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Formation of dicarboxylic acid-terminated monolayers on silicon wafer surface

Serkan Demirci, Tuncer Caykara *

Department of Chemistry, Faculty of Art and Science, Gazi University, 06500 Besevler, Ankara, Turkey

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ABSTRACT

Dicarboxylic acid-terminated monolayers on hydroxylated silicon wafer were prepared via the chemisorption of 3-glycidoxypropyldimethylethoxysilane (GPDMES) molecules and subsequent reaction of the epoxy groups with iminodiacetic acid (IDA). The structure and surface composition of the monolayers were characterized by the means of contact-angle measurement, ellipsometric thickness measurement, reflectance FTIR spectroscopy, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Moreover, we found that the dicarboxylic acid-terminated monolayers on silicon wafer exhibit well-defined contact angle titration curve from which the surface acid dissociation constants were determined. The results were compared with the pK_a values reported in the literature for IDA in aqueous solution. Small difference in the surface pK_a values was attributed to variations of the microenvironment of the acid moieties. These experimental findings provide fundamental knowledge at the molecular level for the preparation of bioactive surfaces of controlled reactivity on silicon substrates.

1. Introduction

The artificial control of chemical and physical properties of hydroxyl-terminated surfaces (e.g. glass and silicon wafers) using organosilane monolayers has recently gained considerable attention in such areas as basic research and bio-applications, since, by selecting precursor molecules with appropriate terminal functional groups (e.g. amine, epoxide, aldehyde, etc.) the functionalities of the hydroxyl-terminated surfaces can be regulated at minute scale [1–3]. Among the various functional groups found to be effective, carboxylic acid groups are particularly important because of their chemical reactivity to DNA [4,5], and proteins [6,7].

Several synthetic routes currently exist for the preparation of carboxylic acid-functionalized monolayers. Extensive study has been reported on the chemisorption of carboxylic acid-terminated thiols on gold surfaces [8,9]. This method has as an advantage that soft lithographic methods such as microcontact printing can be used to obtain precisely defined surfaces [10]. Disadvantages of the method are, however, that the noncovalent Au–S interactions that constitute these monolayers allow for slow but gradual cross-surface diffusion [11] and that these monolayers are easily detached from the Au surface at high temperatures [12]. Hence, there is a growing interest in covalently attached carboxylic acid-terminated monolayers. However, alkoxysilane monolayers terminated with carboxylic acid cannot be directly prepared from alkoxysilane–CO_2H due to the reactivity of carboxylic acid groups with hydroxylated silicon, which competes with the preferred reaction alkoxysilane groups and the substrate.

Surfaces with covalently attached carboxylic acids have been analyzed by a variety of techniques including spectroscopic [13], electrochemical [14] and wetting (contact angle) measurements [15,16]. Due to the high sensitivity and simplicity of operation, contact-angle measurements have been widely used to study carboxylic acid monolayers on gold, such as to monitor the formation process [17], to follow the step-by-step modification [18] and to evaluate kinetic data for surface reactions [19]. Whitesides et al. reported the use of the contact angle titration technique, i.e., determination of the contact angles of a series of buffered water droplets as a function of the pH of the droplet, for studying acid–base reactions of carboxylic acid-terminated monolayers [15]. Creager and Clarke have characterized ω-merkaptoalkanoic acid monolayers on gold by developing a special pretreatment procedure, which gives ideal titration curves (exhibiting a smooth transition between plateau regions at low and high pH) [16]. Wasserman et al. also reported contact angle titration studies of carboxylic acid-terminated alkylsiloxane monolayers on hydroxylated silicon substrates [20].

In this study, the first two-step procedure is described that allows for formation of the dicarboxylic acid-terminated monolayers on silicon wafer surface. The monolayers are prepared in a convenient fashion by the reaction of GPDMES with hydroxyl-terminated silicon surfaces, followed by functionalization reactions, i.e., an epoxy group reaction of GPDMES with IDA that generate the free carboxylic acid groups. The use of IDA in second step is required to prevent the direct reaction of carboxylic acid groups with the hydroxylated silicon, which results in disordered monolayers. In

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* Corresponding author. Tel.: +90 312 2021124; fax: +90 312 2122279.
E-mail address: caykara@gazi.edu.tr (T. Caykara).

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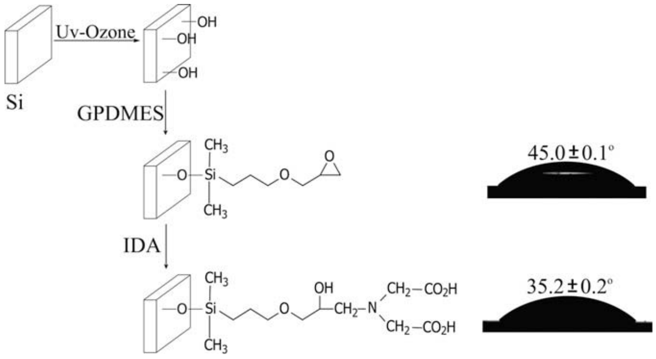

Fig. 1. Schematic representation of the procedure developed for the preparation of the dicarboxylic acid-terminated monolayers. The photographs show a water drop in contact with the silicon surface and the contact angles measured after each step of reaction.

this new approach, direct formation of the free carboxylic acid groups on the surface can be achieved, as demonstrated in Fig. 1. This report also describes our XPS, AFM, reflectance FTIR spectroscopic, ellipsometric and contact angle studies of the formation of dicarboxylic acid-terminated monolayers [–GPDMES–$(CO_2H)_2$] on silicon wafer, and the acid–base properties of the surface. Knowledge of the exact ionization state of the carboxylic moieties is critical importance for the selection of optimal reaction conditions for the immobilization of biomolecules [4,21,22].

2. Experimental

2.1. Materials

All chemicals were of reagent grade or highest available commercial-grade quality and used as received unless otherwise stated. Deionized water (>18.3 MΩ cm) was obtained from a Human Power I Scholar-UV water purification system. (Seoul, Korea). GPDMES (>97%), IDA, and acetone were purchased from Aldrich (Milwauke, USA) and used without further purification. Ethanol (from Aldrich) was dried over 4 Å molecular sieves before use.

2.2. Preparation of silicon substrate

The silicon (1 0 0) wafers (polished one side, n-type, obtained from Shin-etsu, Handoutai, Japan) were cut into strips ((3 cm × 1 cm). They were initially cleaned in ''piranha'' solution, a 3:1 mixture of concentrated H_2SO_4 and H_2O_2 (30%) heated to about 90 °C for 30 min (Caution: ''Piranha'' solution is hazardous oxidizing agent and must be handled with extreme care), followed by copious rinsing with deionized water. Cleaned silicon samples were exposed in UV/ozone chamber (Irvine, CA: Model 42, Jelight Company Inc., USA) for 15 min prior to modification to remove hydrocarbon and produce a hydrophilic surface. The silicon wafers were then modified by the following method.

2.3. Dicarboxylic acid-terminated monolayers on silicon wafer

Formation of the monolayers was achieved in a glove-box under an atmosphere of dry nitrogen. The pretreated hydrophilic substrates were placed into a solution of GPDMES (2 mL) in 10 mL of dried ethanol and allowed to stand in the solution of 24 h without stirring. After the substrates were removed from solution, they were rinsed with acetonitrile (twice), dichloromethane (twice), and ethanol (twice) and dried in a stream of nitrogen.

A substrate covered with a monolayer of GPDMES was placed in a solution of 0.425 M IDA in 10 mL of ethanol–water solvent mixture (1:1, v:v) at 80 °C for 2 h. After the substrate was removed from the solution, it was rinsed with ethanol (twice) and dichloromethane (twice) and dried in a stream of nitrogen.

2.4. Surface characterization

X-ray photoelectron spectra (XPS) of the monolayers on silicon substrate were recorded on a SPECS ESCA spectrometer equipped with a Mg Kα X-ray source. After peak fitting of the C 1s spectra, all the spectra were calibrated in reference to the aliphatic C 1s component at a binding energy of 285.0 eV. Reflectance FTIR spectroscopy was performed under nitrogen purging using a Thermo Nicolet 6700 spectrometer (MCT detector) containing a PIKE grazing angle (80°) attachment. The spectra were taken at a resolution of 4 cm^{-1} after 128-scan accumulation for an acceptable signal/noise ratio. The morphology of the surfaces was recorded on an atomic force microscope (Park Systems XE70 SPM Controller LSF-100 HS). A triangular shaped Si_3N_4 cantilever with integrated tips (Olympus Co. Ltd.) was used to acquire the images in the tapping mode. The normal spring constant of the cantilever was 0.02 N/m. An ellipsometer (DRE, EL X-02C, Ratzeburg, Germany) equipped with a He–Ne laser (λ = 632.8 nm) with an angle of incidence fixed at 70.0° was used to determine the film thickness of the –GPDMES and –GPDMES–$(CO_2H)_2$ monolayers. The film thickness of each sample was calculated by calibrating with known thickness SiO_2 layers on Si(1 0 0) and estimated optical constants for –GPDMES and –GPDMES–$(CO_2H)_2$.

Wetting measurements were performed on an automatic contact angle analyzer combined with a flash camera equipment (model DSA 100, Krüss, Germany) at room temperature. The contact angles reported are thermodynamic equilibrated values of sessile liquid drops of either pure water or buffer solutions. For contact angle titration measurements, the silicon sample was immersed in the buffer solution before the contact angle of that specific buffer recorded. At least five 3.0–5.0-μL drops of each buffer were measured and the average was taken for each point on a pH titration curve. The buffer solutions were prepared according to Britton–Robinson (B–R) procedure [23]. Exact pH values for the buffer solutions were recorded before and after the contact-angle measurements.

3. Results and discussion

High-quality silane monolayers terminated with carboxylic acid groups on silicon wafer surface cannot be prepared directly since carboxylic acids react with hydroxyl-terminated silicon to yield disordered films. Therefore, a new two-step procedure was applied to prepare the structurally well-defined dicarboxylic acid [–$(CO_2H)_2$] terminated monolayers on silicon wafer. The monolayers were formed by the reaction of GPDMES with hydroxylated substrate, followed by an epoxy group reaction of GPDMES with IDA that generated the free carboxylic acid groups. The use of IDA in second step can be prevented the direct reaction of carboxylic acid groups with the hydroxylated silicon, which resulted in disordered monolayers. The thickness measured for the layers before and after the IDA modification process differed from each other in 0.3 nm in average. The static contact angles with water were also measured before and after the IDA modification.

The contact angles of the GPDMES monolayers (θ = 45.0 ± 0.1°) and the IDA modified surface (θ = 35.2 ± 0.2°) reflect the expected hydrophilicity (Fig. 1). However, the contact angle of the –GPDMES monolayer is lower than that of a densely packed (3-glycidoxypropyl)trimethoxysilane (GPTS) monolayer (in the range of 49–55°) [2,24] in spite of the presence of two hydrophobic methyl side groups on the silicon head. This would mean that at full surface