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# Nanoscale surface patterning of diamond utilizing carbon diffusion reaction with a microstructured titanium mold

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ABSTRACT

A novel method was proposed for generating nanoscale surface patterns on single-crystal diamond by carbon diffusion with a microstructured titanium mold under controlled temperature and pressure. The depth, geometry, and surface integrity of the fabricated patterns were investigated by laser micro-Raman spectroscopy and white-light interferometry, and the titanium molds were analyzed by energy dispersive X-ray spectroscopy. The results showed that at specific temperatures and pressures, three-dimensional patterns with a depth of tens of nanometers and sloped/curved walls could be generated on a diamond surface after a few minutes, without causing any surface graphitization. The intensity profile and penetration depth of carbon atoms into the titanium were experimentally measured.

## 1. Introduction

Single-crystal diamond has excellent material properties such as high hardness, thermal conductivity, electrical resistance, and chemical stability, thus it is an important substrate material for cutting tools, power electronics, micro electrical mechanical systems, etc. [1]. There is an increasing demand in industry for the fabrication of large-area micro/nanoscale surface patterns at high precision and low cost. However, due to the high hardness, it is extremely difficult to machine diamond by mechanical methods. Electrical machining can be used to machine sintered poly-crystal diamond [2], but cannot be used for single-crystal diamond due to its insulation properties. Focused ion beam technology can be used to machine diamond, but it is extremely expensive and time- consuming when machining large-area surfaces. Ultra-short pulsed laser has been attempted for machining diamond [3,4], but the surface quality is still low with considerable subsurface damage. In addition, for all the above-mentioned methods, it is difficult to control machining depth at nanometer resolution. In this study, a novel method is proposed to generate nanoscale surface patterns on diamond based on the carbon diffusion reaction with a microstructured titanium mold under controlled temperature and pressure. The resulting depth, geometry, and surface integrity of the patterns were investigated under various conditions. 3D patterns were rapidly fabricated without surface graphitization.

## 2. Mechanism for pattern generation

Though diamond is stable at room temperature, it has high affinity with specific transition metals at a high temperature [5]. Carbon atoms in diamond will diffuse into the transition metals through their contact interface, causing gradual removal of diamond from the surface. As a result, intensive wear occurs to diamond tools when cutting these metals [6–8]. On the other hand, by utilizing the carbon diffusion reaction, a few thermochemical methods have been developed for machining diamond [9–11]. Nevertheless, for ferrous metals Cr, Fe, Co and Ni, catalytic graphitization of diamond occurs before the diffusion reaction [10–12], which causes surface roughening and surface integrity degradation.

In this study, Ti is proposed as a mold material for machining of diamond. Ti is a VI-family metal having 2 *d* electrons. Fig. 1 shows various transition metals plotted with respect to *d* electron number and melting point. Zr, Ta, W, Nb, Mo and Cu have low affinity with diamond due to their high activation energy for carbon diffusion. For other metals, the number of *d* electrons affects the affinity with diamond [13]. Cr, Fe, Co and Ni have 5–8 *d* electrons, thus their affinity with diamond is low. However, their catalytic effect is so strong that upon contact, diamond transforms immediately to graphite before carbon diffusion occurs (Fig. 2(a)). In contrast, Ti and V can react with diamond directly, forming carbides. Ti can absorb carbon atoms from a diamond surface without inducing graphitization (Fig. 2(b)). This unique feature of Ti enables machining of diamond without surface roughening and

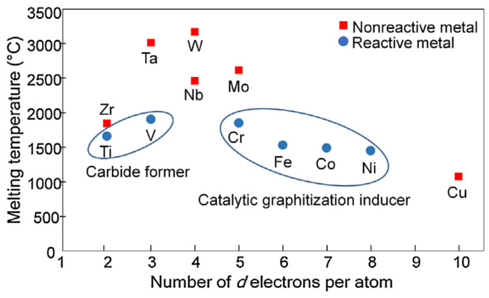

**Fig. 1.** Reactivity with diamond for various transition metals.

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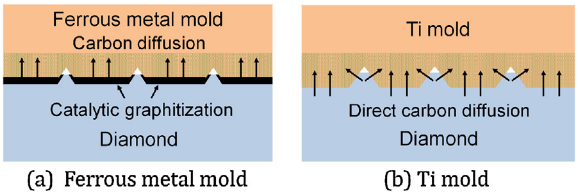


(a) Ferrous metal mold (b) Ti mold

**Fig. 2.** Surface patterning mechanisms of diamond.

graphite residue. When a structured Ti mold is pressed against diamond under high temperature and pressure, carbon atoms are directly absorbed by the Ti. In this way, localized removal of diamond can be realized without leaving a graphite layer. This thermochemical machining method enables the generation of large-area surface patterns by one-step press molding, which provides high productivity, like the nanoimprinting technology.

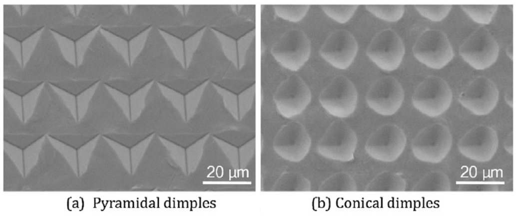
## 3. Experimental procedures

Single-crystal diamond blocks ($3.0 \times 3.0 \times 1.5\ \mathrm{mm}^3$) having (100) surface planes with a mirror finish (surface roughness 1.2 nmSa) were used as the specimens. A nanoindentation system was used to create micro dimples on flat Ti molds having 6 mm diameter, 2 mm thickness, and 10 nmRa surface roughness. Fig. 3 shows SEM photographs of dimples indented on Ti molds by using a Berkovich indenter and a conical indenter. A high-precision molding machine GMP211 (Toshiba Machine Co. Ltd., Japan) was used for the pressing tests, which enables multi-workpiece pressing over an area of 80 mm diameter. Heating was realized by infrared lamps, and temperature was controlled in the range of 600–800 °C with ±1 °C accuracy. Pressing force was controlled with a resolution of 0.98 N to control pressure (~60 MPa). The molding chamber was covered by a quartz tube purged with Ar gas. To prevent stress concentration, 2 mm-thick elastic ceramic sheets were used to cover the diamond sample and the mold from two sides. The patterns formed on the diamond surface were observed using a field emission scanning electron microscope (FE-SEM) (Sirion, FEI Co., USA). The material composition of the mold surface was detected by an energy dispersive X-ray spectroscope (EDS) (XFlash Detector 4010, Bruker Co., Germany). The crystalline structure of the patterns on diamond was characterized by a laser micro-Raman spectroscope (NRS-3100, JASCO Co., Japan). The pattern depth and surface topographies were measured using a white-light interferometer (CCI3D, Taylor Hobson Co., Ltd., UK).

## 4. Results and discussion

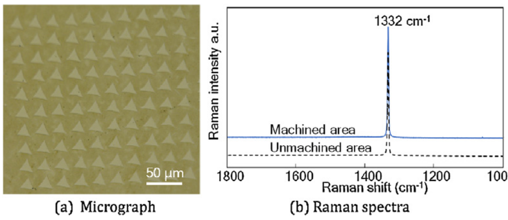
### 4.1. Pattern geometry and surface integrity

Fig. 4(a)is a micrograph of patterns generated on diamond at 800 °C and 30 MPa after a pressing time of 15 min. Triangular patterns were clearly replicated from the pyramidal dimples on the Ti mold (Fig. 3(a)). There was no black graphite residue on the surface after pressing. Fig. 4(b) shows Raman spectra of machined and unmachined surface areas. Both spectra show sharp peaks at 1332 cm$^{-1}$, indicating a structure of single-crystalline diamond without phase transformation. Fig. 5 shows SEM photographs of the patterns at different magnifications. The protruding regions are very smooth (1.2 nmSa), indicating that these regions were unaffected by pressing; whereas the surrounding region is rougher (5.9 nmSa) due to chemical reaction with Ti. Fig. 6 shows a 3D topography and a cross-sectional profile of the patterns. The average height of the protrusions is ~40 nm.



(a) Pyramidal dimples (b) Conical dimples

**Fig. 3.** SEM photographs of micro dimples indented on Ti mold surfaces.



(a) Micrograph (b) Raman spectra

**Fig. 4.** Micrograph and Raman spectra of patterns generated on diamond.

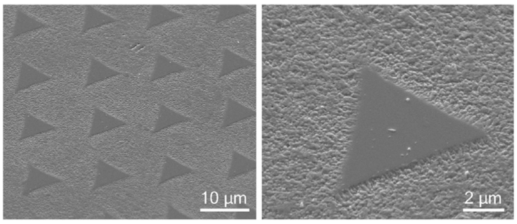
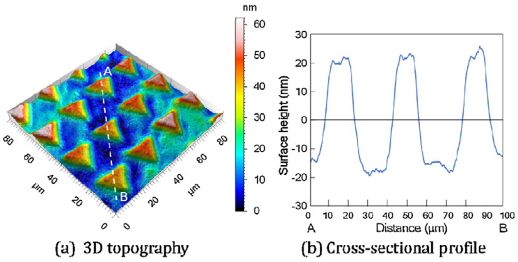


**Fig. 5.** SEM photographs of patterns generated on diamond surface.



(a) 3D topography (b) Cross-sectional profile

**Fig. 6.** 3D topography and cross-sectional profile of patterns in Fig. 5.

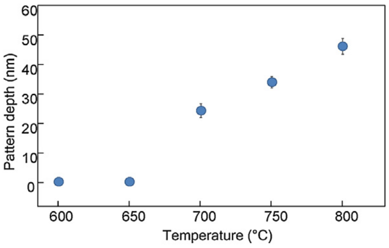
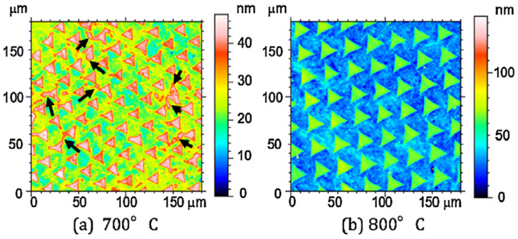


**Fig. 7.** Change of pattern depth with temperature.



(a) 700° C (b) 800° C

**Fig. 8.** Effect of temperature on pattern profile integrity.

### 4.2. Effect of temperature

Pressing tests (15 min each) were performed at temperatures ranging from 600 °C to 800 °C at intervals of 50 °C while the pressure

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