A correlative ToF-SIMS/SPM methodology for probing 3D devices.

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ABSTRACT: With the continuous miniaturization and increasing complexity of the devices used in nanotechnology, there is a pressing need for characterization techniques with nm-scale 3D-spatial resolution. Unfortunately, techniques like Secondary Ion Mass Spectrometry (SIMS) fail to reach the required lateral resolution. For this reason, new concepts and approaches, including the combination of different complementary techniques, have been developed in the last years to try to overcome some of the faced challenges. Beyond the problem of spatial resolution in a 3D SIMS experiment, one is also faced with the impact of changes in topography during the analysis. These are quite difficult to identify, originate from the different sputter rates of the various materials and or phases in a heterogeneous system and are notorious at the interfaces between organic and inorganic layers. As each of these materials will erode at a different velocity, accurate 3D-analysis will require means to establish a spatially resolved relation between ion bombardment time and depth. Inevitably such a non-homogeneous erosion will lead to the development of surface topography. The impact of these effects can be overcome provided one can capture the time and spatially dependent surface erosion (velocity) with high spatial resolution during the course of a profiling experiment. Incorporating a Scanning Probe Microscope (SPM) unit which provides topography measurements with high spatial resolution, into a SIMS tool (e.g. Time of Flight (ToF) SIMS) with means to alternate between SPM and SIMS measurements, is one approach to meet that demand for complementary topographical information allowing accurate 3D chemical imaging. In this paper, the result of integrating a SPM module into a ToF-SIMS system is presented illustrating the improvements in 3D data accuracy which can be obtained when analyzing complex 3D-systems.

1. Introduction

The semiconductor industry is increasingly expanding the library of materials and moving towards advanced heterogeneous systems with 3D architectures, which includes both inorganic materials (e.g. devices and nanolayered systems) and organic materials (e.g. advanced coatings and smart optical films). Obviously, the performance of such complex 3D heterogeneous systems is also determined by the 3D distribution of the elements and chemical compounds. Therefore, the support to their development and understanding requires a metrology solution able to provide the 3D distribution of each constituent with a spatial resolution (both lateral and depth) down to the nanometric scale.

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an extremely surface sensitive technique, which provides both elemental and molecular information on surfaces and thin films. This technique is currently well-established for chemical mapping as well as depth profiling of different organic and inorganic materials and nanolayered systems with a lateral resolution down to 100 nm[1] and a depth resolution down to 5 nm when using large Argon clusters as sputter species.[2]

The generation of a 3D analysis in ToF-SIMS is based on stacking the consecutive 2D images, obtained by the pulsed analysis beam, during the subsequent low energy sputtering steps.[3] However, the 3D analysis of devices/structures exhibiting initially strong topography and/or considerable differences in the sputter yields over the specimen volume (e.g. mixed organic-inorganic systems) is challenging as the ToF-SIMS reconstructed volume suffers from several artifacts. For example, the surface topography of the analyzed sample is currently disregarded in the 3D reconstruction. Instead it is assumed that the analyzed surface is flat and displaying the analyzed volume as a cuboid, leading to strong distortions of the detected depth distributions in the reconstructed 3D volume. Similarly, during the ion beam induced erosion, surface roughness and/or surface topography could build up, especially if the sample is composed of more than one material with different sputter yields and/or crystalline orientations.

In order to obtain a true 3D composition distribution, the time scale of the ToF-SIMS depth profile must be converted into an accurate depth scale (Figure 1) at every X,Y location.

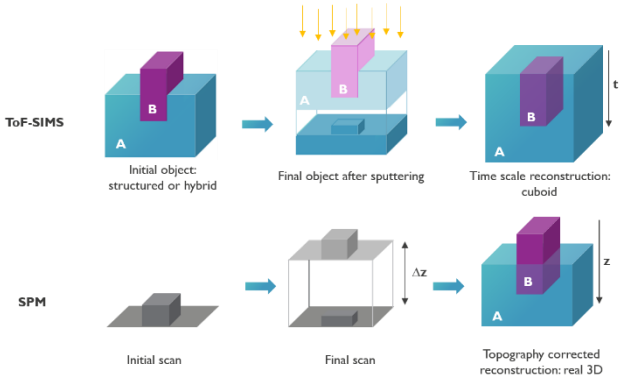


Figure 1. Schematic of the ToF-SIMS/SPM approach.

Provided the heterogeneity is only spatially present and not in depth, *ex-situ* Scanning Probe Microscopy (SPM) experiments before and after sputtering the sample[4,5,6,7,8,9] can be used to perform that conversion as they provide the required complementary information on the surface topography with nanometer resolution.

Unfortunately, the *ex-situ* approach suffers from some limitations. First, the information regarding the sample's topography will be mainly limited to the situation before and after the final ion bombardment. In fact, intermediate information to track the topographical evolution during the sputtering experiment would be quite time consuming since it requires multiples sample's transfers between the two tools.

Moreover, to operate *ex-situ*, the sample will need to be exposed to the air, with the possibility of introducing contaminants on the surface and possible artifacts due to, for example, oxidation. Even though the air exposure can be minimized by using vacuum suitcases, the re-localization of the analyzed zone between the ToF-SIMS and the SPM tools could still be challenging.

A more general solution, avoiding all the issues related to an *ex-situ* approach, is to integrate a SPM system into a ToF-SIMS system allowing for *in-situ* topography analysis during the 3D chemical imaging.

In this work, we present the advantages of such an approach on the example of a hybrid system made of two different organic layers deposited on a silicon array of microstructures. The differences in sputter rates among the components (organic materials vs silicon) and the (initial) micro-scale topography lead to considerable distortions if the standard data analysis protocols which ignore these features are applied. We demonstrate here that the combined ToF-SIMS/ *in-situ* SPM approach provides an unique set of information, i.e. the spatially resolved elemental and chemical information from the ToF-SIMS, and the time dependent topographical information from the *in-situ* SPM analysis, which leads to far more accurate 3D analysis of complex systems.

2. Experimental section

2.1. Combined tool

The tool presented in this study is a combined instrument where the ToF-SIMS and the SPM are integrated in the same UHV analysis chamber (ToF-SIMS NCS, ION-TOF GmbH, Münster, Germany, cfr Figure 2 for its schematic). Thanks to the piezo driven stage, the sample can be moved between the ToF-SIMS and the SPM parts of the instrument with sub-µm precision and high speed. In this way, it is possible to analyze the same region of the specimen with both techniques. The ToF-SIMS analysis is performed using a Bismuth liquid metal cluster ion gun (LMIG) to provide high secondary ion yields, especially for organic materials. In order to avoid strong damage and loss of the molecular information during the sputtering of organic materials, an Argon gas cluster ion beam (GCIB) with energies per atom in the range of 2 eV is used as sputter beam. The SPM unit is designed to provide very accurate information about the surface topography and has a scan range of 80 × 80 × 10 µm^3. As the sputter crater is larger (several hundreds of micrometers) than the scan range of the SPM (80 µm), a special long-distance surface profiler mode is incorporated which allows to measure the correct shape and depth of the sputter craters by stitching several independent SPM segments.

The SPM module can be operated in contact mode, in non-contact and in a variety of dynamic modes including KPFM (Kelvin Probe Force Microscopy) and MFM (Magnetic Force Microscopy), which can provide additional information about the physical properties on a heterogeneous sample.[10] For this study, it was chosen to operate the SPM in tapping mode, mainly due to the presence of organic materials in our hybrid systems. When the cantilever operates in tapping mode, it is excited to oscillate close to its resonant frequency, being only in intermittent contact with the specimen surface. In this way, together with the topography, the phase shift of the cantilever oscillation can be recorded, giving insights on different properties on a heterogeneous sample, such as composition, adhesion, etc...

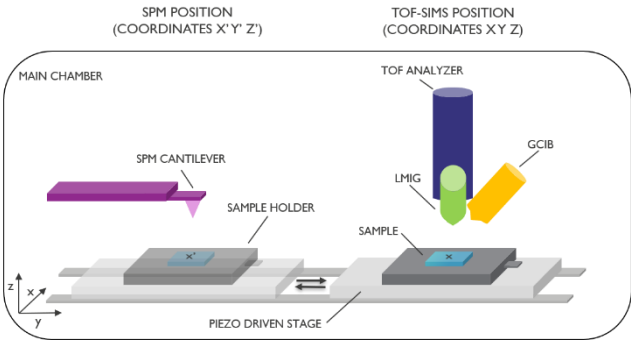


Figure 2. Schematic of the combined ToF-SIMS/SPM tool.

2.2. 3D organic/inorganic microstructures.

A (100) Silicon substrate with native oxide and a dimension of 2 × 2 cm^2 was selected for preparation of the inorganic reference template. The template includes arrays of squares with the dimension of 30 × 30 × 2.4 µm^3 or 5 × 5 × 2.4 µm^3, repeated along an area of 1000 × 1000 µm^2, with a pitch in both lateral directions equal to the trench side (Figure 3). Optical lithography was performed using a Heidelberg uPG101 laser writer and the pattern was transferred into the silicon substrate

with an Oxford plasmalab 100 reactive ion etching (RIE) tool. The inorganic templates were then filled by polystyrene (PS) and Irganox 1010 films. A solution of PS (10300 g/mol) in toluene at a concentration of 150.0 mg/ml was spin-coated (30s at 2000 rpm) onto the Si substrate. After that, the Irganox 1010 layer was deposited by evaporation on top of the PS layer. The latter is the planar reference material for ToF-SIMS developed by the National Physical Laboratory (NPL, Teddington, United Kingdom).[11]

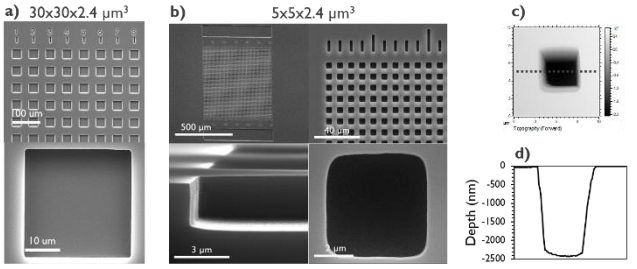


Figure 3. SEM images of (a) 30×30 µm^2 (top view) and (b) 5×5 µm^2 structures (top view and cross-section). c) SPM image for the 5×5 µm^2 bare Si structures. d) Line scan across the SPM image shown in c) in x direction.

The thicknesses of PS and Irganox 1010 films were investigated with optical profilometer and they range between 0.5 and 1 µm for PS and 1 and 2 µm for Irganox 1010, depending on the squares' size, as described in Figure 4. Such a configuration allows the use of the planar organic layers, far from the microstructures area, as a reference for the calibration of the sputter yields and the chemical information.

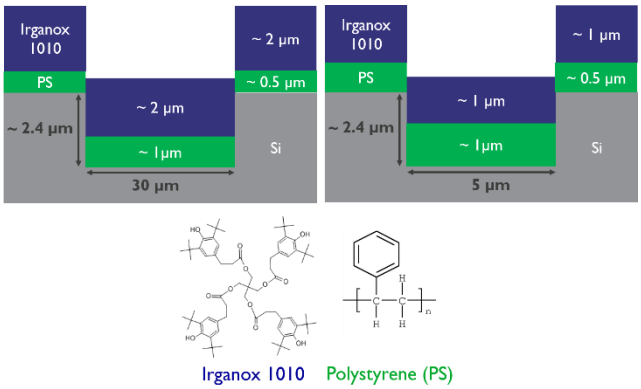


Figure 4. Schematic cross-sectional representation of the structured sample covered with PS and Irganox1010 and their molecular structure.

3. Results and discussion

3.1. Large scale hybrid system: 30 µm squares array filled with organics.

The 30 µm large microstructures filled with PS and Irganox 1010 previously described and presented in Figure 4, were depth profiled using Ar_{5000}^+ 10 keV (0.4 nA, 250 × 250 µm^2) as sputter beam and Bi_3^+ 30 keV (0.05 pA, 50 × 50 µm^2) as primary beam in Fast Imaging mode with delayed extraction to ensure simultaneously good mass (m/Δm > 5000) and lateral resolution (~ 400 nm).[12]

From the depth profile displayed in Figure 5 a, which sums the data over the entire analyzed area, the interfaces between the organic layers both in and outside the trench do not appear very sharp, especially for the PS ion signal. This might suggest a difference in thickness between the two sample's regions (inside and outside the square). In fact, if the reconstruction is separated in two regions (Figure 5 b) i.e. the mesa part (in light blue, inset on the right-hand side) and the square itself (in orange), different sputter times are needed to completely remove the PS layer, confirming a thicker layer inside the square than in the mesa region. Moreover, in the depth profile reconstructed from the square region (in orange), one could erroneously conclude that the two organics, Irganox 1010 and PS, have similar thickness since they are removed in a similar amount of time. However, it is known[13,14], and further supported by the analysis of the Irganox 1010/PS reference layer (outside the micro-structured array), that the sputter yield for Irganox1010 is twice as high as for PS (~35 nm^3/PI for PS and ~73 nm^3/PI for Irganox1010).

This is therefore a perfect example to proof that the combination with the *in-situ* SPM module will improve the data reconstruction of the sample.

Therefore, for the experiment on the array, the ToF-SIMS measurement was alternated with the SPM one at different depths, i.e. the topography was measured at the beginning (top surface, point 0), at the Irganox 1010/PS interface (point 1), at the PS/Si interface (point 2) and at the end of the measurement (in the Si substrate, point 3), as indicated by the inset in Figure 5 a).

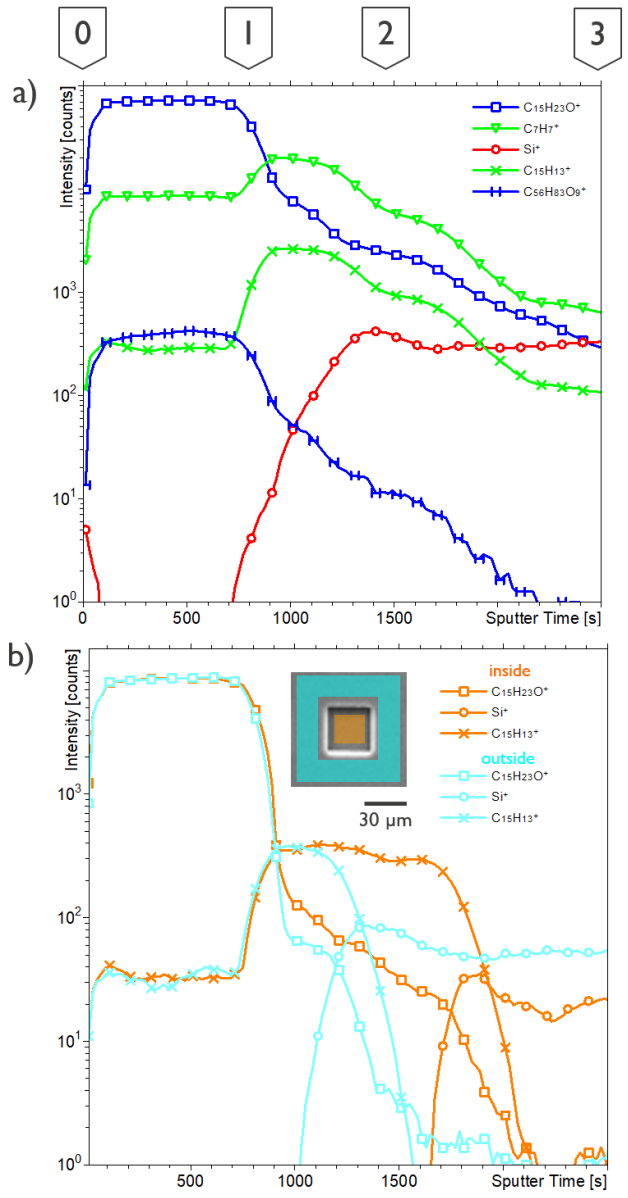


Figure 5. (a) Total area depth profile for 30 µm squares (Irganox 1010 ions in blue, PS ions in green, Si in red). (b) Representative Irganox 1010's fragment ($C_{15}H_{23}O^+$) and PS' fragment ($C_{15}H_{13}^+$) reconstructed from the area inside the squares (in light blue) vs the area outside the squares (in orange).

The SPM analysis was conducted in tapping mode on a 50 × 50 µm² area for the acquisition of images, and along 600 µm for the acquisition of the surface profiles. The surface profiles acquired in X direction (perpendicular to the GCIB orientation) are shown in Figure 6 d). The area scans are used to investigate the surface topography whereas the line scan allowed to obtain information regarding the thickness removed at each sputtering step.

A schematic representation of the topography evolution along the analysis depth is depicted in Figure 6 a) together with the overlays of the ToF-SIMS chemical maps (b) and the SPM images (c, topography, forward direction). Irganox 1010 and PS are represented in blue and in green, respectively, in both drawings (a) and chemical maps (b), while Si is depicted in grey in the drawing and in red in the chemical maps.

At the beginning of the experiment (no sputtering, point 0) the sample surface (and thus ToF-SIMS information) can be simply described by (the signal of) a homogeneous Irganox 1010 layer (Figure 6 a, b) with a thickness difference of 2 µm between the mesa part and the square, based on the SPM image (Figure 6 c).

After reaching the Irganox 1010/PS interface (point 1) all the Irganox 1010 is removed from the mesa and the square, although some counts are still visible at the borders facing the sputter beam. The latter is most likely due to some shadowing which can happen due to the 45° orientation of the Ar (GCIB), together with some redeposition of the organics along the borders. Moreover, Si counts begin to be visible at the square borders, probably because of a thinner layer deposited on the squares' side walls. The topography clearly shows the presence of the organics at the borders and allows to retrieve the information about the Irganox 1010 thickness, being around 2 µm in both regions, as depicted in the sketch (Figure 6 a).

At the PS/Si interface (point 2), the PS is completely removed from the mesa, while it is still present in the square. The Irganox 1010 is still present at the top border but less homogeneous and thinner due to the effect of longer sputtering on the areas previously responsible of the pronounced shadowing effect. This is clearly confirmed by the SPM image, together with the information about the removal of around 500 nm of PS from the two regions.

At the end of the experiment (3), only Si is visible in the structure and some remaining Irganox 1010 on the top wall of the square. The SPM measurements reveal a total thickness of 2 µm for the Irganox 1010 in both regions, and a PS layer thickness of ~500 nm in the mesa and ~1.2 µm in the square.

The spots visible in the SPM images are due to small differences in the organics deposited thickness. In facts, these spots are first Irganox 1010-rich, and then PS-rich, as it can be observed in the ToF-SIMS chemical maps.

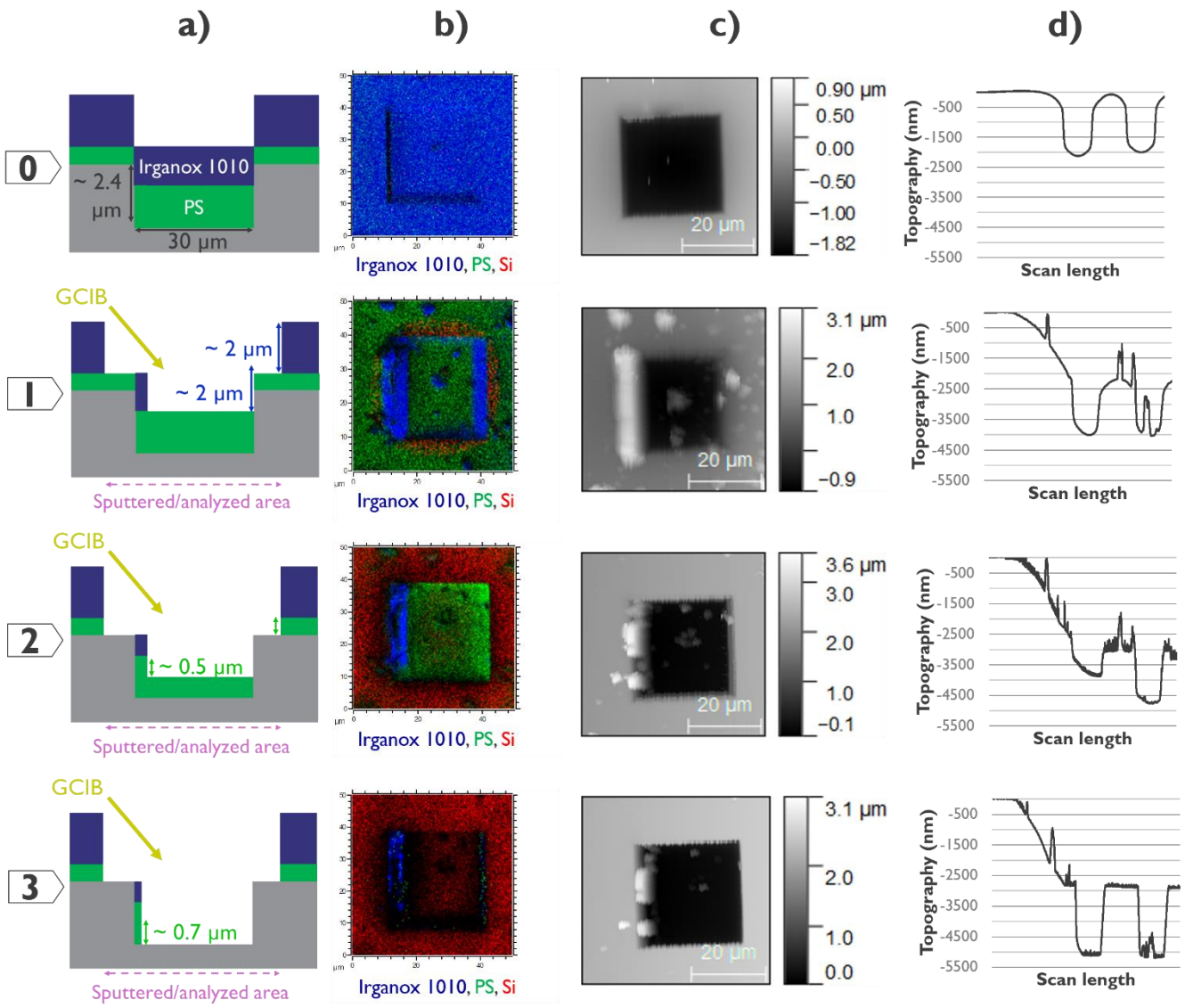


Figure 6. (a) Schematics of topography evolution during sputtering of 30 µm squares sample. (b) Overlay of ToF-SIMS images for Irganox 1010 (blue), PS (green) and Si (red). (c) SPM topographical images. (d) Surface long-range scans in Y direction. Note that both sketch and maps (chemical and topographical) are reported so that the GCIB is always coming from the left-hand side of the images.

Combining the chemical information obtained by ToF-SIMS and the topographical information obtained by SPM, it is possible to generate an accurate 3D view of the 30 µm structure, (Figure 7). Clearly, this is a more truthful representation of the actual 3D structure (see Figure 3) as compared to the cuboid view, which neglects any topographical correction.

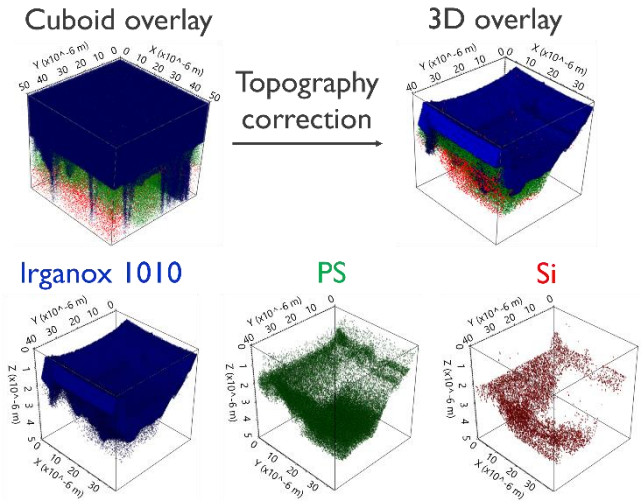


Figure 7. 3D reconstruction for the 30 µm squares (Irganox 1010 ions in blue, PS ions in green, Si in red) without (upper left) and with (upper right) topographical correction based on *in-situ* SPM measurements.

3.2. Smaller scale hybrid system: 5 µm squares array filled with organics.

A similar experiment was conducted on arrays with 5 µm squares in order to assess whether the protocol applied to the larger structures could be transferred to smaller structures with higher aspect ratio. Also in this case, the ToF-SIMS measurement was alternated with the *in-situ* SPM one at several points of the profile: at the beginning (top surface, point 0), at the two interfaces (interface 1, between Irganox 1010 and PS; interface 2, between PS and Si substrate) and at the end of the measurement (in the Si substrate), as indicated by the inset in Figure 8 a).

SPM analysis was performed in the same conditions as for the 30 µm squares. For the ToF-SIMS experiment we maintained the same conditions for the sputter beam. In contrast to the first case study, delayed extraction was not used during the analysis cycles in order to keep the count rate high enough. This however leads to possible mass interferences because of deteriorated mass resolution (nominal for Fast Imaging mode vs $m/\Delta m > 5000$ for Fast Imaging coupled with delayed extraction). For this reason, the Si_2O^+ signal is preferred over the Si^+ to avoid misinterpretation as there is a mass interference at mass 28 with $C_2H_4^+$.

In Figure 8 b), the comparison between the ToF-SIMS chemical maps and SPM images recorded at the four points indicated in (a) is presented.

The same colors as for the 30 µm are used here to indicate the different components: Irganox 1010 (in blue), the PS (in green) and the Si (in red). In the top surface image, the only ions visible are related to the Irganox 1010, as expected.

Even though Irganox 1010 covers the entire sample surface (i.e. mesa and squares), the initial height difference between the mesa part of the array and the squares remains to a certain extent, as shown by the topographical images in Figure 8 c).

As mentioned before, operating the SPM in tapping mode allows to simultaneously collect chemical contrast through the 'phase' image, as reported in Figure 8 d). The SPM phase image shows no contrast on the top surface ("point 0") as only Irganox 1010 is present.

In the Irganox 1010/PS image (Figure 8 b), point 1), the Irganox 1010 signal is only collected from the squares, while the PS is already visible in the mesa part, since at this point all the Irganox 1010 from the mesa was removed. The SPM image (Figure 8 c), point 1) clearly shows the shadowing effect from the 45° orientation of the GCIB, as explained in the previous section. In this case, since the aspect ratio is higher, the effect is even more pronounced, such that the Irganox 1010 inside the squares is only barely sputtered away. The phase image (Figure 8 d), point 1) shows clear contrast between the Irganox 1010 and the PS, matching very well the ToF-SIMS chemical map.

At the PS/Si interface (point 2 in Figure 8), the ToF-SIMS chemical map (Figure 8 b), point 2) still shows Irganox 1010 signal from the squares and PS signal in the mesa part with some Si signal being discernable around the side walls of the structures. This was already observed on the 30 µm squares and is in line with a non-homogeneous distribution of the PS on the surface and bottom of the squares and the side walls.

At the end of the depth profile (point 3 in Figure 8), the PS is completely removed from the mesa part while some organic material still seems to be present inside the squares (Figure 8 b), point 3). This fact is again related to the sputtering of such high aspect ratio structures at 45° (GCIB orientation in this setup). As such, it is possible to successfully perform a depth profile of the mesa regions, with a complete and homogeneous removal of both organic layers and reveal of the Si substrate. In contrast, at the bottom of the squares we are only able to remove part of the Irganox 1010 layer (as shown in Figure 8) as the GCIB sputtering is inhomogeneous over the area (shadowing effect) due to its 45° orientation.

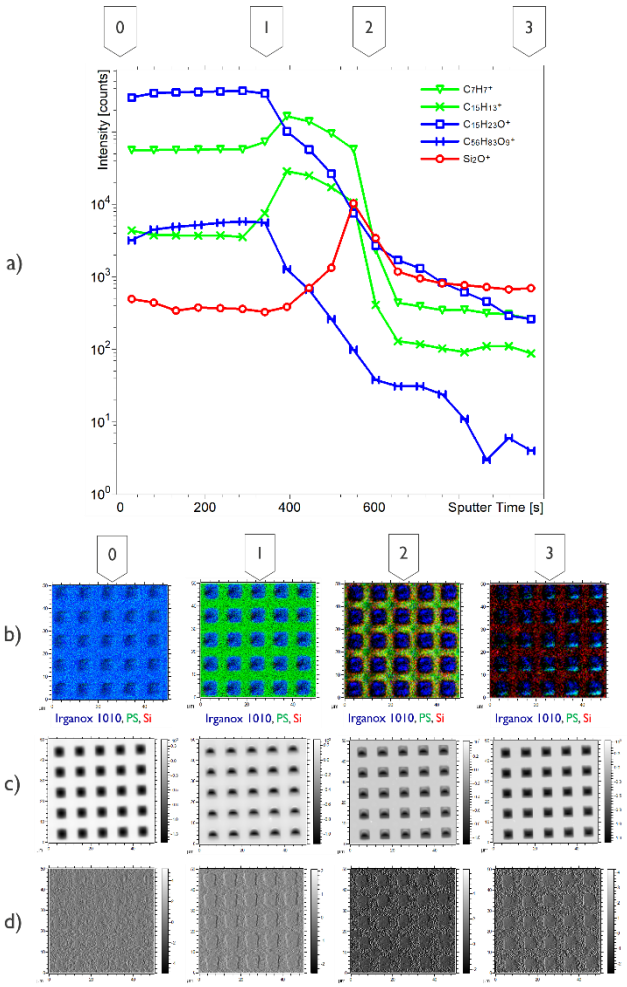


Figure 8. (a) ToF-SIMS depth profile 5 µm squares, (b) ToF-SIMS chemical maps overlay and (c) SPM topography and (d) phase images at the points indicated in the depth profile (a). The orientation of the chemical maps and the SPM images refers to the GCIB coming from the top at 45°.

As an alternative method to the direct crater depth measurement at each point of the depth profile we derived the layers' thickness based on the sputter rate calculated from sputtering PS and Irganox 1010 reference layers. With this method, we estimate that Irganox 1010 and PS were deposited in the mesa part as ~1 µm- and 500 nm-thick layers, respectively, (Figure 9 b, point 0, no sputtering occurred). As previously mentioned, we are not able to completely remove the organics filling within the 5 µm squares, thus this method cannot be applied to the regions inside the squares. At the end of the measurement (Figure 9, point 3), we measured the difference in height between the mesa part (where only Si is now present) and the square. Due to the aforementioned shadowing effect, this is done at two points inside the squares: the upper part, where Irganox 1010 is still detected, and the bottom part, where PS is visible (i.e. Irganox is removed), which yield both ~1.2 µm and ~1.6 µm, respectively. Knowing the total depth of the square without the organic layers (~2.4 µm), we conclude that ~1.2 µm of organic material is still present inside the upper part of the squares (region that suffers more form the shadowing effect) and that ~800 nm of PS are still present inside the squares at the bottom region (where the shadowing effect is less pronounced). Our findings were confirmed by Scanning Electron Microscopy (SEM) on a cross section, as shown in Figure 9 c), with a total thickness of organics of ~1.5 µm and ~2.2 µm, on the mesa and inside the squares, respectively, at point 0, and the remaining ~1.2 µm and ~800 nm of organics at the end of the experiment, in the two regions of the squares.

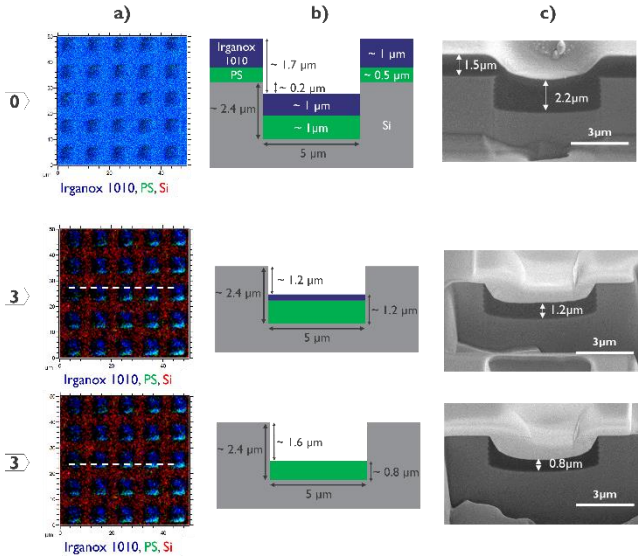


Figure 9. ToF-SIMS chemical maps overlay (a), schematic representation of the sample (b) and SEM on cross-section (c) before (point 0) and after sputtering (point 3), at two different points inside the squares (indicated by the dotted lines on the ToF-SIMS chemical maps). The values displayed in (b) refer to the layers' thickness derived by the sputter rate method presented in the text.

Even though the sputter rate method can be successfully applied to a flat region such as the mesa part, it fails when sputtering is incomplete/inhomogeneous e.g. due to the high aspect ratio of the measured features in combination with the configuration of the ToF-SIMS instrument, i.e. 45° impact angle of the ion columns. It was demonstrated that coupling the ToF-SIMS and the *in-situ* SPM, clear information about the remaining organics inside the squares can be obtained, defining this method as a valuable one to easily determine thickness and morphological evolution of such a hybrid system.

The 3D reconstruction for the sample filled with PS and Irganox 1010 is reported in Figure 10. Here the three layers are clearly displayed at the right depth, as it was derived from the SPM measurements. Irganox 1010 appears at the top as a homogeneous layer on the mesa part while it does not completely fill the squares inside the squares. Its thickness in the mesa part corresponds to the 1 µm we found from the sputter rate calculation. The Irganox 1010 layer's thickness inside the squares and its 3D distribution reflect the shadowing effect from the 45° orientation. The PS signal appears below the Irganox 1010 coating as a homogeneous layer on the mesa part, while likewise reflecting the shadowing effect inside the squares. The Si substrate signal is visible only on the mesa part, where both organic layers have been removed, while it is not detected inside the squares. Thanks to the combination of

the two techniques, it was therefore possible to create an accurate 3D image by combining the ion intensities and the topographical evolution as a function of depth.

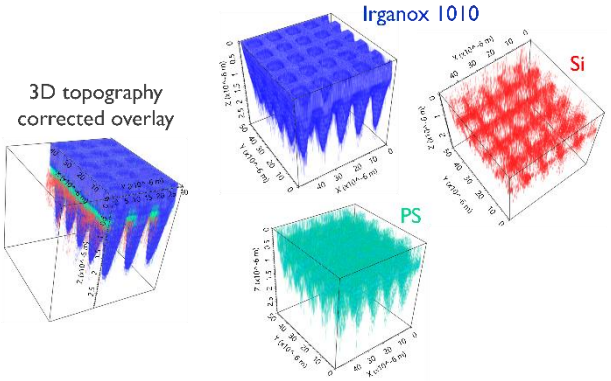


Figure 10. 3D reconstruction for the case of 5 µm structures filled with PS and Irganox 1010.

4. Conclusion

In this study, *in-situ* SPM was used in combination with ToF-SIMS to analyze two silicon micro-patterned systems (5 µm and 30 µm squares) and coated with two different organic films (Irganox 1010 and PS). The *in-situ* SPM was used to obtain topographical information during the sputtering experiment leading to locally determining the time dependent erosion velocity. Based on that information and the resulting topography corrections, a more accurate 3D-representation of the sample could be obtained. For instance, based on that result, it could be established that the deposition of the PS on the mesa part is much thinner as compared to the deposition inside squares. Additionally, it was demonstrated using the SPM phase images that the organic layers were deposited as much thinner layers on the sidewalls of the squares. The detailed topography evolution in combination with the chemical identification from the ToF-SIMS signals, indicated shadowing effects in the sputter erosion of the squares, especially in the 5 µm squares, which can be linked to the 45° angle of the GCIB in our tool configuration.

Overall, the combination of the ToF-SIMS with *in-situ* SPM, represents an important asset to obtain the real 3D information on complex systems with locally varying erosion rates and initial topography.

ASSOCIATED CONTENT

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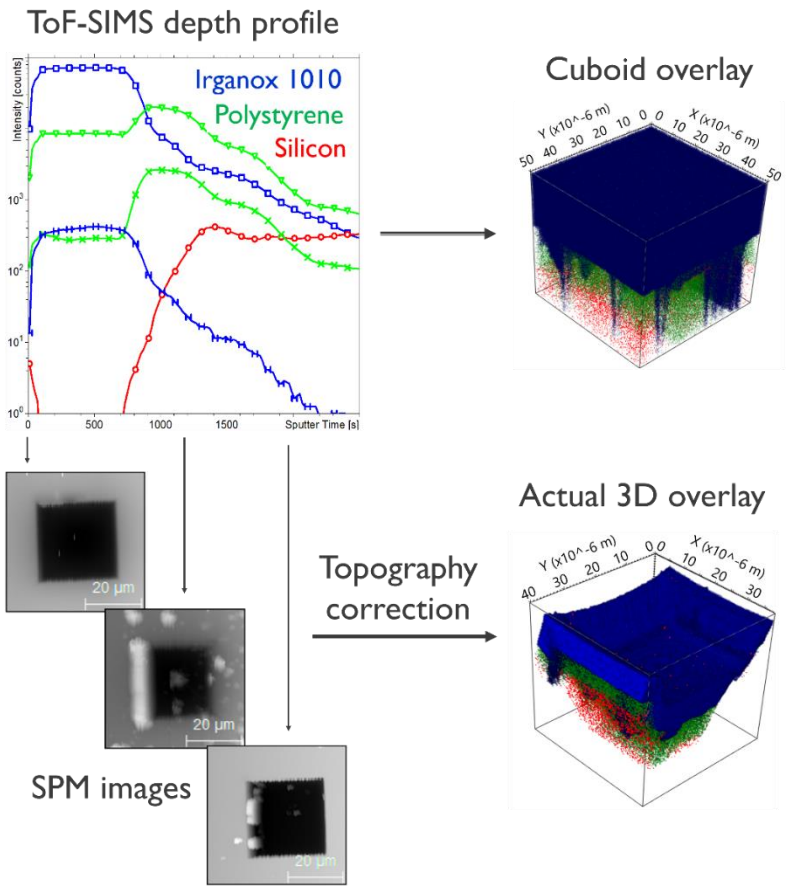
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The standard data analysis protocol, merely considering the ToF-SIMS depth profile, leads to a distorted 3D representation (cuboid overlay), since the differences in sputter rates among the components and the (initial) topography are ignored. However, the coupling with in-situ SPM measurements simultaneously provides the spatially resolved chemical information from the ToF-SIMS, and the time dependent topographical information from the SPM, leading to a far more accurate 3D analysis (actual 3D overlay).