Principal component analysis of TOF-SIMS spectra, images and depth profiles: an industrial perspective

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Abstract

Principal component analysis (PCA) has been successfully applied to time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectra, images and depth profiles. Although SIMS spectral data sets can be small (in comparison to datasets typically discussed in literature from other analytical techniques such as gas or liquid chromatography), each spectrum has thousands of ions resulting in what can be a difficult comparison of samples. Analysis of industrially-derived samples means the identity of most surface species are unknown a priori and samples must be analyzed rapidly to satisfy customer demands. PCA enables rapid assessment of spectral differences (or lack there of) between samples and identification of chemically different areas on sample surfaces for images. Depth profile analysis helps define interfaces and identify low-level components in the system.
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1. Introduction

The quest of the industrial SIMS analyst is to rapidly assess which ions are important in an analysis and to determine their identities. Analytical requests are commonly based on performance issues where samples are designated ''good'' and ''bad'' and the goal is to determine how the surface chemistry affects product performance. Often the chemistry is unknown, creating the potential for a tedious and difficult process. In addition, SIMS spectra are rich with information and, for static SIMS, often contain in excess of 1000 different secondary ion species.

Principal component analysis (PCA) has been applied to SIMS data, but most published applications have been confined to academic labs [1–4]. We have applied PCA to SIMS data in order to more rapidly assess surface chemistry differences between samples, to characterize images and to interpret depth profiles. The chemistries of samples submitted for surface analysis are highly diverse and span almost the entire spectrum of Rohm and Haas businesses including paints, adhesives, electronic materials, electronic devices, ion exchange resins, building products, household and personal care products, and paper.

Compared to several previous literature examples using PCA [1–4], there are several notable differences in the way PCA is used in our industrial analytical lab. In order to prevent analyst bias, almost all data is included in the analysis. Species with masses less than 25 amu are typically excluded due to high intensities with low information. Spectral intensities are typically binned into 0.2 amu bins. Binning has two advantages: the quality of the mass calibration is less crucial due to the size of the bin and the number of data points

analyzed is fewer than if all data were analyzed individually. For multiple species in the same bin, the assumption is the overall intensity will change if one or more of the individual components changes. Models with control samples are not built, but rather PCA is used in a much more qualitative manner. It is rare that we are supplied all appropriate standards or that we receive controlled sample sets. Furthermore, the composition of the sample is often unknown to a large extent as many projects involve materials formulated outside Rohm and Haas or that are exposed to the environment. In addition, we are routinely asked to compare surface chemistries on a very small set of samples (often between two and five) in an analysis time totaling less than 4 h. PCA is usually used on data sets with four samples or more, but has been successfully applied to sample sets with only two samples to bring out very subtle differences. Lastly, the goal of using PCA is to solve performance problems, so less focus is placed on performing the optimum principal component analysis and more focus is placed on the interpretation of the PCA results as they answer the original problem.

2. Experimental

PCA was accomplished using Matlab, The Mathworks and PLS_Toolbox 3.0 (Eigenvector Inc.). SIMS data were acquired on an Ion-TOF IV TOF-SIMS instrument. The methods in this report should be applicable to most types of SIMS data. For mass spectra, intensities are not normalized to total ion intensities since data are generally acquired under the same analysis conditions on the same day. Mean centering is used for spectral data.

For images, data are generally put into 1 amu bins to save analysis time (a 128×128 pixel image is essentially PCA of 16,384 spectra) and to increase the signal level in each bin. Experience in our group has shown that better quality PCA data is obtained by autoscaling the image data instead of mean centering, possibly due to the low signal in each individual pixel.

PCA results are compared to the original data in each case. In part, this is due to binning since the effective mass resolution is decreased. In addition, this verifies the accuracy of the PCA.

3. Applications

In this paper, applications of PCA to several industrial problems are demonstrated. The first project involved SIMS spectra from steel samples with poor and acceptable adhesion to metal-bonding adhesives. In Fig. 1, the first principal component (PC1) scores (a) and loadings (b) of the negative ion spectra from good and bad performing steel are shown. Both sides of each piece of steel were analyzed resulting in a dataset of essentially four samples. Here, we can see that the bad steel (with positive scores) is rich in both
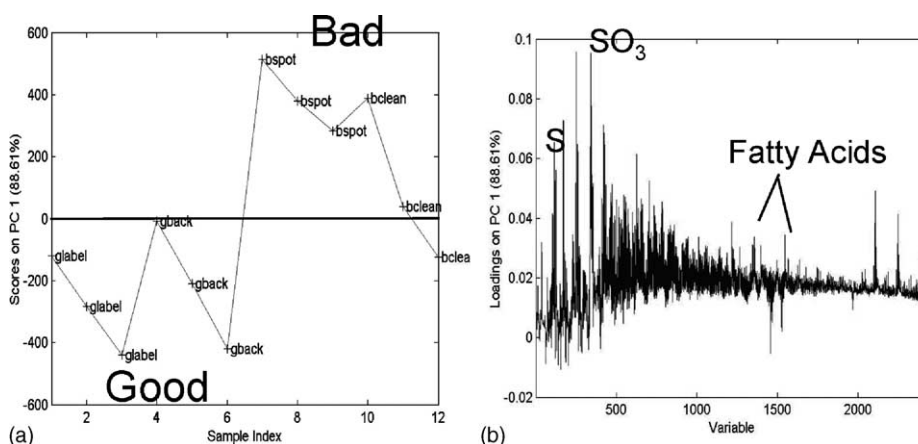

Fig. 1. PC1 of negative ion SIMS data from good and bad steel samples. Scores (a) are on the left and the loading (b) is on the right.

fatty acids and S-containing species (shown in the positive loadings), both of which are known to interfere with adhesion. This can be confirmed with careful examination of the original spectra.

Image analysis was also used to rapidly identify chemical heterogeneity on surfaces. Using PCA, we identified small regions on an electronic device with unique chemistries that were not apparent in the total ion image. Scores associated with each pixel (each is a complete mass spectrum) are mapped into a color scale for each principal component. The result is regions in the image that have clusters of pixels with a certain color. Pixels with the same color have similar chemistry according to the particular principal component.

Interesting clusters of pixels (which often appear as bright spots) in score images should result in a careful examination of the loading for that principal component to understand which ions are associated with that particular region of the image. In Fig. 2, data from a loading from a PCA for an electronic device is shown. The score plot for PC4 indicated some bright spots, which were not apparent in the total ion image, with positive scores. Examination of the loading for PC4 shows indications of Mg, K, Ca, Fe, and Sn that were confirmed through conventional image analysis. Characterization of these regions through the region of interest spectrum alone (spectra generated from selected pixels in an image), shown in Fig. 2, would not have been as straightforward as most of the signal is from hydrocarbons and the only obvious metal is Sn.

PCA has also been applied to depth profiles. Data are extracted into individual spectra at uniform time intervals. In the case below, the chemistry of each layer was known, but PCA was applied to this simple example in order to determine if unique and minor species could be identified. An example of PCA data from a depth profile Fig. 3a and identification of minor components at interfaces is shown in Fig. 3b.

Although the score plot is complicated, there is quite a bit of information that can be quickly extracted. Each inflection point or crossing of the axis corresponds to the start or end of chemical diffusion or the point where the chemistry of a layer becomes constant. Some of these points may correspond to an unexpected or contamination layer. On the right (Fig. 3c), we can see that there are mixed metals and mixed metal oxide species in addition to the pure metal and metal oxides that are significant in PC3. The Ti layer is adjacent to the W and Au layers, but the presence of AuTi and $TiWO_x$ ions was unexpected and could have been overlooked in the conventional analysis. These species have very low intensities (three orders of magnitude less than the major components) in the spectrum from the entire depth profile, yet at certain depths they are quite significant. There is some evidence in the literature that these species may actually be alloys and not just clusters formed during sputtering [5].

PCA also aided greatly in ion assignments in the spectrum. Ions from nominal mass 245 to 250 amu, excluding 249 had a positive loading for PC2. Note that this is not the same pattern as with PC3 shown in
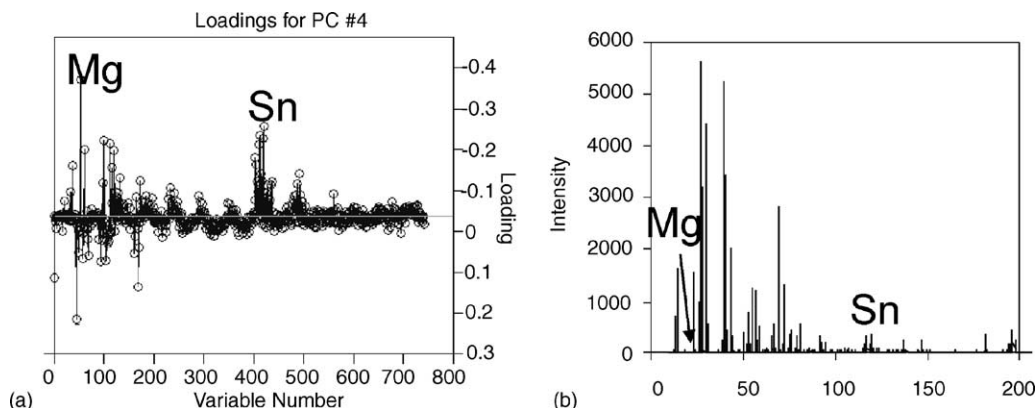

Fig. 2. Loading (a) for PC4 from PCA image analysis of an electronic device on the left. Region of interest spectrum (b) from regions with positive loadings in PC4 on the right. Species in the loading are also labeled with the mass at the start of the bin resulting in a thick black line from overprinting.
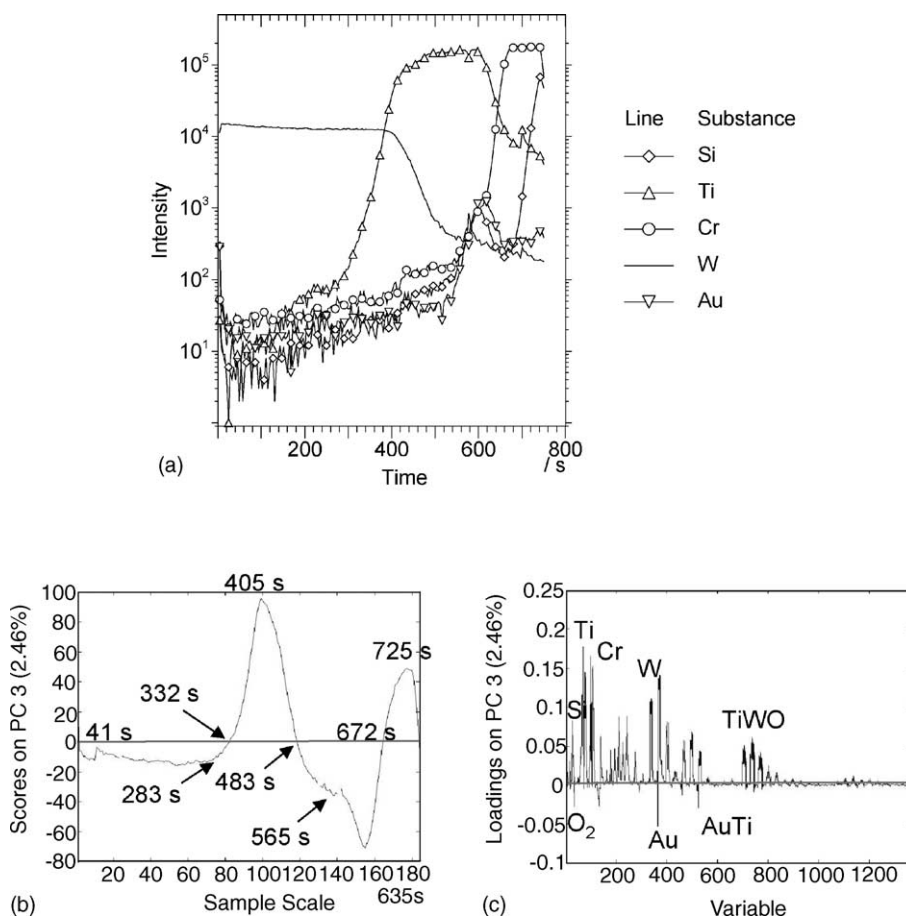
Fig. 3. (a) Positive ion SIMS depth profile of layered device consisting of W over Ti over Cr over Au over Si, PCA of depth profile where scores (b) are plotted for PC3 on the left as a function of profiling time (s) and the loading (c) is on the right.

Fig. 3b and c. Examination of the spectrum in this mass range indicated similar intensities for all of these masses making ion assignments difficult. From the PCA, *m/z* 249 must be from a different species than those adjacent ions because of its negative loading. Other species with negative loadings included Cr, and in fact this ion was assigned to the major isotope of AuCr. A TiWO assignment was made to the ions at *m/z* 246, 247, 248 (major isotope) and 250, but this still left an ion at *m/z* 245 that was unexplained. Realization that Ti had a positive loading led to the conclusion that *m/z* 245 originated from AuTi. Although it is of course possible to come to these same conclusions without PCA, it is always preferable to know which ions may be related and which are unrelated in a spectrum.

4. Conclusions

Application of PCA to industrial sample sets has proven a valuable tool in increasing turnaround times and improving confidence in data analysis. PCA has been successfully applied to spectra, images, and depth profiles. We have found it most appropriate to use PCA when the performance of the sample set seems to indicate an important chemistry difference, but a difference is not obvious in the SIMS data. For sample, sets where the chemistry differences are immediately apparent, PCA is often an extra, unnecessary step. Future development for these techniques should involve the instrument vendors working along side software vendors and interested SIMS analysts in order to develop tools that are easy to use and versatile

enough to meet the needs of a broad range of users. Increasing availability and ease of use will increase the number of interested users.

Acknowledgements

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