Shape-controlled synthesis of diamond crystal by epitaxial growth under high pressure and high temperature conditions*

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In this paper, the diamond epitaxial growth mechanism has been studied in detail by employing several types of diamond as a seed in a catalyst–graphite system under high pressure and high temperature (HPHT) conditions. We find that the diamond nucleation, growth rate, crystal orientation, and morphology are significantly influenced by the original seeds. The smooth surfaces of seeds are beneficial for the fabrication of high-quality diamond. Our results reveal that the diamond morphology is mainly determined by the original shape of seeds in the early growth stage, but it has an adjustment process during the growth and leads to well symmetry. Additionally, we have also established the growth model for the twinned diamond grown on several seeds, and proposed the possible growth processes by tracking the particular shapes of seeds before and after treatment under HPHT conditions. These results suggest that the shape-controlled synthesis of diamond with well morphology can be realized by employing certain suitable diamond seeds. This work is expected to play an important role in the preparation of trustworthy diamond-based electronic and photonic devices.

Keywords: diamond, nucleation, morphology, seed

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1. Introduction

Due to its excellent properties,[1−4] there has been a long history of making extensive use of diamond and the pursuit of the genesis of natural diamond is always of high interest.[5−10] Most of the studies focused on the forming environments of natural diamond[7,11−13] and the effects of the minor elements and impurity diffusion on the diamond crystallization.[8,10,14−18] Generally, while it is confirmed to be a reasonable alternative to investigate the diamond growth mechanism using a catalyst at high pressure and high temperature (HPHT) conditions, there is a lack of generally acknowledged estimates. Recently, diamond epitaxial growth on seeds has been proved to be an effective method to accelerate the nucleation.[19−22] Some valuable information and evidence for diamond nucleation and growth have been obtained.

More recently, both p- and n-type semiconductive diamond have been successfully synthesized by doping.[23−31] Therefore, the shape-controlled synthesis of diamond with well morphology is expected to play an important role in the preparation of diamond p–n junction diodes and has recently received great attention due to its potential applications in the fields of electronic and photonic devices. The moderate growth rate is generally considered to be suitable for the synthesis of high purity diamond during the epitaxial growth process. It is found that the crystal direction and the original shape of the seed play important roles in the formation of diamond morphology.[19] However, the formation process is still unclear. Hirmke *et al.*[21] have investigated the influence of seed particles on the chemical vapour deposition (CVD) diamond and proposed that the obtained diamonds grown on seeds with grain size larger than 5 μm had poor qualities, such as undefined morphology with twining planes and shapes, which is detrimental to further applications in the electronic and photonic fields. Therefore, a deeper understanding of

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the correlation between original seeds and synthesized diamonds is very important for the shape-controlled synthesis of diamond. This will inevitably enhance the prospects for diamond-based electronic and photonic devices and it can also help us to improve existing models for the diamond growth mechanism.

Previously, we have studied the diamond growth mechanism by the seed-assisted method under HPHT conditions, and extensively investigated the nucleation, growth style, and the formation of diamond morphology.[22] Moreover, it is interesting to note that some spontaneous diamonds with irregular shape are also established in the system. Therefore, our present work intends to obtain a broader understanding of the particular influence of the employed seeds on the diamond morphology and the reasons for the appearance of spontaneous nucleation during diamond epitaxial growth process. Here, we employ several different types of seed to synthesize diamonds for studying the epitaxial growth mechanism in detail. In addition, the diamond epitaxial growth on two or more seeds has also been established. According to our observed results, the diamond epitaxial growth mechanism is intensively analysed by tracking particular seed shapes before and after treatment under HPHT conditions. Our work will be greatly helpful for the deep understanding of diamond growth mechanism.

2. Experimental details

Experiments of diamond crystallization were carried out using a china-type large volume cubic high-pressure apparatus (CHPA) (SPD-6×1670) with sample chamber of 38-mm edge length. The schematic diagram of the high pressure apparatus and the growth cell in graphite heater is shown in Fig. 1. The temperature was measured in each experiment by using a Pt RH/Pt Rh6 thermocouple, whose junction was placed near the crystallization ampoule. The starting materials were a high purity graphite (99% purity) as carbon source and an $Fe_{70}Ni_{30}$ alloy powder (200 meshes) as catalyst. To obviously distinguish the original seeds from the new grown diamonds, we choose boron-doped diamonds, black in colour, as the seed crystals, as shown in Fig. 2. The size of the seeds is about 0.1 mm. One type of the seed (S_1) has perfect octahedral shape with smooth surface (Fig. 2(a)). And the other seeds (S_2) are some diamond fragments, some bigger crushed diamond crystals with irregular shapes and face roughnesses (Fig. 2(b)). The graphite powders and $Fe_{70}Ni_{30}$ alloy (1:1, weight ratio) were mixed with seed crystals for 4 hours, and then were machined into an ampoule 38 mm in diameter and 20-mm high for the diamond synthesis.

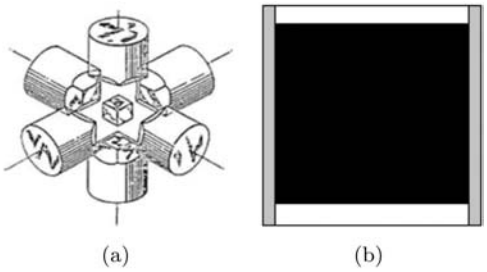


Fig. 1. The schematic diagram of the high pressure apparatus and the diamond growth cell.

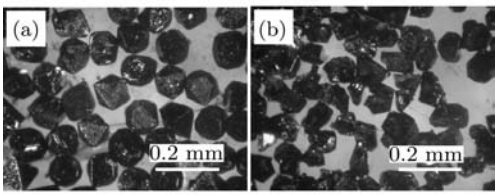


Fig. 2. The optical images of the diamond seed crystals: (a) with perfect octahedral shapes and smooth surfaces (S_1), (b) without integral shapes and smooth faces (S_2).

After the experiments, the crystallization ampoules were first cracked and examined with a binocular microscope. The products were then dissolved in a hot acid mixture of H_2SO_4 and HNO_3 (4:1) to remove the remaining graphite and metal catalyst. The recovered spontaneously nucleated diamonds and seed crystals were studied by using optical microscopy and an LEO 420 scanning electron microscope (SEM). Moreover, several obtained diamonds were separated to examine the interface between the grown diamond and seed crystal by SEM, which is expected to give some clues to the early growth stage.

3. Results and discussion

3.1. Effects of seeds additive on the diamond crystallization in Fe–Ni–C system

The experiments are performed at pressures of 4.6 GPa–5.4 GPa and temperatures ranging from 1340 °C to 1380 °C in the catalyst–graphite system and the experimental results are summarized in Table 1. The diamond growth method can be classified into two categories, including the film growth (FG)

method, and temperature gradient growth (TGG) method. So far high-quality single crystals of diamond have been synthesized using the TGG method. Generally, the seeds on the bottom of the bath are used to initiate diamond growth. However, they are not incorporated into the body of the synthetic crystal, leading to a limit in the fields of electronic devices. Thus, spontaneous diamonds in the system without seed additive (denoted as O) and the diamonds epitaxial growth on seeds S_1 and S_2 (denoted as M and N, respectively) are all obtained by FG method in this study. The diamond epitaxial growth on seeds is observed in systems M and N at 4.6 GPa and 1350 °C (R-2), whereas the spontaneous crystallization of diamond is established till 4.8 GPa in the Fe–Ni–Graphite system (O) (R-7–R-8). We believe that this is due to the higher energy barriers for the diamond spontaneous crystallization than that of the epitaxial growth on seeds. There is no observable difference for the epitaxial growth on the different seeds (S_1 and S_2).

Table 1. Experimental results of diamond crystallization in solvent–graphite system. The (+) and (–) labeled in the table indicate diamond nucleation and growth established or not in the system, respectively.

Run/N	P/GPa	T/°C	Time/min	Diamond growth on seed (O/M/N)	Size/mm (O/M/N)	Spontaneously nucleated diamond (O/M/N)
R-1	4.6	1340	20	–/–/–	/	–/–/–
R-2	4.6	1350	20	–/+/+	0/0.16/0.13	–/–/+
R-3	4.6	1360	20	–/–/–	/	–/–/–
R-4	4.7	1340	30	–/–/–	/	–/–/–
R-5	4.7	1350	30	–/+/+	0/0.25/0.2	–/+/+
R-6	4.7	1360	30	–/+/+	0/0.2/0.18	–/–/+
R-7	4.8	1350	30	+/+/+	0.2/0.35/0.3	+/+/+
R-8	4.8	1360	30	+/+/+	0.25/0.4/0.35	+/+/+
R-9	4.8	1370	30	–/+/+	0/0.35/0.3	–/+/+
R-10	5.0	1380	5	+/+/+	0.15/0.3/0.2	+/+/+
R-11	5.0	1380	10	+/+/+	0.2/0.4/0.3	+/+/+
R-12	5.0	1380	15	+/+/+	0.3/0.5/0.4	+/+/+
R-13	5.0	1380	30	+/+/+	0.5/0.7/0.6	+/+/+
R-14	5.0	1380	60	+/+/+	0.8/1.0/0.9	+/+/+

Besides the diamond growth on the seed, it is important to note that some small diamonds (Fig. 3(a)) are found on the diamond surfaces in the systems N and M. Furthermore, some spontaneously nucleated diamonds are also found at 4.6 GPa (R-2) and 4.7 GPa in systems N and M (R-5), respectively. It indicates that the spontaneously nucleated diamonds formed easier in system N than in system M, in other words, the smooth surfaces of seeds are more effective to suppress the spontaneous nucleation during the diamond epitaxial growth. Since the employed seeds are black in colour, one can easily distinguish the spontaneously nucleated diamonds from the diamond grown on seeds. Most spontaneously nucleated diamonds exhibit an irregular shape, with a yellow colour and are about 200 μm in size, which looks like a stretched cuboctahedron elongated along certain crystal faces. It is clearly seen from the SEM image (Fig. 3(b)) that diamond morphology is specifically novel and the twinned crystal is usually prominent.

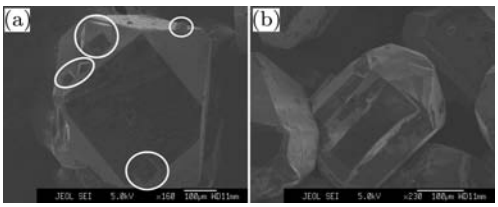


Fig. 3. The SEM images of the spontaneously nucleated diamonds.

At 5.0 GPa, note that the diamond seeds can grow up to 0.3 mm in system M in a 5-min run, while they are up to 0.2 mm only in system N (R-10), indicating the higher growth rate in system M than that in system N at the early growth stage (that is, the crystallization of diamond is easier to establish on seeds with smooth surfaces). With time going on, the growth rates of the diamond in all the systems gradually tend to consistency and no visible discrepancies are found

(runs R-11–R-14). We suggest that it should be due to the self-adjustment process for the rough surfaces of diamond seeds.[21] The continuous and high-quality diamond micro-layers can deposit on the smooth surfaces of the seeds directly, while the rough surfaces of the seeds must go through an adjustment process to obtain some smooth ones, leading to a lower growth rate in system N than in system M. As a result, the excessive diamond nuclei in the system cannot deposit on the diamond roughness surface in time and some spontaneous diamonds are directly formed and grown.

3.2. The correlation between morphology of synthesized diamond and original seed shape

Figure 4 displays the typical optical images of diamond crystals grown on seeds in systems M and N at 5.0 GPa for 30 minutes. The typical diamond grown on seeds S_1 exhibits cubic shape with dominant {100} and minor {111} faces at 1350 °C (Fig. 4(a)) and octahedral shape with dominant {111} and minor {100} faces at 1450 °C (Fig. 4(b)). It is clear that the seeds lie in the centre of the grown diamonds. The new-grown diamond layers generally develop very well, transparent and yellow in colour. Meanwhile, the diamond seeds S_2 are also observed to grow after being treated under HPHT conditions (Figs. 4(c) and 4(d)). However, both the transparency and symmetry of the obtained diamond are worse than those obtained on seeds S_1. And the seed crystals have been deviated from the centre of the obtained diamond because of the non-equivalent growth rate in various directions. The morphology and surface structures of the obtained diamond have been characterized by SEM (Fig. 5). It is clear that the synthesized diamond on seeds S_1 exhibits very perfect morphology (Figs. 5(a) and 5(b)). The surfaces of diamond crystals are smooth and flat, and no observable growth defects are found. The typical diamonds prepared on seeds S_2 exhibit worse symmetry, as shown in Figs. 5(c) and 5(d). The rough surfaces of the original seeds have been smoothed during the moderate growth rates. Some growth striations are found on the diamond surface. However, neither stacking faults on the {100} faces nor twinned planes are detected, which are usually observed at high pressure plasma CVD growth.[32] Additionally, note that the characteristic {100} and {111} faces are dominated, not only following the crystallographic orientations but discounting the original shape of diamond seeds. Thus, we suggest that the use of the rather large seeds for the shape-controlled synthesis of diamond becomes reasonable by the epitaxial growth method under HPHT conditions.

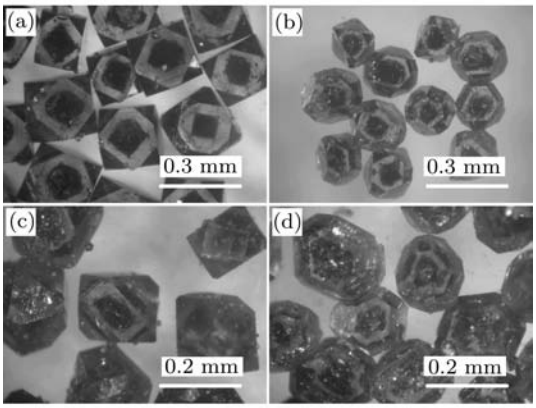


Fig. 4. The optical images of diamond crystals grown on seeds at different temperature conditions: panels (a) and (b) are the diamond crystals grown in system M at 1350 °C and 1450 °C, respectively; panels (c) and (d) show the diamond crystals in system N at 1350 °C and 1450 °C, respectively.

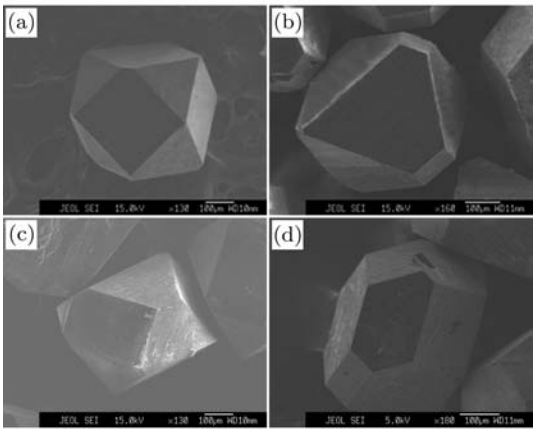


Fig. 5. The SEM images of the diamond crystals grown in system M at 1350 °C (a) and 1450 °C (b), and in system N at 1350 °C (c) and 1450 °C (d).

To further study the correlation between original seed shapes and grown diamond morphology, we prepared some diamond fragments with special shapes as seeds to synthesize diamond. Figure 6(a) shows the optical image of the diamond prepared on the strip fragment. The schematic drawings in the inset images lying at top right corners illustrate the corresponding characterization between the grown diamond and the seed crystal. We can clearly notice that the obtained diamonds also exhibit special strip morphology and the characteristic {100} and {111} faces have been

formed, which elongate along the original shape of the seed crystal (Fig. 6(b)). The diamond morphology is mainly determined by the original seed shape, but the diamonds have an adjustment process to obtain gradual well morphology. The optical image shows the diamond synthesized on some triangular slices in Fig. 6(c). The seed lies in the centre of the diamond and the diamond size only increases from 0.1 mm to 0.16 mm in a 20-min run. Meanwhile, the thickness of the diamond increases up to about 0.1 mm (Fig. 6(d)). This suggests that these diamond seeds grow at a very slow growth rate. In addition, it is important to note that the characteristic {100} and {111} faces are also presented during the later growth process.

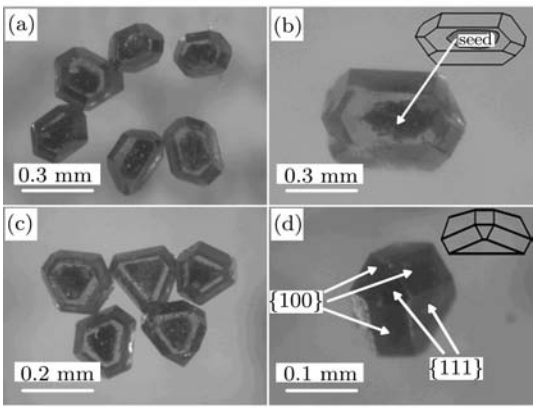


Fig. 6. The optical images of the diamond grown on strip fragments and the triangular slices. We illustrate the schematic drawings of the grown diamond in insets at top right corners of panels (b) and (d) to clarify the correlation between the diamond morphology and shape of the seeds.

3.3. The SEM of the boundary layer between grown diamond and seed crystals

Considering the fact that the boundary layer between grown diamond and the seed crystals plays a key role in fabrication of electronic devices and may give some clues to the diamond growth mechanism at the early growth stage, we thus separate some obtained diamond suitable for examining the growth interface. The SEM images for the interface are shown in Fig. 7. A low-magnification SEM image (Fig. 7(a)) indicates that the diamond seed with smooth surfaces lies in the centre of the diamond and maintains its original shape after treatment under HPHT conditions. The high-magnification SEM image (Fig. 7(b)) clearly shows that the newly grown layers are close to the flat surfaces of seeds and no obvious defects are found. It indicates that the diamond layers are directly deposited on the flat surfaces of seeds, which is suitable for application in the fields of electronic and photonic devices. When seeds have defects on their original surfaces, one can find some boundary layers, as shown in Fig. 7(c). These boundary layers arrange anomalously, on which a great deal of disfigurement appears. However, the grown diamond layers gradually become regular ones layer by layer and parallel to the original surface of the seed. Therefore, diamond morphology is determined by the original surface direction and shape of the seed in the initial growth stage. It is obvious from Fig. 7(d) that some gaps and defects still remain between the seed and the newly grown diamond layers when the diamond grows on seeds with irregular shapes and rough surfaces. The newly grown diamond layers arrange irregularly. Furthermore, a small diamond, just like a spontaneously nucleated diamond 30 μm–40 μm in size, is also found on the surface of the seed. On the basis of the above results, we clarify that one of the most important factors for the fabrication of diamond-based devices using epitaxial growth method is the smooth surfaces of seeds.

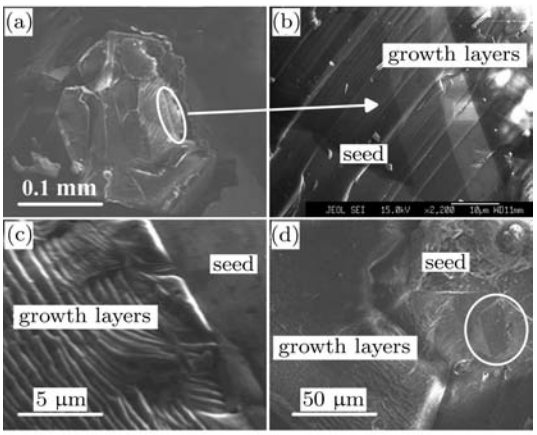


Fig. 7. The SEM micrographs of the interface between the seed and grown layers: panels (a) and (b) are the low- and high-magnification SEM images of the interface grown on the smooth surfaces, respectively; panels (c) and (d) are the SEM images of the interface grown on the diamond seeds with rough surfaces.

3.4. Growth mechanism for the twinned diamond

In order to study the formation of the twinned diamond, the diamond epitaxial growth on several seeds are carried out at 5.4 GPa and 1350 °C–1500 °C. Figure 8(a) demonstrates the typical optical images of the diamond grown on two connected seeds. The two diamond seeds can be considered to be a twin-nucleus.

It is clear that the grown diamond crystal shows nice symmetry and the two seeds maintain their original shapes in the centre of the diamond. The diamond layers deposit on the surfaces of the two seeds and the diamond gradually grows to form a twinned diamond. Figure 8(b) shows another typical growth mode of the twinned diamonds, which separate from each other in the early stage. As the diamonds grow, the space between two diamonds becomes smaller and smaller and then the diamonds would connect with their neighbours to grow into twinning. Note that some surfaces have grown into new integrated facets, and we can conclude that all the facets would ultimately grow into integrated ones. It is noteworthy that {100} and {111} facets of the obtained twinned diamond are formed on the same surface direction as that of the seed crystal.

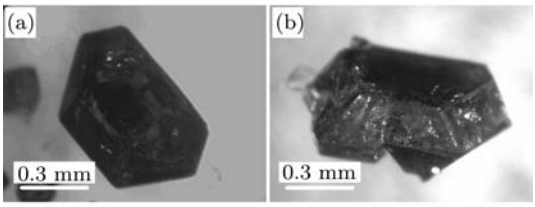


Fig. 8. The typical optical images of the twinned diamond grown on two connected (a) and separated (b) seeds.

Figure 9(a) shows the SEM images of a representative diamond grown on some small diamond seeds at 1450 °C. We can see that the diamond seeds have been gathered together and the obtained diamond is inclined to form a large octahedron. Interestingly, nearly all the original {111} facets of the small diamond seeds arrange regularly in accordance with the grown diamond facets (Fig. 9(b)). It indicates that the diamond seeds have undergone an adjustment process and the seeds arrange regularly to gather together in the early growth stage. Then, a new diamond with octahedral shape is apt to be formed. We describe the formation mechanism for the diamond twinning under higher reaction temperatures in the schematic diagram in Fig. 10, Step I. On the other hand, the obtained diamond grown on the seeds nearly exhibits a typical cub-octahedral morphology at 1350 °C (Fig. 9(c)). Moreover, it is clearly observed from the high-magnification SEM images (Fig. 9(d)) that the original octahedral shape of the employed seeds also has changed into a cub-octahedron shape with obvious {100} faces. This may indicate that a different growth procedure has occurred in the early stage, as given in Fig. 10, Step II. As is well known, the {100} faces are much more stable than {111} faces at low synthetic temperature conditions. Thus, we suggest that the employed seeds grow and some {100} faces have formed in the early stage. Then, a new diamond forms on the seeds with {111} faces and {100} faces arranging regularly. As a result, the obtained diamond exhibits a cub-octahedral shape. In addition, it is interesting to note some veins like dendrites existing on the growing surfaces. This may indicate that the new diamond layers are formed by the expandsion of these veins. Because of the low growth rate, the veins expand slowly and diamond layers cannot be formed quickly. Meanwhile, the sample cell for diamond synthesis is cooled with cycling water from 1450 °C to approximate 200 °C in one minute after experiments. Thus, some veins remain on diamond surface after treatment under HPHT conditions.

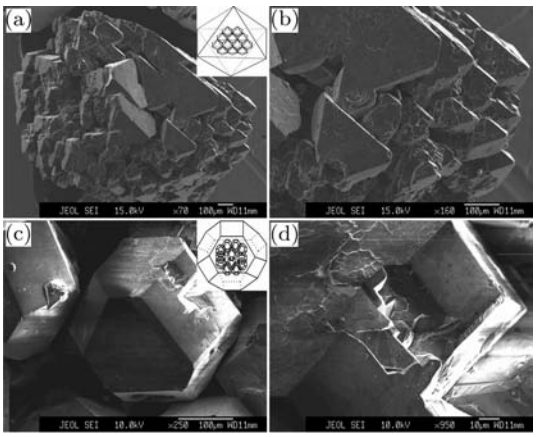


Fig. 9. The SEM images of the representative diamond grown on several seeds at 1450 °C (a), (b) and 1350 °C (c), (d). The right panels are the high-magnification SEM images of the counterparts in the left panels.

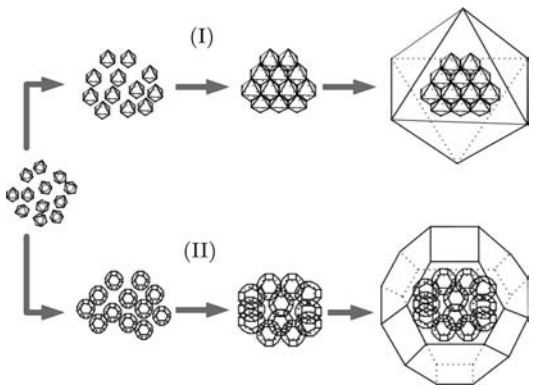


Fig. 10. Schematic drawings (a) and (b) showing the diamond formation process on several diamond seeds at relative high and low temperature conditions, respectively.

4. Conclusion

In this work, we attempt to study the diamond epitaxial growth mechanism employed several types of diamond seeds under HPHT conditions. We find that spontaneously nucleated diamonds formed more easily on the rough surfaces. In addition, the diamond epitaxial growth on two or several seeds has also been established. This work revealed that the shape-controlled synthesis of diamond with well morphology could be realized by employing certain kinds of seeds and it is expected to extend the potential applications of the diamond in the fields of electronic and photonic devices. We suggest that the exploration of diamond epitaxial growth can be helpful for understanding the mechanisms of diamond growth.

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