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Preparation and characterization of vertically columnar boron doped diamond array electrode

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ABSTRACT

A vertically columnar boron doped diamond (BDD) array electrode was fabricated by microwave plasma chemical vapor deposition. Observed by scanning electron microscopy, the fabricated samples were structured with aligned columns whose diameter and height was 8 μm and 12 μm, respectively, and the minimum interval of neighboring columns was 2 μm. The results of electrochemistry measurement showed that the columnar BDD array electrode possessed high oxygen evolution potential and low background current. Besides that, comparing with flat BDD electrode, the columnar BDD array electrode showed higher electrochemical activity (due to its inner active surface being up to 4.25 cm^2), lower impedance of electric double layer, and especially enhanced electrical response signal (2.12 μA/μM, 4 times of flat BDD in glucose detection as a sample). These excellent performances may open the door for the BDD materials to be applied in wide areas including electrochemical detection, electrochemistry degradation, electrochemical synthesis, and so on.

1. Introduction

Electrochemistry, an important part of physical chemistry, is widely involved in the fields of metal industry, environmental science, energy science, imageology, electronics, biology, medical science and so on [1]. Electrode materials play an important role in electrochemical oxidation by influencing the effectiveness of oxidation, degradation pathways, and reaction mechanisms. Different electrode materials (including graphite electrode, glassy carbon electrode, metal electrodes and metal oxide electrodes) have been examined to improve the effectiveness of oxidation and current efficiency [2]. Comparing with these traditional electrode, boron doped diamond (BDD) electrodes obtain following advantages [3–8]: wide electrochemical working potential window in aqueous electrolyte; high mechanical strength and corrosion resistance (even anodic polarization in acidic solution); high resistance to deactivation and long term response stability; and low and stable electric double layer capacitor and voltammetric background current. Therefore, BDD electrode has been investigated extensively in treatment of toxic refractory organic wastewater [9–19], detection of organic compounds and metal ions [20–28], electrosynthesis of organic and inorganic substances [29–31]. However, most studied BDD electrodes are flat with low special surface area and less activity reaction site. Thus they cannot meet the requirements of those applications in sensitivity, efficiency and selectivity [32,33].

To find the methods of improving their performance, the electrochemical process mechanism of organics on BDD electrode was analyzed. The widely acknowledged mechanism considers that organics oxidation and oxygen evolution are carried out through intermediate hydroxyl radicals (produced by water discharge) adsorbed on BDD electrode surface. This mechanism reveals the efficiency of electrocatalytic reaction can be improved by the following methods: increasing the reaction site (area) to promote the quantity of ·OH on electrode surface; increasing the contact between reactant and electrode, and improving products fast release from electrode surface to accelerate electrocatalytic reaction. According to the above analysis, many researches focused on increase of the reaction site (area) by etching BDD film with diamond powder as covering film [34], or depositing BDD on substrates with special micro-structure [35]. In these studies a large increase of reaction site is obtained. However, above mentioned methods always ignore that Warburg impedance (mass transfer resistance) will increase with the morphological nonuniformities of the surface, roughness and porosity [36]. The efficiency of electrochemistry will reduce with the increase of Warburg impedance.

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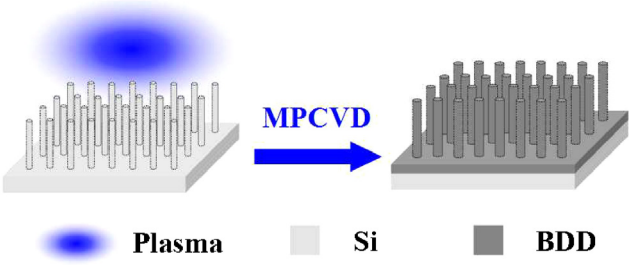

Fig. 1. Schematic diagram of fabrication process of columnar BDD array electrodes.

As mentioned above, the nonuniform structure leads to increase of Warburg impedance. Obviously, a BDD electrode with aligned array structure may solve this contradiction. It can improve the reaction rate not only by increasing the reaction site and electron transfer rate, but also by building a smooth way for the transfer of reactant to electrode surface and products to solution. The aligned array structure can inhibit the increasing of Warburg impedance taken from the three-dimensional structure. However, no report with respect to this topic has been published up to now.

In this work, a vertically aligned BDD electrode was fabricated by depositing BDD onto vertically aligned Si columns. Both its reaction sites and Warburg impedance were evaluated by electrochemical impedance spectroscopy (EIS). Enhanced electrical response signal (glucose detection as a sample) proved that the columnar BDD array electrode performed a higher electrochemical activity and efficiency comparing with flat BDD electrode, successfully.

2. Experimental

2.1. Preparation of columnar BDD array electrode

The Si column array (as the substrate of BDD) was obtained by micro electro mechanical systems (MEMS) techniques [37]. Firstly, SiO_2 film was grown on Si wafer (p-type, 111 plane) by thermally oxidation. Successively, a layer of photoresist was sputtered on the surface of the oxide layer. Subsequently, standard photolithography and microfabrication were performed. The diameter of Si columns and their spacing could be controlled by using various templates. Both the diameter and the spacing of the template used in this work were 5 μm. After photolithography, the unexposed photoresist layer was dissolved with the developer. Following, inductively coupled plasma (ICP) etching was performed to etch SiO_2 layer and Si substrate by C_4F_8 and SF_6-C_4F_8 vicissitudinary, respectively. After removing residual SiO_2, Si column array substrate was obtained.

A microwave plasma chemical vapor deposition (MPCVD) process was used to deposit BDD on the Si column array substrate (Fig. 1). A mixture of CH_4 and H_2 was used as the source gas, wherein the content of CH_4 was varied between 0.5 and 4%. B_2H_6 diluted in H_2 (100 ppm) was employed as a boron doping agent. During the deposition process, the total flow rate, chamber pressure, substrate temperature and deposition duration was 100 sccm, 6 kPa, 500 °C and 6 h, respectively. As a comparison, flat BDD electrode was prepared by depositing BDD on a flat Si substrate under the same conditions.

2.2. Characterization

The general morphology of columnar BDD array electrode was characterized by field emission scanning electron microscopy (FESEM; Hitachi S-4800). Raman spectrum was obtained from Renishaw Micro-Raman System 2000 Spectrometer operated at He–Ne laser excitation (wavelengths 623.8 nm; laser power 35 mW) with a beam spot size of about 2 μm. X-ray diffraction (XRD) was used to identify the crystal of columnar BDD array electrode.

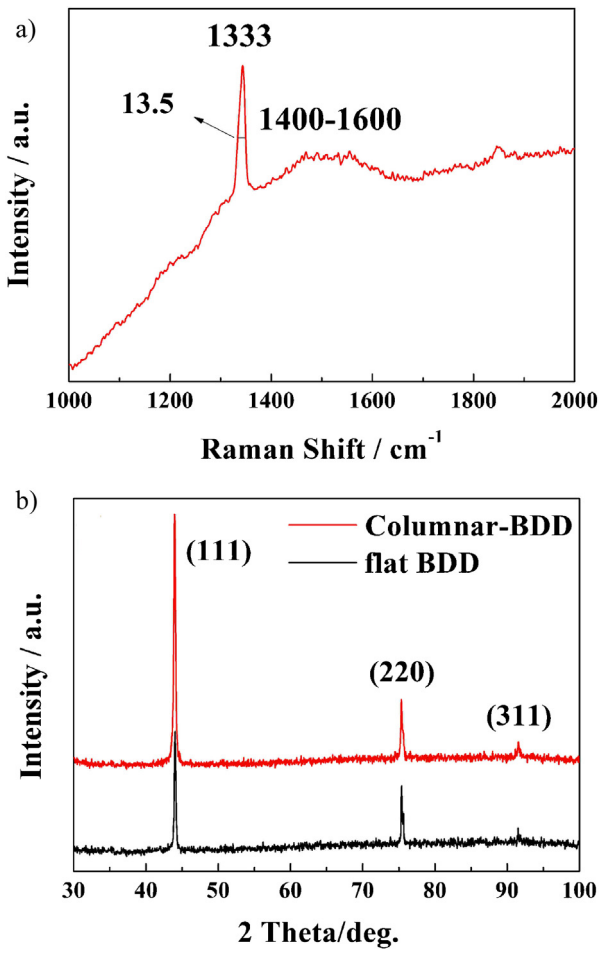

Fig. 2. Raman spectrum (a) and XRD pattern (b) of the columnar BDD array electrode.

Electrochemical experiments were performed on an electrochemical workstation (CH Instruments 650B) at room temperature in a conventional three-electrode electrochemical cell (5 cm of depth and 3 cm of diameter). Columnar BDD array electrode was acted as the working electrode with geometric area 0.725 cm^2. A platinum foil and a saturated calomel electrode (SCE) were used as counter and reference electrode, respectively. The electrochemical redox properties were obtained by the cyclic voltammetry (CV) test in 0.1 M KCl solution containing 1 mM $Fe(CN)_6^{3-/4-}$. The EIS was carried out in 0.1 M KCl solution containing 0.1 mM $Fe(CN)_6^{3-/4-}$. Then the potential window was tested by CV in 0.5 M H_2SO_4 solution at a scan rate of 100 mV s^{-1}. Finally, amperometric response to glucose was carried out in 0.1 M Na_2SO_4 solution with 1 mL glucose solution (50 μM) addition every time. All these tests were conducted on flat BDD electrode for comparison.

3. Results and discussion

3.1. Characterization of columnar BDD array electrode

Raman spectra are very sensitive to the presence of defects and widely used to determine the chemical composition and construction of carbonaceous materials [38]. BDD material could be evaluated according to the intensity ratio of sp^3 and sp^2 hybrid