

1

Semiconductor and Magnetic Material

1.1 INTRODUCTION

Semiconductors are materials having electrical conductivities between those of good conductors and insulators. Semiconductors resistivity varies from 10^{-5} to 10^{+4} Ωm . Similarly resistivity range values 10^{-8} to 10^{+6} Ωm for conductors and from 10^7 to 10^8 Ωm for insulators. Germanium (Ge) and Silicon (Si) are the most commonly used semiconductors and belong to Group-IV of the periodic table. They have resistivity of about 0.6 and 1.5×10^3 Ωm respectively. Also there are certain compound semiconductors such as gallium arsenide (GaAs), indium phosphide (InP), cadmium sulphide (CdS), etc. They are formed by the combination of the elements of groups III and V. Small band gap is another important characteristic of semiconductors. Also the semiconductors have negative temperature coefficient of resistance because the number of carriers in a semiconductor will increase significantly with temperature, resulting in reduction of the resistance of the semiconductor.

1.2 SEMICONDUCTOR MATERIALS (GROUP-IV)

Semiconductors are materials having electrical conductivities between those of good conductors and insulators. The elemental semiconductor such as germanium (Ge) and silicon (Si) belong to Group-IV of the periodic table and have resistivity of about 0.6 and 1.5×10^3 Ωcm respectively. The energy band gaps of these elements of Group-IV at 0 K are given as below:

| | | |
|-------------|---|--------------|
| C (diamond) | → | 5.51 eV |
| Ge | → | 0.75 eV |
| Si | → | 1.16 eV |
| Sn (grey) | → | 0.08 eV |
| Pd | → | \approx eV |

We may say from above list that at room temperature (i.e., 0 K) diamond behaves as an insulator but Ge and Si are treated as semiconductors. In contrary to these Sn and Pd used to work as conductors.

The semiconductor material in pure form is known as intrinsic semiconductor and in impure form it is called extrinsic semiconductor material. The intrinsic semiconductor material is converted to extrinsic one by adding on impurities of pentavalent or trivalent atoms in semiconductor. The process of introduction of impurities in semiconductors in a precisely controlled manner is called *doping*.

1.2.1 COMPOUND SEMICONDUCTOR MATERIALS

Various types of semiconductor materials will be described in this section. Classification of these materials is made according to the positions of constituent atoms of these materials in the periodic table. The different energy band gap material may be obtained from compound semiconductor material. Now we will discuss some of these.

- (a) *Group-IV semiconductor material:* These semiconductor materials have been discussed earlier and for example Diamond, silicon and germanium are the available semiconductor materials of the group.
- (b) *Group-IV compound semiconductors:* Some of the available semiconductor material of such group are: Silicon carbide (SiC) and Silicon germanium (SiGe).
- (c) *Group (III–V) ternary semiconductor alloys:* Some of examples of such semiconductor materials are: Aluminium gallium arsenide (AlGaAs, Al_xGa_{1-x}As), Indium gallium arsenide (InGaAs, In_xGa_{1-x}As), Indium gallium phosphide (InGaP), Aluminium indium arsenide (AlInAs), Aluminium indium antimonide (AlInSb), Gallium arsenide nitride (GaAsN), Gallium arsenide phosphide (GaAsP), Aluminium gallium nitride (AlGaN), Aluminium gallium phosphide (AlGaP), Indium gallium nitride (InGaN) and Indium arsenide antimonide (InAsSb)
- (d) *Group (III–V) quaternary semiconductor alloys:* Aluminium gallium indium phosphide (AlGaInP, also InAlGaP, InGaAlP, AlInGaP), Aluminium gallium arsenide phosphide (AlGaAsP), Indium gallium arsenide phosphide (InGaAsP), Aluminium indium arsenide phosphide (AlInAsP), Aluminium gallium arsenide nitride (AlGaAsN), Indium gallium arsenide nitride (InGaAsN), Indium aluminium arsenide nitride (InAlAsN) and Gallium arsenide antimonide nitride (GaAsSbN) are some examples of semiconductor materials of this category.
- (e) *Group (II–VI) types of semiconductor materials:* Within this category the different types of semiconductors are:
 - (i) *Group (II–VI) secondary semiconductors:* Cadmium selenide (CdSe), Cadmium sulfide (CdS), Cadmium telluride (CdTe), Zinc oxide (ZnO), Zinc selenide (ZnSe), Zinc sulfide (ZnS) and Zinc telluride (ZnTe).
 - (ii) *Group (II–VI) ternary alloy semiconductors:* Cadmium zinc telluride (CdZnTe, CZT), Mercury cadmium telluride (HgCdTe), Mercury zinc telluride (HgZnTe) and Mercury zinc selenide (HgZnSe).

- (f) *Group (IV–VI) types of semiconductor materials:* Within this category the different types of semiconductors may be given as:
- (i) *Group (IV–VI) semiconductors:* Lead Selenide (PbSe), Lead sulfide (PbS), Lead telluride (PbTe), Tin sulfide (SnS), Tin telluride (SnTe).
 - (ii) *Group (IV–VI) ternary semiconductors:* Lead tin telluride (PbSnTe), Thallium tin telluride (Ti_2SnTe_5), Thallium germanium telluride (Ti_2GeTe_5).
- (i) *Group (II–V) types of semiconductor materials:* Within this category the different types of semiconductors may be given as:
- Group (II–V) semiconductors:* Cadmium phosphide (Cd_3P_2), Cadmium arsenide (Cd_3As_2), Cadmium antimonide (Cd_3Sb_2), Zinc phosphide (Zn_3P_2), Zinc arsenide (Zn_3As_2), Zinc antimonide (Zn_3Sb_2).

1.3 OPTO-ELECTRONIC DEVICES SEMICONDUCTOR MATERIALS

We already know that the eye is only sensitive to light of energy ($h\nu$) greater than 1.8 eV and the corresponding wavelength of approximately 0.7 μm . So for light emitting devices the semiconductors of interest must have energy band gaps larger than this limit. Figure 1.1 gives semiconductors that can be used as visible LEDs. Direct band gaps semiconductors indicated by shading are particularly important for electro-luminescent devices. This is because the radiative recombination is a first order transition process (no photon involved). It has been further observed that the quantum efficiency in direct band gap semiconductor material is expected to be much higher than that in indirect band gap semiconductors. For application point of view $\text{GaAs}_{1-x}\text{P}_x$, which is of III-V group compound semiconductor, is of prime importance. The wave vector representation and direct and indirect band gap material concept has been described in Figure 1.2.

The semiconductor material used for light emitting diodes or sources must have energy band gap of more than 1.8 eV. The group of semiconductors which can be used as visible LEDs is shown in Figure 1.1. Direct band gaps semiconductors which are used for electroluminescent devices indicated by shading are particularly important, as we know that the radiative recombination is a first order transition process (no photon involved) and the quantum efficiency is expected to be much higher than that for an indirect band gap semiconductors which are listed in Figure 1.3. From the figure and application point of view, we can say that $\text{GaAs}_{1-x}\text{P}_x$, a III-V group compound is of high importance.

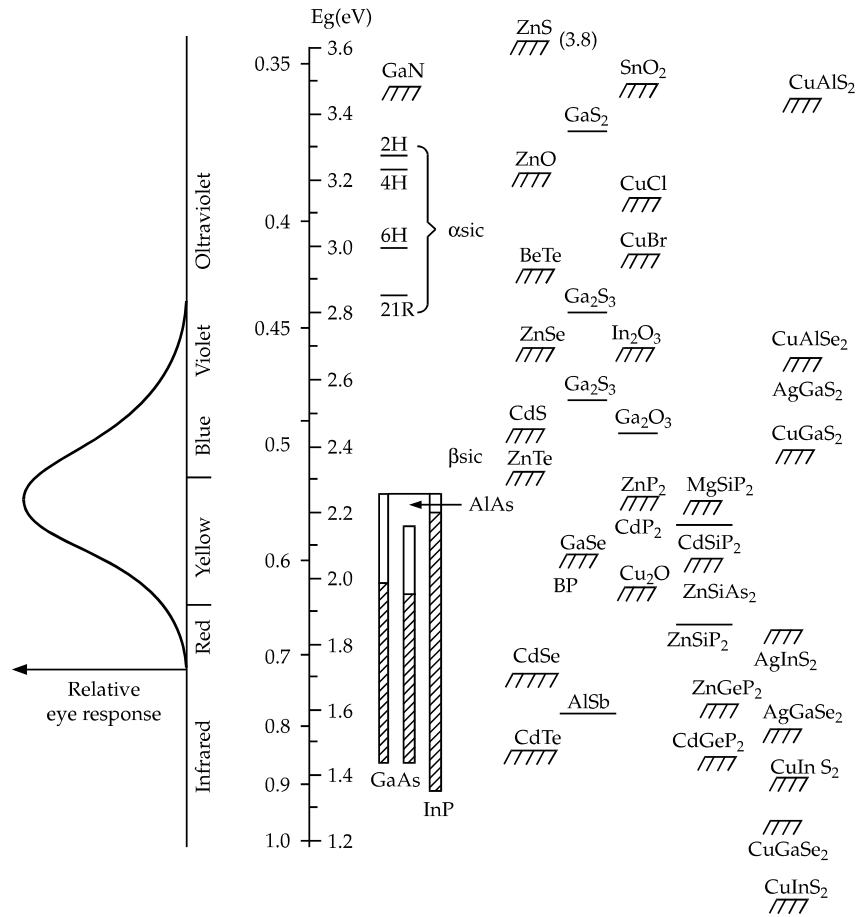


Fig. 1.1 Different semiconductor material.

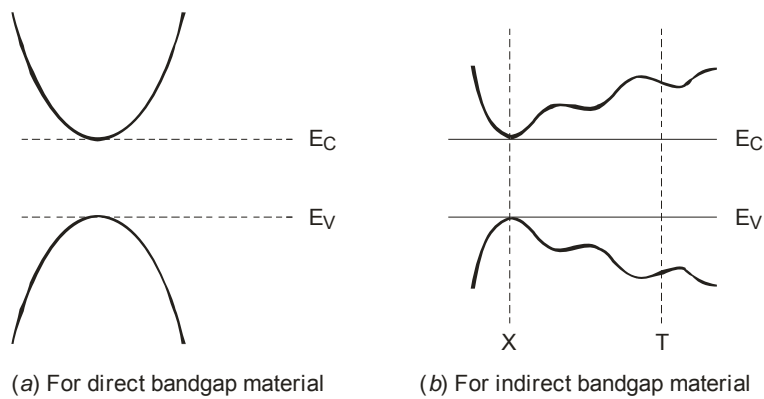


Fig. 1.2 Energy band and wave vector representation of Semiconductor.

The energy gap for $\text{GaAs}_{1-x}\text{P}_x$ as a function of the mole fraction x is depicted in Figure 1.3. For such material the energy gap is direct for $0 < x < 0.45$, and increases from $E_g = 1.424$ eV at $x = 0$ to $E_g = 1.977$ at $x = 0.45$, for $x > 0.45$, this energy gap is indirect. Corresponding energy-momentum plots for selected alloy compositions are shown in Figure 1.3. We can observe that the conduction band has two minima. The direct minimum is the one along the Γ axis. The indirect minimum is the one along the x axis. The holes at the top of the valence band (VB) and the electrons in the direct minimum of the conduction band (CB) have equal momentum however the electrons in the indirect minimum have different momentum. The momentum is conserved for direct band gap semiconductors, such as GaAs and $\text{GaAs}_{1-x}\text{P}_x$ ($x \leq 0.45$). As it has been discussed that the minima of wave vector of conduction band and the maxima of wave vector of valence band are same and hence momentum is conserved. Thus the material will be direct band gap, it is called *k-rule* and the selection of semiconductor material based on the *k-rule* is known as *k-selection rule*. Here *k* denotes wave vector. There is high probability of occurrence as seen in interband transitions. The band gap energy of the semiconductor is then approximately equal to the photon energy. The radiative transition mechanism is predominant in direct band gap materials.

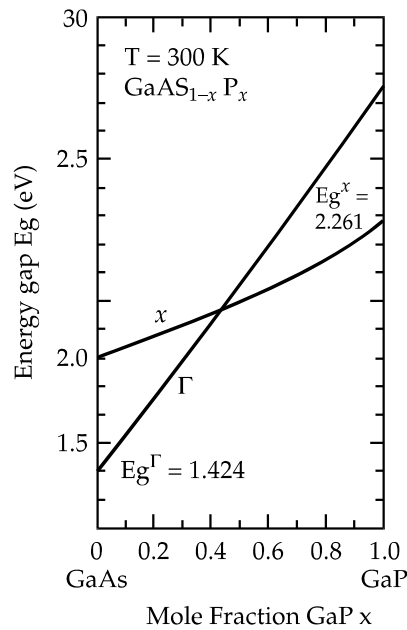


Fig. 1.3. Energy gap Vs mole fraction for $\text{GaAs}_{1-x}\text{P}_x$

However for $\text{GaAs}_{1-x}\text{P}_x$ with $x > 0.45$ and GaP that are indirect bandgap semiconductors, the probability of occurrence for inter band transitions is extremely small. This is because the photons or other scattering agents must participate in the

process in order to conserve momentum. Therefore, for indirect bandgap semiconductors, such as GaP, special recombination centers are incorporated to enhance the radiative process. Incorporating specific impurities such as nitrogen is used to form an efficient radiative recombination center in $\text{GaAs}_{1-x}\text{P}_x$. After introducing the nitrogen, the one nitrogen atom replaces phosphorus atoms in the lattice sites. The electronic core substances of these atoms are different as the outer electronic structure of nitrogen is similar to that of phosphorus (both are group V elements in the periodic table). It is because of this difference an electron trap level close to the conduction band rises. Thus an isoelectronic center is produced which are neutral normally.

Firstly an injected electron is trapped at the center in p -type material. A hole from the valence band is captured from the negatively charged center to form the bound exciton and this electron-hole pair yields a photon with energy equal to the band gap minus energy approximately equal to the binding energy of the center. The momentum of trapped electron is diffused since the trapped electron is highly localized at the center. The probability of direct transition to converse this momentum has greatly increased. In indirect band gap materials for example GaP this radiative recombination mechanism is predominant.

The Figure 1.4 shows introduction of isoelectronic centers. From the figure it is clear that without nitrogen the efficiency drops sharply in the composition range $0.4 < x < 0.5$ as the proximity of the direct-indirect transition at $x = 0.45$. With nitrogen the efficiency is considerably higher for $x > 0.5$, but decreases steadily with increment in x . This is because of the increase in separation between the direct and indirect band gap material. A shift of the peak emission wavelength is shown for nitrogen-doped alloy too. Such thing happen due to binding energy of introduced isoelectronic centers.

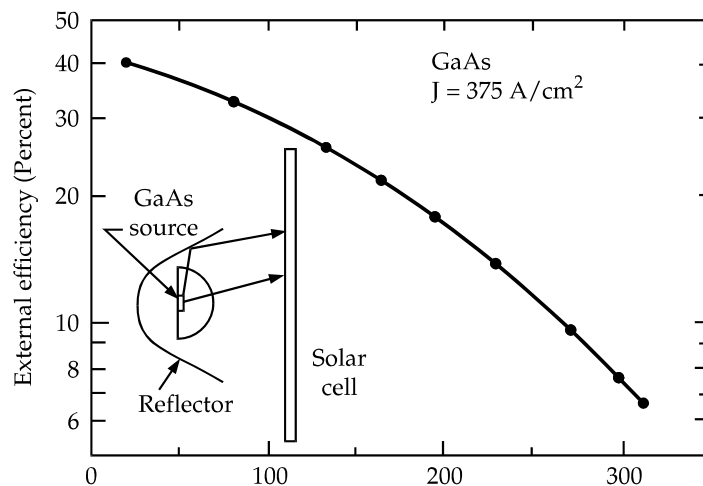


Fig. 1.4 The plot of quantum efficiency Vs alloy composition for $\text{GaAs}_{1-x}\text{P}_x$.

When the nitrogen atom is added in *p*-type material the injected electron is first captured at the center. Such negatively charged center trap a hole from the valence band and constitute the bound exciton. The subsequent annihilation of this electron–hole pair yields a photon. This released photon will have energy of amount band gap minus energy approximately equal to the binding energy of the center. This trapped electron is highly localized at the center since its momentum is diffused. This momentum can be conserved and the probability of direct transition is greatly improved. Hence, the radiative recombination mechanism will become pre-dominant in indirect band gap materials by introduction of such centers.

1.3.1 LAYERED SEMICONDUCTOR

There is existence of another kind of semiconductor materials which is of different form than normal semiconductor materials and it is known as *layered semiconductor materials*. The examples of such materials are: Lead (II) iodide (PbI₂), Molybdenum disulfide (MoS₂), Gallium Selenide (GaSe), Tin sulfide (SnS) and Bismuth sulfide (Bi₂S₃).

1.4 ENERGY BANDS AND ELECTRICAL CONDUCTION

We know that the electrons in solids have energies within certain bands. Similarly the electrons in semiconductor have energies only within particular bands, i.e., between ground state energy which is analogous to electron firmly attached to nuclei of atoms within the material and free electron energy. The energy required for an electron to escape from the surface of material is called free electron energy. In semiconductor material each band will have several discrete quantum states of electrons. Here it should be noted that the major states low energy are filled to a level of energy state known as *valence band*. There is existence of one more energy level in which probability of existence of electron is rare at absolute temperature. This energy level is known as *conduction band*. In conduction band the electron is generally free to move. If we compare the energy band gap between conduction band and valence band in metal and semiconductor we may say that in metal the conduction and valence band overlaps. Hence, the differentiation in metal and a semiconductor may be easily understood.

Therefore, in a semiconductor, electron can be excited to jump to conduction band or higher band from the valence band. For exciting or bringing the electron from valence band to conduction band we must apply energy on electron which will be equal to the energy difference of conduction band to valence band. This energy is known as *energy band gap* and denoted as E_g . The E_g of the particular semiconductor is different from another. Here it should be remembered that the energy of valence band and conduction band is determined with reference to vacuum level and the energy of vacuum level is referred as zero energy state. The valence band is full of electrons and at absolute zero temperature there is no electron in conduction band. Hence valence band does not contribute to the electrical conductivities. As the temperature rises above absolute zero, the electron lying in valence band acquires this thermal energy and moves to the higher

state and may reach the conduction band. The current carrying electrons which are brought to conduction band are called *free electrons*. The electrons which reach the conduction band left behind a vacancy in the valence band. The left vacancy will have a charge which will be equivalent to charge of electron but opposite in nature called as hole or unoccupied states in the valence band. Both, the conduction band electrons and the valence band holes contribute to electrical conductivity. In real sense there is no movement of holes, but the adjacent electron may move to fill this hole, and leave behind a hole at the place from where it has just come. So it means the holes appear to move.

1.5 SEMI-INSULATORS

There is existence of materials which may be considered as *semi-insulators*. The conductivity of such material lies near to that of electrical insulators. These materials are utilized in fabrication of some of the active devices. One of the best possible applications of semi-insulating material is in preparation of substrate for HEMT. The HEMT is very useful transistor for microwave frequency range. The mostly used and popular example of such material is gallium arsenide.

1.6 MAGNETIC SEMICONDUCTORS

The magnetic semiconductor material is one which has properties of both types that is it has properties of ferromagnetism (or a similar response) and semiconductor. If the devices are fabricated by using such materials they will exhibit new kind of control over current conduction. It is known to us that the control of current in semiconductor devices is mainly dependent on control of density of either *n*-type or *p*-type of charge carrier or by both. On the other hand devices integrated by using practical magnetic semiconductors will be controlled by quantum spin state of atoms and up and down spin of atoms of the material too. The fabrication of spin transistor is based on this property (i.e. basic property of spin-electronics).

SUMMARY

The importance of semiconductor material is well known fact and fabrication of semiconductor devices like diodes, transistors, photodiodes and many other devices are based on semiconductor material. In this chapter the study of different semiconductor material has been presented. The chapter highlights on group-IV semiconductor material and properties of these material. The compound semiconductor materials have been also described. The chapter deals with the change of energy band gaps of different compound semiconductor materials on changing their alloy compositions. The group-III-V and group-II-VI secondary, and quaternary alloyed semiconductor material have been described. The concept of introducing isoelectronic centers in indirect band gap semiconductor for increasing radiative transitions has been discussed. In last the semi insulators and layered semiconductors have been described.

MULTIPLE CHOICE QUESTIONS

1. What will happen when nitrogen atoms are added to indirect band gap semiconductor material
 - (a) Material will become pure semiconductor in nature
 - (b) Material will become insulator
 - (c) Isoelectronic centers will be introduced
 - (d) None of these.
2. The energy gap in semiconductor increases on increasing alloy composition in compound semiconductor material.
 - (a) True
 - (b) False
3. What will happen to the material when alloy composition in compound semiconductor material is increased?
 - (a) Material will become conducting in nature
 - (b) Material will become insulator
 - (c) It may work as direct band gap material till alloy composition is less than or equal to 0.45 and after this it will convert to indirect one.
 - (d) None of these.

LONG QUESTIONS

1. Explain direct and indirect band gap material.
2. Discuss the compound semiconductor materials in detail
3. Show how the indirect band gap material can be converted to direct band gap material.
4. What are the different categories of semiconductor material, discuss group IV and group III-V semiconductor material.
5. Explain the band structure and energy bands in semiconductor material
6. Discuss optoelectronic semiconductor material and applications of these.
7. Distinguish between compound and primary semiconductor material.