2nd semester lectures the 4th class

Dr. Ahmed Al-Ghaban

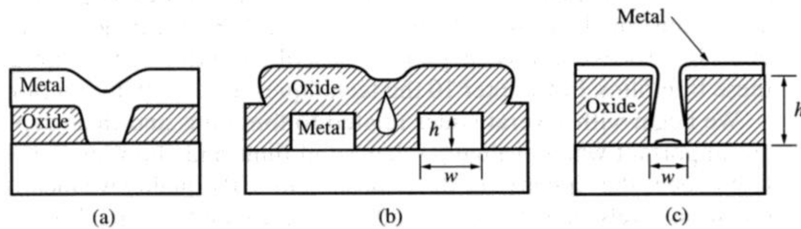
Thin Film Deposition

Topics:

- Chemical Vapor Deposition
- Physical Vapor Deposition
    - Evaporation
    - Sputtering
- Strengths and Weaknesses
- Basic Calculations

Issues related to thin film deposition

- Quality:
  - Composition
  - Defect density (e.g. pinholes)
  - Contamination
  - Mechanical and electrical properties
  - Good adhesion
  - Minimum stress
- Topography
  - Uniform thickness on non-planar surfaces
  - Step coverage
  - Conformal coverage: uniform
  - Space filling in holes, channels
  - Voids

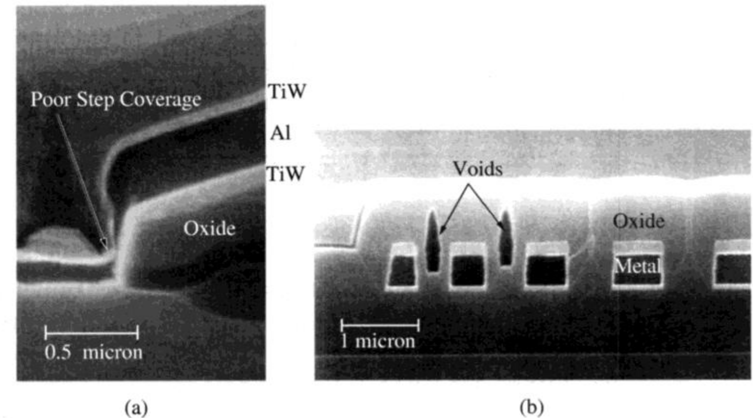


Thin film filling issues:

(a) shows good metal filling of a via or contact hole in a dielectric layer

(b) silicon dioxide dielectric filling the space between metal lines, with poor filling leading to void formation

(c) poor filling of the bottom of a via hole with barrier or metal



SEM photo showing typical coverage and filling problems

Classification of Thin Films

(a) single crystals
(b) epitaxial
(c) polycrystalline
(d) amorphous.

Properties of Thin Films

(a) high surface to volume ratio

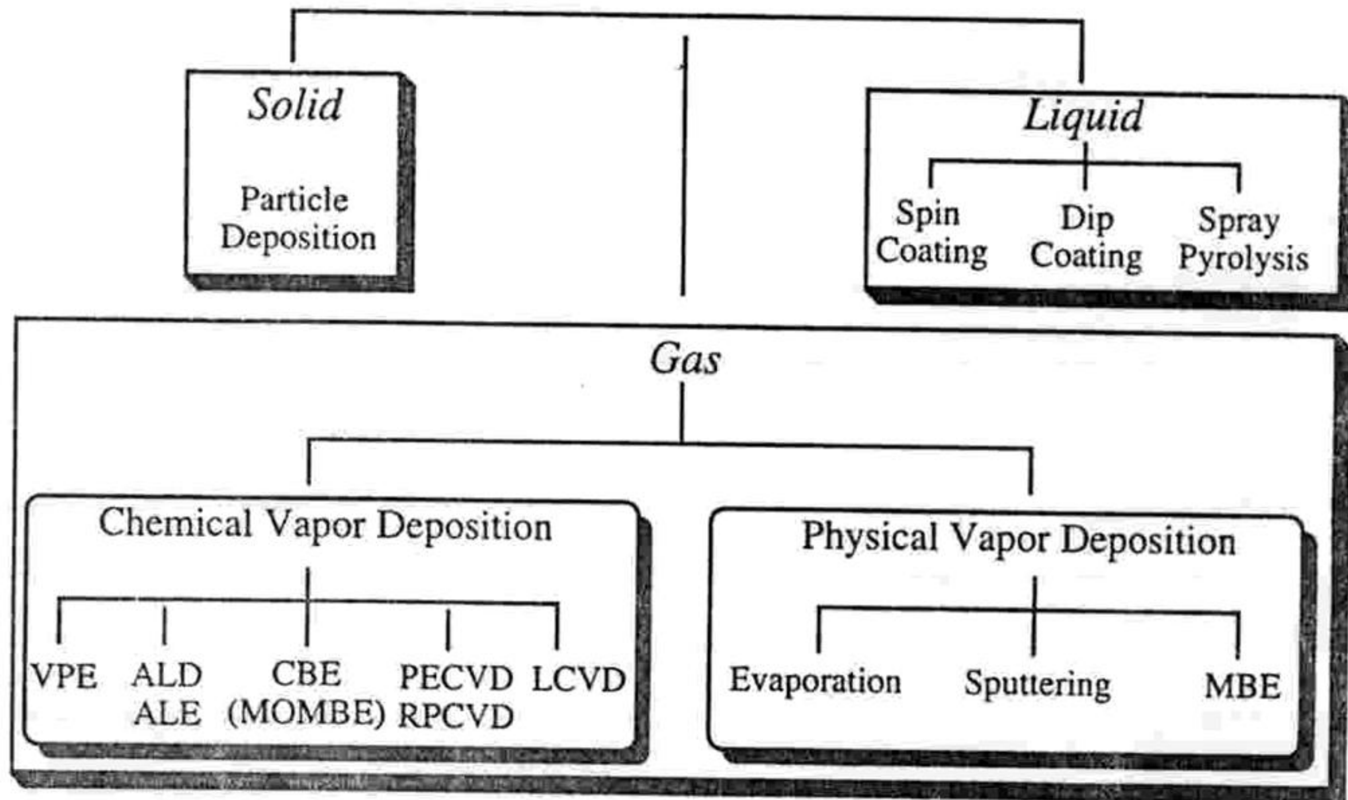
(b) geometrical control (dictated by substrate)

(c) compact

(d) single crystal like properties

Uses of Thin Films

(a) microelectronic devices
(b) telecommunication devices
(c) wear resistant coatings
(d) decorative coatings
(e) optical coatings (windows, solar cells, etc.)
(f) sensors
(g) catalysts



Scheme 5.1 Relationship of different film deposition methods.

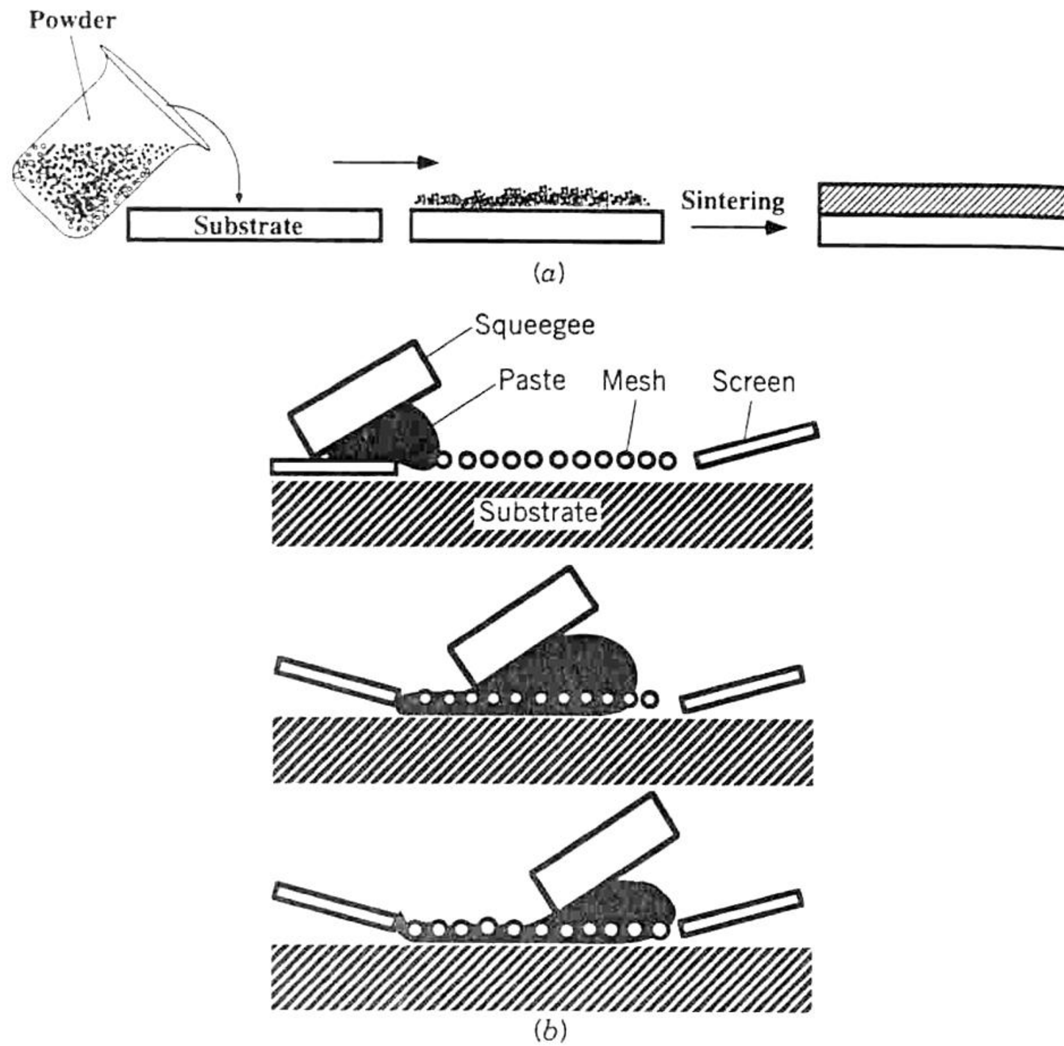


Figure 5.2 Schematic representation of an example of (*a*) solid-state deposition and (*b*) screen printing.

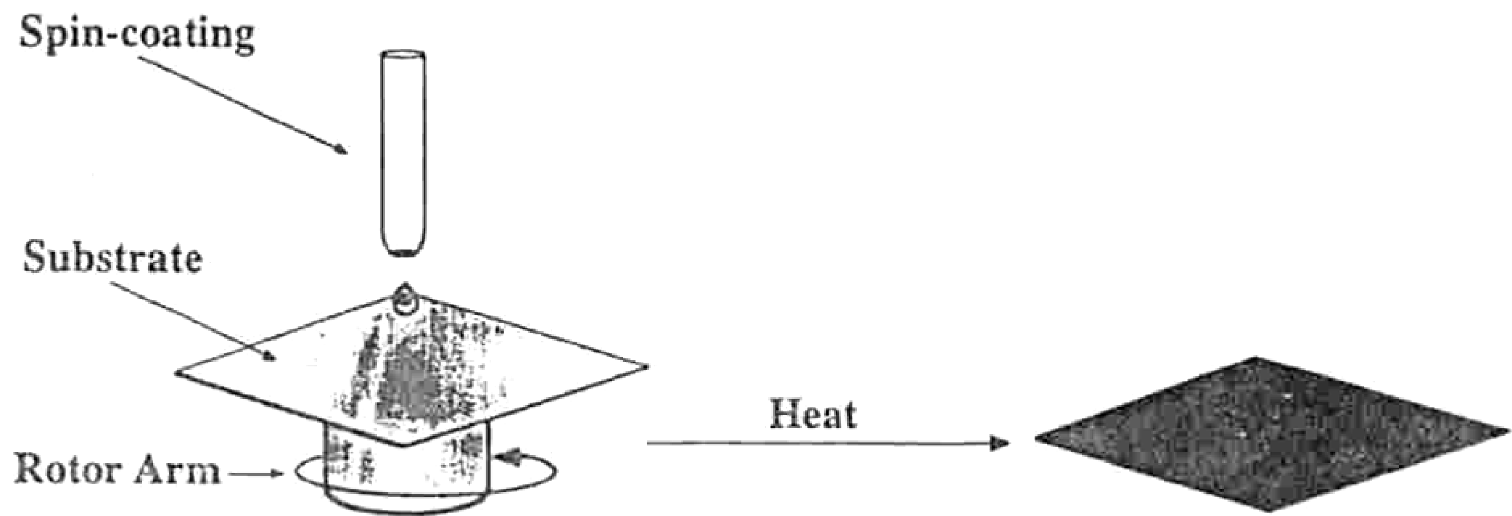
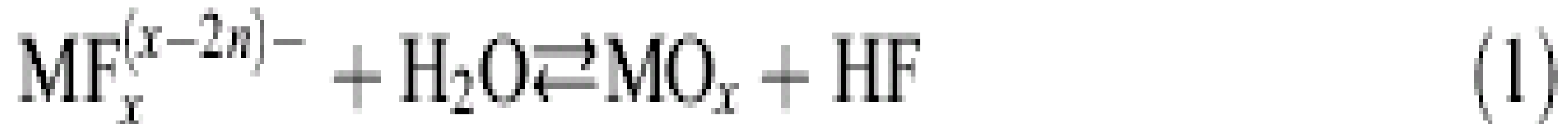
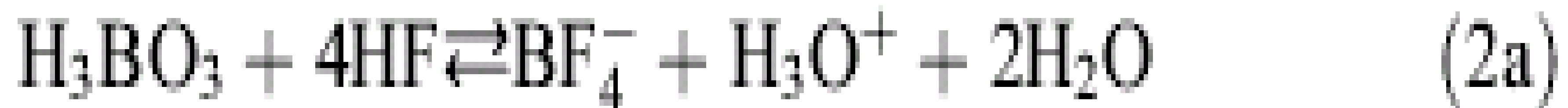


Figure 5.3 Schematic representation of liquid-phase deposition by spin coating.

liquid phase deposition process, LPD)



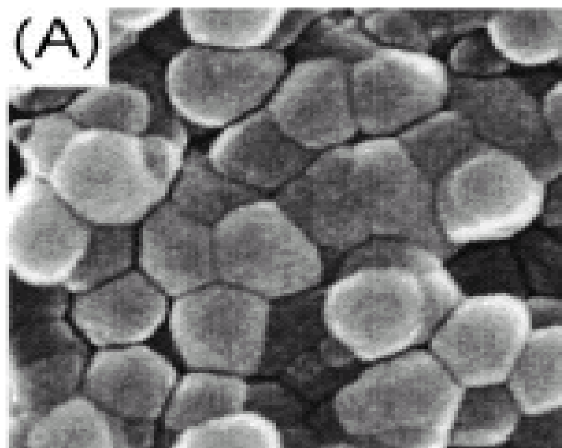
$$MF_x^{(x-2n)-} + H_2O \rightleftarrows MO_x + HF \quad (1)$$

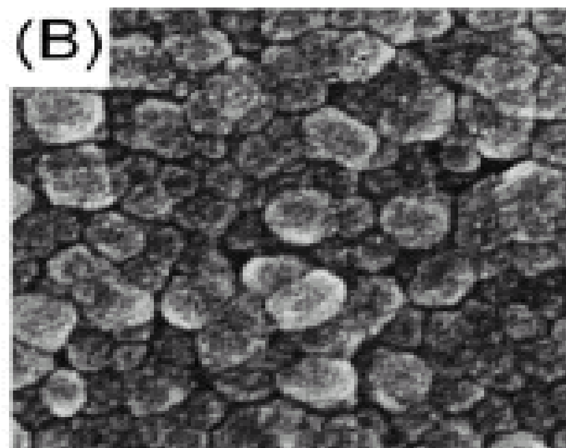


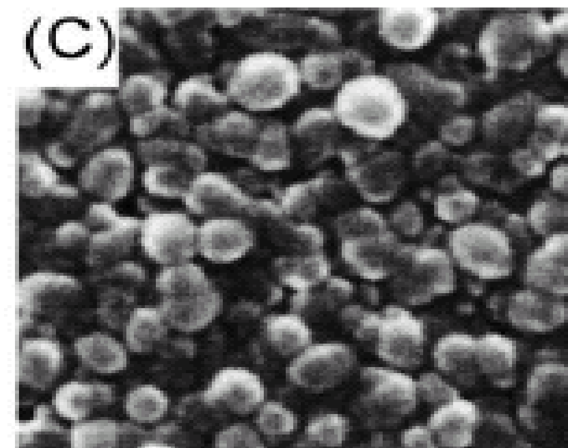
$$H_3BO_3 + 4HF \rightleftarrows BF_4^- + H_3O^+ + 2H_2O \quad (2a)$$

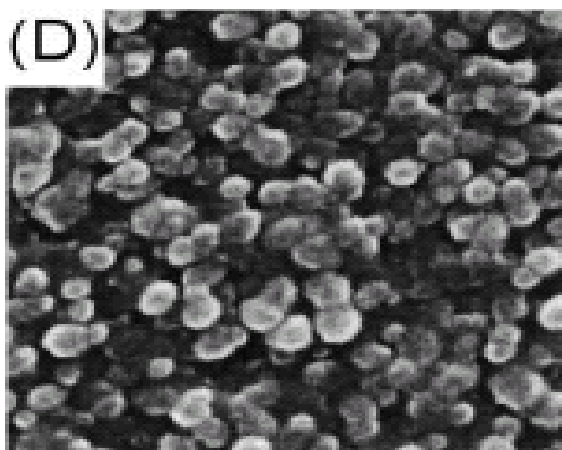
$$Al + 6HF \rightleftarrows H_3AlF_6 + 3/2H_2 \quad (2b)$$

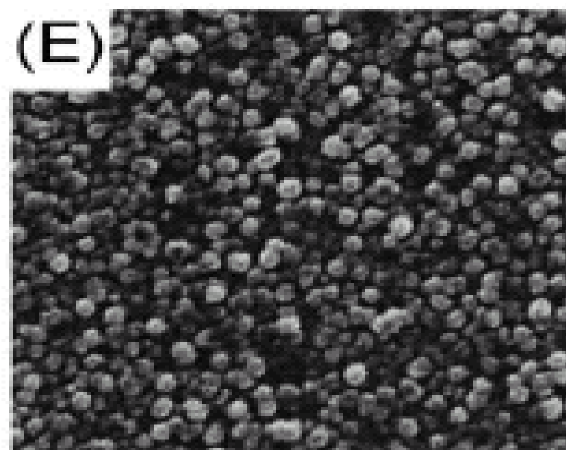
SEM images of the deposited h-FeOOH films at various concentrations. Concentration of H3BO3:
(A) 0.30, (B) 0.40, (C) 0.45, (D) 0.50, (E) 0.55, and (F) 0.60 mol dm^{-3}.

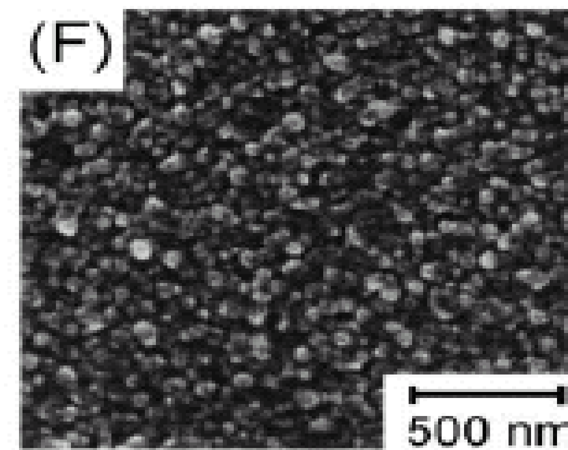












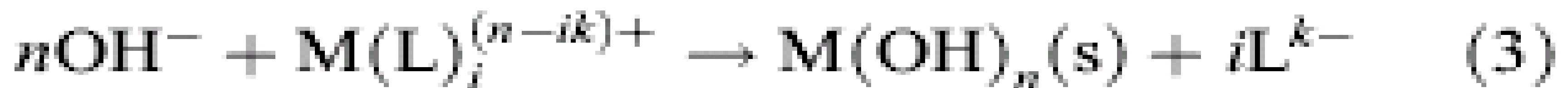
- LPD-grown silica has been widely tested for application in integrated circuit processing,
- and in metal-oxide-semiconductor (MOS)
- and in complementary metal-oxide-semiconductor (CMOS)
- LPD silica is being explored for use in waveguides
- and in MOS solar cells

Chemical bath deposition (CBD)

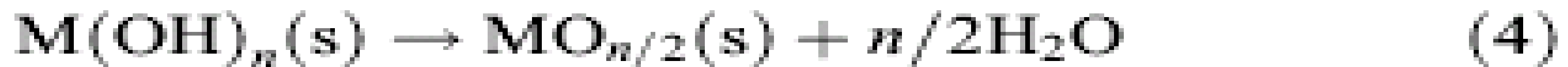
1) complexant-H_2O equilibrium:

2) dissociation of water:

3) displacement of ligands:



4) deprotonation to form oxide:



Some Principles involved

- while the water itself provides oxygen, initially in the form of OH^- ions.
- Hydrolysis can occur even in acidic solutions when the metal cation is easily hydrolyzable,

  as with Fe^{3+} , Ti^{4+} , Zr^{4+} , and Al^{3+}
- CBD requires supersaturated solutions, i.e. the concentrations must exceed the solubility product
- In a closed system, growth cannot continue once the reactants have been depleted below this point, which determines the thickness of the film

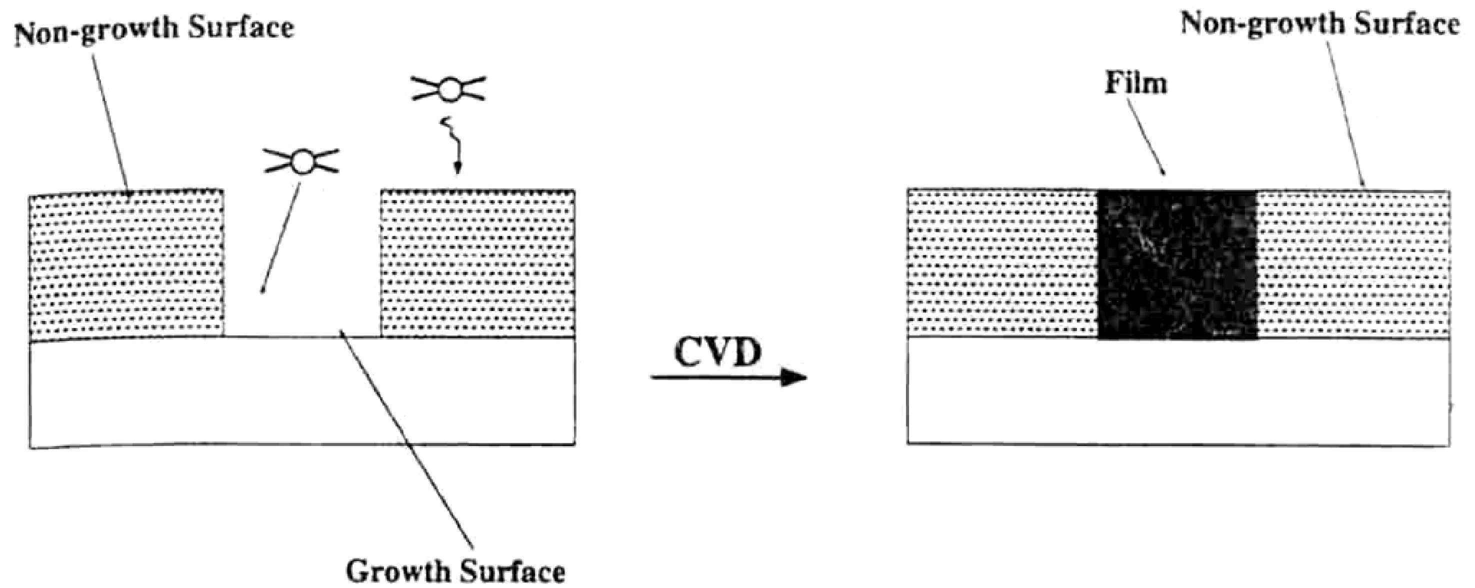
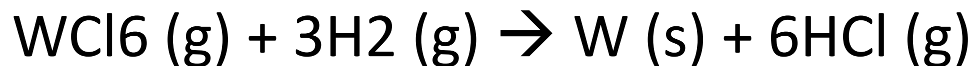


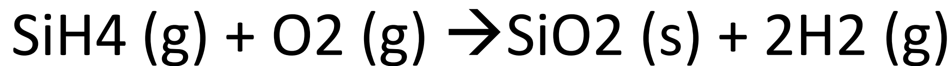
Figure 5.6 Schematic representation of selective deposition.

Chemical Vapor Deposition

- Involves one or more gas phase species which react on a solid surface (substrate) to deposit a solid flim.
- Typically, the reaction is initiated by heating the substrate. Other mechanisms of supplying the activation energy necessary to initiate reactions include: laser CVD, photo CVD, and plasma enhanced CVD.

- Typical Parameters
- Pressure 0.1 torr – 1 atm
  Substrate Temp. 100° C - 1500° C
  Deposition Rate 60Å/min – 300,000Å/min
- The use of organometallic precursors as gas phase species (MOCVD) can result in significant reduction of the substrate temperature.
- Examples


$WCl_6 (g) + 3H_2 (g) \rightarrow W (s) + 6HCl (g)$


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

$6TiCl_4 (g) + 8NH_3 (g) \rightarrow 6TiN (s) + 24HCl (g) + N_2 (g)$

Advantages

- High deposition rates
- Capable of accurate stoichiometry control
- High quality films (low defect concentration)
- No need for high vacuum components
- Favored in industrial settings

Disadvantages

- High operating temperatures
- Toxic Gases
- Generally applicable to binary and elemental films
- Not suitable for production of metastable products

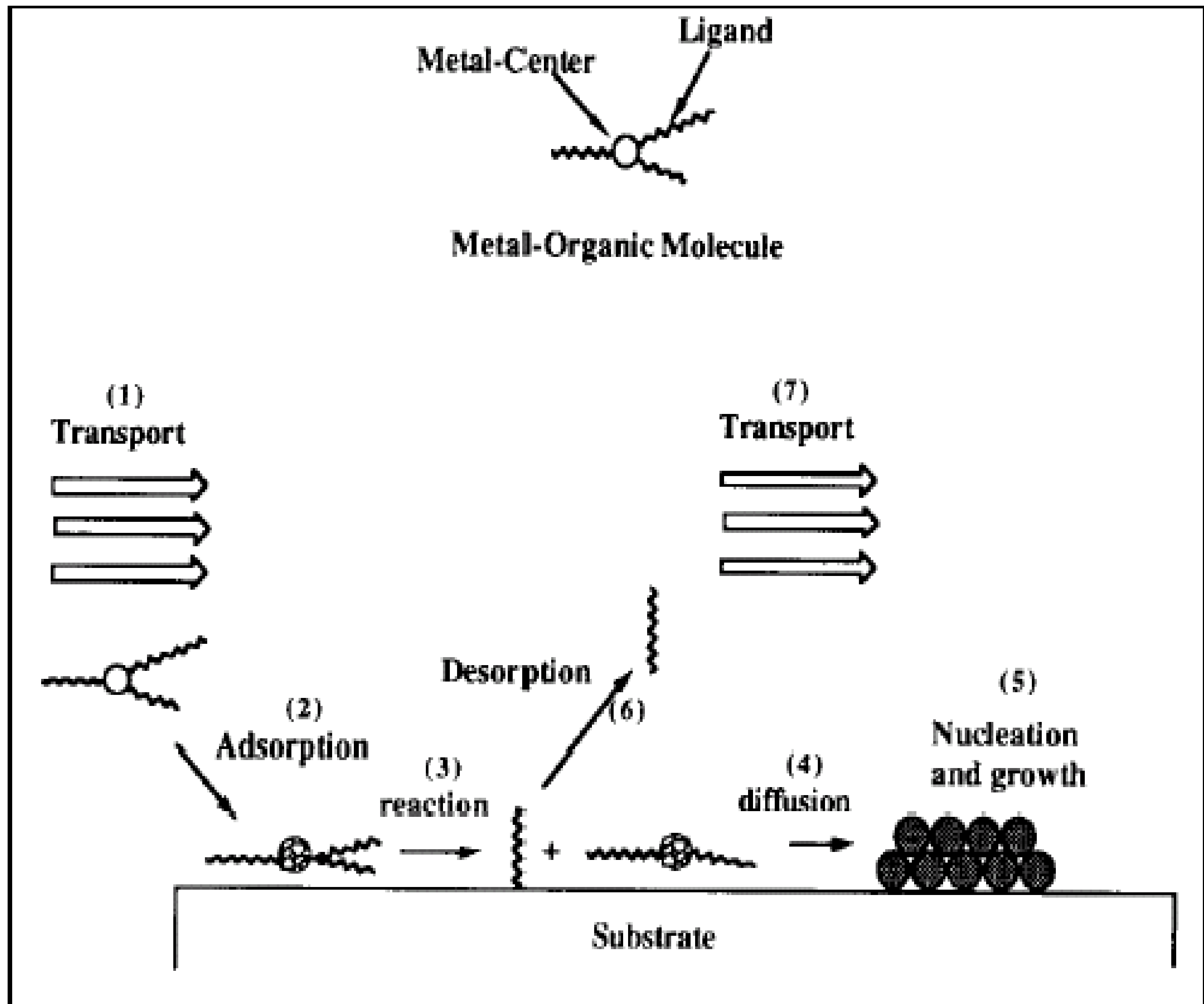


Fig. 2: An illustration of the process occurring in OMCVD.

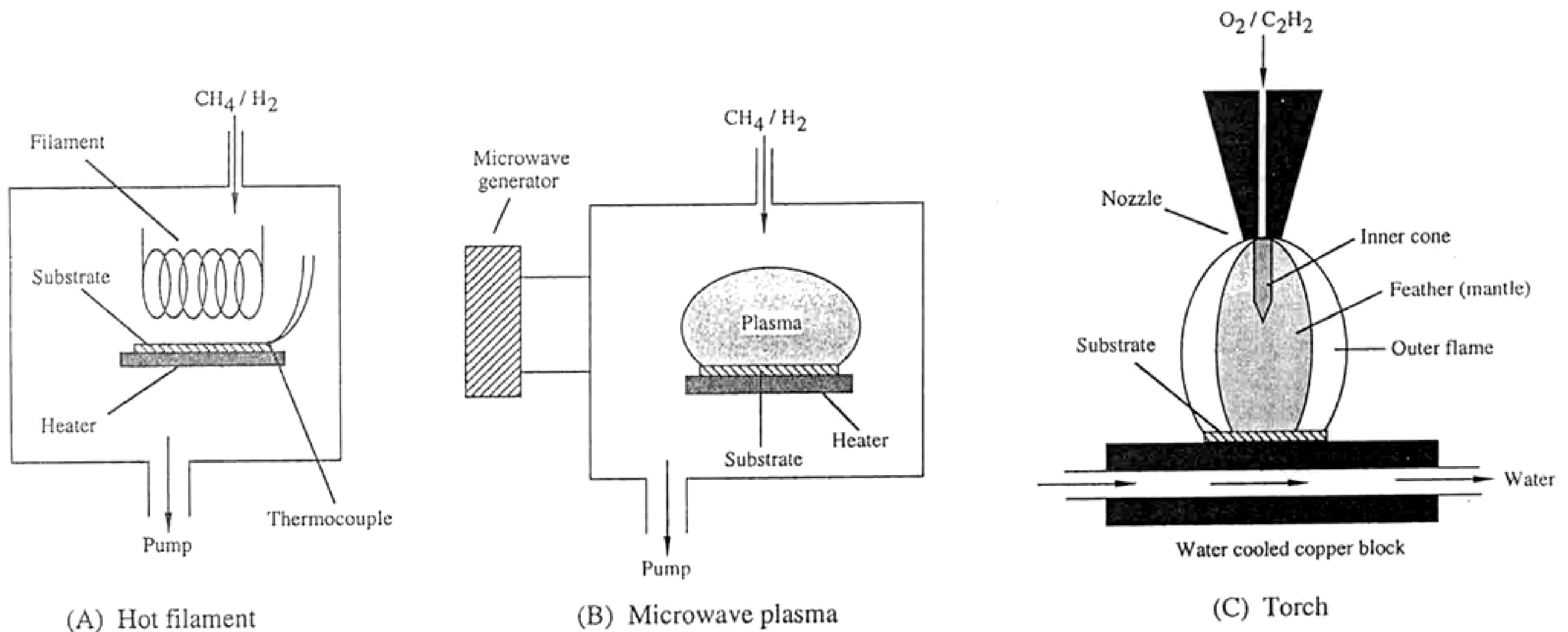


Figure 5.20 Schematic diagrams of three of the most commonly used types of diamond CVD apparatus: (*a*) hot filament reactor; (*b*) microwave-plasma-enhanced CVD reactor; (*c*) oxyacetylene torch.

Highly Organized Carbon Nanotube by Chemical Vapor Deposition

B. Q. Wei, R. Vajtai, Y. Jung, J. Ward, R. Zhang, G. Ramanath, P. M. Ajayan

with flowing argon to 100mTorr and heated gradually to 800 ˚C

SiO_2 layer

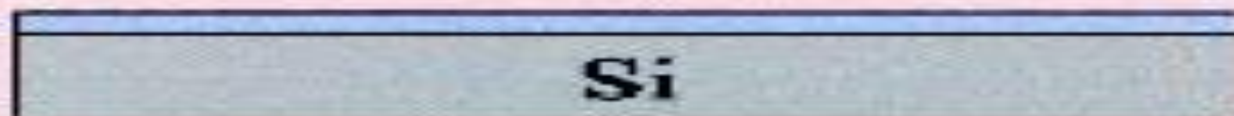
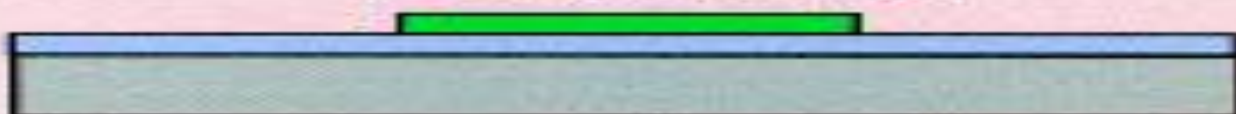
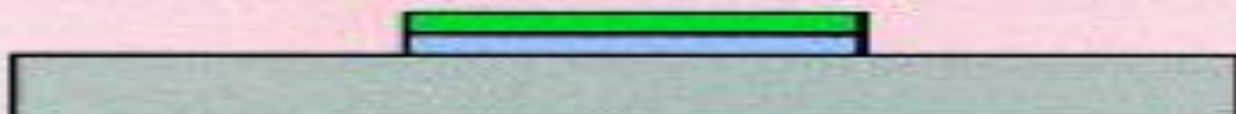


Photo-Resist

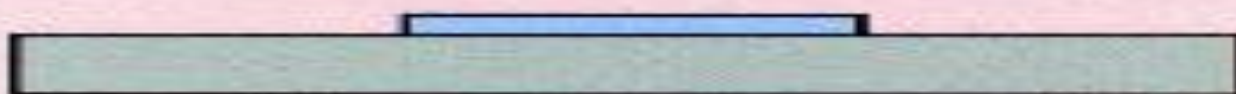
Developing



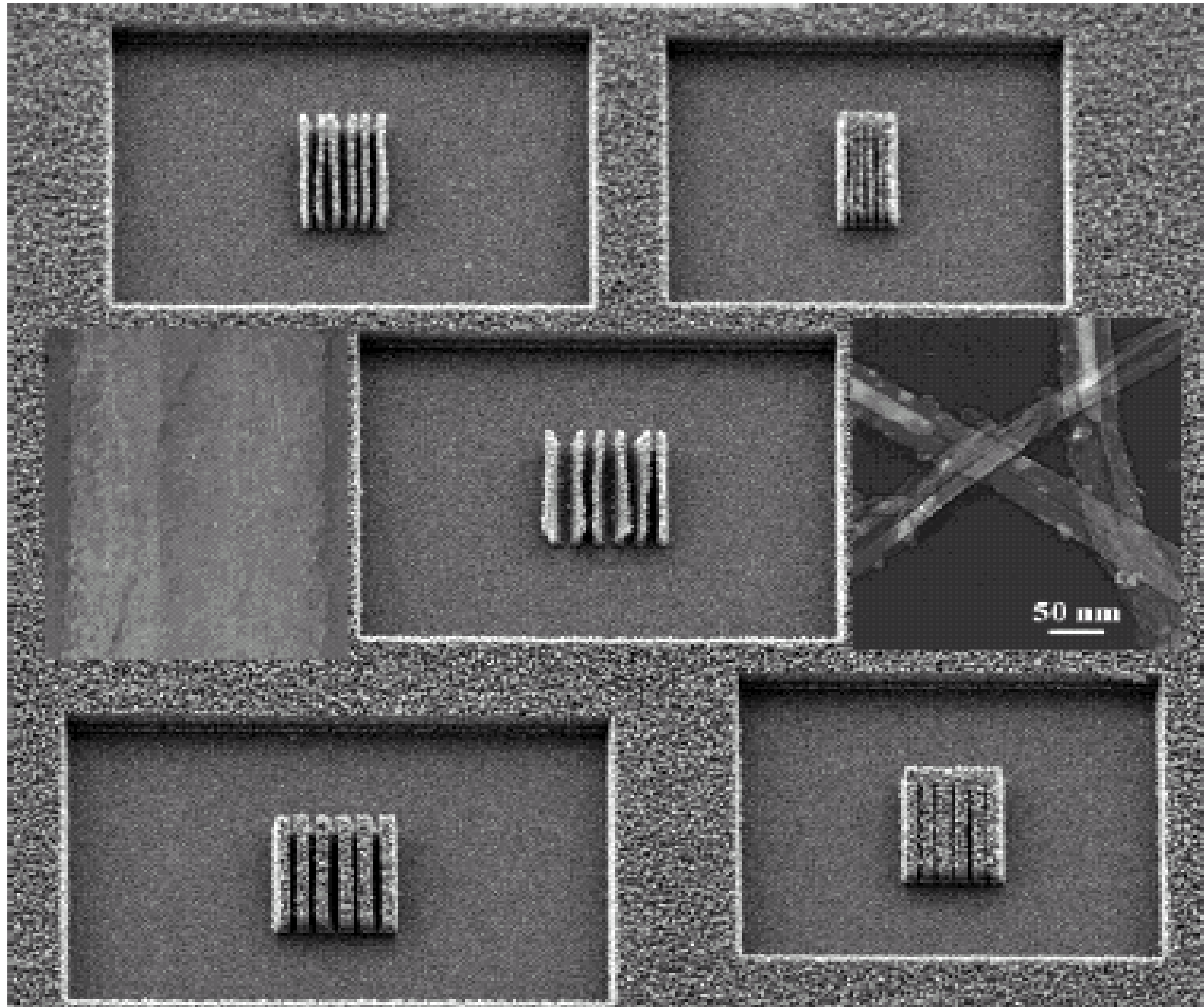
Etching



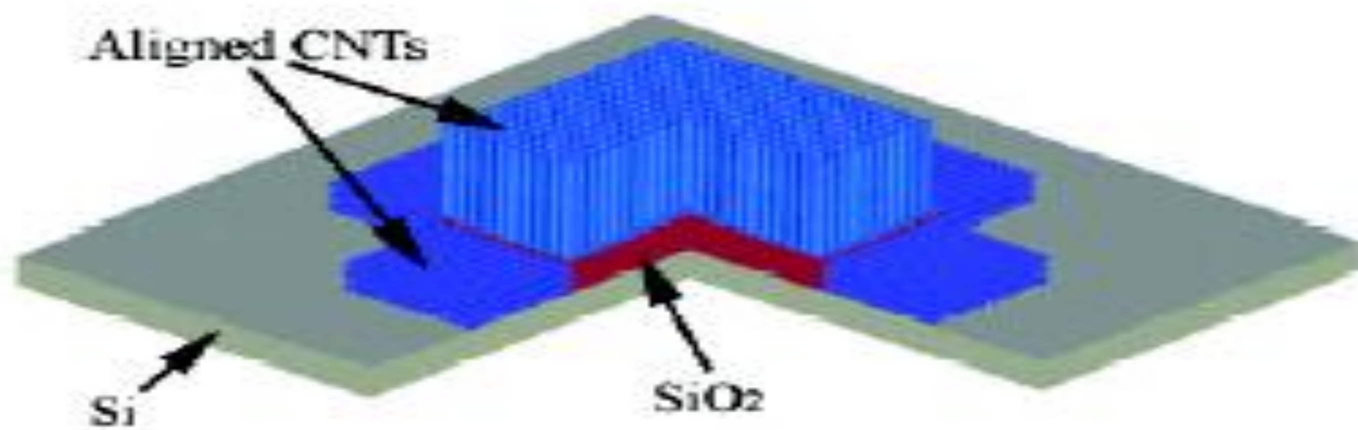
SiO_2/Si Patterns

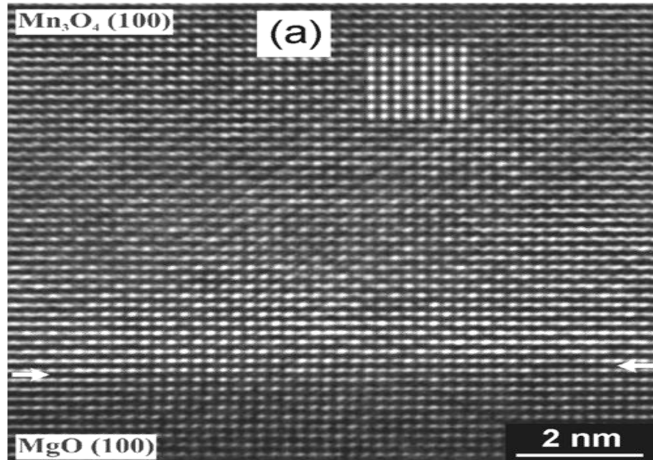


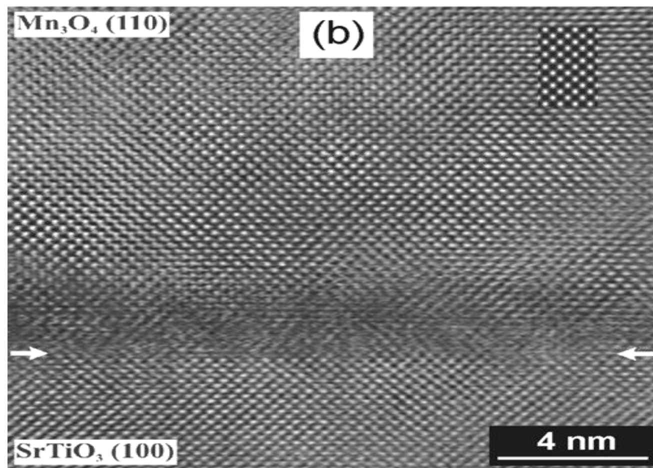
Growth of Nanotubes

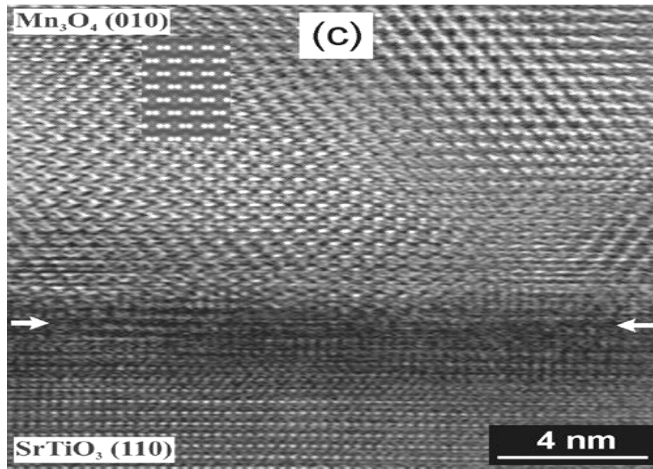

50 nm

20 μm


Aligned CNTs
Si
SiO2







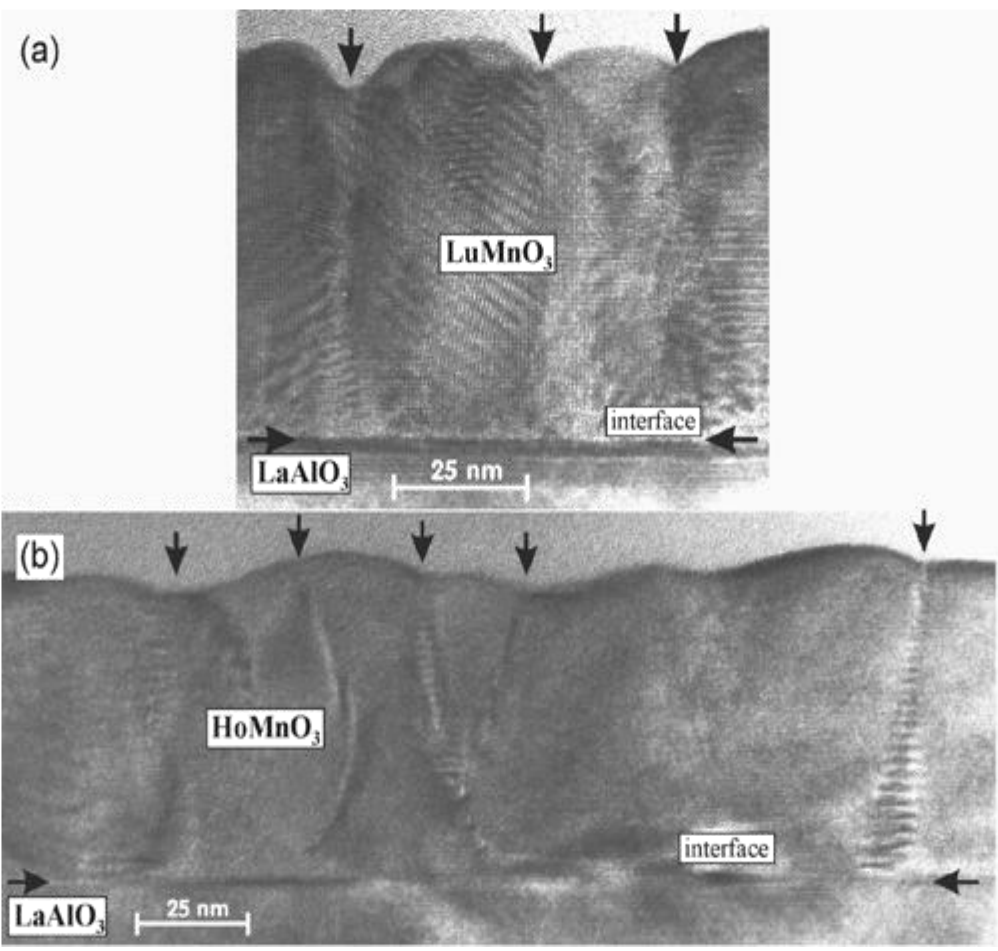
Examples of Epitaxy film

Epitaxial stabilization of oxides in thin films

Gorbenko OY, Samoilenkov SV, Graboy IE, Kaul AR

CHEMISTRY OF MATERIALS

14 (10): 4026-4043 OCT 2002

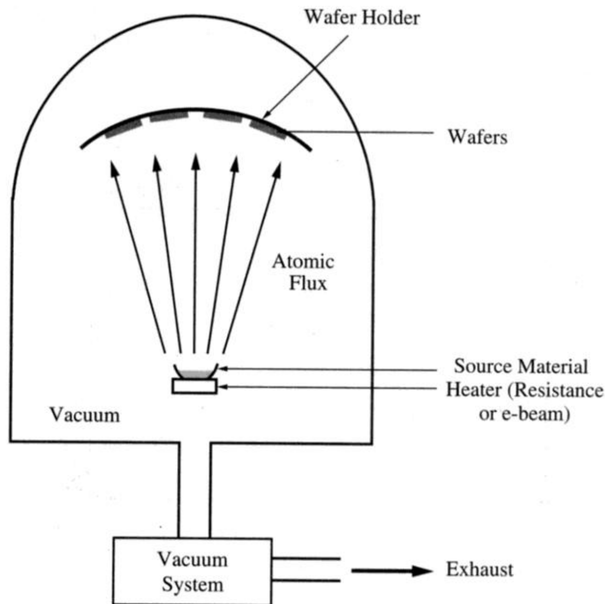


Two types of thin film deposition: CVD and PVD

- CVD
  - Reactive gases interact with substrate
  - Used to deposit Si and dielectrics
  - Good film quality
  - Good step coverage
- PVD
  - Used to deposit metals
  - High purity
  - Line of sight

Physical Vapor Deposition: PVD

2 types: *evaporation* and *sputtering*



Advantages:

Versatile – deposits almost any material

Very few chemical reactions

Little wafer damage

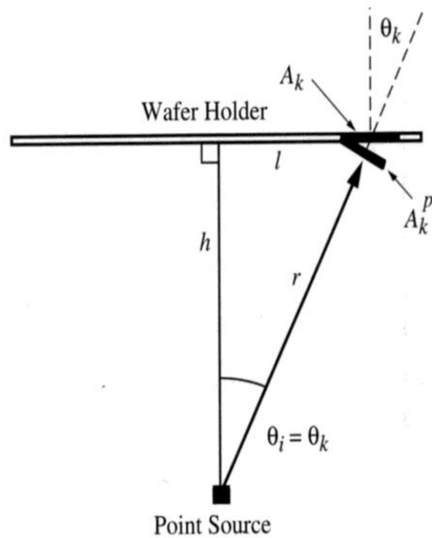
Limitations:

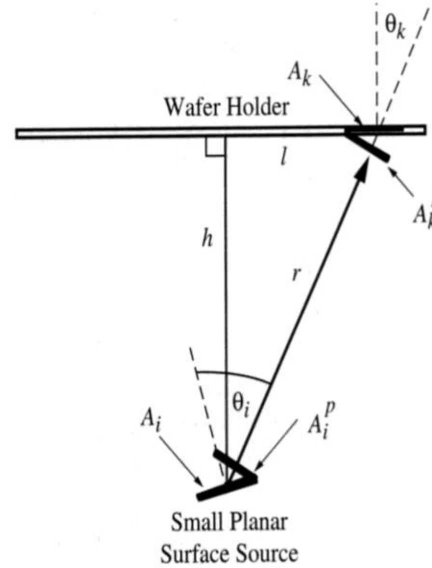
Line-of-sight

Shadowing

Thickness uniformity

Difficult to evaporate materials with low vapor pressures





Geometries of flux and deposition of small areas on a flat wafer holder for (a) a point source and (b) a small planar surface source

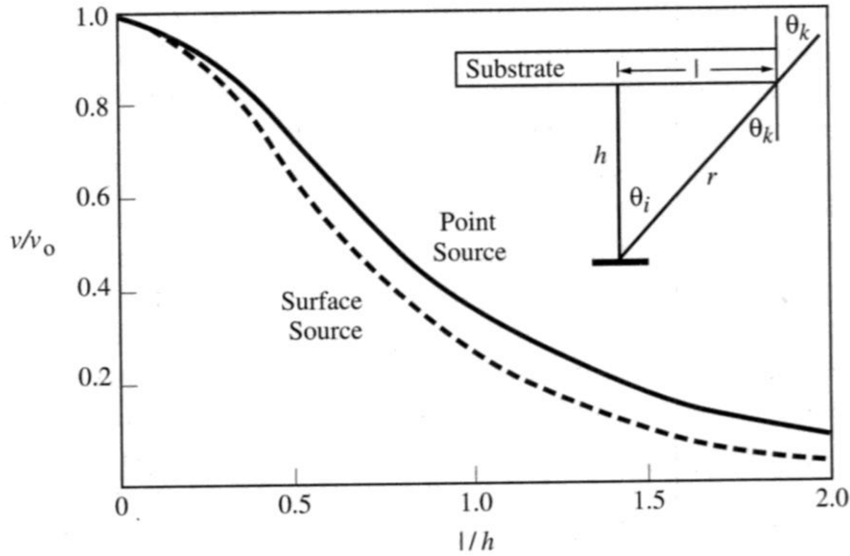
Flux from a point source

$$F_k = \frac{R_{evap}}{\Omega r^2} \cos\theta_k$$

Deposition rate from a surface source:

$$v = \frac{R_{evap}}{\Omega N r^2} \cos\theta_k \cos\theta_i$$

$$R_{evap} = 5.83 \times 10^{-2} A_s \left(\frac{m}{T}\right)^{1/2} P_e$$



Deposition rate of evaporated film as function of position on substrate for point and surface sources. $\theta_i = \theta_k$ in this configuration for both point and surface sources.

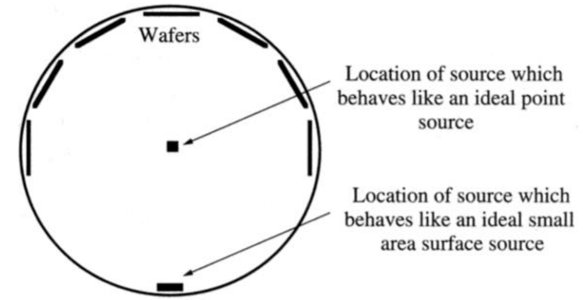


Figure 9–18 Positions of wafers and sources to achieve uniform deposition in evaporation system on all the wafers. Most evaporation sources behave more like a small area surface source and are in that configuration.

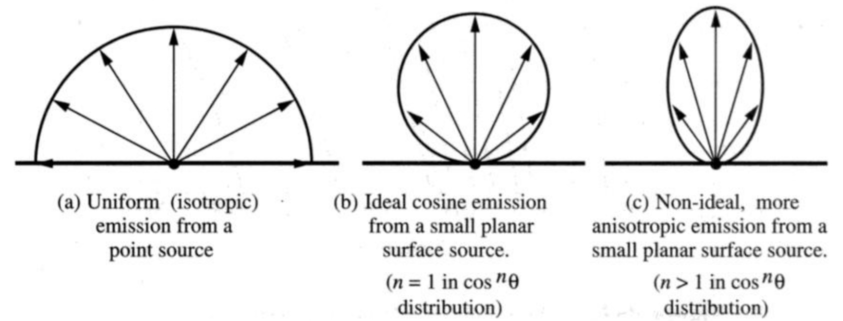


Figure 9–19 Emitted fluxes for point sources and small surface areas sources.

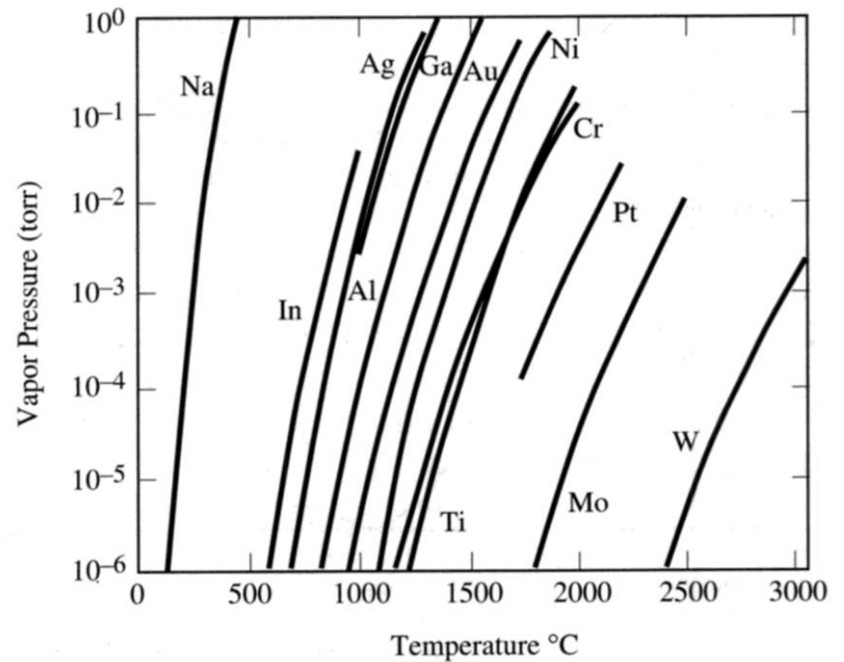
Mean free path λ:

$$\lambda = \frac{kT}{\sqrt{2}\pi d^2 P_e}$$

$k = 1.36 \times 10^{-2}$ erg/at-K

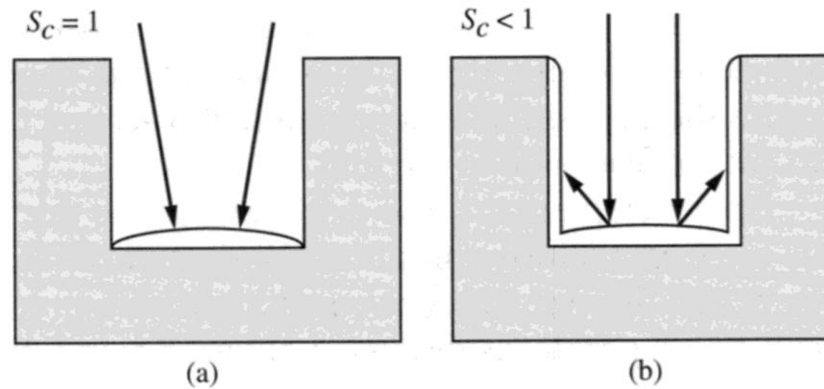
$d \approx .4 \times 10^{-8}$ cm

P_e = partial pressure (torr)



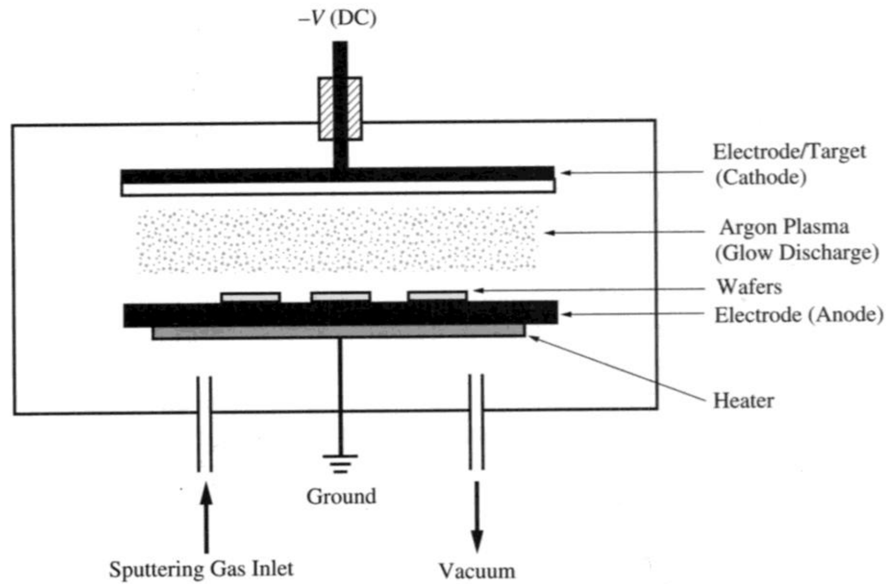
Vapor pressure as a function of temperature of commonly evaporated metals

Sticking coefficient: $S_c = F_{reacted}/F_{incident}$

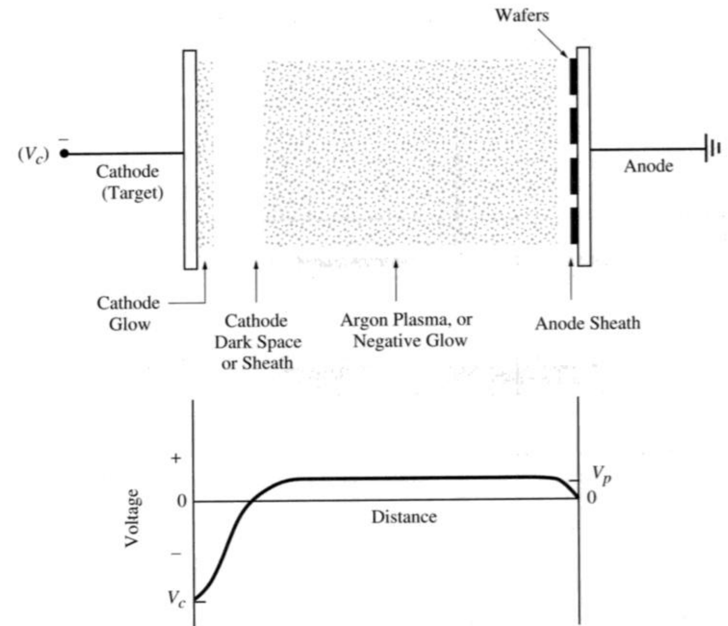


The depositing species have a high sticking coefficient (close to 1) in (a), so that they are deposited where they first strike. In (b) the depositing species have a low sticking coefficient (<<1) so that man are reemitted and deposit elsewhere on the topography, such as the sidewalls.

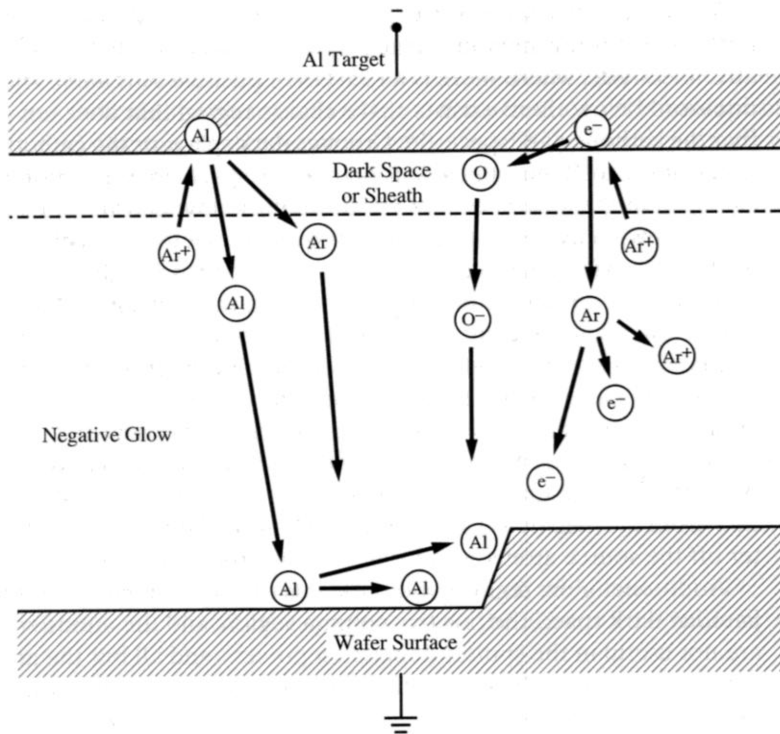
Sputtering



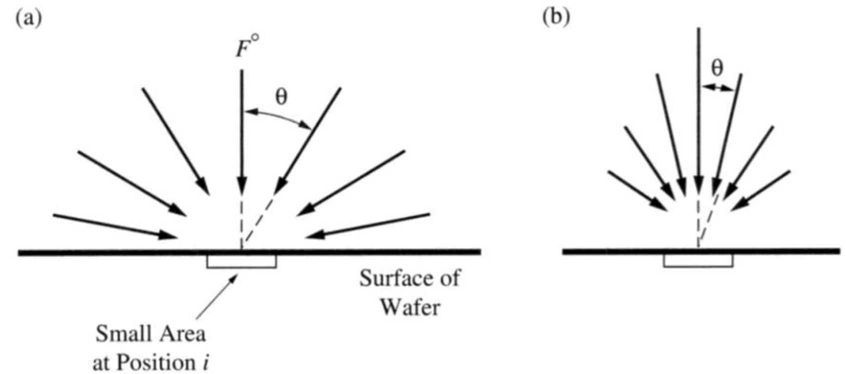
Schematic diagram of DC-powered sputter deposition equipment



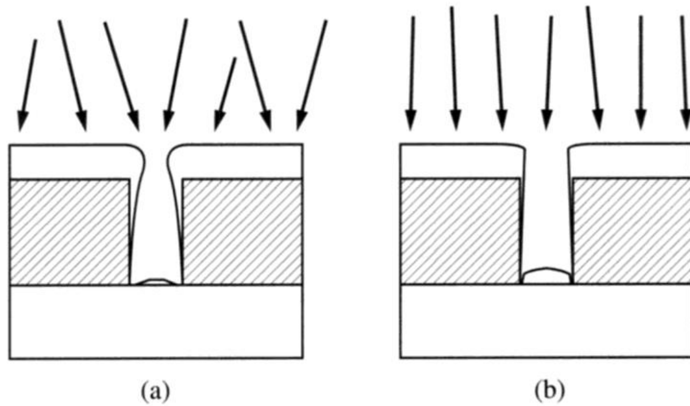
Plasma structure and voltage distribution in DC sputter system



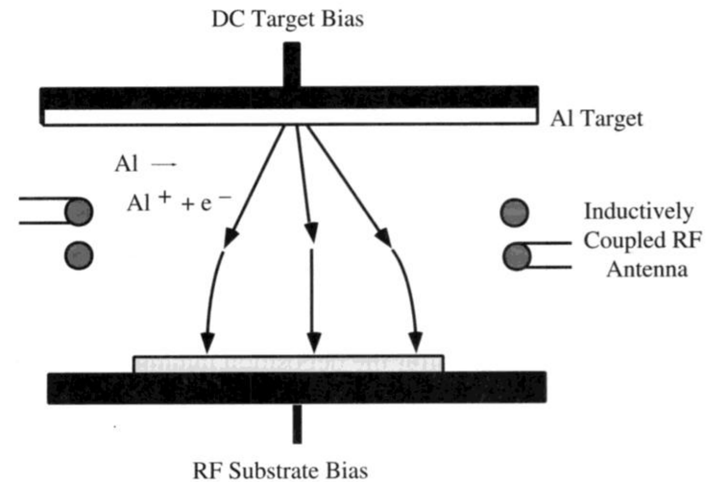
Processes in sputter deposition



Distribution of arrival fluxes for (a) uniform or isotropic arrival distribution and (b) directed or anisotropic arrival distribution. Arrival angle distribution ($\cos^n\theta$) is defined by arrival flux relative to unit surface area. This flux is equal to the normal component of incoming flux, relative to the vertical direction for a horizontal surface.

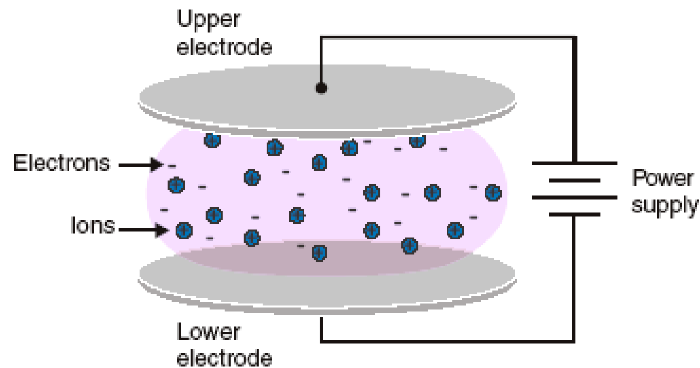


Effect of arrival angle distribution of depositing species on filling trenches or holes. In (a) a relatively wide arrival angle distribution leads to poor bottom filling or coverage, while (b) a narrower arrival angle distribution leads to better bottom filling. The higher the aspect ratio of the feature, the narrower the arrival angle distribution must be for adequate coverage.



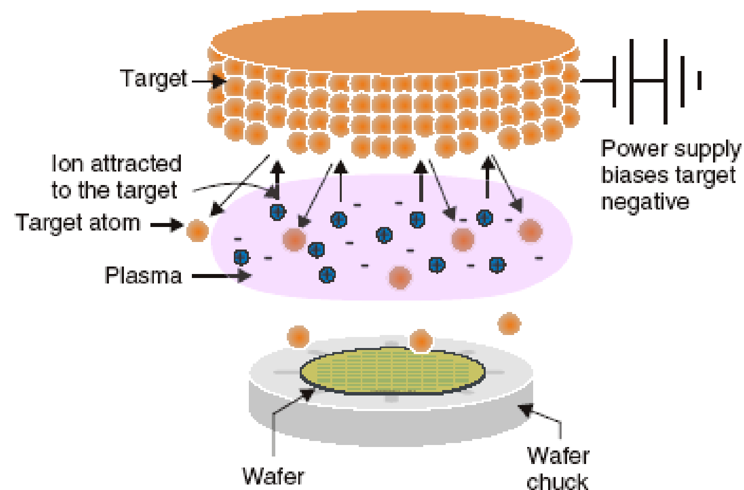
Schematic diagram of ionized sputter deposition system (ionized PVD) showing atomic flux lines

Sputter Deposition



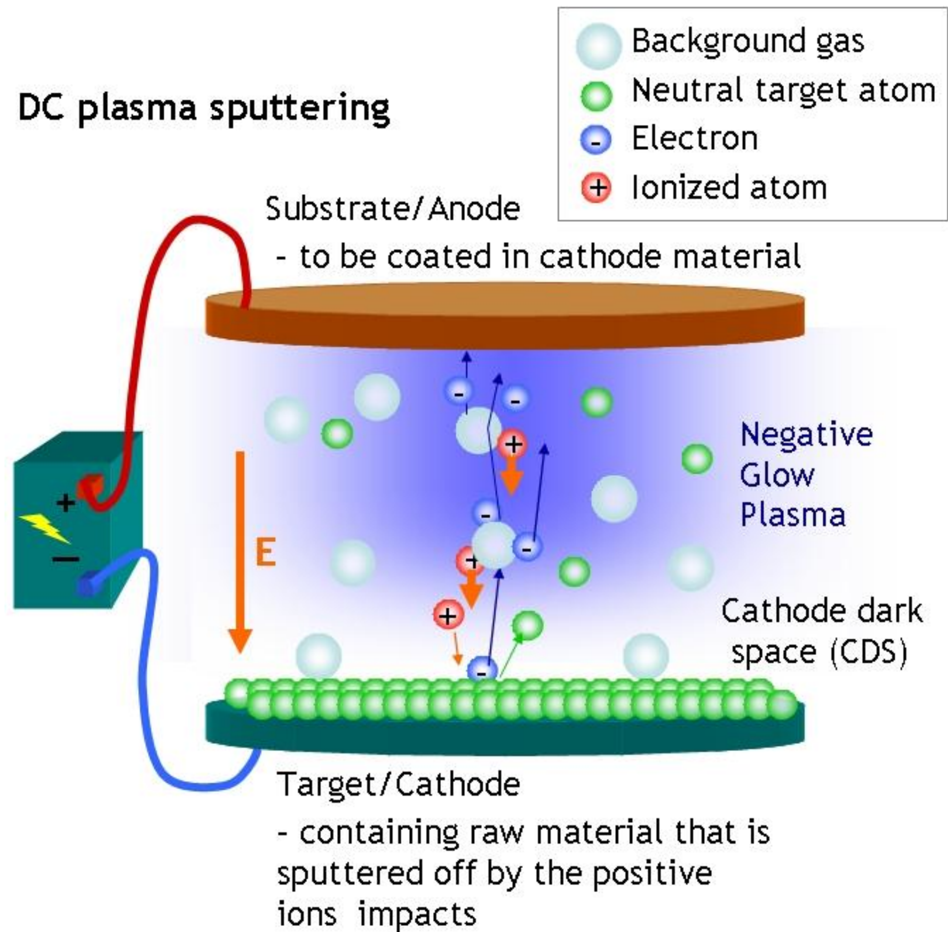
Plasma - a low pressure gas where a high energy field is used to drive ionization creating a large number of ions and free electrons.

Sputter deposition - ions from a plasma are attracted towards a target made of the material to be deposited, the ions strike the target physically knocking target atoms loose, the target atoms then land on the wafer.



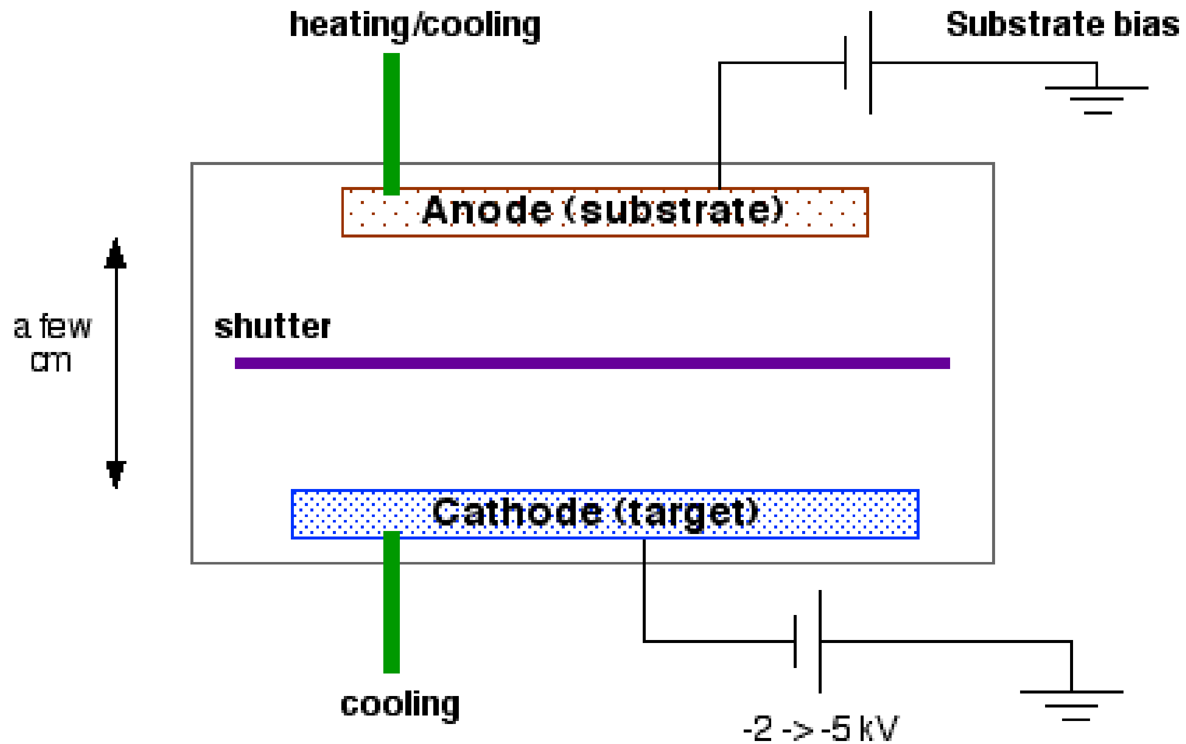
DC Sputter Deposition

Sputter deposition is a physical vapor deposition (PVD) method of depositing thin films by sputtering, that is ejecting, material from a "target," source, which then deposits onto a "substrate," such as a silicon wafer. Sputtered atoms ejected from the target have a wide energy distribution, typically up to tens of eV (100,000 K). The sputtered ions (typically only a small fraction (~1% of the ejected particles are ionized) can ballistically fly from the target in straight lines and impact energetically on the substrates or vacuum chamber (causing resputtering). Energetic ions sputter material off the target which diffuse through the plasma towards the substrate where it is deposited. There is no strong plasma glow around the cathode since it takes a certain distance for the plasma to be generated by electron avalanches started by a few secondary electrons from the sputtering process.



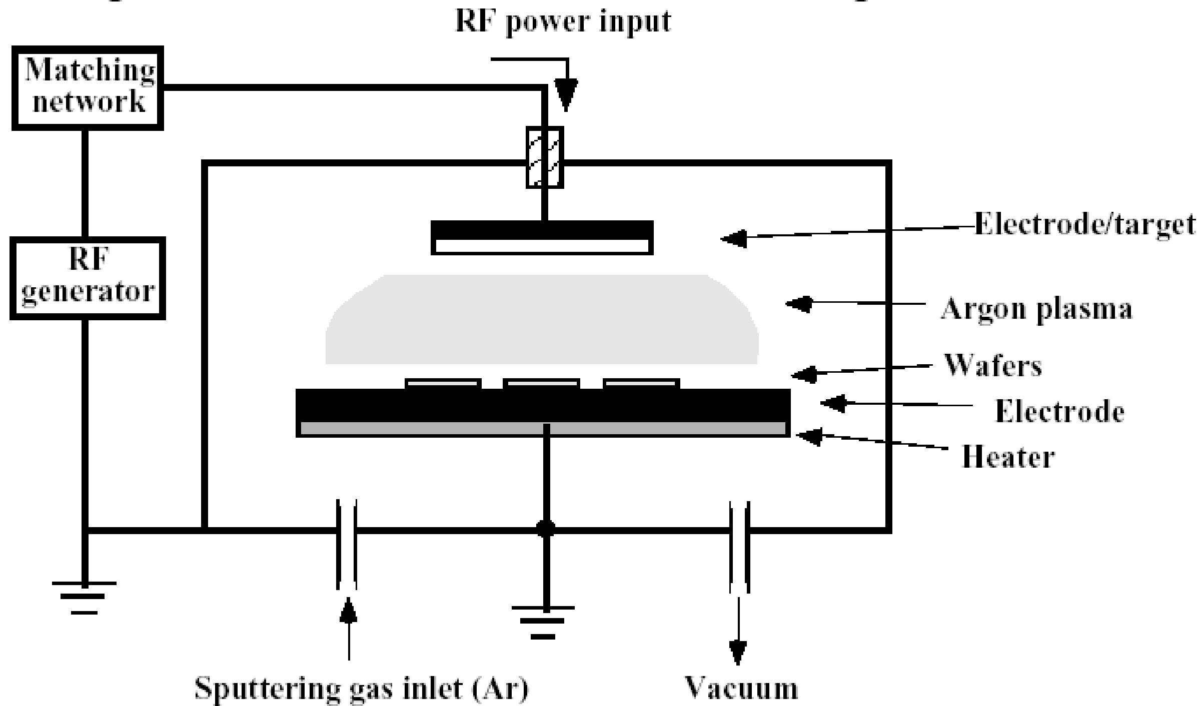
http://en.wikibooks.org/wiki/Microtechnology/Additive_Processes

DC Sputtering



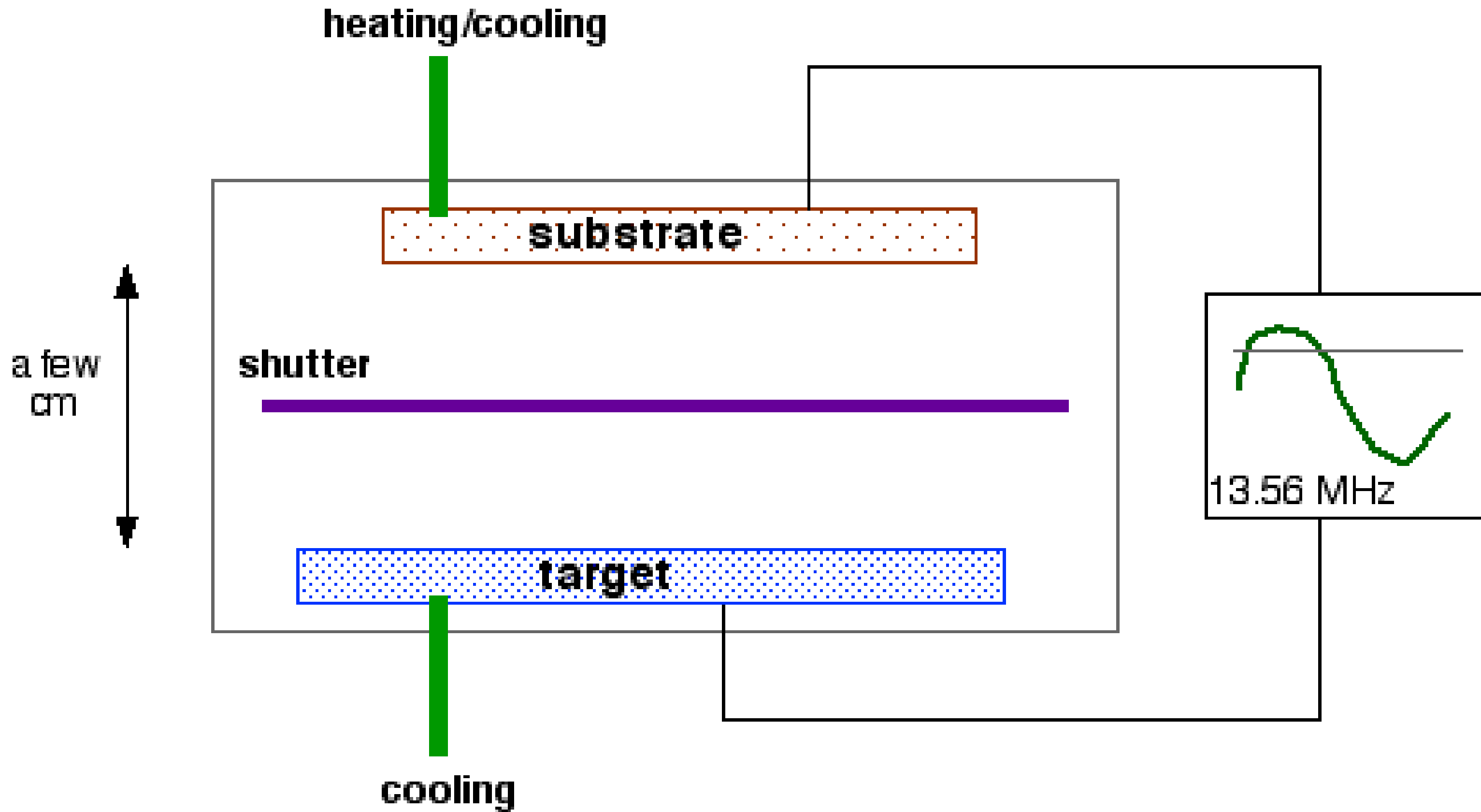
DC Sputtering Schematic

RF Sputter Deposition



RF Sputter Deposition Schematic

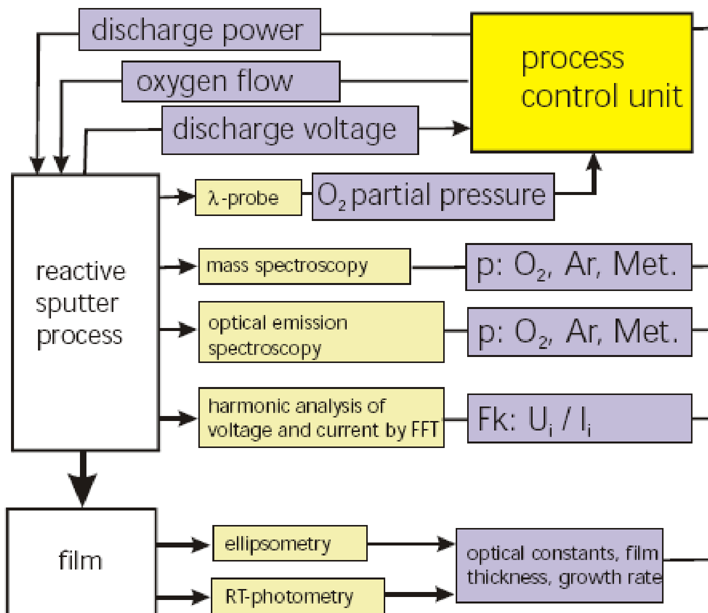
RF Sputter Deposition



RF Sputtering Schematic

Reactive Sputtering

Process control for reactive sputtering



Manipulated variable:
discharge power,
reactive gas flow

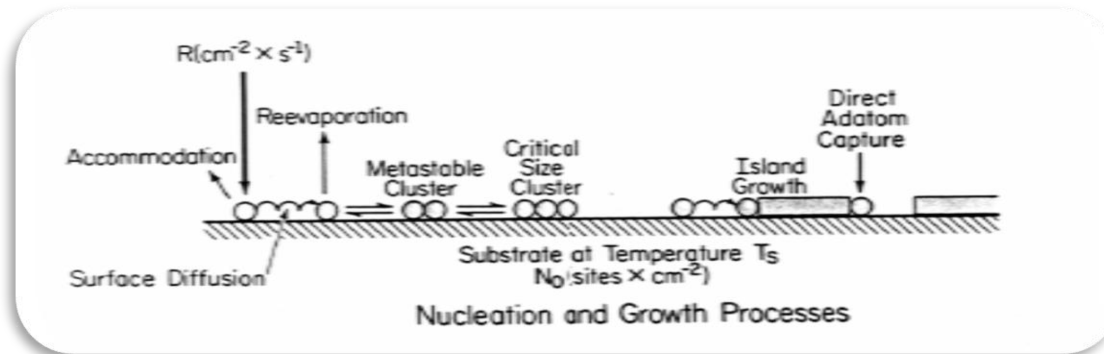
Controlled variable:
optical constants,
partial pressure, voltage,
harmonic analysis
(specific) deposition rate

Process control unit:
PID controller, fuzzy controller,
expert system

➡ **Continuous adjustment of particle fluxes for all materials**

Sit, 2002-05-29

Elements of Thin Film Growth



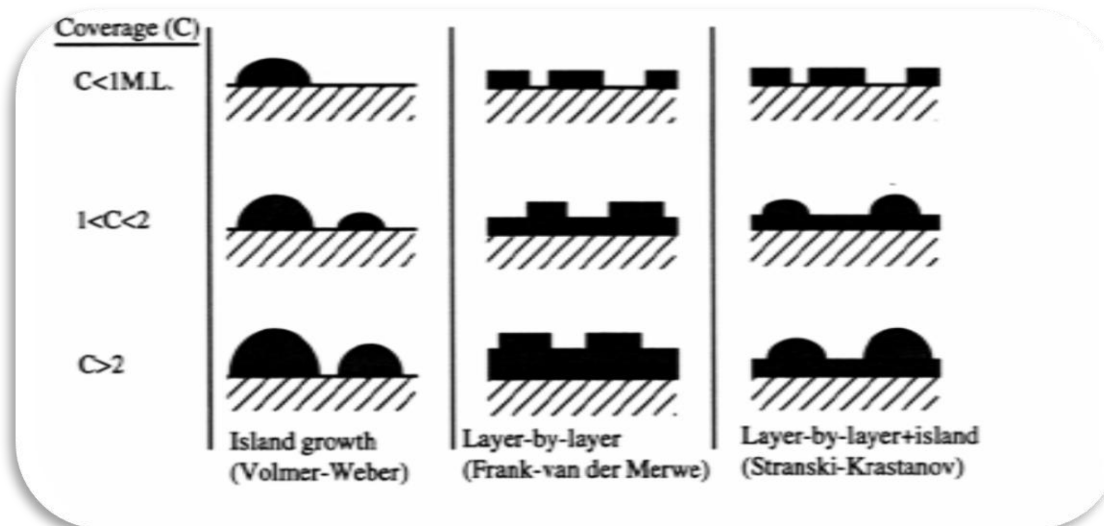
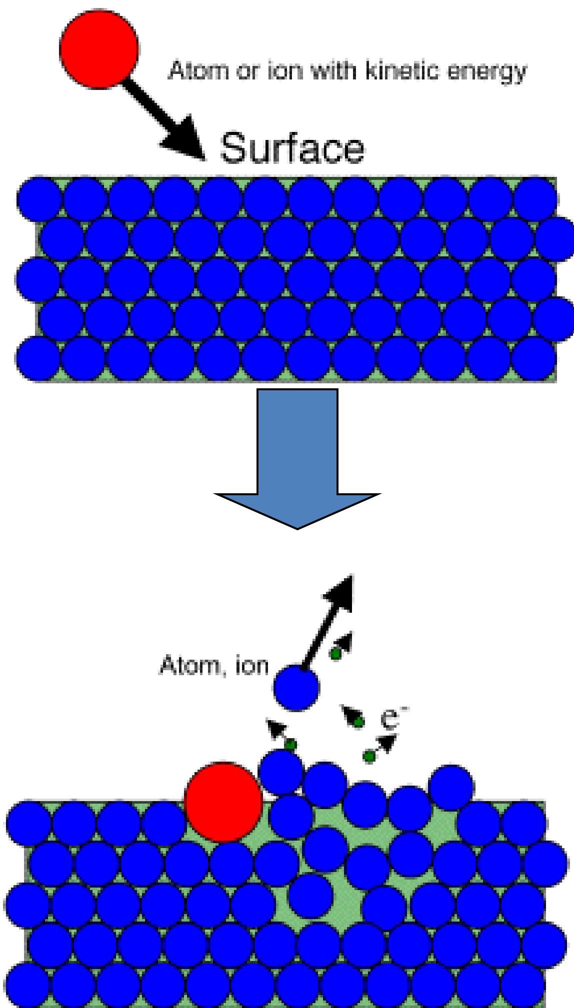


Table 9–1 Common deposition methods for thin films in integrated circuit fabrication

Thin Film	Equipment	Typical Reactions	Comments
Epitaxial silicon	APCVD, LPCVD	$SiH_4 \rightarrow Si + 2H_2$ $SiCl_4 + 2H_2 \rightarrow Si + 4HCl$ Also $SiHCl_3$, SiH_2Cl_2	1000–1250°C. Reduce pressure for lower-temperature deposition.
Polysilicon	LPCVD	Same as epitaxial Si	575–650°C. Grain structure depends on deposition conditions and doping.
Si_3N_4	LPCVD, PECVD	$3SiH_4 + NH_4 \rightarrow Si_3N_4 + 12H_2$	650–800°C for oxidation mask. 200–400°C (PECVD) for passivation.
SiO_2	LPCVD, PECVD, HDPCVD, APCVD	$SiH_4 + O_2 \rightarrow SiO_2 + 2H_2$ $Si(OC_2H_5)_4$ $(+O_3)$ $\rightarrow SiO_2$ + byproducts	200–800°C. 200–500°C (LTO)—may require high T anneal. 25–400°C (TEOS-ozone, PECVD, HDPCVD).
Al	Magnetron sputter deposition		25–300°C (standard deposition). 440–550°C (hot Al for in situ reflow). CVD difficult for alloys (Al-Cu-Si).
Ti and Ti-W	Magnetron sputter deposition (standard, ionized, or collimated)		CVD difficult. Nitrogen can be added to Ti-W to stuff grain boundaries.
W	LPCVD	$2WF_6 + 3SiH_4 \rightarrow 2W + 3SiF_4 + 6H_2$ $WF_6 + 3H_2 \rightarrow W + 6HF$	250–500°C. Blanket deposition with two-step process using both reactions is common.
$TiSi_2$	Sputter and surface reaction	Ti(sputtered) + Si(exposed) $\rightarrow TiSi_2$	Sputter/reaction gives self-aligned silicide.
	Cosputtering or CVD		
TiN	Reactive sputter deposition	$Ti + N_2$ (in plasma) $\rightarrow TiN$	Organometallic source possible for MOCVD deposition.
	CVD	$6TiCl_4 + 8NH_3 \rightarrow 6TiN + 24HCl + N_2$	TiN can also be formed in $TiSi_2$ process.
Cu	Electroplating, electroless, sputtering, CVD	$Cu^{2+} + 2e^- \rightarrow Cu$	Electroplating is most common method today.

Microscopic View of Sputtering



- **The impact of an atom or ion on a surface produces sputtering from the surface as a result of the momentum transfer from the incoming particle. Unlike many other vapor phase techniques there is no melting of the material.**
- **History of Sputtering**
  - The verb to SPUTTER originates from Latin SPUTARE(To emit saliva with noise).
  - Phenomenon first described 150 years ago ...
    Grove (1852) and plücker (1858) first reported vaporization and film formation of metal films by sputtering.
  - Key for understanding discovery of electrons and positive ions in low pressure gas discharges and atom structure (J.J. Thomson, Rutherford), 1897--
  - Other names for SPUTTERING were SPLUTTERING and CATHODE DESINTEGRATION.

ref: www.gencoa.com

Target Erosion

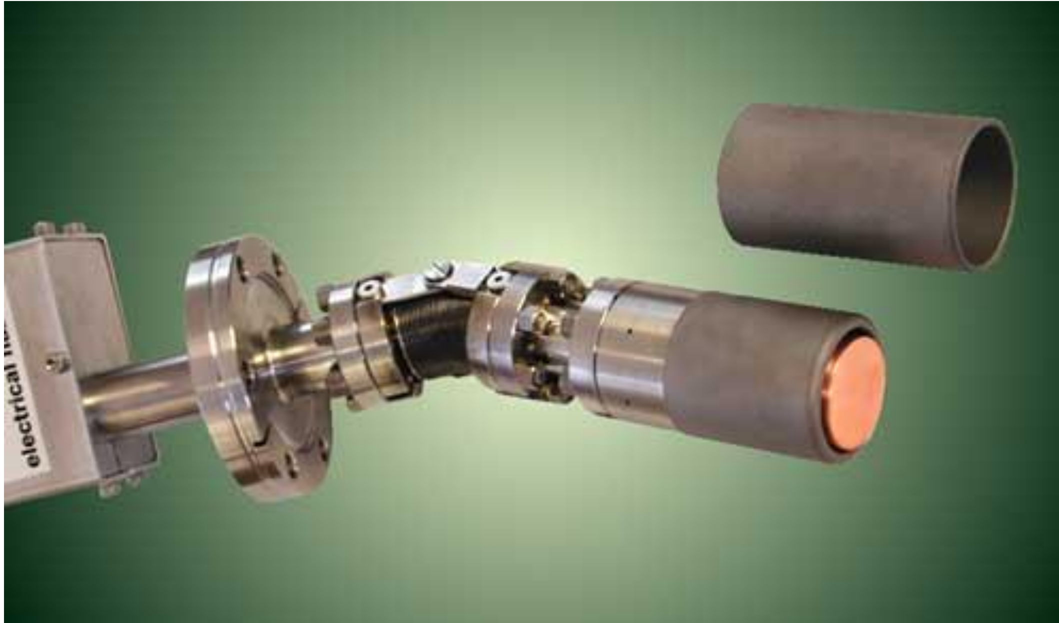
- Target erosion is greatest where the magnetic field and the subsequent plasma density is greatest.
- This leads to inefficient use of target material, particularly in the case of ferromagnetic targets.

ref: www.gencoa.com

Magnetron Guns

ref: www.lesker.com

The Latest in UHV Sputtering



http://www.ajaint.com

- A UHV, magnetron sputter source that fits through the port of a 2.75" CF flange complete with its tilt gimbals assembly.
- The AJA International new A310-XP only needs a 2.75" CF to accommodate the source head, tilt gimbals and gas injection/isolation chimney.
- This revolutionary new design is true UHV - all ceramic to metal construction.

Ion Implantation

Topics:

•Deposition methods

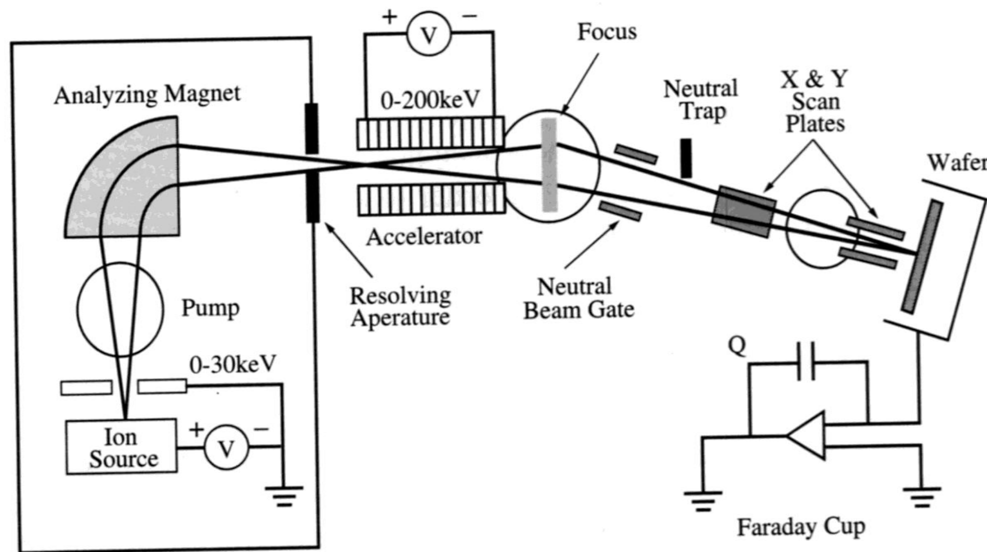
•Implant

-Depth & Distribution

-Masking effects

•Damage annealing

Manufacturing Methods



Schematic of an ion implanter

Ion source: Vaporized solids or gases – e.g., -
- Arsine
- Phosphine
- BF2

Vapors form various species, such as B^{++}, B^{+}, BF^{+}, BF_2^{+}, along with neutral atoms

These gases are **extremely toxic!** Mixed in 15% concentrations with H2

Applying a magnetic induction, **B,** to speeding atoms causes them to bend around the curve of radius R:

$\frac{1}{2} mv^2 = q \cdot \mathbf{v} \times \mathbf{B}$

Velocity can be expressed as:

$\mathbf{v} = \sqrt{(2E/m)} = \sqrt{(2qV_{ext}/m)}$

B can be expressed as a function of current:

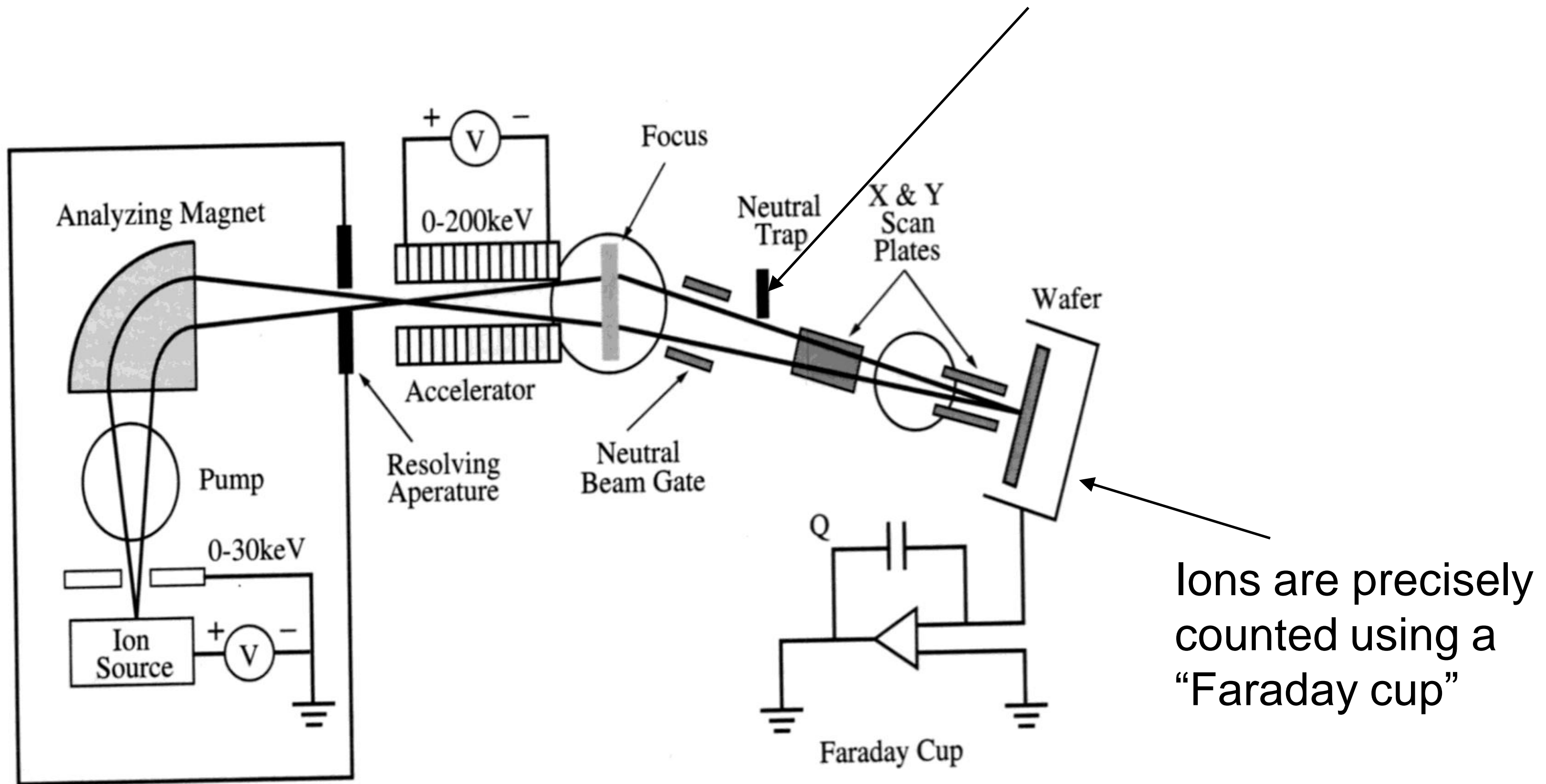
$\mathbf{B} = \alpha I$

Thus

$\sqrt{m} = q/\sqrt{2E}(\alpha R)I$

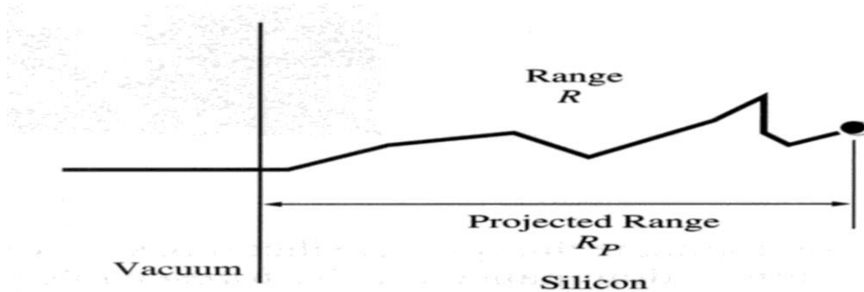
By adjusting current, I, ions can be separated by mass

Neutrals are separated by the electrostatic deviation of the focus beam

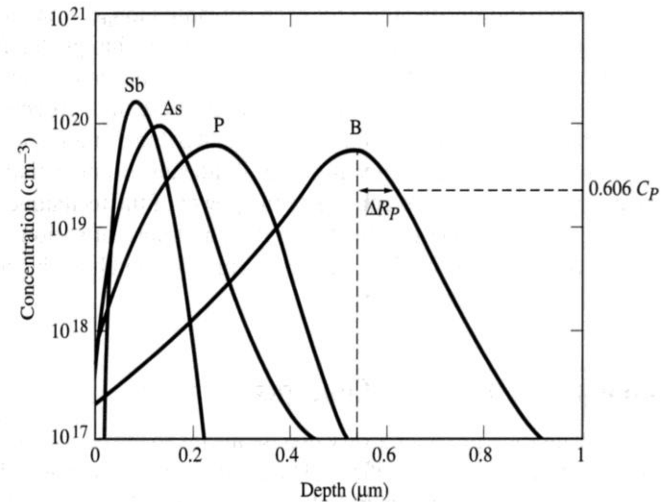


Ions are precisely counted using a "Faraday cup"

Ion Path and Distribution



Schematic of the actual range of an implanted ion and the projected range normal to the surface.

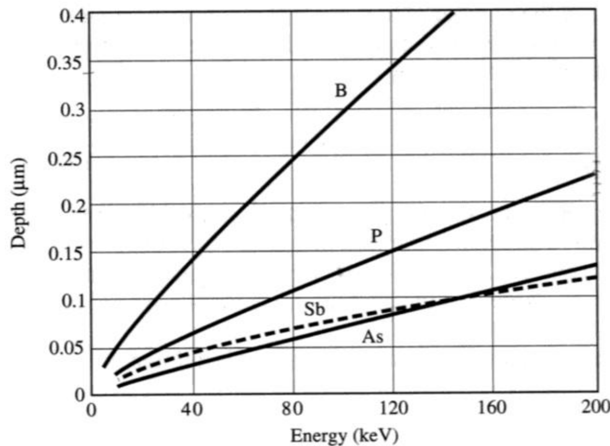


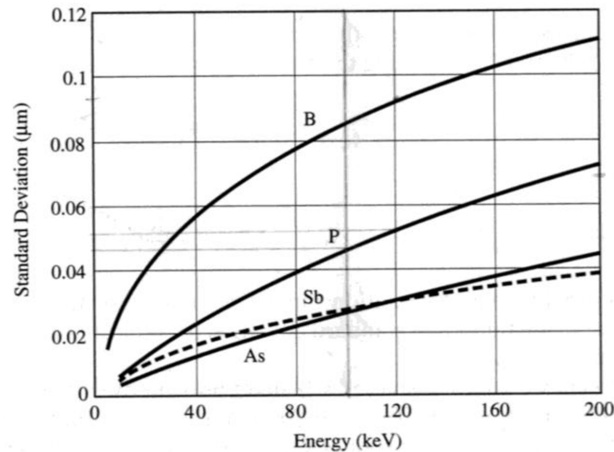
Distribution of ions implanted into crystalline silicon at an energy of 200 keV. Light ions penetrate more deeply, and have more asymmetric distribution than heavy ions.

Definitions: $\mathbf{C_p}$ = peak concentration

$\mathbf{R_p}$ = average projected depth

$\mathbf{\Delta R_p}$ = Standard Deviation = $\sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(x_i-\bar{x})^2}$





Plots of Rp and DRp for common dopants in crystalline Si tilted and rotated to simulate random direction.

Dopant concentration curves are modeled using Gaussian distribution:

$$C(x) = C_p \exp\left(- \frac{\left(x - R_p\right)^2}{2\Delta R_p} \right)$$

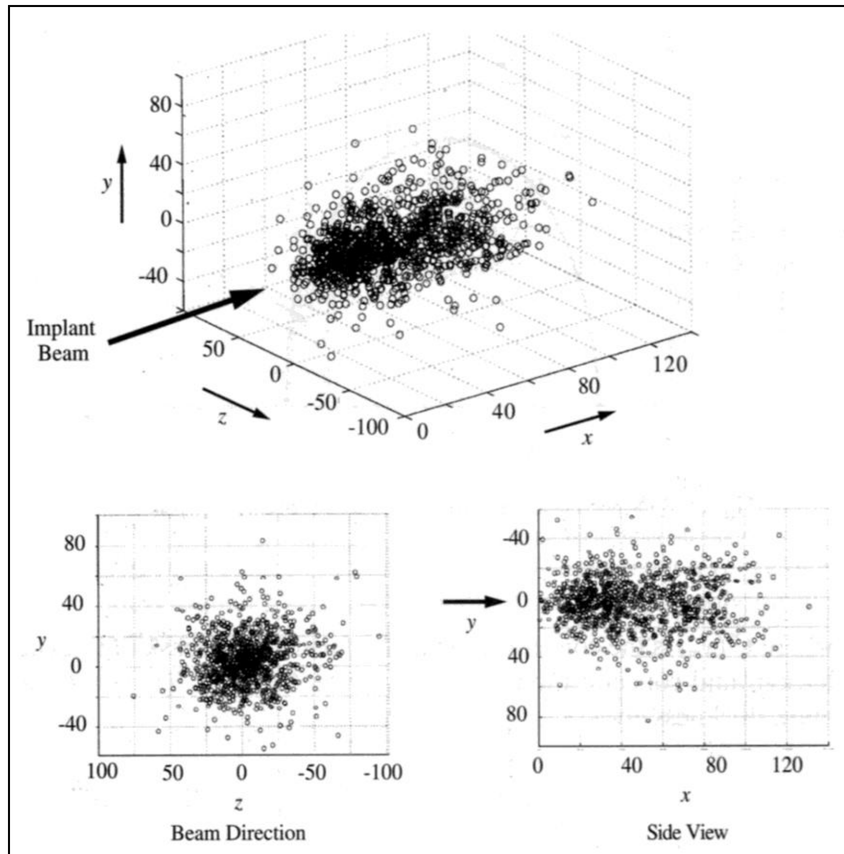
Total number of ions implanted:

$$Q = \int_{-\infty}^{\infty} C(x)dx = \sqrt{2\pi}\Delta R_p C_p$$

This relates the dose to the peak concentration

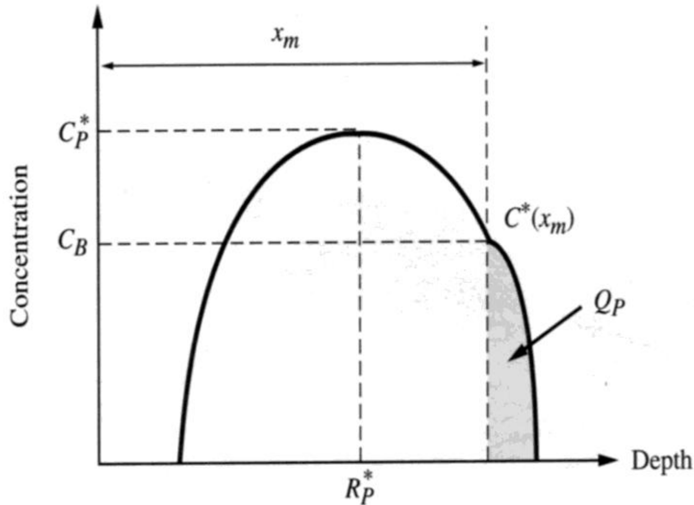
Lateral distributions are also modeled using a Gaussian:

$$C(x,y) = C_{vert}(x)\exp\left(-\frac{y^2}{2\Delta R_{p\perp}^2}\right)$$



Simulated 3D distribution of 1000 P atoms implanted at 35 keV (top). Axis units are nm.

Masking Layers



Schematic of masking process, where dose Q_p penetrates the mask of thickness x_m. * denotes mask

Solving for x_m:

$$C^*(x_m) = C_p^* \exp\left(-\frac{(x_m - R_p^*)^2}{2\Delta R_p^{*2}}\right) \le C_B$$

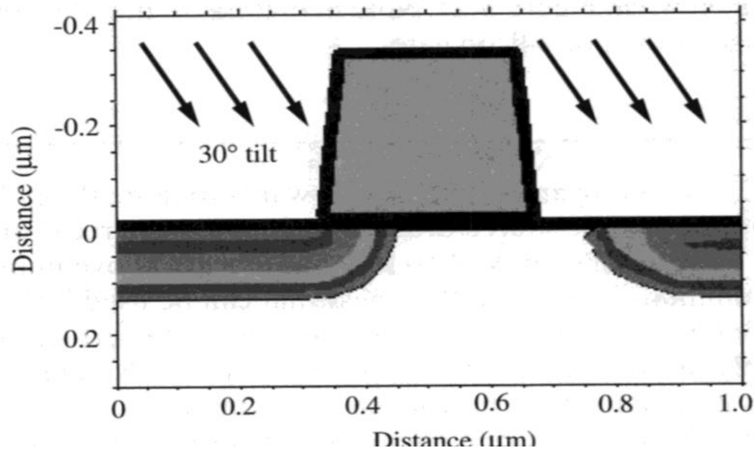
$$x_m = R_p^* + \Delta R_p^* \sqrt{2\ln\left(\frac{C_p^*}{C_B}\right)} = R_p^* + m\Delta R_p^*$$

The dose that penetrates is:

$$Q_p = \frac{Q}{\sqrt{2\pi\Delta R_p^*}} \int_{x_m}^{\infty} \exp - \left[\frac{x - R_p^*}{\sqrt{2}\Delta R_p^*}\right]^2 dx$$

$$Q_p = \frac{Q}{2} erfc\left[\frac{x_m - R_p^*}{\sqrt{2}\Delta R_p^*}\right]$$

Implantation not Perpendicular to Mask



Simulation of 50 keV P implant at a tilt angle of 30°, showing asymmetrical implant distribution and shadowing caused by the gate polysilicon

The dopant distribution resulting from tilt implantation followed by diffusion is given by combining implantation concentration and diffusion equations:

Implantation

$$C(x) = C_p \exp\left[-\frac{\left(x_m - R_p\right)^2}{2\Delta R_p^2}\right]$$

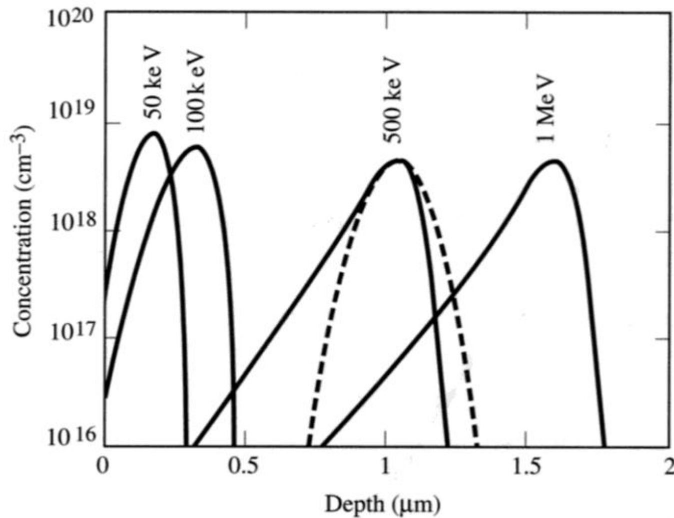
Diffusion

$$C(x) = C(0,t)\exp\left(-\frac{x^2}{4Dt}\right)$$

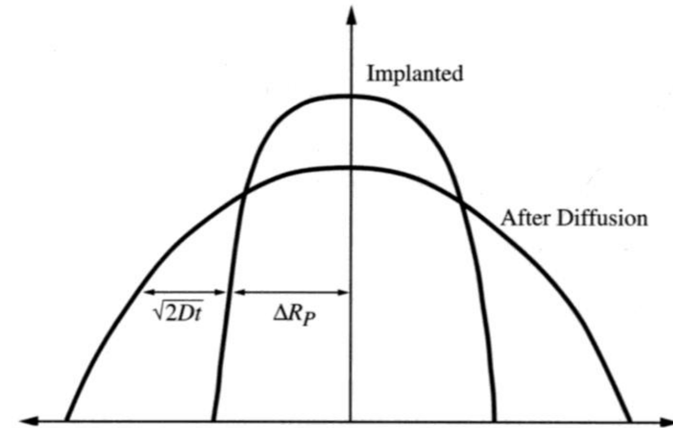
$$C(0,t) = \frac{Q}{2\sqrt{\pi D t}}$$

$$\Rightarrow C(x,t) = \frac{Q}{\sqrt{2\pi\left(\Delta R_p^2 + 2Dt\right)}}\exp\left[-\frac{\left(x - R_p\right)^2}{2\left(\Delta R_p^2 + 2Dt\right)}\right]$$

Actual distributions



Simulated profiles of B implanted in amorphous or polycrystalline Si over a range of energies. Profiles show noticeable skew toward surface due to backscattering of light B ions. Skewed profiles are described by a 4-factor Pearson distribution. Gaussian fit to 500 keV profile is shown by dashed line.



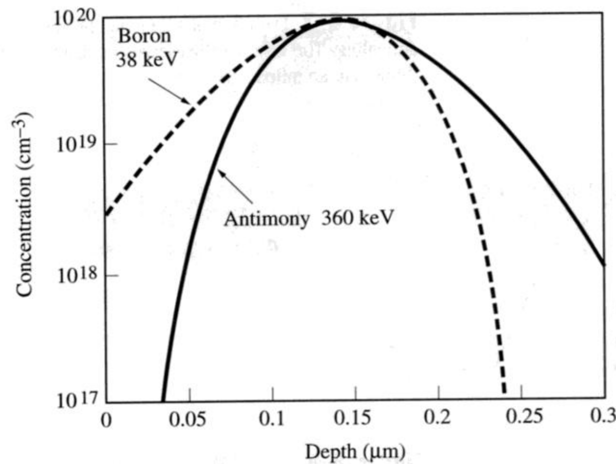
Evolution of Gaussian profile after annealing. The Gaussian preserves its shape as it diffuses in an infinite medium.

To accurately model, we need to include 4 parameters:

1. Projected range, R_p
2. Scatter, ΔR_p
3. "Skewness" due to mass effects, γ
4. *Kurtusis*, or variation due to occasional extremes, β

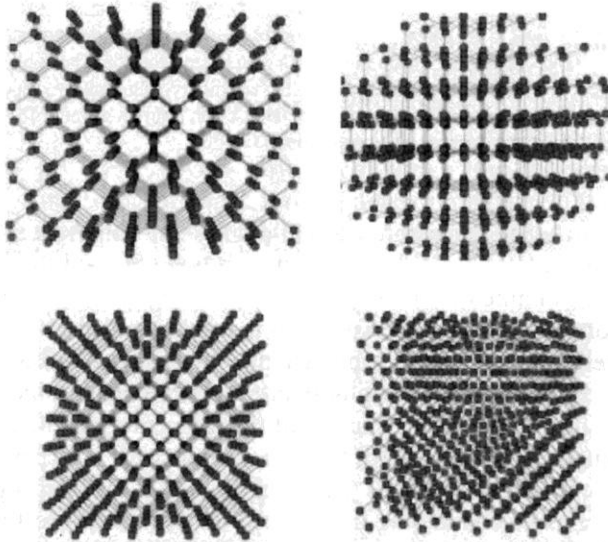
Thus

$$f(\text{curve}) = f(R_p, \Delta R_p, \gamma, \beta)$$

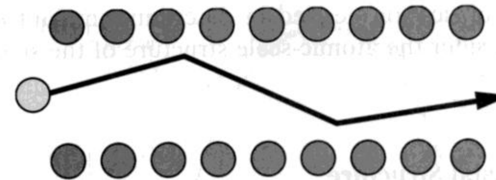


Simulation of ion-implanted B and Sb profiles with implant energy adjusted to give the same range. Light B ion skews toward surface, while heavy antimony ion skews toward bulk.

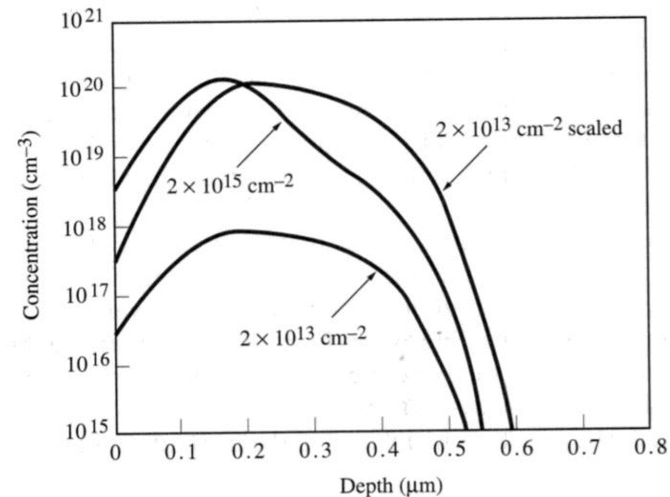
The role of crystal structure



Clockwise from top left: Image of a silicon crystal looking down the 110 axial channels, the 111 planar channels, the 100 axial channels, and with tilt and rotation to simulate a “random” direction



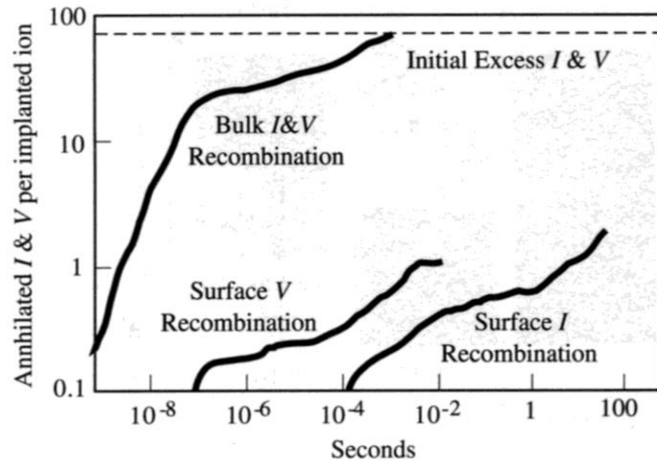
Ions undergo many small angle deflections when traveling in a channel

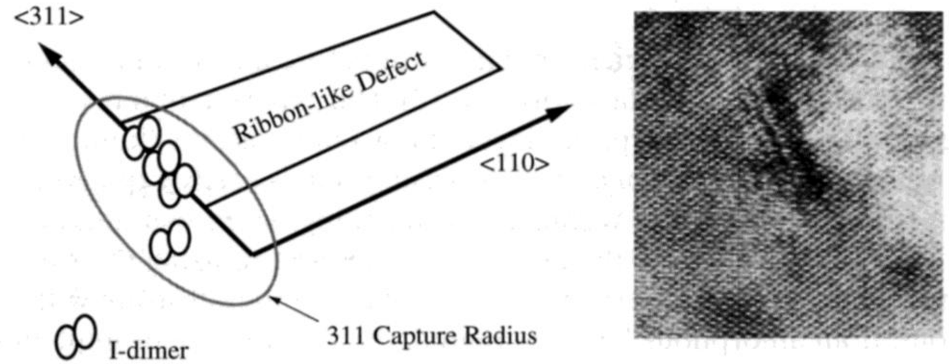


Simulated boron profiles implanted into <100> Si wafers with zero tilt & rotation.

Implantation Damage & Annealing

Goal: to remove damage from implantation and return Si to a crystalline state leaving dopants in substitutional sites.

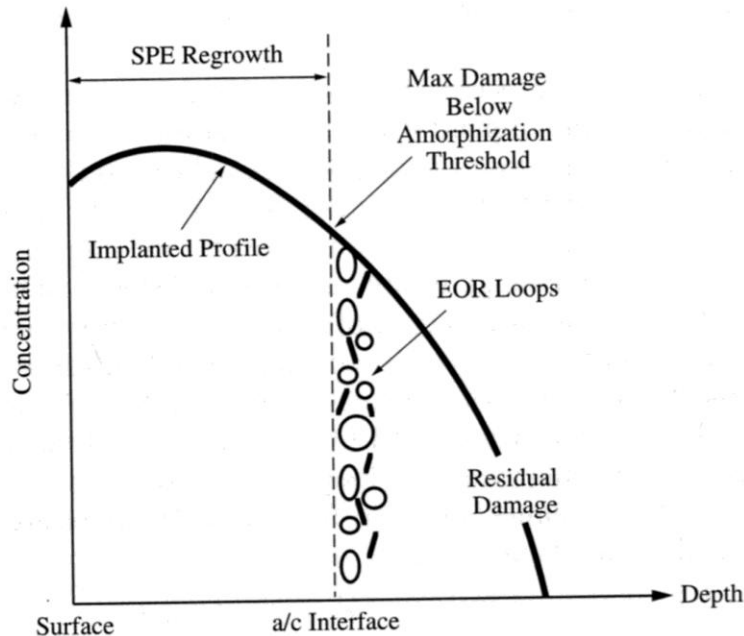




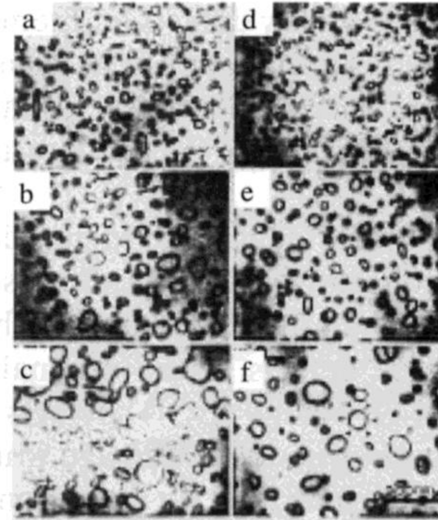
Simulation of recombination of vacancy (V) and interstitial (I) damage resulting from implantation. At 800 ^{o}C, recombination takes place very quickly. After a short time, only excess interstitial clusters remain

Si interstitials condense into ribbons of Si atoms (I-dimers) lying on {311} planes and grow by extending in the <110> directions. On right is a TEM image of clusters

At high temperatures, ribbons condense and grow, creating dislocation loops that populate the boundary between crystalline and amorphous silicon.



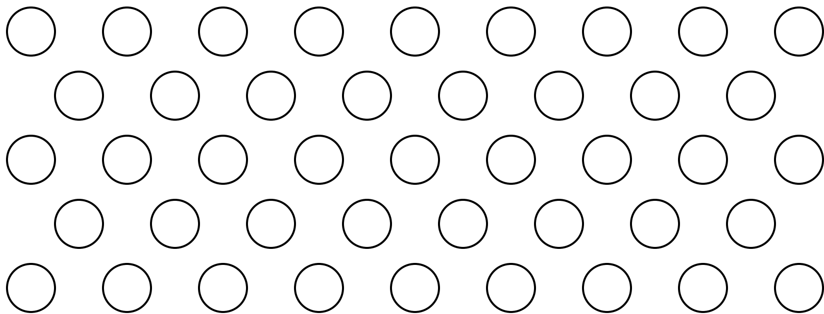
Schematic of stable End-of-Range (EOR) dislocation loops that form at amorphous/crystalline interface



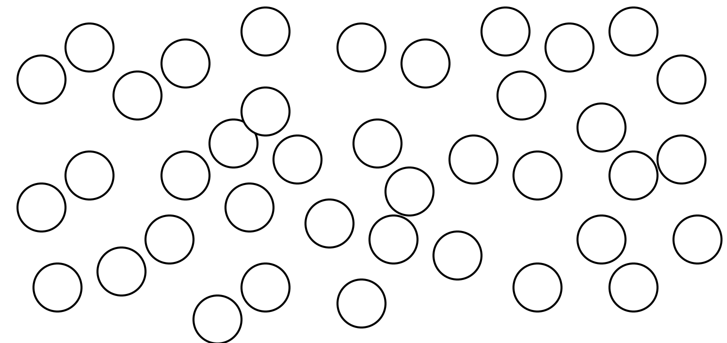
TEM of EOR dislocation loops for annealing times of 5, 60 and 960 minutes at 850 oC (a-c), and for 1, 60 and 400 sec. at 1000 oC (d-f). Loops show some *ripening* (large loops grow at the expense of small loops) but are very stable at typical annealing temperatures.

Implantation Processes: Damage

- Ion collides with lattice atoms and knock them out of lattice grid
- Implant area on substrate becomes amorphous structure



Before Implantation



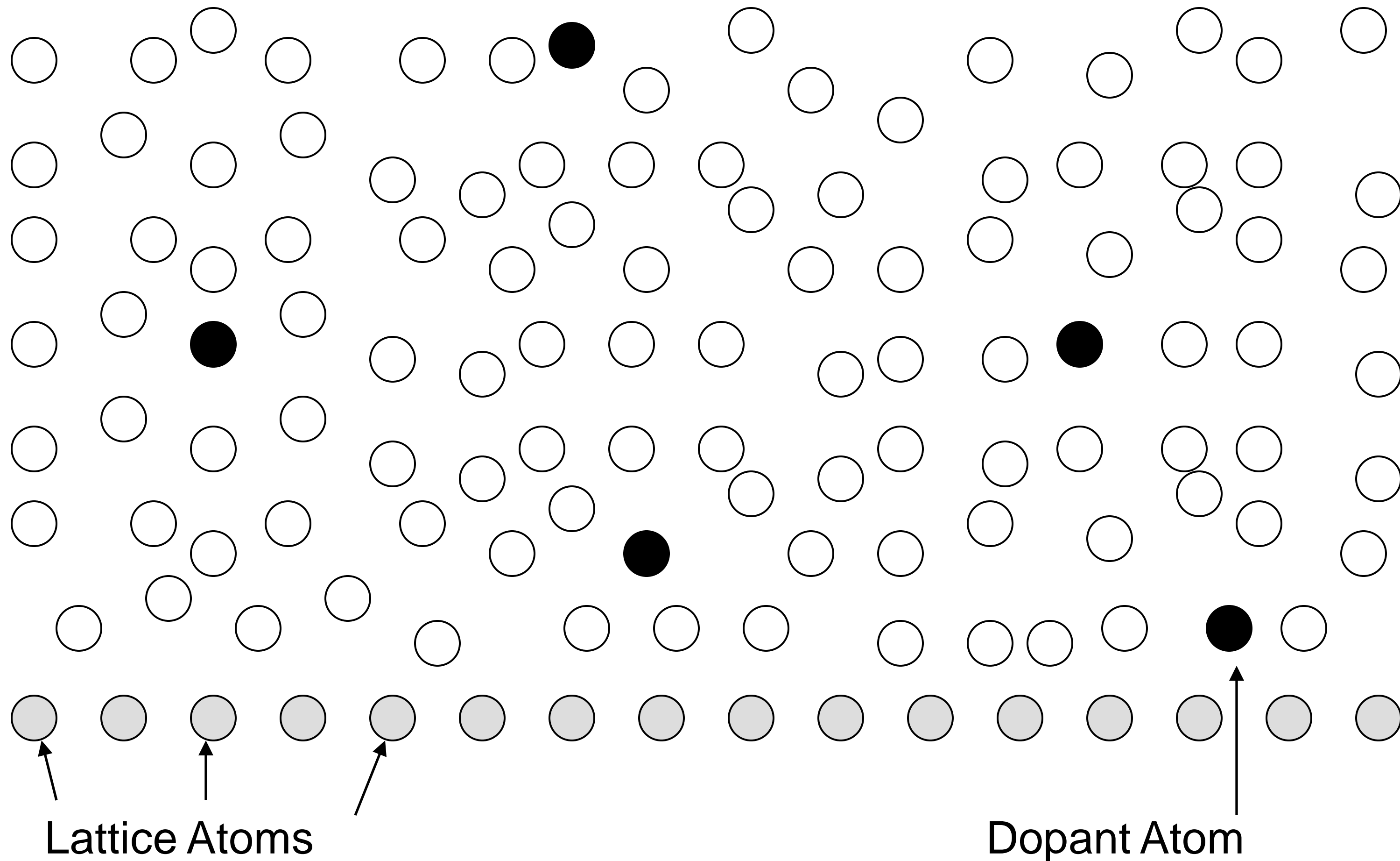
After Implantation

Implantation Processes: Anneal

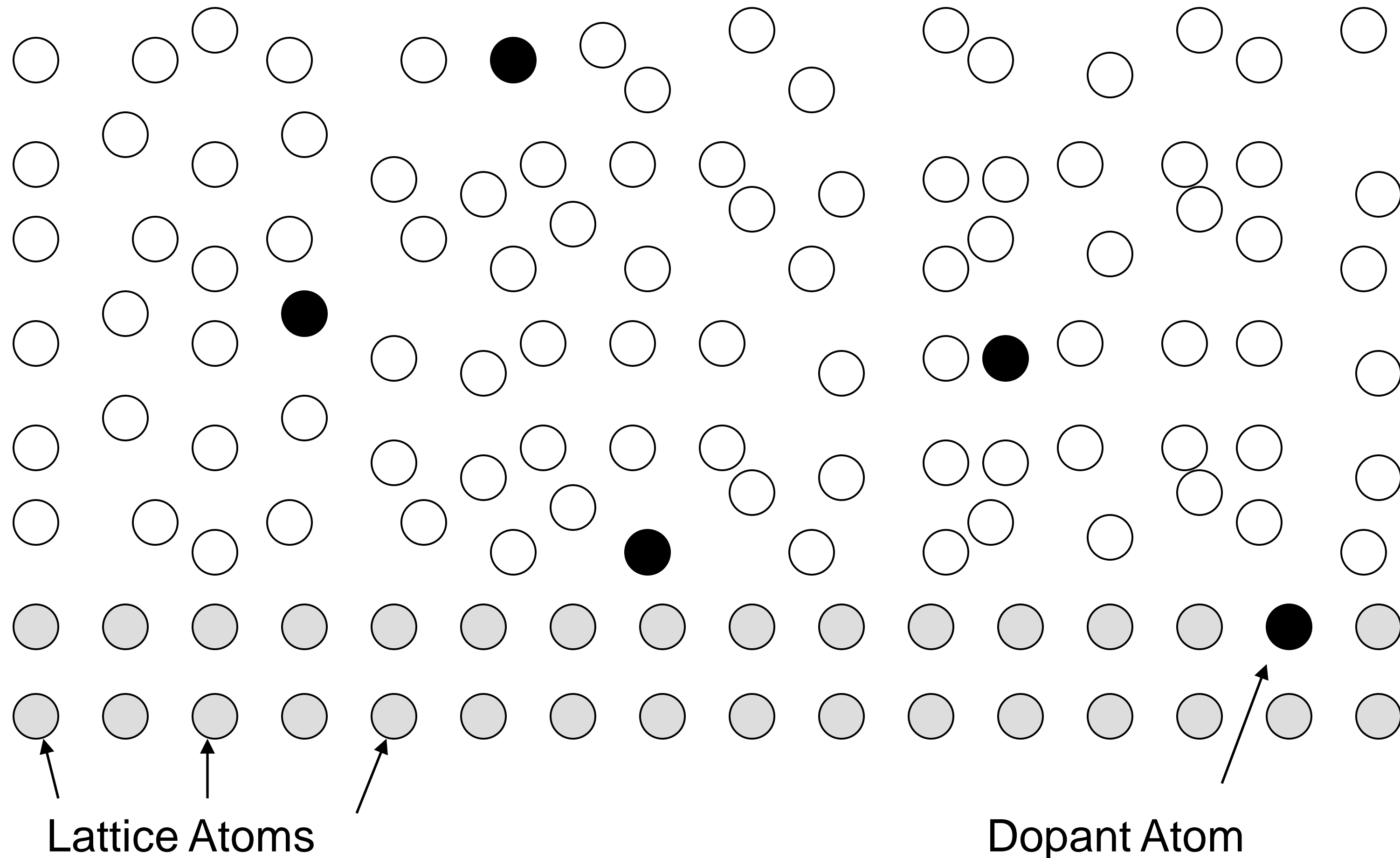
- Dopant atom must in single crystal structure and bond with four silicon atoms to be activated as donor (N-type) or acceptor (P-type)

- Thermal energy from high temperature helps amorphous atoms to recover single crystal structure.

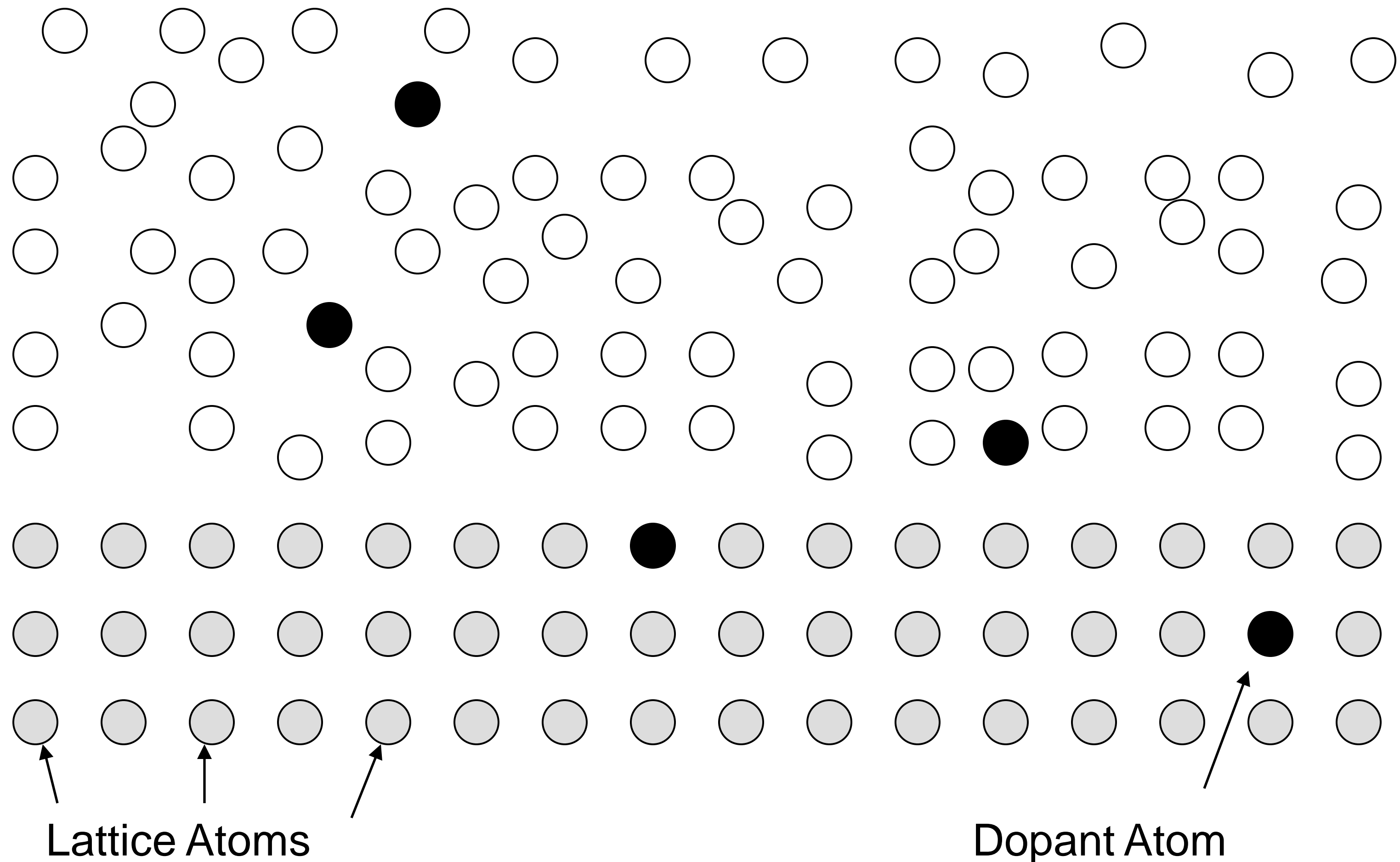
Thermal Annealing



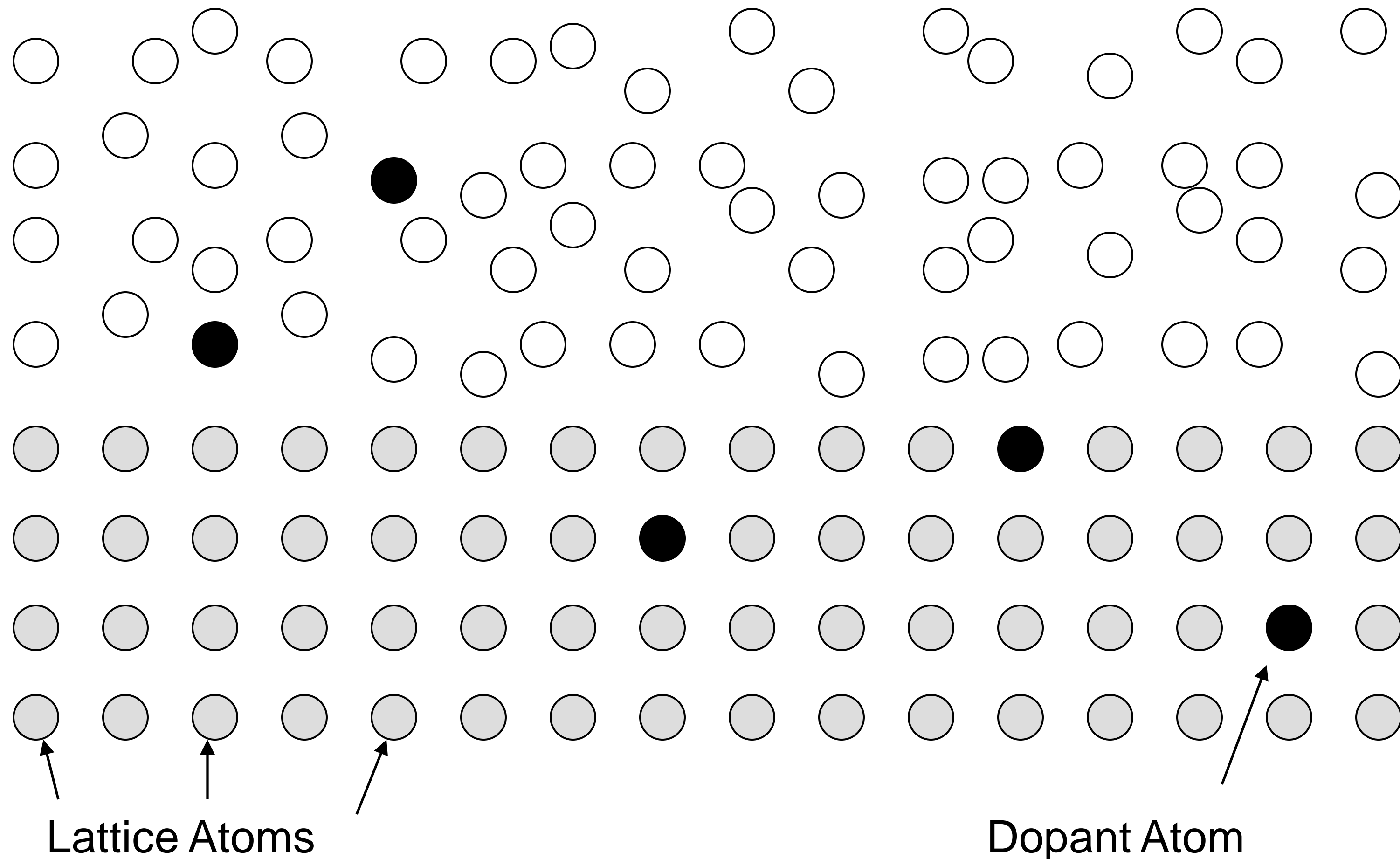
Thermal Annealing



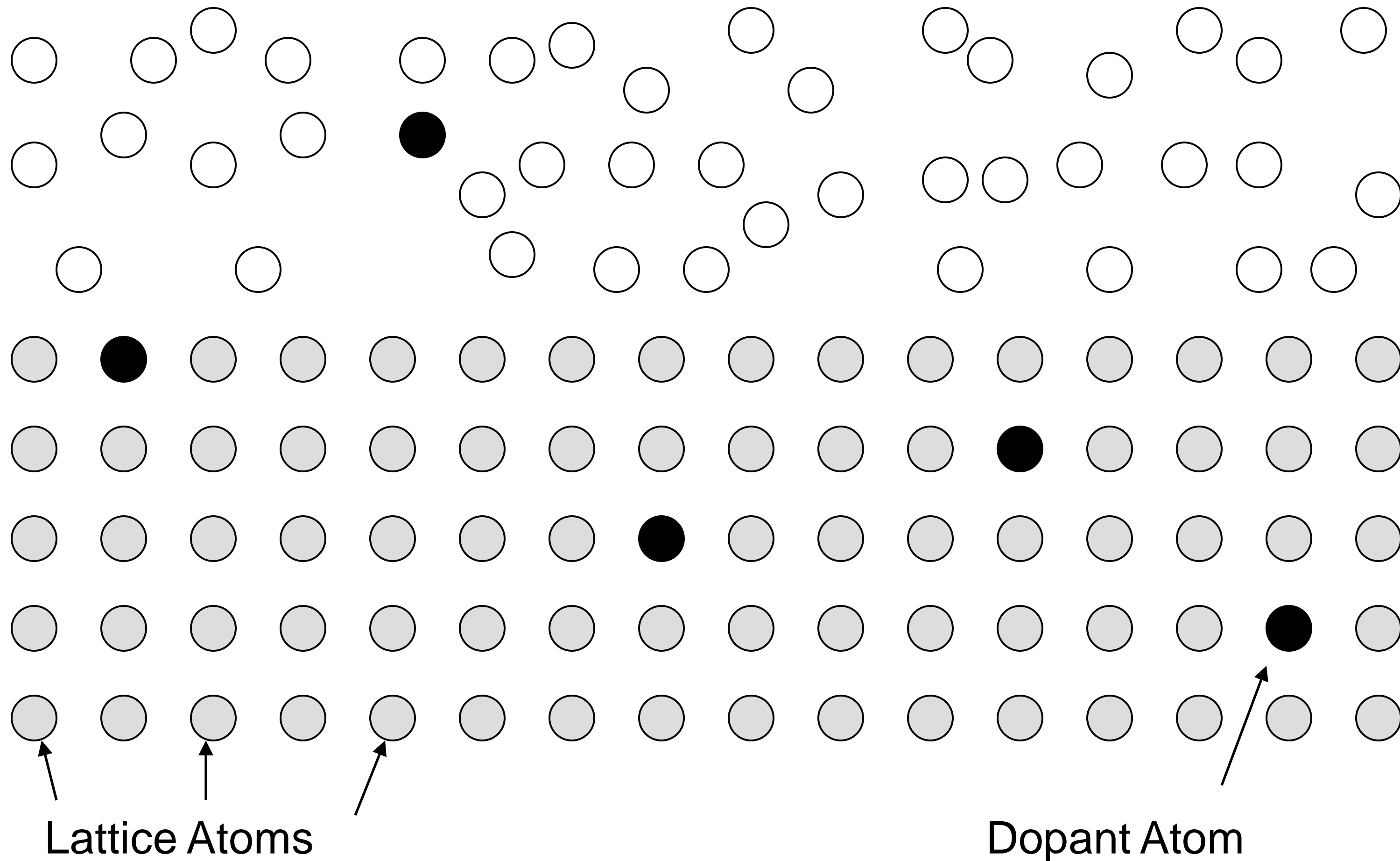
Thermal Annealing



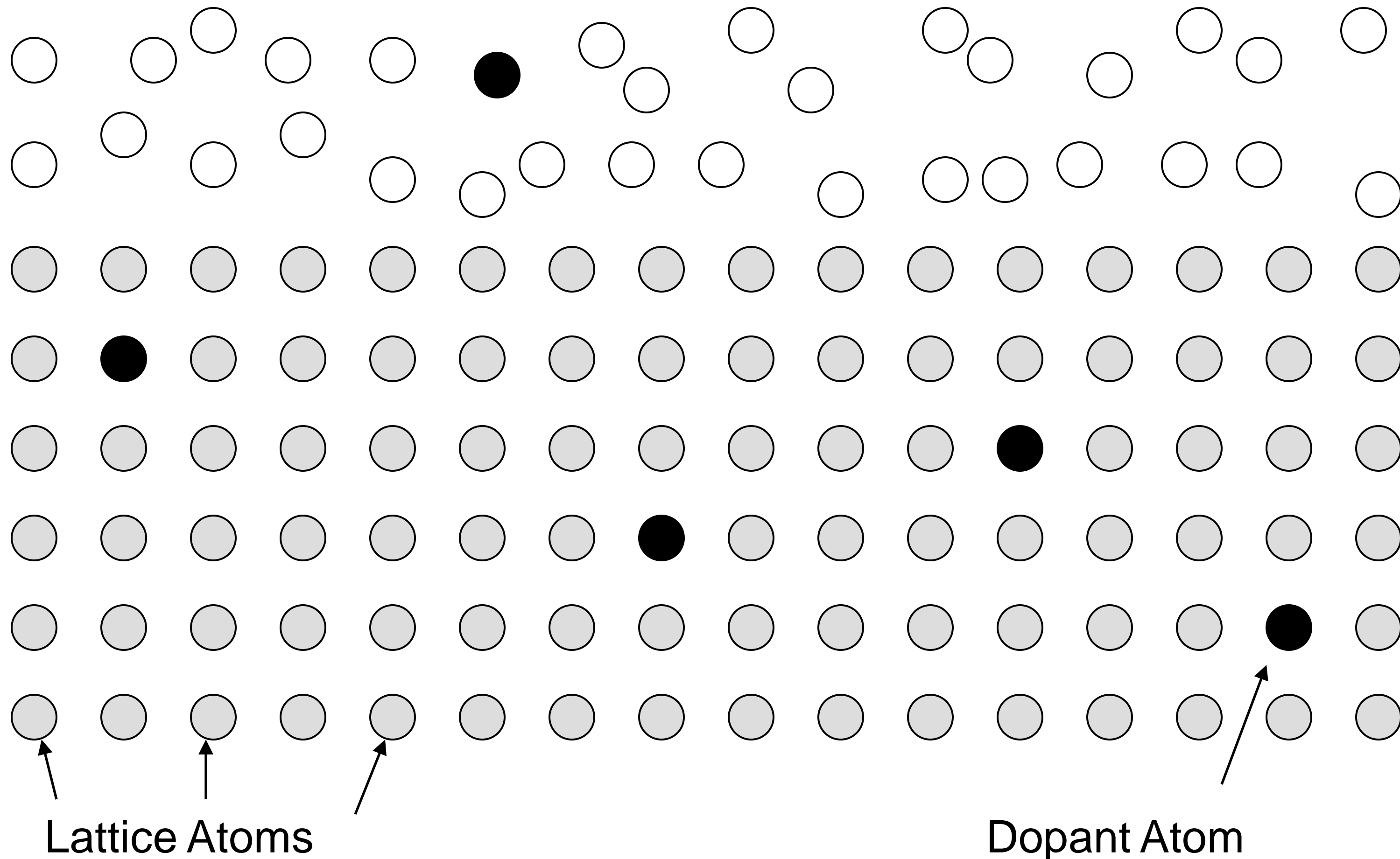
Thermal Annealing



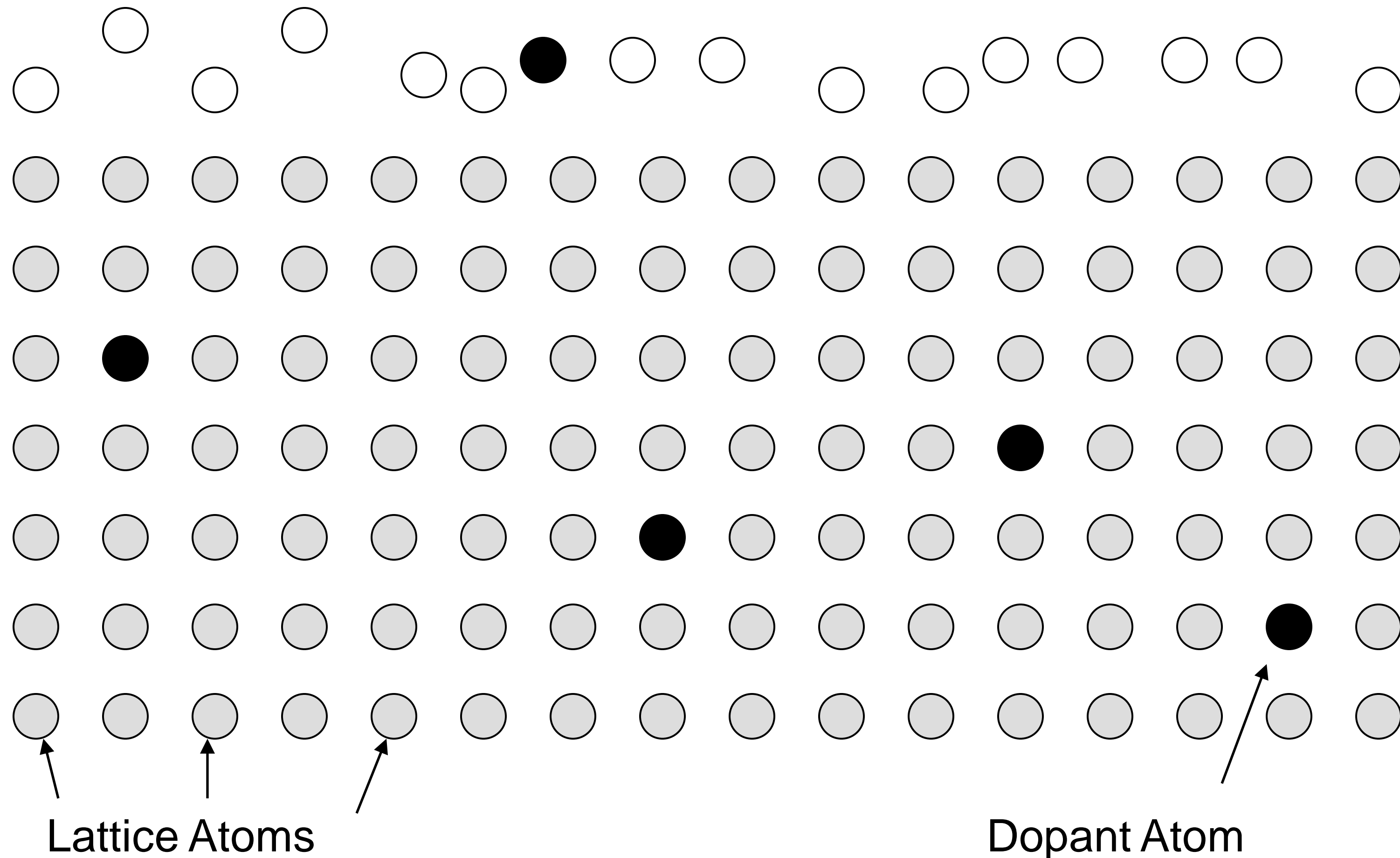
Thermal Annealing



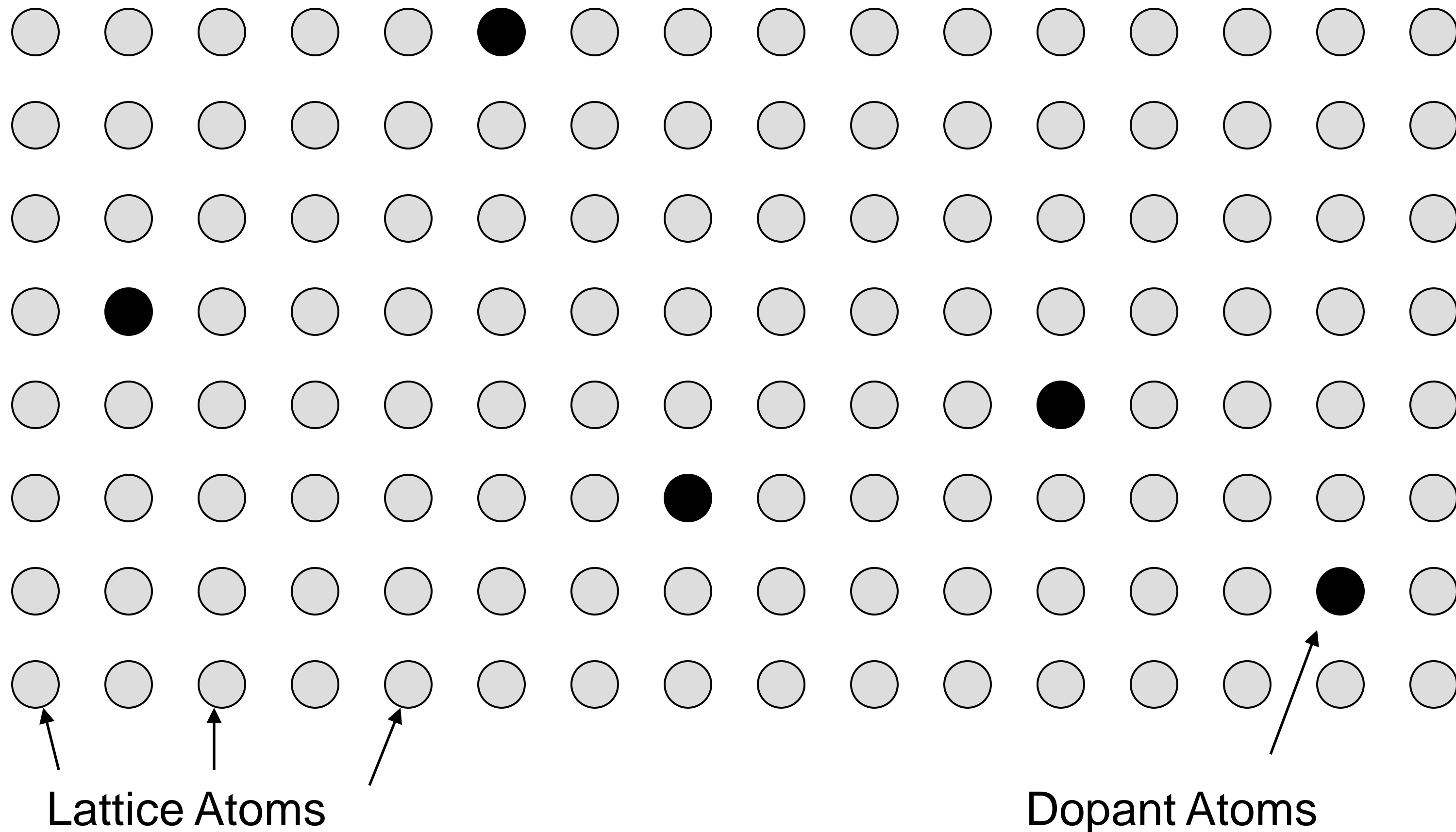
Thermal Annealing



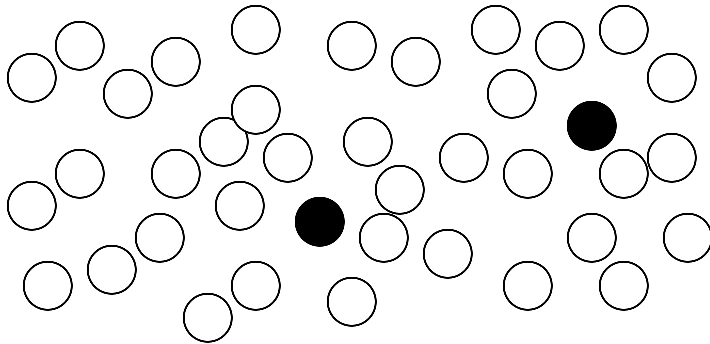
Thermal Annealing



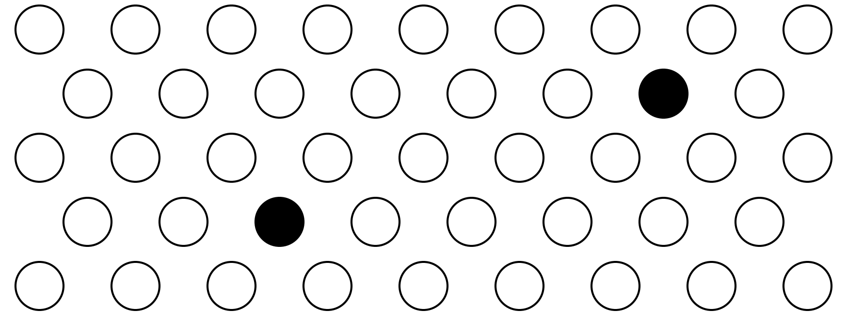
Thermal Annealing



Implantation Processes: Annealing



Before Annealing

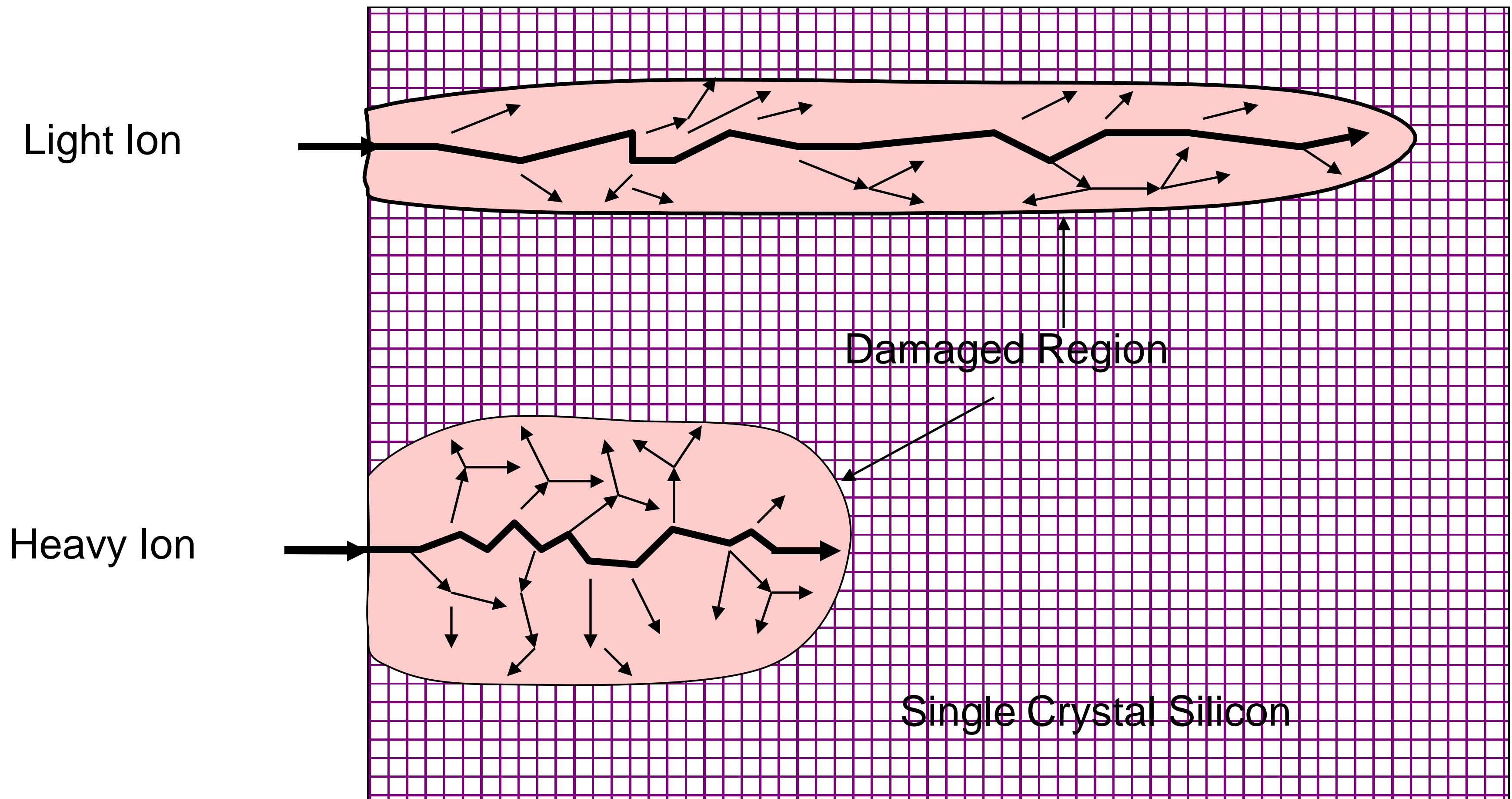


After Annealing

Rapid Thermal Annealing (RTA)

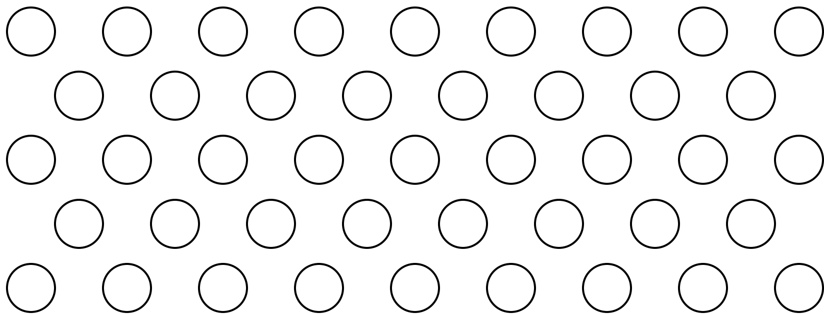
- At high temperature, annealing out pace diffusion
- Rapid thermal process (RTP) is widely used for post-implantation anneal
- RTA is fast (less than a minute), better WTW uniformity, better thermal budget control, and minimized the dopant diffusion

Lattice Damage With One Ion

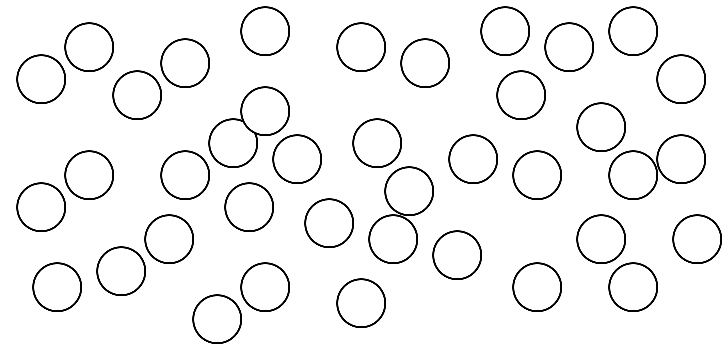


Implantation Processes: Damage

- Ion collides with lattice atoms and knock them out of lattice grid
- Implant area on substrate becomes amorphous structure



Before Implantation



After Implantation

Monte Carlo Simulation of 50keV Boron implanted into Si

SRIM-2000 (v.09)

Ion Type = B (11 amu)
Ion Energy = 50 keV
Ion Angle = 0 degrees

TARGET LAYERS	Depth	Density
Layer 1	5000A	2.321

AtomColors=B/B

Ion Completed= 333(99999)
Backscattered Ions =
Transmitted Ions =

	Range	Straggle
Longitudinal=	1775A	511A
Lateral Proj=	487A	595A
Radial =	753A	365A

Vac./Ion = 323.0

ENERGY LOSS(%)	IONS	RECOILS
Ionization ==>	68.00	7.08
Vacancies ==>	0.21	1.08
Phonons ==>	0.71	22.95