Electrochemistry Communications 75 (2017) 48–51

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Direct SN_1 reaction at oxidized PPF surfaces

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ARTICLE INFO

Article history:
Received 30 November 2016
Received in revised form 21 December 2016
Accepted 27 December 2016
Available online 29 December 2016

Keywords:
Surface functionalization
PPF
SN_1 reaction
Monolayer

ABSTRACT

For comparative purposes, two series of pyrolyzed photoresist film (PPF) substrates are prepared with and without reductive conditions, i.e. in the presence and absence of H_2. Electrochemical and X-ray photoelectron spectroscopy analyses show that PPF substrates prepared in the absence of H_2 possess many more surface oxygen functional groups, mostly hydroxyl groups, than PPF prepared under reductive conditions. These oxidized PPF samples can be advantageously involved in an SN_1 reaction to covalently bind ferrocenyl groups to the surface as (sub-)monolayers.

1. Introduction

Pyrolyzed photoresist film (PPF) is an amorphous carbon material with a structure closely related to that of glassy carbon, while being easier and less costly to produce [1–4]. PPF substrates are attractive because they are easy to obtain, mechanically robust, biocompatible, and have useful electrochemical properties. They also show great versatility in the fabrication of nanostructures [5,6]. PPF substrates have been employed in a large range of applications, including electrochemical sensors [7,8], microelectrochemical systems [9], molecular electronics [10] and modified electrodes [11–14]. Many of these applications involve a surface that has been chemically modified. Indeed, one of the major areas of interest in graphitic materials in general, and PPF in particular, is the possibility of covalently binding molecular groups onto the surface, allowing close control of the morphological and physicochemical properties of the surface layer (thickness, organization, hydrophobicity, etc.). The reductive grafting of diazonium cations is currently the most popular method of modifying the PPF surface [15]. This approach leads to highly stable layers, but these are generally multilayers, with a few exceptions. A method of restricting film growth to (sub) monolayers would be desirable for some applications, and motivates the search for other reactions allowing surface modification with the formation of a robust interface. Plasma iodination to form surface C—I bonds has recently been proposed as a facile and modular approach to functionalization of the PPF surface. The C—I termini are subsequently involved in a photochemical reaction with alkene or alkyne derivatives [16]. More recently, a direct Diels–Alder reaction with anthranilic acids has been demonstrated to produce covalently bound monolayers on PPF and graphene substrates [17]. Upon addition of isoamyl nitrite, anthranilic acid yields an aryne that can graft onto the graphitic surface through a Diels–Alder cycloaddition. Direct reaction between alkyne or alkene compounds and PPF surfaces has been reported to lead to the robust attachment of zinc porphyrin and ferrocene on PPF surfaces via Diels–Alder [4 + 2]- and [2 + 2]-cycloadditions [18].

High pyrolysis temperatures (1100 °C) and a reductive gas atmosphere (pure H_2 or 5% H_2 + 95% N_2) have been shown to yield PPF samples with the lowest oxygen content. These films are slowly oxidized under ambient conditions, with the O/C ratios increasing to as much as 5–6% [1–3]. In this report, we show that the use of a non-reductive atmosphere leads to oxidized PPF "enriched" with surface hydroxyl groups. Used as electrodes, these substrates allow fast electron transfer kinetics with ferricyanide and dopamine. Furthermore, we take advantage of the hydroxyl termini to modify the surface with a (sub-)monolayer of ferrocene via an SN_1 reaction between ferrocenemethanol and the PPF surface in the presence of a strong acid. A comparative investigation with PPF substrates fabricated in the presence of H_2 is carried out, using electrochemical methods and X-ray photoelectron spectroscopy (XPS).

2. Experimental section

2.1. Chemicals

Potassium ferricyanide (98.5%, Acros), dopamine hydrochloride (99%, alfa Aesar) ferrocenemethanol (98%, Alfa Aesar), trifluoroacetic acid (99%, Acros), tetrabutylammonium hexafluorophosphate

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http://dx.doi.org/10.1016/j.elecom.2016.12.016

(Bu_4NPF_6, electrochemical grade, Sigma-Aldrich) were used as received. AZ4562 photoresist resin was from MicroChemicals GmbH.

2.2. Electrochemistry

Electrochemical measurements were performed with an Autolab Electrochemical Analyzer (PGSTAT 30, EcoChemie BV). A three-electrode cell was used with a platinum grid as counter electrode and a saturated calomel electrode (SCE) as reference. The PPF samples were connected with an alligator clip. The electrode area is measured from the immersed surface. The apparent electron transfer kinetic rate constants k_s were estimated through numerical simulations using DigiElch software (version 7, Elchsoft) using the default numerical options and assuming a planar diffusion and application of the Butler–Volmer equation. The charge-transfer coefficient was taken as 0.5.

2.3. XPS

Measurements were performed with an Mg Kα ($h\nu = 1253.6$ eV) X-ray source, using a VSW HA 100 photoelectron spectrometer with a hemispherical photoelectron analyzer. Wide and narrow spectra were acquired with a pass energy of 20 eV. Calibration was performed by setting C 1s at 285 eV. The surface composition was estimated using the integrated peak areas and the corresponding Scofield sensitivity factors. The core level spectra were peak-fitted using CasaXPS software (Casa Software, Ltd., version 2.3.18).

2.4. Preparation of PPF samples

The PPF samples were prepared using a procedure adapted from reference [19]. Briefly, pieces (1.4×1.4 cm^2) of single-side polished n-type Si (100) wafer (Sil'Tronix) were ultrasonically cleaned in a series of solvents, then dried under Ar flow. A small amount of AZ4562 photoresist was spin-coated on the samples (4000 rpm for 30 s). The samples were then soft-baked at 90 °C for 30 min. After cooling, a second layer of photoresist was applied. The samples were pyrolyzed in a tube furnace, using a temperature ramp equal to 10 °C/min until 1100 °C was reached; this temperature was maintained for 1 h, then reduced back to room temperature. During the heating and cooling phases, pure argon or a 95% argon + 5% hydrogen mixture were flowed through the tube furnace at 1 atm. Two series of PPF samples, Ar-PPF and H_2-PPF, were prepared. Finally, the samples were briefly sonicated in acetone, methanol and 2-propanol, then dried with N_2. They were stored at ambient laboratory conditions for at least one week before use.

2.5. Grafting procedure

Surface grafting through surface oxygen groups was performed using a procedure adapted from previously published works [20–22]. Ar-PPF and H_2-PPF samples were soaked in a 1:1 water/acetone v/v solution (10 mL) containing 2×10^{-2} M of ferrocenemethanol. Two drops of concentrated trifluoroacetic acid were added. The reaction was stirred at 45 °C for 2 h and then at room temperature for 20 h. The modified substrates were then rinsed several times with acetone, ultrapure water and acetonitrile.

3. Results and discussion

3.1. XPS analyses

The H_2-PPF and Ar-PPF samples were thoroughly cleaned by ultrasonic rinsing with CH_2Cl_2, acetone and isopropanol, then vacuum pumped overnight before being introduced into the XPS entry chamber. The Ar-PPF samples appear less homogeneous than the H_2-PPF ones to the naked eye, with a black central stripe (c.a. 6–8 mm) flanked by gray edges on each side. C, O and Si elemental species are detected in the XPS survey spectra. The spectrum for H_2-PPF shows the presence of carbon C 1s as a dominant peak (285 eV, 93.4%), oxygen O 1s (533 eV, 5.7%) and a trace of silicon Si 2p (103 eV, 0.9%). The surface composition of Ar-PPF is somewhat different, with the presence of carbon C 1s (285 eV, 37.2%), O 1s (533 eV, 41.4%) and Si 2p (103.6 eV, 21.5%). The Si 2p photoelectron peak at 103.6 eV and the high atomic percentage of oxygen indicate the presence of uncovered SiO_2 in these samples, in agreement with their inhomogeneous aspect. For both samples, a closer inspection of the high-resolution C 1s core level spectra makes it possible to identify several components (Fig. 1). A major component at 285 eV corresponds to C—C or C—H carbons. A variety of different surface oxygen functional groups are detected, namely C–OH groups at 286.5 (±0.3) eV, C═O in surface aldehydes and ketones at 287.8 (±0.3) eV and acid carboxylic groups at 289.3 (±0.3) eV [23].

Interestingly, the amount of surface oxidized functional groups is much larger for Ar-PPF than for H_2-PPF. The ratio of oxidized carbon to total carbon is equal to 0.09 and 0.3 for H_2-PPF and Ar-PPF, respectively. Oxygen functional groups are commonly detected on PPF substrates [1–4]. A pyrolysis temperature greater than 700 °C is required to prepare PPF with a low oxygen content, and 1000–1100 °C was reported to give the best results under forming gas, leading to very low O/C ratios of approximately 0.03 for fresh samples [1–3]. After 24 h under ambient air, the PPF samples are slowly oxidized, with their O/C ratios increasing to as much as 5–6% [2,3]. The C 1s XPS measurements for H_2-PPF are fully consistent with these observations. However, the Ar-PPF contains many more surface oxygen species. A previous report showed that the 2% oxygen content of PPF fabricated under a pure argon atmosphere increased to 10% when stored in air [4]. Moreover, the π-π* shake-up satellite peak, which is clearly observed in the C 1s spectrum for H_2-PPF, is hardly visible for Ar-PPF, indicating a substitution at the level of the phenyl ring [24,25]. This observation is fully consistent with the presence of more oxygenated surface species in Ar-PPF than in H_2-PPF. Another important point worthy of comment concerns the nature of the oxygen surface groups on the Ar-PPF. The peak-fitting

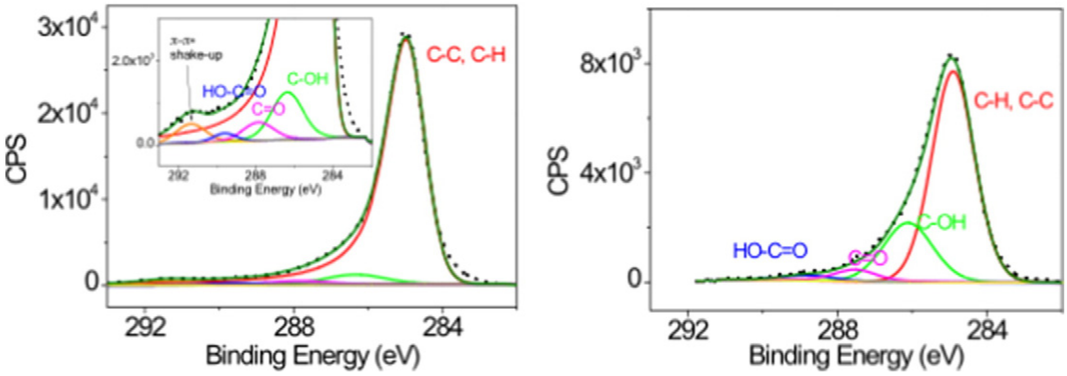

Fig. 1. Peak-fitted C 1s core level spectra for H_2-PPF (left, insert: magnification of the high binding energy side) and Ar-PPF (right).