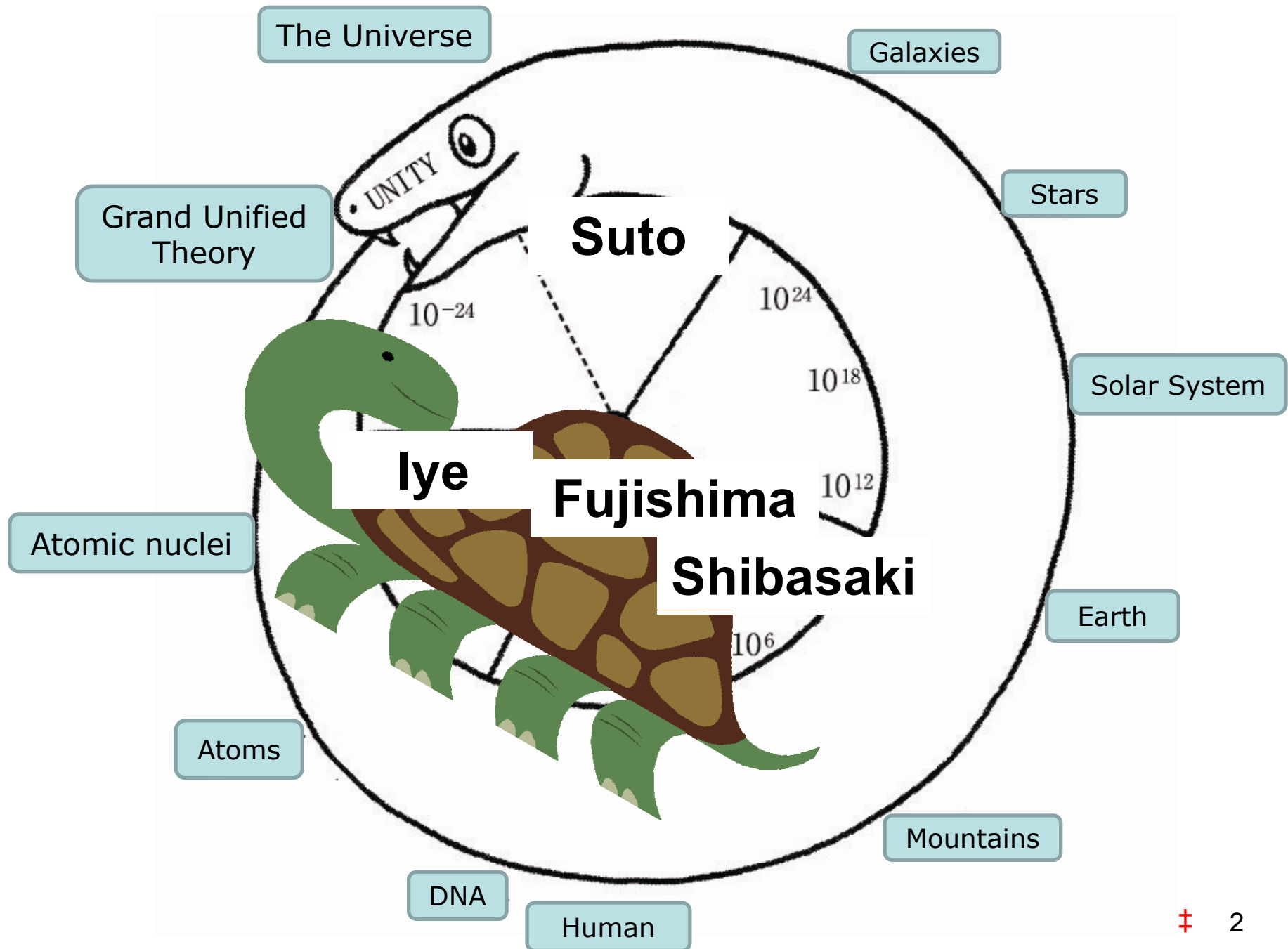


† Source: *Mono-no Okisa (The size of materials)*, Yasushi Suto, 2006, The University of Tokyo Press



Global Focus on Knowledge

# The Production and Application of Matter

Lecture 2: Conjugation (devices)

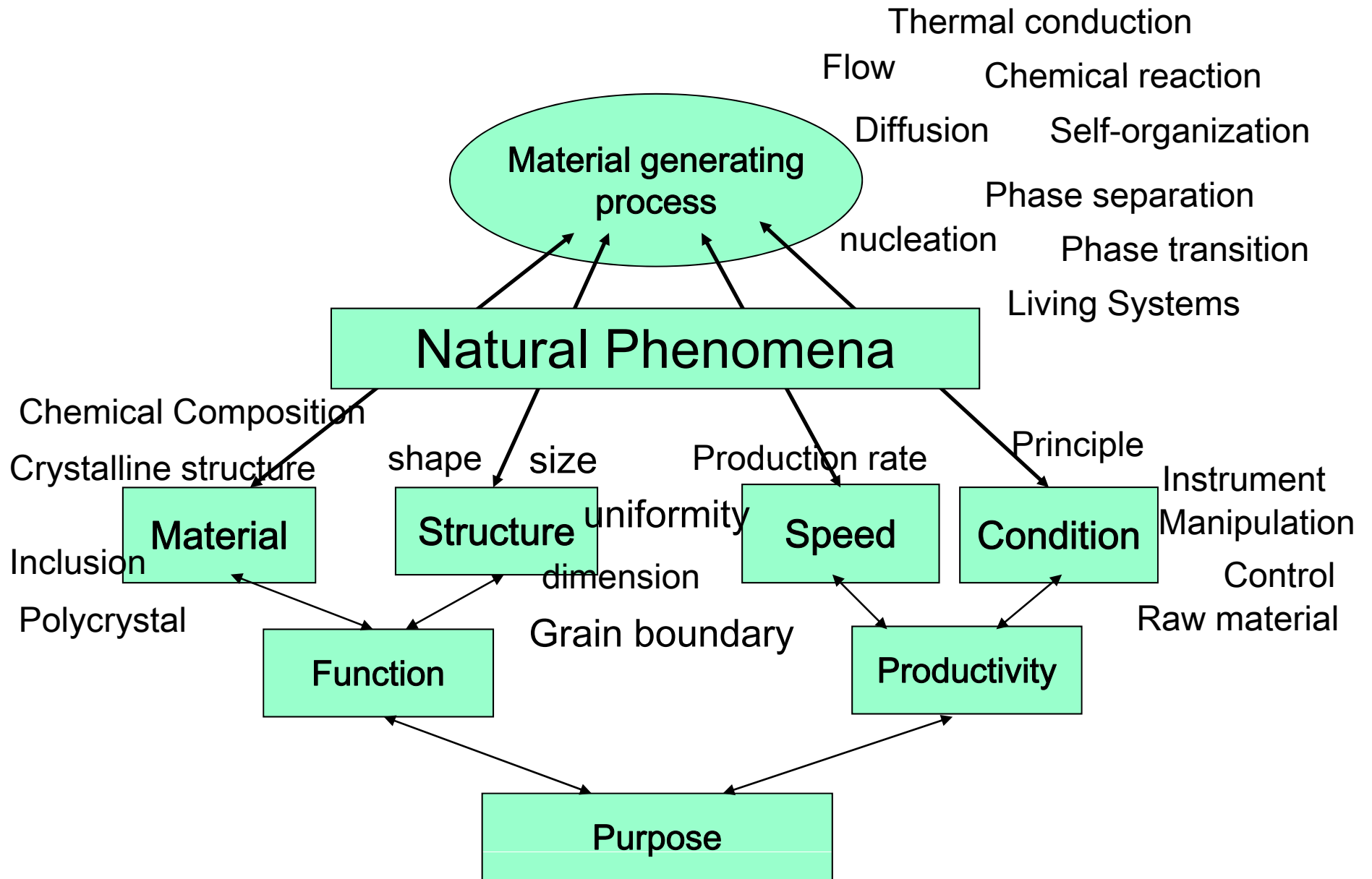
Semiconductors (Si, GaAs)

Soft matters

Hiroshi Komiyama

(the University of Tokyo)

The figures, photos and moving images with #marks attached belong to their copyright holders. Reusing or reproducing them is prohibited unless permission is obtained directly from such copyright holders.



## Introduction

**Semiconductors:** semiconductor devices,  
Optical Fibers, photocatalytic reactor

Composition, Structure (Form and size in particular)  
Speed

Phenomena: Flow, Diffusion, Thermal Conduction

**Soft matters:** Liquid Crystal Displays,  
Color films, Color Filters, Molecular Sensors

Substance (Molecular structure, Molecular Design)  
Structure (Form)

Speed (multilayer coating/ Inkjet Prints) • Conditions  
Phenomena: Self-Organizations, Chemical Reactions,  
Flows (driven by surface tension)

## **II-1. Inorganic Materials**

Semiconductor Devices , Optical Fibers,  
Chemical Reactors

Composition, Structure (Size and Form), Speed

Phenomena: Flow, Diffusion, Thermal Conduction

# Semiconductors

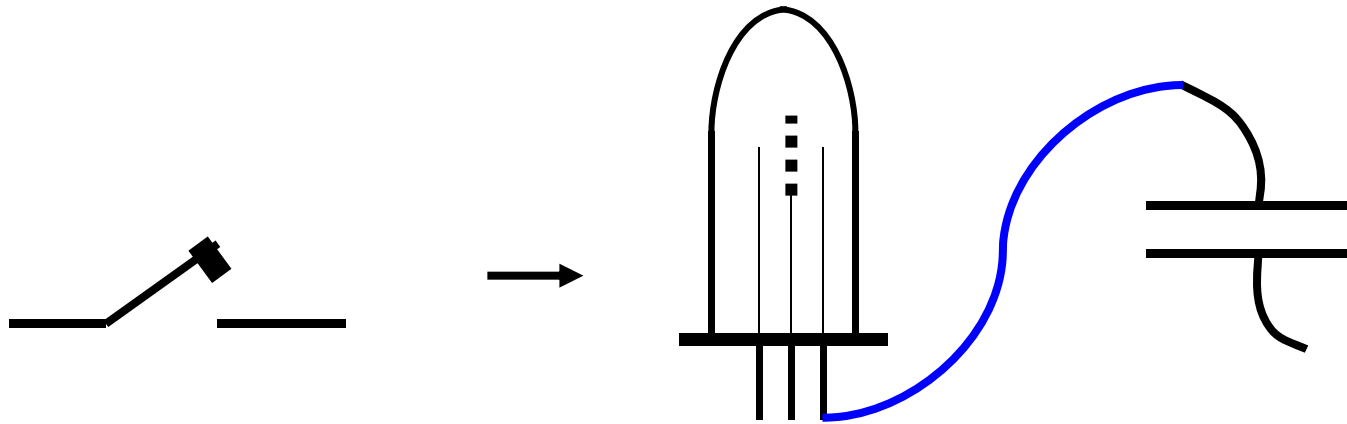
Electric conductance dramatically changes ( $10^{10}$  times) due to impurities, optical irradiations, electric fields

Metals:  $10^{-6} \sim 10^{-4} \Omega\text{-cm}$

Semiconductors:  $10^{-3} \sim 10^8 \Omega\text{-cm}$

Insulators:  $10^{10} \Omega\text{-cm} \sim$

# Memory devices composed of switches and binary cells



Telegrams and  
computations using  
mechanical switches

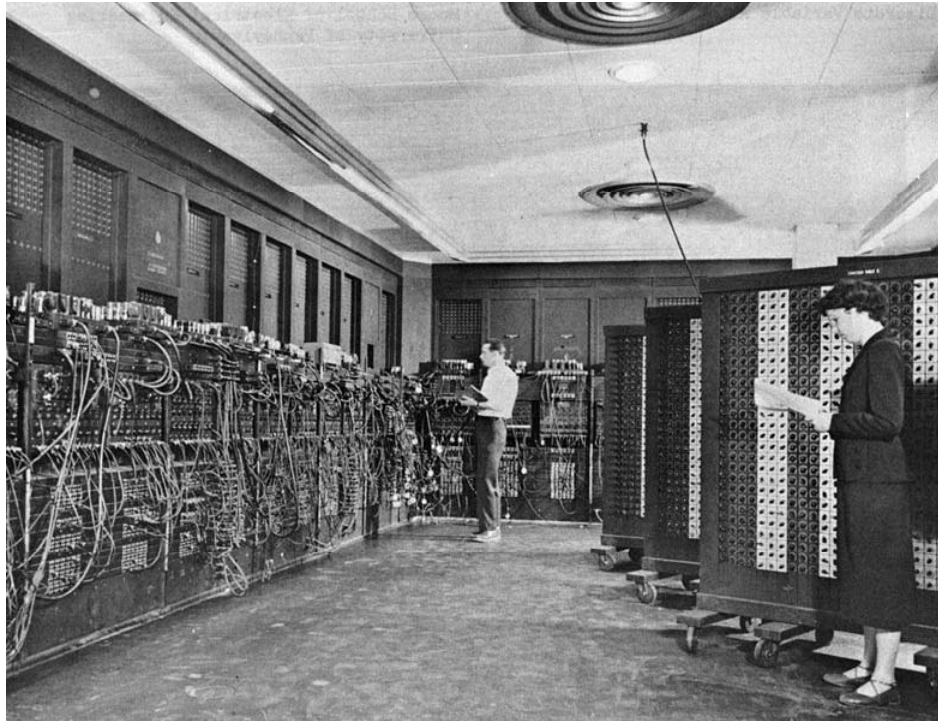
Vacuum tube

Capacitor

$$Q = CV$$



# Vacuum Tube Computers



Source:  
Wikipedia

1946: ENIAC (Electronic Numerical Integrator and Computer)

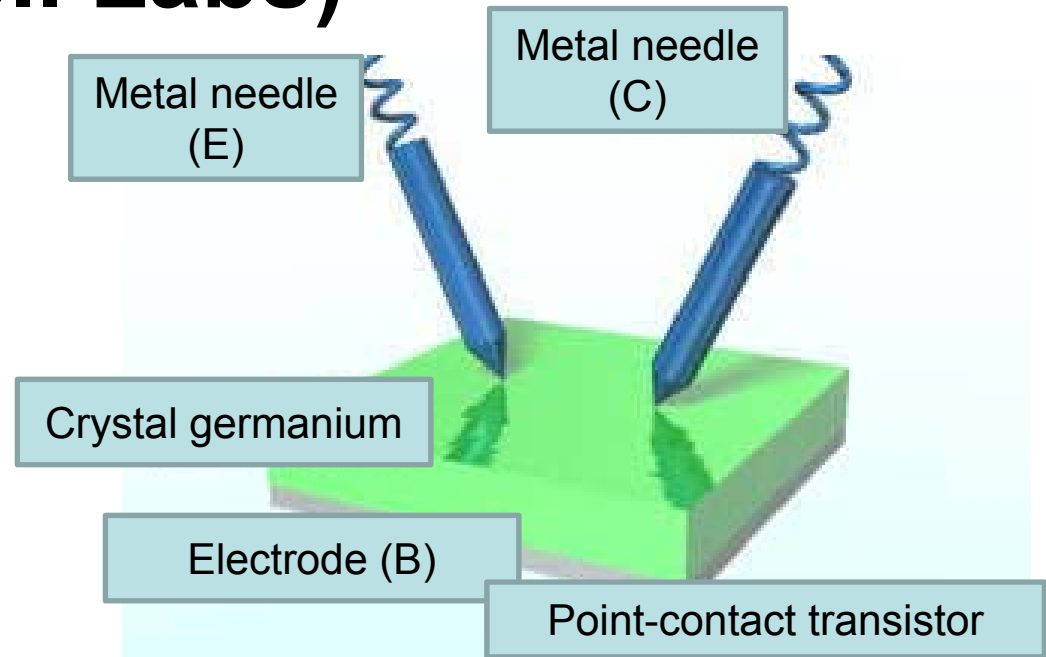
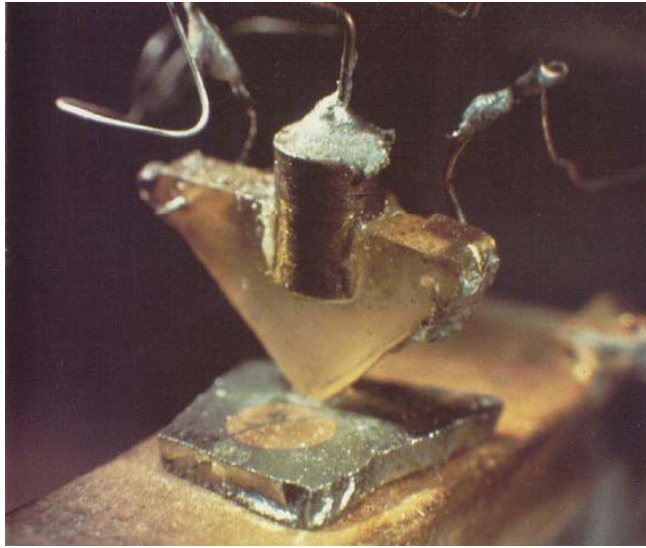
The world's first electric Computer equipped with 18,000 vacuum tubes

It took three seconds to compute a ten-digit ballistic trajectory.

ballistic computing

- power consumption: 140kW
- life span: several hours

# 1947 invention of the transistor (Bell Labs)



**Dec 16, 1947:**

*operation check of the first transistor*

Low energy consumption

High credibility

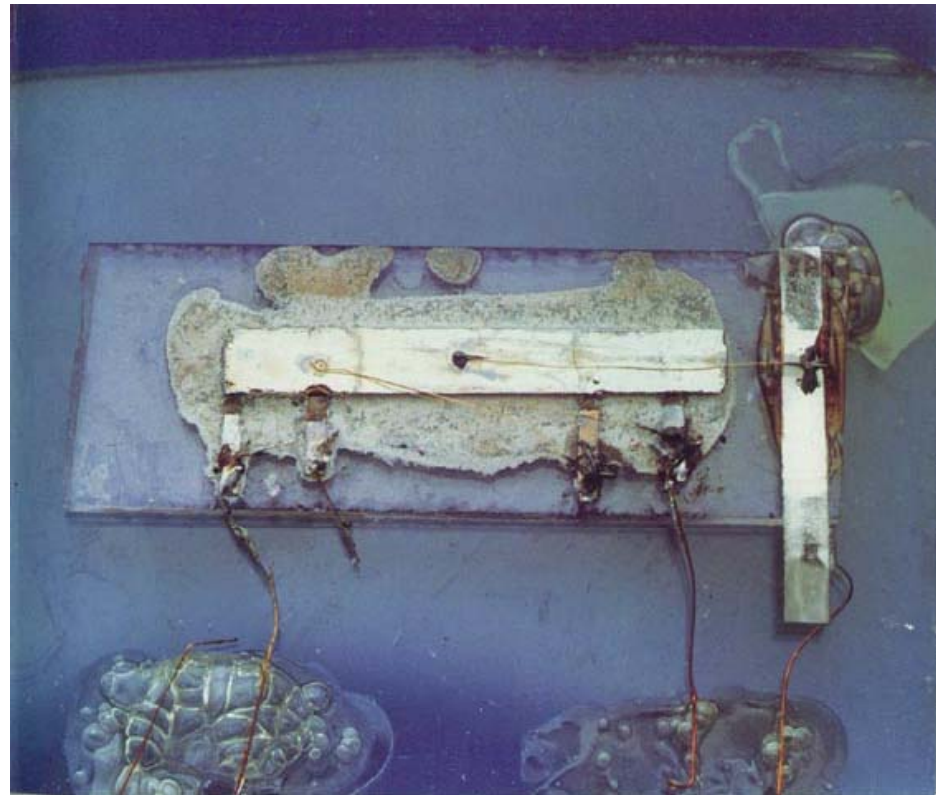
Long lifetime

**W.Brattain, J.Bardeen,  
W.Shockley  
Nobel Prize in Physics (1956)**



# Integration: From Transistors to ICs

- Utilizations of transistors
  - Radar (military purposes)
  - Telephone exchange operation by AT&T (mechanical cable type)
  - Applications to radio receivers (SONY)
  - Large scale computers (IBM)
- transistors were gradually replaced by the ICs



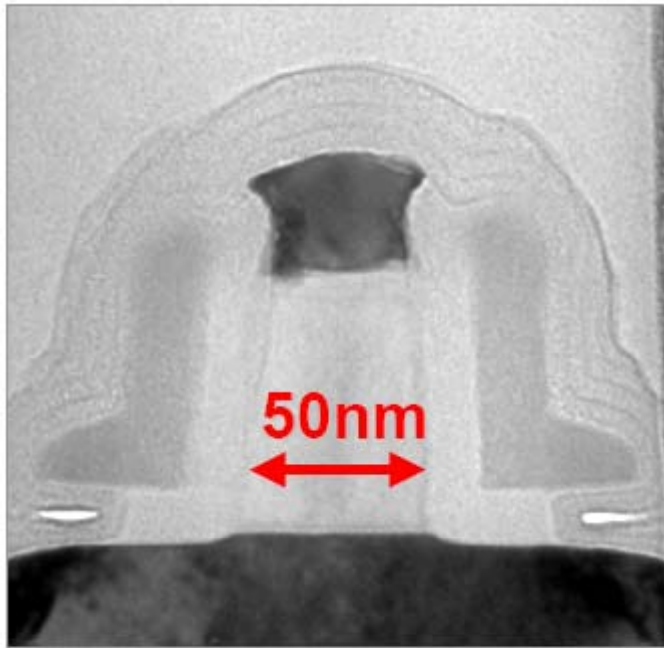
‡ Invented by Dr. Jack Kilby (Texas Instruments Inc. )  
Nobel Prize in Physics (2000)

# Advantages of Integration

- ① High work-rate thanks to miniaturization of transistors  
a transistor that is  $1/k$  times the size of the original works  $k$   
 $\sim k^2$  times faster
- ② Integration of different function enables the realization of multifunction ICs  
mixed loading of CPU, graphic ICs, and Memory chips  
→ realization of a one-chip PC etc.
- ③ Economic efficiency: decrease of prices per bit  
a factory that costs ¥200,000,000,000 produces 10,000,000 wafers every year  
→ ¥200 /chip, ¥60,000 /wafer  
→ ¥600,000,000,000 sales /year

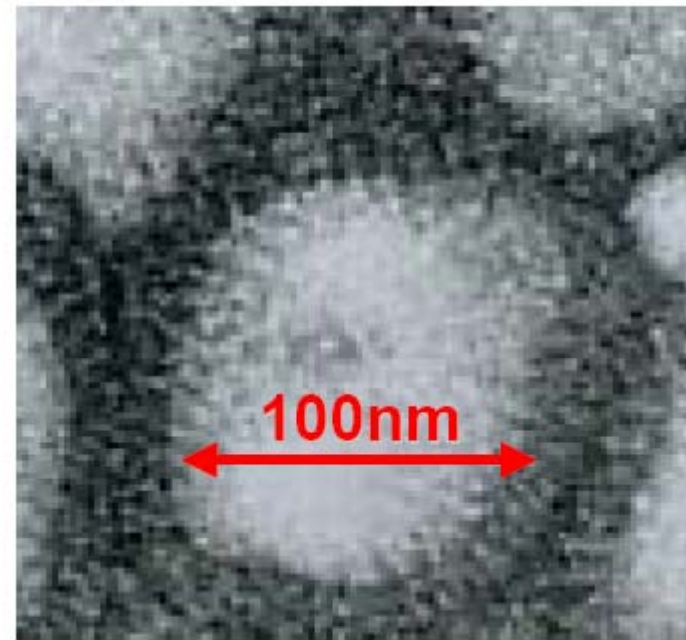
# Already smaller than a Virus

45nm process at present



**Transistor for  
90nm process**

† Source: Intel



**Influenza virus**

† Source: CDC

(Dr. Erskine Palmer, Centers for Disease Control and  
Prevention Public Health Image Library)

# History of Semiconductors

- Vacuum tubes and Solid elements coexisted
- Invention of Transistors (1947)
- Germanium (1950s)
- Silicon, IC (1960s) Integrated Circuit
- ULSI (1970s~) Ultra Large IC
- Semiconductors composed of many kinds of chemical compounds coexist
- GSI, (21<sup>st</sup> Century) Giga-scale Integration
- ???Quantum elements???

# **Driven by the Technology Advancement**

**Anyway, the surface is inevitably oxidized**

Si oxidized film is of good quality

Ge oxidized film is unstable (water soluble)

group III-V semiconductors (e.g. GaAs) are hard to control

## **The Task is Conquerable**

group III-V Semiconductors (e.g. GaAs) is luminous

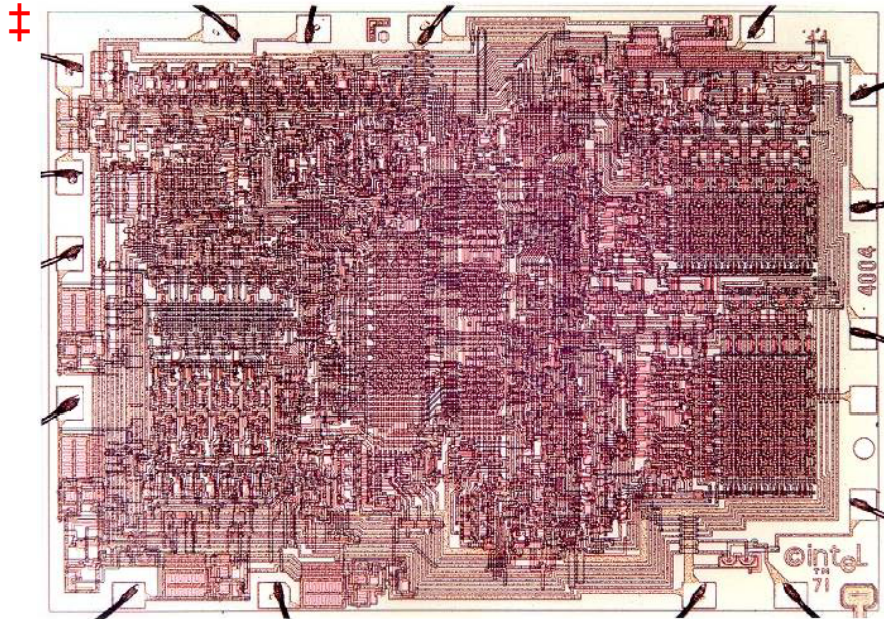
Silicon will be luminous

technology of combinational use

nanodot



**the first CPU in the world  
developed by Intel (1971)**



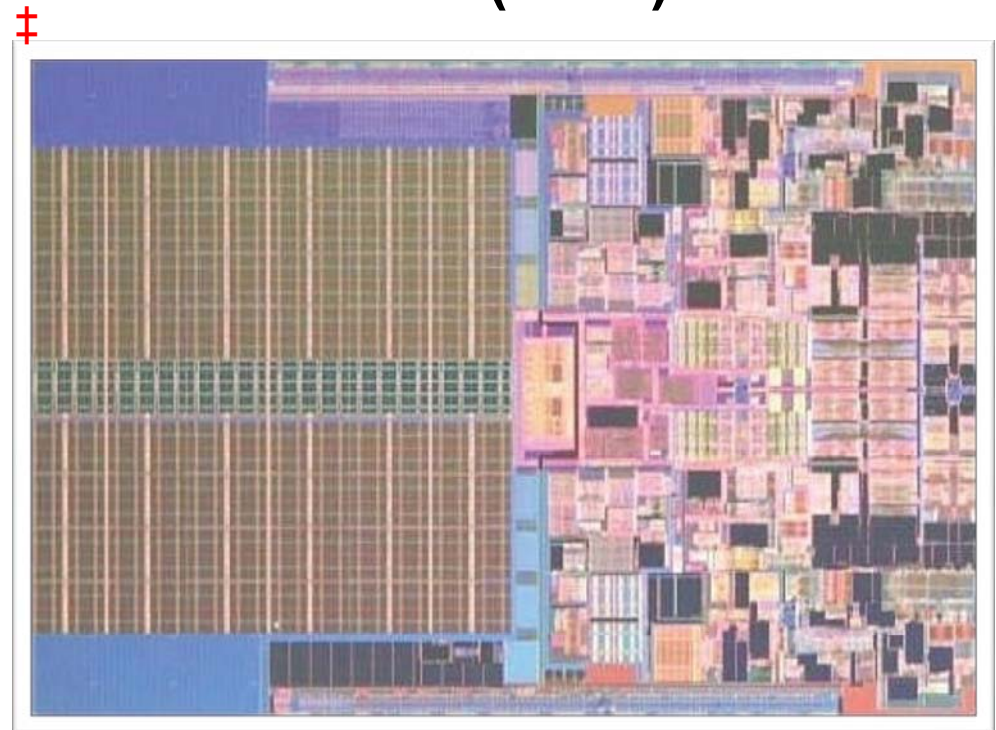
**Developed upon a request from  
Busicom (a Japanese  
Company), as a calculator**

**4004 (CPU)**

**3mm × 4mm, 2237 transistors**

**(Dr. Masatoshi Shima is one of the developers)**

**A processor developed by  
Intel (2008)**



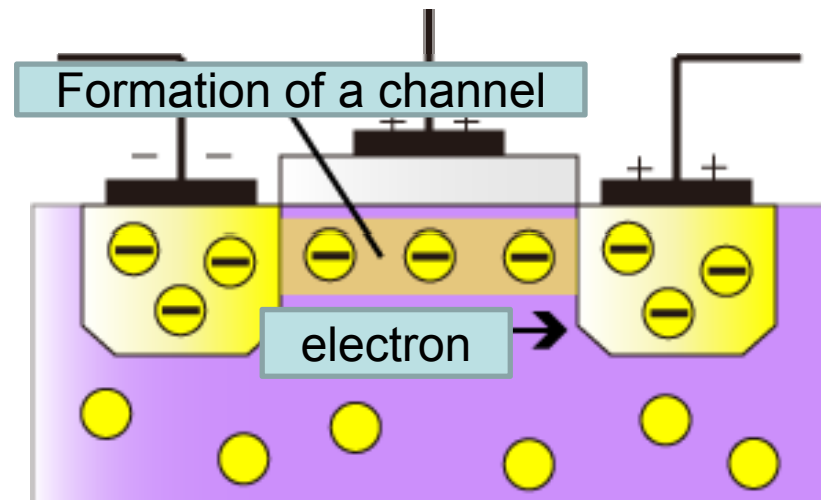
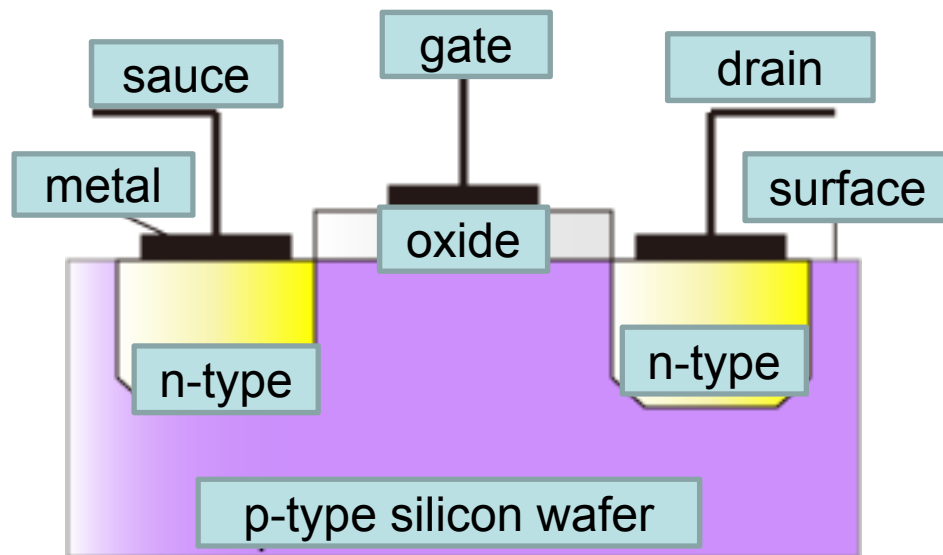
**45nm process**

**Including 410,000,000 transistors**

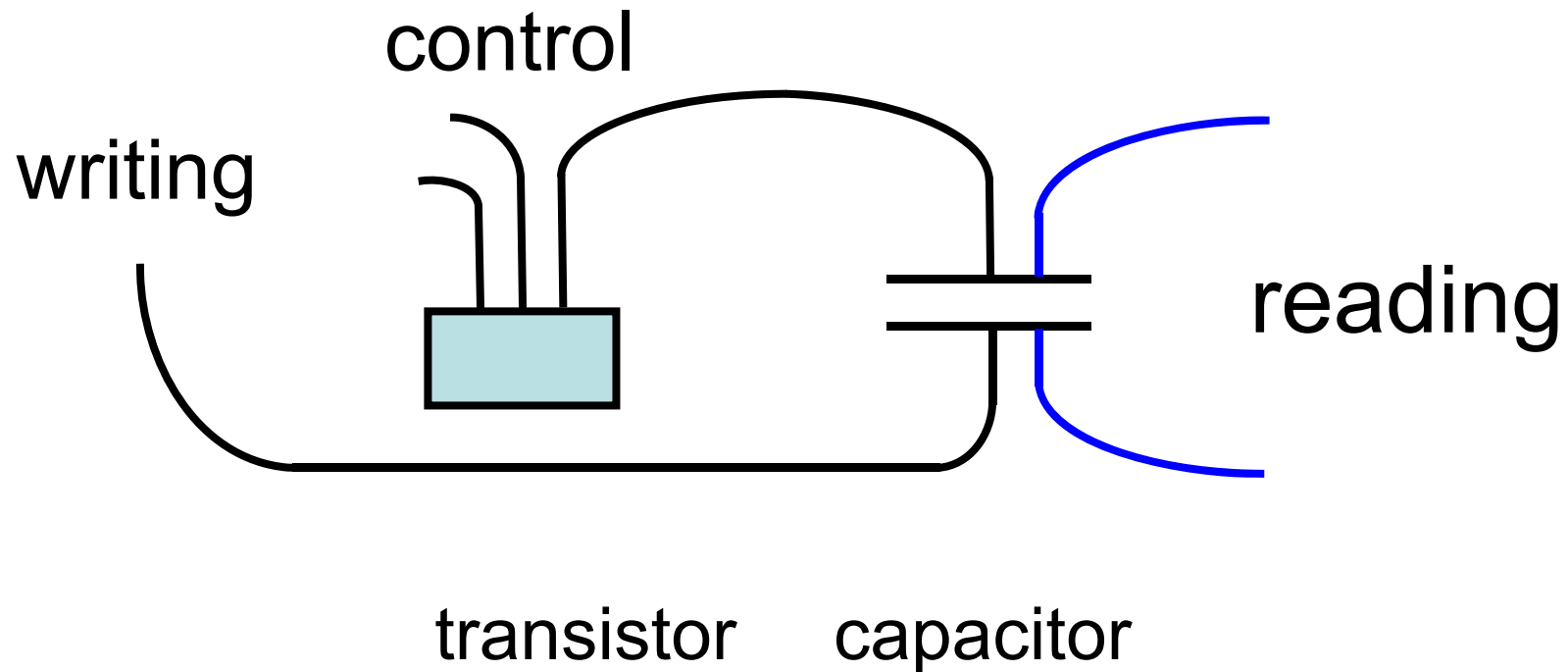


# MOS transistor

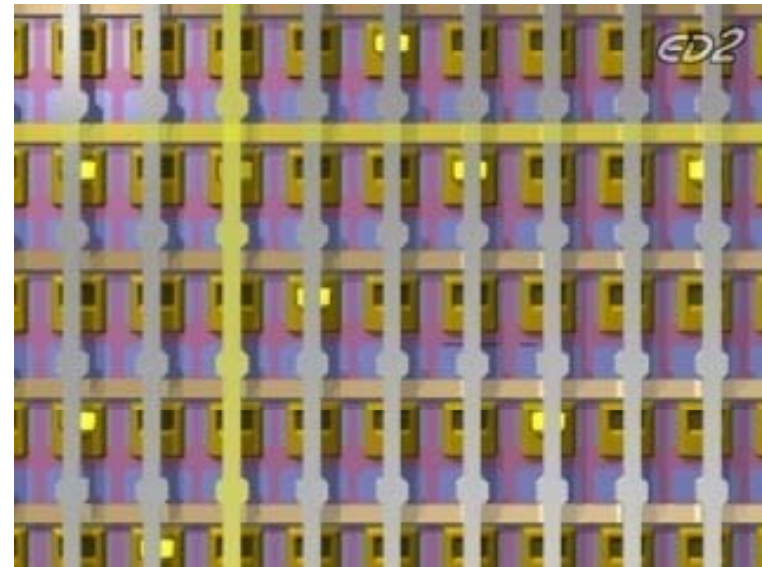
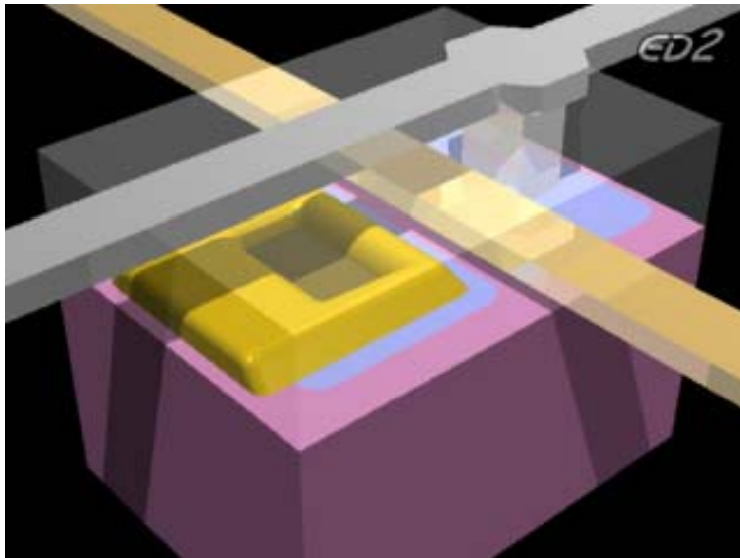
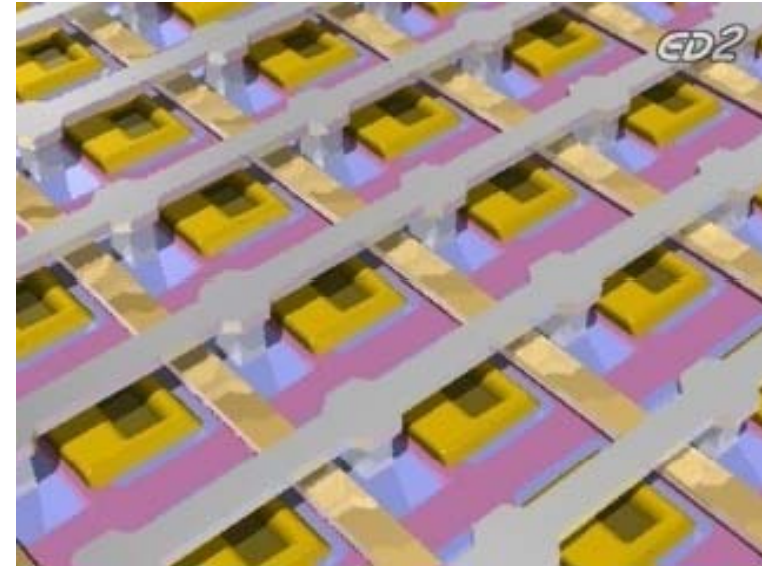
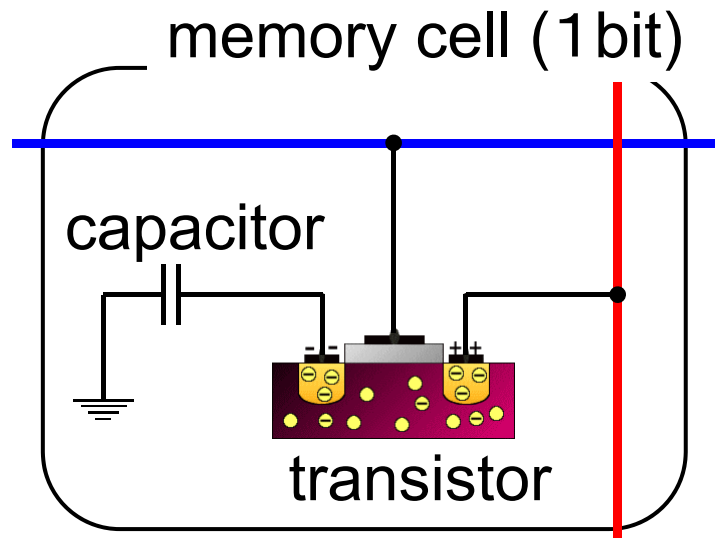
- Metal-Oxide-Semiconductor Structure
- on/off switching the electric current (source to drain) with the voltage at the gate



# A Memory Cell is Made Up of a Control Gate and a Binary Cell



# Structure of DRAM(dynamic random access memory)



# The inevitability of nanotechnology

A memory of  $10^9$  bytes

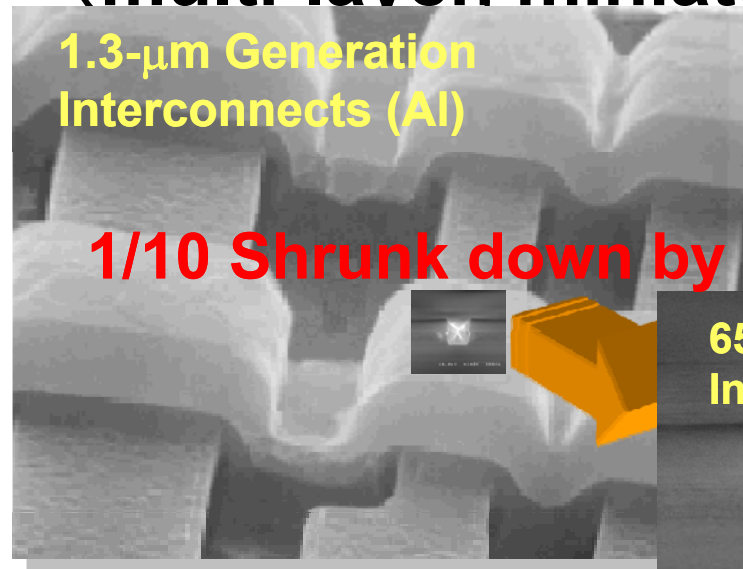
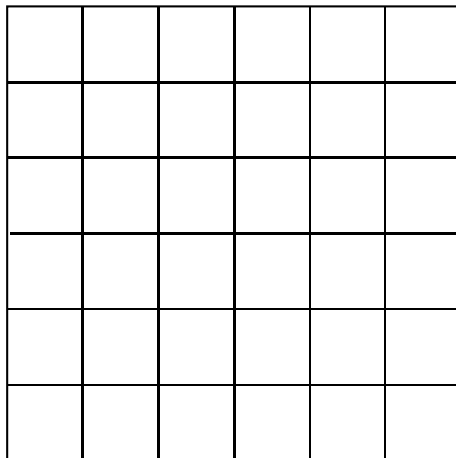
$$= (3 \times 10^4) \times (3 \times 10^4)$$

1 cm  $\times$  1 cm (chip)

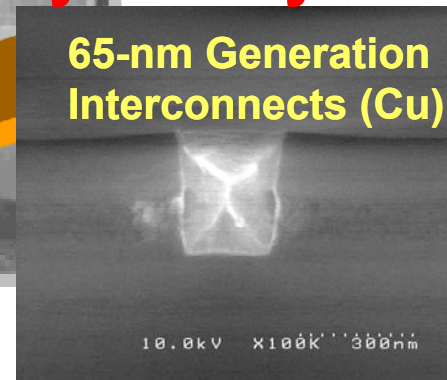
= 0.3  $\mu\text{m}$   $\times$  0.3  $\mu\text{m}$  (element)

**Wiring gets harder**

**(multi-layer. miniaturization)**

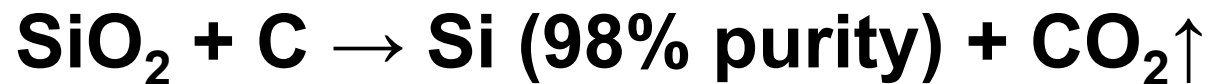


**1/10 Shrunk down by 10-15 years**

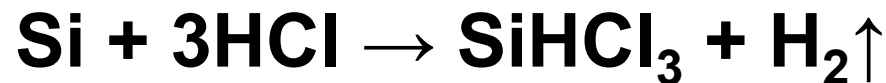


# A process for producing high purity silicon

- ① Reduction of  $\text{SiO}_2$  @  $1200^\circ\text{C}$



- ② Trichlorosilane production



- ③ Distillation and purification



- ④ Synthesis of pure solid Silicon through CVD process



# Producing single crystal Silicon wafers (movie)

the movie here has been removed  
due to a copyright issue.

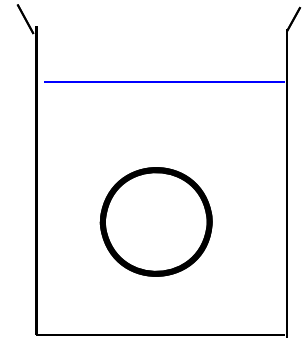
## **CZ (Czochralski) method:**

1. Melting high-purity multi-crystal silicon at high temperature
2. Single crystal growth with seed crystal

**Wafer diameter control  
through pull-up speed and  
temperature distribution**

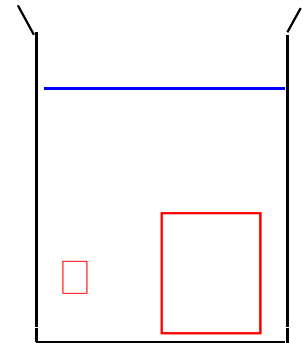
# Q & A What is a nucleation?

**An air bubble vanishes at 90°C  
→ 100°C corresponds to the  
atmospheric pressure**



## **The Stability**

- heat generation and glueing (in vacuum)
- Ostwald ripening
- bubbles are less stable than liquid
- supersaturation (over 100°C) is necessary



**Nucleation is described by the theory of  
statistical mechanics and thermodynamics**

# Common processes for microfabrication

Goal: high production rate, high spatial density, consistent quality

## Pattern formation (lithography)

- ① Photoresist coating
- ② UV ray exposure and image development
- ③ Plasma etching
- ④ Resist removal

Thin membrane producing

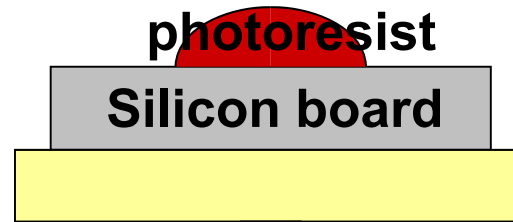
Through PVD, CVD method

Impurity doping (ions)

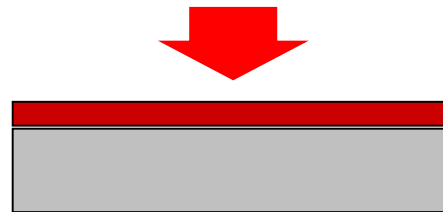




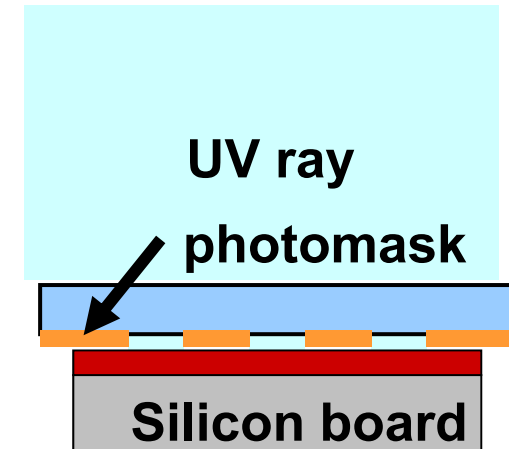
①: photoresist coating



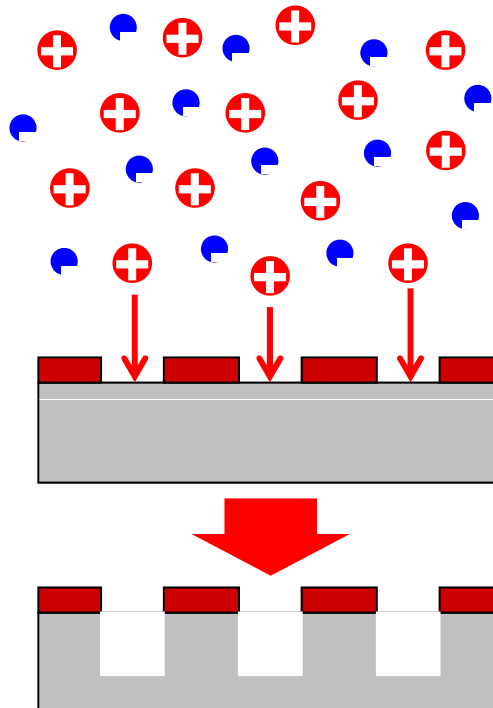
Rapid rotation



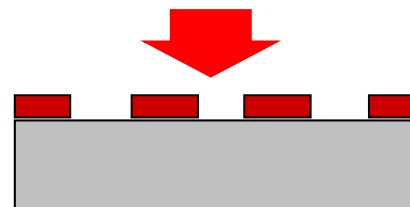
②: UV ray exposure



④: plasma etching



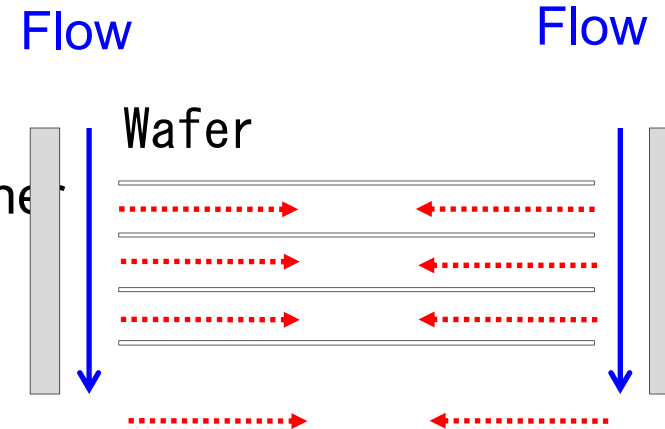
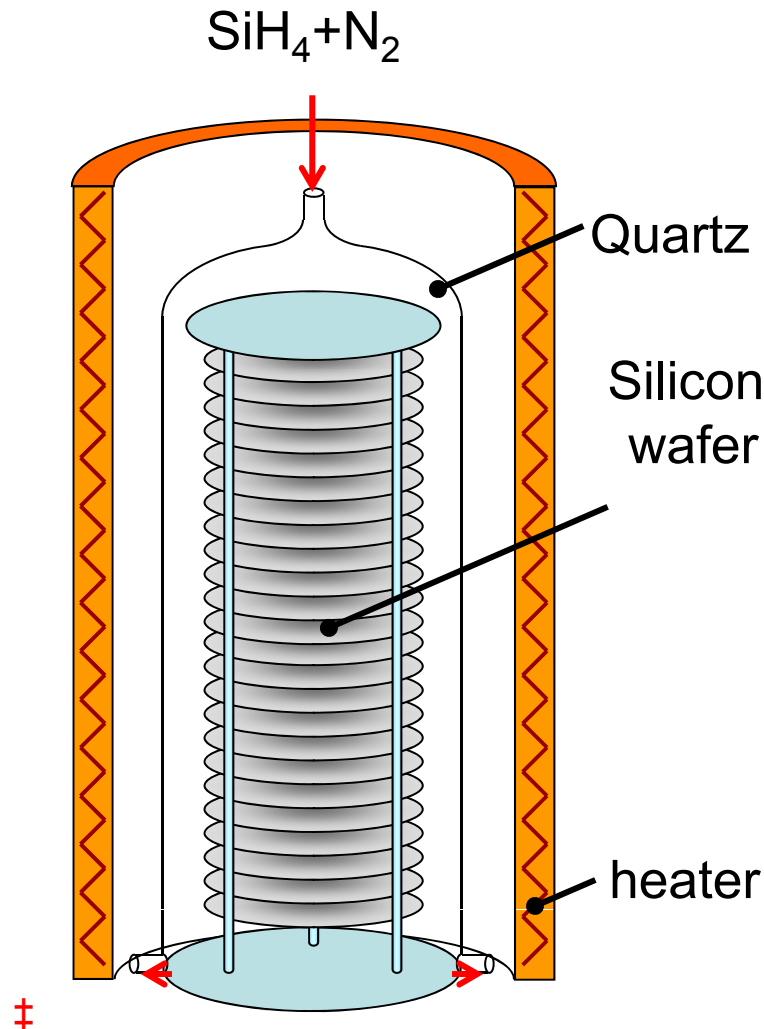
③: image development



†Takeda-Sentanchi Bldg. Clean room  
(The University of Tokyo)

**CVD(chemical vapor deposition) equipment for mass-production**  
**Gas → Chemical Reaction → formation of membrane at the surface**

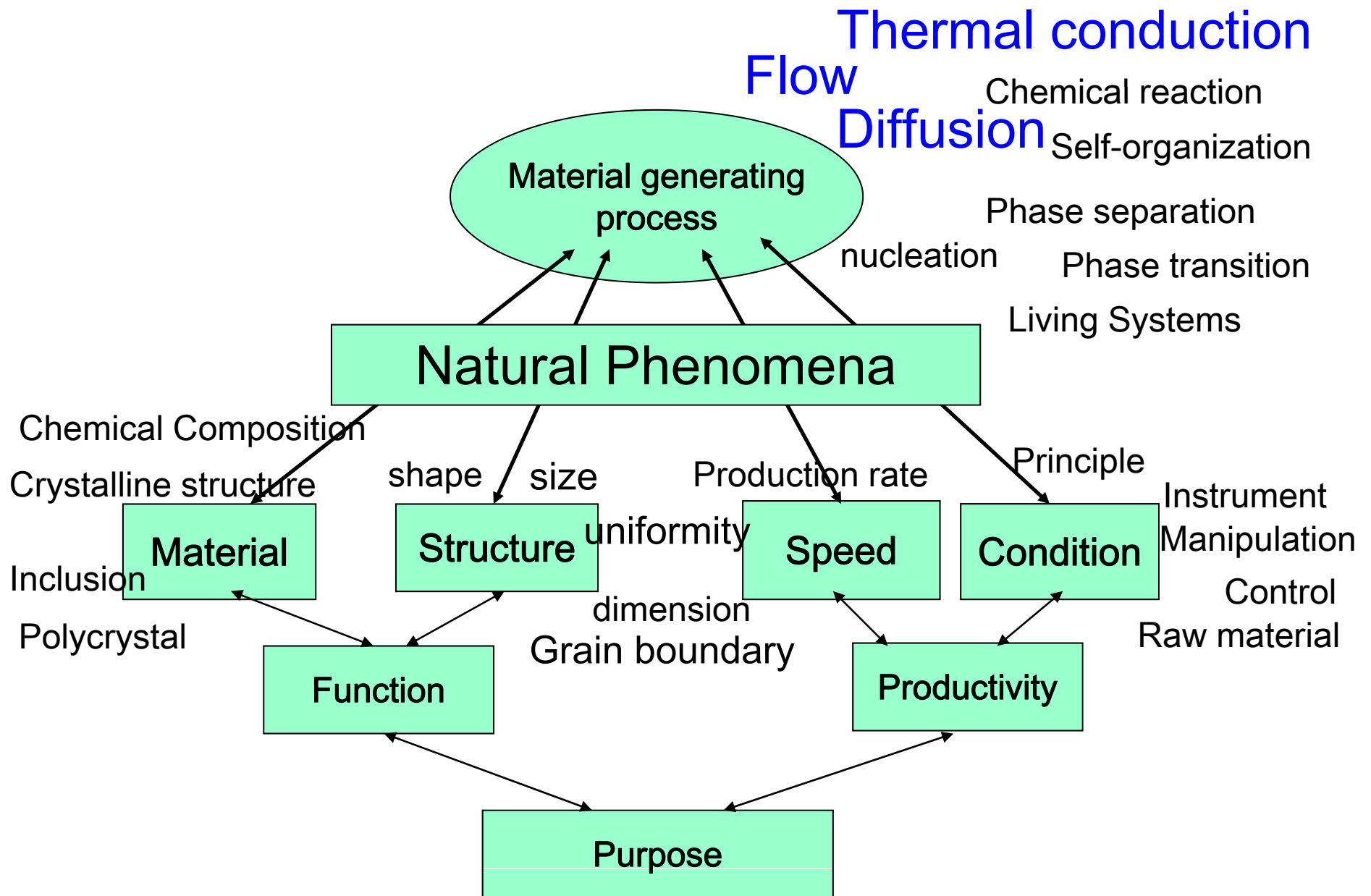
**Flow and Diffusion**



Why does membrane form  
Without flow?



Transmission by flow (in the equipment)  
Transmission by diffusion (on the wafer surface)



## Phenomena (Flow and Diffusion)

- Pulling up a single crystal
  - ✓ Using seed crystals
  - ✓ Avoid nucleation
  - ✓ Precise temperature control
  - ✓ Quiet flow

# Flow: laminar and turbulent flow

- **Laminar flow(not mixed)**
  - ✓ Able to follow streamlines
- **Turbulent flow(well mixed)**
  - ✓ Flow with vortices
  - ✓ Unable to follow streamlines

the movie here has been removed  
due to a copyright issue.

**Reynolds number**

$$Re = \frac{dv\rho}{\mu}$$

$d$  : typical length

$v$  : velocity of fluid

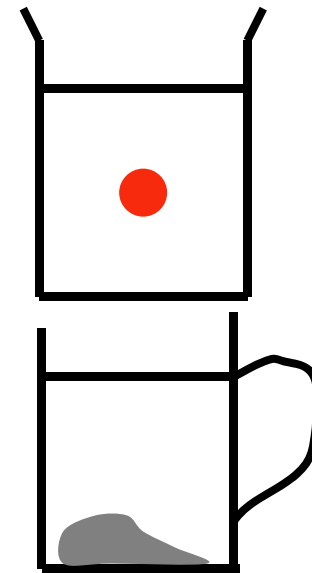
$\rho$  : density of fluid

$\mu$  : viscosity

# Realizing a “diffusion”

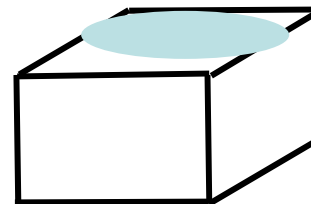
liquid diffusion and solid diffusion

A stain when you put some ink into water



Put a lump of sugar into water,  
and wait without shaking

Coat a block ice with sugar  
Ice with strawberry syrup



‡

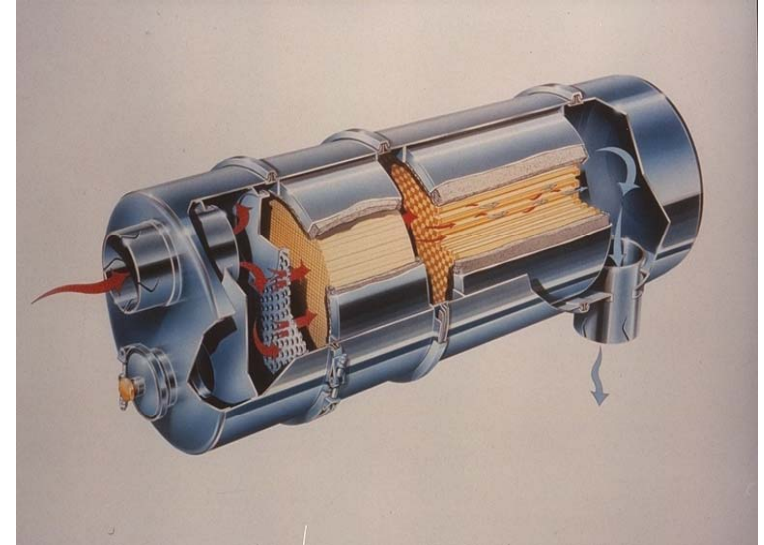
## Honeycomb catalyzer

# Vapor-phase diffusion

Collides 5 billion times per second when running  $0.1 \mu\text{m}$  at the speed of 500 m/s

Automobile emission gas purifying catalyst

Honeycomb type



Unique Patented Johnson Matthey System

Passing through a tube whose diameter is 5mm at 500m/s

All of the molecules make contact with the catalyst on the wall

## Let us return to the main subject...

Molecules on a cup of pure water

One molecule of impurity (electron) in a nanodot

## II-2. Soft matter

LCD displays, Color Films,  
Color Filters, Molecule sensors

**Substance** (molecular structure • molecular design) • **Structure** (form)

**Speed** (multi-layer coating • ink jet) • **Conditions**

**Phenomena**:

Self-Organizing, Chemical reaction, Flow (driven by surface tension )



LCD Displays

Molded plastic products



**Robots**  
(sensors made of  
conductive high  
molecular material)



Amphipathic  
organic molecules

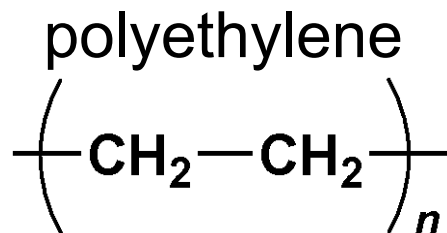


**Micelle** (soap • cosmetics)

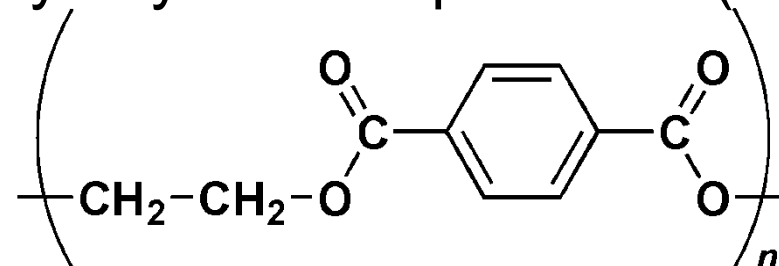


# 1. Characteristics of Soft matter

	Organic material	Inorganic material	metal
	Soft matter	“Hard” matter	
Building block	molecule	atom	
When they show their characteristics	one molecule molecular ensemble	Atomic ensemble	
Bonding force	Intermolecular force (comparatively weak)	Covalent bonding (comparatively strong)	Metallic bonding



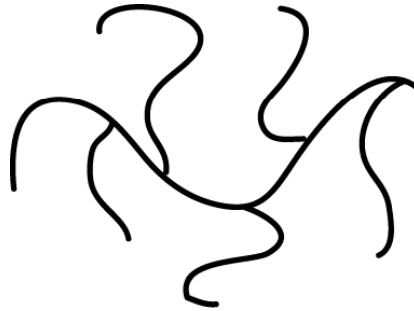
Polyethylene terephthalate (PET)



## 2.1 branched polymer and straight-chain polymer

### Branched polyethylene

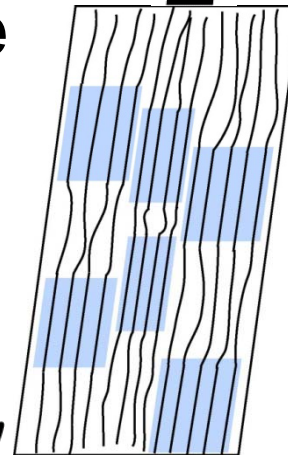
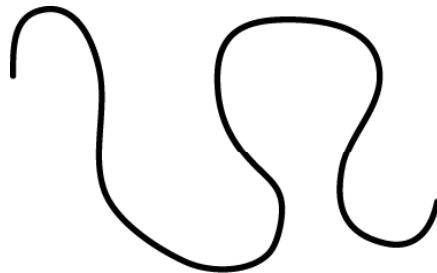
- High pressure, oxygen radical polymerization  
→ irregular structure  
(branched structure)



- soft  
(suitable for film)
- transparent

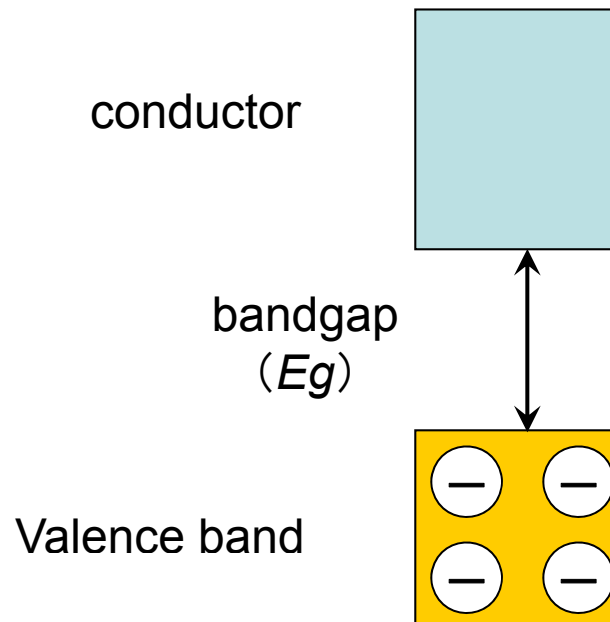
### Straight chain polyethylene

- Low pressure, catalyst polymerization  
→ regular structure  
(normal chain structure)



- large tension strength  
(suitable for textile)
- opaque

## 2.2 polymer semiconductor

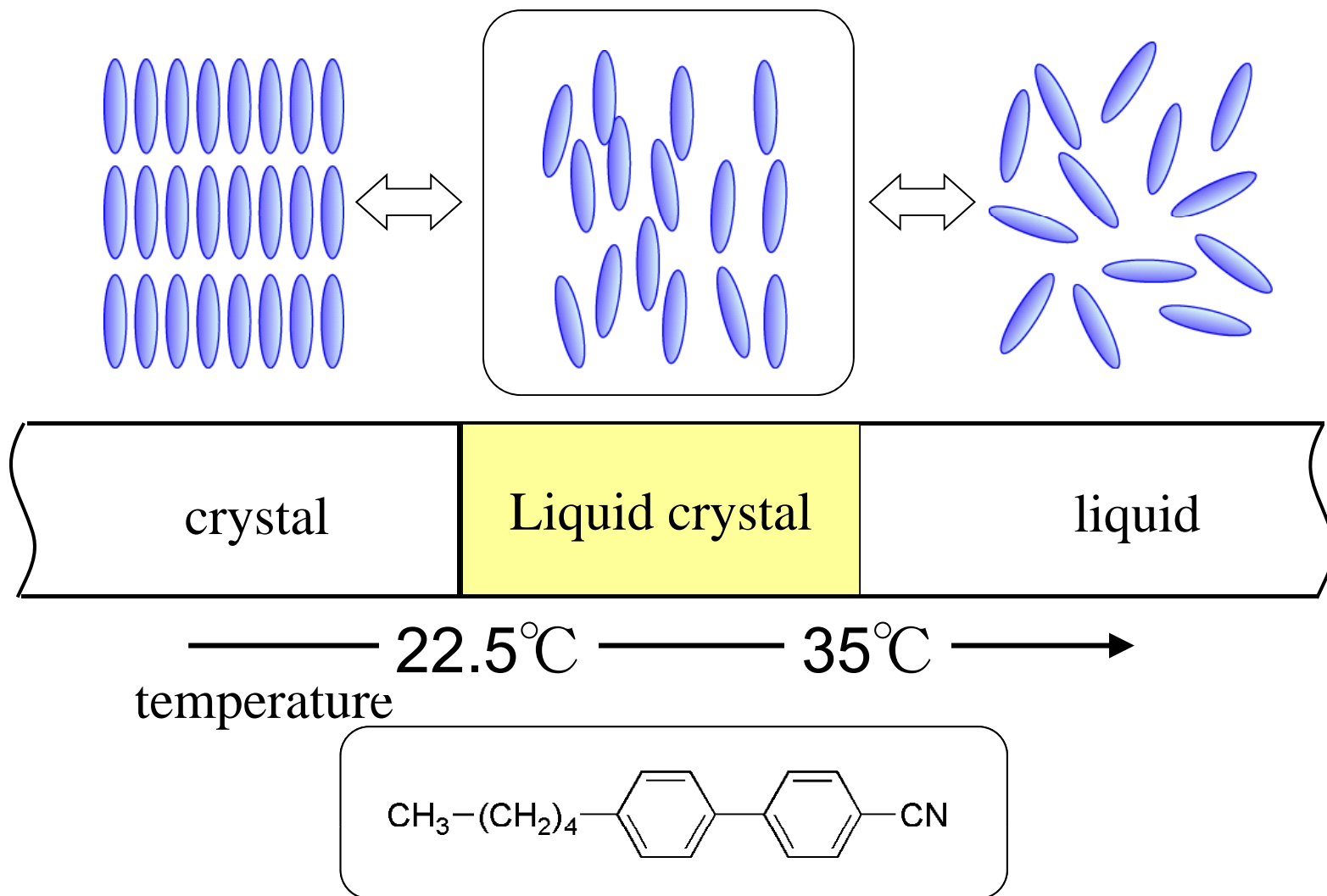


**What are possible with polymer semiconductors**

	compound	$E_g$ (eV)
Conductive polymer	polyacetylene $(\text{—CH=CH—})_n$	1.4
	polythiophene $(\text{—C}_4\text{H}_3\text{S—})_n$	2.0
	PPV $(\text{—C}_6\text{H}_4\text{—CH=CH—})_n$	2.5
Inorganic	Si	1.12
	GaAs	1.42

- flexible as paper, write/delete figures on devices ➡ Electronic paper
- molecular level (nm scale) ➡ Sensors such as Superfine complex elements, and living molecules
- Structure similar to living molecules ➡ Self-restoration
- Semiconductor soft matter is easy to mold and transform
- It is possible to adjust  $E_g$  using chemical modification
- The electric conductivity of doped semiconductor is as high as metals

## 2.3 liquid crystals (functional soft matter)



### 3 manufacturing process : example 1

Making up  $\mu\text{m}$  size structure

**Multilayer structure of photo film  
(multilayer coating, multilayer film formation)**

- controlling laminar flow
- **controlling longitudinal diffusion**
- **controlling drying process**

the movie here has been removed  
due to a copyright issue.

# Is Diffusion good or bad for technologies?

Good

Bad

(application of diffusion) (how to cope with diffusion)

---

Gas phase	Film forming equipment	optic fiber
	Honeycomb catalyst	(particulations in rapid reaction)
	Purification (gas phase or liquid phase)	
Liquid phase	liquid phase reaction (stirring: diffusion of particles of molecular size)	Multilayer film forming (high-speed pull up)
Solid phase	doping	Akashi fiber
	optical fiber (smooth distribution)	(alloying)

---

### 3 manufacturing process : example 2

Making a surface with  $\mu\text{m}$  size structure

**Making Color filter using ink jet mechanism  
(Bottom-up process)**

the movie here has been removed  
due to a copyright issue.

# 4. Nanometer scale manufacturing

## 4. 1 self-assembled phenomenon

Spontaneous structure formation of molecules and atoms (clusters) with their form constant

- formation of fine structure

What to expect ▪ Energy saving

- low environmental burden

Thermo-dynamics	equilibrium	Dissipative system
examples	Crystal Liquid Crystal Self-assembled monolayers Phase separation	Turing model Belousov-Zhabotinsky reaction Liesegang Phenomenon Wind patterns on sand Band on a tropical fish Forest



# Self-assembly : examples

non-equilibrium systems in terms of thermodynamics  
(oscillations in sandhills, forests, and chemical reactions)

## Wind patterns on the Tottori Sand Dunes



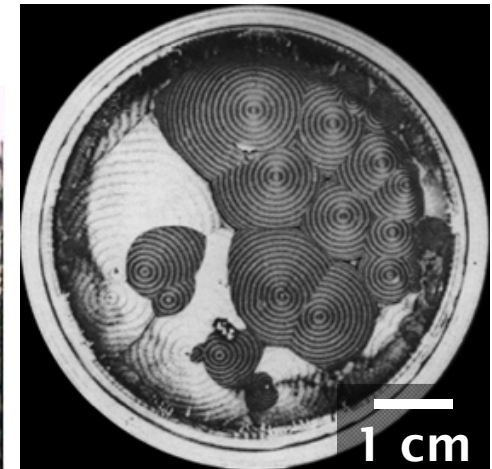
†Tottori Pref., Dept. of Culture and sightseeing,  
Kanko-Seisaku section



## Forest (Mt. Tateshina, Shimagare phenomenon)

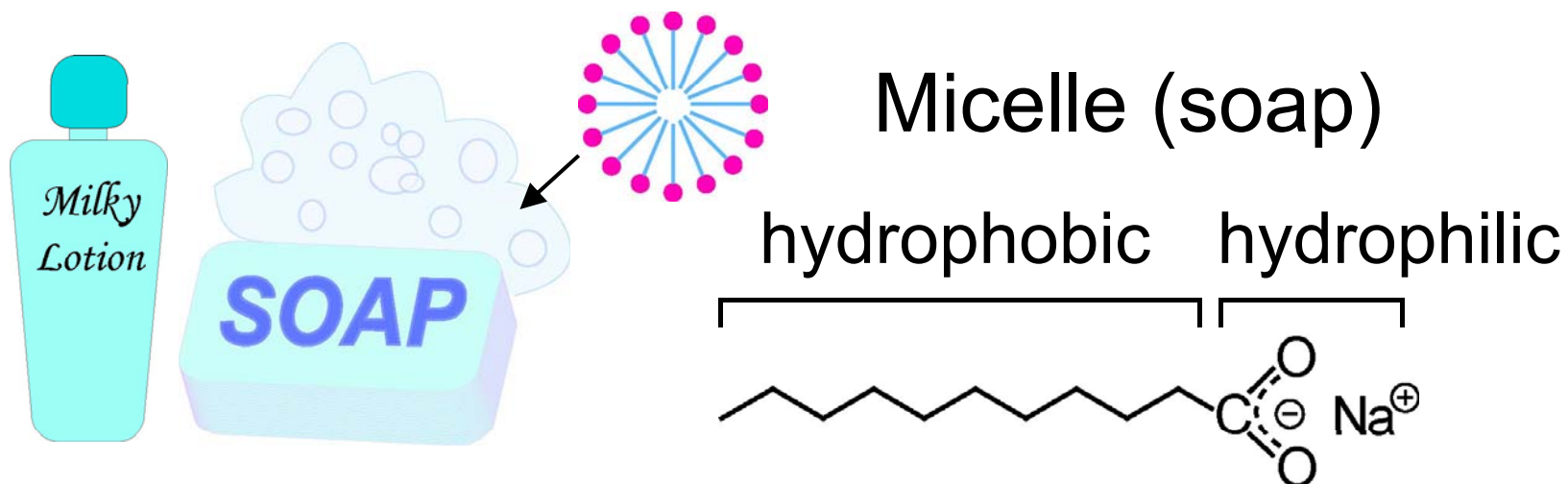
†Nagano Pref., Hara Village, Sightseeing association

Ascorbic acid crystal  
develops along with the  
evaporation of the medium  
(Liesegang Phenomenon)



†K. Iwamoto et al.,  
J. Colloid Interface Sci.  
102, 477 (1984).

## 4. 2 self-assembly of amphipathic molecule

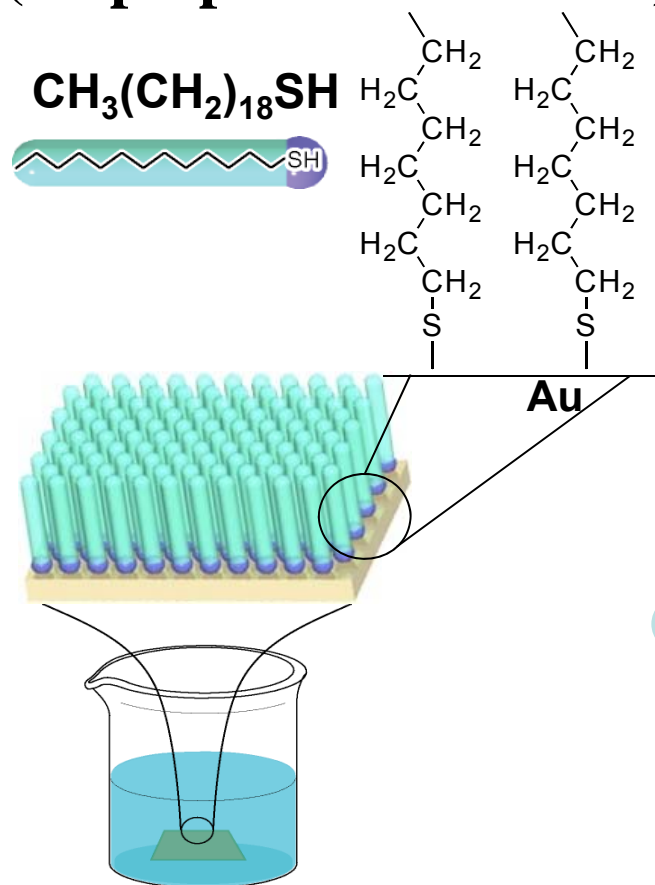


self-assembly on a substrate

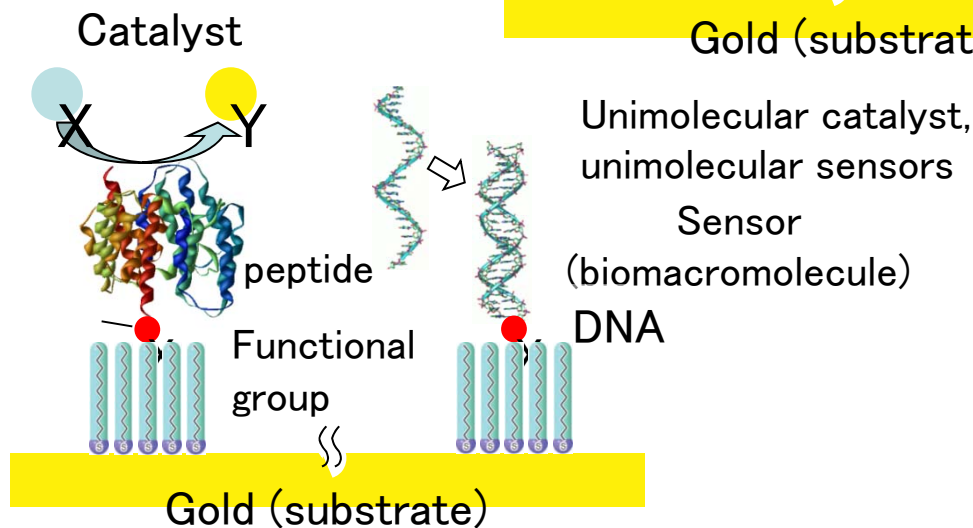
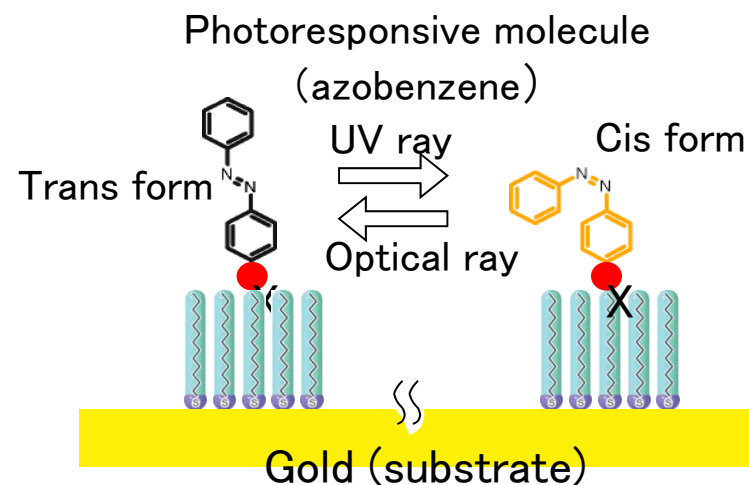
Functionalization at molecular level  
(self-assembled monolayers)

# Self-assembled monolayers (two-dimensional crystallization on a substrate)

(amphipathic molecules)



## Optical memory/sensor



# Surface tension is dominant in microscopic systems

- Surface tension / gravitation

$$\frac{\sigma \times \text{circumference}}{g \rho \times \text{volume}} = \frac{\sigma}{g \rho r^2}$$

the ratio is  $\sim 10^7$   
In micrometer-size  
water droplet

$\sigma$  : surface tension[N m<sup>-1</sup>]

$g$  : gravitational accerelation[m s<sup>-2</sup>]

$\rho$  : density [kg m<sup>-3</sup>]

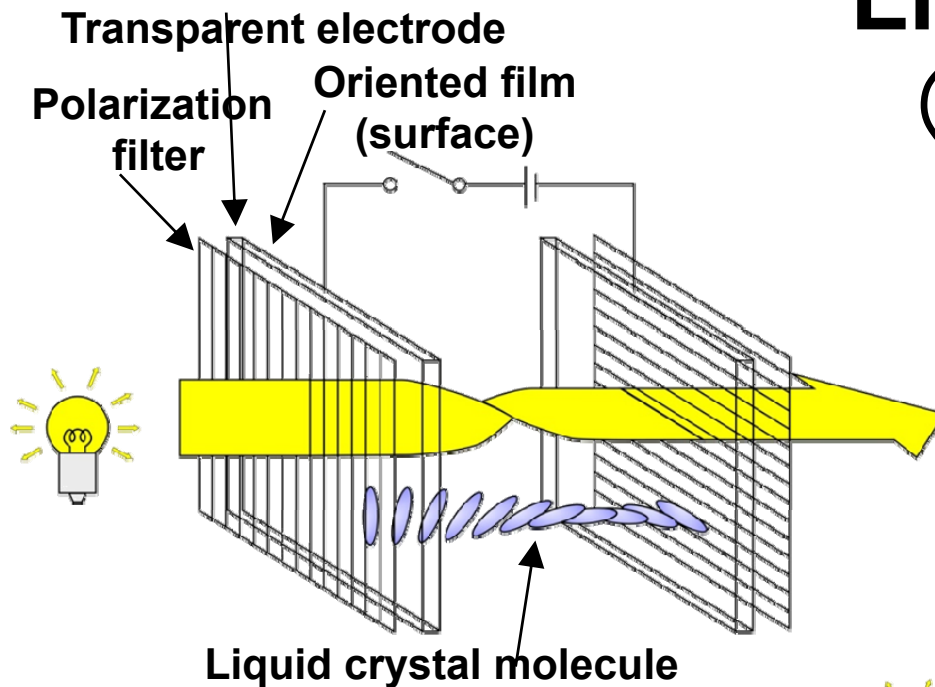
$r$  : radius of droplet [m]

## 4.4 Self-assembling soft matter: Liquid Crystals

4<sup>th</sup> phase of matter : Solid, **LC**, Liquid, Gas

### Liquid Crystal Display (PCs, Mobile phones)

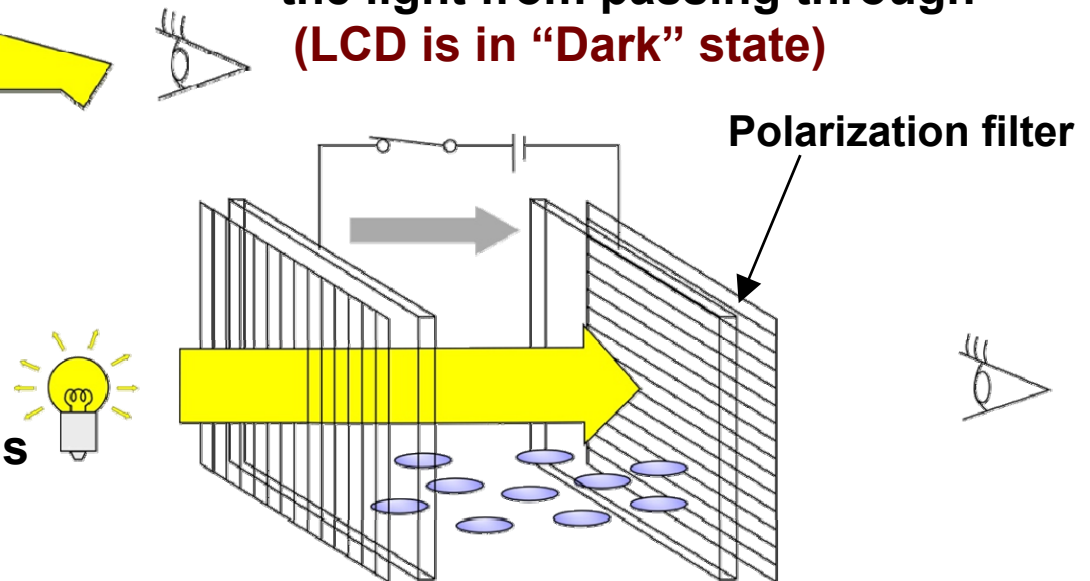
<Electric field ON>

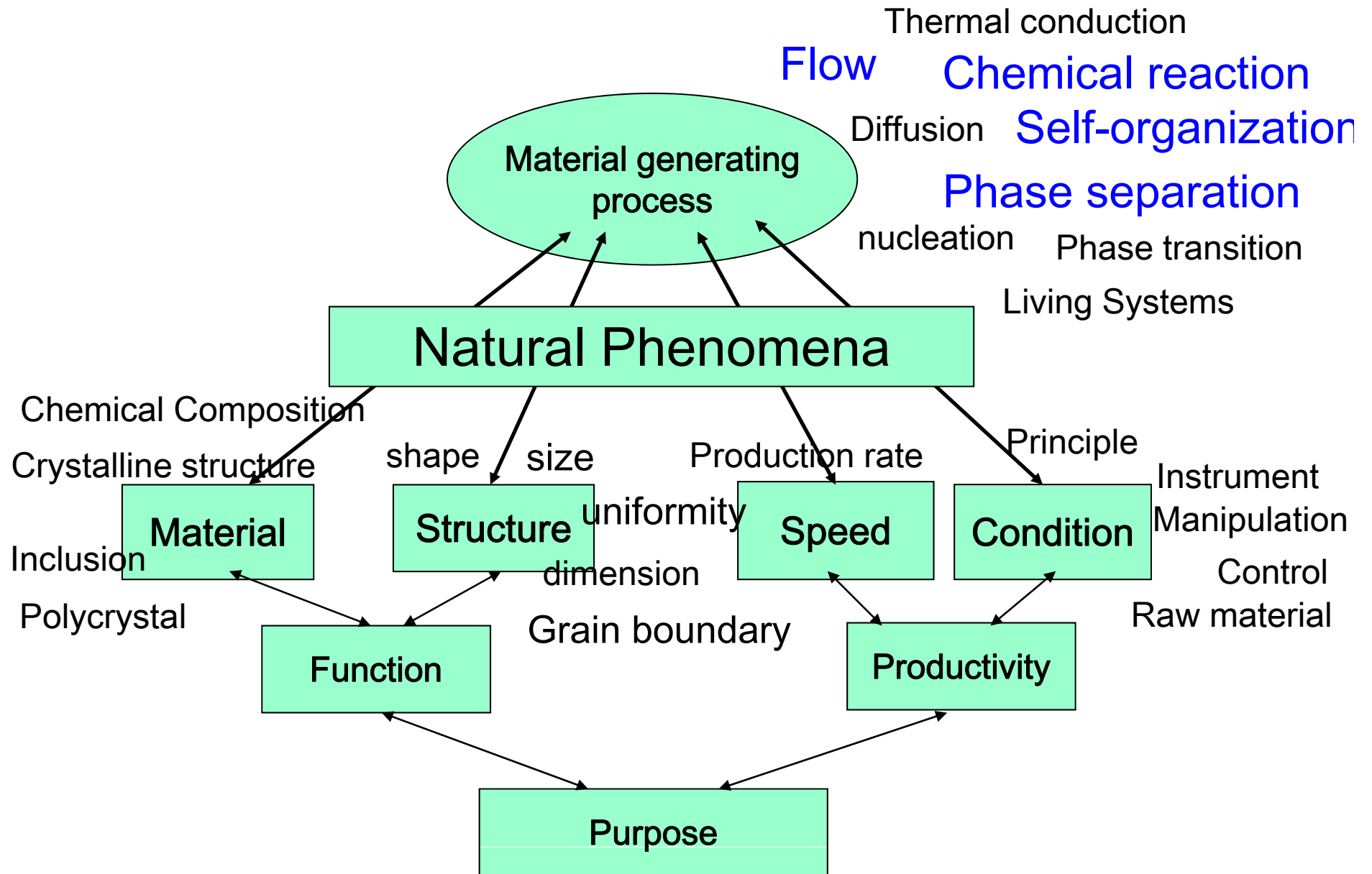


Electric field twists the array of LCs by 90 degrees to rotate the optical polarization surface, making LCD visible ("**Bright**" state )

<Electric field OFF>

a pair of polarization filters keeps the light from passing through  
(LCD is in "**Dark**" state)





## **Q & A cost calculations**

**When 1 automobile costs ¥100 billion,  
100 million cost ¥100 million**

**Cost = (raw material) + (equipment) + (personnel)**

**Reducible cost and non-reducible cost**

**Relocation costs: ¥200 billion → ¥50 billion**

**Misunderstandings about the recycle costs**

**Brush up your ability to predict future prices!**

## Semiconductor devices

### Phenomena

flow : laminar and turbulent flow  
diffusion: Gas, Liquid, Solid  
heat transfer: conduction  
(Thermal conductance  $\times$   
temperature gradient)  
comparison: diffusion  
(diffusion coefficient  $\times$   
concentration gradient)  
radiation, convection  
chemical reaction, self-organization

## Soft matter

Matter and structure  function

Matter (molecule and ensemble  
design)

structure, speed, condition

### phenomena

laminar flow control, diffusion  
control

self-organization

surface tension, marangoni  
convection

phase transition

**Next lecture: Materials science for a sustainable future**