Lecture 1

Introduction to Electronic Materials

Reading:

Pierret 1.1, 1.2, 1.4, 2.1-2.6
The goal of this course is to teach the fundamentals of non-linear circuit elements including diodes, and transistors (BJT and FET), how they are used in circuits and real world applications.

The course takes an “atoms to op-amps” approach in which you learn about the fundamentals of electron movement in semiconductor materials and develop this basic knowledge into how we can construct devices from these materials that can control the flow of electrons in useful ways.

We then extend this knowledge to how these devices can be used to form circuits that perform useful functions on electrical signals.
... Atoms to Everything Else in Optoelectronics

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Modern amplifiers consist of extremely small devices.

Transistors in the above image are only a few microns (µm or 1e-6 meters) on a side. Modern devices have lateral dimensions that are only fractions of a micron (~0.1 µm) and vertical dimensions that may be only a few atoms tall.
Control of Conductivity is the Key to Modern Electronic Devices

- Conductivity, \( \sigma \), is the ease with which a given material conducts electricity.

- Ohms Law: \( V = IR \) or \( J = \sigma E \) where \( J \) is current density and \( E \) is electric field.

  - Metals: High conductivity
  - Insulators: Low Conductivity
  - Semiconductors: Conductivity can be varied by several orders of magnitude.

- It is the ability to control conductivity that make semiconductors useful as “current/voltage control elements”. “Current/Voltage control” is the key to switches (digital logic including microprocessors etc…), amplifiers, LEDs, LASERs, photodetectors, etc…
Atoms contain various “orbitals”, “levels” or “shells” of electrons labeled as n=1, 2, 3, 4, etc… or K, L, M, or N etc… The individual allowed electrons “states” are simply allowed positions (energy and space) within each orbital/level/shell for which an electron can occupy.

- Electrons fill up the levels (fill in the individual states in the levels) from the smallest n shell to the largest occupying “states” (available orbitals) until that orbital is completely filled then going on to the next higher orbital.
- The outer most orbital/level/shell is called the “Valence orbital”. This valence orbital is the only one that participated in the bonding of atoms together to form solids.

Example: Silicon n=1 (2 s), n=2 (2 s and 6 p) and n=3 (2 s and 2 p with 4 unoccupied p states)
• Solids are formed by several methods, including (but not limited to) sharing electrons (covalent bonds) or by columbic attraction of ions (fully ionic) or partial ionic attraction / partial sharing of electrons (partially ionic).
• The method for which the semiconductor forms, particularly whether or not a fixed static di-pole is constructed inside the crystal, effects the way the semiconductor interacts with light.
• Later we will see that covalent bonds tend toward “indirect bandgap” (defined later) materials whereas polar bonds (ionic and partially ionic) tend toward “direct bandgap” materials.

Classifications of Electronic Materials

Materials free from built in static dipoles result from covalent bonds

Materials with built in static dipoles result from partially or fully ionic (polar) bonds
Only the outermost core levels participate in bonding. We call these “Valance orbits” or “Valence Shells”.

For metals, the electrons can jump from the valence orbits (outermost core energy levels of the atom) to any position within the crystal (free to move throughout the crystal) with no “extra energy needed to be supplied”. Thus, “free conducting electrons are prevalent at room temperature.

For insulators, it is VERY DIFFICULT for the electrons to jump from the valence orbits and requires a huge amount of energy to “free the electron” from the atomic core. Thus, few conducting electrons exist.

For semiconductors, the electrons can jump from the valence orbits but does require a small amount of energy to “free the electron” from the atomic core, thus making it a “SEMI-conductor”.

Classifications of Electronic Materials

Valence Electrons can gain energy (thermal, electrical, magnetic or optical energy) and break away from the crystal.

New “Hole” created (empty valence state) that can also move.

Conduction Electrons (free to move throughout the crystal)
Classifications of Electronic Materials

• Since the electrons in the valance orbitals of a solid can have a range of energies and since the free conducting electrons can have a range of energies, semiconductor materials are a sub-class of materials distinguished by the existence of a range of disallowed energies between the energies of the valence electrons (outermost core electrons) and the energies of electrons free to move throughout the material.

• The energy difference (energy gap or bandgap) between the states in which the electron is bound to the atom and when it is free to conduct throughout the crystal is related to the bonding strength of the material, it’s density, the degree of ionicity of the bond, and the chemistry related to the valence of bonding.

• High bond strength materials (diamond, SiC, AlN, GaN etc...) tend to have large energy bandgaps.

• Lower bond strength materials (Si, Ge, InSb, etc...) tend to have smaller energy bandgaps.
Why do the electrons flow when light is present but not flow when light is not present?

Answer, Energy Bandgap (very important concept).
• More formally, the energy gap is derived from the Pauli exclusion principle, where no two electrons occupying the same space, can have the same energy. Thus, as atoms are brought closer towards one another and begin to bond together, their energy levels must split into bands of discrete levels so closely spaced in energy, they can be considered a continuum of allowed energy.

• Strongly bonded materials tend to have small interatomic distances between atoms. Thus, the strongly bonded materials can have larger energy bandgaps than do weakly bonded materials.

• One question that repeatedly comes up: Why does the bandgap form instead of just s and p orbital mixing? While complex beyond this explanation, the answer is in the way the s and p orbitals “hybridize” (mix). As the mixing becomes “severe”, they must separate more fully, leaving a range of energies where no electron can exist – the energy bandgap.
Material Classifications based on Bonding Method

Bonds can be classified as metallic, Ionic, Covalent, and van der Waals.

**Ionic Bonding:** One atom acquires and holds the electron(s) of an adjacent atom. Bonding is coulombic and strong.

**Covalent Bonding:** Atoms share electrons with the surrounding atoms. Bonding is moderately weak.

**Metallic Bonding:** Atoms give up electrons to the surrounding regions, forming an “electron cloud”. Bonding is coulombic but weak due to screening of charge.

**Van der Waals Bonding:** Neutrally charged molecules form dipoles which are attracted to other dipoles. Bonding is extremely weak, but long chains can form.
Consider the case of the group 4 elements, all covalently bonded

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Radius/Lattice Constant</th>
<th>Bandgap</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.91/3.56 Angstroms</td>
<td>5.47 eV</td>
</tr>
<tr>
<td>Si</td>
<td>1.46/5.43 Angstroms</td>
<td>1.12 eV</td>
</tr>
<tr>
<td>Ge</td>
<td>1.52/5.65 Angstroms</td>
<td>0.66 eV</td>
</tr>
<tr>
<td>α-Sn</td>
<td>1.72/6.49 Angstroms</td>
<td>~0.08 eV*</td>
</tr>
<tr>
<td>Pb</td>
<td>1.81/** Angstroms</td>
<td>Metal</td>
</tr>
</tbody>
</table>

*Only has a measurable bandgap near 0K

**Different bonding/Crystal Structure due to unfilled higher orbital states
Classifications of Electronic Materials

Types of Semiconductors:
• Elemental: Silicon or Germanium (Si or Ge)
• Compound: Gallium Arsenide (GaAs), Indium Phosphide (InP), Silicon Carbide (SiC), CdS and many others

Note that the sum of the valence adds to 8, a complete outer shell. I.E. 4+4, 3+5.
Compound Semiconductors: Offer high performance (optical characteristics, higher frequency, higher power) than elemental semiconductors and greater device design flexibility due to mixing of materials.

Binary: GaAs, SiC, etc...

Ternary: Al$_x$Ga$_{1-x}$As, In$_x$Ga$_{1-x}$N where $0<=x<=1$

Quaternary: In$_x$Ga$_{1-x}$As$_y$P$_{1-y}$ where $0<=x<=1$ and $0<=y<=1$

Half the total number of atoms must come from group III (Column III) and the other half the atoms must come from group V (Column V) (or more precisely, IV/IV , III/V, or II/VI combinations) leading to the above “reduced semiconductor notation that emphasizes the equal numbers of anion (higher valence electron group) and cations (lower valence electron group) in the compound.

Example: Assume a compound semiconductor has 25% “atomic” concentrations of Ga, 25% “atomic” In and 50% “atomic” of N. The chemical formula would be:

$$\text{Ga}_{0.25}\text{In}_{0.25}\text{N}_{0.5}$$

But the correct reduced semiconductor formula would be:

$$\text{Ga}_{0.5}\text{In}_{0.5}\text{N}$$
Material Classifications based on Crystal Structure

**Amorphous Materials**
No discernible long range atomic order (no detectable crystal structure). Examples are silicon dioxide (SiO₂), amorphous-Si, silicon nitride (Si₃N₄), and others. Though usually thought of as less perfect than crystalline materials, this class of materials is extremely useful.

**Polycrystalline Materials**
Material consisting of several “domains” of crystalline material. Each domain can be oriented differently than other domains. However, within a single domain, the material is crystalline. The size of the domains may range from cubic nanometers to several cubic centimeters. Many semiconductors are polycrystalline as are most metals.

**Crystalline Materials**
Crystalline materials are characterized by an atomic symmetry that repeats spatially. The shape of the unit cell depends on the bonding of the material. The most common unit cell structures are diamond, zincblende (a derivative of the diamond structure), hexagonal, and rock salt (simple cubic).
Crystalline Order

Water Molecules, H₂O, forming “Snowflakes”

Atoms forming a “Semiconductor”

Need two volunteers... (demo on how a crystal forms naturally due to repulsive electronic bonds)
Crystal Growth: How do we get “Single Crystalline Material”? 

The vast majority of crystalline silicon produced is grown by the Czochralski growth method. In this method, a single crystal seed wafer is brought into contact with a liquid Silicon charge held in a crucible (typically SiO$_2$ but may have a lining of silicon-nitride or other material). The seed is pulled out of the melt, allowing Si to solidify. The solidified material bonds to the seed crystal in the same atomic pattern as the seed crystal.
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*.
How do we create Bandgap Engineered Structures? Epitaxy
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MBE

Partially disassembled MBE system for clarity

RHEED Gun

Effusion Furnaces

Gas Source (oxygen)

Shutter mechanism
Commercial Veeco® MBE
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.

**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). “Luckily”, such poisoning is rare as the pyrophoric (flammable in air) nature of most metal organic means the “victim” is burned severely before he/she can be contaminated.
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.
So much for the introduction. Now on to the meat of the course.