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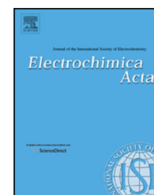

Fabrication of a Microfluidic Device with Boron-doped Diamond Electrodes for Electrochemical Analysis

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ABSTRACT

A prototype microfluidic device using boron-doped diamond (BDD) electrodes patterned on an alumina chip was designed and fabricated. Electrochemical microfluidic devices have advantages in that the amount of sample required is small, the measurement throughput is high, different functions can be integrated on a single device, and they are highly durable. In using the device for the flow injection analysis of oxalic acid, the application of a brief conditioning step ensured that the reproducibility of the current signal was excellent.

Furthermore, the fabricated system also performed as a prototype of “elimination-detection flow system”, in which interfering species are eliminated using “elimination electrodes” prior to the species reaching the “detection electrode”. The fabricated device reduced the current due to interfering species by 78%. Designs of devices to improve this efficiency are also discussed.

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1. Introduction

Over the past two decades, the interest in electrodes made of boron-doped diamond (BDD) has steadily increased, since they possess some unique properties, such as a wide potential window in aqueous solutions, a low background current and an intrinsic high durability, which are all advantages in various electrochemical applications [1–7]. These advantages of BDD in electrochemical analysis are commonly accepted in the analytical field [8,9]. On the other hand, miniaturization and the multi-functionalization of analytical devices in the field of chemical analysis, such as the microfluidic devices used in lab on a chip (LOC) or micro total analytical systems (μ-TAS), has developed alongside the progress in MEMS technologies and the semiconductor industry over the past two decades [10–14]. These microfluidic devices equipped with small-scale laboratory operations require smaller amounts of sample and have decreased throughput time. Electrochemical studies using microfluidic devices have also been carried out because these microelectrochemical techniques can be used in bio/chemical sensors, sample treatment and the regulation of pH as currently realized with traditional macro devices [15–18].

A typical electrochemical microfluidic device is composed of a PDMS block into which channels have been formed as a trench and a glass substrate onto which platinum or gold electrodes have been deposited and patterned [15,19].

With regards to the construction of microfluidic devices using BDD electrodes, there are several problems, such as the difficulty of preparing the film, its poor workability and the limitations of the substrates for growth. Diamond growth apparatus such as chemical vapor deposition (CVD) systems, which may be needed to fabricate the devices on chips, are still not easily available, whereas BDD electrodes themselves are now commercially available. In addition, the substrates onto which the diamond is grown in a CVD system is required to withstand high temperatures, typically over 800 °C [20,21] and also to provide electrical insulation for electrochemical microdivices. Therefore conducting materials such as tungsten, molybdenum, niobium and silicon, which are commonly utilized as substrates for growing polycrystalline BDD, are not available for fabrication of aimed microdevices. Forsberg et al. have reported fabrication of boron-doped nanocrystalline diamond microband electrodes on SiO_2 layer formed on silicon substrate for microfluidic device [22]. Macpherson et al. have reported electrochemical microdevices with BDD electrodes by using an insulating diamond as the substrate [23,24]. They demonstrated fabrication process of coplanar all diamond electrodes of any geometry [25]. On the other hand, BDD microfluidic

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device using a low-cost substrate should be also developed for practical use. Recently, we reported on the fabrication of a chip with BDD electrodes (3-electrode system) on an alumina (Al_2O_3) substrate, which is the most well-known ceramic oxide, for single drop analysis [26,27].

Here, in order to improve the device, microfluidic devices using BDD were fabricated and their electrochemical properties were evaluated with ferricyanide or oxalic acid. Microfluidic devices can be multi-functionalized by placing miniaturized functional units in the fluid channels. Therefore, for example, multi-functional analytical systems, including sample pre-treatments such as upstream elimination of interfering species, can be realized. In the present work, a prototype "elimination-detection flow system" was fabricated using a photolithographic process combined with reactive ion etching (RIE). Four elimination electrodes (EEs) were placed upstream from a detection electrode (DE) in the flow channel. Furthermore, the "prevention efficiency", which is a measure of how much the elimination electrodes prevent current due to interfering species being observed at the detection electrode, was evaluated.

2. Experimental

2.1. Preparation of the BDD electrodes chip

The BDD electrodes chip for the microfluidic device was prepared as follows. The substrate beneath the BDD layer should be electrically insulating in order to isolate the electrodes on each chip. An alumina plate was used as the support substrate because of its low electrical conductivity and high melting point. Prior to the CVD process, the surface of the plate (34 mm × 34 mm × 0.75 mm, Hygente co. ltd., Japan) was scratched with diamond powder on a polishing pad to facilitate nucleation and the wafer was subsequently washed in 2-propanol and deionized water in an ultrasonic bath. The BDD films were deposited on the scratched alumina plate using a microwave plasma-assisted chemical vapor deposition (MPCVD) system (CORNES Technologies/ASTeX, AX-5400). Acetone and trimethoxyborane, respectively, were used for the carbon and boron sources with an atomic ratio of B/C = 1%. Deposition was conducted at 3.0 kW for 2.5 hours [26]. Typical film thicknesses of the BDD films prepared under the above conditions are 3–5 μm.

The design of the device presented in this paper is shown in Fig. 1A. There are seven independent BDD electrodes, which are the counter electrode (CE), a reference electrode (RE) and five working electrodes consisting of a series of four elimination electrodes (EEs) and a detection electrode (DE). For practical electrochemical measurements, the reference electrode was coated with Ag/AgCl ink. Here, the 'elimination' means the function for removing an interfering substance as pretreatment. This function can be performed immediately prior to the detection of a target substance at the detection electrode. To realize this design, the microfabrication technologies such as deep reactive ion etching (Deep-RIE) were used. The fabrication flowchart is shown in Fig. 2.

An oxide layer or metal mask can be used as a hard mask for dry etching BDD [28,29]. Chromium was chosen for the mask to etch the 3-5 μm thick BDD on the alumina substrate. Chromium is a suitable hard mask for the lengthy BDD etching process (15–20 min and more). An SiO_2 layer was used as an interfacial layer between the Cr and the BDD in order to prevent residues of Cr being left on the BDD surface. The SiO_2 and chromium layers were formed on the BDD layer using RF magnetron sputtering (CFS-4ES i-Miller, ShibauraMechatronics Co.). Deposition was conducted with an argon flow rate of 72 sccm, rotation speed of 20 rpm, RF power of 20W, and sputtering times of 20 min for the SiO_2 and 90 min for the Cr. The thicknesses of the SiO_2 and chromium layers were about 100 and 1200 nm, respectively.

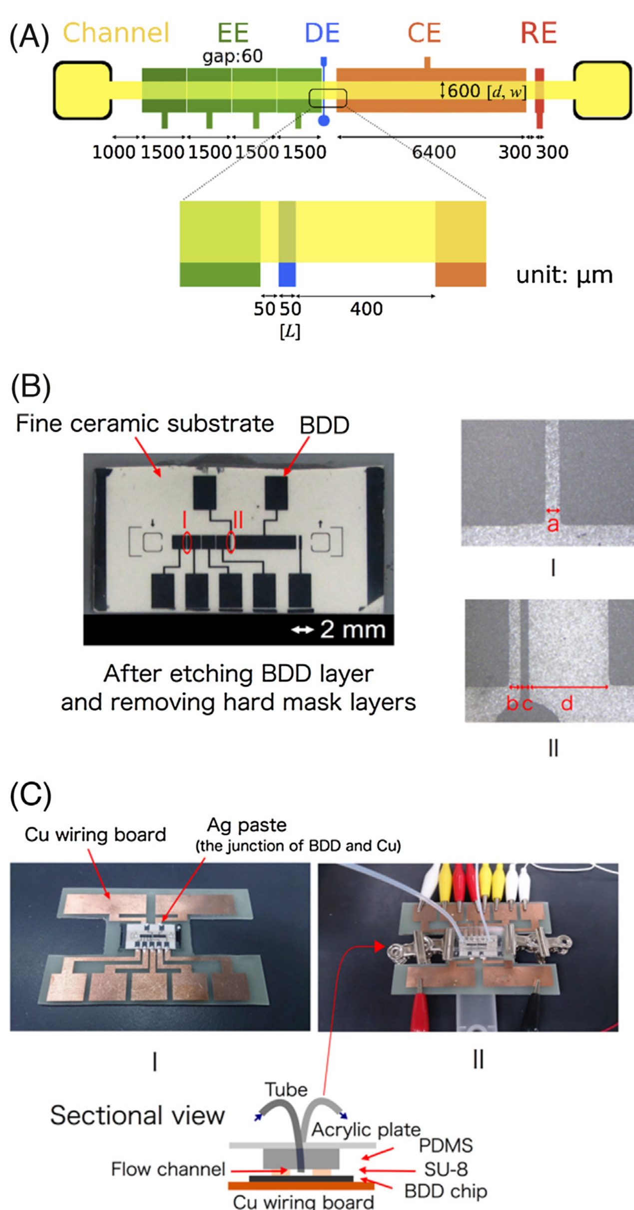

Fig. 1. (A) The design layout of the device. EE, DE, CE and RE represent the Elimination Electrode, the Detection Electrode, the Counter Electrode and the Reference Electrode, respectively. The numbers represent design dimension and the alphabets in the brackets represent parameters used for equation (2), respectively. (B) The substrate after etching the BDD and images from a 3D laser confocal microscope. The image in I shows the gap between two EEs and that in II shows the DE. The lengths designated a∼d are as follows; a: 74.3 μm, b: 62.9 μm, c: 41.4 μm, d: 425.7 μm. (C) The device mounted on a Cu wiring board and a cross sectional view. I: before capping with PDMS, II: after capping with PDMS, and adding the tubes and cables.

The hard mask layers were coated with positive photoresist AZ P4210 (AZ Electronic Materials) and patterned using photolithography. The exposed part of chromium layer was etched using a chromium etchant (Kanto Chemical Co., Inc.) for 10 min. After etching the Cr layer, the exposed part of SiO_2 layer was etched using NLD dry etching apparatus (NLD 570, ULVAC Inc.). The dry etching was done in $C_3H_8 + CHF_3$ etching gas, with flow rates of 20 sccm for both C_3H_8 and CHF_3.

After patterning the hard mask layers, the unmasked part of BDD films were etched using the NLD dry etching apparatus (NLD 570, ULVAC Inc.). The selectivity in etching BDD with the Cr mask was 10:1 (the BDD etch rate was approximately 250 nm/min and

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