Journal of the Korean Chemical Society
2001, *Vol. 45, No. 4*
Printed in the Republic of Korea

수소 플라즈마 에칭과 탄소 확산법에 의한 다이아몬드막 표면의 평탄화

金 聖 薰
신라대학교 신소재 화학과
(2001. 6. 12 접수)

Planarization of the Diamond Film Surface by Using the Hydrogen Plasma Etching with Carbon Diffusion Process

Sung-Hoon Kim
Department of New Materials Chemistry, Nanomaterials Research Center, Silla University, Pusan 617-736, Korea
(Received June 12, 2001)

요 약. 철, 코발트, 니켈 합금을 이용한 탄소확산-수소플라즈마 에칭법으로 다이아몬드 자체막의 표면을 매우 평탄하게 할 수 있었다. 이 방법에서의 다이아몬드 자체막을 합금과 몰리브데늄 기판 사이에 위치시켜 금속-다이아몬드-몰리브데늄(MDM) 샌드위치 형태의 샘플 세트를 이루게 하였다. 이 샘플세트를 마이크로 웨이브 플라즈마 장치에 장착하여 수소 플라즈마를 발생시켜서 기판온도가 섭씨 1,000 이상이 되도록 하였다. 이와 같은 과정들을 탄소확산-수소플라즈마 방법이라고 하였다. 다이아몬드 자체막 표면을 에칭한 후 표면 거칠기, 표면형상, 에칭한 다이아몬드 표면속의 불순물의 침투를 조사하였다. 결론적으로, 탄소 확산-수소 플라즈마 에칭법은 전자 디바이스에 응용할 수 있는 매우 평탄한 다이아몬드 표면을 형성시키는 방법임을 알 수 있다.

ABSTRACT. Planarization of the free-standing diamond film surface as smooth as possible could be obtained by using the hydrogen plasma etching with the diffusion of the carbon species into the metal alloy (Fe, Cr, Ni). For this process, we placed the free-standing diamond film between the metal alloy and the Mo substrate like a metal-diamond-molybdenum (MDM) sandwich. We set the sandwich-type MDM in a microwave-plasma-enhanced chemical vapor deposition (MPECVD) system. The sandwich-type MDM was heated over *ca.* 1000 °C by using the hydrogen plasma. We call this process as the hydrogen plasma etching with carbon diffusion process. After etching the free-standing diamond film surface, we investigated surface roughness, morphologies, and the incorporated impurities on the etched diamond film surface. Finally, we suggest that the hydrogen plasma etching with carbon diffusion process is an adequate etching technique for the fabrication of the diamond film surface applicable to electronic devices.

INTRODUCTION

The achievement of the etching of the diamond film surface is essential to overcome the limitations, mainly caused by the surface roughness, for the practical application of the diamond film to electronic devices.[1,2] However, etching the diamond film surface has been regarded as the most difficult barrier to be overcome, due to the highest hardness and chemical inertness of diamond.[1]

Up to the present, many attempts have been tried to etch the diamond film surface as smooth as possible.[1-3] Among these attempts, the diffusion techniques have been regarded as a promising way to efficiently etch the diamond film surface.[3-8] The mechanism of these techniques were based on the catalytic chemical reaction between diamond and metal substrates, such as Ce,[3]

Mn,[4] Ce-Ni,[5] Fe,[6,7] rare earth metals,[8] and so forth. In this case, diamond could be readily converted into soft carbon species like graphite by the catalysis reaction under the appropriate temperature (600~1,000 °C) condition. Then, the converted soft carbon species diffused into the substrate. As an alternative technique for etching the diamond film surface, a plasma technique, such as ion beam etching,[9-11] reactive ion etching,[12] or electron cyclotron resonance (ECR) plasma,[13] has been introduced. This technique uses active chemical ion species, which could come from O_2,[9,10] Ar,[11] SF_6,[12] air,[13] and so forth. These ion species would react with the protruded diamond grains on the film surface and convert them into soft carbon species. Therefore one could polish the sharp tips of the diamond film surface by etching away the converted soft carbon species. Furthermore, in comparison with a diffusion technique, one might enhance the selectivity of the polished area via the masking process.[13]

Despite many attempts for etching the diamond film, it still requires the enhancement of the etching efficiency and the selectivity for the practical application. In this paper, we introduce a new technique for effectively etching the diamond film surface by combining a diffusion technique and a plasma etching technique. We call this technique as the hydrogen plasma etching with carbon diffusion process. This process can give not only the enhancement of the etching efficiency but also the possibility of the selective polishing by masking process. Detailed processes to obtain a very fine etched state of the diamond film surface, the characteristics of the etched area, and the reason for the enhancement of the etching efficiency are presented and discussed.

EXPERIMENTAL SECTION

For the hydrogen plasma etching with carbon diffusion process, we made the sandwich-type MDM by placing the flat-type metal alloy (Fe, Co, Ni) onto the as-grown surface of free-standing diamond films and mounted them onto the Mo substrate as shown in *Fig.* 1. Before placing the metal alloy onto the film, we polished the metal alloy surface as smooth (below 0.1 μm) as possible. The sandwich-type MDM was set in the reaction chamber of MPECVD system and heated merely by the hydrogen plasma. Free-standing diamond films having

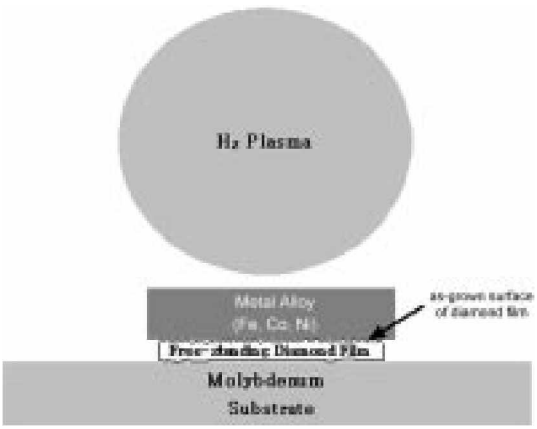

Fig. 1. Schematic diagram of the sandwich-type metal-diamond-molybdenum (MDM) sample set.

ca. 350 μm film thickness were obtained as the previous report.[14]

The detailed conditions for the hydrogen plasma etching with carbon diffusion process of free-standing diamond films are as follows: H_2 gas flow rate = 200 standard cm^3 per minute (sccm), total pressure = 60 Torr, microwave power = 2,000 watt, and reaction time = 20 min, respectively. The substrate was merely heated by the hydrogen plasma and its temperature was measured as *ca.* 1,100 °C by using the optical pyrometer.

After the etching process, the surface roughness and morphologies of the diamond film surface were closely investigated using atomic force microscopy (AFM, PSI CP) and scanning electron microscopy (SEM; Hitachi E-201), respectively. Diamond qualities and the residual impurities of the diamond film surface were also investigated by using micro-Raman (Renishaw 3000) and Auger spectroscopy (VG Scientific, microlab 310-D), respectively.

RESULTS AND DISCUSSION

After the hydrogen plasma etching with carbon diffusion process, we compared the surface morphologies of the diamond film before and after the etching process. *Fig.* 2a and b show the optical photographs of the etched diamond film surface (*Fig.* 2a) with the as-grown diamond film surface (inset of *Fig.* 2a) and the surface of the metal alloy (*Fig.* 2b), which has been placed onto the

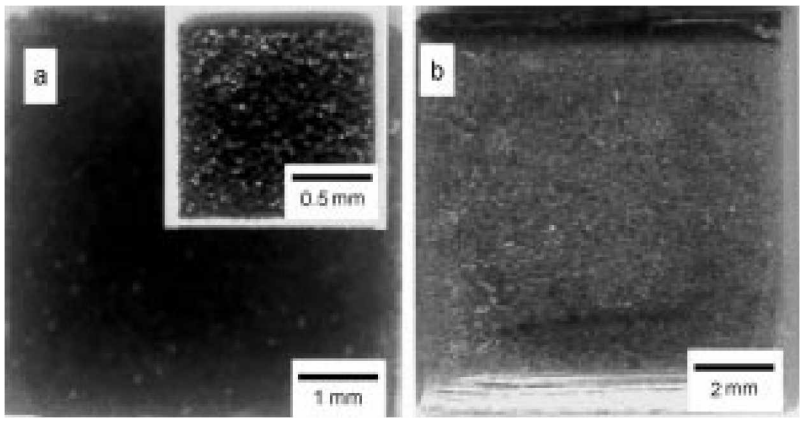

Fig. 2. Optical photographs of (a) the etched diamond film surface with as-grown diamond film surface (inset) and (b) the metal alloy which was placed on the as-grown free-standing diamond film surface.

diamond film surface during the plasma diffusion etching process, respectively. By comparing *Fig.* 2a with its inset, we can obviously observe that a rough surface state of as-grown diamond film transformed into a smooth one by the hydrogen plasma etching with carbon diffusion process. Using the micrometer for thickness measurement, we obtained the film thickness as *ca.* 250 μm. We defined the etching efficiency as the reduced film thickness by the etching process per minute. In this work, the etching efficiency is calculated as *ca.* 5.0 (μm/min). This value is regarded as a higher one for the diamond etching rate, as compared with other reports.[2]

As shown in *Fig.* 2b, we can find a trace of the depressed mark on the metal alloy surface, according to the film shape. It obviously indicates the occurrence of the massive reaction between the film and the metal alloy. So, we suggest that this massive reaction may assist the etching efficiency by pressing the diamond film surface.

We also investigated the detailed surface morphology of the etched surface by using SEM. Compared with the as-grown one (*Fig.* 3b), the under-developed grains and the relatively tiny grains were observed on the etched surface as shown in *Fig.* 3a. Obviously, the under-developed grains (*Fig.* 3a) were able to form a smoother surface, as compared with the well-developed grains (*Fig.* 3b). In addition, the grain size is in proportional to the film thickness, so the relatively tiny grains on the etched surface were considered to be a typical phenomenon after thinning the film thickness by the etching process.

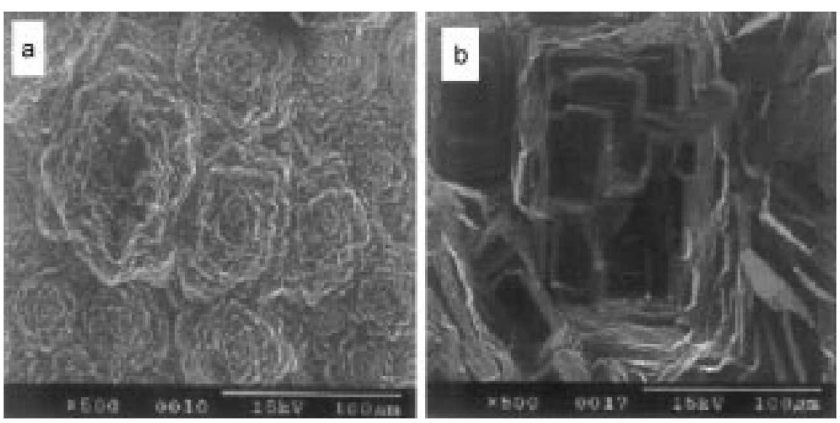

Fig. 3. SEM images of (a) the etched diamond film surface and (b) the as-grown diamond film surface.

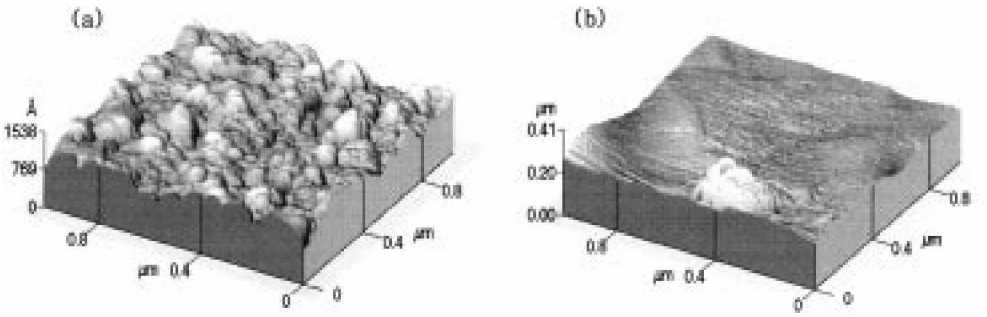

Fig. 4. AFM images of (a) the etched diamond film surface and (b) the metal alloy surface.

Average surface roughness (Ra) of the etched surface, measured by using AFM, shows a comparable value (*ca.* 100 nm) as that of the polished metal alloy surface (compare *Figs* 4a with b). Due to the higher roughness of the free-standing diamond film surface, we could not measure the exact roughness value of the as-grown diamond film surface. However, we consider that the surface roughness value of the as-grown film surface might be over a few tens micrometers, according to the grain size as shown in *Fig.* 3b. So, we can undoubtedly confirm the smoothness of the etched diamond film surface by the hydrogen plasma etching with carbon diffusion process.

From these results, we can suggest that the hydrogen plasma etching with carbon diffusion process can effectively etch the as-grown surface of the free-standing diamond film. Finally, this process could readily lead to a smooth diamond film surface applicable to the diamond electronic devices. We suggest that the cause for these results may be come from the synergy effect of a diffusion process and a plasma etching process as shown in *Fig.* 5. Namely, the hydrogen plasma species would react with the protruded diamond grains on the film surface and could convert them into the soft carbon species like graphite. In addition, the protruded diamond grains could be readily converted into soft carbon species by the catalysis reaction of the metal alloy under the relatively high temperature condition, as the previous report[7]. Then, the converted soft carbon species could be etched away, via $C + 2H_2 \rightarrow CH_4\uparrow$, or diffused into the metal alloy via the solid solution reaction.[8] This is why we call this process as the hydrogen plasma etching with carbon diffusion process.

Undoubtedly, metal components in this metal alloy

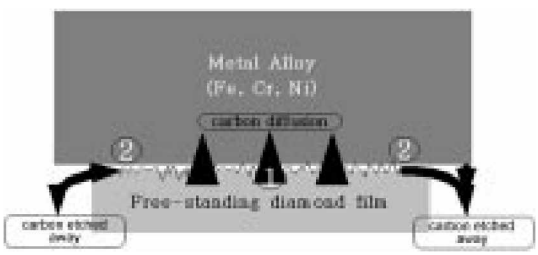

Fig. 5. Schematic diagram of (1) the converted carbon species diffusion into the metal alloy and (2) the etched away of the converted carbon species.

lso have a chance to penetrate into the etched diamond film surface during the etching process and act as impurities in the film. The impurities in diamond film would deteriorate the performance of the diamond electronic devices. To investigate the impurities in the etched diamond film, we carried out Auger spectroscopy measurement as a function of the film depth. *Fig.* 6 shows the depth profile of the etched diamond film. For a depth profile, we sputtered the film at a rate of *ca.* 0.1 nm/sec. We did not find any distinct impurities incorporation, such as Fe, Cr, O, and Ni in the film with the depth. This result reveals that the possibility of the metal components transfer from the metal alloy or the impurities incorporation, which might come from the residual gas in the chamber, into the etched diamond film would be rare during this process.

As shown in *Fig.* 7, the depth profile investigation of the metal alloy was also performed. Noticeably, the carbon component was dominant at the surface of the metal alloy. It obviously reveals that the mass transfer, as a carbon form, has occurred from the diamond film into the

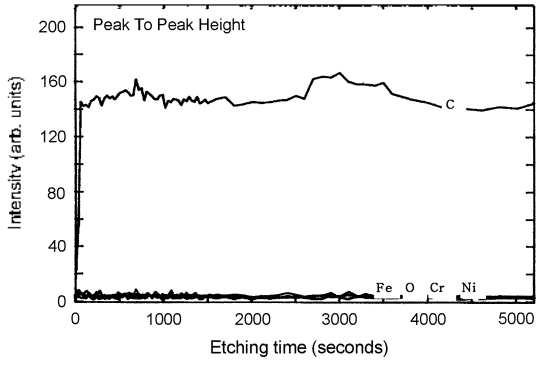

Fig. 6. Auger spectrum of the depth profile for the etched diamond film.

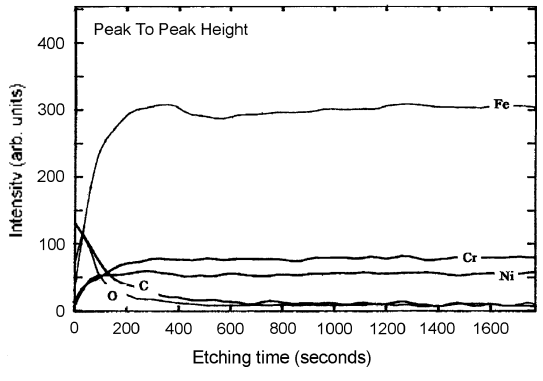

Fig. 7. Auger spectrum of the depth profile for the metal alloy.

metal alloy during this process. The oxygen could be also detected around the surface of the metal alloy (See *Fig.* 7). These results confirm that carbon transfer from the diamond film and oxygen incorporation into the metal alloy would be possible during this process. On the contrary, the metal components transfer from the metal alloy and impurities incorporation from the residual gas into the etched diamond film surface would be rare. We suggest that the different atomic size and the solid solubility may be the main reason to understand the mechanism of these results.[8]

CONCLUSIONS

The hydrogen plasma etching with carbon diffusion process can effectively etch the as-grown surface of the free-standing diamond film via the synergy effect of a diffusion process and a plasma etching process. Furthermore, this process accompanies the pure etched surface without metal components transfer from the metal alloy and the impurities incorporation from the residual gas in the reaction chamber. Consequently, this process can readily produce the smooth and pure diamond film surface applicable to diamond electronic devices.

Acknowledgement. This work was supported by grant No. (2000-1-12100-002-1) from the Basic Research Program of the Korea Science & Engineering Foundation.

REFERENCES

1. Moustakas, T. D. *Synthetic Diamond: Emerging CVD Science and Technology*; Spear K. E., Dismukes J. P., Ed.; John Wiley and Sons Press: New York, U.S.A. 1994; p 145.
2. Malshe, A. P.; Park, B. S.; Brown, W. D.; Naseem, H. A. *Diamond and Related Materials* **1999**, *8*, 1198.
3. Jin, S.; Zhu, W.; Siegrist, T.; Tiefel, T. H.; Kammlott, G. W.; Graebner, J. E.; McCormack, M. *Appl. Phys. Lett.* **1994**, *65*, 2675.
4. Jin, S.; Graebner, J. E.; Tiefel, T. H.; Kammlott, G. W.; Zydzik, G. J. *Diamond and Related Materials* **1992**, *1*, 949.
5. McCormack, M.; Jin, S.; Grabner, J. E.; Tiefel, T. H.; Kammlott, G. W. *Diamond and Related Materials* **1994**, *3*, 254.
6. Jin, S.; Graebner, J. E.; Kammlott, G. W.; Tiefel, T. H.; Kosinski, S. G.; Chen, L. H.; Fastnacht, R. A. *Appl. Phys. Lrtt.* **1992**, *60*, 1948.
7. Tokura, H.; Yoshikawa, M. *Applications of Diamond Films and Related Materials*; Tzeng, Y. Ed.; Elsevier: New York, U.S.A., 1991.
8. Jin, S.; Graebner, J. E.; McCormack, M.; Tiefel, T. H.; Katz, A., Dautremont-Smith, W. C. *Nature* **1993**, *362*, 822.
9. Grogan, D. F.; Zhao, T.; Bovard, B. G.; Macleod, H. A. *Applied Optics* **1992**, *31*, 1483.
10. Bovard, B. G.; Zhao, T.; Macleod, H. A. *Applied Optics*, **1992**, *31*, 2366.
11. Ilias, S.; Sené, G.; Möller, P.; Stambouli, V.; Pascallon, J.; Bouchier, D.; Gicquel, A.; Tardieu, A.; Anger, E.; Ravet, M. F. *Diamond and Related Materials* **1996**, *5*, 835.

12. Vivensang, C.; Erlazzo-Manin, L.; Ravet, M. F.; Turban, G.; Rousseaux, F.; Giequel, A. *Diamond and Related Materials.* **1996**, *5*, 840.
13. Buchkremer-Hermanns, H.; Long, C.; Weiss, H. *Diamond and Related Materials* **1996**, *5*, 845.
14. Kim, S.-H.; Bae, E.-J.; Lee, S.-H.; Kim, Y.-H.; Kim, T.-G.; Lee, S. K.; Kim, D. U. submitted in *Diamond Films and Technology* 2001.