Diamond & Related Materials 66 (2016) 206–212

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Surface patterning of synthetic diamond crystallites using nickel powder

Junsha Wang [a,b], Long Wan [a,*], Jing Chen [a], Jiwang Yan [b]

[a] College of Materials Science and Engineering, Hunan University, Hunan 410082, PR China
[b] Department of Mechanical Engineering, Keio University, Yokohama 223-8522, Japan

ARTICLE INFO

Article history:
Received 30 November 2015
Received in revised form 15 April 2016
Accepted 26 April 2016
Available online 2 May 2016

Keywords:
Synthetic diamond crystallites
Surface patterning
Etch patterns
Nickel powder
Graphitization

ABSTRACT

Nickel powder (Ni) was used as catalyst to form micropatterns on diamond crystallites surface without flowing hydrogen gas. Anisotropic etch patterns on {100} and {111} planes of diamond and the interface of diamond and nickel were analyzed, and the pattern area and etch depth formed at different temperatures were measured quantitatively. Results show that the etch patterns on {100} planes were formed as reversed pyramids, while those on {111} planes were hexagons. Compared to {111} planes, {100} planes had better affinity for nickel. And the formation of cubic nanoparticles on the bottom of the patterns might have been caused by the melting and crystallization of eutectic. An increase in temperature promoted the surface patterning process. At the same temperature, {100} planes were etched more significantly than {111} planes in terms of larger pattern area and deeper etch depth. At 950 °C, the average percentages of pattern area on {100} and {111} planes were 21% and 9%, and the corresponding etch depths were 5.0 μm and 3.0 μm, respectively. Moreover, it was demonstrated that graphitization was the dominant mechanism of the diamond surface patterning process.

1. Introduction

Owing to the advantages in hardness, wear resistance, potential range and chemical stability, diamond has been widely used in precision manufacturing industries [1,2] and biological detection field [3,4]. To increase the surface area or introduce nanopores in two-dimensional diamond film used for electrodes or sensors, much attention has been drawn on diamond surface etching by metals in flowing hydrogen gas. Nickel nanoparticles were prepared on the surface of boron-doped diamond (BDD) by vacuum deposition followed by heat treatment in flowing gas of H_2/N_2 [5]. When Ni/BDD was heated at 700 °C for 2 h, Ni nanoparticles were finely dispersed on BDD surface, but no excavation behavior was observed. However, after the temperature climbed to 900 °C, the surface layer of BDD was excavated vigorously and the excavation degree increased with the heating time. Cyclic voltammogram of BDD shows that the surface area reflected by specific capacitance was enhanced by nearly 15 times through the excavation at 900 °C for 24 h. To achieve pores with controlled shape, diamond oriented in different orientations was selected to be etched by molten Ni particles [6]. After heat treatment, reversed pyramids, channels and triangles were formed on {111}, {110} and {100} planes, respectively. And {111} planes, the most resistant to be etched, were shown to be the stopping planes in etch pits. During such a process, the catalytic gasification of carbon with the help of hydrogen was the mechanism of diamond etching [7].

To create etch pits on surface of polyhedral diamond crystallites used as optical material, cobalt were loaded on diamond surface by impregnation in the nitrate solution [8]. After being heated in H_2/N_2, etch pits similar to those on diamond film were achieved. Using the same method, diamond was etched by iron and iron carbide was probably formed in the process [9]. Although a modicum of success has been attained in diamond etching, the process requires hydrogen as a flowing gas. Most importantly, there is little quantitative analysis about the effect of temperature on the etching extent of diamond. Allowing for the processing cost and safety, we developed a new diamond etching method without flowing hydrogen gas [10]. The feasibility of etching behavior of iron on diamond has been verified, but etch pits were not available on the {111} planes. In this paper, nickel powder was used as the catalyst to etch diamond crystallites. Surprisingly, anisotropic etch patterns were found on {100} and {111} planes. After metal was removed by acid, the pattern area and etch depth on diamond surface were quantified by white light interferometer and laser-probe surface profiling, respectively.

2. Experimental

Synthetic diamond crystallites (LD240) with an average diameter of ~500 μm were bought from Henan Liliang New Material Co., Ltd. And nickel powder with size distribution of 12–52 μm was bought from Zhuzhou Cemented Carbide Group Co., Ltd. To start the experiment, diamond and nickel were mixed in a mass proportion of 1:13. Then the mixtures were wrapped by graphite paper and buried in a graphite crucible full of carbon black. In order to build a closed chamber free from air, the graphite crucible was put into an airtight ceramic crucible with carbon black around. Finally, ceramic crucible was heated in the muffle furnace at a rate of 3 °C/min to 600 °C followed by 2 °C/min to750 °C and

* Corresponding author.
E-mail address: wanlong1799@163.com (L. Wan).

http://dx.doi.org/10.1016/j.diamond.2016.04.010
0925-9635/

1.5 °C/min to the objective temperature and then was retained for one hour. After the heat treatment, diamond was washed by the mixed acid of HCl/HNO_3 to remove the metal.

The surface morphology and element distribution of processed diamond were examined by environment scanning electron microscopy (ESEM, FEI, Inspect S50) and energy dispersive X-ray spectroscopy (EDX, Bruker, XFlash Detector 4010). The structural changes of diamond and nickel were analyzed by micro-Raman spectroscopy (JASCO Corporation, NRS-3100YM, laser wavelength: 532 nm, spectral magnification: ×100, NA: 0.95, laser spot size: 1 μm) and X-ray diffraction (XRD, Bruker, D8 Advance) with Cu Kα radiation. The area and depth of patterns on diamond were quantified using white light interferometer (Taylor Hobson Ltd., CCI 1000) and laser-probe surface profiling (Mitaka Kohki Corporation, MP-3), respectively.

3. Results and discussion

3.1. Morphology observation

Fig. 1 shows the ESEM images of Ni-patterned diamond crystallites at different temperatures. When the heat-treatment temperature was 700 °C, micron-sized mutually orthogonal channels aligned in ⟨100⟩ direction were observed on {100} planes. However, at the ends of channels (indicated by a circle in Fig. 1(a2)), the orientations of sides

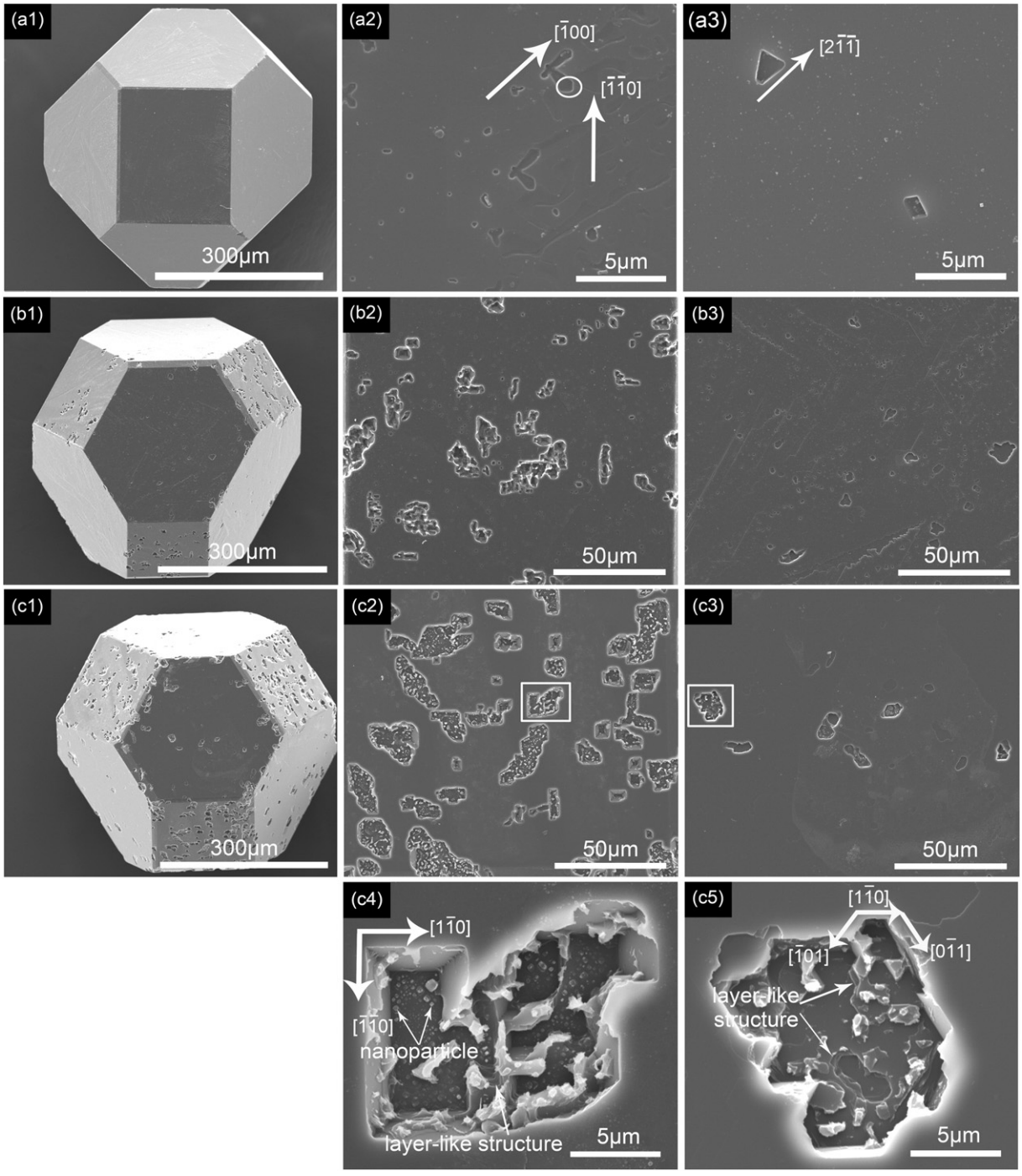

Fig. 1. Morphology of Ni-patterned diamond crystallites heated at (a1) 700 °C, (b1) 800 °C and (c1) 900 °C. ((a2), (b2) and (c2) are the corresponding {100} planes; (a3), (b3) and (c3) are the corresponding {111} planes; (c4) and (c5) are the enlarged square parts in (c2) and (c3), respectively.).