

# Lecture 2: Semiconductors: Introduction

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## 1 Introduction

Metals have electrical conductivity. This is related to the fact that the energy band of the metal consists of *continuous* filled and empty states. This is related to either a half full orbital (alkali metals) or due to overlap between filled and empty orbitals (alkali earth metals). At 0 K the highest filled state is called the **Fermi energy** ( $E_F$ ). Because the energy difference between the states in the outer band is non-existent, at room temperature, electrons can easily move in the metal during application of an external field. The electrons in the outer band of a metal are said to be *delocalized*, i.e. they belong to the entire solid rather than being tied down to a specific atom. These delocalized electrons are responsible for the high conductivity. A schematic for electrical conduction in metals is shown in figure 1.

The formation of energy bands in semiconductors and by extension insulators can be explained in an analogous manner to metals. The difference being that in semiconductors (insulators) there is an energy gap between the filled valence band and the empty conduction band.

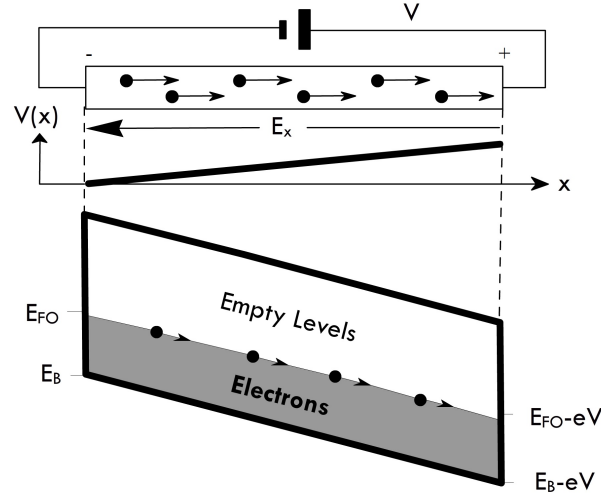


Figure 1: Electrical conduction in metals due to presence of empty electron states in close proximity to filled states. Upon application of an external field electrons move opposite to the field. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

## 2 Band formation in semiconductors

Consider the example of energy band formation in Si (the most dominant in today microelectronics industry). Si has an atomic number of 14 and the electronic configuration is  $1s^2 2s^2 2p^6 3s^2 3p^2$  shown schematically in figure 2. The  $3s^2 3p^2$  forms the outer shell and we can ignore the inner shells as far as electrical conductivity is considered. The  $3s$  and  $3p$  orbitals in Si are close in energy and can hybridize to form  $sp^3$  orbitals. Given that there are 4 electrons a total of 4  $sp^3$  hybrid orbitals are formed. These form 4 bonds that are directed along the corners of a tetrahedron, as shown in figure 3.

Hybridization is a common property of elements of Group IV of the periodic table to which Si belongs to. C which is in top of the group can form a variety of hybrid orbitals ( $sp^3$ ,  $sp^2$ ,  $sp$ ). Both Si and the element below it, Ge, can form  $sp^3$  hybrid orbitals. Sn and Pb (below Ge) are metals with low melting points. In the case of Si, the hybrid orbitals interact the same way that atomic orbitals interact in metals. Consider a bond formed between 2  $sp^3$  hybrid orbitals (1 from each Si atom). The two orbitals can interact to form a bonding ( $\sigma$ ) and anti-bonding ( $\sigma^*$ ) orbital. Since each Si atom will contribute one electron to the bond there will be a total of 2 electrons which will both go to the bonding orbital. Thus, each Si atom can form a

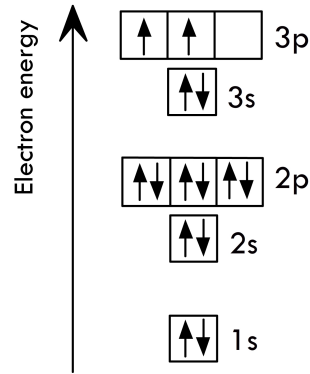


Figure 2: Electronic configuration of Si atom. The 3s and 3p together forms the outer shell while the others form the inner shells. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

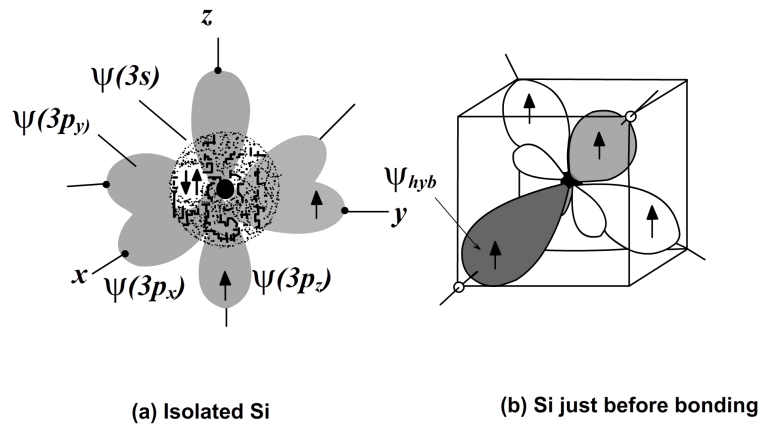


Figure 3: (a) Isolated Si atoms showing the outer shell orbitals. (b) In a solid, these orbitals hybridize to form 4  $sp^3$  orbitals, just before bonding. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

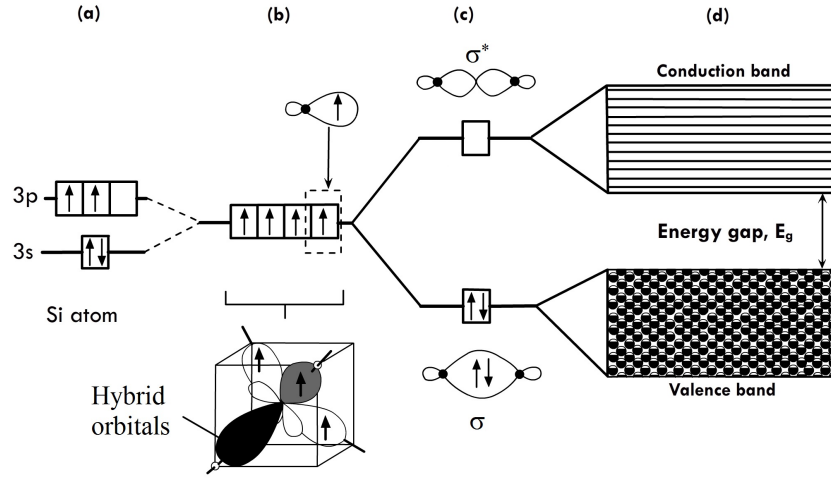


Figure 4: Formation of energy bands in Si. (a) Si atom with 4 electrons in outer shell form (b) 4  $sp^3$  hybrid orbitals. (c) The hybrid orbitals form  $\sigma$  and  $\sigma^*$  orbitals. (d) These orbitals overlap in a solid to form the valence and conduction band. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

bond with 4 other Si atoms and in all cases the bonding orbital ( $\sigma$ ) will be full. A solid will be formed from a large number of these orbitals. When the bonding orbitals interact they will form an energy band, called **valence band**. This valence band will be completely full since the bonding orbital is full. Similarly, the anti-bonding orbitals can interact to form an energy band, called **conduction band**. This will be completely empty. Unlike metals, the valence and conduction band in a semiconductor is separated by a forbidden energy gap, this is called **band gap**. The formation of bands in Si crystal is shown in figure 4.

In the case of Si, the band gap ( $E_g$ ) has a value of 1.11 eV at room temperature (300 K). The same argument for formation of a band gap (filled valence band and empty conduction band with a forbidden energy gap) can be extended to other semiconductors and insulators. The difference between them is related to the magnitude of  $E_g$ . Insulators have a band gap greater than 3 eV while semiconductors have band gap less than 3 eV. This boundary is related to the energy boundary between the visible and UV regions of the spectrum (roughly 400 nm). Some typical values of band gap for different materials are listed in table 1.

Table 1: Room temperature band gap of typical semiconductors and insulators. Materials with band gap less than 3 eV are semiconductors while greater than 3 eV are insulators. ZnO is usually considered a wider band gap semiconductor rather than an insulator.

Material	Band gap (eV)
Si	1.11
Ge	0.67
GaAs	1.43
CdS	2.42
ZnO	3.37
Al <sub>2</sub> O <sub>3</sub>	7.0
SiO <sub>2</sub>	9.0

### 3 Classification of semiconductors

There are different ways of classifying semiconductors depending on the property being measured. One classification that is fairly straightforward is

1. Elemental semiconductors
2. Compound semiconductors

Out of the elemental semiconductors Si and Ge are the most common. There are different type of compound semiconductors - II-VI and III-V are the most common and these can be understood by looking at the portion of the periodic table, shown in figure 5.

Elemental semiconductors (Si and Ge) belong to group IVA of the periodic table. C which is on top of the group is an insulator (diamond) with  $E_g$  of 5.5 eV while Sn and Pb are metals. Compound semiconductors can be formed by combining elements of groups IIIA and VA - the III-Vs. Examples include GaAs, GaP, GaN, InSb. AlN is also a III-V but its band gap is around 6.2 eV making it an insulator. Similarly II-VI compound semiconductors can be formed, examples include ZnO, ZnS, CdSe, CdTe.

Another way of classifying semiconductors based on their band structure is

1. Direct band gap semiconductor
2. Indirect band gap semiconductor

This can be understood from the band picture of the semiconductor, as shown in figure 6. Semiconductors have a filled valence band and an empty

		13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	
		5 <b>B</b> Boron 10.811	6 <b>C</b> Carbon 12.011	7 <b>N</b> Nitrogen 14.00674	8 <b>O</b> Oxygen 15.9994	
	12 IIB 2B	13 <b>Al</b> Aluminum 26.981539	14 <b>Si</b> Silicon 28.0855	15 <b>P</b> Phosphorus 30.973762	16 <b>S</b> Sulfur 32.066	
	30 <b>Zn</b> Zinc 65.39	31 <b>Ga</b> Gallium 69.732	32 <b>Ge</b> Germanium 72.64	33 <b>As</b> Arsenic 74.92159	34 <b>Se</b> Selenium 78.96	
	48 <b>Cd</b> Cadmium 112.411	49 <b>In</b> Indium 114.818	50 <b>Sn</b> Tin 118.71	51 <b>Sb</b> Antimony 121.760	52 <b>Te</b> Tellurium 127.6	
	80 <b>Hg</b> Mercury 200.59	81 <b>Tl</b> Thallium 204.3833	82 <b>Pb</b> Lead 207.2	83 <b>Bi</b> Bismuth 208.98037	84 <b>Po</b> Polonium [208.9824]	

Figure 5: Portion of the periodic table showing the group IV elements and their common dopants. Source <http://chemistry.about.com/od/periodictable/ss/How-To-Use-A-Periodic-Table.htm>

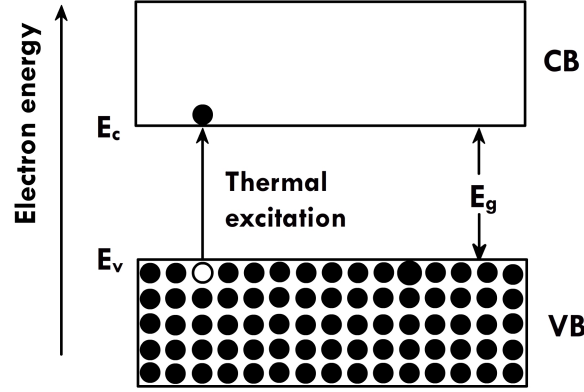


Figure 6: Band picture of a semiconductor showing the full valence band and empty conduction band. The gap between these is called the band gap. At room temperature thermal excitation can cause some electrons to move from valence to conduction band. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

conduction band. Electrons from the valence band can be excited to the conduction band by either thermal excitation or by optical absorption. When the electron returns to the valence band the energy is released either as heat or as photons. In *direct band gap semiconductors* the *dominant mechanism* by which the energy is released (in the absence of defects) *is by photons* (electromagnetic radiation) while in *indirect band gap semiconductors* the energy *is released by phonons* (heat). Direct band gap semiconductors are useful for opto electronic devices like LEDs, and lasers.

The difference between direct and indirect band gap semiconductors is related to their band structure. Electrons in solids have a wave like character. An electron wave is characterized by a wave vector  $\vec{k}$ . Thus, for crystalline materials it is possible to plot  $E$  vs.  $\vec{k}$  diagrams. These are related to the simple band diagrams that show the valence and conduction band. The complete electronic band structure for Si is shown in figure 7.

Without going into the details of the notations in the plot, the 0 eV refers to the top of the valence band and at absolute zero all the energy levels below it are full. This is denoted by the point  $\Gamma_{25'}$ . The line above this,  $L_1$ , has a minimum at point  $X_1$ , which represents the bottom of the conduction band (empty at 0 K). In the case of Si, the valence band maximum and the

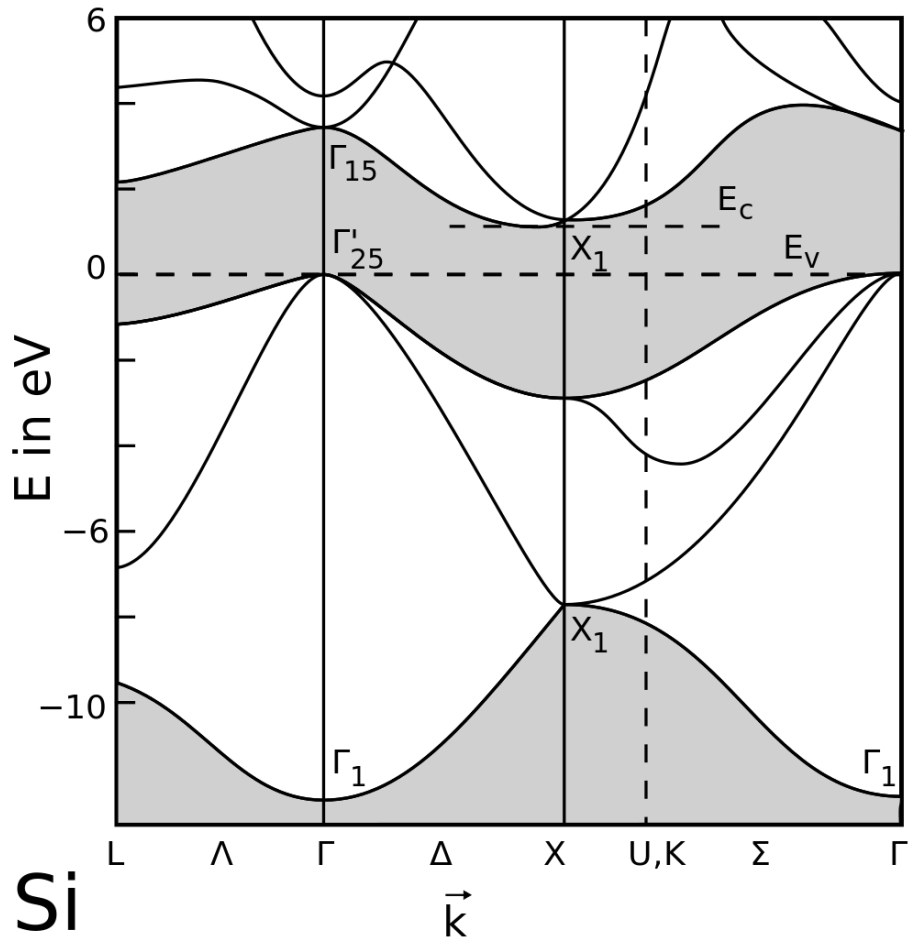


Figure 7: E vs.  $\vec{k}$  diagram for Si. The dotted line at 0 eV is the top of the valence band and the grey region above it is the band gap. The point marked  $X_1$  is the bottom of the conduction band. Source [http://commons.wikimedia.org/wiki/Category:Silicon\\_diagrams](http://commons.wikimedia.org/wiki/Category:Silicon_diagrams)



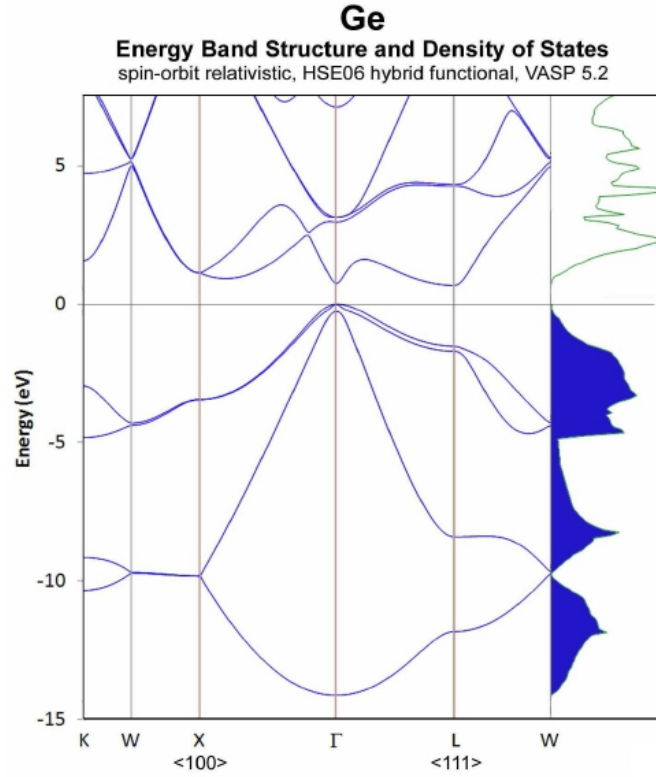


Figure 8: E vs. k diagram for Ge. Ge is also an indirect band gap semiconductor. The portion to the right shows the filled and empty density of states in the valence and conduction band respectively. Source <http://www.materialsdesign.com/appnote/energy-band-structure-germanium>

conduction band minimum are not on top of each other. This makes Si an *indirect band gap semiconductor*. Another example for an indirect band gap semiconductor is Ge, whose band structure is shown in figure 8.

In a direct band gap semiconductor, on the other hand, the top of the valence band and bottom of the conduction band lie on top of each other. An example is GaAs, which is compared to Si in figure 9. Here the maximum at  $L_{4,5}$  is at  $\Gamma_8$  (valence band) and the minimum at  $L_6$  is at  $\Gamma_6$  (conduction band). thus, an electron can get excited from the valence band to the conduction band without change of the wave vector. This can be accomplished easily by absorption of a photon of the appropriate energy. Similarly, an electron from the conduction band can transition to the valence band easily by emission of a photon. In Si and Ge, where the valence band top and conduction band bottom do not line up, this transition requires a change in the

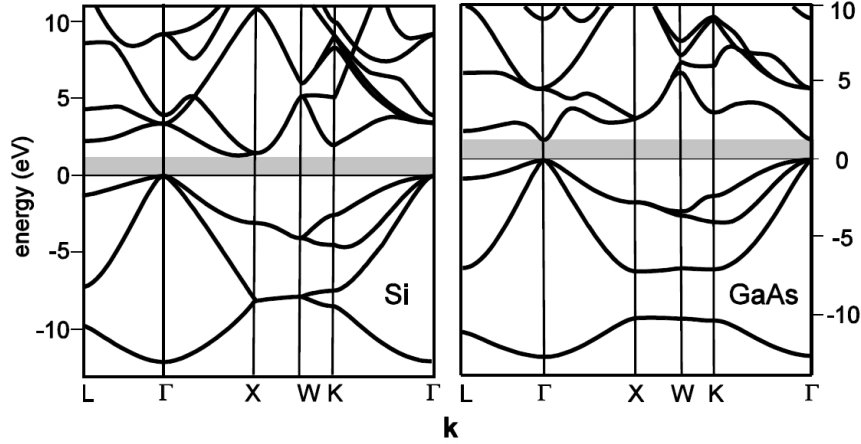


Figure 9: E vs.  $k$  diagram compared for GaAs and Si. GaAs is a direct band gap semiconductor while Si an indirect band gap semiconductor. The grey shaded region represents the band gap. Source <http://users-physics.au.dk/philip/pictures/physicsfigures/node8.html>

electron wave vector. This has to be supplied by the Si lattice, in the form of phonons, so that these are said to be indirect band gap semiconductors.

## 4 Electron effective mass

Electrons in the valence band of Si are bound to the covalent bond between the Si atoms. These electrons are not free to move in the solid. When the electron gets excited to the conduction band they are said to be *delocalized* and can move through the solid. This can be contrasted with metals where the electrons in the valence band are delocalized and are shared with all the atoms in the solid (metallic bond). When an electron in Si gets excited from the valence band to the conduction band it leaves behind a **hole** in the valence band. The hole is the absence of an electron and it is denoted by  $h$  or  $h^+$ . Hole formation is shown schematically in figure 6. The hole can move in the valence band by electron hopping from one bond to another and thus can be said to be delocalized.

When we apply an electric field these electron and holes can move. Consider the motion of free electron and electrons in a solid, in the presence of a field, as shown in figure 10. The electric field goes from positive to negative, so that the electrons travel in the direction opposite to the field. In vacuum the

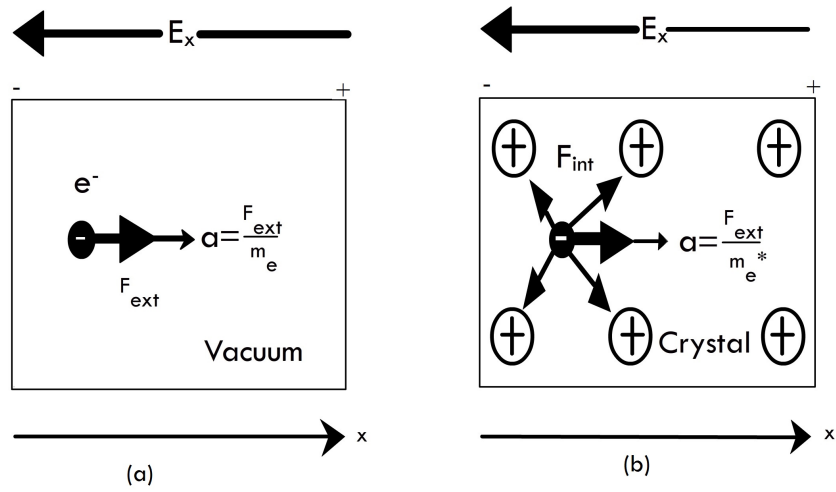


Figure 10: Electron motion in (a) vacuum and (b) solid. In a solid the motion is affected by the interaction with the atoms. This is manifest as an effective mass of the electron. Adapted from *Principles of Electronic Materials* - S.O. Kasap.

acceleration of the electrons ( $a_e$ ) is given by

$$a_e = \frac{eE_x}{m_e} \quad (1)$$

where  $E_x$  is the electric field and  $m_e$  is the rest mass of the electron (ignoring relativistic effects).

In the case of an electron in a solid, under an external field, the interaction with the solid atoms should also be taken into account. Let  $\Sigma F_{int}$  represent the sum of the interaction of the electron with the atoms in the solid. Then the acceleration of the electron, given by using equation 1, is

$$a_e = \frac{eE_x + \Sigma F_{int}}{m_e} \quad (2)$$

The value of the internal forces depends on the location of the electron in the E vs.  $\vec{k}$  landscape and hence equation 2 can be simplified by saying that the electron has an *effective mass*,  $m_e^*$ , so that we can rewrite equation 2 simply as

$$a_e = \frac{eE_x}{m_e^*} \quad (3)$$

The effective mass represents the effect of all the internal forces on the motion of the electron in the conduction band. Similarly, we can define an effective mass,  $m_h^*$ , for the hole movement in the valence band. It should be emphasized that there is no change in the actual mass of the electron but only the representation of the internal forces of the atoms in the solid on the motion of the electron or hole.

For metals like Cu, Ag, or Au the valence electrons are nearly free because they are delocalized and can move easily in the solid. In such cases the effective masses are nearly equal to the rest mass of the electron. In the case of semiconductors, where there is substantial interaction between the electrons in the bonds and the lattice there is a finite deviation. Some typical values of effective masses are tabulated in table 2.

Table 2: Effective masses of electrons and holes in some selected materials. For metals, only electrons are listed since there are no explicit holes in them. For semiconductors, electron effective mass is for the conduction band and hole effective mass is for the valence band.

$\frac{m_e^*}{m_e}$	<b>Cu</b>	<b>Ag</b>	<b>Au</b>	
	1.01	0.99	1.10	
$\frac{m_e^*}{m_e}$	<b>Si</b>	<b>Ge</b>	<b>GaAs</b>	<b>ZnO</b>
	1.09	0.55	0.067	0.29
$\frac{m_h^*}{m_h}$	1.15	0.37	0.45	1.21