

**Determining the Thickness of Aliphatic Alcohol Monolayers Covalently Attached to Silicon  
Oxide Surfaces Using Angle-Resolved X-ray Photoelectron Spectroscopy**

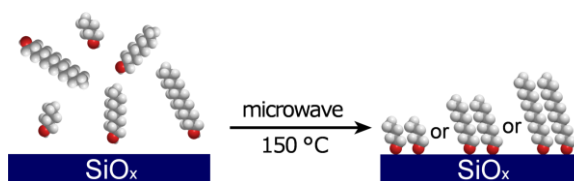
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## Abstract

The thickness of alcohol based monolayers on silicon oxide surfaces were investigated using angle-resolved X-ray photoelectron spectroscopy (ARXPS). Advantages of using alcohols as building blocks for the formation of monolayers include their widespread availability, ease of handling, and stability against side reactions. Recent progress in microwave assisted reactions demonstrated the ease of forming uniform monolayers with alcohol based reagents. The studies shown herein provide a detailed investigation of the thickness of monolayers prepared from a series of aliphatic alcohols of different chain lengths. Monolayers of 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol were each successfully formed through microwave assisted reactions and characterized by ARXPS techniques. The thickness of these monolayers consistently increased by  $\sim 1.0 \text{ \AA}$  for every additional methylene ( $\text{CH}_2$ ) within the hydrocarbon chain of the reagents. Tilt angles of the molecules covalently attached to silicon oxide surfaces were estimated to be  $\sim 35^\circ$  for each type of reagent. These results were consistent with the observations reported for thiol based or silane based monolayers on either gold or silicon oxide surfaces, respectively. The results of this study also suggest that the alcohol based monolayers are uniform at a molecular level.



**Keywords:** angle-resolved X-ray photoelectron spectroscopy (ARXPS); alcohol based monolayers; microwave; silicon oxide surfaces; surface modification

## 1. Introduction

In this article, the thickness of monolayers derived from a microwave-assisted reaction of aliphatic alcohols with silicon oxide surfaces were determined using angle-resolved X-ray photoelectron spectroscopy (ARXPS). The covalent modification of surfaces through the formation of monolayers is being widely pursued for applications that include molecular electronics [1-5], microelectromechanical systems (MEMS) [6-8], and microfluidics [9-13]. The modification of silicon oxide surfaces specifically has been achieved with molecules containing reactive groups, such as silanes [14-16] and phosphonic acids [17-20]. One of the major challenges in forming these monolayers is the potential to achieve multilayer films, intermolecular polymers, and other undesirable side reactions [15, 17, 21-23]. These challenges can result in unpredictable electronic characteristics of the monolayers, as well as non-uniform chemical or physical surface properties. Ultimately, these defects can lead to a detrimental failure of miniaturized devices. Other limitations of using silanes and phosphonic acids as molecular coatings include their limited accessibility, and the relatively high cost to prepare these reagents at the required purity [24].

Alcohol containing compounds have been proposed as an alternative reagent to modify silicon oxide surfaces via the formation of silyl ether (Si–O–C) bonds. The alcohol molecules can form silyl ether bonds with either hydrogen terminated silicon [25-30] or silicon oxides (i.e. silanol terminated surfaces) [31-34]. Minimal side reactions for these processes enable a convenient approach to prepare uniform monolayers, which includes the use of ambient environmental conditions. Our recent work demonstrated the formation of uniform monolayers derived from 1-octanol on various silicon oxide surfaces [33]. This technique is utilized here to form uniform monolayers of a well-defined and tunable thickness as these films can be derived

from a series of aliphatic alcohols of different alkyl chain lengths. Detailed analyses for a series of monolayers formed using aliphatic alcohols of different alkyl chain lengths were performed by ARXPS [35-37]. The results of these analyses were used to determine the overall thickness of each of the monolayers derived from distinct aliphatic alcohol species. The results obtained from these analyses provide insight into the uniformity of the monolayers derived from aliphatic alcohols, and demonstrate a precise control over the thickness of these monolayers on silicon oxide surfaces.

## **2. Experimental**

### **2.1. Reagents and Materials**

Reagents were used as received, which included 30% (v/v) hydrogen peroxide (Fisher Scientific, CAS no. 7722-84-1), sulfuric acid (Anachemia Canada, Inc. ACS reagent grade, CAS no. 7664-93-9), 1-butanol (Caldedon, reagent grade, CAS no. 71-36-3), 1-hexanol (Sigma Aldrich, reagent grade, CAS no. 111-27-3), 1-octanol (Sigma Aldrich, ACS reagent, CAS no. 111-87-5), 1-decanol (Sigma Aldrich, 99%, CAS no. 112-30-1), and 1-dodecanol (Sigma Aldrich, reagent grade 98%, CAS no. 112-53-8). Silicon wafers (test grade, 4", <100>, p-type) with a resistivity between 1 to 10 Ohms·cm with and without a 100-nm thick thermally grown silicon oxide film were purchased from the Nanofabrication Facility in 4D LABS at Simon Fraser University. The wafers were diced into 1 cm by 1 cm square pieces that served as the substrates for the following experiments.

### **2.2. Preparation of Silicon Oxide Surfaces**

Piranha cleaning of the diced substrates was performed to remove surface contamination as described previously [33]. *CAUTION: Piranha solution is a strong oxidizing agent and reacts violently with organic compounds. This solution should be handled with extreme care.* Briefly, the piranha solution was freshly prepared, in which the silicon substrates were immersed for ~1 h. The substrates were subsequently washed with 18 M $\Omega$ ·cm deionized water (Barnstead Nanopure DIiamond water filtration system). A stream of nitrogen (N<sub>2</sub>) gas filtered with a PTFE membrane containing <200 nm pores was used for drying the substrates.

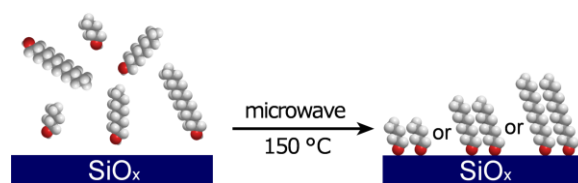
### 2.3. Procedure for the Formation of Monolayers using Aliphatic Alcohols

Each piranha cleaned silicon substrate was placed into a separate quartz tube (Part no. 34042, ATS Scientific Inc.) containing an ~10 mL solution of alcohol (i.e. 1-butanol, 1-hexanol, 1-octanol, 1-decanol, or 1-dodecanol). These quartz tubes were placed into a microwave vessel (Part no. 33806, ATS Scientific Inc.). The closed vessels were radiated with microwaves using a microwave reactor (Ethos Plus Microwave Labstation) for the desired time at a set temperature of 150 °C for 2 h with a ramp time of 5 min. The test tubes were subsequently cooled to room temperature over at least 20 min. The substrates were removed with tweezers from the test tubes, washed sequentially under a stream of acetone and isopropanol (~25 mL each), and dried under a stream of filtered N<sub>2</sub> gas.

### 2.4. Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS)

The ARXPS measurements were conducted using a Kratos Analytical Axis ULTRA DLD system with a monochromatic aluminum source (AlK $\alpha$  of 1486.7 eV) operating at 150 W. Survey scans were acquired using a pass energy of 160 eV, a dwell time of 100 ms, and 1 sweep.

High resolution scans were obtained using a pass energy of 20 eV, a dwell time of 500 ms, and an averaging of 5 scans. The samples were analyzed over a series of different tilt angles. The initial area of analysis was set to 700  $\mu\text{m}$  by 300  $\mu\text{m}$  at a takeoff angle of 0°. The XPS data, such as peak intensities, were analyzed using the Kratos Vision Processing software. The relative sensitivity factors for the relevant species were also obtained through this software package.



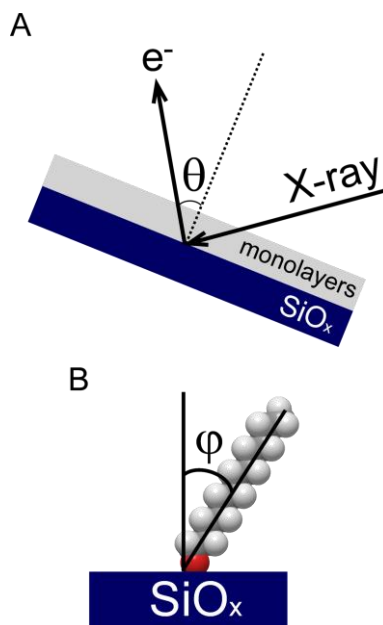
**Scheme 1.** Schematic depiction of the formation of self-assembled monolayers (SAMs) from the microwave assisted reaction of aliphatic alcohols with silicon oxide surfaces.

### 3. Results and discussion

The primary goal of this study was to utilize ARXPS for assessing the thickness of monolayers on silicon oxides derived from aliphatic alcohols. Monolayers were prepared from a series of aliphatic alcohols of increasing chain lengths (Scheme 1). Specifically, we prepared monolayers on silicon oxide surfaces from 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol. Neat alcohol solutions were used during microwave assisted reactions held at a temperature of 150 °C. The substrates were rinsed after these reactions and sonicated in ethanol to ensure minimal physical adsorption of unreacted aliphatic alcohols or other contaminants. Angle-resolved XPS was utilized to assess the coverage, uniformity, and thickness of the monolayers because it has been broadly utilized to analyze the properties of films that have a thickness less than 10 nm [35, 36, 38]. The thickness of the monolayers can be determined from a series of ARXPS measurements. The relative XPS intensity of the carbon signal from the

aliphatic alcohols in the monolayers to the silicon signal from the silicon oxide surfaces are correlated to the angle of these measurements and thickness of the monolayers through the following equation [35, 38, 39]:

$$\ln \left( \frac{I_{C1s}}{I_{Si2p}} \frac{S_{Si}}{S_C} + 1 \right) = \frac{d}{\lambda \cos \theta} \quad (1)$$



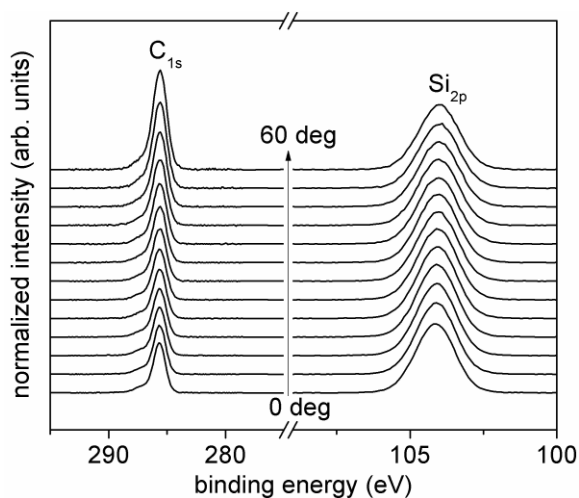
**Fig. 1.** (A) A schematic of the setup for the angle-resolved X-ray photoelectron spectroscopy (ARXPS) measurements, and (B) a schematic of a typical aliphatic alcohol depicting its configuration when covalently attached to the silicon oxide surfaces. The  $\theta$  term is the angle between the photoelectron ejected at the surface and the surface normal. The  $\phi$  term is the tilt angle away from the surface normal adopted by the molecules within the monolayers.

where  $\lambda$  is the attenuation length of the emitted photoelectrons, and  $I_{C1s}$  and  $I_{Si2p}$  are the intensities (e.g., as measured from the peak heights) of the  $C_{1s}$  and  $Si_{2p}$  XPS signals, respectively. The values  $S_{Si}$  and  $S_C$  are the relative sensitivity factors for silicon and carbon, respectively. The

term  $\theta$  is the takeoff angle, and  $d$  is the thickness of the monolayers (Fig. 1A). This calculation assumes that the underlying substrate has a homogeneous chemical composition (i.e. no chemical variation or contamination throughout the substrate). To assess if a homogeneous chemical composition would be measured for the underlying material, ARXPS studies were performed on silicon substrates without monolayers. A 100-nm thick thermally grown silicon oxide film was anticipated to be a suitable material for the substrates in these ARXPS experiments because its chemical composition (i.e.  $\text{SiO}_2$ ) would be homogenous throughout the anticipated penetration depth (typically less than 10 nm) of the photoelectrons obtained during the XPS measurements [36]. A piranha cleaned silicon substrate, on the other hand, would not be a suitable substrate as the thickness of its native oxide layer would be  $\sim 2$  nm [40], which is less than the penetration depth of photoelectrons. The composition of this thinner silicon oxide substrate would, therefore, change significantly over a series of XPS measurements collected at various tilt angles. To demonstrate this variability, a series of ARXPS measurements was collected for piranha cleaned silicon substrates either with or without the 100-nm thermally grown silicon oxide. The peak intensities for the  $\text{Si}_{2p}$  and  $\text{O}_{1s}$  species were compared to assess the changes in chemical composition observed over  $\theta$  values from  $0^\circ$  to  $80^\circ$ . Each of these datasets were collected by varying the angle  $\theta$  in increments of  $10^\circ$  (see Supplementary Data). The ARXPS measurements for the 100-nm thick thermally grown silicon oxide film exhibited a homogenous composition of the  $\text{Si}_{2p}$  and  $\text{O}_{1s}$  species over tilt angles from 0 to  $60^\circ$ . In contrast, the piranha cleaned silicon substrate exhibited a varying relative composition of the  $\text{Si}_{2p}$  and  $\text{O}_{1s}$  species over the same tilt angles. The silicon substrates with the 100-nm thick thermally grown silicon oxide film were utilized to prepare the series of monolayers for the subsequent ARXPS studies, and the determination of the thickness of each of these monolayers.



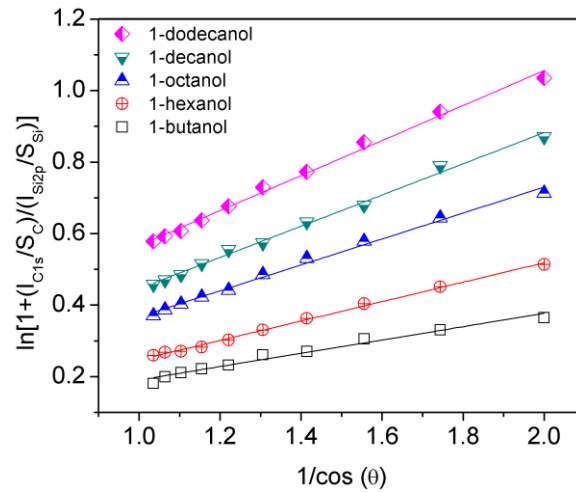
An extensive set of ARXPS measurements were obtained for each of the substrates modified with the monolayers derived from the aliphatic alcohols. These experiments were used to determine the thickness,  $d$ , and the average tilt angle,  $\phi$ , of the bound molecules within the monolayers (Fig. 1B). The high resolution XPS peaks of carbon ( $C_{1s}$ ) and silicon ( $Si_{2p}$ ) were acquired for  $\theta$  values between 0 and 60° at increments of 5°. The  $\theta$  values beyond 60° were not considered for this analysis because these datasets could yield inaccurate results due to



**Fig. 2.** Angle-resolved X-ray photoelectron spectroscopy measurements of 1-dodecanol monolayers on silicon oxide obtained over  $\theta$  values from 0 to 60°. These spectra were normalized against the high resolution spectra of oxygen ( $O_{1s}$ ) species.

contributions from elastic scattering and surface roughness [35]. A series of XPS measurements were obtained for each of the substrates, such as the spectra plotted in Fig. 2 for a substrate coated with 1-dodecanol. The  $C_{1s}$  and  $Si_{2p}$  peaks were normalized against the high resolution oxygen ( $O_{1s}$ ) peaks obtained under the same conditions to enable a direct comparison between each spectrum. While the silicon peak intensities maintained a consistent intensity over the series of  $\theta$  values, carbon peak intensities gradually increased with an increase in  $\theta$ . This result was

expected as the relative elemental composition of the substrate (i.e. the ratio of silicon to oxygen) should be similar regardless of  $\theta$ . On the other hand, the relative increase in the carbon peak intensity with increasing values for  $\theta$  is attributed to the more significant contributions from the organic monolayers in comparison to that of the bulk material (i.e. Si or O). In summary, an increase in the takeoff angle of the ARXPS measurements increased the  $C_{1s}$  signal relative to the  $Si_{2p}$  signal, which was expected for the substrates coated with monolayers.



**Fig. 3.** The plot of  $\ln[1+(I_{C1s}/S_C)/(I_{Si2p}/S_{Si})]$  vs.  $1/\cos(\theta)$  for a series of silicon oxide surfaces coated with monolayers prepared from aliphatic alcohols of increasing chain length. Each set of data was obtained from a series of ARXPS measurements.

The ARXPS measurements were analyzed in further detail to derive the thickness of each of the monolayers. This analysis was performed by comparing the relative peak intensities for carbon and silicon as a function of the tilt angle. Specifically, the term  $\ln[1+(I_{C1s}/S_C)/(I_{Si2p}/S_{Si})]$  was plotted as a function of  $1/\cos(\theta)$ . The plots displayed a linear trend over the datasets associated with each of the substrates. These results suggest that the monolayers were continuous

and uniform, regardless of the alkyl chain length (Fig. 3). On the other hand, the same type of plot obtained from a piranha cleaned silicon substrate supporting only a 100-nm thermally grown oxide film did not show a linear trend for the same analysis of the relative intensities of C<sub>1s</sub> and Si<sub>2p</sub>. The lack of a regular trend observed for the piranha cleaned silicon substrate was attributed to the non-uniform adsorption of volatile carbon based species or miscellaneous

**Table 1.** Estimated film thickness and molecular tilt angles for monolayers derived from aliphatic alcohols on silicon oxide.

	# of carbons	slope	slope error	y-intercept	R <sup>2</sup>	film thickness, d (nm)	molecular length (nm)	tilt angle $\phi$ (°)
1-butanol	4	0.1859	0.0101	0.0052	0.9740	0.46 ± 0.03	0.49	18 ± 6
1-hexanol	6	0.2714	0.0050	0.0244	0.9969	0.68 ± 0.01	0.74	23 ± 2
1-octanol	8	0.3623	0.0104	0.0053	0.9926	0.91 ± 0.03	0.99	23 ± 4
1-decanol	10	0.4362	0.0108	0.0102	0.9945	1.09 ± 0.03	1.2	24 ± 3
1-dodecanol	12	0.4893	0.0130	0.0773	0.9937	1.22 ± 0.03	1.5	35 ± 2

contamination (see Supplementary Data Fig. S2). The thickness of each of the monolayers were calculated from each set of ARXPS data using a  $\lambda$  value of 25 Å [39]. The estimated thicknesses of the monolayers and tilts of the molecules within the series of monolayers prepared from aliphatic alcohols are summarized in Table 1. The calculated average thicknesses were 0.46, 0.68, 0.91, 1.09, and 1.22 nm for the monolayers derived from 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol, respectively. The increase in thickness of the monolayers was proportional to the increase in the chain lengths of the associated aliphatic alcohols. This result indicated that the physical properties of the monolayers were consistent with those of the aliphatic alcohol used to prepare these monolayers.

An average tilt angle ( $\phi$ ) of the monolayers can be estimated based on the monolayer thickness as determined from the analysis of ARXPS measurements. The molecular chain length of each aliphatic alcohol was estimated from their molecular models projected in ChemDraw 3D (see Supplementary Data). The Cartesian coordinates were determined for the oxygen atom and carbon atom at either end of these linear molecules. The distance between these terminal atoms was calculated using the Pythagorean Theorem (see Supplementary Data). The measured thickness of the monolayers were slightly less than the molecular lengths calculated from this model. This observation was anticipated because the monolayers were expected to adopt a tilted position at the silicon oxide surfaces [13]. The molecular tilt angle,  $\phi$ , was an estimate of the angle at which the molecules within the monolayers tilted away from the surface normal (Fig. 1B). The calculated values for  $\phi$  ranged from  $18^\circ$  to  $35^\circ$ , with an average  $\phi$  of  $\sim 24^\circ$ . Tilt angles reported for n-alkanethiol SAMs on gold surfaces range from  $20$  to  $35.3^\circ$ , which were determined using various techniques including ARXPS, ellipsometry, and infrared spectroscopy [13, 41-44]. The tilt angles of molecules within organosilane based monolayers on silicon oxide surfaces are reported to be  $\sim 35^\circ$ . The tilt angles for the species in the alcohol based monolayers are within the ranges of tilt angles reported for these other types of monolayers. This result suggests that the physical properties and the uniformity of the alcohol based monolayers are consistent with organic monolayers derived from other organic precursors, such as alkanethiols or alkylsilanes. The discrepancy in the tilt angles calculated for the series of monolayers derived from the alcohol based reagents could be attributed to experimental errors resulting from ARXPS analyses and/or variations in the structure of the bond between the silicon oxide and the anchoring groups of the monolayers at this interface [13, 43]. The trends observed in the previous studies also indicated that the average increase in thickness of the monolayers per each

addition of a methylene ( $\text{CH}_2$ ) group to the molecular chain was approximately 1.0 to 1.5 Å [45, 46]. The average increase in film thickness of alcohol based monolayers associated with the same addition of a  $\text{CH}_2$  group was determined to be  $\sim 1.0$  Å. Thickness of the alcohol based monolayers derived from microwave-assisted reactions agreed with the measurements from previously studied monolayers, such as thiolates on gold or silane based monolayers on silicon oxide surfaces. The relationship between the chain lengths of organic based monolayers and their overall film thickness is consistent between different types of monolayers.

#### 4. Conclusions

In summary, we have determined the thickness of monolayers derived from the microwave assisted condensation of aliphatic alcohols of different chain lengths on silicon oxide surfaces. Monolayers of 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol formed on silicon oxide surfaces were characterized by angle-resolved X-ray photoelectron spectroscopy (ARXPS), and the peak intensities of  $\text{C}_{1s}$  and  $\text{Si}_{2p}$  were analyzed as a function of changes in the takeoff angle. The average thickness of each of these monolayers were determined to be 0.46, 0.68, 0.91, 1.09, and 1.22 nm corresponding to monolayers derived from 1-butanol, 1-hexanol, 1-octanol, 1-decanol, and 1-dodecanol, respectively. Thickness of the monolayers increased with an increase in the length of the hydrocarbon chain of the aliphatic alcohols. The molecules within the this series of monolayers prepared from species with increasing chain lengths were determined to have an average tilt angle of  $24^\circ$ . The alcohol based monolayers possess a similar film thickness and tilt angle as thiol based monolayers on gold surfaces or silane based monolayers on silicon oxide surfaces, further suggesting a consistency in the physical characteristics of these monolayers.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at (link to be added upon acceptance for publication).

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