Materials Chemistry and Physics 133 (2012) 592–598

Contents lists available at SciVerse ScienceDirect

Materials Chemistry and Physics

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

Materials science communication

Embedding and electropolymerization of terthiophene derivatives in porous n-type silicon

Diyana Badeva[a,*], François Tran-Van[b,1], Layla Beouch[c,2], Claude Chevrot[c,2], Ivania Markova[d,3], Todora Racheva[d,3], Gérard Froyer[a,4]

[a] Equipe Physique des Matériaux et Nanostructures, IMN, B.P. 32229, 44322 Nantes cedex 3, France
[b] Laboratoire de Physico-Chimie des Matériaux et des Electrolytes pour l'Energie (PCM2E), E.A 6299, Université de Tours, Faculté des Sciences et Techniques, Parc de Grandmont, 37200 Tours, France
[c] Laboratoire de Physicochimie des Polymères et des Interfaces, 5, mail Gay-Lussac, F-95031 Cergy-Pontoise Cedex, France
[d] Laboratory of Nanomaterials and Nanotechnologies, University of Chemical Technology and Metallurgy, 8 St. Kliment Ohridski blvd., 1756 Sofia, Bulgaria

ARTICLE INFO

Article history:
Received 21 November 2011
Received in revised form 17 January 2012
Accepted 31 January 2012

Keywords:
Porous silicon
Terthiophene
Oxidation
Filling
Polymerization
Nanocomposite

ABSTRACT

A mesoporous n-type silicon/poly (3′-acetic acid-2,2′-5′,2″ terthiophene)–(Poly (3TAA) nanocomposite was elaborated in order to realize new components for optoelectronics. Non-oxidized and oxidized porous silicon substrates is used and their physical and chemical properties have been studied by different techniques such as transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transformed infrared spectroscopy (FTIR). Terthiophene based conjugated structure has been successfully incorporated inside the pores by capillarity at the melting temperature of the monomer. The filling of the monomer into the porous volume was probed by energy dispersive X-ray spectroscopy (EDX). Polarized infrared absorption spectroscopy results indicated that the monomer molecules show preferential orientation along the pore axis, due to hydrogen bonding, in particular that of the carboxylic groups with silanol-rich oxidized porous silicon surface. The 3TAA monomer molecules embedded in porous silicon matrix were electrochemically polymerized in situ and resonance Raman scattering spectroscopy proved the above-mentioned polymerization.

1. Introduction

Polymeric materials with high nonlinear optical (NLO) properties embedded in a porous silicon matrix have been already investigated by several research groups [1–3] since they are of interest to develop electro-optical devices. The successful penetration of the optically active materials into the porous volume is a key factor to obtain the desired efficient composite material. However, in most studies, there is no indication of the pore filling level with such polymeric materials [4–7]. Several factors contributed to this filling such as porous silicon morphology, surface chemistry and wettability of this surface with the polymeric materials. The optical properties of the resulting composite material depend as well as on the polymer chain organization [8] and the conjugation length along the polymer chains to achieve high third-order nonlinear optical effect [7,9]. In order to finally improve the pore filling we have matched the morphology of the porous silicon matrix and its chemical surface properties with the affinity of the conjugated material. (3′-acetic acid-2,2′-5′,2″ terthiophene)–(3TAA) monomer was chosen due to the carboxylic acid functions which allow hydrogen bonds either with the chemical functions present on the surface of porous silicon or with other 3TAA molecules leading to stacked structures. Through the hydrogen bonds interactions, supramolecular architectures can be achieved within the pores as already observed with diacetylenic monomer bearing carboxylic functional group [9]. Another advantage of this oligotiophene derivative compared to thiophene monomers is to decrease the oxidation potential for electropolymerisation and to minimize the overoxidation of the resulting polymer [10]. In this paper we report for the first time on the successful introduction of the terthiophene derivative in a porous silicon matrix and its specific organization in the confined media and the subsequent in situ electrochemical polymerization leading to the organization of the conjugated macromolecules within the pores.

---

[*] Corresponding author. Tel.: +33 02 4736 6923; fax: +33 02 4736 7073.
E-mail addresses: diyana.badeva@cnrs-imn.fr (D. Badeva), francois.tran@univ-tours.fr (F. Tran-Van), layla.beouch@u-cergy.fr (L. Beouch), claude.chevrot@u-cergy.fr (C. Chevrot), vania@uctm.edu (I. Markova), todora@uctm.edu (T. Racheva), gerard.froyer@cnrs-imn.fr (G. Froyer).
[1] Tel.: +33 02 4736 6953; fax: +33 02 4736 6923.
[2] Tel.: +33 01 3425 7042; fax: +33 01 3425 7071.
[3] Tel.: +359 02 8163 390; fax: +359 02 8685 488.
[4] Tel.: +33 02 4037 3979; fax: +33 02 4037 3995.

0254-0584/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.matchemphys.2012.01.126

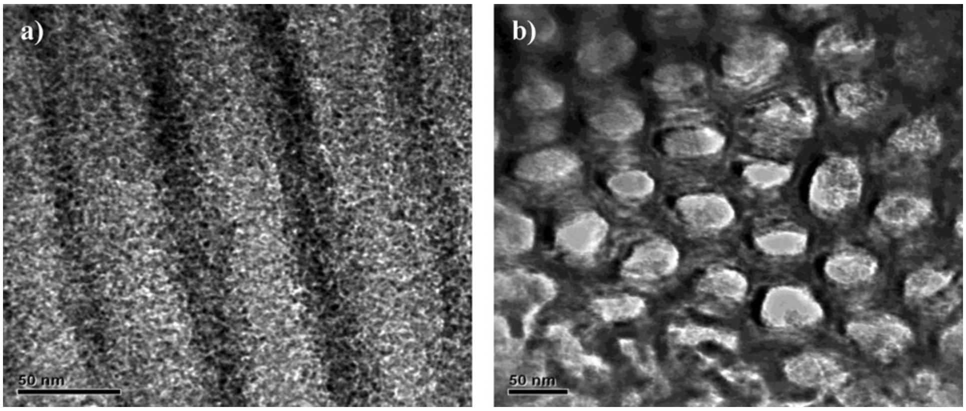

Fig. 1. TEM images of mesoporous structure formed by anodizing n-Si – (a) cross-sectional view, (b) surface view (pore walls are in black).

2. Experimental

2.1. Porous silicon (PSi) preparation

The mesoporous silicon matrix used for the embedding of the organic materials was prepared from crystalline n-type, one-side polished silicon wafer (roughness on polished surface less than 1 nm), purchased from Siltronix, (diameter 100 mm, thickness 85 μm, phosphorous-doped, 100 orientation, $\rho = 0.002–0.010\ \Omega$ cm).

Small pieces – roughly 1.5 cm^2 – were put on the polished side in a Teflon cell in between 2 O-rings delimitating thus a 0.79 cm^2 exposed area to the 1:1 49% HF (aq)/EtOH, v/v used as the electrolyte. The silicon substrates were etched by galvanostatic mode at 344 mA cm^{-2} during 140 s under illumination of a 150 W halogen lamp (lumen at 2550 Im, Color Rendering Index – 100, luminous efficiency – 17 Im/W, detection angle 240° with 180° angle of aperture) set at a 10 cm distance. Under these experimental conditions the porosity of the n-type silicon matrix reaches 65% [11]. The porosity (P) is determined by weighing the silicon substrate both before and after anodisation (m_1 and m_2, respectively) and again after porous silicon layer has been removed (m_3). The porosity is then calculated by the ratio $P = (m_1 - m_2)/(m_1 - m_3)$. The specific surface area of PSi is 140 m^2 g^{-1} determined by BET adsorption measurements [12]. The pore diameter visualized by TEM is ranged from 30 to 50 nm (Fig. 1(a) and (b). The porous layer is 40 μm thick, observed by scanning electron microscopy (SEM) (Fig. 2). This value corresponds to the optimal ratio between the porous layer thickness and that of the crystalline part (85 μm) because higher values of the porous layer thickness will corresponds to higher mechanical constrains that could not be balanced by a larger rigidity of the crystalline part and the sample will explode.

Prior to the transmission optical measurements at 1.3–1.5 μm (the doped silicon absorbs in the IR spectrum) it was necessary to etch the remaining single crystal silicon down to one half of the initial wafer thickness and to obtain a porous layer only. The etching process was performed in the same electrolytic solution (1:1 49% HF (aq)/EtOH, v/v) at higher current density from those used for the porous formation (344 mA cm^{-2}) which ensure electroerosion of the silicon (at a current density higher than Jps). After etching, the porous silicon samples were rinsed with deionized water for 1 min and dried under vacuum for 30 min prior to use.

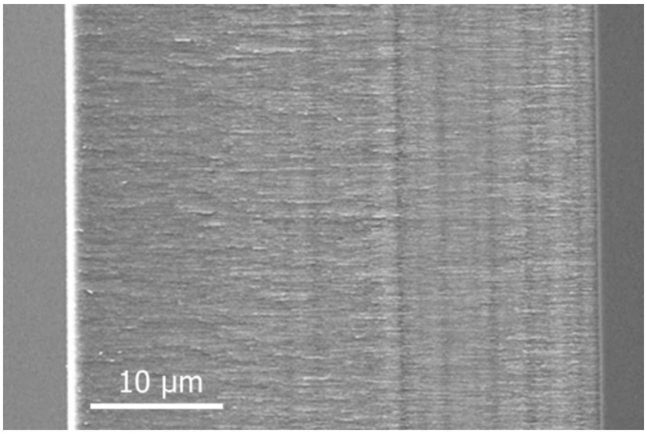

Fig. 2. SEM images of cleaved cross-section sample of the entire PSi layer.

3. Porous silicon oxidation

After preparation the initial hydrophobic porous surface [13] was oxidized by a Piranha solution (6:2 H_2SO_4:H_2O_2 v/v) for 1 min under sonication and 14 min without sonication at room temperature. The samples were carefully rinsed with deionized water and dried under vacuum.

3′-acetic acid-2,2′-5′,2″ terthiophene has been synthesized in five steps by Stille coupling of 2,5-dibromothiophene-3-methylacetate with 2 equivalents of 2-(tributylstannyl)thiophene, followed by acidic hydrolysis of the ester group, using a procedure similar to that of Garnier and co-workers [14]. Total yield: 25% 1H NMR (CDCl3, ppm) 7.36 (q, 1H); 7.23 (m, 3H); 7.13 (q, 1H); 3.8 (s, 2H) [14].

4. Filling of the porous silicon

The oxidized porous silicon samples were covered with the monomer spread as a thin layer of powder on the surface and then installed in a glove box on a hot plate equipped with a temperature regulating system. The porous sample covered by the monomer powder was heated above its melting point (133 °C) under Argon to promote the pore filling. The chemical structure of the monomer after filling was confirmed by Fourier transformed infrared spectroscopy (FTIR) (spectra not shown). The 3TAA was polymerized by a galvanostatic method via an Autolab equipment model PGSTAT 30 (Eco Chemie), interfaced with a computer for data acquisition. Monomers electropolymerization inside the pores was performed in a three electrode conventional cell consisting of a working electrode (porous silicon/3TAA a 0.25 cm^2 substrate surface), a Pt foil 1 cm^2 as counter-electrode and Ag/AgCl/KCl$_{sat}$ as the reference electrode, at constant current of 0.5 mA, with CH_3CN/0. 1 M Lithium perchlorate as electrolyte.