

Optical Properties of Diamond

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Optical Properties of Diamond

A Data Handbook

With 285 Figures and 21 Tables



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Front cover: Electroluminescence of a comb-structured planar p-i-n diode made on a diamond substrate activated with the A-band. The size of the structure is about 1 mm² (courtesy of Dr. A. A. Melnikov).

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Foreword

The unique properties of diamond are responsible for its pre-eminence as a gemstone, and give it a glamour and attraction unprecedented for any other mineral. As the first member of group IV of the periodic table of elements, carbon, in its crystalline form as diamond, has also fascinated scientists for at least 300 years.

Many experimental techniques have been employed in the study of diamond, and of these, optical spectroscopy has proven one of the most fruitful. The absorption line at 415 nm, characteristic of "Cape Yellow" diamonds, was first documented by Walter in 1891. Further work on this absorption, now known as "N3", by the Indian school under Sir C. V. Raman in the 1930s and 1940s led to a basic understanding of the system, which they observed in both absorption and luminescence. The N3 center is a structural defect in the diamond, and the absorption of light occurs by exciting electrons in this defect from one well-defined energy state to another. When the electron returns to the original energy level, luminescence is produced. Detailed studies of natural diamonds over the subsequent 60 years have discovered large numbers of absorption and emission lines, characteristic of different defects.

In 1904 Sir William Crookes showed that a colorless diamond could be turned green by long exposure to radium salts. The spectroscopic study of defect centers created by radiation damage in diamond, and the way in which these centers anneal following heat treatment, began in earnest in the 1950s and continues to the present day, creating new series of absorption and luminescence lines which are not normally found occurring naturally.

In 1955 the dream of converting graphite to diamond became a reality, and of the 100 tones of diamond now produced annually, around 80% is manufactured by the high-pressure, high-temperature (HPHT) route. This "synthetic diamond" or "man-made diamond" has all the desirable mechanical properties associated with diamond which makes it suitable for industrial applications, but the optical properties are quite different from those of the majority of natural diamonds. At present there is considerable interest in the spectroscopy associated with nickel and cobalt, the metals normally used in the synthesis of diamond. Here again we find a large number of absorption and luminescence lines which are not normally seen in natural diamond.

Diamond can also be produced from the gas phase to produce "thin film diamond" by chemical vapor deposition (CVD); in fact, developments of the CVD process over the last 15 years now enable polycrystalline diamond wafers more than 150 mm in diameter and more than 1 mm thick to be produced on a routine basis.

Because this material is grown in a quite different way from natural diamond or HPHT diamond, some of the defects it contains are unique to CVD diamond.

As a result of the intensive research carried out on all forms of diamond, particularly during the last 50 years, a huge number of absorption and luminescence systems have been documented. Some are in the regular scientific journals, others in conference proceedings or special supplements to journals which are more difficult to obtain; some work is found only in Ph.D. theses, and there is a large body of important research on diamond which has been carried out by Russian scientists but not translated into English.

Recognizing the need for a single source of reliable information, Dr Alexander Zaitsev has gathered together all of the known references dealing with optical centers in diamond. This is an ongoing task; new optical centers continue to be discovered while the work is being compiled, but publication of the present volume is a formidable achievement for which the author must be congratulated. It is a book which anyone working on the spectroscopy of defects in diamond will want on their desk, and to which they will make frequent reference.

Professor Alan T. Collins
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To my wife Inga

Preface

Optical properties play an important role in the investigation, characterization, and application of diamond. These optical properties have always made diamond so attractive in its natural beauty, and it still keeps its commercial value today. The unique optical properties of diamond are also one of the main criteria for its industrial use, being the second best property after mechanical hardness.

Many outstanding physical properties of diamond make it an attractive material for optical and optoelectronic applications. Diamond has the widest optical transparency band of all known solids, which ranges from 0.22 μm (fundamental absorption edge) to the far-infrared. Only the intrinsic vibrational absorption band of moderate intensity between 2.5 and 7 μm disturbs the perfection of diamond's transparency in the infrared region. Being transparent in the ultraviolet, visible and infrared spectral regions, diamond provides many opportunities for lattice defects to reveal the optical activity of their electronic and vibrational transitions. The large bandgap energy (5.49 eV) is a particularly favorable condition in the case of luminescence, because the radiative electronic transitions require that both the ground and excited electronic states lie within the bandgap. The high mechanical hardness and thermal conductivity of diamond greatly support its optical applications making diamond optics very stable and resistant in many respects.

When discussing the optical properties of a material its optical centers should be considered carefully, because their properties and abundance determine almost all optical performance of the material. Besides, the content of optical centers is the main parameter of the optical characterization of the material. So far more than 150 vibrational and more than 500 electronic optical centers have been detected in diamond within the spectral range of 20 to 0.17 μm ; that is, between the vacuum ultraviolet and the mid-infrared regions. To fill up this large spectral range diamond possesses many optically active defects of various origins including intrinsic and impurity-related, point and extended defects. Both types of intrinsic point defects (vacancy- and interstitial-related) in diamond can form optical centers. Many impurities are known to form optically active defects in diamond: H, He, Li, B, N, O, Ne, P, Si, As, Ti, Cr, Ni, Co, Zn, Zr, Ag, W, Xe and Tl. Many of the optical centers related to these impurities have been created artificially using doping during growth and, in particular, ion implantation. These centers have never been seen before in pristine natural diamonds. The reason for that is the very short and strong sp^3 hybridized covalent C-C electronic bonds preventing thermodynamical equilibrium (or quasi-equilibrium) incorporation of impurities (even hydrogen) into the diamond lattice. The only remaining possibility is the use of forced methods of

impurity insertion, such as ion implantation. Another reason for the high efficiency of the ion implantation as a method of optical activation of diamond is its inevitable creation of radiation damage. Since the majority of optically active defects in diamond are complexes involving impurity atoms bound to some intrinsic structural defects (vacancies and/or interstitial atoms), defect production is an essential advantage of ion implantation.

The impurities mentioned above are not equally active in creating optical centers in diamond. Some of them, like Si, form only one optical center characteristic of the specie. Others, like N, produce a great number of optical centers throughout the whole optical range of diamond. Nitrogen is an impurity of special importance for diamond. Firstly, nitrogen is responsible for vast majority of impurity-related optical centers. Secondly, many of the most intense and most interesting optical centers for practical applications are known to be nitrogen-related. Nitrogen can form optically active defects in many ways: single isolated nitrogen atoms, multi-atom nitrogen complexes, and complexes of nitrogen atoms with intrinsic lattice defects and with other impurities. Thus the presence of nitrogen in diamond in almost any form immediately changes its optical properties. One of the consequences of high optical activity of nitrogen is the physical classification of diamond based primarily upon nitrogen-related optical absorption.

An important optically related feature of diamond is its high Debye temperature (about 2000 K). Actually this is the highest Debye temperature of those known for any solids. Owing to the high Debye temperature, a remarkable excitation of phonons in the diamond lattice, and consequent electron-phonon coupling with lattice modes in optically active defects, occurs at elevated temperatures. As a result, many optical centers in diamond interact predominantly with local and quasilocal vibrations of the corresponding defects and retain their spectral structures and radiative transition probabilities unaffected to relatively high temperatures. For instance, the H3 or 575 nm nitrogen-related centers exhibit a strong luminescence intensity at temperatures above 500°C.

Being a nondirect bandgap semiconductor, diamond, at first glance, does not appear to be a promising material for light-emitting optoelectronic applications. Indeed, band-to-band radiative transitions in diamond require the participation of phonons, which strongly reduces their probability and makes band-to-band intrinsic luminescence ineffective. However, fortunately the conduction band of diamond has a local minimum in the center of the Brillouin zone, lying at about 7.2 eV above the maximum of the valence band. This peculiarity has a great effect on the probability of the extrinsic radiative transitions occurring at the centers, the excited electronic levels of which lie in proximity to the conduction band. Namely, the wave function of the excited states of such optical centers may possess a considerable local maximum at $\mathbf{k} = 0$. This means that the impulse relaxation required for a quantum assisted electronic transition can easily occur inside the defect via interaction with its quasilocal vibrations. Thus the probability of radiative recombination over such optical centers can be high and even dominant. The light emission efficiency of extrinsic optical centers in diamond is expected to be like that in GaP, which has a bandgap structure analogous to that of diamond, and which is known to be an effective semiconductor for light-emitting diodes.

The physical background of the optical properties of diamond has already been discussed in detail in a number of books and review articles. There is no need to repeat it here. The aim of the present handbook is to present in a systematic manner the experimental and theoretical data on optical properties of diamond accompanied by short explanations and models. This is a handbook, which is supposed to provide a short and quick way to search for concrete information, rather than to give a general view of the subject. It will help diamond researchers to find a reference or assess the level of knowledge of a particular optical feature.

Very often the data obtained by different authors are contradictory. This handbook presents the different points of view equally without any prejudice. The presentation of the information is based on the presumption that all of the experimental data have been obtained correctly (unless the opposite is admitted by the authors themselves). Readers have to form their own opinion based on the facts available and to decide which data or interpretation seem to be more correct. However, in some cases the author of the present handbook gives his opinion; this is marked with (*).

The current understanding of the optical properties of diamonds is sometimes considered as excellent. However this statement is valid only for a few well-known "classical" optical effects (provided they are located in a perfect diamond lattice) and in the case of the basic effects on some main intrinsic and nitrogen-containing defects. The present handbook clearly demonstrates that the number of questions and problems in optics of diamond is growing much faster than the acquisition of reliable data and the elaboration of thought-out answers.

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