Fundamentals of Optoelectronic Materials and Devices

Topic:Chemical vapor deposition (CVD)

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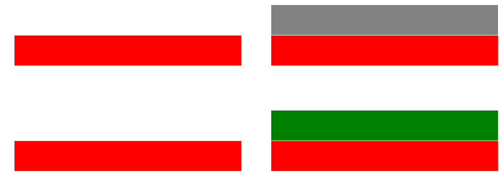
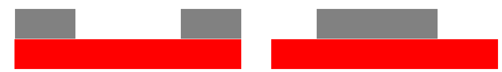
Four wafer-fabrication operations

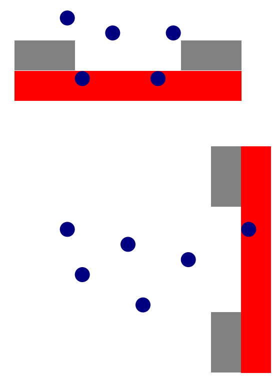
Layering
-Add metal, insulator, semiconductor
 thin layers onto the wafer surface



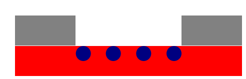
Patterning
-form pattern by removing selected portions
 of added surface layers



Doping
-incorporate dopants into a wafer



Heat treatment
-remove contaminates, repair crystal structure
 of treated wafers



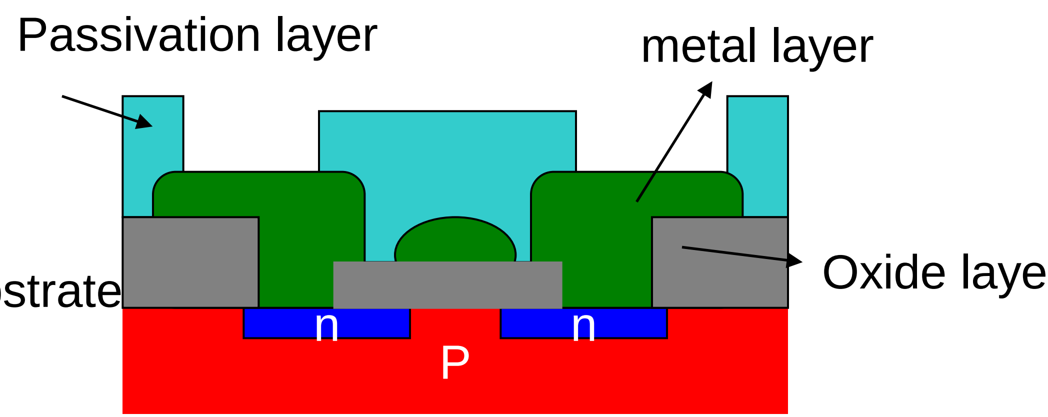
Layering

Tool for layering should be capable to produce layers with

- -high quality
- -uniform thickness
- -great material selection
- -thickness tunable
- -form tight junction with substrate
- -composition tunable

etc….

deposited
layers



Various layering methods were developed to layer a thin film on a wafer

Materials

-Metal, oxide, and semiconductor

Today's lecture references

- Hugh O. Pierson, "Handbook of Chemical Vapor Deposition Principles, Technology and Applications, Noyes Publications
- Hitchman, M.L. and K.F. Jensen, "Chemical Vapor Deposition – principles and applications," ed., Academic Press, San Diego, USA, 1993

Chemical Vapor Deposition (CVD)

- A process can be used to produce thin solid films from gaseous reactants (so-called precursors) via chemical reactions – the most important thin-film deposition process.

- CVD can be extendedly used to produce ultra-fine (nano-sized) particles, fibers, foams, and powders.

- CVD can be used to almost any kinds, any shape, and any size of materials with precise control.

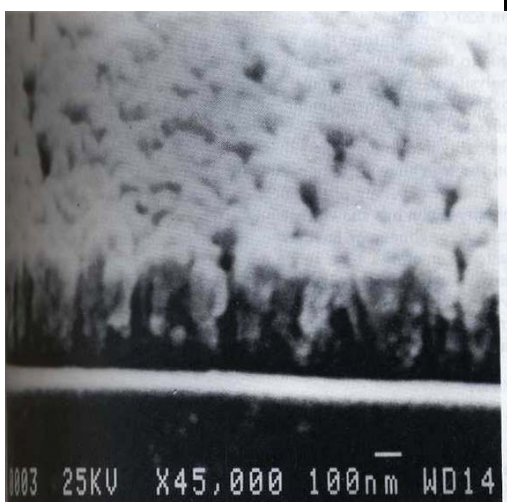
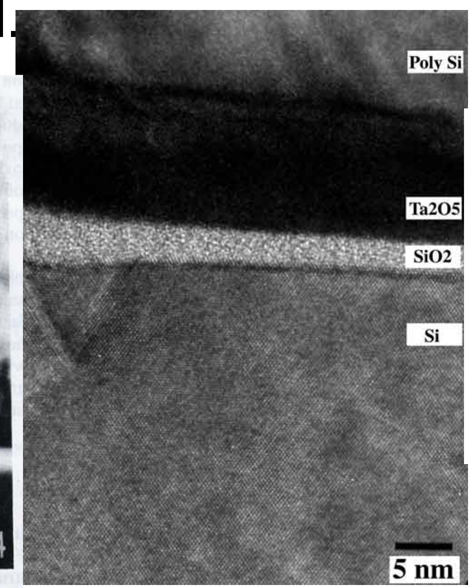
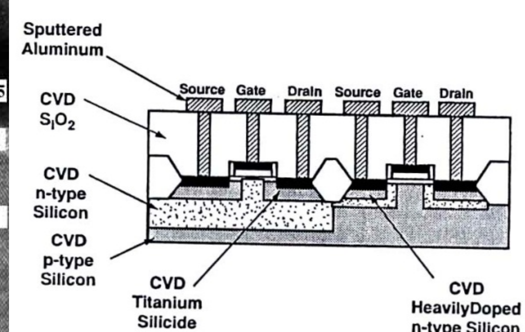
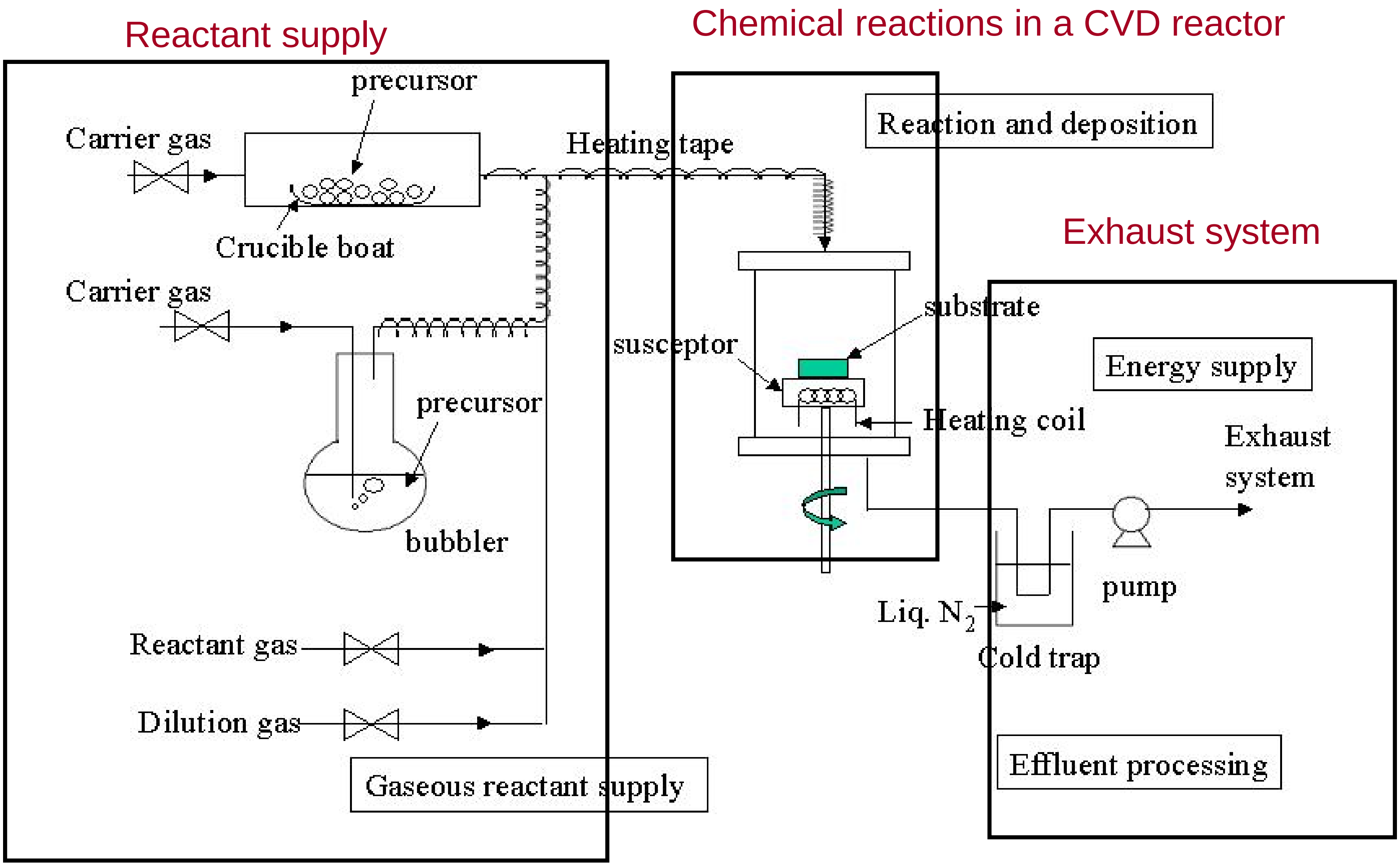


Figure 4.21. Structure of polycrystalline silicon layers (Trainor, 1989).



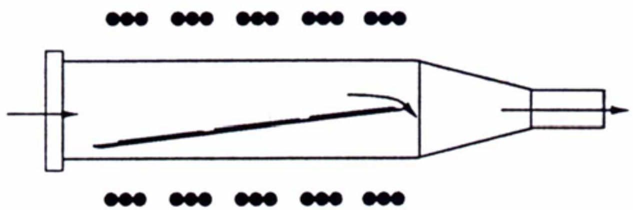


A Typical CVD Apparatus

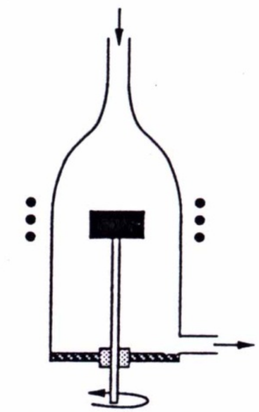


Classification of CVD reactors

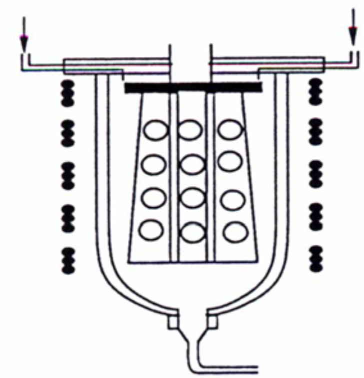
- By reactor configuration:



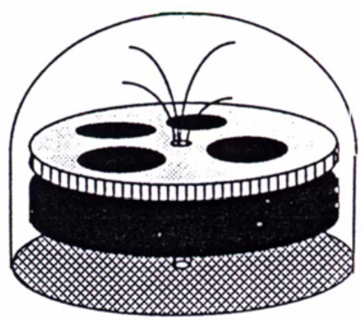
Horizontal CVD Reactor



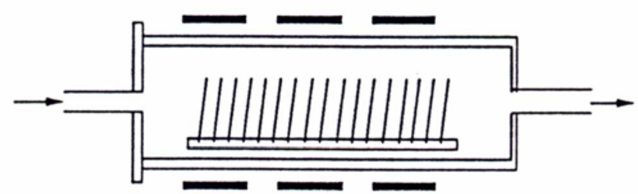
Vertical CVD Reactor



Barrel CVD Reactor



Pancake CVD Reactor

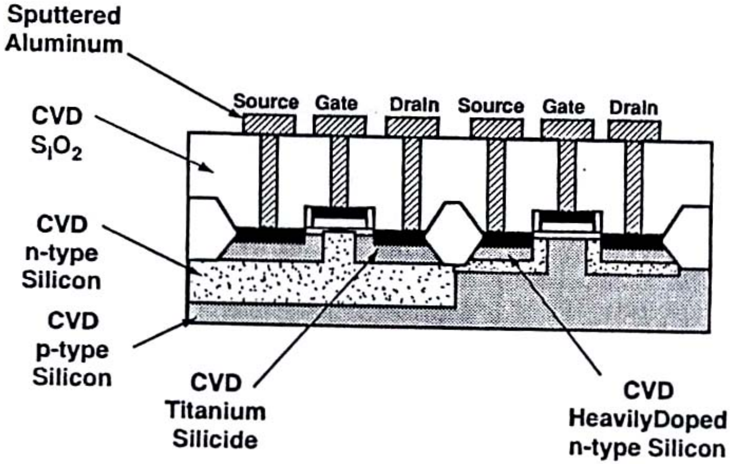


Multiple-Wafer-in-Tube LPCVD Reactor

Hitchman, p. 34

CVD applications in chip fabrication

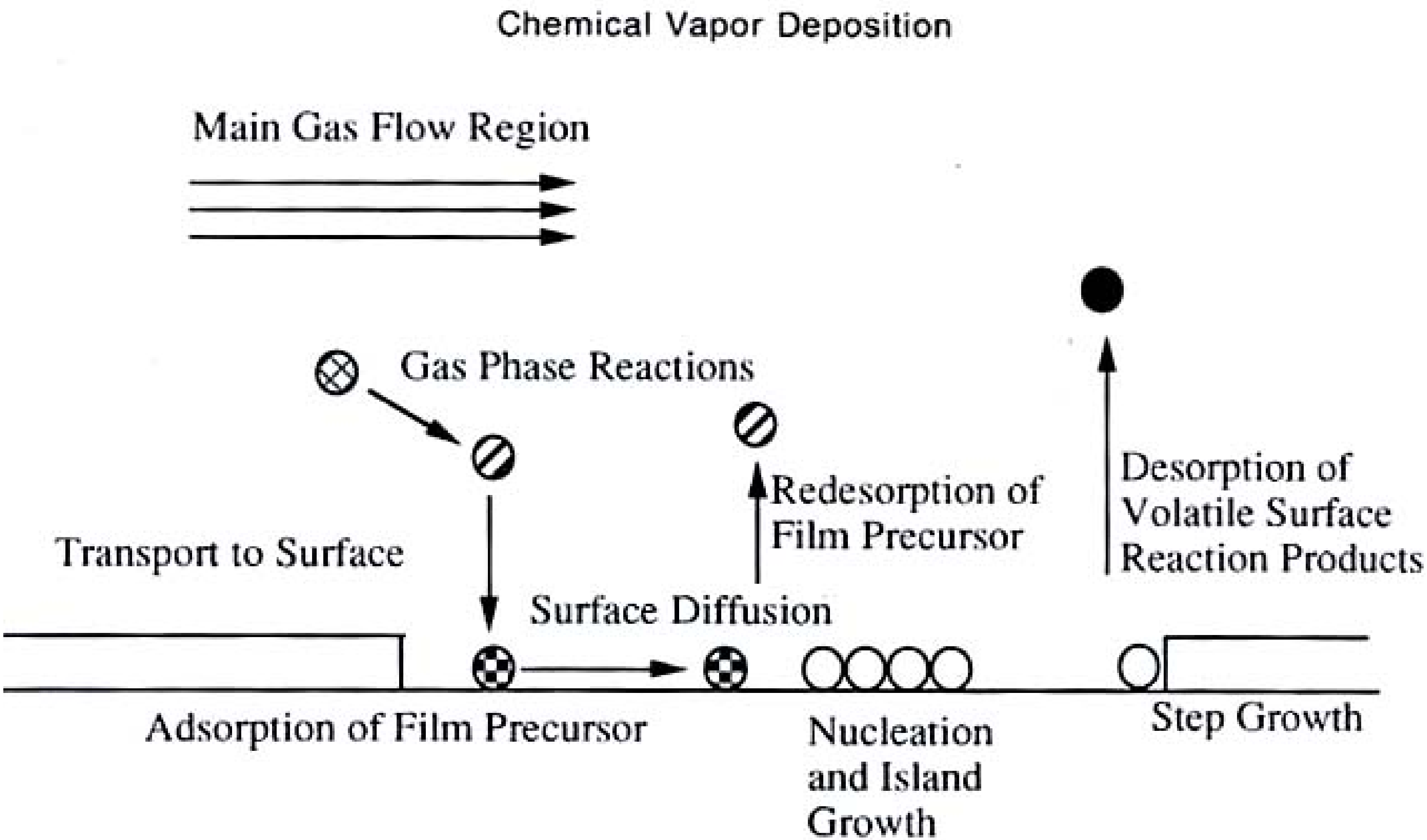
Electrical insulator
Silicon dioxide (SiO2)
-Insulator, diffusion mask, ion-implantation mask, passivation against abrasion, schatches and the penetration of impurities and moisture
Silicon nitride
-Hard, scratch-resistant, excellent diffusion barrier for sodium and water to avoid corrosion



Semiconductors
Silicon, III-V and II-VI semiconductors

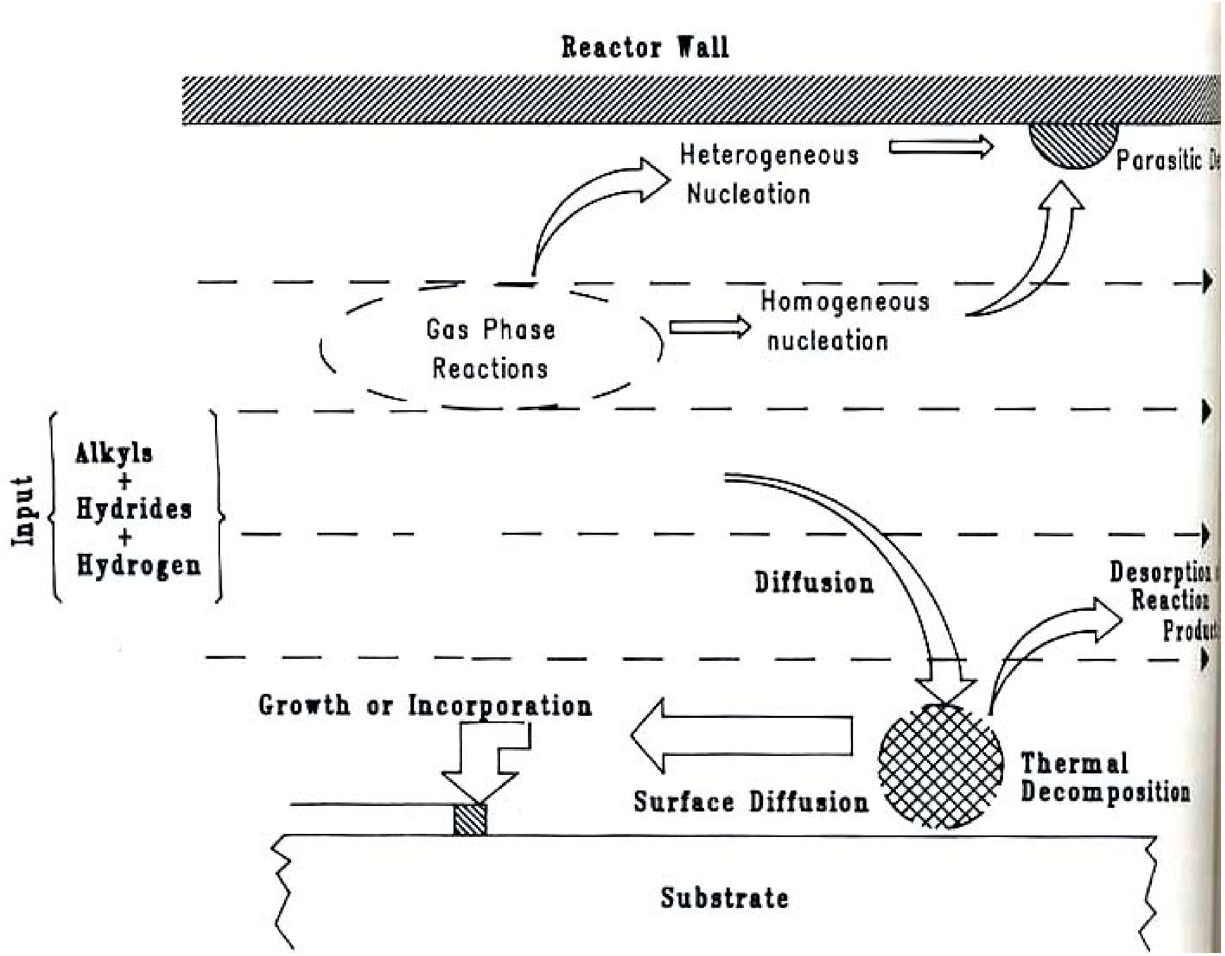
Electrical conductor for interconnection
MoSi2, TiSi2, WSi2, TaSi2, and CoSi2
-Low resistivity, thermal stability, diffusion barrier, mitigation of the electromigration

Scheme of CVD transport and reaction processes



Hitchman p.32

Film growth from chemical reactions in a CVD



Hitchman p 256

Chemistry of CVD

Reactions can occur in either gas-phase and surface, leading to the formation of film precursors and byproducts

Types of reactions

-Pyrolysis, reduction, oxidation, hydrolysis, nitridation, carbidization, diproportionation

Reaction decomposition mechanism

- Gas-phase chemistry
- Surface chemistry

CVD precursors

general characteristics preferred:

1. stability at room temperature – not to react before being transported to reaction zone, easy storage and transfer
2. sufficient volatility at low temperatures – convenient for transportation to reaction zone
3. capability of being produced in a high degree of purity – to avoid introducing contaminants
4. ability to react without producing unwanted side products – to avoid low volatility, toxic side products
5. cost effective enough

Common CVD precursors

halides:

{F, Cl, Br, I} + more electropositive elements ➔

{$AlBr_3$, $AlCl_3$, BCl_3, BF_3, CCl_4, CF_4, $CrCl_2$, $SiCl_4$, $TiCl_4$, WF_6, $ZrBr_4$, $ZrCl_4$…}

metal-organics: (reactive, volatile, moisture sensitive, low decomposition temperatures, not restricted to metals)

M {in IIa, IIb, IIIa, IVa, Va, VIa} + one or more carbon (oxygen) atoms of an organic hydrocarbon groups (alkyls: $-CH_3$, $-C_2H_5$, …; aryls: $-C_6H_5$, …; acetylacetonates: $-OC_5H_8O-$, …) ➔

$(CH_3)_3Al$, $(C_2H_5)_2B$, $(CH_3)_2Cd$, $(C_6H_5)_2Be$, $Ca(C_5H_8O_2)_2$ …

metal carbonyls:

-(CO)- + transition metals with partially filled d-shell ➔

3d : Sc, Ti, V, Cr, Mn, Fe, Co, Ni
4d : Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag
5d : Hf, Ta, W, Re, Os, Ir, Pt, Au

mononuclear, $M(CO)_x$: $Cr(CO)_6$, $Fe(CO)_5$, $Ni(CO)_4$, $W(CO)_6$
dinuclear, $M_2(CO)_x$: $Mn_2(CO)_{12}$, $Fe_2(CO)_9$, $Co_2(CO)_8$
polynuclear : $Fe_3(CO)_{12}$, $Co_4(CO)_{12}$
metal carbonyl complexes: Mn(CO)Cl, $CoNO(CO)_3$

hydrides:

H_2 + {IIIa,IVa,Va,VIa} → AsH_3, B_2H_6, SiH_4, NH_3, …

Chemistry of CVD, often involved reactions

Pyrolysis (thermal decomposition):

hydrocarbon : $CH_4(g) \rightarrow C(s) + 2\,H_2(g)$

hydride : $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

carbonyl : $Ni(CO)_4(g) \rightarrow Ni(s) + 4\,CO(g)$

metal-organics : $CH_3SiCl_3(g) \rightarrow SiC(s) + 3\,HCl(g)$

halide : $WF_6(g) \rightarrow W(s) + 3\,F_2(g)$

Reduction:

hydrogen : $WF_6(g) + 3\,H_2(g) \rightarrow W(s) + 6\,HF(g)$

hydride : $(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3\,CH_4(g)$

metal : $TiI_4(g) + 2\,Zn(s) \rightarrow Ti(s) + 2\,ZnI_2(g)$

Oxidation:

$SiH_4(g) + O_2(g) \rightarrow SiO_2(s) + 2\,H_2(g)$

$SiH_4(g) + 4\,N_2O(g) \rightarrow SiO_2(s) + 4\,N_2(g) + 2\,H_2O(g)$

Hydrolysis:

$SiCl_4(g) + 2\,CO_2(g) + 2\,H_2(g) \rightarrow SiO_2(s) + 4\,HCl(g) + 2\,CO(g)$

$Al_2Cl_6(g) + 3\,H_2O(g) \rightarrow Al_2O_3(s) + 6\,HCl(g)$

Nitridation:

$3\,SiH_4(g) + 4\,NH_3(g) \rightarrow Si_3N_4(s) + 12\,H_2(g)$

$SiH_4(g) + 2\,N_2(g) \rightarrow Si_3N_4(s) + 6\,H_2(g)$

Carbidization:

$TiCl_4(g) + CH_4(g) \rightarrow TiC(s) + 4\,HCl(g)$

$TiCl_4(g) + C(s) + 2\,H_2(g) \rightarrow TiC(s) + 4\,HCl(g)$

Disproportionation:

$2\,GeI_2(g) \rightarrow Ge(s) + GeI_4(g)$

Detailed decomposition mechanism: Silane chemistry

Porolysis of SiH_4 is extremely complex, having 27 reactions, with 120 elementary reactions has been proposed.

Some examples are as follows:

Initial decomposition reaction of SiH_4

$SiH_4 \rightarrow SiH_2 + H_2$ (elimination of H_2)

Homogeneous decomposition

$SiH_2 + H_2 \rightarrow SiH_4$ (reformation of silane)

$SiH_2 + SiH_4 \rightarrow Si_2H_6$ (insert itself into silane)

$SiH_2 + Si_2H_6 \rightarrow Si_3H_8$ (insert itself into disilane)

- Careful temperature and pressure control are critical to lead to expected reactions

Surface reactions: silane decomposition

- $SiH_4 (g) + s \rightarrow H + SiH_3$

  $SiH_3 + s \rightarrow H + SiH_2$

  $2SiH_2 \rightarrow H_2(g) + 2SiH$

  $2SiH \rightarrow H_2(g) + 2s$ + Si film

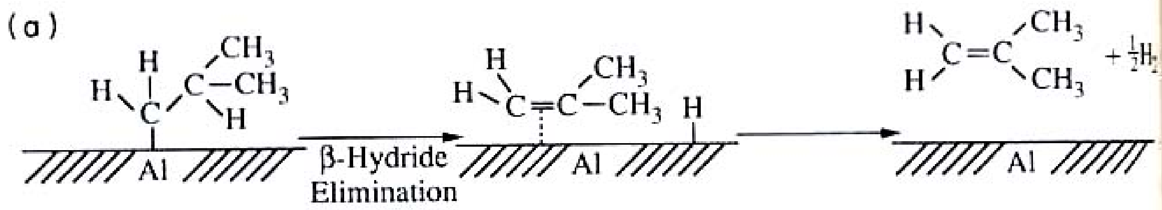
  $2H \rightarrow H_2(g) + 2s$

S: vancant sites and underlining d

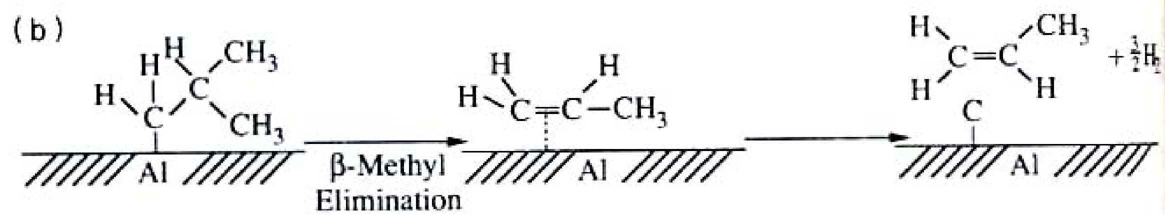
Surface reactions of adsorbed alkyl aluminum compounds

Using triisobutylaluminum as a precursor to deposit aluminum film

175-300C ⟶



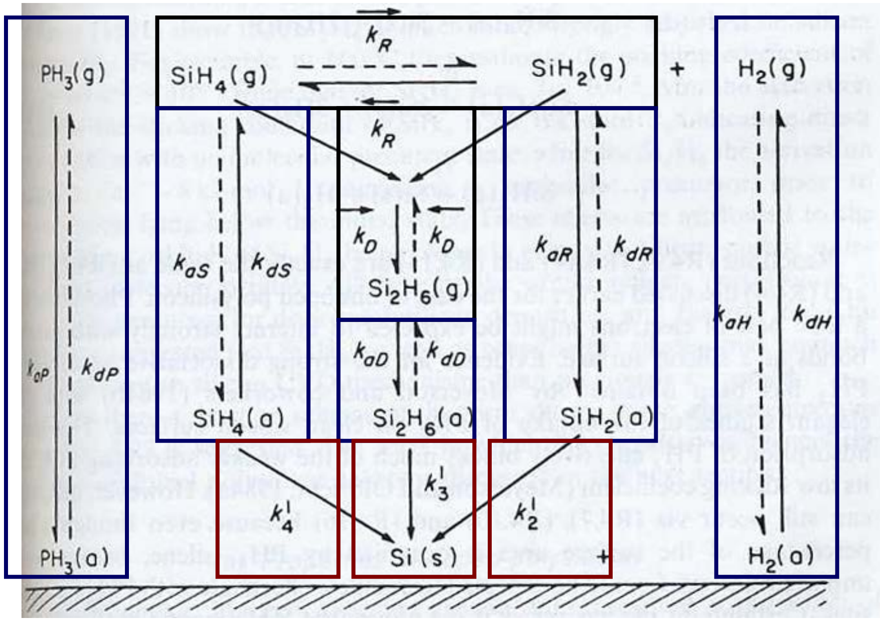
>600C ⟶



-Low temperature (175-300C), high purity Al film was formed because of β-hydride elimination reactions dominate.
-High temperature (>600C), carbon incorporation in aluminum film because of β-Methyl elimination reactions dominate

An example: In-situ phosphorus-doped polycrystalline Si

Precursors: SiH4+PH3/N2   Overall process: SiH4+xPH3/N2 → SiPx + xN2 + (1.5x+2)H2



Growth reactions

k4'

SiH4(a) → Si(s) +2H2(a)

k3'

Si2H6(a) → 2Si(s) + 3H2(a)

k2'

SiH2(a) → Si(s) + H2(a)

Gas-phase reactions:

k_R

SiH4(g) → SiH2(g) + H2 (g)

←

k_R k_D

SiH4(g) + SiH2(g) → Si2H6(g)

←

K_D

Adsorption equilibria

k_{aS}

SiH4(g) → SiH4(a)

←

k_{dS}

k_{aR}

SiH2(g) → SiH2(a)

←

k_{dR}

k_{aD}

Si2H6(g) → Si2H6(a)

←

$k_{aP}k_{dD}$

PH3(g) →PH3(a)

←

$k_{aH}k_{dP}$

H2(g)→H2(a)

←

k_{dH}

Hietchman p 201

Polycrystalline silicon layer

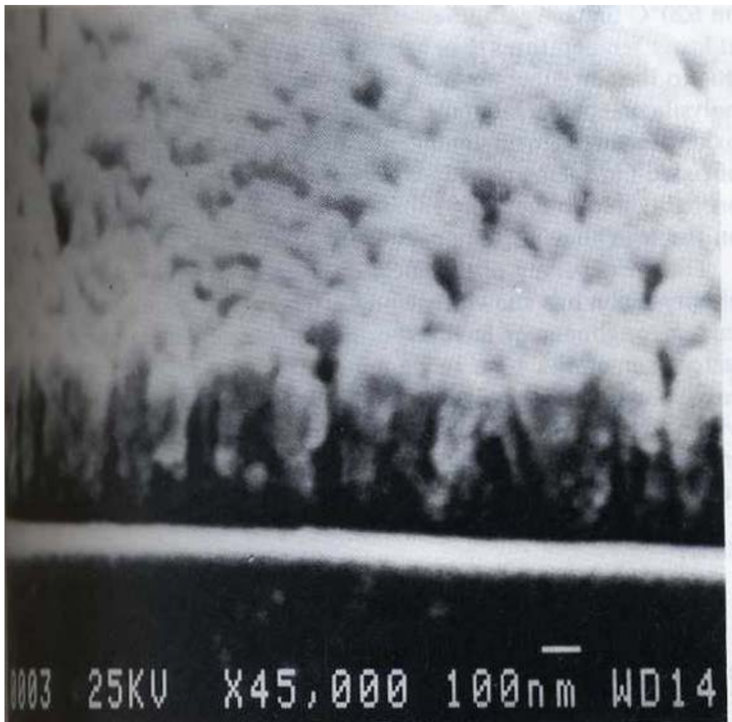
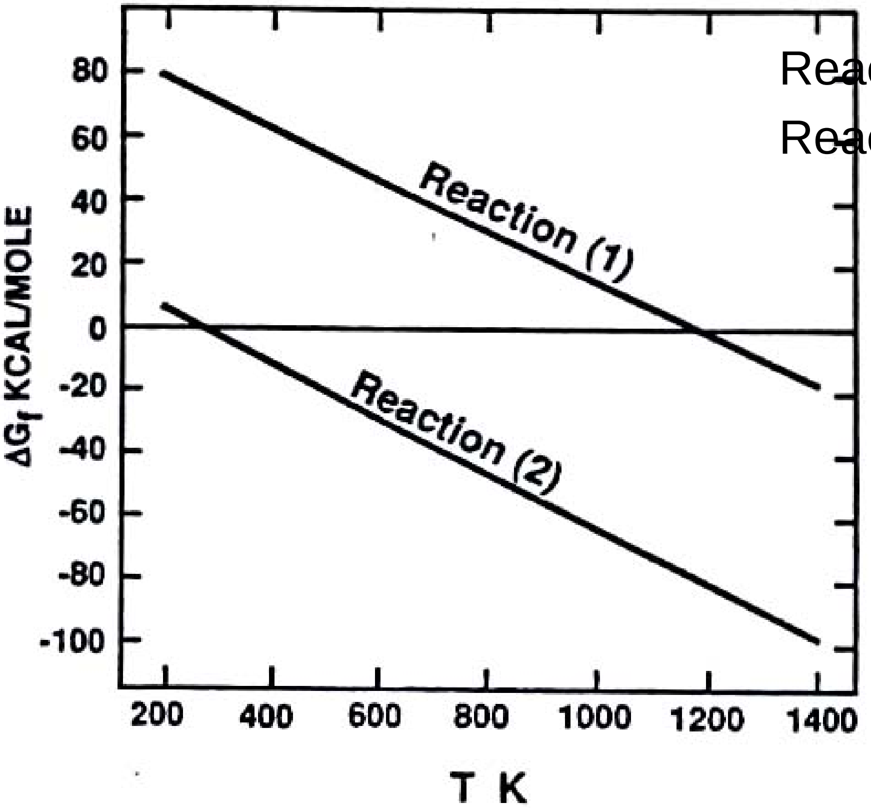


Figure 4.21. Structure of polycrystalline silicon layers (Trainor, 1989).

Thermodynamics of CVD

$\Delta Gr = \Delta Gf + RT \ln Q$

Temperature is raised, ΔGr more negative, and the reaction proceeds.



Reaction 1: $TiCl_4 + 2BCl_3 + 5H_2 \rightarrow TiB_2 + 10\,HCl$

Reaction 2: $TiCl_4 + B_2H_6 \rightarrow TiB_2 + H_2 + 4HCl$

Which reaction is more thermodynamically favoriable?

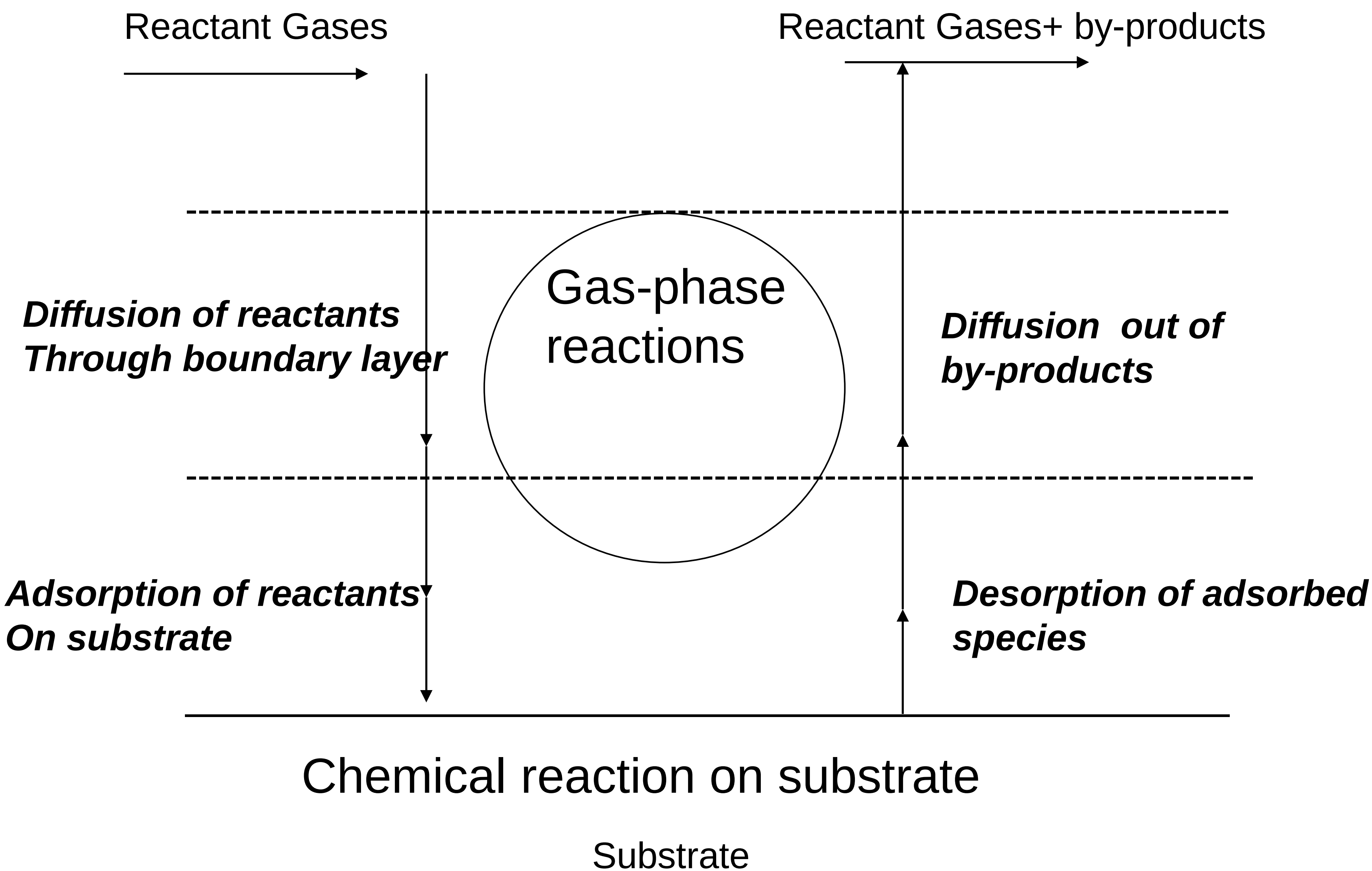
Reaction 2 is more thermodynamically favorable

Pierson P22

Kinetics and Mass transport mechanism

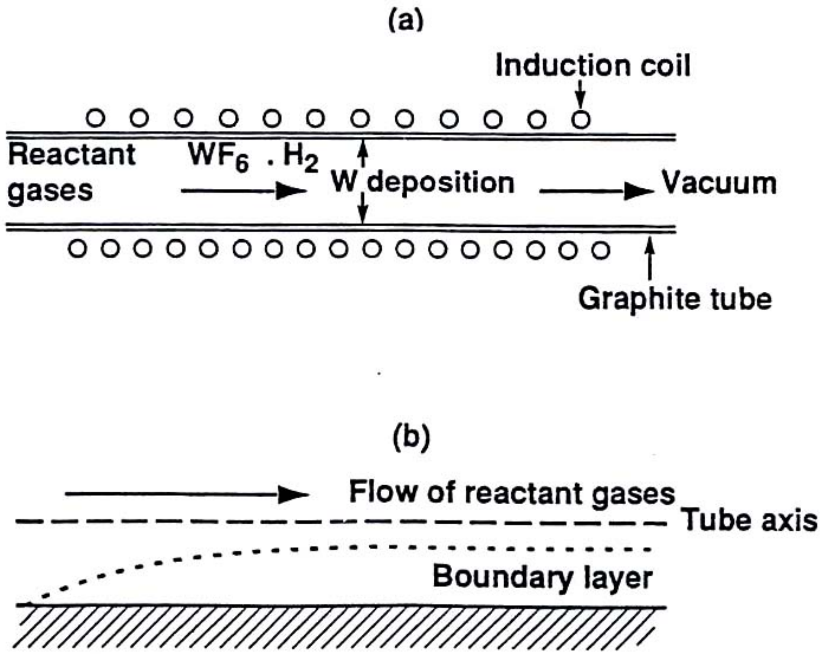
- Deposition sequence
- Boundary layer
- Rate determining steps

Processes contributing to CVD growth



Boundary layer

Reaction: WF6+3H2 →W+6HF



$$D = \sqrt{\frac{x}{R_e}}$$

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

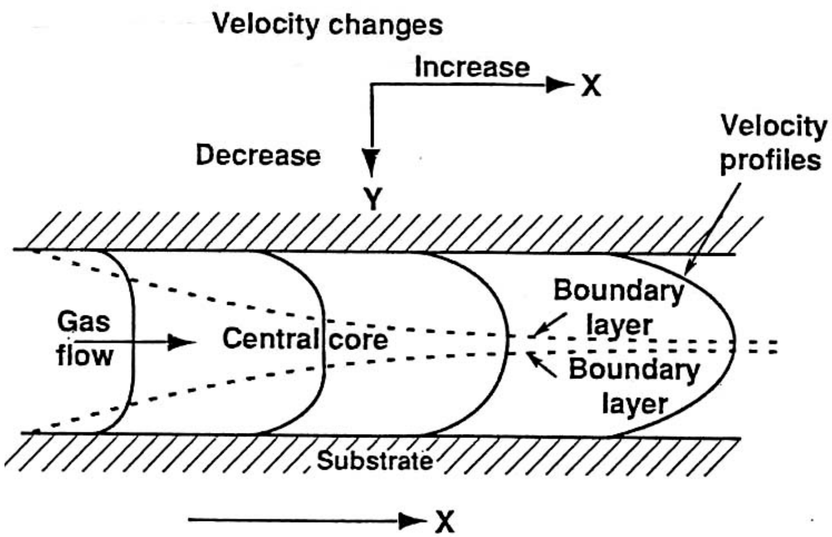
ρ= mass density
u = flow density
x = distance from inlet in flow direction
μ= viscosity

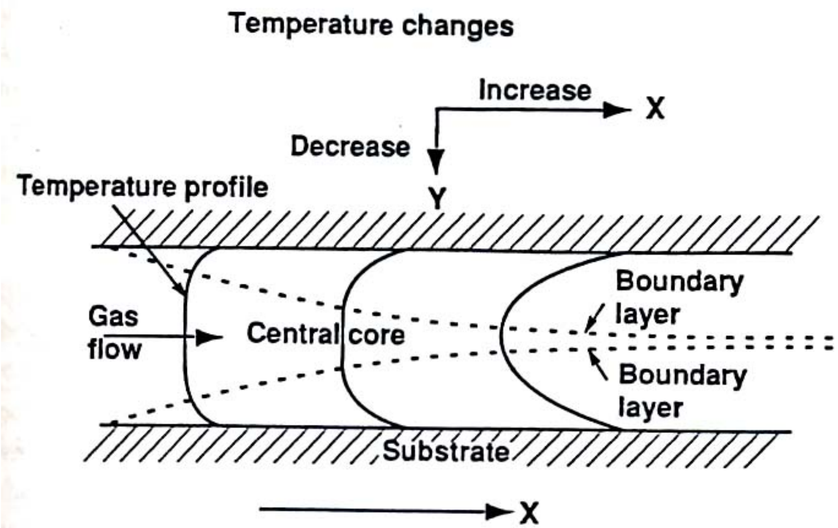
$D \alpha x^{1/2}$ and $u_x^{-1/2}$
$u_x \downarrow \rightarrow D \uparrow$

-Boundary layer: the region in which the flow velocity changes from zero at the wall to the same as the bulk gas speed
-The thickness of the boundary layer increases with lowered gas flow velocity and with farer the distance from the tube inlet

Pierson p28

Velocity and temperature distribution profile





-A steep velocity gradient is noticeable when x is larger

-surface is the hottest

-The shape distribution curve is similar to that of velocity

Reactant Gas is inverse proportional to x

Pierson p30-31

Rate limiting Steps of a CVD reaction

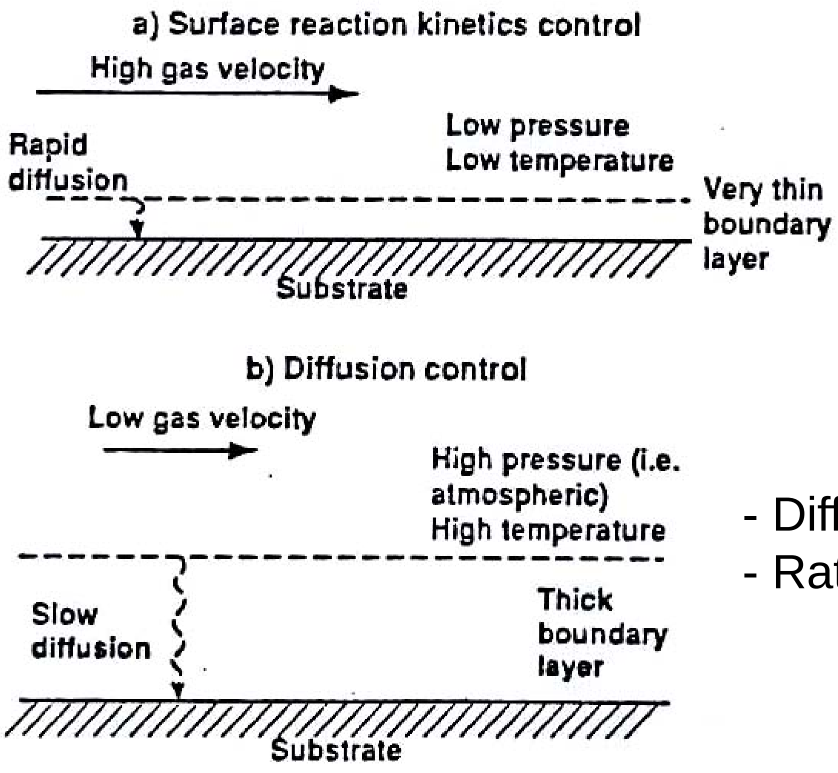


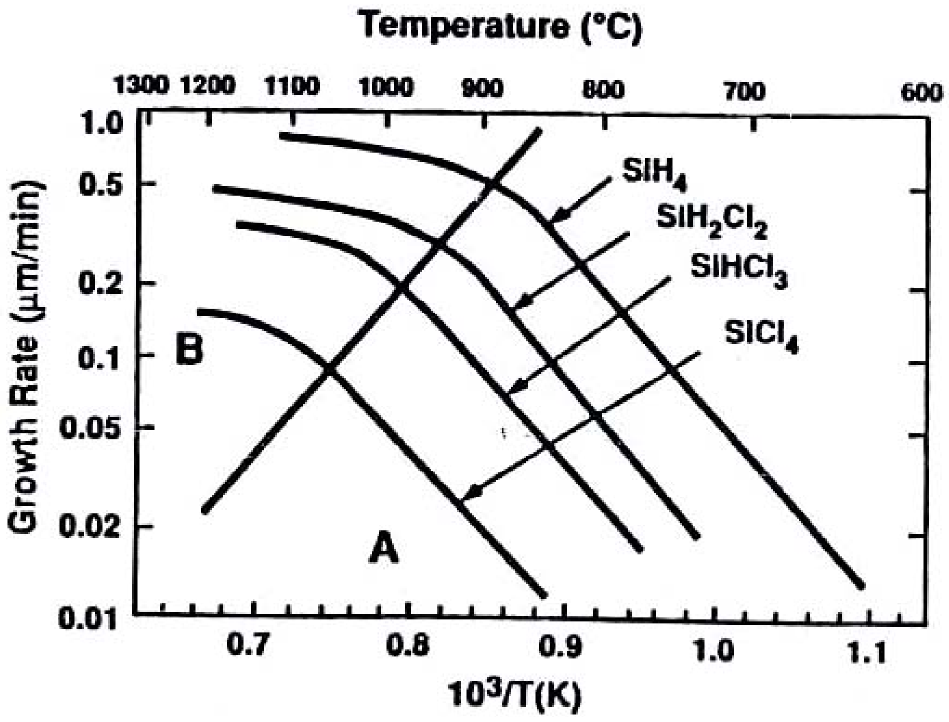
Figure 8. Rate Limiting Steps in a CVD Reaction

- Diffusion is fast due to thin boundary layer
- Rate limiting step is ***surface reaction***

- Diffusion is slow due to thick boundary layer
- Rate limiting step is ***mass transport diffusion***

Pierson p33

T(K) vs growth rate for silicon deposition using various precursors



Area A: lower temperature
*Rate limiting step: (RLS)

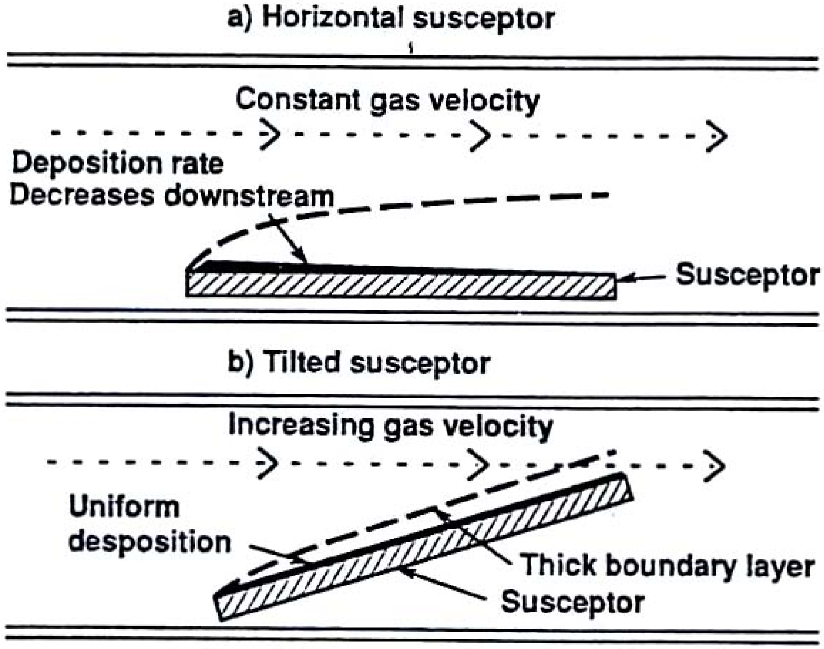
growth rate is low
So, RLS is surface reaction

Area B: higher temperature
*Rate limiting step:

growth rate is high
So, RLS is mass transport diffusion

Pierson p34

Control of deposition uniformity in a tubular reactor



-Deposition rate decreases downstream because of thicker boundary layer along the tube

-Tilted susceptor makes boundary layers thiner because the increase of velocity from constriction of the flow → make the deposition layer more uniform

Pierson p36

Deposition mechanism - Epitaxy

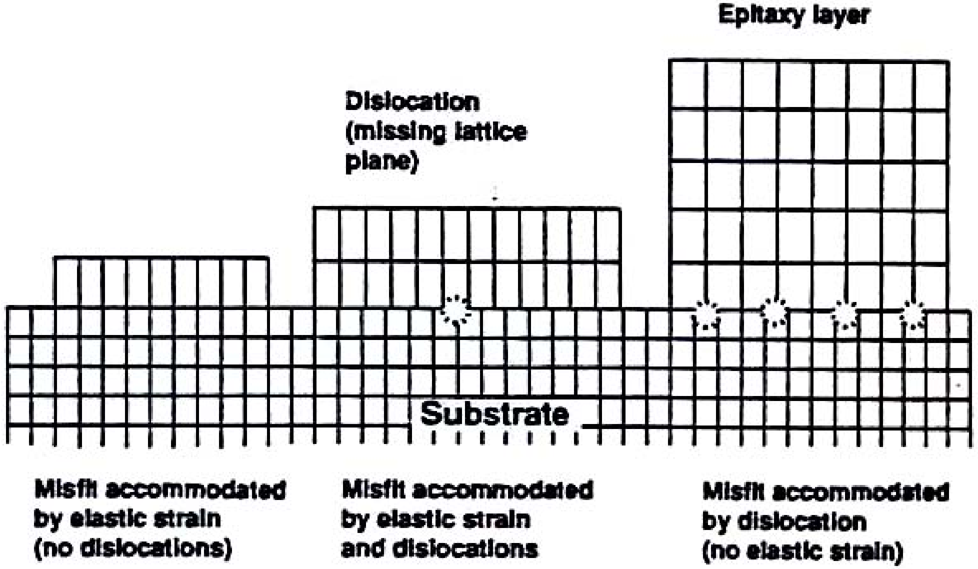
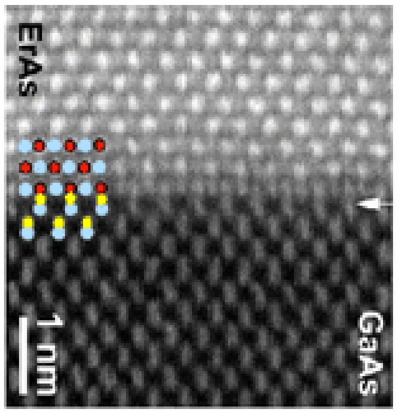


Figure 11. Epitaxy Accommodations of Lattice Mismatch

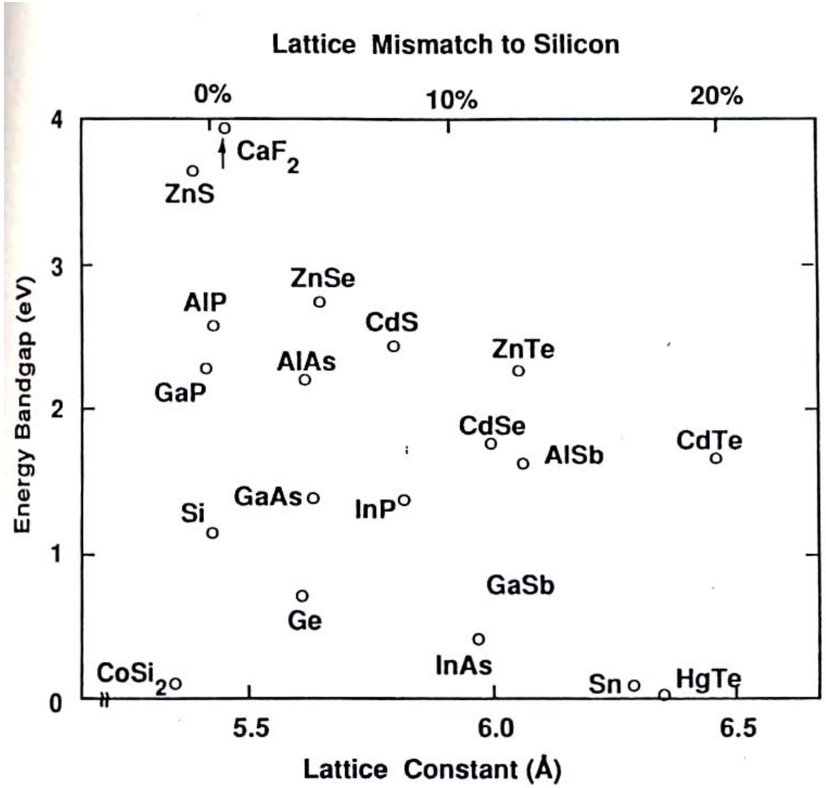
Smooth, pure, defect-free epitaxial ErAs layers on GaAs



Defined as the growth of a crystalline film on a crystalline substrate
-Homoepitaxy – deposited materials are the same as substrate
-Heteroepitaxy - different
-Lattice mismatch of deposited materials with substrate needs to be small

Pierson p 38

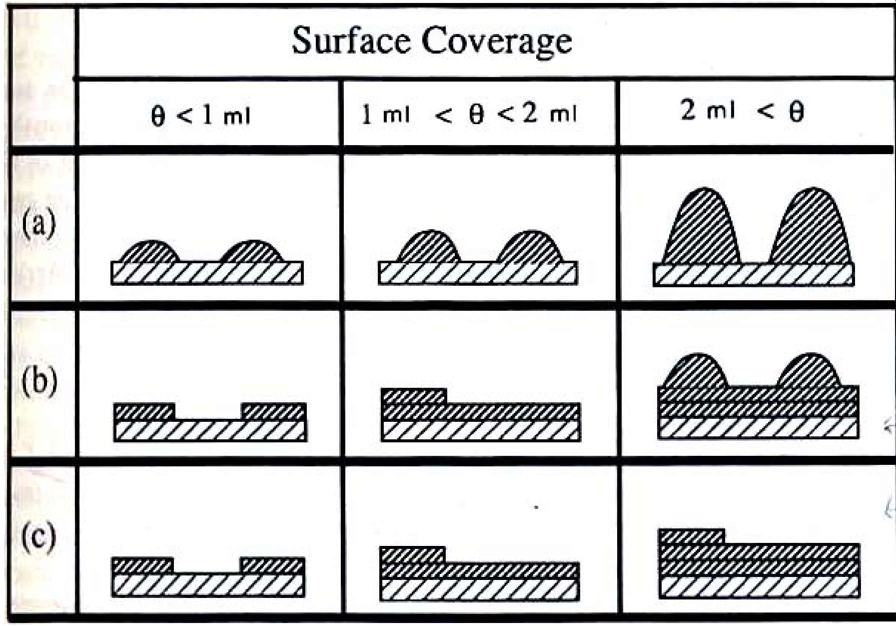
Bandgap and lattice constant of semiconductor



Lattice mismatch larger than 8% is unlikely for deposited materials epitaxially growth on corresponding substrate

Pierson p39

Nucleation and growth modes



Hitchman p37

Three-dimensional island growth-Volmer-Weber growth
film atoms are more strongly bound to each other than to the substrate (Si on SiO2, metals on insulators)
Layer-Plus-island growth-Stranski-Kastanov growth
Combination of two modes
Layer-by-layer-Franck-van der Merwe growth
Film atoms are equally or less strongly bonded to each other than to the substrate (silicon on silicon, homoepitaxy

CVD Processes and Equipment

- Reactant supply
- Reactor types:

-thermal CVD: hot and cold wall reactors

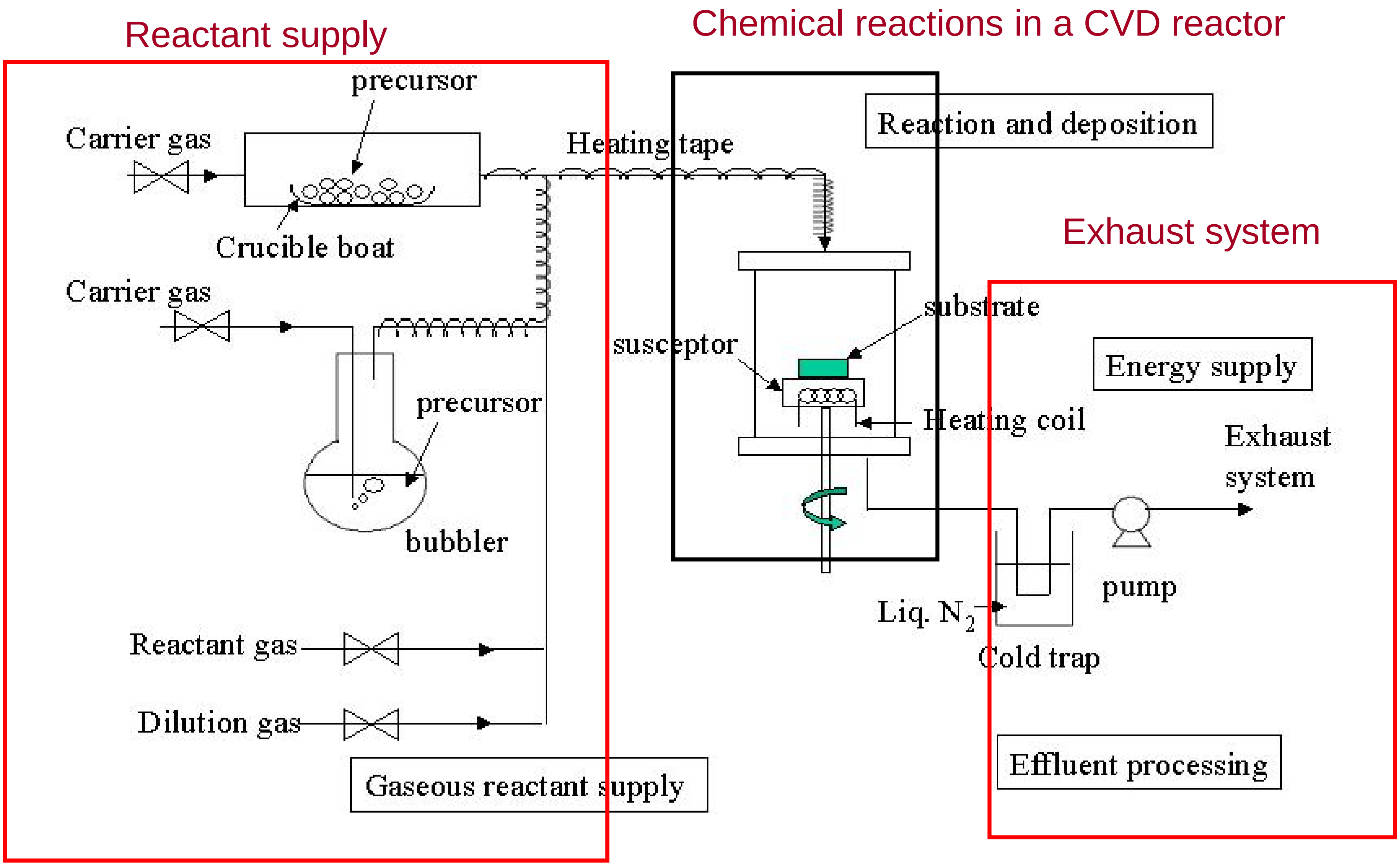
-plasma CVD

-MOCVD

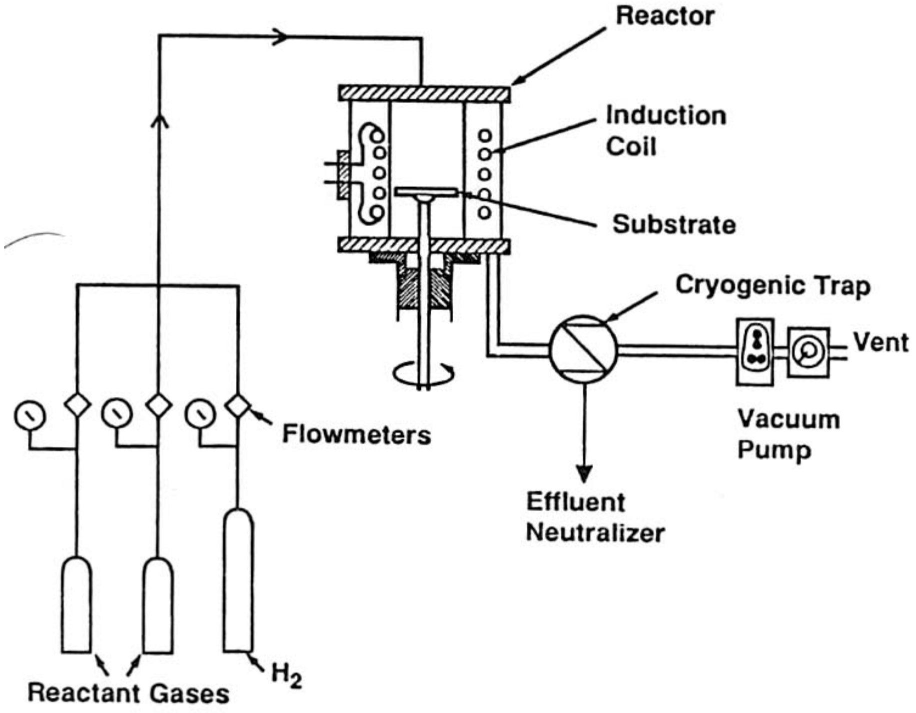
-laser CVD

- Exhaust and by-product disposal

A Typical CVD Apparatus



Reactant supply – gas precursor transport



A gas precursor tank

- Flowmeters to control the transport rate
- Carrier gas like H2 or N2 or O2 is often used

Pierson p84

Reactant supply – liquid and solid precursor transport

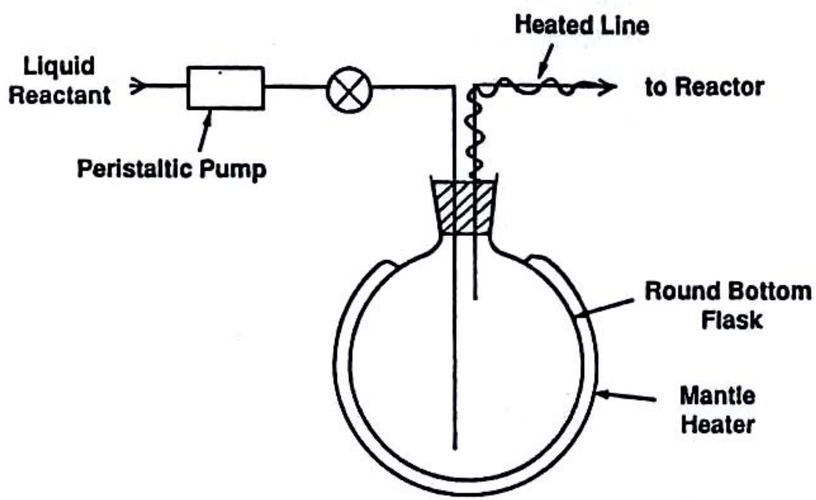
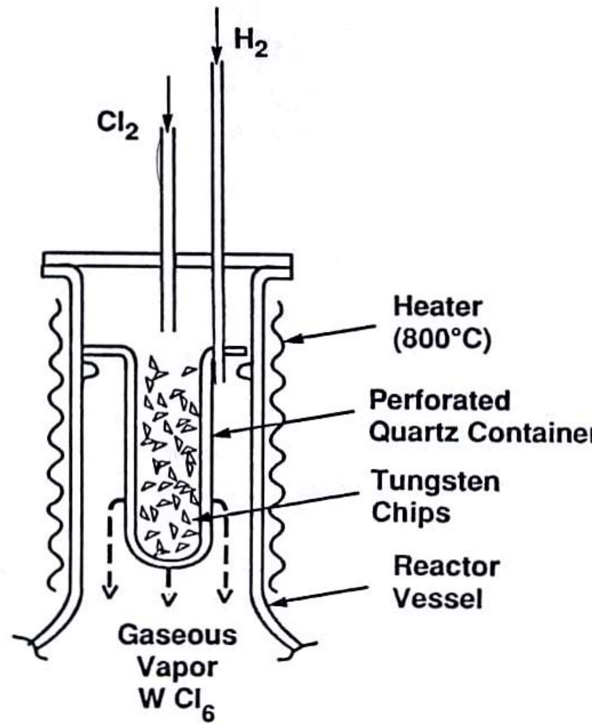


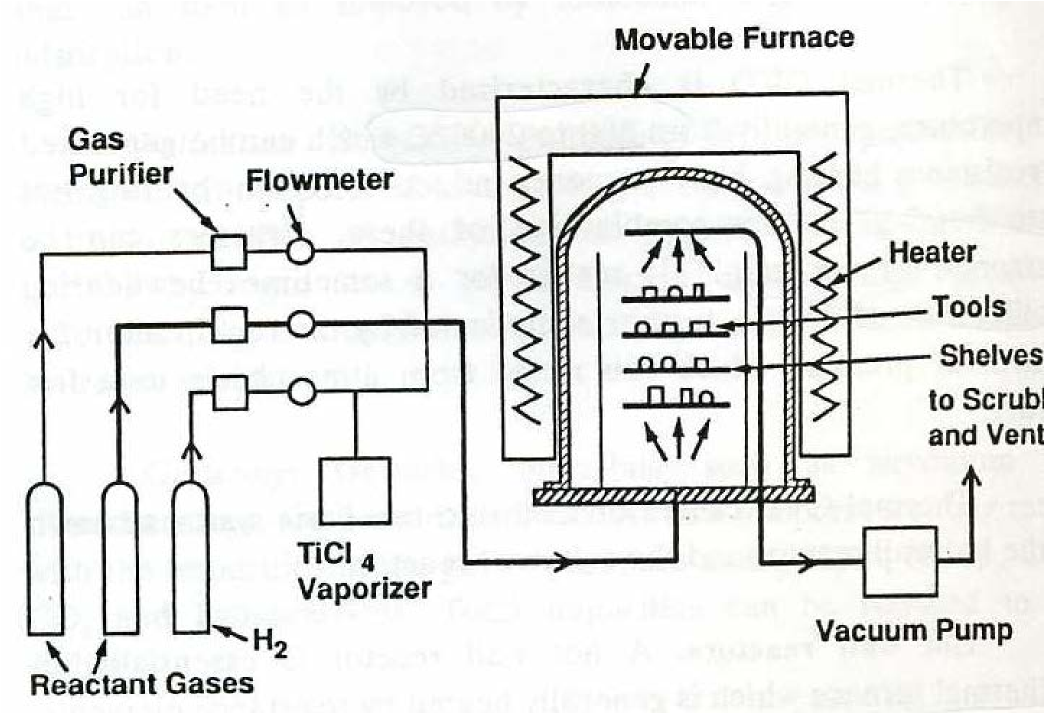
Figure 3. Vaporizer for Liquid Reactant



W(s) + 3 Cl2(g) → WCl6(g) 800 oC
deposition step:
WCl6(g) + 3 H2(g) → W(s) + 6 HCl(g) at 800-1200 oC

Pierson p85-86

Thermal CVD- hot wall reactor

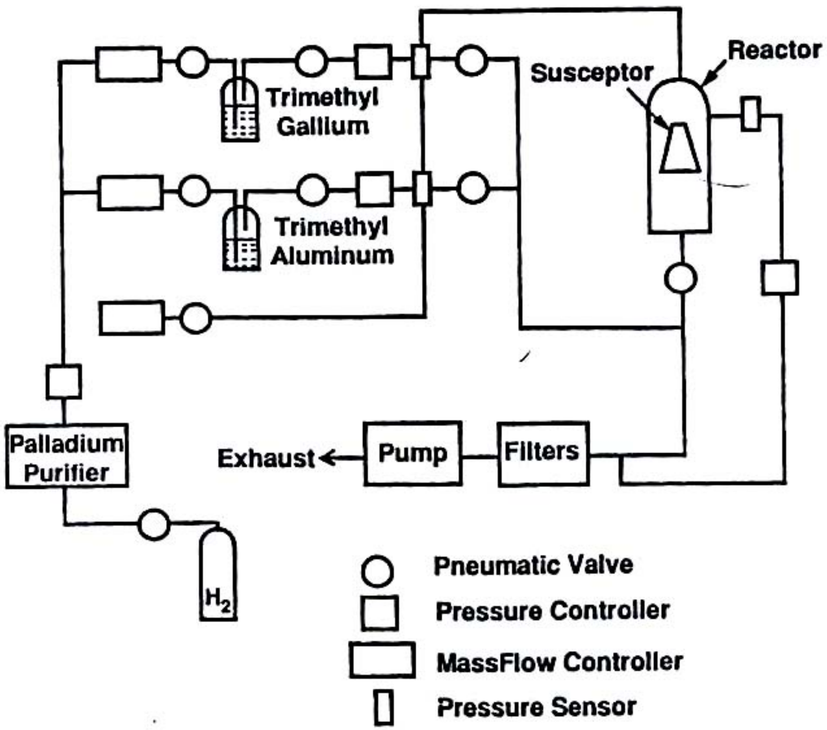


- Isothermal furnace
- Great temperature control
- Deposition occurs everywhere (clean is inconvenient)

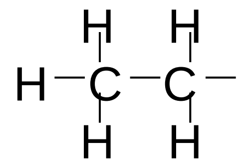
Pierson p90

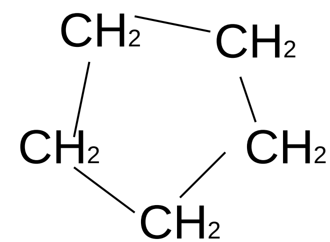
Metallo-Organic CVD (MOCVD)

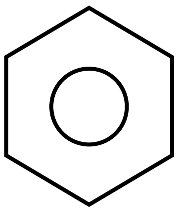
A MOCVD system



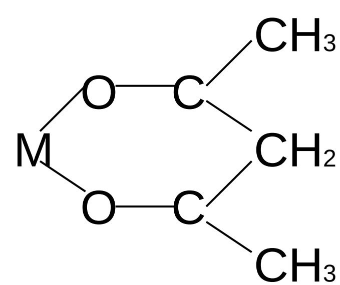
Alkyls or aryls substitute:





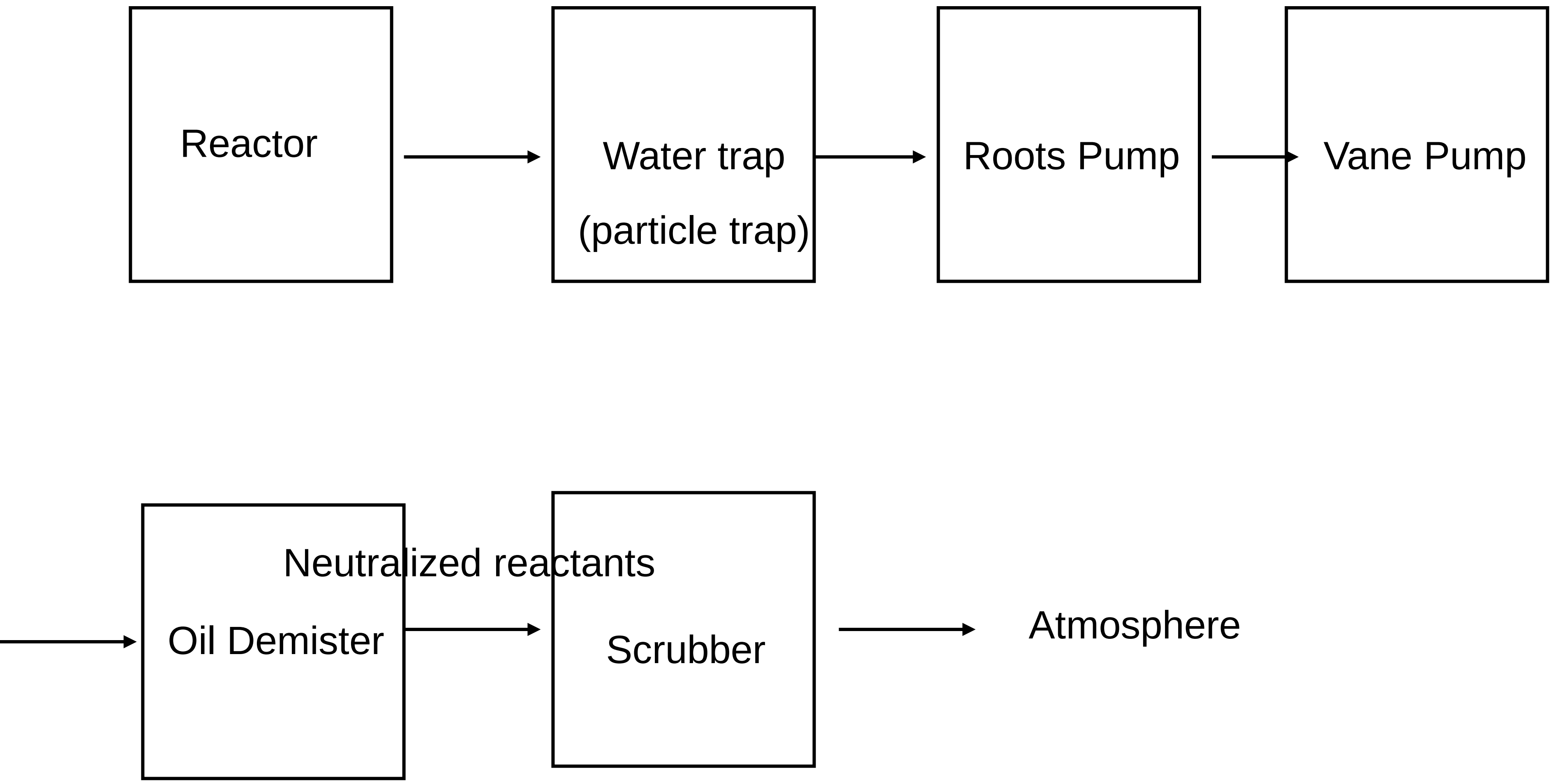


Acetylacetonates (乙酰丙酮基)



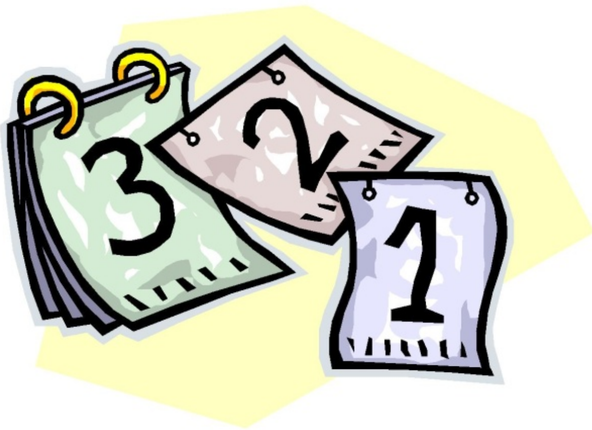
- A CVD system utilizes metallo-organic compounds as precursors.

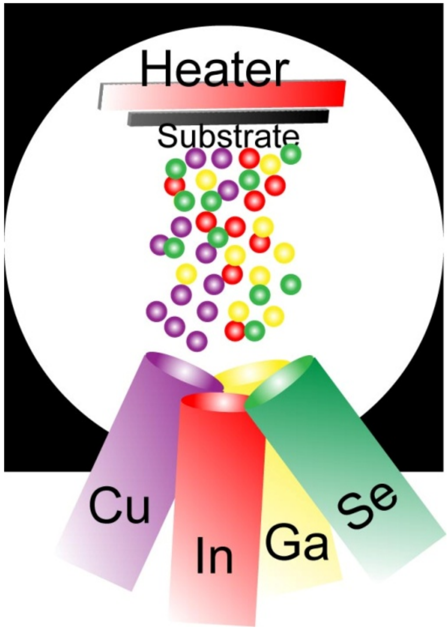
Exhaust system



CVD precursors: toxic, lethal, and pyrophoric

Vacuum-based film deposition





TIME-CONSUMING

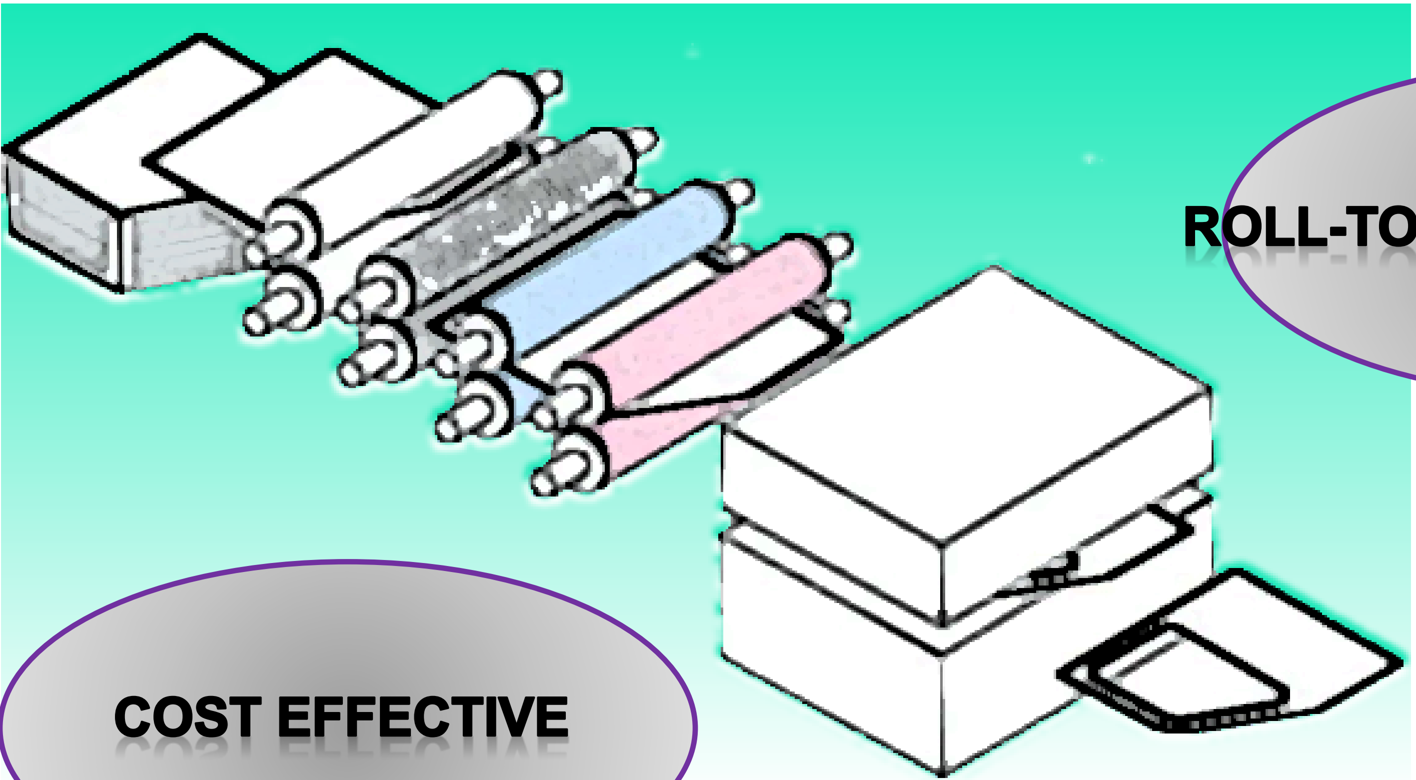
LOW THROUGHPUT

EXPENSIVE

DIFFICULT TO CONTROL STOICHIOMETRY OVER LARGE AREAS

POOR MATERIALS UTILIZATION (30-50%)

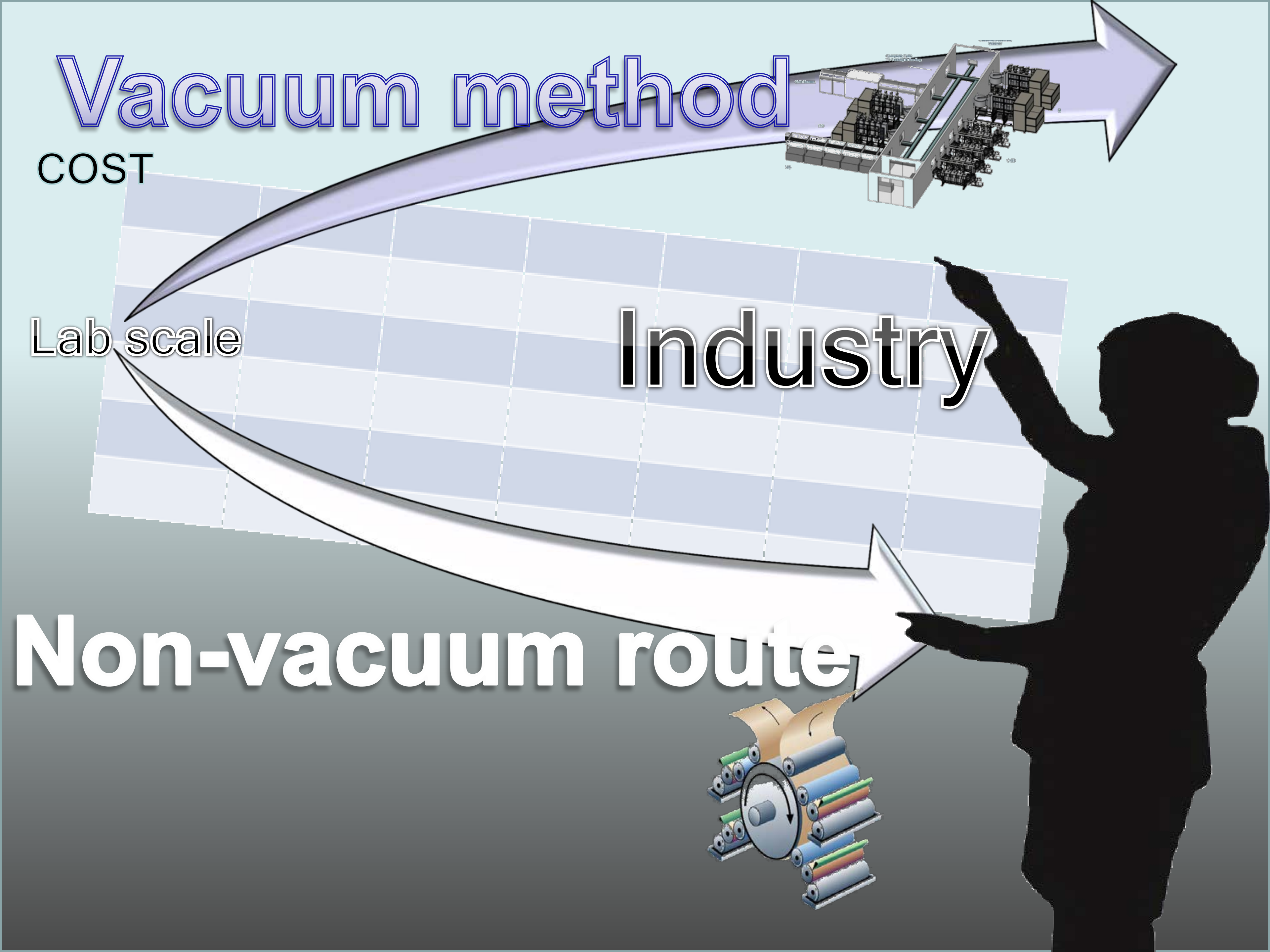
Non-Vacuum Processing



ROLL-TO-ROLL PROCESSIN

COST EFFECTIVE

STOICHIOMETRY CONTROLLABLE


Vacuum method
COST
Lab scale
Industry
Non-vacuum route

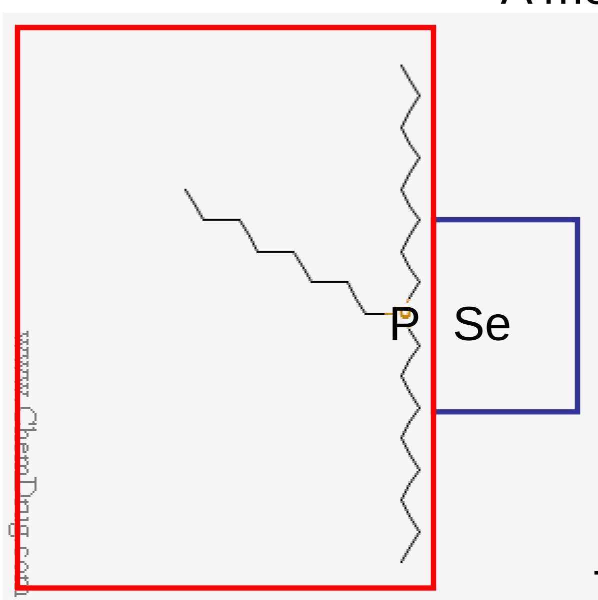
Bottom-up material synthesis

Organic metallic compound

metal source $Cd(CH3)_2$ leaving group$(CH3)_2$

, high reactive (short length)

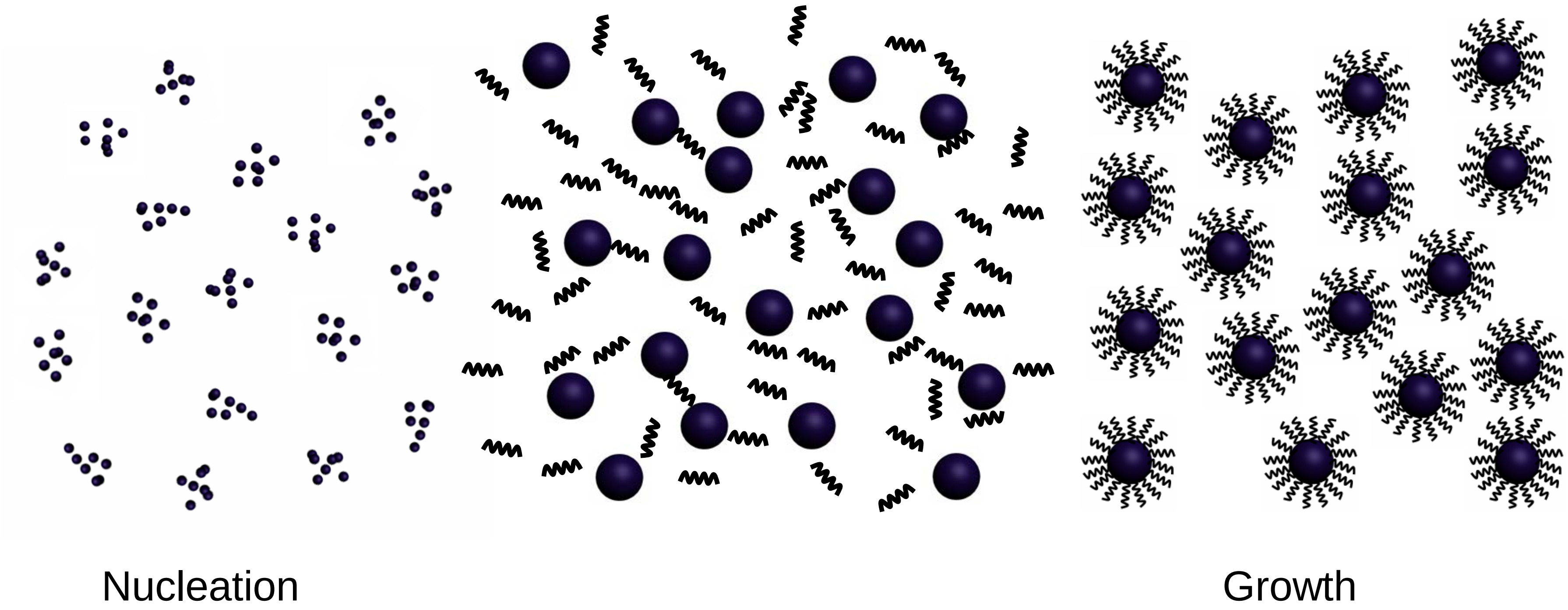
TOP-Se A metal-fat acid complex

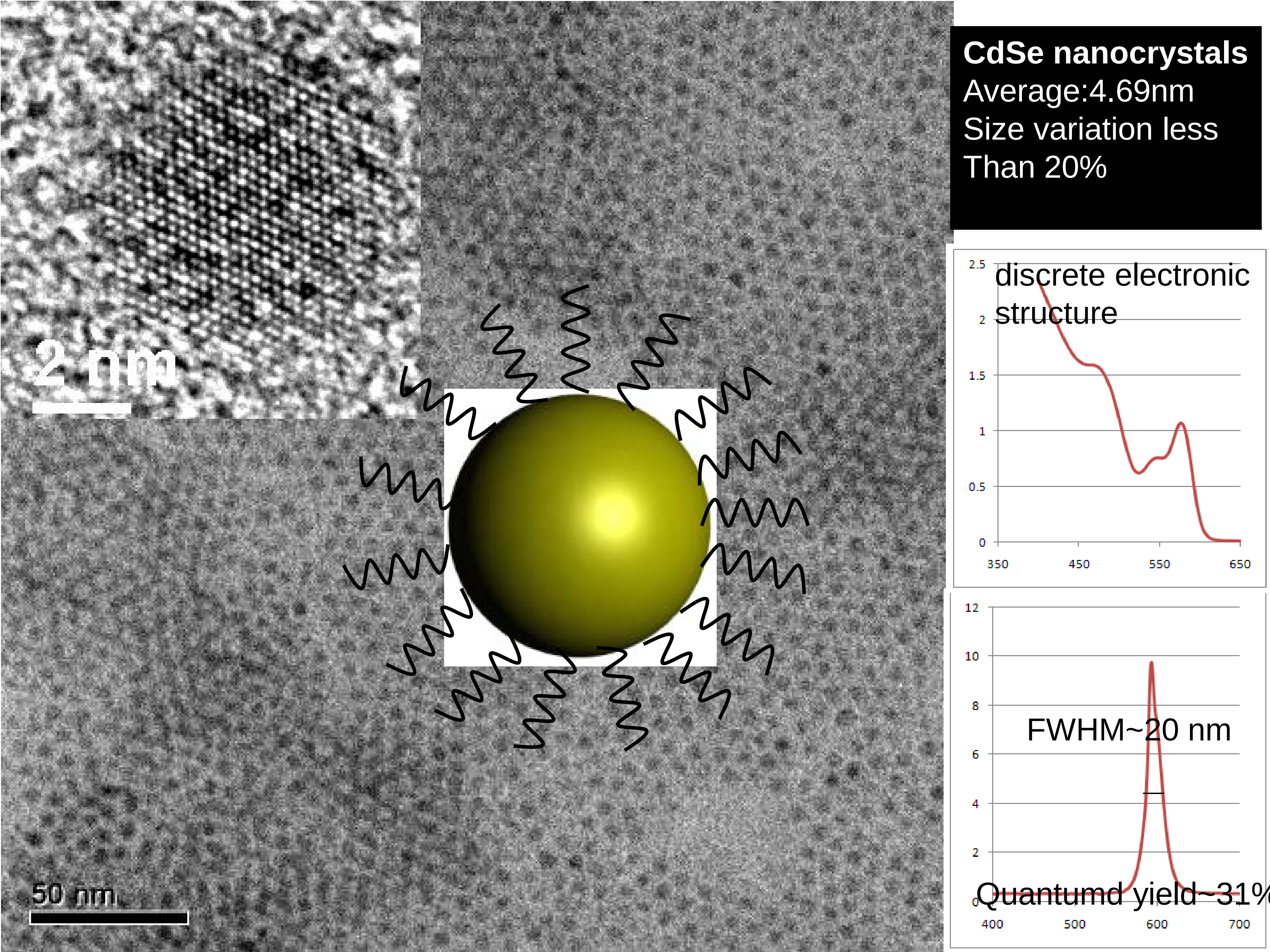


CdSe

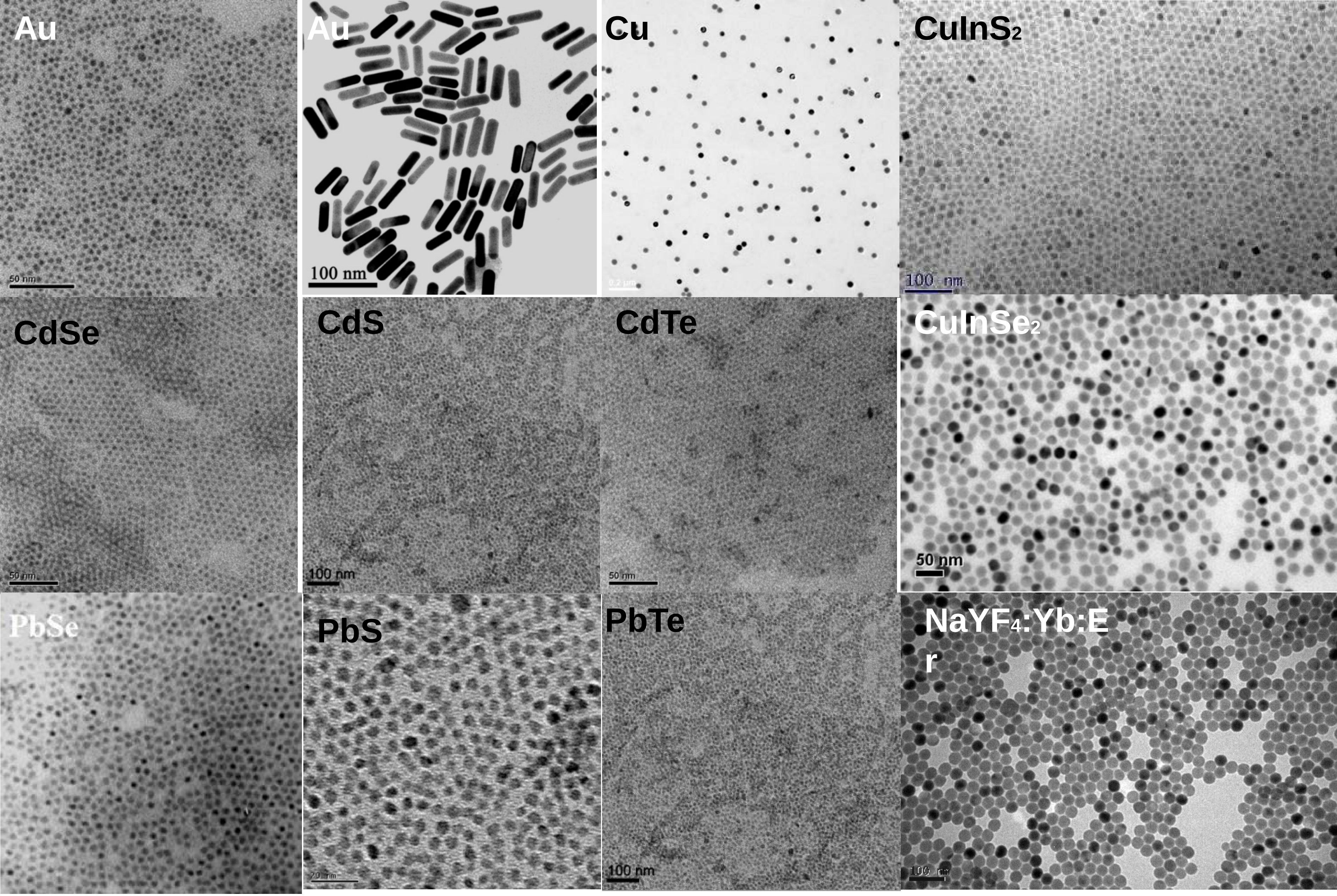
Theoretically, we can make any materials by this approach

Bottom-up material synthesis





CdSe nanocrystals
Average:4.69nm
Size variation less
Than 20%
2 nm
50 nm
discrete electronic
structure
2.5
2
1.5
1
0.5
0
350
450
550
650
12
10
8
6
4
2
0
400
500
600
700
FWHM~20 nm
Quantumd yield~31%



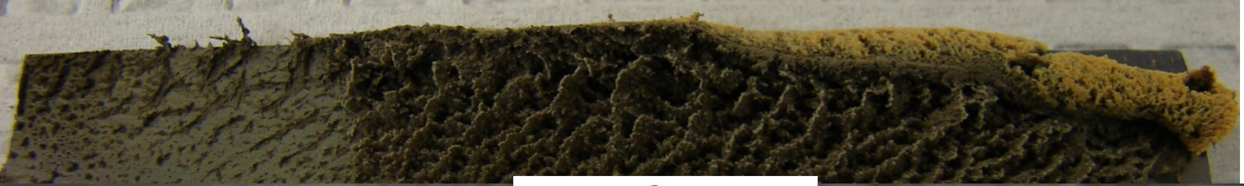
A wide range of nanomaterials you can make for energy applications!

Semiconductor nanocrystals: Cd chalcogenide ; Pb chalcogenide ; Cu-In- chalcogenide

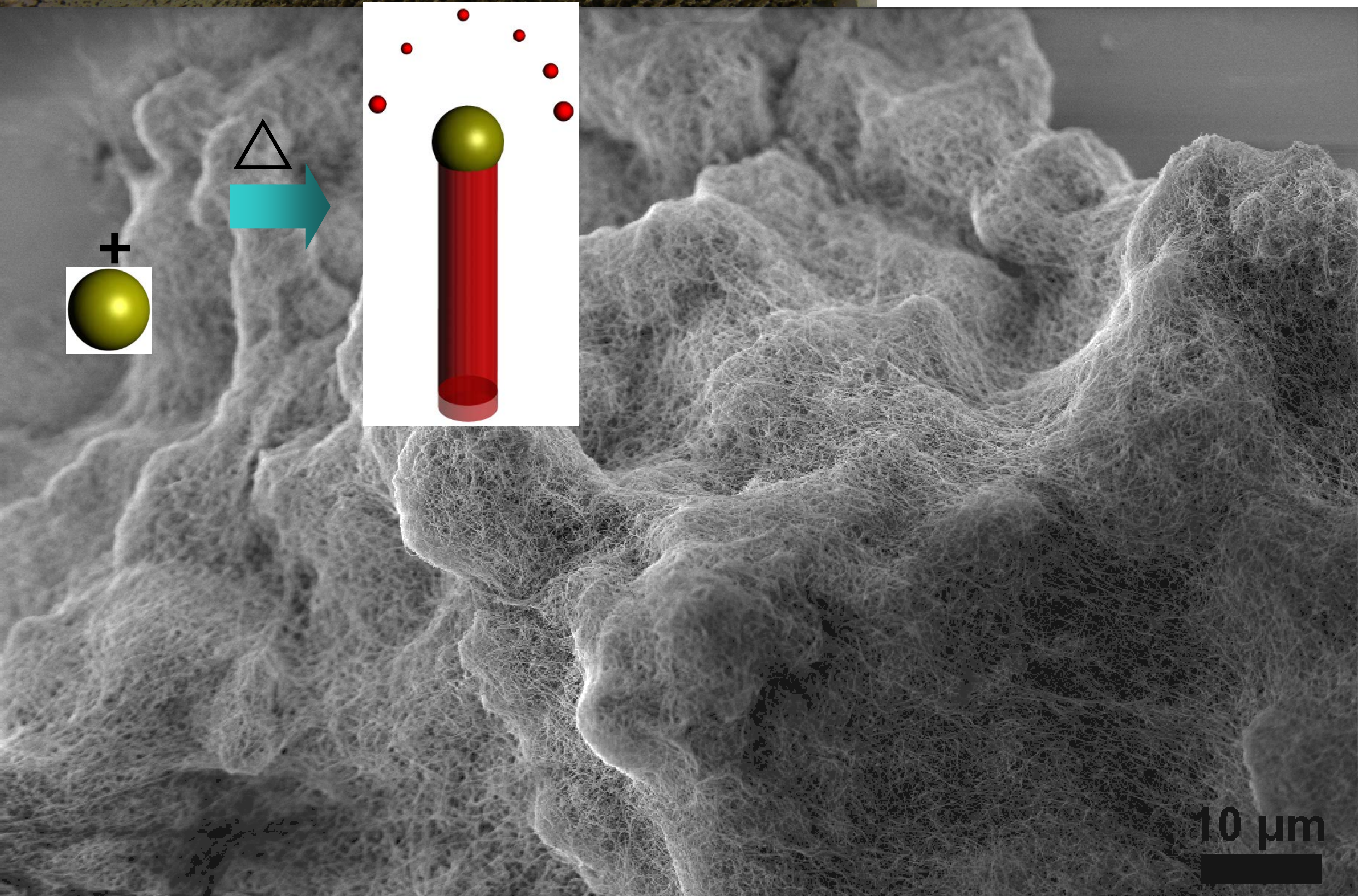
Metal nanostructures: gold and Cu

Upconversion nanocrystal: NaYF4: Yb: Er

段 et al. 未發表數據

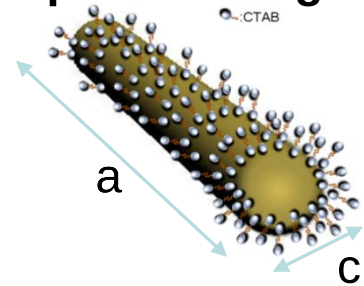


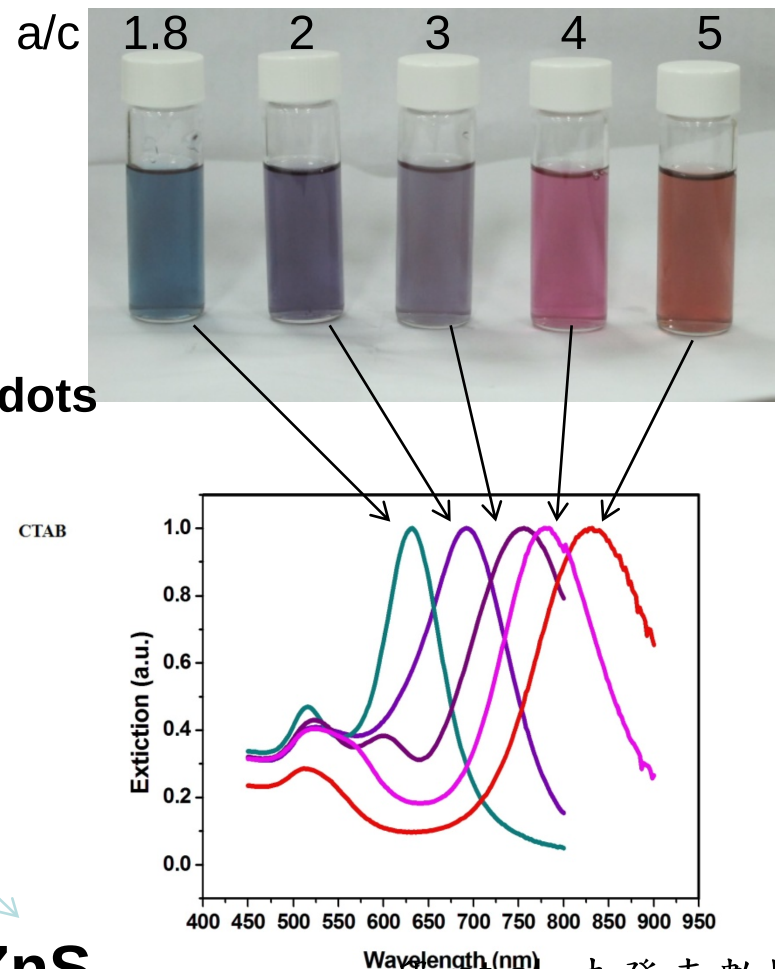
40 mg Si nanowire produced!



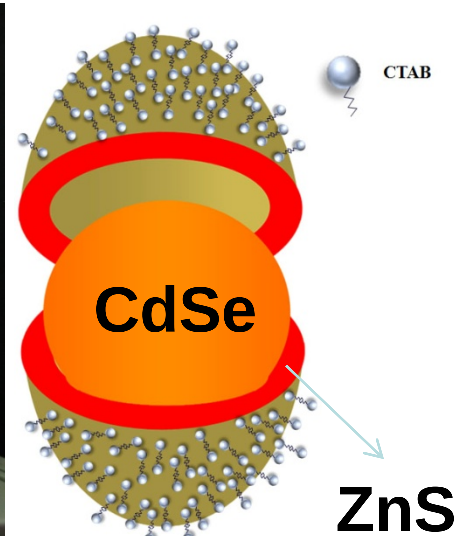
Size Dependent optical properties f CdSe quantum dots

Plasmon absorption tuning of gold nanorods



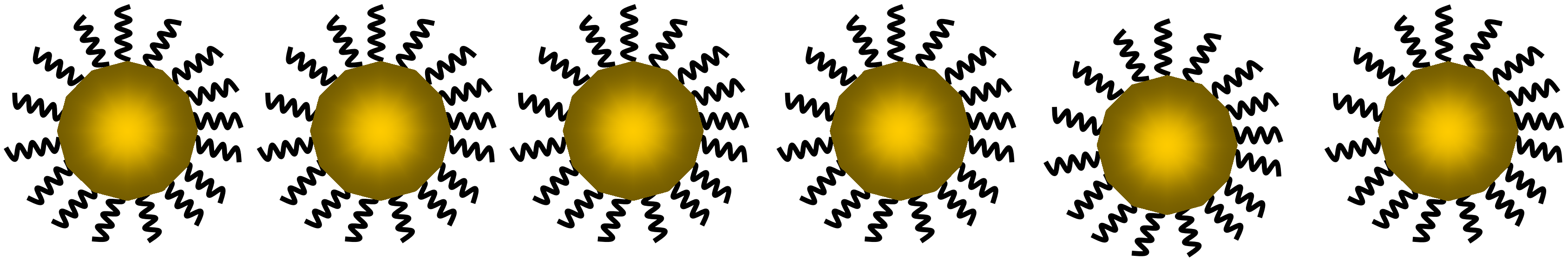


Bright water-soluble CdSe/ZnS/CTAB quantum dots



段 et al. 未發表數據

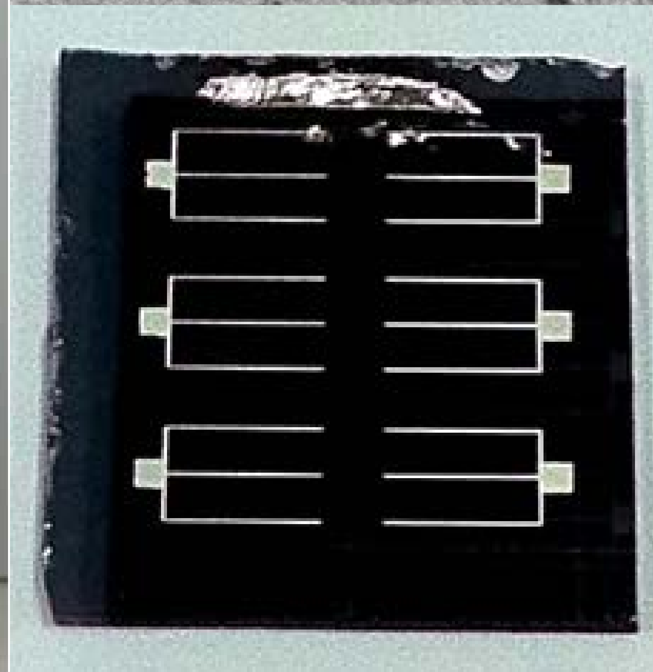
CIGS nanocrystals as ink for thin film solar cell

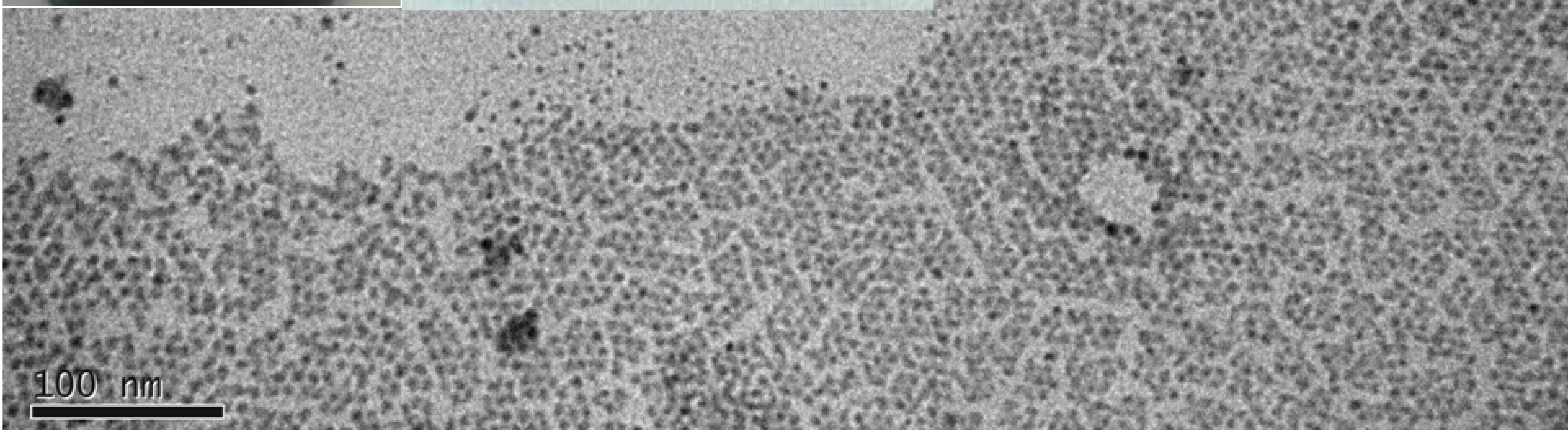


Why?

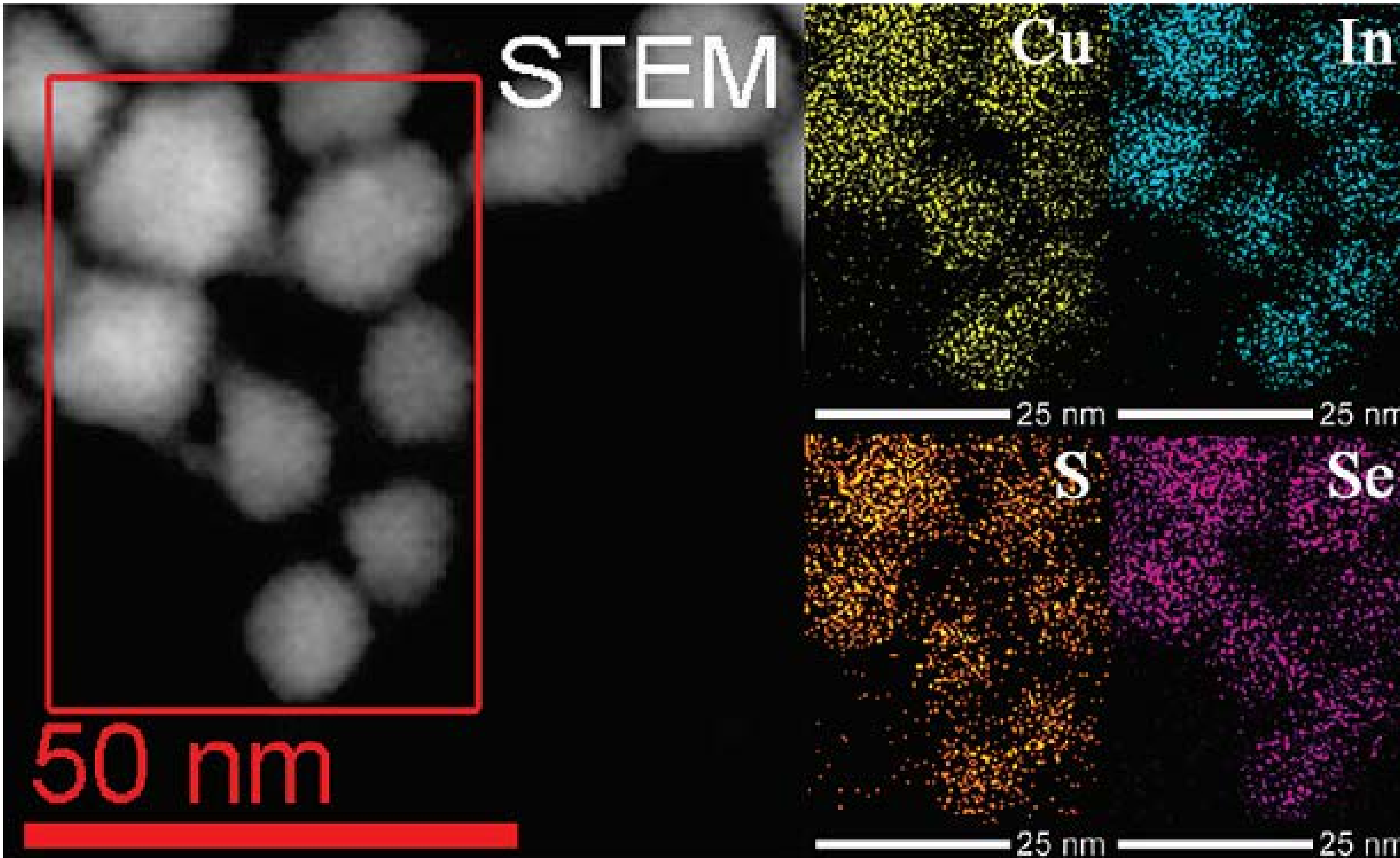
-These nanocrystals are uniform size and composition and stable in solution
-These nanocrystals could be easily accessible in solution-processing procedures, such as dip-coating, in-jet printing, drop-casting and could be implanted for future roll-to-roll fabrication processing.
-These nanocrystals could be easily made in massive quantity using our proposed synthetic strategy.

Nanoparticle ink for CIGS solar cell

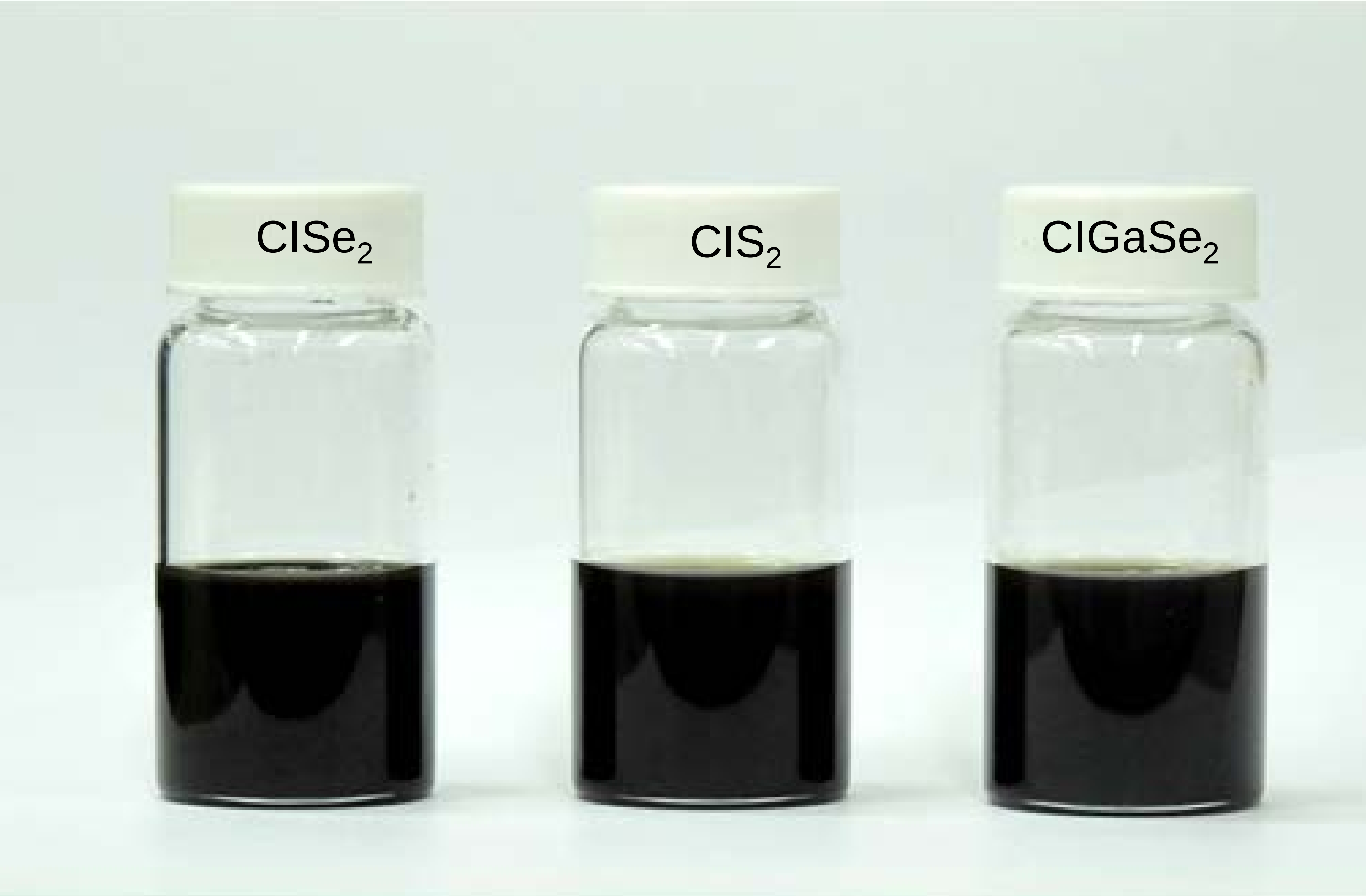




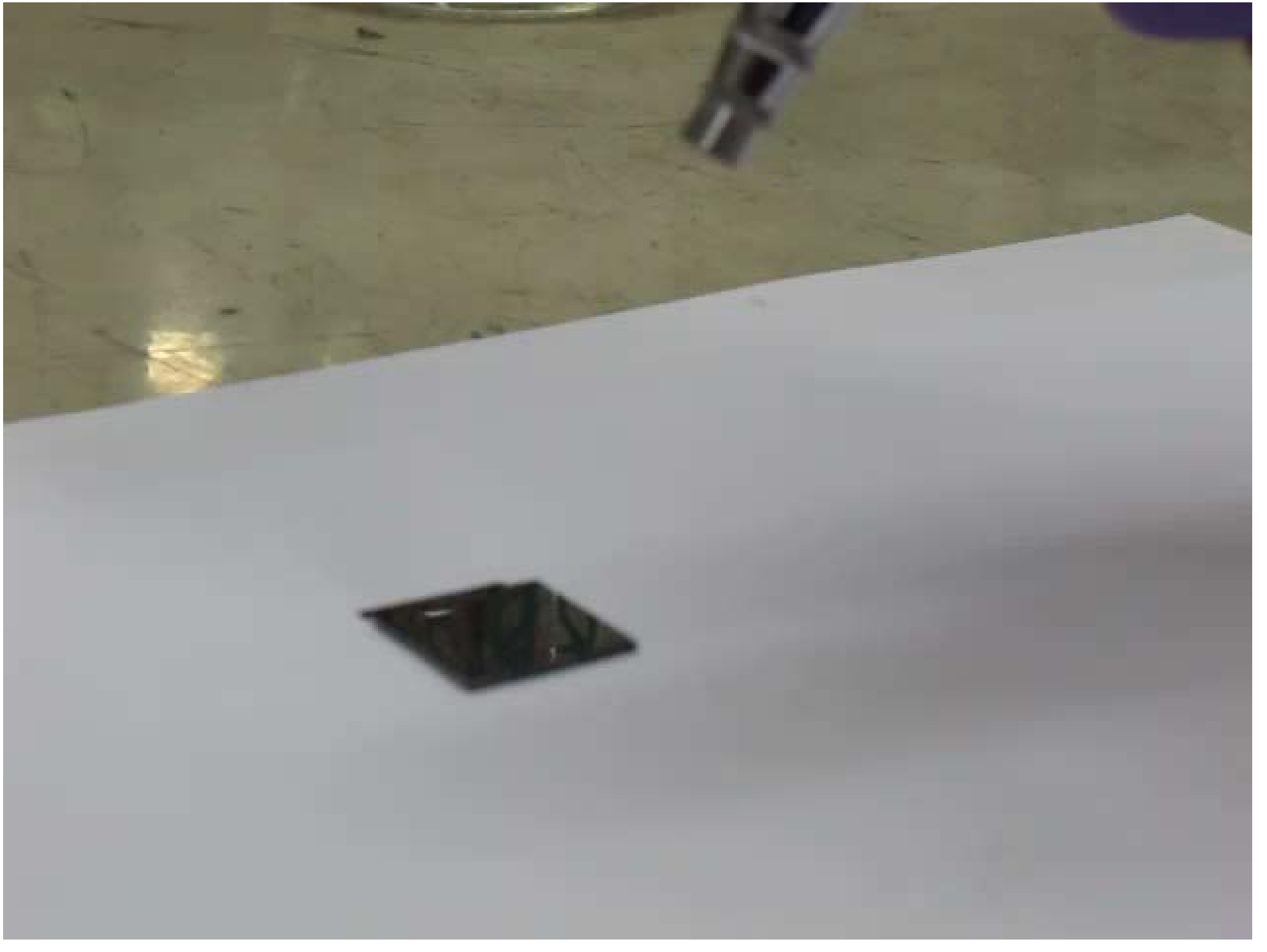
$CuIn(S_{0.5}Se_{0.5})_2$ Nanoparticles



Photos of CIS_2, $CISe_2$, CIGS nanocrystal solution

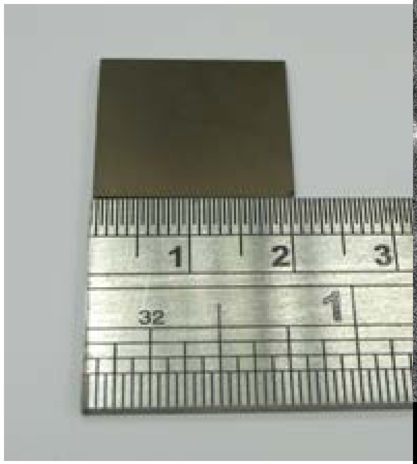


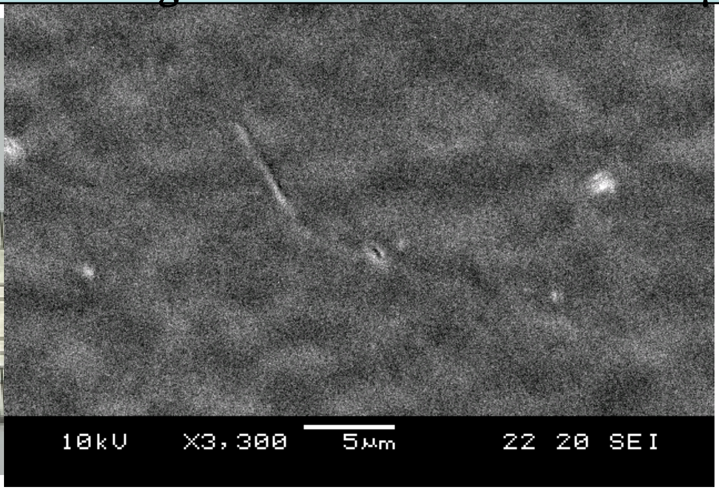
Spray-depositing Nanocrystals on Mo-coated Soda Glass

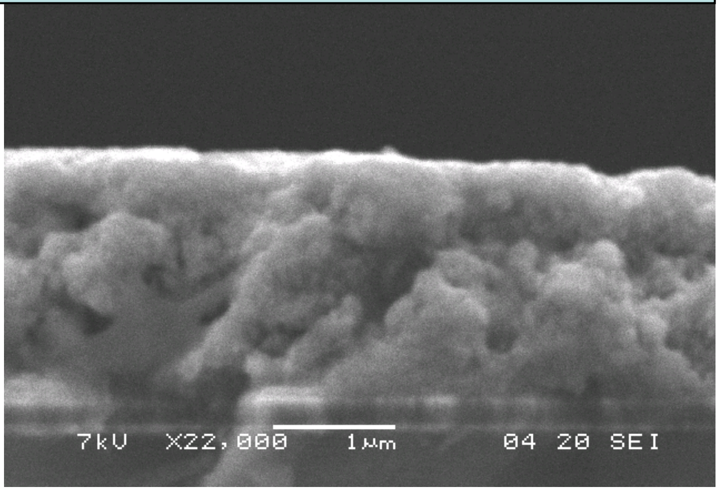


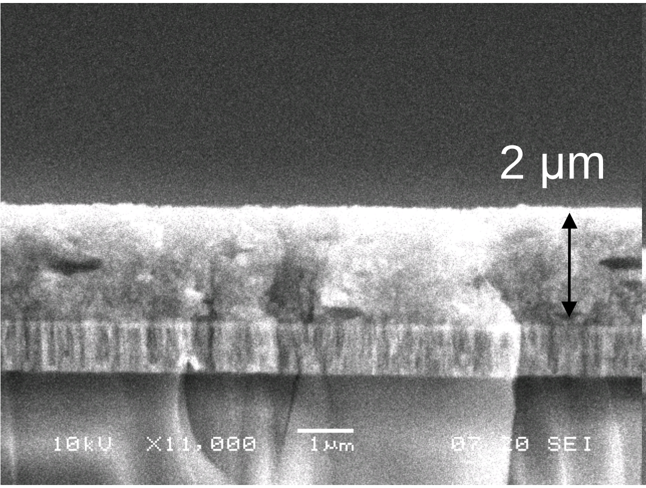
Spray-deposited Film

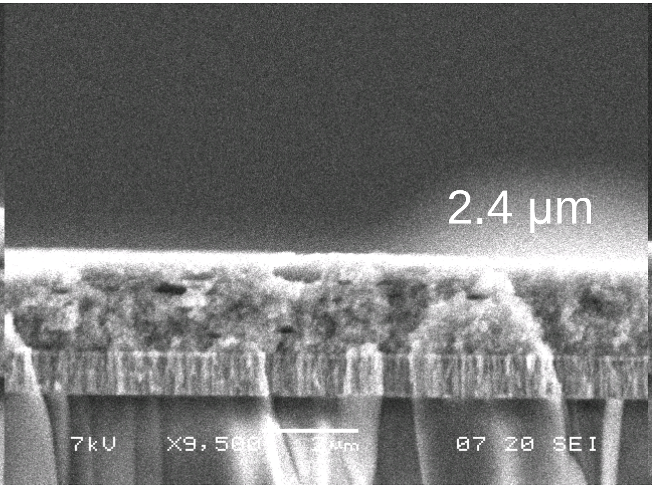
Spray	**concentration : 20mg/ml toluene。 Annealing temp: 500℃。** **Annealing time: 60min。 thickness: ~2µm。**

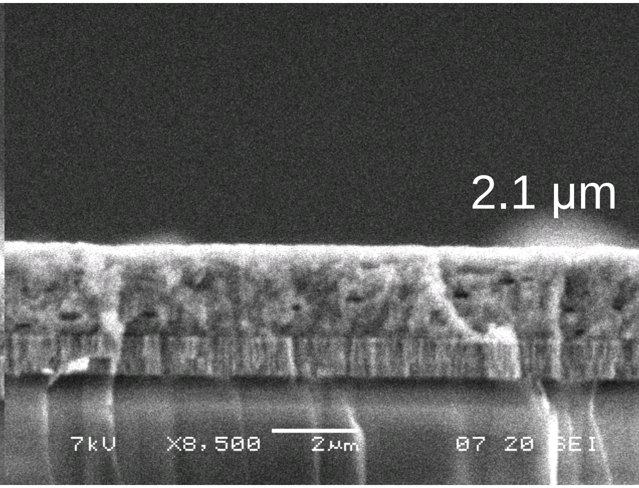




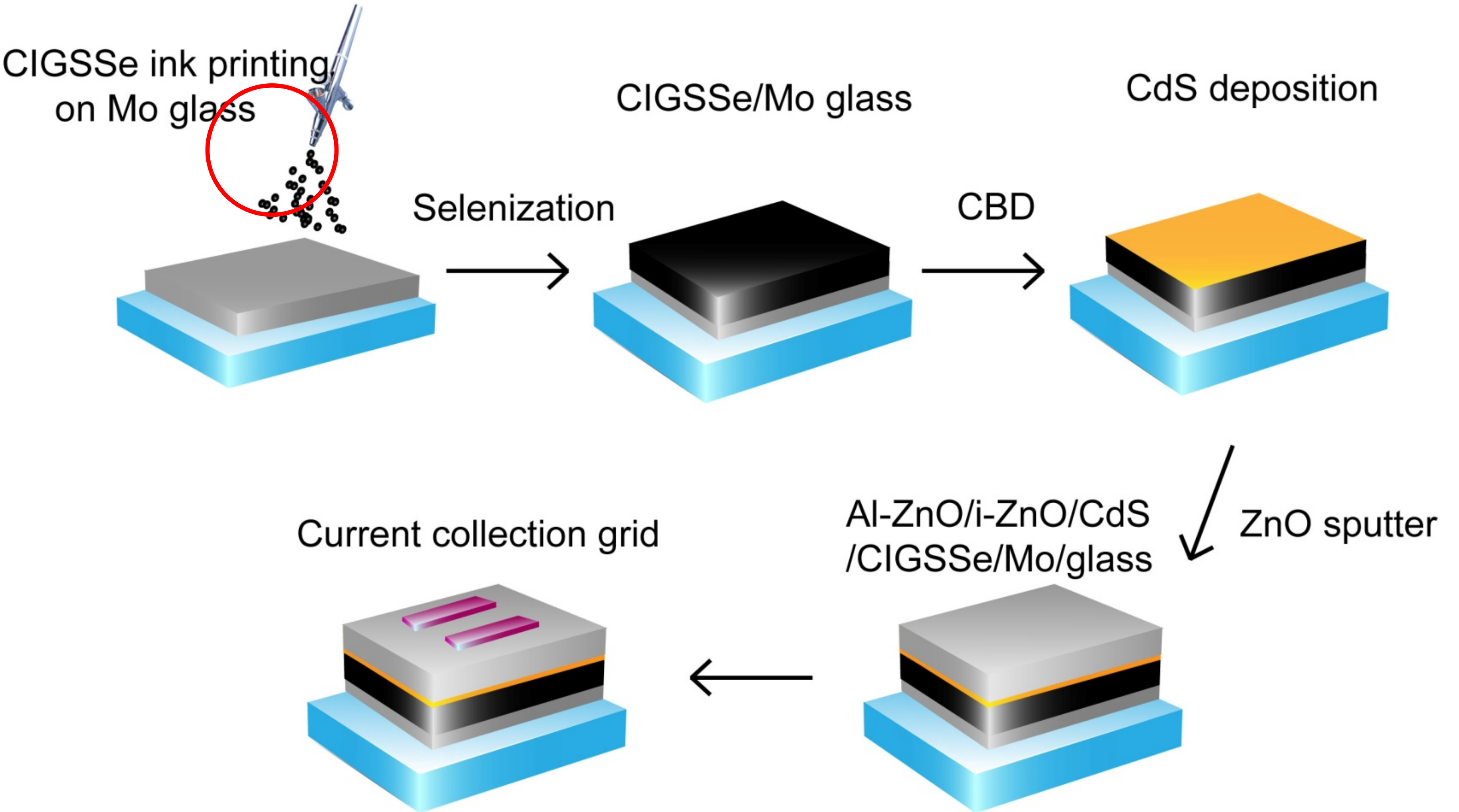




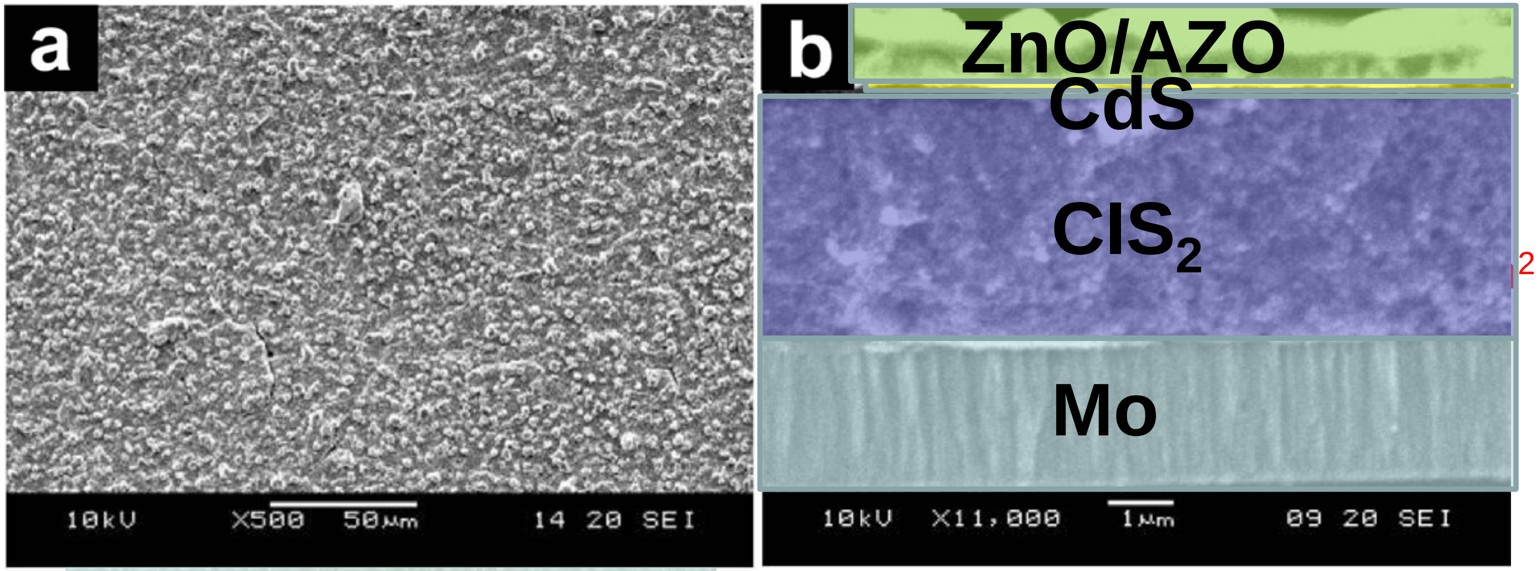


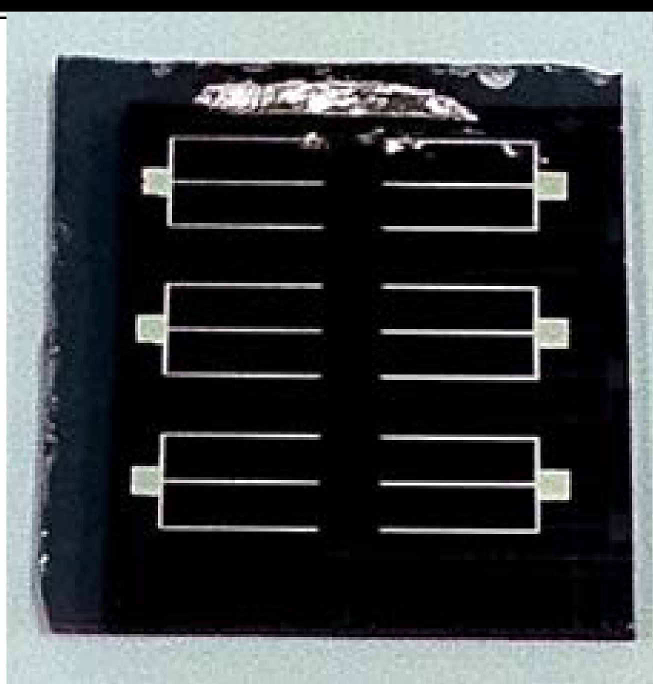


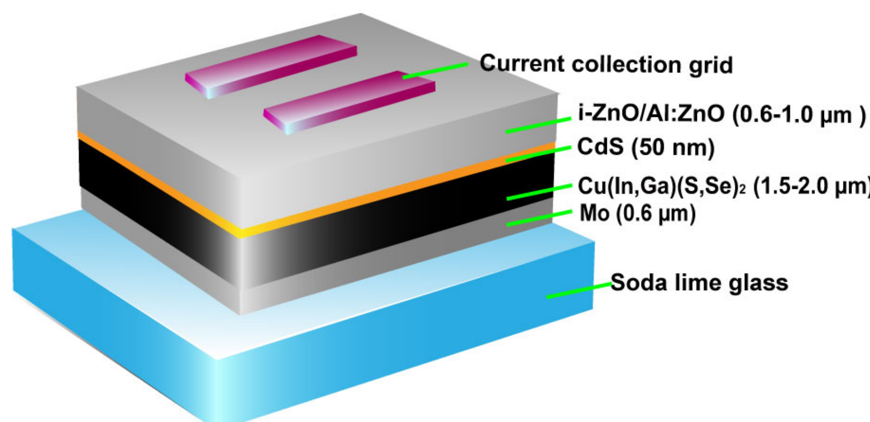
Procedure of CIGS photovoltaic device fabrication



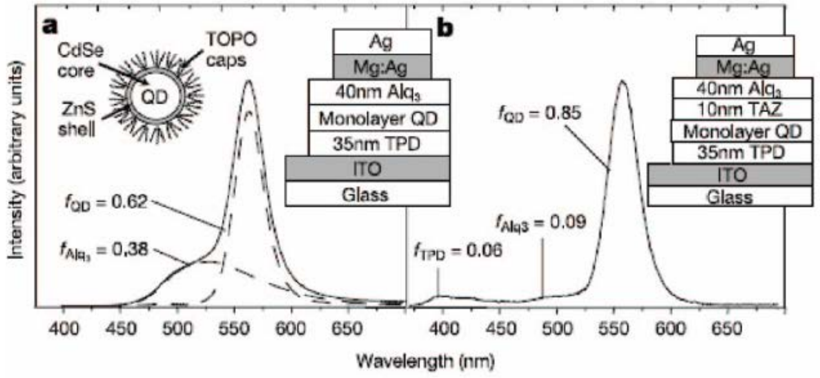
Final Device Efficiency

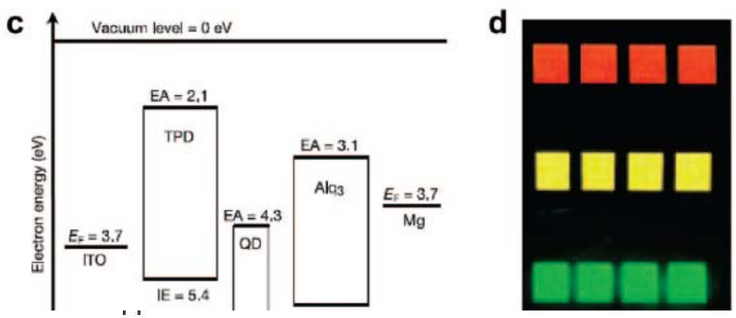


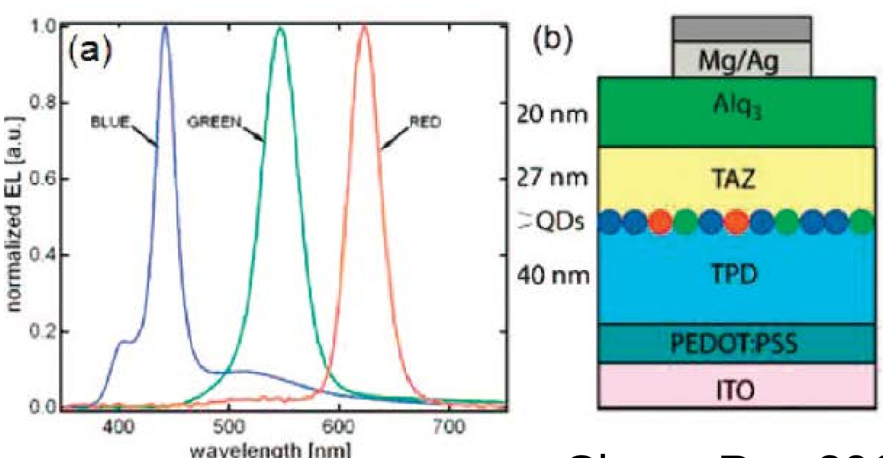




CdSe/ZnS nanocrystal LED







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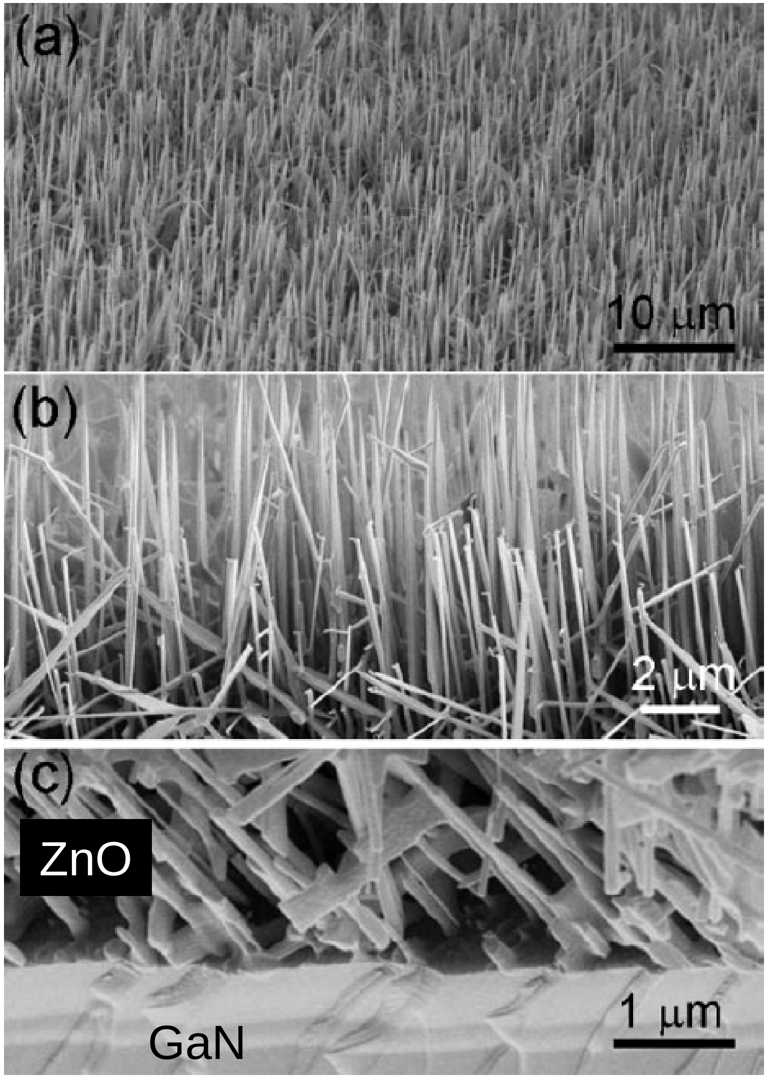
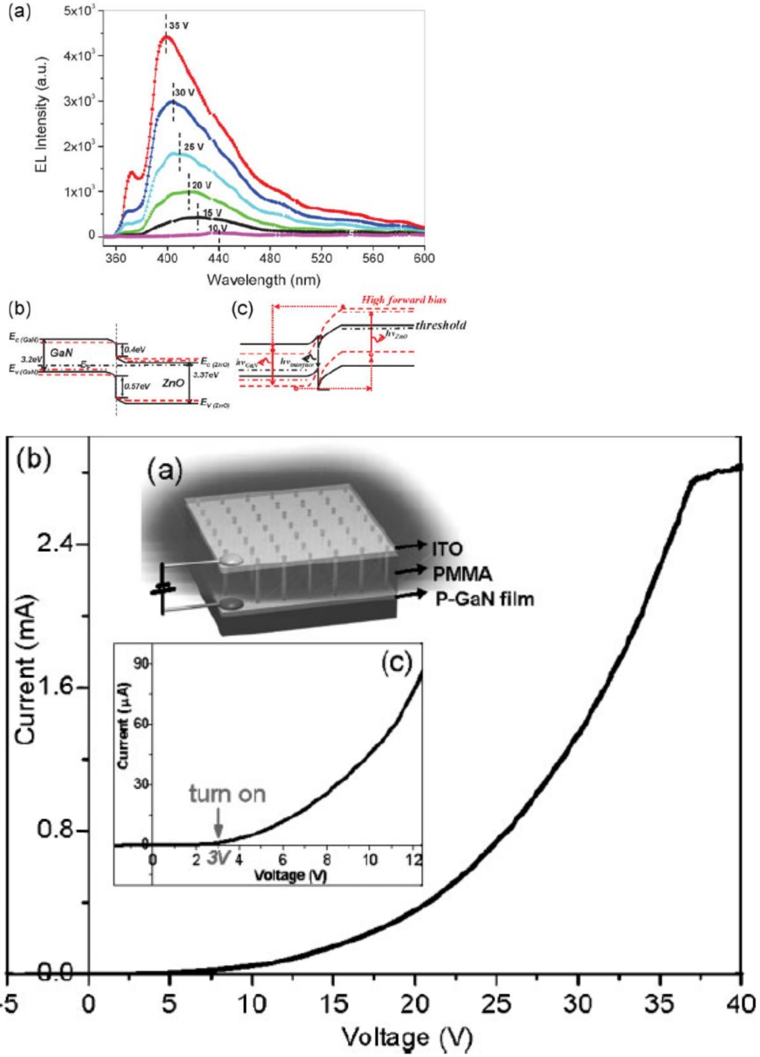
ZnO nanowire /GaN substrate LED





Zhang et al., Adv Mater., 2009

Thanks for your attendance on this class