FC250 Nano- and microtechnologies chapter 4. Basic Microfabrication Techniques - Deposition

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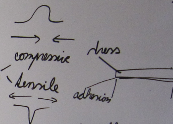
4.3 Thin Film Deposition and Doping

Deposition

important characteristics of films

- etch rate (high for LPCVD-PSG)
- conformality
- mech. properties (hardness, el. modulus, stress



how film stick to subst. depends on
- adhesion
- stress in film

4.3.1 Overview of Deposition Methods

method/processes	specification
evaporative techniques:	
thermal (vacuum) evaporation	resistive heating
	flash evaporation
	arc evaporation
	exploding-wire technique
	laser evaporation
	rf heating
	electron-beam evaporation
molecular beam epitaxy (MBE)	
liquid-phase chemical techniques:	
electro processes	electroplating
	electrolytic anodization
mechanical techniques	spray pyrolysis
liquid phase epitaxy	
gas-phase chemical techniques:	
chemical vapor deposition (CVD)	CVD epitaxy
	metalorganic CVD (MOCVD)
	low-pressure CVD (LPCVD)
	atmospheric-pressure CVD (APCVD)
	atomic layer deposition (ALD)
gas-phase physical-chemical techniques (except plasma and ion beam):	
modifications of CVD	hot filament CVD (HFCVD)
	laser-induced CVD (PCVD)
	photo-enhanced CVD (PHCVD)
	electron enhanced CVD

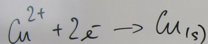
Overview of Deposition Methods

method/processes	specification
	plasma techniques:
sputter deposition	dc sputtering
	rf diode sputtering
	magnetron sputtering
PECVD in low temperature discharges	dc discharge
	rf capacitively coupled plasma (CCP)
	rf inductively coupled plasma (ICP)
	microwave ECR deposition
	microwave resonantor reactor
	atmospheric pressure dielectric barrier discharge (DBD)
	atmospheric pressure glow discharge (APGD)
	atmospheric pressure surface barrier discharge
	etc.
plasma processing in high temperature discharges	vacuum arc
	dc torch
	microwave torch
	etc.
	ion beam techniques:
sputter deposition	ion beam sputtering
	reactive ion beam sputtering
ion deposition	ion beam deposition
	ionized cluster beam deposition (ICB)
dual processes	ion beam assisted deposition (IBAD)
	dual ion beam sputtering

Details of Selected Methods

4.3.2 Electroplating

electroplating ~ 10 μm



Ni

Al

liquid techn.

conductive substr. is a cathode
(or thin film on dielectrics = seed layer)

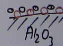
pulsed laser and atomic layer deposition

PLD — PVD

UV laser 1GW in 25ns

ALD — chemical method CVD

Al_2O_3



4.3.2 Thermal Evaporation - Sources for thermal evaporation

Existuje několik typů zdrojů pro napařování, které využívají ohřevu průchodem elektrického proudu:

- **Přímé odporové zahřívání** - Tato metoda je založena na ohřívání materiálu držáku z odporového, těžko tavitelného materiálu, jako je W, Mo, Ta, Nb. Někdy se používá i keramické úpravy povrchu těchto držáků. Tyto zdroje můžeme dále dělit podle tvaru držáku, a tedy způsobu uchycení taveného materiálu.
  - Drátěný držák má formu spirály. Odpařovaný materiál ve tvaru svorky U je na spirále zavěšen. Odpařovaný materiál musí smáčet spirálu, aby se na něj po roztavení nalepil.
  - Drátěný držák má tvar košíku. Napařovaný materiál nesmí košík smáčet, aby po roztavení vytvořil kapku, která nevyteče.
  - Držák má tvar plechové lodičky, v níž je odpařovaný materiál vložen. Lodička je přibližně 0,3 cm hluboká, 10 cm dlouhá a 1 až 2 cm široká. Výkon potřebný pro tyto zdroje je podstatně větší, než v případě drátového uchycení, ale lze deponovat tlustší vrstvy.
  - Zdroj je realizován jako uzavřená pec s jedním nebo více malými otvory, kterými proudí napařovaný materiál.
- **Nepřímé odporové zahřívání** - Kelímek z křemene, grafitu nebo keramiky (např. korundu) je obtočen drátěnou odporovou spirálou.

Pokud má materiál dostatečně vysokou tenzi par před tavením, začne sublimovat a následné kondenzát vytváří tenkou vrstvu. Nevýhodou je nízká depoziční rychlost.

For more details see scanned copy of Smith's book.

Sources using Energetic Beams

- **Jiskrové napařování** Rychlé napařování slitin, či několikasložkových sloučenin, které se normálně mají tendenci rozpadat na složky, lze dosáhnout kapáním malinkých kapek na horký povrch. Dojde tak k separátnímu odpařování na mnoha místech kdy se ale v každém místě odpaří všechny složky.
- **Obloukové napařování.** Zapálením elektrického oblouku mezi dvěma vodivými elektrodami dochází v místě dopadu oblouku k velkému ohřevu materiálu. Teplota je dostatečná i k odpařování Nb a Ta. Tato metoda je také často používá k napařování uhlíku na vzorky pro elektronový mikroskop.
- **Technika explodujícího drátu.** Tato technika je založení na explozi drátku způsobené prudkým ohřevem díky průchodu velkého proudu, řádově 10^6 A/cm^2. Takovéhoto efektu je dosaženo polem kondenzátorů ($\approx$ 10 to 100 μF) nabitým na napětí $\approx$ 1 to 10 kV.
- **RF ohřev.** Pro ohřev materiálu lze použít elektromagnetickou indukci. Ohřev lze aplikovat buď přímo na napařovaný materiál, nebo nepřímo na kelímek v němž je napařovaný materiál uložen.

Sources using Energetic Beams

- **Laserové napařování.** Obrovská intenzita laserového svazku může být použita k ohřevu a odpařování materiálu. Laserový zdroj může být mimo vakuový systém a svazek bývá zaostřen na povrch napařovaného materiálu.
  Pulsed laser deposition (PLD) is a simple technique that uses an intense (1 GW within 25 ns) UV laser (such as KrF excimer) to ablate a target material [7.5]. Plasma is subsequently formed from the target and is deposited on the substrate. Multitarget systems with Auger and RHEED spectroscopes are commercially available. Figure 7.11 shows a typical PLD deposition set-up. The main advantages of the PLD are its simplicity and ability to deposit complex materials with preserved stoichiometry ("stoichiometry transfer"). In addition, fine control over the film thickness can also be achieved by controlling the number of pulses. Stoichiometry transfer allows many complex targets, such as ferroelectrics, superconductors and magnetostrictives to be deposited using PLD. Other materials deposited include oxides, carbides, polymers, and metallic systems (such as FeNdB).

Sources using Energetic Beams

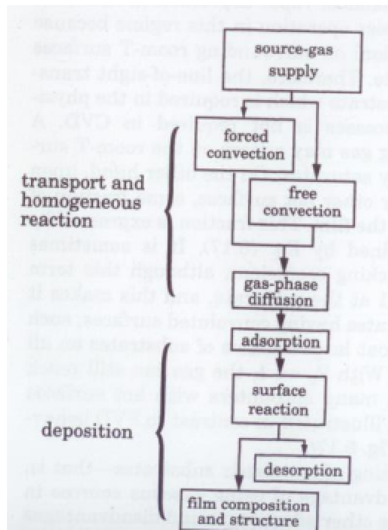
- **Napařování elektronovým svazkem** Napařování použitím odporového zahřívání má velkou nevýhodu v tom, že napařovaný materiál bývá kontaminován materiálem držáku. Také je napařování limotováno vstupním výkonem (došlo by k tavení držáku), což značně ztěžuje napařování materiálů s vysokou teplotou tání. $\Rightarrow$ lze to obejít pomocí elektronového bombardu materiálu.
  Nejjednodušší uspořádání sestává z wolframového vlákna, které je žhaveno a emituje elektrony. Ty jsou následně urychlovány díky přivedení kladného napětí na napařovaný materiál. Elektrony v něm ztrácejí svou energii, čímž materiál ohřívají a dochází k jeho vypařování.

For more details see scanned copy of Smith's book.

Magnetron Sputtering

4.3.4 Chemical Vapor Deposition

. . . constituents of the vapour phase react chemically near or on a substrate surface to form a solid product. Most CVD processes are chosen to be **heterogenous** reactions. Undesirable **homogeneous** reactions in the gas phase nucleate particles that may form powdery deposits and lead to particle contamination.



Gaseous Sources

Let's use practical distinguishment of gas and vapor: gas does not condense when held above room T and below 1-atm partial pressure.
Distinguishing the methods of delivery according to equilibrium vapor pressure p_v:

- sources species having $p_\mathrm{v} < 10^{-2}$ Pa at the wall T of the deposition chamber must by "physically" evaporated (using heat or energy beams) $\Rightarrow$ PVD processes (requiring low-p operation and "line-in-sight" geometry
- materials with $p_\mathrm{v} > 10^{-2}$ Pa at the wall T are used in CVD (can operate at atmospheric pressure or lower - fluid flow $K_n \ll 1$)

Most of elements, with exception of alkali metals and alkaline earths (group IA and IIA) can be converted to gases or to chemical vapors by reacting them with terminating radicals, e. g.

- H
- halogens F, Cl, Br, I
- carbonyl CO
- H-saturated organic radicals R such as methyl CH_3 and ethyl CH_2CH_3

Chemical Reactions in CVD

TABLE 7.1 Typical Overall Reactions Used in CVD

pyrolysis (thermal decomposition)	$SiH_4(g) \rightarrow Si(c) + 2H_2(g)$
	$SiH_2Cl_2(g) \rightarrow Si(c) + 2HCl(g)$
	$CH_4(g) \rightarrow C(\text{diamond or graphite}) + 2H_2(g)$
	$Ni(CO)_4(g) \rightarrow Ni(c) + 4CO(g)$
oxidation	$SiH_4(g) + 2O_2(g) \rightarrow SiO_2(c) + 2H_2O(g)$
	$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(c) + 12H_2(g)$
hydrolysis	$2AlCl_3(g) + 3H_2O(g) \rightarrow Al_2O_3(c) + 6HCl(g)$
reduction	$WF_6(g) + 3H_2(g) \rightarrow W(c) + 6HF(g)$
displacement	$Ga(CH_3)_3(g) + AsH_3(g) \rightarrow GaAs(c) + 3CH_4(g)$
	$ZnCl_2(g) + H_2S(g) \rightarrow ZnS(c) + 2HCl(g)$
	$2TiCl_4(g) + 2NH_3(g) + H_2(g) \rightarrow TiN(c) + 8HCl(g)$

Materials deposited at low temperatures (bellow 600 °C for silicon) are generally **amorphous**. Higher temperatures tend to lead to **polycrystalline** phases. Very high temperatures (typically 900–1100 °C in the case of silicon) are necessary for growing **single-crystal films**.

Deposition Variables

temperature, pressure (from low pressures, i.e., 10–1000 Pa - LPCVD, up to atmospheric pressures - APCVD), input concentration, gas flow rates, reactor geometry, operating principles. Kinetics of the reactions may depend on such factors like substrate material, structure and orientation.

Chemical Reactors

Chemical reactors must provide several basic functions:

- transport of the reactant and diluent gases to the reaction site,
- provide activation energy to the reactants (heat, radiation, plasma),
- maintain a specific system pressure and temperature,
- allow the chemical processes for thin film deposition to proceed optimally,
- remove the by-product gases and vapours.

Reactor geometry affects the gas flow characteristics which, in turn affect the properties of the deposited layer. Two basic flow type reactors:

- Displacement or **plug flow reactor** in which the entering gas displaces the gas already present with no intermixing of successive fluid elements. Plug flow is a simplified and idealized picture of the motion of a fluid, whereby all the fluid elements move with a uniform velocity along parallel streamlines. Mass balance for reactant A involved in a single reaction is very simple: $F_A - (F_A + dF_A) = r_A dV$.
- **Perfectly mixed flow reactor** is the opposite extreme from the plug flow reactor. To approach the ideal mixing pattern, the feed has to be intimately mixed with the contents of the reactor in a time interval that is very small compared to the mean residence time of the fluid flowing through the vessel. The essential feature is the assumption of complete uniformity of concentration and temperature throughout the reactor.

Different CVD Techniques

- CVD epitaxy (see next chapter in presentation) and metal-organic CVD (MOCVD - see Handbook of Thin Film Deposition, ed. S. Krishna, chapter 4.)
  CVD epitaxy or vapour-phase epitaxy (VPE) and metal-organic chemical vapour deposition (MOCVD) are used for growing epitaxial films of e.g. silicon or compound semiconductors. Layers of accurately controlled thickness and dopant profile are required to produce structures of optimal design for device fabrication.
- low pressure and atmospheric pressure CVD
  These two methods are used for deposition of polycrystalline or amorphous materials like polysilicon, silicon nitride and low temperature oxide (LTO).
- ALD

APCVD and LPCVD

The deposition of thin films for semiconductor device manufacture by CVD at atmoshperic pressure (APCVD) was a widely accpeted process in 1976 when equipment for low-pressure CVD (LPCVD) was introduced into the marketplace. At that time, the 3-inch wafer was the predominantly wafer size used in production with some residual presence of smaller wafers and the 4-inch wafer just being introduced into advanced lines.

In the next few years, the LPCVD process became the preferred method for chemical vapour deposition of thin films. The transformation to a new technology that required massive capital expenditure for new equipment took place at a rapid rate throughout the industry. The reason for this rapid change were: (1) a superior film quality, (2) a greatly reduced processing cost, and (3) greatly increased thtoughput per unit of capital investment. Improved film quality also means increased yields and decreased unit costs in an industry that was becoming increasingly competitive.

Atomic Layer Deposition

https://www.youtube.com/watch?v=HUsOMnV65jk This example shows the ALD chemistry for producing HfO2 from gaseous precursors HfCl4 (Cl=green) and H2O (O=red). ALD allows a uniform coating to be applied to complex objects - such as the inside of the fibre optic cable shown here.

https://www.youtube.com/watch?v=XMda8TXLIFk Deposition of TiO_2 using TiCl4 and H2O

4.3.5 Thermal Forming Processes

In the gas phase, **thermal oxidation and nitridation** is a chemical thin-film forming process in which the **substrate itself provides the source for the metal or semiconductor constituent** of the oxide and nitride, respectively. This technique is obviously much more limited than CVD.

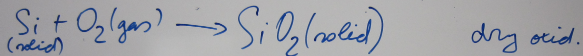
The **thermal oxidation**

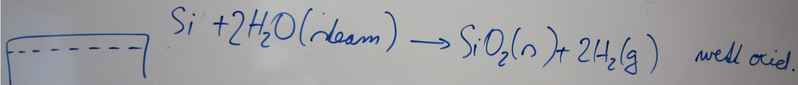
- extremely important applications in Si device technology (very high purity oxide films with high quality Si/SiO_2 interface are required).
- **Thermal oxidation of silicon** surfaces produces glassy films of SiO_2 for protecting highly sensitive p-n junctions and for creating dielectric layers for MOS devices.
  - $T = 700 - 1200 \circ$C
  - dry oxygen or water vapour (steam) as the oxidant; steam oxidation proceeds at a much faster rate than dry oxidation
  - The oxidation rate is a function of the oxidant partial pressure and is controlled essentially by the rate of oxidant diffusion through the growing SiO_2 layer interface, resulting in a decrease of the growth rate with increased oxide thickness.
  - The process is frequently conducted in the presence of hydrochloric acid vapours or vapours of chlorine-containing organic compounds. The HCl vapour formed acts as an effective impurity getter, improving the Si/SiO_2 interface properties and stability.
  - **Si oxidation under elevated pressure** is of technological interest where the temperature must be minimized (VLSI devices): oxidation rate of silicon is $\approx p \Rightarrow$ higher product throughput and/or decreased temperatures. Oxidant: H2O, p up to 10 atm, T usually 750–950 $^\circ$C.

Gas-phase **oxidation of other materials** is of limited technical importance. Examples: metallic Ta films converted by thermal oxidation to tantalum pentoxide for use as antireflection coating in photovoltaic devices and as capacitor elements in microcircuits. Other metal oxides grown thermally: capacitor dielectrics in thin-film devices, improve the bonding with glass in glass-to metal seals, improve corrosion resistance.

Oxidation

Oxidation





900 – 1200°C

⇒ thermal oxide

Doping

Doping

Doping

Si < B p-type; As, P n-type

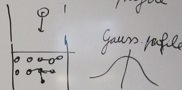
1. diffusion 800°C min, isotropic, use mask

p^{++} very highly doped

micromachining – end point of etching (etch stop)

2. ion implantation

more precise control of
- dose
- profile

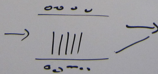


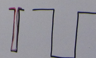
after implantation – annealing necessary

CVD and Epitaxy

for microfabrication: LPCVD 10–100 Pa, 550–900°C; PECVD

SiO_2, Si_3N_4 } dielectr.





polycrystalline Si

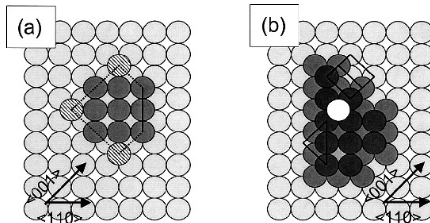
PSG

Introduction to Epitaxy

The world epitaxy = from the Greek "epi" - upon and "taxis" - to arrange ⇒ epitaxial deposition requires ability to add and arrange atoms upon a single crystal surface. Epitaxy is a regularly oriented growth of one crystalline substance upon another.

Specific applications require controlling the crystalline perfection and the dopant concentration in the added layer.

- Homo-epitaxy is growth in which the epitaxial layer is of the same material as the substrate (e. g. Si on Si, GaAs on GaAs).
- Hetero-epitaxy is growth in which the layer is a different material than the substrate (e. g. AlAs on GaAs).



`https://www.slideshare.net/mehmedkoc/ee518-epitaxial-deps07-5695497`
- for process description and vapor phase epitaxy (VPE, also CVD epitaxy)
`https://www.slideshare.net/HrishikeshGhewade/epitaxial-crystal-growth-method?next_slideshow=1`
- for liquid phase epitaxy (LPE) and MBE

Motivation

Epitaxial growth is useful for applications that places stringent demands on the deposited layer:

- high purity
- low deffect density
- abrupt interfaces
- controlled doping profiles
- high reproducibility and uniformity

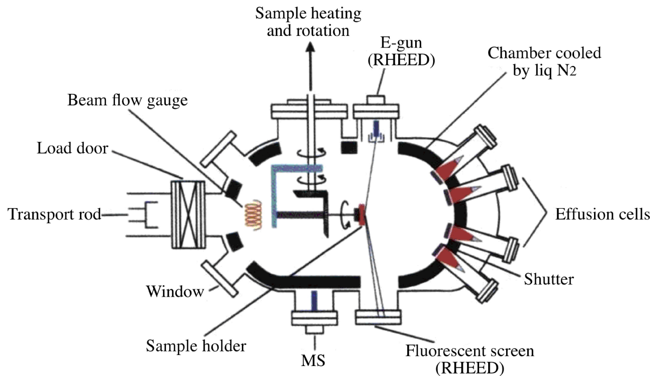
Why homoepitaxy (e. g. Si on Si, GaAs on GaAs)?
Epitaxial films are purer than the substrate and can doped independently.

Molecular Beam Epitaxy

Epitaxe z molekulárních svazků (MBE z anglického molecular beam epitaxy) je sofistikovaná, přesně kontrolovaná metoda pro růst monokrystalické epitaxní vrstvy:

- ve velmi vysokém vakuu (10^{-9} Pa),
- na monokrystalickém substrátu pomalým napařováním jednotlivých atomů či molekul,
- substrát a rostoucí vrstva udržovány na přesně dané teplotě.

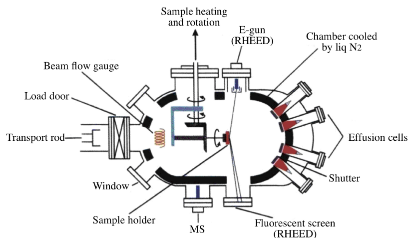
Aparatura pro MBE:



ttp://cnx.org/contents/CyYU5KqY@2/Molecular-Beam-Epitaxy

Molecular Beam Epitaxy

- **Vakuový systém** je velice podobný uspořádání, které je používáno pro analýzu povrchů a kompatibilní s technikou vysokého vakua. Typický systém pro MBE je složen ze čtyř oddělených komor: vstupní komora pro vkládání a vyjímání substrátů, depoziční komora, komora pro analýzu a pomocná komora pro přípravné procesy.
- **Zdroje materiálu** jsou základem každého MBE systému. Musí být schopné poskytovat dostatečnou čistotu a rovnoměrnost napařovaného materiálu.
- **Clona** Jedním ze základních prvků, nutných pro správnou funkci MBE, je clona umístěná na zdroji. Spolu s pomalou rychlostí růstu vrstvy umožňuje kontrolu nad procesem růstu. Požadavkem je schopnost zavřít se během 0,1 s.
- **Manipulace se vzorky.** Vzorky pro MBE jsou uchyceny v molybdenovém držáku pomocí indiového tmelu. Za teploty obvyklé pro MBE je indium tekuté a zajišťuje dobrou přilnavost a převod tepla. Teplota substrátu bývá kontrolována buď termočlánkem, nebo pyrometrem. Obvyklé bývá velké substráty (> 5 cm) nechat během depozice rotovat.



Typy zdrojů pro MBE

- **Knudsenovy cely** jsou standartním zdrojem pro napařování. Vypadají jako hluboké tyglíky uvnitř pece. Pec je vybavena chlazením stěn a termočlánkem. Jsou většinou vyrobeny z odolného kovu jako je Ta, Mo nebo keramiky.
- **Solid Source Cracking Cells.** Některé materiály jako arsen a fosfor se odpařují ve více molekulárních formách. Obvykle platí, že větší molekuly mají vyšší tenzi par a nižší koeficient ulpění při dané teplotě substrátu než měnší molekuly ⇒ výtěžnost lze zvýšit rozbitím větších molekul již ve zdroji. Konstrukce zdroje materiálu v tomto případě odpovídá obvyklé Knudsenově cele s tím rozdílem, že je přidán další ohřev na výstupu z cely, který slouží k rozkladu molekul.
- **Kontinuální zdroj** je typ zdroje pro tekuté materiály (např. rtuť).
- **Zdroj s elektronovým ohřevem** je používán pro těžko tavitelné materiály (W, Co, Ni, Si, Ge).
- **Implantační zdroj** Plyn ze zdroje je ionizován, v některých případech jsou ionty separovány podle hmotnosti. Následně jsou ionty urychleny směrem k substrátu.

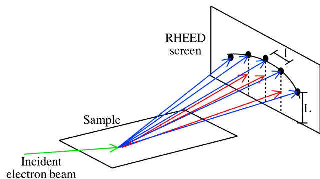
For more details see scanned copy of Handbook of Thin Film Deposition.

`https://www.youtube.com/watch?v=NsGRKSV8yH8&nohtml5=False` Simulation of growth

6.3 Monitoring of Deposition Process

- control of epitaxy - reflectance high-energy electron difraction RHEED

Electrons of energy 5 - 40 keV are directed towards the sample. They reflect from the surface at a very small angle (less than 3°) and are directed onto a screen. These electrons interact with only the top few atomic layers and thus provide information about the surface.



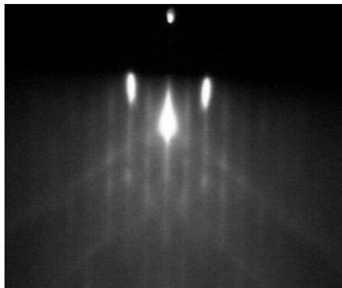


Figure shows a typical pattern on the screen for electrons reflected from a smooth surface, in which constructive interference between some of the electrons reflected from the lattice structure results in lines. If the surface is rough, spots will appear on the screen, also.

For more details see scanned copy of Smith's book.

6.4 CVD Epitaxy

Epitaxial layers can be prepared by a wide range of techniques including evaporation, sputtering and molecular beams. Epitaxial deposition by CVD uses a gaseous transport and chemical reactions. Important application of CVD epitaxy is a production of crystalline silicon (c-Si). With the **silicon epitaxy** radical changes in material properties can be created over small distances within the same crystal. This capability permits the growth of lightly-doped single c-Si on the top of heavily-doped c-Si, n-type Si over p-type Si and vice versa, Si layer with controlled dopant profiles etc.

see Handbook of Thin Film Deposition, ed. S. Krishna, chapter 2.

MOCVD

Metalorganic chemical vapour deposition (MOCVD), metalorganic vapour phase epitaxy (MOVPE), also known as organometallic vapour phase epitaxy (OMVPE)

- a chemical vapour deposition method used to produce single or polycrystalline thin films. It is a highly complex process for growing crystalline layers to create complex semiconductor multilayer structures.
- In contrast to molecular beam epitaxy (MBE) the growth of crystals is by chemical reaction and not physical deposition. This takes place not in a vacuum, but from the gas phase at moderate pressures (10 to 760 Torr). As such, this technique is preferred for the formation of devices incorporating thermodynamically metastable alloys.
- ultra pure gases (metalorganics and hydrides) are injected into a reactor, e. g. $Ga(CH_3)_3$, AsH_3. Unlike traditional silicon semiconductors, these semiconductors may contain combinations of Group III and Group V, Group II and Group VI, Group IV, or Group IV, V and VI elements.

http://www.k-space.com/applications/mocvd/

MOCVD

For example, indium phosphide could be grown in a reactor on a heated substrate by introducing trimethylindium ((CH3)3In) and phosphine (PH3) in a first step. The heated organic precursor molecules decompose in the absence of oxygen - pyrolysis. Pyrolysis leaves the atoms on the substrate surface in the second step. The atoms bond to the substrate surface and a new crystalline layer is grown in the last step. Formation of this epitaxial layer occurs at the substrate surface.

- Required pyrolysis temperature increases with increasing chemical bond strength of the precursor. The more carbon atoms are attached to the central metal atom the weaker the bond. The diffusion of atoms on the substrate surface is affected by atomic steps on the surface.
- The vapor pressure of the metal organic source is an important consideration in MOCVD, since it determines the concentration of the source material in the reaction and the deposition rate.
- A reactor is a chamber made of a material that does not react with the chemicals being used. It must also withstand high temperatures. This chamber is composed by reactor walls, liner, a susceptor, gas injection units, and temperature control units. Usually, the reactor walls are made from stainless steel or quartz. Ceramic or special glasses, such as quartz, are often used as the liner in the reactor chamber between the reactor wall and the susceptor. To prevent overheating, cooling water must be flowing through the channels within the reactor walls.
- A substrate sits on a susceptor which is at a controlled temperature. The susceptor is made from a material resistant to the metalorganic compounds used; graphite is sometimes used. For growing nitrides and related materials, a special coating on the graphite susceptor is necessary to prevent corrosion by ammonia (NH_3) gas.

6.5 Liquid Phase Epitaxy

see https://www.slideshare.net/HrishikeshGhewade/epitaxial-crystal-growth-method?next_slideshow=1

6.6 Atomic Layer Epitaxy

se Smith's book p. 269