Lecture 13 and 14

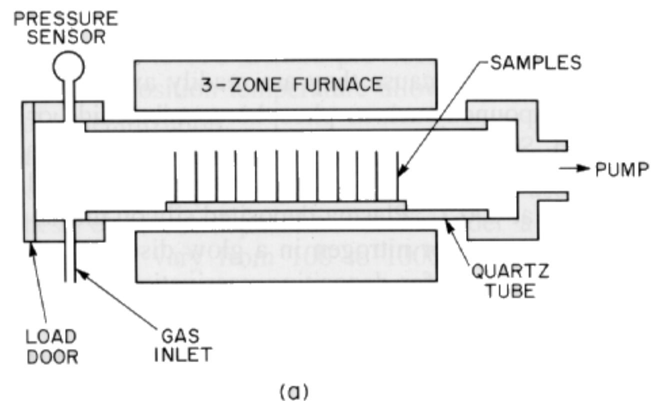
Thin Film Deposition and Epitaxy (Chemical Vapor Deposition, Metal Organic CVD and Molecular Beam Epitaxy)

Reading:

Chapters 13 and 14

Chemical Vapor Deposition

Chemical gas sources are thermally, optically, or electrically (plasma) reacted with a surface to "leave" behind deposits with reaction byproducts pumped out of the reaction tube or vacuum chamber.



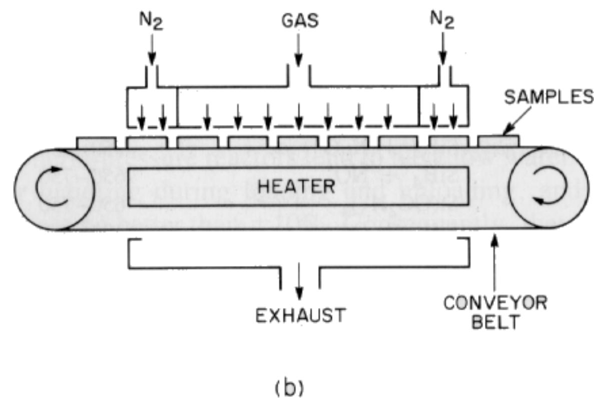


FIGURE 1
Schematic diagrams of CVD reactors: (a) Hot-wall, reduced-pressure reactor. (b) Continuous, atmospheric-pressure reactor.

Four Basic CVD Reactors

1.) Atmospheric Pressure CVD (APCVD)

Advantages: High deposition rates, simple, high throughput
Disadvantages: Poor uniformity, purity is less than LPCVD
Used mainly for thick oxides.

2.) Low Pressure CVD (LPCVD at ~0.2 to 20 torr)

Advantages: Excellent uniformity, purity
Disadvantages: Lower (but reasonable) deposition rates than APCVD
Used for polysilicon deposition, dielectric layer deposition, and doped dielectric deposition.

3.) Metal Organic CVD (MOCVD)

Advantages.: Highly flexible—> can deposit semiconductors, metals, dielectrics
Disadvantages: ***HIGHLY TOXIC!***, Very expensive source material. Environmental disposal costs are high.
Uses: Dominates low cost optical (but not electronic) III-V technology, some metalization processes (W plugs and Cu)

4.) Plasma Enhance CVD

Plasmas are used to force reactions that would not be possible at low temperature.
Advantages.: Uses low temperatures necessary for back end processing.
Disadvantages: Plasma damage typically results.
Used for dielectrics coatings.

LPCVD for Si Technology

Low Pressure Chemical Vapor Deposition (LPCVD) can be used for a variety of materials:

- Polysilicon for gate contacts
- Thick oxides used for isolation between metal interconnects
- Doped oxides useful for global planarization
- Nitrides and other dielectrics for isolation or capacitors (higher K materials for larger capacitance)
- Metals for seed layers for vias and interconnect lines (not typically used for the entire metal line due to slow deposition rate)

Polysilicon

Uses: Gate contact in MOS (prevents metal/oxide reactions) and very short interconnect lines. Also, resistors in analog technologies.

Typically uses Si containing compounds (typically 100% silane, SiH_4, or 20-30% silane/ 80-70% inert gas) are reacted with the wafer at ~0.2 to 1 torr and ~575-650.

The temperature range is limited by:

- Limited by low deposition rate at low temperature end (insufficient thermal energy for the reaction)
- Formation of particles in the gas phase (gas spontaneously reacting before it reaches the wafer) and poor adhesion on the upper temperature end

LPCVD for Si Technology

Deposition rate is limited by reaction rate (controlled by temperature and pressure) and arrival rate (controlled by pressure (remember gas throughput is related to pressure by Q=CP)).

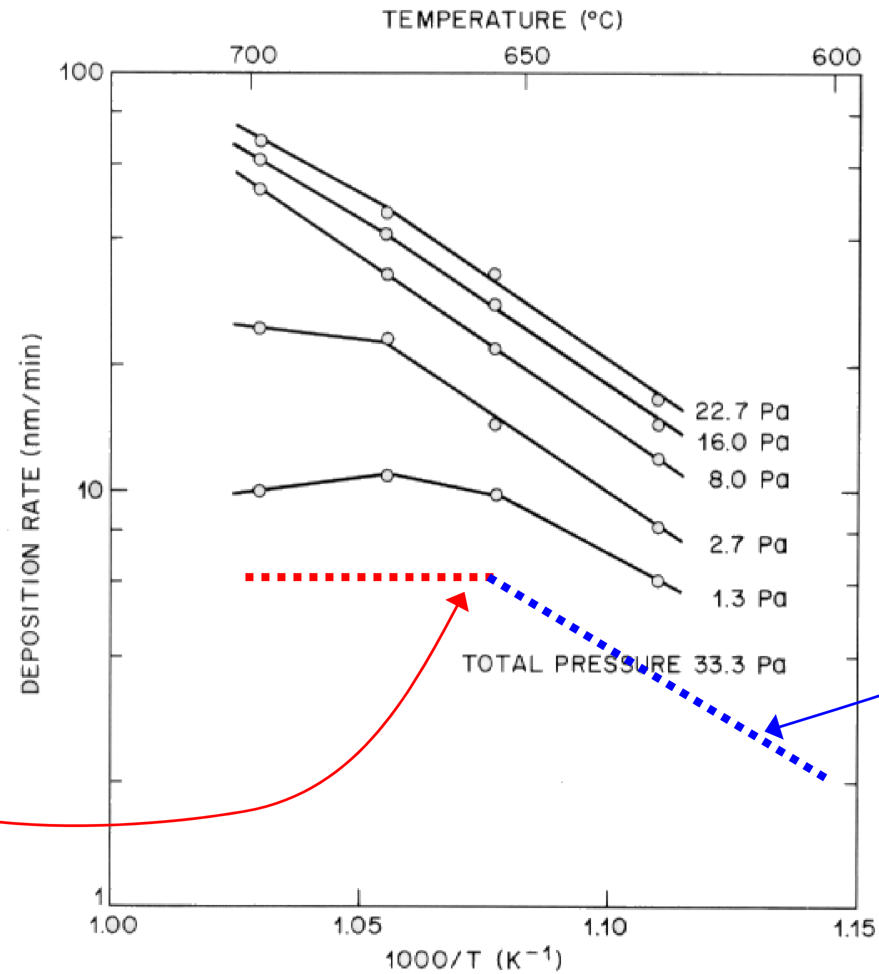


FIGURE 3
Arrhenius plot for polysilicon deposition for different silane partial pressures.

LPCVD for Si Technology

Crystalline Structure is also controlled by temperature.

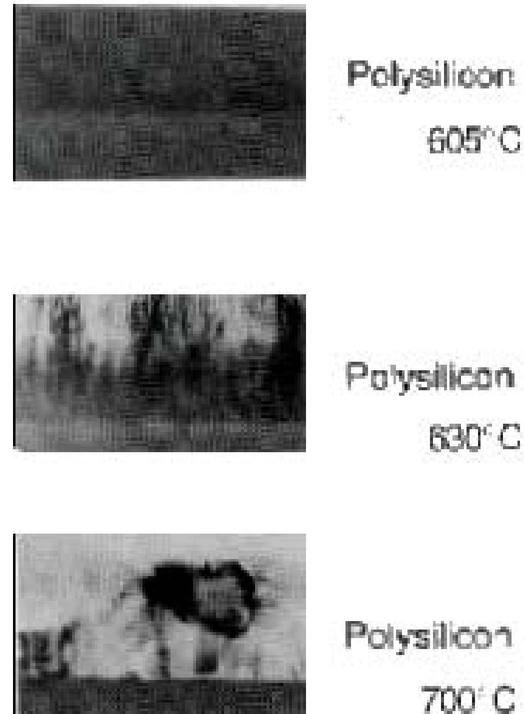


FIGURE 7
TEM cross sections (60,000X) of polysilicon. (a) Amorphous structure deposited at 605°C. (b) Columnar structure deposited at 630°C. (c) Crystalline grains formed by annealing an amorphous sample at 700°C.

Poly-Si can be doped using Diborane (B_2H_6), arsine (AsH_3) or phosphine (PH_3), diffusion (lowest resistivity) or by implantation (highest resistivity). The resistivity can vary from ~10^{-3} to 10^{+5} Ω-cm. Doped poly-Si makes good short interconnect lines

LPCVD of Oxides

Uses:
Undoped: Insulator between multilevel metalization, implantation or diffusion mask, increase thermal oxide thickness for high voltage devices.
Doped: P-doped is used as a multilevel metalization insulator, final passivation layer (prevents ionic diffusion), or a gettering source.

Undoped Oxide Deposition Methods:
Silane $SiH_4 + O_2 \longrightarrow SiO_2 + 2H_2$ < 500 °C (contain H_2O, SiH, and SiOH impurities)
DCS (Dichlorosilane) $SiCl_2H_2 + 2N_2O \longrightarrow SiO_2 + 2N_2 + 2HCL$ (etches) ~900 °C (contains Cl)
TEOS (tetraethoxysilane) $Si(OC_2H_5)_4 \longrightarrow SiO_2$ + many byproducts 650-750 °C
TEOS + Ozone (O_3) Ozone is more reactive and lowers deposition temperatures to ~400 °C

TABLE 3
Properties of silicon dioxide

Deposition	Plasma	$SiH_4 + O_2$	TEOS	$SiCl_2H_2 + N_2O$	Thermal
Temperature (°C)	200	450	700	900	1000
Composition	$SiO_{1.9}(H)$	$SiO_2(H)$	SiO_2	$SiO_2(Cl)$	SiO_2
Step coverage	nonconformal	nonconformal	conformal	conformal	conformal
Thermal stability	loses H	densifies	stable	loses Cl	stable
Density (g/cm^3)	2.3	2.1	2.2	2.2	2.2
Refractive index	1.47	1.44	1.46	1.46	1.46
Stress (10^9dyne/cm^2)	3C–3T	3 T	1 C	3 C	3 C
Dielectric strength (10^6V/cm)	3–6	8	10	10	11
Etch rate, nm/min (100:1 H_2O:HF)	40	6	3	3	2.5
Dielectric constant	4.9	4.3	4.0	—	3.9

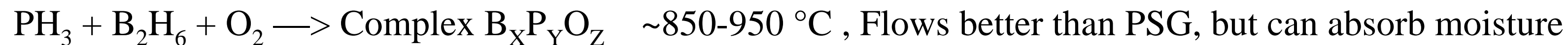
LPCVD of Doped Oxides

Doped Oxide Deposition Methods:

PSG - Phosphorosilicate Glass

$4PH_3 + 5O_2$ ----> $2P_2O_5 + 6H_2$ ~950-1100 °C for flowed glass and <400 for passivation

BPSG - Borophosphorosilicate Glass



$PH_3 + B_2H_6 + O_2$ —> Complex $B_XP_YO_Z$ ~850-950 °C , Flows better than PSG, but can absorb moisture

Doped Oxides (glasses) can be made to "flow" or smooth out. This is particularly useful for smooth interconnects (prevents sharp edges which tend to break metal lines) or for partial global planarization for subsequent lithography steps.

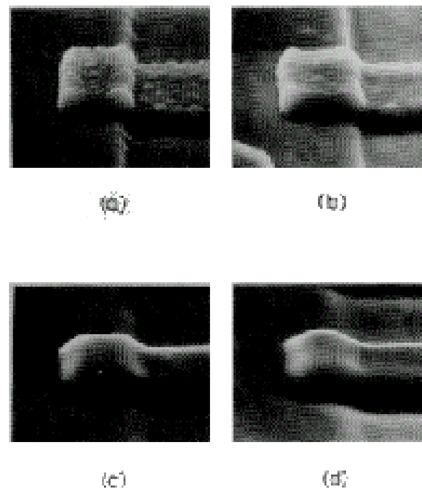


FIGURE 16
SEM photographs (3200X) showing surfaces of 4.6 wt. % P-glass annealed in steam at 1100°C for the following times: (a) 0 min; (b) 20 min; (c) 40 min; (d) 60 min. (*After Adams and Capio, Ref. 34.*)

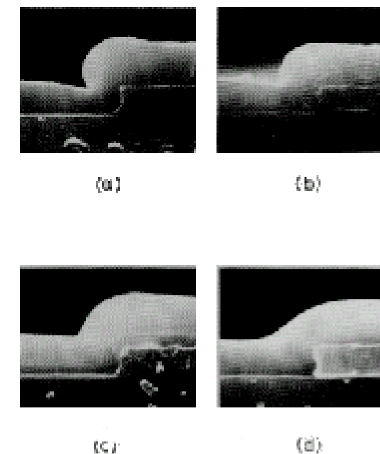
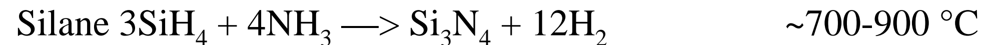
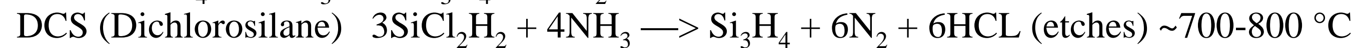


FIGURE 17
SEM cross sections (10,000X) of samples annealed in steam at 1100°C for 20 min for the following weight percent of phosphorus: (a) 0.0 wt. % P; (b) 2.2 wt. % P; (c) 4.6 wt. % P; (d) 7.2 wt. % P. (*After Adams and Capio, Ref. 34.*)

LPCVD of Nitrides

LPCVD of Silicon Nitride


Silane $3SiH_4 + 4NH_3 \longrightarrow Si_3N_4 + 12H_2$ ~700-900 °C


DCS (Dichlorosilane) $3SiCl_2H_2 + 4NH_3 \longrightarrow Si_3H_4 + 6N_2 + 6HCL$ (etches) ~700-800 °C

Contains up to 8% hydrogen

Silicon Nitride is used for encapsulation (sealing up the circuit to prevent contamination from moisture, plastics used in packaging, or air, etc…).
It is sometimes used for a dielectric isolation layer and rarely used as a gate dielectric. Oxide/nitride mixtures known as oxynitrides are sometimes used in FLASH memories.

TABLE 4
Properties of silicon nitride

Deposition	LPCVD	Plasma
Temperature (°C)	700–800	250–350
Composition	$Si_3N_4(H)$	SiN_xH_y
Si/N ratio	0.75	0.8–1.2
Atom % H	4–8	20–25
Refractive index	2.01	1.8–2.5
Density (g/cm^3)	2.9–3.1	2.4–2.8
Dielectric constant	6–7	6–9
Resistivity (ohm-cm)	10^{16}	$10^6 - 10^{15}$
Dielectric strength (10^6 V/cm)	10	5
Energy gap (eV)	5	4–5
Stress (10^9 dyne/cm^2)	10 T	2C–5 T

Alternative CVD Chemistries

TABLE 1
Typical reations for depositing dielectrics and polysilicon.

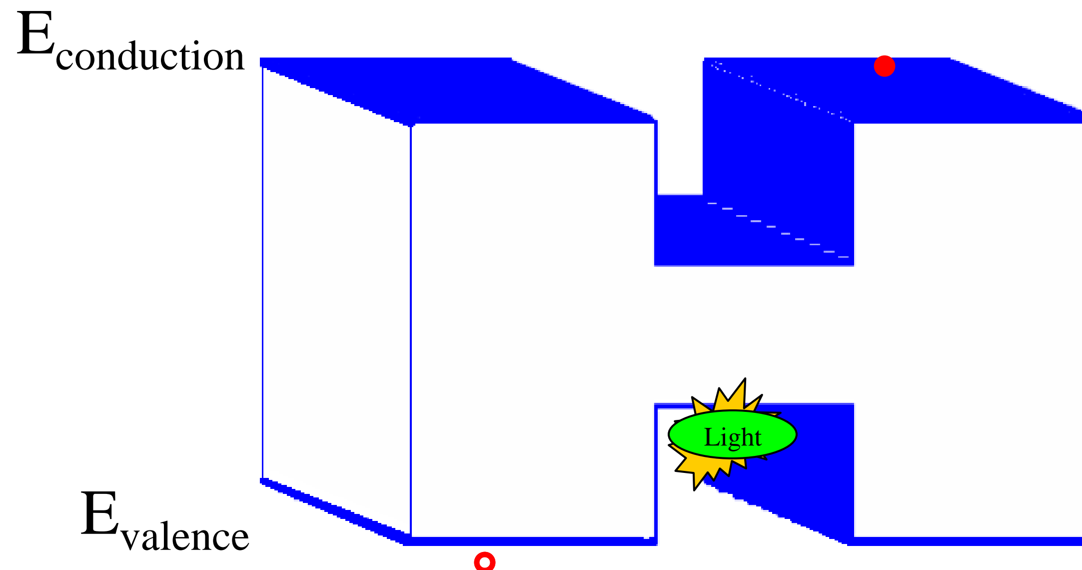
Product	Reactants	Deposition temperature, °C
Silicon dioxide	$SiH_4 + CO_2 + H_2$	850–950
	$SiCl_2H_2 + N_2O$	850–900
	$SiH_4 + N_2O$	750–850
	$SiH_4 + NO$	650–750
	$Si(OC_2H_5)_4$	650–750
	$SiH_4 + O_2$	400–450
Silicon nitride	$SiH_4 + NH_3$	700–900
	$SiCl_2H_2 + NH_3$	650–750
Plasma silicon nitride	$SiH_4 + NH_3$	200–350
	$SiH_4 + N_2$	200–350
Plasma silicon dioxide	$SiH_4 + N_2O$	200–350
Polysilicon	SiH_4	575–650

Epitaxy

Classifications of Electronic Materials

Compound Semiconductors allow us to perform "Bandgap Engineering" by changing the energy bandgap as a function of position. This allows the electrons to see "engineered potentials" that "guide" electrons/holes in specific directions or even "trap" them in specific regions of devices designed by the electrical engineer.

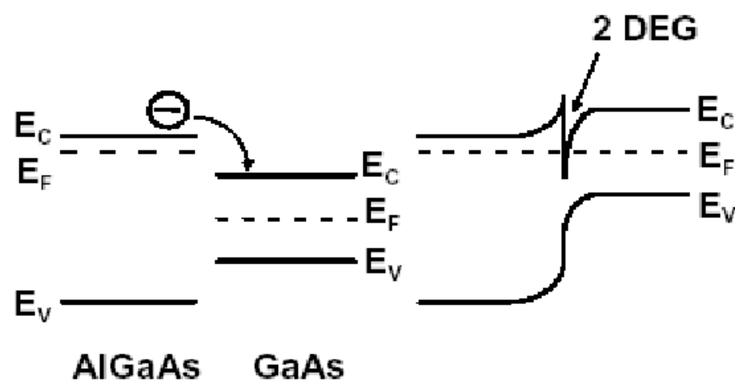
Example: Consider the simplified band diagram of a GaN/ $Ga_{0.75}In_{0.25}N$/ GaN LED structure. Electrons and holes can be "localized" (trapped) in a very small region – enhancing the chance they will interact (recombine). This is great for light emitters!

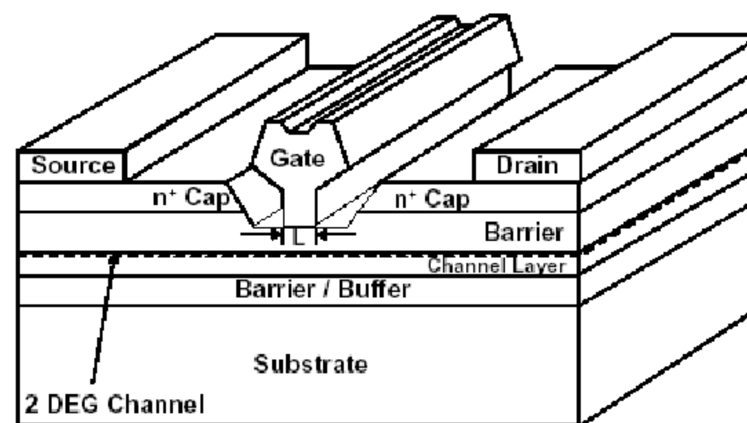


Classifications of Electronic Materials

Compound Semiconductors allow us to perform "Bandgap Engineering" by changing the energy bandgap as a function of position. This allows the electrons to see "engineered potentials" that "guide" electrons/holes in specific directions or even "trap" them in specific regions of devices designed by the electrical engineer.

Example: Consider the band Diagram of a GaAs MODFET. Electrons in the "transistor channel" can be confined in a very thin (50-100 Angstroms) sheet known as a 2 dimensional electron gas (2DEG). This thin layer is very quickly (easily) depleted (emptied of electrons) by application of a gate voltage (repelling electrons) making such transistors very fast. This technology enables high speed communications, modern RADAR and similar applications.





How do we produce these Energy Engineered Structures and Devices?

Epitaxial Semiconductor and Dielectric deposition Techniques:

•"Epitaxial" is derived from the Greek word for skin, more specifically "thin skin". Thin layers of materials are deposited on a substrate

•Temperature and substrate determines the physical structure of the deposited films:

- •Low Temperatures or non-crystalline substrate:
  - •Materials end up with amorphous or polycrystalline materials
- •High Temperature AND Crystalline substrate
  - •Need to have an existing crystalline wafer so as to "seed" the crystallization process.
  - •Films that retain the substrates basic crystal structure are "Epitaxial"

Epitaxy

Single Crystal Semiconductors (Epitaxy, Chapter 14)

We can grow* crystalline semiconductors by raising the temperature to allow more surface migration and by using a crystalline substrate (Si, GaAs, InP wafer, etc…)
===> Single crystal material mimicking the crystal structure of the layers below it.

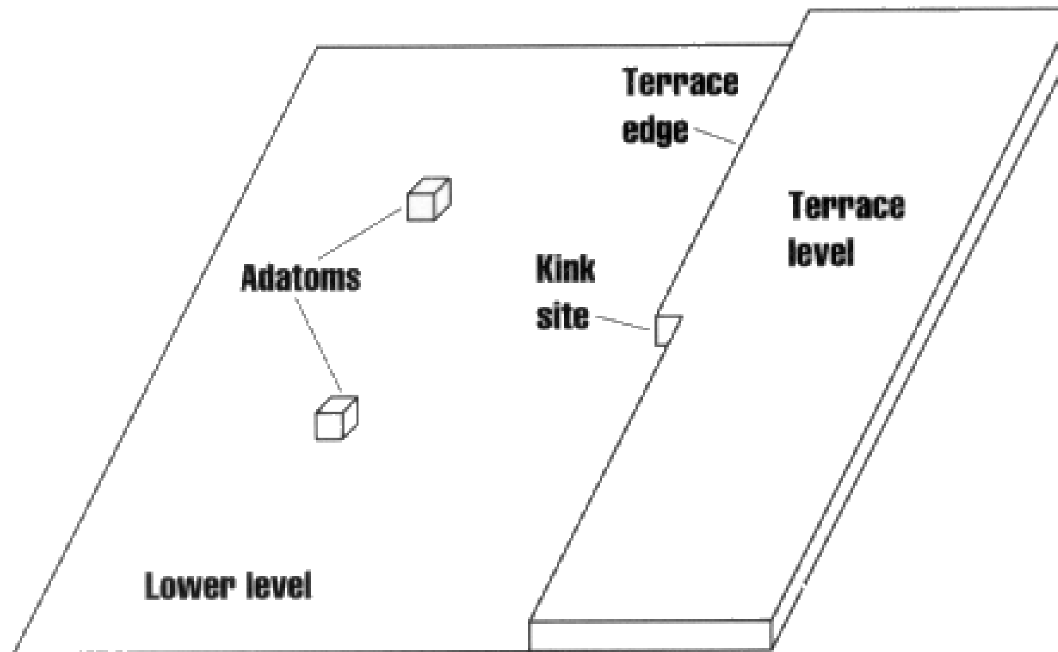
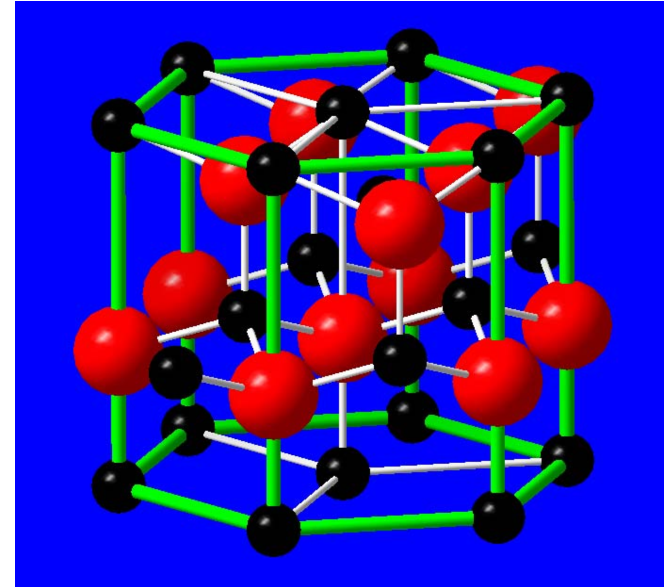


Figure 14-32 A microscopic view of a semiconductor surface during MBE growth or evaporation.

*Instead of the word deposit, we use "grow" to describe the tendency of the deposited material to mimic the crystal structure of crystalline substrate material.

Crystalline Order

Water Molecules, H_2O, forming "Snowflakes"



Atoms forming a "Semiconductor"

Need two volunteers… **(demo on how a crystal forms naturally due to repulsive electronic bonds)**

Epitaxy

Importance of lattice mismatch

The lattice constant of the epitaxially grown layer needs to be close to the lattice constant of the substrate wafer. Otherwise the bonds can not stretch far enough and dislocations will result.

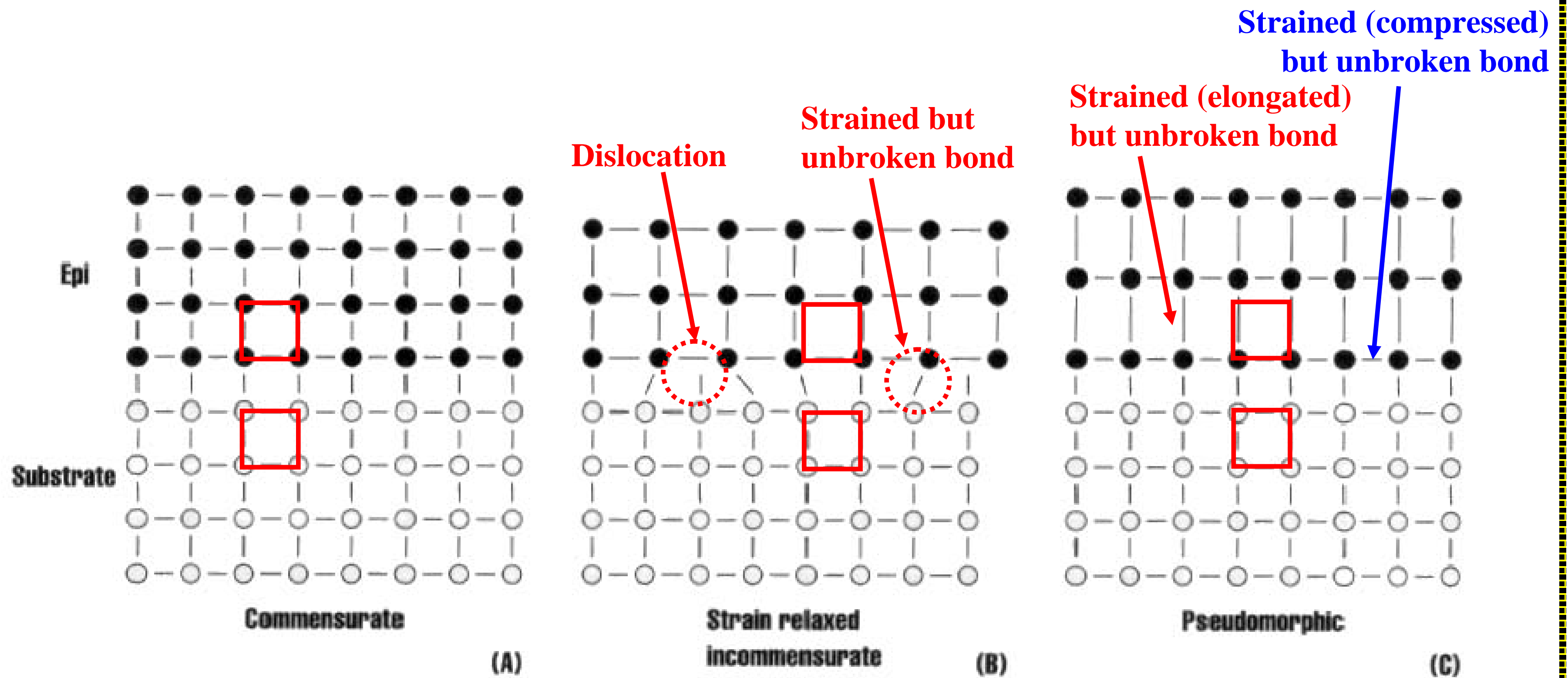


Figure 14-15 Epitaxial growth processes can be divided into (a) commensurate, (b) strain relaxed incommensurate, and (c) incommensurate but pseudomorphic.

Epitaxy

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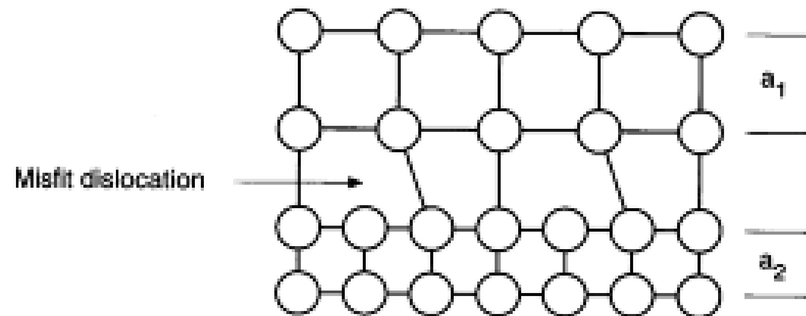


Figure 2.7 Misfit dislocation schematic.

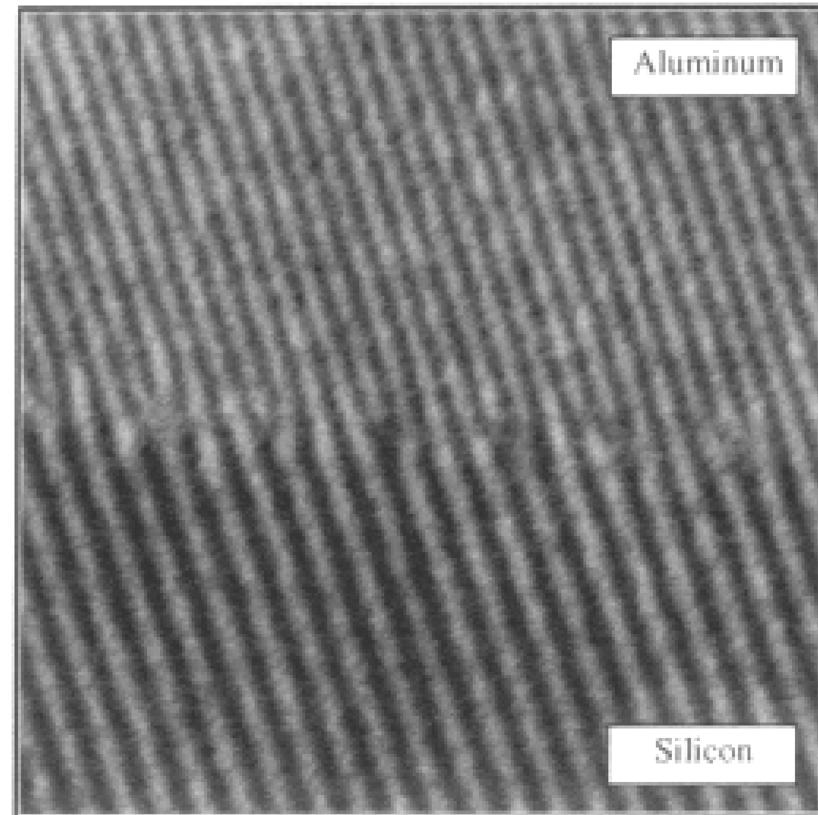


Figure 2.8 A TEM comparable to the schematic of Figure 2.7 that shows the (111) planes of aluminum epitaxially overgrown on silicon and the (111) planes of the silicon substrate.

Silicon Epitaxy

Used for high purity layer growth (alternative/augmenting a denuded zone), can form very thick doped structures (30-100 um) not possible with implantation or diffusion. Such thick, pure layers are often used in power devices with thinner, 1-5 um, are commonly used for many CMOS and bipolar technology.

We want the reaction to occur at the gas/wafer boundary. However, higher temperatures (silane - 650 to 800 C) used for enhanced surface migration also result in gas phase decomposition of Silane resulting in particles. This is very bad as particles tend to fall onto the wafers. Higher quality (fewer defects) material occurs at higher temperatures than 800 C. Instead of silane, chlorosilanes that are more stable up to higher temperatures are more commonly used. Dichlorosilane (SiH_2Cl_2) is the most common and allows growth at ~800 to 1050 °C (higher T is possible).

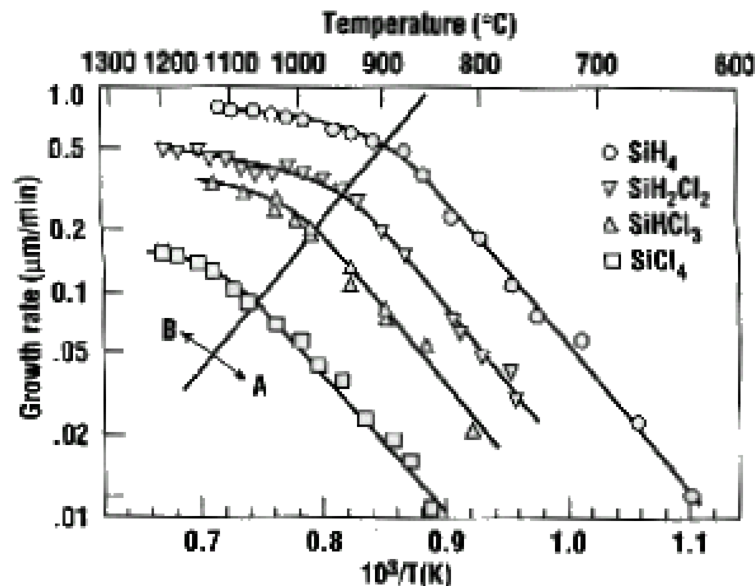


Figure 14.8 Arrhenius behavior of a variety of silicon-containing growth species *(after Eversteyn, reprinted by permission, Philips).*

MOCVD

Primarily used for II-VI, and III-V semiconductors, special metallic oxides and metals.

Metal Organic Chemical Vapor Deposition (MOCVD)

- Many materials that we wish to deposit have very low vapor pressures and thus are difficult to transport via gases.
- One solution is to chemically attach the metal (Ga, Al, Cu, etc…) to an organic compound that has a very high vapor pressure. Organic compounds often have very high vapor pressure (for example, alcohol has a strong odor).
- The organic-metal bond is very weak and can be broken via thermal means on wafer, depositing the metal with the high vapor pressure organic being pumped away.
- Care must be taken to insure little of the organic byproducts are incorporated. Carbon contamination and unintentional Hydrogen incorporation are sometimes a problem.

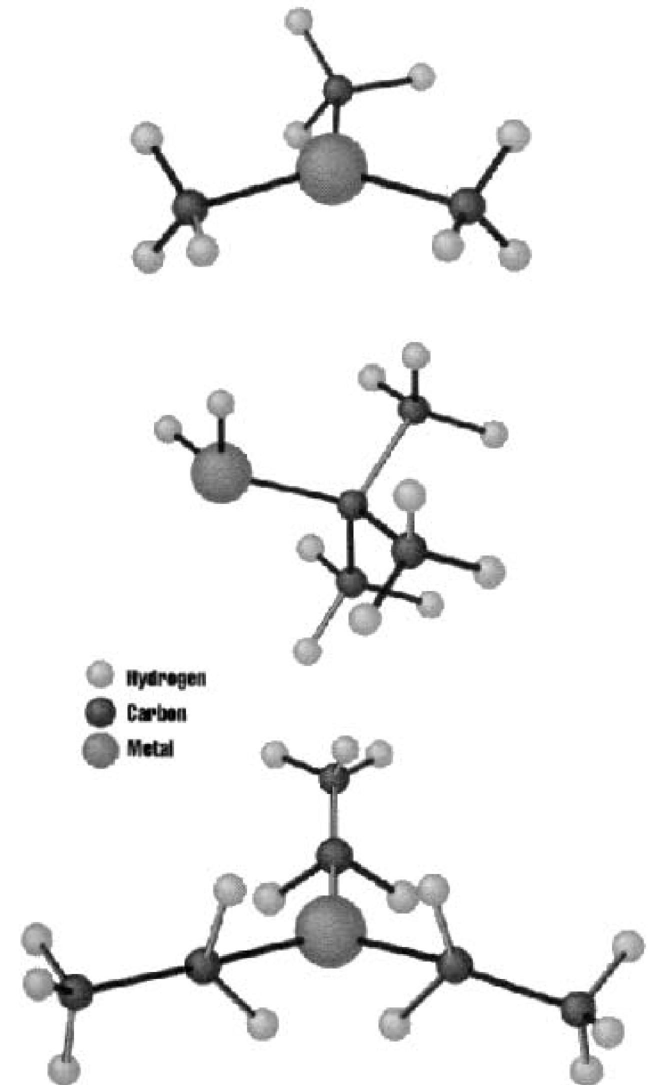
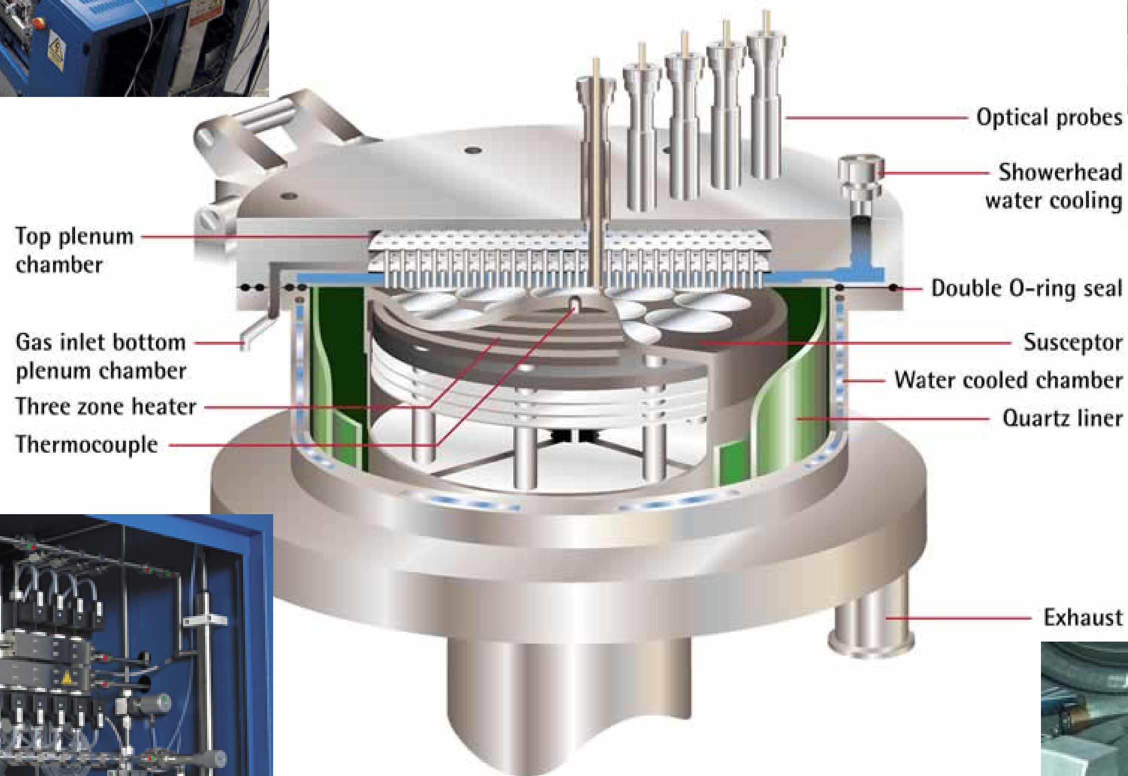


Figure 14-19 Examples of common organometallics used in MOCVD include (from top to bottom): trimethylgallium, tetrabutylarsine, and triethylgallium.

Human Hazard: As the human body absorbs organic compounds very easily, the metal organics are very easily absorbed by humans. Once in the body, the weak metal-organic bond is easily broken, thus, poisoning the body with heavy metals that often can not be easily removed by normal bodily functions. In extreme cases, blood transfusion is the only solution (if caught in time).

Commercial Thomas Swan® MOCVD

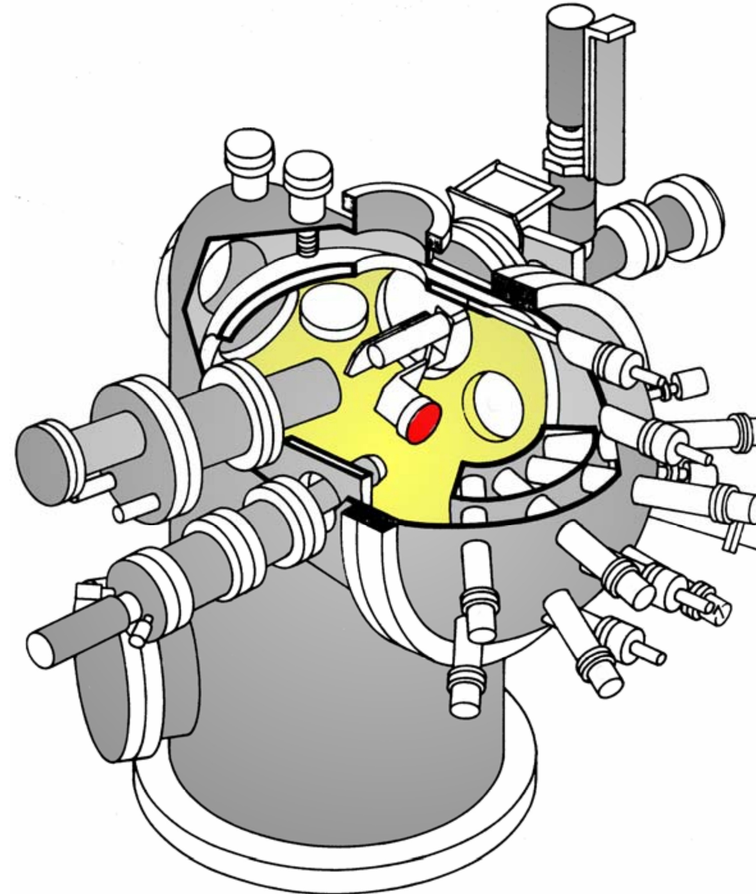


Molecular Beam Epitaxy (MBE)

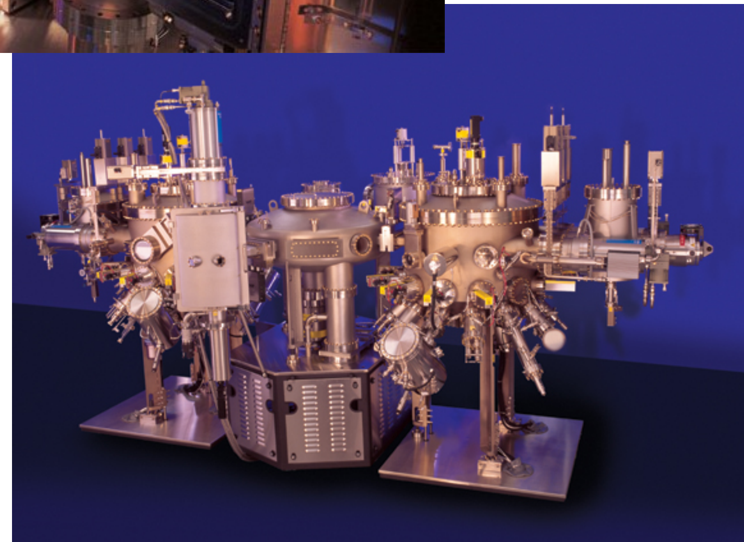
Molecular Beam Epitaxy (MBE)

Dominates III-V electronic market and strong competitor in upper end LASER market
Offers the highest purity material (due to UHV conditions) and the best layer control (almost any fraction of an atomic layer can be deposited and layers can be sequenced one layer at a time (for example Ga then As then Ga etc…).

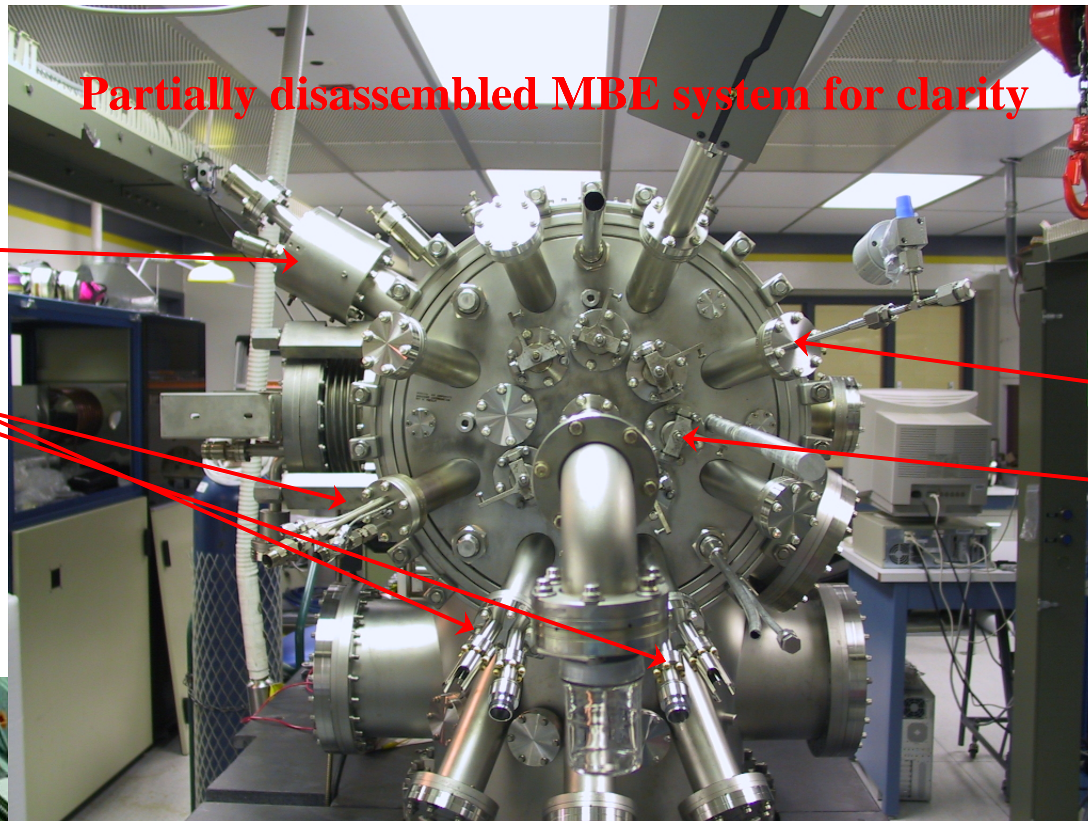
- In an UHV chamber, ultra high purity materials are evaporated.
- Because of the very low pressure, the mean free path is very long (can be hundreds of meters). Thus, the evaporated material travels in a straight line (a molecular beam) toward a hot substrate resulting in highly efficient raw materials usage.
- Once on the substrate, the atom or molecule moves around until it finds an atomic site to chemically bond to.
- Shutters can be used to turn the beam flux on and off
- The flux of atoms/molecules is controlled by the temperature of the "effusion cell" (evaporation source).

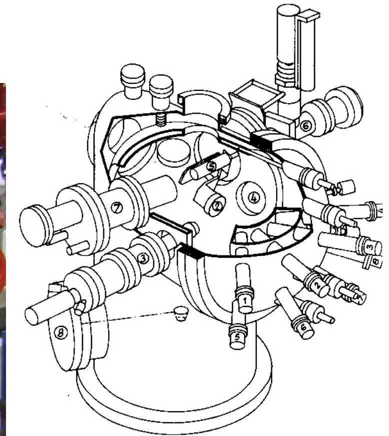


Commercial Veeco® MBE



MBE



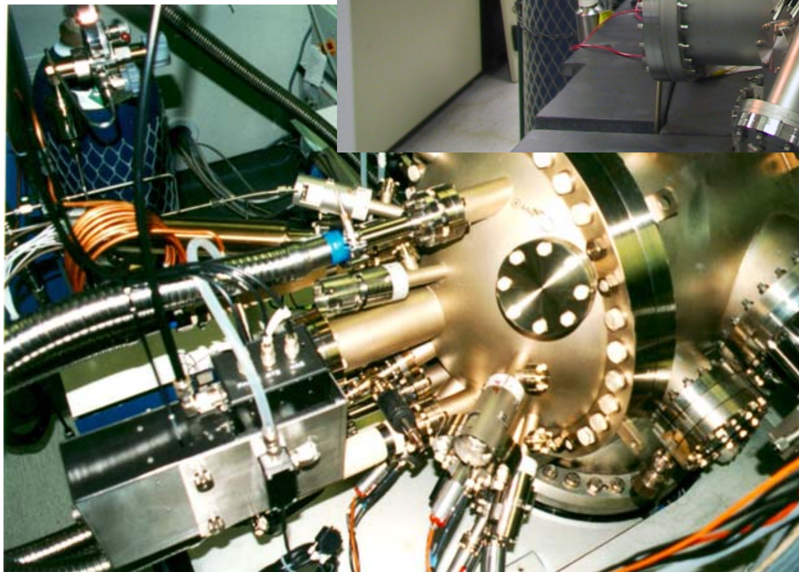


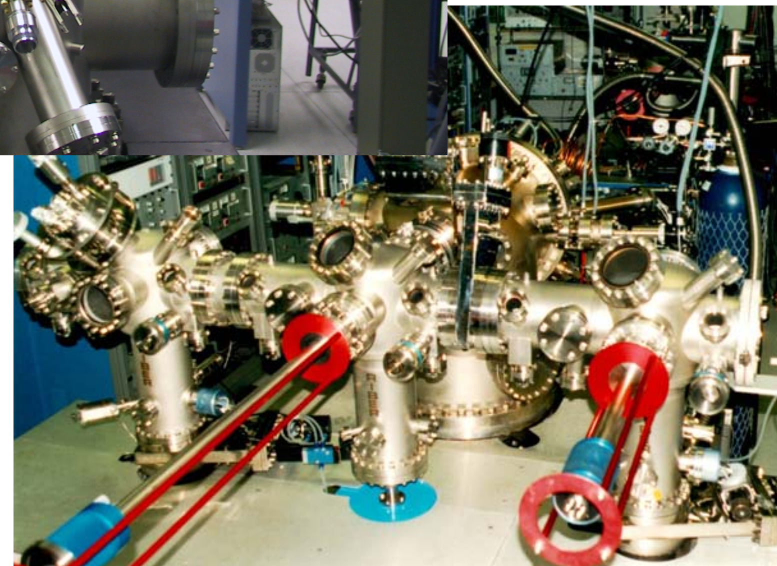
RHEED Gun

Effusion Furnaces

Gas Source (oxygen)

Shutter mechanism

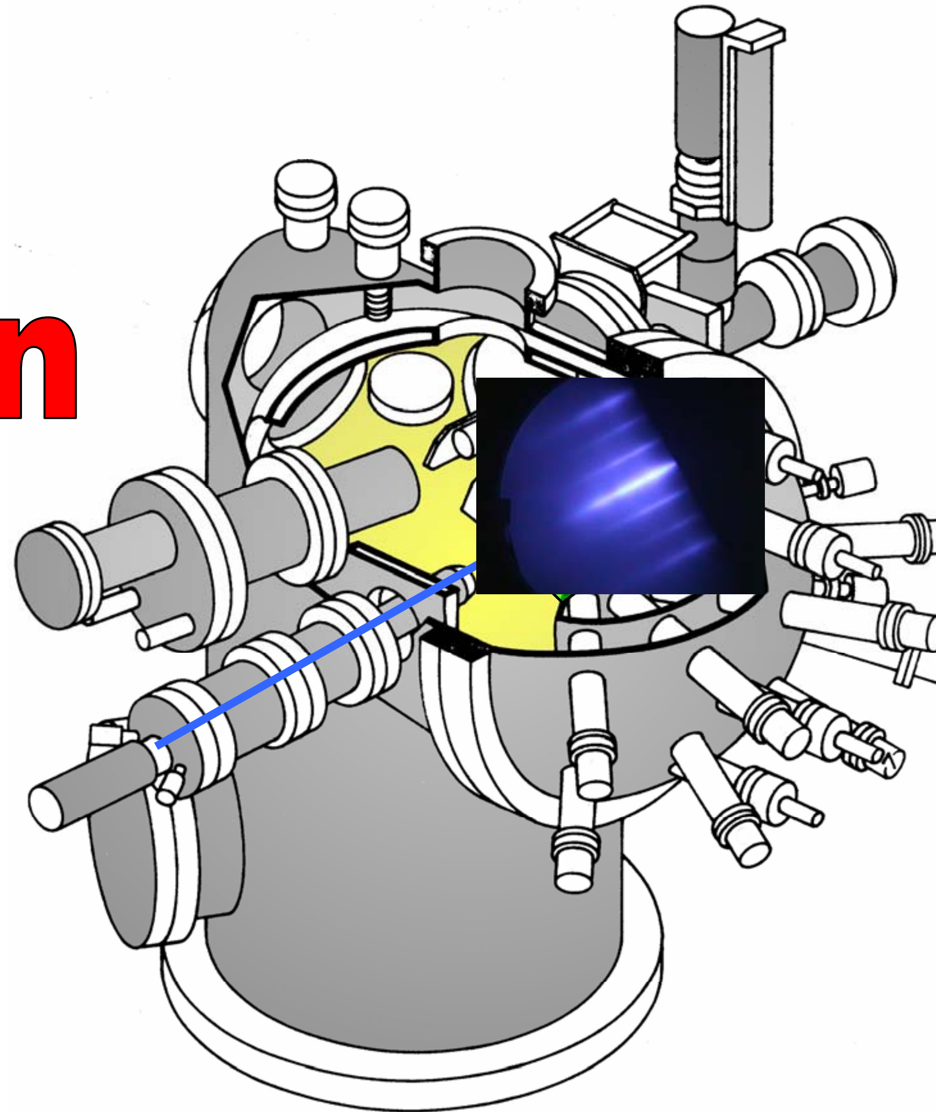




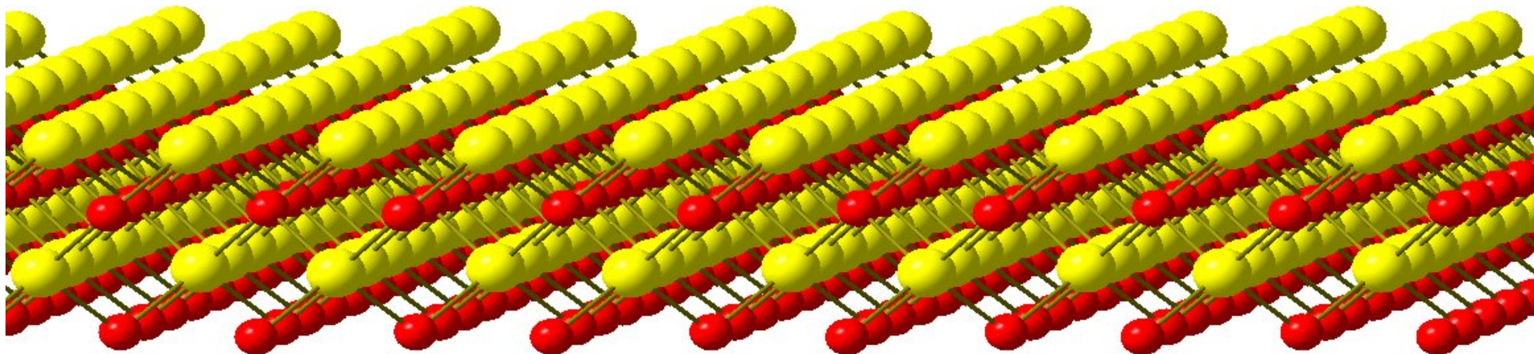
Molecular Beam Epitaxy (MBE)

In

Ga



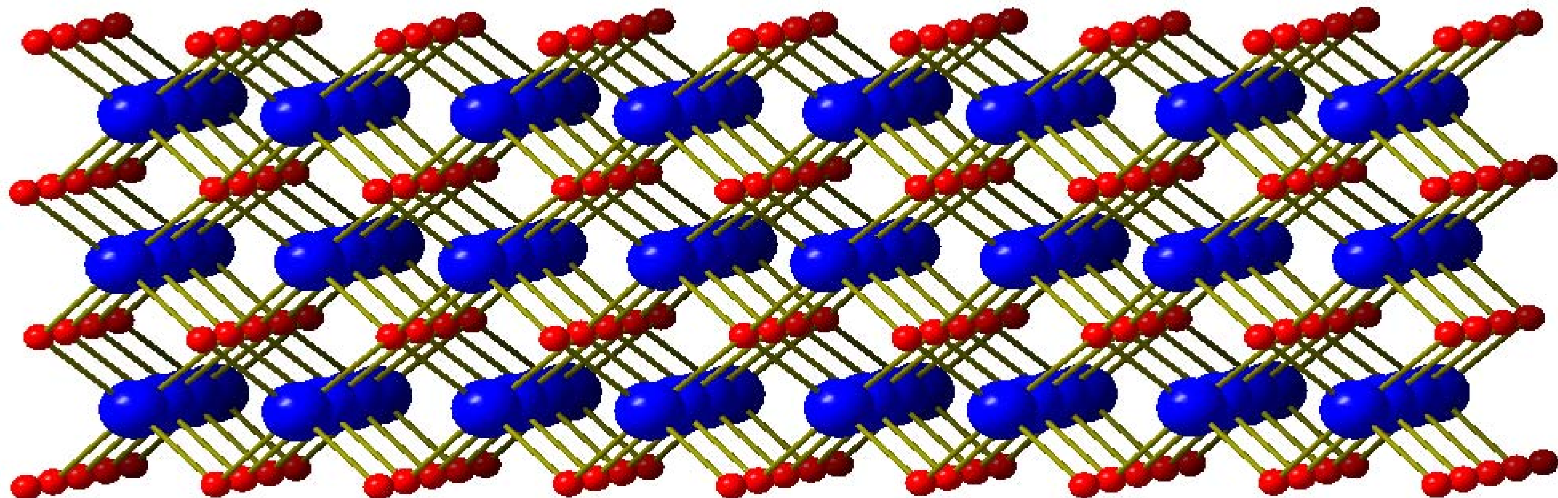
Molecular Beam Epitaxy (MBE)



How do we create Bandgap Engineered Structures? Epitaxy

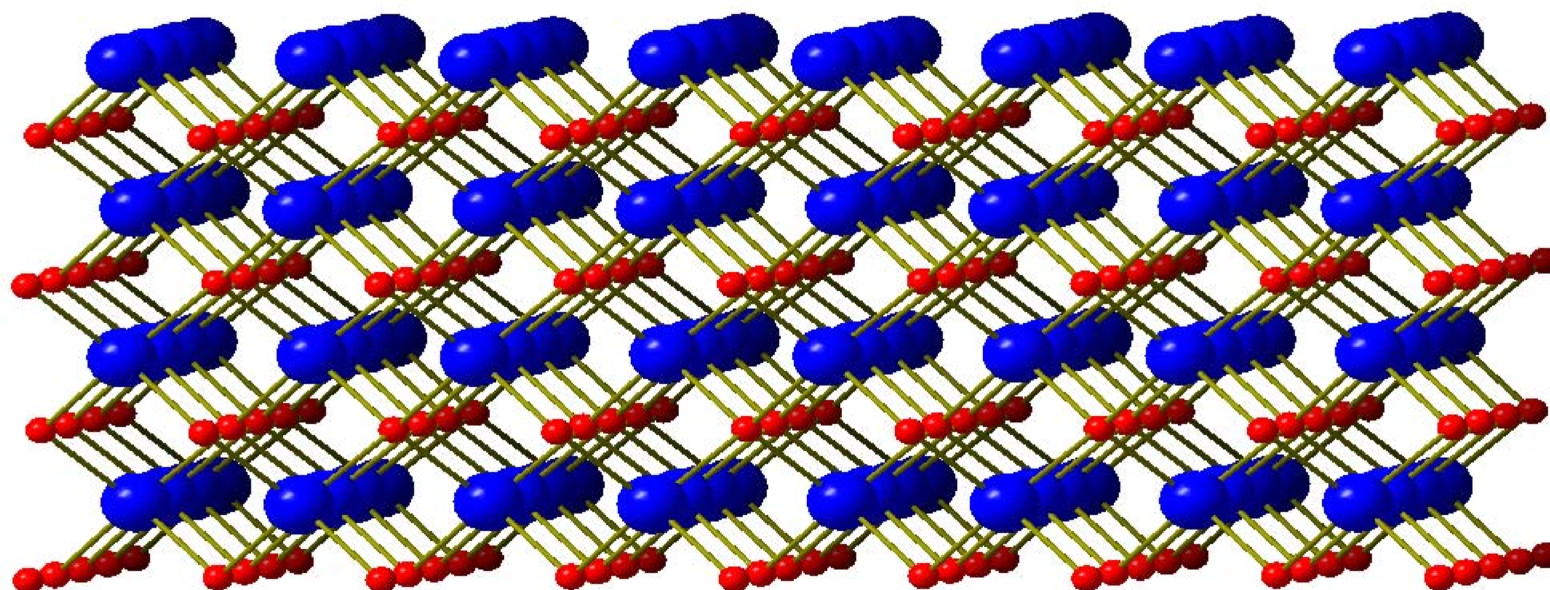
•Repeating a crystalline structure by the atom by atom addition.

•Chemistry controls the epitaxy to insure that, for example, Ga bonds only to N and not Ga-Ga or N-N bonds*.

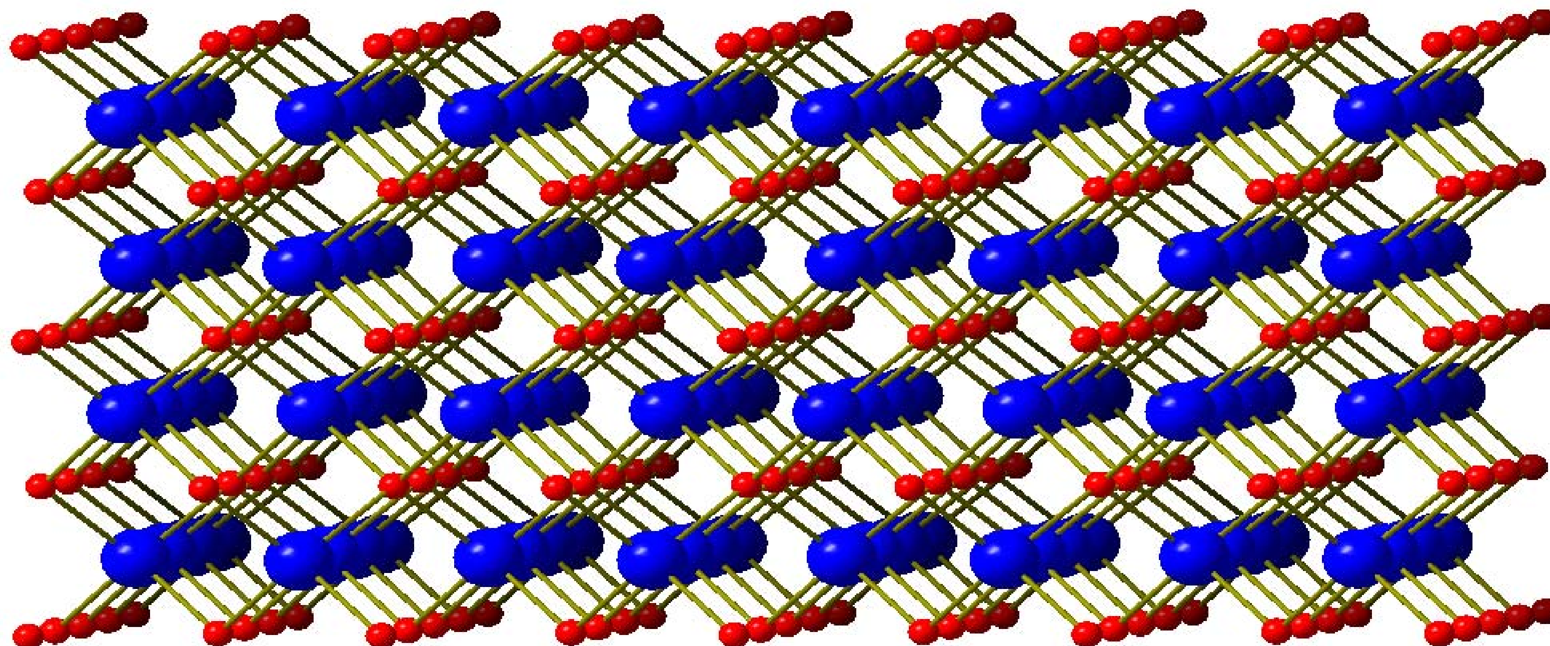


*A small number of "antisite" defects (Ga-Ga or N-N bonds) actually do form but are typically in the parts per trillion concentration.

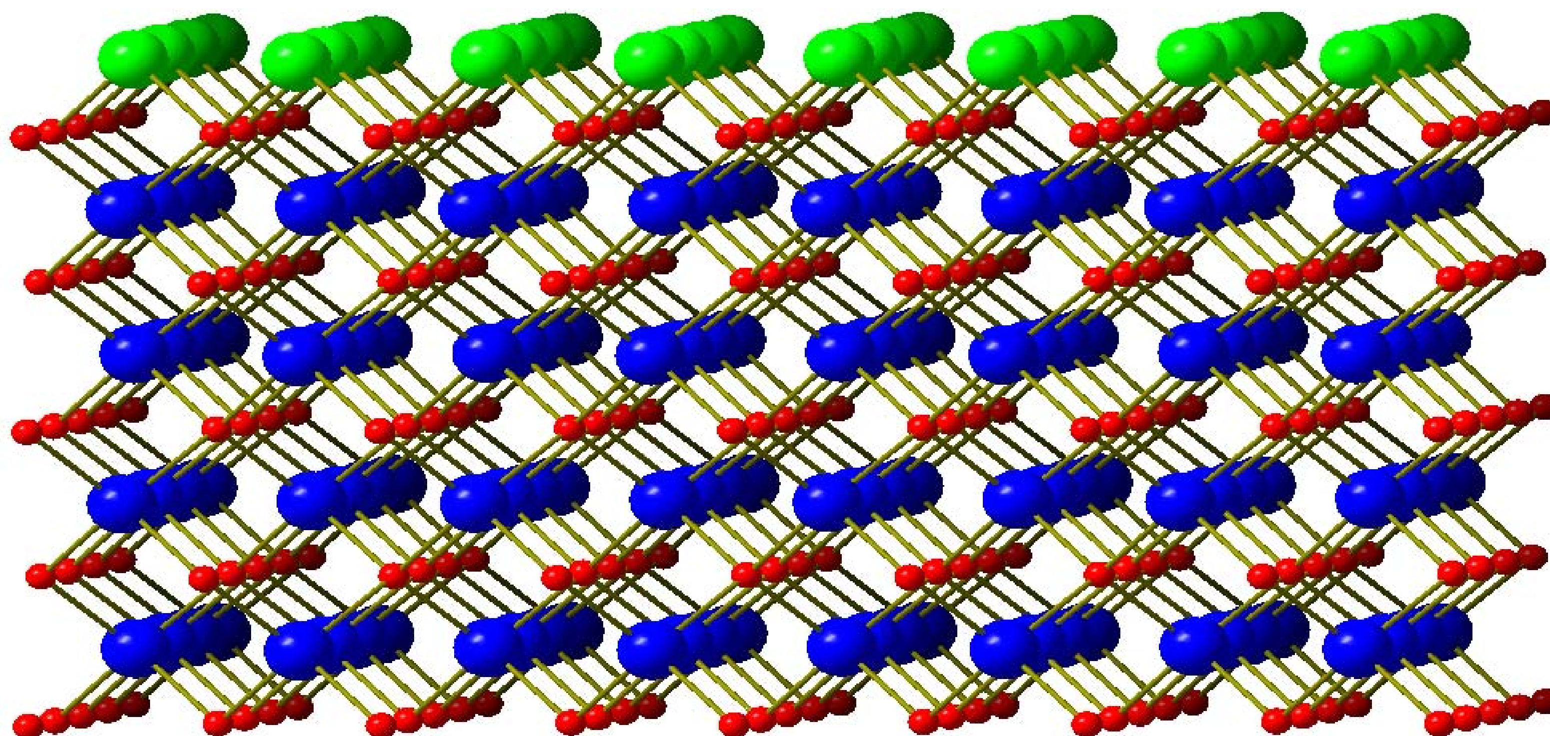
How do we create Bandgap Engineered Structures? Epitaxy



How do we create Bandgap Engineered Structures? Epitaxy



How do we create Bandgap Engineered Structures? Epitaxy



How do we create Bandgap Engineered Structures? Epitaxy

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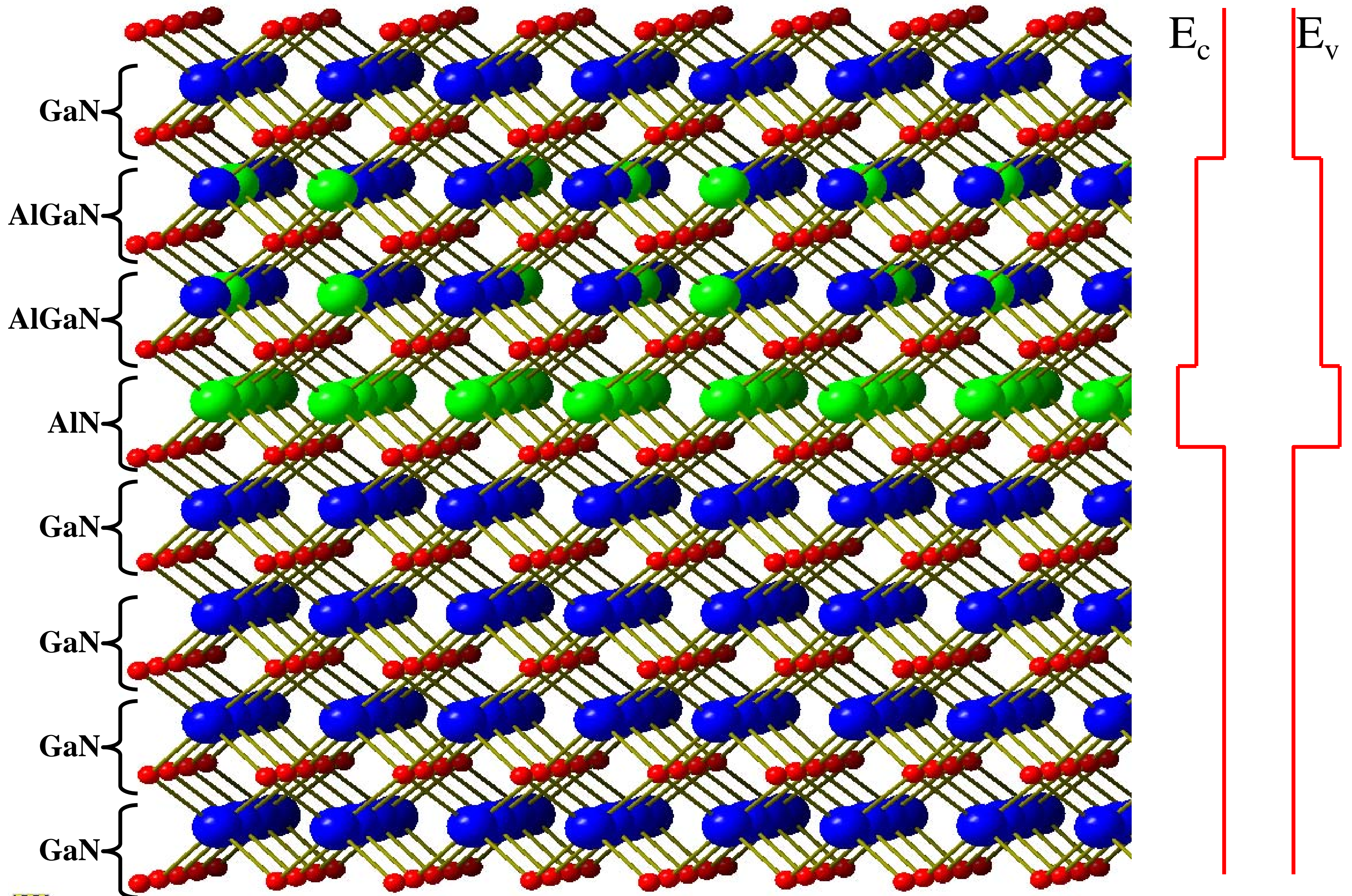
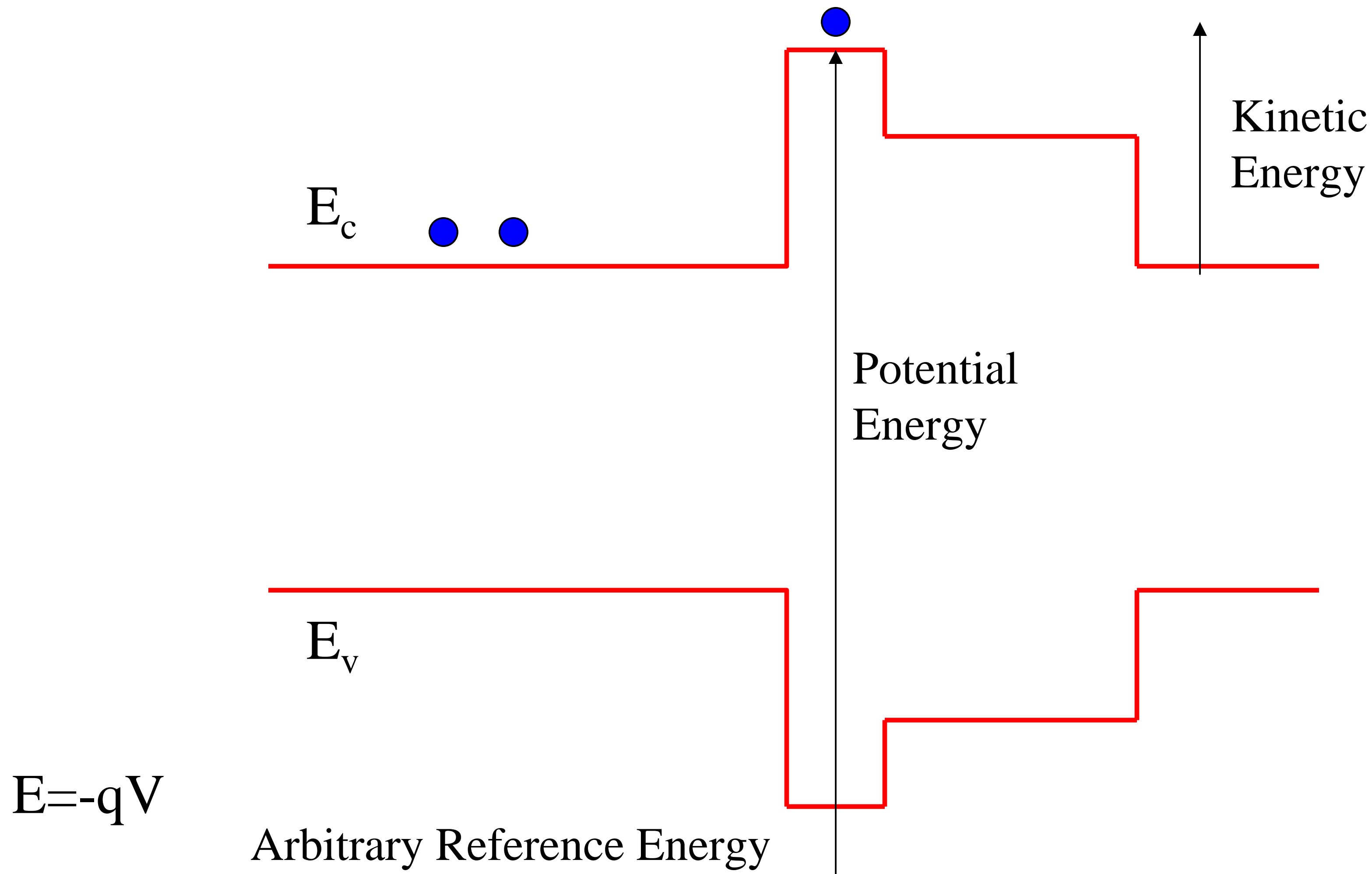


Engineered Energy Behavior in Compound Semiconductors

The potential distributions we will use in this class are all possible/common in device structures. Some may represent "grown in potentials" (quantum wells, etc...) or naturally occurring potentials (parabolic potentials often occur in nature – lattice vibrations for example) including periodic potentials such as lattice atoms.



Plasma Enhanced Chemical Vapor Deposition (PECVD)

Section 13.7 in Campbell

Plasmas can be used to perform low temperature deposition of materials not possible thermally (low thermal energy).

Consider 2 problems:
1.) After metal lines like Aluminum (Si-Al alloy temperature = 577 °C) are deposited, how would you deposit a dielectric layer to isolate the next layer.
Solutions include CVD and PECVD depositions of dielectrics.

2.) After all processing, how would you protect the die?
Solution SiN_X deposition at very low temperature.

We would like to keep process temperatures less than 400 degrees ° C for Si and much lower for GaAs.

When fast diffusing metals like copper are used, this low temperature deposition becomes more important.

Older PECVD systems attempt to randomize gas delivery by operating at higher pressures (~>1 torr), and low induced sheath voltages. The deposited materials have better step coverage due to less shadowing of features (trenches and extrusions)

Most modem systems are based on "Remote Plasma Generation" operating at lower pressures (~0.1 torr) which leads to directionality of the deposition and poorer step coverage. In these systems, the plasma is upstream from the wafer. The "activated species" diffuses downstream to react with wafer. This reduces damage by taking the wafer out of direct contact with the plasma and reduces the bombardment by high energy ions. Using remote systems, very high RF power can be used to create otherwise highly unlikely species (atomic oxygen or nitrogen) without significant ion damage.

Plasma Enhanced Chemical Vapor Deposition (PECVD)

Stoichiometry is not guaranteed in PECVD systems (non-thermal equilibrium). Thus, instead of Si_3N_4 or SiO_2, one obtains Si_XN_Y or SiO_X where x and y can vary (can go from amorphous Silicon to SiN_X or SiO_2)

Due to the rapid deposition without the temperatures required for surface migration (explain term), film tend to be porous (possess holes like a sponge) leading to lower density than thermally grown films. Post deposition anneals (in either 0_2 or NH_3 can help increase the density of the films) but are not common practice (if we are using PECVD instead of CVD, we want low temperatures).

Film stoichiometry and density can be monitored by a COMBINATION of etch rate comparisons to thermally grown films and ellipsometry to determine the index of refraction of the films.

Film stress:
Any dissimilar material deposited on a wafer can cause film stress. This puts a finite limit on the thickness of the film before wafer bowing or film cracking occurs.

Nitrides:
Tend to use SiH_4 (typically diluted for safety in He or Ar) for the Si source and N_2 or NH_3 for the nitrogen source. Films can have very high hydrogen content (>20% atomic).

Oxides:
Tend to use SiH_4 (typically diluted for safety in He or Ar) for the Si source and 0_2 or N_20 for the oxygen source. Use of 0_2 is precluded by "sand" generation by Silane-oxygen pre-reactions minimize gas form. Hydrogen tends to be ~1-10% atomic.

Oxinitrides:
Mixtures of nitrides-oxides can be used to form oxinitrides. These are often used in Flash memory applications where controlled leakage currents and controlled charge storage in the dielectrics are important.

CVD Hazards

Many gases used in CVD systems are toxic (hazardous to humans), corrosive (causes corrosion to stainless steel and other metals), flammable (burns when exposed to an ignition source and an oxygen source), explosive and/or pyrophoric (spontaneously burn or explode in air, moisture or when exposed to oxygen)

TABLE 2
Properties of common gases used in CVD

Gas	Formula	Hazard	Flammable limits in air (vol%)	Exposure limit (ppm)
Ammonia	NH_3	toxic, corrosive	16–25	25
Argon	Ar	inert	—	—
Arsine	AsH_3	toxic	—	0.05
Diborane	B_2H_6	toxic, flammable	1–98	0.1
Dichlorosilane	SiH_2Cl_2	flammable, toxic	4–99	5
Hydrogen	H_2	flammable	4–74	—
Hydrogen chloride	HCl	corrosive, toxic	—	5
Nitrogen	N_2	inert	—	—
Nitrogen oxide	N_2O	oxidizer	—	—
Oxygen	O_2	oxidizer	—	—
Phosphine	PH_3	toxic, flammable	pyrophoric	0.3
Silane	SiH_4	flammable, toxic	pyrophoric	0.5