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Sergei Simakov · Vittorio Scribano · Nikolai Melnik · Victor Pechnikov · Irina Drozdova · Vladimir Vyalov · Mikhail Novikov

Nano and Micro Diamond Formation in Nature

Ultrafine Carbon Particles on Earth and Space

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Contents

Abbreviations

Aq	Water Solution
Antg	Antigirite
Coe	Coesite SiO_2
CVD	Chemical Vapor Deposition
D	Diamond, C
DND	Detonation Nanodiamond Syntheses
Dol	Dolomite $CaMg(CO_3)_2$
En	Enstatite $MgSiO_3$
Fa	Fayalite Fe_2SiO_4
Fo	Forsterite Mg_2SiO_4
FT-t	Fischer–Tropsch-type
FTIR	Fourier Transform Infrared Spectra analysis
G	Graphite, C
Gs	Gaseous
hkl	Diffraction Indexes
HPHT	High Pressure, High Temperature
HRTEM	High-Resolution Transmission Electron Microscope
ICDD	International Center for Diffraction Data
IW	Iron–Wüstite Buffer
KFS	K Feldspar
Liq	Liquid, Melt
Mgt	Magnetite Fe_3O_4
MH	Magnetite-Hematite Buffer
Msn	Magnesium Silicon Nitride $MgSiN_2$
Muas	Muassonite SiC
NASA	National Aeronautics and Space Administration
ND	Nanodiamond
NNO	Nickel–Bunsenite Buffer
OCCs	Oceanic Core Complexes
Ol	Olivine$(Mg, Fe)_2SiO_4$
OM	Organic Matter

Opx	Orthopyroxene (Mg, Fe)SiO_3
Per	Periclase MgO
Pyr	Pyrite FeS_2
QFM	Quartz–Fayalite–Magnetite Buffer
Ro	vitrinite reflectance
S	Solid
SIMS	Secondary Ion Mass Spectrometry analysis
Srp	Serpentine $Mg_2Si_2O_5(OH)_4$
SSZs	Suprasubduction Zones
TEM	Transmission Electron Microscope
SuR	Super Reduced
U–Pb	Uranium-Plumbum
UHP	Ultra High Pressure
UHPT	Ultra High Pressure Temperature
UV	Ultraviolet
WM	Wustite–Magnetite Buffer

Physical Symbols

Å	Angstrom
bar	Unit of Pressure
erg	Unit of Energy
f	Fugacity
G	Gibbs energy
h^3	Volume of carbon atom in diamond
kJ	kilojoules
kV	kilovolts
nm	Nanometer
μm	Micron
P	Pressure
ppm	Parts per million
R	Gaseous Constant
T	Temperature
U	Work of Nuclei Forma
θ	Diffraction angle

Chapter 1
Introduction

Carbon is a many-sided chemical element, as it forms millions of compounds related to both biochemical and geochemical processes. Moreover, elemental carbon occurs in various polymorphs (or allotropes), such as graphite, diamond, amorphous carbon, lonsdaleite, and fullerenes. The physical properties of the different carbon polymorphs vary widely due to the different ways in which the atoms in each are bonded. Diamond is the most compact, Sp^3-bonded, polymorph of carbon, having nearly twice the density of graphite. The study of diamond has seen a recent burst of activity in geochemistry and astrophysics, in novel methods of synthesis, and in the development of useful applications. Diamond is recognized as an extraordinary recorder of astrophysical and geodynamic events that extend from the most remote regions of space to Earth's deep interior. As will be specified later, different types of diamonds have been recognized based on their size, geological occurrence, morphological characteristics, types of solid or fluid inclusions, etc. The processes of formation of some diamond types still raise many contentious questions. The formation of macroscopic diamonds is mainly connected with deep-seated igneous rocks, such as kimberlites and lamproites, and therein mantle xenoliths. To date, in mineralogy, there is no widely accepted definition of a size boundary between kimberlitic microdiamond and macrodiamond. It varies from 0.5 to 1 mm (Chapman and Boxer 2004; Pattison and Levinson 1995). We have assumed 1 mm as the size limit between the microdiamond and macrodiamond. Interestingly, microsized diamonds were also found in metamorphic rocks and ophiolite complexes originating in the graphite stability field. The formation mechanism of these metamorphic rock-hosted diamonds still represents a hotly debated topic.

Currently, the origin of natural nanocarbon particles is still poorly constrained. The family of "nanocarbons" includes the following main components: nanodiamonds, nanosized amorphous carbon, fullerenes, diamondoids, graphene, tubes, onions, horns, rods, cones, peapods, bells, whiskers, platelets, and foam (Shenderova et al. 2002). Diamond structures at the nanoscale (length ~1–100 nm) include pure-phase diamond films, diamond particles, recently fabricated 1-D diamond nanorods,

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and 2-D diamond nanoplatelets. There is a special class of nanodiamond material often called "*ultrananocrystalline*" diamond with the characteristic size of the basic diamond constituents encompassing the range of just a few nanometers that distinguishes it from other diamond-based nanostructures with characteristic sizes below~10 nm (Schrand et al. 2009). The smallest nanometer-sized diamond particles are known mainly in space objects (Tielens et al. 1987; Allamandola et al. 1993). Nanodiamonds in terrestrial rocks are rarely found. They are known in serpentinites, Younger Dryas Boundary layers, coals, and spinel lherzolites (Dubinchuk et al. 1976; Wirth and Rocholl 2003; Tian et al. 2011; Kinzie et al. 2014; Simakov et al. 2015, 2018).

Currently, the creation of new methods of nanocarbon synthesis is one of the urgent tasks of modern technologies. There are three main methods of diamond synthesis:

1. HPHT synthesis of macroscopic diamonds from metal and melts of solvent catalysts at P–T corresponding to the thermodynamic field of diamond stability.
2. DND syntheses at ultrahigh temperatures and pressures.
3. CVD synthesis of diamond films, composites, and coatings at high temperatures and low pressures, corresponding to the field of graphite stability.

In addition, there are rare nano- and micron-sized diamond syntheses at low P–T parameters. Nakano et al. (2002) synthesized nanodiamond particles of 1 nm in size from an interstellar-like organic mixture with water at 150–400 °C at relatively low pressure. Ultrananocrystalline diamonds were synthesized at 220 ° C and the saturated vapor pressure of water using a simple and available hydrocarbon (glucose) (Alzahrani and Alkahtani 2023). Nano- and micron-sized diamonds (up to 1 μm in size) were synthesized by heating a mixture of Li_2CO_3 and nanocarbon particles at 420–550 °C and ambient pressure (Kamali and Fray 2015). Micron-sized diamonds (up to 100 μm) were also synthesized via the interaction between molten aluminum and carbide-containing halide melt at 700–750 °C and ambient pressure (Yolshina et al. 2015). Ishimaru et al. (2001) detected nanodiamond structures in wood charcoal carbonized at 700 °C. In this respect, the book presents the results of theoretical and experimental studies in Chaps. 2 and 3 for a new approach that could be developed for the synthesis of nanodiamonds at low pressures and temperatures.

The first detailed studies on synthetic nanodiamonds were carried out in the 1960s in Russia. The particles of synthetic nanodiamonds contain many impurities and defects; therefore, their density is lower than that of diamond and corresponds to the range of 2.8–3.1 g/cm^3. Nitrogen and ketone, hydrocarbon, carboxyl, and alcohol groups with Sp^3 and Sp^2 hybridizations are present in the impurities of nanodiamonds (Fig. 1.1). It is known that synthesized nanodiamonds display surface bonds terminated with hydrogen and oxygen atoms (Costa et al. 2014; Schrand et al. 2009).

Badziag et al. (1990) suggested that nanodiamonds could be synthesized at low P–T from hydrocarbons with $H/C < 0.25$. Later, Dahl et al. (2003) showed that it is possible to distinguish diamond crystal cages in diamondoids (Sp^3-bonded hydrocarbons), and in this respect, diamond could be defined as the archetypal "macroscopic molecule." Diamondoids occur in crude oils and in gas condensates in remarkable

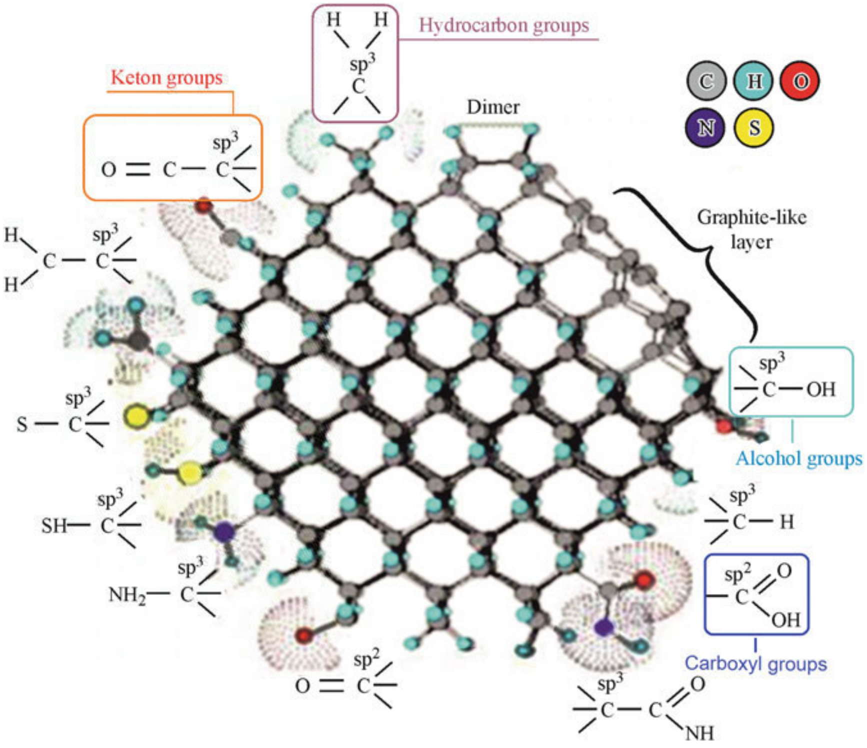

Fig. 1.1 Structures in nanodiamonds in accordance with Schrand et al. (2009) and Costa et al. (2014)

amounts (from 35 to 2,075 ppm, respectively; Nekhaev et al. 2010). They are also known in coals and sediments in the middle and final stages of sediment lithogenesis (Tissot and Welte 1978) with vitrinite reflectances from 1 to 4 R° (Wei et al. 2006, 2007). Dahl et al. (2003) extracted diamond molecules from oil diamondoids containing diamond lattices within their tetrahedral structures and suggested that hydrogen-terminated diamonds and nanometer-sized diamondoid hydrocarbons form a continuous structural series that includes small diamondoids (<1 nm), larger diamondoids (~1–2 nm), nanocrystalline and CVD diamonds (~2 nm–1 mm), and larger macrodiamonds (Dahl et al. 2003). In this respect, E. Osawa (personal communication) considered nanodiamonds to be a larger version of diamondoids (It is interesting to note that Giardini et al. (1982) previously concluded that the genesis of kimberlitic diamonds and oil are connected with each other in the upper mantle). Later, Gebbiea et al. (2018) showed that using diamondoid molecules in CVD syntheses leads to the formation of postcritical diamond nuclei consisting of 26 carbon atoms through the formation of metastable, hydrogen-terminated diamondoid clusters. In this case, the nucleation barrier is four orders smaller than previous estimates.

On the other hand, Costa et al. (2014) showed that nanodiamonds terminated by oxygen functional groups (–COOH) are much more stable in enthalpy than pure graphite and diamond. As a result, they concluded that such surface functional groups may in fact be necessary for nanodiamond formation and persistence. Their presence may explain the occurrence of terminated nanodiamonds under synthetic and natural conditions where pure diamonds would not be stable.

The origin of diamonds in interstellar space has been a topic of intense discussion since the discovery of presolar nanodiamonds in chondrites (Bernatowicz and Zinner 1997). The interstellar nanodiamonds have the highest nitrogen contents from 2,000 to 20,000 ppm (or 0.2–2 wt%), with the main prominent mode at 8,500 ppm. The nitrogen isotopic composition varies from -181 to $-350‰$ of $\delta^{15}N$. They have the lowest carbon isotopic composition, varying from -32 to $-38‰$ of $\delta^{13}C$ (Newton et al. 1995; Russell et al. 1996). Meteoritic nanodiamonds provide information on the nucleosynthesis of evolved stars and the evolution of the astrophysical environment that formed the solar system. The questions of when and how nanodiamonds originate in the cosmos remain open, although comparative microstructural analysis of nanodiamonds extracted from meteorites indicates that the majority of cosmic nanodiamonds are formed by low-pressure vapor condensation processes (Daulton 2006). Several models of their formation have been proposed:

(1) Shock-induced transformation of C–N-rich organics (Saslaw and Gaustad 1969; Blake et al. 1988);
(2) Formation of nanodiamonds in UV-irradiated ices and/or organics (Nuth and Allen 1992);
(3) The CVD-like process (Lewis et al. 1989; Daulton et al. 1996).

Astronomers concluded that 3% of all carbon present in ordinary, carbonaceous, and enstatite chondrite meteorites exists in the form of diamond and that up to 20% of interstellar carbon exists in the form of ultrananocrystalline diamonds (Tielens et al. 1987). They have an average size of 2 nm, and their concentrations reach 1,600 ppm in some cases (Anders and Zinner 1993; Alexander et al. 1998; Zinner 1998). Chondritic nanodiamonds are generally associated with diamondoids (Bauschlicher et al. 2007). Nanodiamonds were also identified by scientists from NASA in the cold molecular clouds formed at low PT. These clouds contain hydroxyl (OH), vapors of water, ammonia, formaldehyde, carbon monoxide, methanol (wood alcohol), ethyl alcohol, and dozens of other more complex molecules. Sellgren (2001) identified the relationship between the interstellar diamond and water ice. Nakano et al. (2002) synthesized nanodiamond particles from a mixture of interstellar-like nitrogen-bearing organics with water at 150–400 °C and lower pressure. They related interstellar diamond formation with organic matter, which mainly consists of glycolic, eicosanoic, and lauric acids, heavy aromatic polycyclic hydrocarbons (phenanthrene) and aromatic hydrocarbons (indene), and nitrogen-bearing organic compounds, such as acetomides and lactamides. Based on these relationships, Kouchi et al. (2005) identified the formation routes of diamonds in the interstellar clouds and parent bodies of carbonaceous chondrites as an ice mixture of H_2O, CO, NH_3, and CH_4 (4:2:2:1). They also