# Handbook on Semiconductors

*Series editor*

T.S. MOSS

Volume 2

# Optical Properties of Solids

*Volume editor*

MINKO BALKANSKI

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# Optical Properties of Solids

*Volume editor*

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# Foreword to Volume 2

Describing the optical properties of semiconductors aims explicitly at understanding the interaction of the radiation field with matter. The investigation of the interaction of photons with a solid generally has two aspects: on the one hand it leads to the possibility of quantitative knowledge of the propagation of light in solids and its applications and on the other hand to the possibility of confronting the experimental evidence with theoretical model representations. Thus the study of optical properties is the interface between the theory of semiconductors and their characterization with their application in view.

For the presentation of the present status in this field we had to choose between a certain number of different schemes.

If we were mainly concerned with selecting characteristics for possible technological applications we should probably have arranged this volume in chapters named after different semiconductors, in which their optical properties would be enumerated. Although recognizing the usefulness of such a presentation, we thought that it would only reach a limited audience of engineers, for whom the continuous up-dating of presented sets of data is important. This would only be possible by continuously rewriting the book or making regular additions.

If, on the other hand, we wanted to emphasize the performances of optical and electrooptical properties of different materials we could not have done it without detailed descriptions of rapidly evolving devices which are treated in a different type of publication.

Our choice is to present the optical properties of semiconductors on the basis of the physical phenomena involved in the interaction of light with semiconductors. Such a presentation gives a direct link with the theory and is the basis of the description of the structure and underlying properties of the materials.

The first chapter, on the optical properties of semiconductors above the absorption edge, is the presentation of a field which parallels the development of the theory of semiconductors and which has presently a particular resurgence of activity due to the development of the use of synchrotron radiation. The determination of the band structure of semiconductors has always been related to the investigation of the optical properties above the energy gap, and new insights have been gained with the introduction of angular resolved photoemission.

The second chapter extends the presentation of the knowledge of band structure by focussing attention on the optical properties of the band populations and their interactions. The energy range investigated is limited to the absorption edge and the phenomenon discussed essentially concerns the interaction of electrons from the lowest conduction band and holes from the highest valence band. The electron–hole condensation is a phenomenon which has excited a large interest in fundamental physics, and its different manifestations enrich the connections of semiconductor physics with other fields like hydrodynamics, for example.

The third chapter presents the optical properties of semiconductor surfaces. With the growing interest in miniaturization, which leads to increasing the surface to volume ratio, the importance of the surface properties in the applications of semiconductors is becoming more and more determinant. Surface physics has always been a difficult field and only recent developments in experimental techniques have provided the possibility for rapid enlightenment. The access to surface states has essentially been through the optical properties, and their review here seems particularly appropriate and useful.

The effects of external forces have always been essential for the determination of the fundamental properties of a system. For semiconductors the systematic investigation of the optical properties in correlation with the external forces has brought important precision, both to the structure and to the dynamics of these materials. The techniques and results of modulation spectroscopy, and the effects of temperature and pressure, are described in chapter four.

The transport properties, determining in many cases the possible use of a given semiconducting material, are characterized by the free carrier parameters directly related to the band structure and density of states. One of the most efficient ways to investigate these parameters is the systematic study of optical properties. Chapter five is devoted to the methods and recent achievements in the investigations of free carrier optical properties, bridging the theoretical understanding between present and potential applications of semiconductors.

Semiconductor lasers is another field where fundamental knowledge of semiconductor physics has led to impressive achievements in technology and opened up a new area for future development: photonics. An important field of action for the first generation in photonics is optical telecommunications, where semiconductors will have to play a major role as light sources, detectors or nonlinear devices. The development of light sources is mainly based on the understanding and operation of radiative recombination giving rise to stimulated or spontaneous photon emission. The fundamentals of this field are treated in chapter six, bringing up to date an important aspect of semiconductor physics which has had a glorious past, an exciting present and probably a very promising future.

Directly related to another field of applications, solar energy conversion, is the photovoltaic effect of semiconductors. This subject is treated in chapter seven, giving a sound basis for further experimental work in this field.

Apparently in most of the measured effects and characteristics considered as determining in the essential functions for application, the electronic structure

and free carrier behaviour seem to play the major role. Nevertheless in a microscopic analysis one has often to face the evidence that phonons are a determining factor in limiting or regulating the macroscopic processes. The fundamental knowledge of phonon properties is mainly gained from the study of their optical properties. Chapter eight is devoted to a summary of the methods of investigation and trends of present knowledge in this field.

A book on optical properties of solids could not be complete in the present day if the nonlinear aspects were not considered. The second order processes and nonlinear optical properties of semiconductors are treated in chapter nine.

Presenting the optical properties of semiconductors in this order we believe offers direct access to the fundamental properties of semiconducting materials, and the possibility to correlate easily the experimental evidence reported here with the theoretical studies presented in Volume 1.

The materials we have brought together should be of interest and use not only to professional research workers in the field but also to engineers in the field of photonics, electronics and semiconductor technology, as well as to students in many areas of physics and technology where fundamental properties of solids are a necessary basis for developing further knowledge of the structure of matter and its eventual use in applications.

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CHAPTER 1

# Optical Properties of Semiconductors above the Band Edge

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*Handbook on Semiconductors*
*edited by T.S. Moss*
*Volume 2, edited by M. Balkanski*

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## 1. Introduction

For a long time optical spectroscopy has been a very powerful tool to study the electronic levels of atoms and molecules. However for solids, and especially for semiconductors, it was only around 1960 that it was realized that the same kind of information could be obtained, in spite of the lifetime broadening and the overlapping of the bands.

This chapter deals with the optical properties of semiconductors above the band gap $E_g$. A large proportion of our knowledge of the energy levels of semiconductors comes from a theoretical analysis of the reflectivity (or the absorption) between $E_g$ and 25–30 eV; we shall be mainly concerned with this energy region. This means that the photon used to probe the crystal, mostly induces transitions between the filled valence bands and the empty conduction bands.

The development of synchrotron radiation in the last few years, has allowed us to go beyond simple reflectivity measurements and use modulation techniques: electroreflectance, thermoreflectance or wavelength modulation. In the same time, additional band structure information (valence bandwidth, density of states) was obtained by photoelectron spectroscopy (ultra-violet and X-rays).

We have arbitrarily chosen to discuss only a limited number of topics and examples, rather than to make a review of all the experiments. Optical measurements, based on synchrotron radiation, have been reviewed in detail recently by Kunz (1976) and Brown (1974).

§ 2 is a reminder of the properties of the frequency dependent complex dielectric function $\epsilon(\omega)$ in the one-electron approximation; the electron–hole interaction and local field effects are also discussed.

§ 3 deals with the band structure of semiconductors. We describe briefly one of the numerous methods used for calculation: the pseudopotential.

A short survey of the experimental techniques, especially synchrotron radiation is given in § 4. In § 5 we illustrate the discussion by a few examples. The first part is a short discussion for the valence to conduction band transitions of GaAs, the second concerns the core to conduction band transitions of different compounds. The importance of many body effects is emphasized by the failure of the one-electron approximation to explain the experimental data.

The last section is devoted to a new, very powerful and promising technique: angular resolved photoemission which allows us to obtain not only the position of the bands, but also the dispersion in energy: $E(\boldsymbol{K})$.

## 2. Optical properties

### 2.1. The one-electron approximation

Almost all of the transitions that contribute to optical properties in semiconductors can be described as one-electron excitations. Collective excitations of many electrons are also possible, but only when the energy of the probing incident photon is of the order of $\hbar\omega_p$, which is the energy of the valence band plasmon. In most semiconductors we have $\hbar\omega_p \geq 15$ eV, an energy range where most valence to conduction band transitions have been exhausted.

In the one-electron approximation, each valence electron is considered as a single particle, moving in a potential $V(r)$, which is the sum of the core potentials and a self-consistent Hartree potential of the other valence electrons.

The response of the solid to the incident electromagnetic field $E(r)$ is described by a complex dielectric function $\epsilon(q, \omega)$, which is frequency- and wave vector-dependent. This tensor can be written as $\epsilon(q, \omega) = \epsilon_1(q, \omega) + i\epsilon_2(q, \omega)$. The energy loss in the crystal is proportional to $\epsilon_2$. Due to the fact that the radiation field varies very little over the atomic dimensions the wave vector dependence is neglected and one has

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega). \tag{1}$$

In the random phase approximation (Ehrenreich and Cohen 1959) the imaginary part $\epsilon_2$ of the dielectric constant is given by

$$\epsilon_2(\omega) = \alpha\omega^{-2} \sum_{v,c} \int_{\text{B.Z.}} 2(2\pi)^{-3} |M_{vc}(\boldsymbol{k})|^2 \delta[\hbar\omega_{vc}(\boldsymbol{k}) - \hbar\omega] \, \mathrm{d}^3k, \tag{2}$$

where $\alpha$ is a constant, the subscripts $v$ and $c$ correspond to the initial and final states respectively and the integration is performed over the Brillouin zone.

$$\hbar\omega_{vc}(\boldsymbol{k}) = E_v(\boldsymbol{k}) - E_c(\boldsymbol{k}) \tag{3}$$

and

$$M_{vc}(\boldsymbol{k}) = \langle u_v | p | u_c \rangle, \tag{4}$$

where $u_v$ and $u_c$ are the periodic parts of the Bloch eigenfunctions of the energies $E_v(\boldsymbol{k})$ and $E_c(\boldsymbol{k})$.

Indirect transitions are neglected because their contribution is negligible.

The integration in the $\boldsymbol{k}$ space can be transformed because

$$\int_{\text{B.Z.}} \mathrm{d}^3k = \int \mathrm{d}S |\nabla_k \omega_{vc}(\boldsymbol{k})|^{-1}, \tag{5}$$

where $S$ is a surface of constant interband energy $\hbar\omega = E_v - E_c$. The result for $\epsilon_2(\omega)$ is

$$\epsilon_2(\omega) = \alpha\omega^{-2} \sum_{v,c} \int 2(2\pi)^{-3} |M_{vc}(\boldsymbol{k})|^2 \, \mathrm{d}S |\nabla_{\boldsymbol{k}} \omega_{vc}(\boldsymbol{k})|^{-1}. \tag{6}$$

The gradient in the denominator allows the integrand to have singularities at some points in $\boldsymbol{k}$ space. Such singularities will dominate $\epsilon_2(\omega)$. The points where they occur ($\nabla_{\boldsymbol{k}} \omega_{vc} = 0$) are called critical points or Van Hove singularities. They are classified into four types $M_0$, $M_1$, $M_2$ and $M_3$ (Van Hove 1953): $M_0$ corresponds to a point where $\omega_{vc}(\boldsymbol{k})$ has a minimum, $M_3$ to a maximum and $M_1$, $M_2$ are saddle points.

Phillips (1956), by using symmetry arguments, showed that there was a minimum set of critical points for each crystal structure. They usually occur at symmetry points.

The Van Hove singularities create structures in the spectrum of $\epsilon_2(\omega)$. Therefore an analysis of the interband transitions curve is a search for critical points. Experimentally we measure the reflectivity; we have to know what the relation is between the reflectivity $R(\omega)$ and the imaginary part of the dielectric constant $\epsilon_2(\omega)$

At normal incidence the complex reflectivity (ratio of reflected to incident electric field) is

$$r = |r| \exp(\mathrm{i}\theta) = (n - 1 + \mathrm{i}K)/(n + 1 + \mathrm{i}K), \tag{7}$$

where $\theta$ is a phase angle, $n$ the refractive index and $K$ the extinction coefficient.

Experimentally we do not measure $r$ but the reflection coefficient

$$R = |r|^2 = (n - 1)^2 + K^2/(n + 1)^2 + K^2. \tag{8}$$

The real and imaginary part of dielectric function $\epsilon(\omega) = \epsilon_1 + \mathrm{i}\epsilon_2$, are related to $n$ and $K$ by the relations

$$\epsilon_1 = n^2 - K^2, \tag{9}$$

$$\epsilon_2 = 2nK. \tag{10}$$

The response to an electromagnetic field must satisfy the requirements of causality; there are Kramers–Krönig relations between $\epsilon_1$ and $\epsilon_2$.

The measurement of $R(\omega)$ over a large energy scale (20–30 eV) allows us to obtain $n$, $K$ and $\epsilon_1$, $\epsilon_2$.

In some cases one can also obtain the absorption coefficient $\alpha$ directly, by measuring the transmission of a thin film of thickness $x$;

$$\alpha = 4\pi K/\lambda = \epsilon_2 \omega/nc, \tag{11}$$

where $\lambda$ is the incident photon wavelength and $c$ the speed of the light. If we neglect the reflections on the faces of the sample

$$T(\omega) = (I/I_0) \exp -\alpha x. \tag{12}$$

The transmission technique is mostly used for studies of core to conduction band transitions, because in their energy range (>20 eV) the normal incidence reflectivity is very low.