Thin Film Deposition

- Physical processes
  - Evaporation: Thermal, E-beam, Laser, Ion-plating.
  - Sputtering: DC, RF, Magnetron, Reactive.
  - Spray: Flame, Plasma.
- Chemical processes
  - Chemical Vapor Deposition (CVD): Thermal, MOCVD, PECVD.
  - Plating: Electroplating, Electroless.
  - Solgel
  - ALE
- Molecular Beam Epitaxy

Vacuum Evaporation

- Heating a source material under vacuum until it evaporates or sublimates.

- The evaporant is deposited onto a substrate to form a film.

- Physical vapor deposition process.

- High deposition rate, simple, easy to use.

- Conductor materials in electronic circuits and devices, dielectric and optical coatings.

Vacuum evaporation

Mean free path of atoms in the vapor > the distance from the source to the substrate.

The mean free path, λ_{mfp}, of particles in air at T = 25 ^{o}C

$$\lambda_{mfp} \approx \frac{5 \times 10^{-3}}{P\text{(torr)}} \quad \text{(cm)}$$

$$\lambda_{mfp} = \frac{1}{n\sigma} \qquad n = P/kT$$

$$\lambda_{mfp} = \frac{kT}{P\sigma} \qquad\qquad \sigma = \pi d^2$$

$$= \frac{411.24 \times 10^{-23}}{P\,(1.21 \times 10^{-18})}$$

For N_2 molecules

$d = 6.2$ Å

$$= \frac{3.40 \times 10^{-3}}{P}$$

Vacuum evaporation

- Deposition rate: Hertz-Knudsen eq.

$R/(cm^2 \cdot s) = C(P'' - P)/(2\pi mkT)^{1/2}$

$R = n \cdot v/4,$

$n = P/kT, \quad v = (8kT/\pi m)^{1/2}$

C: Evaporation coefficient

P'': Evaporant surface vapor pressure

P: Hydrostatic pressure

m: Evaporant molecular weight

k: Boltzmann constant

T: Temperature

Vacuum evaporation

- Evaporation coefficient: Larger for clean surfaces, smaller for contaminated surfaces.

- Deposition rate: Greatly depends on the substrate-to-source geometry.

- Non-uniform thickness on surface: Due to the distance dependence. Knudsen's cosine law, $\cos\theta/r^2$.
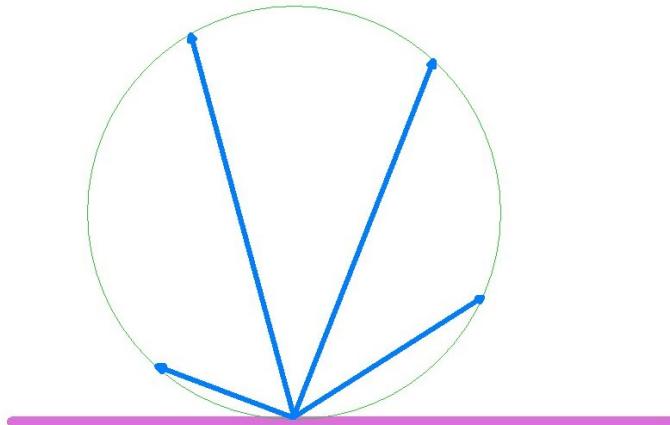
Thermal Evaporation
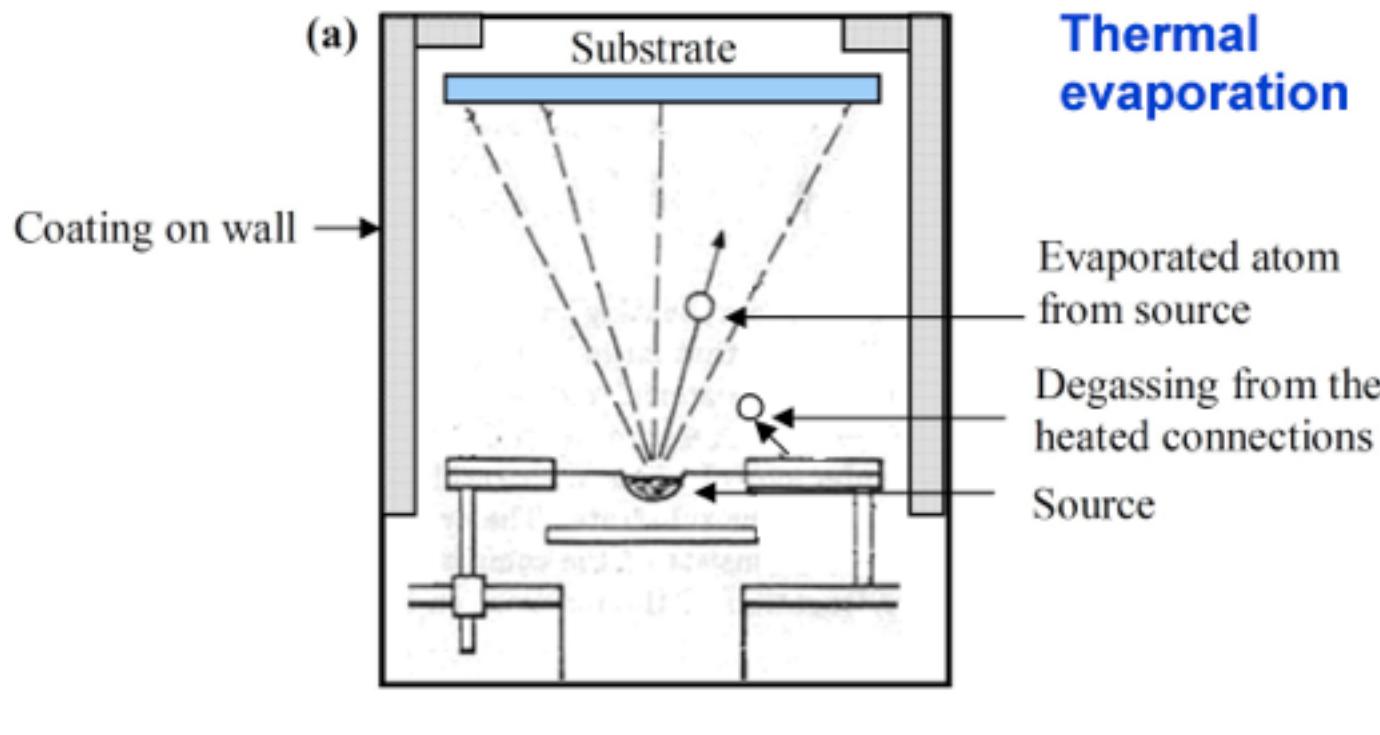
– Difficult: High melting point materials, uniformly heating, rapidly change of deposition rate, reactions between the source and the heating container.

E-beam evaporation

- High energy focused electron beam to heat the source material at a small area.

- Larger deposition rate.

- Water-cooled container (cavity or hearth): No source-container reaction.

- Sweeping or oscillating the e-beam to heat the source material uniformly.

- Multiple hearth sources: Different source materials.
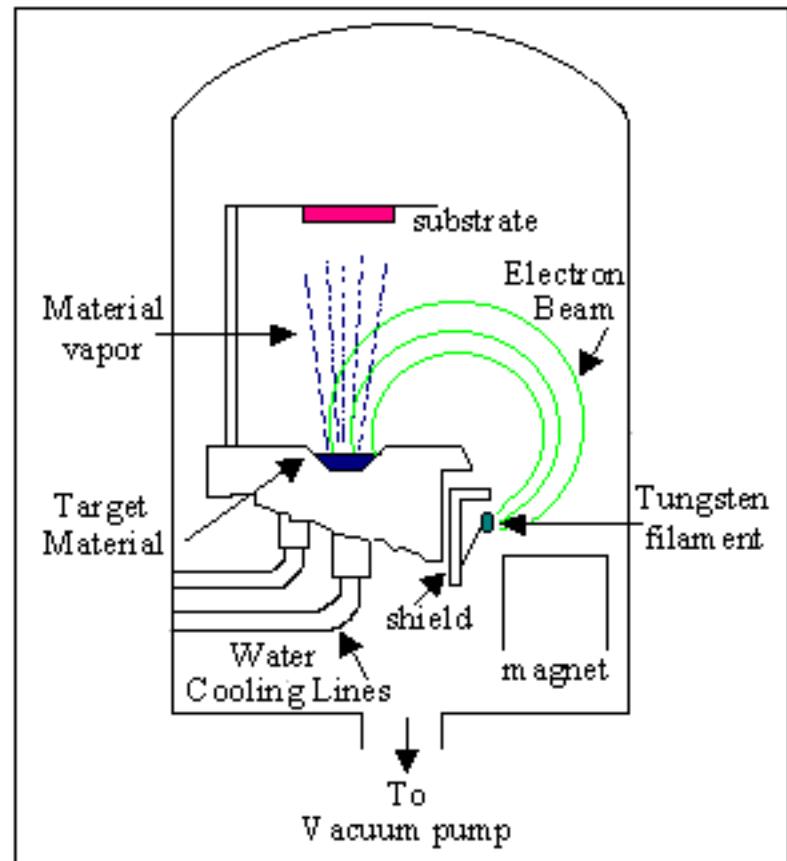
Vapor pressure
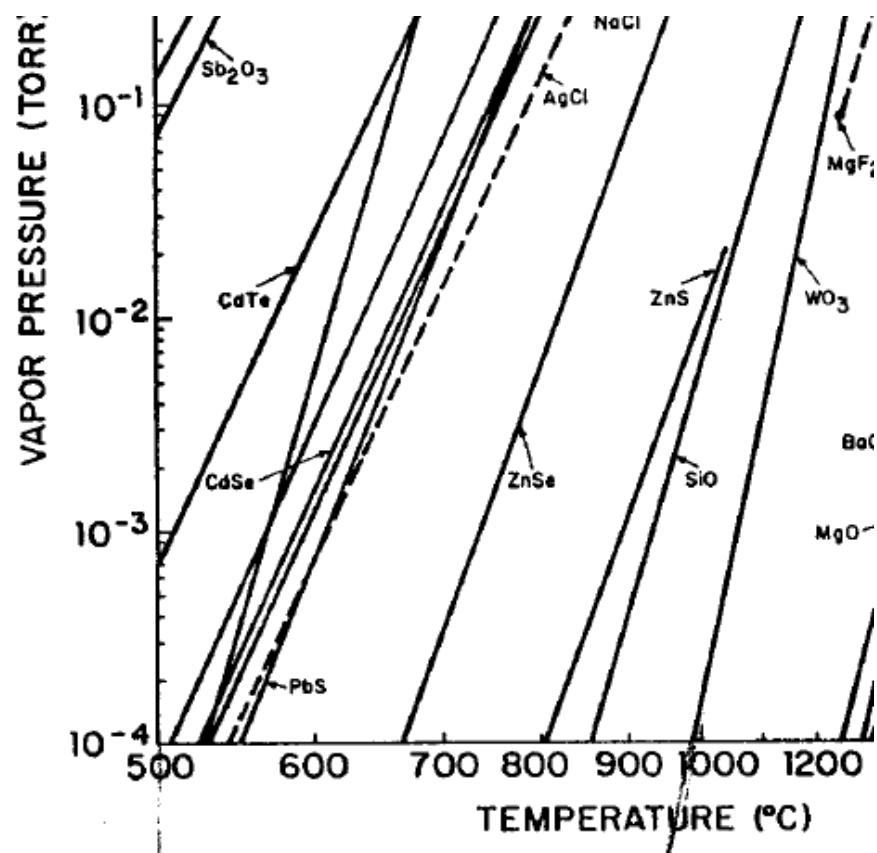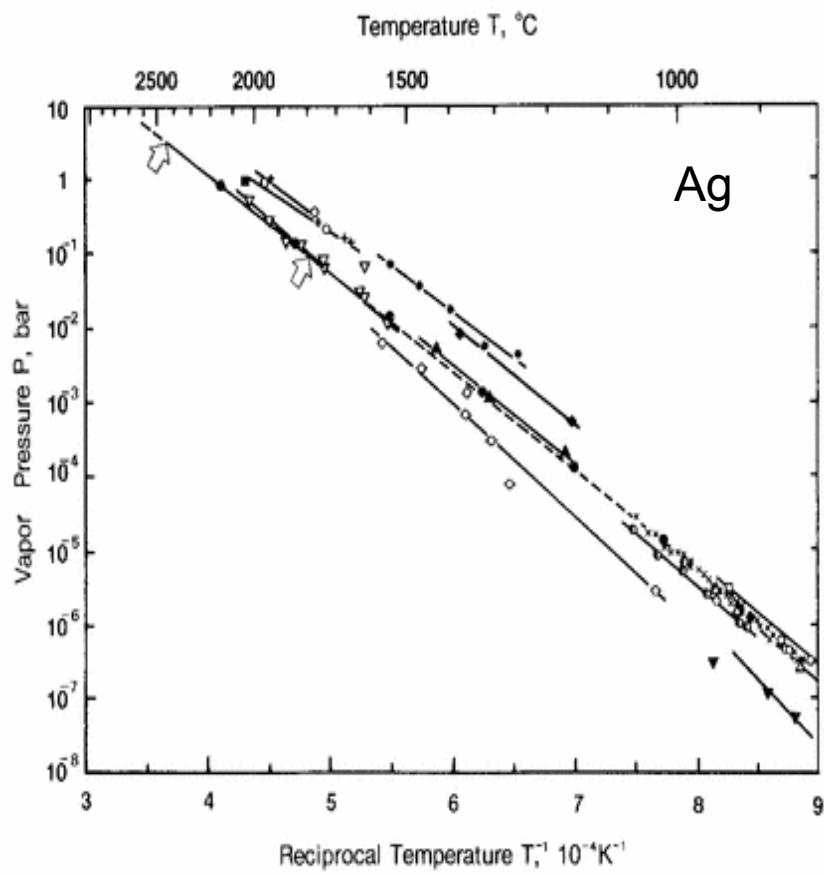
Phase diagram of AuSi
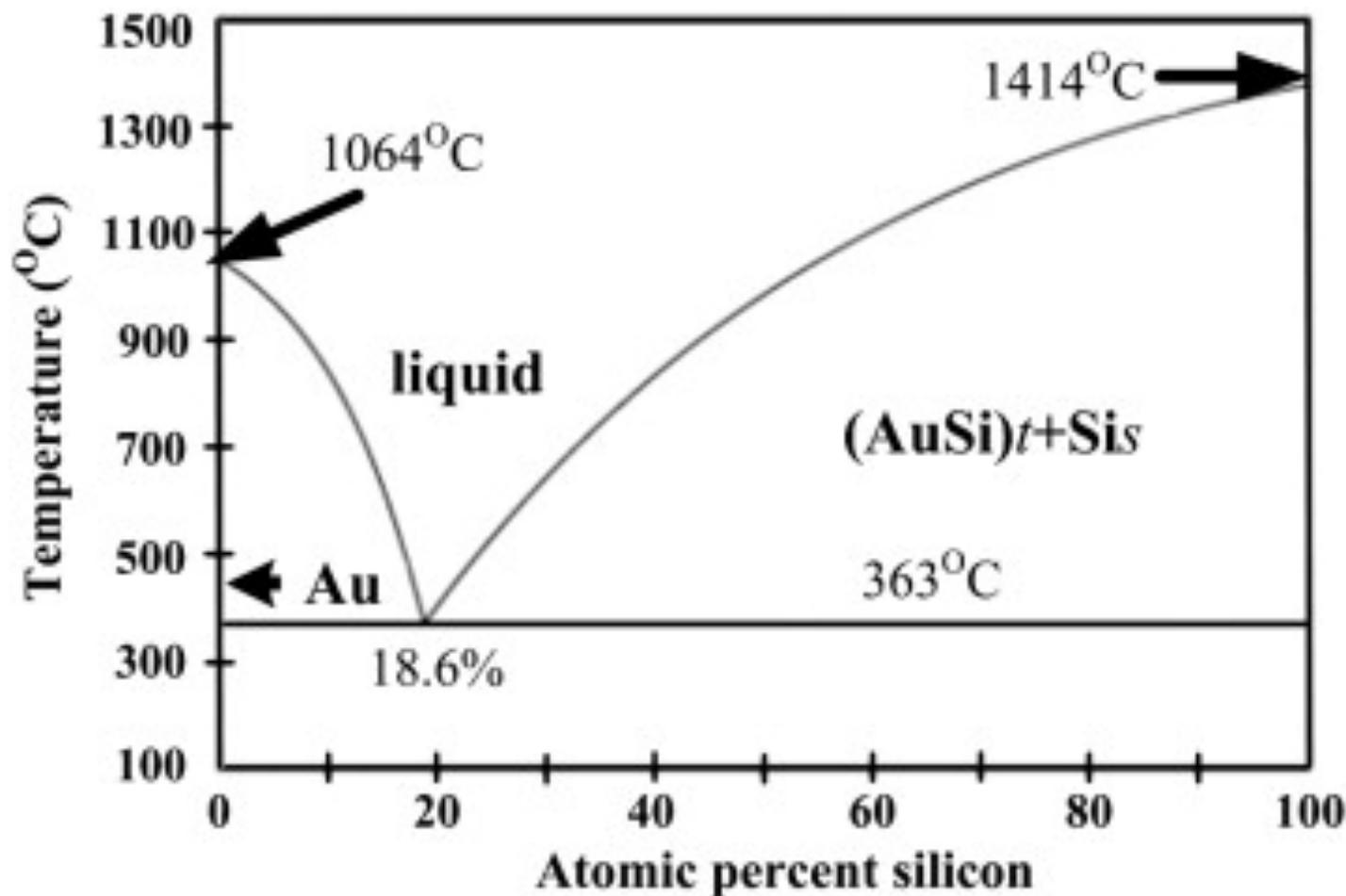
Vacuum evaporation

- Low-energy process: the deposited material condenses onto the substrate with very little kinetic energy.

- Kinetic energy ~ 0.5 eV.

- Sputter deposition: Kinetic energy > 10 eV.

Sputter deposition

- PVD process.

- Bombardment and removal of the cathode material with positive ions from a rare gas discharge.

- Originally developed to deposit refractory metals.

- Now the sputter deposition is able to deposit most materials.

Sputter deposition system
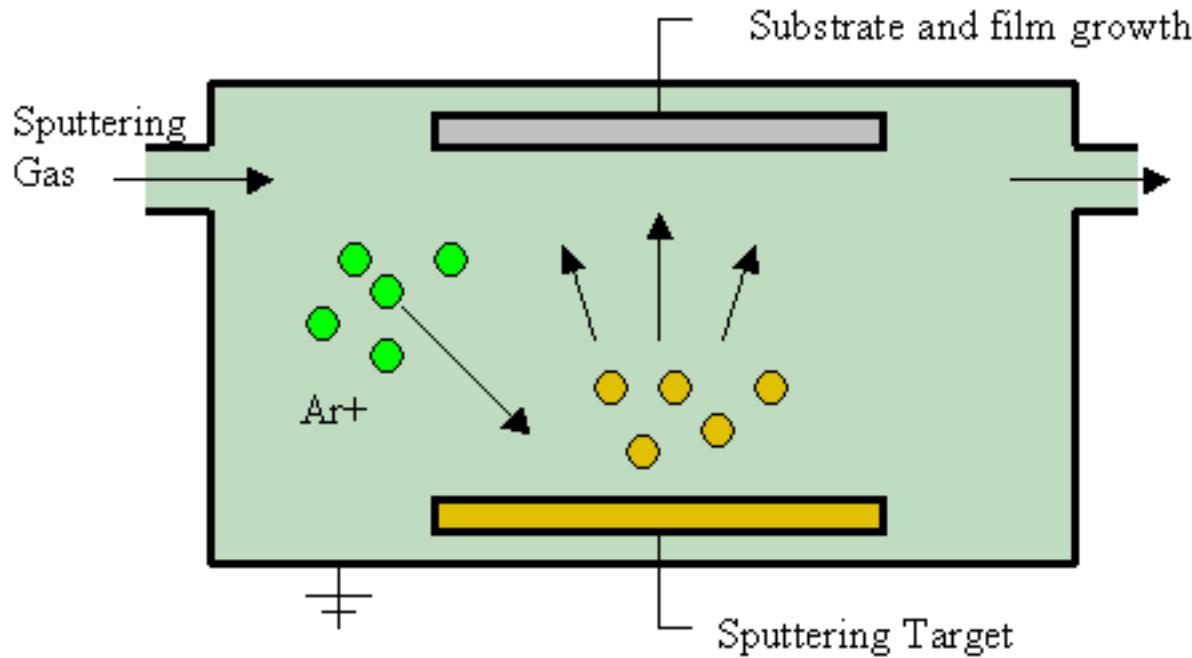
1) vacuum chamber   2) pumping system
3) sputter sources   4) vacuum gauges
5) substrate holder   6) Gas flow supply

# Sputtering Deposition Process

- **Sputtering**
  - Ions are accelerated into target
  - Some of the surface atoms are sputtered off of the target.
  - These sputtered atoms "flow" across the chamber to where they are deposited

Sputtering chamber
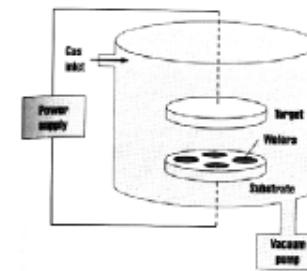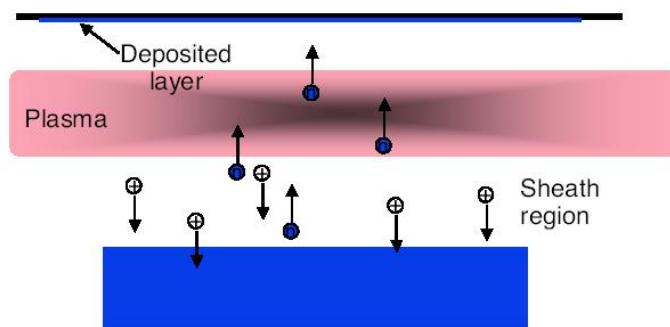
Mechanism of Sputtering

Sputtering involves the collisions of energetic ions with a target surface and the process usually leads to ejection of target atoms.

Incident ion

Reflected ions & neutral

Secondary electrons

sputtered atoms

sputtered atoms

surface

Primary knock-on

lattice atoms
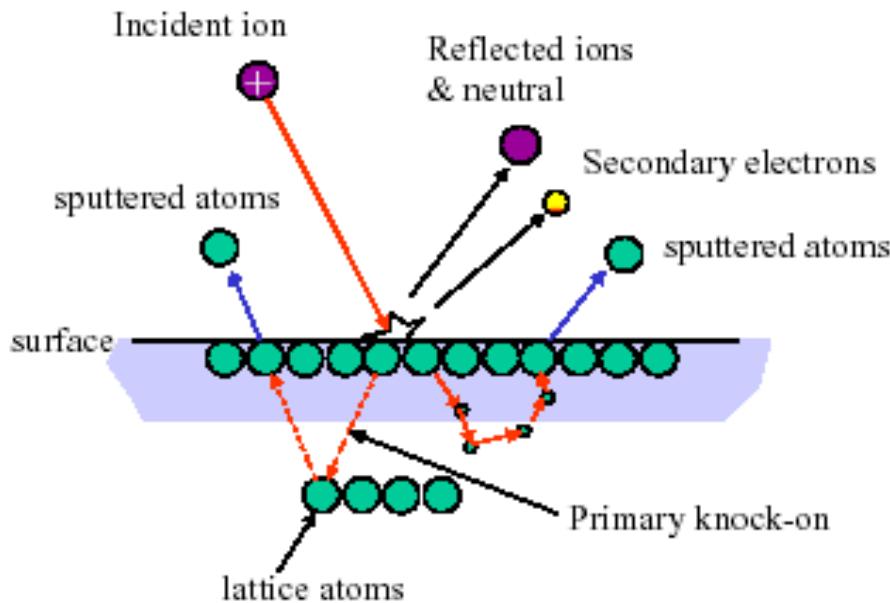
Sputtering process is characterized by sputter yield, S, which is typically in the range of 0.01 and 4 and increase with the mass of metals and energy of the sputtering gas.

Sputter Yield (Cont.)

The sputter yield depends on: (a) the energy of the incident ions; (b) the masses of the ions and target atoms; (c) the binding energy of atoms in the solid and (d) the incident angle of ions.
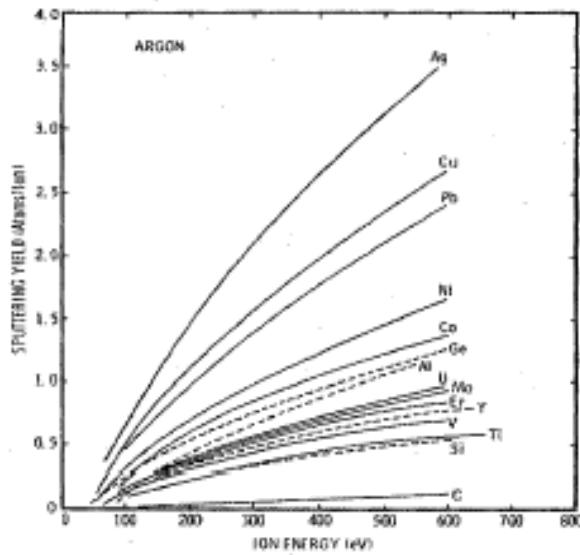
5.5: Variation of sputtering yield with ion energy at normal of incidence. Data from R.V. Stuart and G.K. Wehner, *J. Appl.*

$60^o - 70^o$
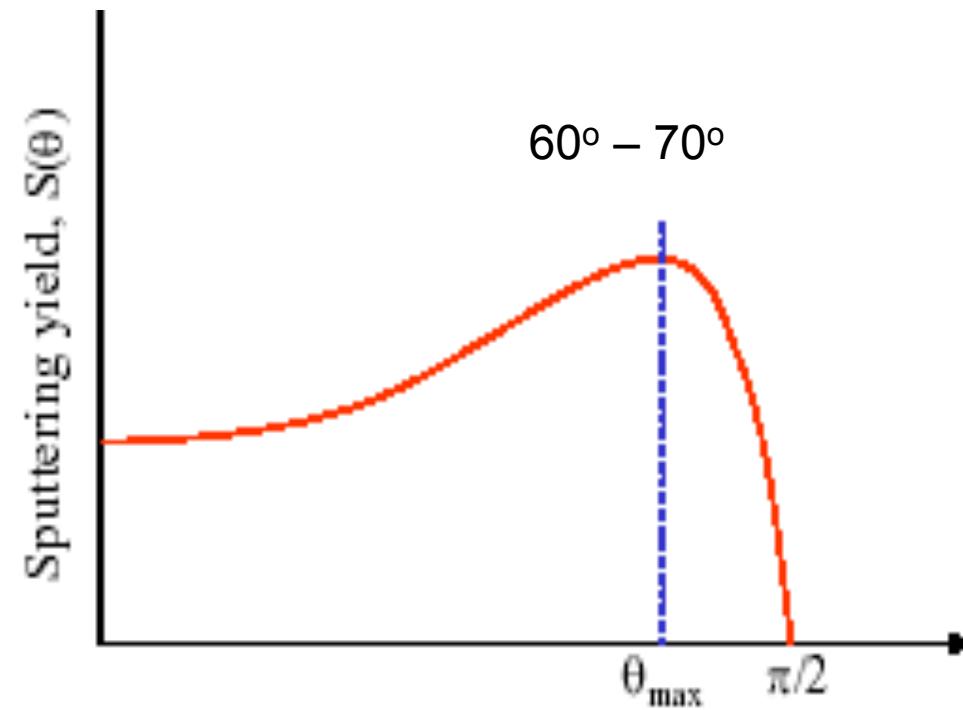
Sputtering Alloy Targets

composition of alloy in film is approximately the same as alloy in target (unlike evaporation)

Alloys

slow diffusion mixing in solids (sputtering)

- target reaches steady state
- surface composition balances sputter yield

High yield material low yield material

High yield material Low yield material
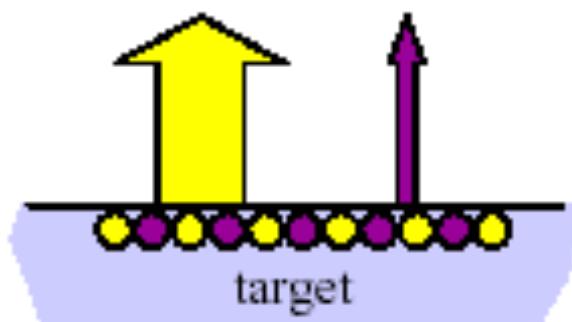
target

target

Before surface equilibrium
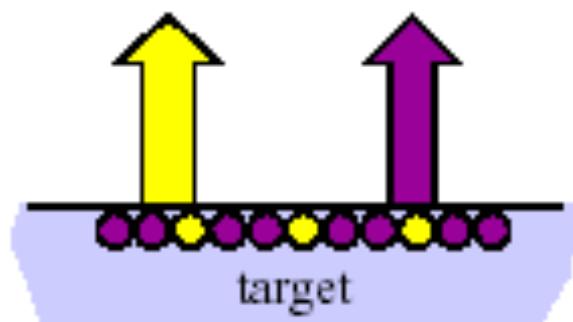
After surface equilibrium

Advantages of sputter deposition

- Elements, alloys and compounds can be sputtered and deposited.

- The sputtering target provides a stable, long-lived vaporization source.

- In some configurations, reactive deposition can be easily accomplished using reactive gaseous species that are activated in plasma.

- The source and substrate can be spaced close together.

- The sputter deposition chamber can have a small volume.

http://www.pfonline.com/articles/069901.html

Disadvantages of Sputter Deposition

- Sputtering rates are low compared to those that can be attained in thermal evaporation.

- Sputtering targets are often expensive and material use may be poor.

- Most of the energy incident on the target becomes heat, which must be removed.

- In reactive sputter deposition, the gas composition must be carefully controlled to prevent poisoning the sputtering target.

http://www.pfonline.com/articles/069901.html

Basic Techniques

- **DC (diode) sputtering**
- **RF (radio frequency) sputtering**
- **Magnetron sputtering**
- **Reactive sputtering**

DC Sputtering

The simplest sputtering technology
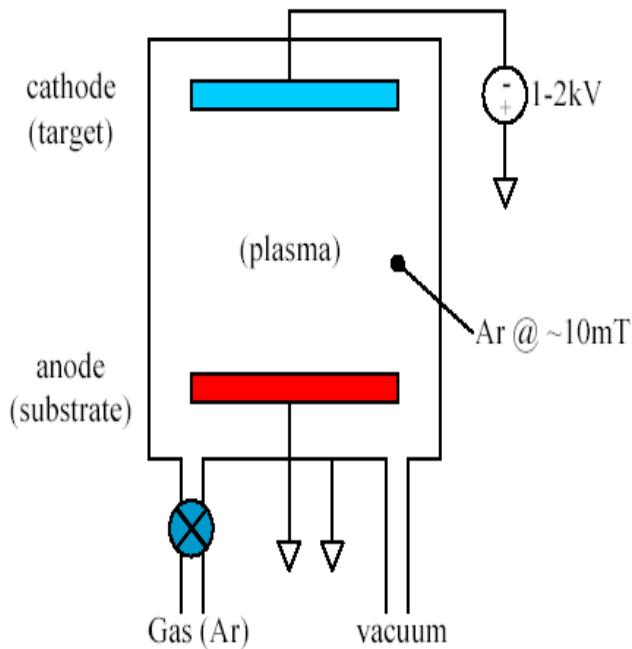
E (e-) < 2eV - no ionization, elastic collisions only
E (e-) > 2eV - inelastic collisions add energy to Ar
❯ ionization (highest energy process, ~15eV)

$$Ar + e^- \rightarrow Ar^+ + 2e^-$$

Note: mass (e-)/mass(Ar) ~ 10^{-5}
- energy transfer small
- e- gain energy via elastic collisions until E>15eV for ionization
- #ions ~ #neutrals ~ 3 x 10^9 cm^{-3} @ 10mT

DC Sputtering (Cont.)

Light e- pulled towards walls faster than ions, leaving slightly more ions in glow region

Light e- move away from cathode faster than ions, leading to a large field, high acceleration of ions into cathode

high-E ions (10keV to 1 MeV) knock target material loose resulting plume of neutrals

new electrons from impact reactions replenish the plasma

http://www.glue.umd.edu/~ddev/me489f/slides/2b_deposition_x6.pdf
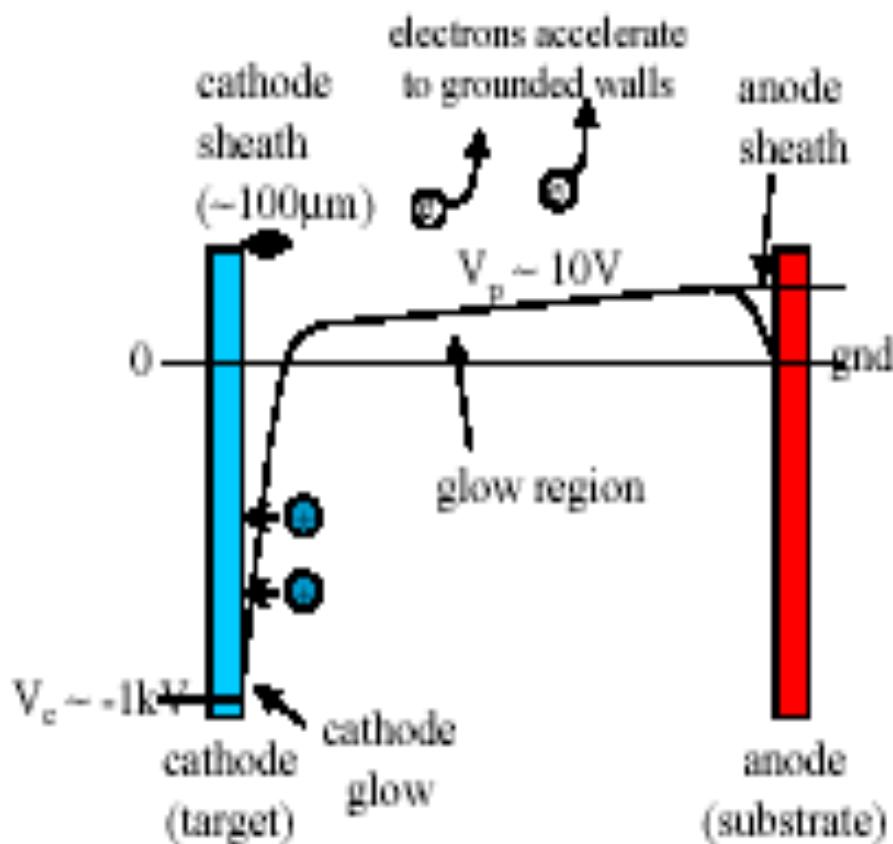
Operating Pressure for DC sputtering

Operating pressure limitations are imposed by the requirement of both the glow discharge and of film deposition.

Optimum deposition rate around 100 mTorr
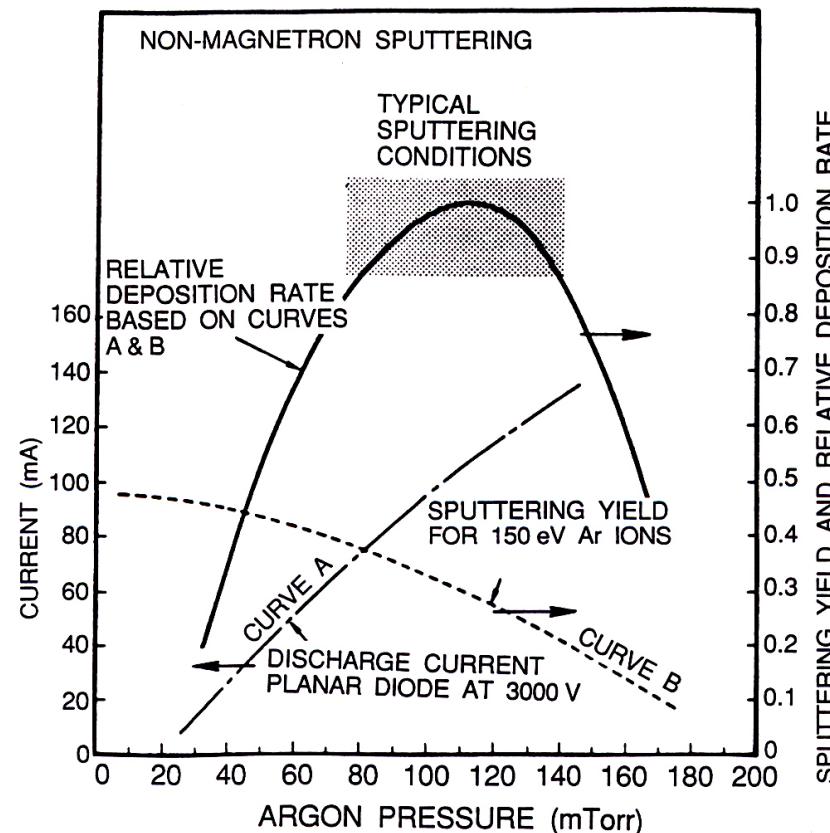
Figure 3-18. Influence of working pressure and current on deposition rate for nonmagnetron sputtering. (From Ref. 23).

Milton Ohring, *Materis Science of Thin Film*, second Edition, P208

Parameters for DC Sputtering

- **Sputter voltage**
  - typically -2 to -5 kV
- **Substrate Bias Voltage**
  - substrate is being bombarded by electrons and ions from target and plasma
    - sputtering film while you deposit
  - neutral atoms deposit independently
  - put negative bias on the substrate to control this
  - can significantly change film properties
- **Deposition rate**
  - changes with Ar pressure
  - increases with sputter yield
    - usually increases with high voltage

http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/
sputtertech.html

RF Sputtering

- DC sputtering - what about dielectrics?
    - in DC systems, positive charge builds up on the cathode (target) need 10^{12} volts to sputter insulators !!

  avoid charge build up by alternating potential

RF sputtering

http://www.uccs.edu/~tchriste/courses/PHYS549/549lectures/
sputtertech.html
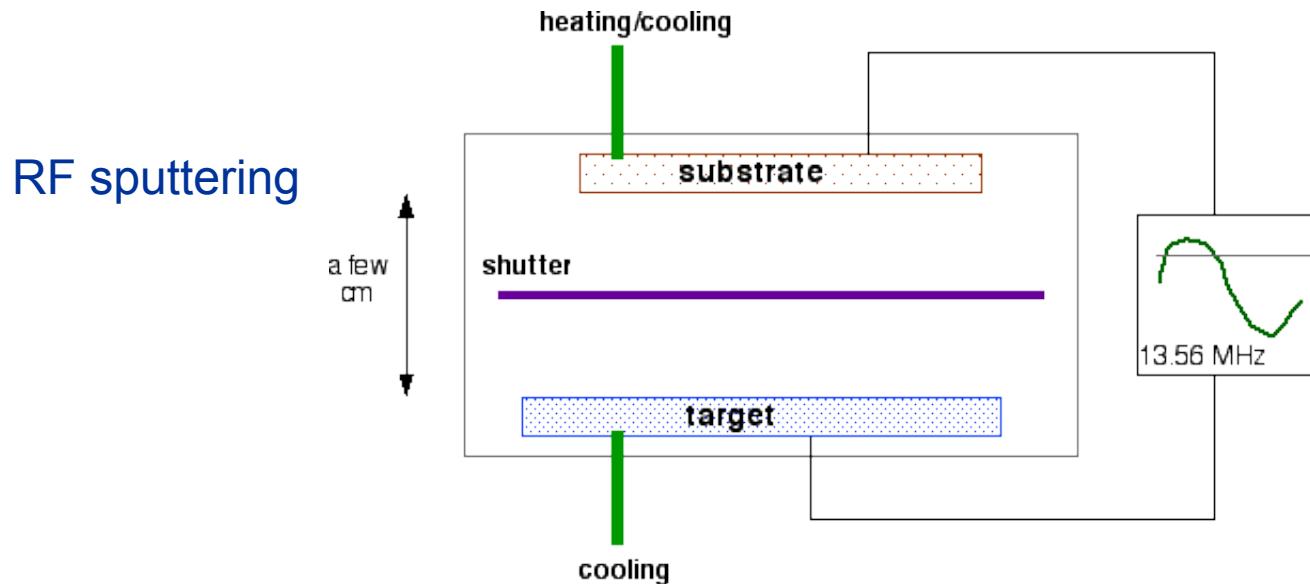
RF Sputtering

- frequencies less than about 50 kHz
  - electrons and ions in plasma are mobile
    - both follow the switching of the anode and cathode
  - basically DC sputtering of both surfaces

- frequencies above about 50 kHz
  - ions (heavy) can no longer follow the switching
  - enough electrons to ionize gases (5~30MHz)

Typically 13.56 MHz is used

Advantages of RF Sputtering

- It works well with insulating targets

- High efficiency

  easier to keep plasma going → can operate at lower
  Ar pressures (1-15 mTorr) → fewer gas collisions
  → more line of sight deposition

http://aultimut.com/aultimut/details.asp?itemid=11

Magnetron Sputter Deposition

❖ Use with DC or RF

• High sputtering efficiency

increase ionization of Ar

– Why? Higher sputter rates at lower Ar pressures (down to 0.5 mTorr)

fewer gas collisions - more line of sight

– How ? increase probability of electrons striking Ar

– increase electron path length

– use electric and magnetic fields

Magnetron Sputtering Principle
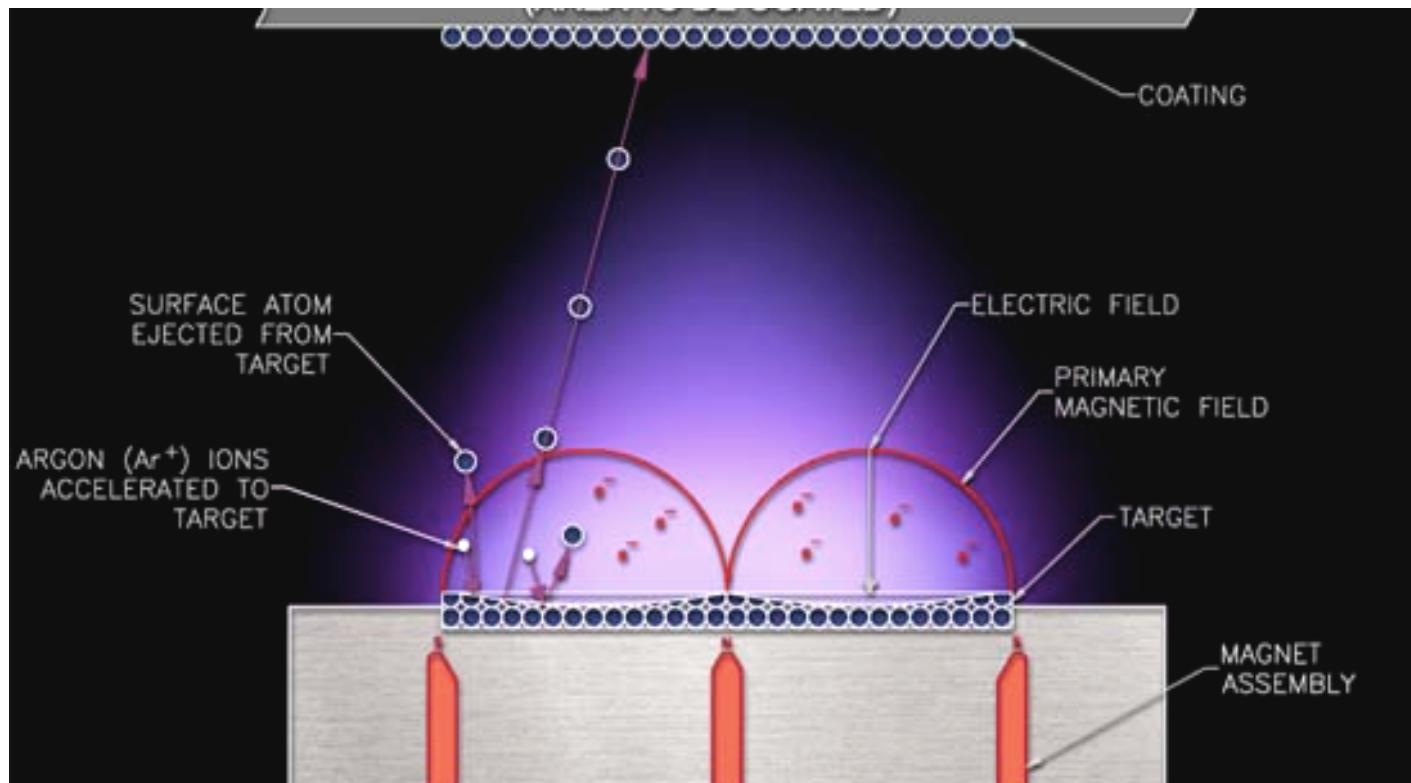
This technology uses powerful magnets to confine the "glow discharge" plasma to the region closest to the target plate. That vastly improves the deposition rate by maintaining a higher density of ions, which makes the electron/gas molecule collision process much more efficient.

Advantages of Magnetron Sputtering

- High deposition rate
- Reducing electron bombardment of substrate
- Extending the operating vacuum range
 - ability to operate at lower pressures

The most widely commercially practiced sputtering method

Parameters for Magnetron Sputtering

- **Deposition pressure : 10^{-3} to 0.1 Pa (10^{-5} to 10^{-3} torr)**

- **Deposition rate : $0.2 \sim 2^{-6}$ m/min (10 times higher than conventional sputtering)**

- **Deposition temperature : 100 to 150 ^{o}C**

Disadvantages for Magnetron Sputtering

- An erosion track in the target
  - This leads to poor efficiency of sputtering yield versus target volume compared to non-magnetron sputtering
- Non-uniform removal of particles from target result in non-uniform films on substrate

http://www.mse.ncsu.edu/WideBandgaps/classes/MAT%20751%20S03/Sputtering/
Magnetron_Ihlefeld.pdf
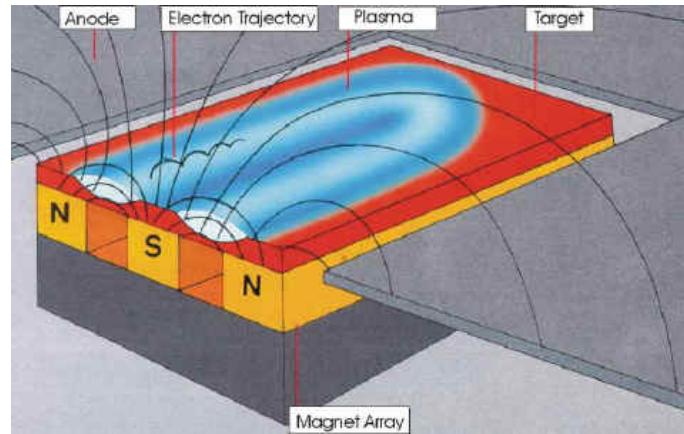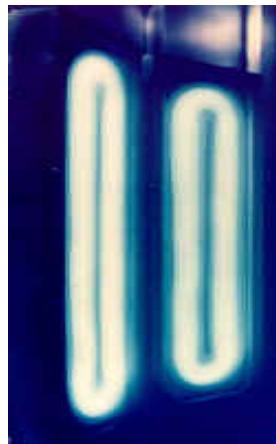
Reactive Sputtering

Sputtering metallic target in the presence of a reactive gas mixed with inert gas (Ar)

• *A mixture of inert +reactive gases used for sputtering*

oxides – Al_2O_3, SiO_2, Ta_2O_5 (O_2)
nitrides – TaN, TiN, Si_3N_4 (N_2, NH_3)
carbides – TiC, WC, SiC (CH_4, C_2H_4, C_3H_8)

Reactive Sputtering (Cont.)

- **chemical reaction takes place on substrate and target**

- **can poison target if chemical reactions are faster than sputter rate**

- **adjust reactive gas flow to get good stoichiometry without incorporating excess gas into film**

Reactive Magnetron Sputtering
Zinc Oxide Thin films

- Zinc oxide is one of the most interesting II/IV compound semiconductors It has been investigated extensively because of its interesting electrical, optical and piezoelectric properties

Reactive sputtering
is the best technique
for Zinc Oxide
deposition.

R. Ondo-Ndong , F. Pascal-Delannoy, A. Boyer, A. Giani, A. Foucaran, Materials Science and Engineering B97 (2003) 68 /73
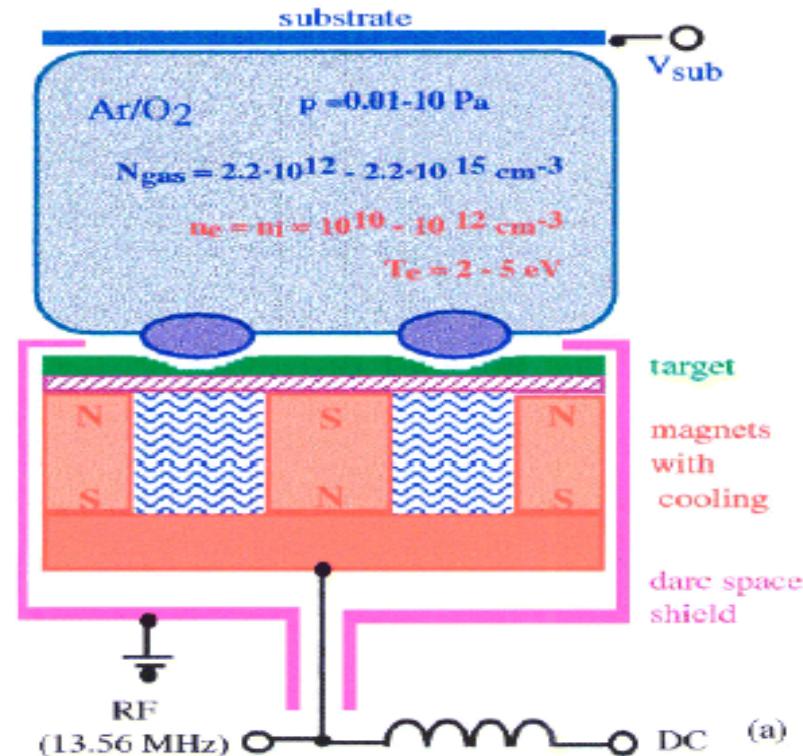
Process Parameters

Quality of the film dependents on deposition conditions, such as substrate temperature, deposition power, deposition pressure and argon–oxygen flow.

Parameters of sputtering deposition of ZnO

Target-substrate distance	50 mm
Sputtering pressure	3.35×10^{-3} Torr
Mixture gas	$A_r + O_2 = 20 - 80\%$
Power RF	100 W
Sputtering time	6 h
Substrate temperature	50–300 °C

Walter Water, Sheng-Yuan Chu,* Materials Letters 55 (2002) 67– 72

Conclusion

- Sputter deposition, also known as physical vapor deposition, or PVD, is a widely used technique for depositing thin metal layers on semiconductor wafers.

- The range of applications of sputtering and the variations of the basic process, is extremely wide.

Chemical vapor deposition

- Reactive carrier gases.

- Transport precursors of desired materials to the substrate surface.

- Gases react with other gases or decompose to produce stable reaction products and deposit on the substrate.

- Most versatile deposition techniques.

- Wide range of chemical reactions, reactants, and applications.

CVD

- Single-crystalline thin films.
- Polycrystalline thin films.
- Amorphous thin films.
- Semiconductors (IV, III-V, II-VI), metals, dielectric, superconductors.
- Microelectronics, optoelectronics, hard and protective coatings.

Chemical vapor deposition (CVD) : overview

- CVD (thermal)
  - APCVD (atmospheric)
  - LPCVD (<10 Pa)
  - VLPCVD (<1.3 Pa)
- PE CVD (plasma enhanced)
- Photon-assisted CVD
- Laser-assisted CVD
- MOCVD

Tensile stress causes concave bending of a thin substrate

Deposited film

Compressive stress causes convex bending of a thin substate

Deposited film
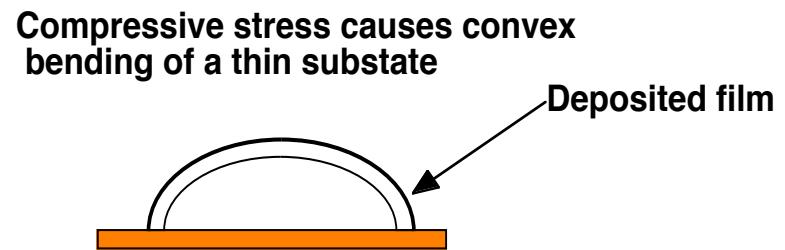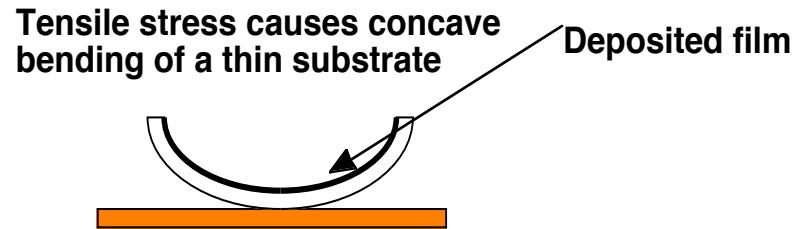
Chemical vapor deposition: reaction mechanisms

- Mass transport of the reactant in the bulk
- Gas-phase reactions (homogeneous)
- Mass transport to the surface
- Adsorption on the surface
- Surface reactions (heterogeneous)
- Surface migration
- Incorporation of film constituents, island formation
- Desorption of by-products
- Mass transport of by-products in bulk

CVD: Diffusive-convective transport of depositing species to a substrate with many intermolecular collisions-driven by a concentration gradient

Main Gas Flow Region

SiH_4

Gas Phase Reactions

Desorption of Volatile Surface Reaction Products

Redesorption of Film Precursor

Transport to Surface

Surface Diffusion

Adsorption of Film Precursor

Nucleation and Island Growth

Step Growth

Si
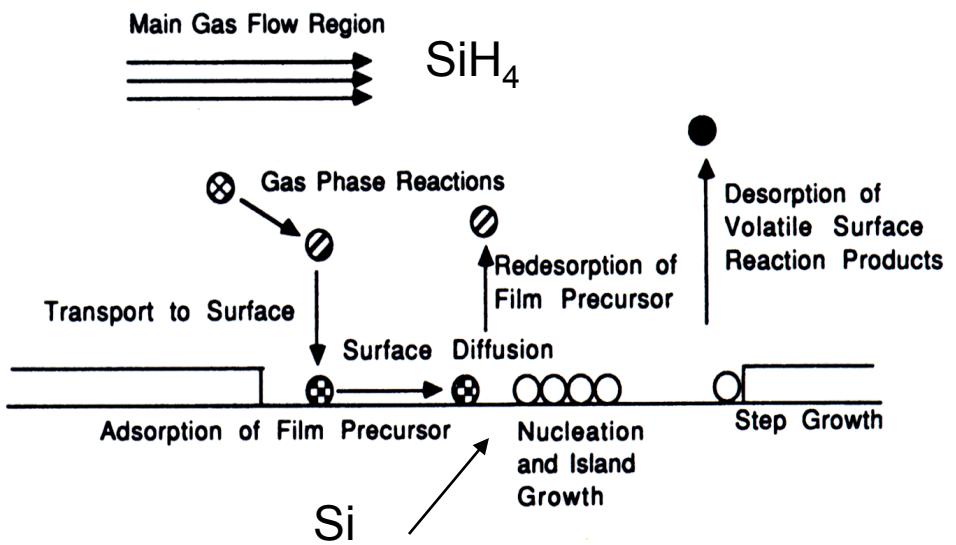
Chemical Vapor Deposition

Precursor → Reactor

Energy → Reactor

Reactor → Solid Products (thin films and powders)

Reactor → Gas Phase products
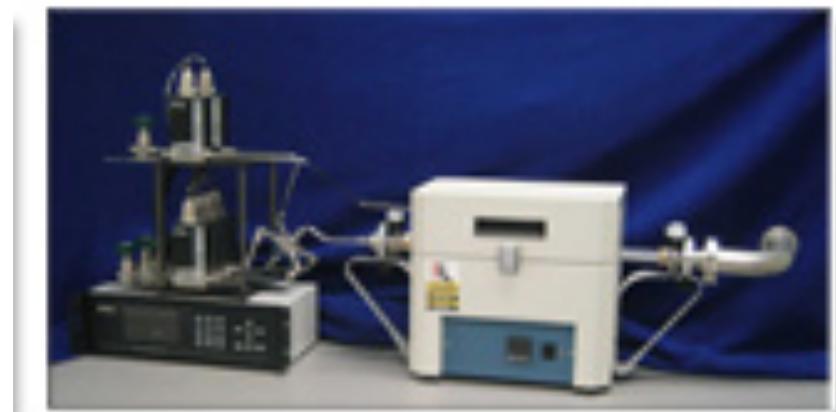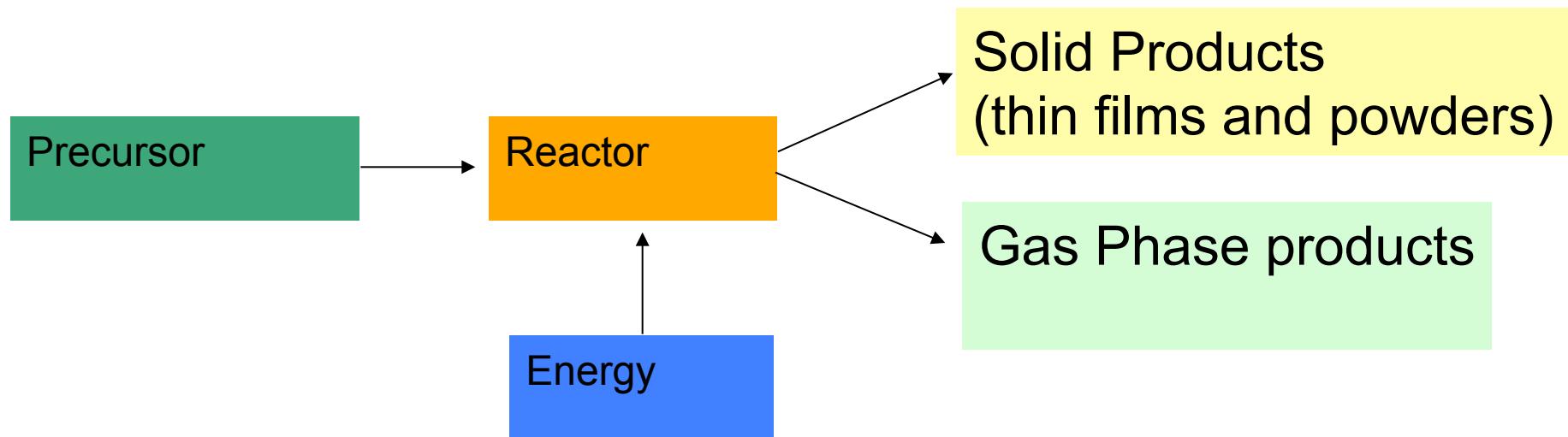
Precursor Considerations

Volatility
    vapor pressure - simple molecules with high vapor pressure are rare
    determined by molecular weight and molecularity (degree polymerized) - result of structure and bonding
    control - temperature, valving

Stability, Reactivity, and Safety
    bond strength, bond dissociation energy - affects process temperature and film composition (purity)
    thermal stability in storage and delivery into the reactor
    reactivity of the precursor and byproducts towards other substances (including biological objects like us)

Single-Source Precursor
    providing more than one element into the film
    simpler delivery system
    uniform elemental distribution at atomic level possible
    limited composition range

Common Precursors
    hydrides: MHx -
SiH4, GeH4, AlH3(NMe3)2, NH3, PH3 ...

    halides: MXy -
TiCl4, TaCl5, MoF6, WF6, ...

    metal-organics -
metal alkyls: AlMe3, AliBu3, Ti(CH2tBu)4 ....
metal alkoxides: Ti(OiPr)4, [Cu(OtBu)]4 ....
metal dialkylamides: Ti(NMe2)4, Cr(NEt2)4 ....
metal diketonates: Cu(acac)2, Pt(hfac)2 ....
metal carbonyls: Fe(CO)5, Ni(CO)4 ....
others: complexes with alkene, allyl, cyclopentadienyl, ... ligands
many precursors have mixed ligands

Energy sources and Reactor types

Thermal Energy
resistive heating - tube furnace
quartz tungsten halogen lamp (very good heat source) - radiant heating
radio-frequency - inductive heating
laser as thermal energy source

Photo Energy
UV-visible light
laser as photo energy source
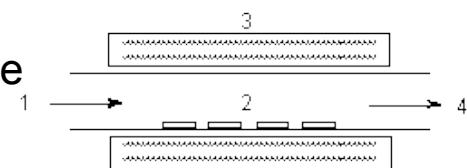
Horizontal Hot-Wall Reactor

Vertical Cold-Wall Reactor

1: precursor in
2: substrates
3: heater or furnace
4: exhaust

RF Power Supply

Parallel Plate Plasma Reactor

RF Power Supply
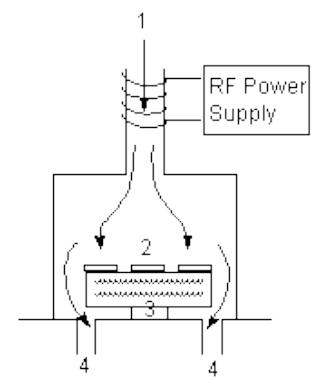
Inductive Tube Remote-Plasma Reactor

PECVD
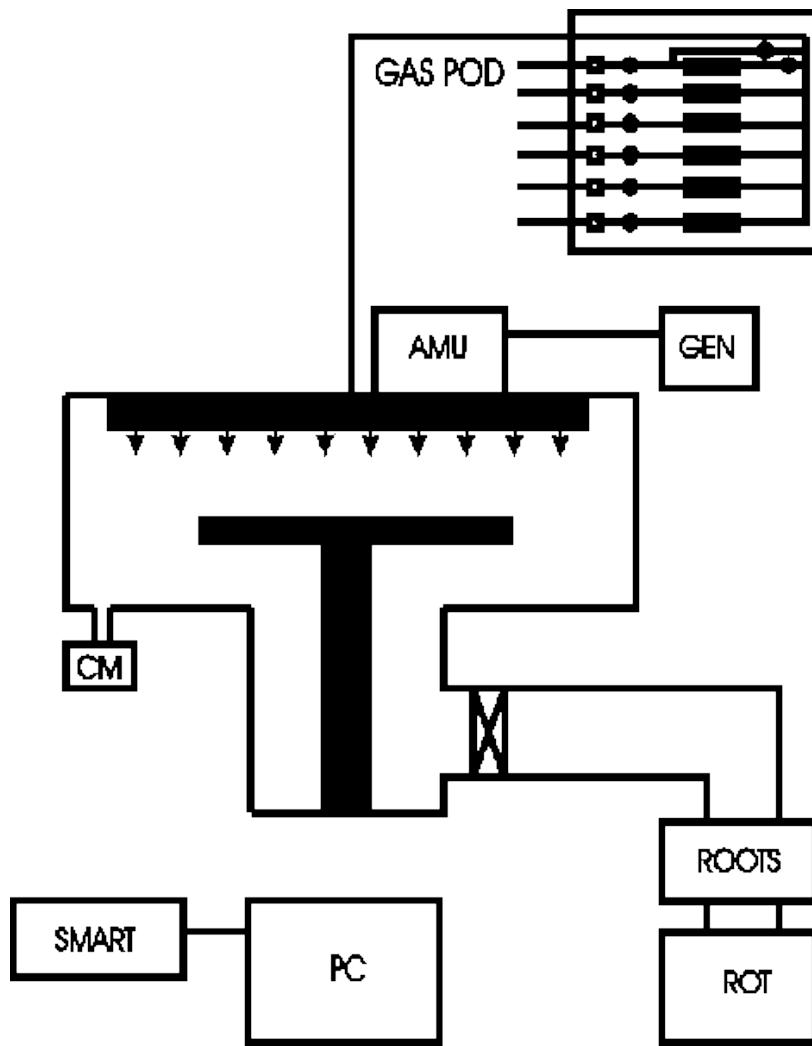
Thermally activated CVD

- Thermal energy (resistance heating, RF-heating, infrared radiation).

- Normal or low pressure.

- Inorganic materials.

MOCVD

- Thermal, glow discharge, ultraviolet radiation.
- Metalorganic compound (MO) gases or liquids.
- Epitaxial growth.
- Semiconductors (III-V, II-VI), high Tc superconductors, dielectric and metal films.

MOCVD

Ga(CH$_3$)$_3$ + AsH$_3$ => 3CH$_4$+GaAs
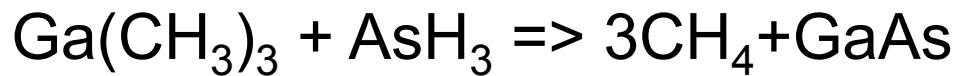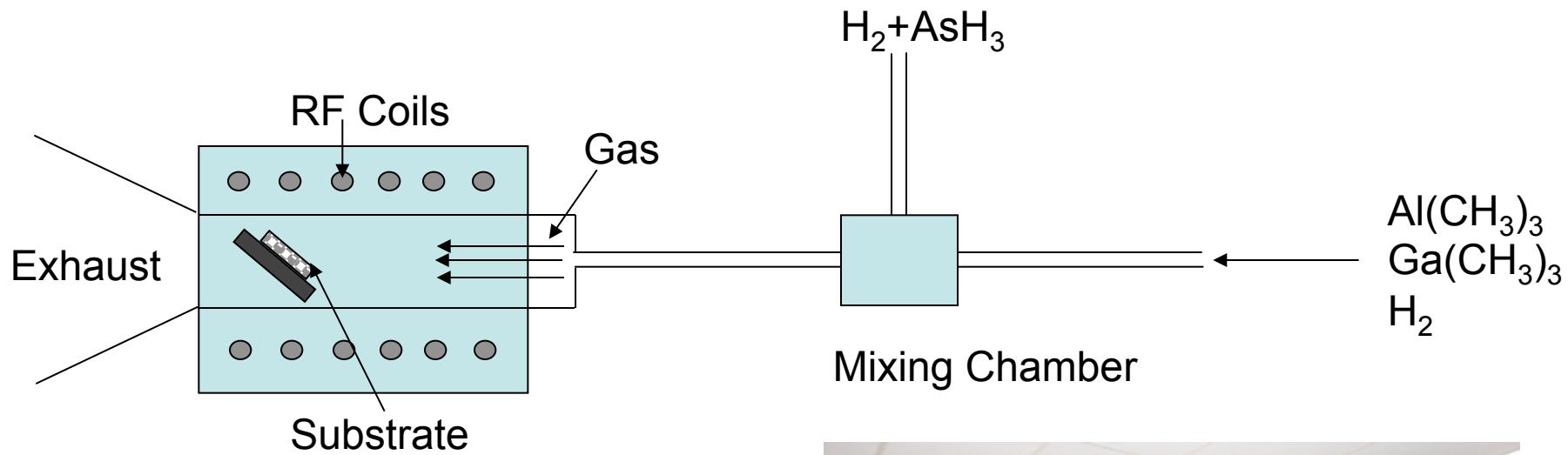
Plasma-enhanced CVD

- Use plasma to ionize and dissociate gases.
- Enhance growth rate.
- Lower temperatures.
- Low pressure.
- Deposite SiO_2, Si_3N_4 (temperature<350°C).

Photo-assisted CVD

- Use light to enhance the reaction rate.

- The effect of radiation is either a local heating of the water or a photochemical reaction.

- Photochemical reaction: Photolytic reaction.

Laser Assisted Vapor Deposition

He

H_2

SiH_4, SF_6, H_2
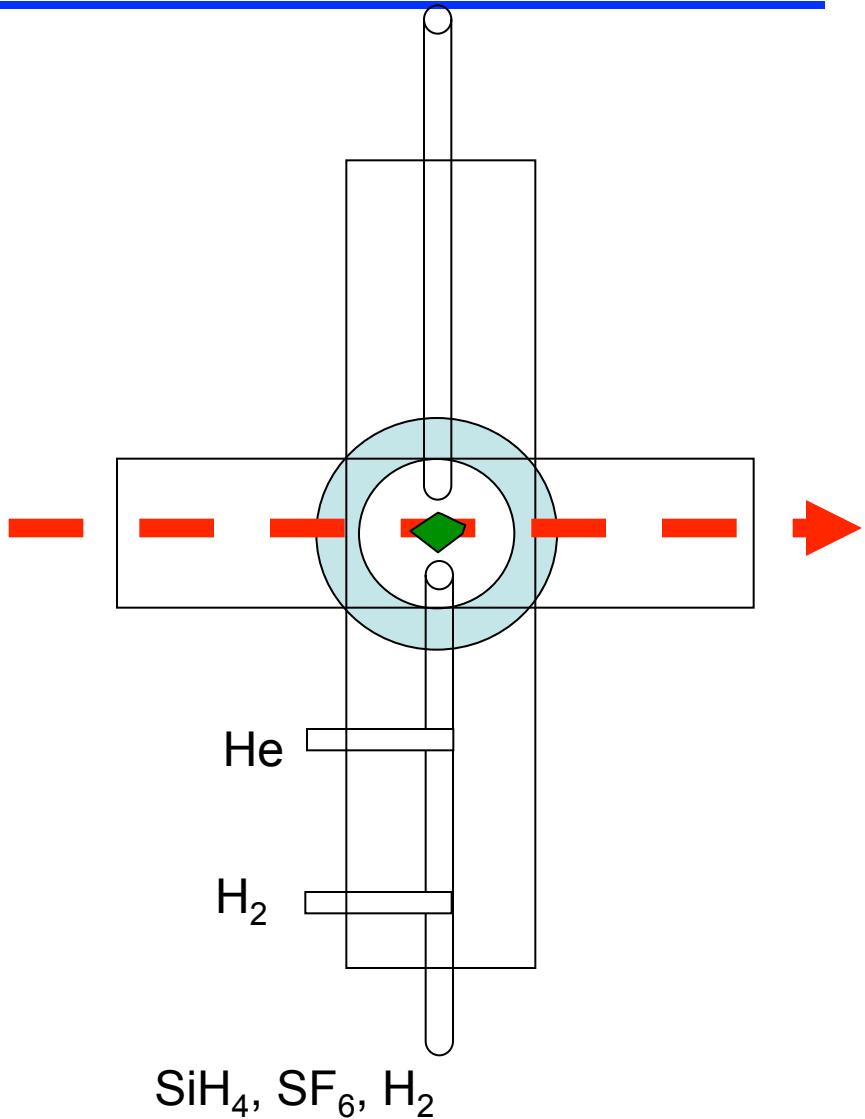
Chemical vapor deposition (CVD) : L-CVD

- The L-CVD method is able to fabricate continuous thin rods and fibres by pulling the substrate away from the stationary laser focus at the linear growth speed of the material while keeping the laser focus on the rod tip, as shown in the Figure . LCVD was first demonstrated for carbon and silicon rods. However, fibers were grown from other substrates including silicon, carbon, boron, oxides, nitrides, carbides, borides, and metals such as aluminium. The L-CVD process can operate at low and high chamber pressures. The growth rate is normally less than 100 μm /s at low chamber pressure (<<1 *bar*). At high chamber pressure (>1 *bar*), high growth rate (>1.1 *mm/s*) has been achieved for small -diameter (< 20 μm) amorphous boron fibers.

Lens

Substrate

Laser focus

Growing fiber
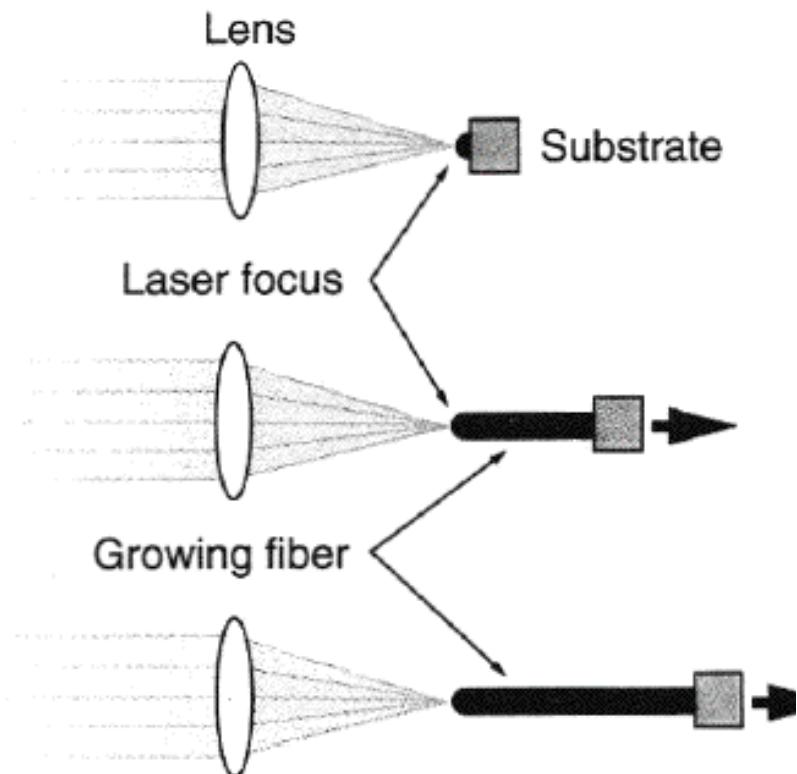
Laser Assisted Catalytic growth
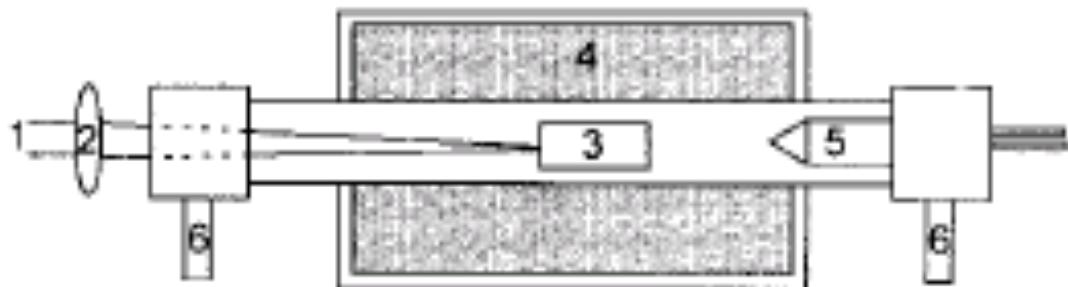
Fig. 2 Schematic of a nanowire growth set up using a combination of laser ablation and vapor-liquid- solid scheme
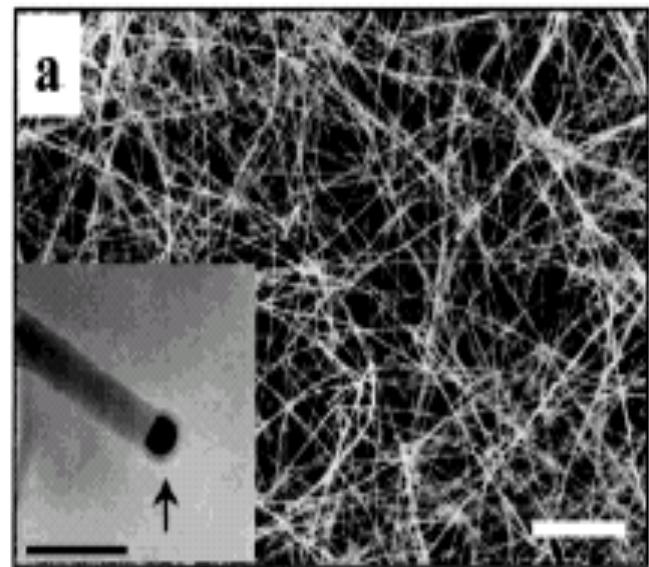

Fig.1 Semiconductor (GaAs) nanowires grown using laser assisted catalytic growth [1ref]. The scale bar corresponds to 50 nm.

Comparison of CVD

- Thermal CVD: Thermal, inorganic sources.
- MOCVD: Thermal, organometallic sources.
- PECVD: Plasma, low temperatures.
- PACVD: Light, low temperatures, selected area.
- ALE: Thermal/light, monolayer control.

Pressure ranges

- TACVD: 10^{-5} – 760 Torr.
- MOCVD: 10 – 760 Torr.
- PECVD: 0.01 – 10 Torr.
- PACVD: 10 – 760 Torr.
- ALE: 0.01 – 760 Torr.

CVD deposition system

- Rough vacuum chamber and sensors.

- Source materials (gas, vapor), gas carriers, gas flow control system.

- Chemical reaction sources: thermal heating (heaters), plasma generating sources to provide the needed energy for the chemical reactions.

- Substrates, holders.

Growth Mechanism

- Gas-phase: homogeneous reaction, diffusion of reactants to the substrate surface (mass transport), desorption of reaction by-products from the surface, diffusion of products into the main gas stream.

- Surface: adsorption of reactants at surface, heterogeneous chemical reactions, surface migration, lattice incorporation.

Pyrolysis

- Thermal decomposition of a compound by heat.
- Hydrides, metal carbonyls, organometallic compounds.
- Non-reversible process.
- Advantages: high reaction efficiency, low temperature, less chemical attack of the substrate.
- Disadvantages: gas-phase nucleation.

Reduction

- Many deposition reactions in CVD.

- Decomposition reaction favoured by the presence of another reactant (usually H_2) which helps to remove one or several of the decomposition products.

- The reversed reaction leads to etching.

- Reversible reaction.

- High temperatures.

Oxidation

- The reaction of a vapor-phas substance with oxygen or oxidant (CO_2, N_2O, NO, O_3), resulting in a solid film (oxide).

- Amorphous dielectric films (SiO_2, Al_2O_3, TiO_2), silicates glasses, oxide semiconductors (ZnO), oxide conductors (SnO_2, In_2O_3), magnetic films (LCMO).

Hydrolysis

- The gaseous compound reacts with externally or in situ formed water vapour leading to the formation of a solid film, usually an oxide.

- Amorphous and epitaxial films.

Nitridation

- The reaction between a gaseous reactant and ammonia (NH_3), nitrogen, hydrazine (N_2H_4) or another nitrogen-containing compound, leading to the formation of a thin nitride film.

- Silicon nitride (Si_3N_4), oxynitrides ($Si_xO_yN_z$, $Al_xO_yN_z$), semiconducting compound nitrides (BN, AlN, GaN), metallic nitrides (TaN, TiN) and superconducting nitrides (NbN).

Chemical Transport

- The transfer of a relatively non-volatile solid source reacting with a transport agent to form a volatile species.

Disproportion

- The dissociation of a reactant species due to its instability at a lower temperature and the formation of another more stable higher-valence chemical species,yielding at the same time the elemental form of the reactant to be deposited.

- A typical reaction: GaCl -> (low temp.) Ga + GaCl$_3$, GaCl<- (high temp.) Ga + GaCl$_3$.

Other reactions in CVD

- Catalysis: enhanced velocity of a reaction.

- Synthesis: a solid film results due to the reaction.

- Photolysis: a reaction due to the absorption of an ultraviolet light.

- Combined reactions: more than one reactions in a reaction.

Atomic Layer Deposition

- Surface controlled for epitaxial growth of single crystal.

- Originally designed for compound semiconductors, II-VI, III-V, oxides, nitrides.

- Epitaxy: Sequential saturated surface reactions to form a monolayer in each sequence.

- Release or exchange of ligands for saturation in each sequence.

ALD Process and Equipments

- Releases sequential precursor gas pulses to deposit a film one layer at a time.
- A first precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. Then a second precursor of gas is introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface.

  Two fundamental mechanisms:
  - *Chemisorption saturation process*
  - *Sequential surface chemical reaction process*

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

Example: ALD cycle for Al$_2$O$_3$ deposition

Tri-methyl aluminum Al(CH$_3$)$_{3(g)}$

Methyl group (CH$_3$)

Hydroxyl (OH) from surface adsorbed H$_2$O

Substrate surface (e.g. Si)
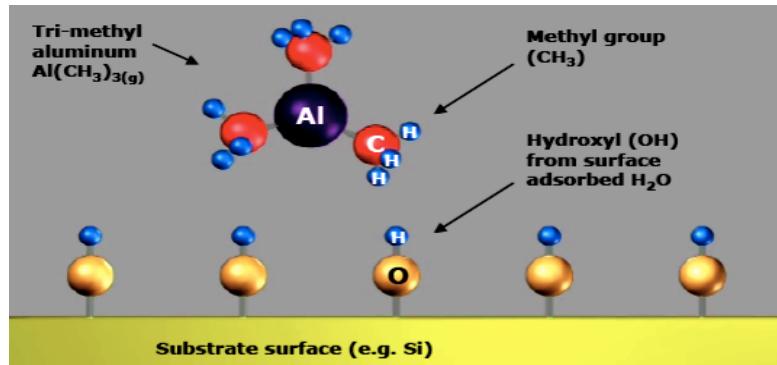
In air H$_2$O vapor is adsorbed on most surfaces, forming a hydroxyl group. With silicon this forms: Si-O-H $_{(s)}$

After placing the substrate in the reactor, Trimethyl Aluminum (TMA) is pulsed into the reaction chamber.

Methane reaction product CH$_4$

Reaction of TMA with OH

Substrate surface (e.g. Si)
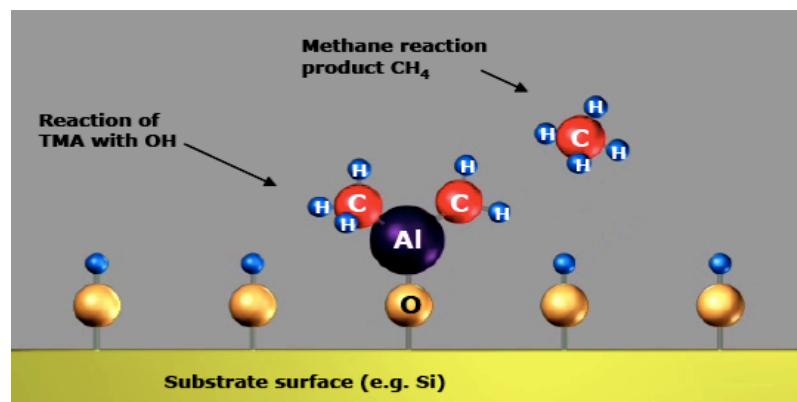
Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, producing methane as the reaction product

$$Al(CH_3)_{3\ (g)} + :Si\text{-}O\text{-}H_{\ (s)} \longrightarrow :Si\text{-}O\text{-}Al(CH_3)_{2\ (s)} + CH_4$$

Excess TMA

Methane reaction product CH$_4$

H
H C
H H
C
Al
**O**

Substrate surface (e.g. Si)
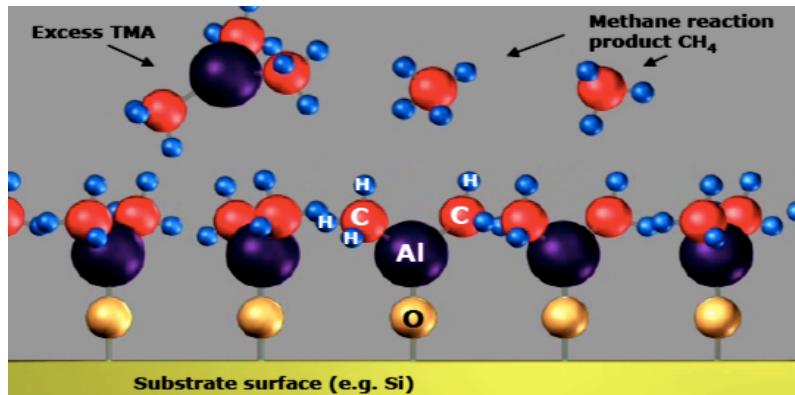
Trimethyl Aluminum (TMA) reacts with the adsorbed hydroxyl groups, until the surface is passivated. TMA does not react with itself, terminating the reaction to one layer. This causes the perfect uniformity of ALD. The excess TMA is pumped away with the methane reaction product.

H$_2$O

H O H

H
H C
H H
C
Al
O
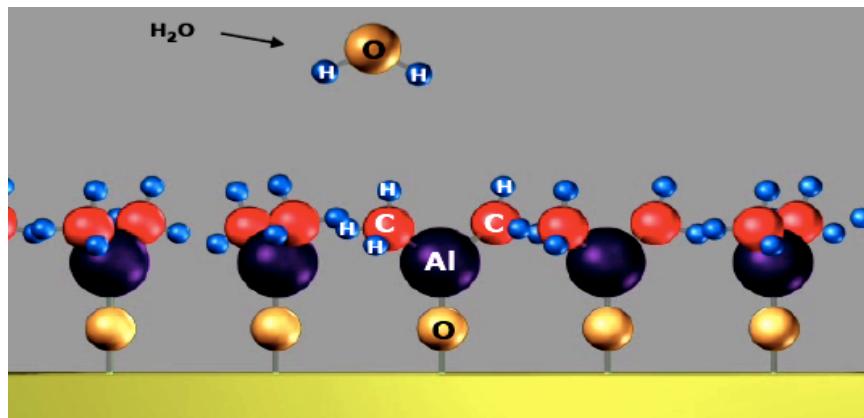
After the TMA and methane reaction product is pumped away, water vapor (H$_2$O) is pulsed into the reaction chamber.
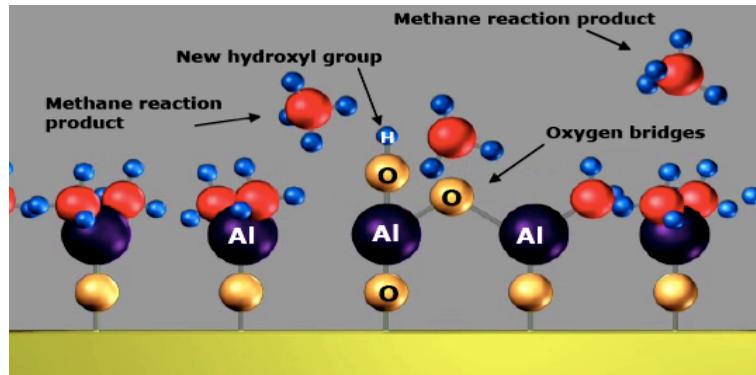
H₂O reacts with the dangling methyl groups on the new surface forming aluminum-oxygen (Al-O) bridges and hydroxyl surface groups, waiting for a new TMA pulse. Again metane is the reaction product.

$$2 \text{ H}_2\text{O}_{(g)} + :\text{Si-O-Al(CH}_3)_2{}_{(s)} \longrightarrow :\text{Si-O-Al(OH)}_2{}_{(s)} + 2 \text{ CH}_4$$
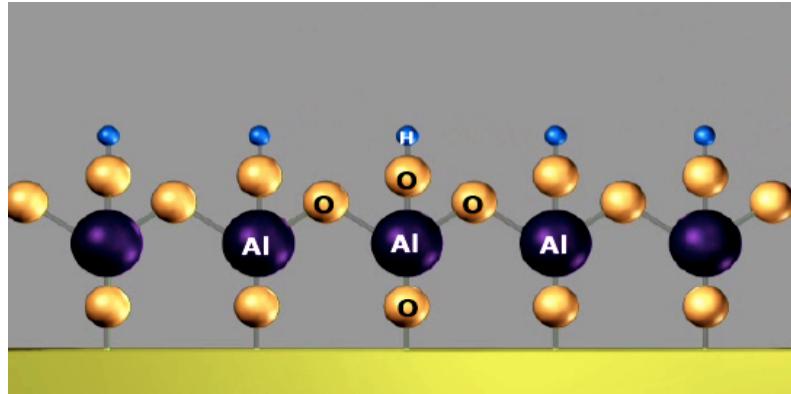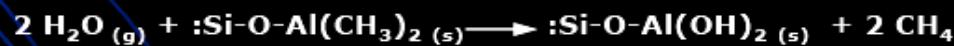
The reaction product methane is pumped away. Excess H₂O vapor does not react with the hydroxyl surface groups, again causing perfect passivation to one atomic layer.

ALD Process and Equipments

- Releases sequential precursor gas pulses to deposit a film one layer at a time.
- A first precursor gas is introduced into the process chamber and produces a monolayer of gas on the wafer surface. Then a second precursor of gas is introduced into the chamber reacting with the first precursor to produce a monolayer of film on the wafer surface.

  Two fundamental mechanisms:
  - *Chemisorption saturation process*
  - *Sequential surface chemical reaction process*

- **Example: ALD cycle for Al$_2$O$_3$ deposition (after 3 cycles)**
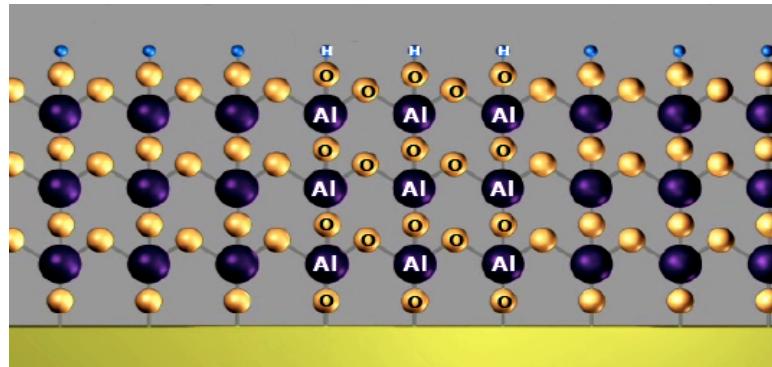
One TMA and one H$_2$O vapor pulse form one cycle. Here three cycles are shown, with approximately 1 Angstrom per cycle. Each cycle including pulsing and pumping takes e.g. 3 sec.

Two reaction steps in each cycle:

$$Al(CH_3)_{3\,(g)} + :Al-O-H_{\,(s)} \longrightarrow :Al-O-Al(CH_3)_{2\,(s)} + CH_4$$

$$2\,H_2O_{\,(g)} + :O-Al(CH_3)_{2\,(s)} \longrightarrow :Al-O-Al(OH)_{2\,(s)} + 2\,CH_4$$

Ref: "Atomic Layer Deposition," Cambridge NanoTech Inc., 24 April 06. <http://www.cambridgenanotech.com/>.

- Advantages
  - Stoichiometric films with large area uniformity and 3D conformality.
  - Precise thickness control.
  - Low temperature deposition possible.
  - Gentle deposition process for sensitive substrates.
- Disadvantages
  - Deposition Rate slower than CVD.
  - Number of different material that can be deposited is fair compared to MBE.

Laser ablation

- Pulsed laser deposition (PLD).
- Ultraviolet (UV) light (~200 nm – 400 nm).
- High energy (> 1 J/cm^2).
- Pulsed, not continuous, laser beam.
- Excimer laser: Gas laser, F$_2$ (157 nm), ArF (193 nm), KrCl (222 nm), KrF (248 nm), XeCl (308 nm), XeF (351 nm).
- Nd^{3+} :YAG laser: Solid state laser, Nd ions, yttrium aluminum garnet (YAG), 1064 nm, frequency doubled to 532 nm, mixed with 1064 nm to produce 355 nm or 266 nm.

PLD system

- Lasers: Excimer laser. 1 to 100 Hz repetition rates, 15 to 50 ns pulse duration.
- Optics: UV windows, mirrors, beam splitters.
- Vacuum chamber, pumps and gauges: High vacuum standard equipments.
- Gas flow: Oxygen.
- Target manipulation: Rotation.
- Substrate holder and heater.

Plating

- Deposition of a metal film using chemical reaction.
- Two types: Electroplating, electroless plating.
- Electroplating: Electrical contact required, conductive substrates, um thick films.
- Electroless plating: No electrical contact required, dielectrics and conductors, thin films.

Plating

- Non-vacuum system.
- Electroplating
- Electroless Plating
- Applications
  - Anticorrosion coatings, interconnect metallization formation.
  - Au, Ni coating for wire bonding.
  - Device interconnections.

Sol-gel coatings

- Resulting from spin coating, dipping or spraying a chemical solution onto a substrate.

- This solution is a stable mixture of suspended precursor particles known as a sol-gel.

- The gel is hardened to form a film by drying, typically in air, at about 100^oC.

Sol-Gel Coatings

- Non-vacuum system.
- Sol-gel
  - Metal alkoxide M(OR)x, R: alkoxy.
  - Sensors, optical coatings, transparent conductors.

Molecular beam epitaxy

- Epitaxy: Continuation of crystal structure from the substrate to the film.

- Single crystalline contaminant-free film.

- Single atomic layer (monolayer) growth.

- Small mismatched lattice constant (<1%).

- Ultrahigh vacuum: $<5\times10^{-11}$ torr.

- Non-epitaxy films: amorphous or polycrystalline.

Molecular Beam Epitaxy
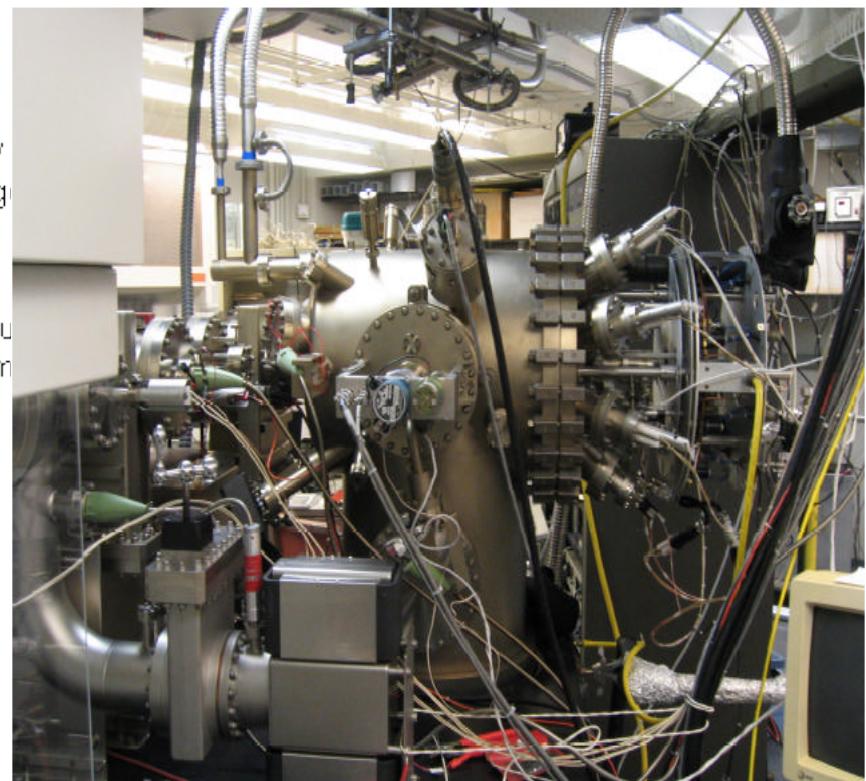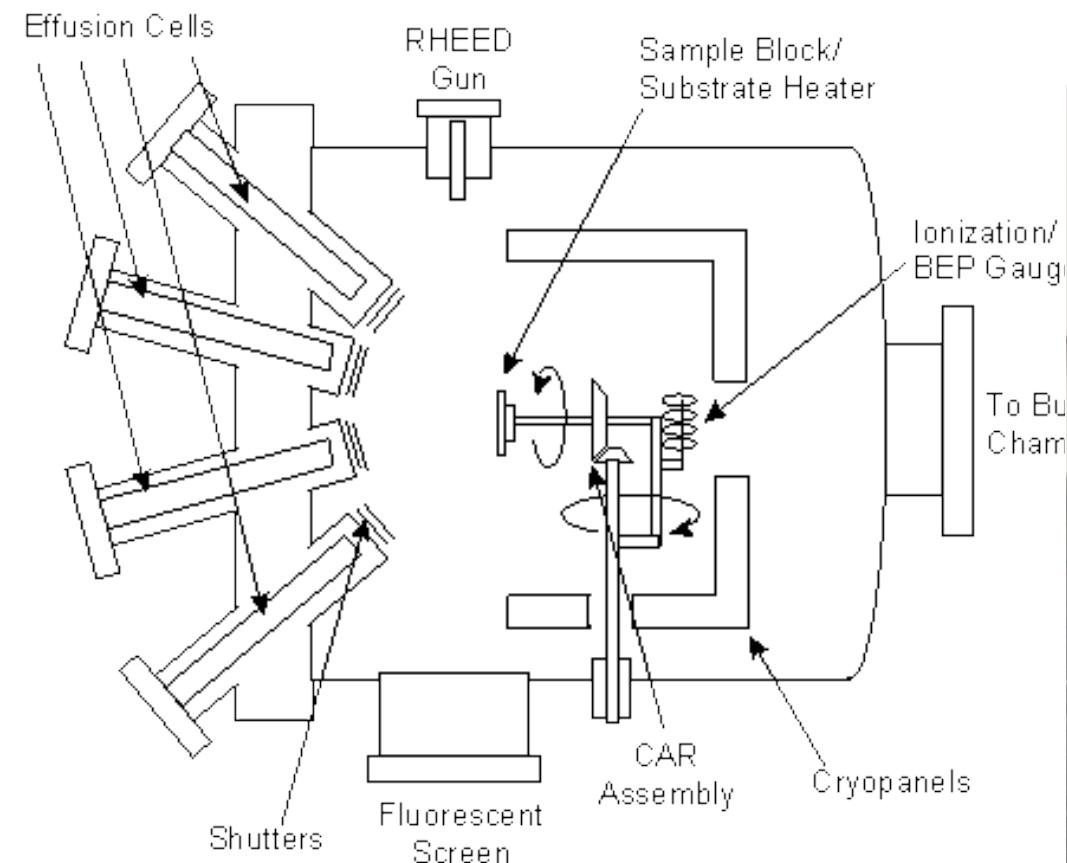
MBE deposition system

- Load lock for substrate loading & unloading.

- Liquid nitrogen shroud to cool the wall.

- Substrate heating: clean surface.

- Film growth: ultrahigh vacuum, shutters to control the flux, in-situ analysis and thickness monitor (RHEED) to control the deposition rate.

RHEED

- Reflection high energy electron diffraction.
- High energy: > 10 KeV.
- Small (grazing) angle incidence (<3°).
- Low depth penetration: < 100 A.
- Lateral ordered structure: Surface structure symmetry, lattice constant.

RHEED

'2 x' Pattern
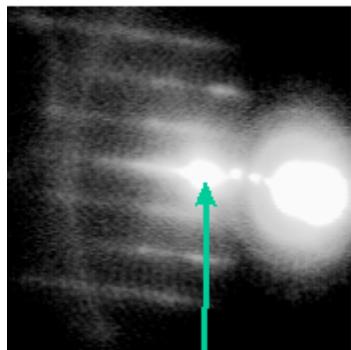
Specular Reflection

'4 x' Pattern
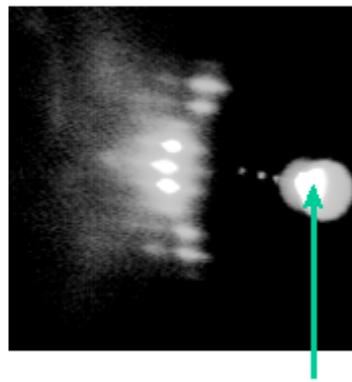
Straight-Through Beam
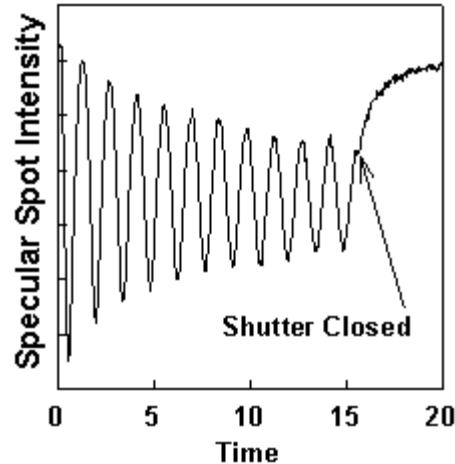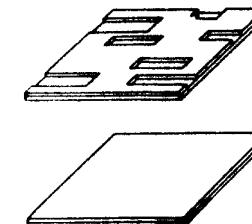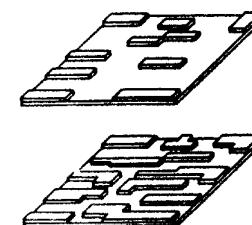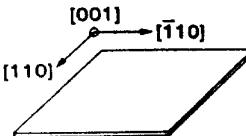
MONOLAYER GROWTH   ELECTRON BEAM   RHEED SIGNAL

[001]   [$\bar{1}$10]   [110]

$\bar{\theta} = 0$

$\bar{\theta} = 0.25$

$\bar{\theta} = 0.5$

$\bar{\theta} = 0.75$

$\bar{\theta} = 1.0$

Specular Spot Intensity

Shutter Closed

0   5   10   15   20

Time

MBE film growth

- Single crystalline substrate with lattice matching to the film.

- Heating (500^oC to 550^oC for GaAs, 700^oC to 900^oC for Si) to remove the surface contamination.

- Layer by layer growth: controlled by high speed shutters and thickness monitor (or RHEED).

Quantum Dots Grown Using MBE

"Electronic Structure of InAs Pyramidal Quantum Dots" :
http://www.sst.nrel.gov/research/InAs.html
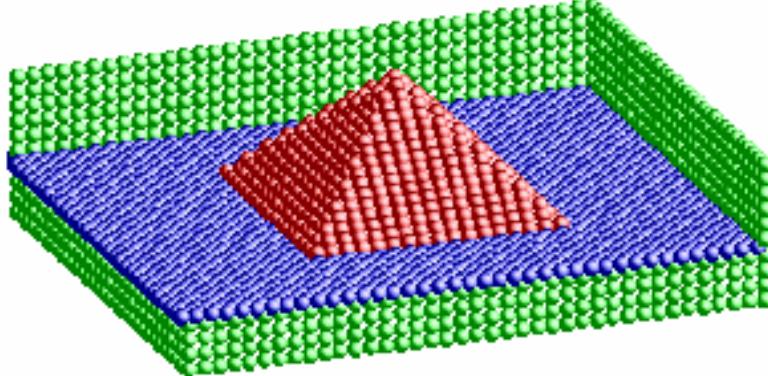
- 🔴 InAs Pyramid
- 🔵 InAs Wetting Layer
- 🟢 GaAs Matrix

AFM
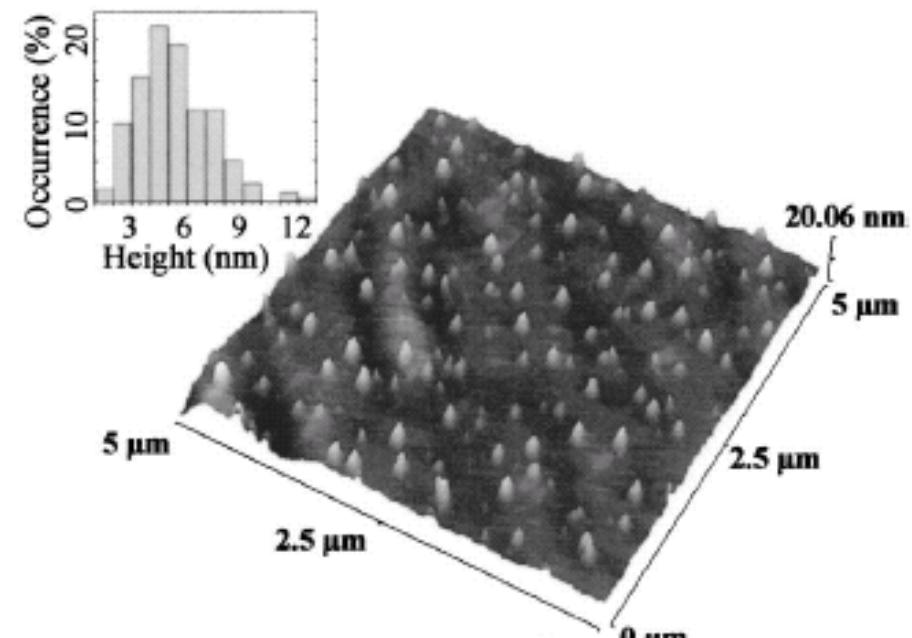
Three-dimensional AFM image of CdSe QDs deposited on ZnCdMgSe barriers. The inset shows a histogram of the QD height [Courtesy: Prof. Tamargo' S group- CCNY].
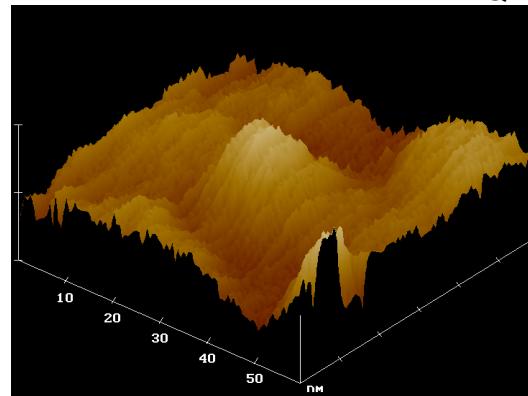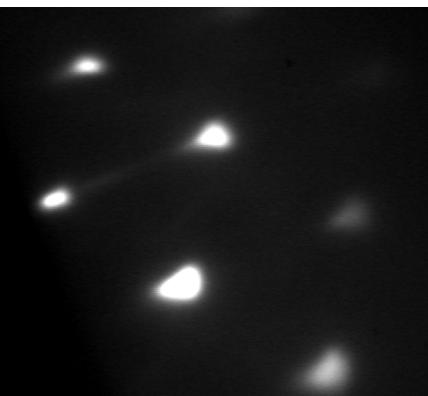
Nanostructure fabrications

- Bottom-up approach: Growth and self-assembly to build nanostructures from atomic or molecular precursors. (There is plenty of room at the bottom).

- Top-down approach: Lithographic patterning to structure macroscopic materials at the nanoscale. ("There is plenty of room at the top", Jean-Marie Lehn).

Nanowire preparations

- Specific substrate crystallographic structures.
- Catalytic growth by a liquid droplet in vapor-liquid-solid process.
- Template: Anodic aluminum oxides.
- Self-assembly.
- Lithography.

Nanoparticle preparation

- Vapor condensation: Metallic and metal oxide ceramic nanoparticles. Inert gas condensation, thin film deposition (sputtering, thermal evaporation, chemical vapor deposition etc.).

- Chemical synthesis: In a liquid medium composed of various reactants. Sol-gel, electrodeposition.

- Solid-state processes: Mechanical processes (Grinding or milling) of bulk materials.