### Mat E 272

### Lecture 25: Electrical properties of materials December 6, 2001

### **Introduction:**

Calcium and copper are both metals; Ca has a valence of +2 (2 electrons per atom) while Cu has a valence of +1 (1 electron per atom). Simply on the basis of numbers of charge carriers per unit volume, we might expect Ca to be a better conductor of electricity. However, this is not the case. Why then is Cu, with half as many valence electrons per atom, a far better electrical conductor than Ca? We will see that the answer lies in the nature of the electronic energy levels (or bands) that form when individual atoms coalesce into a solid. This energy band structure approach also describes the electrical behavior of semiconductors, one of the most technologically significant materials in the last 50 years. We begin with a review of some of the fundamental concepts such as Ohm's law and the nature of energy bands in solids. We will also see how solid solution alloying in metals can have a major impact on the motion of conduction electrons in the resulting alloy, in much the same way as solid solution strengthening affects dislocation motion.

# Introduction

### **Electrical conductivity:**

Did you know that electrical conductivity spans a greater range of values than any other material property? From insulators such as talc and sulfur on one extreme to highly conducting metals such as silver and copper and at the other extreme, this property spans over 20 orders of magnitude!!!

Why is the propagation of electrical current so easy in some materials while almost non-existent in others?



# Definitions

**Electrical conductivity:** 

"a quantitative measure of the ease with which electrical current is propagated in a material in response to an external electric field"

Suppose we place a material in an electric field, of magnitude E. In response to the applied field, charge carriers in the material will drift, or diffuse, down the field gradient.

Empirically, we find that for any given material, the ratio of current density to applied field at constant temperature is a constant, called the electrical conductivity,  $\sigma$  (sigma)

 $\sigma$  is a fundamental material property and varies with temperature

The reciprocal of  $\sigma$  is called the electrical resistivity, and is abbreviated as  $\rho$  (rho)

### **Macroscopic conductivity - Ohm's law**

**Ohm's law:** 

The relationship between applied electric field and current density is more commonly known as Ohm's law:

 $\mathbf{J} = \mathbf{\sigma}\mathbf{E} = \mathbf{\sigma}(\mathbf{d}\mathbf{V}/\mathbf{d}\mathbf{x})$ 

although you may be more familiar with another form of Ohm's law: I = (1/R)V

where "I" is the electrical current, "V" is the voltage drop, and R is the electrical *resistance* (not resistivity in this equation).

Current density can also be written as J = nev, where n is the density of current carriers, v is their drift velocity, and e is the charge of an electron, or  $1.6x10^{-19}$  coulomb.

Units of conductivity are (Ohm-m)<sup>-1</sup>, although (mOhm-m)<sup>-1</sup>, and (mOhm-cm)<sup>-1</sup> are also frequently used. "Ohm" is given a special symbol:  $\Omega$  (Omega)

### **Macroscopic conductivity - Ohm's law**

### **Ohm's law:**

What is the relationship between conductivity,  $\sigma$ , (or resistivity,  $\rho$ ) and resistance, R?

**Resistance depends on the geometry of a material and is NOT a fundamental material property.** 

Conductivity (or resistivity) does NOT depend on the size or shape of a material and IS a fundamental material property.



### **Energy bands:**

In order to understand how materials carry electrical current, we must look first at the allowed energy states for electrons, and how these allowed states are formed. We will use a metal to illustrate the point, but the basic argument applies equally well to any material.

Recall that an <u>isolated</u> atom is characterized by a set of discrete energy shells, or orbitals, within which the electrons are constrained.



As shown at right, there are actually three states corresponding to the 2p subshell.



### **Energy bands:**

When individual atoms come together to form a solid, these energy states split into discrete levels\*, in accordance with the Pauli exclusion principle. If not for the splitting, there would be too many electrons trying to occupy too few energy levels. The splitting and coalescence of energy states is a consequence of the interaction between each atom's wavefunction.

Notice how the discrete energy shells each split into bands. This example corresponds to a hypothetical situation in which 12 atoms coalesce, hence 12 bands for each quantum state.

Imagine if we had 10<sup>23</sup> atoms coming together, the number of bands would be immense and the energy spacing between them would be exceedingly small (*but not continuous*).



Interatomic separation



**Electrons cannot occupy energy levels within the gaps** 

### **Energy bands - metals:**

When energy bands are formed in solids, different arrangements are possible, depending on the initial distribution of electrons within the quantum states of the individual atoms. For example, the 4s subshell in copper is only half full, since it contains 1 valence electron. Thus, there are empty states within this level. In contrast, magnesium contains 2 electrons in its 3s subshell (which is thus filled), but when the individual Mg atoms form a solid, the s and p bands <u>overlap</u>, producing available energy states near the top-most filled band.



### **Energy bands - semiconductors and insulators:**

Notice in particular the two cases shown on the right.

For these materials, there is a <u>forbidden gap</u> between the occupied valence bands and the unoccupied conduction bands. (Conduction bands run throughout the metal and account for electrical conductivity, whereas valence bands correspond to localized electrons).

Such materials are called either semiconductors or insulators, depending on the magnitude of the forbidden energy gap.



Energy (thermal or optical) is required to excite a valence electron across the gap into the conduction band.

# Fermi level

### "Way cool"...

Suppose we cool a material down to 0K (absolute zero). The electrons will fill up energy levels, starting with the lowest (1s), (consistent with the Pauli exclusion principle), until all electrons are accounted for. In this *ground state configuration*, we can identify a highest filled level (and a lowest unoccupied level). The energy level corresponding to the highest occupied level (at 0K) is given a special name; it is called the Fermi energy.

The *Fermi energy* is just a fancy way of identifying the separation, or boundary, between <u>occupied</u> energy levels and <u>unoccupied</u> energy levels. The position of the Fermi energy is important, because it determines whether there are any nearby unoccupied conduction states for electrons to drift from atom to atom. If there are no available conduction states, then no matter how many electrons there are, conduction cannot take place and the electrons are localized.

(Think about a classroom in which every seat is occupied; there may be a lot of students present, but none of them can move because there are no available seats.)

### Fermi level - in a bit more detail

### **Electronic conduction:**

Core electrons (those in low-lying energy states) find it difficult to participate in conduction because in order to move freely through the metal, they would have to push past all the other electrons lying in higher energy states. It would require a lot of energy for this to happen; consequently, core electrons remain localized.

However, for those electrons near the top-most filled levels, only a little bit of energy is needed to "push" them into unoccupied states, <u>if there are available</u> <u>states nearby</u> (in terms of energy). We refer to the density of states (DOS) as the number of available energy states per unit volume.

If the DOS near the top-most filled energy level is high, then there are plenty of places for electrons to become de-localized (or free) and drift throughout the material. However, if the DOS near the top-most filled band is low (or zero), then there are few available states and the electrons remain bound to their respective atoms.

## **Conduction states**

### **Electronic conduction:**

The top figure illustrates what happens when an electron occupying a state near the Fermi energy in a <u>metal</u> receives sufficient thermal energy to be excited into a higher energy state (e.g., in the conduction band). This electron now contributes to the bulk electrical current.

The lower figure depicts the situation in <u>semiconductors</u> and <u>insulators</u>, where there is an *energy gap* between the valence and conduction bands. Much more energy must be imparted to the electron in order for it to overcome the barrier.



# Metal systems

# **Electrical conductivity of metals and alloys:**



Metal	Electrical Conductivity $[(\Omega - m)^{-1}]$	
Silver	$6.8 \times 10^{7}$	
Copper	$6.0 \times 10^{7}$	
Gold	$4.3 \times 10^{7}$	
Aluminum	$3.8 \times 10^{7}$	
Iron	$1.0 \times 10^{7}$	
Brass (70 Cu-30 Zn)	$1.6 \times 10^{7}$	
Platinum	$0.94 \times 10^{7}$	
Plain carbon steel	$0.6 \times 10^{7}$	
Stainless steel	$0.2 \times 10^7$	

Note how the resistivity increases (or how the conductivity decreases) with increasing solute concentration. This is because the solute atoms act as scattering sites, disrupting the otherwise regular periodicity of the lattice.

### From electrons and holes to cell phones and PDAs

Semiconductors form the backbone of our technological society

all microchip processors are based on applications of Si, Ge, and other IIIA-VA and IIB-VIA compounds. In addition, many devices used as sensors are also based on these materials.

What gives semiconductors their unique electrical behavior is the extreme sensitivity (exponential dependence) to the presence of minute quantities of solute, which we refer to as dopants.

The next slide shows an example of how much the resistivity of Si changes upon addition of boron. Make note of the solute concentration; we're talking 13 parts per million (ppm) of boron; this is a fantastically small amount of additive, yet, it is enough to make the resistivity increase by over 4 orders of magnitude!



### The answer lies in the nature of the electronic structure of semiconductors

Let's look at silicon as an example:



Each Si atom has 4 valence electrons which are covalently bonded to its nearest neighbors.

When a phosphorus atom is substituted, since is has 5 valence electrons, all of the covalent bonds are satisfied and there is one electron left over. This extra electron is loosely bound; we say that the P doping introduces *impurity states* within the band gap, so it takes much less energy (on the order of a few meV, or 0.01 eV) for this extra electron to be promoted into the conduction band than for the other bound electrons.

Since the additional electron is loosely bound to its parent atom, only a minute amount of energy is needed to excite it into the conduction band (~ 0.01 eV). There, it can respond to an applied electric field and drift through the crystal.

The loosely bound electron forms a donor state, and may reside only a few meV below the conduction band edge:





Similar behavior is obtained by doping with an element containing *fewer* valence electrons than the solvent, or host material. Such is the case with boron doping in silicon.

The B atom produces an electron *deficiency* and results in formation of an impurity state within the band gap, close to the valence band. Thermal excitation of an electron from the valence band into this acceptor state forms a defect in the valence band, known as a hole. The hole is the active charge carrier and moves in opposite sense as an electron in the conduction band.



### **Temperature effects:**

What happens as a semiconductor is heated up? As more and more electrons acquire sufficient energy to overcome the band gap, the semiconductor becomes a better conductor of electricity. *This is one key distinction between semiconductors and metals; as metals heat up, their electrical conductivity decreases.* 

The conductivity of a semiconductor is described by an Arrhenius equation of the form

$$\sigma = C e^{-\frac{L_g}{2kT}}$$

where E<sub>g</sub> is the magnitude of the band gap, k is Boltzman's constant, and T is the absolute temperature.



### **Example problem**

Problem: If the room temperature (298K) conductivity of <u>intrinsic</u> silicon is 0.0009 (Ohm-m)<sup>-1</sup>, estimate its conductivity at 150°C (= 423K).

Solution: If we know  $\sigma$  at one temperature, we can use this information to find the value of the constant, C, in the Arrhenius equation for conductivity,  $\sigma = Ce^{-\frac{E_g}{2kT}}$ 

Then, we simply substitute this value back into the equation for the desired temperature :

Starting with the given room temperature data:

$$C = \ln\sigma + \frac{E_g}{2kT} = \ln(0.0009) + \frac{1.1eV}{2(8.62x10^{-5}eV/K)(298K)} = 14.4$$
  
then,  
$$\ln\sigma_{423} = C - \frac{E_g}{2kT} = 14.4 - \frac{1.1eV}{2(8.62x10^{-5}eV/K)(423K)} = -0.69$$
  
so  
$$\sigma_{423} = e^{-0.69} = 0.50 \quad (\Omega-m)^{-1}$$

# **Appendix useful electrical units information**

Quantity	Symbol	SI Units	
		Derived	Primary
Electric potential	V	volt	kg-m <sup>2</sup> /s <sup>2</sup> -C
Electric current	Ι	ampere	C/s
Electric field strength	E	volt/meter	kg-m/s <sup>2</sup> -C
Resistance	R	ohm	kg-m <sup>2</sup> /s-C <sup>2</sup>
Resistivity	ρ	ohm-meter	kg-m <sup>3</sup> /s-C <sup>2</sup>
Conductivity	$\sigma$	(ohm-meter) <sup>-1</sup>	s-C <sup>2</sup> /kg-m <sup>3</sup>
Electric charge	Q	coulomb	С
Capacitance	С	farad	s <sup>2</sup> -C <sup>2</sup> /kg-m <sup>2</sup>
Permittivity	e	farad/meter	s <sup>2</sup> C <sup>2</sup> /kg-m <sup>3</sup>
Dielectric constant	$\epsilon_r$	ratio	ratio
Dielectric displacement	D	farad-volt/m <sup>2</sup>	$C/m^2$
Electric polarization	Р	farad-volt/m <sup>2</sup>	$C/m^2$