Rapid 3D Chemical Visualization with Tabletop XUV Laser Mass Spectrometry

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ABSTRACT

Laser ablation in combination with mass spectrometry is a well established methodology to probe chemical composition of a variety of materials, including refractory materials. While using plasma-driven XUV lasers, the drastic reduction of sampled volume is not accompanied by a reduction in sensitivity, which indicates an enhancement of the sample utilization efficiency using XUV. A capillary discharge Ne-like Ar laser operating 46.9nm was utilized demonstrating unprecedented insights. The rapid direct and absolute characterization in 3D of the elemental distribution using XUV laser – time-of-flight (TOF) mass spectrometry is shown here in the case of solar thin films. Elements such as sulphur, zinc and selenium showed similar layered concentration, while sodium, calcium, and silicon may have diffused from the soda-lime glass substrate. Lithium was doped, and is responsible for the development of a granular porous fabric.

Keywords: imaging, mapping, chemical visualization, X-ray laser, XUV, solar cell, thin-film, quasi non-destructive

1. INTRODUCTION

Direct solid sample microanalysis expands the capabilities of traditional chemical analysis in two directions: (i) materials can be measured "*as they are*", with very limited sample preparation; (ii) chemical information is obtained in a space-resolved way. The former is beneficial in terms of (i) speed of the analysis, (ii) minimization of (risks of) artefacts, (iii) possibility to measure composition in the "natural matrix". In some cases, e.g. ceramics, fly ashes, *etc* the matrix is so hard that classical chemical pre-treatment to obtain a representative solution for liquid analysis is not possible.

On the other hand, valuable materials, e.g. cultural heritage, biosamples, *etc* have to be measured rapidly, *in loco*, and in very limited amounts, ideally in a non-destructive approach. Further, solid samples can be characterized by a certain inhomogeneity. The latter is important to understand diffusion processes, purity level, fabric, or consistency of physico-chemical properties, especially for nano-structures, where trace contaminants have huge impact. Therefore, space-resolved analysis (so-called *topochemical* analysis) provides information that bulk methods do not preserve: the distribution function of the analytes. Chemical visualization is thus opening new ways of analysis.

One should be aware of an important difference in *chemical visualization*, i.e. distinguishing between "*imaging*" and "*mapping*"¹. The former refers to a full-block acquisition of a composition pattern that is a direct visualization of the object, while the latter refers to a collection of single data-points, e.g. MS spectra, which are stitched together in post-processing. The difference is substantial for a number of reasons: (i) the *resolution* in imaging depends on the detection method (e.g. pixel), while in mapping depends on the illumination (e.g. spot size); (ii) the *field of view* in imaging depends on the collection aperture and detector size, while in mapping depends on the XYZ stage and is virtually unlimited; (iii) the *data*

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throughput in imaging is a single run, while in mapping is the full sample scanning; (iv) the *visualization fidelity* is, in imaging, dictated by the (distortion of the) *transfer function*, such that systematic or random errors cannot be corrected *a posteriori*, while in mapping the sampling strategy and post-processing method help to mine for the information. In laser ablation MS, the visualization approach bases on mapping.

Classical microanalysis is performed with the aid of probe pulses, which selects the region of interest. *Electron* beams have the highest space resolutions, with the intrinsic limitation that the sample must be conductive or coated. *Ion* beams are limited by strong matrix effects, such that the quantification, i.e. in space and concentration, is not possible. *Coherent photon* beams (lasers) have proven the most flexible sources for microanalysis, with the sole limitation that space resolution is given by the operation wavelength.

The state-of-the-art short wavelength laser utilized for microanalysis has been for long time the excimer at 193nm^{2-7} , with the spatial resolution in the large micron range. The cutting down of the laser wavelength is beneficial to (i) enhance the space resolution, (ii) eliminate elemental fractionation by using a high photon energy, (iii) improve the sample utilization efficiency, by efficient coupling as well as negligible plasma shielding.

The Rocca and the Menoni groups at CSU have been pioneers in both the development of short wavelength lasers as well as their application in mass spectrometry, respectively. A seminal paper by Kuznetsov et al.⁸ demonstrated the capability for nano-scale mass spectrometry (MS). Müller et al.³ showed that this implied a 5 orders of magnitude reduction of sampled mass, which did not turn into an equivalent reduction in MS sensitivity, thus concluding a more efficient sample utilization⁹. The occurrence of fractionation as well as matrix effects is expected to be mitigated compared to ion bombardement techniques, which demands further analysis. The occurrence of doubly charged ions is subject of ongoing research.

The dramatic improvement in sensitivity and space resolution poses issues of distinguishing between sample-related variances (σ_0), due to inhomogeneity (chemistry) or heterogeneity (fabric), as defined in the literature before¹⁰, and analytical method precision (σ_1), which can be unravelled by means of a chemometrical analysis.

Aim of this paper was to address open challenges in the utilization of extreme ultraviolet (XUV) laser for 3D chemical visualization in a semi-quantitative way (signal amplitudes) with TOF mass spectrometry (XUV-TOF). The paper is organized as follows: Sect. 1 is a general introduction to the subject, Sect. 2 summarizes methods and instrumentation utilized for this study, Sect. 3 presents a selection of results, Sect. 4 is a discussion, while Sect. 5 draws main conclusions.

2. METHODS

2.1 Extreme Ultraviolet Laser

The experiments were conducted using the extreme ultraviolet laser ablation time of flight mass spectrometry instrument developed at CSU⁸ and schematically shown in Fig. 1. A capillary discharge XUV-laser ($\lambda = 46.9\text{ nm}$ or 26 eV)¹¹ generated pulses of about $10\text{ }\mu\text{J}$ with duration (FWHM) of about 2 ns and a pulse to pulse energy fluctuation of 10%. Grazing incidence optics were used to collimate the XUV-laser and focus it on the sample using a zone plate. The ablated ions were energy homogenized to 1.5 keV , using the potential difference between the sample and the zone plate, which were set 2.1 mm apart. The zone plate had a central opening of $50\text{ }\mu\text{m}$ in order to allow the ions to be extracted to the time of flight mass analyzer, equipped with a dual micro-channel plate detector (chevron configuration), with 40 mm in diameter active area and 2.31×10^6 electron/ion gain. The folded sample-to-detector distance was ca. 2 m . The entire system occupies an optical table space of $0.6 \times 3\text{ m}$. The mass spectra are processed and stored by a personal computer digitizer (GaGe® EON CS121G1, 12 bits, 1 GS/s). With 50Ω input impedance the amplitude is limited to $\pm 5\text{ V}$. A typical full mass range TOF spectrum is $50\text{ }\mu\text{s}$ (ca. up to 300 m/z) that permitted to obtain the complete elemental coverage⁸.

Figure 1. Schematic sketch of the experimental setup. A XUV-laser pulse at $\lambda = 46.9\text{nm}$ and $\tau = 2\text{ns}$ is delivered by grazing incidence optics to a zone plate, which focuses it on the sample surface. A moving translation stage permits to automate the repetition of shots over a x by y spot matrix on z shots (here $x=10$, $y=10$, $z=10$ shots). Each ablated ensemble is measured by means of XUV-TOF-MS. The photograph show CSU graduate student L. Rush aligning the instrument.

2.2 Data Sampling and Analysis

Raw TOF-MS spectra were calibrated and analyzed using the self-written MATLAB scripts at Empa and direct peak integration was done by signal amplitude summation and baseline subtraction. Typically a XUV-irradiation pattern of 100 points arranged as a 10×10 grid on each electrode was selected as trade-off between sampling duration and representability. The laser spot size was $1\text{ }\mu\text{m}$ while the center-to-center distance between the adjacent points was $2\text{ }\mu\text{m}$. On all the spots 10 consecutive laser pulses of $8\text{ }\mu\text{J}$ were delivered to acquire depth profiles. Averaging of all 1'000 mass spectra per sample provided a representative response with improved signal-to-noise ratio. Peak areas of single pulse spectra were obtained by integration over the baseline corrected corresponding full peak width and extracted to 3D matrices. 2D map stacks were generated by interpolation of the resulting 10×10 grids of peak amplitude for each pulse. The removal of $<100\text{ fg}$ can qualify the method as *quasi* non-destructive as indicated in the literature before¹².

2.3 Samples

Copper zinc tin sulfide selenide (CZTSSe) samples of Kesterite structure were analyzed as reported elsewhere¹³. These are investigated as functional materials in thin film solar cells, which are appreciated as non-toxic alternative to state-of-the-art solutions, e.g. CIGS. The formation of secondary phases can degrade the intrinsic functionality due to so-called shunting currents, which demands detailed 3D insights on the inhomogeneity. The main components of interest were Li (dopant added to enhance the efficiency), Na (contending dopant, destabilizing the lattice and substrate element from soda-lime glass), Si (also in the soda-lime glass substrate), S, Ca (substrate), Cu, Zn, Se, Mo and Sn. The CZTSe concentrations determined by means of bulk ICP-MS analysis were as follows: Cu 13.3%, Zn 10.1%, Se 44.8%, Sn 17.6%.

Figure 2. (a) Mean mass spectra on each layer depth-by-depth, (b) Variances (s^2) on mass spectra on each depth.

3. RESULTS

3.1 Mass Spectra

Each individual laser shot generated a XUV-TOF spectrum with the full elemental contents (entire periodic table). Fig. 2.a shows averages of 10x10 MS data (i.e 100 shots across each x-y layer) per each individual depth, with 10 stacked panels in sequence as a function of depth. A first analysis shows that key elements such as H, C, O, S, often difficult to measure in ICP-MS, are here accessible. Quite interestingly, the isotopic pattern is faithfully reproduced. The peak resolution obtained is close to $R=1'000$, which is in agreement with the specifications of the TOF system utilized⁸. The spectra highlighted occurrence of all main elemental components of Kesterite samples, i.e. Li, Na, Si, S, Ca (*traces*), Cu, Zn, Se, Mo and Sn. Spatial distributions for these elements are shown in the rest of the paper. However impurities such as W, Au, and Hg were also found, which are possibly derived by environmental contamination in the deposition chamber, which is shared in the laboratory. This is an important finding, in order to strictly control the purity of the functional layers, and with that the quality of their operation. The variance within each depth is shown in Fig. 2.b. One observes the correlation with the abundance, in agreement with counting statistics.

3.2 3D Elemental Mappings

The individual 1'000 MS signals (in the previous section we showed the 10 x-y averages for each of the ten z depths) were analyzed in detail, and the peaks of the main components were integrated. The obtained integrals permitted to visualize uncalibrated elemental contents. Calibration would demand utilization of external matrix-matched standard reference materials, which is necessary for the purpose of quantification. However, in the context of this work, aim was to highlight the distributions, and for that, the signal integrals were straightforward.

Figure 3. Elemental mappings for Li, Na, Si, S, Ca, Cu, Zn, Se, Mo and Sn at each of the 10 ablated depthwise layer.

Fig. 3 shows such elemental mapping per each x-y layer and element at the 10 ablated depths. The color scale gives a relative index of the distribution, while the colorbar values permit to obtain the magnitude. Clearly sensitivity factors are different per each individual analyte, which requires external calibration with certified reference materials. It must be

emphasized that the level of details for the material scientist is overwhelming, and opens new ways besides state-of-the-art analytical nano-techniques, such as atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS), X-ray photoemission spectrometry (XPS), etc. Unfortunately, the visualization on the page plane is limiting and does not give the full information as in the digital interaction. Therefore, in the next sections, we will discuss other visualization methods.

Figure 4. Depth mappings for Li, Na, Si, S, Ca, Cu, Zn, Se, Mo and Sn shown as unfolded vertical cross sections. Every 10 points on the X axis one is moving one layer more above the page, for a total of 10 layers.

Figure 5 Block tomoplots for Li, Na, Si, S, Ca, Cu, Zn, Se, Mo and Sn with a 10% signal amplitude cutoff. Note how Na is anticorrelated with S, Cu, Zn, Se, and Sn. Li was doped in stripe domains.

3.3 "Unfolded Bellow" Depth Profile Maps

The visualization of a vertical cross section, i.e. 2D depth profiling, is very insightful to understand the spatial composition of the material. In particular, in a nano-structured porous material, the fabric (heterogeneity) may alter the chemical pattern (inhomogeneity) and hamper the functionality as mentioned above. A new representation method was searched to combine the full scope and insight of available data. The method is understood in analogy to a bellow that is stretched and unfolded. In the block state a series of planes are folded on each other. While unfolding, the maps span over a horizontal stripe. The unfolding period (size of x - y layer) was 10, i.e. every ten points the image shows a new 2D depth profile one cross-section ahead. Fig. 4 shows the visualization of such "unfolded bellow" maps. One observes (i) the granular structure of the material's fabric, (ii) the layering of some elements, e.g. S, Zn, Se, Sn, (ii) the inhomogeneous spotting of Na, Ca, Sn. Studies of the full collection of samples provided robust statistics insights.

3.4 3D Block Visualization

The optimal visualization is accomplished in so-called 3D block "tomoplots" (*tomographic plots*). These can be rotated and sliced to inspect, in the full volume, the elemental distribution. Such tomographic visualization was here frozen into one specific perspective for the representation on paper. Additionally, we have set a 10% signal cutoff to eliminate less informative background, which explains why some plots look clipped. Fig. 5 shows a selection of tomoplots. As mentioned above, one can observe the layered structure (e.g. S, Zn, Se), or the fact that Si may be derived from interdiffusion from the SLG substrate. However, these representations proved weaker for highlighting the granular porous fabric, as shown in the previous section.

4. DISCUSSION

Having carried out the acquisition of a series of XUV-TOF runs, i.e. across x - y as well as z , one may wonder if measurement uncertainties have biased the data, such that sample inhomogeneities are artefacts. ANOVA is a well-established chemometric technique to test the difference between sample means, i.e. whether it is too great to be explained by mere random error. The problem is to consider z samples each with x times y members of layers $L_1, L_2, \dots, L_z$. The 10 means of the samples (times the number of chemical elements) are *computed* as well as the mean of all the values grouped together. The *null hypothesis* to test is that all the samples are drawn from a single population with given mean μ and variance σ_o^2 . One can estimate the variance either from the variation *within* the x - y samples (*layer* inhomogeneity), or *between* the L_z samples (*depth* inhomogeneity).

4.1 Chemometric Analysis

If the null hypothesis is correct, the two estimates of σ_o^2 discussed above should not differ more than a tabulated significance threshold. Otherwise, where the null hypothesis is incorrect, the between sample estimate will be greater than the within sample one because of the depth-wise sample variation. A one-tailed F-test was used, with significance level α (probability that we reject the null hypothesis when it is in fact true, i.e. *Type I* statistical error) set at 2.5%, 1%, and 0.1% (Tab. I).

The scatter of observed values may be attributed to either measurement uncertainties, e.g. laser fluctuations, or to sample inhomogeneities. The one-tailed F-test was thus applied to this data population, with results summarized in Tab. I. Li, Ca, Mo, Sn showed a high degree of variability to consider them affected by the measurement uncertainty, while for Na, Si, S, Cu, Zn, Se there is a certain significance that their inhomogeneity is real, with different α levels.

5. CONCLUSIONS

The analysis of porous inhomogeneous (composition) and heterogeneous (fabric) nano-materials is challenging because the required increase of space resolution may be accompanied by loss of sensitivity and more pronounced measurement errors. The utilization of a tabletop plasma-driven X-ray laser coupled to XUV-TOF has shown unprecedented performance in that sense. A chemometric analysis has shown the level of confidence to the data, providing a robust platform for 3D chemical visualization in a quasi non-destructive approach.

Table 1. Chemometric analysis of data. Here "Samples" are the individual layers ablated with a given number of shots.
Significant threshold from: http://socr.ucla.edu/Applets.dir/F_Table.html

	Li	Na	Si	S	Ca	Cu	Zn	Se	Mo	Sn
<i>Within Sample</i>										
Degrees of Freedom	990	990	990	990	990	990	990	990	990	990
Mean Variance	443.5	1641.5	6.1	35.8	0.283	610.1	23.4	68.3	0.669	39.6
<i>Between Sample</i>										
Degrees of Freedom	9	9	9	9	9	9	9	9	9	9
Variance	39.2	228.2	1.9	10.9	0.009	80.4	7.5	15.9	0.001	4.8
<i>F-test</i> $F_{990,9} =$	11.3	7.2	3.2	3.3	31.6	7.6	3.1	4.3	505.7	8.2
Threshold for $\alpha = 2.5\%$	3.333									
$\alpha = 1\%$	4.311									
$\alpha = 0.1\%$	7.813									
Data Significantly Different	Yes				Yes				Yes	Yes
Significance level		0.1%	2.5%	2.5%		0.1%	2.5%	1%		

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