

Thermal Characterization of Amino-Terminated Self-Assembled Monolayers

Azusa Shida, Hiroyuki Sugimura*, Atsushi Hozumi**, Yutaka Sawada*** and Osamu Takai****

Yokohama City Center for Industrial Technology and Design, 1-1-1 Fukuura, Kanazawa-ku,
Yokohama 236-0004, JAPAN

Fax: 81-45-788-9555, e-mail: azusash@blue.plala.or.jp

* Department of Materials Processing Engineering, Graduate School of Engineering, Nagoya
University, Furo-cho, Chikusa-ku, Nagoya 464-8603, JAPAN

Fax: 81-52-789-3260, e-mail: sugimura@numse.nagoya-u.ac.jp

** National Institute of Advanced Industrial Science and Technology, 2266 -98 Anagahora,
Shimo-shidami, Moriyama-ku, Nagoya 463-8560, JAPAN

Fax: 81-52-736-7182, e-mail: a.hozumi@aist.go.jp

*** Department of Applied Chemistry, Graduate School of Engineering, Tokyo Institute of
Polytechnics, 1583 Iiyama, Atsugi 243-0297, JAPAN

Fax: 81-46-242-3000, e-mail: sawada@chem.t-kougei.ac.jp

**** Center for Integrated Research in Science and Engineering, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464-8603, JAPAN

Fax: 81-52-789-3260, e-mail: takai@otakai.numse.nagoya-u.ac.jp

Three types of amino-terminated self-assembled monolayers were prepared from aminosilanes having different numbers of ethoxy group, such as (3-aminopropyl)triethoxysilane and (3-aminopropyl) dimethylethoxysilane, on Si wafers with a thin oxide film. The structure of the aminosilane films are so complicated that the molecules are likely to have various conformations. Thermal Desorption Spectrometer (TDS) was executed in the range from 333K to 873K in order to clarify the interfacial bonding states of the aminosilane films to the Si substrates. The films showed higher thermal stabilities than the start molecules did. Furthermore, slightly different contact angles of the films were indicating that their interface properties as well as the surfaces possibly govern characteristics of the films. The number of ethoxy group in each of the start molecules influenced the structure of the film and, accordingly, its thermal stability.

Key words: Self-assembled monolayer, Aminosilane, ζ -potentials, Thermal desorption spectrometer

1. INTRODUCTION

Self-assembled monolayer (SAM) has widely been attracted in these decades. Especially alkanethiol or disulfide compounds on Au substrate have been executed intensive studies [1]. Many compounds were applied for the precursor for the SAM. Aminosilane was one of the useful precursors for the SAM. It has various used as fiber adulterants, adhesive joints [2], coupling agents [3], and the coatings on metal [4], so the structure and morphology of these materials are of great interest [5]. Because of the self-assembling of the source molecules, we can obtain the pinhole-free films with lower energy cost. Furthermore, stacking another molecule on the SAM causes more effective functions to the films. In order to use this type of films industrially, the fundamentals of the films such as structures, formations, and durability of the SAM films are much important. Although a few reports for the thermal characterizations of glycine [6] or alkanethiol SAMs [7]

have been reported, there are few reports for the thermal characterizations of the aminosilane SAMs.

In this study, we focused on three types of aminosilanes with different numbers of ethoxy group as the precursor of SAM on Si wafer. The structure or stability of the SAM film has vary with the number of bonding. And we evaluated the impact of thermal stability caused from such interfacial difference, compared with the source aminosilanes.

2. EXPERIMENTAL

Si (100) wafers were cut into 10mm squares and photochemically cleaned by 30min exposure of vacuum ultra violet light ($\lambda=172\text{nm}$) generated from an excimer lamp (Ushio Electric, UER-20, power density 10 mWcm^{-2}). After that, this substrate and a glass bottle filled with 0.8% (vol/vol) aminosilane in diluted toluene were placed together within a PTFE container (65 cm^3) [8]. This container was heated for 60 min in an oven at

373 K. Three types of aminosilanes were used, that is, (3-aminopropyl)triethoxysilane (APS-iii), (3-aminopropyl)diethoxymethylsilane (APS-ii) and (3-aminopropyl)dimethylethoxysilane (APS-i). Those aminosilanes were purchased from Shin-etsu Chemical Co. Ltd, and used no further purification.

Water-contact angles were measured at 298 K in air using an automatic contact angle meter (CA-D, Kyowa Interface Science). The thickness of films was estimated by a spectroscopic ellipsometer (M-550, JASCO). A refractive index of 1.457 was assumed for those films. ζ -potentials were measured by the electrophoretic light scattering spectrophotometer (ELSS; ELS-600, Otsuka Electronics). As the reference particle, polystyrene whose average diameter was 520 nm was used. Each KCl solution containing the reference particles was adjusted to the target pH range with NaOH and HCl [9]. XPS measurement was performed by APEX (ULVAC-PHI) equipped with an Mg-K α X-ray source (1253.6 eV). The thermal deposition spectroscopy (TDS) was performed by EMD-WA1000S/W (ESCO). The specimen was placed on a quartz stage and heated at 873 K at the rate of 60 K min⁻¹. The evolved gas from specimen was monitored by a quadruple mass analyzer (ionization voltage at 70 V).

3. RESULTS AND DISCUSSION

3.1 Formation of the self-assembled aminosilane monolayers

Three types of precursors were used for formation of aminosilane SAMs. The chemical structures of those precursors were shown in Fig. 1. The number of ethoxy group contained with precursors was different from each other. Different types of the interactions with the aminosilane and the silanol oxygen

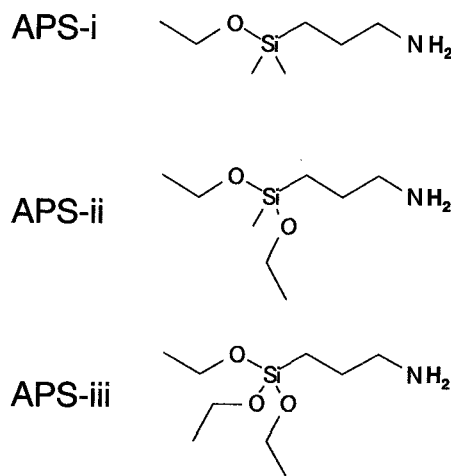


Fig. 1 Chemical structures of precursors of SAMs

onto Si substrate were reported [5, 10-11]. Deposition conditions such as solutions or curing time influenced the interfacial agent of aminosilane onto Si substrate dew to the moiety of aminosilane [12, 13]. For example, for the deposition from water without curing, the amino group was dominantly binding onto the substrate, while for the deposition from toluene without curing, aminosilane adhered downside up [11]. In toluene, the reaction mechanism was thought as follows; ethoxy groups of aminosilane reacted with hydroxyl groups of Si substrate for the silanol oxygen by S_N2 exchange reaction with the loss of Ethanol. The measurement of film thickness by spectroscopic ellipsometer showed that aminosilane films were approximately 3.52 nm thickness. Since this value contained with the thickness of silanol layer (2.91 nm) caused by photocleaning of Si wafer, adjusted aminosilane SAM (APS-i) thickness was 0.61 nm. It was almost the same as the length of the APS-i molecule. The ζ -potentials of the APS-iii SAM film was showed in Fig. 2. The isoelectric point (IEP) was approximately pH 7.8. Only a bare Si wafer, the IEP was below pH 3.0 and in the case of methyl terminated SAM, such as octadecyltrimethoxysilane, it was observed at pH 3.5 to 4.0. The IEP of APS-iii was similar to the IEP of n-(6-aminoethyl)aminopropyltrimethoxysilane. The similar conformation of surface structure showed almost the same value of the IEP [9]. Hence, in this formation, aminosilane can adhered to the Si substrate with ethoxy group and amino group was terminated on top of the surface. Although those aminosilanes took the similar formation to the Si substrate in all three APS, the contact angles of them were slightly different, that is, 20 = 50.2° for APS-i, 20 = 63.8° for APS-ii and 20 = 70.0° for APS-iii SAMs. The occupied area of each

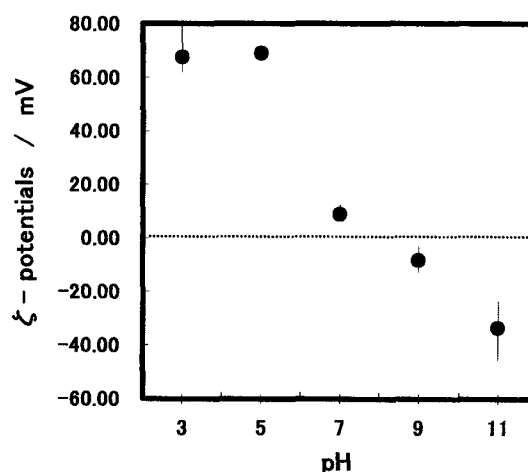


Fig. 2 The ζ -potentials of aminosilane (APS-iii) as a function of pH.

aminosilane was slightly different depends on the number of ethoxy group. Nitrogen atomic contents of each aminosilane SAM was shown in Table I. As each aminosilane had one nitrogen atom in its compound, the density of aminosilane SAM differed from each other. In this condition, as depo, the density of SAM was APS-ii > APS-iii > APS-i. It was assumed that not only the terminated group of the molecules but also packing condition of them on substrate influenced the contact angles of SAM films.

3.2 Thermal characterization of aminosilanes as resources

Prior to the investigation of thermal characterization of SAM films, that of the resource molecules has been executed. After APS-iii was left at rest in air for 100 min, TG-MASS measurement was carried out. The polymerization of silane was started in part. The amount of total gas emission (TIC) by TG-MS showed in Fig. 3. Two large peaks were given in those measurements. One was approximately at 373 K, which contained H₂O and CO₂, the other was at 723 K, the gas contained the fragments relegated $m/z = 42$ and 56 added in the fragments of first peak. Those fragments relegated $\text{--CH}_2\text{CH}_2\text{NH}_2$ and $\text{--CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$. The residual was alkoxysilane without aminopropyl group after heating at 723 K. TG curve indicated that over half of the molecules were lost in air at 723 K.

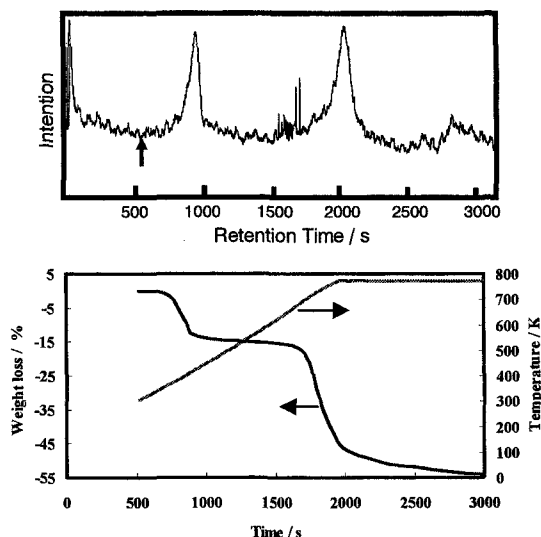


Fig.3 The amount of total emission (TIC ; upper) and weight loss (bottom) of APS-iii resource by TG-MASS. The beginning of the TG measurement was indicated by arrow in the upper.

3.3 Thermal desorption of aminosilane SAM

Total desorption of gas heated toward 873 K was showed in Fig. 4. Amount of total emission was corrected by deposited aminosilane based on the XPS measurement. Two main peaks were appeared during these heat range. One was approximately 600 K, and the other was over 723 K. Molecular mass distribution map was depicted in Fig. 5. At first, relatively small fragments were emitted and desorption of whole precursor was not shown. It indicated that aminosilane SAM films were not exfoliable from the substrate in this temperature range. Large amount of emitted gases were $M/z = 2, 15, 18$ and 28. They were inhere to H₂, CH₃, H₂O and N₂ or $\text{--CH}_2\text{--N}$, respectively. H₂ gas was detected through the whole temperature range. The first peak in Fig. 4 was mostly consisted in H₂O gas. This emission was started at 393 K and continued to the beginning of the emission of CH₃ gas at 733 K. Then N₂ or $\text{--CH}_2\text{--N}$ fragment appeared in 560 K. For the second peak, CH₃ fragment was added in the nitrogen gas. Before and after the heating, changes of the atomic contents of the specimen were shown in Table I. N1s contents derived from amino group were decreased all of the aminosilanes. Especially, APS-i SAM had lost almost all the amino group, although C1s had remained on the substrate. In consideration of XPS and TDS results, the top segment of SAM films, that is NH₂–CH₂–, was sheared off during the heating. After heating, the water contact angles of the SAM films were apt to increase except for the APS-iii SAM film. Since the structure of SAM films partly changed to the methyl terminated one, the water contact angles were increased. APS-iii SAM showed highest rate of the amino group survivals. After the heating, the residue of amino group in APS-iii and APS-ii landed up to the same level. Those phenomena resulted from the number of binding ethoxy group. Hence, only one ethoxy group, APS-i, was too weak to remain its film structure. APS-ii which had two ethoxy groups was better than APS-iii for the adsorption to the substrate, but APS-iii which had supported at three points showed most stability for heating.

Table I Atomic contents of aminosilane SAMs as depo and after heating procedures.

	Contents / atomic%					
	As Depo			After TDS		
	APS-i	APS-ii	APS-iii	APS-i	APS-ii	APS-iii
Si2p	40.3	20.9	36.3	48.9	41.2	37.5
O1s	31.7	27.4	33.7	34.5	30.3	31.9
C1s	25.9	46.8	26.9	16.4	26.7	28.8
N1s	2.2	5.0	3.1	0.2	1.8	1.8

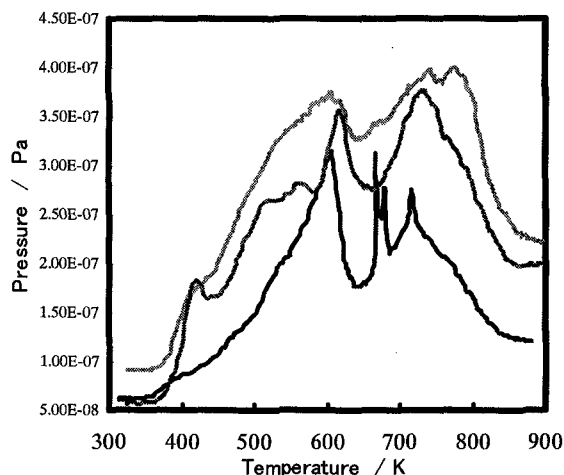


Fig. 4 Total gas desorption of aminosilane SAMs heating procedure from 323 K to 873 K. APS-iii ; upper line, APS-ii ; middle line, APS-i ; bottom line

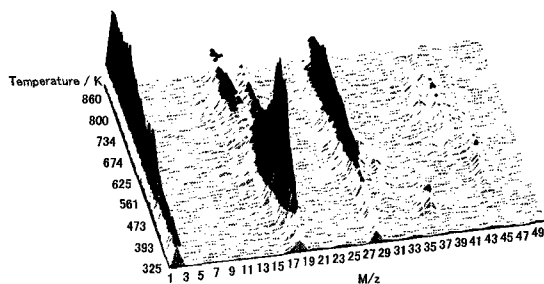


Fig. 5 Molecular mass distribution map of gas emissions of aminosilane SAM (APS-iii) as a function of heating temperature. Temperature was monitored near surface of the specimen.

4. CONCLUSION

Three types of aminosilane with different numbers of ethoxy group were modified as SAM films on Si substrate. Ethoxy group was desorbed from aminosilane, and the residue Si binded to the silanol of the substrate. The heat durability of SAM films was different from the source molecules, and SAM films showed more stable than the source molecules. Having two ethoxy groups, APS-ii, showed the effective packing on the substrate, but three-point supported aminosilane, APS-iii, indicated highest heat stability of SAM films of three all.

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REFERENCES

- [1] A. Ulman, "An Introduction for Ultrathin Organic Films From Langmuir-Brodgett to Self-Assembly", Academic Press, Boston, 1991
- [2] P. A. Heiney, K. Gruneberg, J. Fang, C. Dulcey and R. Shashidhar, *Langmuir*, 16, 2651-2657 (2000)
- [3] C-H, Chiang and J. L. Koenig, *J. Colloid Interface Sci.*, 83 (2), 361-370 (1981)
- [4] M. Rebhan, A. Plagge, M. Rohwerder and M. Stratmann, *Langmuir*, 18, 2577-2581 (2002)
- [5] B. Watts, L. Thomsen, J. R. Fabien and P. C. Dastoor, *Langmuir*, 18, 148-154 (2002)
- [6] G. Tzvetkov, M. G. Ramsey and F. P. Netzer, *Surf. Sci.*, 526 (3), 383-393 (2003)
- [7] C. Kodama and H. Nozoe, *Appl. Surf. Sci.*, 264, 169-170 (2001)
- [8] A. Hozumi, Y. Yokogawa, T. Kameyama, H. Sugimura, K. Hayashi, H. Shirayama and O. Takai, *J. Vac. Sci. Technol. A*, 19 (4), 1812-1816 (2001)
- [9] A. Hozumi, H. Sugimura, Y. Yokogawa, T. Kameyama and O. Takai, *Colls. and Surfs. A*, 182, 257-261 (2001)
- [10] P. Herder, L. Vagberg and P. Stenius, *Colls and Surfs*, 34, 117-132 (1988)
- [11] E. T. Vandenberg, L. Bertilsson, B. Liedberg, K. Uvdal, R. Erlandsson, H. Elwing and I. Lundstrom, *J. Colloid Interface Sci.*, 147 (1), 103-118 (1991)
- [12] K. C. Vrancken, P. V. D. Voort, I. G-D'Hamers, E. F. Vansant and P. Grobet, *J. Chem. Soc. Faraday Trans.*, 88 (21), 3197-3200 (1992)
- [13] G. S. Caravajal, D. E. Leyden, G. R. Quinting and G. E. Maciel, *Anal. Chem.*, 60, 1776-1786 (1988)

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