



Monolayer vs. multilayer self-assembled alkylphosphonate films: X-ray photoelectron spectroscopy studies

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Abstract

Combining functional organic self-assembled monolayers (SAMs) with conventional semiconductor materials is a key step in the development of integrated electronics-based devices. T-BAG (Tethering by Aggregation and Growth) has been shown to be a simple and reliable method to grow SAMs of alkylphosphonates on oxide surfaces. However, distinguishing SAMs from ultra-thin multilayers is a challenge for most conventional surface characterization techniques.

Self-assembled films of octadecylphosphonic acid (ODPA) were deposited on oxide-covered silicon coupons, converted to the corresponding phosphonates, and characterized by high resolution angularly resolved X-ray photoelectron spectroscopy (XPS). It was our goal to distinguish among different bonding configurations for phosphorous in the phosphonate head groups, namely, mono-dentate, bi-dentate or tri-dentate interactions with the oxide surface, as well as to assess quantitatively the near-surface layer composition.

We also present an innovative method that allows us to distinguish between monolayer and multilayer films of ODPA on silicon oxide surfaces. This method is based on differential surface charging effects in XPS. It was found that variation in the ODPA film thickness causes differential responses of various spectral characteristics to an electrical bias applied to the sample during XPS measurements. Both positive and negative applied biases were found to affect the carbon core-level (C1s) line-shape and intensity in the case of the multilayer ODPA film, whereas line-shapes and intensities of all XPS lines measured for the monolayer film were unaffected by the application of a dc bias in the ± 30 V range.

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1. Introduction

Extensive research over the last two decades has shown that modular design of self-assembled monolayers (SAMs) allows for a broad range of applications, from surface coatings to integrated electronics-based devices [1–4]. Understanding the growth and structure of these SAMs is critical for their successful implementation. By definition, SAM films are very thin and, therefore, investigation of

their structure and bonding requires characterization techniques that are sensitive to the first few atomic layers [1].

The formation of SAMs using oxy-acid species can be an acid–base reaction to give a carboxylate or phosphonate complex of a surface metal cation, or one simply involving hydrogen bonded adducts. Phosphonic acid SAMs have been reported on high surface area Al_2O_3 , TiO_2 , ZrO_2 [5] and on planar mica [6], TiO_2 [7] and SiO_2 [8] substrates, although proof of monolayer film formation has been noted only in a few cases. Recently, Gawalt et al., discovered that adhesion and stability of phosphonic SAM films on TiO_2 is greatly enhanced by effective thermal annealing following SAM film formation [7,9,10]. It was proposed that the phosphonic acid molecules in the unheated, as deposited film are simply hydrogen-bonded to the

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substrate, and perhaps also to neighboring molecules. The molecule–molecule interactions (Van-der-Waals and H-bonding) are apparently stronger than substrate–molecule interactions in the as deposited film. Heating then transforms the phosphonic acid monolayer to a phosphonate one; the latter is strongly chemically bonded to the surface. The mechanism proposed for bonding a SAM to silicon is likely similar to that for the Ti oxide surface [7,10].

Characterization of phosphonic acid based SAM films on Si/SiO₂ has already given a nearly complete picture of their structure. These films were characterized by specular reflectance infrared spectroscopy (SRFTIR), atomic force microscopy (AFM), and quartz crystal microgravimetry (QCM) [8]. AFM and SRFTIR analysis indicated the formation of tightly packed films that completely covered the substrate surface. However, the detailed bonding scheme of the phosphonate head group to oxide coated silicon substrates had not been determined. IR is generally a method of choice for the determination of bonding to the surface, but the absorption intensity of monolayer films on silicon oxide is weak, and often even moderate transitions can hardly be detected. To overcome these limitations, XPS could be used to assess changes in the environment for atoms at the interface upon film formation.

One major problem with SAMs characterization is to distinguish between a monolayer film and an ultra-thin (in the range of several nanometers) multilayer film. We now report direct evidence for monolayer film formation using XPS. An innovative method that distinguishes between monolayer and multilayer films of octadecylphosphonic acid (ODPA) on silicon oxide surfaces was developed, based on differential surface charging effects in XPS. Although the application of a small external bias during XPS measurements has been reported as a simple and effective method to detect differential charging of silicon and aluminum oxides [11,12], the present work is the first where application of a dc sample bias during XPS data acquisition is used to distinguish between monolayer and multilayer films of an organic on an oxide surface. We show that XPS characteristics of the monolayer film are unaffected by application of an external bias, which is, therefore, free of differential charging. A multilayer film, on the other hand, displays significant differential charging, which can be easily verified and controlled by application of either positive or negative dc biases. The positive bias may reduce the differential charging by attracting stray electrons from, for example, the ion gauge filament in the vacuum system, while negative bias leads to enhanced differential charging. This allows one to obtain additional information from otherwise unresolved spectral features [13].

2. Experimental

The T-BAG (Tethering by Aggregation and Growth) deposition method was used to prepare ODPA films on the native oxide of silicon [8]. A wafer of single-crystal

Si(100) was cut into 1 cm × 1 cm coupons. The coupons were cleaned by boiling in 1:3 H₂SO₄:H₂O₂ for 45 min followed by extensive rinsing with distilled/deionized water (18.2 MΩ; Milli-Q). The coupons were then boiled in a 1:1 solution of HCl:H₂O₂ for 15 min and were again extensively rinsed with water. Clean silicon coupons were etched with aqueous HF to remove existing oxide and were reoxidized in fuming HNO₃ for 1 min followed by intensive rinsing in Milli-Q water.

ODPA self-assembled on the cleaned Si/SiO₂ surface by holding the coupon vertically in a 40 μM solution of the acid which was dissolved in dry THF (THF (EM Science) was distilled over Na and stored under argon). The solvent is allowed to evaporate at room temperature over about 3 h. Coated coupons were heated in an oven at 140 °C for 36 h, and finally rinsed 3 times with sonication in dry THF for 15 min. Three cycles of T-BAG deposition, baking and intensive rinsing in THF were carried out to deposit a well-ordered, uniform, monolayer film. One T-BAG deposition followed by baking without rinsing in THF was used to deposit a multilayer of ODPA. After deposition, samples were transferred into an UHV system with base pressure of 5×10^{-9} Torr.

XPS data were collected using a Phoibos 150 hemispherical energy analyzer (SPECS) and a monochromatized Al Kα (1486.6 eV) source. The spectrometer was calibrated to the position of the 3d_{5/2} line of sputtered-clean Ag with binding energy 368.25 eV [14] and the C1s line of HOPG at 284.45 eV. Measurements were carried out at three take-off angles: 90°, 40° and 20° between the sample surface and the direction of photoelectrons detected by the analyzer. A pass energy of 30 eV was used for wide range scans (survey), while 10 eV or 15 eV pass energies were used for high resolution measurements of Si2p, C1s, O1s, and P2s regions. For all measurements the binding energy scale was normalized to the position of the SiO₂ (Si2p) peak at 103.8 eV. Curve fitting of the core-level XPS lines was carried out using CasaXPS software with a Gaussian–Lorentzian product function and a non-linear Shirley background subtraction [15]. A Gaussian–Lorentzian mixing ratio was taken as 0.3 for all lines. For quantitative estimations of surface compositions standard atomic photoionization cross-section values from the SPECS database were used [16]. To study charging effects, the sample was biased using a variable dc power supply to ±30 V.

3. Results and discussion

3.1. Self-assembled ODPA films on native oxide coated silicon surface

Normal take-off angle XPS measurements were carried out for the following samples: (i) as deposited ODPA (one T-BAG deposition without baking and rinsing; further referred to as a bulk ODPA film); (ii) the sample after one cycle of T-BAG deposition and baking at 140 °C for 36 h, but without rinsing (further referred to as a multilayer

ODPA film); and (iii) the sample which underwent three cycles of T-BAG deposition, baking and intensive rinsing. The last sample represents a monolayer octadecylphosphonate (ODP) film, as shown in previous AFM, QCM and IR studies [8].

Typical survey spectra of a blank Si surface and a multilayer of ODP on silicon in the 10–600 eV range are shown in Fig. 1. The blank silicon sample shows Si2p, Si2s, O1s, as well as a weak C1s core level lines. After deposition of multilayer ODP, the relative intensities of the C1s and O1s lines increase concurrently with a decrease of intensity of the Si2p and Si2s lines. The insert on Fig. 1 shows the survey scan in the 90–210 eV range where low intensity P2s and P2p peaks can be distinguished. Very pronounced plasmon loss peaks ($2\hbar\omega_B$) of silicon at 134 eV and 186 eV are superimposed on P2s and P2p peaks, respectively. However, the P2s peak at about 192 eV is better separated from the Si-plasmon loss peak; for that reason the P2s, rather than P2p peak, was used for high resolution analysis. The line-shape, position and FWHM of the Si2p_{3/2} peak at 99.6 eV were constant for all types of examined films. However, after deposition of the ODP film, the rel-

ative contribution of SiO₂ peak at 103.8 eV increased compared to the blank Si coupon which can be explained by an increase of silicon oxide thickness after thermal treatment at 140 °C. This increase does not affect the sensitivity of phosphorous detection, since the relative intensity of the silicon plasmon loss peaks, which originate from elemental silicon at 99.6 eV, decreases. Indeed, a very distinct phosphorous peak was observed on a sample with a very thick oxide layer where no plasmon peaks were observed (data not shown).

High resolution XP spectra of P2s, C1s and O1s peaks are shown in Figs. 2–4, respectively, for bulk, multilayer, and monolayer ODP-derived films. The spectrum of the blank silicon coupon is also shown for comparison. The observed P2s binding energy decreases from almost 192.6 eV for bulk, unbound ODP, to 192.3 eV for a multilayer and 191.8 eV for a monolayer film. The low binding energy peak at 186.3 eV is attributed to the silicon plasmon loss peak; it exhibits a regular trend, such as decreasing relative intensity as the thickness of the overlaid organic film increases from a monolayer to a multilayer, and to bulk

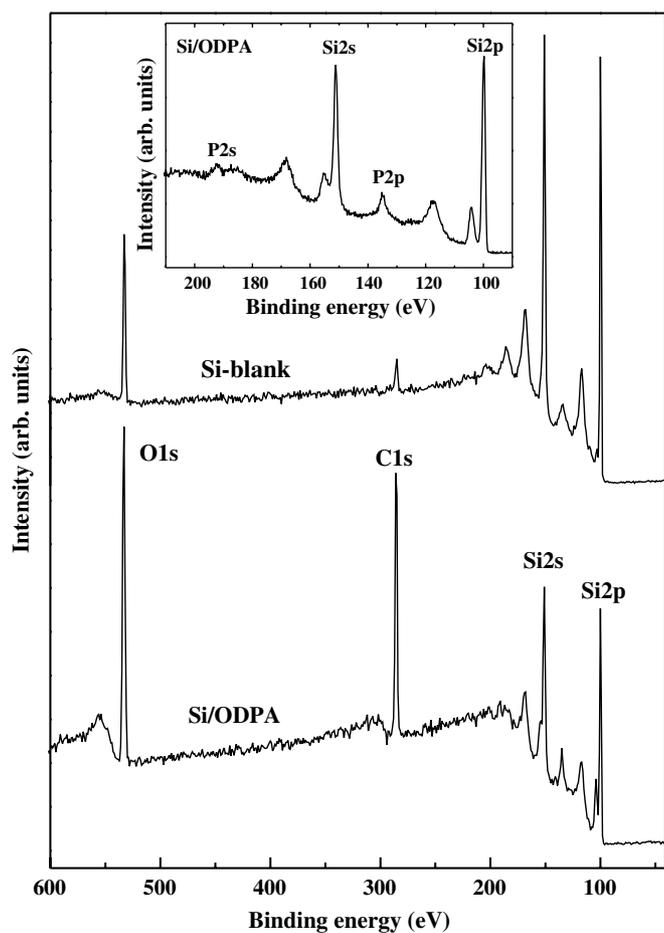


Fig. 1. XPS spectra in the 10–600 eV binding energy range of blank silicon (top) and silicon after multilayer ODP film deposition (bottom). The insert shows the survey scan of a multilayer ODP film on Si in the 90–210 eV range.

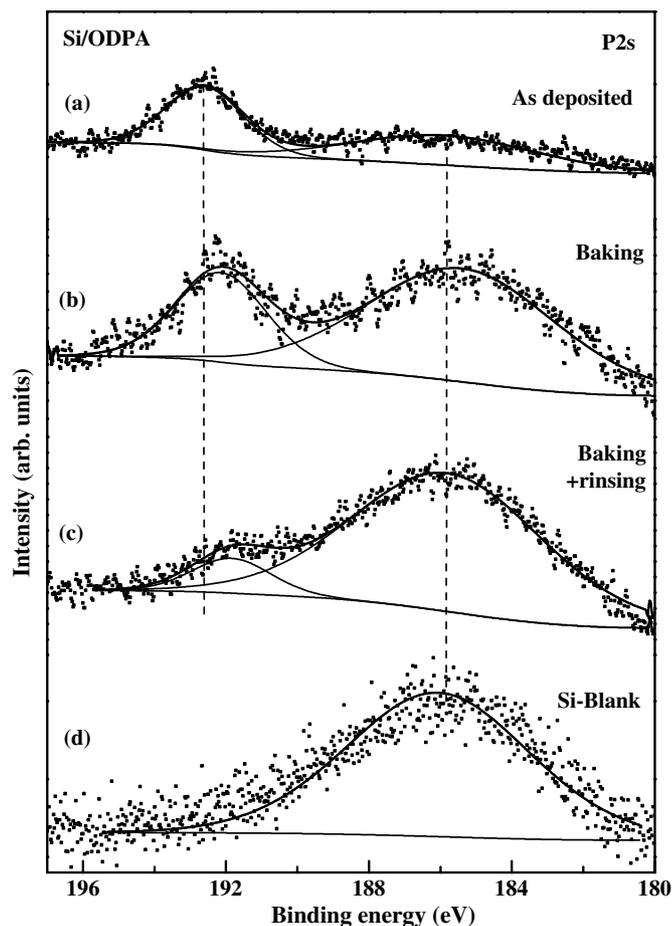


Fig. 2. (a) XPS P2s core level lines measured for an as deposited ODP film on Si (without any treatment), (b) the ODP film after one cycle of T-BAG deposition and baking at 140 °C for 36 h (no rinsing), (c) the ODP-derived film after three cycles of T-BAG deposition, baking and rinsing and (d) XPS spectrum in the 180–197 eV range of a blank Si coupon.

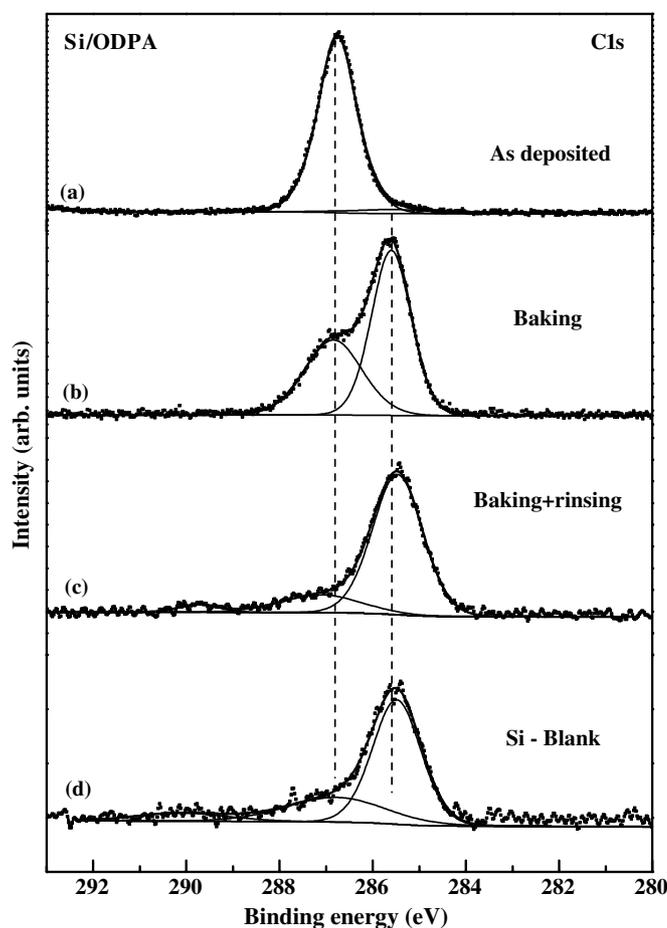


Fig. 3. (a) XPS C1s core level lines measured for an as deposited ODPA film on Si, (b) the ODPA film after one cycle of T-BAG deposition and baking at 140 °C for 36 h (no rinsing), (c) the ODPA-derived film after three cycles of T-BAG deposition, baking and rinsing and (d) a blank Si coupon after standard cleaning process.

ODPA. The interpretation of the binding energy shift of P2s peak is addressed below.

The position and line-shape of C1s peak measured under normal experimental conditions (grounded sample) are different for bulk, multilayer and monolayer ODPA-derived films (see Fig. 3). The spectrum of a bulk ODPA film shows a main C1s peak with a FWHM of 1.2 eV at a binding energy of 286.7 eV and a very low intensity tail at 285.6 eV. For a monolayer film the main C1s peak was located at 285.6 eV, similar to the position of the adventitious carbon contamination detected on a blank silicon coupon. Both carbon peaks measured for a blank sample and a monolayer film show a higher energy tail which can be attributed to the presence of C–O and –O–C=O bonds at about 287.0 eV and 289.5 eV, respectively. The C1s line-shape measured for a multilayer ODPA film is asymmetric and can be satisfactorily fitted with a minimum of two components: the lower binding energy state with a FWHM of 1.0 eV at 285.6 eV and a higher binding energy peak at 286.8 eV with a FWHM of 1.5 eV. These lower and higher binding energy states are seemingly due to two different carbon species on the surface. Based on comparison

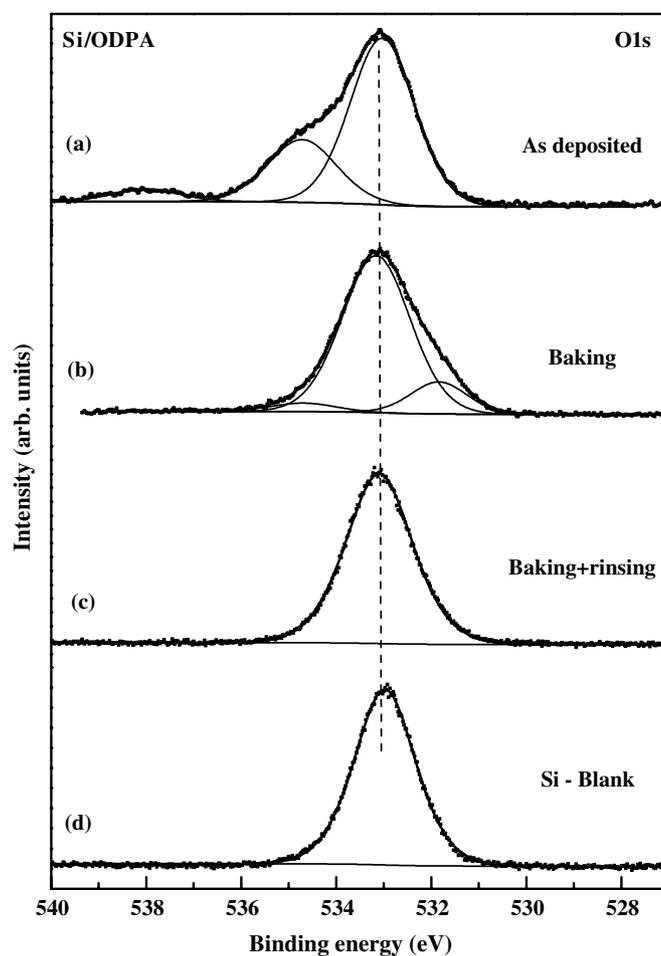


Fig. 4. (a) XPS O1s core level lines measured for an as deposited ODPA film on Si, (b) the ODPA film after one cycle of T-BAG deposition and baking at 140 °C for 36 h (no rinsing), (c) the ODPA film after three cycles of T-BAG deposition, baking and rinsing and (d) a blank Si coupon.

of apparent binding energies, it could be speculated that the lower binding energy state originates from monolayer ODPA that is chemically bonded to the surface; by the same logic, the higher binding energy component would be due to chemically non-bonded, bulk ODPA. However, this big difference in binding energies for chemically identical sp^3 -hybridized carbon atoms is unreasonable. It should be noted that the binding energies and relative amounts of these components were found to be different at different spots on the sample surface, which suggests a correlation between film thickness and characteristics of the C1s core level line. The variation in film thickness, may, in turn, lead to differential charging of the surface and, consequently, a significant shift of the C1s line. It is shown below that the C1s peak shift and variations in line-shape are indeed due to differential surface charging of a thick, multilayer film.

The analysis of O1s core level lines is problematic, since multiple curve-fitting solutions are possible for this peak (see Fig. 4). The O1s line for the blank silicon coupon is at 533.0 eV and has a FWHM of 1.5 eV. This peak contains the main contribution from lattice SiO_2 , as well as from different surface species, such as Si–OH, Si–O–Si

(μ -oxo), C–OH, C=O and –O–C=O, which can hardly be separated, even under high resolution conditions. For bulk ODPA, at least 3 different bonding states of oxygen can be distinguished. The highest binding energy state (538 eV) is most likely due to oxygen of ODPA hydrogen bonded to the silicon oxide surface or to neighboring ODPA molecules. This is consistent with data for water and ice clusters [17] and calculations for formic and acetic acid dimers and formamide oligomers [18]. The O1s component at 534.7 eV is attributed to P=O bonds [19]. The third peak at 533.0 eV, with the maximum intensity and a FWHM of 1.6 eV, consists of different bonding states, including silicon oxide, oxygen from adsorbed contamination, and others [20].

The O1s line for multilayer ODPA film does not show the highest binding energy component at 538 eV (Fig. 4(b)). This is in agreement with the proposed transformation [8] of phosphonic acids hydrogen-bonded to the surface to phosphonates chemically bonded to it. However, the phosphonic acids from the multilayers, non-bonded to the surface, give rise to the low intensity peaks at 534.7 eV (P=O bonds). The peak at 531.8 eV may be due to P–O[−] states [21,22]. The relative population of these states is consistent with the stoichiometric ratio of P=O/POH in a phosphonic acid (1:2). The main O1s peak at 531.1 eV is slightly broadened (FWHM 1.7 eV) and it probably includes the P–O–Si state.

Monolayer ODPA films show an O1s peak which is very similar to that observed for a blank silicon coupon (533.1 eV, 1.6 eV FWHM). No evidence of P=O and P–O[−] bonding states was found here, which indicates a tri-dentate, rather than bi-dentate, or mono-dentate, bonded phosphorus in the ODP head group (see Fig. 5). A similar conclusion was drawn from the XPS analysis of organophosphorus compounds on the Al(111) surface [19].

3.2. Quantitative surface analysis

The elemental composition of analyzed samples was estimated from detailed XPS scans of C1s, O1s, P2s and

Si2p. X-ray photoionization cross-sections of 1.0, 2.93 and 1.18 were used for carbon, oxygen and phosphorus, respectively [16]. The Si2p peak was analyzed using the following values: 0.541 for Si2p_{3/2}, 0.276 for Si2p_{1/2} and 0.899 for Si2p originated from SiO₂. The value for the SiO₂ peak was corrected to account for a minor difference in the photoionization cross-section of Si2p in elemental Si (0.817) and SiO₂ (0.899) [23]. The results are summarized in Table 1. First, the carbon-to-phosphorus ratio for all deposited ODPA films was calculated. For bulk and multilayer ODPA-derived films, the C/P ratio was calculated to be 17.0, which is in a reasonable agreement with the stoichiometric composition of the ODPA (C₁₈H₃₇PO(OH)₂). The total atomic concentration of carbon was used in these cases, assuming that all C1s components originate from the ODPA film on the surface. The validity of this assumption will be addressed below. For the monolayer film, only the main C1s component at 285.6 eV was used in a similar calculation, since the higher binding energy states are earlier attributed to various adsorbed C–O species. The C/P ratio in this case was 18.8, which is within $\pm 5\%$ of the theoretical value. The reasons for a slightly higher carbon concentration and the attenuation of the phosphorus signal are discussed below, based on the angle resolved XPS measurement.

A good indication of the accuracy of quantitative estimations and XPS line analyses may be obtained from a simple calculation of the oxygen balance among different species on the surface. For the blank silicon sample, 3.4 at.% of Si in SiO₂ form requires 6.8 at.% of oxygen. In addition, 0.9 at.% and 0.4 at.% should be included to account for CO and CO₂ species, respectively, based on curve fitting of the C1s peak. The total amount of the calculated 8.1 at.% is consistent with the measured value of 8.6 at.%. For monolayer ODPA, a similar calculation results in a total of 15.0 at.% of oxygen that is needed to account for SiO₂ (9.6 at.%), ODPA (1.5 at.%), CO (2.7 at.%) and CO₂ (1.2 at.%) species. This value is consistent with the 14.9 at.% determined experimentally. Similar estimations for multilayer and bulk ODPA have some uncertainty

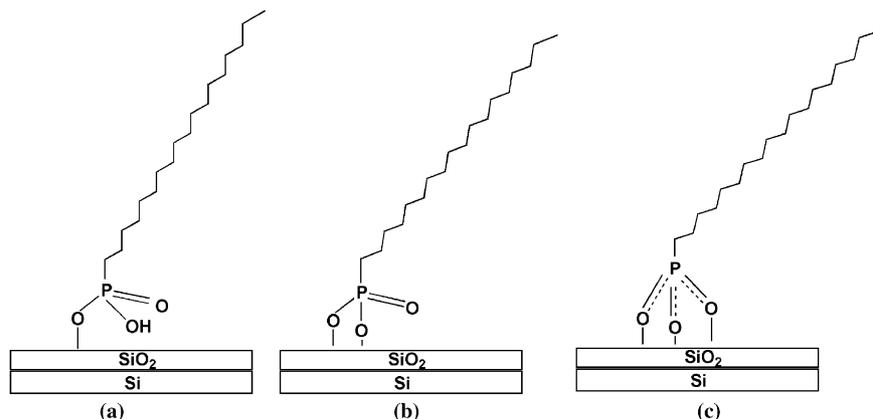


Fig. 5. Different bonding configurations of phosphorus in a phosphonate head group: (a) mono-dentate; (b) bi-dentate; and (c) tri-dentate.

Table 1
The surface elemental composition derived from XPS data of blank Si, monolayer, multilayer, and bulk ODPa films on silicon

Peak	No.	Bonding state	Si-blank	Mono-layer ODP	Multi-layer ODPa	ODPA-bulk
P2s	(1)	ODPA	–	0.5	1.45	2.8
O1s	(2)	Si–O–Si, P–O–Si	8.6	14.9	11.0	9.2
	(3)	P=O	–	–	0.6	3.7
	(4)	P–O [–]	–	–	1.8	–
	(5)	P–O–H...O (H-bonds)	–	–	–	0.7
		O-total	8.6	14.9	13.4	13.6
C1s	(6)	Disordered (due to charging)	–	–	9.8	45.6
	(7)	C–C–H	4.5	9.4	14.9	2.3
	(8)	C=O	0.9	2.7	–	–
	(9)	O–C=O	0.2	0.6	–	–
		C-total	5.6	12.7	24.7	47.9
Si2p	(10)	SiO ₂	3.4	4.8	4.1	2.0
	(11)	Si-elem.	82.5	66.8	56.5	33.7

due to unresolved CO and CO₂ species; they are still, however, in good agreement with experimental data: 12.6 at.% and 12.4 at.% were calculated for multilayer and bulk ODPa films, respectively, vs. 13.4 at.% and 13.6 at.% obtained experimentally.

3.3. Angle resolved XPS measurements

A monolayer ODPa-derived film prepared on Si/SiO₂ was studied using angle-dependent XPS. High resolution spectra of C1s, Si2p, P2s and O1s were acquired at 90°, 40° and 20° between the sample surface plane and the entrance to the electron analyzer. Line-shapes, FWHM, and positions of all peaks remained similar for each take off angle. The intensity of the C1s and P2s peaks increased concomitantly with the decrease in the silicon plasmon loss peak at 186.3 eV due to a relative decrease of the sampling depth and, consequently, a decrease of the elemental silicon contribution to the observed spectrum. The changes for the P2s region measured at normal and grazing take-off angles are shown in Fig. 6. The elemental composition of the surface layer was calculated based on the integral intensities of C1s, O1s, Si2p and P2s peaks, and results are summarized in Table 2. The carbon-to-phosphorus ratio was calculated using the integral intensity of the main (C-1) bonding state, which is attributed to organic film carbon. It is suggested that higher binding energy states (C-2 and C-3) do not originate from a monolayer film. Strictly speaking, these simple calculations are valid only for homogeneous slabs, which is not the case for SAMs; normal incidence measurements more closely approximate this situation. Indeed, the C/P ratio was 18.8, i.e., very close to the stoichiometric C/P ratio in ODPa (18). It increases to 23.7 and 26.0 at 40° and 20° take-off angles, respectively. These results demonstrate the attenuation of the P signal by inelastic scattering in the hydrocarbon tail; significantly these data substantiate our ordered, tails-up monolayer picture of the deposited film and exclude the possibility of randomly oriented ODPa molecules on the surface. Similar general trends

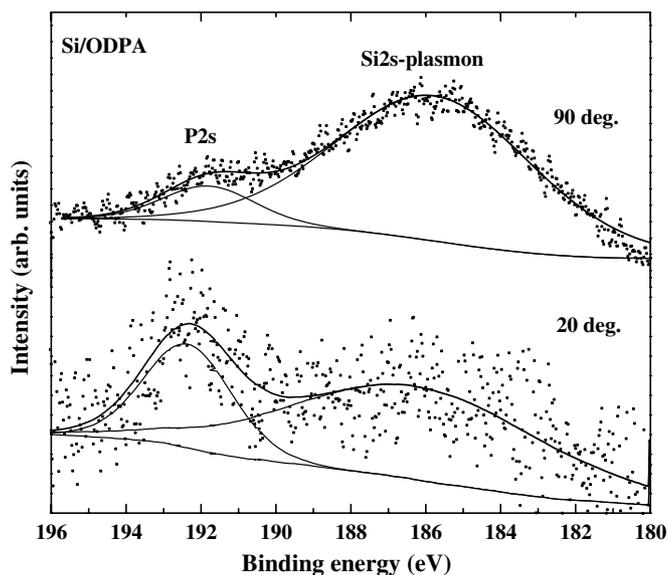


Fig. 6. Angle-dependent XPS of P2s line of a monolayer ODPa film on silicon: take-off angles of 90° (top) and 20° (bottom).

were observed for alkanephosphonate monolayers on Ta(V) oxide surfaces [24] and for SAM of thiols on gold [25].

3.4. Sample biasing during the XPS measurements

To separate intrinsic XPS spectral changes from those caused by a differential surface charging, multilayer and monolayer ODPa-derived films were studied using positive or negative bias applied to the sample in the range of –30 V to +30 V while making the XPS measurements. Variations of C1s and O1s core level lines with this application of negative or positive bias are shown in Fig. 7I and II. A dc bias of ±10 V was chosen to demonstrate all representative changes. The P2s core-level line undergoes similar general changes, and is not shown here for the sake of brevity. All spectra for the same line are plotted on the same energy scale for comparison purposes. The binding

Table 2
Surface elemental composition of a monolayer ODP film on silicon derived from angle-resolved XPS measurements

Take-off angle (degree)	C (at.%)				O (at.%) Total	Si (at.%)		P (at.%) Total	C/P
	Total	C-1	C-2	C-3		Si-elem.	SiO ₂		
90	12.7	9.4	2.7	0.6	14.9	66.8	4.8	0.5	18.8
40	19.2	14.2	4.2	0.8	20.2	51.0	7.7	0.6	23.7
20	33.2	26.0	5.8	1.4	23.0	32.8	9.9	1.0	26.0

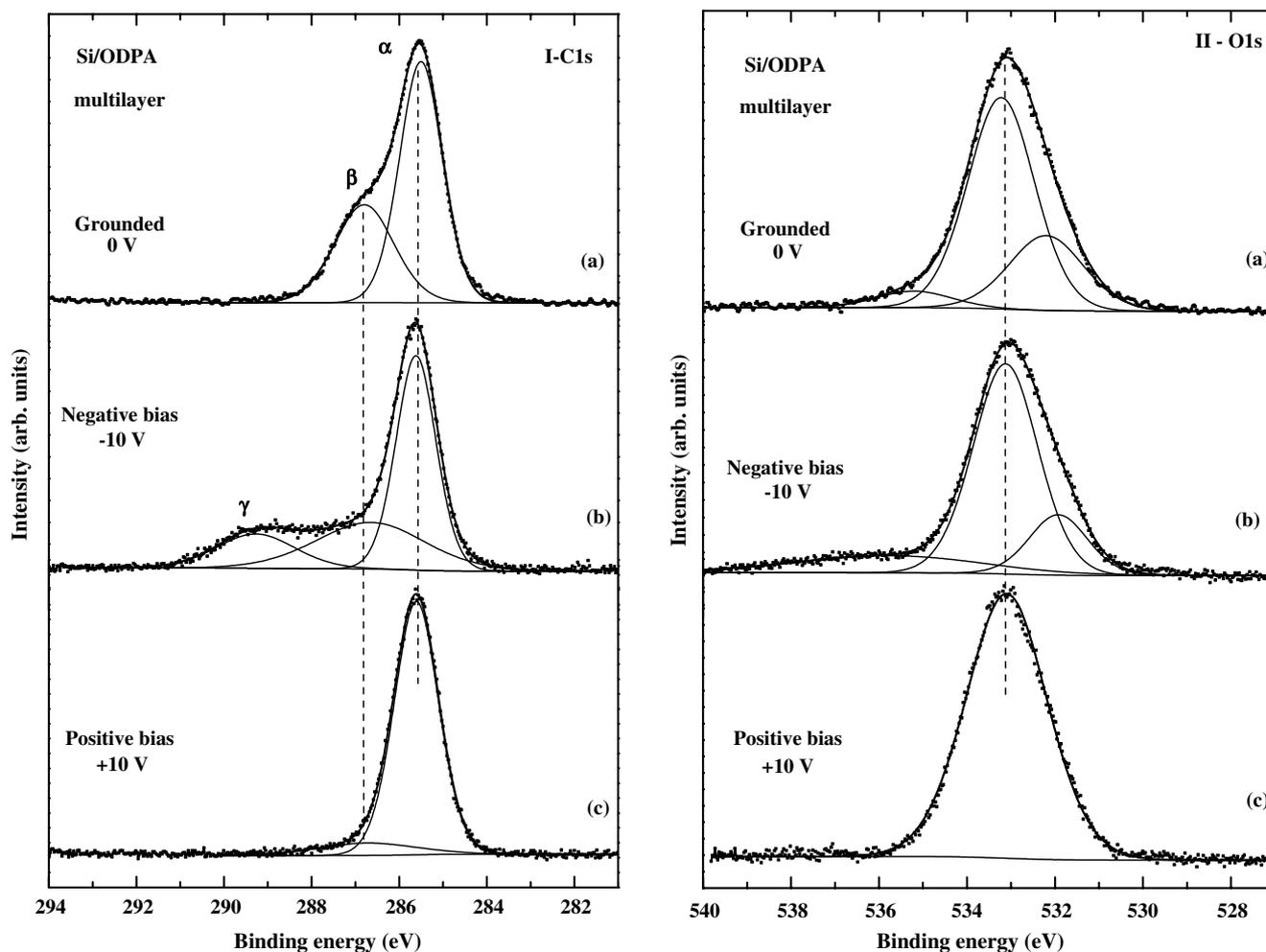


Fig. 7. XPS C1s (I) and O1s (II) core level lines of a multilayer ODP film on silicon measured concurrently with the application of a dc electrical bias to the sample holder: (a) 0 V; (b) –10 V; and (c) +10 V. The binding energy scale is normalized to the position of Si2p peak in silicon oxide at 103.8 eV.

energy scale for all measurements was normalized to the position of the Si2p peak in silicon oxide at 103.8 eV.

The C1s line measured under normal conditions (grounded sample, Fig. 7I (a)) was fitted with two peaks, at 285.6 eV and 286.8 eV. These peaks are denoted by α and β , respectively. In general, the application of a negative bias causes the C1s peak to broaden and to decrease in overall intensity (maximum counts/s value). These changes are gradual and almost saturate beyond –10 V dc bias. Under these conditions spectral fitting required introduction of at least one additional peak at 289.3 eV, denoted by γ , though the FWHM of the β and γ peaks (2.9 eV

and 2.1 eV, respectively) is higher than might be expected for individual bonding states. These peaks are attributed to a number of overlapping lines, which vary by somewhat different values of surface charging that may be closely related to the thickness of the deposited film. The highest binding energy peak, γ , most likely involves the contribution of various C–O bonding states, which were unresolved without application of bias.

Application of a positive bias caused all three peaks to merge into a single C1s line positioned at 285.6 eV with a FWHM of 1.1 eV; a small higher binding energy tail was measured at 286.7 eV. It should be noted that the

application of the positive bias was effective for differential charging neutralization only when the filament of a nude-type ion gauge was brought into operation (it was located near the sample holder). The filament produces a large number of stray electrons; thus, the effect of a positive bias is attraction of stray electrons and neutralization of differential charging, somewhat akin to a flood gun.

Qualitatively similar changes were observed for O1s and P2s peaks, though they were less pronounced than those for C1s: only a small fraction of the O1s peak is due to contributions from ODP molecules from a multilayer, in agreement with the quantitative estimations discussed above. The P2s peak demonstrated the same trend of broadening and splitting into two components: a lower binding energy tail centered at 194.6 eV, which is associated with differentially charged ODP molecules, and a higher intensity component at 192.1 eV. However, the overall intensity of the P2s peak is very low, and its accurate analysis was restricted by low signal-to-noise, even after long acquisition times. Differential charging of multilayer thick films combined with a low intensity of phosphorous signal makes the interpretation of the P2s peak shifts observed for bulk, multilayer and monolayer ODP films difficult. Only a minor shift of the P2s may be expected when P–O–H bonds are converted to P–O–Si states due to the covalent character of the latter and the rather close electronegativities of H (2.1) and Si (1.8).

Positive and negative dc biases were applied to monolayer ODP while acquiring XPS data. In this case no changes of line-shape, FWHM or position (after binding energy scale normalization) were observed for C1s, O1s and P2s peaks. This stability for the C1s peak, measured with +20 V, 0 V and –20 V dc biases, is shown in Fig. 8. From these data, it may be concluded that monolayer ODP on oxide-coated silicon is uniform and thin enough

to be free of differential charging. This conclusion is in good agreement with recent work that discussed controlled surface charging and the use of a flood gun as a probe of vertical positions of atoms in mesoscopic layers [26].

4. Summary and conclusions

High resolution XPS was used to assess the structure and chemical bonding of ODP-derived films on the native oxide of silicon. The main focus of the work was on identification of multilayer vs. monolayer films. Analysis of C1s, O1s and P2s core level lines, combined with an application of a dc electrical bias during spectral acquisition, allows separation of intrinsic chemical information from differential charging effects that are characteristic of multilayer films.

It was found that variation in the ODP film thickness causes different responses of XPS characteristics to sample bias applied during measurements. Both positive and negative biases were found to affect the carbon core-level (C1s) line-shape and intensity of the multilayer phosphonate film, whereas the line-shape and intensity of all XPS lines measured for the monolayer film were stable and not affected by the application of a dc bias in the ± 30 V range. Based on a comparison of the O1s line-shape of monolayer and multilayer films, we suggest that the bonding configuration of phosphorus in a phosphonate head group is tri-dentate, rather than bi-dentate.

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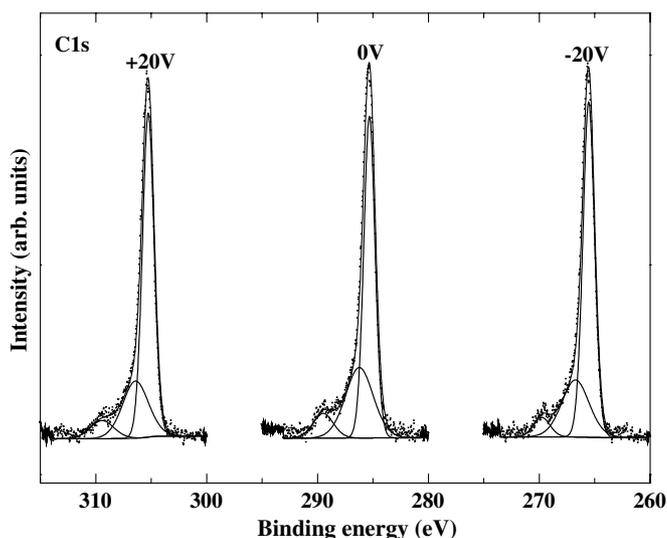


Fig. 8. XPS C1s core level lines of a monolayer ODP film on silicon measured concurrently with the application of a dc electrical bias to the sample holder. Raw data, without a binding energy scale correction, are shown.

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