

Quantification of grafted poly(ethylene glycol)-silanes on silicon by time-of-flight secondary ion mass spectrometry

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Silicon grafted monodisperse poly(ethylene glycol) (PEG) silanes with various PEG chain lengths and mixtures of these were systematically analyzed with static time-of-flight secondary ion mass spectrometry (TOF-SIMS). The mass spectra show differences in the various relative signal intensities, an observation that was used to elucidate important aspects of the grafting process. The relationship between PEG-silane fragment ion abundances and Si⁺ ion abundances were used to (i) qualitatively describe layer thicknesses of grafted mixtures of PEG-silanes on silicon, (ii) construct a calibration curve from which PEG chain length (or molecular mass) can be determined and (iii) quantitatively determine surface mixture compositions of grafted monodisperse PEG-silanes of different chain lengths (3, 7 and 11 PEG units). The results suggest that discrimination does take place in the adsorption process. The PEG-silane with the shorter PEG chain is discriminated for mixtures containing PEG3-silane, whereas the PEG-silane with the longer PEG chain is discriminated in PEG7/PEG11-silane mixtures. The origin of this difference in adsorption behavior is not well understood. Aspects of the grafting process and the TOF-SIMS analyses are discussed. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: time-of-flight secondary ion mass spectrometry; quantification; poly(ethylene glycol); silanes; protein adsorption

INTRODUCTION

Many applications require specific surface properties.¹ Nonspecific protein adsorption is a prerequisite for many biotechnical applications, e.g. optimized cell substrates.¹ or specific recognition in biosensor applications.² The prevention of non-specific adsorption or any non-specific binding is a prerequisite to ensure specific recognition for biosensor applications.² Poly(ethylene glycol)s (PEGs), also known as poly(ethylene oxide) (PEO), are powerful reagents towards providing protein repellent surfaces.³ A lot of effort has been put into modifying surfaces with PEGs in order to make them protein repellent.^{4,5} The surface properties of a PEG layer are dependent on its molecular mass,⁶ interfacial chain density.^{7,8} structural properties⁹ and whether or not the PEG layer is adsorbed or covalently grafted.

It has been shown that grafting of low molecular mass commercially available PEG-silanes on silicon (Fig. 1) yields ultra-thin hydrophilic and stable PEG monolayers with a roughness of <3 Å.¹⁰ Commercially available PEG-silanes are mixtures of PEG oligomers of various chain lengths. It is surprising that large variations in the size of the solute constituents result in such smooth adsorbed films. This behavior could result from at least two different mechanisms. The adsorption process might selectively favor one of the components owing to kinetic or equilibrium differences in reactivity. Another, less plausible, mechanism could be the formation of an umbrella-like layer of longer chain PEGsilanes below which the shorter chain PEG-silanes adsorb without causing an increase in the surface roughness.

In order to understand better why the commercial PEGsilanes exhibit such favorable properties, it is relevant to study the monodisperse PEG-silanes systematically. The properties of grafted monodisperse PEG-silanes and mixtures of these have been examined comprehensively by a multitude of techniques (N. Gadegaard, A. Papra, N. B. Larsen, K. Norrman and F. S. Kamounah, unpublished work). The current work was focused only on the problems associated with quantifying mixture compositions of grafted monodisperse PEG-silanes on silicon surfaces.

In order to determine if the adsorption process selectively favors one of the components owing to kinetic or equilibrium differences in reactivity, it is necessary to quantify the mixture composition on the surface. This is a substantial problem from a characterization point of view, because no obvious characterization techniques exist that can measure the composition of grafted PEG-silane mixtures on silicon

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Figure 1. Reaction scheme for the grafting process. Grafting conditions: 3 mM solution of PEG-silane in toluene (with 0.8 ml l⁻¹ concentrated hydrochloric acid) at room temperature for 18 h.

surfaces. If the PEG-silanes were to be chemically cleaved from the substrate, in order to analyze the composition of the desorbed PEGs or PEG-silanes, there would be no way of knowing whether or not a potential discrimination was caused by the grafting process or the cleavage process. We have employed time-of-flight secondary ion mass spectrometry (TOF-SIMS),¹¹ which is not directly a quantitative technique, to quantify the compositions of various grafted monodisperse PEG-silane mixtures on silicon surfaces.

TOF-SIMS is a powerful tool for obtaining chemical information on surfaces.¹¹ A lot of valuable information can be extracted from a surface mass spectrum, e.g. molecular and structural information, and, as is going to be evident, also quantitative information. TOF-SIMS is a technique based on mass spectrometry and is therefore said not to be a quantitative technique. However, in spite of TOF-SIMS not being a quantitative technique in principle, many workers have made extensive efforts to find ways to use TOF-SIMS quantitatively.^{12–62} Whether or not TOF-SIMS can be said to be quantitative is still debated.

The fundamental reason for mass spectrometry not being directly quantitative in principle is the different response factors associated with different species, i.e. different species produce different signal intensities per unit amount of material. For surface mass spectrometry it makes more sense to use the related property termed the secondary ion yield, which is the number of secondary ions detected relative to the number of primary ions used. The secondary ion yield is influenced by several factors, which are more or less linked, e.g. ionization probability, element type, chemical structure and surface topography and, to complicate things even more, the matrix may influence the secondary ion yield. Matrix effects prevent the signal intensities from the same type of compound on different substrates or different compounds on the same substrate from being compared, which is one of the major problems when trying to use TOF-SIMS quantitatively. However, the PEG-silanes in question differ from each other only in the number of PEG units, i.e. they are structurally and chemically very similar, so it is likely that the matrix effects are similar for all adsorbed molecules in these systems.

There are many examples in the literature reporting quantitative TOF-SIMS.¹²⁻⁶² However, they all have one

thing in common, namely that they employ calibration curves to make TOF-SIMS quantitative. One could argue that a quantification based on a calibration curve should be termed semi-quantitative. To avoid confusion we shall subsequently not distinguish between the terms quantitative and semi-quantitative.

Galuska^{21,22,24} described extensive work regarding the quantification of copolymers and polymer blends, mainly by the use of TOF-SIMS. The systems investigated included copolymers of ethylene and vinyl acetate and copolymers of ethylene and methyl acrylate. He also managed to quantify the fractions of ethylene and propylene in their copolymers, which is noteworthy since these copolymers are entirely hydrogen and carbon based and structurally and chemically very similar. He used a variety of pure C2-C3 copolymers as standards with random sequence distributions, which were verified by ¹³C NMR. The mass spectral differences between polyethylene and polypropylene are, not surprisingly, minor, which means that to make a calibration curve one needs to look at small differences in selected relative signal intensities. Furthermore, there are no unique signals; both polymers produce the same set of signals, but with minor differences in the relative signal intensities, so the signals from each component will be mixed. This will typically result in a non-linear calibration curve. The smaller the ions monitored, the less specific they are, i.e. they can be formed via various reaction channels and originate from different parts of the polymer structure.

In another study, Galuska²³ used TOF-SIMS to determine molecular masses from polymeric surfaces and microscopic phases. He analyzed a variety of elastomers and thermoplastics of known molecular mass and polydispersity index. Once again he studied relative signal intensities and correlated these with the known molecular masses. He obtained non-linear calibration curves that leveled off at ~20 000 mass units, which means that under the given conditions the mass spectra did not change for molecular masses >20 000 mass units. The appearance of TOF-SIMS mass spectra is very sensitive to changes in the chemical and physical surface properties, a fact that Galuska^{21–24} used effectively to quantify mixture compositions and molecular masses.



The approach that Galuska^{21–24} used has general applicability; thus any property for which a property change will result in a change in relative signal intensities can be quantified by constructing a calibration curve. In this work, the same approach was used to illustrate how a potential unknown chain length (or molecular mass) of a monodisperse PEG-silane adsorbed on a silicon surface can be determined from the construction of a calibration curve. Furthermore, it is demonstrated how TOF-SIMS can be used quantitatively to determine binary mixture compositions of grafted monodisperse PEG-silanes on silicon by the use of a calibration.

EXPERIMENTAL

Synthesis

Three monodisperse PEG-silanes were synthesized for this study: (i) a PEG3-silane (three monomers), (ii) a PEG7-silane and (iii) a PEG11-silane. A polydisperse PEG40-silane was also synthesized. Gas chromatographic/mass spectrometric (GC/MS) analysis showed the purities for the PEG3-silane and the PEG7-silane to be \geq 97%. The PEG11-silane partly decomposed during GC/MS and the PEG40-silane was too large to be analyzed using GC/MS.

All chemicals used were products of Fluka (Buchs, Switzerland). The tetrahydrofuran (THF) used in the syntheses was freshly distilled from sodium benzophenone. Toluene was dried using metallic sodium, filtered and stored with activated molecular sieves. Tri(ethylene glycol), tetra(ethylene glycol) and tri(ethylene glycol) monomethyl ether were dried with activated molecular sieves. All reactions were performed under a nitrogen atmosphere.

PEG3-silane

Commercially available tri(ethylene glycol) monomethyl ether was allylated using allyl chloride and *tert*-C₄H₉OK in THF (0–60 °C) to give allyloxytri(ethylene glycol) monomethyl ether. This intermediate was silylated using trimetho-xysilane and H₂PtCl₆ in toluene (90 °C, 96 h) to give the PEG3-silane.

PEG7-silane

Commercially available tri(ethylene glycol) monomethyl ether was chlorinated using thionyl chloride in benzene (pyridine, reflux) to give chloroethyloxydi(ethylene glycol) methyl ether. This intermediate was reacted with commercially available tetra(ethylene glycol) and Na in THF (100 °C) to give hepta(ethylene glycol) monomethyl ether. The hepta(ethylene glycol) monomethyl ether was then allylated with allyl chloride and Na in THF (0–25 °C) to give allyloxyhepta(ethylene glycol) methyl ether. The allyloxyhepta(ethylene glycol) methyl ether is using trimethoxysilane and H₂PtCl₆ in toluene (90 °C, 96 h) to give the PEG7-silane.

PEG11-silane

Commercially available tetra(ethylene glycol) was monoallylated using allyl chloride and NaOH in water (85 °C) to give allyloxytetra(ethylene glycol). This intermediate was then

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monotosylated using *p*-toluenesulfonyl chloride and KOH in dichloromethane (0 °C) to give allyloxytetra(ethylene glycol) tosyl ether. The allyloxytetra(ethylene glycol) tosyl ether was then reacted with hepta(ethylene glycol) monomethyl ether (from the PEG7-silane synthesis) and NaH in THF (0–25 °C) to give allyloxyundeca(ethylene glycol) methyl ether. The allyloxyundeca(ethylene glycol) methyl ether silylated using trimethoxysilane and H₂PtCl₆ in toluene (90 °C, 96 h) to give the PEG11-silane.

PEG40-silane

Commercially available polydisperse tetracosa(ethylene glycol) monomethyl ether was allylated using allyl chloride and *tert*-C₄H₉OK in THF (60 °C, 24 h) to give allyloxytetracosa(ethylene glycol) monomethyl ether. Allyloxytetracosa(ethylene glycol) monomethyl ether was then silylated using trimethoxysilane and H₂PtCl₆ in toluene (90 °C, 96 h) to give the PEG40-silane.

Grafting

We have developed a simple method to coat silicon surfaces, which has been described previously.10 We used silicon wafers (100, single side polished) purchased from Topsil (Frederiksund, Denmark). All chemicals used were products of Fluka (Buchs, Switzerland) and Aldrich (Milwaukee, WI, USA) and used without further purification for the grafting procedure. Ultrapure water was supplied by a Milli-Q system from Millipore (Bedford, MA, USA). The wafers were cut into suitable sizes (a few square centimeters) and cleaned by sonication in ethanol–water (1:1, v/v) for 5 min. The substrate was oxidized in a mixture of hydrogen peroxide (30%, w/v) and sulfuric acid (96%) (20:80, v/v) for 10 min at 120 °C. Caution: the mixture should be used with extreme care owing to its oxidizing power and risk of explosions.63 The wafers were washed with copious amounts of water, sonicated in water for 10 min, blown dry and immersed immediately in the respective solution. Grafting (Fig. 1), was performed in a 3 mM solution of PEG-silane in toluene (with 0.8 m l⁻¹ concentrated hydrochloric acid) at room temperature for 18 h.10 The samples were rinsed in toluene (once), ethanol (twice) and water (twice) and finally sonicated in water for 2 min to remove non-grafted material. The wafers were blown dry and stored dry under ambient conditions.

TOF-SIMS

The TOF-SIMS analyses were performed using a TOF-SIMS IV (ION-TOF, Münster, Germany) operated at a pressure of 5×10^{-9} Torr (with sample, 1 Torr = 133.3 Pa); 15 ns pulses of 15 keV Ga⁺ (primary ions) were bunched to form ion packets with a nominal temporal extent of <0.9 ns at a repetition rate of 10 kHz, which produced a target current of 2.5 pA. These primary ion conditions were used to scan a 500 × 500 µm area of the sample for 30 s. A flood gun was used to prevent built-up charge in the surface. Desorbed secondary ions were accelerated to 2 keV, mass analyzed in the flight tube and post-accelerated to 10 keV before detection. The scan area used (500 × 500 µm) only allowed a mass resolution of ~6000, which was more than enough to resolve all relevant mass spectral peaks. The ion abundances were normalized relative

to the total ion abundance to compensate for differences in the numbers of Ga^+ shots that each sample received together with other instrumental factors. Each sample was analyzed five times at different locations and the average value used. All measurements were repeated with a target current of 200 fA as a test for possible detector saturation. The same results were obtained, but with significantly increased uncertainties caused by the reduced signal intensities.

Ellipsometry

The adsorbed mass per surface area (effective layer thickness) was determined with a Picometer Ellipsometer (Beaglehole Instruments, Wellington, New Zealand) using phase-modulated ellipsometry at the Brewster angle of silicon. The resulting optical parameters were used in the accompanying analysis package for modeling the surface structure in a three-layer model consisting of silicon, silicon oxide and PEG. The refractive index, *n*, of the adsorbed PEG layer was assumed to be 1.46 in the model. This assumption is not critical as modeling shows that variations of the overlayer refractive index of ± 0.02 will affect the calculated layer thickness by only 2%. We analyzed three 0.8 mm diameter spots at different locations on each sample to capture spatial variations and took the average of these measurements as the effective layer thickness.

RESULTS AND DISCUSSION

The samples were all analyzed with TOF-SIMS. The ion bombardment of the sample surfaces results in desorption of fragmented pieces of PEG, of the silane and of the substrate (Fig. 2). TOF-SIMS spectra of the pure monodispersive PEGsilanes grafted on silicon are shown in Fig. 3(a)-(d). The PEG ion series observed are chain cleavage products and analogue ions with one or two hydrogens either added or subtracted. As is evident, the mass spectra show differences in the various relative signal intensities, a fact that will be used to elucidate important aspects of the grafting process.

The sampling depth for static TOF-SIMS is normally said to be \sim 1 nm.¹¹ However, for polymers and oligomers such



as the PEG-silanes in question, there is a paucity of data. We observed a sampling depth, that is significantly larger than 1 nm. Furthermore, the substrate ion, Si⁺, is so small that its escape depth could easily be larger than the PEG-silane fragments. Hence it is not surprising that the substrate signal is detectable for all samples. However, the common surface contaminant silicone oil is also a possible source for the Si⁺ signal. The lack or negligible amount of m/z 147 (Si₂C₅H₁₅O⁺, a very characteristic ion for silicone oil) in the mass spectra, Fig. 3(a)–(d), supports the fact that the samples were not contaminated prior to analysis, so it is safe to assume that all Si⁺ detected originates from the substrate or the silane interface.

Quantification of chain length

For larger PEG-silane chains, the layer will be thicker, and subsequently the likelihood of observing substrate signals will decrease. In Fig. 4, the normalized intensities of various positively charged fragment ions are shown for the PEG3-, PEG7-, PEG11- and PEG40-silane.

The substrate signal (Si⁺) is seen, as expected, to decrease for longer PEG-silane chains. The desorbed ions with the elemental composition SiCH₃O⁺ most likely originate mainly from the silane part of the PEG-silanes (Fig. 2). However, SiCH₃O⁺ can also be formed from the silicon substrate reacting with surrounding organic material. Since the silane group, owing to the chemical bond, is in close vicinity of the surface (Fig. 2), the SiCH₃O⁺ is expected, from wherever it originates, to follow the same qualitative trend as Si⁺. It is evident from Fig. 4 that this is indeed observed.

For larger PEG-silane chains there will be a greater likelihood for larger fragment pieces to be formed [compare Fig. 3(a) with Fig. 3(d)]. Furthermore, from the previous discussion it was suggested that larger PEG-silane chains result in less substrate signal. All this suggests that the abundance of the fragment ions should increase relative to the substrate signal for larger PEG-silane chains. Figure 4 shows the abundances of several fragment ions, and it is evident that the expected trend is observed. The trend is observed for all PEG fragment ions, i.e. the ions shown in Fig. 4 are only a few representative examples. However, the



Figure 2. Possible fragmentation pathways during ionization forming various desorbed fragment ions, which can be detected by the mass spectrometer. Hydrogen abstraction will result in the formation of analogue ion series containing plus or minus one or two hydrogens.



Figure 3. TOF-SIMS of (a) PEG3-, (b) PEG7-, (c) PEG11- and (d) PEG40-silane grafted on silicon. Primary ion, 15 keV Ga⁺; target current, 2.5 pA; scan area, $500 \times 500 \mu$ m. scan time, 30 s; repetition rate, 10 kHz; secondary ion energy, 2 keV; post-acceleration, 10 kV; mass resolution, ~6000. A flood gun was used for charge compensation.

 $C_3H_7O^+$ ion is the only one not to follow the trend. The silane group is connected to the PEG chain via a spacer consisting of propylene. If the spacer, including the oxygen to which it is bound, is cleaved, a $C_3H_7O^+$ ion can be formed if a hydrogen is abstracted from somewhere (Fig. 2). This is one possible explanation for $C_3H_7O^+$ not following the trend. Another possible explanation could be that $C_3H_7O^+$ is a product of a rearrangement. No attempts have been made to investigate this further.

From an analysis of all abundant ions it was found that the abundance of $C_4H_7O^+$ is most sensitive towards changes in the PEG chain length. For the silane part the abundance of SiCH₃O⁺ showed the largest sensitivity towards changes in the PEG chain length. The logarithm of the abundances for these two ions was plotted against the logarithm of the number of PEG units (Fig. 5), which in turn corresponds to the chain length or the molecular mass. Both of these plots can be used as a calibration for a grafted monodisperse PEGsilane sample with an unknown chain length. If the sample is prepared and analyzed in parallel with the standard samples, the signal intensity of $C_4H_7O^+$ or SiCH₃O⁺ will give the chain length.

Quantification of mixture composition

Since the abundance of Si⁺ is inversely proportional to the abundances of PEG fragment ions with an increase in the PEG chain length, the abundance ratio between PEG fragment ions and Si⁺ must be a sensitive measure of changes in the PEG-silane chain length or of the PEG-silane mixture composition. This relationship can be used to determine the surface composition of binary PEG-silane mixtures. If a given PEG fragment/substrate abundance ratio is considered, a crude two-point calibration can be performed based on the pure PEG-silanes, e.g. if the ratio in question is 2 for PEG3-silane and 6 for PEG7-silane, then a ratio of 4 would correspond to 50%. The result is observed to differ slightly depending on which PEG-silane fragment is considered. To compensate for this, the calculations were performed on seven of the most abundant PEG fragment ions (except $C_3H_7O^+$), and average values with corresponding standard





Figure 4. Normalized abundances measured by TOF-SIMS for selected fragment ions for PEG3-, PEG7-, PEG11- and PEG40-silane grafted on silicon. The error bars shown are standard deviations based on five measurements at different locations on the sample surface.

deviations were calculated for binary mixtures of PEG3-, PEG7- and PEG11-silane. The PEG40-silane was excluded to limit the extensiveness of the work. The results are given in Table 1 together with the mixture compositions for the solutions used in the grafting procedure.

As is evident, the mixture compositions for the two PEG3 systems are similar, with values greater than the corresponding solution mixture values. The PEG3-silane was clearly discriminated during the grafting procedure. The PEG7/PEG11 systems behave differently. In contrast to the PEG3 systems, discrimination in the grafting procedure is observed here for the longer PEG-silane. The longer the PEG chain, the less pronounced effect is expected for PEG-silane mixtures of similar size. This is probably the reason

Figure 3. (Continued).





Figure 5. Calibration curves for determination of chain length (or molecular mass) of a grafted PEG-silane on silicon based on the abundance of a PEG chain fragment ion ($C_4H_7O^+$, logarithmic fit) or a silane interface fragment ion (SiCH₃O⁺, linear fit). The error bars shown are standard deviations based on five measurements at five different locations on the sample surface.

 Table 1. PEG-silane mixture compositions in the grafting solutions and the TOF-SIMS measured compositions of grafted PEG-silane mixtures on silicon surfaces^a

Silicon surface PEG3/PEG7	Silicon surface PEG3/PEG11	Silicon surface PEG7/PEG11
(% PEG7)	(% PEG11)	(% PEG11)
52 ± 2	47 ± 4	3 ± 2
80 ± 2	72 ± 4	19 ± 14
81 ± 4	93 ± 2	60 ± 15
	Silicon surface PEG3/PEG7 (% PEG7) 52 ± 2 80 ± 2 81 ± 4	SiliconSiliconsurfacesurfacePEG3/PEG7PEG3/PEG11(% PEG7)(% PEG11) 52 ± 2 47 ± 4 80 ± 2 72 ± 4 81 ± 4 93 ± 2

^a The standard deviations are the result of considering different fragment ions for the quantification.

for the significantly greater standard deviations observed for the PEG7/PEG11 systems compared with the PEG3 systems. We have found no rational explanation for why the shorter PEG-silane is discriminated for two of the systems and the longer PEG-silane is discriminated for one system.

One could argue that our calculated mixture compositions could be a result of discrimination in the desorption process during the TOF-SIMS analysis. In order to confirm that this is not the case, we made the following considerations. A discrimination of the shorter PEG chain will increase the mass per unit surface area (hereafter termed effective layer thickness) and vice versa. Hence, for the PEG3-silane mixtures the expected values for the effective layer thickness versus the solution phase composition should lie above a straight line between the layer thickness of pure PEG3silane and the pure PEG7-silane or PEG11-silane. For the PEG7/PEG11 systems the expected values for the effective layer thickness should, in contrast, lie below a straight line between the layer thickness of pure PEG7-silane and the pure PEG11-silane. The relative abundances between the PEG fragment ions and the substrate ion, Si⁺, must be a qualitative measure of the layer thickness. In Fig. 6, the composition in the solution is plotted against the relative abundances between $C_4H_7O^+$ and Si⁺ for binary mixtures of PEG3-, PEG7- and PEG11-silane. As is evident from Fig. 6, the predicted trend is indeed observed.

One could argue that possible variations in the grafting density could explain the phenomenon in Fig. 6. However, performing the plot without including the substrate signal produces the same qualitative plot, but with considerably larger uncertainty. This rules out the possibility of variations in grafting densities being the cause of the observed phenomenon in Fig. 6.

It could also be argued that an unknown factor could be the cause of the phenomenon with the PEG7/PEG11 mixtures and not the layer thickness. To verify that this is not the case, the effective layer thicknesses were measured with ellipsometry, which is based on a completely different fundamental principle. The result is shown in Fig. 7, and even though the data are somewhat scattered, it is reasonably clear that the thickness values are located above the line for the PEG3-systems and below the line for the PEG7/PEG11 system. This supports the qualitative TOF-SIMS effective layer thickness results presented in Fig. 6.

Our results suggest that discrimination does take place in the adsorption process. The discrimination is dependent on what binary mixture system is considered, hence the mechanism is not well understood. A possible explanation for this observation could be that two or more competing processes exist, e.g. discrimination in the adsorption process and some other unknown process/mechanism that we have not considered. It is highly unlikely that the unknown process is the initially described formation of an umbrella-like layer of longer chain PEG-silanes below which the shorter chain PEG-silanes is situated. Since we are confident that the grafting density is the same in all cases, the 'umbrella' effect would not have any influence on the layer thickness. The 'umbrella' effect would probably have an influence on the relative PEG fragment ion abundances in the TOF-SIMS analysis, i.e. because of the limited probe depth of TOF-SIMS





Figure 6. Normalized relative signal intensities for PEG–substrate measured by TOF-SIMS versus the composition (100, 80, 50, 20 and 0%) in the grafting solution. The dashed line represents the situation when there is no discrimination in the grafting process. The error bars shown are standard deviations based on five measurements at five different locations on the sample surface.



Figure 7. Effective layer thicknesses measured by ellipsometry versus the composition (100, 80, 50, 20 and 0%) in the grafting solution. The dashed line represents the situation when there is no discrimination in the grafting process. The error bars shown are standard deviations based on three measurements at different locations on the sample surface.

with respect to larger molecular fragments. The PEG fragment ions from the shorter PEG-chain would most likely be discriminated. Since the qualitative layer thickness profile in Fig. 6 (TOF-SIMS) is qualitatively consistent with the quantitative layer thickness profile in Fig. 7 (ellipsometry), it supports the fact that the 'umbrella' effect is either non-existent or at most negligible. Furthermore, the 'umbrella' effect would produce inconsistent mixture compositions when calculated from various PEG fragment ion abundances relative to the corresponding Si⁺ abundances. There is no correlation between the size of the PEG fragment ions used in the quantification and the small differences observed for the calculated mixture compositions. This further supports the contention that the 'umbrella' effect is either non-existent or negligible.

CONCLUSIONS

Silicon-grafted monodisperse PEG-silanes with various PEG chain lengths and mixtures of these were systematically analyzed with TOF-SIMS. The mass spectra show differences in the various relative signal intensities, an observation that was used to elucidate important aspects of the grafting process.

The signal intensity of the Si⁺ ion decreases for longer PEG-silane chains as a result of increased layer thickness. The desorbed ions with the elemental composition SiCH₃O⁺ follow the same qualitative trend as Si⁺. The signal intensities of the PEG fragment ions increase relative to the Si⁺ ion signal intensities for larger PEG-silane chains. The C₃H₇O⁺ ion is seen to deviate from this trend. It is suggested that C₃H₇O⁺

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originates from the PEG chain but also from the spacer between the silane and PEG part of the PEG-silane. Another possible explanation could be that $C_3H_7O^+$ is a product of rearrangement.

 $C_4H_7O^+$ was found to be most sensitive towards changes in the PEG chain length. For the silane part the abundance of SiCH₃O⁺ showed the largest sensitivity towards changes in the PEG chain length. The logarithm to the abundances for these two ions was plotted against the logarithm to the number of PEG units, which produced a calibration curve for which a PEG chain length, and thus a molecular mass, can be obtained from the $C_4H_7O^+$ or the SiCH₃O⁺ signal intensity.

The relationship between PEG fragment ion abundances and Si⁺ ion abundances intensities were used to determine the surface composition of binary PEG-silane mixtures. The PEG-silane with the shorter PEG chain is discriminated for mixtures containing PEG3-silane, and the PEG-silane with the longer PEG chain is discriminated in PEG7/PEG11silane mixtures. Our results suggest that discrimination does take place in the adsorption process. The discrimination is dependent on which binary mixture system is considered, hence the mechanism is not well understood.

In order to rule out the possibility of the observed inconsistent discrimination being instrument dependent, the samples were measured with ellipsometry. The resulting layer thickness profile is qualitatively consistent with the qualitative layer thickness profile obtained by TOF-SIMS, which rules out instrument dependence.

It is suggested that the observed inconsistent discrimination could be a result of two or more competing processes, e.g. discrimination in the adsorption process and some other unknown process/mechanism that was not considered. The finding of consistent mixture compositions independently of PEG fragment ion size, and the observation that the layer thickness profile obtained from TOF-SIMS is qualitatively consistent with the corresponding profile measured by ellipsometry, support the conclusion that it is highly unlikely that the unknown process is the formation of an umbrella-like layer of longer chain PEG-silanes below which the shorter chain PEG-silanes are situated.

We believe that we have demonstrated the versatility of TOF-SIMS to (i) qualitatively describe layer thicknesses of grafted mixtures of PEG-silanes on silicon, (ii) construct a calibration curve for which PEG chain length (or molecular mass) can be obtained and (iii) quantitatively determine surface mixture compositions of grafted monodispersive PEG-silanes of different chain lengths.

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