DIAMOND SYNTHESIS BY RF THERMAL PLASMA CVD

Dong-Wha Park and Hyun Park

Department of Chemical Engineering, Inha University
Incheon, 402-751, KOREA

Abstract

Diamond was synthesized on molybdeum substrate by chemical reaction of CH_4 and H_2 using RF thermal plasma. The main Factors of diamond synthesis are the CH_4/H_2 ratio and the substrate temperature. Diamond which has good crystallinity and large density was synthesized, when substrate temperature was 1000℃, and CH_4/H_2 ratio was 0.5%. Diamond was also sythesized by using the organic precursor(ethanol) instead of methane. Diamond which has good quality was synthesized when the flow rates of ethanol is 0.1mℓ/min.

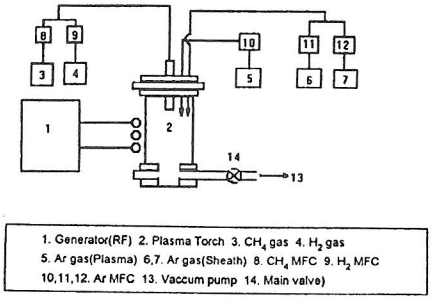
1. Introduction.

The necessity of the source of high temperature increased with increasing the level of the industrial techniques. The reason why thermal plasma is used to the synthesis of materials is that activated atoms, molecules, and radicals are easily formed in plasma, chemical reaction rate is very fast and the limit of chemical equilibrium is overcome in high temperature. Meanwhile, the synthesis of materials likewise diamond of metastable state using plasma is possible. For long ago, diamond has been known that it is synthesized only under the high pressure and temperature[1]. CVD diamond, which has excellent hardness, thermal conductivity, insulating strength and optical transparency, is expected to be applied to cutting tools[2,3], heat-sinks[4,5], windows for optical use[6] etc. The study of the synthesis of diamond by CVD method is actively researched[7-12], because the physical properties of diamond give it almost unlimited application.

In this study in a R.F.(Radio Frequency) thermal plasma CVD system, we attempted to synthesis of diamond on molybdenum substrate by chemical reaction of methane and hydrogen at atmospheric pressure, as well diamond was synthesized by using the liquid organic precursor, ethanol instead of methane. The synthesis of diamond which has good quality was possible, because of the advantages of this R.F. thermal plasma CVD method.

2. Experiment

The experimental apparatus is shown schematically in Fig.1. The apparatus consists of a R.F. plasma torch and its associated power supply , a reaction chamber, a cool-down substrate holder and a gas flow control system. The plasma torch was mounted on the top flange of the reaction chamber and the torch was composed of coaxial double quartz tubes, injection probe and R.F. work coil. The plasma was driven by inductive coupling to a R.F. power supply operating at 4.9MHz with a typical plate power for these experiments of 18~20kW. The inner diameter of water-cooled quartz plasma tube is 44mm. The main plasma gas, argon(flow rate 4~15 l/min), was introduced through the top of the plasma tube. The sheath gas, argon(flow rate 25~35 l/min), was introduced tangential and radial direction with respect to the plasma tube axis, so as to impart swirl, which stabilized the plasma. Experimental conditions are summarized in Table 1. In these experiments molybdenum substrates were pretreated by scratching with 4~6㎛ diamond powder, followed by ultrasonic cleaning in ethanol. Substrate temperature were measured using a two-color optical pyrometer(Wiliamson Tempmatic 8000 series). The pressure in the reaction chamber was 760 torr and deposition time was 1~2 hrs. After the reaction, observation of the products on the molybdenum substrate was made using a scanning electron microscope(SEM) and the identification of the deposits was made by X-ray diffraction analysis and Raman spectroscopy.



1. Generator(RF) 2. Plasma Torch 3. CH_4 gas 4. H_2 gas
5. Ar gas(Plasma) 6,7. Ar gas(Sheath) 8. CH_4 MFC 9. H_2 MFC
10,11,12. Ar MFC 13. Vaccum pump 14. Main valve)

Fig.1. Schematic diagram of experimental apparatus

Table 1. Experimental conditions

Power	16 ~ 22 kW	Ar flow rate A 4 ~ 12 l/min B 10 ~ 15 l/min C 10 ~ 15 l/min carrier	2 l/min
Frequency	4.9 MHz	CH_4 flow rate	54~108 ml/min
Pressure	760 torr	H_2 flow rate	2.5 l/min 200 ml/min
Substrate Temp.	800~1100℃	CH_4/H_2	0.2 ~ 4%
Substrate	Molybdenum		
Deposition Time	1 ~ 2 hr	Ethylalcohol	0.1 ml/min

3. Results and Discussions

3-1. Experimental results of methane to hydrogen ratios.

Experiments were carried out by changing the CH_4/H_2 ratios from 0.2 % to 4% under the condition(power 18~20kW, substrate temperature 1000℃, deposition time 2 hrs and at atmospheric pressure). The results are shown in Fig.2~Fig.4. Fig.2 shows the morphological variation changing the CH_4/H_2 ratios. When the CH_4/H_2 was less than 1 %, it was observed that the particles had good crystallinity.

Especially in the case of 0.5%, it was observed cubo-octahedral structure coexisted diamond crystalline planes (111) and (220). When the CH_4/H_2 ratio was more than 1%, it was observed the shape of diamond particles was changed to ball-like type with few facets, the particle size and density increased. It was inferred that secondary nucleation prevents on existing crystal from growing into a large single crystal. Fig.3 shows the results of X-ray diffraction patterns of the deposited subsrtates. When the CH_4/H_2 ratio is 0.5%, the intensity of diamond crystalline planes(111) and (220) was very dominant, moreover the production of molybdenum carbide such as MoC and Mo_2C increased in some cases with increasing the CH_4/H_2 ratio. Fig.4 shows the results of Raman spectra. When the CH_4/H_2 ratio was 0.5%, it was observed that diamond which has the best crystallinity and purity in all cases. The intensity of the peak decreased around at 1332.5cm^{-1} with increasing the CH_4/H_2 ratio. When the CH_4/H_2 ratio 4 %, it was observed that the weak and broad spectrum at 1400~ 1500cm^{-1}. This spectrum indicated the coexistence of a small amount of non-diamond carbon in the deposited particles. From the above the results, the production of molybdenum carbide increased with increasing the CH_4/H_2 ratio. When the CH_4/H_2 ratio exceeds a certain degree($>$ 3%), it was observed that diamond coexisted non-diamond carbon was synthesized. When the CH_4/H_2 ratio is 0.5%, diamond which has good crystallinity and thick density was synthesizes.

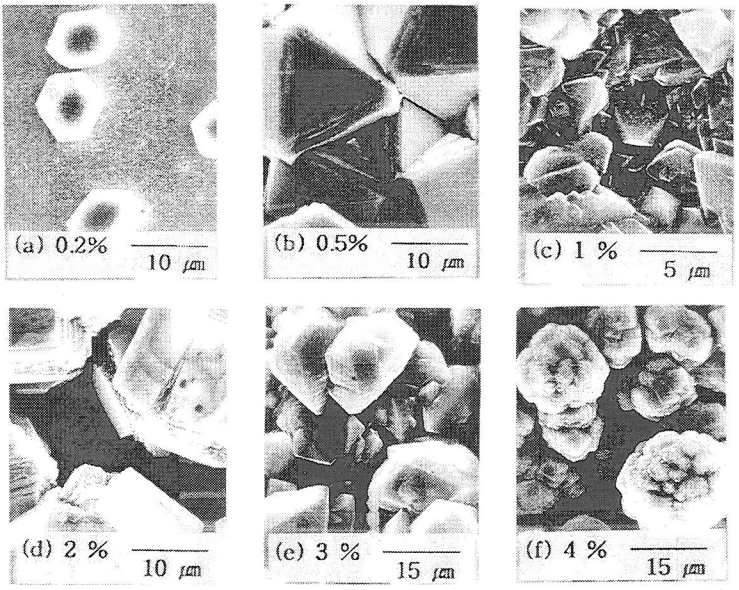


Fig.2. The effect of the ratio of CH_4/H_2

(T_s=1000°C, 760 torr)

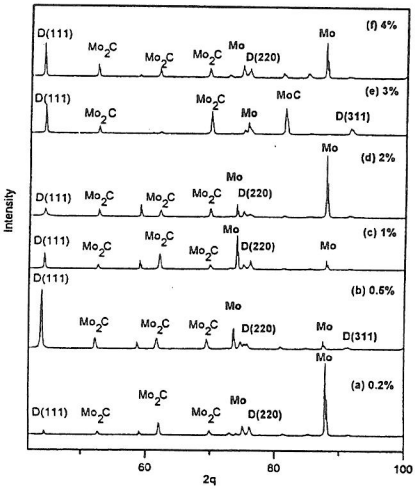


Fig.3. XRD patterns of the deposited diamond (T_s=1000°C, 760 torr)

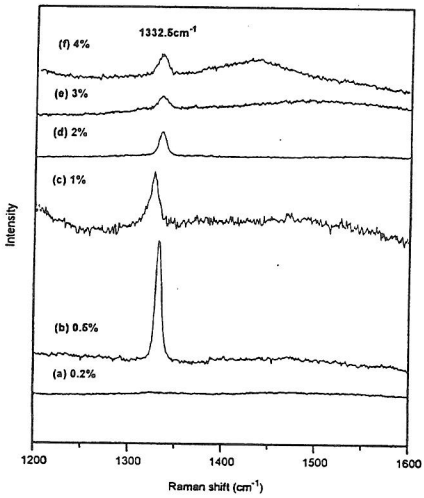


Fig.4. Raman spectra of the deposited diamond (T_s=1000°C, 760torr)

3-2. Experimental results of substrate temperature

Experiments were carried out by changing the substrate temperatures from 800℃ to 1100℃ under the conditions(the CH_4/H_2 ratio 0.5%, power 18~20kW, deposition time 2hrs and at 1 atm). Fig.5 shows the SEM images of surface of the deposited diamond particles at different substrate temperature. In case of 800℃, it was observed that the particles have good crystallinity but density was low. In case of 900℃, it was observed that the density was high in comparison with the case of 800℃. In case of 1000℃, it was observed that diamond which has good crystallinity, the size of crystal and density was synthesized. In case of 1100℃, the crystallinity of particles vanished and the secondary nucleation on existing diamond facets incresed but the size of crystal and density increased.

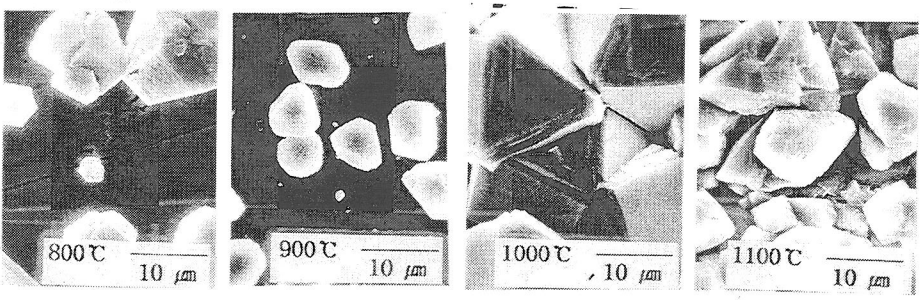


Fig. 5. The effect of the substrate temperature (CH_4/H_2=0.5 %, 760 torr)

Fig.6 shows the results of Raman spectra. The intensity of the peak at 1332.5cm^{-1} increased with increasing the substrate temperature from 800℃ to 1000℃ and the intensity of the peak decreased in case of 1100℃. From the above results, in case of 1000℃, diamond which has good crystallinity and high density was synthesized, the particle size and density increased with increasing the substrate temp.

3-3. Experimental results by using liquid organic precursor.

Diamond was synthesized by using the liquid organic precursor, ethanol. Heated ethanol and carrier gas Ar were flowed into the plasma flame through the injection probe. To avoid the recondensation of ethanol vapor, copper tube which was moved ethanol vapor was wound by the heating coil. Fig.7 shows the SEM images of the morphological variation of the deposited diamond particles under the conditions(power 22kW, substrate temperature 1000℃, deposition time 1 hr and at 1 atm). It was observed cubo-octahedral structure coexisted diamond crystalline planes (111) and (220). In comparison with the case of using methane, a few secondary nucleation on the surface of existing crystal appeared. Fig.8 shows the results of Raman spectra. As a consequence of Raman spectra, it was observed that only one sharp peak at 1332.5cm^{-1}. This peak coincided with the reported value of 1332.5cm^{-1} for natural diamond.

4. Conclusions

1. In R.F.-thermal plasma CVD system, diamond was synthesized on molybdenum substrate by chemical reaction of CH_4 and H_2 at atmospheric pressure. Moreover the synthesis of diamond by using the liquid organic precursor, ethanol instead of CH_4 was possible.
2. Diamond which has good crystallinity and thick density was synthesized when the Ts was 1000℃, the CH_4/H_2 ratio was 0.5%. The secondary nucleation increased with increasing the CH_4/H_2 ratio.
3. Diamond, which has good crystallinity, particle size and density, was synthesized by using the liquid organic precursor, ethanol(0.1 ml/min) instead of methane. The deposited particles were coexisted molybdenum oxide besides diamond particles and molybdenum carbide.

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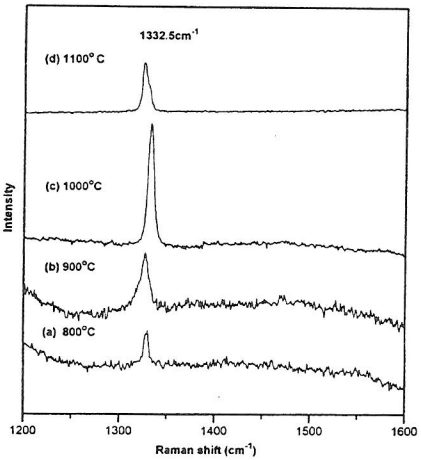

Fig.6. Raman spectra of the deposited diamond (CH_4/H_2 : 0.5%. 760 torr)

Fig.7. SEM (C_2H_5OH=0.1 ml/min, T_s=1000°C, 760 torr)

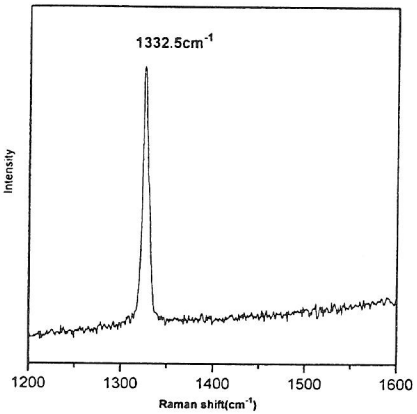

Fig.8 Raman spectra(C_2H_5OH = 0.1 ml/min, Ts = 1273K, 760torr)