

# Growth kinetics and thermodynamic stability of octadecyltrichlorosilane self-assembled monolayer on Si (100) substrate

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## Abstract

We have studied the growth kinetics and thermodynamic stability of octadecyltrichlorosilane (OTS) self-assembled monolayers on Si (100) substrate in order to understand its role in controlling the adhesion and surface hydrophobicity. Time-dependent contact angle measurements, using water as a function of OTS concentration, show rapid monolayer formation in the initial stage followed by a slow attainment of full coverage and the overall kinetics approximately follows the Langmuir adsorption isotherm. The adsorption rate constant ( $k_a = 150 \text{ M}^{-1} \text{ s}^{-1}$ ) is found to be significantly greater than the desorption rate constant ( $k_d = 0.156 \text{ s}^{-1}$ ) while the Gibbs free energy ( $\Delta G_{\text{ads}}$ ) change amounts to  $-4.2 \text{ kcal/mol}$  suggesting thermodynamic stability of OTS monolayer on a silicon surface. Partial monolayer formation by a ‘uniform’ growth mechanism, even at low coverage, is revealed by atomic force microscopy (AFM) in conjunction with grazing angle FTIR spectroscopy. Analysis of the interfacial adhesion properties using Zisman plot suggests a critical surface tension ( $\gamma_c$ ) of  $20.7 \text{ dyn/cm}$  for OTS monolayer on Si (100) surface.

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## 1. Introduction

Ultra-thin organic films like self-assembled monolayers (SAMs) and Langmuir–Blodgett (LB) films are extensively studied due to their fundamental importance in surface modification and also for their diverse potential applications in nanotechnology [1–4]. The presence of a simple monomolecular film on a metallic or semiconducting surface can cause dramatic changes in its surface properties and these SAMs are particularly important due to their ability to control wetting, adhesion, lubrication and corrosion on surfaces and interfaces [1–6]. For example, the presence of SAM on Si (100) surface can tackle the stiction

problem of micro-electromechanical systems (MEMS) by providing a suitable low energy surface coating [7–10]. These types of organic monomolecular films acting as a passivation layer cannot only alleviate capillary forces and direct chemical bonding on Si–O surface, but also reduce electrostatic forces if the terminal group is tailored to possess controlled hydrophobicity. The formation of closely packed, covalently bonded monolayer with tunable chain length and hydrophobic terminal group on silicon oxide surface would eliminate the release stiction and reduce the in-use stiction [7–9]. Usually alkyltrichlorosilane based self-assembled monolayers are used for reducing stiction in silicon micromachines and suitable candidates include octadecyltrichlorosilane (OTS), perfluorodecyltrichlorosilane (FDTS), etc [7–9].

The growth mechanism of OTS-SAM on Si/SiO<sub>2</sub> substrate has been extensively studied in different solvents

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with a wide concentration range [11] using various characterization tools such as FTIR-ATR spectroscopy [12], quartz crystal microbalance [12–14], contact angle technique [12], Atomic force microscopy [11,15], ellipsometry [16] and X-ray reflectivity [17–19]. These studies demonstrate that the growth of trichlorosilane-based SAMs uniquely involves an irreversible covalent cross-linking step [20] and the full coverage (and even in some cases multilayer coverage) is obtained within few minutes to hours depending on the experimental conditions. For example, Maoz and Sagiv were the first to study the kinetics of the monolayer formation of OTS on Si using FTIR spectroscopy and contact angle measurements [12]. Subsequently, qualitative growth kinetics of OTS-SAM were reported by Rozlosnik et al. [11] and Wang and Lieberman [21] by illustrating the important role of solvent selection and humidity control on growth. Although these and several other reports are available on the growth mechanism of SAM formation using different organic molecules by varying the experimental parameters, a quantitative adsorption–desorption rate constant calculation of OTS on Si is missing. This is especially significant for OTS-SAM on Si due to its importance in both micro-machining and microfabrication. Consequently an accurate control of the monolayer growth kinetics is important for establishing a protocol for the construction of closely packed and complete reproducible monolayer on Si surface [1,2].

In the present work we report the adsorption kinetics and thermodynamic stability of OTS monolayer formation on Si (100) by using time-dependent contact angle measurements in accordance with Langmuir adsorption isotherm. The approximate rate constant and Gibbs free energy value estimated within the assumption of this model are in excellent agreement with values reported by independent methods such as quartz crystal microbalance (QCM) and FTIR spectroscopy. The growth mechanism of the OTS-SAM formation is also studied using AFM and FTIR spectroscopy. In addition, the critical surface tension ( $\gamma_c$ ) for OTS monolayer on Si (100) is obtained from the Zisman plot to show the flexibility of SAMs to control the interfacial energy.

## 2. Experimental

*n*-Octadecyltrichlorosilane (OTS),  $\text{CH}_3(\text{CH}_2)_{17}\text{SiCl}_3$  (95%), was obtained from Aldrich, while toluene (99.5%), and ethanol (99.5%) were purchased from Qualigens. Commercially available *n*-type, one-side polished, silicon wafer of (100) orientation with 0.001–0.007  $\Omega\text{-cm}$  resistivity was used as a substrate. These substrates ( $1 \times 1 \text{ cm}^2$ ) were rinsed by milliQplus (18 M $\Omega$  cm) water, sonicated in ethanol and dried under a flow of nitrogen. These wafers were soaked in 10:1 deionized  $\text{H}_2\text{O}:\text{HF}$  solution for 30 s to remove the native  $\text{SiO}_2$  layer followed by soaking in piranha

solution (7:3 concentration  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$ ) for 30 min at 90 °C to grow a fresh oxide layer. These wafers were subsequently rinsed with deionized water, dried in nitrogen and used for further experiments.

Freshly prepared OTS solutions (0.05, 0.1, 0.5 and 1 mM) in toluene were used for the monolayer formation. Silicon wafers were dipped in the OTS solution of a particular concentration and were removed after different time intervals. The contact angle of each sample was measured after washing it several times with the appropriate solvent. These steps were carried out in a nitrogen filled glove box. All measurements of contact angle were performed using water sessile drop with the help of RAME-HART NRL-Model C.A. goniometer. On each sample, contact angle was measured at three different locations and the results were averaged. Critical surface tension of OTS monolayer was measured by using various organic solvents of known surface tension (given in parenthesis dyn/cm) including water (72.1), methanol (22.5), dimethyl sulfoxide (43.5), ethylene glycol (47.3), xylene (28.9), chloroform (26.7), and hexadecane (27.5) [22].

The OTS monolayer was characterized by a grazing angle FTIR spectroscopy on a Perkin Elmer 1615 spectrometer. The bare silicon wafer was used as a background sample and the spectrum was recorded at a resolution of 4  $\text{cm}^{-1}$  over 256 scans at room temperature.

AFM images were obtained using a Nanoscope II (Digital Instruments, Inc) operated at constant height mode with very low applied force (typically under 1 nN). All measurements were performed in ambient conditions using silicon nitride probes mounted on the micro-fabricated cantilever (force constant 0.6 N/m) in the tapping mode to avoid surface damage. The bearing ratio of the digital instrument software was used to estimate the surface coverage of the OTS monolayer. The average thickness of the islands was determined from several random height profiles of the images. Predefined threshold height of the monolayer (2.4 nm) was used for monolayer coverage calculations.

## 3. Results and discussion

Contact angle measurement is one of the important techniques to detect the hydrophobic surface properties of a monolayer despite its poor accuracy and inability to reveal microscopic information. The change in the contact angle roughly indicates the variation in surface chemical composition of the substrate as well as the extent of the monolayer surface coverage [23–26].

Fig. 1 shows the variation of contact angle (with a sessile water drop) as a function of dipping time for different OTS concentrations. Usually a clean Si surface has a contact angle less than 15–20°, which indicates its hydrophilic nature. Soon after the immersion of this substrate on an OTS solution in toluene, the substrate was removed and washed repeatedly with toluene and dried in a stream of nitrogen. This SAM functionalized substrate shows increased contact angle, which is comparably higher than that for Si wafer dipped in pure toluene (without OTS).

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