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ARTICLE TYPE

Molecular packing density of self-assembled monolayer formed from N-(2-aminoethyl)-3-aminopropyltriethoxysilane by a vapor phase process

Hiroyuki Sugimura*[a], Takahiro Moriguchi[a], Masao Kanda[a], Yutaka Sonobayashi[a], Hirohito M. Nishimura[b], Takashi Ichii[a], Kuniaki Murase[a], Shingo Kazama[c]

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The molecular density of an aminosilane self-assembled monolayer formed from N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS) by a vapor phase method has been estimated to be about 3 AEAPS molecules per nm^2 based on chemical labeling, optical absorption spectroscopy and X-ray photoelectron spectroscopy.

Aminosilylation of a solid surface has been widely employed in order to provide chemical functions to the substrate. Onto aminosilylated surfaces, a wide variety of materials can be immobilized. For example, bio-molecules including proteins and DNA have been sucessfully fixed on aminosilylated surfaces.[1] Moreover, organic materials such as polymers, chromophores and acidic molecules have been also chemisorbed to the surfaces.[2] In addition to such organic substances, inorganic materials showed chemical affinities to amino-terminated surfaces as well. Metallic ions have been successfully trapped with surface amino groups through the complex formation between the amino groups and the ions.[3] Metallic colloids and nanoparticles posessing an attractive interaction to amino groups have been immobilized. Chemical deposition of palladium colloid, which served as a catalyst of electroless plating, onto amino-surfaces was applied to metallization of substrates.[4] Much attention has been paid for anchoring gold nanoparticles because of their plasmonic functions.[5] Besides these applications of amino-terminated surfaces as a bese surface for immobilizing molecules, materials and minute objects, surface amino groups have other interesting functions. Such a surface showed an affinity to carbon dioxide and, consequently, is useful for concentration and separation of carbon dioxide molecules.[6] Furthermore, it has been demonstrated that an aminosilyl layer enchanced adhesion of a metallic film to a substrate.[7]

Aminosilylation has been generally conducted by immersing a substrate in a proper solution of an aminosilane precursor. Another relatively new approach is vapor phase methods in which a substrate is exposed to an aminosilane vapor instead of immersing its solution.[8] Polymerization tends to be occurred when tri-functional organosilane is used as a precursor. Thus, organosilane SAMs are prepared with carefully avoiding polymerization. Due to attractive interaction between amino groups and silanol groups which are formed by hydrolysis of the precursor, aminosilane is more readily polymerized. It has been reported that, by the vapor phase methods, polymerization of aminosilane molecules could be reduced and a more uniform self-assembled monolayer was obtainable.[2f,3b,8a] Therefore, the vapor phase aminosilylation is a promising way for all the applications described above. When we use an aminosilylated surface to some applications, one essential question, that is, “how much aminosilane molecules are packed on its surface?”, comes to the front. There has been reported that absolute surface densities of aminosilane monolayers formed by a liquid phase process.[9] In this first report on the estimation of amine density, surface amino groups were first labeled with 4-nitrobenzaldehyde (NBA). NBA molecules were chemisorbed to the monolayer surface through imine bonding. Then, UV-Vis absorbance of nitro groups, from which density of the attached NBA and consequently that of the amino groups of the monolayer surface, were estimated, was measured. The authors have successfully derived absolute molecular densities of a few of alkyl-amionsilane monolayers by assuming that all the amino groups were labeled with NBA. However, considering the size of the aromatic molecule, a part of the surface amino groups might not be labeled due to steric hinderance. On this point, a further improvement thought to be needed.

In this communication, we report on a molecular packing density of an aminosilane self-assembled monolayer (SAM) formed on a fused silica substrate by a vapor phase method. We have employed N-(2-aminoethyl)-3-aminopropyltriethoxysilane (AEAPS) as a precursor for the aminosilane SAM. Di-aminosilane SAM formed from AEAPS is more effective to trap metallic ions than mono-aminosilane SAM.[3b] 2, 4, 6-Trinitrobenzene sulfonic acid (TNBS) acts as a chemical labeling agent for amino groups on the SAM. An advantage of TNBS to NBA is that one TNBS molecule has three nitro groups. Thus, optical absorption due to labeling is expected to be more distinct. From optical absorption with nitro groups of the TNBS molecules attached on the AEAPS-SAM, a surface TNBS density was estimated. Furthermore, a labeling ratio, that is, the ratio between the attached TNBS molecules to the number of the AEAPS molecules consisting of the SAM, was determined based on X-ray photo electron spectroscopy (XPS). Finally, as discussed below, a molecular packing density of our AEAPS-SAM was estimated from these two experimental values.

AEAPS (Chisso Ltd.) and TNBS (Nacalai Tesque, Inc.) was used as received. Ultra pure water with a resistivity of 18 MΩ cm was used throughout this study for all the aqueous solutions and

washing. Quartz glass substrates formed to be 20 mm × 20 mm square with a thickness of 0.2 mm and circle of 8 mm in diameter with a thickness of 0.4 mm were used for optical absorption measurements and for XPS, respectively. After sonicated in ethanol, organic contamination on each substrate was removed by a photochemical cleaning process using active oxygen species generated vacuum ultraviolet light irradiation of oxygen molecules,[8b] so as to be completely hydrophilic with a water-contact angle close to 0°. It is most likely that the substrate surface was terminated with hydroxyl groups. This hydrophilic substrate was aminosilylated with AEAPS by a vapor phase method.[3b] It was placed together with a glass cup filled with 0.1 cm^3 AEAPS liquid diluted with 0.7 cm^3 absolute toluene into a Tefron™ container. The container was sealed with a cap in a dry N_2 atmosphere. Then, the container was heated for 2 hours in an electric oven maintained at a temperature of 373 K. As schematically illustrated in Figure 1a, vaporized AEAPS molecules reacted with surface hydroxyl groups on the substrate, resulting in the formation of a monolayer. This AEAPS-SAM was formed on the both side of the substrate. After the aminosilylation, the sample was sonicated for 20 min successively in absolute toluene, absolute ethanol, 1 mM aq-NaOH and 1 mM aq-HNO_3, in that order. Finally, the sample was rinsed with ultra pure water and then blown dry with a N_2 gas stream. Its thickness was ca. 1.0 nm as confirmed by ellipsometry.[3b]

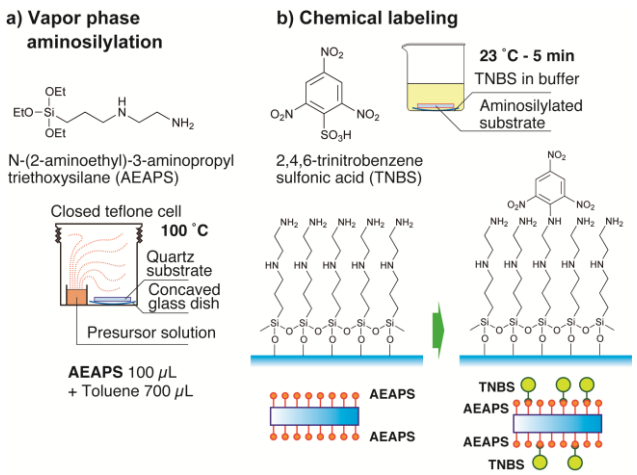

Fig. 1 Sample preparaion. (a) Vapor phase aminosilylation with AEAPS and (b) Chemical labeling with TNBS.

The substrate covered with an AEAPS-SAM was labeled with TNBS. First, 0.1 M aq-Na_2SO_3 and 0.1 M aq-$Na_2H_2PO_4$ were mixed with a volume ration of 1.5:98.5 (Solution A). Second, an aqueous solution of 0.1M $Na_2B_4O_7$ and 0.1 M NaOH was prepared (Solution B). Third, TNBS of 0.1 g was dissolved into warmed pure water of 0.2 cm^3 (Solution C). Finally, the sample was immersed in solution mix (pure water, - 2.5 cm^3, Solution B - 2.4 cm^3 and Solution C - 0.1 cm^3) keeping at a temperature of 23 ˚C. When the immersion was prolonged for 5 min, 10 cm^3 of Solution A was added in order to stop the following chemical reaction.

$$(NO_2)_3\text{-}C_6H_2\text{-}SO_3H + R\text{-}NH_2 \rightarrow (NO_2)_3\text{-}C_6H_2\text{-}NH\text{-}R + H_2SO_3 \quad (1)$$

After this TNBS labeling, the sample was sonicated in ultra pure water for 10 min.

Optical absorption at 420 nm in wavelength was measured by a spectrometer (U-3310, Hitachi, Ltd.). XPS measurements were performed using an XPS apparatus (ESCA3400, Kratos Analytical Ltd.) The X-ray source, Mg *Kα* radiation, was operated at 10 mA and 10 kV. The vacuum level under the measurement was kept at around 10^{-7} Pa.

The AEAPS-SAM/quartz glass sample labeled with TNBS showed an optical absorbance of 0.0129 at 420 nm. Since, AEAPS-SAM and TNBS were present on the both side surfaces of the substrate, the absorbance per one surface is calculated to be 0.0065. If we assume that the adsorbed TNBS molecules are all dissolved into solvent and, then, by storing this solution in an optical measurement cell, its absorbance A is measured, A is expressed by Eq. 2 from Beer-Lambert law.

$$A = \varepsilon L c \quad (2)$$

where ε is molar absorbance coefficient [cm^{-1} l mol^{-1}], L is optical path length [cm] of the cell and c is concentration [mol l^{-1}] of TNBS in solution. When, a cross sectional area of the cell is S [cm^{-2}] and its optical path length is L = 1 [cm], the total amount of TNBS, N [mol], corresponds to the amount of TNBS in a volume of SL, that is, the product of S × 1 [cm^{-3}] and c [mol/l].

$$N = cS \times 10^{-3} \quad (3)$$

In the present case, the molecules are not in the solution, but confined on the sample surface. This situation correspond to a situation that all the molecules are present on the cell wall. However, in this case, its absorbance is same with that of the solution, A, since the total amount of TNBS is same. Thus, we can use the absorbance measured from the TNBS-labeled AEAPS-SAM sample, that is, 0.0065, as the value for A. The area density of TNBS on the sample surface D [mol cm^{-2}] is expressed by Eq. 4.

$$D = N/S = c \times 10^{-3} \quad (4)$$

From Eqs. 2 and 4, D is derived as follows.

$$D = c = A/\varepsilon L = A/\varepsilon \ (L = 1 \text{ cm}) \quad (5)$$

It has been reported that ε of TNBS reacted with a primary amine and chemically bonded to the amine is 22,000 [cm^{-1} l mol^{-1}].[10] Hence, D is calculated to be 3.0×10^{-10} [mol cm^{-2}].

As schematically illustrated in Fig. 1b, it is plausible to consider that a part of the amino groups are not labeled with TNBS due to its steric hinderance. Thus, the labeling ratio must be estimated in order to obtain the true molecular density of the AEAPS-SAM. Figure 2 shows N1s-XPS profiles of the AEAPS-SAM before and after TNBS labeling. The profile **a** is a spectrum of the AEAPS-SAM without TNBS labeling, while the profile **b** is that of the TNBS-labeled AEAPS-SAM. There is a single peak around 399 eV in the spectrum **a**. This peak

corresponds to the sum of nitrogen atoms primary and secondary amines in the AEAPS-SAM. The spectrum **b** has an additional distinct peak corresponding to nitro groups at 405 - 410 eV, which is not present in the spectrum of the bare AEAPS-SAM sample, demonstrating that TNBS molecules are certainly attached to the AEAPS-SAM surface by the labeling process. An area ratio of these two peaks, $A_{\text{amin/nitoro}}$, is estimated to be 1.19. The background of the spectrum was eliminated by drawing a base line using the Shirley algorithm. Since one AEAPS molecule has two amino groups and one TNBS molecule has three nitro groups, a density ratio of AEAPS molecule to TNBS molecule, $R_{\text{AEAPS/TBNS}}$, is shown by Eq. 6.

$$R_{\text{AEAPS/TBNS}} = A_{\text{amin/nitoro}} \times (2/3) = 1.78 \quad (6)$$

This result indicates that 44% of AEAPS is not labeled with TNBS. From the values of D and $R_{\text{AEAPS/TBNS}}$, the density of AEAPS molecules in the SAM, calculated as $D_{\text{AEAPS}} = D \times R_{\text{AEAPS/TBNS}}$, is estimated to be 5.3 mol cm^{-2}. This value corresponds to 3.2 AEAPS molecules per 1 nm^2. Considering errors of the measurements, the last digit is not sufficiently reliable. Thus, we conclude that the molecular packing density of AEAPS is about 3 molecule/nm^2. This value is somewhat smaller than the reported value of 3.9 molecule/nm^2 for an aminopropylsilane monolayer formed by a liquid process.[9] It is considered that, in a liquid process, some of precursor molecules form ordered aggregates in the liquid phase to some extent and, then, adsorb to a substrate surface. This might improve packing density of the resulting monolayer. On the contrary, in a vapor phase process, each precursor molecule adsorbs singularly and randomly to a surface, accordingly, molecular density become sometimes lower than that of a liquid phase SAM.

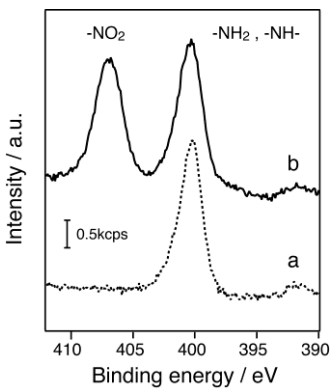

Fig. 2 N1s XPS profiles of (a) AEAPS-SAM before labeling and (b) that labeled with TNBS.

In conclusion, the molecular packing density of the vapor-phase grown AEAPS-SAM on quartz glass was measured based on chemical labeling of amino groups with TNBS. The chemisorbed TNBS density was estimated from optical absorption at 420 nm in wavelength. The labeling ratio of AEAPS/TNBS was determined from XPS by comparing the N1s peak areas corresponding to amino and nitro groups. From these two essential values, we have determined the molecular packing density of AEAPS to be about 3 molecule/nm^2.

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Notes and references

[a] *Department of Materials Science and Engineering, Kyoto University, Kyoto 606-8501, Japan. Fax: +81-75-753-5484; Tel: +81^75^753-9131; E-mail: hiroyuki-sugimura@mtl.kyoto-u.ac.jp*
[b] *Institute for Frontier Medical Sciences, Kyoto University, Kyoto 606-8507, Japan.*
[c] *Chemical Research Group, Research Institute of Innovative Technology for the Earth, Kizugawa, Kyoto, 619-0292 Japan.*

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