Published in final edited form as:

Mater Sci Eng C Mater Biol Appl. 2014 February 1; 35: 283–290. doi:10.1016/j.msec.2013.11.017.

Comparative Study of Solution Phase and Vapor Phase Deposition of Aminosilanes on Silicon Dioxide Surfaces

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Abstract

The uniformity of aminosilane layers typically used for the modification of hydroxyl bearing surfaces such as silicon dioxide is critical for a wide variety of applications, including biosensors. However, in spite of many studies that have been undertaken on surface silanization, there remains a paucity of easy-to-implement deposition methods reproducibly yielding smooth aminosilane monolayers. In this study, solution- and vapor-phase deposition methods for three aminoalkoxysilanes differing in the number of reactive groups (3-aminopropyl triethoxysilane (APTES), 3-aminopropyl methyl diethoxysilane (APMDES) and 3-aminopropyl dimethyl ethoxysilane (APDMES)) were assessed with the aim of identifying methods that yield highly uniform and reproducible silane layers that are resistant to minor procedural variations. Silane film quality was characterized based on measured thickness, hydrophilicity and surface roughness. Additionally, hydrolytic stability of the films was assessed via these thickness and contact angle values following desorption in water. We found that two simple solution-phase methods, an aqueous deposition of APTES and a toluene based deposition of APDMES, yielded high quality silane layers that exhibit comparable characteristics to those deposited via vapor-phase methods.

Keywords

Aminosilane; monolayer; silicon dioxide functionalization

1. Introduction

Organofunctional alkoxysilanes can react with a variety of oxide surfaces that present surface hydroxyl groups (including the oxides of silicon, aluminum, and titanium), resulting in a surface decorated with the organofunctional moiety, thus providing a facile way of modifying the physical and chemical properties of the surface [1,2,3,4]. As a result,

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Supporting Information: Additional data which demonstrates the glutaraldehyde crosslinker stability and IgG immobilization density on films prepared in this work.

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alkoxysilanes find extensive utility in a wide range of applications including as coupling reagents, to probe protein or cell adhesion on a surface and to enable self-assembly or growth of molecules or nanoparticles on a surface [5,6,7,8]. Aminoalkyl alkoxysilanes (or aminosilanes), in particular, have been widely used in protein microarray and biosensor applications to tether proteins or other probe molecules on glass or silicon dioxide surfaces either by noncovalent charge-charge interactions or via bifunctional crosslinkers [9,10].

The reaction between aminosilanes and silicon dioxide surfaces is complex, and is heavily influenced by reaction conditions. The alkoxy groups of alkoxysilanes hydrolyze in the presence of water, forming silanols (Si-OH) [5,11]. The condensation of these silanols results in the formation of siloxane (Si-O-Si) bonds; if this condensation takes place with the silanol groups on a SiO₂ surface, a silane molecule covalently attached to the surface is obtained. Conversely, silanols of different silane molecules can condense with each other, yielding silsesquioxane oligomers or other polymeric structures which can then react with the surface via a single or multiple anchor points [11,12]. Aminosilanes are particularly amenable to these reactions as the amine group on the molecule can catalyze the siloxane formation intra- or inter-molecularly [13].

3-Aminopropyl triethoxysilane (APTES, Figure 1a) is the most commonly used reagent to functionalize silica surfaces with amine groups. Owing to its three reactive alkoxy groups, APTES can form a range of complex layer structures [12]. Because of this, a number of studies have investigated a wide variety of solution-based deposition methods for APTES [13,14,15,16]. Since the alkoxy groups in APTES are susceptible to hydrolysis and subsequent polymerization in the presence of water, anhydrous organic solvents are often preferred for APTES deposition [14,16]. However, some surface water is necessary for the reaction of APTES with a hydroxyl-terminated surface [13]. While ambient moisture usually supplies this necessary water, it also makes the deposition technique highly sensitive to ambient humidity conditions [17]. As a result, the deposition of APTES multilayers and agglomerates despite the use of anhydrous solvents has been widely reported [13,14,16,17].

A uniform surface monolayer of aminosilanes is critical for many applications, particularly in the label-free biosensing area. For example, in resonance-based sensors that rely on the interaction of an evanescent electromagnetic field with the target of interest, thick aminosilane multilayers can move the target-binding events away from the most sensitive regions of the sensor and reduce the quality of the sensor in general [18]. A similar effect has been observed for FET-based sensors whereby increasing the distance of the binding event from the sensing gate surface results in significantly reduced sensitivity [19]. In optical sensors based on the reflectivity of light from a surface, a non-uniform layer causes background reflectivity variations that can complicate data analysis and interpretation. For example, precise control of layer thickness and uniformity is crucial for the successful implementation of the minimum reflectivity condition required for arrayed imaging reflectometry (AIR) biosensors [20]. Thus, it is essential to establish silanization methods that result in uniform aminosilane layers that are reproducible and less susceptible to minor procedural variations. However, although many studies have investigated a range of deposition parameters for aminosilanes, methods of smooth monolayer deposition that are easily implemented in a short period of time without the use of specialized equipment (such as glove boxes or vacuum deposition chambers) are still lacking. Additionally, as described above, most studies have focused on the silanization procedures using APTES; very few have investigated silanization using dialkoxy- and monoalkoxy-silanes and as far as we are aware there are no reports systematically comparing the performance of all three silanes in terms of uniformity and reproducibility of deposition and their hydrolytic stability.

To that end, we investigated solution- and vapor-phase deposition techniques for three different aminosilanes: 3-aminopropyl triethoxysilane (APTES), 3-aminopropyl methyl diethoxysilane (APMDES) and 3-aminopropyl dimethyl ethoxysilane (APDMES) (Figure 1), to determine a method that enabled efficient and uniform silanization of silicon dioxide surfaces. The three aminosilanes were selected based on changing the number of reactive alkoxy groups, while maintaining an identical alkyl linker distance between the silane and amine functional groups. A deposition method from toluene solutions was tested for all three aminosilanes. An aqueous deposition method developed for APTES, which has been shown to deposit monolayers reproducibly, was also tested [5]. Since the vapor-phase deposition of silanes is known to deposit reproducible monolayers [17,21,22], vapor deposition of all three aminosilane layers was tested and compared to solution-phase deposition. The thickness of the layers was monitored using spectroscopic ellipsometry, their topology and hydrophilicity was analyzed using AFM and contact angle goniometry, respectively, and their stability was assessed by studying their desorption characteristics under aqueous conditions.

2. Materials and Methods

2.1 Materials

Silicon wafers with 145 nm of thermally grown oxide were purchased from the Smart System Technology & Commercialization Center, (Canandaigua, NY) and used for all experiments described herein. The wafers were diced into 10 mm × 10 mm chips by American Dicing, Inc. (Liverpool, NY). APTES, APMDES and APDMES were all purchased from Gelest Inc. (Morrisville, PA) and used as received. Anhydrous toluene was obtained by distilling ACS grade toluene (Sigma Aldrich) over sodium. ACS grade methanol was used as received from BDH (Poole Dorset, UK). All other reagents were obtained from Sigma-Aldrich.

2.2. Pre-silanization chip treatment

The diced 10 mm × 10 mm silicon chips were washed in a 3:7 solution of ethanol to 10 M sodium hydroxide for 30 minutes on an orbital shaker. This was followed by thorough rinsing with nanopure water and dried under a stream of nitrogen. The chips were then washed in a piranha solution (3:1 sulfuric acid: 30% hydrogen peroxide) for 30 minutes on an orbital shaker. (CAUTION: Piranha solution is corrosive and can react vigorously with organic materials; use care when handling.) After the wash, chips were thoroughly rinsed with nanopure water and dried under a stream of nitrogen before being subjected to different silanization conditions.

2.3. Silanization procedures

2.3.1. Deposition from toluene solutions—Chips were incubated in a 1% solution of the corresponding aminosilane (APTES, APMDES or APDMES) in anhydrous toluene at room temperature for the desired time period on an orbital shaker. ACS grade toluene was distilled over sodium just before deposition to obtain anhydrous toluene. At the end of aminosilane incubation, the chips were rinsed repeatedly with anhydrous toluene, dried under a stream of nitrogen and baked at 110 °C for 30 minutes.

2.3.2. Aqueous deposition of APTES—A stock solution of 50% methanol, 47.5% APTES and 2.5% nanopure water was prepared and allowed to age for at least one hour at 4 °C. This stock solution could be stored at 4 °C indefinitely. At the time of silanization, the stock solution was diluted 1:500 in methanol (yielding a final APTES concentration in solution of 0.095%), and the chips were incubated in this solution at room temperature for the desired amount of time. At the end of incubation, the chips were thoroughly rinsed with methanol, dried under a stream of nitrogen and baked at 110 °C for 30 minutes.

2.3.3. Vapor-phase deposition—Aminosilanes were vapor-deposited onto plasma cleaned oxide surfaces using a YES-1224P PE-CVD oven (Yield Engineering Systems, Livermore CA), following the procedures outlined by Zhang et al [22]. In brief, the tool was arranged in an active-float-ground plate configuration, with each lot of chips to be functionalized placed on the float plate directly. Following a brief thermalization period to attain a 150 °C chamber temperature under half-atmosphere nitrogen, the chips were oxygen-plasma cleaned for ten minutes under vacuum and then hydrated with 500 μL of nanopure H_2O . After hydration, 500 μL of the silane was injected and allowed a 10 minute soak period to deposit onto the substrates. Following several nitrogen sparges the chips were removed from the chamber and characterized.

2.4. Spectroscopic ellipsometry

Spectroscopic ellipsometry (Alpha-SE, J.A. Woollam) was used to monitor the thickness of the aminosilane layers during deposition and desorption. The thickness of the base silicon dioxide layer was measured after the chips were washed in piranha solution. After silanization, the thickness of the combined oxide and aminosilane layer was measured (the refractive index of the aminosilane layer was assumed to be the same as that of silicon dioxide). The difference was taken as the aminosilane layer thickness.

2.5. Surface characterization

Static water contact angles (CA) on the aminosilane surfaces were measured using a Ramé-Hart goniometer. Measurements were obtained at ambient temperature by placing a 5 μL droplet of water on the chip surface. The resolution of the instrument was $\pm 0.1^\circ$. Surface roughness was characterized via atomic force microscopy (AFM) using a Digital Instruments Nanoscope IIIa or an NT-MDT Solver Next AFM in tapping mode in air using a Si tip (300 kHz, 40 N/m). AFM scans of a 3 $\mu\text{m} \times 3 \mu\text{m}$ area on the chip surface were acquired; two scans were acquired for each surface, each one from a separate chip. Digital Instruments software or Nova P9 2.0.0.443 software was used for the quantitative analysis of AFM images. ImageJ [23] was used to represent the images from the two instruments on the same scale and color scheme.

2.6. Aminosilane desorption in water

Freshly aminosilanized samples were immersed in nanopure water at room temperature, and incubated for time intervals starting at 10 minutes and proceeding to 21 hours. The loss of aminosilane from the surface was monitored by thickness and contact angle measurements.

3. Results and Discussion

The three aminosilanes investigated in our study differ in the number of reactive ethoxy groups (Figure 1). The number of hydrolyzable ethoxy groups directly correlates with the aminosilane molecule's reactivity and its propensity to polymerize. APTES, with three ethoxy groups, can attach to the SiO_2 surface in a number of different ways: a covalent attachment of individual APTES molecules onto surface hydroxyl groups, covalent attachment of lateral 2-dimensional polymer sheets of APTES molecules formed via intermolecular siloxane bonding, or the condensation of APTES molecules into 3-dimensional polymer structures that are anchored to the surface via a few siloxane bonds (or a combination of these) [12]. APMDES has only two reactive groups, and as a result can form fewer possible structures on the SiO_2 surface: covalently attached individual molecules or three-dimensional polymeric structures. Finally, APDMES, with only one alkoxy group, can only form a structure with individual molecules covalently attached to the surface. Although APDMES can form dimers, there are no reactive groups on the dimer itself, and as such it cannot participate in surface modification reactions. Based on this, we expected

APTES to react most aggressively with the surface, with a reduction in reactivity as the number of reactive groups decrease on the other two aminosilanes. To test this, and to establish an optimal reaction time for surface silanization, we investigated the time-dependence of solution-phase aminosilane deposition.

3.1. Time dependence of solution-phase aminosilane deposition

Depositions of APTES, APMDDES and APDMES from a toluene solution and of APTES from an aqueous solution were compared for deposition times ranging from 10 minutes to 60 minutes, at 10-minute intervals (room temperature). The thickness values and the corresponding contact angles obtained from the time-dependence (Figure 2) show dramatic differences between silanes and deposition methods. For APDMES and APMDDES, the aminosilane layer was formed within the first 10 minutes, and longer incubation times did not significantly increase the thickness of the layer. APDMES deposited a thickness of 4.0 ± 0.2 Ångstroms, which is $\sim 60\%$ of the ~ 7 Å expected thickness for a monolayer [24]. This sub-monolayer coverage of APDMES is consistent with other reports of APDMES deposition via vapor-phase and solution-phase methods, and has been attributed to the formation of hydrogen bonds between the amine group of the aminosilane and a silanol group on the SiO_2 surface: this hydrogen bonding prevents the silanol group involved from reacting with another aminosilane molecule, reducing the packing density of silane molecules on the surface [25,26]. The constant thickness of APDMES layers for all deposition times is consistent with the single method of attachment possible for the molecule. The thickness of the APMDDES layer was closer to a monolayer at 8.0 ± 1.0 Å [28]. We did not observe multilayer deposition of this aminosilane over the tested reaction times, in spite of its two reactive groups. The propensity of APTES to form two- and three-dimensional polymer networks was clearly observed in its deposition from toluene solutions, where even a brief 10-minute incubation time yielded a 26.3 ± 0.8 Å thick multilayer of the aminosilane [13]. As incubation time increased, the thickness of the layer continued to increase, a result of the formation of extended polymer networks due to uncontrolled hydrolysis of APTES. For a silanization time of 1 hour, a layer 150 Å thick was obtained. Although the solvent used in our process was anhydrous, no attempt was made to exclude water from the ambient environment, and therefore the ambient humidity was sufficient to cause APTES polymerization. This behavior, however, was not observed in the aqueous APTES deposition method, where APTES was allowed to equilibrate in methanol with a small amount of water over a period of several minutes before being deposited onto the chips. This stock solution was then used throughout the course of the study (several weeks) with no adverse behavior observed. It has been hypothesized that APTES forms stable hydrogen-bonded structures following hydrolysis in water or concentrated alcoholic solutions [5,27]; this likely accounts for the lack of oligomerization under the storage conditions used (47.5% APTES, 50% methanol, 2.5% water). Thus, films formed from this “pre-hydrolyzed” APTES solution are not prone to the multilayer formation observed in APTES layers formed by in-situ hydrolysis of the alkoxy groups. For the aqueous deposition process, the thickness of the aminosilane layer was constant at a little over a monolayer for up to 40 minutes of deposition time, and increased slightly thereafter.

Static water contact angles were measured for the aminosilanized surfaces to characterize their hydrophilicity, and the measured values are in agreement with the observed thickness deposition. In general, upon deposition of the aminosilanes, the static water contact angle of the chips increased from $<10^\circ$ for piranha treated oxide surfaces, to $45\text{--}60^\circ$ for aminosilanized surfaces. An increase in thickness of the aminosilane layer generally corresponded with a decrease in the contact angle, which can be observed for the 50 and 60 minute time-points for aqueous APTES and all times after the 10 minute time-point for toluene APTES. In fact, at 40 minutes of toluene APTES silanization, the contact angle had

dropped to $<10^\circ$ (the same as that of bare oxide), presumably due to a large increase in the number of amine and other hydrophilic groups on the surface. Since shorter reaction times yielded layers closer to a monolayer for APTES deposition, and APMDES and APDMES layers did not change much with increasing reaction times, a 20-minute reaction time was selected for all further characterization of the aminosilane layers (surface morphology and hydrolytic stability).

3.2. Vapor-phase deposition

For vapor-phase deposition, all three silanes deposited layers $\sim 4\text{--}5$ Å thick (4.2 ± 0.3 Å for APTES, 5.4 ± 0.1 Å for APMDES and 4.6 ± 0.2 Å for APDMES) as shown in Figure 3. Thus, we obtained slightly less than monolayer coverage for the silane layers, and no multilayer formation was observed, consistent with literature reports [17,21,22]. The contact angles obtained with vapor-phase deposition were $40 \pm 1^\circ$, $53.9 \pm 0.7^\circ$ and $59.0 \pm 0.8^\circ$ for APTES, APMDES and APDMES, respectively, which were very similar to those obtained for aqueous APTES and toluene APMDES and APDMES solution-phase deposition methods.

3.3. AFM measurements

Spectroscopic ellipsometry and contact angle goniometry are both macroscopic techniques, and provide information about properties averaged over the measurement area ($\sim 1\text{--}2$ mm diameter spot). To examine the surface topology of the aminosilane films on a microscopic scale, we used atomic force microscopy. Representative AFM scans for all the surfaces are shown in Figure 4. RMS roughness values were calculated for each surface and are tabulated in Table 1 (average of two scans per surface, obtained from two different chips).

The differences in the morphologies of films deposited via different methods are clearly seen in the AFM scans. Vapor-phase deposition of all the three aminosilanes produces extremely smooth films, with low surface roughness values (average of 0.2 nm) that are comparable to a clean oxide surface (Table 1). Amongst the solution-phase deposited films, APTES deposited from aqueous solution and APDMES deposited from toluene solution form smooth films with low surface roughness (average values of 0.2 and 0.26 nm, respectively, Table 1) and essentially no surface features. The APDMES results are consistent with the inability of the aminosilane to form, and hence deposit, any structures other than individual molecules on the surface. The lack of any observable polymeric structures in the aqueous APTES film supports the premise that pre-hydrolysis does indeed stabilize hydrolyzed APTES monomers, and they are subsequently deposited as such on the surface. Very different film morphologies were obtained for APTES and APMDES deposited from toluene solution: we observed large agglomerates of aminosilane on both surfaces. In the case of toluene APTES, some agglomerates had a height larger than ~ 300 nm, suggesting that there was extensive 3-dimensional polymerization of APTES. The overall roughness of the film was 20 nm. Combined with the thickness data, this implies that deposition of APTES from a toluene solution produces multilayers interspersed with a number of APTES islands. The number and size of the agglomerates was lower for the APMDES surface than for the APTES surface, which is consistent with the lower reactivity of APMDES. As a result, the overall surface roughness was also much lower, at an average value of 1.3 nm. Additionally, the areas between the APMDES islands were very smooth, with roughness of about 0.2 nm. Combining this information with the thickness data, we can conclude that APMDES deposition from a toluene solution produces films that are predominantly smooth sub-monolayers, but have APMDES islands interspersed over the film area.

3.4. Desorption of aminosilanes in water

The hydrolytic stability of the deposited aminosilane layers is critical for further chip functionalization, usually carried out in an aqueous medium if the goal is that of immobilizing biomolecules (such as antibodies) for the production of biosensors. A number of studies have reported extensive loss of layers prepared from aminopropyl alkoxysilanes upon exposure to water [13,17,26,28]. There are two possible mechanisms responsible for this loss: (a) rinsing with water can remove aminosilane molecules that are weakly hydrogen bonded to the surface [13] and (b) the amine groups can catalyze the hydrolysis of siloxane (Si-O-Si) bonds intra-molecularly via the formation of a five-membered cyclic intermediate, or inter-molecularly, removing aminosilane molecules that are covalently attached to the surface [17,26,28]. To test if the aminosilane identity or deposition procedure had any effect on silane desorption, we immersed them in water (pH = 6.2) for different periods of time, ranging from 10 minutes to 21 hours. The thickness of the films and the water contact angles of the surfaces were measured at each time point to monitor the loss of aminosilanes. The results are shown in Figure 5, where time 0 correlates to no desorption under water (i.e. a dry normal film).

As one would expect, all the three aminosilanes, regardless of the deposition method, exhibited significant desorption from the surface over a period of 21 hours. The decrease in the water contact angles of surfaces is consistent with this loss of organofunctional moieties from the surface. APTES and APDMES layers deposited from toluene solutions were completely removed from the surface at the end of 21 hours, while all the other layers retained some surface aminosilanes. APTES layers deposited from toluene solutions showed the fastest initial rate of desorption. In fact, over a period of 60 minutes, the APTES layer went from a starting thickness of $99.1 \pm 3.2 \text{ \AA}$ to a final thickness of $3.7 \pm 0.3 \text{ \AA}$, suggesting that the APTES multilayers and agglomerates deposited using this method were loosely bound to the surface, and hence washed away within a few minutes of incubation in water. After the 60-minute time point, the toluene APTES layer showed a gradual desorption from the surface, similar to the slow desorption of the other aminosilane layers. Vapor-phase deposited aminosilanes seemed to have a slightly higher stability than solution-phase deposited silanes, as evidenced by the 120 minute time point, where the vapor-phase aminosilanes retained ~50% of the original layer, while the solution-phase aminosilanes (with the exception of APMDDES, which retained ~50% of the original layer) retained <25% of the original layer. However, for the 60-minute time-point (which is usually sufficient for their subsequent functionalization with typical bifunctional cross-linking reagents), layers formed both from vapor and solution deposition methods (except for the toluene APTES layer) retained ~50–70% of the original aminosilane layer.

Of course, a critical parameter of the utility of silanized surfaces is their ability to support subsequent attachment of biomolecules, and stability following the attachment process. We confirmed that the aqueous solution deposited APTES, and APDMES films deposited using anhydrous toluene, retained their ability to covalently attach antibodies to the chip surface even after one hour of desorption in water when compared to no- wash control (Figure S1). Moreover, the silane films showed no significant desorption in buffered solution over a 60-minute period (Figure S2).

Based on the fact that APTES potentially has multiple anchor points on the surface while APDMES can only have one anchor point, one would expect that it would be easier to desorb APDMES from the surface than APTES. However, we did not observe any preferential desorption of APDMES over APTES in our study. This is consistent with the observation of Smith et al. [26] that layers deposited from APTES were not more hydrolytically stable than layers prepared using APDMES. One potential reason for this is that the APTES layers prepared in our study might be predominantly deposited in a covalent

attachment or a 3-dimensional polymerization configuration: for both of these configurations, the individual APTES molecules or APTES polymers could be attached to the surface via a single, or very few anchor points. However, the configuration of APTES films that would be expected to be most resistant to hydrolysis is the 2-dimensional polymerization case, which has the highest number of anchor points and lateral cross-links. The characterization techniques used in this study did not allow us to distinguish between different modes of attachment of the aminosilanes on a molecular level; therefore it was not possible to confirm the exact reason for the equal propensities of APTES and APDMES desorption from the surface.

From literature reports of silanization procedures (Table 2), it is evident that the toluene based deposition of APTES results in a variety of films depending on the deposition conditions, and often results in rough multilayers. This is consistent with the results obtained in our study for the anhydrous toluene deposition method. However, the aqueous APTES deposition method yielded layers that were comparable or better than other APTES layers reported in the literature, particularly in terms of film smoothness and monolayer nature. Very few studies have characterized the deposition of APMDDES or APDMES films. At ~6–8 Å, the thickness of our APMDDES films was consistent with that reported by Moon et al [24]. Our sub-monolayer APDMES films are consistent with the results of Smith et al [26], although monolayer coverages for APDMES have been reported by Moon et al [24].

It is evident from Table 2 that a majority of current literature reports have focused on optimizing silanization procedures using APTES; however, in this study, we undertook a comparative analysis for a variety of deposition methods for three different aminosilanes that can be used for silica surface silanization. This enabled the identification of several combinations of silane molecule/silanization method that yielded uniform and reproducible aminosilane layers, some of which are extremely easy to implement without the need for any specialized equipment. In particular, toluene solution based deposition of APTES and APMDDES were ruled out as potential functionalization methods due to agglomerate formation in the latter and agglomerate and multilayer formation in the former. Toluene based deposition of APDMES, aqueous deposition of APTES, and vapor deposition of the three aminosilanes (APTES, APMDDES and APDMES) all resulted in smooth and reproducible sub-monolayers to monolayers of aminosilanes on the silicon dioxide surface. In terms of convenience of use, the solution-phase methods were more ideal as they could be easily carried out in a wet laboratory environment, while the vapor-phase deposition methods obviously require access to a specialized deposition tool (YES-1224P PE-CVD oven). Additionally, the vapor-phase deposition processes were somewhat prone to contamination by other chemicals used in the oven unless the oven was extensively cleaned between depositions of different chemicals. Furthermore, as with any CVD process, a good deal of effort was invested in validating recipes which reproducibly deposited each film type, as even small changes to the process had a profound effect on film quality.

4. Conclusions

Despite the wide variety of methods available for the functionalization of a silicon dioxide surface with aminosilanes, very few of them actually yield Ångstrom-level reproducibility and uniformity of aminosilane layers required for many applications in a manner that is independent of minor procedural variations. In this study, we investigated the characteristics of layers prepared from three different aminosilanes using solution-phase and vapor-phase deposition methods. A combination of thickness measurements using spectroscopic ellipsometry and surface topological studies using AFM pointed towards a number of deposition methods that yielded sub-monolayer to monolayer films with smooth surface topography. It was determined that the toluene solution deposition of APDMES and the

aqueous solution deposition of APTES yielded silane films with qualities comparable to their films deposited using vapor-phase methods. Although aminosilane layers deposited using all of these methods were prone to hydrolysis in water, they were determined to be sufficiently stable for a period that is usually sufficient for their subsequent functionalization with typical bifunctional cross-linking reagents. Based on the convenience of use and long-term stability, it was concluded that the toluene solution deposition of APDMES and the aqueous solution deposition of APTES were optimal and convenient methods for the functionalization of silicon dioxide surfaces with aminosilanes.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We thank Hsin-I Peng, Brian McIntyre and Sergey Korjanevski for assistance with AFM. We thank Joseph M. Kaule for carrying out the vapor deposition of silanes. Financial support by the National Institutes of Health via NIGMS grant R01GM100788 and via the University of Rochester Human Immunology Center (NIH R24-AL054953) is gratefully acknowledged.

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Highlights

- Various solution-phase aminosilane deposition methods were compared to vapor-phase films
- Films of APTES, APDMES and APMDES were prepared from solution and vapor-phase
- Silane film quality was assessed by thickness, hydrophilicity and surface roughness
- Two solution-phase methods produced silane films comparable to vapor-deposited films.

Figure 1. Structures of the three aminosilane molecules used in our study. **(a)** 3-Aminopropyl triethoxysilane, **(b)** 3-aminopropyl methyl diethoxysilane and **(c)** 3-aminopropyl dimethyl ethoxysilane.

Figure 2. Effect of silanization time on aminosilane film properties for solution-phase deposition. (a) Thickness of the film and (b) Water contact angle for the film. Error bars represent the standard deviation of the measurements from the mean value for three replicate chips.

Figure 3.

Thickness and water contact angle values for the three aminosilanes deposited via vapor-phase method. Error bars correspond to the standard deviation of the measurement from the average measurement of three replicate chips.

Figure 4.

Representative AFM scans of a $3\ \mu\text{m} \times 3\ \mu\text{m}$ area on the aminosilane surfaces. (a) Piranha cleaned oxide surface for reference (b) APTES deposited from toluene (c) APMDDES deposited from toluene (d) APDMES deposited from toluene (e) Aqueous solution-phase deposited APTES (f) Vapor-phase deposited APTES (g) Vapor-phase deposited APMDDES (h) Vapor-phase deposited APDMES (i) Scale bar (all images are represented with a range of 0 to 20 nm).

a **b** **c** **d****Figure 5.**

Aminosilane film characteristics upon desorption in water. Thicknesses (**a**) and water contact angles (**b**) for solution-phase deposited silane layers as a function of desorption time. Thicknesses (**c**) and water contact angles (**d**) for vapor-phase deposited silane layers as a function of desorption time. Error bars represent the standard deviation of the measurements from the mean value for three replicate chips.

Table 1

RMS roughness of the silane surfaces deposited using different methods. The values correspond to the average from two different chips.

Surface	Deposition method	RMS roughness (nm)
Cleaned SiO ₂	Piranha	0.45
APTES	Toluene solution	19.99
APMDES	Toluene solution	1.34
APDMES	Toluene solution	0.26
APTES	Aqueous solution	0.20
APTES	Vapor-phase	0.22
APMDES	Vapor-phase	0.19
APDMES	Vapor-phase	0.18

Table 2

Comparison of our silane layers to other layers deposited using solution phase methods.

Silane	Deposition method	Film characteristics	
		Thickness	Roughness/morphology
APTES[13]	Anh. toluene solution and aqueous solution; 0.4% APTES; 15 minutes – 24 hours reaction time; RT ^a and reflux.	9 Å for anh. toluene, RT, 15 minutes, up to 380 Å for longer reaction times; 3 Å for water, 15 minutes.	Smooth films for toluene, RT, reaction times < 2 hours; agglomerates for higher reaction times, higher temperatures and aqueous solutions.
APTES[14]	Anh. toluene solution; 1, 10 and 33% APTES; 1, 24 and 72 hour reaction times; 25 °C and 75 °C.	No monolayers observed; < 20 Å thickness for 25 °C, 1 hour reaction time; up to 200 Å thick films for 75 °C or longer reaction times.	~0.5 nm for 25 °C, 1 hour reaction time; 0.3 nm for the 72 hour, 75 °C, 10% APTES condition; up to 27 nm for other reaction conditions
APTES	Anh. toluene solution; 2% APTES; 1 hour to 19 hour reaction times; 20 °C and 70 °C.	4 – 57 Å, increases with increasing reaction time.	NR ^b
APTES	Anh. toluene solution; 1% APTES; 30 minutes to 24 hour reaction times; 25 °C.	6 Å at 30 minutes, increases to ~ 100 Å by the end of 72 hours.	NR ^b
APTES[28]	Toluene solution; 1, 10 and 50 mM APTES; 1 hour to 24 hour reaction time; RT and 90 °C.	NR ^b	3.14 nm for RT deposition, 1.28 nm for 90 °C deposition (using 50 mM APTES, 12 hour reaction time).
APTES (this work)	Anh. toluene solution and aqueous solution; 1% APTES for anh. toluene deposition, 0.095% APTES for aqueous deposition; 10 minutes to 60 minutes reaction time; RT.	20 Å at 10 minutes for anh. toluene, increases to ~150 Å at the end of 60 minutes; ~8 Å for up to 30 minutes for aqueous solution, increases to ~17 Å at 60 minutes.	20 nm for anh. toluene deposition at 20 minutes; 0.2 nm for aqueous deposition at 20 minutes.
APMDES	Anh. toluene solution; 1% APMDES; 30 minutes to 24 hour reaction times; 25 °C.	8 Å at 30 minutes, increases to 14 Å by the end of 72 hours.	NR ^b
APMDES (this work)	Anh. toluene solution; 1% APMDES; 10 minutes to 60 minutes reaction time; RT.	6–8 Å for all reaction times.	1.34 nm for 20 minutes reaction time.
APDMES	Anh. toluene solution; 2% APTES; 24 hour reaction time; 20 °C and 70 °C.	3.5/4.7 Å for 20/70 °C.	NR ^b
APDMES	Anh. toluene solution; 1% APDMES; 30 minutes to 24 hour reaction times; 25 °C.	7 Å silane layer for all reaction times.	NR ^b
APDMES (this work)	Anh. toluene solution; 1% APDMES; 10 minutes to 60 minutes reaction time; RT.	~4 Å for all reaction times.	0.26 nm for 20 minutes reaction time.

^aRT: Room temperature.^bNR: Not reported.