

# Chemical Vapor Deposition of Three Aminosilanes on Silicon Dioxide: Surface Characterization, Stability, Effects of Silane Concentration, and Cyanine Dye Adsorption

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Covalently bonded monolayers of two monofunctional aminosilanes (3-aminopropyldimethylethoxysilane, APDMES, and 3-aminopropyldiisopropylethoxysilane, APDIPEs) and one trifunctional aminosilane (3-aminopropytriethoxysilane, APTES) have been deposited on dehydrated silicon substrates by chemical vapor deposition (CVD) at 150 °C and low pressure (a few Torr) using reproducible equipment. Standard surface analytical techniques such as x-ray photoelectron spectroscopy (XPS), contact angle goniometry, spectroscopic ellipsometry, atomic force microscopy, and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) have been employed to characterize the resulting films. These methods indicate that essentially constant surface coverages are obtained over a wide range of gas phase concentrations of the aminosilanes. XPS data further indicate that the N1s/Si2p ratio is higher after CVD with the trifunctional silane (APTES) compared to the monofunctional ones, with a higher N1s/Si2p ratio for APDMES compared to that for APDIPEs. AFM images show an average surface roughness of 0.12–0.15 nm among all three aminosilane films. Stability tests indicate that APDIPEs films retain most of their integrity at pH 10 for several hours and are more stable than APTES or APDMES layers. The films also showed good stability against storage in the laboratory. ToF-SIMS of these samples showed expected peaks, such as CN<sup>-</sup>, as well as CNO<sup>-</sup>, which may arise from an interaction between monolayer amine groups and silanols. Optical absorption measurements on adsorbed cyanine dye at the surface of the aminosilane films show the formation of dimer aggregates on the surface. This is further supported by ellipsometry measurements. The concentration of dye on each surface appears to be consistent with the density of the amines.

## Introduction

Organosilane reagents are commonly used to produce functionalized thin films on silicon oxide and other oxide substrates for a variety of technological applications, and 3-aminopropytriethoxysilane (APTES) is one of the most frequently used of such silanes. Among their applications, APTES and similar aminosilanes may serve as the foundation layer in biosensors and bioarrays,<sup>1–5</sup> increase adhesion in fiberglass–epoxy composites on silica surfaces,<sup>6–8</sup> suppress polymer film dewetting,<sup>4</sup> facilitate production

of arrays of metal nanoparticles on silica substrates,<sup>9</sup> and help probe protein and cell adhesion.<sup>10–13</sup> The morphology and surface concentration of the aminosilane film is crucial for these applications; therefore, producing homogeneous surfaces with controlled packing densities represents an important opportunity. Different reaction conditions have been reported for preparing thin films of APTES and other aminosilanes on silicon wafers, glass, or other oxide substrates.<sup>1,14–24</sup> Although the solution-phase deposition of silanes is the most widely studied method, this

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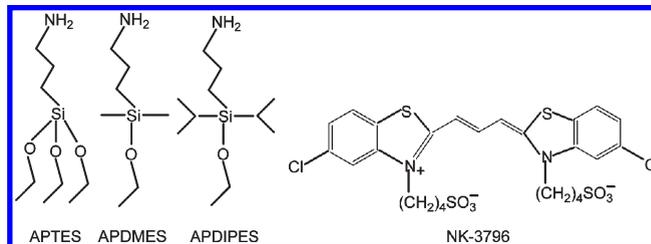
approach is neither environmentally friendly nor is it typically industrially viable because it generates significant amounts of solvent waste. In addition, it is often irreproducible and/or produces poor quality films; in many cases, self-polymerization of APTES in solution, which is difficult to control, remains a major obstacle for production of clean homogeneous silane films.<sup>19</sup> In most cases silane films prepared from solution show irregularities in their morphologies which limits the effectiveness of the films' potential technological applications. The vapor coating procedure described by Fiorilli et al.<sup>20</sup> minimizes, but does not entirely eliminate, the size of the aggregates deposited on the surface of the silane films compared to films prepared from solution. Also, a general problem with aminosilane films appears to be the availability of amino groups on the surfaces of the films.<sup>1</sup> In some cases, this requires further treatment of the films to enhance their efficiency for chemical immobilization, e.g., of biomolecules in the fabrication of biosensors. Such treatment may include additional surface silanization with (typically monofunctional) alkylsilanes (capping agents) to convert the remaining silanol groups into Si–O–Si linkages.

Chemical vapor deposition (CVD) is by far the most effective, simple, and potentially reproducible method for producing homogeneous, covalently bonded, high density, functionalized silane films on silicon and glass surfaces. CVD is much cleaner than the liquid phase approach because the surface is not exposed to impurities that may be in the solvent, and no surface rinsing or cleaning is required after deposition. Clearly, the gas phase approach provides for control of the amount of moisture in the deposition chamber, which limits or eliminates self-polymerization (or dimerization) of the silane. Compared to solution-phase deposition, there have been relatively few reports of the CVD of silanes, which include descriptions of the gas phase deposition of octadecyltrimethoxysilane, fluoroalkyl silanes, and various aminosilanes.<sup>16,20–22,25–31</sup>

In particular, there appears to be no work that explores a series of the important aminosilanes by CVD that includes the sterically hindered APDIPES. To the best of our knowledge, there is also no study that utilizes cyanine dyes as a probe to test the morphology and/or chemistry of functionalized aminosilane films, although an earlier report did discuss the adsorption of a rhodamine 6G on glass slides coated with self-assembled monolayers of phenyltrichlorosilane.<sup>32</sup>

In this work, we explore conditions for preparing controlled, ultrathin, aminosilane films of 3-aminopropyltriethoxysilane (APTES), 3-aminopropyldimethylethoxysilane (APDMES), and 3-aminopropyldiisopropylethoxysilane (APDIPES) (see Scheme 1) on silicon (Si/SiO<sub>2</sub>) substrates. One important purpose of this study is to determine the gas phase concentration of silane that is needed to saturate the surface of a silicon oxide surface. The three silanes were chosen to have obvious structural differences and corresponding reactivities and stabilities in the adsorbed state. That is, APTES has three potential attachment points to the

**Scheme 1. Structures of 3-Aminopropyltriethoxysilane (APTES), 3-Aminopropyldimethylethoxysilane (APDMES), 3-Aminopropyldiisopropylethoxysilane (APDIPES), and 5-Chloro-2-[3-[5-chloro-3-(4-sulfobutyl)-2(3*H*)-benzothiazolyldiene]-1-propenyl]-3-(4-sulfobutyl)-benzothiazolium Hydroxide Triethylamine Salt (NK-3796)**



surface or other silane molecules, while APDMES and APDIPES have only one. Therefore APTES may polymerize, but APDMES and APDIPES are more simple molecules that can only dimerize (of course if they dimerize they cannot covalently bind to the surface). The two methyl groups on APDMES provide some steric hindrance around its silicon atom, and should also give the adsorbed species some measure of hydrophobicity. The two isopropyl groups on APDIPES provide its silicon atom with even greater steric hindrance and more hydrophobic character in the adsorbed state. This additional steric hindrance and hydrophobicity should increase the stability of APDIPES films under extreme pH conditions. This approach has been used to produce chromatographic stationary phases with improved stability.<sup>33</sup> In addition to these observations, we show the morphology and functionality of the prepared films with regards to adsorption of a cyanine dye.

## Experimental Section

**Materials and Chemicals.** Si(100) wafers, polished on one side, were obtained from Montco Silicon Technologies (Spring City, PA). 2-Propanol (99.9%, Sigma, USA), acetone (> 99.5%, Sigma, USA), potassium hydroxide (> 90%, Sigma, USA), and oxygen gas (99.994%, Airgas) were used as received. APTES, APDMES, and APDIPES were purchased from Gelest (Morrisville, PA) and the cyanine dye (NK-3796) was purchased from Hayashibara Biochemical Laboratory, Japan, and used as received.

**Surface Cleaning.** Native oxide-terminated silicon wafers and glass substrates were washed successively with soap and water, 2-propanol, and acetone and then dried under a stream of pure nitrogen gas. Plasma cleaning of the washed slides was performed with a plasma cleaner model PDC-32G from Harrick Plasma (Ithaca, NY) at medium power (10.5 W applied to the rf coil) for ca. 3 min using an air plasma. The thickness of the native oxide was then measured by ellipsometry, after which the surfaces were introduced into the silane deposition system (Scheme 2).

**CVD System.** The YES-1224P Chemical Vapor Deposition System from Yield Engineering Systems (Livermore, CA) incorporates a plasma cleaning/modification capability into a heated vacuum deposition chamber where the internal dimensions of this deposition chamber are 16" (width) × 18" (depth) × 16" (height). Reactive chemicals are vaporized in temperature-controlled flasks and introduced via heated lines to the main chamber. The system allows precise control of chemical volume, reaction temperature, and exposure time. Plasma cleaning can prepare substrates for consistent, repeatable surface reaction, where three types of plates may be used in the YES-1224P: active, ground, and float. Voltages are applied to active plates vis-à-vis any ground plates and/or the walls of the chamber, which are also grounded. Therefore, active plates generally have somewhat higher concentrations of plasma

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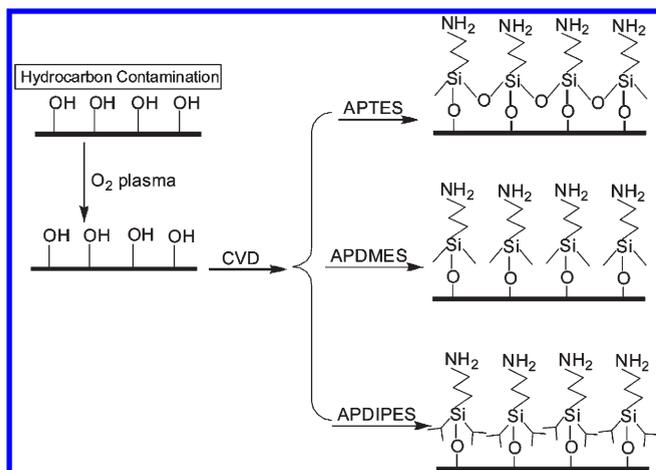
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**Scheme 2. Idealized Representation of Surface Cleaning Followed by Surface Modification with APTES, APDMES, and APDIPES<sup>a</sup>**



<sup>a</sup> Note that because of the relatively few methylene units in them, these short-chain adsorbates are not expected to adopt all trans configurations. That is, the thicknesses of the adsorbed layers are not expected to be the same as the extended lengths of the precursor molecule.

species than do ground plates, and float plates generally have much lower concentrations of such active species.<sup>34</sup>

**CVD of the Aminosilanes.** The entire cleaning, dehydration, and deposition process was performed at 150 °C. To wit, surfaces were first plasma cleaned in the YES-1224P (200 W with high purity O<sub>2</sub> (99.994%) at ca. 0.5 Torr) using a three-plate configuration (active, ground, and float), with the substrates on the float plate. This surface cleaning, which did not increase the thickness of the native oxide,<sup>34</sup> was followed by a dehydration purge to remove residual water from the surfaces. The dehydration purge consisted of evacuating the system to 5 Torr, refilling with N<sub>2</sub> gas to 500 Torr, and evacuating to the base pressure of the recipe setup (1 Torr). An aminosilane (APTES, APDMES, or APDIPES) was then introduced into the sealed chamber, raising the pressure of the deposition chamber to 2–3 Torr. The reaction time of the surface with the gas phase adsorbate was 5 min. After the deposition, three purge cycles were performed, which consisted of addition of N<sub>2</sub> gas, followed by evacuation. These purge cycles were performed for both safety reasons and also to improve the quality of the deposition – they are used to remove residual silane from the chamber before it is opened, and they aid in removing any unreacted silane from the surfaces of the substrates.

**Contact Angle Analysis.** Water contact angles were measured with a Ramé-Hart (model 100-00) contact angle goniometer. The water contact angles, thicknesses (*vide infra*), and XPS N/Si ratios (*vide infra*) reported for the aminosilane surfaces are the averages of measurements obtained from multiple surfaces (sometimes as many as 15–20) prepared over a period of months.

**Spectroscopic Ellipsometry.** Thicknesses of silane films, as well as films with adsorbed cyanine dye, were obtained using an M-2000D instrument from the J.A. Woollam Co. (Lincoln, NE), Inc. The wavelength range was 190.5–989.4 nm, and the angle of incidence was fixed at 75°. The native oxide of silicon dioxide, aminosilane films, and cyanine dye films were modeled using the optical constants of silicon dioxide that were found in the instrument software. This is a valid and widely used approach for ellipsometry of ultrathin organic films,<sup>14,15,24,25</sup> where part of the justification for this approach stems from the similarity of the optical constants of SiO<sub>2</sub> and many other organic materials over a wide range of wavelengths (see, for example, Table 1). Note also that all of the silanes deposited in this study

**Table 1. Optical Constants at 300, 500, and 700 nm of SiO<sub>2</sub>, Polymethylmethacrylate (PMMA), and Polyethylene. These Values Were Obtained from the Instrument Software of Our Spectroscopic Ellipsometer**

material	$n_{300}, k_{300}$	$n_{500}, k_{500}$	$n_{700}, k_{700}$
SiO <sub>2</sub>	1.49, 0	1.47, 0	1.46, 0
PMMA	1.51, $1.5 \times 10^{-4}$	1.49, 0	1.49, 0
polyethylene	1.50, 0	1.49, 0	1.48, 0

will be bonded through at least one Si–O bond, which obviously resembles SiO<sub>2</sub>.

**X-ray Photoelectron Spectroscopy.** XPS was performed with an SSX-100 instrument from Surface Sciences using a monochromatic Al K $\alpha$  source and a hemispherical analyzer.

**Time-of-Flight Secondary Ion Mass Spectrometry.** ToF-SIMS was performed in spectroscopy mode using an ION-TOF TOF-SIMS IV instrument with a two-lens <sup>69</sup>Ga<sup>+</sup> gun. Both positive and negative ion spectra were acquired.

**UV–vis Measurements of the Cyanine Dye Adsorbed on Aminosilane Films.** Glass substrates modified with APTES, APDMES, and APDIPES were analyzed spectrophotometrically using an Agilent 8453 UV–vis spectrophotometer after exposure to an aqueous solution of the cyanine dye.

**AFM Measurements.** Atomic force microscopy (AFM) was performed with a Veeco Dimension V Scanning Probe Microscope.

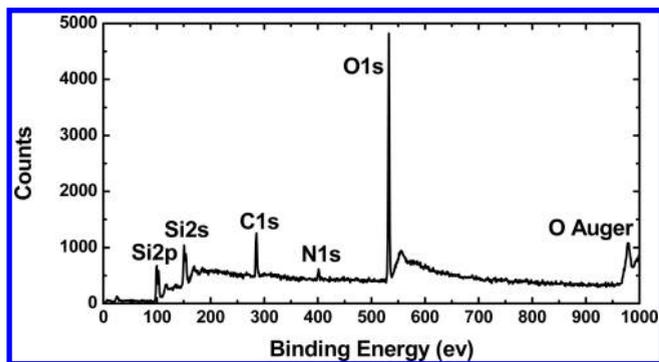
**Stability Tests.** Experiment 1 consisted of immersing aminosilane-coated silicon wafers in a pH 10.0 buffer (potassium carbonate–potassium borate–potassium hydroxide) for either 2 h, 2 h followed by another 2 h, or 4 h. The loss of any aminosilane was determined by the change in the N/Si ratio by XPS. Experiment 2 consisted of six months of storage of the aminosilane-coated surfaces in the laboratory, after which the samples underwent sonication for 3 min in isopropyl alcohol and then for 3 min in acetone, after which they were rinsed with water and dried with a jet of N<sub>2</sub>. The samples were then recharacterized by spectroscopic ellipsometry and water contact angle goniometry (both advancing and receding angles were measured). These samples were also probed by ToF-SIMS.

**Cyanine Dye Adsorption.** Glass slides were immersed in an aqueous solution (0.1 mM) of the cyanine dye (see Scheme 1) for 10 min, removed, rinsed with deionized water, and then dried with a jet of nitrogen gas. The treatment of silicon wafers with the dye solution was accomplished by adding a few drops of the dye solution to the polished surface of a silicon shard (enough to cover the surface), after which it was allowed to stand for 10 min before the excess solution was rinsed away with deionized water, and the slides were again dried with nitrogen gas.

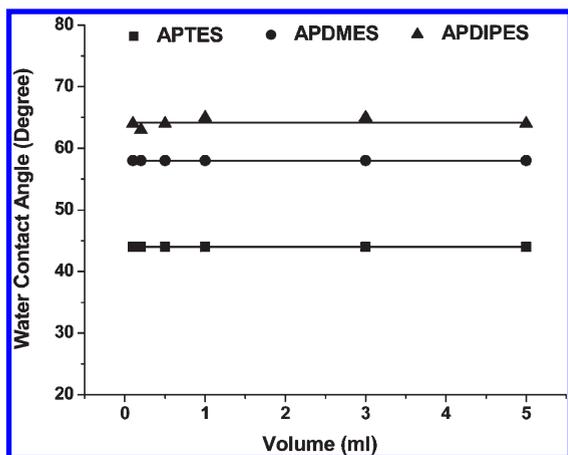
## Results

**A. Thin Film Characterization and Stability.** AFM and XPS were performed on silicon substrates prior to and following aminosilane CVD with 3-aminopropyltriethoxysilane (APTES), 3-aminopropyltrimethylethoxysilane (APDMES), and 3-aminopropyl-diisopropylethoxysilane (APDIPES) (see Scheme 1). As expected, the silicon substrates were initially very smooth, with an rms roughness value of  $0.103 \pm 0.009$  nm. Only a small increase in film roughness was observed after CVD of the aminosilanes. That is, the roughness of the APTES, APDMES, and APDIPES films were  $0.152 \pm 0.005$ ,  $0.104 \pm 0.004$ , and  $0.122 \pm 0.006$  nm, respectively. The films appeared flat and monotonous by AFM; neither the control surface, nor the aminosilane surfaces showed any substantial features in this analysis. Indeed, AFM images of the films of these three silanes suggested complete coverage of their silicon substrates without any indication of rough morphologies. Anderson and co-workers similarly found that vapor phase

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**Figure 1.** A representative XPS survey spectrum of one of our aminosilane (APTES) films on silicon oxide showing the expected signals due to nitrogen (N1s), silicon (Si2p and Si2s), carbon (1s), and oxygen (O1s and Auger signals). There are no unexpected peaks.



**Figure 2.** The advancing water contact angle vs the volume of silane reagent introduced into the deposition chamber.

deposition of an aminosilane (their molecule had two attachment points: 3'-aminopropylmethyldiethoxysilane) produced very smooth surfaces, which were much flatter than those made by solution deposition.<sup>16</sup> Figure 1 is a representative XPS survey scan of the surfaces modified with the three aminosilanes. These survey scans show the expected elemental composition of the surfaces: the presence of silicon, carbon, nitrogen, and oxygen. No N1s signal is present on the bare Si/SiO<sub>2</sub> substrates.

One key purpose of this study was to determine the amount of aminosilane that would be necessary to saturate the surface of an oxidized silicon wafer with a monolayer of an aminosilane. Accordingly, each of the three aminosilanes was deposited at different concentrations; that is, 0.1–5 mL of the silanes were injected into the chamber, which corresponds to concentrations (in the gas phase) of  $(0.1-5) \times (5.7 \times 10^{-5})$ ,  $(0.1-5) \times (7.1 \times 10^{-5})$ , and  $(0.1-5) \times (5.3 \times 10^{-5})$  mol/L of APTES, APDMES, and APDIPES, respectively. Interestingly, even the lowest concentration of the silanes appeared to saturate the surfaces, and this degree of surface saturation did not seem to increase with increasing silane concentration. For example, Figure 2 shows the essentially constant advancing water contact angles of surfaces treated with different concentrations of the three aminosilanes. Clearly, for each of the silanes, the resulting water contact angle does not depend on the concentration of the gas phase reagent. Also, the trend in water contact angles reflects the chemistry of the adsorbates. APTES, with its three ethoxy groups, shows the lowest water contact angles, where unreacted ethoxy groups are expected to be

**Table 2.** Change in XPS N1s/Si2p Ratios for APTES, APDMES, and APDIPES Surfaces after Immersion in a pH 10 Buffer

time	APTES	APDMES	APDIPES
2 h	−22%	−45%	−4%
2 h	−18%	−35%	−1%
2 h + 2 h	−36%	−68%	−19%
4 h continuous	−31%	−58%	−6%

subject to hydrolysis to silanols after the substrates are removed from the oven. APDMES, with its two methyl groups, produces surfaces with substantially higher water contact angles, and there is yet another increase in the water contact angles when two isopropyl groups are present on the silane (APDIPES).

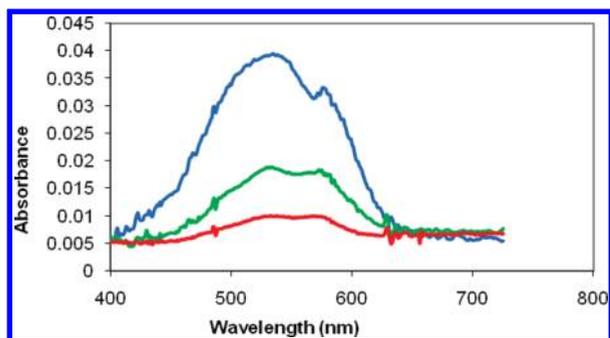
XPS confirms the wetting results, showing approximately the same surface coverage for deposition of a given aminosilane at different concentrations. However, the total amount of surface nitrogen *does* appear to depend on the nature of the adsorbate: the average N1s/Si2p XPS ratios of APTES, APDMES, and APDIPES are  $0.074 \pm 0.010$ ,  $0.058 \pm 0.010$ , and  $0.050 \pm 0.005$ , respectively. That is, APTES shows the highest surface coverage of amine groups, followed by APDMES, which only has one possible attachment point to the surface and some steric hindrance to this site, and finally followed by APDIPES, which also has only one possible attachment point and even greater steric hindrance around this point. Interestingly, ellipsometry shows what appears to be the opposite trend. The thicknesses of the APTES, APDMES, and APDIPES surfaces were  $6.6 \pm 0.5$ ,  $6.5 \pm 0.9$ , and  $8.3 \pm 1.0$  Å, respectively. These results may be a reflection of condensation of APTES molecules at the surface with loss of water versus the permanent methyl and isopropyl groups of APDMES and APDIPES, where especially the isopropyl groups might contribute to the apparent thickness of the film. (Consider that APTES only has three carbon atoms in its alkyl chain bonded to silicon, but APDIPES has nine carbon atoms so bonded.)

Two stability tests were performed on aminosilane films. Experiment 1 consisted of immersing aminosilane-coated surfaces in a pH 10 buffer for different periods of time, after which surface characterization was performed (see Table 2). In this experiment, it was expected *a priori* that the relatively high pH buffer would challenge the SiO<sub>2</sub> substrates along with any covalently attached adsorbates, and that APDIPES would have the greatest stability of the three silanes because of the steric hindrance and hydrophobicity of its isopropyl groups.<sup>33</sup> In the first trial of the experiment, which was repeated, aminosilane films were immersed in the pH 10 buffer for 2 h. As expected, there was very little loss in the nitrogen content of the APDIPES surfaces (ca. 1–4%), as measured by XPS. These losses are probably not statistically significant—it seems reasonable to state that the APDIPES surface was stable, or almost entirely stable, under these conditions. However, the APTES surface showed a significant loss of nitrogen (ca. 20%), and the APDMES surface suffered an even greater loss (ca. 40%). These results suggest that APTES' three reactive groups, which could form a network or attach at more than one place to the surface, are harder to hydrolyze than the singly bonded APDMES molecules. In the second trial, aminosilane surfaces that had been immersed in the pH 10 buffer for 2 h, and then characterized, were again immersed in the pH 10 buffer for an additional 2 h. These results are similar to those obtained in the third trial in which aminosilane surfaces were immersed continuously in the pH 10 buffer for 4 h. In the results from these longer exposures the APDIPES surfaces began to show real loss of nitrogen (ca. 5–20%), but not as great as APTES (ca. 30–35%) or APDMES (ca. 60–65%).

**Table 3. Sample Wetting and Thickness Properties after Six Months of Storage**

property	APTES	APDMES	APDIPES
$\theta_a(\text{H}_2\text{O})$	no change <sup>a</sup>	no change <sup>a</sup>	no change <sup>a</sup>
$\theta_r(\text{H}_2\text{O})$	$31 \pm 1^\circ$	$42 \pm 0^\circ$	$43 \pm 1^\circ$
film thickness	$8.1 \pm 0.2 \text{ \AA}$	$8.3 \pm 1.0 \text{ \AA}$	$8.7 \pm 0.6 \text{ \AA}$

<sup>a</sup> Indicates that there was essentially no change in the advancing water contact angle ( $\theta_a(\text{H}_2\text{O})$ ) of the surfaces after six months of storage in the laboratory.

**Figure 3.** UV-vis absorbance spectra of a cyanine dye adsorbed on APTES (blue), APDMES (green), and APDIPES (red) surfaces.

The second stability test consisted of simply storing aminosilane-coated surfaces in the laboratory for six months. Accordingly, three APTES, three APDMES, and three APDIPES surfaces were stored for six months and then cleaned and reanalyzed by spectroscopic ellipsometry and contact angle goniometry (see Table 3). The thicknesses of the APTES, APDMES, and APDIPES layers increased by  $1.5 \pm 0.5$ ,  $1.8 \pm 1.3$ , and  $0.4 \pm 1.2 \text{ \AA}$ , respectively. These results suggest, perhaps, a small amount of irreversible contamination of the APTES and APDMES surfaces, but little or no contamination of the APDIPES surface. These results are consistent with the greater hydrophobicity (lower surface free energy) of the APDIPES surface contributing to a greater resistance to contamination. The advancing water contact angles of these surfaces were found to be essentially unchanged after six months of storage. Receding water contact angles were also measured and are reported in Table 3. In addition, ToF-SIMS was performed on these surfaces to further characterize them, where peaks corresponding to the following atomic and molecular fragments were found in all the negative ion ToF-SIMS spectra:  $\text{H}^-$ ,  $\text{C}^-$ ,  $\text{CH}^-$ ,  $\text{CH}_2^-$ ,  $\text{O}^-$ ,  $\text{OH}^-$ ,  $\text{C}_2^-$ ,  $\text{C}_2\text{H}^-$ ,  $\text{CN}^-$ ,  $\text{CNO}^-$ ,  $\text{SiO}_2^-$ ,  $\text{SiO}_2\text{H}^-$ ,  $\text{SiO}_3^-$ , and  $\text{SiO}_3\text{H}^-$ . It is significant that the  $\text{CN}^-$  peak was present for all the aminosilanes, as it is characteristically found in the ToF-SIMS spectra of materials that have C–N containing moieties.<sup>35</sup> Interestingly, the  $\text{CNO}^-$  ion, which was also present in all the spectra, may have resulted from amino groups ionically bonded to silanols through  $\text{NH}_2^+/\text{OSi}$  interactions.

**B. Cyanine Dye Adsorption.** Freshly deposited silane films on glass slides and silicon wafers were treated with a 0.1 mM aqueous solution of the cyanine dye shown in Scheme 1. Glass slides were used for UV-vis absorption measurements (Figure 3) and silicon wafers were used for water contact angle and ellipsometry measurements (Table 4). The UV-vis results obtained in Figure 3 are typical of those found in these experiments—the most intense signals come from the APTES surface, followed by the APDMES surface, and finally by the APDIPES surface. Note that dye did not adsorb onto clean glass surfaces, that is, those

**Table 4. Ellipsometry and Water Contact Angle Data Obtained after Dye Treatment. These Data Were Obtained from Three Separate Experiments**

aminosilane	contact angle after dye adsorption	adsorbed dye thickness (Å)
APTES	$32.3 \pm 2.3$	$14.5 \pm 1.2$
APDMES	$51.3 \pm 0.6$	$11.7 \pm 0.8$
APDIPES	$63 \pm 2$	$7 \pm 1$

that were *not* coated with an aminosilane. (See also a duplicate experiment in the Supporting Information, which shows this trend, while also revealing some variability between the runs.) The broad absorbance band centered around 520 nm is attributable to the dimer of the dye, while the monomer absorbs at 563 nm.<sup>36</sup> That is, the dimer and monomer peaks have roughly the same height for the APDIPES and APDMES surfaces, but the dimer peak dominates on the APTES surface. These results seem reasonable in light of both the structure of the dye (*vide infra*) and also the higher number of amine groups on the APTES surface, followed by APDMES, and finally APDIPES (*vide supra*).

Thicknesses of films, as measured by spectroscopic ellipsometry, and water contact angle measurements after dye adsorption are compared in Table 4, where the water contact angles on the dye-coated surfaces decrease going from APDIPES to APDMES to APTES, that is, the more dye that is adsorbed, the lower the water contact angle. This decrease in water contact angles with increase in dye adsorption seems reasonable in light of the quaternary amine on the dye, which will be extremely hydrophilic. One might expect the dye to adsorb through ionic interactions between its two sulfonate groups and two protonated amine groups on an aminosilane surface. If a dye were attached in this manner, one might imagine the dye film thickness to be that of a chain of atoms running through the sulfonate group, the four-carbon alkyl chain, and the five-membered ring. The length of this chain, assuming the chains are standing, would be on the order of 11–14 Å, which is the change in thickness observed for the APTES and APDMES surfaces. If there were only partial coverage of the dye, the change in thickness would be less, for example, 7 Å, as is observed for the APDIPES surface.

**C. Comparison to Previous Vapor Phase Work.** Table 5 provides a comparison of our results to four other APTES/APDMES surfaces reported in the literature, which were deposited by CVD onto silicon, mica, and alumina. It should be noted that different deposition conditions and substrates would be expected to lead to somewhat different aminosilane films. For example, Fiorilli and co-workers reported the water contact angles of APTES surfaces prepared on silica wafers without and with water vapor.<sup>20</sup> Their surfaces prepared without water vapor would be closest to ours and show a water contact angle of  $38^\circ$ , which is not far from our result. Crampton<sup>21</sup> reported APTES deposition on mica in the presence of Hünig's base (diisopropylethylamine) under high (60%) and low (7%) humidity conditions. As expected, the thickness of our APTES film is in quite good agreement with their low humidity result (5.4 Å) and not their high humidity result (10.8 Å). Kurth and Bein<sup>30</sup> obtained similar results for deposition on dry surfaces ( $5 \pm 1 \text{ \AA}$ ) vs water-hydrolyzed surfaces ( $11 \pm 1 \text{ \AA}$ ). Smith and Chen obtained relatively thin (3.5 Å) films after APDMES deposition at  $70^\circ\text{C}$ .<sup>24</sup> Interestingly, our APTES and APDMES films are generally somewhat thicker than all of those reported in Table 5. One possible explanation for this difference is that our higher deposition temperature allows more aminosilane molecules to deposit on the surface, that is, as deposition begins to

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(36) Yao, H.; Isohashi, T.; Kimura, K. *J. Phys. Chem. B* **2007**, *111*, 7176–7183.

Table 5. Comparison to Other Results of Silane Vapor Phase Deposition

silane	thickness	water contact angle ( $\theta_a / \theta_r$ )	roughness	comments (all are vapor phase depositions)
Literature Results				
APTES <sup>20</sup>		38° w/o water vapor 50° w/water vapor	aggregation < 30 nm	3 Torr, 10 min, 80 °C, silicon substrate.
APTES with Hünig's base <sup>21</sup>	5.4 Å (7% rel. humid)			room temperature (RT), mica substrate.
APTES <sup>30</sup>	10.8 Å (60% rel. humid) 5 Å (dry) 11 Å (wet: pretreated w/water vapor)	50° (dry) 65° (wet)		RT, atm. pressure, Al/Al <sub>2</sub> O <sub>3</sub> substrate.
APDMES <sup>24</sup>	3.6 Å	67/42°		deposition at 70 °C on Si/SiO <sub>2</sub> .
Our Results*				
APTES	6.6 Å	44/31°	0.074 ± 0.010 nm	deposition at 150 °C on Si/SiO <sub>2</sub> .
APDMES	6.5 Å	58/42°	0.058 ± 0.010 nm	
APDIPES	8.3 Å	64/43°	0.050 ± 0.005 nm	
Related Silane				
APMDES <sup>16</sup>	10 ± 2 Å	60–65°		RT, 125–150 mmHg

\* Note that our receding contact angles were measured after sample storage in the laboratory. However, because the properties of the surfaces hardly seemed to change after storage, the receding water contact angles measured after the stability test are probably very close to the receding water contact angles that would have been measured initially, had this been done so.

occur, one might expect an increase of steric hindrance around chemisorbed silanes. A higher deposition temperature would be expected to increase mobility of both physisorbed and chemisorbed silanes, ultimately leading to greater surface functionality. By AFM, our aminosilane surfaces are very flat—nearly as flat as bare silicon. Fairly large features were present in Fiorilli's APTES layer.<sup>20</sup> In a study employing a silane related to those we used, Anderson<sup>16</sup> deposited 3-aminopropyl-1-(methyldiethoxysilane) (APMDES), which has only one methyl group instead of the two in our APDMES, at moderately high pressures (125–150 mmHg) in a desiccator. Comparing the thickness of their film to those that Crampton and Bein made under their more humid conditions suggests that Anderson's film has some multilayer character. The overall conclusion that can be drawn from Table 5 is that our results, and in particular our APTES results, are in good agreement with those previously reported and suggest the formation of dense, high-quality surfaces.

### Discussion

The results of our first stability test (immersion in a pH 10 buffer) should be compared to Smith and Chen's study of APDMES and APTES monolayers (prepared in toluene at 70 °C), and an APDMES monolayer prepared by vapor phase deposition at 70 °C, which were immersed in water at 40 °C for 24 or 48 h.<sup>24</sup> After these stability experiments, their APTES monolayers were nearly completely removed, while their APDMES films were up to half removed. In contrast, under basic conditions, we find our APTES monolayers to be more stable than our APDMES films. As noted, our films were prepared at a higher temperature (150 °C), which probably allowed for greater reagent mobility and reactivity and therefore more complete surface coverages. In addition, this higher temperature might allow APTES to bind more frequently through two Si–O bonds, further increasing its stability.

In the report of Smith and Chen, they found an aminosilane *N*-(6-aminohexyl)aminomethyltriethoxysilane ((EtO)<sub>3</sub>SiCH<sub>2</sub>NH(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>, AHAMTES) that yielded monolayers with much greater stability against hydrolysis than APTES or APDMES.<sup>24</sup> They attributed this significant improvement in aminosilane monolayer stability to the inability of AHAMTES to

form five-membered rings by nucleophilic attack of its amine group on its own silicon atom. Such five-membered rings in APTES or APTMES could, in the presence of water, lead to hydrolysis of the Si–O bond, where an amino group on a given silane molecule could similarly attack and help hydrolyze the Si–O bonds of other aminosilane adsorbates.<sup>37</sup> In any case, this earlier work begs the question regarding the enhanced hydrolytic stability of our APDIPES surfaces. Thus, it is not entirely clear whether the stability of our APDIPES surfaces is due to the hydrophobicity of the isopropyl groups, or perhaps more likely, to a combination of this effect with the steric hindrance they provide to their silicon atoms, which would limit both five-member ring formation as well as nucleophilic attack by the nitrogen atom of an adjacent silane.

### Conclusions

Some of the consequences of this work are as follows.

- (1) These results stand in contrast to those obtained in typical liquid phase depositions of silanes. That is, unless the water concentration in a solution is very tightly controlled, for example, the reagents are all very dry, the concentration of an aminosilane in the deposition solution would be expected to strongly influence the thickness of the resulting silane films. In our study, because the number of surface sites is limited, silane concentration over a wide range does not affect surface coverage. As a corollary to this statement, the lack of dependence of surface properties on deposition conditions should lead to robustness in an industrial (or other) process, that is, a small change in silane volume (an important process variable) should have little or no effect on the final film. That is, gas phase silane deposition shows industrial viability.
- (2) The wetting of the silane films is clearly a function of molecular structure. The diisopropyl silane shows a higher water contact angle than the dimethyl silane, which in turn is higher than APTES (the triethoxy-silane).

(37) Etienne, M.; Walcarius, A. *Talanta* **2003**, *59*, 1173–1188.

- (3) The fact that essentially the same films are obtained with either a large or a small volume of any of the three aminosilanes is important because it allows one to use a small volume of the reagent. We assume that the same results will be found with other silanes. Clearly, this will lower the cost of processes and make them more environmentally friendly.
- (4) XPS suggests that we can control the density of the amine groups on a silicon oxide surface by changing the structure of the adsorbate; that is, changing the nature of the groups around the silicon atom in a silane ultimately changes the density of that silane on a surface.
- (5) We can control the hydrolytic stability of adsorbed aminosilanes by changing the structure of the adsorbate. Indeed, the hydrolytic stability is substantially improved when bulky side groups are attached to silicon.
- (6) We appear to be able to control the amount of dye that adsorbs, and its aggregation, on a surface by changing the density of amine groups on the surface.
- (7) This controllable, robust, and clean process provides a straightforward way to make high quality monolayers with active amino groups for semiconductor surface modification, biosurface fabrication, and optical material improvement, *etc.* On the basis of various surface physical properties, this series of aminosilane layers presents multiple choices for practical applications and demonstrates the possibility of producing desirable surface properties by selecting and designing the layer precursors. Properties intermediate between those reported herein could probably be obtained using mixtures of these silanes.

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**Supporting Information Available:** UV-vis and absorbance curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.