Class: 3^{rd}

Subject: Electronic and Magnetic Materials

Lec 2: Semiconductor Materials

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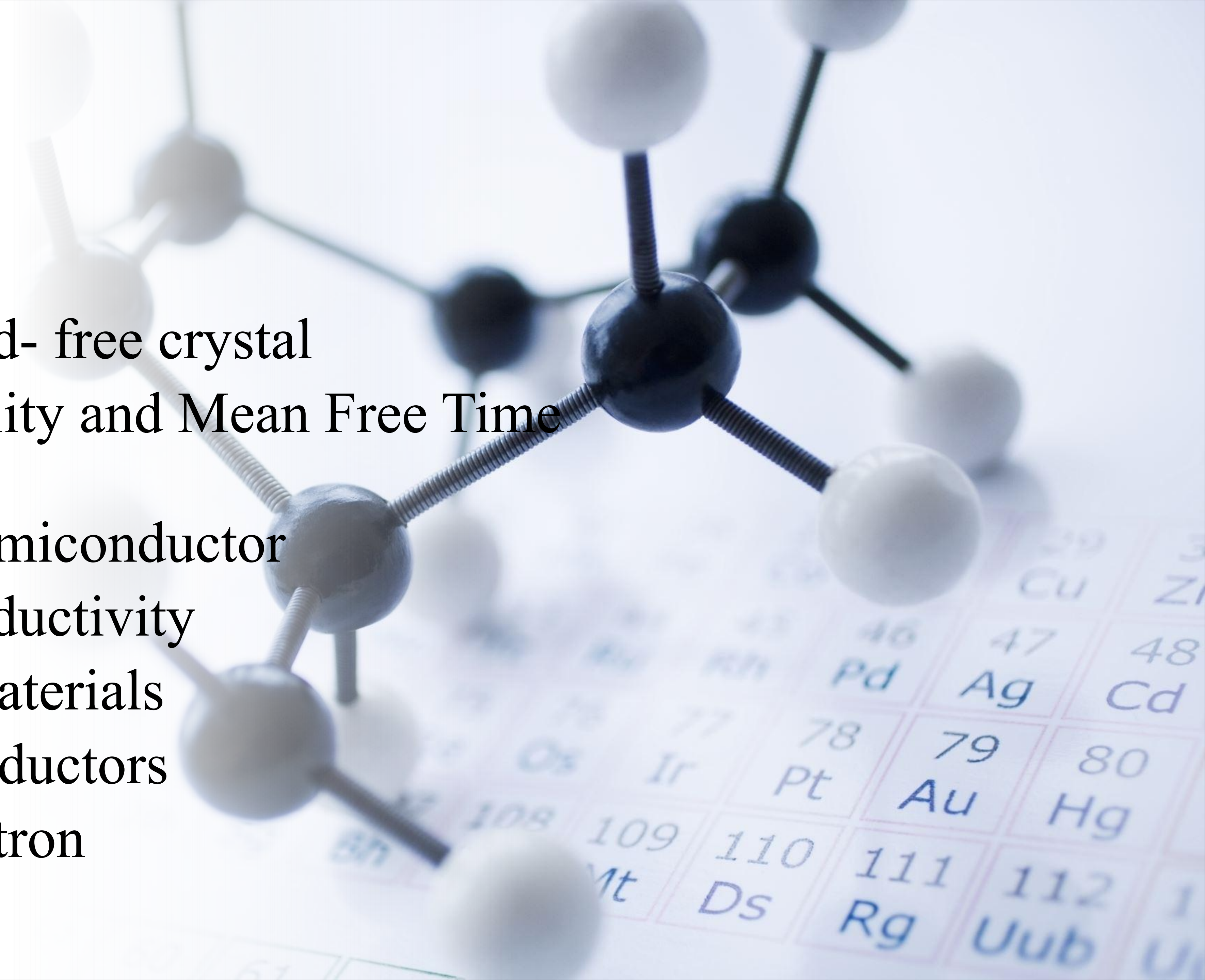
Content



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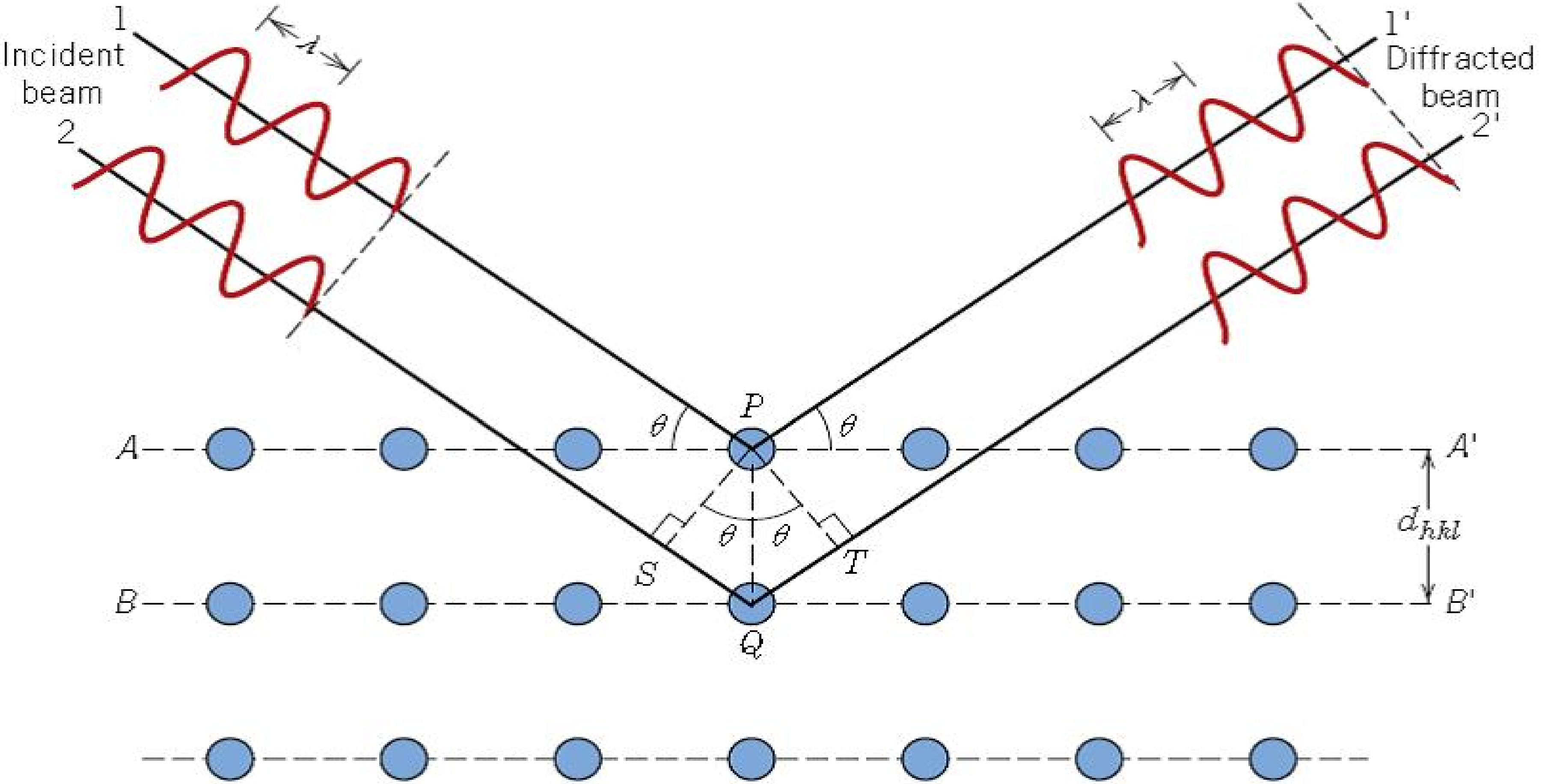
Electrons in a field- free crystal

- An electron moving in a given direction at a constant velocity behaves as a plane wave. The wave interacts with each ionic core and is thereby scattered. Each ion then becomes the source of spherical secondary wavelets in phase with the incident wave. Exactly as was assumed in the discussion of Bragg.
- Diffraction it was concluded there that the secondary wavelets reinforced one another when the condition.

$$n\lambda = 2d\, sin\theta$$

- In this equcation, the expression $2d\, sin\theta$ represents the difference in total path length for two adjacent wavelets. But if $\lambda > 2d,$ as the case for electrons for sufficiently low speed, there is no value of θ for which the path difference can be as much as λ , so that reinforcement can only occur where the path difference is zero. This can only occur in the direction of travel of the original wave which therefore proceeds undiminished in intensity by its encounter with the ions.


1
Incident beam
2
λ
λ
1'
Diffracted beam
2'
P
θ
θ
A
A'
θ
θ
S
T
d_{hkl}
B
B'
Q

- A low energy electons, therefore, is able to move undeflected by a perfectly regular lattice, and behaves as though the ions were not there. We can thus calculate the wave functions for the conduction electrons and determine the expected energy levels by ignoring the presence of the lattice.
- Naturally, in a real metal there are many electrons, all moving in different directions and having different wave functions, but we begin by asking what are the possible wave functions for a single electron in the metal. Then we can add the other electrons, taking care not to violate **pouli's principle.**
- If the electrons are spread uniformly throughout the lattice they cannot be standing waves since in standing waves there are local maxima and minima in the probability distribution. The must therefore be travelling waves since there have uniform intensity every where.
- Now each electron must be confined within the solid but it is not localized near any atom or group of atoms. It can be regarded as orbiting all the atoms in the solid, moving in a curved path of very large radius so that it is (almost) a plane wave. The path will link every atom in the solid so that the ovelall path length is very great.

Collision Probability and Mean Free Time of Electron

The probability of an electron under going collision within time $\delta t,$ so we may let it equal pδt. Take a group of N_O atoms at time t=o. some of these will collide only a short time later, others will be in free flight for longer. To calculate the mean free time we must know how many are left after an orbitrary time t, for the moment we assume that there are N of these.

Between times t and (t+δt) a further small number, $\delta N,$ will have collided. This number δN will be equal to the number N left in the group, multiplied by the probability of collision, p$\delta t,$ for each electron, that is

$$\delta N = NP\delta t$$

The minus sign enters because δN represents a decrease in N. we now find the relation ship between N and t by integrating between t=0 (when N=N_0) and t (when N=N), thus,

$$\int_{N_0}^{N} \frac{dN}{N} =- \int_{o}^{t} P\, dt$$

Performing the integration we find that

$$N=N_0\exp(-Pt)$$

Tells us the number of electrons, δN, which collide between t and (t+δt), and which therefore have a time of free flight equal to t. the average flight time, τ, is given by

$$\tau = \frac{1}{N_0}\int_0^{t=\infty} t dN,$$ by using equ (), we get

$$\tau =- \int_0^{\infty} \frac{N}{N_0} \text{Pt dt}$$

Then

$$\tau =- \int_0^{\infty} pt\, e^{(-Pt)} \text{dt}$$

$$= [t\, e^{(-Pt)}]_0^{\infty} - \frac{1}{P}\int_0^{\infty} P\, e^{(-Pt)} \text{dt}$$

$$= [\, \text{t}e^{(-Pt)}]_0^{\infty} + [\frac{1}{P}\, e^{(-Pt)}]_0^{\infty}$$

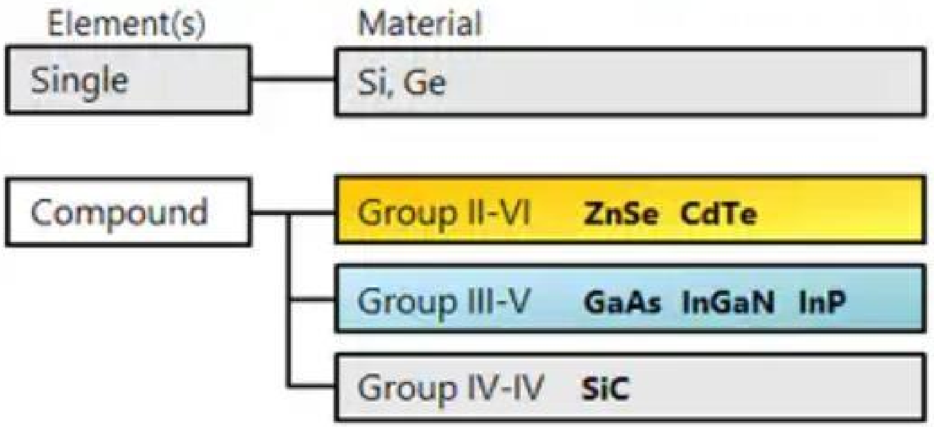
Since the first term is zero at both t=o and t=∞ we finally discover that

$$\tau = \frac{1}{P}$$

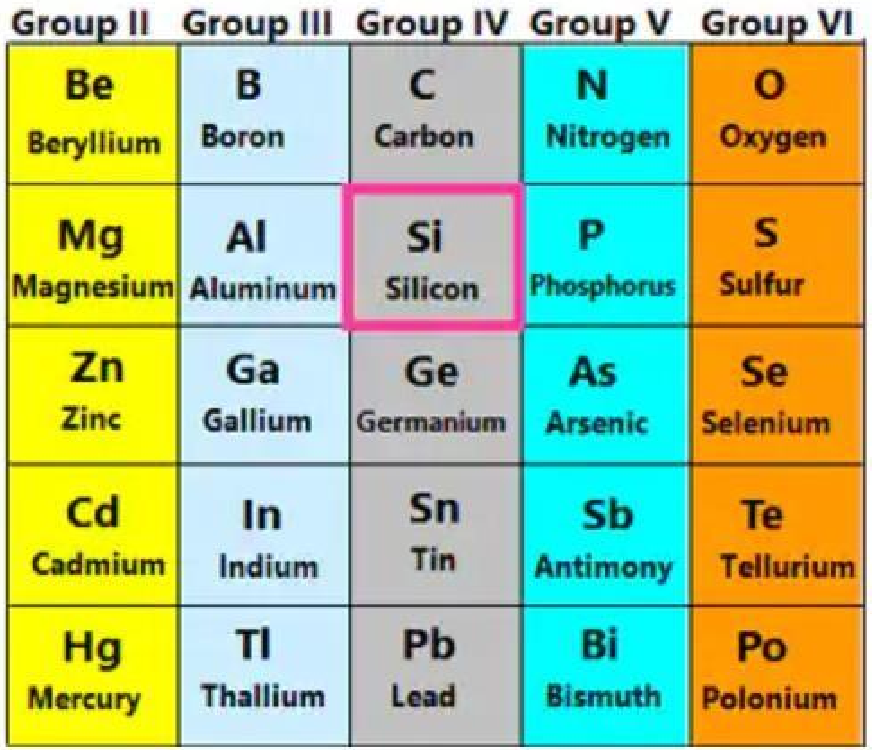
So that the collision probability is just $1/\tau$ per unit time

Introduction of Simconducter

If one examines the electrical resistivites of the elements, particularly of the elements in groups IB, IIB, IIIB, and IVB, it will be seen that they tend to increase with increasing valency. At first sight, this is surprising since increasing valency means an increasing number of loosely bound electrons in the outer shells of the atoms, and an increase in the number of the electrons available might be expected to lead to an increase in electrical conductivity, especially in view of Eq. ($\sigma = n e \mu$). The resistivity of Cu (Group IB is about 1.7×10^{-8} Ω -m) at room temperature while that of germanium (Group IVB in the same period of the table) in the range 10^{-3} to 10^{4} Ω -m, depending on its purity. This phenomenon is directly related to the interatomic bonding in these materials.



Element(s)	Material
Single	Si, Ge
Compound	Group II-VI **ZnSe CdTe**
	Group III-V **GaAs InGaN InP**
	Group IV-IV **SiC**



Group II	Group III	Group IV	Group V	Group VI
Be Beryllium	**B** Boron	**C** Carbon	**N** Nitrogen	**O** Oxygen
Mg Magnesium	**Al** Aluminum	**Si** Silicon	**P** Phosphorus	**S** Sulfur
Zn Zinc	**Ga** Gallium	**Ge** Germanium	**As** Arsenic	**Se** Selenium
Cd Cadmium	**In** Indium	**Sn** Tin	**Sb** Antimony	**Te** Tellurium
Hg Mercury	**Tl** Thallium	**Pb** Lead	**Bi** Bismuth	**Po** Polonium

Bonding and Conductivity

- It will be recalled that the bonding in a metal is visualized in terms of a fixed array of positive ions held in position by a 'sea' of negative charge. The sea consists of the valence electrons which are distributed throughout the solid, i.e., they are shared by all the atoms.
- In the Group IV materials covalent bonds are formed whose distinguishing feature is that the electrons are localized in the bonds. This means that the wave function of a bonding electron is confined to a region of space between adjacent atoms, as depicted in Figs.1.
- In fact, the maximum probability density for the bonding electrons is just midway between the atoms. We show this in the diamond lattice, where for clarity the three-dimensional structure has been unfolded' and drawn in two dimensions. Each bond contains two electrons with opposite spin directions-more than this is not possible owing to Pauli's exclusion principle.

One must not think, however, that these electrons are immobile, condemned forever to stay in the same bond. The probability distributions are smeared out to such an extent that those of neighbouring bonds overlap slightly, and this makes it possible for a pair of electrons in adjacent bonds to change places with one another. Indeed, all the electrons are continually doing so, moving through the network of bonds at great velocity.

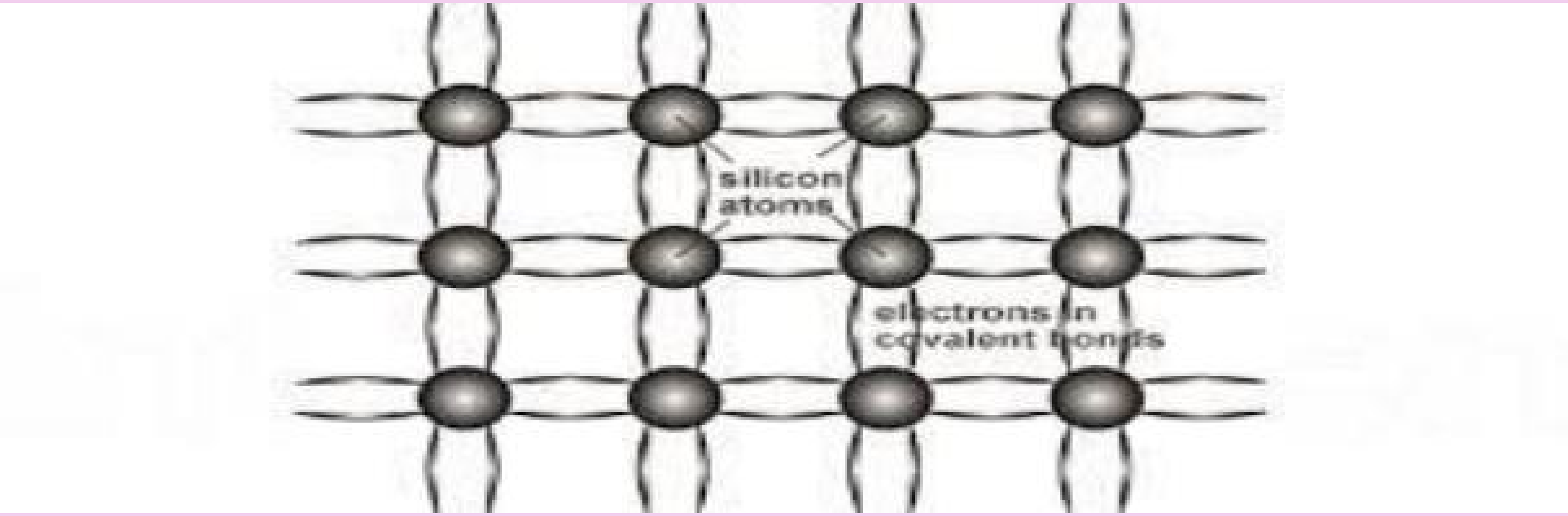


Fig-1 A two-dimensional representation of the covalent bonds in a crystal of C, Si, or Ge, the electron clouds are concentrated between the atoms

Semiconductor Materials

The above argument suggests that a crystal with covalent bonding should be a good insulator, and in some cases this is substantially correct. Our prototype covalent solid. diamond. has a resistivity of $10^{12}(\boldsymbol{\Omega}\text{-m})$ at room temperature, and polymers such as polyethylene and polyvinyl chloride have resistivities of about $10^{15}(\boldsymbol{\Omega}\text{-m})$ in their pure state.

However, two elements silicon and germanium, both of which are of great technological importance, have much lower resistivities. Why is this? If we compare the bond strengths of diamond, silicon, and germanium, we find that they decrease as the atomic weight increases conductivity. It is thus easier to break the bonds in germanium than in silicon, while it is hardest of all to break them in diamond. If the bond is, sufficiently weak, the thermal vibration of the atoms may occasionally be sufficient to sever a bond, even when the temperature is not very high.

Naturally, the higher the temperature, the more likely it is it is that any one bond will be broken, and hence the more bonds will be broken at a given time. Now breaking a bond does not affect the atoms which it joins together-each still has three bonds to keep it in place. But breaking a bond does entail releasing one of the electrons which form it, as shown in Fig. 2.

Thus at any temperature a small proportion of the large number of bonding electrons will be set free. Being no longer confined in the bonds. these electrons may wander freely through the lattice and conduct an electric current.

This is in complete contrast to the situation in a metal, in which all the valence electrons are free to conduct current. The number of free electrons is essentially fixed at a given temperature, although the process of bond rupture by thermal agitation is continuous.

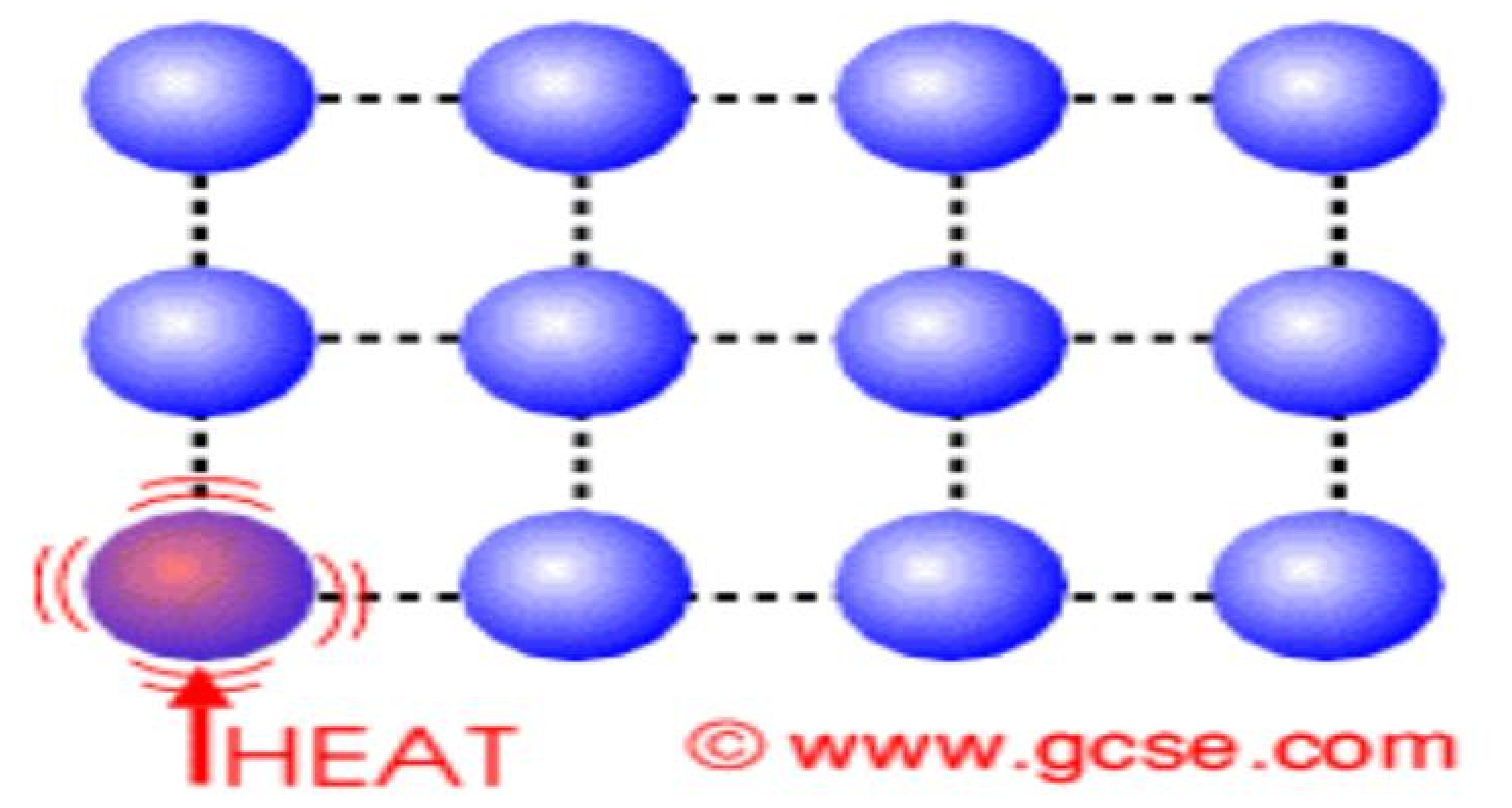


Fig.2: Thermal vibration causes an electron to be freed from one of the bonds

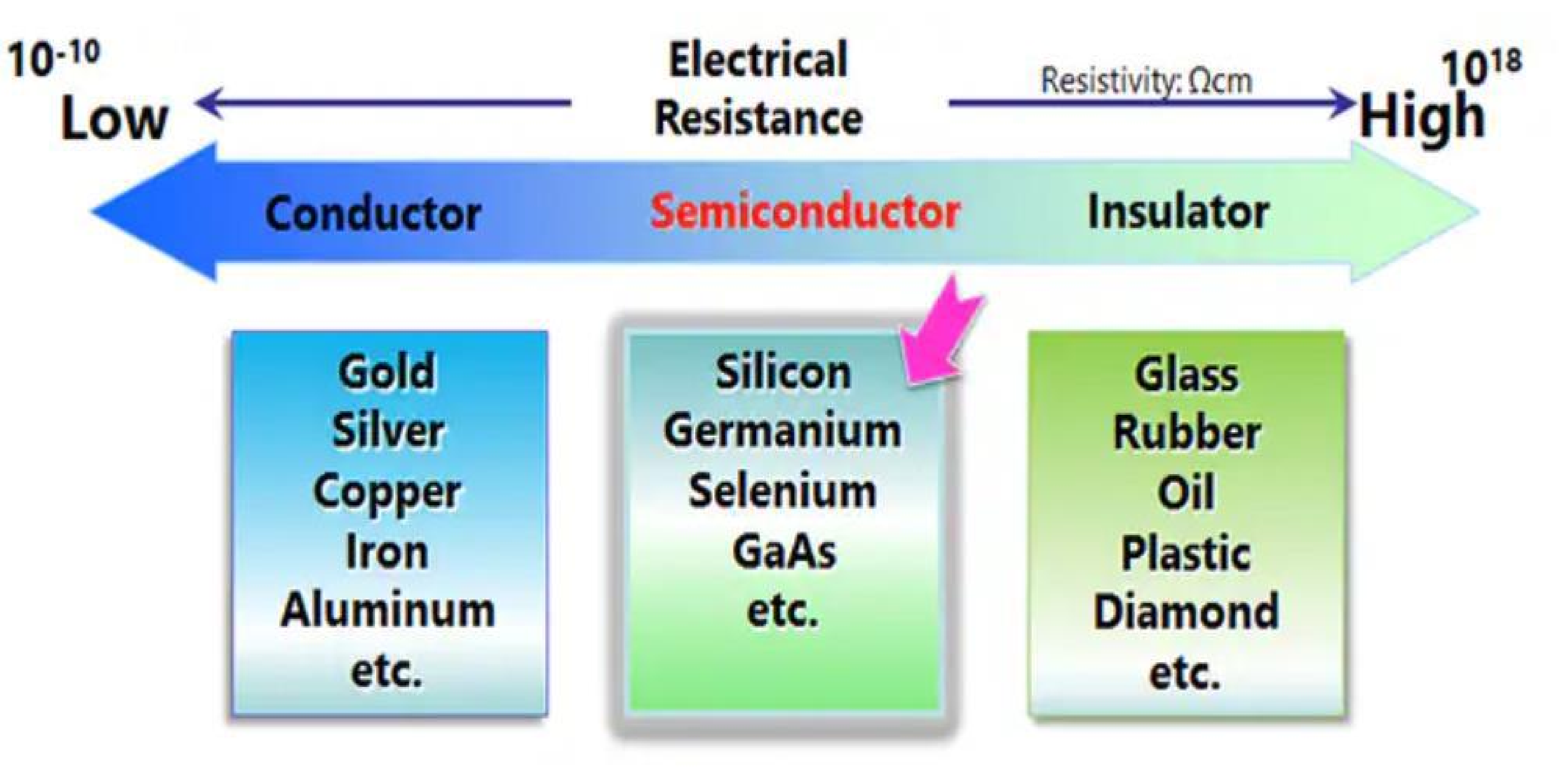
The rate at which electrons are freed is exactly balanced by the rate at which those already free are trapped by an empty bond and lose their freedom. We shall postpone the calculation of the conductivity generated by the presence of free electrons to the next section, for we must now take note of a curious phenomenon which occurs in the bonds.

The freed electrons leave behind them gaps in the bonds, called holes. Since the bonded electrons are in constant motion, these holes are soon filled by nearby electrons.

This necessarily causes the holes to appear in the bonds vacated by the itinerant electrons, and the holes appear to move. In fact the holes move about in much the same random way and as much the same velocity as the electrons in the filled bonds.

We shall now show that the presence of these holes enables the bonded electrons to carry a current in such a way that it appears as if it is conducted by positive charges carried by the holes.

- Semiconductors are materials which have a conductivity between conductors (generally metals) and non-conductors or insulators (such as ceramics). Semiconductors can be compounds, such as gallium arsenide, or pure elements, such as Germanium or silicon.
- Semiconductor materials have physical characteristics that are totally different from those of metals. Whereas metals conduct electricity at all temperatures, semiconductors conduct well at some temperatures and poorly at others.
- In the preceding lecture, it was shown that semiconductors are covalent solids. That is, the atoms form covalent bonds with themselves, the most important being silicon and germanium in Group IV of the periodic. Others may form semiconductor compounds where two or more elements form covalent bonds, such as gallium (Group III) and arsenic (Group V), which combine to form gallium arsenide.



10^{-10} **Low** ← **Electrical Resistance** → Resistivity: Ωcm 10^{18} **High**

Conductor	Semiconductor	Insulator
Gold	Silicon	Glass
Silver	Germanium	Rubber
Copper	Selenium	Oil
Iron	GaAs	Plastic
Aluminum	etc.	Diamond
etc.		etc.

- Germanium is an elemental semiconductor that was used to fabricate the first transistors and solid state devices. But, because it is difficult to process and inhibits device performance, it is rarely used now. The other elemental semiconductor, silicon, is used in approximately 90 percent of the chips fabricated. Silicon’s popularity can be attributed to its abundance in nature and retention of good electrical properties, even at high temperatures. In addition, its silicon dioxide (SiO2) has many properties ideally suited to IC manufacturing.
- Gallium arsenide is classified as a semiconducting compound. Some of its properties, such as faster operating frequencies (two to three times faster than silicon), low heat dissipation, resistance to radiation, and minimal leakage between adjacent components, makes GaAs an important semiconductor for use in high-performance applications. Its drawbacks are the difficulty of growing the ingots and fabricating the ICs.

Typical semiconductor materials used in the fabrication of IC chips are

1. Elemental semiconductors

- Silicon
- Germanium
- Selenium

2. Semiconducting compounds

- Gallium arsenide (GaAs)
- Gallium arsenide–phosphide (FaAsP)
- Indium phosphide (InP)

Excitation of Electrons

When an electron near the top of the valence band (i.e., in a bond) collides with a vibrating atom, it can absorb some of the atom energy and jump into the conduction band. This is just another way to describe how thermal vibrations can break a bond and create an electron-hole pair. The probability of this occurring is just proportional to the probability of an atom having thermal energy greater than Eg , the amount of energy needed to excite the electron. The probability is very nearly proportional to exp(-Eg/KT). The rate of generation of electron-hole pairs is therefore proportional to the same factor.

In equilibrium, the rate of generation of electron-hole pairs must be exactly equal to the rate at which holes and electrons recombine to form fully occupied bonds again. This latter rate must be proportional both to the number of electron per unit volume, n, and to the number of holes per unit volume, p . It is therefore proportional to the product n_p. By equating the rates of generation and recombination, we therefore find that

$$n_p = N_c^2 \exp(-\frac{E_g}{KT}) \ldots\ldots..(1)$$

Where N_C^2 is a proportionality constant.

Since n = p, then we have

$$n = p = N_c exp(-\frac{E_g}{2KT}) \ldots\ldots..(2)$$

This equation can be interpreted as follows:

Since the electrons obey Paulie's principle, they can not be distributed exponentially over the different energy states.

A thorough analyses of the problem shows that in an intrinsic semiconductor the probability of an electron being in quantum state at the bottom of the conduction band is just exp $(-E_g/KT)$. This factor also appears in eq.(2). Of course not all the electrons are in the lowest quantum state in the conduction band, but the vast majority have only a little higher energy. Hence if wa regard the quantity Nc as an effective number of states at the bottom of the band, then the total number of electrons in the band is the number of states Nc multiplie by the probability exp $(-E_g/KT)$ that the state is occupied. That is

$$n = N_c exp(-\frac{E}{2KT})$$

Because N_c is not a number of actual states, it is not a constant, independent of temperature. However, its temperature dependence is small compared to that of the exponential factor in eq.(2), and may safely ignored for our purposes. It also varies but little among the common semiconductors from the typical value of $2.5\times10^{25}m^{-3}$ at 300K.

The electrons in the conduction band and the holes in the valence band may carry current in a similar way to that described for metals. Thus we can use the following eq. to calculate the current density J_n, carried by n free electrons per cubic meter whose drift velocity is V_n:

$$J_n = neV_n$$

Note that J_n. has a positive sign, since both V_n, and e are negative. Similarly the current density J_p, due to the motion of holes in the valence band may be written in terms of their drift velocity $+V_P$,

$$J_p = peV_P$$

Where is the number density of positive holes. The total current density J is then the sum of these

$$\mathrm{J{=}ne}V_n + peV_p \dots\dots\dots\dots\dots\dots.(3)$$

The number of free electrons n and the number of holes p per unit volume are equal (not always) and given by eq.(2) so that we may write the current density

$$\mathrm{J}{=}N_c\left(eV_n + eV_p\right)\exp\left(-\frac{E}{2KT}\right)\dots\dots\dots\dots.(4)$$

Assuming that both the free electrons and the holes behave like the free electrons in a metal, we may use the results of the conduction materials. Thus V_n and V_p, will both be proportional to the electric field ξ and we may divide eq.(3) by ξ to obtain the conductivity:

$$\frac{J}{\xi} = \sigma = N_c\left(e\mu_n + e\mu_p\right)\exp\left(-\frac{K_g}{2KT}\right)\dots\dots\dots\dots\dots\dots.(5)$$

Where $\mu_n \, and \, \mu_p$, are the drift velocities of electrons and of holes respectively in a unit electric field. As before we call $\mu_n \, and \, \mu_p$, the mobilities of electrons and of holes respectively.

In general they will not be equal to one another, but we may expect them both to vary inversely with temperature as we know. However, the exponential in eq.(5) varies more rapidly with temperature and completely dominates the temperature dependence of the whole expression.

Neglecting the temperature dependence of $\mu_n \, and \, \mu_p$, we see that σ arises approximately exponentially with temperature, in marked contrast to metals, for which it falls with rising temperature, The reason is that for semiconductors the number of available charge carriers grows exponentially as the temperature rises, while for metals it is roughly constant. For semiconductors, the rising temperature gives more and more valence electrons enough mergy to jump into the condirction band freeing them and the corresponding hol conduct an electric current.

The experimental values of the conductivity of silicon measured at different temperature T are plotted on a log scale against 1/T in the Fig.3. Exactly as predicted by eq.(5), the points lie very closely on a straight line, the slope of which can be seen by differentiation to be equal to Eg/2K. Using the value for Boltzmann's constant K we can find from the graph that for silicon E =1.15eV.

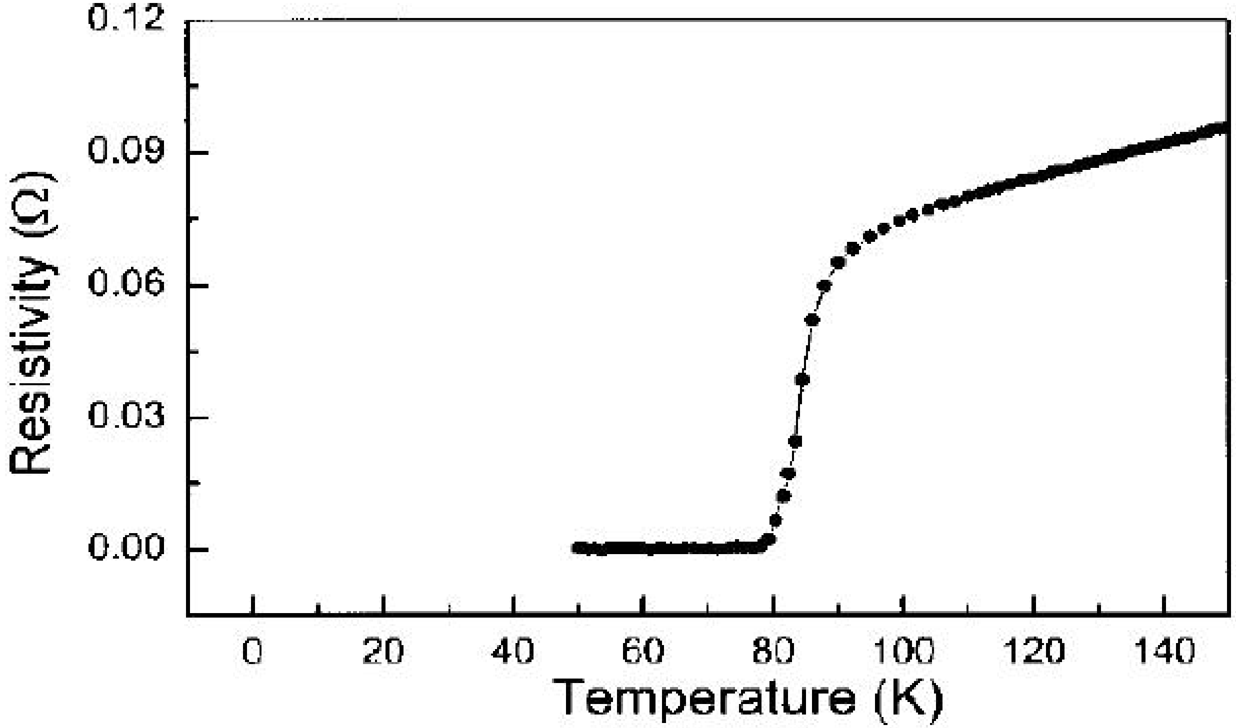


Fig.3: The dependence of the resistivity of silicon on temperature.

Holes and Electrons in Semiconductors

Holes and electrons are the types of charge carriers accountable for the flow of current in semiconductors. Holes (valence electrons) are the positively charged electric charge carrier, whereas electrons are the negatively charged particles. Both electrons and holes are equal in magnitude but opposite in polarity.

Mobility of Electrons and Holes

In a semiconductor, the mobility of electrons is higher than that of the holes. It is mainly because of their different band structures and scattering mechanisms. Electrons travel in the conduction band, whereas holes travel in the valence band. When an electric field is applied, holes cannot move as freely as electrons due to their restricted movement. The elevation of electrons from their inner shells to higher shells results in the creation of holes in semiconductors. Since the holes experience stronger atomic force by the nucleus than electrons, holes have lower mobility.

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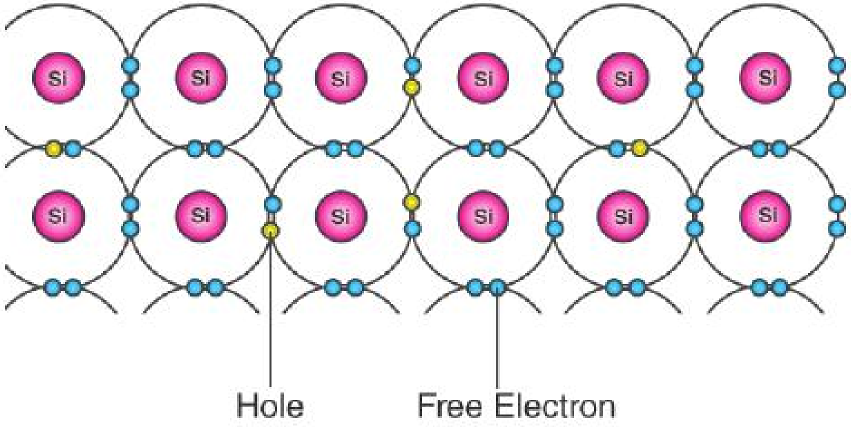
The mobility of a particle in a semiconductor is more, if

- The effective mass of particles is lesser
- The time between scattering events is more

For intrinsic silicon at 300 K, the mobility of electrons is 1500 cm2 (V·s)-1, and the mobility of holes is 475 cm2 (V·s)-1.

The bond model of electrons in silicon of valency 4 is shown below. Here, when one of the free electrons (blue dots) leaves the lattice position, it creates a hole (grey dots). This hole thus created takes the opposite charge of the electron and can be imagined as positive charge carriers moving in the lattice.



Band Theory of Semiconductors

The introduction of band theory happened during the quantum revolution in science. Walter Heitler and Fritz London discovered the energy bands.

We know that the electrons in an atom are present at different energy levels. When we try to assemble a lattice of a solid with N atoms, each level of an atom must split into N levels in the solid. This splitting of sharp and tightly packed energy levels forms Energy Bands. The gap between adjacent bands representing a range of energies that possess no electron is called a Band Gap.

What Is the Fermi Level in Semiconductors

The Fermi level (denoted by EF) is present between the valence and conduction bands. It is the highest occupied molecular orbital at absolute zero. The charge carriers in this state have their own quantum states and generally do not interact with each other. When the temperature rises above absolute zero, these charge carriers will begin to occupy states above the Fermi level.

Properties of Semiconductors

Semiconductors can conduct electricity under preferable conditions or circumstances. This unique property makes it an excellent material to conduct electricity in a controlled manner as required.

Unlike conductors, the charge carriers in semiconductors arise only because of external energy (thermal agitation). It causes a certain number of valence electrons to cross the energy gap and jump into the conduction band, leaving an equal amount of unoccupied energy states, i.e., holes. The conduction due to electrons and holes is equally important.

Why Does the Resistivity of Semiconductors Go Down with Temperature?

The difference in resistivity between conductors and semiconductors is due to their difference in charge carrier density.

The resistivity of semiconductors decreases with temperature because the number of charge carriers increases rapidly with an increase in temperature, making the fractional change, i.e., the temperature coefficient negative.

Some Important Properties of Semiconductors

1. Semiconductors act like insulators at zero Kelvin. On increasing the temperature, they work as conductors.
2. Due to their exceptional electrical properties, semiconductors can be modified by doping to make semiconductor devices suitable for energy conversion, switches and amplifiers.
3. Lesser power losses.
4. Semiconductors are smaller in size and possess less weight.
5. Their resistivity is higher than conductors but lesser than insulators.
6. The resistance of semiconductor materials decreases with an increase in temperature and vice-versa.

Thank you