ABSORPTION

3

The most direct and perhaps the simplest method for probing the band structure of semiconductors is to measure the absorption spectrum. In the absorption process, a photon of a known energy excites an electron from a lower- to a higher-energy state. Thus by inserting a slab of semiconductor at the output of a monochromator and studying the changes in the transmitted radiation, one can discover all the possible transitions an electron can make and learn much about the distribution of states.

Therefore, in this chapter we shall review all the possible transitions: band-to-band, excitons, between subbands, between impurities and bands, transitions by free carriers within a band, and also the resonances due to vibrational states of the lattice and of the impurities. In the following two chapters we shall describe how various optical constants can be obtained, concluding with an illustration of the general experimental procedure for measuring absorption spectra. Absorption is expressed in terms of a coefficient $\alpha(hv)$ which is defined as the relative rate of decrease in light intensity $L(hv)$ along its propagation path:

$$\alpha = \frac{1}{L(hv)} \frac{d[L(hv)]}{dx}$$

3-A Fundamental Absorption

The fundamental absorption refers to band-to-band or to exciton transitions, i.e., to the excitation of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap of the semiconductor. However, because the transitions are subject to certain selection

rules, the estimation of the energy gap from the "absorption edge" is not a straightforward process—even if competing absorption processes can be accounted for.

Because the momentum of a photon, h/λ, (λ is the wavelength of light, thousands of angstroms), is very small compared to the crystal momentum h/a (a is the lattice constant, a few angstroms), the photon-absorption process should conserve the momentum of the electron. The absorption coefficient $\alpha(hv)$ for a given photon energy hv is proportional to the probability P_{if} for the transition from the initial state to the final state and to the density of electrons in the initial state, n_i, and also to the density of available (empty) final states, n_f, and this process must be summed for all possible transitions between states separated by an energy difference equal to hv:

$$\alpha(hv) = A \sum P_{if} n_i n_f \qquad (3-1)$$

In what follows, for simplicity we shall assume that all the lower states are filled and that all the upper states are empty, a condition which is true for undoped semiconductors at 0°K.

3-A-1 ALLOWED DIRECT TRANSITIONS

Let us consider absorption transitions between two direct valleys where all the momentum-conserving transitions are allowed (Fig. 3-1), i.e., the transition probability P_{if} is independent of photon energy. Every initial state at E_i is associated with a final state at E_f such that
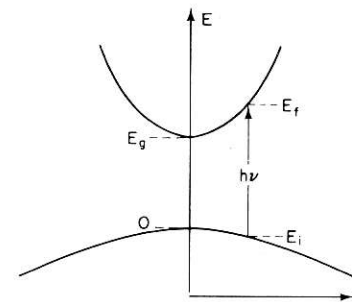
$$E_f = hv - |E_i|$$

Fig. 3-1

But in parabolic bands,

$$E_f - E_g = \frac{h^2 k^2}{2m_e^*}$$

and

$$E_i = \frac{h^2 k^2}{2m_h^*}$$

Therefore,

$$hv - E_g = \frac{h^2 k^2}{2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right)$$

The density of directly associated states can then be found as was done in Sec. 1-A-3:

$$N(hv)\, d(hv) = \frac{8\pi k^2\, dk}{(2\pi)^3}$$

$$= \frac{(2m_r)^{3/2}}{2\pi^2 \hbar^3}(hv - E_g)^{1/2}\, d(hv)$$

where m_r is the reduced mass given by $1/m_r = 1/m_e^* + 1/m_h^*$. Hence the absorption coefficient is

$$\alpha(hv) = A^*(hv - E_g)^{1/2} \tag{3-2}$$

where A^* is given by[1]:

$$A^* \approx \frac{q^2\left(2\dfrac{m_h^* m_e^*}{m_h^* + m_e^*}\right)^{3/2}}{nch^2 m_e^*} \tag{3-3}$$

For an index of refraction $n = 4$ and assuming the hole and electron effective masses equal the free electron mass, one gets

$$\alpha(hv) \approx 2 \times 10^4 (hv - E_g)^{1/2}\ \text{cm}^{-1}$$

hv and E_g being expressed in eV.

3-A-2 FORBIDDEN DIRECT TRANSITIONS

In some materials, quantum selection rules forbid direct transitions at $k = 0$ but allow them at $k \neq 0$, the transition probability increasing with k^2. In the model of Fig. 3-1 this means that the transition probability increases proportionately to $(hv - E_g)$. Since the density of states linked in direct transitions is proportional to $(hv - E_g)^{1/2}$, the absorption coefficient has the following spectral dependence:

$$\alpha(hv) = A'(hv - E_g)^{3/2} \tag{3-4}$$

where A' is given by[1]

$$A' = \frac{4}{3}\frac{q^2\left(\dfrac{m_h^* m_e^*}{m_h^* + m_e^*}\right)^{5/2}}{nch^2 m_e^* m_h^* hv} \tag{3-5}$$

Again, for $n = 4$ and $m_h^* = m_e^* = m$:

$$\alpha(hv) = 1.3 \times 10^4 \frac{(hv - E_g)^{3/2}}{hv}\ \text{cm}^{-1}$$

Note that the hv in the denominator varies slowly compared to $(hv - E_g)^{3/2}$.

[1] J. Bardeen, F. J. Blatt, and L. H. Hall, *Proc. of Atlantic City Photoconductivity Conference* (1954), J. Wiley and Chapman and Hall (1956), p. 146.

3-A-3 INDIRECT TRANSITIONS BETWEEN INDIRECT VALLEYS

When a transition requires a change in both energy and momentum, a double, or two-step, process is required because the photon cannot provide a change in momentum. Momentum is conserved via a phonon interaction as illustrated in Fig. 3-2. A phonon is a quantum of lattice vibration. Although a broad spectrum of phonons is available, only those with the required momentum change are usable. These are usually the longitudinal- and the transverse-acoustic phonons. Each of these phonons has a characteristic energy E_p. Hence to complete the transition E_i to E_f, a phonon is either emitted or absorbed. These two processes are given respectively by

$$\left.\begin{array}{l} hv_e = E_f - E_i + E_p \\ hv_a = E_f - E_i - E_p \end{array}\right\} \tag{3-6}$$
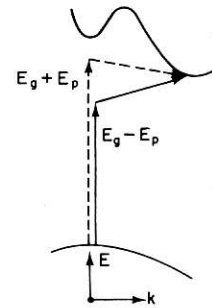

Fig. 3-2

In indirect transitions, all the occupied states of the valence band can connect to all the empty states of the conduction band. The density of initial states at an energy E_i is

$$N(E_i) = \frac{1}{2\pi^2 \hbar^3}(2m_h^*)^{3/2}\, |E_i|^{1/2} \tag{3-7}$$

The density of states at E_f is

$$N(E_f) = \frac{1}{2\pi^2 \hbar^3}(2m_e^*)^{3/2}(E_f - E_g)^{1/2}$$

Substituting Eq. (3-6),

$$N(E_f) = \frac{1}{2\pi^2 \hbar^3}(2m_e^*)^{3/2}(hv - E_g \mp E_p + E_i)^{1/2} \tag{3-8}$$

The absorption coefficient is proportional to the product of the densities of initial states given by Eq. (3-7) and final states given by Eq. (3-8) integrated over all possible combinations of states separated by $hv \pm E_p$; α is also proportional to the probability of interacting with phonons, which is itself

a function $f(N_p)$ of the number N_p of phonon of energy E_p. The number of phonons is given by Bose–Einstein statistics[2]:

$$N_p = \frac{1}{\exp\dfrac{E_p}{kT} - 1} \qquad (3\text{-}9)$$

Hence

$$\alpha(h\nu) = A f(N_p) \int_0^{-(h\nu - E_g \mp E_p)} |E_i|^{1/2} (h\nu - E_g \mp E_p + E_i)^{1/2}\, dE_i \qquad (3\text{-}10)$$

After integration and substituting Eq. (3-9) into (3-10), the absorption coefficient for a transition with phonon absorption is

$$\alpha_a(h\nu) = \frac{A(h\nu - E_g + E_p)^2}{\exp\dfrac{E_p}{kT} - 1} \qquad (3\text{-}11)$$

for $h\nu > E_g - E_p$. The probability of phonon emission is proportional to $N_p + 1$; hence the absorption coefficient for a transition with phonon emission is

$$\alpha_e(h\nu) = \frac{A(h\nu - E_g - E_p)^2}{1 - \exp\left(-\dfrac{E_p}{kT}\right)} \qquad (3\text{-}12)$$

for $h\nu > E_g + E_p$.

Since both phonon emission and phonon absorption are possible when $h\nu > E_g + E_p$, the absorption coefficient is then

$$\alpha(h\nu) = \alpha_a(h\nu) + \alpha_e(h\nu) \qquad (3\text{-}13)$$
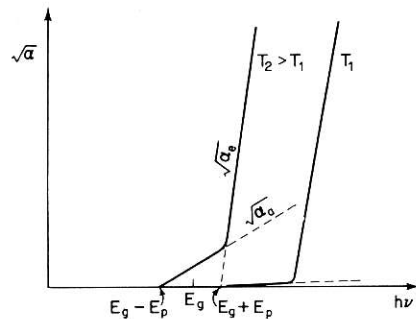
for $h\nu > E_g + E_p$.

Fig. 3-3

[2]S. Wang, *Solid State Electronics*, McGraw-Hill (1966), p. 46.

At very low temperatures, the phonon density is very small [large denominator in Eq. (3-11)]; therefore, α_a is also small. The temperature dependences of α_a and α_e are illustrated in Fig. 3-3, where the square root of α is plotted to yield a linear dependence on $h\nu$. Such a plot, by extrapolation to $\alpha = 0$, gives the values of $E_g - E_p$ and $E_g + E_p$. Note that E_g has been shifted with temperature to reflect the temperature dependence of the energy gap.

As mentioned earlier, there are several types of phonons, one longitudinal-acoustic and two transverse-acoustic, which can participate in the transition process. In fact, they all participate, but with different probabilities.[3]

If the semiconductor is heavily doped, the Fermi level is inside the band (the conduction band in an n-type material) by a quantity ξ_n (Fig. 3-4). Since
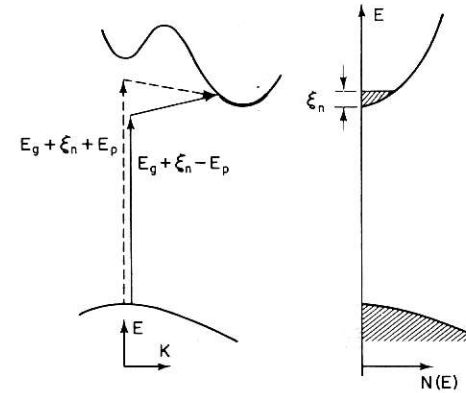

Fig. 3-4 Energy–momentum diagram for degenerate n-type germanium in the [111] direction. Two phonon-assisted transitions are shown to illustrate the usual photon absorption mechanism.

the states below ξ_n are already filled, fundamental transitions to states below $E_g + \xi_n$ are forbidden; hence the absorption edge should shift to higher energies by about ξ_n. The shift of the absorption edge due to band filling is sometimes called the Burstein–Moss shift.[4,5] A calculation of the absorption coefficient was made for heavily doped n-type germanium[6]; the results are reproduced in Fig. 3-5. At 0°K, only the phonon-emission process is possible; $\sqrt{\alpha_e}$ for pure germanium intercepts the abscissa at $E_g + E_p$. The calculated intercept shifts by ξ_n, as expected. The drop of absorption at a given $h\nu > E_g + E_p + \xi_n$ with increasing doping is due to the decrease in the number of available final states.

[3]G. G. MacFarlane, T. P. McLean, J. E. Quarrington, and V. Roberts, *Phys. Rev.* **108**, 1137 (1957) and **111**, 1245 (1958).
[4]E. Burstein, *Phys. Rev.* **93**, 632 (1954).
[5]T. S. Moss, *Proc. Phys. Soc.* (London) **B76**, 775 (1954).
[6]J. I. Pankove and P. Aigrain, *Phys. Rev.* **126**, 956 (1962).