Correlative Microscopy in Life and Materials Science

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Correlative microscopy using SIMS for high-sensitivity elemental mapping

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Important progress and breakthrough developments in materials science and life sciences are more and more often hampered by the absence of adequate analysis techniques. In particular, an analytical tool allowing mapping of samples with both excellent resolution and high-sensitivity chemical information is cruelly missing. Electron Microscopy, Helium Ion Microscopy and Scanning Probe Microscopy are commonly used for high-resolution imaging. However, these techniques have all the same important drawback: they provide no or only very limited chemical information. In electron microscopy, chemical information can be obtained by using techniques like Electron Energy Loss Spectroscopy (EELS) or Energy Dispersive X-ray Spectroscopy (EDS), but the sensitivity is limited. Moreover, these techniques do not permit to distinguish between isotopes, which is a major handicap today due to the increasing use of isotopic labelling, and have limitations in the low mass range. By contrast, Secondary Ion Mass Spectrometry (SIMS) is an extremely powerful technique for analyzing surfaces owing in particular to its excellent sensitivity, high dynamic range, very high mass resolution and ability to differentiate between isotopes.

In order to get chemical information with a highest sensitivity and highest lateral resolution, we have investigated the feasibility of combining SIMS with Transmission Electron Microscopy, Scanning Probe Microscopy and Helium Ion Microscopy and developed three prototype instruments corresponding to the mentioned three combinations of techniques:

- TEM & SIMS: FEI Tecnai F20 equipped with a Ga^+ FIB column and dedicated SIMS extraction optics, mass spectrometer and detectors (figure 1)
- HIM & SIMS: Zeiss ORION Helium Ion Microscope with dedicated SIMS extraction optics, mass spectrometer and detectors [1,2]
- SPM & SIMS: Cameca NanoSIMS 50 with integrated AFM/SPM [3-5]

In order to reach the targeted excellent detection limits with SIMS while using a finely focused analytical probe, high secondary ion yields are crucial. As the intrinsic yields obtained with non-reactive primary ions (as is the case on the TEM & SIMS where a Ga^+ beam is used and on the HIM & SIMS where helium and neon beams are used) are relatively low, we use reactive gas flooding during analysis, namely oxygen flooding for positive secondary ions and cesium flooding for negative secondary ions [1]. With such reactive gas flooding, the yields can be enhanced by up to four orders of magnitude. Based on these yields, we calculated detection limits for various samples under typical analysis conditions for the three combined instruments. An example of the detection limits reached on the HIM & SIMS is shown in figure 2.

By combining the known information channels of TEM, SPM and HIM on the one hand and SIMS on the other hand in one unique and novel analytical and structural tool, new multi-channel nanoanalytical experiments become possible, which open the pathway to qualitatively new types of information about the investigated samples. Different possibilities arise from these in-situ instrument combinations. One can for instance first image in 2D or 3D the sample with TEM/HIM/SPM, then analyze the same zone with SIMS, and finally very precisely overlap the 2 data sets (see example in figure 3 for SPM & SIMS). Another approach consists of first imaging the sample by SIMS to localize hot spots (for instance high concentration of a given element or a given isotope one is interested in), and then to zoom onto this hot spot by TEM/HIM/SPM to identify the feature corresponding to this hot spot. It is important to note that ex-situ multi-technique combinations do not allow the same performances as such an approach is hampered by several limitations, including precise re-localization of analyzed zones after transferring the sample between the standalone instruments and artifacts due to surface oxidation and surface reorganization during sample transfer between the instruments.

The results are very encouraging and the prospects of performing SIMS in combination with TEM, HIM and SPM are very interesting. The combination of high-resolution microscopy and high-sensitivity chemical mapping on a single instrument leads to a new level of correlative microscopy.

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2. D. Dowsett et al., J. Vac. Sci. Technol. B 30 (2012) 06F602
3. T. Wirtz et al., Surf Interface Anal. 45 (1) (2013) 513-516
4. T. Wirtz et al., Rev. Sci. Instrum. 83 (2012) 063702
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Figure 1: TEM & SIMS - Prototype of a combined TEM-SIMS instrument: modified Tecnai F20 equipped with a Ga^+ gun and dedicated SIMS column

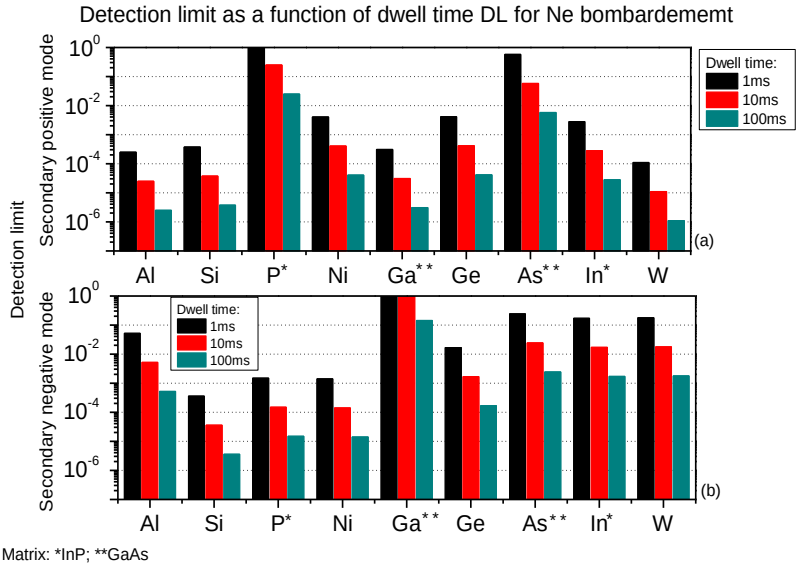

Figure 2: HIM & SIMS - Detection limit for Ne^+ bombardment in secondary positive mode with O_2 flooding (a) and in secondary negative mode with Cs flooding (b). Typical dwell times of 1ms, 10ms and 100ms and a primary ion current of 10 pA are considered.

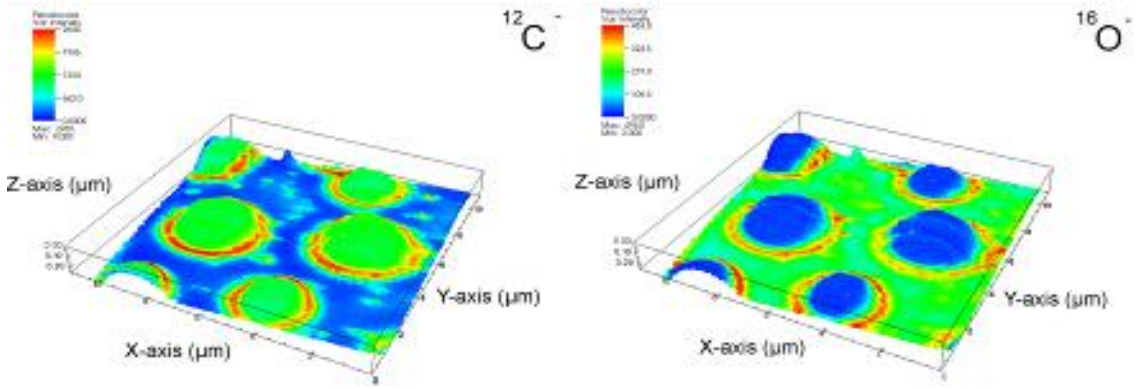

Figure 3: SPM & SIMS - Combined SIMS-SPM 3D reconstruction of a PS/PMMA blend (Field of view: 22.3x17.3 μm^2): (a) $^{12}C^-$ secondary ion signal. (b) $^{16}O^-$ signal, which is characteristic of PMMA [4].