氏名（本籍・生年月日）	張　俊鋒（中国・１９８５年6月２７日）
学位の種類	博士（工　学）
学位記番号	甲　第６０６号
学位授与の日付	平成２６年３月２０日
学位授与の要件	信州大学学位規程第５条第１項該当
学位論文題目	Mechanism of preferential etching of boron-doped diamond electrodes by steam or CO_2 activation
論文審査委員	主査　教　授　杉本　渉 教　授　村上　泰 教　授　沖野　不二雄 准教授　服部　義之 教　授　白石　壮志（群馬大学）

論　文　内　容　の　要　旨

Diamond, a wide-gap insulator, can be converted to a conductor by boron doping. Conductive boron-doped diamond (BDD) is an excellent electrode material for various applications thanks to its wide potential window, chemical and electrochemical stability, and low background current compared to other electrode materials. Fabrication of nanostructured BDD surfaces without loss of other properties is extremely desirable for enhancing its performance (for certain applications). Preferential etching methods have increasingly received attentions for fabricating nanostructured BDD. Steam and carbon dioxide activation are conventional manufacturing processes of activated carbon, whereas they lead to activated carbon with different microstructure. The oxidative etching of diamond {111} and {100} by H_2O and CO_2 at high temperature and high pressure shows different surface features, indicating that relative oxidation rate is different for H_2O and CO_2 and is also sensitive to the diamond structure. In this thesis, steam and CO_2 activation of BDD electrodes were studied with emphasis on the fundamental mechanism of preferential etching for boron-doped polycrystalline diamond electrodes. The non-doped diamond crystallites and films were used for gaining more insight into the activation process. The background of this thesis was introduced in chapter 1. The results are summarized below.

In chapter 2, steam activation of BDD electrodes with different levels of boron doping (800, 2500 and 5000 ppm boron) at 800 °C was conducted, in order to provide detailed insight into the steam-activation process, in particular the difference between the initial reactivity of the {111} and {100} planes against steam activation. The preliminary control experiment with non-diamond crystallites shows that steam activation etches both {111} and {100} plane, although the {111} plane is more easily etched than the {100} plane. An increase in electrical double layer capacitance of BDD electrodes was observed after steam activation, and the enhancement factor was more pronounced for BDD with higher boron content. A 17.5 times increase in roughness was obtained by steam-activation of BDD with 5000 ppm boron. The higher capacitance (surface area) obtained for BDD with higher boron content is attributed to the higher fraction of {111} planes exposed on the surface. The study of non-doped diamond film indicates that the boron is probably not the active site for etching. The mechanism was discussed based on the obtained results, indicating that {111} plane has higher reactivity compared to {100} planes against steam activation. Steam activation is an effective method to increase the active surface area of BDD electrodes and at the same time, enlarge the potential window by removing graphitic impurities.

In chapter 3, CO_2 activation was conducted on BDD electrode composed of a mixture of cubic {100} and triangular {111} orientated planes for investigating the etching behavior. The preliminary experiment on diamond crystallites shows that CO_2 activation leads to preferential etching of {100} and the {111} plane is resistant to activation. For BDD electrode, nanometer sized (5-10 nm) pits were observed on the {100} planes while no change was observable for the {111} planes at 800 °C. When the activation temperature was set to 900 °C, progressive etching of the {100} planes formed larger square pits with size of 200-400 nm along the crystal edges. The study on CO_2 activation of non-doped diamond film indicates that the boron is probably not active site for etching. The mechanism was discussed based on the microscopy and XPS analysis, which indicates that the {100} has higher structure sensitivity than {111} against CO_2 activation. The preferential {100} etching of BDD by CO_2 activation is the opposite of what has been observed in the case of steam activation.

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. The preferential etching by steam and CO_2 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. The obtained results were summarized in chapter 4.