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# Functional Glasses by Coatings or Thin Films

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# Outline

- **General Description of coatings or thin films**
- **New Functionalities of thin films on glasses**
- **Preparation methods for thin films on glass**
- **Some functional glasses by coating or thin films**
  - **Transparent conductive thin films on glass**
  - **Photocatalytic TiO<sub>2</sub> thin films on glass**
  - **Preparation of thin films with Hierarchical structure**
  - **Electrochromic thin films on glass**
- **Summary**



## 1.1 Definition of Coating and Thin Film (from Wikipedia encyclopedia)

**Coating** is a covering that is applied to the surface of an object, usually referred to as the substrate.

Coatings are applied to improve surface properties of the substrate, such as appearance, adhesion, wettability, corrosion resistance, wear resistance, and scratch resistance.

Coatings: liquids, gases or solids

**Thin films** are thin material layers ranging from fractions of a nanometre (monolayer) to several micrometres in thickness. Electronic semiconductor devices and optical coatings are the main applications benefiting from thin film construction.



## 1.2 Characteristics and new functionalities of thin films

Compared with bulk materials:

- **From their thickness and surface or interface**
  - a. Lower melting point due the surface energy
  - b. Selective transmission of reflection from interference
  - c. Change of electrical conductivity due to the inelastic scattering of electrons
  - d. Occurrence of anisotropic magnetic properties
  - e. Occurrence of surface energy level
  - f. Change of transport properties from quantum effect and so on.
- **Metastable State:**

Some properties those not appeared in bulk materials. The properties depend on the preparation method and process.
- **Surface properties:**

For example: photocatalysis, optical reflection, field emission and so on. To save resource and cost.



## 1.3 Classifications of thin films

- **Structure:**
  - a. Phase structure: single crystalline films, poly-crystalline films, nano-crystalline thin films, amorphous thin films
  - b. Microstructure: compact films, porous films, mesoporous thin films
- **Chemical composition:**
  - a. metallic thin films
  - b. inorganic thin films
  - c. organic or polymer thin films
  - d. composite (hybrid) thin films
- **Applications:**
  - a. Structural applications to improve mechanical properties: strength, stiffness, hardness, toughness, abrasive resistance, and so on
  - b. Functional applications to occur new functionalities: electrical, magnetic, optical, electronic, optoelectronic, photonic, thermal, chemical (catalysis, corrosion resistance), biological, photochemical, and so on

## 1.4 Factors to infect properties of thin films

- **Chemical compositions and stoichiometry**
- **microstructure and phase structure**
- **valence state of constituted atom**
- **process**
- **surface structure**
- **homogeneity**
- **thickness**
- **...**



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## 2.1 New Functionalities of Coating glasses

- **Optical:** photoelectric, interference, fluorescence, field-emission, infrared reflective, non-linear, photorefractive
- **Electrical:** high  $T_c$  superconductor, metallic, transparent conducting, Electrical resistivity, silicon semiconductor, dielectric, ferroelectric, piezoelectric, pyro-electric films
- **Magnetic:** giant magnetic resistivity, magnetic memory
- **Thermal:** Thermo-optic films, thermoelectric films
- **Biomedical:** biometals, polymers, apatite, biocomposites
- **Sensitive Films:** Photosensitive, thermo-sensitive, gas-sensitive, humidity-sensitive
- **Chemical:** photocatalytic, wettability,



# 2.2 Applications of Coating glasses

Coating glasses

Solar Cells



Low-e Windows



LEDs



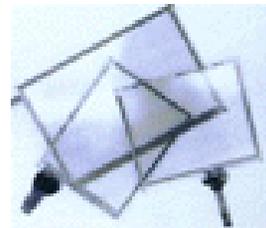
EMI Shielding



FPDs



Touch Panels



AR Coatings



Defrosting Windshields



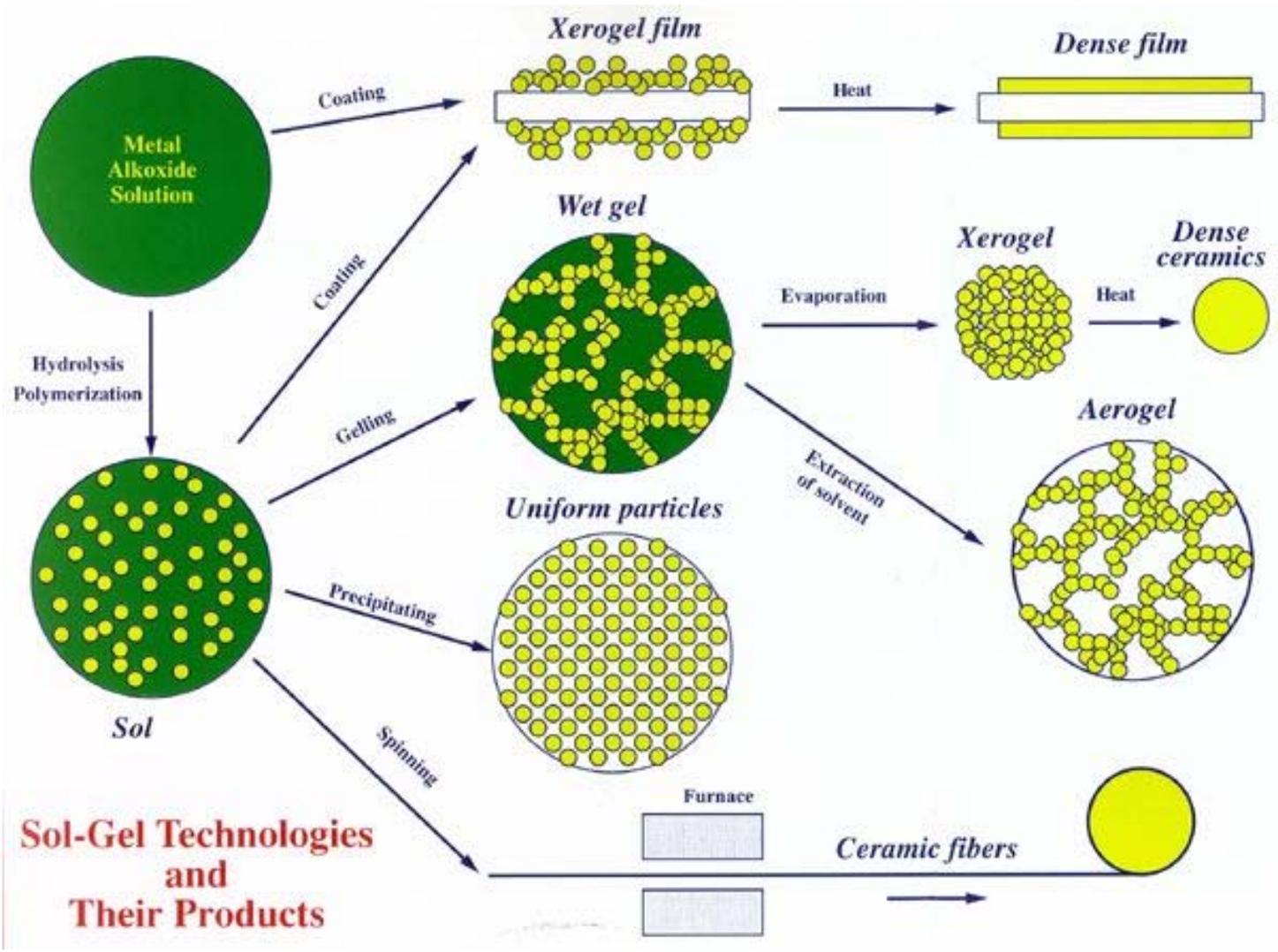


# Outline

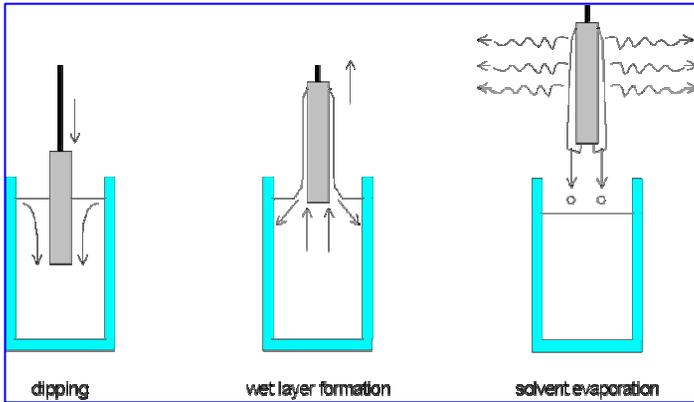
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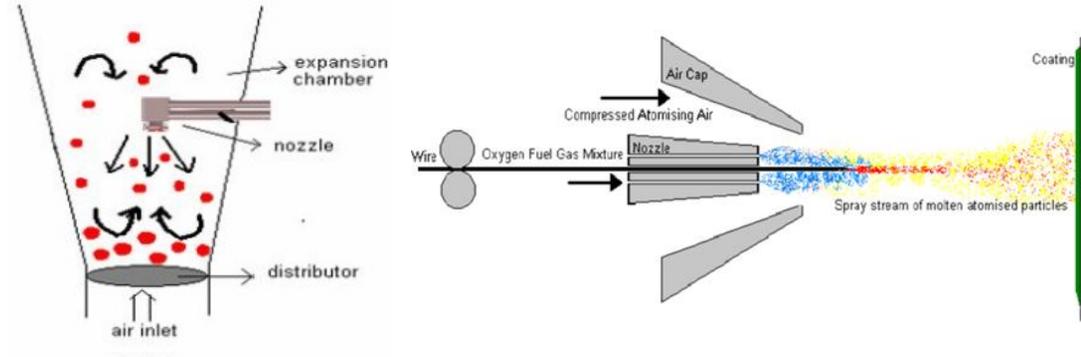
## 3.1 Sol-gel Process



## 3.1.1 Thin films preparation by sol-gel



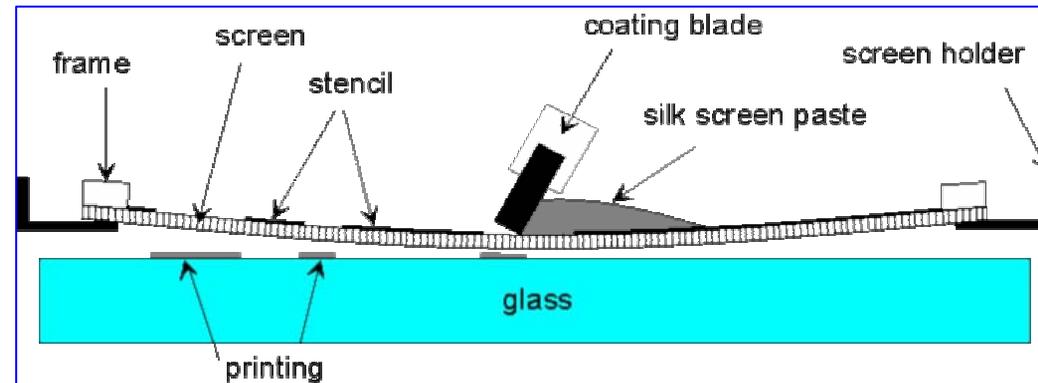
dip coating



spray coating



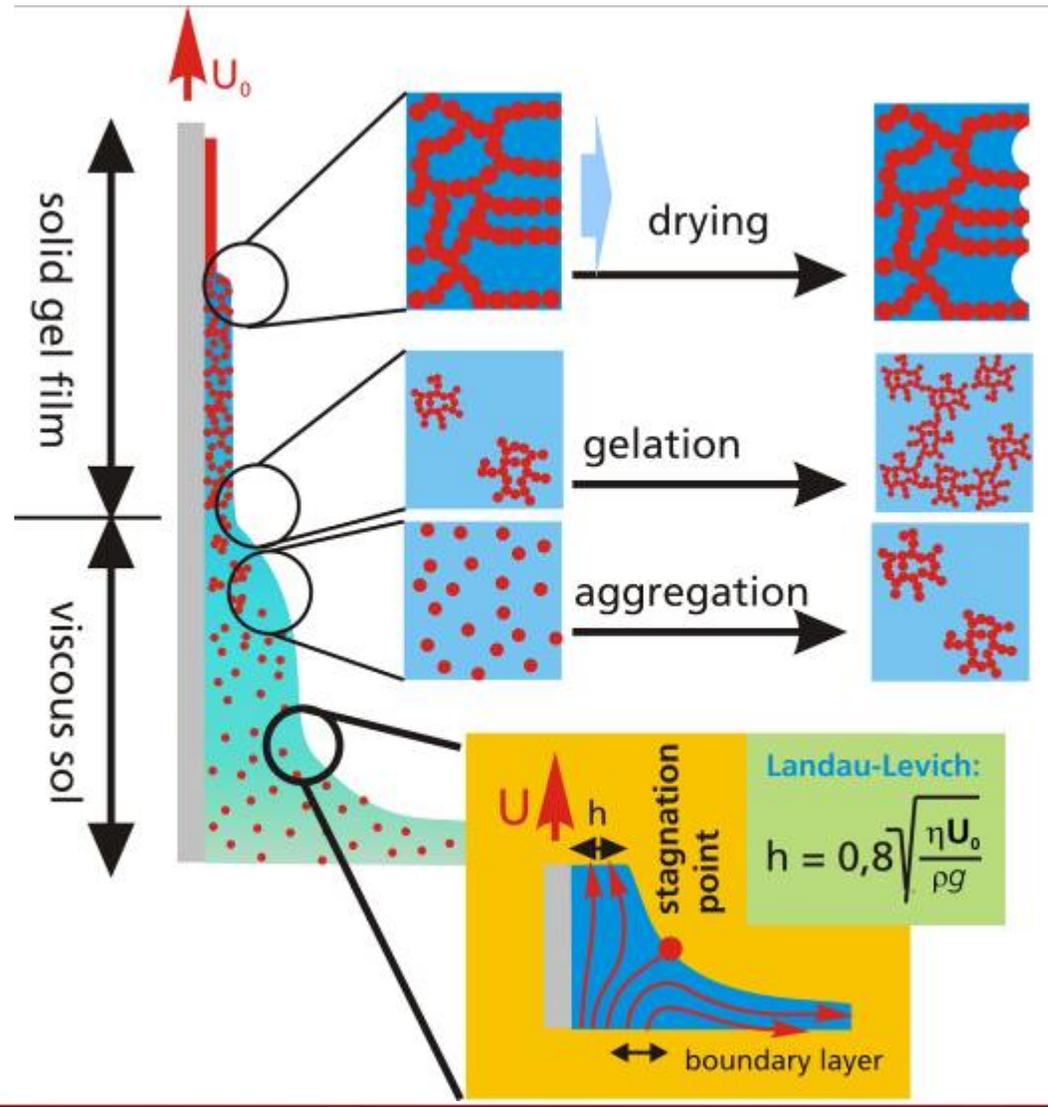
spin coating



screen printing

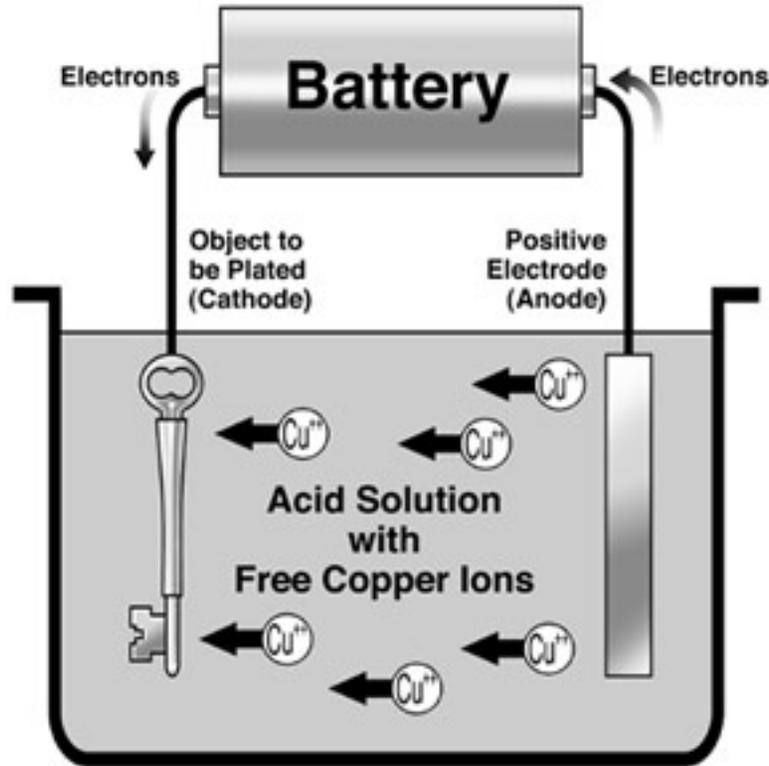


## 3.1.2 Thin Film formation by sol-gel





## 3.2.1 Plating: Electroplating



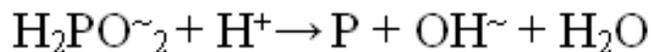
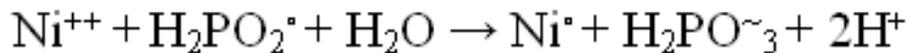
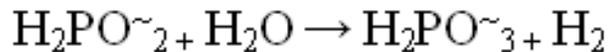
Thin films by EP:  
Silver  
Copper  
Copper alloy  
Nickel  
Sn-Zn alloy  
Chrome alloy  
...

**Electroplating** is a plating process that uses electrical current to reduce cations of a desired material from a solution and coat a conductive object with a thin layer of the material, such as a metal.



## 3.2.2 Plating: Electroless plating

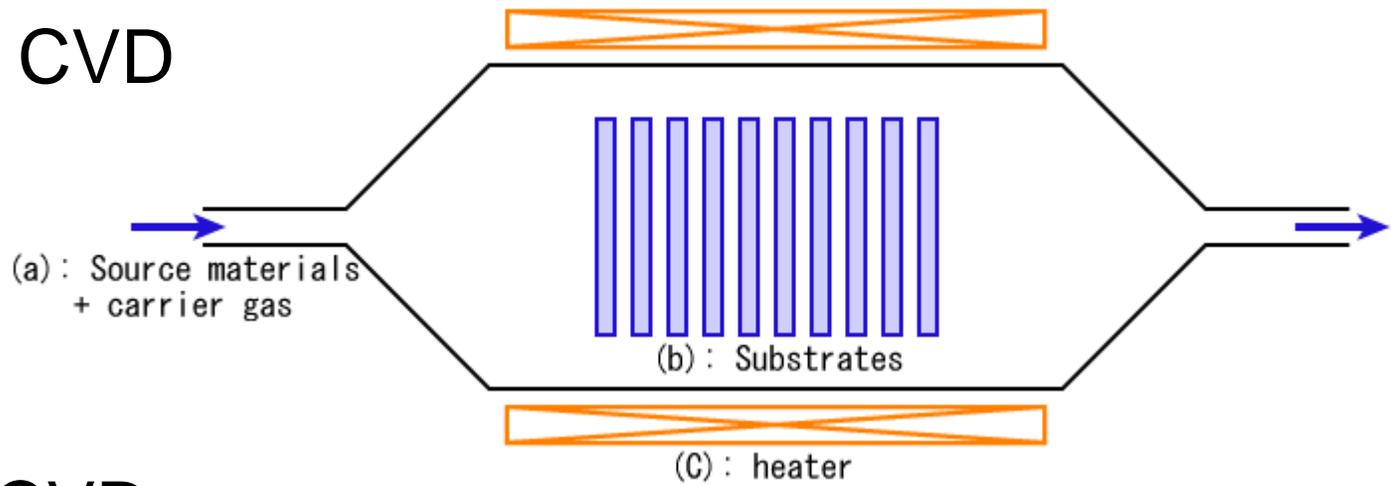
Electroless plating, also known as chemical or auto-catalytic plating, is a non-galvanic type of plating method that involves several simultaneous reactions in an aqueous solution, which occur without the use of external electrical power. The reaction is accomplished when hydrogen is released by a reducing agent, normally sodium hypophosphite, and oxidized thus producing a negative charge on the surface of the part. The most common electroless plating method is electroless nickel plating.



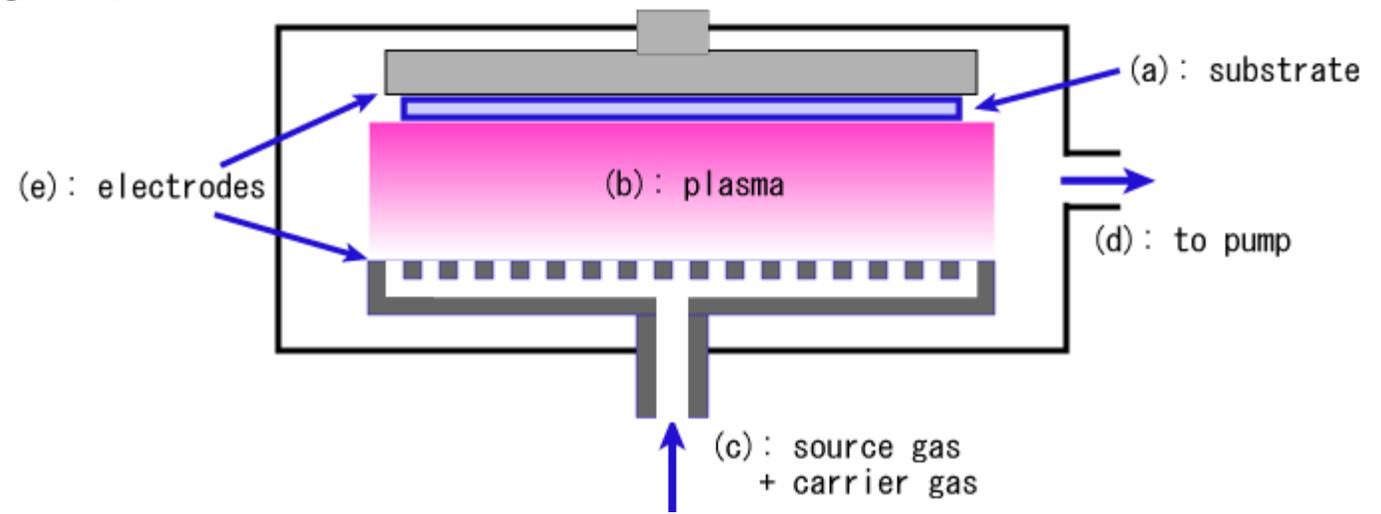


## 3.3 Chemical Vapor Deposition (CVD)

### Thermal CVD



### Plasma CVD





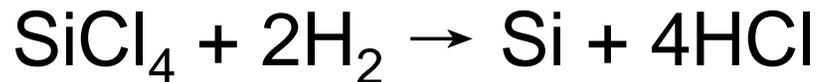
## 3.3.1 Types of chemical vapor deposition

- *Atmospheric pressure CVD (APCVD)*
- *Low-pressure CVD (LPCVD)*
- *Ultrahigh vacuum CVD (UHVCVD) :  $10^{-6}\sim 10^{-8}$ Torr*
- *Plasma-Enhanced CVD (PECVD)*
- *Atomic layer CVD (ALCVD)*
- *Combustion Chemical Vapor Deposition (CCVD)*
- *Hot wire CVD (HWCVD) or catalytic CVD*
- *Metalorganic chemical vapor deposition (MOCVD)*
- *Hybrid Physical-Chemical Vapor Deposition (HPCVD)*
- *Rapid thermal CVD (RTCVD)*
- *Vapor phase epitaxy*

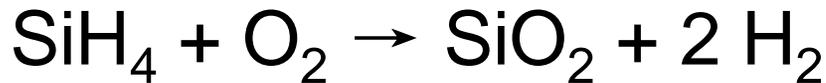


## 3.3.2 Chemical reactions in CVD process

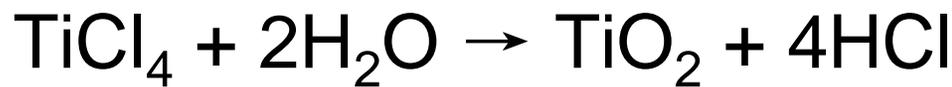
- *Preparation of Silicon thin films*



- *Preparation SiO<sub>2</sub> thin films*



- *Preparation TiO<sub>2</sub> thin films*

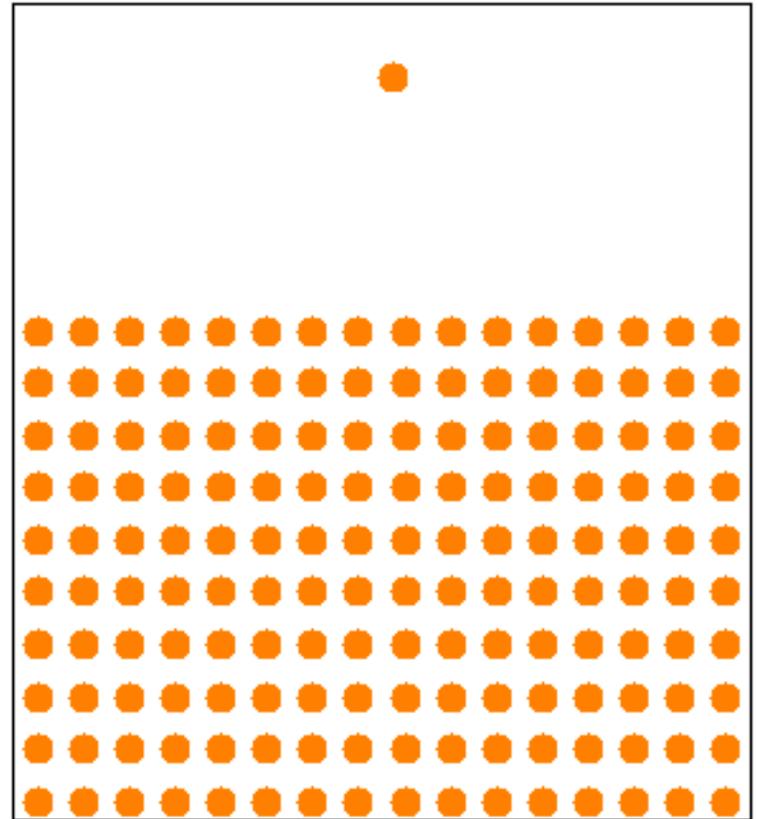




## 3.4 Physical vapor deposition

- Evaporative deposition
- Electron beam physical vapor deposition
- Sputter deposition
- Cathodic Arc Deposition
- Pulsed laser deposition

time 0.0041 ps

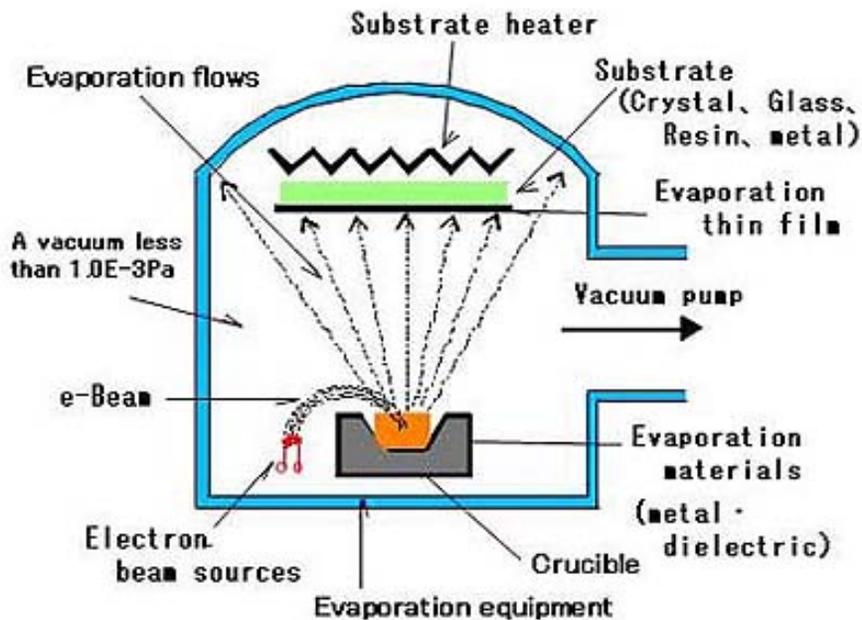


MD simulation of the basic physical process underlying PVD: a single Cu atom deposited on a Cu surface



## 3.4.1 Evaporation deposition

- Two processes: a hot source material evaporates and condenses on the substrate.
- In high vacuum (with a long mean free path), evaporated particles can travel directly to the deposition target without colliding with the background gas. At a typical pressure of  $10^{-4}$  Pa, an 0.4-nm particle has a mean free path of 60 m.
- Evaporated atoms that collide with foreign particles may react with them; for instance, if aluminum is deposited in the presence of oxygen, it will form aluminum oxide.



## Evaporation deposition



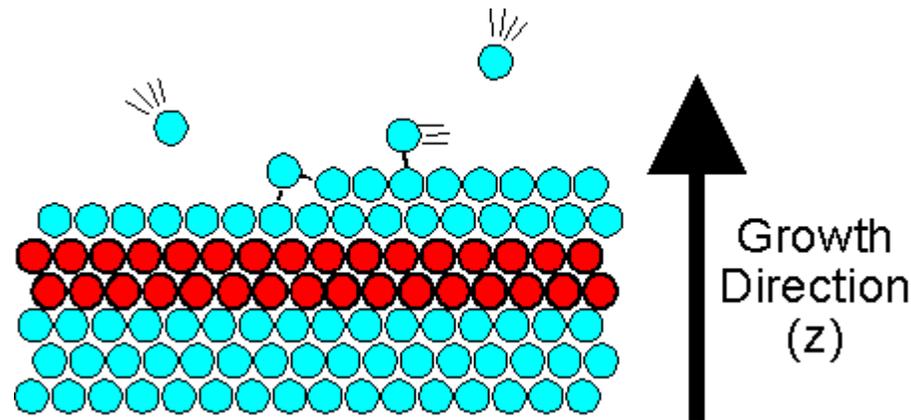
### Main Evaporation Materials

Al	Au
Co	Cr
Cu	Ge
In	Ni
Pb	Pt
Si	Sn
Ti	W
Y	Zn
Al <sub>2</sub> O <sub>3</sub>	BaF <sub>2</sub>
Cr <sub>2</sub> O <sub>3</sub>	HfO <sub>2</sub>
In <sub>2</sub> O <sub>3</sub>	MgF <sub>2</sub>
SiO <sub>2</sub>	SiO
TiO <sub>2</sub>	Ta <sub>2</sub> O <sub>5</sub>
WO <sub>3</sub>	ZnS
Nb <sub>2</sub> O <sub>5</sub>	



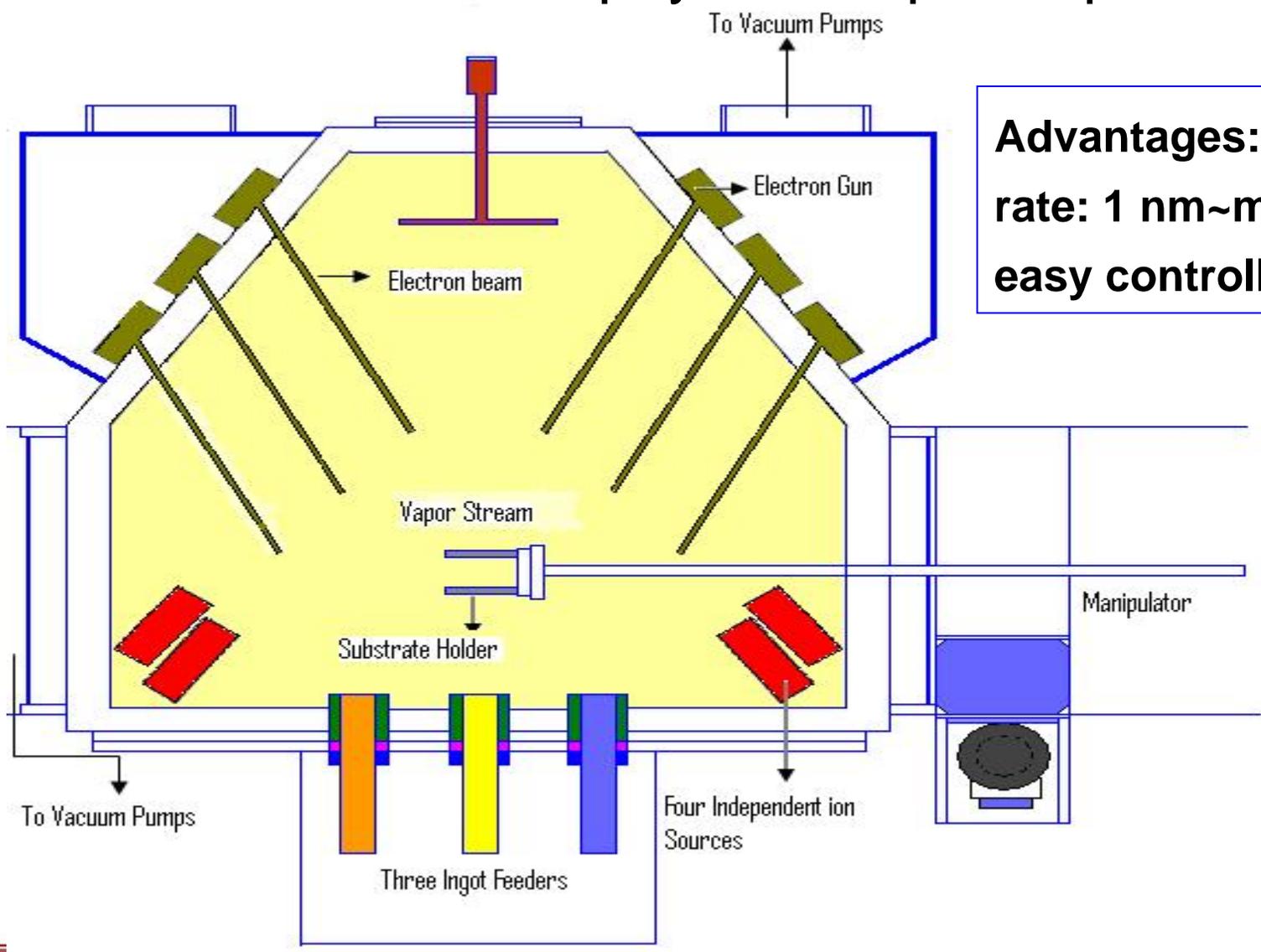
## Molecular beam epitaxy (MBE)

Molecular beam epitaxy takes place in high vacuum or ultra high vacuum ( $10^{-8}$  Pa). The most important aspect of MBE is the slow deposition rate (typically less than 1000 nm per hour), which allows the films to grow epitaxially. The slow deposition rates require proportionally better vacuum to achieve the same impurity levels as other deposition techniques.





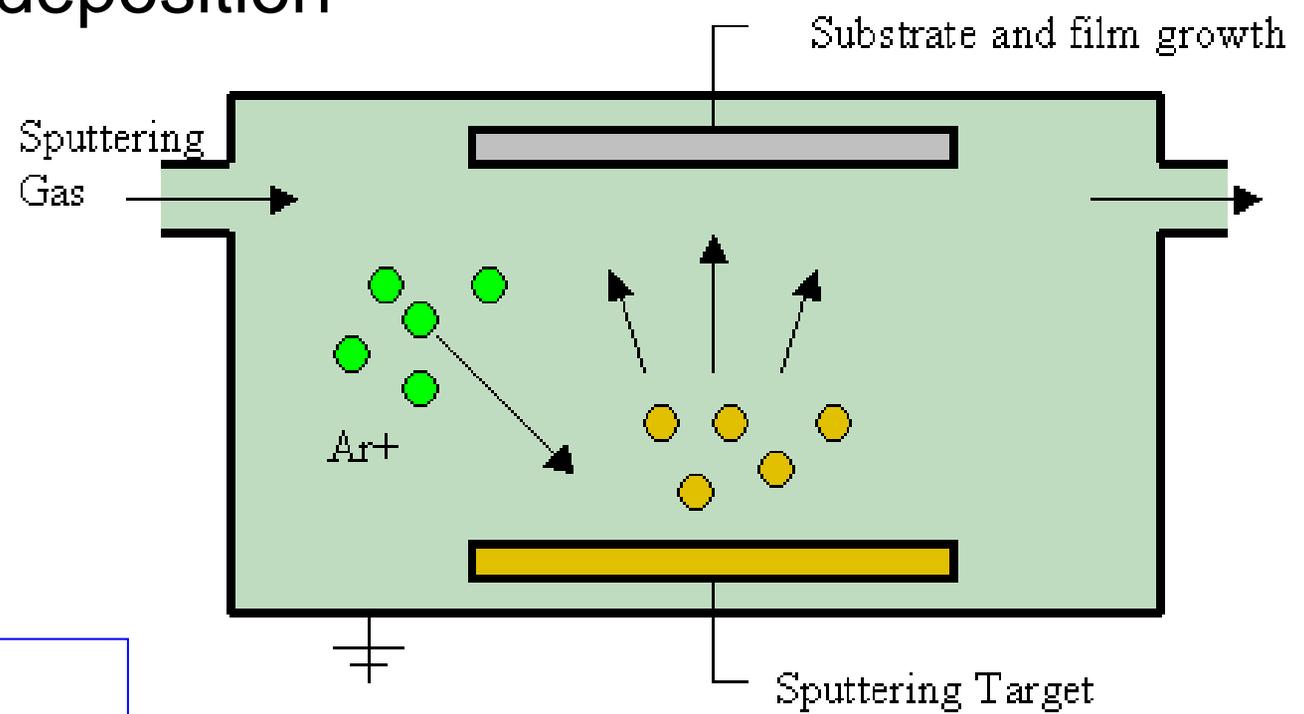
## 3.4.2 Electron beam physical vapor deposition



**Advantages:**  
**rate: 1 nm~microns/min**  
**easy controlling**



## 3.4.3 Sputter deposition

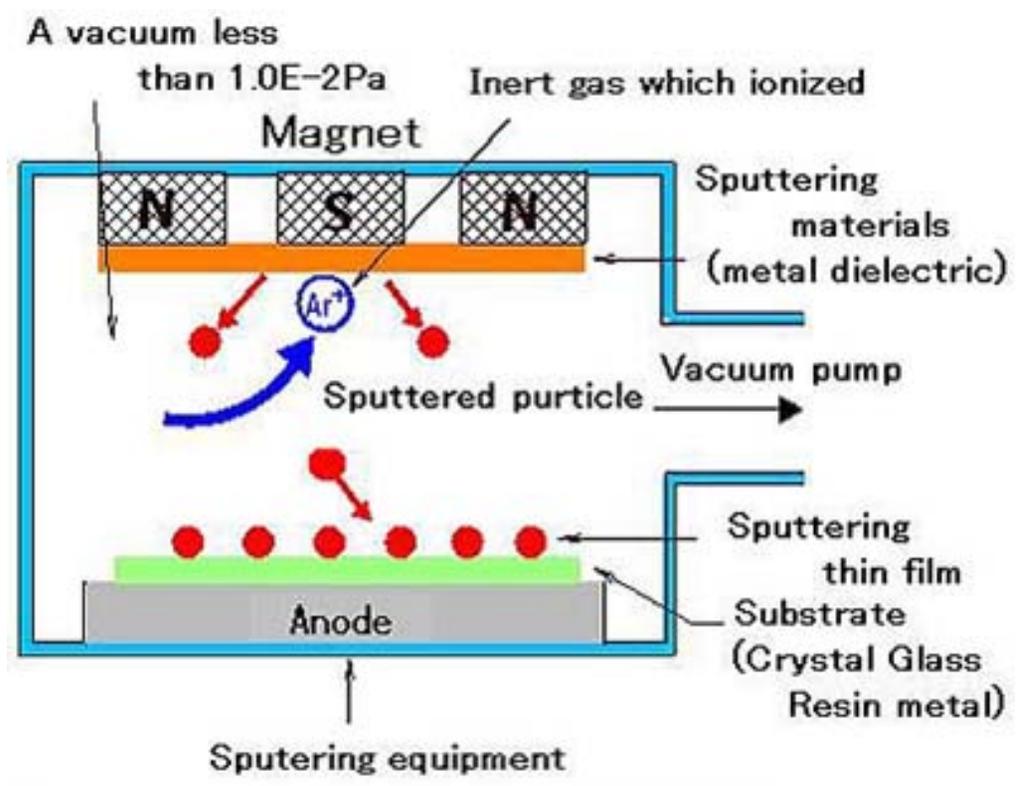


- Advantages:**
- for high  $T_m$  material
  - composition control
  - high speed
  - better adhesion
  - no heating of source

- Disadvantages:**
- structural control difficult
  - layer-by-layer control is difficult



## 3.4.3 Sputter deposition



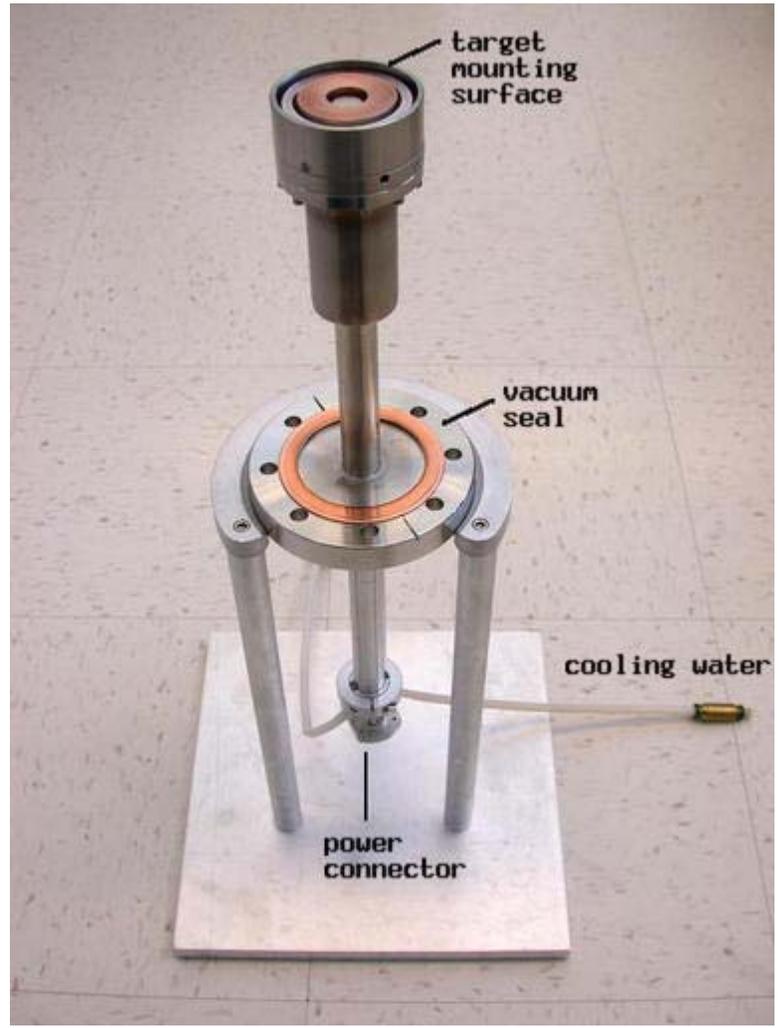
### Magnetron sputtering

### Main Sputtering Materials

Al	Au
Co	Cr
Cu	Mo
Nb	Ni
Pd	Pt
Ru	Si
Sn	Ta
Ti	W
$Al_2O_3$	$Fe_2O_3$
$In_2O_3$	SiN
$SiO_2$	$SnO_2$
$Ta_2O_5$	TiN
$TiO_2$	

## Sputter deposition

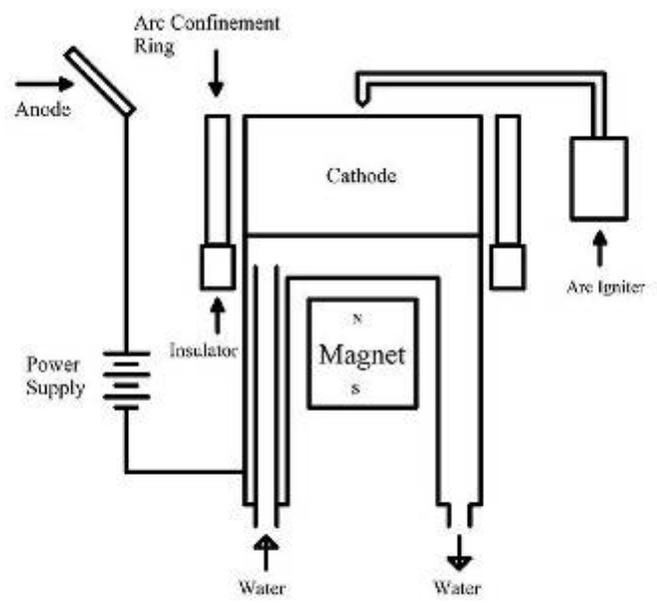
- Ion-beam sputtering
- Reactive sputtering
- Ion-assisted deposition
- High-target-utilization sputtering
- High-power impulse magnetron sputtering
- Gas flow sputtering: hollow cathode effect



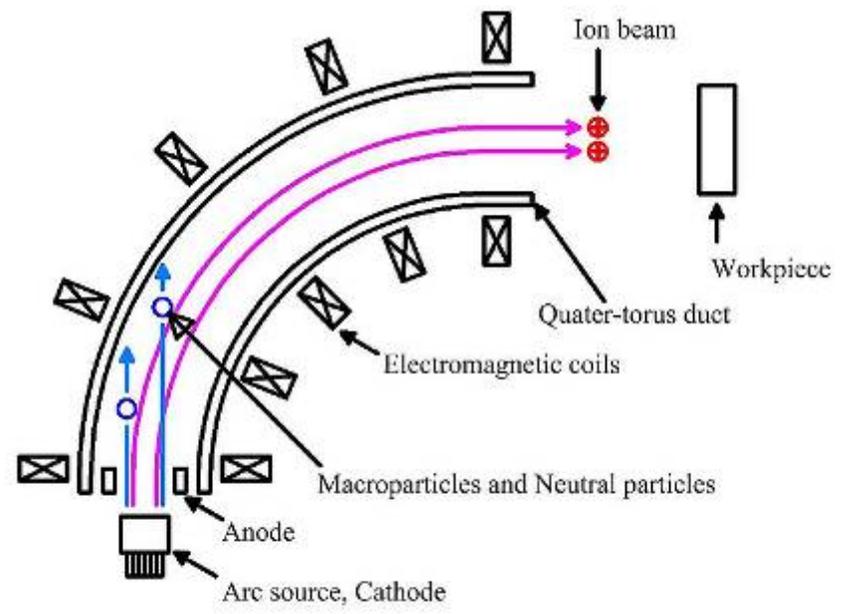
magnetron gun



## 3.4.4 Cathodic arc deposition



Cathodic arc source (Sablev type)



Aksenov's quarter-torus macroparticle filter

The arc evaporation process begins with the striking of a high current, low voltage arc on the surface of a cathode (known as the target) that gives rise to a small, highly energetic emitting area known as a cathode spot. The localized temperature at the cathode spot is extremely high ( $\sim 15000^{\circ}\text{C}$ ), which results in a high velocity (10 km/s) jet of vapourized cathode material, leaving a crater behind on the cathode surface.



## 3.4.5 Pulsed laser deposition

Four stages of PLD:

- Laser ablation of the target material and creation of a plasma
- Dynamic of the plasma
- Deposition of the ablation material on the substrate
- Nucleation and growth of the film on the substrate surface

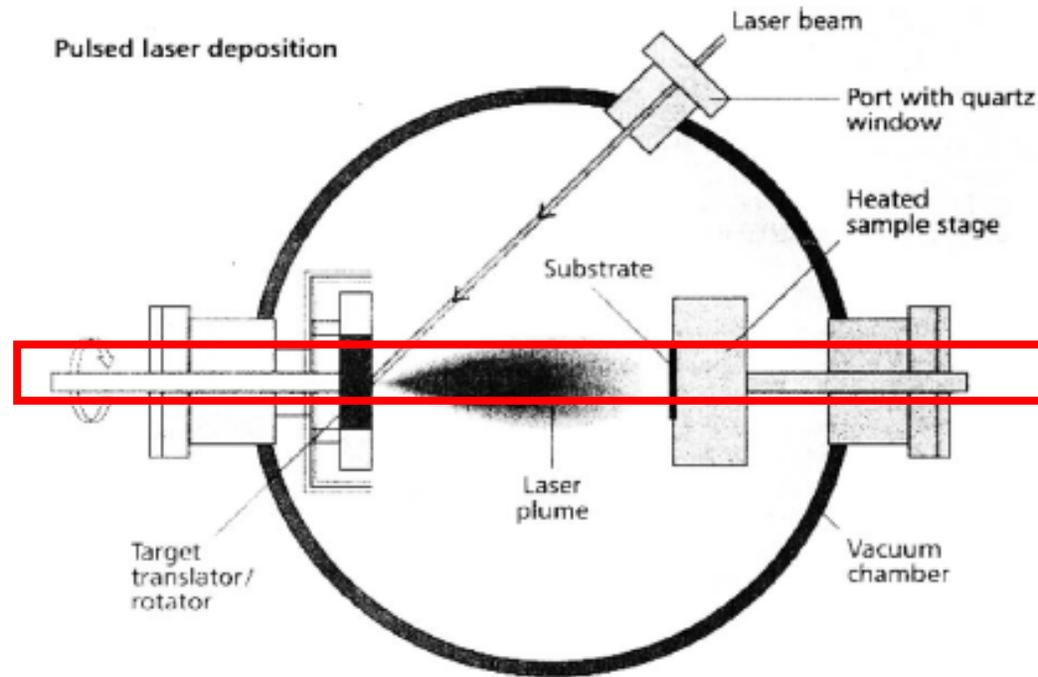
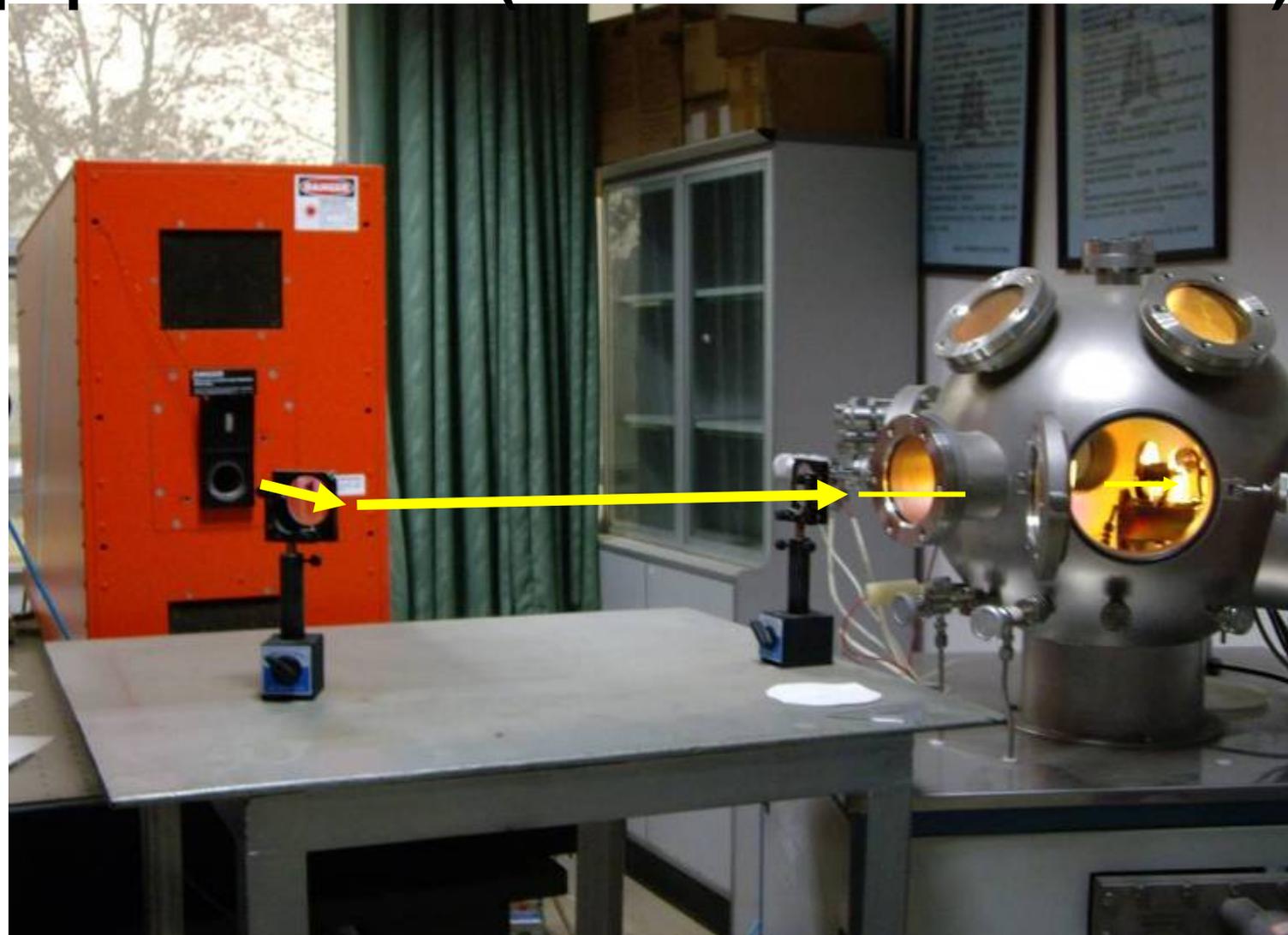


Fig. 1. Scheme of pulsed laser deposition [80].



## Equipment of PLD (KrF excimer laser 248nm)





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## 4.1 Transparent conductive Films on glasses

Type of thin film	Materials
Metals	Au, Ag, Pt, Cu, Rh, Pd, Al
Nitrides	TiN, ZrN
Borides	LaB <sub>4</sub>
Oxides	In <sub>2</sub> O <sub>3</sub> , SnO <sub>2</sub> , ZnO, CdO, Cd <sub>2</sub> SnO <sub>4</sub> , Zn <sub>2</sub> SnO <sub>4</sub>
Polymers	Poly(3,4-ethylenedioxythiophene) (PEDOT), Poly(3,4-ethylenedioxythiophene) PEDOT: Poly(styrene sulphonate) PSS , Poly(4,4-dioctylcyclopentadithiophene)
Carbon nanotubes	C

**The most important functional glasses with many applications: Low-E glasses, electrodes in transparent optoelectronic devices**



## 4.1 Transparent conductive Films on glasses

### 4.1.1 Polymer films

Reported in 1900s as derivatives of polyaniline.

Polymers: derivatives of polyacetylene, polyaniline, polypyrrole or polythiophenes.

Characteristics: conjugated double bonds which allow for conduction. Absorb some of the visible spectrum and significant amounts of the mid to near IR

Band gap: HOMO-LUMO separation that is transparent to visible light.

HOMO: the highest occupied molecular orbital

LUMO: the lowest unoccupied molecular orbital

## 4.1 Transparent conductive Films on glasses

### 4.1.2 CNT thin films

#### Preparation:

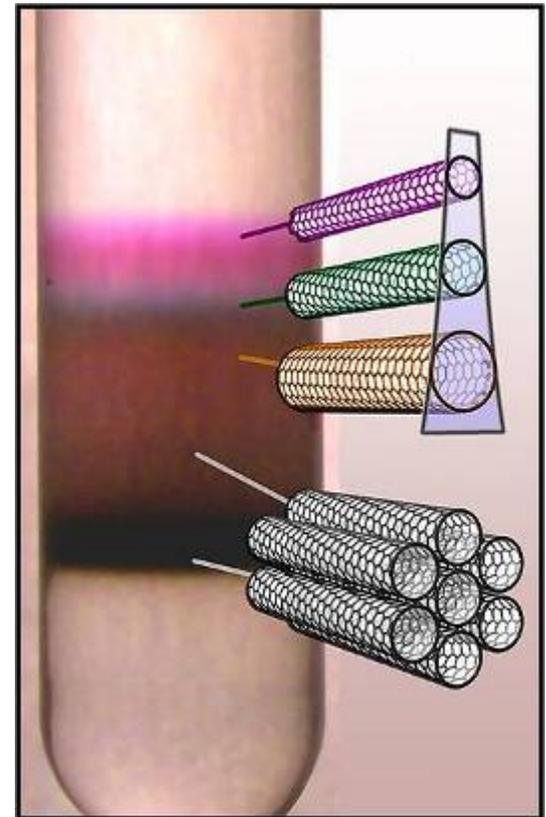
- the CNT growth process
- putting the CNTs in solution,
- creation of the CNT thin film.

#### Advantages:

- high elastic modulus (~1 - 2 TPa)
- high tensile strength (~13 - 53 GPa)
- high conductivity (theoretically  $4 \times 10^9$   $\text{\AA}/\text{cm}^2$ , ~1000 times of Cu).

#### Disadvantages:

- Difficult to prepare homogeneous films



CNTs of various diameters separated within a centrifuge tube. Each distinct diameter results in a different color.



## 4.1 Transparent conductive Films on glasses

### 4.1.3 Metal-based films

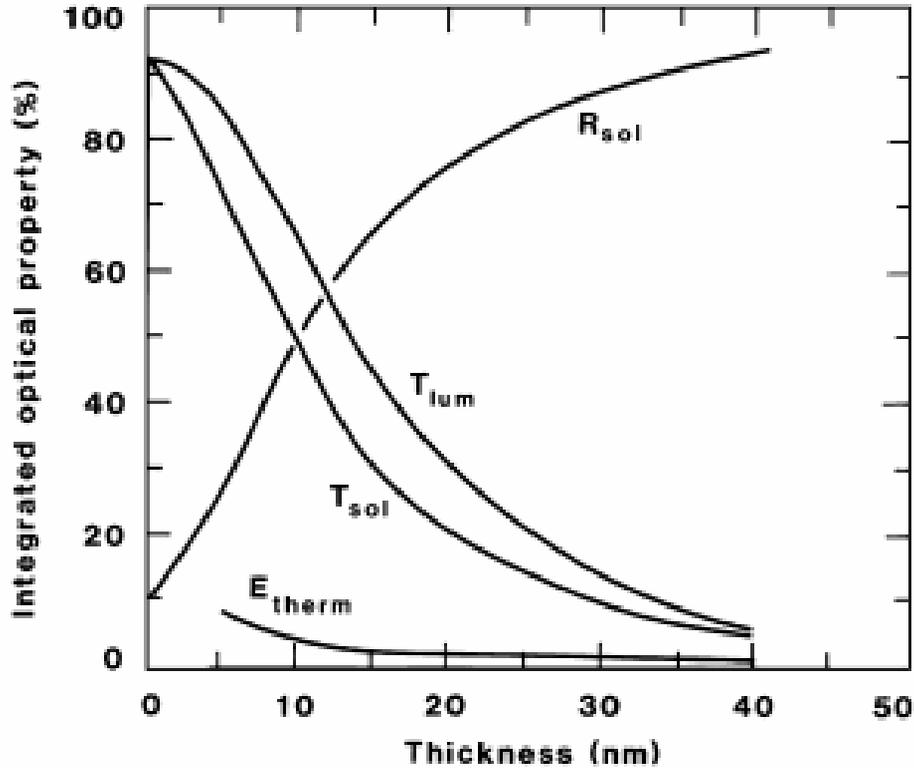
When the thickness is less than 20 nm, the transmittance of metallic film increases and the absorption and reflection decrease with decreasing thickness.

Typical structure:  $\text{Bi}_2\text{O}_3/\text{Au}/\text{Bi}_2\text{O}_3$ ,  $\text{TiO}_2/\text{Ag}/\text{TiO}_2$ . This is based on the principle of interference and often used as the **low-E glass**.

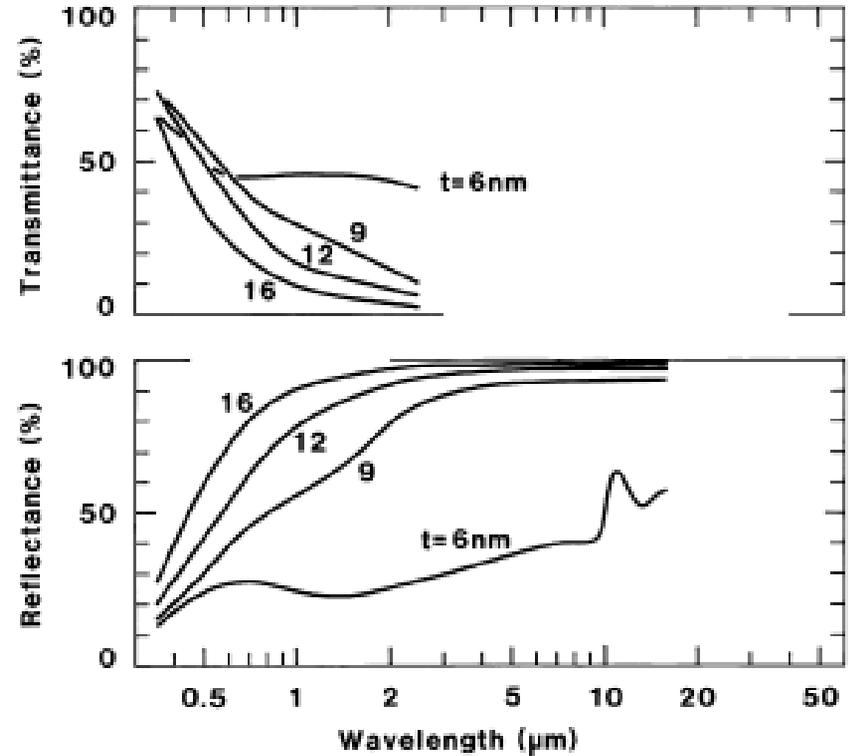


## Emissivity of some materials

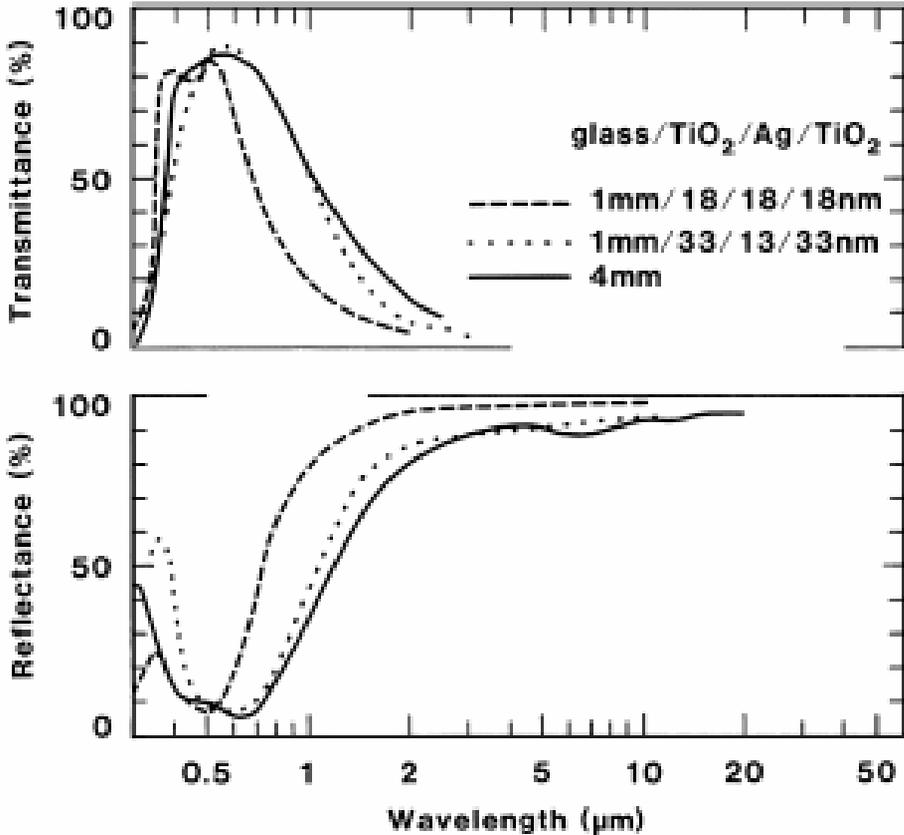
Materials surface	Emittance
Asphalt	0.90-0.98
<b>Aluminum foil</b>	<b>0.03-0.05</b>
Brick	0.93
Concrete	0.85-0.95
Glass (unglazed)	0.95
Fiberglass/cellulose	0.80-0.90
Limestone	0.36-0.90
Marble	0.93
Paper	0.92
Plaster	0.91
<b>Silver</b>	<b>0.02</b>
<b>Steel (mild)</b>	<b>0.12</b>
Wood	0.90



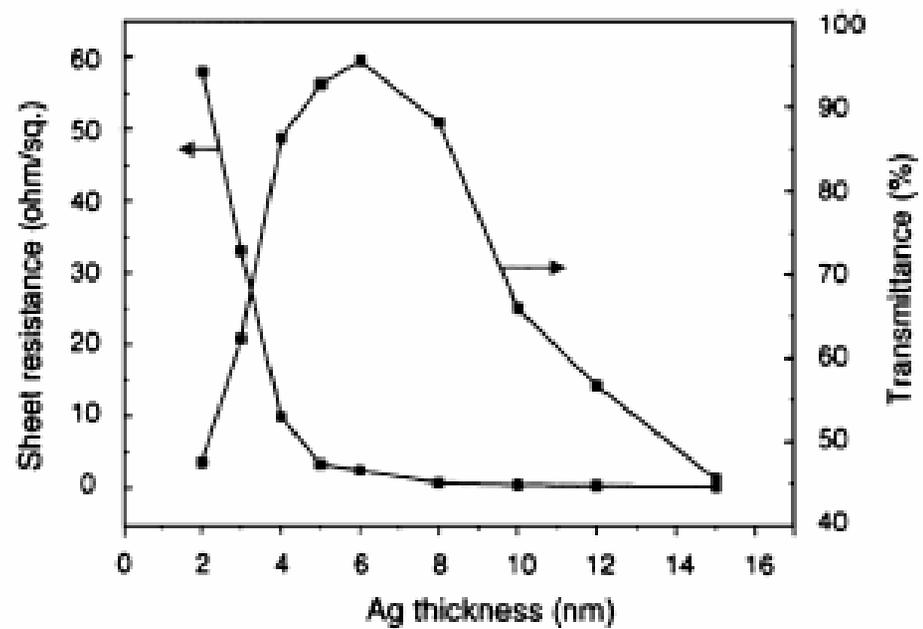
computered plane-parallel Ag layer



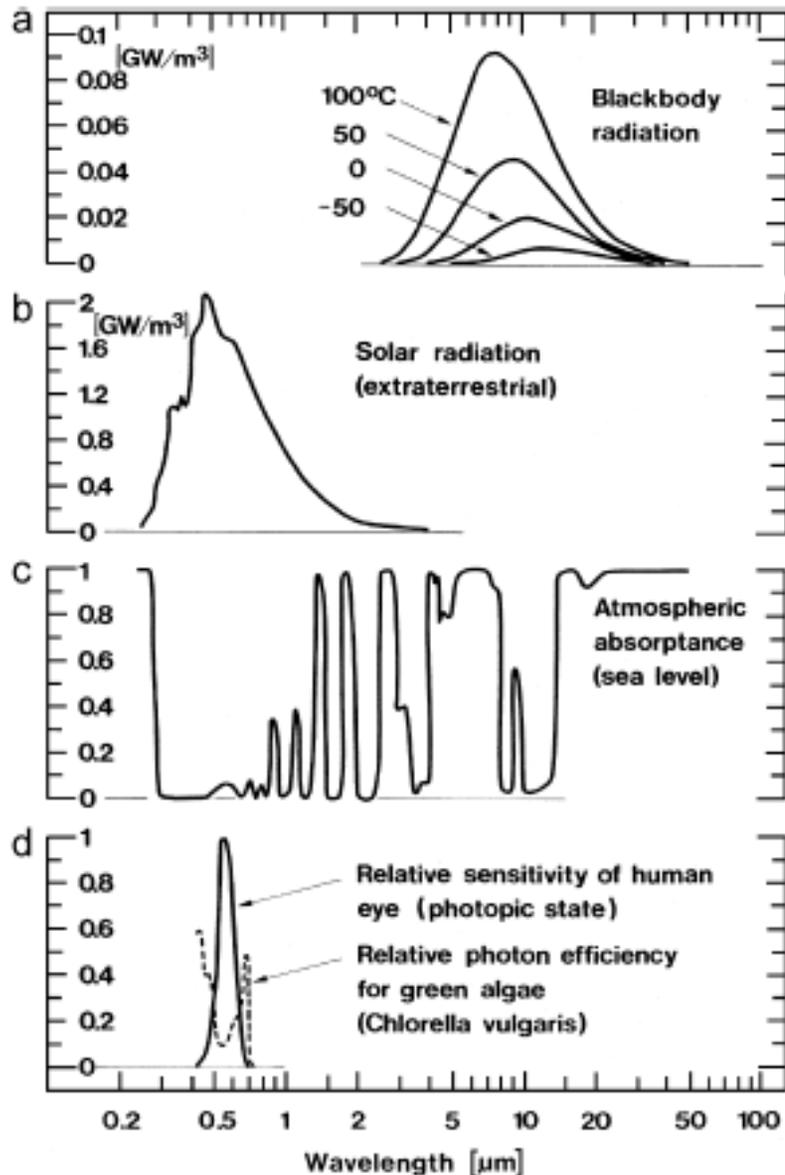
Ag film on glass



### ZnO(20 nm)/Ag/ZnO(20 nm)



Dashed	$T_{lum} > 80\%$	$T_{sol} \approx 50\%$	$R_{sol} \approx 42\%$
Dotted	$T_{lum} > 80\%$	$T_{sol} \approx 67\%$	$R_{sol} \approx 26\%$



These demands have led to two types of thin films, known as “low emittance coatings” (“low- $E$ ”) characterized by

$$T(\lambda) = 1 \quad \text{for} \quad 0.4 < \lambda < 3 \mu m, \quad (3)$$

$$R(\lambda) = 1 \quad \text{for} \quad 3 < \lambda < 50 \mu m \quad (4)$$

and “solar control coatings” characterized by

$$T(\lambda) = 1 \quad \text{for} \quad 0.4 < \lambda < 0.7 \mu m, \quad (5)$$

$$R(\lambda) = 1 \quad \text{for} \quad 0.7 < \lambda < 50 \mu m. \quad (6)$$



## 4.1 Transparent conductive Films on glasses

### 4.1.4 Doped metal oxides

#### Overview:

- fabricated with polycrystalline or amorphous microstructures.
- transmittance of incident light greater than 80%
- conductivities higher than  $10^3 (\Omega \cdot \text{cm})^{-1}$  for efficient carrier transport.

In general, TCOs for use as thin-film electrodes should have a minimum carrier concentration on the order of  $10^{20} \text{ cm}^{-3}$  for low resistivity and a bandgap less than 380 nm to avoid absorption of light over most of the solar spectra. Mobility in these films is limited by ionized impurity scattering and is on the order of  $40 \text{ cm}^2/\text{V}\cdot\text{s}$ .



## 4.1 Transparent conductive Films on glasses

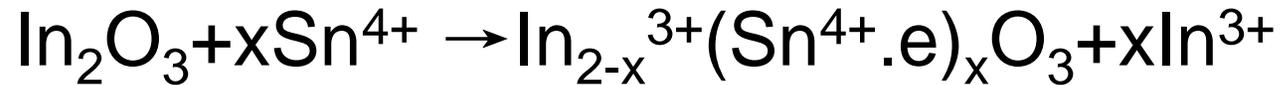
### 4.1.4 Doped metal oxides

- n-type:
  - $\text{In}_2\text{O}_3:\text{Sn}(\text{ITO})$ :  $E_g=3.55-3.75$  eV,  $n=1.9-2.08$
  - $\text{SnO}_2:(\text{F}, \text{Sb}^{5+})$ :  $E_g=3.87-4.3$  eV,  $n=1.8-2$
  - $\text{ZnO}:(\text{In}, \text{Al}, \text{Ga}$  or RE):  $E_g=3.2-3.9$  eV,  $n=1.9-2.2$
- p-type:
  - $\text{ZnO}:(\text{N}, \text{Li})$
  - $\text{SnO}_2:(\text{Al}, \text{In}, \text{Sb}^{3+}, \text{Zn}, \text{Li}, \text{Cu})$
  - $\text{AMO}_2$  type oxides (delafossite structure,  $A=\text{Cu}^{\text{II}}, \text{Sr}$ ,  $M=\text{Ga}, \text{In}, \text{Cr}, \text{Cu}^{\text{III}}$ )



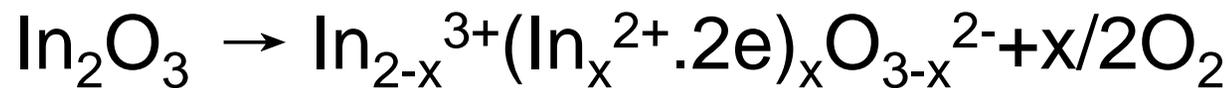
## Mechanism of transparent conductive oxides

In ITO, after doping Sn,



Substitution of  $\text{Sn}^{4+}$  for  $\text{In}^{3+}$  produce one electron.

In the reducing atmosphere,



that is,





## Mechanism of transparent conductive oxides

Dopant: **Shallow donors** near CB (n-type) allow electrons to be excited into CB  
**acceptors** near VB (p-type) allow electrons to jump from VB to the acceptor level, populating the valence band with holes.

An insulator such as an oxide can experience a composition-induced transition to a metallic state given a minimum doping concentration  $n_c$ , determined by:

$$n_c^{1/3} a_H^* = 0.26 \pm 0.05$$

where  $a_H^*$  is the mean ground state Bohr radius. For ITO this value requires a minimum doping concentration of roughly  $10^{19} \text{ cm}^{-3}$ . Above this level, the typically-electrically insulating material becomes metallic and is capable of allowing carrier flow.

## Principal of low-E glass

Relation between emittance and reflectance:

$$\varepsilon = 1 - R$$

Relation between emittance and conductivity:

$$\varepsilon = \sqrt{\frac{8\omega\varepsilon_0}{\sigma}}$$

$\varepsilon$  : emittance,  
 $\varepsilon_0$ : dielectric const in vacuum  
 $\omega$ : angle frequency,  
 $\sigma$ : conductivity

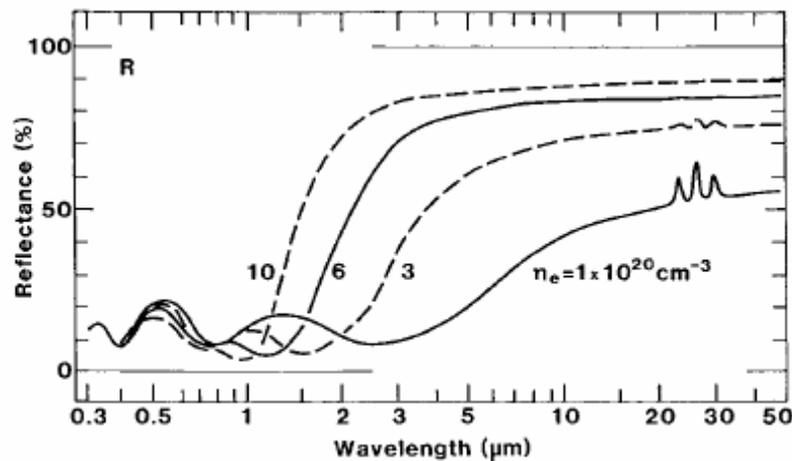
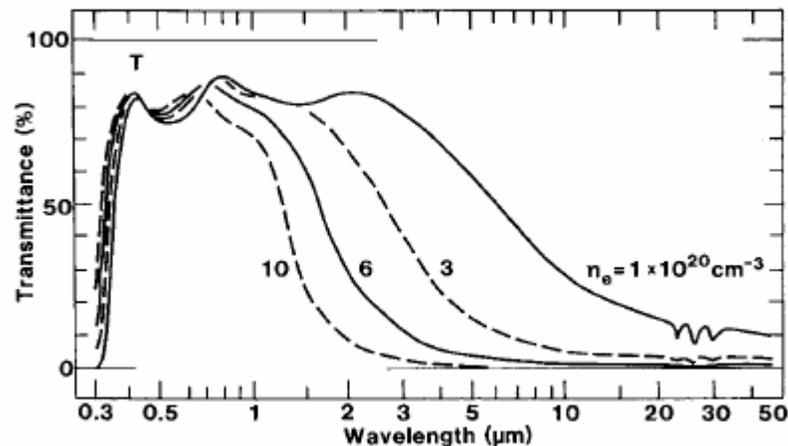
$\lambda$  Starting reflective with Ne and mobility

$$\lambda_p = 2\pi\epsilon_0 \left( \frac{Ne^2}{\epsilon_0 \epsilon_l m^*} - \gamma^2 \right)^{-1/2}$$

Simplifying:

$$R_{IR} = (1 + 0.0053 R_S)^{-2}$$

The smaller  $R_S$ , the larger the  $R_{IR}$



**Wavelength starting reflection with carrier concentration of low-E films**

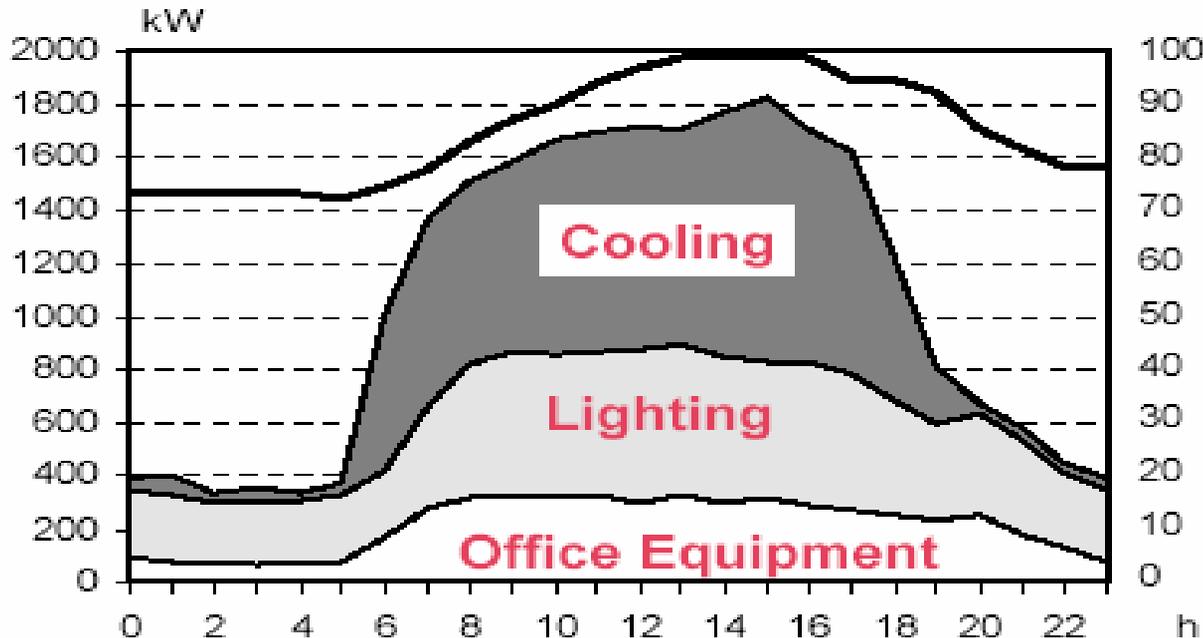
# Application of low-E glass for energy-saving

Energy consumption of building: high as 30-35% of total energy consumption,

Houses: 10~20 kWh / m<sup>2</sup>·yr

Public buildings: 20~60 kWh / m<sup>2</sup>·yr

Large public buildings: 70~300 kWh / m<sup>2</sup>·yr



Typical energy consumption of public building in a summer day



# P-type transparent conductive oxide films

ZnO:(N, Li)                    most extensive studied

SnO<sub>2</sub>:(Al, In, Sb<sup>3+</sup>, Zn, Li, Cu)

AMO<sub>2</sub> type oxides    by Prof. Kawazoe and Hosono in TIT, Japan  
(delafossite structure, A=Cu<sup>II</sup>, Sr, M=Ga, In, Cr, Cu<sup>III</sup>)

The preparation of p-type SnO<sub>2</sub>:Sb (Our researches)

Method: RF sputtering

Target: Sb-SnO<sub>2</sub> ceramic (Sb<sub>2</sub>O<sub>3</sub>:SnO<sub>2</sub> = 0.2:0.8)

Substrate: silica glass and single crystalline Si



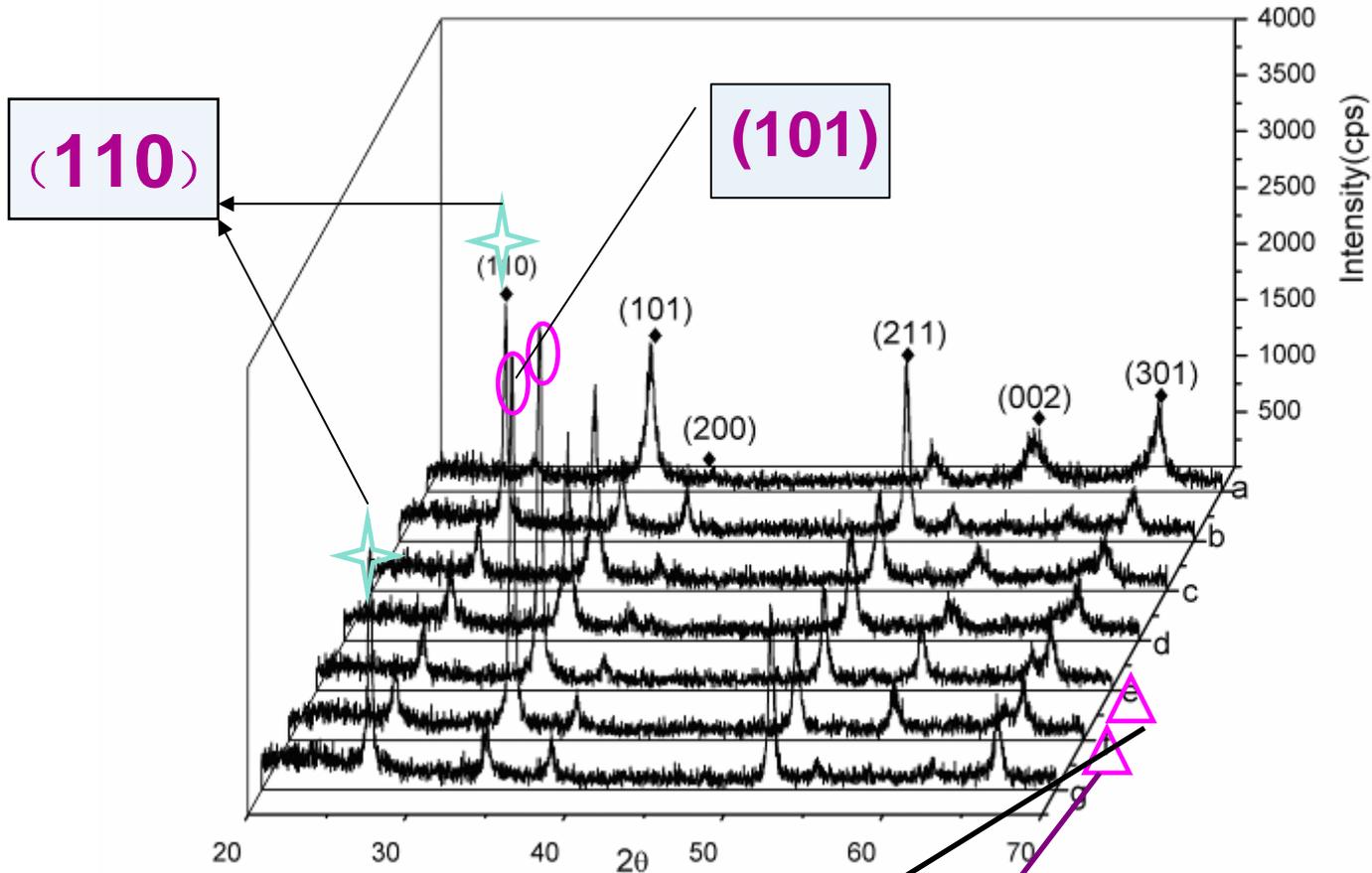
## Electrical properties of ATO films under different annealing temperature

Temperature (°C)	Thickness (μm)	Concentration (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup> )	Resistivity (Ω·cm)	Type
No anneal	0.8	-2.588e+20	2.436e-1	9.9e-2	n
550°C 4h	0.8	-2.32e+20	9.389	2.865e-3	n
600°C 4h	0.8	1.497e+18 -1.618e+18	1.472e+01 1.359e+01	2.832e-1	p/n
700°C 2h	0.8	2.19e+16	3.125e+1	9.12	p
700°C 4h	0.8	5.833e+19	6.465e-1	1.655e-1	p
800°C 4h	0.8	-4.583e+19	9.153	1.488e+1	n

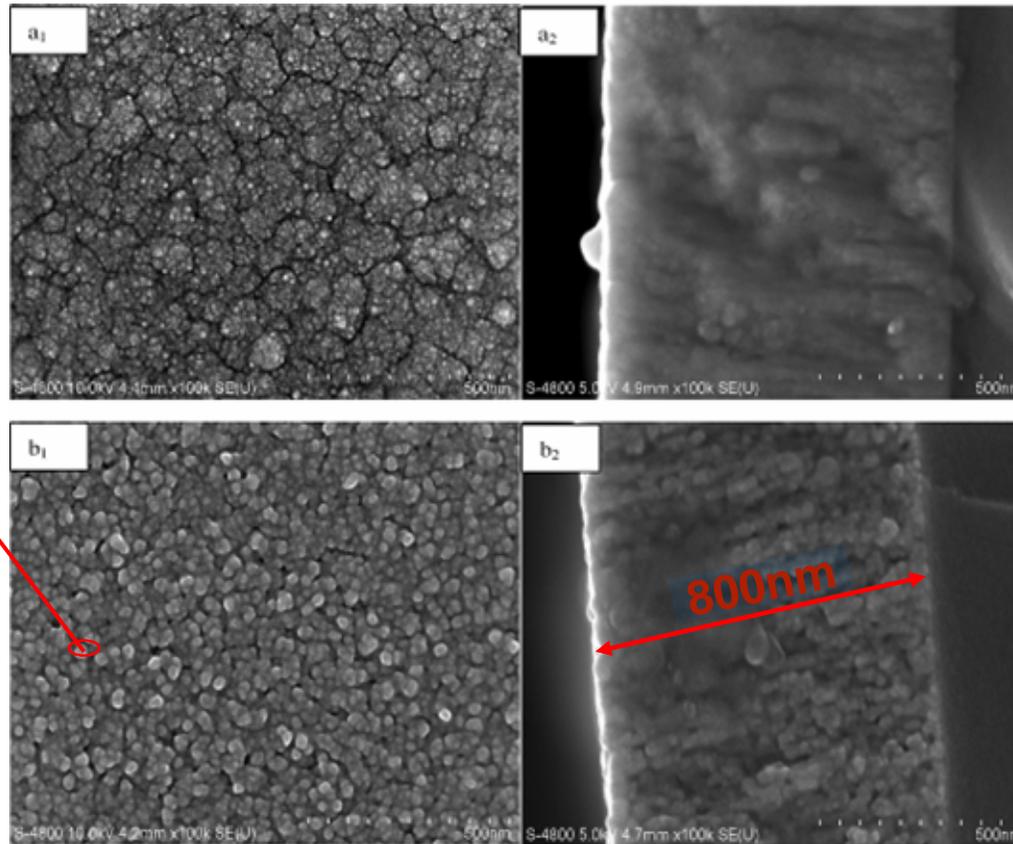
Deposited on quartz substrates  
substrate temp: 200°C

The scattering of carrier is increasing.  
The highest carrier concentration today

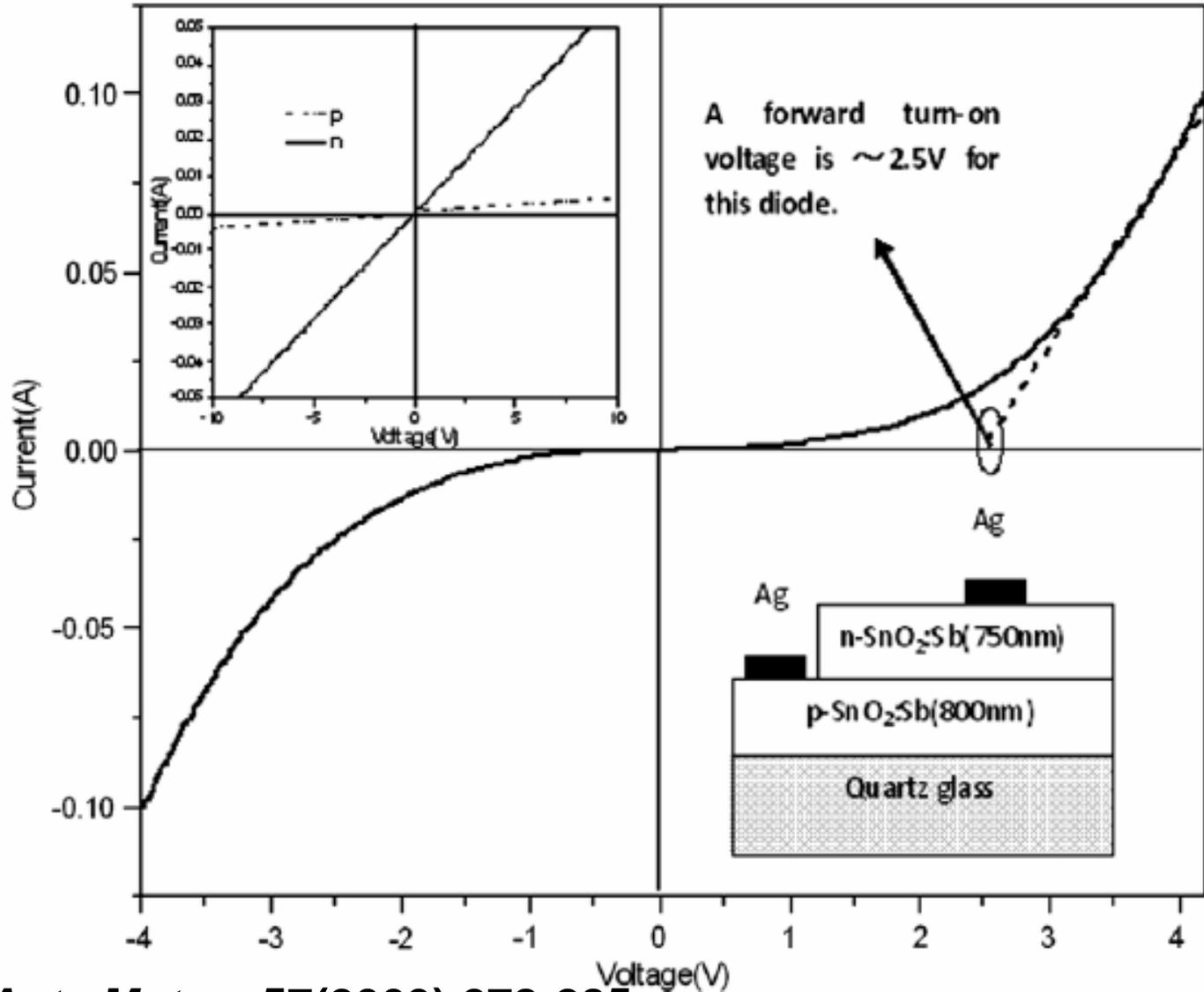
J. Ni et al, *Acta Mater.*, 57(2009) 278-285



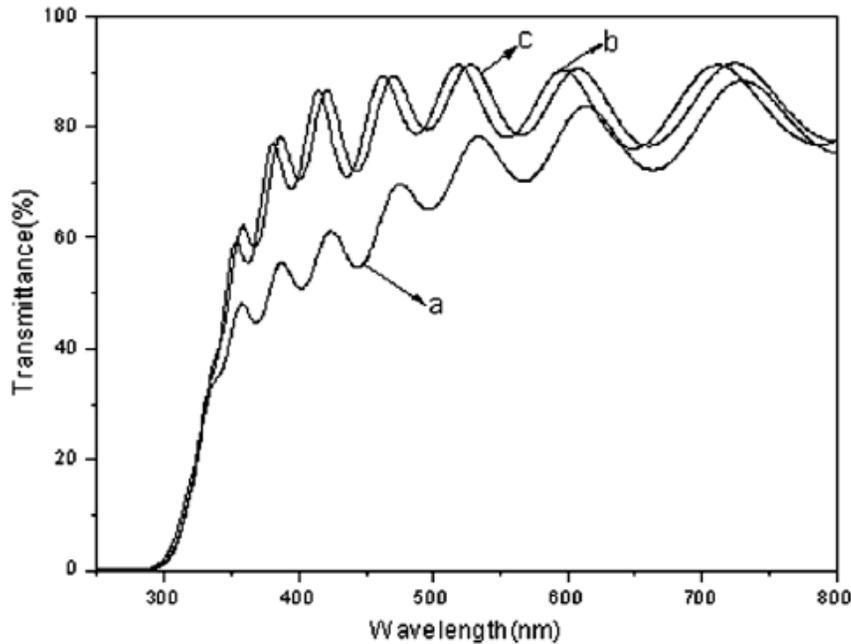
X-ray diffraction spectra of SnO<sub>2</sub>:Sb thin films at different annealing temperature (a: no annealing, b: 823K for 4h, c: 873K for 4h, d :923K for 4h, e:973K for 4h, f :973K for 2h, g: 1073K for 4h)



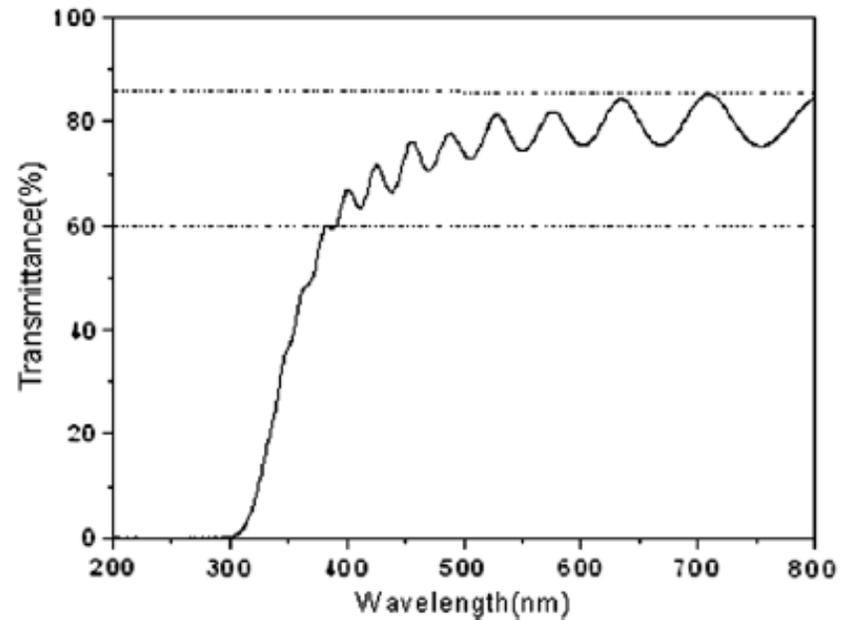
SEM micrographs and image of the cross-section for the ATO films at different annealing temperature (a<sub>1</sub>: micrograph of no annealing, a<sub>2</sub>: cross-section of no annealing; b<sub>1</sub>: micrograph of 973K for 4h, b<sub>2</sub>: cross-section of 973K for 4h)



# Transmittance of p-SnO<sub>2</sub>:Sb thin films and silica glass/ n-ATO/p-ATO p-n junction



transmittance of SnO<sub>2</sub>:Sb thin films



Transmittance of silica/n-ATO/p-ATO  
p-n junction



the influence of the substrate temperature on the electrical properties of the SnO<sub>2</sub>:Sb films.

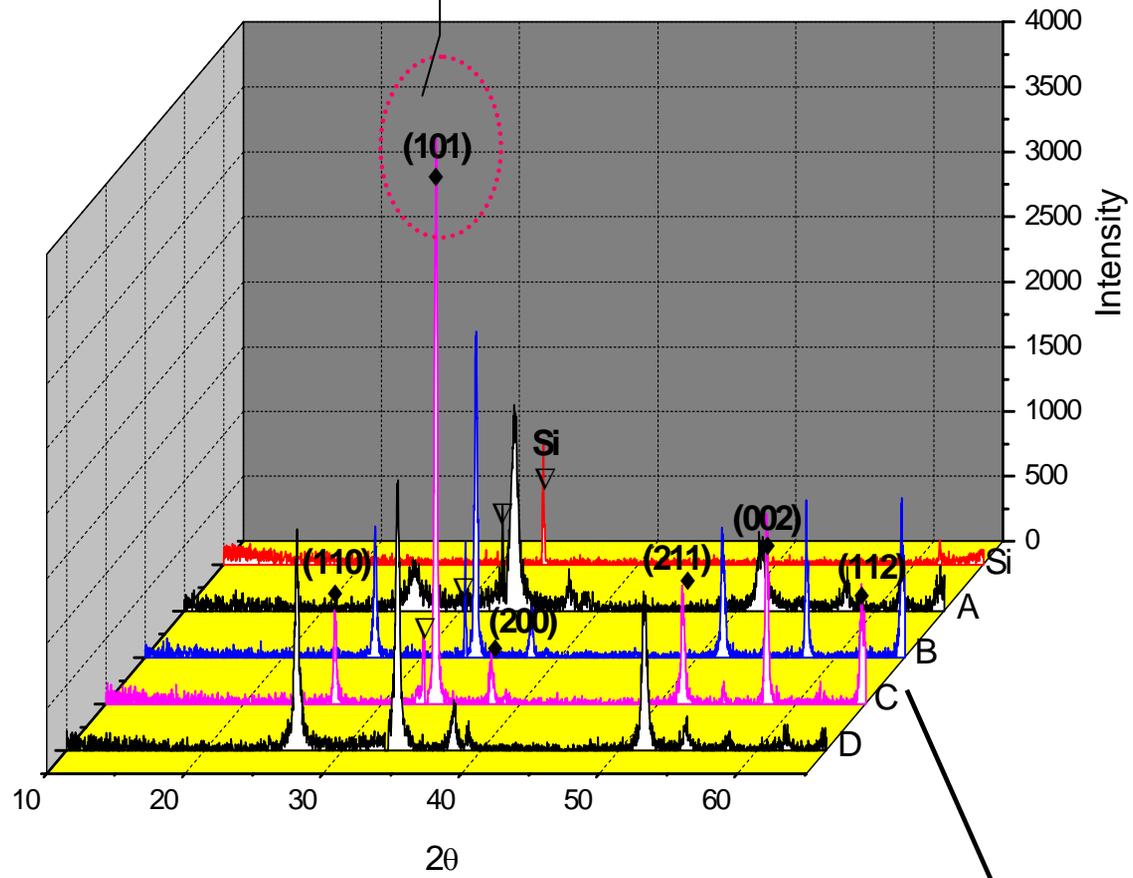
Substrate temperature (°C)	Carrier type	Carrier concentration (cm <sup>-3</sup> )	Carrier Mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Resistivity (Ω cm)
150	P/N	-2.575e+19 2.804e+19	7.28e-1 5.42e-1	3.35e-1
200	P	1.858e+19	1.29	2.59e-1
250	P	1.638e+20	1.87	2.41e-2
300	P	9.288e+19	7.089e-2	9.48e-1

Deposited on Si(100) substrates

Much higher than that of most reported p-type conductors

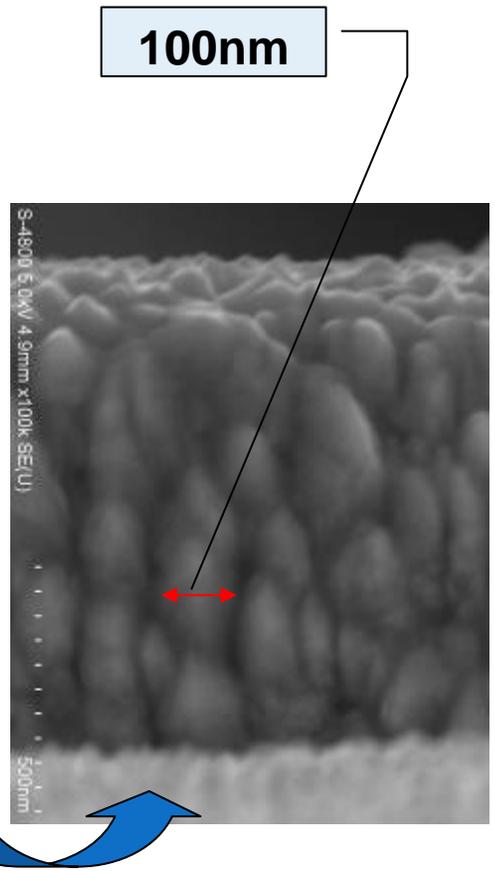
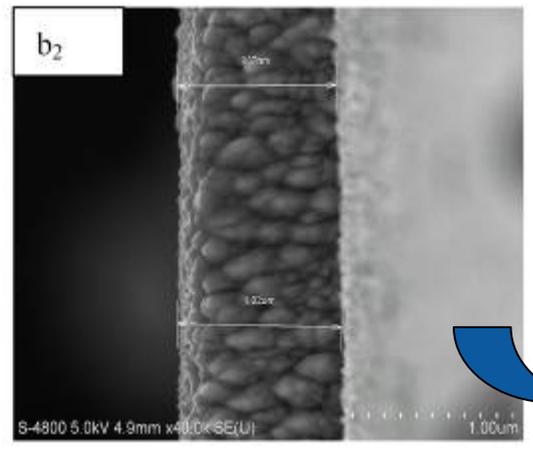
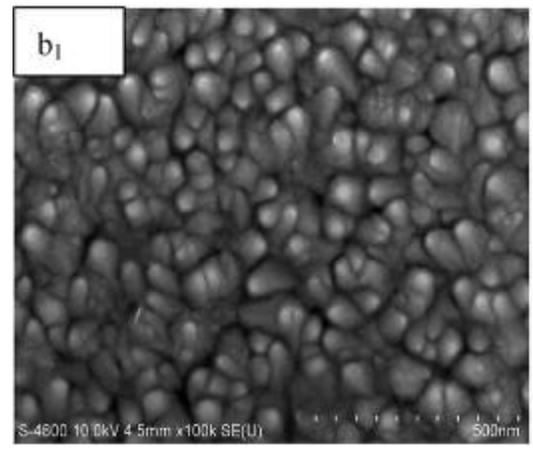
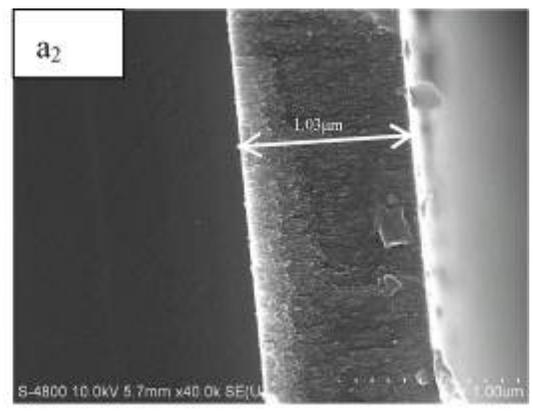
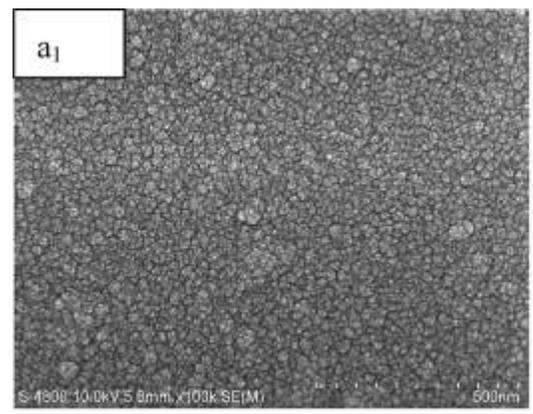


(101)



X-ray diffraction spectra of Si (100) substrate and SnO<sub>2</sub>-Sb thin films deposited at different temperatures (A:150°C, B: 200°C, C: 250°C, D:300°C)

Deposited on **Si(100)** substrates

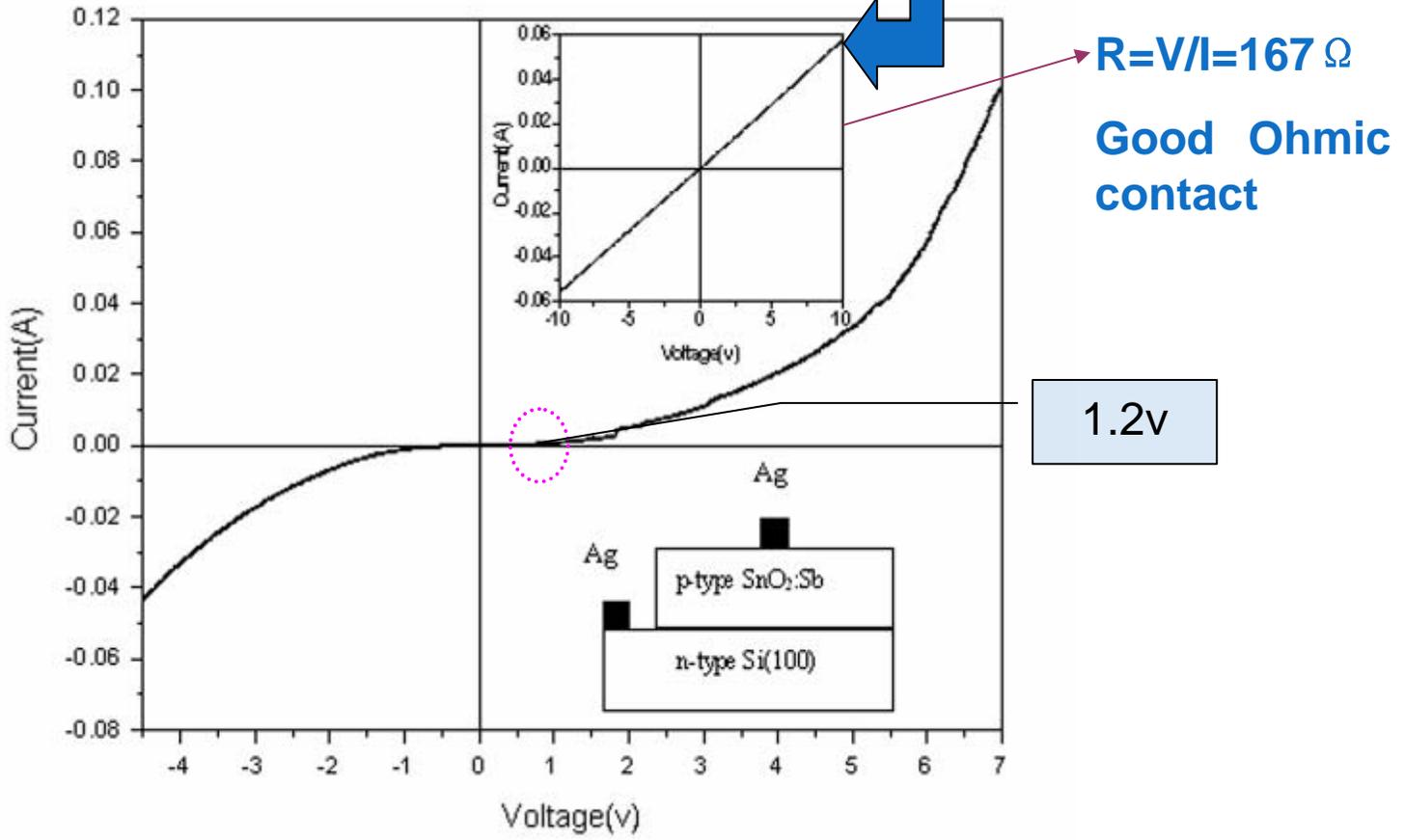


FESEM micrographs and image of the cross-section for the SnO<sub>2</sub>: Sb films deposited at different temperatures (a<sub>1</sub>: micrograph of 150°C, a<sub>2</sub>: cross-section of 150°C; b<sub>1</sub>: micrograph of 250°C, b<sub>2</sub>: cross-section of 250°C).

Deposited on **Si(100)** substrates

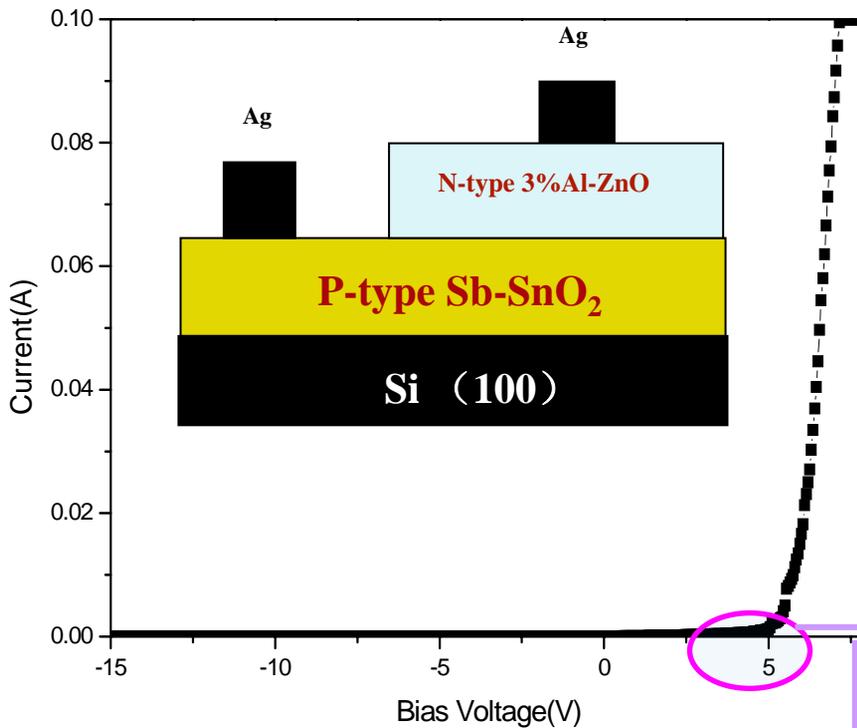
# I-V curve

The upper inset shows the Ohmic contact I-V curve of the Ag electrodes on p-type SnO<sub>2</sub>:Sb film.



I-V characteristics of a p-type SnO<sub>2</sub>:Sb / n-type Si(100) heterojunction. The lower inset shows the schematic structure of the p-type SnO<sub>2</sub>:Sb / n-Si (100) heterojunction. (Notes: the p-type SnO<sub>2</sub>:Sb films were deposited at 250°C)

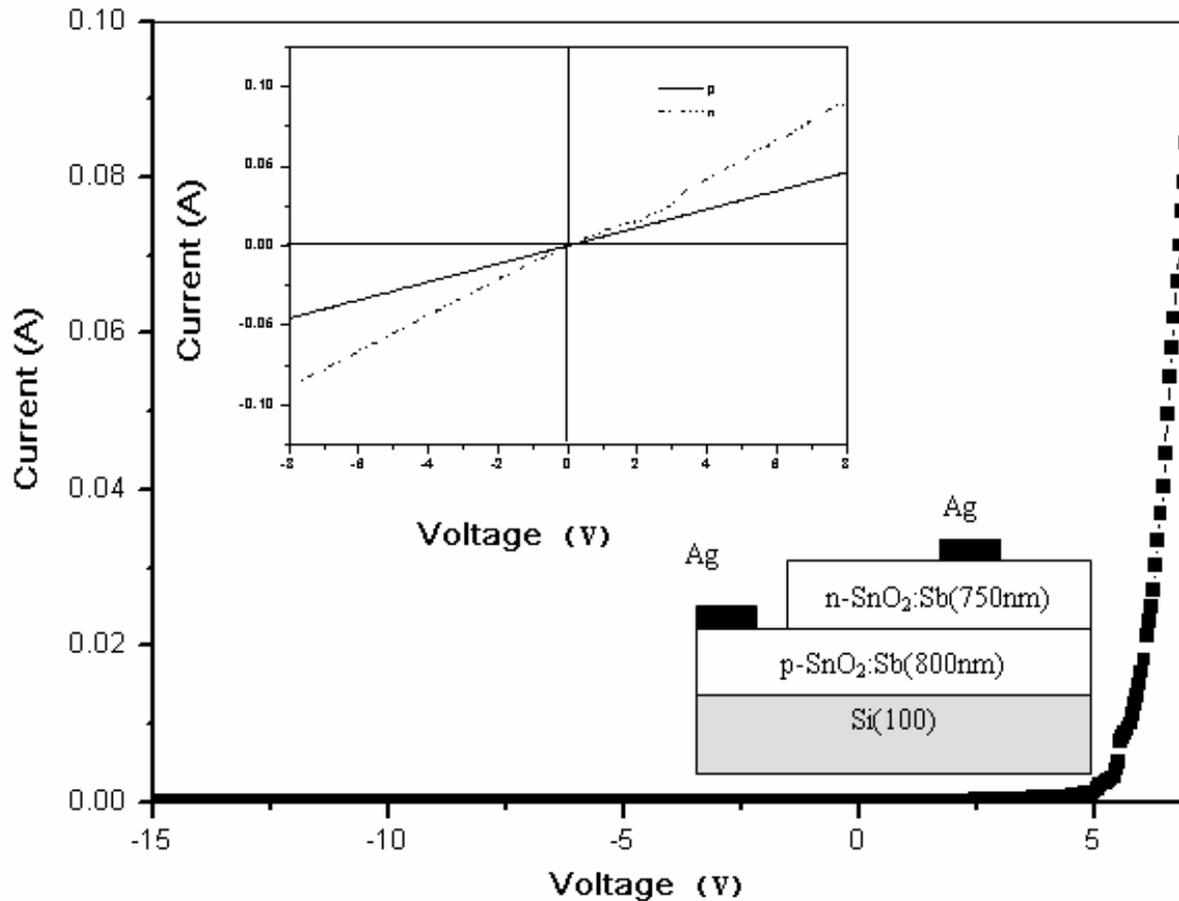
# Transparent hetero p-n junction deposited on Si(100)



the I-V characteristics of p-n junction formed by the n-Al-doped ZnO layer (800 nm)/ p-Sb:SnO<sub>2</sub> layer (800 nm) on a silicon wafer substrate. The Ag electrodes were placed on the n-Al-doped ZnO layer and p-Sb-SnO<sub>2</sub> layer, respectively. The inset shows the device configuration.

A forward turn-on voltage of about 5V for this diode. The power leakage of backward is very small.

# Transparent homo p-n junction deposited on Si(100)



## Anti-reflection of Low-E coating

$$R = \left\{ \frac{(n-1)}{(n+1)} \right\}^2$$

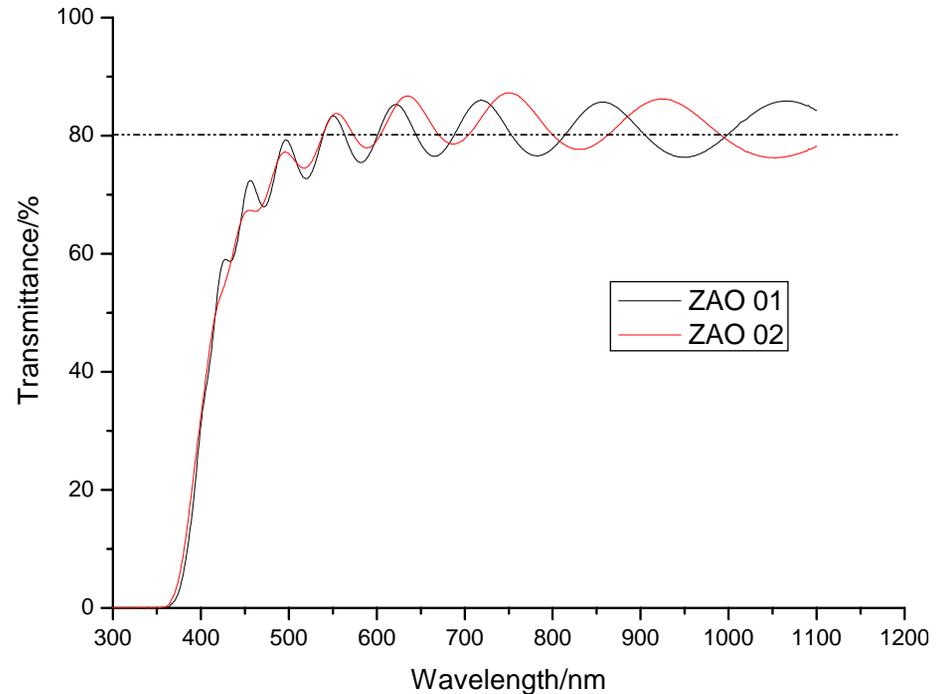
$$T = 1 - R - \alpha$$

R: Reflectance

n: refractive index

T: transmittance

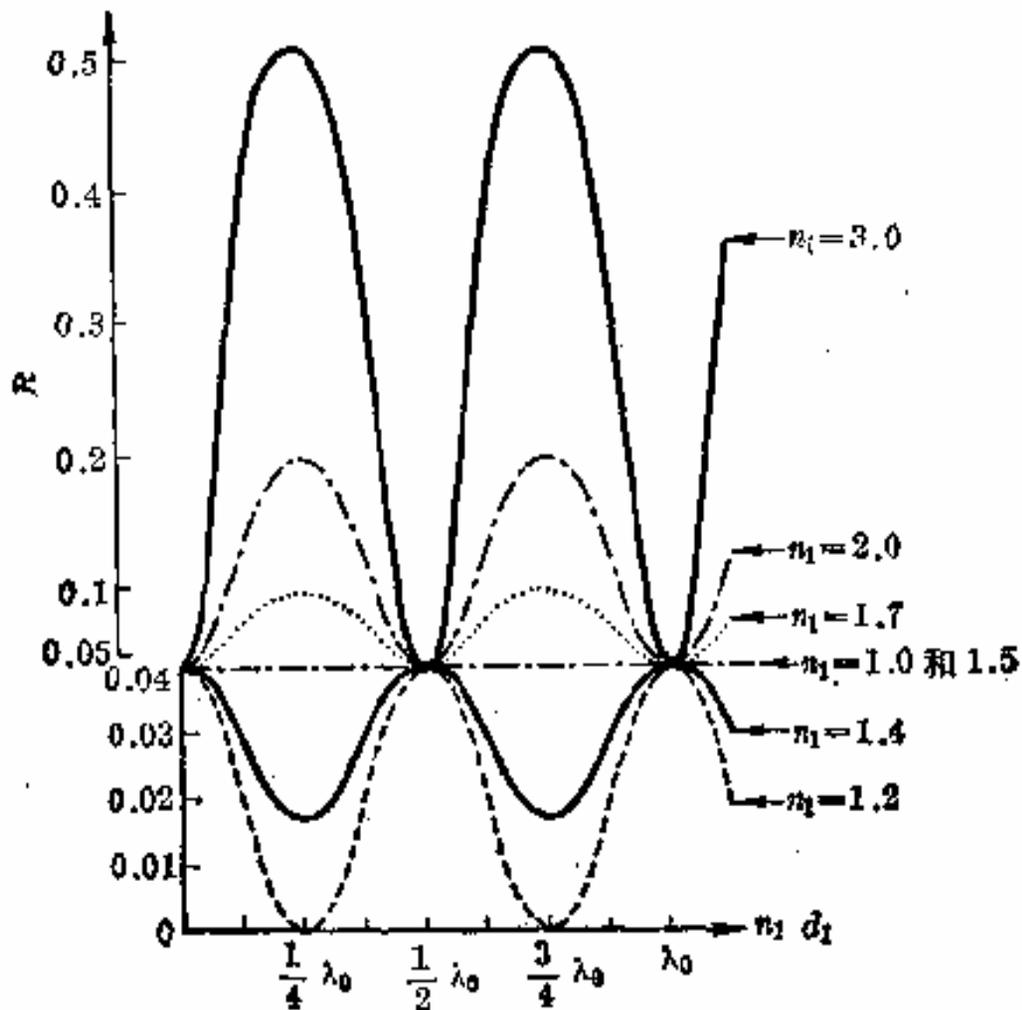
$\alpha$ : absorptance



Transparent conductive oxides with refractive index about 2, then they have large reflectance in visible region.

# Reflectance of single layer dielectric film

$$R_{\lambda,0} = \left( \frac{n_0 - \frac{n_1^2}{n_2}}{n_0 + \frac{n_1^2}{n_2}} \right)^2$$



Relation between reflectance and optical thickness,  $n_1$  for film,  $n_0=1$  for air and  $N_2=1.5$  for glass.

# Types of Antireflection mechanisms

## 1. Interference type:

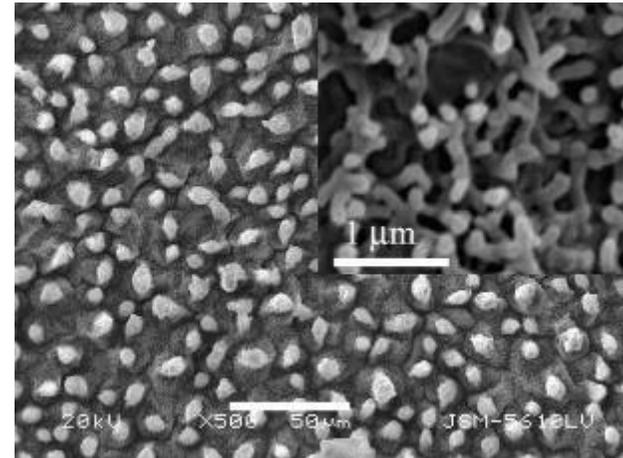
glass/ $\text{TiO}_2$  ( $\text{Ta}_2\text{O}_5$ ,  $\text{Nb}_2\text{O}_5$ ) / $\text{SiO}_2$ /.....

## 2. Modification with surface nano-porous structure

$$n_p^2 = (n^2 - 1)(1 - p) + 1$$

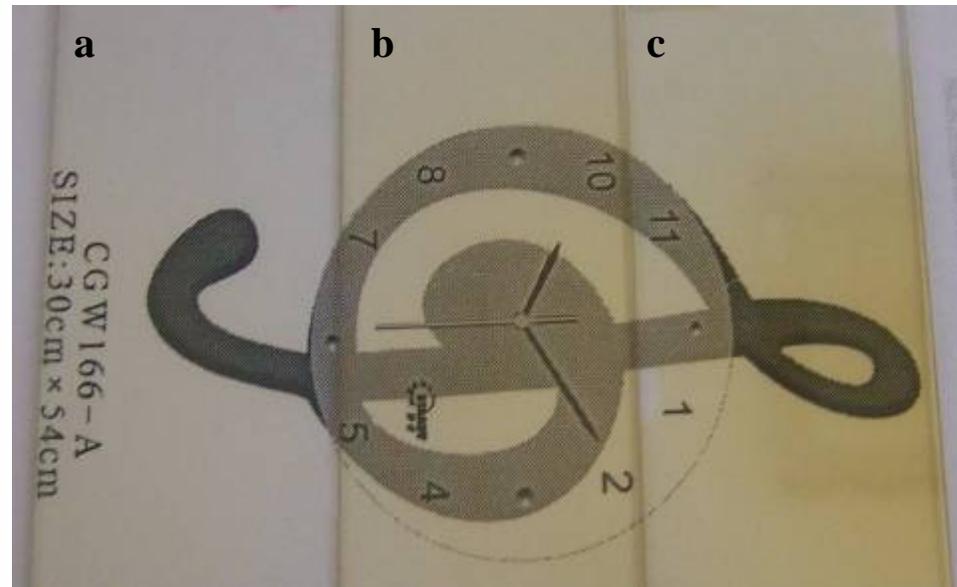
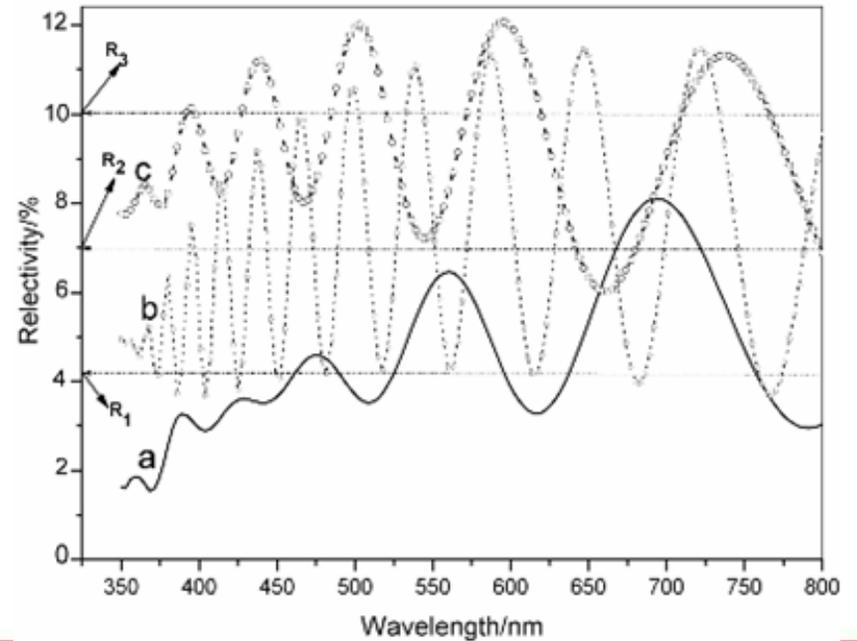
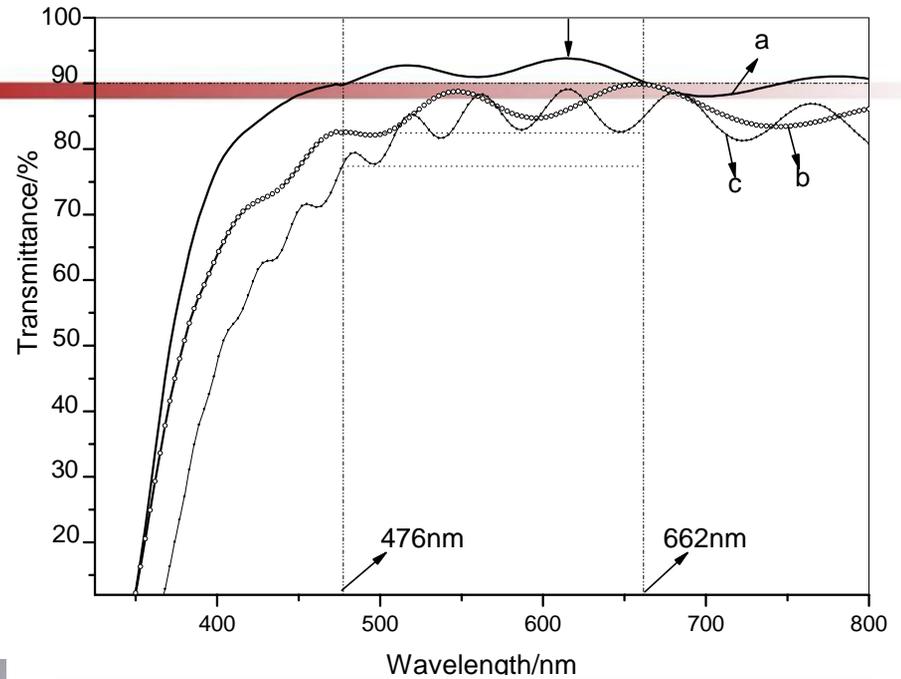
## 3. Absorption type

## 4. Surface structure of lotus leaf

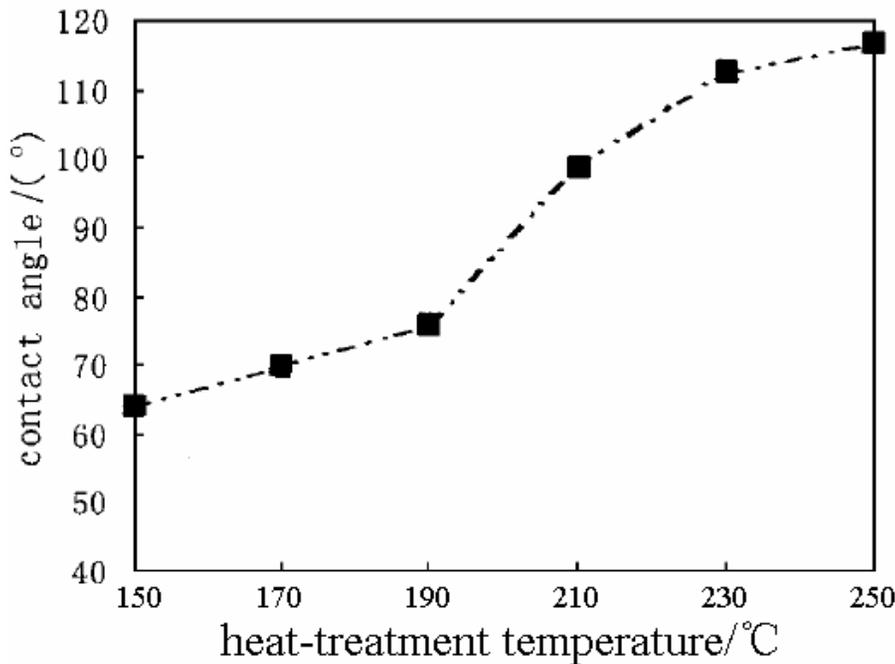
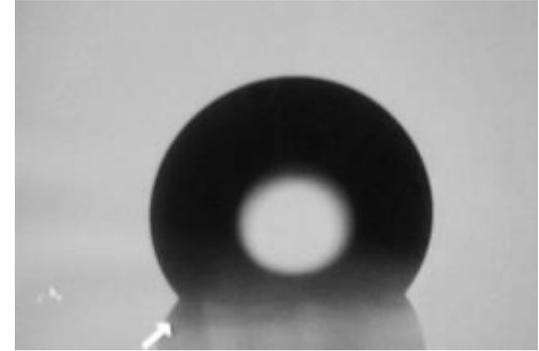


# Interference type

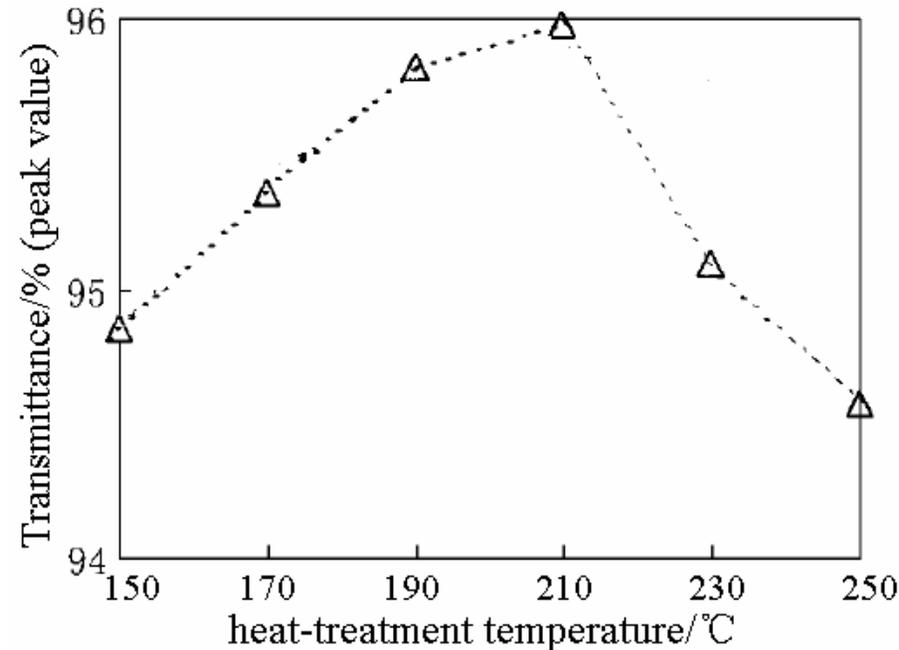
- a:  $\text{SiO}_2(110\text{nm})/\text{AZO}(850\text{nm})/\text{SiO}_2(110\text{nm})$
- b:  $\text{SiO}_2(110\text{nm})/\text{AZO}(850\text{nm})$
- c:  $\text{AZO}(850\text{nm})$



# Nano-porous surface structure of SiO<sub>2</sub> and treatment with hydrophobic agent

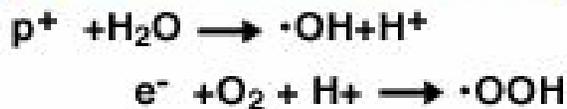
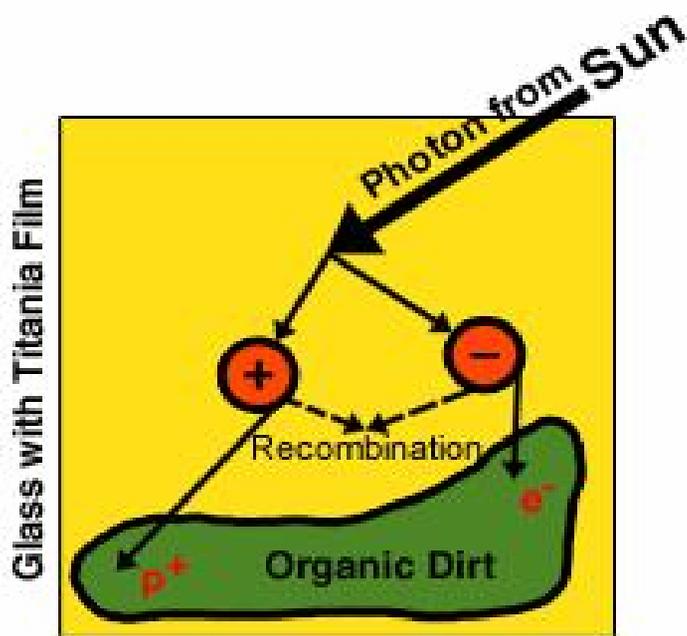


Relation between contact angle and heat-treating temperature



Transmittance with treating temp

## 4.2 Photocatalytic TiO<sub>2</sub> thin films on glass



TiO<sub>2</sub> photocatalist

1972 Honda-Fujishima effect

1970-1990's photolysis of water

photolysis of pollution

materials: powders

1990's dye-sensitized TiO<sub>2</sub> solar cell

1997 photo-induced amphiphilicity

→ TiO<sub>2</sub> photocatalist is suitable  
for degradation of lower content pollution

TiO<sub>2</sub>-based photocatalysis and their evolution



## 4.2 Photocatalytic $\text{TiO}_2$ thin films on glass

### Self-cleaning surface

Super hydrophobic -----fluoropolymer doped  $\text{SiO}_2$

mesoporous  $\text{Al}_2\text{O}_3$

ZnO nano-rod array

Nano-structured polymers

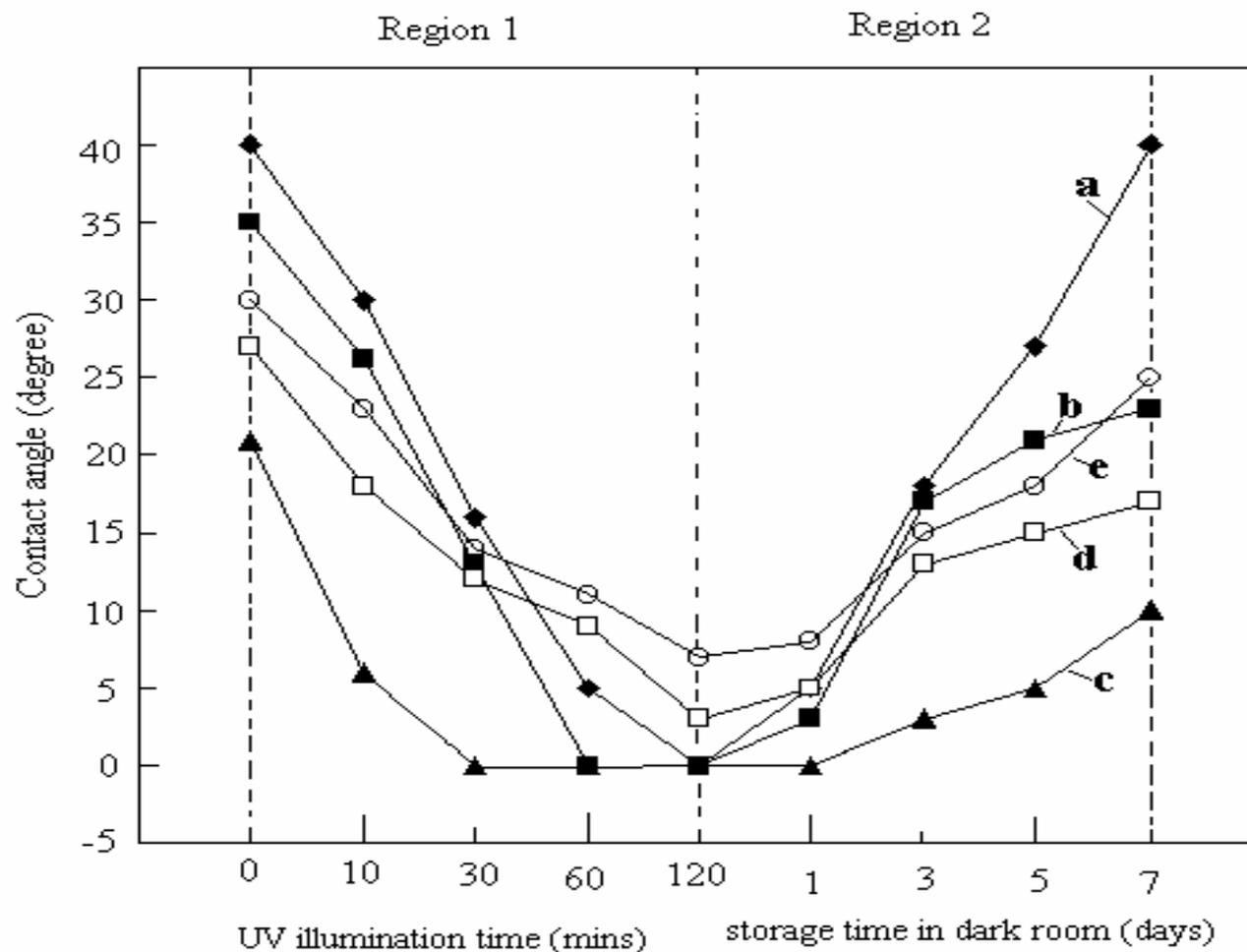
Super hydrophilic-----water soluble materials

$\text{TiO}_2$  photocatalytic property

photoinduced super hydrophilicity

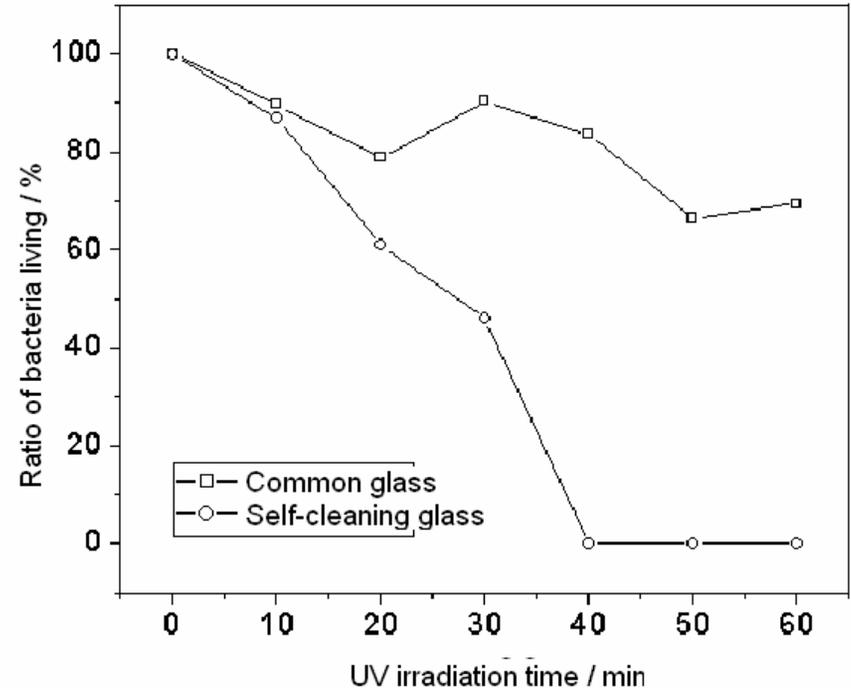
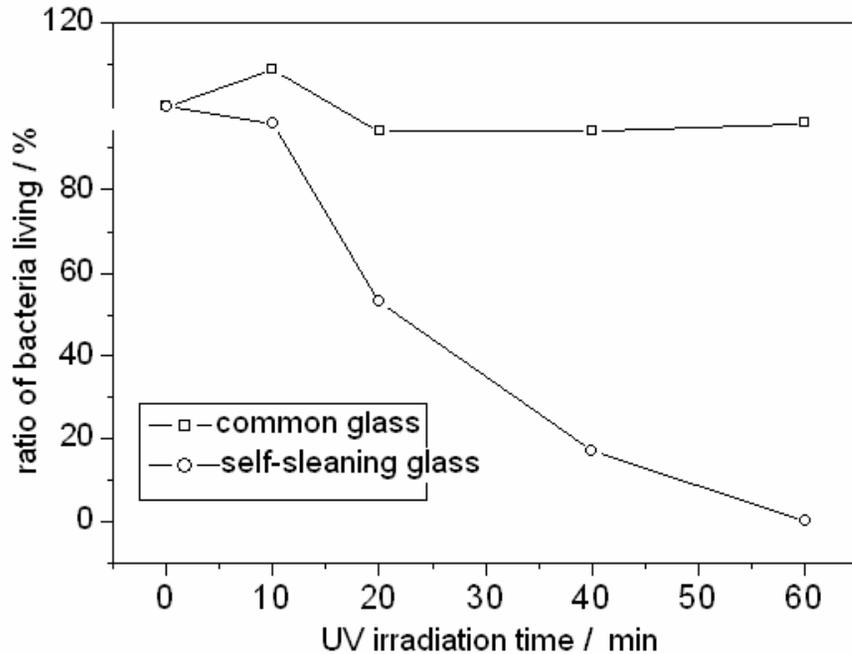
→ self-cleaning surface

# Photoinduced superhydrophilicity of TiO<sub>2</sub> thin films on glass



a: 0g; b: 0.25g; c: 0.5g; d: 1.0g and e: 2g of PEG added to precursor

## Anti-bacteria effect of pure TiO<sub>2</sub> films



**15-W 365-nm UV lamp by Cole-Parmer Instrument Co.,  
average power  $1000 \pm 30 \mu\text{W}/\text{cm}^2$**

**Bacteria: *E. coli* DH5a (left); JM109 (right)**

**concentration:  $1 \times 10^6$  CFC / ml, Temp.:  $25 \pm 1^\circ\text{C}$ ; Humidity: 75%**



## Enhancing anti-bacteria effect **without UV irradiation** by Ag doping (0.1%)

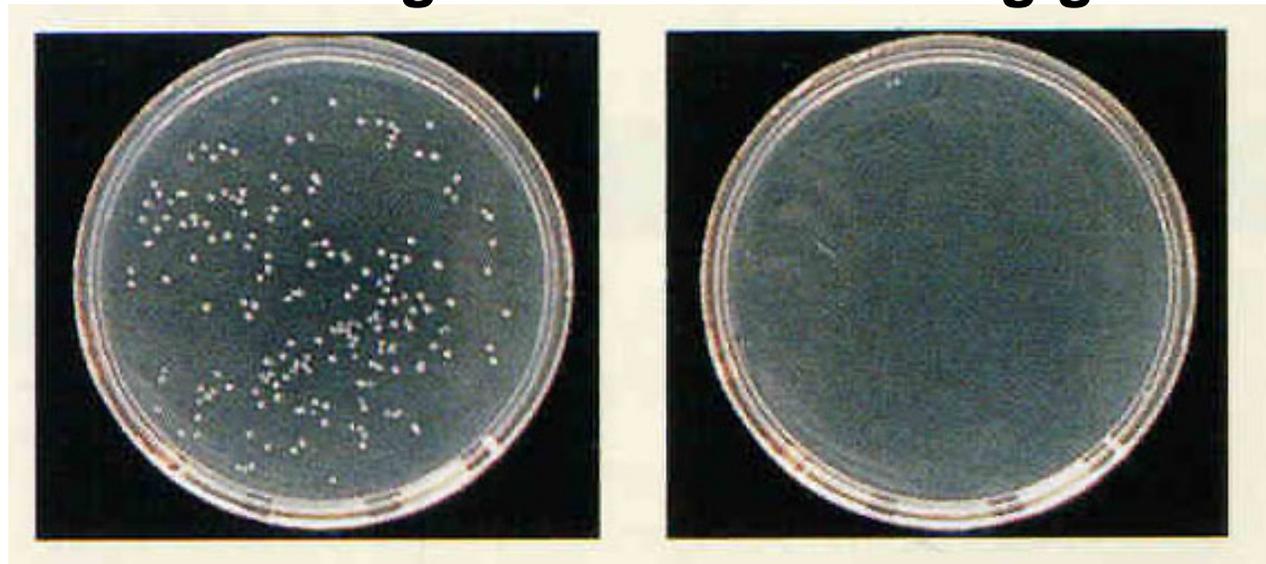
Time of action (h)	Bacteria	Bacteria content (cfu/cm <sup>2</sup> )	Anti-bacteria Ratio (%)
1	Staphylococcus aureus ATCC 6538	$1.9 \times 10^5$	92.63
24	Staphylococcus aureus ATCC 6538	$1.9 \times 10^5$	99.99
24	Escherichia Coli ATCC 25922	$9.0 \times 10^4$	98

This kind of self-cleaning glass will be useful in hospital, refrigeratory, and so on.

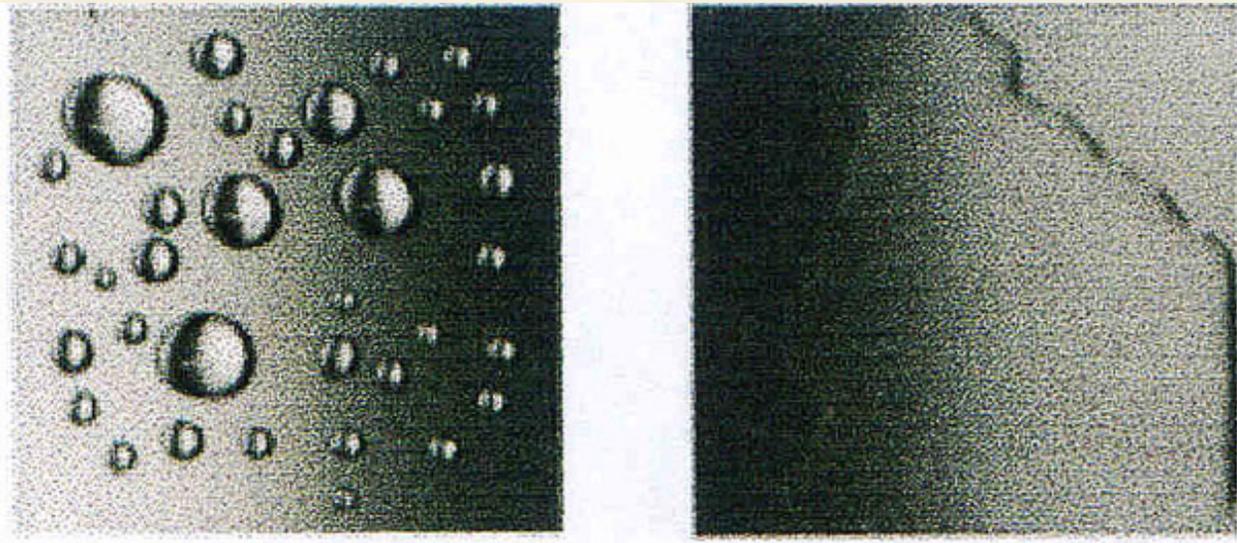
**Common glass**

**self-cleaning glass**

**anti-  
bacteria**

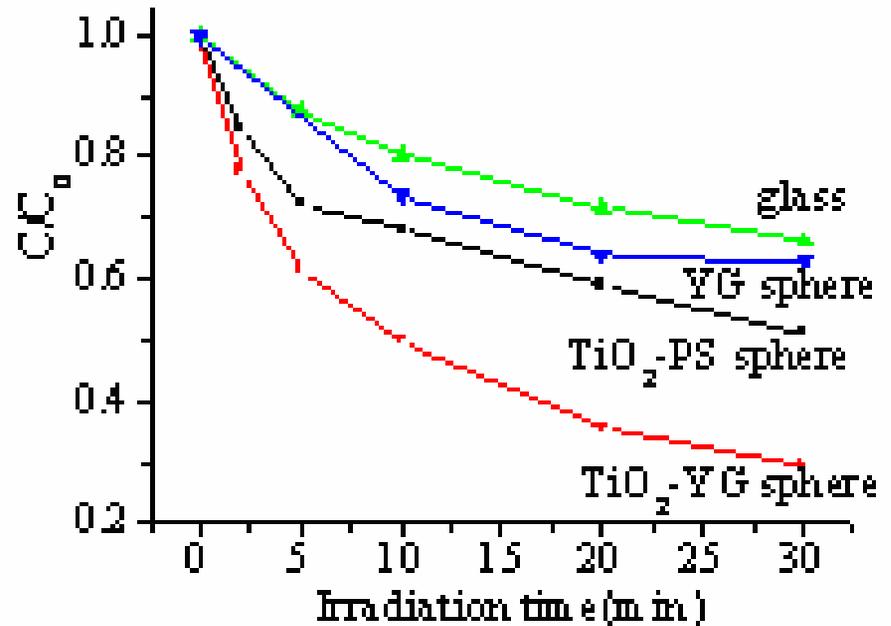
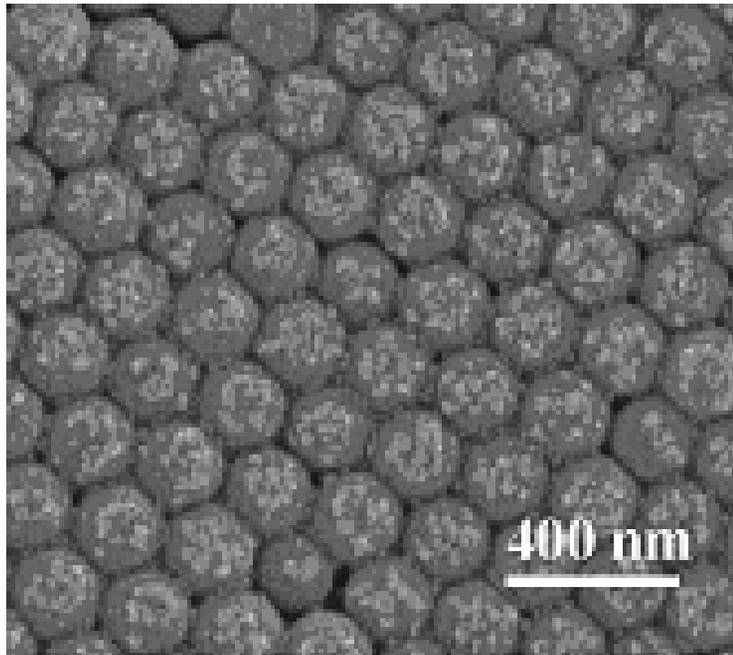


**super hydro-  
philicity**





Enhancing photocatalytic activity of  $\text{TiO}_2$ -based thin films with photonic crystal structure made by the core/shell composite of polymer/ $\text{TiO}_2$



J. Phys. Chem. C 2008, 112, 14973 –14979.



## 4.3 Preparation of oxide thin films with Hierarchical structure by simple magnetron sputtering

Textured coatings: anti-reflection, water-repellent (hydrophobic), and so on.

The use of super hydrophilic type self-cleaning glass will be confused in the environment with high concentration of dust.

Water repellent self-cleaning glass will be very useful in automobiles.

nano-textured  $\text{Al}_2\text{O}_3$

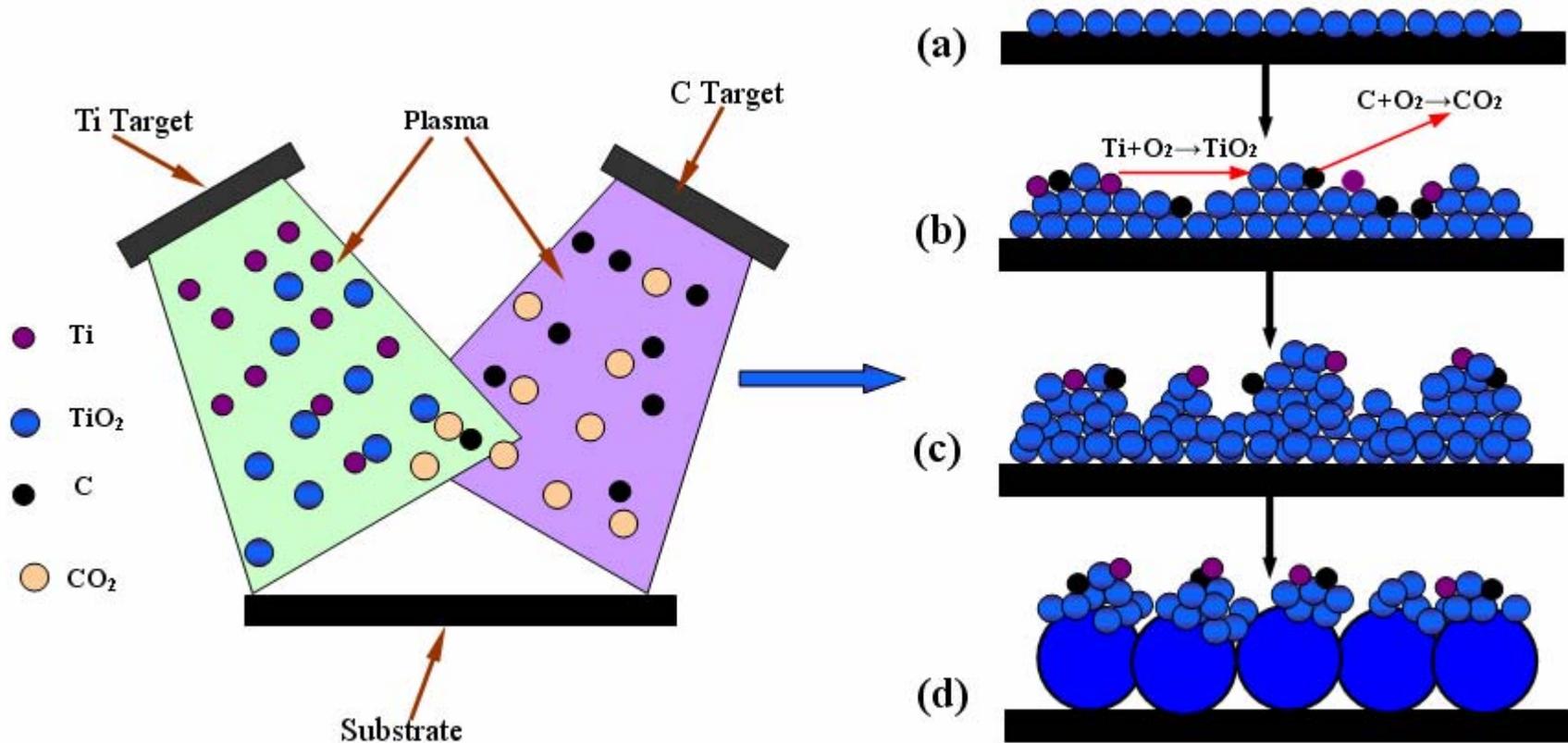
$\text{SiO}_2$  films doped with fluoropolymer

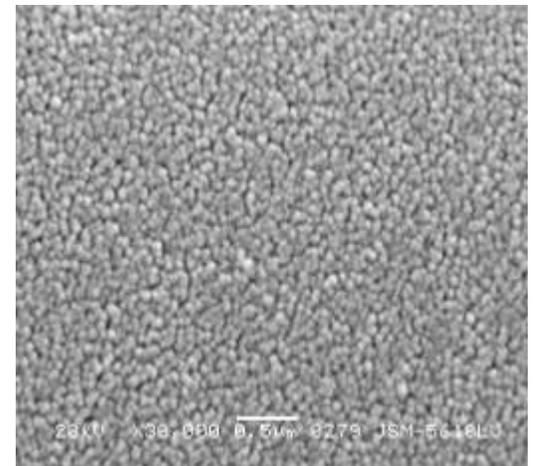
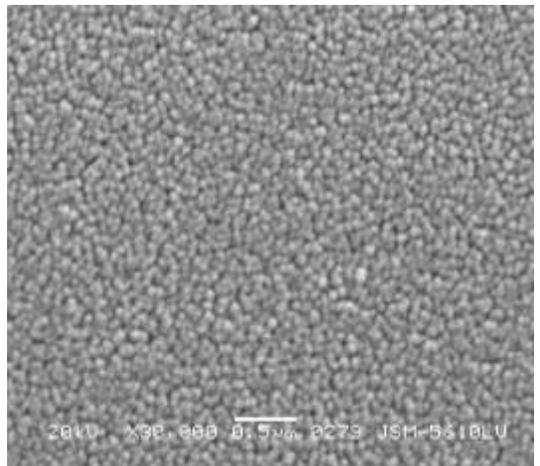
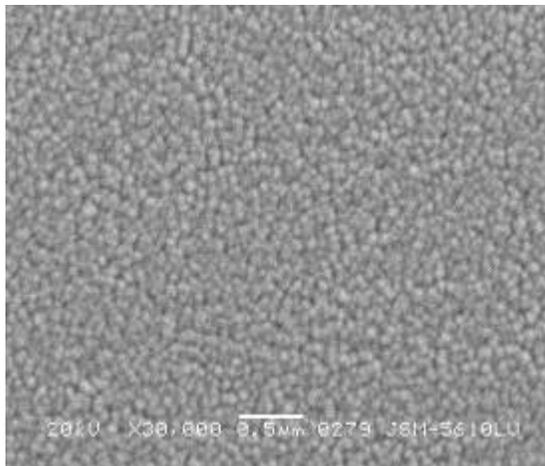
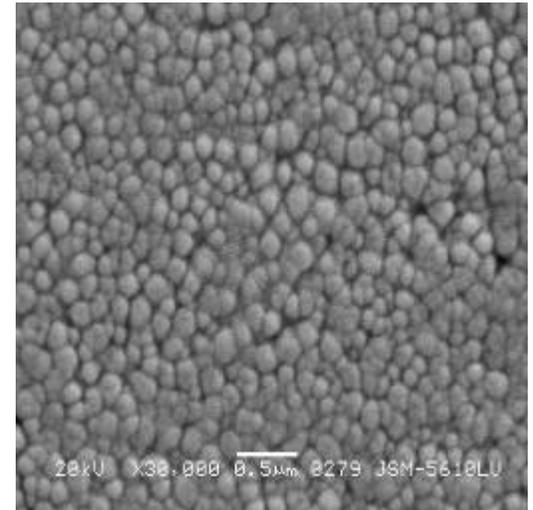
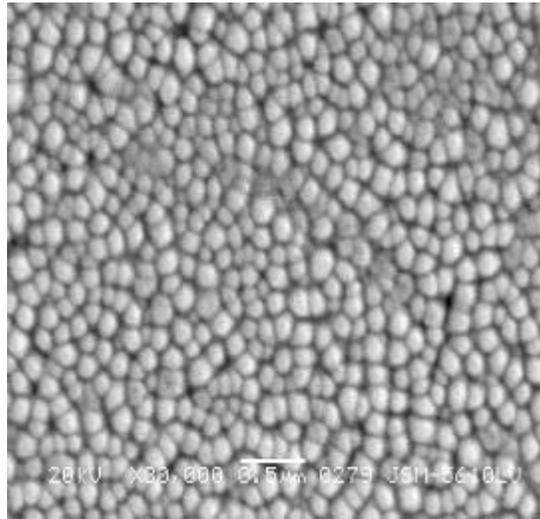
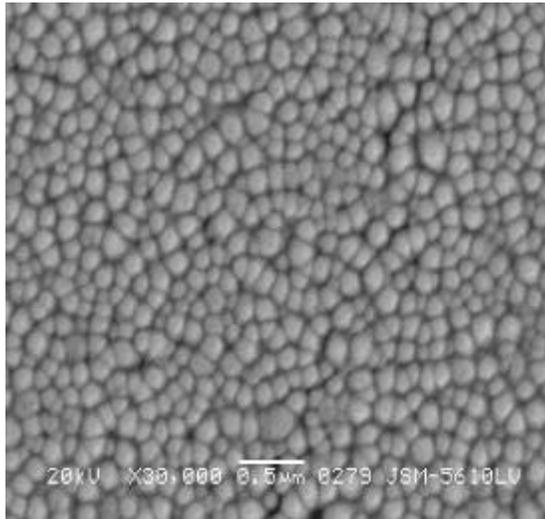
ZnO nano-rod array

Nano-structured polymers

Their preparation is very Complex, often many steps

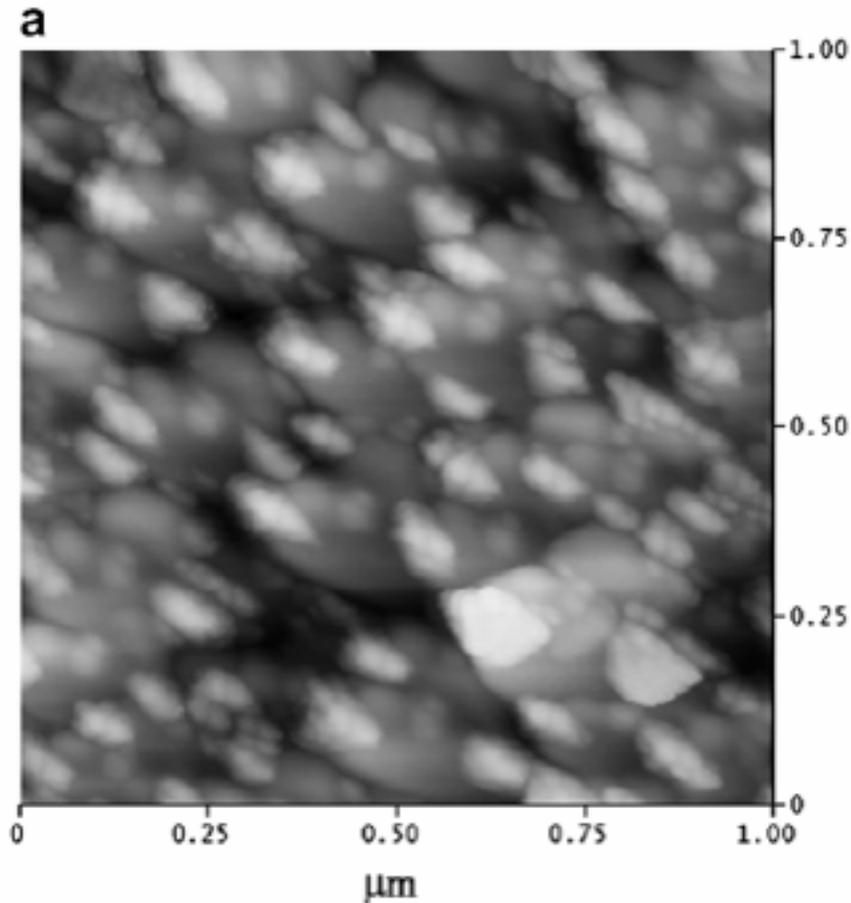
# Carbon-assisted Magnetron sputtering for textured coatings with water-repellent property



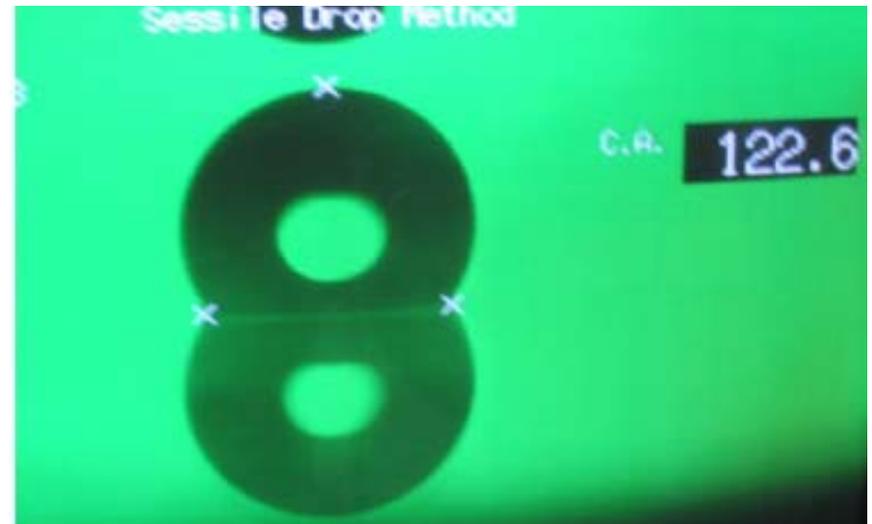


**SEM images of C-assisting sputtered  $\text{TiO}_2$  coatings under different partial pressure of  $\text{O}_2$**

*Y. Xie et al./Chemical Physics Letters 457 (2008) 148–153*



oxygen partial pressure 0.05Pa



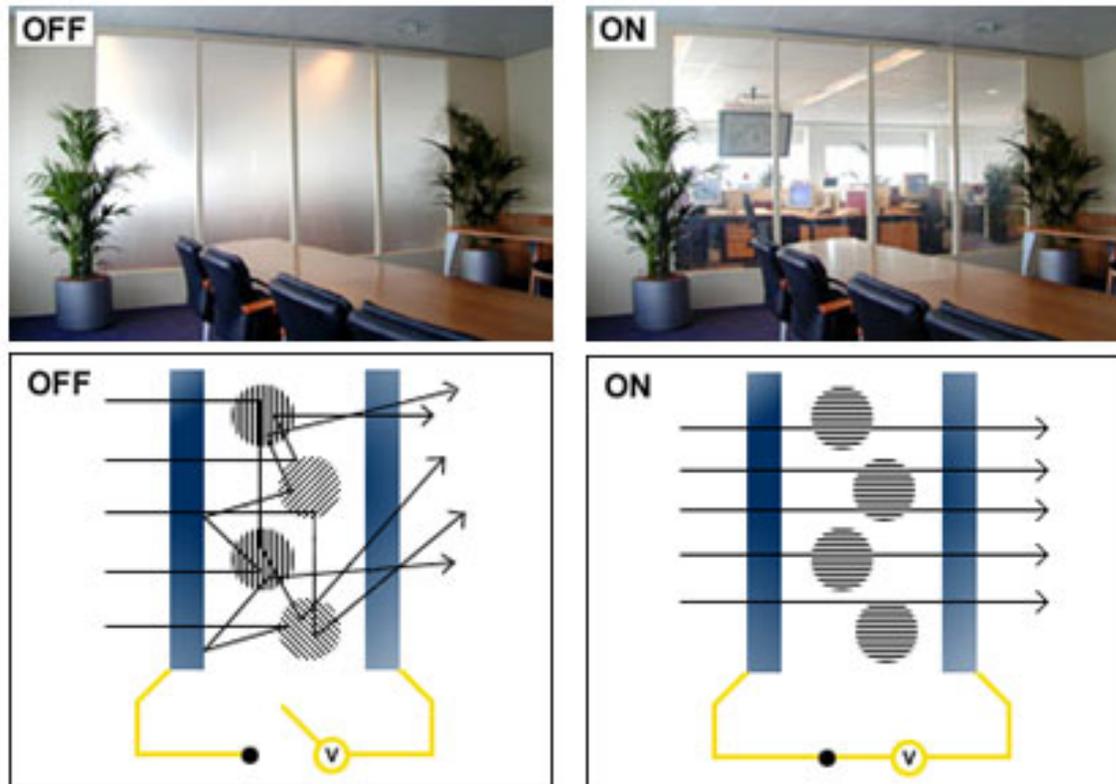
Photograph of water bead on the  
C-assisting sputtered TiO<sub>2</sub> film

## Contact angle of C-assisting sputtered ZnO textural coatings

samples	Sputtering time (min)	sputtering power (W)	Substrate temperature (°C)	Contact angle (°)
A	2	150	300	110.7
B	30	150	300	116.5
C	60	150	300	119.1
D	120	150	300	121.7
<b>E</b>	<b>180</b>	<b>150</b>	<b>300</b>	<b>138.3</b>
F	120	110	300	118.6
G	120	200	300	135.8
H	120	300	300	134.7
I	120	150	100	107
J	120	150	200	127.1

## 4.4 Electrochromic thin films for smart windows

Smart window or switchable window can be realized by using liquid crystal, electrochromic, thermochromic or gas chromic thin films



An example of smart window using electrochromic films



# Electrochromic smart glass and film materials

## Conductive Layer

ITO( $\text{In}_2\text{O}_3:\text{Sn}$ ), FTO( $\text{SnO}_2:\text{F}$ ), AZO( $\text{ZnO}:\text{Al}$ ), CNT(Carbon nanotubes) etc.

## Electrochromic Layer

Inorganic;  $\text{WO}_3$ , NiO,  $\text{IrO}_2$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{VO}_2$ , PB,  
Polymer: PANI(polyaniline), PED-OT

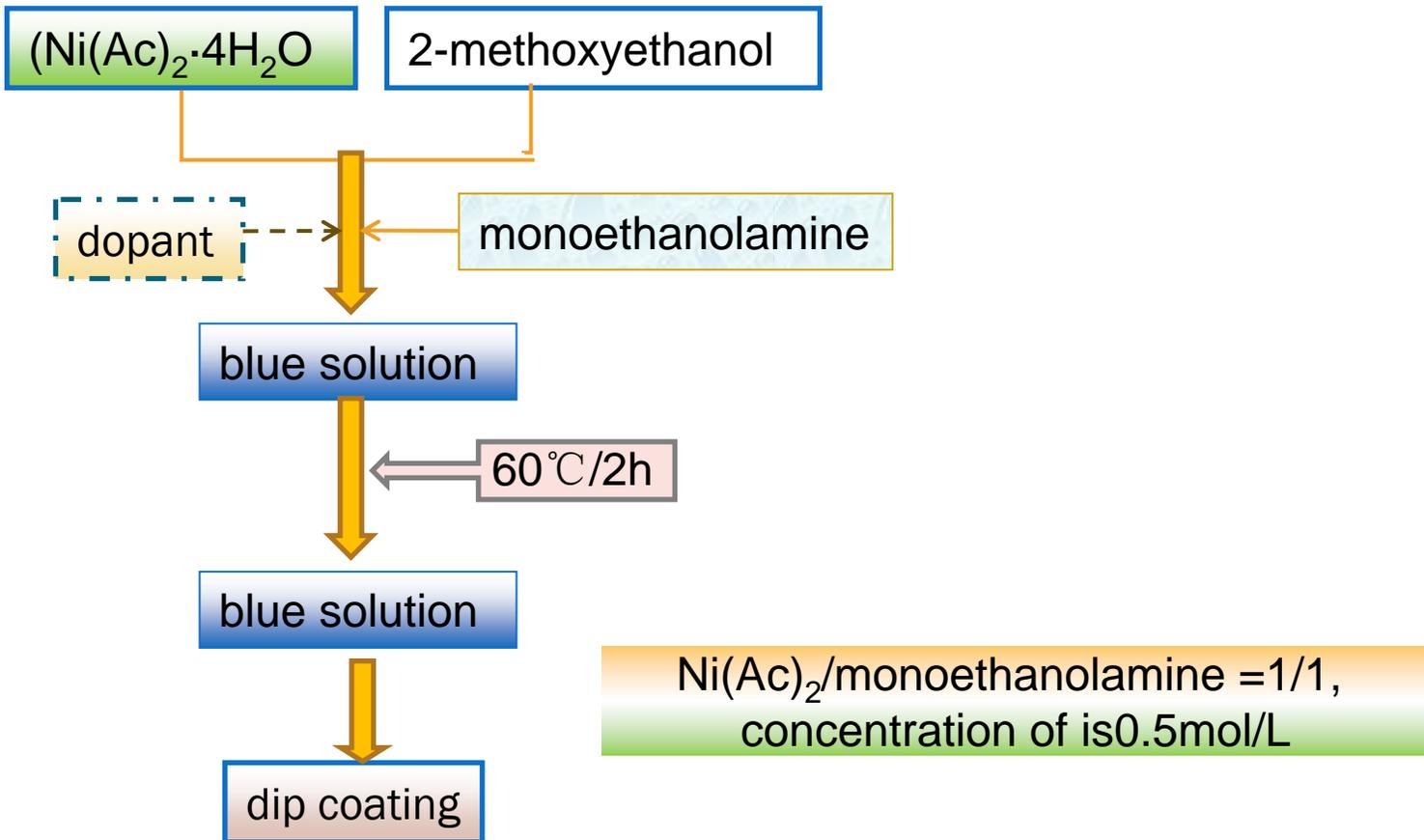
## Ion Conductor

Liquid: KOH, NaOH,  $\text{H}_2\text{SO}_4$   
Solid: LISION, NASICON, Perovskite,  $\text{Ta}_2\text{O}_5$   
Polymer: PC: $\text{LiClO}_4$ , PAMPS

## Ion Storage

$\text{CeO}_2$ ,  $\text{CeO}_2\text{-TiO}_2$ ,  $\text{CeO}_2\text{-ZrO}_2$ ,  $\text{CeO}_2\text{-SnO}_2$ ,  $\text{CeO}_2\text{-SiO}_2$

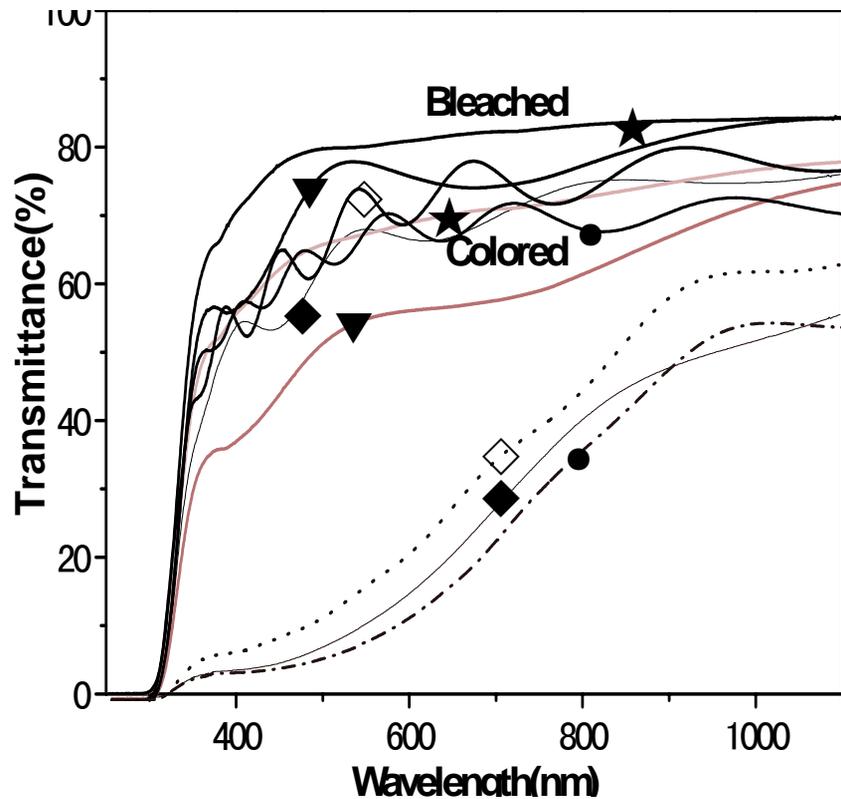
# Preparation of NiO-based electrochromic films



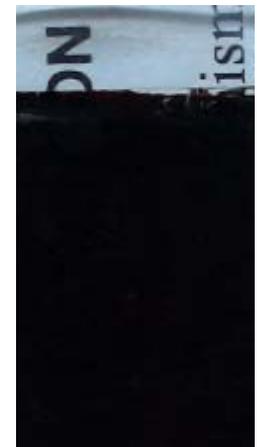
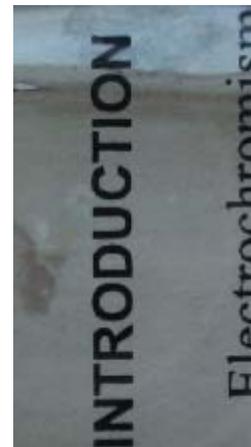
sol-gel process for preparation of NiO-based films



# Electrochromic properties of B<sub>2</sub>O<sub>3</sub>-NiO films



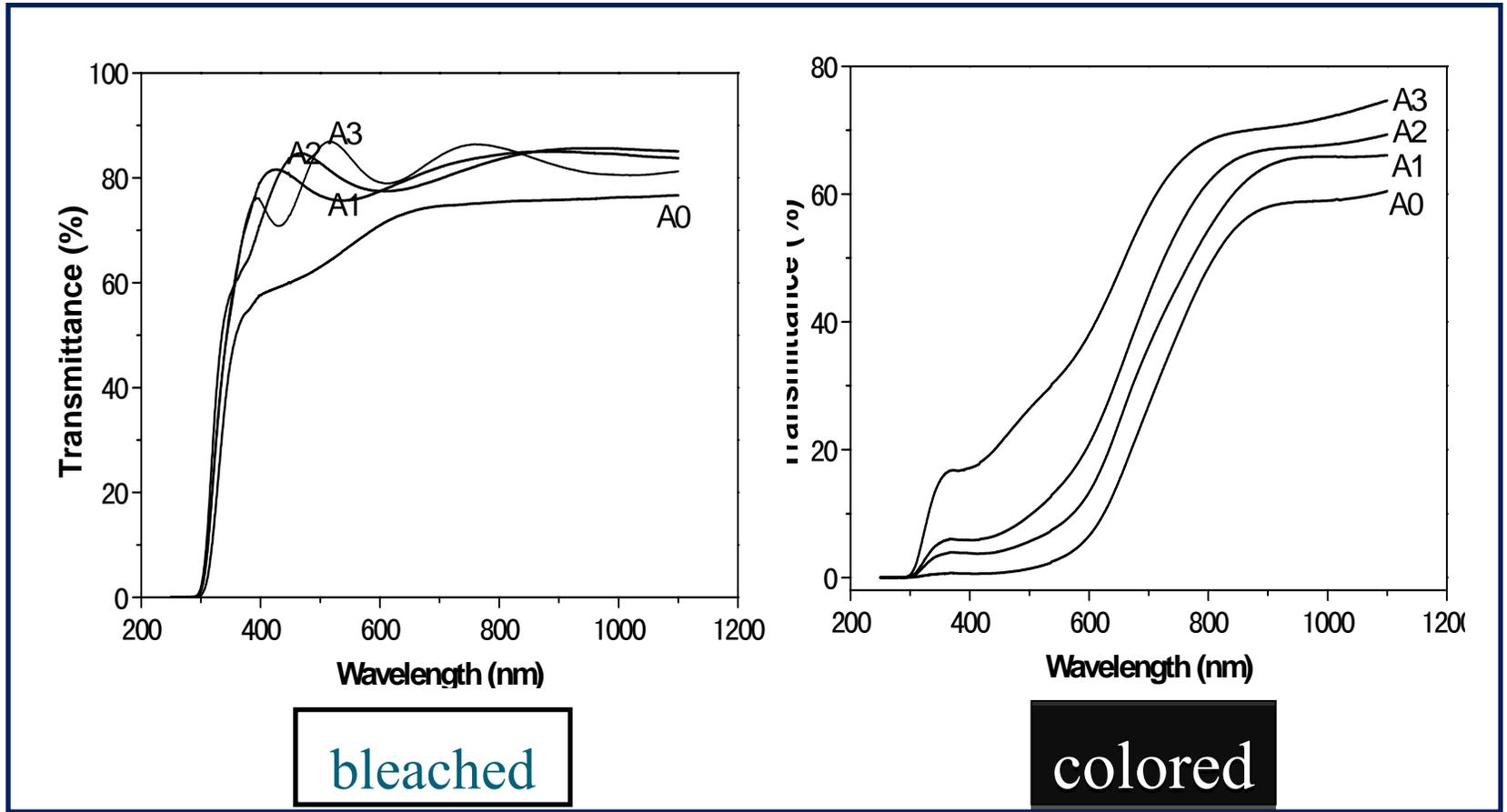
- B0 ★ (0/10)
- B1 ▼ (2/10)
- B2 ◆ (4/10)
- B3 ◇ (6/10)
- B4 ● (8/10)



Doping of B<sub>2</sub>O<sub>3</sub> decreases the transmittance of bleached state and decreases rapidly the transmittance of colored state.



# Addition of $Al_2O_3$ to B2 film improves its property



X. Lou et al. / Progress in Organic Coatings 64 (2009) 300–303

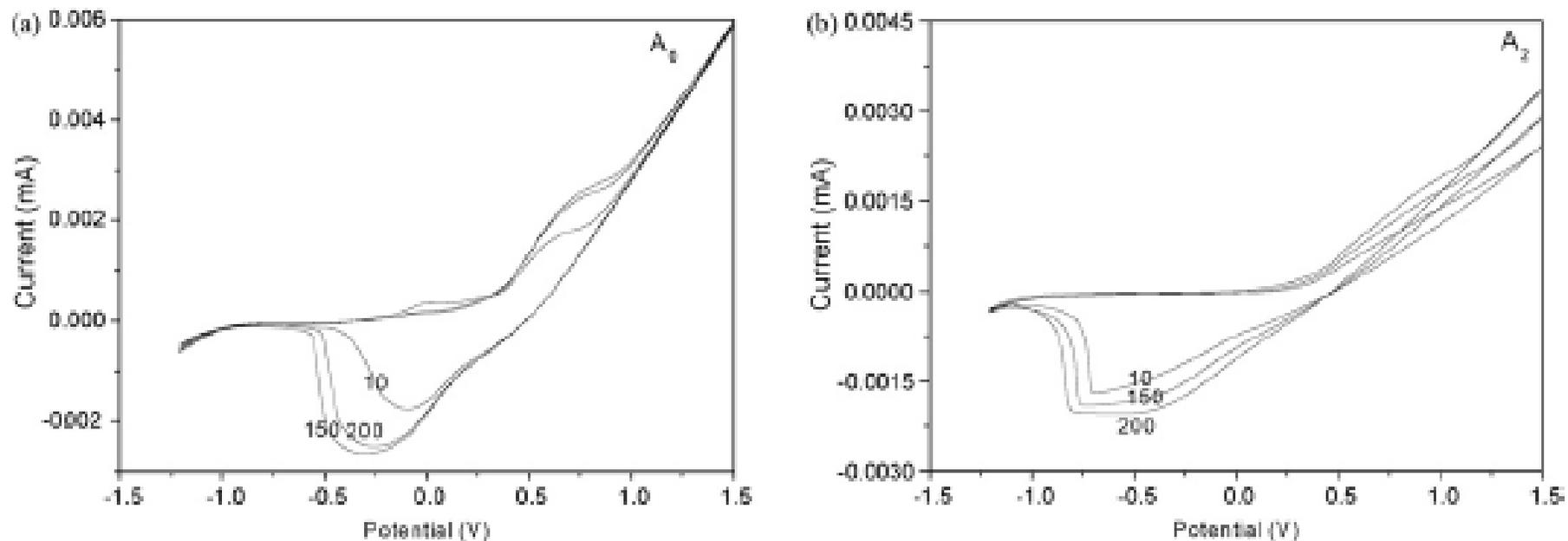
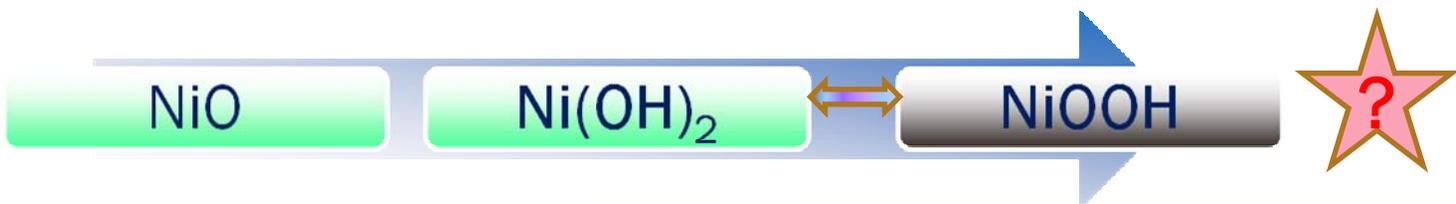
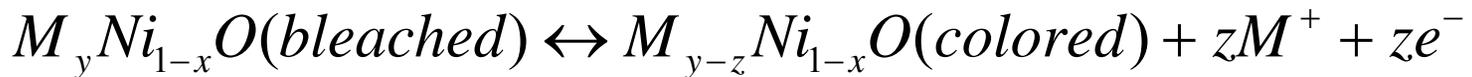
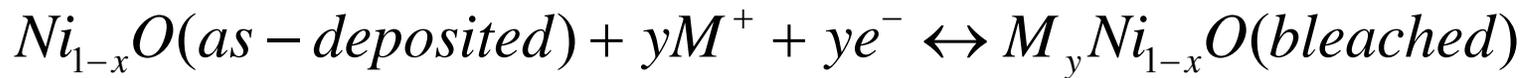
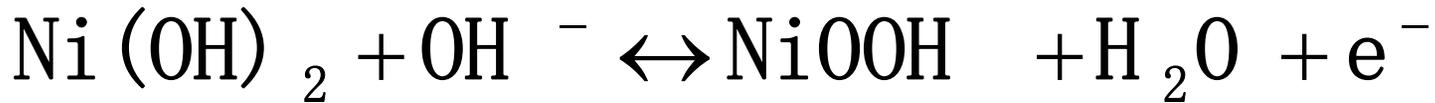


Fig. 3. Cyclic voltammograms of A<sub>0</sub> and A<sub>2</sub> film cycled at 10th, 150th and 200th.



## Mechanism of electrochromism

According to different electrolyte





# Outline

- **General Description of coatings or thin films**
- **New Functionalities of thin films on glasses**
- **Preparation methods for thin films on glass**
- **Some functional glasses by coating or thin films**
  - **Transparent conductive thin films on glass**
  - **Photocatalytic TiO<sub>2</sub> thin films on glass**
  - **Preparation of thin films with Hierarchical structure**
  - **Electrochromic thin films on glass**
- **Summary**



## Summary

1. Coatings or thin films on glass can endue glasses with many new functionalities
2. A number of materials and methods can be used in the production of new functional glasses by coatings or thin films
3. Many functional glasses by coatings or thin films are already applied in our life. But further extensive researches are needed for new functionalities in glass.

## Researches on coatings or thin films on glass in my Lab

objective	Film materials
UV-shielding films	TiO <sub>2</sub> -CeO <sub>2</sub>
Modified Ag-based low-E films	oxide/Ag/isolating layer/oxide
Hydrophobic, anti-reflection	N-TiO <sub>2</sub> ; hierarachical TiO <sub>2</sub> and ZnO, porous SiO <sub>2</sub> -hybrids
TCO, Low-E	N-TCO、 p-TCO (ZnO:Al; SnO <sub>2</sub> :Sb; SnO <sub>2</sub> :F; ITO)
Self-cleaning films	Isolation layer/TiO <sub>2</sub>
Low-E / self-cleaning	TiO <sub>2</sub> /TiN/TiO <sub>2</sub> ; ZnO:Al/TiO <sub>2</sub> ; SnO <sub>2</sub> :Sb/TiO <sub>2</sub> ; ITO/TiO <sub>2</sub>
UV-shielding / IR reflective coating	TiO <sub>2</sub> -CeO <sub>2</sub> / SnO <sub>2</sub> :Sb, TiO <sub>2</sub> -CeO <sub>2</sub> / ZnO:Al
UV shielding / anti-reflective of visible	TiO <sub>2</sub> -CeO <sub>2</sub> / porous SiO <sub>2</sub>
TCO / anti-reflection	ZnO:Al/porous SiO <sub>2</sub> , SnO <sub>2</sub> :Sb/porous SiO <sub>2</sub> , ITO/porous SiO <sub>2</sub>
TCO / anti-reflection by absorption	Oxide / metal(Cr:Ni)/silica; TiN/Si <sub>3</sub> O <sub>4</sub> /SiO <sub>2</sub>
Electrochromic	NiO-based, V <sub>2</sub> O <sub>5</sub> -based
thermochromic	VO <sub>2</sub> -based
One-way transmittance	Dispersed with needle-like nanoparticles
Ionic conductive thin films	Fast ion conductor
Thin film solar cell	CuInGaSe, Si-based, NPSSC



**The 1st production line of self-cleaning glass based on  $\text{TiO}_2$  films in China found in August, 2002**



**The magnetron sputter equipped in my lab which can prepare large area thin films sized  $1200 \times 1000 \text{ mm}^2$ . Using this sputter we complete the research for low-cost preparation of amorphous Si thin film solar cells.**



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# Thank you!

