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Handbook of industrial diamonds and diamond films

Handbook of Industrial Diamonds and Diamond Films
(Eds M Prelas, G Popovici, L K Bigelow)
(New York: Marcel Dekker Inc., 1997)

Over the past years, diamonds, diamond films, and diamond-like carbon films have become of primary importance in many fields of new technology. Several practical applications of these materials have turned out to be commercially viable. However, alongside the attractive qualities of diamond materials, it must be noted that the growth of large diamond monocrystals with given electrophysical properties still remains extremely complex from a technological standpoint. The cost of such crystals is very high, and the problem of their local doping with electrically active impurities remains only partially solved. An alternative and attractive means is based on the synthesis of diamond films from a gas plasma containing ions of carbon and hydrogen.

This book is dedicated to the problem discussed every year at several international conferences (in 1998 they were held in the USA and South Africa). In 1994, a collection of reviews by 30 leading specialists from different countries was published, edited by G Davies [1]. This collection was reviewed in *Physics Uspekhi*. Unfortunately, the book was not published either in Russia or Ukraine, where active work is being carried out in the synthesis of diamond monocrystals, and diamond and diamondlike carbon films.

The book at hand is great in volume — 1214 pages. Among the authors of the 34 chapters are specialists of world renown on physical phenomena in diamonds. It is pleasing to note that the Russian, Belarussian and Ukrainian physicists, V I Nepsha, S M Pimenov, V G Ral'chenko, A G Gontar' and A M Zaĭtsev are among the authors.

The book opens with an article by A T Collins, dedicated to the band structure of diamonds. The article touches a broader range of questions than the contents suggest, since as well as the experimental data, on the basis of which a reliable picture and interpretation of the band structure of diamonds in constructed, it also considers the energy spectra of basic point defects (vacancies) and two electrically active dopants (boron and nitrogen). The contents of the article are largely based on the results of earlier works compiled in Ref. [1], to which have been added the results from the use of synchrotron radiation to find the optical constants for photon energies $h\nu = 5-10$ eV (Logofetidis, 1992). Surprisingly, there is no reference to the well-known theoretical calculations carried out by Bernholz and his colleagues in recent years.

The following review, by P Klausing, covers the morphology of diamond monocrystals grown using the main contemporary methods, natural diamonds, and crystals (grains) in diamond films grown from gas plasma. Notable is the author's interest in several particular types of small diamonds grown at high pressure and temperature (the HPHT method), when it is possible in a fully reproducible manner to control the crystallite morphology with optimal parameters for applications (cutting hard materials).

The author has interesting opinions about the effect of an oxygen dopant on the character of growing diamond crystals.

The article by P Gielisse covers the mechanical properties of the whole range of diamond materials. At present, it is the mechanical properties which give the main uses for diamonds. Gielisse's article includes a precise definition of the properties and fields of employing diamond materials depending on how they were produced and their geometry (small crystals of different forms, films). The properties of natural diamond crystals are also considered. There are tables and graphs allowing a quick orientation in the difficult and very dissimilar field of the technical use of diamond materials. There is an interesting discussion of a specific property which the authors call 'toughness'. By this is meant the limiting value of the pulsed energy which may be released 'almost momentarily' inside the material without destroying it. There is an analogy with processes causing pile-up (clusters) of radiative defects at the end of the passage of heavily charged particles. The author gives approximate formulae, allowing comparison of toughnesses of different types of diamonds.

Chapter 4, by D'Evelin, is dedicated to the surface properties of diamonds. This field, which considerably borders with physical chemistry, is naturally important for practical applications and is of fundamental interest. The current state of knowledge of the properties of diamond surfaces and surface interactions with hydrogen, oxygen, oxides and halogens is put forward. The surface structure of diamonds with planes of the main types (111), (100) and (110) is described in detail. There is an analysis of the chemical reactions of different substances with diamond surfaces (desorption, the interaction of atomic hydrogen with other adsorbed impurities, and surface diffusion). It is a pity that there are no references to the works of Yu V Pleskov (Moscow), which have been published in the leading Russian journals and translated into English.

The article on the heat capacity, heat conductivity and thermal expansion of diamonds, by V I Nepsha (Moscow), presents data on diamond properties, long since defined and recognized as of primary importance in solid-state theory and in application. The author gives the principal important data on the thermal conductivity of diamond crystals enriched in the isotope ^{13}C, whose characteristics were predicted by Berman.

The next chapter, by G Grebner, includes data on the method for obtaining the 'thermal' parameters of diamonds. A great deal of attention is given to the method of measurements in CVD films. Unfortunately, there is no information about the simple and effective methods devised in Moscow by Yu A Kontsev and his colleagues and published in 1995 – 1997.

The largest chapter, by A M Zaĭtsev (Minsk), covers the optical properties of diamonds. This chapter is a monograph in essence. The chapter contents largely coincide or overlap the analogous section of monograph [1], but significantly surpass it in the presentation of data from Russian-speaking

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authors of the countries of the CIS. This chapter, as all the chapters, is excellently illustrated and reflects the tremendous labour of its author [2].

Similar comments may be made for the chapter "Electrical and electronic properties of diamonds" by A G Gontar' (Kiev). As in practically all the review articles, there was a significant quota of references to works on CVD films.

Chapter 10, by K MacNamara, Rutledge and K Glison, includes a detailed description of the experimental methods of research on the main parameters of diamonds. The review is based on works mainly published within recent years including 1995. Its contents primarily reflect the authors' interest in the electronic structure and optical properties of diamonds, partly from analysis of transport phenomena and nonequilibrium electronic processes. The chapter contains valuable material for a wide range of specialists working in the fields of physics and technology not only of diamonds, but of the whole family of wide-band semiconductors. In several of the sections, there are detailed bibliographies (methods based on electron beam scattering, electron microscopy, and X-ray and electron diffraction). As far as we know, this is the first generalization of the possibilities and results of different experimental approaches to the definition of diamond parameters (see Table 1 on page 414 of the book).

Regarding the section on the analysis of data on positron annihilation, we note that this has been developed only in a small number of research centres. At present, it is inaccessible to the majority of researchers.

The large Chapter 11, by D Goodwin and G Butler, is dedicated to the theory and methods of chemical deposition of diamond films from a gas plasma (CVD). As is known, the first experimental results in this field were obtained back in the middle of 50s, but a great interest in carbon films appeared in the early 80s. In the broad bibliography, there are about 20 review articles published since 1987! Particular attention is paid to the role of atomic hydrogen, whose presence in the plasma, according to most published data, is an essential factor in the complex chain of processes in the growth of films. Up to date data on the content of atomic hydrogen in plasma are presented.

A description of the electrophysical and other properties of film grown by CVD makes up a large part of the chapter. These conclusive results are of great interest. The main part of the chapter covers the chemical processes in a plasma interacting with a growing diamond film or other substrate. The authors' conclusions, in agreement with many parallel studies, are that the quality of the films improves with the relative proportion of atomic hydrogen, but on increasing the rate of growth, the number of imperfections invariably rises.

The following chapters (Boseman, Stoner and Glass) contain a review of data on nucleation in the growth of diamonds and on the epitaxial growth of this substance on different substrates, including BN, beryllium oxide BeO, silicon carbide SiC, nickel Ni and cobalt Co. The authors were particularly interested in nucleation processes in the presence of an applied external electric field. To speak of a reliable technology of such processes is evidently premature. The cited literature is mainly very new (1988 – 1995).

The review by Kalish and Prower covers the problem of ion implantation in diamonds and diamond films, including diamond – graphite phase transitions occurring in thin layers, the depth of which can be controlled within certain limits.

It is well known to specialists that ion implantation was used even in the 60s with some success for local doping of diamonds [3]. Natural causes of this are discussed in the book, using literature right up to 1995. Particular attention was paid to the unavoidable radiation defects and phase transitions (amorphization and the transformation from diamond to graphite). Due attention is given to local impulse annealing of implanted diamond layers. The contents should be of interest to specialists working in this direction. Judging by the recent publications, work in this direction is becoming more intense.

The next chapter, by Ral'chenko and Pimenov, gives data on the mechanical treatment of diamond crystals, i.e. such technical methods as cleavage, cutting by mechanical interactions, and the effect of intense laser radiation or electric discharge (spark). A separate section covers methods of polishing diamonds — an old art, which even the philosopher B Spinoza used to practice! Current laser techniques permit excellent results to be obtained quickly and reproducibly. New data are presented for the method of local deposition of diamond films, opening a new direction in solid state electronics, an alternative to local ion milling (see, for example, the microphotograph on p. 1009).

The final chapter (Dreyfus and Fox) is a critical review of data from publications of recent years on active elements of solid state electronics based on diamonds. The authors use a large number of original sources, including publications from 1995. At the beginning, there is a critical analysis of the main classes of diamonds as a material for electronic devices, and also information on the existing methods for creating stable electrical contacts between diamonds and other materials (primarily metals). Further is a discussion of the main ways and possibilities for making devices using diamond. Then there is a valuable reference section for engineers and technologists about existing devices (1982 – 1995), including names, basic parameters and references. This chapter in its entirety should certainly be made available to specialists in the CIS (especially in Russia, Ukraine and Belarus'); however, a publication in *Physics Uspekhi* probably would not be sufficiently comprehensive.

In summary, this book will be of great use to specialists in the field of solid state electronics. In comparison with single-crystal silicon and germanium, where the decisive achievements which have brought us to the current state of microelectronics were made 5 – 7 years after the creation of transistors, diamond is offering stubborn resistance to physicists, chemists and engineers, but progress is being made.

The repetition of a number of facts concerning electrophysical parameters of diamond materials, as well as some differences in the numerical expression of their parameters is unavoidable. The compilers and editors of the book — Mark Prelas, Galina Popovici, and Lewis Bigelow — have, in a short period, published a valuable book for specialists, which should be in every fundamental library covering the fields of applied physics and solid state electronics.

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