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# Effects of Radiation on Semiconductors

EFFECTS OF RADIATION ON SEMICONDUCTORS

DEISTVIE IZLUCHENII NA POLUPROVODNIKI

ДЕЙСТВИЕ ИЗЛУЧЕНИЙ НА ПОЛУПРОВОДНИКИ

# EFFECTS

# OF RADIATION

# ON SEMICONDUCTORS

by

Viktor Sergeevich Vavilov

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$$\left(\frac{c}{b}\right)$$

# PREFACE

The effects of electromagnetic radiation and high-energy particles on semiconductors can be divided into two main processes: (a) the excitation of electrons (the special case is internal ionization, i.e., the generation of excess charge carriers); and (b) disturbance of the periodic structure of the crystal, i.e., the formation of "structural radiation defects." Naturally, investigations of the effects of radiation on semiconductors cannot be considered in isolation. Thus, for example, the problem of "radiation defects" is part of the general problem of crystal lattice defects and the influence of such defects on the processes occurring in semiconductors. The same is true of photoelectric and similar phenomena where the action of the radiation is only the start of a complex chain of nonequilibrium electron processes. Nevertheless, particularly from the point of view of the experimental physicist, the radiation effects discussed in the present book have interesting features: several types of radiation may produce the same result (for example, ionization by photons and by charged particles) or one type of radiation may produce several effects (ionization and radiation−defect formation).

The aim of the author was to consider the most typical problems. The subjects discussed differ widely from one another in the extent to which they have been investigated. An example of a relatively intensively investigated problem is the absorption of infrared radiation by semiconductors − extensive experimental data being available at least for some substances, and theoretical interpretations being available for the majority of cases. An example of an important but neglected problem is the formation and physical nature of the radiation defects in semiconductors. The results of the studies of radiation effects in semiconductors are not only of scientific value but are also essential to the successful solution of several important practical problems, such as:

    a. the direct conversion of solar and nuclear radiation energy into electrical power;

    b. the recording of weak infrared radiation fluxes;

    c. the design of new electromagnetic radiation sources (masers and lasers) using semiconductors;

    d. the counting and determination of the energy and total flux of fast particles and gamma-ray quanta;

    e. the application of semiconductor electronics to nuclear power.

    The solution of each of these problems necessarily involves subjects far removed from the physics of semiconductors. In recent years, several monographs and reviews of Soviet and foreign authors, presenting the advances made toward the solution of these problems, have appeared in the USSR [1-9].

    The contents of the present book reflect to a considerable extent the interests of a team of workers studying the effects of radiation on semiconductors at the P. N. Lebedev Physics Institute of the USSR Academy of Sciences and the author's experience of lecturing to the senior students of the physics faculty of the M. V. Lomonosov Moscow State University.

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*Chapter I*


# ABSORPTION OF LIGHT BY SEMICONDUCTORS


## §1.  Optical Constants of Semiconductors
### and Methods of Determining Them


The absorption of light * by semiconductors and dielectric crys-
tals may be accompanied by photoionization, i.e., the generation
of excess densities of electrons and holes in the conduction and
valence bands, and by electron transitions to excited states.  It
may also be accompanied by other processes (the excitation of
lattice vibrations, interband electron transitions, etc.), but from
the point of view of the problems to be discussed later, it is the
former processes, especially photoionization, that are particular-
ly interesting.

Electrons in a crystal may be divided into the following groups
depending on the nature of their interaction with electromagnetic
radiation:

a.  electrons  in the valence band;

b.  charge carriers (electrons in the conduction band and
holes in the valence band);

c.  electrons localized at defect or impurity levels;

d.  electrons of the inner shells of atoms.

The optical properties of a material are represented by the
refractive index n and the absorption index $\varkappa$, which is also known
as the extinction coefficient.  We shall restrict ourselves to a dis-
cussion of nonmagnetic isotropic media whose permittivity $\varepsilon$ and
conductivity $\sigma$ are scalars.  The value of $\varepsilon$ is found from the ex-
pression

$$\varepsilon = n^2 - \varkappa^2 = 1 + 4\pi\chi. \qquad (1.1)$$

The susceptibility $\chi$ is related to polarization.  Usually,

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*Here, the term "light" represents electromagnetic radiation over a wide range of
wavelengths.
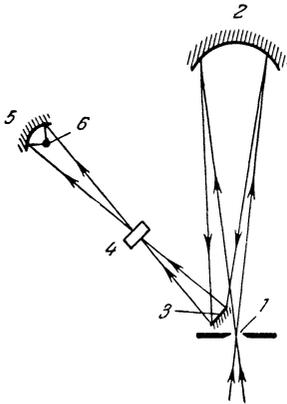
Fig. 1. Measurement of optical transmission in a sample with plane surfaces. 1) Monochromator slit; 2) spherical mirror; 3) plane mirror; 4) sample; 5) elliptical mirror; 6) radiation receiver.

$$\varepsilon \approx n^2, \quad \text{since} \quad n^2 \gg \varkappa^2. \qquad (1.2)$$

The conductivity $\sigma$, which governs the absorption of energy, is given by the formula

$$\sigma = n\varkappa\nu, \qquad (1.3)$$

where $\nu$ is the frequency.*

The experimentally determined absorption coefficient $\alpha$ is related to the absorption index $\varkappa$ by the expression

$$\varkappa = 4\pi\varkappa\frac{\nu}{c} = 4\pi\varkappa\bar{\nu}, \qquad (1.4)$$

where $\bar{\nu} = \nu/c$ is the wave number in cm$^{-1}$.

Data on the optical constants n, $\alpha$, and $\kappa$ are obtained by investigating the transmission of light by the test material, or its reflectivity R. A simple method for making optical measurements on samples of crystals with polished surfaces is shown in Fig. 1. The measured quantity is the transmission T = $I/I_0$, i.e., the ratio of the intensities of the incident $I_0$ and transmitted I light beams. For monochromatic radiation of wavelength $\lambda$

$$T = \frac{I}{I_0} = \frac{(1-R)^2 + 4R\cdot\sin^2\psi}{e^{\alpha d} + R^2 e^{-\alpha d} - 2R\cos 2(\varphi+\psi)}, \qquad (1.5)$$

where d is the sample's thickness, and the values of the angles $\varphi$ and $\psi$ are given by the formulas:

$$\varphi = \frac{4\pi nd}{\lambda}, \quad \psi = \tan^{-1}\frac{2\varkappa}{n^2+\varkappa^2+1}.$$

The term $2R\cos 2(\varphi+\psi)$ represents the interference in a plate-shaped sample. The formula (1.5) also allows for multiple reflection from the surfaces. If we use samples of sufficient thickness or light covering a wide range of the spectrum $\Delta\lambda$, we can avoid interference and use the simple formula

*The conductivity $\sigma$ depends on the optical frequency $\nu$ and, in general, it is not equal to the conductivity $\sigma_0$ at zero or low frequencies.

$$T = \frac{I}{I_0} = \frac{(1-R)^2}{e^{\alpha d} - R^2 e^{-\alpha d}}. \qquad (1.6)$$

The above formula allows for multiple internal reflections, which are important when the transparency and reflectivity are high. The reflectivity of a clean surface, R, for normal incidence is given by the formula

$$R = \frac{(n-1)^2 + \varkappa^2}{(n+1)^2 + \varkappa^2}. \qquad (1.7)$$

Under real conditions, the reflectivity may depend strongly on the state of the surface, in particular on the presence of thin oxide films. To determine the value of $\alpha$, it is convenient to eliminate R by carrying out measurements on samples of different thickness but having the surface treated in the same way. The value of n may be obtained from measurements of the reflectivity or of the interference in thin plates [2].

When the absorption of light by crystals is sufficiently weak, the value of the refractive index, which really represents the volume properties, is found by shaping a given material into a prism and measuring the deviation of a light beam which passes through it [3].

Table 1 gives values of n and $\varepsilon$ for elements of group IV of Mendeleev's table and some intermetallic compounds of the $A_3B_5$ type.

It follows from Eq. (1.7) that in the absence of absorption the transmission of a plane-parallel plate is governed by the value of n.

## § 2.    "Intrinsic" Optical Absorption Band (Fundamental Band)

The existence in all semiconductors of a wide spectral region of very intense absorption, limited on the long-wavelength side by a sharp edge, is due to the fact that the absorption of photons of sufficiently high energy is accompanied by electron transitions from the valence to the conduction band.

In the case of covalent crystals or crystals with weak ionic binding, light of frequency $\nu < (E_g/h)$, where $E_g$ is the "thermal" width of the forbidden band (gap), passes through pure crystals without causing photoionization.

TABLE 1.   Refractive Indices n and Permittivities
ε of Some Semiconductors

| Substance | n | ε | Substance | n | ε |
|-----------|-----|------|-----------|--------|------|
| Diamond | 2.417 | 5.9 | InSb | 3.988• | 15.9 |
| Si | 3.446 • | 11.8 | GaP | 2.97† | 8.4 |
| Ge | 4.006• | 16.0 | GaAs | 3.348• | 11.1 |
| InP | 3.37† | 10.9 | GaSb | 3.748• | 14.0 |
| InAs | 3.428• | 11.7 | AlSb | 3.188• | 10.1 |

•Prism method.
† Reflection data [4].

The readily observed increase in the absorption coefficient
for photons of energies $h\nu > E_g$ allows us to estimate the value
of the forbidden bandwidth.  The nature of the absorption increase
with increasing photon energy, i.e., the shape of the absorption
band edge, is governed by the electron energy-band structure of
the semiconductor.  Absorption processes competing with the "in-
trinsic" absorption and the difficulty of determining exactly small
values of $\alpha$ (beginning with fractions of 1 cm$^{-1}$ or less) usually
prevent us from obtaining very exact values of $E_g$ from the data
on the absorption of light by crystals.  On the other hand, an ap-
proximate value of $E_g$ obtained by this method is reliable and the
method itself is valuable, because of its simplicity, in the initial
studies of new semiconducting materials (an accurate optical meth-
od for determining $E_g$ from the fine structure of the recombina-
tion radiation spectra will be described later, in Chapt. IV).

It is known that in ionic crystals the thermal and optical for-
bidden bandwidths are different.  The optical excitation energy
in these crystals is found to be greater than the thermal excita-
tion energy [5].  This condition can be explained qualitatively
using the Franck-Condon principle, according to which the ex-
cess energy of a system which has absorbed a photon is trans-
formed into the energy of lattice vibrations, in a time considerably
longer than the duration of the act of absorption.

The expression for the absorption coefficient, corresponding
to an electron transition from a state i in the valence band to a
state $f$ in the conduction band without phonon participation, has
the form

$$\alpha = \frac{c}{\nu} |P_{if}|^2 N(h\nu), \tag{1.8}$$

where c is a constant representing the medium, and  N(hν) is the density distribution of the final states over an interval of unit energy.  The matrix element  representing transitions of this type is

$$P_{if} = -i\hbar \int \psi_f^* e_k \,\text{grad}\, \psi_i \, d\tau,$$ (1.9)

where $e_k$ is the polarization vector of radiation with the wave vector **k**; $i = \sqrt{-1}$.  Following Bloch, we can write the wave functions of electrons in the following form:

$$\psi_{kn} = e^{ikr} U_{kn}(r),$$ (1.10)

where $U_{kn}$ are periodic functions with the same period as the lattice, we find that $P_{if}$ vanishes at any point where the following selection rule is not satisfied

$$\boldsymbol{k}_i + \boldsymbol{k} = \boldsymbol{k}_f.$$ (1.11)

Since the wave vectors of an electron in its initial and final states are much greater than the wave vector of a photon, the above selection rule can be expressed also as

$$\boldsymbol{k}_i \approx \boldsymbol{k}_f.$$ (1.12)

Thus, in agreement with the law of conservation of momentum, only the "vertical" transitions without any change in the wave vector are allowed.

A careful study of the fundamental band edge of germanium single crystals, carried out on samples whose thickness was in some cases a fraction of a micron, allowed us to detect the structure shown in Fig. 2 [6].  By the time these experimental results were obtained, it had been shown – by the cyclotron resonance method – that the bottom of the conduction band in germanium crystals did not correspond to the electron wave vector **k** = 0.  The band structure of germanium was calculated theoretically by Herman, whose results are shown schematically in Fig. 3 [7].  In accordance with the above selection rule and Herman's data, the energy threshold for the vertical transitions should correspond to the frequency
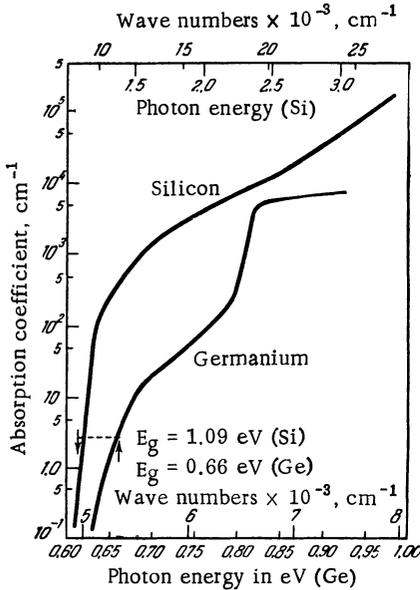
$$\nu' = \frac{1}{h}(E_c' - E_v),$$

Fig. 2. Edge of the fundamental optical absorption band of germanium and silicon single crystals at 300°K [1].
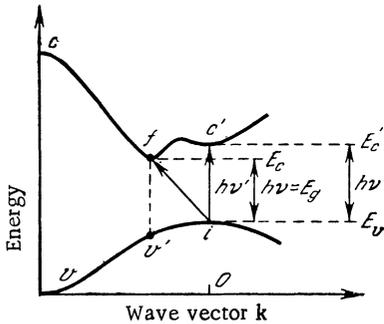


Fig. 3. Energy-band structure of a germanium crystal: v valence band; c conduction band. The complex structure of the valence band is not shown.

which is considerably higher than

$$\nu = \frac{E_g}{h} = \frac{1}{h}(E_c - E_v).$$

However, it is evident from the experimental curve (Fig. 2) that the absorption of a pure germanium single crystal increases strongly at $\nu \approx E_g/h$. To explain this fact, J. Bardeen, F. J. Blatt, and L. H. Hall [8] suggest that in the region of photon energies insufficient for vertical transitions, electron transitions to the conduction band still occur because the selection rule of Eq. (1.12), which should be strictly obeyed in an ideal periodic crystal, is relaxed due to the interaction of electrons with phonons.

Returning to the energy-band structure of Fig. 3, we must follow Herman [7] in assuming that an electron is excited optically from a state i to c' and is then transferred from c' to $f$ emitting or absorbing a phonon. As a result of this, the electron wave vector changes considerably and the whole process can be considered as a "nonvertical" transition from i to $f$ with the absorption of a photon $h\nu \approx E_g$.

Since each of the processes shown in Fig. 3 may involve the emission or absorption of a phonon, the matrix element which gives the transition probability becomes

$$P_{if} = \sum_{m=1}^{4} \frac{P_{im}P_{mc}}{E_m - E_{v'}}, \tag{1.13}$$

where m denotes the intermediate state (c' or v'). The quantities $P_{ic'}$ and $P_{v'f}$ are found from Eq. (1.9). For $P_{iv'}$ and $P_{c'f}$, we have the selection rule

$$\boldsymbol{k}_i = \boldsymbol{k}_f + \boldsymbol{q},$$

where q is the wave vector of a phonon. Assuming that the phonon matrix elements are constant, and that $E_{v'} - E_i \approx E_{c'} - E_f$, Bardeen, Blatt, and Hall [8] have shown that the wavelength dependence of the absorption coefficient for nonvertical transitions should be

$$\alpha_i \sim (h\nu - E_g \pm h\nu_q)^2 \tag{1.14}$$

in the case when transitions are possible for $\boldsymbol{k} = 0$ ($h\nu_q$ represents the phonon energy). In the region of photon energies sufficient for direct (vertical) transitions, beginning with the threshold energy $E_g'$, the absorption coefficient $\alpha_d$ increases, according to the theory, as follows

$$\alpha_d \sim (h\nu - E_g')^{\frac{1}{2}}. \tag{1.15}$$

The considerable difference between the last two expressions can be sometimes used to analyze the experimental data on the form of the absorption band edge and to explain the nature of electron transitions.

Up to now, the absolute values of the photon absorption cross sections * within the fundamental band have not been calculated exactly. We may justifiably assume that when the absorption coefficient is greater than $10^4$ cm$^{-1}$, allowed interband transitions take place in a semiconductor crystal [1].

Figure 4 gives the dependence of the absorption coefficients of germanium and silicon on the difference $\zeta - \zeta_t$ ($\zeta$ is a wave number in general, and $\zeta_t$ are the wave numbers corresponding to the forbidden bandwidth, i.e., $\zeta_t = E_g/hc$). From the curves of Fig. 4, it is evident that the power exponent n in the dependence $\alpha \sim (\zeta - \zeta_t)^n$ at not too high values of $\alpha$ is close to 2.5 for

* We mean here the ratio $\alpha/N$, where N is the number of atoms per cm$^3$ of a crystal.
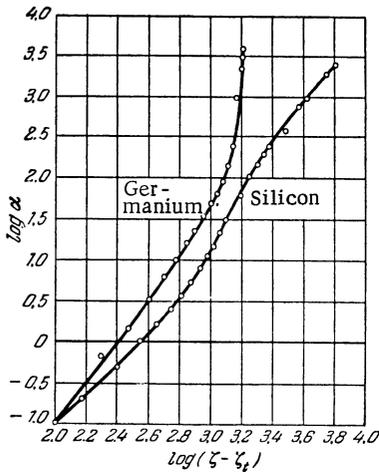
Fig. 4. Dependence of the logarithm of the absorption coefficient on the logarithm of the difference $(\zeta - \zeta_t)$ for germanium and silicon.

germanium and 2.0 for silicon. Both these values are several times greater than the power exponent n = 0.5 which one would expect for vertical transitions. The conduction band of silicon, like that of germanium, has a maximum corresponding to $k \neq 0$ (Fig. 2). Thus the experimental data for germanium and silicon are in agreement with the theory of nonvertical transitions.

The steep rise in the absorption coefficient of germanium crystals near 0.81 eV (Fig. 2) is explained by the fact that this energy corresponds to the threshold for vertical transitions. Comparison of this value with the data on the band structure of germanium, obtained by the other methods mentioned above, allow us to conclude that the minimum in the conduction band corresponding to the origin of coordinates (0, 0, 0) lies above the minimum on the [1, 1, 1] axis. This conclusion regarding the difference of the minimum energies necessary for nonvertical and vertical transitions in germanium is also confirmed by the data on the spectrum of the direct recombination radiation of Ge obtained by J. R. Haynes, which will be discussed in Chapt. IV.

The earlier data on the absorption band edge of Si, obtained by the method of reflection coefficients [9], suggested that the threshold energy for vertical transitions was close to 1.8 eV. However, a direct determination of $\alpha$, as well as a careful study of the recombination radiation spectra, did not confirm this conclusion. According to the measurements of W. C. Dash and R. Newman [6], the vertical separation between the conduction and valence bands at $k = 0$ amounts to 2.5 eV. An analysis of the form of the absorption band edge of PbS, PbTe, and PbSe single crystals, carried out recently by Scanlon [10], who also used the above formulas, gave reliable data on the forbidden bandwidths of these very interesting and important (in infrared technology)
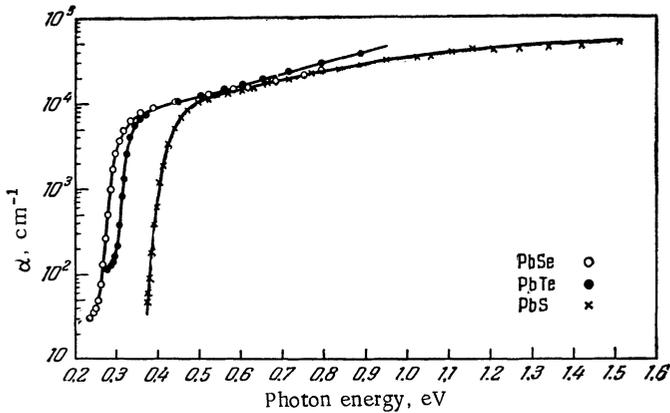
Fig. 5.  Edge of the fundamental absorption band of the semicon-
ducting compounds PbS, PbSe, and PbTe [10].

semiconductors.  As in the case of germanium and silicon, in
earlier work on the absorption of PbS, two different methods were
used for the absorption coefficients ranging from 1 to $10^6$ cm$^{-1}$:
the transmission was measured at low values of $\alpha$ and the re-
flectivity at high values.

The results of these measurements were found to differ.  To
obtain fully reliable data, the following method was adopted. Using
the tendency of PbS-type crystals to cleave along the (100) planes,
a series of single-crystal samples was prepared from several
microns to 1 mm thick, and measuring more than $600 \times 50 \mu$
across.  Then, having improved the focusing part of an infrared
spectrograph, it was possible to measure the transmission through-
out the absorption-edge region of PbS, PbSe, and PbTe (Fig. 5).

The plots shown in  Fig. 6 were used to analyze the form of
the absorption edge.  These plots show clear linear portions cor-
responding to values $\alpha > 3000$ cm$^{-1}$, the extrapolation of which
gives the value of $E_g$ for vertical (direct) transitions (cf. Table 2).
The results of Scanlon should be regarded as more reliable than
the earlier work reporting much higher values of $E_g$ for PbS and
similar compounds [11].

If we plot the dependence of $\alpha^{1/2}$ on $E = h\nu$ (Fig. 7), we find
that in the  $\alpha < 3000$ cm$^{-1}$ region there is an approximately linear
part which may be related to nonvertical electron transitions. The
values of $h\nu = E_g$ for nonvertical transitions   extrapolated to $\alpha=0$