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New Method for Diamond Film Deposition under Different Gravity Conditions

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Abstract : We synthesized diamond from a graphite source in terrestrial and high gravity experiments. Diamond was deposited on silicon substrates. These deposits were characterized by scanning electron microscopy and Raman spectroscopy. The completely closed reaction chamber, which designed and manufactured at Teikyo University of Science and Technology, is easy to install on a centrifuge. We successfully synthesized diamond at high gravity on a large centrifuge at Clarkson University. Compared with terrestrial experiments, high gravity significantly affected the particle size and coverage. Under our experimental conditions, the crystal growth rate was increased at high gravity. This new reaction chamber is also very suitable for space experiments. Even with the limited volume and electric power available in spacecraft, we can install many of our chambers.

1. INTRODUCTION

Materials processing experiments under high gravity with a centrifugal apparatus have given remarkable results recently[1]. Though it had been thought that buoyancy-driven convection is simply increased with increasing gravity in a centrifuge, it has been found that convection can be stabilized with increasing acceleration and that the quality of grown crystals can be unexpectedly improved[2,3].

On the other hand, under the microgravity environment, it is considered that thermal convection is suppressed. Therefore, diffusion becomes the main factor of material transport. Thus it is expected that one can synthesize materials with fewer defects or unique structures and get new information about the growth mechanism of materials.

Diamond possesses superior properties, for example, high hardness, high thermal conductivity, high transparency, high electron and hole mobilities, and a wide bandgap. These unique properties suggest many potential applications.

We planned to synthesize diamond thin films over a wide gravity range, from microgravity up to high gravity. It is expected that one can synthesize higher quality and well-controlled diamond films which have never been synthesized in the terrestrial gravity environment.

The conventional techniques for depositing diamond at low pressure utilize a flow of a hydrocarbon-hydrogen gas mixture with complicated gas tubing for introducing the reaction gas into a reaction

chamber and evacuating reactant gas from it. Beside that, these techniques require a complicated method for generating atomic hydrogen, such as a plasma, hot tungsten filament, or flame. Therefore, these kinds of flow systems are not considered practical for mounting on a spacecraft or on a centrifuge.

For few years, one author (YT) had been concentrated on developing completely closed diamond synthesizing system aimed for microgravity conditions[4-7]. On the other hand, other two authors (LR and WW) have been developing high gravity experimental apparatus for material synthesis. We started our international joint research project on the summer of 1996. With this project, the chamber developed in Japan was installed the centrifuge developed in US. With our preliminary experiments[8], we successfully confirmed that this closed system was very suitable for mounting on large centrifuges and in spacecraft, and synthesized diamond particles under high gravity environment for the first time in the world.

2. EXPERIMENTAL

In 1960s, in the late-USSR, the experimental results was reported for diamond synthesis with graphite Joule heating method on pure hydrogen gas[9]. On the paper, diamond was synthesized on diamond substrate, and the crystal growth rate was very high. After that, many researchers have been concentrated on so called flow system on diamond synthesis, using reaction gas introduction and reactant gas evacuation. In this study, hydrogen gas was introduced at 30 up to 90 Torr into the reaction chamber, in which a graphite rod was mounted on the center. Then the graphite rod was heated, and diamond particles grew on a nearby Si substrate. (In Table 1, basic properties and manufacturers are listed.)

Table 1. Basic properties and manufacturers of graphite

Basic properties and manufacturer		
Manufacturer	S.N.T.	N.C.
Bulk density	1.80	1.75
Open pore / %	8	20.5
Bending strength / M Pa	49	44
Compressing strength / M Pa	93	23
Electrical resistivity / $\mu\,\Omega$cm	1200	1300
Thermal expansion coefficient /x 10^{-6} K^{-1}	5.0	4.2
Thermal conductivity /W m^{-1} K^{-1}	116	110
Ash content / %	0.05*	0.08**
Maximum particle diameter / mm	0.02	classified

S.N.T. ; Shin-Nikka-Technocarbon
N.C. ; Nihon-Carbon
*typical detected elements ; 1ppm(Si), less than 0.1ppm (Fe, Ca, Al, Cr, Cu, K, Ni) less than 0.05ppm (Na)
**detected and undetected elements are classified

In this method, no source gas is introduced and no reactant gas is evacuated during deposition. For high gravity experiments, we installed the chamber on the centrifuge. Particles grown on the substrates were characterized and identified as diamond with SEM and Raman spectroscopy. Diamond particles grown on high gravity environment were confirmed as few times larger that these on terrestrial experiments.

With this completely closed system, we performed approximately 170 depositions, which included more than 60 experiments at high gravity.

Terrestrial experiments

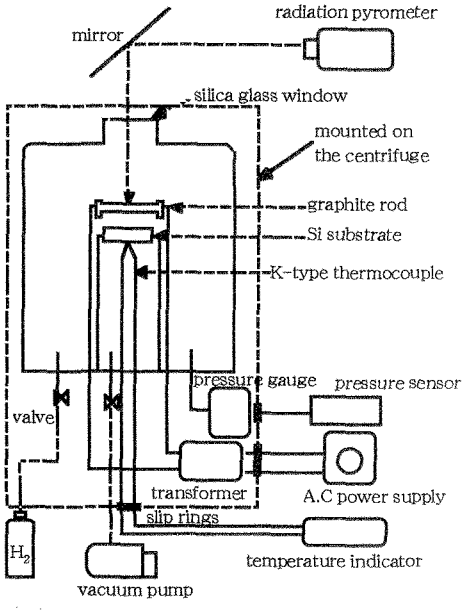
The schematic figure of diamond synthesis apparatus is illustrated in Fig.1. Substrates were mounted 2~4 mm under the graphite rod, and were heated by radiation from the heated graphite rod (1700~1800degC). Besides that, the atomic hydrogen recombination to molecular hydrogen on the substrate surface generate thermal energy[10]. So, in this apparatus, we do not need a substrate heating system in order to synthesize diamond.

Substrate heating

With auxiliary Joule heating of

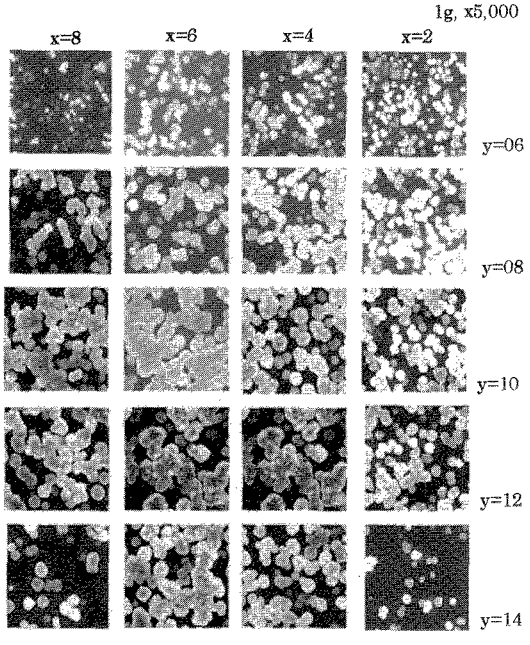
the substrate, synthesized particles on the center of the substrate were not very different, but the area covered by particles

Fig 1. Schematic figure of diamond Synthesis apparatus



was wider. With substrate heating, we can increase the distance between graphite rod and substrate to 4 mm.

Figure 2 ; SEM images of #128 sample



This distance was reported by S. J. Harris et al.[11] as the point of the maxima of calculated and measured methyl radical concentrations from a hot filament.

Substrate setting geometry

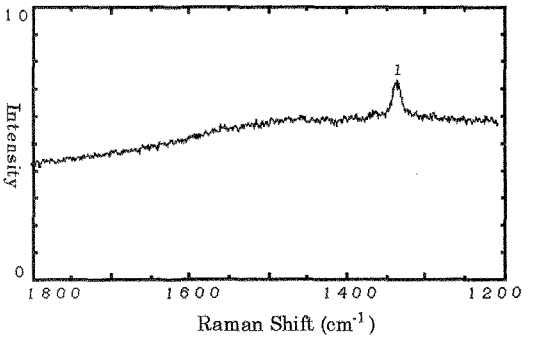
We have two choices to orient the substrate, parallel and perpendicular to the graphite rod. With the parallel geometry, deposits covered a larger area, but there was no big difference at the center of the substrate.

3. RESULTS AND DISCUSSIONS

Particle distribution analysis

Figure 2 shows a scanning electron micrographs of a diamond deposit. For this deposit, four times deposition was accumulated. The deposition times were 40min. each. Hydrogen gas was introduced on 30, 50, 70 and 90 Torr, respectively. The substrate temperature was 740 deg C. The distance between graphite rod and substrate was 2.5mm. Figure 3 shows the Raman spectrum for this deposit. In this

Figure 3; Raman spectrum of #128 sample

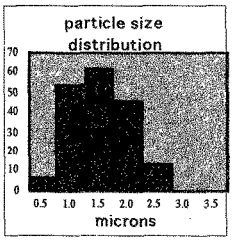


figure, peak notated as 1 was on 1334.0 cm^{-1}, and was confirmed as diamond. In figure 1, 20 photographs are placed with x-coordinates of 2 to 8 mm (from right to left) and y-coordinates of 6 to 14 mm (top to bottom). All photographs were taken as digital image files with the TIF format. With image analysis software (HLImage++97, Western Vision Software U.S.A., Windows 95 version), we could get data for each particles on a photograph, such as x-coordinate, y-coordinate, particle roundness, particle size in x-axis and in y-axis, average radius and so on, and total

area. With these data, we could calculate coverage of area in SEM view which was covered by diamond particles, average radius of all particles, average distance between particles, average separation, and of course count the particle number. For example, four graphs of particle size distribution (x=8, 6, 4 and 2, and y=10) are shown in Figure 4. In this figure,

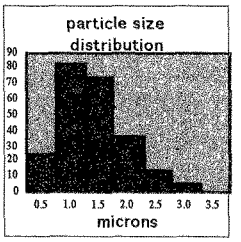
Figure 4; pticle distribution analysis for #128 sample

sample # 128-8-10



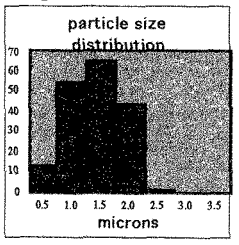
Avg.Radius	0.63
Coverage	58.9%
Avg.Distance	1.56
Avg.Separatn	0.30
particle no.	182

128-6-10 separated



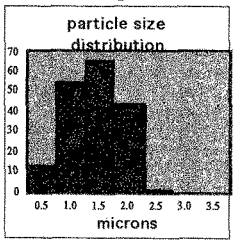
0.57 micron
74.7%
1.26 micron
0.12 micron
234

sample # 128-4-10



Avg.Radius	0.85
Coverage	69.3%
Avg.Distance	1.94
Avg.Separatn	0.24
particle no.	113

128-2-10 separated



0.57 micron
60.0%
1.40 micron
0.26 micron
177

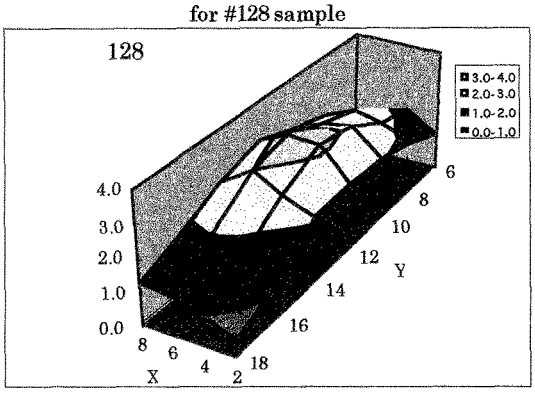
coverage, average radius and other data are listed. Figure 5 shows the overage value distribution for the same deposit.

With these analyses, we can determine the effect of substrate heating, substrate geometry, hydrogen pressure, substrate temperature and so forth.

High gravity experiment

The chamber was mounted on the large centrifuge. Figure 6 shows the typical difference of SEM images between deposits without (top)

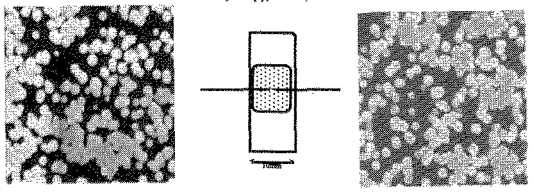
Figure 5; Fraction covered with diamond vs. position for #128 sample



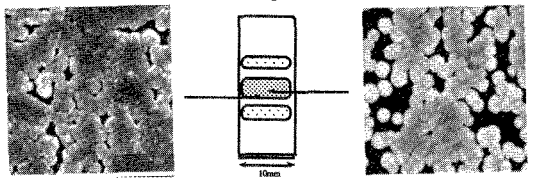
and with (bottom) centrifugation at 2.5g. For these deposits, three times depositions were accumulated. For each deposition, 40min in time, 740 deg C in

Figure 6; SEM images for #110 and #113 sample

#110, 1g, x5,000

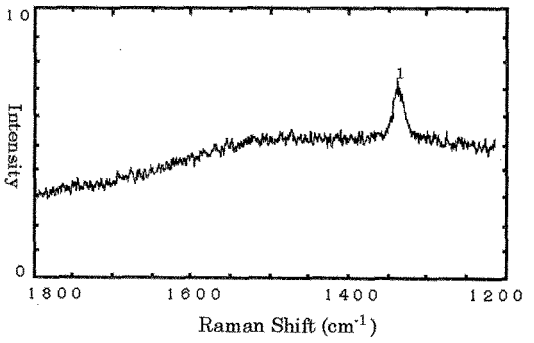


#113, 2.5g, x5,000



substrate temperature, and 2.5mm for distance between graphite rod and substrate. Figure 7 shows the Raman

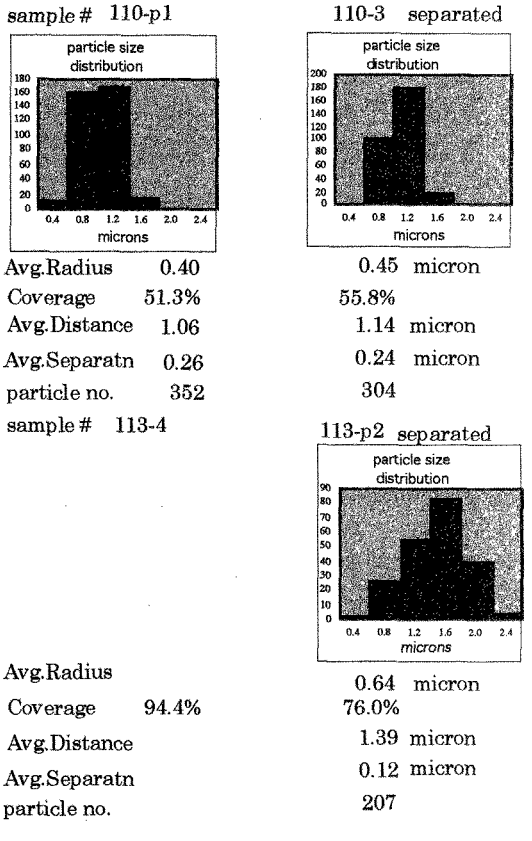
Figure 7; Raman spectrum for #113 sample



spectrum for the deposit at 2.5g

experiment. In this figure, the peak notated as No.1 was on 1337.0cm^{-1}. So, this peak was confirmed as diamond. A similar particle size distribution analysis was performed for some samples for terrestrial and high-g (2.5g) experiments. Figure 8 shows the particle size distribution analysis (same method as shown in figure 4 for figure 6 deposits) for both samples. As shown in figure 6, the SEM photograph of the left bottom, almost all area were covered with diamond particles, so particle size distribution analysis was impossible for this deposit.

Figure 8; particle distribution analysis for #110 and #113 samples



In this particular case, the deposit from high gravity has two to three times larger particles than terrestrial ones, particle coverage was increased.

Appendix

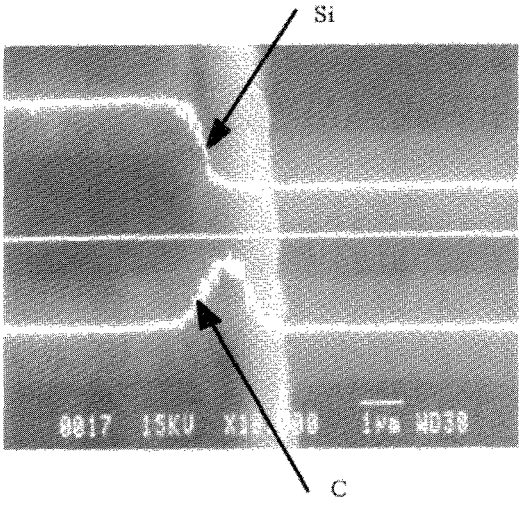
For terrestrial experiment, in Figure 9 shows the cross section of substrate (left) and diamond (center) with SEM, and the line analysis (element analysis) was performed. In this figure, upper line is for silicon, and bottom for carbon. Though the line for Si has sharp edge (arrowed), C has a little bit dull edges on both sides (left and right, arrowed). This might suggest that diamond is not enough grown as complete layer but is still attached particles.

CONCLUSION

Our research for diamond synthesis at high gravity is still in its initial stage.

Though we cannot exactly duplicate the experimental conditions at terrestrial and high-g, we have a clear effect of high gravity on diamond synthesis. Coverage and growth rate were increased. The particle size distribution histograms, Raman spectrometry and other data will be reported on future papers.

Figure 9 ; SEM cross section and element analysis



Diamond synthesis with a completely closed system as reported here might be a very suitable apparatus for space experiments. We will try to synthesize diamond in space with this simple apparatus in the future.

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