NPL

NPL REPORT AS 88

VAMAS TWA 2, 2014:
Sub-project A3(g) Static SIMS Interlaboratory Study: organic depth profiling of mixed materials - Protocol For Analysis

A. G. Shard, R. Havelund, S. J. Spencer, S. A. Smith

MAY 2014

VAMAS TWA 2, 2014: Sub-project A3(g) Static SIMS Interlaboratory Study: organic depth profiling of mixed materials - Protocol For Analysis

A. G. Shard, R. Havelund, S. J. Spencer, S. A. Smith
Analytical Science Division

ABSTRACT

This report describes the protocol for analysis in the VAMAS TWA 2, 2014 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. Reference materials are supplied for this study, comprising layers of Irganox 1010, Irganox 1098 and Fmoc-pentafluoro-L-phenylalanine of known compositions and thicknesses on a silicon substrate. No sample preparation is required from the user and specific guidance is given on sample storage and handling.

© Queen's Printer and Controller of HMSO, 2014

ISSN 1754-2928

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Extracts from this report may be reproduced provided the source is acknowledged and the extract is not taken out of context.

Approved on behalf of NPLML by Ian Gilmore, NPL Fellow.

CONTENTS

1 INTRODUCTION 1
2 TIMETABLE 1
3 THIS PACKAGE 1
4 SAMPLES, HANDLING AND STORAGE 2
5 PROPOSED METHOD 2
6 INSTRUMENT OPERATING CONDITIONS 2
6.1 SPUTTERING ION BEAM 2
6.2 SAMPLE ROTATION. 3
6.3 SAMPLE TEMPERATURE. 3
6.4 CHARGE COMPENSATION. 3
6.5 SIMS ANALYSIS 4
6.5.1 **Table 1.** Minimal list of secondary ions to be recorded for MMK samples. 4
6.5.2 **Table 2.** Minimal list of secondary ions to be recorded for MMF samples. 4
6.6 XPS ANALYSIS 5
7 DATA AQCUISITION 5
7.1 EXAMPLE DATA 5
7.2 USEFUL DATA 6
7.3 DATA REPORTING 6
7.4 DATA INTERPRETATION (OPTIONAL) 6
8 AFTER ANALYSIS 6
9 CONFIDENTIALITY 6
10 ACKNOWLEDGEMENTS 6

1 INTRODUCTION

The ability to depth-profile organic materials and thin films has progressed rapidly, the widespread availability of argon cluster sources means that a significant number of laboratories routinely perform such experiments. In previous VAMAS studies on organic depth profiling, projects A3(e) and A3(f), the excellent repeatability and reproducibility of the method has been demonstrated and these studies have supported the measurement and understanding of sputtering yields and depth resolutions. This understanding is now at an adequate level for most routine analyses. One of the remaining challenges, particularly for secondary ion mass spectrometry, is to find practical methods to convert the depth profile data into compositions.

The purpose of this inter-laboratory study is to determine the influence of the composition of a material upon the signal generated during a depth profile. To conduct this task, participating laboratories are supplied with samples of organic films on silicon wafers. The films are binary mixtures of molecular materials in which the composition is known as a function of depth. The analysis of these samples provides information on composition-dependent sputtering yields, depth resolutions and intensities. It is necessary to use an argon cluster ion sputtering source to participate in this inter-laboratory study.

The specific objectives of this study are: (i) to establish the degree of non-linearity in depth profile intensities with material composition. *i.e.* to identify the "matrix effect"; (ii) to determine whether the matrix effect is consistent between instruments and laboratories and which experimental procedures most strongly influence it; (iii) to test literature or 'in-house' procedures for quantitative analysis (optional).

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

2 TIMETABLE

You should complete the analysis for this work by 31st July 2014. 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, two (or more) organic thin film 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 / / 2014

4 SAMPLES, HANDLING AND STORAGE

Two types of sample are provided: MMK samples are mixtures of Irganox 1010 and Irganox 1098 and MMF are mixtures of Irganox 1010 and Fmoc-pentafluoro-L-phenylalanine. Additionally, a sample of a single material with known thickness is provided. This sample should be used to calibrate the sputtering rate for the conditions and instrument you use prior to analysing the samples.

The samples are stable for more than six months at room temperature and below. 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 in a refrigerator or freezer. The samples should, in any case, be analysed as soon as is convenient and preferably within a month of receipt.

If the samples have been stored cold, allow at least one hour for them to return to room temperature before opening the Fluoroware container. It is vital 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 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.

5 PROPOSED METHOD

The spectrometer should be operated under conditions that give the most stable performance. For the optimum inter-comparison, 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. For users of XPS instruments, section 6.5 should be ignored and for users of SIMS instruments, section 6.6 should be ignored.

6 INSTRUMENT OPERATING CONDITIONS

6.1 SPUTTERING ION BEAM.

The ion beam should be an argon cluster beam and the energy and cluster size selected as those that are most generally used in your laboratory. In case of doubt, 10 keV Ar_{1000}^{+} is suggested. Before analysis, the cluster size should be selected according to your in-house procedures and these detailed in the relevant section of the reporting form. We encourage you to use more than one energy or cluster size for analysis of these samples, since this will widen the scope and relevance of the study.

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 more than +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: from a knife-edge, the image should be converted into a line-scan, which should have the form of an intensity-position sigmoidal curve. The difference between positions at which the intensity is 84% and 16% between the maximum and minimum plateau regions of the curve provides the 2σ width of a Gaussian beam profile, which may be multiplied by 1.18 to obtain the equivalent FWHM, D. It is usually best to fit the curve with an error function, or other suitable function to obtain the best precision. Other methods may be used, according to local practice.

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.

$$N > \frac{2L}{D}$$ 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.

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).

$$A \leq (L - 6D)$$ Expression 2.

6.2 SAMPLE ROTATION.

We do not recommend sample rotation for analysis. If you do use sample rotation, please record and report the rotational frequency and the frame rate of the raster used for the sputtering ion beam.

6.3 SAMPLE TEMPERATURE.

Analysis at room temperature is preferred. However, if there is a likelihood that samples will be heated during analysis, e.g. through the proximity of filaments and other heat sources, sample cooling is recommended. Under no circumstances should the samples be exposed to temperatures of 40°C or higher.

6.4 CHARGE COMPENSATION.

It is necessary to employ low energy electrons to compensate for sample charging that occurs during argon cluster profiling. It has been noted that electron flood guns may cause surface damage to ~20 nm depth over wide areas of the sample which is important for repeat analyses on the same sample. This should not affect the results relevant to this inter-laboratory study because the layers of interest are more than 100 nm deep into the sample. However, it is preferable to minimise exposure to electron irradiation especially if more than one analysis is performed on the same sample.

6.5 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 the 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.

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 ensure that none of the secondary ions are saturating the detector, this is particularly important for the pseudo-molecular ion for Irganox 1098 at 635 Da, which is very intense. 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 30 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 Da from 1176 Da), please record the intensity of all peaks within the vicinity of the peak (e.g. from 1172 Da to 1178 Da). A minimal list of secondary ions that should have their intensities recorded is provided in Tables 1 and 2.

6.5.1 **Table 1.** Minimal list of secondary ions to be recorded for MMK samples.

Irganox 1010		Irganox 1098	
59 Da	$C_2H_3O_2^-$	26 Da	CN^-
277 Da	$C_{17}H_{25}O_3^-$	42 Da	CNO^-
1175 Da	$C_{73}H_{107}O_{12}^-$	635 Da	$C_{40}H_{63}O_4N_2^-$

6.5.2 **Table 2.** Minimal list of secondary ions to be recorded for MMF samples.

Irganox 1010		Fmoc-PFLPA	
41 Da	C_2HO^-	19 Da	F^-
59 Da	$C_2H_3O_2^-$	167 Da	$C_6F_5^-$
231 Da	$C_{16}H_{23}O^-$	476 Da	$C_{24}H_{15}F_5O_4N^-$
1175 Da	$C_{73}H_{107}O_{12}^-$	953 Da	$C_{48}H_{31}F_{10}O_8N_2^-$

6.6 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. For MMK samples, 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. For MMF samples, the background-subtracted and integrated XPS intensity of the C 1s, F 1s, O 1s, N 1s and Si 2p regions should be recorded as a function of sputter time. The sputtering time between analyses should be adjusted so that one set of data is collected at intervals of between 10 nm and 25 nm in depth. This is to ensure that at least three sets of data are acquired within each layer and there is minimal exposure to X-rays during the analysis. Please use the sample of a single material provided in the package, along with the thickness marked on it, to estimate your sputtering rate and therefore the sputtering time between each analysis.

Please ensure that the X-ray source is turned off, or on standby, during sputtering.

The data should be reported as raw intensities without the application of an instrumental transmission function and/or sensitivity factors, and also as atomic% using your standard procedures. If any other elements are detected, please contact Alex Shard, email: alex.shard @ npl.co.uk, immediately.

7 DATA AQCUISITION

7.1 EXAMPLE DATA

An example SIMS profile is given in Figure 1 and an XPS profile is given in Figure 2 with the 8 regions of interest identified. Regions A, B and C at the surface of the sample are ~100 nm thick layers of the pure materials. Regions D, E and F are ~100 nm thick layers of three different mixtures of these materials. Regions G and H are ~200 nm or more thick layers of pure materials with ~3 nm marker layers of the other material within them.

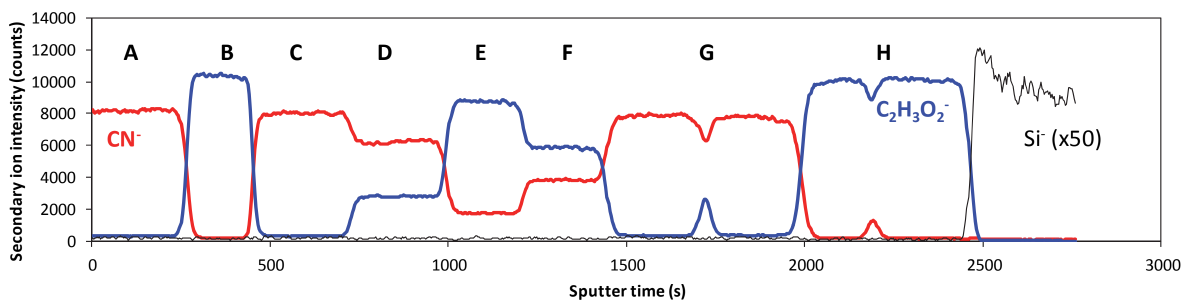

Figure 1. Example SIMS data from an MMK sample.

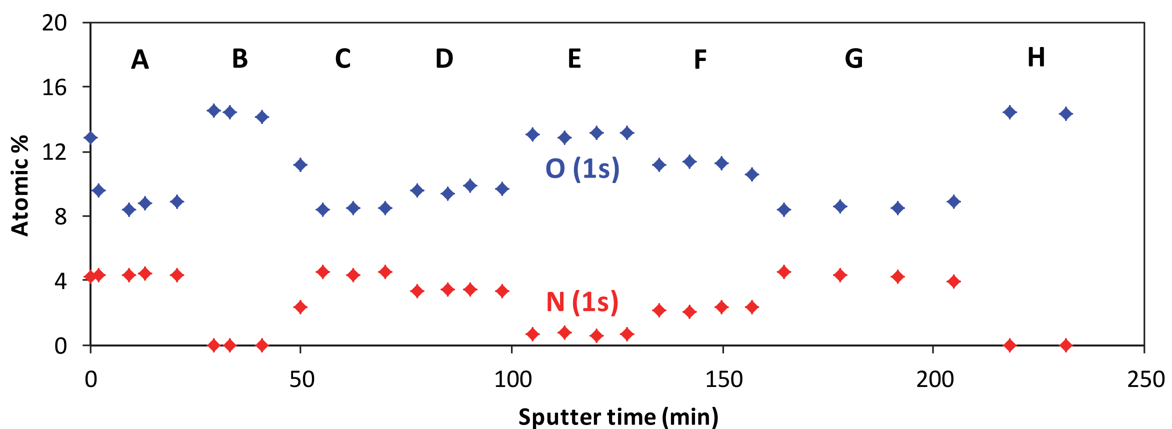

Figure 2. Example XPS data from an MMK sample

7.2 USEFUL DATA

Please check that, within your depth profiles, you can clearly identify all 8 layers. It is not necessary to clearly identify the marker layers in regions G and H and indeed, this may be difficult in XPS depth profiles. If you cannot identify regions A to F please contact Alex Shard, email: alex.shard @ npl.co.uk, immediately.

7.3 DATA REPORTING

An Excel electronic reporting form is supplied as part of this study, please report the data from each profile as a separate Excel spreadsheet within this form. Please ensure that the sputtering time and intensity data is in columns with clear headings and the time column first. Please ensure that each worksheet is uniquely identified and recorded in the data summary sheet.

7.4 DATA INTERPRETATION (OPTIONAL)

XPS users: Use your own in-house procedures to estimate the compositions of layers D, E and F. Please report these and the method you used. The composition of layer F is provided and, in the case of a large discrepancy (a volume fraction difference larger than 0.05) from your calculated value, please contact Alex Shard, email: alex.shard @ npl.co.uk, immediately.

SIMS users: The composition of layer F is provided, please use this information and your in-house procedure to estimate the compositions of layers D and E using secondary ion intensities. Please report these compositions and the method you used.

8 AFTER ANALYSIS

When all analyses are complete, you may keep the sample or dispose of it according to your local procedures. If you are unsure of these, please return the sample to NPL and we will dispose of it for you.

9 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. Please do not to publish your individual results, or any further or different analyses of these materials without consulting or informing NPL. If, for commercial reasons, you do not wish to be identified in our final report, please note this in your report.

10 ACKNOWLEDGEMENTS

This work forms part of the Chemical and Biological programme of the National Measurement System of the UK Department of Business, Innovation and Skills and with additional funding from the European Union through the European Metrology Research Programme (EMRP) projects SurfChem and TREND. The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.