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Time-of-flight secondary ion mass spectrometry in the helium ion microscope

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Abstract

A helium ion microscope, known for high resolution imaging and modification with helium or neon ions, has been equipped with a time-of-flight spectrometer for compositional analysis. Here we report on its design, implementation and show first results of this powerful add-on. Our design considerations were based on the results of detailed ion collision cascade simulations that focus on the physically achievable resolution for various detection limits. Different secondary ion extraction geometries and spectrometer types are considered and compared with respect to the demands and limitations of the microscope. As a result the development and evaluation of a secondary ion extraction optics and time-of-flight spectrometer that allows the parallel measurement of all secondary ion masses is reported. First experimental results demonstrate an excellent mass resolution as well as high-resolution secondary ion imaging capabilities with sub-8 nm lateral resolution. The combination of high resolution secondary electron images and mass-separated sputtered ion distributions have a high potential to answer open questions in microbiology, cell biology, earth sciences and materials research.

Keywords: helium ion microscope, time-of-flight, elemental analysis, secondary ion mass spectrometry, high resolution imaging

1. Introduction

Secondary ion mass spectrometry (SIMS) instruments are commonly optimized for mass resolution, high yields of large molecules or fast sample throughput while high lateral resolution was only of secondary importance for most designs using a magnetic sector [1–4] as well as for time-of-flight (TOF) instruments [5–7]. To achieve highest positive ion yields typically cesium ions are used as primary particles, while a maximum number of negatively charged secondary ions is achieved by utilizing oxygen ions. Commercially available SIMS instruments can reach spot sizes below 50 nm [8] using cesium, gold or bismuth ions [9–11]. Bismuth and gallium ion beams from liquid metal ion sources can be fo-

cusced down to perform SIMS with 20 nm resolution [11–16].

In terms of spatial resolution the existing approaches are limited not by the physical extent of the collision cascade but by the relatively large beam diameter. To achieve the highest possible spatial resolution in SIMS the beam diameter has to be sufficiently smaller than the area that secondary ions are sputtered from. The latter is related to the size of the collision cascade and depends on the primary ion species and energy as well as on the target material.

A helium ion microscope (HIM), equipped with a gas field ion source supplying 30 keV helium or neon ions with an extremely high brightness of up to $10^9 \text{ A cm}^{-2} \text{ sr}^{-1}$, is capable of surface-sensitive imaging with a lateral resolution of 0.5 nm [17–20]. Ion beam milling can be done with 1.8 nm resolution using neon and with 1.3 nm resolution using helium

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ions [21]. It currently provides the smallest beam diameter for both imaging and sputtering and as such would be the ideal candidate for high lateral resolution SIMS imaging. With respect to the implementation of SIMS in the HIM, the secondary ion yield for typical beam parameters [22, 23], possible ion extraction geometries [24] and the expected intermixing of layered structures [25] have been studied in previous work. Recently, TOF spectrometry has been implemented in the HIM to measure the energy of backscattered particles [26–28]. In these studies also the first proof of principle experiments on mass spectrometry of sputtered particles have been demonstrated.

An alternative and more sophisticated SIMS setup inside a HIM including an ion extraction optics and a modified Mattauc-Herzog magnetic sector was recently presented by Wirtz et al. [29–31]. A mass resolution $m/\Delta m$ of up to 300 and a lateral resolution of (10.0 ± 3.6) nm for ${}^7\text{Li}$ (75% to 25%) were demonstrated. However, the current implementation of this device is limited by the finite number of detectors and therefore masses that can be detected simultaneously [31]. The setup presented in this work demonstrates lateral highly resolved material analysis with TOF-SIMS in a HIM, that can detect all masses in parallel. In the literature different definitions of the lateral resolution have been used. Since Wirtz et al. demonstrated the highest lateral resolution so far, we used the same criteria for better comparability (75% to 25%). A comparison of different criteria and peak shapes as well as conversion factors has been published by Saeh [32].

2. Instrument Design

2.1. Theoretical considerations

In commercial SIMS machines the primary ion beam spot size typically exceeds the dimensions of the ions collision cascade. Contrary, in the HIM multiple scattered neon or helium projectiles and recoils will create sputtered particles within an area larger than the sub-nm beam spot. We performed binary collision approximation simulations with TRI3DST [33, 34] and evaluated the spatial origin of sputtered particles. The functions of lateral resolution are shown for example in Fig. 1 for 30 keV helium and neon

ions impinging on amorphous silicon. The normal-

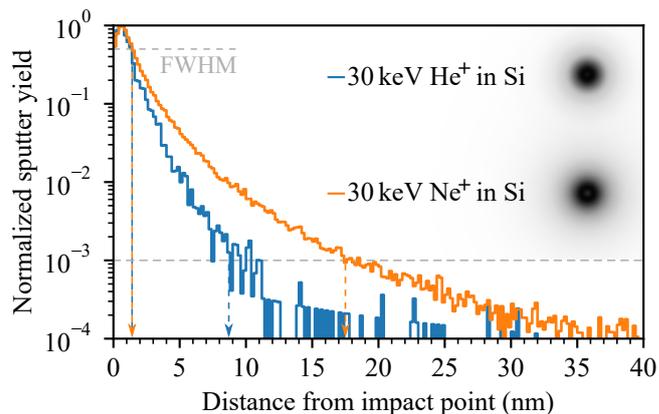


Figure 1: Simulated intensity profiles of sputtered particles in dependence on the distance from the point of impact for 30 keV helium and neon ions in silicon. Emission radii for 50% and 0.1% of the signal intensity are indicated by dashed arrows. The corresponding two-dimensional intensity profiles are shown beside in true dimensions according to the x-axis.

ized sputter yield per area is plotted versus the distance between the primary ion impact site and the emission site. The yield drops to 50% in a radius of 1.2 nm for helium and 1.4 nm for neon. Hence, a diameter of 2.4 nm for helium and 2.9 nm for neon approximate the fundamental achievable lateral resolution for imaging of flat surfaces with SIMS. Other target materials of course show slightly different values. The total ion range decreases for lower primary ion energies and for projectiles with higher atomic number. However, the cross section for nuclear collisions and the probability for multiple scattered particles increases at the same time. Therefore, the size and especially the shape of the intensity profile of sputtered particles depend on multiple parameters. In the surrounding area of a pure occurrence of a material, the sensitivity for low concentration is degraded because of the long tails of the lateral resolution function. A small but not negligible fraction of the primary ion beam can cause sputtering of surface material in a distance of up to several 10 nm. For example the sputtering yield drops to 0.1% in a distance of 8.7 nm from the primary ion impact for helium and 17.4 nm for neon.

An alternative resolution criteria can be given by the diameter that contains 50% of all sputtered particles and has been simulated by Wirtz *et al.* [35] to be 3 nm for 30 keV He and 9 nm for 30 keV Ne. Ac-

108 cording to the TRI3DST [33, 34] simulations used
109 in this work 50 % of all sputtered particles originate
110 from a diameter of 3.6 nm for 30 keV He and 5.9 nm
111 for 30 keV Ne in silicon, respectively. The values
112 are in good agreement for helium but slightly differ
113 for neon projectiles. It has been shown that binary
114 collision approximation simulations deliver similar
115 results as molecular dynamic simulations [36] and
116 experimental data [37]. However, for the prediction
117 of more accurate secondary ion yields especially for
118 non-flat surfaces, three dimensional nanometer sized
119 objects [38] or edge profiles, one has to consider the
120 individual sample geometry, the bulk versus the sur-
121 face composition, the crystalline structure, as well as
122 ion induced heating effects in more advanced simu-
123 lations. As SIMS can only deal with secondary ions
124 one has to include the charge exchange processes
125 at the surface in addition to the above listed points.
126 However, the charge exchange process of sputtered
127 particles at the surface is difficult to predict.

128 For the detection of trace elements in the sam-
129 ple, the achievable lateral resolution is further lim-
130 ited by the finite number of atoms in the interaction
131 volume and the related small number of sputtered
132 ions [22]. Given the small likelihood for a sputtered
133 sample atom to be charged ($\sim 10^{-4}$) one has to re-
134 move approximately 250 nm^3 of material to obtain a
135 single secondary ion on average. Furthermore, the
136 depth resolution in the interaction volume will suffer
137 from ion beam damage and mixing [39–41]. Conse-
138 quently, to maintain low detection limits with shrink-
139 ing object dimensions, maximization of the extrac-
140 tion and detection efficiencies must be major design
141 considerations. The use of oxygen or cesium pri-
142 mary particles to increase the positive or negative ion
143 yields is unfortunately not an option as the micro-
144 scope has so far only been designed by the manufac-
145 turer for the use of helium and neon gas. However, it
146 has been shown that a gas field ion source can also be
147 operated with other gases like hydrogen [42, 43], ni-
148 trogen [43, 44], oxygen [43] or xenon [45]. These ion
149 species could offer many advantages for SIMS and
150 their use will be subject of future investigations. The
151 secondary ion yield can also be enhanced by oxygen
152 gas flooding or cesium coating while using the highly
153 focused Ne or He beam for sputtering [22, 23, 46].

154 2.2. Selection of mass spectrometer

155 A major design goal in the present implementa-
156 tion of SIMS in the HIM was the conservation of
157 the outstanding imaging capabilities as well as the
158 modification performance of the instrument. In or-
159 der to get sufficient signal from the limited amount
160 of sputtered particles the spectrometers extraction,
161 transmission and detection efficiency should be as
162 high as possible. Molecular dynamics simulations
163 and experiments have shown that light atomic pro-
164 jectiles with several keV energy will cause a high
165 molecular fragmentation and mainly produce atomic
166 or short-chain secondary particles [9, 10, 47, 48]. As
167 a consequence the desired mass range doesn't have
168 to exceed 250 u, that would be necessary only for the
169 identification of molecular fragments but not for the
170 detection of single ions or very small molecular frag-
171 ments.

172 For the purpose of mass separation ion traps could
173 be utilized, but they can measure only one mass at a
174 time, they often have a high duty cycle and require
175 a precise ion injection. A magnetic sector mass an-
176 alyzer has less demanding injection conditions and
177 would allow a continuous operation. However, it
178 has to be mounted at the outside of the measurement
179 chamber or the magnetic field has to be shielded from
180 the primary ion beam and the sample region. The
181 spatially mass-separated secondary ions have to be
182 successively detected with either multiple detectors
183 or with a laterally resolving detector. Single ion de-
184 tectors like micro-channel plates are currently not
185 available to cover larger areas and therefore are lim-
186 ited to a certain mass range [31].

187 Time-of-flight has the major advantage that the
188 full kinetic energy or mass range can be measured in
189 parallel and no particles are lost as in a serial mea-
190 surement procedure. Different approaches have been
191 developed in the past to measure the time interval
192 between start and end of the flight path. The time
193 measurement is most commonly stopped by the im-
194 pact of the particle in a detector at the end of the
195 flight path. For the start signal various solutions are
196 available. The time measurement for instance can
197 be triggered by secondary electrons created during
198 the primary ion impact on the sample surface [49].
199 To assign the detected particle to the primary ion
200 that created it, the beam current has to be reduced

201 to less than one primary ion during the maximum
202 flight-time interval. In another approach the mea-
203 surement can be started by secondary electrons that
204 are emitted when secondary particles are transmit-
205 ted through a thin carbon foil [50]. That allows in
206 comparison to the previous approach to increase the
207 primary current until one secondary ion is extracted
208 per maximum flight-time interval. Unfortunately, the
209 efficiency and energy resolution of this type of spec-
210 trometer are rather low for keV particles making this
211 approach not suitable to be applied in the HIM [51].

212 Alternatively, the time measurement can be trig-
213 gered by pulsing the primary or extracted ions [9].
214 In comparison to the latter approach the beam cur-
215 rent does not have to be reduced and an ion pulse can
216 contain a large number of particles. The pulsed ex-
217 traction of secondary ions was not considered for the
218 discussed application due to less sensitivity since the
219 primary ion beam would also cause sample damage
220 when particles are extracted.

221 Consequently, the pulsing of the primary ion beam
222 as the most gentle approach was recently implemented
223 in the HIM [26, 28] to enable backscattering spec-
224 trometry and SIMS as well. Initially, all primary ions
225 can be deflected into a Faraday cup using the existing
226 blanking plates in the HIM. That prevents the ions
227 from leaving the primary column, hitting the sample
228 surface and thus the creation of secondary particles.
229 Lowering of the blanking voltages to ground poten-
230 tial for a short time window allows primary ions to
231 pass the beam blanker until the blanking voltages are
232 applied again. The time difference between trigger-
233 ing the opening of the beam blanker and the mo-
234 ment when primary ions hit the sample surface is al-
235 most constant because of the sharp primary energy
236 [18] and constant propagation times of signals in ca-
237 bles and electronics. Photons that can be created by
238 the primary ion impact can be used to calculate this
239 time difference with the accuracy of the distance be-
240 tween sample and stop detector due to known speed
241 of light [26]. If no photons are available, the time
242 difference must be considered in the time to mass
243 calibration. The spectrometer then just requires a
244 flight tube, a detector at the end and electronics to
245 determine the time difference. For mass spectrome-
246 try the secondary ions have to be accelerated and ex-
247 tracted from the surface in order to obtain a sufficient

248 efficiency. The primary pulse length is adjustable
249 between 20 ns (for best mass resolution) and 250 ns
250 (for highest effective current). The pulse generation
251 and characterization as well as backscattering spec-
252 trometry were studied and described in detail [26]
253 while TOF-SIMS experiments were just performed
254 as proof-of-principle. Here, we present an optimized
255 TOF-SIMS spectrometer to be used with primary ion
256 beam pulsing that has been designed with the above
257 considerations in mind. Compared to the earlier proof-
258 of-principle experiments, it has a higher mass reso-
259 lution and improved lateral resolution.

260 2.3. Secondary ion extraction system

261 For helium or neon projectiles with energies of
262 several keV the sputtering process is dominated by
263 elastic collisions where secondary particles can be
264 emitted into all directions with an energy up to sev-
265 eral eV [52]. An extraction system should be able to
266 collect all positive or negative sputtered ions and di-
267 rect them towards a detector. The sample is negative
268 or positive biased relative to the extraction system
269 to accelerate charged particles of the same charge
270 state to a uniform energy. Possible extraction geome-
271 tries in the HIM have been discussed in the past [24].
272 Dowsett *et al.* [24] showed that a straight nozzle
273 and a flat sample position would lead to an electrical
274 field which is not symmetrical to the extraction opti-
275 cal axis and different sputter emission angles would
276 cause unsymmetrical trajectories and secondary ion
277 beam broadening. The total necessary open diam-
278 eter for a good ion transmission would exceed the
279 optimal working distance between the ion column
280 and the sample surface (approximately 8 mm) while
281 a larger working distance has a negative influence on
282 the focus spot size. Dowsett *et al.* [24] suggested and
283 implemented an electrostatic sector above the sample
284 to reduce these effects.

285 Tilting of the sample and a straight extraction ge-
286 ometry leads to a homogeneous electrical field be-
287 tween the sample surface and the opening of the ex-
288 traction nozzle. A large distance between the sample
289 surface and the extraction system would cause a de-
290 flection, astigmatism and aberrations of the primary
291 ion beam between the ion column and the sample
292 surface. However, shrinking of the extraction sys-
293 tems outer dimension would allow the nozzle to be

294 inserted below the primary column and reduce the
295 extraction distance and the primary beam degrada-
296 tion significantly. Therefore, the tilted straight ex-
297 traction system was selected as the most suitable ge-
298 ometry for the TOF spectrometer. In both designs,
299 the electrostatic sector as well as in the tilted straight
300 extraction geometry, the primary beam has to be post-
301 aligned in the extraction field.

302 The three major requirements for the extraction
303 optics are: (1) a full angular collection meaning that
304 secondary ions emitted in all direction are collected,
305 (2) a low working distance, and (3) a high trans-
306 mission. Secondary goals in the design process in-
307 clude a narrow extracted ion beam, high mass reso-
308 lution of the overall system and mechanical rigidity
309 of the system. Flight time differences caused by dif-
310 ferent secondary ion energies and varying flight path
311 lengths should be minimized for highest mass reso-
312 lution. Those demands could not be satisfied with
313 commercially available solutions that would fit into
314 the limited space.

315 Therefore, a custom solution and extraction op-
316 tics was designed using the advanced ion beam trans-
317 port simulation code package IBSimu [53]. The start-
318 ing conditions for the sputtered ions were chosen ac-
319 cording to a typical angular and energetic distribu-
320 tion spectra of sputtered particles [24, 52] and veri-
321 fied with the angle and energy distribution from
322 TRI3DST. The design of an ion optics is associated
323 with a high number of degrees-of-freedom like dis-
324 tances, diameters, lengths, shape as well as applied
325 voltages on all ion optical elements. Although the
326 time scale for simulating ion trajectories can be as
327 low as some milliseconds nowadays, the simulation
328 of the whole parameter space would not be possible
329 in a finite time. Therefore, an advance optimization
330 strategy can help to find a solution that satisfies the
331 high demands. We developed and applied an evo-
332 lutionary algorithm to evaluate over 2×10^5 different
333 parameter-sets with a total of 10^8 simulated ion tra-
334 jectories. The simulation result which revealed the
335 best overall SIMS extraction performance based on
336 just one single accelerating einzel lens is shown in
337 Fig. 2.

338 A decelerating einzel lens would cause a higher
339 flight time broadening because secondary ions would
340 be slowed down closer to their initial sputter energy,

341 corresponding to larger relative velocity difference.
342 The sample, positioned at a still acceptable working
343 distance of less than 12 mm, has to be tilted towards
344 the extraction nozzle and biased to ± 500 V. Trajec-
345 tories follow symmetrical lines around the extraction
346 axis and the majority of the ions are focused to the
347 end of the flight path. A fine grid at the nozzle en-
348 trance ensures straight field lines and avoids a diver-
349 gent lens effect when ions enter the extraction. The
350 simulations reveal high extraction efficiency and low
351 aberrations of the primary beam. Performance tests
352 shown later in this paper confirm these findings.

353 Additionally, electrostatic steering plates for fine
354 alignment are integrated in the final design. A ren-
355 dering of the overall setup is shown in Fig. 3. The ex-
356 traction nozzle is fully retractable and can be aligned
357 mechanically by micrometer calipers on the outside
358 of the microscope. All parts facing the inside of the
359 measurement chamber are at ground potential and
360 should therefore not influence the microscope per-
361 formance.

362 3. Results and discussion

363 3.1. Mass Spectra

364 In order to evaluate and calibrate the setup, vari-
365 ous well characterized samples have been analyzed.
366 From more than twenty (known) mass peaks the time-
367 of-flight to mass calibration was derived. The cali-
368 brated mass spectra have been rebinned to an equal
369 bin width. A positive ion mass spectrum of a sil-
370 ver surface is shown as an example in Fig. 4. A pri-
371 mary beam of 25 keV Ne^+ with a current of 10 pA
372 was utilized to obtain a high sputter yield while hav-
373 ing a reasonable ion beam spot size. For the used
374 repetition rate of 10 kHz this results in an effective
375 current of approximately 3 fA. As described earlier,
376 longer pulse widths can be applied to reduce the mea-
377 surement time when mass resolution is less impor-
378 tant. Short ion pulses can also cause a broadening of
379 the primary ion beam [27]. For SIMS imaging with
380 highest lateral resolution, a pulse width longer than
381 100 ns should be applied to minimize this broadening
382 effect.

383 Besides both silver isotopes, typical organic molec-
384 ular fragments such as CH_3^+ and C_4H_9^+ with several
385 intermediates and traces of sodium and hydrogen show

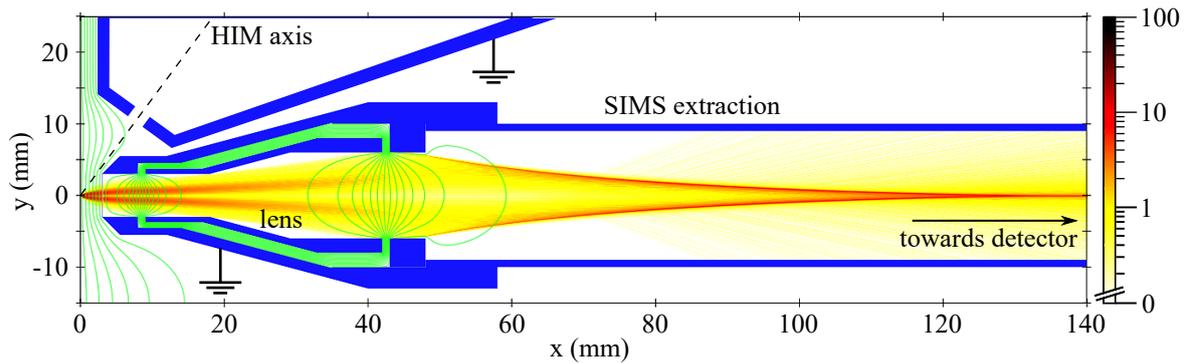


Figure 2: Ion optical simulation of the secondary ion extraction system. Tilted sample is aligned with the y-axis, primary ions incident on the origin of ordinates and create 5000 secondary ions with an initial energy and angular distribution of the sputtered particles. Secondary particle density is calculated and shown on a logarithmic scale.

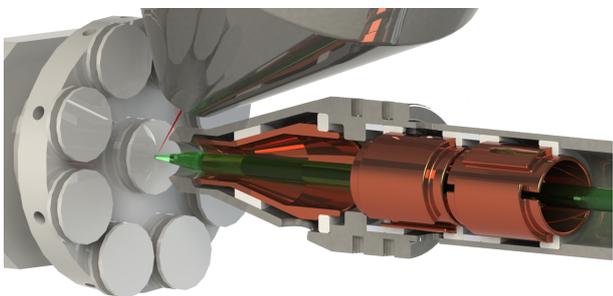


Figure 3: Scheme of primary ion column, sample holder and sectional view of the secondary ion extraction system. Primary ion beam in red, extracted secondary ions in green, electrical isolators white and ion optical elements copper-coloured.

up in the mass spectra. The molecular fragments originate either from surface contamination or from adsorbed residual gas from within the chamber. Although all experiments have been performed at a pressure of $\sim 10^{-7}$ mbar a significant deposition from the gas phase takes place during the acquisition. According to the Hertz-Knudsen-equation, within a typical acquisition time of 10 min more than one monolayer of hydrocarbons attaches the surface from the gas phase. Thus, even *in-situ* plasma cleaning prior to the measurements would be insufficient to completely avoid residual gas mass peaks. Therefore, in future designs a vacuum of at least 10^{-9} mbar would be highly desirable.

Peaks below $m/q = 80$ u show a mean width of (0.26 ± 0.09) u. At these masses, the resolution is sufficient for isotope separation which could be of particular interest in applications like isotope labeling in life science. In all measured spectra the peaks originating from bulk elements are far more broad-

ened than the finite mass resolution of the spectrometer and show an asymmetric peak broadening towards shorter flight times or respectively lower masses. The $^{107}\text{Ag}^+$ peak has full width at half maximum Δm of 1.68 u and the $^{109}\text{Ag}^+$ has a Δm of 1.56 u.

In order to understand the origin of this broadening we simulated the energy and angular distribution of sputtered silver particles. The initial energy distribution of all sputtered particles before extraction has been simulated with TRI3DST [33, 34] (Fig. 5(a) blue). The relative large amount of sputtered particles with energies above 10 eV can be assigned to nuclear collisions with a relatively high energy transfer either with backscattered primary ions or recoils. These scattering events most probably take place below the first monolayers and would therefore in literature be referred as recoils.

Further, the binary collision approximation code is not able to provide the charge state of sputtered particles. The ionization probability of sputtered particles should in general increase towards higher energies [54–56]. For energies below 5 eV or inverse velocities above $5 \mu\text{s}/\text{cm}$ the secondary ion formation is still subject of current research [57, 58]. We did not include the charge state in our simulations since the theoretical models still deviate from the rare experimental data.

The efficiency (extraction and transmission) of the ion extraction system for sputtered particles has been simulated in ion beam transport calculations using IBSimu [53] (Fig. 5(a) green). Since the extraction system was designed to extract secondary ions with energies up to 10 eV, the loss of efficiency at

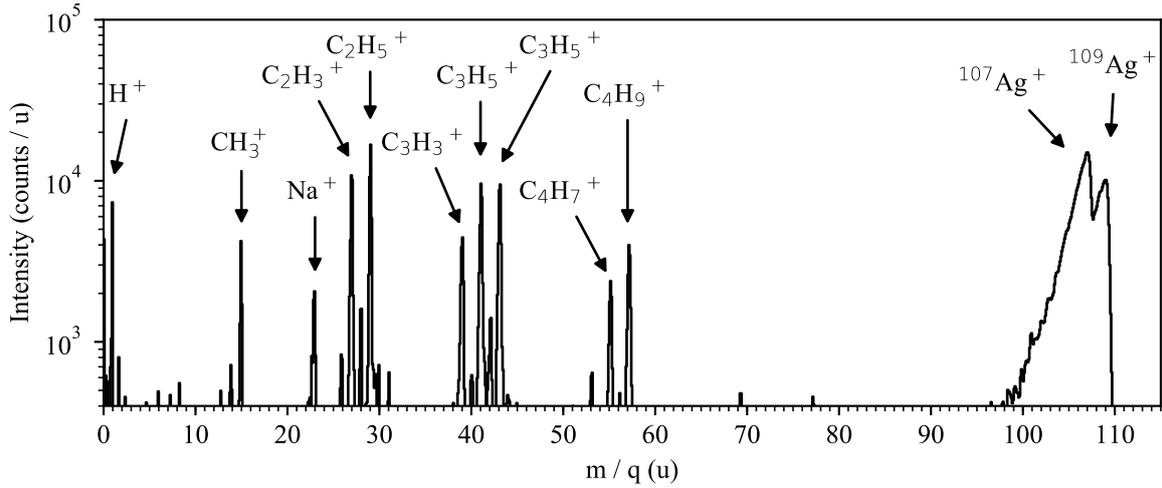


Figure 4: Positive ion mass spectrum of a silver surface (black). Primary beam: 25 keV Ne^+ , 30 ns pulse length, 10 kHz repetition rate, 3 fA effective current, 3×10^{12} ions cm^{-2} .

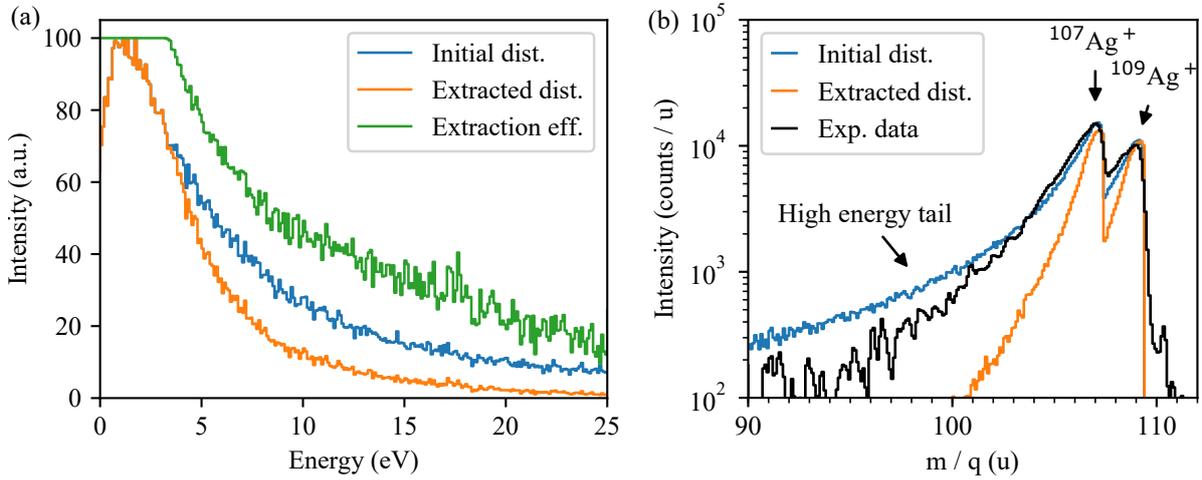


Figure 5: (a) Normalized energy distribution of sputtered Ag particles from TRI3DST summed up over all sputtering angles (blue). Extracted and transmitted particles (orange) according to ion transport simulations using IBSimu [53] and derived efficiency of the SIMS extraction optics (green). (b) Corresponding mass spectra of the initial (blue) and extracted, transmitted silver particle distribution (orange). In comparison the experimental Ag spectrum (black).

439 higher energies is attributed to insufficient focusing
 440 of the einzel lens. The gentle drop of intensities to-
 441 wards higher energies can be explained since a por-
 442 tion of sputtered ions are emitted perpendicular to the
 443 surface and straight into the extraction system and
 444 therefore do not have to be focused by the ion optics.

445 The resulting energy distribution of extracted sput-
 446 tered particles is shown in Fig. 5(a) (orange line).
 447 By comparing initial and extracted intensity we get
 448 a theoretical total efficiency of $(60 \pm 1) \%$ assuming
 449 the energetic and angular distribution extracted from
 450 TRI3DST simulations. The total efficiency for sput-
 451 tered positive or negative ions can be different from

452 this value. Since the ionization probability decreases
 453 at lower energies where the extraction efficiency is
 454 high we expect slightly lower total efficiencies for
 455 charged particles. However, a quantitative estimation
 456 is difficult, since the energy distribution of charged
 457 particles depends on many parameters, including vary-
 458 ing projectile target combinations and even the sam-
 459 ple temperature [59].

460 The described differences in the energy of sput-
 461 tered particles as well as different trajectory lengths
 462 will lead to a broadening of the flight time. Since in
 463 the time to mass calibration a sharp sputtering energy
 464 of 3 eV and a fixed flight path was assumed, these de-

465 viations consequently result in an error of the mass to
466 charge state ratio m/q and therefore contribute to the
467 observed peak broadening. The initial energy distri-
468 bution from TRI3DST has been converted, rebinned
469 and adjusted to the measured signal intensity for both
470 silver isotopes assuming a natural isotope ratio (see
471 Fig. 5(b) in blue). The same has been applied to the
472 data corresponding to the orange line in Fig. 5(b).
473 The discrepancy between experimental data and sim-
474 ulation results (black and orange line in Fig. 5(b)) ac-
475 cording to the above considerations may be attributed
476 to the neglected dependence of the secondary parti-
477 cles charge state on their energy and angle of emis-
478 sion. Another explanation could be misalignment of
479 the extraction optics or ion optical elements which
480 were not considered in the simulation. If a partic-
481 ular charge fraction function of sputtered particles
482 would be known and considered in the above sim-
483 ulations, the simulated and experimental data would
484 be in better agreement. However, the charge fraction
485 as a function of ion energy and emission angle is not
486 available from literature in the energy range applied
487 in this work.

488 Contrary to the bulk signal, the molecular frag-
489 ments exclusively originate from the first atomic lay-
490 ers and a high energy transfer scattering event is un-
491 likely. Those particles can be emitted in a rather
492 soft collision in the recoil cascade and therefore have
493 a narrower energy distribution. A high energy col-
494 lision would also result in higher fragmentation of
495 these molecular fragments.

496 The mass resolution for bulk components can be
497 increased by using a higher acceleration voltage for
498 the secondary ions to reduce the relative ion energy
499 spread. However, this would require a custom sam-
500 ple holder that can be biased to more than ± 500 V.
501 Alternatively, one could use a conventional reflectron
502 TOF design to compensate for the energy spread of
503 sputtered particles. The latter would also result in a
504 higher time or mass resolution due to the extension of
505 the TOF. Therefore, the current setup was designed
506 in a way that a later integration of a reflectron optics
507 is easily possible.

508 3.2. *Imaging SIMS*

509 Besides the analysis of the composition for a cer-
510 tain object of interest, SIMS can be utilized to gener-

511 ate element distribution maps on a very small lateral
512 scale. In this mode, instead of the evaluation of the
513 secondary electron (SE) yield, the yield of sputtered
514 ions is used for contrast generation. Both, the total
515 ion yield as well as the particular yield of a single
516 ion mass can deliver valuable information that are
517 not accessible from SE images. While a total ion
518 yield image reveals good element contrast, mass se-
519 lected mapping allows the precise determination of
520 the location and the distribution of one particular el-
521 ement.

522 Examples for both imaging modes are shown in
523 Fig. 6 for two different samples. A copper trans-
524 mission electron microscopy grid on top of copper
525 scotch tape Fig. 6(a-c) and a NaCl micro and nano-
526 crystal on a silicon substrate Fig. 6(e-i). Table salt
527 was crushed on a silicon substrate to get micrometer
528 and nanometer sized crystals of NaCl. It provides a
529 sample with high yield of positive sodium and nega-
530 tive chlorine ions that is easy to obtain and prepare to
531 reproduce the shown results. Additionally, the inte-
532 grated mass spectrum (sum of all pixels) of the latter
533 sample is seen in Fig. 6(i). The dwell time (data ac-
534 quisition time per pixel) was chosen to be a couple of
535 milliseconds to ensure multiple primary ion pulses in
536 each pixel.

537 Fig. 6(c) represents a demagnification of the area
538 shown in Fig. 6(b). It reveals the area of the previous
539 imaging by a higher intensity, an effect that can be at-
540 tributed to the removal of surface contaminants, sur-
541 face roughening, or compositional changes induced
542 by the ion beam.

543 For the secondary electron images in Fig. 6(d) an
544 ion fluence of 10^{14} $\text{Ne}^+\text{cm}^{-2}$ was applied whereas the
545 SIMS measurement in Fig. 6(e-g, i) was done with
546 3.8×10^{12} $\text{Ne}^+\text{cm}^{-2}$ and in Fig. 6(h) with
547 2.1×10^{15} $\text{Ne}^+\text{cm}^{-2}$. The irradiated areas typically
548 suffer from severe sample damage and in this case
549 from sputtering in the exposed area and redeposition
550 close by (indicated by green arrows in Fig. 6(d)).
551 They are visible as black squares with a bright sur-
552 rounding on the presented NaCl micro-crystal in the
553 post-SIMS secondary electron image (see Fig. 6(d)).

554 The lateral resolution of the presented setup was
555 studied on multiple edges with different orientations.
556 Therefore a NaCl micro-crystal was partially irradi-
557 ated, on the area indicated by dotted lines in Fig. 7(a),

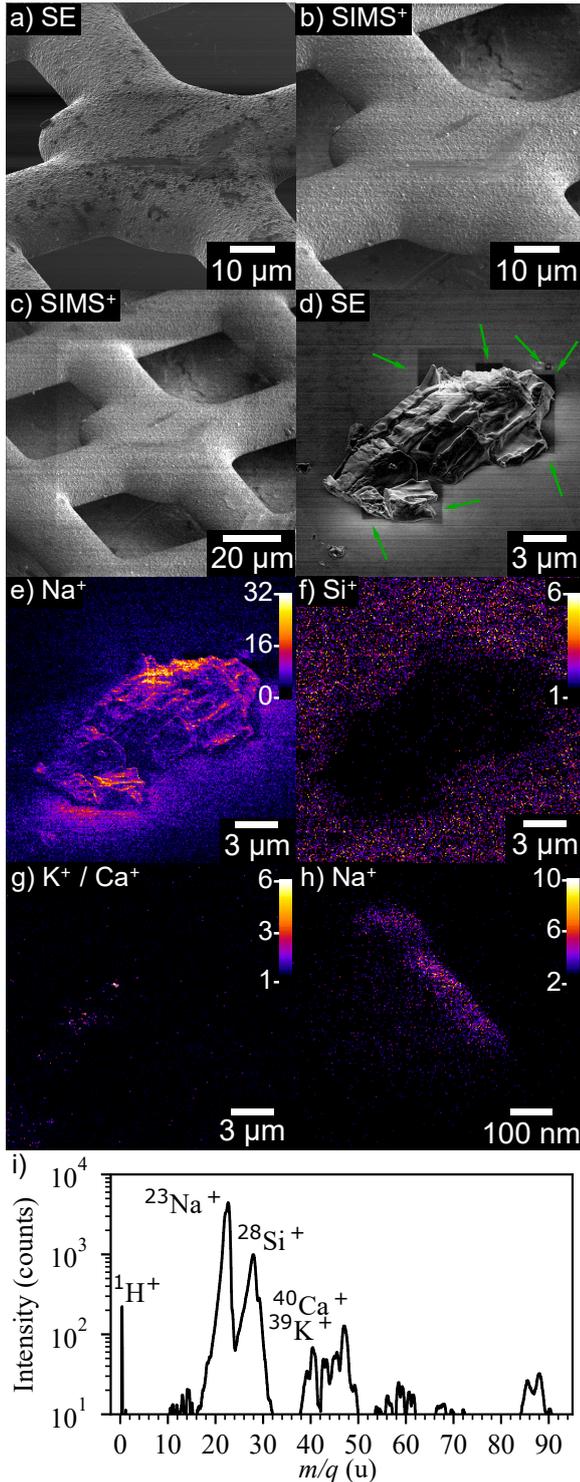


Figure 6: Images of a transmission electron microscope grid as generated by a 25 keV Ne^+ beam (a-c) (1024×1024 pixels). The contrast is generated by secondary electron yield (a) and the positive secondary ion yield (b,c). Secondary electron image, ablation in exposed areas and sputter redeposition close by is indicated by green arrows (d), SIMS element maps (e-g) and integrated SIMS spectrum (i) of a NaCl micro-crystal and Na^+ map of a NaCl nano-crystal (h). The measurements (e-i) were recorded with 25 keV Ne^+ , a pixel resolution of 256×256 , 150 ns pulses with 18 kHz repetition rate and 2.5 fA effective current. A $20 \mu\text{m}$ (e-g) / 700 nm (h) field of view, 15 ms (e-g) / 10 ms (h) dwell time per pixel and a total acquisition time of 16 min was used in (e-g) or rather 11 min in (h). The color of maps represents the number of counts per pixel (see color scale).

558 with the spectrometer inserted and the extraction field
 559 applied. The irradiation was performed with a 0.5 pA,
 560 unpulsed 25 keV neon ion beam using a fluence of
 561 around $10^{18} \text{ Ne}^+ \text{ cm}^{-2}$ at 54° incident angle. Dur-
 562 ing the irradiation and the measurements the sample
 563 holder was tilted towards the extraction system, see
 564 Fig. 2. All of the following milling and analysis steps
 565 have been performed with the inserted ion extraction
 566 optics and with enabled extraction bias.

567 The majority of the measured sputtered ions in
 568 positive mode are sodium ions (see Fig. 6(i)). To
 569 avoid a low duty cycle and a reduced effective beam
 570 current, an unpulsed beam was used for imaging to
 571 get a better signal to noise ratio in the same measur-
 572 ing time. The total sputtered ion yield was used to
 573 create an image contrast which is influenced for ex-
 574 ample by the elemental composition and the charge
 575 state of secondary particles. The latter is itself in-
 576 fluenced by the surface chemistry and the local work
 577 function. Furthermore, the collision cascade and the
 578 extraction efficiency depend on the surface topogra-
 579 phy which dominates in the present case the contrast
 580 mechanism.

581 The signal intensity, and therefore the amount of
 582 sputtered ions that can be measured in the irradiated
 583 areas of the sample is lower compared to the unirra-
 584 diated area. The sodium chloride crystal was either
 585 partially or completely removed in the milled area.
 586 The lower total yield of positive secondary ions in the
 587 irradiated area can be explained by a reduced extrac-
 588 tion efficiency and a reduced emission of secondary
 589 ions from the milled trenches [60, 61]. The signal
 590 intensity however is higher directly next to the irra-
 591 diated areas. This is specially seen on those edges
 592 that are on the top left of the trenches. The secondary
 593 electron yield dependence on the incident angle and
 594 on surface topography has been investigated before
 595 in scanning electron microscopes [62] and focused
 596 ion beam instruments including HIMs [63–65]. Sec-
 597 ondary electrons as well as ions are created when
 598 the primary ion enters the sample surface, but more
 599 importantly for this effect, also when the primary
 600 ion or secondary particles leave the sample. There-
 601 fore a similar signal enhancement on edges and to-
 602 pographic effects are expected for the secondary ion
 603 yield as well. This is in agreement with binary colli-
 604 sion approximation (BCA) simulations [33, 34]. The

605 enhanced secondary ion yield from surface edges was
 606 also observed in other SIMS measurements in the
 607 HIM [31].

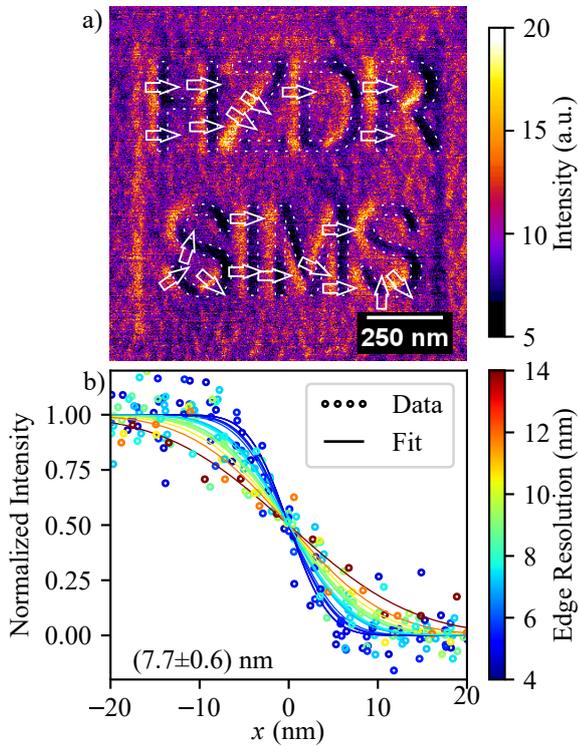


Figure 7: NaCl crystal with ion beam engraved text (marked by dotted lines) as imaged using the total positive secondary ion yield (a). Measurement time of 105 s, 0.5 pA, unpulsed 25 keV neon ion beam, 20 μm aperture, spot control 4 or crossover position at -211 nm, 400×400 pixels and a field of view of 1.2 μm . The number of secondary ions per pixel has been estimated based on the secondary ion yield per primary ion measured in Fig. 6(i). 20 edge profiles have been extracted from the areas indicated by the arrows in the total ion yield image. Each of these edge profiles was averaged over a width of 12 pixels respectively 36 nm, normalized and fitted by an error function (b). For better visualization the edge profiles have been aligned to the fitted center of the error function. Data points as well as fit functions are colored according to their edge resolution (75 % to 25 %). The mean edge resolution evaluates to (7.7 ± 0.6) nm.

608 Several edge profiles were extracted from the total
 609 positive secondary ion image (see Fig. 7(a)), averaged
 610 as indicated by the width of the arrow (12 consecutive
 611 lines or 36 nm each), normalized and fitted by a simple
 612 error function (b). The lateral resolution was defined as
 613 the intensity drop from 75 % to 25 % and indicated as
 614 color of the particular data points and fit functions. The
 615 mean edge resolution obtained from the 20 averaged edge
 616 profiles is 7.7 nm with a standard deviation of 0.6 nm.

618 We thus demonstrated that sputtered particles can
 619 be extracted with a lateral resolution close to the fun-
 620 damental limit of SIMS on flat samples, which has
 621 been estimated to be 3 nm (see Fig. 1). It should be
 622 emphasized that the lateral resolution alone does not
 623 take into account the sensitivity to certain ions. It
 624 will therefore not be possible to extract sufficient ions
 625 of each sample component from a sputter volume
 626 whose diameter is in the order of the lateral resolu-
 627 tion. Therefore, highest lateral resolution is achieved
 628 exclusively for elements providing a high secondary
 629 ion yield.

630 Additionally, it has to be mentioned that our mea-
 631 surements were not carried out on a flat surface and
 632 are therefore not directly comparable with the simu-
 633 lation results. Furthermore, due to the sputtering
 634 process the surface topography changes continuously
 635 which will certainly influence the shape of edges dur-
 636 ing the data acquisition. Although we demonstrated
 637 highest lateral resolution of 7.7 nm, the ultimate res-
 638 olution could not be achieved in this work since the
 639 low signal intensity and the quickly occurring sam-
 640 ple damage hamper the precise focusing of the pri-
 641 mary ion beam in the applied extraction field. In
 642 future work the influence of the extraction field on
 643 the primary ion beam will be studied to speed up the
 644 switching between normal secondary electron imag-
 645 ing and material analysis using SIMS.

646 4. Conclusions

647 TOF-SIMS was implemented in a HIM with a
 648 tilted and biased sample and a straight secondary ion
 649 extraction geometry. The implemented setup was
 650 simulated with IBSimu, optimized for a high effi-
 651 ciency using an evolutionary algorithm and experi-
 652 mentally studied on various samples. High transmis-
 653 sion, a mass resolution of 0.3 u and 8 nm edge reso-
 654 lution have been demonstrated.

655 Sample damage and detection limits which are
 656 a function of the sputtered volume used during the
 657 analysis of nano structures are a fundamental limita-
 658 tion of sputtering based analysis methods in particu-
 659 lar for the low amount of available sample material.
 660 However, with the demonstrated mass resolution and
 661 the resulting ability to separate isotopes for light el-
 662 ements in combination with the record lateral reso-

663 lution give the method a large potential for material
664 analysis in life sciences, material science and other
665 research fields.

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