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Diamond microcrystallites formation through the phase transition graphite→liquid→diamond

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Abstract. The paper presents the results of synthesizing the diamond microparticles (3 to 5 μm) in a spark discharge in hydrogen at the low pressure (100 Torr). The obtained growth rate $\sim 5 \mu\text{m/s}$ is uniquely high. Our analysis of the nature of particles by using SEM and Raman spectroscopy demonstrates that these particles are cubic high quality diamond. Using the result of SIM images after cross-cutting of the sample by FIB, it is concluded that diamond does not grow on the substrate and running process is not CVD. Discussing the theory of the spark discharge, it is suggested that the process occurs at high pressures and temperatures. A hypothesis of diamond formation through a diffusion mechanism of the direct phase transition is presented.

Keywords: diamond microparticle, spark discharge, direct phase transition, threefold point of the phase diagram.

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1. Introduction

Synthesis of diamond has attracted attention ever since it was established in 1797 that diamond is a crystalline form of carbon. From the time of announcement in 1955 of a process for artificial diamond synthesis with a molten transition metal solvent-catalyst at pressure where diamond is the thermodynamically stable phase, the topic of diamond and diamond films (DF) growth and application has been on the top of research activity in the whole world still now. In spite of the fact that many technologies of diamond and DF deposition are developed, structural and physical properties of synthesis products are well studied, the unexpected preparation of fullerenes in 1991 year and then nanotubes, success in deposition of nanodiamonds [1] show that the issues in the field of diamond and diamond like materials have a lot of unknown up to date.

As known, the methods of diamond synthesis at low pressures, where it is metastable, are divided into physical and chemical vapor deposition (CVD) [2]. The physical methods are based on the diamond growth from supersaturating carbon vapor. The CVD methods are characterized by the chain of vapor transport reactions in hydrocarbon or hydrocarbon-hydrogen mixtures. The gas activation is provided by thermal, electrical, chemical, photochemical, or combined methods [3]. Diamond growth takes place through formation of chemical bonds between carbon atoms.

Because in our experiment the diamond synthesis runs by the way characterized as physical (but new physical), it is useful to remind some aspects of the known physical methods. In one of his numerous reviews [4], B.V. Spitsyn mentioned that Brinkman *et al.* was among the first to suggest a diamond growth from carbon vapor obtained by the high temperature graphite sublimation. Carbon transferring from a graphite source occurs in vacuum or gas. Diamond can be grown on a silicon substrate, quartz glass, stainless steel and other materials. However, the best results are obtained when diamond grows on the facet of natural diamond. The growth rate depends on the technology conditions. The growth rate increase is the most actual problem up to now. In Table, there are some examples of diamond film physical deposition from carbon ions of medium energy, which was characterized by the high growth rate and big coated area [4].

In this paper, the diamond microparticles are obtained as a result of d.c. discharge between two graphite rods at low pressure 100 Torr in a chamber. The issues concerning with determination of the growth mechanism type, elucidation of the discharge type, discharge mechanism and characteristics of the pressure and temperature in the area of discharge are discussed.

The diamond particles were characterized using micro-Raman spectroscopy fulfilled on the JASCO spectrometer of NPS-1000 type. In the course of measurements, a laser beam with the wavelength 532.07 nm

Table. Some deposition parameters and basic properties of DF prepared from carbon atoms and ions.

N	Deposition method	Starting substances (sputtering or plasma-forming gas)	Temperature, K	Substrate material	Linear rate, nm/s	Maximum thickness of film, μm	Diameter of substrate, mm
1	Arc in inert gas	Graphite (Ar)	300	Si, stainless steel, glass	5	10	–
2	Arc in inert gas	Graphite	300	Si, Ni, NaCl, KCl	–	0.5	–
3	Double beam	Graphite (Ar)	300	NaCl, quartz glass, hard alloy	–	–	–
4	Double beam	Graphite, diamond (Ar)	453	NaCl, KCl	2×10^{-3}	3×10^{-2}	10
5	Duoplasmatron	Graphite	298-323	Quartz glass, Si, Ni, KCl	0.5	0.1	50

and 1 μm spot size was focused onto the crystallites. The images of diamond particles were obtained using JEOL field-emission scanning electron microscope (SEM). Scanning ion microscopy (SIM) was fulfilled after cross cutting the sample by a focused ion beam (FIB) of gallium. Experimental results were obtained in Department of Environmental and Materials Science, Teikyo University of Science & Technology, Japan.

2. Technology of preparation

Synthesis of diamond particles were performed using the equipment for carbon deposition JEOL, JEE-5B modified with additional pipes to inlet gases to reaction chamber. The experiments were carried out without hydrogen (in vacuum), with hydrogen (100 Torr) and in the mixture Ar/H₂ (100 Torr). The graphite rods were fixed in position end-to-end in special holders. The graphite rods were given by Mitsubishi Pensil CO., LTD. The shape of graphite rods were cylindrical, diameter 3 mm with sharp tip (diameter 1–2 mm). Four shapes of sharp tips were used in all the set of experiments. We used silicon, Al₂O₃ ceramics and non-alkaline glass substrates. Distance between graphite rods and substrate was 5 and 10 mm. The position of substrates was also changed (up-and-down) relatively to graphite rods in various experiments. Before the process, the substrates and graphite rods were ultrasonically treated in liquid acetone.

Approaching d.c. discharge the applied voltage has been increased to 7–8 V for 30 s. Within this time interval, the graphite rods were heated and began to emit. After the moment of discharge appearance, the applied voltage was maintained for 10 s in the first group of experiments and 1 s in the second one. The current reached 25 A. The discharge was accompanied with bright emission and crackling sound. Then the voltage was removed and the process stopped. The temperature in discharge area was observed with two-colored pyrometer (CHINO, IR-AQ and IR-GAG). In the illumination area, the temperature reached 2400 °C. The substrate was heated due to illumination of discharge and rods. The substrate temperature was controlled by a

K-type thermo-couple attached to the back of the substrate and reached 300 °C in its maximum.

As a product of synthesis, the graphite flake, amorphous carbon films and diamond microparticles in quantity 2 to 4 particles per the rectangular 1.5×1.0 cm² were obtained on all the types of substrates.

3. SEM and Raman spectroscopy results

SEM images of obtained diamond particles (Fig. 1) demonstrate that synthesized diamonds obviously have a cubic shape with the upper facets (311) or (711) and

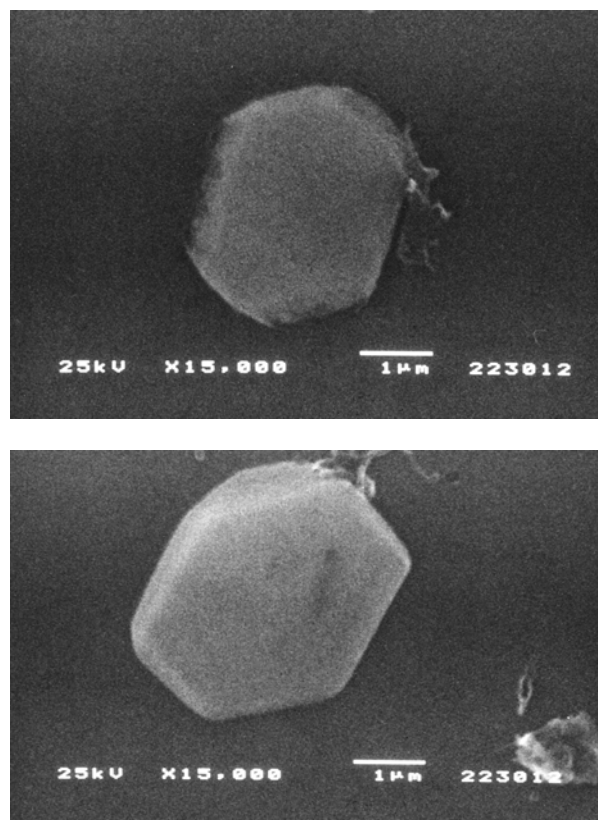


Fig. 1. SEM images of two different diamond particles.

lateral facets (110) or (101). The presented cubic shape is also typical for spontaneous diamond synthesis. This result is in a good correlation with the fact [2] that at high temperature of supersaturating vapor it is observed the plasma-chemical growth of diamond with dominant cube faces. From SEM images, it is seen that diamond particle sizes are 3 to 5 μm . Hence, the obtained growth rate could reach $\sim 3\text{--}5 \mu\text{m/s}$ proceeding from the discharge appearance time 1 s.

The analysis of Raman spectra (Fig. 2) confirms the diamond nature of particles. Spectrum exhibits the first-order diamond peak centered at $1330 - 1332 \text{ cm}^{-1}$. The high intensity of the diamond peak, its small full-width at half-maximum ($5.42\text{--}6.32 \text{ cm}^{-1}$) and small contribution of the graphite phase demonstrate the high quality of the diamond crystal particles. The Raman analyses were also carried out on deposited areas surrounding the diamond crystals: there are graphite flakes in the center of the sample (directly under the place of the graphite tips contact) and then areas that have D and G signals usually characterizing diamond-like carbon films.

4. Discussion of the results

What do the presented results have new and unusual? The first question which is necessary to be answered what synthesis method occurs in this process: plasma-chemical or physical. Initially it was declared [5] that the process of growth was chemical vapor deposition. In usual CVD [4], the hydrocarbon radicals are deposited on the surface of a heated substrate and form the diamond and graphite nucleation centers. Following this fact in our experiments, the chamber was modified specially to inlet hydrogen with the goal to get hydrogen ions that would interact with activated carbon. It should be mentioned that in experiments without hydrogen the

diamond particles were not obtained. Hydrogen inlet promoted diamond synthesis. But the growth rate $3\text{--}5 \mu\text{m/s}$ obtained in our experiments is unique high. Thus, the growth rates for diamond deposited using the chemical vapor deposition method lie within the range 0.1 to $1.4 \mu\text{m/h}$ for the optimal conditions [4].

To elucidate the process of growth, the cross cutting of samples in the place of diamond particle position was carried out by the focused gallium ion beam. The results of SIM (Fig. 3a, b) fulfilled in the place of cutting deny the initial version of CVD as a running process. Both physical and plasma-chemical methods of diamond particle growth at low pressures are based on the fact that nucleation and the following growth occur on the substrate. That is why nature, temperature and treatment of substrate influence on the deposition result very strongly. But in the obtained results (Fig. 3), it is evident that particles do not nucleate on the substrate because

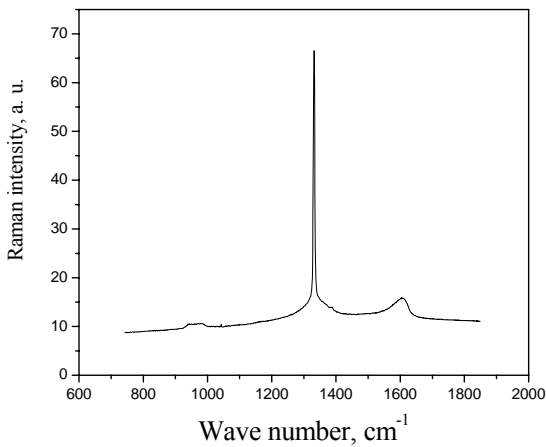
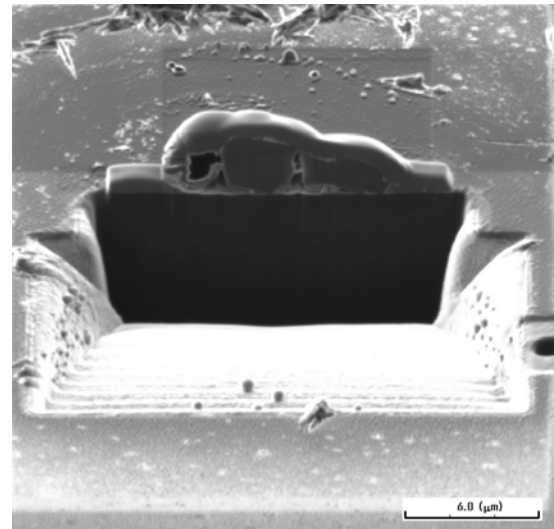
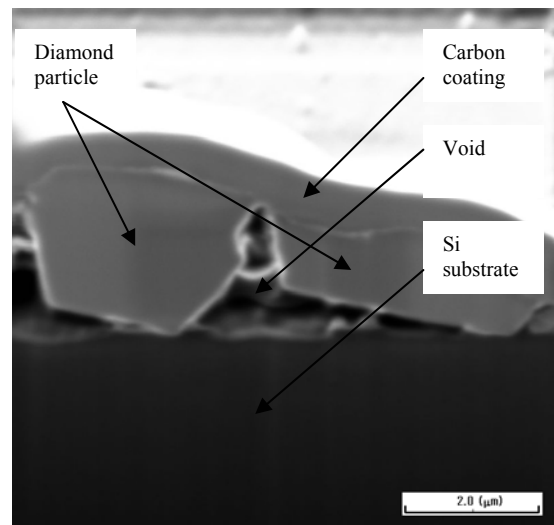


Fig. 2. Micro-Raman spectrum of the crystal, which indicates the peak at 1331.885 cm^{-1} that is characteristic for diamond.



a



b

Fig. 3. SIM images of the cross-section of the substrate with diamond particles under small (a) and bigger (b) magnification.

only corner of particles lies on it. In comparison, the cross cutting of the substrate with diamond deposited by hot filament CVD shows that particle lies on the substrate by a whole face and hence grows on the substrate (Fig. 4). Possibly in our case the diamond particle “drops” on the substrate. So, the running process is not CVD. This conclusion coincide with that reported in [6], where it was put under doubt the plasma-chemical nature of the growth of diamond microparticles that were obtained as a result of a pulse discharge between two sharpened tips (~0.5 mm in diameter) of graphitic electrodes. In the experiment [6], the carbon plasma is formed by an electric pulse discharge (20 – 100 ms) at the huge current (~800 – 1,000 A) and pressure (0.01 – 0.05 Torr). It was detected ~10 to 50 diamond microparticles (10 – 100 μm) per square centimeter [6]. Because these microparticles do not stick to the substrate and are easy removed, it was concluded that they dropped on the substrate. But authors did not explain how and where microparticles form in this case.

The second issue of doubts about plasma-chemical nature of obtained diamond is the extremely high growth rate (~3...5 μm/s) that is higher than that in known publications [7-14]. The only rate 500–100 μm/s calculated in [6] exceeds that of our results.

The additional fact opposing the plasma-chemical process is independence of nature, temperature and position of the substrates, which is in contrast to our results and those of the work [6]. And finally, the arrangement of microparticles is also strange from the viewpoint of CVD. The matter is that microparticles are located not in the area directly under a place of discharge but further (Fig. 5). In the beginning, there are areas like amorphous carbon films, which are formed at temperatures considerably less than the diamond growth

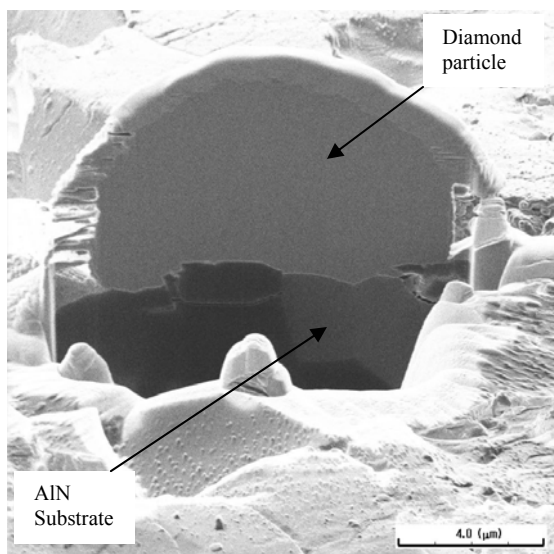


Fig. 4. SIM images of the cross-section of the substrate with CVD diamond particles.

temperature. Then, there are located areas with a small amount of diamond particles (2 to 4 particles per area of $1.5 \times 1.0 \text{ cm}^2$). Hence, from the direction of the temperature gradient, the assumption of diamond growth on the substrate is unreal.

It is possible to conclude that diamond particles in our experiments are formed by some physical mechanism. The known physical mechanism assumes growth from supersaturated carbon vapor on the substrate. In our experiment, supersaturated carbon vapor could be obtained as a result of heating of graphite rods at big direct current running and reaching in its maximum 25 A. However, the particles do not nucleate on the substrate. We assume that diamond particles process formation occurs in the place of contact of graphite tips [15]. The results with different shape of graphite tips prove this idea. Diamond microparticles could not be formed in experiments with cylindrical rods (diameter 3 mm) and were synthesized only in the case of sharpened tips (1-2 mm). Sharpening of the end leads to the electric field strength increase within the discharge range. Hence, the electric characteristics determine the synthesis. That is why, the next question concerns with the process in the discharge place. Because the process is accompanied of crackling that is peculiarity of spark discharge [16], in the beginning the discharge was determined as a spark [5, 15]. However, it is known [16] that the spark discharge appears at relatively high gas pressure what is close to the atmospheric one or higher. In our experiments, the pressure is only 100 Torr. Strong heating of graphite rods at high current resulting in graphite evaporation despite of the fact that graphite is refractory material. As graphite vapor is ionized, ions have weak mobility, so the pressure in discharge place increases and could reach the atmospheric one. Assuming that the process is the spark discharge, the gas temperature in the discharge channel reaches the value of the order of 10,000 °C [16]. Such sharp temperature increase for a short time of spark being generates very strong and instant (exposure type) increase in the gas pressure that leads to characteristic crackling. In this case, the process of diamond formation does not run at low pressure and should be characterized as the process occurring at a high temperature and high pressure. In this

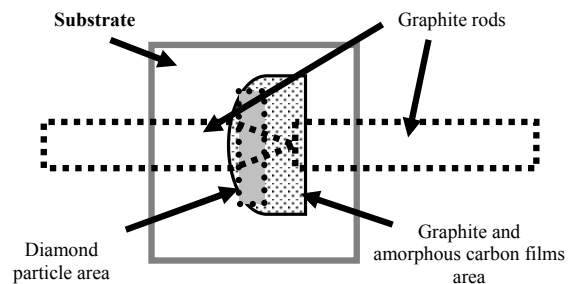


Fig. 5. Alignment of graphite rods, substrate and location of products of synthesis.

situation, it should be taken into account another mechanism of diamond synthesis. That is why, these papers suggest the hypothesis of diamond formation through the mechanism of the direct phase transition of the first order at the high pressure. From the data [17] the phase transition graphite→diamond at shock compression takes place within the pressure range 200 to 400 kbar, the volume effect of transformation composes 18 %. According to our estimating calculation, the temperature at 200 kbar is 470 K, at 400 kbar – 770 K, at 600 kbar – 1300 K [17]. Diamond synthesized under shock compression of pure graphite without special introduction of additives – coolers and not dissipated in cooled matrix has a cubic structure in stored after compression samples. In work [17], it is mentioned the results of Bandy who got transformation graphite→diamond for 6 – 8 s at the temperature 4000 K due to application of pulse heating the pressed graphite samples using a discharge from a powerful condenser battery. For cubic diamond synthesis at the pressure 140 kbar and temperature 3000 K, it was necessary 4 ms. In our experiments, the registered temperature in the discharge area reached 2400 °C, process runs 1 and 10 s, diamond has the cubic structure, which is close to the mentioned above data [17].

The next issue is elucidation of the mechanism of phase transition: martensite or diffusion. It is known [17] that structure of forming phase and degree of crystal perfection depends on the mechanism of the direct phase transition. As to make the X-ray structural analysis of obtained particles is not obviously possible because of their small sizes and difficulties to find them on the substrate with account of their small amount (2 to 4 particles on the sample), so making the conclusion of the mechanism responsible for the phase transition could be done by some indirect way. The transformation observed by us is very fast (~1 s), which is characteristic of the martensite mechanism. But the temperature in our process is high, while the martensite transformation occurs at low temperatures. That is why, most likely the character of the transformation observed in our experiments is diffusion. If we return to SEM images of the obtained particles (Fig. 1), we could see that the diamond single crystal has a “tail”. This tail could be stiffened fused part of melting graphite. The formation of separated single crystals grown in the whisker shape is characteristic for crystals prepared from melt [17] as well as in our case. Moreover, through melting only diffusion growth of a new phase is possible [17]. But if diamond formation goes by the diffusion way from melting graphite, it is possible that we discovered experimental proof of existence of threefold point of transition graphite→liquid→diamond on the known carbon diagram of state [18], theoretically predicted but earlier not observed. It was mentioned [18] that from the Bandy estimation the threefold point graphite→liquid→diamond takes place at the pressure 12 GPa and temperature 4000 K on the carbon diagram of state.

The described mechanism of diamond formation could explain the results of our experiments and those of the work [6]. The difference between our results and [6] includes the size and amount of diamond microparticles. Apparently larger size and bigger amount of microdiamonds in [6] is based on the usage of graphite of very high purity (99.999 %). While in our experiments, we use graphite of the mark P-41 consisting of graphite and amorphous carbon and hence possessing more defects and impurities. The next divergence with the data [6] concerns with hydrogen influence. In the work [6], hydrogen was introduced to the chamber in the latter set of experiments specially to check the hypothesis of plasma-chemical reaction. However, its presence does not influence on the results. Hydrogen changes neither particle size nor their shape. By contrast, in our experiments the diamond particles are obtained only with hydrogen. This fact was the initial reason to support that this process was CVD, because as is known [2] hydrogen availability is the necessary component of diamond plasma-chemical deposition. Apparently, in our process hydrogen acts as a cooling medium for crystallizing diamond particles. Changing of gas in the chamber from pure H₂ to mixture H₂/Ar in relation 2:98 at the total pressure 100 Torr leads to the result that pure cubic diamond is not discovered. It means that the size of gas molecules, their amount and composition has a big importance and influence on the process kinetics.

It should be marked that our conclusion is made on assumption that the discharge is of the spark type. But the discharge mechanism is not completely clear. In the work [19], it is approved that at the distance d between cathode and anode less than 5 cm the atmospheric air is breakdowned by not streamer but Townsend mechanism of duplication of avalanches. In our case, the position of electrode is end-to-end and d is very short. From the abovementioned information, it means that mechanism is not streamer like and hence the discharge is not spark. To elucidate the breakdown mechanism, we should note that one from the tips of graphite electrodes is sharp what creates the increasing of electric field strength. Yu.P. Rayzer writes [19] that due to sharp dependence of the coefficient of electron duplication α on the electric field strength E it is enough to get an overvoltage approximately 10 % for creation of the streamer even in this interval, while at a static voltage the breakdown is Townsend. Competition between mechanisms of avalanche duplication and streamer takes place, and result could be declined in one or another side. For example, the streamer mechanism would be dominant at the overvoltage increase or due to introduction of another additional gas that decreases the coefficient of secondary electron emission, which suppresses the process of avalanche duplication. So, the spark discharge is possible in our case.

If, nevertheless, to start with the fact that the pressure in the place of contact of graphite rods is unknown and the initial pressure is 100 Torr, so from the

determination [19] of the process running at $pd < 1000$ Torr·cm, where p is the pressure and d is the distance between the anode and cathode, the discharge is characterized as the decaying one passing into the process of a current increase up to the arc discharge. In this case, explaining the result of the phase transition graphite→diamond is possible via the process of explosion emission described in the work [19]. At the breakdown of vacuum interval with strong sharpening electrode (cathode or anode) the sharp current increasing after some time leads to explosion of the tip and plasma emission from it. Explosion of electrode materials (graphite in our case) occurs as a result of emission on the tip of plenty joule heat from current of autoelectronic emission and then in the process of heating from the current of thermoautoelectronic emission. The current density from tip surrounded by plasma reaches $10^8 - 10^9$ A/cm². While the electrons take off from the surface, the new electrons come to this place from the bulk of material. I.e., in the graphite near the emitting surface, the current of a huge density proceeds. This current heats graphite till explosion-like evaporation of microledge. It is known [19] that at the currents 15 to 20 A the arch becomes sibilant. At the further increase of the current, the torch of heated vapor goes off from anode spot. The temperature in the anode spot reaches 4200 K. In our experiment, the current increase goes on up to 25 A. Hence, it is possible to assume that the process of evaporation and explosion-like evaporation of graphite take place without the molten phase. But if only the evaporation process is running, the diamond formation is going through the known physical mechanism of growth *on the substrate*. However, the presence of “tail” in Fig. 1 connected with the cubic diamond insists on the version of melt. So, a most likely the breakdown mechanism is streamer and discharge is spark.

5. Conclusion

As a result of the spark discharge between two graphite rods in hydrogen at the low pressure 100 Torr in the chamber, the diamond microparticles 3 to 5 μm are obtained on the silicon, Al₂O₃ ceramics and non-alkaline glass substrates. The reached growth rate 3 to 5 μm/s is very high. Diamond nature of particles is confirmed by the results of SEM and micro-Raman analyses. Cross cutting the diamond particles by FIB demonstrates that synthesis does not occur on the substrate, which denies the known CVD mechanism and physical mechanism of formation at low pressures. The hypothesis of diamond synthesis through direct phase transition of the first order graphite→liquid→diamond via the diffusion mechanism at high temperatures and pressures has been proposed. The high temperatures and pressures are generated by the process in the spark discharge. In this case, hydrogen plays a role of cooling ambient. The obtained results could be experimental proofs of existence of threefold point on the phase diagram of carbon and demonstrates the new way to create diamond microparticles.

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