

## Analysis of single-crystal diamond growth by using microwave plasma CVD

Hideaki Yamada,

Akiyoshi Chayahara, Yoshiaki Mokuno, Shinya Ohmagari, and Shin-ichi Shikata

*National Institute of Advanced Industrial Science and Technology (AIST)  
1-8-31 Midoriga-oka, Ikeda, Osaka 563-8577, Japan*

Single crystal diamond growth by using microwave plasma chemical vapor deposition was studied numerically as well as experimentally. Recent development of wafer processing made us possible to prepare inch-size wafers, which are close to or even larger than a quarter of the wavelength of the microwave. In this case, non-uniformity becomes obvious. To specify the origin of the non-uniformity, radical distributions were numerically studied. Comparison with experiments suggests possible importance of uniformities of the substrate temperature and  $\text{CH}_x$  ( $x < 3$ ) near the top-surface of the substrate.

### 1. Background

From the bulk power system to the electric vehicles, the power management is one of the indispensable elemental technologies for energy-saving society. Power semiconductor materials such as SiC and GaN have been expected to be key materials in this field owing to their material constants; they are superior to those of Si. Then, those of diamond are even better than above mentioned materials [1].

For realization of their industrial use, establishment of processing to prepare high-quality crystals over inch-size area with low cost is necessary as in the cases of GaN and SiC. Artificial way to produce diamond was firstly reported in 50's by using high-pressure-high-temperature method (HPHT). This method, however, requires huge apparatus and is considered to be impractical for fabrication of wafers with inch size area. Actually, inch size crystal by using HPHT has never been reported to the best of author's knowledge. Then, in 80's, microwave plasma chemical vapor deposition (MWPCVD) was found to be another way to synthesize diamond. Though, on the other hand, it has been still hard to enlarge the size of a seed single crystal diamond. Commercially available size of single crystal diamond (SCD) is typically several millimeters which is much smaller than the wavelength of the microwave (approximately 12 mm for 2.45 GHz of MW frequency).

In recent 10 years, we have developed techniques to enlarge the size of SCD and processing to prepare freestanding wafers [2-4]. Then, we reported a 2 inch size ( $40 \times 60 \text{ mm}^2$  area) SCD mosaic wafer [5]. Now, the size of SCD is comparable to the wavelength and non-uniformity in the growth rate and quality becomes remarkable [5, 6]. Therefore, we started

to study distributions of temperatures, radicals and reactions among them by using numerical simulations [7, 8]. In this report, we present growth rate distributions based on these numerical results and its comparison with experimental results. Then, based on these results, possible mechanism of the origin of the non-uniformity is discussed.

### 2. Experimental

SCD wafers were prepared by a commercially available setup [AX6500 produced by Seki diamond systems of Cornes Technologies, Ltd.]. Frequency of the MW is 2.45 GHz, and the imposed power is typically 5-8 kW to maintain the substrate temperature around 1100 °C. The gas pressure was set to be 0.1-0.2 atms. Details of typical growth condition can be found in our literature [2-6].

### 3. Simulation

A fluid based model was originally developed where the governing equations were reduced into a simple set [7, 8]. Calculation domain was prepared as the same with the structure of the experimental setup, i.e. AX6500.

### 4. Results and discussion

We have observed decrease of the growth rate in edge region when the size of substrate is larger than almost 1-inch. For example, we have measured 40% drop in growth rate, for substrate with 40 mm edge.

Simulation was conducted for the discharge condition similar to the experiment, where the substrate temperature is assumed to be constant just for simplicity. Calculation of the distribution of H ( $\text{CH}_3$ ) near the substrate top surface gives relatively (non-)uniform distribution of H ( $\text{CH}_3$ ). Because H

is concentrated at the center of the discharge region and recombination of  $\text{CH}_3$  with H is enhanced there,  $\text{CH}_3$  concentration is low in the central region above the top surface of the substrate. Substituting this result into a theoretical model to estimate the growth rate [9],

Growth rate=

$$\frac{C_1 \sqrt{T_s} \text{CH}_3}{C_2 \exp(a_1/T_s) + C_3 \exp(a_2/T_s) + 1 + f(T_s) \text{H}_2/\text{H}},$$

where  $C \cdot a$  are constants and  $f = f(T_s)$  is a algebraic function of the substrate temperature, one may notice that the absolute value of the numerically-estimated growth rate is consistent with that obtained in experiment. On the other hand, as for its uniformity, one may also notice that the growth rate increases in radial direction, which is opposite to the experimental observation.

As one possible reason to explain this discrepancy is the non-uniformity of the substrate temperature. Actually, substrate temperature is not uniform in experiments and the equation also has dependence on it. However, to explain 40% decrease of the growth rate, decrease of the substrate temperature more than 200 °C. Therefore, there is other mechanisms which cause the non-uniformity.

We noticed that, for relatively high power (density) discharge as in the present case, hydrocarbon radicals  $\text{CH}_x$  ( $x < 3$ ) as well as  $\text{CH}_3$  are also generated and these are not negligible anymore. Figure 1 shows typical distributions of H,  $\text{CH}_3$  and C around the top surface of the substrate.

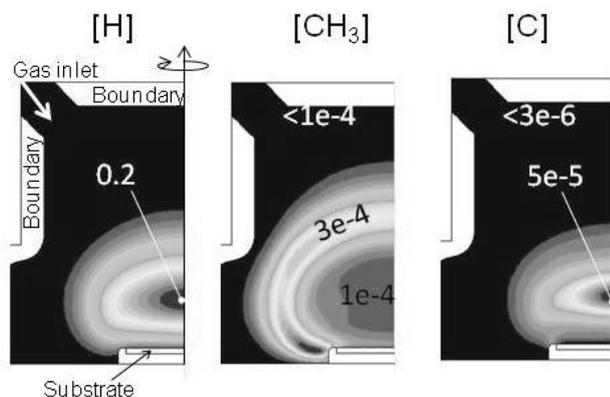


Fig.1. Contours of mole fractions of (left) H,  $\text{CH}_3$ , and C (right) for 16kPa/3kW. Substrate temperature was assumed to be uniform. The diameter of the substrate in this case is 2 inch.

Different from  $\text{CH}_3$ , C concentrates around the central region. While the concentration of C is almost ten times smaller than that of  $\text{CH}_3$ , its

reaction probability is much higher than  $\text{CH}_3$ ; molecular dynamics simulation suggests that reaction probability of C is 10 times higher than that of  $\text{CH}_3$  [10]. This result suggests that C would have a role as a possible precursor of the growth in addition to  $\text{CH}_3$ . This may be a possible cause of the non-uniformity of the growth rate. While its mechanism is still unclear, atomic C may react with the top surface of the substrate and enhances the growth around the central region.

## 6. Summary

We have conducted experiments of the growth of SCD over inch size area by using MWPCVD. In addition, numerical simulation was conducted under the corresponding condition with the experiments. We found that the absolute value of the experimentally-obtained growth rate is consistent with that numerically-obtained one. If the substrate temperature is assumed to be completely uniform, however, experimentally obtained non-uniformity of the growth rate cannot be explained. From the comparison of the numerical results with the experiments, uniformity of the substrate temperature would be important factor. In addition, contribution of  $\text{CH}_x$  ( $x < 3$ ) as well as  $\text{CH}_3$  on the crystal growth may possibly have some contributions on the uniformity.

## Acknowledgments

This work was partially supported by JSPS KAKENHI Grant Number 25820129.

## References

- [1] S. Koizumi, C. E. Nebel and M. Nesladek: *Physics and Applications of CVD Diamond* (Wiley-VCH, Weinheim, 2008), Chap. 3, p.30.
- [2] A. Chayahara, Y. Mokuno, Y. Horino, et al.: *Diamond Relat. Mater.* **13** (2004) 1954.
- [3] Y. Mokuno, A. Chayahara, H. Yamada, et al.: *Diamond Relat. Mater.* **18** (2009) 1258.
- [4] H. Yamada, A. Chayahara, Y. Mokuno, et al.: *Appl. Phys. Express* **3** (2010) 051301.
- [5] H. Yamada, A. Chayahara, Y. Mokuno, et al.: *Appl. Phys. Lett.* **104** (2014) 102110.
- [6] H. Yamada, A. Chayahara, Y. Mokuno, et al.: *Diamond Relat. Mater.* **33** (2013) 27.
- [7] H. Yamada, A. Chayahara and Y. Mokuno: *J. Appl. Phys.* **101** (2007) 063302.
- [8] H. Yamada: *Jpn. J. Appl. Phys.* **51** (2012) 090105.
- [9] Y.A. Mankelevich, A.T. Rakhimov and N.V. Suetin: *Diamond Relat. Mater.* **5** (1996) 888.
- [10] M. Eckert, E. Neyts and A. Bogaerts: *J. Phys. D: Appl. Phys.* **41** (2008) 032006.