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Lecture 8: Functional glasses by coatings or thin films

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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_2 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, wetability, 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 emmission 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, fluoresence, field-emmission, infrared reflective, non-linear, photorefractive
- Electrical: high Tc 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

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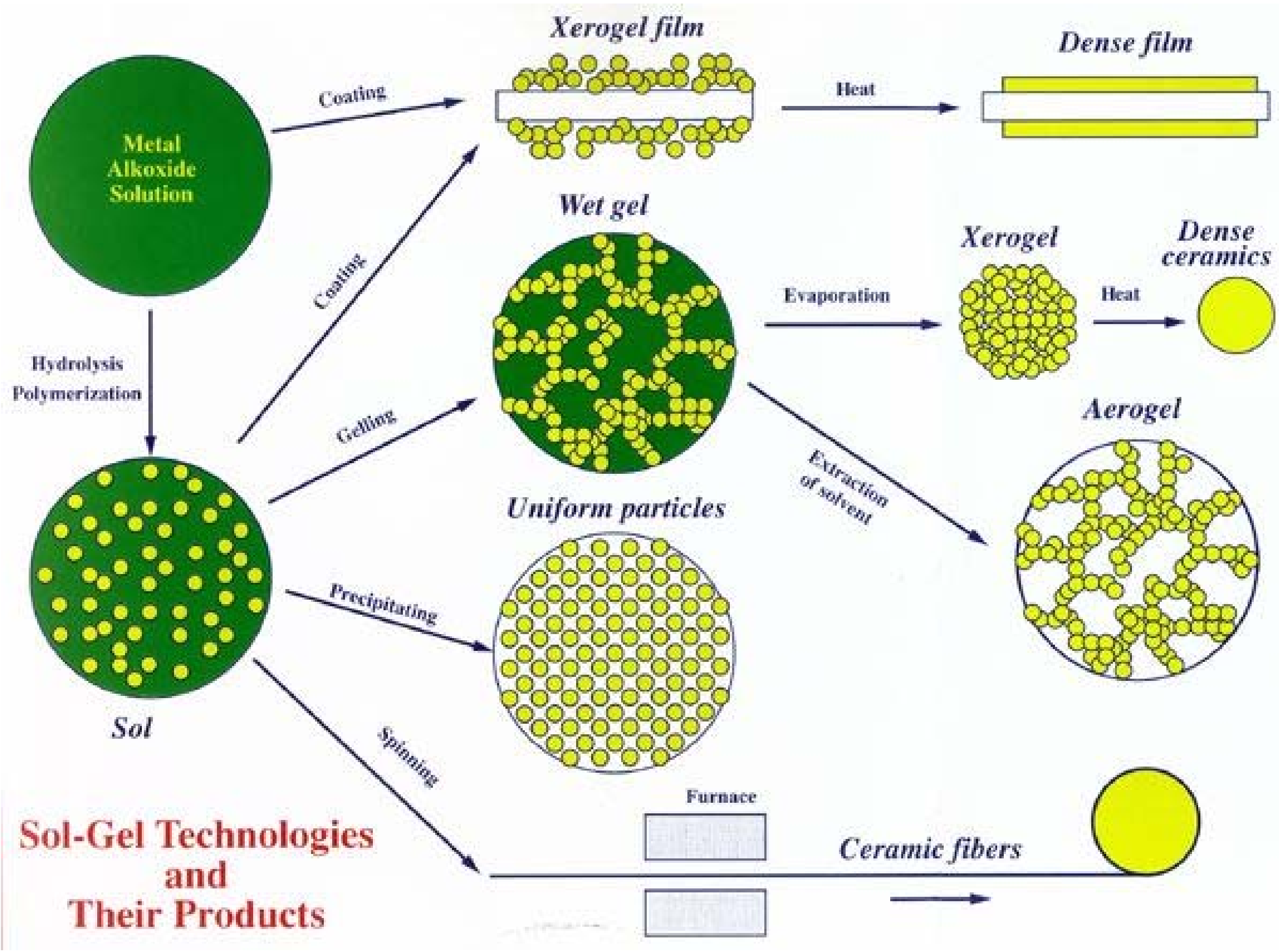
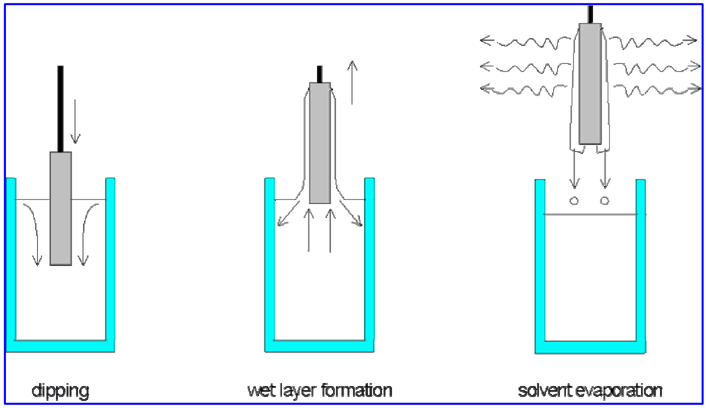
3.1 Sol-gel Process

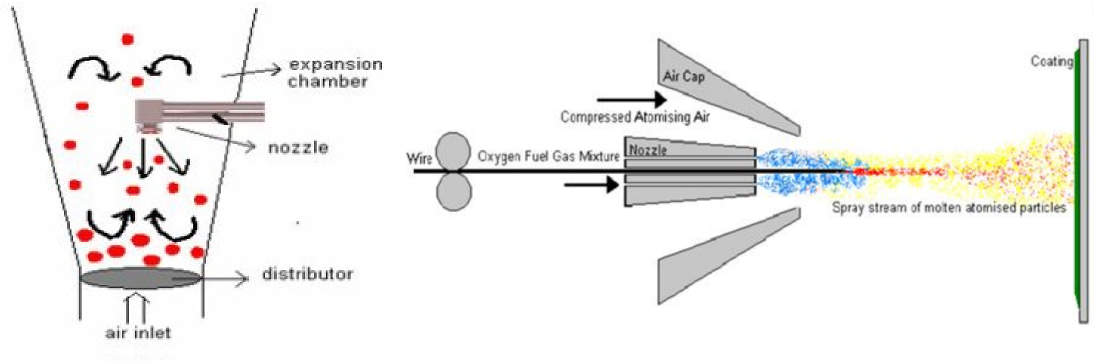


Preparation methods

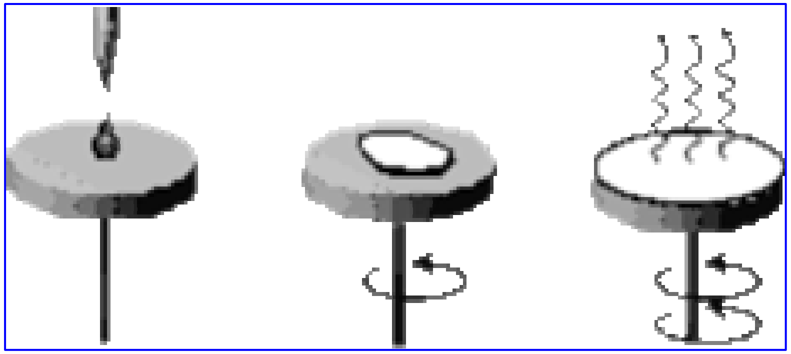
3.1.1 Thin films preparation by sol-gel



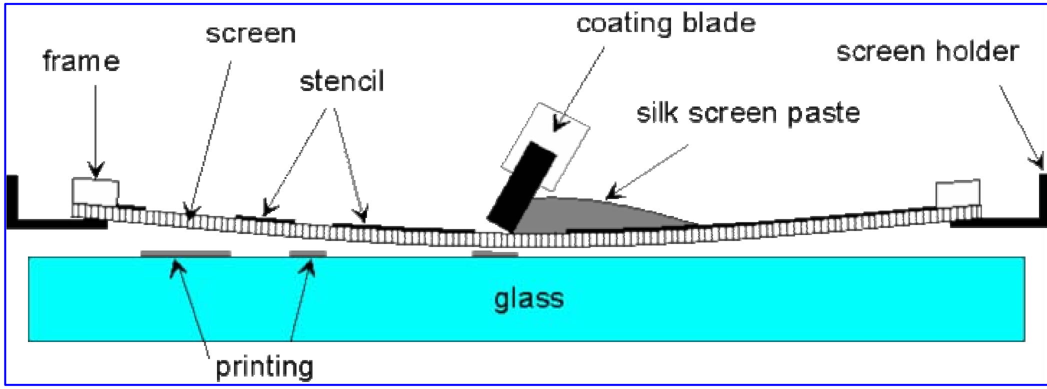
dip coating



spray coating

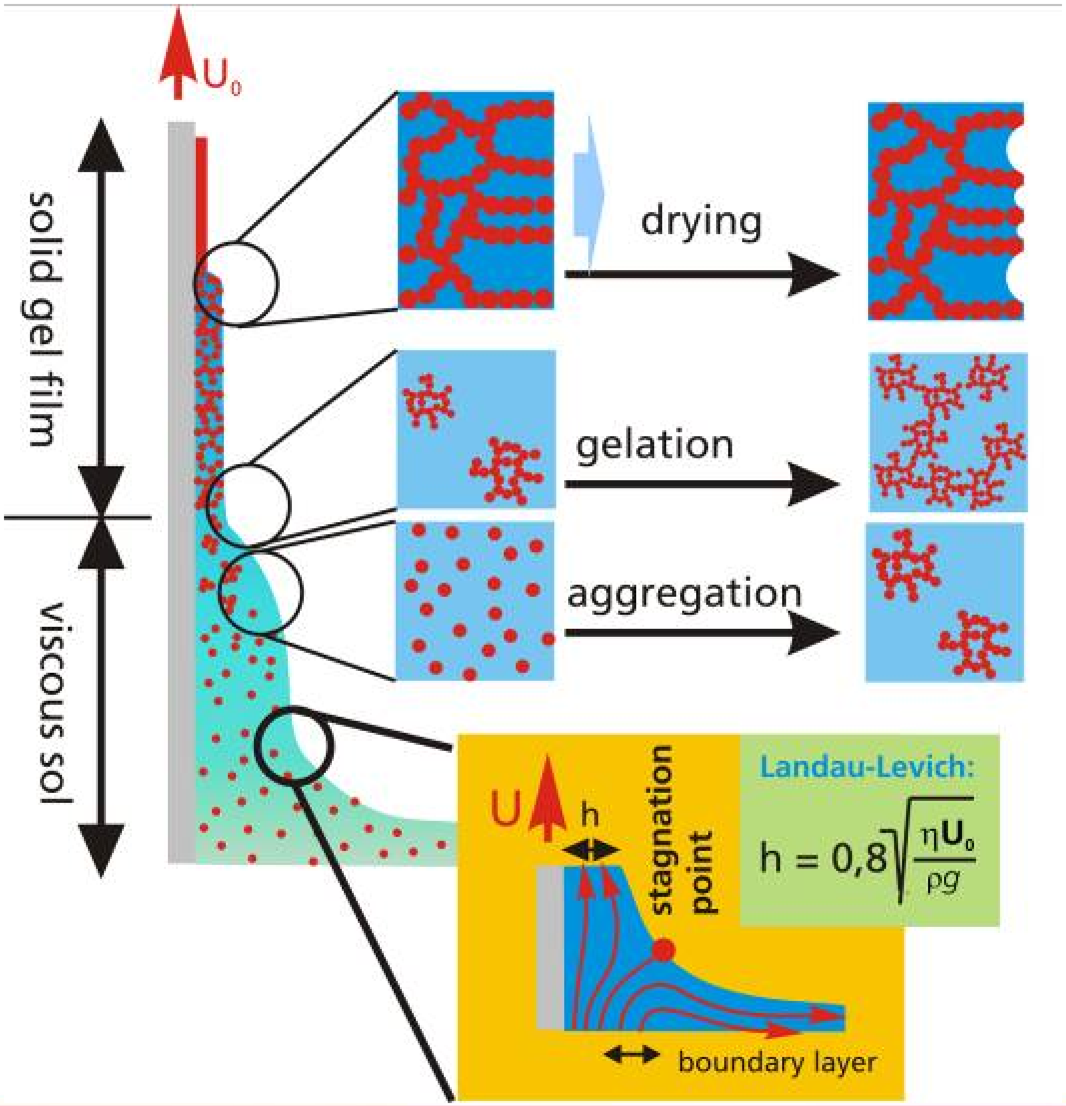


spin coating

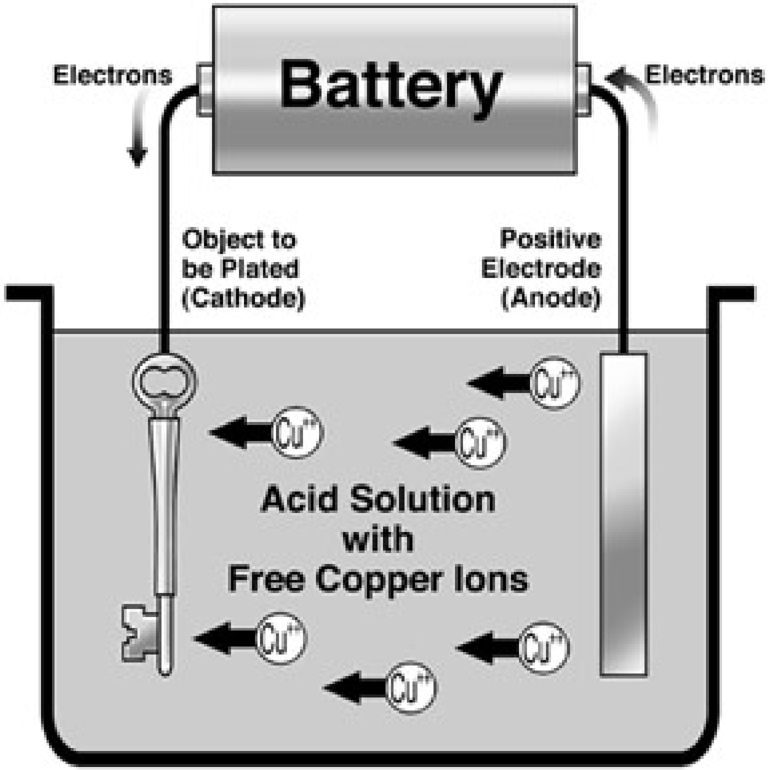


screen printing

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.

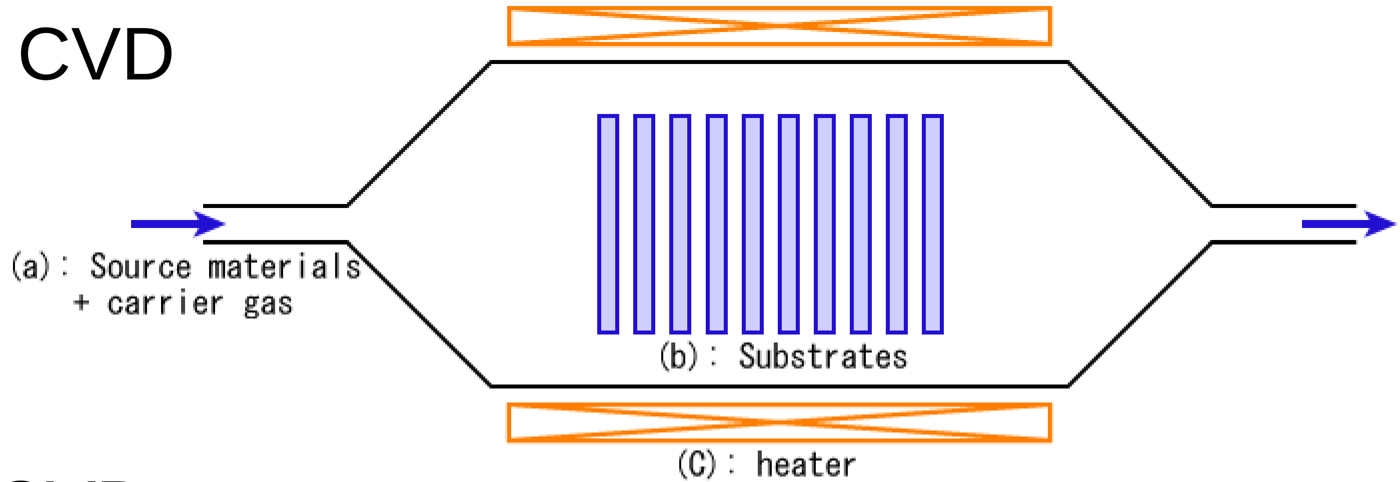
$$H_2PO^-_2 + H_2O \rightarrow H_2PO^-_3 + H_2$$

$$Ni^{++} + H_2PO_2^- + H_2O \rightarrow Ni^{\circ} + H_2PO^-_3 + 2H^+$$

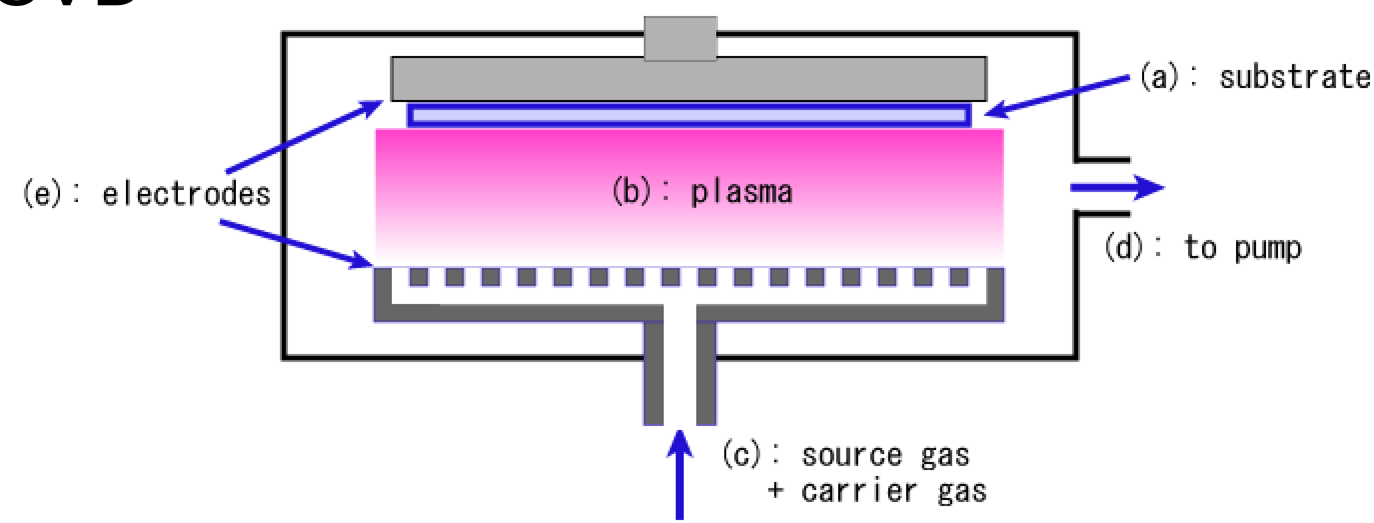
$$H_2PO^-_2 + H^+ \rightarrow P + OH^- + H_2O$$

3.3 Chemical Vapor Deposition (CVD)

Thermal CVD



Plasma CVD



3.3.1Types of chemical vapor deposition

- *Atmospheric pressure CVD* (APCVD)
- *Low-pressure CVD* (LPCVD)
- *Ultrahigh vacuum CVD* (UHVCVD)： 10^{-6}~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*

$$SiH_4 \rightarrow Si + 2H_2$$

$$SiCl_4 + 2H_2 \rightarrow Si + 4HCl$$

- *Preparation SiO_2 thin films*

$$SiH_4 + O_2 \rightarrow SiO_2 + 2\,H_2$$

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$$

$$SiCl_2H_2 + 2\,N_2O \rightarrow SiO_2 + 2\,N_2 + 2\,HCl$$

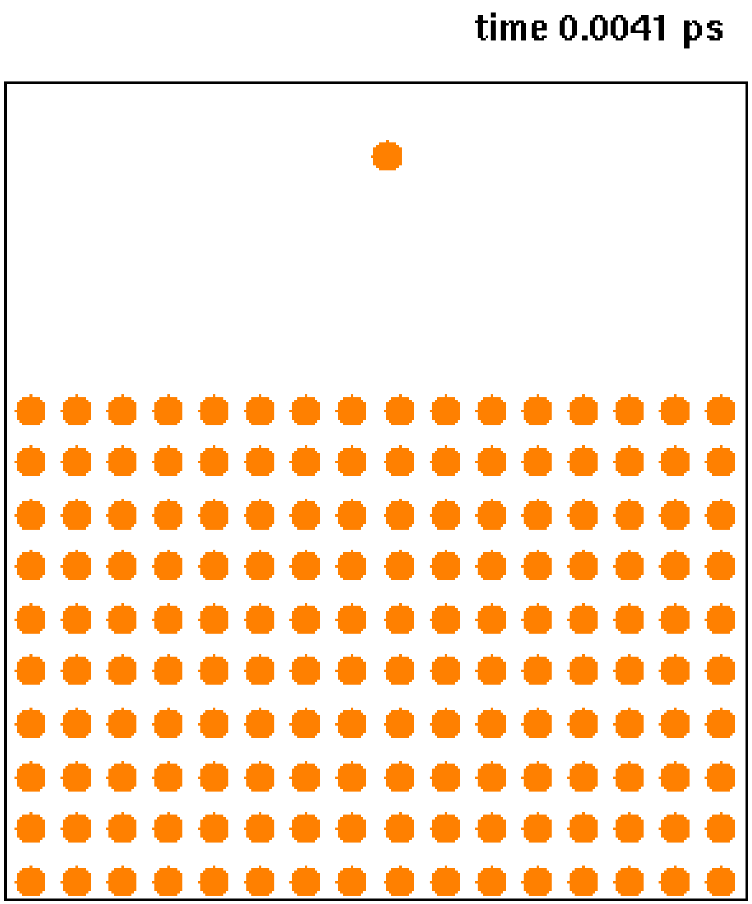
$$Si(OC_2H_5)_4 \rightarrow SiO_2 + \text{byproducts}$$

- *Preparation TiO_2 thin films*

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

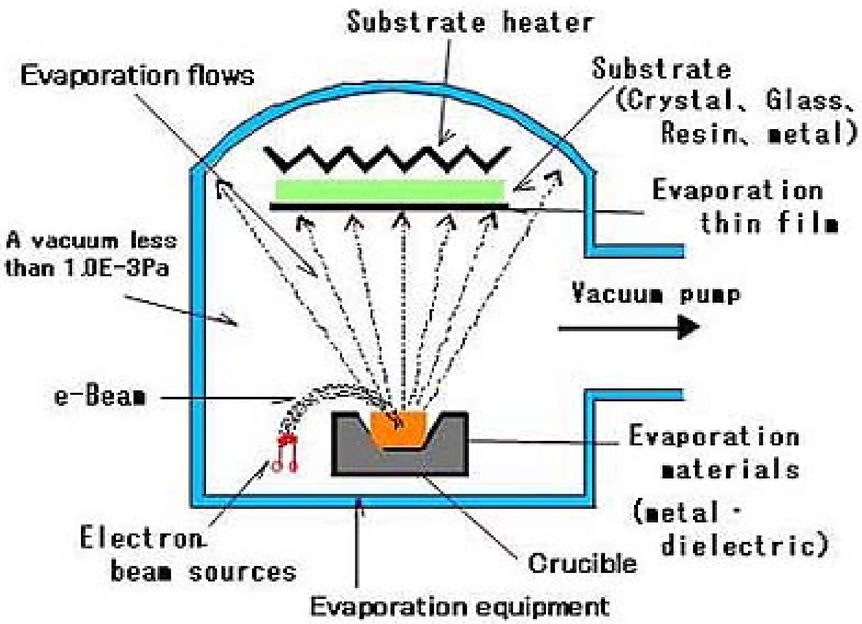
3.4 Physical vapor deposition

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



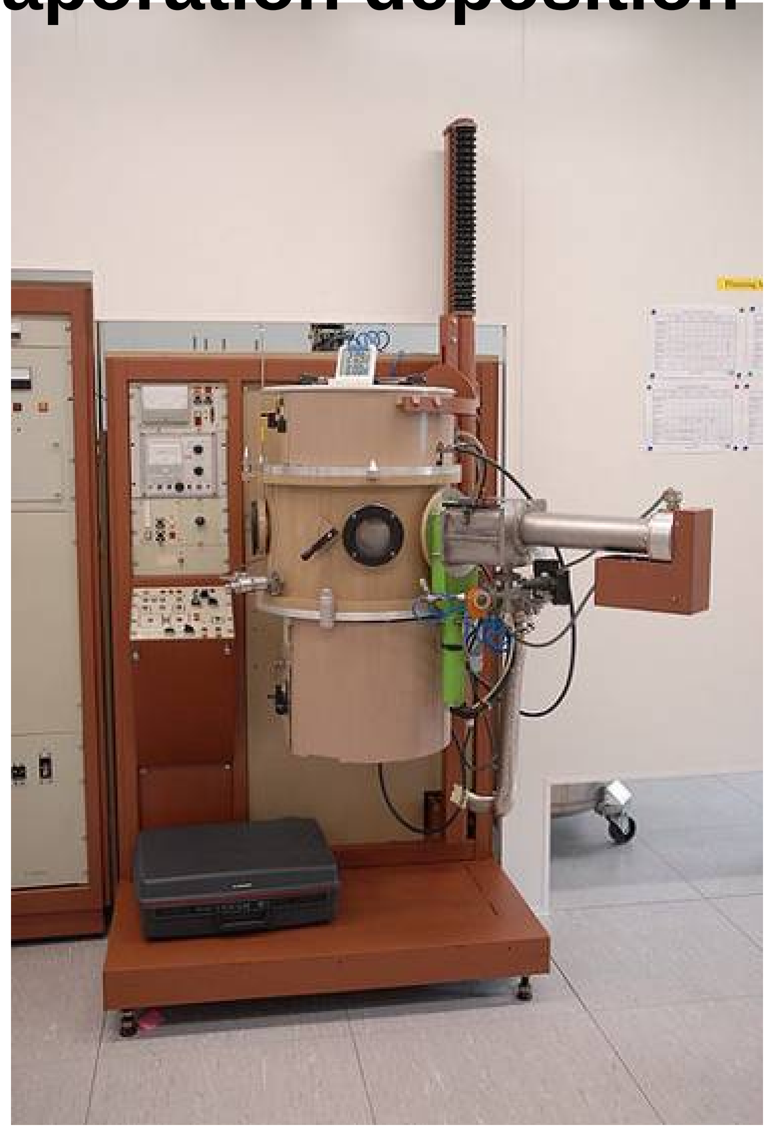
MD simulation of the basic physical process underlying PVD: a single Cu atom deposited on a Cu surface

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

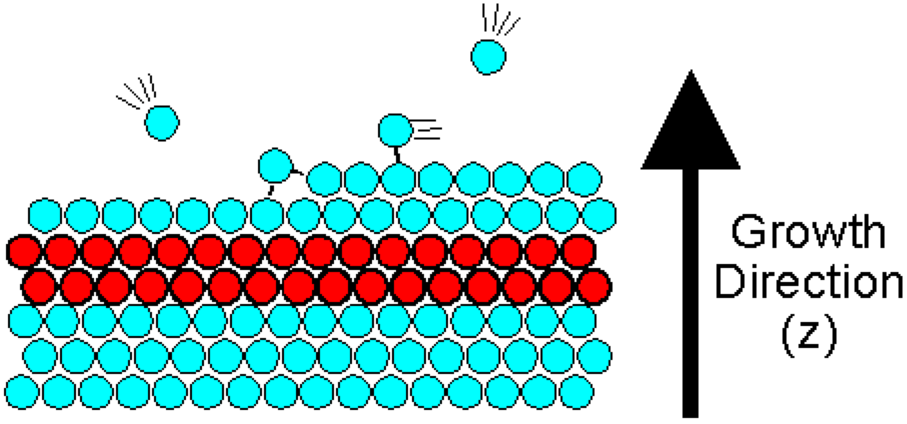


Main Evaporation Materials

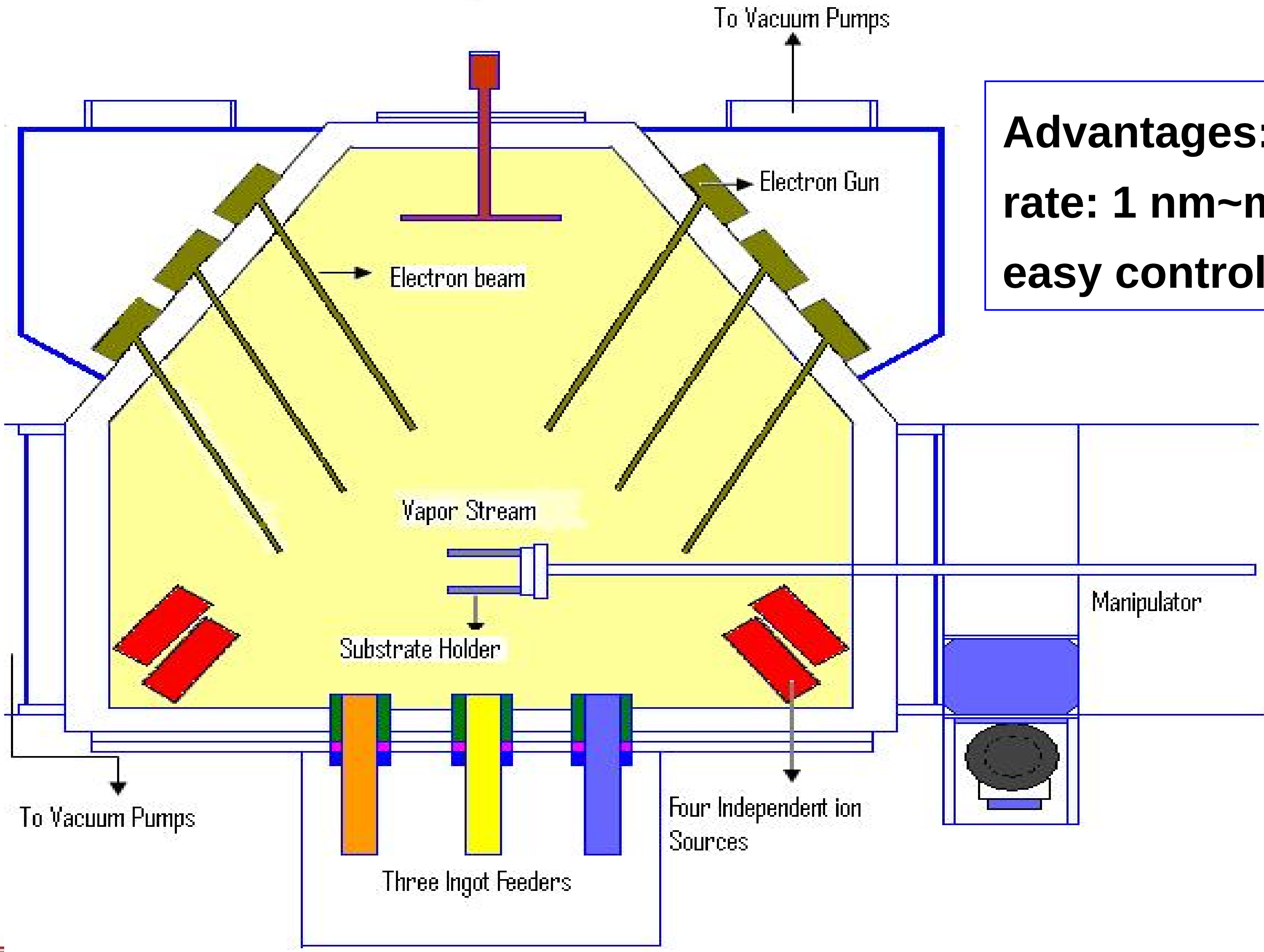
Al	Au
Co	Cr
Cu	Ge
In	Ni
Pb	Pt
Si	Sn
Ti	W
Y	Zn
Al_2O_3	BaF_2
Cr_2O_3	HfO_2
In_2O_3	MgF_2
SiO_2	SiO
TiO_2	Ta_2O_5
WO_3	ZnS
Nb_2O_5	

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

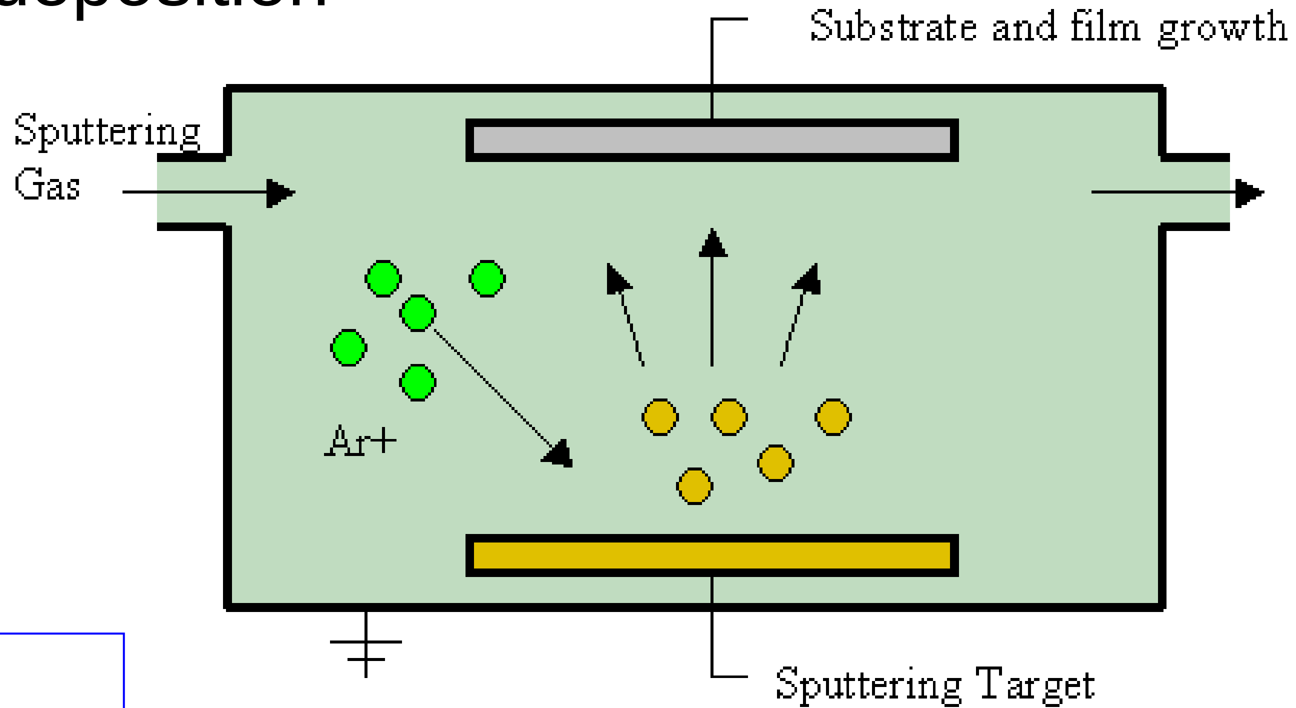


Advantages:

rate: 1 nm~microns/min

easy controlling

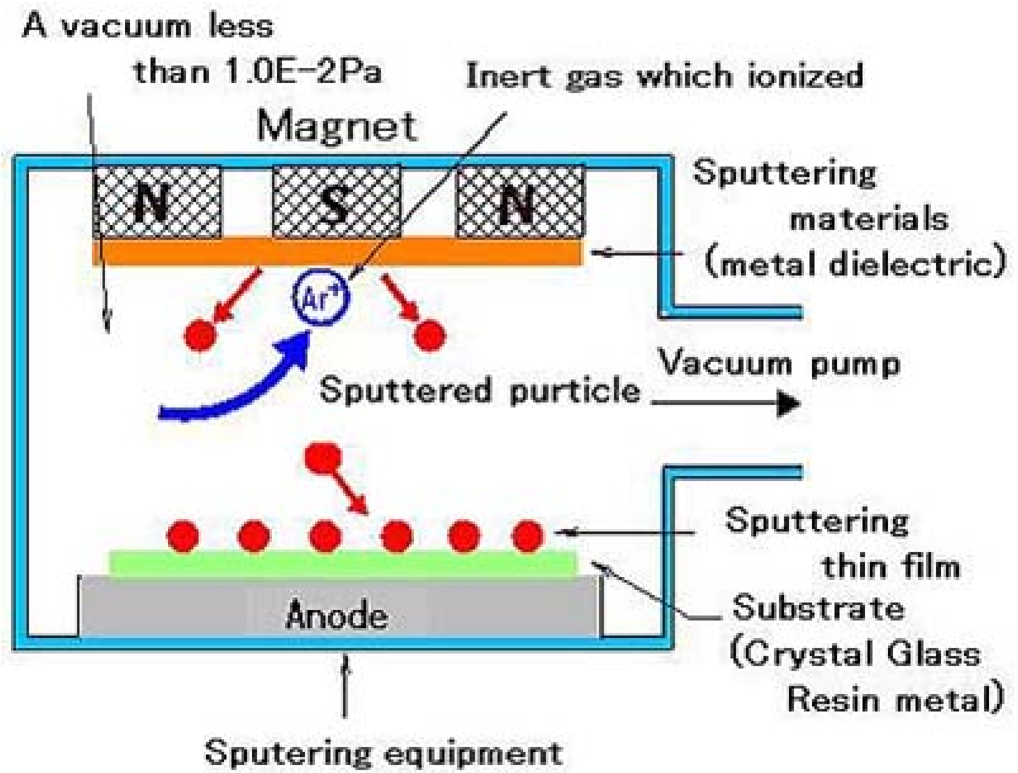
3.4.3 Sputter deposition



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

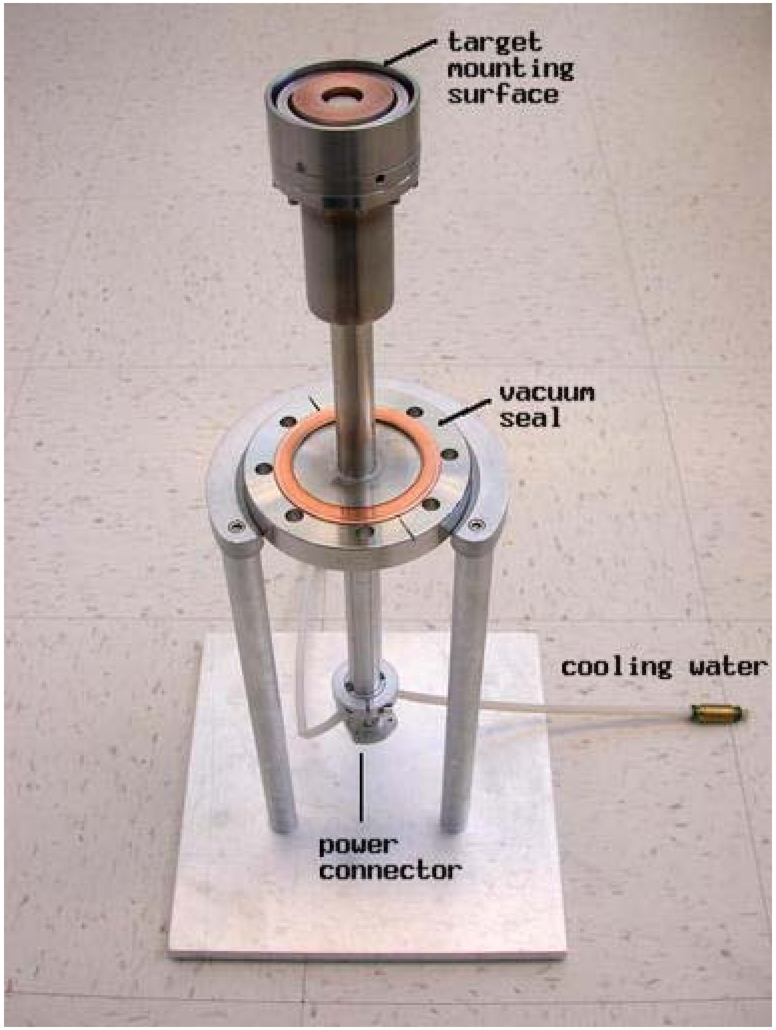
Main Sputtering Materials

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	

Preparation methods

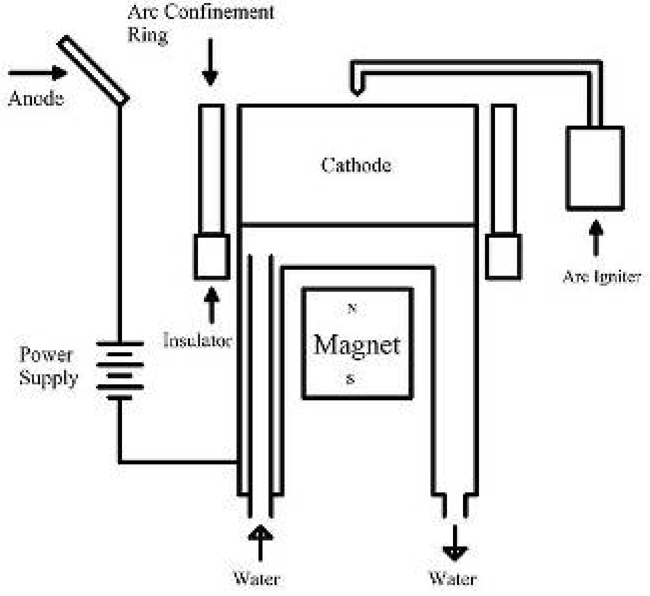
Sputter deposition

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

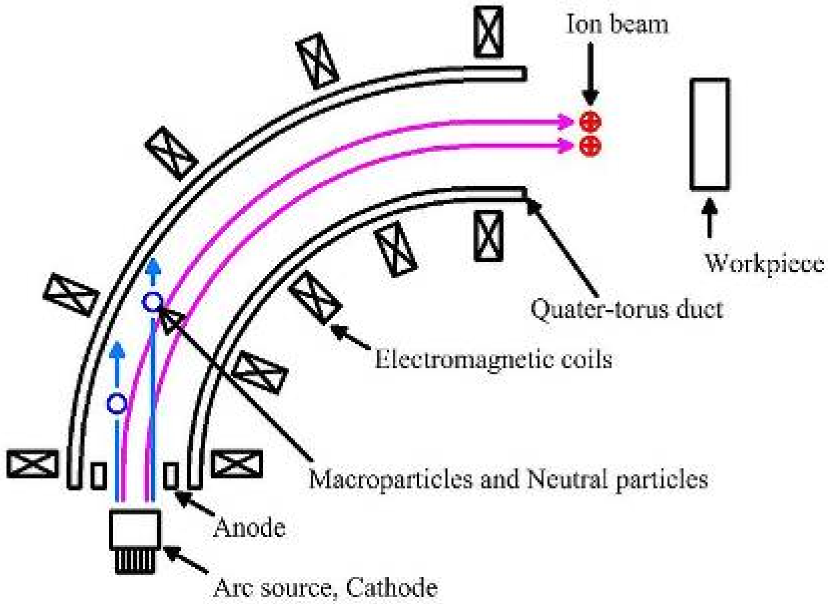


magnetron gun

3.4.4 Cathodic arc deposition



Cathodic arc source (Sablev type)



Aksenov's quater-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 (~ 15000° 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

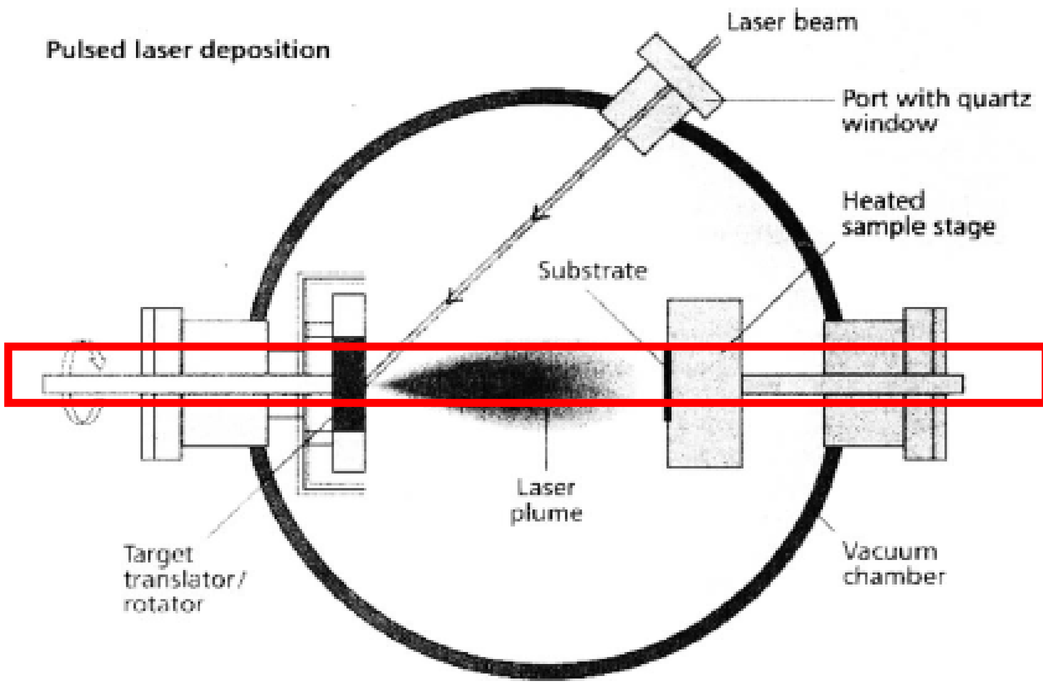
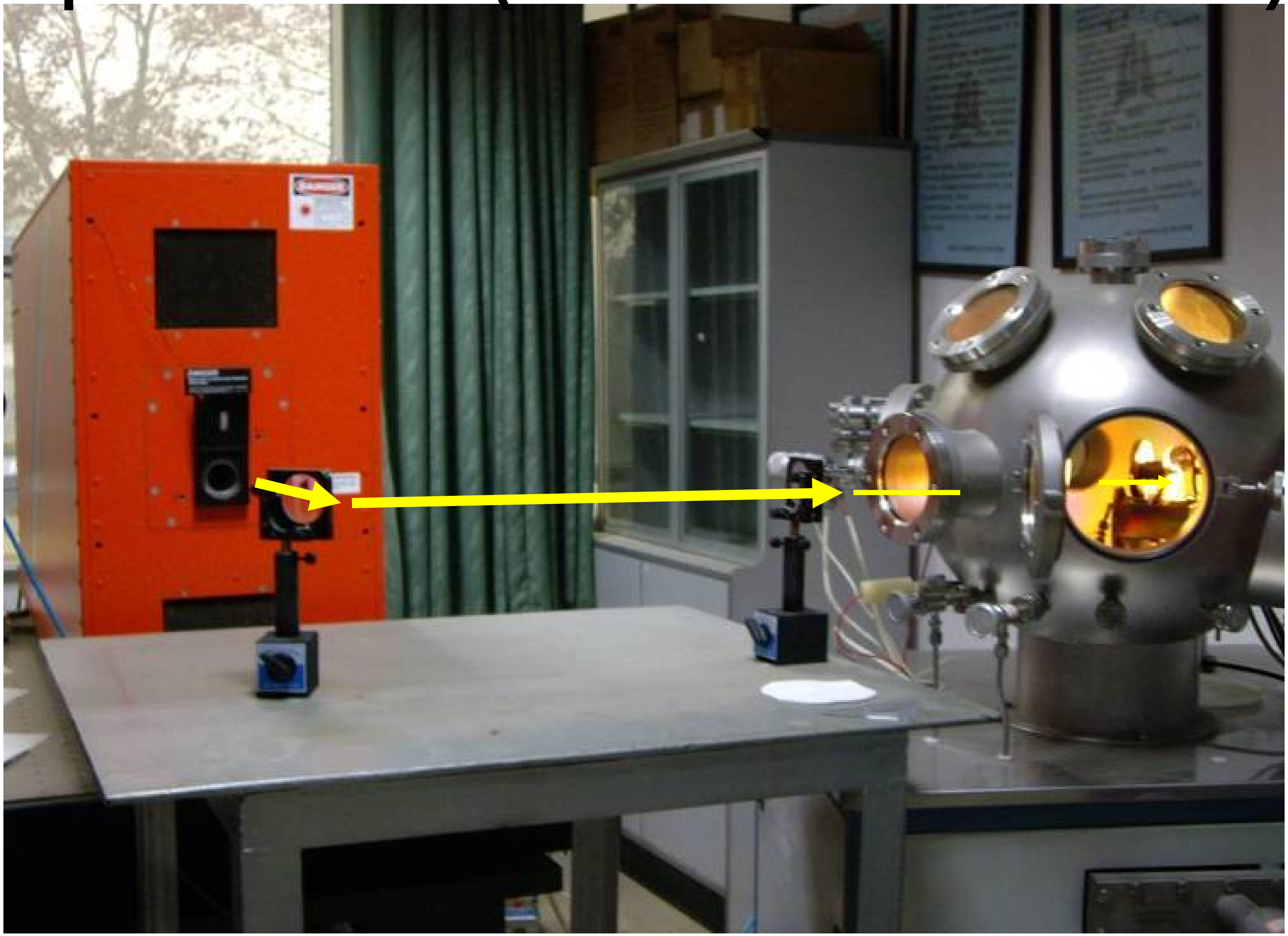


Fig. 1. Scheme of pulsed laser deposition [80].

P. Schenck, D.L. Kaiser, Chem. Britain 39 (5) (2003) 45.

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_4
Oxides	In_2O_3, SnO_2, ZnO, CdO, Cd_2SnO_4, Zn_2SnO_4
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: HUMO-LUMO separation that is transparent to visible light.

HOMO：the highest occupied molecular orbital
LUMO：the lowest unoccupied molecular orbital

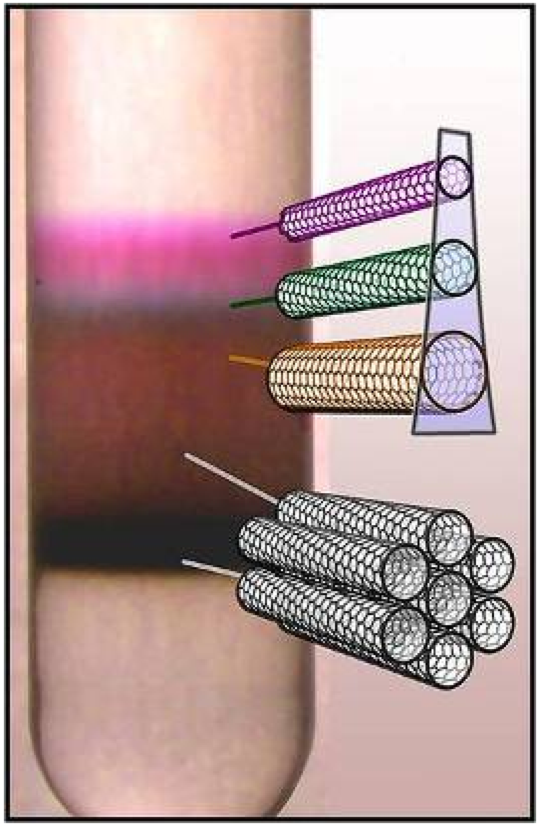
4.1 Transparent conductive Films on glasses

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 4x10^{9} Å/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

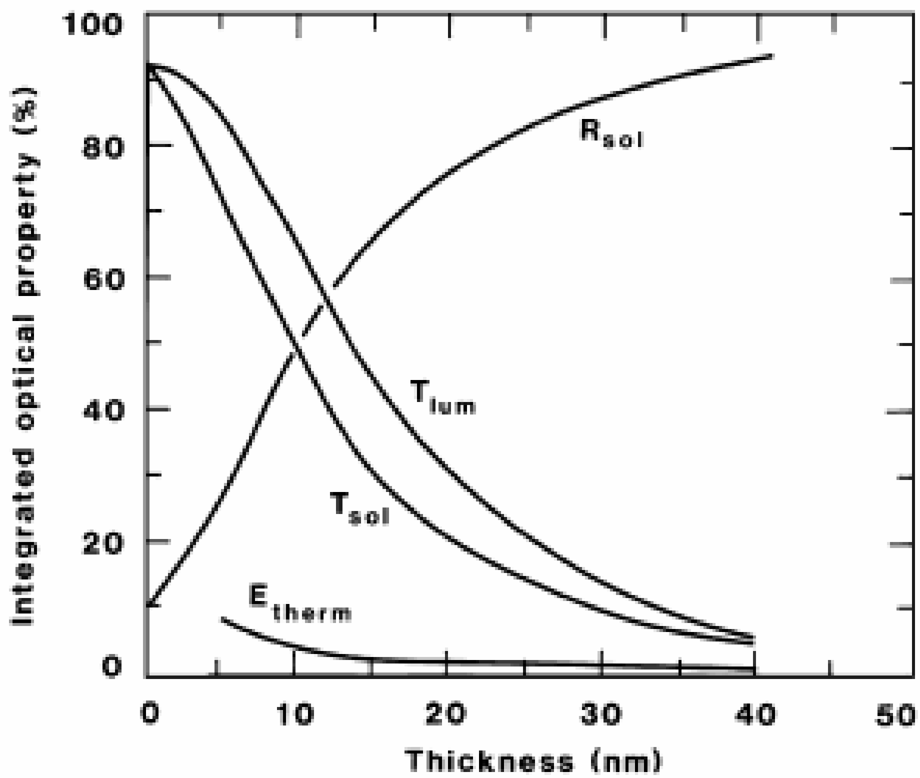
4.1.3 Metal-based films

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

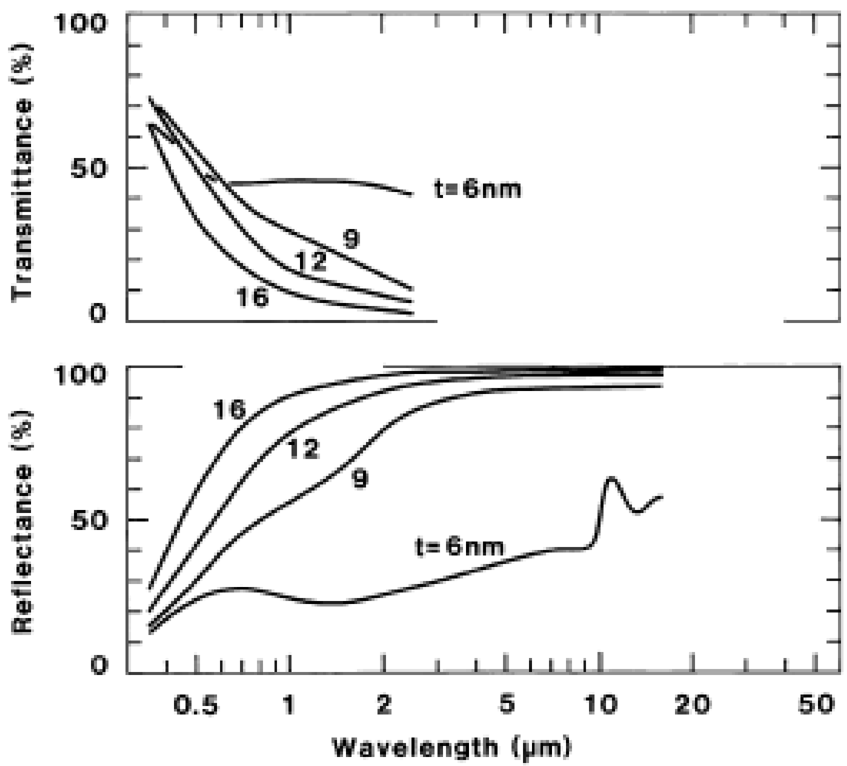
Typical structure: Bi_2O_3/Au/Bi_2O_3, TiO_2/Ag/TiO_2. This is based on the principle of interference and often used as the low-E glass.

Emissivity of some materials

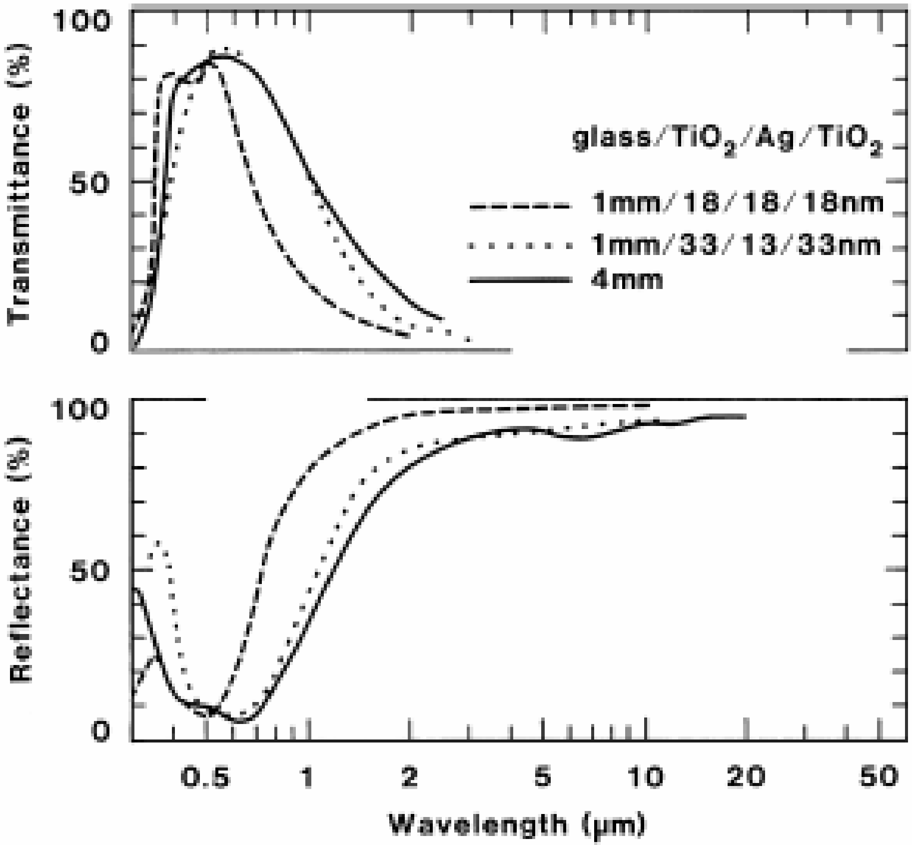
Materials surface	Emittance
Asphalt	0.90-0.98
Aluminum foil	0.03-0.05
Brick	0.93
Concrete	0.85-0.95
Glass (unglazed)	0.95
Fiberglass/cellulose	0.80-0.90
Limestone	0.36-0.90
Marble	0.93
Paper	0.92
Plaster	0.91
Silver	0.02
Steel (mild)	0.12
Wood	0.90



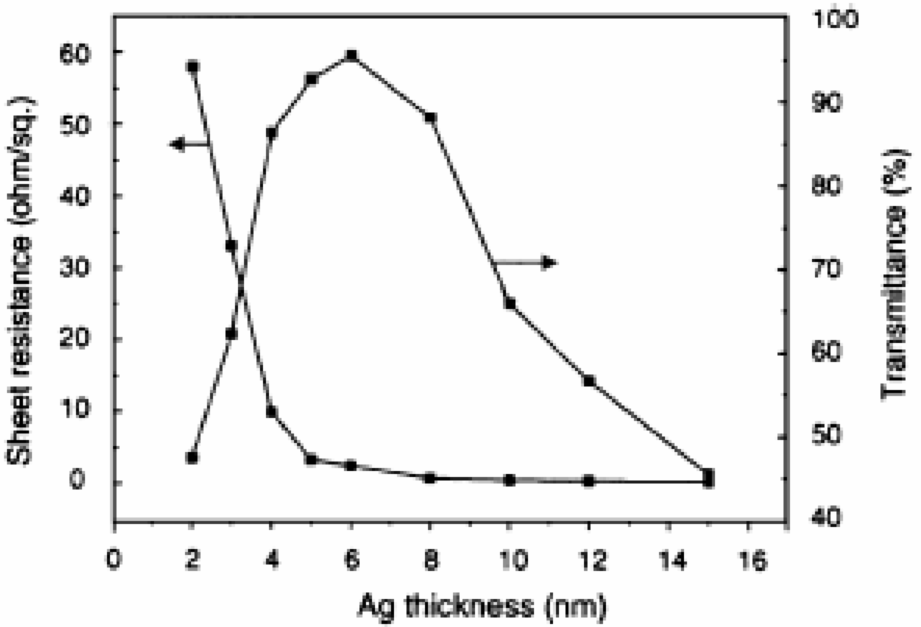
computered plane-parallel Ag layer



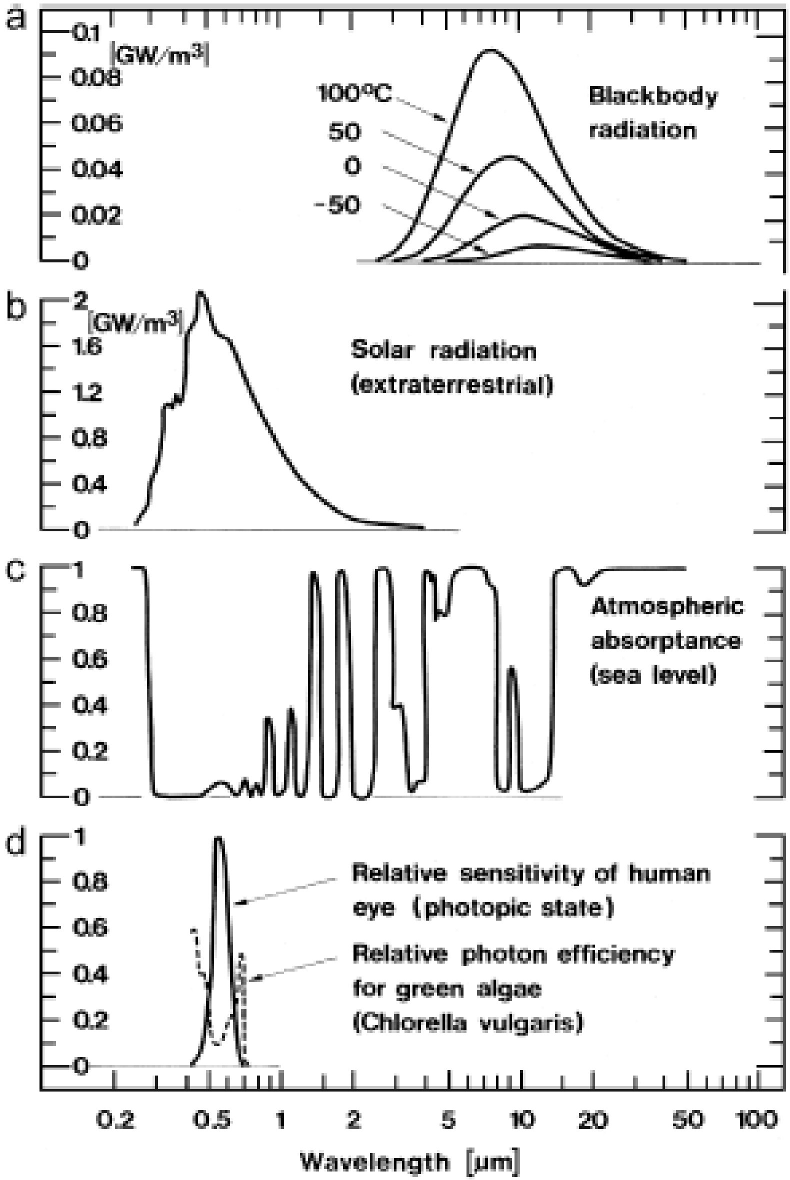
Ag film on glass



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



Dashed	T_{lum}>80%	T_{sol}≈50%	R_{sol}≈42%
Dotted	T_{lum}>80%	T_{sol}≈67%	R_{sol}≈26%



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

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

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

and "solar control coatings" characterized by

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

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

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 (Ω-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} 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 cm^2/V-s.

4.1 Transparent conductive Films on glasses

4.1.4 Doped metal oxides

- n-type:
  - In_2O_3:Sn(ITO): E_g=3.55-3.75 eV, n=1.9-2.08
  - SnO_2:(F, Sb^{5+}): E_g=3.87-4.3 eV, n=1.8-2
  - ZnO:(In, Al, Ga or RE): Eg=3.2-3.9 eV, n=1.9-2.2
- p-type:
  - ZnO:(N, Li)
  - SnO_2:(Al, In, Sb^{3+}, Zn, Li, Cu)
  - AMO_2 type oxides (delafossite structure, A=Cu^{II},Sr, M=Ga, In, Cr, Cu^{III})

Mechanism of transparent conductive oxides

In ITO, after doping Sn,

$$In_2O_3 + xSn^{4+} \rightarrow In_{2-x}^{3+}(Sn^{4+}.e)_xO_3 + xIn^{3+}$$

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

In the reducing atmosphere,

$$In_2O_3 \rightarrow In_{2-x}^{3+}(In_x^{2+}.2e)_xO_{3-x}^{2-} + x/2O_2$$

that is,

$$O_O^x \leftrightarrow V_O^{\bullet\bullet} + 0.5O_2(g) + 2e'$$

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} 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:

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

ε ***: emittance,***
ε_0**:dielectric const in vacuum**
ω**: angle frequency,**
σ**: conductivity**

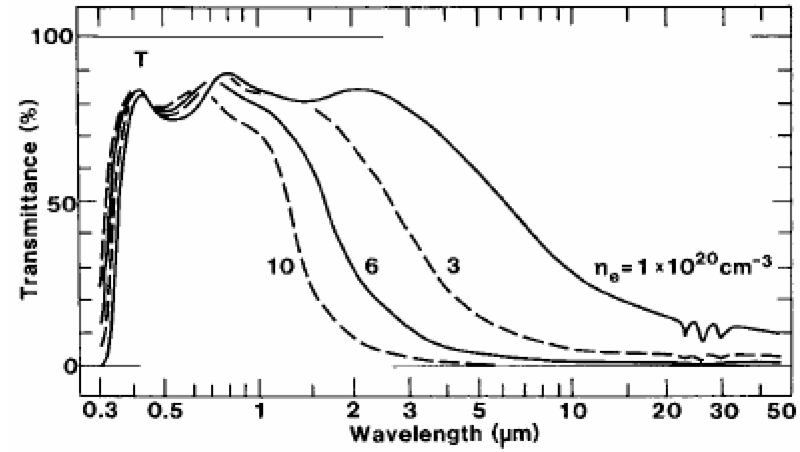
λ Starting reflective with Ne and mobility

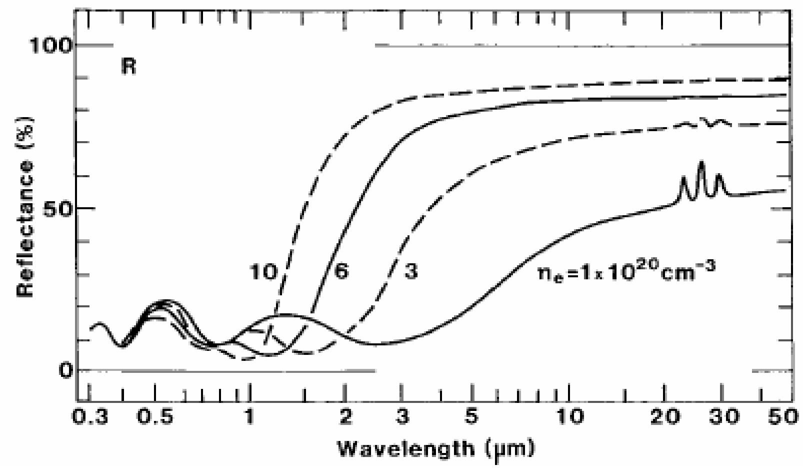
$$\lambda_p = 2\pi c_0 \left(\frac{Ne^2}{\varepsilon_0 \varepsilon_l m^*} - \gamma^2 \right)^{-1/2}$$

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

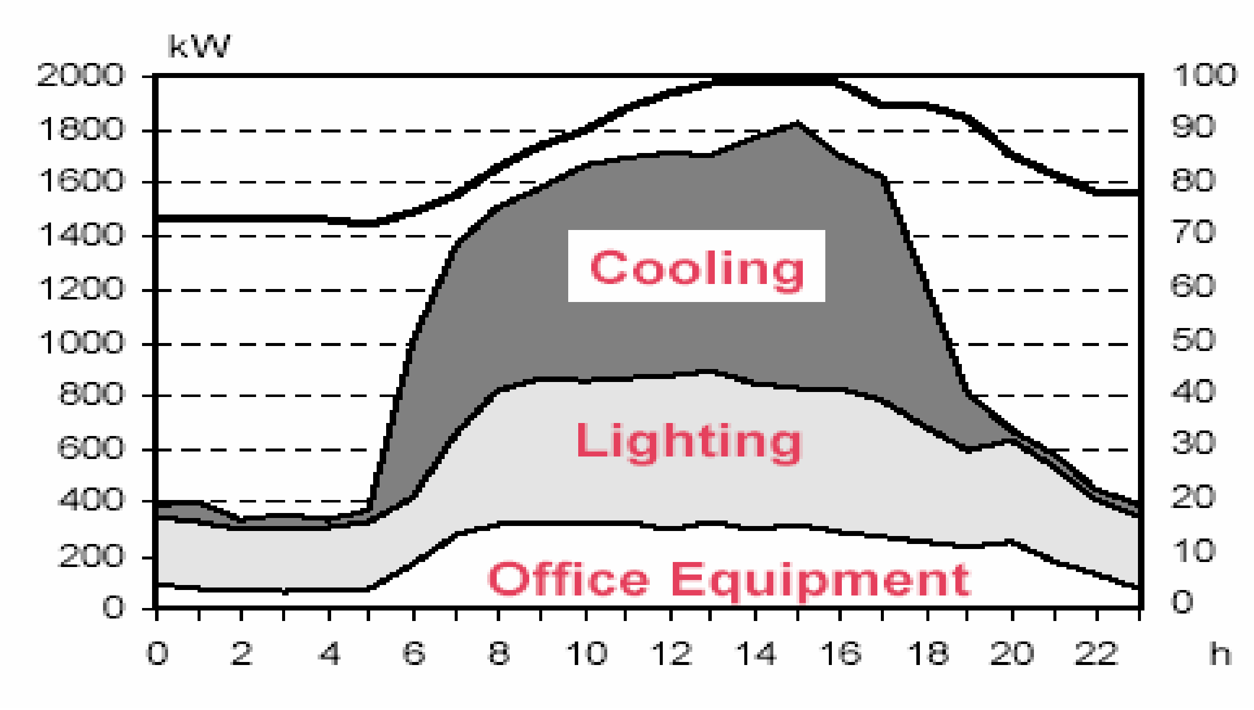
Application of low-E glass for energy-saving

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

Houses：**10～20 kWh / m²·yr**

Public buildings：20～60 kWh / m²·yr

Large public buildings：70～300 kWh / m²·yr



Typical energy consumption of public building in a summer day

P-type transparent conductive oxide films

ZnO:(N, Li) most extensive studied
SnO_2:(Al, In, Sb^{3+}, Zn, Li, Cu)
AMO_2 type oxides by Prof. Kawazoe and Hosono in TIT, Japan
(delafossite structure, A=Cu^{II},Sr, M=Ga,In, Cr, Cu^{III})

The preparation of p-type SnO_2:Sb (Our researches)

Method：RF sputtering
Target：Sb-SnO_2ceramic(Sb_2O_3:SnO_2 = 0.2:0.8)
Substrate：silica glass and single crystalline Si

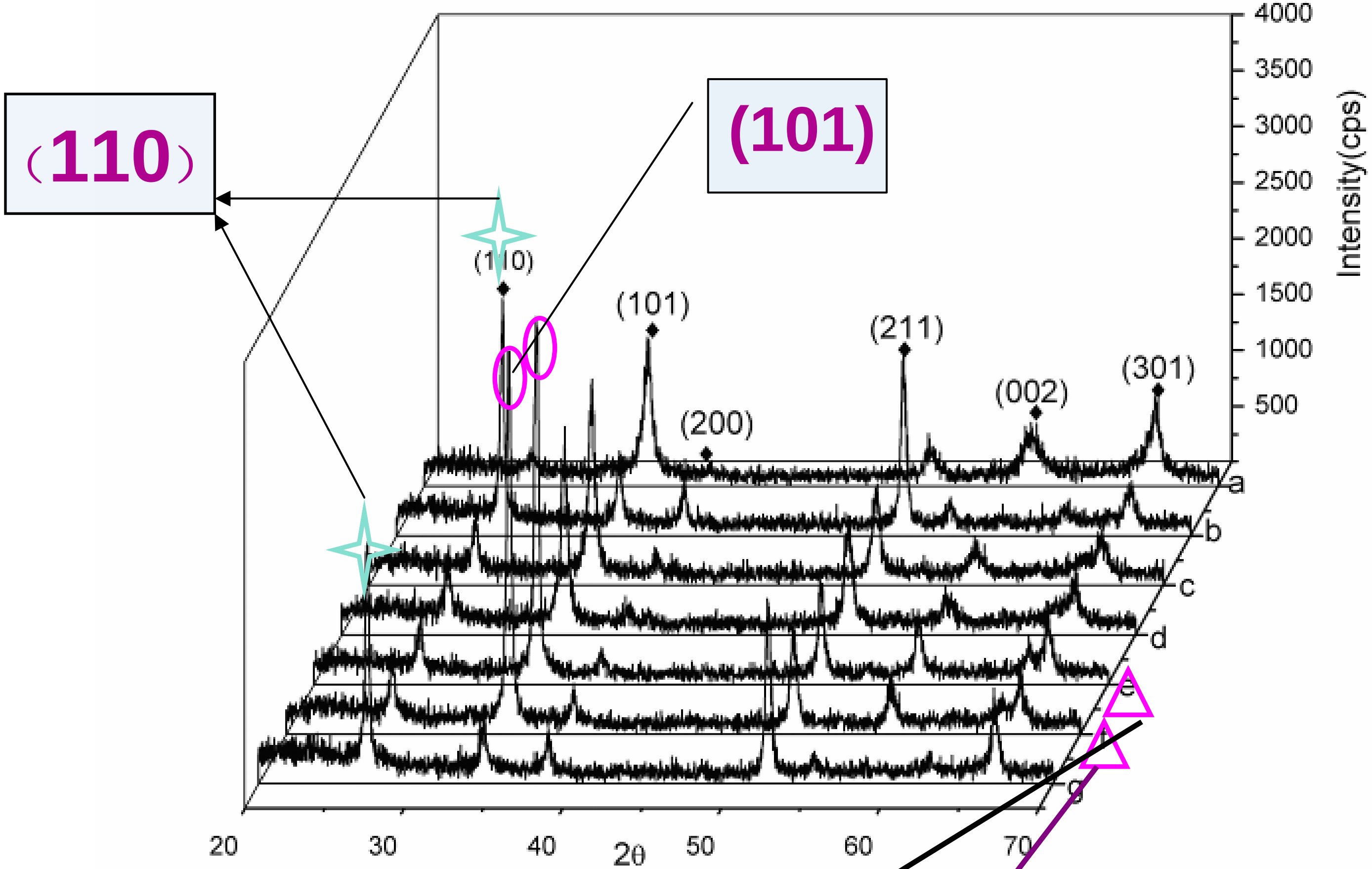
Electrical properties of ATO films under different annealing temperature

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

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

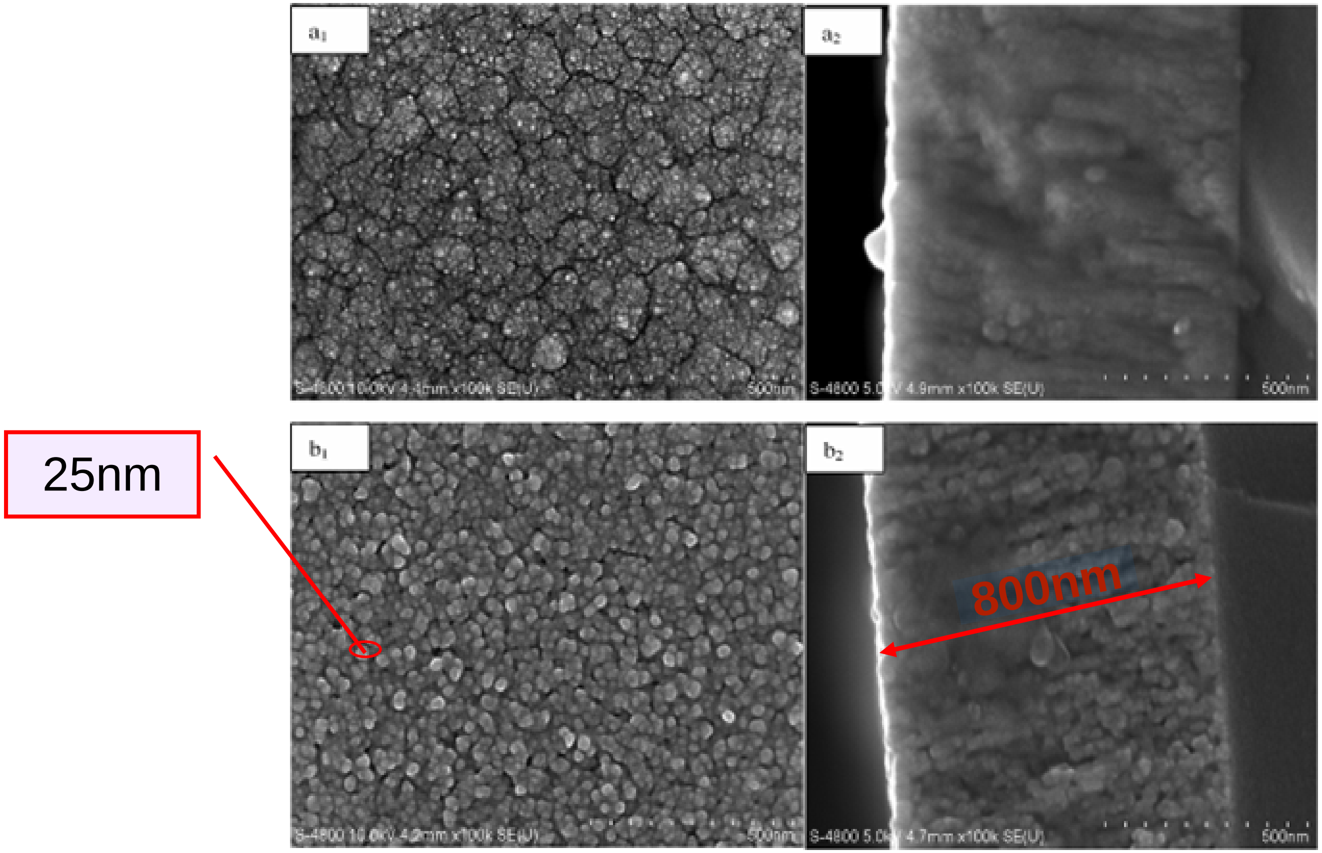
Deposited on quartz substrates
substrate temp: 200℃

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



X-ray diffraction spectra of SnO_2: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)

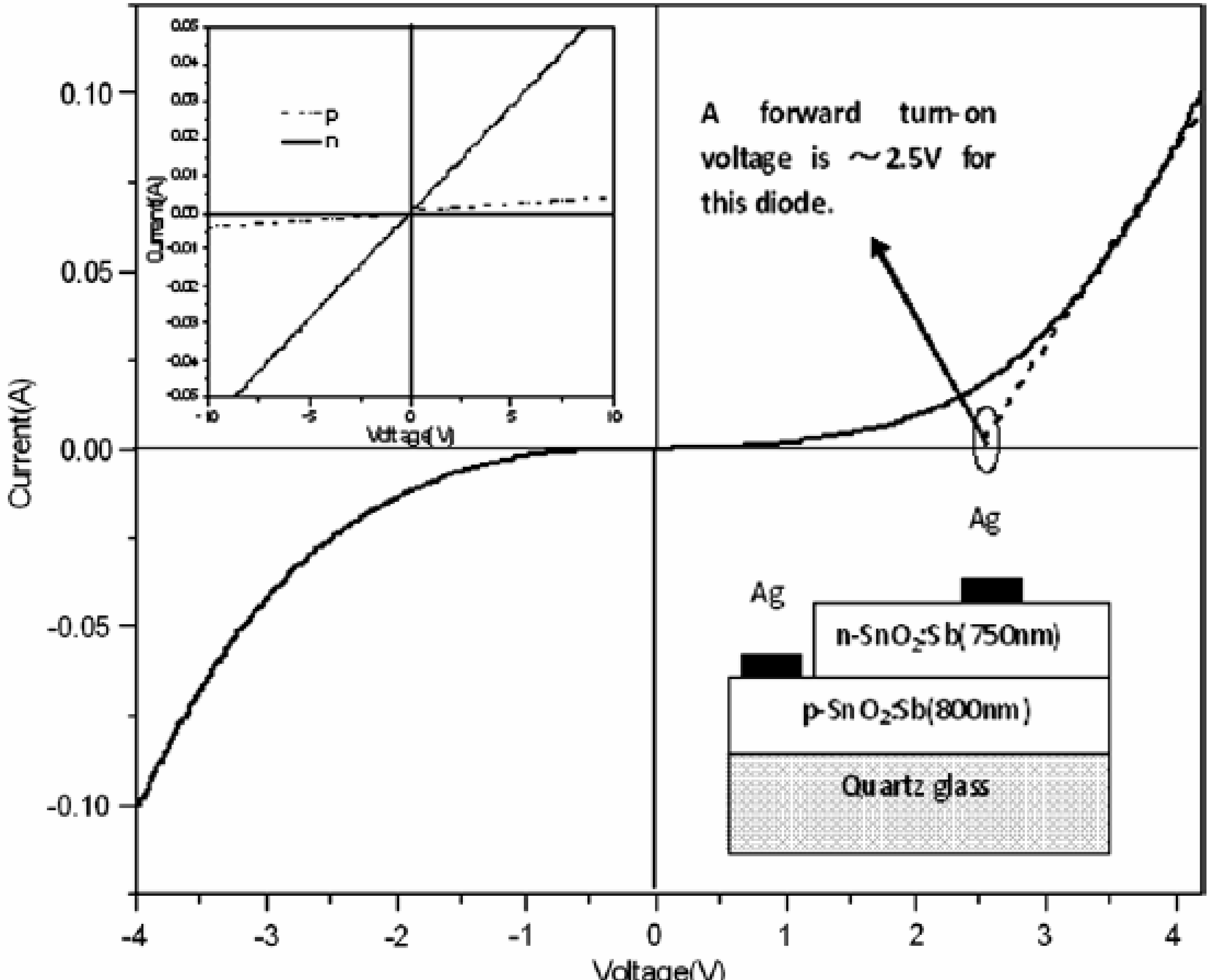
J. Ni et al, *Acta Mater.*, 57(2009) 278-285 **Deposited on quartz substrates**



SEM micrographs and image of the cross-section for the ATO films at different annealing temperature（a_1: micrograph of no annealing, a_2: cross-section of no annealing; b_1: micrograph of 973K for 4h, b_2: cross-section of 973K for 4h）

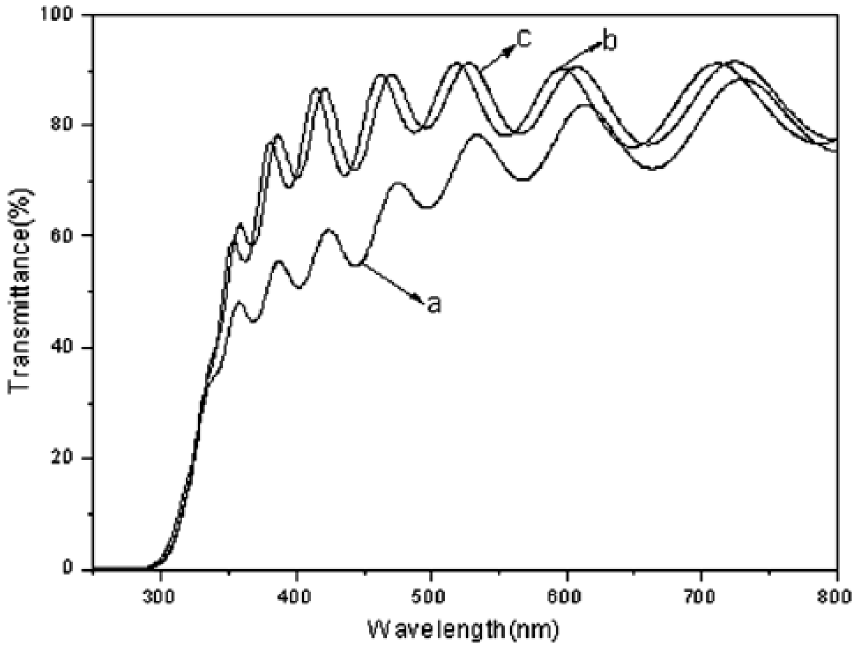
J. Ni et al, *Acta Mater.*, 57(2009) 278-285

Deposited on quartz substrates

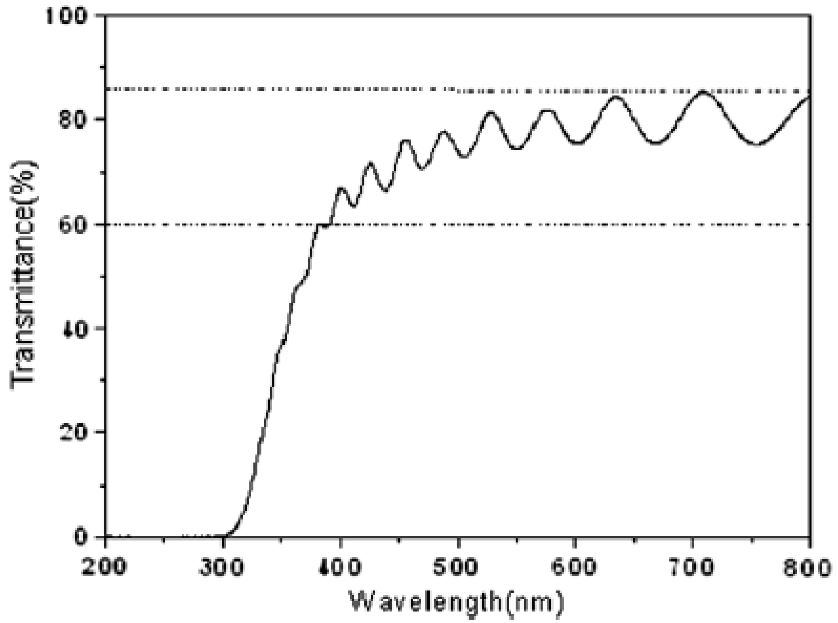


J. Ni et al, *Acta Mater.*, 57(2009) 278-285

Transmittance of p-SnO_2:Sb thin films and silica glass/ n-ATO/p-ATO p-n junction



transmittance of SnO_2:Sb thin films



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

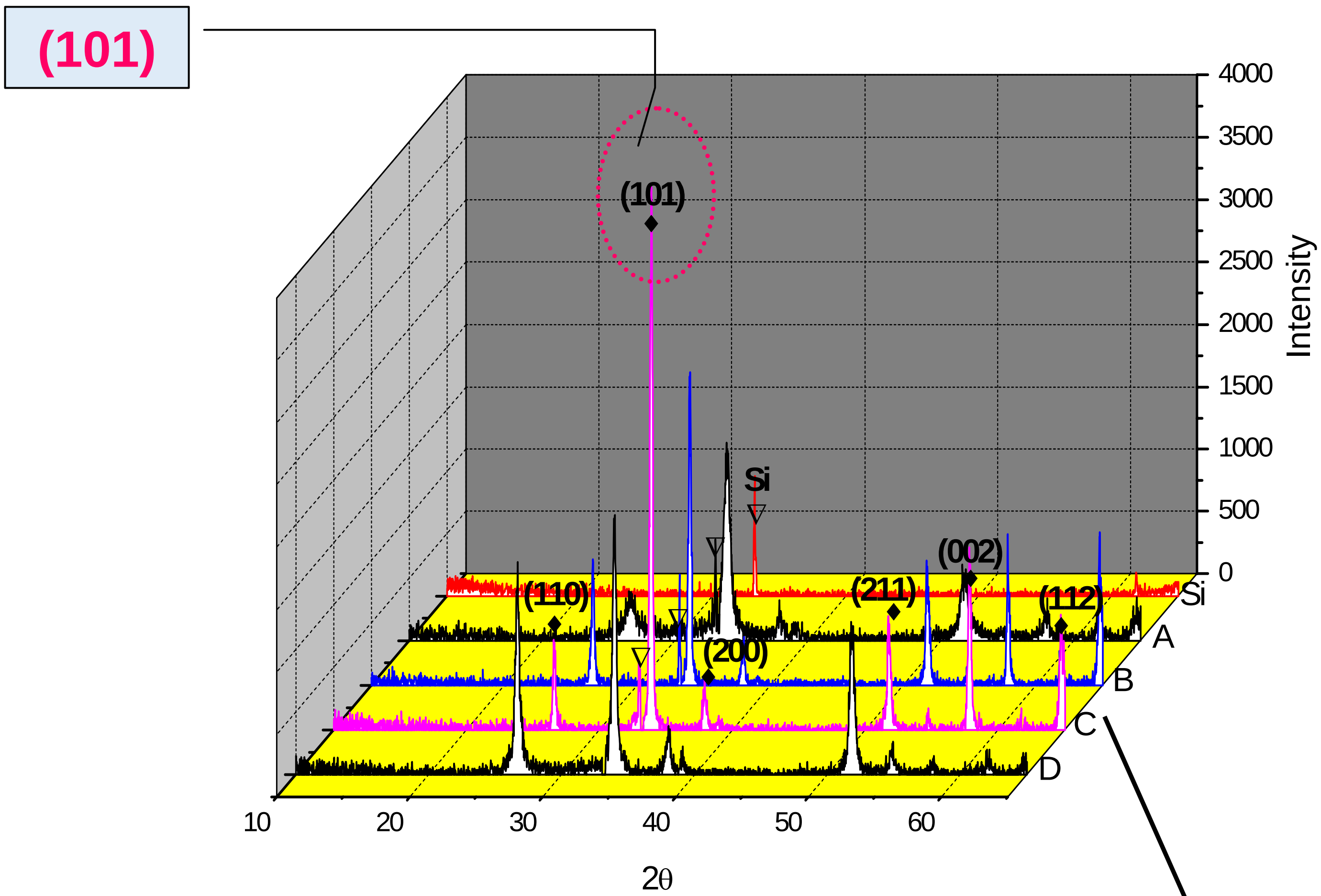
J. Ni et al, *Acta Mater.*, 57(2009) 278-285

the influence of the substrate temperature on the electrical properties of the SnO_2:Sb films.

Substrate temperature (℃)	Carrier type	Carrier concentration (cm^{-3})	Carrier Mobility ($cm^2V^{-1}s^{-1}$)	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

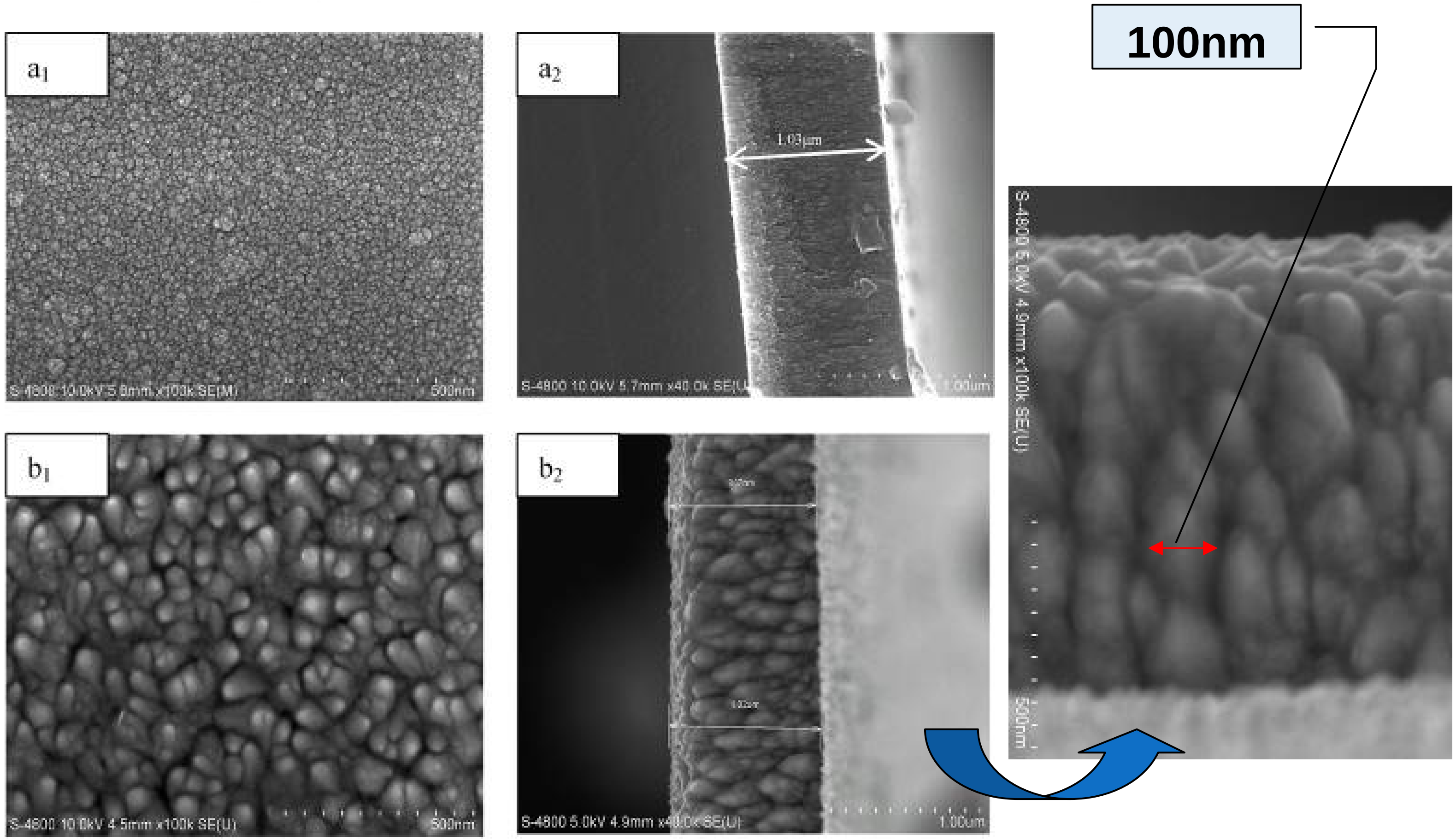
Much higher than that of most reported p-type conductors

Deposited on Si(100) substrates



X-ray diffraction spectra of Si (100) substrate and SnO_2:Sb thin films deposited at different temperatures (A:150℃, B: 200℃, C: 250℃, D:300℃)

Deposited on Si(100) substrates

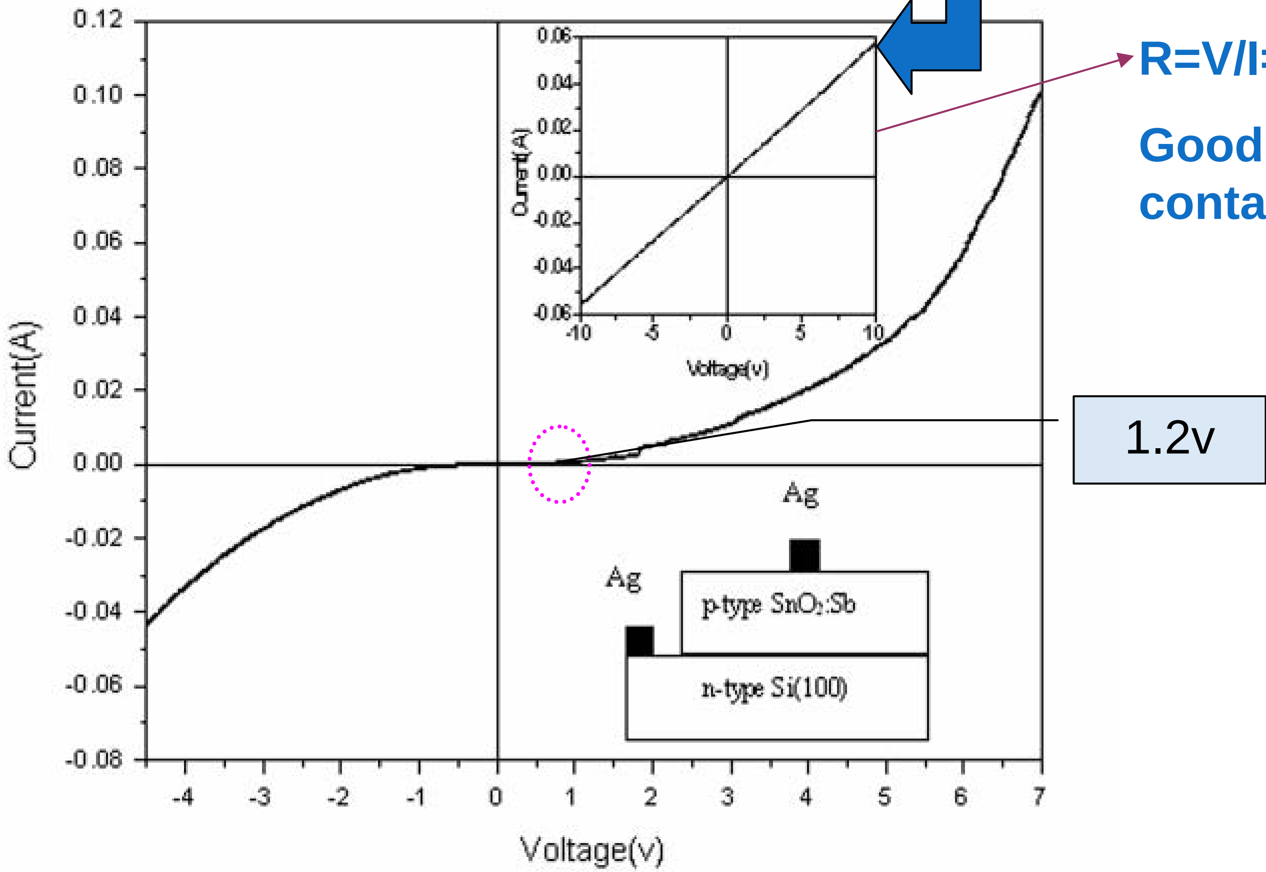


FESEM micrographs and image of the cross-section for the SnO_2: Sb films deposited at different temperatures (a_1: micrograph of 150℃, a_2: cross-section of 150℃; b_1: micrograph of 250℃, b_2: cross-section of 250℃).

Deposited on Si(100) substrates

The upper inset shows the Ohmic contact I–V curve of the Ag electrodes on p-type SnO_2:Sb film.

I-V curve

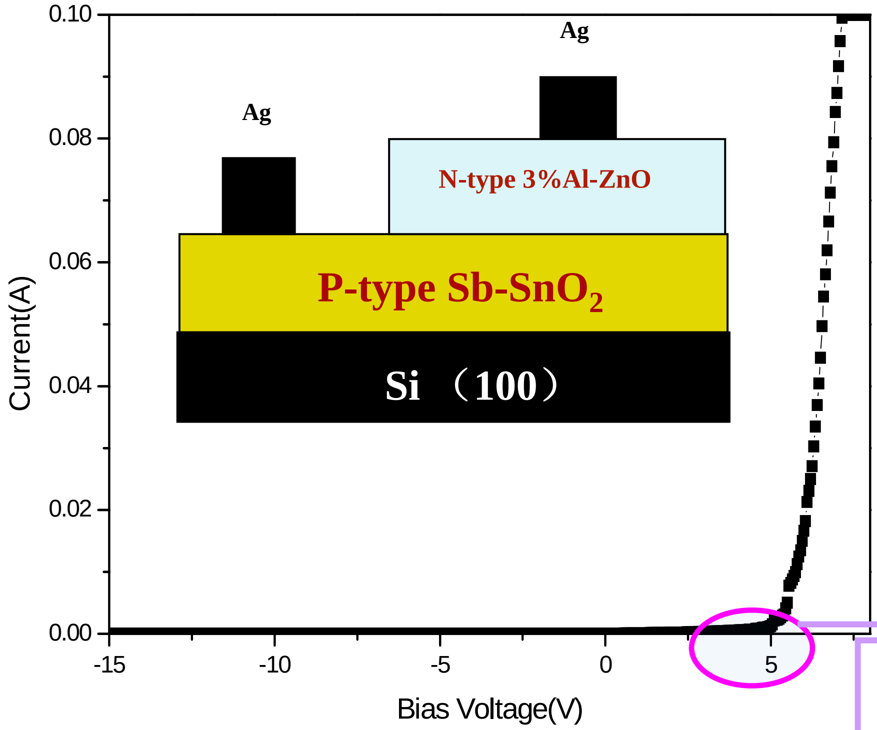


R=V/I=167Ω

Good Ohmic contact

I–V characteristics of a p-type SnO_2:Sb /n-type Si(100) heterojunction. The lower inset shows the schematic structure of the p-type SnO_2:Sb /n-Si (100) heterojunction. (Notes: the p-type SnO_2:Sb films were deposited at 250℃)

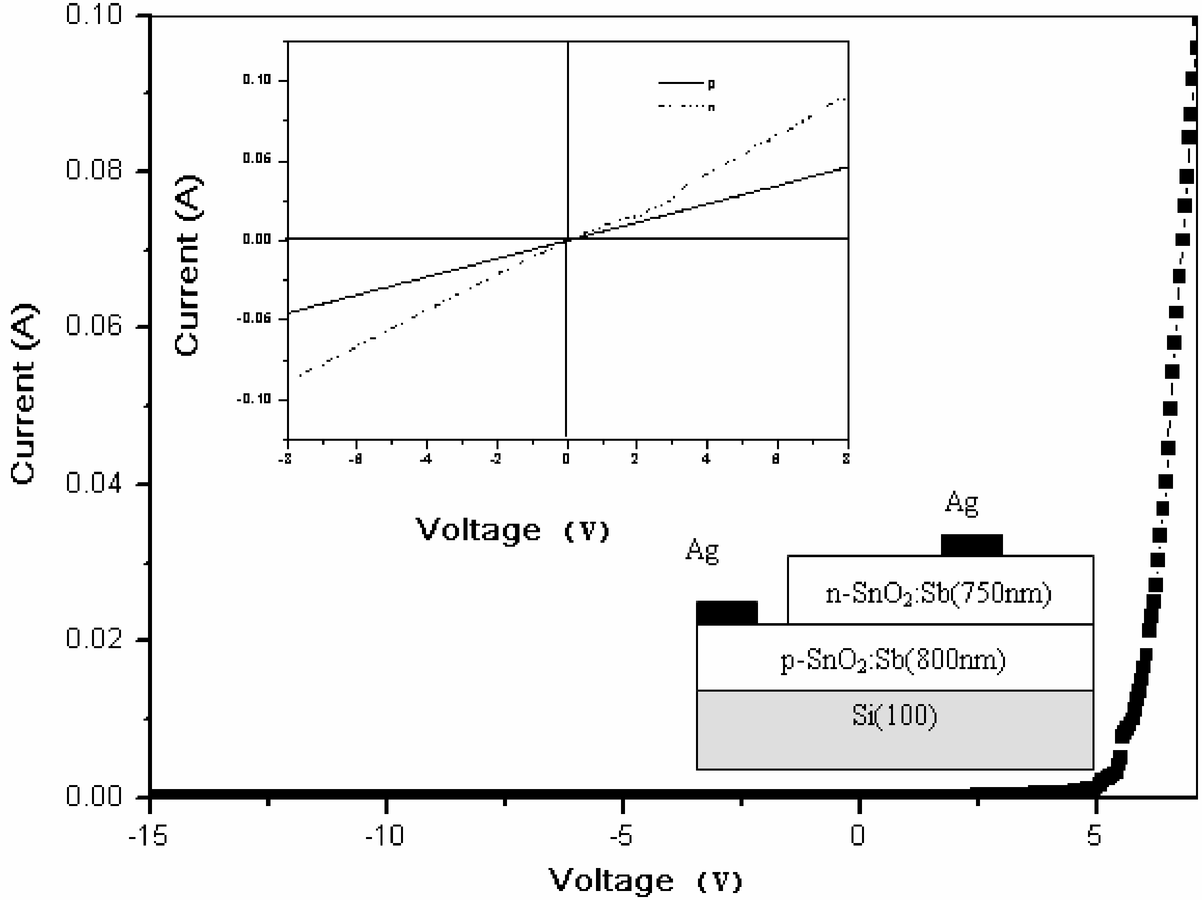
Transparent hetero p-n junction deposited on Si(100)



the I-V characteristics of p-n junction formed by the n-Al-doped ZnO layer (800 nm)/ p-Sb:SnO_2 layer (800 nm) on a silicon wafer substrate. The Ag electrodes were placed on the n-Al-doped ZnO layer and p-Sb-SnO_2 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

$$R = \{(n-1) / (n+1)\}^2$$

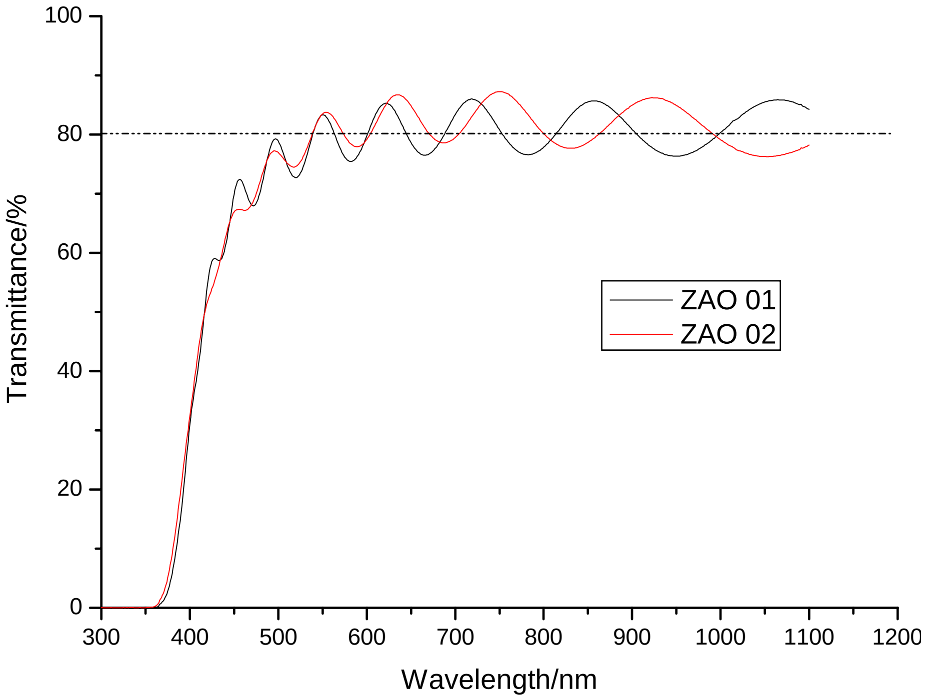
$$T = 1 - R - \alpha$$

R： Reflectance

n： refractive index

T： transmittance

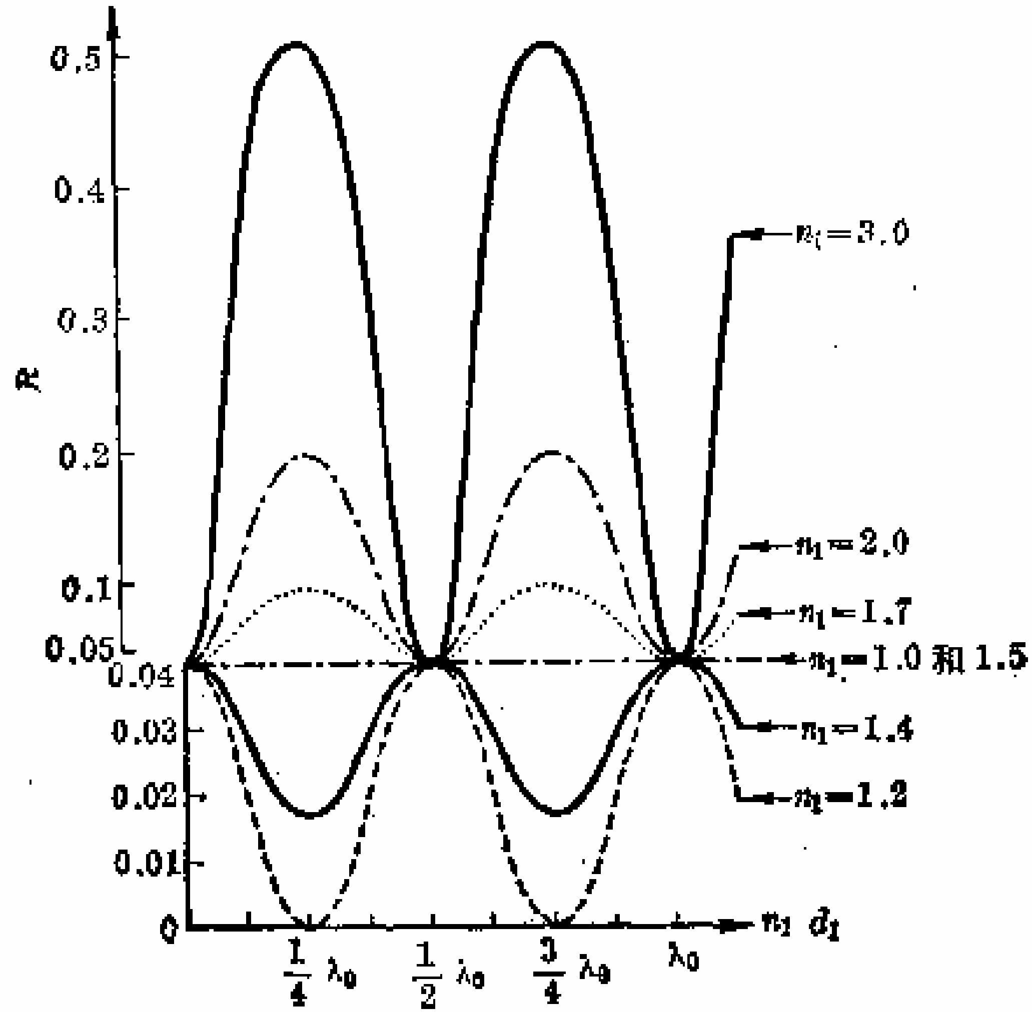
α： absorptance



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

Reflectance of single layer dielectric film

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



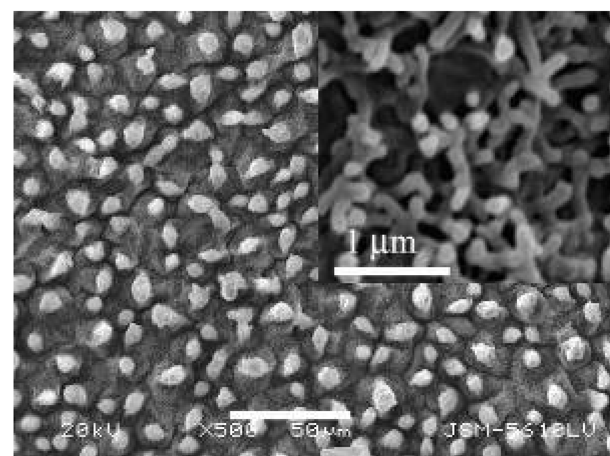
Relation between reflectance and optical thickness, n_1 for film, n_0=1 for air and N_2=1.5 for glass.

Types of Antireflection mechanisms

1. **Interference type:**
   glass/TiO_2（Ta_2O_5，Nb_2O_5）/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**

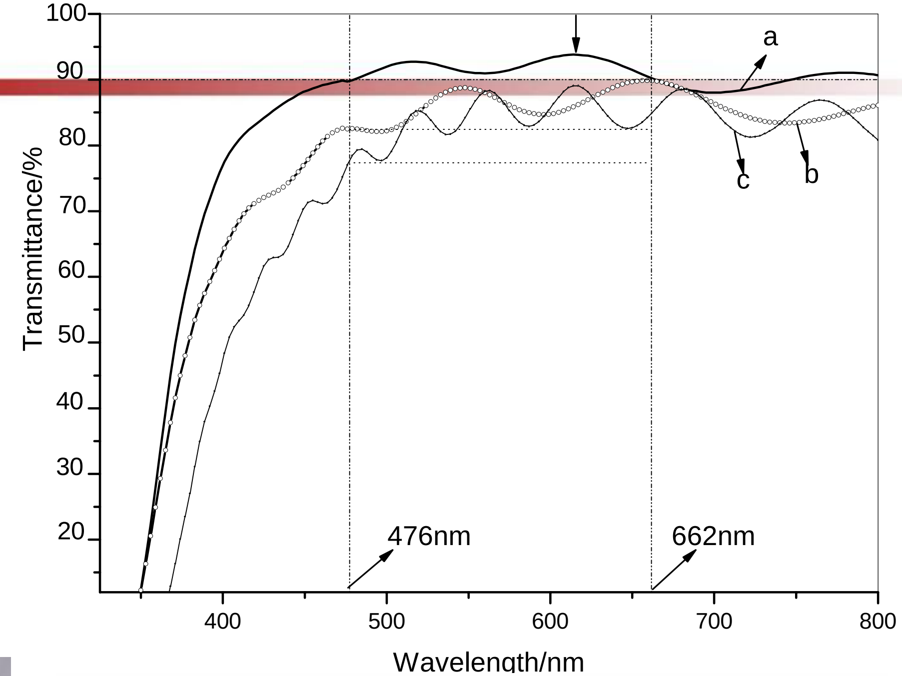


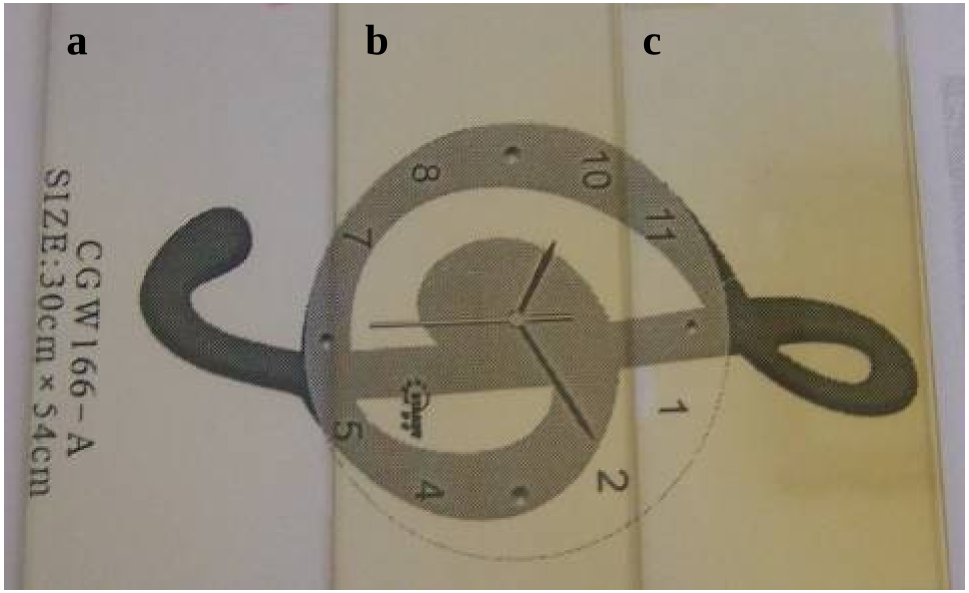
Interference type

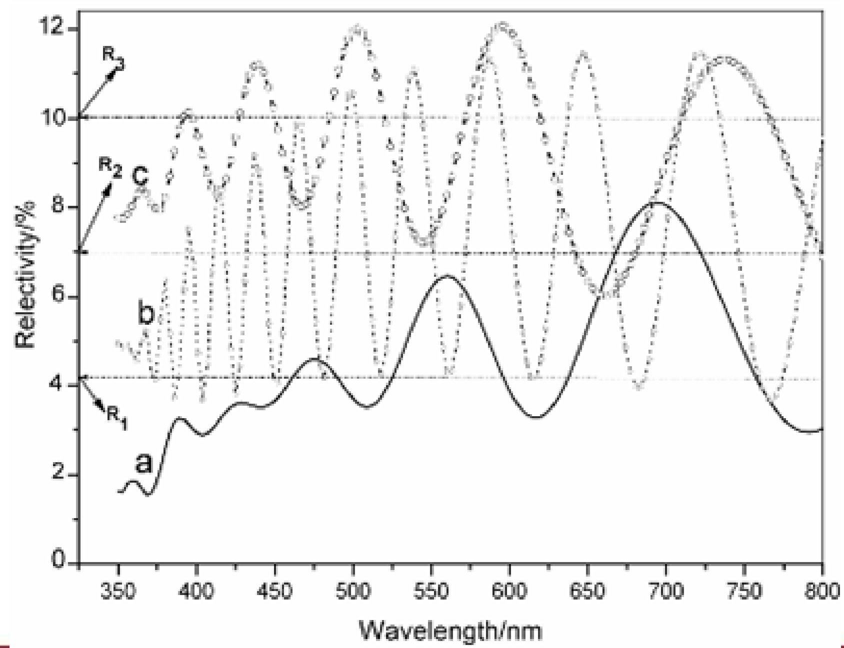
a: SiO_2(110nm)/AZO(850nm)/SiO_2(110nm)

b: SiO_2(110nm)/AZO(850nm)

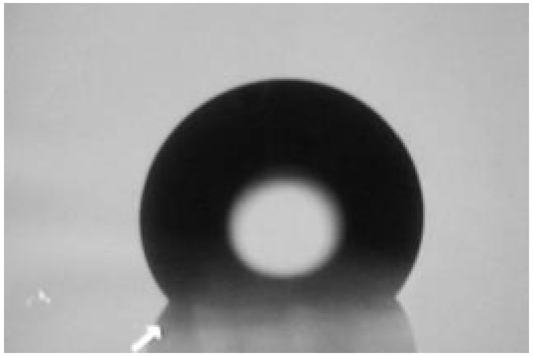
c: AZO(850nm)

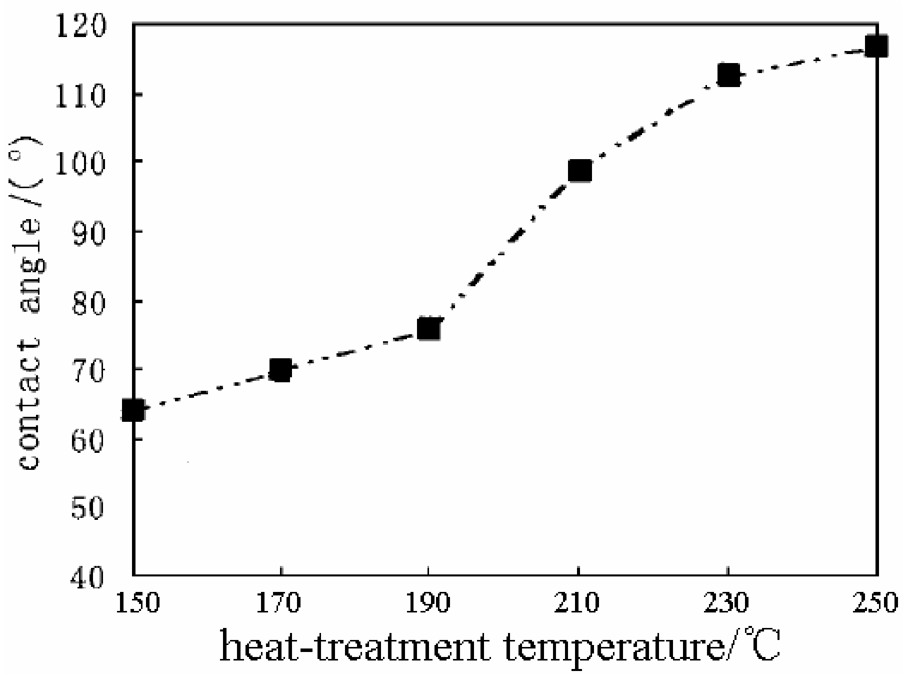




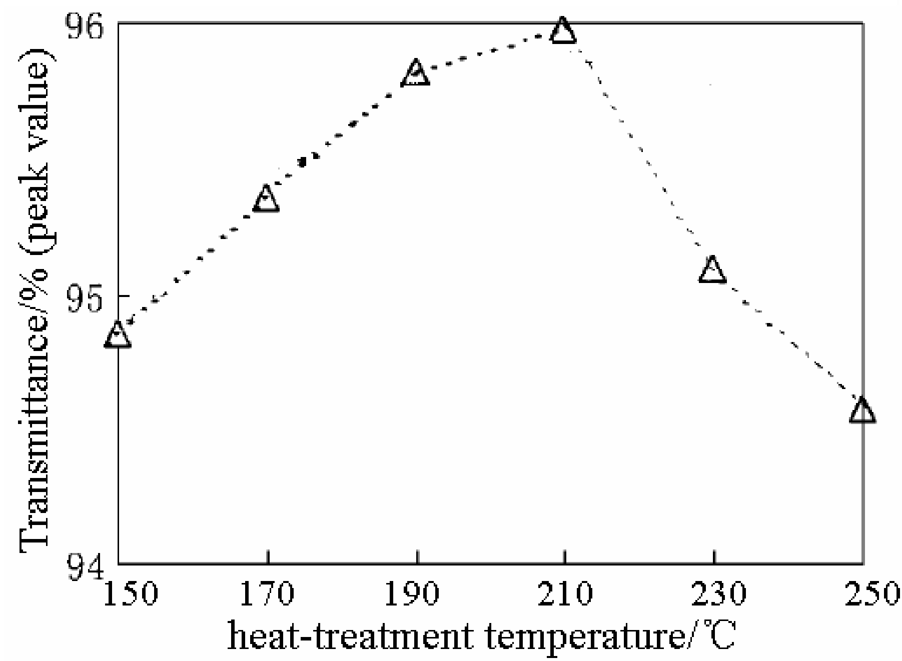


Nano-porous surface structure of SiO_2 and treatment with hydrophobic agent



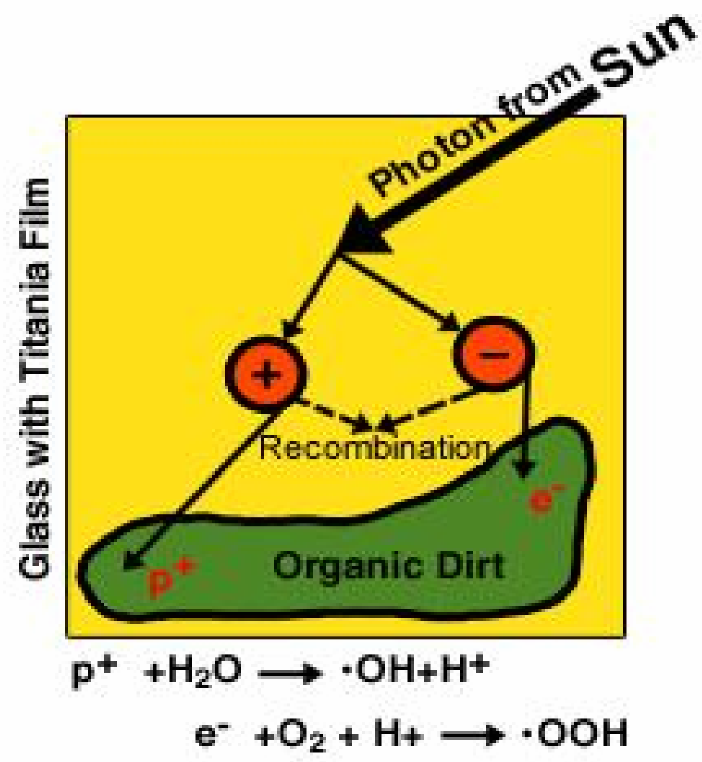


Relation between contact angle and heat-treating temperature



Transmittance with treating temp

4.2 Photocatalytic TiO_2 thin films on glass



TiO_2 photocatalist

1972 Honda-Fujishima effect

1970-1990's photolysis of water

photolysis of polution

materials: powders

1990's dye-sensitized TiO2 solar cell

1997 photo-induced amphiphilicity

⟶ TiO2 photocatalist is suitable for degradation of lower content polutions

TiO_2-based photocatalysis and their evolution

4.2 Photocatalytic TiO_2 thin films on glass

Self-cleaning surface

Super hydrophobic -------fluoropolymer doped SiO_2

mesoporous Al_2O_3

ZnO nano-rod array

Nano-structured polymers

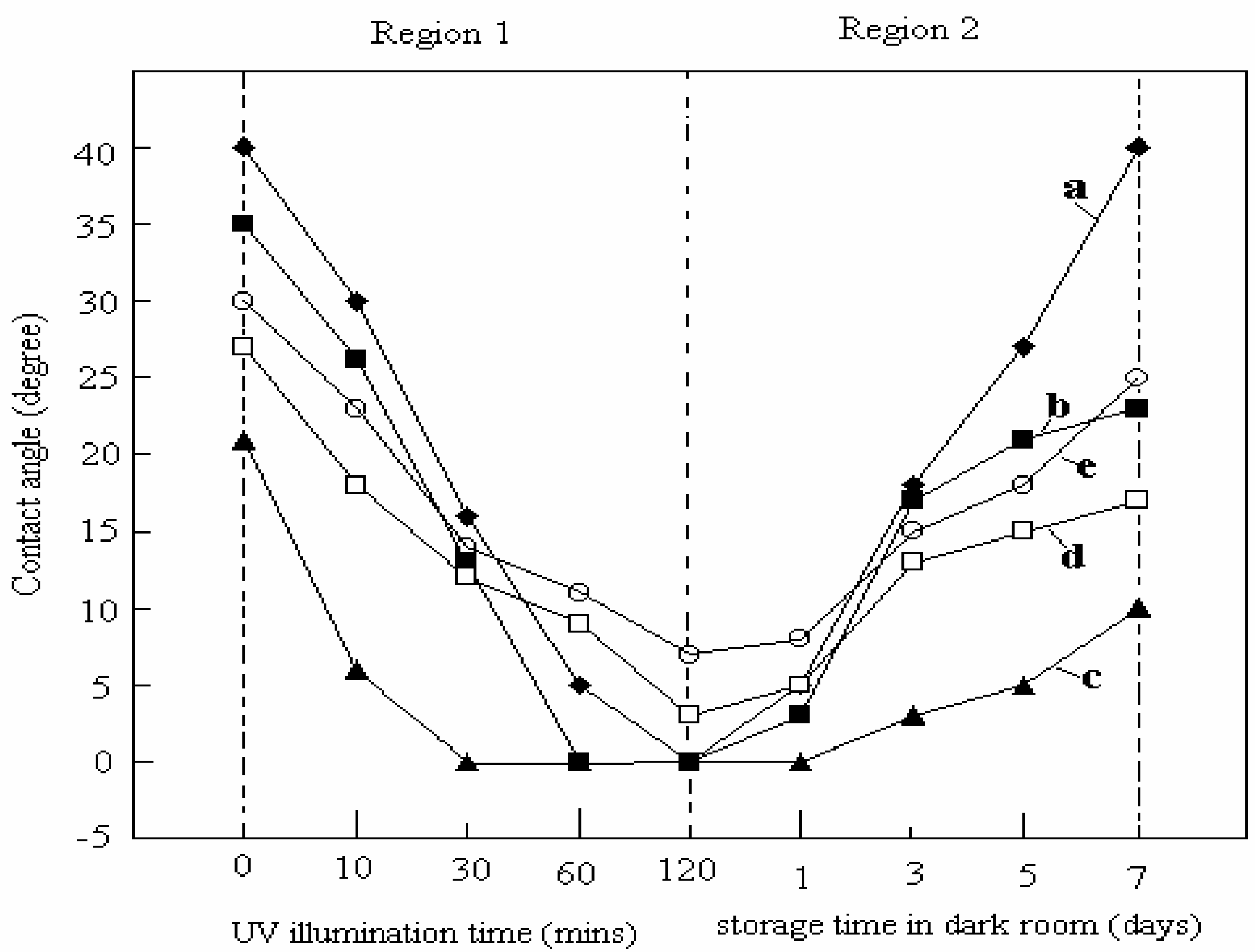
Super hydrophilic-------water soluble materials

TiO_2 photocatalytic property

photoinduced super hydrophilicity

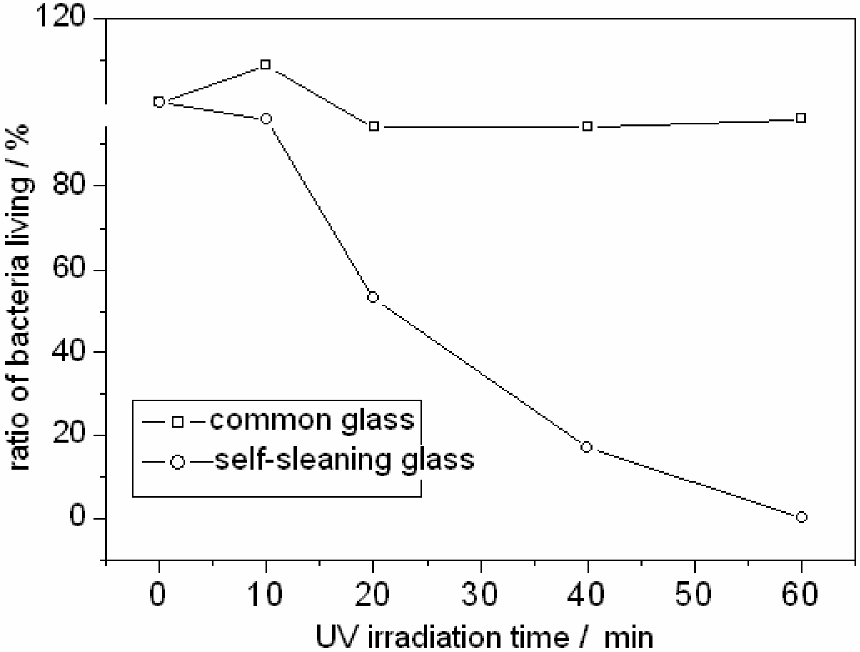
→ self-cleaning surface

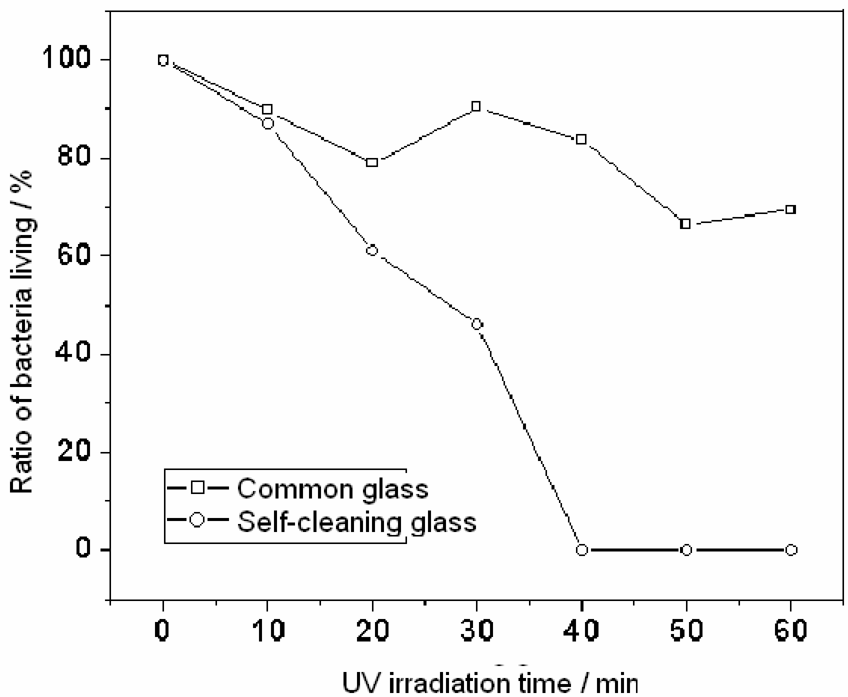
Photoinduced superhydrophilicity of TiO_2 thin films on glass



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_2 films





15-W 365-nm UV lamp by Cole-Parmer Instrument Co., average power 1000 ± 30 μW/cm^2
Bacteria: *E.Coli.* DH5a (left); JM109 (right)
concentration: 1×10^6 CFC / ml, Temp.: 25 ± 1^{o}C; Humidity: 75%

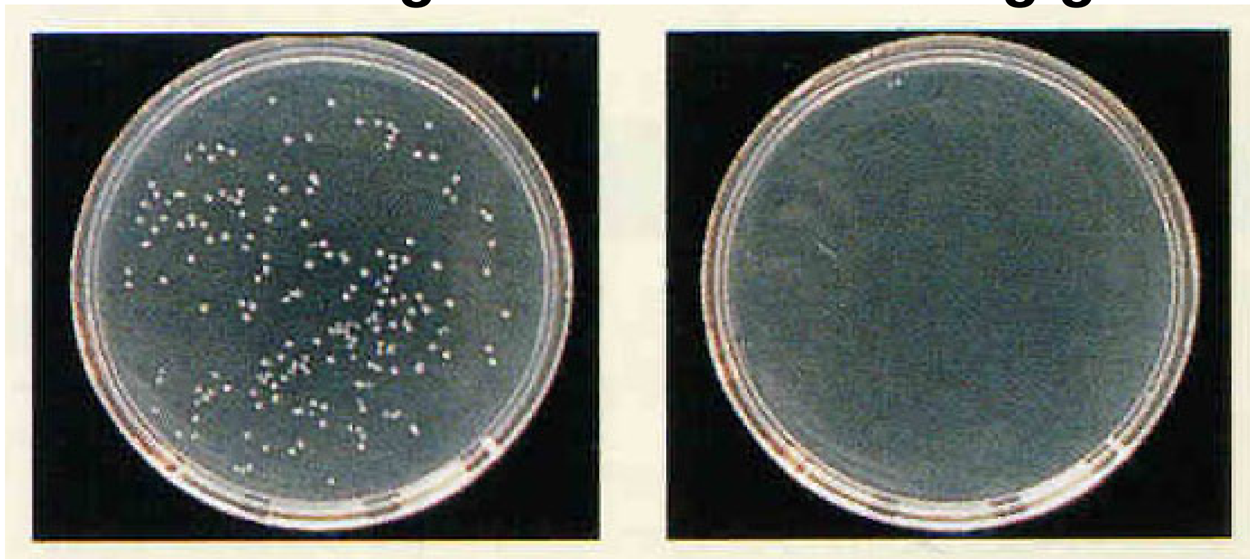
Enhancing anti-bacteria effect without UV irradiation by Ag doping (0.1%)

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

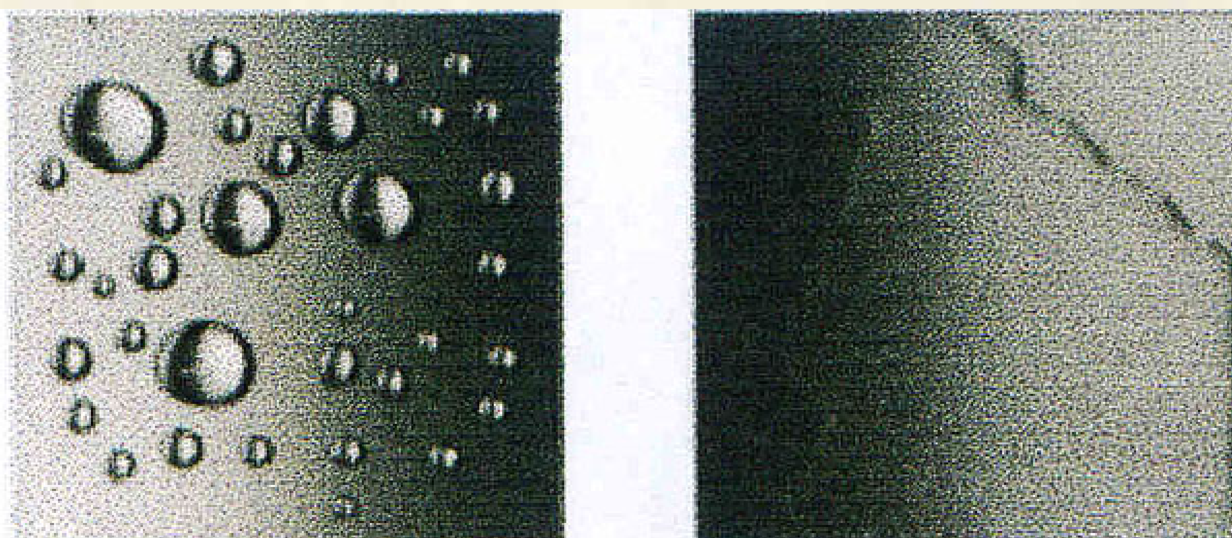
This kind of self-cleaning glass will be useful in hospital, refrigeratory, and so on.

Common glass **self-cleaning glass**

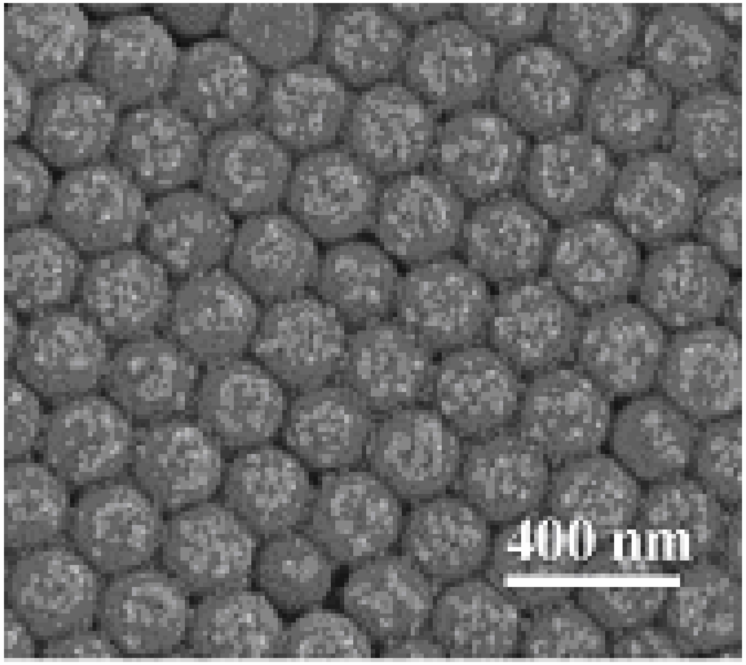
anti-bacteria

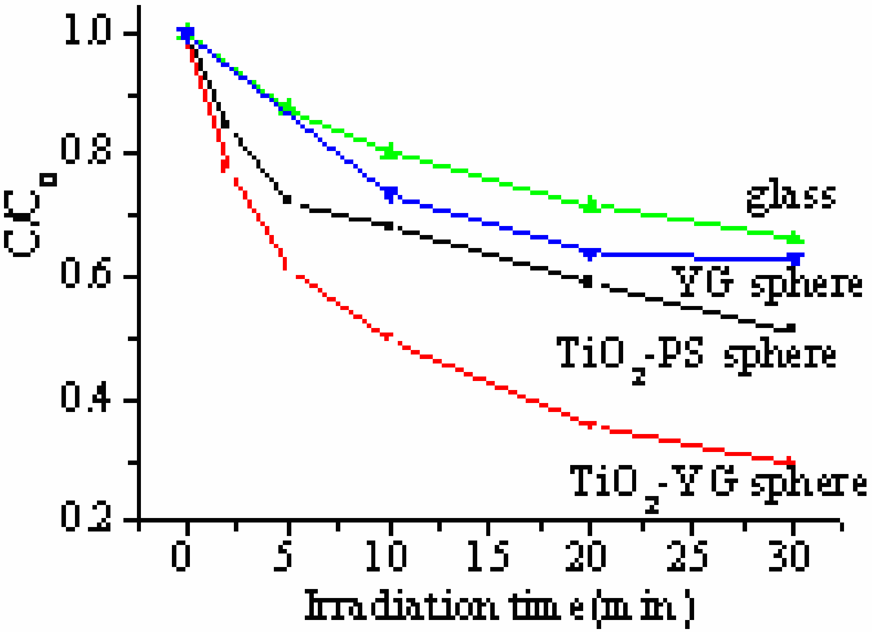


super hydro-philicity



Enhancing photocatalytic activity of TiO_2-based thin films with photonic crystal structure made by the core/shell composite of polymer/TiO_2





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

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

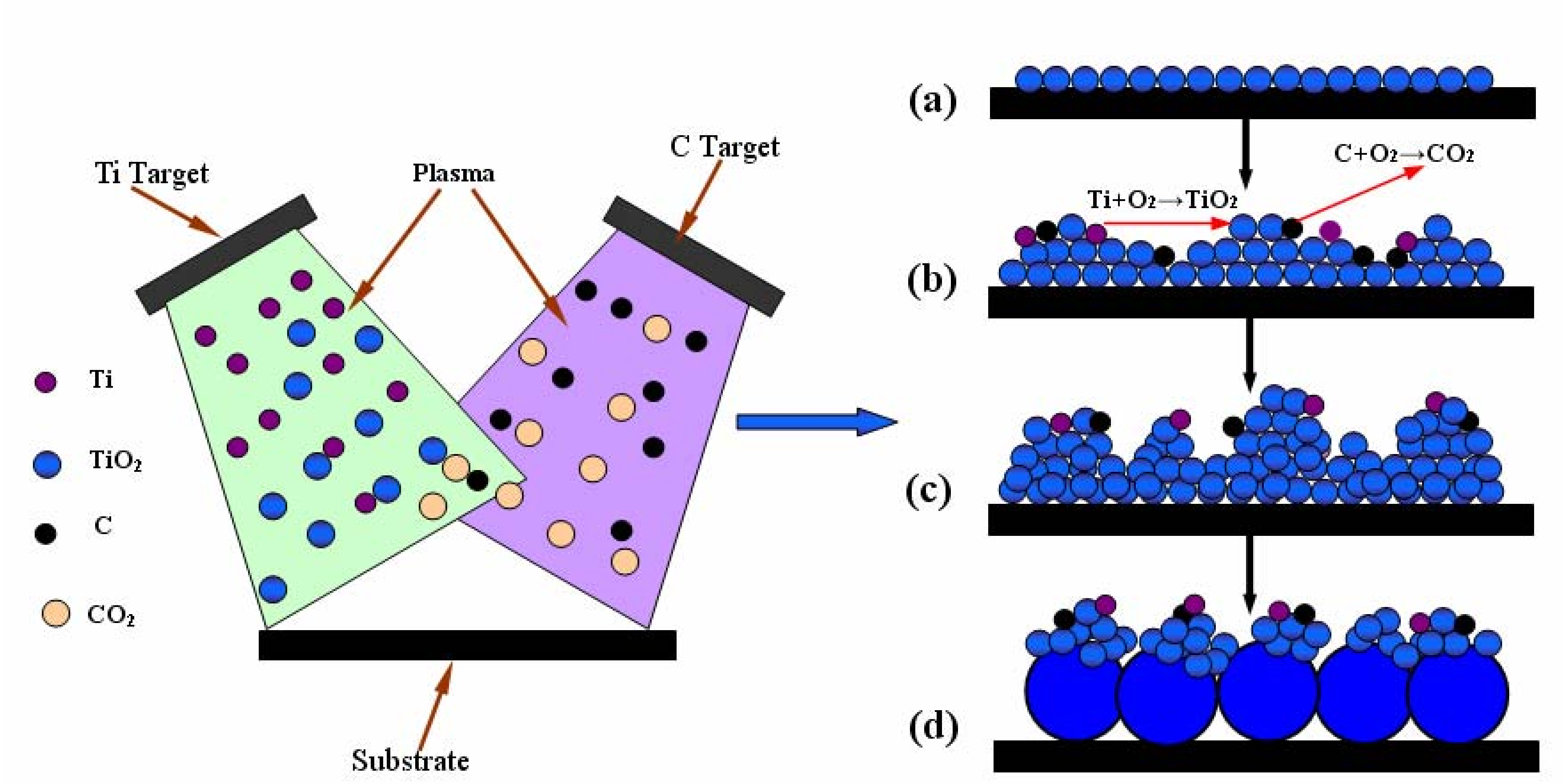
Textured coatings: anti-reflection, water-repellent (hydrophobic), and so on.

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.

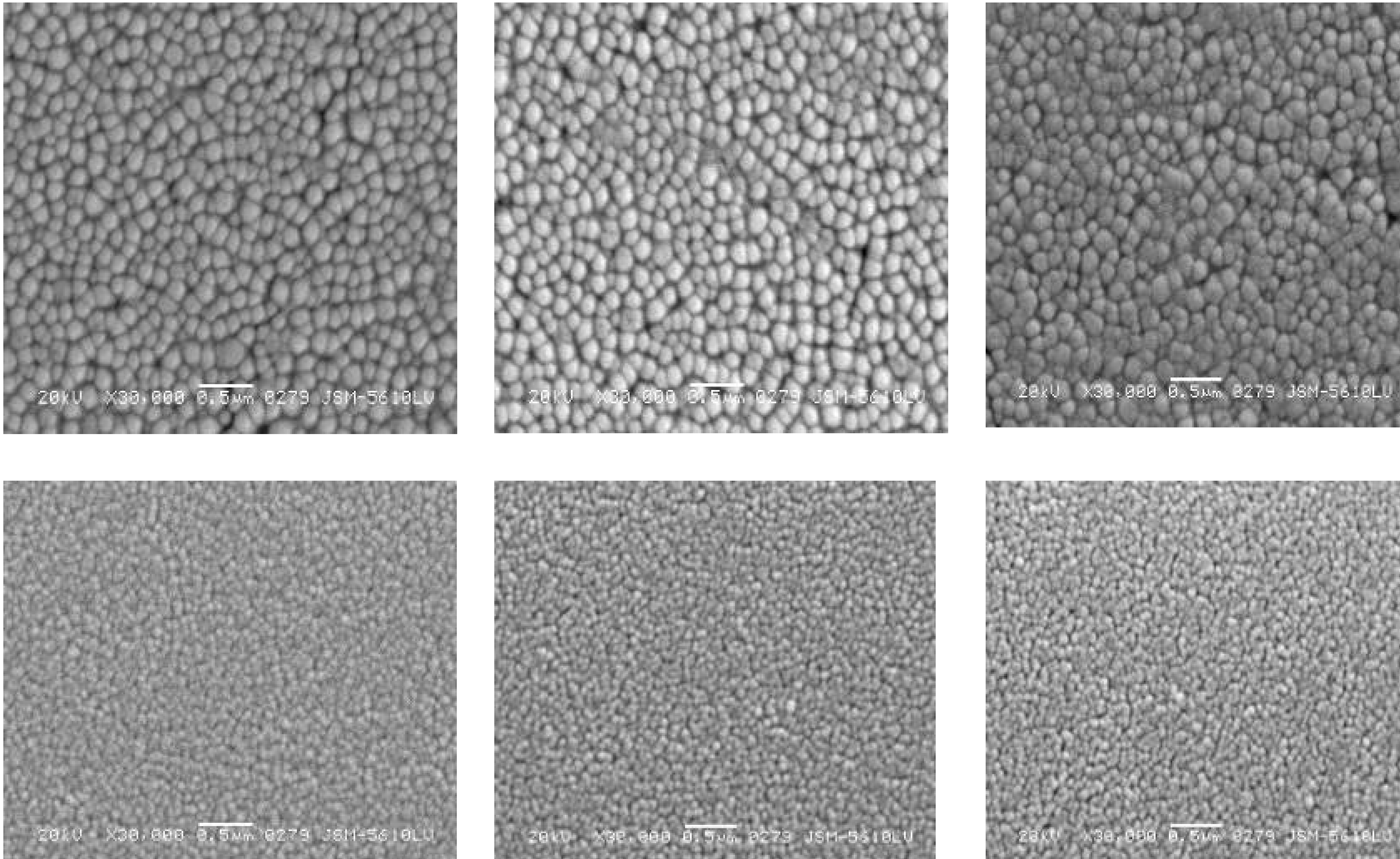
nano-textured Al_2O_3
SiO_2 films doped with fluoropolymer
ZnO nano-rod array
Nano-structured polymers

Their preparation is very Complex, often many steps

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

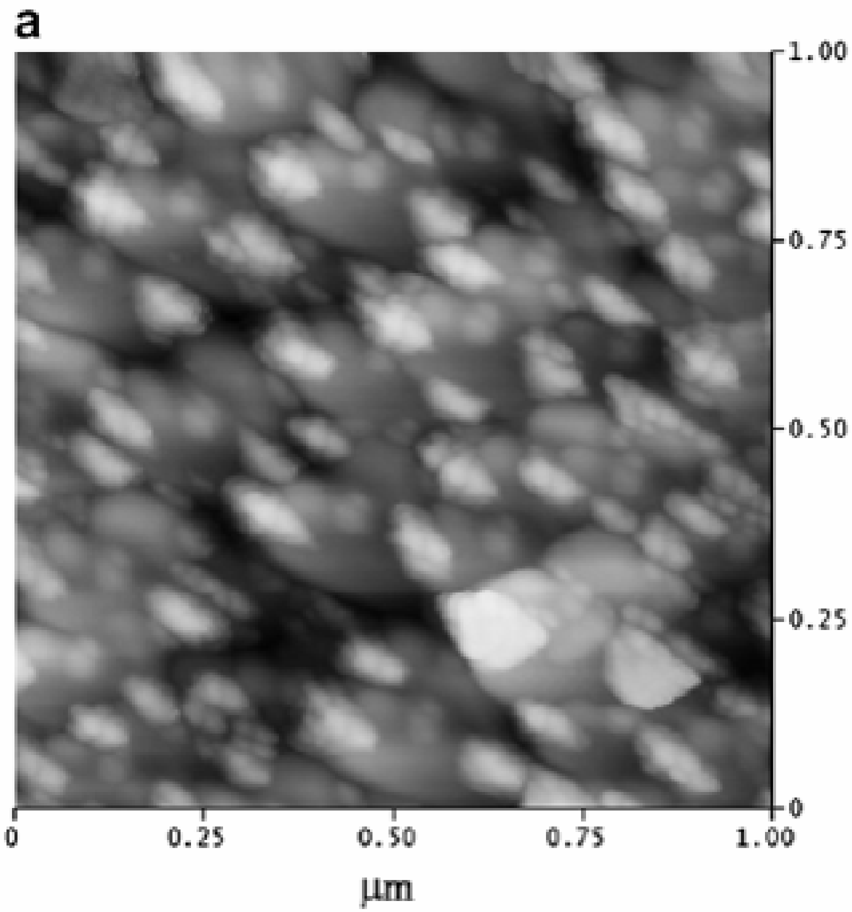


Y. Xie et al. / Chemical Physics Letters 457 (2008) 148–153

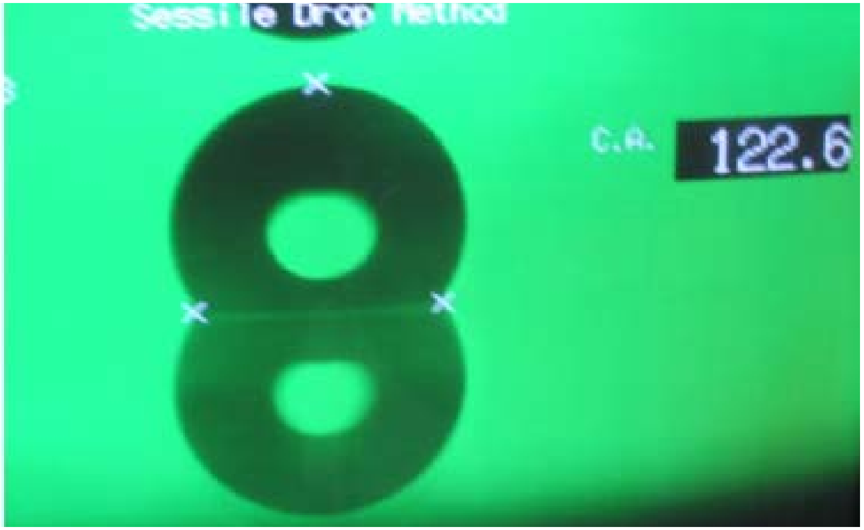


SEM images of C-assisting sputtered TiO_2 coatings under different partial pressure of O_2

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



oxygen partial presure 0.05Pa



Photograph of water bead on the C-assisting sputtered TiO_2 film

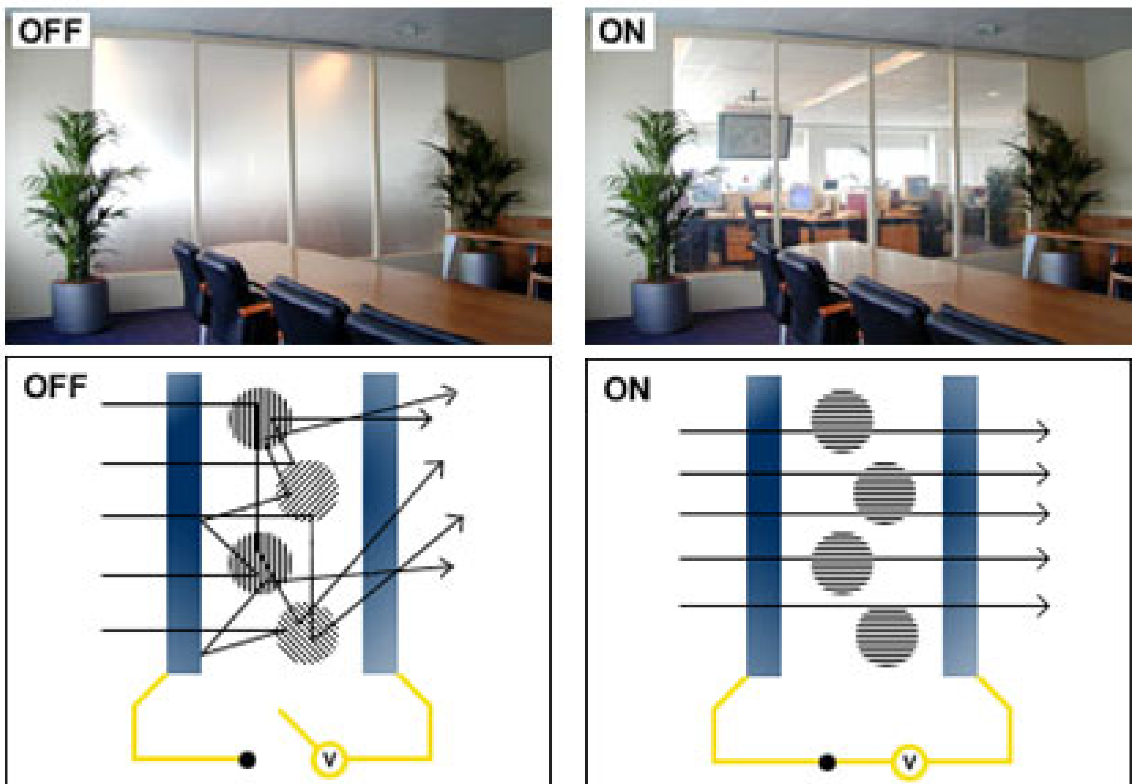
Y. Xie et al. / Chemical Physics Letters 457 (2008) 148–153

Contact angle of C-assisting sputtered ZnO textural coatings

samples	Sputtering time（min）	sputtering power (W)	Substrate temperature（℃）	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
E	180	150	300	138.3
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 eletrochromic films

Electrochromic smart glass and film materials

Conductive Layer

ITO(In_2O_3:Sn), FTO(SnO_2:F),AZO(ZnO:Al),CNT(Carbon nanotubes) etc.

Electrochromic Layer

Inorganic; WO_3,NiO,IrO_2,Nb_2O_5, VO_2,PB,
Polymer: PANI(polyaniline),PED-OT

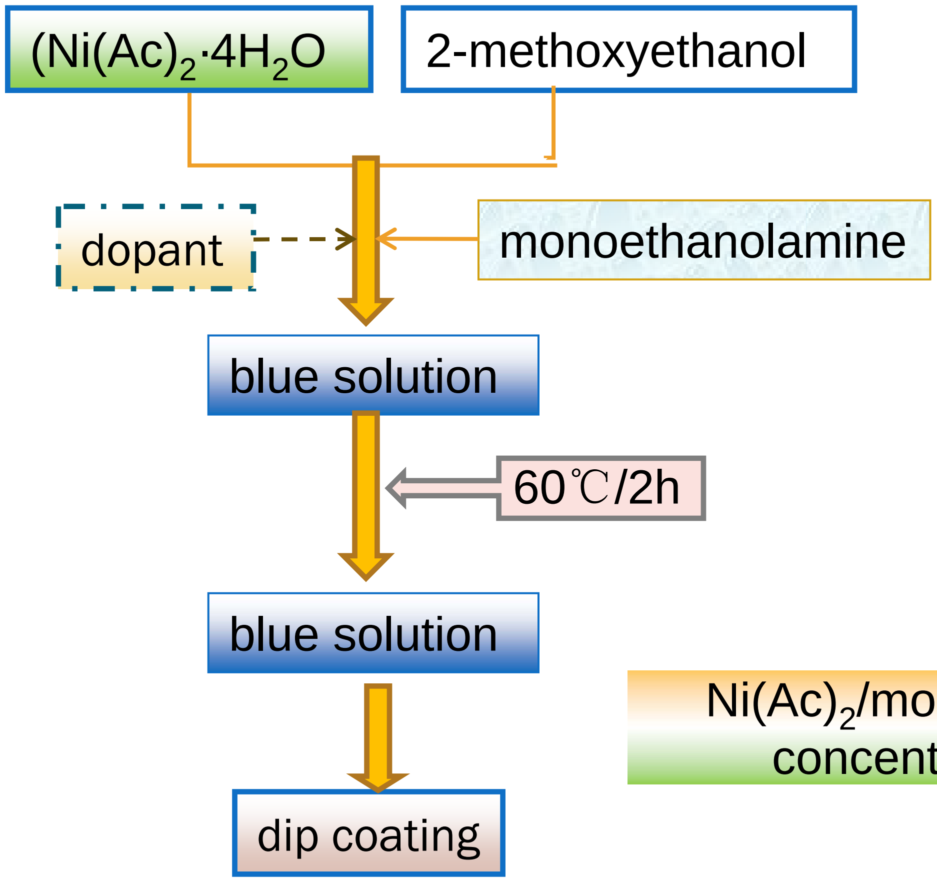
Ion Conductor

Liquid: KOH,NaOH,H_2SO_4
Solid: LISION,NASICON,Perovsike,Ta_2O_5
Polymer: PC:$LiClO_4$,PAMPS

Ion Storage

CeO_2, CeO_2-TiO_2, CeO_2-ZrO_2,CeO_2-SnO_2,CeO_2-SiO_2

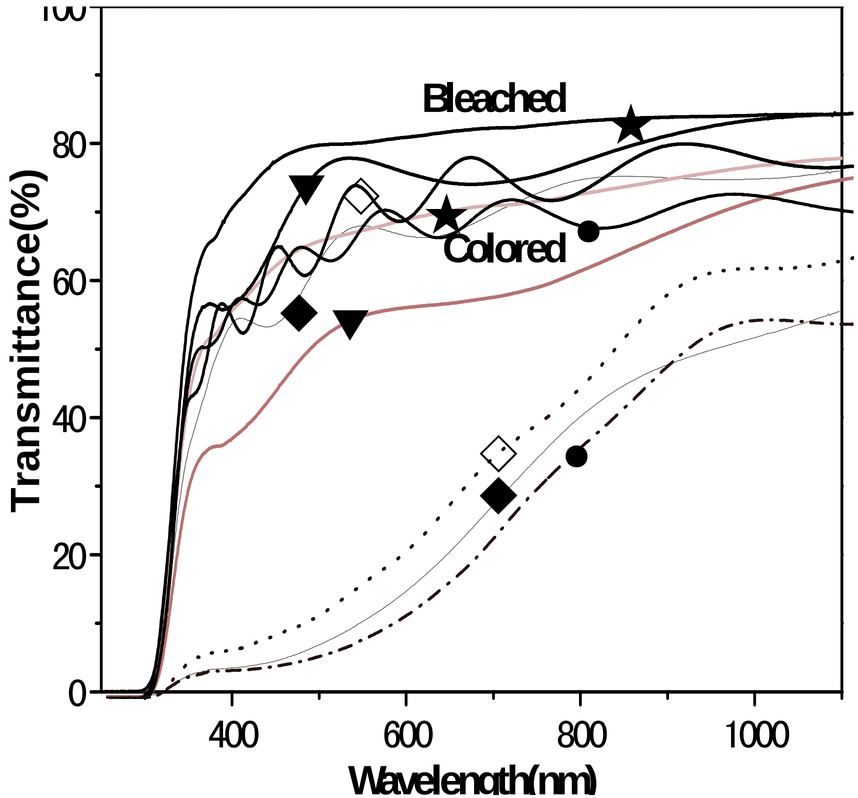
Preparation of NiO-based electrochromic films



$Ni(Ac)_2$/monoethanolamine =1/1, concentration of is0.5mol/L

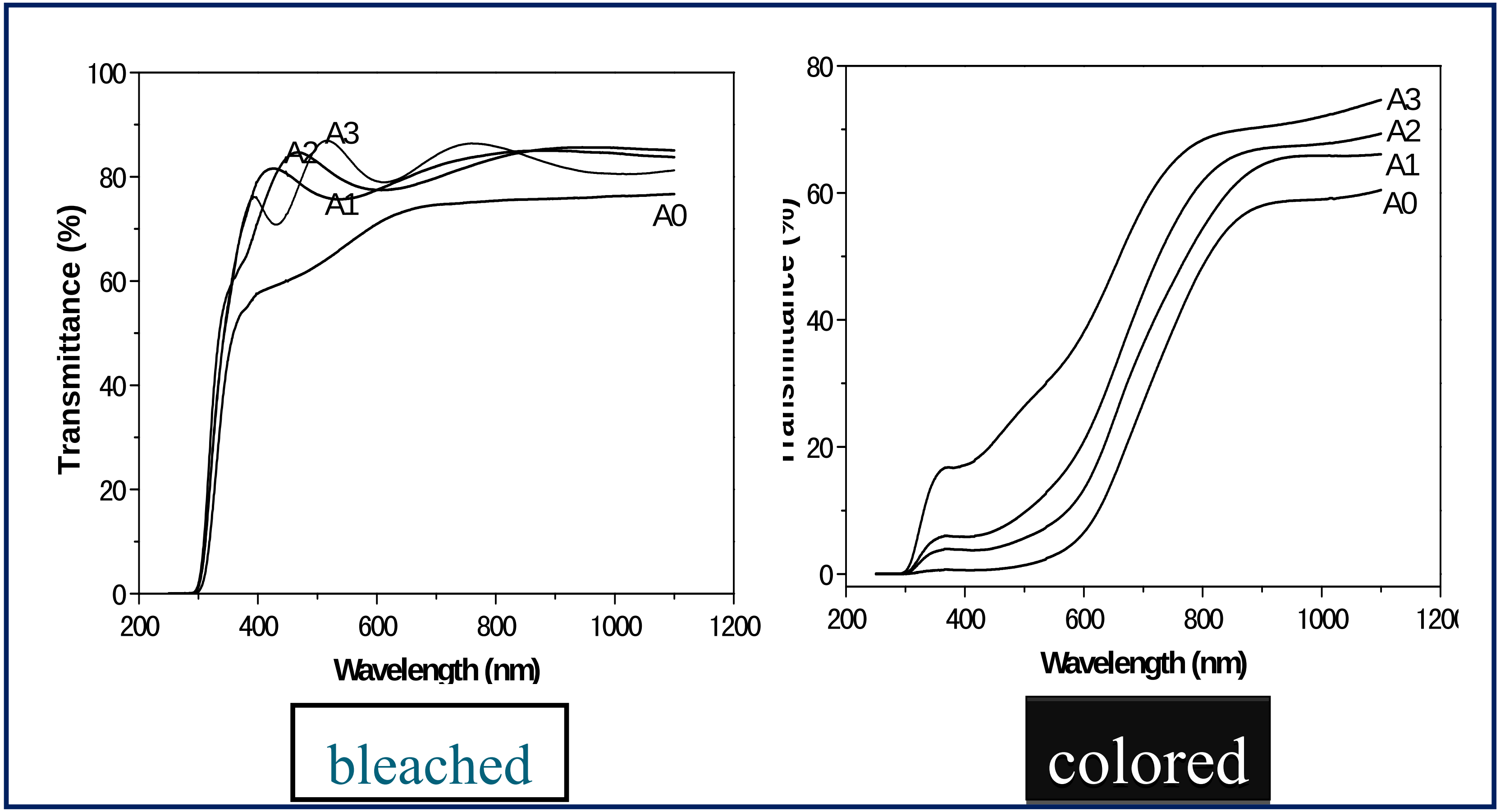
sol-gel process for preparation of NiO-based films

Electrochromic properties of B_2O_3-NiO films

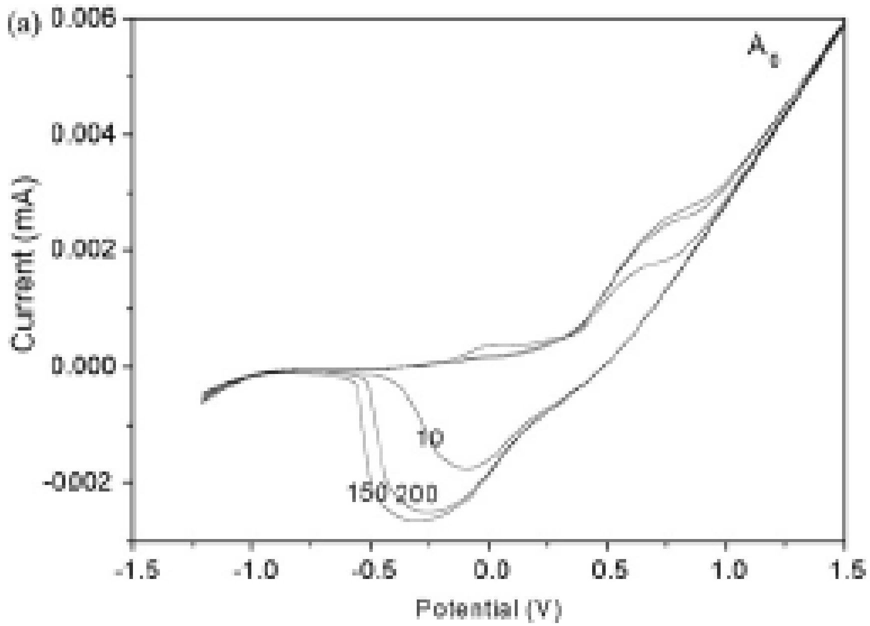


Doping of B_2O_3 decreases the transmittance of bleached state and decreases rapidly the transmittance of colored state.

Addition of Al_2O_3 to B2 film improves its property



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



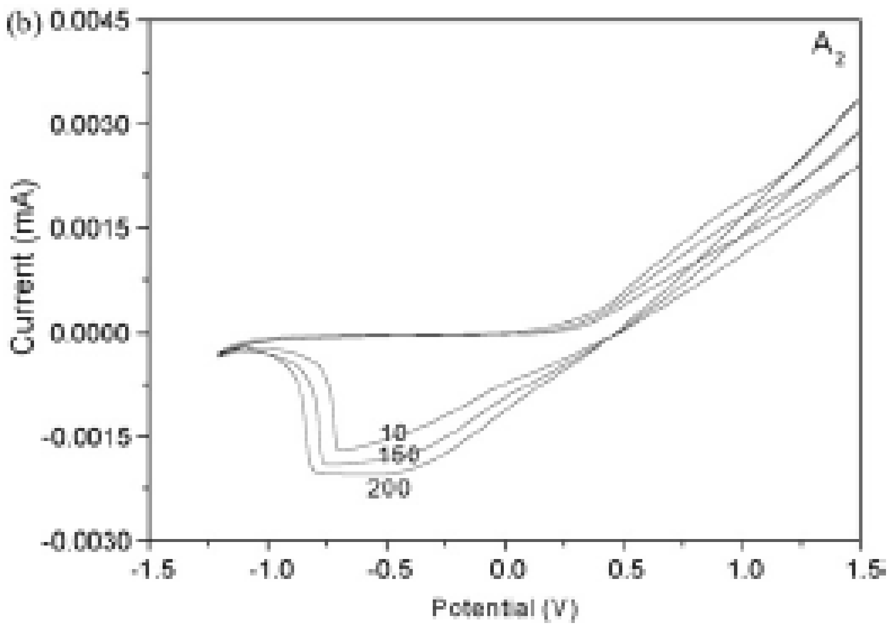


Fig. 3. Cyclic voltammograms of A_0 and A_2 film cycled at 10th, 150th and 200th.

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

Mechanism of electrochromism

According to different electrolyte

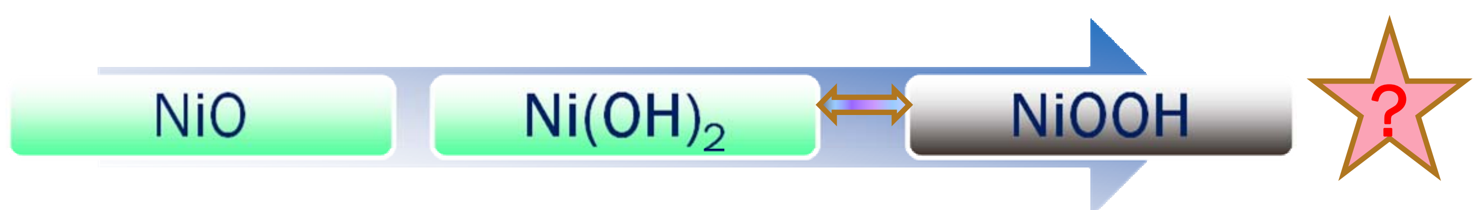
$$+OH^{-} \leftrightarrow NiOOH + e^{-}$$

$$Ni(OH)_2 + OH^{-} \leftrightarrow NiOOH + H_2O + e^{-}$$

$$Ni(OH)_2 \leftrightarrow NiOOH + H^{+} + e^{-}$$

$$Ni_{1-x}O(as-deposited) + yM^{+} + ye^{-} \leftrightarrow M_yNi_{1-x}O(bleached)$$

$$M_yNi_{1-x}O(bleached) \leftrightarrow M_{y-z}Ni_{1-x}O(colored) + zM^{+} + ze^{-}$$



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 TiO2 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_2-CeO_2
Modified Ag-based low-E films	oxide/Ag/isolating layer/oxide
Hydrophobic, anti-reflection	N-TiO_2； hierarachical TiO_2 and ZnO， porous SiO_2-hybrids
TCO, Low-E	N-TCO、p-TCO（ZnO:Al； SnO_2:Sb； SnO_2:F； ITO）
Self-cleaning films	Isolation layer/TiO_2
Low-E / self-cleaning	TiO_2/TiN/TiO_2； ZnO:Al/TiO_2； SnO_2:Sb/TiO_2； ITO/TiO_2
UV-shielding / IR reflective coating	TiO_2-CeO_2 / SnO_2:Sb， TiO_2-CeO_2 / ZnO:Al
UV shielding / anti-reflective of visible	TiO_2-CeO_2 / porous SiO_2
TCO / anti-reflection	ZnO:Al/porous SiO_2, SnO_2:Sb/porous SiO_2, ITO/porous SiO_2
TCO / anti-reflection by absorption	Oxide / metal(Cr:Ni)/silica； TiN/Si_3O_4/SiO_2
Electrochromic	NiO-based， V_2O_5-based
thermochromic	VO_2-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 TiO_2 films in China found in August, 2002

The magnetron sputter equiped in my lab which can prepare large area thin films sized 1200 x 1000 mm^2. Using this sputter we complete the research for low-cost preparation of amorphous Si thin film solar cells.

Thank you!