RESEARCH ARTICLE

Topography and Field Effects in Secondary Ion Mass Spectrometry – Part I: Conducting Samples

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Abstract

Quantitative chemical characterization of surfaces with topography by secondary ion mass spectrometry (SIMS) remains a significant challenge due to the lack of systematic and validated measurement methods. In this study, we combine an experimental approach using a simple model system with computer simulation using SIMION, to understand and quantify the key factors that give rise to unwanted topographic artefacts in SIMS images of conducting samples with microscale topography. Experimental data are acquired for gold wires (diameters 33 to 125 μm) mounted onto silicon wafers. Significant loss of ion intensities and shadowing arise from the distortion of the extraction field, and the chemical analysis over the whole of the sample surface is difficult. For large primary ion incidence angles of $\geq 55^\circ$ to the surface normal, a fraction of the primary ions are scattered from the target and impact the substrate, emitting secondary ions that may be mistaken as originating from the wire. For conducting samples, topographic field effects may be reduced by the use of a smaller extraction voltage and an extraction delay. The effects of an extraction delay on ion intensities, mass resolution and time-of-flight are studied, and its application is demonstrated on an anisotropically etched silicon sample. The use of a simple sample holder with a V-shaped groove to reduce topographic field effects for wires is also presented. Using these results, we provide clear guidance to analysts for the diagnosis and identification of topography effects in SIMS, and present key recommendations to minimize them in practical analysis.

Key words: Static SIMS, Topography, Imaging, Delayed extraction, Extraction voltage, Ion scattering, Field effects, Extraction field

Introduction

Many technological devices possess significant surface topography, including microfluidic systems, MEMS, composite materials, catalysts, electronics, sensors and

biomedical devices. The functionality and activity of these components is often critically dependent on their nanoscale surface chemistry and molecular interactions. An example is the analysis of microfluidic channels for wetting and other properties. Secondary ion mass spectrometry (SIMS) is a promising technique for the study of surfaces due to its chemical sensitivity and specificity. However, significant topographic features in the scale of tens or even hundreds of microns are commonly encountered on these samples. This can cause many unwanted artefacts in SIMS spectra and images [1–4], which significantly hinder data interpretation

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and quantification. As a result, chemical characterization of surfaces with microscale topography remains a significant challenge due to the lack of systematic and validated measurement methods.

The analysis of topographic samples is different from the analysis of flat uniform surfaces in many aspects and these are discussed in detail in this paper. These issues broadly fall into four categories:

- (i) Practical issues: Appropriate sample mounting for topographic samples is essential to minimize field effects, to optimize the sample surface potential (for insulating samples) or to reduce sample charging [5].
- (ii) Simple geometry effects: Due to the difference in the angle of the primary ion beam and the analyzer with respect to the sample, the image coordinates can be distorted, and geometrical shadowing can occur when an area of the sample is not accessible to the primary ion beam.
- (iii) Sputtering behavior: Many sputtering parameters are a function of the primary ion incidence angle, which varies across samples with topography. This includes sputtering yields [6] and the energy and angular distribution of emitted secondary ions [7, 8]. For organic samples, changes to the spectra such as the relative intensity of organic fragments have been observed at different incidence angles [1].
- (iv) Instrumental response: This arises from the extraction and mass analysis of secondary ions from a sample with topography. For example, secondary ions entering the analyzer at large angles may be lost because of limited analyzer acceptance. For instruments with pulsed primary ions, the time-of-flight for secondary ions originating from different heights or positions may be shifted, leading to poorer overall mass resolution. It has been shown that, for samples with moderate topography, the resulting time-of-flight shift can be used to estimate the local height and partly restore the mass resolution [2, 9].

This study primarily concerns time-of-flight SIMS (ToF-SIMS) instruments. There are essentially two types of instrument design—pulsed primary ion source (currently covers most instruments) and DC primary ion source and pulsed analyzer (a recent new design [10]). Here, we study the effects (i) to (iv) which apply generally to both instrument designs. One important difference between the two designs is that in the pulsed primary ion type, the ion pulse is used to trigger the time-of-flight measurements for secondary ions, and the mass resolution depends on, amongst other parameters, the spread of flight times of the secondary ions. This gives rise to poorer mass resolution for topographic samples since higher sample features may have shorter flight times. In the pulsed analyzer design [10] the secondary ions pass continuously into the analyzer (like conventional liquid chromatography mass spectrometers).

The secondary ions are subsequently bunched in time and then pulsed into a time-of-flight analyzer. Consequently, the mass position and mass resolution are expected to be approximately independent of the topography. We note in the text where parts of this study are not relevant to these instrument types.

The topographic effects described in this paper are also relevant to SIMS instruments with non time-of-flight analyzer designs, such as quadrupole or magnetic sector instruments, which are expected to be affected similarly by sample mounting, geometry, sputtering behavior and the distortion of the ion extraction field. We will not discuss these instruments in detail, but much of this work will be applicable to these instruments.

In this paper, we report on the effects of topography for conducting samples. Elsewhere, in Part II, we extend our studies to insulating samples using poly(ethylene terephthalate) (PET) fibers [11]. We aim to understand and quantify the key factors that give rise to unwanted topographical artefacts in ToF-SIMS and provide guidance to recognize and reduce these artefacts. This is done by combining an experimental approach using simple model systems with computer modelling using SIMION. Our model systems consist of conducting gold wires, with nominal diameters of 33 μm , 60 μm and 125 μm . These are chosen since gold is a model conductor exhibiting a few clear mass peaks, and gold wires have well-controlled geometries and are easy to obtain in a range of diameters. This allows us to study the variation of topographic field effects as a function of feature size at a scale that is relevant to many real devices. For samples with sub-micron topography, the field effects are minimal and they are not studied here. Improvements after instrumental optimization are then demonstrated on an anisotropically etched silicon sample. To help with practical analysis, we investigate the benefits of a simple sample holder with a V-shaped groove to reduce topographic field effects. Elsewhere, using hair fibers with multi-component coatings, we study the rapid processing of high-resolution ToF-SIMS images for samples with topography using multivariate methods such as principal component analysis (PCA) and multivariate curve resolution (MCR) [12].

Experimental

Gold wires (with nominal diameters of 33 μm , 60 μm and 125 μm) are obtained from Goodfellow (Goodfellow Cambridge Ltd., Huntingdon, UK) and used as received, without additional cleaning. The wires are mounted flat on a clean silicon substrate using the method shown in Figure S.1 in the Supplementary Information. As we shall see later, it is important that the wire is mounted in good contact with the substrate. To do this, first, a section of the wire is held under tension and mounted onto the substrate by the application of silver dag (Agar Scientific) at each end. Two additional wires are then held perpendicular to the first wire and mounted on top, roughly a quarter of the distance from the

ends of the first. The perpendicular wires hold down the first wire such that the central area for analysis (marked on Figure S.1) is in good contact with the substrate. Naturally, the wire cannot be in perfect contact with the substrate, so the gap between the wire and the substrate is estimated using an optical microscope. This is done by measuring the difference in the stage height between the positions where the center of the wire and the substrate come into optical focus, and then subtracting from this the nominal diameter of the wire. We find that good surface contact can be achieved between the wire and the substrate using this mounting method, and the gap can be kept to less than 5 μm .

The anisotropically etched silicon sample consists of a Si (001) surface, where the oxide surface is photolithographically patterned and the exposed areas are etched in ethylene diamine pyrocatechol to a depth of 40 μm . This produces multiple polyhedra with eight (331) faces and four (111) faces. The full details of the sample are provided in Ref. [13].

SIMS analyses are conducted using an ION-TOF IV instrument (ION-TOF GmbH, Germany) of single-stage reflectron design [14]. For all experiments, the analyzer reflector voltage is set to +20 V and an extraction gap of 1.5 mm between the sample and the extraction cone is used. For extraction voltage experiments, the sample is kept at ground potential and a constant extraction voltage (variable between -500 V and -2000 V) is applied to the analyzer extraction cone to extract positive secondary ions. This provides an extraction field that roughly covers the regime used in most ToF-SIMS instruments. For extraction delay experiments, the extraction voltage (set at -2000 V) is pulsed so that it switches on several tens of ns after the pulsed primary ions hit the sample. Standard analyzer lens and reflector settings are used without further optimization. For each analyzer setting, a positive ion image is obtained for each wire diameter using a focused Bi^+ liquid metal ion gun at 25 keV energy, incident at $\theta=45^\circ$ to the sample normal for a flat sample. Images are acquired using an ion beam raster of 256×256 pixels. All secondary ion images are presented in the traditional manner with the x and y coordinates in the plane of a flat sample surface. Image analysis is conducted in Matlab v7.3 (The MathWorks, Inc., Natick, MA, USA) using custom routines. The intensities are first summed over the observed length of the wire for an improved signal to noise ratio. Since the wire radius and the image field of view are known *a priori*, the originating positions of the ions (expressed as an angle ψ on the wire respect to the extraction direction) is calculated for each pixel using simple geometry, and these are used to generate an angular intensity profile for each wire image.

Computer modelling is carried out to calculate the extraction field and secondary ion trajectories, as follows. Models are set up in an ion optics simulation software, SIMION 8.0 (Scientific Instrument Services Inc., Ringoes, NJ, USA), by placing cylinders of specified diameters on a flat conductive substrate (both at ground potential). A flat extraction plate is placed 1.5 mm above the substrate to

approximate the entrance of the analyzer cone. Unless otherwise stated, the extraction voltage is kept at -2000 V and positive secondary ions are emitted from the wire and the substrate surface with an initial energy of 2 eV at a direction normal to the surface. The velocities and trajectories of the secondary ions as they accelerate towards the analyzer entrance are recorded and analyzed. We make the simple assumption that the angular acceptance of the analyzer is 4° , and that secondary ions travelling with an angle of more than 4° to the extraction plate normal as they enter the analyzer are unavailable for detection. This allows us to visualize and explain the essential topographic field effects observed experimentally but does not provide quantitative results, since our simple SIMION model does not take into account the secondary ion optics of the analyzer system, including focusing lens, apertures and the use of dynamic emittance matching [15], which have an effect on the ion trajectories and acceptance of the system.

Results for a Gold Wire

Topographic Field Effects

The total secondary ion images of a gold wire, with a diameter of 125 μm , are shown in Figure 1. The wire is orientated with its axes either parallel to the azimuth of the

Figure 1. Total ion images of a gold wire with diameter 125 μm using 25 keV Bi^+ primary ions. (a) Parallel alignment, linear intensity scale. The field of view on the substrate surface is $500 \mu\text{m} \times 500 \mu\text{m}$. (b) Parallel alignment, logarithmic intensity scale, field of view $500 \mu\text{m} \times 500 \mu\text{m}$. (c) Perpendicular alignment, linear intensity scale, field of view $625 \mu\text{m} \times 625 \mu\text{m}$. (d) Perpendicular alignment, logarithmic intensity scale, field of view $625 \mu\text{m} \times 625 \mu\text{m}$. In perpendicular alignment, the observed position of the wire in the SIMS image (O), actual position of the wire if viewed from above (A) and the shadow region (S) are marked by arrows

incoming primary ion beam direction ('parallel alignment') or perpendicular to it ('perpendicular alignment'), and the total ion intensities are shown in both linear and logarithmic scales. It is clear that the topography critically limits the regions from which sputtered secondary ions may be detected, and chemical analysis over the whole area is difficult. We first focus on the results for parallel alignment. Only a thin central region of the wire can be detected with significant intensity, and signals from the substrate are 'shadowed' in the vicinity of the wire. The loss of ion intensities is caused by the severe distortion of the extraction field in the presence of the conducting wire, and can be simulated using SIMION. Figure 2a shows the SIMION results along the cross-section of the wire. This shows the equipotential lines (pink) and example ion trajectories (red / blue) from a conducting wire and the surrounding substrate for secondary ions emitted normal to the surfaces with kinetic energy of 2 eV. The equipotential lines are curved around the conducting sample, and the secondary ions acquire a large transverse velocity component as they are accelerated towards the mass analyzer extraction cone. Secondary ions from the sides of the wire and the adjacent substrate, with trajectories shown by red lines, are lost due to the limited angular acceptance of the single reflectron analyzer [6], which is approximately 4° . Because of the significant topography of this example, the field effects completely dominate over the increase in the sputtering yields expected at grazing angles of incidence. Therefore we do not see a strong enhancement of secondary ion intensities at the sides of the wire, which is observed sometimes for smaller wires or for insulating fibers where topographic field effects are much less significant [1, 11, 12, 16]. Here we study these topographic effects in detail and provide recommendations to analysts for their reduction.

Observable Width of Wire and Shadow Size

The extent of topographic effects for gold wires, for different diameters and extraction voltages, can be quantified using the total secondary ion images obtained experimentally. Figure 2b shows the size of the substrate shadow, defined by the position where the substrate secondary ion intensity has fallen to 10% of the plateau value for large distances from the wire, for experimental data from gold wires with diameters of 33 μm , 60 μm and 125 μm . For wires that are in good contact with the substrate (solid lines), the shadow size follows a power law for the wire diameter with an exponent of ~ 1.2 for each extraction voltage, i.e. it is disproportionately more pronounced for larger wires. The shadow size also increases sharply for poorly mounted wires that are raised from the substrate (dotted lines). This can be explained by the increased curvature of the extraction field, as the equipotential lines must contour around the raised samples. Figure 2c shows the observable width of the wires, defined as the full width half maximum of the thin central region in the total ion images. Poor mounting (dotted lines)

Figure 2. (a) SIMION simulation of a conducting wire, with a diameter of 125 μm , on a conducting substrate, showing the equipotential lines of the extraction field (pink lines) and the trajectory of sputtered secondary ions from the substrate and the wire. Assuming an analyzer angular acceptance of 4° , the ions that are detected are shown in blue, and the ions that are lost are shown in red. The extraction gap is 1.5 mm and the extraction voltage is -2000 V. (b) Experimental results using 25 keV Bi^+ primary ions for gold wires of different diameters (D) and mounting gap from the silicon substrate (G), as a function of the extraction voltage from -500 to -2000 V, showing the size of the substrate shadow. For zero extraction voltage, the geometric shadows are shown. (c) Experimental results showing the observable width of the gold wires in μm as a function of the extraction voltage

drastically increases the topographic effects and reduces the observable width. Typically, for well-mounted samples (solid lines) only 15 μm of the wires may be observed regardless of the wire diameter. Expressed in terms of the angle, ψ , on the wire with respect to the extraction direction, only ions from $|\psi| \leq 26^\circ$, 13° and 7° can be detected from the 33 μm , 60 μm and 125 μm wires, respectively. Since the area available to the primary ion beam is $|\psi| \leq 90^\circ$, this represents a severe limitation to the chemical analysis of the wire surface. The topographic features observed here are in good qualitative agreement with those reported using a PHI nanoTOF instrument [17], but differences in the magnitudes of these effects arise from the different extraction voltage, extraction gap and analyzer design of the nanoTOF instrument.

From Figure 2b and c, it is clear that sample mounting is crucial for the analysis of topographic samples, and it is recommended that conducting samples are in good contact with a flat conductive substrate, which minimizes the distortion in the extraction field. For wires or fibers this can be achieved, for example, using the method shown in Figure S.1 in the Supplementary Information. For all samples, topographic effects can be reduced by the use of a smaller extraction voltage. This will be discussed in more detail later.

Effect of Sample Alignment

We now return to the images of the 125 μm gold wire acquired in perpendicular alignment, shown in Figure 1c and d in the linear and logarithmic intensity scale, respectively. Due to geometry, the images are spatially distorted along the direction of the primary ion beam, which is incident from the right hand side. For angles of incidence other than normal (typically, $\theta = 45^\circ$ is used), the coordinates of the image are not simply the xy spatial coordinate on the sample, but are dependent on the height z . Features with a height z are projected by a distance $d = z/\tan\theta$ to the left of the true position, as illustrated in Figure 1 in Ref. [1]. The effect on the wire in perpendicular alignment is marked on Figure 1d. The substrate shadow is marked by arrow 'S' on the figure. The wire should be in the middle of the shadow region if viewed from above (marked by arrow 'A'), but it is recorded to the left instead (marked by arrow 'O'). The perceived diameter of the wire is also increased by $\sqrt{2}$ to around 176 μm . Careful analysis of the data shows that the strongest intensities, which appear on the left hand side of the observed position of the wire, actually occur at the center of the wire ($\psi = 0^\circ$). Little intensity enhancement is observed on the left hand side of this bright area, despite the larger primary ion angle of incidence compared to the right hand side. Therefore, as in the horizontal alignment, the topographic field effect dominates the intensities in this image rather than the angle of incidence. Later, we present a method using an extraction delay to reduce field effects so that the intensity changes due to the angle of incidence could be observed. In general, the relative extent of geometric

distortions, angle of incidence and field effects are not trivial to predict, especially for a sample without well-characterised topography. It is recommended that samples should be analyzed in an orientation that minimizes geometrical distortions, if possible. For the remainder of the study, we shall focus only on wires in the parallel alignment.

Effects for Different Secondary Ions

So far we have only examined the total ion intensities. The study of individual ion images show that the extent of topographic effects also varies for different secondary ions. Figure 3 shows the scaled secondary ion intensities of different species (at around unit mass resolution) as a function of their originating position (angle ψ on the wire) for a 60 μm gold wire. The data are scaled to the intensity at the center of the wire, $\psi = 0^\circ$. In the intense central region $|\psi| \leq 15^\circ$, all secondary ions shown vary in unison with the total ion intensity, with the exception of Au^+ , which has a larger observable width. To an analyst, the spectrum at $\psi = 15^\circ$ may be mistaken for 'cleaner' wire material, with much weaker organic peaks, than the spectrum at the center of the wire at $\psi = 0^\circ$. For larger angles $|\psi| \geq 30^\circ$, the scaled intensity of Au^+ is more than an order of magnitude larger than Au_3^+ . The strong enhancement of secondary ions C_2H_3^+ , C_2H_4^+ and Si^+ are unrelated to this and will be discussed separately in the next section. The significant difference between Au^+ and Au_3^+ intensities is due to sputtered monatomic ions (e.g. Au^+) having, on average, higher kinetic energies than organic or cluster ions (e.g. C_2H_3^+ or Au_3^+) [18]. To understand this, Monte Carlo simulations are carried out using SIMION on the trajectory of secondary ions emitted from the wire surface with different kinetic energies (2 eV or

Figure 3. The angular intensity profile of secondary ions acquired from a 60 μm gold wire using 25 keV Bi^+ primary ions with an extraction voltage of -2000 V, scaled to their respective ion intensity at the center of the wire, $\psi = 0^\circ$. The inset diagram shows the angle ψ on the wire with respect to the extraction direction

7 eV), over a range of emission angles with respect to the normal of the wire surface. The results are shown in Figure S.2 in the Supplementary Information. We make the simple assumption that the analyzer has an angular acceptance angle of $<4^\circ$, so that ions travelling at a direction larger than 4° to the analyzer axis at the point of entry are not detected. We find that for larger angles ψ on the wire, the strong topographic field effects mean that detection is not possible except for ions emitted with a larger initial energy in the direction of the extractor. Thus, the observable width is larger for atomic secondary ions with higher kinetic energies, in agreement with the experimental data. Similarly, SIMION predicts that the substrate shadow is smaller for atomic secondary ions, which is also observed.

Scattering of the Primary Ions

Figure 3 also shows that for many secondary ions, notably at nominal mass 28 u (covering Si^+ and C_2H_4^+), a large enhancement effect which peaks at $\psi=57^\circ$ can be observed. The complete absence of the enhancement for Au^+ and Au_3^+ ions characteristic of the wire shows that it is not simply owing to an increased sputtering yield at grazing incidence angles. We find that the enhancement is caused by the scattering of the Bi^+ primary ions from the gold surface at large angles of incidence, which has been suggested previously [3]. Scattering results in a delayed and broadened secondary ion intensity contribution to the time-of-flight spectra. This is shown in Figure S.3 in the Supplementary Information for the H^+ peak from different regions of a 125 μm gold wire, before and after in-situ sputter cleaning to remove carbonaceous contamination. H^+ ions emitted from the center of the wire (red) arrive a few ns before those emitted from the substrate (blue), since they are produced closer to the extractor. Before sputter cleaning (Figure S.3a), at the side of the wire where the enhancement effect is observed, the regional spectrum (green) reveals two distinct contributions, one from the wire surface and one delayed, broadened contribution. The broadened contribution is also observed on other secondary ions and is not limited to H^+ . After sputter cleaning (Figure S.3b), most of the H^+ are removed from the wire surface, and the signal reduces by two orders of magnitude at the center of the wire, although there is still a significant amount remaining on the silicon substrate. However, at the side of the wire, the broadened contribution is still significant and has the same intensity ratio to the substrate signal. The broadened contribution can be explained by a fraction of the scattered primary ions hitting the substrate at a location away from the shadow region, emitting secondary ions that are recorded by the instrument at the location of the wire after a delay of several ns. Our data show that primary ion scattering is important for a primary ion incidence angle of $\geq 55^\circ$ to the surface normal, and chemical components identified as localized to these areas may in fact originate from the surrounding regions. To diagnose these effects, a high mass resolution

image using a bunched primary ion beam is useful to provide necessary mass resolution to identify the broadened contribution caused by scattering.

Optimizing Parameters

Extraction Voltage

We have already seen from Figure 2 that using a smaller extraction voltage can reduce the extent of topographic effects in ToF-SIMS images of conducting samples. For example, the observable width of the gold wire is improved by $\sim 35\%$ when the extraction voltage is reduced from -2000 V to -500 V. As shown by the Monte Carlo simulations (Figure S.2b and Figure S.2d in the Supplementary Information), at a smaller extraction voltage, the maximum angle ψ on the wire from which ions can be detected is increased. However, at the center of the wire ($\psi=0^\circ$), only secondary ions emitted with a narrower range of emission angles can be detected. This is because the ions that are emitted with an initial direction off-normal to the analyzer axis receive less “pull” towards the analyzer at smaller extraction voltages, and are consequently more likely to be lost due to the limited angular acceptance. Thus, using a smaller extraction voltage improves the intensities at the wire sides at a cost of reducing the intensities at the center of the wire and from the substrate. For many analyzer systems where the extraction voltage determines the ion energy during time-of-flight, using a smaller extraction voltage increases the data acquisition time, since the flight time required for measuring mass m using extraction voltage E is proportional to $(m/E)^{1/2}$. For these systems, using a smaller extraction voltage may reduce the mass resolution as the natural spread in the kinetic energies of sputtered secondary ions becomes a larger fraction of the total ion energy. Thus, a compromise has to be reached about the optimal reduction of topographic effects and the extraction voltage for each application.

Extraction Delay

Topographic field effects can also be reduced via the use of an extraction delay, for instrument designs with pulsed primary ions. Here, the extraction voltage is switched on several tens of nanoseconds after the sputtering event, when the sputtered secondary ions have drifted away from the sample surface into a region where the extraction field would be less distorted by the topographic sample. The use of an extraction delay in SIMS has a similar effect as in secondary neutral mass spectrometry (SNMS), where sputtered neutrals drift freely until they are post-ionized by a pulsed laser beam and extracted. It has been shown that field effects are considerably reduced in SNMS compared with SIMS for the analysis of microparticles [3].

In the following, we study the use of extraction delay to reduce topographic field effects in SIMS using an extraction

Figure 4. The use of extraction delay for the reduction of topographic field effects. This applies only to pulsed primary ion design instruments. **(a)** SIMION simulation of the effects of 50 ns extraction delay on a gold wire with a diameter of 125 μm . This shows the curved equipotential lines of the extraction field (pink lines), and the trajectory of sputtered secondary ions both before the extraction voltage is switched on (green) and afterwards (blue). All ions are detected assuming an analyzer angular acceptance of 4° . **(b)** Experimental results for a 60 μm gold wire using 25 keV Bi^+ primary ions, showing the total ion images in logarithmic intensity scale, for extraction delays of 0 ns, 50 ns, 90 ns and 150 ns. The maximum intensity per pixel are 1983, 1391, 714 and 593 counts, respectively. The field of view on the substrate surface is 500 $\mu\text{m} \times 500 \mu\text{m}$. **(c)** The observable width of the wire (red), the size of the substrate shadow (orange), the integrated intensity of the Au^+ peak (green) and the full width half maximum peak width (blue), as a function of the extraction delay, shown by their % change with respect to the value at zero extraction delay. **(d)** The time-of-flight and peak shape of Au^+ secondary ions for an extraction delay of 0 ns to 90 ns

voltage of -2000 V and standard analyzer lens and reflector settings. Figure 4a shows the SIMION simulation results for an extraction delay of 50 ns. For comparison, the wire diameter, extraction voltage and extraction gap are the same as those used in Figure 2a. The secondary ions drift in a straight trajectory away from the surface (green lines), until the extraction voltage is switched on some time later and they are quickly accelerated towards the analyzer (blue lines). Compared to Figure 2a, the flight paths towards the analyzer are less affected by topography, and the detection of the ions emitted from the sides of the wire and the substrate improves substantially, with all secondary ions travelling within the analyzer acceptance angle of 4° . Figure 4b shows the total ion images of a 60 μm gold wire for a range of extraction delays. The observable width of the wire (red) and the shadow size (orange) are plotted in Figure 4c by their percentage change with respect to the value at zero extraction delay. With an extraction delay of 70 ns, the observable width of Au^+ is increased by 26%, and the substrate shadow is reduced by 42%. However, the use of an extraction delay has a large effect on secondary ion intensities, mass resolution and the ability to identify high mass species. We now study these effects in more detail.

Figure 4d shows the time-of-flight spectra of the Au^+ secondary ion signals from a 60 μm gold wire, for different extraction delays. From this, the integrated intensities (green) and peak widths (blue) of the Au^+ peak are plotted in Figure 4c. We first consider the effect of extraction delay on the secondary ion intensity. On a flat sample, an extraction delay always causes a loss in intensity, which drops rapidly as the secondary ions eventually drift out of the extraction region. For a topographic sample, owing to improved analyzer acceptance due to the reduction of topographic effects, the integrated intensity of Au^+ ions

increases by more than 40% with an extraction delay of 50 ns before dropping at larger extraction delays. Second, we consider the effect on the time-of-flight and mass resolution. As the extraction delay is increased, the time-of-flight of Au^+ reduces and reaches a minimum at 70 ns before increasing rapidly again. This is observed for all secondary ions, and the extraction delay to achieve the minimum flight time is dependent on the ion mass and kinetic energy. This can be explained as follows. If the extraction voltage is switched on when the secondary ions are at a height h above the sample, then they will only acquire a fraction of the extraction energy. For a flat conducting sample, the fraction would be $1-h/d$, where d is the extraction gap. As a consequence, extraction delay leads to a reduced speed of secondary ions as they enter the analyzer, which affects their flight paths and their final flight times to the detector. At large extraction delays (e.g. for Au^+ ions beyond 90 ns), the drift distance h is large, and the low ion velocity means that these ions have a long flight time compared to those extracted normally. However, at smaller extraction delays (e.g. for Au^+ ions at 50 ns), the moderate reduction in ion velocity is more than compensated by the reduced penetration of these lower energy ions into the ion mirror in the reflectron analyzer. Thus these ions have a shorter flight path than ions at full energy, which results in an overall reduced time-of-flight to the detector. This behavior is by design and normally employed to improve the time focus at the detector by compensating for different secondary ion energies on emission. Here it has important consequences on the practical use of extraction delay. We observe in Figure 4d that the minimum time-of-flight typically signifies the extraction delay beyond which the energy compensation of the analyzer becomes ineffective, and the mass resolution degrades rapidly. With a high extraction delay, the peak shape thus becomes asymmetric with a large tail. Further SIMION simulations were carried out on a model of a complete reflectron instrument, provided by Green et al. and described in Ref. [19]. This shows that, for a flat sample, the minimum time-of-flight occurs when the secondary ions are extracted from a certain height above the surface, regardless of their mass and kinetic energies on emission. Using experimental data from a flat silicon wafer, the height is estimated to be about $60\text{ }\mu\text{m}$ above the surface, equivalent to a loss of 80 eV in extraction energy. Note that it is not straightforward to compensate for this by optimizing the spectrometer, since secondary ions with different masses and energies will drift to different heights under an extraction delay, thus the optimization of the energy compensation for one ion will generally lead to the loss of mass resolution for another. The loss in signal and mass resolution is particularly acute for low mass secondary ions, since the drift distance for a particular extraction delay and ion energy is proportional to $m^{-1/2}$.

The effects described above represent limitations to the use of extraction delay for the reduction of topographic effects. The optimal extraction delay for a sample depends

on the size of the topographic features, the mass of the secondary ions of interest, their kinetic energies on sputtering and the compromise between mass resolution, signal intensity and the extent of topographic effects. Using data from a flat silicon wafer, we present our recommendations in Figure 5 for the extraction delay required for an organic or cluster secondary ion with mass m . Curve A shows the extraction delay, t_1 , required to obtain minimum time-of-flight for the ion under study. The mass resolution and signal intensity begin to degrade from this point. Curve B shows the upper limit extraction delay, t_2 , where the peak has severely broadened but the peak shape is still fairly symmetrical and Gaussian, acceptable for basic identification. At this point, the secondary ion intensity has degraded by typically a factor of two. The recommended analysis region lies below curve B. Often a large extraction delay required for high mass and slow moving secondary ions leads to the loss of low mass and fast moving secondary ions, which are required for the mass calibration of the data. Line C shows the maximum extraction delay that retains sufficient signal for CH_x peaks for basic mass calibration. Beyond this, it is necessary to compare the spectra obtained using a low extraction delay for the identification of high mass peaks.

We can estimate the size of topographic features, the topographic effects of which may be minimized by a particular extraction delay, using the distance that the secondary ions have drifted away from the surface. Assuming the emitted ions have a kinetic energy of 2 eV, the upper

Figure 5. Recommendation plot for the optimal use of extraction delay for organic or cluster secondary ions, with an extraction voltage of -2000 V . This applies only to pulsed primary ion design instruments. Curve A shows the extraction delay, t_1 , required to obtain minimum time-of-flight, and curve B shows the upper limit extraction delay, t_2 , beyond which the peak shape ceases to be useful. Line C shows the maximum extraction delay required to maintain sufficient signal for low mass ions for the basic mass calibration of the data. The recommended analysis region lies below curve B. The estimated sizes of topographic features, whose effects may be minimized by the chosen extraction delay, are shown in brackets

limit extraction delay t_2 occurs at a drift distance of 240 μm . For minimum time-of-flight, t_1 , this distance is 60 μm . From Figure 2a, we can see that the drift distance generally needs to be 3–4 times the size of topographic features for the effective removal of field curvature caused by sample topography. To help analysts, the suggested size of topographic features for each extraction delay is labelled in Figure 5. This simple estimate is in good agreement with experimental data obtained for Au_3^+ secondary ions (mass 591 u) from a 60 μm gold wire, which shows no improvements in the observable width after an extraction delay of 250 ns, approximately equivalent to a drift distance of 200 μm . Using Figure 5, an extraction delay may be quickly selected, depending on the desired compromise between mass resolution, signal intensity and topographic effects.

Finally, we note that an extraction delay is only useful for short primary ion pulse widths, where the pulse width is much smaller than the extraction delay. An extraction delay can also cause a shift of the image along the primary ion beam azimuth direction, as the beam ceases to be deflected by the extraction field. On some instruments, the setting at which the extraction delay is 0 ns may not be well defined and analysts should increase the delay incrementally until a change in the spectra is observed.

Improved Sample Mounting

Where possible, topographic field effects can also be reduced significantly using special sample mounting methods to minimize the distortion of the extraction field. Whilst the simple method shown in Figure S.1 in the Supplementary Information produces good results for the analysis of a single conducting wire, and is relatively quick to implement, topographic field effects can be strongly reduced if a number of wires are mounted adjacent to each other in a parallel close-packed fashion. The disadvantages of this method are that it is relatively time consuming and that signal from the sides of the wires may not be available due to the close

proximity of another sample. To address these issues, we use SIMION to design a special sample holder which could effectively counteract the distortion of the extraction field arising from a conducting wire. The criteria are that the holder must be easy to use and be applicable to wires with a range of diameters. We find that a single V-shaped groove cut into a sample block, with the wire mounted such that it is laying flat at the bottom, provides good results. The simulation and experimental results for the sample holder are shown in Figure 6. The SIMION simulation (Figure 6a) shows an optimal design with the angle of the groove at 30° to the horizontal and a groove depth of 450 μm . Secondary ions emitted from the side of the wire are deflected by the groove towards the analyzer, and the groove acts as a simple focusing lens for the secondary ions. All ions arrive at the analyzer entrance with an angle of $<2^\circ$ and are therefore available for detection. Figure 6b and c show such a device in practice using a 125 μm gold wire. The total ion image is shown in linear and logarithmic intensity scale, for comparison with Figure 1a and b, respectively. Although it is clear that topographic field effects are still important, the sample holder substantially reduces this and the observable width of the wire is increased to 31.2 μm , equivalent to $|\psi| \leq 15^\circ$ on the wire. This represents a $\sim 115\%$ improvement over previous results with the wire mounted on a flat silicon wafer. The sample holder also significantly reduces shadow regions on the substrate, although the substrate intensities are now uneven because of the surface roughness of the sample holder. This very simple prototype device significantly reduces topographic field effects with the benefit that the mass resolution is not strongly affected.

Example Application – Anisotropically Etched Silicon Surface

In this section, we demonstrate the practical application of extraction delay for the reduction of topographic field effects on a more complex sample. SIMS analysis is carried out on

Figure 6. The use of a V-groove sample holder to reduce topographic field effects for conducting wires. The angle of the groove is 30° to the horizontal and the groove depth is 450 μm . (a) SIMION simulation of the secondary ions emitted from a 125 μm wire. This shows the curved equipotential lines of the extraction field (pink lines), and the trajectory of sputtered secondary ions (blue lines). All ions are detected assuming an analyzer angular acceptance of 4° . (b) Experimental results using 25 keV Bi^+ primary ions for a 125 μm gold wire mounted on the V-groove sample holder, field of view 500 $\mu\text{m} \times 500 \mu\text{m}$, acquired using a primary ion beam raster of 128×128 pixels, showing the total ion image in linear intensity scale, and (c) logarithmic intensity scale

an anisotropically etched silicon sample, obtained from Prutton *et al* [13]. This sample has been previously used to evaluate topographic effects in Auger electron spectroscopy [13]. The height of the polyhedra are 40 μm , with sloping surfaces that are inclined at 46.5° or 54.7° to the horizontal plane as calculated from the crystal structure. The total ion image without an extraction delay, obtained using a Bi^+ primary ion beam incident at $\theta=45^\circ$ to the horizontal from the right hand side, is shown in Figure 7a. Clear contrast is observed due to topography. First, few secondary ions can be detected from the sloping surfaces because of strong topographic field effects, except at locations where a sloping surface is immediately adjacent to another near the bottom of the polyhedra. An example of this is marked on the figure

Figure 7. Total ion images of an anisotropically etched Si sample using 25 keV Bi^+ primary ions, with (a) no extraction delay (b) 110 ns extraction delay. The intensities are shown in logarithmic scale and the field of view assuming a flat sample surface is $500\ \mu\text{m} \times 500\ \mu\text{m}$. (c) Total ion image acquired using 25 keV Bi^+ primary ions with 130 ns extraction delay (log scale), field of view $290\ \mu\text{m} \times 290\ \mu\text{m}$, showing the regions of interest on different faces. (d) Relative ion yields of PDMS characteristic peak ($\text{C}_5\text{H}_{15}\text{OSi}_2^+$) as a function of primary ion angles of incidence, using Bi^+ and Bi_3^+ primary ions with 130 ns extraction delay, for the regions of interest defined in (c). The intensities are normalized to their values at 72.3°

by arrow A. Here, the extraction equipotential lines form a ‘V’ shape as they must curve around the conducting surface, and this significantly improves the acceptance of secondary ions from the sloping surfaces, similar to our V-groove device discussed earlier. Second, a large increase of intensities at grazing incidence angles can be observed, marked on the figure by arrow B. The increase is approximately three times compared with the top surface of the polyhedra, despite the strong field effects on these sloping surfaces. It is clear that field effects and primary ion angles of incidence are both significant mechanisms of topographic contrast in this image.

To reduce topographic field effects and reveal the variations in secondary ion yields at different primary ion angles of incidence, Figure 7b shows the total ion image obtained on the same area when an extraction delay of 110 ns is applied. The overall topographic contrasts are reduced significantly and it is possible to detect secondary ions originating from the entirety of the sample surface. The increase in secondary ion intensities at grazing angles of incidence is now more than 5 times due to the strong reduction of field effects. To investigate further, Figure 7c shows the total ion image obtained using an extraction delay of 130 ns, with the primary ion beam azimuth aligned with the edges of the polyhedra. The differences in the ion yields on the different sloping surfaces are now clear. We specify five regions of interest, marked A to E on the figure. From these regions of interest, the relative ion yields as a function of the angles of incidence (calculated from the geometry of the sample) are plotted in Figure 7d, for images acquired using Bi^+ and Bi_3^+ primary ions. We use the $\text{C}_5\text{H}_{15}\text{OSi}_2^+$ peak (nominal mass 147 u), characteristic of the polydimethylsiloxane (PDMS), a mobile surface contaminant that is fairly evenly distributed on the surface. The extraction delay chosen is below the upper limit of 150 ns (curve B on Figure 5) for this ion. The intensities are normalized to their values at the maximum incidence angle of 72.3° . We find that the ion yields using Bi_3^+ have a weaker dependence on the angle of incidence compared to Bi^+ . This is expected from the non-linear enhancement of cluster ion sputtering. Although we cannot completely eliminate the field effects, for example, the angle of incidence dependence of the ion yields for Bi^+ does not follow the expected $\sec^2\theta$ distribution, it is clear that useful semi-quantitative SIMS intensities can still be obtained from highly topographic samples using the simple recommendations presented here. Notwithstanding the reduction in mass resolution and the loss of intensities for lower mass ions, an extraction delay can be extremely helpful for analysts trying to localize molecular components on a highly topographic surface, where they are not interested in the behavior of smaller fragment peaks. Our results also suggest that cluster ion beams further reduce the dependence of secondary ion yields on the primary ion angle of incidence, and thus can be used to reduce topographic contrast in ToF-SIMS images. We expect this to be especially beneficial for samples with much smaller topo-

graphic features, where the image contrast is dominated by the different primary ion angle of incidence rather than topographic field effects, for example the analysis of surfaces with sub-micron topography.

Conclusions and Recommendations

We have conducted a detailed study of the key factors that give rise to topographic artefacts in ToF-SIMS images of conducting samples. Aside from simple geometry effects, the majority of unwanted topographic contrast can be accounted for by topographic field effects (where the distortion of the extraction field by the presence of the sample cause the loss of secondary ion signals) or by variations in the primary ion incidence angle. Using these results, we recommend the following for conducting samples:

- (1) If possible, topographic samples should be analyzed in an orientation that minimizes geometrical distortions, for example, by aligning wires or fibers parallel to the primary ion beam azimuth.
- (2) Samples should be mounted in such a way as to minimize the distortions of the extraction field, if possible. Wires or fibers should be mounted in good contact with a flat conductive substrate (following Figure S.1 in the Supplementary Information), mounted parallel to each other in a close-packed fashion, or in a V-groove sample holder (Figure 6) to reduce field effects.
- (3) The field effects caused by topography may be reduced by using a smaller extraction voltage or an extraction delay. An extraction voltage of -500 V for positive ions is found to be useful for the instrument used in this study. Extraction delay is only applicable to pulsed primary ion design instruments and has a significant effect on mass resolution and signal intensity. Figure 5 provides a simple guide for the extraction delay suitable for a given size of topographic features and secondary ion.
- (4) The variation of secondary ion yields with the primary ion incidence angle is also a significant cause of topographic contrast. This can be reduced using a cluster ion beam such as Bi_3^+ instead of Bi^+ .
- (5) At large angles of incidence, primary ions may be scattered from one region of the sample to another. Scattering may be diagnosed using a high mass resolution image acquired with a bunched primary beam.

Complementary recommendations for insulating samples are presented in the second part of this study [11]. In the future, improved mass spectrometer designs would be crucial to further reduce topographic effects and enable the applications of SIMS to a wider range of industrial samples. This could be achieved, for example, by increasing the angular acceptance of the analyzer, or by extending the usefulness of extraction delay using more sophisticated energy compensation and methods to restore mass resolution.

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