The Korean Journal of Ceramics, 4 [1] 1 - 4 (1998)

Deposition of Diamond Film by Hydrogen-oxyacetylene Combustion Flame

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(Received November 5, 1996)

Diamond film was deposited on Mo substrate at atmospheric pressure using a combustion flame apparatus with the addition of H_2. At a temperature above 1000°C, parts of the film were converted into graphites and these were etched by hydrogen atoms. With increasing C_2H_2/O_2 ratio, the nucleation density of the film increased. But the greater part of the film was formed with cauliflower-shaped amorphous carbon. These amorphous carbon were crystallized by etching amorphous carbon.

Key Words : Diamond film, Oxygen acetylene combustion flame

I. Introduction

Diamond has many outstanding physical and chemical properties, which make it desirable for mechanical, thermal, optical and electronic applications. Its high hardness, strength, chemical resistance and low coefficient of friction make it an ideal material for abrasives, wear-resistant surfaces, tool coatings and corrosion barriers. The ultraviolet visible infrared transparency makes it suitable for optical applications, such as windows, lens coating and X-ray lithography masks. Its high thermal conductivity and good electrical insulation make diamond film a good heat diffuser material for high power semiconductor devices, thus allowing a high degree of circuit integration and denser packaging with fewer thermal problems.[1,2]

Hirose[3,4] first reported a new method of diamond synthesis using oxygen acetylene combustion flames at atmospheric pressure. In the oxygen acetylene combustion flame technique, the temperature of the oxyacetylene flames is up to 3000°C at inner core near the nozzle edge, thus ionizes the hydrocarbon gas and produce the chemical active species for diamond deposition.[5] Apart from the high growth rates, this simple technique, which only requires low equipment investment, can produce high quality diamond films/crystals with optical transparency in the visible light range, as well as in the infrared and ultraviolet ranges.[6-8] In this paper, we studied reaction mechanism of diamond deposition and discussed the effects of processing parameters in order to produce high-quality, high growth rate diamond films.

II. Experimental Procedures

The experimental apparatus is schematically shown in Fig. 1. A brazing nozzle(1 mm I.D.) was positioned vertically above the substrate. Mo substrate was mounted on a water-cooled holder made of copper in order to control the substrate temperature. The distance between the torch nozzle and the substrate was maintained between 3 and 20 mm, and the deposition time varied from 30 min to 5 h. The reaction gases used were acetylene, oxygen and hydrogen. Acetylene(C_2H_2) was passed through an activated charcoal filter to remove the residual acetone and purity of O_2 and H_2 gases used were above 99% without further purification.[9] The experimental conditions were shown in Table 1. Mo substrate with diameter of 2.54 cm was polished with sandpapers, and then supersonically treated using 5 μm diamond powder. The substrate temperature was measured with an optical pyrometer.

The deposited films were characterized using SEM (scanning electron microscopy, Hitachi X-650), XRD(X-ray diffractometer, Philips PW 1710) and Raman spectroscopy.

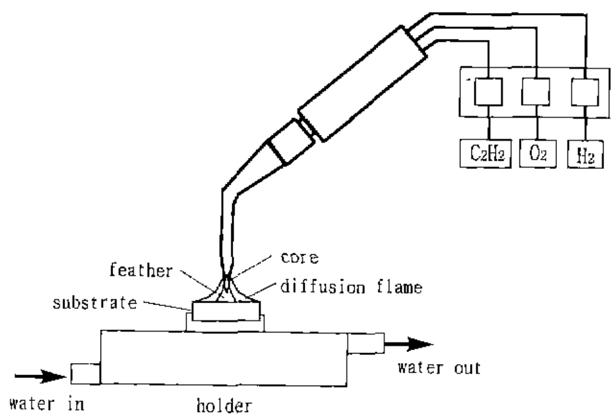

Fig. 1. Schematic diagrasm of the experimental apparatus.

Table 1. Experimental Conditions

torch nozzle I.D. 1 mm	pressure 760 torr
C_2H_2 flow rate 0.9~1.7 l/min	C_2H_2/O_2 ratio 0.93~1.15
O_2 flow rate 0.9~1.47 l/min	H_2/O_2 ratio 0~1.0
H_2 flow rate 0.37~1.47 l/min	substrate temperature 750~1100°C
total flow 1.9~4.64 l/min	time 30 min~5 hr

III. Results and Discussion

1. The effect of substrate temperature

Fig. 2 shows the morphologies of the films deposited at various substrate temperature. There were observed a few of crystallites at 830°C(a). With increasing the temperature, nucleation density of the film increased gradually but those particles were formed to amorphous phase as shown in Fig. 2(c), (d).

X-ray diffraction patterns of the films deposited at various substrate temperature was shown in Fig. 3. These patterns compared with the standard peak values of diamond such as d(111)=2.06(2θ=43.9°C, d(220)=1.26(2θ=75.3°). There was observed strong peak of Mo substrate and weak peak of diamond in Fig. 3(a). The peaks of diamond were sharpened at 900°C as shown in Fig. 3(b). With increasing substrate temperature, the peak intensities of diamond significantly decreased and the peaks of Mo_2C and Mo were sharpened(Fig. 3(c), (d)).

From these results, it is considered that crystal phase was formed at lower temperature but, nucleation density of on the substrate was low because hydrogen atoms were not so activated in low temperature. The greater part of the film was formed with amorphous phase.

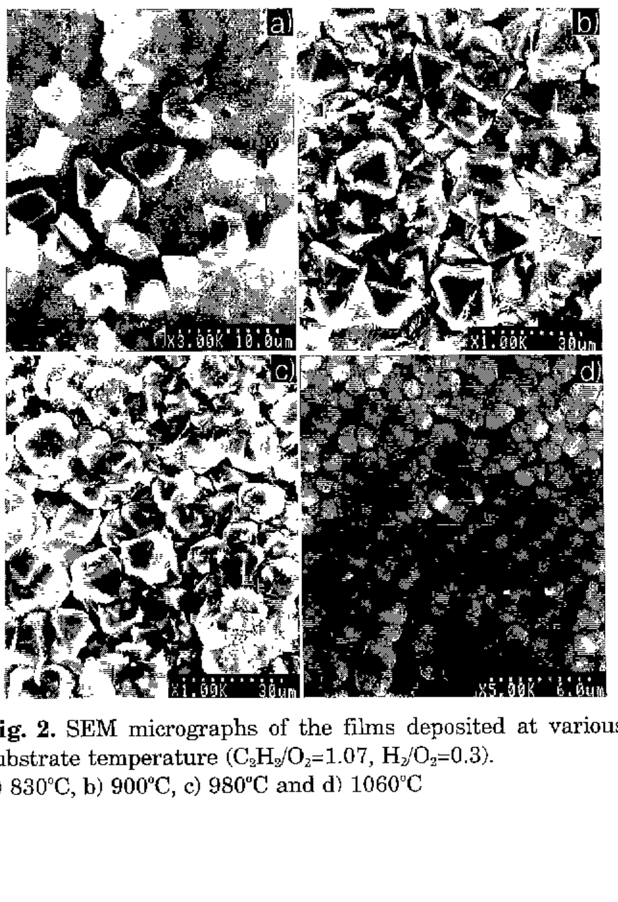

Fig. 2. SEM micrographs of the films deposited at various substrate temperature (C_2H_2/O_2=1.07, H_2/O_2=0.3).
a) 830°C, b) 900°C, c) 980°C and d) 1060°C

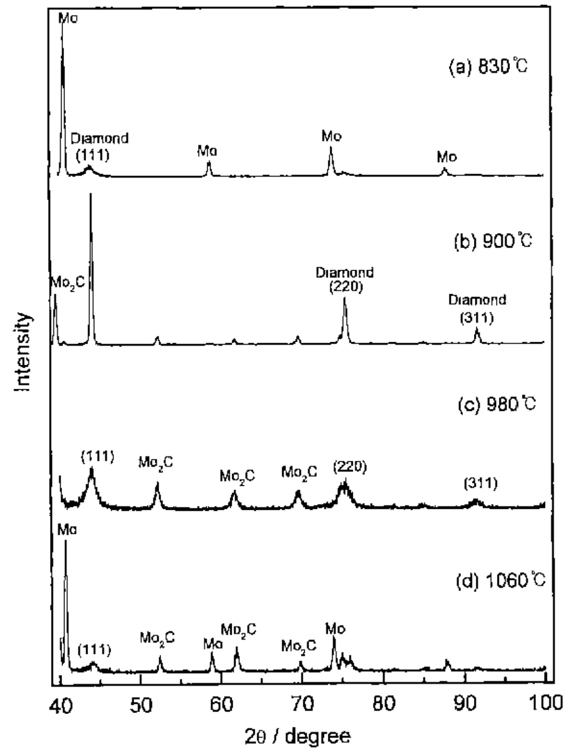

Fig. 3. X-ray diffraction pattrerns of the films deposited at various substrate temperature (C_2H_2/O_2=1.07, H_2/O_2=0.3).
a) 830°C, b) 900°C, c) 980°C and d) 1060°C

2. The effect of C_2H_2/O_2 ratio

The morphologies of the films deposited at various acetylene to oxygen ratios were observed in Fig. 4. In case of C_2H_2/O_2<1.07, the films were more crystallized. Especially, at C_2H_2/O_2=1.0, diamond films showed cubo-octahedral structure of (100), (111) and crystallinity was the greatest In case of C_2H_2/O_2>1.07, crystals changed to cauliflower-shaped amorphous carbon. With increasing C_2H_2/O_2, C-radicals more increased than oxygen and hydrogen etchant. Therefore, films were not etched properly so, formed with amorphous carbon.[12]

X-ray diffraction patterns of the films were shown in Fig. 5. In condition of the C_2H_2/O_2 ratio below 0.97, diamond crystal was not detected as shown in (a). It was supposed that nucleation density on the substrate was very low. As the C_2H_2/O_2 ratio increased, diamond peaks increased sharply. However, when the C_2H_2/O_2 ratio was over 1.07, diamond peaks were eleminated and Mo_2C peaks increased.

3. The effect of H_2/O_2 ratio

It was reported that hydrogen atoms play an important role in surface activating and etching thus, in-

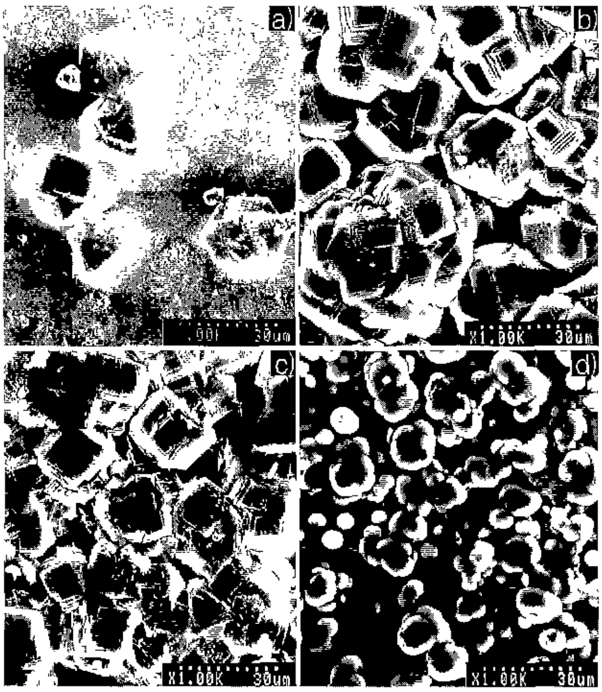

Fig. 4. SEM micrographs of the films deposited at various C_2H_2/O_2 ration (T_s=900°C, H_2/O_2=0.3).
a) 0.97, b) 1.0, c) 1.07 and d) 1.15

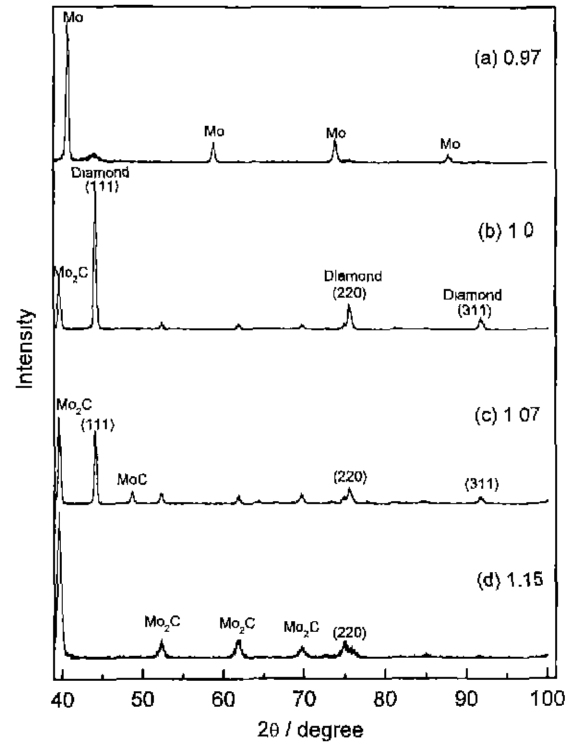

Fig. 5. X-ray diffraction patterns of the films deposited at various C_2H_2/O_2 ratio (T_s=900°C, H_2/O_2=0.3).
a) 0.97, b) 1.0, c) 1.07 and d) 1.15

crease the stability of diamond nuclei and improve the film quality.[14,15] The effect of hydrogen gas was observed as shown in Fig. 6. The film was formed with amorphous carbon in the C_2H_2/O_2 atmosphere. As adding hydrogen gas, the particles deposited on the substrate were crystallized. However, if the the H_2/O_2 ratio was too high, the crystal was not deposited properly due to rapid etching by super-saturated hydrogen.

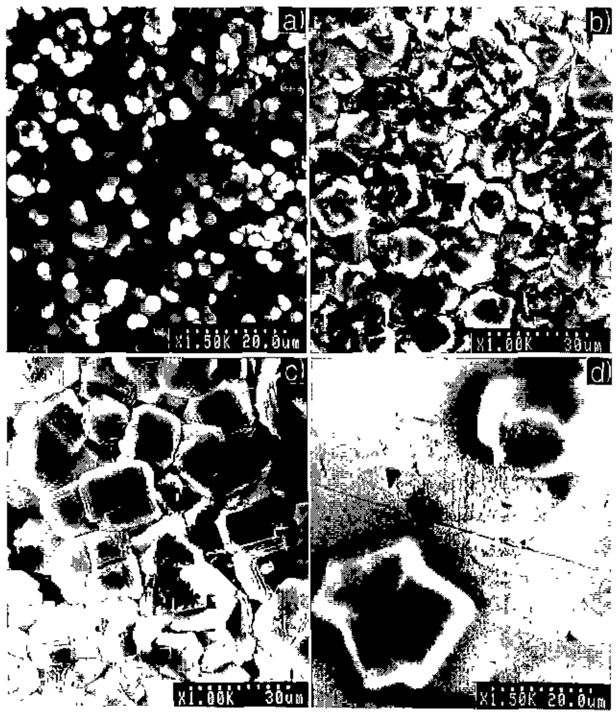

Fig. 6. SEM micrographs of the films deposited at various H_2/O_2 ratio (T_s=900°C, C_2H_2/O_2=1.0).
a) 0, b) 0.3, c) 0.5 and d) 0.7

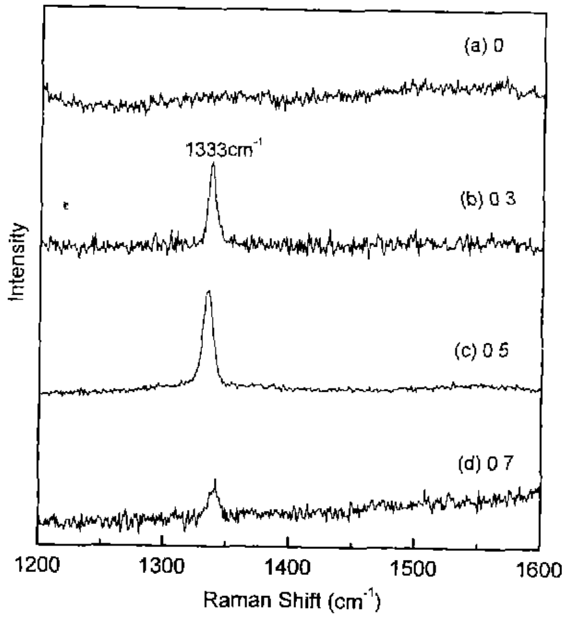

Fig. 7. Raman spectrums of the films deposited at various H_2/O_2 ratio (T_s=900°C, C_2H_2/O_2=1.0).
a) 0, b) 0.3, c) 0.5 and d) 0.7

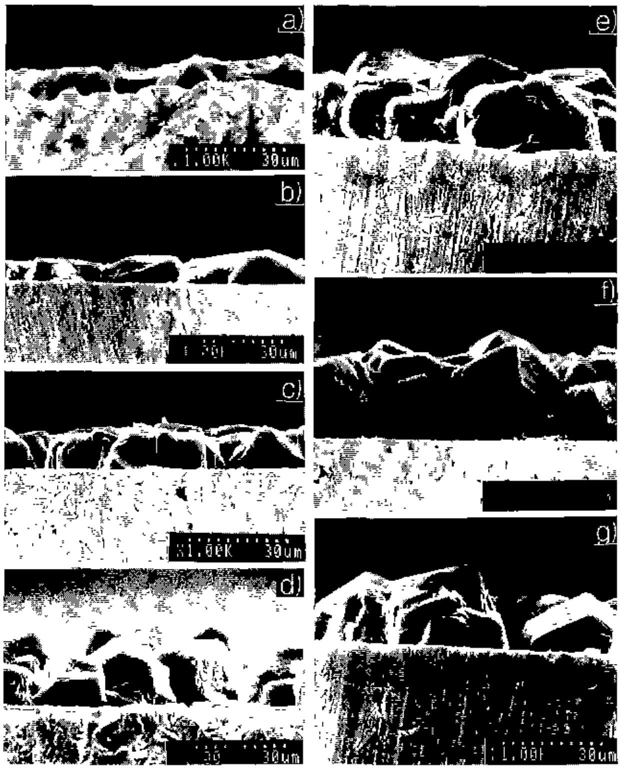

Fig. 8. SEM micrographs of the films deposited at various depodition time (T_s=900°C, C_2H_2/O_2=1.0, H_2/O_2=0.5)
a) 0.5 hr, b) 1 hr, c) 1.5 hr, d) 2 hr, e) 3 hr, f) 4 hr and g) 5 hr

Raman spectras of the films deposited at various H_2/O_2 ratio were shown in Fig. 7. The sharp peaks near the standard 1332 cm^{-1} were due to SP^3-bond crystalline diamond. With increasing H_2/O_2 ratio, diamond peak was developed but, in condition of H_2/O_2 ratio over 0.7, diamond peak was weak because deposited particles etched by supersaturated hydrogen atoms.

From these results, it was noted that hydrogen atoms were improved the film composition by etching amorphous carbon.

In condition of C_2H_2/O_2=1.0, H_2/O_2=0.5 and Ts(substrate temperature)=900°C, the results of cross sectional view of the films were shown in Fig. 8. With increasing deposition time up to 2 hours, the thickness of the film increased but, there was not significant change after 3 hours.

IV. Conclusion

In this paper, diamond film was deposited by hydrogen-oxyacetylene combustion flame. The results indicated that :

1. With increasing substrate temperature, film growth rate increased due to high nucleation density of diamond on substrate. At temperature above 1000°C, parts of the films were formed to amorphous phase.

2. With increasing the C_2H_2/O_2 ratio, growth rate was increased. But crystals were cauliflower-shaped and most part of the films with amorphous carbon were deposited.

3. With addition of H_2, the nucleation density of diamond increased by the improvement of surface activity. Hydrogen gas improved the film quality by etching amorphous carbon.

With increasing deposition time, the thickness of diamond film increased but, there was not significant change after 3 hours. And in condition of T_s=900°C, C_2H_2/O_2=1.0 and H_2/O_2=0.5, the film were covered with crystalline diamond.

Acknowledgement

The authors wishes to acknowledge financial support of the Korea Research Foundation made in the program year of 1997.

References

1. N. Fujimori, A. Doi, Jap. Pat. Appl. JP86, 251(120), Nov. 8 (1986).
2. Sumitomo Electric Industries, Ltd., Jap. Pat. Appl. JP60/57993, April.3 (1985).
3. Y. Hirose, Porc. of 1st Int. Conf. on New Diamond Science and Technology, (Japan New Diamond Forum) Tokyo, 38 (1988).
4. Y. Hirose, Y. Terasawa, "Synthesis of diamond thin film by thermal CVD using organic compounds", *Jpn. J. Appl. Phys.*, **25**, 519 (1986).
5. E. Meeks, R. J. Kee and D. S. Dandy, "Computational simulation of diamond chemical vapor deposition im premixed $C_2H_2/O_2/H_2$ and CH_4/O_2-strained flames", *Combustion and Flame*, **92**, 144 (1993).
6. W Zhu, B. H. Tan, J. Ahn, H. S. Tan, "Studies of diamond films/crystals synthesized by oxyacetylene combustion flame technique", *J. Mat. Sci.*, **30**, 2130 (1995).
7. M. Murayama, K. Uchida, "Synthesis of uniform diamond films by flat flame combusiton of acetylene/hydrogen/oxygen mixture", *Combustion and Flame*, **91**, 239 (1992).
8. W. A. Carrington, L. M. Hanssen, K. A. Snail, D B. Oakes and J. E. Butler, "Diamond growth in O_2+C_2H4 and O_2+C_2H_2 flames", *Metall. Trans. A*, **20A**, 1282 (1989).
9. C. M. Marks, H. R. Burris, J. Grun, K. A. Snail, "Studies of turbulent oxyacetylene flames used for diamond growth", *J. Appl. Phys.*, **73**, 755 (1993).
10. Y. Matsui, H. Yabe and Y. Hirose, "The growth mechanism of diamond crystals in acetylene flames", *Jap. J. Appl. Phys.*, **29**, 1552 (1990).
11. B W. Yu and S. L. Girshick, "Atomic carbon vapor as a diamond growth precursor in thermal plasmas", *J. Appl. Phys*, **75**, 3914 (1994).
12. G. Zhimeng, Y. Sheng, L. Heyi, "The roles of hydrogen in deposition of diamond film using hydrogen-oxyacetylene combustion flame", *J. Mat. Sci. Lett.*, **14**, 244 (1995).