

Characterization of Self-Assembled Organic Films Using Differential Charging in X-ray Photoelectron Spectroscopy

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Differential charging is often regarded as a problem in X-ray photoelectron spectroscopic studies, especially for insulating or partially conducting samples. Application of a positive bias can reduce the effect of differential charging by attracting stray electrons from the system, thereby compensating for the electron loss. On the other hand, differential charging effect can be enhanced by the application of a negative bias to the sample during spectrum acquisition. The successful use of the differential charging technique to distinguish between multi- and monolayer organophosphonate films on oxide-covered silicon has been reported. A detailed description of this technique is now presented which shows how differential charging can be used as an important tool for the characterization of self-assembled films deposited on various surfaces. The dependence of this technique on the conductivity of the substrate has been investigated by studying the spectral behavior of the deposited films of phosphonic acid on conducting, semiconducting, and insulating samples (stainless steel, silicon, and glass). Application of either positive or negative dc electrical bias affects the carbon core-level (C1s) line shape and intensity, which is dependent on the atom's physical location above the surface.

Introduction

Self-assembled monolayers (SAMs) are widely used to modify conductor and semiconductor surfaces and have applications in fields such as electronic devices or biological sensors;¹ understanding the growth and structure of these SAMs is key to their successful implementation in these devices. In this context, the uniformity of SAMs is of great importance and the presence of multilayer islands is undesirable. However, distinguishing SAMs from ultrathin multilayers can be a challenge for most conventional surface characterization techniques. The T-BAG method (tethering by aggregation and growth) has been shown to be simple and reliable to grow SAMs of alkylphosphonic acids on oxide surfaces.² SAM films are by definition very thin, and therefore, investigation of structure and bonding in SAMs requires characterization techniques that are sensitive to only a few atomic layers. XPS analysis of organic SAM films has been widely used to provide information on film structure, composition, and bonding.^{3,4} However, sample charging is often a problem when using XPS to analyze insulating or only partially conducting materials such as these SAM films due to the incomplete neutralization of the photoemitted electrons.^{5–10} The low-energy

electron flood-gun technique has been used successfully for the neutralization of these excess electrons.^{11–13} An alternative approach to this problem is to use an external bias, as first reported by Dickinson et al.¹⁴ However, there is a fundamental difference between the two methods. For the electron flood-gun technique, excess electrons are supplied by an external source located above the sample, and thus results are independent of the conductivity of the sample. Moreover, over-neutralization leading to an excess of negative charge on the surface is also possible, especially for the samples with poor conductivity. In the latter case, the flow of electrons is from the ground to the sample and is, therefore, dependent on the conductivity of the sample.

Since the early development of surface analytical techniques, charging effects have been widely observed and reported to be problematic.^{15,16} However, surface charging has also been shown to yield chemical, physical, and structural information.^{12,13,17–23} The increasing use of charging effects to provide sample information is reflected in extensive work by Suzer et al.^{24–29}

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Recently we have demonstrated the use of charging to derive information about the thickness of the organic film on various surfaces.³ Charging can be troublesome when different regions of the sample experience different electrical potential, leading to differential charging. This can arise when the sample is composed of various materials of different electrical conductivity. Havercroft et al., have utilized such differential charging to obtain chemical information on aluminum alloys where a complex surface chemistry includes surface contamination.³⁰ A similar situation could also arise where a nonuniform thin film is deposited on a surface. Thus, in principle, an ideal SAM film could be distinguished from a nonuniform, yet ultrathin multilayer, film by the detection of differential surface charging in the latter case. We have shown this to be the case for SAMs of alkylphosphonic acid deposited on the native oxide of silicon by the T-BAG technique.³ Here we describe the concept of differential charging and further elaborate the use of this technique for the characterization of SAMs grown on three different substrates: stainless steel (SS), the native oxide of silicon, and glass. We also discuss the effect of substrate conductivity on the efficiency of the external biasing for differential charging neutralization.

Experimental Section

Sample Preparations. Coupons (approximately $1 \times 1 \text{ cm}^2$) of stainless steel, silicon, and glass were used as conducting, semiconducting, and insulating surfaces, respectively. T-BAG was used here to prepare octadecylphosphonic acid (ODPA) films on these surfaces; a detailed description of the deposition method has been presented elsewhere.² ODPA self-assembles on the precleaned coupons by holding them vertically in a $25 \mu\text{M}$ solution of the acid in dry THF. The solvent is allowed to evaporate at room temperature, and the coated coupons are then heated in an oven at 140°C for 48 h after which they are cleaned in a series of organic solvents to remove any multilayers. Three cycles of depositions with multiple rinsing and sonication in methanol have been used to obtain a monolayer film, whereas multilayer films were obtained by one T-BAG deposition followed by baking without rinsing. Three samples, a clean reference substrate, a monolayer ODPA film, and multilayer ODPA on each of the three substrate materials were prepared and transferred into the UHV system (base pressure of 5×10^{-9} Torr) for XPS analysis.

Analysis. All samples were analyzed by XPS using a Phoibos 150 hemispherical energy analyzer (SPECs) and a monochromatic Al source (1486.6 eV). The spectrometer was calibrated to the position of the $3d_{5/2}$ line of sputter-cleaned Ag at a binding energy of 368.25 eV and the C1s line of HOPG at 284.5 eV.³¹ A pass energy of 30 eV was used for wide-range scans, while 10 or 15 eV pass energies were used for high resolution measurements. All samples were attached to the sample holder by a stainless steel pin to ensure good electrical contact. The external electrical bias was applied with a variable dc power supply connected to the sample holder plate via a feed-through pin, as shown in Figure 1. Electrical bias in the range of +30 to -30 V was applied. Curve fitting of the core XPS lines was carried out using CasaXPS software³² with a Gaussian–Lorentzian product function and a nonlinear Shirley background subtraction.³³

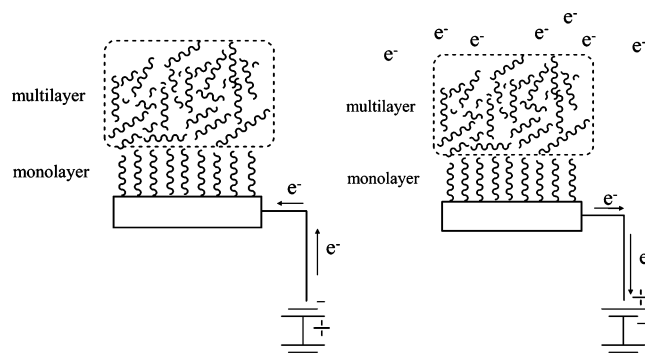


Figure 1. Schematic drawing of charge compensation for a monolayer and a multilayer film (left) on application of negative bias and (right) on the application of a positive bias.

Results and Discussion

Differential charging was used to distinguish between a multilayer and a monolayer film deposited on conducting, semiconducting, and insulating samples. The principle of this method is shown schematically in Figure 1. SAMs of phosphonic acid are grown on oxide surfaces by the T-BAG method. The lack of uniformity of the deposited film and/or the presence of multilayers might lead to the differential charging of the surface during XPS measurements. Electron compensation or neutralization of the film regions lying closer to the substrate is easy compared with that for regions physically further removed from the sample surface. This leads to differential charging in the same species depending on the distance of such regions from the sample surface. This differential charging can be amplified or reduced by the application of external biasing. On application of a negative bias, electron compensation near the surface takes place easily, whereas this is not the case for regions of the film farther from the surface, so differential charging is amplified in this case. On application of a positive bias, stray electrons from filaments in the vacuum system are attracted to the surface and thus compensate the loss of electrons from the film components at the top layer, thereby decreasing differential charging. In this study, the filament of a nude-type ion-gauge was turned on to supply stray electrons along with the application of positive bias. It has been shown in our previous work that the differential charging and application of the external bias affect mainly the position and shape of the C1s peak, while O1s and P2s lines, originating from the deposited ODPA, are less affected.³

Multilayer ODPA on the Native Oxide of Silicon. The survey scan of a silicon sample in the range of 90–300 eV is shown in Figure 2, as is that for the sample after deposition of a multilayer ODPA film. The silicon sample shows Si2p, Si2s, and a low-intensity C1s peak, which is mainly due to adventitious carbon contamination. The O1s peak is observed at about 530 eV (not shown in the figure). After deposition of multilayer ODPA, the relative intensities of the C1s and O1s lines increase concomitantly with a decrease in intensity of the Si2p and Si2s lines. In addition, a low-intensity P2s peak can also be identified, whereas the P2p peak is superimposed on the very pronounced plasmon loss peaks ($2\hbar\omega_B$) of silicon at 134 eV.

High-resolution XP spectra of Si2p, C1s, and O1s lines were measured for the silicon sample using positive or negative bias applied to the sample in the range of +30 to -30 V while recording XPS measurements (Supporting Information). No variations of C1s or other line-shapes or intensities were observed, indicating that adventitious carbon contamination is very thin and/or uniform. Thus, no differential charging is generated during the measurements of the native oxide of silicon.

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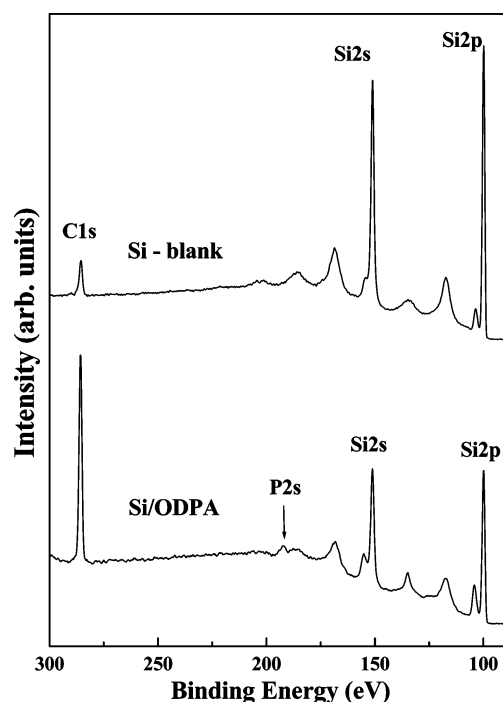


Figure 2. Typical survey scan in the 300–90 eV range of silicon sample (top) and silicon sample after deposition of multilayer ODPa film (bottom).

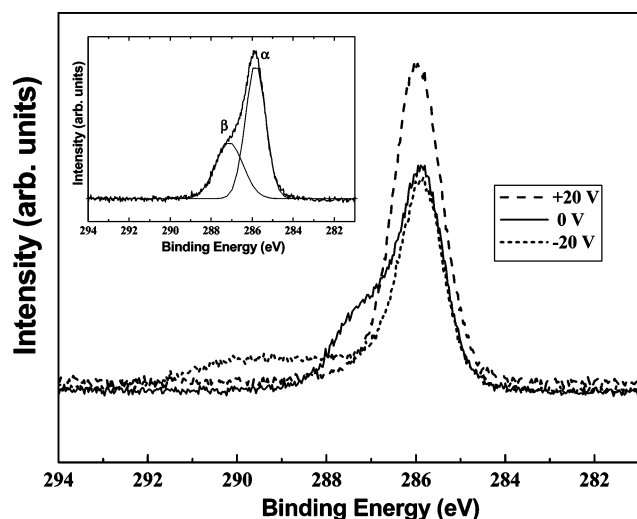


Figure 3. XPS C1s core level lines of a multilayer ODPa film on silicon measured concurrently with the application of a dc electrical bias to the sample holder. The binding energy corresponding to the applied potential has been corrected for the grounded sample. The insert shows the fit of the C1s line measured without external bias.

The C1s line measured with and without sample biasing for multilayer ODPa deposited on silicon is shown in Figure 3. The line-shape observed for the unbiased sample is asymmetrical with a well-defined shoulder on the higher-binding-energy side. This line may be fit to two peaks, at 285.6 and 286.8 eV, denoted as α and β , respectively (see the insert in Figure 3). This usually indicates that there are two different types of carbon species present on the surface. However, on application of a positive bias, all the peaks merge to produce a single line positioned at 285.6 eV. This is consistent with there being only one type of carbon (aliphatic) present on the surface; the α and β peaks are caused by differential charging of the surface. Theoretically, this differential charging can be increased by the application of a negative potential; this is observed, as shown in Figure 4. The

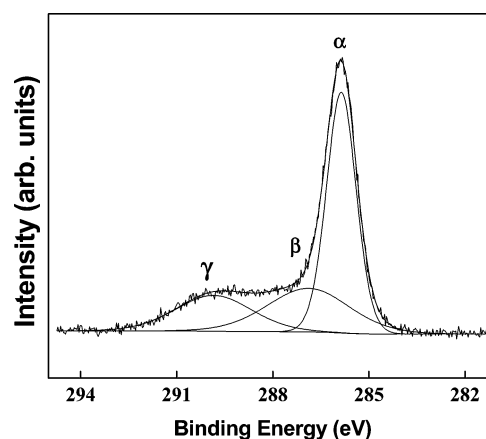


Figure 4. XPS C1s core level line of a multilayer ODPa film on silicon measured concurrently with the application of -20 V dc electrical bias. The α , β , and γ peaks are introduced to fit the curve and they can be attributed to a number of overlapping lines, which vary by different values of surface charging.

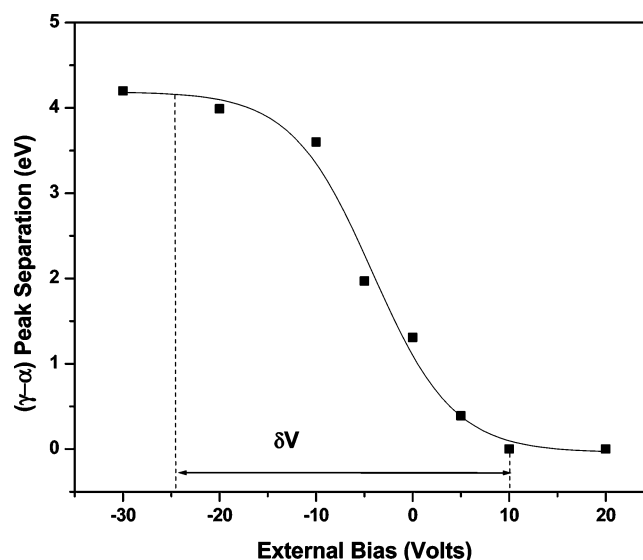


Figure 5. Plot of (γ - α) peak separation vs the applied potential for the C1s core level lines of a multilayer ODPa film on silicon. " δV " is the difference in the negative and positive potential after which there is no further peak separation.

application of -20 V external bias leads to the broadening of the peaks, and curve-fitting required at least one additional peak at 289.3 eV (denoted as γ in Figure 4).

The fwhm's of β and γ peaks (2.9 and 2.1 eV) are much higher than might be expected for an individual bonding state (ca. 1 eV under the experimental conditions used in the present work). This can be attributed to the presence of a number of overlapping lines which vary according to different amounts of surface charging. It is observed that application of negative bias increases the broadening of the peak, whereas application of positive bias decreases the broadening. The relationship between the α and γ peaks separation and the external supplied voltage is shown in Figure 5. It can be seen that the application of negative bias below -25 V or positive bias above +10 V does not affect the peak separation significantly. " δV " is defined as the difference between these two potentials. The broadening of the peak may probably correlate with the thickness of the organic film on the surface. In this regard, a sigmoidal curve can be fit to these data and a correlation can be established between the thickness of the organic film and the voltage required to stabilize the peak. In addition to film thickness, other factors may be present such as

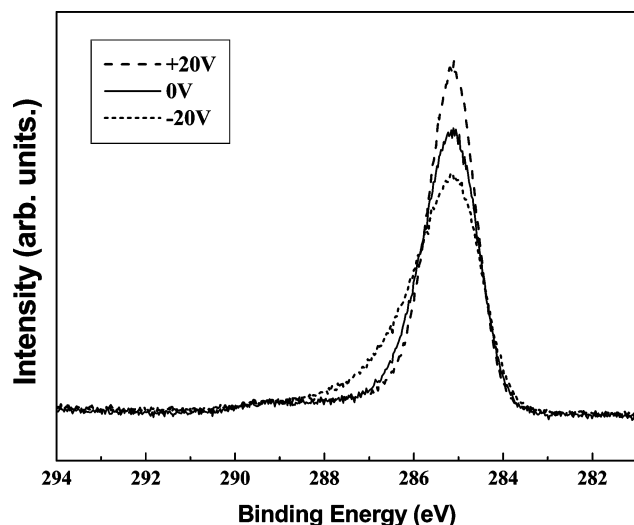


Figure 6. XPS C1s core level lines of a multilayer ODPa film on SS measured concurrently with the application of a dc electrical bias to the sample holder. The binding energy corresponding to the applied potential has been subtracted to show a better comparison.

the conductivity and roughness of the surface on which δV can depend. Further studies have to be carried out to determine this correlation. Additional control of the flow of the electrons to the surface may be achieved by using a well-controlled flood gun. This has been demonstrated by Cohen and co-workers to measure the conductivity of the organic layers on the surface.^{34,35} It should also be emphasized that there was no change in the peak shape or intensity of Si2p and Si2s lines, which further indicates that differential charging originates from variation in thickness of the deposited organic film on the surface.

Multilayers of ODPa on Stainless Steel and Glass Substrates. The dependence of differential charging and its compensation by sample biasing on the conductivity of the substrate was studied for an ODPa film deposited on glass and SS samples. The effect of external bias on the C1s region of the ODPa on SS is shown in Figure 6. An important point here is the absence of any clear evidence of surface charging when no bias is applied. However, on application of negative bias, there is clear evidence of peak broadening concomitant with a decrease in overall intensity. The application of positive bias reduced the effect of differential charging, and as a result, a higher-intensity and more symmetric peak at 285.3 eV was observed. Thus, the same general trends were observed on application of positive and negative sample biases during spectral acquisition either for conductive SS or the semiconductive silicon substrate coated with a thin native oxide film. However, in the case of SS, the peak separation is less pronounced compared to that observed on silicon. Nevertheless, this peak can be fit with a number of overlapping lines which vary by different values depending on their surface charging. The C1s region of the blank SS sample and the sample with monolayer film remained unchanged by the application of external bias (see Supporting Information).

Not surprisingly, the glass surface had the highest initial surface charging, as it is an insulating material. Surface charging was so intense that the peaks shifted during spectral acquisition. The spectra were stabilized by the application of +10 V external bias simultaneously with the operation of a nude ion gauge (as an electron source) in the vicinity of the sample holder. Detailed scans, which require higher acquisition times, showed increased

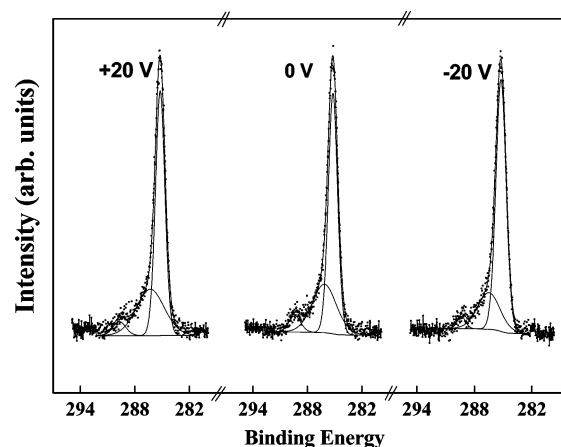


Figure 7. XPS C1s core level lines of a monolayer ODPa film on silicon measured concurrently with the application of a dc electrical bias to the sample holder. The binding energy corresponding to the applied potential has been subtracted for clarity.

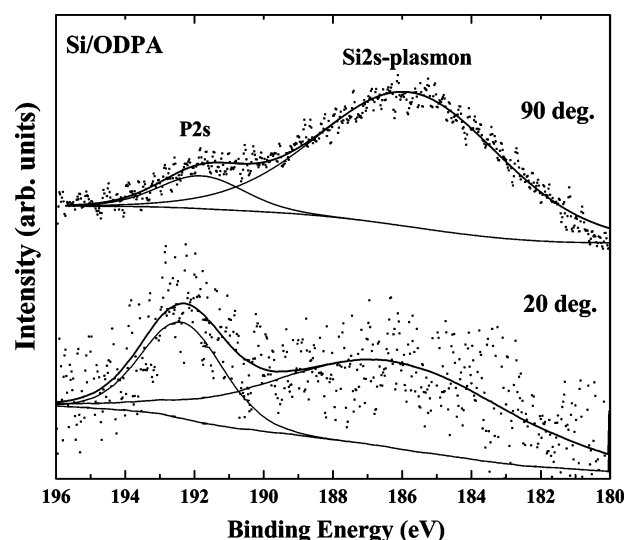


Figure 8. Angle-dependent XPS of P2s line of a monolayer ODPa film on silicon: takeoff angles of 90° (top) and 20° (bottom).

charging, and peaks shifted during acquisition. This made it difficult to study the effect of differential charging on this sample. This illustrates the fact that using a positive external bias with an ion gauge can be used to compensate only small charging problems when a monochromatic X-ray source is used for XPS measurements.

Monolayer of ODPa on Silicon. Monolayer ODPa films were deposited on the native oxide of silicon and studied using this biasing technique. The C1s region of the Si sample with a monolayer film on the surface measured under different conditions, 0, -20, and +20 V of external bias, is shown in Figure 7. It is evident from the graph that application of positive and negative bias had no effect on the intensity or shape of the C1s line. However, one might conclude that multiple rinsings with sonication might have removed any film from the surface, and therefore, similar results are observed as for a clean surface. This had been ruled out by a detailed quantitative XPS analysis in our earlier work, which confirmed the presence of phosphorus on the surface.³ Angle resolved studies were conducted in the phosphorus region, and as shown in Figure 8, the intensity of the P2s peak (192.1 eV) increased appreciably in the case of grazing incidence (20°), as compared to normal incidence (90°). The Si2p peak remained the same on application of negative and positive bias as expected.

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Conclusions

Differential surface charging has been used to distinguish between a multilayer and a monolayer phosphonate film on the oxide surfaces of silicon, SS, and glass. A correlation can be established between the thickness of the film and the value of the external electrical bias (δV) required to stabilize the broadening of the C1s core level line in the XP spectra. It has also been demonstrated that the application of a positive bias along with the presence of an electron source (ion gauge in the vicinity of the sample holder) can act as an inexpensive electron

flood gun to overcome small charging problems that are inherent to high-resolution monochromatic XPS measurements.

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Supporting Information Available: XPS C1s core level lines of a reference silicon sample measured concurrently with the application of a dc electrical bias to the sample holder. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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