The Korean Journal of Ceramics, **2** [4] 184 - 187 (1996)

Nucleation of CVD Diamond on Various Substrate Materials

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(Received November 5, 1996)

Diamod nucleation by mw assisted CVD was examined various conditions namely, (1) diamond nucleation on variour substrate materials, such as Si, cubic BN, pyrolytic BN and AlN, (2) AST(Activated species transport) method which promote nucleation of diamond on single crystal and polycrystalline alumina substrate was developed. (3) Effect of bias enhancement of nucleation on single crystalline Si was examined, and finally (4) DST (Double step treatment) method was developed to enhance diamond nucleation on Ni In this method, we separated carbon diffusing process into Ni, carbon precipitating process from the inside of Ni and diamond precipitation process

Key words : Microwave plasma CVD, Nucleation od Diamond, Method of enhancement of diamond nucleation

I. Introduction

It is known that the substrate holder contaminate diamond in microwave-CVD process. We investigated boron content in the diamond film deposited on a Si single crystal using hBN as holder material.[1] Boron was detected in the diamond film by SIMS. Such result indicates to an idea of control nucleation density of diamond particle using various holder materials. Among them, diamond holder is most interesting to supply carbon source to the substrate. Because, diamond species will transfer to the substrate.

Spitsyn[2] has reported the transport of carbon species from graphite source to diamond substrate in a closed tube by the hot filament method. We named such method was carried was carried out by surrounding the substrate with diamond powder. Alumina ceramic amd saphire substrate were used.[3] We have tried another approach to increase uncleation density of the diamond, which plant substrate with fine cluster diamond particle. This method could be increased uncleation density.[4]

Yugo *et al*[5] have shown that the nucleation density of diamond on mirror-polished silicon substrates was markedly increased by negative biasing the substrate, so-called bias enhancement nucleation (BEN). We studied the variation of diamond nucleation density in plasma CVD as a function of BEN conditions.[6]

We present a method of increase nucleation density on Ni substrate avoiding graphite deposition on the surface by double step heat treatment (DST).

In this paper, we discuss and compared various methods for the enhancement of nucleation density of diamond in plasma CVD method.

II. Experimental

NIRIM type microwave plasma CVD apparatus (2.45 GHz) was used throughout the study. Mixed methane and hydrogen gas of various contents were used.

The relation between input power and substrate temperature measured by optical thermometer. Diamond particle deposited on the substrates were observed by scanning elecron microscope (SEM, JEOL JSM-5200). The X-ray photoelectron spectroscopy (XPS, Perkin Elmer, ESCA A5500) was used for the measurements.

1. Activated species transport

In a simple example of AST method, we placed diamond powder around the substrate. As shown in Fig. 2. SEM image of the diamond particles on alumina and sapphire showed distinct enhancement of nucleation density by AST method. In this case, 1% methane and hydrogen mixed gas of 40 torr was used at 900-1000°C for 2 h to deposit diamond in a microwave plasma CVD Grain size of the diamond powder used as a carbon source surrounding the substrate was 165-197 μm. We chnaged grain size of diamond powder, but no difference of the sizes of the deposited diamond. An XRD pattern and Raman shift of the diamond deposited on alumina suggested no distinct difference of quality of the diamond film.

We tried deposition of diamond using pure hydrogen by AST method. If carbon species could be activated and transported from the source zone onto the substrate sur-

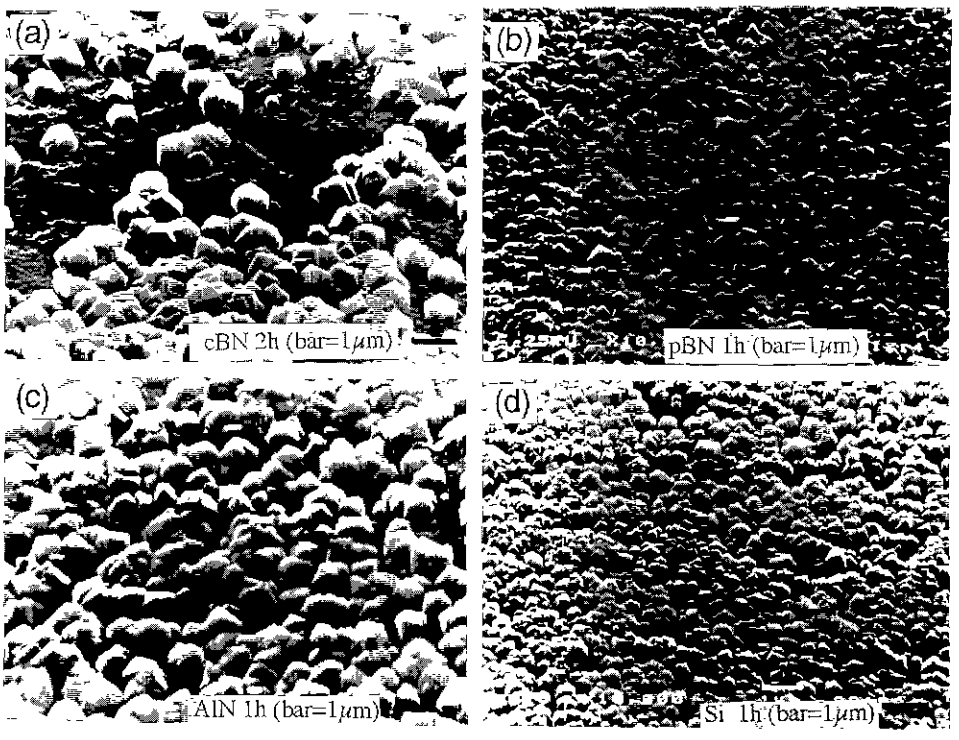

Fig. 1. SEM images of the diamond film deposited on cBN, pBN, AlN ceramics Si. The condition of the deposition: substrate temperature 850°C measured by optical thermometer, gas concentration $CH_4(H_2+CH_4)$=0.6%, gas flow sccm, gas pressure 40 torr, substrate holder alumina

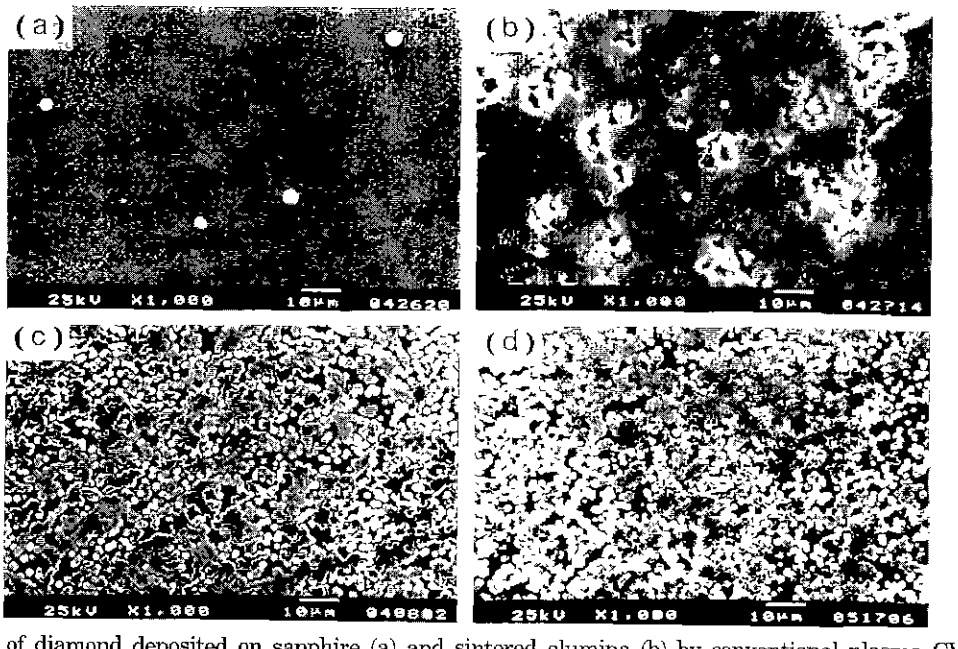

Fig. 2. SEM images of diamond deposited on sapphire (a) and sintered alumina (b) by conventional plasma CVD method. These data showed very small nucleation density of diamond (c) and (d) show almost film like diamond deposition by AST on sapphire and on alumina, respectively. It must be noted that secondary nucleation of diamond showing multi-layered structure is observed.

face in AST method. diamond deposition may occur in pure hydrogen. We found occasionally diamond particles but results were not reproducible.

Spitsyn *et al.*[2] have shown that chemical trasport from the graphite source to natural diamond seed was occured in hydrogen gas. This mechanism can be explained due to rapid etching of carbon from graphite surface and temperature gradient between graphite and diamond. Tem-

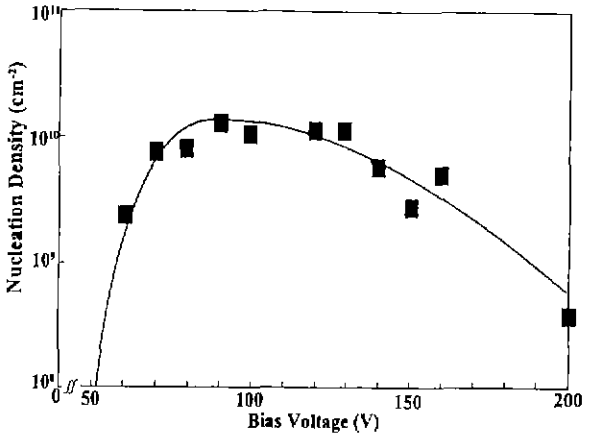

Fig. 3. Nucleation density as a function of bias voltage obtained under the following conditions. Pressure in reacter 15 torr, methane concentration 30%, deposition time 8 min, microwave power 900 W.

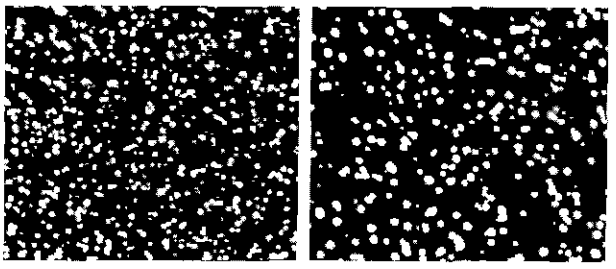

Fig. 4. SEM images of diamond particles deposited under 80 V bias (a) and 140 V bias (b) in 30% methane 15 torr gas at 900 W of microwave power for 8 min.

perature gradient in our experiment may be small or reversible. At the initial stage of AST, the concentration gradient of diamond species could be assumed and it decreases with increasing amount of diamond deposition. This scheme can well explain the preferential secondary nucleation on the as-grown diamond surface observed later stage of the deposition by AST.

We believe that AST method can be increase nucleation density at the initial stage of deposition. If we could found way to increase surface migration of diamond particle and to avoid secondary nucleation on diamond.

2. Bias enhancement nucleation

Nucleation density of diamond particle on mirror-polished Si is shown in Fig. 3. Nucleation density was changed with bias voltage and showed a peak at about 90 volt. The data was obtained in 15 torr gas pressure, 30% methane concentration at 900 W of microwave power for 8 min. The SEM photographs of the diamond with changing vias voltage are also illustrated in Fig. 4.

Figure 5 shows an X-ray photoelectron spectrum (XPS) to analyze bonding energy of carbon formed before the diamond nucleation. Duration of the deposition were select-

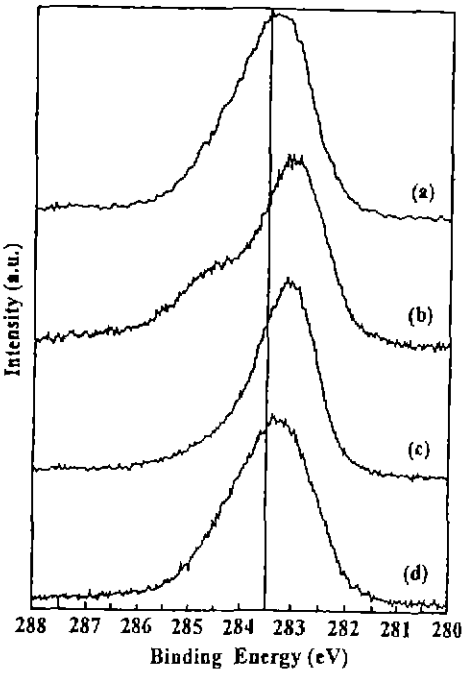

Fig. 5. XPS of carbon ls of the substrate at 50 V bias, 8 min. (a) and 80 V bias for 3 min. (b) 100 V bias for 3 min. (c) and 200 V bias for 3 min.

ed for 3 min. to observe pre-deposition stage. The C_{1s} spectra of the specimen treated at 80 V and 100 V shifted to the lower energy side indicating increase of sp^3 component of amorphous carbon or SiC. The increase in the concentration of sp^3 bond in carbon phase may enhance the diamond nucleation.

This conclusion is consistent with the mechanism suggetsed by Yugo *et al*[5]: carbon ion is accelerated to the substrated by the bias voltage to form sp^2 noncrystalline clusters, but these clusters were removed and transformed into sp^3 clusters through collision of carbon ions and etching by hydrogen ion.

The similation based on (1) optimum voltage to get high nucleation density and (2) energy loss of precursor by the migration on the surface could be valid BEN process in such as data shown in Fig. 3.

III. Results and Discussion

1. Deposition of diamond the ceramic substrate

We tried diamond deposition on pyrolytic BN (pBN), high pressure sintered high cubic BN polycrystal, AlN substrates. We used 40 torr gas of 0.6% methane content and deposited at 850°C for various time between 5 and 180 min. Si substrate used as a standard to evaluate nucleation density of the diamond. The substrates were polished using 6 μm and 3 μm diamond powder and then lapped by 0-1 μm diamond powder. Figure 1. showed typical SEM photographs of diamond particles deposited on substrates. Nucleation density of diamond on AlN, pBN were almost similar to the Si. The uncleation density of

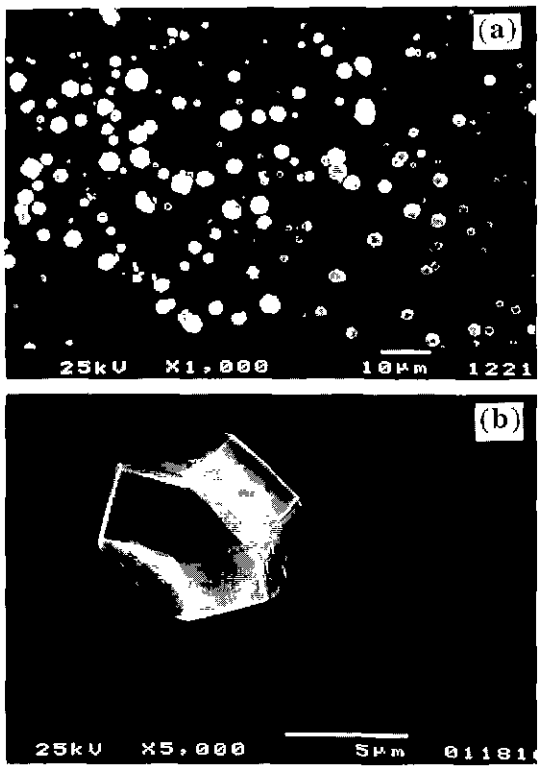

Fig. 6. (a) Diamond particle deposited on polycrystalline Ni substrate by DST method. The diffusion process was carried out at 1050°C for 1h under 85 torrr 3% methane and then deposition process: 950°C for 1.5 h ander 45 torr 3% methane cocentration. (b) enlarged photograph of the diamond particle showing regular cubo-octahedral morphology.

diamond, however, was smaller on cBN. No obvious increase of the nucleation density was observed after 30 min. deposition and final grain size of diamond was ranging 0.3-0.6 μm for all substrates examined in this study.

We can conclude at least that the nuceation density of the diamond were same order of magnitude for the examined substrates because these substrate have same order of lattice mismatch to the diamond. We have no reasonable explanation of relatively lower density of cBN because cBN has smallest lattice mismatch among the substrates examined in this study.

2. Double step heat treatment for the diamond deposition on nickel

As Ni react with hydrocarbon at hight temperature, graphite or amorphous carbon are easily formed on the suface of Ni. Diamond formed with small nucleation density on the graphite deposited on the Ni. Longer depositing time (about 10 h) was needed to get obvious deposition by conventional single step deposition.[7] We developed double stage heat treatment (DST) for diamond deposition on Ni. In this process, we treated Ni substrate at 1050°C in 3% methane of 85 torr pressure for 0.5 h to diffuse carbon into Ni, then we decreased temperarure suddenly to 950°C and kept for such as 1.5 h to deposite diamond on Ni. Lattice parameter of Ni of the sample quenched from 1050°C was mesured by XRD technique. It was located intermediate value between starting Ni and HPHT treated Ni in graphite. This data suggested diffusion of carbon into Ni at relatively high temperature in plasma. The quched and maintaining stage at 950°C, we can deduce that carbon species precipitate on the Ni surface because carbon was super saturated in Ni at 950°C.

We observed diamond deposition on Ni as shown in Fig. 6(a) and (b) showing about 3-4 μm size deposition of diamond particles which showed regular octahedral morphology.

We believe this process can applicate the deposition of diamond on the substrates of highly carbon soluble metals such as Ni, Co and Fe.

References

1. H. Hirai, O. Fukunaga and O. Odawara, "Effect of Microwave Power on Hydrogen Content in Chemically Vapor Deposited Diamond Film," *J. Am. Ceram. Soc.*, **74**[1], 1715-18 (1991).
2. B V. Spitsyn, L. L. Bouilov and B. V. Deryagin "Vapor Growth of Diamond on Diamond and Other Surfaces," *J. Cryst. Growth*, **52**, 219-26 (1981).
3. Xin Qiao, O. Fukunaga, N. Shinoda and K Yui, "Enhancement of diamond nucleation on alumina substrates by the activated species transport method," *Diamond and Related Materi.* **5**[10], 1096-1102.
4. O. Fukunaga, "Prepartion of Functional Diamond Film by CVD Method," *Res. Report Asahi Glass Fundation*, **61**, 301-11 (1992), in Japanese.
5. S Yugo, T, Kanai and T. Kimura, "A new method for the generation of diamond nuclei by plasma CVD," *Diamond and Related Mater.*, **1**[2/4], 388-91 (1992).
6. Y. Ma, T. Tsurumi, N. Shinoda and O. Fukunaga, "Effect of bias enhanced nucleation on the nucleation density of diamond in microwave plasma CVD," *Diamond and Related Mater*, **4**[12], 1325-30 (1995).
7. R. Haubner, A. Lindlbauer and B. Lux, "Diamond deposition on chromium, cobalt and nickel substrates by microwave plasma chemical vapour deposition," *Diamond and Related Mater.*, **2**[12], 1505-15 (1993).