



Influence of boron concentration on growth characteristic and electro-catalytic performance of boron-doped diamond electrodes prepared by direct current plasma chemical vapor deposition

Yujie Feng^{a,*}, Jiangwei Lv^a, Junfeng Liu^a, Na Gao^a, Hongyan Peng^b, Yuqiang Chen^b

^a State Key Laboratory of Urban Water Resources and Environment, Harbin Institute of Technology, No. 73, Huanghe Road, Harbin 150090, China

^b Physics Department, Mudanjiang Normal College, Mudanjiang 157012, China

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ABSTRACT

A series of boron-doped diamond (BDD) electrodes were prepared by direct current plasma chemical vapor deposition (DC-PCVD) with different compositions of $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3$ gas mixture. A maximum growth rate of $0.65 \text{ mg cm}^{-2} \text{ h}^{-1}$ was obtained with $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3$ ratio of 4/190/10 and this growth condition was also a turning point for discharge plasma stability which arose from the addition of $\text{B}(\text{OCH}_3)_3$ that changed electron energy distribution and influenced the plasma reaction. The surface coating structure and electro-catalytic performance of the BDD electrodes were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, Hall test, and electrochemical measurement and electro-catalytic oxidation in phenol solution. It is suggested that the boron doping level and the thermal stress in the films are the main factors affecting the electro-catalytic characteristics of the electrodes. Low boron doping level with $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3$ ratio of 4/199/1 decreased the films electrical conductivity and its electro-catalytic activity. When the carrier concentration in the films reached around 10^{20} cm^{-3} with $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3$ ratio over a range of 4/195/5–4/185/15, the thermal stress in the films was the key reason that influenced the electro-catalytic activity of the electrodes for its effect on diamond lattice expansion. Therefore, the BDD electrode with modest $\text{CH}_4/\text{H}_2/\text{B}(\text{OCH}_3)_3$ ratio of 4/190/10 possessed the best phenol removal efficiency.

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1. Introduction

Industrial wastewater might contain toxic and non-biodegradable organic substrates, which are not available for conventional biological treatment. Electrochemical oxidation process, as one of advanced oxidation processes (AOPs), has attracted considerable attention for its potential application in oxidizing a broad range of biorefractory organic pollutants [1–3]. The effectiveness of electrochemical oxidation for wastewater treatment is mainly dependent on the properties of the electrode materials and the conditions of the electrolysis. Traditional metal electrodes and some DSA electrodes have been investigated extensively such as platinum [4], ruthenium dioxide [5], lead dioxide [6], and tin dioxide [7]. The deficiencies of these electrodes might be concluded as low current efficiency and low stability that arise from low oxygen evolution over-potential [8], corrosion of the coatings and substrates [9] and fouling or poisoning of the active surfaces [10]. Thus, there is a need for developing new electrode

materials that have high stability, high activity and low cost for wastewater treatment. Since Tenne et al. reported the first usage of boron-doped diamond (BDD) electrodes for pollutant removal in 1993 [11], there has been increasing interest in the synthetic diamond electrodes to oxidize a wide variety of organic compounds [12–14]. BDD electrodes possess several favorable electrochemical properties, including a wide potential window in aqueous media, low background current, high stability and corrosion resistance in acid and alkaline solution [15]. Thus, BDD electrodes are currently considered to be one of the most promising electrode materials for electrochemical oxidation process.

Various chemical vapor deposition (CVD) techniques have been invented and applied to fabricate diamond films, including hot filament CVD (HFCVD) [16], microwave plasma CVD (MPCVD) [17], plasma enhanced CVD [18], electron assisted CVD [19], etc. Among all of them, direct current plasma chemical vapor deposition (DC-PCVD) is one of CVD techniques initially proposed by Suzuki et al. [20] in the early 1987. Based on glow discharge to acquire high hydrogen dissociation, the advantage of DC-PCVD is its high efficiency and high growth rate, which is superior to widely used HFCVD and MPCVD. The stability of the DC glow discharge is crucial for diamond films growth by DC-PCVD, especially for doping

* Corresponding author. Tel.: +86 451 86283068; fax: +86 451 82373516.
E-mail address: yujief@hit.edu.cn (Y. Feng).

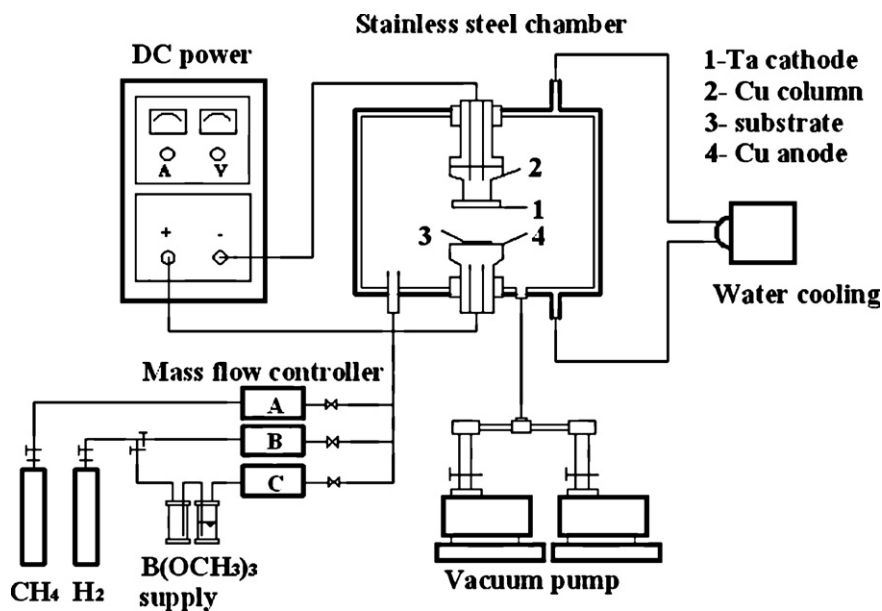


Fig. 1. Schematic diagram of DC-PCVD system.

diamond films deposition which needs to add dopant gases or vapors to a conventional methane hydrogen gas mixture. Lee et al. found that the addition of Ar and nitrogen in the gas mixture would cause unstable plasma and change the quality and morphology of diamond films [21]. Due to the difficulty of sustaining stable plasma, there are few reports with regard to the addition of other gases in deposition of doping diamond films by DC-PCVD. Our previous research found that boron dopant concentration was a key growth parameter for plasma stability when preparing BDD films and that properly control this parameter can acquire stable DC plasma conditions [22].

Diamond in its pure form is an insulator with a wide band gap of 5.5 eV. Addition of proper amounts of dopants, such as B, P and N, can enhance the electrical conductivity of the diamond films [23,24]. Diamond films doped with boron (p-type) could obtain low electrical resistivity ($\sim 10^{-3} \Omega \text{ cm}$) and be used as electrode materials [25]. For BDD electrodes preparation by DC-PCVD, high boron doping level in the film could improve the electrical conductivity of the electrode. However, high concentration of boron dopant in the preparation process usually causes glow discharge breakdown and finally destroys the active surface [22]. Thus, it is important to control the boron dopant concentration in the gas phase to sustain stable glow discharge plasma and to optimize this growth parameter to acquire BDD electrodes with high electrical conductivity and high electro-catalytic activity.

In this work we prepared a series of BDD electrodes with different boron dopant concentrations in the gas phase by DC-PCVD. The effects of boron dopant concentration on growth characteristic and electro-catalytic performance of BDD electrodes were characterized by SEM, XRD, Raman spectroscopy, Hall test and phenol degradation.

2. Experiments

2.1. Electrode fabrication

BDD films were deposited on p-type monocrystalline Si (1 1 1) substrates using a DC-PCVD system (Fig. 1). A stainless steel chamber was used as deposition reactor. The DC glow discharge was sustained between tantalum cathode with a diameter of 70 mm

and water-cooled copper anode. The surface of the Si substrate was cleaned in a dilute HF solution to remove oxide layer, and then scratched with diamond paste to enhance the nucleation of diamond particles during the initial growth stage, finally washed with alcohol to remove polishing debris from the scratches. The source gas was a mixture of ultrahigh purity CH₄ (99.999%) and H₂ (99.999%) regulated by mass flow controller "A" and "B", and B(OCH₃)₃ was used as boron source. The B(OCH₃)₃ concentration in the source gas was controlled by regulating the output of a carrier gas (H₂) (mass flow controller "C") which flowed through the liquid B(OCH₃)₃ source in a bubbler. The substrate temperature was monitored with optical pyrometer (Sciample technology Co. Ltd., China). Four BDD electrodes with CH₄/H₂/B(OCH₃)₃ ratio of 4/199/1 (sample A), 4/195/5 (sample B), 4/190/10 (sample C) and 4/185/15 (sample D) were prepared, respectively. The detailed growth parameters were shown in Table 1.

2.2. Growth characteristic and surface structure of BDD electrodes

The average growth rates (G) of the BDD films over the whole film area were calculated by measuring the film weight change before (W_1) and after (W_2) deposition at various growth time (t) and at various film areas (A) according to the following equation:

$$G(\text{mg cm}^{-2} \text{ h}^{-1}) = (W_2 - W_1)/(t \times A) \quad (1)$$

The crystal morphology of BDD electrodes was characterized by field emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). Raman measurement was carried out over a frequency range of 200–2000 cm^{-1} on the Raman spectrometer (inVia Raman, Renishaw Corporation, UK) with an excitation wavelength of 514.5 nm of Ar ion laser. X-ray diffraction patterns of BDD electrodes were recorded on a D/max-2200/PC XRD instrument (Rigaku Co. Ltd., Tokyo, Japan), using Cu K α radiation and a graphite monochromator at an operating voltage of 40 kV and current of 20 mA. A scanning speed of 2°/min with a sample interval of 0.02° was used. Carrier concentration of BDD electrode was determined by ET9000 Hall system (East Changing Technologies, Inc., China).

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