



Analysis of the uptake of chlorotrimethylsilane on glass from toluene solution-phase depositions



Aniket Maharanwar, Jeffery J. Weimer*

Materials Science Program, Department of Chemistry, Department of Chemical & Materials Engineering, The University of Alabama in Huntsville, 301 Sparkman Drive, Huntsville, AL 35899, United States

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ABSTRACT

The uptake of chlorotrimethylsilane on glass from toluene is proposed to follow a defined reaction model. Static contact angles θ_m are measured on glass exposed to a range of solution concentrations for $t = 20$ min. The uptake is potentially sensitive to residual moisture. Fractional surface coverage f_c is calculated from three models, direct conversion $f_c \propto \theta_m$, a patchy layer $f_c \propto \cos(\theta_m)$, and a micro-heterogeneous surface $f_c \propto (1 + \cos(\theta_m))^2$. Phase contrast images in atomic force microscopy show uniform coverage and thereby favor the micro-heterogeneous model. Calibrations of f_c against the intensity of an R-Si peak from x-ray photoelectron spectroscopy favor the direct or micro-heterogeneous model. The uptake reaction is a two step process. The first step is equilibrium Langmuir adsorption/desorption to physisorbed silane. The second is an irreversible, first-order, rate-determining step. The equation $f_c = 1 - \exp(-k_{rds} t K_{eq} C / (1 + K_{eq} C))$ is applied using weighted regression analysis. The parameters weighted from all three coverage models are $\langle K_{eq} \rangle = 35 \pm 14 \text{ M}^{-1}$ and $\langle k_{rds} \rangle = 0.219 \pm 0.053 \text{ min}^{-1}$.

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1. Introduction

Surfaces of glass-based materials are ubiquitously functionalized using silanes, especially to convert them from hydrophilic to hydrophobic. One of the smallest of the silanes for the job is chlorotrimethylsilane ($(\text{CH}_3)_3\text{SiCl}$ or CTMS) (also listed as trimethylchlorosilane TMCS in the literature). The CTMS¹ molecule is ideal for fundamental uptake studies because complications from cross-linking reactions in solution and steric issues during deposition should be reduced compared to those found with multi-functional silanes and larger-chain alkyls, respectively. Its small size also offers the potential to change surface chemistry without significantly changing surface topography or, as important in some applications, without adding an additional, highly-undesired thickness to a surface.

A number of studies report on the deposition of CTMS on glass-based surfaces, primarily in applications to increase the hydrophobicity of the surface. Deposition methods include vapor phase [1–15], pure liquid [16,17], and solutions of benzene [18], cyclohexane [19,20], hexane [2,21–26], toluene [7,8,11,17,27–29], alcohols

[30–32], dichloromethane [33], and xylene [34]. Selections of the literature have reported on the uptake or reaction of CTMS as a function of surface pretreatment [2,4], type of glass [2], solution concentration [19,20,27,29,32,35], immersion time [19,22,29,32], or deposition temperature [4,7,29]. As expected, increasing solution concentration and exposure time increases water contact angle and therefore hydrophobicity, but only up to a limiting extent. The uptake at full coverage on different substrates has been calculated from experiments [6] or models [10,36]. The value in the latter case ranges between 0.72, 0.785, and 0.953 depending on the assumed size and packing geometry of the tri-methyl end groups on the bonded CTMS. By comparison, the experimental study shows that 97% coverage was obtained on glass beads exposed to vapor. The contact angle for full coverage of CTMS/glass has been reported as 70° [6], $75^\circ \pm 2^\circ$ [15], $\approx 80^\circ$ [10], 84.5° [36], and up to 90° for a quartz-glass [33].

In the framework of the extensive background literature, the goal of this work is to analyze the solution-phase deposition of CTMS on glass in a fundamental and comparative way. The objectives are to characterize how the chemistry and structure of the surface changes with CTMS deposition, to model the uptake using first-principles kinetic and thermodynamic equations, and to relate the findings to prior studies of corresponding relevance. The concentration of CTMS in toluene is varied at a constant deposition time and temperature. Contact angles are measured, and the chemistry and topography of the surfaces are characterized

* Corresponding author: .

E-mail address: Jeffrey.Weimer@UAH.edu (J.J. Weimer).

¹ CTMS - chlorotrimethylsilane, XPS - x-ray photoelectron spectroscopy, AFM - atomic force microscopy, DI - distilled water, MeOH - methanol, MTCS - methyl-trichlorosilane.

with atomic force microscopy (AFM) and x-ray photoelectron spectroscopy (XPS). The equilibrium behavior of the silane reaction is examined in experiments with step-function changes in solution concentration. Relative surface coverage is calculated from contact angle measurements using three different conversion equations. The values are fit as a function of solution concentration with a two-step, equilibrium adsorption + kinetic reaction model. The outcome is a report on how the surface chemistry and topography of glass are affected by CTMS as well as a functional, first-principles relationship between fractional coverage and solution concentration.

2. Materials and methods

2.1. Materials

Type No. 1 borosilicate cover slips (regular glass) of size 18 mm $\times$ 18 mm were purchased from Fisher Scientific. The CTMS (redistilled, 99+%) was purchased from Sigma Aldrich (Milwaukee, WI) and stored in a glove bag under N_2 purge until needed. The cleaning chemicals methanol (methanol - MeOH, $\geq 98\%$), hydrochloric acid (HCl, 36.5–38.0%), and concentrated sulfuric acid (H_2SO_4 , $\geq 95.5\%$) were bought from Fisher Scientific. The toluene solvent for the silane solution ($\geq 99.5\%$) was purchased from Sigma Aldrich. Ultra-pure deionized or distilled water (DI) was obtained from Fisher Scientific or from an in-house distillation unit.

2.2. Methods

2.2.1. Cleaning and coating glass with CTMS

Literature has demonstrated that organic contaminants present on glass can be effectively removed with a mixture of MeOH and HCl [37,38]. Subsequent treatment with concentrated H_2SO_4 is proposed to form metal soluble salts from the metal oxide contaminants present on the surface. This results in the removal of the contaminants from the surface. Rinsing glass with DI water then is stated to leave behind a uniform layer of hydroxyl groups on the surface.

The above principles were utilized in this study. As a first step, the glass was kept in MeOH : HCL (1:1) for 30 min. This was followed by exhaustive rinsing of the samples with DI until no schlieren lines were observed. Next, the samples were kept in concentrated H_2SO_4 bath for 30 min. The samples were then rinsed with DI. The cleaned samples were stored in a DI water bath for future use in the functionalization treatment. Care was taken throughout the wet-chemistry cleaning to not let the samples superimpose on each other. They were dried under fume hood prior to functionalization.

Three to five glass substrates were functionalized over a range of ten incremental steps in solution concentrations from 0.13 vol% to 10 vol% CTMS. A Labnet Labpette micropipette having a capacity in the range of 20 μ L - 250 μ L was used to extract the requisite amount of silane to add to a known starting amount of toluene. Glass sample vials were cleaned thoroughly and heated up in an oven for 120 $^{\circ}$ C–150 $^{\circ}$ C. They were cooled down to room temperature in the oven and then removed to a glove box purged with N_2 . While in the glove box, they were rinsed with a silane solution at a specific concentration and then filled with a clean aliquot of that same silane solution. The clean, dry glass samples were immersed fully in the silane solution in the vials. The glass samples were oriented vertically so that only their edges touched the walls of the vials. The vials were covered with a cap and kept in the glove box until the samples were removed for analysis. Immersion time was constant at 20 min.

2.2.2. Equilibrium testing

For equilibrium tests, two sets of four glass samples each were initially functionalized using two different concentration values. One set used a low concentration of 0.25 vol% while the other used a high concentration of 5 vol%. After 20 min, two samples from each bath were removed. With the remaining two samples still immersed in solution, the concentrations were immediately switched. The low concentration was increased to high by adding CTMS, and the high concentration was diluted to low by adding toluene. Two sets of two samples each with concentration values of 0.25 vol% and 5 vol% were also kept in solution for 24 h.

2.2.3. Characterizing

Contact angle measurements were obtained with a ramé-hart model 290 F4 series automated goniometer (Ramé-Hart Instrument Co., Succasunna, NJ, USA). Droplets measuring 4 μ were dispensed from a stainless steel needle onto glass samples by the static sessile drop method. The goniometer apparatus included a camera, light source, and DROPimage software for automatic acquisition and calculation of contact angles. Contact angles of DI on a Teflon standard were measured to ensure proper calibration. Experiments were carried out at room temperature. Contact angles were measured within 10 s of the drop being placed. Drops were measured ten times in rapid succession. A total of five drops were dispensed onto each glass sample. Each drop was measured before dispensing an additional drop.

Imaging for AFM was done using a Dimension 3000 instrument (previously from Digital Instruments Inc., Santa Barbara CA). Images were captured at a fixed scan size of 10 μ m $\times$ 10 μ m with a nominal scan rate of 0.4–0.5 Hz. The scans were done in tapping mode using a cantilever with a nominal resonance frequency of 200–300 kHz and using optimum values for amplitude set point, integral gain, and proportional gain. No baseline function was removed from the line scans of the raw images, and height and phase contrast mode images were captured simultaneously. Imaging was done on three samples clean and at 1 vol% concentration over at least three regions per sample. Images were processed with XY second order plane fitting and flattening tools to remove scan-line disparities before display.

One set of samples was prepared for analysis using XPS. All samples were cleaned together. The samples were immersed for 20 min at different volume concentrations of CTMS. The XPS characterization was done using a Perkin-Elmer PHI 5000 VersaProbe I. The take-off angle (relative to the surface plane) was 45 $^{\circ}$ with an analysis spot size of 100 μ m and monochromatic Al x-rays at a power of 28.9 W. Charging was neutralized with con-current ion and electron beam neutralizers. Survey scans as well as high-resolution scans of O 1s, C 1s and Si 2p were taken from three different regions on each sample. Before display, the high-resolution peaks were all shifted by the same offset required to put C 1s for the clean sample at 283.6 eV.

2.2.4. Data analysis

Left and right values from ten images were averaged for each drop dispensed to correct for tilt in the sample. Measurements of five drops per sample with three to four samples per concentration produced an array of 150–200 contact angles per solution concentration. The average and standard uncertainty of the array was calculated in a spreadsheet as the representative measured contact angle θ_m and its standard measurement uncertainty $\delta\theta_m$. Another method that could be used instead is to calculate the average and standard uncertainty per drop from the ten images, calculate the weighted average and standard uncertainty per sample from the five drops, and calculate a weighted average and standard uncertainty per solution concentration from the three to four samples per solution concentration. This alternative approach should give

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