Optical Properties of Condensed Matter and Applications
Wiley Series in Materials for Electronic and Optoelectronic Applications

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Optical Properties of Condensed Matter and Applications

Edited by

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Series Preface

WILEY SERIES IN MATERIALS FOR ELECTRONIC AND OPTOELECTRONIC APPLICATIONS

This book series is devoted to the rapidly developing class of materials used for electronic and optoelectronic applications. It is designed to provide much-needed information on the fundamental scientific principles of these materials, together with how these are employed in technological applications. The books are aimed at postgraduate students, researchers, and technologists engaged in research, development, and the study of materials in electronics and photonics, and at industrial scientists developing new materials, devices, and circuits for the electronic, optoelectronic, and communications industries. The development of new electronic and optoelectronic materials depends not only on materials engineering at a practical level, but also on a clear understanding of the properties of materials, and the fundamental science behind these properties. It is the properties of a material that eventually determine its usefulness in an application. The series therefore also includes such titles as electrical conduction in solids, optical properties, thermal properties, etc., all with applications and examples of materials in electronics and optoelectronics. The characterization of materials is also covered within the series in as much as it is impossible to develop new materials without the proper characterization of their structure and properties. Structure–property relationships have always been fundamentally and intrinsically important to materials science and engineering.

Materials science is well known for being one of the most interdisciplinary sciences. It is the interdisciplinary aspect of materials science that has led to many exciting discoveries, new materials, and new applications. It is not unusual to find scientists with a chemical engineering background working on materials projects with applications in electronics. In selecting titles for the series, we have tried to maintain the interdisciplinary aspect of the field, and hence its excitement to researchers in this field.

PETER CAPPER
SAFA KASAP
ARTHUR WILLOUGHBY
Optical properties and their experimental measurements represent one of the most important scientific endeavors in the history of materials research. Advances made to date in photonic devices that have enabled optical communications could not have been achieved without a proper understanding of the optical properties of materials and how these properties influence the overall device performance. Today, research on optical properties of materials draws on not only physicists, who used to be the usual traditional researchers in this field, but also scientists and engineers from widely different disciplines. Although there are several books in the market on optical properties of materials, they have tended to be either too theoretical or so general that they do not include some of the recent and exciting advances. In some cases, the books are too specialized. More significantly, most of these books do not present all the recent advances in the field in one accessible volume. Therefore, it is intended here to have a single volume covering from fundamentals to applications, with up-to-date advances in the field, and a book that is useful to practitioners.

Following a semiquantitative approach, this book summarizes the basic concepts, with examples and applications, and reviews some recent developments in the study of optical properties of condensed-matter systems. It covers examples and applications in the field of electronic and optoelectronic materials, including organic polymers, inorganic glasses, and photonic crystals. An attempt is made to cover both the experimental and theoretical developments in any field presented in this book, which consists of 16 chapters contributed by very experienced and well known scientists and groups on different aspects of optoelectronic properties of condensed matter. Most chapters are presented to be relatively independent with minimal cross-referencing, and chapters with complementary contents are arranged together to facilitate a reader with cross-referencing.

In chapters 1 and 2 by Kasap, coworkers and collaborators, the fundamental optical properties of materials are concisely reviewed and these chapters are expected to refresh the readers with basics and provide some useful optical relations for experimentalists. In chapter 3, Shimakawa et al. present an up to date review of the optical properties of disordered condensed matter, both the theory and experiments, and chapter 4 by Singh and Ruda covers the concept of excitons for crystalline and non-crystalline materials. In chapter 5, Aoki has presented a comprehensive review of experimental advances in the techniques of observing photoluminescence together with recent luminescence results for amorphous semiconductors, and chapter 6 by Singh deals with theoretical advances in the field of photoluminescence and photoinduced changes in non-crystalline condensed-matter systems. Thus, the contents of chapters 5 and 6 are complementary. In chapter 7 by Kugler et al., recent advances in the simulation and understanding of the light-induced volume changes in chalcogenide glasses are presented. Chapter 8 by Edgar covers an extensive discussion on the optical properties of glasses. In chapter 9, Ruda and Matsuura present a comprehensive review of properties and applications of photonic crystals. In chapter 10, Tanaka
has presented an up to date review of the nonlinear optical properties of photonic glasses. Chapter 11 by Kobayashi and Naito discusses the fundamental optical properties of organic semiconductors, and in chapter 12 Zhu has presented a comprehensive review of the applications of organic semiconductors. These two chapters are also complementary. In chapter 13, Truong and Tanemura have presented the optical properties of thin films and their applications. Chapter 14 by Kielbasa et al. presents a detailed review of the optical properties of materials with negative refractive index and their applications. In chapter 15, Singh and Oh have discussed the excitonic processes in quantum wells, and in chapter 16, Murayama and Oka have presented the optical properties and spin dynamics of diluted magnetic semiconductor nanostructures.

The aim of the book is to present its readers with the recent developments in theoretical and experimental aspects of novel optical properties of condensed matter and applications. Accomplishments and technical challenges in device applications are also discussed. The readership of the book is expected to be senior undergraduate and postgraduate students, R&D staff, and teaching and research professionals.

JAI SINGH

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1 Fundamental Optical Properties of Materials I

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1.1 Introduction

Optical properties of a material change or affect the characteristics of light passing through it by modifying its propagation vector or intensity. Two of the most important optical properties are the refractive index \(n\) and the extinction coefficient \(K\), which are generically called optical constants; though some authors include other optical coefficients within this terminology. The latter is related to the attenuation or absorption coefficient \(\alpha\). In this chapter we present the complex refractive index, the frequency or wavelength dependence of \(n\) and \(K\), so-called dispersion relations, how \(n\) and \(K\) are interrelated, and how \(n\) and \(K\) can be determined by studying the transmission as a function of wavelength through a thin film of the material. Physical insights into \(n\) and \(K\) are provided in Chapter 2.
The optical properties of various materials, with $n$ and $K$ being the most important, are available in the literature in one form or another, either published in journals, books and handbooks or posted on websites of various researchers, organizations (e.g., NIST) or companies (e.g., Schott Glass). Nonetheless, the reader is referred to the works of Wolfe [1.1], Klocek [1.2], Palik [1.3, 1.4], Ward [1.5], Efimov [1.6], Palik and Ghosh [1.7], Nikogosyan [1.8], and Weaver and Frederikse [1.9] for the optical properties of a wide range of materials. Adachi’s books on the optical constants of semiconductors are highly recommended [1.10–1.12] along with Madelung’s third edition of ‘Semiconductors: Data Handbook’ [1.13]. There are, of course, other books and handbooks that also contain optical constants in various chapters; see, for example, references [1.14–1.17].

There are available a number of experimental techniques for measuring $n$ and $K$, some of which have been summarized by Simmons and Potter [1.18]. For example, ellipsometry measures changes in the polarization of light incident on a sample to sensitively characterize surfaces and thin films. The interaction of incident polarized light with the sample causes a polarization change in the light, which may then be measured by analysing the light reflected from the sample. Recently, Collins has provided an extensive in-depth review of ellipsometry for optical measurements [1.19]. One of the most popular and convenient optical measurements involves passing a monochromatic light through a thin sample, and measuring the transmitted intensity as a function of wavelength, $T(\lambda)$, using a simple spectrophotometer. For thin samples on a thick transparent substrate, the transmission spectrum shows oscillations in $T(\lambda)$ with the wavelength due to interferences within the thin film. Swanepoel’s technique uses the $T(\lambda)$ measurement to determine $n$ and $K$, as described in Section 1.4.

1.2 OPTICAL CONSTANTS

One of the most important optical constants of a material is its refractive index, which in general depends on the wavelength of the electromagnetic wave, through a relationship called dispersion. In materials where an electromagnetic wave can lose its energy during its propagation, the refractive index becomes complex. The real part is usually the refractive index, $n$, and the imaginary part is called the extinction coefficient, $K$. In this section, the refractive index and extinction coefficient will be presented in detail along with some common dispersion relations. A more practical and a semiquantitative approach is taken along the lines in [1.18, 1.20, 1.21] rather than a full dedication to rigour and mathematical derivations. More analytical approaches can be found in other texts, e.g. [1.22].

1.2.1 Refractive index and extinction coefficient

The refractive index of an optical or dielectric medium, $n$, is the ratio of the velocity of light $c$ in vacuum to its velocity $\nu$ in the medium; $n = c/\nu$. Using this and Maxwell’s equations, one obtains the well known Maxwell’s formula for the refractive index of a substance as $n = \sqrt{\varepsilon_r \mu_r}$, where $\varepsilon_r$ is the static dielectric constant or relative permittivity and $\mu_r$ the relative permeability. As $\mu = 1$ for nonmagnetic substances, one gets $n = \sqrt{\varepsilon_r}$, which is very useful in relating the dielectric properties to optical properties of materials at any particular frequency of interest. As $\varepsilon_r$ depends on the wavelength of light, the refractive index also
depends on the wavelength of light, and this dependence is called dispersion. In addition to dispersion, an electromagnetic wave propagating through a lossy medium experiences attenuation, which means it loses its energy, due to various loss mechanisms such as the generation of phonons (lattice waves), photogeneration, free carrier absorption, scattering, etc. In such materials, the refractive index becomes a complex function of the frequency of the light wave. The complex refractive index, denoted usually by \( n^* \), with real part \( n \), and imaginary part \( K \), called the extinction coefficient, is related to the complex relative permittivity, \( \varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \), by:

\[
n^* = n - jK = \sqrt{\varepsilon_r} = \sqrt{\varepsilon_r' - j\varepsilon_r''}
\]  

(1.1a)

where \( \varepsilon_r' \) and \( \varepsilon_r'' \) are, respectively, the real and imaginary parts of \( \varepsilon_r \). Equation (1.1b) gives:

\[
n^2 - K^2 = \varepsilon_r' \quad \text{and} \quad 2nK = \varepsilon_r''
\]  

(1.1b)

In explicit terms, \( n \) and \( K \) can be obtained as:

\[
n = (1/2)^{1/2}[ (\varepsilon_r'^2 + \varepsilon_r''^2)^{1/2} + \varepsilon_r' ]^{1/2}
\]  

(1.2a)

\[
K = (1/2)^{1/2}[ (\varepsilon_r'^2 + \varepsilon_r''^2)^{1/2} - \varepsilon_r' ]^{1/2}
\]  

(1.2b)

The optical constants \( n \) and \( K \) can be determined by measuring the reflectance from the surface of a material as a function of polarization and the angle of incidence. For normal incidence, the reflection coefficient, \( r \), is obtained as

\[
r = \frac{1-n^*}{1+n^*} = \frac{1-n+jK}{1+n-jK}
\]  

(1.3)

The reflectance \( R \) is then defined by:

\[
R = |r|^2 = \frac{(1-n+jK)^2}{(1+n-jK)^2} = \frac{(1-n)^2 + K^2}{(1+n)^2 + K^2}
\]  

(1.4)

Notice that whenever \( K \) is large, for example over a range of wavelengths, the absorption is strong, and the reflectance is almost unity. The light is then reflected, and any light in the medium is highly attenuated. (Typical sample calculations and applications may be found in ref. [1.20].)

Optical properties of materials are typically presented by showing the frequency dependences (dispersion relations) of either \( n \) and \( K \) or \( \varepsilon_r' \) and \( \varepsilon_r'' \). An intuitive guide to explaining dispersion in insulators is based on a single-oscillator model in which the electric field in the light induces forced dipole oscillations in the material (displaces the electron shells to oscillate about the positive nucleus) with a single resonant frequency \( \omega_0 \). The frequency dependences of \( \varepsilon_r' \) and \( \varepsilon_r'' \) are then obtained as:

\[
\varepsilon_r' = 1 + \frac{N_{at}}{\varepsilon_o} \alpha_1' \quad \text{and} \quad \varepsilon_r'' = 1 + \frac{N_{at}}{\varepsilon_o} \alpha_2''
\]  

(1.5)
where \( N_{at} \) is the number of atoms per unit volume, \( \varepsilon_0 \) is the vacuum permittivity, and \( \alpha' \) and \( \alpha'' \) are the real and imaginary parts of the electronic polarizability, given respectively by:

\[
\alpha' = \frac{1 - (\omega/\omega_o)^2}{\left[1 - (\omega/\omega_o)^2\right]^2 + (\gamma/\omega_o)^2 (\omega/\omega_o)^2}
\]  

(1.6a)

and

\[
\alpha'' = \frac{(\gamma/\omega_o)(\omega/\omega_o)}{\left[1 - (\omega/\omega_o)^2\right]^2 + (\gamma/\omega_o)^2 (\omega/\omega_o)^2}
\]  

(1.6b)

where \( \alpha_{eo} \) is the DC polarizability corresponding to \( \omega = 0 \) and \( \gamma \) is the loss coefficient that characterizes the electromagnetic (EM) wave losses within the material system. Using Equations (1.1)–(1.2) and (1.5)–(1.6), the frequency dependence of \( n \) and \( K \) can be studied. Figure 1.1(a) shows the dependence of \( n \) and \( K \) on the normalized frequency \( \omega/\omega_o \) for a simple single electronic dipole oscillator of resonance frequency \( \omega_o \).

It is seen that \( n \) and \( K \) peak close to \( \omega = \omega_o \). If a material has a \( \varepsilon'' \gg \varepsilon' \), then \( \varepsilon_r = -j\varepsilon'' \) and \( n = K \approx \sqrt{\varepsilon''/2} \) is obtained from Equation (1.1b). Figure 1.1(b) shows the dependence of the reflectance \( R \) on the frequency. It is observed that \( R \) reaches its maximum value at a frequency slightly above \( \omega = \omega_o \), and then remains high until \( \omega \) reaches nearly \( 3\omega_o \); thus the reflectance is substantial while absorption is strong. The normal dispersion region is the frequency range below \( \omega_o \) where \( n \) falls as the frequency decreases, that is, \( n \) decreases as the wavelength \( \lambda \) increases. The anomalous dispersion region is the frequency range above \( \omega_o \) where \( n \) decreases as \( \omega \) increases. Below \( \omega_o \), \( K \) is small and if \( \varepsilon_{dc} \) is \( \varepsilon_r(0) \), then \( n \) becomes:

![Figure 1.1](image-url)

**Figure 1.1** Refractive index, \( n \) and extinction coefficient \( K \) obtained from a single electronic dipole oscillator model. (a) \( n \) and \( K \) versus normalized frequency and (b) Reflectance versus normalized frequency [Reproduced from S.O. Kasap, *Principles of Electronic Materials and Devices*, 3rd Edition, McGraw-Hill, Boston, 2005]
Since, $\lambda = 2\pi c/\omega$, defining $\lambda_0 = 2\pi c/\omega_o$ as the resonance wavelength, one gets:

$$n^2 = 1 + (\varepsilon_{\infty} - 1) \frac{\omega_o^2}{\omega_o^2 - \omega^2}; \quad \omega < \omega_o$$  \hspace{1cm} (1.7)$$

While intuitively useful, the dispersion relation in Equation (1.8) is far too simple. More rigorously, we have to consider the dipole oscillator quantum mechanically which means a photon excites the oscillator to a higher energy level, see, for example, Fox [1.21] or Simmons and Potter [1.18]. The result is that we would have a series of $\frac{\lambda^2}{\lambda^2 - \lambda_i^2}$ terms with various weighting factors $A_i$ that add to unity, where $\lambda_i$ represents different resonance wavelengths. The weighting factors $A_i$ involve quantum mechanical matrix elements.

Figure 1.2 shows the complex relative permittivity and the complex refractive index of crystalline silicon in terms of photon energy $h\nu$. For photon energies below the bandgap energy (1.1 eV), both $\varepsilon''$ and $K$ are negligible and $n$ is close to 3.7. Both $\varepsilon''$ and $K$ increase and change strongly as the photon energy becomes greater than 3 eV, far beyond the bandgap energy. Notice that both $\varepsilon'$ and $n$ peak at $h\nu \approx 3.5$ eV, which corresponds to a direct photoexcitation process, electrons excited from the valence band to the conduction band, as discussed later.

1.2.2 $n$ and $K$, and Kramers–Kronig relations

If we know the frequency dependence of the real part, $\varepsilon'$, of the relative permittivity of a material, then by using the Kramers–Kronig relations between the real and the imaginary

$$n^2 = 1 + (\varepsilon_{\infty} - 1) \frac{\lambda^2}{\lambda^2 - \lambda_o^2}; \quad \lambda > \lambda_o$$  \hspace{1cm} (1.8)$$

\begin{figure}[h]
\centering
\begin{subfigure}[h]{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{fig1a.png}
\caption{(a) Complex relative permittivity of a silicon crystal as a function of photon energy plotted in terms of real ($\varepsilon'$) and imaginary ($\varepsilon''$) parts.}
\end{subfigure} \hspace{1cm}
\begin{subfigure}[h]{0.4\textwidth}
\centering
\includegraphics[width=\textwidth]{fig1b.png}
\caption{(b) Optical properties of a silicon crystal versus photon energy in terms of real ($n$) and imaginary ($K$) parts of the complex refractive index [Data extracted from D.E. Aspnes and A.A. Studna, Phys. Rev. B, 27, 985 (1983)].}
\end{subfigure}
\end{figure}
parts we can determine the frequency dependence of the imaginary part \( \varepsilon'' \), and vice versa. The transform requires that we know the frequency dependence of either the real or imaginary part over as wide a range of frequencies as possible, ideally from zero (DC) to infinity, and that the material has linear behaviour, i.e., it has a relative permittivity that is independent of the applied field. The Kramers–Kronig relations for the relative permittivity \( \varepsilon_r = \varepsilon'_r - j\varepsilon''_r \) are given by [1.23, 1.24] (see also Appendix 1C in [1.18])

\[
\varepsilon'_r(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\omega'\varepsilon''_r(\omega')}{\omega'^2 - \omega^2} \, d\omega'
\]

(1.9a)

and

\[
\varepsilon''_r(\omega) = \frac{2\omega}{\pi} P \int_0^\infty \frac{\varepsilon'_r(\omega')}{\omega'^2 - \omega^2} \, d\omega'
\]

(1.9b)

where \( \omega' \) is the integration variable, \( P \) represents the Cauchy principal value of the integral, and the singularity at \( \omega = \omega' \) is avoided. [A negative sign is inserted in Equation (1.9b) if we take \( \varepsilon_r = \varepsilon'_r + j\varepsilon''_r \)]

Similarly one can relate the real and imaginary parts of the polarizability, \( \alpha'(\omega) \) and \( \alpha''(\omega) \), and those of the complex refractive index, \( n(\omega) \) and \( K(\omega) \) as well. For \( n^* = n(\omega) - jK(\omega) \),

\[
n(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{K(\omega')}{\omega' - \omega} \, d\omega' \quad \text{and} \quad K(\omega) = \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon''_r(\omega')}{\omega' - \omega} \, d\omega'
\]

(1.10)

A negative sign is needed in the second term if we use \( n^* = n(\omega) + jK(\omega) \). It should be emphasized that the optical constants \( n \) and \( K \) have to obey what are called \textit{f-sum rules} [1.25]. For example, the integration of \([n(\omega) - 1]\) over all frequencies must be zero, and the integration of \( \omega K(\omega) \) over all frequencies gives \((\pi/2)\omega_p^2\), where \( \omega_p = h(4\pi N Ze^2/m_e)^{1/2} \) is the free-electron plasma frequency in which \( N \) is the atomic concentration, \( Z \) is the total number of electrons per atom, and \( e \) and \( m_e \) are the charge and mass of the electron. The \textit{f-sum rules} provide a consistency check and enable various constants to be interrelated.

### 1.3 REFRACTIVE INDEX AND DISPERSION

There are several popular models describing the spectral dependence of refractive index \( n \) in a material. Most of these are described below though some, such as the infrared refractive index, are covered under Reststrahlen absorption in Chapter 2 since it is closely related to the coupling of the EM wave to lattice vibrations. The most popular dispersion relation in optical materials is probably the Sellmeier relationship since one can sum any number of resonance-type terms to get as wide a range of wavelength dependence as possible. However, its main drawback is that it does not accurately represent the refractive index when there is a contribution arising from free carriers in narrow-bandgap or doped semiconductors.
1.3.1 Cauchy dispersion relation

In the Cauchy relationship, the dispersion relationship between the refractive index \(n\) and wavelength of light \(\lambda\) is commonly stated in the following form:

\[
n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{1.11}
\]

where \(A\), \(B\), and \(C\) are material-dependent specific constants. Equation (1.11) is known as Cauchy’s formula and it is typically used in the visible spectrum region for various optical glasses and is applies to normal dispersion, when \(n\) decreases with increasing \(\lambda\) [1.26, 1.27]. The third term is sometimes dropped for a simpler representation of \(n\) versus \(\lambda\) behaviour. The original expression was a series in terms of the wavelength, \(\lambda\), or frequency, \(\omega\), or photon energy \(\hbar \omega\) of light as:

\[
n = a_0 + a_2 \lambda^{-2} + a_4 \lambda^{-4} + a_6 \lambda^{-6} + \ldots \lambda > \lambda_{th} \tag{1.12a}
\]

or

\[
n = n_0 + n_2 (\hbar \omega)^2 + n_4 (\hbar \omega)^4 + n_6 (\hbar \omega)^6 + \ldots \hbar \omega < \hbar \omega_{th} \tag{1.12b}
\]

where \(\hbar \omega\) is the photon energy, \(\hbar \omega_{th} = hc/\lambda_{th}\) is the optical excitation threshold (e.g., bandgap energy), \(a_0, a_2, \ldots\) and \(n_0, n_2, \ldots\) are constants. It has been found that a Cauchy relation in the following form [1.28]:

\[
n = n_{-2} (\hbar \omega)^{-2} + n_0 + n_2 (\hbar \omega)^2 + n_4 (\hbar \omega)^4 \tag{1.13}
\]

can be used satisfactorily over a wide range of photon energies. The dispersion parameters of Equation (1.13) are listed in Table 1 for a few selected materials over specific photon energy ranges.

Cauchy’s dispersion relations given in Equations (1.11–1.13) were originally called the elastic-ether theory of the refractive index. It has been widely used for many materials although, in recent years, many researchers have preferred to use the Sellmeier equation described below.

1.3.2 Sellmeier dispersion equation

The Sellmeier equation is an empirical relation between the refractive index \(n\) of a substance and wavelength \(\lambda\) of light in the form of a series of single-dipole oscillator terms each of which has the usual \(\lambda^2/(\lambda^2 - \lambda_i^2)\) dependence as in

\[
n^2 = 1 + \frac{A_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{A_2 \lambda^2}{\lambda^2 - \lambda_2^2} + \frac{A_3 \lambda^2}{\lambda^2 - \lambda_3^2} + \ldots \tag{1.14}
\]

where \(\lambda_i\) is a constant, and \(A_1, A_2, A_3, \lambda_1, \lambda_2\) and \(\lambda_3\) are called Sellmeier coefficients, which are determined by fitting this expression to the experimental data. The actual Sellmeier