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Application of XPS spectral subtraction and multivariate analysis for the characterization of Ar^+ ion beam modified polyimide surfaces

Svitlana Pylypenko, Kateryna Artyushkova, Julia E. Fulghum *

Department of Chemical and Nuclear Engineering, University of New Mexico, 209 Farris Engineering Center, Albuquerque, NM 87131, United States

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ABSTRACT

This paper presents results of a detailed X-ray photoelectron spectroscopy (XPS) characterization of complex changes at a polyimide surface resulting from Ar^+ ion beam modification. The changes in chemical composition in the surface layer lead to formation of a layer that can act as an alignment layer for liquid crystals. The goal of this paper is to report on the result of a combination of spectral subtraction and multivariate analysis for analysis of XPS spectra. Principal component analysis (PCA), applied to curve-fitting results of difference spectra and multivariate curve resolution (MCR), applied to raw spectra, provided consistent results, and allowed for extraction of chemical anisotropy, defining factor in the ion beam (IB) alignment mechanism. This study demonstrated that more detailed chemical information about complex systems can be obtained through application of multivariate analysis to XPS spectra and curve-fits. Further, this approach can be effectively used in the characterization of various complex materials to link chemical structure to their properties.

1. Introduction

One common use of X-ray photoelectron spectroscopy (XPS) is in the analysis of surface modifications, which requires data from multiple samples. As the number of samples and/or areas on the sample analyzed in a particular experiment, as well as the number of elements present in the sample and parameters that were used to modify the material increase, the data sets become progressively larger and more complex. The generation of large and/or complex XPS data sets raises new data processing issues ranging from consistency of data analysis to data correlation and comparison. One important goal in the development of XPS is to maximize the information obtained from data, while reducing acquisition time. Success requires effectively utilizing all available information, including peak area, peak shape and binding energy, to provide qualitative and quantitative information about the elements present at the surface and the chemical environment of each element.

For polymer materials XPS peaks are often rather broad, while chemical shifts occur over a relatively narrow energy range. Evaluation of the chemical state of elements from high-resolution XPS spectra requires peak deconvolution through curve-fitting. Curve-fit procedures even when performed by an experienced user, according to known or tabulated chemical shifts, are subjective and can result in non-unique curve-fits. For C 1s photopeaks, minor components and components due to secondary shifts, can be overlooked as they occur at the same binding energy (BE) as major components.

Characterization of materials with similar composition or analysis of changes due to modification of material can require the detection of small changes in a series of spectra [1]. For studies of material modification, the situation may be even more complicated, as new species that are created as a result of chemical modification or treatment may appear at the same BE as species present in the starting material. Resolving minor components located close to a more significant component requires an effective method for comparing spectra from a set of similar spectra.

Fitting the spectrum using model peaks is one approach. The line-shapes defined from the model spectra (e.g. acquired from pure standards or the starting material) can be used as synthetic components in a peak curve-fitting model. This approach can be advantageous when the problem is to assess the relative contribution from one or several spectra, which serve as model spectra, into another spectrum. This method of curve-fit was demonstrated to be effective in the studies of polymer blends [2] and catalyst structures [3]. However, model-based curve-fits can be applied only when model compounds and spectra are available. Additionally, the assumption that a percentage of a pure standard is unchanged in the mixture or in surface-modified samples is not always valid. Another way to curve-fit a series of complex spectra

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* Corresponding author.
E-mail address: jfulghum@unm.edu (J.E. Fulghum).

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with irregular chemical changes is to mathematically manipulate the spectra, such as through spectral subtraction. This method allows for enhancement of differences in the spectra and detection of small changes in the surface composition.

Multivariate techniques are often utilized as an alternative to, or in combination with, conventional curve-fitting as they facilitate reducing the dimensionality of large data sets, resolving overlapped components in spectra, and extracting subtleties in the data. They also offer an excellent tool for visualization of complex data sets, simplifying the interpretation of results. One of the most widely used, principal component analysis (PCA) transforms the matrix comprised of the experimental data into a few principal components. Multivariate self-modeling curve resolution (MCR) method is one of the extensions of PCA that allows the extraction of positive spectral profiles from an unresolved mixture. In this paper we demonstrate applications of conventional curve-fitting, and PCA applied to curve-fits obtained after spectral subtraction. MCR analyses have utilized an Alternating Least Squares (ALS) algorithm and was applied to the raw high-resolution XPS spectra. These various approaches were used to study surface-modified polyimide layers. The polymer was modified by irradiation with an Ar^+ ion beam, resulting in the changes in the chemical composition of the surface layer. Ar^+ ion beam exposure can be used to make substrates that can act as an alignment layers for liquid crystals in liquid crystal devices [4–9]. Multiple effects, including topography and chemical anisotropy, can be involved in the mechanism of alignment of liquid crystals by Ar^+ beam exposure [10,11]. It is thought that IB alignment is based on angular selective destruction and rearrangement of the surface material that creates orientational order on the initially isotropic surface [10]. It is clear that in order to understand the mechanism of IB alignment, the initial structure and the changes in chemical states at the surface of the polymer induced by Ar^+ ion beam irradiation should be thoroughly investigated. XPS is the technique of choice for surface chemical characterization of the uppermost molecular layer of polymers, and has been recently utilized in the extraction of chemical anisotropy [12].

2. Experimental

Polyimide films were prepared by spin-coating a solution of the polyamic acid (PI 2555, from Dupont) on ITO/glass substrates. The coated substrates were soft-baked at 90 °C for 1 min and then hard-baked at 250 °C for 1 h. Ar^+ ion beam exposure of polymer films was conducted using the Ar^+ ion gun on the Kratos AXIS Ultra photoelectron spectrometer. The substrates were bombarded at a 45° angle to the surface plane using a 2 keV beam energy.

XPS measurements were performed with a Kratos Axis Ultra X-ray photoelectron spectrometer using a monochromatic Al Kα source operating at 300 W, and charge compensation using low energy electrons. The base pressure was about 2×10^{-10} Torr, and operating pressure was around 2×10^{-9} Torr. Survey and high-resolution spectra were acquired at pass energies of 80 and 20 eV and step size of 1 and 0.1 eV, respectively. In the rotation experiment, XPS analyses were performed for three IB bombarded samples and one unbombarded reference sample. Quantification was based on the analysis of three areas per sample. For details of the rotation experiments please refer to Section 3.

Data analysis and quantification were performed using the Vision software provided by the manufacturer and CasaXPS (http://www.casaxps.com/). Spectra were corrected for background, charge-referenced to carbon at 285 eV, and curve-fitted with 70% Gaussian/30% Lorentzian functions of constrained width. The width of peaks, dictated by FWHM of monochromatic source, analyzer settings and element (electron shell), in the curve-fit of C 1s, O 1s and N 1s were set to be 0.9, 1.2 and 1.0, respectively. Spectral subtraction, followed by curve-fitting of the difference spectra, was performed using CasaXPS software. Standard deviations were on the order of 1%.

Multivariate analysis was performed in the MATLAB environment using an in-house graphical user interface based on the 4.1 PLS_Toolbox. The MCR routine was downloaded from http://www.ub.edu/gesq/mcr/mcr.htm. Prior to PCA analysis, mean scaling was applied to the data sets consisting of curve-fits of single elements. The spectral preprocessing prior to the MCR was consistent with processing employed in quantitative XPS. Straight-line backgrounds were subtracted from C 1s spectra prior to MCR. All spectra were calibrated so that the hydrocarbon peak is at 285 eV. No scaling of data was done for MCR analysis with non-negativity constrains.

3. Results and discussion

3.1. Initial XPS characterization

Table 1 lists changes in elemental concentrations in the polyimide surface resulting from Ar^+ beam exposure. Averages of 3 areas per samples for 3 samples are shown with standard deviations on the order of 1%. Survey and high-resolution XPS spectra of carbon, oxygen and nitrogen were acquired before and after Ar^+ beam exposure for various times. The most significant changes in the surface layer occur in the first 20 min of IB irradiation. Ar^+ beam exposure appears to selectively deplete oxygen and nitrogen.

The curve-fits for PI 2555 before IB exposure and after 10 min of IB bombardment, along with the polyimide structure, are shown in Fig. 1. The different carbon chemical environments in the PI 2555 structure will give rise to multiple overlapping peaks in the C 1s spectra [13]. Initially, this theoretical composition was used to evaluate the number and positions of the components required to fit C 1s. Then the curve-fitting procedure was performed and amounts/positions of the components were adjusted as necessary to take into account experimental composition. The curve-fit obtained from the unbombarded polymer was used as the starting point for analysis of the C 1s photopeak from the bombarded polyimide. Changes in the spectrum necessitated the addition of additional components, and the area and positions of all components were then adjusted to obtain the best fit.

As shown in Fig. 1a, the C 1s peak of unexposed polyimide contains eight carbon species. The peak at 288.6 eV is the carbonyl carbon of the imide ring, the peak at 285.5 eV is $C^*{-}C{=}O$ connected to the carbonyl carbon, which connects two phenyl rings on the backbone of the polymer chain, and the peak at 285.3 eV is saturated hydrocarbons. The decrease in their intensities after ion beam exposure is apparently associated with the loss of oxygen and nitrogen, as the $C^*{-}C{=}O$ and the imide ring are destroyed (Fig. 1b). The curve-fits of O 1s and N 1s (not shown) also indicate a decrease in concentrations of nitrogen and oxygen in the imide ring. These observations suggest that the

Table 1
Changes of C, O and N content and their relative ratios in PI 2555 as a function of Ar^+ beam exposure time.

IB time (min)	C (%)	O (%)	N (%)	C/O	C/N
0	77.4	16.6	6.0	4.7	13.0
1	78.7	15.4	5.9	5.1	13.3
5	82.9	11.4	5.7	7.3	14.7
10	86.9	7.5	5.6	11.6	15.5
12.5	88.4	6.5	5.1	13.6	17.3
15	88.9	6.2	4.9	14.3	18.1
17.5	90.3	5.1	4.6	17.8	19.5
20	90.4	4.9	4.7	18.3	19.3