



Surface structure and electrochemical characteristics of boron-doped diamond exposed to rf N₂-plasma

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ABSTRACT

Epitaxial (100)-oriented diamond layer with boron doping above 10^{20} cm^{-3} was exposed to an RF N₂ plasma, the resulting surface structure and electrochemical characteristics were investigated. The N₂ plasma treatment was combined with *in vacuo* pre-heating to remove adsorbates and with surface shielding to reduce plasma-induced corrosion. X-ray photoemission spectroscopy revealed full nitrogenation of the surface with the presence of C–N and C=N bond structures. Anodic treatment in 0.1 M KOH in the oxygen evolution range generated nitrogen–oxygen bonds and carbon–oxygen functionalities which partially substitute the initial nitrogen-termination. The nitrogenated and electrochemically polarised diamond electrode exhibited higher catalytic activity to [Fe(CN)₆]^{3–/4–} but slower to [Ru(NH₃)₆]^{3+/2+} redox reactions, as compared to an identical diamond electrode with fully oxygen-terminated surface.

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1. Introduction

Diamond has been considered as an interesting material for electrochemical sensing and for electron device applications due to the unique combination of electronic transport properties, electrochemical behaviour, chemical stability and robustness [1,2]. But in many cases the properties of diamond devices are strongly influenced by termination of the active surface area by functional groups of different types, as it has been demonstrated for the cases of hydrogen-, oxygen- and fluorine-terminated surfaces [1–9]. Each surface bond structure can be characterised by a specific dipole and dangling bond configuration. This may lead to a variety of electrochemical responses of diamond to redox systems [3,6–10] and vary also the projected flat-band condition of capacitance–potential plots in aqueous solutions [8,11–13]. The latter characteristics could be related to electronic surface states induced by the surface functional groups, which pin the surface Fermi level thus inducing energy band bending at the surface [12–14]. Besides, surface termination affects also the pH sensing characteristics of diamond-based ion sensitive field effect transistors (ISFETs) [4,15].

In this regard, nitrogen-termination of diamond could be also very interesting for chemical sensing: Amino-groups on diamond surface have been also used for anchoring the organic molecules by photo-chemical reactions [16,17]. Diamond-based ISFETs with an aminated surface demonstrated a sensitivity in wide range of

pH [18]. Besides, amino-terminated diamond has been proven to be a favourable material for the adsorption of metallic nano-particles in electrolytes [19].

However it should be noted that the characteristics of diamond electrodes are very sensitive to the methods of surface processing, which could be a wet or photo-chemistry, electrochemical polarisation or exposure to plasma. Especially processing in a RF plasma reactor has been found as very “aggressive” to the diamond surface [20,21]. It could corrode the surface in a nanometre range, also resulting in a non-diamond carbon phase [21]. Such defects modify the electronic surface barrier in contact with electrolytes and also degrade the response to redox reactions [8,20,21]. A reduced electrochemical response has been also reported for diamond electrodes exposed to a NH₃/N₂ plasma in a RF-reactor [22]. At such conditions, the true behaviour of surface functional groups could be masked by the activity related to plasma-induced defects. Recently we proposed an improved method of plasma exposure where the plasma-induced corrosion of diamond surface is suppressed [23]. This method includes pre-heating in vacuum to remove adsorbates and shielding the surface during the plasma treatment. Following this recipe we processed the surface of single crystalline epitaxial diamond in an RF N₂ plasma reported here. The induced surface functionalities and the electrochemical characteristics of the processed diamond electrode were analysed. We investigated also the effect of anodic polarisation in alkaline electrolyte on the surface characteristics. The experiments were done using with diamond epi-layers with the concentration of boron acceptors above the full activation limit of 10^{20} cm^{-3} . Such

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highly doped diamond layers are potentially interesting for electrodes [2] and for ISFETs with a boron delta-doped channel [24].

2. Experimental

The boron-doped epitaxial layers were grown on two identical high-temperature high-pressure synthetic diamond substrates with (1 0 0)-oriented surface. The CVD growth was conducted in a microwave-assisted chemical vapour deposition reactor system using a boron rod as the doping source [25]. The achieved level of boron doping was about $4 \times 10^{20} \text{ cm}^{-3}$, as evaluated from the corresponding capacitance–potential plots in electrolytes, see Ref. [13] for details. Average peak-to-peak roughness of the as-grown epitaxial surfaces was below 1 nm as measured by atomic force microscopy (AFM). The thickness of the boron-doped layers was approx. 30 nm.

As already mentioned, the route of sample preparation and surface treatment in plasma followed a recently developed recipe verified in the experiments on fluorine-terminated diamond [23]. It included (i) wet chemical oxidation of the as-grown diamond surface, (ii) sample pre-heating in ultra-high vacuum and (iii) exposure to RF plasma at room temperature without breaking the vacuum with shielding the diamond surface against high-energy ions. In the step (i), the as-grown diamond samples were exposed to a wet chemical treatment in hot $\text{H}_2\text{O}_2:\text{H}_2\text{SO}_4$ (1:2) mixture followed by rinsing in de-ionised water. Such chemical oxidation removes carbon–hydrogen surface bonds and the associated *p*-type surface conductivity, which appear after diamond growth in hydrogen-rich atmosphere [26]. The electronic surface properties of the resulting oxygen-terminated diamond in electrolytes have been extensively discussed in the literature in the past [11–13]. Therefore, one of the diamond samples with identical doping, however with oxygen-terminated surface, was used as reference during the electrochemical measurements.

The exposure of diamond sample to N_2 -plasma was carried out in a RF barrel reactor with background pressure below 10^{-7} mbar and with integrated heater in the sample holder. Thermal desorption of oxygen from the diamond surface could be expected at temperatures about 600 °C [27]. Thus in step (ii) of our experiment, the initially oxidised diamond sample was pre-heated in ultra-high vacuum to a temperature of 740 °C for 15 min. After cooling down the annealed sample to room temperature, the chamber was filled with N_2 gas (5.0, Messer Gas) up to a pressure of 2×10^{-2} mbar. In the next step (iii) the plasma treatment was performed at an RF input power of 30 W for 2 min. During this exposure the sample was fixed to a grounded metallic holder so that the sample's surface was facing the chamber wall. By this shielding we attempted to reduce the damage of the diamond surface caused by energetic ions in the plasma. As a proof, AFM analysis detected no increase of the surface roughness in the sub-nanometre range, similar to the report in [23].

The X-ray photoemission spectra (XPS) were acquired at normal (0°) emission angle with a VG ESCALAB210 electron spectrometer equipped with monochromatized $\text{AlK}\alpha$ (1486.6 eV) radiation source with an overall resolution of 0.32 eV. The binding-energy scale of the instrument was calibrated by means of a gold reference samples (Au 4f: 84.0 eV). The XPS measurement chamber was attached to the RF plasma reactor. Using the integrated interlocks and movable sample holders it was possible to characterise the plasma-exposed sample by XPS without breaking the vacuum. By processing the XPS data, the signal intensities were calculated by integrating the appropriate core lines using voigt line shape after Shirley type background subtraction. Besides, the recorded spectra were corrected by the energy-dependent sensitivity factor of the measurement instrument. The parameters of the instrumental sen-

sitivity were integrated into the data acquisition software. Thus, the ratios of the spectroscopy peaks discussed below were taken by calculating the integrated intensities of the corresponding photoelectron signals, and corrected by the instrumental sensitivity.

The XPS analysis was combined with electrochemical study of the nitrogen-terminated surface. For this purpose the processed sample was packaged as electrochemical electrode. The electrochemical response to $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$ / $[\text{Fe}(\text{CN}_6)]^{3-/4-}$ redox reactions was recorded at three steps of the surface processing: (I) as-exposed to N_2 plasma, (II) after anodic polarisation in 0.1 M KOH and (III) after rinsing the polarised electrode in de-ionised water and drying by nitrogen gas flow. The characteristics of the nitrogen-terminated electrode were compared to an identically grown diamond sample with fully oxygen-terminated surface by electrochemical polarisation. The two electrodes were mounted on copper holders, contacted with silver paste and passivated using a removable Teflon-based adhesive tape. The perforated opening of 1 mm in the passivation determined the active electrode area in contact to the electrolytes.

3. Results and discussion

3.1. XPS analysis

3.1.1. As-exposed surface

The high-resolution photoemission spectrum of the C1s line of the as-nitrogenated surface measured *in vacuo* (i.e. without breaking vacuum after the plasma exposure) is shown in Fig. 1a. The corresponding overview spectrum in the figure's inset revealed no traces of oxygen, which had been obviously removed during the annealing at 740 °C temperature. Deconvolution of the C1s spectrum identified three components: the bulk sp^3 peak at the energy of 284.1 eV (C1 in Fig. 1a) and two surface components C2 and C3 shifted to higher energies. The position of the bulk peak was in agreement with the previous reports on similar epitaxial diamond layers in the as-grown state and after chemical and various plasma treatments [13,21]. The two other components C2 and C3 were positioned at 285.1 eV and 286.7 eV energies. It may be worth noticing that no additional signal was resolved in the 283 eV energy range, and which would be related to a non-diamond carbon phase on the surface. In Ref. [21] a spectral component below 284 eV has been detected after *direct* exposure of epitaxial diamond to CF_4/O_2 or O_2 plasmas in RF barrel reactor without shielding the exposed surface. Such a peak is usually attributed to amorphous carbon due to plasma-induced corrosion. In the present study, neither amorphous carbon components were detected by XPS, nor were traces of surface corrosion detected by AFM. We believe that the obtained quality of the surface was related to the geometry of the grounded electrode in the reactor chamber and shielding.

According to the literature data on nitrogenated carbon films and organic compounds, the shifted spectral components of the C1s spectrum at 285.1 eV and 286.7 eV energies could be associated with C=N and C–N bonds respectively [28–30]. The ratio of the integrated peak intensities $I_{\text{C3}}/I_{\text{C2}}$ was approx. 0.2. This could indicate the prevalence of surface bond structures containing imine groups. Further details on the as-prepared surface were obtained by analysing the corresponding N1s spectrum in Fig. 2a. The shown spectrum represented a broad band positioned at 399.5 eV energy. It was characterised by a featureless structure and full width at half magnitude of approx. 2.5 eV. It could be deconvoluted into two components N1 and N2 at approx. 399.1 eV and 400.0 eV, as shown in the figure. The fitting revealed no noticeable traces of components at 398 eV and 402 eV energy ranges, and which would be related to C≡N and to N–N bonds respectively [30,31].

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