



A vapor phase deposition of self-assembled monolayers: Vinyl-terminated films of volatile silanes on silicon oxide substrates

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ABSTRACT

Vinyl-terminated self-assembled monolayers (SAMs) offer significant flexibility for further chemical modification and can serve as a versatile starting point for a tailoring of surface properties. A vapor phase deposition of such films would offer advantages in cases where the preparation from solution is not an option or not desired, for example in connection with silicon microstructures such as micro-electromechanical systems. We show that SAMs of 9-decyltrichlorosilane ($\text{CH}_2=\text{CH}-(\text{CH}_2)_8-\text{SiCl}_3$), 10-undecyltrichlorosilane ($\text{CH}_2=\text{CH}-(\text{CH}_2)_9-\text{SiCl}_3$), 14-pentadecyltrichlorosilane ($\text{CH}_2=\text{CH}-(\text{CH}_2)_{13}-\text{SiCl}_3$), decyltrichlorosilane ($\text{CH}_3-(\text{CH}_2)_9-\text{SiCl}_3$), and octadecanetrichlorosilane ($\text{CH}_3-(\text{CH}_2)_{17}-\text{SiCl}_3$) can be prepared both from solution and from the vapor phase. The resulting layers were compared by static contact angle measurements, ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy to determine their surface wettability, the film thickness, the smoothness and homogeneity of the respective films, and their chemical composition and each method gave films of comparable quality. Deposition of functionalized SAMs from the vapor phase is rare. Here we report the parameters for the preparation of well-ordered vinyl-terminated SAMs from the vapor phase.

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1. Introduction

The deposition of ultrathin organic films on surfaces as functional coatings is an important research area. Self-assembled monolayers (SAMs) are playing an increasingly important role here because of their ease of preparation and the flexibility they offer in terms of the surface chemistry. Of particular interest in the formation of SAMs are silanes, since they can be attached to a large variety of different substrates containing hydroxyl or oxide groups, e.g. silicon and glass [1,2]. In addition, organosilane monolayers are physically [3,4], thermally [5,6], and chemically stable [7]. One area where the modification of silicon (oxide) surfaces is of pivotal importance is micro-electromechanical systems (MEMS) [8] and their yet smaller equivalents of nano-electromechanical systems (NEMS). MEMS and NEMS are most often made of silicon because of its desirable mechanical properties [8].

The majority of work regarding the deposition and the modification of SAM films on SiO_x substrates was achieved by wet chemistry, i.e. by immersion of the substrates into a diluted solution of the surfactant. An organosilane SAM on a silicon substrate was reported by Sagiv in 1980 [1]. Since then SAMs of silane molecules with many different functional groups have been prepared from solution, see for example Refs. [9,10]. One example of a film with a functional group

is vinyl-terminated SAMs [11]. They offer the possibility for further chemical modification in subsequent steps [12–14] and are therefore also potentially interesting for the surface functionalization of MEMS. The majority of functional films applied to MEMS so far are hydrophobic anti-stiction coatings, e.g. [6,15–18], which are deposited in a single step procedure. The immersion of MEMS into a solution of a surfactant however is in general not an option and does not produce films of reliable quality, because a liquid will not necessarily be able to wet all parts of a microstructure due to microscopic air bubbles that are frequently attached to microstructures in liquids and that are difficult to remove. Therefore alternative coating procedures have to be used. A vapor phase deposition of a SAM can eliminate some of the problems encountered in wet chemistry [17,19]. It has been found that vapor phase methods can form higher quality monolayers of silanes on silicon [20], because aggregated organosilane molecules do not vaporize and deposit on the surface, unlike in the liquid phase process. The experimental parameters leading to high quality vapor phase deposited films however are not a priori known. While methyl-terminated and fluorinated silane films deposited from the gas phase have been studied, see for example Refs. [17,18,21–26], information about the preparation of high quality vinyl-terminated silane films from the vapor phase and their characterization is not available. Since vinyl-terminated films have some flexibility for further chemical modification, for example via oxidation [2], addition [10], a Heck type reaction [2], or metathesis [12,14], they offer potential as a starting point for a tailored functionalization of silicon

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microstructures such as MEMS with a variety of chemical groups. This is only useful however if high quality monolayer films can be prepared from the vapor phase.

We now report the preparation of three different vinyl-terminated silane films on silicon–silicon dioxide (Si/SiO₂) substrates from the vapor phase. The films are characterized in terms of their surface wettability, film thickness, smoothness and homogeneity, as well as their chemical composition. For comparison we have also prepared the corresponding films from solution. In addition, two well-known methyl-terminated films of simple alkane based trichlorosilanes were prepared from both solution and the vapor phase and used as a reference.

2. Experimental details

2.1. Pre-treatment of the silicon substrates

Commercially available n-type, one-side polished silicon (100) wafers (Wacker, Munich, Germany) were used as substrates. The silicon wafers were cut into 1.5 × 1.5 cm² pieces and cleaned in four successive steps [27]: exposition to an ozone atmosphere for 30 min was followed by washing in a solution of conc. H₂SO₄ (95%, Fisher Scientific, Leicestershire, UK) and 30% H₂O₂ (Fisher Scientific) (2:1) at 70 °C for 15 min (*Caution: "piranha" solution reacts violently with many organic materials and should be handled with care*). Samples were then washed in a solution of conc. NH₄OH (35%, Fisher Scientific), deionized (DI) water, 30% H₂O₂ (1:5:1) at 70 °C for 15 min, and finally in a solution of conc. HCl (36%, Fisher Scientific), DI water, and 30% H₂O₂ (1:6:1) at 70 °C for 15 min. After each step the substrates were rinsed with DI water and dried under nitrogen. The preparation of SAMs followed immediately after the cleaning procedure.

Clean SiO_x substrates typically displayed roughness root mean square (RMS) values of ~70 pm over an area of 5 × 5 μm² determined with atomic force microscopy. Similar values are reported in the literature [28].

2.2. Surfactants

Vinyl-terminated trichlorosilanes were synthesized with alkyl chain lengths of 10 (9-decenytrichlorosilane (CH₂=CH-(CH₂)₈-SiCl₃) **1**, 11 (10-undecenytrichlorosilane (CH₂=CH-(CH₂)₉-SiCl₃) **2**, and 15 carbon atoms: 14-pentadecenytrichlorosilane (CH₂=CH-(CH₂)₁₃-SiCl₃) **3** (Fig. 1). A general synthetic pathway to compounds **1–3** is

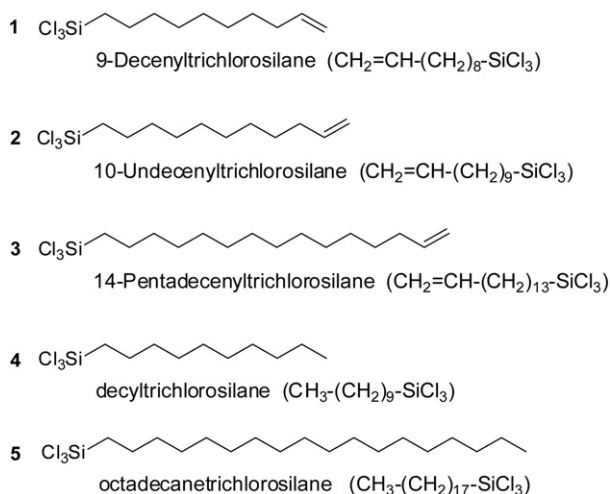


Fig. 1. Molecules used for the formation of SAMs on silicon substrates deposited from solution and from the vapor phase.

shown in Fig. 2. We used a modification of the methodology described by Hostetler et al. [29]. The purity of the prepared compounds was similar to values reported in the literature [30].

Commercially available methyl-terminated surfactants decyltrichlorosilane (CH₃-(CH₂)₉-SiCl₃) **4**, and octadecanetri-chlorosilane (CH₃-(CH₂)₁₇-SiCl₃) **5** (Alfa Aesar, Lancashire, UK), were used as reference compounds (Fig. 1). Monolayers of all surfactants were prepared on freshly cleaned silicon wafers.

2.3. Preparation of alkyl- and alkenyl-trichlorosilane monolayers

Three methods were used to prepare covalently attached layers of trichlorosilane molecules on silicon wafers. These were (1) from toluene, (2) (a) from the vapor phase of the surfactant under reduced ambient pressure, and (2) (b) from the vapor phase of the surfactant under atmospheric pressure.

2.3.1. Solution deposition

Cleaned silicon wafers were placed in glass vials and 5 mL of 1 mM solutions of the precursor molecules in toluene was added. The substrates remained in the solution for 24 h at room temperature. After adsorption, samples were withdrawn from the solution, rinsed with toluene, dichloromethane, and DI water, and then placed in a desiccator. In order to remove larger polymerized aggregates that were physically adsorbed on the substrates, the samples were sonicated sequentially in toluene, dichloromethane, and DI water for 15 min each.

2.3.2. Vapor phase deposition

Cleaned silicon wafers were transferred to sealed flasks (100 mL capacity) containing either i) 0.05 mL or ii) 0.15 mL of one of the trichlorosilane precursor molecules in a separate open vessel. There was no direct contact between the liquid surfactant and the substrate during preparation. In i) the air from the flask was evacuated by using a vacuum pump for a few seconds to reduce the pressure to ~400 Pa, while ii) was carried out under atmospheric pressure. Each of the reactions was left for 4 days at 60 °C in case of the shorter molecules **1**, **2**, and **4**, and for 3 days at 70 °C in case of the longer molecules **3** and **5**. After the adsorption, the substrates were treated in the same way as the samples prepared from solution.

All films were characterized by contact angle measurements, ellipsometry, X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM).

2.4. SAM characterization

2.4.1. Contact angle measurements

Water contact angles (DI water) were measured with a G10 goniometer microscope (KRÜSS GmbH, Hamburg, Germany) under ambient conditions at room temperature. Droplets of ~3 μL were dispensed from a microburette. All reported values are the average of three measurements taken from different places of the surface.

2.4.2. Ellipsometry

The thickness of the SAMs was measured with an M-2000DI™ spectroscopic ellipsometer (J. A. Woollam Co., Inc., USA). Thickness values were extracted from fits to the data taken from 45 to 70° in steps of 5° over wavelengths from 200 to 1000 nm. The sample surface was modeled as a Si substrate with an oxide layer and a Cauchy layer. The thickness of the silicon oxide after the oxidative cleaning treatment was 16 ± 1 Å (average of three samples). The thickness of the monolayer films was calculated with a refraction index of 1.45 [31,32]. The error based on the observed variation of the thickness of the organic films prepared under identical conditions was ~2 Å.

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