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Absolute Surface Density of the Amine Group of the Aminosilylated Thin Layers: Ultraviolet−Visible Spectroscopy, Second Harmonic Generation, and Synchrotron-Radiation Photoelectron Spectroscopy Study

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The surface of a fused silica and oxidized silicon wafer (SiO_2/Si(100)) was treated with (3-aminopropyl)triethoxysilane (**1**), (3-aminopropyl)diethoxymethylsilane (**2**), and (3-aminopropyl)ethoxydimethylsilane (**3**) for 72 h in solution. Thickness of the aminosilylated film out of **1** increases rapidly, and it turns out to be around 100 Å in 72 h. Rather slow increase of the thickness is observed for **2**, which produces the layers of 8 and 14 Å in 10 and 72 h, respectively. The reagent **3** produces the monolayers of constant thickness 7−8 Å during the whole span of the reaction. The aminosilane layer was allowed to react with 4-nitrobenzaldehyde to form an imine, and absorbance (A_{surf}) of the imine was recorded by UV−vis spectroscopy. The imine was hydrolyzed in a known volume of water to produce 4-nitrobenzaldehyde, and subsequently its absorbance was measured. Thus observed number of the aldehyde molecules is equivalent to the number of the imine molecules on the surface. With the known surface area of the substrates, the absolute surface density of the imine, that is, the reactive amine group on the surface, was calculated. At an early stage of the aminosilylation with **2**, a surface density of 3.9 amine groups per 100 Å^2 was measured. A relatively low value was observed for **3**. It is also observed that **1** produces a multilayer with rough surface morphology, of which surface density increases sharply by the reaction time. Tilt angle of the imine was estimated from the A_{surf} and the absolute surface density. The angles vary among 23−47° depending on the reaction condition. Second harmonic generation of a laser light of 1064 nm was observed for the imine-formed substrates. X-ray photoelectron spectroscopy utilizing a synchrotron radiation source, in particular for the N(1s) binding energy region, confirmed the chemical transformation. Also, it is observed that the nitro group of the imine is cleaved by X-rays.

Introduction

Aminosilylation of hydroxy-bearing surfaces finds numerous applications in chromatography and immobilization of molecules of interest such as enzyme, antibody, and inorganic catalysts.[1] In all these applications the reactive primary amine group exposed on the surfaces is utilized. Through the self-assembly[2] various types of molecules are identified to form molecular layers on the aminosilylated flat surface.[3−5]

The chemical and physical natures of the aminosilylated thin layer are of the utmost importance, because they influence crucially a morphology and a surface density of the self-assembled molecules. The deceptively simple reaction between the aminosilane coupling agents and the hydroxy-bearing surfaces has been studied by quartz-crystal microbalance,[6] X-ray photoelectron spectroscopy,[7] and ^{13}C cross polarized magic angle spinning NMR spectroscopy.[8b−d] Its mechanism for the reaction was proposed.[8] We previously reported an analysis of the aminosilylated layers with UV−vis spectroscopy and ellipsometry.[4a] Relative surface density of the amines was determined by transforming the group into an aromatic imine and subsequent measuring of UV−vis absorption. However, an uncertainty still persists because the absorption depends upon the tilt angle of the chromophores.

Herein, we wish to report a determination of the *absolute* surface density of the amine group of aminosilylated layers, where a UV−vis spectrophotometer is a primary analytical tool. The layer was also analyzed with ellip-

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sometry, synchrotron-radiation photoelectron spectroscopy, and second harmonic generation.

Experimental Section

General Information. The silane coupling agents (SCA) **2** and **3** were purchased from Gelest, Inc., and were stored under nitrogen. All other chemicals including the coupling agent **1** are of reagent grade from Aldrich Chemical Co. Anhydrous toluene and ethanol were from Aldrich Chemical Co. and used as received. All solvents for self-assembly process are of HPLC grade from Mallinckrodt Chemical Co. The UV grade fused silica plates (30 × 10 × 1.0 mm or 25 × 10 × 1.8 mm; surface figure, $>2\lambda$) were purchased from CVI Laser Co. The polished prime Si(100) wafers (dopant, phosphorus; resistivity, 1.5−2.1 Ω·cm) were purchased from MEMC Electronic Materials, Inc. The substrates were thoroughly cleaned by a procedure described elsewhere.[4a,b] UV−vis spectra were recorded on Hewlett-Packard diode-array 8452A and 8453 spectrophotometers. 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 a 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.

Aminosilylation. Clean substrates were immersed into anhydrous toluene solution (20 mL) containing an SCA (0.2 mL) under nitrogen atmosphere. The substrates were placed in solution at 25 °C. The reaction time was varied from 30 min to 72 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 cases the 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.

Ellipsometry. Thickness of the samples was measured with an automatic ellipsometer as described earlier.[4a]

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

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

Hydrolysis. The imine-formed substrates were immersed in water (10 mL) containing acetic acid (0.02 mL), and the aqueous solution was heated at 30 °C for 1 h. Typically, two pieces of the substrates were enough to get reliable absorbance data. Absorbance of produced 4-nitrobenzaldehyde ($\epsilon_{max} = 1.45 \times 10^4$ M^{-1} cm^{-1} in water or 0.2% acetic acid) can be measured by sampling out an aliquot of the solution. For recovery of the aminosilylated layers, the substrates were washed with water and sonicated in water for 2 min.

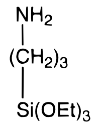
Second Harmonic Generation. The nonlinear optical properties of the thin films were investigated using second harmonic generation (SHG) in a transmission geometry. The SHG measurements were made under nonresonant conditions using the 1064 nm, 6 ns output of a Q-switched Nd:YAG laser (Spectron, SL802), operating with a repetition rate of 10 Hz. The horizontally polarized laser beam was focused onto a sample with a lens of focal length 20 cm. The beam diameter irradiated on the sample was approximately 1 mm. The sample was mounted on a motorized rotation stage, of which resolution was 0.3°. A Glan-Thompson linear polarizer was employed to detect the light of p-polarization. The second harmonic radiation was separated from the fundamental by using IR-blocking filters and band-pass filters (532.0 ± 1.5 nm). SHG was detected by a photomultiplier tube (Hamamatsu, R928), and its intensity was averaged by a boxcar integrator (SRS, SR250). The level of output signal from the boxcar integrator was monitored by an oscilloscope. A 3 mm-thick, *y*-cut quartz single crystal ($d_{11} = 1.1 \times 10^{-9}$ esu) was used as a reference.

X-ray Photoelectron Spectroscopy. The present photoemission experiments were performed at the 2B1 spherical grating monochromator (SGM) beamline of the Pohang Light Source.[9] The light source has a typical SGM with five gratings and can deliver photon energies from 12 to 1230 eV. The monochromator consists of a fixed entrance slit, five gratings, and a movable exit slit. The prefocusing mirror is located inside a shielding wall, and there is a refocusing system to deflect the photon beam to the two sample positions. At the end of the beamline, a typical experimental chamber for photoemission spectroscopy is installed. The chamber is equipped with surface analysis tools, such as a 125 mm hemispherical analyzer for photoemission spectroscopy, a reverse-view low-energy electron diffraction system, an electron gun for Auger electron spectroscopy, and an ion sputtering gun. During the experiments, the base pressure of the experimental chamber was kept at 1×10^{-10} Torr. All measurements were made with a take-off angle of 45°. The overall energy resolution (monochromator plus analyzer) was estimated to be 1.18 eV by measuring the Fermi edge of gold.

The photon energy can be selected to give the most-enhanced photoemission intensity and/or the most well resolved surface-related structure in the spectra.[10] For a survey scan, a grating (HEG2) was selected for a photon energy of 800 eV. Meanwhile, another grating (HEG1) and a photon energy of 500.8 eV were selected for the largest photoionization cross section of the N 1s orbital. In the particular case, the typical cross section is *ca.* 5 × 10^5 barns. Electron binding energies were calibrated against the C 1s emission at $E_b = 284.6$ eV. Collected data were analyzed with a least-squares fit routine.[11] Quantitative analysis was performed using a Shirley background subtraction routine.

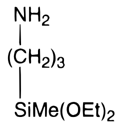
Results and Discussion

Aminosilylation. 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, (3-aminopropyl)triethoxysilane (APRTS) (**1**), (3-aminopropyl)diethoxymethylsilane (APRDMS) (**2**), and (3-aminopropyl)ethoxydimethylsilane (APREMS) (**3**). Properties of the films were measured at 30 min, 10 h, 24 h, 48 h, and 72 h of the reaction time.



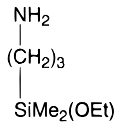
$NH_2(CH_2)_3Si(OEt)_3$

1



$NH_2(CH_2)_3SiMe(OEt)_2$

2



$NH_2(CH_2)_3SiMe_2(OEt)$

3

Thickness. Ellipsometry was utilized to determine thickness of the aminosilylated layers on silicon wafers. As in Figure 1, all the reagents gave thin layers of 6, 8, and 7 Å thickness in 30 min. For each run of the reaction the measured values are reproducible except reagent **1**. For **1**, the rates of film growth are different from batch to batch. However, the thickness of the layer invariably increased with the reaction time. Typically films of 50−100 Å thickness were obtained in 72 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. For **2**, the thickness increases slowly so that a film of 14 Å is formed in 72 h.

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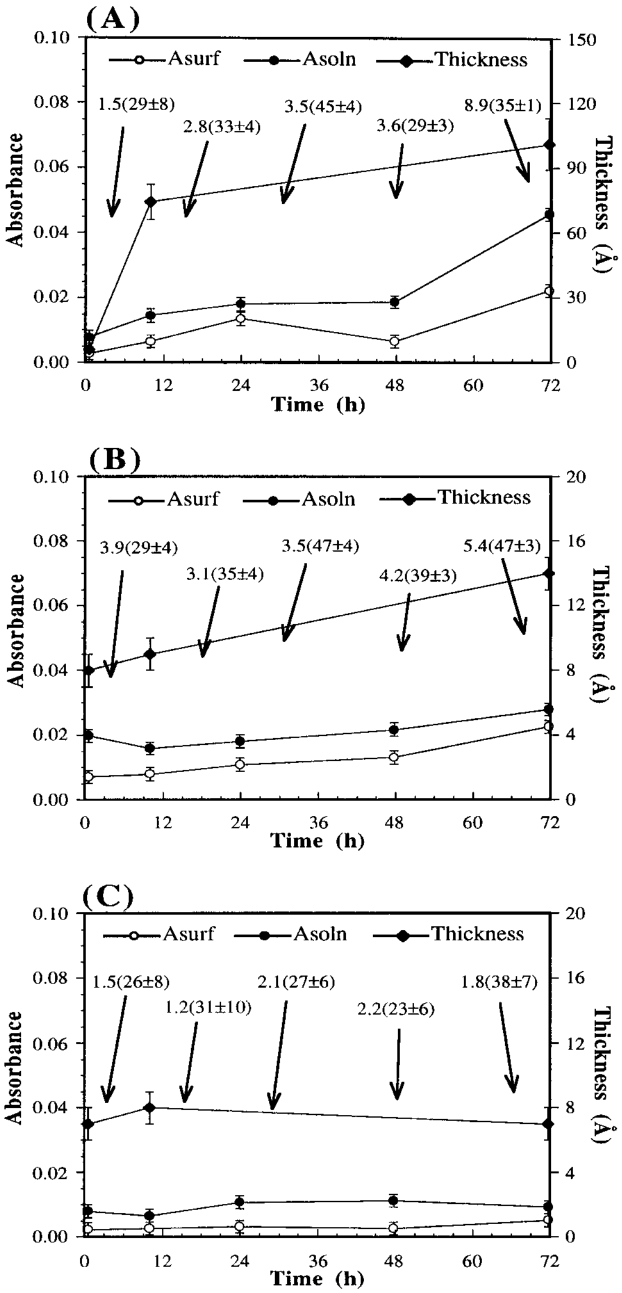
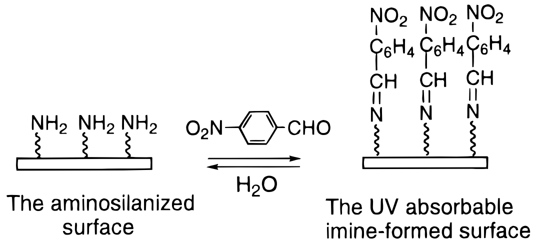


Figure 1. Thickness (◆) of the aminosilane layers measured at various reaction times; absorbance (○) of the imines (A_{surf}) and converted absorbance (●) from the produced 4-nitrobenzaldehyde: (A) for APRTS (**1**), (B) for APRDMS (**2**), (C) for APREMS (**3**). The numbers in Figure 1 represent the absolute density of the amines per 100 Å^2, and the numbers in parentheses show the tilt angle ($\langle\theta\rangle$) of the imines at these points. The calculated thickness and measured absorbance have typically an error of ±1 Å and 0.001, respectively.

Contrastingly, for **3** the measured thickness is constant after 30 min of the reaction.

It is interesting to observe such a distinctive difference among the reagents of the similar structure. 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.[12] It has been proposed that alkoxysilane and chlorosilane reagents hydrolyze first to form hydroxysilane compounds. Subsequently the latter compounds dehydrate to form siloxane bridges not only among the hydroxysilanes but between the hydroxysilanes and the hydroxyl groups on the silica surfaces.[1a,b,8,10] In the mechanism the trialkoxysilane compound naturally has the highest chance of forming a three-dimensional network leading to the formation of thick films during the self-assembly, and the dialkoxysilane analog has a lower chance. However, the monoalkoxysilane is not able to form multilayers. Therefore, our observation on the thickness fits perfectly in the last mechanism.

Scheme 1



For **3**, the observed thickness is constant during the whole span of the reaction and very close to the calculated one.[14] Thus, the formed layers can be regarded as the monolayers. For **2**, the observed value is very close to that of the monolayer at the beginning of the reaction, but the thickness increases slowly to double its value in 72 h. Therefore, it can be said that a quasi-monolayer is formed when a relatively short time is allowed for **2**. Contrastingly, a double layer is formed when a longer reaction time such as 72 h is allowed. For **1**, at a very early stage of the reaction the thickness of the film should be close to that of the monolayer. On the later stage, it is obvious that it forms a thick multilayer. It is clearly not easy to control the rate of the multilayer formation, and inhomogeneity of the films should be problematic. At any stage of the reaction, **1** produces inhomogeneous films lacking uniformity.

Imine Formation. Surface density of the amine group is of great concern, because it determines the density of self-assembled molecules on top of the aminosilylated layer, eventually all other physical and chemical properties of the layer. Naturally, there has been a strong need to establish a direct method determining density of the amine functionality exposed on the surfaces. Because the commonly used aminosilane reagents, **1**, **2**, and **3**, do not have a chromophore for UV–vis spectroscopy, measuring the surface density is no simple task.

An imine formation (Scheme 1) between the amine group and 4-nitrobenzaldehyde was chosen to transform the nonabsorbing aminosilylated layers into UV–visible absorbing layers.[15] The condensation usually can be driven by removal of water. However, use of a large excess of 4-nitrobenzaldehyde in anhydrous solvents also drives the reaction complete. Indeed, the imine formation is complete in 3 h with a large excess of 4-nitrobenzaldehyde. No increase of the absorbance after 3 h confirms the completeness of the reaction.

The imines with the layer from **1**–**3** show an absorption sharp enough to assign its $\lambda_{\max}$ as 284–288 nm.[4a] These values are very close to that of 4-nitrobenzylidene *tert*-butylamine in solvents of medium polarity (282 nm). For **1**, the relatively weak absorbance (0.0027) was observed at an early stage of the reaction as in Figure 1. Overall,

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[12] Corriu, R. J. P.; Guerin, C. *Adv. Organmet. Chem.* **1982**, *20*, 265–312.

[13] Tredgold, R. H. *Order in Thin Organic Films*; Cambridge University: Cambridge, 1994.

[14] The calculated and averaged distance between hydrogens of the amine group and oxygens for **1** is 6.6 Å.

[15] Use of the reaction for other purposes appears in ref 5.

the absorbance continuously increases with the reaction time. In 72 h, the absorbance eventually becomes the highest value, 0.0288. For **2**, a moderate absorbance (0.0071) was observed at the beginning of the reaction, and the value increases rather slowly with the reaction time. The absorbance reaches 0.0226 in 72 h. Relatively low and constant absorbances (0.0023−0.0052) were observed for **3** during the whole span of the reaction.

Out of their absorbances, relative surface density of the imines, that is, the reactive amines, could be compared, if the tilt angles of the aromatic chromophore were assumed to be constant. Under the assumption, it can be said that **1** produces a multilayer of the highest surface density and **3** a monolayer of the lowest one in 72 h. Interestingly, **2** produces a film of the highest surface density in 30 min, and it is quite true even for 10 h. For the longer reaction time, **1** exceeds in the surface density. However, information on the tilt angles of the chromophore is required for the reliable interpretation.

For control experiments, silane reagents lacking of the amine group such as *n*-butyldichlorosilane and *n*-hexyltrimethoxysilane were selected. Successful silanization was confirmed with ellipsometry and contact angle measurement. In particular, a catalytic amount of triethylamine was used to facilitate the silanization with the latter reagent. For both cases, no increase of UV−vis absorption was observed. Therefore, neither the imine formation nor physisorption of the aldehyde occurred. The control experiment eliminates the possibility that the aldehyde adsorbs on the aminosilylated surface physically.

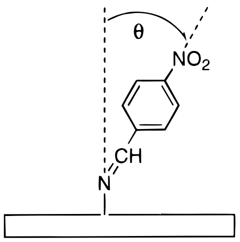
Absolute Surface Density of the Imine. Hydrolysis of the imine is important because it enables us to restore the analyzed surface to its original state, the aminosilanized surface for further application. Moreover, by measuring surface area of the substrates and the amount of 4-nitrobenzaldehyde from the hydrolysis, the absolute surface density of the imines can be calculated.[16] For example, an absorbance of 0.004 55 was observed when two pieces of the imine-formed substrates with **1** were hydrolyzed in 0.2% aqueous acetic acid (10.0 mL). The independently measured extinction coefficient gave 3.15 × 10^{-9} mol of 4-nitrobenzaldehyde. With a measured surface area (1.25 × 10^{17} Å^2), the absolute density of 1.52/100 Å^2 was calculated. For **1**, the initial density (1.5/100 Å^2) keeps increasing with the reaction time, in particular, rapidly after 48 h. Eventually the density reaches 8.9/100 Å^2 in 72 h. Because a molecule of the imine occupies ca. 20 Å^2, the higher value of the absolute density than five confirms the rough aminosilylated surface morphology produced from **1**. For **2**, the density is rather constant up to 48 h. The values (3.1−4.2/100 Å^2) are well in accord with the number of hydroxyl group of substrates (4.6/100 Å^2)[17] and the number of self-assembled azobenzene (4.0/100 Å^2).[18] However, the density becomes 5.4/100 Å^2 in 72 h. The increase of the density probably reflects the formation of rough surface as the increase of the thickness. For **3**, the density is rather constant (1.2−2.2) throughout the reaction time. The constancy is in harmony with the constant thickness and A_{surf}.

It is noteworthy that among the reagents **2** produces films of the highest absolute density (ca. 4/100 Å^2) at 30 min and 10 h of reaction time. Because the films can be regarded as the monolayers or the quasimonolayers at these stages, aminosilylation with **2** in a short period of reaction time should be the best choice to get a uniform aminosilylated layer of the highest surface density of the reactive amine group. Alternatively, when the perfect monolayer is required, use of **3** is recommended. However, the lower density of the amine group (ca. 2/100 Å^2) is a drawback.

Tilt Angles. The tilt angle of the chromophore from the surface normal (θ) can be obtained from the absorbance of the imine-formed substrate (A_{surf}) and the A_{soln} (eq 1).[19] Absorbance of the imine (A_{soln}) can be simply derived from the absolute surface density. For example, an absolute density of 1.52/100 Å^2 can be converted into a concentration of 2.53 × 10^{-10} mol cm^{-2}/*d*, where *d* is the film thickness. Because a path length of the beam is 2*d*, and because the measured extinction coefficient of a model compound, 4-nitrobenzylidene *tert*-butylamine is 1.55 × 10^7 cm^2/mol,[20] A_{soln} turns out to be 0.0078. It is an absorbance as if the imine molecules were in the random orientation like in solution. In Figure 1 the closed circles represent the values (A_{soln}).

As shown in Figure 1, tilt angle of the chromophore at early stage is 29 ± 8° and has increased to 35 ± 1° in 72 h for **1**. Because of the low value of the absorbances, which is barely larger than the experimental error (±0.001), uncertainty is significant at the early stage and is reduced at the later stage. For **2**, the value varies from 29 ± 4° to 47 ± 4°. For **3**, the value starts at 26 ± 8° and ends up with 38 ± 7°. Due to low absorbance during the entire span of the reaction, the values have a large relative error for the last case. In general, it seems that the value increases with the reaction time. However, a rather large relative error deters from putting a significance on the change. Overall, these values are in the range of 23 and 47° and are quite well in accord with the previously reported values of self-assembled aromatic hromophores.[21]

$$\sin^2 \langle\theta\rangle = 2A_{surf}/(3A_{soln}) \qquad (1)$$



Chemical Stability of the Imines. The imine in solution is susceptible to hydrolysis even at the ambient condition. The reduction of UV−vis absorption of the imine-formed substrate is observed and should be a result of the hydrolysis of the imine on the surface. Alternatively, the diminution of UV−vis absorption could be attributed to the decrease of the tilt angle (θ). However, concomitant

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[16] When the density of the amine on a flat surface is greater than 4−5/100 Å^2, the conversion to the imine could be lower than 100% due to the steric problem. In the particular case, the absolute density of the imine should be smaller than the density of the amine. The difference between the two values is reduced for a rough surface but will never go to zero.

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[19] Buscher, C. T.; McBranch, D. Li, D. *J. Am. Chem. Soc.* **1996**, *118*, 2950−2953.

[20] The extinction coefficients are 1.55 × 10^7, 1.51 × 10^7 , 1.55 × 10^7, and 1.58 × 10^7 cm^2/mol in dichloromethane, chloroform, acetonitrile, and methanol, respectively. The averaged value is 1.55 × 10^7 cm^2/mol.

[21] Tilman, N.; Ulman, A., Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *111*, 6136−6144.

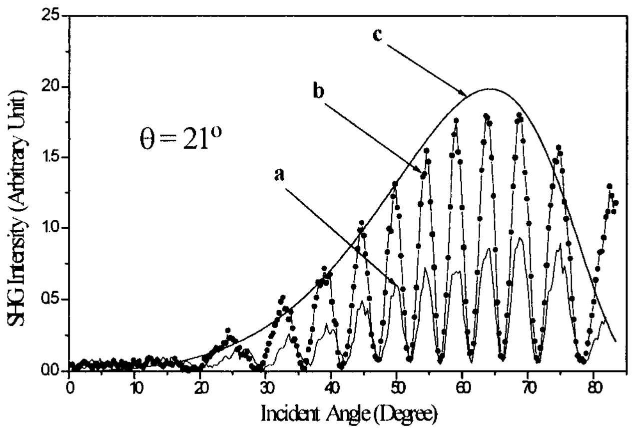

Figure 2. SHG intensity as a function of fundamental light (1064 nm) incident angle from a fused silica surface (a) and one having an imine molecular layer on both sides (b). Data points for the bare surface are deleted for clarity. The calculated curve c was obtained when the tilt angle of the chromophore is set to be 21°.

decrease of SHG intensity excludes the possibility (*vide infra*). Therefore, it is clear that the hydrolysis is the sole reason for the reduction of A_{surf}. In particular, absorbance at 284 nm decreases with the time when a sample was exposed to the atmosphere. An initial decrease of the absorbance can be expressed by an exponent, which is typical for the first-order kinetics. A half-life from an extrapolation is 38 h. However, the rate of the hydrolysis decreased after the initial decay so that 52% of the absorbance disappeared in 5 days. Because humidity is a crucial factor determining the rate of the hydrolysis, the rate varies when the samples are exposed in the uncontrolled atmosphere. Exposure time to the air should be minimal when the samples are analyzed, and they should be stored in a desiccator.

Second Harmonic Generation. The aromatic imine on the surfaces can be also analyzed by observing second harmonic generation (SHG). Tilt angle of the chromophore, that is, the aromatic imine, can be calculated from an angle dependence of the SHG intensity ($I^{2\omega}$).[22] In particular, when a noncentrosymmetric layer exists on both sides of the substrate, a characteristic interference pattern is observed. Fitting the envelope of the interferrogram gives the tilt angle of the chromophore.

Figure 2 shows a typical interferogram of the imine-formed substrates. The envelope of the simulated interferogram is fairly matched with the observed one except at large angles. The data above 75° are deleted for the calculation, and the simulated curve fits best in the observed envelope when the angle is set to be 21°.[17a,23] Because the substrate was prepared with **2** for 30 min for the particular case, it can be said that the angle coincides modestly with the one from UV−vis spectroscopy (29 ± 4°). However, the significant discrepancy between the observed and simulated envelopes deteriorates the reliability of the analysis.

Discrepancy can be originated from the following two major reasons. The first one is a weak intensity of SHG from the imine. This is primarily due to the low molecular hyperpolarizability (β) of the aromatic imine lacking of the extensive conjugation such as in stilbene and azobenzene. The observed SHG intensity is obviously larger than that of the bare and aminosilylated surfaces. The intensity of SHG out of the bare surface is close to half of that of the imine-formed substrate. The aminosilylated substrate also gives almost the same intensity and pattern of SHG as the bare surface. Unfortunately, it is not possible to separate the effect of the bare or aminosilylated surface from the SHG of the imine-formed substrates, not only because chemical species present on the surfaces keep being changed on each step of the chemical transformation but also because determining all the signs of the *b* of the involved species is not possible. Therefore, a simple subtraction is by no means applicable. Also, at this level of intensity, a noise level of the employed laser system can easily distort the interference pattern. The second one is arising from the hydrolysis. Typically it takes about 2 h to collect data for 90°. During the measurement, the hydrolysis can proceed far enough to affect the interferrogram (*vide supra*). The decrease of the SHG intensity by the exposure time was also observed, which confirms the hydrolysis. Therefore, only approximate tilt angle of the imine can be obtained from the SHG interferogram for this particular case.

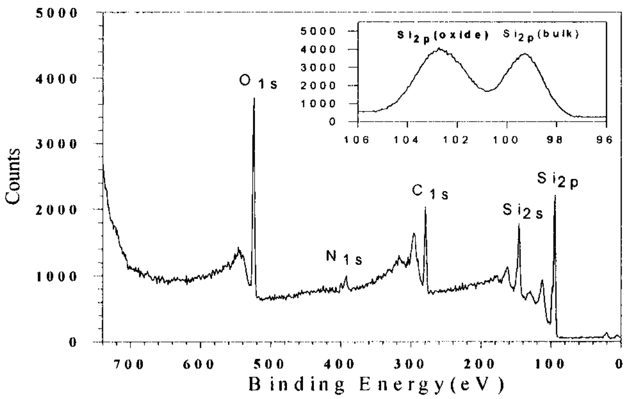

Figure 3. XPS spectrum of the imine-derivatized substrate from a survey scan. The examined substrate has a thin layer enough to show Si(2p) bulk band as shown in the inset.

Nevertheless, for the destructive interference, the SHG intensity goes to nearly zero, which reflects the homogeneity of the imine molecular layers. A very similar pattern of SHG was observed for samples prepared with **1**. For samples of **3**, SHG of the imine was barely discernible, which reflects the low density of the imine.

Synchrotron-Radiation Photoelectron Spectroscopy. A synchrotron radiation source was utilized for variable energy X-ray photoelectron spectroscopy (XPS). An X-ray of 500 eV was selected for the enhanced sensitivity for N(1s). In particular, N(1s) binding energy region was scrutinized to elucidate the involved chemical transformation. A survey scan (Figure 3) for the film from **2** shows the bands from O(1s), N(1s), C(1s), Si(2s), and Si(2p). The two Si(2p) bands originated from silicon oxide together with the siloxane (*ca.* 103 eV) and bulk silicon (99.1 eV) are evident as in the inset. In XPS for the thick aminosilylated surface prepared from **1**, the band from the bulk silicon is absent. The thick layer shows larger C(1s) and N(1s) bands and smaller Si and O(1s) bands.

To follow the change along the imine formation, aminosilylated substrates of 8 Å thickness and 5.1 amines/100 Å^2 were prepared with **2**, and an averaged spectrum out of 20 scans was obtained.[24] As in Figure 4a, the N(1s) band observed for the aminosilylated surface is a doublet of which the major peak is known as that from free amine (399.7 eV) and another peak is known as that from the

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[22] Li, D.; Ratner, M. A.; Marks, T. J.; Zhang, C.; Yang, J.; Wong, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 7389−7390.

[23] A commercially available program, Mathematica, was used for the calculation.

[24] Typically, 3−5 min is required for a scan.

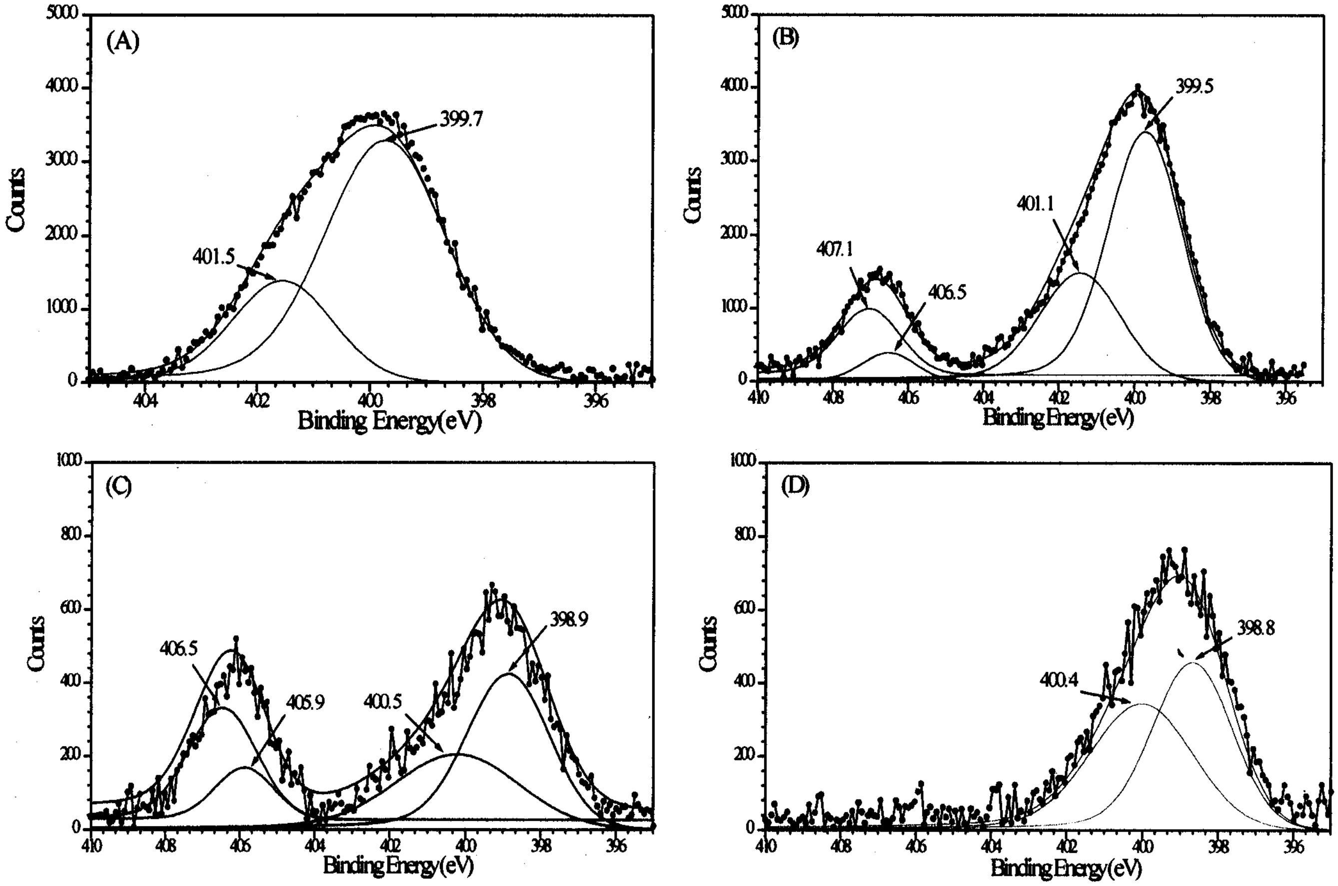

Figure 4. XPS spectra showing N(1s) energy region: (A) for an aminosilylated substrate (20 scans); (B) for the imine-derivatized substrate (20 scans); (C) for the imine-derivatized substrate (the first scan); (D) for the imine-derivatized substrate (the 20th scan).

protonated amine (401.5 eV).[7a,c,25] The amine was transformed into the imine, and data are averaged to give the spectrum (Figure 4b) after 20 scans of data collection. In the spectrum, two bands are observed in the N(1s) region. The band of lower binding energy is from the imine group, and the band of the higher binding energy is from the nitro group. The former band should be originated solely from the imine nitrogen, because all of the amine group is transformed into the imine. Deconvolution of the band gives the two peaks at 399.5 and 401.1 eV, where the intensity of the first one is larger. Position of these peaks fairly well coincides with the reported value.[26] Overall, N(1s) binding energy of the imine is very close to that of the amine. It is not clear why there are two types of the imine nitrogen at this moment. The nitro band can be deconvoluted into two peaks centering at 406.5 and 407.1 eV. Also, it is known that N(1s) of the nitro group has a binding energy of 406 eV.[25,27] Therefore, it is confirmed again with X-ray photoelectron spectroscopy that the aminosilylated surface was transformed successfully into the imine-formed surface with 4-nitrobenzaldehyde.

It is interesting to find that the nitro band is relatively large at the beginning of the irradiation (Figure 4c), is reduced as the irradiation continues, and totally disappears in 53 min (Figure 4d). After the X-ray was irradiated on a spot until disappearance of the nitro band, new spots were analyzed. The intensity of the band is fully restored for the other spots, but again reduced to zero as the irradiation. Contrastingly, the imine band did not change at all during the whole process. Also, the intensity of the C(1s) band arising from the aromatic carbons (285.1 eV) never decreased. When the samples are irradiated with X-ray of 450, 525, and 550 eV, the rates of the disappearance are comparable to that for 500 eV.[28] It is the most appropriate to conclude that the bond between the nitro group and the phenyl is cleaved by the X-ray.[29]

Conclusion

Absolute density of the amine group on the aminosilylated surfaces can be obtained by UV−vis spectroscopy. Imine formation enables us to measure the relative density, and the hydrolysis of the imine in a known volume of solvents makes it possible to measure the absolute density. Aminosilane reagents of a similar chemical structure provide aminosilylated layers of different thickness and density of the amine. Analysis of the molecular layers with X-ray photoelectron spectroscopy and nonlinear optical spectroscopy confirmed the chemical transformation on the surfaces.

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(26) Fally, F.; Doneux, C.; Riga, J.; Verbist, J. J. *J. Appl. Polym. Sci.* **1995**, *56*, 597−614.

(27) (a) Liu, G.; Freund, M. S. *Chem. Mater.* **1996**, *8*, 1164−1166. (b) Liu, Y.-C.; McCreery, R. L. *J. Am. Chem. Soc.* **1995**, *117*, 11254−11259.

(28) Photon flux of the four different energies is almost constant.

(29) The selective cleavage of the nitro group is unprecedented to the best of our knowledge.