

# Preface

The optical spectroscopy of impurities in bulk semiconductors and insulators is a field of research that has been actively investigated in the last 60 years, resulting in a huge amount of published results. With time, there has been an evolution of the spectroscopic techniques toward higher spectral resolutions necessary for the observation of important spectroscopic details. There has been also a parallel evolution of the materials studied toward a better control of their impurity content and of their isotopic composition, to the resurgence of interest for materials like diamond, silicon carbide, or zinc oxide, and to the study of new materials like the nitrides and the magnetic semiconductors. The growth of the interest for the properties of hydrogen in semiconductors has also been a constant of the last 30 years. Last, but not least, optical spectroscopy has also been determinant in the study of quasi-monoisotopic materials made of nearly a single isotope.

One of the goals of optical spectroscopy of defects and impurity centres is to help in the determination of their atomic structure (chemical composition and symmetry in the host lattice), and when possible, of their electronic properties, in order to better understand their other physical properties, for their eventual use in various processes, or for mere curiosity and understanding. This is generally possible for not too complicated and reasonably localized centres, known as point defects, as opposed to extended defects. This requires the identification of good-quality spectra, which can be facilitated when isotope shifts are observed, and when measurements under uniaxial mechanical stresses or magnetic fields can be performed. This is not in general sufficient and when applicable, additional methods involving the electronic and nuclear spins of the atoms of the centres (electron spin resonance or ESR, electron nuclear double resonance or ENDOR) must be used. Important information on the atomic structure and location of defect atoms can also be obtained from the results of channelling measurements of alpha particles along specific crystalline orientations and from the interpretation of extended X-rays fine structure (EXAFS) measurements. The concentrations of electrically active centres are obtained by electrical methods like Hall effect measurements, and some of the energy levels of these centres can be obtained by deep-level transient spectroscopy

(DLTS). At a more general level, impurity concentrations can also be obtained by secondary ions mass spectroscopy (SIMS).

The atomic structures and electronic and vibrational properties of impurities and defects have often been confirmed or predicted from *ab initio* calculations. Different methods associated with these calculations have been of a great help to elucidate the thermodynamic stability and the vibrational spectra of impurity centres, and when different possibilities existed, such calculations have allowed making a choice based on thermodynamic arguments.

Three methods are mainly used in optical spectroscopy of impurity centres in semiconductors and insulators. One is absorption spectroscopy and the other one is based on photoluminescence. In absorption spectroscopy, the spectral characteristics of the radiation transmitted or reflected by a sample is analysed. In usual photoluminescence experiments, an intense optical excitation beam, generally at photon energies larger than the band gap, is focussed on the sample, and radiative transitions emitted by the sample at lower energies are recorded. In Raman scattering experiment, the external excitation must be monochromatic and at low temperature, one records weak photoluminescence lines at energies equal to the difference between that of the excitation line and of transitions of the centres with specific selection rules (Stokes lines). Each of these methods has its specific advantages and limitations.

One goal of optical absorption spectroscopy, which is a non-destructive technique, is the routine analysis of semiconductor materials (impurity concentration and homogeneity). A prerequisite is the existence of calibration factors of the absorption. These calibrations are obtained from the correlation of absorption coefficients or integrated absorption of well-identified features with atomic or defects concentration, obtained by ESR, SIMS, activation analysis, or atomic absorption analysis.

This book is the second volume of an ensemble devoted to the presentation of the optical absorption of impurities and defects in semiconductors and insulators. The first one, entitled "Optical Absorption of Impurities and Defects in Semiconducting Crystals I. Hydrogen-Like Centres" dealt with the electronic spectroscopy of centres whose electronic excited states are close to the first electronic continua of the crystals (conduction and valence bands).

The present volume is complementary to the preceding one, which was focussed on electrically active dopants. This one deals with two types of absorption: the first one is electronic and due to transitions between levels generally separated by energies representing a notable fraction of the band gap of the semiconductors, and associated with so-called deep-level centres or more shortly deep centres. Depending on the value of the band gap of the material, these transitions can occur in the ultraviolet, visible, or near-infrared region. The second type of absorption studied in this book is due to the vibration of isolated impurity atoms or impurity complexes, and it generally occurs in the infrared when purely vibrational. One advantage of this latter type of absorption is that it is a form of solid-state molecular spectroscopy which is independent of the electrical activity of the centres. These two fields cover also parts of the authors' experimental work during many years

and the presentation given here can look somewhat biased but we think, however, it reflects the situation in these domains, without pretending to be exhaustive.

Deep-level centres are defects or impurities that have energy levels generally located well below the conduction band minimum and well above the valence band maximum. They are found in the native state in crystals like diamond or aluminium oxide ( $Al_2O_3$ ) and they are responsible for the different colours found for these crystals. They can also be produced in these crystals by thermal treatments at high temperature or by irradiation with high-energy particles, and this is used indeed to produce artificially coloured gemstones. In semiconductors, they are due to metallic impurities like transition metals and to defect centres produced by high-energy irradiation of various origins. Deep centres can play important roles in semiconductor devices as they often act as recombination centres for charge carriers and therefore affect minority carrier life times. Deep centres associated with some metal atoms can also be useful for obtaining semi-insulating materials that can serve as substrates for devices technology. For instance, state-of-the-art bulk “pure” gallium arsenide would be p-type because of residual carbon; the natural introduction during crystal growth of  $As_{Ga}$  anti-site defects, which act as double-donors, allows pinning the Fermi level around mid-gap and therefore obtaining materials with resistivity about  $10^8 \Omega \text{ cm}$  at room temperature. In the same spirit, state-of-the-art “pure” indium phosphide is n-type because of residual sulphur, the main contaminant of phosphorus, and doping with iron, a mid-gap acceptor, allows InP substrates to be grown with high resistivity.

Electrical measurements, including space-charge techniques (DLTS), are indeed techniques privileged for their high sensitivity to investigate deep-level centres in semiconductors. However, they are not so efficient for identifying precisely the microscopic structure of the defects involved. Most of the centres with deep levels display electronic transitions which can be detected by absorption or photoluminescence spectroscopy, which help elucidate their physical properties and atomic structures.

In semiconducting and insulating crystals, centres involving foreign atoms (FAs) with masses significantly smaller than those of the atom(s) of the crystal can give vibrational modes at frequencies higher than those of the lattice vibrations. Such FAs can be residual impurities of the starting materials used in crystal growth (e.g. carbon in silicon), but also impurities or components of gases used during crystal growth or thermal processes (e.g. hydrogen, carbon, or nitrogen), or constituents or impurities of materials used to contain the molten material before crystal growth (e.g. boron, oxygen, or nitrogen). These modes do not propagate in the crystal and remain localized in the vicinity of the centres, hence their denomination of localized vibrational modes (LVMs), and when they produce a dipole moment, they can be observed in absorption. The role of the masses of the FAs in the frequencies of these LVMs implies the existence of isotope shifts of these modes when the FAs are not mono-isotopic, and this property is very useful for the chemical identification of the FAs. As for the electronic transitions, the concentration of centres can also be obtained from the intensities of the LVMs when a suitable calibration factor exists.

Chapter 1 starts with basic definitions necessary for the understanding of the subject, followed by sections summarizing different physical properties of the centres discussed later. It ends with indications of the terminology used in the description of the spectroscopic features, sometimes in relation to ESR spectra for the paramagnetic centres.

An overview of the bulk optical properties of the semiconducting crystals necessary to understand the spectroscopic properties of impurities and defects is provided in Chap. 2.

Chapter 3 describes the principles of absorption spectroscopy in solids, the main types of optical instruments used for this purpose, together with additional techniques to cool and compress samples, or to submit them to magnetic fields.

Electronic absorption of deep centres is discussed in Chap. 4. For this topic, we have been obliged to make a choice that we hope to be representative. A first category of centres includes some intrinsic and extrinsic radiation defects in silicon. Another one concerns the impurity centres and defects in diamond, with a special part devoted to nitrogen. For the third one, we consider EL2 in GaAs, and the last part is devoted to some transition metals in different semiconducting crystals.

The principles of the vibrational spectroscopy of impurity centres and defects are presented at the beginning of Chap. 5. We have also added some hints on the calculation methods used to predict the most stable atomic structures for defect centres and to obtain vibrational frequencies. The need to make a classification in the vibrational spectra of impurity and defects have led us to present in this chapter those related to substitutional FAs, isolated, paired, or complexed, after the general presentation. We have roughly followed the columns of the periodic table, with an inversion between carbon and boron because of the general conclusions which can be drawn from the results on carbon, especially in GaAs.

The vibrational spectra of interstitial atoms and related centres are presented in Chap. 6, with an important part related to oxygen. Hydrogen is nearly absent from this chapter as its vibrational properties are discussed in Chap. 8.

A large part of Chap. 7 is devoted to FAs sometimes classified as quasi-substitutional or off-centre, well represented by the oxygen-vacancy centre in silicon and germanium. We have also added in this chapter the features related to the C- and B-related irradiation defects.

Chapter 8 deals with the vibrational transitions of centre where hydrogen is involved. The centres first considered are the intrinsic defects containing one or several hydrogen atoms bonded to crystal atoms. A large part is devoted to the vibrational properties of the isolated  $H_2$  molecule in III–V compounds and in elemental semiconductors. The spectroscopy of complexes of hydrogen with FAs is divided into two parts. One concerns the centres resulting from the interaction with isoelectronic and interstitial atoms. The other one deals with the centres formed when the electrical activity of donors and acceptors is passivated by hydrogen. We have tried to describe in the last part the spectroscopy of some hydrogen-related centres whose origin is not clear.

This book is primarily intended for students and scientists interested in the optical properties of semiconductors, but it should be also useful to scientists and

engineers interested or involved in the characterization of semiconductors. For the understanding of the principles underlying the experimental data, an elementary knowledge of quantum mechanics and of group theory applied to solid-state physics and spectroscopy is required.

The writing of different parts of this book has benefited from oral or e-mail discussions with Brian Bech Nielsen, Jacques Chevallier, Paul Clauws, Alan Collins, Monique Combescot, Denis Côte, Gordon Davies, Stephan Estreicher, Robert Jones, Kurt Lassmann, Michael Stavola, Wilhelm Ulrici, Hiroshi Yamada-Kaneta, and George Watkins. Gordon Davies deserves special thanks for having accepted to write the foreword and for many valuable suggestions.

We are also indebted to Vladimir Akhmetov, Horst Bettin, Naomi Fujita, Christian Julien, Ludmila Khirunenko, Edvard Lavrov, Matthew McCluskey, Vladimir Markevich, Leonid Murin, Roland Pässler, Adele Sassella, Wilhelm Ulrici, and Ralf Vogelgesang for kindly sending information or figures used in the book. Warm thanks are addressed to Georg Bosshart for providing a very good photograph of the Dresden Green diamond and information on the Allnatt diamond.

The help and the suggestions of Claude Naud for a substantial part of the spectroscopic results obtained in our laboratories are gratefully acknowledged.

We wish to thank Bernard Perrin, director of the Institut des NanoSciences de Paris (INSP), for allowing one of us (BP) to co-write this book within the frame of this Institute.

Finally, let Claus Ascheron be thanked for his patience during the preparation of the manuscript, Adelheid Duhm for her support in the editing phase and Deepa Gopalakrishnan for her help in correcting the proofs.

Paris, France  
July 2011

Bernard Pajot  
Bernard Clerjaud

Optical Absorption of Impurities and Defects in  
Semiconducting Crystals  
Electronic Absorption of Deep Centres and Vibrational  
Spectra

Pajot, B.; Clerjaud, B.

2013, XXVIII, 512 p., Hardcover

ISBN: 978-3-642-18017-0