Quantitative XPS Analysis of PEG-Modified Silicon Surfaces

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Poly(ethylene glycol) (PEG) films were covalently coupled to silicon surfaces using a solution phase and a vapor phase technique. These methods are targeted for creating nonfouling PEG films on silicon bio-microsystems. We used X-ray photoelectron spectroscopy (XPS) to better understand and analyze PEG functionalized silicon surfaces. Elemental surface composition was obtained from survey spectra for various PEG modified surfaces. Further, high-resolution C-1s scans were taken to ensure the presence of the characteristic C−O bond, which confirms the coupling of PEG on the silicon surface. Percent C−O was analyzed theoretically to better understand the formation of thin PEG films on silicon surfaces. Also, the thickness of the PEG film was estimated using the standard overlayer model.

Introduction

Poly(ethylene glycol) (PEG) films are of extreme importance to the field of biomedical engineering due to their ability to control biomolecular interactions with device surface. They have been used to prevent biofouling in bio-microsystems, tissue engineering applications, drug delivery, and cell patterning.[1-4] PEG is known to have unique properties in aqueous environments, acting much like a molecular windshield wiper. When a biomolecule such as a protein approaches the surface, the PEG chains which are in constant motion will wipe off the molecule from the surface, thus preventing biofouling.[5]

In this study, we have prepared two types of PEG modified silicon surfaces: one by solution phase and the other by a vapor phase reaction. We used X-ray photoelectron spectroscopy (XPS) to characterize unmodified and PEG modified silicon surfaces. XPS is an extremely sensitive technique, which can help us better understand the characteristics of the prepared surfaces. Survey scans were taken to determine the surface elemental composition for various PEG modified surfaces. Further, high-resolution C1s scans were taken to ensure the presence of the characteristic C−O bond for PEG on the surface. The percentage of C−O bond present on the surface is directly related to the PEG grafting density. Hence, formation of this bond for various concentrations was fitted to a Langmuir-type model and for reaction times was fitted to an exponential association model to better understand the phenomenon of film formation. Further, the intensities of Si2p peaks before and after PEG modification were used to estimate film thickness using the standard overlayer method.[6] The standard overlayer method calculates the thickness of the film using the intensities of Si2p peaks before and after modification with PEG.

Experimental Section

Materials. 3-aminopropyltrimethoxysilane, PEG (M_w = 1000), toluene, hydrogen peroxide (30%), hydrochloric acid

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(50%), ammonium hydroxide, triethylamine, silicon tetrachloride, ethylene oxide, and boron trifluoride were purchased from Sigma Chemical Company (St. Louis, MO). Silicon wafers, P-type, boron doped with ⟨100⟩ orientation were purchased from Atomergic Chemetals Corp. (Farmingdale, NY).

Preparation of PEG Modified Surfaces. PEG modified surfaces were prepared using the following two different techniques as described below. The surfaces were cleaned and hydrophilized using the standard RCA procedure which involves treating surfaces at 80 °C for 15 min in solutions of 1:1:5 proportions of $NH_4OH:H_2O_2(30\%):DI$ water and 1:1:6 proportions of $HCl(50\%):H_2O_2(30\%):DI$ water, respectively.

Solution Phase Reaction. PEG immobilization on the silicon surfaces using the solution phase reaction was achieved using a covalent coupling technique.[7,8] This technique forms more stable films compared to physical adsorption on the surface. In this technique, a PEG-silane is formed by reacting PEG with silicon tetrachloride in the presence of triethylamine as a catalyst. The reaction results in the formation of $PEG-OSiCl_3$ which would then react with the trace level −OH on silicon to form a network of Si−O−Si bonds resulting in immobilization of PEG on the surface.[9-12] The PEG-silane formation and its immobilization on the silicon substrates was performed in anhydrous conditions to prevent hydrolysis and undesired side reactions. Various concentrations of PEG (10, 20, and 50 mmol) and immobilization time (1, 2, and 4 h) were used to form PEG films with various compositions.

Vapor Phase Reaction. Ethylene oxide in the vapor phase was used to grow PEG on a silicon surface.[13] Surfaces were first silanized with a reactive end group silane like 3-aminotripropyltrimethoxysilane (APTMS) in the vapor phase. Boron trifluoride was used as a gas catalyst with ethylene oxide. This allows reaction sites to be made available for the attachment of reactive ethylene oxide molecules followed by an additional polymerization reaction to form PEG on the surface. PEG composition can be controlled by the concentration of ethylene oxide and the polymerization reaction time. The reaction was terminated by flowing inert gas over the surface after an appropriate time. Various concentrations of ethylene oxide (10, 20, and 40 mmol/cm^2 of surface area) and immobilization times

TABLE 1: XPS Elemental Composition for Unmodified and PEG Modified Silicon Surfaces

	clean silicon	solution phase reaction						vapor phase reaction					
		10 mmol	20 mmol	50 mmol	1 h	2 h	4 h	10 mmol	20 mmol	40 mmol	1 h	2 h	4 h
% Si	54.2	31.8	21.3	17.4	31.8	28.4	22.9	10.7	10.9	14.4	10.7	12.1	14.2
% C	13.2	21.6	27.3	29.5	21.6	23.2	27.9	63.1	66.2	69.3	63.1	66.7	68.9
% O	32.5	46.4	51.4	53.1	46.5	48.3	49.1	13.8	11.5	8.1	13.8	10.2	9.8
% N	−	−	−	−	−	−	−	12.4	11.4	8.2	12.4	11.0	7.9

(1, 2, and 4 h) were used to form PEG films of various compositions.

X-ray Photoelectron Spectroscopy Analysis (XPS). To determine the surface composition of PEG modified-surfaces, XPS analysis was conducted on a Perkin-Elmer 5600 XPS/SIMS instrument with a monochromatic Al Kα X-ray source (1486.6 eV) with an Omni Focus III small area lens and multichannel detector. A concentric hemispherical analyzer (CHA) was operated in the constant analyzer transmission mode to measure the binding energies of emitted photoelectrons. The binding energy scale was calibrated by the Au4f$_{7/2}$ peak at 83.9 eV, and the linearity was verified by the Cu3p$_{1/2}$ and Cu2p$_{3/2}$ peaks at 76.5 and 932.5 eV, respectively. Survey spectra were collected from 0 to 1100 eV with a pass energy of 188 eV, and high-resolution spectra were collected for each element detected with a pass energy of 23.5 eV. Survey and high-resolution spectra were collected at 65° take off angle, defined as the angle spanned by the electron path to the analyzer and the sample surface. All spectra were referenced by setting the hydrocarbon C1s peak to 285.0 eV to compensate for residual charging effects. Data for percent atomic composition and atomic ratios were calculated using the manufacturer supplied sensitivity factor. The high-resolution C1s peaks were analyzed using the peak fit software provided by the instrument manufacturer.

Results and Disscussion

XPS Survey Spectra. XPS analysis was performed to ascertain the presence of PEG on the surface of silicon. Survey spectra for an unmodified and PEG-modified surface illustrate clearly the change in carbon and silicon composition of the silicon surface before and after PEG modification. There is a sharp increase in the C1s (285 eV) peak and a decrease in the Si2p (100 eV) peak for the PEG-modified surface compared to unmodified silicon (not shown). This trend was observed for all of the PEG modified surfaces prepared using various concentrations (solution phase: PEG concentration, vapor phase: ethylene oxide concentration) and immobilization times.

Table 1 highlights the surface elemental composition for various PEG films formed by solution phase and vapor phase reaction deduced from the survey spectra using the software provided with the XPS instrument. PEG modified silicon surfaces show an increase in carbon concentration as well as a slight increase in oxygen concentration and a decrease in silicon concentration compared to unmodified silicon. This trend was followed both with increasing concentration and reaction time indicating formation of densely packed PEG films on the surface.

High-Resolution C1s Scans. High-resolution C1s scans provided more precise information about PEG grafting as a function of concentration and reaction time. The main carbon peak at 285 eV is the hydrocarbon or the C−C peak. The peak at a shift of −1.5 eV from the C−C peak is the carbonyl or the C−O peak, a characteristic of PEG coupling. Presence of this peak in all of the modified surfaces suggests the presence of PEG moieties.

Further, we see a substantial increase in the intensity of the C−O peak with an increase in concentration and reaction time.

(a) Solution phase reaction
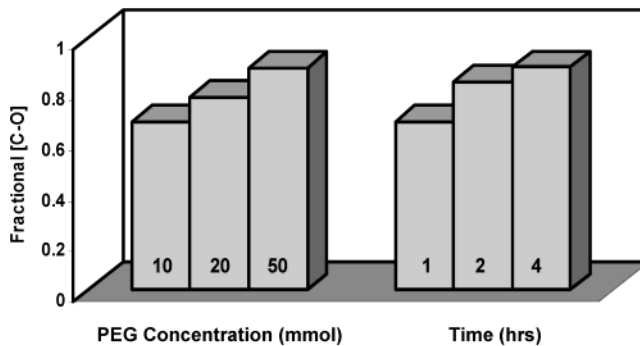

(b) Vapor phase reaction
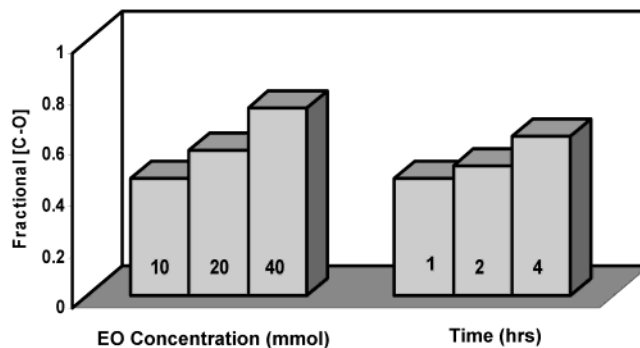
Figure 1. Fractional [C−O] variations with concentration and reaction time for (a) solution phase reaction and (b) vapor phase reaction.

To extract quantitative information from this observation, the curve fitting software supplied with the instrument was used to calculate the relative contribution of the two peaks ([C−O] and [C−C]) to the total carbon concentration. A convolution of Gaussian components was assumed for all peak shapes. The fractional area of the [C−O] peak was now taken as a measure of PEG grafting. Figure 1 shows the variation in the [C−O] fractional concentration with both the concentration and reaction time.

Theoretical Analysis of PEG Film Formation. Our investigations at different concentrations and reaction times suggest that PEG film formation is strongly influenced by these parameters. It is, therefore, realized that a theoretical analysis of this behavior would be useful in developing a refined understanding of the PEG film formation. Furthermore, this can be useful for preparing the PEG films of desired grafting density without the need for exhaustive experimentation.

Therefore, we examined the effect of concentration and immobilization time on formation of [C−O] bonds using the Langmuir-type model.[14] The Langmuir-type model is derived on the basis of assumptions that all of the binding sites are with equal energy and only one molecule adsorbs on one binding site, which are of an independent nature. This suggests that, if this model is followed, surfaces should achieve saturation with monolayer formation. This model was originally developed for gas adsorption and was used as a first approach to describe the

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J. Phys. Chem. B, Vol. 108, No. 17, 2004 **5187**
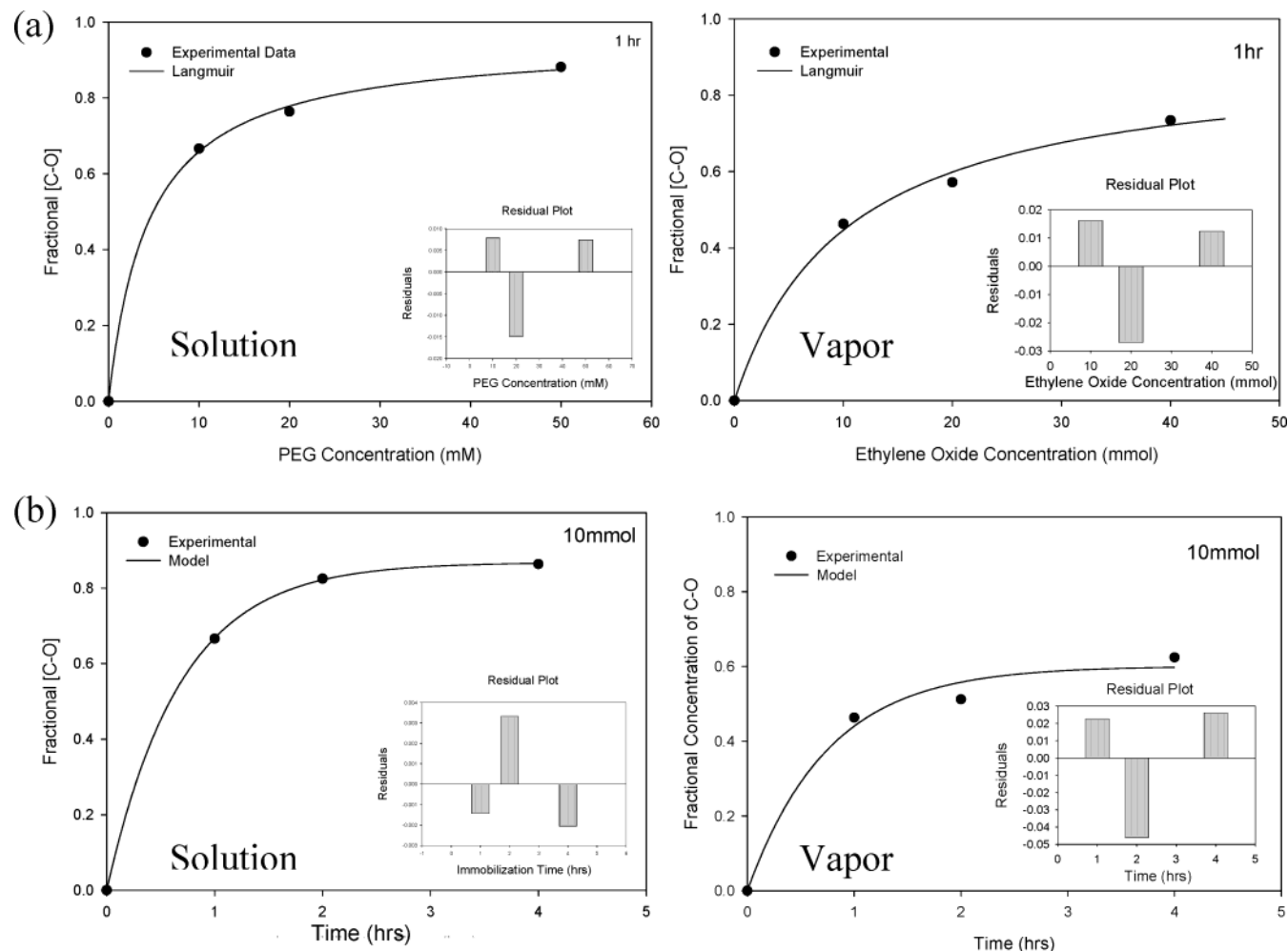
Figure 2. (a) Langmuir-type and (b) exponential association model fit for PEG film formation. Fractional [C—O] is considered as a measure of PEG grafting.

adsorption behavior of a variety of molecules ranging from gases to large molecules such as proteins.[15–16] Therefore, it was of great interest to examine PEG film formation in this study using this model

$$\text{Langmuir-type model: } y = \frac{a_L x}{(b_L + x)}$$

where x is the initial PEG concentration, y is the grafting density in terms of formation of C—O bond, a_L is the maximum grafting density of the PEG film using Langmuir-type model, and b_L is the dissociation constant for Langmuir-type model (i.e., inverse of association constant and signifies strength of PEG-silicon interaction).

It must be noted here that the value of x and y are not the equilibrium values in this study. Figure 2a shows the modeling fit for PEG films formed by solution and vapor phase reactions. As we can see, the Langmuir-type model fits well for variation in concentration as indicated by the lower standard error and high coefficient of correlation (Table 2).

The time course of PEG film was examined using the Exponential association model. This model shows exponential growth of the PEG film and is given by the following equation:

$$y = a(1 - \exp(-bx))$$

where a and b are the parameter characterizing the exponential growth.

TABLE 2: Model Parameters for Langmuir-Type and Exponential Association Models from XPS Data for PEG Film Formation on Silicon Surfaces

	solution phase reaction		vapor phase reaction	
	Langmuir	exponential	Langmuir	exponential
a	0.9521	0.89	0.9079	0.6010
b	4.461	1.352	10.3256	1.3184
standard error	0.013	0.016	0.0239	0.0408
R^2	0.999	0.999	0.9980	0.9926

The grafting kinetics for PEG film formation in this study followed the exponential association model (Figure 2(b)). The model parameters are given in Table 2.

Film Thickness from XPS Data. Estimation of PEG film thickness is extremely important since these films will be applied to biomedical devices with micro- and nanometer size features. Ellipsometry is generally used to measure film thickness. However, due to the refractive index differences, it cannot be used in some cases. In such cases, film thickness can be determined from the attenuation of XPS signals from the substrate material before and after modification. The thickness of PEG films can then be estimated using the standard uniform overlayer model, which is given by the following equation:

$$I_{Si} = I_{Si}^0 \exp\left(-\frac{t}{L_{Si} \sin \theta}\right)$$

where I_{Si}^0 is the intensity of Si2p peaks from clean silicon

TABLE 3: Thickness Estimation from Standard Overlayer Model Using XPS Intensities of Si2p Peaks [$I_0 = 4480$ eV, $L = 3.13$ nm, $\theta = 65'°$][a]

	solution phase reaction						vapor phase reaction					
	10 mmol	20 mmol	50 mmol	1 h	2 h	4 h	10 mmol	20 mmol	40 mmol	1 h	2 h	4 h
I (eV)	2394	1452	1115	2394	1641	1345	3355	3000	2050	3355	2800	2637
t (nm)	1.75	3.20	3.95	1.75	2.85	3.41	0.82	1.14	2.22	0.82	1.32	1.50

[a] I, intensity of Al2p peaks; t, thickness.

substrate, I_{Si} is the intensity of Si2p peaks from PEG modified silicon surface, L_{Si} is the electron attenuation length for Si peaks, and θ is the take off angle for XPS measurements

To obtain the film thickness from this equation, the electron attenuation lengths (EAL) for the Si2p peak needs to be calculated. The calculations are performed using NIST SRD-82 software[17] based on the kinetic energy (KE) of the electrons, photoionization asymmetry parameter (β), ineleastic mean free path (IMFP), and transport mean free path (TMFP). The KE of the electrons is defined as the difference between X-ray energy and the core electron binding energy (BE) of aluminum. The X-ray energy for Al kα source is 1486.6 eV.[18] The values of BE were obtained from NIST X-ray Photoelectron Spectroscopy Database SRD 20 version 3.1[19] and values of β were obtained from Band et al.[20] Using the EAL, the take off angle for measurement and the intensities of Si2p peaks the thickness of the film was calculated in this investigation (Table 3). Noticeably, the film formed by the two techniques described are very thin ranging from 0.8 to 3.5 nm. This analysis suggests that PEG films of different thickness can be prepared by varying concentration and reaction time depending upon the requirement. We see that, as the concentration and reaction time increase, the PEG films thickness first increases and later reaches a saturation value at higher concentration and reaction time.

Conclusions

In this work, we focused on XPS characterization and a theoretical analysis of two different types of PEG modified silicon surfaces created using a solution phase and a vapor phase technique. Our results confirmed the presence of PEG on silicon surface formed by both methods and demonstrated that we could achieve different grafting densities of PEG on silicon substrates by varying the concentration and reaction time. Also, the formation of characteristic [C−O] bonds on various PEG modified surfaces was modeled using the Langmuir-type and exponential association model. Further, the estimations for film thickness using the standard overlayer model suggested formation of very thin films on the surface. This analysis may provide a framework for creating PEG films of desired thickness for silicon-based bio-microsystems.

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