# Introduction to Nanotechnology


**Kuei-Hsien Chen**: IAMS, Academia Sinica & CCMS, NTU
Ph.D. 1989 Harvard University

**Hossein hosseinkhani**: GIBE, NTUST
Ph.D. Kyoto University

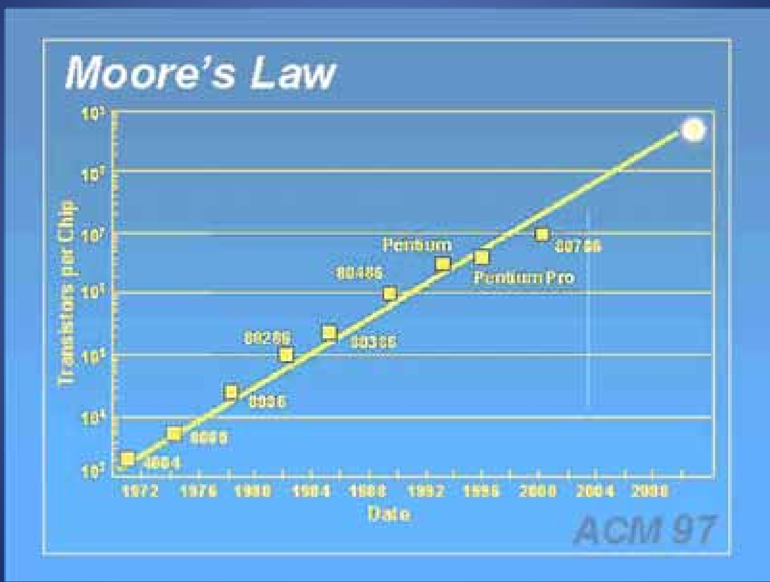
**Chunwei Chen**: MSE, NTU
Ph.D. Cambridge University

**Li-Chyong Chen**: CCMS, NTU
Ph.D. 1989 Harvard University

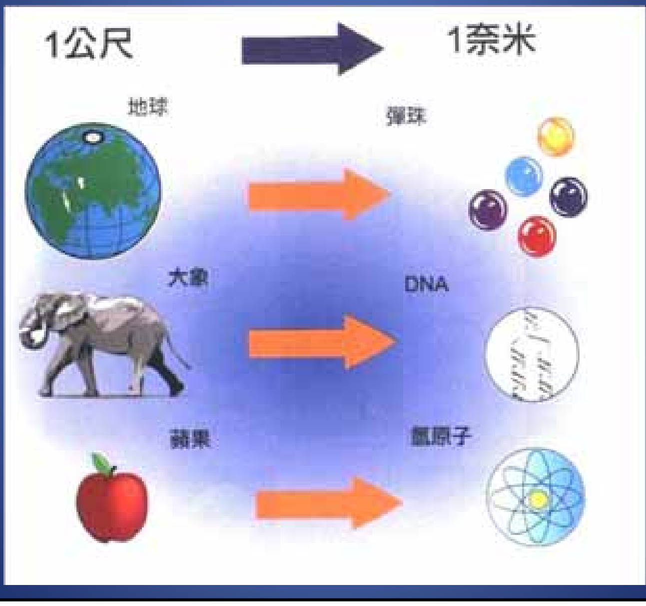




# Moore's Law



# What is Nano?




# Scale

- Meter (m)
- Millimeter (mm) = $10^{-3}$ m
- Micrometer (μm) = $10^{-6}$ m
- Nanometer (nm) = $10^{-9}$ m
- Picometer (pm) = $10^{-12}$ m
- Femtometer (fm) =$10^{-15}$ m
- Attometer (am) = $10^{-18}$ m ?

- Second (s)
- Millisecond (ms) = $10^{-3}$ s
- Microsecond (μs) = $10^{-6}$ s
- Nanosecond (ns) = $10^{-9}$ s
- Picosecond (ps) = $10^{-12}$ s
- Femtosecond (fs) =$10^{-15}$ s
- Attosecond (as) = $10^{-18}$ s

## Pressure

- 1 Pa = 1 $Nm^{-2}$ = $10^{-5}$ bar = 7.501 * $10^{-3}$ mm Hg (torr)
- 1 atm = 760 mm Hg = 1.013 bar

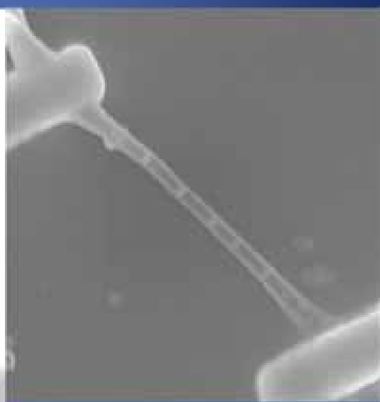
## Energy

- 1 cal = 4.184 J
- 1 eV = 1.602 * $10^{-19}$ J = 23.06 kcal/mole
- 1 kWh = 3.6 * $10^{6}$ J
- 1 BTU = 1055 J

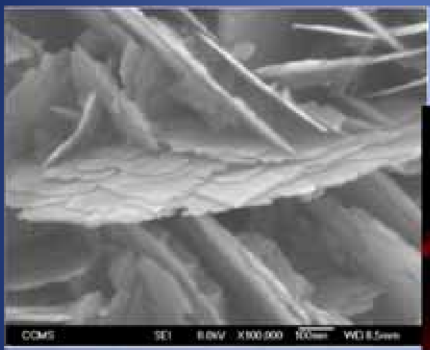
## Power

- 1 W = 1 $Js^{-1}$
- 1 hp = 746 W

# SEM

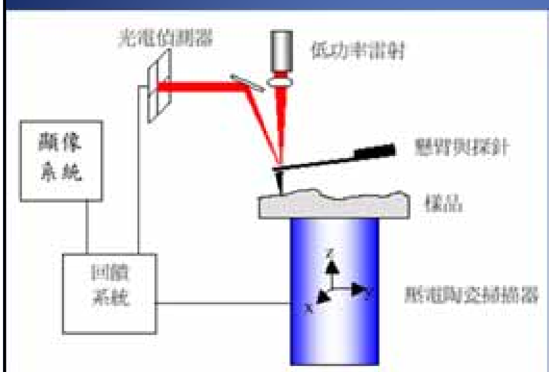


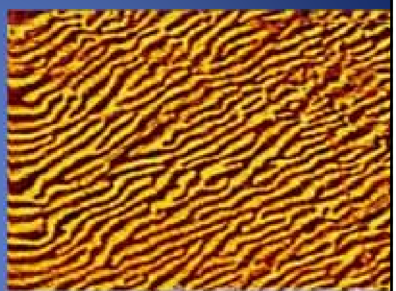
# SEM

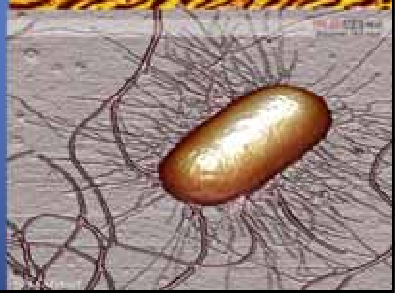



First Place
in Science as Art, MRS-2008

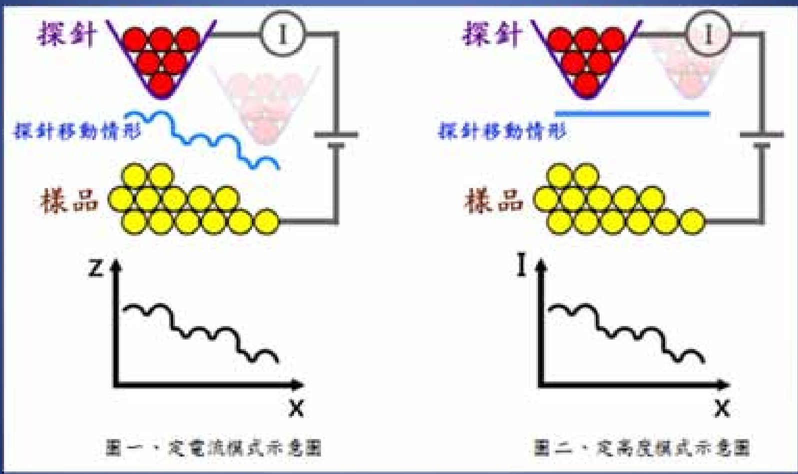
# AFM


光電偵測器
低功率雷射
懸臂與探針
樣品
顯像系統
回饋系統
壓電陶瓷掃描器

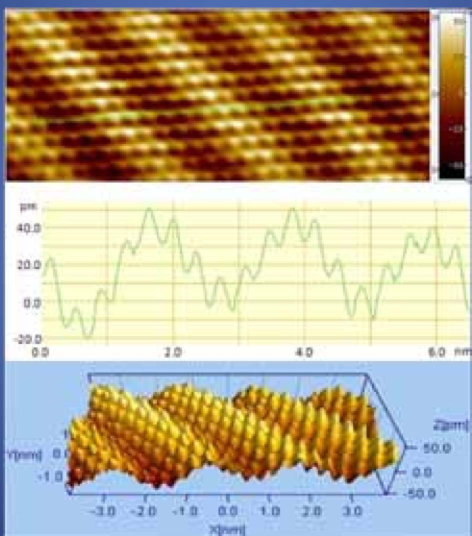




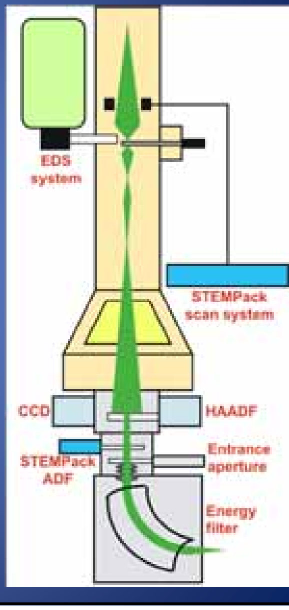
# STM


探針
I
探針移動情形
樣品
Z
X
圖一、定電流模式示意圖
探針
I
探針移動情形
樣品
I
X
圖二、定高度模式示意圖

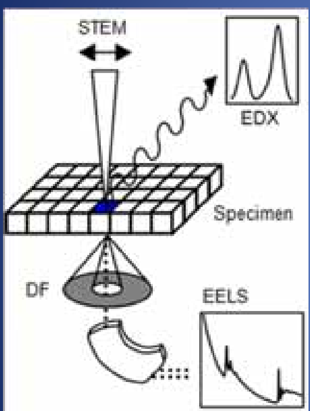
# STM

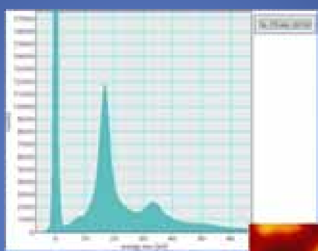

pm
40.0
20.0
0.0
-20.0
0.0
2.0
4.0
6.0 nm
Z[pm]
50.0
0.0
-50.0
Y[nm]
-1.0
-3.0 -2.0 -1.0 0.0 1.0 2.0 3.0
X[nm]

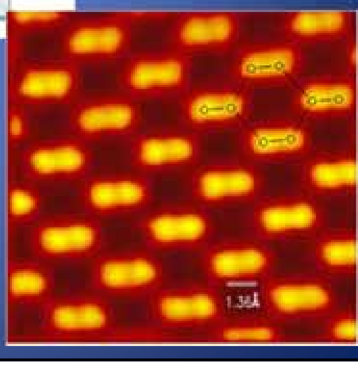
# TEM


EDS system
STEMPack scan system
CCD
HAADF
STEMPack ADF
Entrance aperture
Energy filter

# TEM (EELS)


STEM
EDX
Specimen
DF
EELS

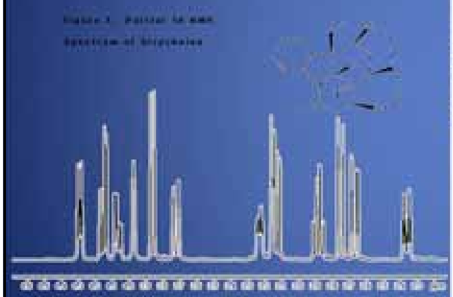


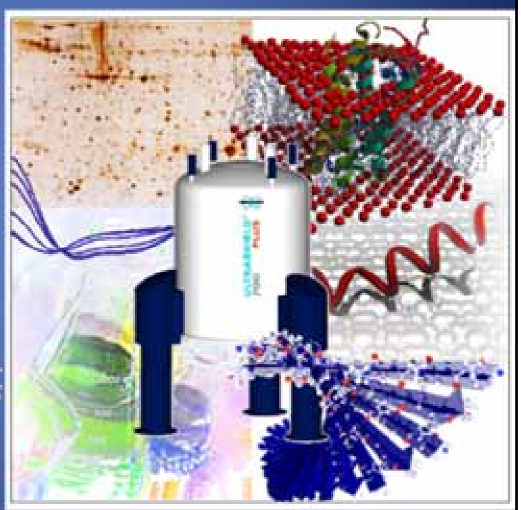

1.36Å

# Composition Analysis

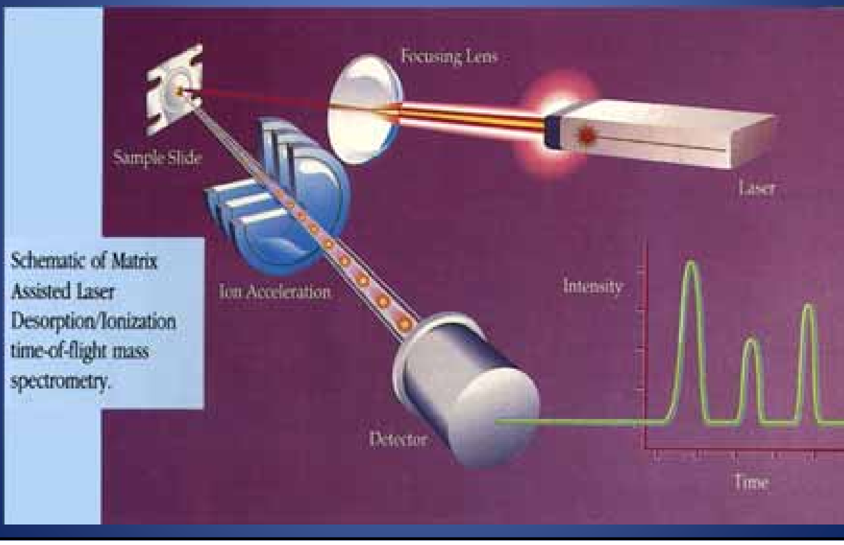
1. EL （元素分析儀）
2. EDS (X射線能量散佈分析儀)
3. AES (歐傑電子光譜)
4. NMR （核磁共振波譜分析）
5. ICP MASS (電子耦合電漿質譜)
6. MALDI （Matrix-assisted laser desorption/ionization）

# NMR, MRI





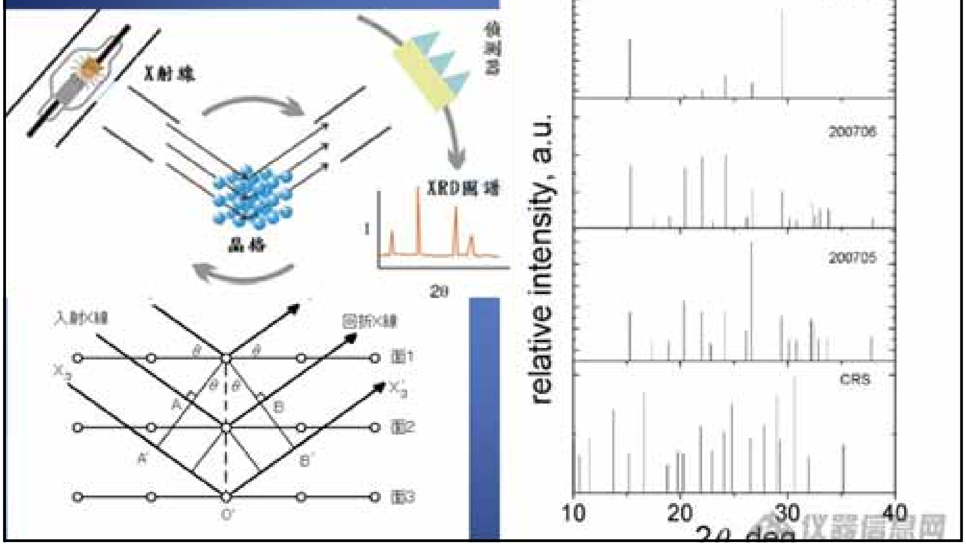
# MALDI （Matrix-assisted laser desorption/ionization)



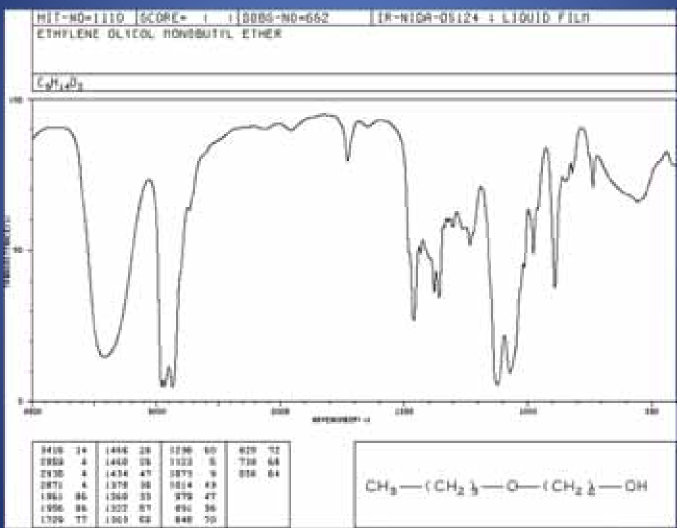

# Structure Analysis

1. XRD (X光繞射)
2. TEM (穿透式電子顯微鏡)
3. FTIR (紅外光譜）
4. Raman （拉曼光譜）

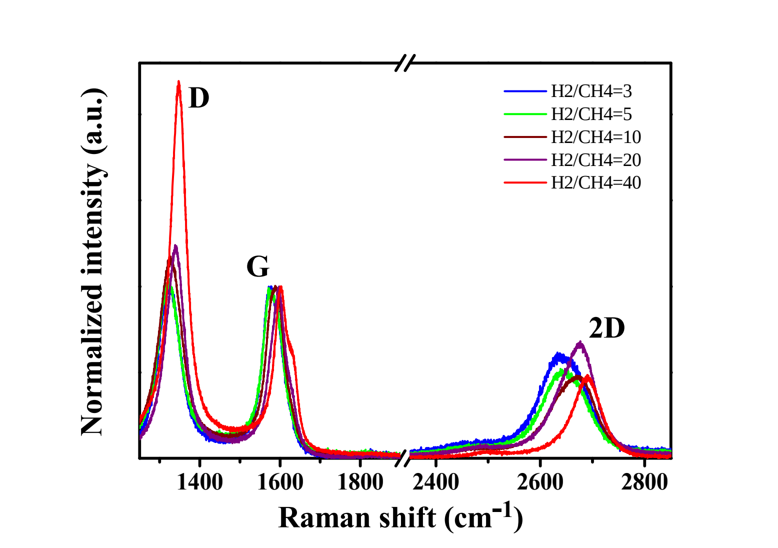
# XRD (X光繞射)




# FTIR (紅外光譜)(鍵結 )



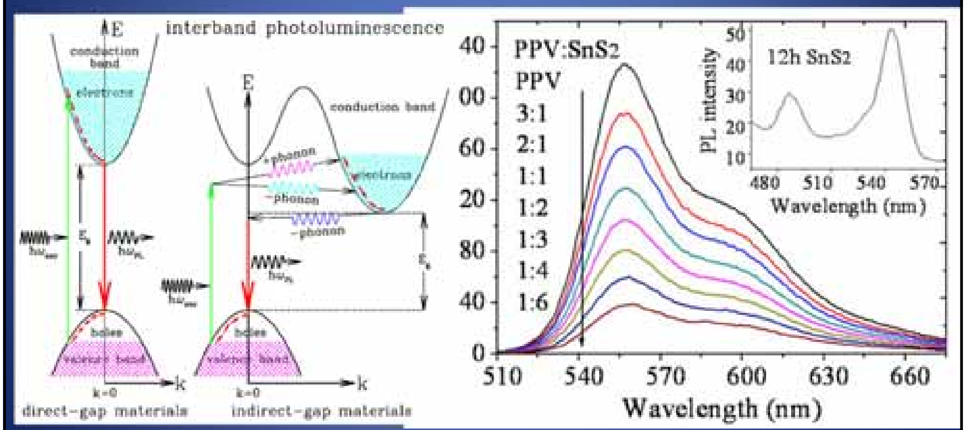
# Raman （拉曼光譜)



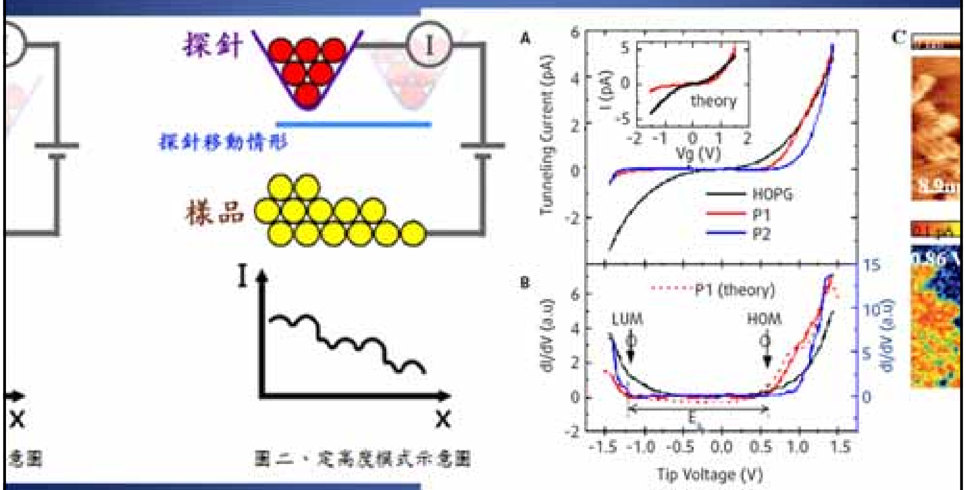

# Electronic properties

1. Optical Absorption (吸收光譜)
2. Photoluminescence (螢光光譜)
3. STS (掃描穿隧顯微術)
4. XPS ( X光電子光譜 )
5. 同步輻射測量(SRRC)

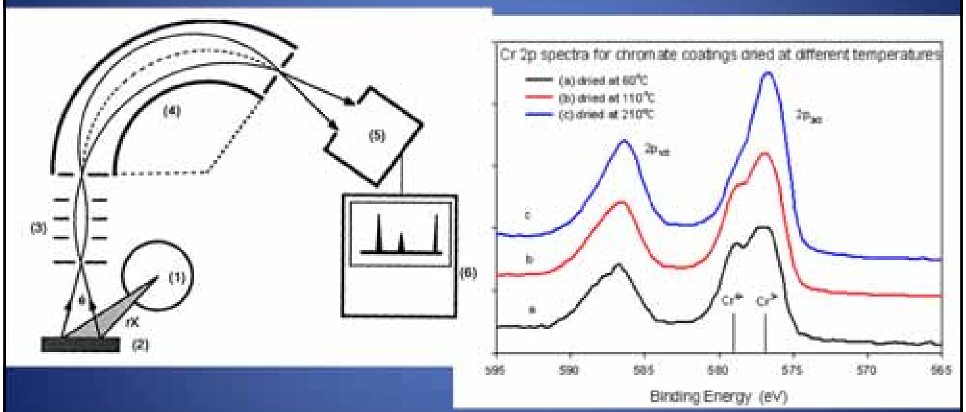
# Photoluminescence (PL & CL)



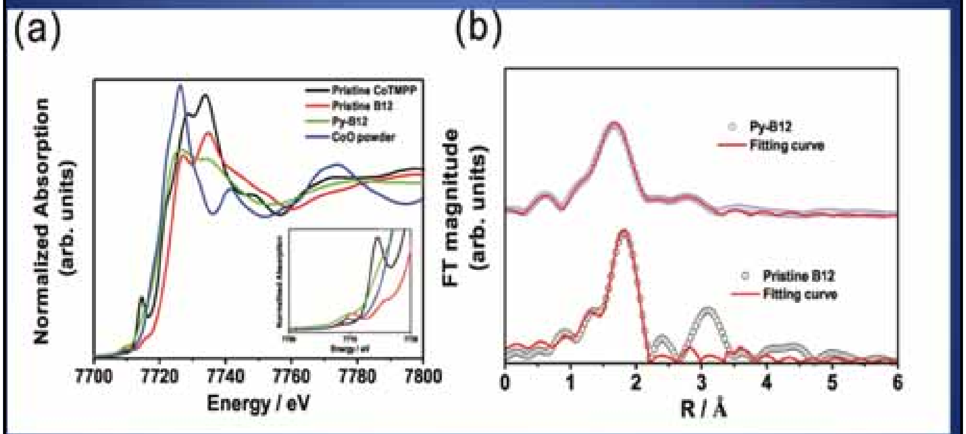

# STS (掃描穿隧顯微術)



# XPS ( X光電子光譜)




# 同步輻射測量(SRRC)

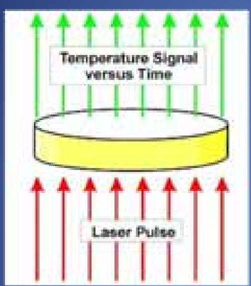


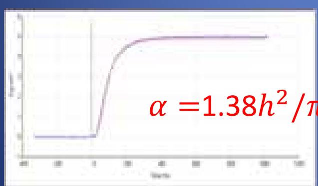

## (XANES & EXAFS)

# Other Thermal and Magnetic Measurements

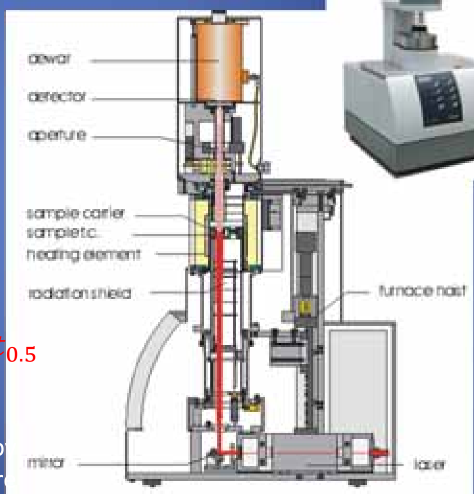
1. 熱傳導係數測量(Thermal conductivity)
2. 熱重分析(TGA)
3. 熱分析儀 (DSC)

## Thermal Diffusivity Measurement



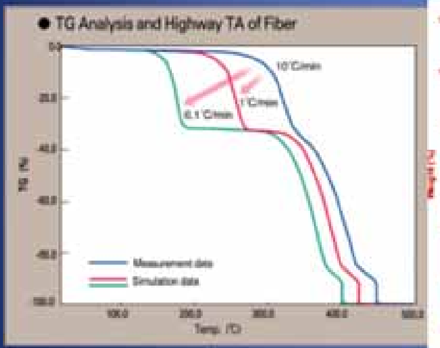
$\alpha = 1.38 h^2 / \pi^2 t_{0.5}$

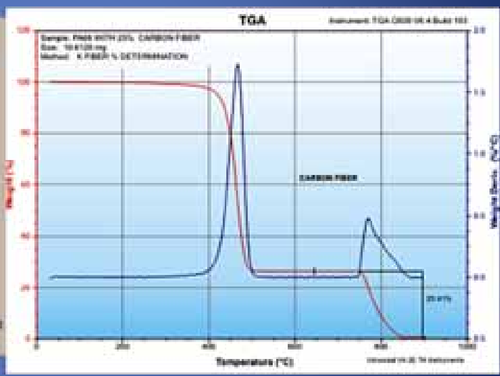


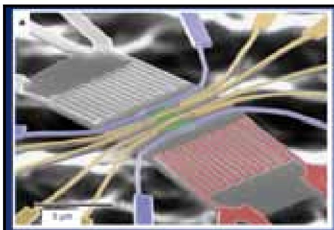

We can get the thermal diffusivity b measure the "half-time" of temperatur increase resulted from laser heating.

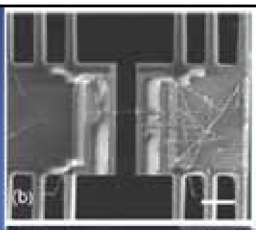
Cooperator: Dr. Y. Chen's lab

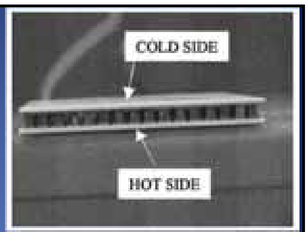
# TGA & DSC



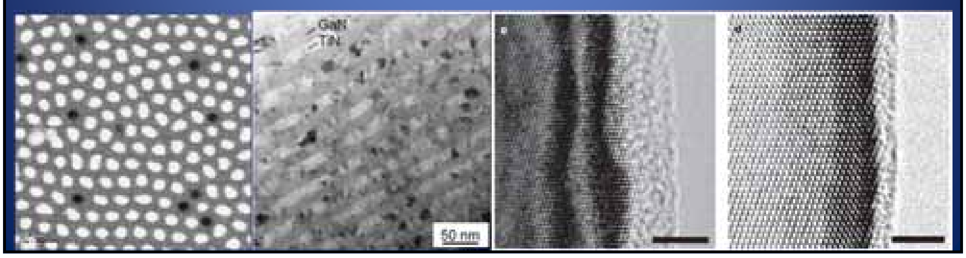



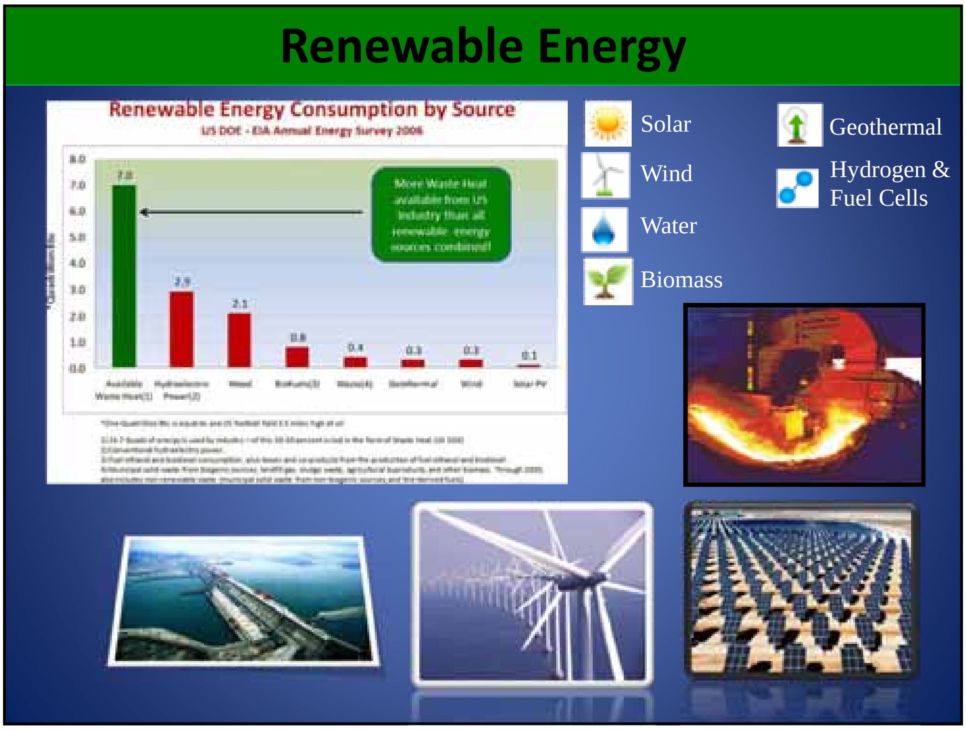



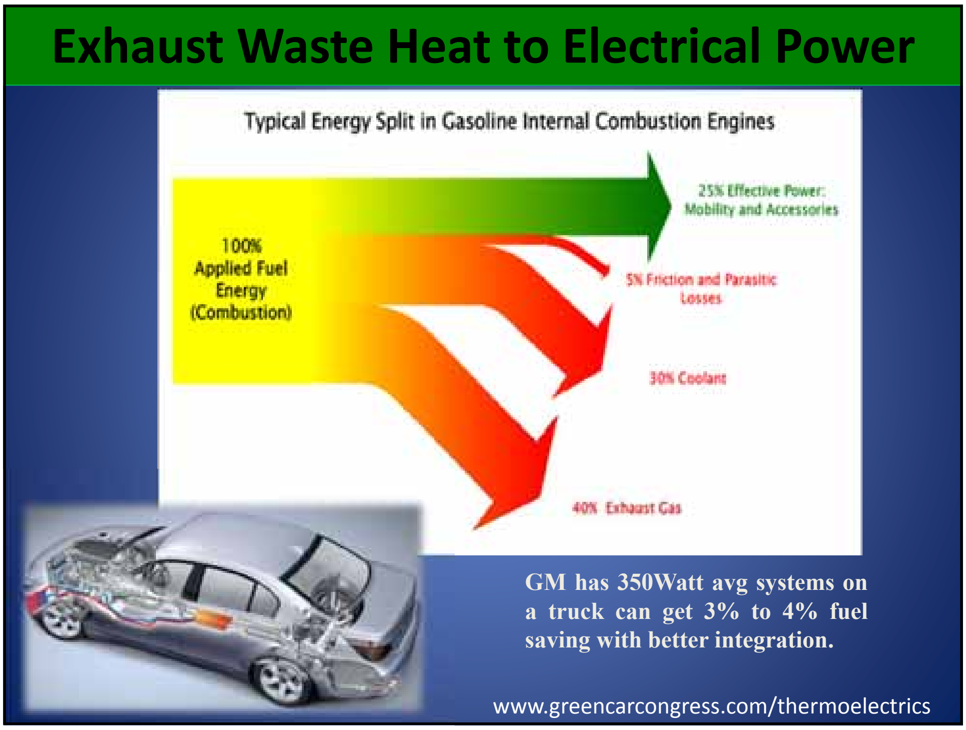




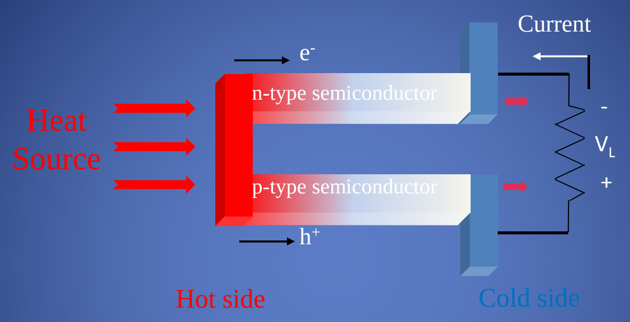

# Nanomaterials for Thermoelectric Applications

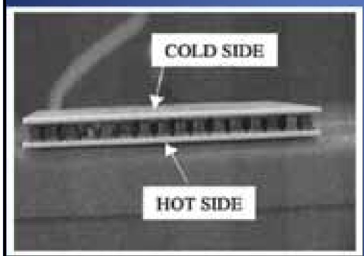



Renewable Energy
Renewable Energy Consumption by Source
US DOE - EIA Annual Energy Survey 2006
More Waste Heat available from US Industry than all renewable energy sources combined!
7.0
2.9
2.1
0.8
0.4
0.3
0.3
0.1
Solar
Wind
Water
Biomass
Geothermal
Hydrogen &
Fuel Cells


Exhaust Waste Heat to Electrical Power
Typical Energy Split in Gasoline Internal Combustion Engines
100%
Applied Fuel
Energy
(Combustion)
25% Effective Power:
Mobility and Accessories
5% Friction and Parasitic
Losses
30% Coolant
40% Exhaust Gas
GM has 350Watt avg systems on a truck can get 3% to 4% fuel saving with better integration.
www.greencarcongress.com/thermoelectrics

# TE Generator Working Principle




Electron flow

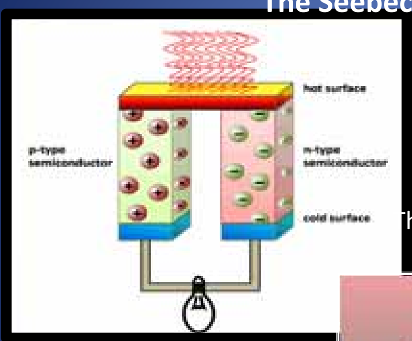
Hole flow

Total current flow

Chen et al., Intl. Mater. Rev. 48(2003)45

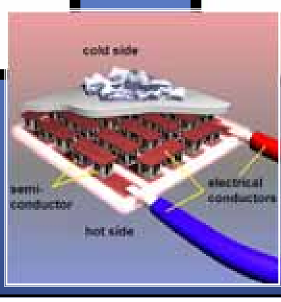
# TE Generator Working Principle

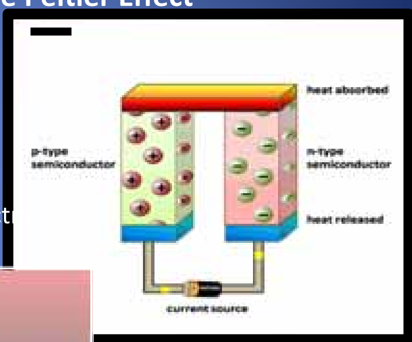
**The Seebeck and the Peltier Effect**




Thermoelectric
Power Generation

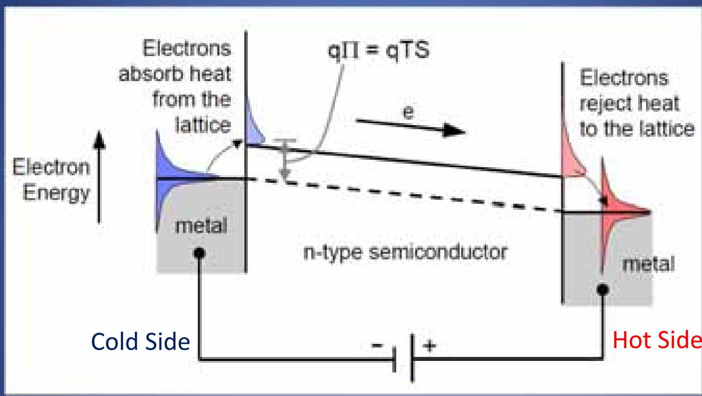
Thermoelect
Device




Thermoelectric
Cooling

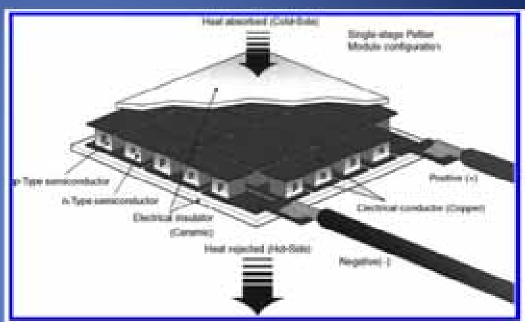
# The Peltier Effect (1834)



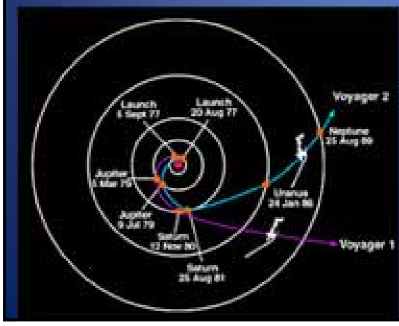

Driven by an applied potential, electrons (holes) absorb heat from the lattice at the cold side, and reject heat to the lattice at the hot side →Refrigeration.

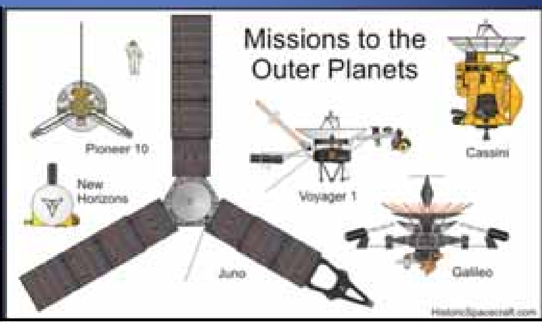
# Benefits of Thermoelectric devices

- ✓ No moving elements
- ✓ No working fluids and gases
- ✓ Low-noise operation
- ✓ Reduced size and weight
- ✓ High reliability — KRYOTHERM guarantees lifetimes of more than 200,000 hours for our TEDs
- ✓ Easy switching from cooling to heating mode

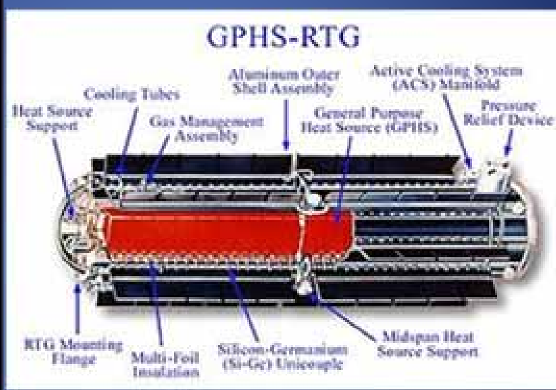



# Example of TE Devices: Voyagers

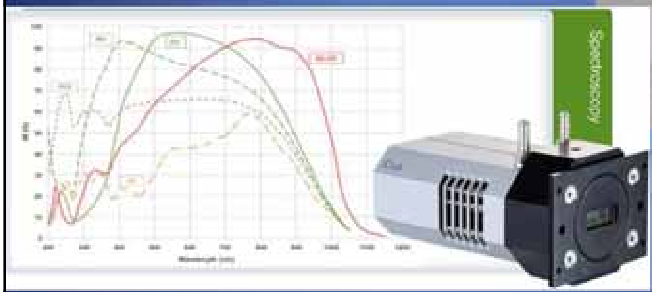




# Example of TE Devices: RTG



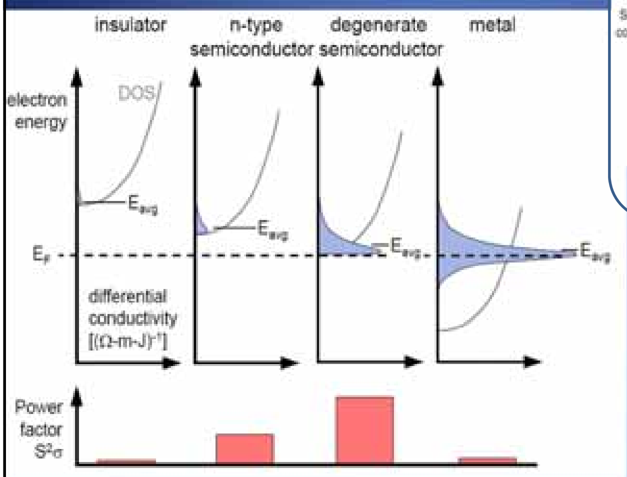

Radioisotope thermoelectric generator (RTG, RITEG)

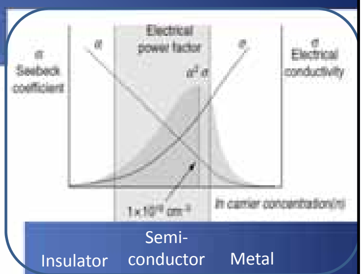
## Example of TE Devices: CCD Cooling


Koolatron P-27 Voyager - A Thermoelectric Cooler - 12 Volt Cooler ($139.95)

## Differential Electron Conductivity




"Power factor"

$$ZT = \frac{S^2\sigma}{k}T$$

# Selection of Thermoelectric Materials

$$Z = \frac{S^2\sigma}{\kappa}$$

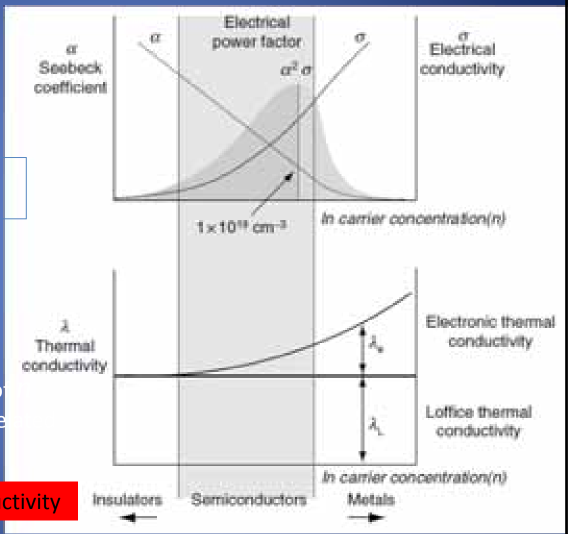
Electrical conductivity $\sigma$
Thermal conductivity $\kappa$
Seebeck coefficient $S$

Free carrier density $n$

The thermal conductivity
$$\kappa = \kappa_{Lattice} + \kappa_{Electron}$$

Lattice part is roughly independent o
while the electronic part is directly re
to the electrical conductivity

High power factor, Low thermal conductivity

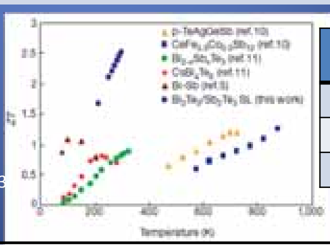



Schematic dependence of electrical conductivity, Seebeck coefficient, power factor, and thermal conductivity on concentration of free carriers.

# ZT in This Decade

| Year | Journal | Materials | ZT | T(K) | Institute |
|---|---|---|---|---|---|
| 2011 | Nature | $PbTe_{1-x}Se_x$ (Buck) | 1.8 | 850K | MS, California Institute of Technology |
| 2009 | Nature | $In_4Se_{3-d}$ (Buck) | 1.5 | 700K | Samsung |
| 2008 | Nature | Si (52nm rough NWs) | 0.6 | 300K | Berkeley |
| 2008 | Nature | Si (20nm NWs) | 1.0 | 200K | CE, California Institute of Technology |
| 2008 | Science | BiSeTe (buck) | 1.5 | 400K | Physics, Boston College |
| 2004 | Science | $AgPb_mSbTe_{2+m}$ (buck) | 2.1 | 800K | Michigan State University |
| 2003 | Nature | $Bi_2Te_3/Pb_2Te_3$ SL | 2.6 | 300K | Research Triangle Institute |
| 2002 | Science | PbSeTe/PbTe SL | 1.6 | 300K | Massachusetts Institute of Technology |
| Before | | | ~1 | | |


Y. Z Pei et al, Nature 473, 66 (2011)
J. S. Rhyee et al, Nature 459, 965 (2009)
A. I. Hochbaum et al, Nature 451, 163 (2008)
A. I. Boukai et al, Nature 451, 168 (2008)
B. Poudel et al,Science 320, 634 (2008)
K. F. Hsu et al, Science 303, 818 (2004)
R. Venkatasubramanian et al, Nature 413 597 (2003
T. C. Harman et al, Science 297, 2229 (2002)


| Nature Materials | Publication |
|---|---|
| 2011 | 4 |
| 2010 | 4 |
| 2003-2009 | 13 |

# ZT & Efficiency

**Efficiency η**

$$\eta = \frac{T_H - T_C}{T_H} \frac{\sqrt{1+ZT} - 1}{\sqrt{1+ZT} + T_C/T_H}$$

**Efficiency examples**

| $ZT$ | $T_H$/K | $T_C$/K | η |
|---|---|---|---|
| 0.5 | 673 | 373 | 5.6% |
| 1 | 673 | 373 | 9.4% |
| 2 | 673 | 373 | 14.3% |
| 3 | 673 | 373 | 17.4% |
| 3 | 773 | 373 | 20.8% |
| 3 | 873 | 373 | 23.6% |

**Figure-of-merit *ZT***

$$ZT = T\frac{S^2\sigma}{\kappa}$$

**Thermal conductivity k**

$$\kappa = \kappa_L + \kappa_{el}$$

**Thermal conductivity k**

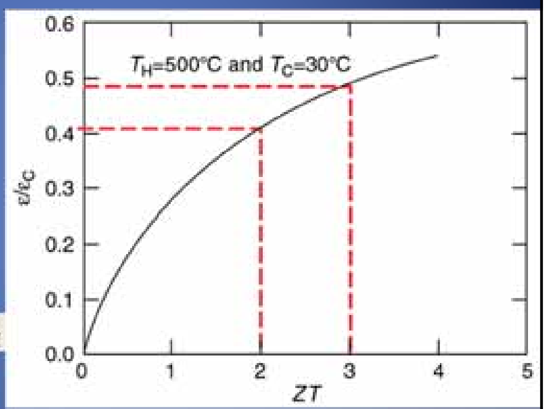
$$\kappa_{el} = L_0 \sigma T$$

- To match a refrigerator, an effective ZT= 4 is needed
- To efficiently recover waste heat from car, ZT = 2 is needed

# Efficiency and *ZT*

$$\eta_{TE} = \eta_C \left( \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+\frac{T_C}{T_H}} \right)$$

Carnot efficiency, $\eta_C = (T_H - T_C)/T_H$



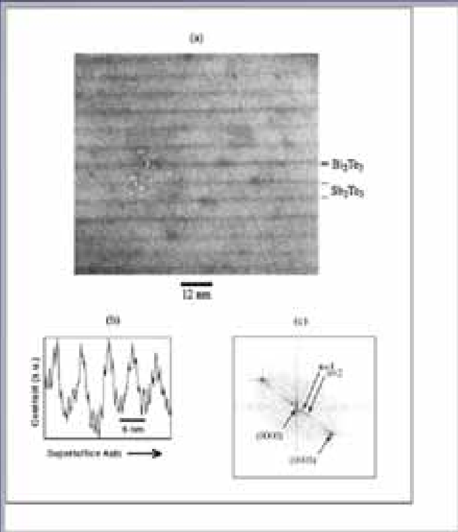
## New Approaches

- New Bulk Materials
  - Skutterudites (Rensselaer, Oak Ridge, JPL, 1992)
    - Cage-structures with rattling atoms to scatter phonons
  - Novel Chalcogenides and Clathrates (Michigan State and Arizona, 1994)
    - Complex Variations of $Bi_2Te_3$ to reduce phonon mean-free paths
- Nano-scale Materials
  - Low-Dimensional Structures (MIT, MIT Lincoln Labs, 1992)
    - Quantum-confinement to Enhance Density of states which increase Seebeck coefficient
  - Nano-scale Superlattices (RTI, 1992)
    - **Phonon-blocking** from acoustic mismatch between superlattice components but **electron-transmitting** due to negligible electron-energy offsets
  - Heterostructure Thermionics (UCSB, Oak Ridge, 1996)
    - Thermionic-like effects using energy barriers that can be controlled in hetero-structures

## New Progresses

- Cs $Bi_4Te_6$ (Michigan State University)
  - Bulk Materials with a ZT~ 0.8 at 225K but less than 0.8 at 300K (*Science* **287**, 1024-1027, 2000)
- Filled Skuterrudites (JPL)
  - Bulk materials with a ZT ~1.35 at 900K (Proc. Of 15th International Conf. On Thermoelectrics, 1996)
- PbTe/PbTeSe Quantum-dots (Harman, MIT Lincoln Labs.)
  - ZT~ 1.6 at 300K based on cooling data (*Science* 297, Sep. 2002)
- $Bi_2Te_3/Sb_2Te_3$ Superlattices (RTI)
  - ZT~2.4 at 300K in devices with all properties measured at the same place, same time, with current flowing and verified by two independent techniques (*Nature*, 597-602, Oct. 2001)

# Nanostructured Superlattice

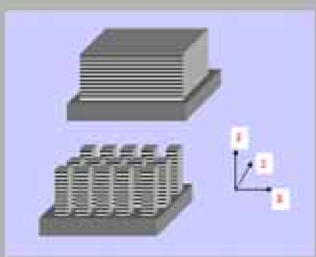


Applied Physics Letters, 75, 1104 (1999)

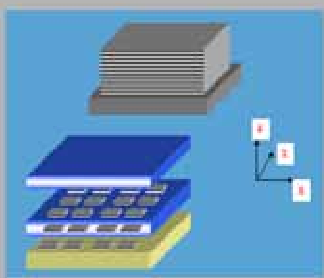
- 10Å/50Å $Bi_2Te_3/Sb_2Te_3$ Structure
- Optimized for disrupting heat transport while enhancing electron transport perpendicular to the superlattice interfaces

# New Ideas

- Combine Phonon-Blocking, Electron-Transmitting Structures Along Heat Flow with Orthogonal Quantum-Confinement for ZT in the range of 4 to 5?

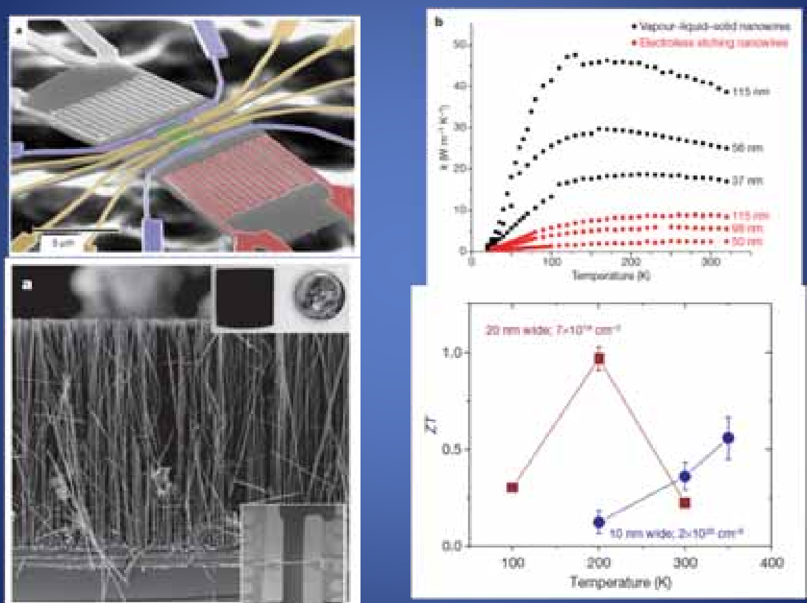


Layered SL Patterned to form 1-di Quantum-Wires – **Orthogonal Quantum Confinement**



Layered SL Patterned to form Quantum-Boxes – **Orthogonal Quantum Confinement**

# Si Nanowires as an Efficient TE Material

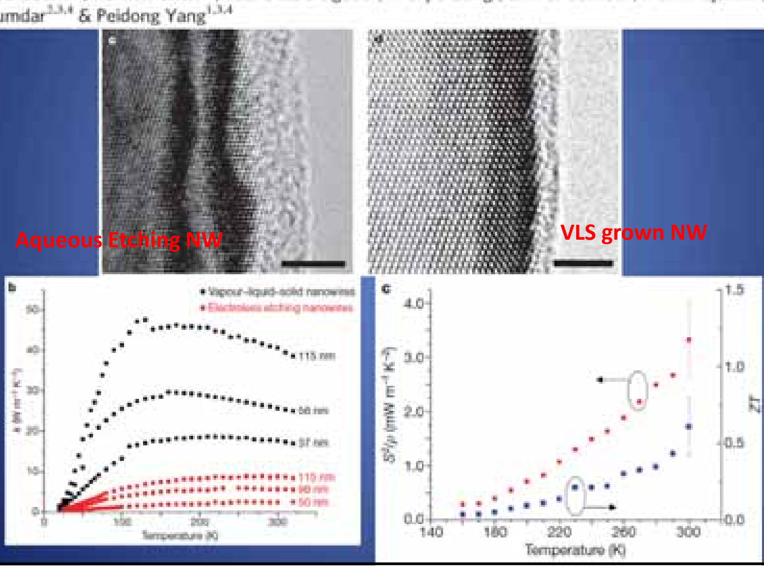


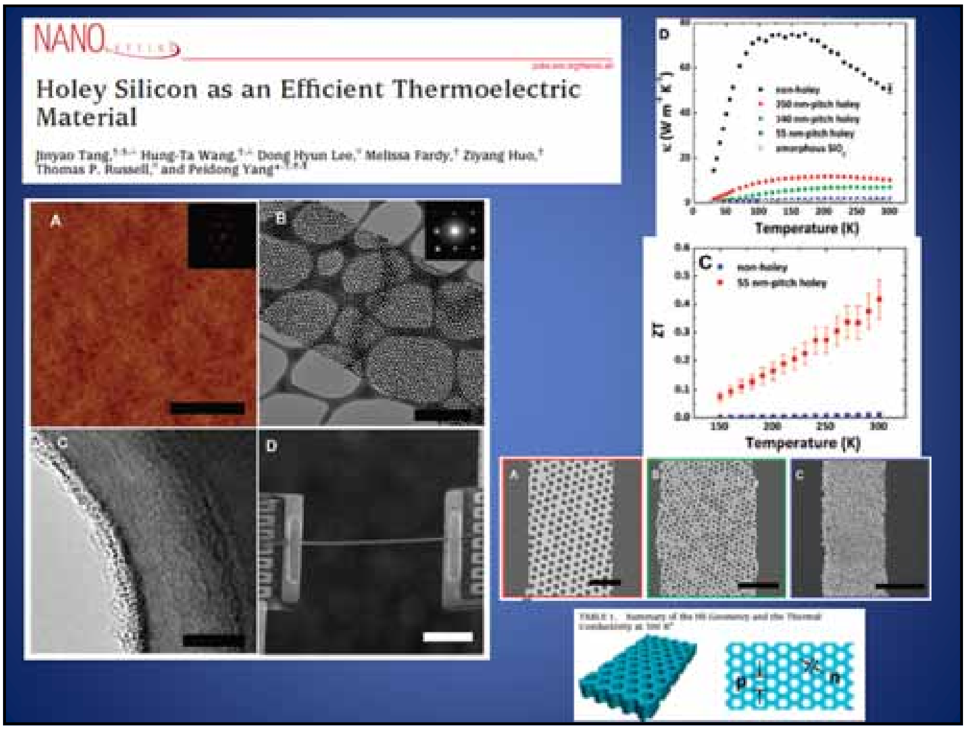

Akram I. Boukai *et al*, Nature **451** 168(2007)

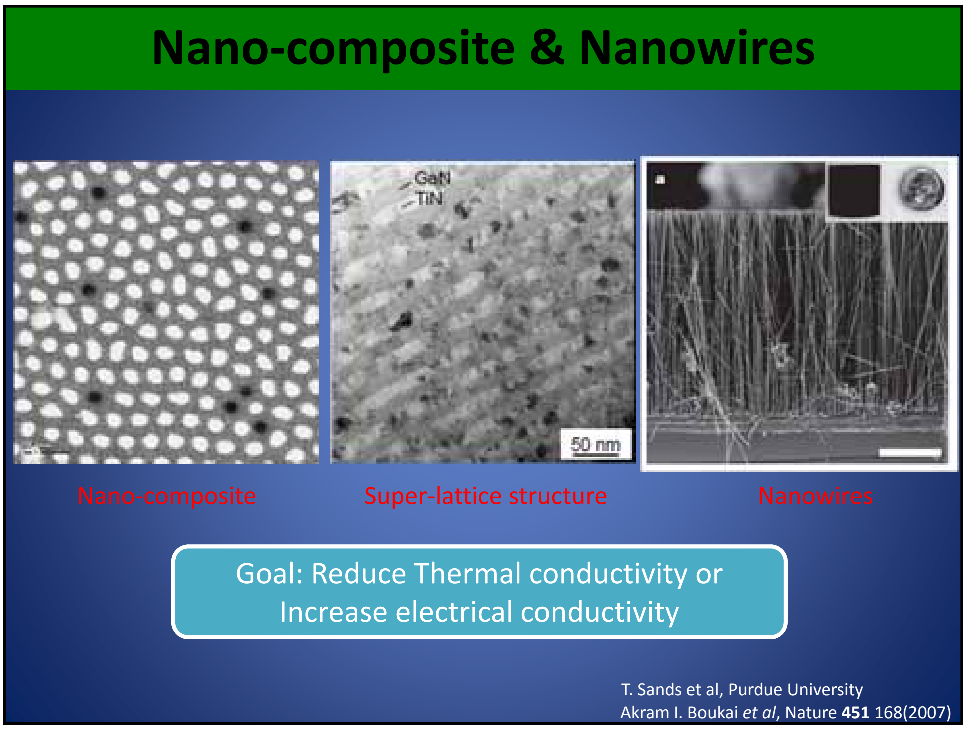
Vol 451|10 January 2008|doi:10.1038/nature06381 nature

## Enhanced thermoelectric performance of rough silicon nanowires

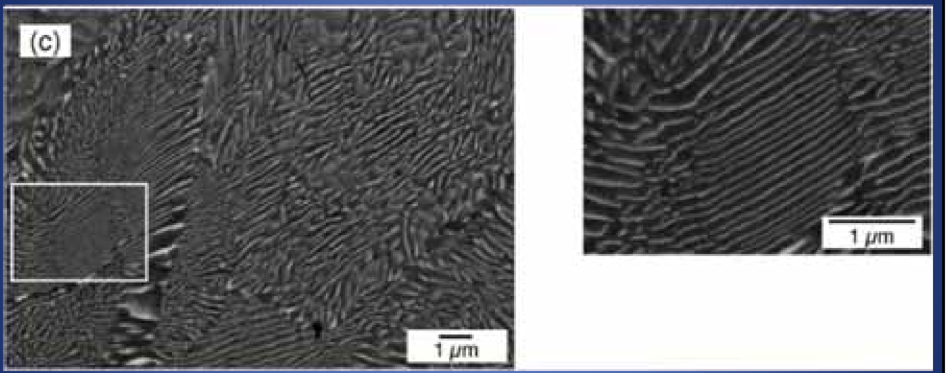
Allon I. Hochbaum[1]*, Renkun Chen[2]*, Raul Diaz Delgado[1], Wenjie Liang[1], Erik C. Garnett[1], Mark Najarian[3], Arun Majumdar[2,3,4] & Peidong Yang[1,3,4]




NANO LETTERS
Holey Silicon as an Efficient Thermoelectric Material
Jinyao Tang, Hung-Ta Wang, Dong Hyun Lee, Melissa Fardy, Ziyang Huo, Thomas P. Russell, and Peidong Yang
Temperature (K)
non-holey
55 nm-pitch holey
ZT
Temperature (K)


Nano-composite & Nanowires
GaN
TiN
50 nm
Nano-composite
Super-lattice structure
Nanowires
Goal: Reduce Thermal conductivity or Increase electrical conductivity
T. Sands et al, Purdue University
Akram I. Boukai et al, Nature 451 168(2007)

## Lamellae of Thermoelectric PbTe and Sb2Te3

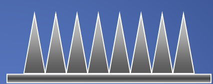



Jeffrey Snyder Chem. Mater., Vol. 19, No. 4, 2007 765

## 1-D Nano Materials in AML

*JACS 123, 2791 (2001)*
*APL 81, 22 (2002)*
*JACS 127, 2820 (2005)*
*APL 90, 213104 (2007)*
*Adv. Func. Mater. (2008)*
*Small 4, 925 (2008)*
*Electrochem. Comm. 11, 850 (2009)*
*Anal. Chem. 81, 36 (2009)*
***Angew. Chem. Int. Ed. 49, 5966 (2010)***

**Wire/Rod**

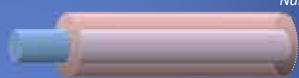


**Nanotip**

*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, 1938 (2009)*

*APL 81, 4189 (2002)*
*Adv. Func. Mater. 12, 687 (2002)*
*APL 86, 203119 (2005)*
*JACS 128, 8368 (2006)*
*PRB 75, 195429 (2007)*
*J. Power Sources 171, 55 (2007)*
*JACS 130, 3543 (2008)*
*J. Power Sources 190, 279 (2009)*

**Tube**



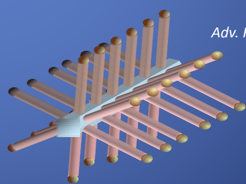
**Core-shell**

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

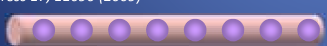
*Chapter 9, pp. 259-309, Nanowires and nanobelts, Kluwer (2004)*
*Adv. Func. Mater. 16, 537 (2006)*
*APL 90, 123109 (2007)*
*Adv. Mater. 19, 4524 (2007)*
*Opt. Express 17, 11690 (2009)*

**Belt**

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



**Brush**

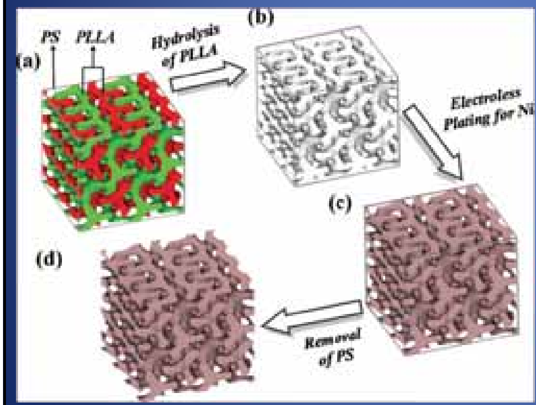


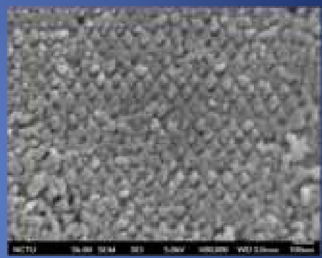
*Adv. Mater. 14, 1847 (2002)*
***Nature Mater. 5, 102 (2006)***

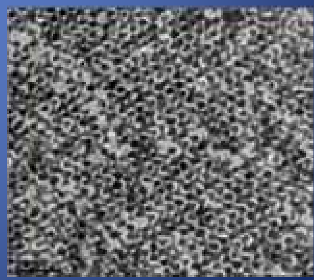
**Peapod**

***Other related:***
*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, 259 (2009)*
***Angew. Chem. 48,7586 (2009)***
***J. Mater. Chem. (2010)***

# Nanocomposites





# TE Measurement

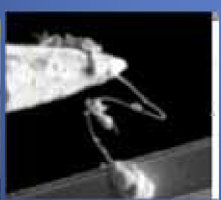

Multiwall carbon nanotube


Silver nanowire

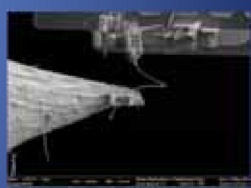

ZnO nanowire


$Ga_2O_3$ nanowire


Undoped Si nanowire

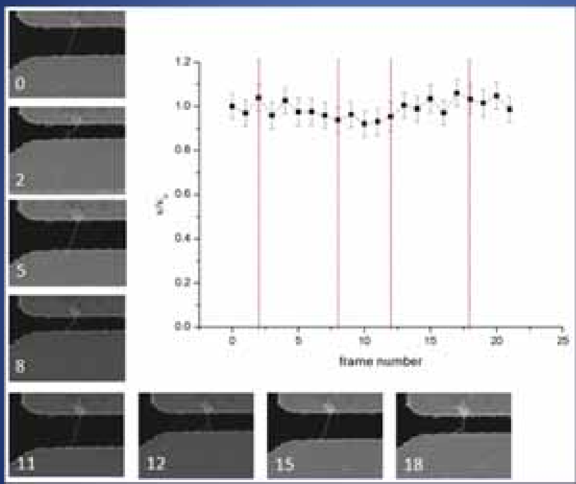

P-type Si nanowire

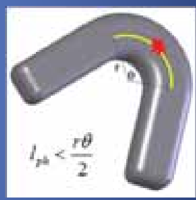

N-type Si nanowire


SiGe nanowire

Thermal conductivities remain intact under extreme strain

## *SWCNT goes beyond the theoretical limit of 1D ballistic phonon transport*




No changes of thermal conductivity is observed even when the bending radius of curvature is less than the phonon mean free path.

## Perspective

- Nanotechnology provides great opportunity for Thermoelectric materials.
- Demonstration of high ZT materials is yet to come.