Diamond & Related Materials 49 (2014) 62–71

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

New electrochemically improved tetrahedral amorphous carbon films for biological applications

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ARTICLE INFO

Article history:
Received 8 May 2014
Received in revised form 13 August 2014
Accepted 18 August 2014
Available online 27 August 2014

Keywords:
Tetrahedral amorphous carbon
Thin films
Electrochemistry
Dopamine
Biomaterials

ABSTRACT

Carbon based materials have been frequently used to detect different biomolecules. For example high sp^3 containing hydrogen free diamond-like carbon (DLC) possesses many properties that are beneficial for biosensor applications. Unfortunately, the sensitivities of the DLC electrodes are typically low. Here we demonstrate that by introducing topography on the DLC surface and by varying its layer thickness, it is possible to significantly increase the sensitivity of DLC thin film electrodes towards dopamine. The electrode structures are characterized in detail by atomic force microscopy (AFM) and conductive atomic force microscopy (C-AFM) as well as by transmission electron microscopy (TEM) combined with electron energy loss spectroscopy (EELS). With cyclic voltammetry (CV) measurements we demonstrate that the new improved DLC electrode has a very wide water window, but at the same time it also exhibits fast electron transfer rate at the electrode/solution interface. In addition, it is shown that the sensitivity towards dopamine is increased up to two orders of magnitude in comparison to the previously fabricated DLC films, which are used as benchmarks in this investigation. Finally, it is shown, based on the cyclic voltammetry measurements that dopamine exhibits highly complex behavior on top of these carbon electrodes.

1. Introduction

Monitoring the state of the human body and its functions by network of wirelessly interconnected sensors is a scientific, economic and technological challenge of utmost importance. If combined with the ability to stimulate these sensor/actuator networks could act as the user interface between living and electronic worlds. At this specific interface the information can be gathered by a network of sensors. In the case of electrochemical sensors, the electrode is the element which is in immediate contact with the biological environment. Thus, the operation of the interface between biological system and electronic device relies on the functionality of this electrode.

The rate of the electrochemical reactions is significantly influenced by the nature of the electrode surface [1]. The kinetics of oxygen and hydrogen evolution is significantly slower on carbon than on most commonly used metal electrodes [2]. The resulting wide potential window is one of the reasons for the widespread use of carbon materials for electrodes. Amorphous diamond-like carbon (DLC) is a non-crystalline carbon with high fraction of diamond-like (sp^3) bonds [3]. DLC coatings are characterized by excellent physical properties (high hardness, high elastic modulus) as well as chemical inertness to any acids, alkaline solutions, and organic solvents [3]. We have recently shown that DLC electrodes are exceptionally stable in phosphate buffered saline (PBS) solution, but can still be utilized to detect biomolecules by inducing local electrochemically active spots on the otherwise inert DLC electrode [4]. Furthermore, DLC in its many forms is an attractive electrode material because of its antifouling properties and general biocompatibility [5–17].

Neurotransmitters, such as dopamine, provide the important communication link between neurons. Abnormal dopamine transmission has been associated with several neurological disorders, e.g. Parkinson's disease, schizophrenia, and Huntington's disease [18]. For therapeutic purposes, an accurate determination of dopamine level in situ would be highly desirable. When dopamine is oxidized two electrons and two protons are transferred [2,19,20]. These electrons can be detected with cyclic voltammetry, for instance. The primary challenge here is that the concentration of dopamine in the extracellular fluid is very low (0.01–1 μM) [20]. Secondly, the released dopamine is rapidly cleared from the extracellular space. Thus, the sensor must not only be

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http://dx.doi.org/10.1016/j.diamond.2014.08.007
0925-9635/

sensitive and selective, but it should also have a fast response time. The third challenge is long term stability, which is confronted by the adsorption of oxidation products leading to the fouling of the electrode.

As stated above, the motivation to use DLC thin films as bioelectrodes lies for example in their biocompatibility, easy processability, compatibility with current CMOS processes, mechanical robustness, and excellent corrosion resistance. Unfortunately, the sensitivity of DLC coated electrodes towards, for example dopamine, is typically not high enough if other more electrochemically active materials are not combined with the DLC matrix [4]. The purpose of this work is to show that by utilizing a specific deposition process for DLC thin film electrode system, it is possible to achieve not only chemically very inert, but at the same time electrochemically active electrode material. The microstructure as well as the electrochemical properties of the DLC films will be characterized in detail. Here our previous DLC coatings with approximately the same sp^3 content will be used as the benchmark. The main differences between the two coatings will be discussed and the factors most likely contributing to the observed very different electrochemical behavior will be rationalized.

2. Experimental

The substrate materials used were either p- or n-type Si(100) wafers (Ultrasil and Okmetic). Two different kinds of samples were fabricated for the electrochemical investigations. In both cases the samples consisted of Ti interlayer and layer of tetrahedral amorphous carbon, although different types of processing conditions and experimental setup were used.

In the first case, direct current (DC) magnetron sputtering system and dual filtered cathodic arc deposition system were used for titanium and carbon deposition, respectively. It is to be noted that both systems are installed in one deposition chamber. The highly conductive p-type boron-doped (100) Si wafers with 0.001–0.002 $\Omega \cdot$cm resistivity were utilized. All wafers were cleaned by standard RCA-cleaning procedure before the deposition. Samples were placed in the rotating holder (rotational velocity used was 20 rpm). The vacuum in the chamber was pumped down by dry scroll vacuum pump (Edwards XDS10) and by cryo pump Cryo-Torr (Helix Technology Corporation). In order to achieve a low vacuum, a high vacuum throttle valve was used. DC-magnetron sputtering system was equipped by circular and water-cooled magnetron sputtering source with 2 in. Ti target (Kurt J. Lesker Company) and DC generator (DCO2 BP). The shutter was utilized for controlling the sputtering time. Pre-sputtering of 2 min was carried out for cleaning the surface of Ti target. Titanium interlayers were deposited under the following deposition conditions: discharge power was fixed at 100 W, total pressure was 0.67 Pa, Ar gas flow rate was 28 sccm, deposition temperature was close to room temperature, and deposition time was 350 s. Cathodic arc deposition system purchased from Lawrence Berkeley National Laboratory was equipped the 90° bent magnetic filter for the reduction of the macroparticle contamination. Two 99.997% graphite rods (Goodfellow) of the diameter of 6.35 mm were used as the carbon cathodes, which were surrounded by a cylindrical anode. The arc current pulses had the amplitude of 0.7 kA and 0.6 ms pulse width. Each pulse was triggered at 1 Hz frequency. The 2.6 mF capacitor bank was charged to 400 V. The number of pulses was 360. The distance between the substrate holder and the filter was about 20 cm. Total pressure during the deposition process was no less than $1.3 \cdot 10^{-4}$ Pa. These electrodes are marked in the subsequent analyses as improved ta-C (IMP-ta-C).

In the second case, the deposition was done by using another experimental set-up. The 70 L deposition chamber was pumped with an oil diffusion pump to base pressure of 1×10^{-3} Pa. The samples were mounted by hanging in rotating carrousel with planetary rotation of the substrate holders. The full rotation time of the carrousel was about 25 s. The chamber has two arc sources and one ion source on the chamber walls. Prior to deposition the samples were etched by using a griddles argon ion source. The titanium coating was deposited by using a continuous current arc source equipped with 60° magnetic filtering. The arc current used was 55 A and the duration of the deposition was 35 s. For the carbon a 2.6 mF capacitor bank was charged to 200 V and the arc was triggered with ignition electrodes. The maximum pulse current was 3 kA and the pulse width was about 0.3 ms. Each pulse was triggered separately at 1 Hz frequency. The deposition rate during the pulse was about 1.4×10^{15} ions/cm^2, as measured from the growth rate of a carbon layer on a flat silicon substrate. The distance from the cathode varied between 150 and 300 mm during the deposition due to sample rotation. The average carbon ion energy has been previously measured to be 40–50 eV using an electrostatic probe. It may be assumed that all carbon in the plasma is ionized. These electrodes are subsequently marked as reference ta-C (REF-ta-C).

The morphology of the fabricated samples was studied with optical microscopy (Leica), and scanning electron microscopy (SEM) (Hitachi-4700). Scanning probe microscope Ntegra Aura (NT-MDT Company) with variable measuring facilities was used to carry out atomic force microscopy (AFM), spreading resistance microscopy or in other words conductive-AFM (SRM or C-AFM) and current–voltage spectroscopy, as well as scanning tunneling microscopy (STM). The measurements were carried out in 'scanning by sample' mode with the use of two different measuring heads. In the case of conductive AFM, a diamond coated conductive probe (DCP10) was mounted to special probe holder designed for the current measurements under the varied voltage applied to the probe. The measurements were performed in the contact regime. The typical curvature of radius of the tip used was about 100 nm and the force constant of the cantilevers was nominally 11.5 N/m. In the case of STM measurements, STM head and TT10 Bruker etched tungsten tip (length was 8 mm, diameter was 0.25 mm) were used. Tip height was chosen to give the tip current of 0.2 nA under the tip (bias) voltage of 0.5 V. Dependencies of the tunneling current on the voltage applied to the sample were obtained from STM. In both cases of current–voltage characteristic measurements, dependences were the average of, at least, 50 measurements in different points. Bitmap images (topography and current maps) were processed with free software Gwyddion 2.34.

Samples were further characterized by X-ray reflection (XRR) analysis performed via Philips X'Pert Pro diffractometer (CuKα, $\lambda = 1.5405$ Å, acceleration voltage: 40 kV, anode current: 40 mA) and visible Raman spectroscopy with the use of WITec alpha 300 spectrometer (laser wave length was 532 nm, exposure time was 0.1 s, and spectrum wave number was in the range of 450 to 3900 cm^{-1}). All spectra obtained were processed by an average of 100 spectra and a background subtraction. The thickness of deposited layers was measured by means of a profilometer (Dektac).

Cross-sectional TEM samples were prepared conventionally by grinding, polishing and dimpling the specimen until its thickness was below 10 μm, followed by Ar ion milling performed using a PIPS Ion miller (Gatan USA). High-resolution transmission electron microscopy (HRTEM) was performed using a double-aberration-corrected JEOL 2200FS microscope and a JEOL 2100 (JEOL, Japan) microscope equipped with a field emission gun (FEG) operating at 200 kV. Moreover, the JEOL 2100 microscope was used to perform scanning transmission electron microscopy (STEM) using high angle annular dark-field (HAADF) imaging. The JEOL 2200FS TEM was equipped with an energy dispersive X-ray (EDX) spectrometer for elemental analysis and the JEOL 2100 was equipped with the Gatan image filter (GIF) for electron energy-loss spectroscopy (EELS). A Gatan 4k × 4k UltraScan 4000 CCD camera was employed for digital recording of the HRTEM images.

Cyclic voltammetry (CV) was carried out with Gamry Reference 600 Potentiostat/Galvanostat/ZRA. Contact was made to the backside of the sample by using Cu wire and Ag adhesive. The sample was placed inside a polycarbonate sample holder which protected completely the sides and back of the electrode. Hole with a diameter of 8 mm in the sample holder allowed the solution to reach contact with the electrode. Water window was measured in 0.15 M sulfuric acid and the dopamine measurements utilized different concentrations of dopamine in phosphate buffered saline (PBS) solution. Sweep rate was typically set to 50 mV/s. The reference electrode was Ag/AgCl skinny reference electrode