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Anisotropy of synthetic diamond in catalytic etching using iron powder

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ABSTRACT

This paper demonstrated a novel technique for catalytic etching of synthetic diamond crystallites using iron (Fe) powder without flowing gas. The effect of temperature on the etching behaviour on different crystal planes of diamond was investigated. The surface morphology and surface roughness of the processed diamond were examined by scanning electron microscope (SEM) and laser-probe surface profiling. In addition, the material composition of the Fe-treated diamond was characterized using micro-Raman spectroscopy and the distribution of chemical elements and structural changes on Fe-loaded diamond surfaces were analyzed by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD), respectively. Results showed that at the same temperature the {1 0 0} plane was etched faster than the {1 1 1} plane, and that the etching rate of both {1 0 0} and {1 1 1} plane increased with temperature. The etch pits on {1 0 0} plane were reversed pyramid with flat {1 1 1} walls, while the etch holes on {1 1 1} plane were characterized with flat bottom. It was also demonstrated that graphitization of diamond and subsequent carbon diffusion in molten iron were two main factors resulting in the removal of carbon from the diamond surface.

1. Introduction

Owing to the exceptional mechanical properties, such as high hardness, high wear resistance and its ability to form extremely sharp cutting edges, diamond has been widely used in precision manufacturing industries [1,2]. To improve the functionality of diamond and to increase its applicability to other related fields, extensive research is being done concerning surface modification of diamond. Extant literature on gasification of carbon suggests that in the presence of hydrogen, graphite will gasify into methane and furthermore, transition metals can accelerate the gasification process significantly [3,4]. Studies on gasification of graphite have also showed the formation of etch channels [5] and tunnels [6], which led to the subsequent development of the process known as metal catalytic hydrogenation of diamond.

The earliest efforts concerning diamond patterning using Fe, Ni and Pt films under hydrogen atmosphere led to a lore of metallic iron being the most active catalyst [7]. Afterwards, Chepurov et al. [8–10] performed etching of synthetic diamond crystallites with iron particles loaded in a hydrogen atmosphere to investigate the anisotropic etching patterns on different crystal planes. Their results showed that the irregular channels with flat bottom appeared on the {1 1 1} face, while linear cavities were formed on the {1 0 0} and the {1 1 0} faces. It was also observed that etching on the {1 1 1} plane of synthetic diamond proceeded in tangential direction whereas in natural diamond etching occurred preferentially in a normal direction [11]. However, when synthetic diamond crystallites were etched using iron particles which were reduced from ferric chloride by hydrogen gas, etching along the tangential direction was completely absent. Instead, the iron particles penetrated deeper into the volume of diamond leading to the formation of nano pits and tunnels [12]. Most surprisingly, the anisotropy of etching was found non-existent as well [13].

Since then, series of attempts have been made to optimize the etching process by varying the preparative methods and the annealing atmosphere of metal-diamond mixture. An impregnation method was developed to load the ferric nitrate on diamond crystallites and the effect of crystal plane on the etching behaviour at 900 °C in a flowing gas mixture of H_2 (10%) + N_2 (90%) was investigated [14]. Results showed that nanochannels with flat walls perpendicular to the surface were formed on the {1 1 1} plane, while an array of etch pits on the {1 0 0} plane reflecting the atomic arrangements on the corresponding surface was identified. Additionally, the formation of iron carbide-like particles during the iron

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etching process was also postulated. More recently, a simple technique to etch the diamond by self-assembled metals under mixed hydrogen and nitrogen atmosphere was proposed [15]. According to this method, thin iron layers were vacuum evaporated on the {1 0 0}-oriented diamond film and different etching temperatures and holding times were compared. Observations at 800 °C indicated that except the edge part, no etching occurred. Further heating at 900 °C resulted in the formation of some vacant etch pits and channels because Fe particles slipped out of the pits. Under the same conditions, an increase in annealing time led to the appearance of obvious etch pits and channels with four flat walls.

Hence, the above literatures suggest that although a modicum of success has been attained in etching diamond surface using iron but the process requires the use of hydrogen as a flowing gas. Using hydrogen gas increases processing cost and may cause safety problems. From this meaning, it is necessary to develop research on diamond etching without using flowing hydrogen gas. However, up to date, very little has been done to etch diamond without flowing hydrogen. The primary objective of this study was to eliminate the need of a flowing gas while etching diamond using iron. Most importantly, there is no systematic study evident in the literature which would show the dependence of temperature on the anisotropic etching behaviour of synthetic diamond which partly motivated this study as well. Accordingly, the methodology of the experiments and the observations gathered from the experiments are being discussed in this paper.

2. Experimental details

This experimental study made use of diamond crystallites (LD 240 from Henan Liliang New Material Co., Ltd.) with average diameter of 0.5 mm and iron particles with size distribution of 2–10 μm. As for the process of sample preparation, diamond and iron powder in a weight ratio of 1–13 were mixed thoroughly using stirring rod. In order to ensure a close contact between the diamond crystallites and iron powder, the mixture was gently pressed by slide glasses. Subsequently, samples were wrapped with the graphite paper to avoid the influence of oxygen from air on the etching process. Then, samples were placed in the graphite crucible full of carbon black powder, which was set in a closed ceramic crucible with carbon black. Finally the ceramic crucible with sample contained was moved into the muffle furnace. Heating rate from room temperature to 600 °C was set at 3 °C/min which changed to 2 °C/min until 750 °C. In order to ensure the close contact between the surfaces of melt iron and diamond, the heating rate was then slowed to 1.5 °C/min. After the temperature reached the objective etching temperature, it was retained for one hour. After the catalytic treatment, the annealed bulk samples were rinsed in aqua regia ($HCl:HNO_3 = 3:1$) to remove the excess iron particles and the specimens were labelled as Fe-treated diamond. The surfaces of the Fe-treated diamond were measured using a laser probe and maximum Peak-to-Valley (P–V) value was used as an index for characterizing the extent of etching. The surface morphology and distribution of chemical elements of the specimens were done using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometer (EDX) while the chemical composition was characterized by X-ray diffraction (XRD).

3. Results

3.1. Surface morphology of diamond crystallites

Fig. 1 shows the morphology of pristine crystallites of synthetic diamond. The as-received synthetic diamond crystallites had cubo-octahedral structure i.e. eight surfaces oriented on the {1 1 1} plane and six surfaces oriented on the {1 0 0} plane while

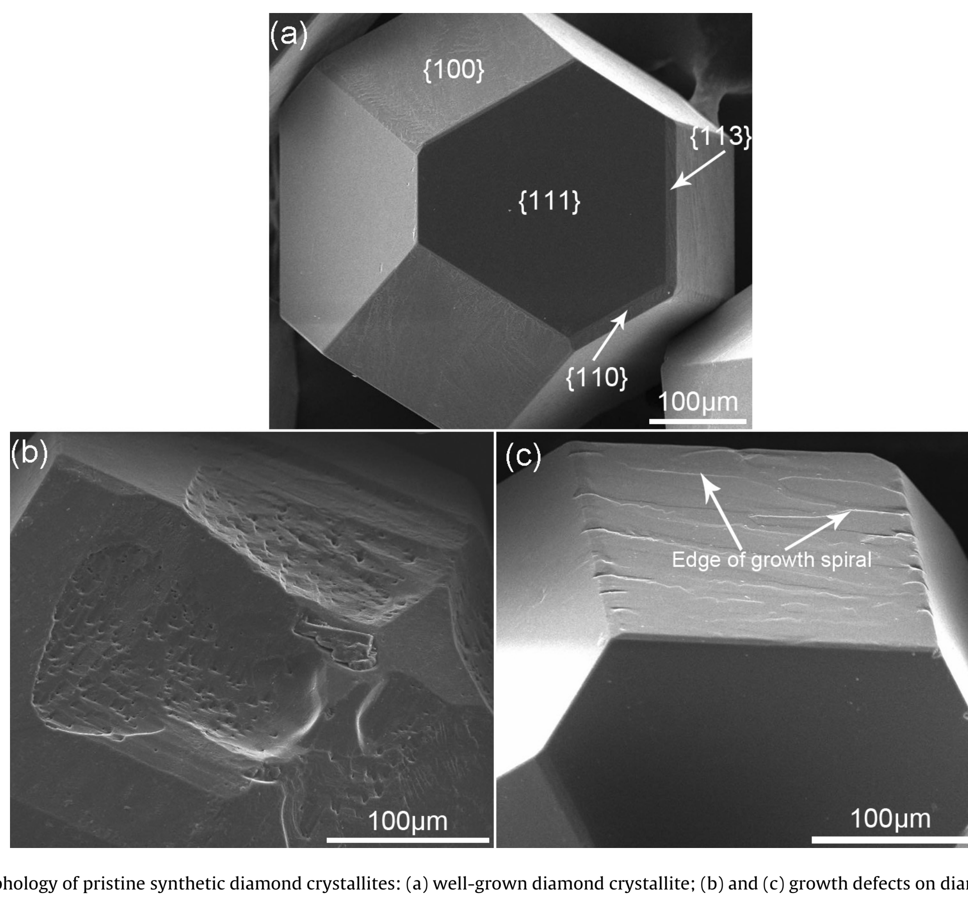

Fig. 1. Morphology of pristine synthetic diamond crystallites: (a) well-grown diamond crystallite; (b) and (c) growth defects on diamond surfaces.