Future Nanomaterials

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1. Introduction

❑ The incipient of nanoscience & nanotechnology

"There is Plenty of Room at the Bottom", lecture by Richard P. Feynman, December 1959:

"I would like to describe a field, in which little has been done, but in which an enormous amount can be done in principle… it might tell us much of great interest about strange phenomena that occur in complex situations… it would have an enormous number of technical applications. What I want to talk about is the problem of manipulating and controlling things on a small scale… there is room – you can decrease the size of things in a practical way. I now want to show that there is plenty of room… according to the laws of physics."

- Today nanoscience & nanotechnology has become a major multidisciplinary research field with impacts ranging from fundamental physics to medicine.

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Why “nano”?

- Understanding the physical & chemical principles down to atomic and molecular scales.
- Designing and manipulating atomic/molecular-scale physical & chemical characteristics and processes.

❑ A short list of applications:

- High-density miniaturized “smart” devices & data storage
- “Smart” materials with designed properties
- Ultra-sensitive detectors for medical to defense applications
- Space exploration
- Telecommunications
- Quantum information technology
- DNA sequencing (& engineering)
- Improved medicine (e.g. targeted-cell treatment and drug delivery)
- Efficient photovoltaic cells, batteries & hydrogen storage for energy applications
- Flexible and energy-efficient display
- Metrology
- Filtering, detoxication and desalination
- Bioengineering, etc.

Interdisciplinary nature & technical issues

- **Disciplines involved in nanoscience & nanotechnology:**

  Physics, chemistry, biology, surface & material sciences, electrical engineering, mechanical engineering.

- **Technical requirements for nanoscale research:**

  - Nano-fabrication
    - The "top-down" approach
    - The "bottom-up" approach
  - Nano-instrumentation/characterization
  - Nano-materials/devices
  - Integrating & functionalizing nano-systems

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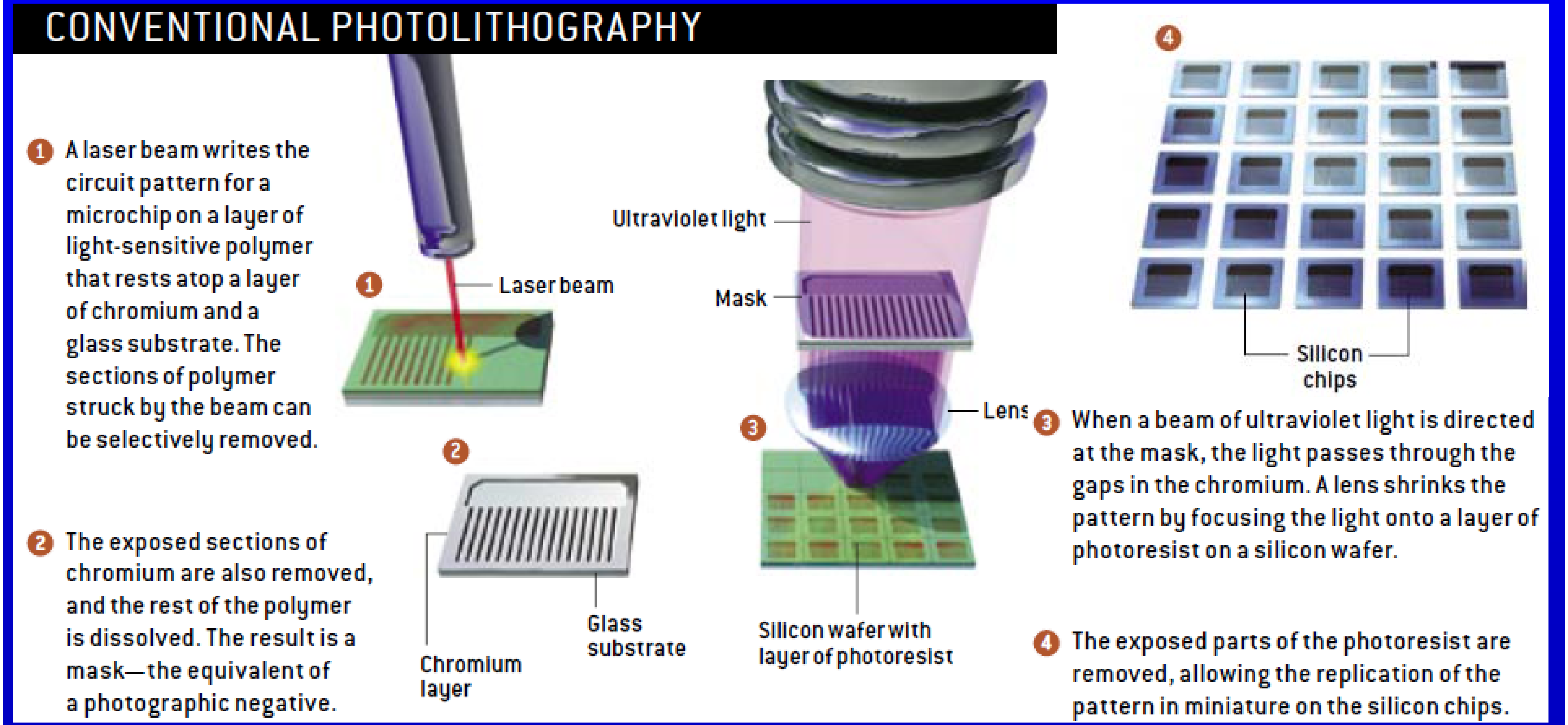
2. Nanofabrication Technologies

❑ The "top-down" approach

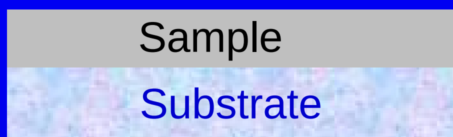
- Lithographic techniques: including optical, electron-beam and focused-ion-beam (FIB) lithography for processing inorganic materials.

[G. M. Whitesides & J. C. Love, Scientific America (2007)]

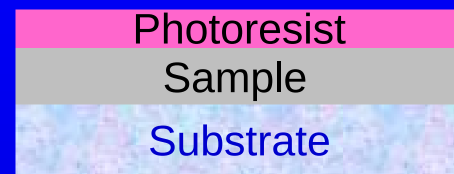


Basic procedure of photolithography

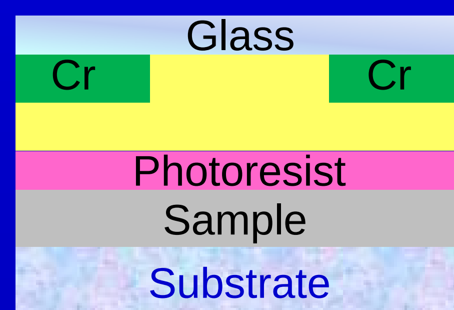
1) Prepare sample surface:
Remove contaminants & moisture.



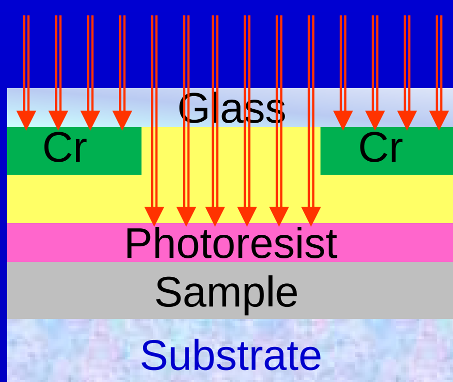
2) Apply photoresist:
Apply adhesion promoter, spin-coat photo-resist & pre-bake.



3) Align photomask:
A photomask may be developed by laser patterning a layer of light-sensitive polymer on top of a Cr and glass substrate.



4) Exposure to UV light:
Chemical change occurred in the photoresist exposed to light, which transferred patterns from the mask.



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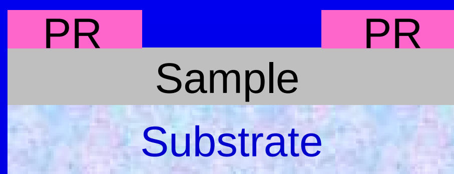
Basic procedure of photolithography (cont.)

5) Develop & remove photoresist:
Perform post-exposure bake & apply developer to remove exposed resist.

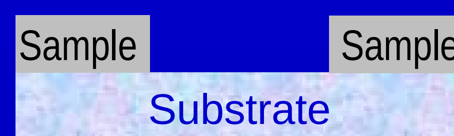


6) Etch exposed sample:
Perform either chemical (wet) or plasma (dry) etching to remove exposed parts of the sample.

- **Primary advantages:**
  - Cost effective.
  - Precise control of the shape & size.

- **Disadvantages:**
  - Required flat surfaces.
  - Difficult for creating non-flat features.
  - Necessity for extremely clean conditions.

7) Remove leftover photoresist:
The remaining photoresist may be removed either by a liquid resist stripper or by oxygen plasma.



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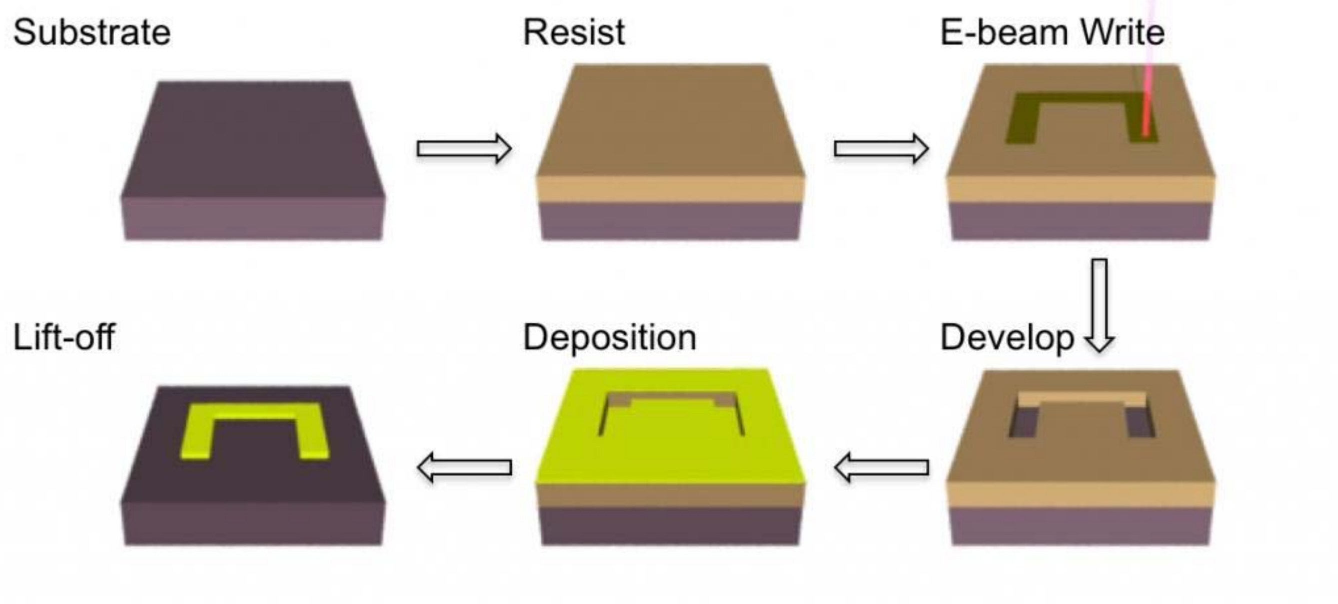
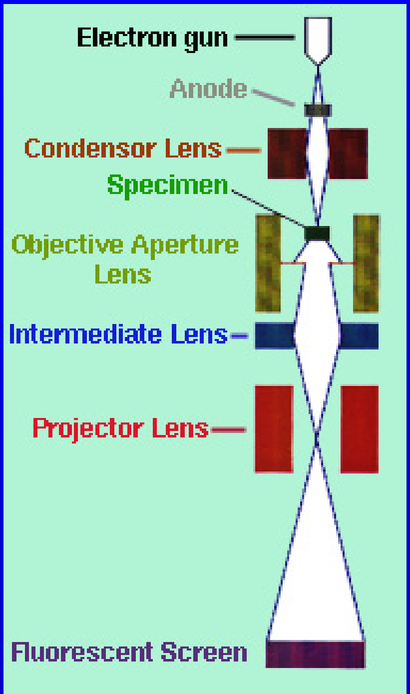
Electron-beam (e-beam) lithography

- Electron beam lithography is the practice of emitting a beam of electrons in a patterned fashion across a surface covered with a resist and of selectively developing regions of the resist ("developing").



"Maskless" lithography using electron beam



- Primary advantage:
  High resolution (~ a few nanometers)
- Disadvantage:
  Low throughput (~ 10^7 times lower than that of photolithography)

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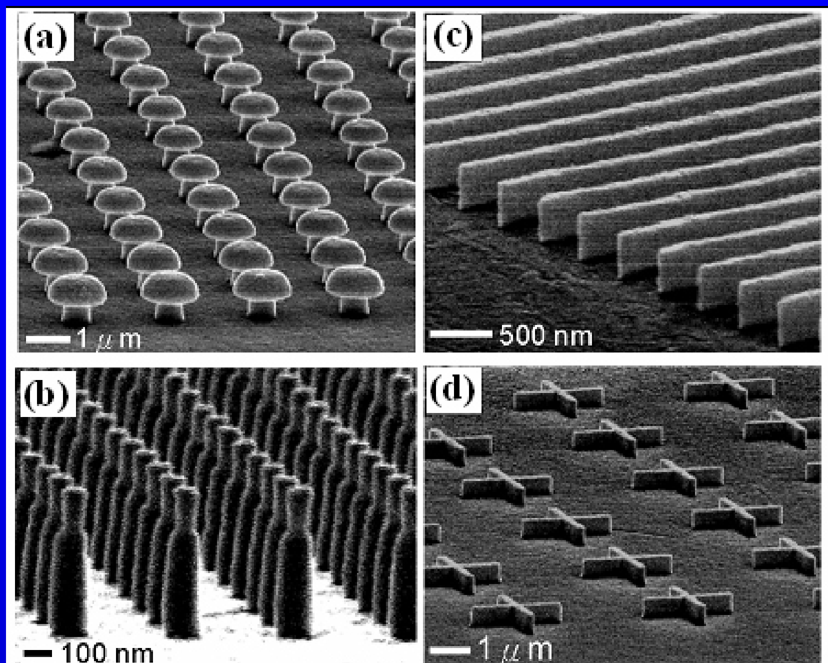
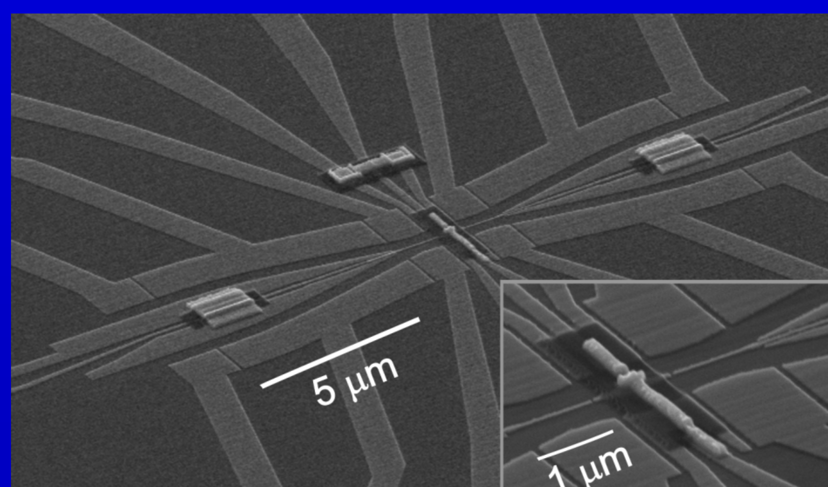
Examples of nanostructures by e-beam lithography



(Academia Sinica, Taiwan)

(220px-EB)

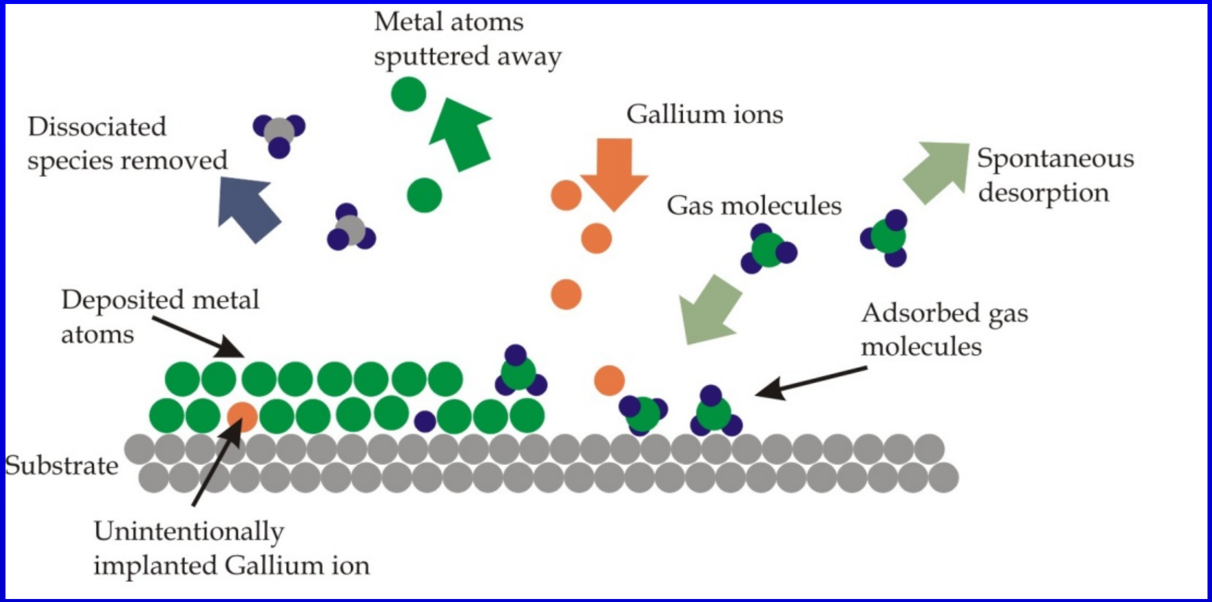


(Cambridge University)

Focus ion beam lithography & microscopy

- Focused ion beam (FIB) systems operate in a similar fashion to a scanning electron microscope (SEM) except, rather than a beam of electrons, FIB systems use a finely focused beam of ions (usually gallium) that can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling.

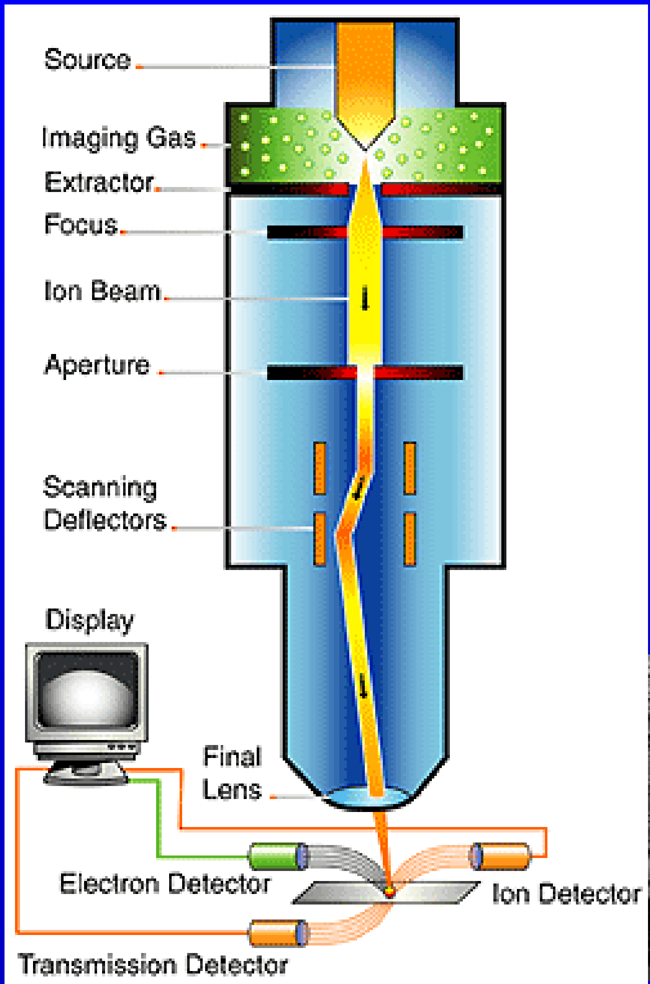
The Principle of FIB operation:



- The gallium (Ga+) primary ion beam hits the sample surface and sputters a small amount of material, which leaves the surface in forms of secondary ions, neutral atoms, or secondary electrons. As the primary beam rasters on the sample surface, the signal from the sputtered ions or secondary electrons is collected to form an image. A FIB can also be used to deposit material via ion beam induced deposition.

Examples of focused-ion-beam (FIB) lithography

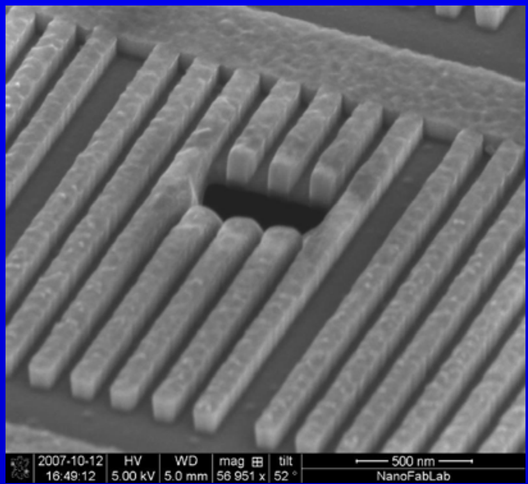
Block diagram for a realistic FIB system:

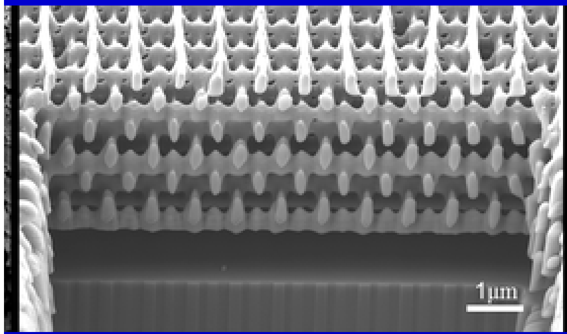


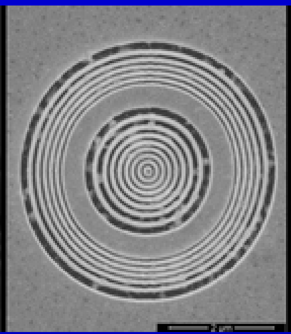
(From www.waynadnoticsboard.com)

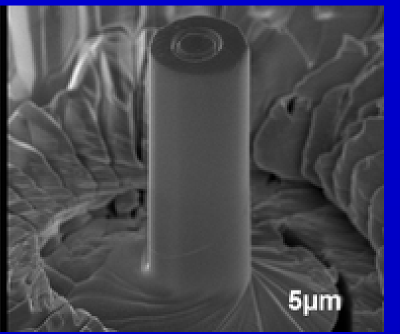
Image of a commercial FIB system:

Ni-grating by FIB (www.spie.org)









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Comparison between e-beam and FIB lithography

- Unlike an electron microscope, FIB is inherently destructive to the specimen. When the high-energy Ga-ions strike the sample, they will sputter atoms from the surface, and will also be implanted into the top few nanometers of the surface so that the surface will become amorphous.

- FIB has used as a micro- and nano-machining tool, to modify or machine materials at the micro- and nano-scale. The high level of surface interaction has also been exploited in *patterned doping of semiconductors* and for *maskless implantation*.

- At lower beam currents, FIB imaging resolution is comparable to that of SEM in terms of imaging topography, but its two imaging modes with *secondary electrons* and *secondary ions* offer many advantages over SEM. For instance, FIB secondary electron images show intense *grain orientation contrast*. FIB secondary ion images also reveal *chemical differences*.

- A new development in using ***helium*** and ***neon*** ions in the FIB is a good compromise between the pros and cons of the FIB and SEM.

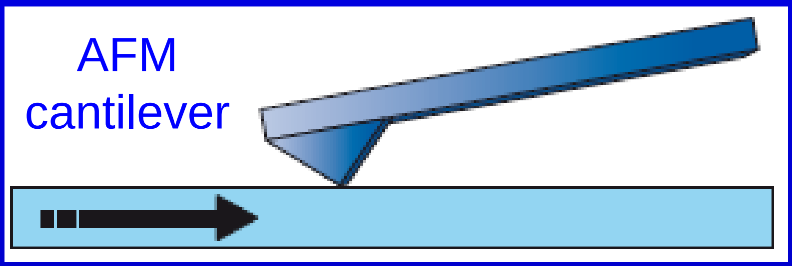
Example of FIB secondary electron imaging of grain boundaries of a specimen

Example of the "bottom-up" approach: Scanning probe lithography

- Scanning probe lithography involves either delivery of energy or delivery of material: [Ref.: K. Salaita et al. Nature Nanotech. **2**, 145 (2007)]

(Delivery of energy)

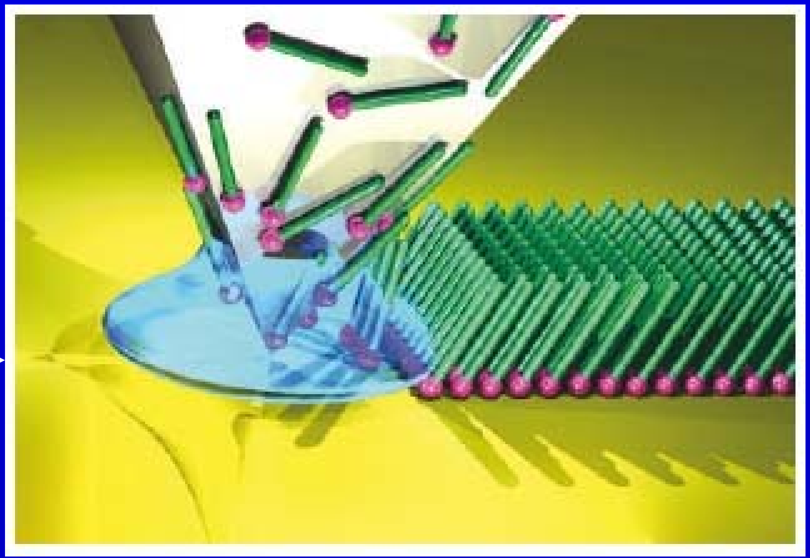
Nano-grating, nano-shaving, anodic oxidation, the "Millipede"



(Delivery of material)

Dip-pen nano-lithography (DPN) & variations of DPN

DPN is a direct-write lithographic tool that allows soft and hard "ink" coated on scanning probe tips to be printed onto surfaces with high registration & resolution.



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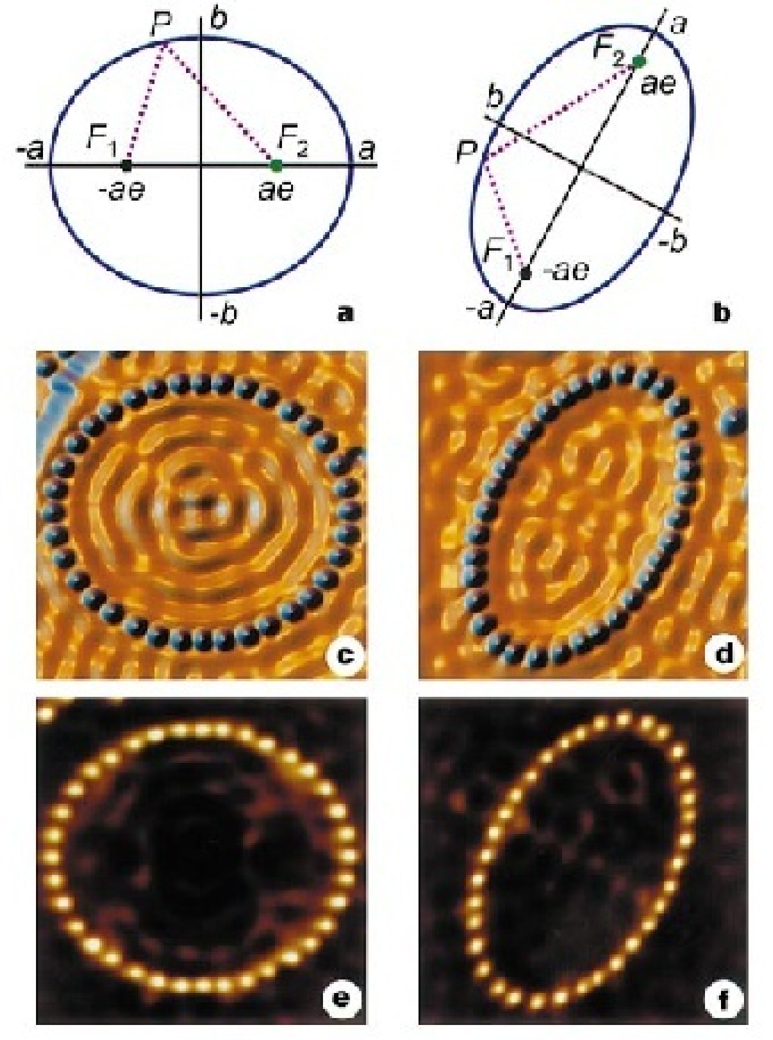
Example of "bottom-up" approach: Atomic-scale fabrication with scanning tunneling microscope (STM)

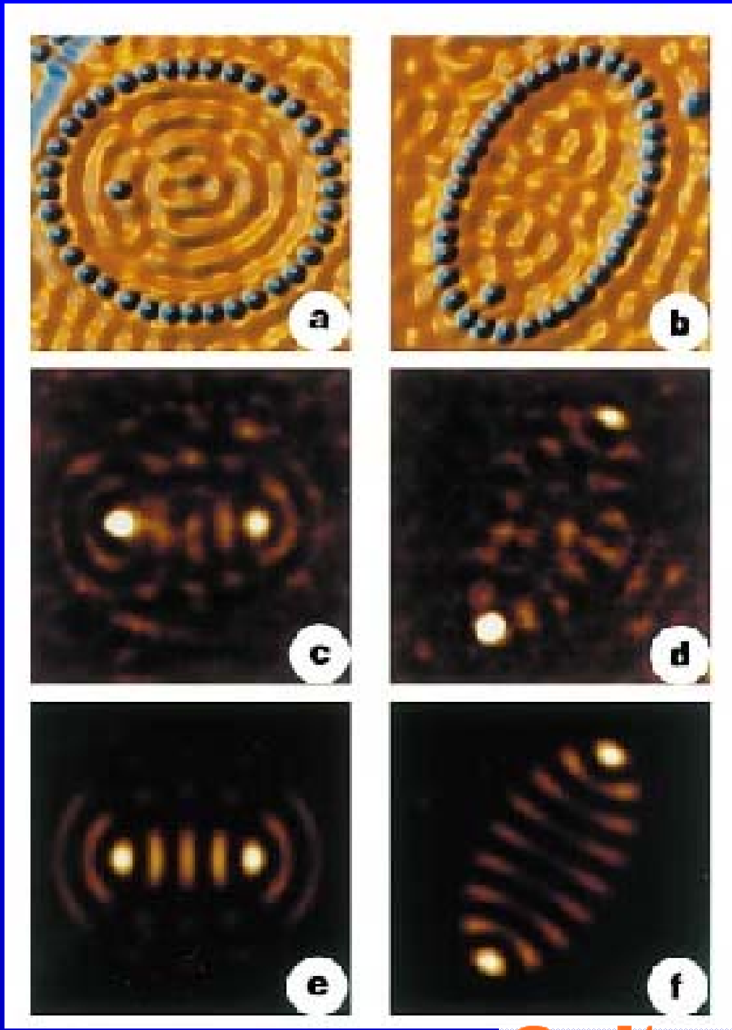
- Using an STM tip to manipulate Co atoms on top of Cu(111):

Manoharan et al., Nature 403 (2000)

"quantum corrals"

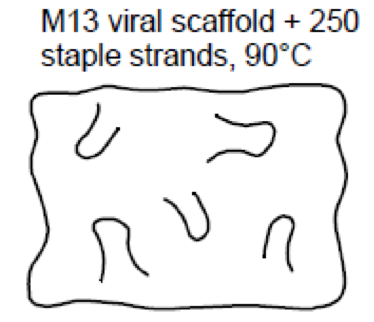


"quantum mirage"



Example of "bottom-up" approach: Folding DNA to form nanoscale shapes & patterns

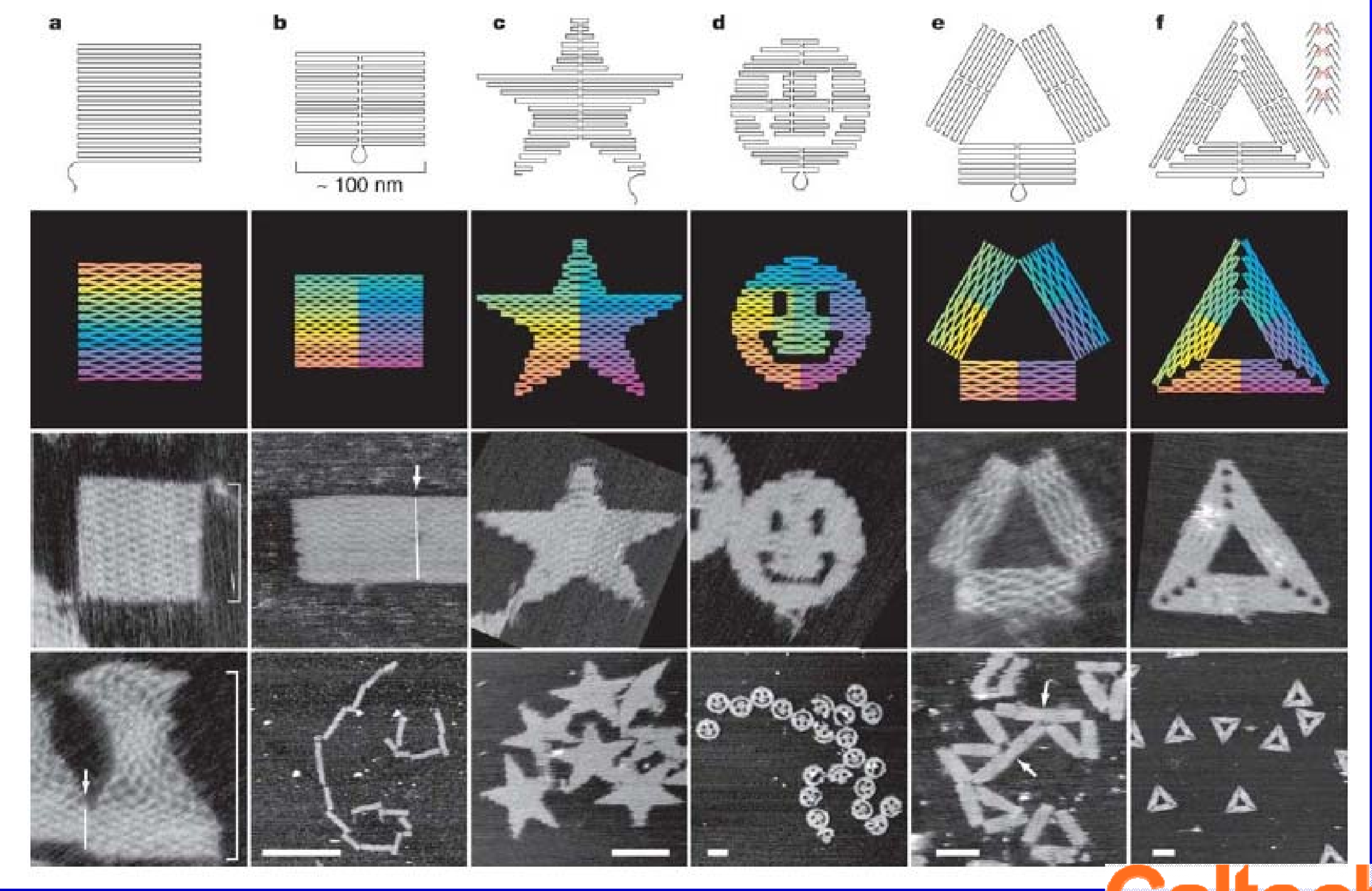
- DNA nanostructures such as origami may be created by using ~200 small synthetic DNA strands ("staples") to fold a long single-stranded DNA scaffold.
- This approach can create arbitrary two-dimensional and three-dimensional shapes.



~ 6 nm per pixel;
~ 2 nm per stack

Watson-Crick base pairing:
A ⟷ T
C ⟷ G

P.W.K. Rothemund, Nature 440 (2006).



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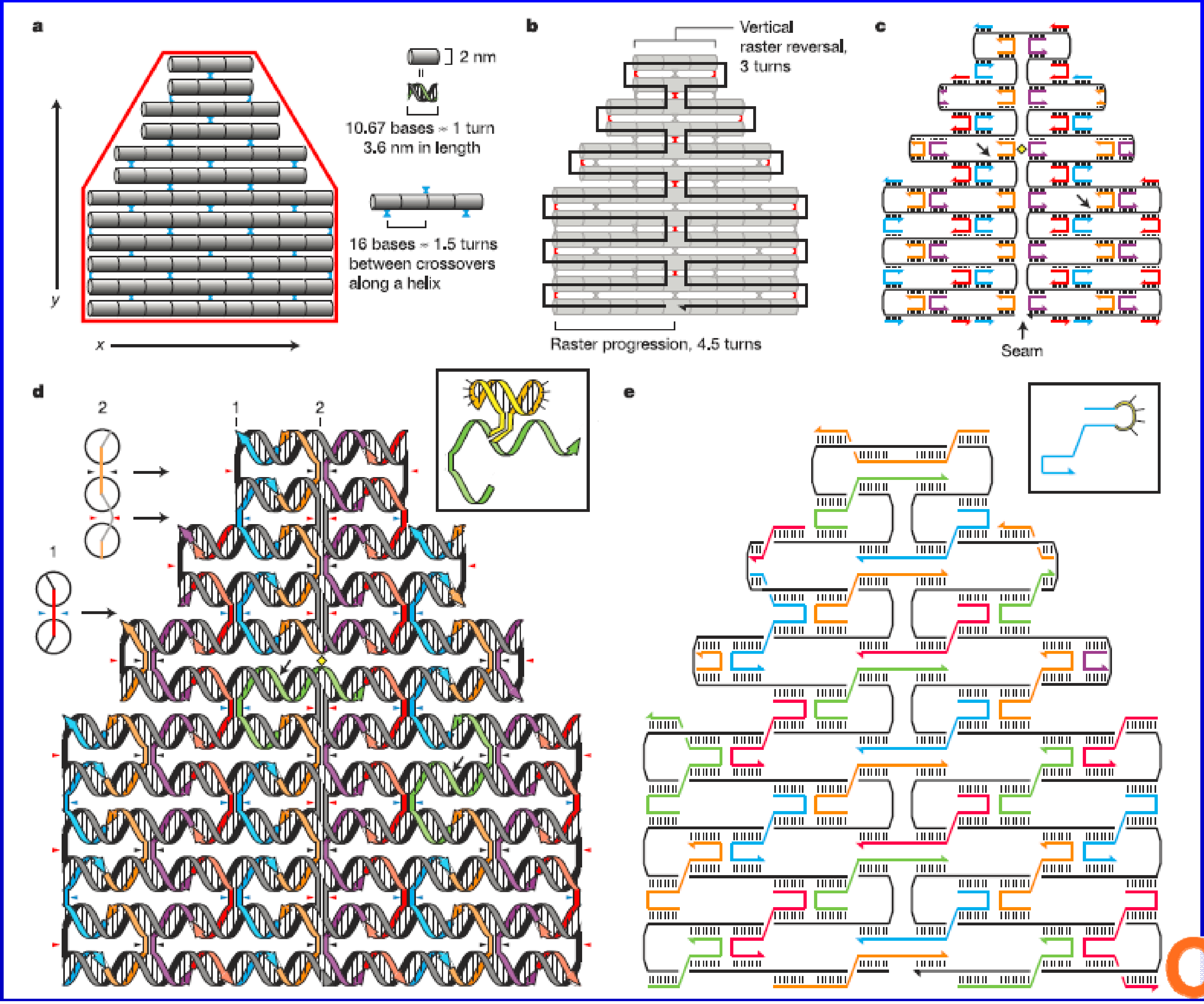
Basics of DNA nano-patterning (Rothemund, 2006)



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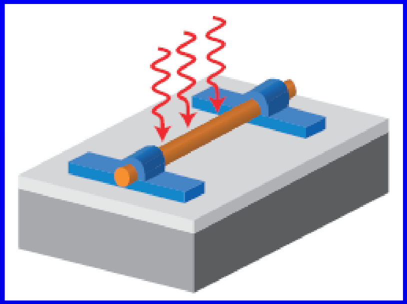
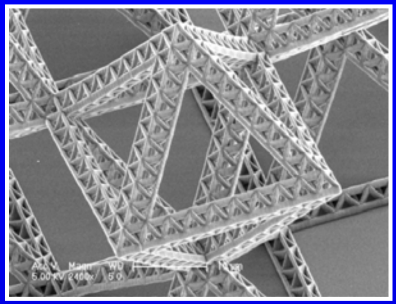
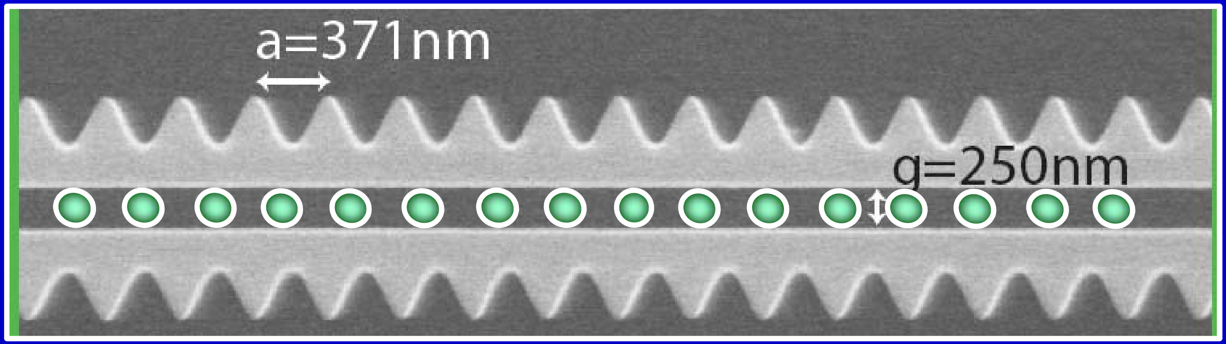
3. Examples & Applications of Nano Meta-Materials

❑ Representative nano meta-materials

- Quantum dots
- Nanowires
- Nano-photonics
- Nano-truss materials
- Quantum matter assembled from single atoms & photons







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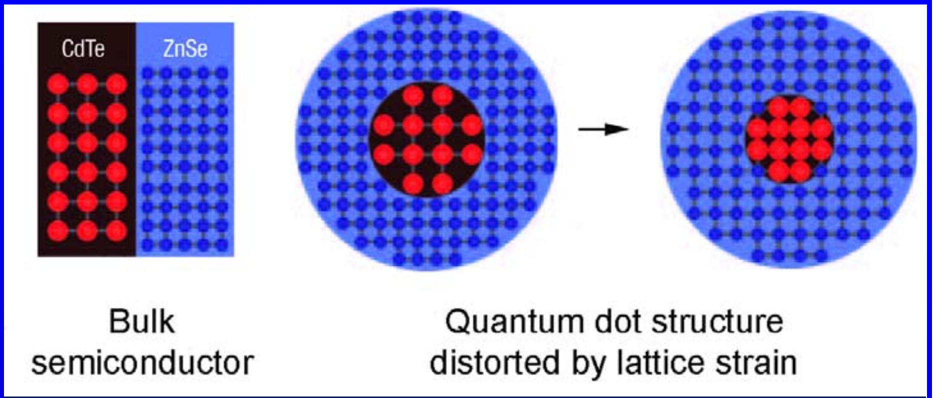
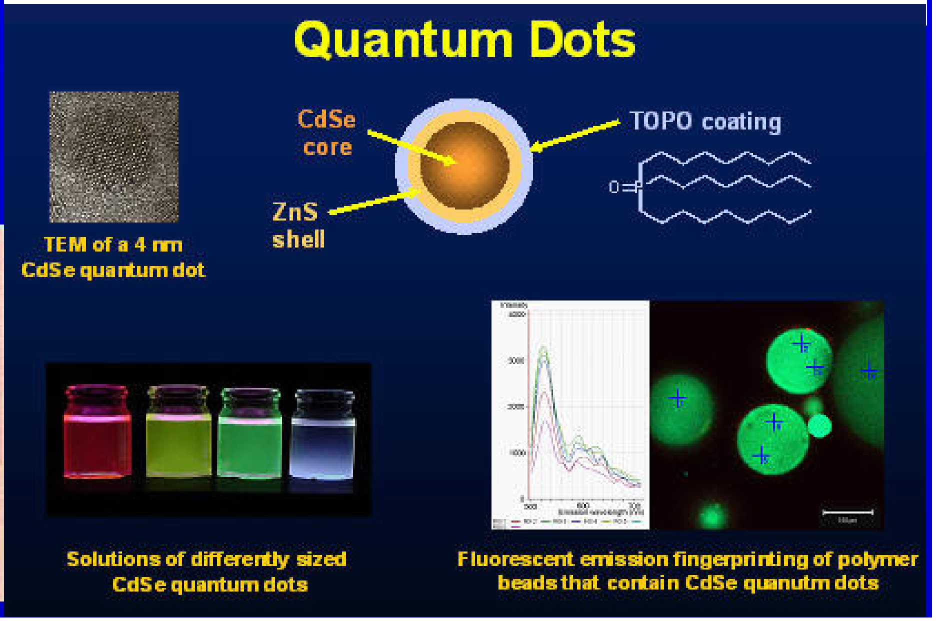
Quantum Dots

- A *quantum dot* is a *semiconductor nanostructure* that confines the motion of conduction-band electrons, valence-band holes, or excitons (bound pairs of conduction band electrons and valence band holes) in all three spatial directions.

- The confinement can be due to *electrostatic potentials* (generated by external electrodes, doping, strain, impurities), *the presence of an interface* between different semiconductor materials (*e.g.* in core-shell nanocrystal systems), *the presence of the semiconductor surface* (*e.g.* semiconductor nanocrystal), or a combination of all of the above.



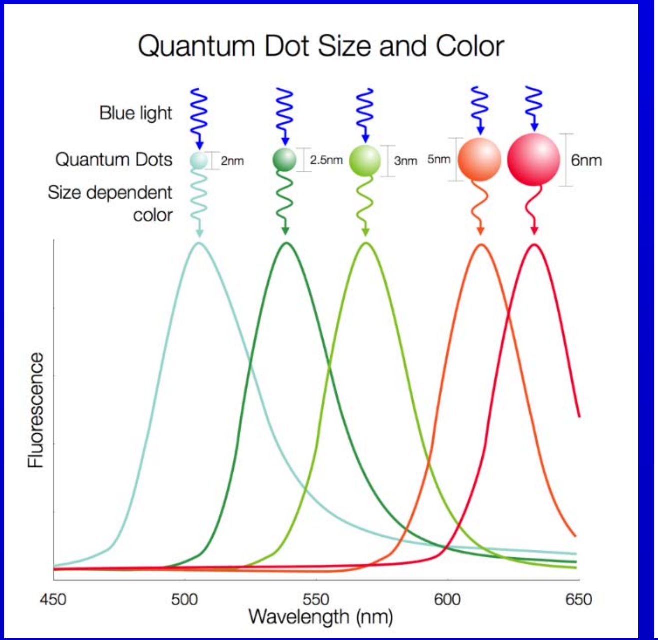


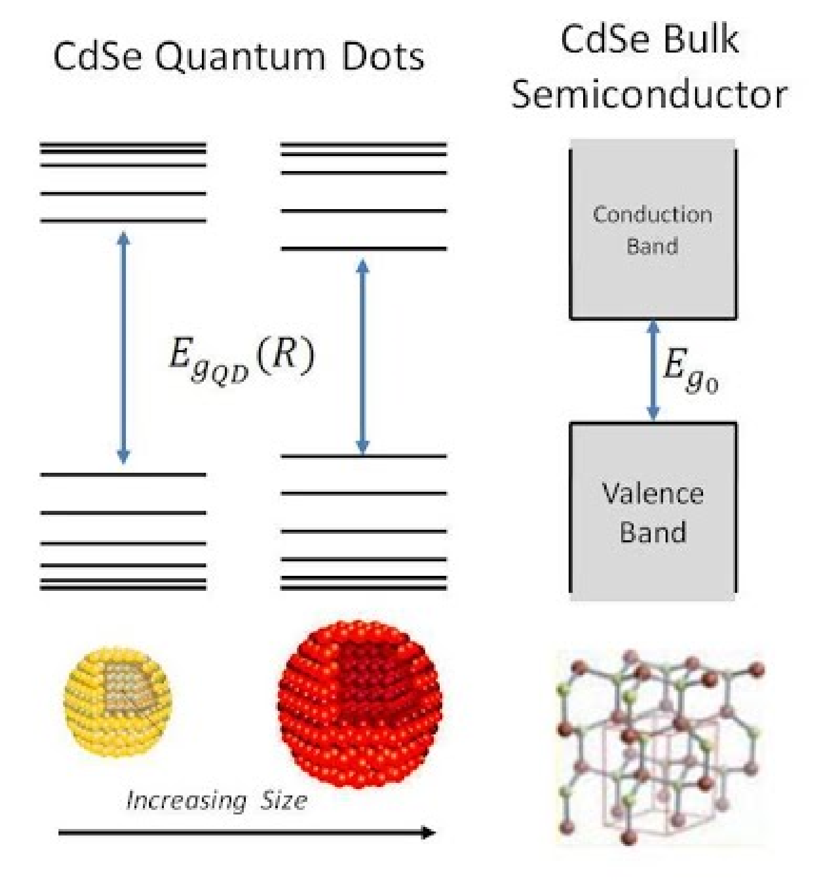
Lithographically created quantum dots:

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

Properties of quantum dots

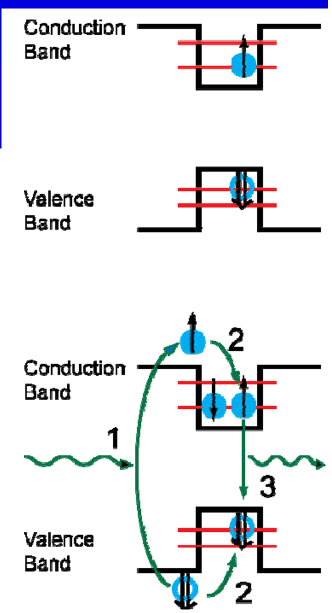
- A quantum dot has a discrete quantized energy spectrum, which are reminiscent of atomic spectra and so quantum dots are also known as ***artificial atoms***.
- The electronic wave functions are spatially localized within the quantum dot, but extend over many periods of the crystal lattice.
- Colloidal semiconductor nanocrystals can be as small as 2 to 10 nanometers.
- Self-assembled quantum dots are typically between 10 and 50 nm in size.
- Quantum dots fabricated by lithographically patterning can have lateral dimensions exceeding 100 nanometers.



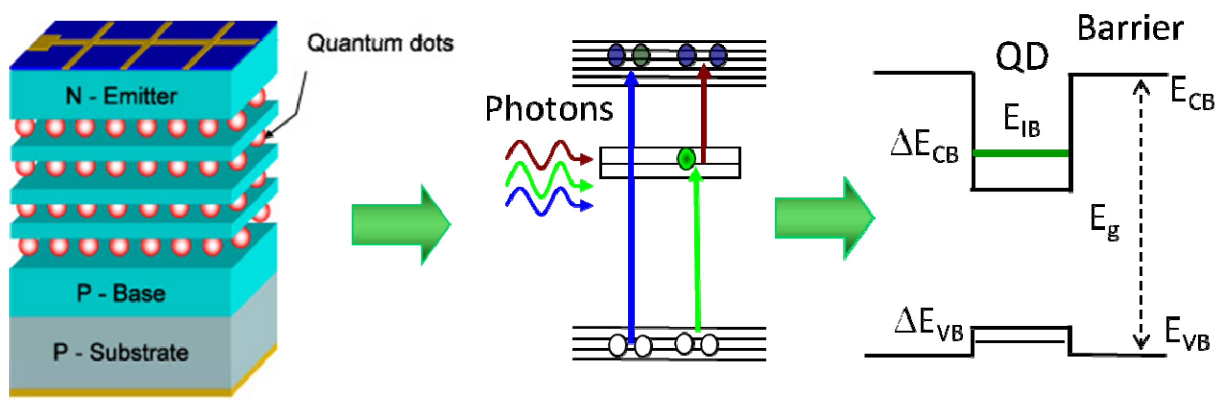


Applications of quantum dots

- Quantum dots are particularly significant for optical applications because of their high extinction coefficient. Examples of optical applications include diode laser, photovoltaic devices, light emitting diodes (LEDs), photodetectors, photocatalysts.
- Quantum dot technology is one of the most promising candidates for use in ***solid-state quantum computation***. By applying small voltages to the leads, the flow of electrons through the quantum dot can be controlled and thereby precise measurements of the spin and other properties therein can be made.
- Quantum dots are far more superior to organic dyes in terms of their brightness and stability, and are therefore ideal for various types of biological applications, such as highly sensitive cellular imaging, tracking of molecules and cells over extended periods of time, *in vitro* imaging of pre-labeled cells, etc.



Incorporation of quantum dots in solar cells for efficient light harvesting

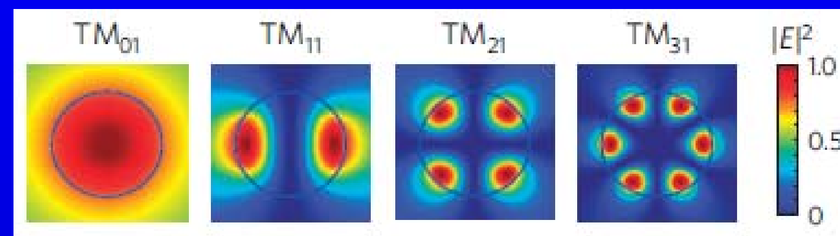


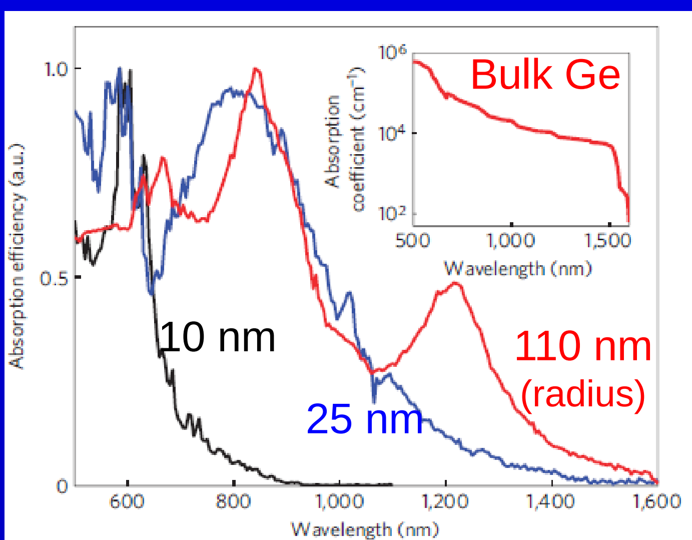
Schematic of operating principle and energy band diagram of proposed III-(As, SB)solar cell

Semiconducting nanowires

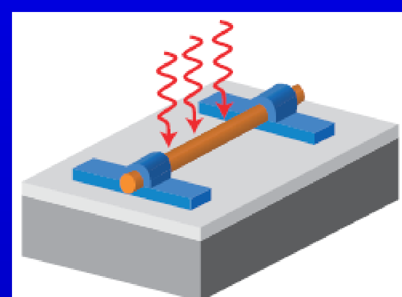
- Semiconducting nanowires (NWs) have been demonstrated to be highly versatile optoelectronic components for a wide variety of applications, including:

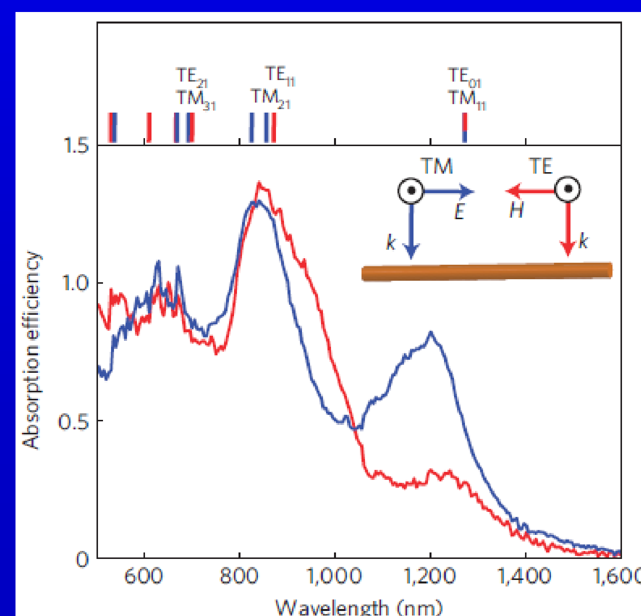
  * polarization-sensitive photodetectors & arrays with sub-wavelength resolution;
  * polarization-sensitive nano-avalanche photodiodes (APDs) w/ gains up to 10^5;
  * optical modulators & nano-waveguides;
  * nano-LEDs and nano-lasers ;
  * solar cells, biomedical sensors, etc.





L. Y. Cao et al. (2009)





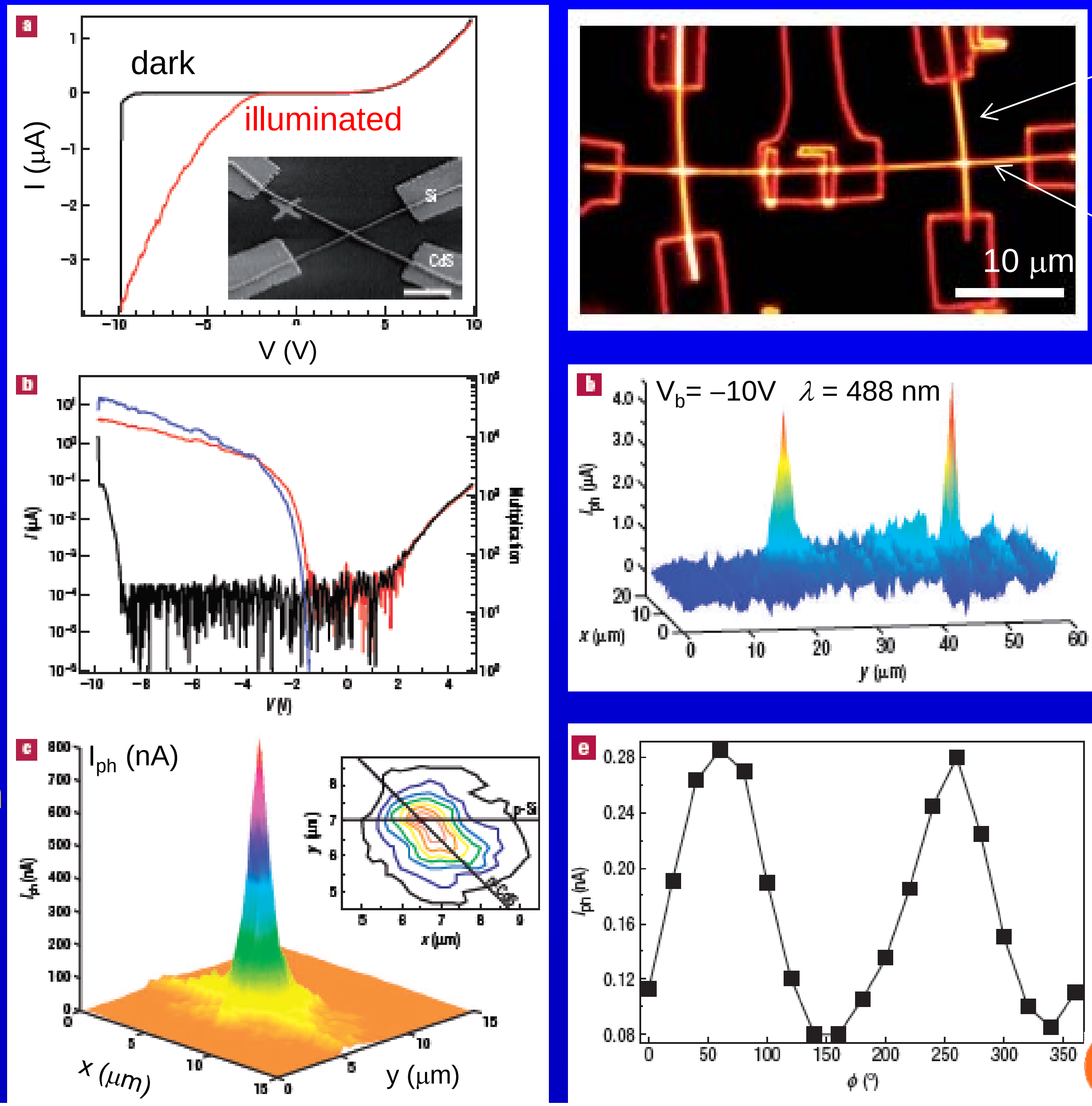
Polarization-sensitive & spatially resolved nano-APDs

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

Gain up to 10^5

Spatial resolution better than 250nm (sub-wavelength)

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



No cross talk

Polarization -sensitive

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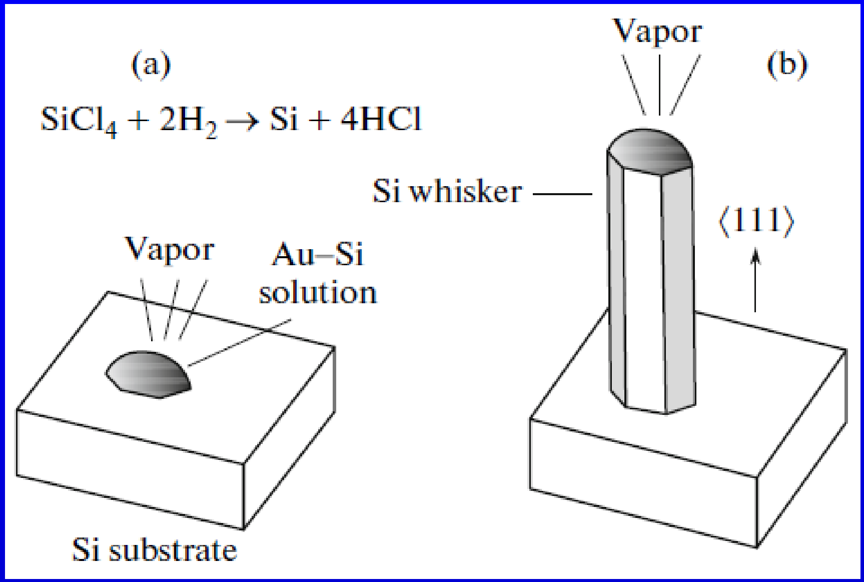
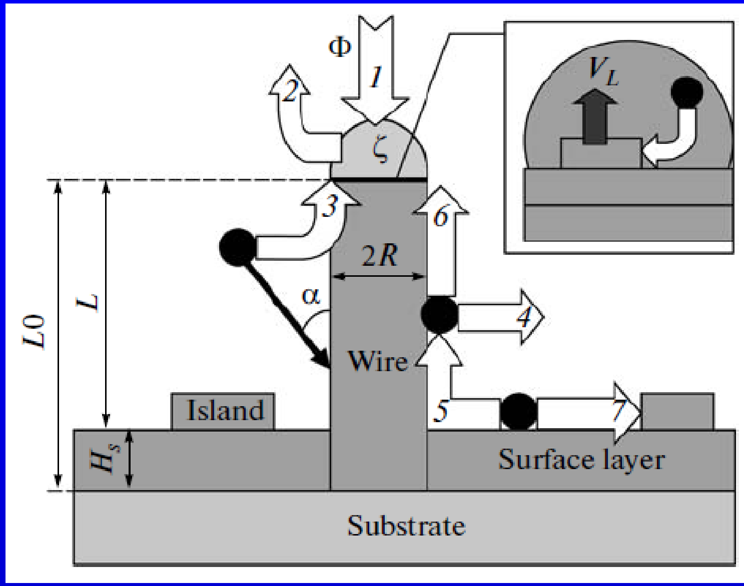
Fabrication of NWs

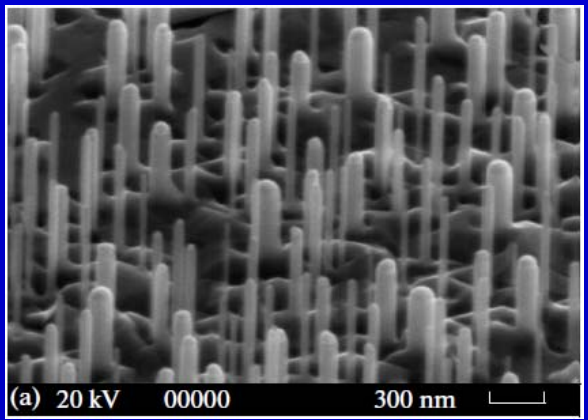
- Mechanism of the growth vapor-liquid-crystal:

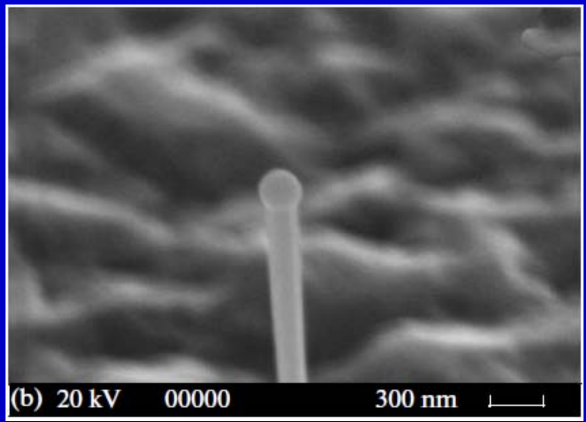
V. G. Dubrovskiia et al., Semiconductors 43, (2009)





An ensemble of GaAs-NWs grown by MBE





An individual GaAs-NW

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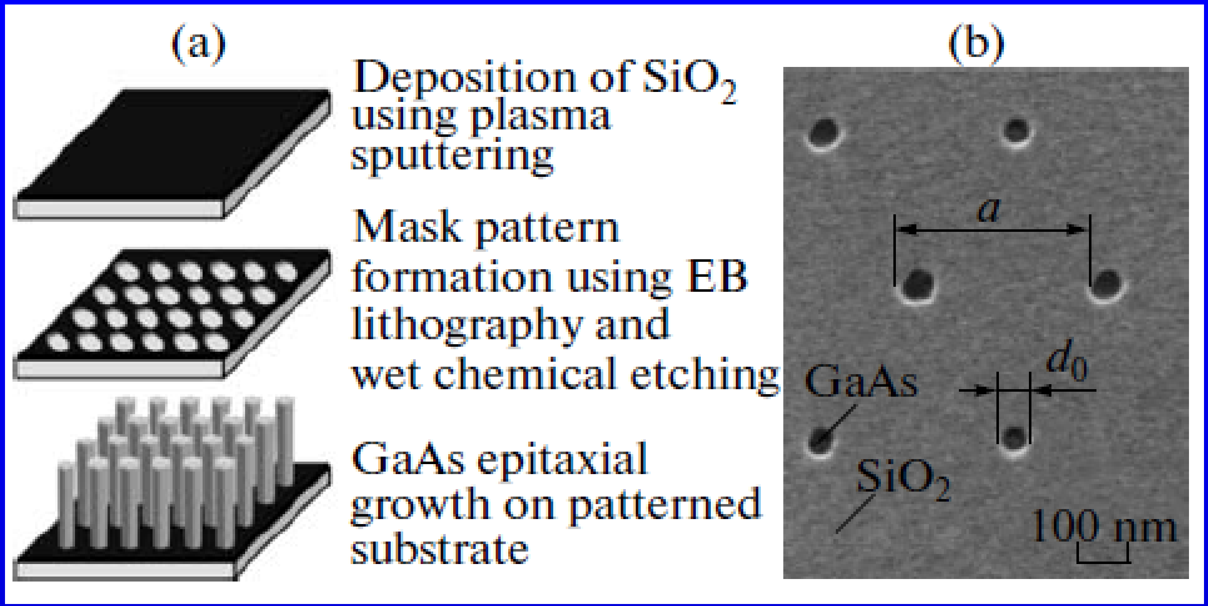
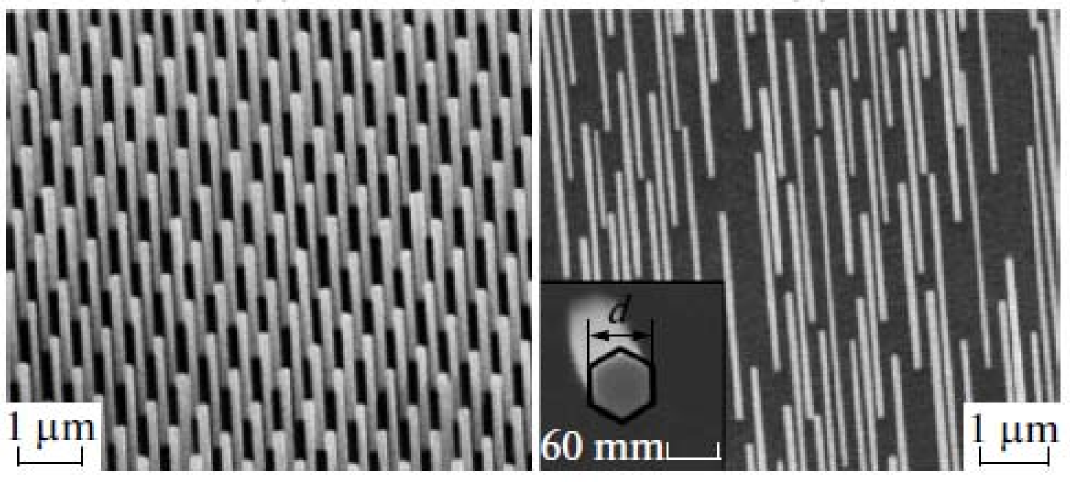
Fabrication of NWs (cont.)

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 GaAs (111) surface for d_0 = 200 nm:



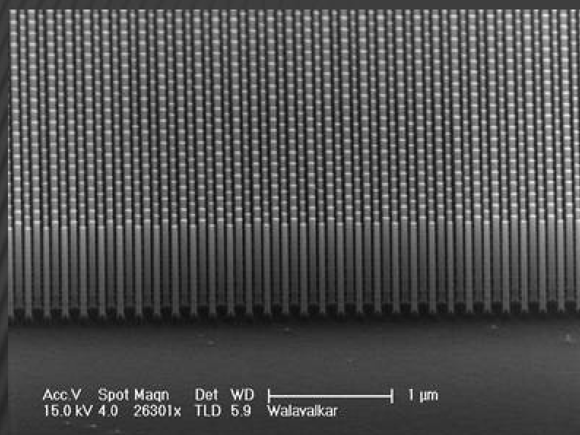
GaAs-NWs grown on GaAs (111) surface for d_0 = 50 nm

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

Combined effects of strain & quantum confinement: Strained Si nano-pillars

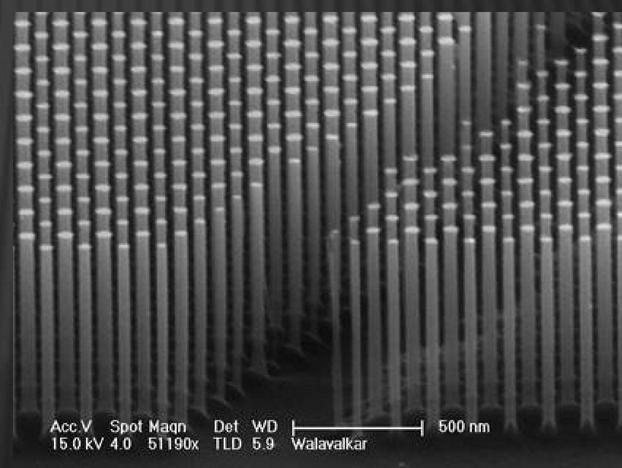
- When silicon pillars are oxidized, the silicon lattice expands by approximately 40%, which leaves the adjacent un-oxidized silicon under tremendous tensile strain. In nano-pillars, this strain can increase to a point where the silicon oxidation process is self-limited, leaving 2 ~ 10 nm wide strained Si cores within a SiO_2 shells.

Professor Axel Scherer's group at Caltech



A 5 minute etch provides excellent surface and sidewall quality

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



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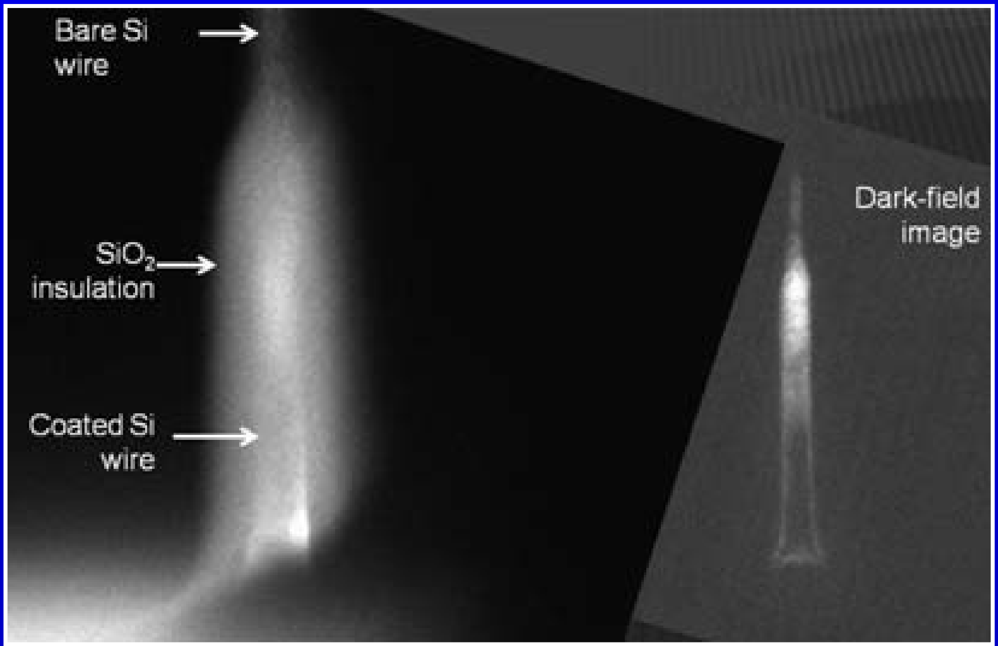
Quantum confinement by thermal oxidation

- The size of silicon nano-pillars can be further decreased by thermal oxidation.
- The final nano-pillar diameter is controlled by the oxidation temperature.



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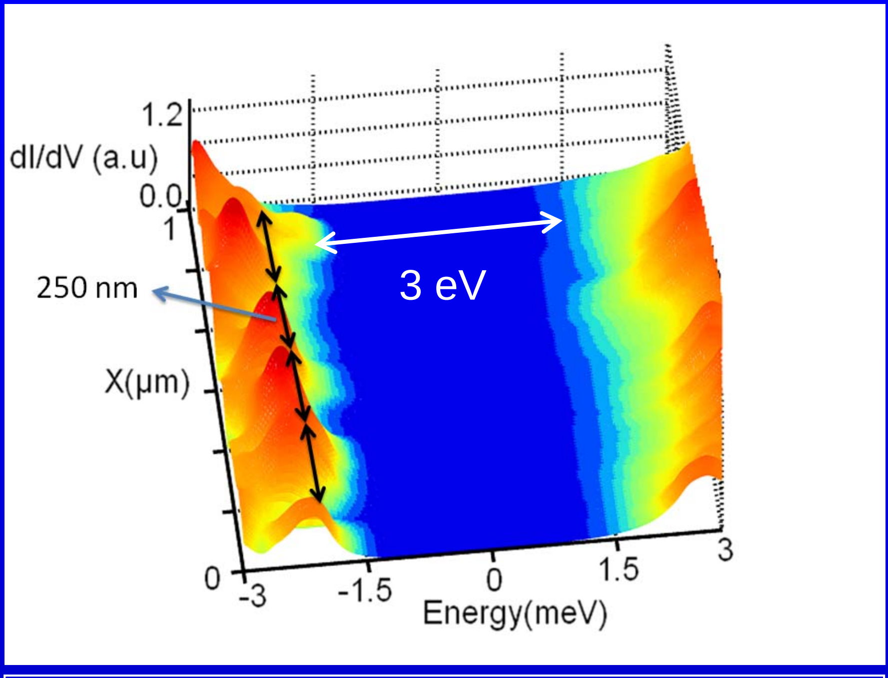
STM studies of oxidized silicon nano-pillars

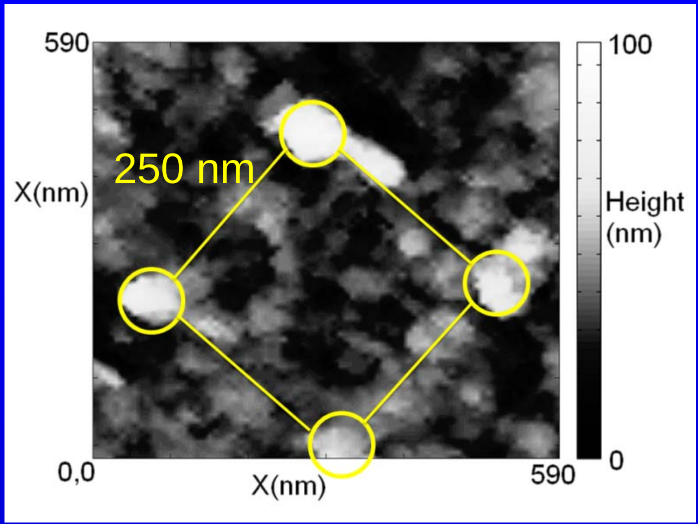
Spatially resolved spectroscopy of HF-etched silicon nano-pillars



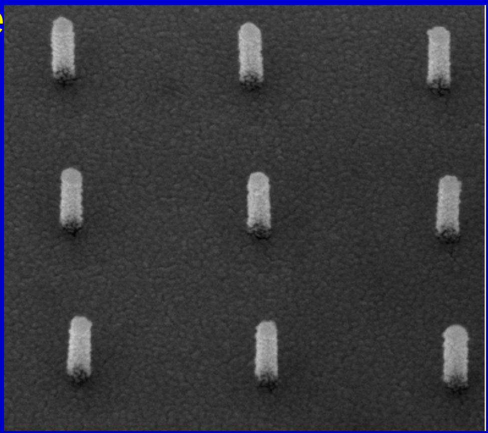
The energy gap increases from indirect ~ 1.1 eV gap for crystalline Si to direct ~ 3 eV for the strained Si nano-pillars.

→ The energy gap may be controlled by the temperature of oxidation

Surface topography from STM after HF chemical etching



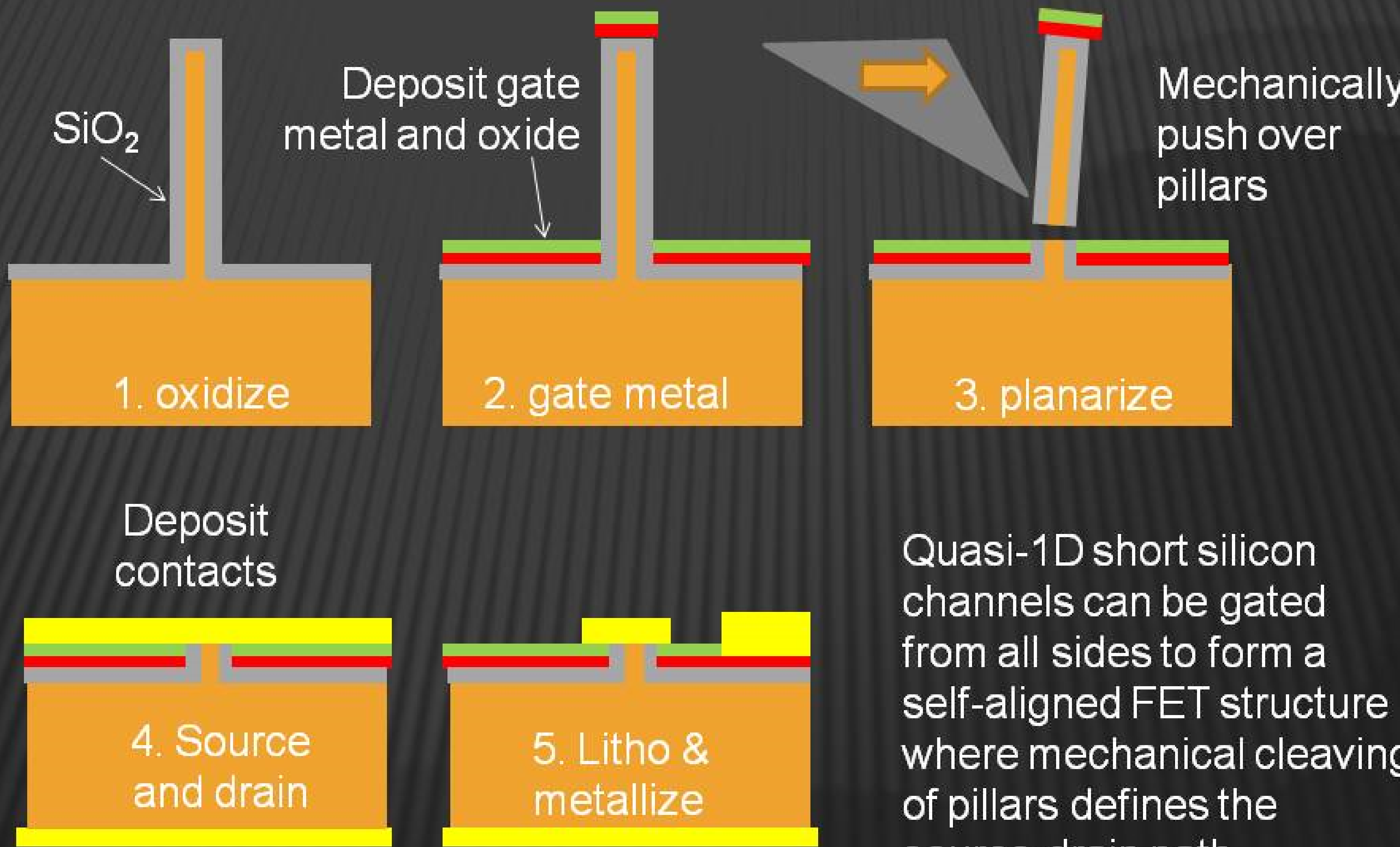
SEM image before HF chemical etching:



G. K. Drayna, M. L. Teague, & N.-C. Yeh, (unpublished)

Caltech

Making a transistor out of a strained Si nano-pillar



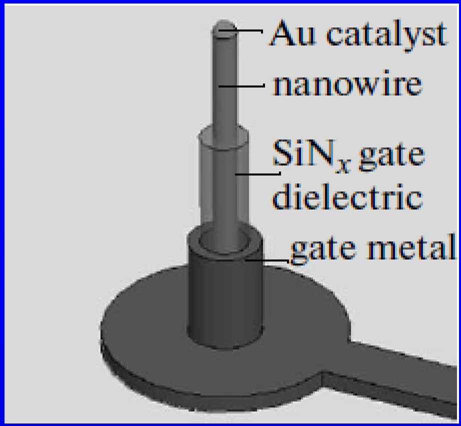
Quasi-1D short silicon channels can be gated from all sides to form a self-aligned FET structure where mechanical cleaving of pillars defines the source-drain path

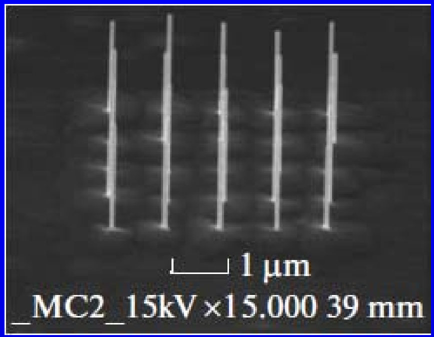
(Courtesy of Axel Scherer)

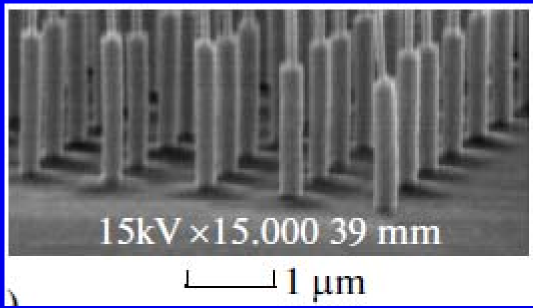
Caltech

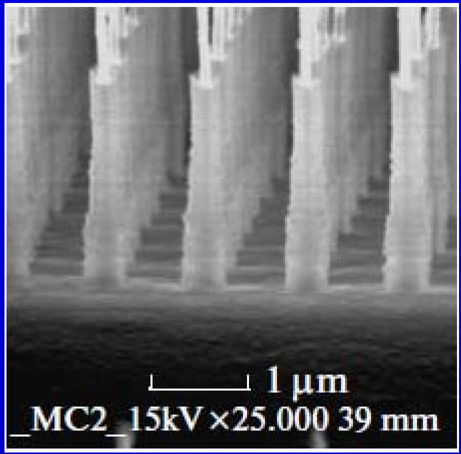
Examples of NW-based transistors

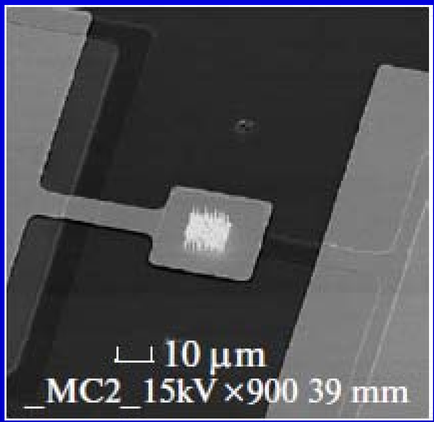
- Similar transistor structures have been demonstrated in InAs nanowires with larger diameters and separations:

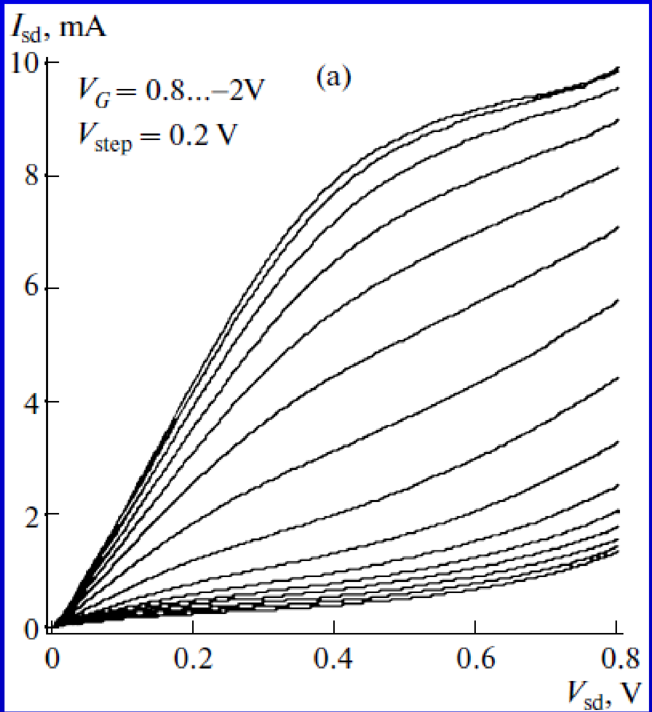












V. G. Dubrovskiia et al., Semiconductors 43, (2009)

Photonic Crystals

- Photonic crystals consist of periodic dielectric or metal-dielectric nanostructures that affect the propagation of electromagnetic waves (EM) in the same way as the periodic potential in a semiconductor crystal affects the electron motion by defining allowed and forbidden electronic energy bands.

- The periodicity of the photonic crystal structure must be around half the wavelength of the electromagnetic waves that are to be diffracted. This is ~200 nm (blue) to 350 nm (red) for photonic crystals operating in the visible part of the spectrum.

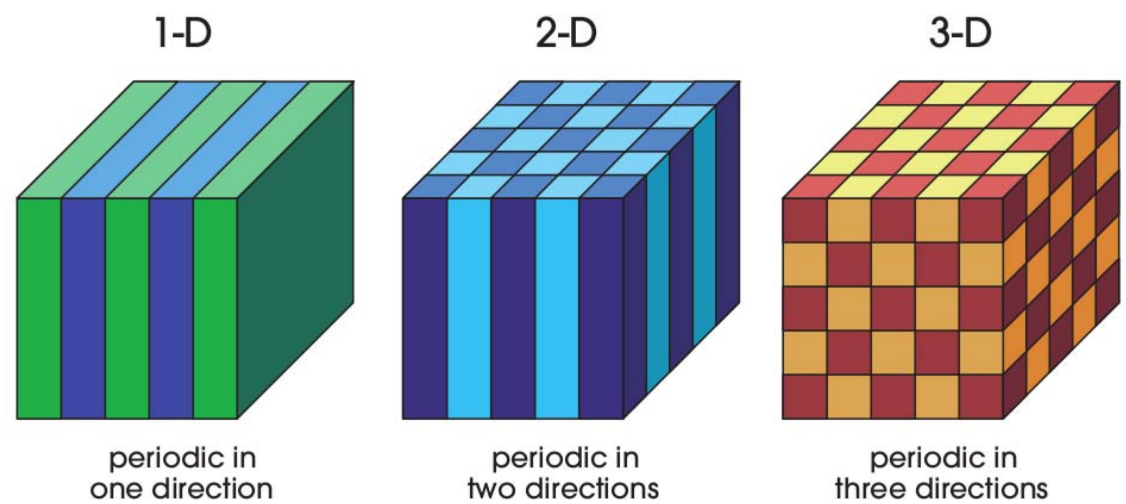
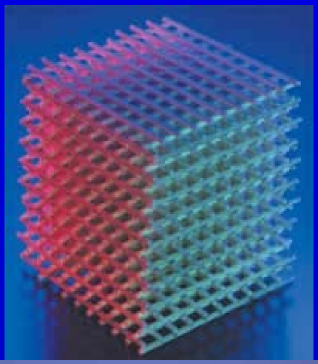
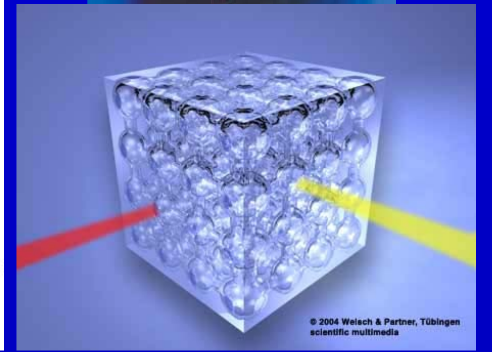


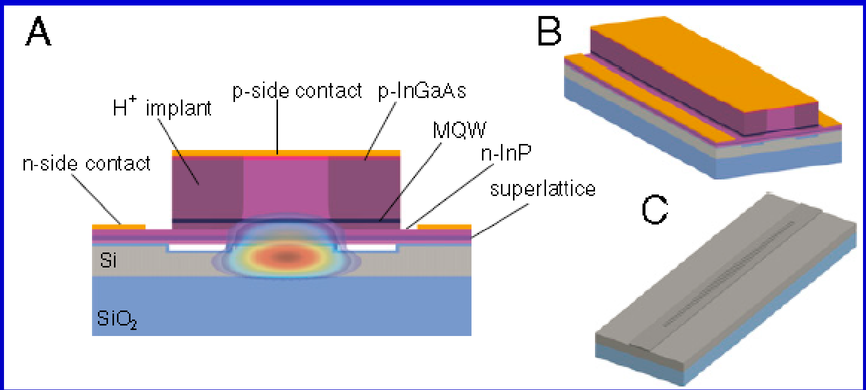
Figure 1: Simple examples of one-, two-, and three-dimensional photonic crystals. The different colors represent materials with different dielectric constants. The defining feature of a photonic crystal is the periodicity of dielectric material along one or more axes.





Nano-Photonics

- Nano-photonics is the study of light-matter interaction on the nanometer scale.
- Although normal optical components cannot focus light to nanoscales, it is possible to squeeze light into nanoscales using such techniques as ***surface plasmons***, localized surface plasmons around nanoscale metal objects, and the nanoscale apertures and nanoscale sharp tips used in near-field scanning optical microscopy (NSOM) and photo-assisted STM.
- Metals are an effective way to confine light to far below the wavelength. Therefore, visible light can be confined to the nanoscale via metallic nanostructures, such as nanoscale tips, gaps, etc. This effect is based on the principle that the permittivity of a metal is typically very large and negative below the plasma frequency of the metal (usually ultraviolet).



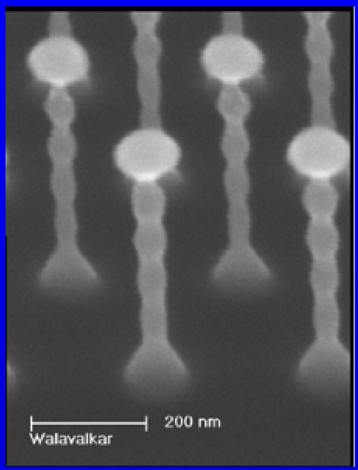
High-coherence semiconducting laser for faster internet (Prof. Amnon Yariv, Caltech)

PNAS 111, 2879 (2014)

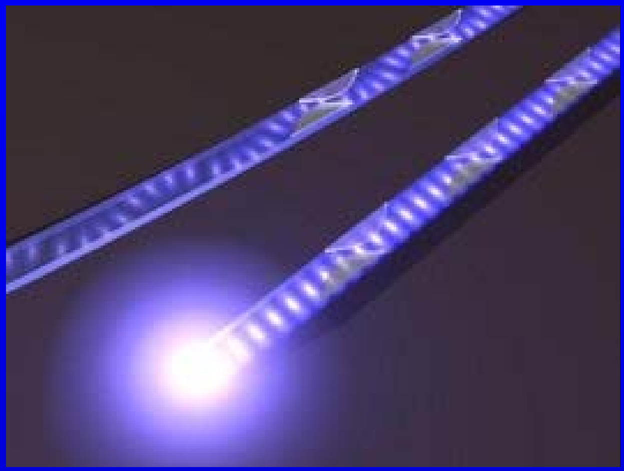
Achieving unprecedented spectral purity for laser (18 kHz, ~20 times narrower frequency range relative to the S-DFB laser currently employed for worldwide optical-fiber network) by incorporating nano-scale corrugations in silicon layer .

Applications of Nano-Photonics

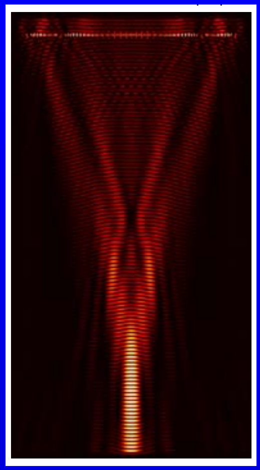
- Silicon nano-pillars for varying photoluminescence (A. Scherer)



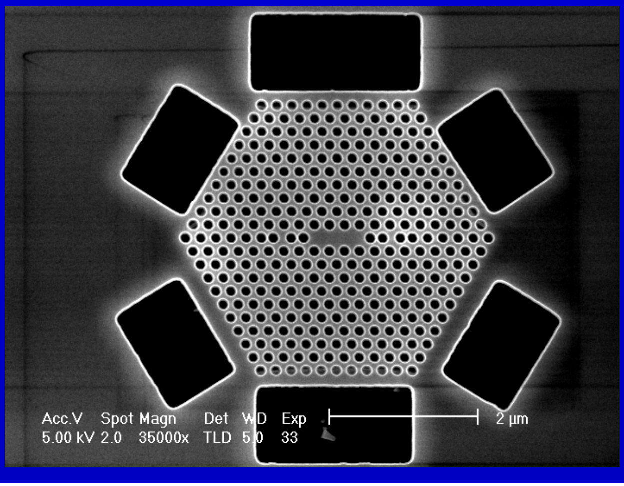
- Nanophotonics for miniaturized vertical cavity laser (A. Scherer)



- Planar silicon lens (A. Faraon)



- Diamond photonic crystal

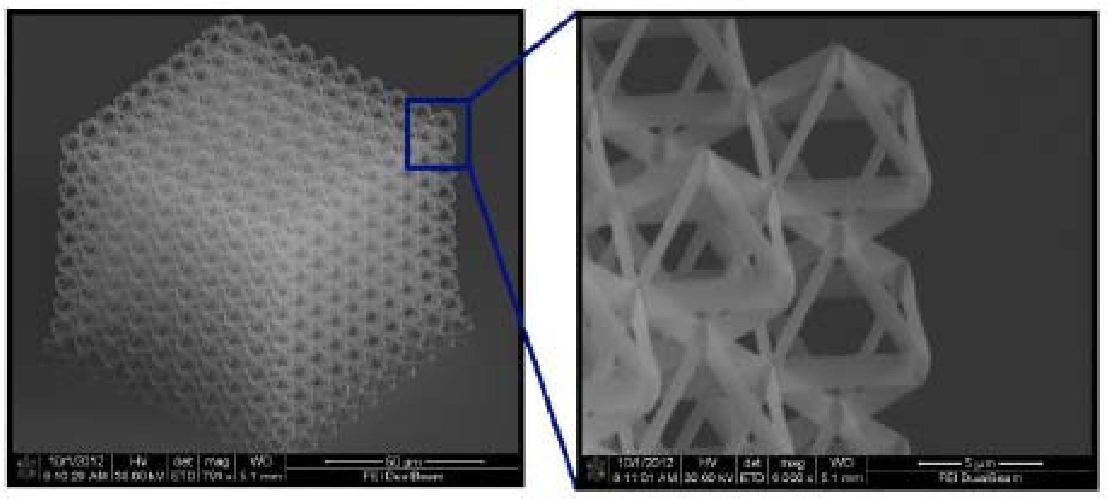


(A. Faraon)

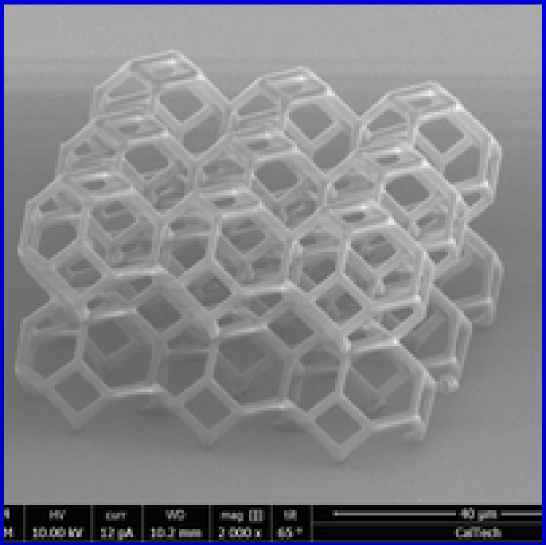
- ➢ Nano-photonic materials & devices for plasmonic waveguides & printing
- ➢ Photonic bandgap materials & photonic crystals
- ➢ On-chip manipulation of light
- ➢ Quantum information S&T with quantum objects embedded in nanoscale photonic devices

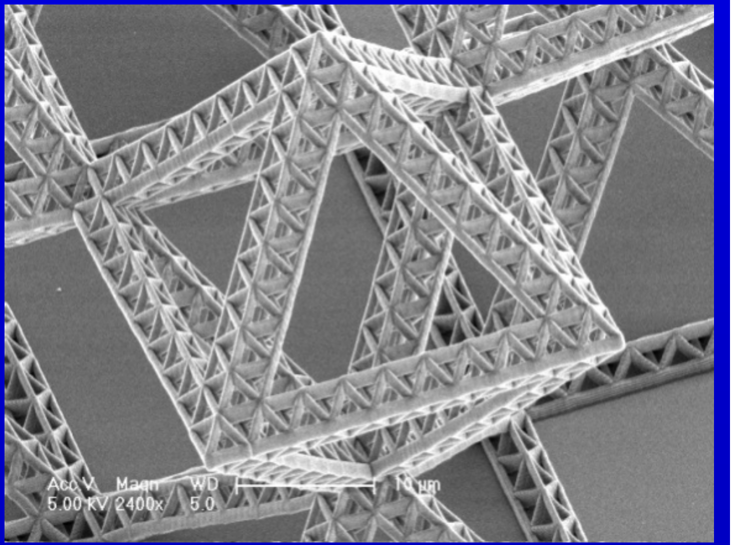
Nano-truss materials

- Creating and studying ultra-light materials with superior thermo-mechanical properties via combination of three-dimensional (3D) hierarchical architectures and nanoscale material size effects (Julia Greer, Caltech)



SEM image of various 3D truss structures created by direct laser writing & two-photon lithography on polymer scaffolds followed by ALD or CVD for depositing desirable metals on the scaffolds

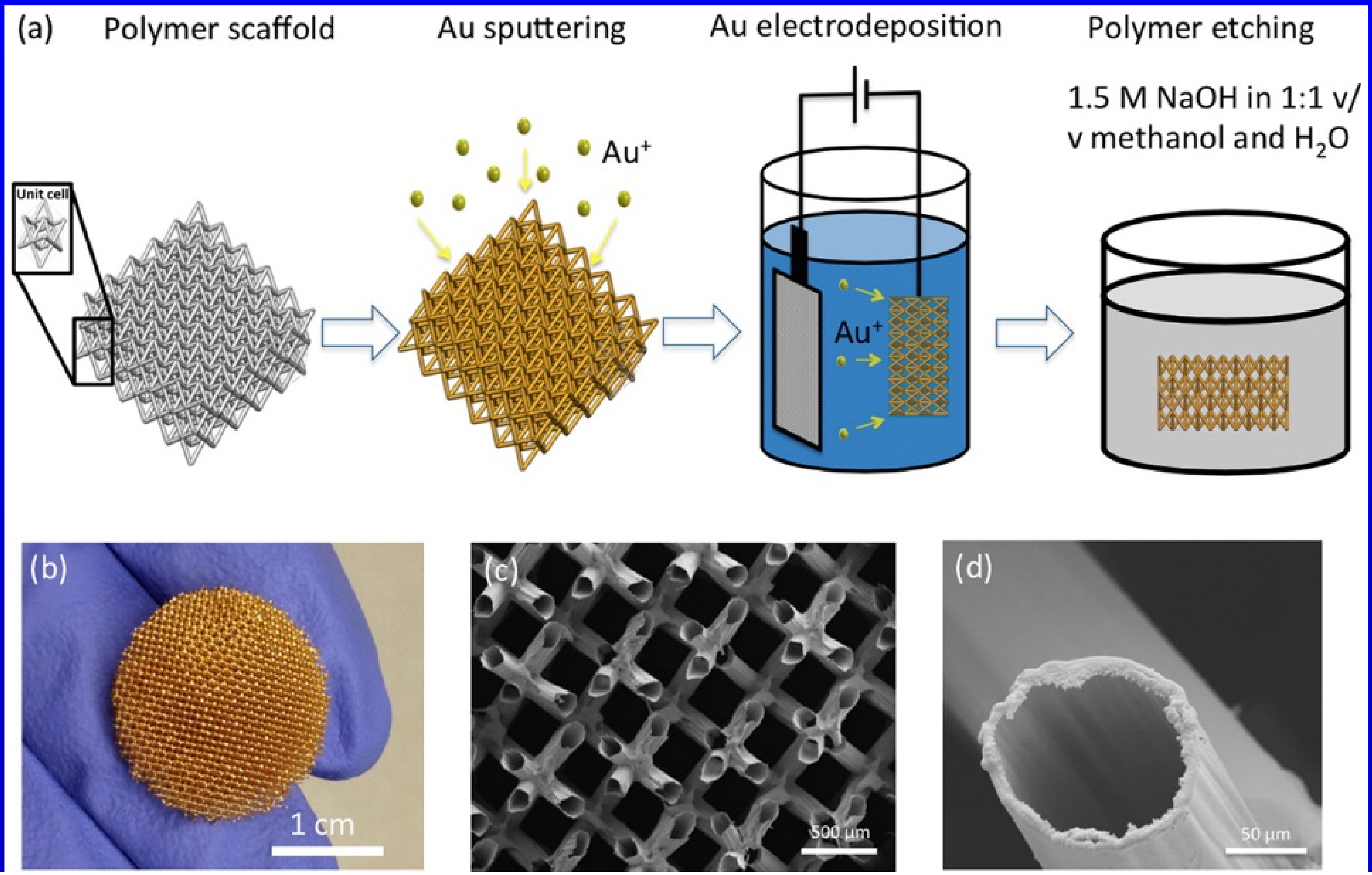




Potential applications of nano-truss materials

- Using a 3D gold truss microstructure with periodic pores and independently tunable surface compositions as a Li-O_2 battery cathode, demonstrating improved stability, strong mechanical robustness, and enhanced surface areas for better catalytic activity for oxygen reduction reaction.

C. Xu *et al.*, ACS Nano **9**, 5876 (2015)



Quantum matter assembled from single atoms & photons

(H. Jeff Kimble & Oskar Painter)

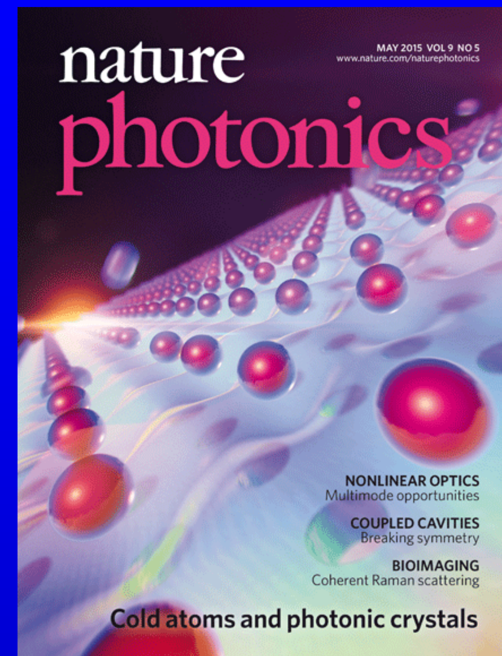
- **Technical approach**

  This research effort employs nano-photonic techniques to develop unique quantum “meta-matter” that consists of assemblies of nanostructured dielectric materials and optically-trapped ultra-cold atoms, with the atom-atom interactions mediated by photons.

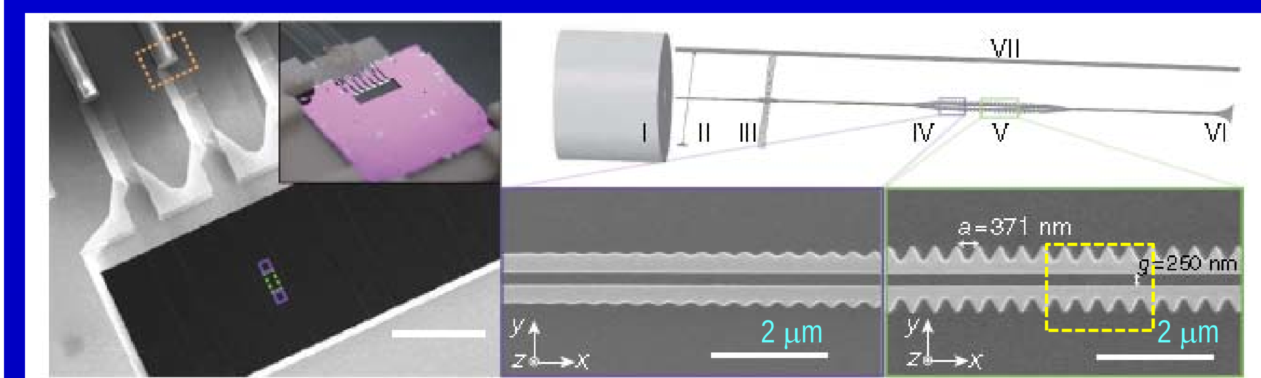
- **Ultimate objective**

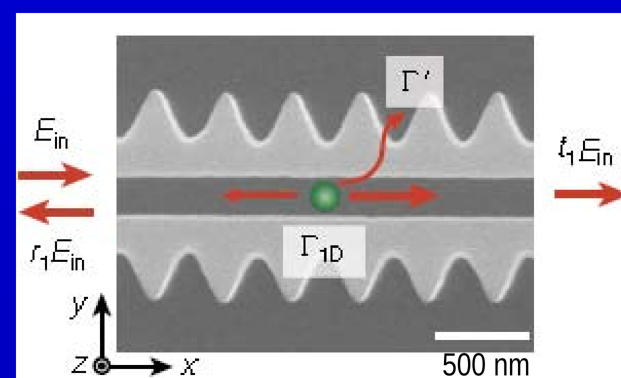
  These novel quantum materials will expand our understanding of new quantum states of matter and enable new quantum information technologies.

Nature Photonics 9, 326 (2015)



Nature Communications 5, 3808 (2014)



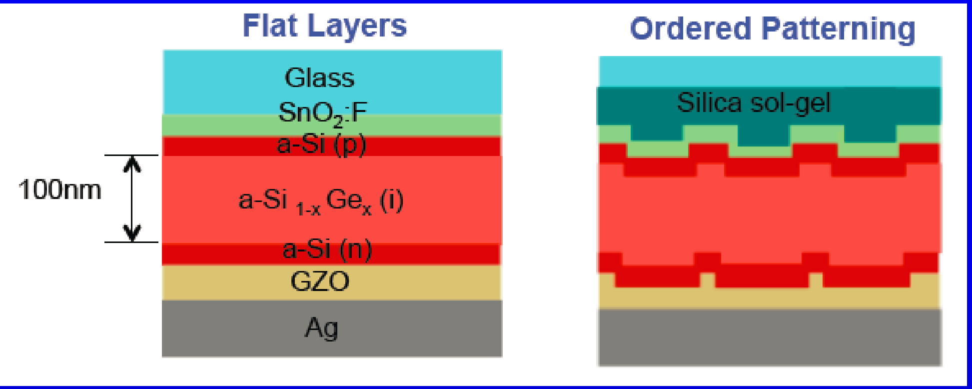


Nanotechnology for Sustainability

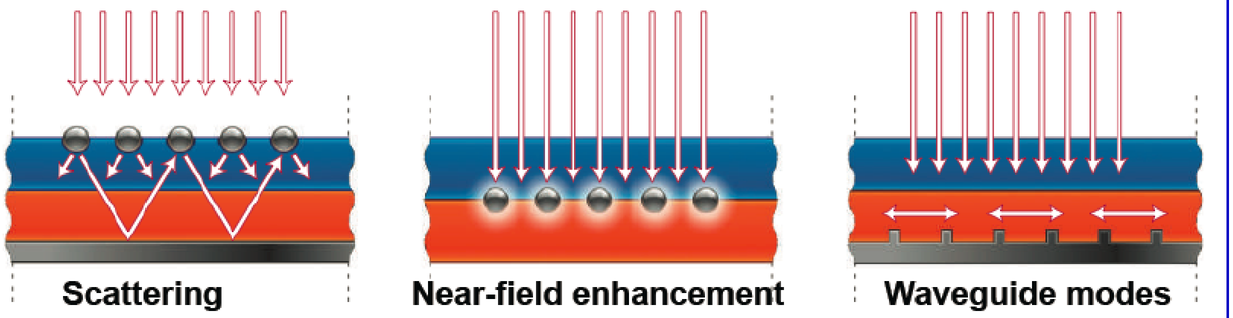
- Strategy for better solar cells:
  (Harry Atwater)

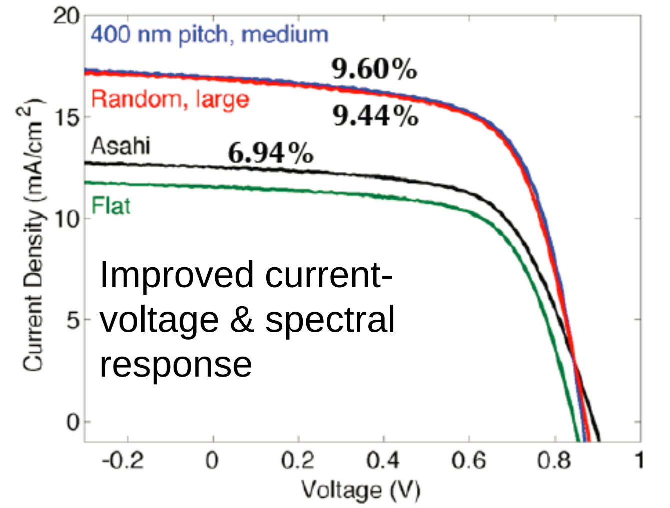
-- Light management in thin film cells;
-- Light trapping in a-Si/a-SiGe cells;
-- Random and nano-imprinted texture designs;
-- Combined optical & electrical modeling.

a-Si_xGe_{1-x}:H cell light trapping structures



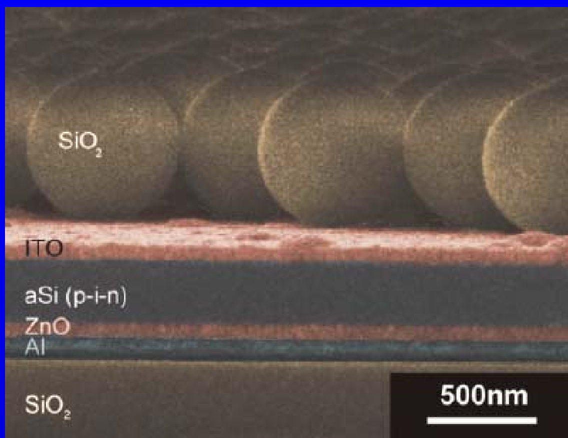
- Plasmonic photovoltaics for light trapping:





Nanotechnology for Sustainability

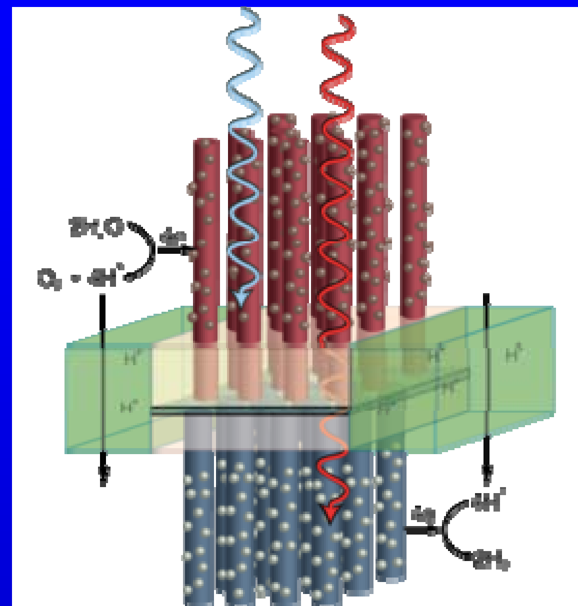
- Enhancing the photovoltaic efficiency via nano-engineering



Amorphous Si solar cells with resonant nano-particles on top

(Harry Atwater)

- Nano-structures for water splitting

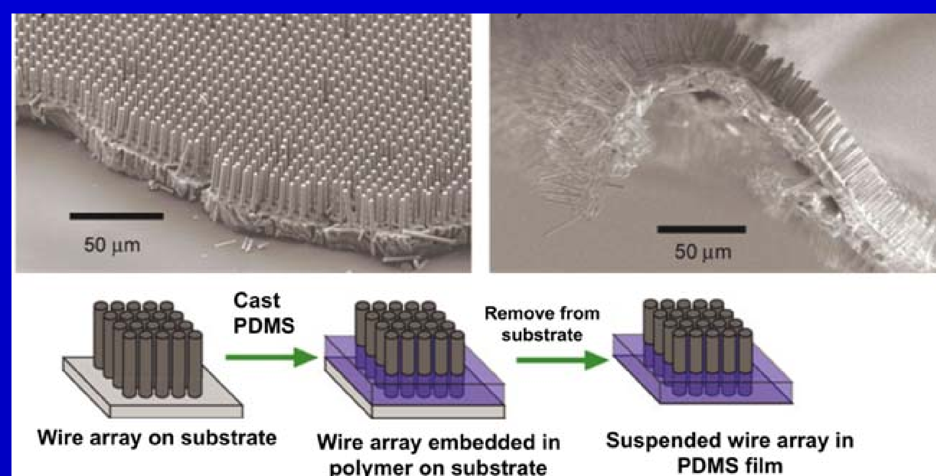


Nano-structured arrays of anodes & cathodes with oxidation and reduction catalysts and a central conductive membrane for ion exchange.

(Nate Lewis)

- Polymer-embedded silicon nano-wire arrays for flexible solar cells

(Harry Atwater & Nate Lewis)



4. Graphene: A Wonder Nanomaterial for S&T

The rise of graphene

- Unique physical properties
- Promising applications
- Major challenges for graphene-based technologies

A recent breakthrough

- Room-temperature scalable production of high-quality graphene

New research directions

- Nanoscale "strain engineering" of electronics & optoelectronics
- Next generation of interconnects
- Graphene-based photovoltaic cells
- Graphene nanoribbons for supercapacitors & energy storage

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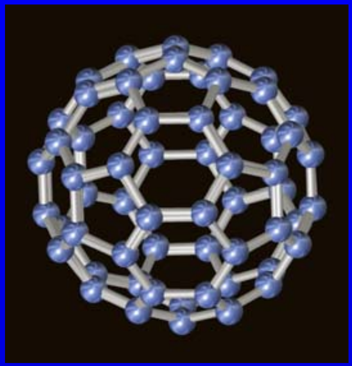
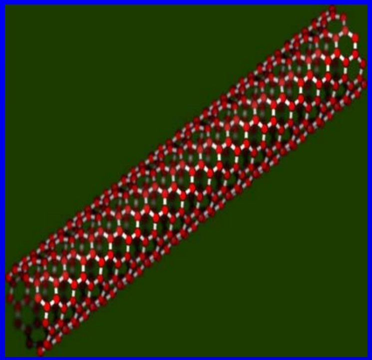
The Rise of Graphene

Carbon structures in different dimensions:

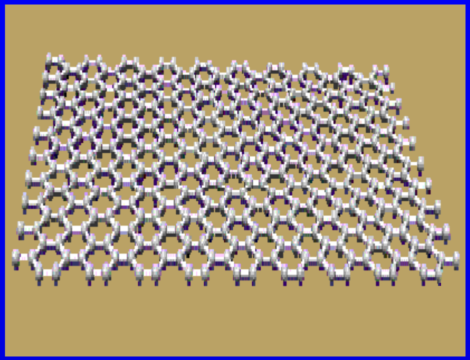
0D



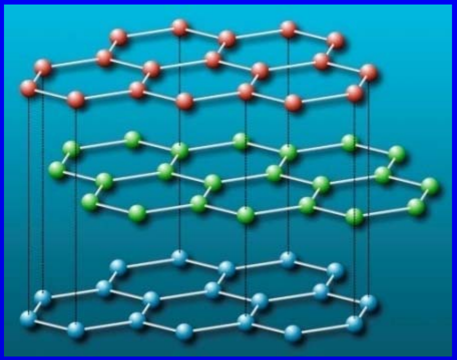
1D



2D



3D



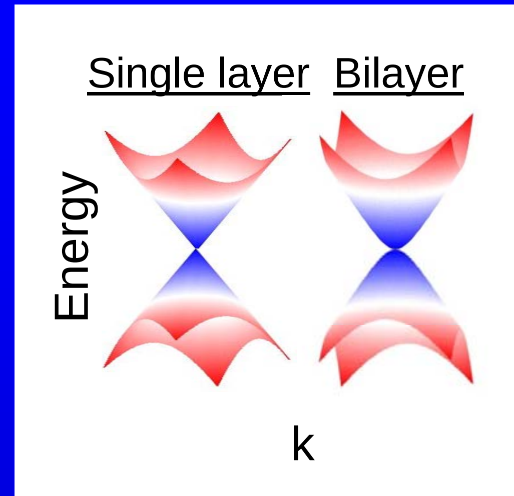
- Graphene consists of a monolayer of carbon atoms in a honeycomb lattice.
- Unique properties promising for a wide range of applications.
- First experimental isolation by Geim's group in 2004.
  [Novoselov et al, Science (2005).]
- Nobel prize in physics (2010) to Geim and Novoselov.

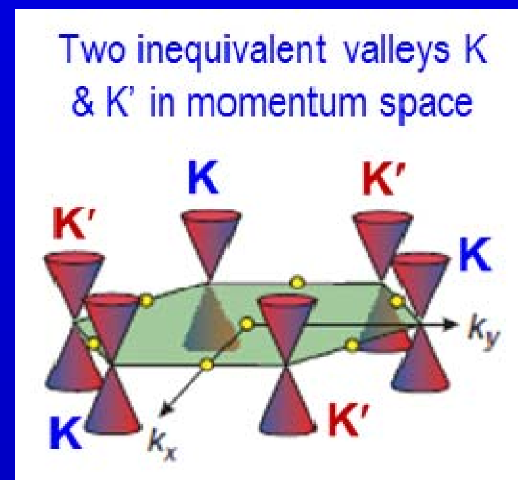
Review of unique properties of graphene

Unique physical properties:

- Massless Dirac fermions near the Dirac point (K, K').
- Klein tunneling.
- Anomalous quantum Hall effect.
- High thermal conductivity (~5000 W/mK).
- High current-carrying density (~ mA/μm width).
- High mobility (~ 20,000 cm^2/Vs in as-prepared samples, up to 300,000 cm^2/Vs if suspended).

  ⇔ Compared with silicon @ 2,000 cm^2/Vs
- Supports ballistic transport over large distances.
- Novel edge states.





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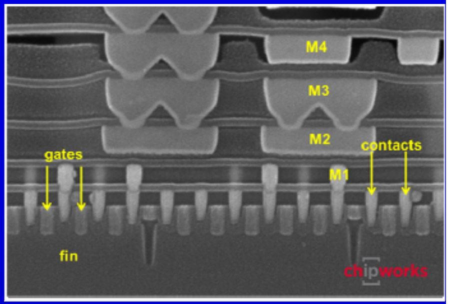
Promising Applications of Graphene

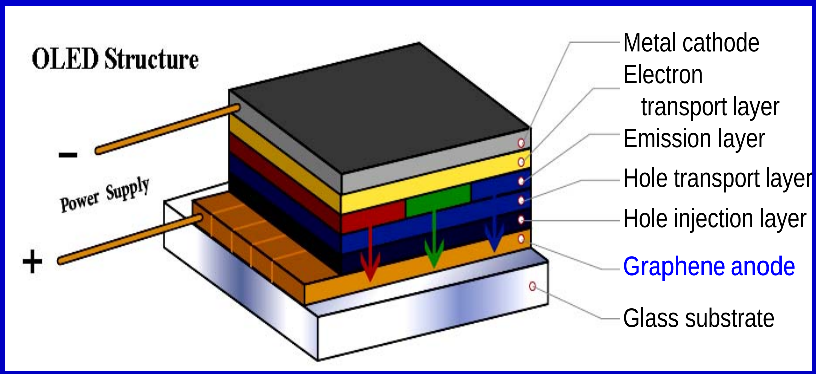
- Optoelectronic applications:
  - ➢ Solar cells, fuel cells, LED, displays, photo-detectors, lasers, etc.

- Electronic applications:
  - ➢ Non-volatile atomic switches for memory storage & stochastic algorithms;
  - ➢ Field-effect transistors (FET) for logics; super-capacitors;
  - ➢ 2D $\rightarrow$ compatible with lithographic techniques for beyond Si-CMOS, *e.g.*, new generation of interconnects.

- Chemical and biological applications:
  - ➢ Various types of sensors based on graphene; DNA sequencing;
  - ➢ Filtering and detoxication, etc.



- Spintronic applications:
  - ➢ Pure carbon room-temperature magnets, etc.
- Mechanical applications:
  - ➢ Super-lubricant; ultra-strong membrane, etc.
- Materials applications:
  - ➢ Metallic surface passivation, etc.



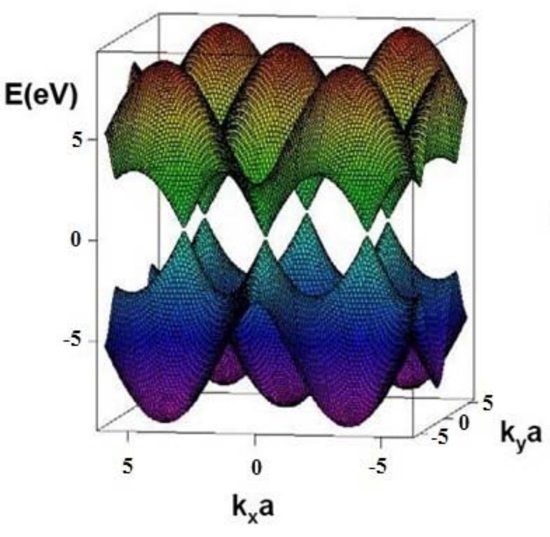
Electronic Bandstructures of Graphene

- In the tight binding approximation and assuming a perfectly ordered infinite system, there are 3 covalently bonded sp^2 and 1 $2p_z$ conduction electrons.
- The resulting $E_{2D}(k)$ band structure is

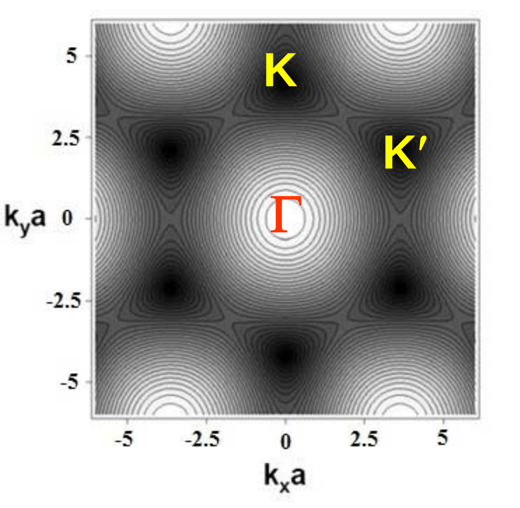
Near the "Dirac points" K & K'

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

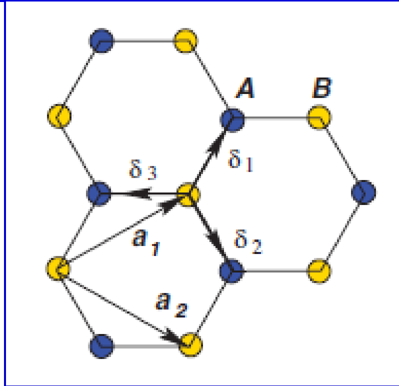
The energy dispersion relation of 2D graphene:



First Brillouin zone in the reciprocal space:

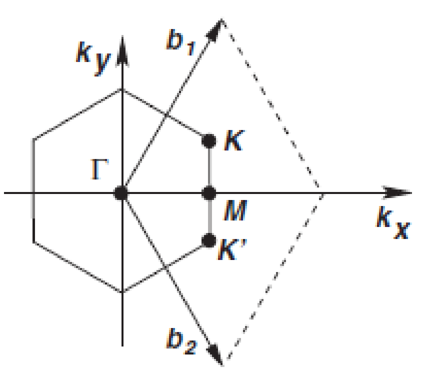


Two sublattices in the real space:



(Two lattice vectors a_1 and a_2)

The first Brillouin zone of graphene:



(Non-equivalent K and K′ valleys)

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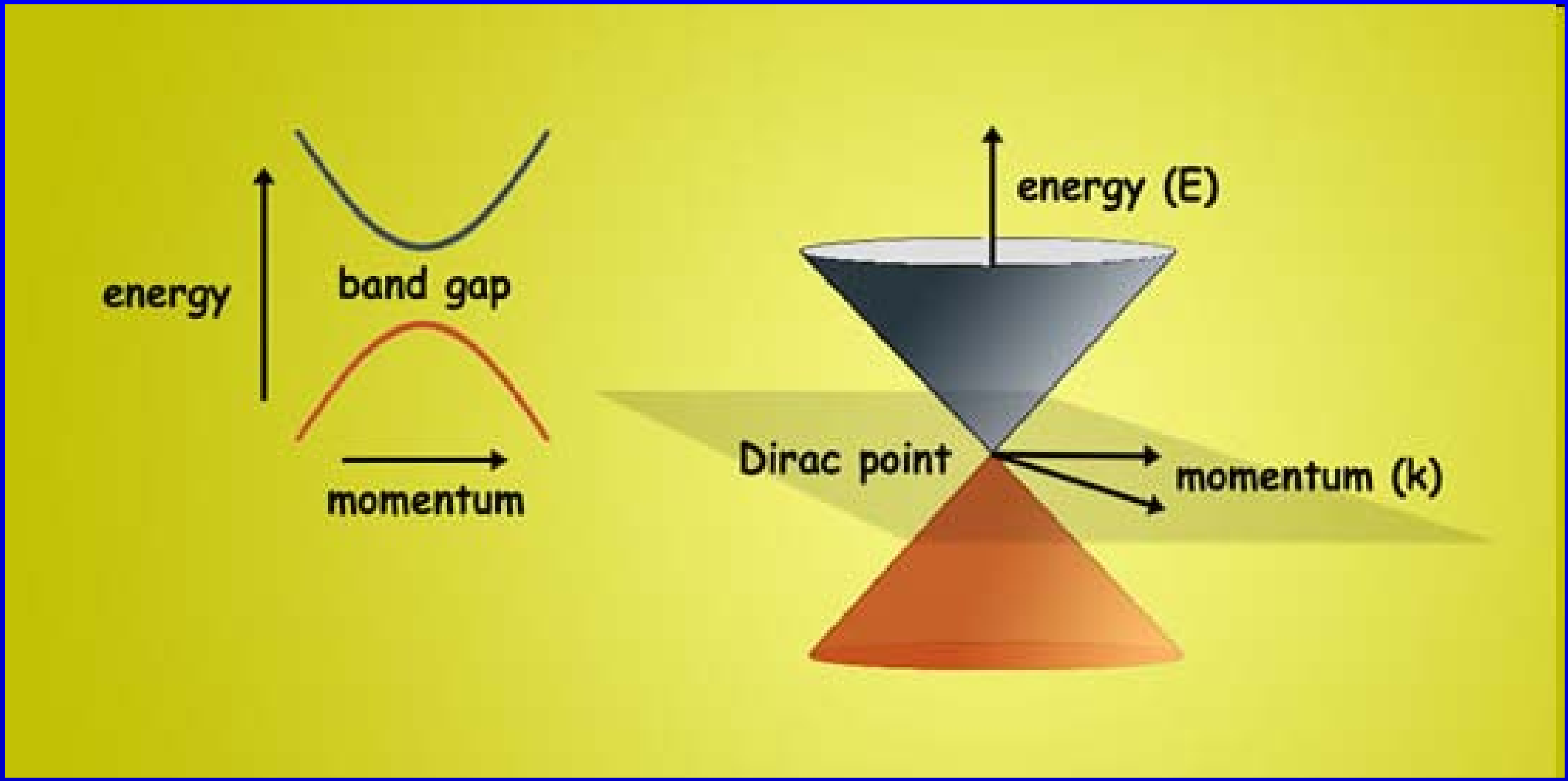
Dirac Cones & Semi-metallic Properties of Graphene

Conventional semiconductors (with finite energy gaps):

Semi-metallic Graphene (with zero-energy gap):



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

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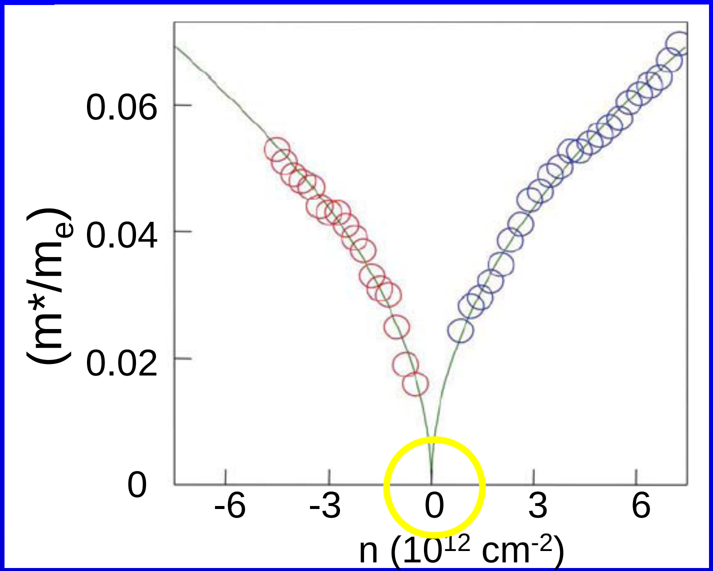
Massless Dirac Fermions & Linear Dispersion Relation

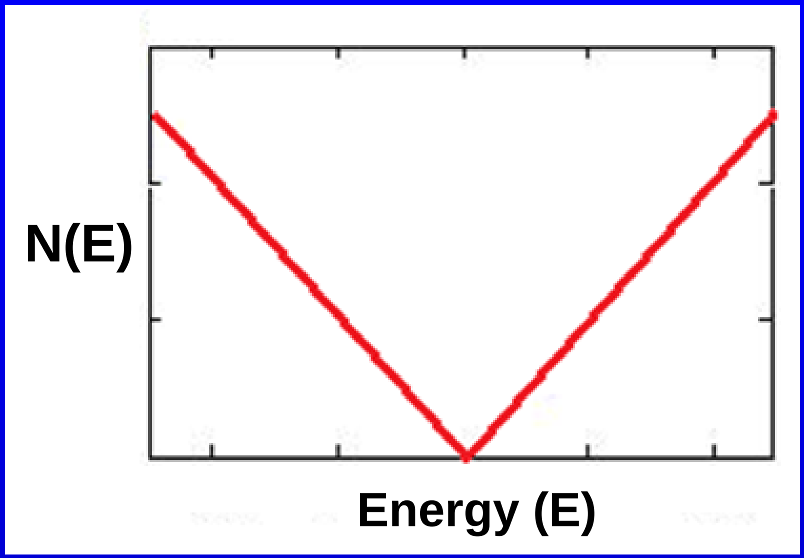
Cyclotron mass of carriers



Cyclotron mass: $m^* = (n\pi)^{1/2}/v_F$
Fermi velocity: $v_F \sim 10^6$ m/s
Carrier areal density: n

→ Carriers are massless at the Dirac point.

Electronic density of states N(E)



- The energy dispersion relation $E(k) \sim \pm \hbar v_f |\mathbf{k}|$ and 2D nature leads to a linear density of states $N(E) \sim |E - E_{Dirac}|$ that vanishes at the Dirac point E_{Dirac}.

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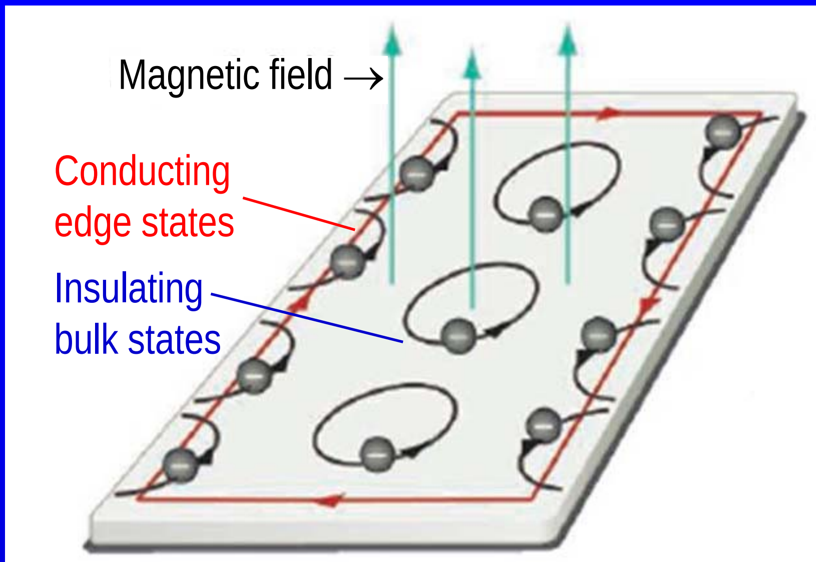
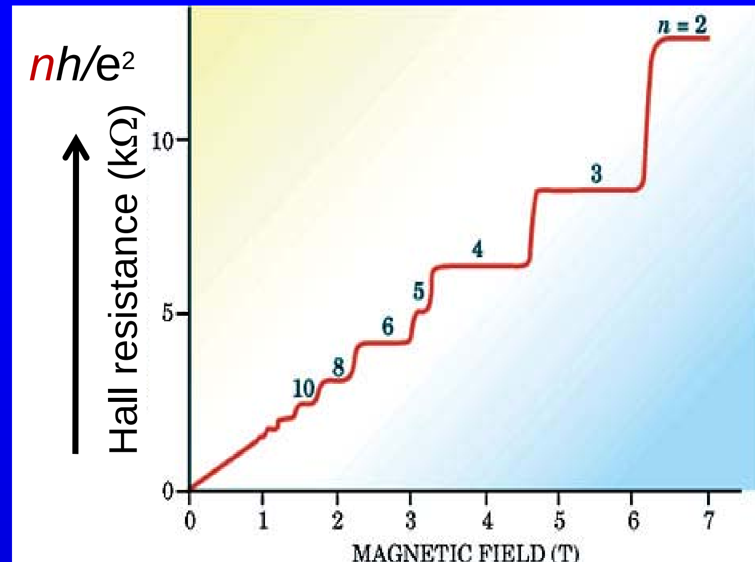
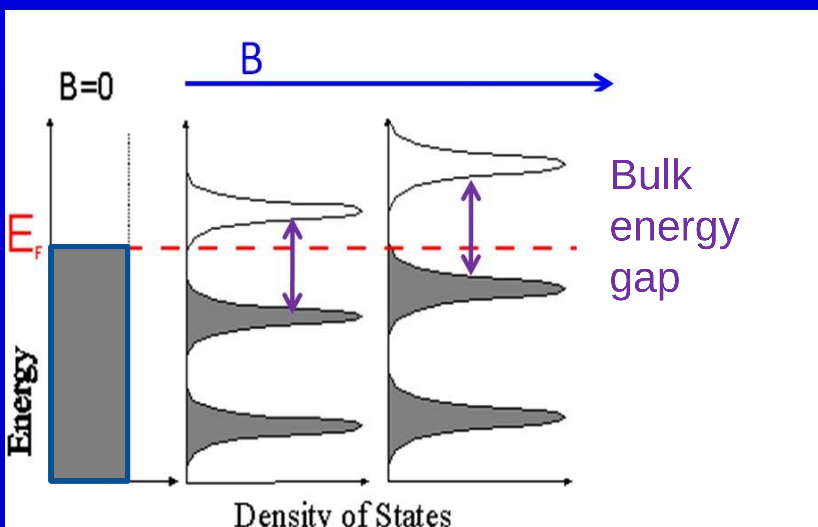
Integer Quantum Hall effect (IQHE)





Broken time-reversal symmetry



Hall conductance: $\sigma_{xy} = \boldsymbol{n}(e^2/h)$

n: Chern number (edge states)

$$n = \frac{1}{2\pi}\int_{BZ}[\nabla_{\mathbf{k}} \times \mathbf{A}(k_x, k_y)]_z d^2\mathbf{k}$$

$$\mathbf{A} = -i\langle u_{\mathbf{k}}|\nabla_k|u_{\mathbf{k}}\rangle$$

Topological properties (TKNN invariant)

Finite *n* → topologically protected edge-states

Magnetic field-induced quantum Hall effects (QHE) in graphene

- In graphene, the carrier density (n) is related to the energy (E), momentum (k) and Fermi velocity (v_F) by the relations (for $B = 0$):

$$n = (k_F)^2/\pi = (E/v_F)^2/\pi$$

- For $B > 0$, the cyclotron frequency (ω_c) is given by:

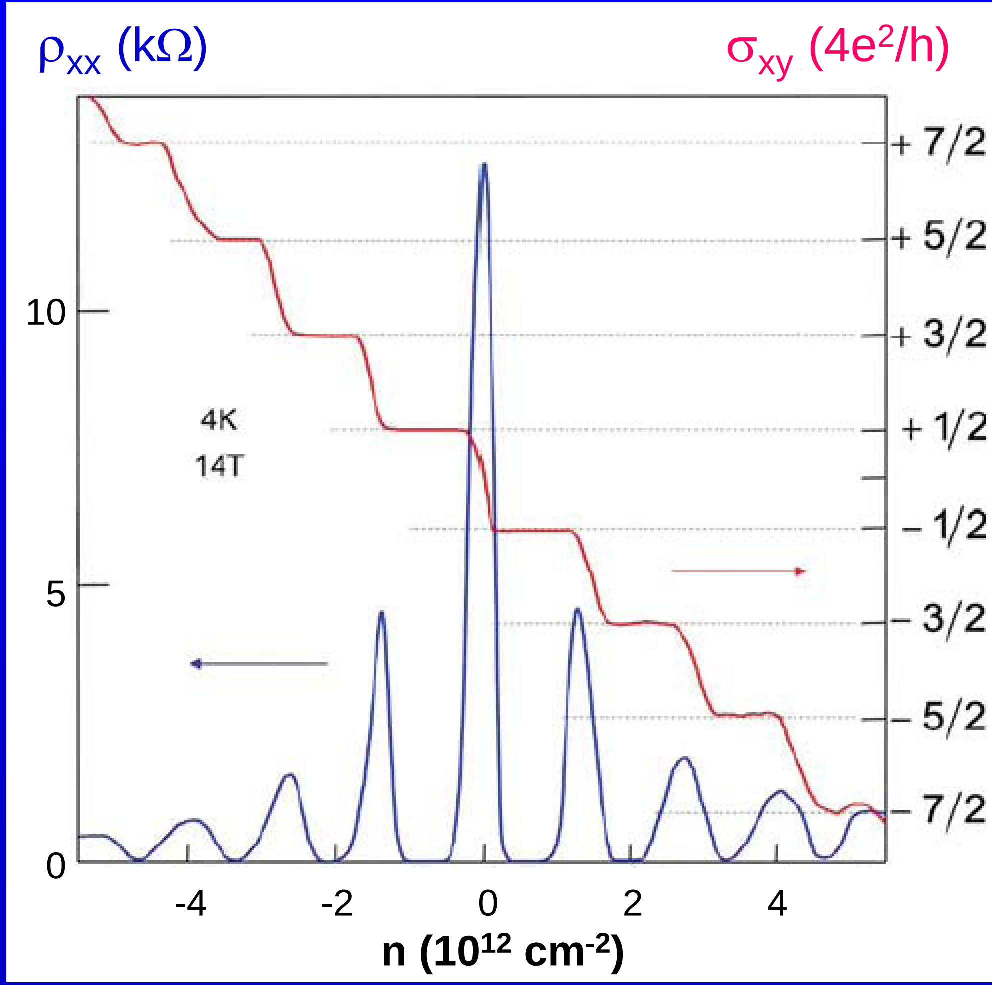
$$\omega_c = 2^{1/2}(v_F/l_B) = (2eB)^{1/2}v_F$$

- Landau levels:

$$E_n = \mathrm{sgn}(n)\sqrt{2e\hbar v_F^2 B|n|}$$

Longitudinal resistivity

Hall conductivity



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Gauge fields induced by intrinsic disorder

Strained-induced pseudo-magnetic field & quantum Hall effect

- A two-dimensional strain field $u_{ij}(x,y)$ on graphene leads to a gauge **A** :

$$\mathbf{A} = \frac{-(\partial \ln t/\partial \ln a)}{a}\begin{pmatrix} u_{xx} - u_{yy} \\ -2u_{xy} \end{pmatrix} \equiv \frac{\beta}{a}\begin{pmatrix} u_{xx} - u_{yy} \\ -2u_{xy} \end{pmatrix}$$

t: nearest hopping constant
x-axis: along the zigzag direction

a: lattice constant
$\beta = 2 \sim 3$

- A non-trivial gauge **A** leads to a pseudo-magnetic field $\mathbf{B}_s$ and a magnetic length l_B:

$$\mathbf{B}_S = \nabla \times \mathbf{A} \qquad (\ell_B)^{-2} \equiv \frac{2\pi B_s}{\Phi_0} = \frac{\beta}{a}\left(\frac{\bar{u}}{L}\right) \sim \frac{\beta}{aL}\left(\frac{z_0}{L}\right)^2$$

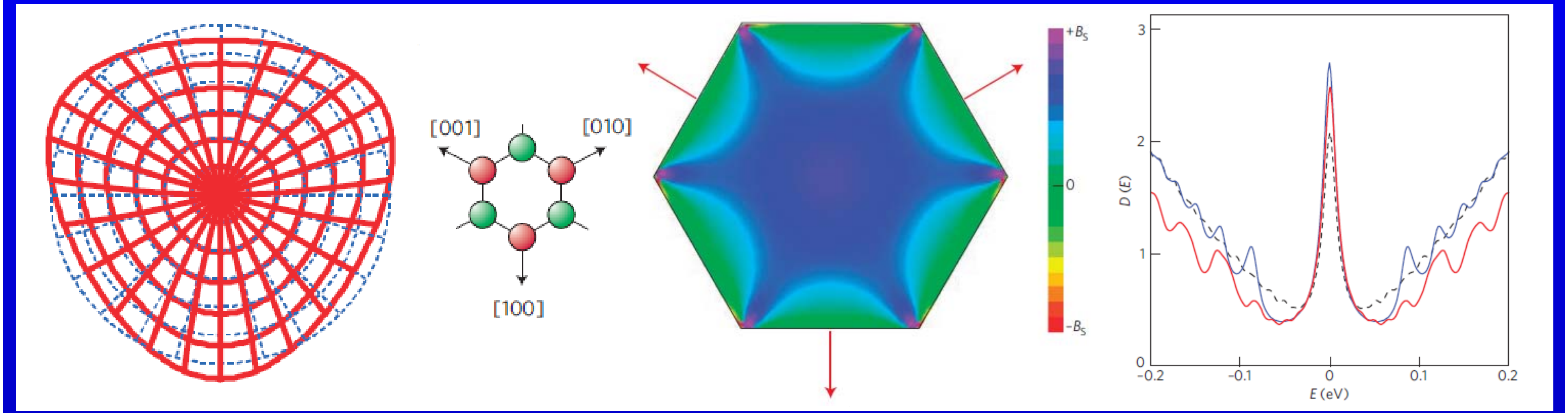
z_0: height fluctuation
u: displacement field

L: length of strained region
Φ_0: flux quantum

Strain-induced pseudo-magnetic fields & quantum Hall effects (QHE)

- The occurrence of strain-induced zero-field quantum Hall effect (QHE) will lead to sharp peaks in the density of states (DOS) at discrete energy levels E_n that can be directly detected with STM.

- Example: strain-induced pseudo-magnetic fields & Landau levels in graphene



shear strain on graphene

strain-induced pseudo-magnetic fields B_S

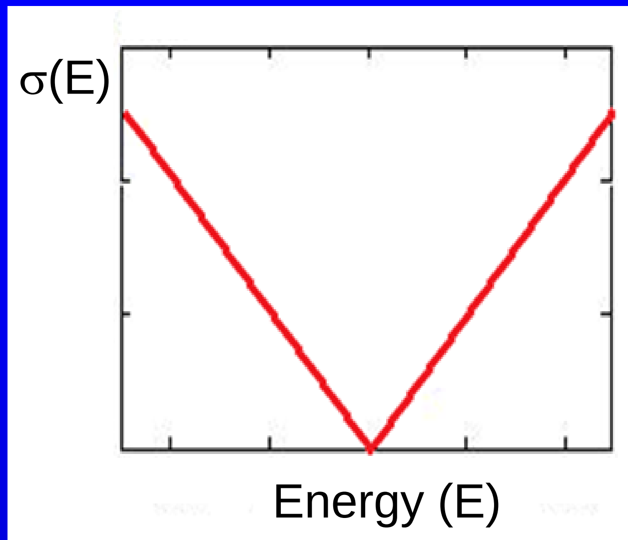
DOS-vs-energy for strained graphene under various Bs

F. Guinea *et al*, Nat. Phys. **6** (2010)

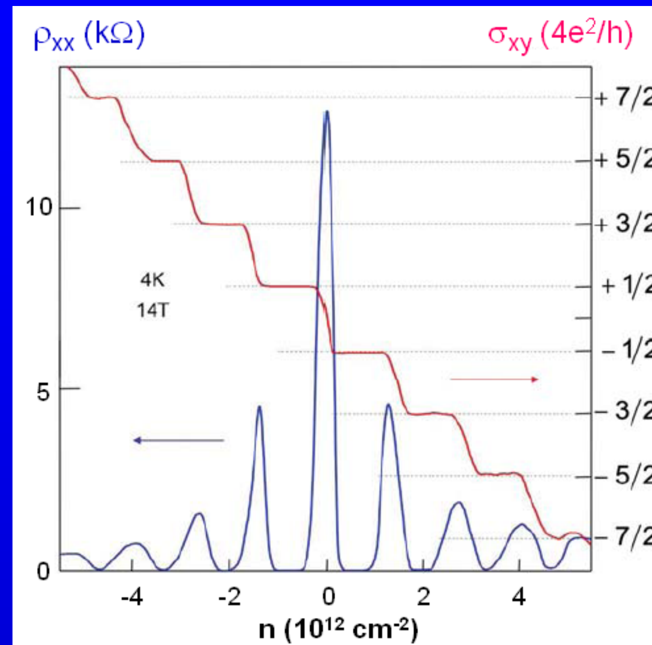
Caltech

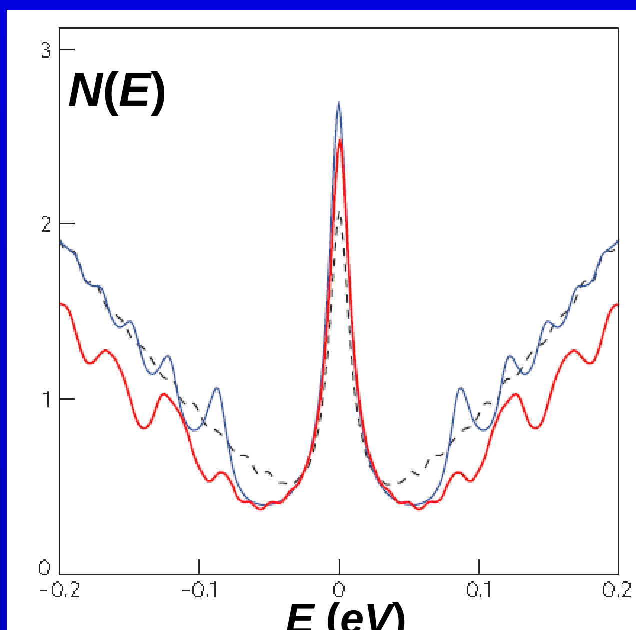
Comparison of graphene conductance in zero, finite and pseudo magnetic fields

Zero-field
(H = 0)



Finite field
(H > 0)





Strain-induced pseudo-magnetic field ($B_S >> 0$)

F. Guinea *et al*, Nat. Phys. 6 (2010)

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New Breakthroughs & Superior Properties of Room-Temperature Grown Graphene

❖ Consequences of high-temperature processing:

- ❑ Incompatibility with current technology for lithographic device processing
  - Growth temperature too high, surfaces too rough & defect density too high for most lithographic processes.

- ❑ Combined strain-induced pseudo-magnetic fields and charging effects could reduce the electronic mobility by orders of magnitude
  - Consistent with experimental findings

- ❑ High-density of growth defects result in compromises of mechanical integrity
  - Graphene samples typically flakes off into small pieces upon transfer from the growth substrate to other surfaces

Solution:

- ➢ Room-temperature growth of large-area high-quality graphene on Cu substrates

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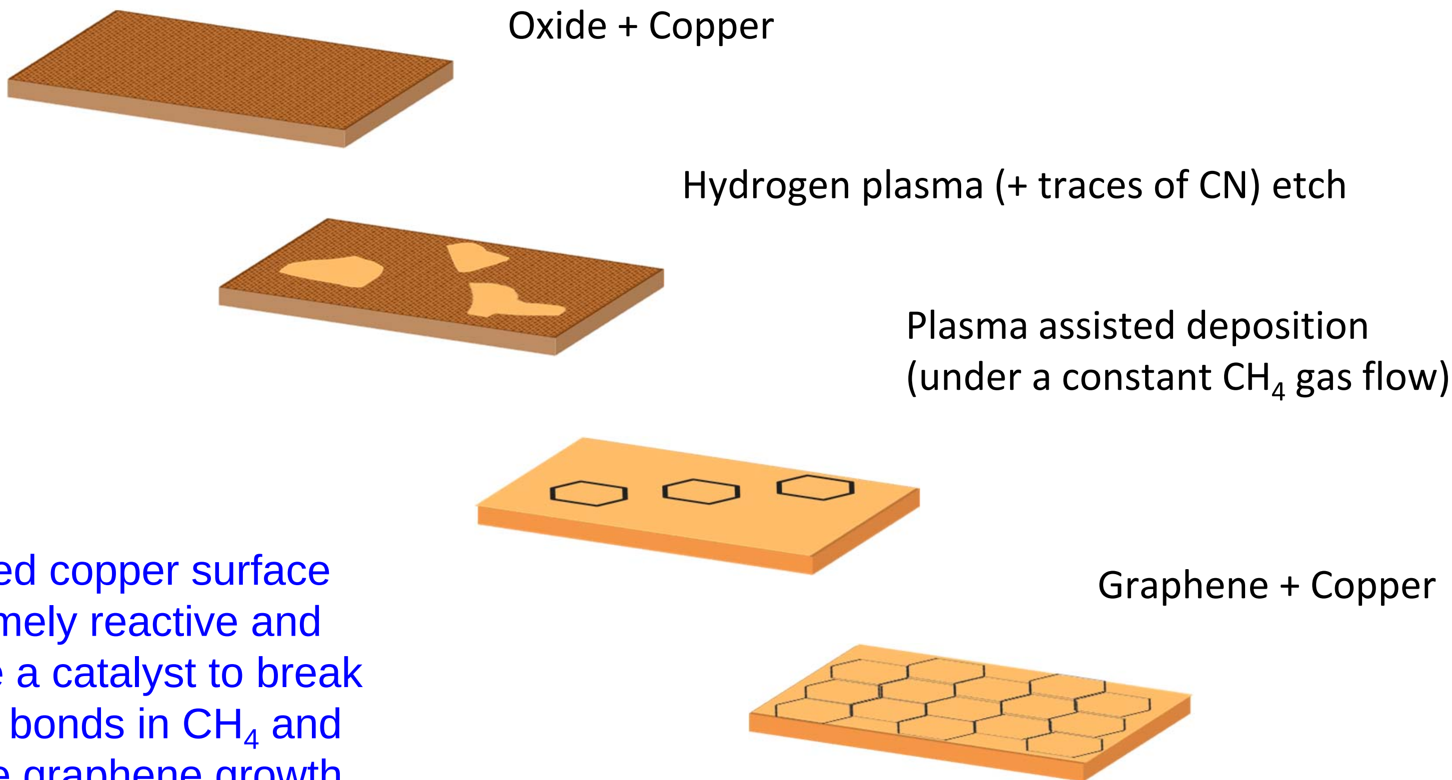
A new growth mechanism w/ plasma assistance



A cleaned copper surface is extremely reactive and acts like a catalyst to break the C-H bonds in CH_4 and nucleate graphene growth.

In contrast to the high-temperature CVD process where copper reaches nearly its melting point so that carbon dissolves into copper until it saturates and then nucleate into graphene sheets.

Promising low-temperature growth for high-quality large-area graphene

- **Superior crystalline properties & mechanical integrity:**
  - Much reduced strain & much smoother surface morphology.
  - Single crystalline samples (up to 1 cm^2) & fewer defect densities.
  - Much higher & consistent electrical mobility (~ 60,000 cm^2/V-s at 300 K).
  - Single-step fast growth (5 ~ 15 minutes).

- **High-quality spectral characteristics over ~ cm^2 areas:**
  - Reproducible controlled process for monolayer growth.
  - Controllable multi-layer growth.
  - Industrial-size growth may be achievable.

➡ **Many large-scale electrical & mechanical applications become feasible.**

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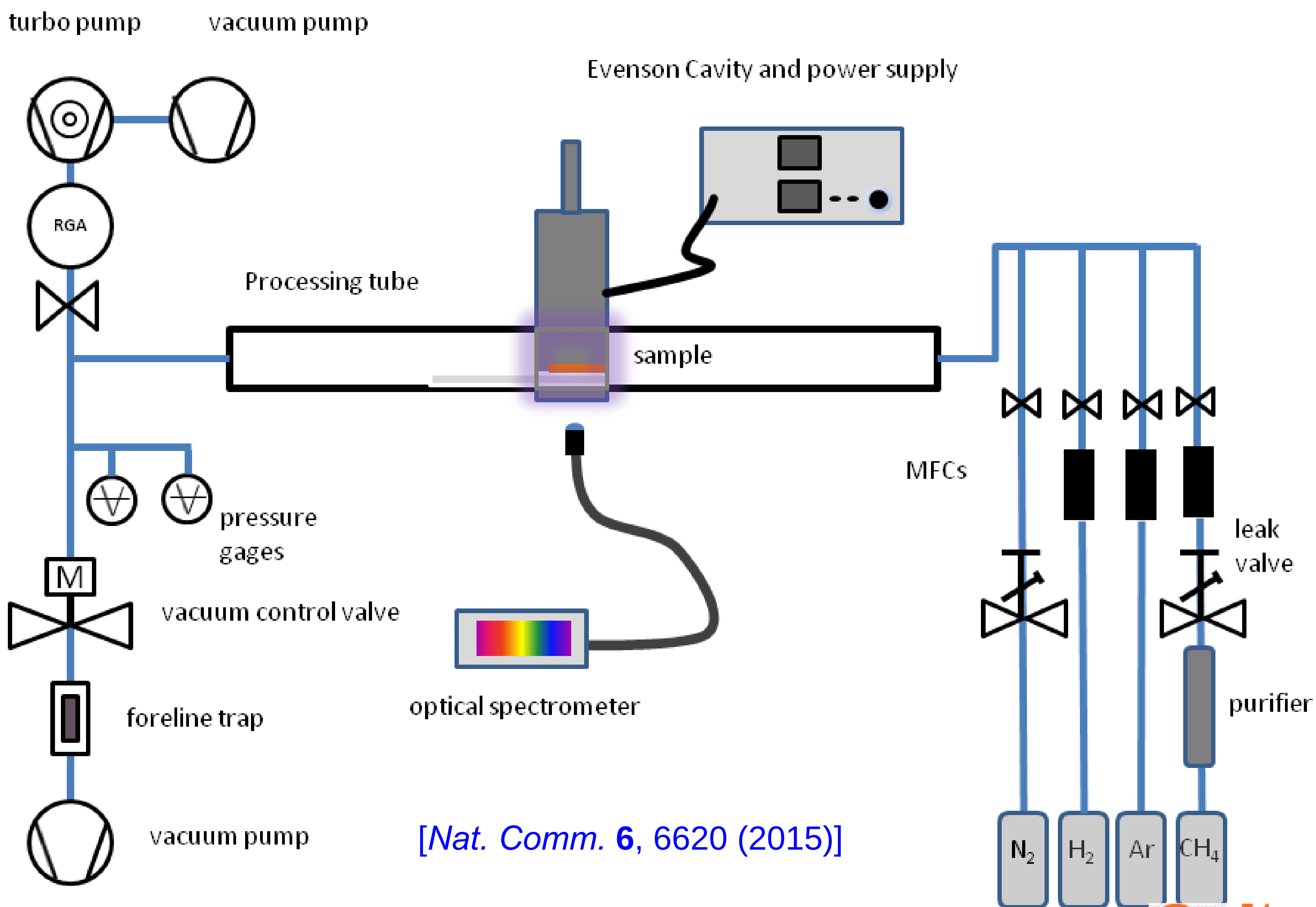
Experimental setup of the PECVD growth system



[*Nat. Comm.* **6**, 6620 (2015)]

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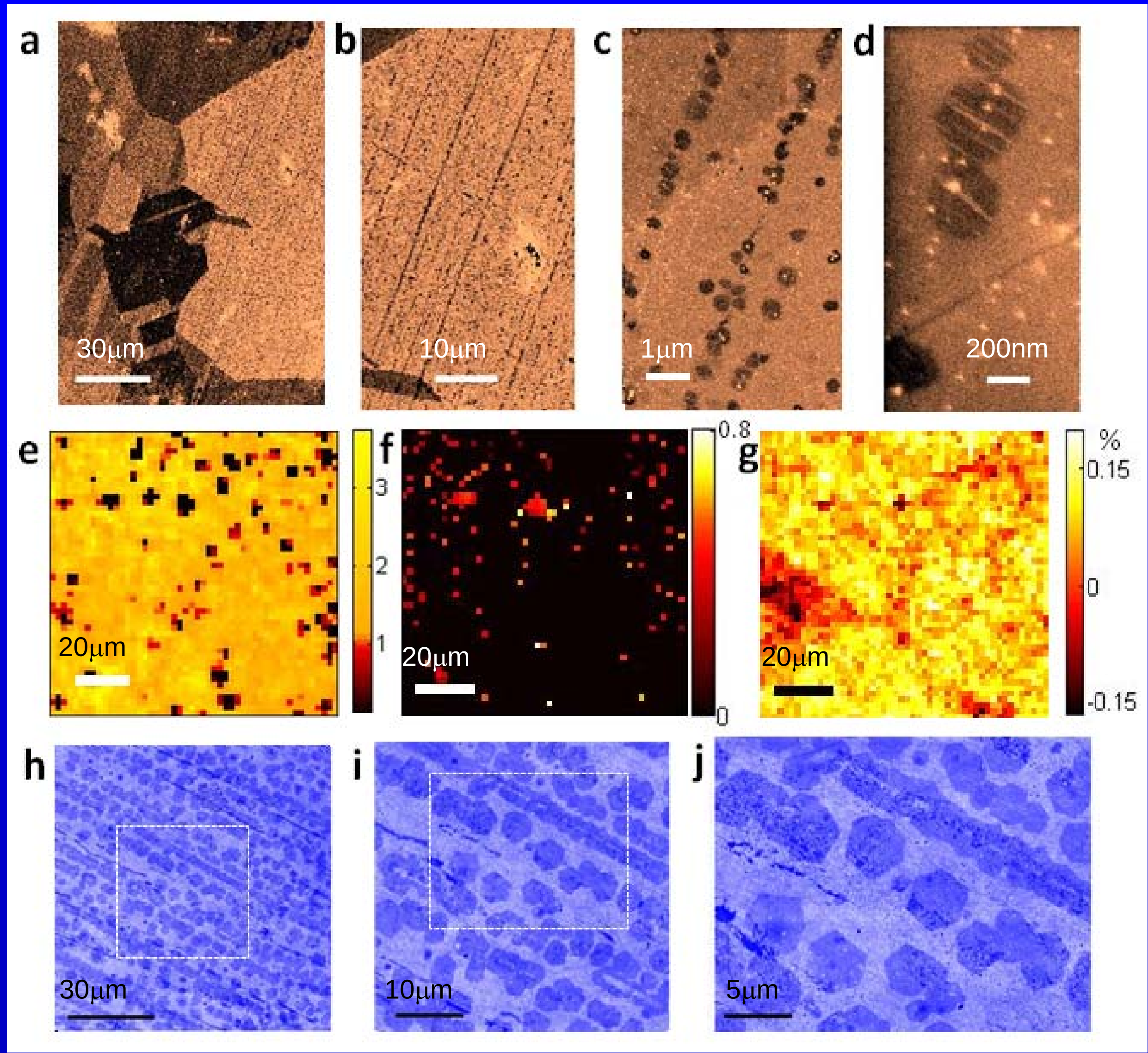
Guided growth of graphene by low-temperature PECVD

a)-d): SEM images of early-stage PECVD-growth of graphene on copper

e): 2D/G Raman spectral map of a monolayer PECVD graphene; f): D/G Raman spectral map of the same area; g): Strain map of the same

h)-i): SEM images of second layer graphene growth

[*Nat. Comm.* **6**, 6620 (2015)]



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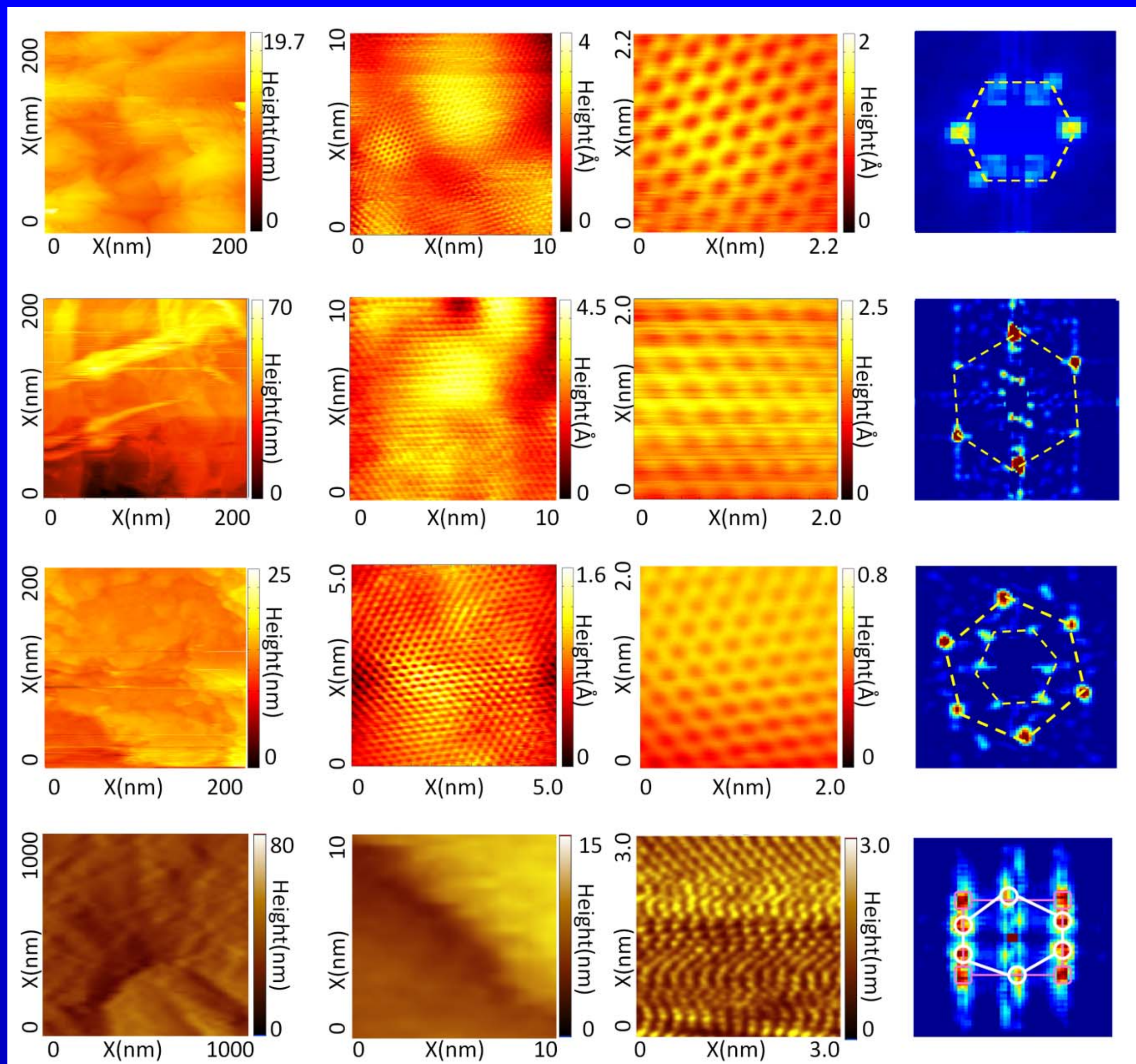
Comparison of the atomic order between high-T & LT-grown graphene



LT-grown on Cu foil — Largely ordered structure w/ slight distortion

LT-grown on Cu (100) — Microscopically ordered structure w/ Moiré patterns

LT-grown on Cu (111) — Microscopically ordered structure w/ Moiré patterns

High-T grown on Cu foil — Severely distorted atomic structures

Caltech

Comparison of microscopic strain between high-T & LT-grown graphene

LT-grown on Cu foil

Small strain

LT-grown on Cu (100)

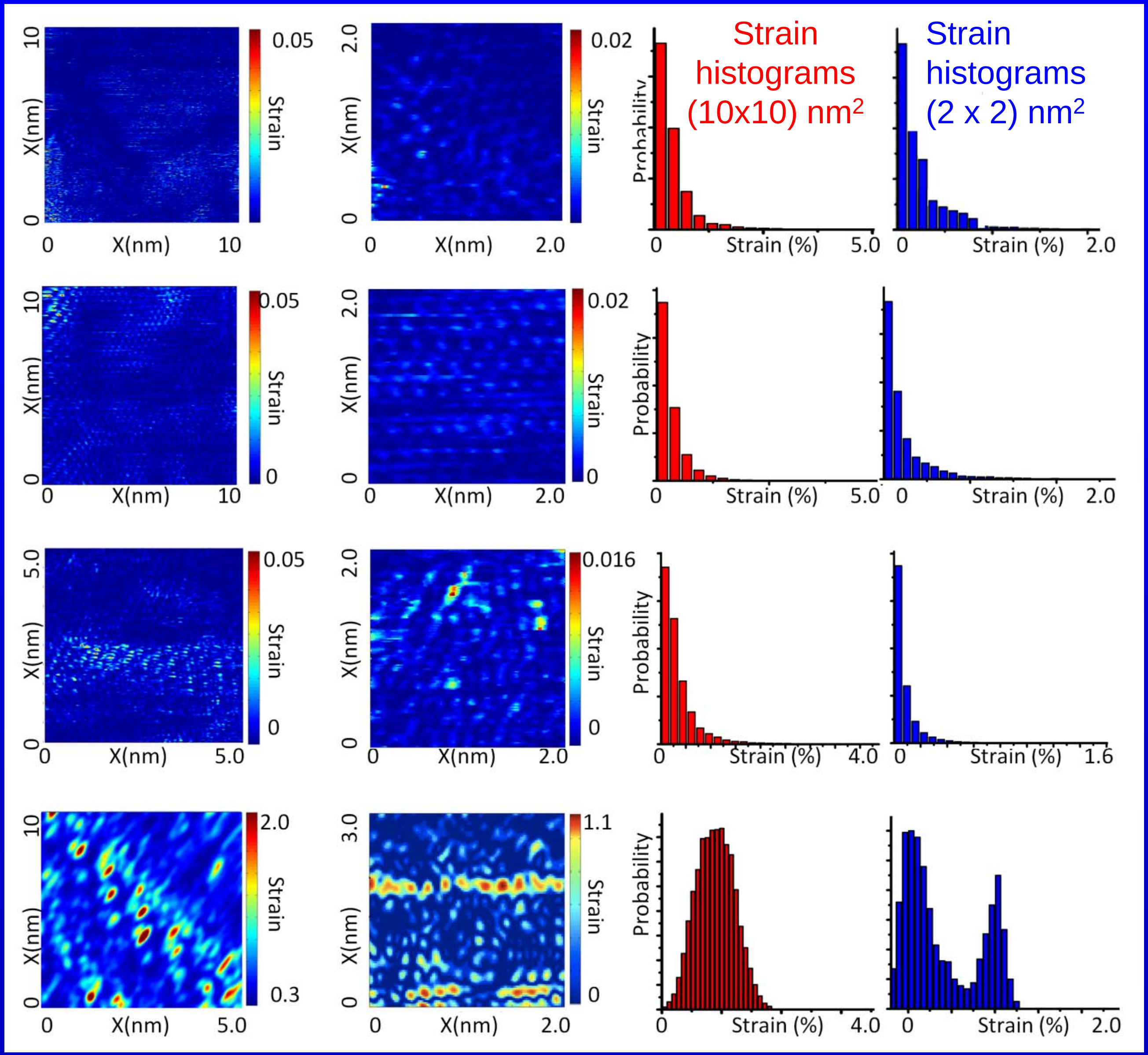
Small strain

LT-grown on Cu (111)

Smallest strain

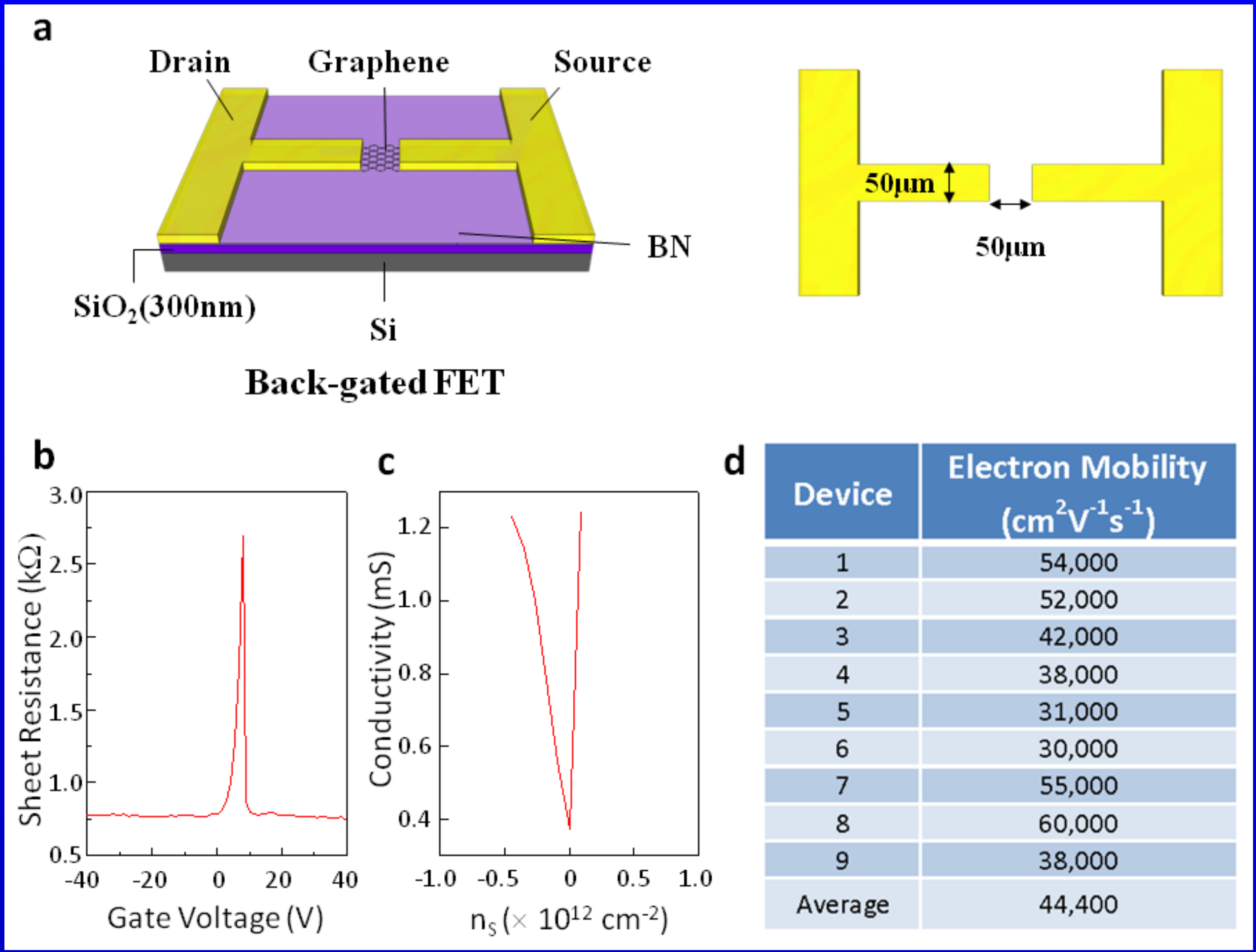
High-T grown on Cu foil

Large & non-uniform strain



Intrinsic field-effect mobility measurements of LT-grown graphene

- Intrinsic field-effect mobility of large RT-graphene (~ 1 cm^2) & transferred to BN:
  - ➢ Mobility ~ 60,000 cm^2/V-s at 300 K, determined from the slope of σ-*vs.*-*n*.



Device	Electron Mobility ($cm^2V^{-1}s^{-1}$)
1	54,000
2	52,000
3	42,000
4	38,000
5	31,000
6	30,000
7	55,000
8	60,000
9	38,000
Average	44,400

⇔ Better than the highest mobility (~ 37,000 cm^2/V-s) taken at 4.2 K on high-temperature CVD-grown graphene transferred to BN.

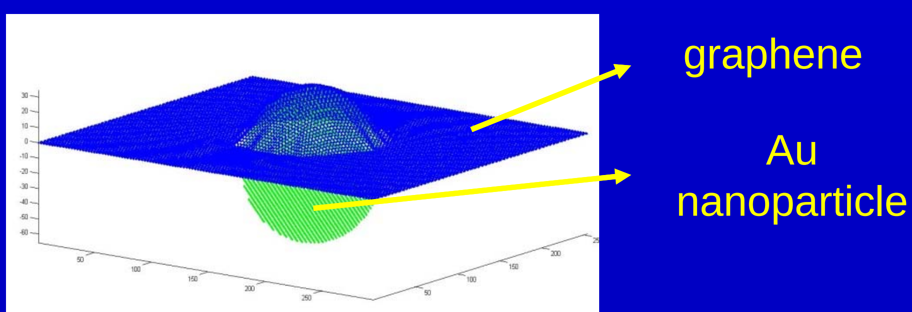
[*Nat. Comm.* **6**, 6620 (2015)]

Caltech

Theoretical simulations of nano-scale strain engineering via molecular dynamics (MD)

- LAMMPS – http://lammps.sandia.gov
- Create a monolayer graphene sheet and an Au nanoparticle
- Fix the boundary atoms of the graphene
- Move up the particle and relax the whole system until it's in the equilibrium states.
- Calculate
  - displacement field of carbon atoms: u_x, u_y, h
  - strain tensor: u_{xx}, u_{yy}, u_{xy}
  - gauge potential: A_x, A_y
  - pseudomagnetic field: B_s

N.-C. Yeh *et al.*, Acta Mechanica Sinica 32, 497 (2016)



$$u_{xx} = \frac{\partial u_x}{\partial x} + \frac{1}{2}\left(\frac{\partial h}{\partial x}\right)^2 \qquad u_{yy} = \frac{\partial u_y}{\partial y} + \frac{1}{2}\left(\frac{\partial h}{\partial y}\right)^2$$

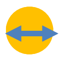
$$u_{xy} = \frac{1}{2}\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) + \frac{1}{2}\frac{\partial h}{\partial x}\frac{\partial h}{\partial y}$$

$$A_x(\vec{r}) = \frac{\beta}{a}[u_{xx}(\vec{r}) - u_{yy}(\vec{r})]$$

$$A_y(\vec{r}) = -2\frac{\beta}{a}u_{xy}(\vec{r}) \qquad B_s = |\nabla \times \mathbf{A}|$$

Simulation of graphene on nanoparticles

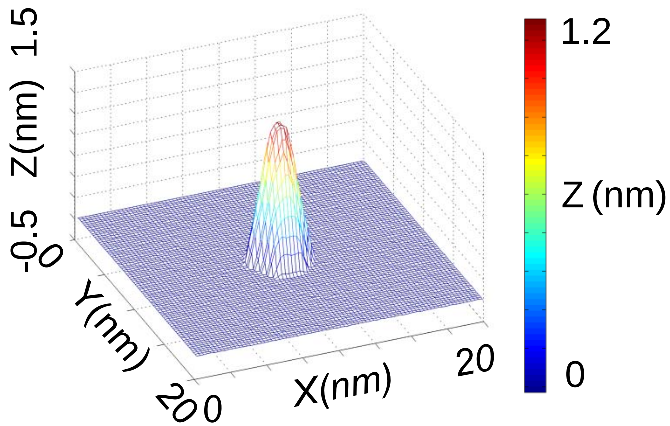
Au nanoparticle
diameter = 2.4nm

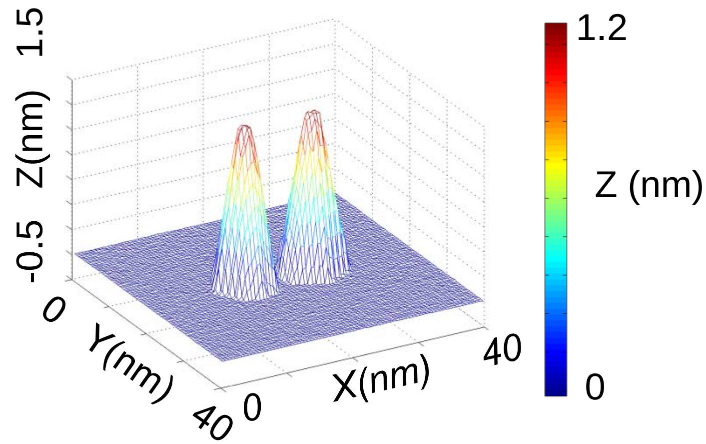


Graphene/Single Au nanoparticle

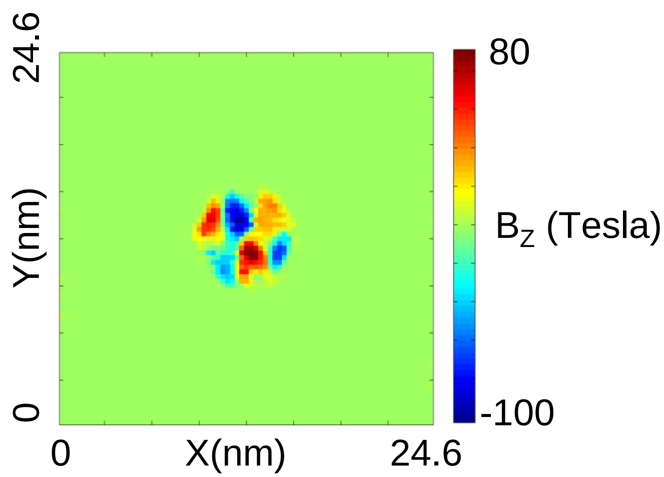
Graphene/Two Au nanoparticles

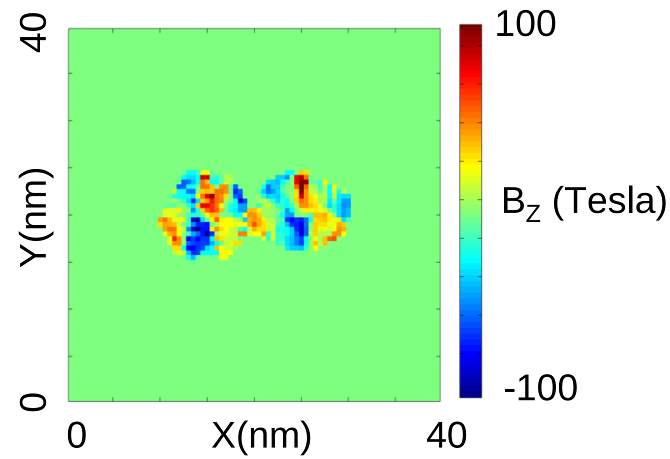
Graphene topography





Pseudomagnetic field





N.-C. Yeh *et al.*, Acta Mech. Sin. 32, 497(2016)

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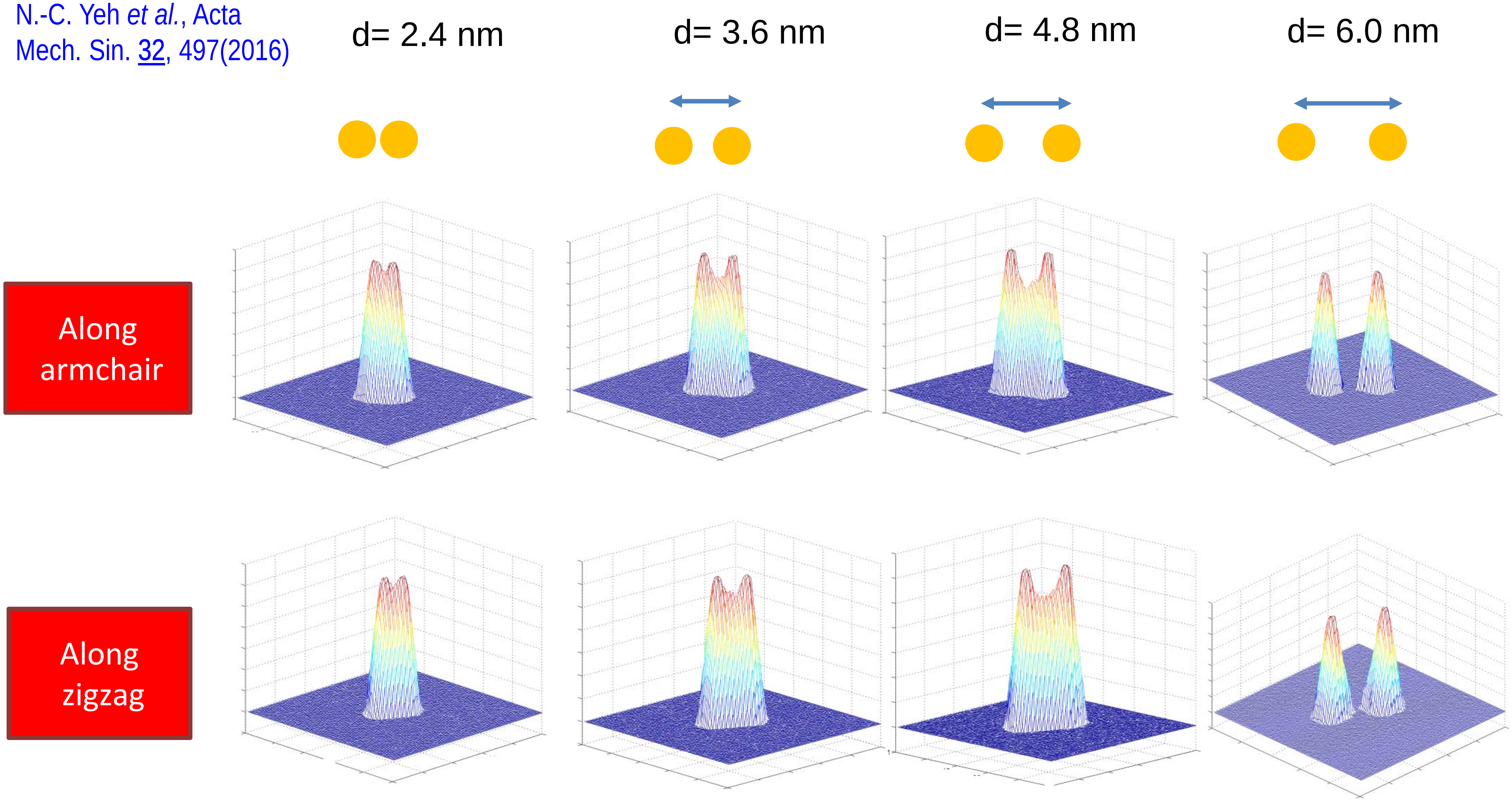
Topography evolution of graphene on two Au nanoparticles

N.-C. Yeh *et al.*, Acta Mech. Sin. <u>32</u>, 497(2016)



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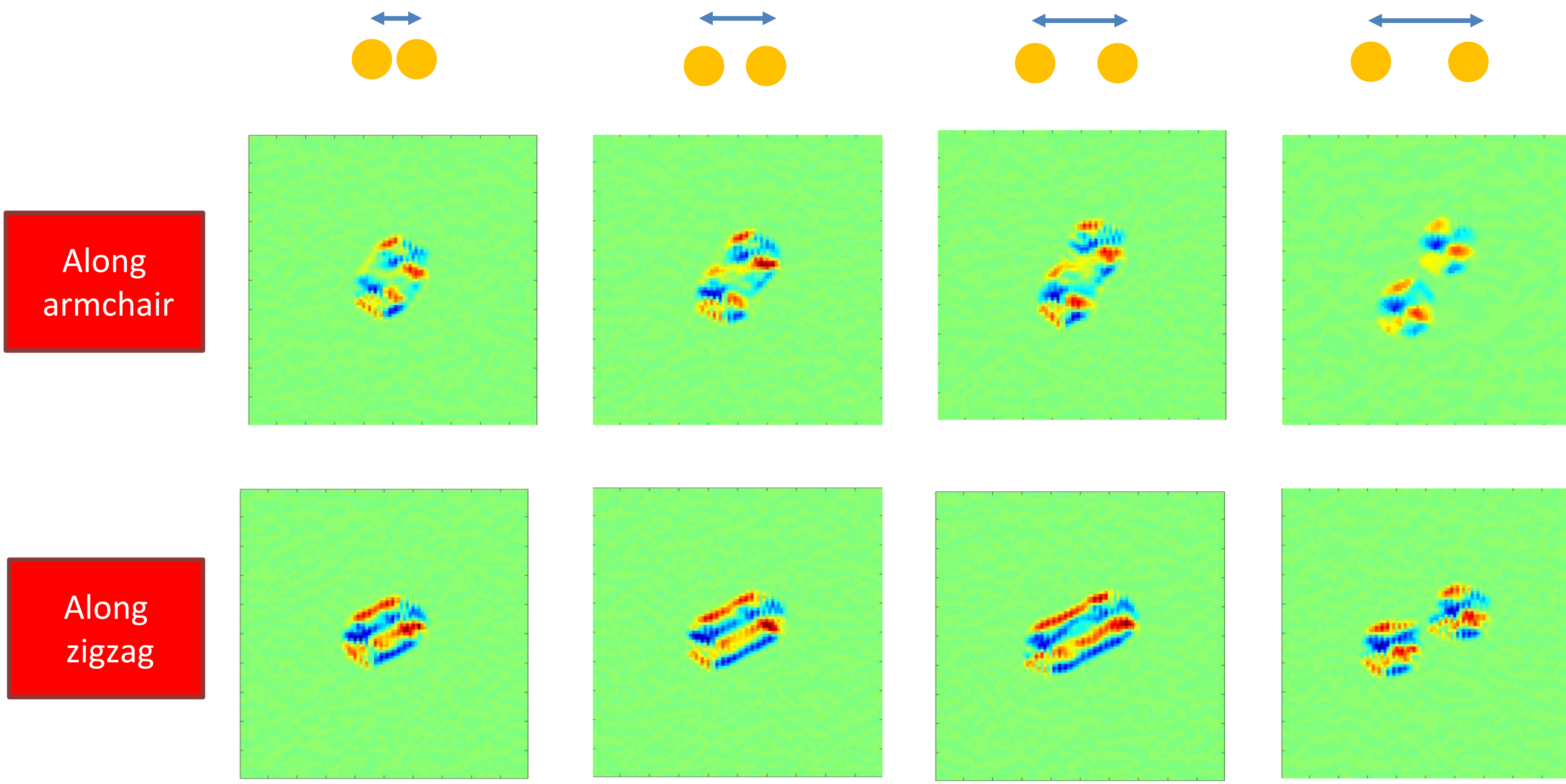
Pseudomagnetic field evolution of graphene on Au nanoparticles

N.-C. Yeh *et al.*, Acta Mech. Sin. (2016)

d= 2.4 nm d= 3.6 nm d= 4.8 nm d= 6.0 nm



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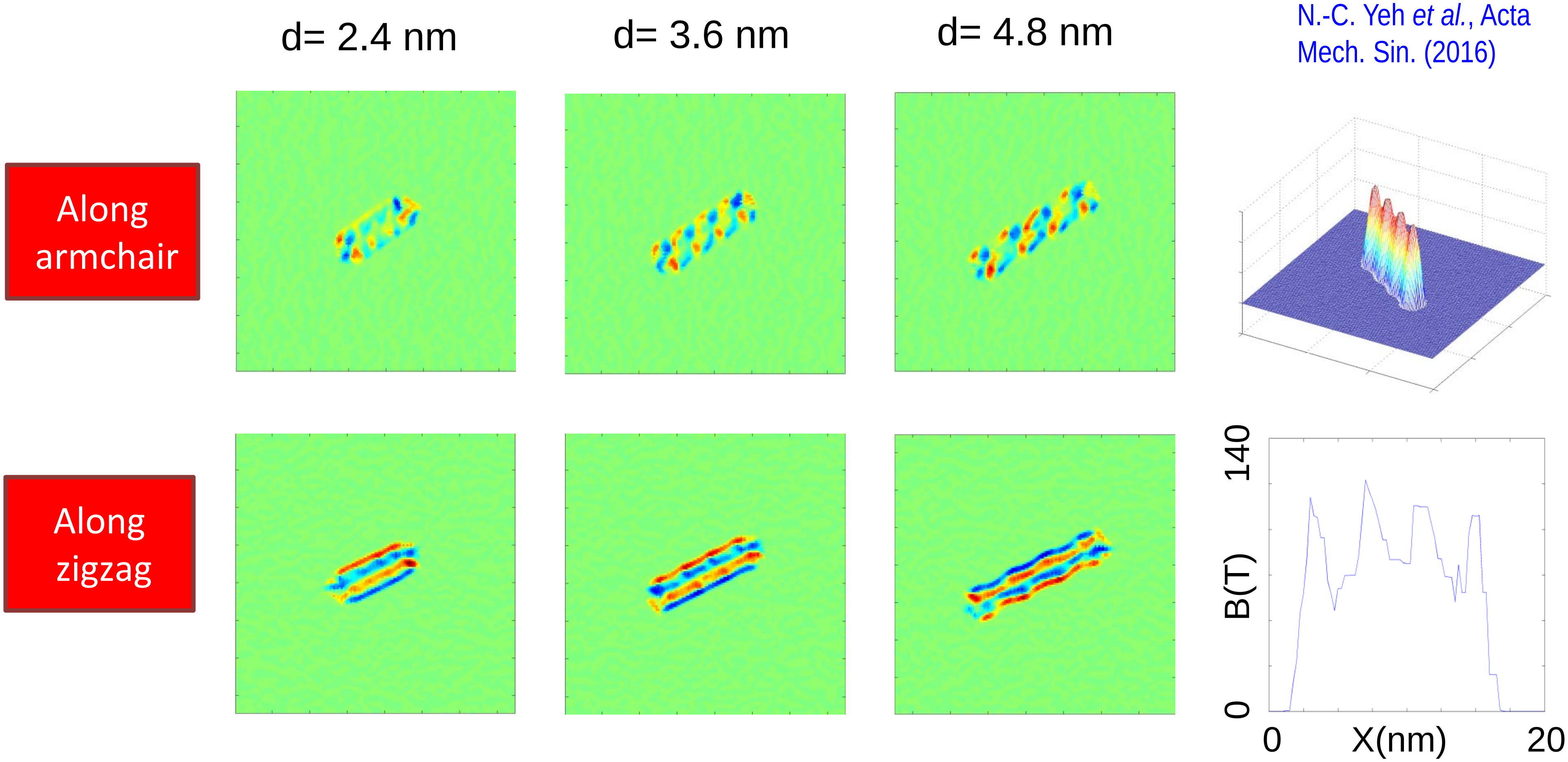
Pseudomagnetic field evolution of graphene on four Au nanoparticles

N.-C. Yeh *et al.*, Acta Mech. Sin. (2016)

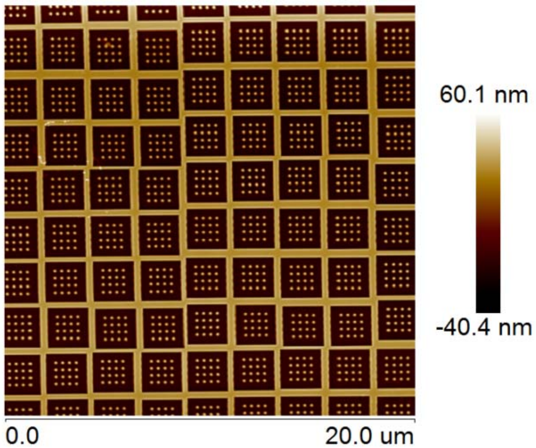


Changing the closely spaced nanoparticles to an extended ridge would provide uniform pseudo-magnetic fields with alternating signs, suitable for using as the “undulators” for accelerating single-valley Dirac fermions.

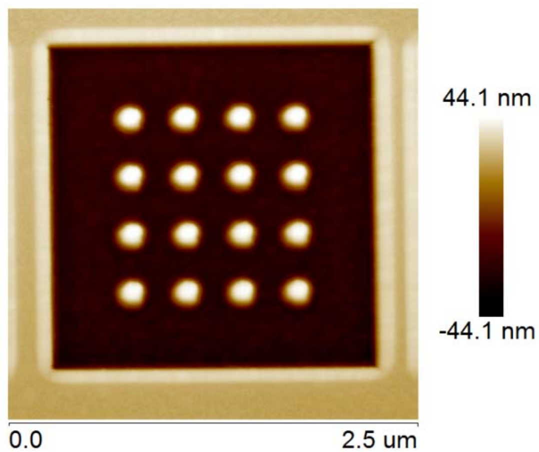
Caltech

Graphene/BN/Si-nanostructures (Method: focused ion beam)

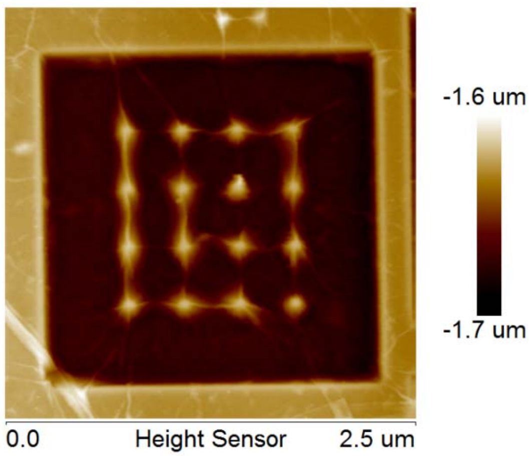
AFM image of Si nanostructures

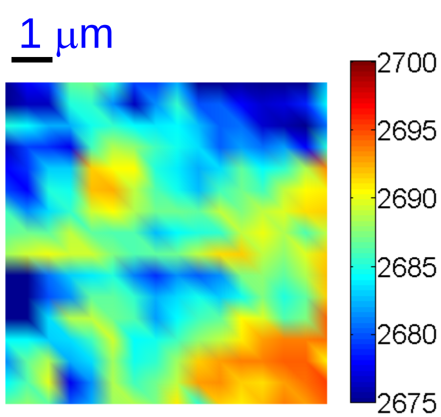


AFM image of BN/Si nanostructures

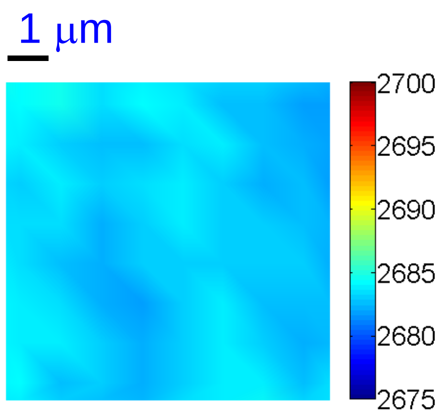


AFM image of Graphene/BN/Si nanostructures

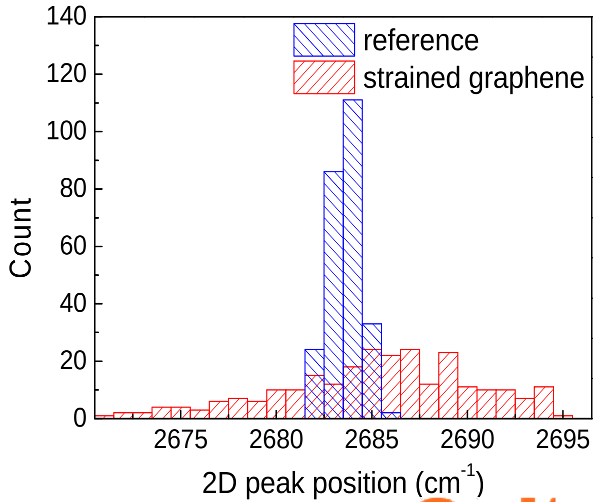




2D Raman peak position map on strained area



2D peak position map on unstrained area



N.-C. Yeh *et al.*, Acta Mech. Sin. (2016)

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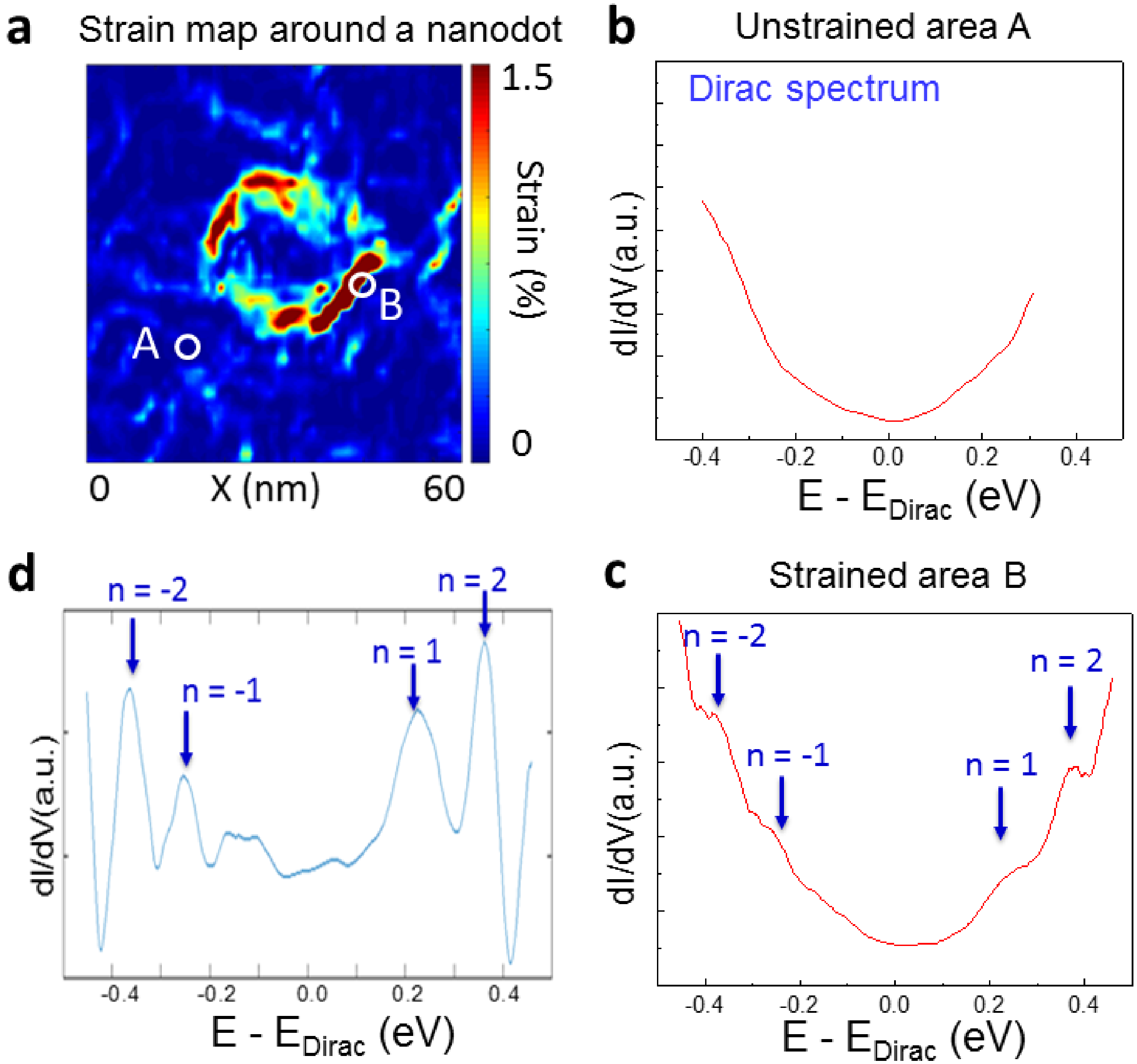
STM topography and spectroscopy on graphene/BN/Au-nanoparticles

- Evidence for strain-induced pseudo-magnetic fields:



From $|E - E_{Dirac}|$

$$= \mathrm{sgn}(n)\sqrt{2e\hbar v_F^2 B_s |n|},$$

we find B_S ~ 55 Tesla.

N.-C. Yeh *et al.*, Acta Mech. Sin. (2016)

New Research Directions

1) Nanoscale strain engineering of graphene

2) PECVD growth of graphene for next generation interconnects

3) Materials development for graphene-based photovoltaic & fuel cells

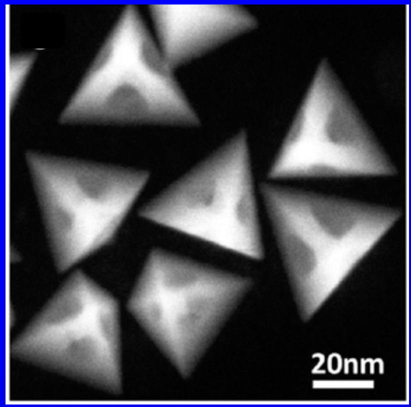
4) Developing GNRs for supercapacitors & energy storage

Caltech

1) Nanoscale strain engineering of graphene

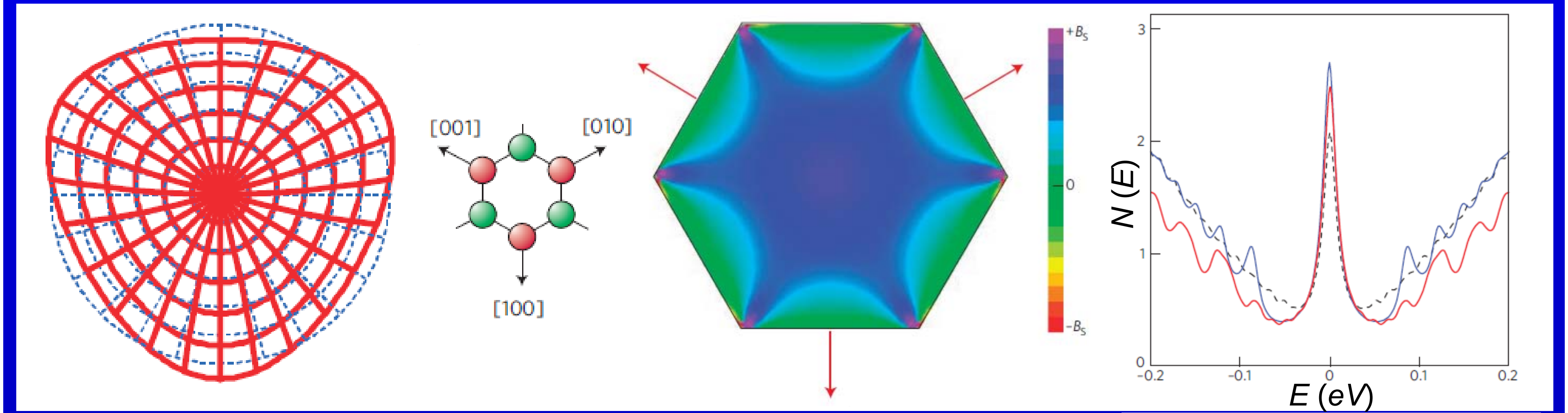
- Developed better nanostructures:

Palladium tetrahedron nanocrystals



30 nm palladium (Pd) tetrahedron nanocrystals dispersed in EtOH

- Tetrahedron nanostructures created better defined pseudo-magnetic fields



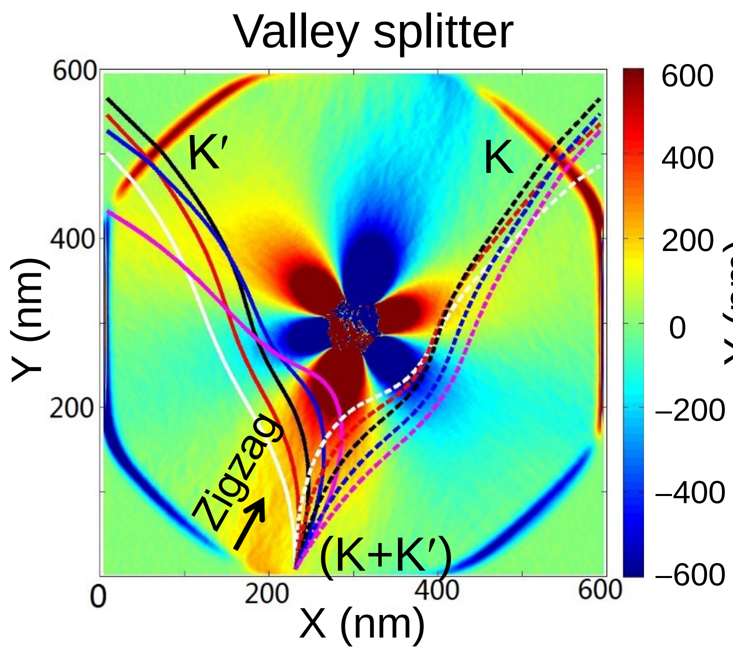
shear strain on graphene

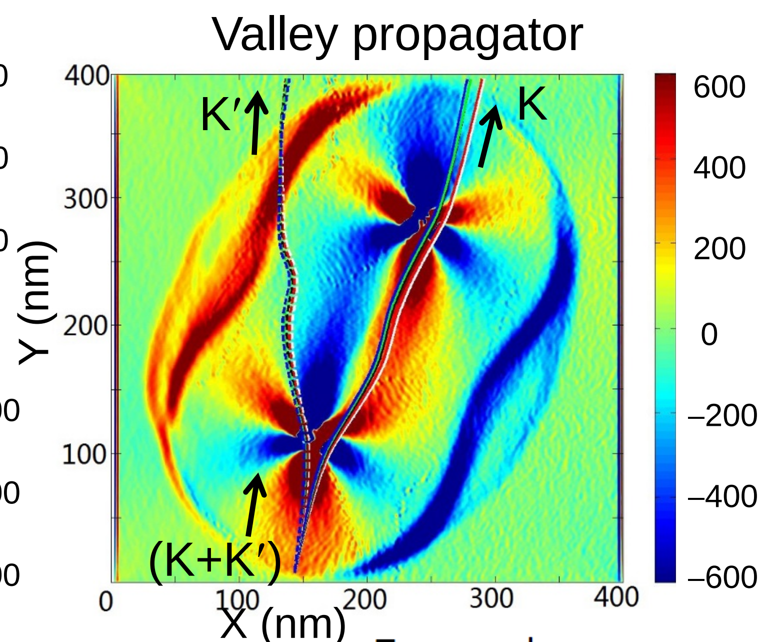
strain-induced pseudo-magnetic fields B_S

DOS-vs-energy for strained graphene under various Bs

F. Guinea *et al*, Nat. Phys. 6 (2010)

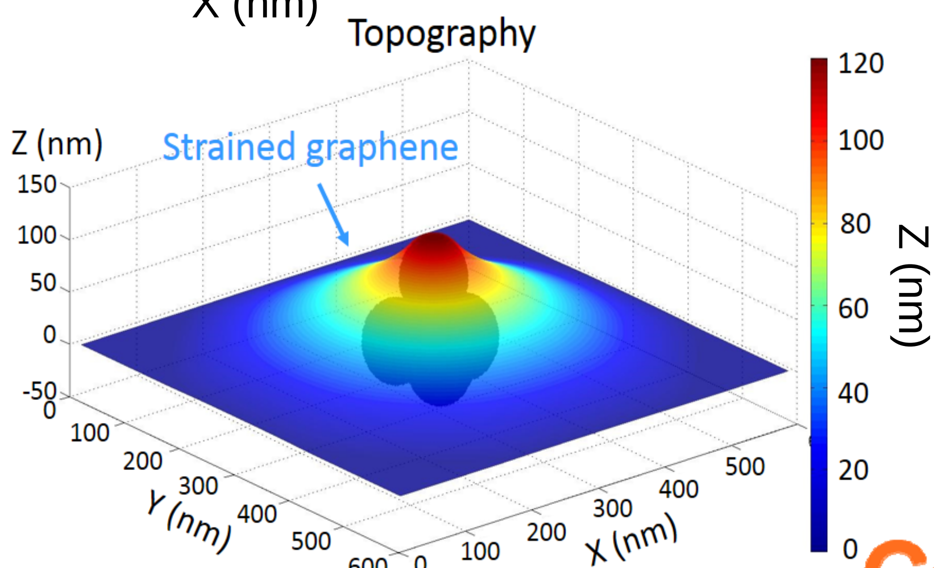
Realistic valleytronic devices based on strain-engineered graphene-on-nanostructures





Proper alignment of valley-splitters may become a valley-propagator that can enable the transport of valley-polarized Dirac fermions

Valley-dependent Dirac fermion trajectories through the spatially varying pseudo-magnetic fields of a valley-splitter



Graphene over a tetrahedron-like nanostructure can create pseudo-magnetic fields that break the valley (pseudo-spin) degeneracy

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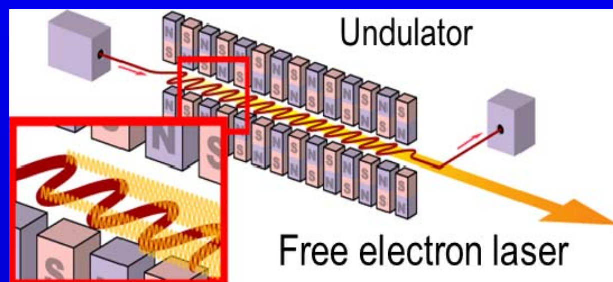
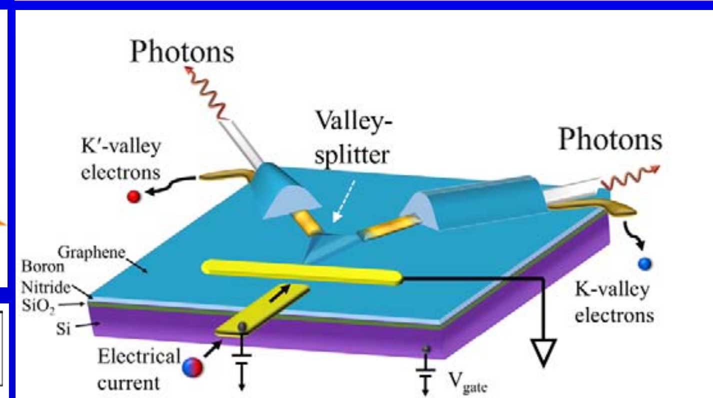
Nanoscale strain-engineering of graphene

- The two degenerate valleys K and K' are effectively two opposite pseudo-spins, which may be separated by strain-induced pseudo-magnetic fields, leading to valleytronics that can provide:

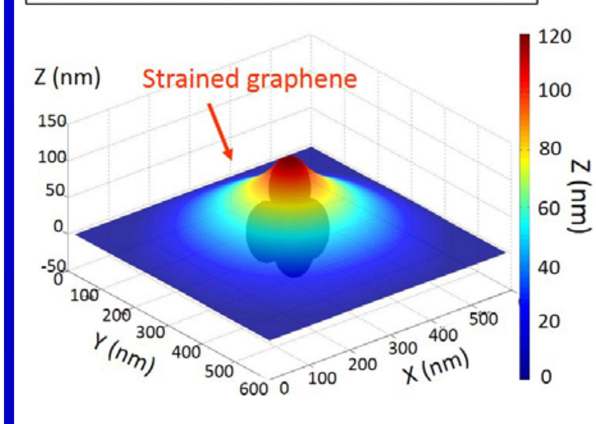
1) high fidelity in quantum communication;
2) controllability by polarized lights;
3) possible generation of photons.

Nanoscale strain-engineered, graphene-based free electron laser

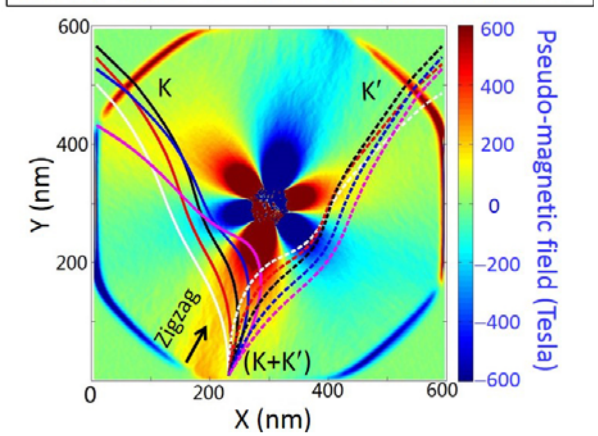


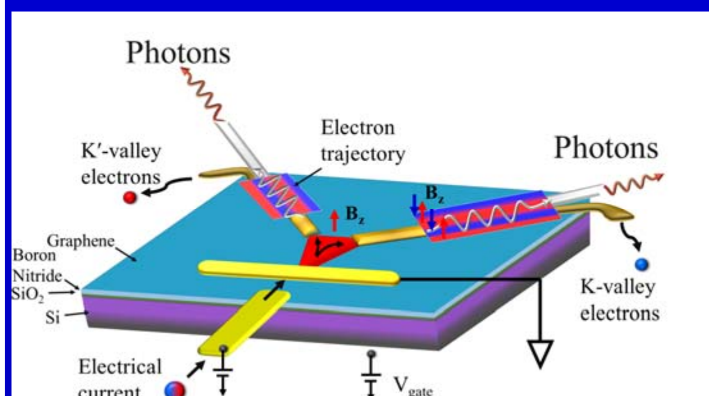


Topography of a "valley-splitter" consisting of graphene on a tetrahedron-like nanostructure



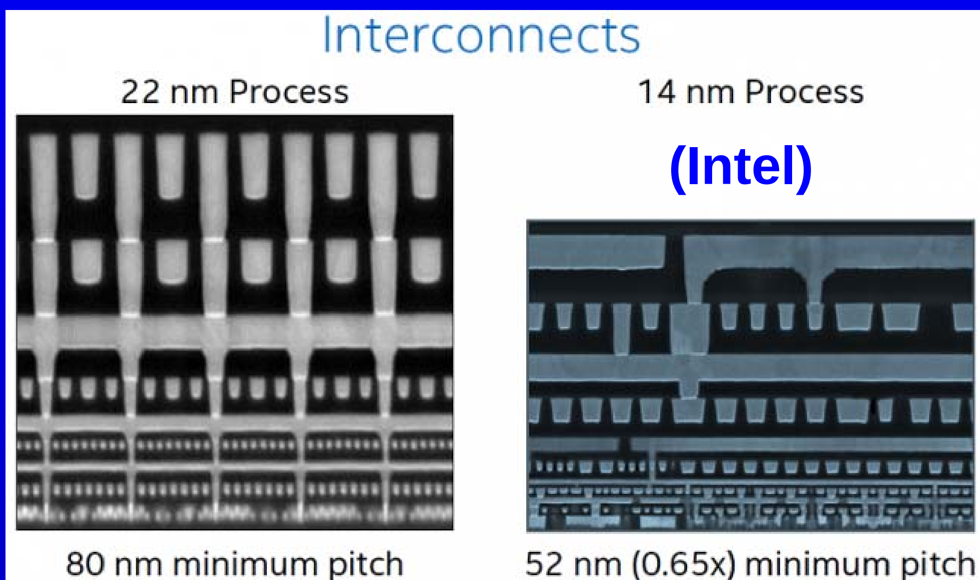
Generating valley-polarized currents in graphene by passing degenerate currents through a valley splitter

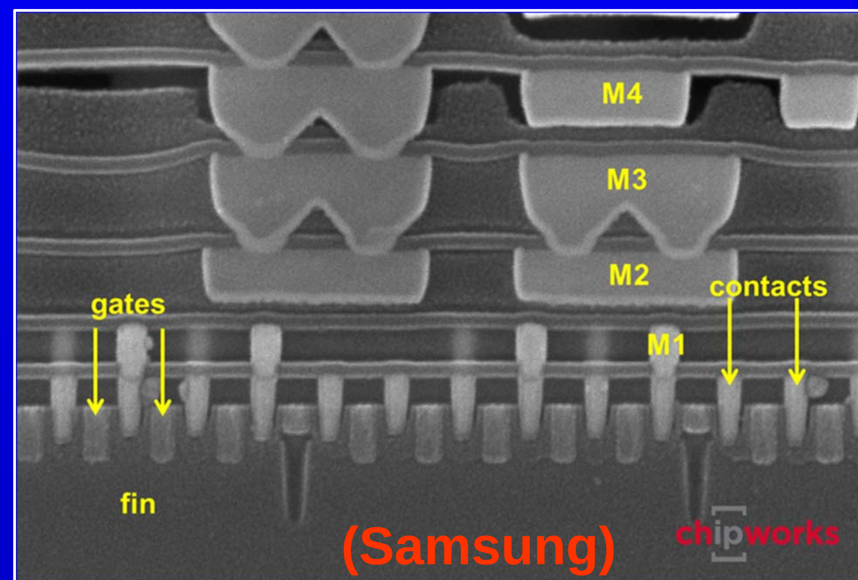




2) Next generation interconnects in integrated circuits (IC's)

- The continuing demand of miniaturizing electronic components in IC's has imposed serious challenges to the existing technology for interconnects:
  - ❖ Increasing narrower copper interconnects become granular and resistive.
  - ❖ Severe diffusion of copper into silicon, leading to strong energy dissipation, reduced lifetime and compromised reliability.





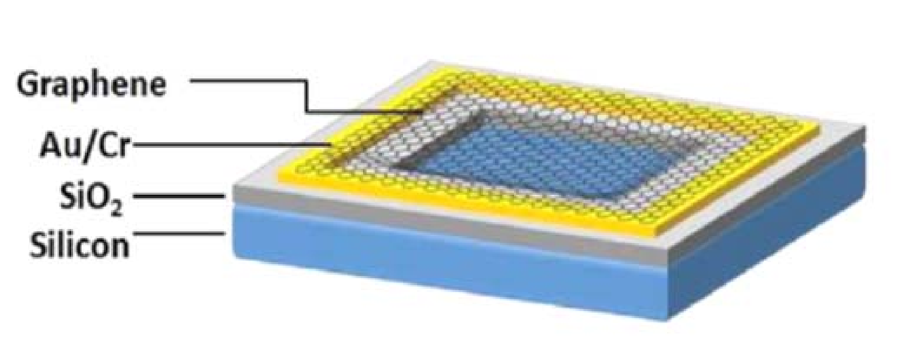
- **<u>Possible solution</u>:**

  Deposit graphene layers on copper interconnects to 1) prevent copper from diffusing into silicon and 2) to increase electrical & thermal conductivity.

Caltech

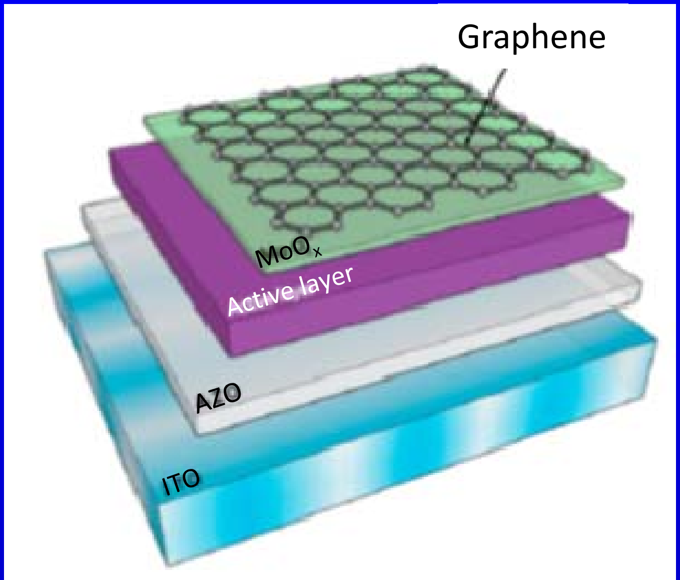
3) Three types of graphene-based broadband photovoltaic cells

[1] Hybrid graphene-Schottky photovoltaic cells
(Frequency range: Infrared)



<u>Challenges</u>: enhancing light absorption; better graphene work function & mobility.

[2] Inverted graphene-based organic photovoltaic cells
(Frequency range: Optical)



<u>Challenges</u>: Improving the lifetime by identifying and then minimizing environmental aging effects.

[3] "All-graphene" photovoltaic cells
(Frequency range: Infrared to THz)

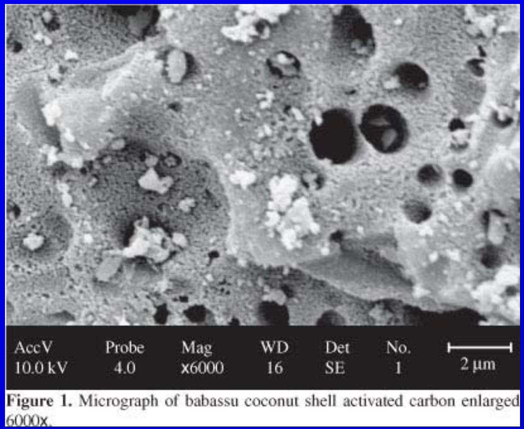
⇒ Replacing silicon by hydrogen-doped graphene, or "graphane"

<u>Challenges</u>: creating stable energy gaps in graphene; controlling the size of the gap.

Caltech

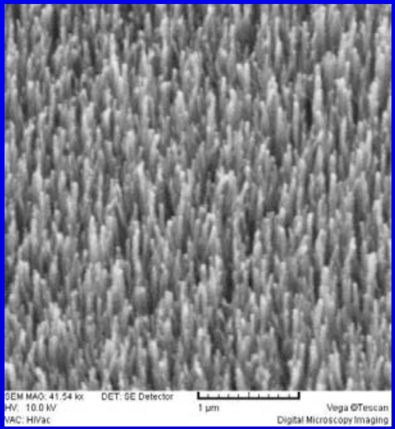
4) GNRs for supercapacitor applications

- Current supercapacitors for energy storage utilize activated carbon, which only store charges primarily on its surface.
- Carbon nanotubes (CNTs) are promising, but uncontrollable variables and high costs are inhibitors for commercial applications.



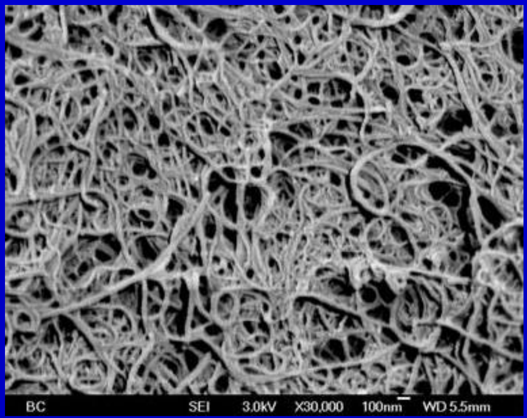
Activated Carbon

Used in currently available super-capacitors; 2D surface storage



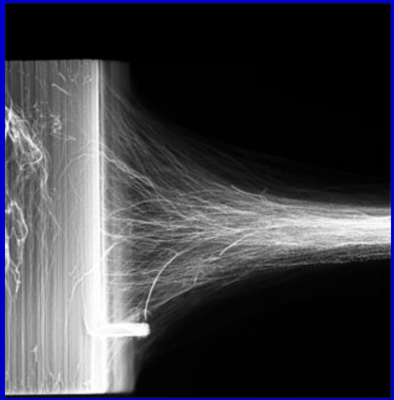
CNT Forest

Used in the MIT method



CNT Paper

Poor alignment for conductivity, packing factor is relatively low



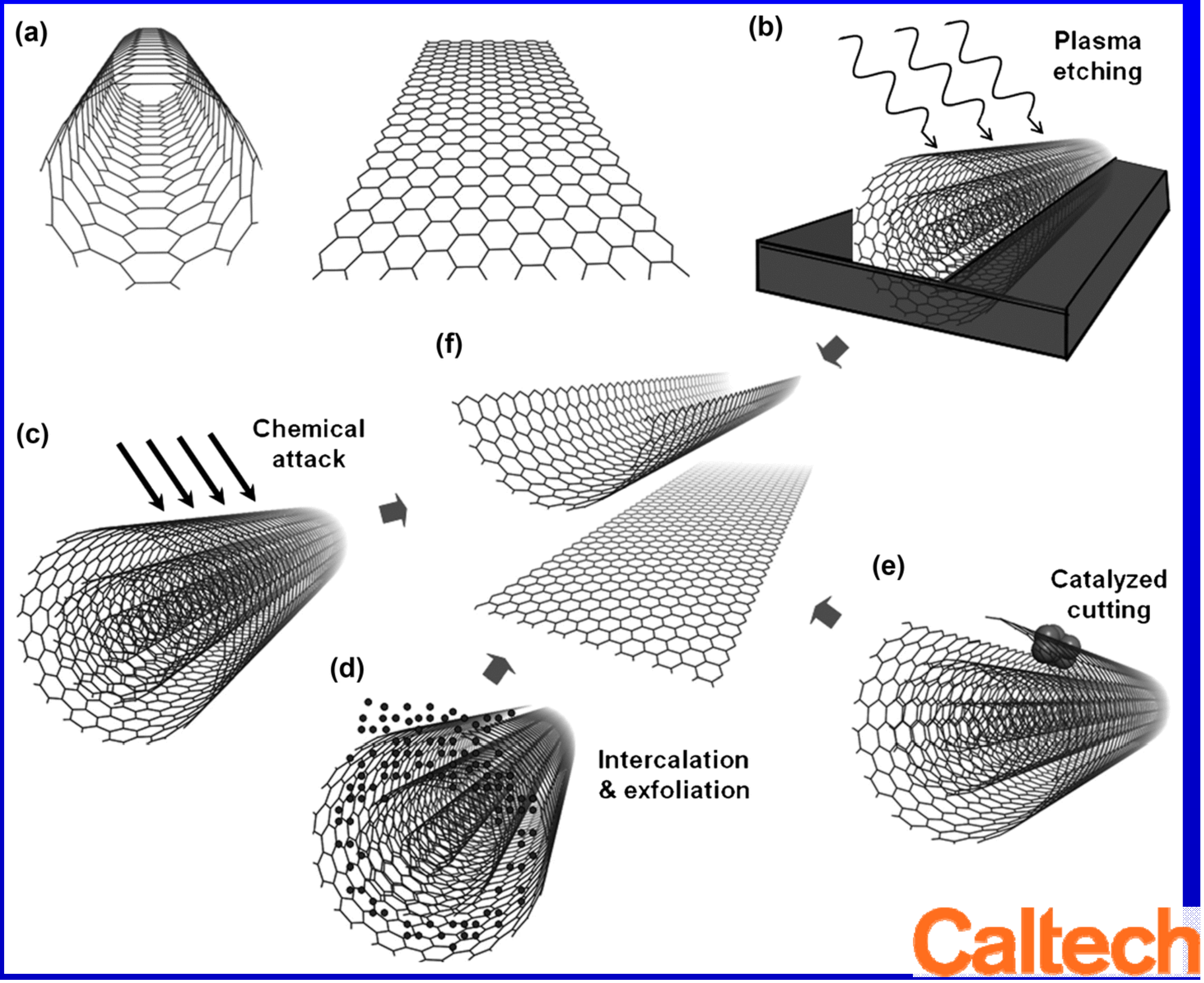
CNT Filaments

This method allows for 3D structures with a high packing factor, high strength and large surface area

GNRs for supercapacitor applications

- Graphene nanoribbons (GNRs) are even better candidates than CNTs for charge storage, provided that they can be mass produced at a low cost.

Unzipping CNTs
into GNRs

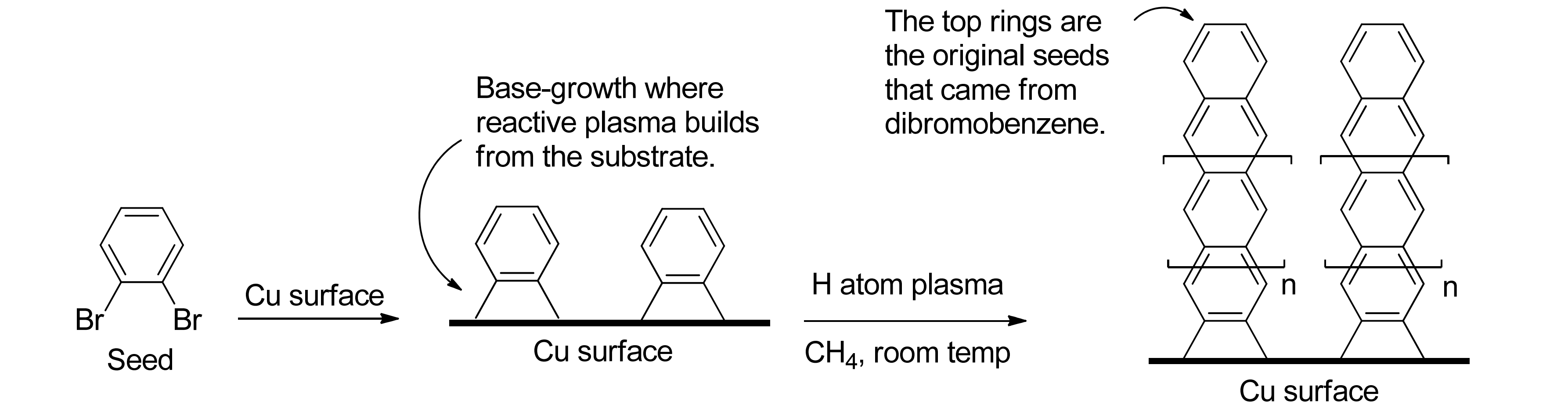


- Exploring seeded growth of GNRs by means of low-temperature PECVD technique.

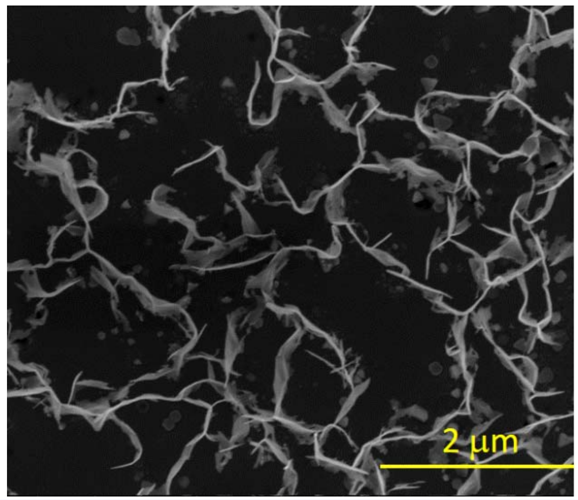
Caltech

New success in fast growth of high-quality graphene nanoribbons (GNRs)

- Seeded PECVD growth of GNRs: [C.-C. Hsu, M. L. Teague, J. Tour and N.-C. Yeh (2016)]



- SEM image of GNRs:

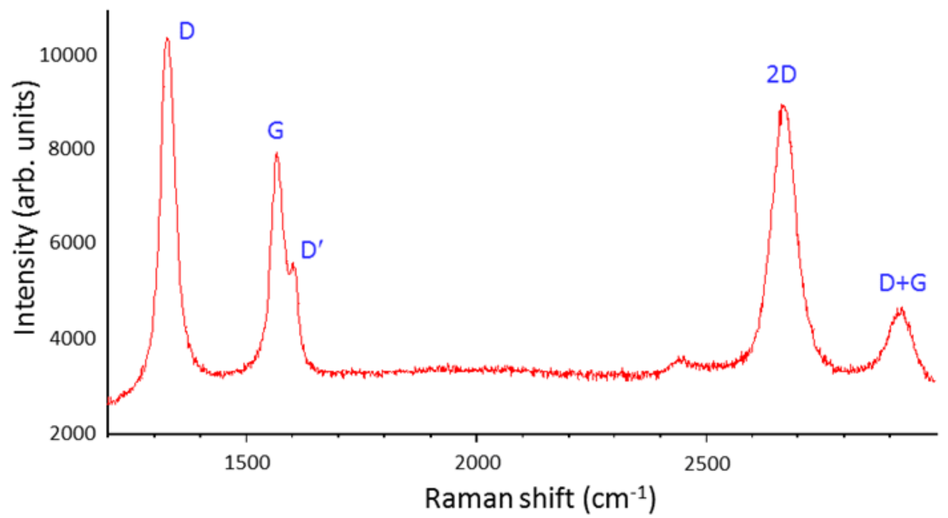


(Lengths ~ 10μm)

(widths <~ 10nm)

(10 minutes of growth)

- Raman spectroscopy of GNRs:

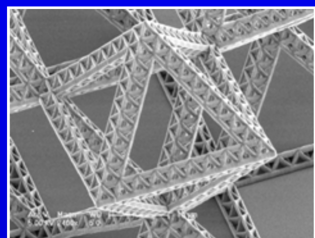


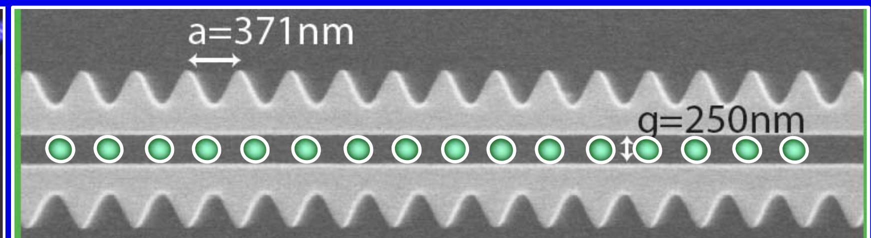
5. Summary & Outlook

- Creative nanofabrication and materials synthesis methods can enable new nanomaterials and nano meta-materials with novel functionalities for the advances of science and technology.

- Examples of nano meta-materials:

  Quantum dots, semiconducting nanowires, nano-photonic systems, nano-truss materials, quantum matter assembled from atoms & photons, etc.



➡ Applications to quantum science & technology, energy & sustainability, bio- & medical engineering, space exploration, etc.

- New breakthrough in graphene synthesis & related research is promising for a new era of graphene-based technologies.