

Surface characterizations of mono-, di-, and tri-aminosilane treated glass substrates

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Received 16 December 2005; accepted 17 March 2006

Available online 27 March 2006

Abstract

The surface properties and structure of mono-, di-, and tri-aminosilane treated glass surfaces were investigated using surface analytical techniques including X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, atomic force microscopy (AFM), and streaming potential. An optimized dip-coating process was demonstrated to produce roughly silane monolayer coverage on the glass surface. The surface charge measurements indicated that aminosilanization converts the glass surface from negative to positive potentials at neutral pH values. Higher positive streaming potential was observed for tri- compared with mono- and di-aminosilane treated glass surfaces. For all aminosilane treated glass samples, the high-resolution N 1s XPS spectra indicated a preferential orientation of the protonated amino-groups towards the glass surface whereas the free amino groups were protruding outward. This study aimed to obtain uniform, reproducibly thin, strongly adhering, internally cross-linked, and high positively charged aminosilane-coated glass surfaces for the attachment of DNA fragments used in microarraying experiments.

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Keywords: Glass surface; Aminosilane; Microarrays; XPS; Molecular orientation; Raman

1. Introduction

Thin films of functional organosilane molecules on solid surfaces have found important industrial applications, such as supports for biomolecules [1] and catalysts [2], advanced composite materials [3], and synthesis of chromatographic supports [4]. With the general formula $(X)_3SiY$, where X is an alkoxy ($-OCH_3$ or $-OCH_2CH_3$) or halogen ($-Cl$) ligand and Y is an organofunctional group (aminopropyl, methacryloxy, glycidoxy, vinyl, etc.), the bifunctional organosilane molecules undergo two different types of chemical reactions. The alkoxy groups ($-OR$) hydrolyze in an aqueous environment, producing hydroxyl groups, one or more of which may undergo condensation and elimination reactions with surface $-OH$ groups

commonly found on inorganic surfaces as well as on neighboring organosilane molecules. The reactivity of the Y-functional group is utilized for attachment of additional moieties or as a coupling agent to bond with secondary surfaces [5–7].

Generally, alkoxy silane molecules hydrolyze rapidly in water forming isolated monomers, cyclic oligomers, and large intramolecular cyclics [5,8,9]. The control over which species predominates is determined by silane type, concentration, pH, temperature, storage condition, and time. For instance, the low concentration (1%, w/w) of aminopropyltriethoxysilane (APS) in aqueous solution ($pK \approx 8.5$) is stable and forms trisilanol monomers and very low molecular weight oligomeric cyclics [5]. The adsorption mechanism of APS on glass surfaces has been extensively studied [10–14]. In addition to the siloxane ($Si-O-Si$) linkages [10], very strong hydrogen bonds between amino groups of the silanes and the surface silanol groups are formed [15]. The H-bonding has been proved using FTIR [11], ^{13}C MAS NMR [12], and X-ray photoelectron spectroscopies [13,14]. Furthermore, the amino group itself is believed to act

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as a catalyst and enhance the adsorption rate of APS molecules on the glass surface [16,17].

It has been experimentally observed [18] that APS-coating layer on solid surface is not uniform but instead forms “islands” with dimensions large enough to be detected by SEM. The polysiloxane structure inside such islands is also non-uniform and is composed of a 3D graded network (the cross-linking density is graded along the island thickness) [19,20]. Inside such islands, the inner part forms a layer of silane monomers that is highly cross-linked with both the substrates and top silane molecules. The outer part, which is exposed to environment, has open structure with low cross-linking density and high fraction of loosely bonded molecules [6]. From the technological point of view, silane coatings for adhesion promotion applications should offer a robust and internally cross-linked layer of reproducible thickness. Such characteristics cannot be achieved for multilayer coatings with high possibility of “islands” formation. For example, DNA microarrays utilizing organosilane coatings often have significant experimental variability due to the various difficulties in producing uniform coatings [21].

In the present study, mono-, di-, and tri-aminosilanes are applied to glass surface using an optimized dip-coating process with the objective to obtain a robust monolayer coating with high accessible number of amino groups and high positive surface charge for DNA microarray applications. We have generated a calibration curve for the thickness, thus the silane-coating layer on glass samples can be semi-quantitatively measured using X-ray photoelectron spectroscopy (XPS). The properties and structure of the silane-coating layers were characterized using XPS, atomic force microscopy (AFM), Raman spectroscopy, and streaming potentials. Furthermore, we have explored the molecular orientations of different aminosilane molecules on the glass surface using angle resolved XPS N 1s analysis.

2. Materials and methods

2.1. Materials

Low self-fluorescence microscopic slides ($1 \times 25 \times 75$ mm) were supplied by Schott AG (Jena, Germany). Glasses include borosilicate 1, borosilicate 2, soda-lime silicate, and synthetic fused silica. Silicon wafers were also used in this study (*n*-type; Wafernet, San Jose, CA) whereby the surface was comprised of a thin (40 ± 0.5 Å) SiO₂ layer. Three aminosilane compounds (Gelest Inc.) were used without further purification: 3-aminopropyltriethoxysilane (APS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA), and (3-trimethoxysilylpropyl) diethylenetriamine (DETA). The chemical structures of these compounds are schematically represented in Fig. 1. Concentrated HCl and NaOH solutions (research grade; Aldrich Chem. Co.) were diluted to obtain the desired concentrations. The solvents were HPLC grade (Aldrich Chem. Co.) and used without further purification. All references to H₂O in the text refer to water obtained from a Nanopure™ purification system (resistivity > 18 MΩ cm).

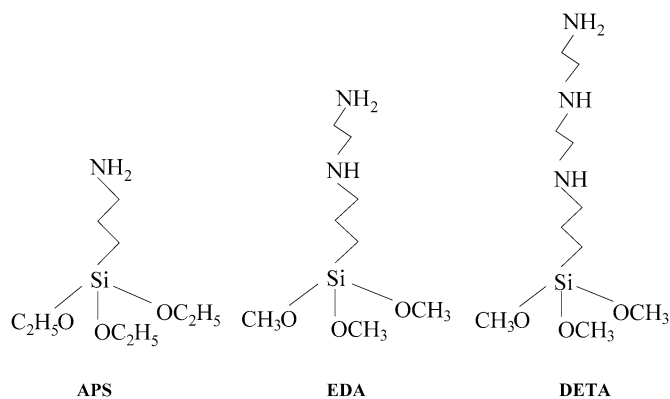


Fig. 1. Schematic structures for 3-aminopropyltriethoxysilane (APS), *N*-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA), and (3-trimethoxysilylpropyl) diethylenetriamine (DETA).

2.2. Sample preparation

2.2.1. Dip coating

Glass substrates were cleaned using a general glass cleaning protocol: immersion in NaOH (2.5 M) solution for 24 h, sonication in H₂O for 10 min, immersion in HCl (0.1 M) for 15 min, sonication in H₂O for 10 min and immersion in methanol for 5 min prior to the silanization step.

Silanization of the samples were performed by dip coating in 1% aqueous solutions of silane for 15 min. Post-treatment steps include shaking in methanol for 5 min, rinsing in H₂O for 10 min and finally spin drying (2000 rpm) for 5 min. The coated slides were baked at 110 °C for 15 min and stored in a vacuum desiccator prior to analysis.

2.2.2. Pulsed CVD coating

Due to the small differences between the refractive index of both glass substrate and the organosilane film, ellipsometry cannot measure the organosilane film thicknesses on glass surfaces [22]. To obtain information on the thickness of the silane film, a silicon wafer was substituted for the glass substrates. Using a pulsed CVD technique (ThinSonic pulsed ultrasonic CVD; Sono-Tech Corp.), different APS film thicknesses were deposited on silicon wafers. The pulsed ultrasonic method is a process in which the precursor is delivered to the ultrasonic nozzle through a series of automatically controlled solenoid valves. The experimental apparatus is described in detail elsewhere [23]. The precursor is atomized at the tip of the nozzle and introduced into a low-pressure reaction chamber in a near-vapor-phase state (~ 15 μm drop diameter). Nozzle power, volume of pulses and number of pulses were varied to obtain the desired coating thicknesses. All of the silicon wafer substrates were first cleaned in NH₄OH:H₂O₂:H₂O (1:1:5) solution before the silane deposition step. The substrates were heated (120 °C) in situ for 15 min prior to the pulses injections. A control sample was prepared as described above excluding the deposition step. Silane layer thicknesses on the Si wafer samples were measured using an ellipsometer (Gaertner L116C). Dip-coated Si wafer samples were also prepared by immersion in 1% APS (aqueous) solution for 15 min; some samples were dried under N₂ without any post-washing steps,

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