Research Article

Metastable Nanosized Diamond Formation from Fluid Phase

S. K. Simakov,[1] V. T. Dubinchuk,[2] M. P. Novikov,[3] and N. N. Melnik[4]

[1] *Geological Department, St. Petersburg University, 7/9 Universitetskaya Nab., St. Petersburg, 199034, Russia*
[2] *Fedorovskiy All Russian Mineral Research Institute, Moscow 119017, Russia*
[3] *Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka 142432, Russia*
[4] *Lebedev Physics Institute, Russian Academy of Sciences, Moscow 117924, Russia*

Correspondence should be addressed to S. K. Simakov, simakov@ap1250.spb.edu

There is evidence that part of kimberlitic microdiamonds was formed at low P-T parameters corresponding to graphite stability. Microdiamonds were also discovered in ultramafic, volcanic, and different metamorphic crust rocks formed at low P-T parameters. The formation of these diamonds is probably caused by introduction of metasomatic fluids at metastable P-T parameters. In our experiments nanosized (70–80 nm) diamonds were synthesized at earth crust P-T parameters from fluid phase. Their presence was confirmed by Raman spectroscopy and electronic microscopy methods.

1. Introduction

The formation of the bulk of Earth diamonds is due to the deep upper mantle rocks formed at P and T corresponded to diamond thermodynamic stability. Meanwhile there is evidence that part of kimberlitic diamonds (with size less than 1 mm) was formed at lower P-T parameters corresponding to graphite stability, probably caused by introduction of metasomatic fluids [1]. Microdiamonds were also discovered in ultramafic rocks of Kamchatka [2] and in vulcanoclastic komatiite of French Guiana [3]. Nanocrystalline diamonds were found in garnet pyroxenite xenoliths of Hawaiyan and Gissar basaltes [4, 5]. Over the last 40 years microdiamonds have also been founded in the different earth crustal rocks [6–11] including the organic matrix [12, 13]. The most famous and important deposit of crustal microdiamonds is Kokchetave massive situated in Northern Kazakhstan [11]. It is located within the western part of a metamorphic belt which is interpreted as a megamelange that comprises structural units underlain by HP and UHP rocks. Diamondiferous varieties of the UHP rocks form a narrow (nearly 1 km thick), NE-trending band; they comprise less than one percent of the total UHP rock volume. Parageneses of rock-forming minerals indicate conditions of amphibolite or granulite metamorphic facies. Individual relicts of UHP minerals commonly occur as microinclusions in zircons and garnets. The economically important diamondiferous zone consists of variegated rocks, from silicate to essentially carbonate varieties with a wide spectrum of mineral assemblages. The maximum diamond grade is observed in hydrothermal metasomatic zones. Diamondiferous bodies are branching linear zones which do not coincide with structure of hosting metamorphic bodies. Morphology of these zones reflects the pathways of fluids along the weakened zones [14]. Diamonds mainly associate with graphite, and the main mineral diamond inclusions are graphite, carbonate, and water [15]. De Corte et al. [16] and Korsakov and Shatsky [17] show that Kokchetave graphites and diamonds have formed from one fluid source. Pechnikov and Kaminsky [14] come to the conclusion that diamonds are products of an open disequilibrium system with input of reactants and partial removal of products at a relatively low temperature level (500–600°C, see [18]) and pressure. Crystallization of diamonds occurred synchronously to the deposition of graphite. Kokchetave diamonds have anomaly high concentration of N in comparing with kimberlitic [15].

Diamond has been a unique material, which has attracted the attention of man through the ages. Ever since it became known (around 1797) that diamond is essentially crystallized carbon, several attempts were made to synthesize diamonds artificially from other forms of carbon. As a result, understanding the exact conditions for its thermodynamical

stability and development of experimental techniques to achieve these conditions in the laboratory led to the successful synthesis of diamond in the early 1950s. Ever since more and more researches have opened up newer methods of diamond synthesis and at present, these can be roadly classified as follows:

(1) a catalytic conversion of graphite to diamond at high T and P,

(2) metastable growth on accelerated carbon ions on diamond seeds or substrates at low pressures. These syntheses may be conveniently divided into three categories: hot flament chemical vapor deposition (CVD), high-frequency plasma-assisted chemical vapor deposition, and deposition chemical plasma discharge.

2. Theory of Metastable Nanodiamond Formation

Metastable phases can form from precursors with high chemical potential if the activation barriers to more stable phases are sufficiently high. As the precursors fall in energy, they can be trapped in a metastable configuration. Formation of a metastable phase depends on selecting conditions where rates of competing processes to undesired products are low. The phase diagram of carbon shows that under normal conditions diamond is a metastable form of carbon. This, however, need not mean that diamond crystallization cannot occur under these conditions. The free-energy of carbon atoms in methane and carbon monoxide carbon vapour may be even higher than that of carbon in the diamond form, if the temperature is not too high. During the decomposition of such compounds by suitable means, the carbon atoms, during its fall from a state of higher free-energy, could pause at the level of diamond instead of going all the way down to that of graphite. Such phenomena, wherein pauses at metastable states occur, are well known in many other chemical systems (for silica system, e.g.). Metastable phases have been found to grow in the stability field of other phases when its nucleation and growth are facilitated, for instance, by providing seeds of the required phase or a substrate, which allows epitaxial overgrowth [19].

For diamond, it has been argued that crystallization in a P-T regime, where diamond is actually thermodynamically unstable with respect to graphite, may be possible due to kinetic factors. Deryagin and Fedoseev [20] have shown that diamonds can grow from methane-rich fluid at metastable P-T conditions on the diamond seeds. Chauhan et al. [21] showed that addition of hydrogen to the hydrocarbon gas phase suppressed the growth rate of graphite more than it suppressed the growth rate of diamond, resulting in higher diamond yields. Individual faceted diamond crystals without the use of a diamond seed crystal were obtained on the basis of this effect [22]. Other researchers have shown that metastable diamond formation is possible without using seeds. Badziag et al. [23] showed that nanometer-sized diamonds could be more stable than graphite when formed from hydrocarbons with an H/C ratio of more than 0.24.

Subsequent work has shown that the addition of oxygen to the hydrocarbon gases can stabilize the diamond nucleus formation in the P-T field of graphite stability [24].

Fedoseev et al. [25] show that critical radii of graphite and diamond nuclei depend upon to surface energy (σ), atomic volume of carbon (V), and chemical potential of the resaturation ($\triangle \mu$):

$$r = 2\frac{\sigma V}{\triangle \mu}. \tag{1}$$

for diamond (d) and graphite (g) σ could be taken as 2 and 0.5 J/mole correspondingly [25]. Then r_g/r_d ratio could be expressed by the following formulation:

$$\frac{r_g}{r_d} = 0.2\frac{\triangle \mu_d}{\triangle \mu_g}. \tag{2}$$

From another side chemical potentials of the resaturation for diamond and graphite could be expressed by the following formulations:

$$\triangle \mu_g = \mathrm{RTln}\left(\frac{Pi}{Pi_g}\right), \tag{3}$$

$$\triangle \mu_d = \mathrm{RTln}\left(\frac{Pi}{Pi_d}\right). \tag{4}$$

As follows from (2) and (4) (where Pi and $Pi_{g,d}$ are the real and equilibrium pressures of carbonaceous gases, resp.), (r_g/r_d) is also connected with the ratio between real and calculated equilibrium pressures of carbonaceous gases in the C-O-H system. In this system, the composition of the mixture depends on P-T-f_{O_2} conditions; therefore, it is possible to select f_{O_2} conditions, at which the diamond nucleus formation is more stable than the graphite one ($r_g > r_d$) in the field of graphite stability [24]. From this model, it follows that the preferable f_{O_2} for diamond formation at 700°C and 5 kbar is 2 log units lower than the QFM buffer, which corresponds to the water-rich fluid [26]. It is explained the fact of maximum diamond grade observed in hydrothermal metasomatic zones of Kokchetave deposite [14] and closed to the composition of gaseous inclusions in Kokchetave diamonds [15]. This theoretical conclusion coincides with the established fact that diamond is more stable in an oxygen environment than graphite because oxygen reduces graphite to a greater degree than diamond [27]. Bachmann et al. [28] have shown that the synthesis of diamonds under metastable conditions corresponds to the narrow fluid composition in the C-O-H system.

Noteworthy for metastable diamond formation is the role of nitrogen. The stabilized role of nitrogen can be explained by the facts that N is the main crystallochemical mixture in kimberlitic diamonds [29]. Korolev et al. [30] noted a stabilized role of nitrogen for the diamond synthesis from the carbonate-silicate system at high P-T conditions. The reaction of interaction between methane and nitrogen is a possible way of metastable diamond formation [31]:

$$\mathrm{N_2 + 1.5CH_4 \longrightarrow 1.5C + 2NH_3}. \tag{I}$$
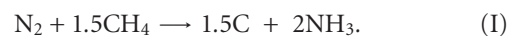
From this reaction the equilibrium pressures of methane under the diamond nucleus could be expressed as

$$lgf_{CH4} = \frac{2lg\,f_{NH3} - lg\,f_{N2} - lg\,K_I}{1.5}. \tag{5}$$

Nitrogen could intrude into the diamond structure according to reaction for ammonium disruption [32]:

$$NH_3 \longrightarrow N^{+3} + 3H^{--}. \tag{II}$$
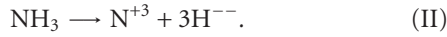
In this case, the pressure of ammonium equilibrated with the growing diamond would decrease. The ammonia decrease will result in methane decrease (5). This suggests that $\triangle\mu_d$ and r_g/r_d increase (see (2) and (4)), accompanied by increased diamond growth. It is supported by the fact of a high concentration of N in Kokchetave diamonds [18, 33] .

3. Diamond Synthesis

We provided the formation of free carbon from carbon-bearing gases at 500°C and total pressure of 1000 bar. The sources of carbon-bearing gases and nitrogen were liquid organic matters. The mixture was heated in the titanium (BT-8 alloy) high-pressure reactor. The run duration was 5–7 days. Using X-ray diffraction to characterize the experimental products, nanographite was identified [34]. After this, the products were treated in concentrated $HClO_4$ to remove any graphite. In the rest product there were white and opaque particles. Raman and photoluminescence (PL) spectra were recorded on a U-1000 spectrometer with the microscope setup. Argon laser radiation (488 nm) was used for excitation. The laser exciting radiation was focused to a spot in $\sim 10^4$ nm diameter. This allowed us to study the homogeneous and transition areas of the sample surface and monitor any laser heating effect on the sample. The Raman spectra were recorded with a resolution of 1–5 cm^{-1}. The results of the analyses are shown in Figure 1. Curve 1 is the Raman spectra (RS) of opaque samples. From the form of a spectrum, it appears that these samples are strongly disordered graphite. For white samples RS spectrum is shown as curve 2. In Figure 1, RS spectra of diamond (D) and disordered graphite (G) are providing for comparison. Comparing these spectra it is possible to draw a conclusion that the cleaned samples contain atoms of carbon with sp^3 bonds. Based on a comparison of curve 2 with that for pure diamond, there is a high probability that the white material represents microparticles of diamond. The nature of wide bands in region 1120–1300 cm^{-1} is not yet clear and requires the further studying.

The powder that remained after washing was loaded in colloidal solution in amyl acetate and then applied onto a water surface. The thin film obtained was transferred onto a grid for electron microscopic investigation. Samples were studied with a Tecnai-12 transmission electron microscope (TEM) at an accelerating voltage of 120 kV equipped with a "Gotana" camera system. The carrier film typically contained 70–80 nm sized particles of different forms (Figure 2). Diamonds were diagnosed in the particles by microdiffraction method. Microdiffractions corresponding to diamond
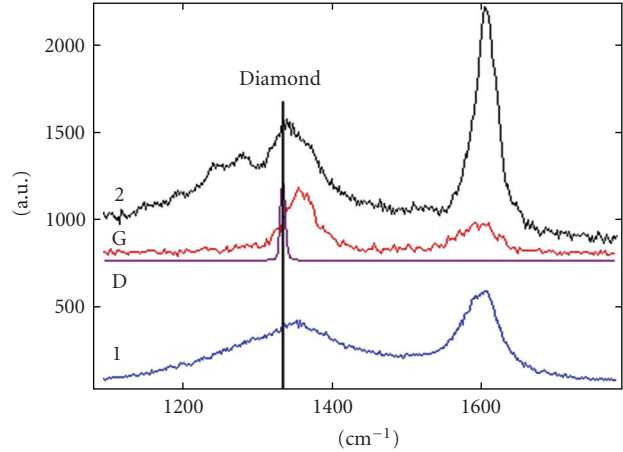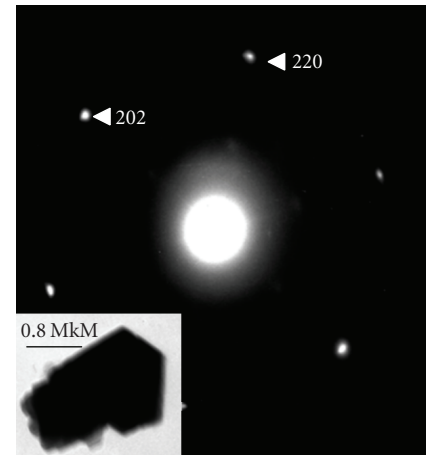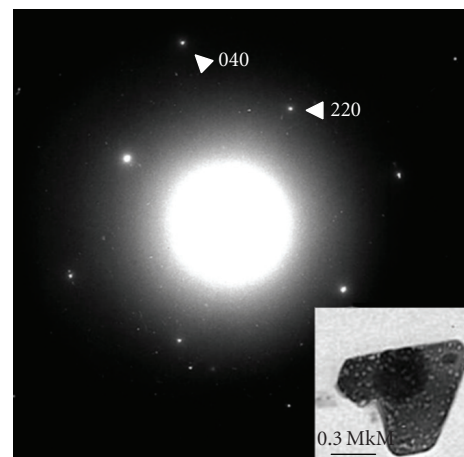

FIGURE 1: RS spectra of different samples. 1: opaque samples; 2: white coloring samples; D: diamond; G: graphite.

(a)

(b)

FIGURE 2: Microdiffractions and form of the diamond, zone axis's [111] (a) and [001] (b) correspondingly.

TABLE 1: Comparison of interplanar spacings based on the microdiffraction pattern in Figure 2 with data on diamond presented in the ASTM database (card 06-0675) (in angstream).

Hkl	ASTM	$d_{calc}A$
	diamond	
<220>	1.26	1.26
220	1.26	1.26
040	0.88	0.88

Interplanar spacings determined from Figures 2(a) and 2(b) coincide with those for diamond (a = 3,55A°) presented in the ASTM database (card 06-0675)-(Table 1) and correspond to Fd3m spacing group. None of the known cubic phases have such interplanar spacings in ASTM. In another particles graphite, chaoite, cubic carbon, carbides, and lonsdaleite were diagnosed by the same method [34, 35].

4. Conclusion

Thus the results indicate that diamond could be formed from carbon-bearing fluids at low temperatures and pressures without diamond or another seeds. The presence of nitrogen can stabilize diamond formation at metastable conditions. From it follows that microdiamonds could be formed from fluids in crustal and magmatic rocks at P-T parameters corresponding to graphite stability.

Acknowledgment

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