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VAMAS TWA 2, 2009: Sub-project A3(d) Static SIMS Interlaboratory Study – Part II: organic depth profiling by cluster ion beams - Protocol For Analysis

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VAMAS TWA 2, 2009: Sub-project A3(d) Static SIMS Interlaboratory Study – Part II: organic depth profiling by cluster ion beams - Protocol For Analysis

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ABSTRACT

This report describes the protocol for analysis in the VAMAS TWA 2, 2009 organic depth profiling study. Procedures for setting the sputter ion beams and analysis regions are provided to ensure the equivalence of data between different instruments. A single reference material is supplied for this study, alternating layers of Irganox1010 and Irganox3114 of total thickness ~400 nm on a silicon substrate. No sample preparation is required from the user and specific guidance is given on sample handling.

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Approved on behalf of the Managing Director, NPL
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1 INTRODUCTION.

In the last ten years, sputter depth profiling of organic materials has received much attention. This interest has stemmed from the development of cluster ion sources, although monatomic sources have also been used for this purpose. The general findings of previous studies using cluster ion beams are that the initial sputtering yields, in terms of a volume or mass of sputtered material, is similar for many organic materials under identical experimental conditions. However, the sputtering yield generally does not remain constant and declines with increasing ion dose in a fashion that appears to be strongly dependent upon both the material and the experimental conditions.

The purpose of this inter-laboratory study is to relate experimental conditions to two important analytical parameters: The (dose-dependent) sputtering yield and depth resolution. To conduct this task, participating institutions are supplied with one or more samples of an organic film with marker layers at known depths[(1)]. More than one sample has been sent to those participants that require them and have given a valid reason, for example: because they cannot focus their ion beam sufficiently and require extra samples to complete objective 2; or because they intend to undertake extensive studies under objective 3. The samples are from a consistent batch to eliminate the material dependency so allowing the influence of experimental conditions to be evaluated. The specific objectives are: (i) To assess the ability of a particular experimental arrangement to perform useful depth profiles for the selected organic material; (ii) To determine the repeatability of organic depth profiling; (iii) To investigate experimental parameters for depth profiling (optional).

If you are unsure of any part of this protocol please contact Alex Shard, email: alex.shard @ npl.co.uk

2 TIME TABLE

You should complete the analysis for this work by 30th June 2009. If you cannot do so and you need extra time please inform alex.shard @ npl.co.uk.

3 THIS PACKAGE

This package contains this protocol, one (or more) organic multilayer sample(s), as noted above, on silicon wafer(s). These are individually packaged in fluoroware containers wrapped in aluminium foil to exclude light and sealed in a plastic bag. The organic multilayer is on the side of the silicon wafer facing the concave base of the fluoroware container. Inspect the packaging to check if it has been opened by customs and if the integrity of the samples has been compromised. If you are in doubt contact NPL. Please notify us that everything is received in order.

☐ I have emailed NPL that all is OK with the sample(s) on / / 2009

4 PROPOSED METHOD

The spectrometer should be operated under conditions that give the most stable performance. For the optimum intercomparison, a common set of operating conditions is needed, however due to the variety of instruments available, no single set of conditions can do this. Instead we give general conditions for guidance to improve comparability.

5 INSTRUMENT OPERATING CONDITIONS

5.1 SPUTTERING ION BEAM

The ion beam current should be measured using a suitable Faraday cup. If your system does not have one, a simple but accurate device may be made using a drilled hole, aligned to the ion beam, with a depth more than 5 times the diameter. Alternatively, measure the ion beam current with an electrometer with a +10 V bias on the sample holder. The ion beam current should be measured both before and after each depth profile to establish whether there has been any change during the profiling.

The raster area may be calculated, or set, by imaging a calibrated grid with secondary electron detection. The beam diameter may be estimated from a secondary electron image taken from a grid or a knife-edge: the difference between positions at which the intensity is 84% and 16% between the maximum and minimum plateau regions provides *D*, the full width at half maximum (FWHM) of a Gaussian beam profile.

The number of raster lines, *N*, should be set so that the spacing between lines (= *L* / *N*) is less than half the FWHM of the sputtering ion beam, where *L* is one of the raster dimensions (the length of one of the sides of the sputtered area). In the case of a Gaussian beam profile, this ensures that the ion dose within the central region of the sputtered area is evenly distributed. Thus, Expression 1 needs to be satisfied when selecting the raster dimension or number of raster lines.

$$N > \frac{2L}{D} \qquad \text{Expression 1}$$

In setting the raster size, consideration should be given to the useful analysis area. This should be restricted to the centre of the sputtered area to avoid the border close to the edge of the sputtered area that receives a lower dose than the centre. The width of the 'border' can be conservatively estimated as 1.5 times the FWHM of the sputtering beam diameter to obtain ~0.01% variation in dose across the analysed region. In this regard, the spatial resolution of the analytical technique should also be taken into consideration as the technique may sample areas that have received a lower dose. For example, if a separate, relatively highly focussed ion beam is used for analysis, this estimate is valid. However, if the sputtering ion beam is also used for analysis, the 'border' may be conservatively estimated as 3 times the FWHM of the ion beam diameter. A pictorial representation of the 'border' and analysis regions is provided in figure A1 in the appendix.

For consistency, we recommend that the analysis area be selected to satisfy Expression 2, where *A* is the relevant analysis dimension (the length of one of the sides of the analysed area).

$$A \leq (L - 6D) \qquad \text{Expression 2}$$

5.2 SIMS ANALYSIS

Use your preferred ion source and energy for spectroscopic analysis. Please use the guide in the previous section (5.1) to select an appropriate analytical area in the centre of the sputtered area.

Negative secondary ions should be detected, and intensities for selected ions recorded as a function of sputter time. Please note whether the intensities are dead time-corrected or not. It is preferable to apply such a correction, please see part I of this study for details.

If a separate ion source is used for analysis, the analysis primary ion beam current should be less than 10^{-4} times the sputtering ion current. Please record the primary ion beam current in the same manner described in the previous section for the sputter ion beam (5.1). To align the ion beams:

(1) move to a fresh area of the sample;
(2) obtain a secondary ion image over as large an area as possible using the analysis source {no features should be observed};
(3) set the sputter beam raster size to zero and irradiate the sample for at least 10 seconds {NOTE: it is advisable to set detector potentials to zero during this step};
(4) re-image the sample as in step (2), a dark area or spot with low secondary ion yield should now be visible {if not, it is likely that your ion beams are grossly misaligned or that the sample is at the wrong height};
(5) centre the analysis area on the dark area and select an appropriate raster dimension for the analysis and sputter beams;
(6) move to a fresh area of the sample, at least 500 μm away and perform the analysis.

Intensities should be integrated using a unit mass resolution, because charging during sputtering may alter the time of flight of secondary ions (see note on charge compensation below, 5.4). If possible, record the raw data and then analyse the data using the mass spectrum of the complete dataset to guide the position and width of the windows for each signal. If it is impossible to resolve the high mass peaks from neighbouring peaks (e.g. 1175 U from 1176 U), please record the intensity of all peaks within the vicinity of the peak (e.g. from 1172 U to 1178 U). A minimal list of secondary ions that should have their intensities recorded is provided in table 1.

Table 1 – Negative secondary ions for analysis

Matrix material (Irganox 1010)		Marker material (Irganox 3114)	
41 u	C_2HO^-	26 u	CN^-
59 u	$C_2H_3O_2^-$	42 u	CNO^-
175 u	$C_{12}H_{15}O^-$	346 u	$C_{18}H_{24}N_3O_4^-$
231 u	$C_{16}H_{23}O^-$	564 u	$C_{33}H_{46}N_3O_5^-$
277 u	$C_{17}H_{25}O_3^-$		
1175 u	$C_{73}H_{107}O_{12}^-$		

5.3 XPS ANALYSIS

The area of analysis for XPS should be in the centre of the sputtered area and the size selected so that there is no overlap with the 'border' defined in section 5.1. The background-subtracted and integrated XPS intensity of the C 1s, O 1s, N 1s and Si 2p regions should be recorded as a function of sputter time. The data should be reported as raw intensities without the application of an instrumental transmission function and/or sensitivity factors. If any other elements are detected, please contact Alex Shard, email: alex.shard @ npl.co.uk, immediately.

The marker material (Irganox 3114) contains approximately 5 at% nitrogen (excluding hydrogen), whilst the matrix contains none. Acquisition parameters should be selected to ensure that good intensity (at least 10^3 counts) for N 1s is attained for the first marker layer. A high analyser pass energy (e.g. 80 eV or more) is therefore recommended.

5.4 CHARGE COMPENSATION

During the depth profiling of these multi-layers with C_{60} ions, a small shift in the time-of-flight of secondary ions is observed which may be attributable to surface charge. For other sputtering ion species, sample charging may be a significant problem, therefore we recommend that electron flood charge compensation be used during depth profiling of the multilayers.

6 SAMPLE PREPARATION AND SAMPLE HANDLING

SIMS is, of course, very sensitive to trace contaminations and it is vital, therefore, that the samples are kept clean and are analysed as soon as possible after the Fluoroware containers are opened. Samples should only be handled at their edge using cleaned metal tweezers held using powderless polyethylene gloves. Vinyl gloves, often used in clean rooms, are coated with a release agent from the moulding process, and should not be used. The release agent is very mobile and quickly contaminates the samples. This may lead to poor measurement reproducibility and poor quality data.

The samples are stable for up to six months at room temperature. Some degradation of the outermost matrix layer is evident after this time, but this degradation is minimal if the samples are stored in the dark. The marker layers are not affected over this period. The samples should, in any case, be analysed as soon as is convenient and preferably within a month of receipt.

The silicon wafer sample is 10 mm × 10 mm, but the coated area is 8 mm × 8 mm and should be easily identified by a visual inspection. Please avoid the edges of the coated area, we recommend that analysis is performed within a 6 mm × 6 mm area in the centre of the coated region.

Each sample is individually coded and may have variations in layer thicknesses compared to other samples. The thicknesses of each layer on each sample are individually known and recorded at NPL. If you have more than one sample, it is important that you ensure that you record which sample has been used to acquire which set(s) of data.

7 DATA ACQUISITION

We now give specific guidance for each of the three objectives of this study.

7.1 OBJECTIVE 1: Assessing the ability to perform organic depth profiles

In the context of this interlaboratory study, a successful depth profile is one in which at least one of the marker layers within the sample can be clearly identified using at least one of the detection signals. An example dataset from a successful profile is shown in the appendix in figure A2. If none of the marker layers can be clearly resolved during the depth profile then this constitutes an unsuccessful profile. Depth profiles should be classified as ‘successful’ or ‘unsuccessful’ using this criterion. If your first depth profile is unsuccessful, do not proceed to objective 2, although you may proceed to objective 3 should you choose to.

7.2 OBJECTIVE 2: Determining the repeatability of organic depth profiles

Perform three depth profiles on the sample(s) on three different days using the same experimental set up and as close to the same conditions as possible. These datasets will be analysed by NPL to determine the repeatability of organic depth profiling using your experimental set up. We will also determine the variation in the sputtering yield and the depth resolution with ion dose. This information will be used to compare different experimental arrangements within the final report and, where possible, to determine the reproducibility of depth profiling in different laboratories which use the same experimental arrangement.

7.3 OBJECTIVE 3: (OPTIONAL) Investigate experimental parameters for depth profiling

If you have the time and capability, please conduct profiles using different experimental conditions (for example: ion energy; ion current; incidence angle; substrate temperature; rotation during sputtering). These data will be valuable in determining the optimal conditions for organic depth profiling. We would be grateful if you could send these data to us also, although we appreciate that you may not want it to be included within our final report, please see the note on confidentiality below (section 10).

8 AFTER ANALYSIS

When all analyses are complete, return the sample to its container. The Irganox container shall then be wrapped in aluminium foil (as it was sent). Return the sample to NPL by courier using the original packaging. If you wish to be informed of the layer thicknesses for your sample(s), please request this information once the samples have been returned.

9 DATA REPORTING FORMAT

The preferred data formats for the three depth profiles at 7.2 and any further profiles at 7.3 are:

1)
As an Excel spreadsheet within the electronic reporting form: Please ensure that the time and intensity data is in columns with clear headings and the time column first. Please ensure that the worksheet is uniquely identified and recorded in the data summary sheet.

2)
As ASCII data, in the format shown in Table 2. “Channel ID X” means a textual identifier of the signal for which intensities are being reported, e.g. “42 U”, “564 U”, “C 1s”, “N 1s” etc. Please ensure that the ASCII file for each dataset is uniquely identified and recorded in the data summary sheet.

Table 2 - Format for ASCII data

Column 1	Column 2	Column 3	Column 4
Time (s)	Intensity (counts)	Intensity (counts)	Intensity (counts)
	“Channel ID 1”	“Channel ID 2”	“Channel ID 3”
value 1	value 1	value 1	value 1
value 2	value 2	value 2	value 2
...	...	...	...

If you would like to send data using an alternative format, please contact alex.shard @ npl.co.uk

The preferred method for returning data and forms is by email. Alternately send the data on a CD ROM.

10 CONFIDENTIALITY

The samples supplied in this interlaboratory study are not certified reference materials, but have been produced to the best of our abilities. They are sent to you in confidence, and if there are any problems with them we ask that you contact us immediately so that we can determine whether the problem is generic or restricted to a single batch or sample. If, for commercial reasons, you do not wish to be identified in our final report, please note this in your report.

ACKNOWLEDGEMENTS

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REFERENCES

1. A G Shard, F M Green, P J Brewer, M P Seah and I S Gilmore, *J. Phys. Chem. B* **112** 2596 (2008).

APPENDIX

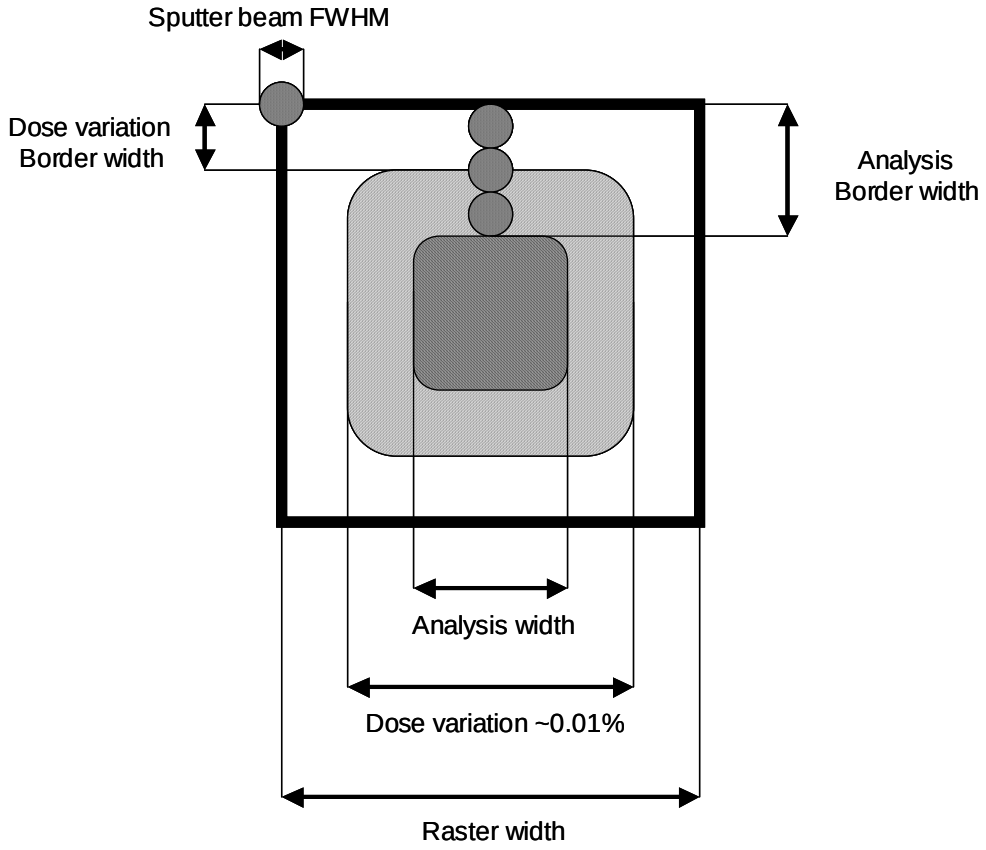

Figure A1: Diagrammatic representation of the recommended analysis width for depth profiling in relationship to the beam diameter and constant dose regions. At the edge of the rastered area the dose is half that at the centre of the rastered area and the corners receive a quarter of the central dose.

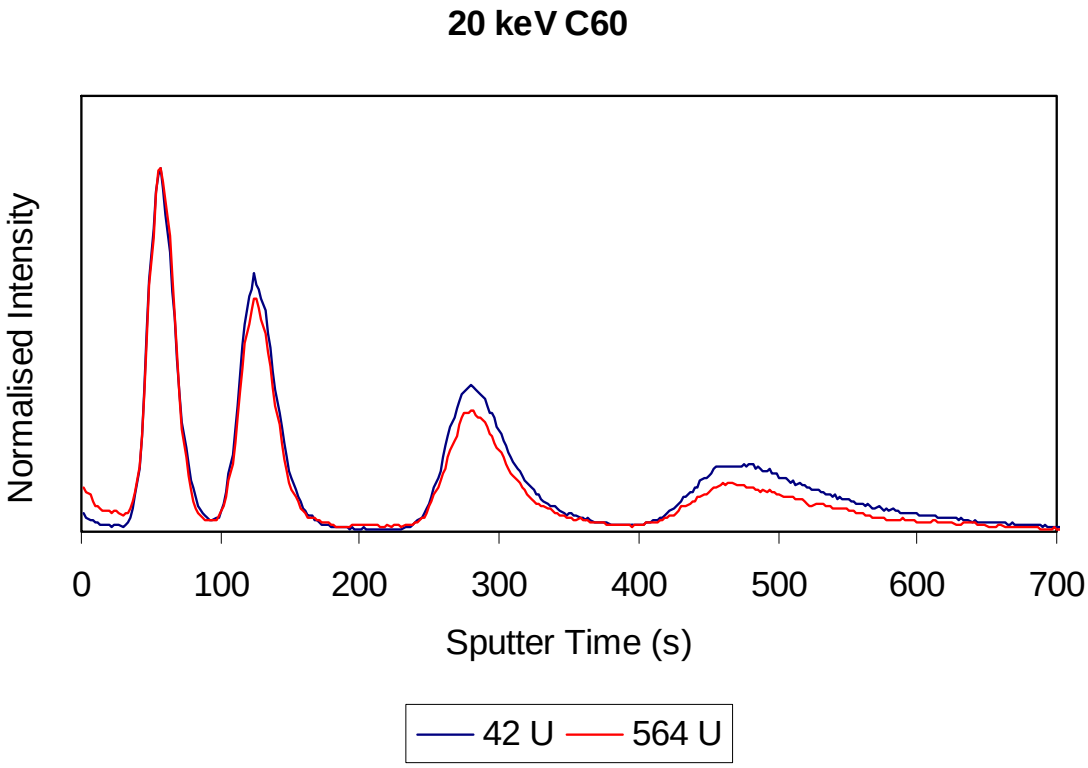

Figure A2: Example negative secondary ion signals from marker layers during a successful TOF SIMS organic depth profile.