



Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A short route of covalent biofunctionalization of silicon surfaces

Ahmed Arafat*, Muhammad A. Daous¹

Chemical & Materials Engineering Department, King Abdulaziz University, P.O. Box 80204, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 3 October 2010
Received in revised form
28 November 2010
Accepted 7 December 2010
Available online 16 December 2010

Keywords:

Silicon
Biofunctionalization
Biosensor
DNA
Non-specific
Adsorption

ABSTRACT

Covalently attached organic monolayers on etched Si(1 1 1) surfaces were prepared by heating solutions of 1-alkenes and 1-alkynes in a refluxing mesitylene. Surface modification was monitored by measurement of the static water contact angle, X-ray photoelectron spectroscopy (XPS), infrared reflection absorption spectroscopy (IRRAS), and atomic force microscopy (AFM). Flat and clean *N*-hydroxysuccinimide (NHS)-ester-terminated/1-decyl mixed monolayers were covalently attached in one step onto a silicon surface. This procedure allows a mild and rapid functionalization of the surface by substitution of the NHS-ester moieties with amines at room temperature. The NHS-ester groups were shown to be fully intact onto the surface. The surface reactivity of the NHS-ester moieties toward amines was qualitatively and quantitatively evaluated via the reaction with methoxytetraethyleneglycolamine (TEGamine) and finally functionalized with single strand and complete DNA molecules.

Moreover, domains of DNA were selectively immobilized, on silicon surface making use of TEGamine, which acts as protein repelling agent and therefore prevented non-specific DNA adsorption. The resulting DNA-modified surfaces have shown excellent specificity, and chemical and thermal stability under hybridization conditions.

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1. Introduction

Designing and controlling the surface chemical properties of silicon and silicon-related surfaces through the immobilization of biomolecules receives an increasing attention regarding the development of advanced biochip, bioarray and biosensor technologies [1,2]. Extensive investigations have been devoted to the chemical functionalization of hydride-terminated silicon surfaces by covalent attachment of organic molecules and their subsequent transformations [3,4]. Such modifications enhance the stability of these surfaces and displays very good electronic properties compared to those formed on silicon oxide surfaces [5]. The ease and excellent reproducibility of the chemical modification protocol, and the possibility of photo-patterning of hydrogen-terminated silicon surfaces under laboratory conditions are a real asset for developing silicon surfaces as biosensor platforms [6–9].

Strother et al. have explored the chemical derivatization of hydrogen-terminated silicon surfaces for direct attachment of DNA. They found that the DNA-modified surfaces exhibited a high den-

sity of binding sites and a high specificity and stability to the hybridization conditions [10,11]. Although direct immobilization of DNA on chemically modified silicon surfaces was reported, other important criteria for using crystalline silicon in such applications still need to be met. These include: (i) organic functional groups should be made available and accessible on the semiconductor surface to facilitate the immobilization of chemical and biological species on these surfaces. (ii) Provide a specific interaction between the surface functional group and the target molecule to immobilize in order to avoid non-specific adsorption of the target on the surface, and (iii) provide a good stability of the surface monolayer in physiological environments to allow for reusability of such devices as well as to minimize the loss of material during chemical manipulations of the surface. Furthermore, utilizing crystalline silicon offers the possibility of using well-established microfabrication methods for the integration of diverse chemical and biochemical functionality into microelectronic platforms, and the use of intrinsic properties of silicon to detect molecular events occurring on the surface [12–14]. Electrical detection of molecular interactions on the surface, however, requires good electronic properties and a low density of surface states of the organic monolayer/silicon interface.

Recently, different strategies for the chemical functionalization and passivation of hydrogen-terminated silicon and porous silicon under various conditions were developed. Simple and functional 1-alkenes to form organic monolayers covalently attached to the semiconductor surface through Si–C bonds have been utilized. For example, reaction of ester-terminated alkenes with Si(1 1 1)–H led

* Corresponding author. Permanent address: Chemistry Department, Faculty of Science, Helwan University, 17790 Helwan, Cairo, Egypt.

Tel.: +202 25552467/+966 552006920; fax: +202 25552468/+966 6952257.

E-mail addresses: akhamis@kau.edu.sa (A. Arafat), mdaous@kau.edu.sa (M.A. Daous).

¹ Tel.: +966 552006920; fax: +966 6952257.