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Diamond Synthesis by a Graphite Rod Heating under Normal and High Gravity Environment

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Abstract

The authors already conducted a series of diamond thin film synthesis under high gravity with a centrifugal facility with DC-plasma CVD method. In present paper, the results of high gravity experiments with graphite rod heating will be reported. The effect of high gravity was confirmed by 1 G ~ 50 G experiments. On the bases of the experimental results of 1 G ~ 50 G experiments, 70 G experiments were performed. With 70 G experiments, diamond particles with (100) and (111) surfaces were observed. And the maximum particle size was 5 microns in diameter. In present study, high gravity effects for diamond synthesis were confirmed and reported.

1. Introduction

In DC-plasma CVD diamond synthesis, gaseous species on the reaction chamber were detected and analyzed with OES (optical emission spectroscopy), under terrestrial and high gravity environment.[1)] And we expected that synthesized diamond particles might have some different morphology comparing with terrestrial conditions.

Early experiments showed the actual possibility of growing diamond thin films by using a DC-plasma CVD source. Subsequently, a number of enhancements and features were experimentally recognized in the high gravity CVD process, namely;

- increase in the nucleation site density;
- increase in the deposition rate;
- increase in the particle size;
- change in the crystal morphology from (111) facet diamond to (100) facet dominant;
- improved uniformity. [2)]

From the results of diamond synthesis under high gravity using graphite rod for carbon source, authors have designated that the combination of closed system and graphite rod Joule heating are suitable experimental methodology under high gravity experiments.[3)] To understand the effect of gravity on diamond synthesis in CVD with the graphite rod heating method, a series of high gravity experiments have been conducted. The present paper reports the results the authors have obtained from 1G up to 70G in a centrifugal apparatus.

2. Graphite rod Joule heating

Graphite rods were used as a solid carbon source and heater for activation of hydrogen gas to hydrogen radicals.[4)] Silicon (100) wafers were used as substrate. Hydrogen gas was introduced into the reaction chamber at the suitable initial pressure, 80 Torr. A graphite rod was heated with Joule heating. Substrate temperature was measured with R-type thermocouple attached to the substrate.

Temperature of the graphite heater was measured with the two-color pyrometer through a silica glass window on the wall of the chamber. The substrate temperature was 780 degree C, and the graphite rod temperature was 2200 degree C, respectively. **Figure 1** shows a photograph of substrate and graphite rod.

3. Model for cyclic hydrogen reaction

The model was based on the gas chromatographic analysis, wherein CH_4, C_2H_2, C_2H_4, C_2H_6 species were detected while diamond synthesis was going-on.[4)] We thought that present experimental results have revealed the reaction mechanisms on the diamond synthesis for the closed system as follows.

Initially installed in the chamber were pure hydrogen gas and solid carbon only. When the graphite rod was heated up,

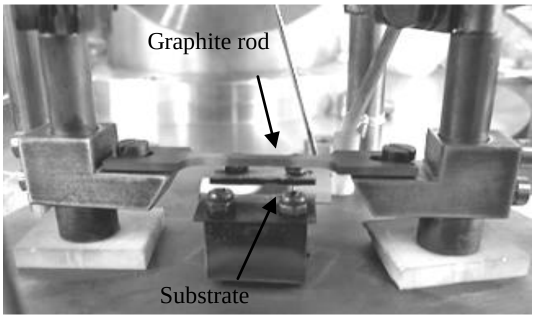

Fig.1 A photograph of substrate and graphite rod

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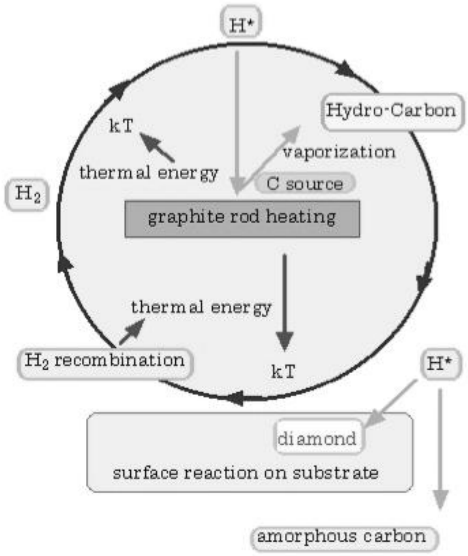

Fig.2 Model for cyclic hydrogen reaction

hydrogen molecules were activated to H radicals. Then H radicals reacted with carbon to generate hydrocarbon, typically methane. On the substrate, hydrocarbon generated amorphous carbon and diamond at same time. And hydrogen radicals composed amorphous carbon selectively and recomposed to hydrogen molecules again. In this way, the completely closed system works without hydrogen consumption. **Figure 2** shows our reaction model with schematic drawing. [4)]

4. High gravity facility

Figure 3 gives the overall view of the high gravity centrifuge facility developed in the present study. This facility is installed in a 1.45 m deep pit in a laboratory floor. The total length is 4.22 m and the main part in this facility. This drum, made of 304 stainless steel, has 1.06 m inner diameter and 0.97 m length. Although the fluctuation of the acceleration vector in the chamber at a relatively low rotation speed, due to the gravitational acceleration, is rather appreciable compared to those ordinary high gravity facilities with a rotating arm and a hinged process chamber, this geometrical structure was selected after the following considerations:

(1) high gravity conditions 10 – 100 G should be necessary to confirm the gravitational effects;
(2) relatively small rotation diameter was preferred to establish a substantial gravity gradient in the chamber, if required; and
(3) the facility should be easily scaled up for practical purposes in the future.

The maximum design rotation speed of this facility is

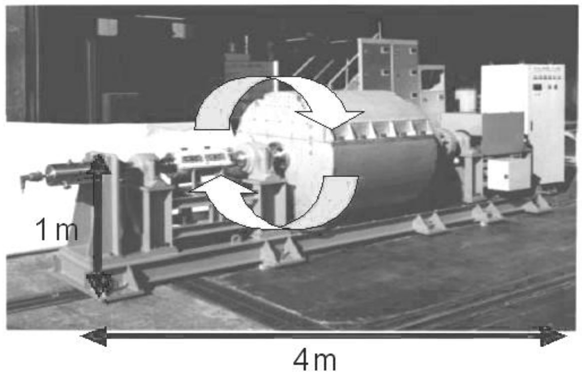

Fig.3 High gravity centrifugal facility

limited up to 550 rpm, but 100 G at the substrate position was attained at 495 rpm in the present CVD apparatus. The rotational balance was adjusted with putting pieces of counterweight on proper positions of the drum surface so that centrifuge drum can be held at an arbitrary position. If the rotational balance is adjusted more precisely, a higher maximum rotational speed of up to 750 rpm will be attainable.

As for power supply to the chamber, three independent electric power lines are available in the centrifugal drum through slip rings. The capability of the slip rings is 50 V/100 A, 100 V/20 A, and 1000 V/1 A line was employed.

All the experimental data in the centrifuge drum are transmitted to a data acquisition system through another slop ring which allows 12 pairs of data transmission including four special leads for R-type thermocouples.

The CVD chamber installed in the centrifuge drum is evacuated via 1/2 inches evacuation line, and an additional four 1/4 inches lines are available for gas supply. A magnetic fluid seal connects these lines in the centrifuge drum with evacuation and gas supply system outside the drum. The magnetic fluid seal is cooled by a copper jacket in which cooling water is circulated so that the outgas from the warmed magnetic fluids in the seal due to high speed rotation can be prevented.

Although no cooling procedure was require in the present study, cooling water can also be introduced at one end of the facility and flows out from the other end, and employed for the connection. All these cables and pipes run in the 143 mm diameter rotation shaft.

The rotation of the centrifugal drum is operated by a 75 kW motor and a rubber belt, and the rotational speed is controlled by a programmable inverter.[5)]

5. High gravity experiments

After the chamber was evacuated, a pure hydrogen gas was introduced into the chamber. After all procedures were completed, the rotation of the drum started. These experiments yielded the substrate temperature around 780 degree C. The experimental conditions were as follows:

In the previous experiments, the substrate temperature did problem, we adjusted the distance between substrate and not rise enough as planned temperature. To solve this the graphite rod from 6.0 mm to 4.5 mm so that the substrate temperature could be maintained at the same temperature, 780 degree C, in all the gravity conditions from 1 G to 70 G. To keep substrate temperature, 780 degree C, we controlled electric energy.

Diamond was considered to be synthesized with surface reaction on the substrate. And substrate temperature is the most important factor for diamond synthesis. To compare results, we should control substrate temperature. **Table 1**, **Table 2** and **Table 3** show experimental conditions.

Table 1 Experimental conditions for 1, 10, 25, 50G experiments

Gravity / G	1	10	25	50
Substrate	Si			
Distance; substrate-graphite rod / mm	5.5			
Reaction time / min	40			
Pressure (H_2) / Torr	80			
Planned substrate temperature / degree C	780			
Measured substrate temperature / degree C	784	780	780	779

Table 2 Experimental conditions for 50 G experiments

Gravity / G	50			
Substrate	Si			
Distance; substrate-graphite rod / mm	6.0	5.5	5.0	4.5
Reaction time / min	40			
Pressure (H_2) / Torr	80			
Planned substrate temperature / degree C	780			
Measured substrate temperature / degree C	776	779	778	763

Table 3 Experimental conditions for 70 G experiment

Gravity / G	70
Substrate	Si
Distance; substrate-graphite rod / mm	4.5
Reaction time / min	40
Pressure (H_2) / Torr	80
Planned substrate temperature / degree C	780
Measured substrate temperature / degree C	779

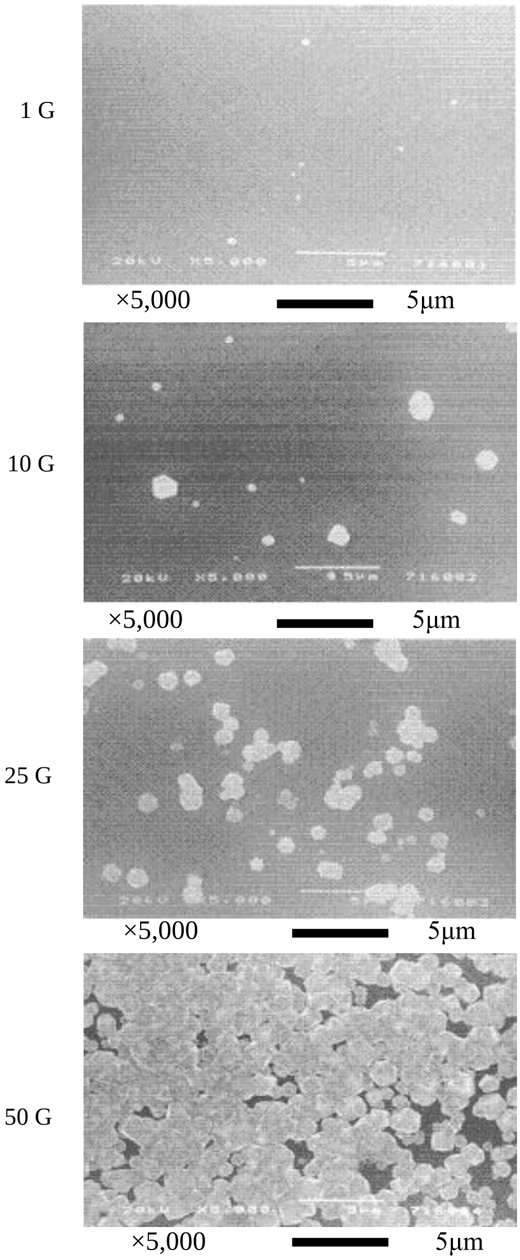

Fig.4 SEM micrographs for 1, 10, 25, 50 G experiments

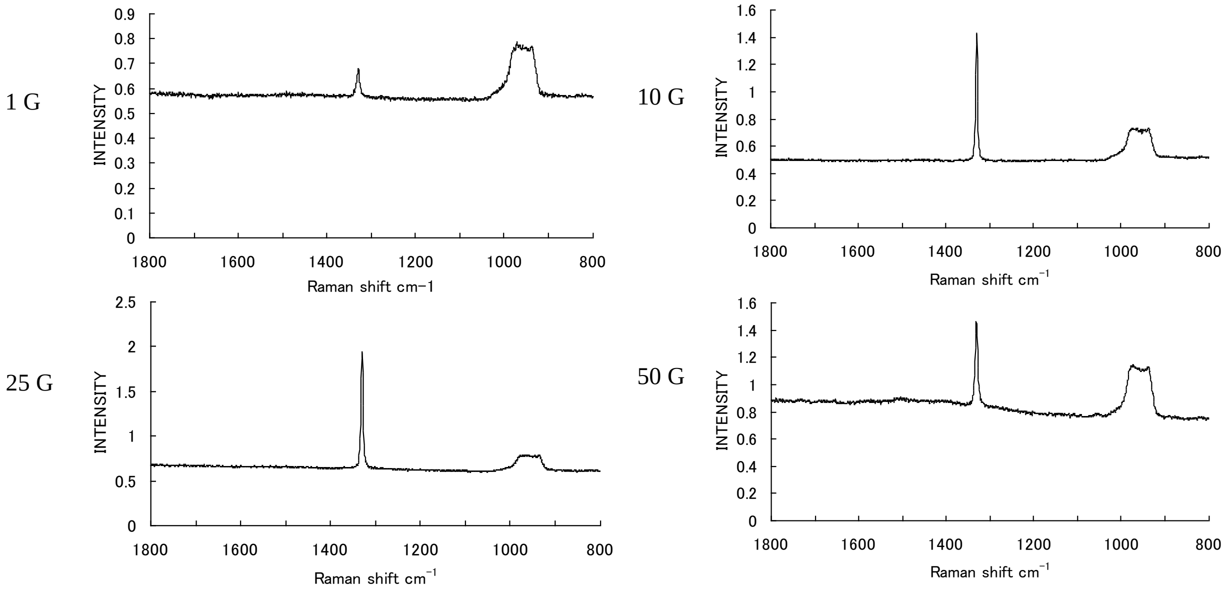

Fig.5 Raman spectra for 1, 10, 25, 50 G experiments

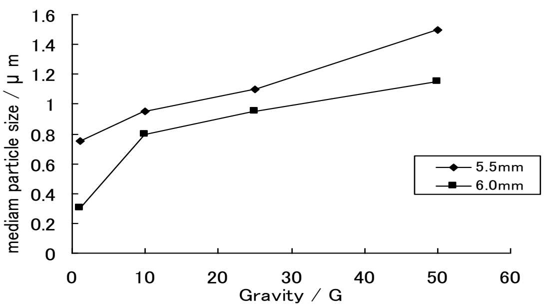

Fig.6 Particle size vs. gravity

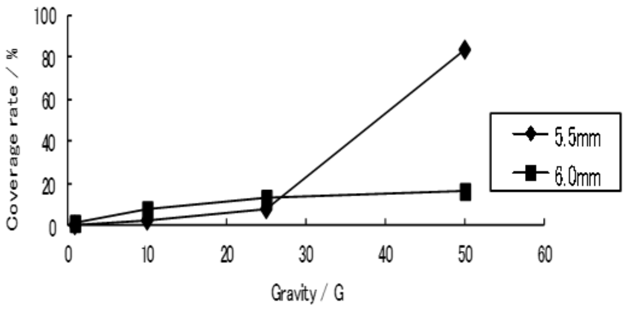

Fig.7 Coverage rate vs. gravity

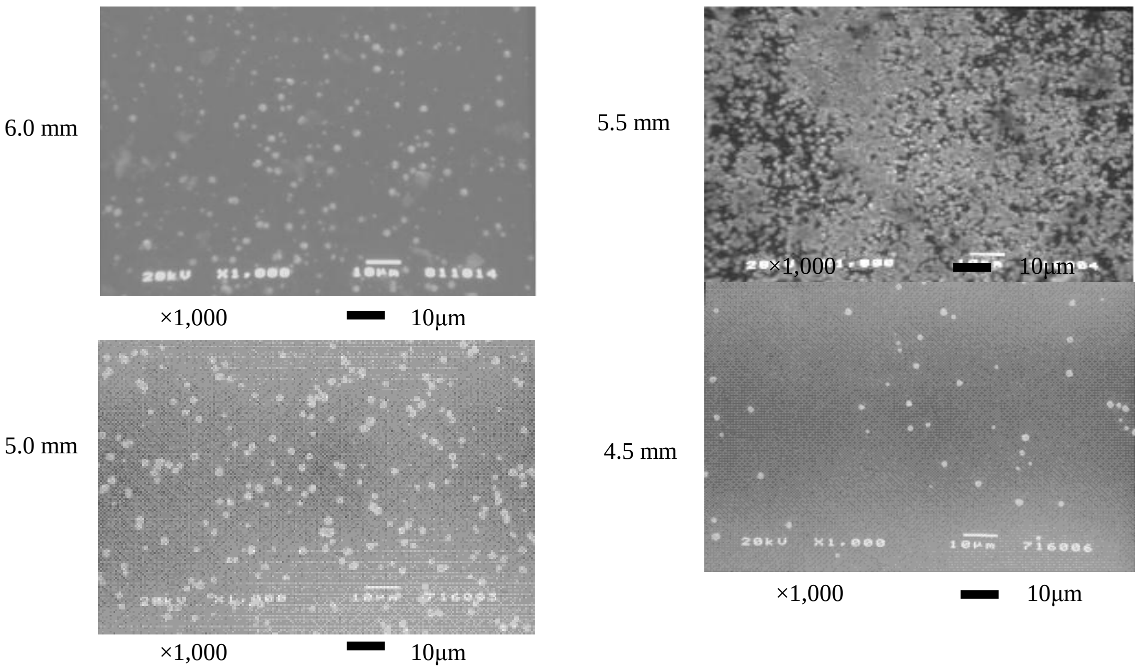

Fig.8 SEM micrographs for 50 G experiments

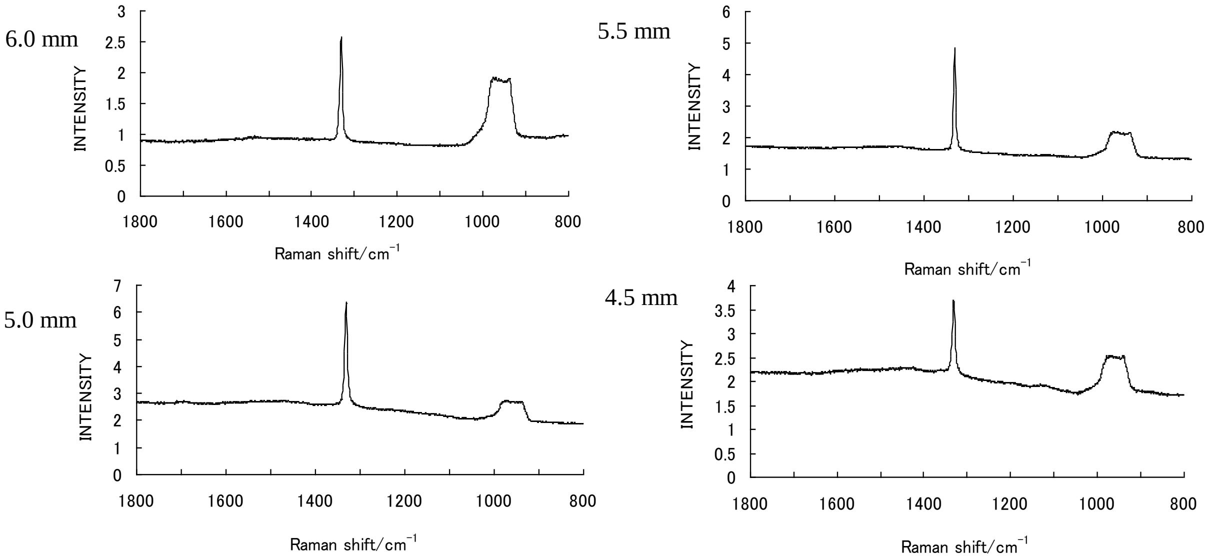

Fig.9 Raman sprctra for 50 G experiments

6. Results and Discussion

On Raman spectra, the strong peaks on 1333 cm^{-1} were assigned to diamond crystal structure. Broad peaks on 900-1000 cm^{-1} were come from Si substrates. Graphite peaks, G-band on 1580 cm^{-1} and D-band on 1355 cm^{-1}, were rarely observed on **Fig.9**.

Figure 4 shows SEM photographs of synthesized particles on the center of the substrate for 1 G ~ 50 G experiments. The increments of particle sizes and coverage rate with increasing gravity were confirmed. **Figure 5** shows Raman spectra for 1 G ~ 50 G experiments. In 1 G experiment, the peak on 1333 cm^{-1} was very weak. It signified that the particle was very small in this case. Fig. 6 and Fig. 7 show graphs of particle size vs. gravity and coverage rate vs. gravity, respectively. With increasing gravity, particle sizes and coverage rates are increasing.

When we fixed the maximum gravity of 50 G in our experiments, it was observed in **Fig. 8** that particle sizes were almost the same, approximately 1 micron, even under the different distances between the graphite rod and the substrate. However, the highest coverage rate was found with the experiment of distance 5.5 mm experiment. To keep the substrate temperature as at 780 degree C, while the distance between substrate and graphite rod increase from 4.5 to 6.0 mm, graphite rod temperature must be increase. Thermal convection, express by Grashof number,

$Gr = L^3 \beta g(T_1 - T_0) / \nu^2$, is proportional to temperature difference $(T_1 - T_0)$. L stands for typical size for the calculation, β for thermal expansion coefficient, g for gravity, ν for kinematic viscosity. When graphite rod temperature, here as T_1 , was increased and kept same substrate temperature, here as T_0 , in Grashof equation, thermal convection was induced. If increment of coverage rate was the effect of thermal convection, the maximum coverage rate must be confirmed on the experiment of distance 6.0 mm experiment. But the maximum coverage rate was found on the experiment of distance 5.5 mm. So, the increment of coverage rate might be not only the effect of thermal convection but also other factor, such as the concentrations of hydro-carbon and/or hydrogen radicals on the surface of the substrate. **Figure 10** shows SEM photograph for 70 G experiment. Diamond particles with (100) and (111) surface were observed. The maximum particle size was 5 microns with 70 G experiment. **Figure 11** shows Raman spectrum for 70 G experiments. Characteristic diamond peak, 1333cm^{-1} was confirmed.

With SEM photographs and Raman spectra, diamond synthesis was confirmed in all experiments. And we found increment of particle size and coverage rate with increasing gravity.

We couldn't measure graphite rod temperature because of indicator's fault. Since the graphite rod temperature could not be monitored in high gravity conditions, real graphite rod temperatures were unknown throughout all the high gravity experiments. In the meanwhile, electric power imposed to the graphite rod was increased nearly up to the limit of apparatus in the highest gravity condition to maintain the desired substrate temperature in all the gravity conditions. If the graphite temperature could be maintained at a constant temperature in all the gravity conditions, the

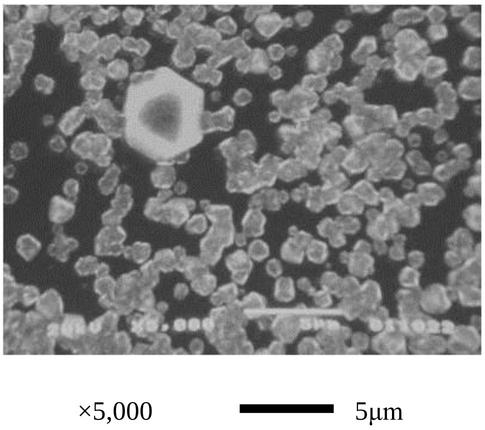

Fig.10 SEM micrograph for 70 G experiments

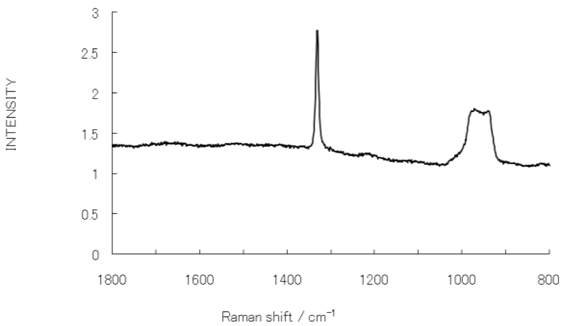

Fig.11 Raman spectrum for 70 G experiments

effect for gravity would be more clearly discussed. To this end, the installation of an auxiliary heater for the substrate, as reported in [6], will be one of the solutions.

7. Conclusions

With the present experiments, the particle sizes and coverage rates were increased with gravity increment.

The effect of high gravity obtained in the DC-plasma method[2] was confirmed again in the present graphite rod Joule heating method.

With the present graphite rod Joule heating and the DC-plasma method, the effect of high gravity was confirmed. In near future, if we could perform experiments with various experimental conditions, we can obtain clearer effects of high gravity.

Reference

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