What is Materials Science and Engineering (MSE)?

• In general, MSE bridges disciplines of applied physics, chemistry, biology, and engineering. The science of materials helps you to understand the fundamental structure-property relations in materials, while the engineering of materials enables you to learn how to process materials and determine the properties of the finished product.

• Materials Scientists and Engineers are specialists who are totally involved in the investigation and design of materials.
The study of MSE is about interrelationships:

- **Structure**
- **Properties**
- **Performance**
- **Processing**

- There are many facets of **structure** and purpose of this course is to put them into perspective.
- Fundamental building blocks of materials are **atoms** and the chemical interactions, resulting in the formation of **bonds** that derive from the **electronic structure** of atoms, which play a critical role in determining the **structure** and **properties** of materials.
- This tendency of atoms to bond to one another gives rise to the condensed phases of matter – liquids, crystals, glasses, etc.
- Materials with the same chemical composition but different **structures** often have different **properties**, for example of Al₂O₃ (on left).
- Thus, we need to understand not only what materials are made of, but also how their constituents (atoms, ions or molecules) are arranged and their microstructure, in order to understand the properties of materials.
Types of Materials

- **Metals**: Metallic bonding $\rightarrow$ non-directional sharing of electrons giving structures of very high coordination and high density.
  - Composed of one or more (alloys) metallic elements (e.g. Ti, Al, Ni, Cr) and often also nonmetallic elements (e.g. C, N, O) in small amounts.
  - In general, have high strength, ductility (capable of large amounts of deformation without fracture), and fracture toughness.
  - In general, high thermal & electrical conductivity (conduction by electron transport), opaque, reflective.

- **Ceramics**: Mixed Ionic bonding (most) $\rightarrow$ non-directional transfer of electrons giving structures of high coordination and Covalent bonding (some) $\rightarrow$ directional sharing of electrons giving structures of low coordination and low density.
  - Compounds of metallic & non-metallic elements (oxides, carbides, nitrides, chlorides, ...)
  - Strong, elastic/stiff, hard yet they are often brittle (lack ductility), glassy.
  - Non-conducting (insulators) with very high heat resistance (refractory).

- **Intermetallics**: Mixed metallic and ionic/covalent bonding
  - Compounds of metallic & metalloid elements (e.g., silicides like MoSi$_2$)
  - Compromise between ceramic and metallic properties: brittle and high melting, but have some toughness due to metallicity.
Types of Materials (continued)

• **Polymers/plastics:** Covalent bonding in the chain and secondary bonding (e.g., VDW) between the chains
  – Organic compounds based on carbon, hydrogen and other non-metallic elements (e.g. O, N and Si). Very large molecular structures.
  – Soft, ductile (easily formed into complex shapes), low strength, low density
  – non-conducting (insulators) with low heat resistance

• **Electronic materials (semiconductors):** Mixed Ionic (some) and Covalent bonding (most)
  – Conductivity between metals and ceramics/polymers.

• Composites
Course Objectives

You will learn about:

- **Structure** of materials at different size/length scales:
  1. Electronic structure
  2. Atomic structure
  3. Crystal structure (crystallography)
  4. Nano/Micro structure
  5. Macrostructure

- How these structures may dictate material properties

This course will help you to:

- Classify/characterize different material structures and use materials properly
- Realize new design opportunities with materials

*MAKE SURE YOU KNOW CHAPTERS 2 (ATOMIC STRUCTURE & BONDING) AND 3 (CRYSTAL STRUCTURE) IN INTRODUCTION TO MATERIALS SCIENCE AND ENGINEERING BOOK, *e.g.* CALLISTER.

*YOU SHOULD HAVE TAKEN AN INTRODUCTION TO MATERIALS SCI/ENG COURSE, *e.g.*, MTSE 3000 or ENGR 3450
What does Structure of Materials Mean?

• The structure of materials concerns the quantitative description of the arrangements of the components that make up the material on all relevant length scales.

• The atoms in a material can be bound to one another in a great variety of ways, and often knowledge of some details about the arrangements in a small grouping of just a few atoms can provide useful structural descriptors.
  • A descriptor provides a precise quantitative characterization of some aspect of structure.

• For such a group we will use generic term, polyatomic ensemble, which can take many forms:

• To characterize impurities/defects in material, since real materials rarely have homogeneous/perfect structures, it is useful to know their average concentration and average relative separation distance (averaging over small volumes) rather than to know the precise location of each impurity.
  • Compositional inhomogeneities may be deliberately introduced to provide a particular functionality of the material…
<table>
<thead>
<tr>
<th>Structural feature</th>
<th>Dimension (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>atomic bonding</td>
<td>$&lt; 10^{-10}$</td>
</tr>
<tr>
<td>missing/extra atoms</td>
<td>$10^{-10}$</td>
</tr>
<tr>
<td>crystals (ordered atoms)</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>second phase particles</td>
<td>$10^{-8}$</td>
</tr>
<tr>
<td>crystal texturing</td>
<td>$&gt; 10^{-6}$</td>
</tr>
</tbody>
</table>

Structure has many dimensions.
Different Approaches

Science-driven approach

Design-driven approach

From Professor Michael Ashby, University of Cambridge, UK.
If a material is **crystalline**, descriptors based on theory of **crystallography** can be used to quantify the crystal structure, i.e. kind of average, ideal reference state combined with number, type and distribution of imperfections.

These structural features of the average environment around each atom are quantifiable and constitute **long-range order (LRO)**, which is the **major structural descriptor** for specifying the structure of crystalline materials.
Non-Crystalline Structural Descriptors

- If a material is non-crystalline, there is no ideal reference state for comparison with the real structure, thus more difficult to quantify.

- A portion of a 2-D continuous random network structure of a compound with formula $A_2B_3$:

![Fig. A 2-D continuous random network structure in a stoichiometric $A_2B_3$ compound.](image)

- This structure is non-crystalline because it lacks spatial periodicity.
- However, the structure is not completely random, since each $A$ atom is bonded to three $B$ atoms and each $B$ atom is bonded to two $A$ atoms. Also, there is a characteristic distance between $A$-$B$ separation (bond length) and the angles formed by the $A$-$B$-$A$ and $B$-$A$-$B$ bonds fall within a narrow range.

- These structural features of the average environment around each atom are quantifiable and constitute short-range order (SRO), which is the major descriptor for specifying the structure of non-crystalline (amorphous) materials, such as glass.
Example of LRO and SRO

Porous SiO$_2$-FeC film (amorphous) on single crystal Si wafer

Transmission electron microscope (TEM) image
Materials are not always perfectly ordered arrays of atom or ions

Polycrystalline ZnO thin film

Planar stacking faults (2-D area defect) “denoted by arrows” \(\rightarrow\) missing or extra row of ions in the lattice.

- An interfacial defect that exists within above ZnO hexagonal closed packed (HCP) stacking sequence \(\rightarrow\) disruption in lattice.
Materials are not always perfectly ordered arrays of atom or ions.

Polycrystalline ZnO thin film

Edge dislocations (1-D line defect) “denoted by arrow”

Burgers vector

Edge dislocation line
• The physical and chemical properties of materials are strongly influenced by the interatomic bonds and thus by the outermost valence electrons.

• Elusive goal of structural chemistry is the determination of a material’s structure from knowledge of its constituents’ chemical bonding.

• The primary reason for a general lack of a predictive theory of structure is that the bonding between atoms is extremely variable:
  • Many examples in terms of structural state and bonding, e.g., TiCl$_2$ (s) and TiCl$_4$ (l)…..

• Thus, you must be careful in assigning a particular type of bonding to given atom/ion pairs and the inadequacy in using stoichiometric formulas to predict material structures.
Ground State Electron Configurations of the Elements

Hybridization in carbon:

- **ns**
- **s**
- **p**
- **sp**

Hybridization is change from atomic orbitals to form new bonding orbitals (or hybrid orbitals).

- The driving force for the formation of hybrid orbitals is a lower energy state for the valence e-'s.

- Hybridization in carbon:
  - ns
  - np

4f
5f
S and P Orbitals

• A 1s orbital may be considered as a spherical distribution of negative charge (electron cloud), which becomes more diffuse as the distance from the nucleus increases.

• 2s orbitals are similar in shape, but the radius of the electron cloud is larger.

• \(ns^2\) configuration if electrons completely fill the \(s\) orbital.

• \(p\)-orbitals consist of electron clouds with a node at the nucleus of the atom.

• There are three such orbitals, oriented at right angles to one another:

\(np^6\) configuration if electrons completely fill the \(p\) orbital.
Hybridization in Covalent Structures

• Hybridization is the change from atomic orbitals to form new bonding orbitals (hybrid orbitals).
• The driving force for the formation of hybrid orbitals is a lower energy state for the valence e–’s
• **Covalently bonded structures:**
  • sharing of electrons by overlapping orbitals.
  • highly **directional**: when a bond is formed, electron density is increased along a line connecting the two bonding atoms.
  • formed from atoms that have both $s$ and $p$ valence electrons available (elements on right hand side of periodic table with relatively high electronegativities).
  • the formation of $sp$ hybrid orbitals results in 4 equivalent $sp^3$ orbitals with same energy directed towards the vertices of a tetrahedron (occurs in **group 4** atoms such as C (diamond), Si, and Ge as well as SiC), the geometry of these orbitals leads to the 4-fold coordination of covalent structures.

*Shaded circles represent neighboring atom positions.*
Diamond Cubic Crystal Structure

Examples:
C (diamond), Si, & Ge [tetrahedrally coordinated structure]
The formation of pseudo-tetrahedral arrangements are found even when there are fewer than 4 nearest neighbors. In these cases the lone (non-bonding) pair of electrons complete the tetrahedron.

For example hybridization in group 5 (P, As, Sb) and group 6 (S, Se, Te) atoms leads to 4 $sp^3$ orbitals that have a tetrahedral arrangement, even though some of the ligands are non-bonding lone pairs.

- Shaded circles represent neighboring atom positions.
- Dots represent electrons in lone pair orbitals.

Phosphorous:

Sulfur: