Laboratory XPS Imaging: Improved Procedures and Data Analysis

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Laboratory XPS imaging has changed dramatically with the most recent generation of XPS instrumentation. Image acquisition times of seconds to minutes have transformed XPS imaging from a novelty to a routine analysis method. This transition has been facilitated by the development of focused x-ray sources, new analyzers and improved detection systems. Methods of image acquisition, and current capabilities will be demonstrated, and speculations about future developments will be offered.

This enhanced surface chemical characterization of heterogeneous samples comes at the cost of increasing complexity in the XPS data sets acquired. For example, in a spectra-from-images experiment, images are acquired as a function of binding energy. The resulting multi-spectral imaging data set is a complex data structure, requiring more sophisticated analysis methods than visual inspection, if the data are to be interpreted effectively. We will discuss a variety of multivariate analysis methods that can be utilized to assist in the evaluation of large data sets

New opportunities for multi-technique correlations also arise from the improved spatial resolution and decreased data acquisition times. A variety of techniques, including FTIR, AFM and TOF-SIMS have spatial resolutions comparable to, or better than XPS, making correlative analyses possible. Examples demonstrating the additional information obtained when XPS measurements are combined with imaging FTIR or AFM will be shown. Considerations in comparison of images of very different spatial resolutions will be discussed.

Introduction.

The objective of XPS imaging is to quantitatively map surface elemental and chemical distributions for heterogeneous or patterned samples. New approaches to photoelectron imaging have developed in recent generations of commercial instrumentation. A spatial resolution of several microns is now achievable with acquisition times of minutes rather than hours [1]. Imaging can be used to locate a region from which to acquire small area spectra, to display chemical or elemental state distributions or to map overlayer thicknesses.

Improvements in spatial resolution and data acquisition times for a variety of analytical instrumentation, in combination with improvements in imaging XPS, allow for new approaches to the chemical characterization of complex heterogeneous materials. This article discusses several different approaches that are now possible for the characterization of complex materials.

Experimental details and data acquisition

The XPS spectra and images were acquired on a Kratos AXIS Ultra photoelectron spectrometer using a monochromatic Al K$\forall$ source operating at 300W. The base pressure was $2x10^{-10}$ Torr, and the operating pressure was $2x10^{-9}$ Torr. Charge compensation was accomplished using low energy electrons.

The Kratos XPS has a spatial resolution of down to 2-3 μm's in images [2]. This instrument features a recent development in XPS instrumentation: the spherical mirror analyzer. This analyzer provides real time chemical state and elemental imaging. Using a standard input lens, the photoelectrons pass through the outer hemisphere into a spherical mirror analyzer and back to the detector plane. The spatial relationship of electrons emitted from the surface is maintained, allowing for real time detection using a microchannel plate detector.

Example 1. Images-to-spectra experiment

Project description

X-ray photoelectron spectroscopy (XPS) has not previously been utilized to evaluate the chemical changes which occur in Si(100) as a result of Ga^+ beam bombardment during focused ion beam (FIB) milling. This study evaluates the utility of high spatial resolution XPS analysis in the analysis of FIB specimens, which are typically 5 μm wide x 30 μm long x 100 nm thick. Images-to-spectra datasets are utilized in order to obtain spectra from smaller areas than are possible through acquisition of small area spectra.

Experimental details

The degree of oxidation on the surface of a FIB-milled Si (100) specimen was determined by extracting Si 2p spectra from a set of high spatial resolution Si 2p images. For the images-to-spectra experiment, a series of Si 2p images were collected in 0.2 eV steps over a binding energy (BE) range of 94.0 eV to 104.0 eV. Each high spatial resolution image was acquired at a pass energy of 80 eV for 1 hour. A single pixel was selected from one of the images and the intensity for that pixel was used as a single point in the spectrum. The spectrum was developed by plotting pixel intensities as a function of BE. The result was a single spectrum extracted from the series of images.

Results and discussion

Si oxidation in the FIB-milled sample is evaluated using an images-to-spectra data set. The images displayed in Fig. 1a) are 200 μm^2 and contain 256 x 256 pixels, thus Si 2p spectra which are extracted from single pixels resulted in analysis areas of approximately 1 μm^2. The locations on the FIB specimen from which single-pixel spectra were extracted are shown in Fig. 1b).

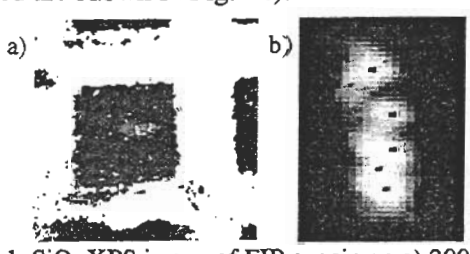

Figure 1. SiO_2 XPS image of FIB specimen a) 200x200 μm^2 ; b) region selected for extraction of Si 2p spectra.

Two of the extracted Si 2p spectra are shown in Fig. 2. The Si 2p spectra extracted from the images-to-spectra dataset were curve-fit in order to semi-quantitatively determine the relative concentrations of Si^0 and Si^{+4} at each of the six pixel locations. The Si 2p spectra extracted from the specimen shortly after FIB-milling contained an average of 24% Si^{+4} (SiO_2), while the same sample contained an average of 44 % Si^{+4} after 4 months.

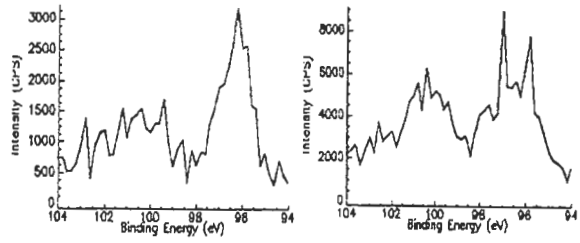

Figure 2. Si 2p spectra from a single pixel (~1:m^2), a) as-received and b) after 4 months

Conclusions

The spectra acquired from the image data sets show clear differences between the as-received and aged FIB sample. It is important to evaluate the limitations of small area spectroscopy on this small sample and to consider alternate data collection methods, such as imaging and images-to-spectra datasets presented here. For this sample, the Si 2p high resolution spectra, which were collected from areas 15 μm in diameter were less useful than the spectra-from-images results. The 15 μm spectra include a sampled area which is larger than the FIB specimen, while the spectra-from-images can be restricted to selected regions of the specimen. [3].

Example 2. Multivariate Data Analysis

Project description.

The recent improvements in analytical instrumentation also increase the complexity in the datasets which are acquired. Multidimensional imaging data sets such as the images-to-spectra experiment discussed above present challenges for qualitative and quantitative analysis. Multivariate analysis (MVA) methods can aid the analyst in interpreting the vast amount of information resulting from multi-dimensional data set acquisitions.

The sample for this project was collected from carbonate rocks found on the shores of Lake

Alchichica in Mexico. This alkaline lake is situated in a volcanic crater and is rich in Mg. The rocks are white with rough surfaces, and green and brown features in the holes and contain 10 different elements. (Fig. 3) Medium magnification (350x350 microns) images and backgrounds were acquired from areas of interest. 11 chemical images (9 elements and 2 types of carbon) acquired from the same area on the sample are evaluated as a multivariate image data set.

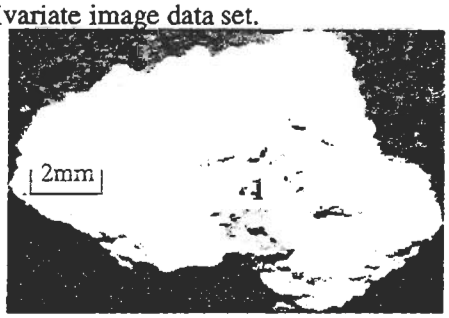

Figure 3. Carbonate rock

This project utilizes photoelectron imaging in combination with MVA in order to characterize compositional variation as a function of color variation, and to identify the types of carbonic materials and magnesium compounds (carbonates or oxides) present. Surface analysis of this sample represents a different challenge than the FIB sample. Although the sample is large, the analytical signals depend not only on the surface composition but also upon the local topography. Scatter diagrams, principal component analysis (PCA) and classification are used to evaluate the extent of artifacts in the images and to distinguish between the regions varying in chemical composition vs. topography.

Data Analysis.

Large image data sets can be analyzed using Multivariate Image Analysis (MIA). The goal of MIA methods is to extract significant information from an image data set while reducing the dimensionality of the data. PCA divides information into orthogonal components by transforming multivariate images into a number of *score* images. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. The objective is to identify images which are globally correlated or anti-correlated. This information can be displayed as *loadings* of the different maps and the pixels, which are responsible for the correlations, can be displayed as component images. Component images may be easier to interpret than pure variable images. One of the most important uses of principal components is in scatter plots of one PC image against another.

A scatter diagram, or two-dimensional histogram, yields information about the intensity relationships between two or more elemental or chemical maps, leading to the calculation of chemical phase maps. The scatter diagram results in groupings of points, which reflect different classes of pixels present in the two images. This approach provides a rapid analysis of the images's content in terms of correlation (points along the first diagonal) and anti-correlation (points along the second diagonal). If a cluster of representative points, or part of a cluster, in the scatter diagram is selected, the group of points can be backprojected to the regions of the image which contribute to the cluster. After the back projection, the spatial relationship of pixels possessing a chemical similarity can be studied.

Classification is the process of assigning data to one of a fixed number of possible classes. The goal is to convert the numerical image data into descriptive labels that categorize different surface materials or conditions. Phase maps, images that show the spatial distribution of a particular phase, are obtained from classification. Unsupervised classification uses statistical techniques to group n-dimensional data into natural spectral classes.

Results and discussion.

Spectroscopic analysis of multiple areas on the sample distinguishes major categories of regions existing in the sample. Areas on the white part of

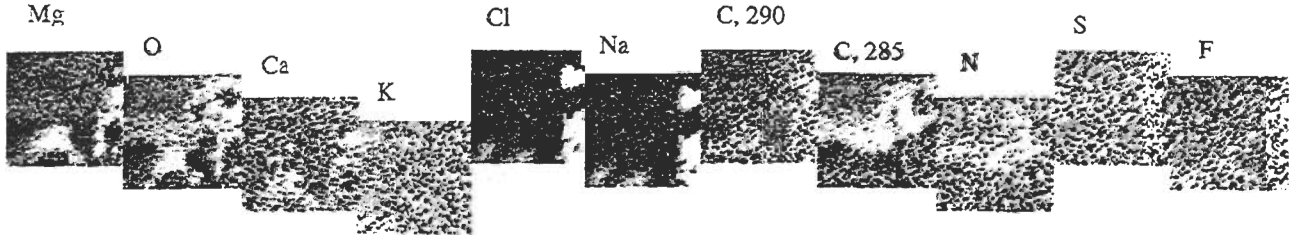

Figure 4. 350x350 ăm XPS images acquired from area 1 on the sample shown in Fig. 3

sample are enriched in Ca and Mg carbonates oxides and depleted in C and N, while areas on colored part of the sample are enriched in N- aining organics. A third group of areas, aining both white and colored regions on the ple, are enriched in Na and Cl.

An example of the information that can be ined from image analysis is presented for area 1, ted in the green part of the sample on Fig. 3 re 4). From spectroscopic analysis, it is evident this area is depleted in O, Mg, K, Ca and ched in C and N.

Application of PCA to background-corrected ges results in a three-component model. (Figure he 1st PC image is very similar to the O and Mg ges. Indeed its loading has the highest ribution from O, Mg, Ca and the C component 90 eV, allowing for identification of the 1st ponent as Mg and Ca carbonates. The 2nd ponent image is similar to the inverse of Cl and and the loading shows the highest negative ribution due to Cl and Na. The 3rd PC image is lar to the image of the C component at 285 eV laid on the inverse of the Mg and Ca images. highest contribution to this component is due to at 285 eV, N, Ca and Mg. Components esenting three distinct chemical phases, Ca and carbonates, sodium chloride and N-containing on, are thus extracted by PCA.

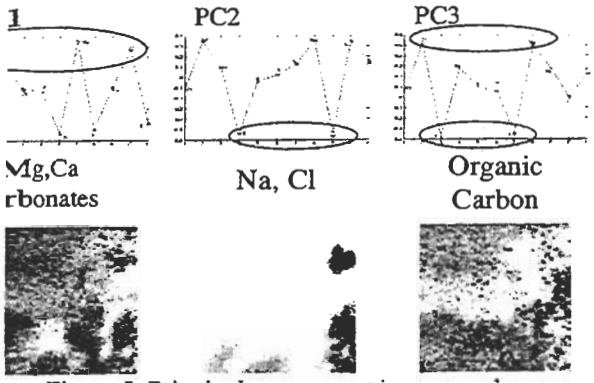

Figure 5. Principal component images and loadings for 3-component model

The scatter plot of the 1st vs the 2nd principal ponent images results in a cloud consisting of an with the highest concentration of points along 1st diagonal and a less dense cloud around it. (Fig. The cloud is divided into three parts and projected to the original image. This is an active procedure in which the analyst decides how to divide the scatter plot based on external knowledge available, such as chemical/elemental images and PC images. The first two principal components show the spatial representation of two phases: carbonates and sodium chloride on a background. The scatter plot of PC1 vs PC3 results in a larger spread of points. The division of this scatter plot into three parts provides additional details on the chemical phases present in the sample. Three chemical and one topographic phase are identified using scatter plot analysis of PC images.

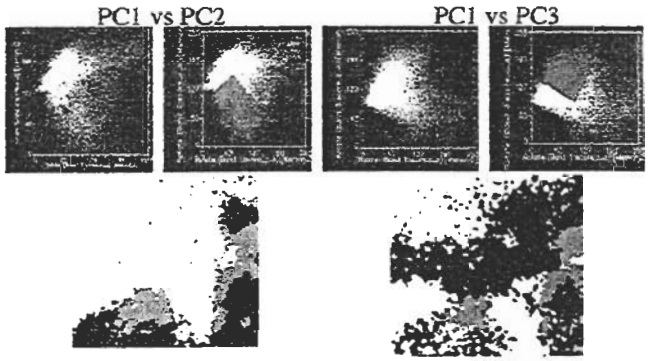

Figure 6.Scatter plot of principal component vs each other. Original scatter plot, scatter plot with areas selected and areas backprojected to original images are shown

Unsupervised classification was also applied to the images. The 4-classes model obtained is shown in Fig. 7. Topographic background, sodium chloride, a carbonate phase and organic carbon are classified. Small area C 1s high resolution spectra were acquired from identified phases, confirming this analysis. It is observed that both organic and inorganic carbon are present in this area on the sample. Post-classification statistics allow for quantitative conclusions on the percentage each phase occupies.

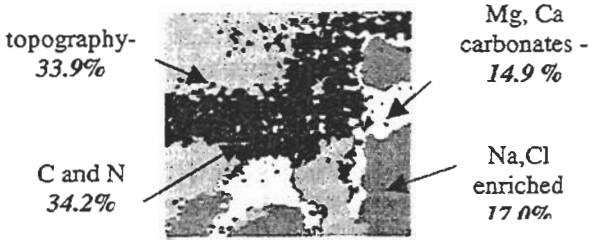

Figure 7. Unsupervised classification. 4-classes model.

Conclusions.

The application of MVA methods extracts chemical information from large data sets. Chemical phases and topographical artifacts can be separated

through application of PCA, scatter plot and classification analyses.

Example 3. Technique correlation

Project Description.

Multivariate methods applied to data sets from a single technique can enhance data interpretation, and therefore contribute to a more complete understanding of sample structure. Complete characterization of a complex material, however, requires information not only on the surface or bulk chemical components, but also on stereometric features such as size, distance, and homogeneity in three-dimensional space. Combining data acquired from the same area on the sample by different techniques, i.e. from XPS, FTIR, TOF-SIMS and AFM, should reveal more information than would be obtained if each data type was processed separately.

Image correlation and registration aspects must be taken into account for direct correlative studies. Differences in technique sampling properties, such as sampling depth; field of view (FOV), spatial resolution and, the hardest and most important part, image alignment must be considered.

At this stage of instrumentation development, commercially available FTIR and XPS instruments offer similar characteristics, such as rapid, real-time imaging with comparable lateral resolution and, critically, comparable image fields, allowing for direct correlative studies. XPS samples approximately the top 10 nm of the film, while the FTIR images acquired in transmission mode are representative of the total film. This direct correlation allows for evaluation of the extent of phase separation and phase segregation in multicomponent systems.

Atomic force microscopy (AFM) is widely used for the determination of the topography of surfaces of solid materials with resolution down to atomic resolution in special cases. Phase imaging goes beyond simple topographical mapping to detect variations in composition, adhesion, viscoelasticity, and perhaps, other properties. It is critical to identify phases present in AFM phase images. By using relatively large scanned areas, the AFM images can be correlated with XPS images to assist in identification of phases. XPS and AFM image correlation is a much more complicated task than XPS/FTIR correlation as a result of significantly different image properties.

A patterned sample, consisting of 6 äm lines of polymer deposited on an indium tin oxide (ITO) substrate, and a polymer blend of 50%/50% poly(vinyl chloride), PVC, and poly(methyl methacrylate), PMMA are utilized in these correlative studies.

Results and discussion.

Figure 8 compares FTIR and XPS images acquired from the same areas on two different polymer blend samples. The XPS images have been rotated to facilitate comparison. Both the XPS and FTIR images from blends of low molecular weight PMMA (Fig. 8a) show large, intense PVC-enriched features. The XPS images of high molecular weight PMMA samples, in Figure 8b, show less contrast and fewer distinct features. The FTIR images from these two films show more contrast, but the shape and size of PVC-enriched areas are similar to those on the XPS images.

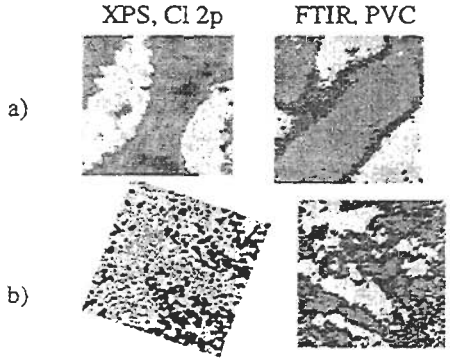

Figure 8. 350x350 äm XPS and FTIR images acquired from the same area on the sample for 2 regions a) and b)

This study is the first to demonstrate that XPS and FTIR images and spectra can be acquired from the same areas of samples in order to correlate micro- and macro properties at the surface and in the bulk of heterogeneous polymer blends [4,5].

To correlate AFM and XPS images, properties of images from both techniques have to be compared and matched. Initially a patterned sample with known properties is used to design the procedure for XPS/AFM correlation, and then this procedure is applied to XPS and AFM images acquired from the polymer blend.

If a large scanned area is used, there is overlap between the field of view in AFM and XPS images.

The biggest difference in the image properties of the two techniques is clearly spatial resolution. The resolution in XPS images is 2-5 microns, while that in AFM images is ~nanometers. For image correlation, the AFM images can be deresolved by applying a median convolution filter, in order to approximate the XPS resolution. Figure 9 shows 20x20 μm original and deresolved AFM images together with a cropped XPS image of the same size from a polymer blend. The shape and size of features observed in XPS and deresolved AFM images are similar.

Figure 9. Comparison of original, deresolved AFM and cropped XPS imaged from 50%/50% PVC/ PMMA blend

For a quantitative comparison of images from the two techniques, unsupervised classification can be applied to AFM topographic and phase images as well as XPS images. Post-classification statistics will then provide the percentage of the image each class occupies. This approach first was applied to the patterned sample. A 2-phase model is classified in which phase 1 represents the ITO substrate, while phase 2 represents the 6 äm lines of deposited polymer. Table 1 shows the %ITO resulting from image classification applied to 4 AFM and 24 XPS images of three different sizes. Both methods give statistically similar results.

Table 1. Classification results from deresolved AFM and cropped XPS images on patterned sample

	% ITO from image classification		
Image size	AFM Topography	AFM Phase	XPS
30x30 μm	50.3 ±0.8	50.5 ±9.3	48.7 ±1.3
50x50 μm	50.2 ±0.8	49.6 ±5.5	48.8 ±0.4
100x100 μm	50.1 ±1.1	44.1 ±2.6	48.3 ±0.9

The same procedure was applied to AFM and XPS images acquired from 25%/75%, 50%/50% and 75%/25% PVC/PMMA blends. Figure 10 shows the good correlation obtained between the XPS and AFM classification results.

The hardest task in direct correlative studies is image alignment. If the same areas are to be analyzed using XPS and AFM, the analysis area must be located using both techniques. Marking the small areas analyzed using the AFM requires a more sophisticated approach than using a felt pen or locator grids. One alternative is to draw a box around the analysis area using contact mode AFM. Figure 11 shows the areas marked by the AFM in optical and XPS images. This method allows for AFM and XPS analysis of the same sample areas, providing a new method for identifying phases in AFM images or for correlation of topography with surface chemistry.

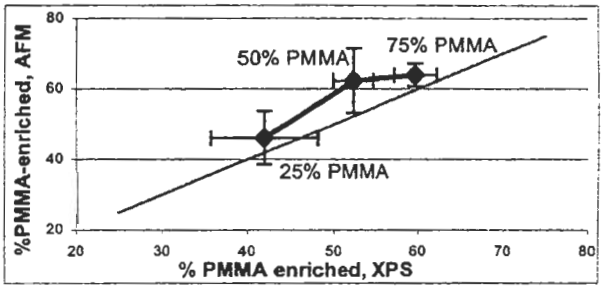

Figure 10. Classification results applied to XPS and AFM images from PVC/PMMA blend

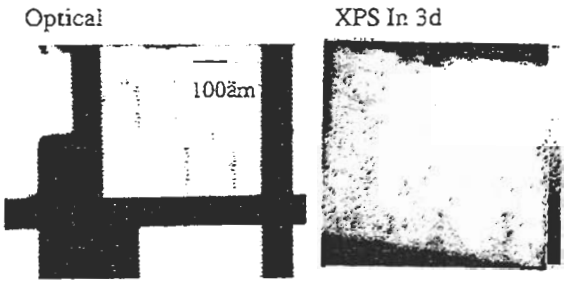

Figure 11. Two boxes drawn with AFM tip. Left – optical and right – 350x350 äm XPS In 3d images

Conclusions

The development of rapid imaging capabilities in a variety of techniques facilitates multitechnique analysis. Although new methods of sample preparation and data correlation are required, this effort will result in correlated surface and bulk chemical characterization.

General conclusions

Current laboratory photoelectron imaging capabilities allow for characterization of complex, heterogeneous materials which could not previously be effectively analyzed using XPS. Large data sets result, however, from samples containing multiple chemical phases, which are heterogeneously distributed. The use of MVA methods dramatically improves the chemical information which can be extracted from these data sets. Surface chemical characterization of materials can be enhanced through correlation of bulk or topographic information. The overlap in field of view between XPS, FTIR and AFM offers new possibilities for non-destructive 3-D sample characterization.

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