

Metastable nanosized diamond formation from a C-H-O fluid system

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The model of nanosized diamond particles formation at metastable P-T parameters from a C-H-O fluid system is presented. It explains the hydrothermal formation and growth of diamond and the specifics of chemical vapor deposition (CVD) diamond synthesis gas mixtures at low P-T parameters. Further, the model explains the genesis of interstellar nanodiamond formations in space and the genesis of metamorphic microdiamonds in shallow depth Earth rocks. In contrast to models where many possible reactions are considered, the present model makes the simplest possible assumptions about the key processes, and is then able to account for various tendencies seen in experimental data.

I. INTRODUCTION

The optimal gas system composition for metastable diamond formation has been debated in many publications over a long period of time. Badziag et al.¹ came to the conclusion that nanometer-sized diamonds could be more stable than graphite when formed from hydrocarbons with an H/C ratio of approximately 0.24. Simakov² has shown that the addition of oxygen to the hydrocarbon gases can stabilize diamond nucleus formation in the *P-T* field of graphite stability. The question of whether diamond can be grown under hydrothermal conditions mimicking those under which it is formed within the Earth has also long been debated.^{3,4} Roy et al.⁵ have made a detailed study of the hydrothermal growth of diamond in C-H-O and C-H-O-halogen systems. Shimansky et al.⁶ have claimed hydrothermal growth of diamond but no details were given on the composition of the liquid and the characterization of the phases. Zhao et al.⁷ have demonstrated diamond hydrothermal synthesis from a mixture of glassy carbon, powdered nickel, diamond seeds, and water at 800 °C and 1.4 kbar. Bachmann et al.⁸ have analyzed gaseous compositions of the 78 different chemical vapor deposition (CVD) diamond syntheses and summarized the results in the form of an atomic C-H-O phase diagram. They concluded that the exact nature of the source gases was unimportant for most diamond CVD processes and that, at typical process temperatures and pressures, it was only the relative ratios of C, H, and O that controlled deposition. The diagram partitions into three distinct regions associated with: (i) diamond growth, centered on the C-O tie line where the input mol fractions of carbon and oxygen are equal; (ii) no growth, lying below the C-O tie line; and (iii) nondiamond growth, located above the C-O tie line. The triangularly

shaped “diamond domain” is adjusted along the CO line of the diagram and is limited by the lines $X_{C/(O+O)} \approx 0.57$ on the carbon-rich side and $X_{C/(O+O)} \approx 0.45$ on the oxygen-rich side (see Fig. 1 in Bachmann et al.⁸). The main part of the synthesis compositions lies in the middle part of the domain between methane and acetylene lines, but only the smaller portion corresponds to hydrogen. Experiments by Marinelli et al.⁹ using a variety of hydrocarbon/CO₂ gas mixtures confirmed the presence of three such regions, and also refined the position of the boundaries between them. Later, Ford¹⁰ and Eaton¹¹ confirmed the main concept of the Bachmann scheme, namely, the existence of a single compositional diamond domain in a C-O-H triangular diagram, in which the overall gas compositions are plotted.

II. BACKGROUND

For diamond, it has been argued that crystallization under *P-T* conditions where diamond is actually thermodynamically unstable with respect to graphite is possible due to kinetic factors.^{12,13} Nanosize diamond particles have an energetic advantage over graphitic particles of the same size, and could be more stable under low *P-T* conditions.^{1,14–16} Fedoseev et al.¹⁷ have shown that critical radii of graphite and diamond nuclei depend upon the surface energy (σ), atomic volume of carbon (V), and chemical potential of the resaturation ($\Delta\mu$):

$$r_g/r_d = V_g\sigma_g\Delta\mu_d/V_d\sigma_d\Delta\mu_g \quad , \quad (1)$$

where the surface energy σ of nanosized diamond (d) or graphite (g) particles depends upon the temperature and size of the particles.¹⁸ From the σ_g/σ_d relation given in Nuth¹⁹ and from Gamarnik¹⁵ it follows that for nanoparticles, $V_g\sigma_g/V_d\sigma_d \approx 1$. The r_g/r_d ratio can then be expressed as:

$$r_g/r_d = \Delta\mu_d/\Delta\mu_g \quad . \quad (2)$$

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The chemical potentials of the resaturation for diamond and graphite can then be expressed as follows:

$$\Delta\mu_g = RT\ln(P_i/P_{i_g}) \quad , \quad (3)$$

$$\Delta\mu_d = RT\ln(P_i/P_{i_d}) \quad , \quad (4)$$

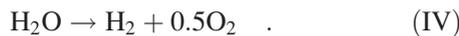
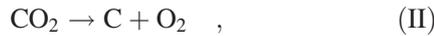
where P_i and $P_{i_{g,d}}$ are the real and equilibrium pressures of carbonaceous gases.

From Eqs. (2)–(4), the ratio of r_g/r_d depends on the ratio between real and calculated equilibrium pressures of carbonaceous gases. Within the range of graphite stability, $P_{i_g} < P_{i_d}$, which corresponds to the preferred graphite formation from fluid phase. The condition of preferred diamond formation corresponds to $P_{i_g} > P_{i_d}$. The difference between $\Delta\mu_g$ and $\Delta\mu_d$ depends upon the difference of P_i/P_{i_g} and P_i/P_{i_d} , and at lower $P_{i_{car}}$ the difference tends to zero, which corresponds to the optimal condition of diamond formation from a gaseous mixture within the range of graphite stability.

In a hydrocarbon-hydrogen mixture, the gas-solid reaction of hydrocarbon shedding can be proposed for carbon formation in a fluid:



Subsequent work has shown that the addition of oxygen to the hydrocarbon gases can stabilize diamond nucleus formation in the P - T range of graphite stability.² This conclusion coincides with the established fact that diamond is more stable in the oxygen environment than graphite, because oxygen reduces graphite to a greater degree than diamond.²⁰ In the C-O-H system, the following gas-solid reaction can be proposed in addition to reaction (I):



Calculations done for the C-O-H system show that $P_{\text{CH}_4(\text{car})}$ is low within the range of the system, close to the upper limit of carbon stability by oxygen (CCO buffer).²¹ Within this range $P_{\text{CH}_4(\text{g})} \approx P_{\text{CH}_4(\text{d})}$, which corresponds to diamond nucleus stabilization (Fig. 1). From the calculations it follows that there are three types of gaseous mixtures equilibrated with free carbon. The fluid changes composition from CO_2 - H_2O - CH_4 to CO_2 - H_2O - H_2 and to CO - H_2 with decreased pressure and increased temperature (Figs. 1 and 2), which corresponds to the relationships established for the C-H-O system by Eaton and Sunkara.¹¹ At T and P corresponding to CVD synthesis, CO - H_2 compositions exist; while at P - T conditions corresponding to hydrothermal growth, CO_2 - H_2O - CH_4 compositions exist (Fig. 1). Therefore, nanodiamond stable

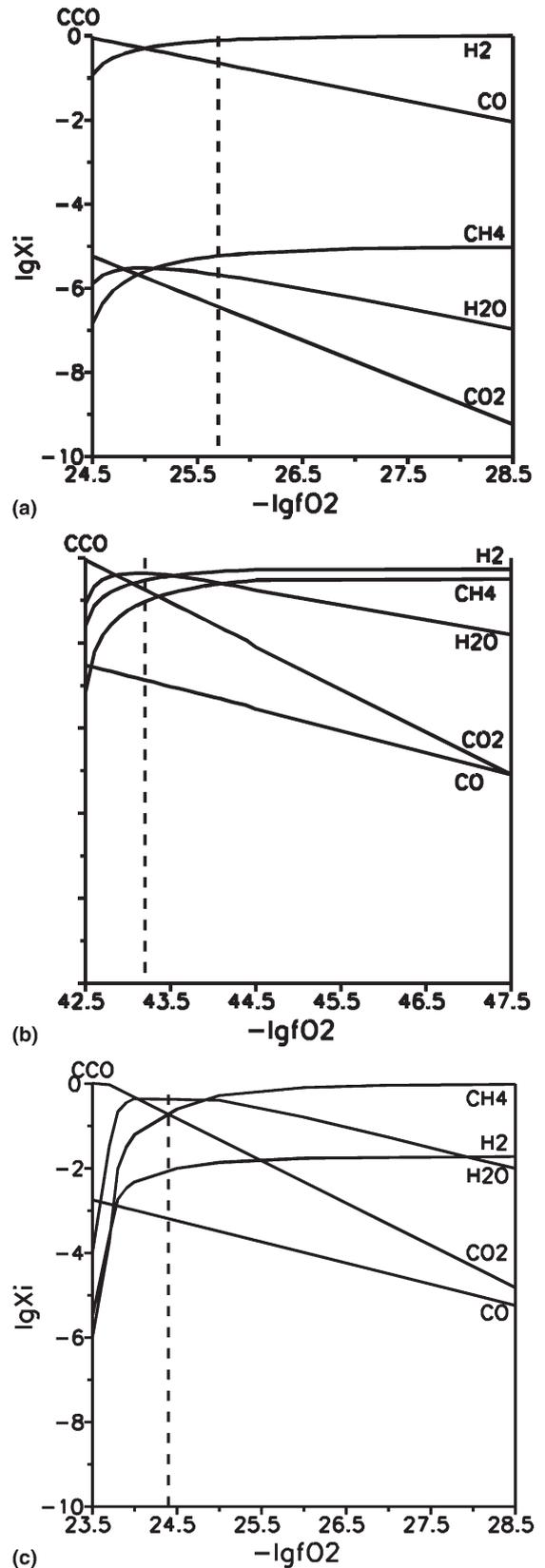


FIG. 1. Variation of compositions of C-O-H system: (a) at 1000 °C and 10^{-3} bar, (b) at 250 °C and 10^{-3} bar, (c) at 500 °C and 1 kbar. CCO denotes the upper limit of carbon by oxygen. The dotted line denotes the boundary of the range of diamond preferable growth.

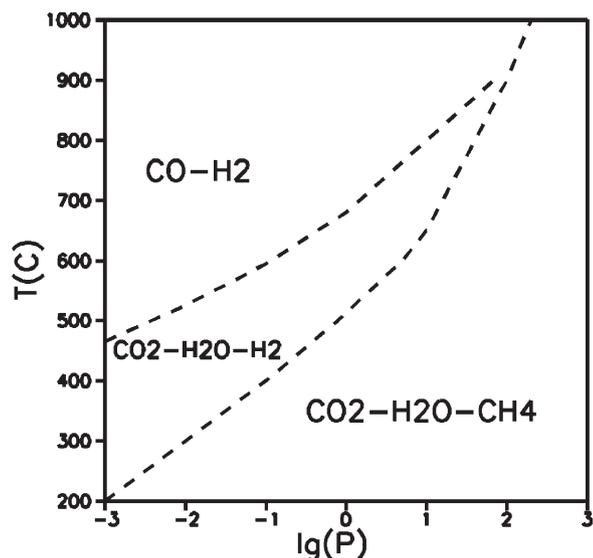


FIG. 2. Variation of composition of the C-O-H system with pressure and temperature.

compositions vary from $\text{CO}_2\text{-H}_2\text{O}$ to CO-H_2 , expanding with the increase in temperature and decrease in pressure (Figs. 1 and 2). From the model, it follows that at all P - T conditions there are three distinct regions in the C-O-H system connected with the degree of oxygen fugacity. The no-growth carbon region lies beyond the CCO buffer. At CVD conditions, the buffer corresponds to CO composition; and at hydrothermal conditions, the buffer corresponds to CO_2 . The diamond-growth region lies lower than the CCO buffer. Under CVD conditions, the buffer corresponds to CO-H_2 compositions; and at hydrothermal conditions, the buffer corresponds to $\text{CO}_2\text{-H}_2\text{O}$ (Fig. 1). The graphite growth region lies below the diamond-stable region. Under CVD conditions, this region corresponds to H_2 composition; and under hydrothermal conditions, this region corresponds to H_2 and CH_4 (Fig. 1). In the C-O-H system, the diamond-growth region forms a half-parabolic domain extended between CO and CO_2 composition and the acetone-ethanol line of the diagram (Fig. 3). The vertex of the parabola is situated near the crossing of the acetone-ethanol and CO lines (Fig. 3). The axis of the parabola corresponds to the CO line up to the CO composition of the diagram. The two parts inside the domain should be considered: (i) CVD, and (ii) hydrothermal. The CVD part lies on the CO line and below. It is limited by the CO composition and the line $X_{\text{C}/(\text{O}+\text{O})} \approx 0.41$ on the carbon-rich side of the diagram (Fig. 3) and corresponds to the CO-H_2 CVD compositions at pressures lower than 1 atm (Fig. 2). The hydrothermal part lies beyond the CVD region and is limited by the CO_2 composition on the carbon-rich side of the diagram (Fig. 3). It corresponds to the hydrothermal $\text{CO}_2\text{-H}_2\text{O-H}_2$ (CH_4) compositions over the wide range of P - T conditions (Fig. 2).

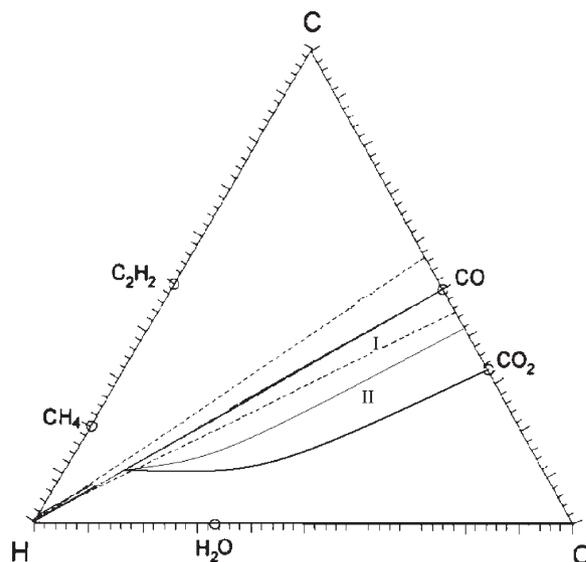


FIG. 3. Atomic C-O-H diagram with half-parabolic nanodiamond domain. (I) field of the CVD synthesis, (II) field of the hydrothermal syntheses.

III. EXPERIMENTS

The possibility of nanodiamond formation from C-O-H fluids at hydrothermal temperatures and pressures without seeds was proved experimentally.²² The syntheses were prepared at 500°C and a total pressure of nearly 1000 bar within the fluid organic matter. In the experiments, a water-alcohol solution was used as the source of the free carbon. The mixture was heated in a high-pressure reactor with a total volume of 500 cm^3 . The run duration was 5–7 days. Raman spectra show that the synthesized products contain atoms of carbon with sp^3 bonds. Samples were studied under a transmission electron microscope. Diamonds were diagnosed as 70–80 nm-sized particles of different forms; some of them reached $1\ \mu\text{m}$ (Fig. 4).

IV. RESULTS AND DISCUSSION

Although the thermodynamic treatment should be limited to hot-filament CVD, the results will provide some guidelines for plasma processing regarding the effect of the independent variables on the microstructural evolution. Sommer et al.²³ and Wang et al.²⁴ developed a thermodynamic analysis of diamond CVD based on a quasi-equilibrium model, where nonequilibrium steady state depositions of diamond and graphite were analyzed using equilibrium thermodynamics. Following Fig. 3, the CVD region of our domain covers most of the Bacmann⁸ and Marinelli⁹ experimental points lying on the CO line and below it. The model also explains the data found in Marinelli et al.,⁹ that the addition of hydrocarbons to pure CO_2 first initiates diamond growth, and then graphite growth [Figs. 1(b) and 1(c)].

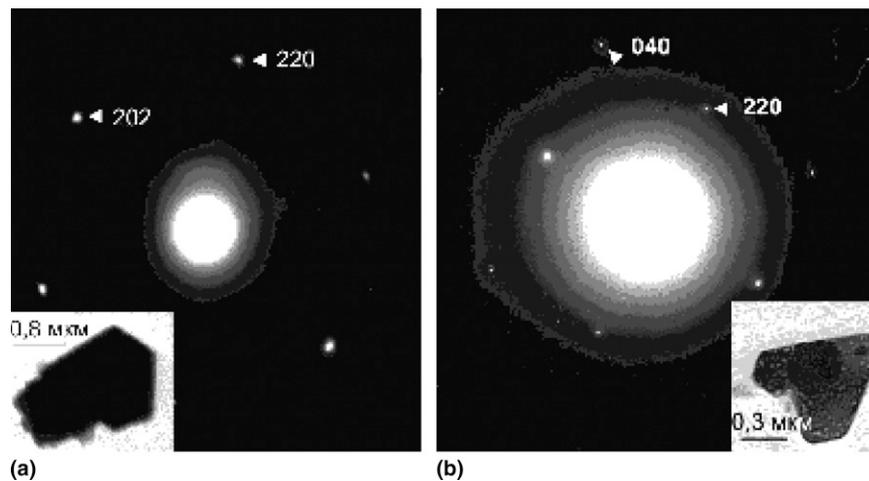


FIG. 4. Microdiffractions and form of the diamond, (a) zone axis [111] and (b) zone axis [001].

As a result, it is possible to conclude that the model could provide a common basis for low-pressure diamond CVD and hydrothermal methods. By means of this model, special relations between very different source gases and gas mixtures become clear.

The origin of diamonds in interstellar space has been a topic of intense discussion since the discovery of presolar nanodiamonds in chondrites.²⁵ Meteoritic nanodiamonds provide information on the nucleosynthesis of evolved stars and the evolution of the astrophysical environment that formed the solar system. Sellgren²⁶ identified the relationship between the interstellar diamond and water ice. Nakano et al.²⁷ studied interstellar diamond formation in relation to organic matter. Based on these relationships, Kouch et al.²⁸ identified new formation routes of diamond in the interstellar clouds and parent bodies of carbonaceous chondrites during laboratory experiments. The new formation route was found from the ice mixture of H₂O, CO, NH₃, and CH₄ (4:2:2:1). 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.²⁹ The fluid calculations performed at 250 °C and 10⁻³ bar show that the diamond stability range here corresponds to CO₂ and H₂O compositions of the fluid [Fig. 1(b)]. This explains the relationship of interstellar diamonds with water.²⁶

Microdiamonds and nanodiamonds have also been found in shallow earth rocks formed at *P-T* conditions corresponding to graphite thermodynamic stability.³⁰⁻³⁴ The highest grade is observed in hydrothermal metasomatic zones of the Kokchetave metamorphic massive situated in Northern Kazakhstan.³⁵ The fluid calculations performed at *P-T* conditions corresponded to hydrothermal metasomatic zones of the Kokchetave metamorphic massive formation (500 °C and 1 kbar) show that the

diamond stability range here corresponds to CO₂ and H₂O compositions of the fluid [Fig. 1(c)]. This explains the relationship of the Kokchetave microdiamonds with water and carbon dioxide.³⁶

The model presented shows that nanosized diamond particles could be formed from carbon-bearing fluids at low temperatures and pressures without seeds in the range of the upper limit of carbon stability in oxygen. It explains the hydrothermal formation and growth of diamond and the specificity of the CVD diamond synthesis gas compositions at low *P-T* conditions, as well as the genesis of interstellar nanodiamonds in space and of nanodiamonds and microdiamonds in the shallow depth metamorphic Earth rocks at *P-T* conditions corresponding to graphite stability. In contrast to models where many possible reactions are considered, the present model makes the simplest possible assumptions about the key processes, and is then able to account for various tendencies seen in experimental and natural data. The determined relations may help to develop new models needed for diamond formation and deposition.

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REFERENCES

1. P. Badziag, W.S. Verwoerd, W.P. Ellis, and N.R. Greimer: Nanometer-sized diamonds are more stable than graphite. *Nature* **343**, 244 (1990).
2. S.K. Simakov: Thermodynamic estimation of oxygen-hydrogen conditions influence on diamond and graphite critical nucleus formation at processes of methane destruction at low pressures. *Russ. J. Phys. Chem.* **69**, 346 (1995).
3. V.S. Shatsky and N.V. Sobolev: Origin of diamonds in metamorphic rocks. *Dokl. Akad. Nauk* **331**, 217 (1993).

4. R.C. DeVries, R. Roy, S. Somiy, and S. Yamada: A review of liquid phase systems pertinent to diamond synthesis. *Trans. Mater. Res. Soc. Jpn.* **14B**, 1421 (1994).
5. R. Roy, D. Ravichandran, P. Ravindranathan, and A. Badzian: Evidence for hydrothermal growth of diamond in the C-H-O and C-H-O halogen system. *J. Mater. Res.* **11**, 1164 (1996).
6. A. Szymanski, E. Abgarowicz, A. Bakon, A. Niedbalska, R. Salacinski, and J. Sentek: Diamond formed at low pressures and temperatures through liquid-phase hydrothermal synthesis. *Diamond Relat. Mater.* **4**, 234 (1995).
7. X-Z. Zhao, R. Rustum, A.C. Kuruvilla, and A. Badzian: Hydrothermal growth of diamond in metal-C-H₂O systems. *Nature* **385**, 513 (1996).
8. P.K. Bachmann, D. Leers, and H. Lydtin: Towards a general concept of diamond chemical vapour deposition. *Diamond Relat. Mater.* **1**, 1 (1991).
9. M. Marinelli, E. Milani, M. Montuori, A. Paoletti, A. Tebano, G. Balestrino, and P. Paroli: Compositional and spectroscopic study of the growth of diamond films from several gaseous mixtures. *J. Appl. Phys.* **76**, 5702 (1994).
10. I.J.J. Ford: Boundaries of the diamond domain in the C-H-O diagram of carbon film deposition. *J. Phys. D: Appl. Phys.* **29**, 2229 (1996).
11. S.C. Eaton and M.K. Sunkara: Construction of a new C-H-O ternary diagram for diamond deposition from the vapor phase. *Diamond Relat. Mater.* **9**, 1320 (2000).
12. B.V. Deryagin and D.V. Fedoseev: *Growth of Diamond and Graphite from the Gas Phase* (Nauka, Moscow, 1977), p. 115.
13. S.P. Chauhan, J.C. Angus, and N.C.J. Gardner: Kinetics of carbon deposition on diamond powder. *J. Appl. Phys.* **47**, 4746 (1976).
14. E.F. Chaikovskii and G.H. Rosenberg: Phase diagram of carbon and possibility of diamond formation at low pressures. *Dokl. Akad. Nauk* **279**, 1372 (1984).
15. M.Y. Gamarnik: Energetical preference of diamond nanoparticles. *Phys. Rev. B: Condens. Matter* **54**, 2150 (1996).
16. V.L. Tawson and M.G. Abramovich: Polymorphism of crystals and phases size effect: Transformation diamond to graphite. *Dokl. Akad. Nauk* **287**, 291 (1986).
17. D.V. Fedoseev, B.V. Deryagin, I.G. Varshavskaya, and A.S. Semenova-Tyan-Shanskaya: *Diamond Crystallization* (Nauka, Moscow, 1984), p. 134.
18. M.N. Magomedov: About the relationship of surface energy with size and form of nanocrystals. *Phys. Tverd. Tela* **46**, 924 (2004).
19. J.A. Nuth: Small-particle physics and interstellar diamonds. *Nature* **329**, 589 (1987).
20. T. Kawato and K. Kondo: Effects of oxygen on CVD diamond synthesis. *Jpn. J. Appl. Phys.* **26**, 1429 (1987).
21. S.K. Simakov: Redox state of Earth's upper mantle peridotites under the ancient cratons and its connection with diamond genesis. *Geochim. Cosmochim. Acta* **62**, 1811 (1998).
22. S.K. Simakov, V.T. Dubinchuk, M.P. Novikov, and N.N. Melnik: Low-pressure-temperature, metastable nanosized diamond and diamond-like phases formation without seeds, in *NDNC-2008, the 2nd Annual Conference of New Diamonds and Nanocarbons* (Elsevier, Taipei, 2008), p. 219.
23. M. Sommer, K. Mui, and F.W. Smith: Thermodynamic analysis of the chemical vapor deposition of diamond films. *Solid State Commun.* **69**, 775 (1989).
24. R.B. Wang, M. Sommer, and F.W. Smith: The deposition of diamond films via the oxyacetylene torch: Experimental results and thermodynamic predictions. *J. Cryst. Growth* **119**, 271 (1992).
25. T. Bernatowicz and E. Zinner: Astrophysical implications of the laboratory study of presolar materials, in *Proceedings of the AIP Conference* (Elsevier, Woodbury, NY, 1997), p. 748.
26. K. Sellgren: Aromatic hydrocarbons, diamonds, and fullerenes in interstellar space: Puzzles to be solved by laboratory and theoretical astrochemistry. *Spectrochim. Acta* **57**, 627 (2001).
27. H. Nakano, A. Kouchi, M. Arakawa, Y. Kimura, C. Kaito, H. Ohno, and T. Hondoh: Alteration of interstellar organic materials in meteorites' parent bodies: A novel route in diamond formation. *Proc. Japan Acad. Ser. B* **78**, 277 (2002).
28. A. Kouchi, H. Nakano, Y. Kimura, and C. Kaito: Novel routes for diamond formation in interstellar ices and meteoritic parent bodies. *Astrophys. J.* **626**, L129 (2005).
29. T.L. Daulton: Extraterrestrial nanodiamonds in the cosmos, in *Ultrananocrystalline Diamond*, edited by O. Shenderova and D. Gruen (William-Andrew, Norwich, UK, 2006), p. 23.
30. O.M. Rozen, U.M. Zorin, and A.A. Zayachkovsky: Diamond foundation in connection of precambrian eclogites of Kokchetav massive. *Dokl. Akad. Nauk* **203**, 674 (1972).
31. L.F. Dobrzhinetskaya, E.A. Eide, R.B. Larsen, B.A. Sturt, R.G. Tronnes, D.C. Smith, W.R. Taylor, and T.V. Posukhova: Microdiamonds in high-grade metamorphic rocks of the Western Gneiss region, Norway. *Geology* **23**, 597 (1995).
32. N.V. Sobolev and V.S. Shatsky: Diamond inclusions in garnets from metamorphic rocks; A new environment for diamond formation. *Nature* **343**, 742 (1990).
33. M.I. Novgorodova and A.V. Rasskazov: High-pressure carbon mineral phase formation as a result of heat explosion at shift transformation of graphite. *Dokl. Akad. Nauk* **322**, 379 (1992).
34. R. Wirth and A. Rocholl: Nanocrystalline diamonds from the Earth's mantle underneath Hawaii. *Earth Planet. Sci. Lett.* **211**, 357 (2003).
35. V.A. Pechnikov and F.V. Kaminsky: Diamond potential of metamorphic rocks in the Kokchetav Massif, northern Kazakhstan. *Eur. J. Mineral.* **20**, 395 (2008).
36. K. De Corte, P. Cartigny, V.S. Shatsky, P. De Paepe, M.V. Sobolev, and M. Jovay: Characteristics of microdiamond from UHPM rocks of the Kokchetav massif (Kazakhstan), in *Proceedings of the 7th International Kimberlite Conference*, edited by J.J. Gurney, L.G. Gurney, M.D. Pascoe, and S.H. Richardson (Elsevier, Cape Town, 1999), p. 174.