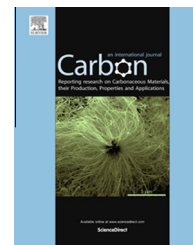


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# Preferential {100} etching of boron-doped diamond electrodes and diamond particles by CO<sub>2</sub> activation

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## ABSTRACT

The etching behavior of polycrystalline boron-doped diamond (BDD) electrodes and diamond particles with gaseous CO<sub>2</sub> at 800 and 900 °C was investigated by field-emission scanning electron microscopy, atomic force microscopy and X-ray photoelectron spectroscopy. Polycrystalline BDD (800 ppm), composed of a mixture of cubic {100} and triangular {111} orientated planes, was used so as to pursue the possibility of preferential etching by high temperature CO<sub>2</sub> treatment. Nanometer sized pits were observed on the {100} planes while no change was observable for the {111} planes when the activation temperature was 800 °C. The difference in the etching behavior by CO<sub>2</sub> with regard to the different planes was clarified using diamond particles and comparing with steam activation. The results demonstrate that CO<sub>2</sub> activation leads to preferential {100} etching, whereas steam-activation results in preferential {111} etching.

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## 1. Introduction

The etching of diamond has been studied both from fundamental standpoints [1–7] as well as for practical applications in conductive diamond electrodes [8–12]. The oxidative etching of diamond with O<sub>2</sub> and O<sub>2</sub>/H<sub>2</sub>O, as well as thermal and hyperthermal atomic oxygen have indicated that the {100} planes are more erosion resistant compared to the {111} planes [1–7]. A similar phenomenon was also observed in the case of H<sub>2</sub>O etching of conductive boron-doped diamond (BDD), where steam activation of BDD lead to preferential etching of the {111} planes [13,14]. In addition to O<sub>2</sub> and H<sub>2</sub>O, CO<sub>2</sub> is also a common oxidative etchant. CO<sub>2</sub> activation has been widely used to prepare activated carbon, and is known to lead to activated carbon with a different microstructure compared to steam activation [15–20]. Despite the abundant work on the preparation of activated carbon via CO<sub>2</sub> and steam activation, information on the reaction

between CO<sub>2</sub> and diamond is scarce. The oxidative etching of diamond in kimberlite melts at high temperatures and high pressures have shown that oxidation of diamond with CO<sub>2</sub> and H<sub>2</sub>O produce different surface features on {111} and {100} planes [21,22]. To the best of our knowledge, the reaction between CO<sub>2</sub> and boron-doped diamond has not been studied yet. These studies motivated us to study the CO<sub>2</sub> activation of boron-doped diamond. We anticipated that in contrast to the {111} etching observed by steam activation in boron-doped diamond [13,14], CO<sub>2</sub> activation may lead to preferential etching of the {100} planes.

Polycrystalline BDD is grown on substrates mainly by CVD processes and consists of randomly oriented crystallites with a mixture of cubic {100} and triangular {111} orientated planes exposed on the surface. Since electrocatalysis and redox reactions are both surface sensitive, BDD with preferential planes exposed to the surface would contribute to a better understanding of the kinetics and electrochemical

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activity of BDD surfaces. The ratio of the exposed planes in BDD electrodes is governed by the CVD conditions and is not easily controlled. For example, highly boron-doped BDD are composed mainly of {111} planes, thus it is difficult to grow diamond films with {100} orientation with high levels of boron doping. The higher level of boron doping in {111} has been suggested to be the cause of higher electron transfer kinetics for redox couples such as  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$  and  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  for {111} than {100} [23,24].

In this study,  $\text{CO}_2$  activation is conducted on polycrystalline boron-doped diamond composed of a mixture of {111} and {100} planes, as well as non-doped diamond crystallites to investigate the etching behavior of doped-diamond surfaces. The etching behavior of different planes is characterized by microscopy and the preferential etching by  $\text{CO}_2$  is compared and discussed with activation using steam as the oxidative etchant.

## 2. Experimental section

Boron-doped polycrystalline diamond (800 ppm) was synthesized by hot filament-assisted chemical vapor deposition on a Nb substrate ( $2 \times 2 \text{ cm}^2$ ) following previous procedures [25,26]. The electrode with the BDD layer facing up was positioned in a silica boat and set in a silica furnace tube. The furnace temperature was raised to the activation temperature (800 or 900 °C) at a rate of  $5^\circ\text{C min}^{-1}$  under flowing  $\text{N}_2$  (99.99995%). When the activation temperature was reached,  $\text{N}_2$  gas was changed to  $\text{CO}_2$  gas ( $200 \text{ mL min}^{-1}$ ) and held for 2 h. Finally, the samples were cooled down to room temperature under flowing  $\text{N}_2$ . The samples will be denoted as a-BDD (800 °C) and a-BDD (900 °C) for BDD activated at 800 and 900 °C, respectively. Steam activation was conducted in a similar fashion to  $\text{CO}_2$  activation. Instead of  $\text{CO}_2$  gas, ultrapure water ( $>18 \text{ M}\Omega \text{ cm}$ ) was introduced into the silica furnace tube at saturated vapor pressure (40 °C) with  $\text{N}_2$  as the carrier gas at a flow rate of  $100 \text{ mL min}^{-1}$ . Activation using both  $\text{CO}_2$  and steam was conducted in an open system with the outlet gas exposed to atmospheric pressure.

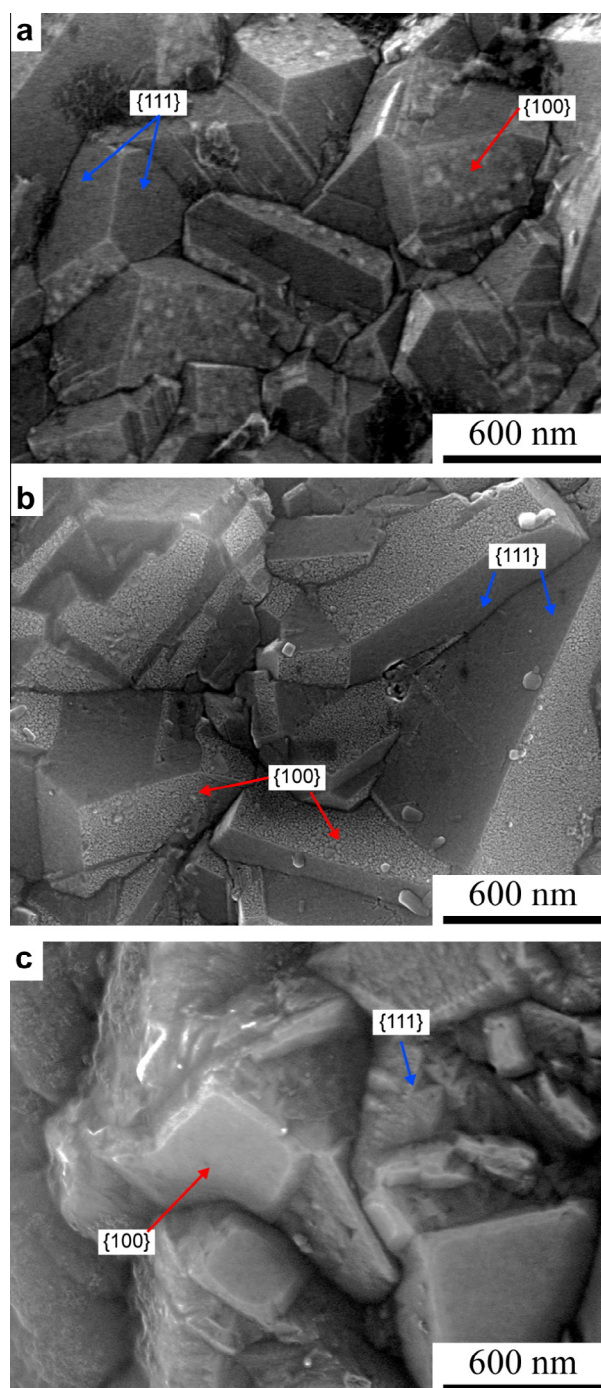
The etching of pure diamond by  $\text{CO}_2$  activation and steam activation was conducted using as-received diamond crystallites with an average diameter of  $300 \mu\text{m}$  (TOMEI DIAMOND Co. Ltd., IMS-25). The diamond crystallites have a cubo-octahedral structure with well-defined {111} and {100} planes (Supplementary material Fig. S1).

A field emission-scanning electron microscope (FE-SEM; Hitachi S-5000) was used for morphological observation. Atomic force microscopy (Bruker, Digital Instruments Nanoscope III ADC 5) was performed in air using silicon cantilevers (Bruker, NCHV-A) and a  $130 \mu\text{m}$  scanner (AS-130V). X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD X-ray photoelectron spectrometer with spectral resolution of approximately 0.8 eV using a standard Mg K $\alpha$  (1256.6 eV) X-ray source operated at 15 mA and 15 kV. All binding energies were referenced to Au (4f $_{7/2}$ ) at 83.7 eV. The C1s spectra were fitted with asymmetric mixed Gaussian-Lorentzian sum functions using the XPS peak fitting software XPSpeak (version 4.1). The microstructure of BDD was characterized by Raman spectroscopy (Kaiser Optical Systems, Inc.,

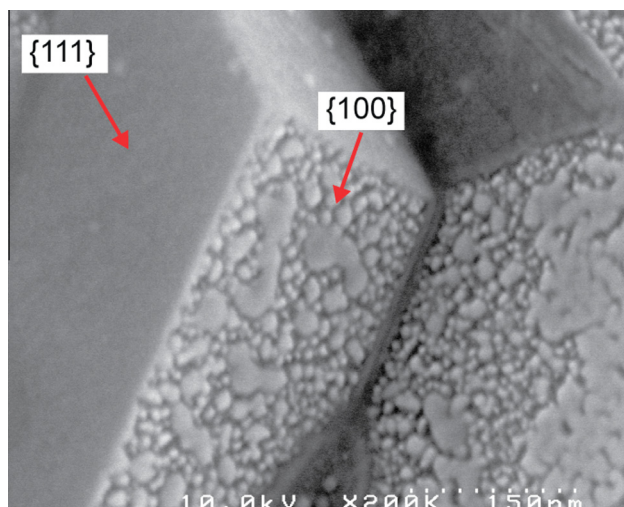
Raman Microscope System 3000) with a YAG laser (excitation wavelength 532 nm) as the excitation source.

## 3. Results and discussion

The pristine BDD (800 ppm boron) electrode consists of randomly oriented crystallites with a mixture of cubic {100} and triangular {111} orientated planes exposed on the surface, as shown in Fig. 1a. The {100} and {111} planes can be



**Fig. 1 – Typical HR-SEM images of (a) pristine BDD, (b)  $\text{CO}_2$  and (c) steam-activated BDD at 800 °C, respectively. (A colour version of this figure can be viewed online.)**



**Fig. 2 – Enlarged image of CO<sub>2</sub>-activated BDD at 800 °C. (A colour version of this figure can be viewed online.)**

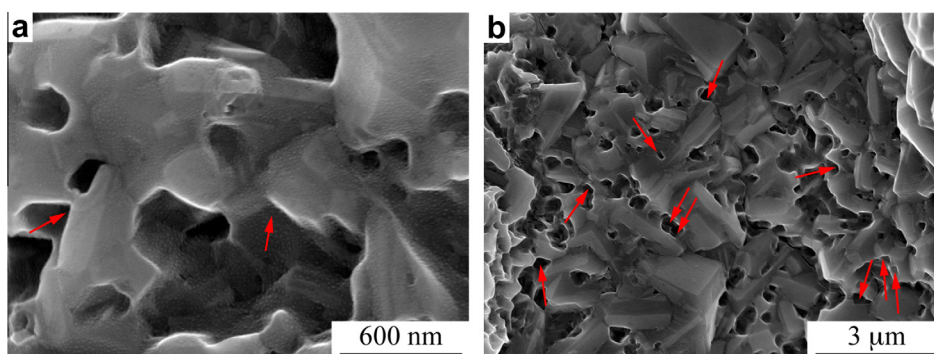
identified by their shape as well as the difference in contrast in the FE-SEM images. In FE-SEM images obtained with secondary electrons, the cubic {100} planes appear as regions with slightly brighter contrast compared to the triangular {111} planes due to different electron affinity [27]. Some inhomogeneity in the contrast is observed on the {100} surface, which may suggest inhomogeneity by partial atmospheric oxidation of the surface.

A typical FE-SEM image of BDD after CO<sub>2</sub> activation at 800 °C is shown in Fig. 1b (see Supplementary material Fig. S1 for low-magnification images). For a-BDD (800 °C), numerous nanopits (5–10 nm) can be observed on the {100} planes, while no etching is evident on the {111} planes, which is more clearly seen in the images at higher magnification (Fig. 2). For the steam-activated BDD (Fig. 1c), many pits in the shape of trigon or deformed trigon are formed on the {111} plane, while no etching is evident on the {100} plane. FE-SEM images of a-BDD (900 °C) reveals progressive etching of the {100} planes at 900 °C forms larger square pits with size of 200–400 nm along the crystal edges (shown with red arrows in Fig. 3), resulting in a macro-porous texture. Etching is so se-

vere at 900 °C, that the {111} planes are no longer able to be distinguished after CO<sub>2</sub> activation. In the case of activated carbon, CO<sub>2</sub> first produces narrow micropores and then the pores are widened as activation progresses [15–20]. If the mechanism of CO<sub>2</sub> activation of BDD is similar to that of activated carbon, then the activation at 900 °C can be attributed to the widening of the nanopits to form large (200–400 nm) square pits.

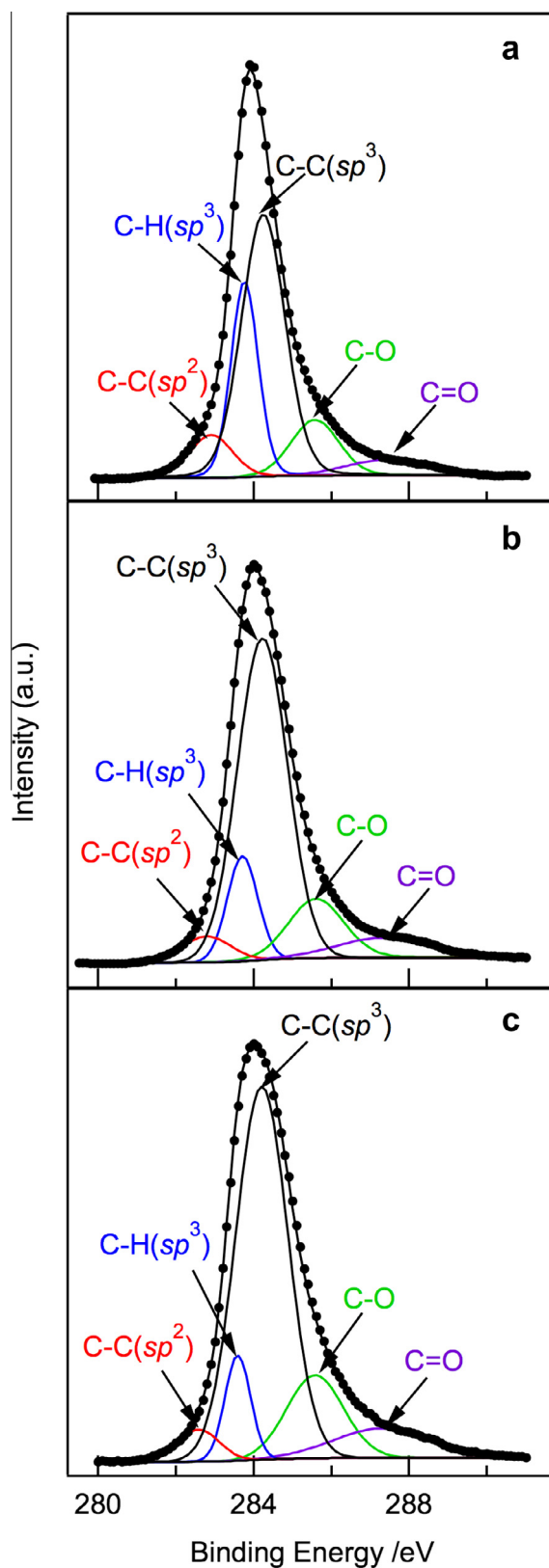
XPS data was acquired to investigate the change in the carbon species on the surface of BDD (Fig. 4). The relative abundance of the five carbon species obtained from the XPS data is shown in Fig. 5. The percentage of C–C(sp<sup>2</sup>) decreased from 8.2% for pristine BDD to 4–5% for the CO<sub>2</sub>-activated BDD, indicating the removal of graphitic impurity by CO<sub>2</sub> activation. This observation was also supported by Raman spectroscopy (see Supplementary material). Oxygen functional groups (C–O, C=O) in pristine BDD is due to partial atmospheric oxidation. After CO<sub>2</sub> activation at 800 °C, the relative abundance of C=O increased from 5.6% to 7.7% without any obvious change in the C–O. CO<sub>2</sub> activation at 900 °C leads to a further increase in C=O content to 9.2% and an increase in C–O from 11.8% to 15.2% compared to the pristine BDD. The abundance of C–H decreases from 23.7% for the pristine BDD to 8.8% for CO<sub>2</sub> activated BDD at 900 °C. C=O is known to form on the {100} plane after oxidation of hydrogen-terminated diamond [28,29]. A similar trend has been reported for anodic oxidation of BDD, producing C–O and C=O on the {100} plane, while C–O is generated on the {111} plane [30]. Coupled with the FE-SEM images showing the preferential etching of the {100} plane, the increase in C=O can thus be associated to the partial oxidation of the {100} plane. Although the conditions of oxidation are different, the trend in the kinetics of oxidation by CO<sub>2</sub> activation seems to be similar to oxidation of diamond and anodic oxidation of BDD.

In order to gain more macroscopic insight into the activation process, large non-doped diamond crystallites were subjected to CO<sub>2</sub> activation. Comparative experiments by steam activation was also conducted to clarify the preferential etching behavior. Typical FE-SEM images of diamond particles after CO<sub>2</sub> and steam activation at 900 °C for 2 h are shown in Fig. 6. After CO<sub>2</sub> activation, the {100} plane is rigorously etched with square pits (around 200–400 nm) with pit density of 5.7 pits μm<sup>−2</sup> (Fig. 6(b)). Etching of the {111} plane is less



**Fig. 3 – Typical HR-SEM images of CO<sub>2</sub>-activated BDD at 900 °C: (a) high and (b) low-magnification. (A colour version of this figure can be viewed online.)**





**Fig. 4** – C1s spectra of (a) pristine BDD and CO<sub>2</sub>-activated BDD at (b) 800 °C and (c) 900 °C for 2 h. (A colour version of this figure can be viewed online.)

obvious with some point-bottomed trigons in the size of 100–300 nm (Fig. 6(b')). The trigonal pit density ( $0.1 \text{ pits } \mu\text{m}^{-2}$ ) is

similar to the defect density of pristine diamond {111} plane, suggesting that the etching occurs at the defect sites. On the

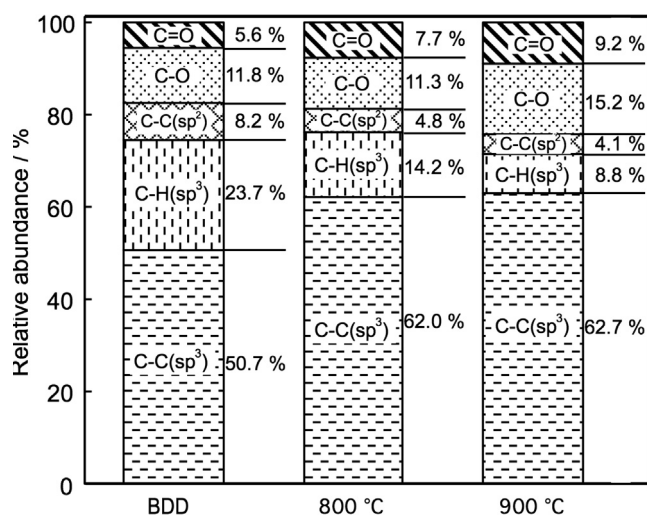


Fig. 5 – Relative abundance of the carbon species based on XPS analysis on BDD.

contrary, steam activation induces a very different surface feature compared to CO<sub>2</sub> activation. The {100} plane of steam-activated diamond (Fig. 6(c)) has point-bottomed square shaped pits with large size of 0.5–2  $\mu\text{m}$  and pit density of 0.8 pits  $\mu\text{m}^{-2}$ . The {111} plane has 0.5–3  $\mu\text{m}$  sized triangular pits with pit density of 0.13 pits  $\mu\text{m}^{-2}$  (Fig. 6(c')). Many steps can be observed on the walls of the triangular pits on the steam-activated {111} plane.

The surface roughness ( $R$ ) was obtained from AFM images shown in Fig. 7. Before activation, the roughness is  $R < 10$  nm for both {111} and {100} planes. For CO<sub>2</sub> activation, increase in roughness of only the {100} plane ( $R = 102$  nm) is apparent, and no obvious change can be observed for {111} plane ( $R = 10$  nm). Thus CO<sub>2</sub> activation leads to preferential etching of {100} and the {111} plane is resistant to activation. The roughness of the steam-activated {111} plane is  $R = 169$  nm, approximately two times higher than steam-activated {100} plane ( $R = 89$  nm). Steam activation etches both {111} and {100} plane, although the {111} plane gives a more roughened surface than the {100} plane. Since preferential etching was

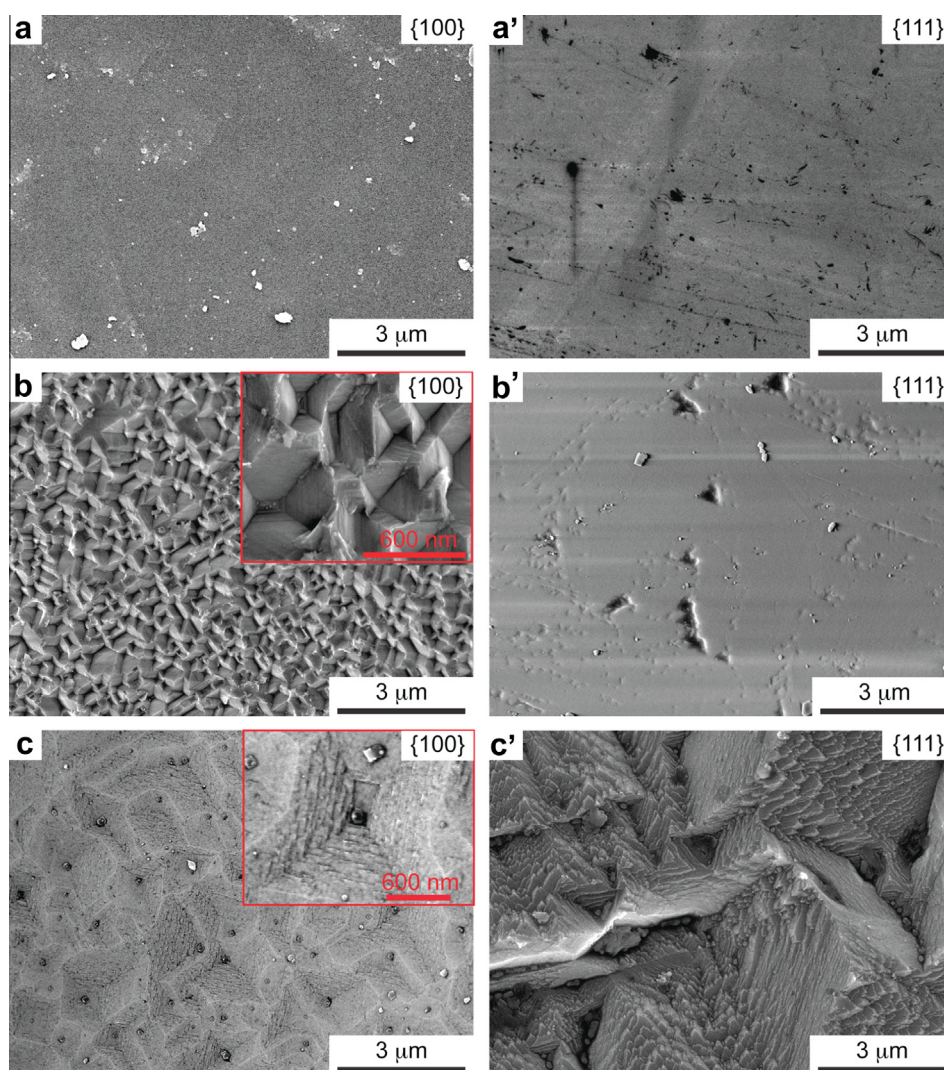
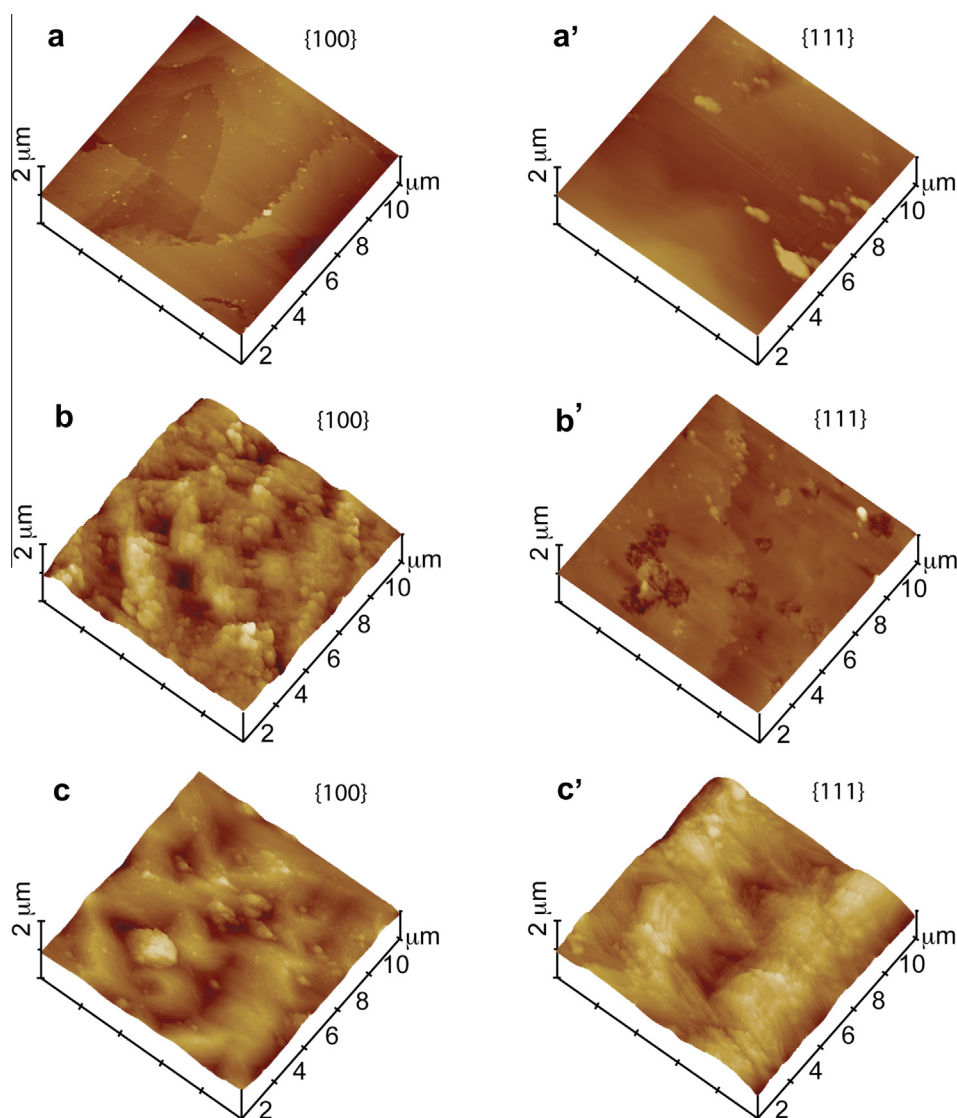


Fig. 6 – Typical SEM images of {100} and {111} plane of (a, a') pristine diamond, (b, b') CO<sub>2</sub> and (c, c') steam-activated diamond at 900 °C for 2 h. (A colour version of this figure can be viewed online.)



**Fig. 7** – Typical AFM tapping mode images of {100} and {111} plane of (a, a') pristine diamond, (b, b') CO<sub>2</sub> and (c, c') steam-activated diamond at 900 °C for 2 h.

observed for non-doped diamond, we presume that boron is probably not the active site for etching. However, since the amount of CO<sub>2</sub>-etchable {100} planes are less abundant for highly doped BDDs, it is anticipated that different etching results would be obtained for different doping level. Steam-activation would most likely result in higher degree of etching compared to CO<sub>2</sub>-activation for highly doped BDD, and vice versa for lower boron-containing BDD.

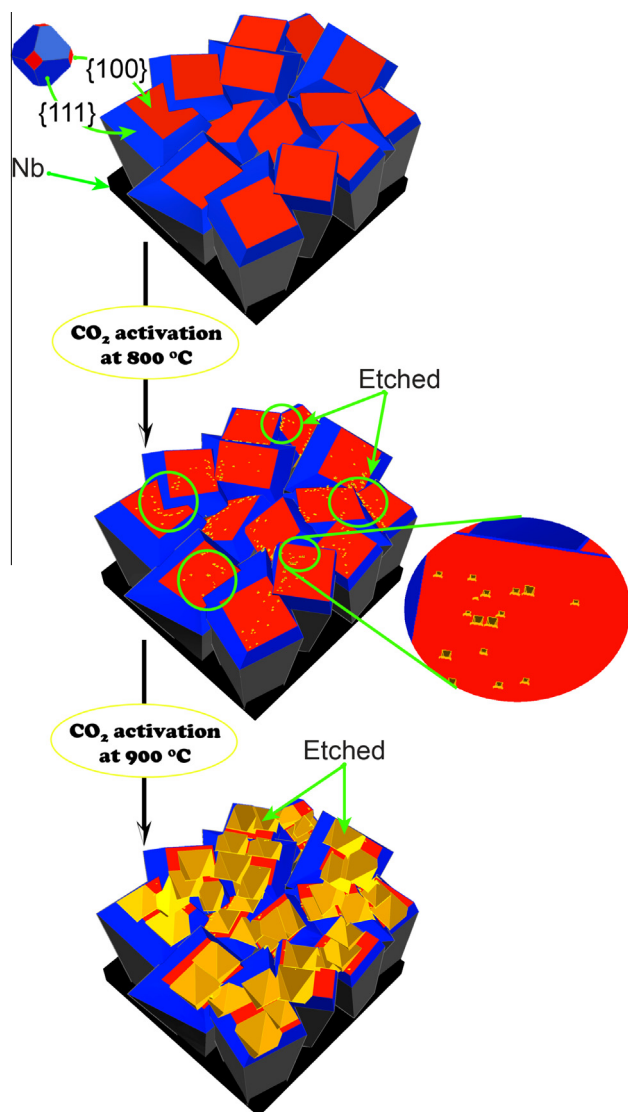
Based on the obtained results, the CO<sub>2</sub>-activation mechanism of polycrystalline BDD is discussed. The oxidative etching of diamond in kimberlite melts at high temperatures and high pressures has been reported [21,22]. In these studies, the relative oxidation rate is different for H<sub>2</sub>O or CO<sub>2</sub> and is also sensitive to the diamond plane [21,22]. The structure sensitive oxidation has been explained by the difference in the position and distance between the open bonds in the diamond lattice being different along the diamond lattice [21,22]. It is assumed that the preferential oxidation of BDD is similar to

that of these high temperature high pressure conditions to some extent. The macroscopic view of the CO<sub>2</sub> activation process of BDD is schematically illustrated in Fig. 8. CO<sub>2</sub> activation at 800 °C leads to mild etching of {100} planes, forming numerous nanopits (5–10 nm) on the {100} plane. When the activation temperature is raised to 900 °C, progressive etching of {100} plane occurs with widening of the pores, resulting in the formation of large square pits (200–400 nm) along the crystal edges.

#### 4. Conclusion

CO<sub>2</sub> activation of boron-doped diamond and diamond surfaces was conducted and compared with steam-activated surfaces. To the best of our knowledge, this is the first report on the CO<sub>2</sub> activation of diamond or boron-doped diamond under atmospheric pressure. Preferential etching of {100}





**Fig. 8 – Schematic illustration of the CO<sub>2</sub>-activation process of polycrystalline BDD.**

planes was observed for CO<sub>2</sub> activation at 800 °C, forming numerous nanopits (5–10 nm). At this temperature, etching of the {111} surface is minimal. A macroporous surface composed of 200–400 nm pits was obtained when the activation temperature was set to 900 °C. Raman and XPS analysis supported the preferential etching of the {100} plane. The preferential etching behavior of boron-doped and non-doped diamond is the opposite of what has been observed in the case of steam activation. The results obtained in this work provide a simple and effective method to control the etching of specific surfaces of sp<sup>3</sup> carbon. The preferential etching by CO<sub>2</sub> and steam may allow one to fabricate BDD electrodes with different exposed surfaces at the same doping level, which is difficult to achieve under typical CVD procedures. This work provides a simple and effective method to control the preferential orientation ({111} or {100}) of BDD surface, which can afford a better understanding behind the fundamental electrochemical behavior of specific BDD surfaces.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.carbon.2013.12.109>.

## REFERENCES

- [1] Evans T, Sauter H. Etching of diamond surface with gases. *Philos Mag* 1961;6(63):429–40.
- [2] De Theije FK, Van Der Laag NJ, Plomp M, Van Enckevort WJP. A surface topographic investigation of 001 diamond surfaces etched in oxygen. *Philos Mag A* 2000;80:725–45.
- [3] De Theije FK, Roy O, Van Der Laag NJ, Van Enckevort WJP. Oxidative etching of diamond. *Diamond Relat Mater* 2000;9(3–6):929–34.
- [4] De Theije FK, Van Veenendaal E, Van Enckevort WJP, Vileg E. Oxidative etching of cleaved synthetic diamond 111 surfaces. *Surf Sci* 2001;492(1–2):91–105.
- [5] Shpilman Z, Gouzman I, Grossman E, Shen L, Minton TK, Paci JT, et al. Oxidation and etching of CVD diamond by thermal and hyperthermal atomic oxygen. *J Phys Chem C* 2010;114(44):18996–9003.
- [6] Paci JT, Schatz GC, Minton TK. Theoretical studies of the erosion of (100) and (111) diamond surfaces by hyperthermal O(<sup>3</sup>P). *J Phys Chem C* 2011;115(30):14770–7.
- [7] Paci JT, Minton TK, Schatz GC. Hyperthermal oxidation of graphite and diamond. *Acc Chem Res* 2012;45(11):1973–81.
- [8] Masuda H, Yanagishita T, Yasui K, Nishio K, Yagi I, Rao TN, et al. Synthesis of well-aligned diamond nanocylinders. *Adv Mater* 2001;13:247–9.
- [9] Terashima C, Arihara K, Okazaki S, Shichi T, Tryk DA, Shirafuji T, et al. Fabrication of vertically aligned diamond whiskers from highly boron-doped diamond by oxygen plasma etching. *ACS Appl Mater Interfaces* 2011;3:177–82.
- [10] Yang N, Uetsuka H, Osawa E, Nebel CE. Vertically aligned nanowires from boron-doped diamond. *Nano Lett* 2008;8(11):3572–6.
- [11] Takasu Y, Konishi S, Sugimoto W, Murakami Y. Catalytic formation of nanochannels in the surface layers of diamonds by metal nanoparticles. *Electrochim Solid-State Lett* 2006;9(7):C114–7.
- [12] Ohashi T, Sugimoto W, Takasu Y. Catalytic roughening of surface layers of BDD for various applications. *Electrochim Acta* 2009;54(22):5223–9.
- [13] Ohashi T, Zhang J, Takasu Y, Sugimoto W. Steam activation of boron doped diamond electrodes. *Electrochim Acta* 2011;56(16):5599–604.
- [14] Zhang J, Nakai T, Uno M, Nishiki Y, Sugimoto W. Effect of the boron content on the steam activation of boron-doped diamond electrodes. *Carbon* 2013;65:206–13.
- [15] Rodríguez-Reinoso F, Molina-Sabio M, González MT. The use of steam and CO<sub>2</sub> as activating agents in the preparation of activated carbons. *Carbon* 1995;33(1):15–23.
- [16] Molina-Sabio M, Gonzalez MT, Rodriguez-Reinoso F, Sepiilveda-Escribano A. Effect of steam and carbon dioxide activation in the micropore size distribution of activated carbon. *Carbon* 1996;34(4):505–9.

- [17] Linares-Solano A, Salinas-Martínez de Lecea C, Cazorla-Amorós D, Martín-Gullón I. Porosity development during CO<sub>2</sub> and steam activation in a fluidized bed reactor. *Energy Fuels* 2000;14(1):142–9.
- [18] Pastor-Villegas J, Durán-Valle CJ. Pore structure of activated carbons prepared by carbon dioxide and steam activation at different temperatures from extracted rockrose. *Carbon* 2002;40(3):397–402.
- [19] Román S, González JF, González-García CM, Zamora F. Control of pore development during CO<sub>2</sub> and steam activation of olive stone. *Fuel Process Technol* 2008;89(8):715–20.
- [20] González JF, Román S, González-García CM, Valente Nabais JM, Luis Ortiz A. Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation. *Ind Eng Chem Res* 2009;48(16):7474–81.
- [21] Fedortchouk Y, Canil D, Semenets E. Mechanisms of diamond oxidation and their bearing on the fluid composition in kimberlite magmas. *Am Mineral* 2007;92(7):1200–12.
- [22] Fedortchouk Y, Manghnani MH, Hushur A, Shiryaev A, Nestola F. An atomic force microscopy study of diamond dissolution features: the effect of H<sub>2</sub>O and CO<sub>2</sub> in the fluid on diamond morphology. *Am Mineral* 2011;96(11–12):1768–75.
- [23] Pleskov YV, Evstefeeva YE, Varnin VP, Teremetskaya IG. Synthetic semiconductor diamond electrodes: electro-chemical characteristics of homoepitaxial boron-doped films grown at the (111), (110), and (100) faces of diamond crystals. *Russ J Electrochem* 2004;40:1023–9.
- [24] Pleskov YV, Evstefeeva YE, Krotova MD, Varnin VP, Teremetskaya IG. Synthetic semiconductor diamond electrodes: electrochemical behaviour of homoepitaxial boron-doped films orientated as (111), (110), and (100) faces. *J Electroanal Chem* 2006;595:168–74.
- [25] Hattori S, Doi M, Takahashi E, Kurosu T, Nara M, Nakamatsu S, et al. Electrolytic decomposition of amaranth dyestuff using diamond electrodes. *J Appl Electrochem* 2003;33:85–91.
- [26] Katsuki N, Takahashi E, Toyoda M, Kurosu T, Iido M, Wakita S. Water electrolysis using diamond thin-film electrodes. *J Electrochem Soc* 1998;145(7):2358–61.
- [27] Ushizawa K, Watanabe K, Ando T, Sakaguchi I, Nishitani-Gamo M, Sato Y, et al. Boron concentration dependence of Raman spectra on 100 and 111 facets of B-doped CVD diamond. *Diamond Relat Mater* 1998;7(11–12):1719–22.
- [28] Pehrsson PE, Mercer TW. Oxidation of heated diamond C(100): H surfaces. *Surf Sci* 2000;460:74–90.
- [29] Pehrsson PE, Mercer TW. Oxidation of the hydrogenated diamond (100) surface. *Surf Sci* 2000;460:49–66.
- [30] Kondo T, Honda K, Tryk DA, Fujishima A. Covalent modification of single-crystal diamond electrode surfaces. *J Electrochem Soc* 2005;152(1):E18–23.