

## CHAPTER I

### HEAVILY DOPED SEMICONDUCTORS



#### 1.1 Introduction.

When the studies of semiconductor began, physicists and engineers had to contend with impure semiconductors containing  $10^{19}$ - $10^{20}$   $\text{cm}^{-3}$  of foreign impurities. The techniques for preparing pure semiconducting single crystals were developed. And while the gradual reduction of the impurity concentration achieved, new properties of these impure crystals were discovered and applied in practical devices. Finally it became clear that the technology of semiconductor devices required not crystals of maximum purity but crystal with impurities introduced in precisely known amounts.

Up to 1958, all semiconductor devices were made of lightly doped semiconductors containing not more than  $10^{16}$  impurities per  $\text{cm}^3$ . These impurities, being isolated, formed narrow states in the band gap for electrons or holes. After that technology begin to return to crystals containing impurities in amounts reaching  $10^{20}$   $\text{cm}^{-3}$ , heavily doped. Some applications of such heavily doped semiconductors are used in laser, light emitting diodes and some active components of solid state systems, i.e., bipolar transistor.

Heavily doped semiconductors are only a part of the more general problem of disordered systems.

#### 1.2 Disordered Systems.<sup>1-4</sup>

A system of particles is called disordered if there is no

long-range order in the distribution of the particles. For the charge carriers (electrons or holes) an equivalent definition is that, a condensed macroscopic system is called disordered if the potential energy of the charge carrier is spatially nonperiodic. Liquids, amorphous, glassy substances, disordered alloys and heavily doped semiconductors are some examples of disordered systems<sup>1</sup>.

The disordered materials mentioned above might be very different physically. However, the theory of electronic structures is common feature of all disordered systems. The discussion of disordered materials has been based on highly simplified model band structures. It begin with perfect and imperfect crystals, and observing the effects of increasing disorder on the electronic structures.

The universal structural feature of perfect crystals is their periodicity. The one - electron Hamiltonian satisfies the equation

$$H(\vec{p}, \vec{r}) = H(\vec{p}, \vec{r} + \vec{\ell}) \quad 1.2.1$$

for any translational vector  $\vec{\ell}$  of direct lattices.

Then, by the Bloch's theorem, the eigenfunctions  $\psi_{nk}$  of  $H$  are such that

$$\psi_{nk}(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} U_{nk}(\vec{r}) \quad 1.2.2$$

where  $U_{nk}(\vec{r})$  is periodic functions with the periodicity of the direct lattices,

$$U_{nk}(\vec{r} + \vec{\ell}) = U_{nk}(\vec{r}) . \quad 1.2.3$$

$\vec{k}$  is the wave vector and  $n = 1, 2, 3, \dots$  is so-called band index.

All eigenfunctions (1.2.2) are extended. An electron described by (1.2.1) goes everywhere in the crystal with equal probability just as in the free electron case. The energy spectrum of the electron consists of continuous bands at allowed levels separated by forbidden gaps. The density of states  $\rho(E)$  goes to zero at the band edges as the square root of the energy (Fig.1.1).

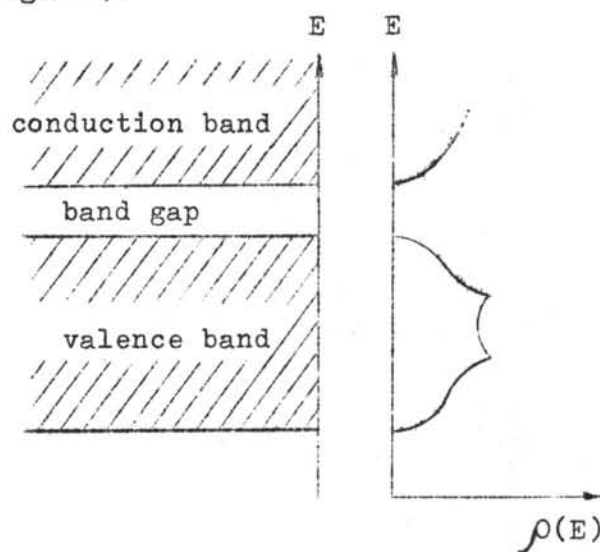


Fig.1.1 Energy band scheme of perfect crystals.

Now, let us consider a crystal containing a single localized imperfection such as an impurity. If the localized change  $\Delta V$  produced by the imperfection in the crystal potential  $V$  is weak, we can use the Born approximation to obtain the solution of the scattering problem. The result is that the states remain extended. The change in the density of states is small and the sharp band edges remain. As  $\Delta V$  increases beyond a certain critical value, the energy state splits off the band as a

$\delta$  - function in the band gap. This state is bound to and localized around the imperfection. Both attractive and repulsive localized potential changes can bind an electron in the crystal in localized states. A strong repulsive change can push a localized state above the upper bound of the continuum, in the same way that an attractive potential can push the localized state below the lower bound of the continuum (Fig.1.2a).

The next step is to consider an imperfect crystal. Consider the case of low but finite concentration of random distribution of individual imperfection.

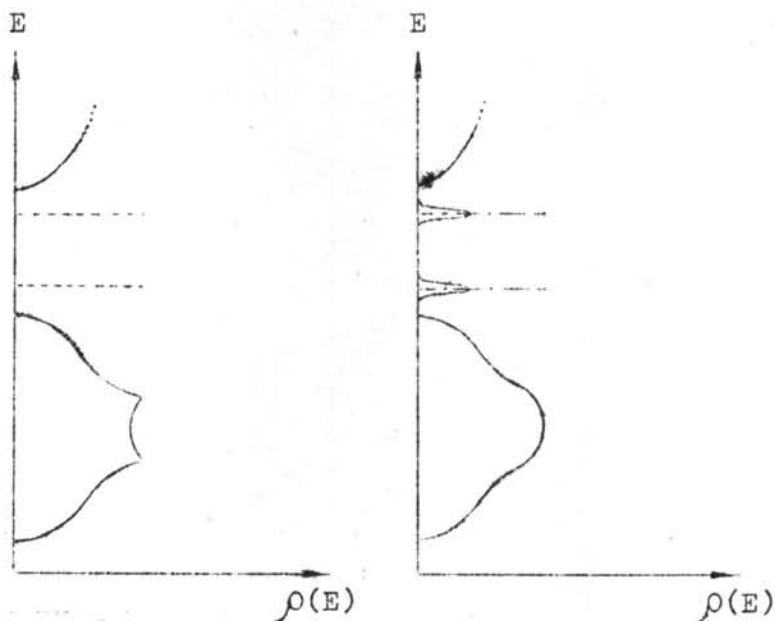


Fig. 1.2a.

Fig. 1.2b.

Fig.1.2 Density of states  $\rho(E)$  as a function of energy  $E$  for  
 a. a crystal containing only one localized imperfection,  
 b. a crystal containing a low concentration of localized imperfections.

For weak scattering potential, the electron wave functions remain extended. Since the concentration of imperfection is much smaller than the concentration of regular atoms, the change in the density of states to be small. When each  $\Delta V$  is large enough, there will be a non-zero density of states inside the gap with a peak expected around the position of the bound state corresponding to a single impurity. If the concentration is high enough, individual localized states broaden to form an imperfection band (Fig.1.2b). If the imperfections were regularly arranged in a superlattice there would be a narrow imperfection band with sharp edges possessing the typical features stemming from the periodicity.

As the randomness increases, the band becomes broader. For  $E_c < E < E'_c$ , the states remain extended. At the energies  $E_c, E'_c$  they change abruptly from extended to localized states. So that for  $E < E_c$  and  $E > E'_c$  there are tails of localized states (Fig.1.3). The energies  $E_c$  and  $E'_c$  are called mobility edges.

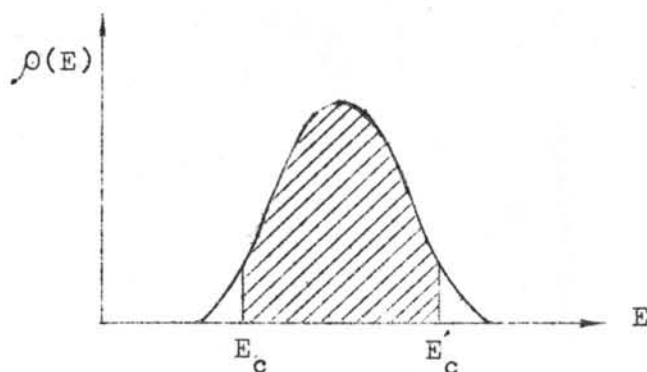


Fig.1.3 The density of states of an isolated energy band in a disordered material. There is a band of extended states inside the energies  $E_c$  and  $E'_c$  with tails of localized states outside.

To determine the existence of band gap in disordered materials, photon absorption can be used. The fact that glass is transparent shows that amorphous  $\text{SiO}_2$  has a band gap of several electron volts. The shape of the absorption edge indicates the way the density of states behaves near the band edges. The absorption coefficient  $\alpha(\omega)$  drops markedly at some threshold frequency  $\omega_0$  which is close to that of the crystalline materials. Two types of behavior are observed ; sharp edge and optical tail.

In the case of sharp edge,  $\alpha(\omega)$  is practically zero at  $\omega < \omega_0$ . For the existence of the tail  $\alpha(\omega)$  is approximated by an exponential function of frequency  $\omega$ , where  $\omega < \omega_0$

$$\alpha(\omega) \approx \exp\left(\frac{h(\omega - \omega_0)}{W}\right) \quad 1.2.4$$

$W$  is a characteristic energy

The d.c. conductivity at low temperature gives the most direct way of distinguishing between localized and extended states. An electron or hole in a localized state has zero mobility whereas the extended states have a finite mobility. The measurements of the Knight shift and of the nuclear relaxation time confirm the idea of the electron states in a gap as being localized.

### 1.3 Heavily Doped Semiconductors. 5-9

In pure semiconductor crystals, the periodic structure of ionic cores causes the energy spectrum of electronic structure of the crystals to form into continuous allowed bands separated by forbidden gaps. Edges of these bands are sharply cut - off. When impurities are introduced into the periodic crystal

the extra carriers (electrons for donor impurities and holes for accepters) would change the band structure. In the case of low concentration of impurities, the impurity atoms are far apart and there are no interaction between them. Each impurity form a localized state in an energy gap below a conduction band for donor level and above valence band for acceptor level (Fig.1.2).

To simplify the calculation, for example, of donor state the hydrogenic model is used to approximate the system of an individual impurity with an electron. For an isotropic material which dielectric constant  $\epsilon$ , the effect of host atoms can be crudely explained in terms of effective mass  $m_e^*$  of an electron. By solving the Schrödinger equation with hydrogenic Hamiltonian one obtain the donor state lying at an energy

$$E_d = \frac{m_e^* e^4}{2\hbar^2 \epsilon^2} \quad 1.3.1$$

below the conduction band edge. In the same maner an acceptor state lies at an energy

$$E_a = \frac{m_h^* e^4}{2\hbar^2 \epsilon^2} \quad 1.3.2$$

above the valence band edge.  $m_h^*$  is an effective mass of hole carrier.

As mention earlier, at sufficiently low concentration the states closely resemble individual impurity state. When the concentration,  $\bar{n}$ , is increased further the range of impurity potential can exceed the impurity separation. The localized states grow in spatial extention until some of

states have finite amplitude throughout the material. These impurity states broaden to form impurity band. A state broadens symmetrically above and below its original position and the values of  $E_d$  and  $E_a$  become smaller. Experimental results of reduction in these energies are shown in Fig.1.4. The ionization energies vanish in Ge and Si at different concentrations. Since in Si the impurity states are more highly localized, a greater impurity concentration is required in Si for the same wave overlap as in Ge.

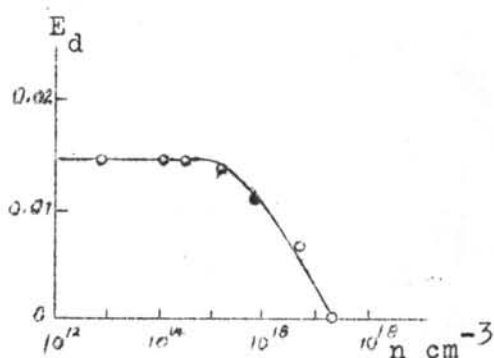


Fig.1.4a. Dependence of the ionization energy of donors in germanium on their concentration.

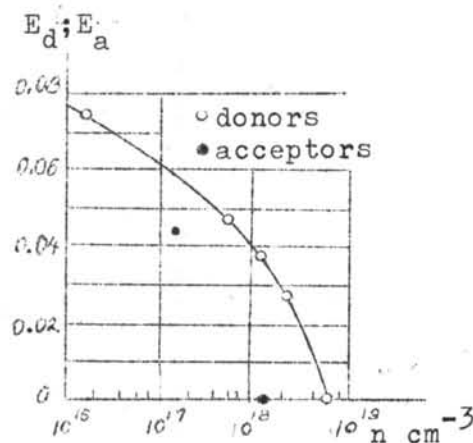


Fig.1.4b. Dependence of the ionization energies of donors and acceptors in silicon on their concentrations.

In real system the impurity atoms are distributed randomly. The random impurity potential has fluctuations of varying shape and size distributed throughout the semiconductor. These fluctuations produce localized tail states above and below the impurity band. Large fluctuations are less than small ones so a tail of density of states decreases away from the band edge.



Let us define the dimensionless quantity  $\bar{N}^{-1/3} a^*$ . This quantity directly relates to the average separation distance between impurity atoms as

$$\frac{r_s}{a^*} = \left(\frac{3}{4\pi}\right)^{1/3} \frac{1}{\bar{N}^{-1/3} a^*}, \quad 1.3.3$$

where  $a^*$  is an effective Bohr radius defined by

$$a^* = \frac{\hbar^2 \epsilon}{m^* e^2}. \quad 1.3.4$$

The calculation shows that the upper edge of impurity band merges into the unperturbed conduction band at  $\bar{N}^{-1/3} a^* \approx 0.18$  and the Fermi level enters the conduction band at  $\bar{N}^{-1/3} a^* \approx 0.43$ , hence a separated band model is not tenable at these doping levels.<sup>1</sup>

A quantitative theory is possible at higher impurity densities. The theory is usually based on the approximation of linear screening. The screened potential at any point is given by a superposition of individually screened Coulomb impurity potential. For linear screening the electron - impurity potential energy may be written as

$$V(\vec{r}) = \sum_i v(\vec{r} - \vec{R}_i), \quad 1.3.5$$

where

$$v(\vec{r} - \vec{R}_i) = \frac{-e^2}{\epsilon |\vec{r} - \vec{R}_i|} \exp \left[ -Q |\vec{r} - \vec{R}_i| \right] \quad 1.3.6$$

the screened Coulomb potential energy of electron at point  $\vec{r}$  respect to impurity at point  $\vec{R}_i$ . The reciprocal screening length is given in

the Thomas - Fermi approximation by

$$Q^2 = \frac{4\pi e^2}{\epsilon} \int_0^{\infty} \rho(E) \left( -\frac{\partial f}{\partial E} \right) dE \quad 1.3.7$$

where

$$f = \left\{ 1 + \exp \left[ \frac{E - E_f}{kT} \right] \right\}^{-1} \quad 1.3.8$$

is the Fermi - Dirac distribution function and  $\rho(E)$  is the band density of states. If the screening is due to electrons in several bands, or electrons and holes  $Q^2 = \sum_i Q_i^2$  where  $Q_i^2$  is calculated from (1.3.7) for each band. The effectiveness of carriers screening is determined by the relative magnitudes of the screening length and the effective Bohr radius. If  $Qa^* > 1$ , the screening is more effective and the effect of impurity potentials is less important. It should be noted that when  $\rho(E)$  is calculated it will depend on  $Q$  through the potential  $V(\bar{r})$ . Therefore  $Q$  and  $E_f$  for a given concentration  $N$  can be obtained in a self-consistent calculation<sup>6</sup>. However,  $Q$  can be approximated by using the unperturbed band density of states in (1.3.7) if the Fermi level is high above the band edge, Hence, the reciprocal screening length can be approximated as

$$Q^2 = 4 \left( \frac{3}{\pi} \right)^{1/3} \left( \frac{n}{a^*} \right)^{1/3} \quad 1.3.9$$

Note that, the screened Coulomb potential mentioned above contain crudely the exchange and correlation effects of the electron-electron interaction.

The calculation of  $\rho(E)$  can be approached in many ways.

However, by using a semiclassical approximation, Kane has calculated the density of states near the conduction band edge and obtained

$$\rho(E) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{3/2} n^{1/2} Y(E/n), \quad 1.3.10$$

where

$$Y(x) = \pi^{-1/2} \int_{-\infty}^x (x-\zeta)^{1/2} \exp(-\zeta^2) d\zeta \quad 1.3.11$$

The semiclassical approximation is a limitation on the accuracy of the theory. The tail states that calculated by this theorem are an over estimate.

Halperin and Lax<sup>8</sup> used a quantum mechanical theory to improve the accuracy of  $\rho(E)$ . They proposed that  $\rho(E)$  can be represent in the form of,

$$\rho(E) = C a(E) \exp(-b(E)/2\xi) \quad 1.3.12$$

C and  $\xi$  are constants.  $a(E)$  and  $b(E)$  can be evaluated in numerical table not analytic form. But the process of calculation is cumbersome since it involves solving the Hartree type equation.

Recently Sa-yakanit<sup>9</sup> has used the Feynman path integral technique to acheive an analytical form of  $\rho(E)$ . This work gives the same form of  $\rho(E)$  as propose by (1.3.12). This new approach can be used to evaluate Kane's equation (1.3.10) or gives numerical results the same values as calculated by Halperin and Lax by using appropriate conditions.