Influence of diamond-etching conditions on the fabrication of diamond microneedles by a thermochemical reaction of Ni in an H₂ atmosphere

Koji KOYAMA¹,²,¹, Seong-Woo KIM¹ and Mamoru YOSHIMOTO²

¹Adamant Namiki Precision Jewel Co., Ltd., Adachi, Tokyo 123–8511, Japan
²Tokyo Institute of Technology, Yokohama, Kanagawa 226–8502, Japan

We examined the influence of diamond-etching conditions on microneedles fabricated by a thermochemical reaction between a Ni film with pinholes and a diamond (100) wafer in an H₂ atmosphere. The diamond microneedles fabricated by varying the annealing temperatures and thickness of the Ni film coated on the diamond were characterized by scanning electron microscopy. Relatively uniform and long diamond microneedles, with diameters of about 1 µm and heights of about 20 µm, were obtained by annealing for 6 h at 850 °C. For Ni films thicker than 1 µm, microneedles with inverted conical shape were obtained, whereas those fabricated with thinner Ni films exhibited a conical shape.

Key-words: Ni, Thermochemical diamond etching, Diamond microneedle, Shape control, Taper angle

[Received February 8, 2021; Accepted May 7, 2021]

Owing to its ultimate properties, diamond has a wide range of applications, including in machining tools, heat spreaders, audio components, and optical parts. In addition, diamond is predicted to be one of the key materials for future electronic devices, such as wide-gap semiconductors and quantum sensors. As the appropriate form for future electronic devices, such as wide-gap semiconductors and quantum sensors, diamond is predicted to be one of the key materials for future electronic devices. In this work, we examined the influence of diamond-etching conditions on microneedles fabricated by a thermochemical reaction of Ni in an H₂ atmosphere. The diamond microneedles fabricated by varying the annealing temperatures and thickness of the Ni film coated on the diamond were characterized by scanning electron microscopy. Relatively uniform and long diamond microneedles, with diameters of about 1 µm and heights of about 20 µm, were obtained by annealing for 6 h at 850 °C. For Ni films thicker than 1 µm, microneedles with inverted conical shape were obtained, whereas those fabricated with thinner Ni films exhibited a conical shape.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words: Ni, Thermochemical diamond etching, Diamond microneedle, Shape control, Taper angle

[Received February 8, 2021; Accepted May 7, 2021]

Owing to its ultimate properties, diamond has a wide range of applications, including in machining tools, heat spreaders, audio components, and optical parts. In addition, diamond is predicted to be one of the key materials for future electronic devices, such as wide-gap semiconductors and quantum sensors. As the appropriate form for future electronic devices, such as wide-gap semiconductors and quantum sensors, diamond is predicted to be one of the key materials for future electronic devices. In this work, we examined the influence of diamond-etching conditions on microneedles fabricated by a thermochemical reaction of Ni in an H₂ atmosphere. The diamond microneedles fabricated by varying the annealing temperatures and thickness of the Ni film coated on the diamond were characterized by scanning electron microscopy. Relatively uniform and long diamond microneedles, with diameters of about 1 µm and heights of about 20 µm, were obtained by annealing for 6 h at 850 °C. For Ni films thicker than 1 µm, microneedles with inverted conical shape were obtained, whereas those fabricated with thinner Ni films exhibited a conical shape.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words: Ni, Thermochemical diamond etching, Diamond microneedle, Shape control, Taper angle

[Received February 8, 2021; Accepted May 7, 2021]

Owing to its ultimate properties, diamond has a wide range of applications, including in machining tools, heat spreaders, audio components, and optical parts. In addition, diamond is predicted to be one of the key materials for future electronic devices, such as wide-gap semiconductors and quantum sensors. As the appropriate form for future electronic devices, such as wide-gap semiconductors and quantum sensors, diamond is predicted to be one of the key materials for future electronic devices. In this work, we examined the influence of diamond-etching conditions on microneedles fabricated by a thermochemical reaction of Ni in an H₂ atmosphere. The diamond microneedles fabricated by varying the annealing temperatures and thickness of the Ni film coated on the diamond were characterized by scanning electron microscopy. Relatively uniform and long diamond microneedles, with diameters of about 1 µm and heights of about 20 µm, were obtained by annealing for 6 h at 850 °C. For Ni films thicker than 1 µm, microneedles with inverted conical shape were obtained, whereas those fabricated with thinner Ni films exhibited a conical shape.

©2021 The Ceramic Society of Japan. All rights reserved.

Key-words: Ni, Thermochemical diamond etching, Diamond microneedle, Shape control, Taper angle

[Received February 8, 2021; Accepted May 7, 2021]
microneedles obtained by varying the annealing temperature and the thickness of the Ni films coated on the diamond (100) wafers were characterized by scanning electron microscopy (SEM).

Commercially available high-pressure high-temperature (HPHT)-synthesized diamond (100) wafers (SUMICRYSTAL, 4 × 4 × 0.5 mm³) were used to examine the effect of etching conditions on the fabrication of the microneedles. Typical average offset angle and its standard deviation toward (100) direction on (100) plane for eleven diamond wafers were estimated to be 0.12° and 0.06°, respectively. The fabrication process, which employs Ni-diamond thermochemical-etching, is schematically shown in Fig. 1. First, the HPHT diamond wafers were planarized using a home-built Scaife polishing machine. The surface roughness (Ra) of the diamond wafers were less than 0.2 nm, which were measured by atomic force microscopy (AFM, Hitachi High-Technologies; AFM5400L).

Next, a Ni film was deposited on the polished diamond wafer using a home-built sputtering apparatus. The output power, Ar-gas flow rate, and gas pressure during the sputtering were 100 W, 12.2 sccm, and 0.2 Pa, respectively. The thickness of the Ni film was varied from 1.0 to 2.0 μm. To obtain the microneedle, pinholes were randomly created on the Ni film by femtosecond laser ablation (wavelength: 780 nm, pulse width: 250 fs, Cyber Laser, IFRIT), as shown in Fig. 1(3). The diameter of the pinholes was controlled by varying the laser-irradiated pulse number and/or laser beam scanning. The diameter and the density of the pinholes on the Ni film employed in this experiment were about 1 μm and 5000 pieces/mm², respectively. By the way, it might be possible to make the well-aligned pinholes when we use a laser ablation system with precisely controlled XY stage. We also confirmed the penetration of the pinholes into the Ni film using an optical microscope with transmitted light, as shown in the inset of Fig. 1(3).

To investigate the relationship between the annealing temperature and the fabricated diamond microneedles, the diamond wafers coated with 1-μm-thick Ni films were annealed in 100% atmospheric H₂ gas using a home-built annealing furnace. The annealing temperatures were varied from 700 to 1000 °C. The annealing time and H₂-gas flow rate were 6 h and 1 L/min, respectively. The appearance of the obtained microneedles was observed with an SEM (JEOL, JSM-63). Crystallinity of the fabricated diamond microneedle was evaluated by Raman spectroscopy (Jasco; NRS-1000). The microneedle was removed from the diamond wafer annealed at 850 °C and then put on a glass plate for the Raman measurement.

We also examined the influence of the thickness of the Ni films on the shape of the fabricated microneedles. Three HPHT diamond wafers with Ni-film thicknesses of 1.0, 1.3, and 2.0 μm were prepared. Pinholes of about 1-μm diameter were created on the Ni films. The annealing temperature and time were 850 °C and 6 h, respectively. The shape of the microneedles was observed using SEM.

Figure 2 shows the variation of the annealing temperature with the height of the microneedles fabricated with the 1.0-μm-thick Ni film and annealed for 6 h. The average height of ten microneedles was estimated. The insets of Fig. 2 are the SEM images of the microneedles, and they show the surface of the Ni film, including the microhole, after annealing at various temperatures. The gray-colored areas indicate the Ni film, which was confirmed by energy-dispersive X-ray spectroscopy. As shown in the SEM images, diamond microneedles were obtained when annealed at temperatures from 800 to 950 °C. Diamond microneedles, as well as the pinholes, were not clearly observed on the Ni film annealed at 700 °C. This could be a result of a slower rate of thermochemical-etching at 700 °C, as well as the filling of the pinholes due to the hydrogen-diagnosis-related deformation of the Ni film near the pinholes. As for our experiments, we could obtain the data on the Ni layer behavior after thermochemical-etching for the case of annealing at 800 °C, which was estimated from surface profiles measured with a laser profiler before/after the Ni layer removal. As a result, it was found that the Ni layer thickness after thermochemical-etching was estimated to be about 0.8 ± 0.1 μm, which was approximately 20% thinner than that before the thermochemical-etching. This decrease in Ni layer thickness might indicate the diffusion of Ni element into the diamond during thermochemical-etching reaction.

The side surfaces of the microneedles annealed at 950 °C were relatively rougher than those of the microneedles annealed at other temperatures, suggesting intense etching of the surfaces of the diamond microneedle with Ni element supplied from the pinhole edge of the Ni film. The sample annealed at 1000 °C showed no microneedles and the Ni film exhibited a considerably uneven surface, as
shown in the insets of Fig. 2. It is assumed that there are two possible mechanisms for no microneedle fabrication at 1000 °C as follows. (1) The Ni film would etch not only vertically but also horizontally to the diamond surface. As a result, the microneedles became thinner and rougher with increasing the annealing temperature until 950 °C. Finally, all the microneedles were completely etched at 1000 °C. (2) As reported previously, hydrogen and carbon diffusion would reduce melting point of the thin Ni film, resulting in closure of the pinhole on the Ni film because of liquefaction of Ni near the pinholes. Relatively uniform and long diamond microneedles of about 1 μm in diameter at the top and 20 μm in height were obtained when annealed for 6 h at 850 °C.

Figure 3 shows Raman spectrum of the microneedle fabricated at 850 °C.

Fig. 3. Raman spectrum of the microneedle fabricated at 850 °C.

Figure 4 shows the SEM images of the microneedles fabricated with different Ni-film thicknesses and annealed 6 h at 850 °C: (a) 1.0 μm, (b) 1.3 μm, and (c) 2.0 μm. The average taper angles at the tip of the microneedle are indicated on the figures.

Fig. 4. SEM images of the microneedles fabricated with different Ni-film thicknesses and annealed 6 h at 850 °C: (a) 1.0 μm, (b) 1.3 μm, and (c) 2.0 μm. The average taper angles at the tip of the microneedles are indicated on the figures.

Figure 2. Variation of the annealing temperature with average height of microneedles annealed for 6 h (Ni film thickness of 1.0 μm). The insets (SEM images) show the microneedles formed at various temperatures. Upper and lower images are top view and bird view, respectively.
The change in the shape of the fabricated microneedles from a conical to an inverted conical shape, as the thickness of the Ni films varied (Fig. 4) is interesting from the scientific and practical viewpoints. It is interesting to discuss the reason why the microneedle shape depends on the Ni film thickness even though there are not so enough experimental results at present. It could be partly attributed to the additional etching of the diamond microneedles by the Ni element supplied from the sidewalls of the Ni pinholes. The carbon and hydrogen elements could catalytically react and desorb as methane, which is similar to the reaction in the diamond etching with Ni nanoparticles as previously reported. On the other hand, the ratio of the pinhole diameter to the Ni-film thickness also seems to be a factor controlling the shape of the obtained microneedles. So that, in case of the same pinhole diameter, the thicker Ni film sidewall might supply relatively more Ni element to the microneedle, which would make the microneedles inverted conical. To clarify the present Ni-film thickness dependence of the microneedle shape, there is a need for further atomic-scale investigations on the composition distribution of Ni or C elements in the diamond microneedles and the Ni film near the pinholes. In addition, to understand the present process, it might be necessary to consider the role of the hydrogen element dissolved in the Ni film.

In summary, we investigated the influence of annealing temperature and Ni-film thickness on the thermochemical-etching reaction between Ni films and diamond (100) wafers in an H₂ atmosphere. This was carried out in an attempt to develop advanced technology for fabricating diamond microneedles. Relatively uniform and long diamond microneedles were obtained at an annealing temperature of 850 °C. The diameter at the top and the height of the fabricated microneedles were about 1 and 20 µm, respectively. The taper angle and the shape of the microneedles varied with the thickness of the Ni film deposited on the diamond wafer. For Ni films thicker than 1 µm, the fabricated microneedles had an inverted conical shape, whereas the thinner Ni films yielded conical microneedles. These results would contribute to not only the improvement of the microneedle fabrication techniques but also the creation of new diamond-based device applications.

References
1) T. Matsumoto, H. Kato, K. Oyama, T. Makino, M. Ogura, D. Takeuchi, T. Inokuma, N. Tokuda and S. Yamasaki, Sci. Rep.-UK, 6, 31585 (2016).
2) P. Sfyushev, M. Nesladek, E. Bourgeois, M. Gulk, J. Hruby, T. Yamamoto, M. Trupke, T. Teraji, J. Isoya and F. Jelezko, Science, 363, 728–731 (2019).
3) N. Fujimori, J. Ceram. Soc. Jpn., 99, 1063–1068 (1991).
4) S. Ikeza and M. Yoshio, J. Ceram. Soc. Jpn., 109, 542–549 (2001) [in Japanese].
5) A. Caspi, Gems Gemol., 33, 102–121 (1997).
6) H. Minami, K. Watanabe, K. Masui and N. Nabekura, J. Soc. Electr.-Mach. Eng., 44, 17–24 (2010).
7) Y. Ando, Y. Nishibayashi, H. Furuta, K. Kobashi, T. Hirao and K. Oura, Diam. Relat. Mater., 12, 1681–1684 (2003).
8) N. Oi, M. Inaba, S. Okubo, I. Tsuyuzaki, T. Kagura, S. Onoda, A. Hiraiva and H. Kawarada, Sci. Rep., 8, 10660 (2018).
9) A. P. Grigoriev and V. V. Kovalsky, Indiaqua, 39, 47–54 (1984).
10) A. P. Grigoriev, S. K. Lifshits and P. P. Shamaev, U. S. Patent No. 4339304, July 13 (1982).
11) A. P. Grigoriev, S. K. Lifshits and P. P. Shamaev, Jpn. Patent No. 1563060, June 12 (1990).
12) H. Al Mehedi, J. C. Arnault, D. Eon, C. Hébert, D. Carole, F. Omnes and E. Gheeraert, Carbon, 59, 448–456 (2013).
13) V. G. Ralchenko, T. V. Kononenko, S. M. Pimenov, N. V. Chernenko, E. N. Loubnin, V. Y. Armeyev and A. Y. Zlobin, Diam. Relat. Mater., 2, 904–909 (1993).
14) W. Smirnov, J. J. Hees, D. Brink, W. Müller-Sebert, A. Kriele, O. A. Williams and C. E. Nebel, Appl. Phys. Lett., 97, 073117 (2010).
15) N. M. Kazuchits, M. S. Rusetksy, V. N. Kuzuchits and A. M. Zaitsev, Diam. Relat. Mater., 64, 202–207 (2016).
16) Y. Imoto and J. Yan, Appl. Surf. Sci., 404, 318–325 (2017).
17) M. Nagai, K. Nakanishi, H. Takahashi, H. Kato, T. Makino, S. Yamasaki, T. Matsumoto, T. Inokuma and N. Tokuda, Sci. Rep., 8, 6687 (2018).
18) H. Aida, S.-W. Kim, K. Ikejiri, Y. Kawamata, K. Koyama, H. Kodama and A. Sawabe, Appl. Phys. Express, 9, 035504 (2016).
19) H. Aida, S.-W. Kim, K. Ikejiri, D. Fujii, Y. Kawamata, K. Koyama, H. Kodama and A. Sawabe, Diam. Relat. Mater., 75, 34–38 (2017).
20) H. Aida, K. Ikejiri, S.-W. Kim, K. Koyama, Y. Kawamata, H. Kodama and A. Sawabe, Diam. Relat. Mater., 66, 77–82 (2016).
21) S.-W. Kim, Y. Kawamata, R. Takaya, K. Koyama and M. Kasu, Appl. Phys. Lett., 117, 202102 (2020).
22) N. T. Gladkich, R. Niedermayer and K. Spiegel, Phys. Status Solidi B, 152, 181–192 (1966).
23) P. C. Yang, W. Liu, R. Schlesser, C. A. Wilden, R. F. Davis, J. T. Prater and Z. Sitar, J. Cryst. Growth, 187, 81–88 (1998).
24) A. Pundt, Adv. Eng. Mater., 6, 11–21 (2004).
25) M. Pitter, M. B. Hugenschmidt and R. J. Behm, Jpn. J. Appl. Phys., 36, 3635–3638 (1997).