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Experimental study of the organic ion intensity distribution in the ion imaging of coated polymer fibres with S-SIMS

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ABSTRACT

Time-of-Flight Static Secondary Ion Mass Spectrometry excels in probing the molecular composition of the outer monolayer of flat samples with a lateral resolution in the sub-μm range. However, the method faces significant methodological problems in the case of non-conducting samples with high topography or surface curvature, such as fibres, yarns or fabrics. Specifically, the useful secondary ion yield in a given spot on the fibre depends on the local incidence angle, the height above the earthed sample holder, the position relative to the axis of the mass analyser and the extent of the local surface charging. This study has focused on the empiric reduction of the useful ion yield variations observed in the ion images of fibres with diameter of 25 and 100 μm. Up to now, most literature data consider the analysis of fibres positioned along or perpendicular to the projection of the projectile beam in the plane of the sample surface because these specific geometries facilitate the interpretation of the ion images. However, it has been discovered that the diagonal orientation of the fibre in the field-of-view largely reduces the ion yield variations for fibres with a small diameter (25 μm). The situation is different for fibres with a diameter of 100 μm. In that case, the ion images contain no secondary ion counts for the pixels referring to a significant part of the fibre. In particular, the resulting lack of delineation between the shadow zone in the front of the fibre and the boundary of the fibre hampers the practical use of the ion images A fourfold decrease of the extraction voltage or a 20% increase of the distance between sample holder and extraction electrode is found to improve the detection of secondary ions from the part of the fibre facing towards the impinging primary ion beam. These observations have been tentatively related to the mass analyser acceptance and its dependence on the delicate balance between conflicting effects such as field strength and curvature of the field lines, secondary ion emission angle and initial kinetic energy and difference in local surface potential due to the position in the extraction field and charge build-up during analysis.

1. Introduction

Nowadays, textile industry deploys booming R&D activities focused on the development of functionalised fibres and their use in new and eco-friendly composites. Use of functionalised fibres gives particular properties to textile, such as anti-microbial activity [1], protection against electrostatic charging [2], self-cleaning properties [3,4] and fire-retardation [5]. Other developments even include the use of polymer-based organic materials to create photovoltaic textile structures [6] and smart textile incorporating hardware for information technology applications [7]. Intensive research also explores the use of renewable biomaterials such as wood fibres to replace glass fibres or traditional oil-based polymer fibres in eco-composites [8]. The success of coated fibres and the composite materials largely depends on the adhesion between the successively applied layers or between the reinforcing fibres and the surrounding matrix. Often, additives are used to improve these adhesive interactions. So-called grafting agents can be added to functionalise the fibre during processing and, thereby, ensure perfect interaction with the matrix. These components must be present at a specific interface to be efficient. Hence, the development of high-tech fibres used in advanced textile or composite applications requires molecular analysis of solids at the sub-μm or even at the nm scale. Analytically speaking, this is a demanding task for which high molecular specificity and an extreme limit-of-detection (LOD) must be combined with a good lateral and depth resolution. At this moment, time-of-flight static secondary ion mass spectrometry (ToF-S-SIMS) emerges as the method of choice because of its capability to provide full molecular information

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allowing unexpected compounds to be identified. Furthermore, the information depth is as good as one monolayer [9] and molecular imaging is feasible with a spot as small as 150 nm [10]. The LOD of only 10^4 organic molecules in the analysed micro-volume approaches the physical limit of mass spectrometry [11].

However, current instrumentation is designed for nano-scale analysis of materials with minimal topography [12], such as flat surfaces and coatings or nano-fibres with a diameter of less then a few μm [13]. Hence, serious complications arise when the instrument is used for the analysis of materials, such as fibres, yarns or fabrics, featuring a curvature or surface topography in excess of several tens of μm.

An early application of fibre analysis has been reported by Groenewold et al. [14,15] with the imaging of cocaine on textile and surfactants from a shampoo on dog hair. The secondary ion images show an even distribution of the shampoo residues along the axis of the fibre but, surprisingly, not in the radial direction. The effects of the local incidence angle on the useful secondary ion yield have been investigated by Rangarajan et al. [16]. It has been found that the orientation of glass and graphite fibre axis relative to the analysis beam direction is of importance to rationalise the secondary ion intensities detected from the fibre. Avci et al. [17] have studied conducting and insulating wires to determine the effect of sample conductivity on the mean kinetic energy of the secondary ions, averaged over the total fibre. Lee et al. [18,19] have used modelling of the extraction field distortion in the analysis of conducting gold wires or insulating polyethylene terephthalate (PET) fibres to explain qualitatively the intensity distributions seen in the secondary ion images.

From a theoretical point of view, it can be anticipated that the difference of the useful secondary ion yield between different points on a fibre depends on a variety of parameters such as the local incidence angle of the primary ion beam, the emission energy and emission angle of the secondary ion, the potential at the point from which the ion is generated, the effects of the fibre conductivity and the surface charging on the extraction field as well as the acceptance of the mass spectrometer. Current instrumentation does not allow the different effects to be studied separately. Although literature studies reveal interesting concepts about some of these aspects, no information about the relative importance of the different effects is available yet.

The purpose of this paper is a purely experimental study of the differences in the useful secondary ion yield at different spots along fibres with a diameter of 25 μm and 100 μm. Specifically, insulating PET fibres with a diameter of 25 μm and 100 μm have been coated with cetyl trimethyl ammonium bromide (CTAB) because of its favourable secondary ion yield. Unlike most of the experiments described in the literature, the fibres have been analysed systematically in different orientations relative to the projection of the primary ion beam in the plane of the sample holder and the secondary ion intensity profiles perpendicular to the fibre axis have been measured as guiding parameters to optimise the analysis.

2. Experimental

2.1. Sample preparation

Monofilament PET fibres with a diameter of 25 and 100 μm were kindly provided by Centexbel (Ghent, Belgium). The fibres were dip-coated in a concentrated solution of CTAB in deionised water and dried in a stream of hot air. The coated fibres were fixed on an aluminium substrate or silicon wafer (N-type, 14.5–20 ohm cm, Montco Silicon, Spring City, PA, USA) with clamps to ensure good contact of the fibre with the substrate. The loaded substrate was mounted on the top mount sample holder of the ToF-S-SIMS.

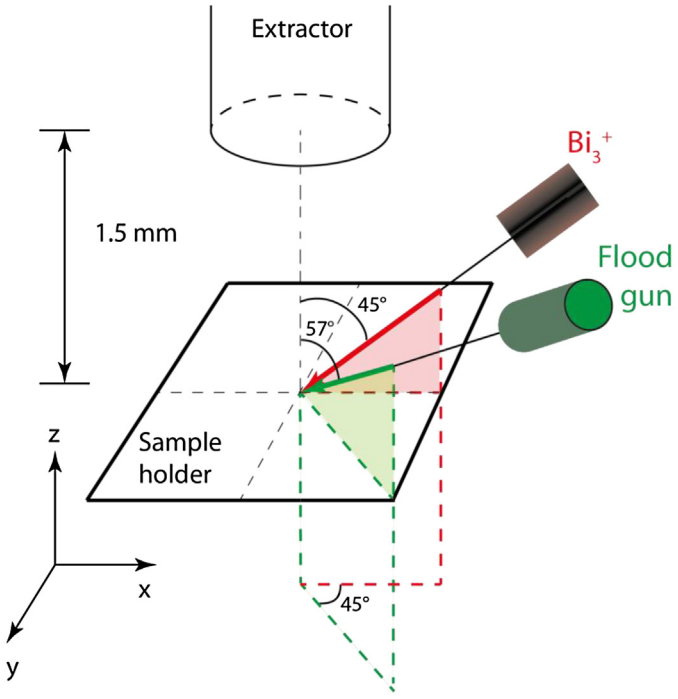

Fig. 1. Orientation of the Bi primary ion source and electron flood gun with respect to the sample surface in the TOF-S-SIMS instrument used.

2.2. ToF-S-SIMS analysis

Positive ion mass spectra from the surface of a fibre with diameter of 100 μm were recorded, using a TOF-SIMS V (ION-TOF, Münster, Germany) and a 25 keV Bi_3^+ liquid metal ion gun (LMIG) in the high current bunched mode, featuring a mass resolution of 1800 (FWHM at H^+ peak) and a beam spot diameter smaller than 2 μm. As illustrated in Fig. 1, the gun was aligned in a 45° orientation with respect to the sample holder. Ion images were recorded in the burst-alignment mode, yielding a beam spot diameter of 300 nm. Images were acquired from a region of typically 100 μm × 100 μm (25 μm fibre diameter) or 300 μm × 300 μm (100 μm fibre diameter) during 15 scans with a resolution of 256 × 256 pixels or 512 × 512 pixels, respectively. The ion dose densities were 1.2×10^{12} cm^{-2} and 2.8×10^{12} cm^{-2} for the analysis of the fibres with diameter of 100 μm and 25 μm, respectively. Electron flooding was applied in all experiments. The electron flood gun was mounted under an angle of 57° with respect to the normal on the sample holder and an angle of 45° with respect to the LMIG (cf. Fig. 1). The energy of the electrons was 21 eV. To optimise the secondary ion intensity detected from fibres with a diameter of 100 μm, the extraction voltage was varied between 500 and 2000 V and the distance of the sample substrate to the extraction electrode was varied between 1.5 and 2.1 mm.

3. Results and discussion

To facilitate the discussion of the results later on, it might be profitable to briefly outline current concepts on the formation and collection of secondary ions generated from large fibres. Fig. 2 gives a schematic overview of the different issues that might be of importance for homogeneous fibres. The green, red and orange zones simply refer to spots from which different secondary ion intensities are expected. The next discussion will be confined to the ion imaging of fibres of which the axis is perpendicular to the primary ion beam, i.e. the so-called vertical orientation (cf. infra).