



Influence of the atomic nitrogen content in amorphous carbon nitride thin films on the modulation of their polarizable interfaces properties

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ABSTRACT

Amorphous carbon nitride (a-CNx) thin films possessing different nitrogen contents ($0.12 \leq x \leq 0.30$) have been synthesized by the DC cathodic reactive magnetron sputtering technique on transparent glass/indium tin oxide (ITO) substrates. They were characterized ex-situ by using two microscopy techniques: scanning electron microscopy (SEM) and atomic force microscopy (AFM), a spectroscopic technique: X-ray photoelectron spectroscopy (XPS), and in solution by using electrochemical methods: cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). The results obtained with these methods have permitted to highlight why a-CN0.30, the a-CNx sample with the highest nitrogen content among those investigated in this work, behaves both as a dielectrical material (low electronic conductivity) and as an ideally polarizable interface (high polarization resistance). For this purpose, the role of both the ionic strength and the overpotential were investigated in blocking electrode conditions, i.e. only in the presence of the supporting electrolyte. It was observed that the interfacial capacitance can be strongly electrically modulated with the ionic charge concentration and with the applied overpotential. The understanding of the behaviour of a-CNx materials presents a great challenge for their integration in new microfluidic transistor type devices in view of the elaboration of polarizable interface flow-field effect transistors (PI-FFETs).

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1. Introduction

In the last years, amorphous carbon nitride (a-CNx) thin films were abundantly investigated. In particular, electrochemically pre-treatments were developed to improve their surface electrochemical reactivity [1–10]. Most of the time, a low atomic nitrogen content was selected for a-CNx thin film elaboration and cathodic and/or anodic electrochemical pre-treatments were empirically optimized in an acidic or alkaline medium, respectively. For this purpose, correlations between electrochemical properties and chemical composition, and between conductivity measurements and electrochemical reactivity of these films were investigated. In

these studies, the atomic nitrogen and carbon contents in a-CNx thin films were determined by XPS [4,11–13]. Indeed, it has been previously reported that local variation of the sp^2 and sp^3 type bonding arrangements of nitrogen and carbon atoms induced local conductivity and electrochemical reactivity variations on the a-CNx surface [7,14,15], which played a key role on the a-CNx electrochemical properties. These results were in agreement with the literature where it was reported that sp^3 C–N groups act as insulating sites while sp^2 C=C groups favor high conductivity areas [11,16–18]. Additionally, an increase of C_{sp^2}/C_{sp^3} Raman band ratio reveals a transition towards a more graphitic microstructure in the a-CNx layer [19–21]. These studies have permitted the control and the exploitation of the surface chemistry of a-CNx [7] for the development of electroanalytical procedures allowing the detection and the separation of biomolecules with biological interest such as ascorbic acid and dopamine [8,22], or a drug called furosemide [10].

In 2010, Plecis et al. [23] were the first ones to successfully

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exploit *a*-CN_x layers to produce a polarizable interface (PI) in microfluidic transistors using the Flow-Field Effect Transistors (FFETs) configuration [24,25]. It was thus an alternative to the conventional metal-insulator-electrolyte systems (MIE-FFETs) for controlling electro-osmotic flows (EOF) in microfluidics [26–28]. Indeed, in such microdevices, no charge transfer reaction (case of MIE-FFETs) from or towards the conducting layer takes place in the potential window or must be negligible (case of PI-FFETs) whatever the overpotential applied [23,29,30]. As a matter of fact, in the MIE configuration, the control of the EOF is strongly narrowed by the low value of the serial capacitance of the dielectrical film covering the electrodes. This limitation obviously does not exist with the PI configuration. However, in this later development [23], the authors often observed a deterioration of the *a*-CN_x PI whose origin was not entirely understood. We put forward two reasons: (i) the *a*-CN_x composition on glass was not optimized although the FFET was evidenced, and (ii) the absence of potential regulation system because neither a reference electrode nor an adapted apparatus have been used and connected to the first PI-FFET prototype to precisely measure the potential difference between the liquid at microchannel entrance and the lateral electrode. If the applied potential difference is larger than the potential window, it could entail degradation either on the cathodic side by disruption of the film due to hydrogen evolution or on the anodic side by erosion and formation of carbon dioxide.

In this work, we provide an answer to the first problematics. For this purpose, we optimized amorphous carbon nitride (*a*-CN_x) deposition on transparent and conductive glass/ITO slides so that it fully complies only the PI requirements mentioned above. Electrochemical measurements were performed in a conventional electrochemical cell to precisely control the PI potential. As mentioned previously, these polarizable glass slides were not electrochemically pre-treated as traditionally investigated in the literature in order to enhance or catalyze its electroanalytical performances. In this work, we focused our attention on the moderately high nitrogen contents ($P(N_2)/P_{tot}$ reaching up to 30%) and their detrimental effects on the kinetics of Faradaic reactions. These results are important for a better knowledge of the interfacial phenomena occurring at *a*-CN_x electrode/aqueous solution interfaces mainly when a high atomic nitrogen content is present in the *a*-CN_x material.

2. Materials and methods

2.1. Elaboration of glass/ITO/*a*-CN_x samples

Glass/ITO samples possessing a square resistance of 30 Ω were purchased from SOLEMS (Palaiseau, France). They were first cleaned with ethanol, acetone, and bi-distilled water, and then submitted to a radiofrequency ion etching (13.56 MHz) in the reactor (model MP 300S, PLASSYS S.A., France). *a*-CN_x thin films were deposited on glass/ITO substrates using the DC reactive magnetron sputtering technique, a graphite target and a Ar/N₂ plasma with a total pressure of 0.4 Pa. The different N₂ partial pressures used in this work were 3, 7, 15 or 30% of the total pressure. The thin films were deposited with a power of 200 W for 20 min. The *a*-CN_x samples were characterized by XPS, SEM and AFM.

2.2. Glass/ITO/*a*-CN_x electrode preparation

For electrochemical characterization, the *a*-CN_x samples were elaborated as mentioned above. However, a hollow plexiglass cylinder with a 6 mm internal diameter was glued in a vertical position on the prepared *a*-CN_x sample. Thereafter, the periphery and

the portion of the *a*-CN_x sample situated outside of the cylinder were both coated with epoxy resin in order to expose only a reproducible electrode area (0.282 cm²) situated inside the cylinder to the electrolytic solution (See Scheme 1).

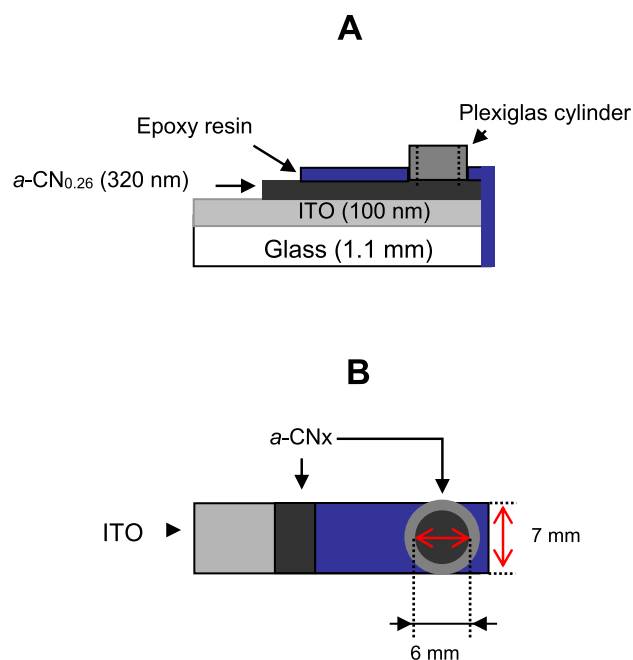
2.3. Apparatus

A scanning electron microscope (S440, LEICA) with a tungsten filament was used for analyzing the detailed morphology of glass/ITO/*a*-CN_x electrodes before and after they were coated with epoxy.

The AFM equipment used is a Molecular Imaging apparatus composed with a Pico-LE base equipped with a micro positioning device. This latter allows a precise positioning of the AFM tip on the *x*-*y* plane of the sample. A wide area scanner (100 μm × 100 μm) was also used together with a photo-detector, and an AFM nose suitable for AFM experiments in conductive mode. To measure local electrical conductivity, the current sensing mode of AFM (CS-AFM) was used to record I-E curves on randomly selected zones of the sample. For that purpose, CS-AFM probes purchased from Nano-AndMore (France) and made from a rectangular cantilever bearing a silicon tip coated with a PtIr5 alloy (spring constant: 2,8 N m⁻¹, curvature radius: 15 nm) were used.

The XPS measurements were carried out on a SPECS instrument (Phoibos MCD 150 analyzer), using an MgKα X-ray source with a power of 150 W. The angle of analysis was equal to 90° with respect to the sample surface and the C 1s, O 1s, and N 1s spectra were recorded with a pass energy of 10 eV.

Electrochemical measurements were performed by using a Bio-Logic SP-300 potentiostat with the EC-lab software. Experiments were performed with a three-electrode cell arrangement. Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) experiments were carried out in blocking electrode conditions, *i. e.* in the presence of the supporting electrolyte only. The polarization curves were plotted from –1.5 V to +1.5 V using a 50 mV s⁻¹ scan rate. The EIS spectra were plotted using a frequency range from 10 kHz to 50 mHz with 5 points per decade.



Scheme 1. Schematic representation of the *a*-CN_x working electrode deposited on glass/ITO substrates. Not to scale. A. Cross-section. B. Top view.

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