Epitaxy
Epitaxial Growth

• Epitaxy means the growth of a single crystal film on top of a crystalline substrate.

• For most thin film applications (hard and soft coatings, optical coatings, protective coatings) it is of little importance.

• However, for semiconductor thin film technology it is crucial.
Types of Epitaxy

• Homoepitaxy
  – The film and the substrate are the same material.
  – Often used in Si on Si growth.
  – Epitaxially grown layers are purer than the substrate and can be doped independently of it.

• Heteroepitaxy
  – Film and substrate are different materials.
  – Eg: AlAs on GaAs growth
  – Allows for optoelectronic structures and band gap engineered devices.
Heteroepitaxy

• Trying to grow a layer of a different material on top of a substrate leads to unmatched lattice parameters.

• This will cause strained or relaxed growth and can lead to interfacial defects.

• Such deviations from normal would lead to changes in the electronic, optic, thermal and mechanical properties of the films.
Lattice Strains

- For many applications nearly **matched** lattices are desired to minimize defects and increase electron mobility.

- As the mismatch gets larger, the film material may **strain** to accommodate the lattice structure of the substrate. This is the case during the early stages of film formation (pseudomorphic growth) and with materials of the same lattice structure. The Si-Ge system is an example.

- If strain accommodation is not possible then dislocation defects at the interface may form leading to **relaxed** epitaxy and the film returns to its original lattice structure above the interface.

- **Lattice misfit** is defined as:

\[
\tilde{\varepsilon} = \frac{a_0(s) - a_0(f)}{a_0(f)}
\]

where \(a_0(s/f)\) are the lattice constants of the substrate and the film.
Metal-Semiconductor Heteroepitaxy

- Metal-semiconductor structures are used for contact applications.
- While not essential, epitaxial growth allows increased electron mobility through a junction.
- Examples:
  - CoSi$_2$ or NiSi$_2$ on Si. Since the lattice mismatch is small (all around 5.4 Å) and the crystal structures are similar, interfaces are remarkably defect free.
  - Fe on GaAs is similarly possible since the lattice size of Fe is about half of GaAs.
  - The lattice constants of Al and Ag are $\sim1/\sqrt{2}$ of GaAs. In this case the crystal orientation of the film is rotated with respect to the substrate. A few layers of intervening metal (such as Fe or Ga) can be deposited to foster epitaxy.
Tilted Layer Epitaxy

- It is possible to have a misorientation between the crystal plane of the film and the substrate.
- As a result the surface breaks up in to an array of terraces of variable length and height.
- Then the film growth occurs by step advancement along the terraces (step - flow process).

Epitaxial Tilting of GaN Grown on Vicinal Surfaces of Sapphire (Huang, et.al.)
Lattice Misfits and Defects

- If the lattice mismatch is less than ~9%, the initial layers of film will grow pseudomorphically.
- Therefore very thin films strain elastically to have the same inter-atomic spacing as the substrate.
- As film thickness increases, the rising strain will eventually cause a series of misfit dislocations separated by regions of relatively good fit. As such they are equilibrium theories.
- There is a critical film thickness, $d_c$, beyond which dislocations are introduced.
- In most cases pseudomorphic growth occurs until $f d_c = b/2$, where $b$ is the size of the film unit cell.
Defects $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$ Films

- The GeSi/Si system has a large lattice misfit built in and as such is not an equilibrium system.
- This results in a large number of dislocations with few regions of good fit and the theory breaks down.
- Rippled surfaces and pyramidal tips are typical.
Types and Sources of Defects

- Defects reduce electron mobility, carrier concentration and optical efficiency.
- Current levels in Si are 1-10 defects/cm².
- Defects can propagate from the substrate as a screw dislocations.
- Dopants and impurities can cause edge and point dislocations.
- Another type of defect is the stacking faults where the stacking order of successive layers do not follow a specific order.
Formation of Misfit Dislocations

• They generally originate from threading dislocations at the film-substrate interface.
• The dislocation pierces through the substrate and the film.
• As it grows, it glides and bends in a slip plane.
• Above the critical thickness \( (d_c) \) the increasing strain allows a break and the film dislocation separates from the originating defect, leaving behind a stable misfit dislocation.
Epitaxy of Compound Semiconductors

• Most compound semiconductors are from the III-V group of materials (GaAs, InP, etc.) although II-VI materials are also used (ZnO, CdSe, CdS).

• Stochiometric adjustments allow control of the band structures and lattice constants.

• This affects both the electrical, thermal and optical properties and the epitaxial nature of the film.
Optical Properties of Compound Semiconductor

• Optical emission from semiconductors requires energy and momentum conservation. While the energy of the emitted photon can come from an excited electron returning to its ground state, such a transition may require extra momentum which the photon cannot supply (photons have minimal momentum).

• Materials that require extra momentum are called indirect semiconductors. Silicon and Germanium are examples (which is why we do not have Si lasers).

• In contrast direct gap semiconductors do not require a momentum change and can emit a photon efficiently. GaAs, ZnO, GaN and many of their alloys are in this class and are used in LEDs and semiconductor lasers.
Other Properties of Compound Semiconductors

- For direct gap semiconductors, the band gap energy determines the wavelength (color) of the light that will be emitted. Various III-V alloys are used to cover most areas from the UV (GaN) to the NIR (GaAs) to the IR (InSb).

- The various alloys also offer a spectrum of lattice constants for lattice matching. GaAs and AlAs interfaces have minimal misfit and negligible dislocations.

- Thermal expansion coefficients are also comparable.
Devices and Applications

- **Optoelectronic Devices**
  - Using the direct gap nature for efficient light emission and the stochiometric flexibility for epitaxial purity, most lasers are made with compound semiconductors.

- **High Speed Electronic Devices**
  - The higher electron mobilities of compound semiconductors allow for operation in the microwave range (1 – 1000 GHz).
  - The heterojunction nature also increases the gain and efficiency of amplifiers made from these devices.
GaIN Light Emitting Devices

- While materials with wide band gaps exist (AlN, GaN, ZnO) it has been difficult to get commercial blue/violet laser sources.
- Main difficulties lie in p-doping these materials and the high density of defects at the heterojunctions. Lack of suitable lattice matched substrates contribute to this problem.
- Current technology uses GaN for this region of the spectrum.
- p-doping was achieved using Mg. Also interface defects were reduced with a buffer layer over the sapphire substrate.
Liquid Phase Epitaxy (LPE)

- LPE involves the precipitation of a crystalline film from a supersaturated melt on to a substrate.
- The temperature is increased until a phase transition occurs and then reduced for precipitation.
- By controlling cooling rates the kinetics of layer growth can be controlled.
- Once can have either continuous reduction with the substrate (equilibrium cooling) or separate reduction in increments followed by contact with the substrate (step cooling).
- It is a low cost method yielding films of controlled composition, thickness and lower dislocation densities.
- Disadvantages are rough surfaces and poor thickness uniformity.
CVD Epitaxy (MOCVD)

- The CVD process is carried out at a pressure around 0.5 – 760 torr and at temperatures hundreds of degrees lower than the substrate melt temperature.
- The precursors are metalorganic. The reactions can produce high quality epitaxial layers of III-V semiconductors with very good thickness control allowing quantum well structures to be manufactured.
- Examples:
  - TMGa + AsH$_3$ at 650 – 750 °C for GaAs.
  - TMGa + NH$_3$ at 800 °C for GaN.
  - TEIn + PH$_3$ at 725 °C for InP.
Molecular Beam Epitaxy (MBE)

- The environment is highly controlled ($P \sim 10^{-10}$ torr).
- One or more evaporated beams of atoms react with the substrate to yield a film.
- For epitaxial growth the surface diffusion-incorporation time has to be less than one layer’s deposition time. This limits the technique to being a low temperature one.
- Semiconductor and dopant sources are arrayed around the substrate. Each source and the substrate can be individually heated. Shutters control exposure to each species.
- The sources can be solid source (for arsenide compounds) or gas source (for phosphorus compounds).
MBE vs. MOCVD

- Both techniques can produce highly epitaxial films with excellent abruptness, allowing thin layers to be formed.
- The UHV of MBE allows for better in situ diagnostic techniques to be employed.
- Substrate temperatures are lower in MBE.
- MBE is relatively safer.
- MOCVD has a higher growth rate and less downtime.
- It also has no issues regarding phosphor deposition.
Silicon Heteroepitaxy

While Si is not the ideal material from an electronic and optical point of view, its abundance, ease of processing and availability of a good native oxide have made it the backbone of semiconductor industry.

Combining Si substrates with compound semiconductor films would enable higher optoelectronic functionality and higher speeds.

However, there are severe lattice mismatch and chemical compatibility issues between Si and most III-V alloys that preclude direct growth.

Wafer Bonding
  - The III-V epi-layer is grown on a lattice matched substrate and bonded to a Si wafer by heat and pressure. The lattice matched substrate is then removed by etching leaving the Si/III-V structure behind.