Formation of Uniform Aminosilane Thin Layers: An Imine Formation To Measure Relative Surface Density of the Amine Group

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The surface of a fused silica and oxidized silicon wafer (SiO_2/Si(100)) was treated with (4-aminophenyl)trimethoxysilane (**1**), (3-aminopropyl)triethoxysilane (**2**), (3-aminopropyl)diethoxymethylsilane (**3**), and (3-aminopropyl)ethoxydimethylsilane (**4**) in solution. The thickness of thus formed aminosilane layers was determined with ellipsometry. In most cases silane coupling agents produce monolayers of 6−10 Å thickness, but reagent **2** gives multilayers with variable thickness (6−100 Å) depending upon the dipping time. The aminosilane layers were allowed to react with 4-nitrobenzaldehyde, and formation of the corresponding imines was confirmed by UV−vis spectroscopy. Relative surface density of the amines was calculated from the observed absorbance. In aqueous medium the imines were easily hydrolyzed to regenerate the amine group. The process, the formation, and the subsequent hydrolysis of the imines, can be repeated several times without any noticeable degradation of the absorption characteristics. The ellipsometric data and the measured absorbance show that **3** gives the most uniform molecular layer with the highest surface density of the amine functionality. Meanwhile, **2** provides multilayers lacking uniformity, and the other reagents produce uniform thin layers but with lower surface density of the amine.

Introduction

Slanization, in particular aminosilanization, of hydroxyl-bearing surfaces finds numerous applications in immobilization of molecules of biological interest such as enzyme and antibody, immobilization of inorganic catalysts, modification of electrodes, chromatography, and building foundation for self-assembly.[1] In all these application the reactive primary amine group exposed on the surfaces is utilized. On the aminosilanized surface, various types of molecules including ionic polymer,[2] nonlinear optical chromophores,[3,4] fullerene,[5] porphyrin,[6] transition metal complexes,[7] and even inorganic colloidal particles[8] are identified to form molecular layers through self-assembly.

The chemical and physical natures of the aminosilanized thin layer are of the utmost importance, because they influence crucially a morphology and a surface density of the immobilized or the self-assembled molecules. The deceptively simple reaction between the aminosilane coupling agents and the hydroxyl-bearing surfaces has been studied by optical ellipsometry, reflection−absorption infrared spectroscopy, quartz-crystal microbalance,[9] X-ray photoelectron spectroscopy,[10] and ^{13}C cross polarized magic angle spinning NMR spectroscopy.[10a] Bein showed that (3-aminopropyl)triethoxysilane (APRTS) provides a monolayer (5.3 silanes/nm^2; thickness of 7 Å) in the vapor phase adsorption,[11] and a layer with increased loading (6.4 silanes/nm^2; thickness of 11 Å) in the solution phase.[9a] Also, it is shown that APRTS forms a multilayer in the solution phase, while (3-aminopropyl)ethoxydimethylsilane (APREMS) forms a monolayer on silicas.[10a] Reactions of the alkoxysilane coupling agents with the hydroxyl-bearing surfaces have been studied, and their mechanisms were proposed.[12]

Herein, we wish to report an analysis of aminosilanized layers with ellipsometry and UV−vis spectrophotometry. Several typical aminosilane reagents, all of these are commercially available, were selected and tested whether they can produce uniform, compact, and thin aminosilane layers. To measure relative density of the nonabsorbing

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amine groups, an imine formation with 4-nitrobenzaldehyde was applied.

Experimental Section

General Procedures. Procedures. The silane coupling agents (SCA) **1**, **3**, and **4** were purchased from Gelest, Inc. SCA **3** and **4** were stored under nitrogen. All other chemicals including the coupling agent **2** are of reagent grade from Aldrich Chemical Co. Anhydrous toluene and methanol were from Aldrich Chemical Co. and used as received. All solvents for the self-assembly process are of HPLC grade from Mallinckrodt Chemical Co. The UV grade fused silica plates (30 × 10 × 1.5 mm; surface figure > 2λ) were purchased from the CVI Laser Co. The polished prime Si(100) wafers (dopant, phosphorus resistivity, 1.5−2.1 $\Omega\cdot$cm) were purchased from MEMC Electronic Materials, Inc. UV−vis spectra were recorded on a Hewlett-Packard diode-array 8452A spectrophotometer. Contact angles were measured with face contact angle meters (Model CA-D and CA-DT) from Kyowa Interface Science Co. Deionized water (18 MΩ/cm) was obtained by passing distilled water through Barnstead E-pure 3-Module System. In order to avoid grease contamination during the silanization process, Teflon sleeves or gaskets were used for joints of the glassware.

Cleaning. The substrates were thoroughly cleaned by a procedure described elsewhere.[3b] Fused silica beakers were used to avoid possible interference of metal ions. The substrates were washed with copious amounts of deionized water and dried in vacuum. The water contact angle was typically less than 5°. Whenever the measured value is above 5°, the cleaning process is repeated until satisfactory.

Solution-Phase Silanization. Thus prepared substrates were immersed into anhydrous toluene solution (20 mL) containing an SCA (10 mg for **1**, 0.2 mL for **2**−**4**) under nitrogen atmosphere. The substrates were placed in solution at 25 °C. The reaction times were varied from several minutes to 24 h. After the silanization they were washed with toluene and baked for 30 min at 120 °C. Subsequently the substrates were sonicated in toluene, a mixture of toluene and methanol (v/v = 1/1), and methanol. For each sonication step, 2 min was allowed. Finally the substrates were dried under vacuum. In most of cases thus formed silanized substrates were used immediately for the next steps. When the substrates were stored under argon atmosphere and used later, no difference was found.

Formation of the Imines. The silanized substrates were immersed into anhydrous methanol (25 mL) containing 4-nitrobenzaldehyde (10 mg), acetic acid (0.02 mL), and Linde 4-Å molecular sieve (*ca.* 1 g) under argon atmosphere. The substrates were immersed in the solution at 50 °C for 3 h. After the condensation the substrates were washed with methanol and sonicated in methanol for 2 min. Finally the substrates were dried under vacuum.

Hydrolysis. The imine-formed substrates were immersed in water (15 mL) containing acetic acid (0.02 mL), and the aqueous solution was heated at 30 °C for 1 h. The substrates were washed with water and sonicated in water for 2 min.

Ellipsometry. All measurements were taken on an automatic ellipsometer (Rudolph AutoEL-II) equipped with a HeNe laser (632.8 nm). The imaginary and real refractive index of the silicon wafer were measured prior to the silanization. The aminosilane thin layers were analyzed again after the film formation. The reported refractive indices of the bulk materials (n = 1.421 (**2**), 1.427 (**3**, **4**)) are used for the calculation except for **1**, of which index is assumed as 1.421. The thickness was calculated using the three-phase model with a program (DafIBM) from Rudolph Research Co. The angle of incidence was 70°. More than five spots for a sample were measured, and for a spot Δ and Ψ were recorded at least three times. The calculated film thickness has typically an error of ±1 Å.

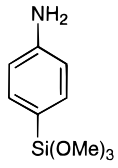
UV−vis Spectrometry. All spectra were recorded after baseline correction with a HP built-in program. Spectra of the substrates with and without the thin layers were recorded and corrected in order to measure their absorbance.

4-Nitrobenzylidene *tert*-Butylamine. The compound is prepared as described previously,[13] and its λ_{max} and extinction coefficient in various solvents have been measured. (λ_{max}, ϵ_{max}, solvent) = (282 nm, 1.56 × 10^7 cm^2/mol; CH_2Cl_2); (282 nm, 1.51 × 10^7 cm^2/mol, $CHCl_3$); (282 nm, 1.55 ×10^7 cm^2/mol; CH_3CN); (277 nm, 1.58 × 10^7 cm^2/mol, CH_3OH).

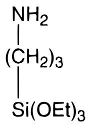
Results and Discussion

Aminosilanization. Several typical aminosilane reagents were selected and purchased. These include (4-aminophenyl)trimethoxysilane (APHTS) (**1**), (3-aminopropyl)triethoxysilane (APRTS) (**2**), (3-aminopropyl)diethoxymethylsilane (APRDMS) (**3**), and (3-aminopropyl)ethoxydimethylsilane (APREMS)(**4**). Reagents **2**, **3**, and **4** have been frequently used for the aminosilanization of substrates such as silicon wafers, fused silica, and silica gel. Reagent **1** has been included because it has a chromophore which can absorb UV light rather strongly. When this forms a thin layer on a fused silica, valuable information on the layer might be retrieved out of UV−vis spectroscopy.

Properly prepared substrates such as silicon wafers (SiO_2/Si(100)) and fused silica plates were allowed to react at room temperature with the reagents dissolved in anhydrous toluene under nitrogen atmosphere. Anhydrous condition was maintained to protect the reagents from a hydrolysis leading to a gel. Substrates were taken out at various reaction times to measure their surface properties.

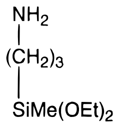


1



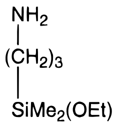
$H_2N(CH_2)_3Si(OEt)_3$

2



$H_2N(CH_2)_3SiMe(OEt)_2$

3



$H_2N(CH_2)_3SiMe_2(OEt)$

4

Thickness. Ellipsometry showed thickness of the aminosilanized layers on silicon wafers. As in Figure 1, all the reagents gave thin layers of 10, 6, 9, and 7 Å thickness, respectively, in 10 min. For each run of the reaction the measured values are reproducible except the reagent **2**. The thickness of the layer from reagent **2** invariably increased with the reaction time. However, the rates of film growth are different from batch to batch. Typically films of 50−100 Å thickness were obtained in 24 h. Moreover, the ellipsometric data of the thick film vary significantly (±5 Å) from site to site. The observation reflects inhomogeneity of the thus formed thick film. Contrastingly, for **1**, **3**, and **4** the thickness did not change significantly after 10 min of reaction. It is not certain at this point why **2** produces thick films. Nucleophilic substitution of alkoxy groups by the amine group, which will connect the layers to form the multilayer, cannot be a plausible mechanism, because alkoxysilanes are resistant to nucleophilic attack of the primary amines.[14] It has been proposed that alkoxysilane and chlorosilane reagents hydrolyze first to form hydroxysilane compounds and then dehydrate to form siloxane bridges not only among the hydroxysilanes but between the hydroxysilanes and the hydroxyl groups on the silica surfaces.[1a,d] In the mechanism the trialkoxysilane compound naturally has a higher chance of forming a three-dimensional network leading to the formation of thick films during the self-assembly. As for **1**, steric bulkiness of the phenyl group might discourage the formation of the network.

For **4**, the observed thicknesses are very close to the calculated one, but for **1** and **3,** the observed thicknesses

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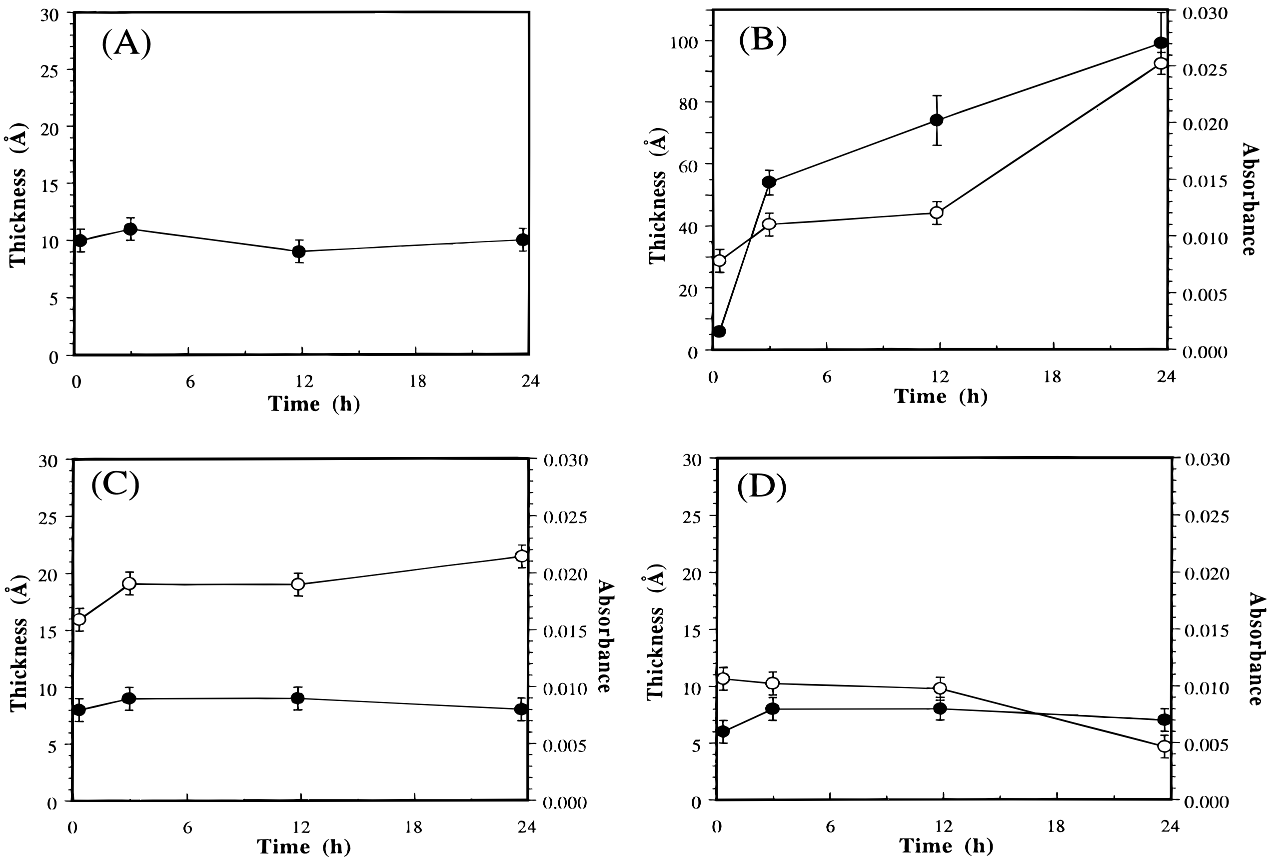
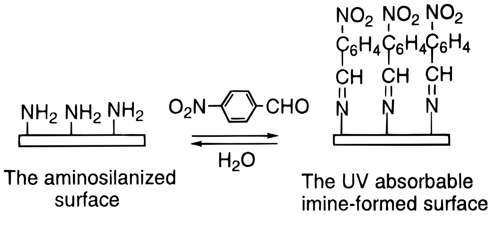


Figure 1. Thickness (●) of the aminosilane layers measured at various reaction times and absorbances (○) of the imines at these points (A) for APHTS (**1**), (B) for APRTS (**2**), (C) for APRDMS (**3**), and (D) for APREMS) (**4**). Absorbances for APHTS are omitted due to broadness of the absorption. The calculated thickness and measured absorbance have typically an error of ±1 Å and 0.001, respectively.

are slightly large.[15] The discrepancy of the observed value from the calculated one could originate from several factors resulting in errors in ellipsometry. Also, higher density of the aminosilane of the layer from **3** (*vide infra*) might result in such a difference. Alternately, formation of a tilted double layer can be speculated to explain the observed thickness. However, it is hard to explain why the reaction for building-up a multilayer does stop at the second layer even when plenty of time is allowed. Therefore, the layers from **1**, **3**, and **4** can be best described by the monolayers.

Measurement of Surface Density of the Amine Group with UV−vis Spectroscopy. Surface density of the amine group is of great concern, because it determines the density of self-assembled molecules on top of the aminosilanized layer, eventually, all other physical and chemical properties of the layer. Due to the UV absorbing nature of the aminosilane layer from **1**, its UV−vis spectra have been examined. The spectra show an absorption centering at 246 nm.[16] Out of its absorbance, surface density can be roughly calculated with an assumption that the averaged extinction coefficient of the chromophore in solvents can be applied for the self-assembled chromophore.[17] Thus calculated surface density of the amine group is 2.5 amines/100 Å^2. The density is significantly lower than the number of hydroxyl group of substrates (4.6)[18] and that of self-assembled azobenzene molecules (4.0).[19] However, lack of information about the average orientation of the chromophore deteriorates the reliability.

Scheme 1



Because popular aminosilane reagents (**2**−**4**) do not have a chromophore, measuring the surface density is no simple task. There has been a strong need to establish a direct method determining density of the amine functionality exposed on the surfaces. Several spectroscopic methods and quartz-crystal microbalance were applied to measure the density, but these methods tend to give total density in the thin layers rather than the surface density.

An imine formation (Scheme 1) between the amine group and 4-nitrobenzaldehyde was chosen to transform the nonabsorbing aminosilanized layers into absorbing lay-

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(15) The distances between hydrogens of the amine group and oxygens are calculated, and averaged. The values for **1** and **2** are 7.2 and 6.6 Å, respectively.

(16) In chloroform as well as in dichloromethane, the observed λ_{max} of the reagent **1** is 246 nm.

(17) The observed extinction coefficients are 1.35×10^7, 1.19×10^7, 1.88×10^7, and 1.46×10^7 cm^2/mol in dichloromethane, chloroform, acetonitrile, and methanol, respectively. The averaged value is 1.47×10^7 cm^2/mol.

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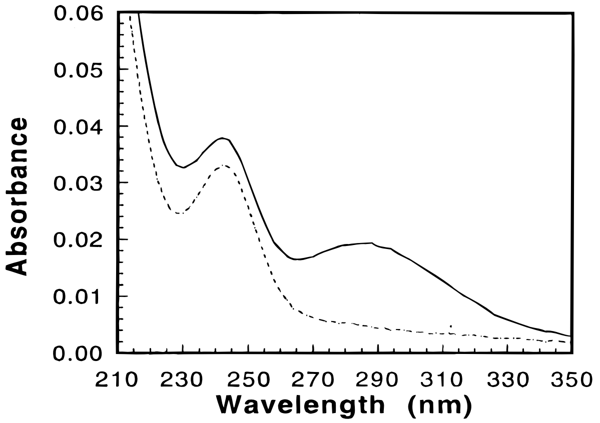

Figure 2. UV−vis spectra of the aminosilane layer (- - -) from APRDMS (**3**) and the corresponding imine-formed layer (—). Hydrolysis of the imine gives the spectrum of the original aminosilane layer. Subsequent formation of the imine restores the spectrum of the imine layer. The two-step process can be repeated several times without deteriorating the absorption characteristics.

ers.[20] If the average orientation (i.e., tilt angle) of the chromophore of each sample can be assumed to be almost the same, absorbance of the imines can used to determine the relative surface density of the chromophore as well as the amine group exposed on the surfaces.

The condensation usually can be driven by removal of water. Also use of a large excess of 4-nitrobenzaldehyde favors the forward reaction to give a quantitative yield. Indeed, the imine formation is complete in the presence of a molecular sieve, acetic acid, and a large excess of 4-nitrobenzaldehyde in 3 h. The absorbance of the imines does not increase after this. It is found that the condensation is not complete without the molecular sieve and acetic acid.

The imine formed with the layer from **1** shows only a broad absorption; thereby λ_{max} of the spectrum is unable to be assigned. Contrastingly, the imines with the layer from **2**−**4** show an absorption sharp enough to assign their λ_{max} as 286−288 nm (Figure 2). These values are very close to that of 4-nitrobenzylidene *tert*-butylamine in solvents of medium polarity (282 nm). As in Figure 1, relatively weak absorbance (0.0078) was observed from reagent **2** at the early stage of the reaction. The absorbance does not increase significantly until 12 h and increases up to 0.025 at 24 h. Therefore, **2** produces a multilayer of 50 Å thickness with a low density of the amine group in 12 h and a multilayer of 100 Å thickness with a relative high density in 24 h. **4** produces a thin layer during the whole span of reaction time, The relative weak absorbances indicate the low density of the amine groups on the surface. It is noteworthy that **3** always gives a uniform thin layer of 9 ± 1 Å thickness with a stronger absorbance after 10 min. The absorbances measured between 3 and 24 h can be converted into 3.7−4.2 of the amine groups in 100 Å^2, when the averaged extinction coefficient (1.55×10^7 cm^2/mol) was used for the calculation.[21,22] Therefore, it can be concluded that the aminosilane reagent **3** produces the aminosilanized layer with the highest uniformity and surface density.

Hydrolysis. Hydrolysis of the imine is important because it enables us to restore the analyzed surface to its original state, the aminosilanized surface, for further application. It is demonstrated that thus formed imine on the layer from **3** can be completely hydrolyzed in a mild condition in an hour. As in Figure 2, the process, the imine formation and the subsequent hydrolysis, can be repeated several times without deteriorating the UV−vis absorption characteristics. Therefore, the amine group can be perfectly restored after the imine formation and spectroscopic measurements for the next application.

Conclusion

Among several aminosilane reagents tested, (3-aminopropyl)diethoxymethylsilane (**3**) produces a monolayer of the highest primary amine density on the surface of fused silica and oxidized silicon wafer. Density of the amine group on the surface can be monitored by UV−vis spectroscopy when the nonabsorbing functional group is transformed into the aromatic imine. Moreover, the imine can be quantitatively hydrolyzed in an aqueous medium to regenerate the original primary amine group. The facile and quantitative nature of the hydrolysis enables us to measure the density of the amine group without degrading the nature of the aminosilanized surfaces.

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[21] Because both sides of the substrates absorb the light, the observed absorbances are divided by two and transformed into a unit of surface density as in the following: $S = A/(2\epsilon_{av}) = 0.0214/(2 \times 1.55 \times 10^7\ \text{cm}^2/\text{mol}) = 6.90 \times 10^{-10}\ \text{mol/cm}^2 = 4.16$ molecules/100 Å^2.

[22] The measurable maximal density might be limited by the volume of the imines.