



Synthesis of nanopolycrystalline mesoporous diamond from periodic mesoporous carbon: Mesoporosity increases with increasing synthesis pressure

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ABSTRACT

We report the catalyst-free synthesis of monolithic mesoporous nanopolycrystalline diamond from periodic mesoporous carbon at pressures between 15 and 21 GPa and a temperature of 1300 °C. We investigated the pressure-dependence of the porosity with 3-dimensional electron tomography. We have observed that surface areas increase from 56 to 90, 138 m² g⁻¹, and porosities increase from 10, 24, to 33% for materials produced at 15, 18, and 21 GPa, respectively. The increased porosity at higher pressure may be due to the earlier onset of the nucleation of diamond at higher pressure.

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Diamond is the hardest known material. Bundy et al. first produced the synthetic diamond at high pressure and high temperature in 1955 [1]. The hardness of single-crystalline diamond varies from about 60–120 GPa, depending on the crystallographic plane and direction of measurement [2]. However, due to the existence of well-defined crystal planes single-crystalline diamond has only a moderate toughness, which limits its industrial application. On the contrary, polycrystalline diamond possesses a high volume fraction of grain boundaries that can block the crack propagation process, resulting in greater toughness and a more isotropic hardness [3]. According to the Hall-Patch effect, mechanical properties of materials can be strengthened by reducing grain size, i.e. increasing number of grain boundaries, thus nanopolycrystalline diamond is considered to be an effective method for improving mechanical properties [4]. Conventional polycrystalline diamond contains binder materials of metal (Co, Ni) or ceramic (SiC) that can degrade the mechanical properties and thermal stability. Irifune et al. first synthesized nano-polycrystalline diamond by direct conversion of graphite without aid of any catalyst at high pressure

(>12 GPa) and high temperature (>2300 °C) [5]. The diamond is obtained as a transparent monolith and thus no binder is required for the production of tools. But the ultra-high synthesis condition is a major obstacle for large-scale production of nanopolycrystalline diamond. Nanopolycrystalline diamond has also been synthesized from other carbon precursors, e.g. annealed nano-diamond [6], ball-milled graphite [7], non-graphitic carbons (amorphous carbon, fullerene, quasi-amorphous soot, carbon black) [8,9] etc. Nanopolycrystalline diamond with ultra-high hardness has been obtained by introducing twin boundaries using multi-core carbon onion precursors [10].

Recently, periodic mesoporous carbon CMK-8 was explored as a precursor for nanopolycrystalline diamond [11]. The hypothesis behind the work was that porous forms of carbon are more reactive at high pressure, which would allow for the formation of nanopolycrystalline diamond at lower temperature. Indeed, a phase transformation into nanopolycrystalline diamond was observed from a temperature of 1300 °C at a pressure of 21 GPa [11]. Surprisingly the nanopolycrystalline diamond was found to be mesoporous. The porosity in the material was attributed to the low transformation temperature at which the synthesis is kinetically controlled, leading to incomplete densification and the formation of a porous diamond material as a metastable phase. However, the

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porosity of the materials was only qualitatively characterized, and no detailed information about pore volumes and pore size distributions were given. Also no investigations were carried out to determine the minimal pressure required for the formation of nanopolycrystalline diamond and the dependence of pressure on the porosity. Further, it was not investigated if CMK-8 is the only precursor that can be used for the synthesis of porous diamond, or if other periodic mesoporous carbons with other pore structures can also be used. It has recently been reported that diamond nanocrystals can also be synthesized from periodic mesoporous SBA-15 type carbon at 14 GPa pressure and temperature of 1300–1400 °C [12]. However, the high pressure behavior of SBA-15 above this pressure is currently unknown.

Here, we report the synthesis of mesoporous, monolithic, transparent, nanopolycrystalline diamond at pressures between 15 GPa and 21 GPa and a temperature of 1300 °C from SBA-15 type periodic mesoporous carbon. The synthesized diamond has been characterized with X-ray diffraction, Raman spectroscopy and transmission electron microscopy. We then quantified the porosity with 3-D electron tomography. Surprisingly, with increasing pressure, the porosity in the diamond increases. Electron tomography measurements indicated that surface areas are 56, 90, 138 m² g^{−1} and porosities are 10, 24, 33% for the product materials synthesized at 15, 18, 21 GPa respectively.

For the synthesis of diamond under high-pressure high-temperature conditions a periodic mesoporous carbon material with cylindrical pores (SBA-15 type) was used as a precursor, which was synthesized according to the reported procedure [12,13]. The precursor SBA-15 type periodic mesoporous carbon material has a pore size of 5.3 nm, a BET surface area of ~650 m² g^{−1} and a pore volume of 0.6 cm³/g [12]. The high-pressure experiments were performed using an 8/3 cell assembly (Fig. S1) in a multianvil apparatus. The samples were compressed to 15, 18, and 21 GPa and heated at temperatures of 1300 °C for 180 min respectively. The starting material was placed in the chamber surrounded by an alumina sliver, a cylindrical Re heater, and a LaCrO₃ sleeve for thermal insulation. The whole assembly was placed inside a Cr₂O₃ doped MgO octahedron with an edge length of 8 mm. The octahedron was placed inside eight corner-truncated (truncated edge length 3 mm) tungsten carbide cubes. Pyrophyllite gaskets were used to separate the tungsten carbide cubes from each other. The temperature was measured using a W5%Re–W26%Re wire as thermocouple (C-type) which was implemented into the assembly. The sample was compressed to the desired pressure at a rate of 2 GPa/h at room temperature and then heated to the final temperature at a rate of 50 °C/min. After the final temperature was reached, the temperature was kept constant for 3 h. Then, the pressure was released at a rate of 2 GPa/h. After ambient pressure was reached, the sample was extracted from the alumina sleeve for characterization and analysis.

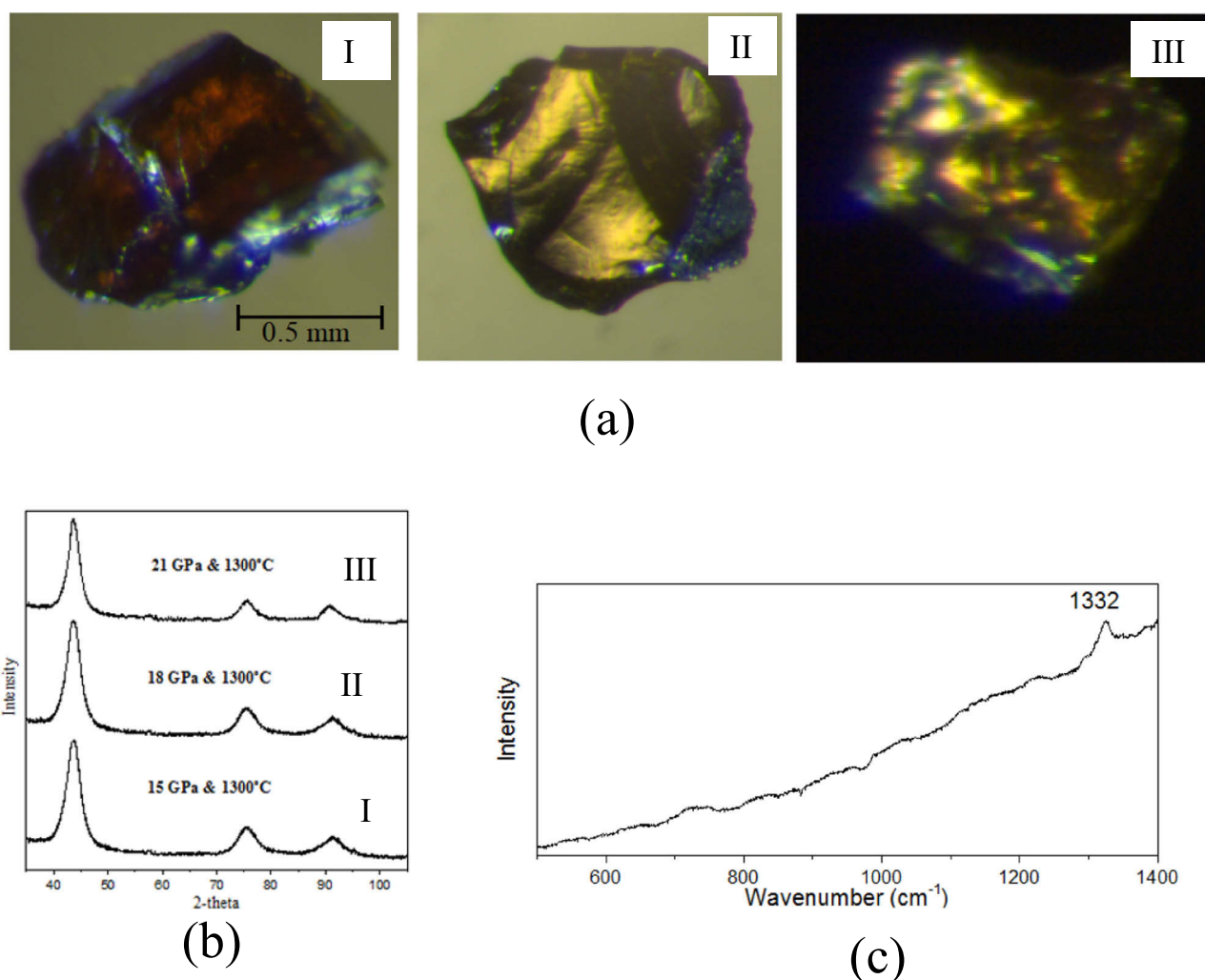


Fig. 1. (a) The optical microscopy image, and (b) XRD pattern (CuKα) of the product materials synthesized at (I) 15 GPa–1300 °C, (II) 18 GPa–1300 °C and (III) 21 GPa–1300 °C; (c) The Raman ($\lambda_{\text{ex}} = 532$ nm) spectra of no polycrystalline diamond synthesized at 15 GPa and 1300 °C.

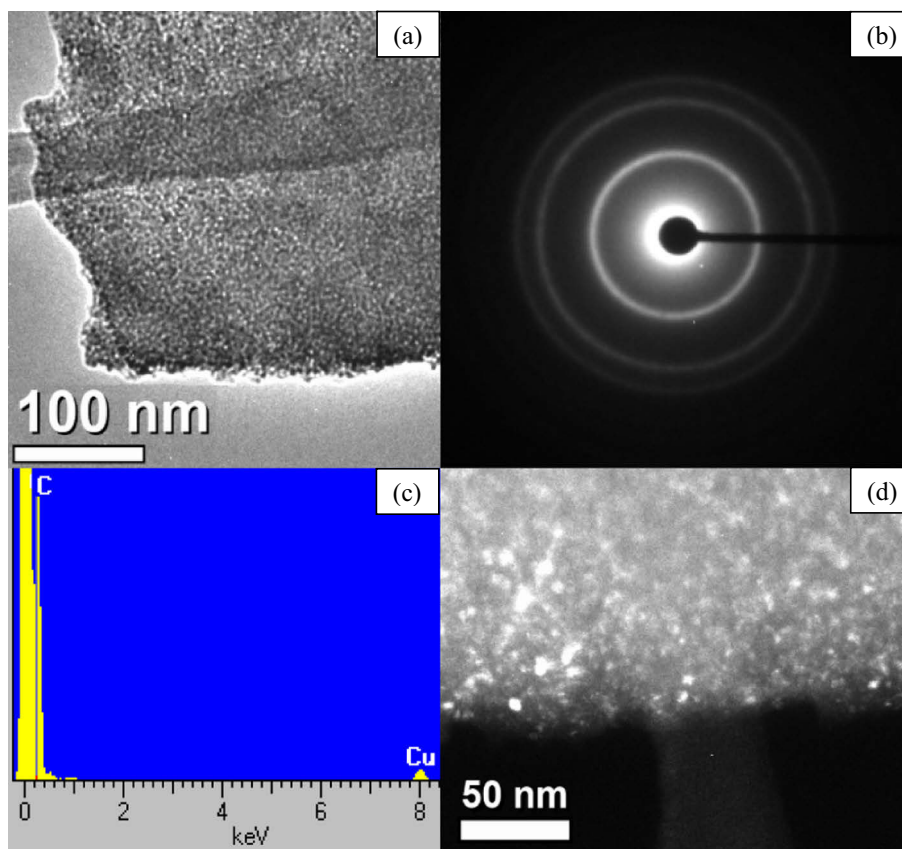


Fig. 2. (a) TEM, (b) SAED, (c) EDS pattern and (d) TEM Dark Field image corresponding to the first diffraction ring of (c) of mesoporous diamond synthesized at 15 GPa and 1300 °C.

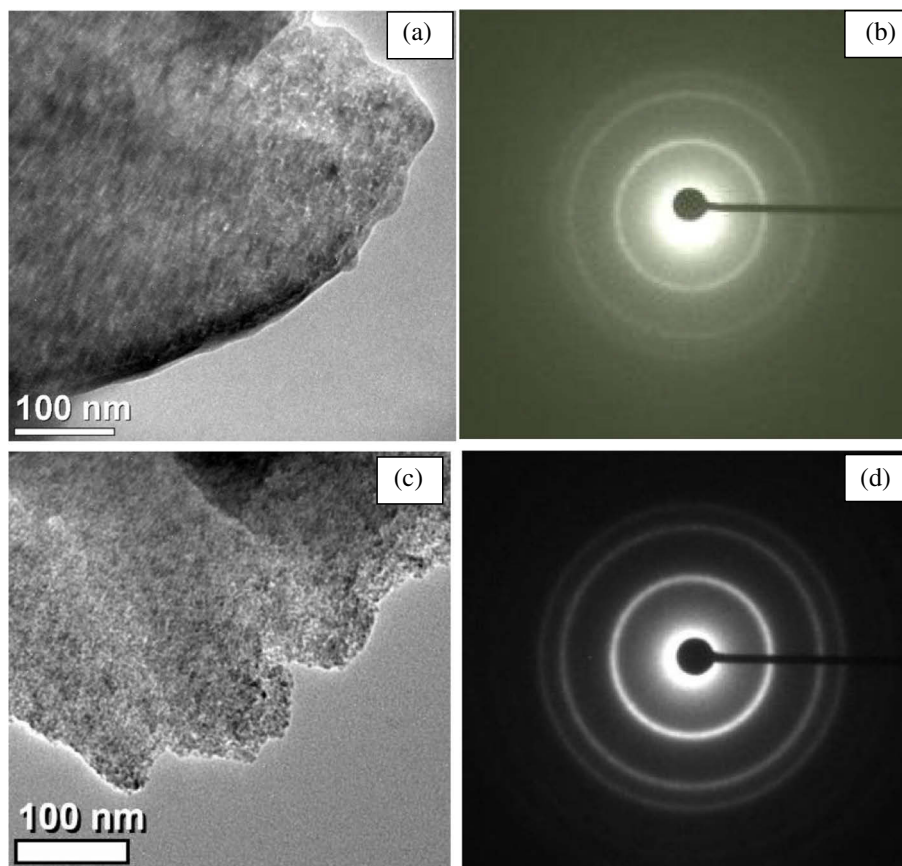


Fig. 3. (a) TEM and (b) SAED of mesoporous diamond synthesized at 18 GPa and 1300 °C; (c) TEM and (d) SAED of mesoporous diamond synthesized at 21 GPa and 1300 °C.

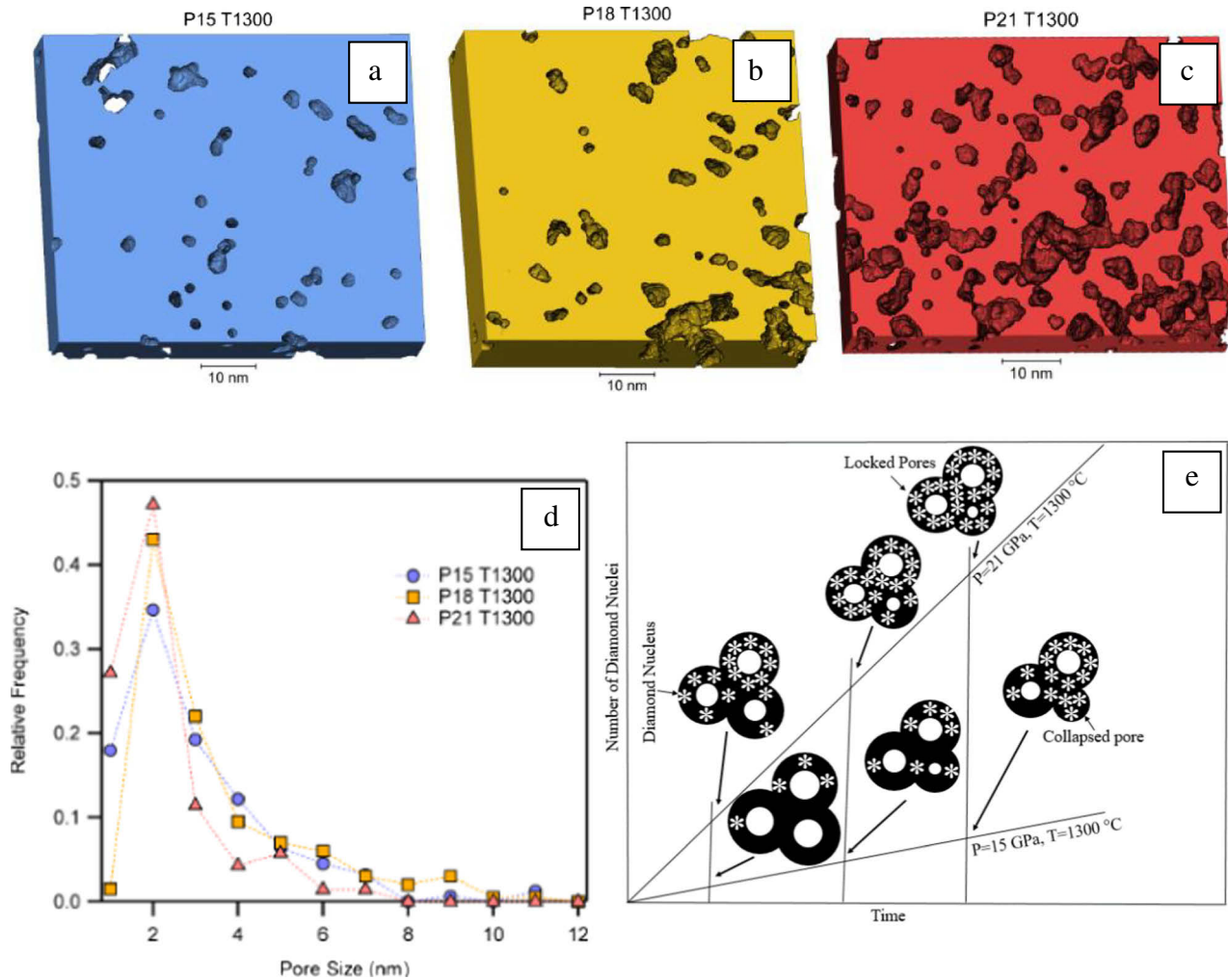


Fig. 4. (a)–(c) 3-D visualization and (d) pore size analysis using electron tomography of product materials synthesized at pressures 15 GPa, 18 GPa, 21 GPa and temperature of 1300 °C; (e) Evolution of Diamond Nuclei with time: at higher pressure (21 GPa, 1300 °C), Diamond Nuclei evolve faster causing more “Locked Pores”; while at lower pressure (15 GPa, 1300 °C), Diamond Nuclei evolve slowly with time leading to more collapsed pores.

The mesoporous carbon that was subjected to a pressure of 15 GPa and a temperature of 1300 °C for 3 h yielded a transparent monolithic material with a brown color indicating the formation of nanopolycrystalline diamond (Fig. 1a). X-ray diffraction (XRD) data confirmed the presence of crystalline, cubic diamond (Fig. 1b). The reflections can be indexed as 111, 220, and 311 reflections. The broadness of the peaks suggests nanocrystallinity of the sample. The crystal size can be calculated using Scherrer's formula [14] (Table S1), as around 5 nm.

Additionally, the formation of diamond was confirmed by Raman spectroscopy (using 532 nm green laser) under ambient conditions [15,16]. The Raman spectrum shows only one first-order Raman line at 1332 cm^{-1} indicating the presence of pure cubic diamond (Fig. 1c). The high background is due to the fluorescence of diamond.

To gain insight into the morphology of the diamond obtained, we investigated the product with transmission electron microscopy (TEM). A TEM image of the material obtained at 15 GPa indicates a porous morphology with a mesoscale texture (Fig. 2a). The pore system does not exhibit periodic order. To investigate whether the porous particles were crystalline, we performed selected area electron diffraction (SAED). The electron diffraction pattern revealed concentric diffraction rings that are expected for nanopolycrystalline materials (Fig. 2b). This is consistent with the transparent monolithic nature of the product. The well-resolved diffraction rings of the SAED pattern can be indexed to (111), (220) and (311) with corresponding d spacings of 0.2068,

0.1261, and 0.1074 nm that can all be attributed to the cubic diamond lattice.

It clearly excludes the presence of another crystalline phase (e.g. graphite). The optical transparency of the product and sharp diffraction contrast observed in TEM images rules out the possibility of a mesostructured composite of an sp^2 -hybridized form of carbon and diamond. The combined TEM and SAED data suggests that the diffraction contrast observed in TEM is due to mesoporosity rather than the presence of a second phase. We have also performed energy-dispersive x-ray (EDX) spectroscopy experiments that confirmed that no other element but carbon is present (Fig. 2c). Nanopolycrystallinity is also confirmed by dark field imaging which shows ~5–10 nm sized crystals (bright areas) contributing to the first diffraction ring in SAED (Fig. 2d) which almost the same as calculated from X-ray diffraction data with Scherrer's formula (Table S1).

Table 1

Pore volume, porosity and surface area measured with electron tomography of the product material synthesized at pressures of 15, 18 and 21 GPa and temperature of 1300 °C.

Synthesis condition P (GPa), T (°C)	Pore volume (cm^3/g)	Porosity (%)	Surface area ($\text{m}^2\text{ g}^{-1}$)
15, 1300	0.0291	10	56
18, 1300	0.0697	24	90
21, 1300	0.095	33	138

In order to better understand the effect of pressure on porosity, we performed additional experiments at different pressures (18 and 21 GPa) keeping the temperature constant (1300 °C). The synthesized products were again obtained as a transparent monolithic material indicating the formation of nanopolycrystalline diamond (Fig. 1a). With increasing pressure, the color of the product changes from brown to light yellow. X-ray diffraction (XRD) data confirmed the presence of crystalline, cubic diamond (Fig. 1b) with 111, 220, and 311 reflections. TEM image and SAED patterns also indicated the formation of mesoporous nanopolycrystalline diamond (Fig. 3).

We then analyzed the materials synthesized at 15, 18, and 21 GPa with electron tomography to obtain quantitative information about the surface area, pore size distribution and porosity. The details about 3-D electron tomography method and the data analysis procedure have been added in the supporting information.

The 3-D electron tomography shows a very similar pore size distribution centered around 2 nm for the three samples (Fig. 4a–d). The surface area and pore volume are 56 m² g^{−1} and 10%, respectively for the diamond material obtained at 15 GPa–1300 °C synthesis condition. Unexpectedly, increasing the synthesis pressure to 18 and 21 GPa, increases the porosity and surface area in the product materials (Table 1), which is contradictory to the conventional behavior.

Solid-state structures tend to be close-packed minimizing the “empty space” between atoms. Therefore, special conditions are required to form porous structures to overcome the tendency of close-packing. The most commonly-used strategy for creating porous materials is the templating method [17,18]. Porous materials exposed to high pressure (>1 GPa) generally undergo pore collapse [19–25]. For example, periodic mesoporous silica MCM-41 undergoes pore collapse at room temperature in the MPa pressure range [24]. Tolbert et al. have demonstrated that the mesopores of MCM-41 can elastically and reversibly deform at high pressure and ambient temperature [26,27]. We have observed that our synthesized nanopolycrystalline diamond is mesoporous in nature, despite extreme synthesis condition and the porosity increases with increasing synthesis pressure. At first glance, it would be expected that the porosity of the products decrease with increasing pressure because pressure favors denser phases over porous phases, however the opposite was experimentally observed. The reason may be that a higher pressure facilitates the nucleation of diamond, which leads to the formation of more pores between the diamond nuclei. Because the phase transformation occurs at an earlier stage there is less time for the pores in the sp²-carbon to fully collapse before the onset of the phase transformation. After the diamond nuclei have formed, the elimination of the porosity in the diamond is hindered due to the high kinetic inertness of the diamond nanoparticles (Fig. 4e).

In summary, we have synthesized transparent, mesoporous, nanopolycrystalline diamond monoliths from periodic mesoporous SBA-15 type carbon at pressures between 15 and 21 GPa and a temperature of 1300 °C. Electron tomography provided quantitative information about pore volume, pore size distribution, and surface area. From electron tomography measurement, we concluded that with increasing synthesis pressure condition, the porosity and the surface area of nanopolycrystalline diamond increase. This behavior may be due to

the fact that with increasing pressure, diamond nucleation is facilitated which leads to a higher porosity. The results further show that the synthesis of mesoporous, nanopolycrystalline diamond does not require a specific precursor mesopore structure, and that the minimal pressure required to produce mesoporous, nanopolycrystalline diamond from SBA-15 type periodic mesoporous carbon is 15 GPa with a temperature of 1300 °C.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scriptamat.2018.10.024>.

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