



Electron transport determines the electrochemical properties of tetrahedral amorphous carbon (ta-C) thin films



Tommi Palomäki^a, Niklas Wester^b, Miguel A. Caro^{a,c}, Sami Sainio^a, Vera Protopopova^b, Jari Koskinen^b, Tomi Laurila^{a,*}

^a Department of Electrical Engineering and Automation, School of Electrical Engineering, Aalto University, Espoo, Finland

^b Department of Materials Science and Engineering, School of Chemical Technology, Aalto University, Espoo, Finland

^c COMP Centre of Excellence in Computational Nanoscience, Department of Applied Physics, Aalto University, Espoo, Finland

ARTICLE INFO

Article history:

Received 16 August 2016

Received in revised form 16 December 2016

Accepted 16 December 2016

Available online 19 December 2016

Keywords:

tetrahedral amorphous carbon

electron transfer

electron transport

film thickness

electrochemical properties

ABSTRACT

Amorphous carbon based electrodes are very promising for electrochemical sensing applications. In order to better understand their structure-function relationship, the effect of film thickness on the electrochemical properties of tetrahedral amorphous carbon (ta-C) electrodes was investigated. ta-C thin films of 7, 15, 30, 50 and 100 nm were characterized in detail with Raman spectroscopy, transmission electron microscopy (TEM), conductive atomic force microscopy (c-AFM), scanning tunneling spectroscopy (STS) and X-ray absorption spectroscopy (XAS) to assess (i) the surface properties of the films, (ii) the effect of film thickness on their structure and electrical properties and (iii) the subsequent correlation with their electrochemistry. The electrochemical properties were investigated by cyclic voltammetry (CV) using two different outer-sphere redox probes, Ru(NH₃)₆^{3+/2+} and FcMeOH, and by electrochemical impedance spectroscopy (EIS). Computational simulations using density functional theory (DFT) were carried out to rationalize the experimental findings. The characterization results showed that the sp²/sp³ ratio increased with decreasing ta-C film thickness. This correlated with a decrease in mobility gap value and an increase in the average current through the films, which was also consistent with the computational results. XAS indicated that the surface of the ta-C films was always identical and composed of a sp²-rich layer. The CV measurements indicated reversible reaction kinetics for both outer-sphere redox probes at 7 and 15 nm ta-C films with a change to quasi-reversible behavior at a thickness of around 30 nm. The charge transfer resistance, obtained from EIS measurements, decreased with decreasing film thickness in accordance with the CV results. Based on the characterization and electrochemical results, we conclude that the reaction kinetics in the case of outer-sphere redox systems is determined mainly by the electron *transport* through the films and not the electron *transfer* between the redox probe and the electrode surface, since the surface region is expected to be identical in all the ta-C films. Finally, it was shown that a titanium interlayer between the Si substrate and ta-C significantly affected the electrical and electrochemical properties of the electrodes, further emphasizing the role of electron transport through the film in determining the electrochemical behavior of ta-C.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Diamond-like carbon (DLC) is a promising electrode material owing to its unique electrochemical properties such as chemical inertness, wide potential window and low background current.

Thus, DLC has been used in analytical applications for detecting biomolecules such as neurotransmitters [1–3], glucose [4], and heavy metals [5]. The basic electrochemical properties and response of DLC to several redox systems have also been investigated [6–9] and recently reviewed [10]. The unique electrochemical properties of DLC are conferred by the high sp³ fraction that also makes it a pseudo band gap semiconductor. A form of highly sp³-bonded DLC that has electrochemical properties

* Corresponding author. Tel.: +358 503414375

E-mail address: tomi.laurila@aalto.fi (T. Laurila).

close to those of diamond is referred to as tetrahedral amorphous carbon (ta-C). It is generally claimed that the low density of states (DOS) around the Fermi level hinders heterogeneous electron transfer to ta-C and semiconductors in general [11,12]. Accordingly, doping with nitrogen has been commonly used to improve the electrical properties of ta-C and enhance electron transfer [8,9].

It has been shown that the structure and electrical properties of ta-C are heavily dependent on film thickness [13,14]. A decrease in film thickness leads to an increase in the sp^2/sp^3 ratio and decrease in the mobility gap [13,15]. Therefore, controlling the thickness of ta-C may be another effective way in addition to doping to enhance electron transfer. In our previous study, we showed that the structural changes associated with film thickness strongly correlated with the electrical properties of ta-C and might have implications for their electrochemical properties as well [15]. Furthermore, the surface of ta-C is composed, irrespective of the bulk sp^3 fraction, of a low-density sp^2 -rich layer [16–18]. This layer has been shown to be responsible for a relatively high local DOS at the surface of highly sp^3 -bonded amorphous carbon (a-C) with computational simulations [19]. This is in contrast with the conventional view that attributes a low DOS around the Fermi level to diamond-like carbon materials [1].

In this paper, we investigate in depth the effect of film thickness on the electrochemical properties of ta-C with the use of physical and structural (Raman spectroscopy, TEM, STS, c-AFM, XAS) as well as electrochemical characterization methods (CV, EIS). Additionally, computational simulations utilizing density functional theory (DFT) are used to rationalize the experimental findings. Based on the results, we challenge the conventional view that relates the high sp^3 fraction in ta-C thin films to the slow electron transfer kinetics in the case of outer-sphere redox systems. Instead, we propose that it is actually the electron transport through the ta-C films that explains the observed reaction kinetics.

2. Experimental

2.1. Deposition of ta-C films

ta-C thin films of 4, 7, 15, 30, 50 and 100 nm were deposited on a titanium adhesion layer on top of highly conductive boron-doped p-type (100) Si wafers with 0.001–0.002 Ωcm resistivity (Ultrasil, USA). Before deposition, the samples were cleaned by standard RCA-cleaning procedure and by ultrasonication for 3 min in HPLC grade acetone (Sigma-Aldrich). The 20 nm thick Ti adhesion layers were deposited by means of direct-current magnetron sputtering (DC-MS) and ta-C films were deposited with a filtered cathodic vacuum arc (FCVA) system. Samples were deposited at a distance of either 110 or 220 mm.

Both deposition systems were installed inside the same cylindrical 125 l stainless steel chamber with a dry-scroll vacuum pump (Edwards XDS10) and a Cryo-Torr (CTI Cryogenics CT8F) cryo pump. The magnetron sputtering system was equipped with a circular, water-cooled 2-inch Ti target (Kurt J. Lesker Company) and a DC generator (DCO2 BP). The following deposition parameters were used: discharge power fixed at 100 W, total pressure of 0.67 Pa, Ar gas flow rate of 29 sccm, and deposition times of 60 s (110 mm) and 350 s (220 mm). The Ti target was cleaned by a pre-sputtering of 120 s prior to all depositions.

The FCVA deposition system (Lawrence Berkeley National Laboratory, USA) was equipped with a 45° bent magnetic filter to reduce macroparticle contamination and two cathodes in a dual cathode configuration. Graphite cathodes (Goodfellow) with 6.35 mm diameter and 99.95% purity were used. A pulse forming network (PFN) was used to strike the triggerless arc with a frequency of 1 Hz. The PFN was controlled with custom-made National Instruments hardware and LabView software. The 2.6 mF

capacitor bank was charged to 400 V resulting in an arc current of 0.7 kA and pulse width of 0.6 ms. The total pressure during the deposition process was below 1×10^{-4} Pa.

During the depositions the samples were at floating potential and rotation was used to ensure homogeneous film deposition (rotational velocity 20 rpm). Ti and ta-C films with varying thicknesses were deposited on silicon and the deposition rates at both target distances were determined by contact profilometry (Dektac XT).

In order to study the electrochemical properties and influence of Ti on the ta-C electrodes, a titanium film without ta-C was also prepared as described above.

2.2. Raman spectroscopy

Visible Raman spectroscopy (LabRAM HR, Jobin Yvon Horiba) was used to study the bonding configuration of the ta-C films. The system was equipped with an argon laser (wavelength of 488 nm, power 10 mW) and BX41 (Olympus) microscope and 100x objective lens with a spot diameter of less than 1 μm . The I_D/I_G ratios of the acquired Raman spectra were determined by fitting a double Gaussian function.

2.3. Transmission electron microscopy (TEM)

Cross-sectional TEM samples were prepared conventionally by grinding, polishing and dimpling the sample until its thickness was below 10 μm , followed by Ar ion milling with a PIPS Ion miller (Gatan USA). High-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2100 (JEOL, Japan) microscope equipped with a field emission gun (FEG) operating at 200 kV. A Gatan 4k \times 4k UltraScan 4000 CCD camera was employed for digital recording of the HRTEM images. The microscope was equipped with the Gatan image filter (GIF) for electron energy loss spectroscopy (EELS). A C_{60} EELS spectrum was taken as the reference [20] and the proportion of sp^2 -bonded carbon atoms was calculated using the method reported by Cuomo et al. [21].

2.4. Conductive atomic force microscopy (c-AFM)

An Ntegra Aura scanning probe microscope (NT-MDT) was used for contact and conductive AFM (spreading resistance microscopy) measurements. The measurements were carried out in scanning-by-sample mode with the use of a universal measuring head equipped with a probe holder designed for current measurements and diamond-coated conductive probes (DCP10 and HA_HP_DCP). C-AFM was performed in single-pass mode, which permitted the simultaneous acquisition of topography maps, roughness data, current maps, current distribution and the average current J_{SR} flowing through the studied sample area under an applied probe voltage of 0.5 V.

2.5. Scanning tunneling spectroscopy (STS)

Investigation of the density of states (DOS) near the Fermi level and mobility band gap measurements were carried out with STS in ambient air conditions with an Ntegra Aura scanning probe microscope (NT-MDT). Tunneling current-voltage characteristics and differential conductivity were measured at different randomly chosen surface areas of the studied films by the interrupted-feedback technique. At least 10 measurements were done for each point to reduce the possible error from tip-sample spacing variation. The tip current and tip voltage were 0.2 nA and 0.5 V, respectively.

Download English Version:

<https://daneshyari.com/en/article/4767340>

Download Persian Version:

<https://daneshyari.com/article/4767340>

[Daneshyari.com](https://daneshyari.com)