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Development of Large Diamond Synthesis by Double Test Tubes Hot Filament Chemical Vapor Deposition

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Abstract*—In this research, "diamond" synthesis device by double test tubes hot filament chemical vapor deposition (HFCVD) was developed and proposed. Remaining hydrogen was reused for the maximum utilization of resources. In addition, this diamond synthesis device is capable to synthesis diamond continuously of up to 60 h per time. As a result, large diamond as large as 1.85 mm and 1.73 mm can be produced from the synthesis of three times with 180 h in total. Moreover, after each synthesis, the quality of diamond crystal was improved by annealing in hydrogen atmosphere. The crystal size was measured and physical characteristics of diamond were analyzed using scanning electron microscopy (SEM). The increasing rate of diamond crystal size after each synthesis was also examined. In addition, electrical properties of the synthetic diamond was compared with natural diamond from room temperature (25°C) to 200°C. The synthetic diamond has the resistance of 1337.28 MΩ, which the natural diamond has the resistance of 1428.67 MΩ. Temperature changes has no effect on the resistance of the diamond crystal. Moreover, the synthetic diamond was confirmed to be diamond using Raman spectroscopy. It has the same peak as the natural diamond at the Raman shift of 1332 cm^{-1}.

***Index Terms*—Double test tubes HFCVD, Large Diamond**

I. Introduction

THE synthesis of diamond by hot filament chemical vapor deposition (HFCVD) is another synthesis method with low cost and high safety. Nevertheless, to obtain large diamond crystal, long continuous synthesis period is required and hence lots of hydrogen is needed. Hydrogen after synthesis is vented without reuse.

Therefore, this research reused the hydrogen after synthesis by building another diamond synthesis device. As a result, numbers of diamond can be synthesized from each experiment using the same amount of hydrogen, which is 10 ml/min. In addition, the size and quality of the synthetic diamond was analyzed. The synthetic diamond is as large as 1.85 mm and 1.73 mm from the total synthesis period of 180 h. Moreover, to confirm that the synthetic diamond is diamond and is the same as natural diamond, Raman spectroscopy was applied, which the peak of Raman shift at 1332 cm^{-1} was observed.

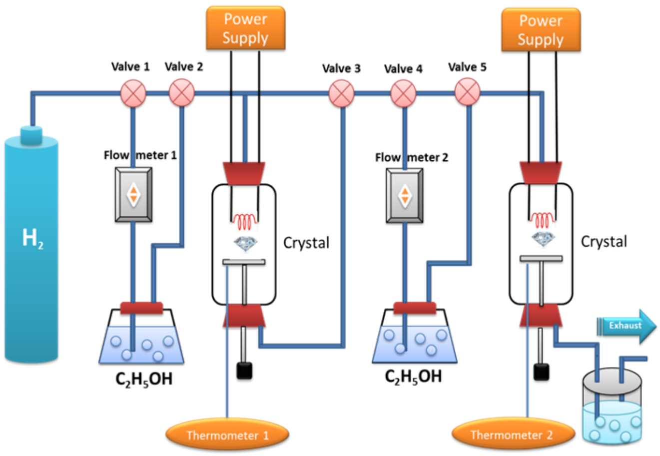

Fig. 1. Diamond synthesis system by double test tubes HFCVD.

In general, to obtain large synthetic diamond, long synthesis time is required. Moreover, graphite is always found in diamond crystal. Therefore, it is a must to improve the quality of diamond crystal through annealing method in hydrogen atmosphere with appropriate control of annealing duration and temperature.

Surface morphology of the synthetic diamond was analyzed using scanning electron microscopy (SEM). The synthetic diamond was confirmed its perfect diamond characteristics using Raman spectroscopy, which Raman shift at 1332 cm^{-1} shall be observed. Electrical properties of the synthetic diamond compares to the natural diamond can be specified through the relationship between current and voltage.

II. Methodology

The synthesis of diamond was conducted using hot filament chemical vapor deposition (HFCVD)[1] method. Hydrogen was applied as carrier gas to transport ethyl alcohol (C_2H_5OH) into the system at the flow rate of 10 ml/min. Ethyl alcohol was decomposed using a heating coil at the temperature of 2000°C. The reaction is as written in

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(1). After that, carbon atoms will be deposited on the silicon base, which its temperature was controlled at approximately 900°C, for 60, 120 and 180 h, sequentially.

$$C_2H_5OH \xrightarrow[2000^{\circ}C]{\triangle} 2C + H_2O + 2H_2 \qquad (1)$$

In addition, each synthesis of diamond, the synthetic diamonds were annealed in hydrogen atmosphere for 9 min at 900°C to improve the quality of the synthetic diamond. After that, characteristics of the annealed diamond crystals were analyzed using SEM before continue the synthesis to 120 and 180 h, sequentially. Moreover, to confirm that the synthetic diamonds are diamond, Raman spectroscopy was applied and compared peaks with the natural diamond, which the Raman spectrum is as shown in Table I below.

After that, current and voltage of the synthetic diamond at 180 h, which their sizes are 1.85 mm and 1.73 mm, were measured to compare the resistance with the natural diamond. Two silver electrodes were connected, then bias voltage from 3 to 15 V to measure electrical properties of the diamond crystal. The temperature was also varied from 25 to 200°C[3]. The test circuit is as shown in Fig. 2.

TABLE I
ANALYSIS OF CARBON TYPE USING RAMA SPECTROSCOPY [2]

Peak position(cm^{-1})	Type of carbon	Description
~1140	Small size(<0.1 µm) cubic diamond	Occasionally observed in diamond films with very small grain size (<0.1 µm).
1315-1326	Hexagonaldiamond	Broad band, observed in shock wave produced diamond.
1332	Cubicdiamond	First order peak with FWHM of $19cm^{-1}$for natural diamond.
1345	Amorphous carbon	Broad band, it becomes a shoulder of the 1550 cm^{-1}band when the material is hydrogenated.
1355	Microcrystalline graphite	Observed in material with small grain size.
1550	Amorphous or diamond-like carbon	Broad band.
1580	Graphite	First order peak.
2458	Cubic diamond	Second order peak.
2710	Microcrystalline graphite	Second order peak.
3240	Graphite	Second order peak.

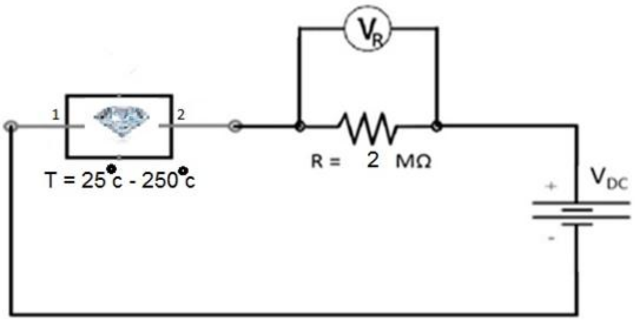

Fig. 2. Circuit to find relationship between current and voltage of diamond crystal.

Voltage and current flew through the diamond crystal was recorded to find the resistance of the diamond crystal as written in (2) and (3), respectively.

$$V_{(Diamond)} = V_{DC} - V_R \qquad (2)$$

$$I_{(Diamond)} = V_R / R \qquad (3)$$

Values of current and voltage will be plotted to find the relationship between current and voltage. The resistance of the diamond crystal is equal to the inversed of the slope of the graph.

III. RESULTS AND DISCUSSION

From the synthesis of diamond crystal for 60 h by HFCVD method on silicon base at 900°C and annealing of the diamond crystal in hydrogen atmosphere for 9 min to improve the quality of the diamond crystal, it was found that carbon was formed continuously into a crystal and it is large in size. Surface morphology of synthetic diamonds analyzed by SEM are as illustrate in Fig. 3A and 3B. The confirmation that the synthetic diamonds are diamond was confirmed using Raman as shown in Fig. 4A and 4B.

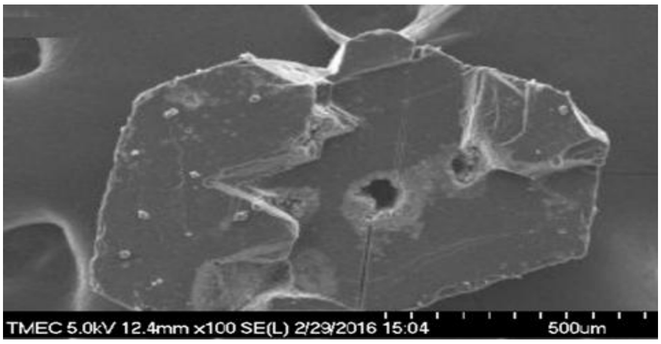

Fig. 3A. 0.96 mm diamond crystal.

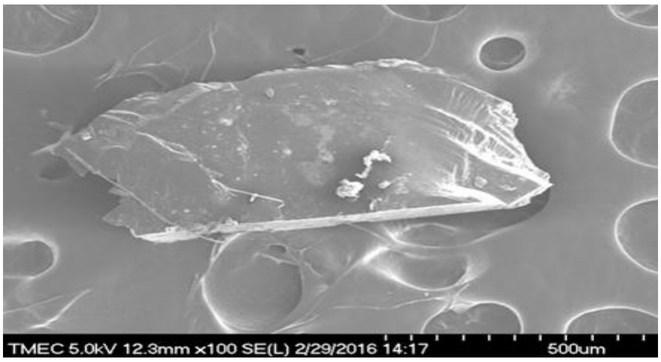

Fig. 3B. 0.89 mm diamond crystal.

According to Fig. 3A and 3B, which illustrates the surface morphology of the synthetic diamond from SEM, it is clear that the synthetic diamond is in crystal form with the size of 0.96 and 0.89 mm, respectively.

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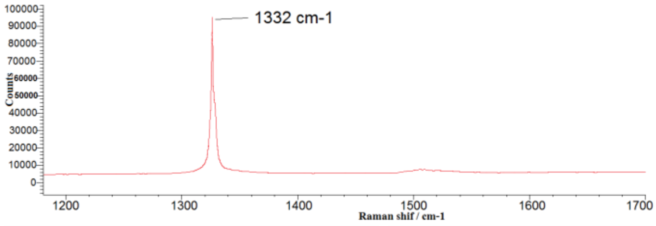

Fig. 4A. Raman spectrum of 0.96 mm diamond crystal.

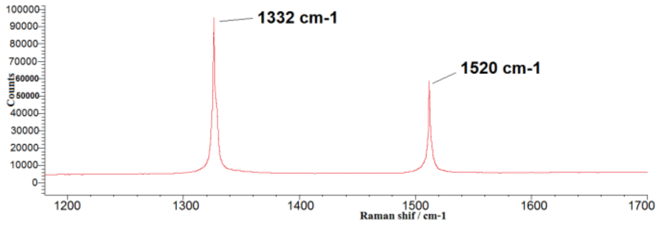

Fig. 4B. Raman spectrum of 0.89 mm diamond crystal.

Figure 4A and 4B show Raman spectrum from Raman spectroscopy. Single peak of Raman shift at 1332 cm^{-1} was observed as illustrate in Fig. 4A. When compare the peak with Raman spectrum table, it indicated that it is absolutely "diamond". However, in Fig. 4B, Raman shift at 1332 cm^{-1} is also observed but there is also the other peak at the Raman shift of 1580 cm^{-1}. When the Raman shift was compare with Raman spectrum in Table I, Raman shift of 1580 cm^{-1} is graphite. Therefore, this diamond crystal is not absolutely diamond. However, after each synthesis, there was crystal quality improvement by annealing and hence the annealing duration was increased from 9 min to 12 min.

After that, the synthetic diamonds were synthesized for another 60 h, which the total synthesis time is 120 h, and annealed in hydrogen atmosphere for 12 min. The crystal of the synthetic diamonds are as shown in Fig. 5A and 5B.

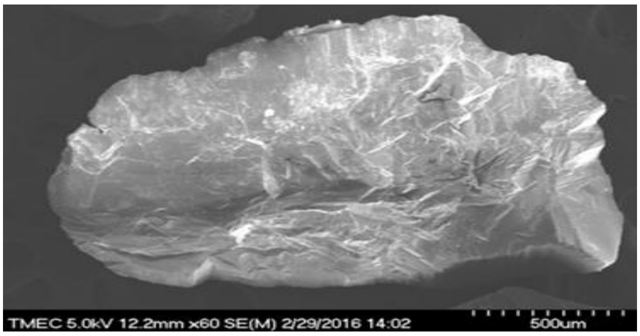

Figure 5A 1.45 mm diamond crystal.

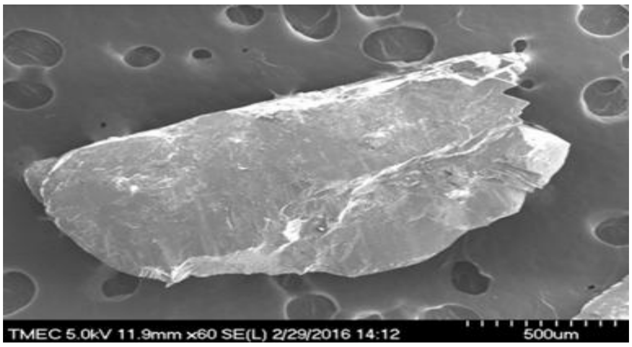

Fig. 5B. 1.36 mm diamond crystal.

Moreover, the synthetic diamonds were found to be perfect diamond as the single Raman shift at 1332 cm^{-1} was observed for both synthetic diamonds as illustrates in Fig. 6A and 6B.

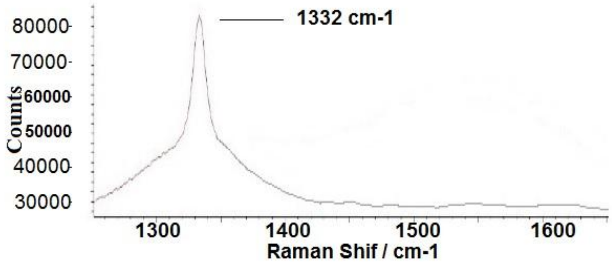

Fig. 6A. Raman spectrum of 1.45 mm diamond crystal.

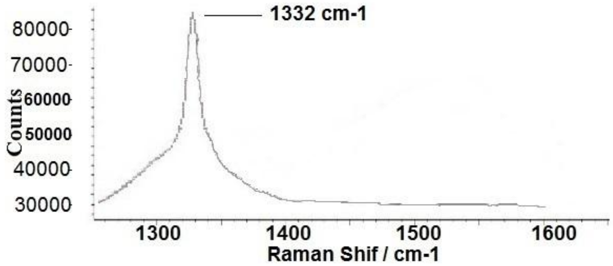

Fig. 6B. Raman spectrum of 1.36 mm diamond crystal.

This indicated that the synthetic diamonds are extremely perfect. Therefore, the synthetic diamonds were synthetized for another 60 h, which the total synthesis time is 180 h. Surface morphology of both synthetic diamonds from SEM are as shown in Fig. 7A and 7B.

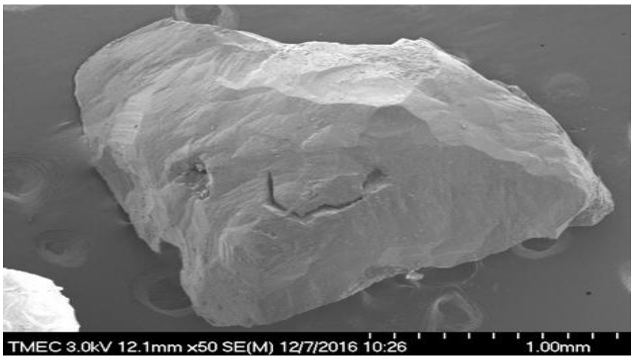

Figure 7A 1.85 mm diamond crystal.

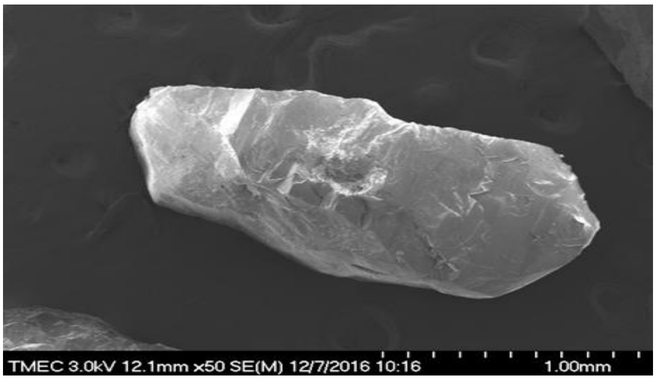

Fig. 7B. 1.73 mm diamond crystal.

According to Fig. 7A and 7B, the diamond crystals are 1.85 mm and 1.73 mm in size, respectively. In addition, they are diamond crystal with the same crystal structure as the natural diamond from Raman spectrum as shown in Fig. 8.

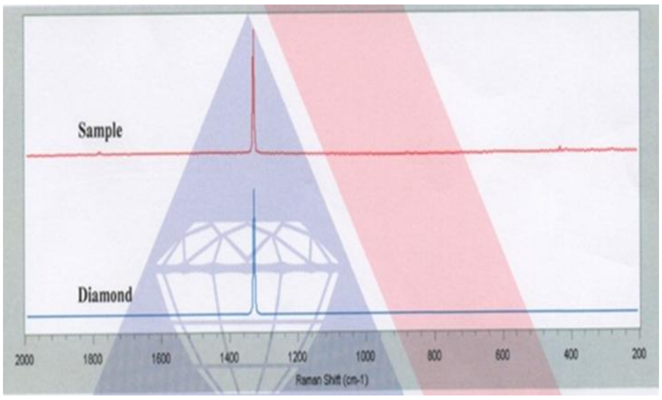

Fig. 8. Raman spectrum of the synthetic diamond (Sample) and the natural diamond (Diamond).

When the diamond properties were confirmed using Raman spectroscopy to compare with the natural diamond, it was found that its responses were all the same as the natural diamond[4].

Then the diamond crystal growth rate was analyzed. The measured diamond crystal size at various times was plotted. As can be seen from Figure 9, the first 60 h of the synthesis, the growth rate is as high as 16 µm/h and decreased with time. The growth rate is summarized in Table 2.

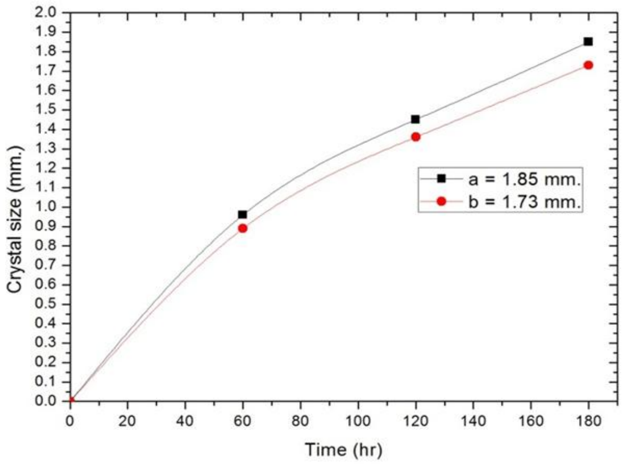

Fig. 9.Relationship of diamond crystal size and synthetic time.

TABLE II
GROWTH RATE AT EACH SYNTHETIC PERIOD

Crystal	Growth Rate in the 1st Period (µm/h)	Growth Rate in the 1st Period (µm/h)	Growth Rate in the 1st Period (µm/h)
a	16.00	8.16	6.66
b	14.83	7.83	6.16

Then, the relationship between current and voltage of 180 h synthetic diamond with diamond crystal size of 1.85 mm was compared with the natural diamond with similar size. The result is as shown in Fig. 10 and 11.

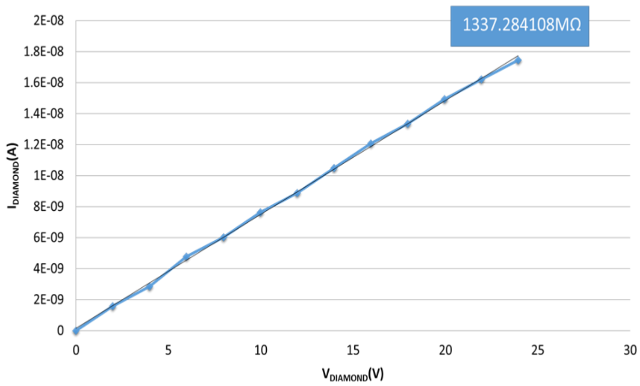

Fig. 10. Relationship between current and voltage of the synthetic diamond.

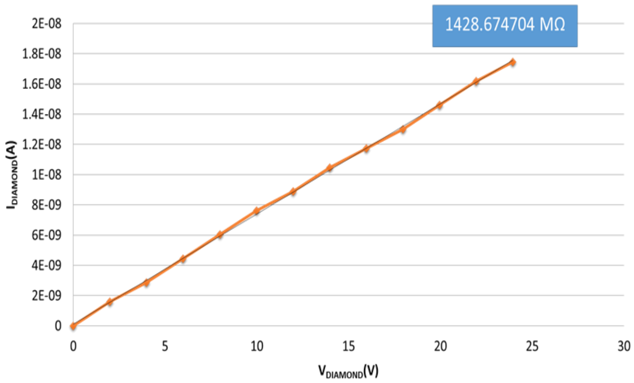

Fig. 11. Relationship between current and voltage of the natural diamond.

When varied temperature with the synthetic diamond from 25 to 200°C, it was found that the temperature changes has minor effect on the resistance of the synthetic diamond as shown in Fig. 12.

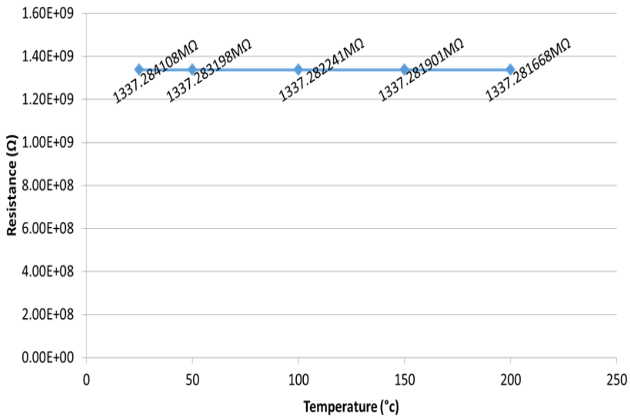

Fig. 12.Relationship of synthetic diamond and temperature.

Finally, resistance was calculated from the inversed of slope of the plot between current and voltage of the synthetic diamond. The resistance of the synthetic diamond is equal to 1337.28 MΩ. The resistance of the natural diamond is 1428.67 MΩ.

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IV. Conclusion

Thy synthesis of large and complete diamond crystal using double test tubes HFCVD, two large diamond crystals of 1.85 mm and 1.73 mm were achieved.

With long synthesis period of 180 h, perfect diamond crystals similar to the natural diamond were obtained. In addition, temperature has no effect on electrical properties of the synthetic diamonds.

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