

# INTRODUCTION TO ELECTRONIC MATERIALS SCIENCE

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## 1.1 INTRODUCTION

Materials science can be thought of as a combination of the sciences of chemistry and physics within a backdrop of engineering. Chemistry helps to define the synthetic pathways, and provides the chemical makeup of a material, as well as its molecular structure. Physics provides an understanding of the ordering (or lack thereof) of atoms and molecules and electronic structure, and physics also provides the basic principles that enable a description of materials properties. The combined information provided by physics and chemistry about a material leads to the determination and correlation of materials properties with the process used to prepare the material, and with the materials structure and morphology. The properties once determined and understood are exploited through judicious engineering. In a sense engineering brings focus to the properties that materials possess, and to the material itself if suitable applications are found. Evidence for the leadership of engineering is witnessed by the many national goals that pervade the national research funding agencies such as nanotechnology, biotechnology, and microelectronics. In each of these fields the advantages of certain materials properties are extolled. The goals in every case include the preparation of new materials with enhanced properties for particular engineering objectives.

Materials science as we know it today finds its origins in traditional metallurgy and metallurgical engineering departments. Consequently many university materials science curricula and textbooks in use in these curricula are heavily weighted toward traditional topics related to metallurgy. More modern areas are relegated toward special topics courses and textbooks covering selected areas. This text is aimed toward electronic materials science where the engineering objective is better materials for microelectronics and photonics.

While there has been growing interest and understanding in electronic materials for centuries, there was a major revolution in electronics that began in the late 1940s with the invention of the transistor by Bardeen, Brattain, and Shockley. This invention irreversibly changed the entire electronics arena. Essentially before this time all active electronic circuits components were made of closely spaced similar metal elements (electron-emitting filaments, grids, electrodes) contained within a glass vacuum envelope, so-called vacuum tubes. These devices could switch currents, provide amplification and rectification, and along with passive components enable the construction of radios, televisions, and even analog and digital computers. About the early electronic devices based on vacuum tubes, it is amusing to recall that these early electronic marvels were all larger than today's versions. None were larger than the early (1960s) analog and digital computers that used vacuum tubes, and that filled large rooms and even entire buildings, but had less computing power than the laptop with which this text is written. Then, after the invention of the transistor, it was more than 10 years before the ideas about the solid state devices could be truly felt with the implementation of reliable discrete transistors replacing vacuum tubes on the electronics market, and in all kinds of consumer devices. During this period of incubation from invention to widespread applications, there were somewhat dormant areas of science and engineering that became very active and made major advances that were spurred on by the potential markets for the new solid state devices. First it was realized that single crystals of semiconductor electronic materials had to be made in large quantities rather than in laboratory sizes and with crystalline perfection and chemical purity never before imagined in manufacturing. Then the notion of electronic band structure that derived from the earliest days of quantum mechanics had to be modernized and understood for the new solid state electronic materials. From the new results of electronic energy band structure, doping could be understood, and the role of crystallographic defects became central to electronics materials. Lattice diffusion of dopants into crystals developed greatly in this era. It was also realized that the new class of electronic devices would require the joining of different solid state materials such as metals with semiconductors with insulators in every permutation. Thus there was renewed interest in phase equilibria, not only to understand the important metallurgical transformations that govern steel and other alloys but, with emphasis on alloys between electronically dissimilar materials and with homogeneity ranges, so as to understand atomic vacancies and correlate crystal lattice vacancies with resulting electronic properties. Along with all these advances in understanding and practice of the solid state since the invention of the transistor, another invention came to the fore that also revolutionized the way we live. This invention is the integrated circuit (IC). The integrated circuit enables the configuring of solid state electronic materials in order to fabricate devices such as transistors and rectifiers on the surface of semiconductors, and to link them all together to make a complete electronic system or subsystem to be further linked. The IC has paved the way for all the modern electronic devices especially the digital devices that perform logic and memory. In addition to enabling the efficient manufacture of multiple solid state devices, the IC paved the way for another major revolution, namely nanotechnology or nanoscience. The very heart of the IC, as it is implemented with planar technology, enables the downward size scaling to present device dimensions in the nanoscale range. The areas of electronic materials science and microelectronics are clearly the forerunners of nanotechnology, and many of the techniques developed for ICs are fully integrated into modern nanotechnology. Thus the areas of electronics materials/microelectronics and nanotechnology are intimately related in that it is clear that microelectronics is the predecessor of nanotechnology, and that advances in nanotech-

nology will undoubtedly impact microelectronics. As microelectronics took hold of all the devices we use, the area of optical devices or photonics also developed using the solid state ideas about materials as well as the ability to integrate optical and electronic devices on a chip.

The study of electronic materials science must then include the factors that enable a material to be prepared and understood, and its properties determined and optimized for defined applications, in particular, electronics and/or photonics applications. These typical factors selected for study comprise the names of Chapters 2 through 11: Structure, Diffraction, Defects, Phase Equilibria, Diffusion, Mechanical Properties (two chapters), Electronic Structure, Electronic Properties, and Devices. Many of these topics and chapters have the same names one finds in traditional materials science texts, and that is no accident. It is clear that a foundation in traditional materials science is implicit in electronics materials science. The difference is in emphasis, since as a practical matter one text or one course cannot do it all. In the following paragraphs the reasons are discussed why these headings are chosen for a study of electronics materials science, and the emphasis is explained.

## 1.2 STRUCTURE AND DIFFRACTION

Materials science is often described as being comprised of structure-property relationships. In this context structure refers not only to the arrangement of the basic building blocks, or long-range ordering but also to the chemical structure or short-range ordering. This more complete notion of ordering is discussed early in Chapter 2 of this text with the appropriate nomenclature, and this theme is revisited many times throughout the book. Different structures can represent both different chemical bonding and different arrangements of atoms and/or molecules, and possibly even different states of aggregation (roughness, large grained, etc.). All these structural aspects can lead to different properties, including electronic and optical properties. It is important to use a consistent nomenclature to identify the unique structural features so that materials scientists communicate in a standard language. These topics are discussed in Chapter 2 on the structure of solids.

In Chapter 3 on diffraction we study the determination of crystal structure. The basic idea that underlies this important family of techniques, diffraction techniques, is the principle of superposition. It will be seen in the text that much of the fundamentals of materials science can be understood by referring to a few the basic tenets of chemistry and physics. Among the tenets that are continually revisited is the superposition principle that is used for diffraction, mechanical properties, and electronic structure (with the first review of this tenet in Chapter 3 and again more thoroughly in Chapter 9). For example, the nature of a wave function that is used to describe an electron can be understood by considering the wave function to be made up of many waves in a complex blend, namely the notion of modulation.

Later in Chapter 3 the concept of reciprocal space is introduced. The idea follows from the notion that it is important in science to operate in the coordinate space most appropriate to the system. It is found that for crystal structure obtained by diffraction, reciprocal distances correlate the structure with diffraction experiments.

From a study of structure and diffraction one may glean the erroneous idea that only, or at least mostly, crystalline materials are important in materials science and electronic materials science. This is far from the truth, but it is a natural tendency that follows from

paying close and early attention to only perfect crystals. In fact a large fraction of useful materials in all fields are not crystalline at all (e.g., the dielectrics used in microelectronic ICs), and another large fraction is partially crystalline (alloys used for contacts in microelectronics) or at least defective in their crystalline nature. However, the nonperfectly crystalline materials are more difficult to describe universally and simply. That is to say, each material must be described using a number of structural aspects where crystallinity may be one of the important aspects. However, as is usual in science, the ideal state is the easiest to describe thoroughly, and this is the reason why virtually all studies of materials science commence with a discussion of ideal or perfect crystals.

Also electronic structure that is discussed in Chapter 9 on electronic structure is important for determining many properties particularly electrical properties. It will be seen in Chapter 9 that the structure of the material will greatly influence the electronic structure and in turn the electronic and optical properties.

### 1.3 DEFECTS

To dispel the misleading attention to perfect crystals, in Chapter 4 on defects in solids we look at different kinds of defects. The definitions for several of the more common material defects are discussed. It has been found over and over that simple structural defects such as substitutional and interstitial defects can alter electrical properties and mass transport via diffusion by orders of magnitude, while at the same time hardly affect the melting point or the thermal conductivity for a material. Furthermore line defects are implicated as the main factor in the plastic deformation of crystalline materials. The notion of grain boundaries as the boundaries in between single crystal grains is also implicated in the mechanical properties of materials and in electronic properties of polycrystalline semiconductors. Thus both the structure and its level of perfection provide a backdrop from which the behavior and properties of a material are understood, particularly, electronic materials.

Also in Chapter 4 another fundamental tenet of materials science is introduced and used liberally in following chapters. This tenet is the Boltzmann distribution from which both equilibrium thermodynamics and activation energies, or energy barriers, for processes can be understood. This concept is introduced by considering a simple two allowed state problem, and assessing how two energetically distinct states separated by a difference in energy,  $\Delta E$ , can be populated. The result is a familiar exponential term  $e^{-\Delta E/kT}$  often referred to as the Boltzmann factor. However, in the field of chemical kinetics an Arrhenius factor with the same form as the Boltzmann factor is often discussed in relation to the velocity of chemical reactions, but the Arrhenius factor is often introduced without adequate discussion about its origin, or at best as an empirical result. The importance of this idea is such that it is introduced and discussed early in the text. Furthermore the laws of thermodynamics derive from the average or statistical nature of atoms or compounds that comprise a material. This statistical notion is crucial toward the understanding the average properties of a macroscopic piece of a material that contains a large number of atoms and/or molecules. Such thermodynamics properties include the phase of the material, the vapor pressure, and decomposition temperature. On the other hand, quantum mechanics may be required to understand the properties that depend on the specific interactions of atoms and/or molecules within a material such as the absorption or emission of light and the electronic and thermal conductivity.

## 1.4 DIFFUSION

In virtually all solid state reactions and transformation, matter moves; that is, atoms and/or molecules are transported to and from the reaction site. Often in the solid state that motion is by a random process, and such random processes are termed diffusive processes. Early in Chapter 5 on diffusion in solids the form for a variety of diffusion equations are compared, and it is observed that seemingly unrelated phenomena are governed by equations with the same form, namely there is a flux in response to a force. That flux (with units of amount/area  $\cdot$  time) can be matter, heat, charge, energy, and so on. Even the famous Schroedinger equation of quantum mechanics (see Chapter 9) has the form of a diffusion equation. Although only mass diffusion is covered in Chapter 5, heat transport, for example, involves the solution of similar equations.

In the field of mass diffusion many treatments deal purely with the underlying physics that enable random matter transport, while other approaches deal exclusively with the mathematics of solving the differential diffusion equations. In Chapter 5 both areas are addressed. In addition another fundamental tenet in materials science is introduced, namely the random walk problem. While applied strictly to diffusion in this chapter, the random walk problem yields insight into how random processes can yield simple understandable results precisely because of the assumed randomness of the system. This is a powerful idea that helps hone the intuition of a materials scientist who must often deal with seemingly unsolvable problems involving randomness and complexity. In the field of electronic materials diffusion plays a central role that includes the transport of dopants, other point defects (vacancies and impurities, and electronic carrier diffusion in electronic and optical devices.

## 1.5 PHASE EQUILIBRIA

Traditional introductory materials science texts usually cover the topic of phase equilibria adequately for understanding electronic materials. The main reason is based on the fact that most introductory materials science texts emphasize metallurgical materials, namely metals and alloys, even though these texts have often been modernized with the addition of polymers and electronic materials. Metallurgy deals extensively with mixed composition alloys such as steel. An understanding of steel and other important alloys requires a detailed knowledge of the phase diagram for the system, in order to know under what conditions to expect certain alloy phases and the composition of the phases. However, oftentimes advanced physics and chemistry courses spend little time on this topic, and while some forms of phase equilibrium are covered in undergraduate chemistry courses, solid state phase diagrams are often barely mentioned. It is clear, however, that modern trends in materials science and electronic materials science include complex materials that can have several phases and wide homogeneity (stoichiometry) ranges. Included in the kinds of electronic and photonic materials in which phase equilibria are important are modern binary semiconductors that are used extensively for both electronic and optical devices, ceramic superconductors, alloy superconductors, magnetic alloys, high dielectric constant insulators, and polymer blends.

In Chapter 6 on phase equilibria we provide simple derivations of the Gibbs phase rule and the lever rule and outlines the procedure to estimate phase diagrams from known thermodynamic data. All materials scientists deal with the formation of phases from some primal state, and hence often the initial stage of phase formation, nucleation

becomes important in determining final product morphologies. For this reason nucleation is added in the chapter. An understanding of nucleation phenomena is also important to the understanding of the processes that are used to prepare the thin films used for most modern electronic and optical devices.

## 1.6 MECHANICAL PROPERTIES

In the first of the two chapters on mechanical properties the emphasis is the development of the basic ideas and the resulting relationships among the elastic constants. In Chapter 7 on the elasticity property of solids, these constants are used to describe the behavior of materials that deform elastically, which means that as forces are applied, the material deforms, but the material returns to its original state as the forces are removed. Most materials exhibit this behavior when small forces are applied for short periods of time. There is more interest when larger forces are applied that leave a material permanently deformed or even causes fracture of the material, since deformation and failure relate the usefulness of a material for fabricating products such as cars, bridges, and homes. However, as was the case for structure, first the simpler ideal case of elasticity is considered and then consideration is given to a more complicated behavior called plasticity. In Chapter 8 on the plasticity property of solids the underlying ideas are presented for permanent deformation or plasticity. The implication of dislocations for the plastic deformation of crystalline materials is discussed and creep is briefly discussed. In this chapter the deformation of noncrystalline materials such as polymers is discussed, and several models that are used to interpret the mechanical response of these kinds of materials are developed.

In microelectronics and photonics many of the devices are constructed by layering films of dissimilar materials. Therefore differences in thermal expansion as well as chemical incompatibilities at the interfaces can lead to performance and reliability issues for the devices. Furthermore many of the extreme structural features and extremely small sizes of features of the modern devices can exacerbate the mechanical issues that may exist for planar and larger devices. In addition the applications of forces on a crystal lattice can alter the atomic spacing and therefore affect the electronic nature, meaning the electronic energy band structure, of a material. A full analysis of these complicated structural and electronic issues is beyond the scope of this text, but a first-order treatment of the important relationships properties is essential so that advanced study and appreciation of the implications of mechanical properties can be accomplished.

Many modern microelectronics products such as computer chips are fabricated from thin films of dissimilar materials. Also, once the layered structures are formed, the products go through various temperature cycles as part of the further processing. These structures are prone to the development of stresses that can lead to device failure and to shorter useful lifetimes. Consequently the mechanical issues of thermal expansion, stresses, and defect formation that are crucial to further study of electronic material reliability are covered in these two chapters.

## 1.7 ELECTRONIC STRUCTURE

In Chapter 9 on electronic structure we consider another aspect of the structure of materials, namely the electronic structure. The basic ideas relating to electronic structure

include a consideration of the arrangement of atoms and molecules as was introduced in Chapters 2 and 3 plus the addition of a consideration of the interactions of the atoms or molecules in their various structural motifs. The interactions among atoms and molecules is handled using quantum mechanics. Quantum mechanics enables chemists to estimate, if not calculate, the structure of many important molecules using the Schrödinger equation. Similarly quantum mechanics enables the calculation of the allowed and disallowed energies for the electrons in an array of atoms or molecules in condensed phases, such as liquids or solids. The allowed energies are called energy bands, and the disallowed energies are called the forbidden energy gaps (FEG) or simply band gaps. An old (1931) but useful model for the calculation of electronic energy band structure for solids is presented, the Kronig-Penney (KP) model. Despite its simplicity the KP model contains many of the important physical ideas that are used in more modern models, but without difficult mathematics. Consequently the KP model is useful as a vehicle to understand the origin of allowed electronic energy bands and gaps, but the KP model does not enable quantitative estimations of energy bands. Nonetheless, many important conclusions can be made regarding the electronic structure of materials using the KP model. Associated with the energy band structure is an extensive nomenclature and representation language, and this language is introduced to describe electron energy band structure. In this chapter there is heavy reliance on the structural ideas and reciprocal space that were introduced in Chapters 2 and 3.

It is clear that fundamental to understanding electronic and optical properties of solids and the devices is the electronic energy band structure; thus Chapters 10 and 11 make heavy use of the ideas developed in this chapter. Furthermore modern ideas about nanotechnology that include quantum well structures, quantum dots, and other small intricate structures are understood in terms of the energy band structure and the comparisons that are made to larger devices.

## 1.8 ELECTRONIC PROPERTIES AND DEVICES

In Chapter 10 on electronic properties we make heavy use of the results from Chapter 9, in particular, the electronic energy band structure, and adds to this development the use of the statistics for electrons, namely Fermi statistics. An estimate is made about the number of electronic states for materials, the so-called density of states (DOS) is calculated. From the energy band structure, the density of states (DOS), and the probability for occupancy, the Fermi-Dirac distribution function, the electronic arrangement for solids is deduced. From this arrangement the electronic nature of the materials is revealed, and resulting properties are understood. The different kinds of electronic materials are also discussed: conductors, semiconductors, superconductors, and non-conductors. Electronic conduction is treated both classically and in terms of quantum mechanical ideas. For superconduction the popular BCS theory is introduced. Lastly in Chapter 10 the electronic nature of organic materials is introduced, and since many of the organic materials in use are amorphous, the electronic nature of amorphous materials is discussed. In the final chapter, Chapter 11 on junctions, devices, and the nanoscale, we reach a point where we can distill the ideas developed in Chapters 9 and 10 that are fundamental to designing and understanding electronic and optical devices. Virtually all modern electronic and optical devices use the junctions of materials. Thus in Chapter 11 we commence with junctions and the electronics implications of joining dissimilar materials. From junctions, passive devices that do not change flowing currents or applied

potentials can be constructed such as thermocouples and solid state refrigerators. Then, using various junctions, this chapter introduces electronic devices that are important in today's microelectronic technology such as diodes, solar cells, transistors, and the devices that comprise computer chips. The basic ideas about optical devices are introduced with examples. The last section deals with nanotechnology and the kinds of devices that will emerge from ongoing research in fabricating nanoscale structures from materials.

## 1.9 ELECTRONIC MATERIALS SCIENCE

Modern science and technology requires highly trained materials scientists who can function in diverse areas such as metallurgy, biology, ceramics, electronics, and optics, to name several fields. It is clear that there are many commonalities in the fields. For example, for all solid state materials, structure with all its implications is important. For biology, molecular structure is more important than is electronic energy band structure at this juncture in development. That is not to say that with the development of biomaterials and nanotechnology the future will bring bio-inspired electronic and optical devices. For many fields structural defects are important as are mechanical properties. For the fields of electronics and optics, electronic structure and properties are fundamental to understand the resulting devices. However, defects and mechanical interactions are also crucial. Thus topics in this text were chosen more as a matter of practicality, in that to adequately cover all areas of importance to electronic materials would result in an impractically large text. Careful choices had to be made in selecting the most germane material for electronic materials science.