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Introductory concepts

Many photoelectric phenomena are describable in terms of a set of basic concepts involving electron activity in semiconductors. These include optical absorption by which free carriers are created, electrical transport by which free carriers contribute to the electrical conductivity of the material, and the capture of free carriers leading either to recombination or trapping.

1.1 Overview

These effects are illustrated in Figure 1.1. Intrinsic optical absorption in Figure 1.1(*a*) corresponds to the raising of an electron from the valence band to the conduction band. Extrinsic optical absorption corresponds to the raising of an electron from an imperfection to the conduction band as in Figure 1.1(*b*), or the raising of an electron from the valence band to an imperfection in Figure 1.1(*c*).

Optical absorption is described quantitatively through the absorption constant α. In the simplest case, neglecting reflection or interference effects, if light of intensity I_0 is incident on a material of thickness d with absorption constant α, the intensity of the transmitted light I is given approximately by Beer's Law,

$$I = I_0 \exp(-\alpha d) \tag{1.1}$$

A free electron may be captured at an imperfection as in Figure 1.1(*d*), or a free hole may be captured at an imperfection as in Figure 1.1(*e*). The capture process is described through a capture coefficient β such that the rate of capture R of a species with density n by a species with density N is given by

$$R = \beta n N \tag{1.2}$$

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The capture coefficient β is often expressed as the product of a capture cross section S and the average thermal velocity v of the free carrier.

$$\beta = \langle S(E)v(E)\rangle = Sv \tag{1.3}$$

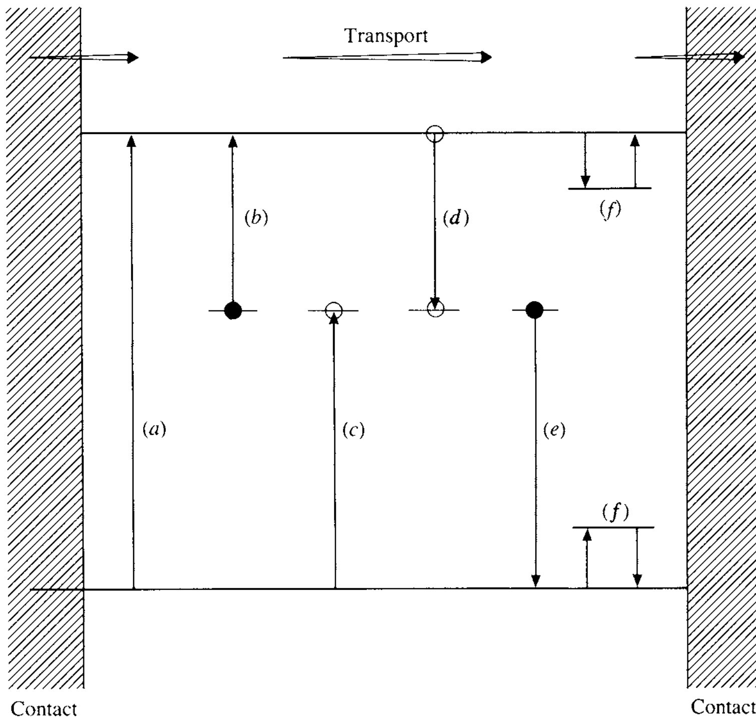
where the implied averages are over electron energy. The magnitude of β depends on the details of the capture process.

When capture of an electron (or hole) leads to recombination with a hole (or electron), a recombination process has occurred. The lifetime of a free carrier, τ, i.e., the average time the carrier is free before recombining, is given by

$$\tau = 1/\beta N \tag{1.4}$$

Comparison with Eq. (1.2) shows that the rate of capture (in this case the rate of recombination) is equal to n/τ. Since in steady state the rate of recombination must be equal to the rate of excitation G (per

Figure 1.1. Major transitions and phenomena associated with photoelectronic effects in homogeneous semiconductors. (*a*) intrinsic absorption, (*b*) and (*c*) extrinsic absorption, (*d*) and (*e*) capture and recombination, (*f*) trapping and detrapping.



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unit volume per second), we have the basic relationship that

$$n = G\tau \tag{1.5}$$

This is a fundamental relationship in the discussion of all photoelectronic phenomena. It has the characteristic of a basic truism, applicable to many different types of situations, stating that the average density (m^{-3}) of a species present at a given time is given by the product of the rate at which the species is being generated ($m^{-3}\,s^{-1}$) multiplied by the average lifetime of a member of the species (s). If more than one type of recombination process is present, the individual recombination rates add.

A captured carrier at an imperfection may do one of two things: (i) recombine with a carrier of the opposite type, as just described, or (ii) be thermally reexcited to the nearest energy band before recombination occurs. In the latter case the imperfection is referred to as a trap, and the capture and release processes are called trapping and detrapping. Figure 1.1(f) shows such a trapping and detrapping situation. If R_c is the capture rate of free carriers with density n by imperfections with density N, such that $R_c = \beta n N$, and if R_d is the thermal detrapping rate given by $n_t \nu \exp(-\Delta E/kT)$, where n_t is the density of trapped carriers, ν is a characteristic 'attempt to escape frequency,' and ΔE is the activation energy for detrapping, then the imperfection acts like a recombination center if $R_c > R_d$ but like a trap if $R_c < R_d$. We develop these concepts more completely later.

The physical situation of electrical current flow under illumination pictured in Figure 1.1 involves two other considerations: the effect of the contacts, and the nature of the transport of free carriers. Both of these must be considered in further detail.

The ability of the contacts to replenish carriers to maintain charge neutrality in the material (properties of an ohmic contact) if carriers are drawn out of the opposite contact by an electric field plays a key role in determining the kind of phenomena observed. The general effect of electrical contacts between a metal and a semiconductor under illumination can be described in terms of three classes of behavior: (a) blocking contacts, (b) ohmic contacts, and (c) injecting contacts. The characteristic dependence of current on applied voltage for these three types of contacts is shown in Figure 1.2. A qualitative description of the phenomena given below is followed by a more quantitative discussion in Section 1.4.

A blocking contact as in Figure 1.2(a) is unable to replenish carriers created by photoexcitation when they are drawn out of the material by

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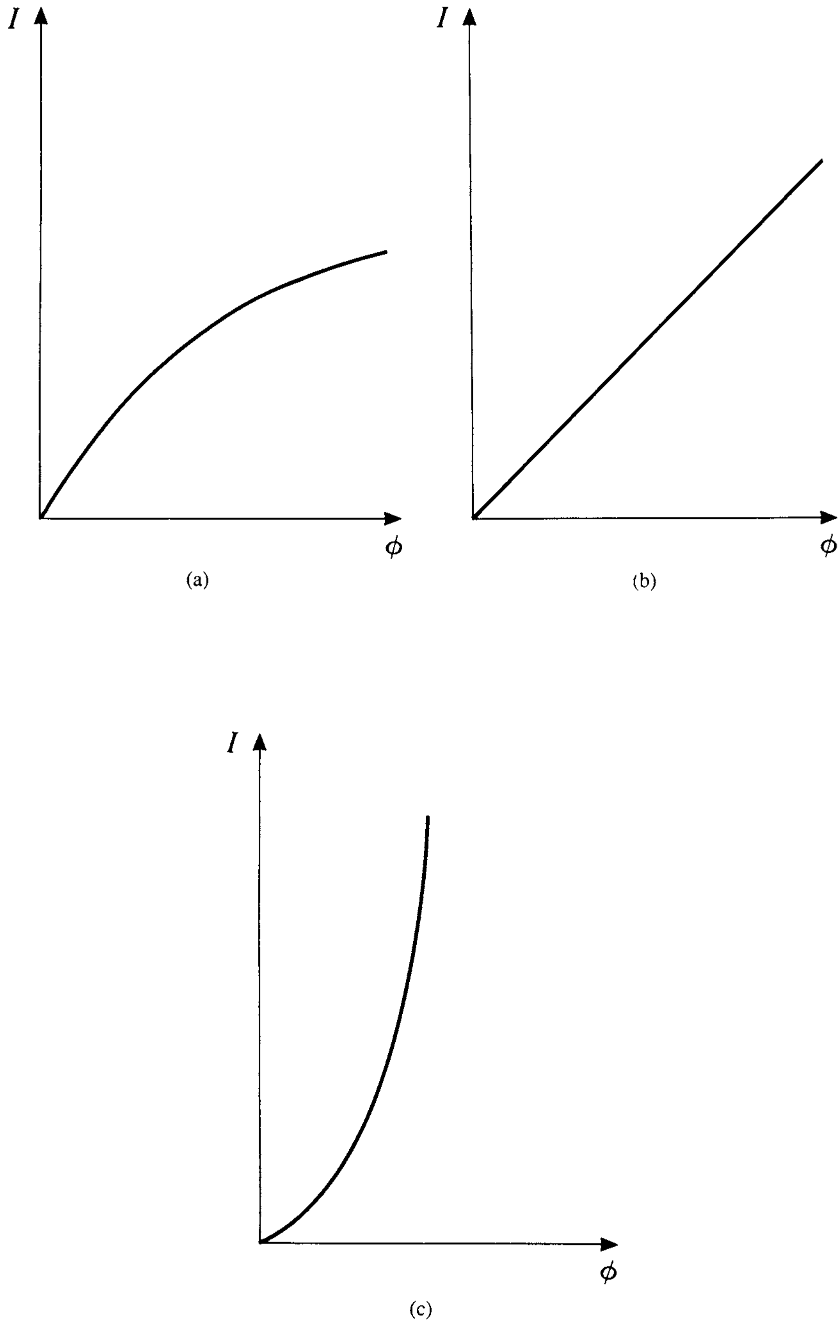
Figure 1.2. Major variations of current with applied voltage for (*a*) a blocking contact, (*b*) an ohmic contact, and (*c*) an injecting contact.



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an applied electric field. The current varies less than linearly with applied voltage, and may become saturated.

An ohmic contact as in Figure 1.2(*b*) is able to replenish carriers created by photoexcitation when they are drawn out of the material by an applied electric field. The contacts contribute negligible electrical resistance, and current varies linearly with applied voltage with a slope equal to the reciprocal of the resistance of the bulk semiconductor.

An injecting contact as in Figure 1.2(*c*) is an ohmic contact at low applied electric fields that is being operated under sufficiently high applied electric field that carriers drawn in from the contact have time to cross the material in the electric field before the material is able to achieve charge neutrality by dielectric relaxation. The result is a regime in which the material is not electrically neutral, and the current flow is called 'space-charge-limited.'

The actual transport process, as usually described in terms of scattering effects or carrier mobility, determines how the change in free carrier density due to illumination affects the actual electrical conductivity. The total current density $\mathbf{J}_{\text{tot}}$ can be expressed as the sum of a drift current $\mathbf{J}_{\text{dr}}$ and a diffusion current $\mathbf{J}_{\text{df}}$:

$$\mathbf{J}_{\text{tot}} = \mathbf{J}_{\text{dr}} + \mathbf{J}_{\text{df}} \tag{1.6}$$

The drift current due to free electrons, for example, is given by

$$\mathbf{J}_{\text{drn}} = \sigma_{\text{n}} \mathscr{E} \tag{1.7}$$

where σ_{n} is the electrical conductivity, $\sigma = nq\mu_{\text{n}}$ for conductivity due to electrons, with n the density of free electrons, q the charge per electron, and μ_{n} the electron mobility, and $\mathscr{E}$ is the electric field. The mobility can be written as

$$\mu_{\text{n}} = (q/m_{\text{n}}^*)\tau_{\text{sc}} \tag{1.8}$$

where m_{n}^* is the effective mass of the electron and τ_{sc} is the scattering relaxation time for electrons, the average time between electron scattering events.

The electron drift current can also be written as

$$\mathbf{J}_{\text{drn}} = nq\mathbf{v}_{\text{dn}} \tag{1.9}$$

where $\mathbf{v}_{\text{dn}}$ is the electron drift velocity, such that

$$\mathbf{v}_{\text{dn}} = \mu_{\text{n}} \mathscr{E} \tag{1.10}$$

The electron diffusion current can be expressed as

$$\mathbf{J}_{\text{dfn}} = qD_{\text{n}}\nabla n \tag{1.11}$$

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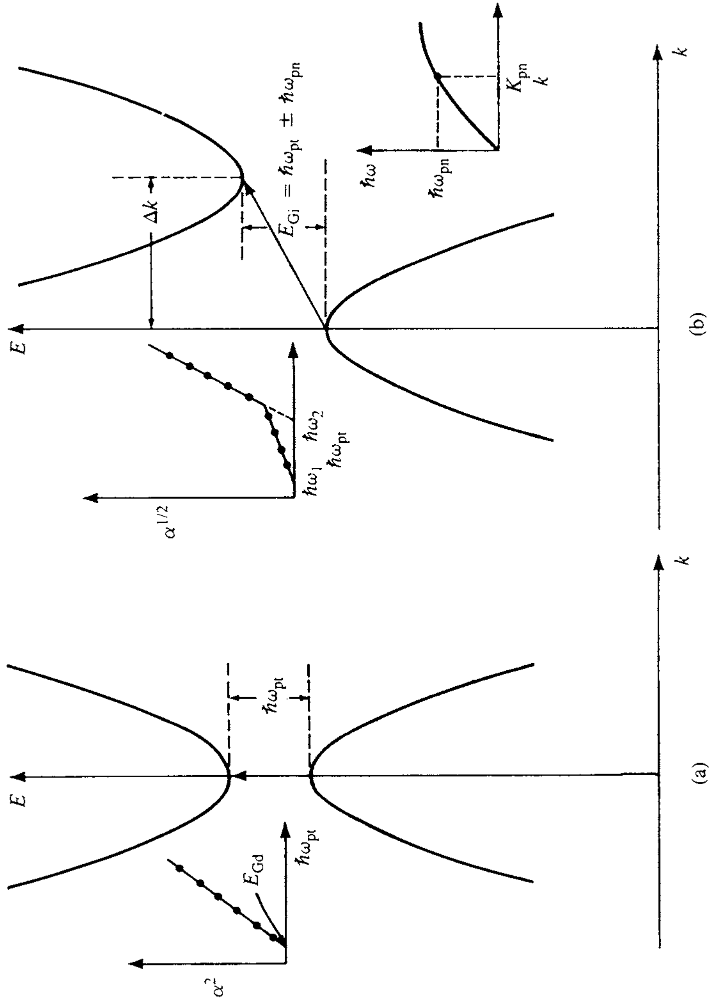

Figure 1.3. (*a*) Intrinsic direct absorption, and (*b*) intrinsic indirect absorption. Inserts show the variation of absorption constant α with photon energy $\hbar\omega_{pt}$ expected for each type of absorption, and a typical phonon dispersion curve for the indirect material involving a phonon in the transition with energy $\hbar\omega_{pn}$ and wavevector K_{pn}.

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where the electron diffusion coefficient D_n is given by

$$D_n = \mu_n kT/q \tag{1.12}$$

1.2 Intrinsic optical absorption

Intrinsic optical absorption corresponds to photoexcitation of an electron from the valence band to the conduction band. If the minimum of the conduction band is at the same point in **k**-space as the maximum of the valence band, as shown in Figure 1.3(*a*), a vertical transition occurs involving only the absorption of a photon. Such a transition is called a direct optical transition. The minimum photon energy for absorption $\hbar\omega_{min} = E_{Gd}$, where E_{Gd} is the direct bandgap of the material, and the change in k upon making a transition $\Delta k = K_{photon} \approx 0$. This is because the momentum associated with the photon is very small (of the order of 1/500) compared to the width of the Brillouin zone and can be effectively neglected.

If the minimum of the conduction band is at a different point in **k**-space from the maximum of the valence band, as shown in Figure 1.3(*b*), an optical transition from the top of the valence band to the bottom of the conduction band must involve the absorption of a photon and a simultaneous absorption or emission of a phonon. In this case $E_{Gi} = \hbar\omega_{min} \pm E_{phonon}$, where E_{Gi} is the indirect bandgap of the material and E_{phonon} is the energy of the phonon involved in the process; a positive sign corresponds to phonon absorption, and a negative sign to phonon emission. The change in k upon an indirect optical absorption is given by $\Delta k = K_{phonon}$.

To calculate the magnitude of the absorption constant α associated with an intrinsic optical transition, a quantum mechanical perturbation calculation must be carried out in which the effect of the light is treated as a perturbation in the basic Schroedinger equation.[1] For a direct transition, the transition probability depends only on the square of the matrix element involving the interaction of the light with the electrons, and is hence a first-order process. The final result is a variation of α for photon energies $\hbar\omega \geq E_{Gd}$ corresponding to

$$\alpha^2 = (\hbar\omega - E_{Gd}) \tag{1.13}$$

so that a plot of α^2 vs $\hbar\omega$ gives a straight line with intercept of E_{Gd}, as shown in Figure 1.3(*a*). Direct optical transitions are characterized by a rapid increase in α for $\hbar\omega > E_{Gd}$ to values of the order of 10^6–$10^7\ \mathrm{m}^{-1}$, so that only a thin film of the material is required to absorb most of the light.

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Quantum mechanical calculation of α for indirect optical transitions gives a transition probability that is proportional to the product of the square of the matrix element for photon–electron interaction and the square of the matrix element for phonon–electron interaction. The actual form of α is given by

$$\alpha \propto \langle n \rangle (\hbar\omega + E_{pn} - E_{Gi})^2 + (1 + \langle n \rangle)(\hbar\omega - E_{pn} - E_{Gi})^2 \tag{1.14}$$

where

$$\langle n \rangle = [\exp(E_{pn}/kT) - 1]^{-1} \tag{1.15}$$

is the Bose–Einstein distribution. The first term in Eq. (1.14) corresponds to optical absorption with absorption of a phonon, and the second to optical absorption with emission of a phonon. The magnitude of the αs obtained are smaller than for direct absorption since they correspond to a second-order process. The magnitudes of α for photon energies slightly larger then E_{Gi} are of the order of $10^4\ \mathrm{m}^{-1}$. A plot of $\alpha^{1/2}$ vs $\hbar\omega$, as shown in Figure 1.3(b), consists of two straight lines, one corresponding to absorption of a phonon, and the other to emission of a phonon. If these two straight lines intersect the $\hbar\omega$ axis at $\hbar\omega_1$ and $\hbar\omega_2$ with $\hbar\omega_1 < \hbar\omega_2$, $E_{Gi} = (\hbar\omega_1 + \hbar\omega_2)/2$ and $E_{pn} = (\hbar\omega_2 - \hbar\omega_1)/2$.

A specific example is given in Figure 1.4 for the case of Ge at 300 K that has both a direct bandgap at $\mathbf{k} = 0$ and an indirect bandgap with conduction band minimum at the (111) zone face. $E_{Gi} = 0.68$ eV and for $E < 0.8$ eV, the value of α is less than or equal to $10^4\ \mathrm{m}^{-1}$; $E_{Gd} = 0.81$ eV and for $E > 0.8$ eV, the value of α is about $10^6\ \mathrm{m}^{-1}$. If the penetration depth d is defined as $1/\alpha$, effectively the distance over which the intensity is reduced by a factor of e, then d is about 100 μm for the indirect absorption range, and 1 μm for the direct absorption range.

Several critical effects dependent on the type of intrinsic optical excitation may be summarized as follows.

(1) For a direct bandgap material (such as GaAs or CdTe) optical absorption occurs near the surface of a material; for an indirect bandgap material (such as Si or GaP) light penetrates much deeper into the material.

(2) For direct bandgap materials, the magnitude of the intrinsic photoconductivity (defined as the increase in conductivity caused by intrinsic absorption) depends critically on the surface lifetime; in indirect materials the surface lifetime is much less important.

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(3) If a direct bandgap material is used in a p–n junction type of device where junction collection of photoexcited carriers is important, a shorter diffusion length L ($L = (D\tau)^{1/2}$) is required for carrier collection by the junction; in an indirect material a larger L is necessary if all of the photoexcited carriers are to be collected.

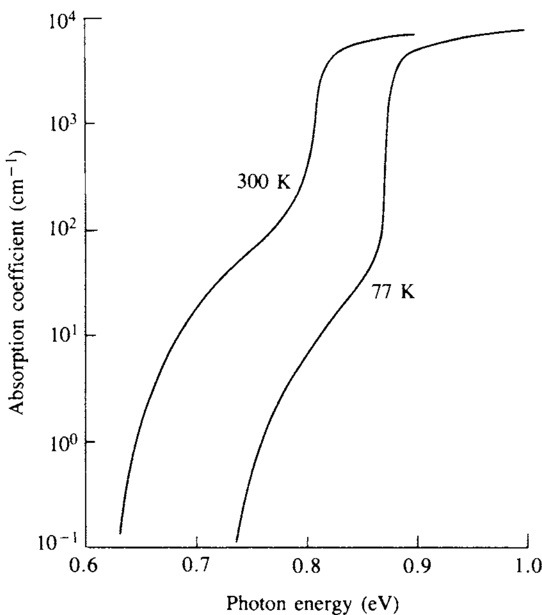
(4) Direct bandgap materials have a higher intrinsic luminescence efficiency associated with a recombination of electrons and holes with emission of photons because of a shorter value of radiative recombination lifetime; indirect materials have a lower intrinsic luminescence efficiency, since the longer lifetime for radiative recombination allows competing processes for non-radiative recombination to become important.

1.3 Extrinsic optical absorption

Absorption involving imperfections is called extrinsic optical absorption. The absorption constant is proportional to the density of absorbing centers N,

$$\alpha = S_0 N \tag{1.16}$$

Figure 1.4. Dependence of absorption constant on photon energy for Ge. (After W. C. Dash and R. Newman, *Phys. Rev.* **99,** 1151 (1955).)



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with a proportionality constant S_0 that is called the optical cross section for the absorption process. The magnitude and dependence on photon energy of S_0 have been calculated by a variety of quantum mechanical approximations.

Two extreme cases may be considered: (i) the case of an imperfection with a small ionization energy (a shallow imperfection) for which the uncertainty in position of a bound carrier Δx is large, yielding a small uncertainty in Δk; and (ii) the other extreme of an imperfection with a large ionization energy (a deep imperfection) for which the wavefunction of the bound carrier is localized and the uncertainty Δk is large.

A hydrogenic model can be applied to the case of a shallow imperfection in the electric dipole approximation, assuming a transition from a ground state like that of hydrogen to a final state consisting of a plane wave. The ionization energy of the imperfection E_I can be expressed in terms of the ionization energy of the hydrogen atom E_H, the effective mass of the free carriers m^*, the free carrier mass m_0 and the dielectric constant of the material ϵ, as

$$E_I = E_H[(m^*/m_0)/\epsilon^2] \tag{1.17}$$

and the dependence of S_0 on photon energy is given by

$$S_0(\hbar\omega) \propto (\hbar\omega - E_I)^{3/2}/(\hbar\omega)^5 \tag{1.18}$$

which increases rapidly for $\hbar\omega > E_I$ and shows a relatively sharp maximum for $\hbar\omega = (10/7)E_I$.

A variety of models has been developed to treat the case of deep imperfections.[2] The simplest of these is the delta function model for the imperfection potential that leads to

$$S_0(\hbar\omega) \propto (\hbar\omega - E_I)^{3/2}/(\hbar\omega)^3 \tag{1.19}$$

which increases rapidly for $\hbar\omega > E_I$ and shows a relatively broad maximum for $\hbar\omega = 2E_I$.

The magnitude of S_0 at the maximum for a variety of models lies between 10^{-19} and 10^{-21} m^2 with a value of about 10^{-20} m^2 being a reasonable approximation in most cases.

1.4 Electrical contacts

In order to make measurements of the free carrier density or the electrical conductivity in a semiconductor, it is ordinarily necessary to make electrical contact to the material, usually with metallic contacts. Alternative methods exist, to be sure, such as measurements

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