2D Nanostructures

Thin Films

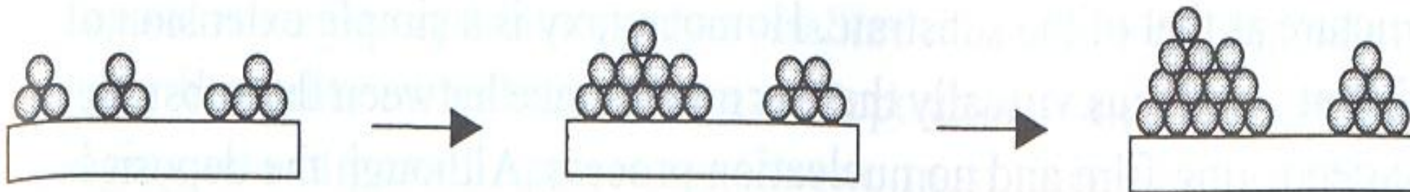
- Film growth methods
  - Vapour-phase deposition
    - Evaporation
    - Molecular beam epitaxy (MBE)
    - Sputtering
    - Chemical vapour deposition (CVD)
    - Atomic Layer deposition (ALD)
  - Liquid-based growth
    - Electrochemical deposition
    - Chemical Bath deposition (CBD or **CSD**)
    - Langmuir-Blodgett films
    - Self-assembled monolayers (SAMs)

- **Film deposition**
  - Involves predominantly heterogeneous processes
    - Heterogeneous chemical reactions
    - Evaporation
    - Adsorption & desorption on growth surfaces
    - Heterogeneous nucleation & surface desorption on growth surfaces
  - Most film deposition & characterization processes are conducted under vacuum

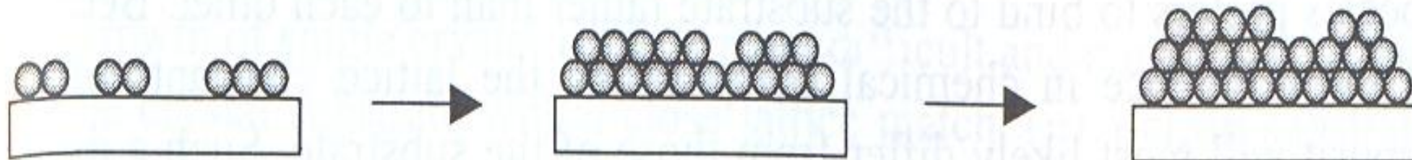
Fundamentals of film growth

- Thin film growth involves nucleation and growth on the substrate or growth surface
- Crystallinity & microstructure of film is determined by nucleation process
- 3 Basic nucleation modes
  - Island growth
    - Growth species are more strongly bonded to each other than to the substrate
    - Islands coalesce to form a continuous film
      - E.g. metals on insulator substrates, alkali halides, graphite and mica substrates
  - Layer growth
    - Growth species are bound more strongly to the substrate than to each other
    - 1st complete monolayer is formed before the deposition of 2nd layer occurs
    - Involves in situ developed stress due to lattice mismatch between the deposit and the substrate
      - e.g. epitaxial growth of single crystal films
  - Island-layer growth
    - combination of layer growth and island growth

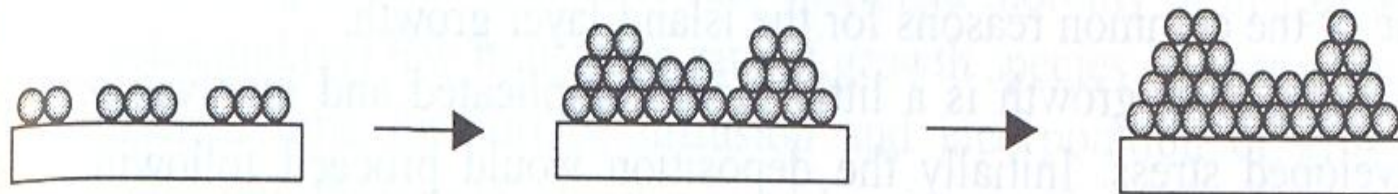
3 Basic nucleation modes



Island or Volmer–Weber growth



Layer or Frank–van der Merwe growth



Island-layer or Stranski–Krastonov growth

Effect of growth conditions

- Nucleation models and mechanisms are applicable to the formation of single crystal, polycrystalline and amorphous deposit, and of inorganic, organic and hybrid deposit
- Whether the deposit is single crystalline, polycrystalline or amorphous depends on the growth conditions and the substrate

Growth of single crystal films is most difficult and requires:

- Growth of single crystal films is most difficult and requires:
  - (i) a single crystal substrate with a close lattice match
  - (ii) a clean surface so as to avoid possible 2° nucleation
  - (iii) a high growth temperature so as to ensure sufficient mobility of the growth species
  - (iv) low impinging rate of growth species so as to ensure sufficient time for surface diffusion and incorporation of growth species into the crystal structure and for structural relaxation before the arrival of next growth species

Deposition of amorphous films

- Deposition of amorphous films typically occurs
- (i) when a low growth temperature is applied, there is a insufficient surface mobility of growth species, and/or
- (ii) When the influx of growth species onto the growth surface is very high, growth species does not have enough time to find the growth sites with the lowest energy.

Growth of polycrystalline crystalline films

- Conditions for the growth of polycrystalline films
- Intermediate between conditions of single crystal growth and amorphous film deposition
  - moderate temperature to ensure a reasonable surface mobility of growth species
  - High impinging flux of growth species

Epitaxy

- The growth or formation of single crystal on top of a single crystal substrate
- Homoepitaxy
  - is to grow film on the substrate, in which both are the same material
  - No lattice mismatch between films and substrates
  - Uses
    - to grow better quality film
    - to introduce dopants into the grown film
- Heteroepitaxy
  - Films & substrates are different materials
  - Lattice mismatch between films and substrates
- Application of epitaxy: electronic industry

Physical vapour deposition (PVD)

- PVD is a process of transferring growth species from a source or target and deposit them on a substrate to form a film.
- The process proceeds atomically and mostly involves no chemical reactions.
- Methods for the removal of growth species
  - Evaporation
    - The growth species are removed from the source by thermal means
  - Sputtering
    - Atoms or molecules are dislodged from solid target through impact of gaseous ions (plasma)

Evaporation

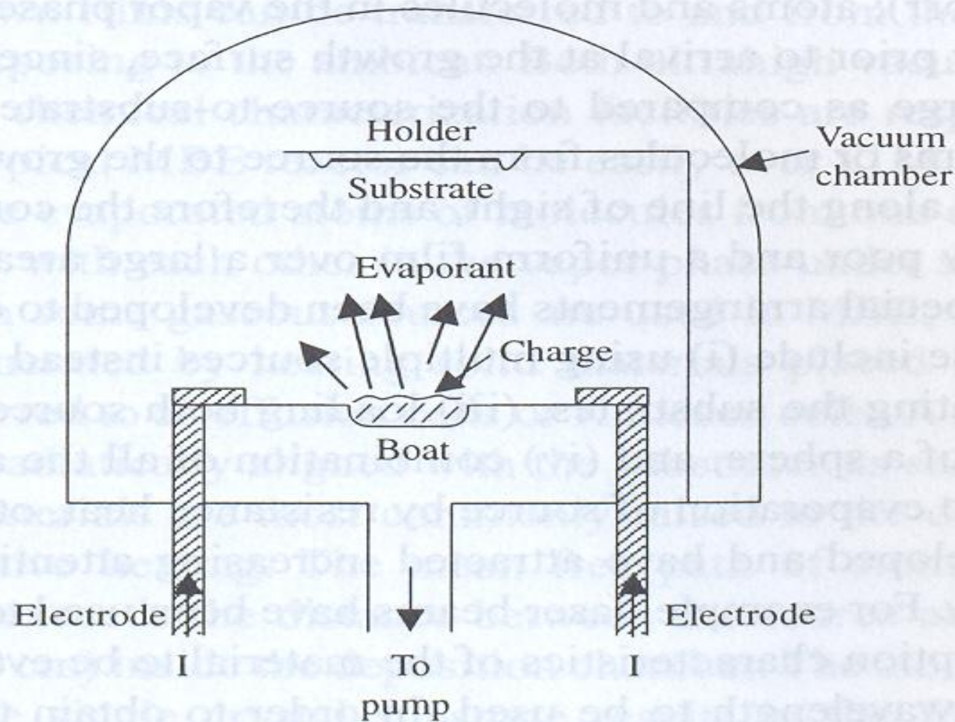
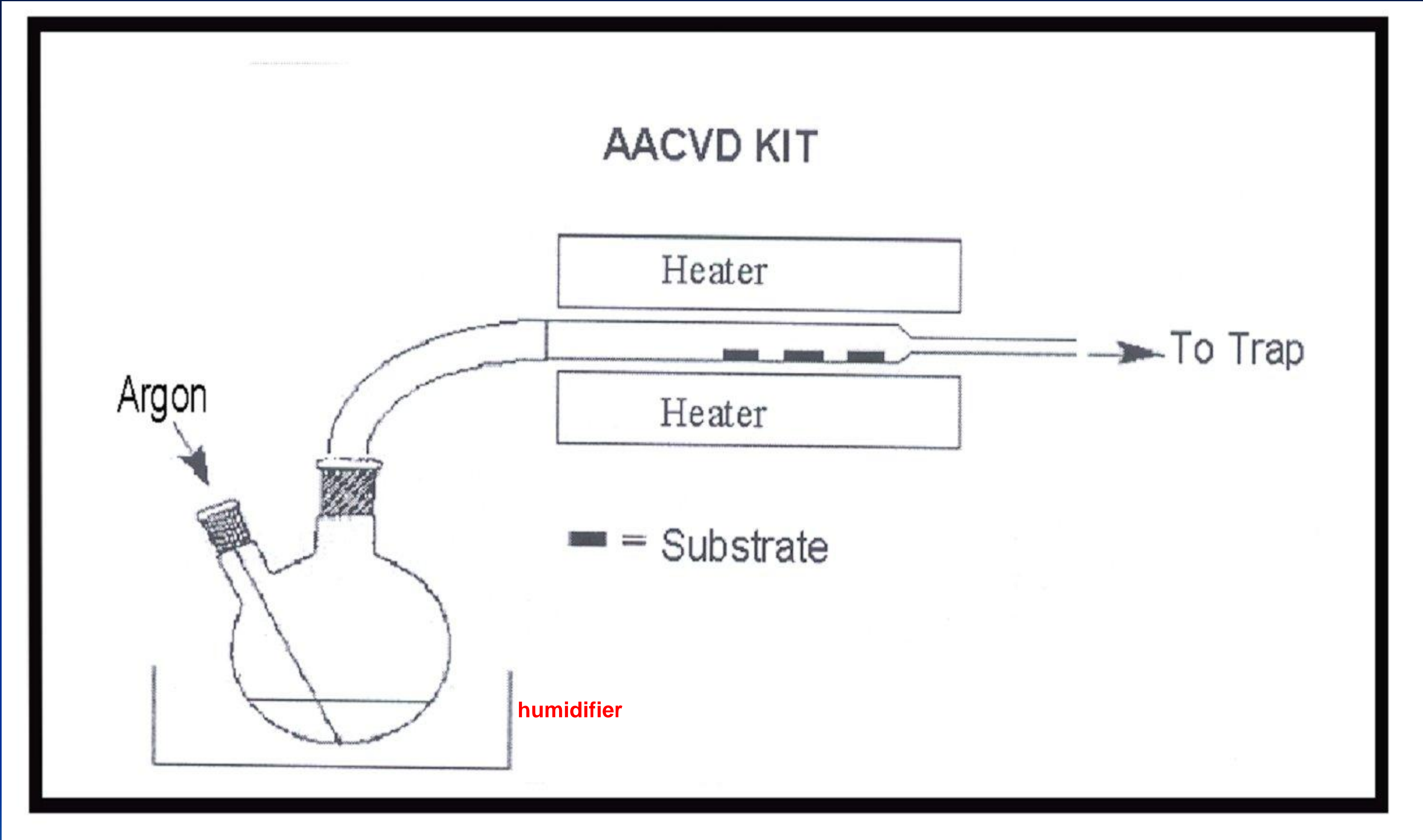


Fig. 5.6. A typical evaporation system consisting of an evaporation source to vaporize the desired material and a substrate located at an appropriate distance facing the evaporation source. Both the source and the substrate are located in a vacuum chamber.



Aerosol-assisted chemical vapor deposition (AACVD)

Evaporation

- The desired vapour pressure of source material can be generated by simply heating the source to elevated temperatures
- The concentration of the growth species in the gas phase can be easily controlled by varying the source temperature and the flux of the carrier gas
- The resulting vapour composition often differs from the source composition due to pyrolysis, decomposition and dissociation
- It is difficult to deposit complex films. When a mixture of elements or compounds is used as a source for the growth of a complex film
  - One element may evaporate faster than the another resulting in the depletion of the first element
- Deposition of thin films by evaporation is carried out in a low pressure (10^{-3} ~10^{-10} torr). It is difficult to obtain a uniform thin film over a large area.
- To overcome this shortfall
  - Multiple sources are used instead of single point source
  - The substrate is rotated

Sputtering

- Sputtering is to use energetic ions to knock atoms or molecules out from a target that acts as one electrode and subsequently deposit them on a substrate acting as another electrode

Sputtering…dc discharge system

- Ionization of inert gas e.g. Ar (by electric field or dc voltage)
- when inert gas ions strike the cathode (source target), neutral target atoms are ejected
- These atoms pass through the discharge and deposit on the opposite electrode (the substrate with growing film
- Other negatively charged species also bombard and interact with the surface of the substrate or grown film

Deposition of insulating film

- Apply an alternate electric field to generate plasma between two electrodes
- Typical RF frequencies: 5 – 30 MHz
- 13.56 MHz reserved for plasma processing by the Federal Communications Commission
- The target self-biases to a negative potential and behaves like a dc target
  - Electrons are more mobile than ions and have little difficulty in following the periodic change in the electric field
- To prevent simultaneous sputtering on the grown film or substrate, the sputter target must be an insulator and be capacitatively coupled to the RF generator
- Sputtering a mixture of elements/compounds will not result in a change of composition in the target and thus the composition of the vapour phase will be the same as that of the target and remain the same during the deposition.

Evaporation vs Sputtering

Evaporation	Sputtering
Uses low pressures (10^{-3} – 10^{-10} torr)	Requires a relatively high pressure (~100 torr)
Atoms/molecules in evaporation chamber do not collide with each other prior to arrival at the growth site	Atoms/molecules in sputtering collide with each other prior to arrival at the growth site
Evaporation is desirable by thermodynamic equilibrium	Sputtering is not desirable by thermodynamic equilibrium
The growth surface is not activated in evaporation	The growth surface is constantly under electron bombardment and thus is highly energetic
The evaporated films consist of large grains	The sputtered films consist of smaller grains with better adhesion to the substrates
Fractionation of multi-component systems is a serious challenge	The composition of the target and the film can be the same

Laser ablation

- Uses laser beams to evaporate the material
- Absorption characteristics of the material to be evaporated determine the laser wavelength to be used
- Pulsed laser beams are generally used in order to obtain high power density.
- Laser ablation is an effective technique for the deposition of complex metal oxides such as high Tc superconductor films.
- Advantage of Laser ablation
  - The composition of the vapour phase can be controlled as that in the source
- Disadvantage of Laser ablation
  - Complex system design
  - Not always possible to find desired laser wavelength for evaporation
  - Low energy conversion efficiency

Electron beam evaporation

- Limited to electrically conductive source
- Advantages
  - Wide range of controlled evaporation rate due to a high power density
  - Low contamination

Arc evaporation

- Used for evaporation of electrically conductive source.

Molecular beam epitaxy (MBE)

- A special case of evaporation for single crystal film growth, with highly controlled evaporation of a variety of sources in ultrahigh-vacuum of typically ~10^{-10} torr.
- Consists of realtime structural and chemical characterization capability
  - (high energy electron diffraction (RHEED)
  - X-ray photoelectric spectroscopy (XPS)
  - Auger electron spectroscopy (AES)
  - Can also be attached to other analytical instruments

MBE: Effusion cells

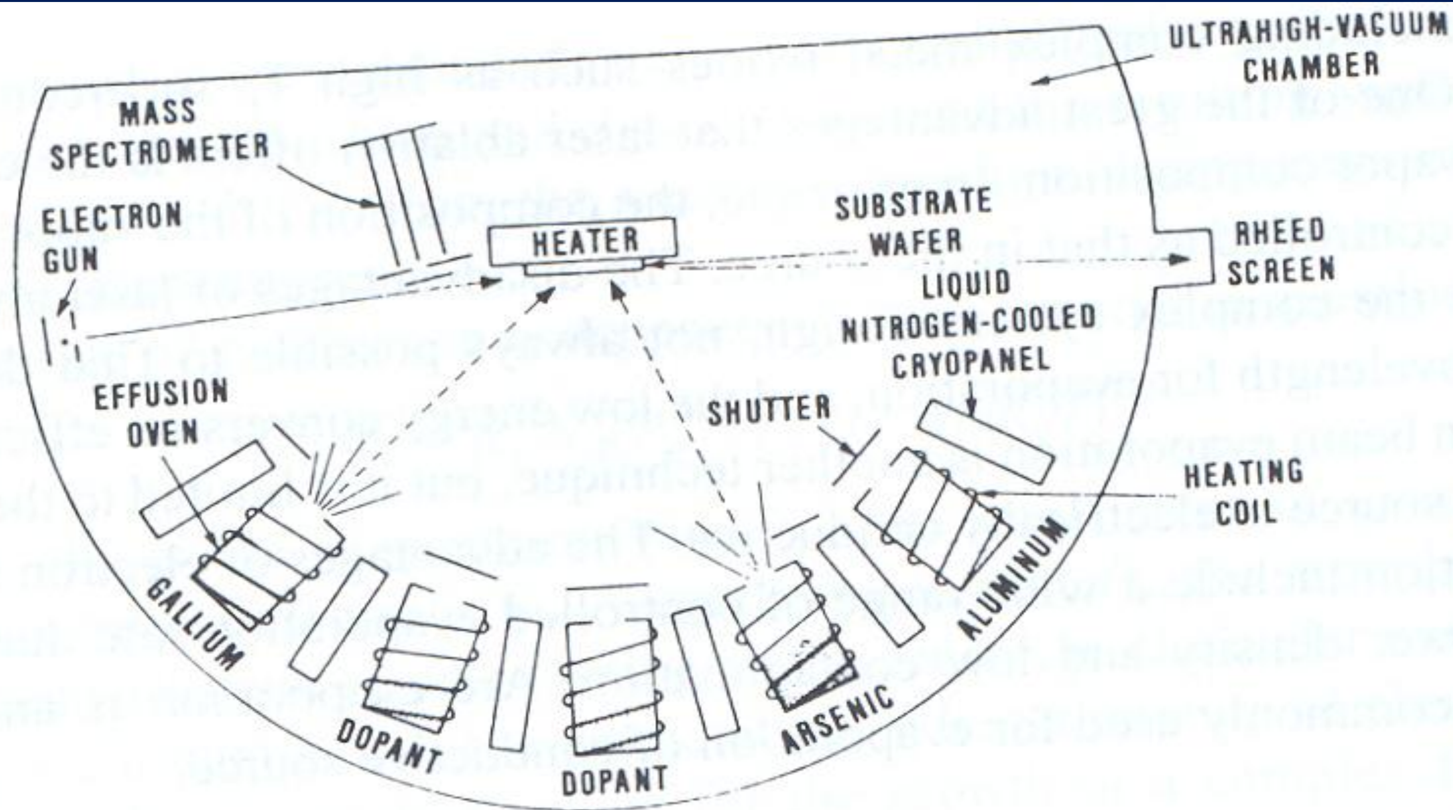


Fig. 5.7. Schematic showing a number of effusion cells radiatically aligned with the substrates.

MBE

- In MBE the evaporated atoms or molecules from one or more sources do not interact with each other in the vapour phase under such low pressure
- Most molecular beams are generated by heating solid materials placed in source cells (aka effusion cells or Knudssen cells)
- The atoms or molecules striking on the single crystal substrate results in the formation of the desired epitaxial film.
- The extremely clean environment, the slow growth rate, and independent control of the evaporation of individual sources enable the precise fabrication of nanostructures and nanomaterials at a single atomic layer
- Highly pure film can be obtained
  - UH vacuum environment ensures absence impurity or contamination
- Minimal formation of crystal defects
  - Slow growth rate ensures sufficient surface diffusion and relaxation
- Precise control of chemical composition of the deposit possible
  - Evaporation of sources controlled individually

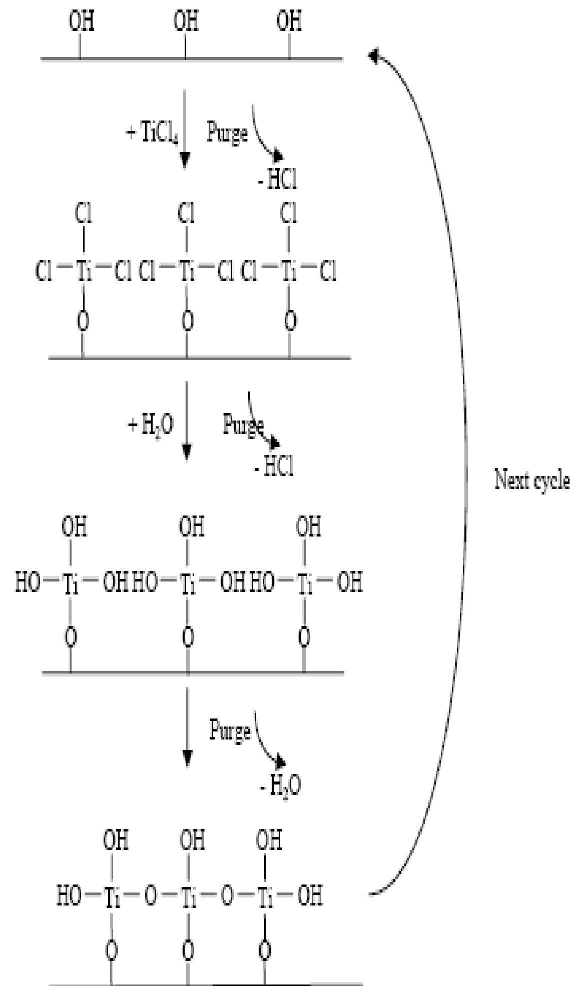
Main attributes of MBE

- A low growth temperature that limits diffusion and hyper abrupt interfaces
- A slow growth rate that ensures a well controlled 2D growth at a rate of 1 μm/h. A very smooth surface and interface is achievable through controlling the growth at the monoatomic layer level.
- A simple growth mechanism compared to other film growth techniques ensures better understanding due to the ability of individually controlled evaporation of sources
- A variety of in situ analysis capabilities provide invaluable information for the understanding and refining of the process

Atomic Layer Deposition (ALD)

- ALD is aka - atomic layer epitaxy (ALE) - atomic layer growth (ALG) - atomic layer CVD (ALCVD) - molecular layer epitaxy (MLE)
- differs significantly from other thin film deposition methods.
- The most distinctive feature of ALD is self-limiting growth nature, each time only one atomic or molecular layer can grow.
- Therefore, ALD offers the best possibility of controlling the film thickness and surface smoothness in truly nanometer or sub-nanometer range.
- ALD can be considered as a special modification of the chemical vapor deposition, or a combination of vapor-phase self-assembly and surface reaction.
- Typical ALD process
  - Surface is first activated by chemical reaction.
  - When precursor molecules are introduced into the deposition chamber, they react with the active surface species and form chemical bonds with the substrate.
  - Since the precursor molecules do not react with each other, no more than one molecular layer could be deposited at this stage.
  - Next, the monolayer of precursor molecules that chemically bonded to the substrate is activated again through surface reaction.
  - Either the same or different precursor molecules are subsequently introduced to the deposition chamber and react with the activated monolayer previously deposited.
  - As the steps repeat, more molecular or atomic layers are deposited in the way one layer at a time.

The process of titania film growth by ALD.



- Substrate Hydroxylation
- Introduction of titanium precursor (titanium tetrachloride).
- Precursor will react with the surface hydroxyl groups through a surface condensation reaction
- $Cl_3Ti\text{-}O\text{-}Me + H_2O \rightarrow (HO)_3Ti\text{-}O\text{-}Me + HCl$
- Neighboring hydrolyzed Ti precursors subsequently condensate to form Ti-O-Ti linkage:
- $(HO)_3Ti\text{-}O\text{-}Me + (HO)_3Ti\text{-}O\text{-}Me \rightarrow Me\text{-}O\text{-}Ti(OH)_2\text{-}O\text{-}Ti\ (HO)_2\text{-}O\text{-}Me + H_2O$
- By-product HCl and excess H_2O removed from the reaction chamber.

ZnS film growth

- Precursors: $ZnCl_2$ and H_2S
- Chemisorb $ZnCl_2$ on substrate
- Introduce H_2S to react with $ZnCl_2$ to deposit a monolayer of ZnS on substrate
- HCl is released as a by-product.

Thin Films Deposited by ALD

Table 5.1. Thin Film Materials Deposited by ALD[1,2]

II-VI compounds	ZnS, ZnSe, ZnTe, $ZnS_{1-x}Se_x$, CaS, SrS, BaS, $SrS_{1-x}Se_x$ CdS, CdTe, MnTe, HgTe, $Hg_{1-x}Cd_xTe$, $Cd_{1-x}Mn_xTe$
II-VI based phosphors	ZnS:M (M = Mn, Tb, Tm), CaS:M (M = Eu, Ce, Tb, Pb), SrS:M (M = Ce, Tb, Pb, Mn, Cu)
III-V compounds	GaAs, AlAs, AlP, InP, GaP, InAs, $Al_xGa_{1-x}As$, $Ga_xIn_{1-x}As$, $Ga_xIn_{1-x}P$
Nitrides	AlN, GaN, InN, SiN_x, TiN, TaN, Ta_3N_5, NbN, MoN, W_2N, Ti-Si-N
Oxides	Al_2O_3, TiO_2, ZrO_2, HfO_2, Ta_2O_5, Nb_2O_5, Y_2O_3, MgO, CeO_2, SiO_2, La_2O_3, $SrTiO_3$, $BaTiO_3$, $Bi_xTi_yO_z$, In_2O_3, In_2O_3:Sn, In_2O_3:F, In_2O_3:Zr, SnO_2, SnO_2:Sb, ZnO, ZnO:Al, Ga_2O_3, NiO, CoO_x, $YBa_2Cu_3O_{7-x}$, $LaCoO_3$, $LaNiO_3$
Fluorides	CaF_2, SrF_2, ZnF_2
Elements	Si, Ge, Cu, Mo, Ta, W
Others	La_2S_3, PbS, In_2S_3, $CuGaS_2$, SiC

Requirements for ALD Precursors

Table 5.2. Requirements for ALD Precursors

Requirement	Comments
Volatility	For efficient transportation, a rough limit of 0.1 Torr at the applicable maximum source temperature
	Preferably liquids or gases
No self-decomposition	Would destroy the self-limiting film growth mechanism
Aggressive and complete reactions	Ensure fast completion of the surface reactions and thereby short cycle times
	Lead to high film purity
	No problems of gas phase reactions
No etching of the film or substrate material	No competing reaction pathways
	Would prevent the film growth
No dissolution to the film	Would destroy the self-limiting film growth mechanism
Un-reactive byproduct	To avoid corrosion
	Byproduct re-adsorption may decrease the growth rate
Sufficient purity	To meet the requirements specific to each process
Inexpensive	
Easy to synthesize & handle	
Nontoxic and environmentally friendly	

Sol-Gel Dip-Coating