

Deposition Techniques

EE 2520

1 Introduction

Slide #3

1. Any microfabrication of devices be it MEMS or CMOS involves deposition, patterning and etching steps.
2. Successive layers are deposited, patterned and etched to fabricate the complex stacked structure that provide the desired functionality
3. The toolbox of deposition is extensive as depicted in Fig.1 and gives a wide range of choices for the process engineering
4. The deposition techniques can be classified into either chemical vapor deposition or physical vapor deposition
5. Aspect ratio (H/W), side wall coverage, voids are the key metrics for choosing the deposition technique as shown in Fig.2

Process	Abbreviation	Temperature Range	Method
Chemical Vapor Deposition	CVD	500 - 1100°C	Gas phase, chemical
Low Pressure Chemical Vapor Deposition	LPCVD	500 - 800°C	Gas phase, low pressure chemistry
Metal-Organic Chemical Vapor Deposition	MOCVD	600 - 1200°C	Gas phase chemistry
Plasma Enhanced Chemical Vapor Deposition	PECVD	300 - 450°C	Plasma chemistry
Atomic Layer Deposition	ALD	100 - 400°C	Chemistry
Plasma Sputtering	Sputtering	100 - 300°C	Physical deposition
Evaporation	Evaporation	100 - 500°C	Physical deposition
Molecular Beam Evaporation	MBE	100 - 400°C	Physical deposition

Figure 1: Various Deposition Techniques

6. Desirable Traits of Deposition

- The film should have the desired composition, low contaminates, good electrical and mechanical properties.
- The film should have uniform thickness across wafer and also wafer-to-wafer.
- The film should have good step coverage also known as conformal deposition
- The film should be devoid of voids.
- The film should be amenable to planarization

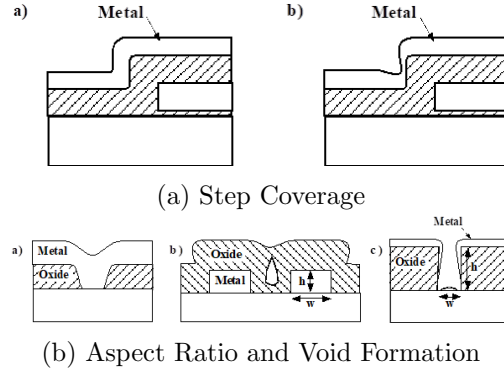


Figure 2: Metrics for Deposition

2 Chemical Vapor Deposition

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1. Chemical Vapor Deposition (CVD) systems use reactive gases that undergo thermal decomposition and deposit a layer on the wafer surface
2. When the term CVD is used without any prefix, the pressure inside the chamber is assumed to be atmospheric. It is also referred to as Atmospheric Pressure Chemical Vapor Deposition and the schematic is shown in Fig.3

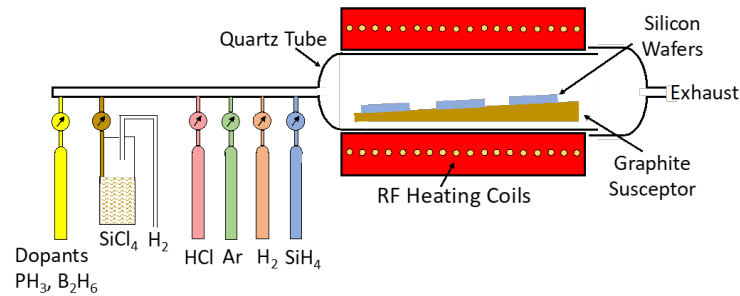


Figure 3: Typical APCVD Set up

3. Deposition of silicon film can be done through CVD by decomposing Silane



4. Si films may be crystalline if they are deposited on a crystalline substrate with appropriate processing conditions
5. Deposition crystalline silicon on top of Silicon is beneficial for the following reasons
 - Resistivity of silicon grown by CZ method is restricted to 10- ($\Omega - \text{cm}$) because of the existence of oxygen and other impurities from the quartz crucible. Such impurities can be reduced by CVD

- Growth of lightly doped substrate on heavily doped substrate is possible. This is typically used in CMOS devices to avoid latchup
6. The term "Epitaxy" refers to deposition/growth of a crystalline material over a crystalline substrate
 7. If a film of a different crystalline material is grown on the substrate, then the term "heteroepitaxy" is used
 8. The growth of different size atoms on the substrate causes strain and often causes defects if the layer is too thick
 9. Strain is used to modify the mobility of the carriers in the channel of CMOS device by growing strained SiGe/SiC source/drain regions
 10. At an atomic level, depositing atoms find a site on the substrate where they attach and continue the layer growth
 11. The growth at an atomistic level occurs via several nucleation mechanisms such as surface nucleation, ledge nucleation and kink nucleation as shown in Fig.4

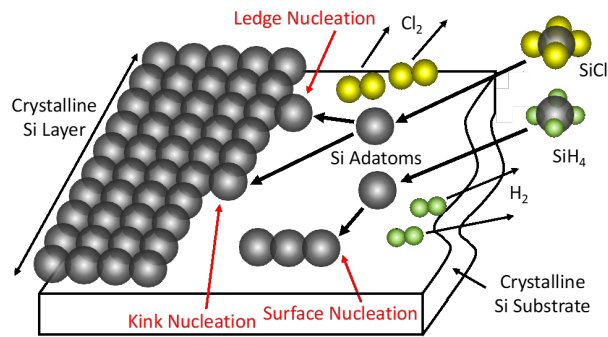


Figure 4: Nucleation mechanisms in CVD

12. At epitaxy temperatures, which are high, the hot walls would decompose the gas before it gets onto the wafer and thus creates non uniformity
13. Most epitaxial systems use "warm wall" with wall temperature being much cooler than the wafer temperature
14. The physics of layer growth consists of mass transport of the reactants followed by surface reactions
15. The diffusion flux through the growing layer that plays an important role in oxidation kinetics **doesn't** exist because the reactions occur on top of the surface

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16. Fig.5 shows the fluxes that contribute the film growth.
17. The flux of reactant species from the gas phase to the wafer surface is given by

$$F_1 = h_G(C_g - C_s) \quad (2)$$

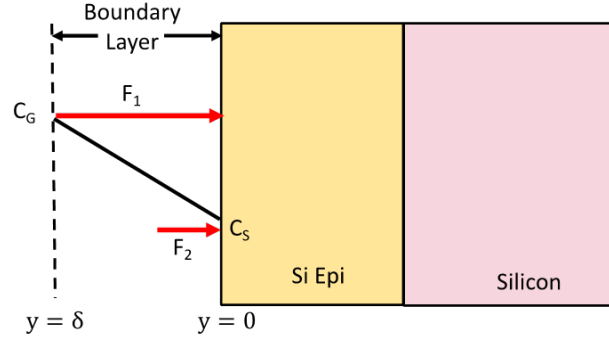


Figure 5: Types of flux in CVD processes

18. The $(C_g - C_s)$ (*molecules cm⁻³*) is the concentration of the reactant species at the boundary layer between the freely flowing gas region and the substrate surface
19. The concentration gradient acts as the driving force to move reactants to the surface with h_G (*cm sec⁻¹*) being the mass transfer coefficient.
20. Assuming first order kinetics, the flux consumed by the reaction at the surface is given by

$$F_2 = K_s C_s \quad (3)$$

21. C_s (*molecules cm⁻³*) is the concentration at the surface and K_s (*cm sec⁻¹*) is the concentration of the reacting species.
22. At the steady state, the concentration at the surface is given by

$$C_s = C_G \left(1 + \frac{K_s}{h_G} \right)^{-1} \quad (4)$$

23. The growth rate of the film is given by

$$\nu = \frac{F}{N} = \frac{K_s h_G}{K_s + h_G} \frac{C_G}{N} \quad (5)$$

24. ν is the growth rate of the film and N is the number of molecules/atoms incorporated per unit volume in the film
25. The concentration of the reactant molecules is typically a small fraction of the total gas flow, as usually a carrier gas is used to move the reactant gas along the reactor while minimizing the amount of more expensive reactant gas required for growth.
26. The growth can be written as
27. The growth rate of the film is given by

$$\nu = \frac{F}{N} = \frac{K_s h_G}{K_s + h_G} \frac{C_T Y}{N} \quad (6)$$

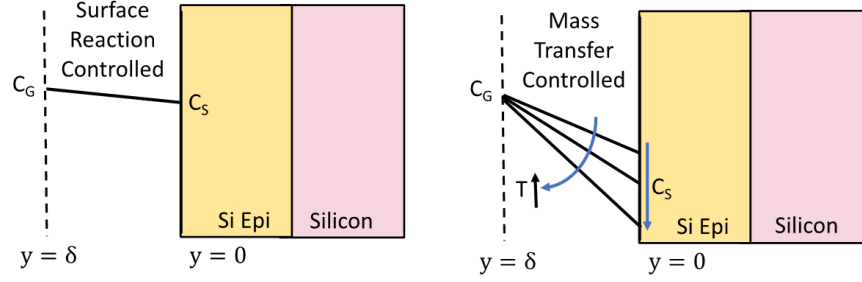


Figure 6: Limiting cases in the growth rates

28. $Y = \frac{C_G}{C_T}$ is the mole fraction of the reactant gas
29. The two limiting cases are indicated in Fig.6

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30. If $K_s \ll h_G$, the reaction regime is known as surface reaction-controlled regime. The mass transfer is relatively fast, while the slower surface reaction determines the deposition rate which is given by

$$\nu \approx K_s \frac{C_T Y}{N} \quad (7)$$

31. If $h_G \ll K_s$, the reaction regime is known as mass transfer-controlled regime. The mass transfer is relatively slow, while the faster surface reaction determines the deposition rate which is given by

$$\nu \approx h_G \frac{C_T Y}{N} \quad (8)$$

32. The growth rate is constant in both regimes. There is no explicit time dependency

33. Fundamentally, this is because the gas-phase diffusion process here corresponds to mass transport across a boundary layer of constant thickness.

34. the mass transport coefficient can be written as

$$h_G = \frac{D_G}{\delta} \quad (9)$$

where D_G is the gas phase diffusion coefficient of the reacting species across a boundary layer of constant thickness δ

35. Even though there is a diffusion term, the transport coefficient h_G is relatively independent of temperature because gas-phase diffusion has a much lower temperature dependence than solid-phase diffusion.
36. While the growth velocities in both regimes are constant with time, there is a very strong difference in the temperature dependence of the growth kinetics in these two different regimes.

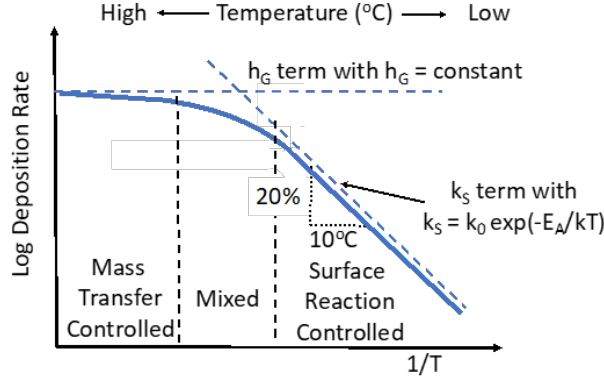


Figure 7: The two limiting regimes

37. The temperature dependence comes about because the surface reactions are exponentially activated with temperature, as shown in Fig.7

38. The surface reactions are exponentially activated, so that k_s is given by

$$k_s = k_0 \exp\left(-\frac{E_A}{kT}\right) \quad (10)$$

39. In the temperature regime, a small change in temperature causes a large change in the deposition rate.

40. While these films are being deposited, they can also be doped in situ. The common dopant source gases are arsine (AsH_3), phosphine (PH_3), and diborane (B_2H_6).

41. Since the silicon density is $5 \times 10^{22} \text{ cm}^{-3}$ and the doping density might be on the order of $10^{15} - 10^{20} \text{ cm}^{-3}$ for lightly and highly doped silicon, the amount of dopant source gas is a small fraction of the silicon-containing gas.

42. It can be more problematic to grow a lightly doped epilayer on a heavily doped substrate.

43. The lightly doped layer tends to get extra doping from two sources.

- The first is simple solid-state diffusion from the doped substrate that is well modeled by complementary error function diffusion into an infinite medium, given by

$$C(x, t) = \frac{C}{2} \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (11)$$

- Here, $x \approx 0$ is at the substrate epitaxial interface. The assumption of infinite medium is valid because the growth velocity is much faster than the diffusion from the substrate (i.e $vt \gg \sqrt{Dt}$)
- The second source of doping is caused by dopant atoms from the front side, backside or side of the wafer evaporating into the gas phase and redepositing on the growing film. Empirically this follows an exponential decay and is modeled by

$$C(x) = C^*_s \exp\left(-\frac{x}{L}\right) \quad (12)$$

- where C_s^* is an effective surface concentration and L is an experimentally determined decay length. A schematic of this "autodoping" is shown in Fig.9

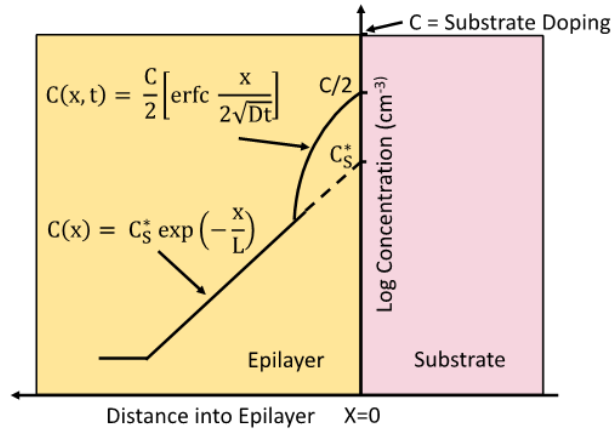


Figure 8: The two limiting regimes

- - Some of these anomalous effects can be countered by growing the epitaxial layer faster than the diffusion processes take place. Thus, silane (SiH_4) growth at high temperatures can minimize these effects.
44. Fig.?? shows the growth rate in different silicon-containing gases with silane growth in the mass-flow-limited regime being the fastest.

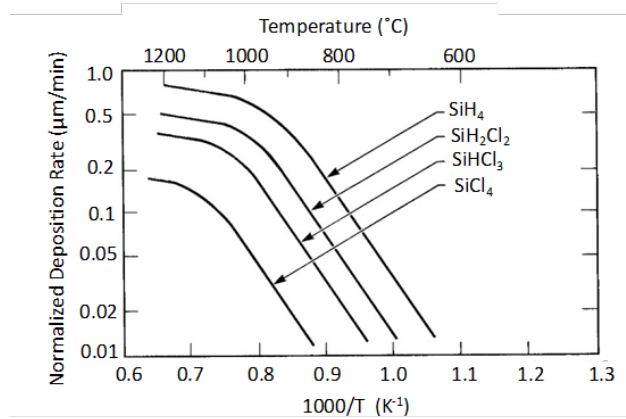


Figure 9: Growth Rates of Silicon

45. Silane is a very dangerous, explosive gas because of its instability. Silane is more reactive than the other Si-containing gases so one would expect the growth rate to be higher.
46. The chlorosilanes tend to deposit selectively on silicon rather than on exposed oxides, so growing strained SiGe source/drain regions with Si- and Ge-doped chlorosilanes would form selectively deposited regions in the exposed source/drain region and not on the oxide isolation structures. The chlorine helps remove any silicon that nucleates on the insulation regions.

47. The chlorosilanes are also less likely to decompose in the gas phase, preventing random particulate deposition.
48. There is however a problem with epitaxial growth in the mass-flow-dominated regime. The uniformity of growth is very sensitive to the gas flow and concentration. Thus, methods to uniformly distribute the gas using showerhead gas distribution systems in single-wafer systems are used.

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2.1 Heteroepitaxy

1. When different materials are epitaxially grown on top of one another, the term heteroepitaxy is used.
2. Fig.10 shows a range of semiconductors with their band gap and lattice constant.

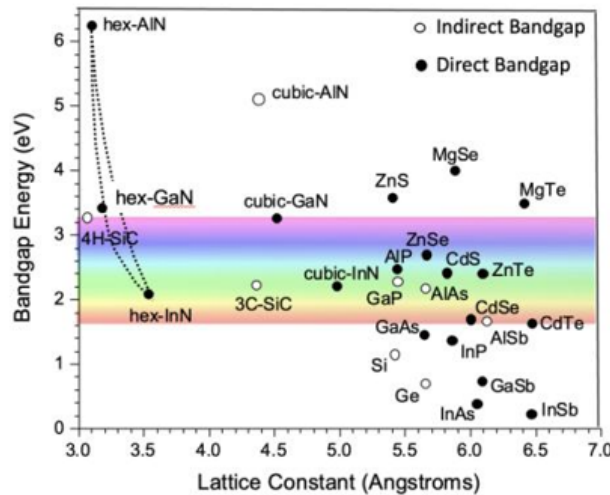


Figure 10: Lattice Constants

3. Materials with the same lattice constant can be easily grown using lattice-matched unstrained heteroepitaxy without creating defects, such as the GaAs/AlAs materials. This allows the bandgap of AlGaAs alloys to be tuned in these direct-bandgap materials.
4. Materials with different lattice constants can also be grown using strained heteroepitaxy, such as the SiGe layers indicated in the yellow region.
5. Strained SiGe heteroepitaxy was used to improve device mobility in PMOS channels starting with the 90 nm node. Lattice matching of Ge on Si is shown in Fig.11
6. Compressive strain in a recessed source/drain is introduced by growing SiGe epitaxy on the Si substrate, enabling increased channel mobility in PMOS devices.

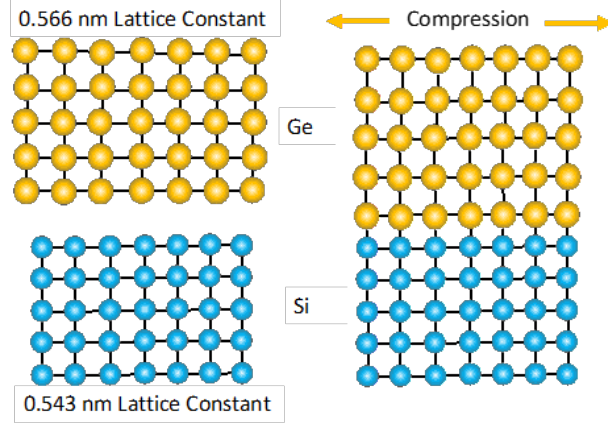


Figure 11: SiGe lattice

7. The Ge or SiGe grown epitaxial film is forced to adopt the smaller silicon lattice spacing because the thin film is grown on a much thicker substrate. This causes the SiGe regions to push laterally on the PMOS channel region.
8. There are limits on the Ge concentration and the thickness of the SiGe layers that can be grown. Beyond a certain threshold or critical thickness, dislocations form in the grown layers as shown in Fig.12.

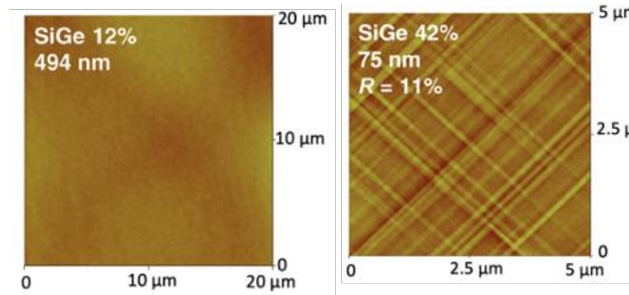


Figure 12: Dislocation formation at high concentration of Ge

9. To grow GaN on Si, a series of barrier layers and buffer layers are required, illustrated in Fig.13. The barrier layer is needed to prevent Si interdiffusion into the GaN layer and the buffer layer is required to reduce the dislocation density caused by the severe lattice mismatch. Several anneals of the buffer layer to cause purposeful relaxation of the strain may be required, along with optimized grading of the buffer layer before a high-quality GaN layer can be grown.

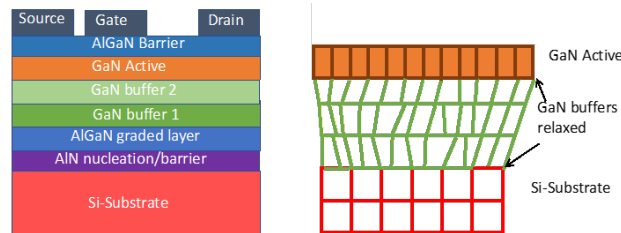


Figure 13: Buffer layers growth for lattice matching

10. GaN layers can only be grown with high quality on (111) Si, whereas most CMOS circuitry is grown on (100) wafers.
11. GaN has a hexagonal crystal structure while silicon is a cubic crystal. Growing such radically different crystals by heteroepitaxy is only possible because the surface of the silicon (111) crystal has a hexagonal atomic layout that forms a useable seed for the GaN crystal.

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3 Low Pressure Chemical Vapor Deposition (LPCVD)

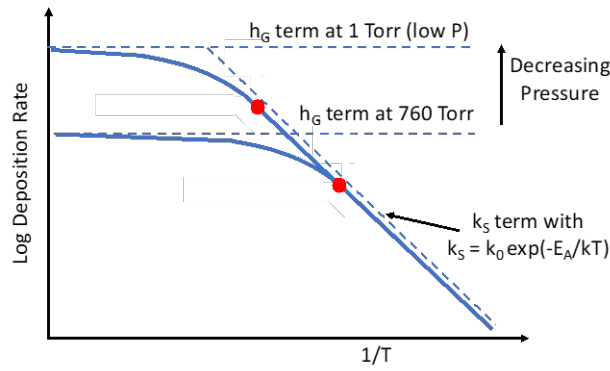


Figure 14: LPCVD

1. Growth in the mass-transfer-controlled regime provides the fastest growth rates at higher temperatures compared to growth in the surface-reaction-limited regime. But it is much more difficult to control gas flows and achieve uniformity and reproducibility than it is to control temperature accurately.
2. Growth in the surface-limited regime offers the prospect of uniform, controllable growth rates.
3. Growth rates decrease exponentially in the surface-dominated regime.
4. In the mass-flow-dominated regime, the growth velocity is

$$V \cong h_g \frac{C_T}{N} Y \quad (13)$$

$$h_g = \frac{D_G}{\delta} \quad (14)$$

5. The key point is that reducing the pressure increases the mean-free path of the reactants, so the diffusivity D_G of the reactants increases.

6. D_G is inversely proportional to the pressure

$$D_G = \frac{1}{P_{total}} \quad (15)$$

7. Decreasing the total pressure P_{total} from 760 torr(1atm) to 1 torr, a typical LPCVD pressure, increases D_G by 760 times.
8. Decreasing P_{total} also increases the boundary layer thickness δ but only by a factor of 3 to 10 times.
9. The net effect is that the mass transport increases by about 100 times.
10. Since h_G is much larger at lower pressures, the deposition velocity is not limited by the mass transfer of reactants through the boundary layer and the diffusion-limited growth curve shifts up as shown in figure.
11. This means that higher growth rates can be achieved at lower pressures, increasing the throughput of the deposition process.
12. The two red dots in Fig.14 show possible operating points at atmospheric pressure (lower dot) and at 1 Torr (upper dot).
13. Because the deposition rate is no longer sensitive to the gas flows, the wafers can be stacked close together and processed in parallel with no loss of uniformity as shown in Fig.15.

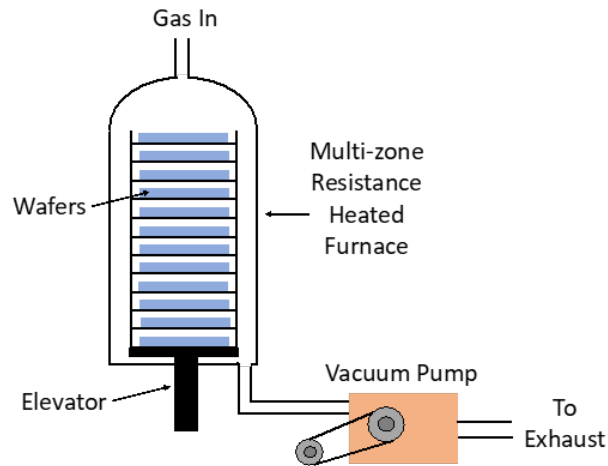


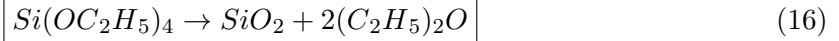
Figure 15: LPCVD

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4 Metal Organic Chemical Vapor Deposition

1. Low temperature deposition techniques are sought after as they allow depositions on temperature-sensitive materials while not affecting any prior steps, such as doping profiles.

- Efforts were put in to develop more thermally unstable gas precursors that decomposed at lower temperatures and allowed deposition of the desired materials.
- Replacing the silanes or chlorosilanes with more unstable organic-silicon gases such tetraethyl ortho-silicate (TEOS) allowed lower-temperature deposition of silicon dioxide via the reaction



- Note that ethanol is C_2H_5OH , so the tetra refers to the 4 ethanol-like organic groups that attach to the si, decomposing to give silicon dioxide and a diethyl ether volatile byproduct.
- MOCVD is chemical vapor deposition method with different precursors, but its key advantage is that it enables a low-temperature deposition reaction and the enormous diversity of the precursors provides a method for depositing stacks of many different semiconductor compounds. Typical precursors are shown in Fig.16

Metal	+	Organic	→	Metal-Organic Precursor
Common Metals		Common Organics		Common MOCVD Precursors
Gallium				Tri or Tetra methyl = TM
Aluminum				Triethyl= TE
Indium				Triisopropyl = TiP
Arsenic		Methyl		Dimethyl = DM
Antimony				Diethyl = DE
Zinc				Trimethylgallium (TMGa)
Cadium				Triethylgallium (TEGa)
Telluride		Ethyl		Triisopropylgallium (TiPGa)
Germanium				Trimethylaluminum (TMAI)
				Trimethylindium (TMIn)
				Triethylindium (TEIn)
				Trimethylarsenic (TMAs)
				Trimethylantimony (TMSb)
		Isopropyl		Dimethylzinc (DMZn)
				Diethylzinc (DEZn)
				Dimethylcadmium (DMCd)
				Dimethyltellurium (DMTe)
				Diethyltellurium (DETe)
				Tetramethylgermanium (TMGe)

Figure 16: MOCVD Precursors

- The low-temperature reactions allow abrupt interfaces to be formed between different layers.

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- The technique is flexible enough to grow essentially all the III-V and II-VI alloys, including ternary and quaternary compounds. It can grow multilayer heterostructures and superlattices with abrupt interfaces.

8. It is simple to synthesize organic precursors like trimethylgallium $\text{Ga}(\text{CH}_3)_3$ and these precursors can be designed to pyrolyze (decompose due to heat) at low temperatures. This allows reaction to occur between the group III organometallics and the group V hydrides as shown in Fig.17 to deposit compound semiconductors such as

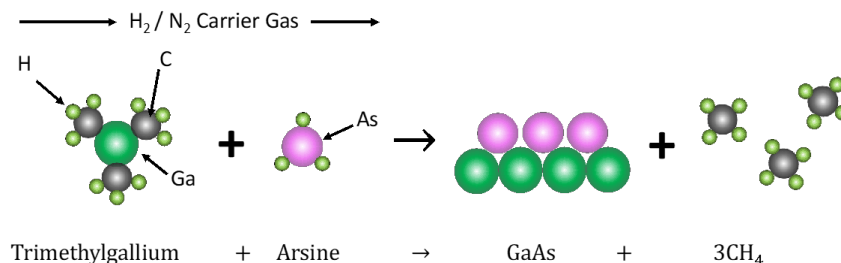
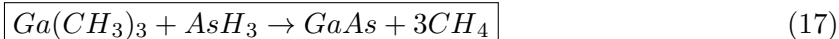


Figure 17: MOCVD Deposition of GaAs

9. This reaction can be generalized for the III-V compounds to a simplified reaction



10. Where M is the group III element, such as Al, Ga, or In; V is the group V element, such as Sb, P or As; and O_P is an organic precursor subunit, such as CH_3 or C_2H_5 .
11. The formation of the semiconductor is basically an acid-base reaction. The group III metal alkyls are strong acids and the group V hydrides are strong bases, making the formation of the binary semiconductor favorable. The reaction is sometimes referred to as a Lewis acid-base reaction, indicating that there is a transfer of two electrons during the product formation.
12. To produce a metal-organic precursor such as trimethylgallium requires some elementary chemistry. Gallium can be purified by reacting with chlorine, producing gallium trichloride. Standard "methylating agents", like methyl magnesium iodide, are routine chemical reagents that result from the ready insertion of active magnesium or lithium metals into carbon-halogen bonds like methyl iodide. The resultant "organometallic" species will transfer the methyl group to metals that are more noble in the metallic form (as gallium is relative to magnesium). In other words, the formation of trimethylgallium from standard methyl lithium or methyl magnesium halide precursors is thermodynamically favored.
13. MOCVD Precursor
- must be volatile, so that it can be transported from a heated bubbler by a carrier gas such as H_2 or N_2 to the heated susceptor where pyrolysis or catalytic decomposition can occur
 - must be sufficiently stable during transport in the gas phase so that it does not decompose, and it should not react with the other precursors until it encounters the heated substrate.

- There rapid pyrolysis should occur for both components and the semiconductor layer can be formed.
- 14.
 15. When the organic radical is small, such as trimethyl $(\text{CH}_3)_3$, it becomes more stable and the temperature of decomposition is high. When the organic radical is big, such as triethyl $(\text{C}_2\text{H}_5)_3$, the temperature of decomposition is low and in this case the growth temperature will be low but there is the possibility of unwanted parasitic reactions in the gas phase. The strength of the metal-organic (M-O) bond is a measure of the stability of the organic precursor.
 16. For many compounds based on Ga, In, As, Al and P, the growth rates under As-rich conditions have been shown to be linearly dependent on the partial pressure of the metal-alkyl species, so that it is limited by the arrival rate of the column III organometallics, indicating a first- order reaction. The growth rate is relatively independent of temperature over a wide range 500°C to 800°C). The purity of the III-V films does improve monotonically with lower temperatures due to decreased carbon and silicon incorporation in the layers.
 17. Empirically, MOCVD growth is largely mass-transport limited such that the epilayer growth rate is mostly, controlled by diffusion of the Group III precursor through a boundary layer of thickness δ .
 18. the growth is in the mass transfer limited regime, where the mass transfer coefficient $h_g = D_G/\delta$ dominates, and D_G has a relatively weak temperature dependence. Control of growth rate and the achievement of uniform film growth depends on achieving a uniform metal alkyl flux over the substrate, illustrating the importance of careful hydrodynamic design.
 19. The gas distribution and hydrodynamics in the reactor have a major effect on the epilayer thickness, uniformity and the abruptness of the layer growth.
 20. The reactor schematic in Fig.19 shows cold wall reactor with inductive heating of the substrate with a uniform boundary layer.
 21. To prevent premature decomposition of the precursors, the susceptor and substrate must be the hottest part of the growth chamber so that the gas precursors are cracked near the substrate and the epitaxial film can be grown.

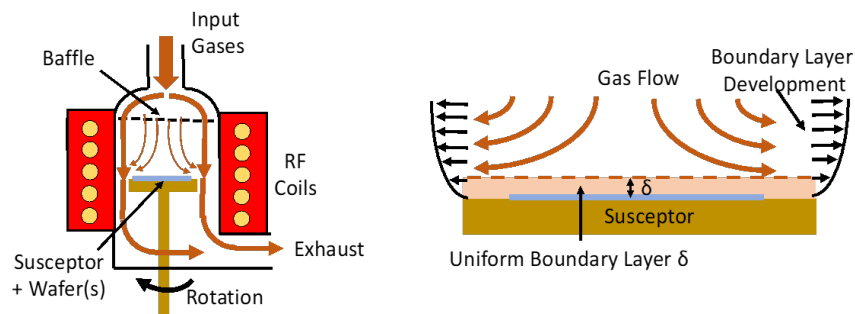


Figure 18: MOCVD Set up

5 Plasma Enhanced Chemical Vapor Deposition

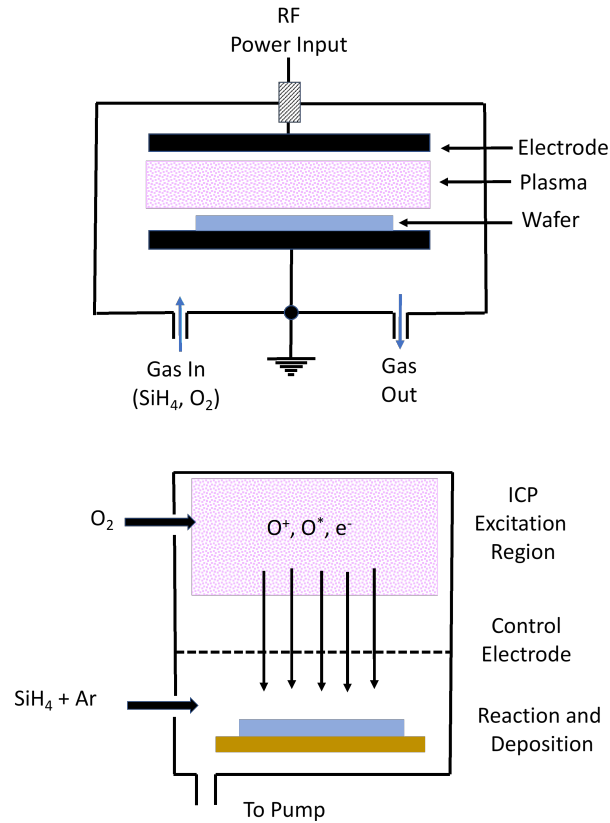


Figure 19: PECVD

1. PECVD systems are often parallel-plate plasma systems where the main purpose of the plasma is to break apart the source gases and enhance the deposition rates, as illustrated in Fig.?? and with the plasma physics described in detail in references figures.
2. The plasma provides a very strong source of radicals so the deposition rate becomes mass- 34 transport-dominated and shows very little temperature dependence.
3. The plasma is composed of ions, electrons and excited neutral species (radicals) in a weakly ionized gas.
4. A large range of films can be deposited (oxides, nitrides, silicon, metals) and the deposited films are usually non-stoichiometric.
5. For example plasma deposited silicon dioxide is not SiO_2 , but instead SiO_x where $x < 2$.
6. Ions, electrons and radicals are generated in the plasma and just as in etch plasmas the radicals are the dominant excited species. A simple example shows the energy needed to create a silane radical versus an ionized silane molecule:



$$\boxed{SiH_4 + e^- \rightarrow SiH_4^+ + 2e^- (\Delta E \sim 12.2eV)} \quad (20)$$

showing that it is much easier to create a cal than an ionized species.

7. It is the combination of radical reactions on the surface along with ion bombardment that determines the film deposition rate and quality.
8. At too high pressures, the neutrals decrease the ability of the electrons to gain sufficient energy because there are too many collisions. At too low pressures, the electrons do not collide with enough other molecules to sustain the plasma and create species for the reaction. Thus, the pressure range for PECVD is limited to approximately 50 mTorr to 1 Torr, while HD-PECVD can use lower pressures in the main chamber (≈ 5 mTorr) to create longer mean free paths with fewer collisions, giving a more directional ion flux onto the wafers.