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Organosilane self-assembled monolayers formed at the vapour/solid interface

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Self-assembly of organosilane molecules at the vapour/solid interface under atmospheric pressure conditions was explored in order to form a monolayer on oxide-covered silicon substrates. Three types of precursors were employed: *n*-octadecyltrimethoxysilane (ODS: $H_3C(CH_2)_{17}Si(OCH_3)_3$), *n*-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS: $H_2N(CH_2)_6NH(CH_2)_3Si(OCH_3)_3$) and fluoroalkylsilane (FAS: heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane, $F_3C(CF_2)_7(CH_2)_2Si(OCH_3)_3$). Characteristics of these self-assembled monolayers (SAMs) formed at a temperature of 100–150 °C were studied based on ellipsometry and x-ray photoelectron spectroscopy. Chemical properties of the monolayers were characterized further by water contact angle and ζ-potential measurements. The SAMs formed from ODS and FAS were hydrophobic so as to show water contact angles of >100°, whereas that of the SAM formed from AHAPS was ~60°. ζ-potentials and isoelectric points (IEPs) of SiO_2 substrates covered with each of the SAMs were measured and compared with a naked SiO_2 substrate. The IEPs of the SiO_2 substrate covered with the ODS- or FAS-SAM was pH 3.5–4.0, which was almost the same as those of polyethylene and polytetrafluoroethylene plates, whereas that of the naked SiO_2 substrate was pH ~2.0, as predicted from results on silica particles. In the case of the AHAPS-SAM, its surface was positively charged under acidic conditions due to protonation of surface amino groups. Consequently, the AHAPS-SAM-covered substrate showed an IEP of pH 7.5–8.0. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: organosilane self-assembled monolayer; silicon oxide; chemical vapour deposition; water contact angle; x-ray photoelectron spectroscopy; ζ-potential

INTRODUCTION

Organic thin films have been applied frequently to modify the chemical and physical properties of solid surfaces. In particular, the class of organic films known as self-assembled monolayers (SAMs), spontaneously formed on certain substrates through chemisorption of organic molecules, have attracted considerable attention because of their structures with highly ordered molecules and the simplicity of the preparation process.[1] Among various SAMs, organosilane SAMs formed on hydroxyl (OH)-bearing oxide surfaces through the chemical reaction of organosilane molecules with OH sites on the surfaces are promising for practical applications, because the SAMs are markedly stable mechanically and chemically due to the strong immobilization through siloxane bondings. Such organosilane SAMs were usually prepared at the liquid/solid interface by simply immersing a substrate in a solution of precursor molecules.[2,3]

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Here, we report the recent progress in our research on the self-assembly of organosilane molecules at the vapour/solid interface. Besides the liquid-phase process usually applied to SAM preparation, the vapour-phase process is also promising, particularly because it has no need for the use of the large amount of solvents necessary in the liquid-phase processes. Furthermore, the deposition of aggregated organosilane molecules, which frequently degrades the quality of the SAMs, is expected to be smaller in the vapour-phase method than in the liquid-phase method, because such aggregated molecules have lower vapour pressure and are rarely vaporized. Thus, the vapour-phase method is considered to be practically convenient. Nevertheless, there have been only a small number of studies on the preparation of organosilane SAMs from the vapour phase.[4–13] Because the method depends on whether a precursor can vaporize or not, it is not widely applicable at present. Exploring the vapour-phase preparation of organosilane SAMs is thus of importance for developing surface modification technologies of oxide materials.

EXPERIMENTAL

Sample plates cut from n-type Si(100) wafers (Shin-etsu, Handoutai) were photochemically cleaned by exposing to

vacuum ultraviolet (VUV) light generated from an excimer lamp (Ushio Electric, UER20-172V, $\lambda = 172$ nm with a power density of 10 mW cm^{-2}).[10] Because the light at this wavelength range is strongly absorbed by atmospheric oxygen, it can propagate through a long distance only in a vacuum. This is the reason why such a light is generally called VUV. In this study, we used this VUV light in air with a short irradiation distance. Table 1 summarizes water contact angles of the Si substrate at various VUV exposure times. The substrates were VUV-irradiated in air at a distance of 10 mm from the lamp to each of the substrates. Before the VUV irradiation, the Si substrate shows a water contact angle of ~60° due to contamination. However, the water contact angle becomes smaller with an increase in VUV exposure. At an exposure of >2 min, the substrate becomes completely wet with water. Because the water contact angle of this strongly hydrophilic substrate was too small to be measured by a contact angle meter, it was expressed as <5°. Short-wavelength radiation in this range dissociatively excites the carbon–carbon and carbon–hydrogen bonds of organic molecules.[14] Furthermore, the light produces oxygen atoms and ozone molecules due to photoexcitation of atmospheric oxygen molecules.[15] Consequently, organic materials are decomposed by direct photoexcitation and by the following oxidation by active oxygen species. Note that this cleaning method is different from the conventional UV/ozone cleaning method because atomic oxygen is generated directly and contributes as well as ozone. Thus, the photoirradiated samples are cleaned by this photochemical elimination of surface organic contamination. The sample surfaces became covered with a thin silicon oxide (SiO_2) layer ~2 nm thick and the surface was completely hydrophilic with a contact angle with water of <5°. The surface was most likely terminated with hydroxyl (OH) groups. In this study, we photocleaned the samples with VUV exposure for 10 min.

The SAMs were formed through a simple method described as follows. Three types of precursors were employed: *n*-octadecyltrimethoxysilane (ODS: $H_3C(CH_2)_{17}Si(OCH_3)_3$; Tokyo Kasei Organic Chemicals), *n*-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS: $H_2N(CH_2)_6NH(CH_2)_3Si(OCH_3)_3$; Gelest Inc.) and fluoroalkylsilane (FAS: heptadecafluoro-1,1,2,2-tetrahydro-decyl-1-trimethoxysilane, $F_3C(CF_2)_7(CH_2)_2Si(OCH_3)_3$; Shin-etsu Chemical). The chemical structures of these precursors and their corresponding SAMs are shown in Fig. 1. A photocleaned SiO_2/Si plate was placed together with a glass cup filled with organosilane liquid into a 65 cm^3 Teflon™ container. When ODS and FAS were employed, the cleaned samples were placed together with a glass cup filled with 0.2 cm^3 organosilane liquid. The container was sealed with a cap and placed in an oven maintained at 150 °C. In the case of AHAPS, a glass cup was filled with 0.1 cm^3 organosilane liquid diluted with 0.7 cm^3 toluene under a dry nitrogen atmosphere in order to avoid gelation of AHAPS through polymerization. A lower temperature of 100 °C was employed for AHAPS in order to minimize polymerization of AHAPS in toluene. Subsequently, each of the samples treated with AHAPS were sonicated for 20 min successively in dehydrated ethanol and dehydrated toluene. Then, the samples were sonicated further in NaOH (1 mM) and HNO_3 (1 mM) to remove excessively adsorbed AHAPS molecules as described in the following section. We employed a sonication time of 20 min for each of the basic and acidic washings, because a longer sonication might cause degradation of the monolayer. Finally, the samples were rinsed with Milli-Q water and blown dry with a nitrogen gas stream. In most cases, these AHAPS-treated samples were used immediately for the next steps, because amino-terminated surfaces highly attract impurities from ambient air.[16]

Table 1. Water contact angles of Si substrates photochemically cleaned through VUV exposure in air

VUV exposure (min)	0	0.5	1	1.5	2
Contact angle (degree)	60	50	38	19	<5

The thicknesses of the deposited films were measured using an ellipsometer (Plasmos, SP2300) with an He–Ne laser as a light source. The angle of incidence for the measurements was set at 70°. We calculated each sample's monolayer thickness using the refractive index of Si (3.875 − 0.023i) and assuming that the monolayer and the native oxide on the Si substrate were transparent at this wavelength and had the same refractive index of 1.46. Because the resulting value was the sum of the thicknesses of the monolayer and the native oxide, the actual monolayer thickness was determined by subtracting the oxide thickness from the total. Before monolayer coating, the thickness of the native oxide layer of each sample was measured. We estimated the oxide thickness on the silicon substrate to be 2.0 nm by measuring >100 samples.

The chemical properties of the deposited films were characterized further by water contact angle measurement, x-ray photoelectron spectroscopy and ζ-potential measurement. Water contact angles of the samples were measured at 298 K in air using an automatic contact angle meter (CA-X, Kyowa Interface Science) and applying the sessile drop method. The XPS spectra of the samples were measured using Mg Kα radiation (ESCA3400, Shimadzu). The binding energy scales were referenced to 285.0 eV as determined by the locations of the

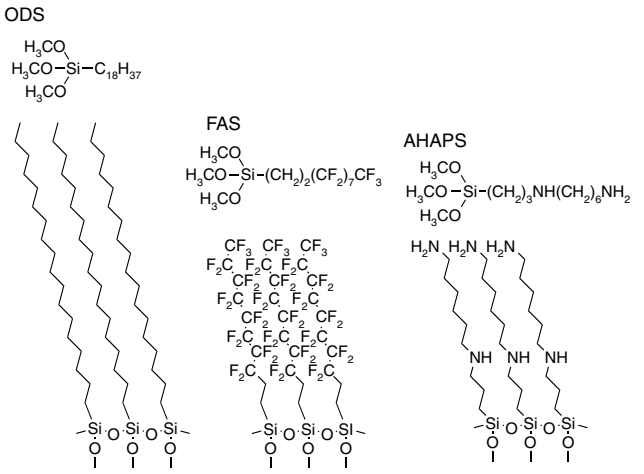

Figure 1. Chemical structures of ODS-, FAS- and AHAPS-SAMs and their precursors.

maximum peaks on the C 1s spectra of hydrocarbon (CH_x), associated with adventitious contamination. The ζ-potentials of SiO_2/Si plates covered with each of the SAMs and of a bare SiO_2/Si plate photochemically cleaned were measured at a temperature of 298 K by the use of an electrophoretic light scattering spectrophotometer (ELS-600, Otsuka Electronics). A solution containing 1 mM KCl as supporting electrolyte was used, adjusting its pH over the range of 3–11 by adding HCl or NaOH. Details of these ζ-potential measurements have been described elsewhere.[17]

RESULTS AND DISCUSSION

Organosilane molecules in a vapour or liquid phase react with OH groups on an oxide surface, resulting in the formation of a SAM as illustrated in Fig. 1. Figures 2 and 3 follow the formation of ODS-, FAS- and AHAPS-SAMs. When an SiO_2/Si substrate is treated with ODS or FAS it becomes hydrophobic, as shown in Fig. 2. The water contact angles of the ODS- and FAS-treated substrates increased with an increase in reaction time at the initial stage of chemical vapour deposition (CVD). However, they hardly increased when the CVD process had been prolonged for 3 and 1 h in the cases of ODS and FAS-treated substrates, respectively. The water contact angles of the ODS- and FAS-treated substrates reached 105° and 112°, respectively. The XPS C 1s spectra of the deposited films are shown in Fig. 4. The spectrum of the film prepared from ODS (Fig. 4(a)) consists almost of a single peak centred at 285.0 eV, indicating that a hydrocarbon film corresponding to its precursor was formed. On the other hand, the spectrum of the film prepared from FAS (Fig. 4(b)) could be resolved into six features centred at binding energies of 283.5–283.6, 285.0, 286.6–286.7, 290.5, 291.7–291.9 and 294.1 eV, which were identified according to the reported chemical shifts.[18] These components correspond to Si–C, C–C, C–O, $-\underline{C}F_2-CH_2-$, $-CF_2-CF_2-$ and $\underline{C}F_3-CF_2-$ groups, respectively. The film deposited form FAS is a fluorocarbon film which is more hydrophobic than the hydrocarbon film.

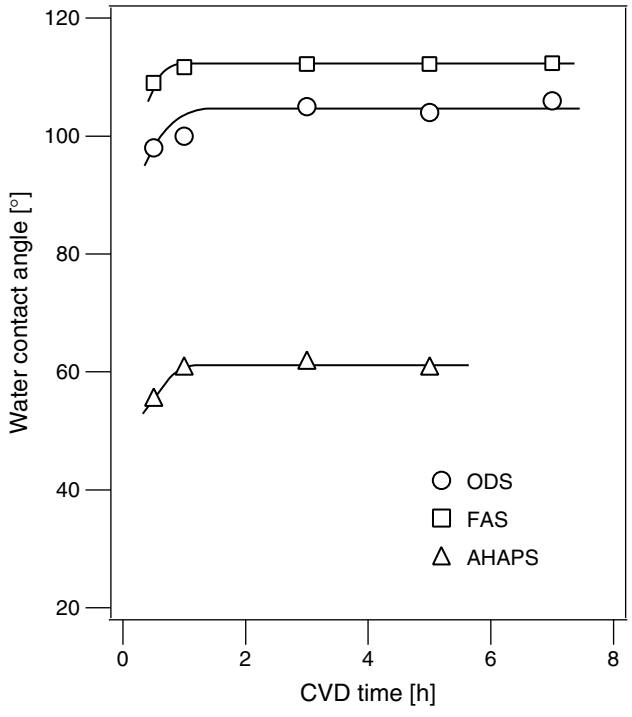

Figure 2. Water contact angles of the SAMs.

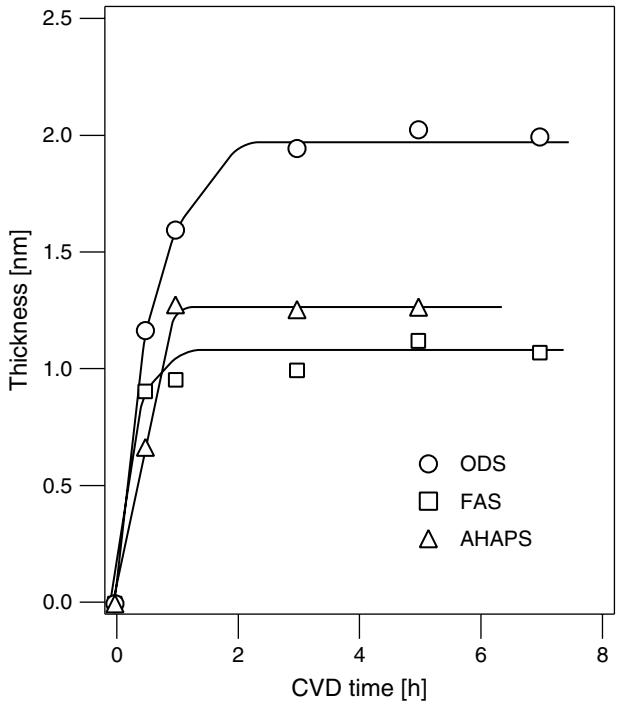

Figure 3. Thicknesses of the SAMs.

As clearly demonstrated in Fig. 3, the thicknesses of the films grown on the ODS- and FAS-treated substrates increase and stop increasing similarly. A film of 2 nm thick was grown on the ODS-treated substrate at a reaction time of >3 h, whereas a film of 1.1 nm thick was formed on the substrate treated with FAS for >1 hour. These thicknesses of the deposited films are shorter than the lengths of the corresponding precursor molecules, which were calculated to be 2.35 and 1.34 nm for ODS and FAS, respectively, using Molecular Orbital Package (Version 7). Both deposited films are thus considered to be monomolecular layers composed of packed molecules inclined by >30° to normal. The ODS has a vapour pressure of 2 Torr at 150 °C, whereas FAS's vapour pressure is 1 Torr at 86 °C. Thus, FAS is expected to show a higher vapour pressure than ODS at our preparation temperature of 150 °C, which is why ODS took longer to form a monolayer than FAS did.

Besides ODS and FAS, AHAPS also forms a monolayer. Its thickness reaches 1.3 nm at a reaction time of 1 h and remained unchanged even when the reaction time was extended up to 5 h. However, unlike the other SAMs prepared from ODS and FAS, the AHAPS-SAM formation was not reproducible when it was conducted without sonication in organic solvents and in ionic solutions. Because an amino group in the aminosilane molecule, i.e. $-NH_2$ or –NH–, may form a hydrogen or ionic bond with a methoxysilane group or its hydrolysis form, i.e., $\equiv SiOCH_3$ or $\equiv SiOH$, respectively, in another aminosilane molecule, AHAPS molecules are thought to form aggregates and to

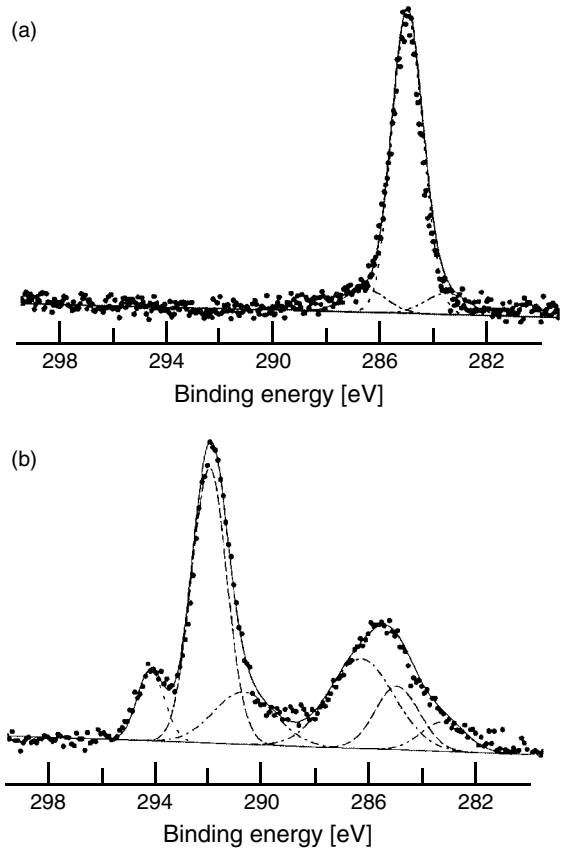

Figure 4. The XPS C 1s spectra of ODS- and FAS-SAMs. Both of the SAMs were prepared by CVD with a reaction time of 5 h.

be further adsorbed on the AHAPS-SAM surface. Indeed, thicknesses of the AHAPS deposits prior to the sonication were sometimes 2–3 times greater than the true thickness of the AHAPS-SAM. A considerable amount of AHAPS molecules were thought to be adsorbed on the SAM surface.[18] The thickness of the AHAPS-SAM, i.e. 1.3 nm, is slightly smaller than the calculated molecular length of 1.48 nm. The adsorbed AHAPS molecules formed a monolayer but probably inclined ~25° to normal. Although simply physisorbed AHAPS molecules can be removed by sonication in organic solvents, the chemisorbed AHAPS molecules through hydrogen and ionic bondings still remain, which is why the sonication in ionic solutions was needed.

Water contact angles of the AHAPS-treated substrates also increased with the reaction time, as indicated by the open triangles in Fig. 2. The saturated value was ~60°, in good agreement with those of the entirely amino-terminated SAMs reported in the literature.[20–22] The atomic ratio of nitrogen to carbon (N/C) of the AHAPS-SAM was estimated to be ~0.17 from XPS. This is slightly smaller than that of the chemical formula of the AHAPS molecule (N/C = 0.19), probably due to adventitious carbon contaminants on its surface. As shown in Fig. 5, an N 1s XPS peak consists of at least two chemical components with binding energies of 399.6 and 400.9 eV. The former is assigned to –NH– and $-NH_2$ groups, whereas the later corresponds to protonated amino groups, i.e. $-NH_3^+$ The AHAPS-SAM is found to be protonated partially, probably due to washing in the acidic solution in the preparation process.

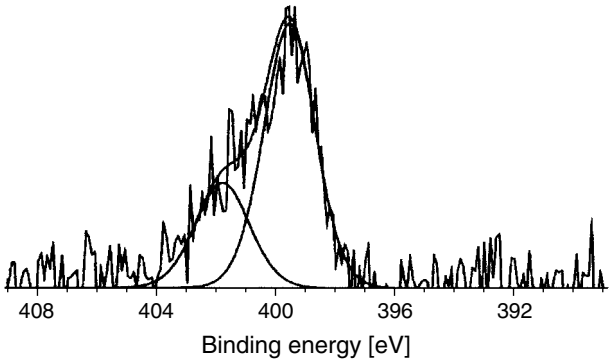

Figure 5. The XPS N 1s spectra of the AHAPS-SAM. The SAM was prepared by CVD with a reaction time of 3 h.

Figure 6 depicts the variation in ζ-potentials of the ODS-SAM- (open circle), FAS-SAM- (open square) and, AHAPS-SAM (open triangle)-covered and uncovered SiO_2/Si substrates (closed circle). Each ζ-potential was estimated from the average of the values measured three times. The error of the ζ-potentials was about ±5 mV. In the pH range 3–11, the SiO_2/Si substrate shows negative ζ-potentials of ~25–82 mV due to partial ionization of the surface silanol groups (SiOH) to -SiO^-, similar to silica particles.[23,24] Although there are no isoelectric points (IEPs) in this pH range, by extrapolating the potential curve the IEP of the SiO_2/Si substrate is estimated to be pH 2.0, coinciding with the reported IEP of silica.[25]

The pH dependence of the ζ-potentials for the ODS- and FAS-SAMs on the SiO_2/Si substrates is significantly different from those of the naked SiO_2/Si substrate. These ζ-potential vs. pH curves are nearly identical in shape and magnitude over the entire pH range. From the potential

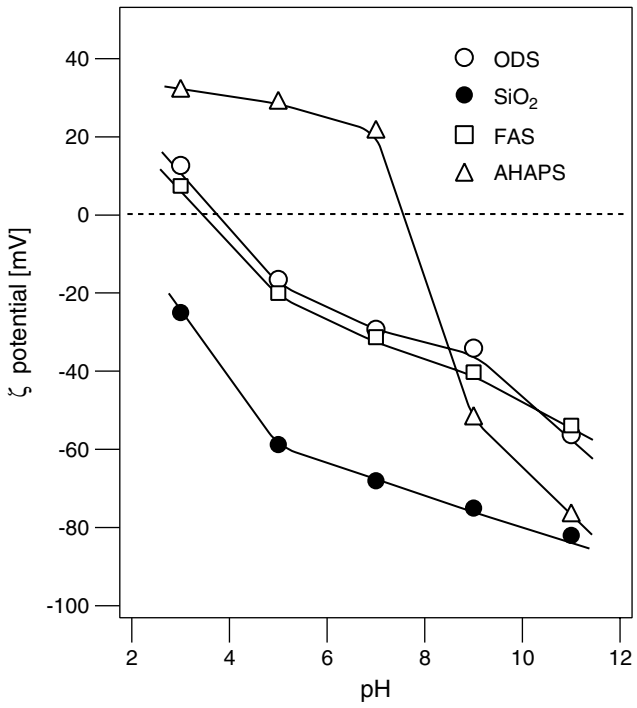

Figure 6. The ζ-potentials of the SAM-covered and naked SiO_2/Si substrates in the pH range 3–11.

curves, the negative ζ-potentials of the ODS- and FAS-SAM- covered SiO_2/Si substrates are ~35–65% lower in magnitude than those of the naked SiO_2/Si substrate. This is attributable to the reduction of the number of silanol groups on the SiO_2/Si surface because they are consumed through the covalent bonding at the SAM SiO_2/Si interface. Furthermore, the IEPs of the ODS- and FAS-SAM- covered SiO_2/Si substrates are estimated to be pH 3.5–4.0. This IEP value is higher than the IEP of the naked SiO_2/Si substrate, which is pH 2.0, and is almost the same as the IEPs of polyethylene and polytetrafluoroethylene plates, whose surfaces are terminated with $-CH_2-$ and $-CF_2-$ groups, respectively.[17] On the other hand, the AHAPS-SAM shows an IEP of pH 7.5–8.0. Its ζ-potentials are positive below pH 7.0. Under such acidic conditions, amino groups on the AHAPS-SAM are considered to be protonated to $-NH_3^+$. On the contrary, under basic conditions, the amino groups are probably converted to $-NH^-$ or $-NH_3O^-$ due to deprotonation or attachment of hydroxyl anions, resulting in large negative ζ-potentials as shown in Fig. 6.

CONCLUSION

Self-assembly of organosilane molecules at the vapour/solid interface was explored in order to modify the chemical properties of oxide-covered Si substrates. Similar to the liquid-phase self-assembly processes, monolayers were successfully formed. Onto the SiO_2/Si substrates, organosilane SAMs were formed at a temperature of 100–150 °C using three types of precursors, i.e. ODS, FAS and AHAPS, which had terminal functional groups of $-CH_3$, $-CF_3$, $-NH_2$, respectively. Based on ellipsometry and XPS, SAMs composed of the corresponding precursor molecules were confirmed to be formed. Chemical properties of the SAMs were characterized further by contact angle and ζ-potential measurements. The SAMs formed from ODS and FAS were so hydrophobic that they showed water contact angles of >105°, whereas that of AHAPS-SAM was ~60°. The IEPs of the ODS- and FAS-SAMs were in the range of pH 3.5–4.0, which was almost the same as those of polyethylene and polytetrafluoroethylene plates, whereas that of the naked substrate was pH ~2.0. The ζ-potentials of the AHAPS-SAM were positive under acidic conditions due to protonation of surface $-NH_2$ groups. Consequently, the AHAPS-SAM showed an IEP of pH 7.5–8.0.

Acknowledgements

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