나노소재합성개론

2025-2

3. Synthesis of Nanomaterials - I (Physical Methods)

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.2.2 Laser Vapourization (Ablation)

- Vapourization of the material is effected using pulses of laser beam of high power

- The set up is an Ultra High Vacuum (UHV) or high vacuum system equipped with inert or reactive gas introduction facility, laser beam, solid target and cooled substrate.

- Usually laser operating in the UV range such as excimer (excited monomers) laser (see Table 3.1) is necessary because other wavelengths like IR or visible are often reflected by surfaces of some metals.

Gas	F_2	ArF	KrCl	KrF	XeCl	XeF
λ, nm	157	193	222	249	308	350

Table 3.1 Wavelengths of some commonly used excimer lasers

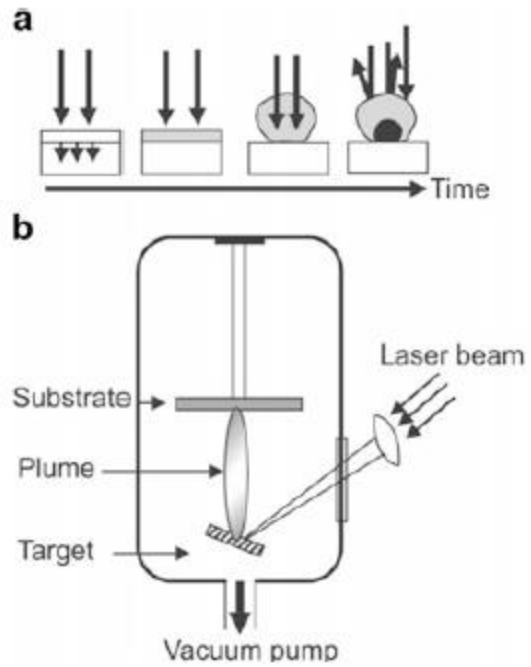
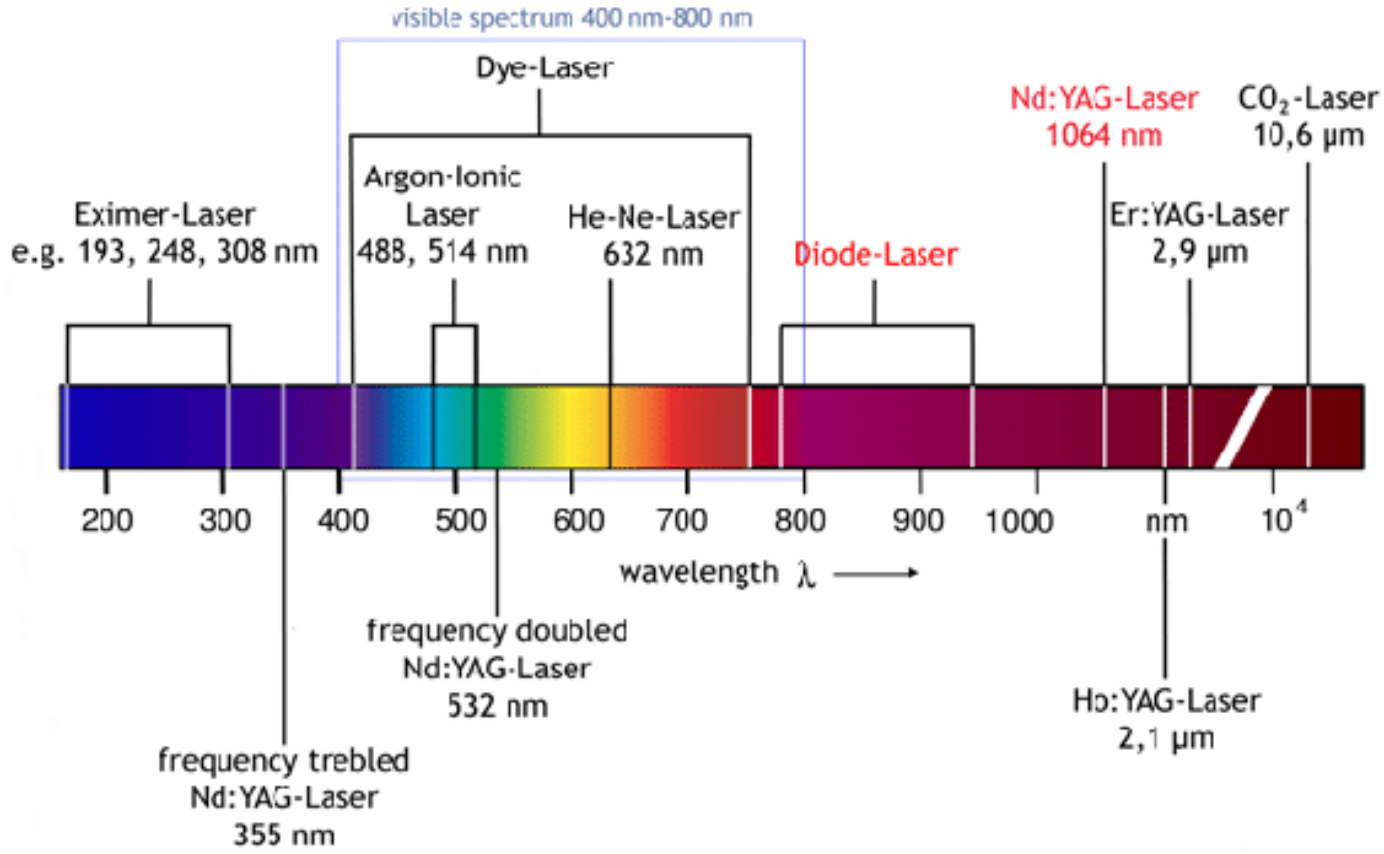


Fig. 3.8 (a) Sequence of material evaporation by laser beam interaction with a target material. (b) Laser deposition schematic apparatus

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.2.2 Laser Vapourization (Ablation)



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3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.2.2 Laser Vapourization (Ablation)

- A powerful beam of laser evaporates the atoms from a solid source and atoms collide with inert gas atoms (or reactive gases) and cool on them forming clusters.
- They condense on the cooled substrate. The method is often known as laser ablation.
- Gas pressure is very critical in determining the particle size and distribution.
- Simultaneous evaporation of another material and mixing the two evaporated materials in inert gas leads to the formation of alloys or compounds.
- This method can produce some novel phases of the materials which are not normally formed.
- For example Single Wall Carbon Nanotubes (SWNT) are mostly synthesized by this method.

3. Synthesis of Nanomaterials I (Physical Methods)

3.2 Methods Based on Evaporation

3.2.2 Laser Pyolysis

- Another method of thin films synthesis using lasers is known as 'laser pyrolysis' or laser-assisted deposition.

- A mixture of reactant gases is decomposed using a powerful laser beam in presence of some inert gas like helium or argon

- Atoms or molecules of decomposed reactant gases collide with inert gas atoms and interact with each other, grow and are then deposited on cooled substrate.

  ➡ Many nanoparticles of materials like Al_2O_3, WC and Si_3N_4

- Gas pressure plays an important role in deciding the particle sizes and their distribution.

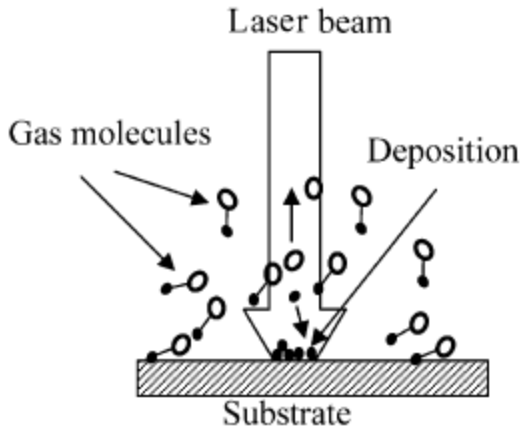


Fig. 3.9 Schematic diagram depicting laser pyrolysis

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

- Sputter deposition is a widely used thin film deposition technique, specially to obtain stoichiometric thin films (i.e. without changing the composition of the original material) from target material

- Target material may be some alloy, ceramic or compound and Sputtering is also effective in producing non-porous compact films
- Sputtering is a very good technique to deposit multilayer films for mirrors or magnetic films for spintronics applications.
- In sputter deposition, some inert gas ions like ArC are incident on a target at a high energy.
- Depending on the energy of ions, ratio of ion mass to that of target atoms mass, the ion-target interaction can be a complex phenomenon

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

- The ions become neutral at the surface but due to their energy, incident ions may get implanted, get bounced back, create collision cascades in target atoms, displace some of the atoms in the target creating vacancies, interstitials and other defects, desorb some adsorbates, create photons while loosing energy to target atoms or even sputter out some target atoms/molecules, clusters, ions and secondary electrons.

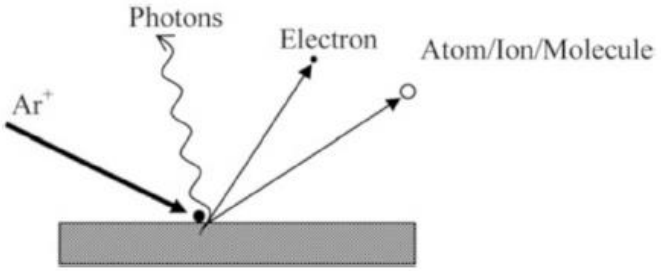


Fig. 3.10 Interaction of an ion with target

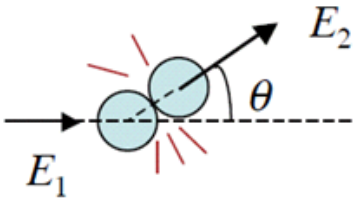
- Sputter yield for different elements with same incident ion having same energy varies in general.
- This would lead one to think that from a target consisting of two different elements or more, the one having higher sputter yield should get incorporated in larger quantity than the others.
- However high sputter yield elements get depleted fast and other elements also make contribution. Thus the stoichiometry is achieved in the deposited film.

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

Sputtering yield

Elastic energy transfer



$$\frac{E_2}{E_1} \propto \frac{4M_1M_2}{(M_1+M_2)^2}\cos^2\theta$$

E_2 is greatest for $M_1=M_2$.
There is also inelastic energy transfer, which leads to secondary electrons emission…

$$Y = \frac{\text{sputtered atoms}}{\text{bombing ions}} = \alpha \frac{Mm}{(M+m)^2}\frac{E_m}{U_M}$$

M : mass of target atom

m : mass of bombing ion

E_m : kinetic energy of bombing ion

U_M : Bonding energy of target metal

α : depends on striking /incident angle

- Sputter yield Y: the number of sputtered atoms per impinging ion.
- Obviously, the higher yield, the higher sputter deposition rate.
- Sputter yield is 1-3: not too much difference for different materials.
- 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.
- The yield is rather insensitive to the target temperature except at very high temperatures where it show an apparent rapid increase due to the accompanying thermal evaporation.

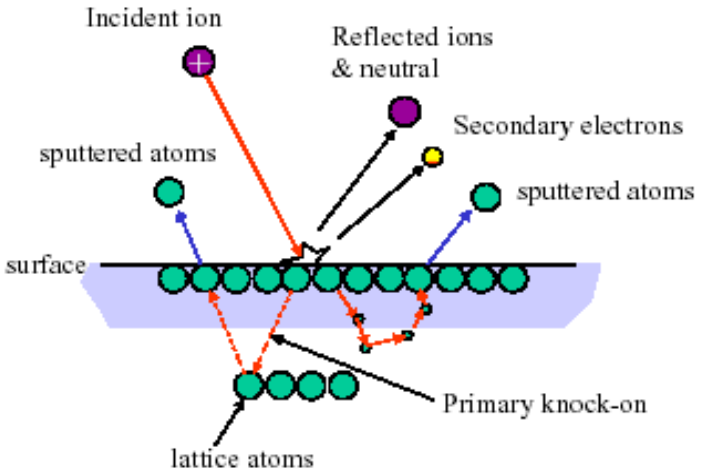
3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

Mechanisms of sputtering and alloy sputtering

The ion impact may set up a series of collisions between atoms of the target, possibly leading to the ejection of some of these atoms. This ejection process is known as sputtering.

Here we are interested in sputter deposition. Of course sputter can also be used as an etching method (the substrate to be etched will be the 'target'), which is called sputter etching.

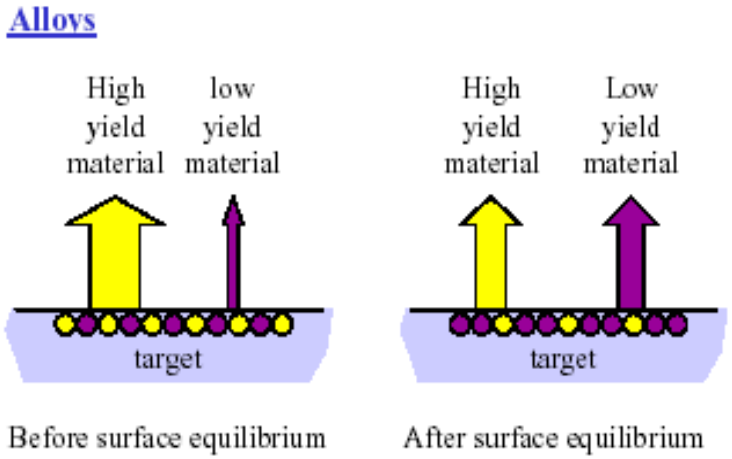


For Alloys

Unlike evaporation, composition of alloy in film is approximately the same as target.

Target NOT melted, slow *diffusion* (no material flow) mixing.

When target reaches steady state, surface composition balances sputter yield.



3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

Advantages:

- Able to deposit a wide variety of metals, insulators, alloys and composites.
- Replication of target composition in the deposited films.
- Capable of in-situ cleaning prior to film deposition by reversing the potential on the electrodes .
- Better film quality and step coverage than evaporation.
- This is partly because adatoms are more energetic, and film is 'densified' by in-situ ion bombardment, and it is easier to heat up to high T than evaporation that is in vacuum.
- More reproducible deposition control – same deposition rate for same process parameters (not true for evaporation), so easy film thickness control via time.
- Can use large area targets for uniform thickness over large substrates.
- Sufficient target material for many depositions.
- No x-ray damage.

Disadvantages:

- Substrate damage due to ion bombardment or UV generated by plasma.
- Higher pressures 1 –100 mtorr ($< 10^{-5}$ torr in evaporation), more contaminations unless using ultra clean gasses and ultra clean targets.
- Deposition rate of some materials quite low.
- Some materials (e.g., organics) degrade due to ionic bombardment.
- Most of the energy incident on the target becomes heat, which must be removed.

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

- Sputtering process can be run in DC or RF mode (insulator must be run in RF mode)
- Major process parameters:
  - Operation pressure (~1-100mTorr)
  - Power (few 100W)
  - For DC sputtering, voltage -2 to -5kV.
  - Additional substrate bias voltage.
  - Substrate temperature (20-700^{o}C)

In addition to IC industry, a wide range of industrial products use sputtering: LCD, computer hard drives, hard coatings for tools, metals on plastics.

It is more widely used for industry than evaporator, partly because that, for evaporation:

- There are very few things (rate and substrate temperature) one can do to tailor film property.
- The step coverage is poor.
- It is not suitable for compound or alloy deposition.
- Considerable materials are deposited on chamber walls and wasted.

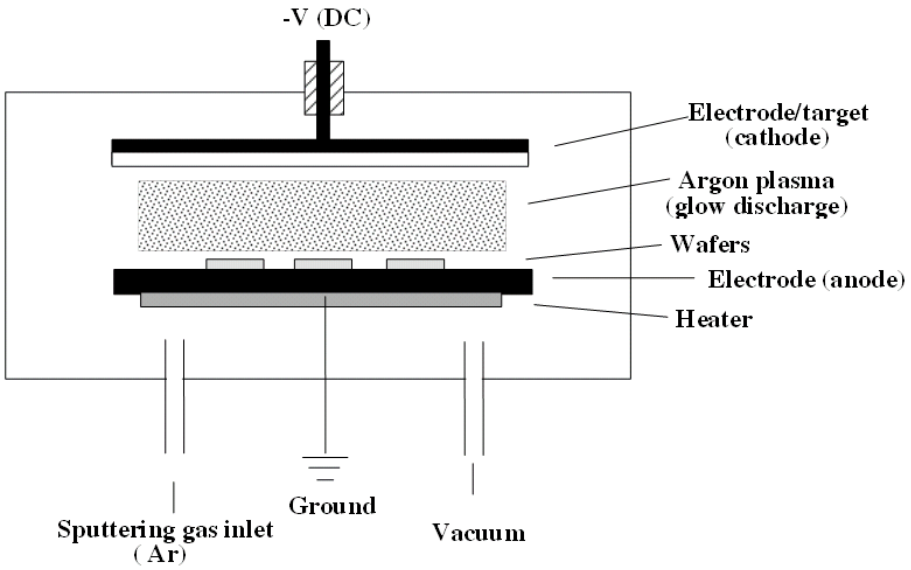
Targets for sputter deposition.

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

3.3.1 DC Sputtering

- This is a very straight forward technique of deposition, in which sputter target is held at high negative voltage and substrate may be at positive, ground or floating potential



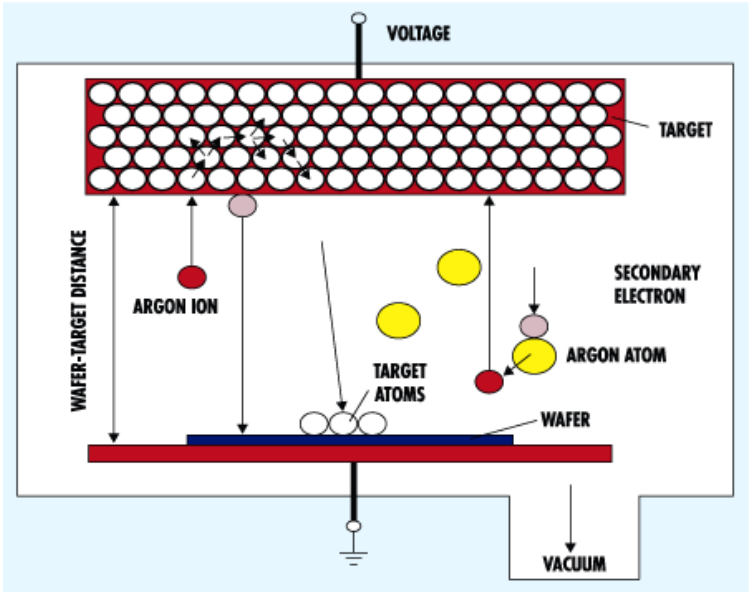


Fig. Schematic diagram of DC-powered sputter deposition equipment.

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

3.3.1 DC Sputtering

- Plasma is needed to make the gas conductive, and generated ions can then be accelerated to strike the target.
- Higher pressures than evaporation: 1-100 mTorr.
- Better at depositing alloys and compounds than evaporation.
- The plasma contains ≈ equal numbers of positive argon ions and electrons as well as neutral argon atoms. Typically only <0.01% atoms are ionized!

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

3.3.1 DC Sputtering

DC plasma

Plasma is ionized gas, with nearly equal number of ions and electrons, plus neutrals (un-ionized molecules including those at ground state and excited state; free radicals such as atomic O, H, F – but no free radicals for Ar plasma).

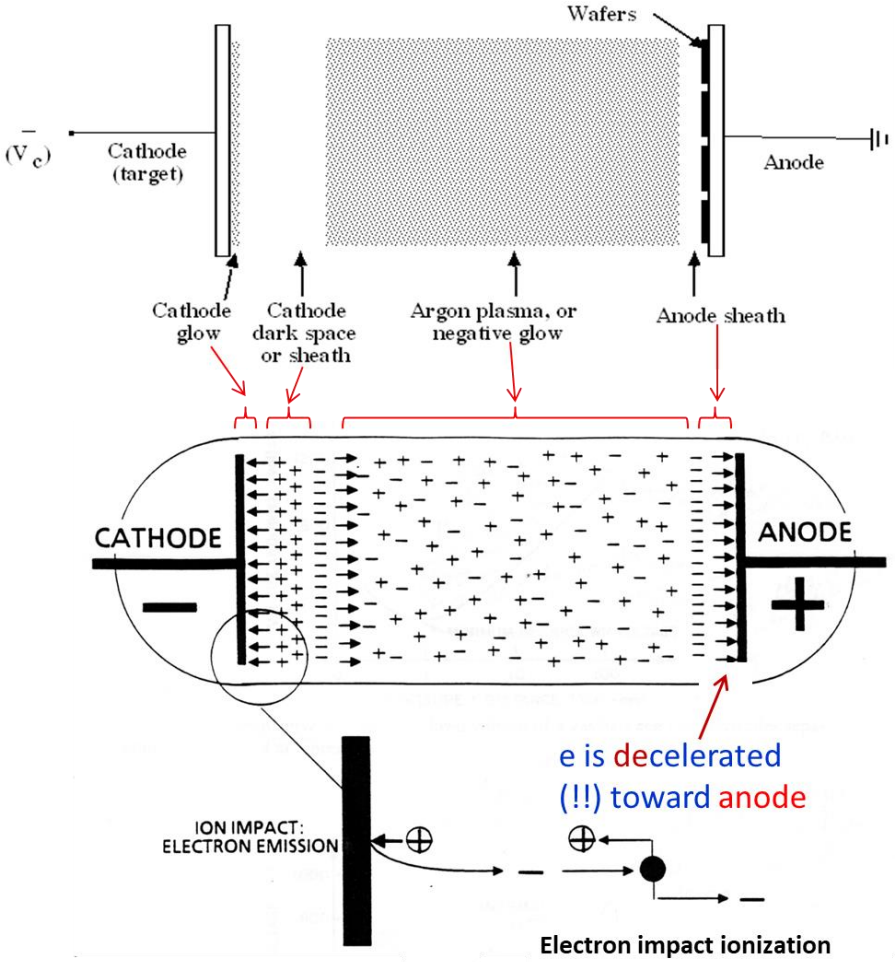
Glow is due to de-excitation of excited Ar.

So glow only exists where there are lots of electrons to excite Ar.

Cathode glow region: very close to cathode, secondary electrons are created by Ar bombardment of target material.

Cathode dark space/sheath: electrons pass too fast with little excitation.

Anode sheath: electrons lost to anode due to its faster *random* movement.



3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

3.3.2 Reactive sputtering

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

- Sputtering a compound target may not give what one wants.
- This doesn't mean reactive sputtering will give what one wants – it is just one more thing to try with.
- Certainly reactive sputtering can be done using DC sputtering, whereas compound target (insulating) can only be used for RF sputtering.
- Chemical reaction takes place on substrate and target.
- Can "poison" target if chemical reactions are faster than sputter rate.
- Need to adjust reactive gas flow to get good composition (e.g. SiO_2 rather than SiO_{2-x}) without incorporating excess gas into film.

A mixture of inert + reactive gases used for sputtering:

Oxides – Al_2O_3, SiO_2, Ta_2O_5 (O_2 mixed with Ar)

Nitrides – TaN, TiN, Si_3N_4 (N_2, NH_3, mixed with Ar)

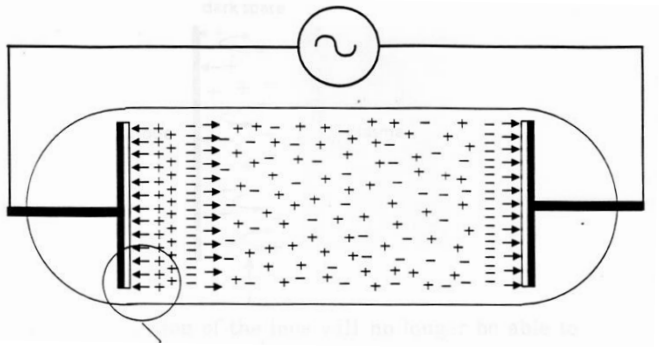
Carbides – TiC, WC, SiC (CH_4, C_2H_4, C_3H_8, mixed with Ar)

3. Synthesis of Nanomaterials I (Physical Methods)

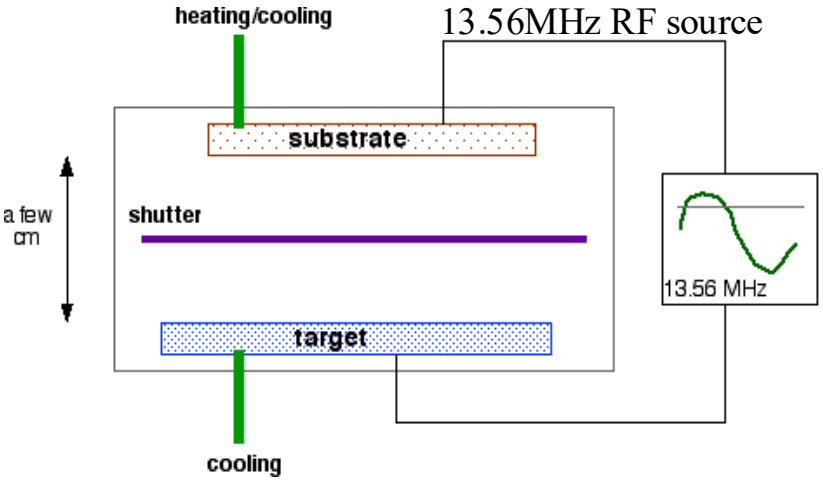
3.3 Sputter Deposition

3.3.2 RF sputtering

- Good for insulating materials because, positive charge (Ar^+) build up on the cathode (target) in DC sputtering systems. Alternating potential can avoid charge buildup
- When frequencies less than ~50kHz, both electrons and ions can follow the switching of the anode and cathode, basically DC sputtering of both surfaces.
- When frequencies well above ~50kHz, ions (heavy) can no longer follow the switching, and electrons can neutralize positive charge buildup on each electrode during each half cycle.
- As now electrons gain energy directly from RF powder (no need of secondary electrons to maintain plasma), and oscillating electrons are more efficient to ionize the gas, RF sputter is capable of running in lower pressure (1-15 mTorr), so fewer gas collisions and more line of sight deposition.



Switch polarities before the target surface saturates with ions.



3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

3.3.2 RF sputtering

- For symmetric target-substrate configuration, sputtering of both surfaces will occur, though in the opposite half cycles.
- When the electrode areas are not equal, the field must be higher at the smaller electrode (higher current density), to maintain overall current continuity.
- It was found that voltage drop across the dark sheath of the two electrodes satisfy the relation: (A is the area of the electrode)

$$\frac{V_1}{V_2} = \left(\frac{A_2}{A_1}\right)^m \quad \text{(m = 1-2 experimentally)}$$

- Thus by making the target electrode much smaller, sputtering occurs "only" on the target.
- Wafer electrode can also be connected to chamber walls, further increasing V_2/V_1.

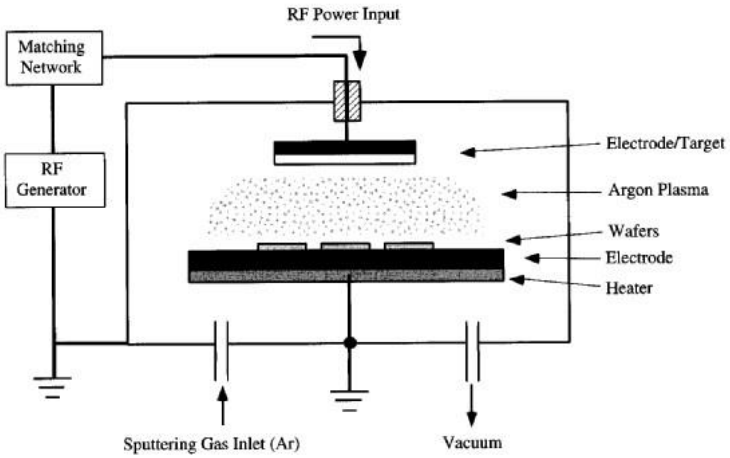
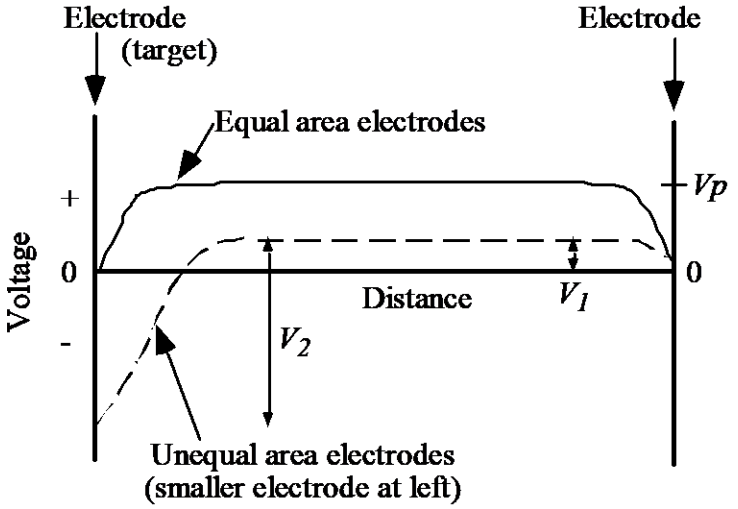


Figure 9–28 Schematic diagram of RF-powered sputter deposition system.



3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

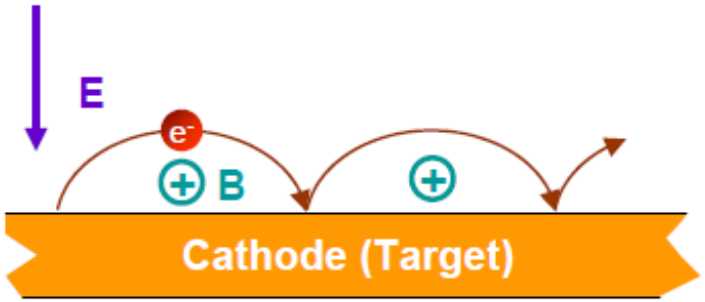
3.3.3 Magnetron Sputtering

- In DC & RF sputtering, the efficiency of ionization from energetic collisions between the electrons and gas atoms is low.
- Most electrons lose energy in non-ionizing collisions or are collected by the electrodes.
- Oscillating RF fields increasing ionization efficiency marginally.
- Hence, deposition rates are low.
- To increase deposition rates, magnets are used to increase the percentage of electrons that take part in ionization events, increasing the ionization efficiency.
- A magnetic field is applied at right angles to the electric field by placing large magnets behind the target.
- This traps electrons near the target surface and causes them to move in a spiral motion until they collide with an Ar atom.
- The ionization and sputtering efficiencies are increased significantly - deposition rates increase by 10-100×, to 1 μm per minute.
- Unintentional wafer heating is reduced since the dense plasma is confined near the target and ion loss to the wafers is less.
- A lower Ar pressure (to 0.5mTorr, can still sustain plasma) can be utilized since ionization efficiency is larger which can improve film quality as less argon will be incorporated into the film.
- Magnetron sputtering can be done in DC or RF, but more often it is done in DC as cooling of insulating targets is difficult in RF systems.

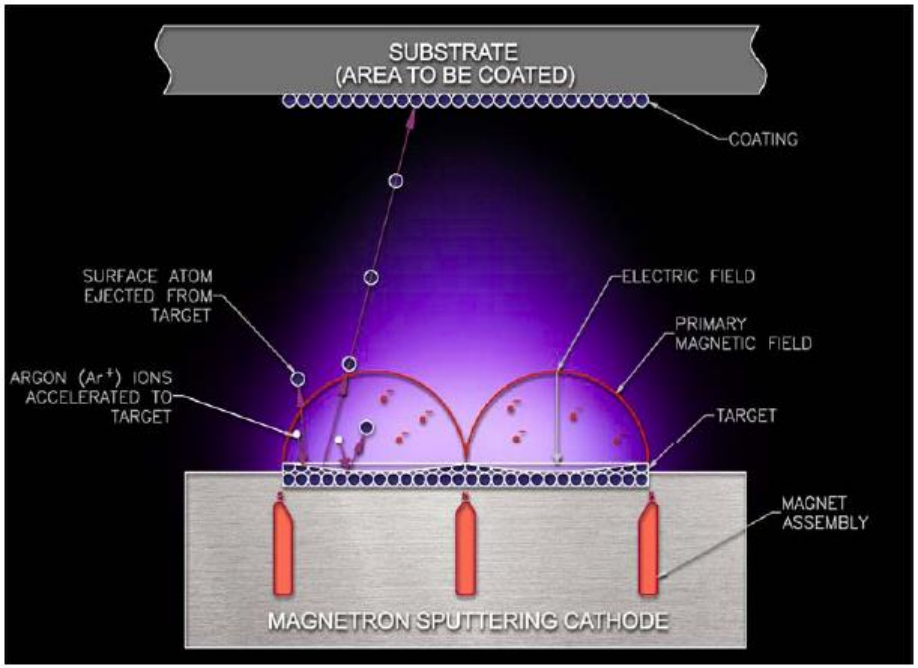
3. Synthesis of Nanomaterials I (Physical Methods)

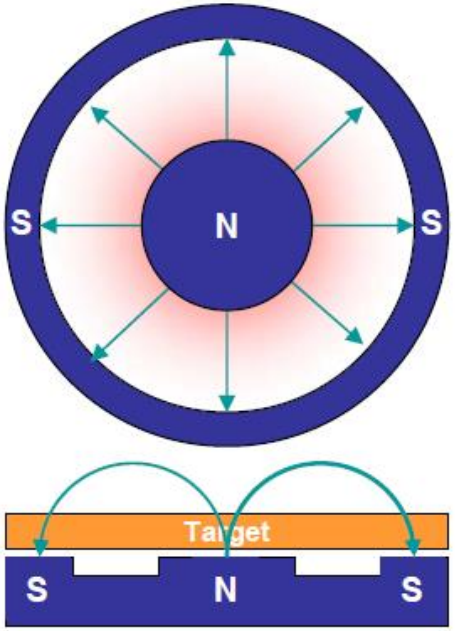
3.3 Sputter Deposition

3.3.3 Magnetron Sputtering



Orbital motion of electrons increases probability that they will collide with neutral species and create ions.





Magnetron sputtering for high density of plasma near target.

3. Synthesis of Nanomaterials I (Physical Methods)

3.3 Sputter Deposition

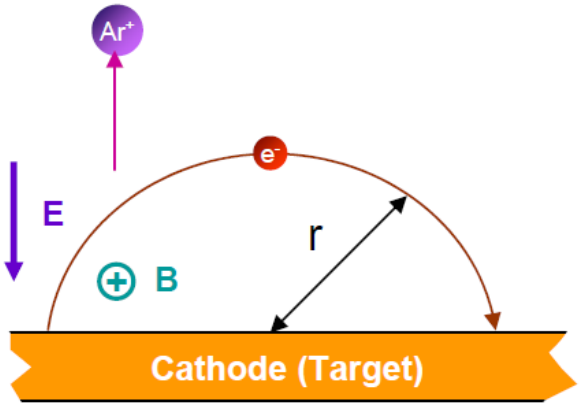
3.3.3 Magnetron Sputtering

Impact of magnetic field on ions

Hoping radius r:

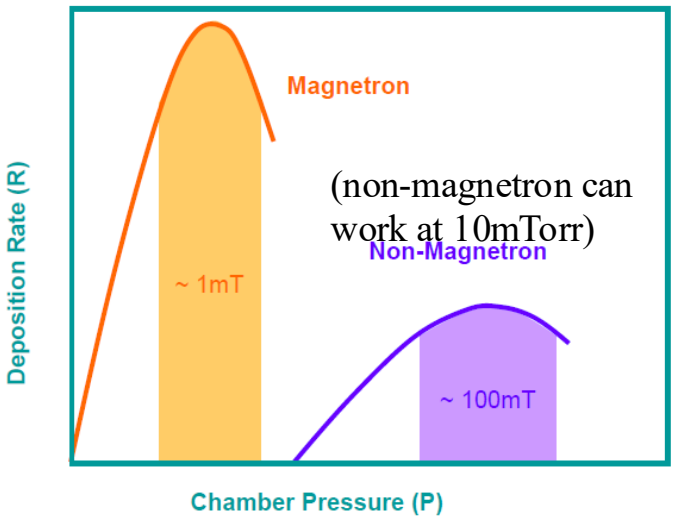
$$r \sim \frac{1}{B}\sqrt{\frac{2m}{e}V_d}$$

V_d: voltage drop across dark space/sheath (~100V)
B: magnetic field (~100G)
For electron: r~0.3cm
For Ar^+ ion: r~81cm



As a result:

- Current density (proportional to ionization rate) increases by 100 times.
- Required discharge pressure drops 100 times.
- Deposition rate increases 100 times.



3. Synthesis of Nanomaterials I (Physical Methods)

Comparison of evaporation and sputtering

EVAPORATION	SPUTTERING
low energy atoms	higher energy atoms
high vacuum path • few collisions • line of sight deposition • little gas in film	low vacuum, plasma path • many collisions • less line of sight deposition • gas in film
larger grain size	smaller grain size
fewer grain orientations	many grain orientations
poorer adhesion	better adhesion

3. Synthesis of Nanomaterials I (Physical Methods)

Comparison of evaporation and sputtering

Evaporation	Sputtering
Low energy atoms (~ 0.1 eV)	High energy atoms / ions (1 – 10 eV) • denser film • smaller grain size • better adhesion
High Vacuum • directional, good for lift-off • lower impurity	Low Vacuum • poor directionality, better step coverage • gas atom implanted in the film
Point Source • poor uniformity	Parallel Plate Source • better uniformity
Component Evaporate at Different Rate • poor stoichiometry	All Component Sputtered with Similar Rate • maintain stoichiometry

3. Synthesis of Nanomaterials I (Physical Methods)

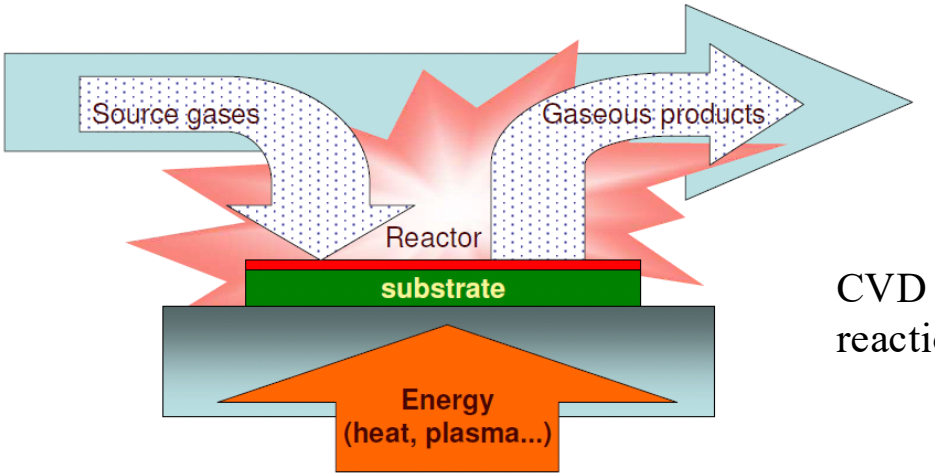
Comparison of evaporation and sputtering

	Evaporation	Sputtering
Rate	Thousand atomic layers per second (e.g. 0.5 μm/min for Al)	One atomic layer per second
Choice of materials	Limited	Almost unlimited
Purity	Better (no gas inclusions, very high vacuum)	Possibility of incorporating impurities (low-medium vacuum range)
Substrate heating	Very low	Unless magnetron is used substrate heating can be substantial
Surface damage	Very low, with e-beam x-ray damage is possible	Ionic bombardment damage
In-situ cleaning	Not an option	Easily done with a sputter etch
Alloy compositions, stochiometry	Little or no control	Alloy composition can be tightly controlled
X-ray damage	Only with e-beam evaporation	Radiation and particle damage is possible
Changes in source material	Easy	Expensive
Decomposition of material	High	Low
Scaling-up	Difficult	Good
Uniformity	Difficult	Easy over large areas
Capital Equipment	Low cost	More expensive
Number of depositions	Only one deposition per charge	Many depositions can be carried out per target
Thickness control	Not easy to control	Several controls possible
Adhesion	Often poor	Excellent
Shadowing effect	Large	Small
Film properties (e.g. grain size and step coverage)	Difficult to control	Control by bias, pressure, substrate heat

3. Synthesis of Nanomaterials I (Physical Methods)

3.4 Chemical Vapor Deposition (CVD)

- Chemical vapour deposition, a hybrid method using chemicals in vapour phase is conventionally used to obtain coatings of a variety of inorganic or organic materials.



CVD : deposit film through chemical reaction and surface absorption.

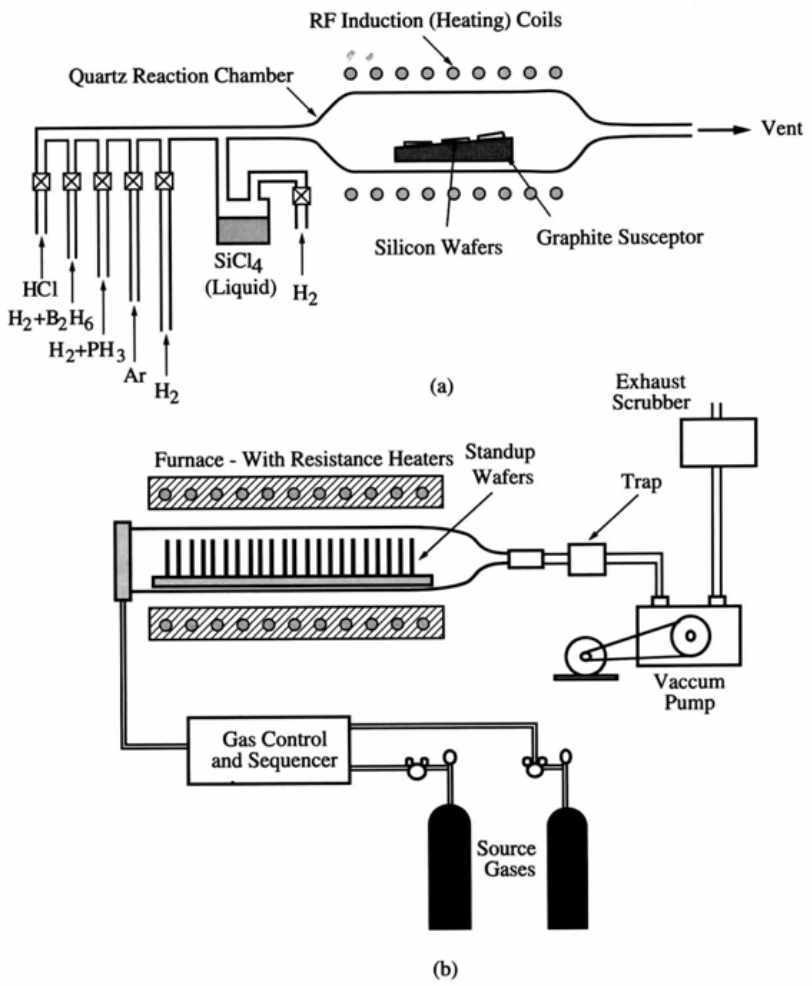
CVD steps:

- Introduce reactive gases to the chamber.
- Activate gases (decomposition) by heat or plasma.
- Gas absorption by substrate surface .
- Reaction take place on substrate surface, film firmed.
- Transport of volatile byproducts away form substrate.
- Exhaust waste.

3. Synthesis of Nanomaterials I (Physical Methods)

3.4 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) systems



Atmospheric cold-wall system used for deposition of epitaxial silicon. ($SiCl_4 + 2H_2 \rightarrow Si + 4HCl$)

Low pressure hot-wall system used for deposition of polycrystalline and amorphous films, such as poly-silicon and silicon dioxide.

3. Synthesis of Nanomaterials I (Physical Methods)

3.4 Chemical Vapor Deposition (CVD)

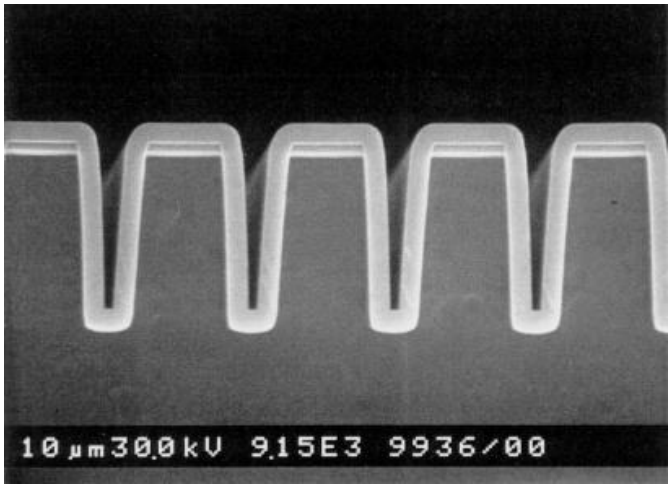
CVD advantages and disadvantages (as compared to physical vapor deposition)

Advantages:

- High growth rates possible, good reproducibility.
- Can deposit materials which are hard to evaporate.
- Can grow epitaxial films. In this case also termed as “vapor phase epitaxy (VPE)”. For instance, MOCVD (metal-organic CVD) is also called OMVPE (organo-metallic VPE).
- Generally better film quality, more conformal step coverage (see image below).

Disadvantages:

- High process temperatures.
- Complex processes, toxic and corrosive gasses.
- Film may not be pure (hydrogen incorporation…).



3. Synthesis of Nanomaterials I (Physical Methods)

3.4 Chemical Vapor Deposition (CVD)

Types of CVD reactions

- **Thermal decomposition**

  AB(g) ---> A(s) + B(g)

  Si deposition from Silane at 650°C: $SiH_4(g) \rightarrow Si(s) + 2H_2(g)$

  $Ni(CO)_4(g) \rightarrow Ni(s) + 4CO(g)$ (180°C)

- **Reduction (using H_2)**

  $AX(g) + H_2(g) \rightarrow A(s) + HX(g)$

  W deposition at 300°C: $WF_6(g) + 3H_2(g) \rightarrow W(s) + 6HF(g)$

  $SiCl_4(g) + 2H_2(g) \rightarrow Si(s) + 4HCl$ (1200°C)

- **Oxidation (using O_2)**

  $AX(g) + O_2(g) \rightarrow AO(s) + [O]X(g)$

  SiO_2 deposition from silane and oxygen at 450°C (lower temp than thermal oxidation):
  $SiH_4(g) + O_2(g)$ ---> $SiO_2(s) + 2H_2(g)$

  $2AlCl_3(g) + 3H_2(g) + 3CO_2(g) \rightarrow Al_2O_3 + 3CO + 6HCl$ (1000°C)

  (O is more electronegative than Cl)

- **Compound formation (using NH_3 or H_2O)**

  $AX(g) + NH_3(g) \rightarrow AN(s) + HX(g)$ or $AX(g) + H_2O(g) \rightarrow AO(s) + HX(g)$

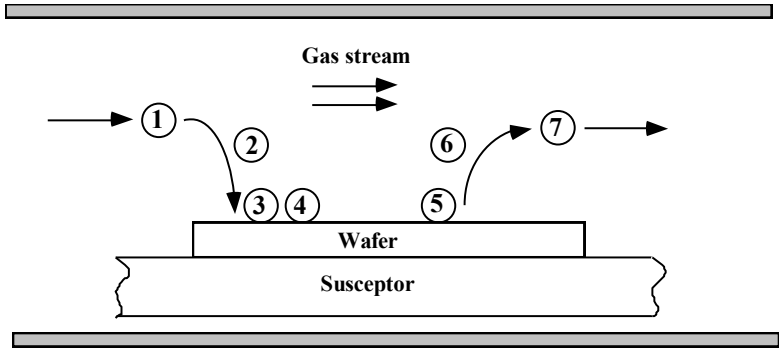
  Deposit wear resistant film (BN) at 1100°C: $BF_3(g) + NH_3(g) \rightarrow BN(s) + 3HF(g)$

  $(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4$ (650 – 750°C)

3. Synthesis of Nanomaterials I (Physical Methods)

3.4 Chemical Vapor Deposition (CVD)

Steps involved in a CVD process



Reaction rate may be limited by:

- Gas transport to/from surface.
- Surface chemical reaction rate that depends strongly on temperature.

1. Transport of reactants to the deposition region.
2. Transport of reactants from the main gas stream through the boundary layer to the wafer surface.
3. Adsorption of reactants on the wafer surface.
4. Surface reactions, including: chemical decomposition or reaction, surface migration to attachment sites (kinks and ledges); site incorporation; and other surface reactions (emission and redeposition for example).
5. Desorption of byproducts.
6. Transport of byproducts through boundary layer.
7. Transport of byproducts away from the deposition region.

Steps 2-5 are most important for growth rate.
Steps 3-5 are closely related and can be grouped together as “surface reaction” processes.

Next

3. Synthesis of Nanomaterials - II (Chemical Methods)