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Application of FIB-TOF-SIMS technique for elemental characterization of new thin film energy devices

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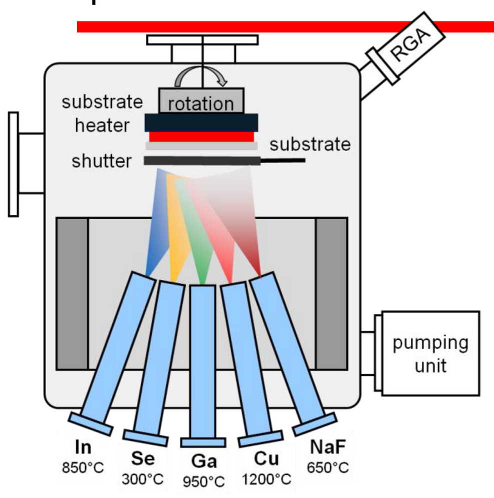
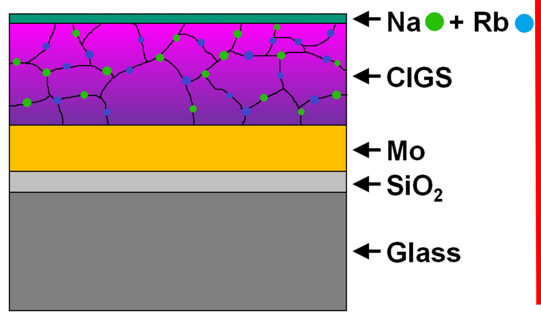
ABSTRACT

In this work we present an application of a high resolution Focused Ion Beam Time-of-Flight Secondary Ion Mass Spectrometry (FIB-TOF-SIMS) technique in high vacuum environment for analysing new energy devices based on multilayer structures. In particular, micron-scale Cu(In,Ga)Se_2 (CIGS) thin films for solar cell applications and thin films involved in Li-ion solid state batteries were investigated using a depth profiling mode to represent their elemental compositions in a three-dimensional space. This has allowed the dedicated layer distribution as well as inter-layer diffusion of elements to be accessed. Moreover, in some cases lateral chemical imaging has revealed material segregation at the grain boundaries. This has enabled the grain size to be measured with the precision down to hundreds of nanometers. Additionally, in order to verify the effect of sample topology on the acquired FIB-TOF-SIMS signals, the sample surface was imagined during the FIB sputtering with FIB SE (Secondary Electrons). Complementary, the sample surface was analysed using an in-situ SEM (Scanning Electron Microscopy) before and after the FIB-TOF-SIMS measurements. The evolution of the surface morphology and roughness during FIB-TOF-SIMS measurements was observed. In summary, the conducted studies have delivered important information on the quality of the material fabrication process that ultimately determines the functionality of the devices.

Cu(In,Ga)Se_2 (CIGS) thin film



- Sample fabrication: multi-stage co-evaporation of Cu, In and Ga in a Se atmosphere
- Post-deposition treatments (PSTs): sequential evaporation of NaF and RbF in Se atmosphere after CIGS growth
- Goal: an increase of net free carrier (hole) concentration and reducing the recombination at CdS/CIGS junction
- The bandgap is determined by the In/Ga concentration varying from 1.0 eV for pure $CuInSe_2$ and 1.7 eV for pure $CuGaSe_2$. A Ga/In grading means a bandgap grading across the thickness
- Average Cu/(Ga+In) ratio: 0.86 (under-stoichiometric Cu concentration)
- Bandgap (In/Ga) grading through the thickness: min. bandgap (absorption edge) ≈ 1.15 eV



Al-doped $Li_7La_3Zr_2O_{12}$ (Al:LLZO) as solid-state electrolyte

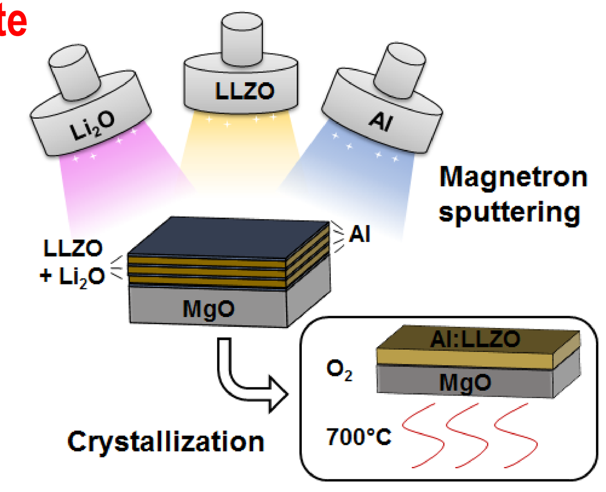
- Sample fabrication: magnetron sputtering
- Ionic conductivity depends on crystalline phase

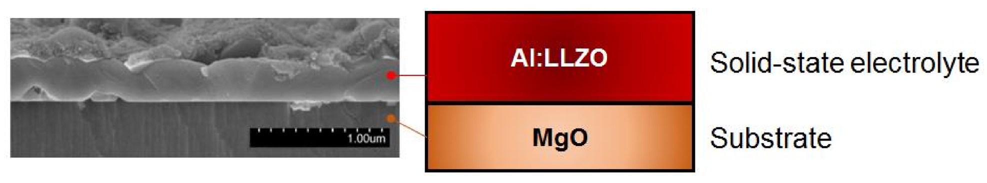
Tetragonal ~10^{-6} S/cm ⟷ Cubic ~10^{-4} S/cm — Not stable at RT

- Doping stabilizes cubic phase at RT

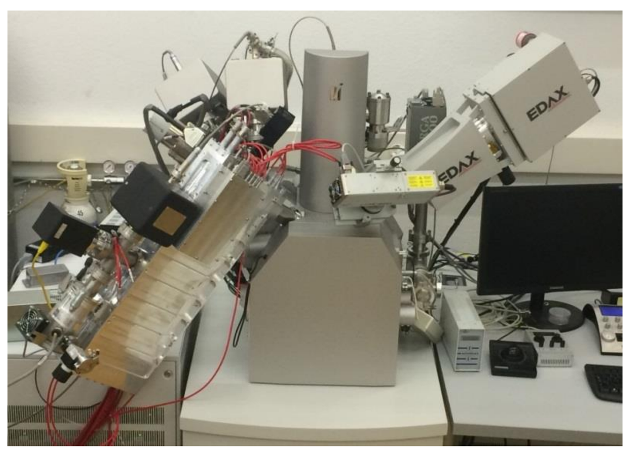
$Li_{7(-x)}La_{3(-y)}Zr_{2(-z)}O_{12}$ — Al^{3+} | Ga^{3+}_x; Nd^{3+}_y | Sr^{2+}_y; Ta^{5+}_z

- Properties:
  - → High Li-ion conductivity
  - → Wide electrochemical stability window
  - → High thermal and mechanical stability
  - → Properties tuneable with doping



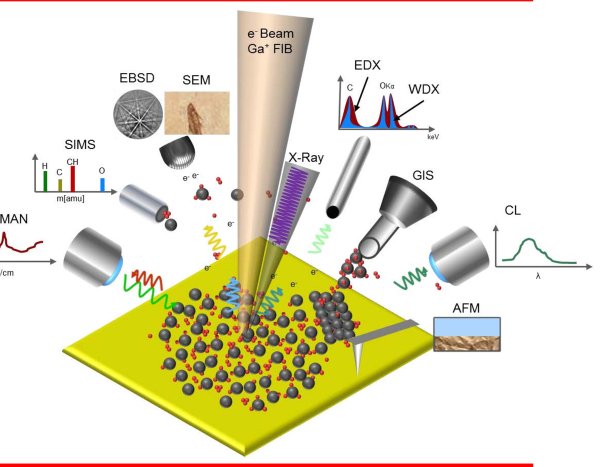


FIB-TOF-SIMS

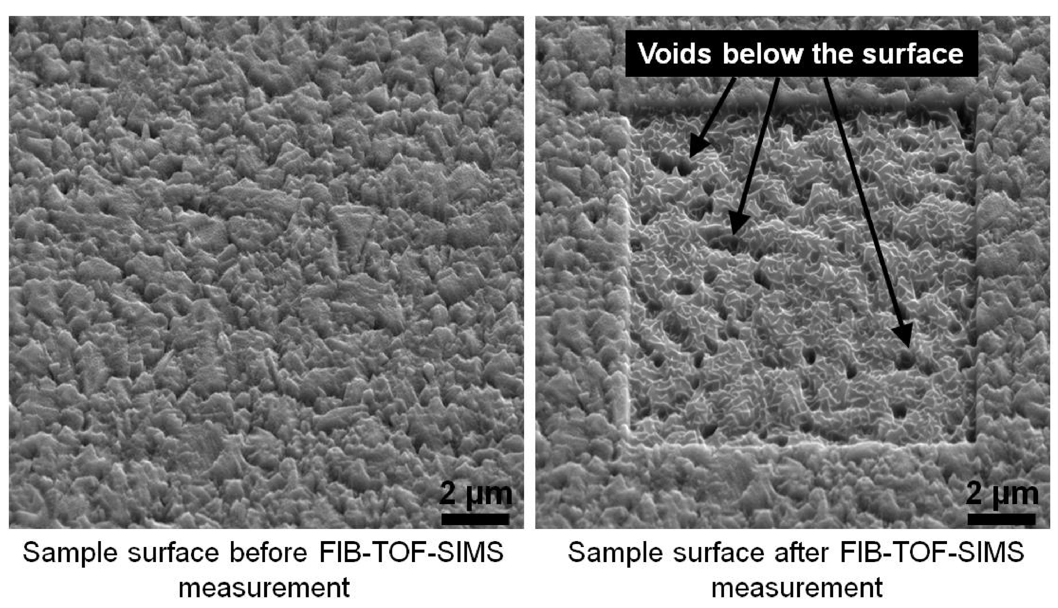


- 3D elemental characterization
- Detection of all ionized atoms and molecules
- Isotope recognition
- Element mass-to-charge ratio is proportional to the ion time-of-flight
- Quantification is not possible due to the matrix effect
- Ion yield depends on the chemical surface state
- Lateral resolution of ≈50 nm is determined by the beam size and the collision cascade
- Depth resolution depends on the beam energy and can be as low as 10 nm

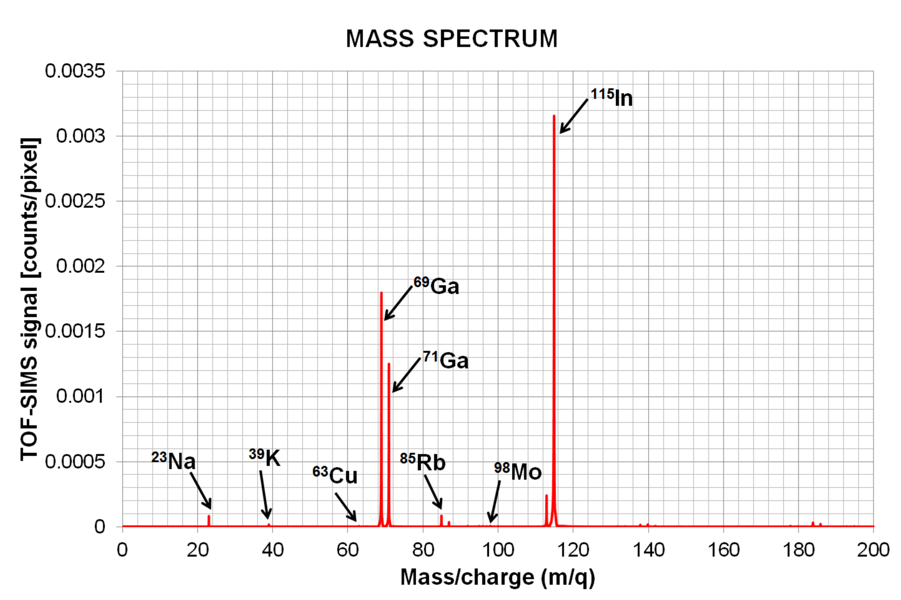
Experimental conditions:
- I_{FIB} = 180 pA
- E_{FIB} = 30 keV
- ROI = 10 µm x 10 µm
- t_{dwell} = 16.2 µs
- Resolution 512 x 512

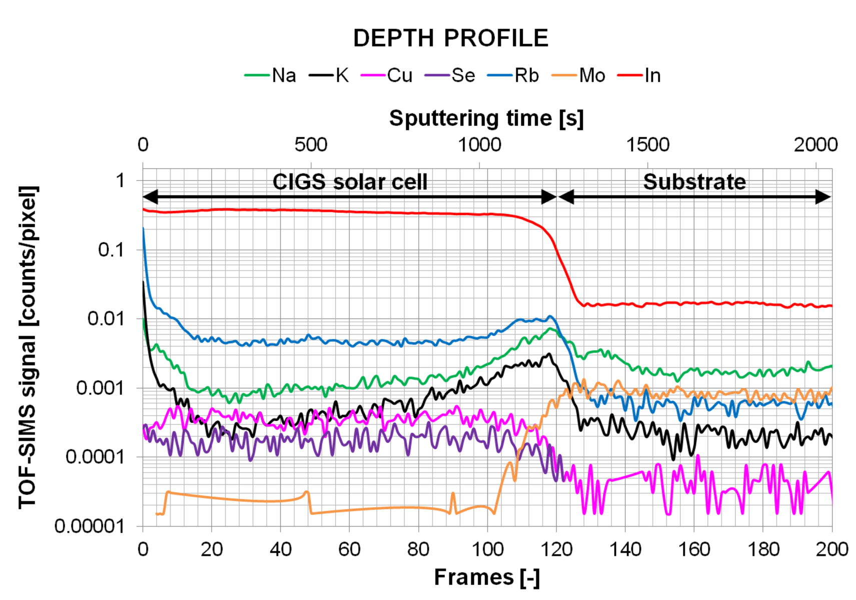


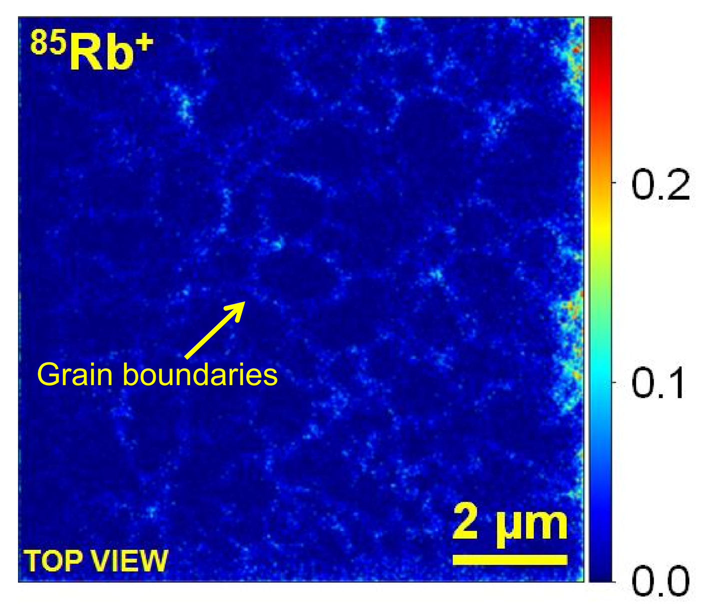
CIGS thin film



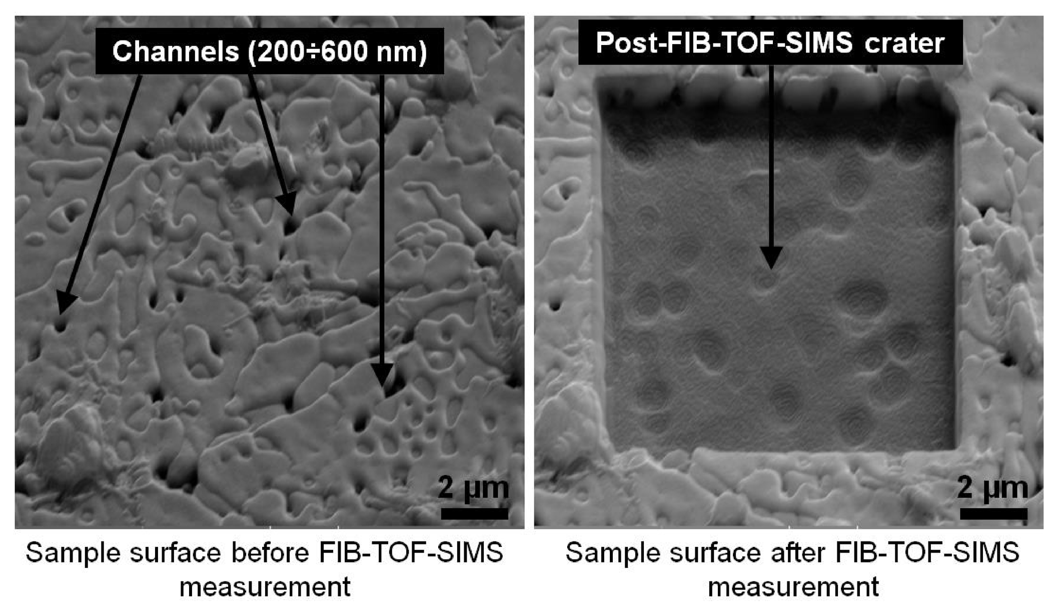
Sample surface before FIB-TOF-SIMS measurement — Sample surface after FIB-TOF-SIMS measurement



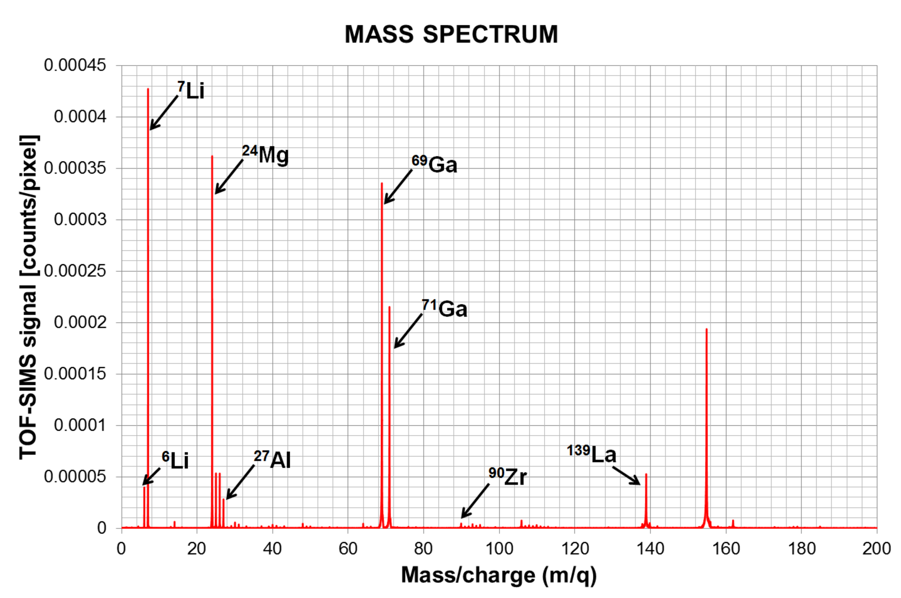


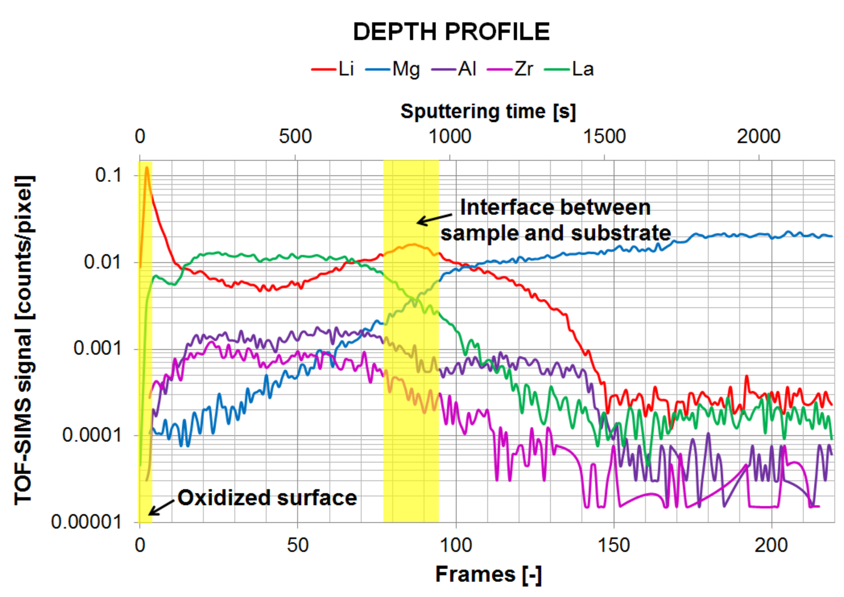


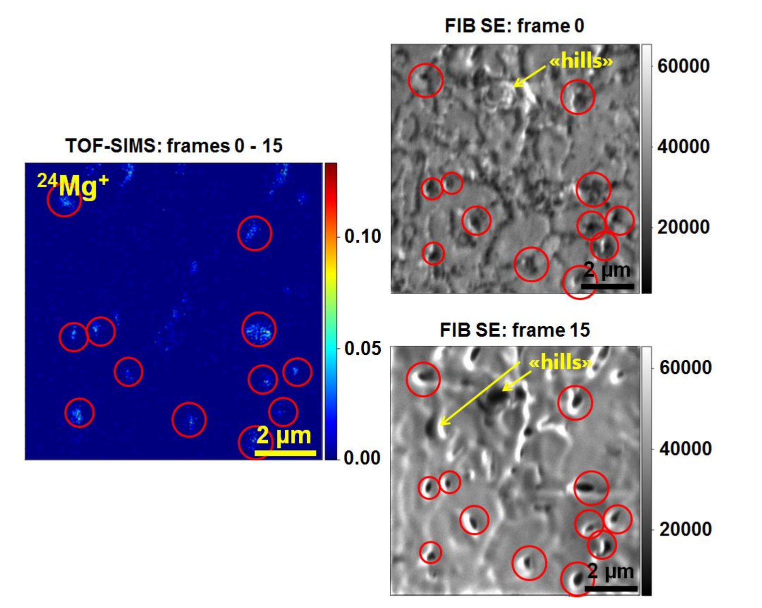
Al:LLZO as solid-state electrolyte

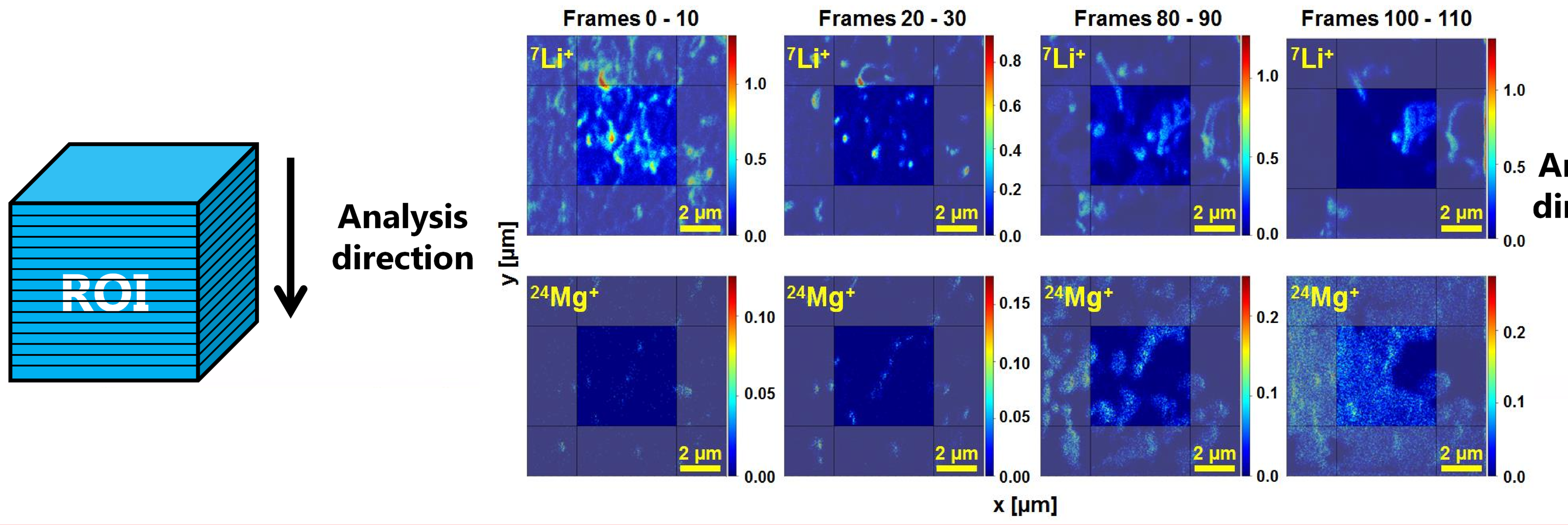


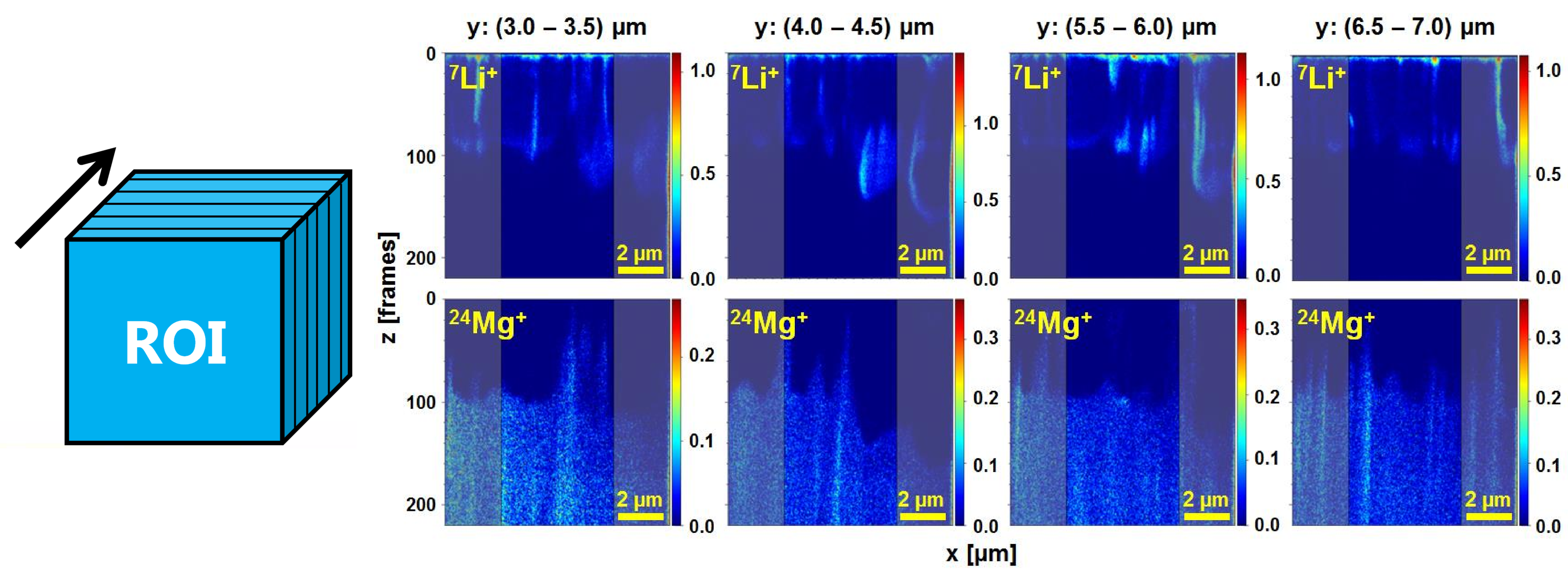
Sample surface before FIB-TOF-SIMS measurement — Sample surface after FIB-TOF-SIMS measurement











CONCLUSIONS

- The FIB-TOF-SIMS technique used in high vacuum conditions has allowed detecting all major elements of CIGS solar cells and thin films involved in Li-ion solid state batteries to be detected.
- The interfaces between active parts of thin film energy devices and substrates were well-distinguished during the TOF-SIMS depth profile measurements. Increased TOF-SIMS signal acquired within first 3-4 frames probably results from the surface oxidation as oxygen increases positive ion yields.
- $^{85}Rb^+$ has agglomerated on the grain boundaries of CIGS solar cell giving there an increased TOF-SIMS signal. This has allowed the size of the grains to be assessed. The measured values were in the range of (0.3 – 2.0) µm.
- The distribution of Li in the solid state electrolyte of the Li battery was inhomogeneous. Li grains were observed in the regions close to the sample surface whilst deeper the structure has formed more uniformly. The Mg signal measured with TOF-SIMS indicates that the MgO substrate roughness was significant. Moreover, Mg channels connecting the substrate with the sample surface were observed.
- The studies have demonstrated that the FIB-TOF-SIMS method used in HV has a great potential for 3D elemental characterization of thin film energy devices. This can deliver important information for optimizing the fabrication process and therefore lead to improved performance of the materials.