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Electrochemical impedance spectroscopy of polycrystalline boron doped diamond layers with hydrogen and oxygen terminated surface

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ABSTRACT

This work is a systematic study of electrochemical impedance spectroscopy of high quality polycrystalline boron doped diamond films with varying boron content (from semiconducting to metallic behavior) and with different surface terminations (hydrogen or oxygen) in aqueous electrolyte solution. The films were grown by microwave plasma enhanced chemical vapor deposition. The concentration of acceptors (N_A) was determined from the Mott-Schottky plots and the values were compared with those from neutron depth profiling and Raman spectroscopy. The N_A values are in a good agreement across the different techniques, ranging from ca. $1.2 \cdot 10^{20}$ cm^{-3} for semiconducting samples up to ca. $2 \cdot 10^{21}$ cm^{-3} for heavily doped films with metallic conductivity. The films with hydrogen terminated surface exhibit lower values of both the flat band potentials (E_{fb}) and the N_A values, compared to the films with oxygen terminated surface.

1. Introduction

Polycrystalline boron doped diamond (BDD) is a complicated system whose electrochemical properties are influenced by many factors, such as boron doping level, morphological features (grain boundaries and point defects), non-diamond impurity content (especially sp^2 carbon), crystallographic orientation and surface termination [1–6]. Diamond can be modified by different surface functional groups ranging from simple heteroatom-termination of the carbonaceous skeleton to targeted chemical modifications for achieving specific electrochemical [1,4] and photoelectrochemical [7–9] functions. The most common surface terminations include oxygen (OT) and hydrogen (HT) atoms, which is associated with different wettability of the diamond (HT surface is hydrophobic, OT surface is hydrophilic). Further significant difference between hydrogen and oxygen terminated surface is in an electron affinity. The negative electron affinity (NEA) is a result of the C–H dipole at the hydrogenated diamond surface and the positive electron affinity (PEA) is caused by the C–O dipole at the oxygenated surface [5,10–12]. The electrochemical properties of BDD with hydrogen or oxygen terminated surface have been studied by several authors [1, 11–20]. Electrochemical impedance spectroscopy (EIS) is a useful technique to study the double-layer structure and charge transfer at surface modified BDD films. The impedance spectra can be fitted using equivalent circuits that correspond to the processes occurring at the electrolyte/BDD interface. The simplest equivalent circuit is the so-called Randles circuit, in which the Helmholtz capacitance and its corresponding parallel resistor [1,5,8,15,21–23], as well as the Warburg element [15,20] are neglected. From the Mott-Schottky plots, obtained from EIS measurements, it is possible to determine the concentration of active acceptors (N_A) of BDD films. There are also other techniques for determining the acceptor concentration of BDD such as the neutron depth profiling (NDP), secondary ion mass spectroscopy (SIMS), Raman spectroscopy and Hall-effect measurements [24] which also provide the concentration of acceptors in bulk or in the surface.

However, a specific feature of EIS is that it selectively maps the active acceptors in a thin space-charge (accumulation) layer underneath the surface. Although there is a bulky literature about impedance spectra and Mott-Schottky plots on diamond electrodes, the subject is far from being fully understood and consistent. Individual experimental works show large spread of results, such as flatband potentials (which range from about 0 to 4 V vs. SHE) [1,17,20,25–28] and also several different equivalent circuits were used for spectra fitting (see Fig. S1 in Supplementary data). Quite often, the actually applied circuit is not specified in the source works [17–19,29–31] but we may assume that they employed the simplest Randles-type RC circuit with pure capacitor like in [23]. Denisenko et al. [26] proposed a circuit with two RC elements in series, to account for a separation of space-charge layer and double layer at the interface. A replacement of simple capacitor with constant-phase element (CPE) and inclusion of Warburg impedance has been presented in several works [15,20,32]. A variant of Deniseko's

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model [26] with one CPE instead of capacitor was used in [21,22]. Yet more complex circuits with elements representing surface states are discussed in [27]. However, a systematic comparison of these circuits is less frequent in the literature. One exception is the work by Garrido at al. [15]. They compared the quality of fitting to two different R-CPE circuits: with or without the Warburg element, the latter provided more accurate matching with experimental spectra.

To address these questions, we present here a comparative study using several different circuits, pointing at possibilities and limitations of this approach. More specifically, we have carried out an electrochemical impedance study of high quality polycrystalline boron doped diamond films prepared by microwave plasma enhanced chemical vapor deposition with various boron doping level and with hydrogen and oxygen terminated surface, respectively. Acceptor concentration (N_A) of BDD films from impedance measurements (EIS), neutron depth profiling (NDP) and Raman spectroscopy were compared.

2. Experimental section

2.1. Preparation of BDD layers

The polycrystalline boron doped diamond (BDD) films were deposited on fused silica substrates in an ASTeX 5010 series Microwave Plasma Enhanced Chemical Vapor Deposition (MPECVD) reactor. The samples were grown in a conventional CH_4/H_2 plasma and doping was induced by trimethyl boron gas $B(CH_3)_3$. The growth conditions were: B/C ratio in the gas phase 500, 2000 and 8000 ppm, pressure 47.7 mBar, temperature 710 °C, methane content 0.5% and deposition time 480 min. These synthetic conditions are identical to those used in our previous work [2]. The surface of BDD films was terminated with hydrogen (HT BDD) and oxygen (OT BDD), respectively. Surface termination was realized by plasmatic treatment in hydrogen (oxygen) plasma at pressure of 30 mBar and temperature of 500 °C for 10 min. Samples were cooled down to room temperature under constant flow of hydrogen (oxygen). The BDD films in work [2] were as-grown, i.e. with hydrogen terminated diamond surface. For a contact angle measurements 1.5 μl volume of distilled water was used to make a droplet on the surface of BDD film using a micropipette. The images of sessile droplets were taken using a commercial digital camera (Canon IXUS 500 HS). The contact angle was determined by fitting of droplet using the open source image processing software ImageJ with Contact Angle plug-in.

2.2. Methods for BDD films characterization

Electrochemical measurements (impedance spectroscopy and cyclic voltammetry) were performed using a three electrode system in aqueous phosphate buffer solution pH 7.00 (PBS, Sigma Aldrich). The BDD films with hydrogen or oxygen terminated surface were used as working electrodes (Ag contact with Au wire insulated by epoxy coating), platinum mesh was a counter electrode and an Ag/AgCl electrode (sat. KCl) was a reference. The electrochemical impedance spectra were measured in the frequency range from 100 kHz to 0.1 Hz and in the bias voltage range from 0.9 V to −0.9 V using an AUTOLAB PGSTAT128N potentiostat with the frequency response analyzer (EcoChemie). The measurement was controlled by the GPES4 and FRA software. All electrochemical measurements were carried out in Ar atmosphere. The physical surface area of the BDD electrodes was determined from the roughness factor of ca. 2.5 estimated from the double-layer capacitance. The total boron concentration (depth profile) in BDD films was determined with a neutron depth profiling (NDP) method with an error of ±10% at standard ambient conditions [33]. Raman spectra were excited using 633 nm (1.96 eV) or 457 nm (2.71 eV) laser wavelength and recorded by a Labram HR spectrometer (Horiba Jobin-Yvon) interfaced to an Olympus microscope (objective 100×). Alternatively, a WITEC spectrometer with a 532 nm (2.33 eV) laser excitation in a highly confocal setup (100× objective and 25 μm fiber optics) was used. The spectrometers were calibrated by the F_{1g} mode of Si at 520.2 cm^{-1}.

3. Results

Polycrystalline BDD thin films with an approximate thickness of 2 μm were grown by MPECVD on quartz substrates. The surfaces of these as-grown films can be considered mostly as H-terminated owing to the reduction conditions during growth, however, the surface termination cannot be regarded as unambiguously defined for surface-sensitive studies like EIS. The surface morphology evaluated by AFM and the structural properties (presence of graphitic or amorphous phases, boron doping level) analyzed by micro-Raman spectroscopy of the as-grown BDD films have been detailed in our previous work [2]. The BDD films show well-defined and faceted crystals (ca. 450 nm in size), and almost no graphitic or amorphous carbon impurities. For further studies, the BDD samples were first treated in hydrogen plasma to achieve fully H-terminated surface. Subsequently, after the completion of all relevant experiments (see below), the BDD samples were treated in oxygen plasma to acquire the O-terminated surface. The surface contact angles were 92° for H-terminated BDD and 12° for O-terminated BDD, respectively. This confirms high efficiency of hydrogen and oxygen treatments (Fig. 1).

Electrochemical impedance spectra were measured on boron doped diamond (BDD) films with hydrogen or oxygen terminated surface. Fig. 2 shows experimental data corresponding to selected potentials for the whole frequency range (AC impedance Nyquist plots; imaginary part vs. real part of complex impedance for different frequencies) of BDD films with hydrogen (HT BDD) and oxygen terminated surface (OT BDD). Fig. 3 shows the equivalent circuit used for fitting the experimental data which takes into account the diffusion phenomena [15,20]. In this circuit the ohmic resistance R_s of the electrolyte solution, electrodes, contacts etc. is in series with the parallel combination of the space charge capacitance (BDD/electrolyte interface) represented by constant phase element (CPE) and its associated resistance (R_1) in series with diffusion impedance Z_w, the so-called Warburg element. This equivalent circuit (Fig. 3) provided the best fits to experimental spectra; other possible circuits are shown in Supplementary content (Fig. S1) with the corresponding fits to Nyquist plots in Fig. S2. By comparing the individual fits in Figs. 2 and S2, we can conclude that the circuit with CPE and Warburg impedance (Fig. 3) gives the best matching.

The impedance of a CPE equals:

$$Z_{CPE} = B(i\omega)^{-\beta} \quad (1)$$

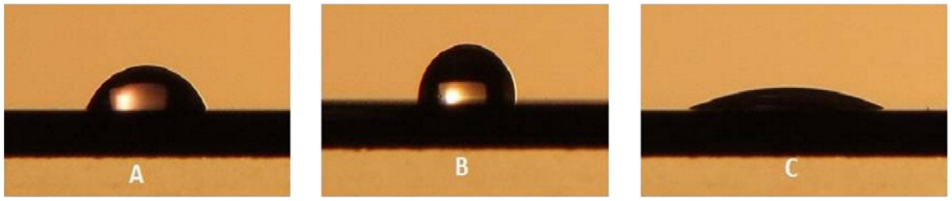

Fig. 1. Contact angle of A) as-grown, B) hydrogen terminated and C) oxygen terminated surface of boron doped diamond film.