



Chemical modification of chromium oxide surfaces using organosilanes

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ABSTRACT

Alkylsiloxane layers that were prepared by reaction of alkyltrichlorosilanes, alkyltriethoxysilanes, and mono-, di- and trihydridoalkylsilanes with chromium oxide surfaces were assessed in terms of their hydrophobicity. Two general conditions were studied, in the vapor phase at elevated temperatures (70 °C) and in solution at 70 °C. The surfaces were characterized by contact angle analysis and X-ray photoelectron spectroscopy (XPS). The kinetics of the solution phase reactions of *n*-octadecylsilane and *n*-octadecyltrichlorosilane were also studied. Hydrophobic monolayers were achieved in all cases, but subtle differences in structure were found.

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1. Introduction

Chemical modification of solid metal oxide surfaces using organic reagents can create materials with desired solid–liquid and solid–vapor interactions. This chemistry has been used in wide ranges of applications in sensor technology, optical and electronic devices, lithographic patterning, wetting and adhesion [1–6]. These modifications include the adsorption of alkanethiols [7,8], dialkyl disulfides [9,10] and dialkyl sulfides [11] on gold, alkanethiol and alkanedithiols on GaAs(001) [12], fatty acids on alumina [13,14], alcohols and amines on platinum [15], organosilicon hydrides [16,17], phosphates [18] and alkanephosphonic acids [19] on titanium, and organosilanes on silicon surfaces [20–23].

Organosilanes ($R_{3-n}SiX_{n+1}$) having up to three hydrolyzable groups in the molecule (where $X = Cl, OR$ and NMe_2) have been widely used to modify surfaces, forming a large variety of organosilicon monolayers and thin films [1,20,21]. Chlorosilanes and alkoxy silanes are quite sensitive to moisture and therefore they require very specific reaction conditions. The byproducts of the reactions of commonly used chloro- and ethoxysilanes (HCl and ethanol) are reported to be problematic and can interfere with the monolayer formation and affect its structure [24]. The preparation of monolayers using hydrosilanes ($R_{3-n}SiH_{n+1}$) on a wide range of metal oxide surfaces reported by Fadeev and co-workers

[16,17,25], has advantages over other silane coupling agents because reaction conditions are relatively clean and the byproduct is molecular hydrogen (H_2), that does not interfere with monolayer formation. A disadvantage is that much fewer hydrosilanes are commercially available and that they are expensive. We had a specific interest in chromium oxide surface modification and carried out comparison studies of monolayers prepared with chloro-, ethoxy- and hydrosilanes to determine the latitude of reagent choice.

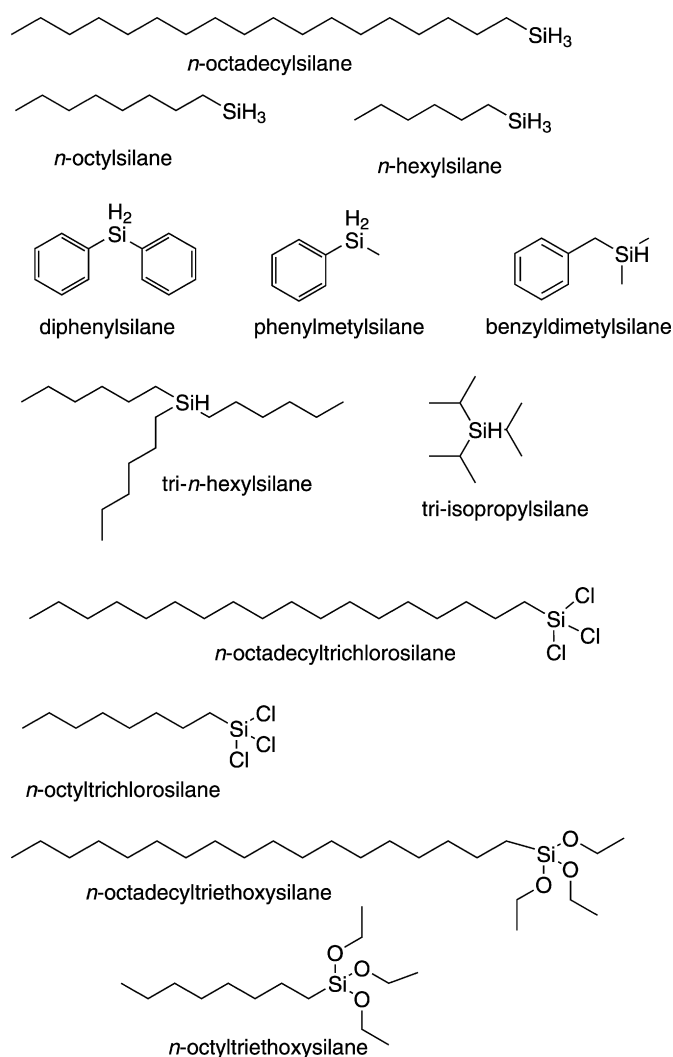
Several groups have studied the formation of organic thin films on chromium surfaces using different modifying reagents. These include the assembly of the surfactants myristic acid [26] and dodecylsulfate [27], deposition of Langmuir–Blodgett films of phthalocyanines [28] and polyimides [29] and the adsorption of electroactive species containing isonitrile and thiol functional groups [30]. Reactions of octadecylsilane [16] and octadecyltriethoxysilane [31] with chromium oxide have been reported, however sparse data are provided and comparisons between these monolayers have not been made. Octadecylsiloxane layers provided sufficient selectivity to pattern the underlying chromium layer by electron lithography [30].

This paper reports the study of chromium oxide surfaces prepared using several reactive classes of silanes and different conditions. Reactions of triethoxysilanes, trichlorosilanes and mono-, di-, and trihydrosilanes were carried out in both vapor and solution phase. Kinetics of reactions of *n*-octadecylsilane ($n-C_{18}H_{37}SiH_3$) and *n*-octadecyltrichlorosilane ($n-C_{18}H_{37}SiCl_3$) in solution were investigated. Scheme 1 summarizes the variables addressed. The surfaces were characterized by contact angle analysis and X-ray photoelectron spectroscopy (XPS).

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Scheme 1. Organosilanes used for the chemical modification of chromium.

2. Experimental

2.1. Materials

All chemicals were used as received unless noted otherwise. Toluene, hexane (HPLC grade), heptane (HPLC grade), methylene chloride (HPLC grade), 2-propanol and acetone were purchased from Fisher. Ethanol was purchased from VWR. All silane reagents, $n\text{-C}_{18}\text{H}_{37}\text{SiH}_3$, $n\text{-octylsilane}$ ($n\text{-C}_8\text{H}_{17}\text{SiH}_3$), $n\text{-hexylsilane}$ ($n\text{-C}_6\text{H}_{13}\text{SiH}_3$), diphenylsilane ($(\text{C}_6\text{H}_5)_2\text{SiH}_2$), phenylmethylsilane ($\text{C}_6\text{H}_5\text{CH}_2\text{SiH}_2$), benzyldimethylsilane ($\text{C}_7\text{H}_7(\text{CH}_3)_2\text{SiH}$), tri- n -hexylsilane ($(n\text{-C}_6\text{H}_{13})_3\text{SiH}$), tri-isopropylsilane ($(i\text{-C}_3\text{H}_7)_3\text{SiH}$), $n\text{-C}_{18}\text{H}_{37}\text{-SiCl}_3$, $n\text{-octyltrichlorosilane}$ ($n\text{-C}_8\text{H}_{17}\text{SiCl}_3$), $n\text{-octadecyltriethoxysilane}$ ($n\text{-C}_{18}\text{H}_{37}\text{Si}(\text{OC}_2\text{H}_5)_3$) and $n\text{-octyltriethoxysilane}$ ($n\text{-C}_8\text{H}_{17}\text{-Si}(\text{OC}_2\text{H}_5)_3$) were purchased from Gelest. Anhydrous heptane, anhydrous toluene and ethyldiisopropyl amine (EDIPA) were purchased from Aldrich. Water was purified using a Millipore Milli-Q system that involves reverse osmosis, ion exchange and filtration steps; we refer to water purified by this method as Milli-Q water. Silicon-supported chromium wafers (the chromium layer on the silicon was ~ 1000 Å thick) were cleaned using a Harrick Scientific O_2 plasma cleaner at high power settings for 5 min. Water completely wets the O_2 -plasma cleaned chromium surface.

2.2. Characterization

XPS spectra were obtained with a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. Depth profiling was done by collecting spectra at 15° and 75° takeoff angles with respect to the plane of the sample surface. The analysis at 15° has a penetration depth of ~ 10 Å and that at 75° corresponds to a penetration depth of ~ 40 Å [32]. Contact angle measurements were made with a Ramè-Hart telescopic goniometer and a Gilmont syringe with a 24-gauge flat-tipped needle. Milli-Q water was used as a probe liquid. Advancing and receding contact angles were recorded while the water was added and withdrawn from the drop, respectively. The values are averages of 4–5 measurements made on different areas of samples.

2.3. Reaction of chromium oxide surfaces with alkylchlorosilanes and alkylethoxysilanes in the vapor phase

Chromium wafers were cleaned as described above. The wafers were immediately placed in a custom-made wafer holder and suspended in a Schlenk tube containing 0.5 mL of alkylchlorosilane or alkylethoxysilane. There was no contact between the silane and the substrates. Reactions were run at 70°C for 3 days. The wafers were isolated and rinsed with toluene, 2-propanol, ethanol, ethanol-water (1:1), and Milli-Q water in this order, and then dried in a clean oven at 125°C for 10 min. (The wafers modified with octadecyltrichlorosilane or octadecyltriethoxysilane were extracted with hexane in a Soxhlet apparatus for 2 h before the rinsing steps.)

2.4. Reaction of chromium oxide surfaces with alkylchlorosilanes in solution

Chromium wafers were cleaned as described above. The wafers were immediately placed into the reaction flask. The reaction flask was similar to the one that was used for the vapor phase reactions with the exception that the top included a 4 mm Teflon stopcock and joint capped with a rubber septum to facilitate additions *via* syringe under an inert atmosphere. Clean wafers were covered with anhydrous toluene (15 mL) containing ethyldiisopropylamine (EDIPA) (0.17 mL; 10^{-3} mol). $n\text{-Octadecyltrichlorosilane}$ (0.5 mL) was added *via* syringe. Reactions were carried out at 70°C for 3 days or as otherwise noted. The modified wafers were rinsed and handled as described for the vapor phase reactions.

2.5. Reaction of chromium oxide surfaces with hydridosilanes in vapor phase

Chromium wafers were cleaned as described above. The wafers were immediately placed in a custom-made wafer holder and suspended in a Schlenk tube containing 1 mL of hydridosilane. There was no contact between the silane and the substrates. Reactions were carried out at 70°C for 3 days. The wafers were isolated and rinsed with heptane, methylene chloride, ethanol, acetone and Milli-Q water in this order, and then dried in a clean oven at 125°C for 10 min.

2.6. Reaction of chromium oxide surfaces with hydridosilanes in solution

Chromium wafers were cleaned as described above and introduced to the same reaction tube described above. Anhydrous heptane (~ 25 mL) was transferred *via* cannula to the reaction tube and hydridosilane (1 mL) was added *via* syringe. Reactions were run at 70°C for 3 days unless otherwise noted. The modified wafers were rinsed and handled as described for the vapor phase reactions.

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