Introduction to Nanophysics

Prof. J. Raynien Kwo

Department of Physics

National Tsing Hua University

Feb. 21, 2013

What is the size for a “nano” ?

One (nm) equals to 1/1000000000 (10^{-9}) meter

10^{-3} m , **Macro**

10^{-6} m , **Micro**

10^{-9} m , **Meso**

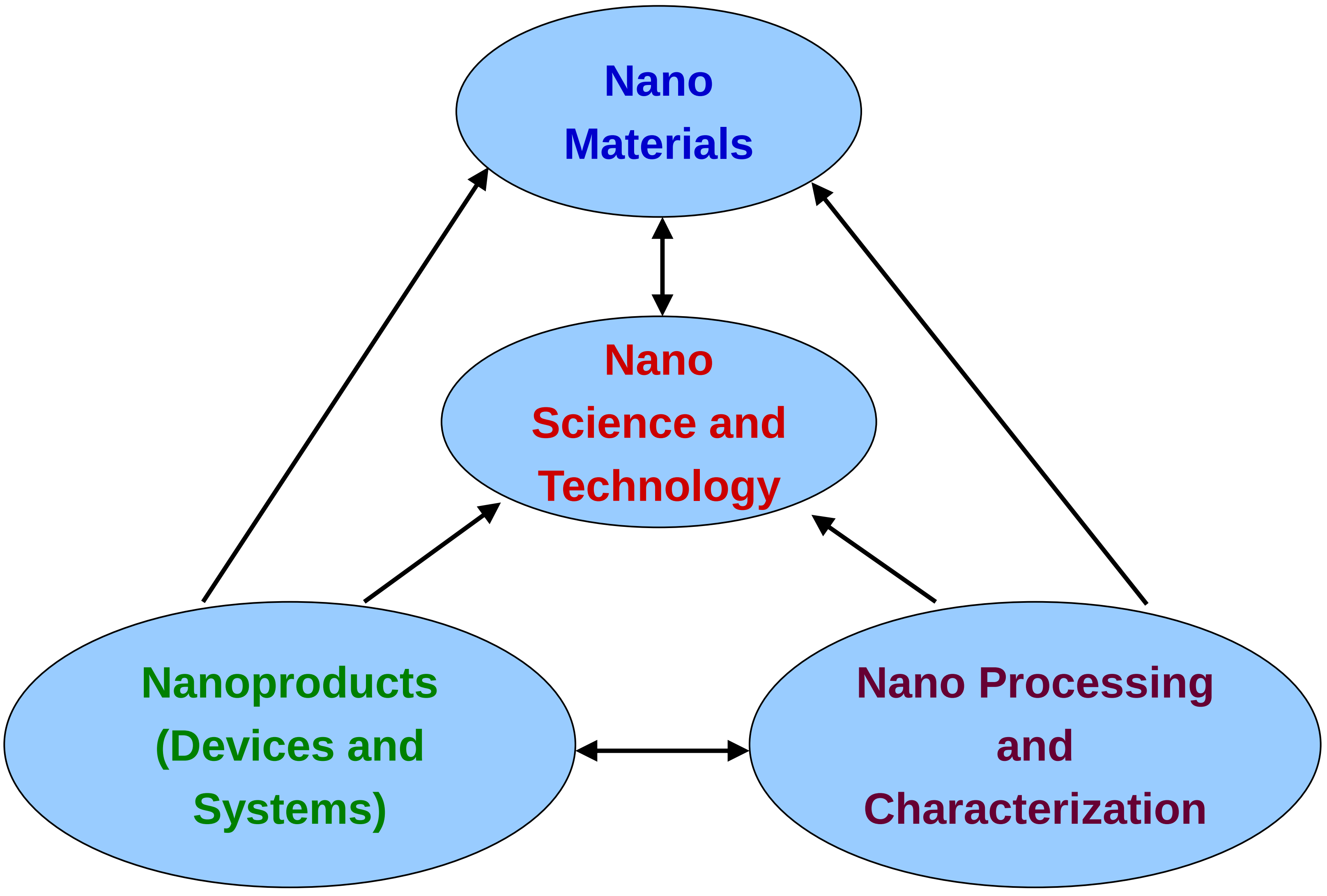
R. Feymann Already Knew about this !

" There's plenty of room at the bottom ! " in 1959.

Physicists noticed the "Nano " as early as .....

- 4th Century, Roman glassmaker: the color of glasses can be changed by mixing in metal particles
- In 1883, Films containing silver halides for photography were invented by George Eastman, founder of Koda.k
- 1908, Gustay Mie first provided the explanation of the size dependence of color.
- Vision from Feynman in 1959: "There is plenty room at the bottom", and also recognized there are plenty of nature-given nanostructures in biological systems.
- 1950-1960, small metal particles were investigated by physicists.
- 1957, Ralph Landauer realized the importance of quantum mechanics plays in devices with small scales.
- Before 1997 => **mesoscopic** (or low dimensional) physics : quantum dots, wells, wires.....are known already.

Major Topics of Nanoscience and Technology



What is the Nano Technology?

- **Science and Technology Down scaling to size under100 nm:**

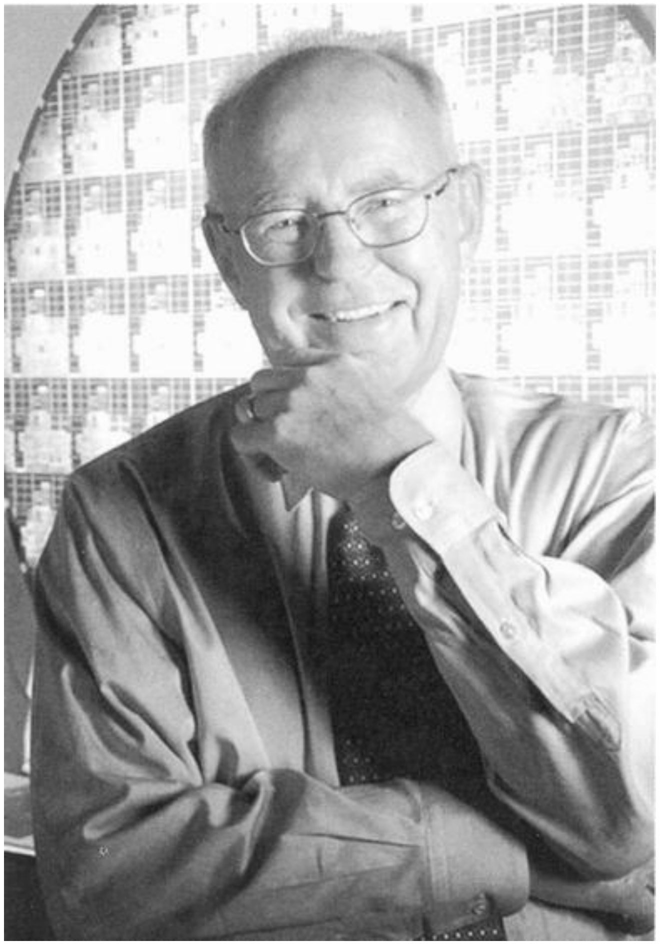
  Via the "Top-down" lithographic pattering.
  -- Moore's law !

- **Manipulate the atomic and molecular structures："Bottom-up" nano materials, growth and assembly.**

  Feymann: There's plenty of room at the bottom

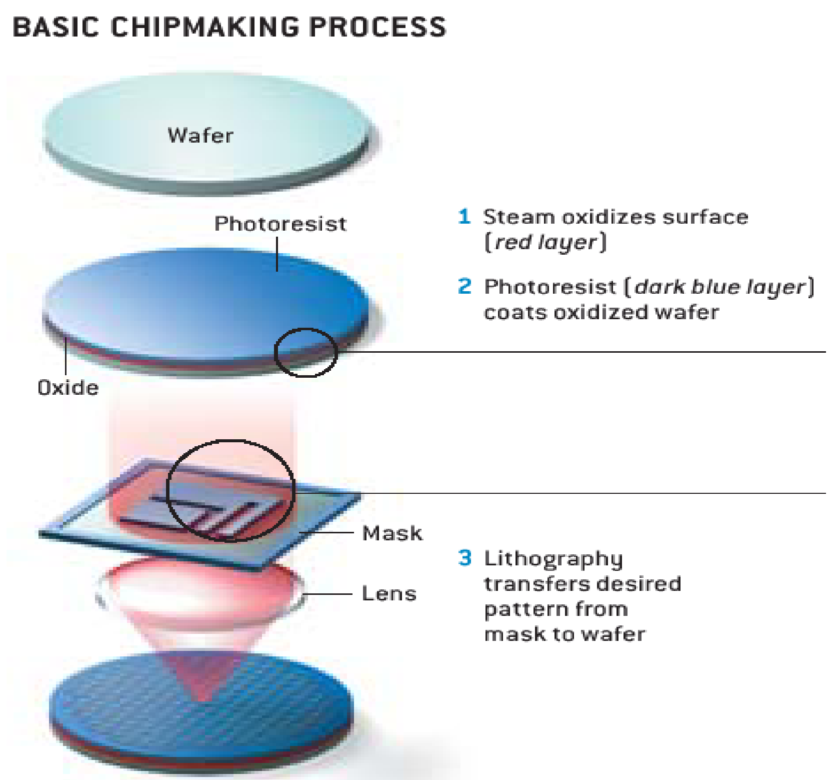
Major Driving Force pushing for Nano

Is due to the bottle neck met in Microelectronics



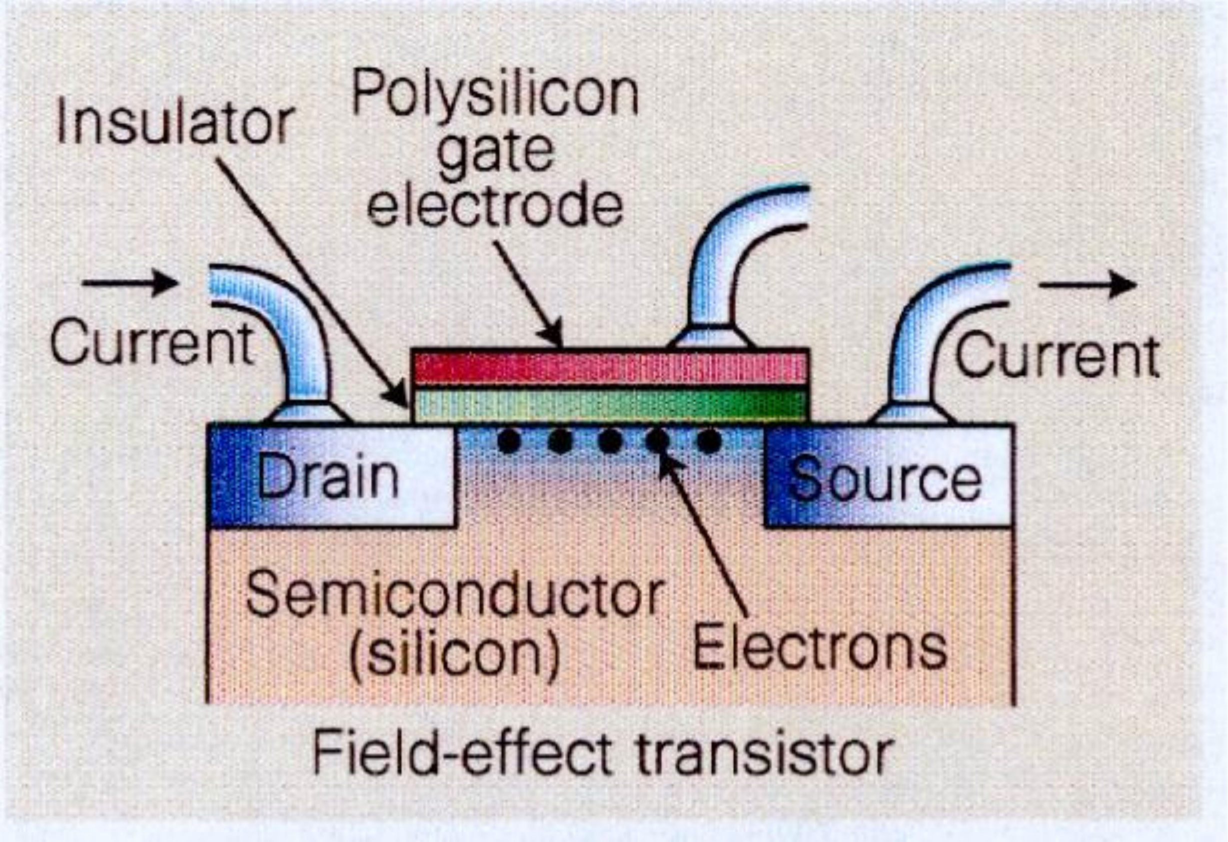
Moore's Law :

A 30% decrease in the size of printed dimensions every two years.



囊括凝體物理重要
平臺的兩個現代電
子科技之基礎元件

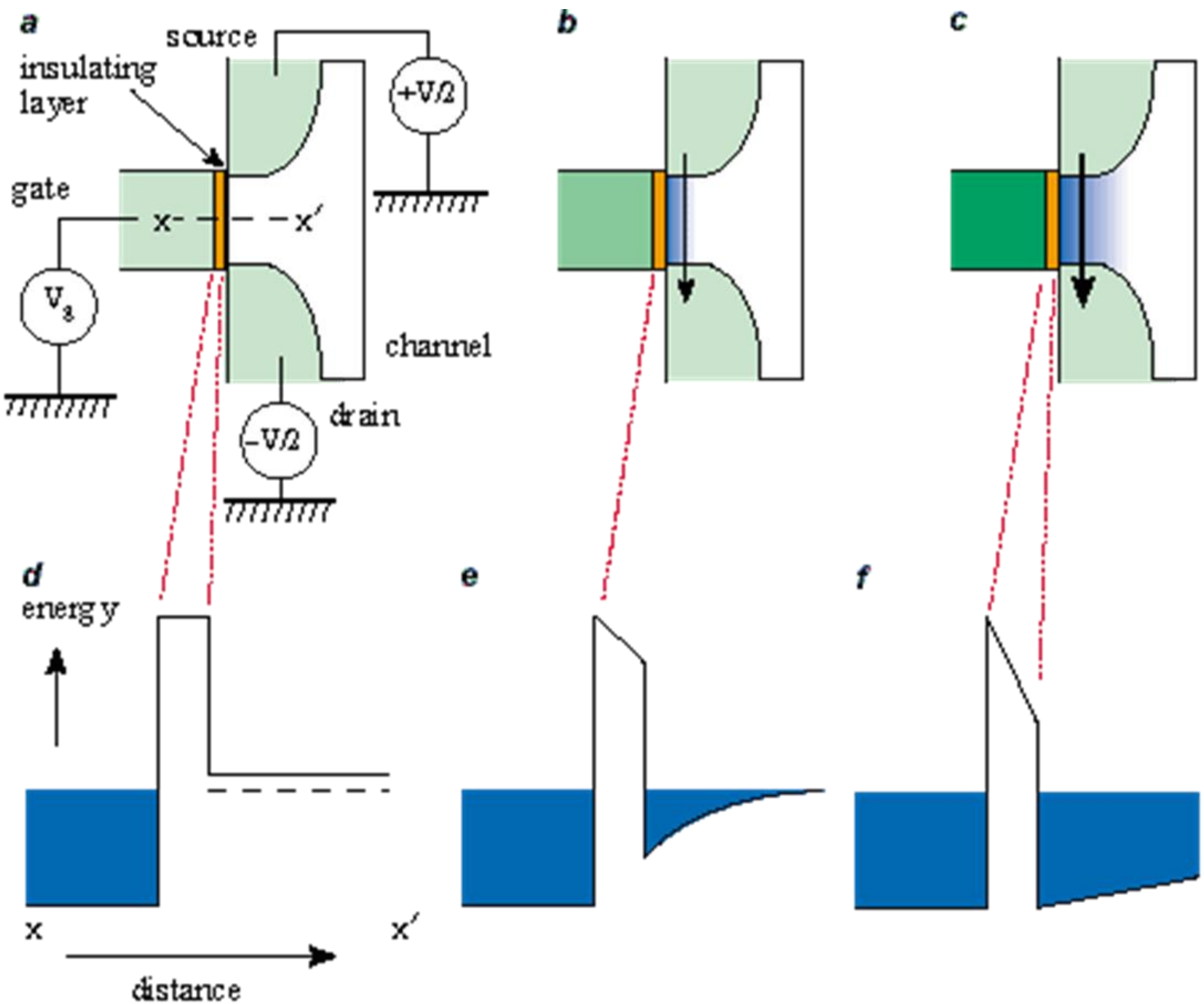
Metal-Oxide-Feld Effect Transistor



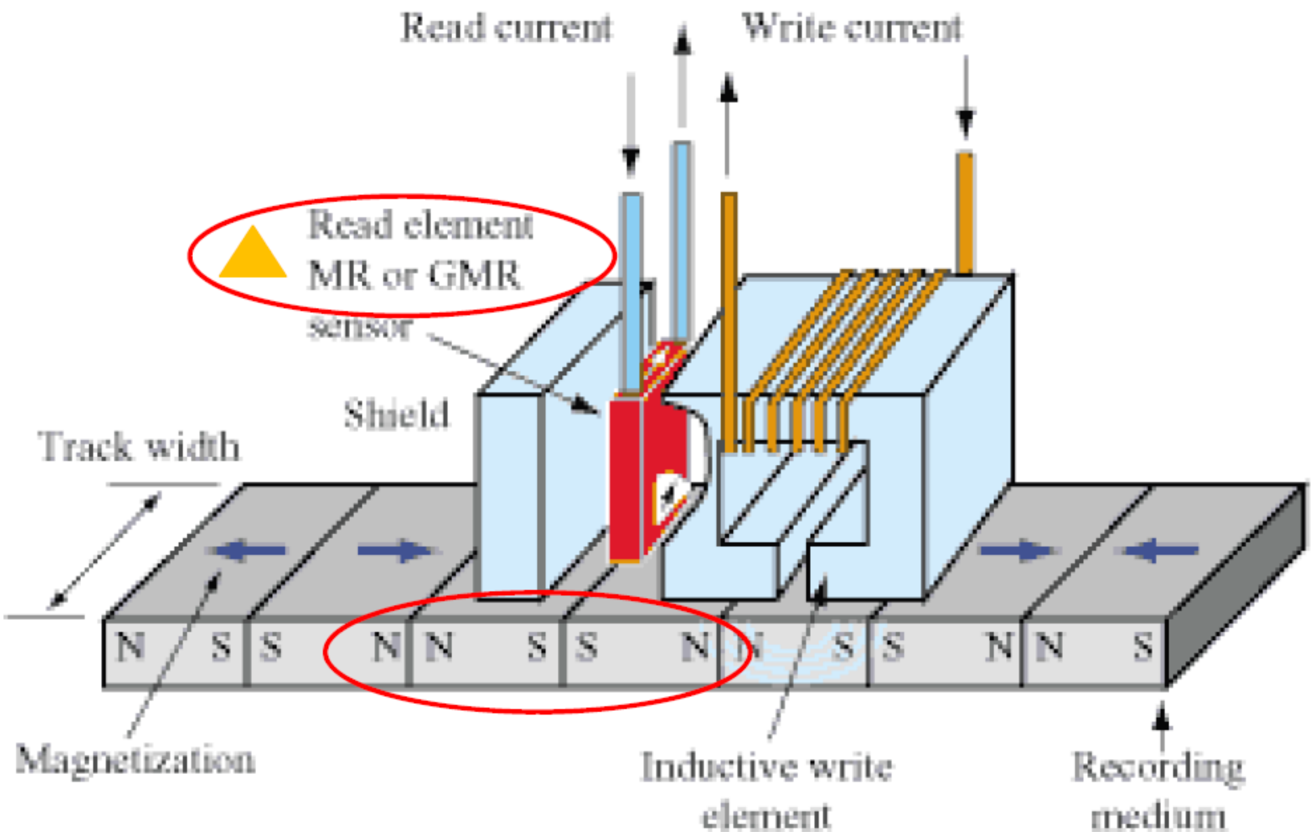
1960 Kahng and Atalla, First MOSFET

1970 First IC, 1 kbit, 750 khz microprocessor

電子科技之基礎--MOSFET
(metal-oxide-semiconductor field-effect transistor)



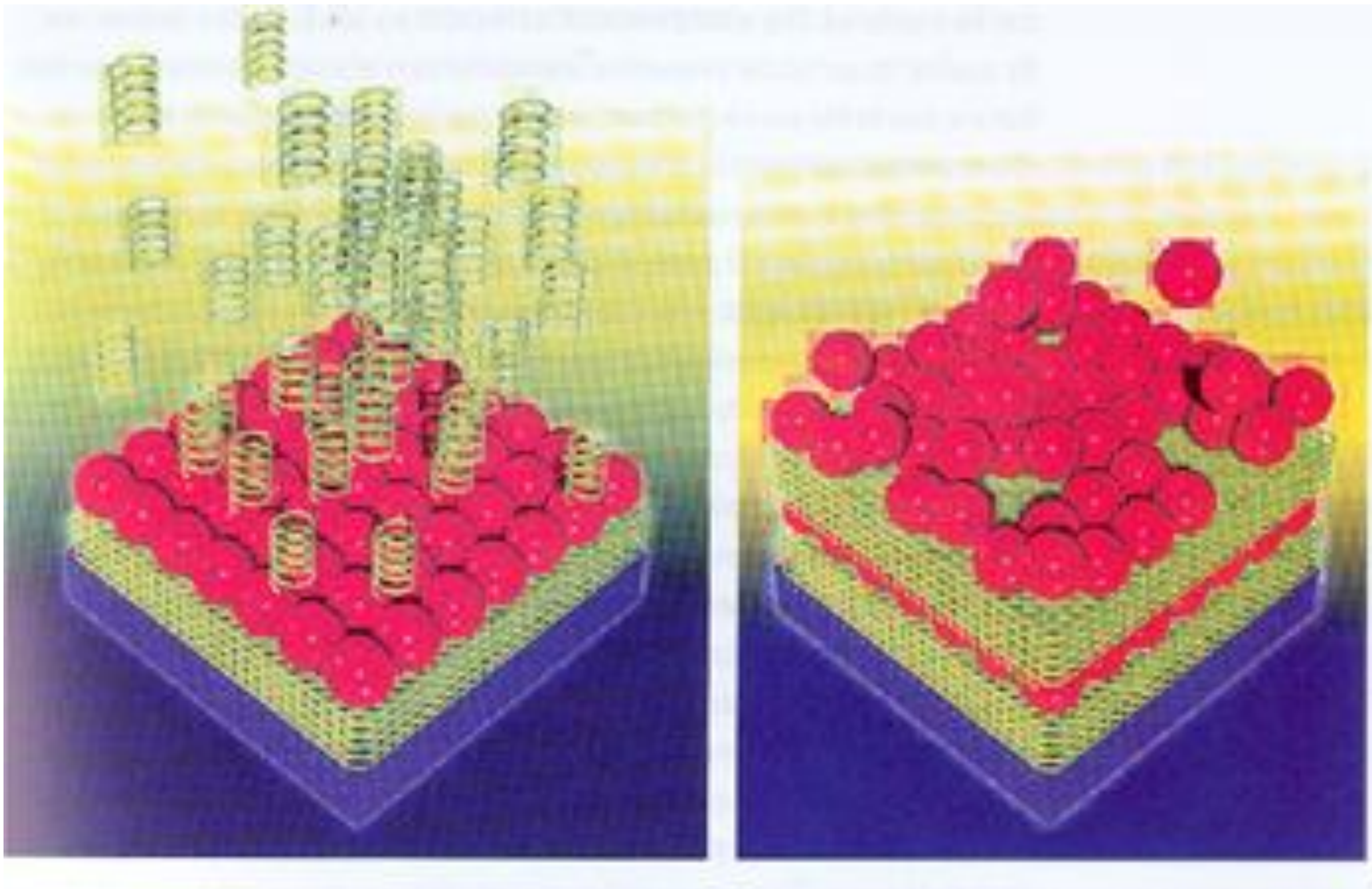
電子科技之基礎--磁記錄



Read current
Write current
Read element
MR or GMR
sensor
Shield
Track width
N S S N N S S N N S S N N S
Magnetization
Inductive write
element
Recording
medium

Bottom-up Nano systems & Self-Assembly

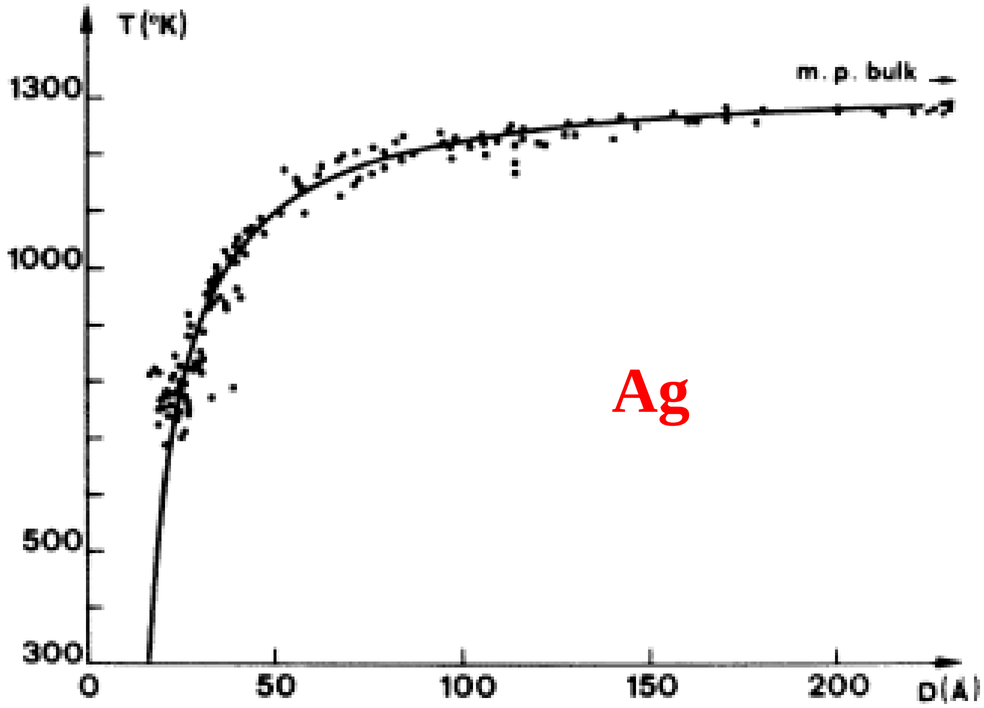
enabling of designing large molecules and nano materials



The First Lesson :

Bulk-to-nano Transition

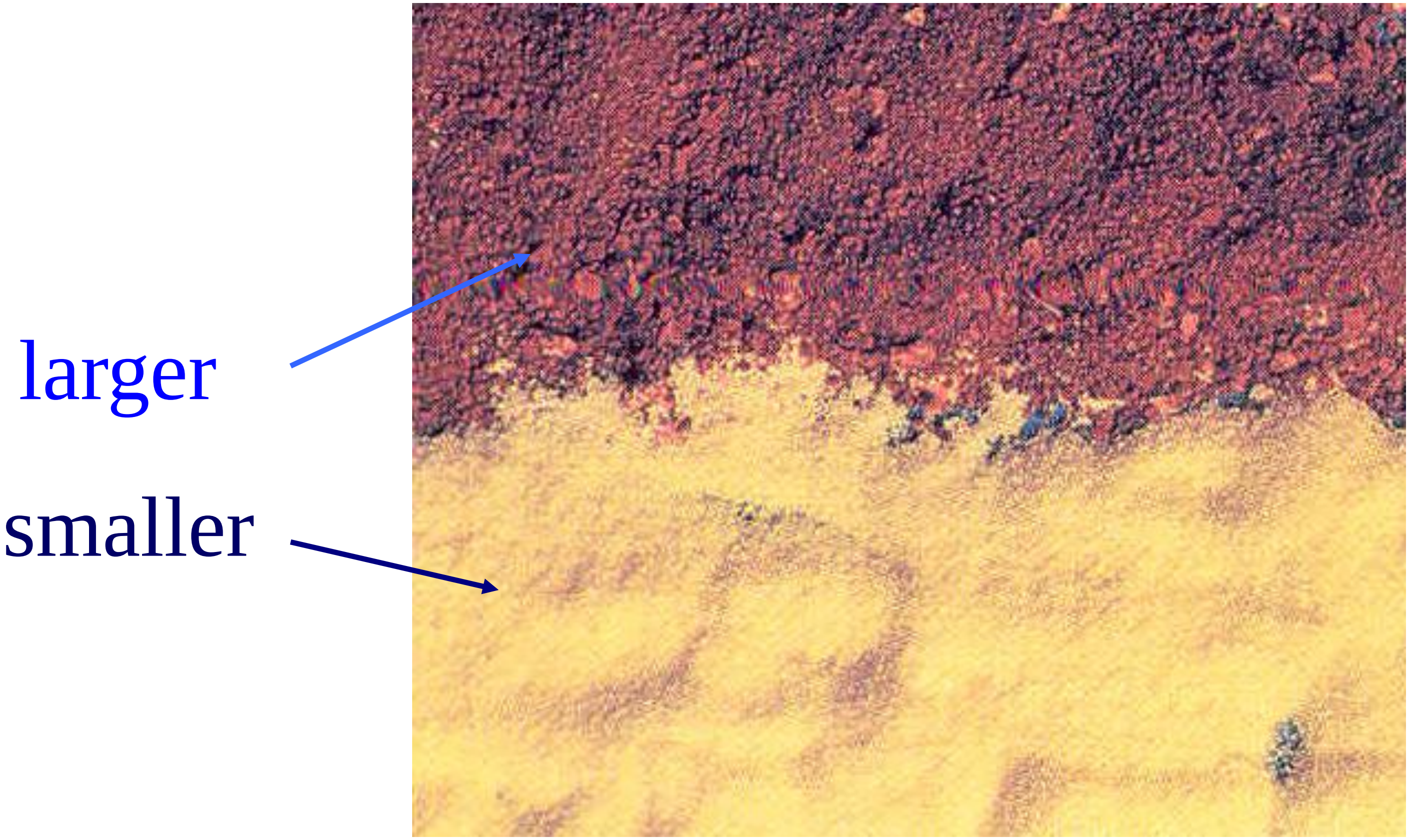
Ex: size-dependence of melting temperature



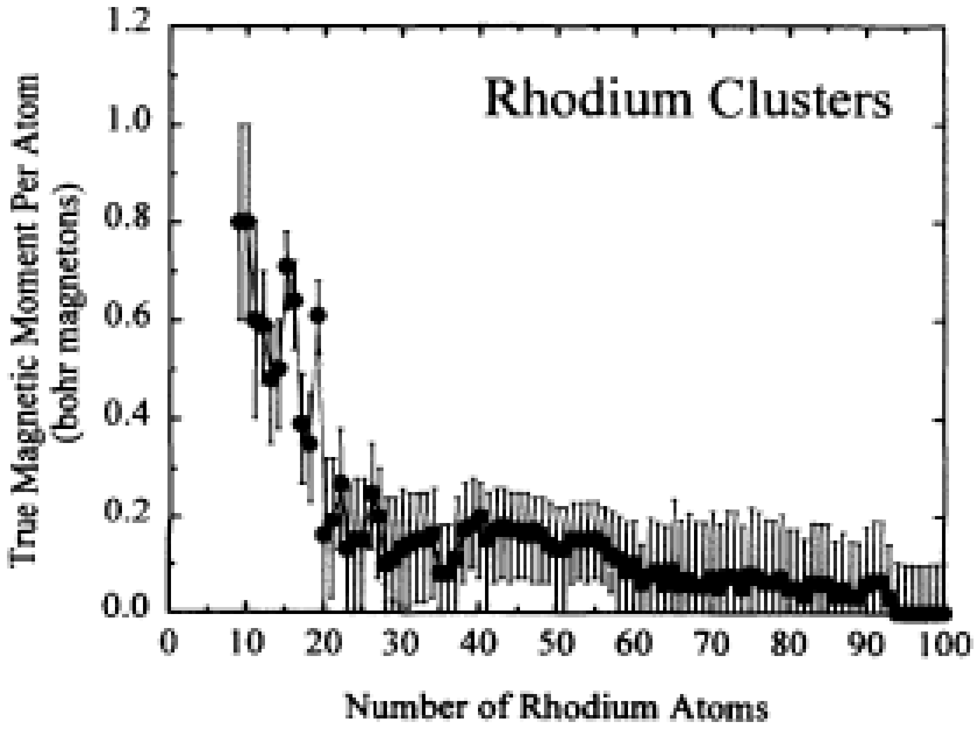
Ph. Buffat and J-P. Borel, Phys. Rev. A13, 2287 (1976)

Ex: size-dependence of color

powered cadmium selenide



Ex: size-dependence of magnetism



A. J. Cox et al. Phys. Rev. B49, 12295 (1994)

The Second Lesson :

- The ability of growing the nano scale materials and structures

- The ability of detecting and manipulating on the nano scale.

(I) Advance in thin film growth:

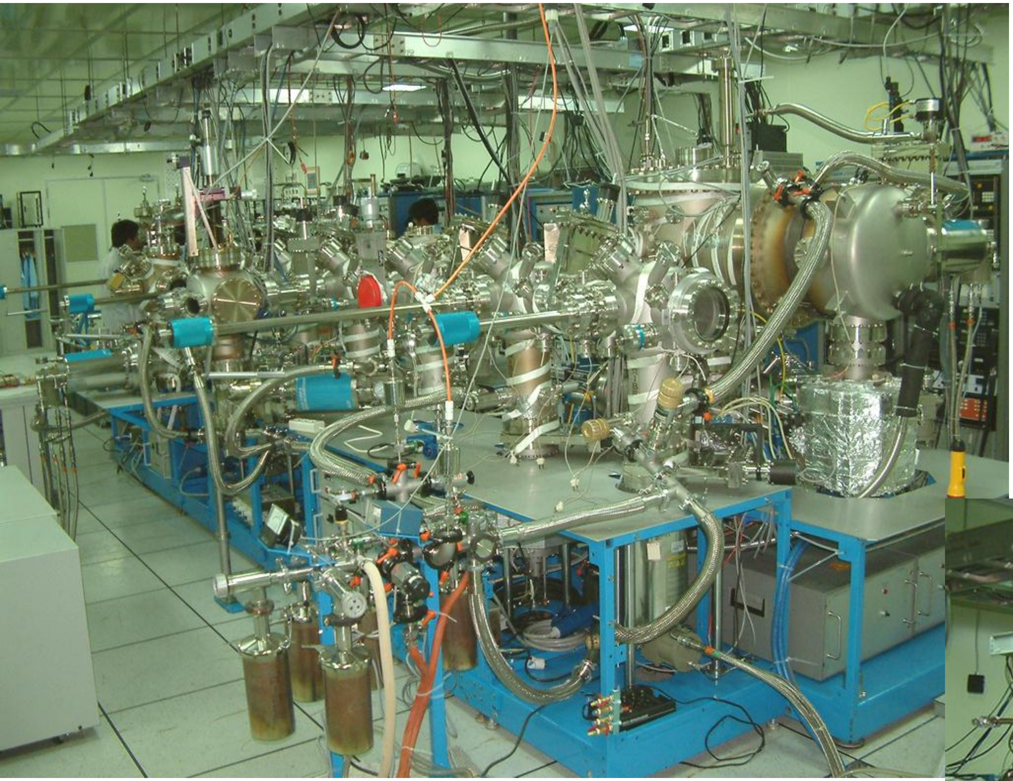
Such as Molecular Beam Epitaxy, atomic layer depostion, laser MBE, etc…

- For Nano electronics in metals, oxides, and semiconductors

(II) Detection at nano scale : STM, AFM, MFM, STEM, Cs-TEM

- In 1982, Binning, and Rohrer in IBM invented scanning tunneling microscope.
- In 1986, Binning, Quate, and Gerber invented the atomic force microscope AFM.

Integrated MBE Multi-chamber System



Now located in the Nano Technology Center, ITRI, Hsin Chu, Taiwan

For Metal, Oxide and Semiconductor Films On the Nano scale

Scanning Tunneling Microscope (STM)

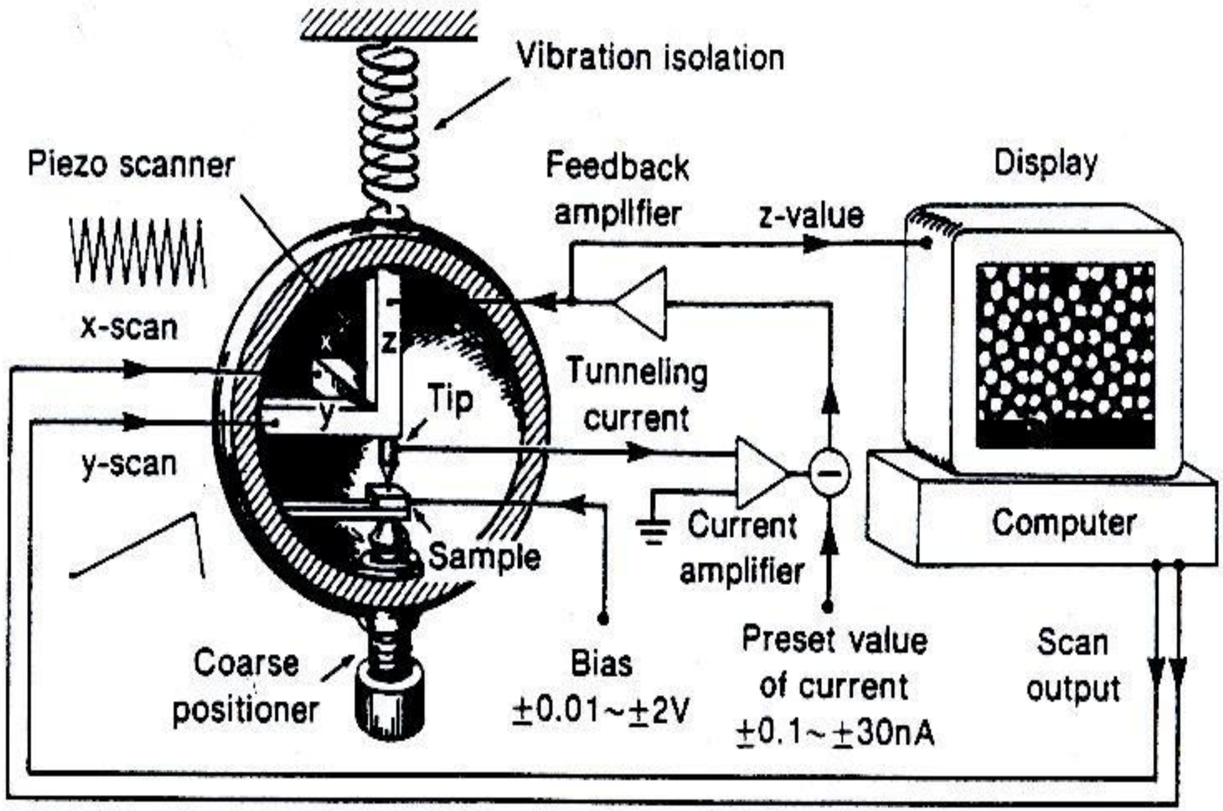
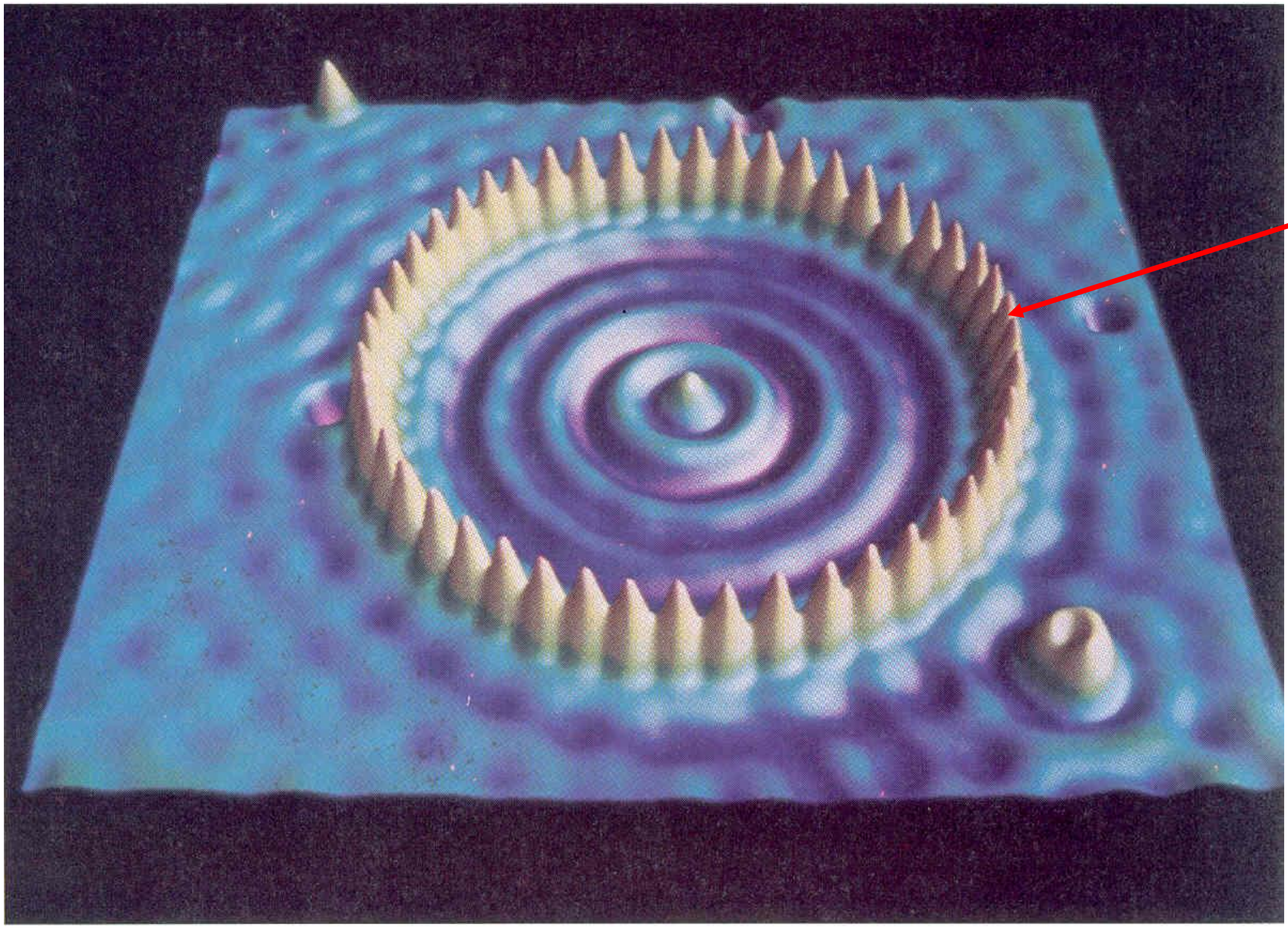


Figure 1.10 Scanning tunneling microscope. (From C. Julian Chen, *Introduction to Scanning Tunneling Microscopy*, Oxford: Oxford University Press, 1993.)

Quantum Corral

of 7.13 nm radius, 48 Fe atoms

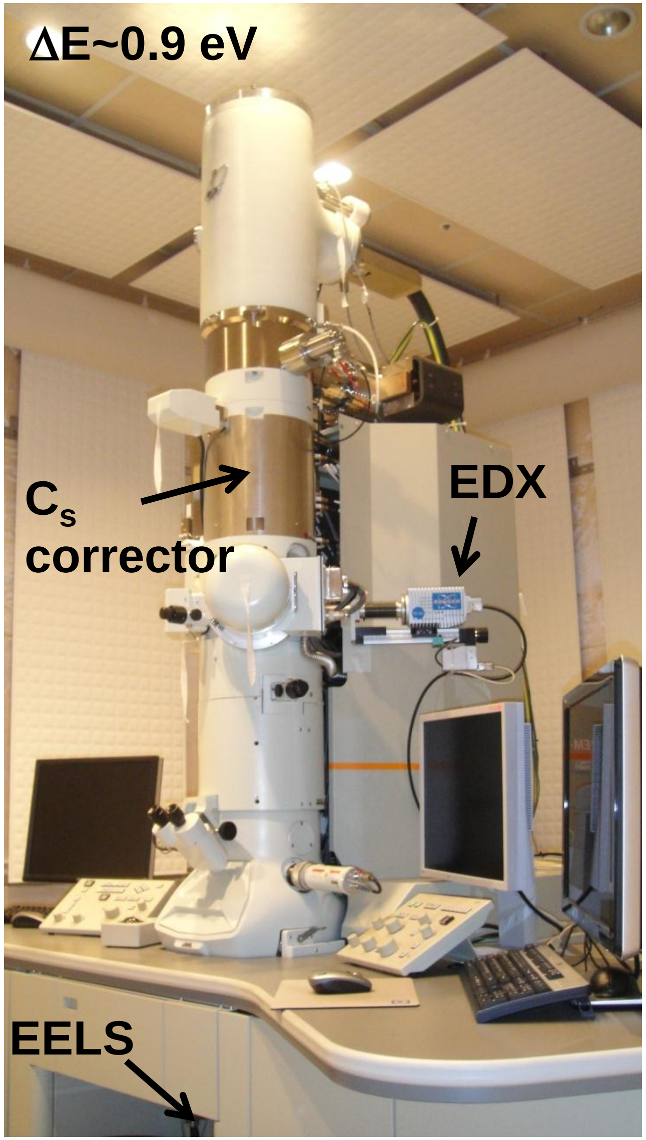


Crommue, Luts, and Eigler, Science 262, 218-220, 1993

Scanning Transmission Electron Microscope Laboratory

2-Å STEM

1-Å STEM

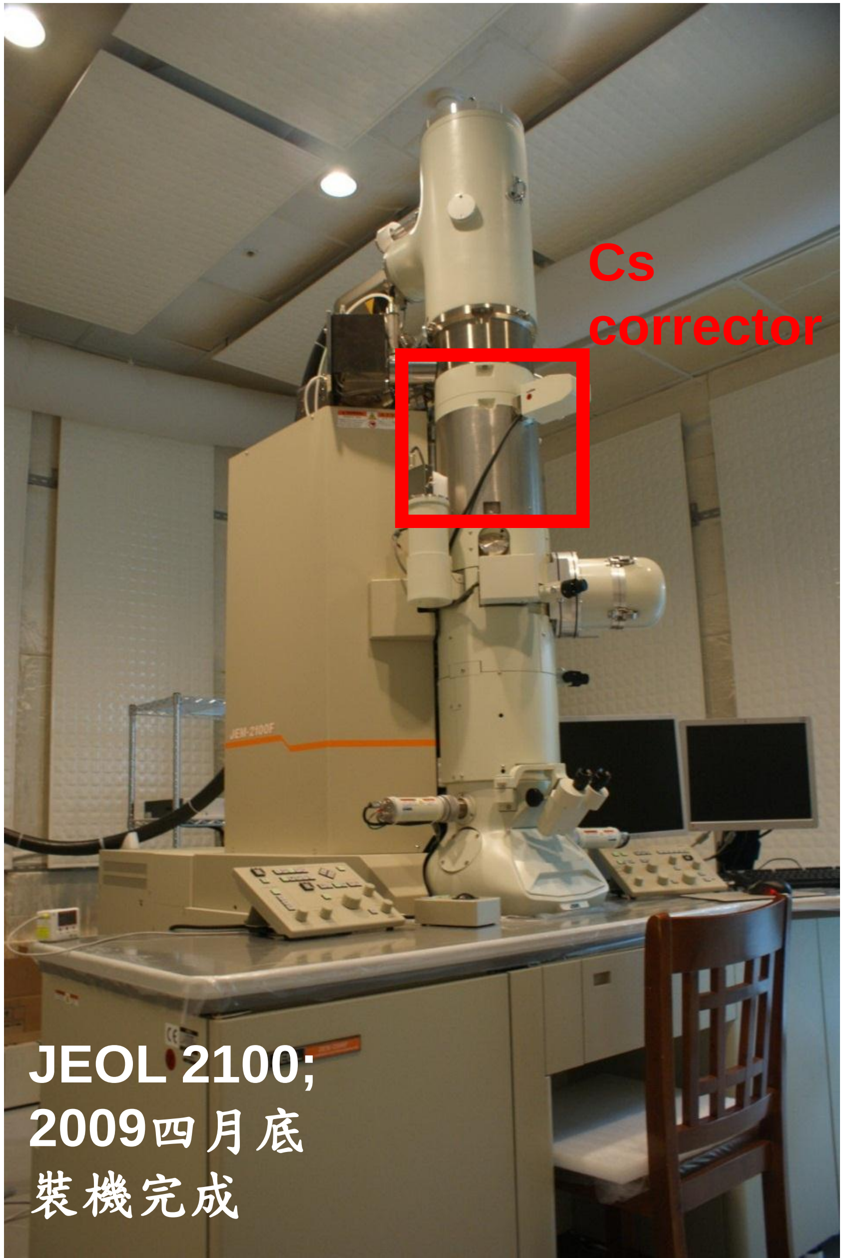


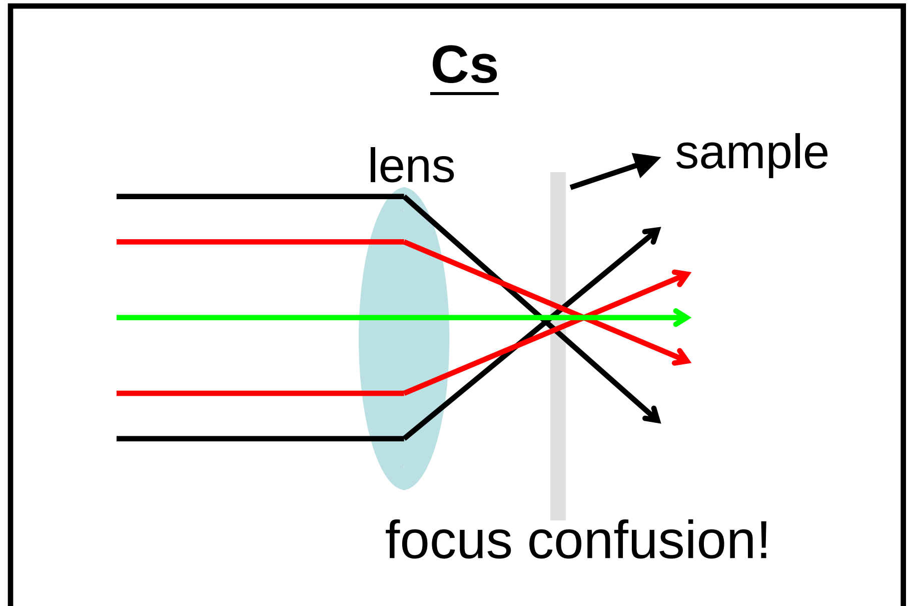
Prof. C. H. Chen and

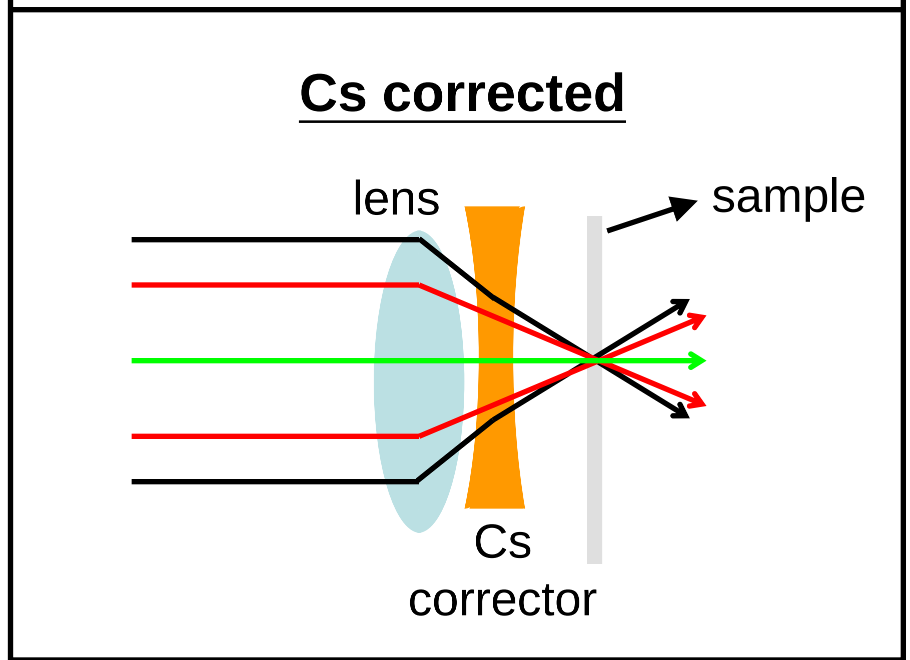
Dr. M.-W. Chu.

Spherical Aberration Corrected (球面相差)

Cs-STEM by C. H. Chen at CCMS, NTU

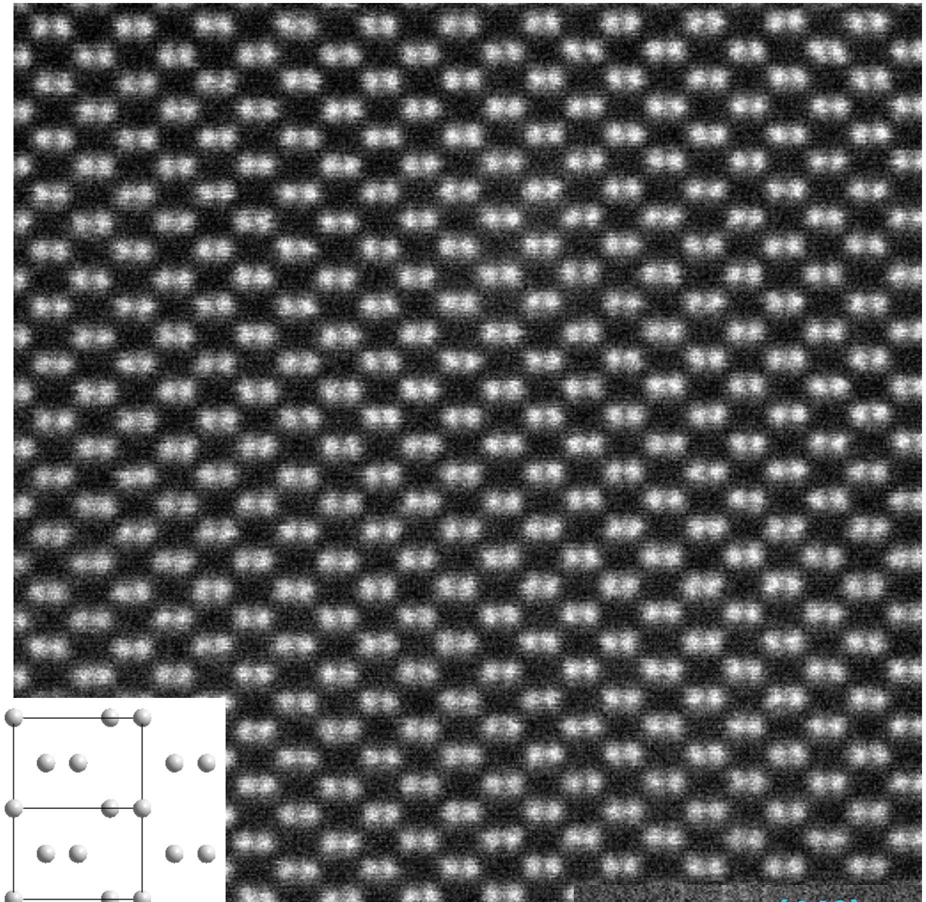




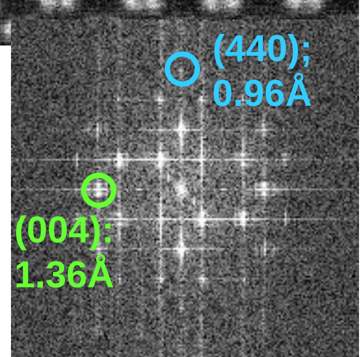


High-Angle ADF: Si dumbbell, 1.36 Å spacing

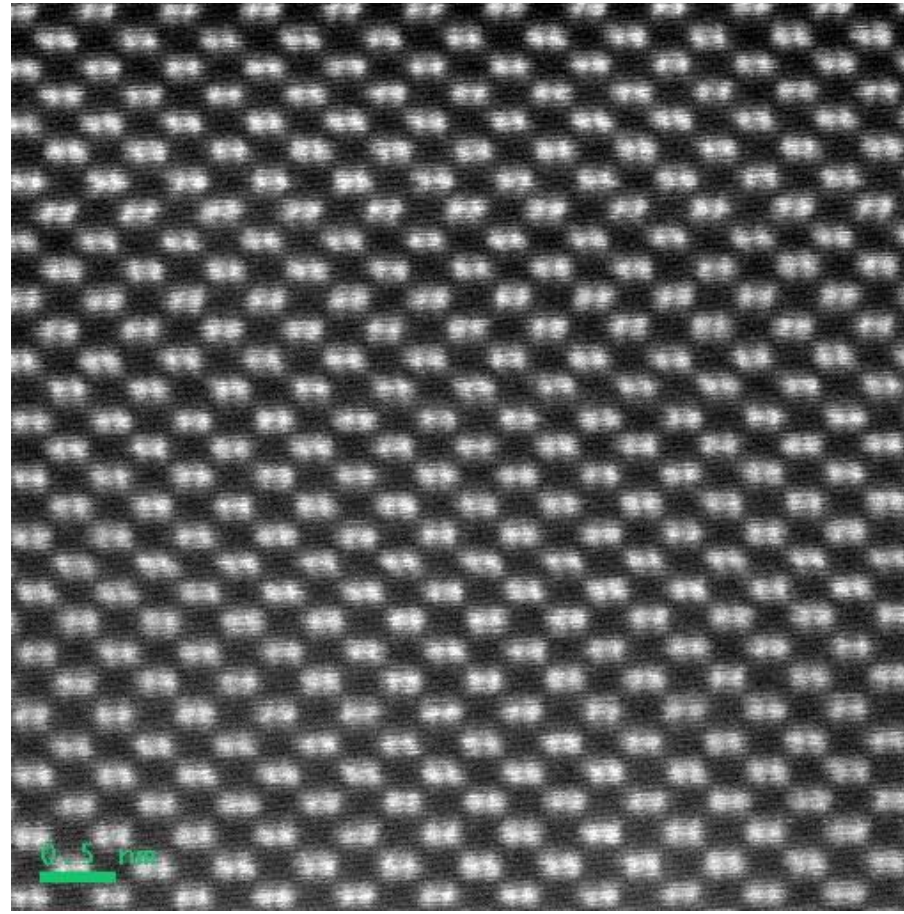
15s exposure



Si [110]

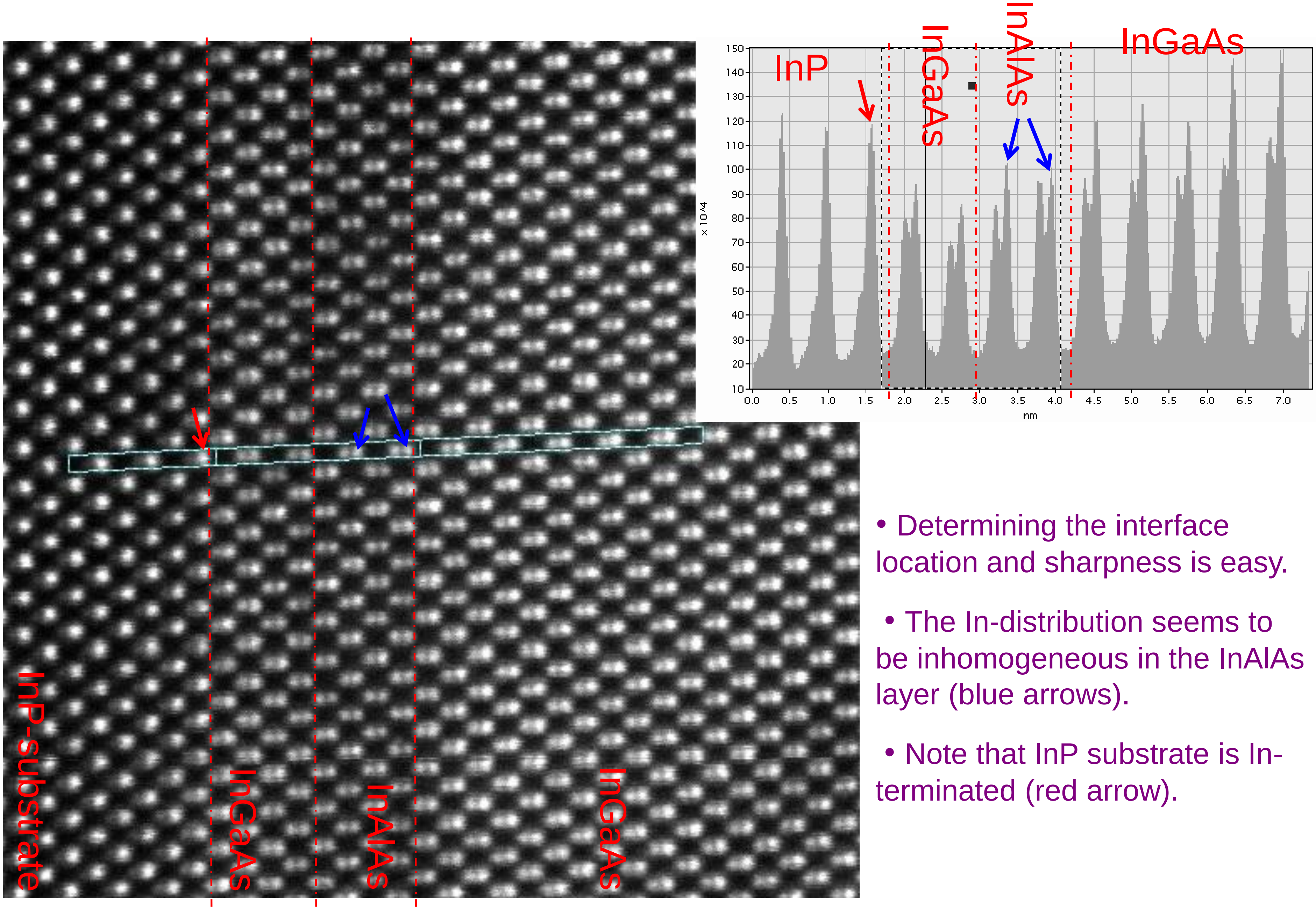


60s exposure



Drift ~1Å/min !!

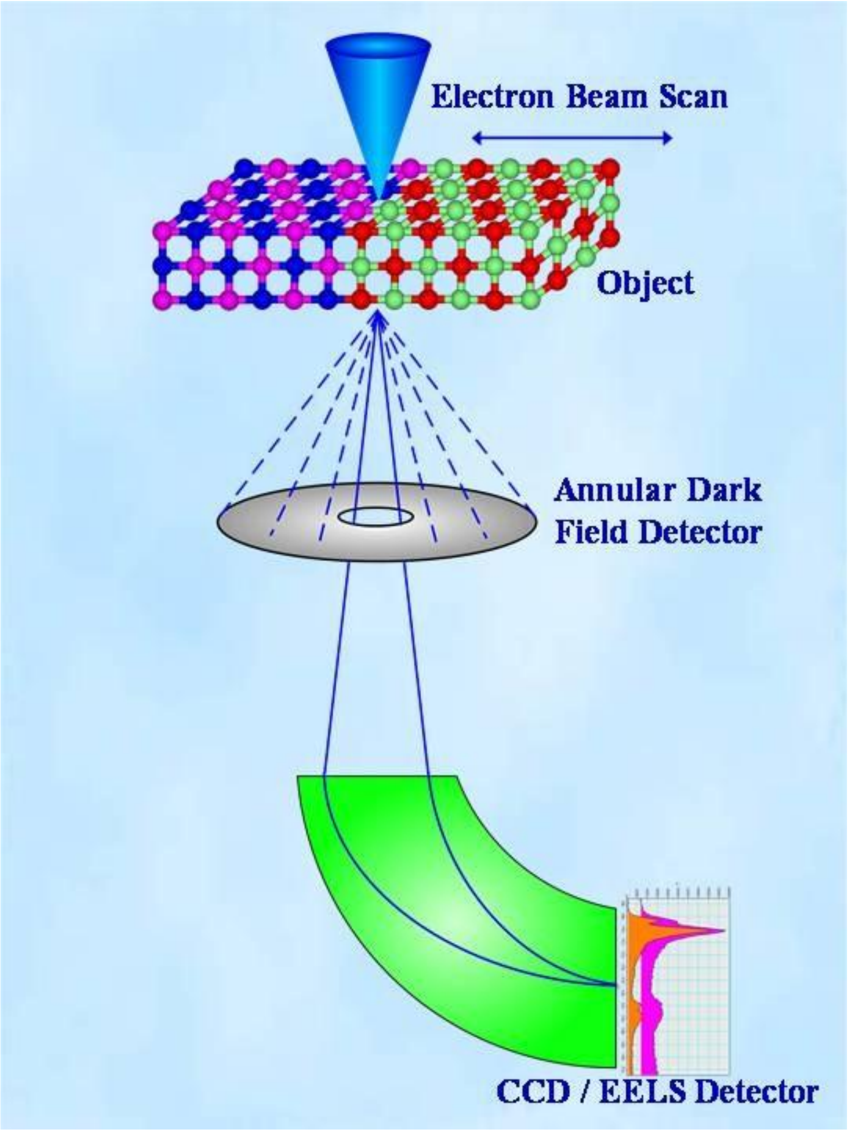
InGaAs/InAlAs superlattices on InP Substrate

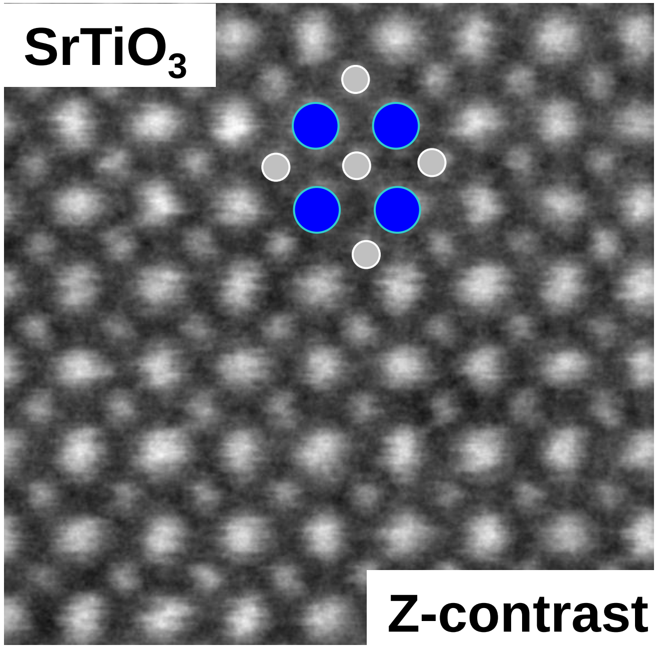


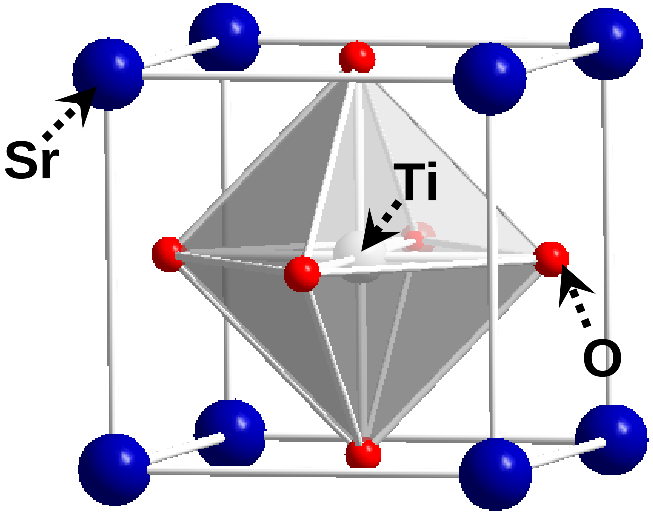
- Determining the interface location and sharpness is easy.
- The In-distribution seems to be inhomogeneous in the InAlAs layer (blue arrows).
- Note that InP substrate is In-terminated (red arrow).

Atomic Resolution STEM Imaging: Z-contrast

2-Å Electron Probe

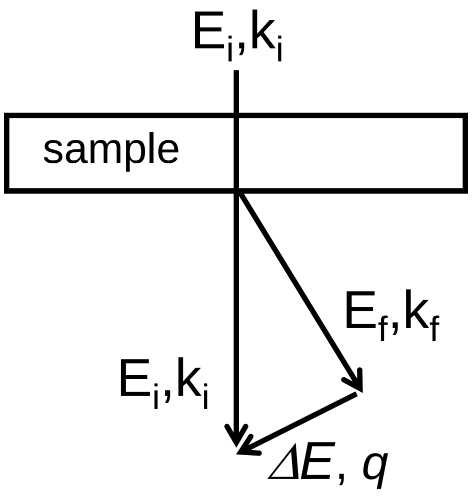






cubic; *a* = 3.905 Å

Electronic Exc.: Electron Energy-Loss Spectroscopy (EELS)



$$\Delta E = E_i - E_f$$

$$q = k_i - k_f$$

Coulomb Interaction

$$v(r) = \sum_j \frac{e^2}{\left| r - r_j \right|}$$

$$= \sum_q v_q \rho_q e^{iqr}$$

, where ρ_q the electron density operator

Inelastic Scattering (ΔE) Probability

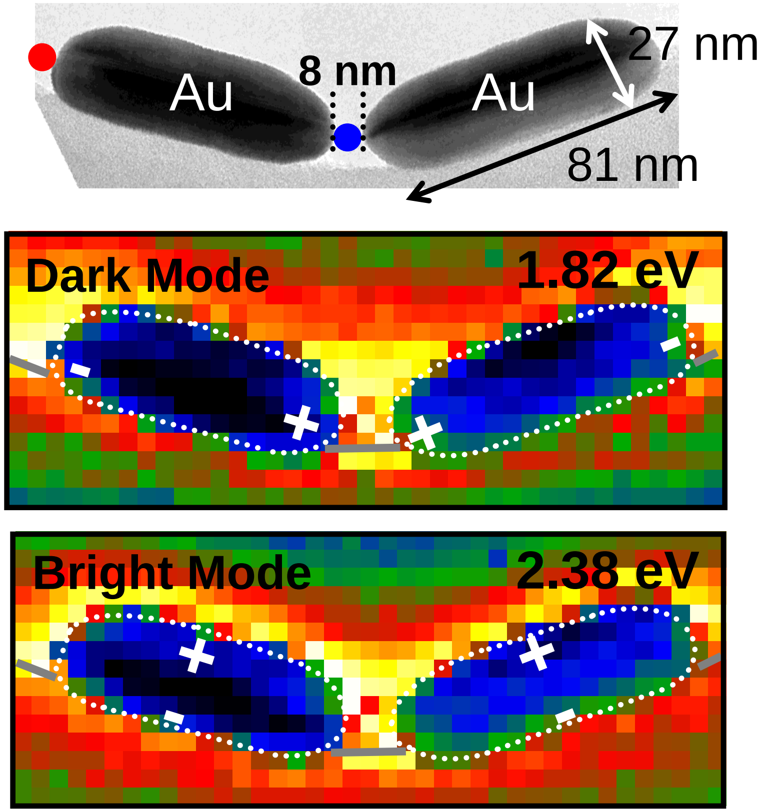
$$\frac{d^2\sigma}{d\Omega d\Delta E} \sim \sum_f \left| \langle \psi_f \left| v(q) \right| \psi_i \rangle \right|^2 \delta(E_i - E_f - \Delta E)$$

$$\sim \frac{1}{q^4} \cdot S(\omega, q) \longrightarrow \text{X-ray}$$

$$\sim \frac{1}{q^2} \cdot \mathrm{Im}\left[\frac{1}{\varepsilon(\omega, q)} \right] \longrightarrow \text{EELS}$$

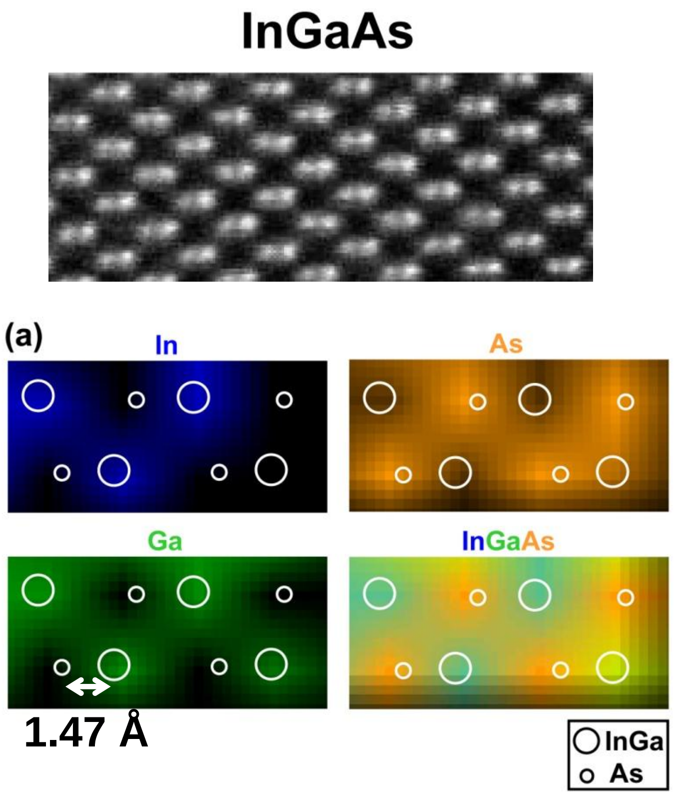
Spectral Imaging at Ultimate Spatial Resolution

Plasmonic Mapping: STEM-EELS (2-Å Probe)



M.-W. Chu *et al*., Nano Lett. **9**, 399 (2009).

Chemical Mapping: STEM-EDX (1-Å Probe)



M.-W. Chu *et al*., Phys. Rev. Lett. **104**, 196101 (2010).

The Third Lesson:

The importance of Quantum Physics

The cause for variation of scaling

- Influence of Boundary
  --Increase of proportion of boundaries
  --Existence of surface / edge modes
  --Geometrical reconstruction

- Decrease of the number of particles
  decrease of confinement , increase of purturbation

- Different scaling for different physical entity

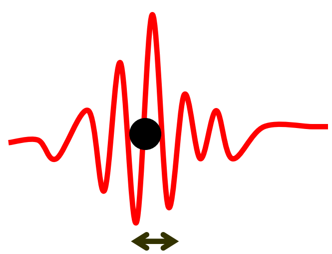
Quantum Effect:

=> Most likely to have new breakthough !

The connection of materials wave with mechanics

h = Planck constant
(6.626×10^{-34} joule-sec)

DeBroglie:
$\lambda = h/p$



λ

Einstein:
$E=h\nu=p^2/2m$

Wave length

Free electrons $\lambda_{th}(300K) = 6.2nm$

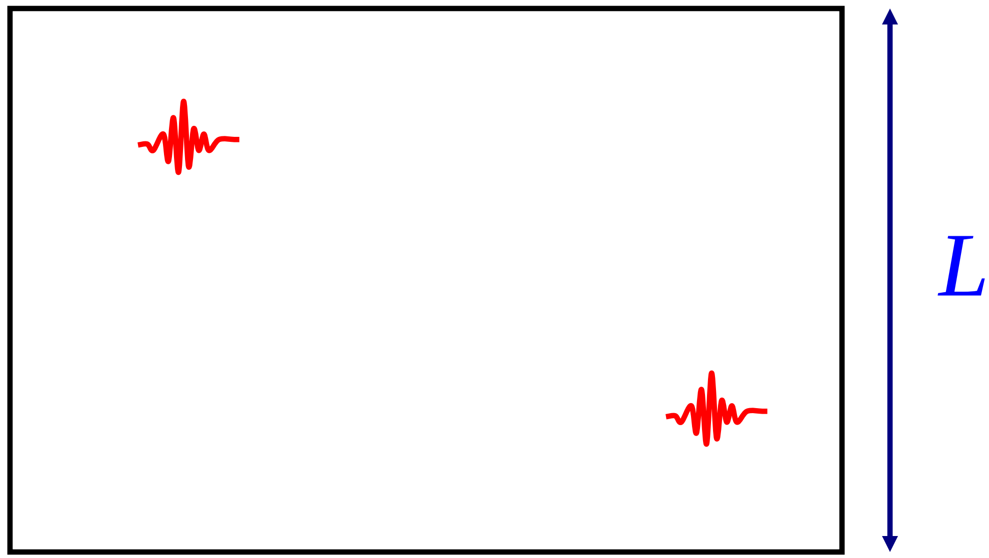
Semiconductors $10nm \le \lambda \le 100nm)$

Atoms $(300K) \le 0.2nm$

Bulk Limit ⟺ Nano Limit

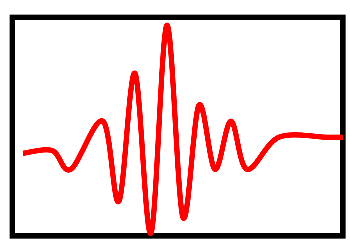
Bulk materials

$\lambda \ll L$



Nano

$\lambda \sim L$

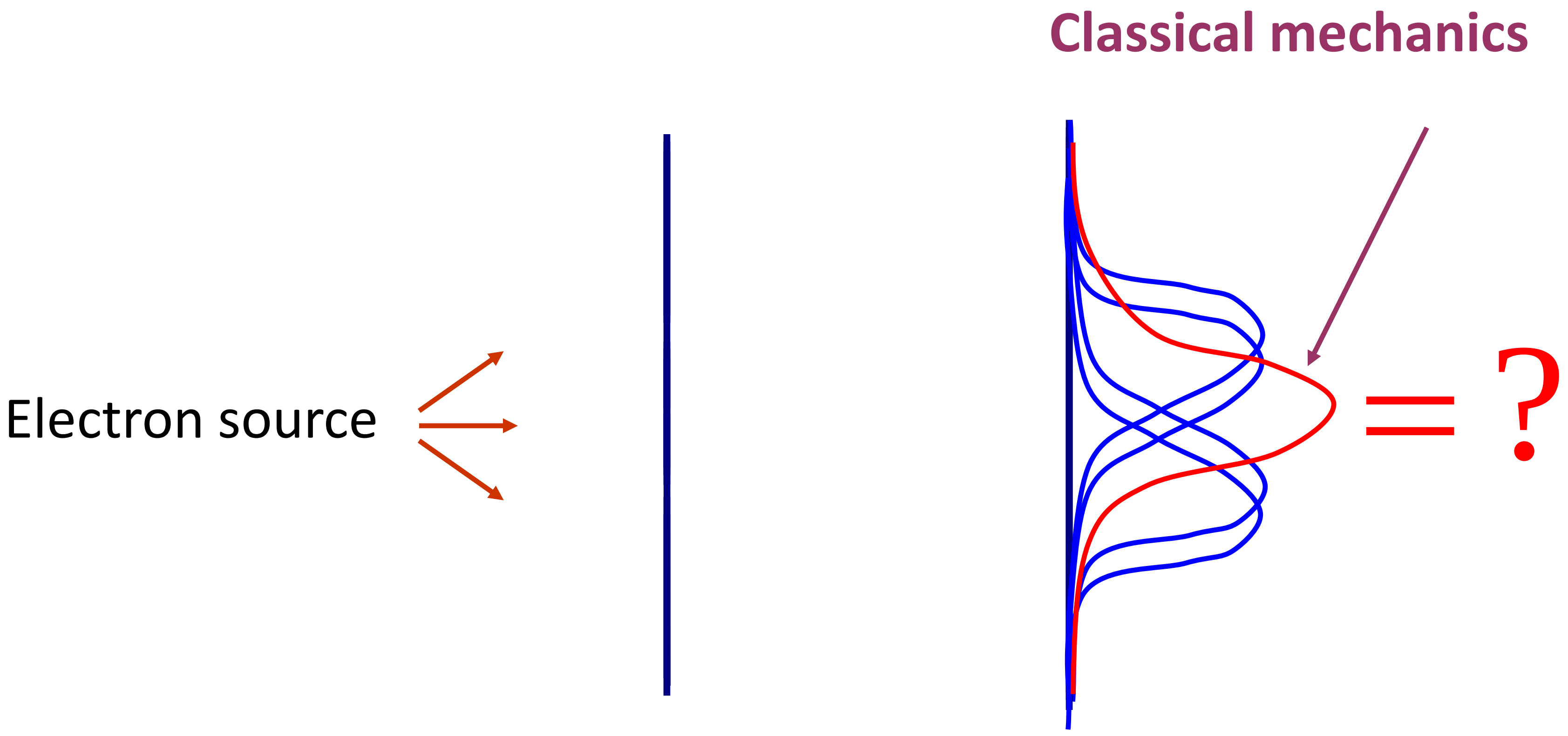


Major Qauntum Effect at the nano scale

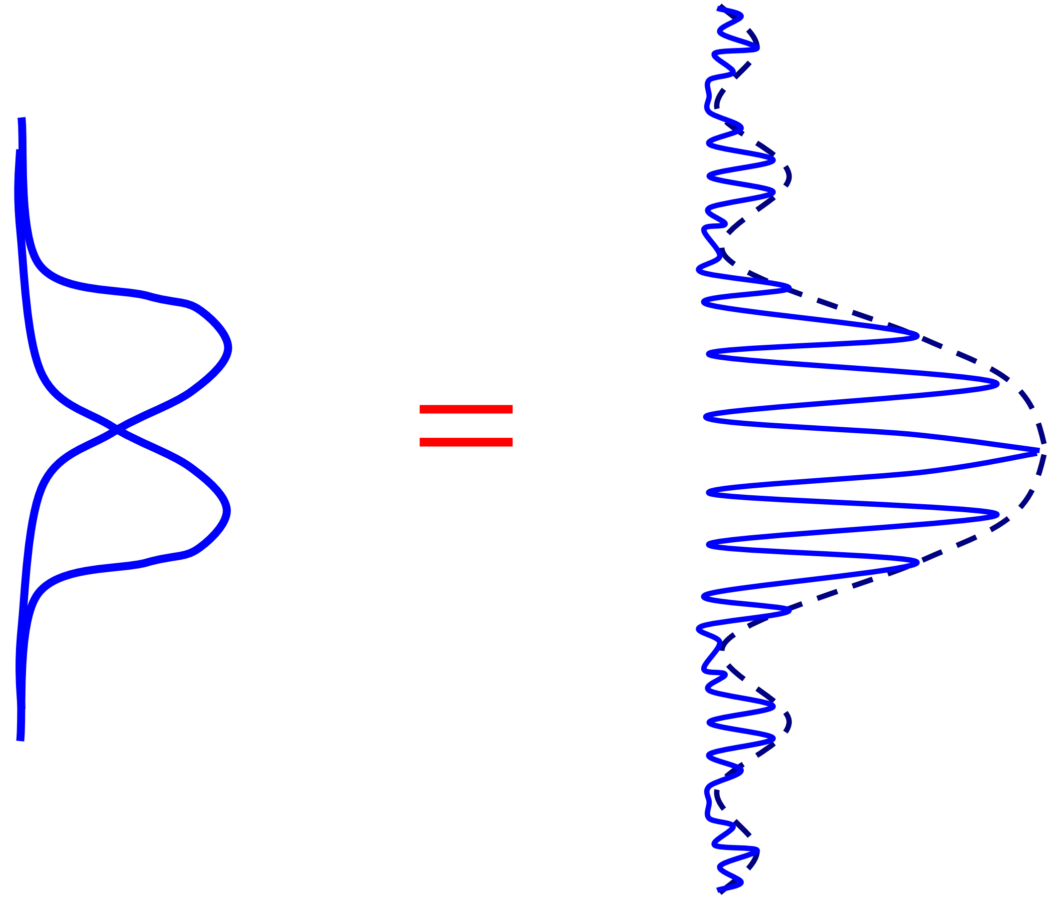
- Interference
- Quantization
- Tunneling
- Quantum Spin

(I) Interference

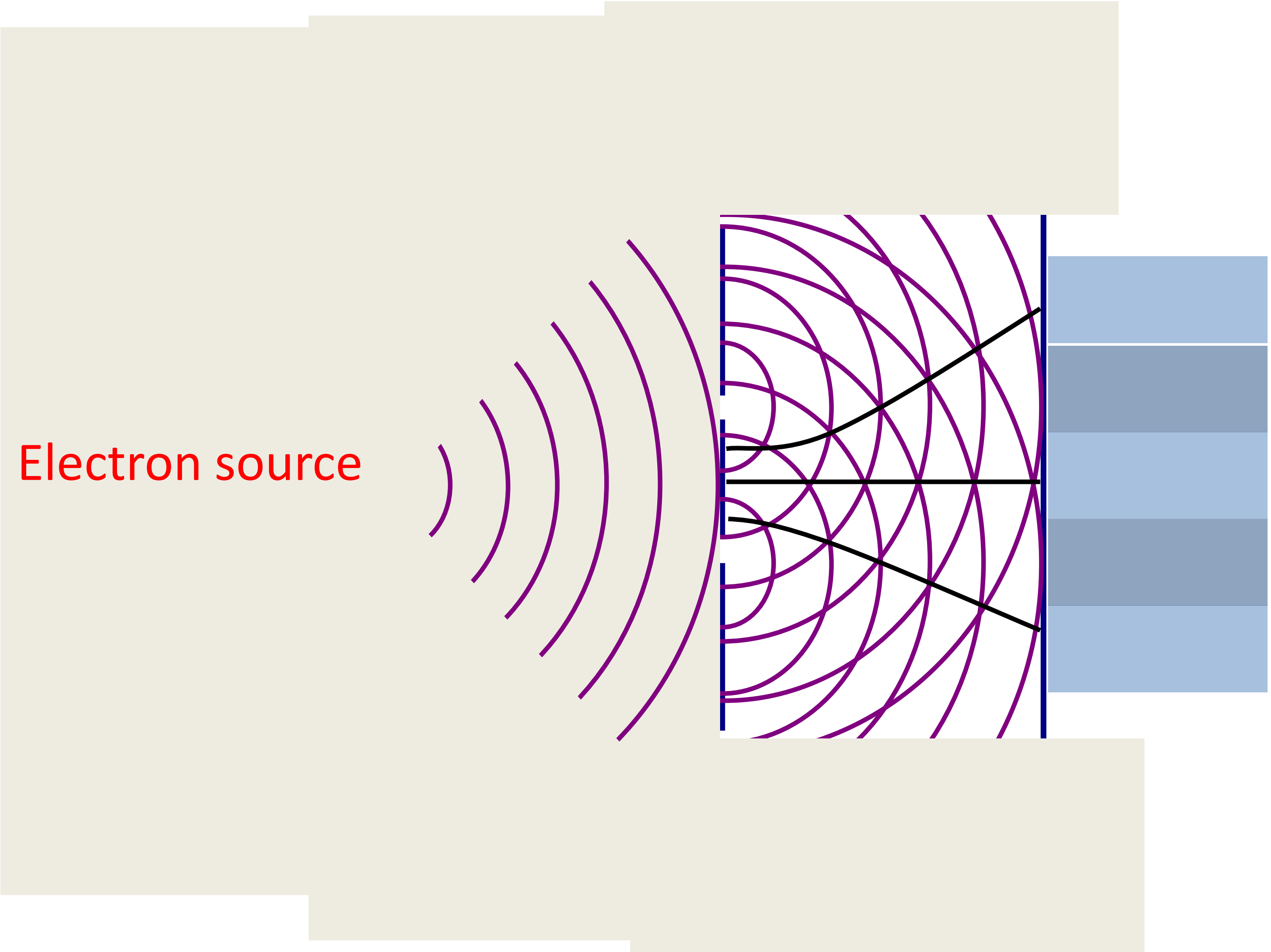
The wonder of electron in waves

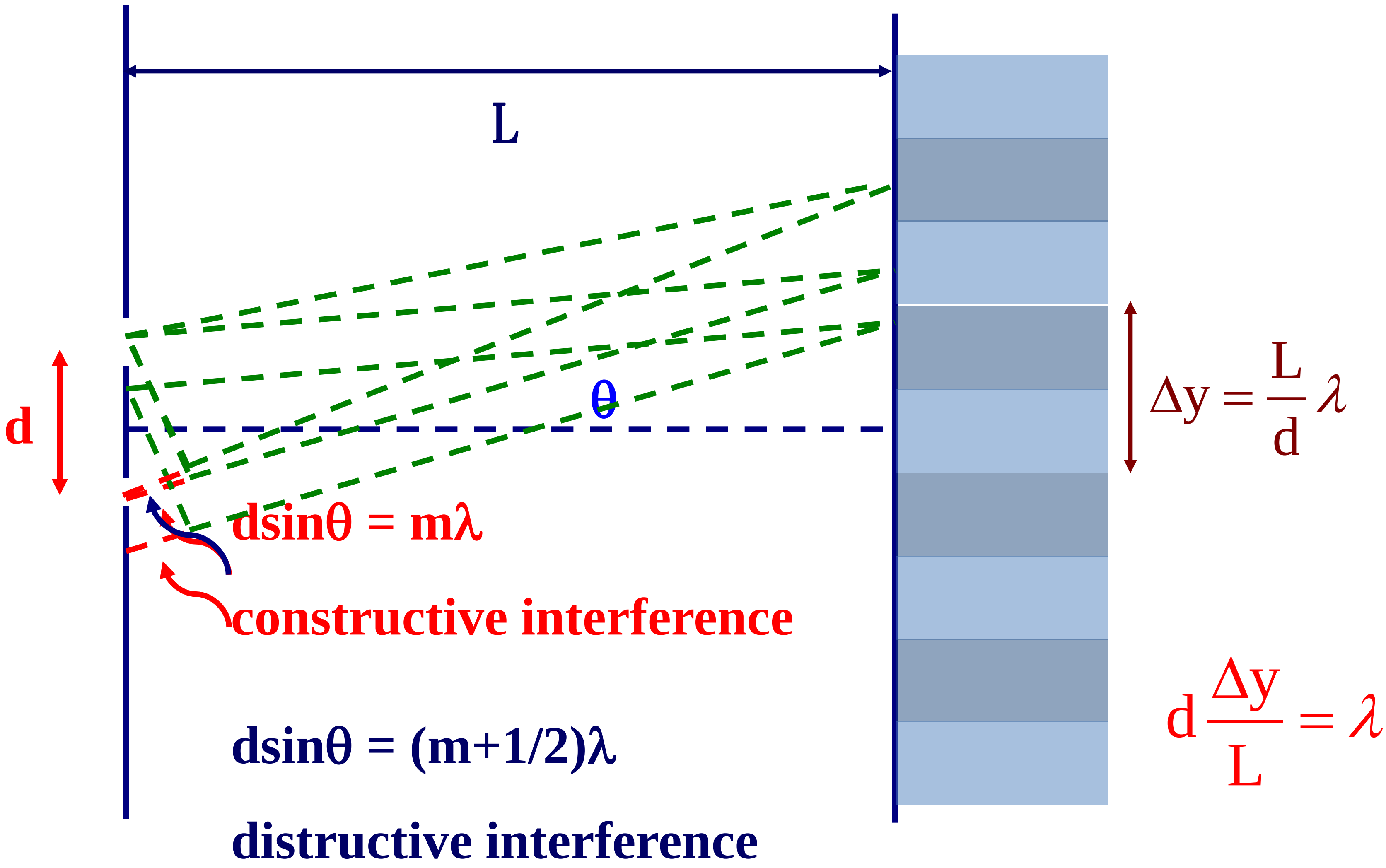


The wave property of electrons



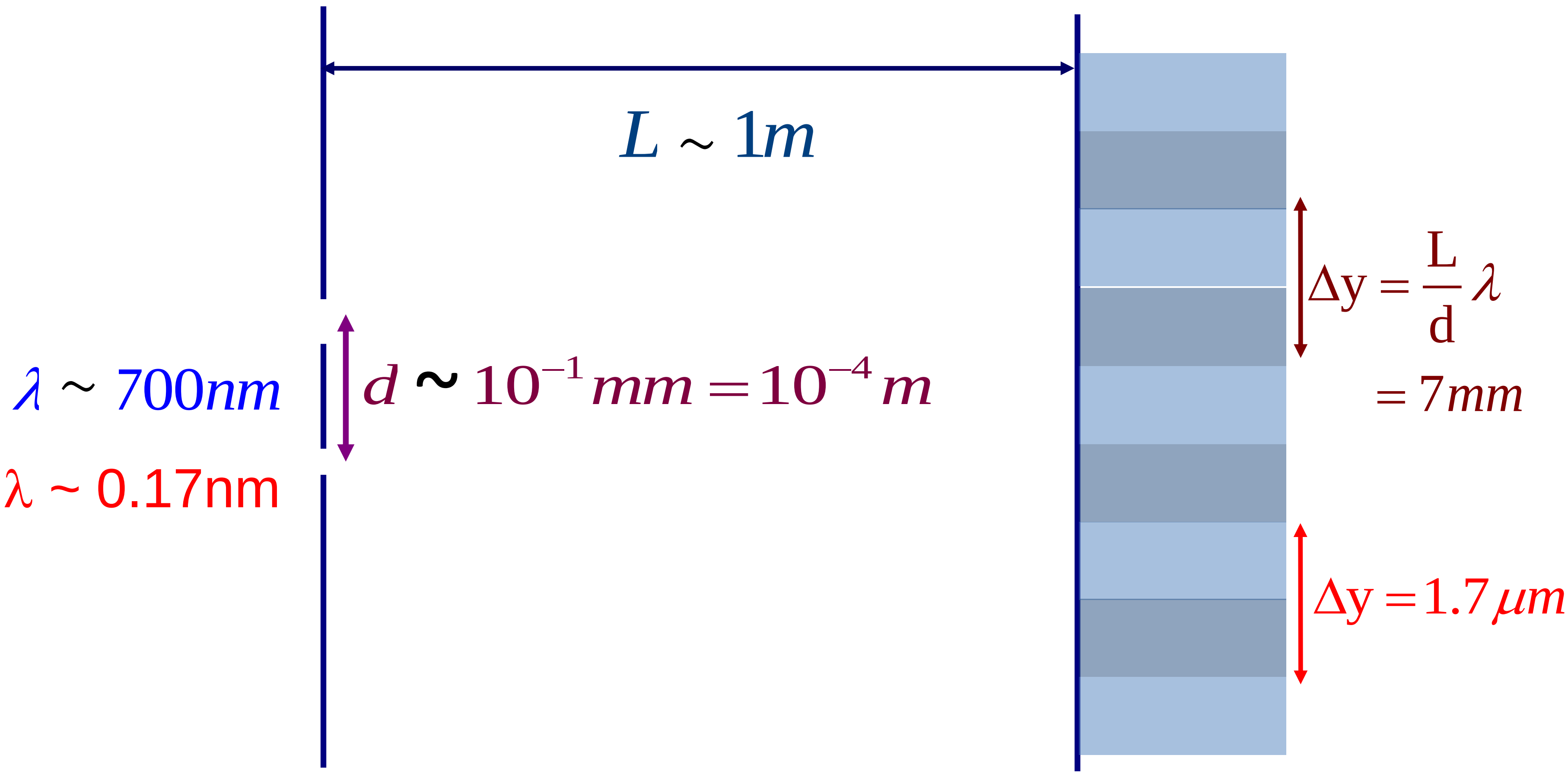
Double Slit Interference of Electrons





L
d
θ
$\Delta y = \frac{L}{d}\lambda$
dsinθ = mλ
constructive interference
dsinθ = (m+1/2)λ
distructive interference
$d\frac{\Delta y}{L} = \lambda$

~


$L \sim 1m$
$\lambda \sim 700nm$
$\lambda \sim 0.17nm$
$d \sim 10^{-1} mm = 10^{-4} m$
$\Delta y = \frac{L}{d}\lambda$
$= 7mm$
$\Delta y = 1.7 \mu m$

(II) Quantization

Confinement of the materials wave

↓

Standing Wave

↓

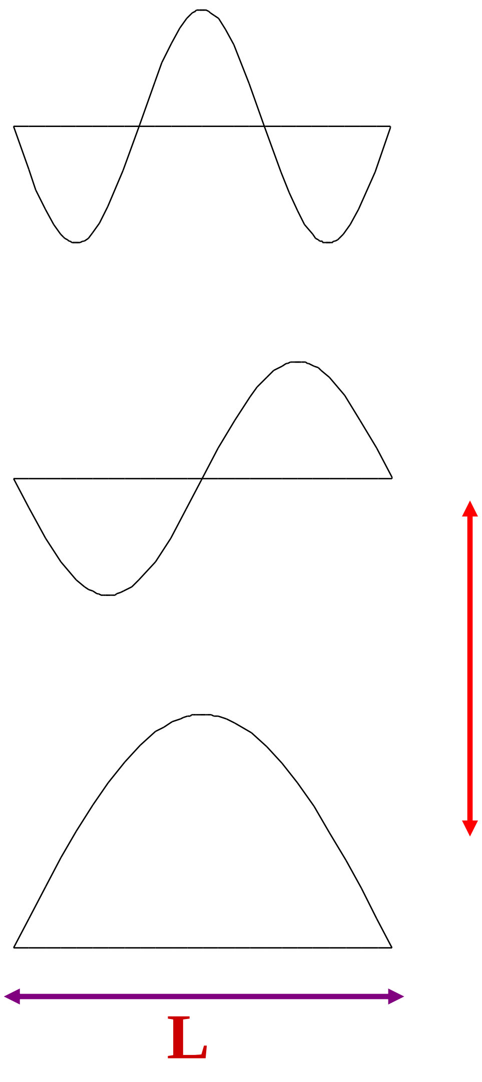
Quantizations

The Qauntization of Energy

$n = 3$

$n = 2$

$n = 1$



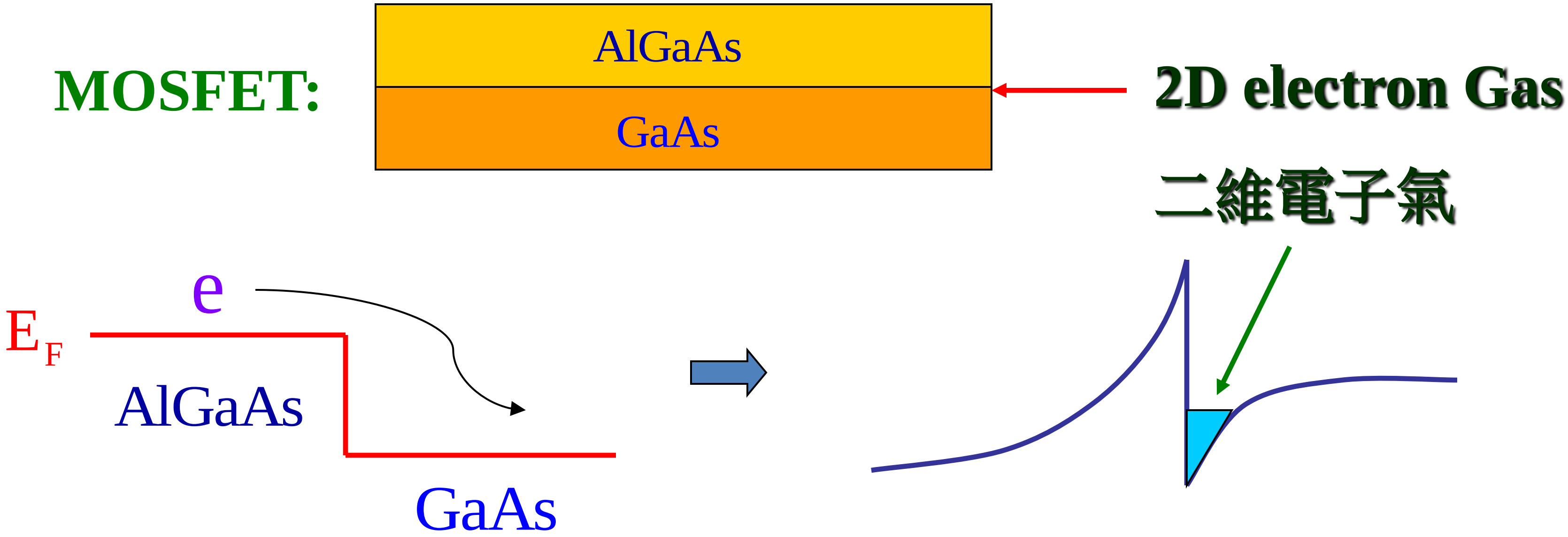
$\delta E \propto 1/L^2$

$$L = \frac{n}{2}\lambda$$

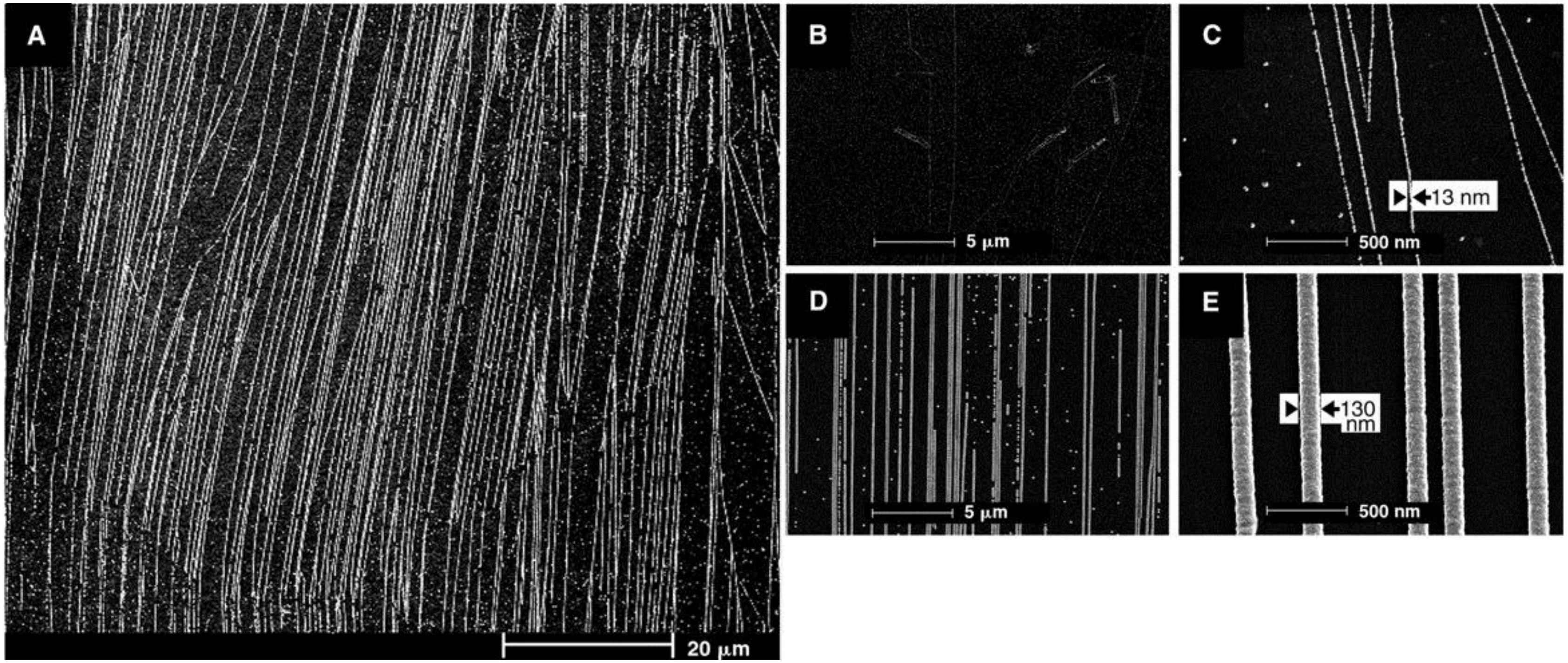
$$p = \frac{h}{\lambda} = \frac{nh}{2L}$$

$$E_n = \frac{p^2}{2m} = \frac{n^2h^2}{8mL^2}$$

Quantum well: 1D confinement



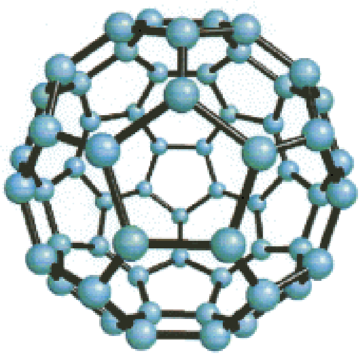
Quantum wire: 2 D-Confinement



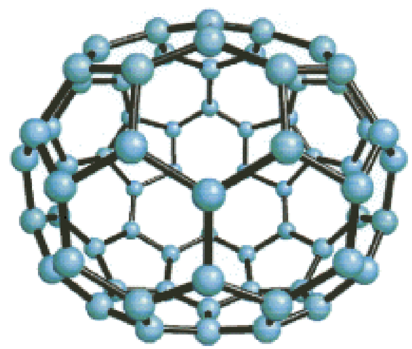
SEM images of MoO_x nanowires on graphite surfaces

Science **290**, 2120-2123, (2000)

Quantum dot: 3 D - Confinement

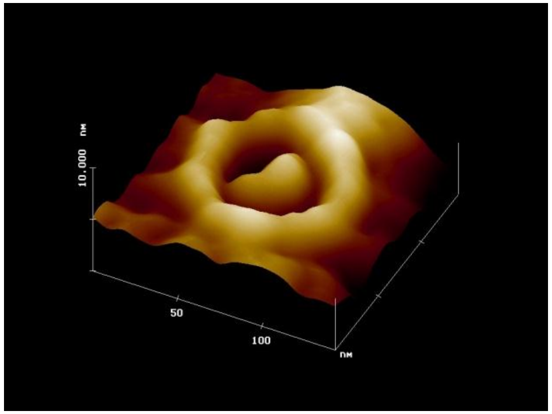


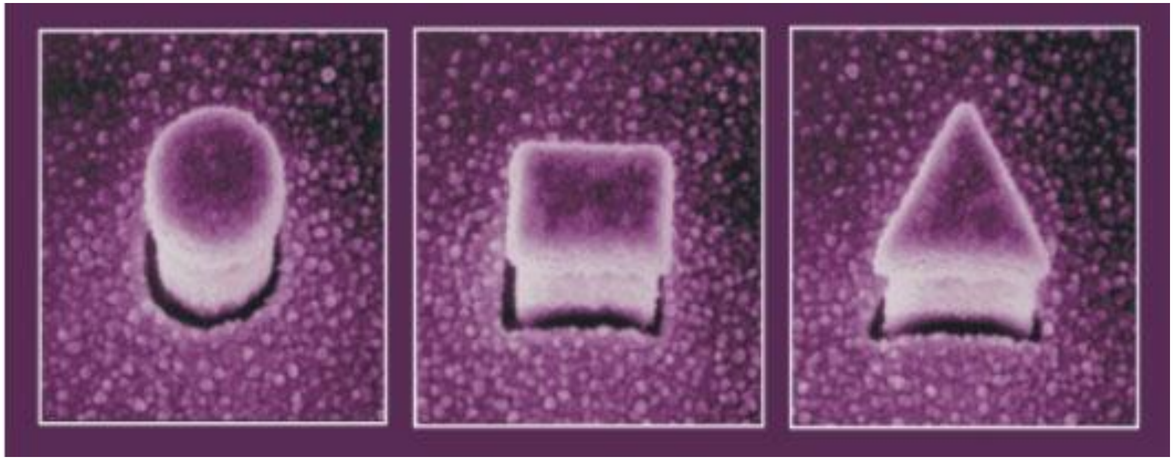
C_{60}



C_{70}

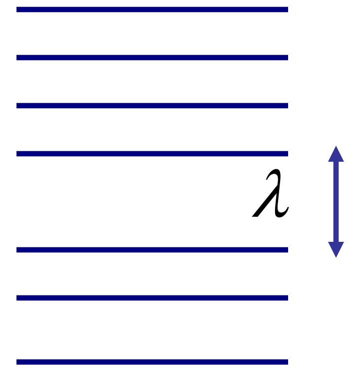
Quantum Dots of various shape





Absorption in scattering
From red to yellow

larger λ_0

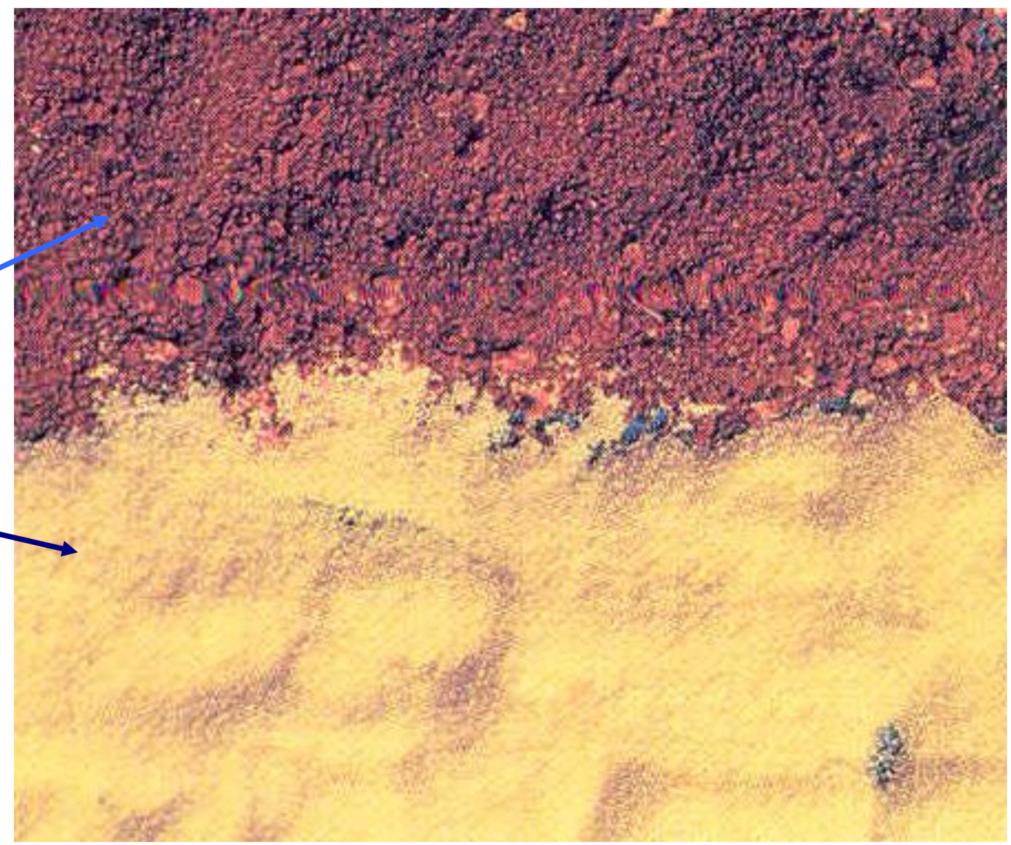


$$E = hc/\lambda \propto 1/L^2$$

powdered Cadmium Selenide

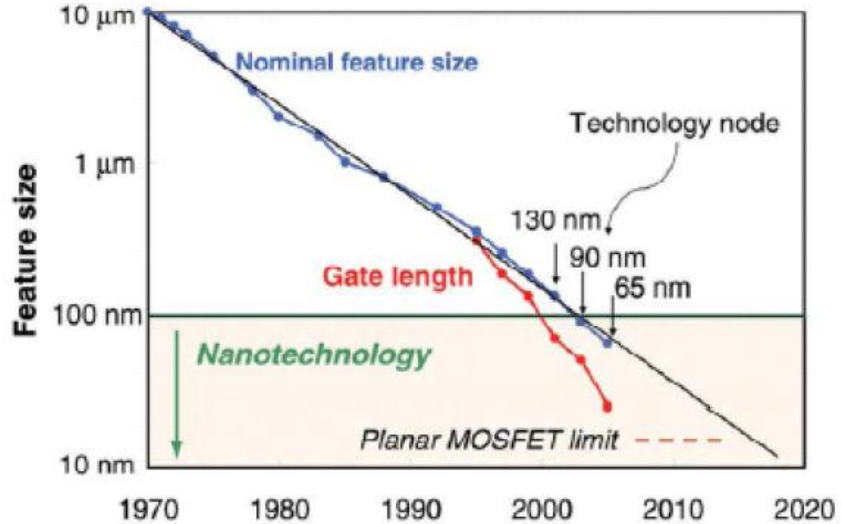
larger

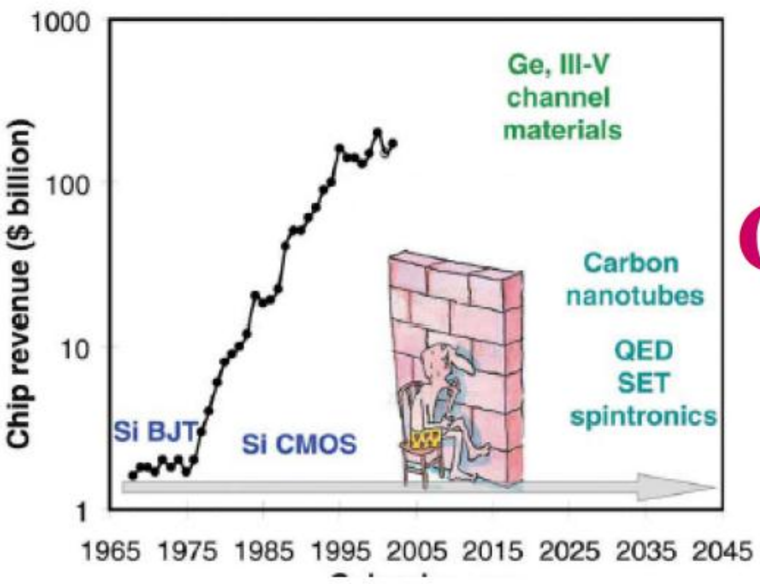
smaller



Background for search new platform

Scaling limit of Si MOSFET
& superparamagnetism



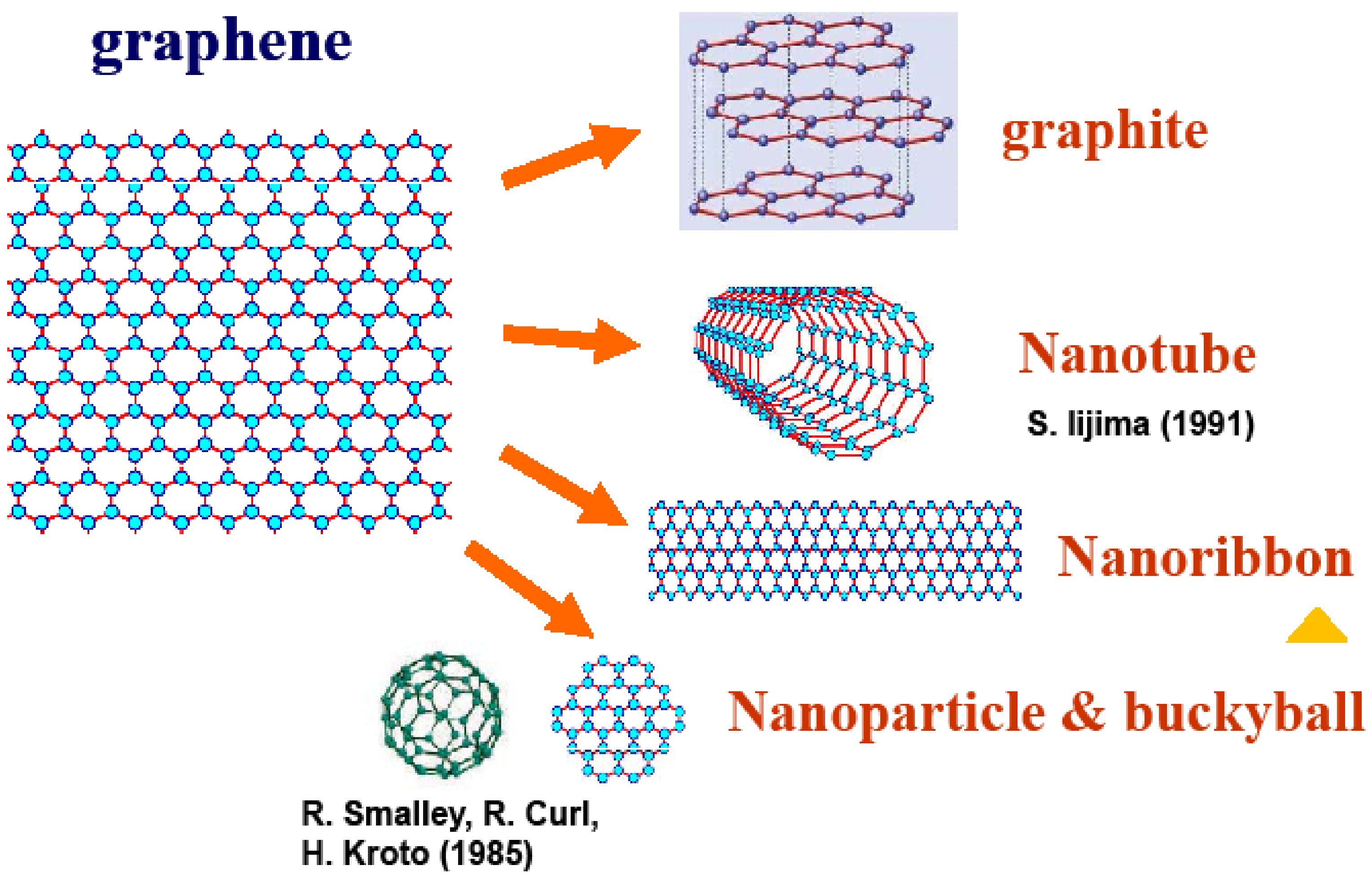


Carbon era?

Thompson and Parthasarathy, Materialstoday 9, 20, 2006

The Advent of Carbon Era ?

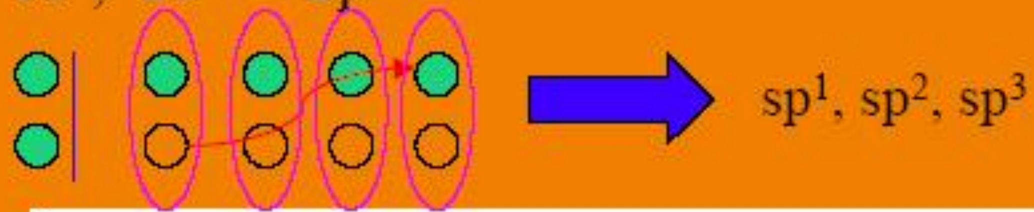
Diversity of carbon forms

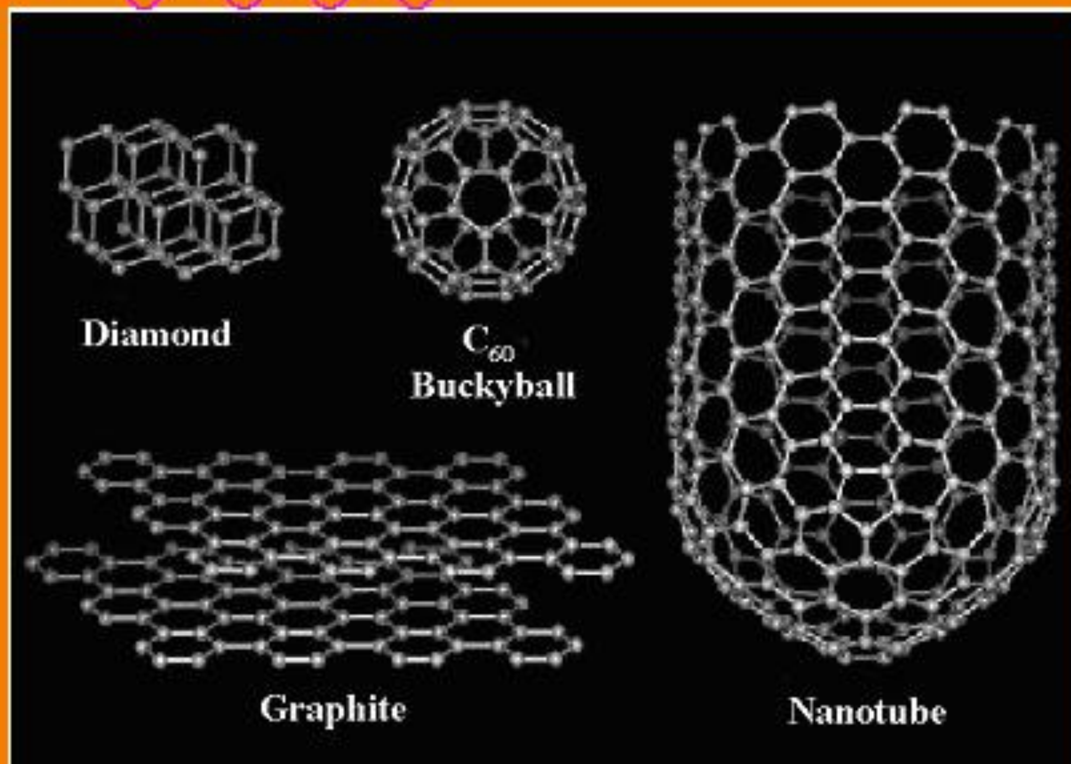


Carbon Nanotube

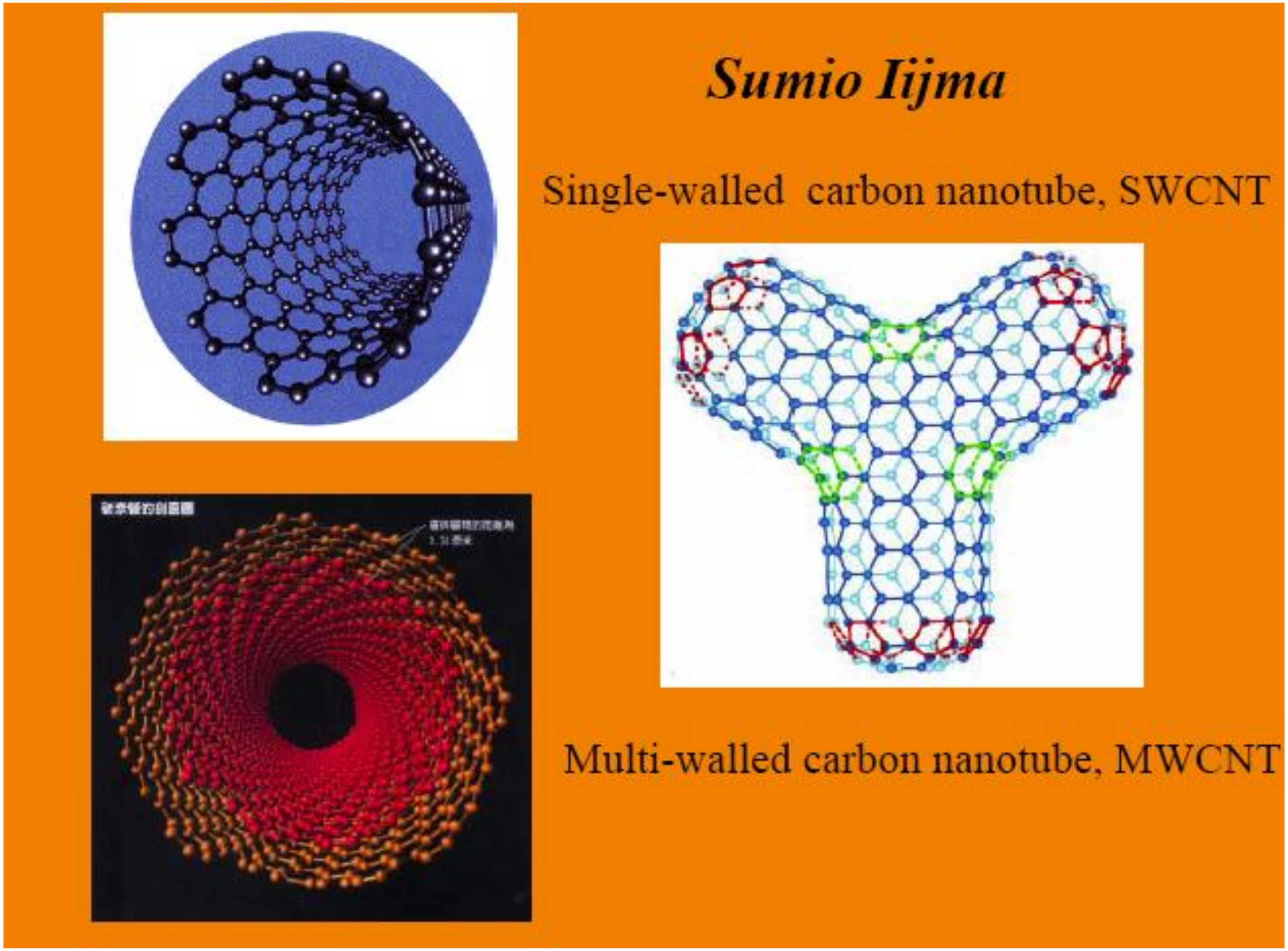
- Structure of carbon nonatubes

Carbon: $1s^2$, $2s^1$ $2p^3$





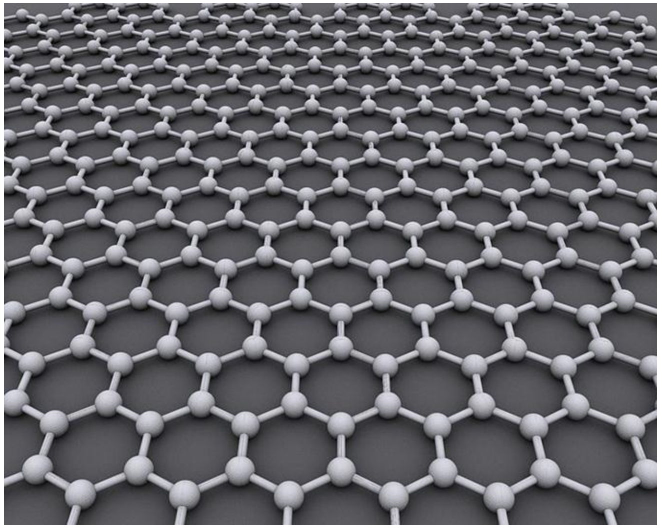
Carbon Nanotube



Carbon Nanotube based Transistors / Electronics

Unexpected realization of graphene sheet

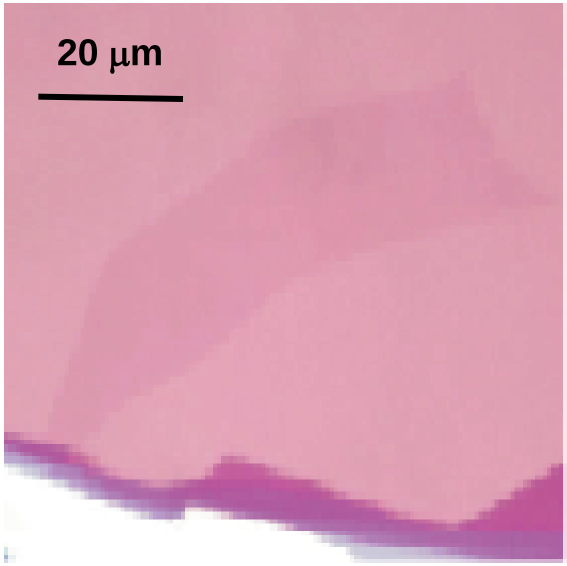
mechanically exfoliated graphene sheets



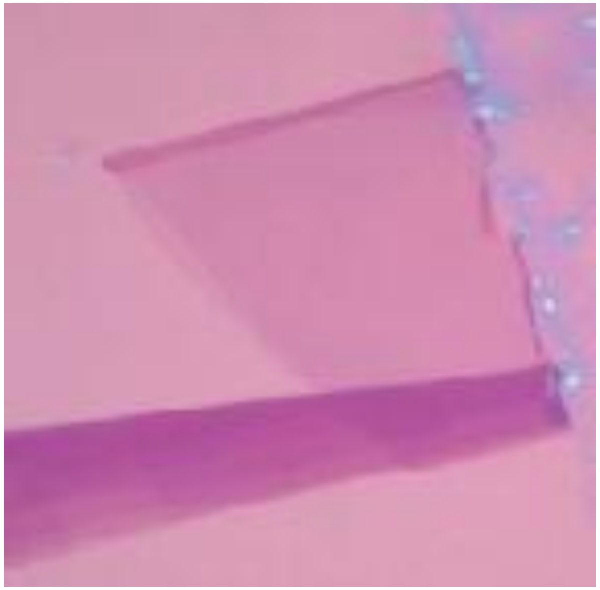
AFM image of single-layer graphene on SiO_2
K.S. Novoselove et al., Science 306, 666 (2004)

Exfoliated Graphene Monolayers and Bilayers

Reflecting microscope images.



Monolayer



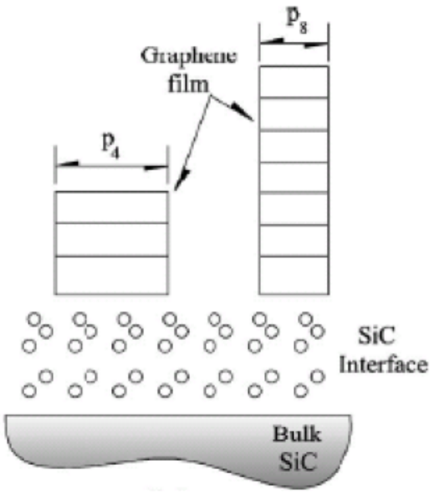
Bilayer

K. S. Novoselov *et al.*, *Science* **306**, 666 (2004).

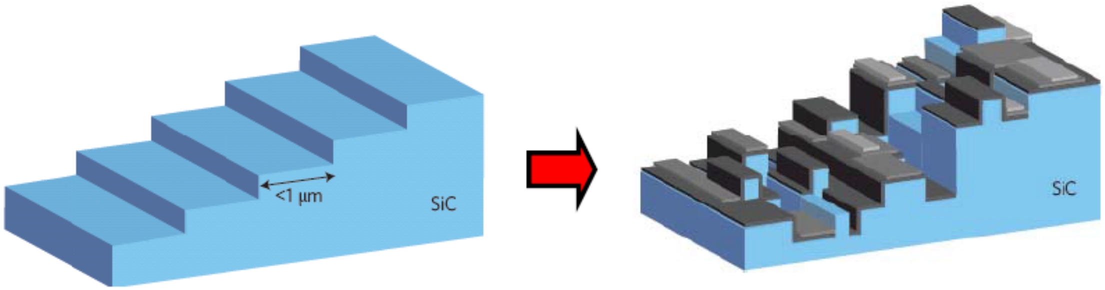
Epitaxial growth of graphene

Epitaxial graphene grown on SiC(0001) surfaces

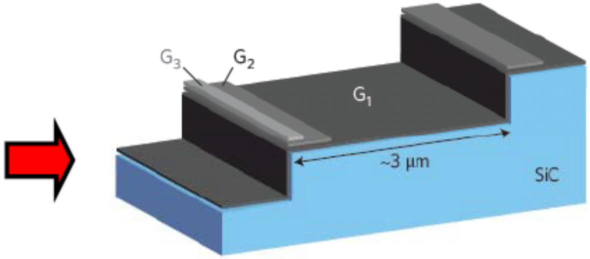
One often ends up with multi-layers of graphene with small grains 30nm-200nm



Recent progress:

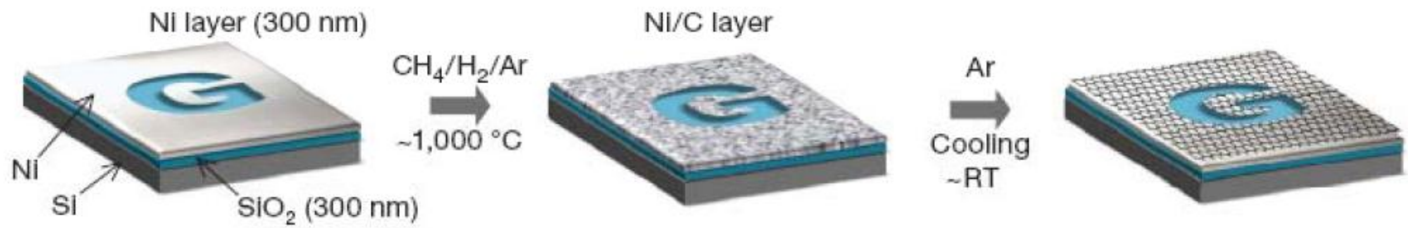


UHV

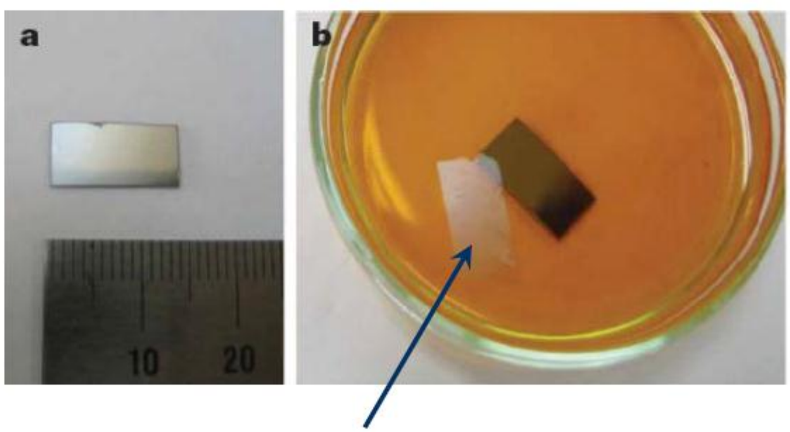


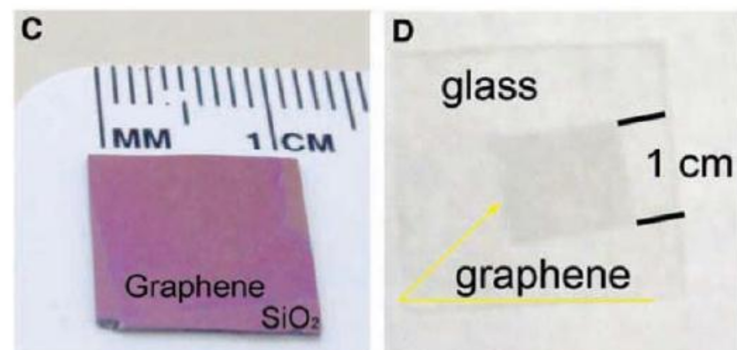
In the presence of pressurized Ar
K.V. Emvsev et al., Nature Materials 8, 203 (2009)

CVD graphene on metal substrates



Etching and transfer

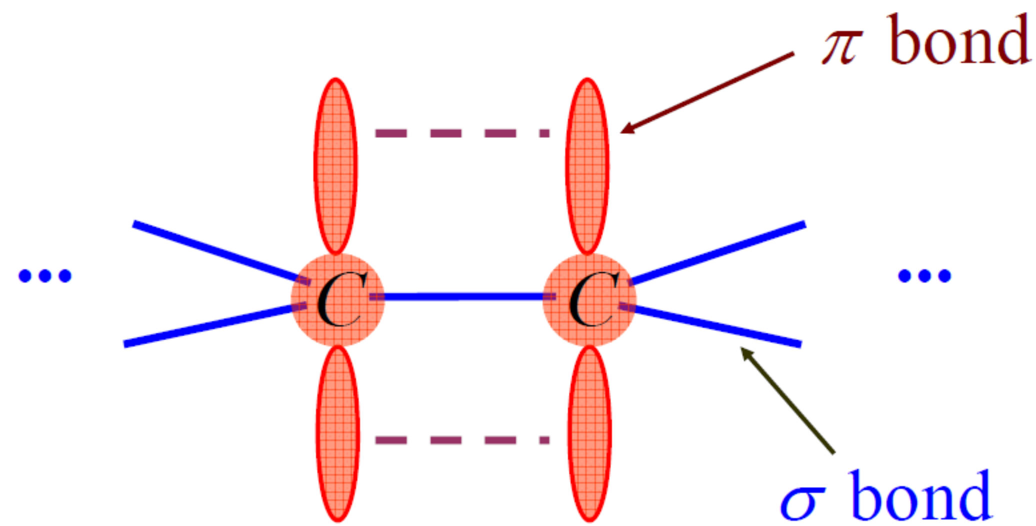




Cu: Li et al., Science 324, 1312 (2009)

Floating graphene after Ni being etched
Ni: Kim et al., Nature 457, 706 (2009)

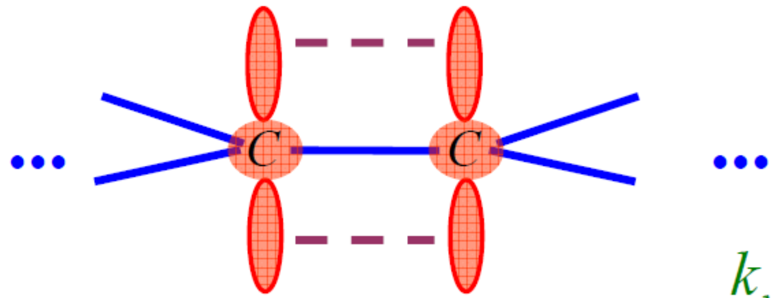
Element of Carbon Network

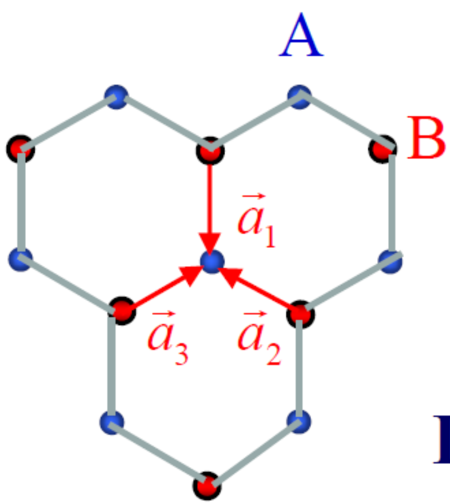


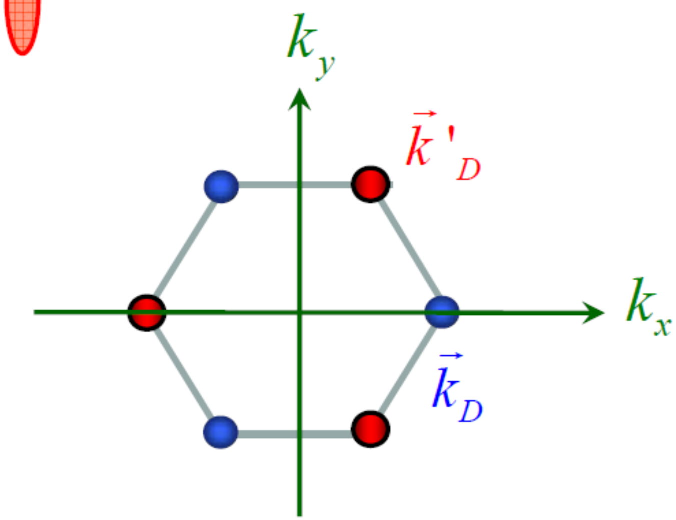
Carbon $1S^2\,\underbrace{2S^2\,2P^2}$

4 electrons in σ bonds (SP^2) + π bond or SP^3

Parent spectrum
Two dimensional Dirac Fermions





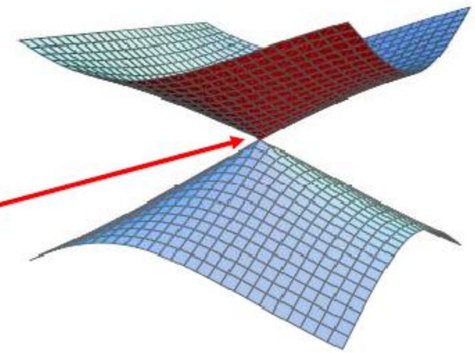


Dirac points

$$e^{i\vec{k}_D\cdot\vec{a}_n} = 1,\ e^{i2\pi/3},\ e^{i4\pi/3} \Leftrightarrow \sum_n e^{i\vec{k}_D\cdot\vec{a}_n} = 0$$

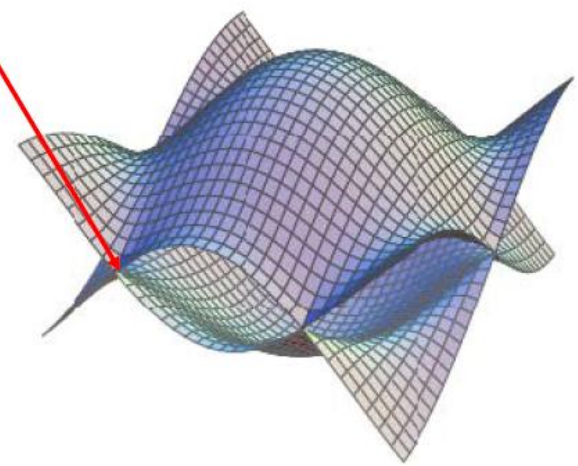
Quasi-Dirac Fermions

$E = \hbar \upsilon k$ with $m = 0$



Dirac points

New playground for testing relativistic QM and QED!

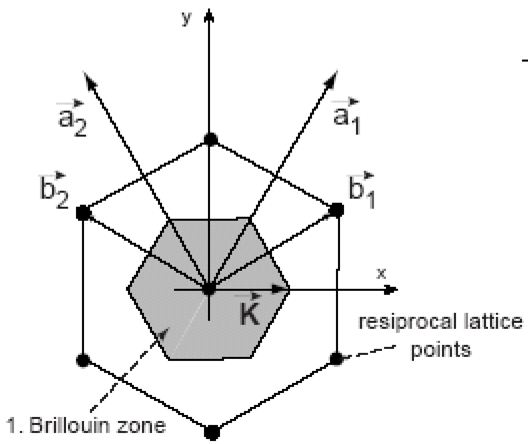


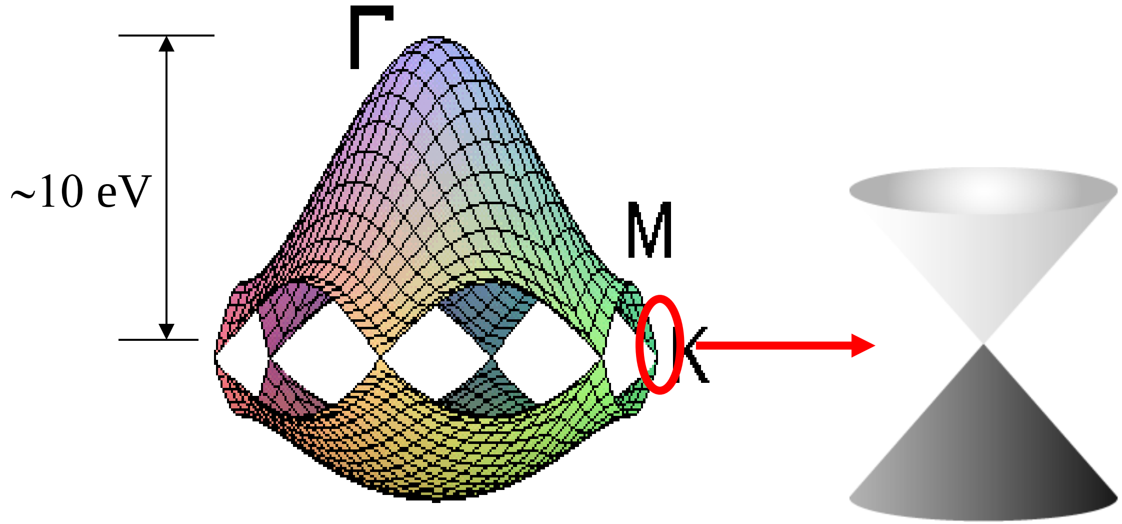
Not exactly Dirac Fermions

$\upsilon \approx c / 300$

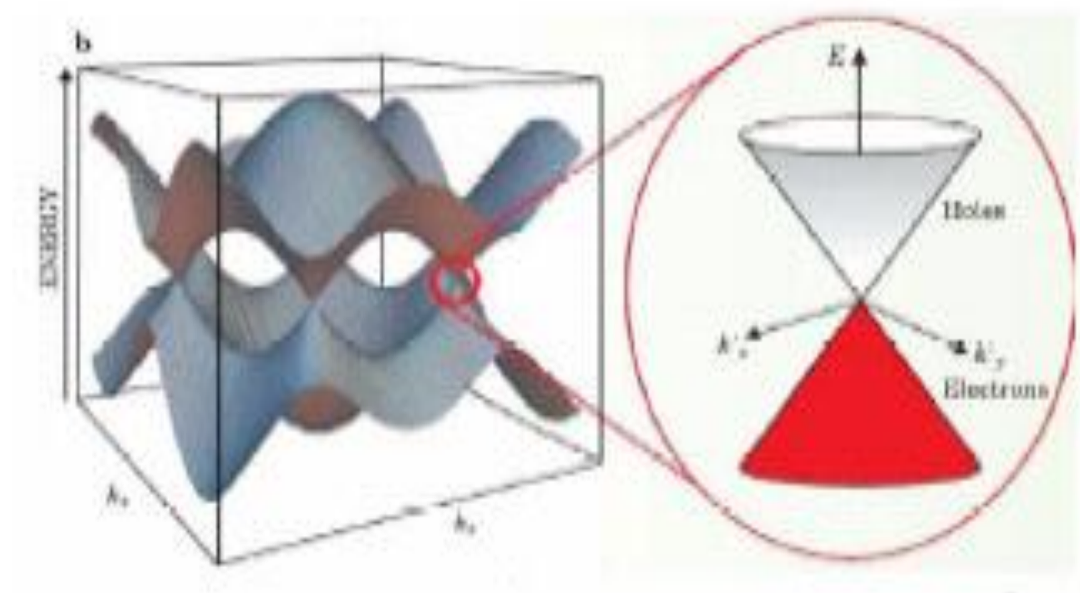
$k_D \neq 0$ and inter-Dirac point scatterings!

Band Structure near K Points





Relativistic Dirac fermion.



Super-Qualities

- $m^* = 0$ expect huge mobility

Carrier mobility: 200000 $cm^2/V.s$

(Geim, 2008, 300K, $n \approx 10^{13} cm^{-2}$)

Ballistic transport at micronscale

Epitaxial graphene: 2000 $cm^2/V.s$ **(27K)** $\lambda_\phi \geq 1 \mu m$

CVD graphene: 4050 $cm^2/V.s$ **(room temp)**

Si 1500 $cm^2/V.s$ **high speed GaAs 8500** $cm^2/V.s$

InSb (undoped) 77000 $cm^2/V.s$

- Thermal conductivity (room temp)

$\approx 5 \times 10^3 W m^{-1} K^{-1}$ ~ 10 × Cu or Al

General Properties of Graphene

Electrically:

High mobility at room temperature,
Large current carrying capability

Mechanically:

Large Young's modulus.

Thermally:

High thermal conductance.

Exotic Behaviors

-Quantum Hall effect

-Barry Phase

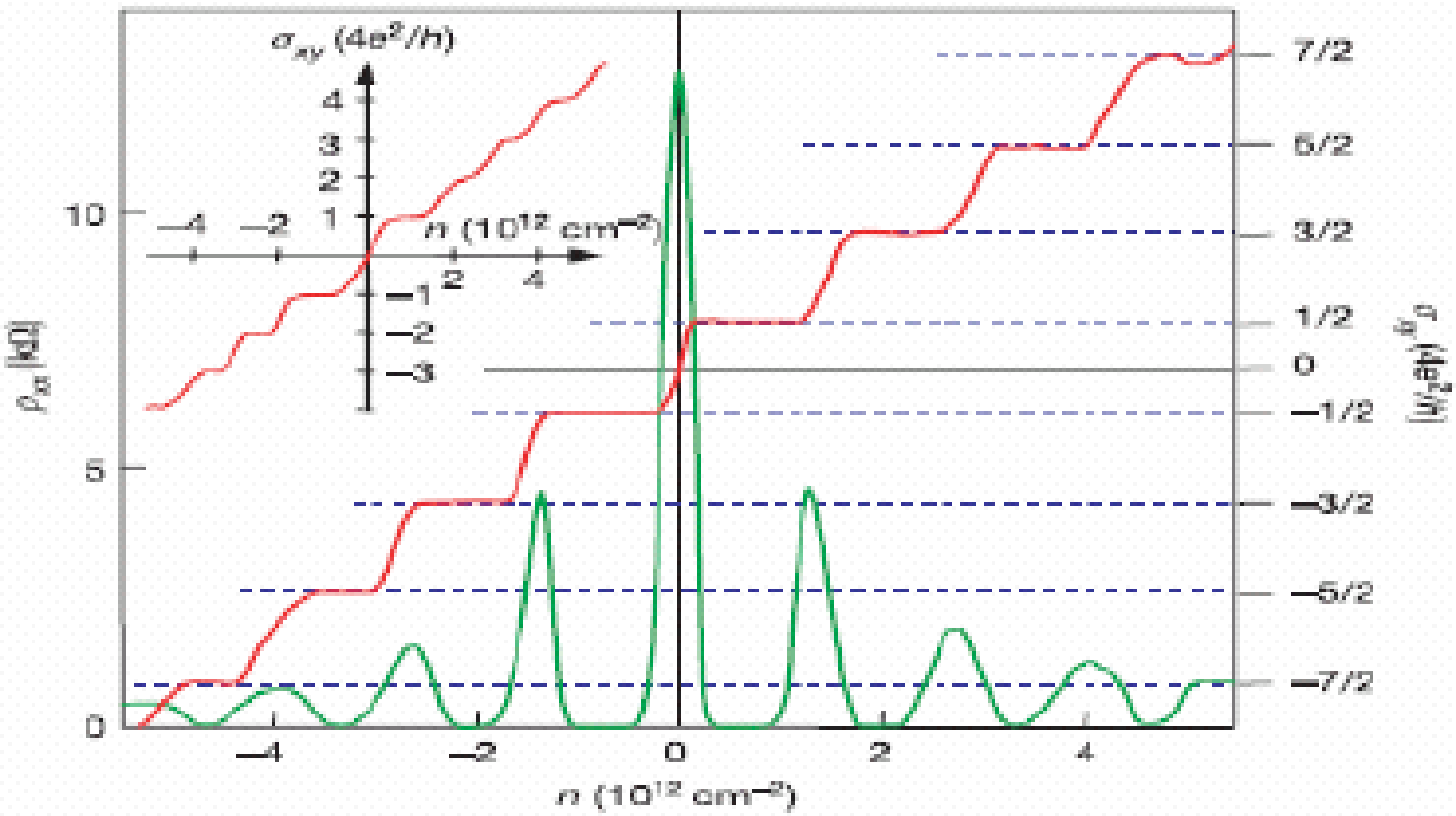
-Ballistic transport

-Klein's paradox

-Others

-
-

Quantum Hall Effect

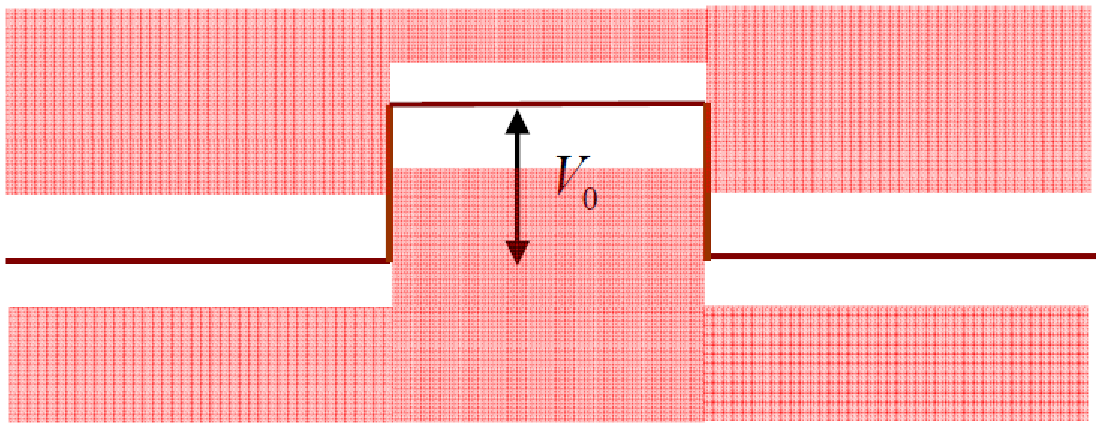


$$\sigma_{xy} = \frac{4e^2}{h}\left(N + \frac{1}{2}\right)$$

Y. Zhang et al, *Nature* **438**, 201(2005)

Electron scattering from a potential barrier

Potential complication: Klein Paradox (1929)



$$T \rightarrow 1 \text{ as } V_0 \Rightarrow m_0c^2$$

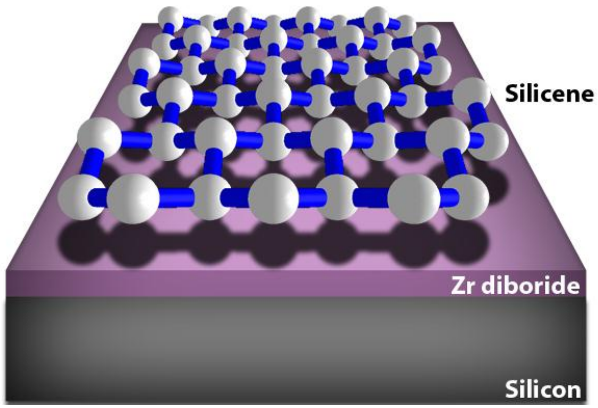
As the potential approaches infinity, the reflection diminishes,
the electron always transmittes

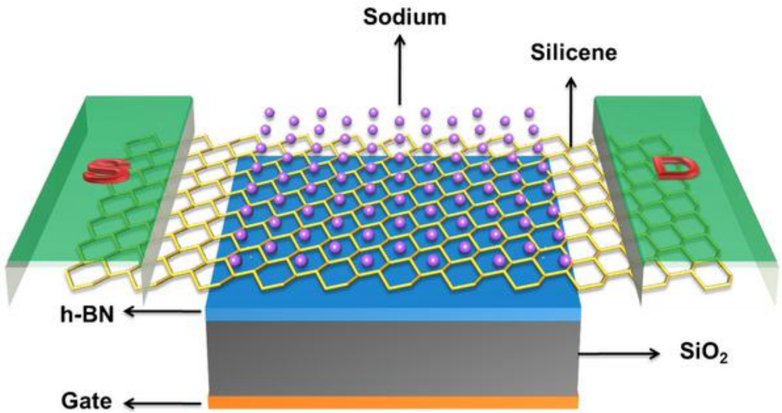
No confinement for electrons

On/off ratio is reduced in graphene FET

Another emerging wonder material : Silicene

- Graphene-like two-dimensional silicon
- Could be more compatible with existing silicon-based electronics
- Potential application as a high-performance field effect transistor

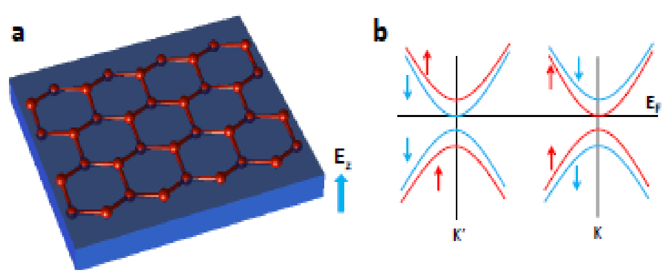


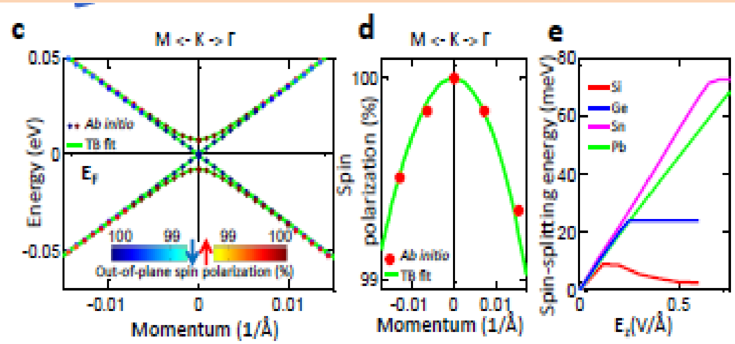


Nature, Scientific Reports **2**, # 853, 2012

To grow Silicene, Germanine, and even Tinene on insulating or semiconducting substrate.

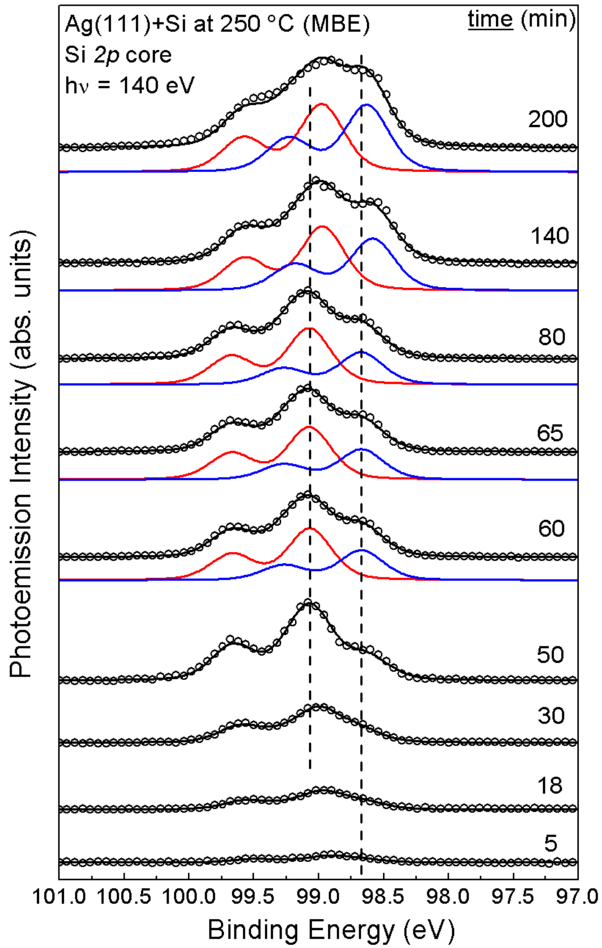
Superconductivity in alkaline or alkaline earth elements doped silicene (CaC_6 T_c=13K; $CaSi_6$ T_c = ?)





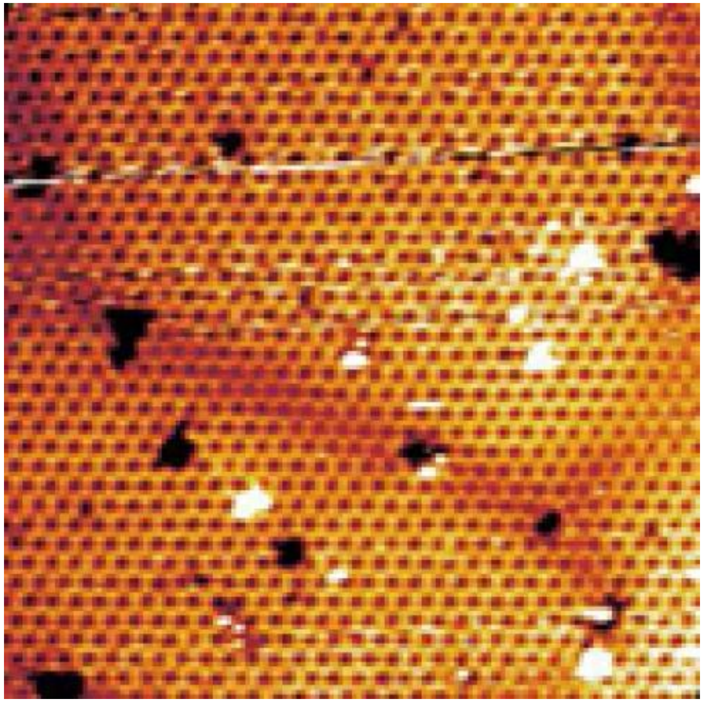
Combined spectroscopic and microscopic study underway

Synchrotron radiation core level photoemission from NSRRC

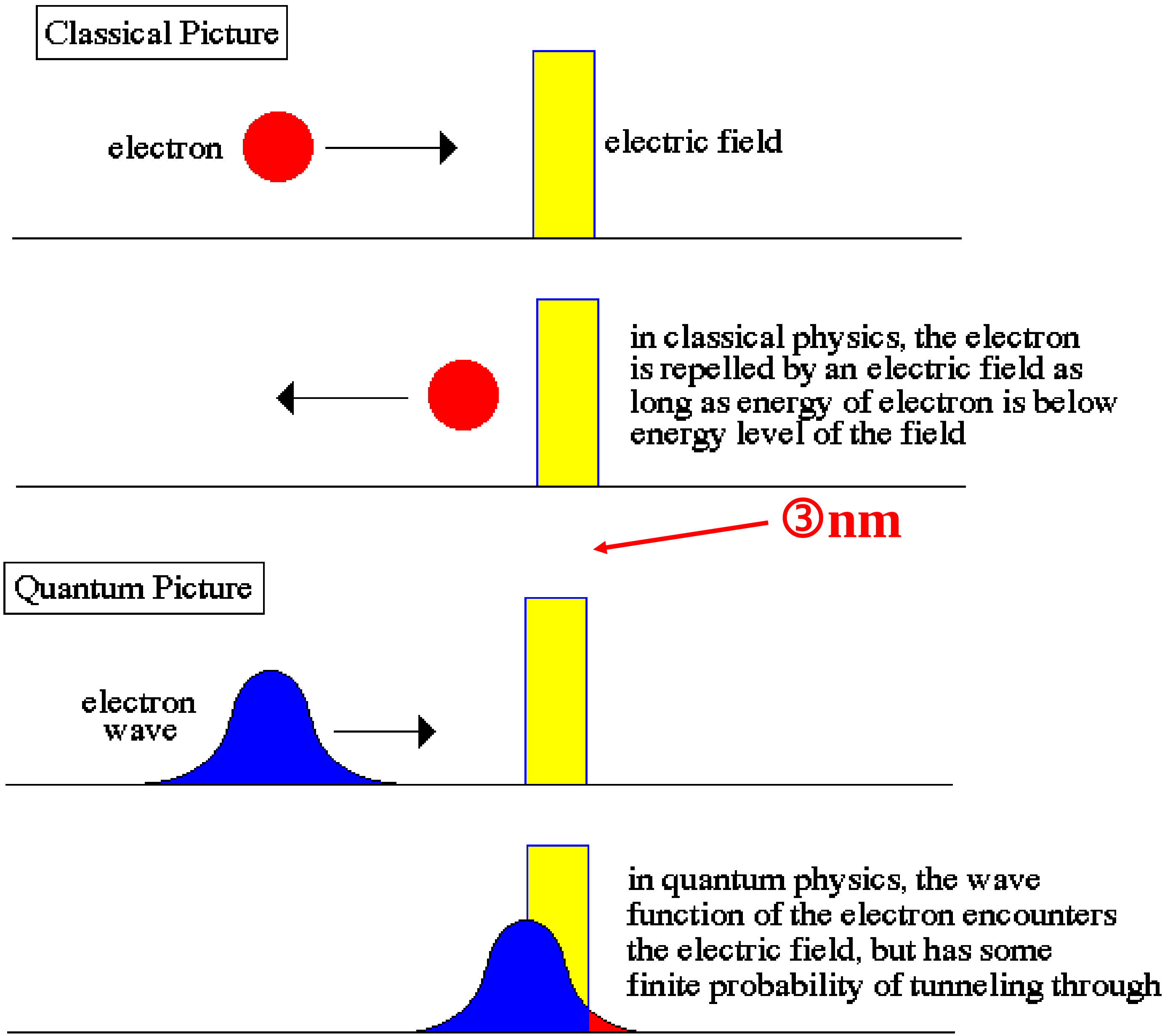


60s = 1 ML

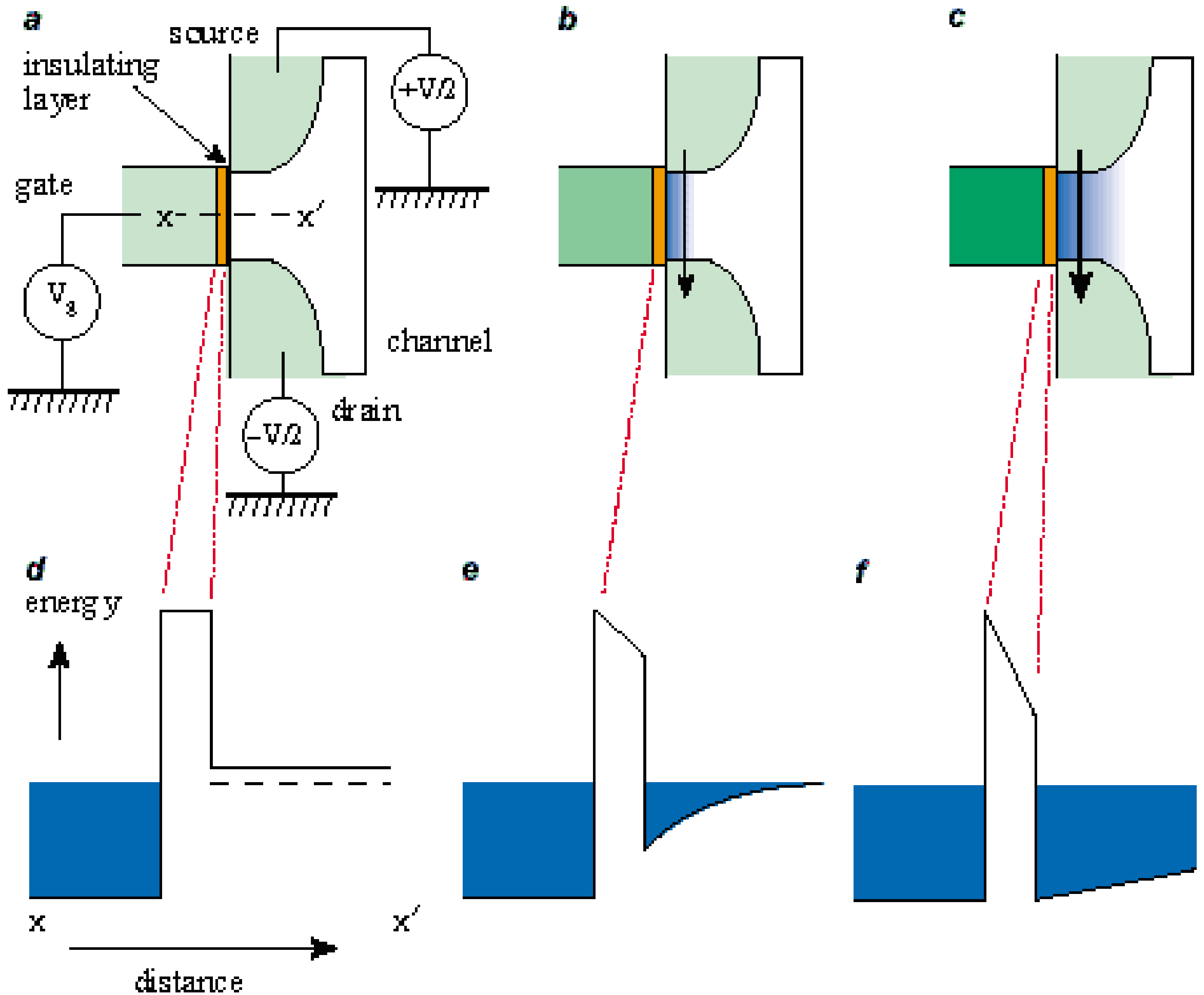
Scanning Tunneling Microscopy



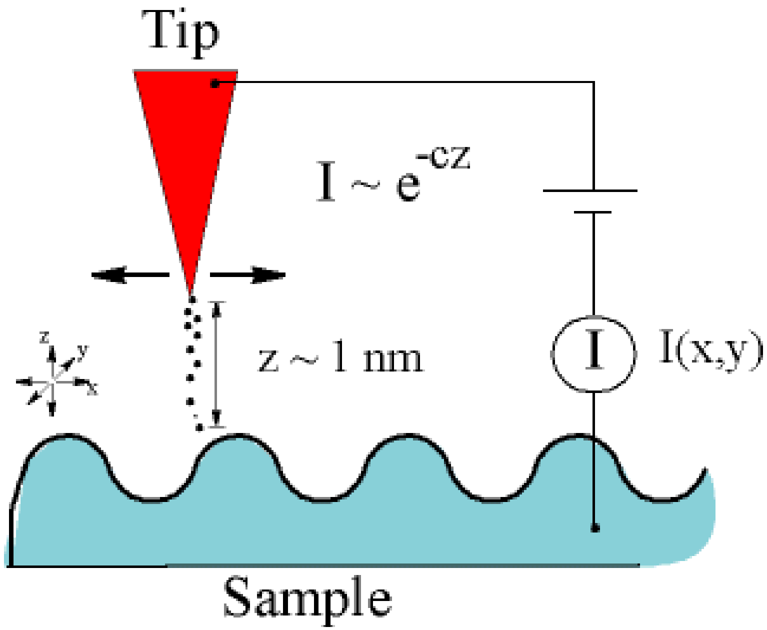
(III) Tunneling


Classical Picture
electron
electric field
in classical physics, the electron is repelled by an electric field as long as energy of electron is below energy level of the field
③nm
Quantum Picture
electron wave
in quantum physics, the wave function of the electron encounters the electric field, but has some finite probability of tunneling through

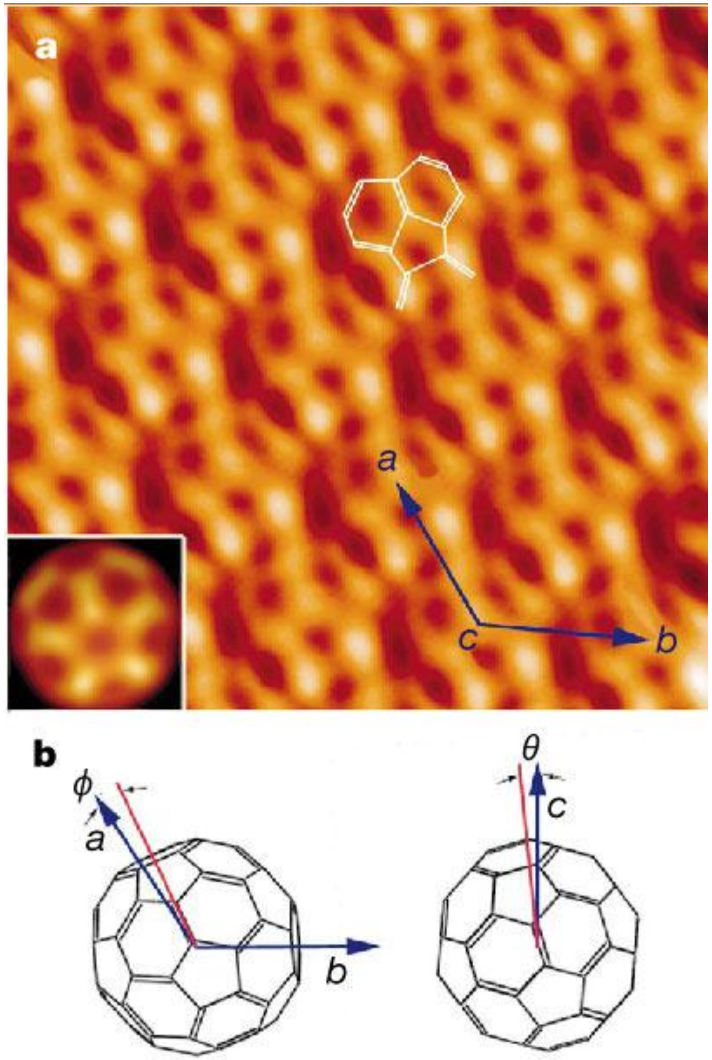
Quantum Tunneling is the major effect for the failure of Transistor at nano scale



Scanning Tunneling Microscope (STM) – Physicist used to detect the nano structures



Nature 409, 304(2001)

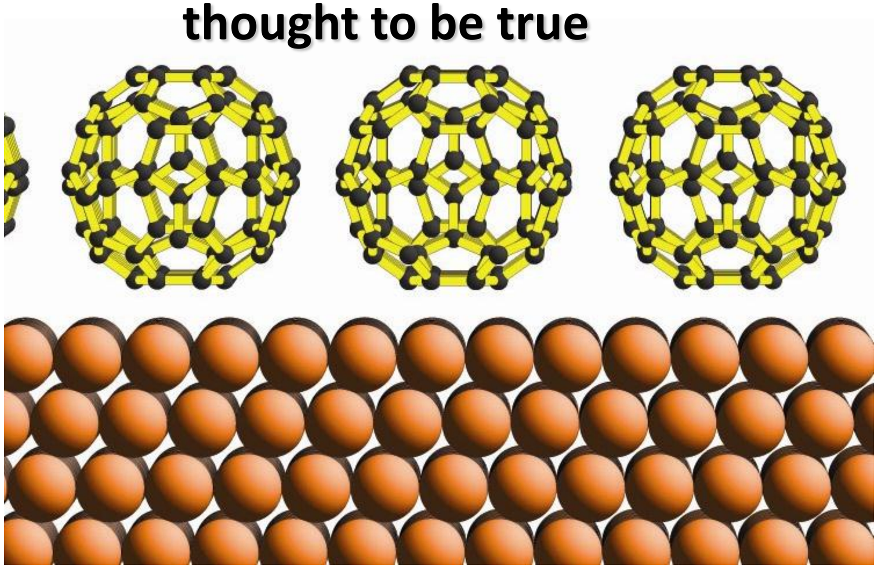


Doping-structure correlation at fullerene/metal interface (interface engineering)

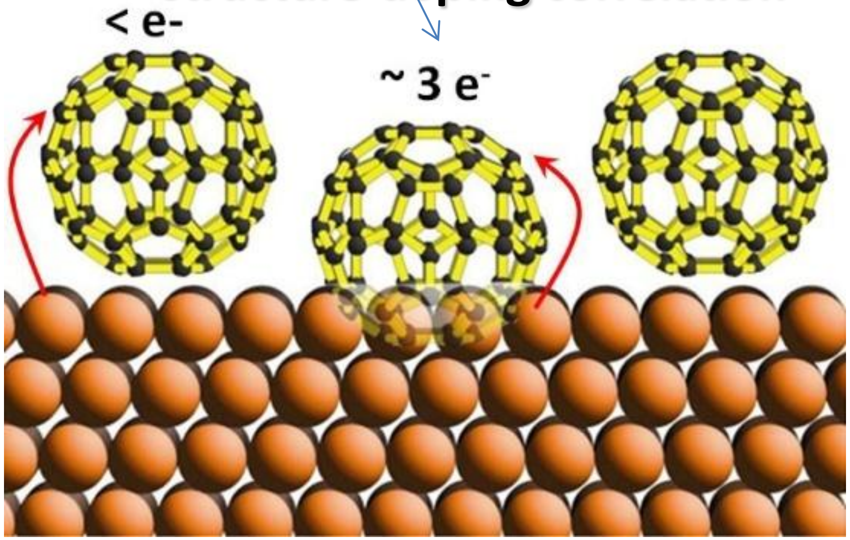
C_{60}/Cu(111) case:

"optimal" doping (e.g., 3 e^- per C_{60}) achieved purely through interface reconstruction.
Combined techniques of STS, STM, PES, LEED I-V, and ab-initio theory are used in this study.

Naïve case!
thought to be true



Reality…
structure-doping correlation



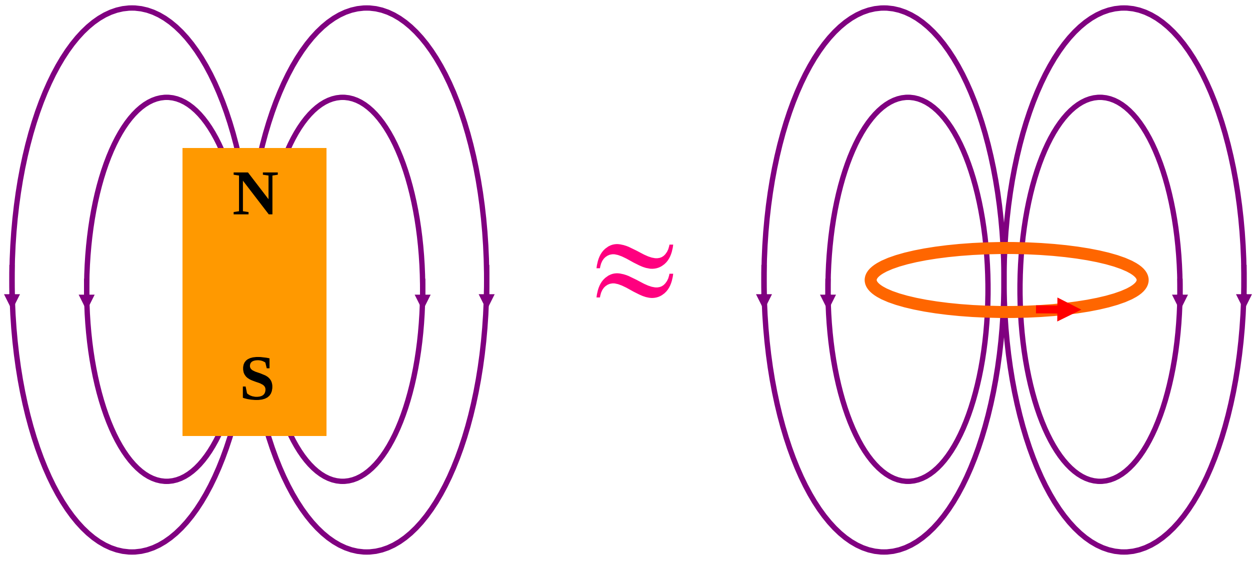
Implication: electronic property of molecule-electrode contact must consider structural details at the interface

W. W. Pai et al., Phys. Rev. Lett. 104, 036103 (2010)

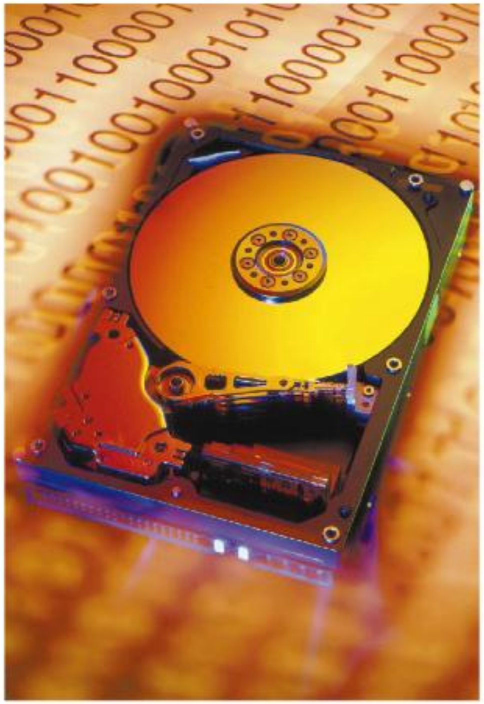
(IV) Quantum Spin

Spin and Nano technology

Electron Spin is the smallest unit of magetism,
Came from Quantum Mechanics



Often being used for magnetic recording ~30 billion market



Well read: spintronics has dramatically increased data storage densities in hard drives.

Spintronics ⇔ Electronics

New generation of computer

Compulttion and storage in one shot

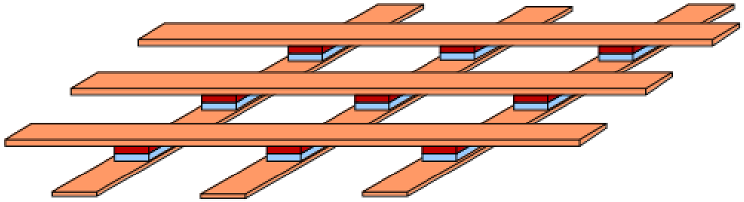
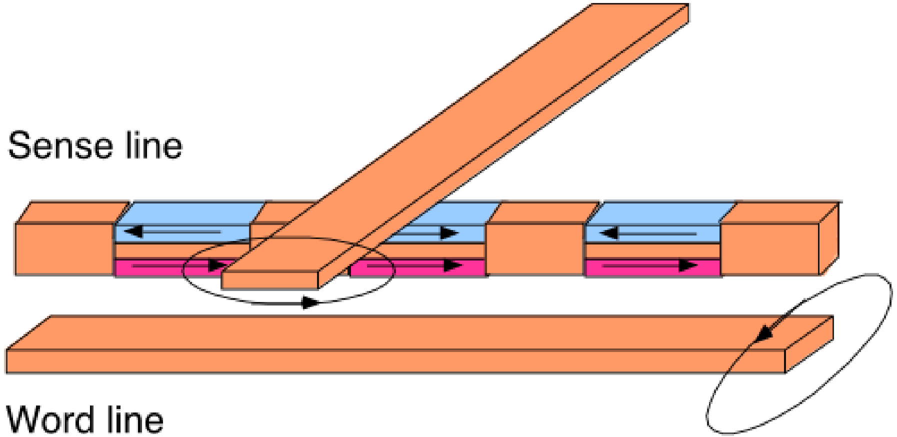


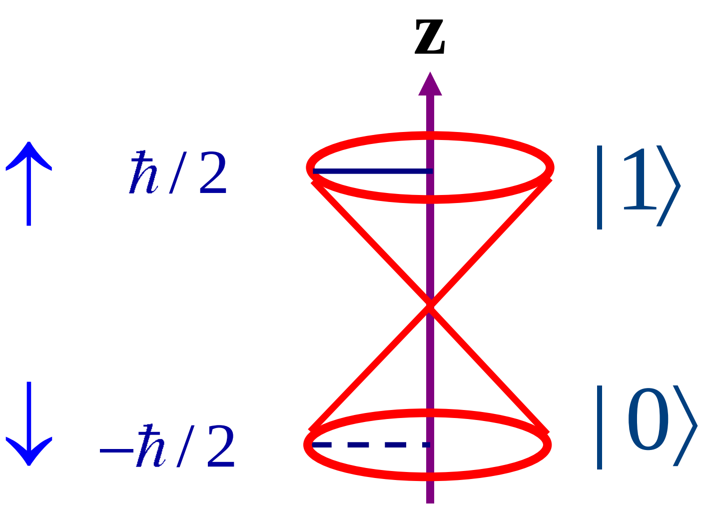
Fig. 7. A schematic representation of RAM that is constructed of magnetic tunnel junctions connected together in a point contact array. The conducting wires provide current to the junctions and permit voltage measurements to be made. They also enable the manipulation of the magnetization of the elements by carrying currents both above and below the magnetic junctions to create magnetic fields.



When turn-on, it is ready!

Quantum behavior of ferromagnets

-Spin as a quantum qubit

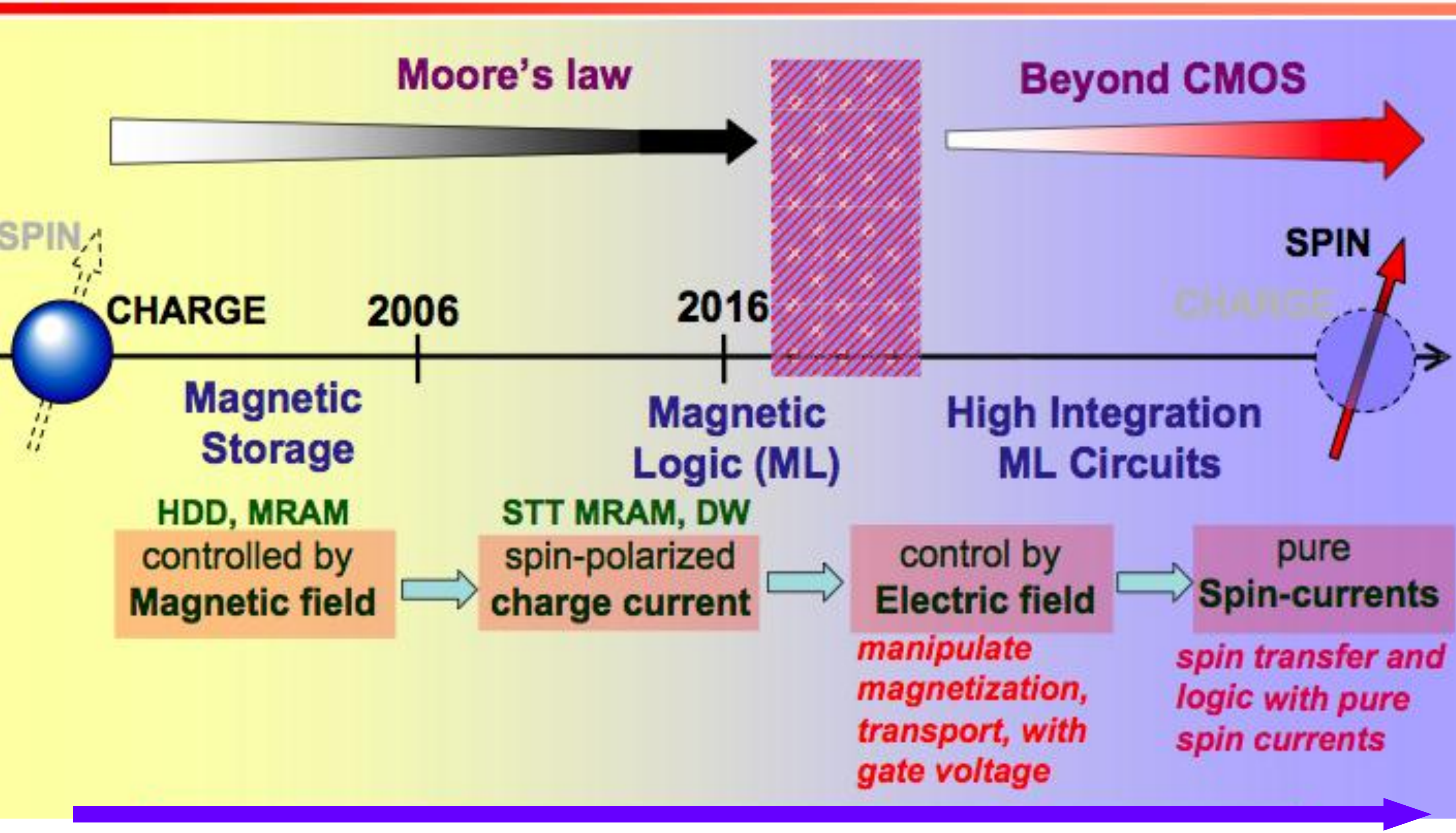


$$qubit = \alpha\,|0\rangle + \beta\,|1\rangle$$

Due to superposition

More information!

Tentative roadmap



Can we take the "charge" out of Spintronics ?

To generate pure spin current !

Courtesy Claude Chappert, Université Paris Su, INTERMAG 2008, Madrid, Spain

Spintronics vs Electronics

- ✓ Reducing the heat generated in traditional electronics is a major driving force for developing spintronics.
- ✓ Spin-based transistors do not strictly rely on the raising or lowering of electrostatic barriers, hence it may overcome scaling limits in charge-based transistors.
- ✓ Spin transport in semiconductors may lead to dissipationless transfer of information by pure spin currents.
- ✓ Allow computer speed and power consumption to move beyond limitations of current technologies.

Reliable generation of pure spin currents !

- ✓ Spin Hall effect (2004)
- ✓ Spin Pumping (2006)
- ✓ Inverse Spin Hall effect (2006)
- ✓ Spin Seebeck effect (2008)
- ✓ Spin Caloritronics (2010)

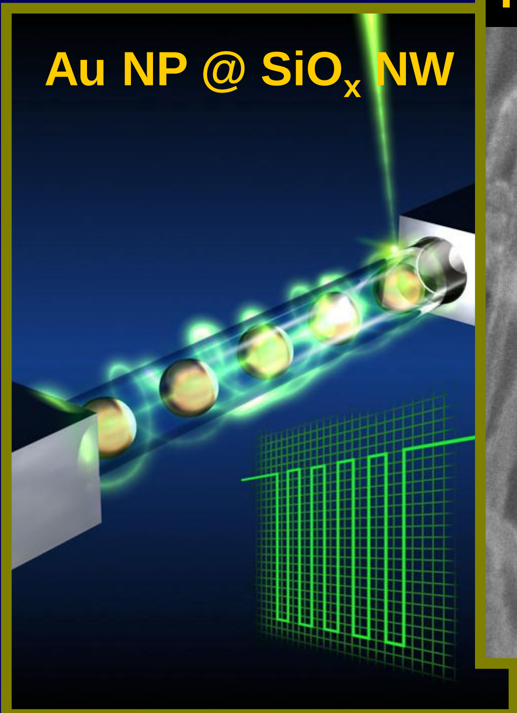
Major Qauntum Effect at the nano scale

- Interference
- Quantization
- Tunneling
- Quantum Spin

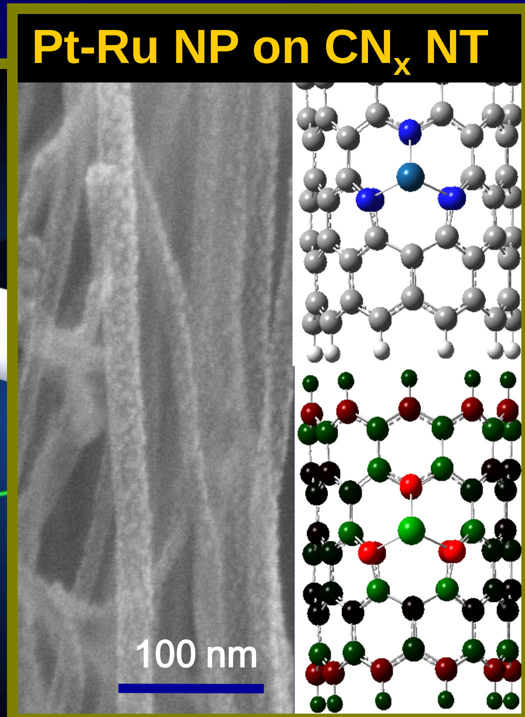
The Fourth Lesson:

Innovations of nano structures and nano materials for various applications

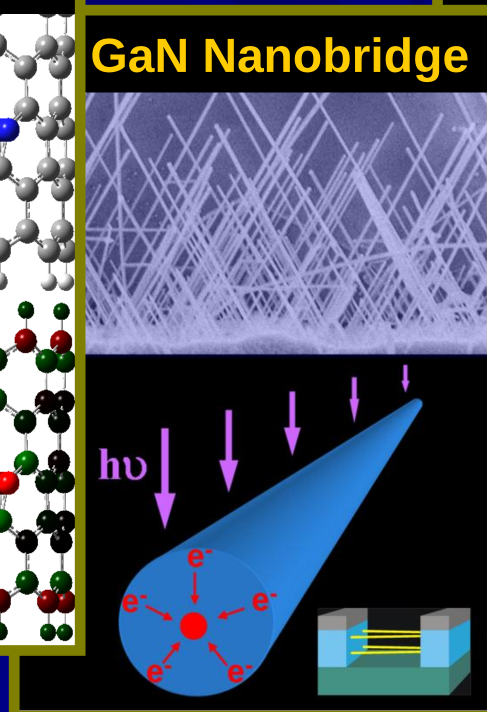
Overview of Advanced Materials Laboratory



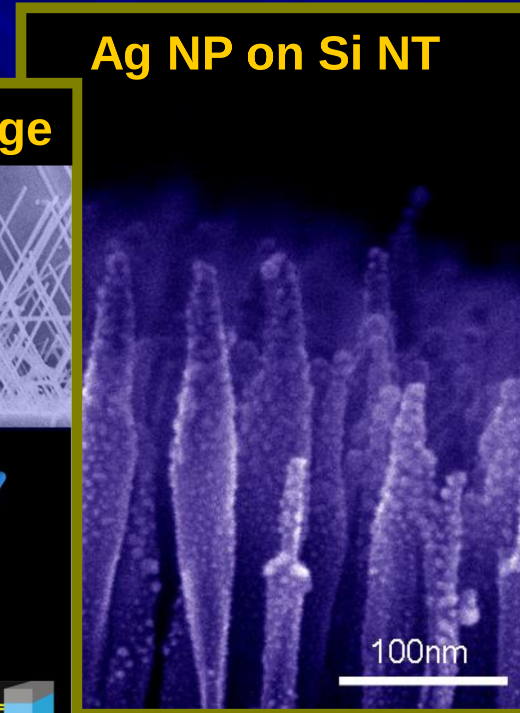
Color-selective Optical Switch, SPR-enhanced Sensor



Fuel Cells, Supercapacitors



High-gain Photo-detector, Solar Cells, Bio-sensor



SERS: Molecule/Bio-sensing

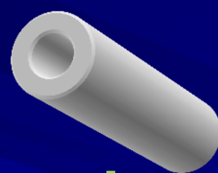
Li-Chyong Chen
Center for Condensed Matter Sciences
National Taiwan University

The Nano-world at CCMS-AML:

a Fruitful Research Field with Technology Implications

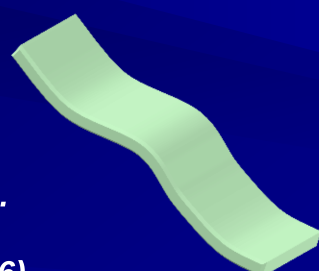
Wire/Rod

JACS 123, 2791 (2001)
APL 81, 22 (2002)
JACS 127, 2820 (2005)
APL 88, 241905 (2006)
APL 90, 213104 (2007)
Adv. Func. Mater. 18, 938 (2008)
Small 4, 925 (2008)
Analytical Chem. 81, 36 (2009)



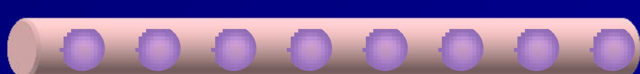
Tube

APL 79, 3179 (2001)
APL 81, 4189 (2002)
Adv. Func. Mater. 12, 687 (2002)
APL 86, 203119 (2005)
Chem. Mater. 17, 3749 (2005)
JACS 128, 8368 (2006)
PRB 75, 195429 (2007)
JACS 130, 3543 (2008)



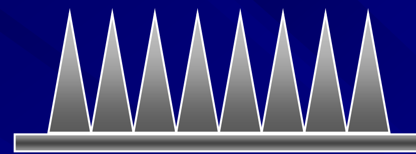
Belt

Chapter 9, pp. 259-309, Nanowires and nanobelts, Z.L. Wang Ed., Kluwer (2004)
Adv. Func. Mater. 16, 537 (2006)
APL 90, 123109 (2007)
Adv. Mater. 19, 4524 (2007)



Peapod

Adv. Mater. 14, 1847 (2002)
Nature Mater. 5, 102 (2006)

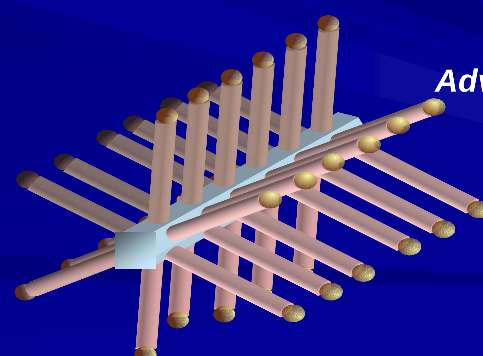


Nanotip

APL 83, 1420 (2003)
Nano. Lett. 4, 471 (2004)
Chem. Mater. 17, 553 (2005)
Adv. Func. Mater. 15, 783 (2005)
APL 86, 203119 (2005)
US Patent 6,960,528,B2
APL 89, 143105 (2006)
Nature Nanotech. 2, 170 (2007)
Nano Lett. 9, 1839 (2009

Core-shell

APL 81, 1312 (2002)
Nano. Lett. 3, 537 (2003)



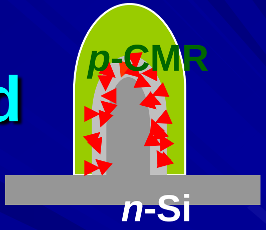
Brush

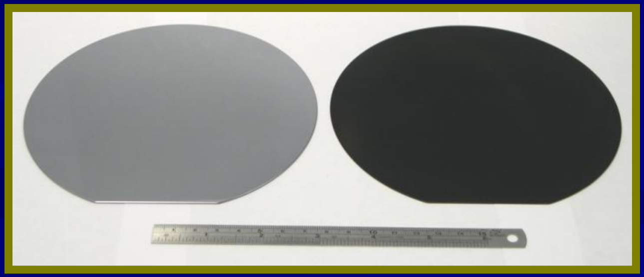
Adv. Func. Mater. 14, 233 (2004)

Other Thin Films:
APL 86, 21911 (2005)
APL 86, 83104 (2005)
APL 86, 161901 (2005)
APL 87, 261915 (2005)
JVST B 24, 87 (2006)
APL 88, 73515 (2006)
Adv. Mater. 21, 759 (2009)

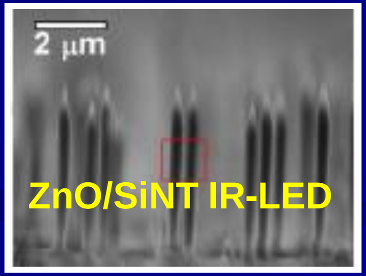
Si Nanotips-Array and their Hetero-junctions: On-chip, IC-compatible

* Antireflection:
  Broadband (uv-terahertz), Omnidirectional (>70º)
* Electroluminescence in ZnO/SiNTs:
  IR emission, x10 higher; turn-on ~3V, x2 lower than film
* Magneto-resistance in LSMO/SiNTs:
  Room-temp. MR at lower bias and magnetic field

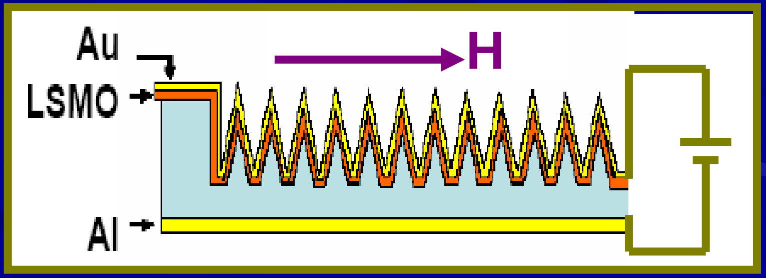




Nature-Nanotechnology
2 (2007) 770



Nano Letters
9 (2009) 1839



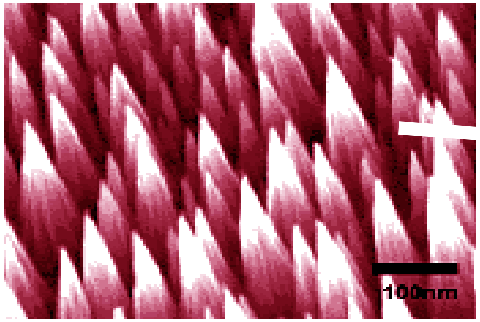
Promising high-density memory:
On-going

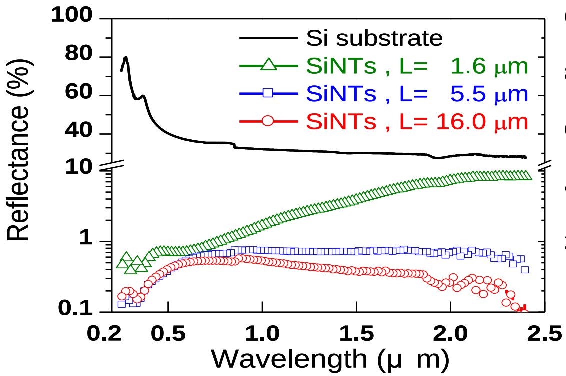
A Man-made Moth Eye

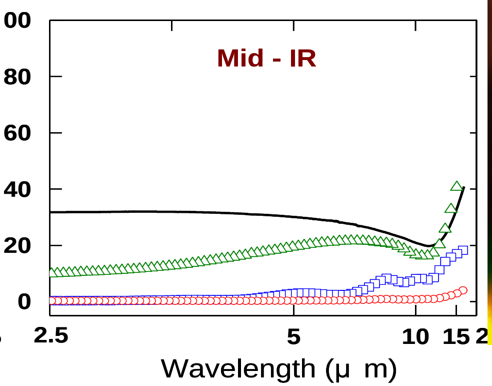
Broadband and Quasi-omni-directional Anti-reflection Properties with Biomimetic Silicon Nanostructure

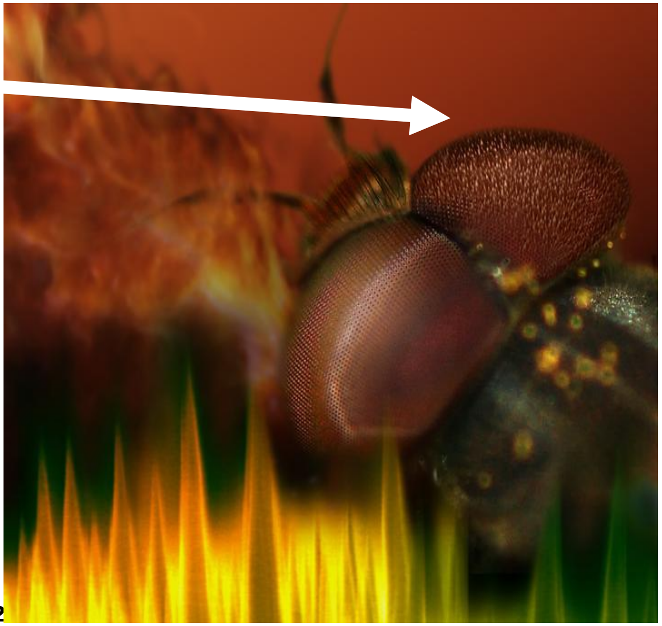
Y. F. Huang, et al., Nature Nanotechnology 2, 770-774 (2007) & US Patent 2005

Featured by NPG Asia Materials, March 2008









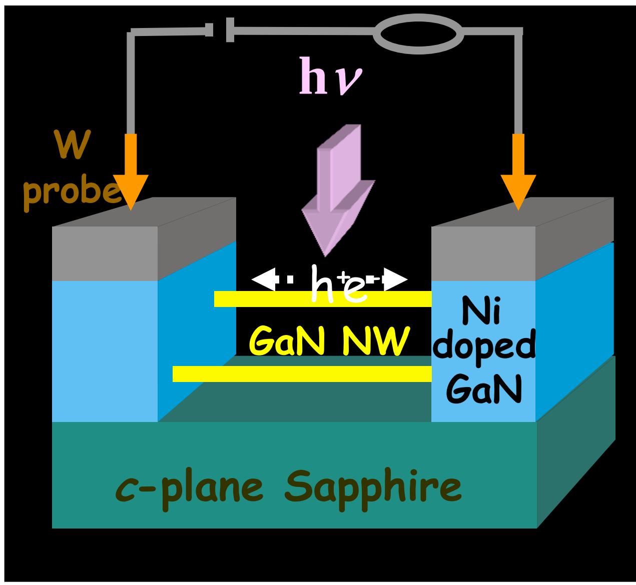
Many plants and animals have tiny surface structures that absorb certain wavelengths of light. These naturally formed nanostructures provide the colors in butterfly wings, camouflage for cicadas and enable moths to capture as much light as possible when flying at night.

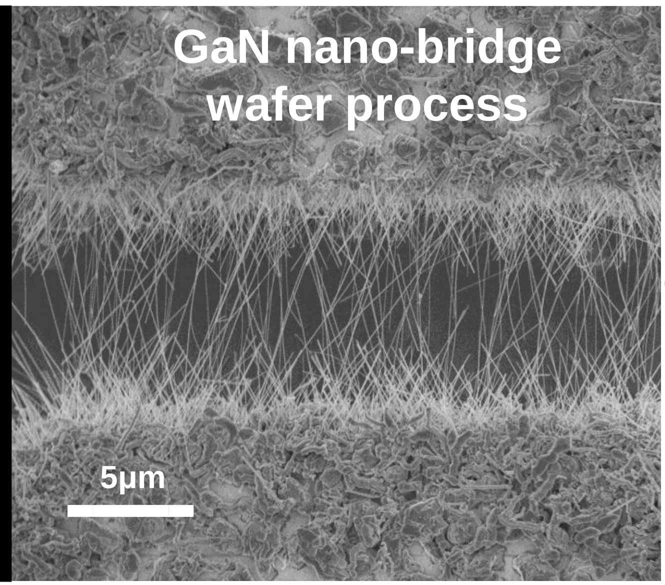
Now, we have created nanostructure surfaces which mimic moth eye and surpass its function in anti-reflection in that they absorb almost all incident light.

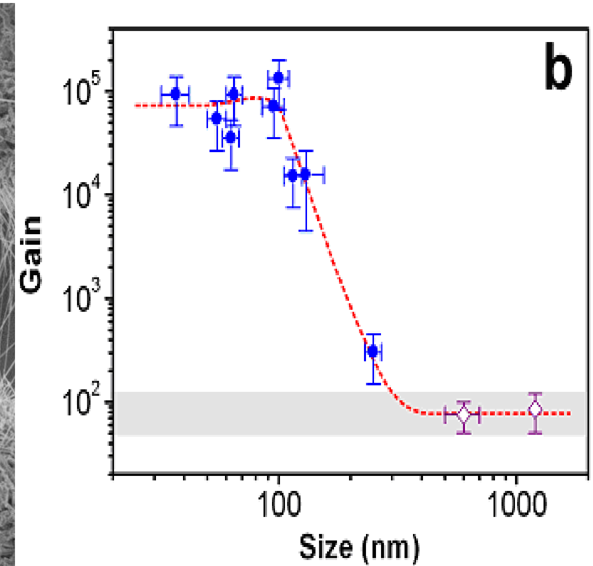
Building a Nano-scale Bridge On-chip

On-chip Fabrication of Well Aligned and Contact Barrier-Free GaN Nanobridge Devices with Ultrahigh Photocurrent Responsivity

R. S. Chen, et al., Small 4, 925-929 (2008)







- Nanowire: Naturally formed core-shell structure, 1D electron gas-like property
- On-chip process for building GaN nanobridge devices, which provide a large surface area, short transport path, and high responsivity for next-generation sensors and detectors

A Color-selective Nanoswitch

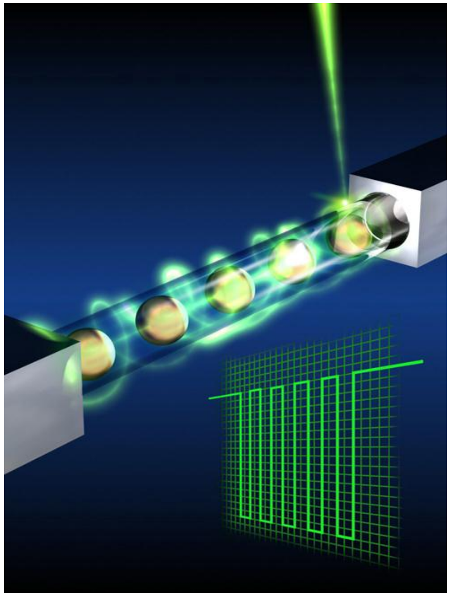
Photosensitive Gold Nanoparticle-embedded Dielectric Nanowires

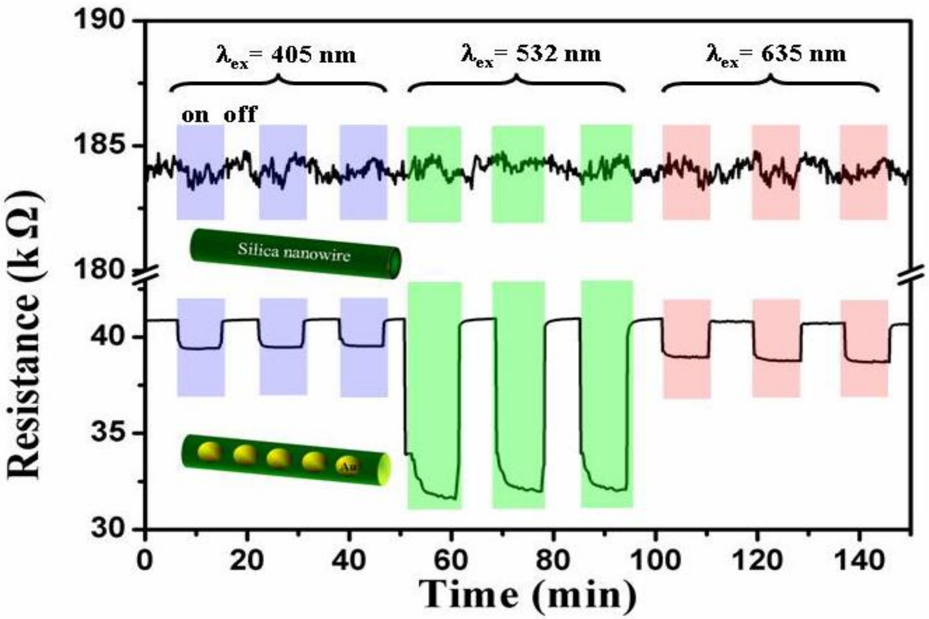
M. S. Hu, et al., Nature Materials 5, 102-106 (2006)

A Fast Breaking Paper

(in each individual field, only 1 was selected bimonthly among the Highly Cited Papers)

(http://esi-topics.com/fbp/2007/august07-Li-ChyongChen.html)





In ancient Arabian story of “Ali Baba and the Forty Thieves”, the treasure is in a cave, of which the mouth is sealed by magic. It opens on the words "Open Sesame" and seals itself on the words "Close Sesame".

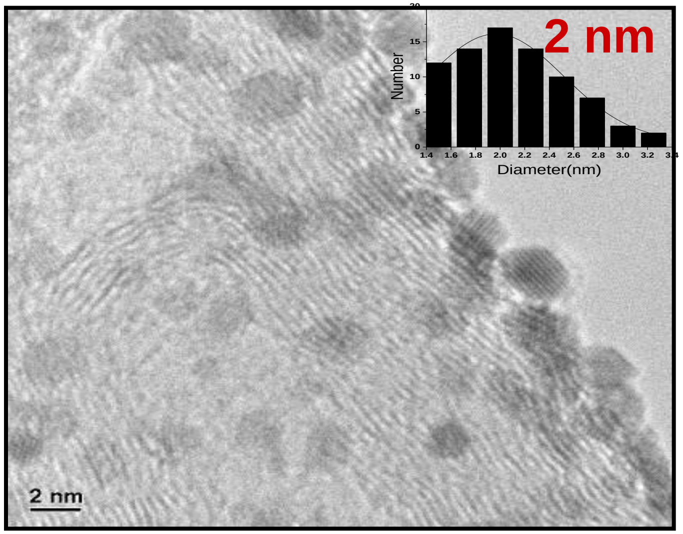
The nanopeapod (i.e., gold nanoparticle-embedded dielectric nanowire) will open to green light but shut for lights of other colors.

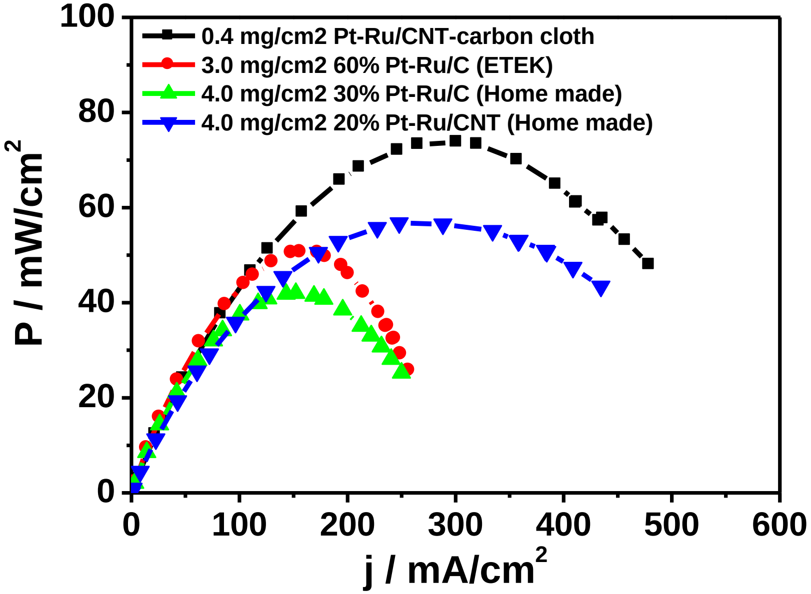
Next-generation Energy Solution (I): Fuel Cell with Low-loading of Precious Metals

Ultrafine Pt Nanoparticles Uniformly Dispersed on Arrayed Carbon Nanotubes with High Electrochemical Activity at Low Loading of Precious Metal

C. L. Sun, et al., Chemistry of Materials 17, 3749-3753 (2005)

C. H. Wang, et al., J. Power Sources 171, 55-62 (2007)





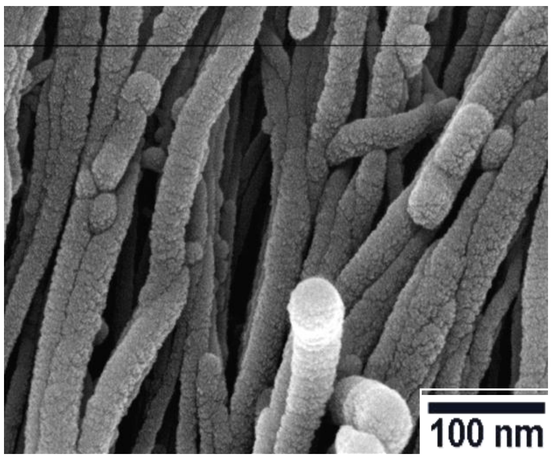
- Direct methanol fuel cell is promising power generator with a wide range of applications from portable electronic devices to automobiles.
- Nanotubes-Pt/Ru composites are highly efficient in loading precious metals. Only **one tenth** of metal loading, in comparison to the conventional, is needed.

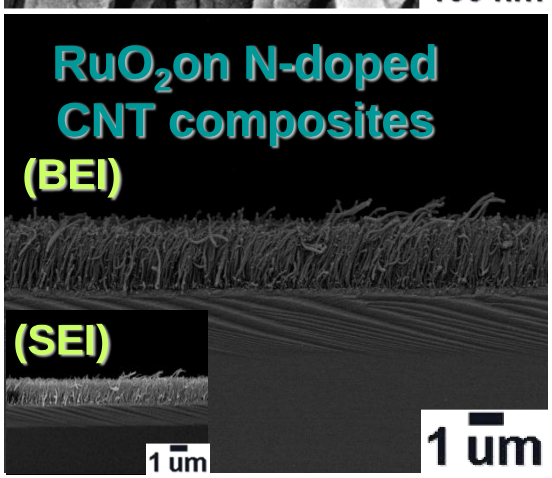
Next-generation Energy Solution (II): High-performance Supercapacitor

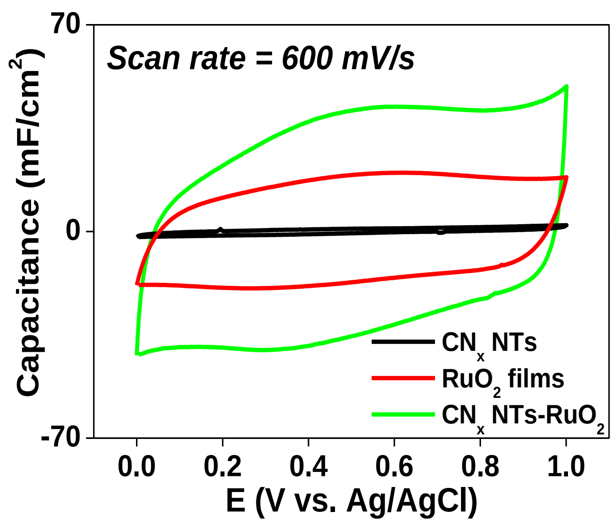
Ultrafast Charging-discharging Capacitive Property of RuO_2 Nanoparticles on Carbon Nanotubes Using Nitrogen Incorporation

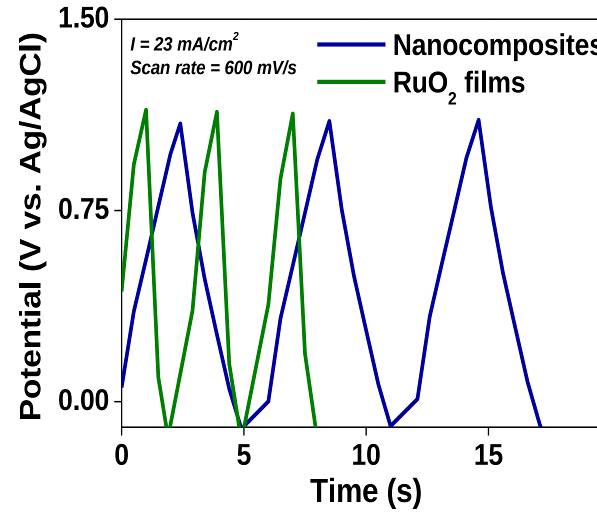
W. C. Fang, et al., Electrochemistry Communications 9, 239-244 (2007)

W. C. Fang, et al., J. Electrochemical Society 155, K15-K18 (2008)









- **4 fold increase in capacitance**
- **Optimal capacitance of *1380 F/g at 600 mV/s* (theory: 1450 F/g)**
- **Output current as high as *23 mA/cm²***
- **Stable at high scan rate**
- **10 fold increase in charge-discharge rate**

The Fifth Lesson:

Nano photonics

and

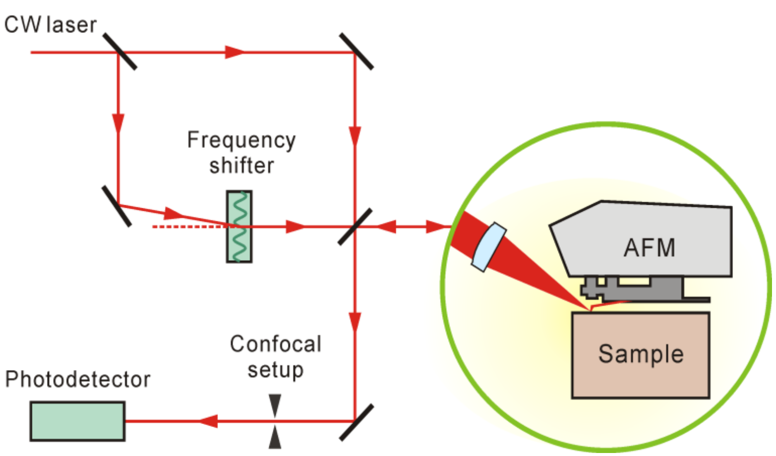
Bio-applications

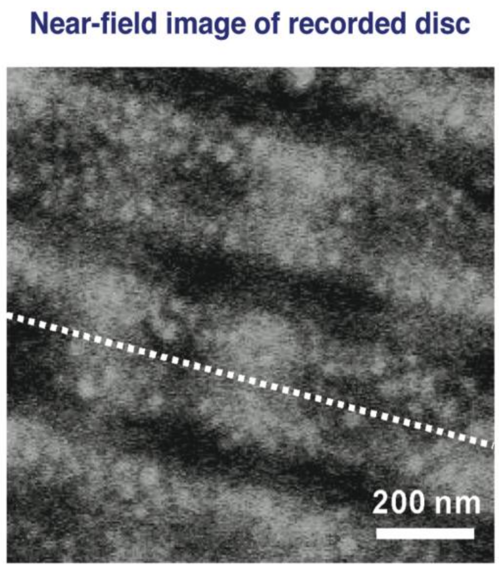
Nano-photonics and Plasmonics

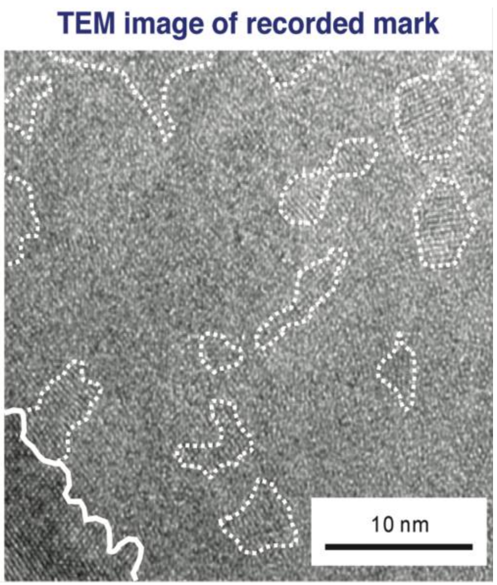
Near-field examination of blue-ray discs

Dr. Juen-Kai Wang, CCMS, NTU

S-SNOM setup



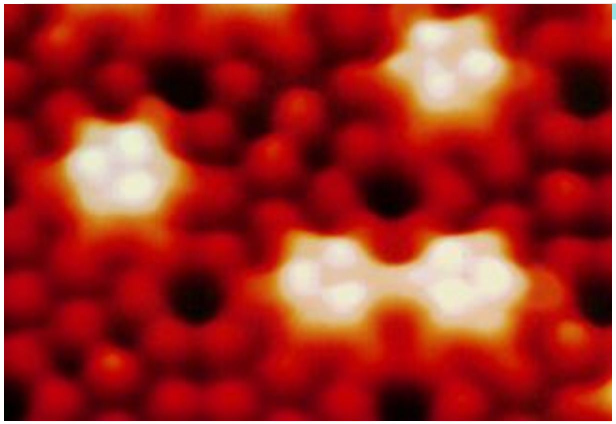
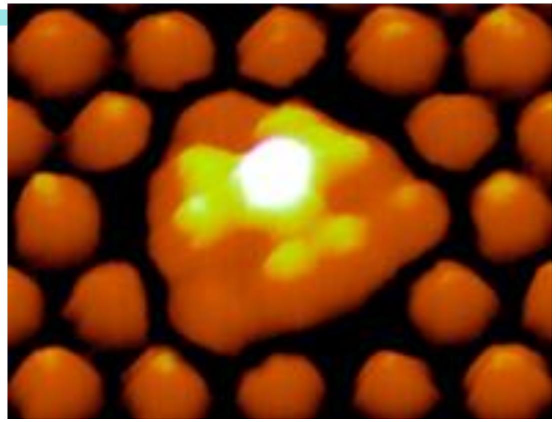
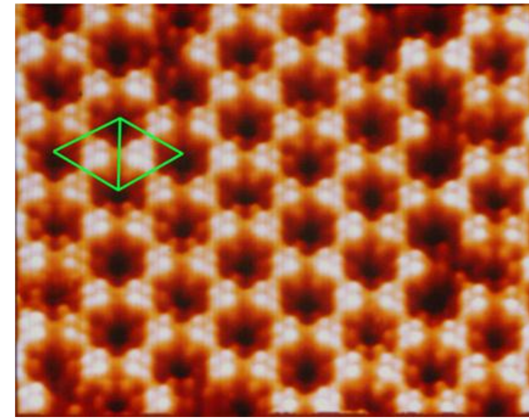
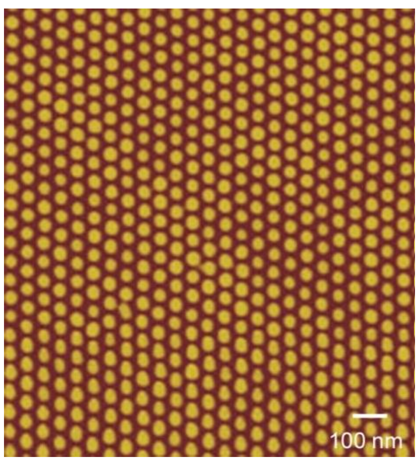


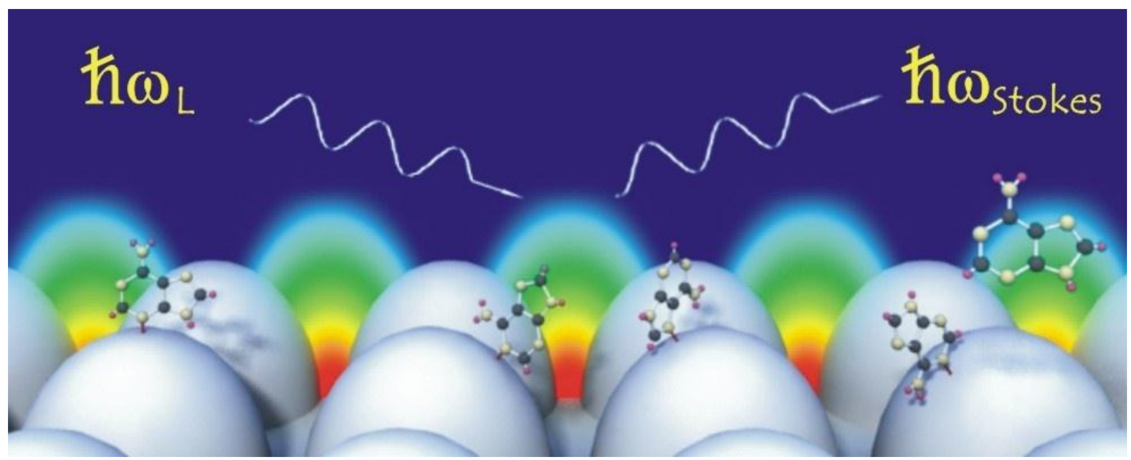


- **Scattering-type SNOM reveals sub-10 nm optical signature.**
- The optical contrasts of the dark and the bright regions in near-field image of phase-change layer correspond to amorphous and polycrystalline AgInSbTe, respectively.
- Small bright spots with a size of ~30 nm emerge within the dark region, corresponding to the nano-sized ordered domains in the TEM image.
- **s-SNOM provides a direct optical probe in nanometer scale for high density optical storage media.**

J. Y. Chu et al., Appl. Phys. Lett. 95, 103105 (2009).

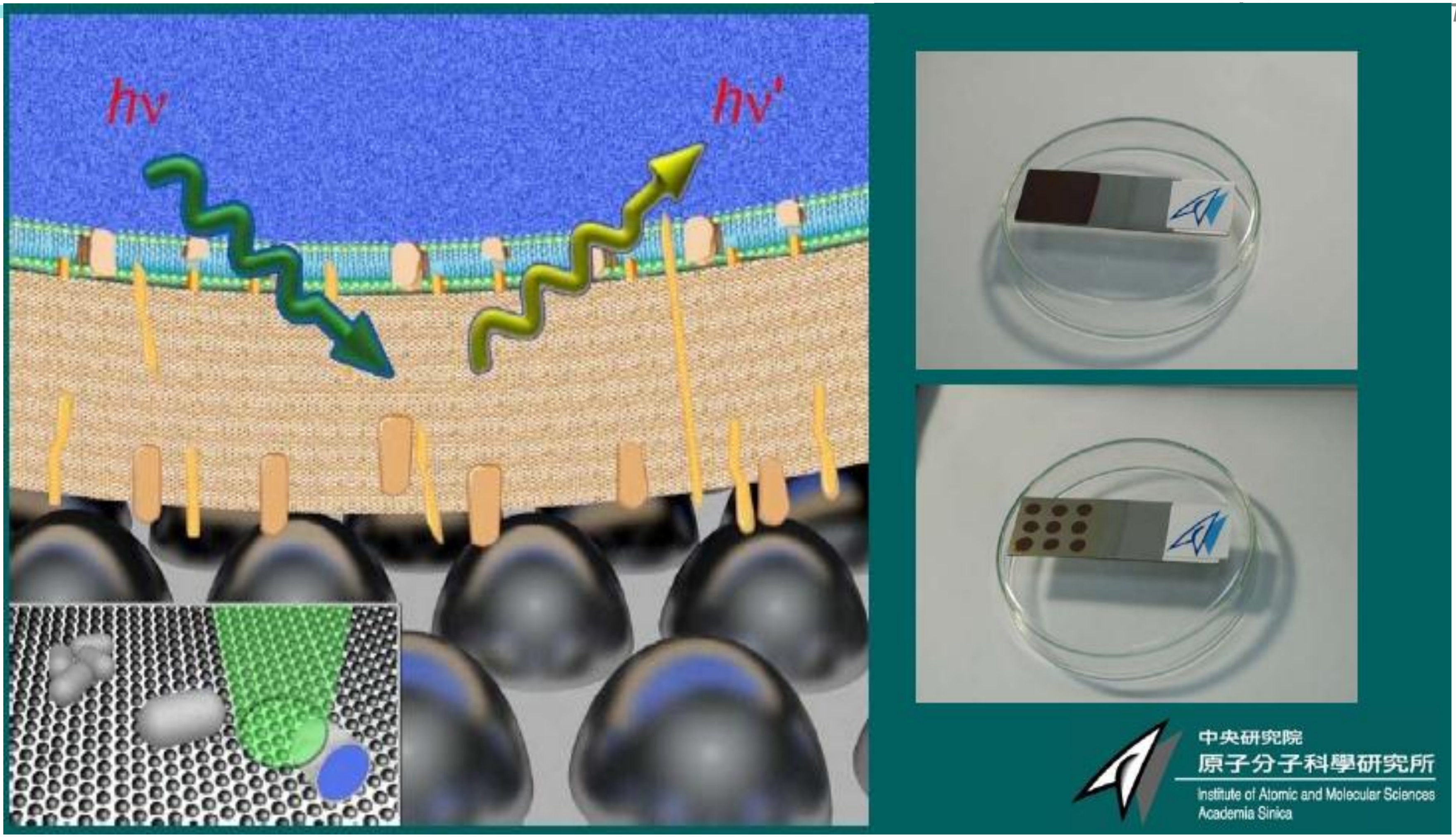
Creating Monodispersed Ordered Arrays of Surface-Magic-Clusters and Anodic Alumia Nanochannels by Constrained Self-organization



Prof. Yuh-Lin Wang 王玉麟
IAMS Academia Sinica, Taiwan

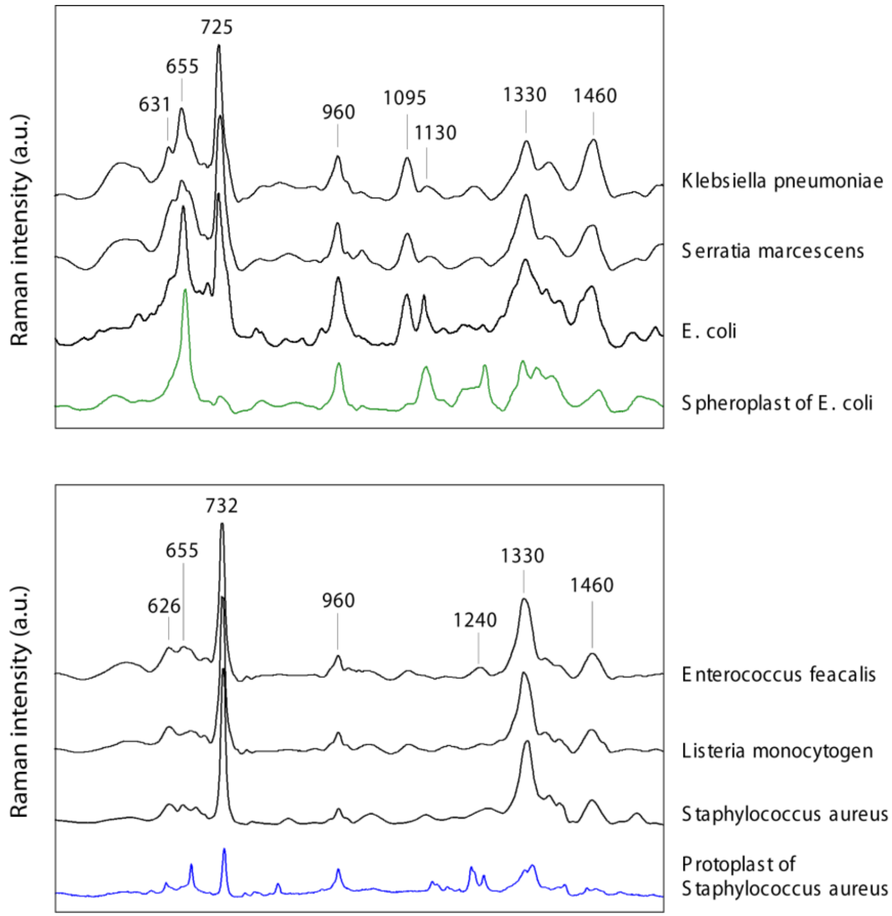
A High Sensitivity and High Speed Biomedical Diagnostic Technology using SERS

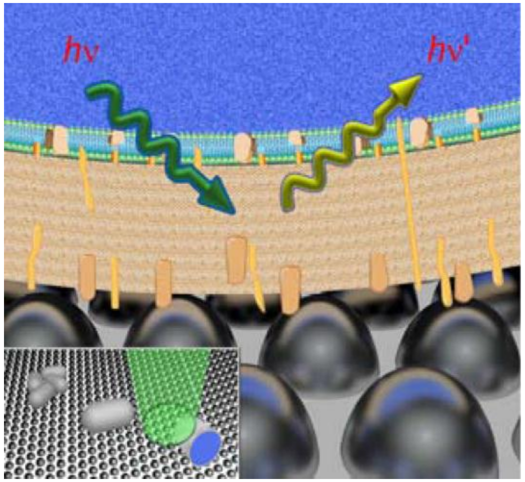


Prof. Yuh-Lin Wang 王玉麟
IAMS Academia Sinica, Taiwan

SERS detection of bacterial cell wall

Dr. Juen-Kai Wang, CCMS, NTU





- Sensitive and stable SERS profiles based on our substrates readily reflect different bacterial cell walls found in Gram-positive, Gram-negative, and mycobacteria group.
- Characteristic changes in SERS profile are recognized in the drug-sensitive bacteria of antibiotic exposure, which could be used to differentiate them from the drug-resistant ones.

H.-H. Wang et al., Adv. Mater. 18, 491 (2006); T.-T. Liu et al., PLoS ONE 4, e5470 (2009).

The End