General Materials Science

Byungwoo Park
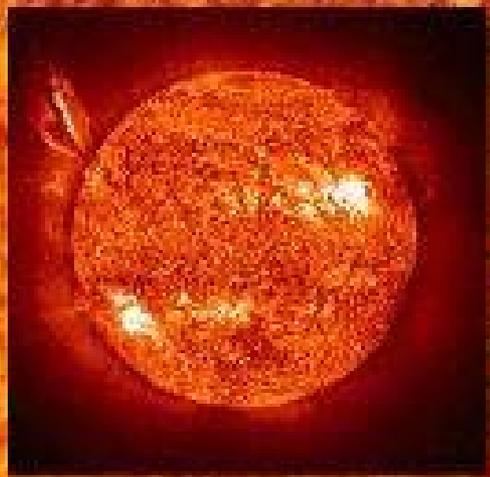
Department of Materials Science and Engineering
Seoul National University

http://bp.snu.ac.kr

Earth shown
for size comparison

Google Earth

Nanoscale Control: Nanomaterials for Energy

White LED

PDP

Cellular Phone

MP3

Phosphor

Fuel Cell

Nanomaterials for Energy

Solar Cell

Li⁺ Battery

Solar Panel

Portable Devices

Laptop

PMP

Global Warming: How to Win?

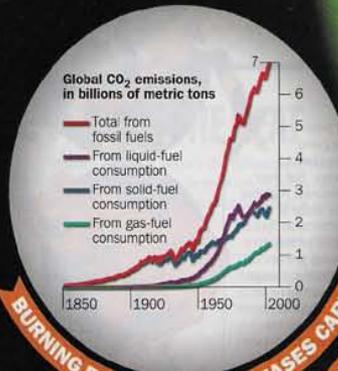*TIME* (2008)

Hard Times: The End of Prosperity?

TIME (2008)

VICIOUS CYCLES

The debate over whether Earth is warming up is over. Now we're learning that climate disruptions feed off one another in accelerating spirals of destruction. Scientists fear we may be approaching the point of no return
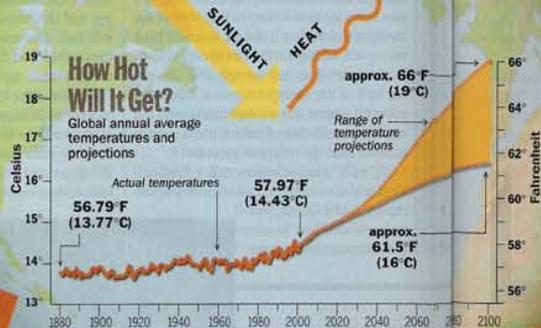
TIME graphic by Joe Lertola; reported by Missy Adams

THE GREENHOUSE EFFECT

Without the **greenhouse effect**, life on Earth would not be possible. Energy from the sun is absorbed by the planet and radiated back out as heat. Atmospheric gases like **carbon dioxide** trap that heat and keep it from leaking into space. That's what keeps us warm at night.

But as humans pour ever increasing amounts of greenhouse gases into the atmosphere, more of the sun's **heat gets trapped**, and the planet gets a fever

SUNLIGHT   HEAT

Greenhouse effect

How Hot Will It Get?
Global annual average temperatures and projections

Range of temperature projections

approx. 66°F (19°C)

Actual temperatures

57.97°F (14.43°C)

56.79°F (13.77°C)

approx. 61.5°F (16°C)

Celsius / Fahrenheit

1880 1900 1920 1940 1960 1980 2000 2020 2040 2060 280 2100

WASHING ASHORE The ice at the North Pole is floating, so as it melts, the sea level won't change much. But the massive ice sheets over Antarctica and Greenland are another story. If both melted completely, sea levels could rise nearly 220 ft. (72 m). That's a worst-case scenario. But the melting is accelerating, and sea levels are projected to rise gradually, threatening low-lying communities

MELTING ICE RAISES SEA LEVELS

Global average sea-level rise, in meters
Projections of several models

2000   2050   2100

INUNDATING LOW COASTAL AREAS

cold water, so it floats on the surface. As it reaches Europe and releases its heat, the current grows denser and sinks, flowing back to the south and crossing under the northbound Gulf Stream until it reaches the tropics and starts to warm again. The cycle works splendidly, provided the water remains salty enough. But if it becomes diluted by freshwater, the salt concentration drops, and the water gets lighter, idling on top and stalling the current. Last December, researchers associated with Britain's National Oceanography Center reported that one component of the system that drives the Gulf Stream has slowed about 30% since 1957. It's the increased release of Arctic and Greenland meltwater that appears to be causing the problem, introducing a gush of freshwater that's overwhelming the natural cycle. In a global-warming world, it's unlikely that any amount of cooling that resulted from this would be sufficient to support glaciers, but it could make things awfully uncomfortable.

"The big worry is that the whole climate of Europe will change," says Adrian Luckman, senior lecturer in geography at the University of Wales, Swansea. "We in the U.K. are on the same latitude as Alaska. The reason we can live here is the Gulf Stream."

DROUGHT

AS FAST AS GLOBAL WARMING IS TRANSFORMing the oceans and the ice caps, it's having an even more immediate effect on land. People, animals and plants living in dry, mountainous regions like the western U.S. make it through summer thanks to snowpack that collects on peaks all winter and slowly melts off in warm months. Lately the early arrival of spring and the unusually blistering summers have caused the snowpack to melt too early, so that by the time it's needed, it's largely gone. Climatologist Philip Mote of the University of Washington has compared decades of snowpack levels in Washington, Oregon and California and found that they are a fraction of what they were in the 1940s, and some snowpacks have vanished entirely.

Global warming is tipping other regions of the world into drought in different ways. Higher temperatures bake moisture out of soil faster, causing dry regions that live at the margins to cross the line into full-blown crisis. Meanwhile, El Niño events—the warm pooling of Pacific waters that periodically drives worldwide climate patterns and has been occurring more frequently in global-warming years—further inhibit precipitation

BURNING FOSSIL FUELS RELEASES CARBON

Global CO2 emissions, in billions of metric tons
- Total from fossil fuels
- From liquid-fuel consumption
- From solid-fuel consumption
- From gas-fuel consumption

1850   1900   1950   2000

FUELING THE FIRE The amount of carbon dioxide in the atmosphere is climbing fast. Most of it comes from burning fuels for energy—gasoline in cars or coal for electricity, for example. The U.S., with less than 5% of the world's population, produces one-quarter of all greenhouse gases

SPREADING THE PAIN Deforestation, ▶ through clear-cutting or burning, sows havoc far beyond the affected area. The fires release still more carbon into the atmosphere, fewer plants survive to convert CO2 into oxygen, and scorched soil absorbs more heat and retains less water, increasing droughts

BURNING FORESTS

Plants take in CO2

Fires release carbon

Less carbon absorbed
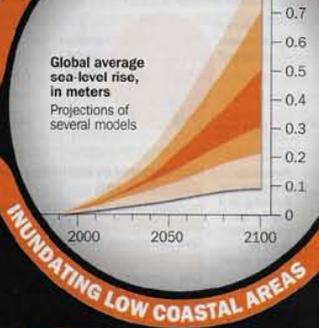
Soil dries out

REDUCES OXYGEN AND INCREASES DROUGHT

MELT POLAR ICE AND PERMAFROST

Summer sea-ice extent
Current
2030 (est.)

THAWING OUT The North Pole may be seasonally ice free by 2050. Melting permafrost will release vast amounts of trapped carbon into the air

Near-surface permafrost
- 1980-99
- 2080-99 (est.)

RISING TEMPERATURES

WHICH MEANS LESS ICE

SPEEDING UP Ice reflects nearly all the sun's energy that hits it. As the planet's ice melts, more of that energy is absorbed by Earth—which further raises the temperature. That, in turn, makes the remaining ice melt quicker

LESS ICE MEANS MORE HEAT

20% reflected by vegetation and dark soil

10% reflected by ocean water

90% reflected by ice

Sources: Intergovernmental Panel on Climate Change, Third Assessment Report; NOAA; NASA; National Snow and Ice Data Center; Carbon Dioxide Information Analysis Center; National Center for Atmospheric Research; U.S. Global Change Research Program; Goddard Institute for Space Studies

35

GLOBAL WARMING

More and more
land is being
devastated by drought...

MOONSCAPE Cattle struggle across parched land in Ethiopia. The amount of the earth's surface afflicted by drought has more than doubled since the 1970s

BOBBY HAAS—NATIONAL GEOGRAPHIC IMAGE COLLECTION

GLOBAL WARMING

Polar ice caps are melting faster than ever...

AT SEA In the Canadian high Arctic, a polar bear negotiates what was once solid ice. Bears are drowning as warmer waters widen the distance from floe to floe

ARCTICNET—NCE

PHYSICS TODAY

APRIL 2002

EARTH AT NIGHT: composite satellite image

SPECIAL ISSUE: THE ENERGY CHALLENGE

Ascension Island (1970~1990)

百年の愚行 *(ONE HUNDRED YEARS OF IDIOCY), 2002*
Tetsuya Ozaki
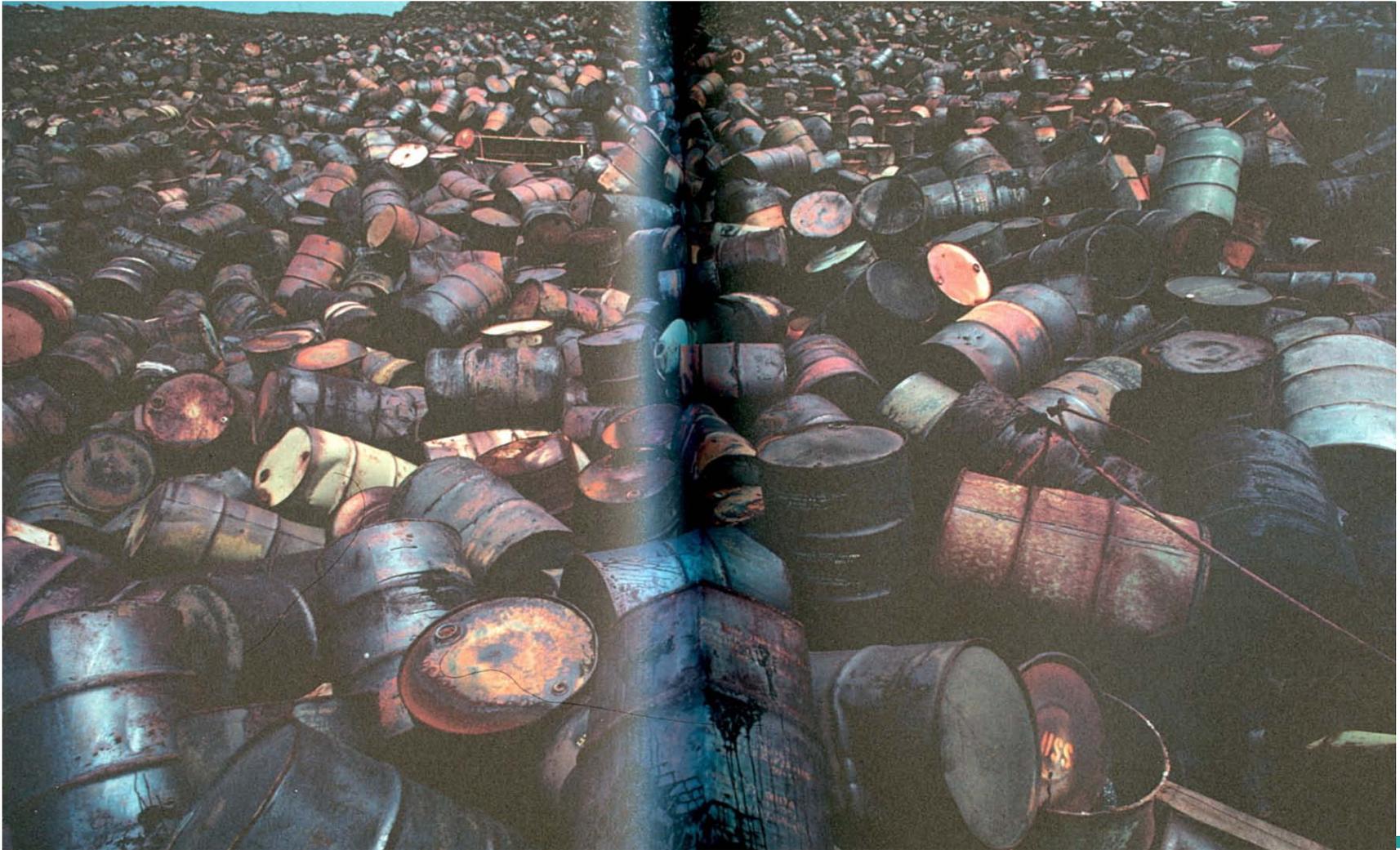
百年の愚行 (ONE HUNDRED YEARS OF IDIOCY), 2002

Argentina / Buenos Aires (1993)

百年の愚行 (ONE HUNDRED YEARS OF IDIOCY), 2002

Philippine / Lubango (1996)

百年の愚行 (ONE HUNDRED YEARS OF IDIOCY), 2002

Zaire / Goma (1994)

cholera

百年の愚行 (ONE HUNDRED YEARS OF IDIOCY), 2002
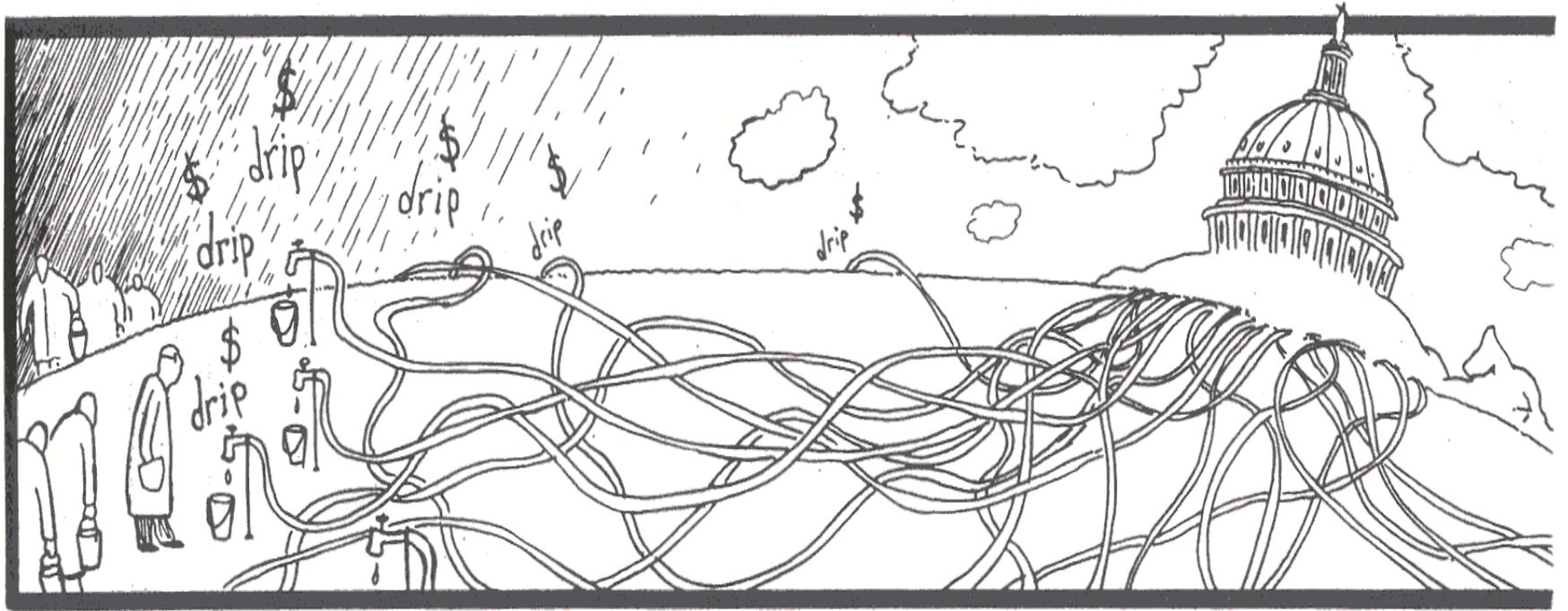
Science vs. Art
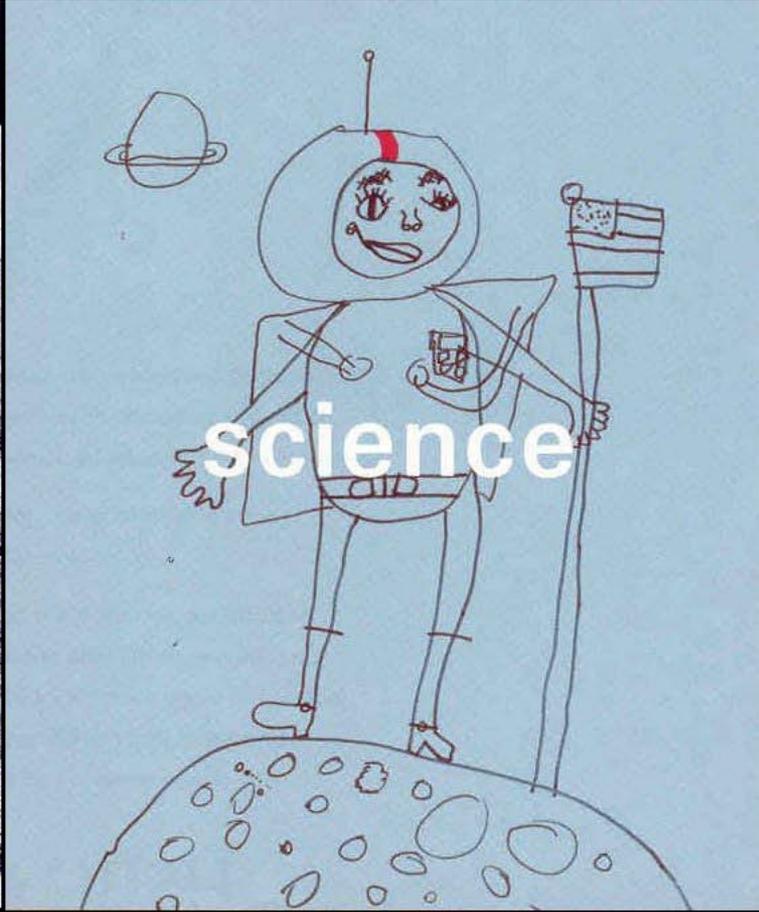
Synthesis/Control of Nanostructures for Desirable Applications
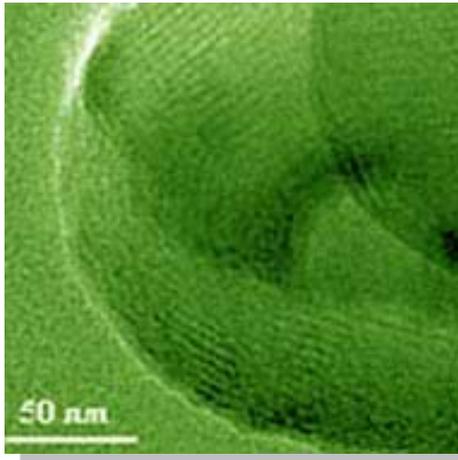
Mesoporous Structure
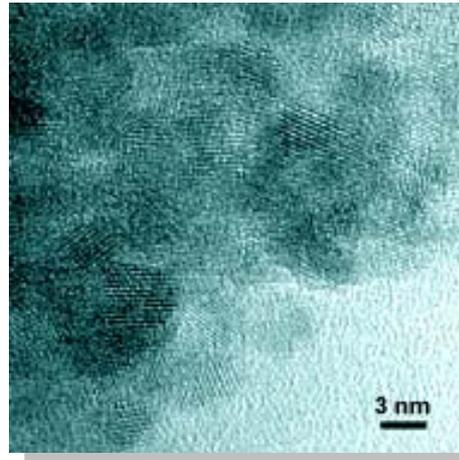
Oxide Nanoparticles
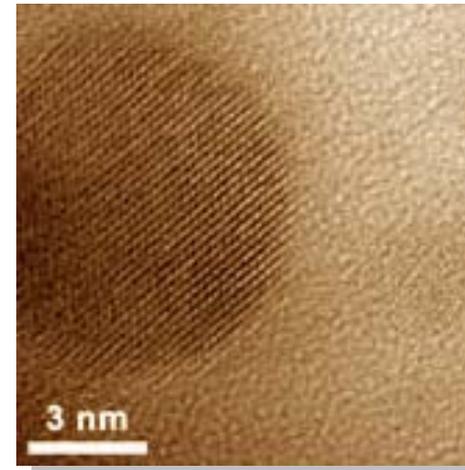
Semiconductor Nanoparticles
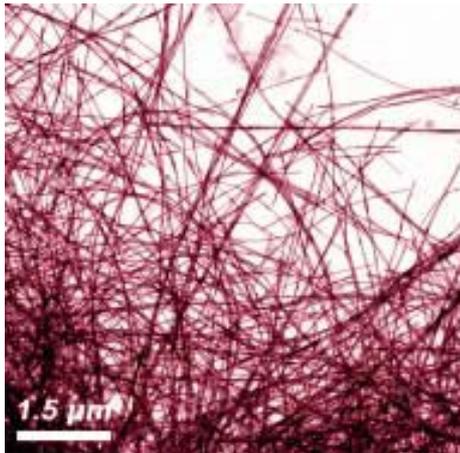
Nanowires
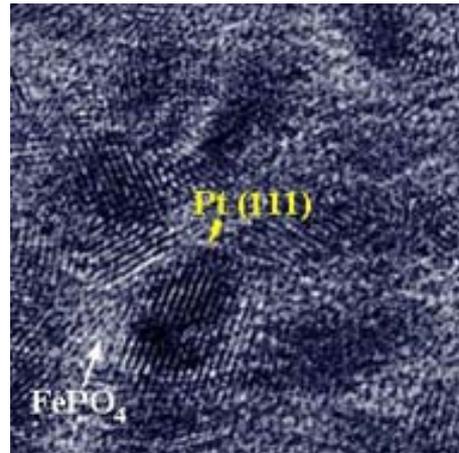
Nanocomposites
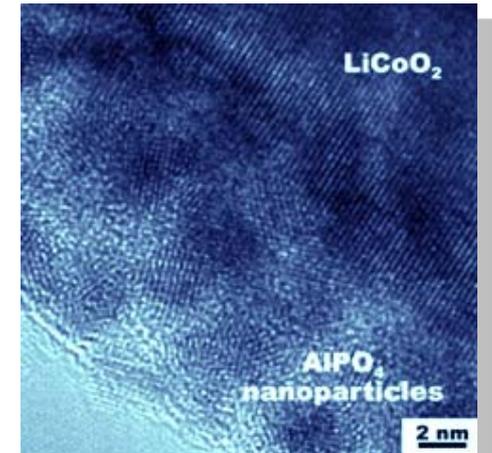
Nanoscale Coating

A Nanoscale (Nanocar) Vehicle
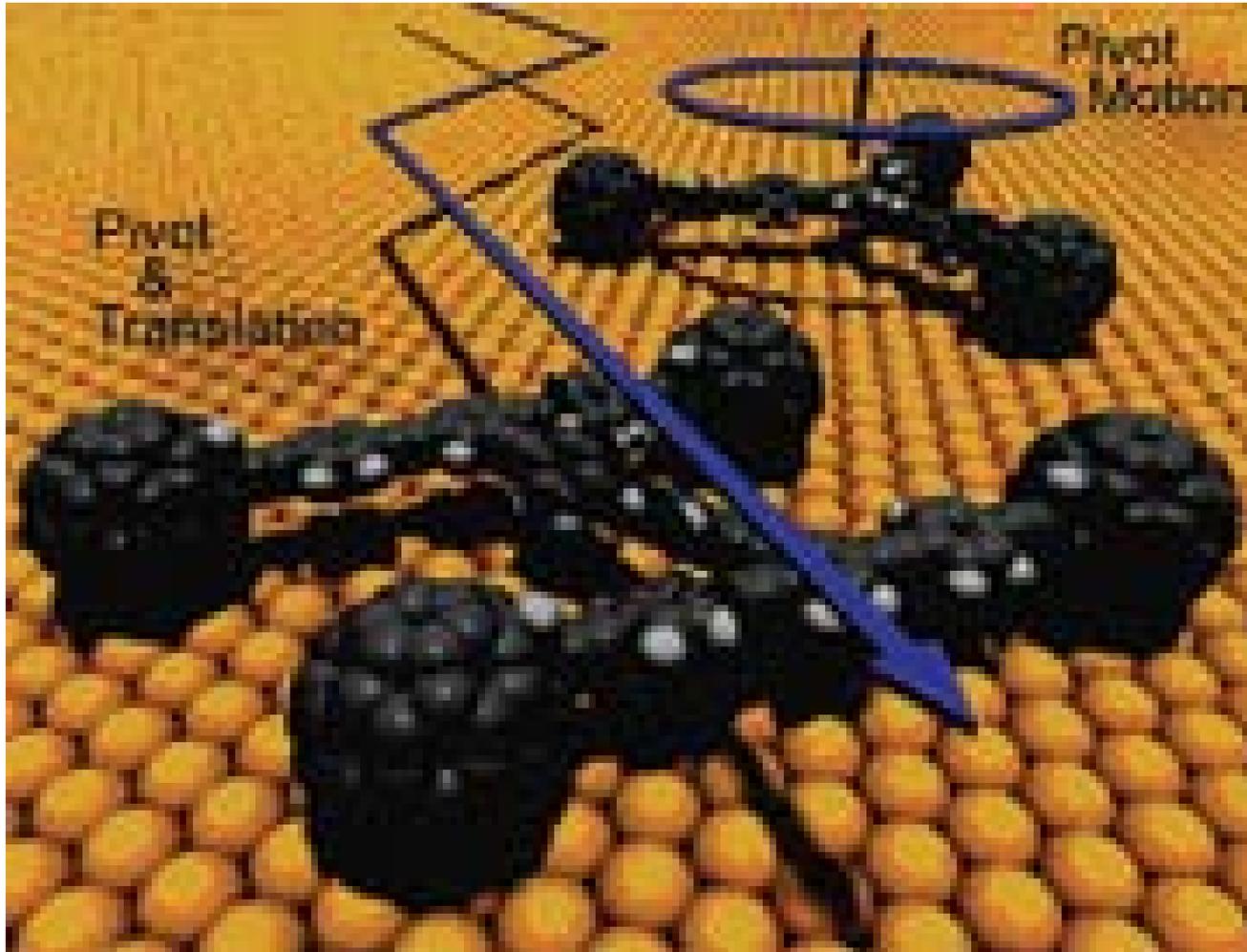
James M. Tour's Group
Rice University
Science **315, 1199 (2006)**
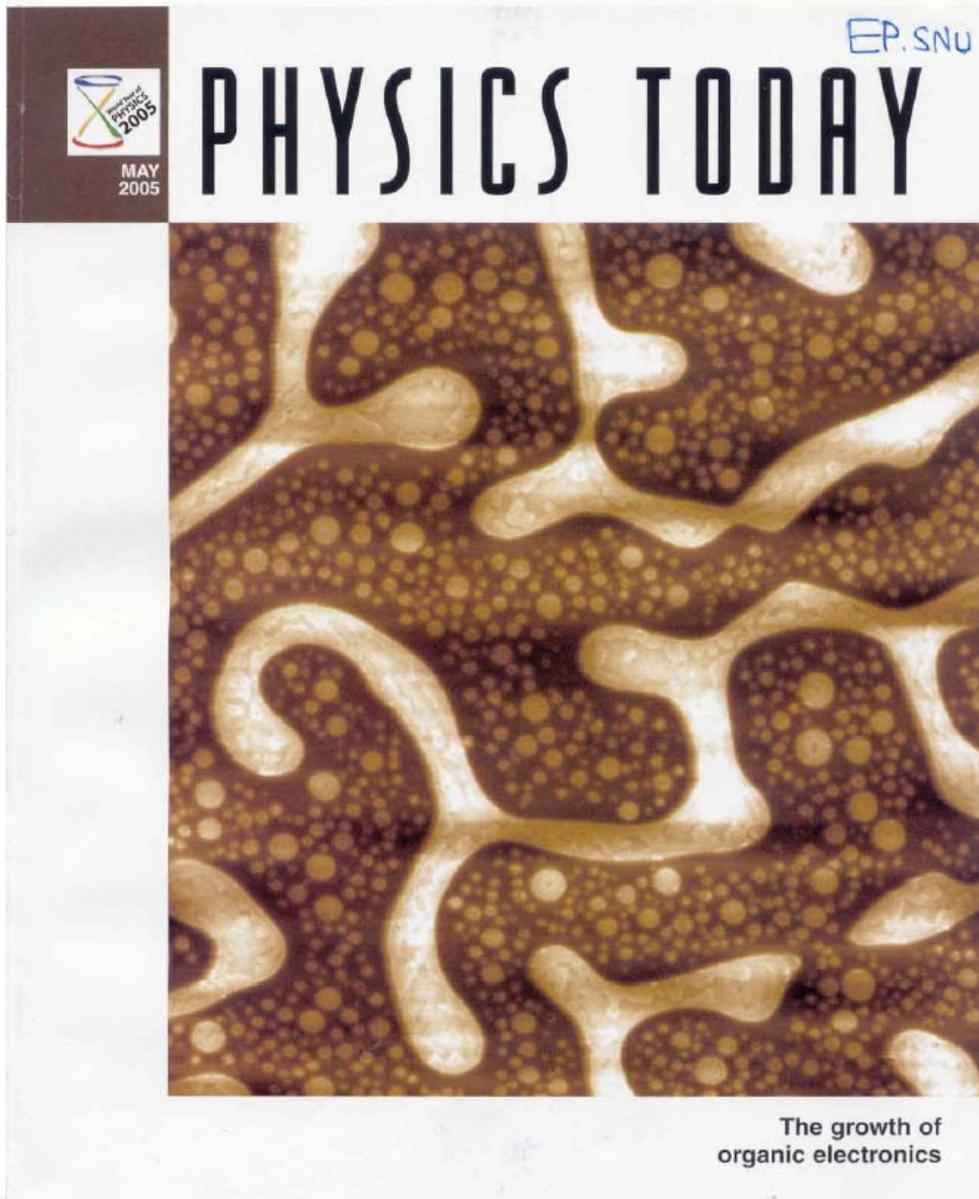
The growth of organic electronics
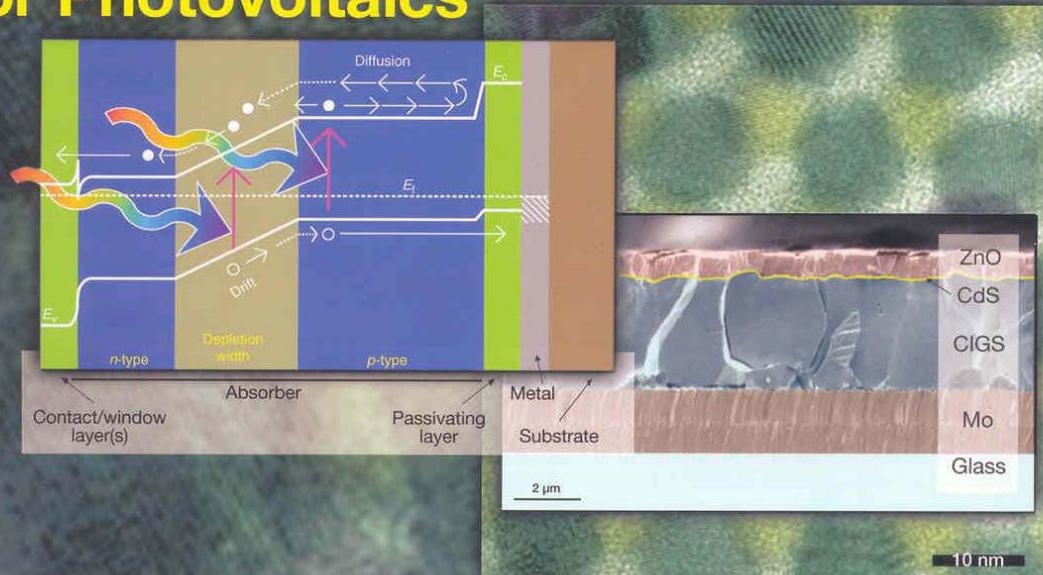
Photovoltaic Conversion Efficiencies & Novel Conducting Polymers

Photovoltaic conversion efficiencies

	Laboratory best*	Thermodynamic limit
Single junction		31%
Silicon (crystalline)	25%	
Silicon (nanocrystalline)	10%	
Gallium arsenide	25%	
Dye sensitized	10%	
Organic	3%	
Multijunction	32%	66%
Concentrated sunlight (single junction)	28%	41%
Carrier multiplication		42%

*As verified by the National Renewable Energy Laboratory. Organic cell efficiencies of up to 5% have been reported in the literature.
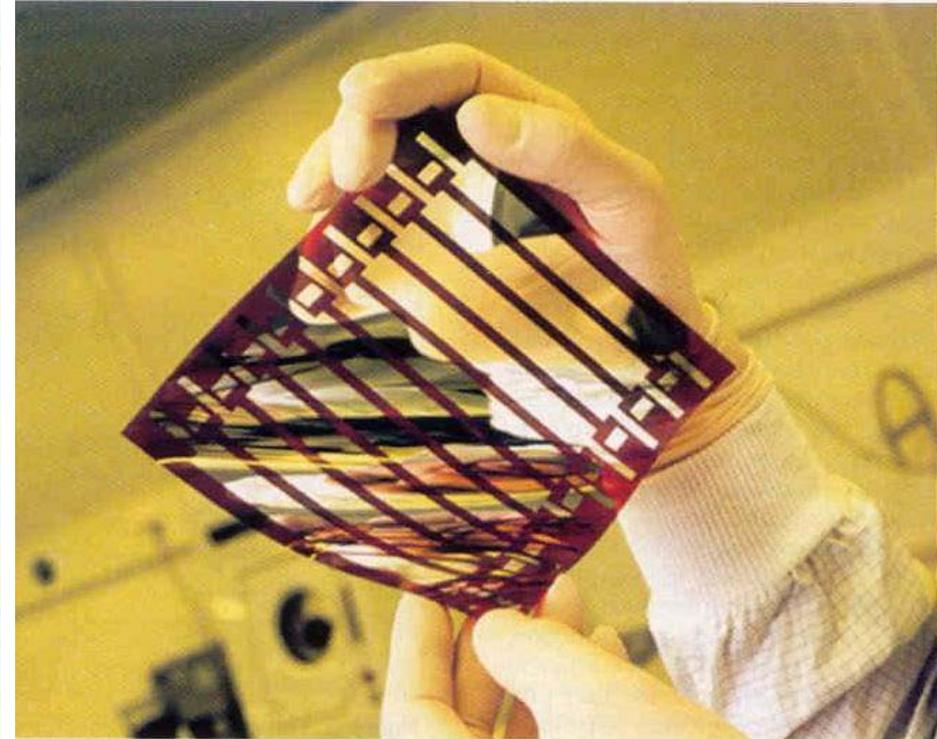
Figure 2. **Novel conducting polymers** enable solar cells that are flexible, inexpensive, and versatile. The new materials can be coated or printed onto flexible or rigid surfaces. (Image courtesy of Konarka Technologies.)

Physics Today (March 2007)

Solar Energy Conversion

Figure 1. Solar photons convert naturally into three forms of energy—electricity, chemical fuel, and heat—that link seamlessly with existing energy chains. Despite the enormous energy flux supplied by the Sun, the three conversion routes supply only a tiny fraction of our current and future energy needs. Solar electricity, at between 5 and 10 times the cost of electricity from fossil fuels, supplies just 0.015% of the world's electricity demand. Solar fuel, in the form of biomass, accounts for approximately 11% of world fuel use, but the majority of that is harvested unsustainably. Solar heat provides 0.3% of the energy used for heating space and water. It is anticipated that by the year 2030 the world demand for electricity will double and the demands for fuel and heat will increase by 60%. The utilization gap between solar energy's potential and our use of it can be overcome by raising the efficiency of the conversion processes, which are all well below their theoretical limits.

Physics Today (March 2007)
G. W. Crabtree and N. S. Lewis

Environment-Friendly Power Sources

Mobile Electronics

Hyundai Motors

Carbon

40 nm   백금 나노입자
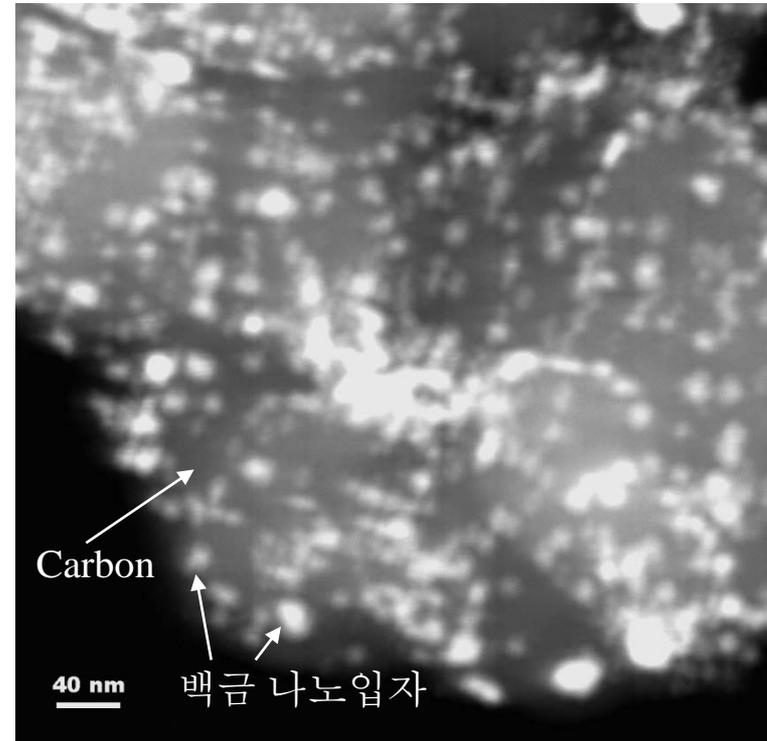
High-Technology Electronics Equipments
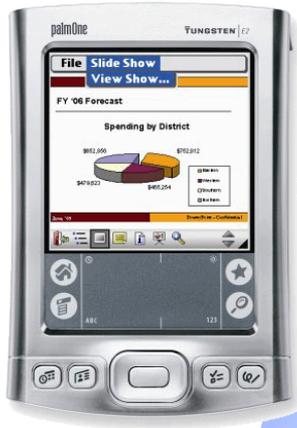
PDA

Laptop Computer

Mobile Phone

MP3 Player

PMP

Digital Camera

Microelectronics

Thin-Film Battery
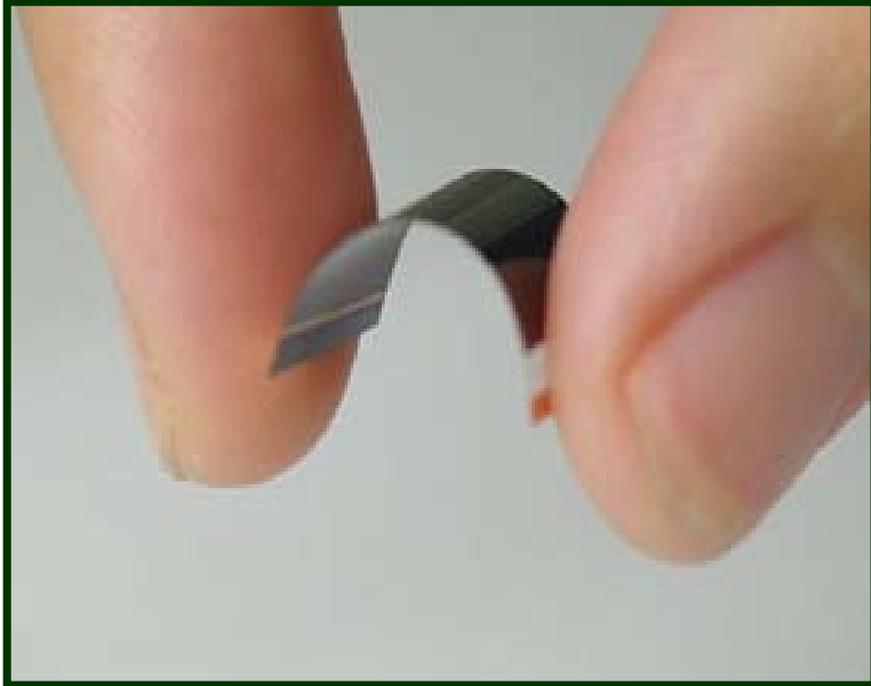
- **Smart Card**
- **Portable Sensors**
- **ID Tags**
- **SRAM**

Capsule-Type Endoscope

Micro Syringe
Micro Optics
Temp.Sensor, PH Sensor, Chemica Sensor
Micro pump
Fixing Mechanism
Tissue Compatible Material
RF-Comm. Module
DC-DC Converter
Micro Gripper
Hardness Sensor
Signal,Processor, System-on-Chip
Wireless Power Trans.Module
Extension/ contraction Mechanism
Micro Battery
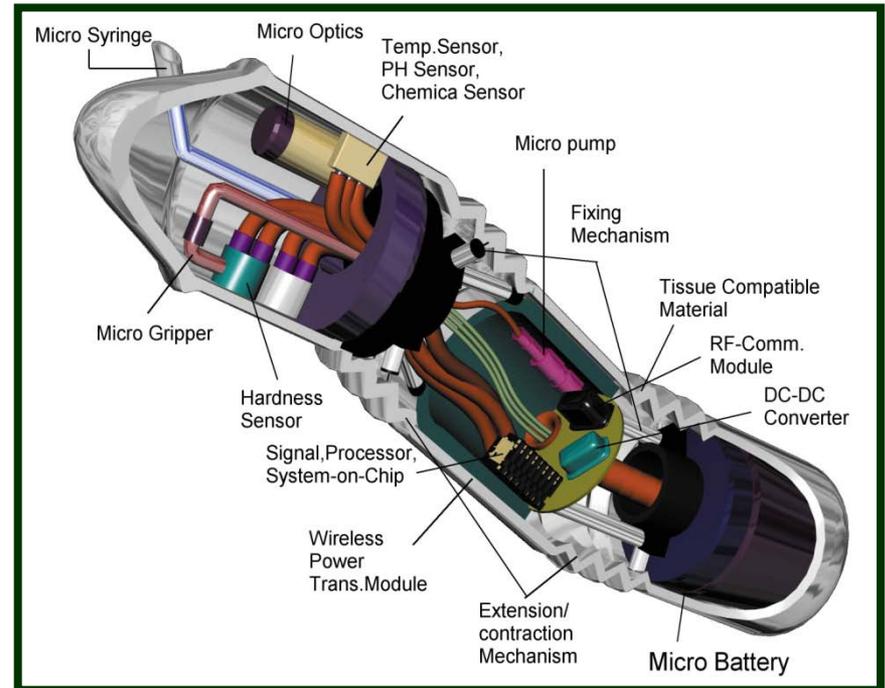
- **Sensors**
- **RF Communication**

— ADVANCED MATERIALS —

❖ **What is a Scientific Paper?**

A paper is not just an archival device for storing a completed research program. It is a structure for *planning* your research in progress.

❖ **Why do I do the work?**

❖ **What are the central motivations and hypothesis?**

Prof. George M. Whitesides
Department of Chemistry and Chemical Biology
Harvard University
Cambridge, MA 02138 (U.S.A.)

Adv. Mater. (2004)

Thermodynamics = Why

Phase Transformations = How

Attractive Research

Phase Transformations of Nanomaterials

Activated ← How do phase transformations occur?

G
$(= H - TS)$

Metastable

Thermodynamic Driving Force

Equilibrium

Configurational Coordinates
(for ~10^4 atoms)
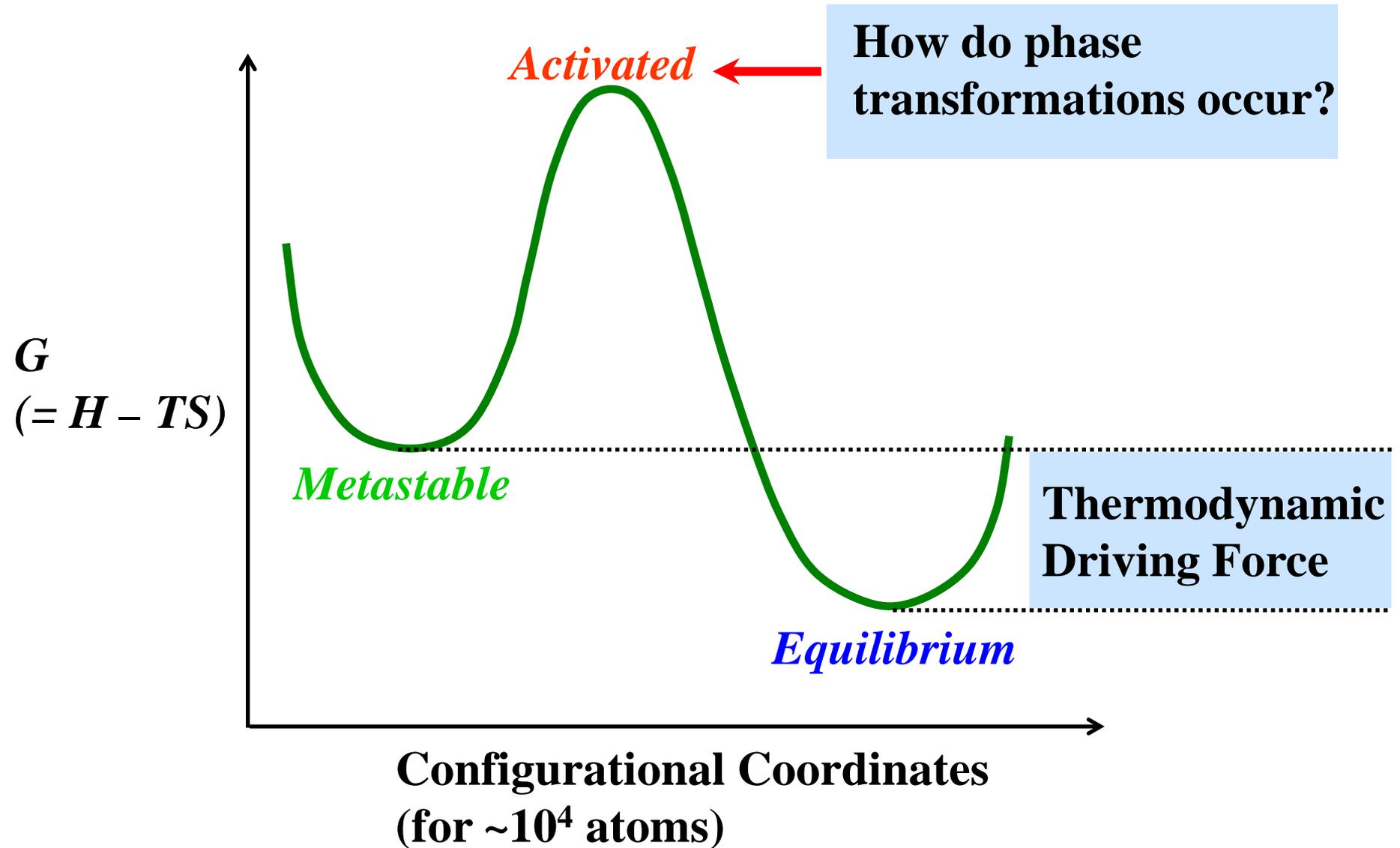
Prof. David Turnbull

Jeju Island (Aug. 2005)

Vitamin C

http://www.3dchem.com/
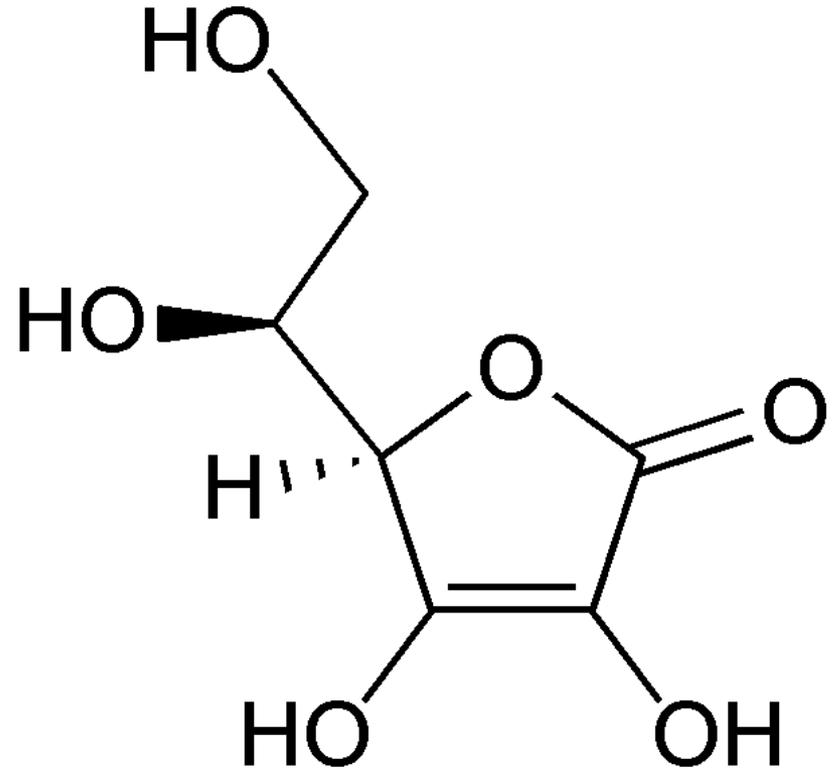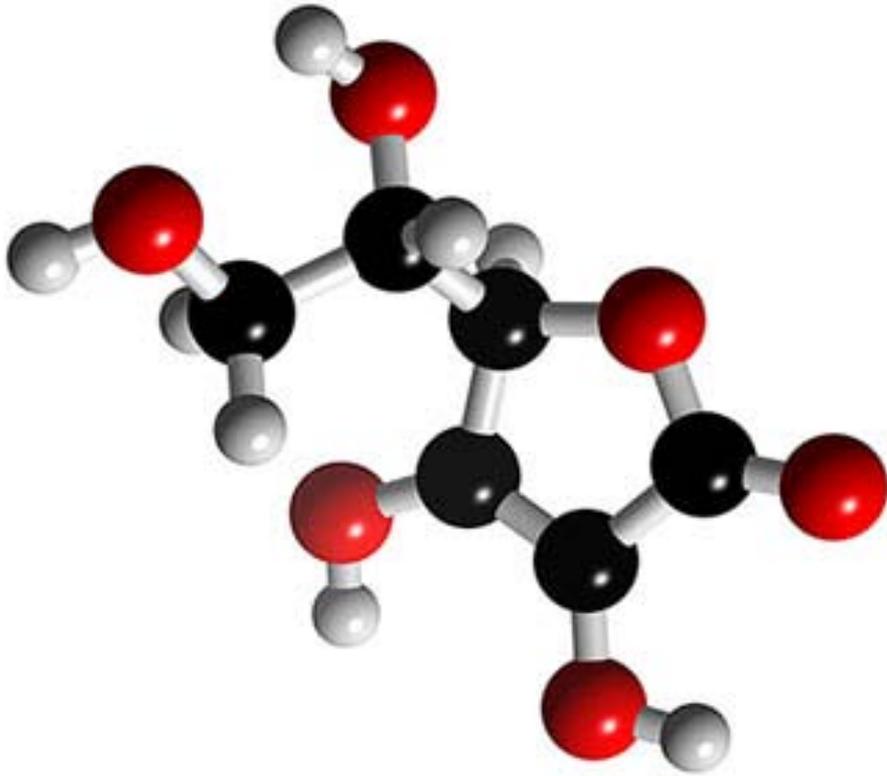
Gibbs Free Energy

Low Temperature — Enthalpy

$H - TS$

High Temperature — Entropy
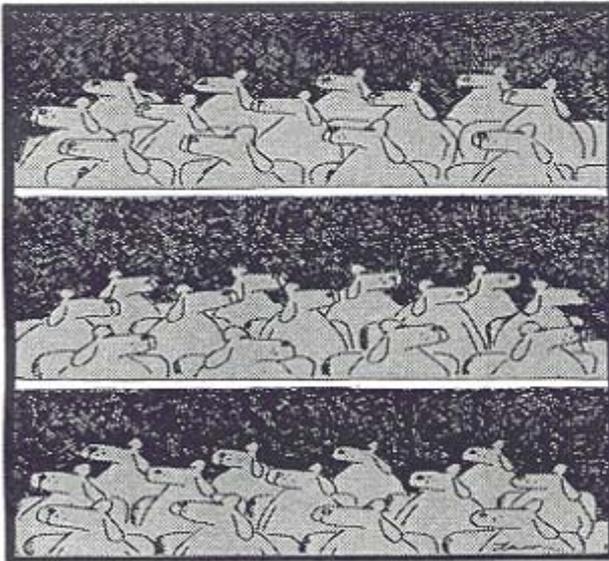
At the popular dog film, *Man Throwing Sticks*

Out of Order
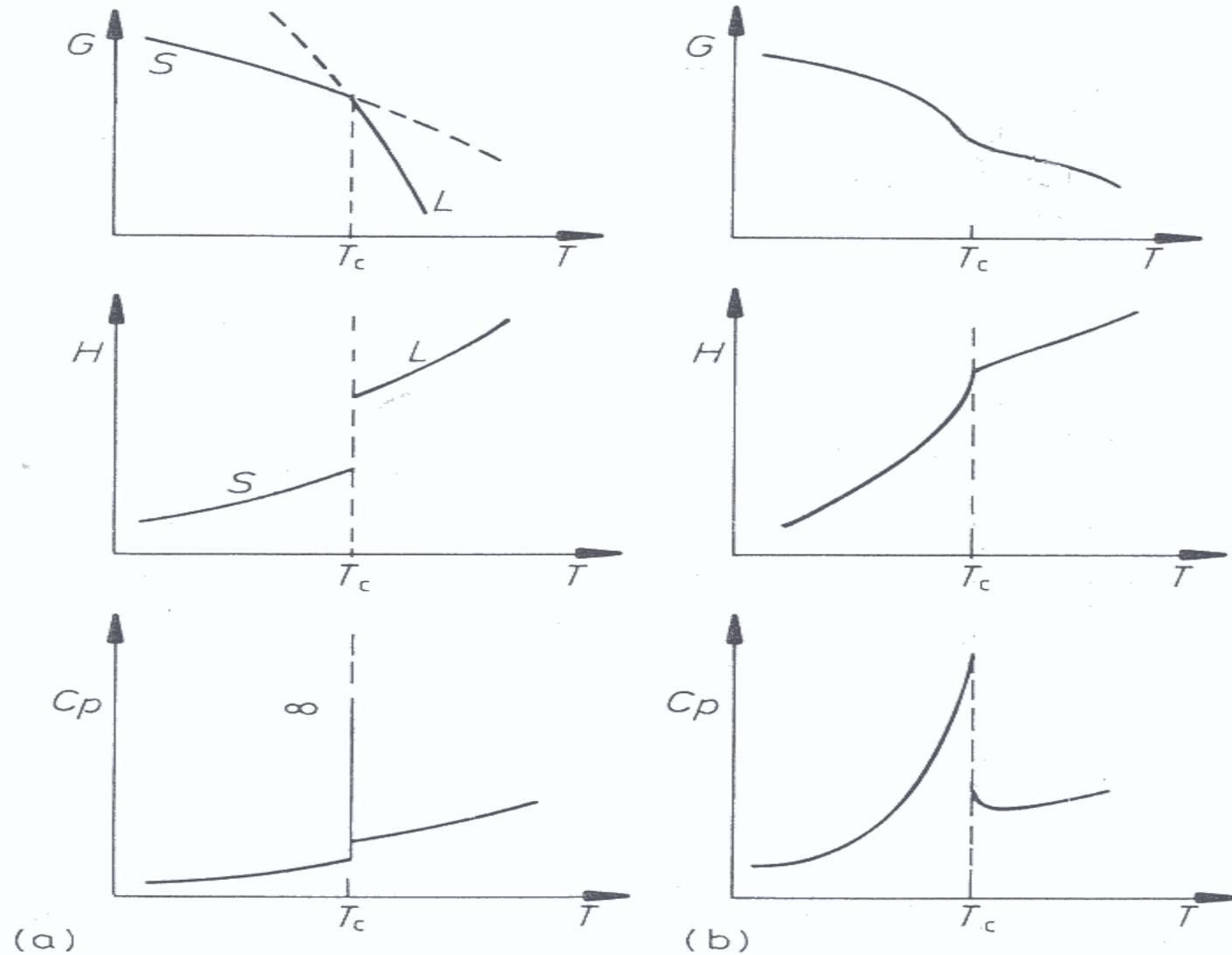
Fig. 5.82   The thermodynamic characteristics of   (a) first-order   and   (b) second-order phase transformations.

First-Order Transition
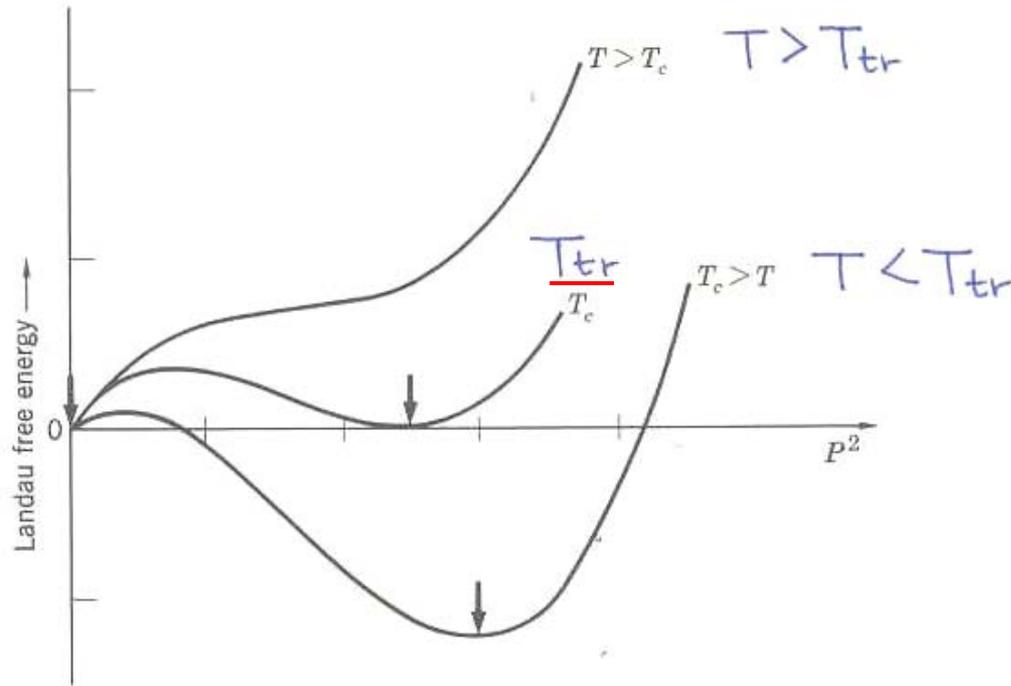
Figure 15 Landau free energy function versus (polarization)^2 in a first-order transition, at representative temperatures. At T_c the Landau function has equal minima at $P = 0$ and at a finite P as shown. For T below T_c the absolute minimum is at larger values of P; as T passes through T_c there is a discontinuous change in the position of the absolute minimum. The arrows mark the minima.

[15]J. A. Gonzalo, Phys. Rev. **144**, 662 (1966); P. P. Craig, Phys. Letters **20**, 140 (1966).

Heat Capacity of Second-Order Transition
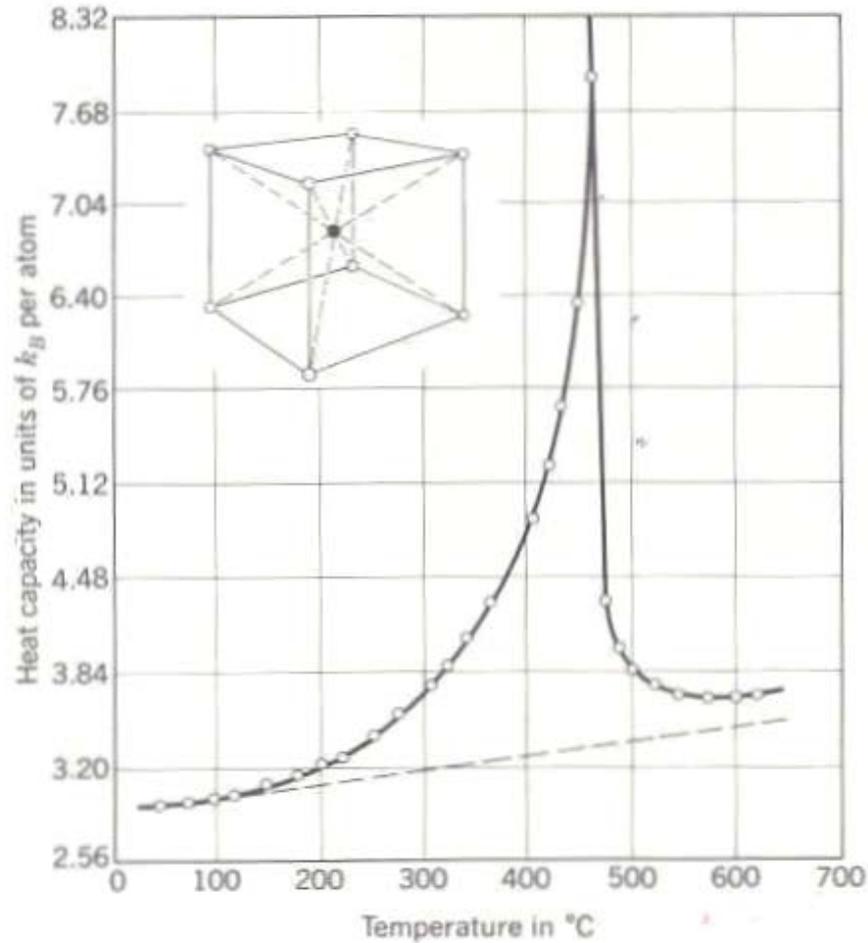
Figure 21 Heat capacity versus temperature of CuZn (β-brass) alloy. [After F. C. Nix and W. Shockley, Revs. Mod. Physics **10**, 1 (1938).]

The general problem of the stability of microstructure

Centre of mass

The minimum work required to render unstable is a measure of metastability

Metastable equilibrium

Unstable equilibrium

Stable equilibrium

Metastability

Instability

Fig. 1.1. Difference between metastability and instability. (After Cahn 1968, courtesy of A.I.M.E.)

Stability of Nanostructures – Free Energy

The general problem of the stability of microstructure

Fig. 1.2. The change in free energy of an atom as it takes part in a transition. The 'reaction coordinate' is any variable defining the progress along the reaction path.
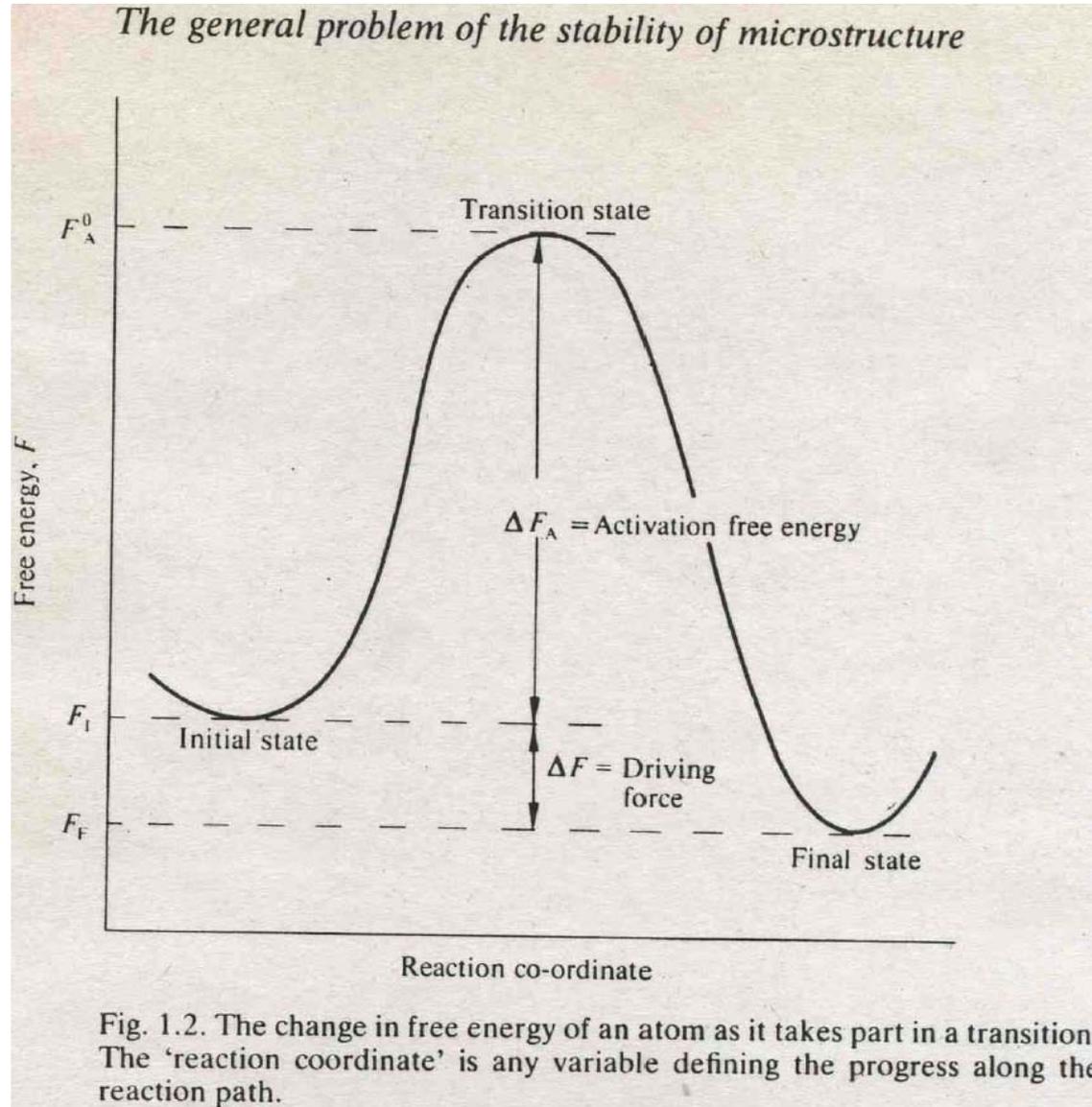
Two General Cooling Paths – Crystalline vs. Amorphous Phases
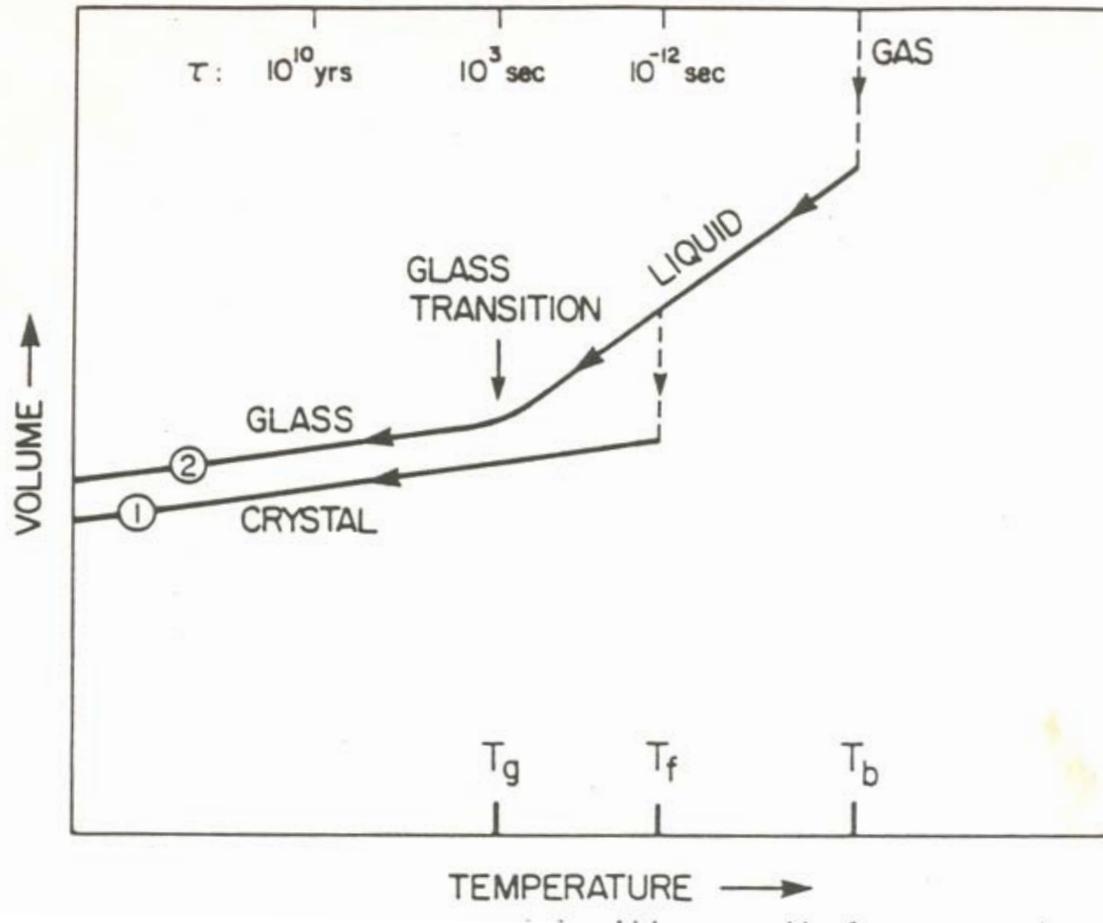
Route ①: path to the crystalline solid state

➔ discontinuous

Route ②: rapid quenching to the amorphous solid

➔ continuous

Schematic Sketches of Atomic Arrangements

(a) CRYSTAL   (b) GLASS   (c) GAS
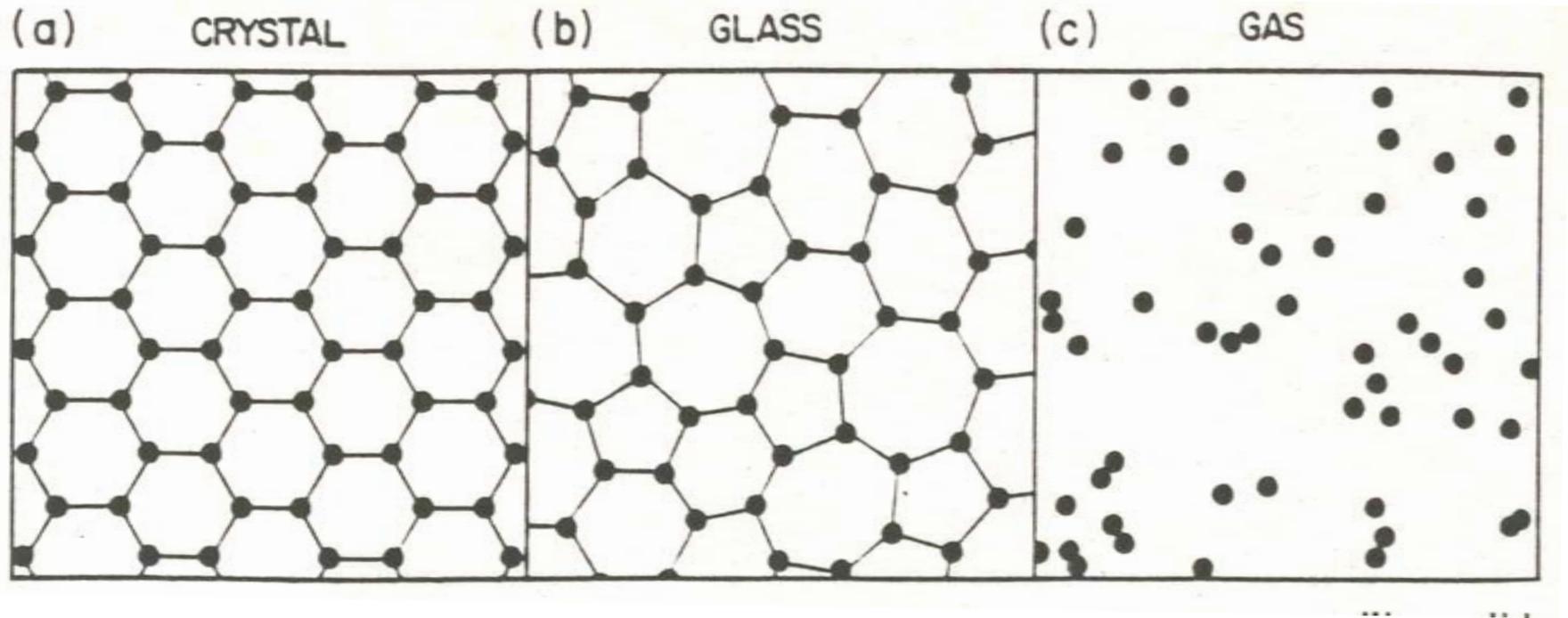
(a) Crystal = The bond lengths and angles are exactly (almost) equal.

(b) Amorphous = High degree of local correlation.

(c) Gas = The particles are rarely correlated.

Glass-Transition Temperature vs. Cooling Rate
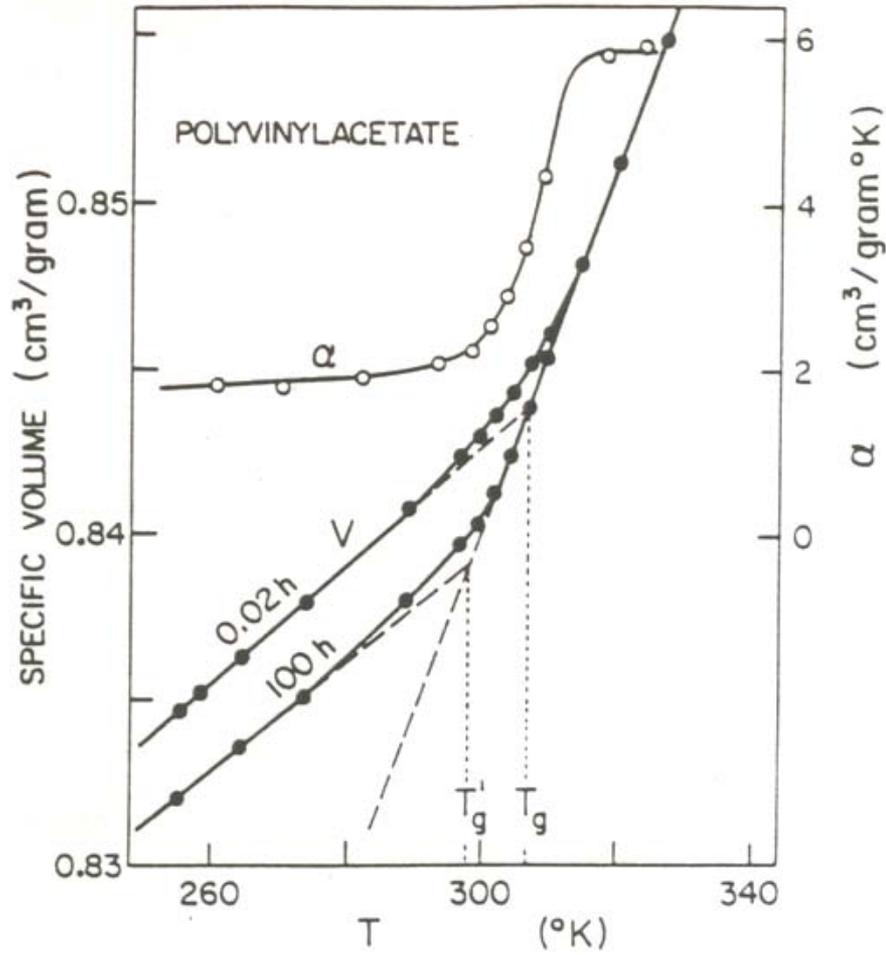
Liquid–glass transition

Relaxation

Relaxation

KAL

Specific Heat of Amorphous Phase
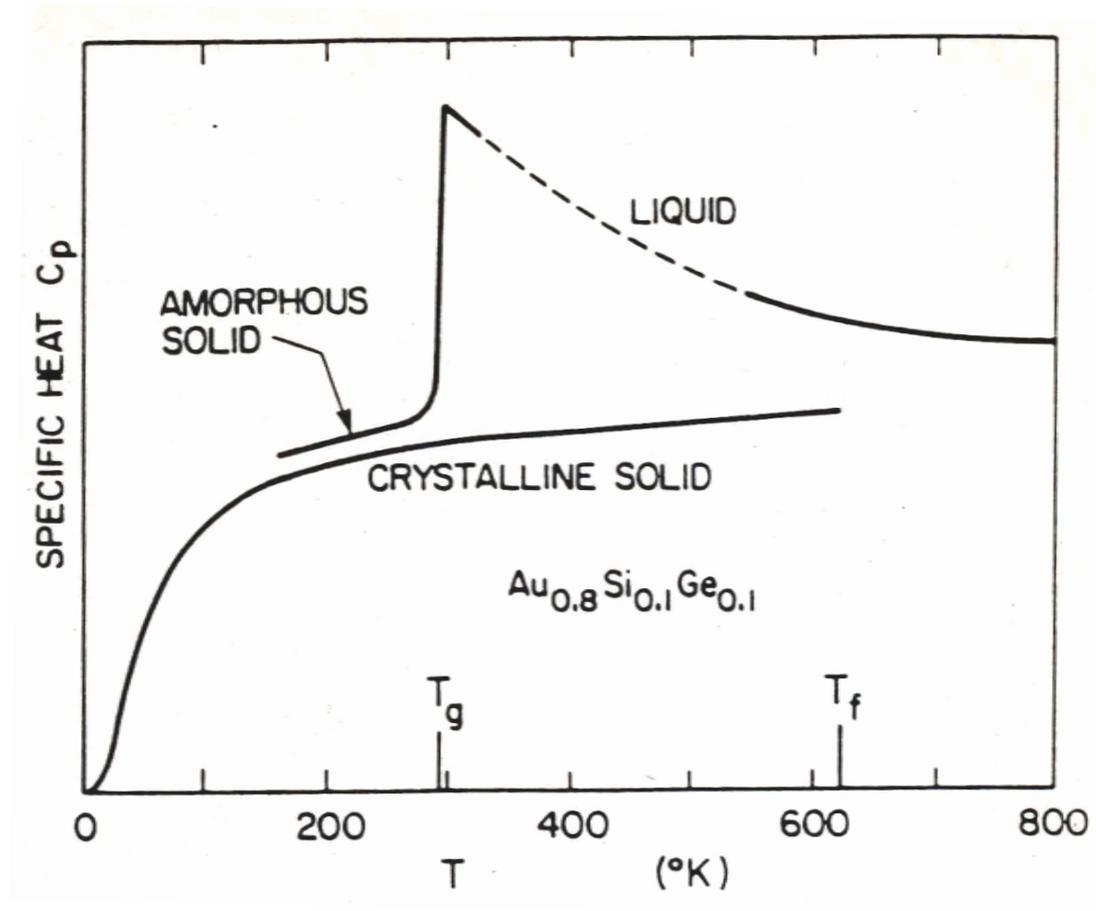
No Latent Heat **Second-Order Transition** **Glass - Liquid Transition**

Examples of Applications for Amorphous Solids

TABLE 1.2 Some examples of applications of amorphous solids

Type of Amorphous Solid	Representative Material	Application	Special Properties Used
Oxide glass	$(SiO_2)_{0.8}(Na_2O)_{0.2}$	Window glass, etc.	Transparency, solidity, formability as large sheets
Oxide glass	$(SiO_2)_{0.9}(GeO_2)_{0.1}$	Fiber optic waveguides for communications networks	Ultratransparency, purity, formability as uniform fibers
Organic polymer	Polystyrene	Structural materials, "plastics"	Strength, light weight, ease of processing
Chalcogenide glass	Se, As_2Se_3	Xerography	Photoconductivity, formability as large-area films
Amorphous semiconductor	$Te_{0.8}Ge_{0.2}$	Computer-memory elements	Electric-field-induced amorphous $\leftrightarrow$ crystalline transformation
Amorphous semiconductor	$Si_{0.9}H_{0.1}$	Solar cells	Photovoltaic optical properties, large-area thin films
Metallic glass	$Fe_{0.8}B_{0.2}$	Transformer cores	Ferromagnetism, low loss, formability as long ribbons

Amorphous InGaZnO Semiconductor for Thin-Film Transistor (TFT)

Diffusion

- Redistribution of atoms from regions of high concentration of mobile species to regions of low concentration.
- It occurs at all temperatures.
- The diffusivity has an exponential dependence on *T*.

Random Walk

final

initial
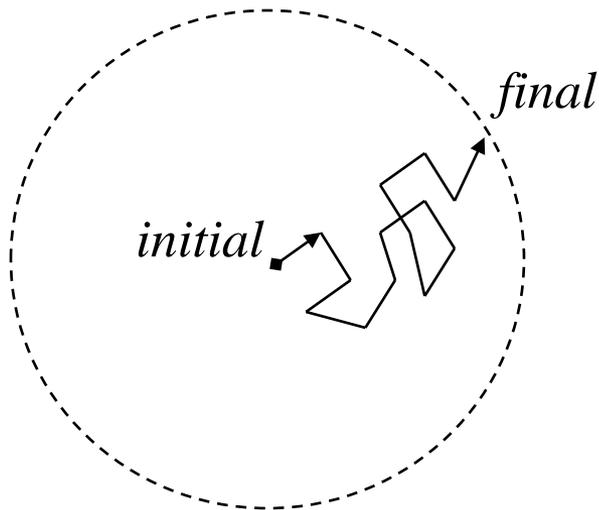
Age of Universe ~ 10^{17} sec (${10^{10}}$ years)

Gas : $D \sim 1$ cm^2/s $\longrightarrow$ $(Dt)^{1/2} \sim 3000$ km

Liquid : $D \sim 10^{-5}$ cm^2/s $\longrightarrow$ $(Dt)^{1/2} \sim 10$ km

Solid : $D \sim 10^{-8}$ cm^2/s $\longrightarrow$ $(Dt)^{1/2} \sim 300$ m

Fick's Law

Fick's 1st Law

$$\vec{J} = -D\frac{\partial C}{\partial x}$$

$\vec{J}$: diffusive flux (atoms/cm^2•sec)

D : diffusion coefficient (cm^2/sec)

C : atomic concentration (atoms/cm^3)

X : distance (cm)

Fick's 2nd Law

If D is independent of C, then

$$\nabla \cdot \vec{J} + \frac{\partial C}{\partial t} = 0 \qquad \Longrightarrow \qquad D\frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t}$$

General Materials Science   BP

How Do Atoms Diffuse?

<Vacancy Mechanism>

<Interstitial Mechanism>

(a)   (b)

(a) Direct interstitial mechanism

(a) Before jumping

(b) After jumping into the right-hand side

(b) Direct exchange of a pair of atoms

(c) Ring mechanism
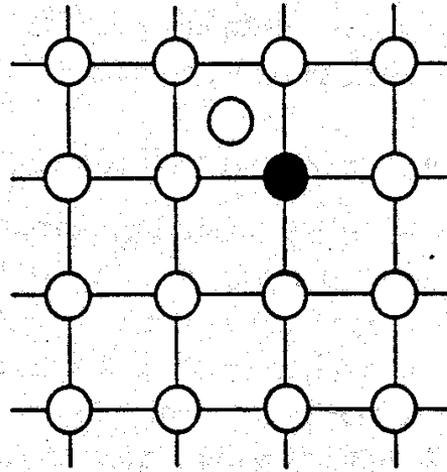
(a) Interstitial Si has approached substitutional Au.
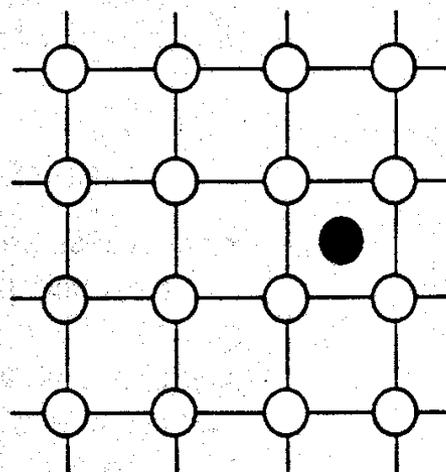
(b) Au has exchanged its original position with Si.
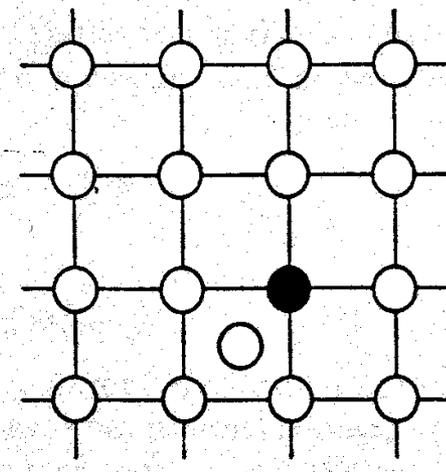
(c) Au has re-occupied a regular site by kicking a Si atom into an interstice.

ex) Au diffusion in *c*-Si

How Fast? – Thermal Activation
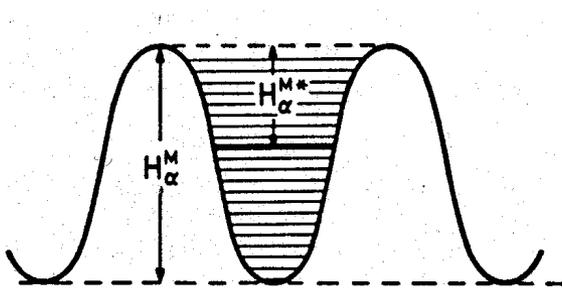
Thermally assisted energy-release mechanism via the vibrational state marked by the heavy horizontal line.

For interstitial diffusion

$$D = D_0 \exp\left(-\frac{\Delta H_m}{k_B T} \right)$$

Activation enthalpy : $Q = \Delta H_m \sim$ 1 eV

Prefactor: $D_0 \sim 10^{-2} - 10^{-3}$ cm^2/sec

For substitutional diffusion

$$D = D_0 \exp\left(-\frac{\Delta H_f + \Delta H_m}{k_B T} \right)$$

Activation enthalpy : $Q = \Delta H_f + \Delta H_m \sim$ 3 - 5 eV

Prefactor: $D_0 \sim 10 - 10^{-1}$ cm^2/sec

Several Points for Self Diffusion

(1) Rough correlation between Q ($= \Delta H_f + \Delta H_m$) and T_m

Interatomic bond strength (cohesive energy) $\uparrow$ $\longrightarrow$ Q $\uparrow$ T_m $\uparrow$ D $\downarrow$

$$\boxed{Q \sim 20\, k_B T_m}$$ $k_B = 8.617 \times 10^{-5}$ eV/K

(2) Temperature Dependence

For Ge self-diffusion

$D = 4.4$ cm^2/s $\times$ exp(-3.4 eV/$k_B T$)

$T_m = 1211$ K $D = 3.1 \bullet 10^2$ Å^2/s $(Dt)^{1/2} \sim 1000$ Å
$T_m = 298$ K $D = 1.4 \bullet 10^{-41}$ Å^2/s $(Dt)^{1/2} \sim 10^{-19}$ Å
For $t = 1$ hour

(3) Measurements (S.I.M.S.)

By deposition (~ 200 Å)

Si^{28} Si^{29} Si^{28}
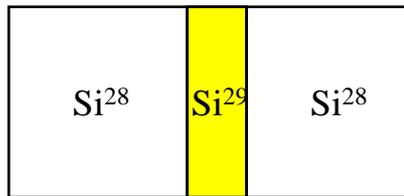
Implant Si^{29} ~ 100 keV

Si^{28}

5000 Å
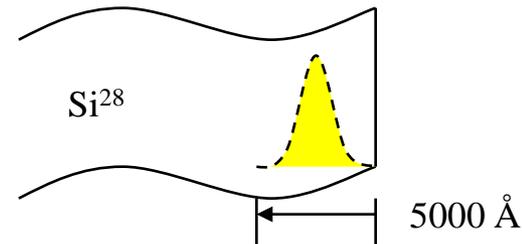
Solution to the Diffusion Equation

Governing Equation $\longrightarrow$ $\boxed{D \cdot \nabla^2 C = \dfrac{\partial C}{\partial t}}$

$D > 0$
D independent of C
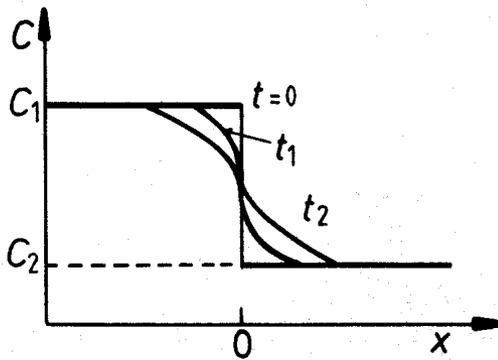
$$C(x) = \frac{C_1 + C_2}{2} - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

$$erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z \exp(-y^2)\,dy$$
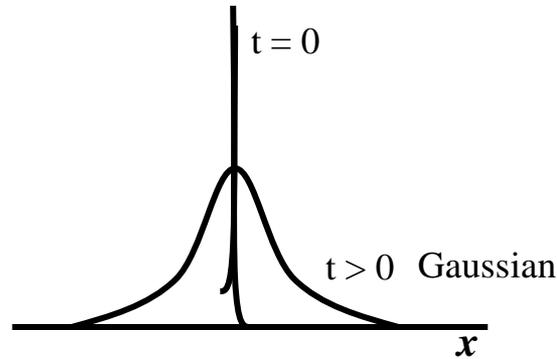
$$C(x) = \frac{Area}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$
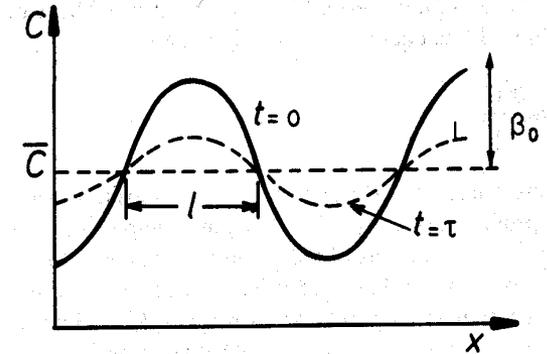
$$C(x) = \overline{C} + \beta_0 \sin\left(\frac{\pi x}{l}\right)\exp\left(\frac{-t}{\tau}\right)$$

$$\tau = \frac{l^2}{\pi^2 D}$$

Superlattice (Si/SiGe)

Empirical Survey of Self Diffusion

D [cm^2/s]

- 10^0 — vapor
- 10^{-4} — liquid
- 10^{-5} — amorphous
- 10^{-8}
- defect
- crystal
- 10^{-20}

boiling   melting

high T   **low T** T_m/T
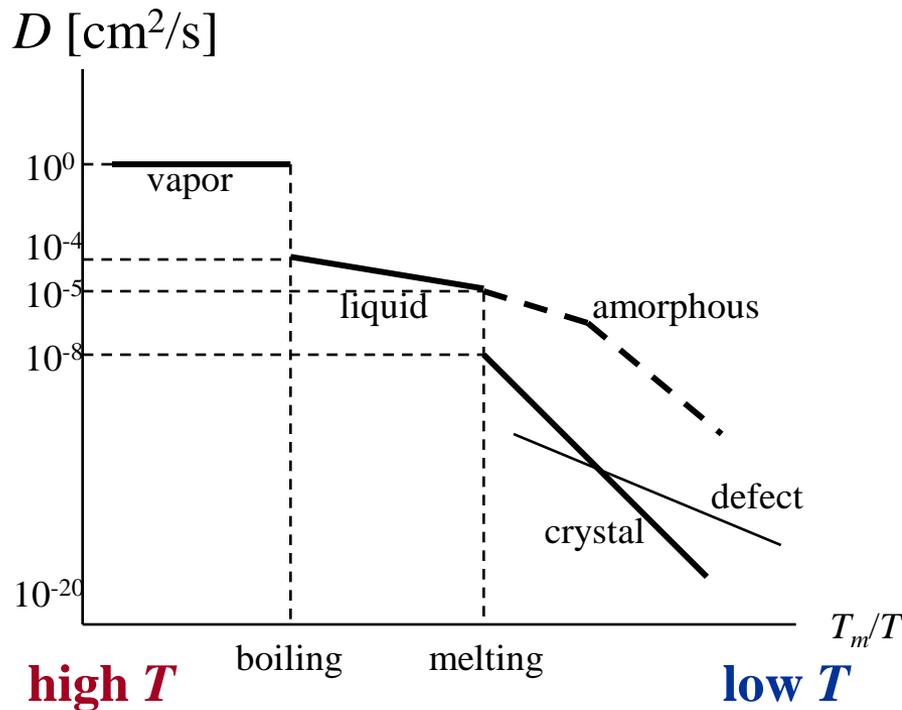
* Extended Structural Defects

- Dislocation
- Grain boundary
- Short circuit: easy diffusion path
  dominant at low T

* Structure

- fcc: $D(T_m) \sim 10^{-8}$ cm^2/s
- bcc: $D(T_m) \sim 10^{-7}$ cm^2/s
- diamond: $D(T_m) \sim 10^{-12}$ cm^2/s

Self Diffusivity
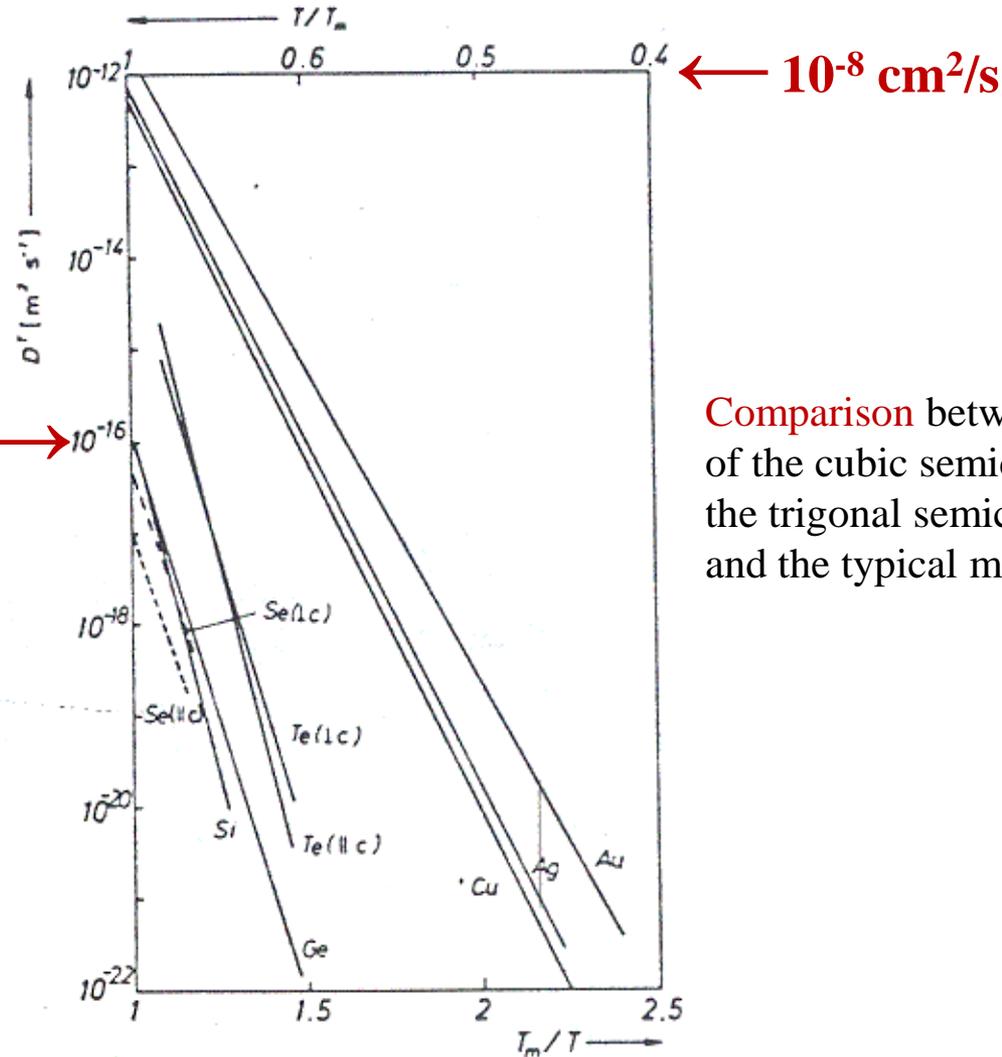
Comparison between the self-diffusivities of the cubic semiconductors Ge and Si, the trigonal semiconductors Te and Se, and the typical metals Cu, Ag, and Au.

Self Diffusion in Ge
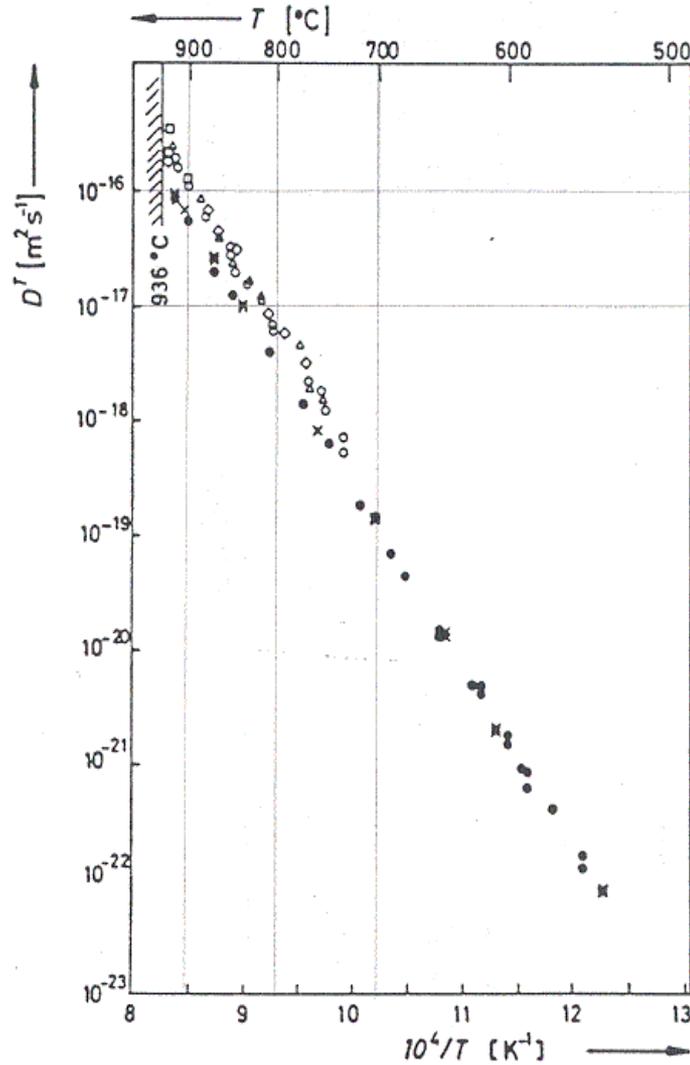
$\longleftarrow$ 10^{-12} cm^2/s

Tracer self-diffusion coefficient of Ge as a function of temperature. Data are from various groups.

Self Diffusion in Si
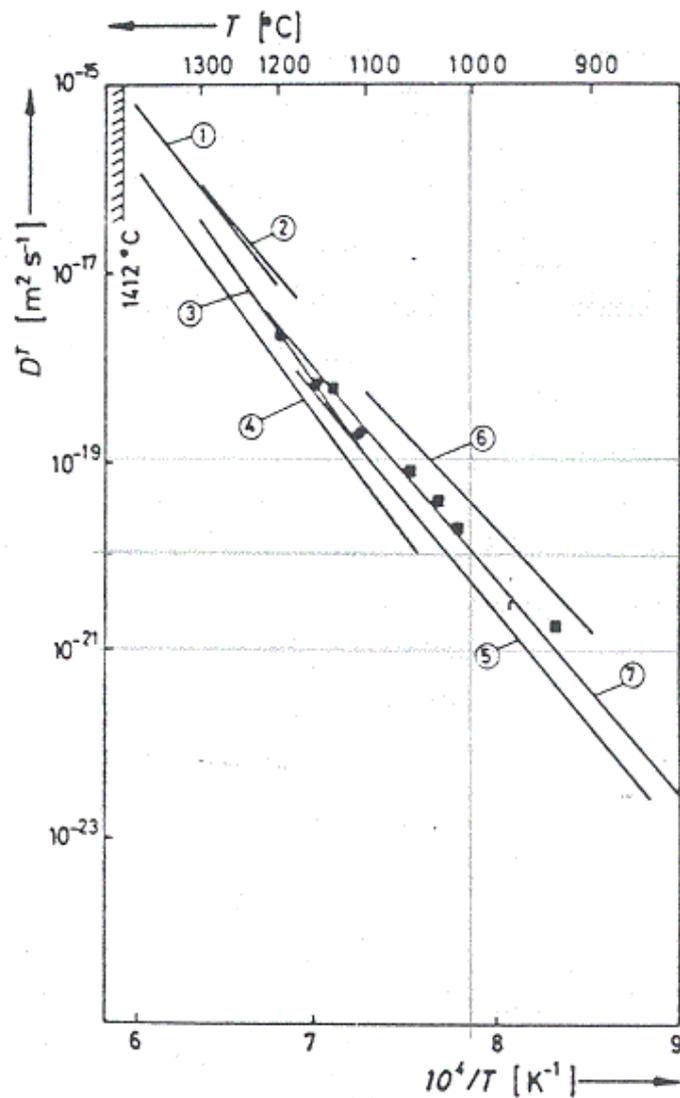
10^{-12} cm²/s

Tracer self-diffusion coefficient of Si as a function of temperature from various groups. Deviations may arise from several reasons which need to be further investigated.

10^{-4} cm²/s

10^{-12} cm²/s

Survey of the diffusivities of foreign atoms in silicon. Foreign atoms include Cu, Ni, Li, Fe, O, C; group Ⅲ (Al, Ga, As); group Ⅴ (P, As, Sb); and Ge.
For comparison, Si self-diffusion data are included.

Device Applications

- **In semiconductor devices, solute atoms control electrical conductivity and *n*-type (or *p*-type) doping.**

- **Concentration and distribution of dopants play a critical role in the device operation.**
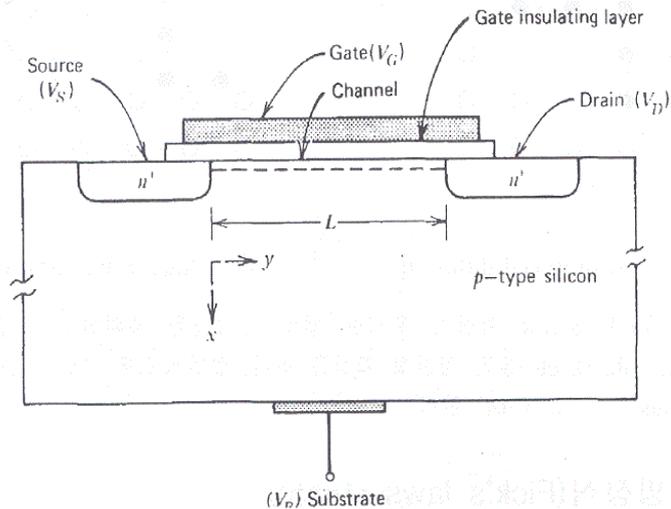
MOSFET (Metal Oxide Semiconductor Field Effect Transistor)
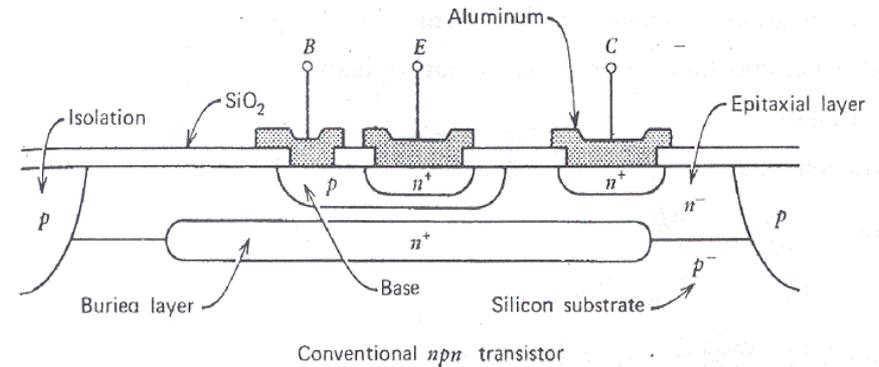
BJT (Bipolar Junction Transistor)

DIFFUSION ON SEMICONDUCTOR SURFACES

Atomic-resolution imaging techniques show that a good deal of surface physics can be understood with elementary statistical mechanics, but some surprisingly complex behaviors occur even in simple systems.

Harold J. W. Zandvliet, Bene Poelsema, and Brian S. Swartzentruber

Semiconductor devices continue to get ever smaller, which means that individual defects play an increasingly important role in their performance. In the process of fabricating more innovative, better performing devices, crystal growers have developed an amazing intuition about how atoms and molecules behave on crystal surfaces. Their intuition, formed from knowledge of fundamental atomic-scale processes and honed through experience, concerns such questions as where atoms and molecules stick, how they interact with each other and the substrate, and how they diffuse.

rapidly and quickly finds another atom with which to form an adsorbed dimer. Adsorbed dimers can be bound either on top of, or between, the substrate dimer rows and can have their dimer bonds oriented parallel or perpendicular to the rows. Dimers on top of the substrate rows can rotate, changing their orientation from parallel to perpendicular and back. They can also diffuse, both along and across substrate rows. The stability of binding sites, along with rotational and diffusion barriers, can all be readily extracted from real-time scanning tunneling microscopy (STM) experiments—with the help of elemen-

Individual Si Atom and Dimer on Si (001)
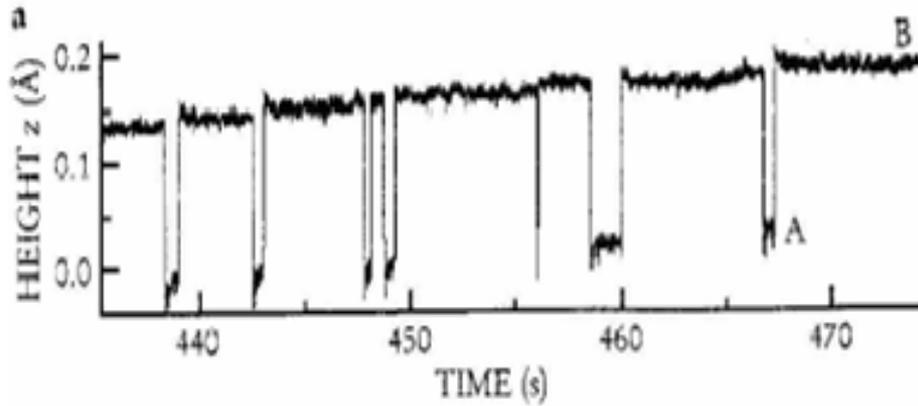
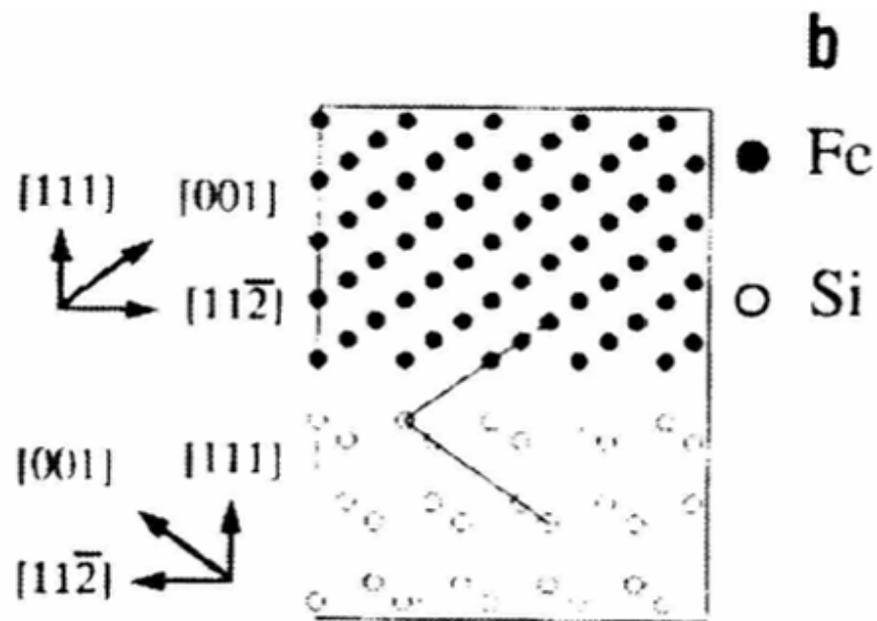**Height z as function of time**
(Scanning tunneling microscope tip)

- Transition between A and B
- Different transition rates
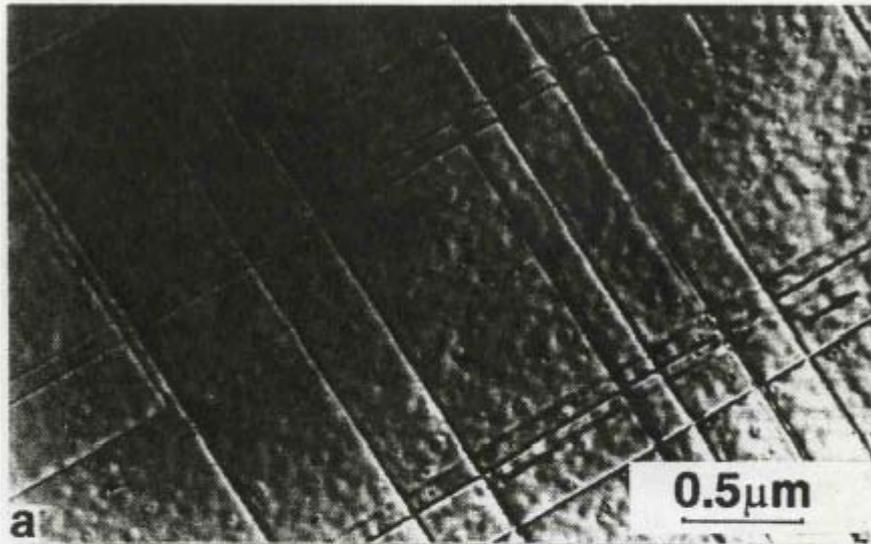

~0.5 eV
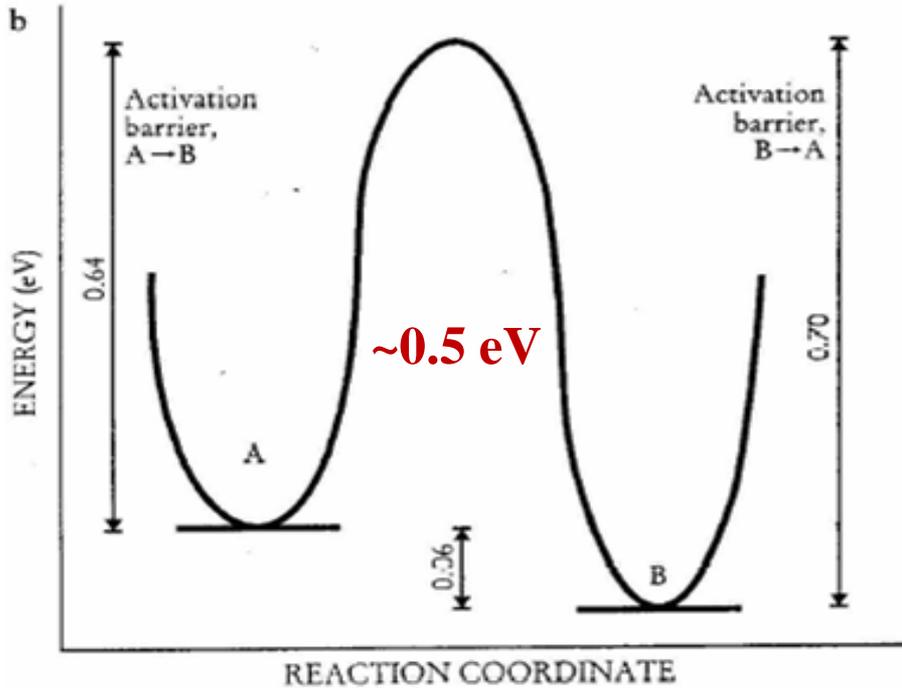
Energy vs. coordinate

a

Fe

Si [1$\bar{1}$0]   2 nm
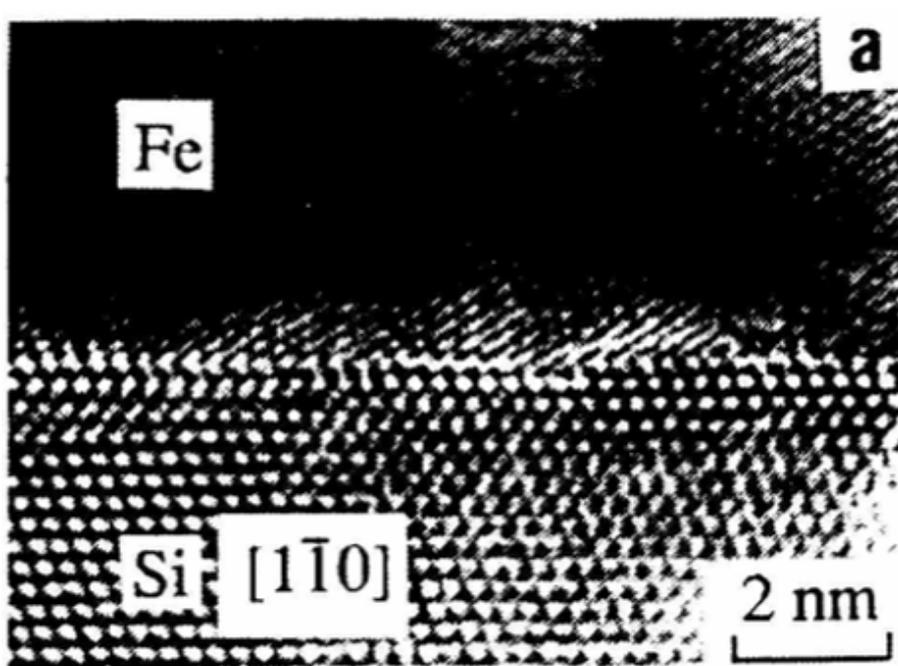
Atomic image of α–Fe/Si interface along [110] Si direction.

b

[111] [001]

[11$\bar{2}$]

[001] [111]

[11$\bar{2}$]

● Fe

○ Si

Appl. Phys. Lett.

A schematic diagram showing the twinned epitaxy.

Plan-View TEM: $Si_{1-x}Ge_x$ Epitaxy on Si (001)

The average dislocation distance
- measured directly.
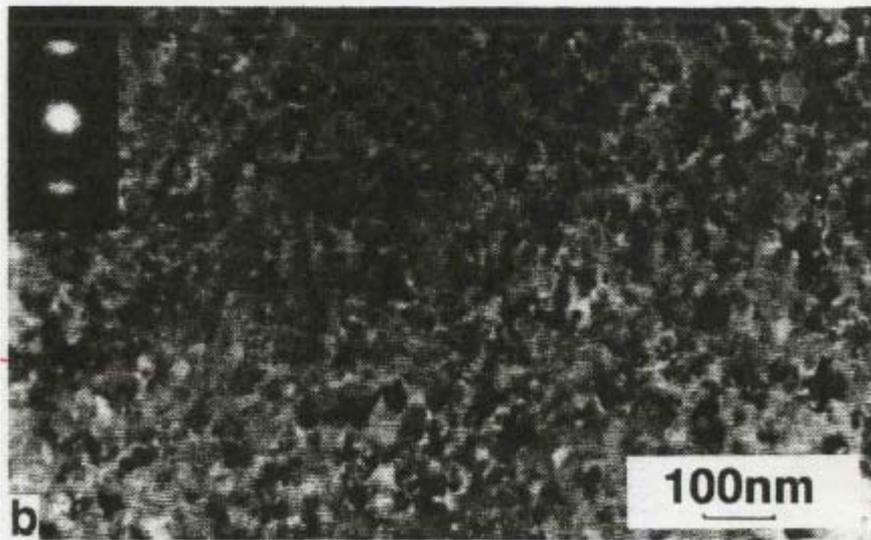
Distance of Moire' fringes

20 μm
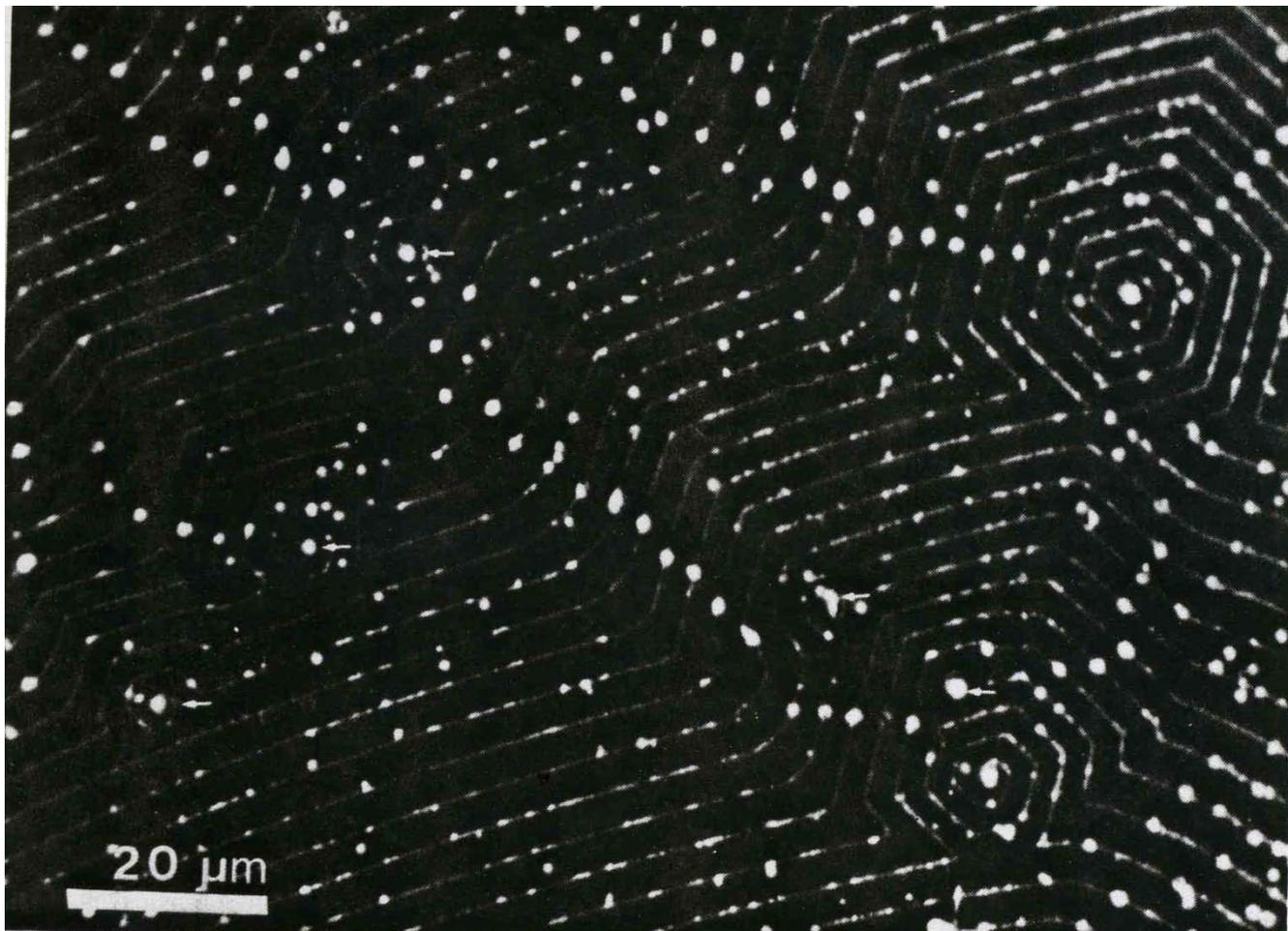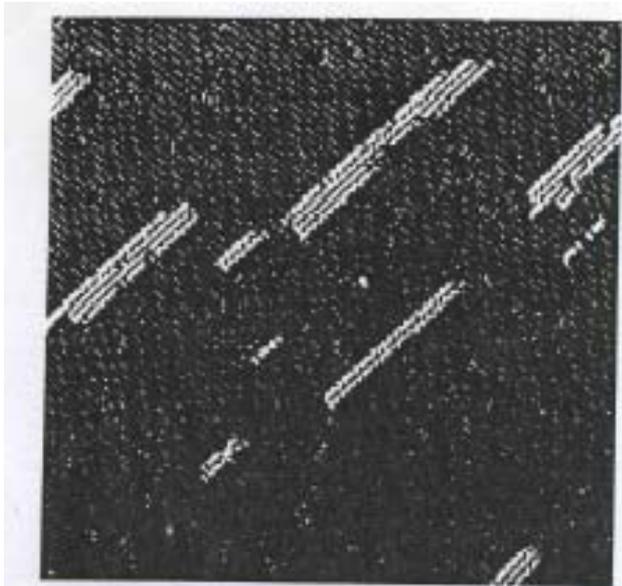
Islands – anisotropic
Measured by STM

60 nm × 60 nm
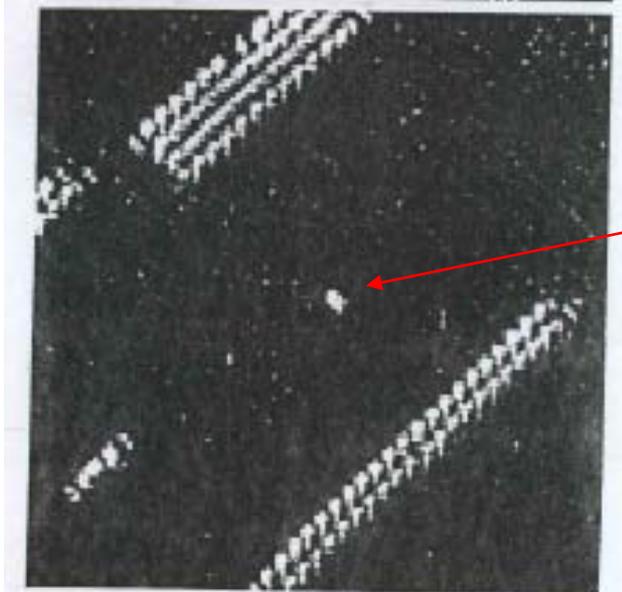
Single dimer

25 nm × 25 nm

Growth Characteristics – Silicon (001) Surface
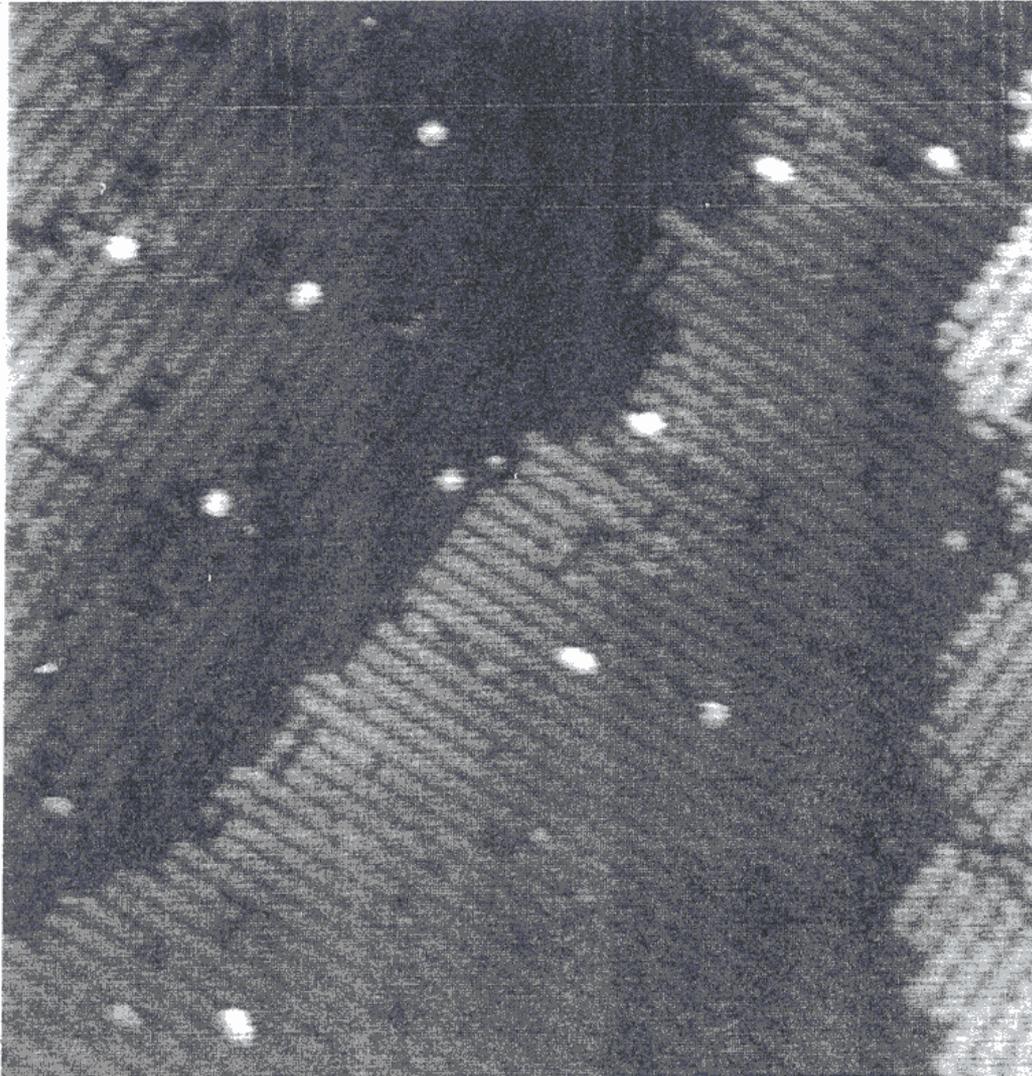
FIGURE 1. A SCANNING tunneling microscope image of a silicon (001) surface after the deposition of a small amount of Si at room temperature. The image shows two single-layer steps (the jagged interfaces) separating three terraces. Because of the tetrahedral bonding configuration in the silicon lattice, dimer row directions are orthogonal on terraces joined by a single-layer step. The area pictured is 30 × 30 nm.
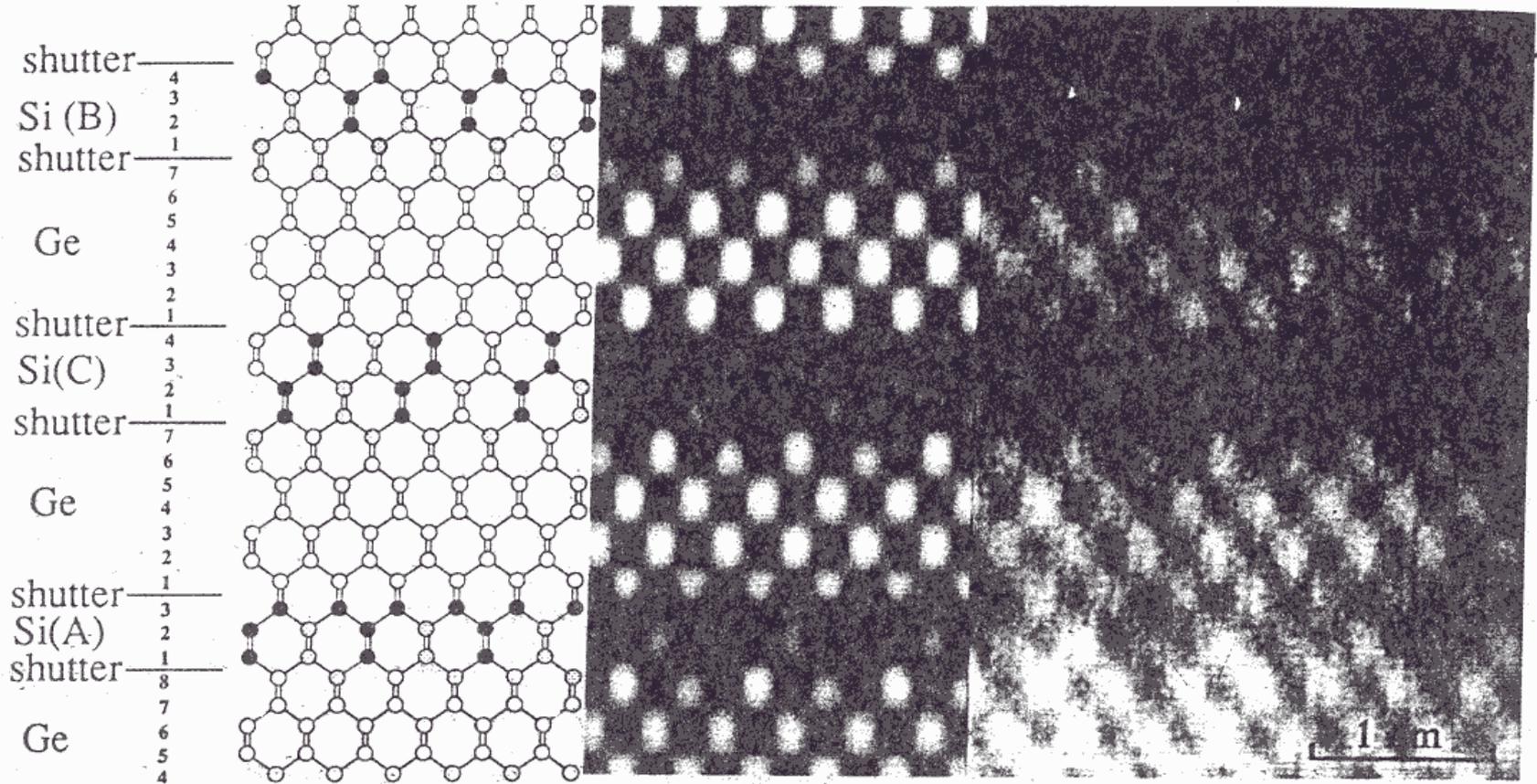
FIG. 4. A [110] Z-contrast electron microscope image of a nominal $(Si_4Ge_8)_{24}$ superlattice revealing unexpectedly complex interfacial arrangements that developed during growth. The schematic and simulation show the structures expected to arise through a Si/Ge atomic exchange process at growing step edge [D. E. Jesson, S. J. Pennycook, and J.-M. Baribeau, Phys. Rev. Lett., 66, 750 (1991)]. Open circles represent Ge columns, solid circles Si columns, and shaded circles alloy columns.
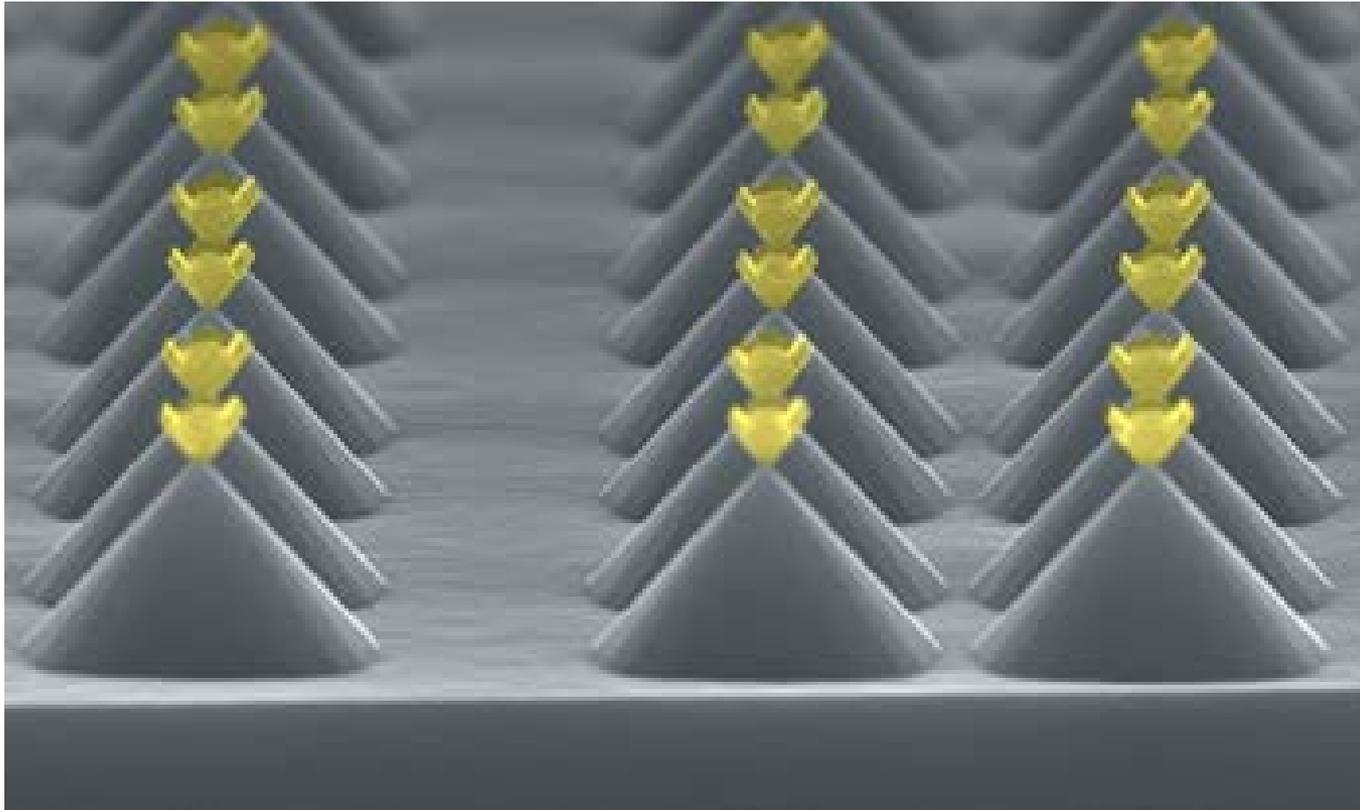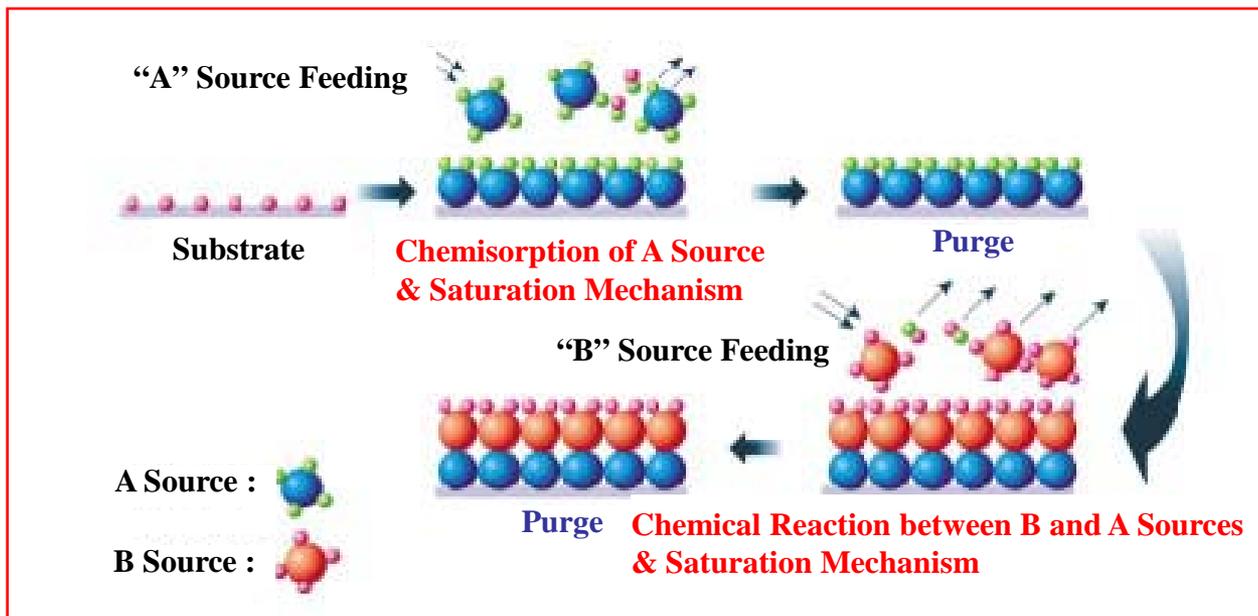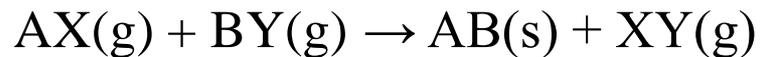
Joel Henzie and Teri W. Odom, Northwestern University, J. Phys. Chem. B (2006)

The orientation-dependent optical properties of the nanoparticle arrays have revealed new insight into the interaction between light and materials at the nanoscale. These structures are also being explored in applications such as chemical /biological sensing and nanophotonics.
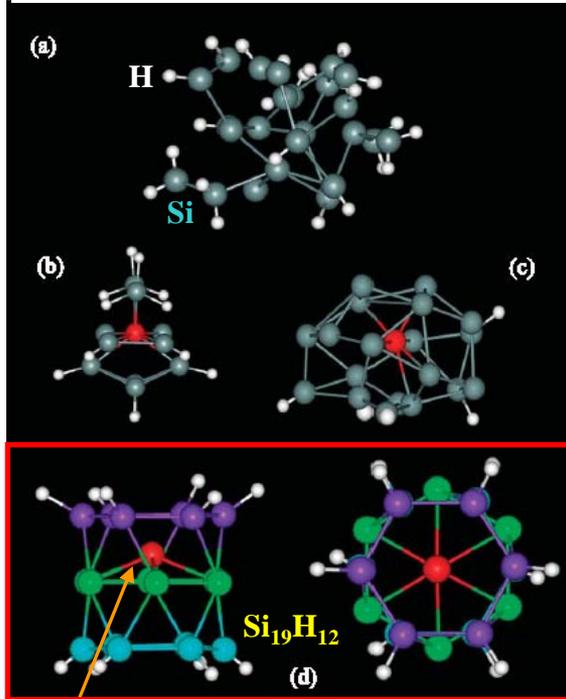
Atomic Layer Deposition (ALD)

$$AX(g) + BY(g) \rightarrow AB(s) + XY(g)$$

"A" Source Feeding

Substrate

Chemisorption of A Source & Saturation Mechanism

Purge

"B" Source Feeding

A Source :

B Source :

Purge

Chemical Reaction between B and A Sources & Saturation Mechanism

---

Advantages of ALD
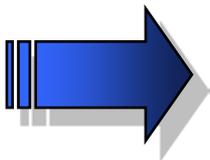
- **Accurate and simple thickness control.**
- **Good reproducibility.**
- **Sharp interfaces.**
- **Low processing temperature.**
- **Uniform, conformal, and dense films.**

Controlled Growth of Silicon Nanocrystals in a Plasma Reactor

Hydrogenated Si nanoparticles
in SiH_4 plasma reactor @ 300 K

Electron density of $Si_{19}H_{12}$ isomer
with cylindrical configuration

Phys. Rev. Lett. **95**, 165502 (2005)

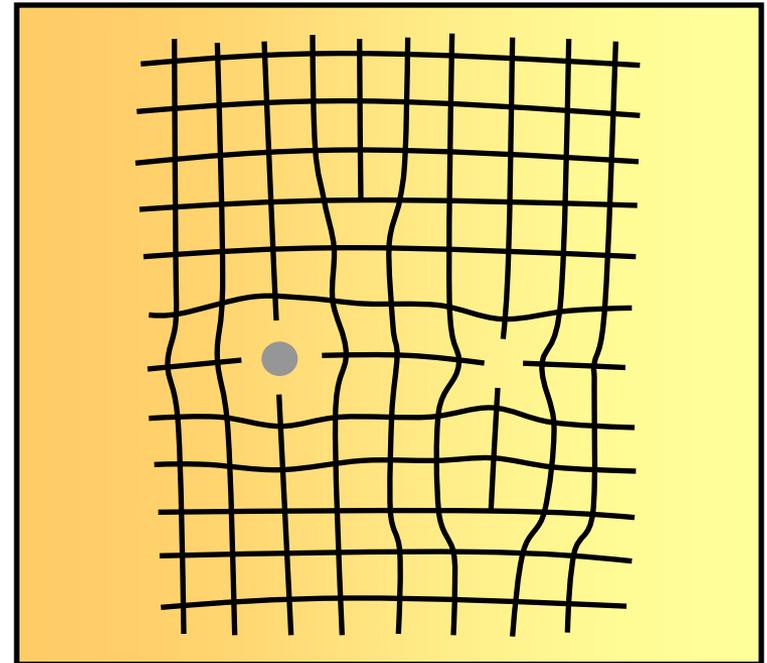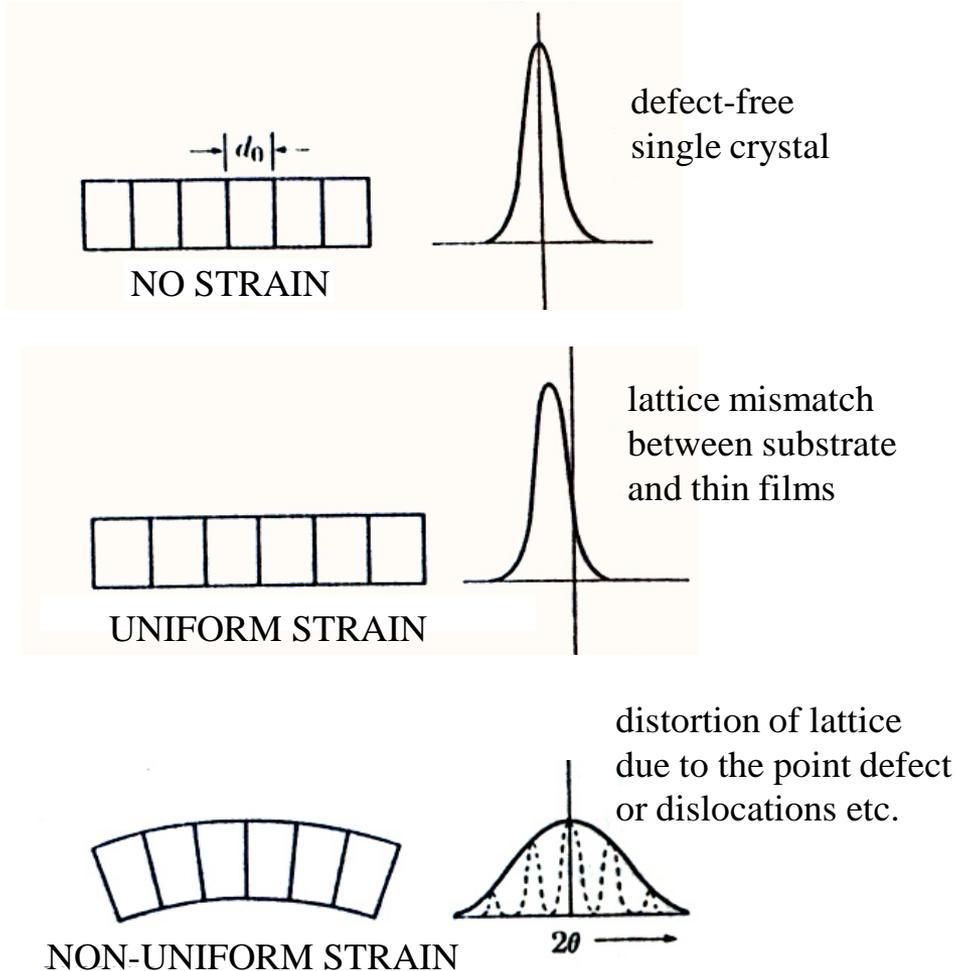**H**

Si

$Si_{19}H_{12}$

(Large dipole moment
→ "off center" of internal Si)

Strong permanent dipole moment (1.9 D)
→ 2 building blocks align themselves
→ Beginning of nanowire formation
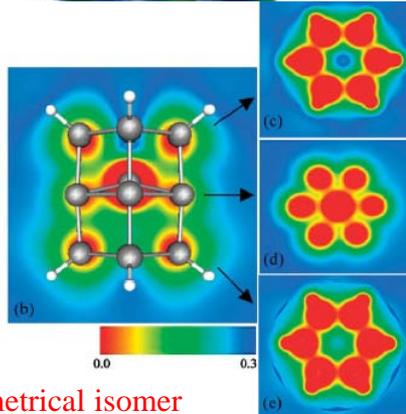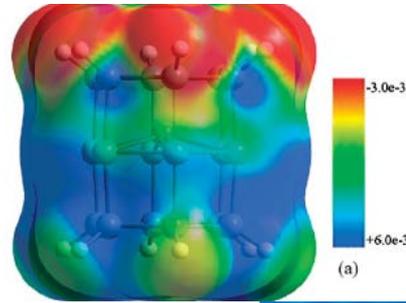
Geometrical isomer
(30° rotation of center hexagon ring)
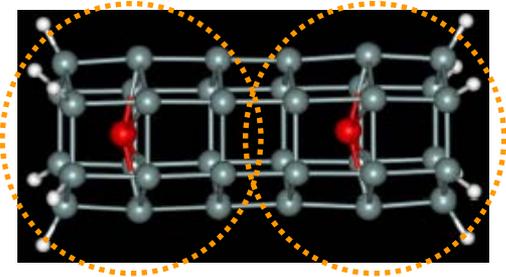
Molecular Dynamic (MD) Simulations 이용:
CVD Plasma -- Si Nanostructures의 Growth Mechanisms

Amorphous, H-Rich Crystalline, Poor Crystalline, or Tubelike $Si_{19}H_{12}$

Non-Uniform Distribution of Local Strain

defect-free
single crystal

NO STRAIN

lattice mismatch
between substrate
and thin films

UNIFORM STRAIN

distortion of lattice
due to the point defect
or dislocations etc.

NON-UNIFORM STRAIN

2θ

Non-Uniform Local Strain

*Point Defects, Off-Stoichiometry,
Stacking Faults, Dislocations, etc.*

A SURFACE VIEW OF ETCHING

Experiments conducted with scanning tunneling microscopes in ultrahigh vacuum reveal a fascinating, step-by-step picture of the etching process.

John J. Boland and John H. Weaver

Chemical etching has been practiced since at least the late Middle Ages. In its early form, it involved coating an object, such as a metal plate, with wax, carefully patterning the hardened wax by cutting down through it with a sharpened tool to expose but not penetrate the object's surface and then exposing the object to an etching solution, typically an acid. With time, the etchant molecules in the solution would react with atoms of the exposed surface to form reaction products that would dissolve, thereby removing material from the surface.

exposed to gaseous molecules, rather than to liquids, and the etch products are desorbed into the vapor. Since desorption requires energy to break surface bonds, temperatures as high as 900 K may be needed. In many cases, therefore, it is advantageous to alter the surface chemistry and enhance the formation of volatile species. Numerous so-called assisted etching techniques have been developed to increase etching rates, to achieve directed or anisotropic etching and to make etching possible, at reduced temperatures, for even the most inert materials.
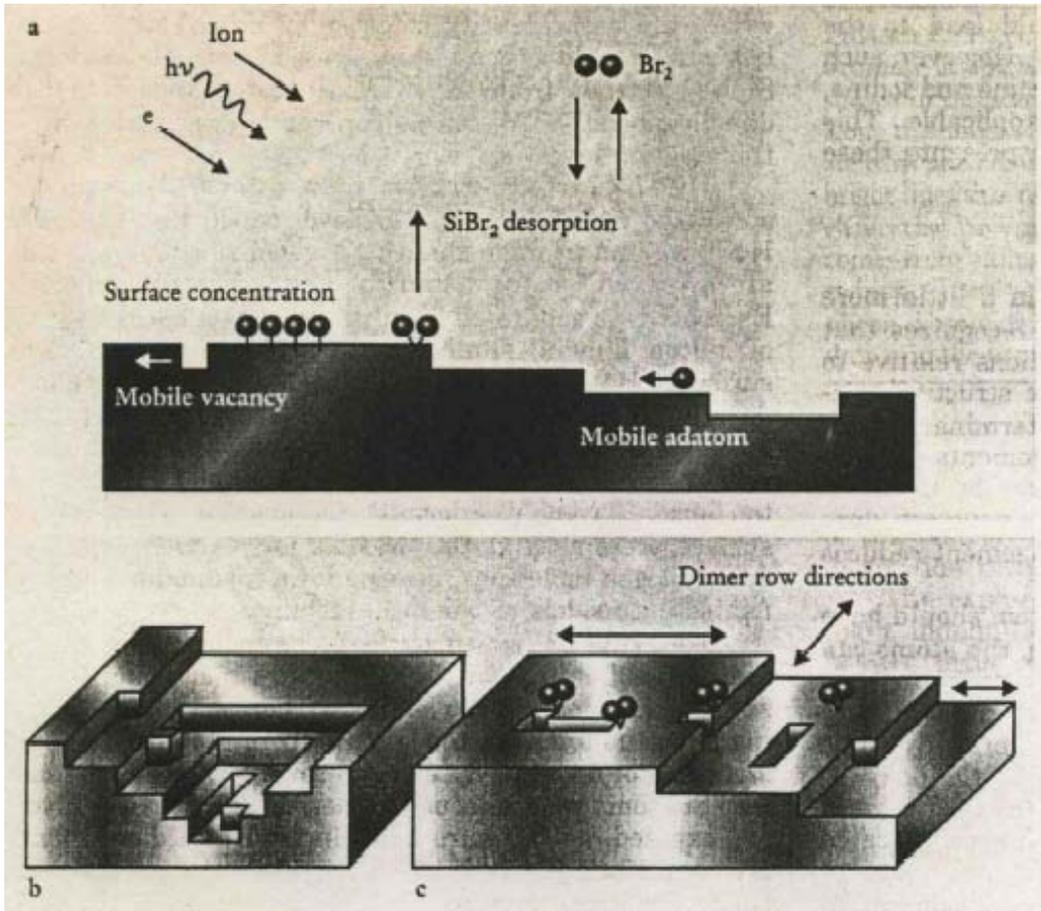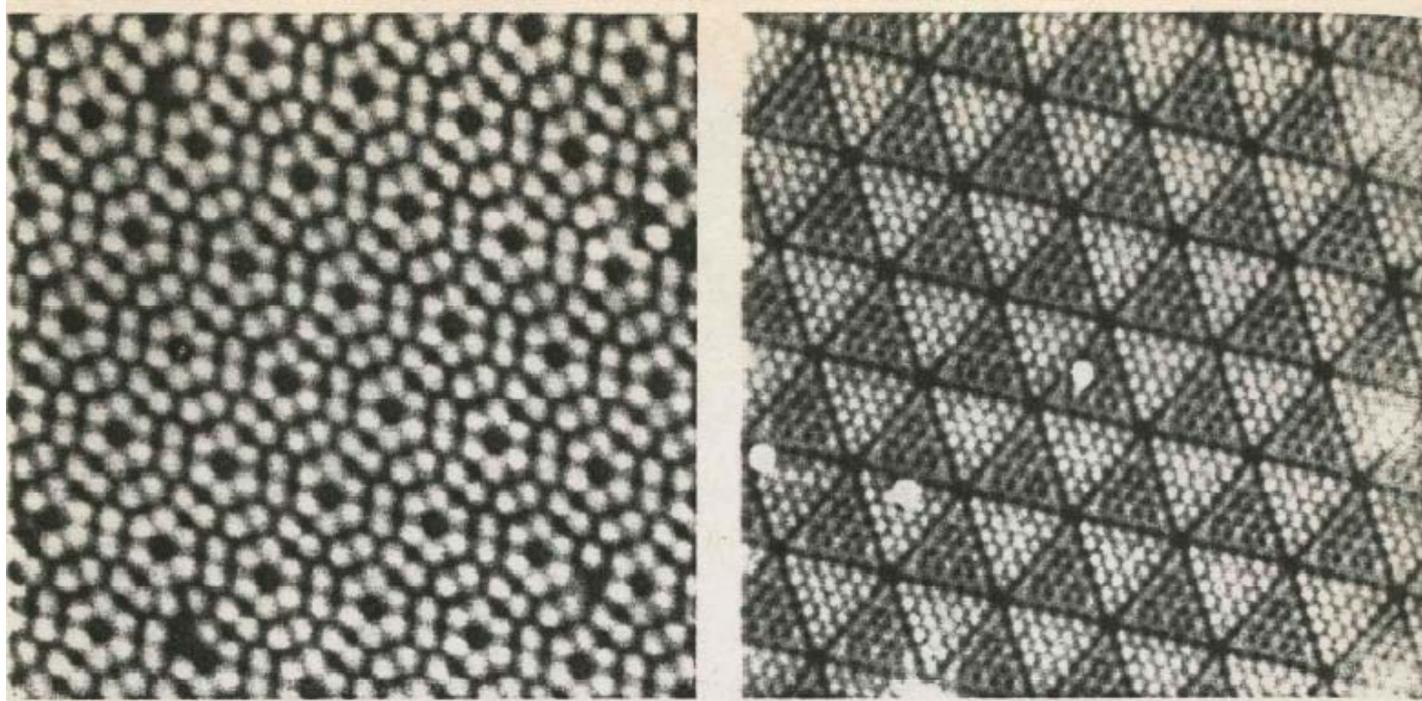
(a) Being exposed primarily to bromine molecules, but also to electrons, protons and ions

(b) Deeply indented surface
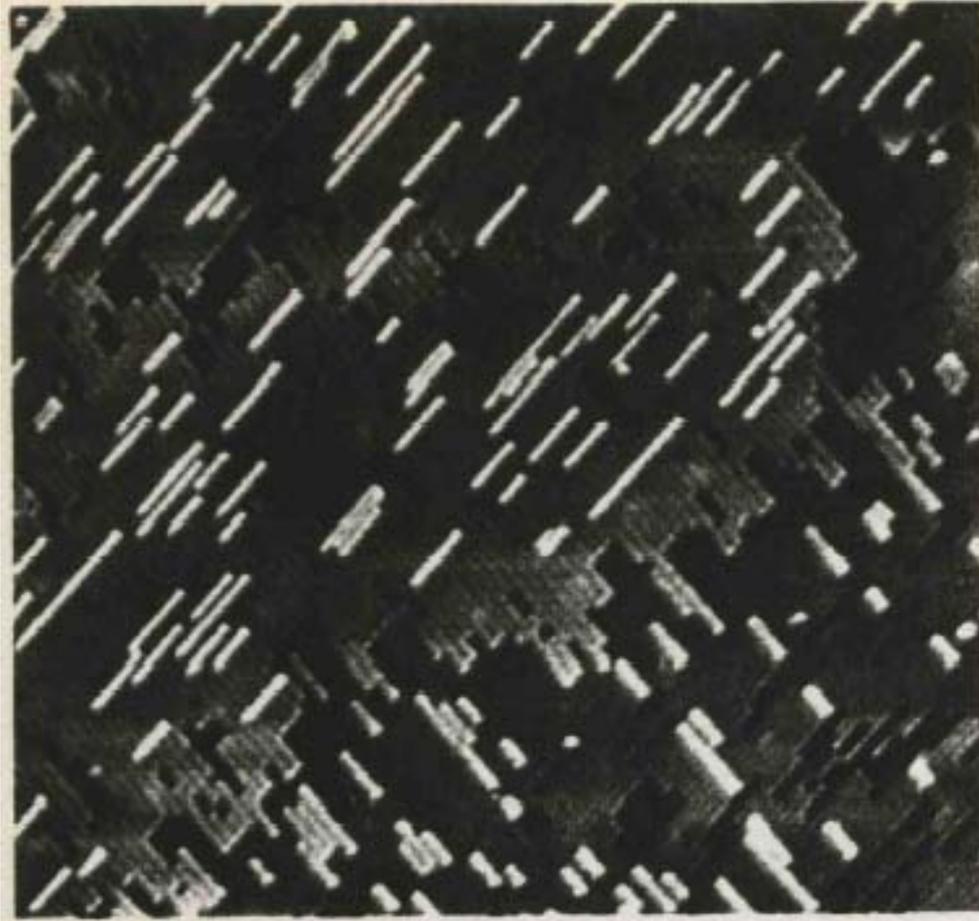
(c) Desorption at different surface sites.

Before and after the removal of adatoms from a reconstructed 7 × 7 (111) surface as imaged by STM

| The adatom layer of the clean Si(111) 7 × 7 surface. | The rest layer following removal of the adatom layer by bromine etching at 675 K. |

The dark areas represent pits, one atom layer deep.

The bright lines are silicon dimer chain.

Ferromagnetic Domains in a Single Crystal

Single Crystal Ni
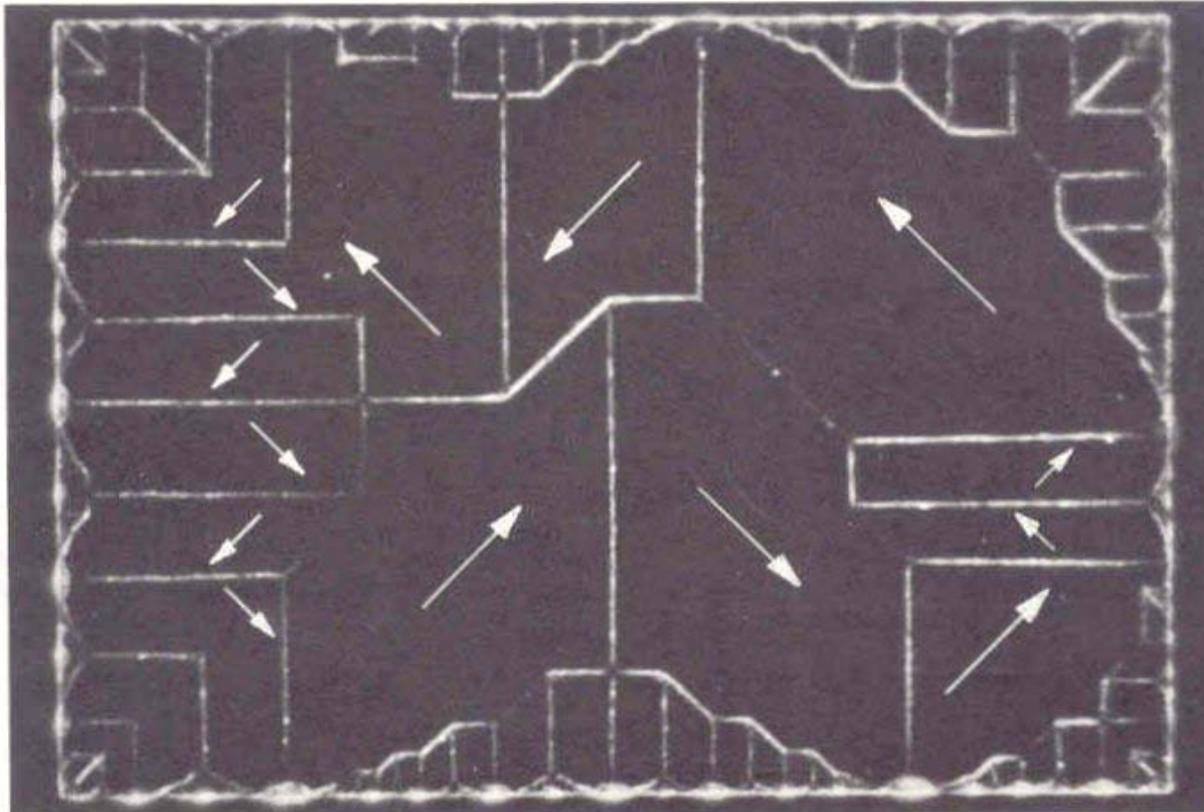
C—Ni

Figure 27 Ferromagnetic domain pattern on a single crystal platelet of nickel. The domain boundaries are made visible by the Bitter technique. The direction of magnetization within a domain is determined by observing growth or contraction of the domain in a magnetic field. (After R. W. De Blois.)
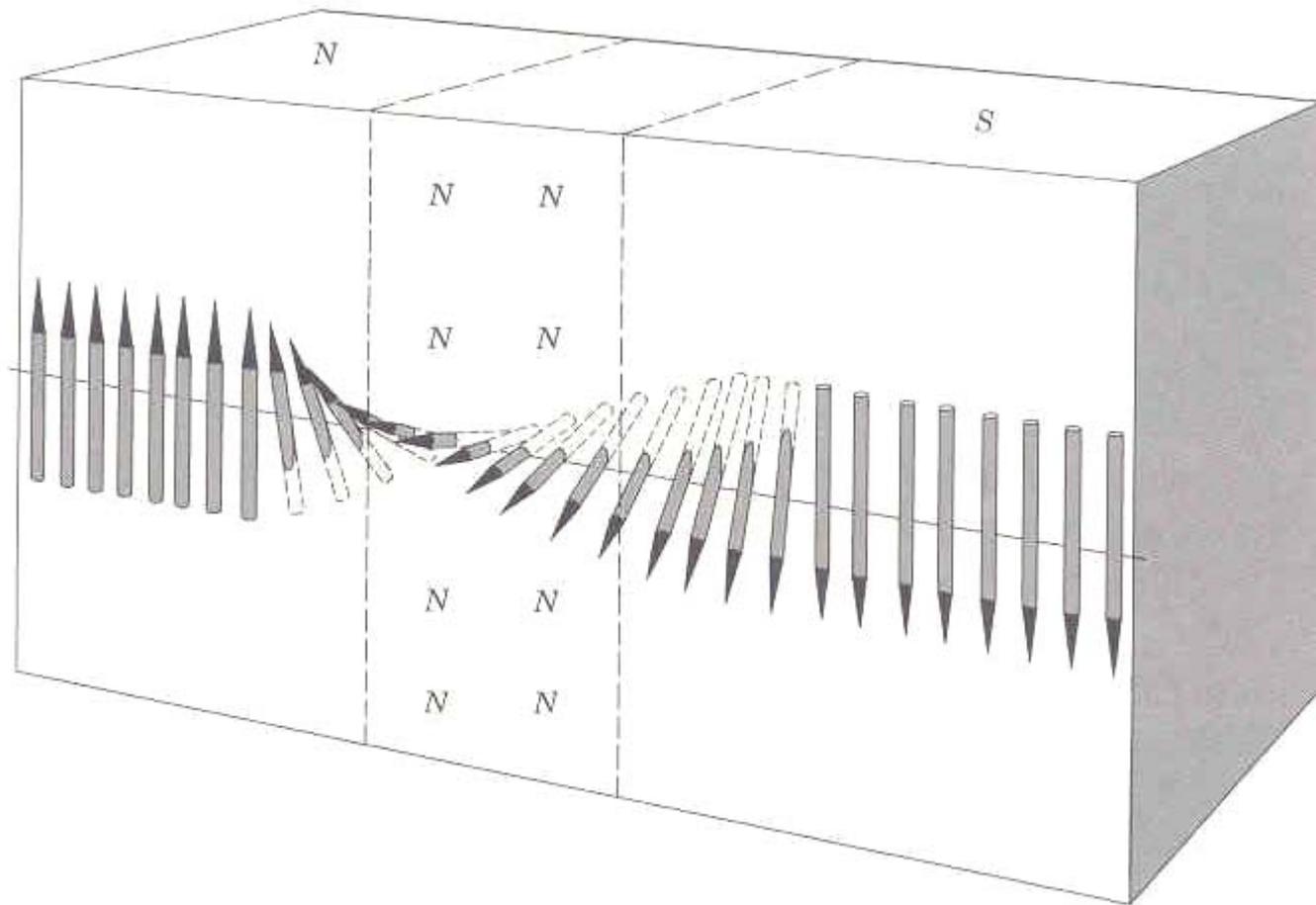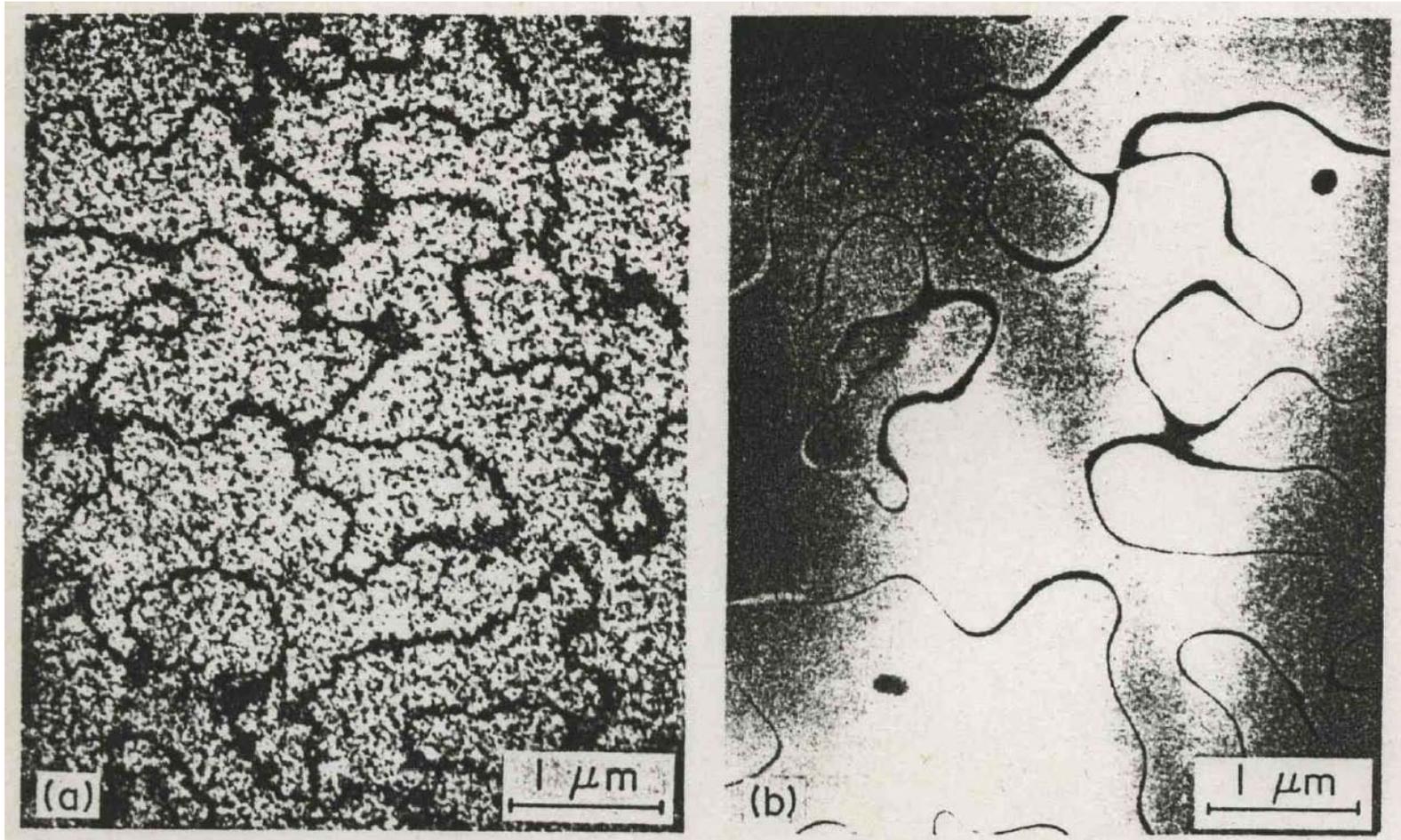
Figure 32 The structure of the Bloch wall separating domains. In iron the thickness of the transition region is about 300 lattice constants.

Domain Size (L) vs. Correlation Length of Fluctuations (ξ)
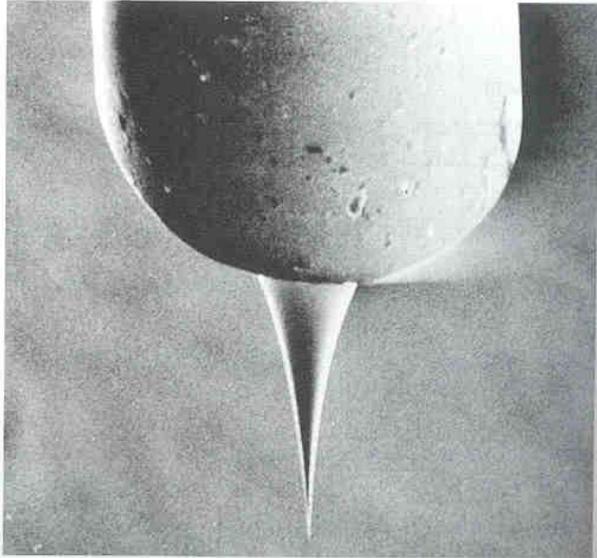

ξ : *Correlation Lengths of Fluctuations*

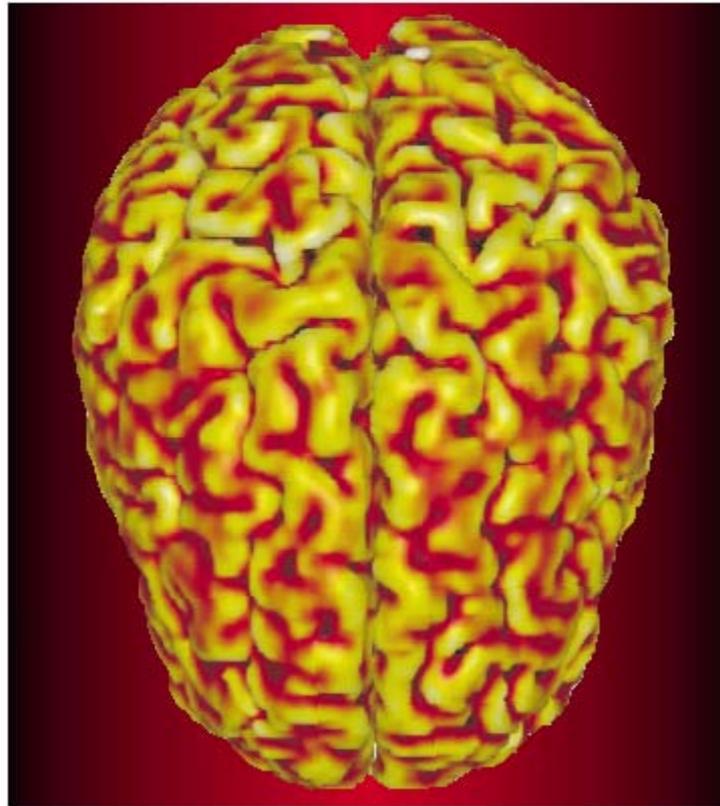L : *Domain Size*
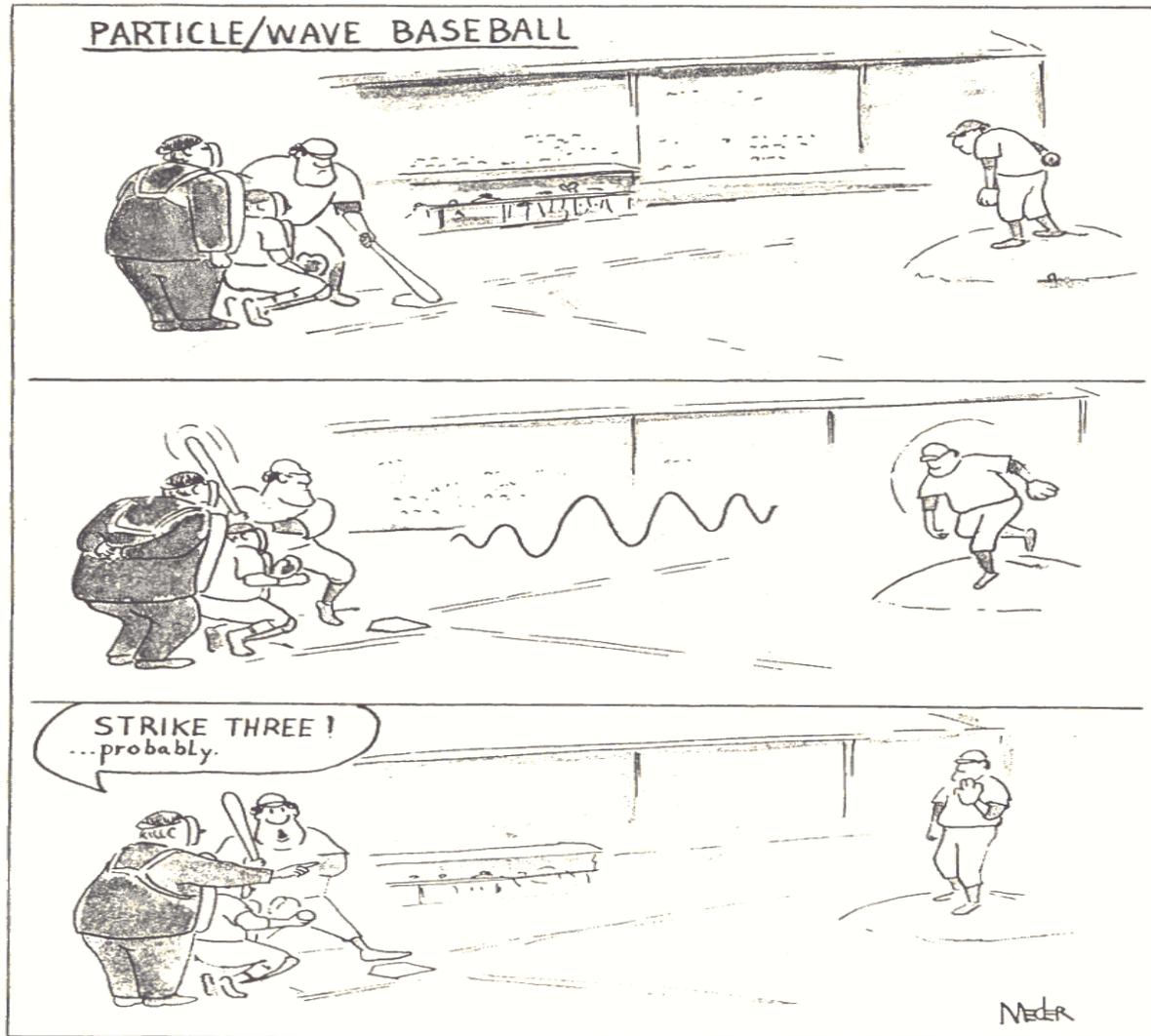
Scanning Tunneling Microscopy

The tungsten probe of
a scanning tunneling microscope.
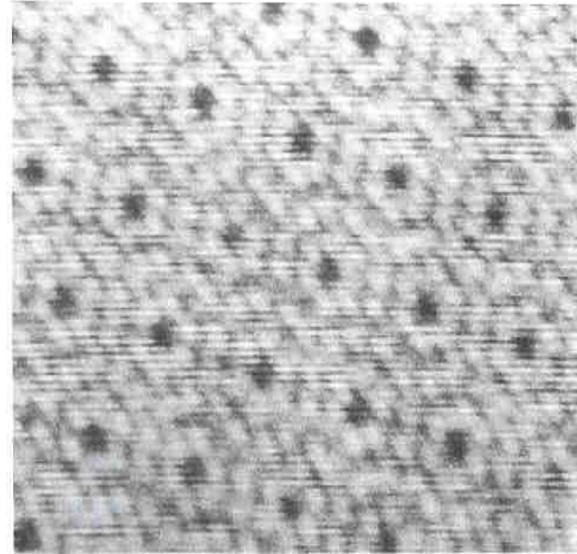
Silicon atoms on Si (111) surface of a
silicon single crystal form a repeated
pattern (produced by STM).

Reconstructing the brain activity from magnetic-resonance imaging.

If in some cataclysm, all scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or atomic fact, or whatever you wish to call it) that all things are made of atoms.

R. P. Feynman

''The Feynman Lectures on Physics''
Addison-Wesley Publishing Company
Reading, Massachusetts
Vol. 1, p. 1–2, 1963
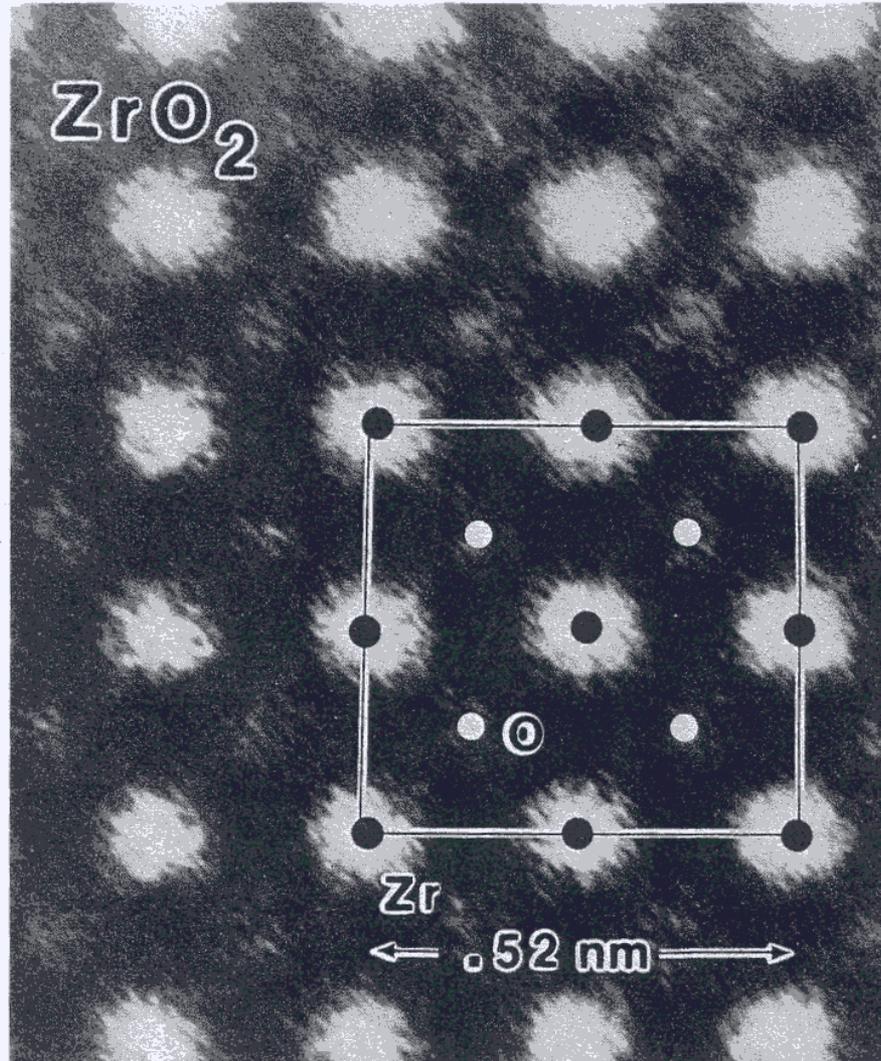
The atomic-resolution electron microscope permits imaging of the regular arrangement of atoms in a crystalline structure. For this ceramic material, the arrangement of zirconium and oxygen ions can be compared with the atomic-scale geometry of Figure 3.4-3. (Courtesy of R. Gronsky, National Center for Electron Microscopy, Berkeley, California)

Schematic Structure of CH_4: sp^3 Orbital
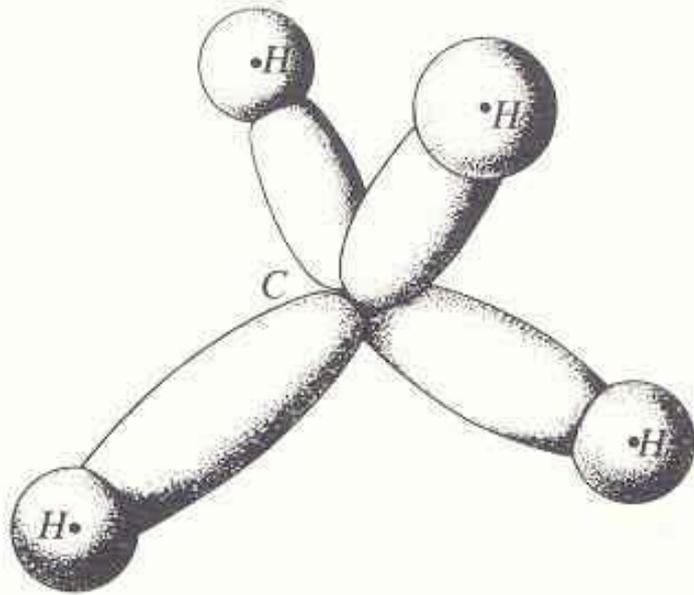
SP^3

FIGURE 10

Schematic structure of the methane molecule. The sp^3 orbitals produce bonds arranged like the straight lines joining the center of a tetrahedron to its four corners (angles of 109°28').
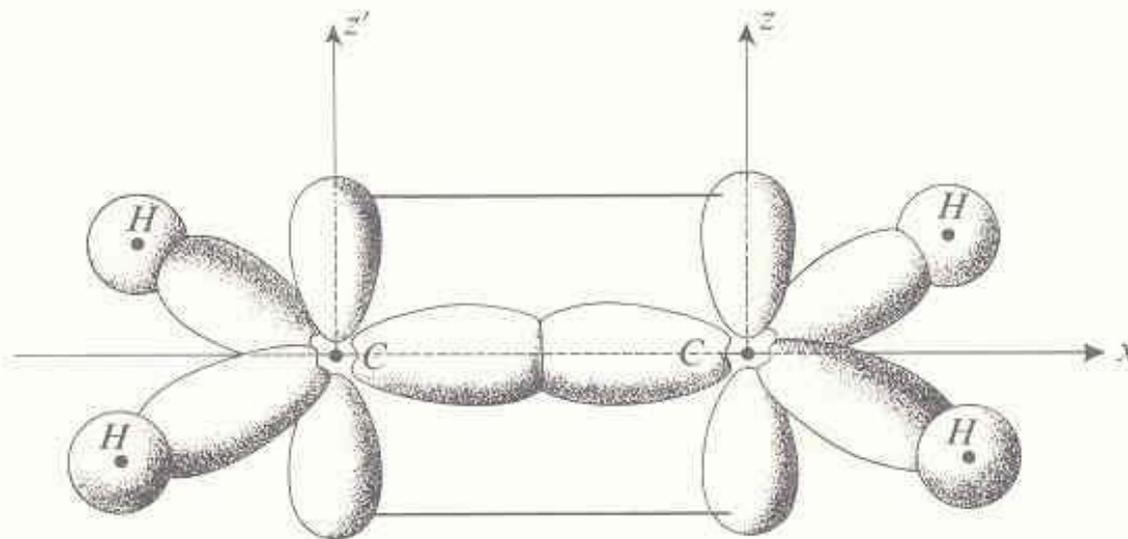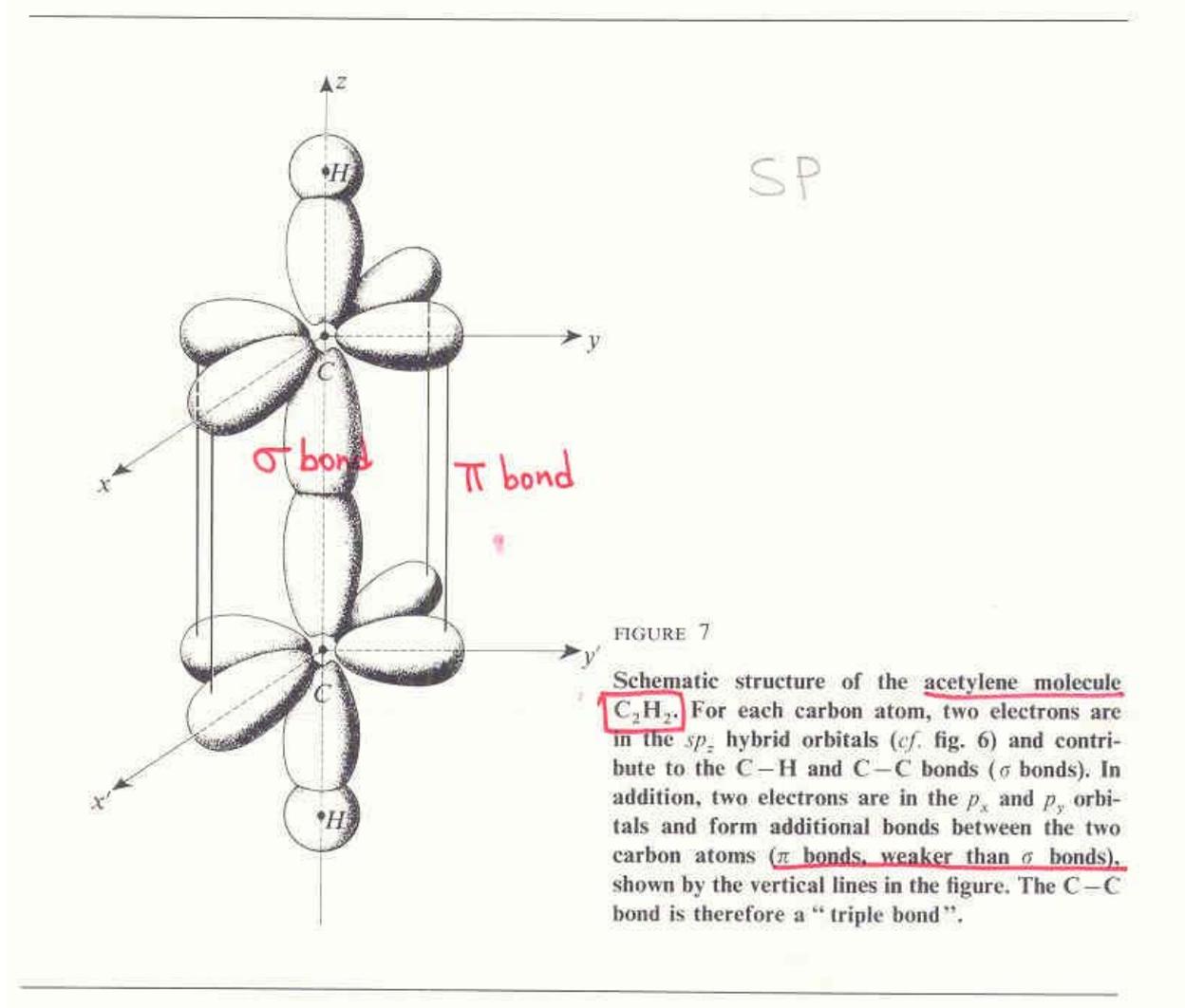
Schematic Structure of C₂H₄: sp² Orbital

FIGURE 9

Schematic structure of the ethylene molecule C_2H_4. The two carbon atoms form a double bond with each other : one σ bond due to sp^2 orbitals of the type of those shown in figure 8 (the other two sp^2 hybrid orbitals at 120° with this one form the C − H bonds), and one π bond, due to the overlapping of the p_z orbitals.

SP

σ bond

π bond

FIGURE 7

Schematic structure of the acetylene molecule C_2H_2. For each carbon atom, two electrons are in the sp_z hybrid orbitals (cf. fig. 6) and contribute to the C−H and C−C bonds (σ bonds). In addition, two electrons are in the p_x and p_y orbitals and form additional bonds between the two carbon atoms (π bonds, weaker than σ bonds), shown by the vertical lines in the figure. The C−C bond is therefore a "triple bond".

Fig. 1 Electron diffraction pattern from a $Ga_{1.0}Mg_{1.8}Zn_{2.1}$ icosahedral crystal in a melt-spun ribbon.
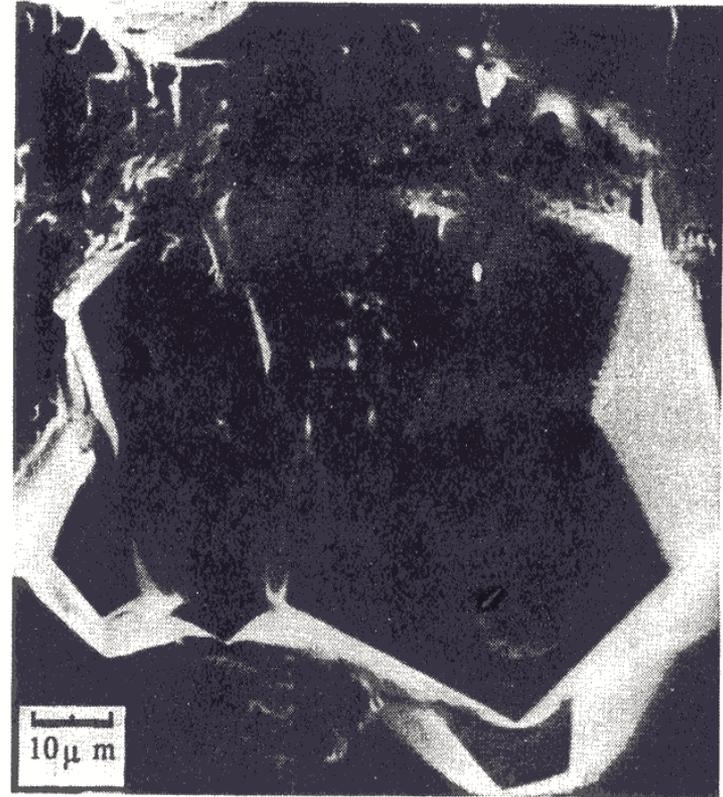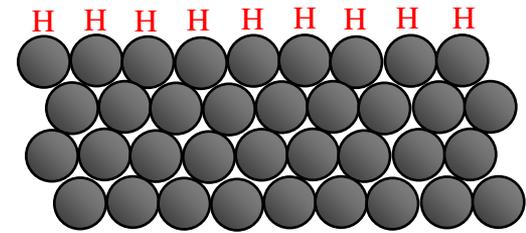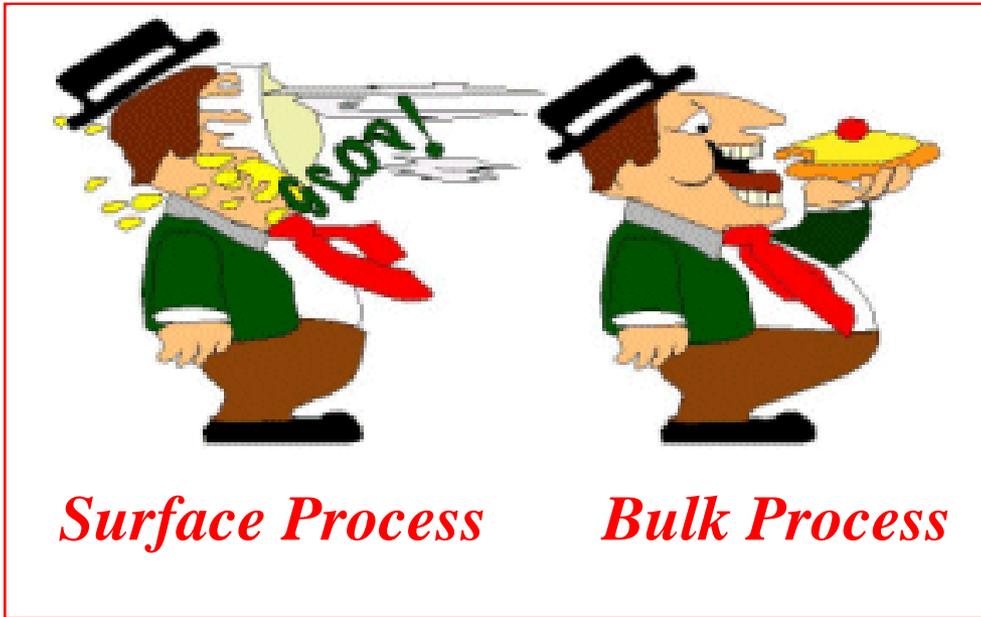

Fig. 3 Scanning electron micrograph of icosahedral crystals with pentagonal dodecahedral growth morphology found in a shrinkage cavity of a slowly cooled $Ga_{1.0}Mg_{2.1}Zn_{3.0}$ingot.
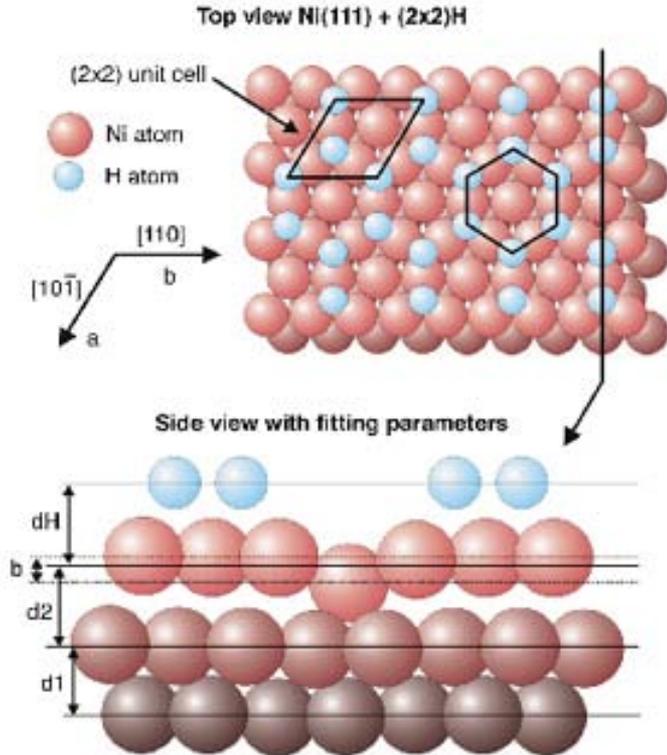
Adsorption vs. Absorption

Adsorption　　Absorption

Surface Process　　*Bulk Process*

H adsorption on Si

Dr. K. L. Yeung (Hong Kong Univ.)
http://teaching.ust.hk/~ceng511/notes/

Adsorption vs. Absorption

Top view Ni(111) + (2x2)H

(2x2) unit cell

● Ni atom
○ H atom

[110] b

[10$\bar{1}$] a

Side view with fitting parameters

dH
b
d2
d1

- The model of the UHV low-T p(2×2) structure of H adsorbed on Ni(111) proposed. The fitting parameters of the atomic model are shown.
- The values of these parameters found from our SXRD data compare well with the ones found from the LEED study.
- K. Müller's group (Universität Erlangen-Nürnberg, Germany) *Phys. Rev. B* **47**, 15969 (1993)

Hydrogen-induced restructuring of close-packed metal surfaces: H/Ni(111) and H/Fe(110)

L. Hammer, H. Landskron, W. Nichtl-Pecher, A. Fricke, K. Heinz, and K. Müller
Festkörperphysik, Universität Erlangen-Nürnberg, Staudt-Strasse 7, D-8520 Erlangen, Germany
(Received 4 March 1993)

We report that hydrogen can induce surface reconstructions by adsorption even on close-packed substrates. New low-energy electron-diffraction analyses for H/Ni(111) and H/Fe(110) show that consideration of reconstruction is essential for a convincing experiment-theory fit as well as for reliable determination of the adsorption site. There are two different types of reconstruction: Hydrogen pulls nickel atoms out of the surface but pushes iron atoms towards the bulk. These findings are mirrored by a different sign of work-function change for both systems and demonstrate the correlation between geometric and electronic structure.
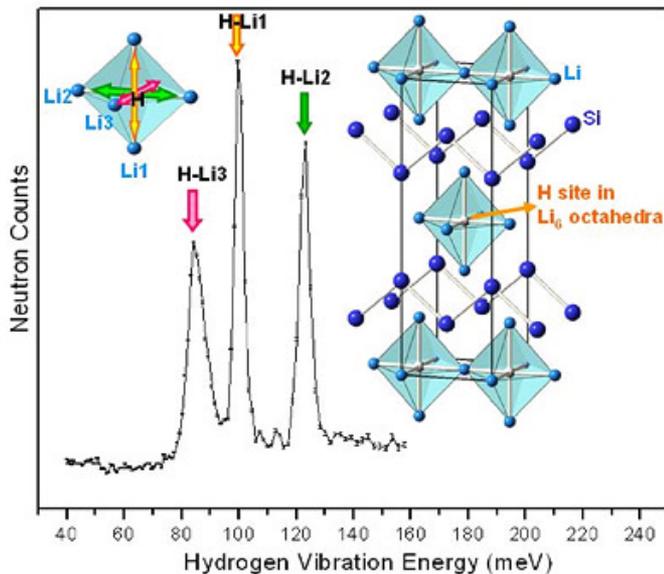
Metal Hydride – Hydrogen Storage
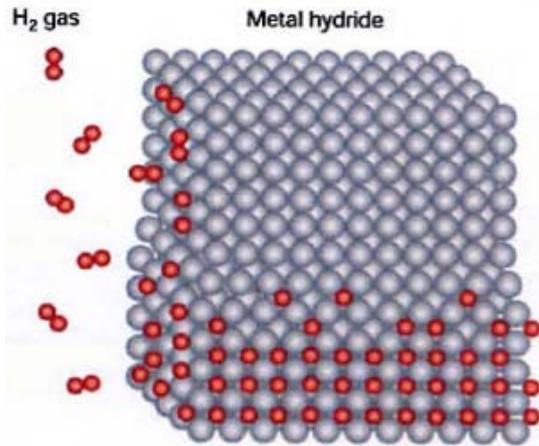
Schematic of Metal Hydride
from MRS Bulletin **27** (2002)
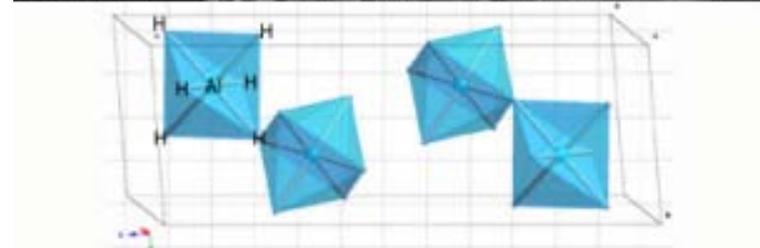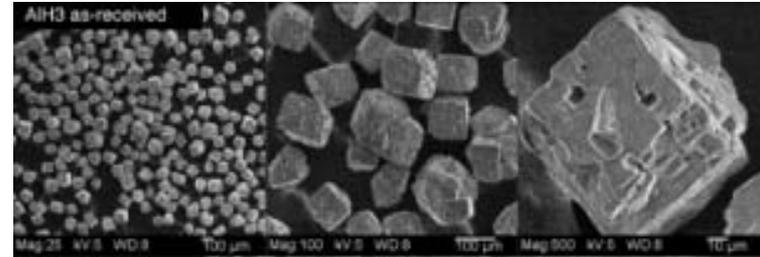
SEM and Crystal Structure of **AlH₃**
DOW Chem. Co.
http://www.dow.com

Structure and Vibration of Hydrogen Atoms bound in **Li₄Si₂H**
University of Maryland
http://www.mse.umd.edu/research/spotlight/h-storage.html

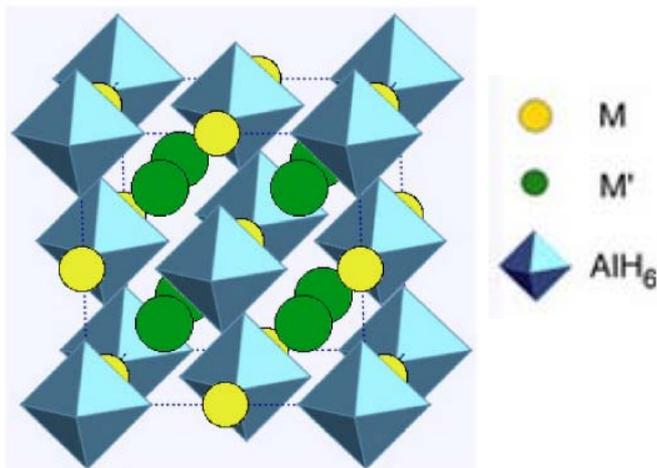# *Metal Hydride – Hydrogen Storage*

FIG. 7. (Color online) Structural diagram of $M_2M'AlH_6$ showing AlH_6 octahedra, M cations (large) and M' cations (small).

J. Graetz *et al*.
Phys. Rev. B **71**, 184115 (2005)

Structures and thermodynamics of the mixed alkali alanates

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The thermodynamics and structural properties of the hexahydride alanates ($M_2M'AlH_6$) with the elpasolite structure have been investigated. A series of mixed alkali alanates (Na_2LiAlH_6, K_2LiAlH_6, and K_2NaAlH_6) were synthesized and found to reversibly absorb and desorb hydrogen without the need for a catalyst. Pressure-composition isotherms were measured to investigate the thermodynamics of the absorption and desorption reactions with hydrogen. Isotherms for catalyzed (4 mol% $TiCl_3$) and uncatalyzed Na_2LiAlH_6 exhibited an increase in kinetics, but no change in the bulk thermodynamics with the addition of a dopant. A structural analysis using synchrotron x-ray diffraction showed that these compounds favor the $Fm\overline{3}m$ space group with the smaller ion (M') occupying an octahedral site. These results demonstrate that appropriate cation substitutions can be used to stabilize or destabilize the material and may provide an avenue to improving the unfavorable thermodynamics of a number of materials with promising gravimetric hydrogen densities.
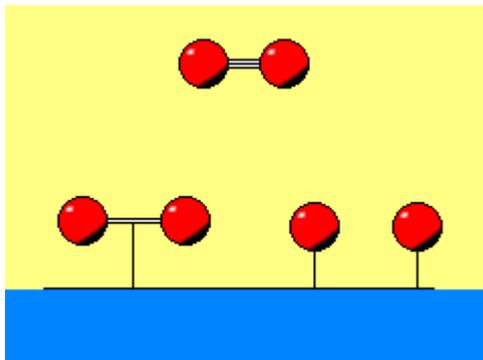
Types of Adsorption Modes
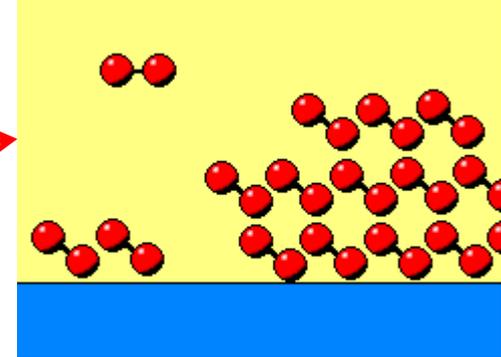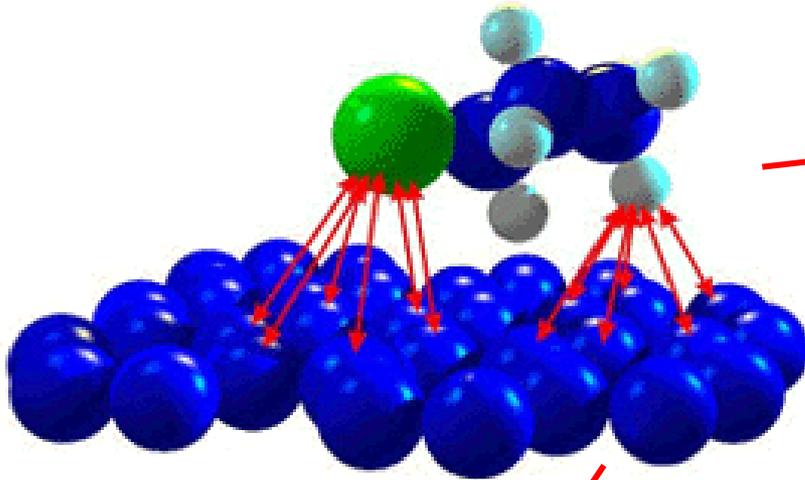
Physical Adsorption or
Physisorption

Bonding between molecules and surface is by **weak van der Waals forces**.

Chemical bond is formed between molecules and surface.

Chemical Adsorption or
Chemisorption

Dr. K. L. Yeung (Hong Kong Univ.)
http://teaching.ust.hk/~ceng511/notes/

MRS Spring Meeting

Mountaineering

Covalent Bonding