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Grafting of functionalized polymer on porous silicon surface using Grignard reagent

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ABSTRACT

Recently, considerable attention has been paid to the manipulation and the control of the physicochemical properties of porous silicon surfaces because of their crucial importance to the modern microelectronics industry. Hybrid structures consisting of deposited polymer on porous silicon surfaces are important to applications in microelectronics, photovoltaics and sensors (Ensafi et al., 2016; Kashyout et al., 2015; Osorio et al.; 2015; Hejjo et al., 2002) [1–4]. In many cases, the polymer can provide excellent mechanical and chemical protection of the substrate, changes the electrochemical interface characteristics of the substrate, and provides new ways to the functionalization of porous silicon surfaces for molecular recognition and sensing. In this work, porous silicon surface was modified by anodic treatment in ethynylmagnesium bromide electrolyte leading to the formation of a polymeric layer bearing some bromine substituents. Subsequently, the formed polymer is functionalized with amine molecules containing functional groups (carboxylic acid or pyridine) by a substitution reaction between bromine sites and amine groups (Hofmann reaction). The chemical composition of the modified porous silicon surfaces was investigated and the grafting of polymeric chains and functional groups on the porous silicon surface was confirmed by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) which displayed the principal characteristic peaks attributed to the different functional groups. Furthermore, the surface of the material was examined by scanning electron microscopy (SEM).

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1. Introduction

Porous silicon is a promising material for numerous applications [1–4] and significant research efforts have been devoted over the past two decades to further advance its electronic, optical, chemical and physical properties [5,6]. Especially, interfacing porous silicon with organic materials has become the subject of many investigations to enable target applications in different fields [7,8].

The functionalization of porous silicon surfaces by macromolecules constitutes an attractive approach for designing novel microsystems for several applications; such as sensors for detection of toxic gases and removal of pollutants from aqueous solutions [9,10].

The advantages of these polymeric/silicon nanosystems are their ease of fabrication, a high sensitivity and the most important is their room temperature operation.

With the progress in polymerization methods, it is possible to prepare well-defined grafted polymer chains on various substrate surfaces by a variety of techniques using solvents such as dip and spin coating, aerosol, electrochemical... or depositions from solid states (vacuum evaporation, plasma polymerization).

This paper focused on the anodization of hydrogenated porous silicon surface in anhydrous ethynylmagnesium bromide (Grignard reagent) for the grafting of aliphatic polymer on the surface [11]. When unsaturated precursor is used, polymer ultrathin film is synthesized at the surface; it is bonded through covalent Si-C bonds and exhibited an excellent adherence. The formed polymeric layer contains some remaining bromine substituents whereby amine molecules having either an acid character namely 4(2- amino ethyl) benzoic acid or a basic character namely 4(amino methyl) pyridine, are attached by substitution of bromine sites (Hofmann reaction). The obtained surfaces now bearing functional groups (carboxylic

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acid or pyridine) could be used as chelating sites to remove pollutants from aqueous solutions.

2. Experimental

2.1. Materials

Tetrahydrofuran (THF), 0.5 M ethynylmagnesium bromide in THF, N,N dimethyl sulfoxid (DMSO), 1,2 dichlorobenzene (DCB), 4-(2- amino ethyl) benzoic acid hydrochloride 97% and 4(amino methyl) pyridine were purchased from Aldrich and were used as received.

The silicon substrates are pieces of double side polished silicon (p type Si(100)), 525 μm thickness and 1–10 Ωcm resistivity.

Nanostructured porous silicon (PSi) layers were formed by the electrochemical anodization of Silicon in (HF 35%, H₂O 35% and ethanol 30%) mixture under a constant current density of 20 mA cm^{-2} for 1 min.

2.2. Polymer grafting from ethynylmagnesium bromide

Ethynylmagnesium bromide was provided in THF solvent. Prior to grafting the polymeric chains, THF was substituted by DCB solvent. This substitution was carried out by adding DCB to the

Grignard solution and then reconcentrating it by evaporating THF using a vacuum pump. This procedure was repeated twice in order to ensure a good substitution yield.

PSi surface was modified by anodic treatment in ethynylmagnesium bromide electrolyte for 5 min at a current density of 1.6 mA cm^{-2} in a nitrogen-purged glove box. This reaction leads to the formation of polymeric layer covalently anchored to PSi surface. The formed polymer film was washed extensively with organic solvents.

2.3. Aliphatic polymer functionalization through substitution reaction

PSi/polymer nanostructure was immersed in 4-(2- amino ethyl) benzoic acid/DMF solution or in 4(amino methyl) pyridine/THF solution at room temperature. The study of the chemical substitution reaction of bromine atoms by amines was carried out for various times ranging from 4 to 16 h, and different concentrations (1 M and 2 M for 4(amino methyl pyridine)) and 0.3 M and 0.5 M for 4-(2- amino ethyl) benzoic acid.

2.4. Surface characterization

X-ray photoelectron spectroscopy (XPS) measurements were performed with ESCALAB 220 XL spectrometer from vacuum Gen-

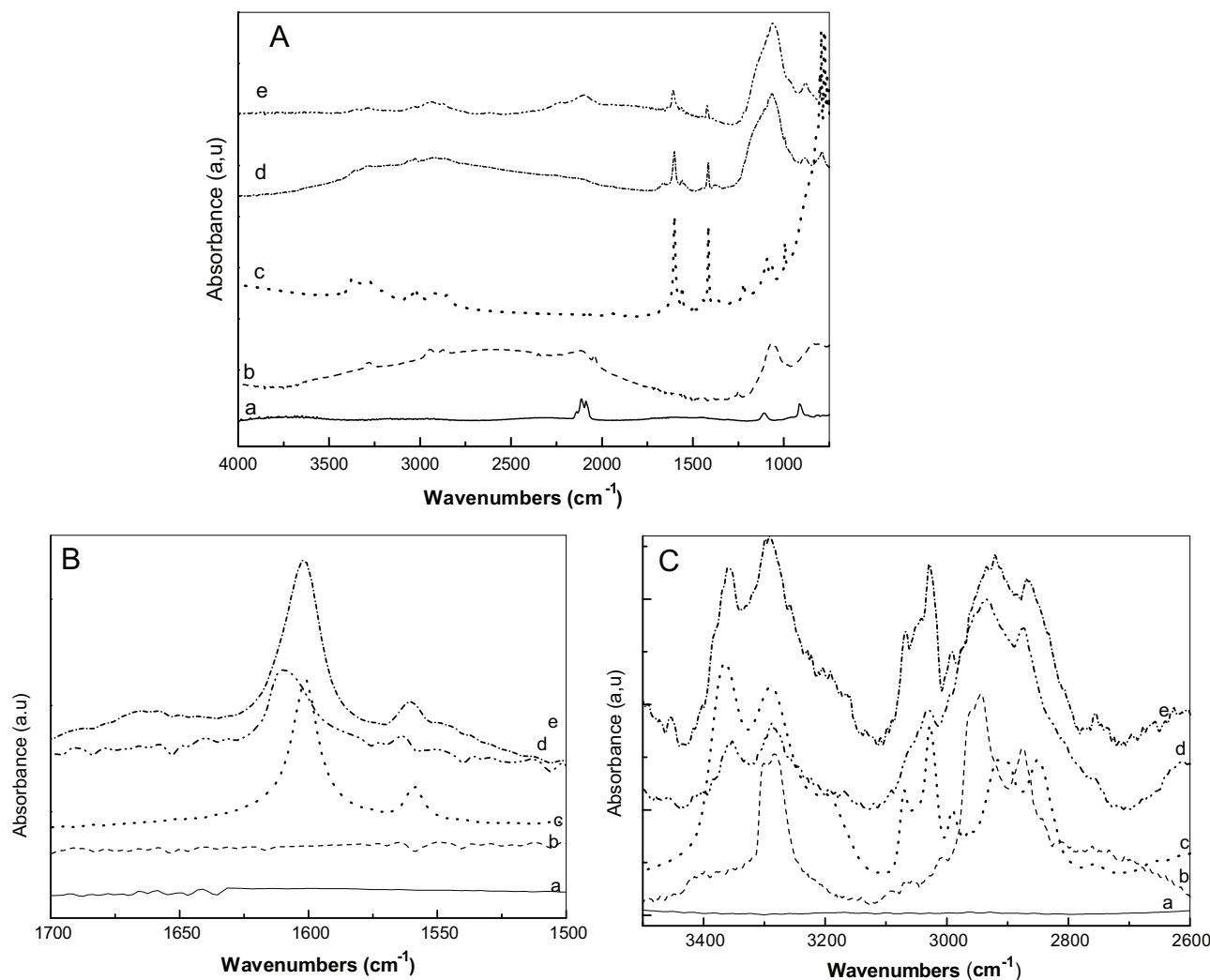


Fig. 1. FTIR spectra of (a) PSi surface, (b) PSi/Aliphatic polymer, (c) 4(amino methyl) pyridine, (d) PSi/Aliphatic polymer/4(amino methyl) pyridine ($t=4\text{ h}$), (e) PSi/Aliphatic polymer/4(amino methyl) pyridine ($t=16\text{ h}$). (A) The FTIR spectra in 4000–750 cm^{-1} range. (B) The FTIR spectra in 1700–1500 cm^{-1} range. (C) The FTIR spectra in 3500–2600 cm^{-1} range.

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