# Diamond synthesis using tubular hot-hoil CVD

Ippei Tanaka[1], Masashi Higami[*2] and Yasunori Harada[1]

[1] *Graduate School of Engineering, University of Hyogo2167 Shosha, Himeji, Hyogo 671-2280 Japan*
[2] *Department of Engineering, University of Hyogo2167 Shosha, Himeji, Hyogo 671-2280, Japan*

In this study, the effects of the tube temperature and gas flow rate on diamond synthesis using tubular hot-foil CVD were investigated. CH4 and H2 gases with a CH4 concentration of 1 % %were used as process gases. The tube was heated through resistance heating, and the temperature ranged from 1500 °C to 1650 °C. The H2 gas flow rate was varied from 500 to 1000 SCCM. The deposition rate increased with the tube temperature. A maximum deposition rate of 13.5 µm/h was achieved at a temperature of 1650 °C with a $H_2$ gas flow rate of 1000 SCCM. Consequently, the tubular hot-foil CVD method can be used to obtain diamond films at a deposition rate exceeding 10 µm/h.

***Keywords:*** *diamond, chemical vapor deposition, film*

## 1. Introduction

Diamond coatings have attractive properties such as high hardness and low friction. Diamond films can be used as cutting tools and mechanical components.

Microwave plasma chemical vapor deposition and the hot-filament method (HFCVD) are the main methods used for producing diamond coatings. In particular, HFCVD can be obtained by depositing polycrystalline diamond films to decompose a gas mixture consisting of a hydrocarbon in hydrogen using a metal filament heated to approximately 2000 °C. In addition, the HFCVD system allows films to be coated in three-dimensional shapes or over large areas. However, this method has a low deposition rate of ~1 µm/h. Although a high deposition rate can be achieved through a high gas temperature, the gas temperature around the substrate becomes lower than that of the filament.

Takamori et al. reported that single-crystalline diamond films were obtained by two-layer filament arrangement in HFCVD system. The deposition rate reached 17.9 µm/h at a filament temperature of 3000℃[1)]. On the other hand, High-speed jet deposition of thermally activated gas has been developed[2)]. In this method, a high-speed jet of the source gas is injected into the inner channel of a cylindrical reactor for the thermal activation of gases. Although a deposition rate of 20 µm/h was achieved, the diamond morphology consisted of particles at a heating power of 1700–1800 W.

We have proposed a tubular hot-foil CVD, in which a filament is replaced with a tube in HFCVD. Tubular hot foil CVD can effectively decompose the source gas through the heated tube. This method can be used to grow diamond films at low electric power and high deposition rates. We have previously reported that diamond films were deposited by tubular hot foil CVD, and the deposition rate was 3 µm/h at a tube temperature of 1500 °C. However, to improve the deposition rate of diamonds using this technique, several issues remain. In particular, the deposition rate was expected to depend on the tube temperature.

In this paper, the effects of tube temperature and gas flow rate on diamond synthesis using tubular hot-foil CVD was investigated.

*2 Student, University of Hyogo

## 2. Experiment

Diamond films were deposited by a hand-made CVD apparatus. A scratched Si wafer was used as substrate. Tantalum foil served as the tube. $CH_4$ and $H_2$ gases with a 1% $CH_4$ concentration were used as process gases. The tube was heated through resistance heating, and the temperature ranged from 1500 °C to 1650 °C. The deposition time was fixed at one hour.

The temperature was measured using a radiation thermometer. The deposits were imaged using scanning electron microscopy (SEM), and the film thickness was determined from the SEM cross-sectional images. The deposition rate was calculated by dividing the film thickness by deposition time. Raman spectroscopy was used to evaluate the quality of the diamond films.

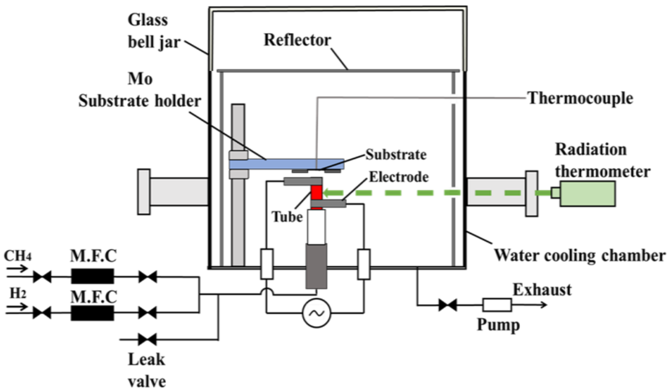


Fig.1 Schematic diagram of CVD apparatus.

Table 1 Synthesis condition.

| Experiment number | 1 | 2 |
|---|---|---|
| $CH_4$ concentration % | 1 | 1 |
| $H_2$ flow rate, SCCM | 500, 700, 900, 1000 | 1000 |
| Pressure, kPa | 4 | 4 |
| Tube temperature, °C | 1650 | 1500, 1600, 1650 |
| Distance between substrate and gas injection port, mm | 3 | 3 |
| Deposition time, h | 1 | 1 |

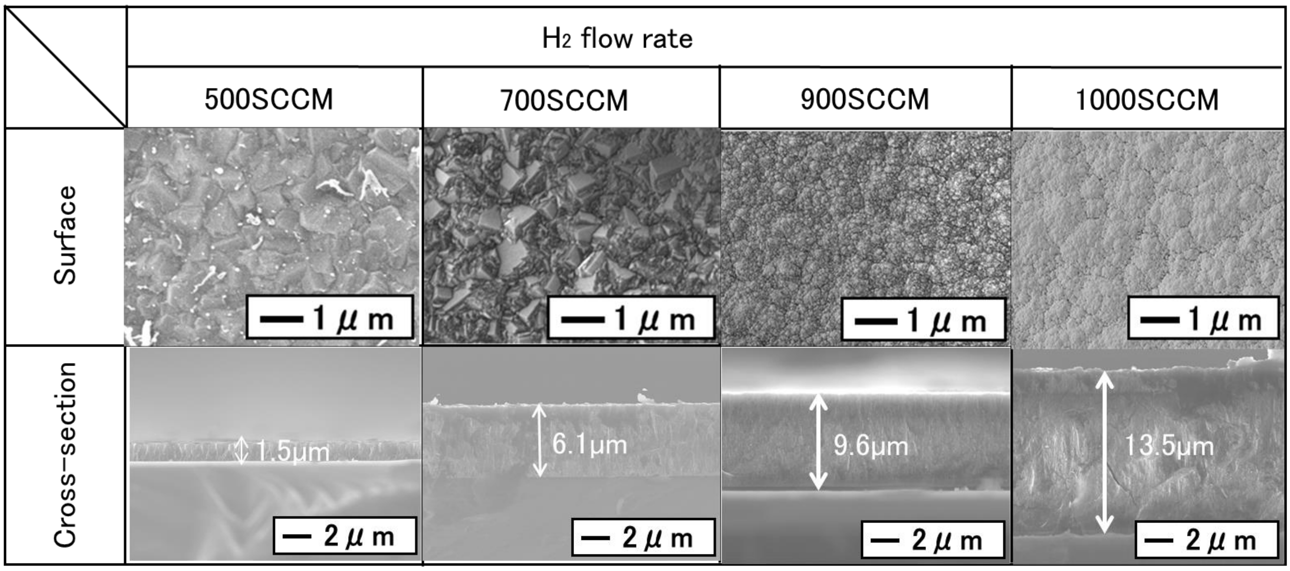

Fig.2 Surface and cross-sectional SEM images of films deposited at different $H_2$ flow rates.

## 3. Results

### 3.1 Effect of gas flow rate

The substrate temperature was increased with increasing $H_2$ flow rate such as from 653 to 743°C. Fig.2 shows Surface and cross-sectional SEM images of films. The grain size decreased with an increase in the $H_2$ flow rate. Well-faceted films were observed at 500 and 700 SCCM. In contrast, a grain size of approximately 0.04-0.05 μm was observed at 900 and 1000 SCCM. The deposition rate was increased with increasing tube temperature. The highest deposition rate of 13.5μm/h was obtained at 1000 SCCM.

In the Raman spectra, the peak at 1333 $cm^{-1}$ related to diamond was observed under all conditions. Additionally, the G band at approximately 1580 $cm^{-1}$ was also confirmed. With an increase in the $H_2$ flow rate, the intensity ratio of the diamond to the G band ($I_{dia}/I_G$) decreased.

### 3.2 Effect of tube temperatures

The substrate temperature increased with an increase in the tube temperature from 673 to 743°C. From SEM images, the grain size was decreased with increasing tube temperature. Well-faceted films were observed at 1500°C. On the other hand, the grain size of about 0.04 μm was observed at 1650 °C. The deposition rate was increased with increasing tube temperature. The highest deposition rate (13.5μm/h) was obtained at 1650 °C. In Raman spectra, the peak of 1333$cm^{-1}$ related to the diamond was observed at all conditions. In addition, the presence of the G band was confirmed. With increasing tube temperature, $I_{dia}/I_G$ decreased, and the half-width at half-maximum of the diamond peak increased.

## 4. Discussion

Fig.3 shows relationship between substrate temperature and deposition rate. The deposition rate increased with the $H_2$ flow rate and tube temperature. In HFCVD, the deposition rate is affected by the substrate and filament temperatures. It should be noted that the deposition rate was greater than 13 μm/h at 1650 °C. This result indicates that the warm gas was carried to the substrate by increasing the gas flow and tube temperature. In addition, higher tube temperatures accelerated the decomposition of $CH_4$. Therefore, the FWHM of the diamond peak in the Raman spectra decreased.

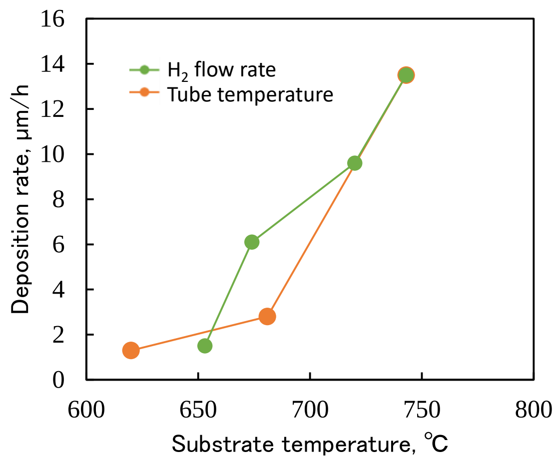

Fig.3 Relationship between substrate temperature and deposition rate

## 5. Conclusions

This work shows how the tube temperature and total flow rate affect the deposition rate of diamond films prepared by the tubular hot-foil CVD method. Moreover, the proposed method achieves a deposition rate exceeding 10 μm/h.


## Acknowledgments

The present work was supported by the OSG Fund 2022.


## References


1) Y. Takamori et al.: Diam. Relat. Mater. **118** (2021) 108515.
2) Yu.V. Fedoseeva et al.: Materials **13** (2020) 219.