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Carbon thin films as electrode material in neural sensing

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ABSTRACT

For therapeutic purposes, an accurate measurement of dopamine levels in situ would be highly desirable. A novel strategy for the selective determination of dopamine concentrations based on carbon thin film electrodes is presented in this paper. Traditionally, in order to make diamond films conductive, they are doped with different concentration of boron atoms. Here, carbon thin films with varying conductivities were achieved by unbalanced magnetron sputtering. The benefit of the method is that it can be performed at room temperature consequently broadening the selection of suitable substrates. The carbon thin films had a wide potential window, which showed strong dependence on conductivity. The potential window was largest (4.6 V) with the most resistive carbon thin film. On the other hand, the sensitivity of the electrode toward dopamine was not significantly affected by the conductivity. In addition, relatively similar behavior with respect to the dopamine oxidation was observed between various surfaces. The slight differences observed in the electrochemical behavior among the thin films are most likely caused by 1) different conductivities and/or 2) different surface charges and subsequent differences in the chemical properties of the surfaces. In conclusion, it can be stated that a-C thin film is a very potential neural sensing material.

1. Introduction

Neurotransmitters, such as dopamine, are the chemicals that communicate information throughout our brain and body. Abnormal dopamine transmission has been connected with several neurological and psychiatric disorders, e.g. Parkinson's disease, schizophrenia, and Huntington's disease [1]. The accurate measurement of neurotransmitters would provide a better understanding of these diseases and a tool to follow up the output of the treatments. For example, deep brain stimulation (DBS) is increasingly being used as the treatment for Parkinson's disease and feedback control has great potential to improve efficacy, reduce side effects and decrease the cost of the treatment. Most of the attention with this respect has been focused on recording potential biomarkers, such as dopamine, directly from the basal ganglia [2].

Dopamine can be oxidized by electrochemical methods, and thus they are frequently used for the determination of the concentration of dopamine. The primary challenge in dopamine detection is that the concentration of dopamine in the extracellular fluid is low (0.01–1 μM) [3,4], while the amounts of the main detection interferers, which undergo oxidation within the same potential window as dopamine, are several orders of magnitude higher. Secondly, the released dopamine is rapidly cleared from the extracellular space. Accordingly, the sensor must be sensitive, selective and fast. The final challenge is the long term stability, which is confronted by the adsorption of oxidation products leading to the fouling of the electrode.

The rate of the electrochemical reactions is significantly influenced by the nature of the electrode surface. The kinetics of oxygen and hydrogen evolution is significantly slower on carbon than on most commonly used metal electrodes [5]. 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. Modified DLCs have been applied to various engineering fields, such as magnetic hard disk coatings, wear-protective coatings, razor blades, engine parts, and biomedical coatings [6,7]. 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 [8]. Furthermore, DLC is an attractive electrode material because of its antifouling properties [9,10]. For example, DLC resisted in static conditions adhesion of *Staphylococcus aureus* and *Staphylococcus epidermidis* compared to titanium, tantalum and chromium [11–13]. On the other hand, patterned DLC coatings improved the biocompatibility of silicon surfaces [14–16], making it an attractive material for area-array electrodes.

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Traditionally, in order to make diamond films conductive, they are doped with different concentration of boron atoms. Boron doped diamond (BDD) is an excellent electrode material owing to its large potential window in aqueous solution, low background current, fast electron transfer kinetics and stability [17]. These characteristics of diamond electrodes have been employed in a number of applications. Unfortunately, chemical vapor deposition, used for BDD coating, requires high temperatures (>800 °C), which limits the choice of substrate materials.

Recently, sp^2 and sp^3 hybrid carbon materials, called nanocarbon films, have been developed by employing the electron cyclotron resonance (ECR) sputtering method. This technique provides a nanocrystalline sp^2 and sp^3 mixed bond structure with an atomically flat surface (surface roughness of 0.05–0.1 nm) and high conductivity without doping [18]. Nanocarbon films have the required sp^3 bonded carbon structure that exhibits the wide potential window. In addition sp^2-carbon is very important for obtaining the electrode activity needed to oxidize the target molecule. These films have been successfully applied for DNA electroanalysis [19,20]. Here we present a novel way of making sp^2 and sp^3 hybrid carbon material with varying conductivity at room temperature and demonstrate its feasibility for electrochemical detection of dopamine.

2. Experiment details

Four different electrode materials were compared in this study: (i) nanocrystalline conducting carbon (nc-C) and (ii) insulating amorphous carbon films (ta-C, Table 1) on silicon, (iii) silicon itself and (iv) commercial BDD (Windsor Scientific, UK).

2.1. nc-C coatings

Conductive carbon films were deposited by a carbon film unbalanced magnetron (CFUBM) at various target power densities and by adding hydrogen. The substrate materials used were highly doped n++ Si (100). The cylindrical target was pure graphite (99.99%) with a diameter of 100 mm. It was discharged with directly current power supply. Before deposition, base pressure was reduced 3×10^{-5} Torr using diffusion and rotary pump. Prior to deposition the Si wafer was treatment by Ar plasma pre-cleaning with a bias of −700 V and a working pressure of 100 mTorr. Working pressure was fixed to 3 mTorr. The carbon film deposition rates are shown in Table 1. The deposition rate was controlled by adjusting the target power density in the rage of 10–30 W/cm^2. The substrate temperature has been measured to be up to 200 °C depending on the target power and the surface temperature of 270 °C at the highest was detected.

The coating thickness was kept at 0.5 μm. A surface profilometer (KLA Tencor Alpha-Step ASIQ) was used to measure the thickness of the carbon films.

Table 1
Coating conditions, resistivity and surface roughness of the samples. For comparison, the surface roughness of the commercial BDD electrode is given.

Sample	Coating thickness (nm)	Working pressure (mTorr)	Deposition rate (nm/min)	Resistivity	Surface roughness (nm)
nc-C1	500	3	120	0.03 Ωcm	2.5
nc-C2	500	3	36	3.60 Ωcm	1.2
nc-C3	500	3	18	60 Ωcm	1.1
nc-C4	500	3	3	200 Ωcm	2.8
nc-C5	500	3 (H_2 7% mixing)	105	5×10^6 Ω	1.6
ta-C	30	0.01	6	$>> 10^6$ Ωcm	0.33
BDD					1.0

2.2. Control ta-C coatings

The substrate materials used were highly doped n++ Si (111) wafers (Okmetic). First, the Si wafers were etched in buffered HF solution and dried in flowing nitrogen right before the deposition.

Prior to the coating, the samples were cleaned by argon ion beam sputtering. A 20 μm thick layer of titanium was sputtered to enhance the ta-C layer adhesion. ta-C was deposited using cathodic arc deposition. The capacitor bank of 2.6 mF capacitance was discharged yielding a current pulse with a frequency of 1 Hz, a maximum current of about 3 kA and a half width of 150 μs. An accumulation of about 1.4×10^{15} atoms cm^{-2} during each pulse was obtained. The sample holder was rotated with the rotation axis perpendicular to the direction of the plasma plume.

2.3. AFM

AFM measurements were done using PSIA XE-100 Advanced Scanning Probe Microscope with MicroMasch type B contact silicon cantilever (nominal radius of tip curvature < 35 nm, tip height 15–20 μm, tip cone angle < 20°, resonant frequency 105 kHz, force constant 2.0 N/m) using tapping mode. AFM scan rate was 1 Hz and the scanned areas were between 1 and 100 μm in height and width.

2.4. Resistivity of nanocrystalline coatings

The electrical resistivity of the carbon film was measured by 4-point probe (CMT-SR-1000N). The probe current was in the range from 10 nA to 100 mA.

2.5. Cyclic voltammetry

Cyclic voltammetry measurements were made using a potentiostat (QuadStat, eDAQ Pty Ltd, Denistone East, Australia) attached to a recording unit (e-corder 821, eDAQ) and computer. Echem software (ADInstruments Pty ltd, Castle Hill, Australia) was used to enter the parameters of the experiment and control the potentiostat. A titanium rod with 2.5 μm thick coating of platinum (ET078, eDAQ) served as the counter electrode and a commercial Ag/AgCl electrode (Sarissa Biomedical Ltd., Coventry, UK) was used as the reference. All measurements were made in a Faraday cage (VistaShield, Gamry Instruments, Warminster, USA) to avoid electrical interference.

The potential window was determined in nitrogen purged 0.15 M H_2SO_4 (Merck KGaA, Darmstadt, Germany) with pH 0.55 at a scan rate of 400 mV/s. Then the potential was cycled approximately 20 to 25 times until a steady-state CV was obtained. The capacitive currents were measured at −0.15 V vs Ag/AgCl in H_2SO_4 from steady state CVs.

The ability to detect dopamine was assessed with cyclic voltammetry in nitrogen purged phosphate buffered saline (PBS) with 5 nM–100 μM dopamine (Sigma-Aldrich, St. Louis, USA) at a scan rate of 400 mV/s. The initial potential was chosen as 0 V, since no redox reactions occurred at that potential. Three cycles were scanned at each dopamine concentration.

3. Results and discussion

3.1. Surface characteristics

High concentration of sp^2 in the nc-C and high concentration of sp^3 (80–85%) in ta-C films was detected by applying XPS, Raman and TEM as reported earlier [21,22]. The nc-C films presented a smooth surface, with an average surface roughness of 1–3 nm (Table 1). The roughness depends on the deposition parameters as described in more detail elsewhere [23]. Table 1 shows the measured resistivity of the samples. The most conductive surface has a resistivity of 0.03 Ωcm whereas the hydrogenated carbon and control ta-C are practically insulators.