Transactions of the Materials Research Society of Japan 33[2] 377-380 (2008)

Electrochemical properties of CVD diamond

Hidehiko Ohtsu, Kazuya Yasuda*, Kazuya Koyama**, Yukihiro Sakamoto***, Satoshi Yamashita***, Matsufumi Takaya***

Graduate student, Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-8588, Japan
Fax: 81-047-478-0309, e-mail: hidehiko_ohtsu@yahoo.co.jp
*Yoshino Denka Kogyo Inc.,2849 Koshigaya, Koshigaya-shi, Saitama 344-0023, Japan
Fax: 81-048-966-0507, e-mail: yasuda@yoshinodenka.com
** National Institute of Advanced Industrial Science and Technology,
16-3, Onogawa, Tsukuba 305-8069, Japan
Fax: 81-0298-61-8458, e-mail: k-koyama@aist.go.jp
***Chiba Institute of Technology, 2-17-1 Tsudanuma, Narashino, Chiba 275-8588, Japan
Fax: 81-047-478-0516, e-mail: yukihiro.sakamoto@it-chiba.ac.jp

Diamond was synthesized by microwave plasma CVD and hot filament CVD. (111) textured diamond films were synthesized from CH_4-H_2 reaction gas system and (100) textured films were synthesized from CO-H_2 reaction gas system using microwave plasma CVD, respectively. Boron doped and non-doped CVD diamond films were synthesized using hot filament CVD from CH_4-H_2 reaction gas system with B_4C as a dopant. An electrochemical property was estimated by a cyclic voltammetry.

From the SEM observation, polycrystalline diamond films were observed. For samples prepared by microwave plasma CVD method, (111) texture films and (100) textured films were obtained from different reaction gas systems. Also polycrystalline CVD diamond films were observed both boron doped and non-doped samples using hot filament CVD. From the estimation of Raman spectroscopy, peaks of diamond were obtained at 1333 cm^{-1} in their Raman spectra.

As a result of cyclic voltammetry, the potential windows were broad. The areas of the potential window of CVD diamond films were different respectively and they were depended on growth conditions and CVD methods.

Key words: CVD, diamond, microwave, hot filament, cyclic voltammetry

1. INTRODUCTION

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, and chemical inertness. As one of properties of diamond, chemical inertness is very important to apply CVD diamond for the electrode of electrolysis in the electrolyte of wide range of pH. And high current density can be obtained because of its electric conductivity and high thermal conductivity.

On the other hand, proportions of natural diamond and man-made diamond are granular and to obtain large size diamond plate is very difficult. However, their features can made not only grain but also film by using CVD methods. In this report, the electrochemical properties were studied on the CVD diamond prepared by microwave plasma CVD and hot filament CVD. Also the electrochemical measurement by cyclic voltammetry was carried out using these diamond thin films, and the characteristic of the CVD diamond electrode was evaluated, and the possibility of CVD diamond to be used as electrode material was examined.

2. EXPERIMENTAL METHODS

2.1 Diamond synthesis

Two different CVD methods, microwave plasma CVD and hot filament CVD, were used for diamond synthesis. Schematic illustration of microwave plasma CVD apparatus was shown in Figure 1.Two kinds of diamond thin film were synthesized on silicon substrate using a CH_4-H_2 reaction gas system or a CO-H_2 reaction gas system. Each synthesis condition were shown in Table Ⅰ.

Boron doped diamond thin film was synthesized with hot filament CVD method. Schematic illustration of hot filament CVD apparatus installed with Ta filament and substrate was shown in Figure 2. Reaction gases were used CH_4 and H_2 . Boron was doped by using B_4C installed in hot filament CVD apparatus. The synthesis condition was shown in Table Ⅱ.

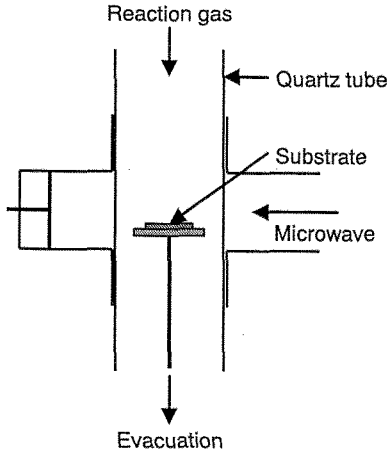

Fig. 1 Schematic illustration of microwave plasma CVD apparatus.

Table I Synthesis condition of microwave plasma CVD.

Reaction gas	CH_4 / H_2	CO / H_2
Substrate	Si	Si
CH_4 flow rate (cm^3/min)	1	—
CO flow rate (cm^3/min)	—	30
H_2 flow rate (cm^3/min)	100	100
Microwave power (W)	400	400
Pressure (kPa)	5.3	5.3
Substrate temp. (K)	1093 ~1113	1093 ~1113
Reaction time (h)	5	5

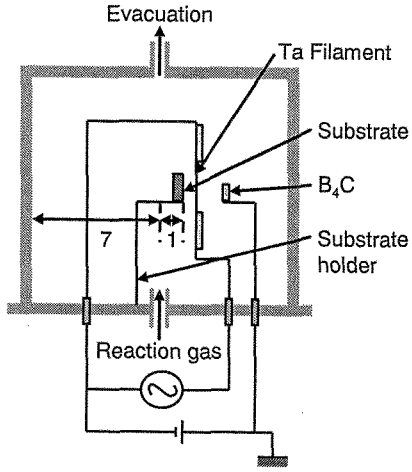

Fig. 2 Schematic illustration of hot filament CVD apparatus.

Table II Synthesis condition of hot filament CVD.

Reaction gas	CH_4 / H_2
Substrate	Si
CH_4 flow rate (cm^3/min)	3
H_2 flow rate (cm^3/min)	100
Distance between filament and substrate (mm)	4
Bias voltage (V)	100
Pressure (kPa)	4.0
Filament temp. (K)	2273
Reaction time (h)	3

2.2 Electrochemical measurement.

The schematic illustration of electrochemical measurement system was shown in Figure 3. Solartron1280B was used as a potentiostat. The diamond thin film electrode was used for working electrode, and the platinum electrode was used for counter electrode and saturation Ag/AgCl electrode was used for reference electrode, respectively. The electrolyte was adjusted to pH=3, 9.5, 12 by using H_2SO_4 and NaOH on the basis of 0.05M Na_2SO_4 solution, respectively.

The experiment was swept from rest potential to negative potential up to -3.0V at sweep speed 50mV/s after rest potential was measured, and, in addition, swept to positive potential up to 3.0V.

This operation was repeated in 10 cycles, and the cyclic voltammogram was made, and the change of the shape was examined. Diamond thin film electrode was synthetically evaluated based on result of surface observation by SEM in before and after the electrochemical measurement and qualitative evaluation by the Raman spectroscopy.

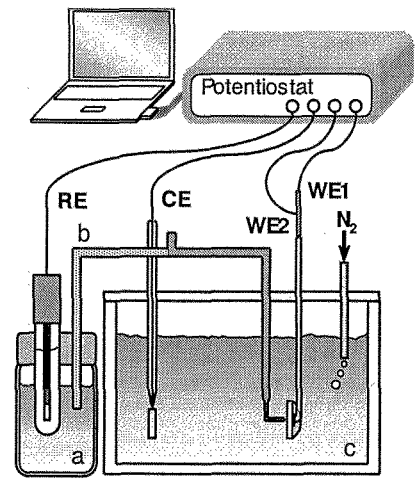

Fig. 3 Electrochemical measurement apparatus.
RE: SSE, CE: Pt, WE: diamond
a: KCl(sat.) solution
b: Salt bridge(KCl sat.)
c: 0.05 M Na_2SO_4 soluition

3. RESULTS AND DISCUSSION.

3.1 Morphologies and qualities of CVD diamond

Morphology and Raman spectra of each CVD diamond thin films synthesized by either method were almost similar. SEM images of the diamond thin film made by micro wave plasma CVD method by using CH_4-H_2 and CO-H_2 mixed gas for the reactant gas were shown in Figure 4(a) and (b). Moreover, SEM image of the Boron doped diamond thin film made from hot filament CVD method was shown in Figure 4(c).

From the SEM observation, polycrystalline diamond films were observed. Diamond thin film that used the CH_4 gas shown in Figure 4(a) was made of the diamond crystal of 2μm or less. (111) textured diamond films were synthesized

from CH_4-H_2 reaction gas system using microwave plasma CVD. Diamond thin film that used the CO gas shown in Figure 4(b) was made of diamond crystal type that consisted of about 2-3μm clearness and single a particle. (100) textured diamond films were synthesized from CO-H_2 reaction gas system using microwave plasma CVD. The Boron doped hot filament CVD diamond thin film shown in Figure 4(c) piled up closely the diamond crystal of about 2-4μm. (111) textured diamond films were synthesized from CO-H_2 reaction gas system using microwave plasma CVD.

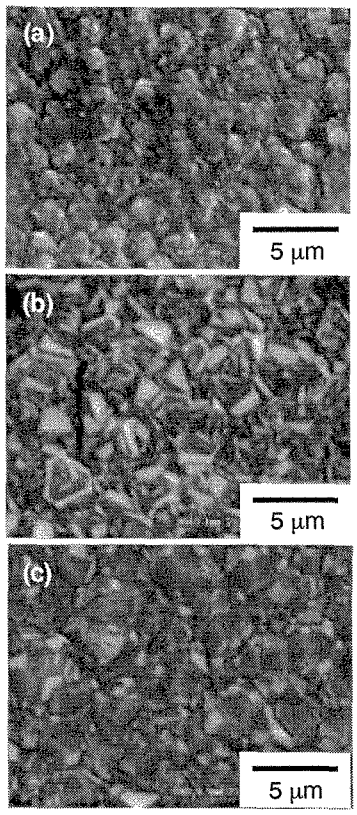

Fig. 4 SEM images of the synthetic CVD diamond film electrode.
(a) Microwave plasma CVD(CH_4/ H_2)
(b) Microwave plasma CVD(CO/ H_2)
(c) Hot filament CVD(BDD)

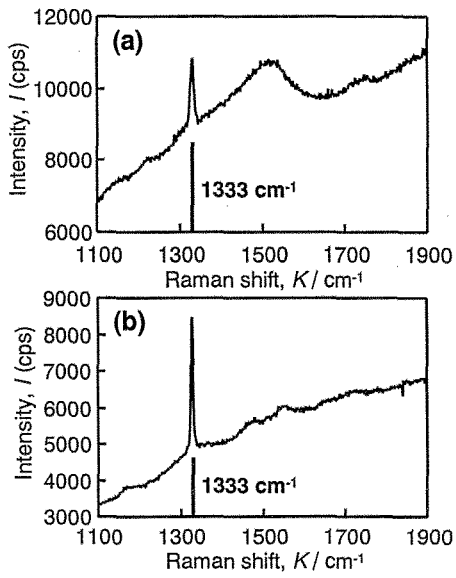

Fig. 5 Raman spectrum of the synthetic CVD diamond film electrode.
(a) Microwave plasma CVD(CO/ H_2)
(b) Hot filament CVD(BDD)

Raman spectrum of diamond thin film of microwave plasma CVD and of hot filament CVD of Boron doped were shown in Figure 5(a), and (b). From the estimation of Raman spectroscopy, peaks of diamond were obtained at 1333 cm^{-1} in their Raman spectra. Additionally, the broad peak of the DLC component was also observed near 1550cm^{-1}.

3.2 Electrochemical properties

The cyclic voltammogram of the obtained each diamond thin film electrode hardly changed in each electrolysis condition even if it repeated ten times, and stability and reproducibility were excellent. The cyclic voltammogram at the pH=12 of the microwave CVD diamond film electrode used CO was shown in Figure 6. The hydrogen was generated at -1.2V vs.SSE, and the oxygen was generated at 1.2V vs.SSE. The potential window was about 2.4V. The range of hydrogen and oxygen generated potential in the other pH solution was about -0.90～2.1V vs.SSE at pH=3, and it was about -1.2～1.8V vs.SSE at pH=9.5. Both of the potential window were about 3.0V.

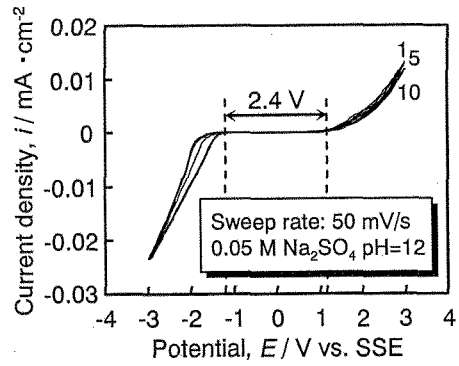

Fig. 6 Cyclic voltammogram of the microwave plasma CVD diamond film electrode using CO/ H_2.

Next, cyclic voltammogram at the pH=12 of the Boron doped hot filament CVD diamond film electrode was shown in Figure 7. The range of hydrogen and oxygen generated potential was about -1.8～1V vs.SSE at pH12, and the potential window was about 2.7V.

The potential range in which hydrogen and oxygen in the other pH solution generated was about -1.5～1.7V vs.SSE at pH=3, and it was about -1.6～1.7V vs.SSE at pH=9.5. And, the potential window was 3.1V and 3.3V respectively.

When cycle number increased, potential of the oxygen generation was shifted to nobel direction and the potential of the hydrogen generation was shifted to the base direction. As for the Boron doped diamond thin film electrode, the current density of the oxygen generation and the hydrogen generation was ten times as large as that of non dope diamond thin film.

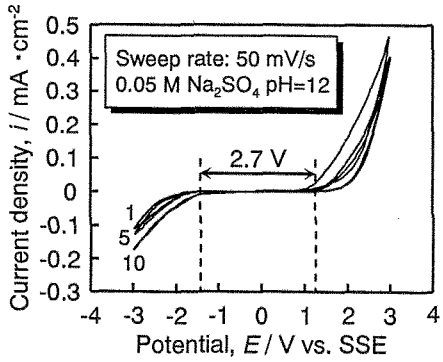

Fig. 7 Cyclic voltammogram of the hot filament CVD diamond film electrode(BDD).

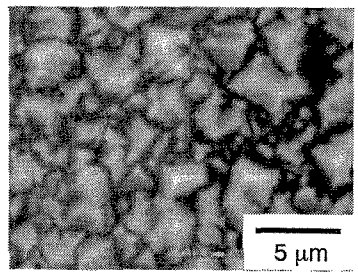

Fig. 8 SEM image of the hot filament CVD diamond film after the electrochemical measurement.

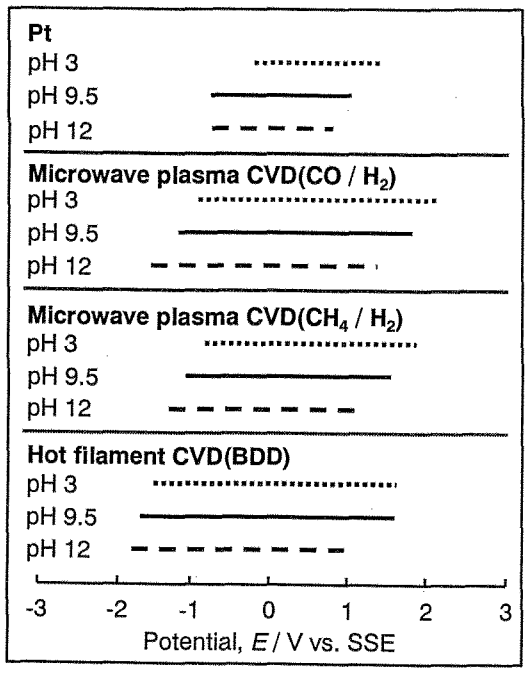

Fig. 9 Measured potential window.

SEM image of the Boron doped CVD diamond film after the electrochemical measurement was shown in Figure 8. As for the surface morphology, it was almost changeless and the Raman spectrum was also almost changeless.

Including the Pt electrode, the potential window after ten cycles in the electrolyte of each pH of two kinds of no dope diamond thin film electrode and boron dope diamond thin film electrodes were shown in Figure 9.

In comparison with the platinum electrode, the potential window of diamond thin film electrode were extended near 2V. As for this, the diamond thin film electrode can be possible for the material with the high overvoltage, and it is effective for the precipitation of the metal. Moreover, and, the potential of the oxygen evolution shifted on the non dope diamond thin film electrode to the base direction with the rise in pH, and the oxygen became easy to be generated. However, the potential hardly changed on the boron dope diamond thin film electrode, even if pH changed.

4. CONCLUSIONS

As a result of estimation of electro-chemical properties of CVD diamond prepared by using microwave plasma CVD and hot filament CVD, conclusions are follows,

1. From the SEM observation, (111) textured diamond films were synthesized from CH_4-H_2 reaction gas system and (100) textured films were synthesized from CO-H_2 reaction gas system using microwave plasma CVD, respectively.

Also polycrystalline CVD diamond films were observed Boron doped samples using hot filament CVD. From the estimation of Raman spectroscopy, peaks of diamond were obtained at 1333 cm^{-1} in their Raman spectra.

2. As a result of cyclic voltammetry, the potential window of the CVD diamond thin films were extended in comparison with the platinum electrode in either pH solution at about 2V. The areas of the potential window of CVD diamond films were different respectively and they were depended on growth conditions and CVD methods.

3. The current density of Boron dope CVD diamond electrode was ten times higher than non dope CVD diamond. And surface morphology and the quality of CVD diamonds were not changed after electrochemical measurement.

References

[1] Mutsukazu Kamo, Yoichiro Sato, Seiichiro Matsumoto, and Nobuo Setaka; J. of Crystal Growth, 62, 642 (1983)

[2]Seiichoro Matsumoto, Yoichiro Sato, Masayuki Tsutsumi, Nobuo Setaka; J. of Material Science, 17, 3106 (1982)

[3] Hidehiko Ohtsu, Kazuya Yasuda, Kazuya Koyama, Yukihiro Sakamoto, Satoshi Yamashita, Matsufumi Takaya; 58th annual meeting of the International Society of Electrochemistry (2007)

(Recieved September 30, 2007 ; Accepted December 30, 2007)