Effect of Nitrogen Addition on Delamination of Synthesized Diamond Films by Flame Combustion Method Using High-Purity Acetylene

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Diamond films have been synthesized by flame combustion using a mixture of commercial acetylene and oxygen gas, but the flame combustion conditions were unstable, owing to the use of commercial acetylene. This is due to the variable purity of commercial acetylene that includes dissolved impurities. Therefore, in this study, high-purity acetylene was used to synthesize diamond films; it was obtained through special dissolution of pure acetylene of stable and high purity. To obtain good quality diamond films and to achieve good adhesion, diamond films were synthesized by stable flame combustion using a mixture of high-purity acetylene and oxygen gas with nitrogen gas added as the diamond promotion agent; nitrogen flow rate was carefully varied in the range of 0.333~0.667 cm$^3$/s. According to the results, the optimal nitrogen flow rate was 0.500 cm$^3$/s, and good quality diamond films were synthesized. The synthesized crystallites also showed almost uniform size and high density. Moreover, as nitrogen flow rate was further increased or decreased from 0.500 cm$^3$/s, the diamond quality of the synthesized films was reduced. The delamination of films synthesized with varying the nitrogen flow rates was prevented at a very high probability. In particular, the delamination of the films synthesized at a nitrogen flow rate of 0.500 cm$^3$/s was completely prevented. To investigate the effects of nitrogen addition on the synthesized diamond films and film delamination, the nitrogen density of synthesized films was analyzed. The nitrogen density of the films synthesized with nitrogen addition was higher than that of the films synthesized without nitrogen addition. The nitrogen density of the synthesized films was increased by nitrogen addition. Thus, nitrogen addition to high-purity acetylene affects diamond synthesis. Moreover, the crystallite morphology of synthesized diamond films can be changed by varying the nitrogen flow rate.

Key Words: Synthesized Diamond Films, Flame Combustion, High-Purity Acetylene, Nitrogen Addition, Delamination

1. Introduction

Owing to its excellent properties, namely, high thermal conductivity, high hardness and high wear resistance, diamond is widely used in the industry, such as in the manufacture of cutting and polishing tools. Diamond films have long been considered a coating material of dental cutting tools1); thus, diamond has been extensively studied for use as a coating material of medical devices2). From these studies, it is thought that if diamond films can be directly synthesized on the surface of various materials and good adhesion can be achieved, surface improvement in terms of high hardness and ultimately in terms of wear resistance can be realized. Therefore, the expansion of diamond application in various fields is expected.

The flame combustion method enables the synthesis of diamond using acetylene-oxygen gas (C$_2$H$_2$/O$_2$) flame combustion in ambient atmosphere3)-4). It has various advantages over other methods, such as high synthesis speed and the safety and low cost of the equipment used; these advantages are desirable in the industrial market. In the flame combustion method, the enlargement of the area of the synthesized diamond5), the synthesis of large single-crystal diamond6) and the synthesis of diamond films for application in electronic devices7) have been investigated. However, to date, the factors affecting diamond synthesis remain to be determined and no means of precisely controlling this method has yet been established. Moreover, during cooling, most diamond films delaminate as a result of thermal stress. We previously synthesized diamond films on a Mo substrate surface by the flame combustion method8)-14). To prevent diamond film delamination for the synthesis of good diamond films, a three-step synthesis method was proposed9) and its optimal conditions were determined10)-14).
Diamond films have been synthesized by flame combustion using a mixture of commercial acetylene and oxygen gas. However, the flame combustion conditions are unstable, owing to the use of commercial acetylene during the synthesis of diamond films. This is due to the variable purity (91.5–98.5%) of commercial acetylene as a result of dissolved impurities. Therefore, in this study, high-purity acetylene was used; it was obtained through special dissolution of pure acetylene of stable and high purity (more than 99.5%). Generally, high-purity acetylene is used for atomic absorption spectrometry. We considered that the flame combustion conditions become stable with the use of high-purity acetylene gas, and that good diamond films and good adhesion can be achieved by this method. Thus, diamond synthesis was conducted by stable flame combustion using a mixture of high-purity acetylene and oxygen gas. Nitrogen gas, as a diamond promotion agent, was added to the high-purity acetylene-oxygen mixture gas to synthesize diamond films. We confirmed that a nitrogen flow rate range of 0.333–0.667 cm³/s was optimal for diamond synthesis. However, the delamination of the synthesized films was not evaluated in this range.

In this study, to obtain good quality diamond films and to achieve good adhesion, diamond films were synthesized by stable flame combustion using a mixture of high-purity acetylene and oxygen gas with the addition of nitrogen gas. A three-step synthesis method was used to prevent film delamination. Nitrogen flow rate was carefully varied in the range of 0.333–0.667 cm³/s. Moreover, to compare the synthesized films and film delamination, films were also synthesized without nitrogen addition (nitrogen flow rate, 0.000 cm³/s). The effects of nitrogen flow rate on the synthesized films and film delamination were investigated. The nitrogen density of the films synthesized with and without nitrogen addition was determined. We proved that nitrogen addition to high-purity acetylene affects diamond synthesis. Good diamond films and good adhesion were synthesized with a stable flame combustion using a mixture of high-purity acetylene and oxygen gas with an optimal amount of nitrogen gas added. Moreover, the crystallite morphology of the synthesized films was changed by varying the nitrogen flow rate. The synthesized films were analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) analysis and secondary ion mass spectrometry (SIMS), and the results of the analysis were discussed.

2. Experimental details

2.1. Substrate

Molybdenum (Mo) of 99.9% purity was used as the substrate for synthesizing diamond because it has a high melting point and can easily produce carbide as a result of the low diffusion coefficient of carbon. A Mo rod of 10 mm in diameter was used; it was cut into disk-shaped fragments of about 3 mm thickness. As a pretreatment to prevent the delamination, scratch processing, in which a substrate surface is ground with emery paper in one direction, was performed. Furthermore, as growth nuclei for the diamond synthesis, diamond seed particles of about 0.25 μm in diameter were dispersed in acetone; the Mo substrate was added, and seed attachment processing was performed for 30 minutes with an ultrasonic syringe.

2.2. Experimental equipment

The experimental equipment is shown in Fig. 1. A 100 × 100 × 55 mm³ copper box was used for cooling. Cooling water was poured into this box and the film surface temperature was kept constant. A noncontact infrared radiation thermometer was used to measure the film surface temperature during the synthesis. As a support for cooling, a Mo rod of 10 mm in diameter was set vertically at the center of the box and fixed to a table by a flange. The Mo substrate was attached to this Mo rod. For efficient cooling, thermally conductive Ag paste was applied between the Mo substrate and the Mo rod. They were glued in the furnace at 473 K.

The cooling box was put on a stage. Since it was capable of moving vertically, the distance from the cooling waterside to the film surface was changed, and film surface temperature was controlled. A stepping motor was set on the stage and controlled by the stage controller.

To stabilize the flame combustion, high-purity acetylene was used as fuel for the synthesis; this was obtained through special dissolution of pure acetylene of stable purity (more than 99.5%). Here, oxygen was used as the fuel for the synthesis. Moreover, nitrogen gas was added as the diamond promotion agent to the mixture of high-purity acetylene and oxygen gas to synthesize...
diamond films. A burner was used for welding. Mixed gas was introduced into the burner and combusted. The diameter of the exit of the burner was 1 mm. In addition, a mass flow controller was used as the gas flow meter, which could control gas flow rate precisely and display flow quantity digitally.

2.3. Three-step synthesis method

We have found some appropriate synthesis conditions for synthesizing tough diamond films\(^9\), but the films obtained delaminate at a synthesis temperature less than 1300 K (low temperature) and are of high quality. Although tough films could be synthesized at more than 1400 K (high temperature), they were of low quality.

A three-step synthesis method was proposed to prevent film delamination\(^9\). In this method, the film surface temperature is changed three times during the synthesis. The first step of the method is performed at 1423 K. This was because high bonding strength can be achieved at high temperatures, even though good diamond films are not synthesized. The intermediate layer that works as the buffer phase for thermal stress reduction is synthesized on the Mo substrate in the first step. With high bonding strength achieved by the layer, delamination is prevented. The second step is performed at 1223 K, because a good diamond phase can be synthesized at this temperature. To obtain sufficient thickness of the film, the third step is performed at 1323 K. In the first step, diamond is synthesized, and Mo\(_2\)C is also deposited on the substrate. Thus, the first-step layer has the diamond and Mo\(_2\)C phases (multilayer). In the second and third steps, diamond is synthesized. In this study, the average thickness of the synthesized film by the three-step method was 30 \(\mu\)m per hour.

2.4. Synthetic conditions

The synthetic conditions are shown in Table 1. We previously determined these conditions\(^9\)\(^\text{-}^\text{14}\), which are optimal for preventing delamination during the synthesis of diamond films.

We have confirmed that scratching treatment on the substrate surface affects delamination\(^9\), and that delamination could be most easily prevented by scratching with emery paper of \#400 grain size (scratching treatment \#400). Thus, diamond films were synthesized on the substrate surface with scratching treatment \#400. Here, the measured surface roughness \(R_s\) (arithmetical mean deviation of the assessed profile) of the scratching treatment \#400 was 0.18 \(\mu\)m\(^3\).

An outline of the flame combustion is shown in Fig. 2. The flame combustion consists of a flame inner cone, acetylene feather and an outer luminous layer. Diamond was synthesized in the acetylene feather area. The distance of the flame inner cone from the Mo substrate surface, \(d\), is shown in the figure. During the synthesis, when the distance was changed, diamond film synthesis and delamination were affected, because the acetylene feather area changed. When the distance was short, the diamond growth rate was high, and when the distance was long, the diamond growth rate was low. We have confirmed that the delamination at \(d = 1.5\) mm during the diamond film synthesis could be effectively prevented\(^9\). Therefore, diamond films were synthesized at \(d = 1.5\) mm.

The ratio of oxygen flow rate \(F_o\) to acetylene flow rate \(F_a\) was set to \(R_f = F_o/F_a = 0.90\), because delamination-free crystallite growth could be realized at \(R_f = 0.90\)\(^9\).

In this study, to investigate the synthesis and delamination of the diamond films, nitrogen flow rate was varied. The changes in nitrogen flow rate are shown in Table 2. We confirmed that the nitrogen flow rate range of 0.333\(-\)0.667 cm\(^3\)/s was the diamond synthesis condition range. Thus, nitrogen flow rate was carefully varied in the range of 0.333\(-\)0.667 cm\(^3\)/s. Moreover, to compare the synthesized films and film delamination, the synthesis was conducted without nitrogen addition (nitrogen flow rate 0.000 cm\(^3\)/s).

The synthetic time for each of the three steps in the method

<table>
<thead>
<tr>
<th>Table 1 Conditions for diamond syntheses.</th>
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<tr>
<td>Reaction gas</td>
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<tr>
<td>Film surface temperature</td>
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<tr>
<td>Pressure</td>
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<tr>
<td>Substrate surface roughness, (R_s)</td>
</tr>
<tr>
<td>Inner cone-to-substrate distance</td>
</tr>
<tr>
<td>C(_2)H(_2) Flow rate, (F_a)</td>
</tr>
<tr>
<td>O(_2) Flow rate, (F_o)</td>
</tr>
<tr>
<td>Flow ratio, (R_f = F_o/F_a)</td>
</tr>
</tbody>
</table>

Fig. 2 Outline figure of flame combustion.
used was set to 1200 s, and the total synthesis time of all three steps was set to 1 h.\textsuperscript{19,10}

3. Experimental results and discussion

3.1. Effects of nitrogen flow rate on delamination

The results of the delamination of the films synthesized with varying the nitrogen flow rate are shown in Table 3, which shows the percentage of numbers of delaminated specimens synthesized at the same nitrogen flow rate. ‘Nondelamination’ means that no interfacial delamination occurred, and the film remained on the substrate. ‘Half-delamination’ means that the film remained on more than half the area of the substrate. ‘Delamination’ means that interfacial delamination occurred, and most of the film did not remain on the substrate. All delaminated specimens were observed. From the results, it was confirmed that delamination occurred at the interface between each of the synthesized film and the substrate.

In Table 3, the delamination of the synthesized films in all cases was successfully prevented at a very high probability. Moreover, the half-delamination of the films synthesized with varying the nitrogen flow rate was also prevented. In particular, the delamination of the synthesized films in Case 5 (nitrogen flow rate, 0.500 cm\textsuperscript{3}/s) was completely prevented. The delamination was prevented simply by varying the nitrogen flow rate. However, the delamination in other cases except Case 5 was not completely protected. In all cases except Case 5, a small difference in the percentage of nondelamination was observed. We considered that the change in nitrogen flow rate had some effects on the delamination of the synthesized films.

3.2. Investigation of SEM images of films synthesized with varying the nitrogen flow rate

The films synthesized with varying the nitrogen flow rate were analyzed by scanning electron microscopy (SEM: JEOL JSM-5800).

<table>
<thead>
<tr>
<th>Case</th>
<th>N\textsubscript{2} flow rate, $F_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>0.000 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 2</td>
<td>0.333 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 3</td>
<td>0.417 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 4</td>
<td>0.458 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 5</td>
<td>0.500 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 6</td>
<td>0.542 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 7</td>
<td>0.583 cm\textsuperscript{3}/s</td>
</tr>
<tr>
<td>Case 8</td>
<td>0.667 cm\textsuperscript{3}/s</td>
</tr>
</tbody>
</table>

Table 2 Conditions of nitrogen flow addition.

<table>
<thead>
<tr>
<th></th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
<th>Case 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nondelamination</td>
<td>83.3%</td>
<td>83.3%</td>
<td>91.7%</td>
<td>91.7%</td>
</tr>
<tr>
<td>Half delamination</td>
<td>8.3%</td>
<td>16.7%</td>
<td>0.0%</td>
<td>0.0%</td>
</tr>
<tr>
<td>Delamination</td>
<td>8.3%</td>
<td>0.0%</td>
<td>8.3%</td>
<td>8.3%</td>
</tr>
</tbody>
</table>

Table 3 Results of delamination induced by varying the nitrogen flow rate.

SEM images of the films synthesized with varying the nitrogen flow rate (Cases 1 ~ 8) are shown in Fig. 3. Figs. 3(a) ~ (h) show the films synthesized in Cases 1 (0.000 cm\textsuperscript{3}/s) ~ 8 (0.667 cm\textsuperscript{3}/s), respectively. In the SEM image in Fig. 3(a),\textsuperscript{16} the synthesized crystallites showed a ball-like morphology. The ball-like structure is a mixture of graphite and diamond crystallites.\textsuperscript{12,17} Since graphite crystallites cannot be etched away, the synthesized crystallites develop a ball-like morphology.

In the SEM image in Fig. 3(b),\textsuperscript{16} the synthesized crystallites showed no ball-like morphology. The crystallites shown here could be etched compared with those in Case 1 (without nitrogen addition). Thus, we considered that the nitrogen addition affected the etching process.

In the SEM images in Figs. 3(c) and (d), the synthesized crystallites could be easily etched compared with the crystallites in Case 2 (with a small amount of nitrogen added). They showed a nearly octahedral morphology. Moreover, they showed nearly uniform size compared with the crystallites in Case 2. As the amount of nitrogen added increased, the synthesized diamond crystallites showed better properties than the crystallites synthesized with a small amount of nitrogen added.

In the SEM image in Fig. 3(e),\textsuperscript{16} the synthesized crystallites could be easily etched compared with the crystallites in Case 4, and diamond crystallites could still grow. They showed an almost octahedral morphology, and thus were considered good diamond crystallites. They also showed almost uniform size and high density. When nitrogen gas was added to the mixture of high-purity acetylene and oxygen gas for the synthesis of diamond films, the optimal amount of nitrogen added promoted the etching of crystallites and the growth of crystallites of uniform size. In this experiment, the optimal nitrogen flow rate was 0.500 cm\textsuperscript{3}/s.

In the SEM image in Fig. 3(f), the synthesized crystallites
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Fig. 3(a) SEM image of the synthesized film in Case 1.

Fig. 3(b) SEM image of the synthesized film in Case 2.

Fig. 3(c) SEM image of the synthesized film in Case 3.

Fig. 3(d) SEM image of the synthesized film in Case 4.

Fig. 3(e) SEM image of the synthesized film in Case 5.

Fig. 3(f) SEM image of the synthesized film in Case 6.

Fig. 3(g) SEM image of the synthesized film in Case 7.

Fig. 3(h) SEM image of the synthesized film in Case 8.
could not be etched compared with the crystallites in Case 5. Moreover, they showed nonuniform size compared with the crystallites in Case 5.

In the SEM images in Figs. 3(g) and (h), the synthesized crystallites could not be easily etched compared with the crystallites in Case 5, and the synthesized crystallites showed an almost ball-like morphology. Furthermore, they showed nonuniform size. As the amount of nitrogen added increased from the optimal amount, the synthesized diamond crystallites showed worse properties than the crystallites synthesized with an optimal amount of nitrogen added.

3.3. Investigation of XRD patterns of films synthesized with varying the nitrogen flow rate

The films synthesized with varying the nitrogen flow rate were analyzed by X-ray diffraction (XRD: JEOL JDX-3530) analysis. Typical XRD patterns of the films synthesized with varying the nitrogen flow rate (Cases 1 and 5) are shown in Fig. 4(a) and (b). Figs. 4(a) and (b) show the films synthesized in Cases 1 (0.000 cm$^3$/s) and 5 (0.500 cm$^3$/s), respectively.

In the XRD pattern in Fig. 4(a), a small peak showing existence of diamond could be confirmed. Peaks showing the existence of diamond (111) and (220) surfaces were also confirmed. A small diamond was synthesized.

In the XRD pattern in Fig. 4(b), it is shown that, as the amount of nitrogen added increased, peaks showing the existence of diamond could be confirmed. Peaks showing the existence of diamond (111) and (220) surfaces were clearly confirmed; the peak of the diamond (111) surface was very distinct. The synthesized diamond crystallites showed better properties than the crystallites in Case 1. In the SEM and XRD results, the synthesized diamond crystallites in Case 5 showed an almost octahedral morphology, and thus were considered good quality diamond crystallites.

3.4. Effects of nitrogen addition on the properties of synthesized diamond films and film delamination

From the experimental results, we discussed the effects of nitrogen addition on the properties of synthesized diamond films. When nitrogen gas was not added to the mixture of high-purity acetylene and oxygen gas, the synthesized crystallites showed a ball-like morphology. Moreover, in the SEM and XRD results, the synthesized films were not good diamond films. Previously, when diamond films were synthesized using commercial acetylene gas under the same conditions used in this study, good diamond films with octahedral crystallites were obtained. This might be due to the fact that the crystallites could be etched. We considered that the reason for the difference in results is the difference between the components of commercial acetylene gas and high-purity acetylene gas.

Several researchers have shown that nitrogen addition affects the morphology of synthesized diamond crystallites. Therefore, in this study, nitrogen gas was added to a mixture of high-purity acetylene and oxygen gas to synthesize diamond films. And, nitrogen flow rate was carefully varied. In the SEM and XRD results, as nitrogen flow rate was increased from 0.333 cm$^3$/s to 0.500 cm$^3$/s, the synthesized crystallites showed etchability and an almost octahedral structure, and the synthesized films were considered good quality diamond films. Moreover, the synthesized crystallites showed uniform size. As nitrogen flow rate was further increased from 0.500 cm$^3$/s, the synthesized crystallites showed nonetchability and a ball-like structure. Therefore, it was clear that excessive increase in the amount of nitrogen added reduced the diamond quality of the synthesized films. The diamond quality of the synthesized films was improved by adding an optimal amount of nitrogen to the mixture of high-purity acetylene and oxygen gas. In this experiment, the optimal nitrogen flow rate was 0.500 cm$^3$/s.

The delamination of films synthesized with varying the nitrogen
flow rate was prevented at a very high probability. In particular,
the delamination of the films synthesized at a nitrogen flow rate
of 0.500 cm$^3$/s was completely prevented; the delaminations in
other cases were not. The reason for this was that the diamond
crystallites synthesized at the optimal nitrogen flow rate of 0.500
$cm^3/s$ were etchability and good quality diamond crystallites.
Moreover, the synthesized crystallites showed almost uniform
size and high density. So, adhesive areas between synthesized
film and the substrate were large. Therefore, the adhesive strength
was high, resulting in the prevention of delamination. However,
the delamination in other cases except Case 5 was not completely
protected. The reason for this was that the crystallites synthesized
at other cases were not good quality diamond crystallites. And,
the synthesized crystallites were not uniform size and high
density. Therefore, adhesive areas between synthesized film and
the substrate were small. So, the adhesive strength of other cases
was lower than the adhesive strength of nitrogen flow rate of 0.500
cm$^3$/s.

The delamination of the synthesized diamond films in all the
cases was prevented at a very high probability. In this regard, the
following other reasons are given. The films were synthesized
using the three-step synthesis method, which is effective in
preventing delamination. Moreover, films were synthesized under
the previously determined optimal conditions$^{10-14}$ to prevent
delamination.

We considered$^{15}$ that the diamond quality of the synthesized
films was improved by adding an optimal amount of nitrogen.
In general, diamonds are sorted by the amount of nitrogen they
contain. The properties of diamonds change with a change in the
amount of nitrogen in the diamond.$^{21}$ Consequently, nitrogen is a
very important factor for diamond synthesis. Thus, we considered
that nitrogen is taken up in diamonds during their growth, and that
nitrogen is the main factor that determines diamond properties.
Here, the amount of nitrogen in high-purity acetylene was
investigated and found to be 0.01~0.17%, which was negligible.
However, the amount of nitrogen in commercial acetylene is
0.8~2.5%$^{16}$. From results, the diamond quality of the synthesized
diamond films was changed by varying the nitrogen flow rate.
This reason for this is the difference in nitrogen amount between
high-purity acetylene and commercial acetylene. Previously,
the effect of oxygen on the etching of diamond crystallites was
confirmed in diamond films synthesized using commercial
acetylene gas$^{3,17}$. In this study, we considered that nitrogen
promoted the etching effect of oxygen. Therefore, the etching of
synthesized crystallites progressed, and the quality of synthesized
diamond films was improved. When nitrogen flow rate was
increased too much, an oversupply of nitrogen was created.
This prevented the etching effect of oxygen, and as a result, the
diamond quality of the synthesized films was not improved. We
considered$^{22}$ that the reason for this was that CN-radicals in the
acetylene feather of the flame combustion being affected.

We confirmed that good diamond films and good adhesion
can be synthesized by stable flame combustion using a mixture
of high-purity acetylene and oxygen gas with the addition of
an optimal amount of nitrogen gas. Moreover, the crystallite
morphology of synthesized diamond films can be changed by
varying the nitrogen flow rate.

3.5. Determination of nitrogen density of synthesized films

To investigate the effects of nitrogen addition on the properties
of synthesized diamond films and film delamination, the nitrogen
density of films synthesized with nitrogen and without nitrogen
addition was analyzed. Here, to determine the nitrogen density
of synthesized films, secondary ion mass spectrometry (SIMS: by
Foundation for Promotion of Material Science and Technology
of Japan) was used. The synthesized films with optimal nitrogen
(flow rate: 0.500 cm$^3$/s) addition and without nitrogen addition
(flow rate: 0.000 cm$^3$/s) were evaluated. The nitrogen densities
of the synthesized films determined by SIMS analysis are shown
in Fig. 5. In the figure, the ordinate shows the nitrogen density of
the synthesized films and the abscissa shows the depth from the
surface of the synthesized films. In Fig. 5, the nitrogen density
of the synthesized film at nearly 1.0 $μm$ depth from the surface
of the film synthesized with nitrogen addition was $1×10^{-3}$ atom
% (10 ppm). On the other hand, the nitrogen density of the
synthesized film at nearly 1.0 $μm$ depth from the surface of the
film synthesized without nitrogen addition was $2×10^{-4}$ atom % (2
ppm). From the comparison of the results of SIMS analysis, the
nitrogen density of the films synthesized with nitrogen addition
was larger than that of the films synthesized without nitrogen
addition. Therefore, the nitrogen density of the synthesized film
was increased by adding an optimal amount of nitrogen. We were thus able to prove that the addition of nitrogen as a diamond promotion ingredient to high-purity acetylene gas affects diamond synthesis and film delamination.

4. Conclusions

In this study, to obtain good-quality diamond films and to achieve good adhesion, diamond films were synthesized by stable flame combustion using a mixture of high-purity acetylene and oxygen gas with nitrogen addition. A three-step synthesis method was used to prevent film delamination. Nitrogen flow rate was carefully varied in the range of 0.333~0.667 cm$^3$/s. The effects of varying the nitrogen flow rate on diamond film synthesis and delamination were investigated. Moreover, to investigate the effects of nitrogen addition on the properties of diamond films and film delamination, including nitrogen density of films synthesized with and without nitrogen addition were analyzed.

(1) In the SEM and XRD results, the synthesized diamond crystallites at the nitrogen flow rate of 0.500 cm$^3$/s showed an almost octahedral morphology, and thus were considered good quality diamond crystallites. In this experiment, the optimal nitrogen flow rate was 0.500 cm$^3$/s, and good quality diamond films were obtained. The synthesized crystallites showed almost uniform size and high density. Moreover, as nitrogen flow rate was further increased or decreased from 0.500 cm$^3$/s, the diamond quality of the synthesized films was reduced. The diamond quality of the synthesized films was improved by adding an optimal amount of nitrogen to the mixture of high-purity acetylene and oxygen gas.

(2) The delamination of films synthesized with varying the nitrogen flow rates was prevented at a very high probability. In particular, the delamination of the films synthesized at a nitrogen flow rate of 0.500 cm$^3$/s was completely prevented. The reason for this was that the diamond crystallites synthesized at an optimal nitrogen flow rate of 0.500 cm$^3$/s were good quality diamond crystallites.

(3) From the comparison of the results of SIMS analysis, the nitrogen density of the films synthesized with nitrogen addition was higher than that of the films synthesized without nitrogen addition. Therefore, the nitrogen density of the synthesized film was increased by adding an optimal amount of nitrogen. Thus, nitrogen addition to high-purity acetylene affects diamond synthesis.

We were thus able to prove that the addition of nitrogen as a diamond promotion ingredient to high-purity acetylene gas affects diamond synthesis and film delamination. We also confirmed that good diamond films and good adhesion can be synthesized by stable flame combustion using a mixture of high-purity acetylene and oxygen gas with the addition of an optimal amount of nitrogen gas. Moreover, the crystallite morphology of synthesized films can be changed by varying the nitrogen flow rate.

References