

Synthesis of diamond film and UNCD on BeCu substrate by hot filament CVD

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Diamond film and ultrananocrystalline diamond (UNCD) film were synthesized on BeCu alloy substrate by using hot filament CVD apparatus. We succeed in the synthesis of diamond film and Boron-doped electrically conductive diamond film on the substrate. Moreover, UNCD film was successfully synthesized by the CVD apparatus, although this film was not electrically conductive electrically conductive. At the first stage of the CVD process for UNCD, needle-shape deposits appeared. A two-step process, that is, the synthesis of UNCD and then boron-doped diamond, was effective for the synthesis of the electrically conductive diamond film having smooth surface.

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1. Introduction

In the field of semiconductor manufacturing, all products are checked after the “front-end process” and after the post process. For these test processes, the electrical contacts are pushed to the electrode of the measured products, and then a current is applied to the products via the electrical contacts. For “the post process”, the shape of the electrical contact is complicated because the setting for the measurement must be established. In general, Au-coated BeCu alloy or Au-coated carbon tool steel was used as the electrical contacts because these materials are easily deformed.

For the electrical contact material used in the test process during semiconductor manufacturing, the following properties are required: wear resistance, high electrical conductivity, and antifouling property. It is well known that diamond is a very hard material. Therefore, a lot of research studies have been performed for the application of diamond as a cutting tool.¹⁾ Moreover, it is known that boron-doped diamond contacts electricity and that heavily doped diamond is a superconductor.²⁾ Diamond is difficult to bond to other materials. This property is a disadvantage in the application of diamond in many cases. However, this property is suitable for electrical contacts in semiconductor manufacturing. As mentioned above, the electrically conductive diamond coating has properties necessary for an electrical contact material to be used in the testing process of semiconductor manufacturing. Therefore, if an electrical conductive diamond film is applied to the coating of electrical contacts, a high performance electrical contact could be fabricated. We have attempted to use electrically conductive diamond film as a coating for electrical contacts for use in the testing process in semiconductor manufacturing.³⁾ However, we must optimize the synthesis conditions for practical use. There are various kinds of shapes of electrical contacts in the testing process. For the probe-type, an uneven surface is favorable because it can break through the oxidized surface of the electrode for the product. Therefore, the conventional electrically conductive diamond film synthesized by CVD process is suitable for the

coating of the probe-type electrical contact because the surface is usually uneven. On the other hand, for the blade-type electrical contact, a flat surface is favorable because the contact point must slide on the electrode surface. Therefore, the electrically conductive ultrananocrystalline diamond (UNCD) is suitable for the coating of the blade-type electrical contact because its surface is rather smooth.

In semiconductor manufacturing testing processes, BeCu alloy is used as the base material for the electrical contact because the BeCu alloy has the highest hardness (~1400 MPa) of alloys based on Cu and because the electrical conductivity of the BeCu alloy is relatively high. Moreover, BeCu alloy is used as a structural material in various fields because of its workability. Therefore, the coating of the BeCu alloy with the diamond film or UNCD should be significant for various applications.

Some research studies have already been performed for the diamond deposition on a Cu substrate.^{4)–13)} However, most of these studies were performed not for the coating with the diamond for mechanical use but for the epitaxial growth of the diamond synthesized by CVD process. As for the BeCu alloy substrate, there is few reports for the deposition of diamond film except for our study.³⁾

Some studies have reported the deposition of UNCD. Although the UNCD consists of not the pure diamond phase but a hybrid material that contains sp^3 carbons and sp^2 carbons, the surface of the UNCD is smoother than that of the conventional diamond film synthesized by CVD process. Therefore, studies have investigated the use of UNCD as a MEMS material.¹⁵⁾ Although a few researchers have used a hot filament CVD apparatus for the synthesis of the UNCD,¹⁶⁾ most of the samples have been synthesized by a microwave plasma CVD apparatus.¹⁷⁾ Moreover, Si was used as the substrate in the CVD process. As for the BeCu alloy substrate, few papers have appeared thus far.¹⁴⁾ The purpose of this research was to apply coating containing a nanostructure diamond film on the seal of diamond anvil cell. Therefore, using hot filament CVD apparatus, the synthesis of electroconductive diamond on BeCu alloy for electrical application and coating with UNCD on BeCu alloy substrate is valuable for new applications of diamond material. In this study, we attempted to

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Table 1. The CVD conditions for synthesis on the BeCu alloy substrate

	H ₂ /CCM	TMB diluted with H ₂ /CCM	CH ₄ /CCM	CH ₄ concentration	Power /W	Distance /mm	Time /hour	Holder
1-1	200	20	2	0.9	250	7	2	porcelain
1-2	195	0	5	2.5	300	4-6	2	porcelain or Cu
1-3	195	20	5	2.3	300	5	2	Cu
1-4	141	20	5	3.0	250	4	2	Cu
1-5	100	20	5	4.0	250	4	2	Cu
1-6	75	20	5	5.0	250	4	2	Cu

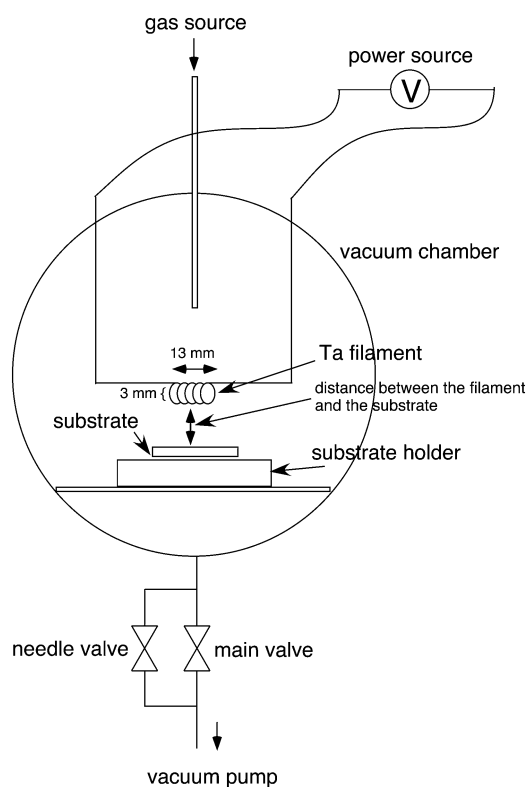


Fig. 1. Schematic of the CVD apparatus used in this study.

synthesize electroconductive diamond and electroconductive UNCD on a BeCu alloy as a base for the application of electrical contact.

2. Experimental

The BeCu alloy (alloy25, 5 mm*5 mm*0.25 mm) was used as the substrate of the CVD process. A hot filament CVD apparatus was used for the CVD synthesis process in this study. The schematic of the CVD apparatus used in this study is shown in Fig. 1. The apparatus has a filament, measuring 13 mm*3 mm, in a vacuum chamber. The vacuum chamber was vacuumed by an oil-sealed rotary vacuum pump. The gas sources were introduced in the vacuum chamber, whose pressure was controlled by a needle valve. A tantalum filament was used for the CVD process. For the CVD process of the diamond film, CH₄, H₂, and H₂-diluted trimethylboron (TMB) (910 ppm) were used as gaseous source. The synthesis conditions are summarized in Table 1. For the synthesis of UNCD, CH₄, H₂, Ar, and N₂ were used as gaseous source. The synthesis conditions are summarized in Tables 2-4. The surface morphologies of the samples were observed by SEM. Raman spectrometry (excitation wavelength: 532 nm) was used for confirmation of the crystal phases of the deposits. AFM measurements were also performed for the observation of the

Table 2. CVD conditions for the synthesis of UNCD film

	Ar /CCM	H ₂ /CCM	CH ₄ /CCM	CH ₄ /(CH ₄ + H ₂) × 100 /%	Ar /(Ar + H ₂) × 100 /%
2-1	80	120	3.0	2.44	40
2-2	80	120	2.0	1.64	40
2-3	80	120	1.2	0.99	40
2-4	80	120	1.0	0.83	40
2-5	80	120	0.8	0.66	40
2-6	80	120	0.6	0.50	40

Table 3. CVD conditions for the synthesis of UNCD film and boron-doped UNCD film

	Ar/ccm	N ₂ /ccm	H ₂ /ccm	TMB/CCM	CH ₄ /ccm
3-1	80	20	120	0	3
3-2	60	40	120	0	3
3-3	40	40	120	0	3
3-4	0	80	120	0	3
3-5	0	40	160	0	3
3-6	80	20	100	20	3
3-7	0	80	100	20	3

Table 4. CVD conditions for two step process

	H ₂ /CCM	TMB/CCM	CH ₄ /CCM	distance/mm
4-1	100	20	5	3
4-2	100	20	5	4
4-3	100	20	5	5
4-4	100	20	5	6
4-5	100	20	5	7
4-6	100	20	5	8

surface roughness of the samples. The electrical conductance of the samples was checked by a simple circuit tester.

3. Results and discussion

3.1 CVD diamond

3.1.1 Non-doping

We have already synthesized the diamond film on a W substrate. In this case, a porcelain insulator block was used for the substrate holder. The synthesis conditions for the W substrate are listed as (1-1) in Table 1. The SEM image of the sample of the synthesis condition of (1-1) on the BeCu substrate was shown in Fig. 2. It is known that the diamond particles synthesized by CVD process were covered with (100) plane and (111) plane when the quality of the diamond particles was not low. Therefore, the deposits in Fig. 2 should not be diamond particles. It is known that the substrate-surface temperature at ca. 800-1000 degrees C is needed for diamond synthesis by CVD method. The substrate-surface temperature of the samples in this

study could be lower than the suitable temperature because of high thermal conductivity of BeCu substrate ($105 \text{ W m}^{-1} \text{ K}^{-1}$). Therefore, a shorter distance between the filament and the substrate (4–6 mm) was investigated for (1–2) in Table 1 using a porcelain substrate. However, the BeCu alloy substrate melted at these distances. The thermal energy derived from the electrical power applied to the filament must heat the BeCu alloy substrate. The melting point of BeCu alloys is ca. 900 degrees C. Because the porcelain insulator block used as the substrate holder should have low thermal conductivity, the BeCu alloy substrate should be hotter than 900 degrees C. Diamond synthesis on a Cu substrate has been reported.^{4)–13)} The melting point of Cu (1084.62 degrees C) is higher than that of BeCu alloy. The lower melting point of BeCu alloy should make CVD synthesis of diamond difficult because this melting point was similar to the suitable temperature for diamond deposition. To suppress the temperature of the substrate, the electrical powder applied to the filament was reduced to 200 W. When the input power was 200 W, the BeCu alloy substrates did not melt when the distance between the filament and the substrate was 4–7 mm, the BeCu alloy substrate did not melt. However, no diamond was deposited on the substrates. Electrical power of 200 W could be insufficient for the synthesis of diamond because the gaseous sources, such as CH_4 and H_2 , may not be activated. The low CH_4 concentration

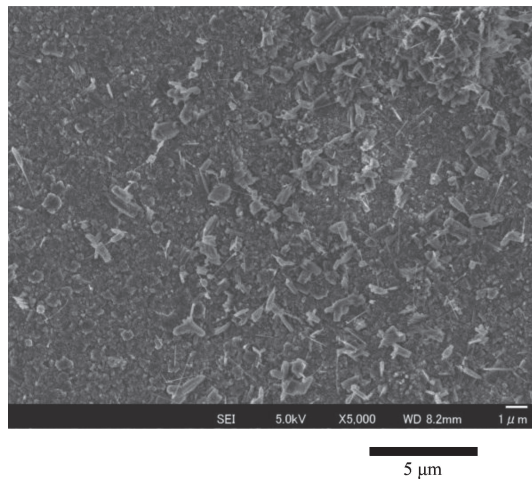


Fig. 2. SEM image of the sample after the process of (1–1) listed in Table 1.

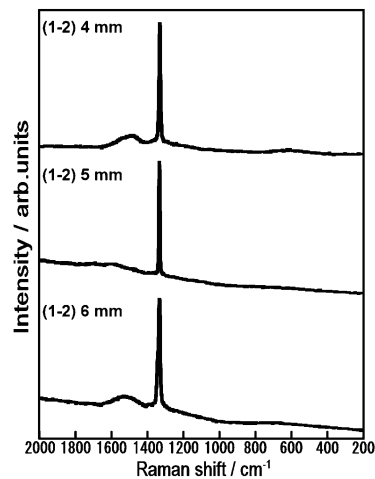


Fig. 4. Raman spectra of the sample after the processes of (1–2), (1–4), (1–5), and (1–6) listed in Table 1 using the Cu substrate.

also may be one of the reasons for the absence of diamond deposition because the nucleation density on the non-carbide substrate, such as Cu, was poor.¹⁸⁾ In order to synthesize the diamond, the following improvements were performed:

1. higher electrical power (to activate of the gaseous source)
2. Cu-plate substrate holder for heat sink (to diffuse heat)
3. higher CH_4 concentration (2.5%) (to enhance the nucleation density)

The synthesis processes were performed under the conditions for (1–2) in Table 1 using a Cu substrate. SEM images of the samples are shown in Fig. 3. The shapes of the deposits were the typical form of a diamond film. The Raman spectra of the samples are shown in Fig. 4. There was a sharp peak at

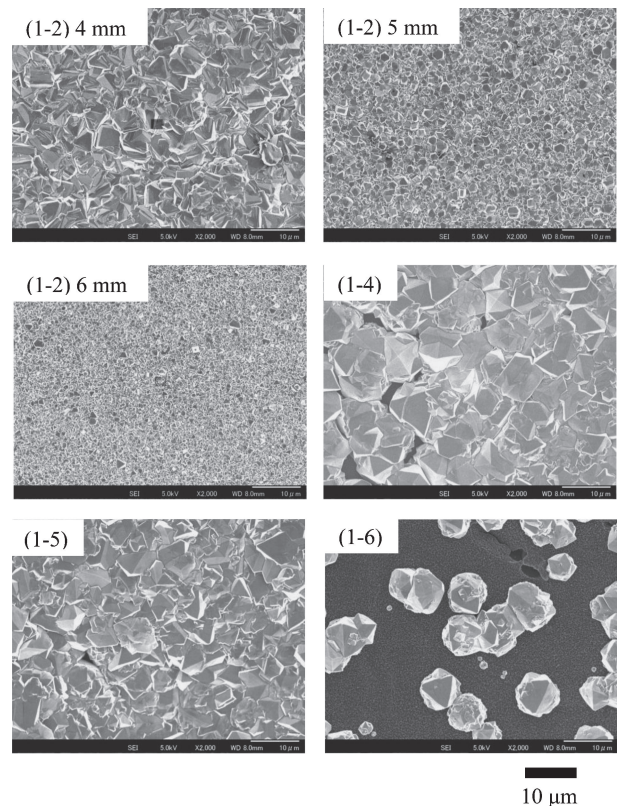


Fig. 3. SEM images of the sample after the processes of (1–2), (1–4), (1–5), and (1–6) listed in Table 1 using the Cu substrate.

ca. 1333 cm^{-1} , which was assigned to the diamond phase, in the Raman spectra of the samples although a small broad peak also appeared at ca. 1500 cm^{-1} , which was assigned to a non-diamond phase. When the CH_4 concentration was 2.5% and the distance between the filament and the substrate was from 4 to 6 mm, the diamond film was successfully deposited on the BeCu substrate. The grain size decreased as increasing the distance. The reason for the decrement should be not the increase in the nucleation density but the decrease in the growth rate of diamond. The reason why the number of sample particles decreased along with the distance between the filament and the substrate should be that larger grains covered smaller grains.

3.1.2 Boron-doping

Based on the above experimental results, the deposition of boron-doped diamond film was attempted to synthesize an electrically conductive diamond film on a BeCu substrate. Hydrogen-diluted trimethylboron (TMB) (910 ppm) was added to the gaseous source. The synthesis conditions are summarized in (1–3) to (1–6) in Table 1. The (1–3) condition was unsuitable for diamond synthesis; that is, there was no deposit related to diamond. We used high CH_4 concentrations (condition 1–4 to 1–6) because we postulated from the section 3.1.1 results that the low CH_4 concentration was the reason for the failure (even though this concentration is commonly used for diamond synthesis on a conventional substrate such as Si). The SEM images are shown in Fig. 3. When the CH_4 concentration was 3–5%, diamond particles were deposited on the substrate, although the nucleation density for the sample at 5% was low. An excessive CH_4 concentration may be detrimental for diamond synthesis on the BeCu substrate. The Raman spectrum of light boron-doped diamond is similar to that of non-doped diamond;¹⁹⁾ there is a sharp peak at 1333 cm^{-1} . The Raman spectra in Fig. 4 for samples (1–4)–(1–6) indicate that the shape of the spectra were similar to those of the heavy boron-doped diamond.¹⁹⁾ The conduction test using a circuit tester indicated that the deposits were electrically conductive.

Based on these experimental results, we can presume that a higher CH_4 concentration (more than 2.5 but less than 5%) than the conventional concentration for diamond synthesis on Si substrate (0.5–3%) is necessary for the synthesis of diamond film on BeCu substrate. Jiang et al. reported that the interlayer was deposited before the deposition of diamond phase when diamond synthesis was performed on Cu, which is the primary constituent of the BeCu alloy.⁴⁾ Therefore, we can presume that the non-diamond phase deposited on the BeCu substrate as the interlayer. The BeCu alloy used in this study contains small amounts of Fe, Co, and Ni. It is known that these elements tend to prevent diamond from being deposited on the substrate. These elements might be the reason for the need for a higher CH_4 concentration in the CVD process.

3.2 UNCD

3.2.1 Non-doping

Next, we attempted to synthesize the UNCD film on a BeCu substrate. May et al. reported UNCD synthesis on a Si substrate using a hot filament CVD apparatus.²⁰⁾ They used the gaseous source mixture of CH_4 , H_2 , and Ar. The results of their study indicated that UNCD could be deposited at $\text{Ar}/(\text{Ar}+\text{H}_2)^*100 = 0.14\text{--}0.86$. The addition of Ar was necessary for the synthesis of UNCD. Based on the experimental conditions, the percentage of the added Ar gas was fixed as summarized in Table 2. The SEM images of the samples are shown in Fig. 5(A). The average grain size of the deposits was 0.7–2.1 μm , which should mean that these

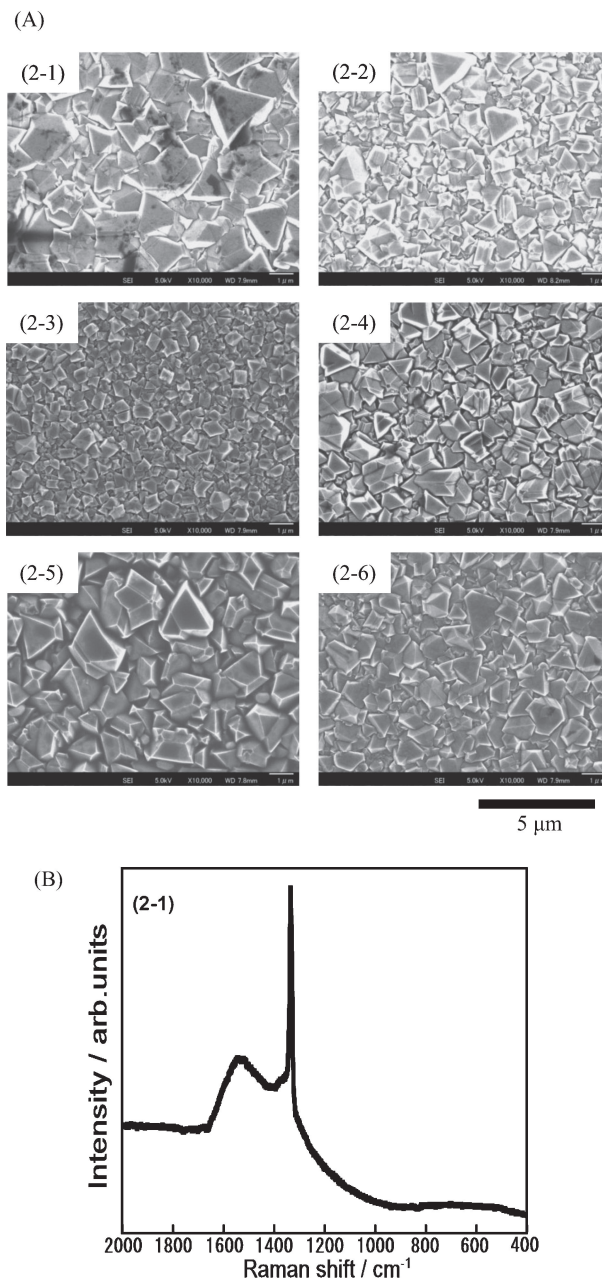


Fig. 5. (A) SEM images of the sample after the process listed in Table 2 (B) Raman spectra of the sample after the process listed in Table 2.

grains were of a different size than those of UNCD. Moreover, the shapes of all the samples were not those of UNCD, but rather of conventional diamond synthesized by CVD process. The Raman spectra supported this conclusion as shown in Fig. 5(B). In order to find the best synthesis conditions for UNCD, we tried to increase the Ar concentration in the gaseous source. However, we could not complete the CVD process because the Ta filament broke during the process. The addition of Ar gas should be the reason for the filament break. In order to make a breakthrough, nitrogen gas was added to the gaseous source as summarized at (3–1)–(3–5) in Table 3. The SEM images and the Raman spectra of the samples are shown in Fig. 6(A) and Fig. 6(B). The surface morphology and the Raman spectra of the samples were similar to those of the UNCD reported by Kuzmany.²¹⁾ Therefore, these data showed that UNCD film could be successfully deposited on

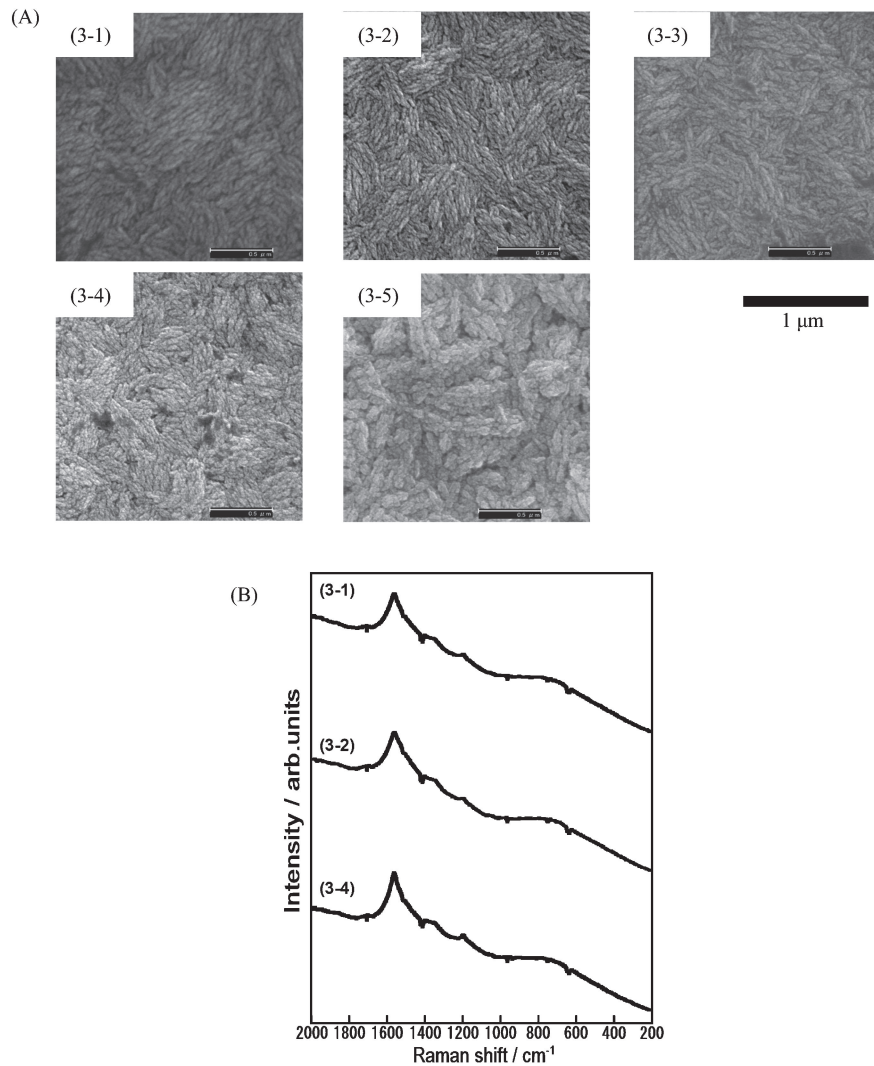


Fig. 6. (A) SEM images of the sample after the processes of (3-1), (3-2), (3-3), (3-4), and (3-5) listed in Table 3 (B) Raman spectra of the sample after the processes of (3-1), (3-2), (3-3), (3-4), and (3-5) listed in Table 3.

BeCu alloy substrate. These experimental results should mean that the addition of N_2 gas was necessary for the deposition of UNCD on BeCu alloy substrate, whereas the addition of Ar gas had no practical impact on the synthesis. The peaks at 1562 , 1356 , and 1120 – 1190 cm^{-1} were assigned to G peak, D peak, and trans-polyacetylene structure, respectively. The G peak is derived from graphitic structure, and the D peak is derived from amorphous structure. These peaks are generally observed in Raman spectra for diamond-like carbon. In some research reports, peaks at 1140 and 1470 cm^{-1} were indirect evidence of the presence of a nanocrystalline diamond structure.²²⁾ In this study, these peaks were unclear. However, because the Raman spectra reported for UNCD were also unclear,²³⁾ we can consider that the samples in this study were UNCD.

In order to investigate the growth process of UNCD, CVD process was performed for short time. SEM images are shown in Fig. 7(A). There were many needle-shape deposits on the sample synthesized for 15 min. The width of the deposits increased when the CVD process was performed for 30 min. The shape seemed to be intermediate for UNCD. The Raman spectra for the samples are shown in Fig. 7(B). The shape of the spectra changed as synthesis time increased. The presumed deposition process from the experimental results of SEM and Raman is as follows;

1. First, the needle-shape deposits, whose structures are not UNCD, appear on the substrate surface.
2. The width of the deposits increase after ca. 30 min. The structures of the broadened deposits are UNCD.
3. The broadened deposits cover the substrate surface.

In a previous report, the Si plate was used as a substrate for UNCD film in the hot filament CVD process.¹⁶⁾ From the structure of the UNCD cross-section, it has been proposed that of UNCD's deposition mechanism was different from that of conventional diamond synthesized by CVD process.¹⁷⁾ The deposition of nanosized diamond particles is for UNCD, whereas the columnar growth is for the conventional diamond synthesized by CVD process. Moreover, it was reported that in the case of the synthesis of UNCD film, the particles whose grain size were a few nanometers were deposited on the substrate.²⁴⁾ The particles were deposited because the high re-nucleation rate of the hydrogen poor plasma led to the continuous nucleation of new crystals, limiting the maximum grain size. In the case of this study, we noticed that the needle-shape particles appeared at the first stage of UNCD synthesis. However, the presumed deposition process of this study is different from that of the previous reports. The kind of substrate for diamond synthesis by the CVD process was categorized into three types;²⁵⁾ (i) those that form carbides, (ii)

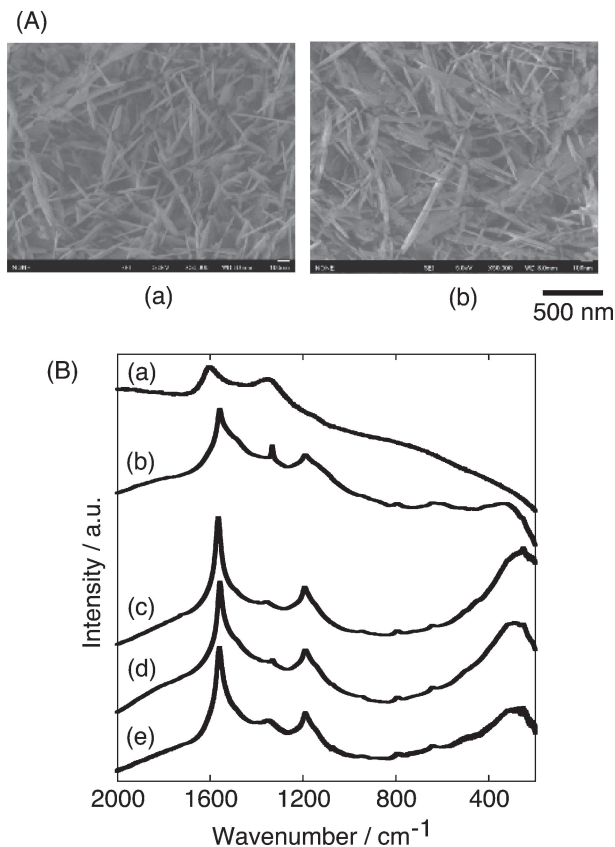


Fig. 7. (A) SEM images and (B) Raman spectra for the samples. (a), 15 min.; (b), 30 min.; (c), 1 h; (d), 1.5 h; (e), 2 h.

those that do not form carbides but can dissolve carbon, (iii) those that neither form carbides nor dissolve carbon. Because silicon is type (i), carbide can be synthesized as the interlayer that can bind between the substrate and the deposits. However, because BeCu alloy is categorized as type (iii), the deposit mechanism on BeCu substrate should be different from that on Si substrate. This may be the reason for the difference in the reported synthesis condition. For the deposition of UNCD, a carbon-rich layer might have to exist on the substrate. If this idea is correct, then in the case of Si substrate, the carbon-rich carbide layer should form at the initial step of the CVD process. In the case of the BeCu substrate, the needle-shape carbon particles, which should be a carbon-rich layer, acted as a carbon-rich layer.

The deposition time dependence of the root mean square (RMS) of surface roughness measured by AFM is shown in Fig. 8(A). As reference, the RMS values after the synthesis of conventional diamond by CVD process for 2 h on other substrates are shown in Fig. 8(B). The RMS values in Fig. 8(B) increased after the CVD process. This should mean that the surface roughness was enhanced with the deposition of diamond. However, the RMS value decreased when the CVD synthesis of UNCD in this study was performed on the BeCu substrate. Moreover, the RMS value was almost independent of the deposition time at more than 1 h. These results could mean that the proposed reaction mechanism (continuous nucleation of new crystals, resulting in the limitation of the maximum grain size) progressed during the UNCD deposition process after the growth of needle type deposits toward UNCD.

The samples were not electrical conductors based on the results of the conduction test using a circuit tester. Some papers reported

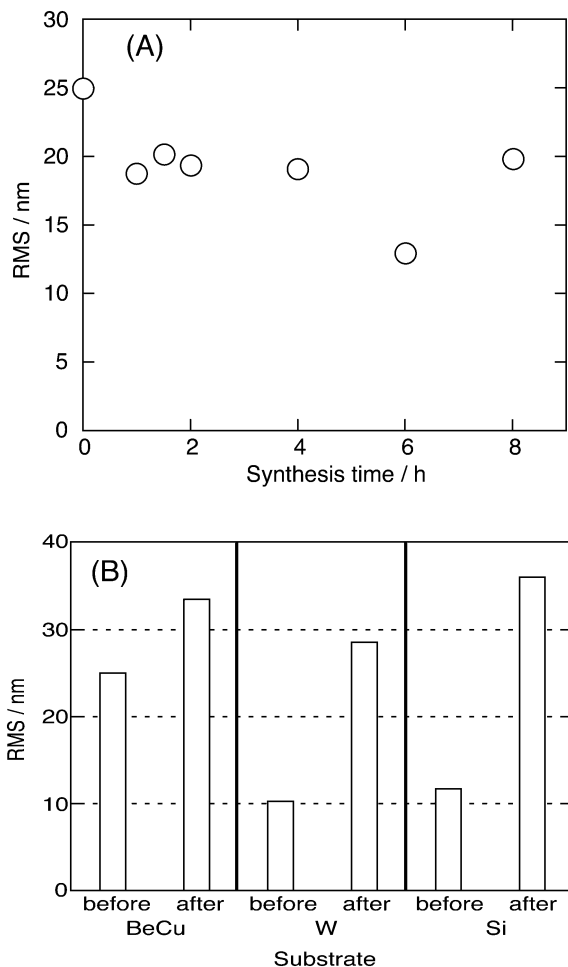


Fig. 8. (A) The deposition time dependence of the root mean square (RMS) of surface roughness (B) The RMS values after the synthesis of CVD diamond for 2 h on other substrates.

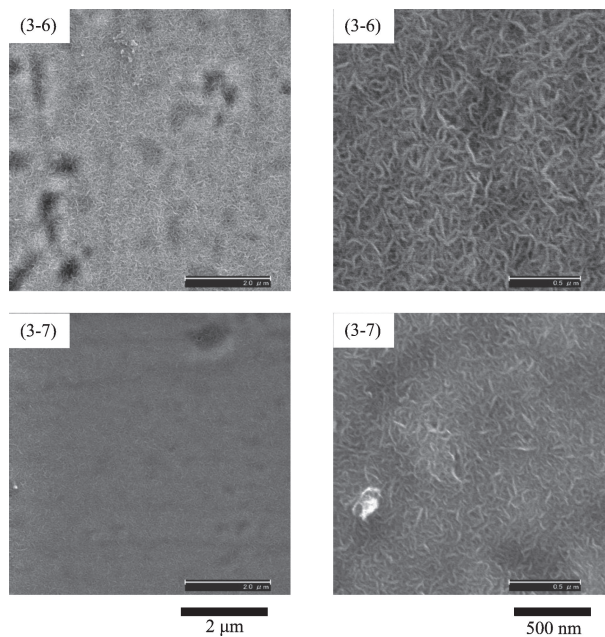


Fig. 9. SEM images of the sample after the processes of (3-6) and (3-7) listed in Table 3.

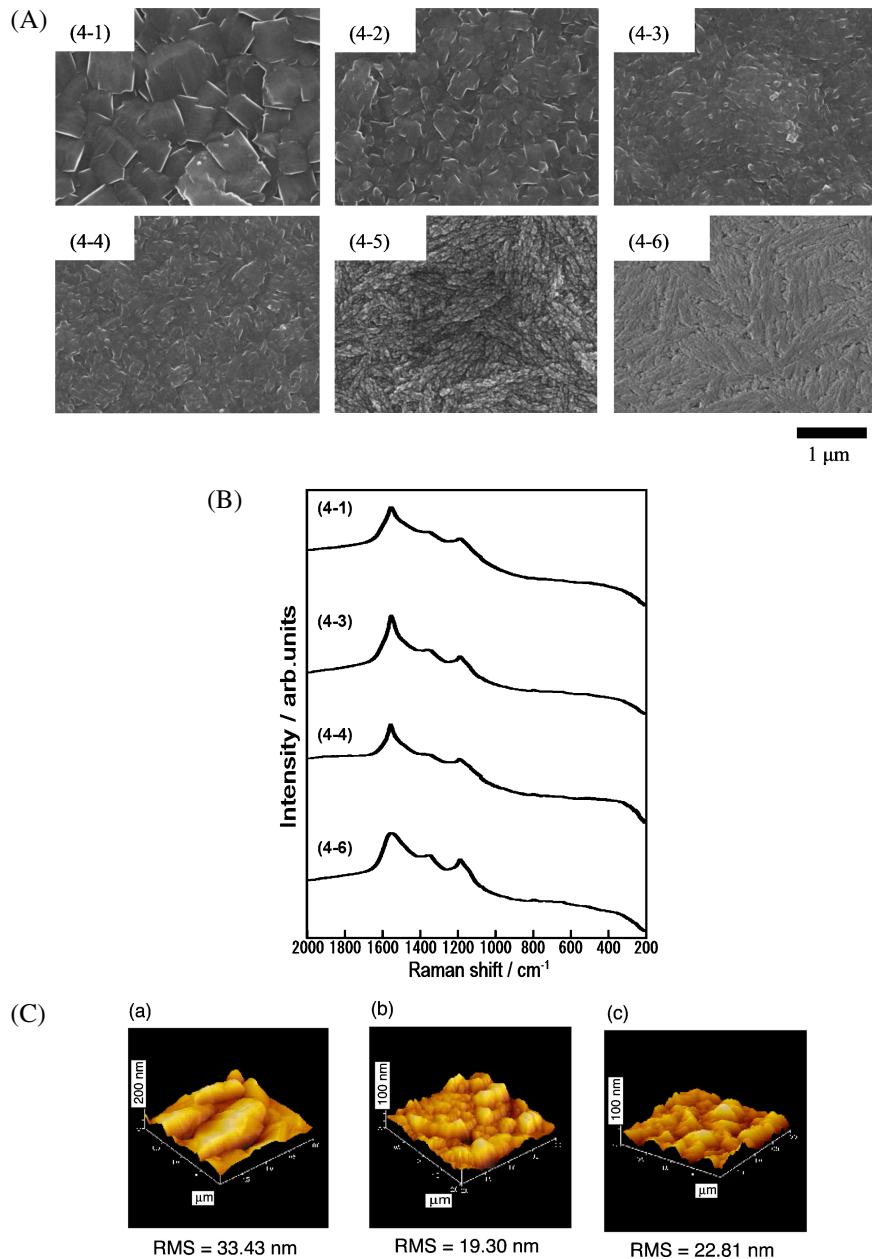


Fig. 10. (Color online) (A) SEM images of the sample after the process listed in Table 4. (B) Raman spectra of the sample after the process listed in Table 4. (C) AFM images of the samples. (a), the sample of (1–5); (b), the sample of (3–1); (c), the sample of (4–2).

the synthesis of an electrical conductive UNCD.²⁴⁾ Most of these films were prepared not by the hot filament CVD but by the microwave plasma CVD method. For the sample prepared from the gaseous source containing N₂, the electrical conduction of the films was caused by an impurity that contained nitrogen in the grain boundary.²⁴⁾ Therefore, the boundary condition of the films prepared by the hot filament CVD method may be different from that of the films prepared by the microwave plasma CVD method.

3.2.2 Boron doping

We synthesize UNCD on a BeCu alloy substrate, as mentioned in section 3.2.1. However, we could not confirm the electrical conduction of the deposited film. Boron doping, therefore, was used to improve the electrical conductivity of the film. The conditions are listed as (3–6)–(3–7) in Table 3. The SEM images of the samples are shown in Fig. 9. The surface morphology

of the sample was obviously different from that of UNCD. Moreover, the samples were not electrical conductors based on the results of the continuity test using a circuit tester. The elemental analysis by EDX indicated that the constituent elements on the surface after the CVD process were C (11.6 mol %), Cu (3.07 mol %), B (42.7 mol %), N (42.6 mol %), and Co (1.19 × 10⁻² mol %). These data also should suggest that there was no UNCD on the substrate after the CVD process because the percentage of C was small. The addition of TMB should have a negative effect on the synthesis of the UNCD on the BeCu alloy, at least in the case of the hot filament CVD method at a high TMB concentration.

3.3 Two-step process

In order to realize an electrically conductive UNCD film on the BeCu alloy substrate, we planned the following strategy.

First step: cover BeCu alloy substrate with UNCD film

Second step: deposit very thin electrically conductive diamond on the surface

In the first step, the surface of the BeCu alloy substrate is covered with UNCD film as the basis for the smooth coating. In the second step, a very thin electrically conductive diamond is deposited on the surface in order to electrical conductivity without changing the smoothness of the surface.

The condition for the first step is (3-1) in Table 3, and the condition for the second step is listed in Table 4. SEM images of the samples are shown in Fig. 10(A). In spite of the short CVD time, that is, only 15 min, the surface morphology drastically changed when the distance between the filament and the substrate was short, such as 3 mm. The surfaces after the second step were uniform. The Raman spectra for the samples are shown in Fig. 10(B). These spectra indicated that the conditions of the films after the second process were almost same as those before the second process. The reason for the similarity of the spectra should be that the thickness of the anisotropic deposits during the second process was very thin or that the deposits synthesized during the first process were anisotropically etched during the second process. The CH₄ concentrations for the second process were 4%, which is higher than the CH₄ concentration used in conventional diamond synthesis by CVD process. Therefore, we could presume that the reason for the similarity in the spectra was not the etching, but the thinness of the deposits. This result should mean that the two-step process can be used to coat the BeCu alloy. The AFM images of the samples are shown in Fig. 10(C). The surface roughness after the two-step process was the almost same as that before the two-step process. Therefore, the two-step process should be effective for the synthesis of boron-doped diamond having smooth surface. A continuity test using the circuit tester confirmed that the samples, which were prepared at a 6 mm or less distance between the proximal end of the filament and the substrate surface, had electrical conductivity. The simple test using the circuit tester showed that the electrical resistance decreased with the decreasing distance between the filament and the substrate, whereas the samples prepared at 7 mm or more still had high electrical resistance. The surface morphology of the samples having high electrical resistivity was very similar to that of the surface before the second step. Because the distance between the filament and the substrate was too great for the CVD process, no deposit should be on the substrate during the second step. When the second step was performed without the first step, there was no deposit on the substrate. Therefore, the first step should affect the condition after the second step. The deposit of first step might act as the basis for the second step, because the surface morphology drastically changed in spite of the short CVD time.

4. Conclusions

A beryllium-copper alloy plate was used as a substrate of diamond film and UNCD film for a hot filament CVD apparatus. Moderate electrical power, relatively high CH₄ concentration (more than 2.5 and less than 5%), and moderate heat diffusion were necessary for diamond synthesis on BeCu alloy substrate. For the deposition of UNCD film, nitrogen gas was indispensable although argon gas was not needed for the synthesis. The addi-

tion of N₂ did not effectively improve the electrical conductivity of UNCD film in this study. Two-step processes, that is, the synthesis of UNCD film and then the synthesis of a very thin boron-doped diamond film, were performed in order to realize an electrically conductive smooth-surface film. After the second step, the surface of the film was electrical conductive, although the deposition time of the second step was very short (15 min).

References

- 1) B. Lux and R. Haubner, *Ceram. Int.*, **22**, 347–351 (1996).
- 2) Y. Takano, *J. Phys.: Condens. Matter*, **21**, 253201 (2009).
- 3) H. Amano, T. Tsubota, N. Murakami, T. Ohno, S. Sawada, T. Suenaga and H. Nagahata, *Diamond Relat. Mater.*, **24**, 195–200 (2012).
- 4) N. Jiang, L. C. Wang, J. H. Won, M. H. Jeon, Y. Mori, A. Hatta, T. Ito, T. Sasaki and A. Hiraki, *Diamond Relat. Mater.*, **6**, 743–746 (1997).
- 5) M. Vedawyas, G. Sivananthan and Ashok Kumar, *Mater. Sci. Eng., B*, **78**, 16–21 (2000).
- 6) L. Constant and F. Le Normand, *Thin Solid Films*, **516**, 691–695 (2008).
- 7) C. Li, K. C. Feng, Y. J. Fei, H. T. Yuan, Y. Y. Xiong and K. Feng, *Appl. Surf. Sci.*, **207**, 169–175 (2003).
- 8) N. Ali, Q. H. Fan, W. Ahmed, I. U. Hassan, C. A. Rego and I. P. O'Hare, *Thin Solid Films*, **355–356**, 162–166 (1999).
- 9) K.-L. Chuang, L. Chang and C.-A. Lu, *Mater. Chem. Phys.*, **72**, 176–180 (2001).
- 10) O. Shin-ichi, S. Yamashita, K. Kataoka and T. Ishikura, *Jpn. J. Appl. Phys.*, **32**, L200–L203 (1993).
- 11) M. Ece, B. Oral and J. Patscheider, *Diamond Relat. Mater.*, **5**, 211–216 (1996).
- 12) L. Constant, C. Speisser and F. Le Normand, *Surf. Sci.*, **387**, 28–43 (1997).
- 13) Q. H. Fan, E. Pereira and J. Gracio, *J. Mater. Sci.*, **34**, 1353–1365 (1999).
- 14) S. A. Catledge and Y. K. Vohra, *J. Mater. Res.*, **23**, 2373–2381 (2008).
- 15) A. R. Krauss, O. Auciello, D. M. Gruen, A. Jayatissa, A. Sumant, J. Tucek, D. C. Mancini, N. Moldovan, A. Erdenir, D. Ersoy, M. N. Gardos, H. G. Busmann, E. M. Meyer and M. Q. Ding, *Diamond Relat. Mater.*, **10**, 1952–1961 (2001).
- 16) J. G. Buijnsters and L. Vazquez, *J. Phys. Chem. C*, **115**, 9681–9691 (2011).
- 17) J. E. Butler and A. V. Sumant, *Chem. Vap. Deposition*, **14**, 145–160 (2008).
- 18) C.-M. Niu, G. Tsagaropoulos, J. Baglio, K. Dwight and A. Wold, *J. Solid State Chem.*, **91**, 47–56 (1991).
- 19) R. J. Zhang, S. T. Lee and Y. W. Lam, *Diamond Relat. Mater.*, **5**, 1288–1294 (1996).
- 20) P. W. May and Y. A. Mankelevich, *J. Appl. Phys.*, **100**, 024301 (2006).
- 21) H. Kuzmany, R. Pfeiffer, N. Salk and B. Günther, *Carbon*, **42**, 911–917 (2004).
- 22) Y. S. Zou, Z. X. Li and Y. F. Wu, *Vacuum*, **84**, 1347–1352 (2010).
- 23) James Birrell, J. E. Gerbi, O. Auciello, J. M. Gibson, D. M. Gruen and J. A. Carlisle, *J. Appl. Phys.*, **93**, 5606–5612 (2003).
- 24) O. A. Williams and M. Nesladek, *Phys. Status Solidi., A Appl. Mater. Sci.*, **203**, 3375–3386 (2006).
- 25) M. Vedawyas, G. Sivananthan and A. Kumar, *Mater. Sci. Eng., B*, **78**, 16–21 (2000).