Depth Profile Characterization of Layered Materials Using ToFSIMS Hyperspectral Imaging Coupled with Sputtering

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Abstract IASIM16

DEPTH PROFILE CHARACTERIZATION OF LAYERED MATERIALS USING TOFSIMS HYPERSPECTRAL IMAGING COUPLED WITH SPUTTERING

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Key Words: ToFSIMS, depth profiling, hyperspectral, PCA, MCR

Time-of-Flight Secondary-Ion-Mass Spectroscopy (ToFSIMS) is a useful hyperspectral imaging tool for characterization of surfaces. When coupled with sputtering, images can be acquired at a sequence of depths resulting in a time-series of images that can be used to characterize a material at a succession of depths several nanometers deep. ToF-SIMS measurements were acquired from a bilayer of C3F6 and Poly(N-isopropylacrylamide) (PNIPAM) plasma polymers on a silicon wafer at 50 sputter depths (corresponding to approximately 200 nm) and the resulting images were analyzed collectively using principal components analysis (PCA), maximum autocorrelation factors (MAF) and multivariate curve resolution (MCR). The results of the different techniques were consistent between each other and could be easily interpreted from a chemical and physical perspective. This was largely attributed to the high selectivity of the measurement technique. Although any of the three data analysis methodologies could be employed satisfactorily in practice, PCA and MCR provided the most chemically meaningful and easy to interpret results and showed clear evidence of what material was present at each layer and identified analytes not easily identified using traditional univariate analysis of the data. For example, Figure 1 shows MCR Factor 3 at all sputter depths, *d*, indicating it is associated with the top layer and Figure 2 shows the MCR contributions for six factors. The different layers are clearly apparent in Figure 2.

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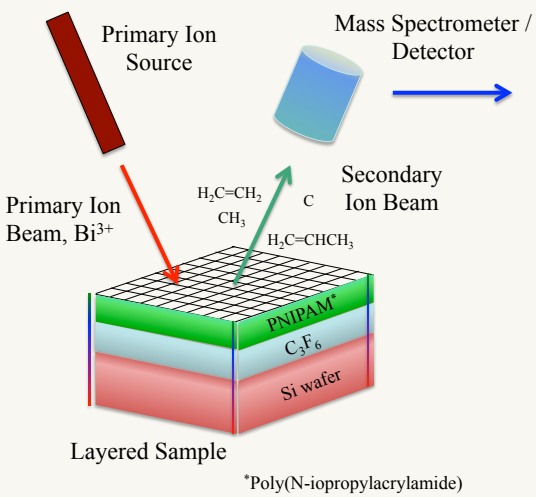
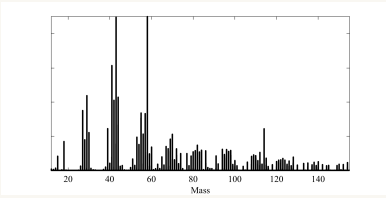
Secondary Ion Mass Spectrometry (SIMS)



*Poly(N-iopropylacrylamide)



The primary ion source is rastered over the sample surface to obtain a hyperspectral image.

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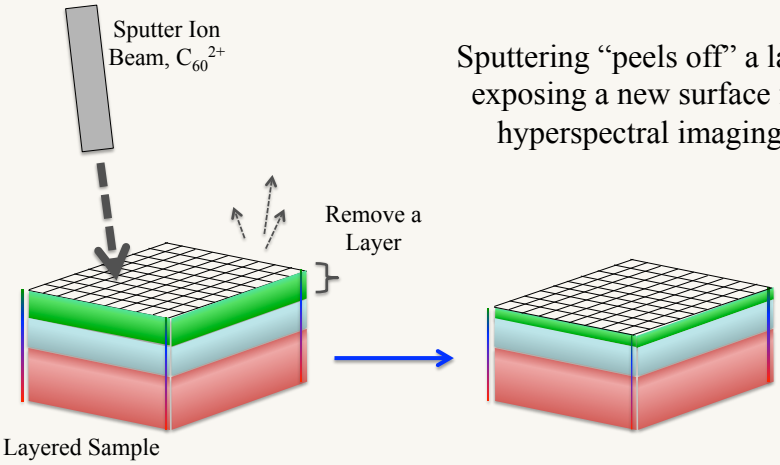
Sputtering → Depth Profiling



Sputtering "peels off" a layer exposing a new surface for hyperspectral imaging.

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ToF-SIMS Imaging & Depth Profiling

- The primary beam is scanned over the surface
  - mass channel spectrum (time of flight) at each pixel
  - 256x256 hyperspectral image of the surface
- Depth profiling is achieved by sputtering
  - multiple hyperspectral images at 50 different depths (~200 nm depth profile)
- 256x256x406[+]x50 reduced to 85x85x300x50
  - use mean of 3x3 windows, remove edge pixels, remove highest mass channels

[+]integrated from thousands of peaks

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Data Analysis

- Principal Components Analysis (PCA)
  - orthogonal scores / loadings
- Maximum Autocorrelation Factors (MAF)
  - directly related to whitened PCA to focus on spatially autocorrelated signal
- Multivariate Curve Resolution (MCR)
  - attempt to obtain pure component, non-negative scores and factors that are more physically interpretable
- Use Poisson scaling and 1-norm
  - allows lower signal (higher mass channels) to influence the model

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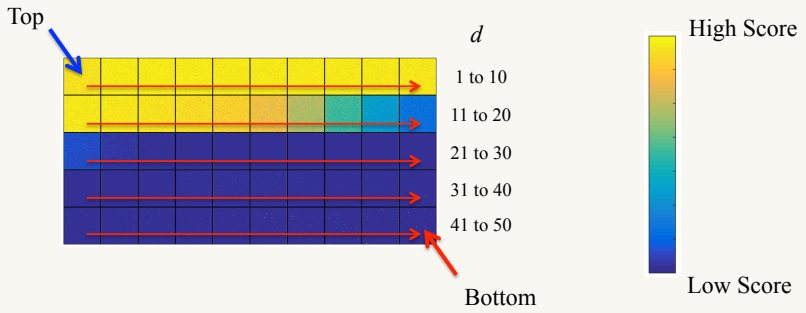
Example Image



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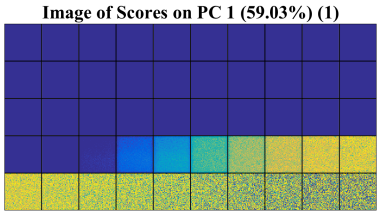
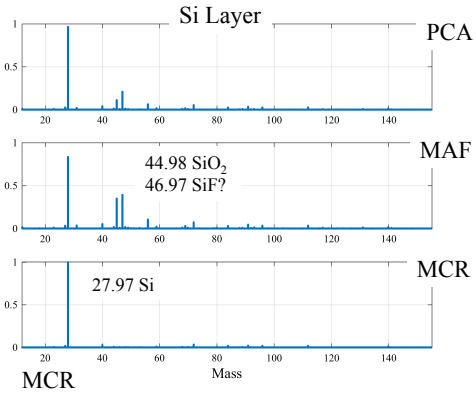
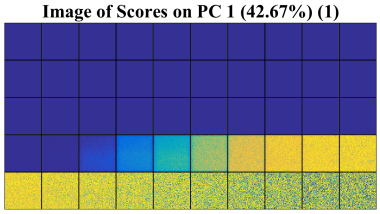
PCA

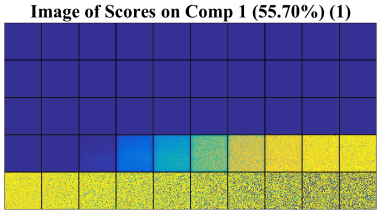




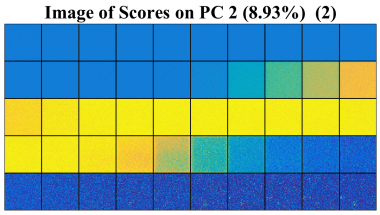
MAF

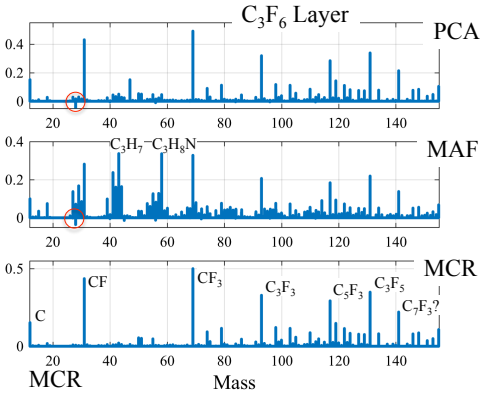


MCR

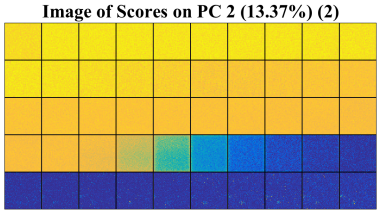


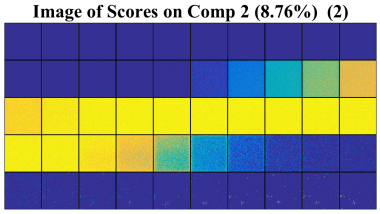
PCA





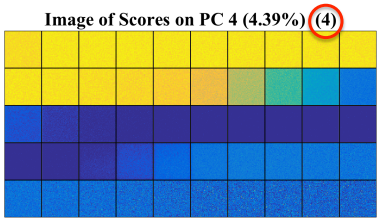
MAF



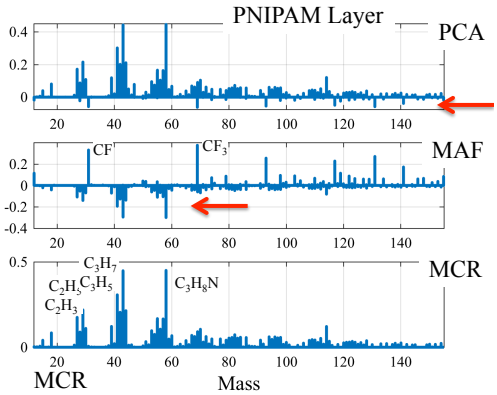


MAF Factor 2 includes Top and Middle Layers

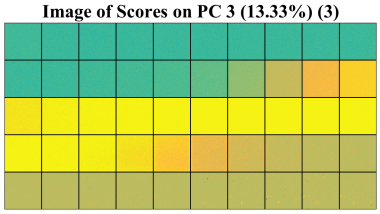
PCA

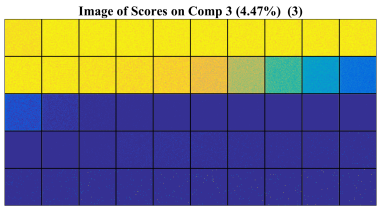


PCA Factor 4 is the Top Layer



MAF

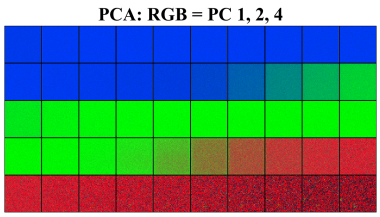


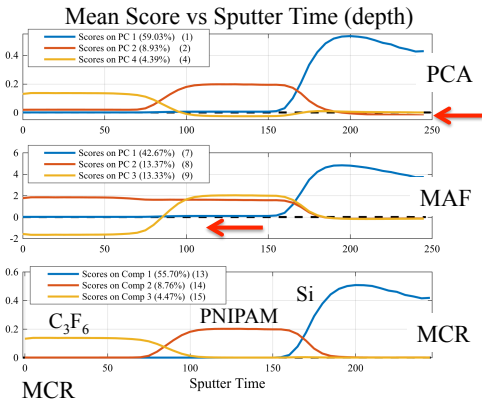


MAF Factor 3 includes Bottom and Middle Layers

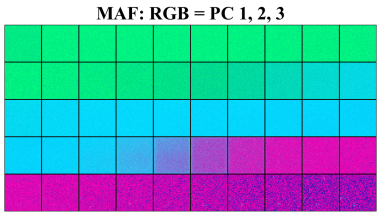
MCR Factor 3 is the Top Layer

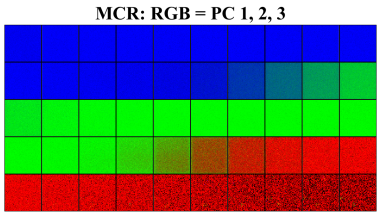
PCA



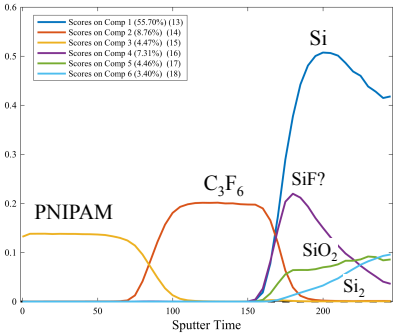


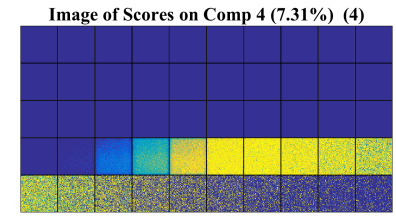
MAF

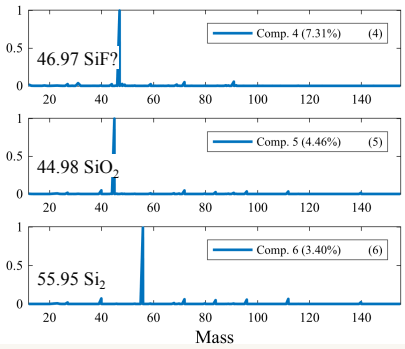




MCR Factors 4, 5 & 6







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Conclusions

- Results are consistent across analysis methods PCA, MAF & MCR. Observed differences are attributable to different objective functions.
  - PCA maximizes variance and retains orthogonal scores & loadings. Easy to use and reproduce. Interpretability of results attributed to high selectivity in the ToF-SIMS measurements.
  - MAF maximizes variance relative to first spatial difference and retains orthogonal scores & "unwhitened" loadings. Easy to use. Interpretabilty suffered in this example due to rotational ambiguity.
  - MCR finds end-members satisfying non-negativity. Can take effort to obtain good results but ease in this example attributed to high selectivity in the ToF-SIMS measurements. Most easily interpreted attributed to non-negativity (and non-orthogonality of scores & loadings).

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