

# The Advent of Carbon Era ?

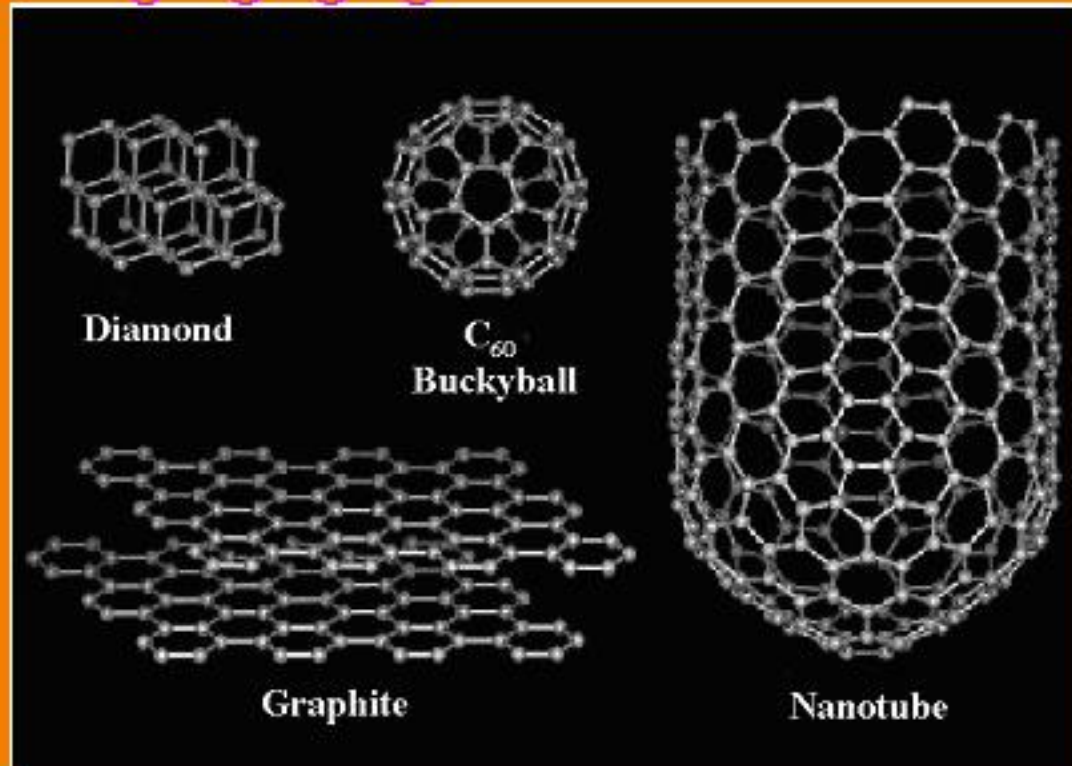
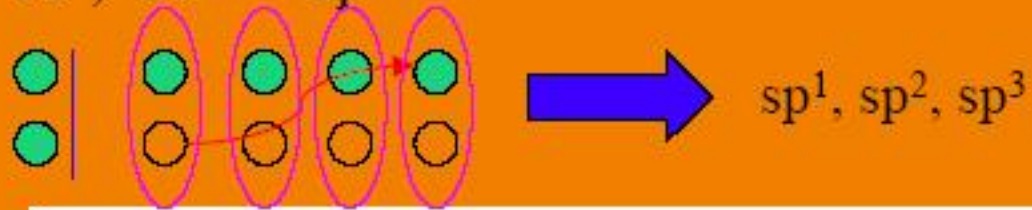
The Physics of Graphene:

- Possibility of relativistic electronics and spintronics

# Carbon Nanotube

+ Structure of carbon nanotubes

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

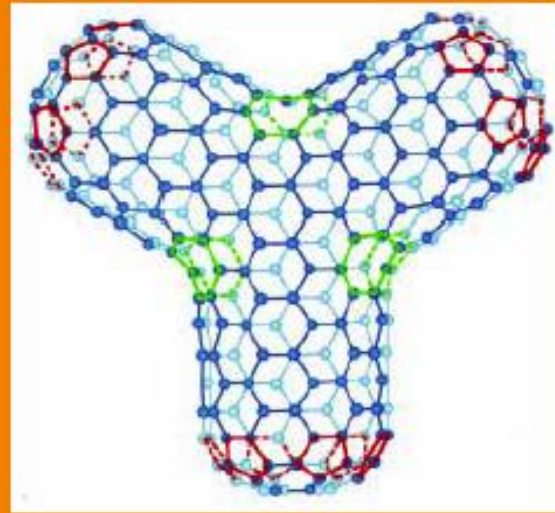


# Carbon Nanotube

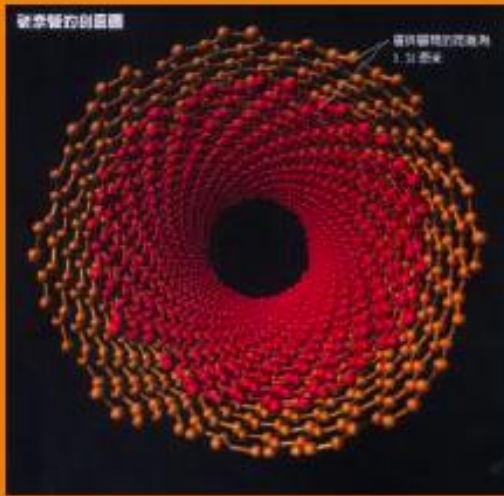


*Sumio Iijima*

Single-walled carbon nanotube, SWCNT



Multi-walled carbon nanotube, MWCNT



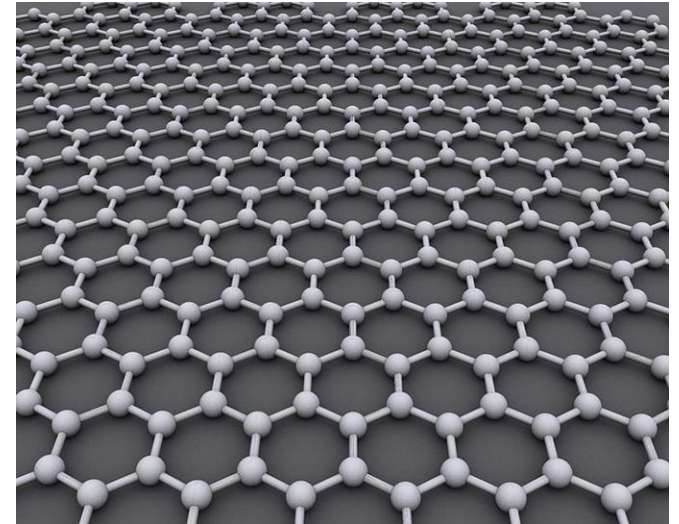
## Carbon Nanotube based Transistors / Electronics

# Unexpected realization of graphene sheet

(⇐



mechanically exfoliated graphene sheets





AFM image of single-layer graphene on  $\text{SiO}_2$   
K.S. Novoselove et al., Science 306, 666 (2004)

# **(III) Tunneling and Nano-electronics**

### Classical Picture

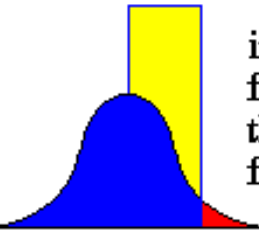
electron   electric field 

  in classical physics, the electron is repelled by an electric field as long as energy of electron is below energy level of the field

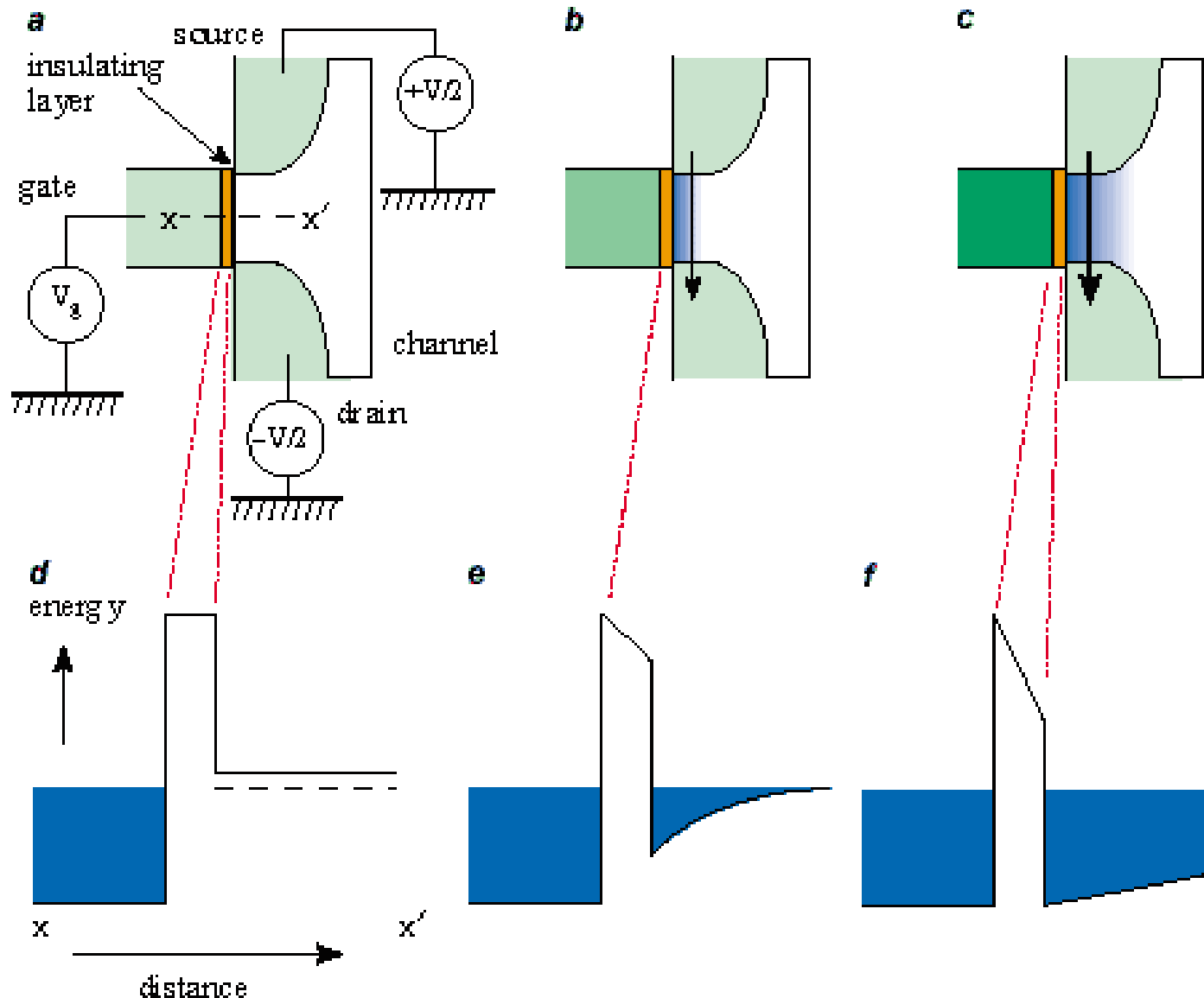
### Quantum Picture

electron wave  

 ③nm

 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





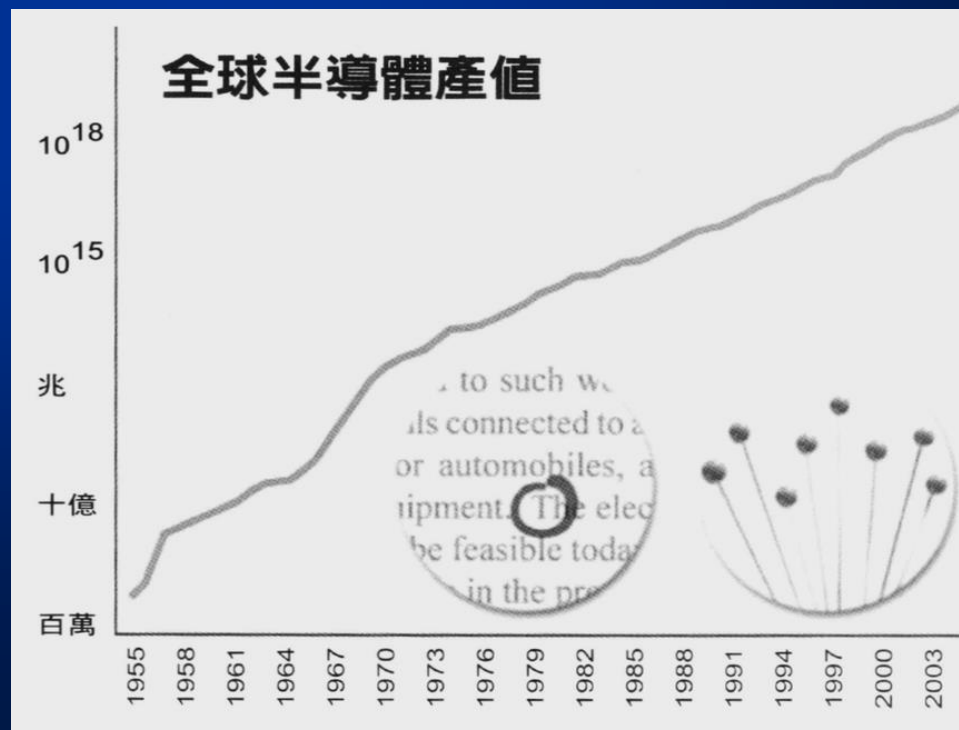
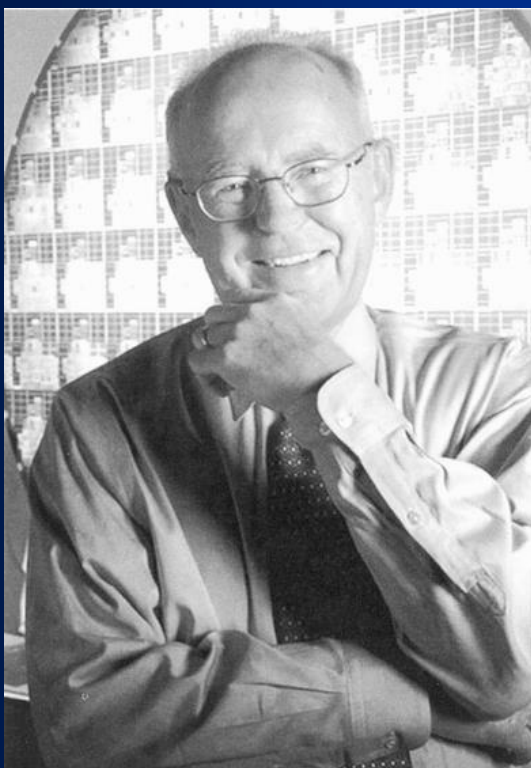
# 近來大力推動奈米科技的背景

## 來自微電子學可能遭遇瓶頸的考慮

### Moore's Law : 摩爾定律

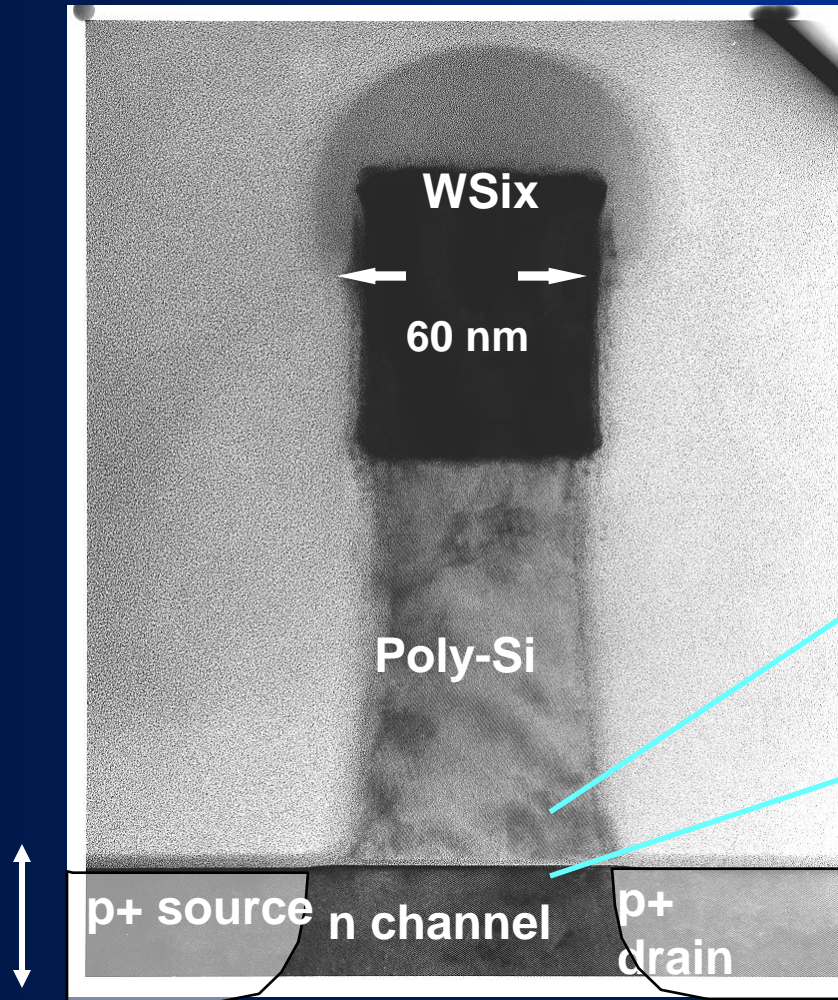
A 30% decrease in the size of  
printed dimensions every 1.5 years.

矽晶上電子原件數每1年半會增加一倍

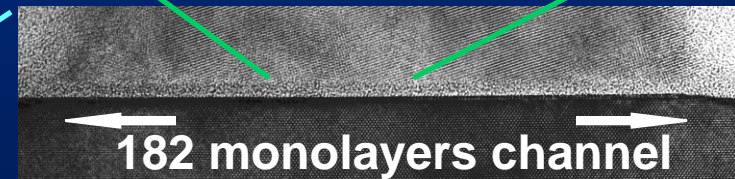
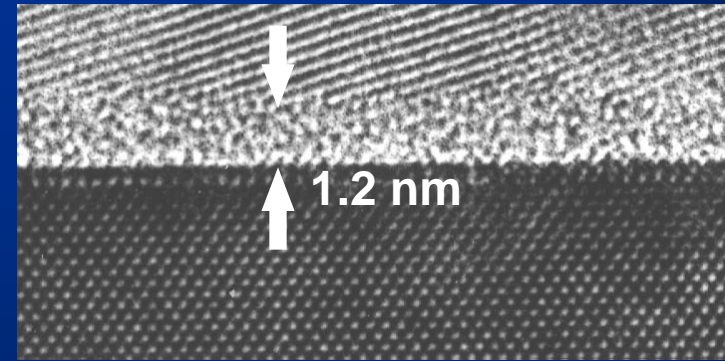




# Scaling Limits to CMOS Technology



Gate Oxide ~ 5 Si Atoms thick !



Shrinking the junction depth  $\Rightarrow$  increasing the carrier concentration



# CMOS scaling, When do we stop ?

**Reliability:** 25 ~~22~~ ~~18~~ ~~16~~ Å

processing and yield issue

**Tunneling :** 15 Å

Design Issue: chosen for 1 A/cm<sup>2</sup> leakage

$I_{\text{on}}/I_{\text{off}} \gg 1$  at 12 Å

**Bonding:**

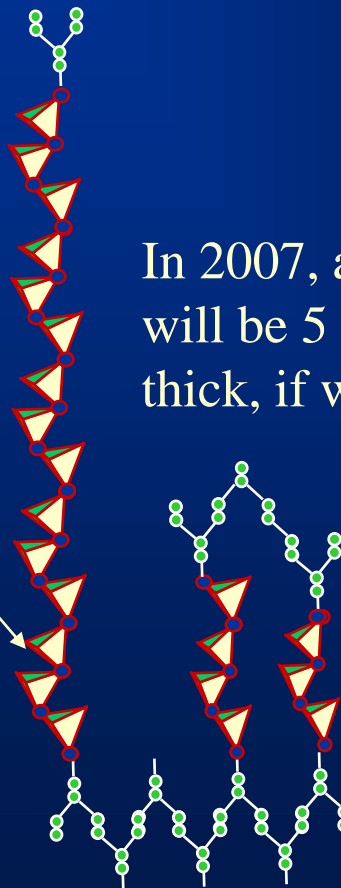
Fundamental Issues---

- how many atoms do we need to get bulk-like properties?  
EELS -- Minimal 4 atomic layers !!
- Is the interface electronically abrupt?
- Can we control roughness?

In 1997, a gate oxide was 25 silicon atoms thick.

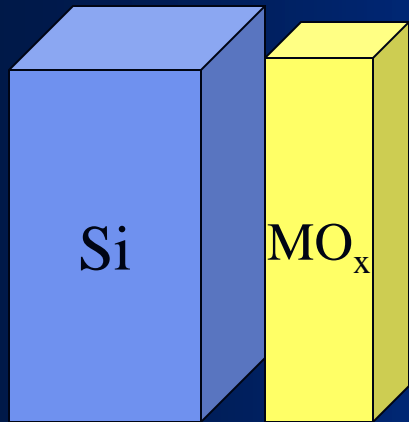
In 2007, a gate oxide will be 5 silicon atoms thick, if we still use SiO<sub>2</sub>

and at least 2 of those 5 atoms will be at the interfaces.





# Fundamental Materials Selection Guidelines



- Thermodynamic stability in contact with Si to 750°C and higher. **(Hubbard and Schlom)**  
**Alkaline earth oxide, IIIB, IVB oxide and rare earth oxide**
- Dielectric constant, band gap, and conduction band offset
- Defect related leakage,  
substantially less than SiO<sub>2</sub> at  $t_{eq} < 1.5$  nm
- Low interfacial state density  $D_{it} < 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$
- Low oxygen diffusivity
- Crystallization temperature  $> 1000^\circ\text{C}$



$t_{eq}$  : **equivalent oxide thickness (EOT) to be under 1.0 nm**

$$t_{eq} = t_{ox} \kappa_{\text{SiO}_2} / \kappa_{ox}$$



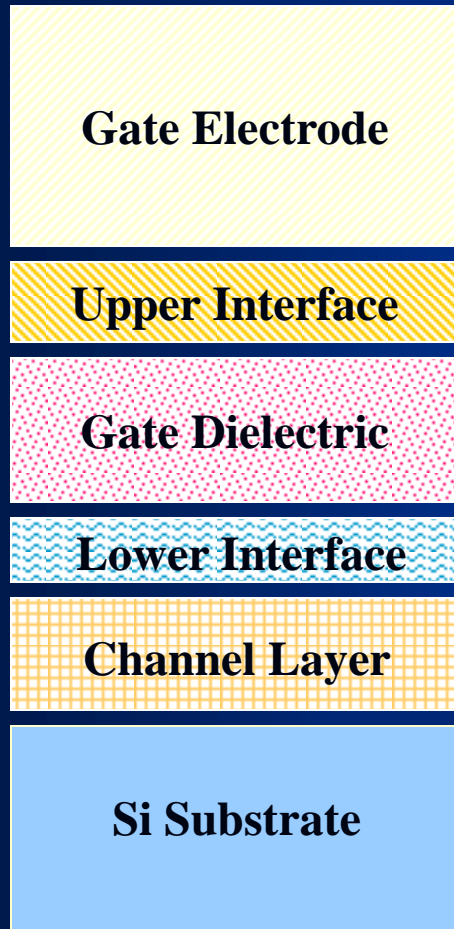
# Basic Characteristics of Binary Oxide Dielectrics

Dielectrics	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Y <sub>2</sub> O <sub>3</sub>	HfO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>	ZrO <sub>2</sub>	La <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>
Dielectric constant	3.9	9.0	18	20	25	27	30	80
Band gap (eV)	9.0	8.8	5.5	5.7	4.5	7.8	4.3	3.0
Band offset (eV)	3.2	2.5	2.3	1.5	1.0	1.4	2.3	1.2
Free energy of formation MO <sub>x</sub> +Si <sub>2</sub> → M+ SiO <sub>2</sub> @727C, Kcal/mole of MO <sub>x</sub>	-	63.4	116.8	47.6	-52.5	42.3	98.5	7.5
Stability of amorphous phase	High	High	High	Low	Low	Low	High	High
Silicide formation ?	-	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Hydroxide formation ?	-	Some	Yes	Some	Some	Some	Yes	Some
Oxygen diffusivity @950C (cm <sup>2</sup> /sec)	2x 10 <sup>-14</sup>	5x 10 <sup>-25</sup>	?	?	?	10 <sup>-12</sup>	?	10 <sup>-13</sup>



# Integration Issues for High $\kappa$ Gate Stack

## FET Gate Stack



## Critical Integration Issues

- Morphology dependence of leakage  
*Amorphous vs crystalline films?*
- Interfacial structures
- Thermal stability
- Gate electrode compatibility
- Reliability

## Fundamental Limitations

- Fixed charge
- Dopant depletion in poly-Si gate
- Dopant diffusion
- Increasing field in the channel region

# Si CMOS Device Scaling – Beyond 22 nm node

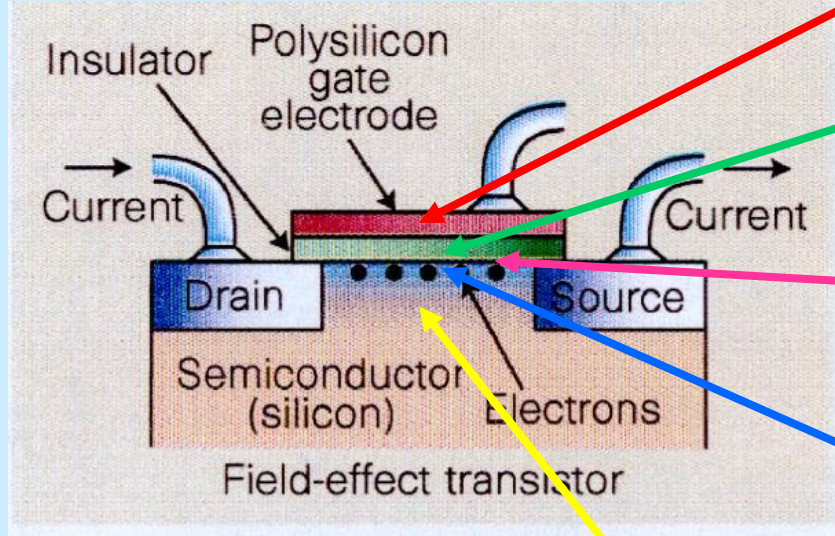
## High $\kappa$ , Metal gates, and High mobility channel

### 1947 First Transistor



The Transistor  
50th Anniversary: 1947–1997

### 1960 First MOSFET



**Metal Gate**

**High  $\kappa$  gate dielectric**

**Oxide/semiconductor interface**

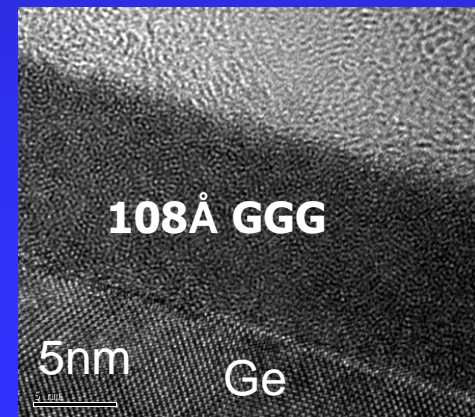
**High mobility channel**

**Integration of Ge, III-V with Si**

**Moore's Law: The number of transistors per square inch doubles every 18 months**

Shorter gate length  $L$   
Thinner gate dielectrics  $t_{ox}$

**Driving force :**  
**High speed**  
**Low power consumption**  
**High package density**



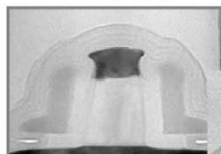


# Intel Transistor Scaling and Research Roadmap

## Transistor Scaling and Research Roadmap

90nm Node

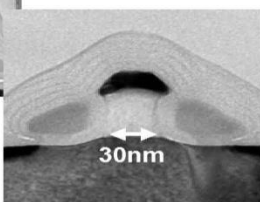
2003



50nm Length  
(Production)

65nm Node

2005



30nm Length  
(Development)

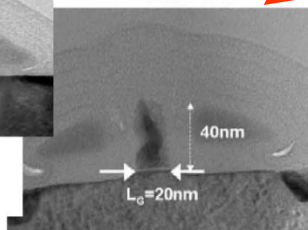
Uniaxial  
Strain

SiGe S/D PMOS

1.2nm Ultra-thin SiO<sub>2</sub>

45nm Node

2007

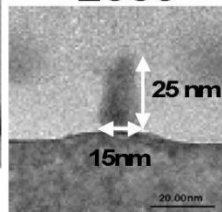


20nm Length  
(Development)

High-K &  
Metal-Gate  
Options

32nm Node

2009

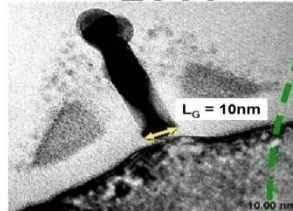


15nm Length  
(Research)

Non-planar Tri-Gate  
Architecture Option

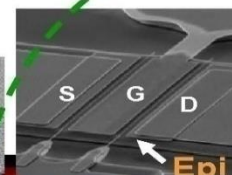
22nm Node

2011

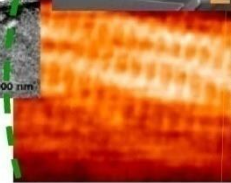


10nm Length  
(Research)

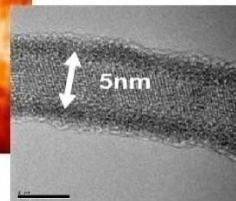
2015-2019  
Research



III-V Device  
Prototype  
(Research)



C-nanotube  
Prototype  
(Research)



Nanowire  
Prototype  
(Research)

Robert Chau, Intel, ICSICT 2004

*More non-silicon elements introduced*

# Science and Technology of Ultimate CMOS

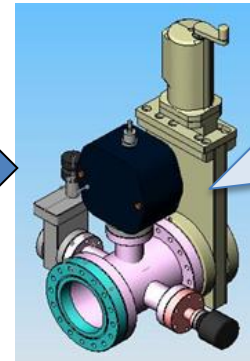
## The Ultimate CMOS – End of road map

**To achieve higher speed and lower power consumption**

R&D of III-V InGaAs MOSFET state-of-art technology below 7 nm node,  
by combining advanced analysis of spectroscopy/microscopy/quantum transport/theoretical modeling



- In-situ ALD of oxide integrated with MBE
- Tailor reconstructed surface to be Ga-rich
- Controlled chemical reaction route and species



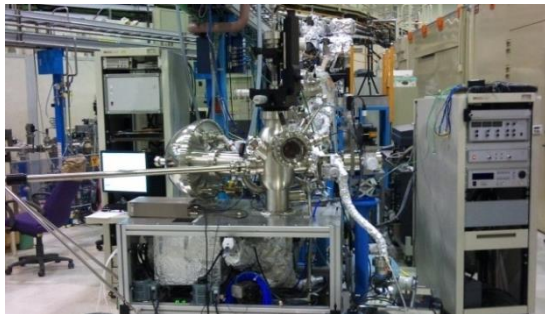
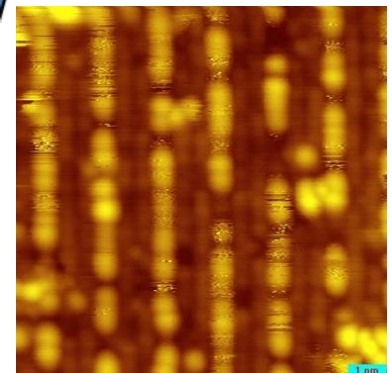
Portable UHV chamber for transfer 2" wafers in  $3 \times 10^{-10}$  torr for PES and STM analysis



High resolution synchrotron radiation photoemission spectroscopy in NSRRC by Dr. T.W. Pi.



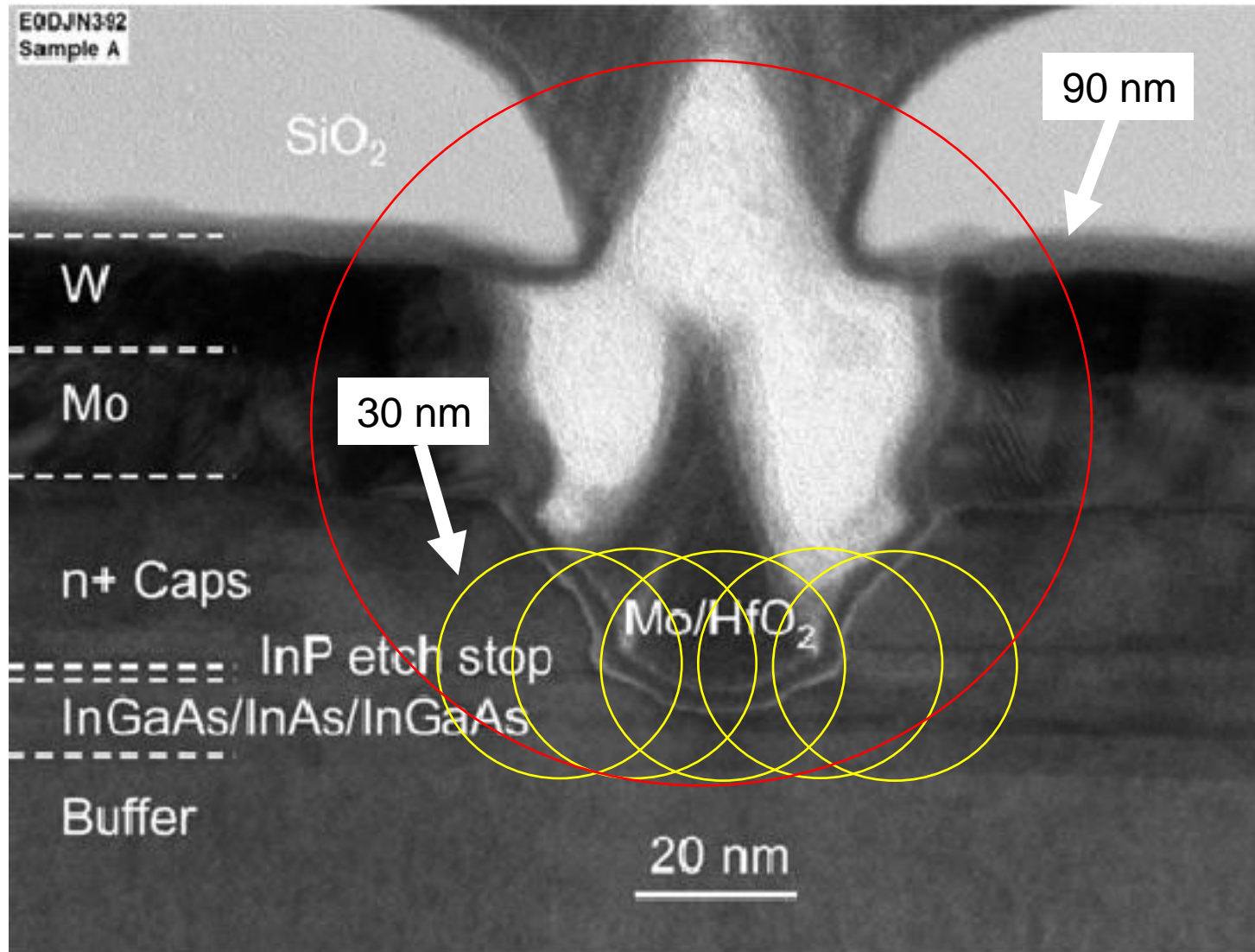
InGaAs surface reconstructed at 77K



RT and LT STM/STS study by Dr. W.W. Pi at CCMS/NTU



# Bragg Ptychography on III-V MOSFETs with gate length $< 30$ nm

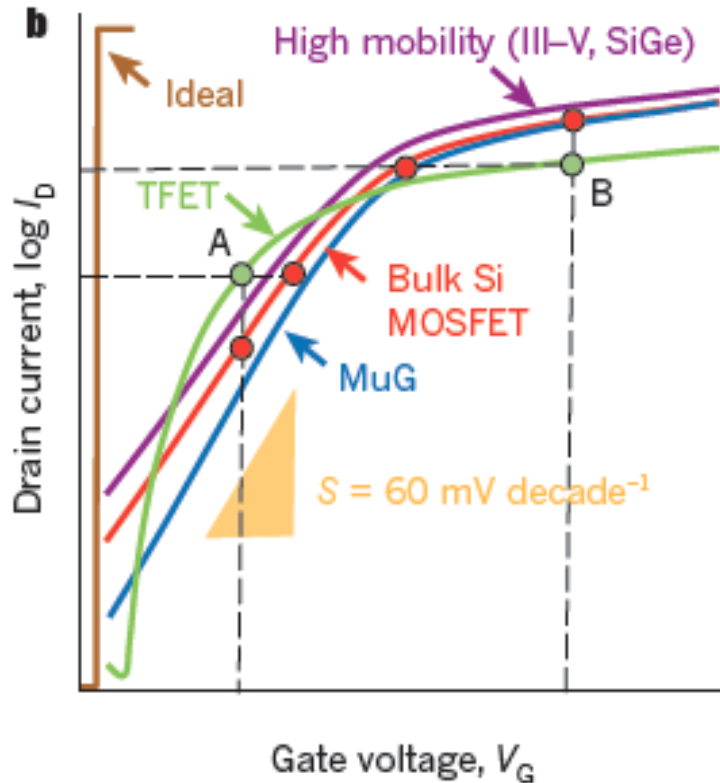


# Tunneling-FETs offer sharper turn-on devices compared to MOSFETs

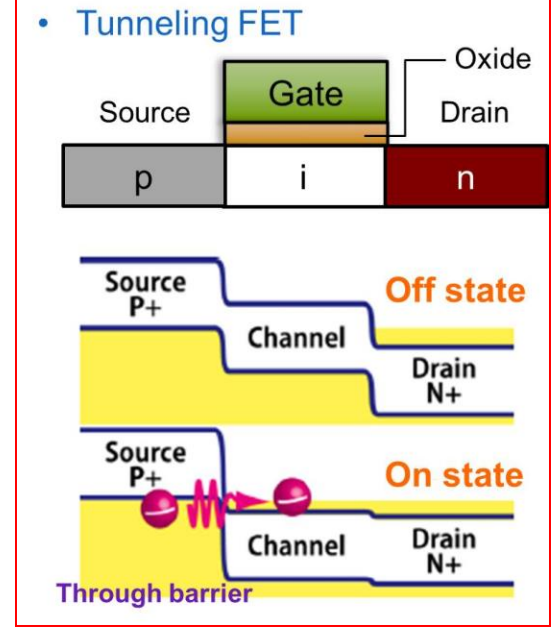
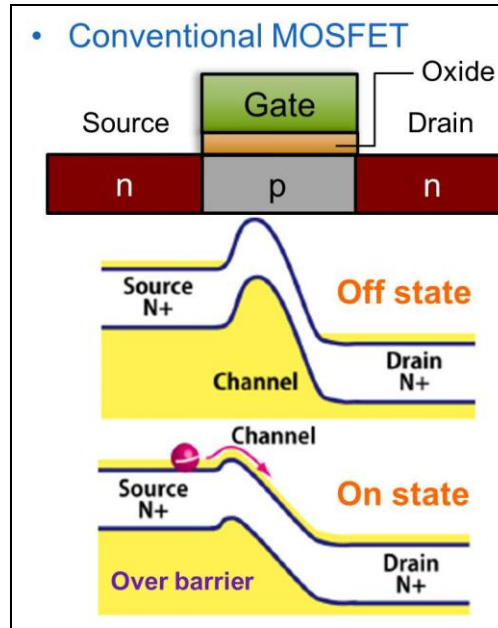
Lower  $V_{DD}$  to lower switching energy ( $P_{active} \sim C \cdot V_{DD}^2$ )

Better performance for ultra low-power applications

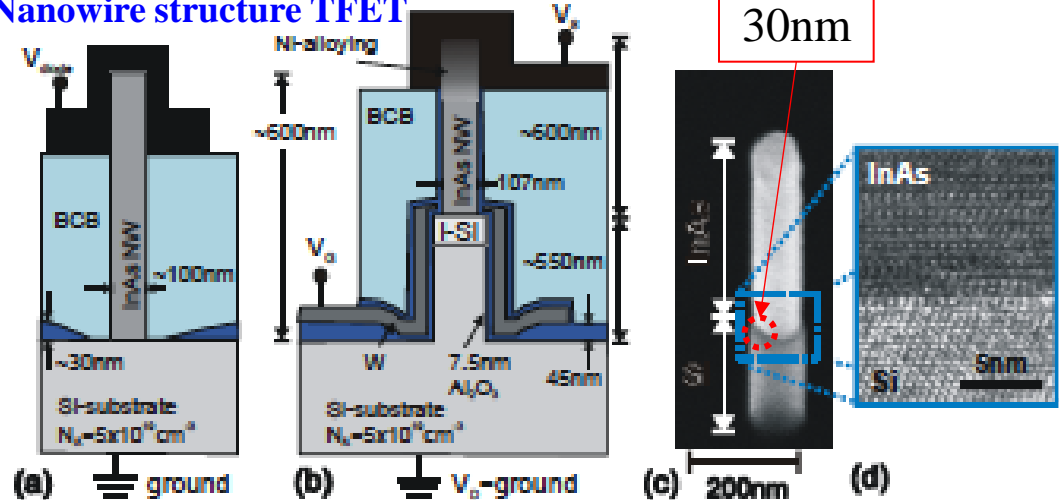
## Atomic Model Prediction



A. M. Ionescu et al.,  
*Nature* **479**, 329 (2011).



## Nanowire structure TFET

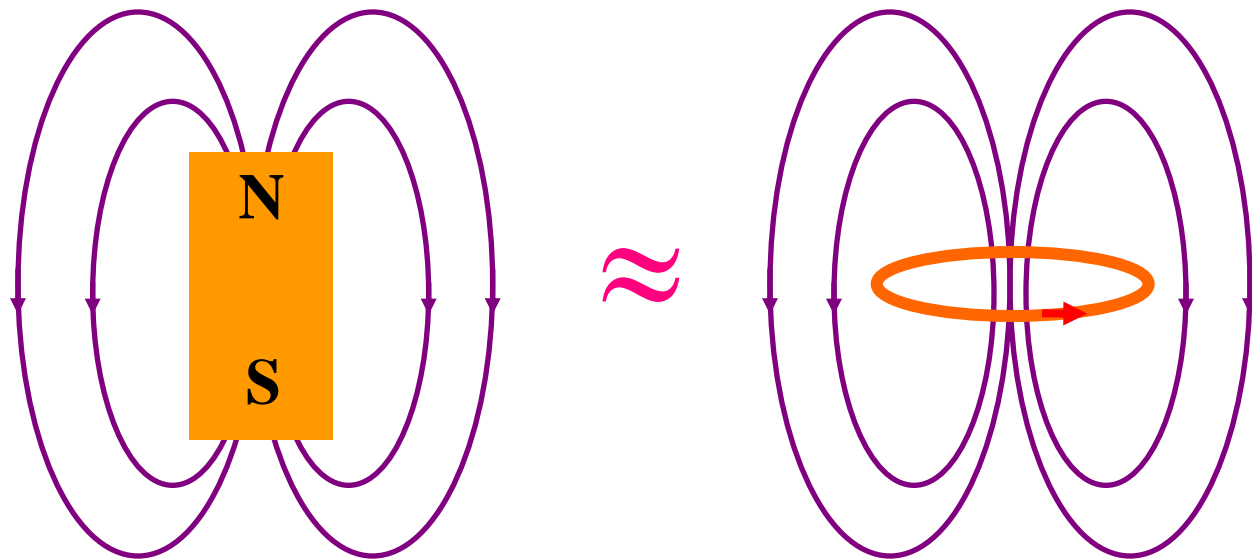


H. Riel et al., *IEDM* 391 (2012).

# **(IV) Quantum Spin**

# Spin and Nano technology

**Electron Spin is the smallest unit of magnetism,  
came from Quantum Mechanics**



**Often being used for  
magnetic recording  
~30 billion market**

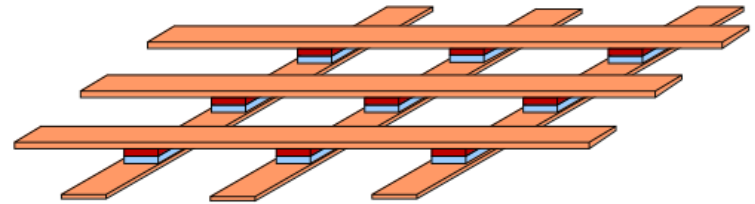
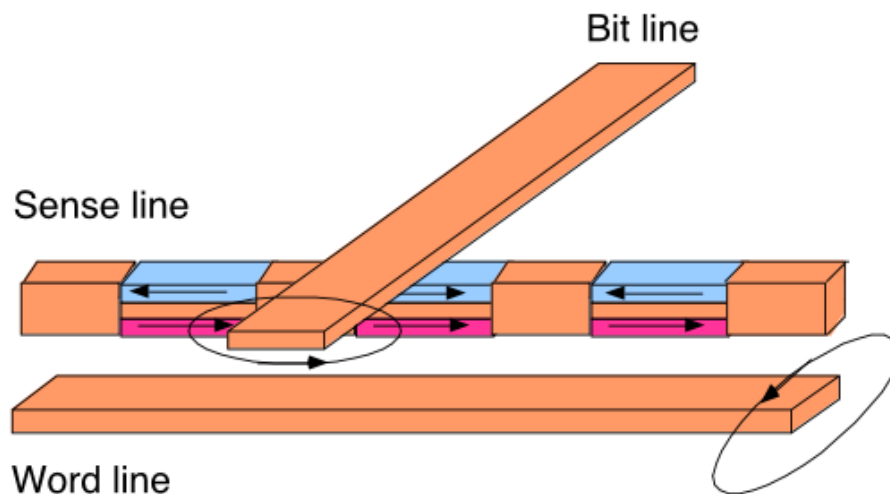


Well read: spintronics has dramatically increased data storage densities in hard drives.

**Spintronics  $\Leftrightarrow$  Electronics**

# New generation of computer

Computation and storage  
in one shot

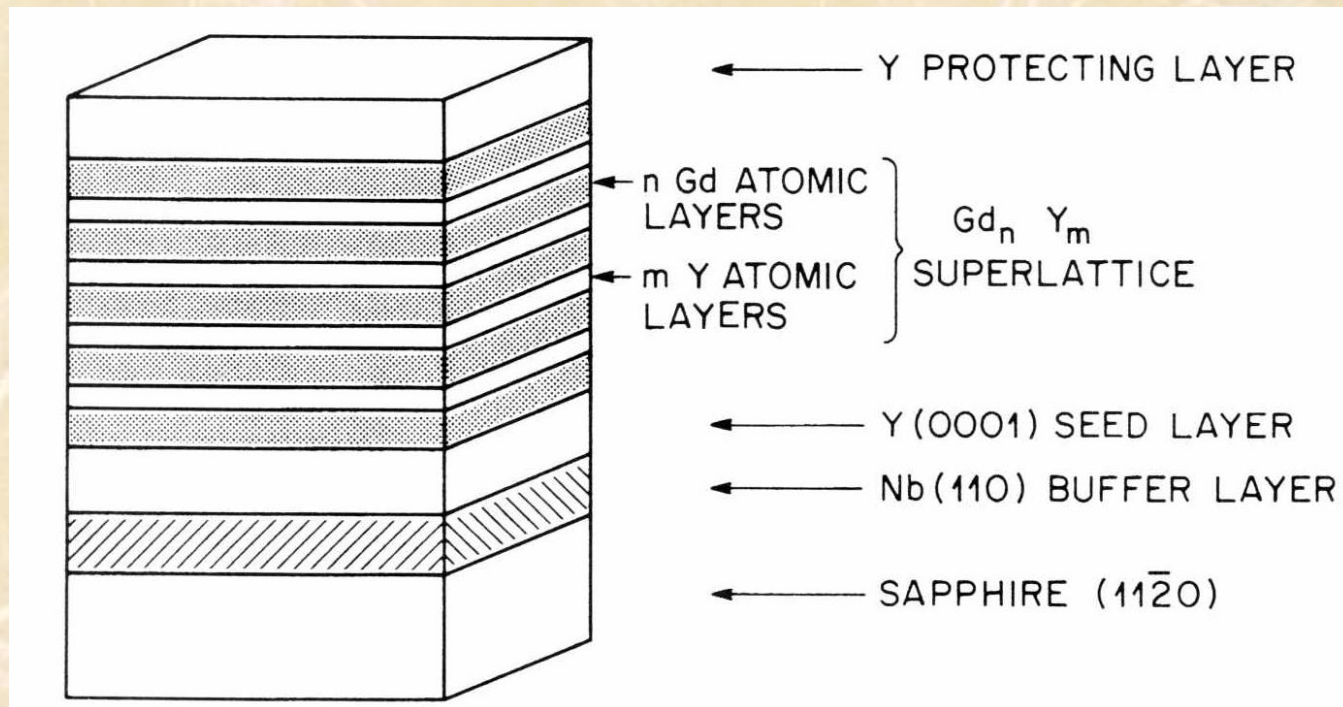


**Fig. 7.** A schematic representation of RAM that is constructed of magnetic tunnel junctions connected together in a point contact array. The conducting wires provide current to the junctions and permit voltage measurements to be made. They also enable the manipulation of the magnetization of the elements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

When turn-on,  
it is ready!

# Artificial Superlattice

- Matching the structural periodicity with physical length scale of **superconductivity and magnetism**
- Modulation of physical properties

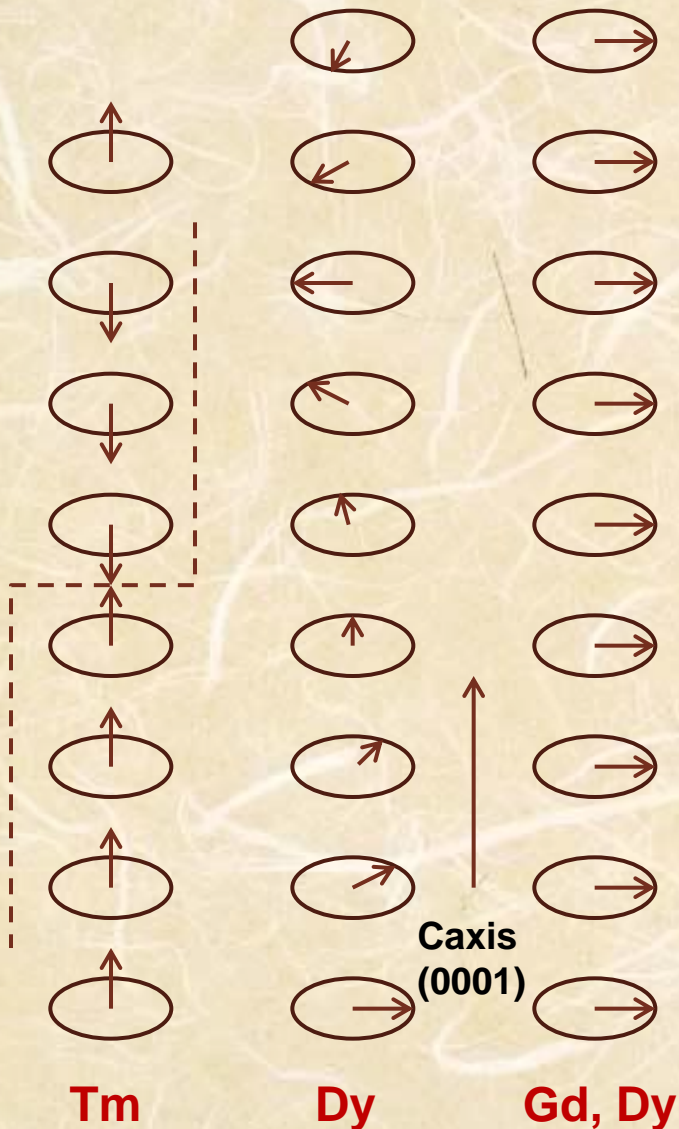


## Invention of metal molecular beam epitaxy in 1981

- Single crystal epitaxial superlattices with Atomically abrupt interfaces

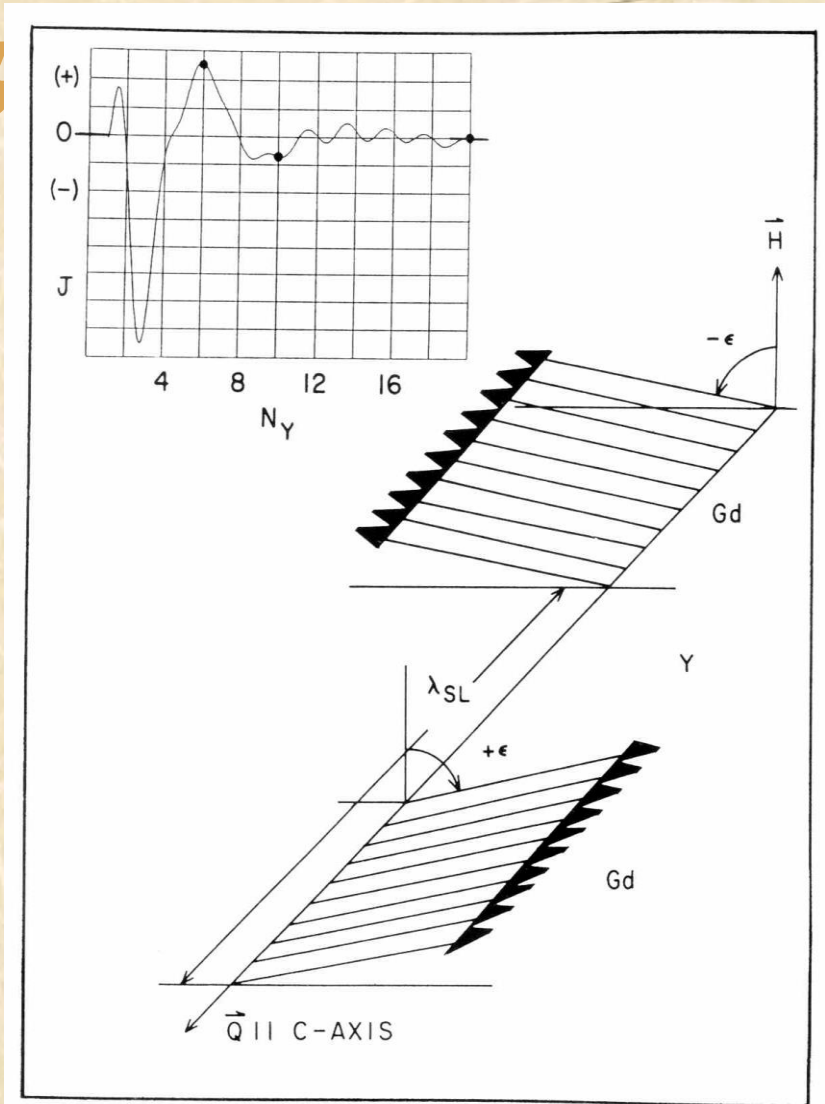
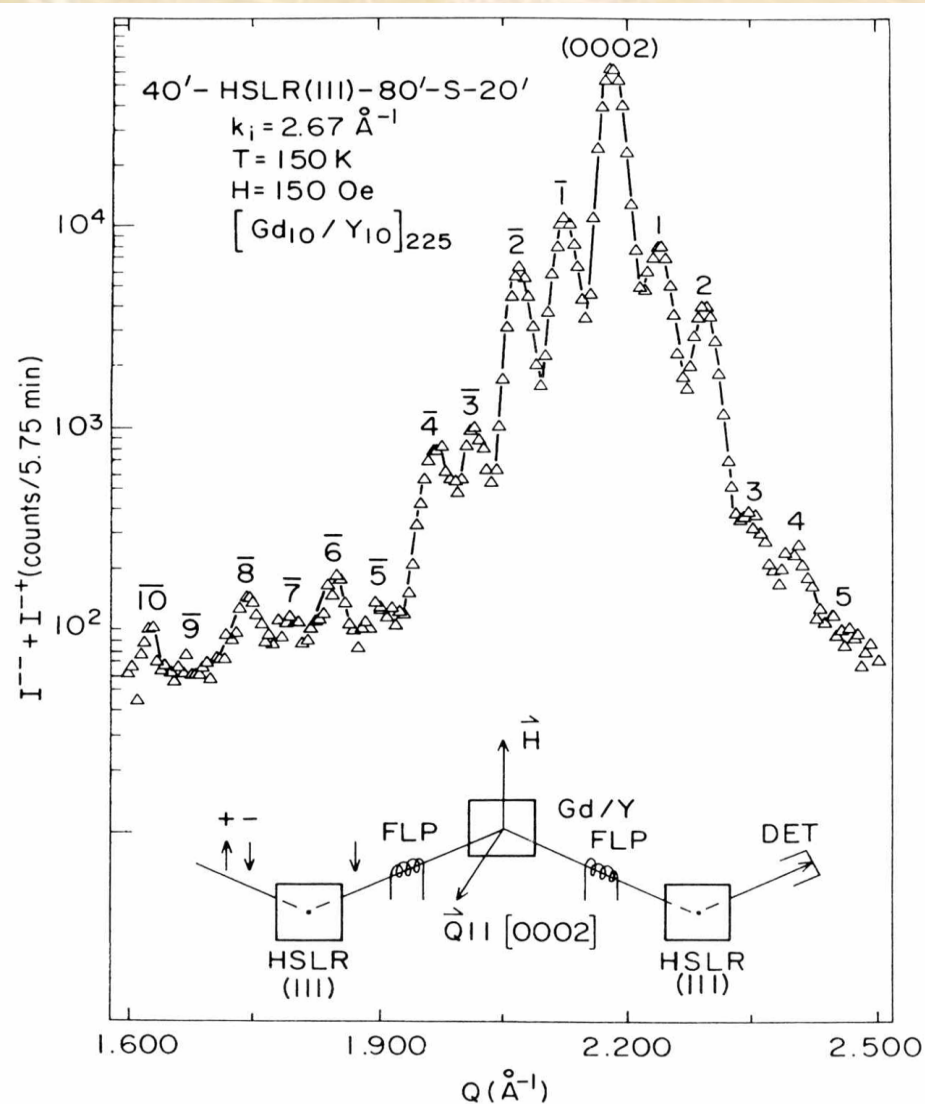
# HCP crystal structure

- Similar crystal- chemical nature of rare earth forms coherent superlattices
- Metallic superlattice effect
  - Long range nature of the indirect exchange interaction
  - Magnetic coupling of magnetic rare earth through non – magnetic Y, Lu
  - Modulation of magnetic properties of Gd - Y Superlattices
  - Spin structure modification of Tm - Y, Dy - Y Superlattices
- 2-dimensional magnetism
- Interfacial magnetism



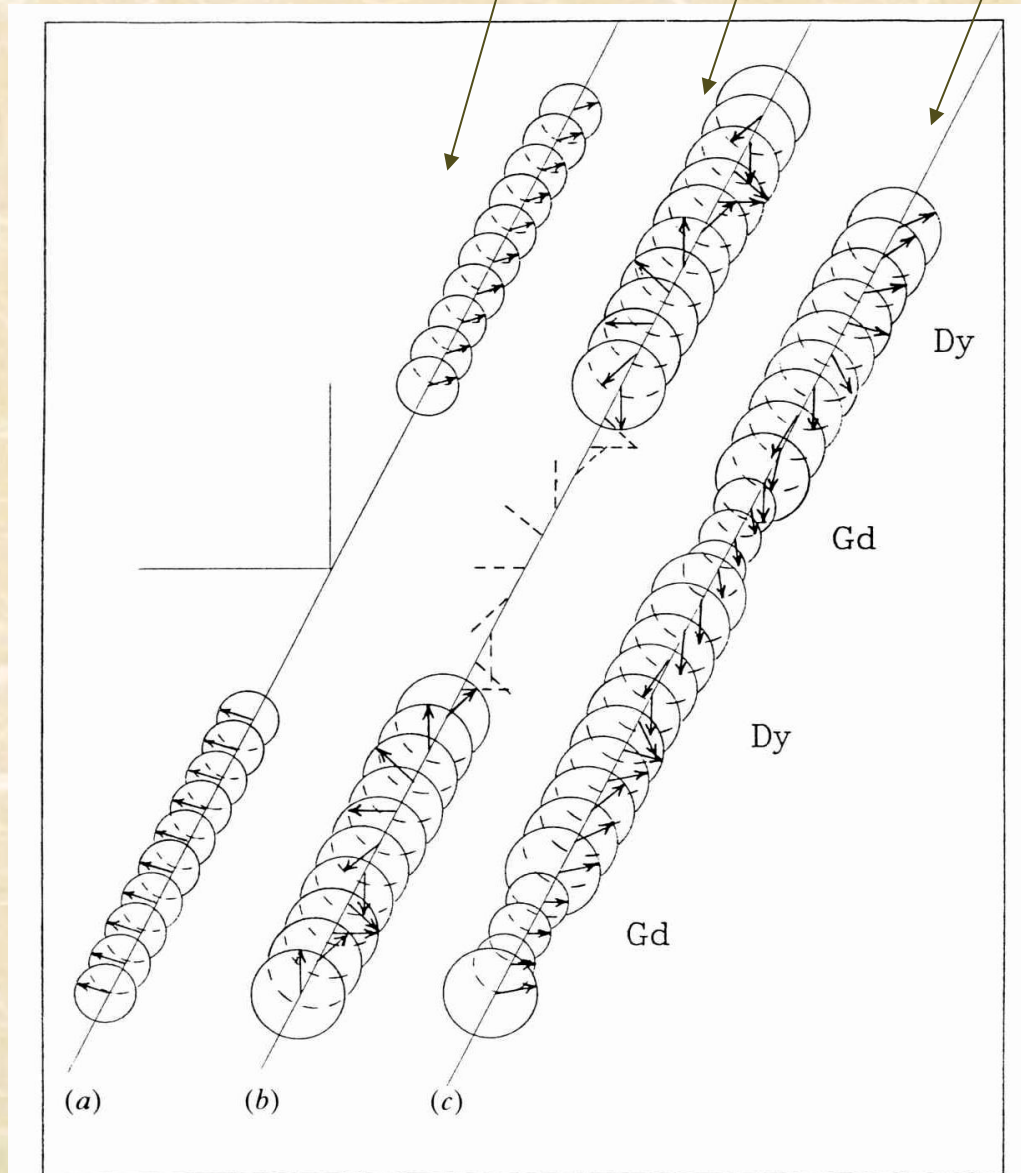
Spin structures of heavy rare - earths

# Neutron Diffraction Studies of the $\text{Gd}_5\text{-Y}_{10}$ Magnetic Superlattice – Antiferromagnetically coupled



# Spin Structure Tailoring in artificial Superlattices

**Gd-Y Dy-Y Gd-Dy**



1984-1989

# Giant Magnetoresistance(GMR)

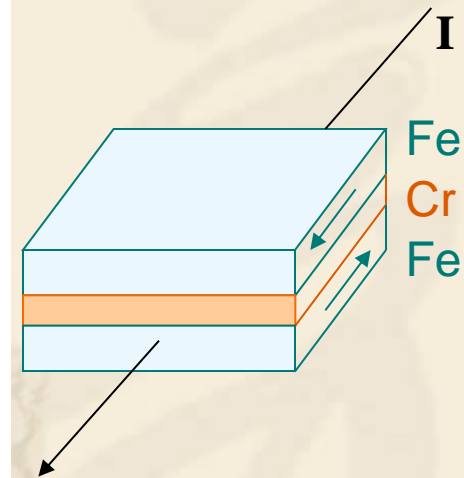
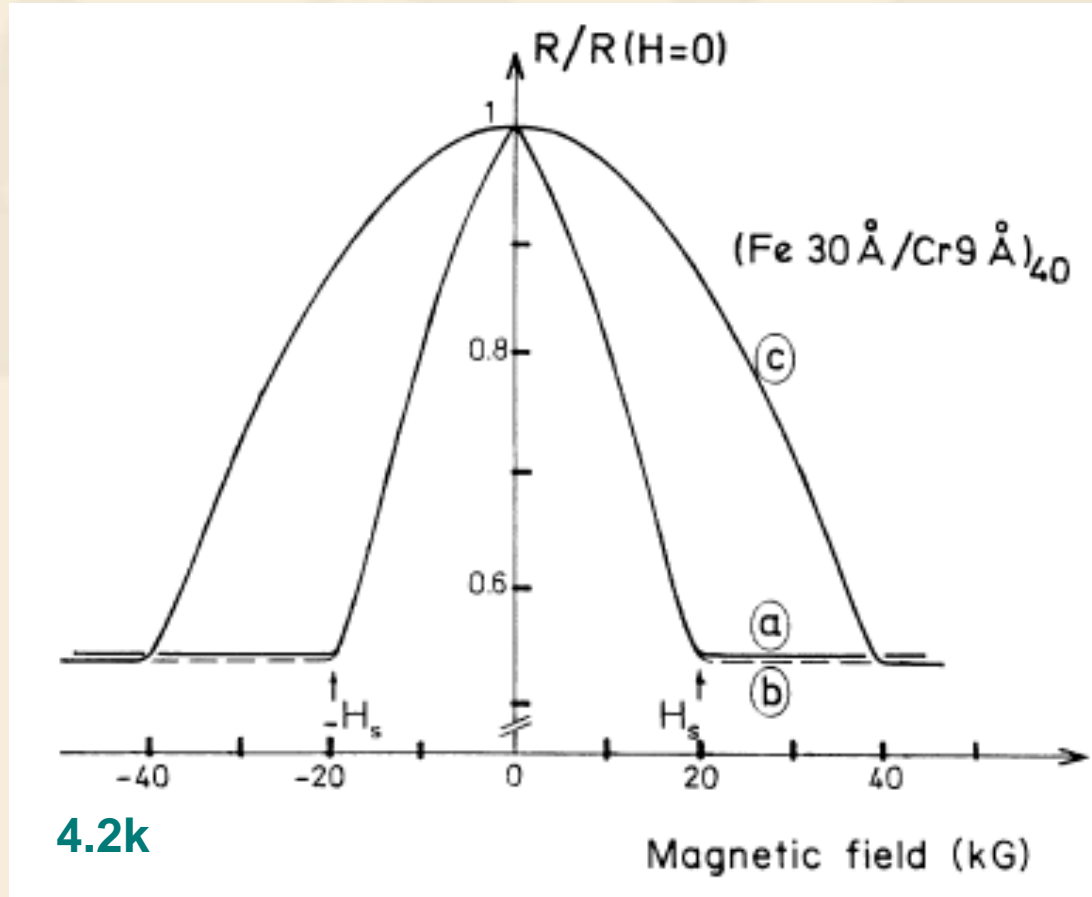
## ❖ What is GMR?

- ✦ GMR is a very large change in electrical resistance that is observed in a ferromagnet/paramagnet multilayer structure.
- ✦ Resistance change occurs when the relative orientations of the magnetic moments in alternate ferromagnetic layers change as a function of applied field.
- ✦ The total resistance of this material is lowest when the magnetic orientations of the ferromagnetic layers are aligned, is highest when the orientations are anti-aligned.

Ferro.
Para.
Ferro.
Ferro.
Para.
Ferro.
Para.
Ferro.

M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, and F. Petroff,  
*Phys. Rev. Lett.*, **61**, 2472 (1988).

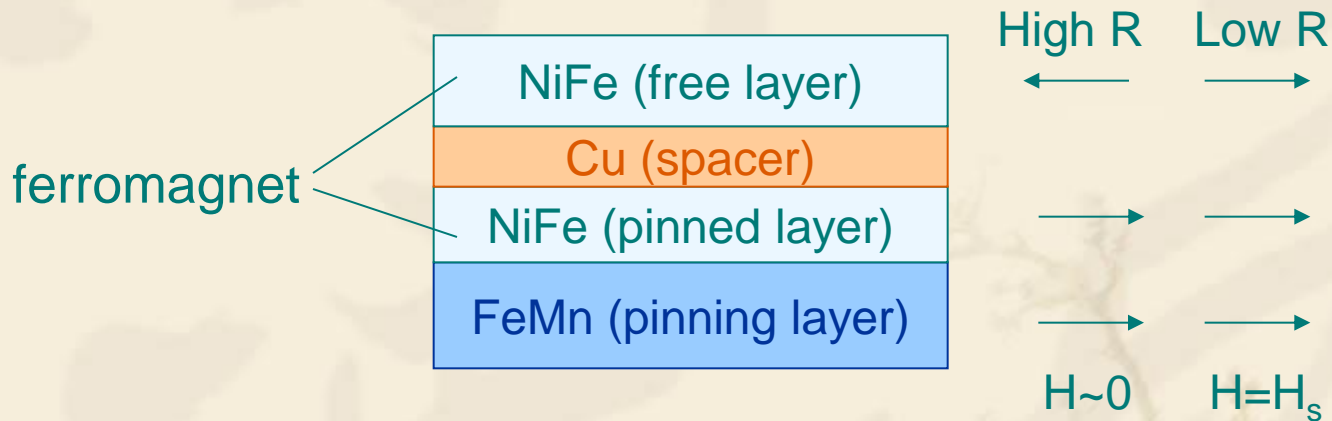
# First Evidence of GMR



$H_s$  corresponds to the field at which all layer magnetizations point along the field direction.

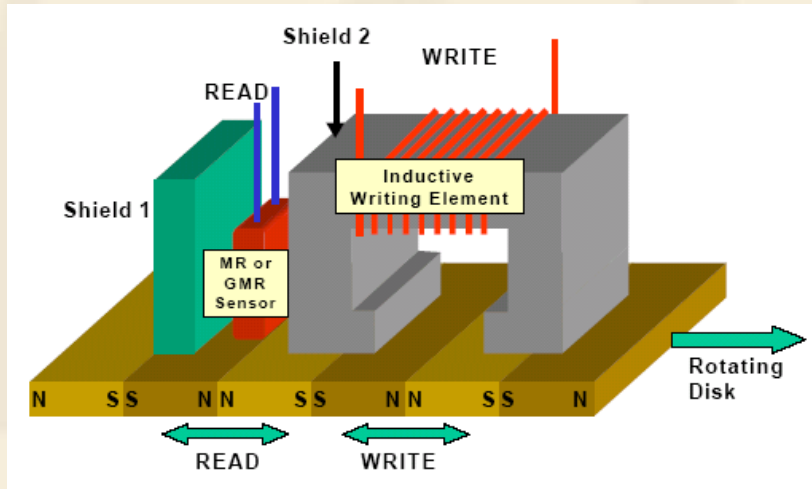
# Spin-Valve GMR

- ✧ The simple structure of Spin-valve GMR is



- ✧ The magnetisation of the top permalloy layer is free to rotate as the field is varied. Second permalloy layer is fixed due to its exchange interaction with the iron–manganese layer.

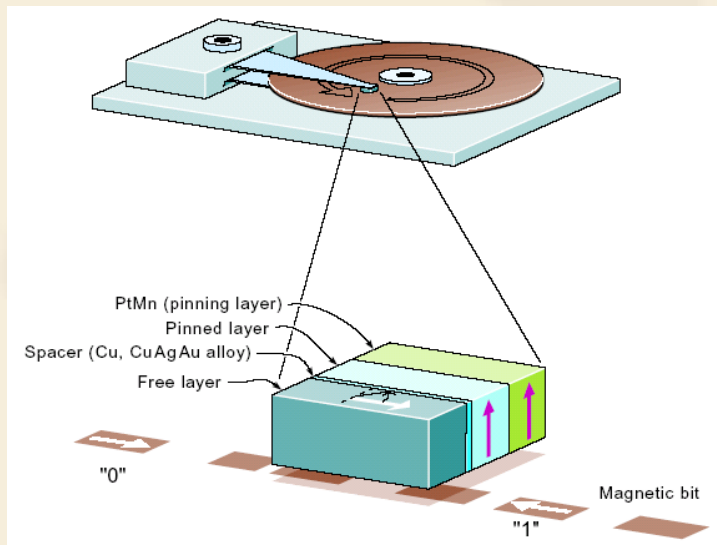
# GMR Spin Valve Reading Head



✧ Magnetization is stored as a “0” in one direction and as a “1” in the other. This is the magnetic field sensed by the GMR head.

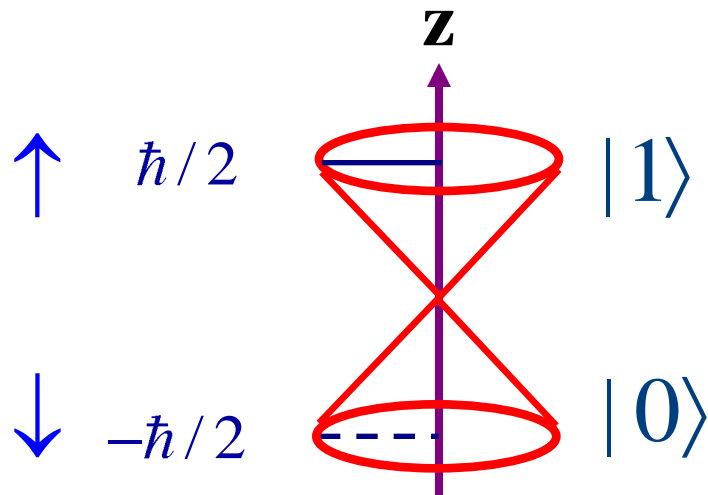
✧ When the head passes over these magnetic bits, the magnetization direction of the free layer in the head responds to the field in each bit by rotating either up or down.

✧ The resulting change in the resistance is sensed by the voltage across the GMR head (current passing through the GMR element is constant).



# Quantum behavior of ferromagnets

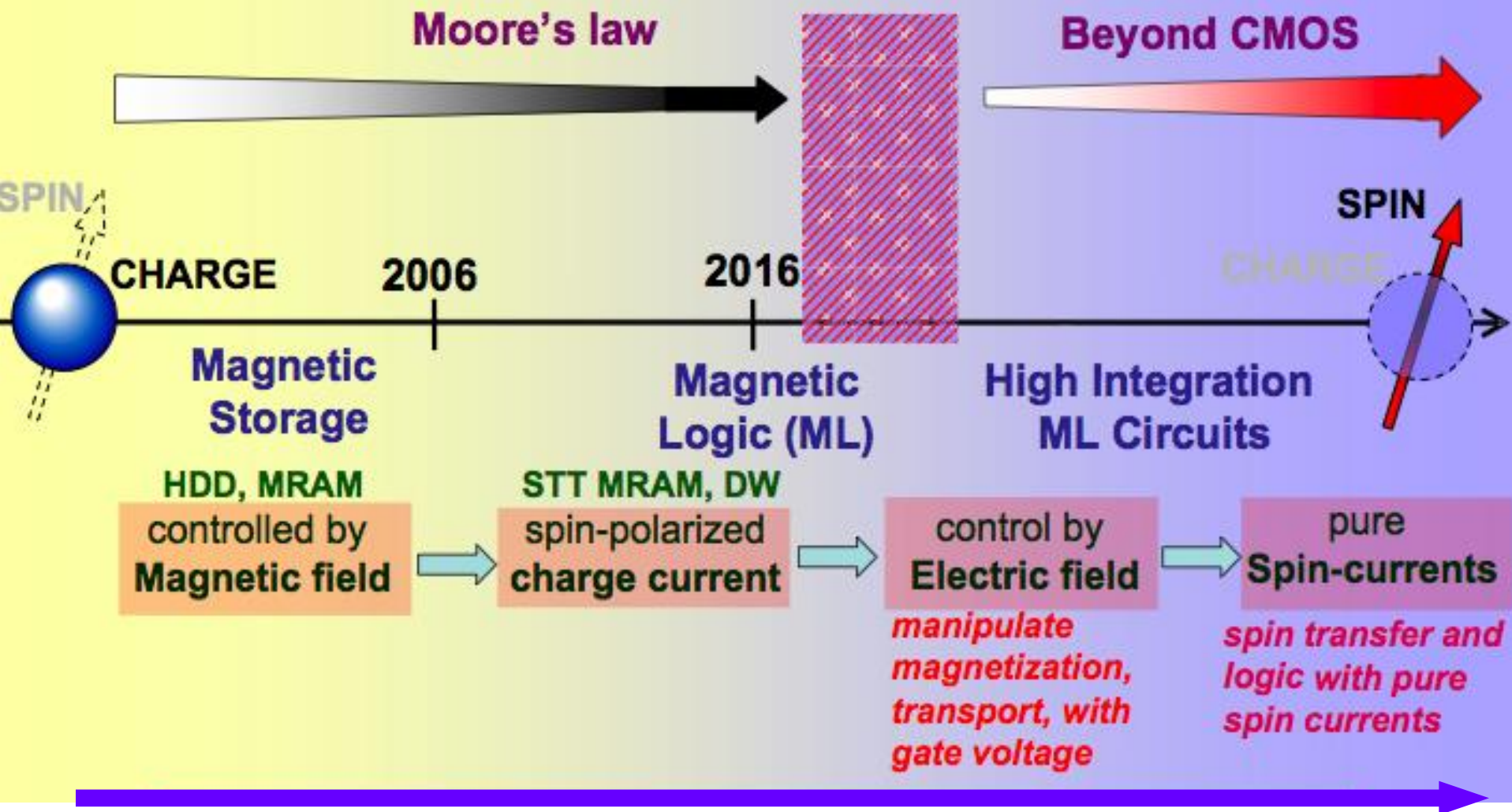
## -Spin as a quantum qubit



$$\text{qubit} = \alpha |0\rangle + \beta |1\rangle$$

**Due to superposition  
More information!**

# Tentative roadmap



**Can we take the “charge” out of Spintronics ?  
To generate pure spin current !**

# *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 Quantum Effect at the nano scale

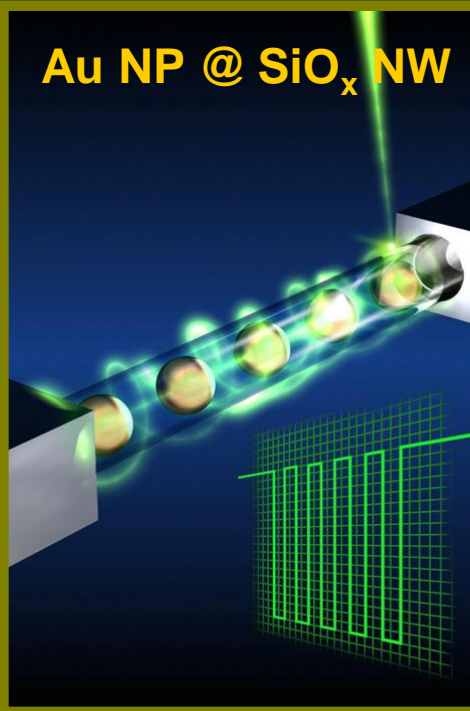
- Interference
- Quantization
- Tunneling
- Quantum Spin

**The Fourth Lesson:**

**Innovations of  
nano structures and  
nano materials  
for various applications**

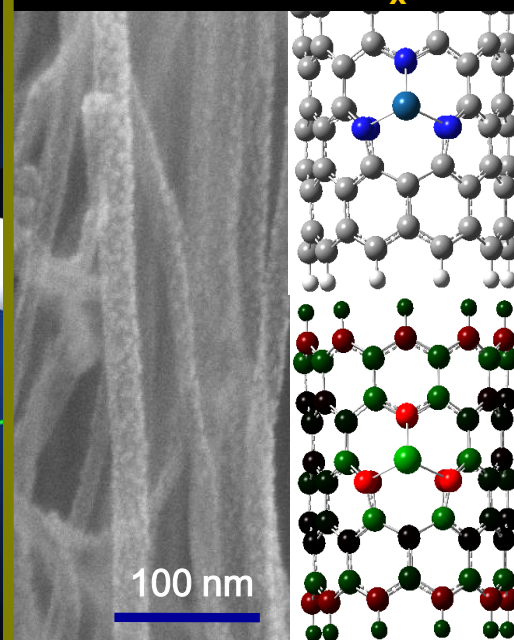
# Overview of Advanced Materials Laboratory

**Au NP @ SiO<sub>x</sub> NW**



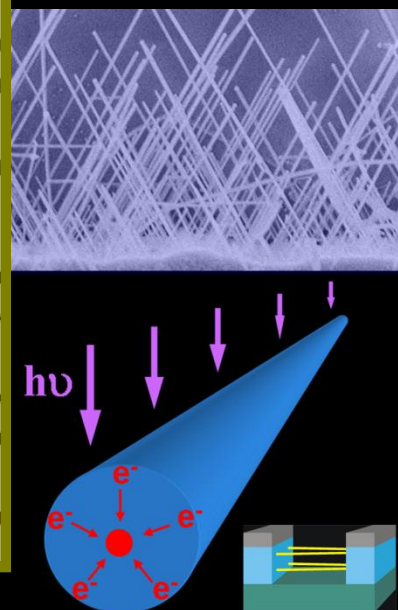
Color-selective Optical Switch, SPR-enhanced Sensor

**Pt-Ru NP on CN<sub>x</sub> NT**



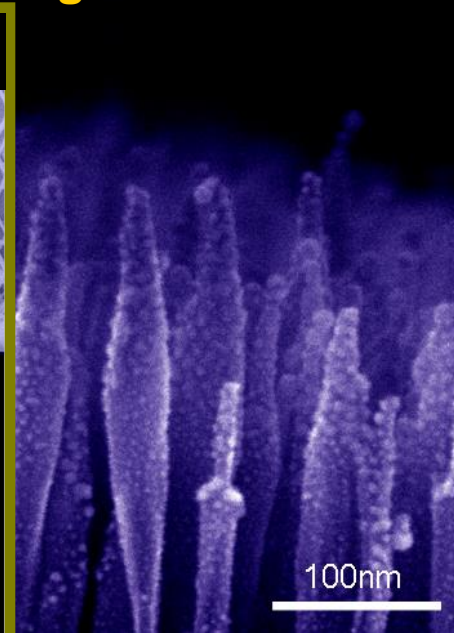
Fuel Cells, Supercapacitors

**GaN Nanobridge**



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

**Ag NP on Si NT**



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

*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)

*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)

Chapter 9, pp. 259-309,  
*Nanowires and nanobelts*, Z.L.

Wang Ed., Kluwer (2004)

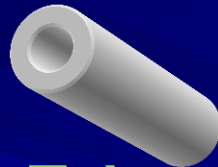
*Adv. Func. Mater.* 16, 537 (2006)

*APL* 90, 123109 (2007)

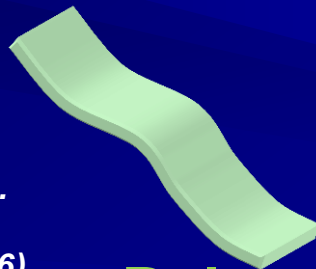
*Adv. Mater.* 19, 4524 (2007)



**Wire/Rod**



**Tube**



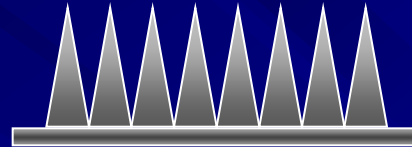
**Belt**



**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)

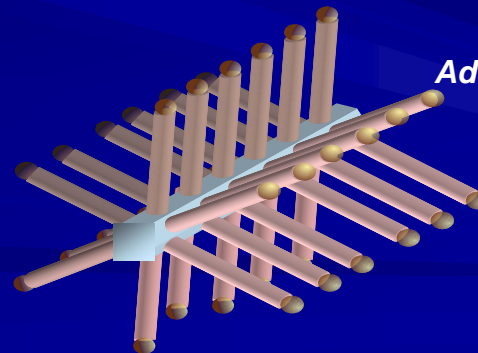
*Nano Lett.* 9, 1839 (2009)



**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)

# A Color-selective Nanoswitch

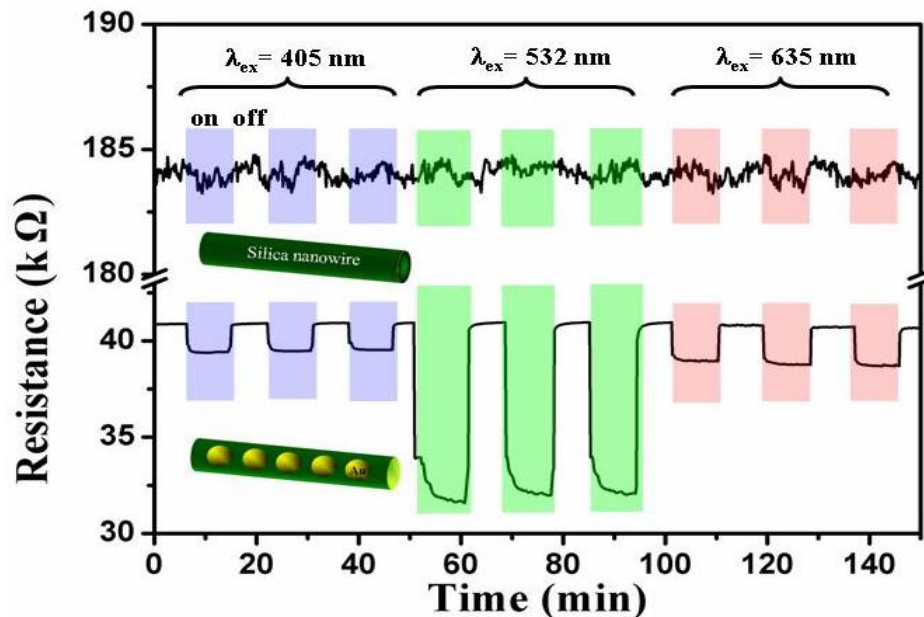
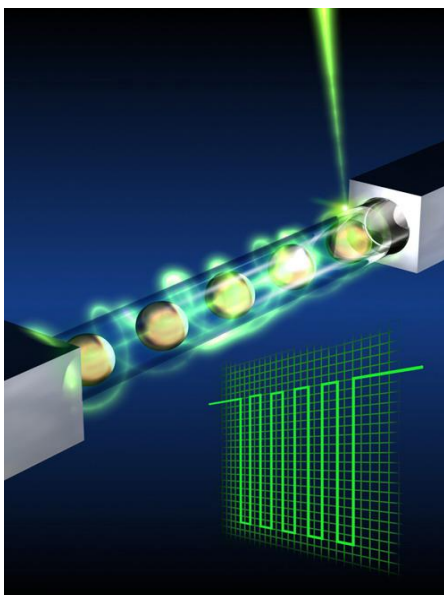
## Photosensitive Gold Nanoparticle-embedded Dielectric Nanowires

*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.

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

- \* Antireflection:

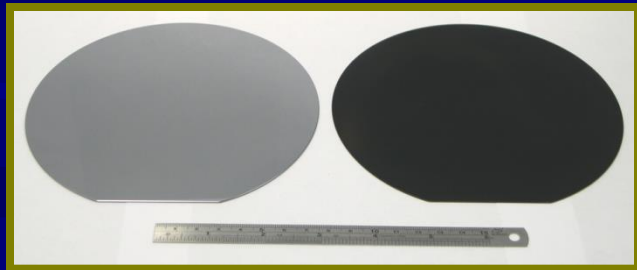
Broadband (uv-terahertz), Omnidirectional ( $>70^\circ$ )

- \* Electroluminescence in ZnO/SiNTs:

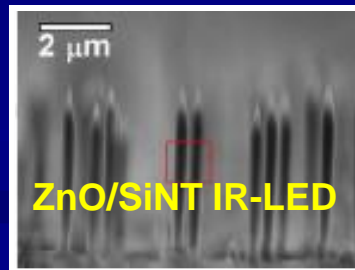
IR emission, x10 higher; turn-on  $\sim 3\text{V}$ , x2 lower than film

- \* Magneto-resistance in LSMO/SiNTs:

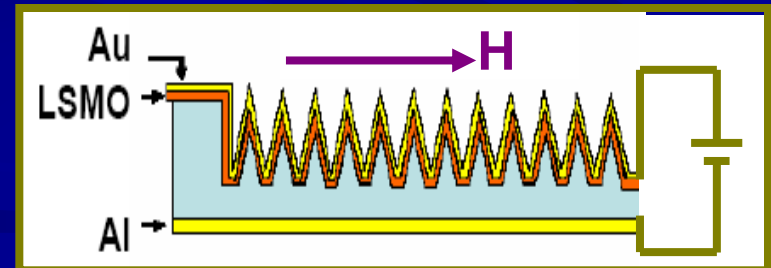
Room-temp. MR at lower bias and magnetic field



Nature-Nanotechnology  
2 (2007) 770



Nano Letters  
9 (2009) 1839



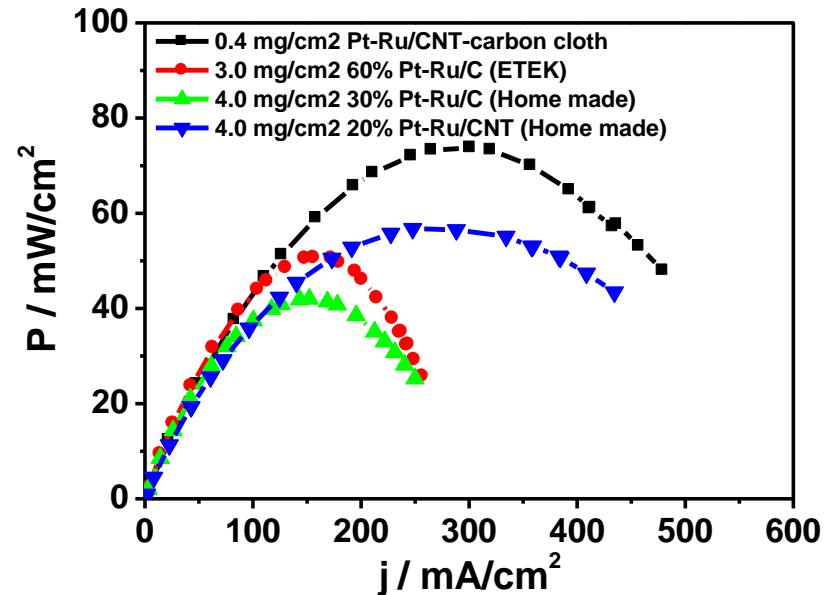
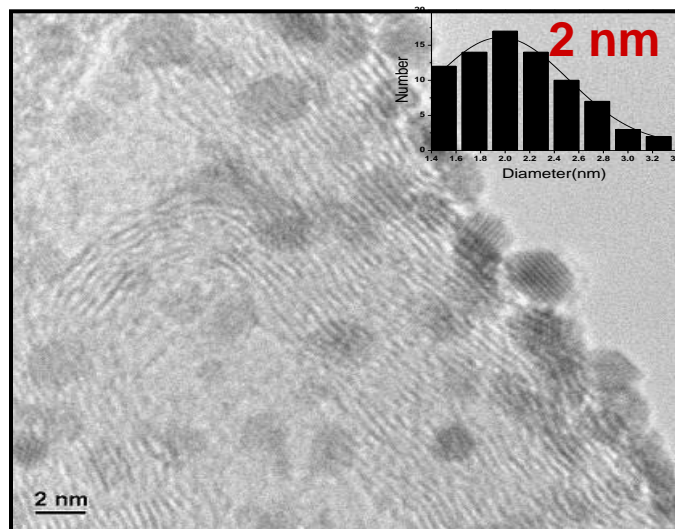
Promising high-density memory:  
On-going

# 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)*



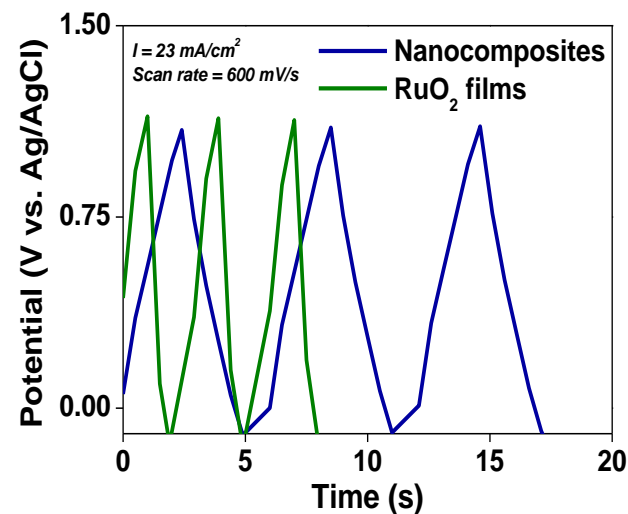
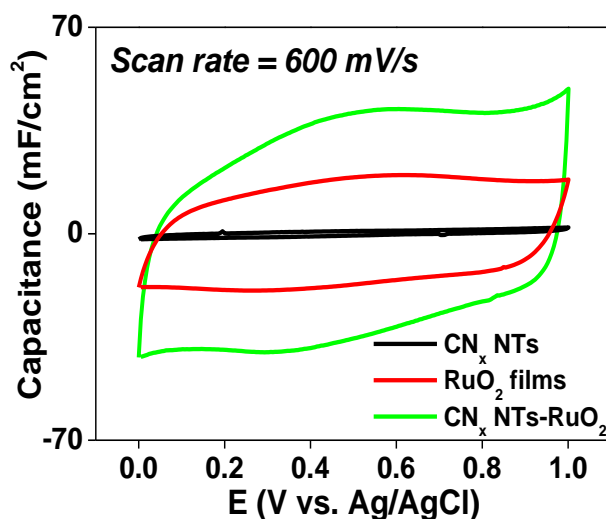
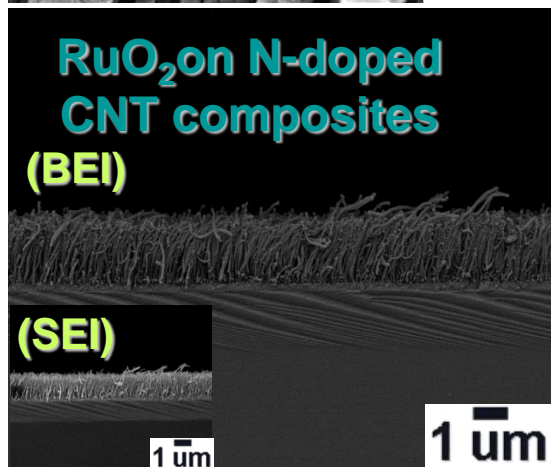
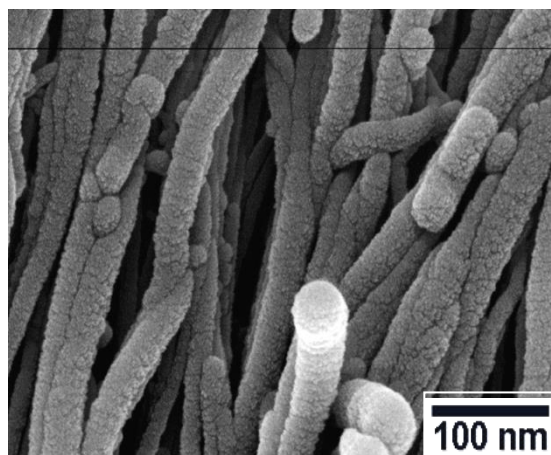
- Direct methanol fuel cell is promising power generator with a wide range of applications from portable electronic devices to automobiles.
- Nanotubes-Pt/Ru composites are highly efficient in loading precious metals. Only **one tenth** of metal loading, in comparison to the conventional, is needed.

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

## Ultrafast Charging-discharging Capacitive Property of RuO<sub>2</sub> 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)



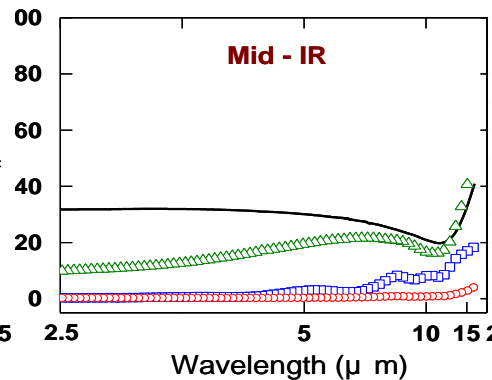
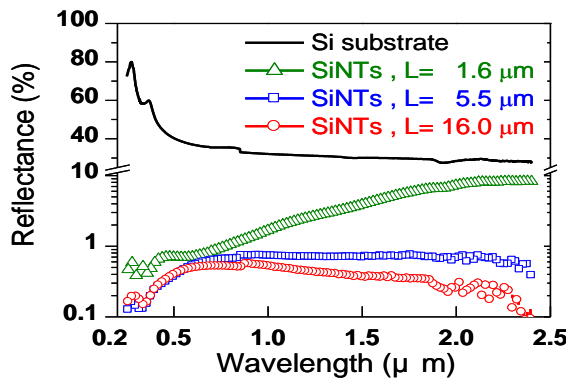
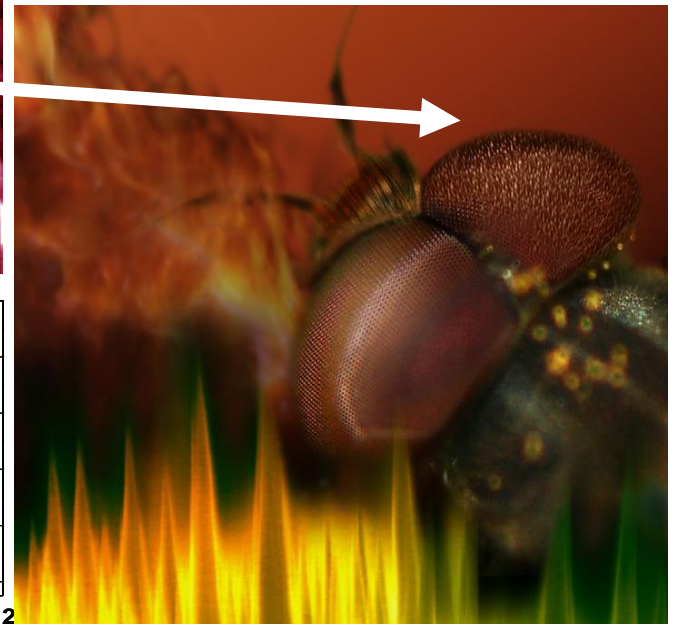
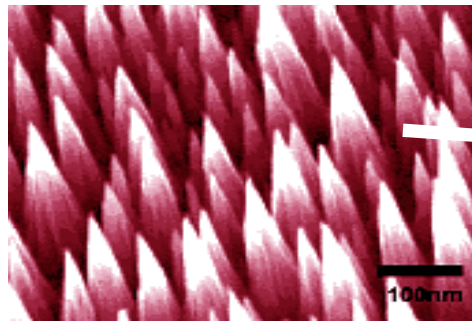
- 4 fold increase in capacitance
- Optimal capacitance of 1380 F/g at 600 mV/s (theory: 1450 F/g)
- Output current as high as 23 mA/cm<sup>2</sup>
- Stable at high scan rate
- 10 fold increase in charge-discharge rate

# 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**

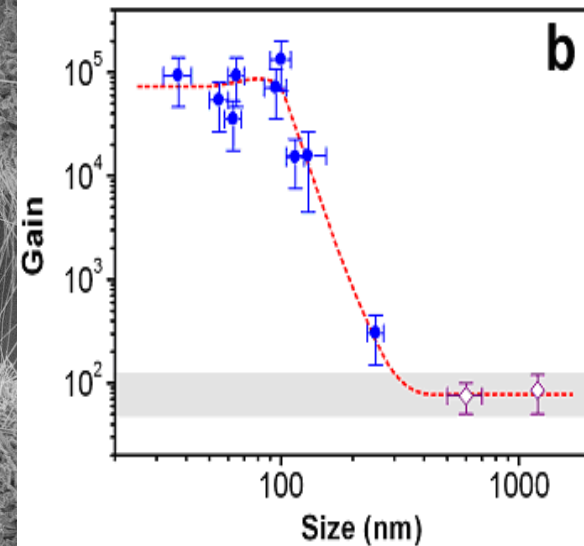
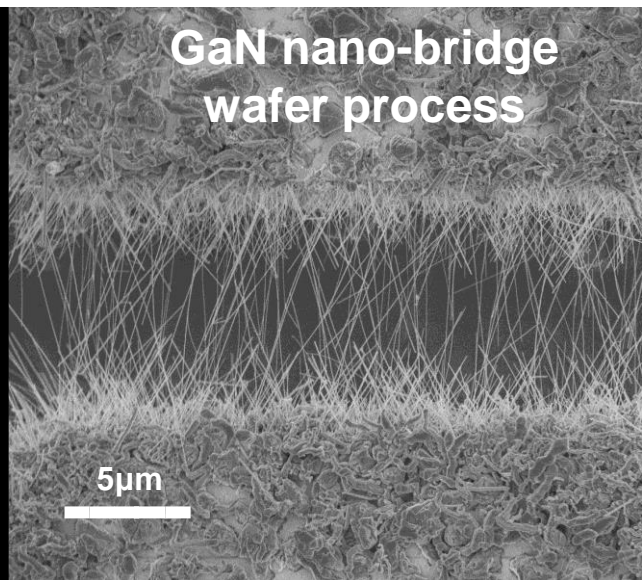
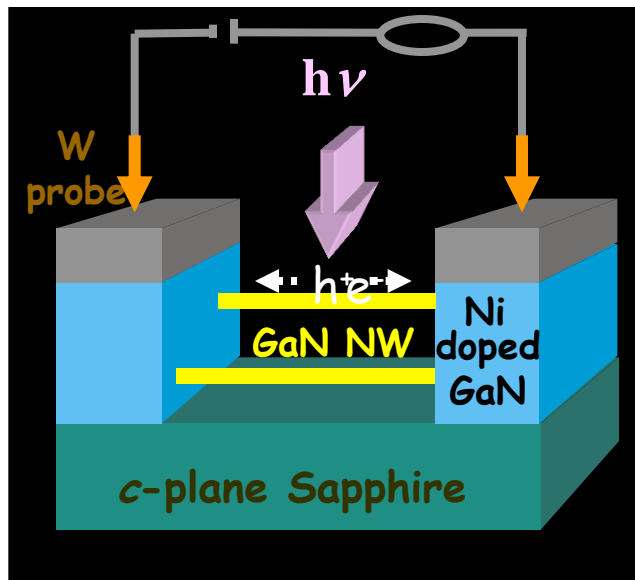


Many plants and animals have tiny surface structures that absorb certain wavelengths of light. These naturally formed nanostructures provide the colors in butterfly wings, camouflage for cicadas and enable moths to capture as much light as possible when flying at night. Now, we have created nanostructure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

# **The Fifth Lesson:**

**Nano photonics**

**and**

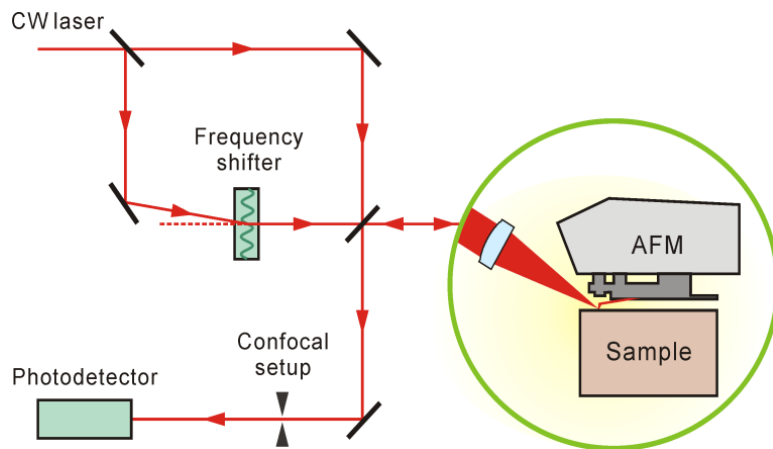
**Bio-applications**

# Nano-photonics and Plasmonics

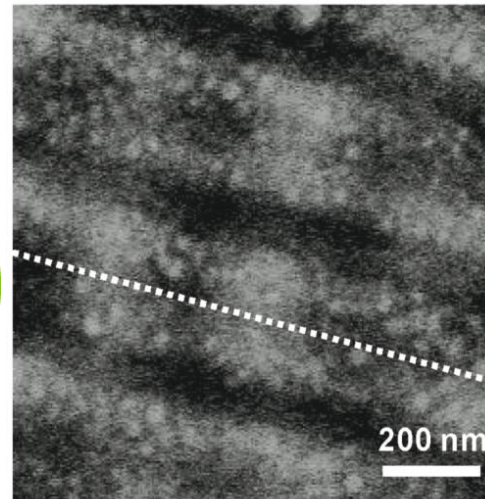
## Near-field examination of blue-ray discs

Dr. Juen-Kai Wang, CCMS, NTU

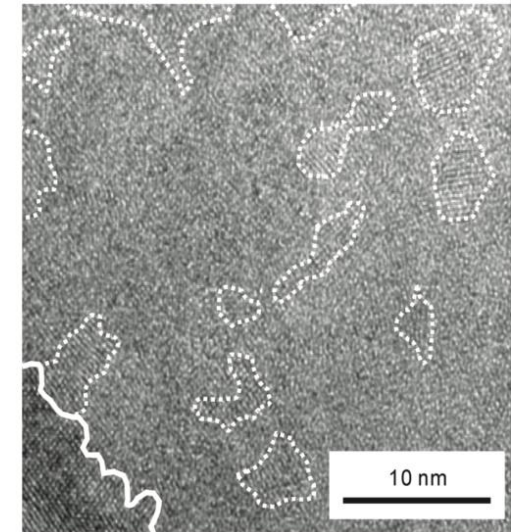
### S-SNOM setup



Near-field image of recorded disc

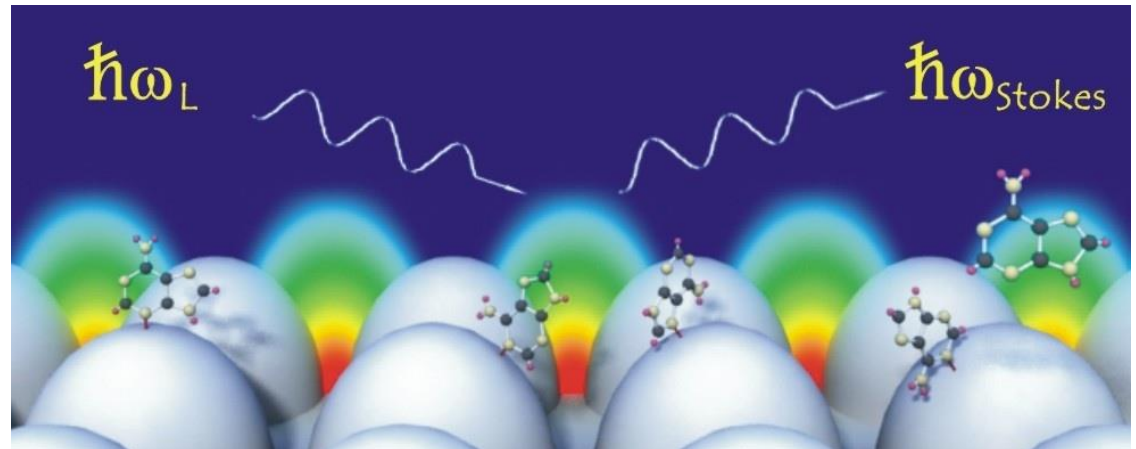
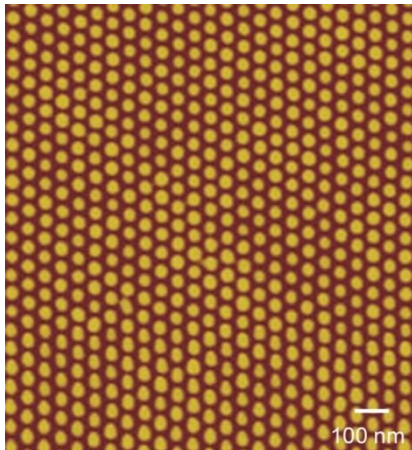
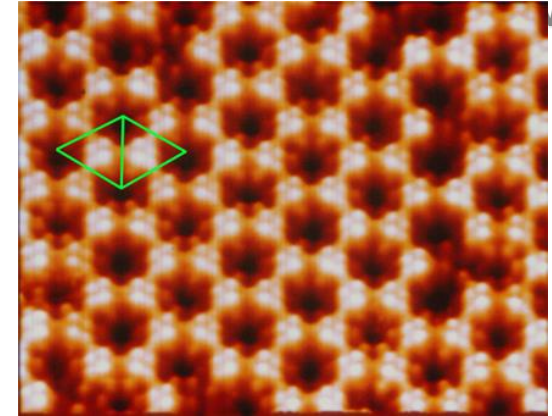
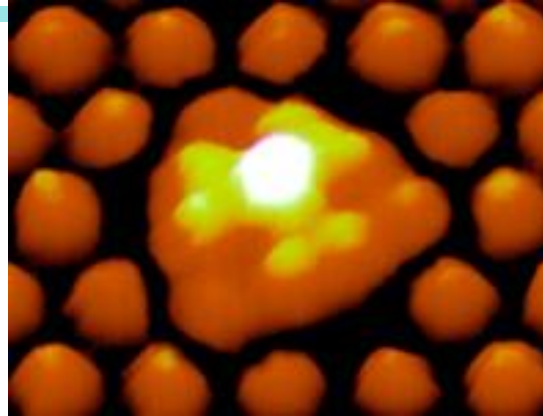
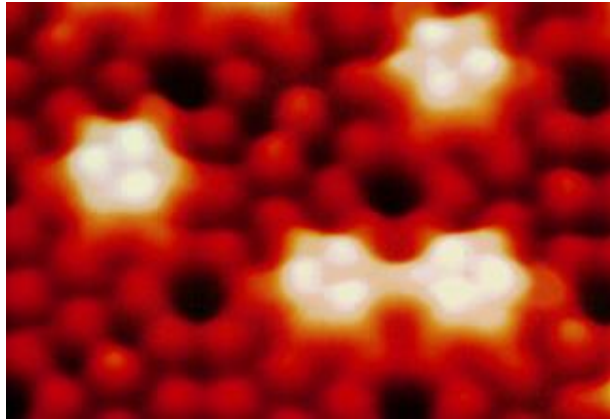


TEM image of recorded mark



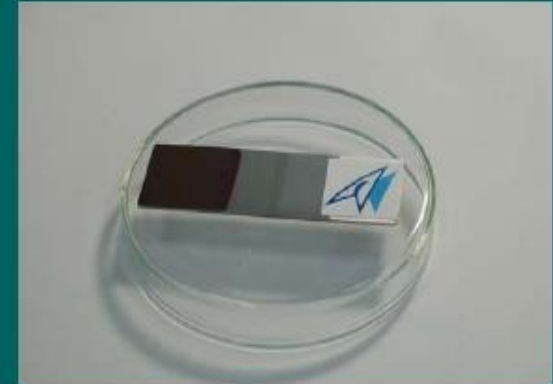
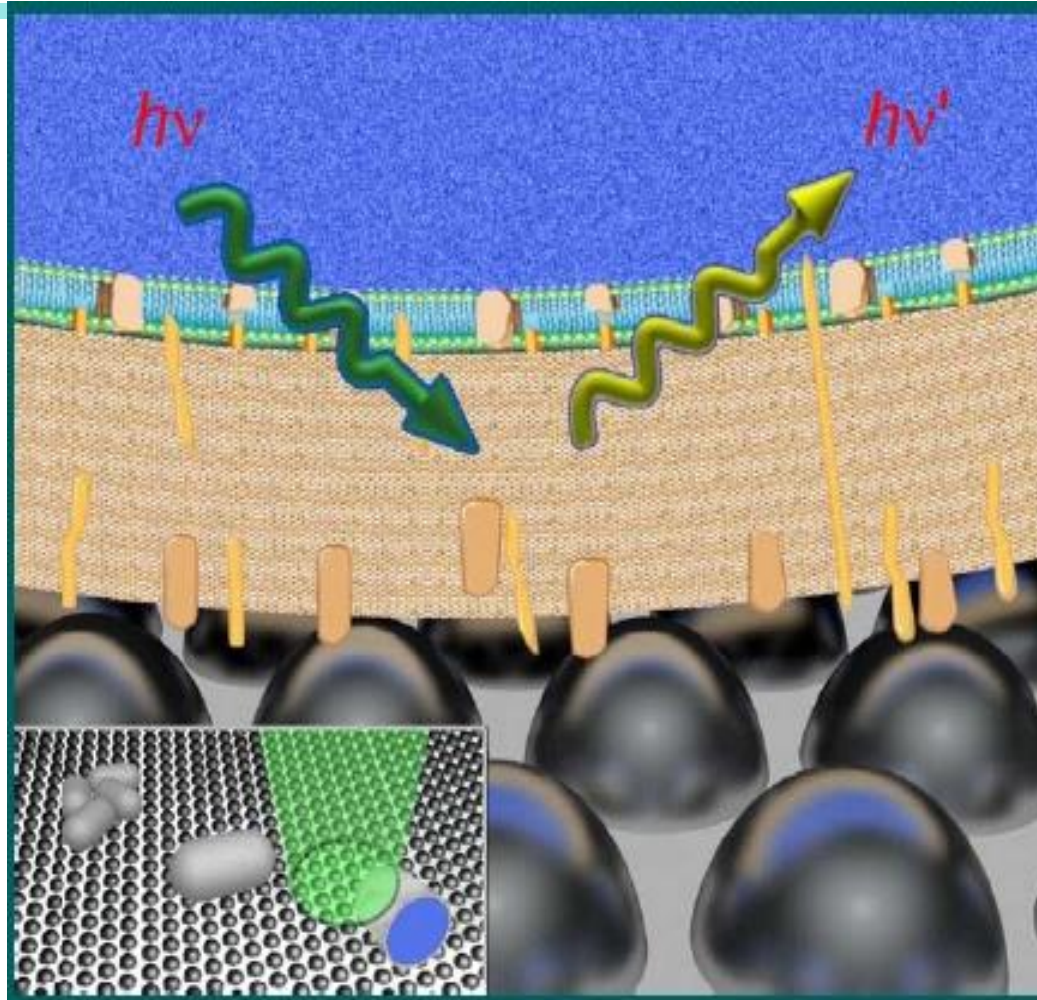
- **Scattering-type SNOM reveals sub-10 nm optical signature.**
- The optical contrasts of the dark and the bright regions in near-field image of phase-change layer correspond to amorphous and polycrystalline AgInSbTe, respectively.
- Small bright spots with a size of ~30 nm emerge within the dark region, 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.**

# Creating Monodispersed Ordered Arrays of Surface-Magic-Clusters and Anodic Alumina 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

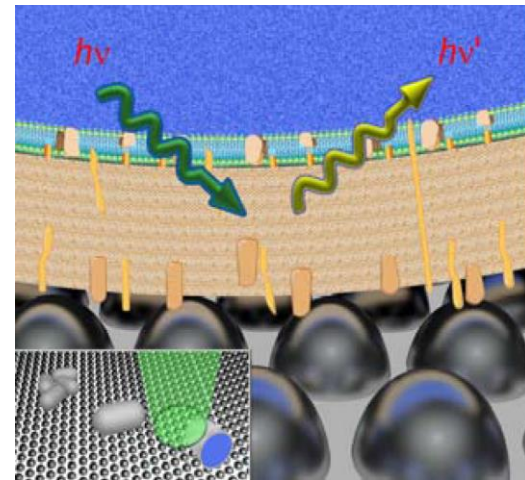
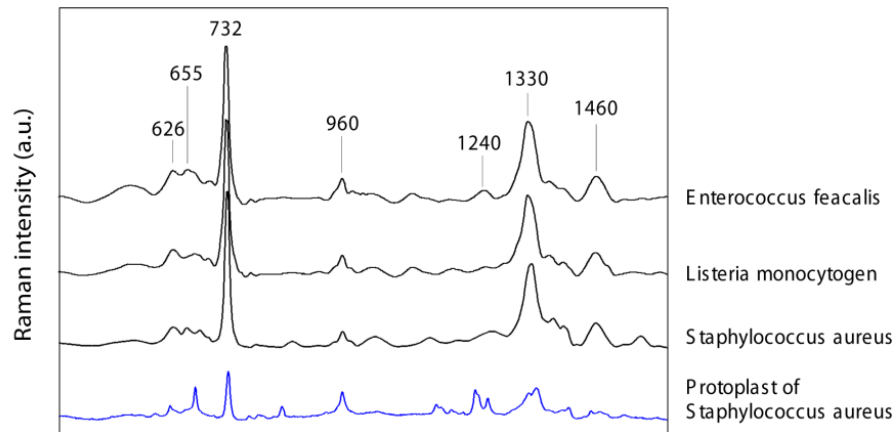
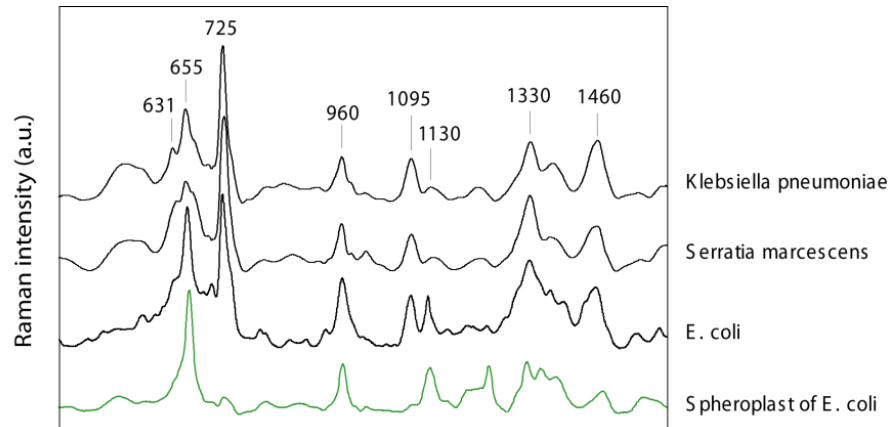


中央研究院  
原子分子科學研究所  
Institute of Atomic and Molecular Sciences  
Academia Sinica

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.

# Papers to read

- “Observation of a Magnetic Antiphase Domain Structure with Long-Range Order in a Synthetic Gd-Y Superlattice”, C. F. Majkrzak, J. W. Cable, J. Kwo, M. Hong, D. B. McWhan, Y. Yafet, J. V. Waszczak, and C. Vettier, *Phys. Rev. Lett.* **56**, 2700, (1986).
- M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, *Phys. Rev. Lett.*, **61**, 2472 (1988).
- “High k gate dielectrics  $\text{Gd}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  for Si”, J. Kwo\*, M. Hong, A.R. Kortan, K. T. Queeney, Y. J. Chabal, J. P. Mannaerts, T. Boone, J. J. Krajewski, A. M. Sergent, and J. M. Rosamilia, *Appl. Phys. Lett.*, **77**, 130, (2000).
- “Epitaxial Cubic  $\text{Gd}_2\text{O}_3$  as a Dielectric for GaAs Passivation”, M. Hong, J. Kwo, A. R. Kortan, J. P. Mannaerts, and A. M. Sergent, *Science*, **283**, 1897, (1999).
- “Observation of the Spin Hall Effect in Semiconductors”, Y. K. Kato, R. C. Myers, A. C. Gossard, D. D. Awschalom\*, *Science* **306**, 1910 (2004).
- “Tunnel field-effect transistors as energy-efficient electronic switches”, A. M. Ionescu, and H. Riel, *Nature*, **479**, 329 (2011).