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Editorial

The Many Facets of Diamond Crystals

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Abstract: This special issue is intended to serve as a multidisciplinary forum covering broad aspects of the science, technology, and application of synthetic and natural diamonds. This special issue contains 12 papers, which highlight recent investigations and developments in diamond research related to the diverse problems of natural diamond genesis, diamond synthesis and growth using CVD and HPHT techniques, and the use of diamond in both traditional applications, such as mechanical machining of materials, and the new recently emerged areas, such as quantum technologies. The results presented in the contributions collected in this special issue clearly demonstrate that diamond occupies a very special place in modern science and technology. After decades of research, this structurally very simple material still poses many intriguing scientific questions and technological challenges. It seems undoubted that diamond will remain the center of attraction for many researchers for many years to come.

Keywords: diamond; high pressure high temperature; chemical vapor deposition; defects and impurities; color centers; carbon isotopes; structural defects; crystal morphology

1. Introduction

Diamonds, which possess a remarkable range of extreme and outstanding properties superior to other materials, have been attracting huge interest as a versatile and technologically useful material. Advances in diamond synthesis and growth techniques have paved the way for this unique material to many existent and prospective applications, which now range from optics and electronics to biomedicine and quantum computing. Besides its importance as the strategic future of electronic material, diamond has been the classical model object of fundamental research in solid-state physics, chemistry, and engineering. Diamond occupies a very special place in the Earth sciences, where it serves as an invaluable source of information about the Earth's interior. Of course, being the king of gems, diamond is the key stone for the gem industry and gemological science.

Diamond is an allotrope form of carbon that is thermodynamically stable at high pressures. It has a face centered cubic structure with each carbon atom covalently bonded to its four nearest neighbors in a regular tetrahedron. This structural arrangement coinciding with the sp3 hybrid orbitals of carbon yields a rigid framework, which combined with the strength of the C-C bond gives rise to many outstanding properties of diamond.

At first sight, the idea proposed by the editorial team of *Crystals* to organize a special issue dedicated to diamond crystals seemed somewhat perplexing inasmuch as diamond is truly a multidisciplinary subject and the issue will inevitably be composed of contributions from very different areas of diamond research that may complicate its overall comprehension. On the other hand, as it frequently happens, solutions to some particular issue may lie just a step aside of the subject area and breakthroughs are only possible with a multidisciplinary approach. Diamond is such a case. To structure the editorial introduction to this special issue, I conventionally divide the subjects into what concerns natural diamonds and synthetic diamonds. The former are mainly considered in the Earth sciences and the latter in the material science, physics, and engineering.

2. Some Facets of Natural Diamond Crystals

Considering the importance of diamond in the Earth sciences, I cannot help quoting the famous dictum of the eminent scientist Sir Charles Frank: If "A snowflake is a letter to us from the sky" (Nakaga) then "a diamond is a letter to us from the depths, and a letter more worth reading since we can visit the sky". Indeed, most diamonds are known to form at the depths of 140–200 km and brought to the surface by ancient volcanic activity. Due to the exceptional mechanical strength and chemical inertness of diamond, it can bring to the surface the specimens of the deep Earth interiors in an unchanged form. For decades, diamond research in the Earth sciences has been dominated by the studies of inclusions hosted in natural diamonds as well the specific rocks called xenoliths, which host diamonds. A wealth of information has been gathered from these studies. It has been established that most of natural diamonds can be assigned to the two major parageneses: peridotitic and eclogitic [1–4]. By the use of radiogenic isotopes in the minerals trapped within diamond it is found that diamonds are very old, down to 3.0 Ga, that is about two-thirds of the age of the Earth, and the youngest being around 1.0 Ga and possibly less [5]. These and subsequent studies on mineral and fluid inclusions in diamond have laid the foundation for our understanding of the geochemical and mineralogical environment of diamond formation in the Earth's mantle.

In recent decades there has been clear trend in natural diamond studies consisting in paying more attention to the internal structure and properties of diamond itself rather than to focus just on the entrapped inclusions. The real structure of natural diamond crystals can be considered a storehouse for genetically valuable information. Recently, numerous investigations have been undertaken to extract and decipher this diamond message. In their contribution, Giovanna Agrosi, Gioacchino Tempesta, Giancarlo Della Ventura, Mariangella Cestelli Guidi, Mark Hutchison, Paolo Nimis, and Fabrizio Nestola studied diamond crystals from Sao Luiz (Juina, Brazil) [6]. Diamonds from Juina, Brazil, are well-known examples of superdeep diamond crystals formed under sublithospheric conditions at depths greater than 400 km [7]. Such superdeep diamonds are very rare and their investigations provide paramount information about the physical and chemical conditions in the Earth's regions as deep as the mantle transition zone and the lower mantle [8,9]. Using X-ray diffraction topography and FTIR micro-spectroscopy, the authors show that the studied crystals demonstrate features, which are commonly associated with deformation processes by solid-state diffusion creep under high pressure and high temperature. These observations testify the very deep origin of the Juina diamonds.

Detailed studies of the internal structure of diamond derived from different sources may help to establish possible connections between the primary kimberlitic sources and secondary alluvial placers. Alexey Ragozin, Dmitry Zedgenizov, Konstantin Kuper, and Yuri Palyanov consider in their contribution specific diamonds from the Zarnitsa kimperlite pipe (Yakutia) that show transition morphologies between octahedron and rounded rhombic dodecahedron and have sectorial mosaic-block structure [10]. Such diamonds have not been previously reported for any other known kimberlite pipes of the Yakutian diamondiferous province but, as shown in this paper, demonstrate some similarities in the internal structure with diamonds from the alluvial placers of the Siberian Platform. However, the authors come to an important conclusion that, despite the physical resemblance and the similarity of the internal structure, diamond crystals from the Zarnitsa kimberlite pipe and the rounded diamonds from the alluvial placers were formed due to essentially different processes. Diamonds from the Zarnitsa kimberlite pipe evolve from polycrystalline cores to monocrystals, while an alluvial placer diamond splits up the spherulite-like structure.

The problem of the origin of alluvial diamonds is further considered in the contribution from Alexey Ragozin, Dmitry Zedgenizov, Konstantin Kuper, Viktoria Kalinina, and Alexey Zemnukhov, who studied the internal structure of yellow cuboid diamonds from alluvial placers of the Northeastern Siberian platform [11]. Rich diamond alluvial placer deposits are located in this region and the primary sources of the diamonds in these placers have not been discovered yet. An intriguing question here is that the studied cuboid diamonds constitute approximately 7–7.5% of the alluvial placer diamond collection, while diamonds with similar habit are infrequent in Siberian kimberlites and in amount do not exceed 2% of the total diamonds found in the region. It is therefore thought that the kimberlites discovered in the Siberian platform are unlikely to be the source of these diamond placers. The presented paper, being a part of an extensive study of alluvial diamonds from the Northeastern Siberian platform, provides new information on the internal structure of diamonds from these placers and contributes to solving the challenging puzzle of their origin.

Diamond is composed of carbon, which exists in nature in two stable isotopes ^{12}C and ^{13}C with average abundances of 98.9% and 1.1%, respectively. Natural diamonds are known to demonstrate slight variations of the carbon isotope composition, which is measured in parts per thousand (permil) relative to the standard (PDB, a fossil belemnite). A lot of valuable information has been gained from the isotopic studies on diamond (see reviews [12,13]). For instance, diamonds of the two main parageneses, peridotitic and eclogitic, show clear differences in the carbon isotope compositions, which is thought to be due to different carbon sources for peridotitic and eclogitic diamonds. However, the overall picture is much more complicated, and to explain the heterogeneous distribution of carbon isotopes in natural diamond crystals two major models are considered: (1) changing of the carbon source; and (2) fractionation of a fluid over the course of diamond crystallization. Vadim Reutsky, Piotr Kowalski, Yuri Palyanov, EIMF, and Michael Wiedenbeck in their contribution provided clear evidence of carbon and nitrogen fractionation related to the growing surfaces of a diamond [14]. This work is a vivid example of the importance of the experimental modelling contribution to solving the problems of natural diamond genesis [15–18]. By studying diamonds produced in high pressure high temperature experiments with various growth systems, the authors demonstrate that regardless of the bulk composition of the system, there exists a measurable fractionation of carbon isotopes and nitrogen impurity on the surface of diamond itself. The ab initio calculations of carbon isotope fractionation on different crystallographic faces of diamond also support this conclusion.

3. Some Facets of Synthetic Diamond Crystals

The modern era of diamond as a technological material began in the 1950s after the first reports on the successful synthesis of diamond through the high pressure high temperature (HPHT) technique [19,20]. The subsequent rapid development of the technologies for a mass production of diamond abrasive grids and powders has revolutionized many branches of the manufacturing, mining, and construction industries. As research and developments on synthesis and growth of diamond has further progressed, along with our growing understanding of the unique properties of diamond, new, sometimes quite unexpected, areas of diamond applications have been opening. Today, approaching the end of the second decade of the 21st century, we can see that diamond has entered many important technologies where not only its mechanical properties but its other exceptional properties are utilized. This process is steadily developing. Now, one very promising area to be engaged with diamond is connected with the so-called quantum technologies emerging over the last 10–15 years. It turns that color centers in diamonds represent a suitable platform for realizing solid-state single-photon sources, which are indispensable for the quantum physics technologies [21,22]. The most outstanding example of such color centers in diamond is the negatively charged nitrogen-vacancy (NV) center proving to be a promising system for quantum information processing [23], nanoscale electromagnetic field sensing [24,25], plasmonics [26], and biolabeling [27,28]. A number of impressive examples of using the NV centers in diamond has been demonstrated recently, including experiments on the loophole Bell inequality test [29], and nanoscale imaging magnetometry under ambient conditions [30]. In their contribution, Ettore Bernardi, Richard Nelz, Selda Sonusen, and Elke Neu review recent progress in nanoscale sensing using nitrogen-vacancy centers in single-crystal diamond [31]. After a comprehensive introduction of the nanoscale sensing based on individual nitrogen vacancy centers they consider two key challenges of the field: (1) the creation of highly-coherent, shallow NV centers less than 10 nm below the surface of a diamond crystal; and (2) the fabrication of tip-like photonic nanostructures that enable efficient fluorescence collection and can be used for scanning probe imaging based on color centers with nanoscale resolution. They discuss several approaches for creating optimal, shallow NV centers, and conclude that enhanced sensitivities and resolution in NV-based imaging are feasible in the nearest future.

The NV-based single-photon sources are known to suffer from a disadvantage connected with spectrally broad emission of the NV centers. Therefore, active research has also been undertaken to find out other optical centers in diamond with properties suitable for the novel applications [32]. Recently, silicon-vacancy [33,34], germanium-vacancy [35–37], and tin-vacancy [38,39] centers have been demonstrated to possess characteristics that are promising for single-photon applications. In addition, attempts at creating optical centers related to other impurities in diamond, such as Ni [40], Cr [41], and Eu [42] have been reported. In this context, the contribution by Vladimir Nadolinny, Andrey Komarovskikh, and Yuri Palyanov provides a comprehensive review of point defects in diamond related to the incorporation of large impurity atoms into the diamond crystal lattice [43]. Special emphasis is given to nickel, which is commonly used as a solvent-catalyst in high pressure high temperature (HPHT) diamond synthesis and growth. It is shown that at sufficiently low growth temperatures, nickel atoms occupy a substitutional position in the diamond lattice forming a defect with Td symmetry. The large Ni-C bond length (~2 Å) gives rise to a significant strain around the growth defect; the strain can be relaxed due to the displacement of one of the nearest carbon atoms to the interstitial position at high annealing temperatures. In this case, the nickel atom shifts and forms the so-called double semi-vacancy defect; the observed HFS of ^{13}C and ^{14}N confirms the proposed structure. Besides the nickel, the incorporation of titanium, cobalt, phosphorus, silicon, and germanium impurities into the diamond structure are discussed in the review. These impurity atoms have large atomic radii; a formation of double semi-vacancy defects is energetically favorable for them. The nickel, cobalt, and titanium are catalysts and nitrogen getters in the HPHT synthesis, that is why the resulting impurity defects are of interest. At the same time, doping with phosphorus, silicon, and germanium is promising for high-tech applications. For example, high-power semiconductor devices have already been constructed; silicon- and germanium-vacancy centers are perspective single-photon light sources that can be used in quantum communication systems. I believe that this review can serve as a reference book for the researchers studying defects in diamond.

The progress in the development of new diamond-based technologies is inseparably linked to research and development into the synthesis and growth of this material. At present, bulk diamond crystals are produced using two main methods, chemical vapor deposition (CVD) and growth at high pressure high temperature (HPHT) conditions. HPHT diamond synthesis and growth relies on the catalytic ability of some substances to convert graphite to diamond at the conditions of thermodynamic stability of diamond. These substances are commonly termed to as solvent-catalysts and are typically represented by transition-metal melts, especially Fe, Ni, and Co and their alloys. In recent decades, active research on synthesis and growth of diamond at HPHT conditions has been carried out using a variety of solvent-catalysts, both metallic and non-metallic. The main objectives of these investigations are connected with the fundamental aspects of diamond nucleation and growth, modeling natural diamond-forming processes, and the development of new routes of synthesizing diamond crystals with specific and unusual properties. In their contribution, Yuri Palyanov, Igor Kupriyanov, Yuri Borzdov, Denis Nechaev, and Yuliya Bataleva study HPHT diamond crystallization in the Mg-Si-C system [44]. The Mg-based solvent-catalysts have recently focused considerable attention, which is caused by the following main findings [45–49]: from these catalysts, diamond crystallizes in the kinetically controlled regime with high growth rates, up to 8.5 mm/h; the produced diamond crystals are nitrogen-free type II; effective doping of diamond with silicon and germanium impurities, creating silicon-vacancy and germanium-vacancy color centers, is possible. By studying diamond crystallization in the Mg-Si-C system at 7.5 GPa and 1800 °C with the Mg-Si compositions spanning the range from the Mg-C to Si-C end-systems the effect of the Mg/Si ratio on the graphite-to-diamond conversion degree, diamond crystal morphology, and optical properties is established and discussed [44].

The CVD technology of diamond growth has advanced tremendously to the extent that single-crystal diamond can now be produced with an unprecedentedly low impurity content, down to less than a one-part-per-billion level. One of the challenging problems lying in the focus of the current research is reaching the control over the extended defects, such as dislocations [50]. These defects affect electronic and optical properties of diamond and should be overcome for the most demanding applications. It is frequently mentioned that, in silicon technology, the elimination of dislocations was a major step in microelectronics. It has been established that with careful selection of diamond substrates and applying special surface treatments and tailored growth conditions, the dislocation content of the produced diamonds can be significantly reduced [51]. One of the approaches useful to suppress the dislocation content is the epitaxial lateral overgrowth (ELO), which has been successively applied for other semiconductor materials (GaN, GaAs, etc.) [52]. It consists of filtering dislocations by promoting lateral growth from a substrate that is partly covered by an appropriate mask. Recently, Tallaire et al. [53] have shown that using lateral growth over a macroscopic hole made in the diamond substrate it is possible to produce diamond crystals with significantly reduced dislocation density. Following this general approach, Fengnan Li, Jingwen Zhang, Xiaoliang Wang, Minghui Zhang, and Hongxing Wang describe in their contribution a way to produce low dislocation density single crystalline diamond by two-step epitaxial lateral overgrowth [54]. They show that using substrate processing, such as patterning with inductively coupled plasma (ICP) etching and metallization, it is possible to stimulate diamond lateral growth in the CVD process. The diamond films produced by the two-step ELO show much reduced content of dislocation related etching pits. The proposed method seems very promising for technological applications.

Chemical vapor deposition is a versatile technique allowing diamond growth on various substrates. Since the early stages of CVD diamond growth, it has been recognized that many tools used for material machining would significantly benefit from being covered with a thin film of diamond. Nowadays, diamond coated tools and instruments with increased hardness and durability are omnipresent in the modern industry. However, as described in the contribution by Evgeny Ashkinazi, Roman Khmelnitskii, Vadim Sedov, Andrew Khomich, Alexander Khomich, and Viktor Ralchenko, even in this field which appears well established and widely used in practice, there is still room for further research and development [55]. The functional properties of the cutting tools can further be enhanced if bilayered or multilayered micro- and nanocrystalline diamond coatings are applied. To take all advantages of such coatings, one has to pay special attention to nanocrystalline diamond (NCD) growth on microcrystalline diamond (MCD) film/substrate. The question of how nanocrystalline diamond is deposited on different crystallographic faces of single crystal diamond substrates is considered in this contribution and the results obtained are important for making proper choices for the growth conditions enabling uniform NCD layers on MCD films.

The advancements seen over the last decades in diamond science and technology rely on the detailed knowledge and understanding of the basic properties of diamond, which were intensively investigated in the past and continue to be an area of active research. Most of the extreme material properties of diamond are related to its unique lattice and corresponding phonon spectrum. One of the important tool for probing the vibrational spectrum of diamond is the Raman scattering. The Raman spectrum of diamond bears important information on the optical phonon lifetime and its temperature dependence provides insights into anharmonicity of the lattice vibrations. In addition, both the position and linewidth of the Raman peak are sensitive to the lattice imperfections and commonly used as a measure of crystalline quality of diamond and diamond-related materials. In order to use this property of the diamond Raman spectrum to full extent, it is important to understand the physical mechanisms behind the effect of defects and impurities on the vibrational properties of diamond. This appealing question is considered in the contribution by Nikolay Surovtsev and Igor Kupriyanov, who studied the effect of nitrogen impurities on the Raman line width in diamond [56]. They show that the defect-induced broadening of the diamond Raman line is temperature independent and comes from the optical phonon scattering on the defects.

Diamond is known to be an ideal material for solid-state detectors of ionizing radiation and high-energy particles. Indeed, in this particular niche, diamond has found diverse applications in biomedical sciences [57,58] and high-energy physics [59]. It is sufficient to mention the ATLAS and CMS experiments at the Large Hadron Collider (LHC), both of which include diamond detectors and have been involved, for example, in the search, discovery, and exploration of the elusive Higgs boson. A challenging problem for solid-state detectors is the radiation damage under high-energy loads, resulting in performance degradation. Solving this issue demands clear understanding of the fundamental physics behind the interaction of various high-energy particles with the detector material, diamond in our case. In addition, this question is also important for the process of ion implantation, which is frequently used to modify diamond properties [60]. Yury Belousov in his contribution reports in-depth theoretical calculations of the time evolution of radiation defects induced by negative pions and muons in diamond, silicon, and germanium [61]. Radiation damage of diamond by these particles is not commonly considered, but since they are the products of the interaction of high-energy protons with a target, the corresponding radiation defects may be important for the relevant applications.

As it is already noted, owing to its outstanding mechanical and physicochemical properties, diamond dominates in ultra-precision machining of various metallic and non-metallic materials. There is however one critical limitation. Diamond cannot be used for machining of ferrous metals because of the severe tool wear rate. This hinders many important applications where ultra-precision machining of steel alloys is required. In order to reduce this catastrophic tool wear, certain process modifications have been proposed in the literature, including use of different carbon-saturated atmospheres [62], cryogenic [63], and ultrasonic assisted [64] turning, and others. However, the problem has not been still solved satisfactorily, that stimulates further investigations. In their contribution, Lai Zou, Yun Huang, Ming Zhou, and Guijian Xiao report the results of a series of thermal analysis experiments simulating the wear process of single crystal diamond [65]. The aim of this study is to investigate the thermochemical wear of diamond surface catalyzed by iron at elevated temperatures under different gas atmospheres, leading to a better understanding of the mechanisms of diamond tool wear in machining of ferrous materials.

4. Conclusions

Summarizing, this special issue contains 12 papers which highlight recent investigations and developments in diamond research related to the diverse problems of natural diamond genesis, diamond synthesis and growth using CVD and HPHT techniques, and the use of diamond in both traditional applications, such as mechanical machining of materials, and recently emerged areas, such as quantum technologies. The results presented in the contributions collected in this special issue clearly demonstrate that diamond occupies a very special place in the modern science and technology. After decades of research, this structurally simple material still poses many intriguing scientific questions and technological challenges. It seems undoubted that diamond will remain the center of attention for many researchers for many years to come. It is very tempting to finish this editorial with the famous slogan of the De Beers' advertising line, which has just celebrated its 70th anniversary, "A diamond is forever".

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