# DIAMOND DEPOSITION ON THE SUBSTRATE PRETREATED IN $N_2$-$C_2H_2$ PLASMA

Shinya NARUMI, Takayasu SATO, Shigeru ITO and Kazuo AKASHI

Department of Industrial and Engineering Chemistry, Faculty of Science
and Technology, Science University of Tokyo, 2641, Yamazaki, Noda-
city, Chiba, 278, Japan

## Abstract

Diamond film was deposited on Ti or Fe substrate without any mechanical pretreatment. Generally the mechanical pretreatment for substrate is essential for the deposition of diamond film on it by CVD. It is supposed that C-C bond formed on the surface of the substrate by pretreatment in $N_2$-$C_2H_2$ r.f.(4MHz) plasma generated inductively, plays an important role, in order to promote diamond growth. High quality diamond film was obtained on the pretreated substrate in a short time by the combustion flame CVD. Thus it was demonstrated that this pretreatment is very useful to get high quality diamond film on the substrate without any mechanical pretreatment.

## 1. Introduction

It is well known that mechanical polishing of the surface of various substrates with diamond powder or diamond paste enhances the nucleation density of diamond. The mechanism of commonly applied scratching(polishing) or ultrasonic treatment to promote diamond deposition is not so well understood[1,2]. Iijima et al.[3] have shown the evidence of a high density diamond residue after the mechanical pretreatment, and believe that diamond growth is, in effect, homoepitaxial growth on the residue. But Dennig and Stevenson[4] have also shown that diamond nucleates on sharp geometric features like edges and apexes, without the presence of diamond residue. Plasma treatment, in this work, can produce both C-C bond and the roughness on the surface of the substrate. It is expected for the plasma pretreatment to have the same effect as above-mentioned, and in the recent study, the possibility of the continuous operation of plasma pretreatment and plasma diamond deposition was discussed. A part of this work has already been reported in [5].

## 2. Experimental

Ti substrate was pretreated by r.f. plasma nitriding and carbonitriding processes. Fig.1 shows a schematic illustration of the pretreatment apparatus. The conditions of these pretreatments are following; gas pressure: 45Pa, gas composition: $N_2$:$C_2H_2$=100-90:0-10, substrate temperature: 600-800℃, plasma power: 4kW(4MHz), reaction time: 1-2 hours. The deposition of diamond on the substrates pretreated in these ways was tried. Fig.2 is a schematic illustration of the diamond deposition apparatus. The conditions of diamond deposition are as follows: Gas composition ; $O_2/C_2H_2$=0.87, Total flow rate; 6.45l/min, Substrate temperature; 350-600℃, Reaction time; 10-60min. For comparison, using the surface scratched substrate, the combustion flame CVD for the diamond deposition was also carried out. Here the scratching pretreatment was done for 1 hour with diamond particles (~5 μ m) or SiC particles (~5 μ m) suspended in ethyl alcohol by using an ultra sonic cleaner and then the substrate was washed in acetone for 5 minutes. The surface of the pretreated substrate was investigated by ESCA and AFM. The deposited diamond was characterized by SEM and Raman spectroscopy.

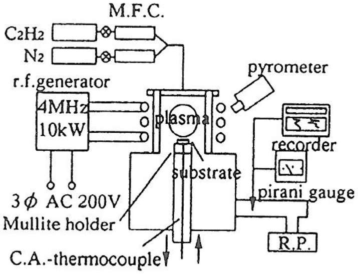


Fig.1. Apparatus for pretreatment

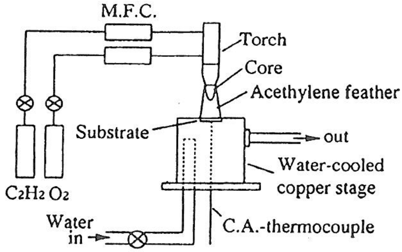
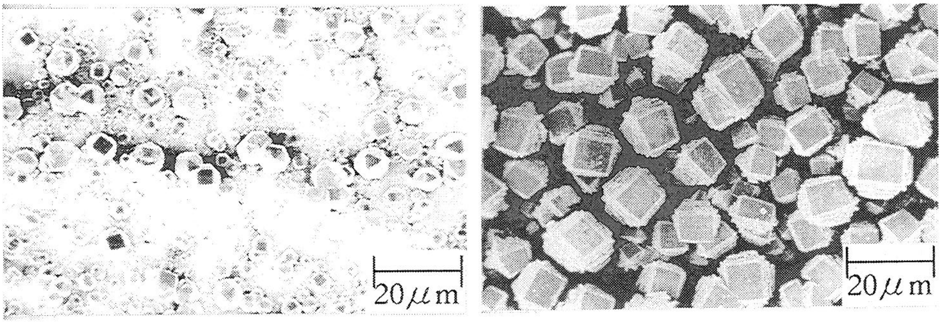


Fig.2. Apparatus for diamond CVD

## 3. Results and discussion

### 3.1 Diamond deposition on Ti(C,N)

Using the Ti substrate pretreated by plasma nitriding, the diamond deposits obtained for 30min and 60min were not films but particles, as shown in Fig.3. On the other hand, as shown in Fig.4, diamond film formed on the plasma carbonitrided substrate in a short time, that is only 10 minutes. Fig.5 shows the result of ESCA measurement, in which C-C bond was detected on this modified surface. The micro-roughness of the surface was measured by AFM. There was hardly any difference in the micro-roughness of the substrates pretreated in $N_2$ and $N_2$-$C_2H_2$ plasma, so the deposition of diamond film must be much enhanced by the presence of carbon species on the surface of the substrate.



(a) (b)

Fig.3. SEM images of diamond deposited on plasma nitrided Ti at 800℃ (Deposition time of diamond (a) 30min (b) 60min)

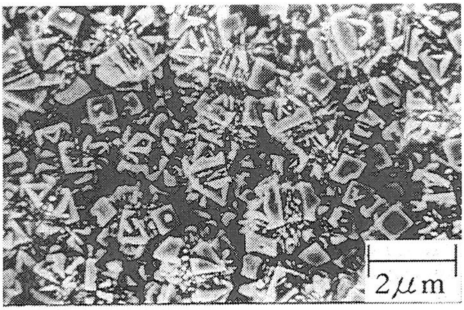


Fig.4. SEM image of diamond deposited on plasma carbonitrided Ti at 700℃, $C_2H_2$ 10%(Deposition time of diamond 10min)

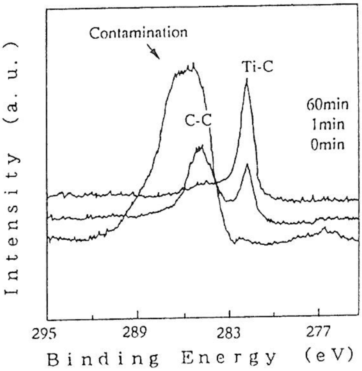


Fig.5. ESCA spectra of plasma carbonitrided Ti(Pretreatment temperature 700℃, $C_2H_2$ 10%)

Moreover, the effect of plasma carbonitriding pretreatment on the deposition of diamond was investigated by changing the gas composition ($C_2H_2$: 1,3,10%) and the substrate temperature (600,700,800℃). It was estimated from Raman spectroscopy that high quality diamond film is obtained at 700℃ with the gas composition of 10% $C_2H_2$. Raman spectrum of diamond film deposited for 30 minutes on the substrate pretreated in above condition was compared with that of diamond film deposited for 30 minutes on the substrate scratched by diamond particles or SiC particles, as shown in Fig.6. It shows that high quality diamond is obtained on the substrate prepared by plasma carbonitriding. SEM images of diamond were shown in Fig.7.

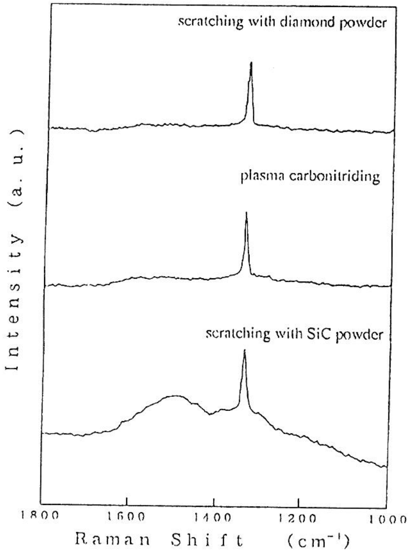
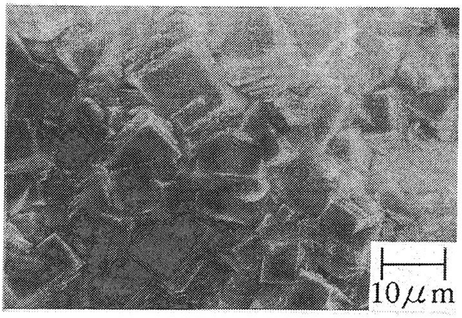
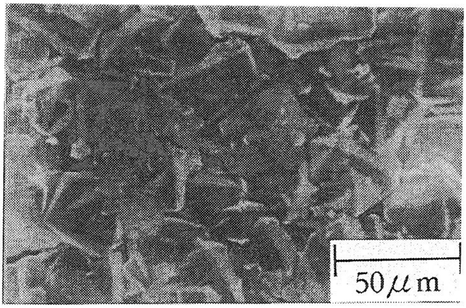


Fig. 6 . Raman spectra of diamond film deposited on substrate after various pretreatments
(deposition time of diamond 30min)



scratching with diamond powder



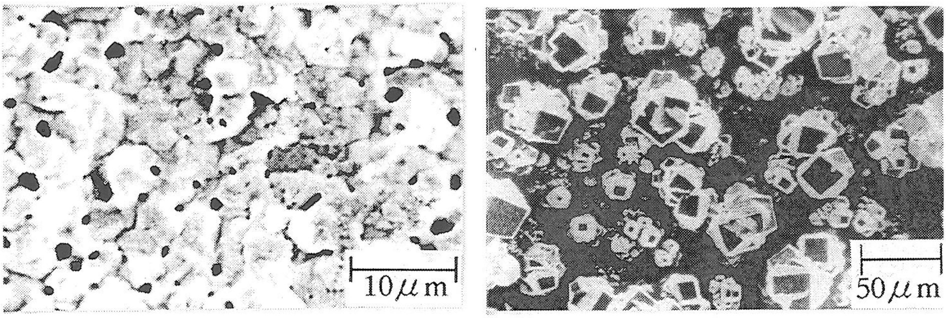
plasma carbonitriding ($C_2H_2$ 10%,700℃)

Fig.7. SEM images of diamond deposited on the substrates after various pretreatments

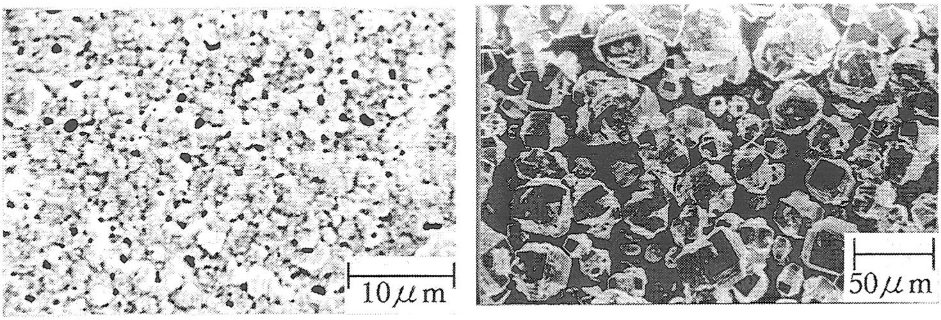
### 3.2 Diamond deposition on Fe(C,N)

Metallic substrate like as Fe, Ni, Co or Pt does not form stable carbides but dissolves carbon, therefore, carbon diffusion into such substrate occurs until the entire substrate is saturated with it. This carbon diffusion can cause melting of the substrate and formation of graphitic and amorphous carbon. It is thought that plasma nitriding or carbonitriding plays a role of barrier layer for carbon diffusion.

At first diamond deposition on the substrate pretreated by plasma nitriding was carried out. Fig.8 shows SEM images of nitrided Fe substrates and diamond deposited on them. As shown in Fig.8, diamond particles were obtained on nitrided Fe substrate(cf. Diamond deposition on Fe substrate under this condition causes melting of the substrate due to carbon diffusion). It seems that nitrided layer plays a role of barrier layer for carbon diffusion. And it is observed that the surface morphology affects the diamond nucleation density.



nitriding temperature: 420℃

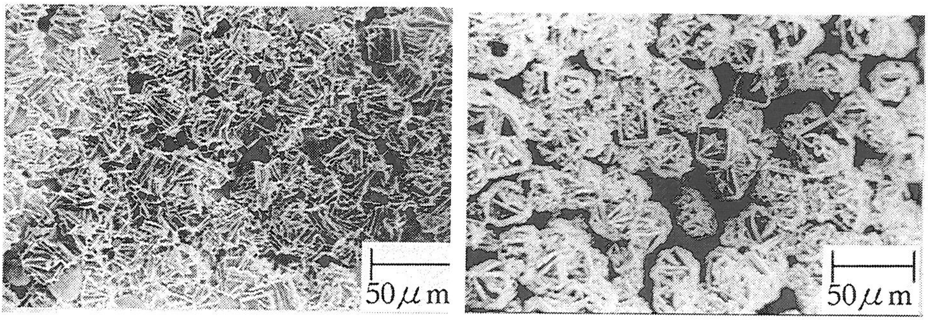


nitriding temperature: 380℃

Fig.8. SEM images of the nitrided Fe substrate(left) and diamond deposited on them(right) (deposition temperature of diamond: 350℃, deposition time: 30min)

Second, using the substrate pretreated by plasma carbonitriding($C_2H_2$ 1%, 380,420℃), diamond was deposited. As shown in Fig.9, diamond film was obtained for 30min. On the other hand, diamond was not deposited on the carbonitrided($C_2H_2$ 3%, 10%) substrate, because the deposit was burned. In the latter case, it is thought that excess carbon species on the surface of the modified substrate caused a large quantity of graphitic component and burning of the deposit.

As these results, it seemed that the surface morphology affected the diamond nucleation density but diamond nucleation and growth were much enhanced by the presence of carbon species on the surface of the modified substrate.



carbonitriding temperature: 420℃ carbonitriding temperature: 380℃

Fig.9. SEM images of diamond deposited on the carbonitrided ($C_2H_2$ 1%) Fe (deposition temperature of diamond: 350℃, deposition time: 30min)

## 4. Conclusions

The investigation of deposition of diamond film without any mechanical treatment was carried out. The deposits obtained on the substrates pretreated by plasma nitriding were not diamond films but particles. On the other hand, diamond films can be formed on the plasma carbonitrided substrates in a short time. The quality of diamond film on the plasma carbonitrided substrate was almost same as that on the substrate scratched by diamond particles.

In this work, it seems that the nucleation density is affected in surface morphology but the diamond nucleation and growth is much enhanced by presence of carbon species on the surface of the modified substrate.

## References

[1] W.A. Yarbrough and R. Messier, Science 247, 688(1990)
[2] W.A. Yarbrough, Mater. Sci. Monographs 73, 25(1991)
[3] S. Iijima, Y. Aikawa and K. Baba, Appl. Phys. Lett. 57, 2646(1990)
[4] P.A. Dennig and D.A. Stevenson, Appl. Phys. Lett. 59, 1562(1991)
[5] T. Sato, M. Negishi and K. Akashi, Hyomen Gijutsu, 45, 1, 106(1994)