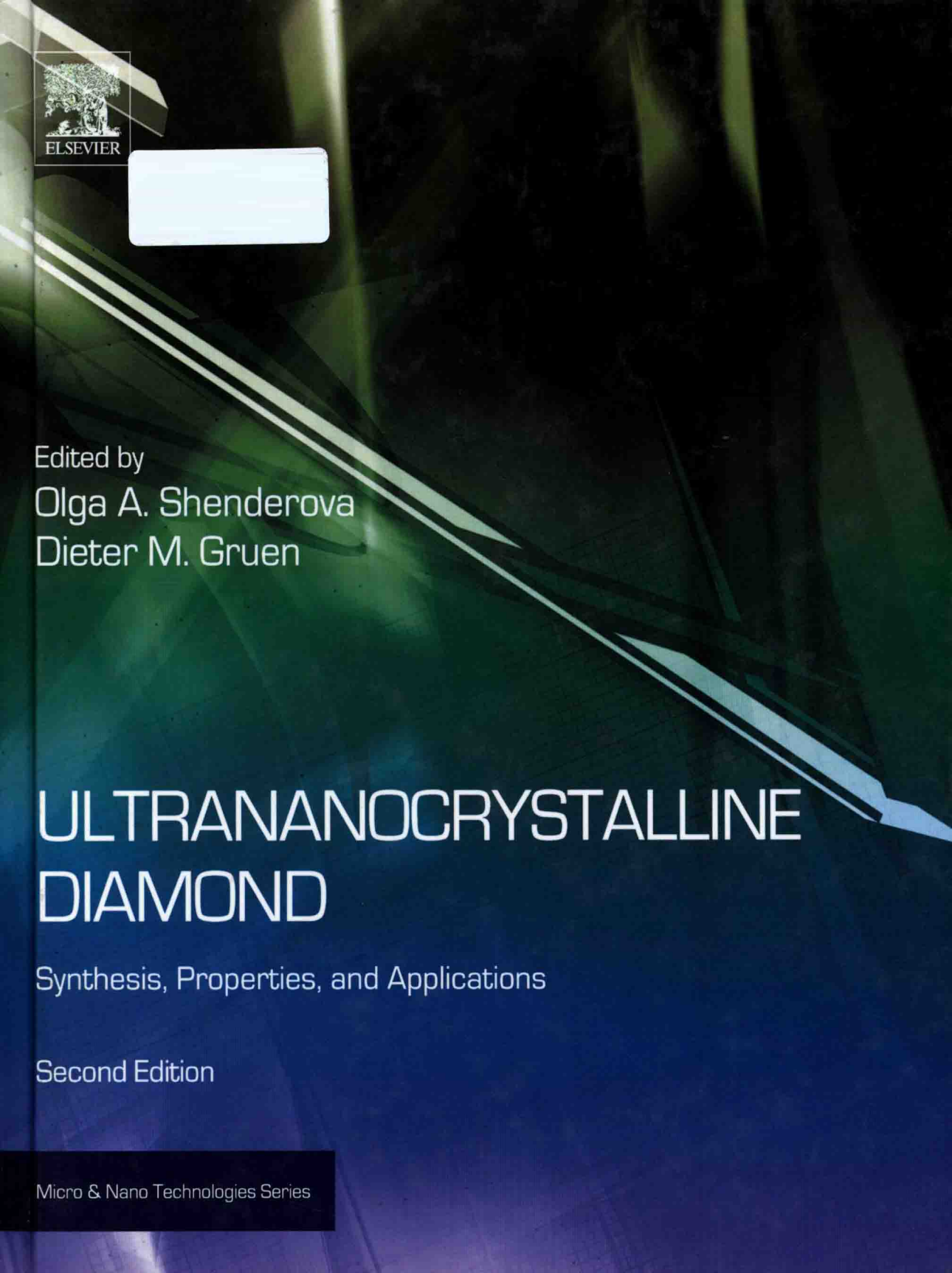
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Edited by
Olga A. Shenderova
Dieter M. Gruen
ULTRANANOCRYSTALLINE DIAMOND
Synthesis, Properties, and Applications
Second Edition
Micro & Nano Technologies Series

Ultrananocrystalline Diamond

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Ultrananocrystalline Diamond

Preface

The first edition of *Ultrananocrystalline Diamond* was published in 2006, revealing vast synergistic relationships between two communities of scientists working largely independently with ultrananocrystalline diamond (UNCD) in one of two forms: as a dispersed powder made by detonation techniques and as a chemical vapor deposited film. Since then, important events have taken place in the fields of nanostructured carbon materials in general and UNCD in particular. The discovery of graphene was awarded the Nobel Prize in Physics in 2010, spawning further interest in carbon nanostructures worldwide. Nanostructured diamond experienced important advances in synthesis, processing, characterization, and applications, accelerated by a widely expanding research community working with UNCD. The key purpose of this second edition of the book is to give a broad overview of the forefront of research in the UNCD field, providing a focus for and giving direction to the next generation of experimental and theoretical developments.

Nanoscale diamond particles were first produced by detonation in the USSR in the 1960s, but they remained essentially unknown to the rest of the world until the end of the 1980s. Since then, a number of important breakthroughs in purification, surface functionalization, and deagglomeration led to wider interest in these particles with diameters as small as 4–5 nm, which are now known as detonation nanodiamond (DND). DND is utilized in such applications as polishing, nanocomposites, and different areas of medicine. Another class of nanoscale diamond particles is nanodiamond produced by milling of high-pressure high-temperature diamond microcrystals providing nanoscale diamond particles containing intrinsic color centers aimed at revolutionizing biomedical imaging and quantum optics applications. Research on the synthesis of UNCD films began in the early 1990s when Gruen conceived the idea of using fullerene and later hydrocarbon molecules as carbon sources in hydrogen-poor noble gas microwave plasmas so as to achieve very high renucleation rates. The films, composed of 5–10 nm randomly oriented diamond crystallites with sharp grain boundaries, have many fascinating properties not possessed by conventional microcrystalline diamond films. The discovery and subsequent development of UNCD films has already resulted in a variety of novel applications. Some of these have reached the stage of commercialization while others are likely to follow this path as the technology continues to mature.

The content of the book is divided into three parts. The first part provides an overview of basic information and recent advances in synthesis and processing of UNCD. The second part addresses advances in nanodiamond characterization and properties measurements. The third part provides in-depth discussions of several emerging applications of UNCD films and nanoparticulate diamond.

The book starts with a chapter by Barnard on modeling of nanodiamond particle stability including studies on the distribution of incidental impurities and functional defects such as photoluminescent color centers. A summary of numerous synthetic

means to produce nanoscale diamond particles that have been reported up to date is given in the chapter by Danilenko, the inventor of DND, and Shenderova. The chapter emphasizes that development of novel DND synthesis approaches is required that will significantly increase production volume and purity while decreasing aggregate sizes of as-synthesized DND. Colloidal suspensions of individual DND particles of only 4–5 nm in size (so-called single-digit nanodiamond) recently became available, as described in the chapter by Osawa and coworkers. The availability of single-digit DND particles has broadened perspectives on the application of nanodiamond particles in composites and nanomedicine. The chapter by Kuznetsov and Butenko discusses conditions of nanodiamond phase transformation through graphitization that has important practical implications. A number of modern techniques based on electron, X-ray, RF wave, and visible light interaction with materials recently helped to reveal several key questions about the structure, morphology, and presence of nitrogen impurities in DNDs. These findings are discussed in the chapter by Vlasov, Turner, Tendeloo, and Shiryev. The chapter by Zvyagin and Manson reviews the basic luminescent properties of nitrogen-vacancy (NV) color centers in diamond nanoparticles, with a focus on the hotly debated mechanisms of ground spin-state polarization and the mechanisms of photoconversion that affects photostability. Progress toward unveiling the influence of the nanometer-proximal diamond surface on the emission properties of NV centers is also addressed. Neitzel, Mochalin, and Gogotsi discuss recent advances in surface chemistry of nanodiamond and nanodiamond–polymer composites, while M. Ivanov and D. Ivanov critically examine applications of nanodiamond and other ultradispersed carbon particles in lubricating oils for reduction of wear and friction. There is increasing evidence that nanodiamonds can be effectively utilized as a platform for a variety of diagnostic and therapeutic applications. Dean Ho and colleagues demonstrate the powerful therapeutic sequestering and targeting effect of nanodiamonds and its potential for improving the ability to treat a broad spectrum of diseases such as cancer. During the pursuit for novel uses of nanoparticles, it is imperative to independently assess the biocompatibility of nanosized particles. The chapter by Schrand, concluding the book, reviews the current literature on nanodiamond biocompatibility, addresses the current methods for studying biocompatibility, and discusses specific factors responsible for nanodiamond biocompatibility through the exploration of *in vitro* and *in vivo* data.

Advances in research and development of particulate nanodiamonds are discussed in parallel with progress in the area of UNCD films. The synthesis of UNCD films both by microwave and by hot-filament techniques is discussed in the chapter by Asmussen, Grotjohn, and Schuelke. Attention is paid to theory, modeling, and diagnostics as well as to the scaling up of microwave plasma machines for the growth of homogeneous UNCD films on 8" diameter and larger wafer sizes. Cost-effective development of such processes will be key to the rapidity with which UNCD films will penetrate the marketplace.

The reasons for the unique properties of UNCD films are to be found in the fundamental ways in which UNCD particles differ from larger diamond crystallites. In particular, the highly unusual rehybridized bonding at the ubiquitous UNCD grain

boundaries is reexamined using a combination of molecular dynamics and density functional tight-binding calculations. This sophisticated approach allows Adiga, Zapol, and Curtiss to draw conclusions concerning the thermal stability and the effect of annealing on sp^2/sp^3 hybridization ratios in UNCD films. These authors also examine the complex bonding relationships that can exist for carbon nanotubes reacting with the reconstructed diamond (100)-(2 × 1) surface revealing unexpected energetically stable nanotunnel structures.

Using secondary ion mass spectrometric measurements, Michaelson and Hoffman have shown that UNCD films incorporate about 5 atomic percent hydrogen during synthesis, a fact not explicitly taken into account in the work of Adiga et al. The work of Michaelson and Hoffman explores in detail the effect by means of which hydrogen increases by several hundred degrees the thermal stability of the films relative to that found for diamond particles. Detailed studies involving isotopic exchange, Raman and high-resolution electron energy-loss spectroscopy, and theoretical calculations allow them to conclude that this effect is primarily due to "grain boundary stabilization" arising from incorporated hydrogen atoms bonded to sp^2-bonded carbon atoms located at internal grain surfaces.

About 10 years ago, Gruen and his collaborators found that the progressive substitution of nitrogen for argon in the synthesis gas causes UNCD films to attain electrical conductivities that reach several hundred S/cm for 20% additions of nitrogen. A chapter by Arenal explores this phenomenon in detail and concludes that it depends on the formation of 3–5 nm diamond crystallites bonded end to end so as to form 80–100 nm long diamond filaments surrounded by a graphene-like sheath that is 2–3 layers thick. It is thought that complex interactions of UNCD crystallites with thermally unstable polymeric HCN, polynitrile, and polyacetylene precursors may be involved in the formation of these highly unusual densely interwoven electrically conducting "diamond wires."

A chapter by Auciello reviews the production of UNCD MEMS and NEMS structures using both selective film deposition and photolithographic coupled with reactive ion etching techniques. Device applications frequently require the integration of UNCD films with dissimilar materials in film form including piezoelectric oxides, metal films, and biological materials for a new generation of biological applications. The range of devices developed up to now include RF MEMS/NEMS resonators, piezoactuated NEMS switches, UNCD AFM tips, and MEMS/NEMS biomedical devices and biosensors.

Synthesis and properties of core/shell nanocarbon ensembles including UNCD/graphene ensembles are described in a chapter by Gruen. The goal is to create new classes of materials with energy conversion efficiencies that can compete with electromagnetic induction. The new approach to thermoelectricity focuses on increasing the "present" and "transported" electronic entropy by the use of biphasic ensembles. Decoupling the thermopower from the carrier density in this way would enable hitherto unrealized values of power factors. This ambitious approach to thermoelectricity requires a detailed understanding of the processes associated with transport of entropy across interfaces and in a temperature gradient. Early

experimental results are reported on two of the nanocarbon model systems that have been explored in this challenging effort up to now.

We hope that this present book will attract the attention of scientists working in other areas of nanostructured materials on the opportunities for applications offered by UNCD in its various forms. We believe that a wide variety of new, unexplored areas of research within carbon nanostructures and particularly still exist.

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