Journal of Visualized Experiments

3D depth profile reconstruction of segregated impurities with secondary ion mass spectrometry technique
--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE61065R2
Full Title:	3D depth profile reconstruction of segregated impurities with secondary ion mass spectrometry technique
Section/Category:	JoVE Chemistry
Keywords:	secondary ion mass spectrometry; SIMS; gallium nitride; defect selective etching; dislocation, impurity; oxygen
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Additional Information:	
Question	Response
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Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Warsaw, Poland

Dear Editor and Reviewers,

I am pleased to submit a protocol entitled "Three dimensional localization of segregated impurities with secondary ion mass spectrometry technique" by Paweł Piotr Michałowski, Sebastian Złotnik, Iwona Jóźwik, Adrianna Chamryga and Mariusz Rudziński for consideration for publication in JoVE.

The proposed protocol combines excellent detection limits of secondary ion mass spectrometry (SIMS) technique with reasonable spatial resolution and allows to obtain realistic three dimensional distribution of segregated impurities/dopants in solid state materials. Three major issues are discussed and addressed: i) non-uniformity of the detector is compensated by flat-field correction; ii) vacuum background contribution (parasitic oxygen counts coming from residual gases present in the analysis chamber) is estimated and subtracted; iii) all experiments are performed within stable timespan of the primary ion source. Wet chemical etching can be used to reveal position and types of dislocations in a material and then the SIMS result can be superimposed on images obtained from scanning electron microscope and thus the position of agglomerated impurities can be related to position of certain defects. The method is fast and does not require sophisticated sample preparation stage but requires a high quality and stable ion source and the whole measurement should be perform fast to avoid deterioration of the primary beam parameters.

Our work is focused on detection of oxygen in gallium nitride samples but the proposed method can be easily adapted to other materials and/or detected elements where non-uniform distribution is expected. Therefore we believe that our work will be interesting for other scientists.

Sincerely,

Paweł Piotr Michałowski

1 **TITLE:**
2 3D Depth Profile Reconstruction of Segregated Impurities using Secondary Ion Mass
3 Spectrometry
4
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18
23 **SUMMARY:**
24 The presented method describes how to identify and solve measurement artifacts related to
25 secondary ion mass spectrometry as well as obtain realistic 3D distributions of
26 impurities/dopants in solid state materials.
27
28 **ABSTRACT:**
29 The presented protocol combines excellent detection limits (1 ppm to 1 ppb) using secondary
30 ion mass spectrometry (SIMS) with reasonable spatial resolution (~1 μm). Furthermore, it
31 describes how to obtain realistic three-dimensional (3D) distributions of segregated
32 impurities/dopants in solid state materials. Direct 3D depth profile reconstruction is often
33 difficult to achieve due to SIMS-related measurement artifacts. Presented here is a method to
34 identify and solve this challenge. Three major issues are discussed, including the i)
35 nonuniformity of the detector being compensated by flat-field correction; ii) vacuum
36 background contribution (parasitic oxygen counts from residual gases present in the analysis
37 chamber) being estimated and subtracted; and iii) the performance of all steps within a stable
38 timespan of the primary ion source. Wet chemical etching is used to reveal the position and
39 types of dislocation in a material, then the SIMS result is superimposed on images obtained via
40 scanning electron microscopy (SEM). Thus, the position of agglomerated impurities can be
41 related to the position of certain defects. The method is fast and does not require sophisticated
42 sample preparation stage; however, it requires a high-quality, stable ion source, and the entire
43 measurement must be performed quickly to avoid deterioration of the primary beam
44 parameters.

45
46 **INTRODUCTION:**
47
48 Secondary ion mass spectrometry (SIMS) is a well-known technique used for contamination
49 monitoring with excellent detection limits[1-6]. Vacuum background contribution can be
50 problematic for light elements (e.g., hydrogen, carbon, nitrogen, oxygen), which may be
51 present in the form of residual gases in a measurement chamber. Peres et al. previously
52 established a technique to estimate background contribution; thus, a realistic concentration of
53 contaminating atoms can be determined[7].
54
55 In many materials, the distribution of contaminating atoms is not uniform. The case of gallium
56 nitride (GaN) is particularly interesting, as it is predicted that oxygen mainly decorates screw
57 and mixed dislocations[8-11]. Considering that most analytical methods lack sensitivity or spatial
58 resolution to detect low concentration contaminating atoms, it is essential to develop a SIMS
59 measurement procedure that is capable of 3D localization of segregated impurities[12].
60
61 While many SIMS spectrometers are equipped with position sensitive detectors, a direct 3D
62 reconstruction of a depth profile is insufficient to obtain realistic distribution of oxygen atoms
63 in a GaN sample. Imperfection of the detector may distort the image and prevent researchers
64 from obtaining a realistic distribution of contaminating atoms. However, a large problem is
65 vacuum background contribution, as usually >90% of registered oxygen counts originate from
66 residual gases present in the analysis chamber. Presented here is a method to identify and
67 adequately solve each of these challenges.
68
69 Nonuniformity of the detector can be tested on a blank silicon wafer. Even a long integration
70 time can lead to the observation of some secondary ion image nonuniformity, due to varying
71 sensitivity of each channel in a microchannel plate detector. Therefore, flat-field correction is
72 needed to obtain high-quality images of 3D distributions of segregated atoms.
73
74 Vacuum background contribution is related to a flux of contaminating atoms from the vacuum
75 adsorbed onto the analyzing area. Considering that the process is dynamic (i.e., the sample
76 surface is constantly sputtered by the primary beam), it can be assumed that each point of the
77 analyzed area has the same probability to adsorb these oxygen atoms. Furthermore, they are
78 almost immediately sputtered and do have not enough time to segregate. Therefore, a
79 statistical approach is the most efficient. Random elimination of 90% (or more) of oxygen
80 counts should reveal regions where oxygen is agglomerated.
81
82 It should be noted that the stability of the primary beam is crucial for this type of experiment.
83 After some time, the intensity and homogeneity of the beam deteriorates, which reduces the
84 quality of the image. It is therefore essential to estimate a timespan of stable operation of the
85 beam and perform all experiments before the beam becomes unstable. The protocol can be
86 easily used for other materials and detected elements at which nonuniform distribution is
87 expected. It is particularly interesting to combine this with wet chemical etching, which reveals
88 the positions and types of dislocation. Thus, the position of agglomerated impurities can be

89   correlated to position of defects.

91   **PROTOCOL:**

93   **1. Defect selective etching**

95   1.1. Solid etchant preparation

97   1.1.1. Prepare a eutectic mixture of strong bases of potassium hydroxide (KOH) and sodium
98   hydroxide (NaOH), together with magnesium oxide (MgO), by dissolving and mixing the
99   composing alkali hydroxides and metal oxide in distilled water. Keep stoichiometric quantities
100 of 53.6/37.3/9.1 at % of NaOH, KOH, and MgO, respectively[13]. MgO addition increases the
101 etchant viscosity such that it remains on the Ga-polar surface and does not flow over the edges
102 to the N-polar surface[13,14]. All chemicals used should be practical grade quality.

104 1.1.2. Heat the mixture in a flask on a hot plate to 200 °C and agitate by magnetic stirring for 1
105 h (above the melting point of the KOH-NaOH eutectic point).

107 1.1.3. Cool the mixture to ~100 °C by reducing the temperature of a hot plate to completely
108 evaporate the remaining liquid. This step depends on flask size and water volume, so it may
109 require several minutes up to 1 h.

111 1.1.4. Transfer the solid etchant (denoted as E+M) into a dried bottle, avoiding exposure to
112 moisture.

114 CAUTION: KOH and NaOH may cause skin irritation and eye damage. Work with gloves and
115 goggles. The protocol can also be paused here.

117 1.2. Defect selective etching

119 1.2.1. Prepare a clean GaN surface for the analysis. GaN that is epitaxially grown on sapphire is
120 used in the following steps[12].

122 1.2.2. Place the GaN sample on a hot plate heated to ~450 °C. Place the thermocouple near the
123 sample to precisely read the real temperature.

125 1.2.3. Place a piece of solid E+M etchant on top of the GaN and leave for 3 min.

127 1.2.4. Take the sample from the hot plate and place in a beaker with hot HCl for 3–5 min to
128 eliminate remaining E+M.

130 1.2.5. Remove the sample from HCl and insert in a beaker with deionized (DI) water and
131 ultrasonic bath for 5–10 min.

133   1.2.6. Dry the sample by N_2 blowing.

135   CAUTION: HCl may cause skin irritation and eye damage. Work with gloves and goggles. Avoid
136   getting burnt. The protocol can also be paused here.

138   **2. Scanning electron microscopy observation**

140   2.1. Mark the sample (e.g., with an L-shaped scratch using a diamond pen cutter).

142   2.2. Mount the sample on a metal stub dedicated to the SEM model to be used, using a
143   conductive adhesive (i.e., double-sided carbon conductive tape or a similar material). Use
144   gloves during sample preparation and transfer to avoid grease contamination from hands.

146   2.3. Add a piece of the tape from step 2.2 to connect the sample surface with a metal stub to
147   prevent charge buildup on the specimen surface. Alternatively, a sputtered coating with
148   conductive material (~10 nm thick) can be applied to prevent charging effects.

150   2.4. Acquire at least three high-resolution SEM micrographs (ideally, a minimum of five) of a top
151   view of the sample. Each image should display an area of at least 25 µm x 25 µm. Avoid taking
152   images from the surface regions with macroscopic surface defects. **Figure 1** presents a typical
153   result.

155   2.5. Note the exact position of each picture with a respect to the L-shaped marker.

157   NOTE: The protocol can be paused here.

159   **3. Secondary ion mass spectrometry measurements**

161   3.1. Tool calibration

163   3.1.1. Calibrate the SIMS equipment using negative polarity, Cs primary ions with 7–13 keV
164   impact energy. Align the secondary and primary beams. Keep the beam as small as possible (at
165   least 1 µm in diameter), as the lateral resolution is predetermined by the size of the beam.

167   3.1.2. Prepare five-seven settings for beams with various ion current density. For simplicity,
168   keep the size of the beam intact, and change the beam current . Measure the beam current and
169   size of the beam[15]. In the following steps, beam currents of 5 nA, 10 nA, 15 nA, 20 nA, 30 nA,
170   and 50 nA and a spot size 1 of µm are used.

172   3.1.3. Use a 50 µm x 50 µm raster size and 35 µm x 35 µm analysis area for the following steps.
173   Choose 256 x 256 pixels for spatial resolution. If not specified otherwise, use a standard
174   integration time for each signal (typically 1–2 s).

176   3.2. Primary source stability

177

3.2.1. Choose a setting with a moderate beam current (15–20 nA).

3.2.2. Obtain a series of images using $^{30}Si_2^-$ secondary ion for a blank silicon wafer. For each image, integrate the signal for 5–10 min.

3.2.3. Perform pixel-to-pixel comparisons of all images with the first image. If >5% of pixels show a >5% difference from the first image, this indicates that the beam became unstable. Note the timespan of the beam stability.

3.3. Measurement

NOTE: The following steps are performed within a stable timespan of the beam.

3.3.1. Follow the procedure described by Peres et al. to estimate the background level of oxygen contamination in the measurement chamber[7]. For each measurement, there is no need to obtain the absolute values of oxygen concentration, as the intensity ratio of $^{16}O^-$ and $^{69}Ga^-$ signals is sufficient.

3.3.2. Use different beam settings than those prepared in step 3.1.2. Perform at least five measurements for each beam setting. Obtain a depth profile using $^{16}O^-$ secondary ion, reach a ~200 nm depth, and measure the intensity of $^{69}Ga^-$ secondary ion by integrating the signal for 10–15 s. Do not perform this in regions where SEM images have been obtained.

3.3.3. Plot the intensity ratio of $^{16}O^-$ and $^{69}Ga^-$ signals as a function of the inversed primary current density (there is no need to calculate absolute values). A good linear fit is expected (here, $R^2 = 0.997$). Estimate the vacuum background contribution as shown on **Figure 2**.

3.3.4. Choose an intense beam (30 nA) for the following steps. Obtain an image that will be used for flat-field correction. Use a $^{30}Si_2^-$ secondary ion for a blank silicon wafer. Integrate the signal for 5–10 min. **Figure 3** presents a typical result.

3.3.5. Perform depth profile measurements in the same regions where SEM images have been obtained. Using a $^{16}O^-$ secondary ion, integrate the signal for 3–5 s for each data point.

NOTE: The protocol can be paused here.

4. Data treatment

4.1. Reconstruct a 3D image from a depth profile.

4.2. Perform flat-field correction: pixel-to-pixel normalize each $^{16}O^-$ ion image using a reference image obtained in step 3.3.4. **Figure 4A** presents raw data and **Figure 4B** presents the image after the flat-field correction.

221
222 4.3. Estimate vacuum background contribution from a plot obtained in step 3.3.2. There is no
223 need to calculate absolute values; however, note the specific percentage of total counts that
224 can be attributed to vacuum background contribution. A value between 90%–95% is typical for
225 such an experiment.
226
227 4.4. Subtract the vacuum background contribution: randomly eliminate 90%–95% of the
228 registered $^{16}O^-$ counts. **Figure 4C** presents a typical result for a single plane.
229
230 4.5. Plot the remaining counts as a 3D image. **Figure 5** presents a typical result.
231
232 4.6. Integrate signals from all data points and superimpose the 2D image on the previously
233 obtained SEM image using any image editor software with layer support. Treat the SEM image
234 as background. A layer containing SIMS results should only contain actual counts as colored
235 pixels (delete the white regions in between). Add ~30% of transparency to this layer. **Figure 6**
236 presents a typical result
237
238 **REPRESENTATIVE RESULTS:**
239
240 Very clear pillar-shaped structures should be observed in the 3D image. More oxygen should be
241 agglomerated in a region closer to the surface, since the etching process introduces more
242 oxygen that can diffuse through the sample. **Figure 7** presents a 3D image of raw data and an
243 animation of how the reduction procedure reveals the final result. **Figure 4C** also presents a
244 typical result for a single plane.
245
246 The SIMS image superimposed on the SEM image reveals that oxygen is agglomerated along
247 cores of largest etch pits. These can be attributed to mixed/screw dislocations[15]. It should be
248 noted that if the core is smaller than the size of a primary beam, the secondary image will
249 inherit the size and shape of the primary beam. In suboptimal experiments, a random
250 distribution of oxygen counts can be seen (**Figure 8**). **Figure 9** presents a situation in which the
251 beam becomes unstable during the experiment. Specifically, the quality is high for a region so
252 close to the surface, but it gradually deteriorates during the experiment.
253
254 **FIGURE LEGENDS:**
255
256 **Figure 1: SEM micrographs of etch pits revealed on GaN surface using E+M etch.** The
257 parameters were set at 450 °C for 3 min. The inset depicts a magnified micrograph with
258 revealed hexagonal pits generated on dislocation cores. The two biggest pits (>500 nm)
259 represent dislocations with screw component of the Burgers vector. This figure has been
260 reproduced with permission[12].
261
262 **Figure 2: Average O_2 concentration vs. inverse primary current density $1/J_{pr}$.** Vacuum
263 background contribution can be estimated from the plot. Error bars represent the SD of each
264 data set (five measurements).

265

266   **Figure 3: A typical $^{30}Si_2^-$ secondary ion image for a blank silicon wafer.** Intensity differences are
267   caused by nonuniformity of the detector.

268

269   **Figure 4: Typical plane view of oxygen counts distribution measured in 3D mode.** Shown are
270   images **(**A) from raw data, (B) after flat-field correction, and (C) after subtraction of vacuum
271   background contribution. This figure has been adapted with permission[12].

272

273   **Figure 5: 3D view of oxygen counts in a 5 μm x 5 μm x 1 μm cuboid**. For better visibility, the z-
274   scale is elongated. See **Supplemental Figure 1** for animation. This figure has been adapted with
275   permission[12].

276

277   **Figure 6: Lateral distribution of oxygen secondary ions (blue pixels) projected on an SEM
278   micrograph.** Despite SIMS-related artifacts (lateral resolution determined by size of the primary
279   beam), a clear correlation between the positions of largest pits and oxygen are observed. This
280   figure has been adapted with permission[12].

281

282   **Figure 7: Animation showing how the reduction procedure is performed.** At the beginning of
283   the procedure, all counts are present, then for each layer, 90% of counts are randomly
284   eliminated.

285

286   **Figure 8: Random distribution of oxygen counts in suboptimal experiment.**

287

288   **Figure 9: Experiment performed with an unstable beam.** The quality deceases with sputtering
289   depth.

290

291   **DISCUSSION:**

292

293   Issues of nonuniformity of the detector and vacuum background contribution are easy to solve
294   by flat-field correction and subtraction of parasitic counts, respectively. The subtraction
295   procedure is not perfect, as it may subtract a contribution where oxygen has been
296   agglomerated. In contrast, at the other position, it will leave the background count unaffected;
297   thus, some artificial counts may still be present while some real counts are reduced.
298   Nevertheless, it is efficient and sensitive enough to provide acceptable results.

299

300   The primary beam instability is the most problematic, as deterioration of the primary beam
301   parameters will blur the secondary ion image; thus, no reliable information about the sample
302   can be obtained. Section 3.2 in the protocol is particularly important. For instance, for a well-
303   aligned beam, the first $^{30}Si_2^-$ secondary ion image reflects nonuniformity of the detector, but
304   after some time, the image will start to change. This is caused by deterioration of primary beam
305   parameters (i.e., primary current loss, defocusing, position drift, etc.). It is therefore important
306   to estimate the timespan of beam stability. It is advised to start the experiment 2–3 h after
307   initialization of the beam, as it is typically more stable.

308

309 If the experiment is performed within a stable timespan of the beam and the result is still not
310 satisfactory, it is advised to consider the quality of the primary beam. For a small primary beam,
311 it is more challenging to confirm sufficient quality by observing a secondary ion image only. It is
312 therefore advised to perform atomic force microscopy roughness tests at the crater bottom
313 after sputtering ~1 μm of a very flat material (i.e., a blank silicon wafer). If the root mean
314 squared is above 1 nm, then further optimization of the primary beam is required.
315
316 The size of the beam limits the lateral resolution of this method. SIMS can image features that
317 are smaller than the beam size, but the secondary ion image will inherit the shape and size of
318 the primary ion beam. If a distance between two features is smaller than the size of the beam,
319 the secondary ion image will blur them together. Despite these issues, the method allows users
320 to obtain a realistic 3D distribution of impurities/dopants in solid state samples. Furthermore,
321 any spatial segregation of atoms can be correlated to the position of defects and interfaces.
322
323 For GaN-based structures (i.e., oxygen-decorated), dislocations acting as local nonradiative
324 recombination centers are responsible for n-type conductivity. For other materials any
325 inhomogeneity of the dopant/contaminating atoms distribution may have major impacts on the
326 performance of a device. Thus, the protocol is particularly useful for failure analysis and
327 optimization of growth and processing procedures.
328

332
333 **DISCLOSURES:**
334 The authors have nothing to disclose.
335

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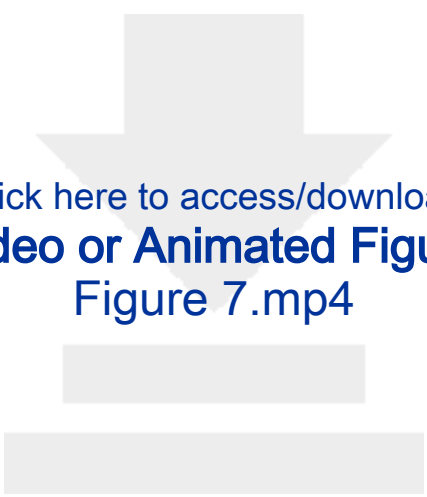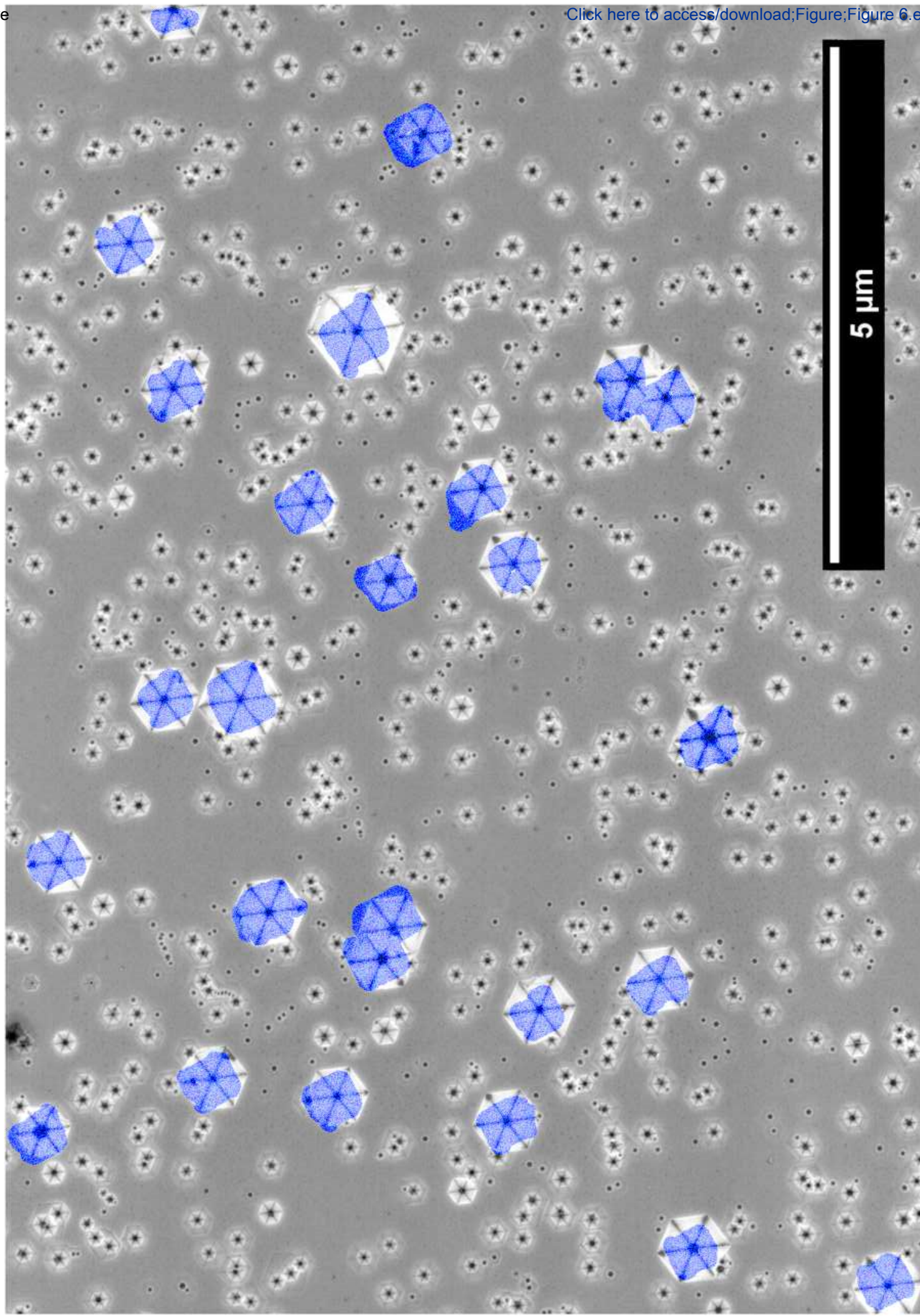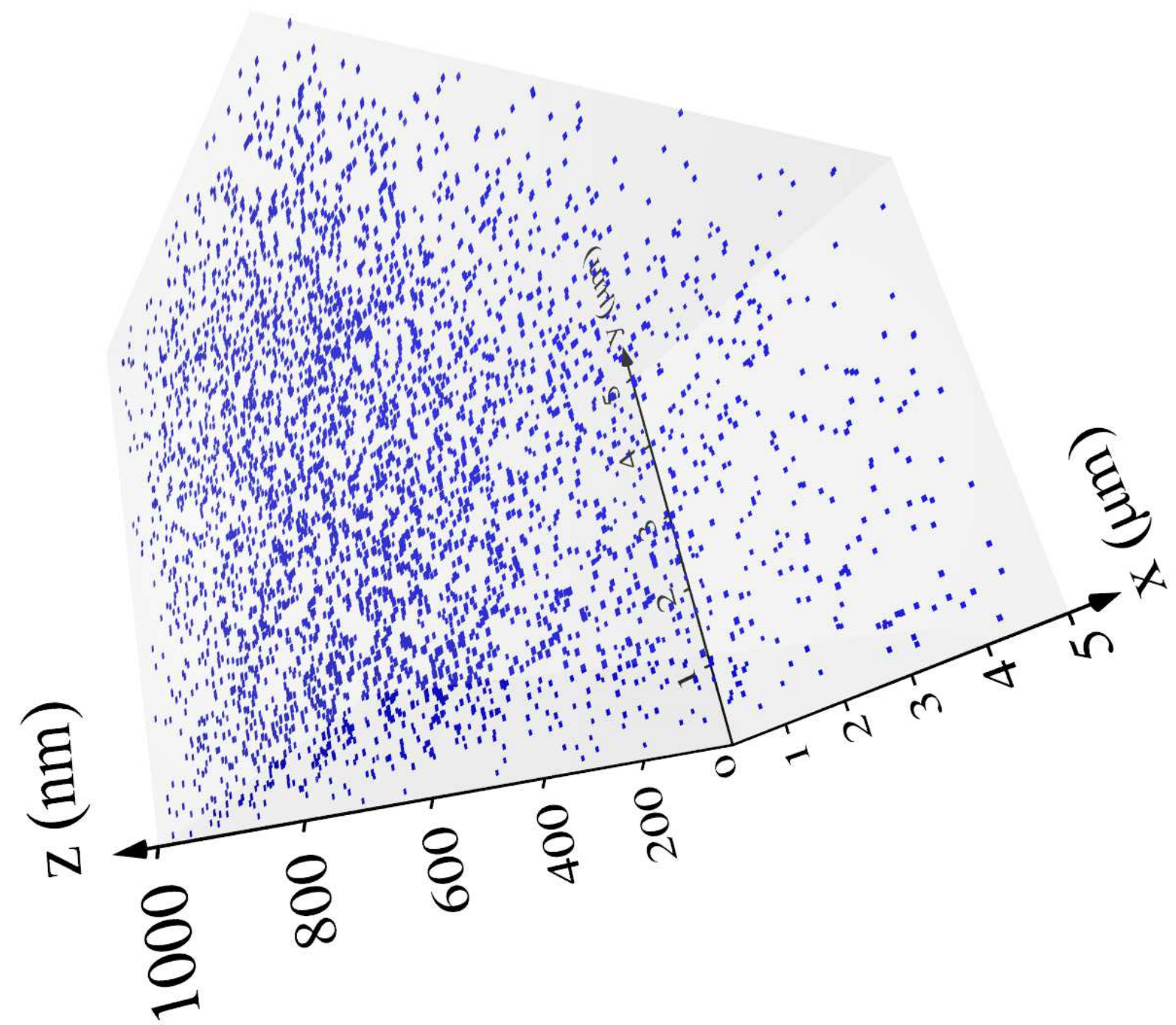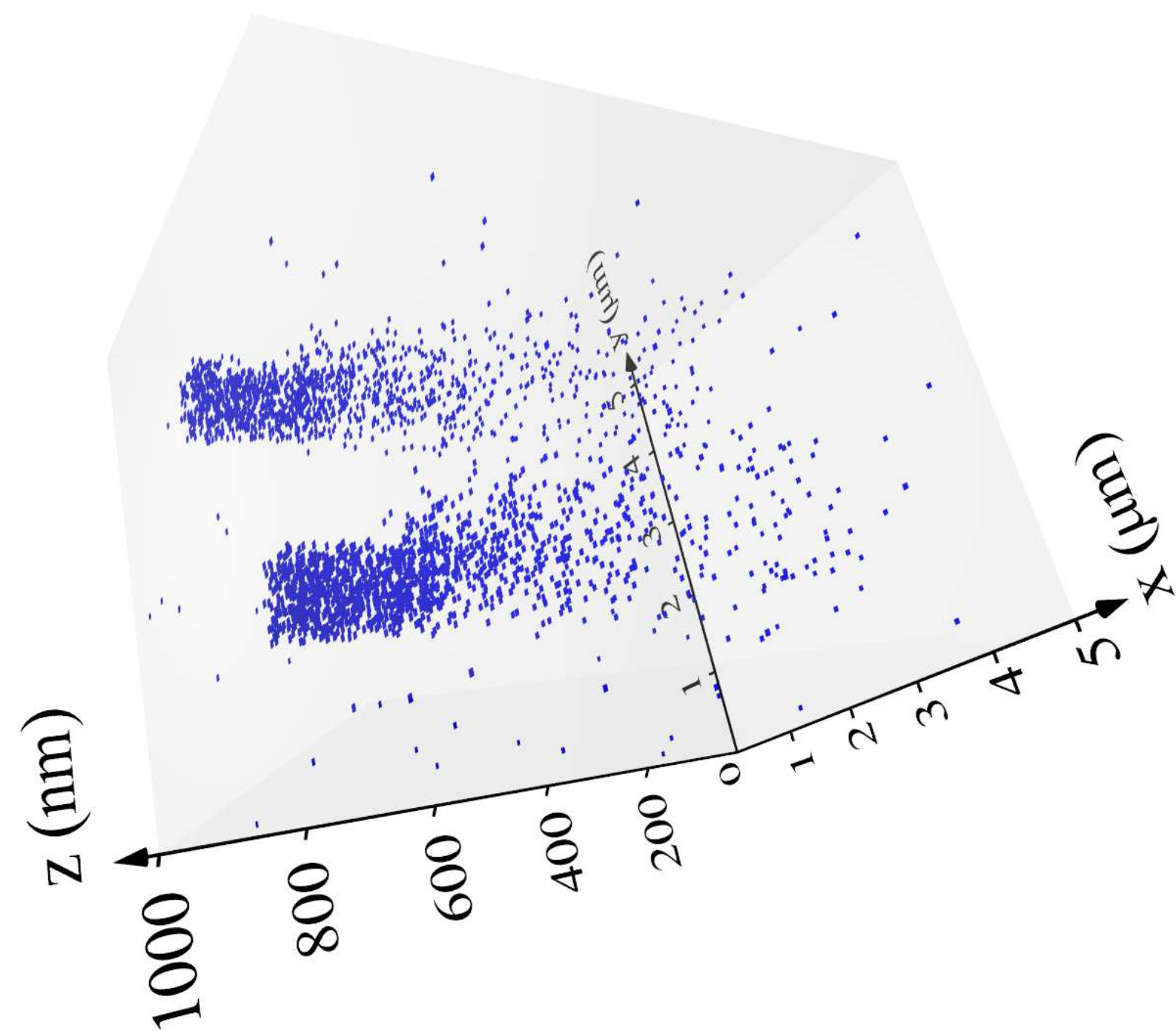
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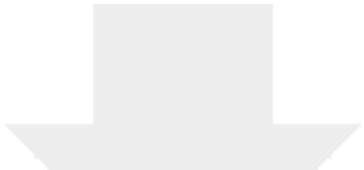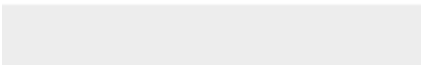
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Video or Animated Figure
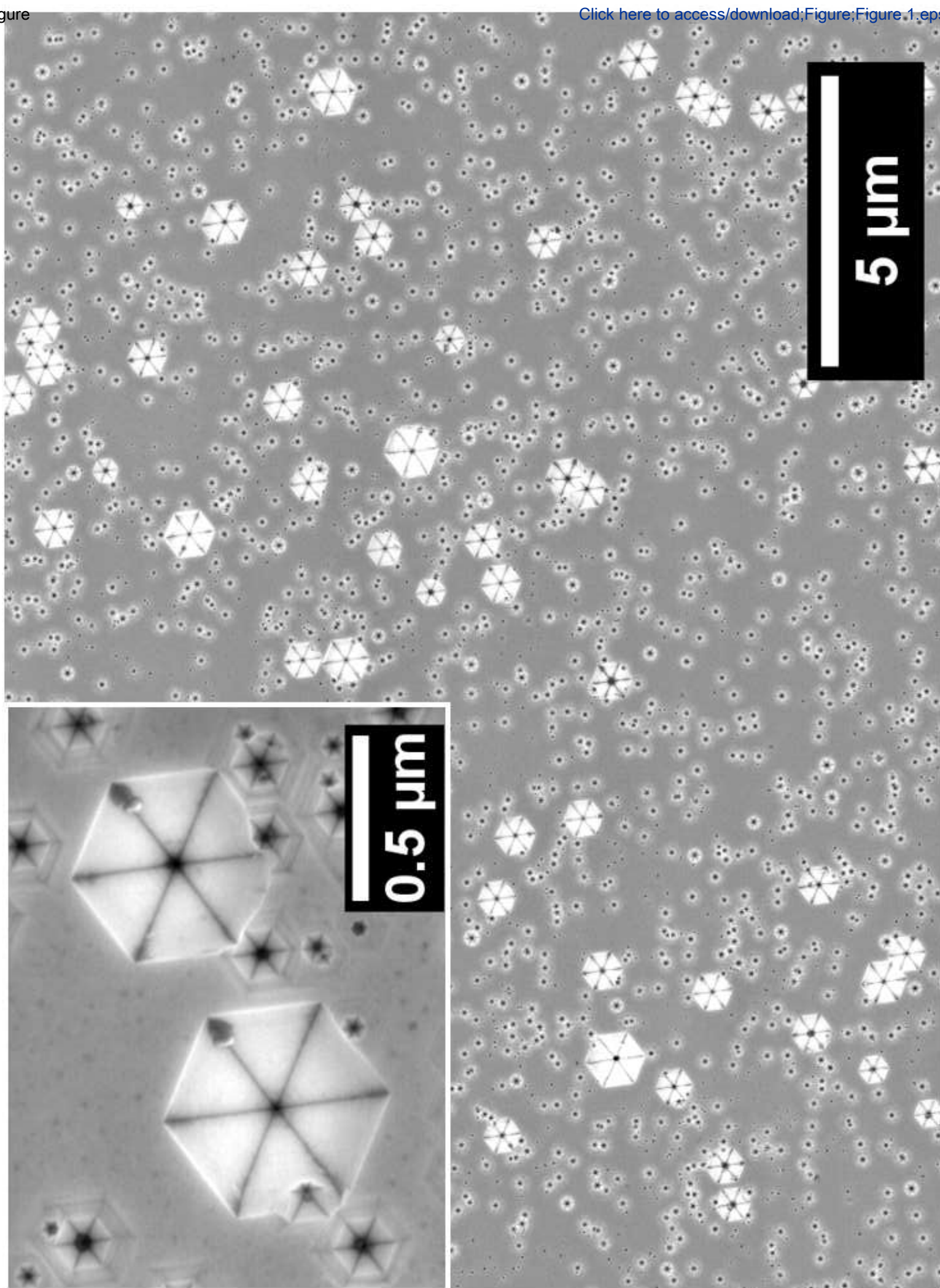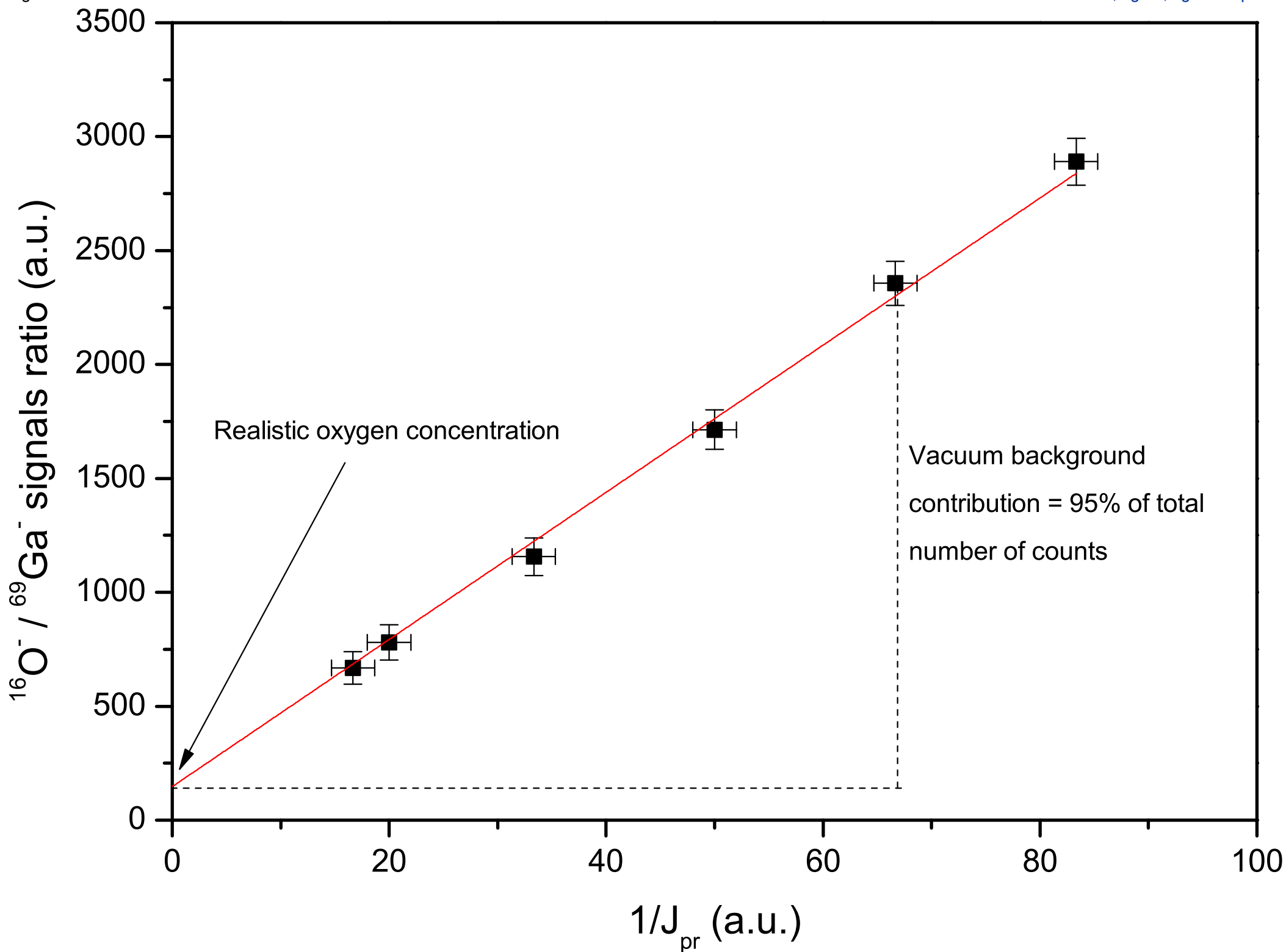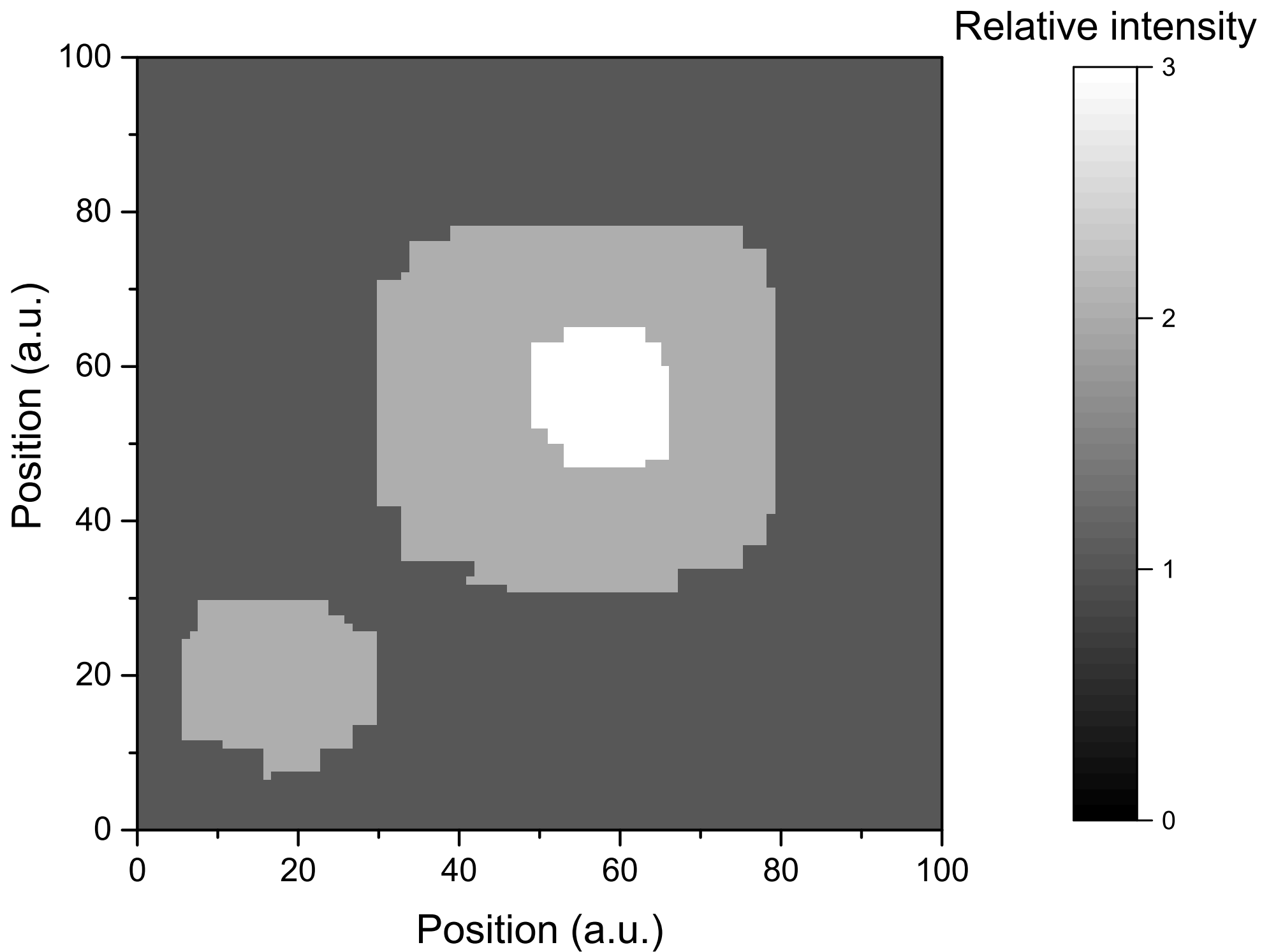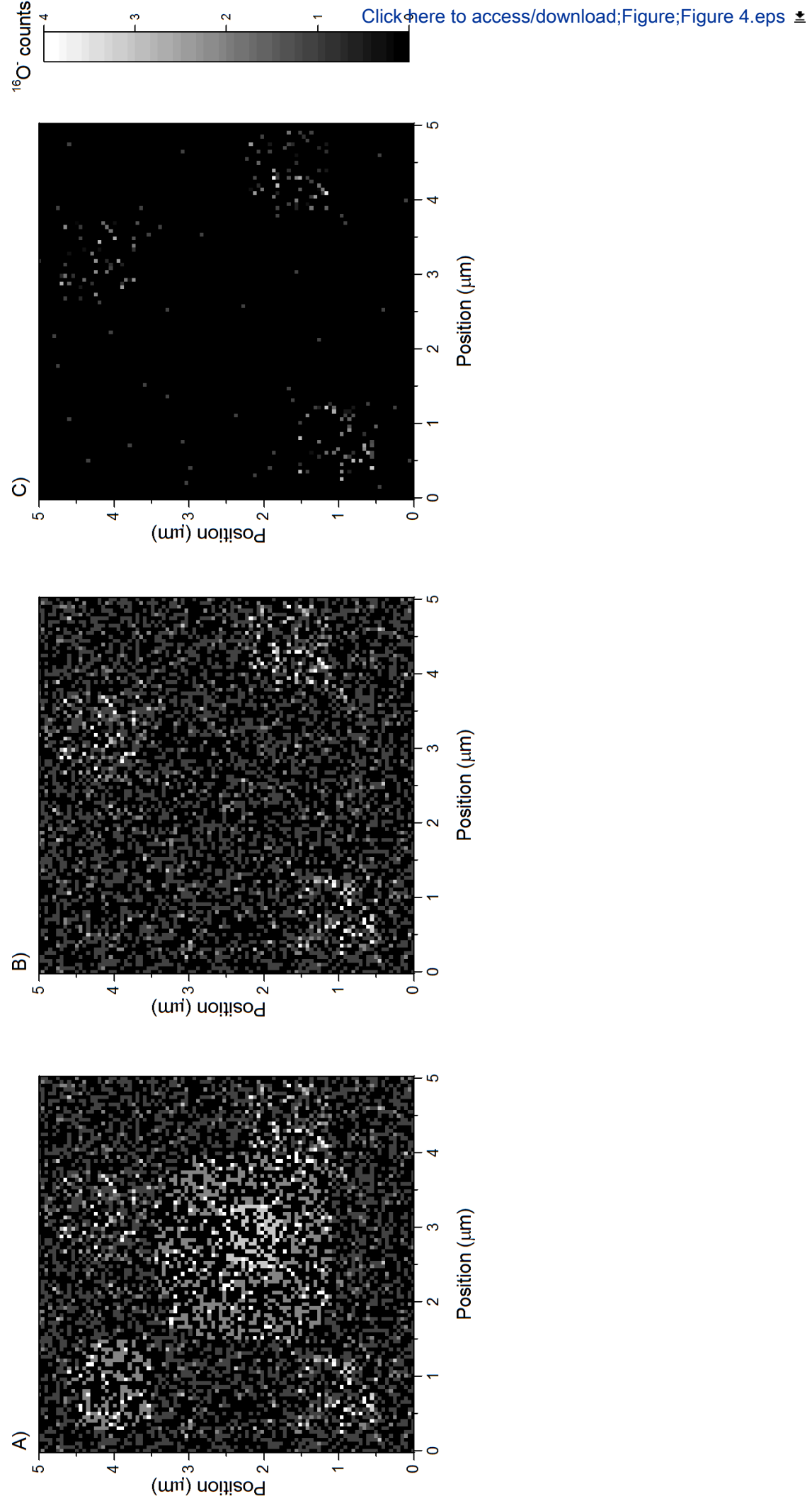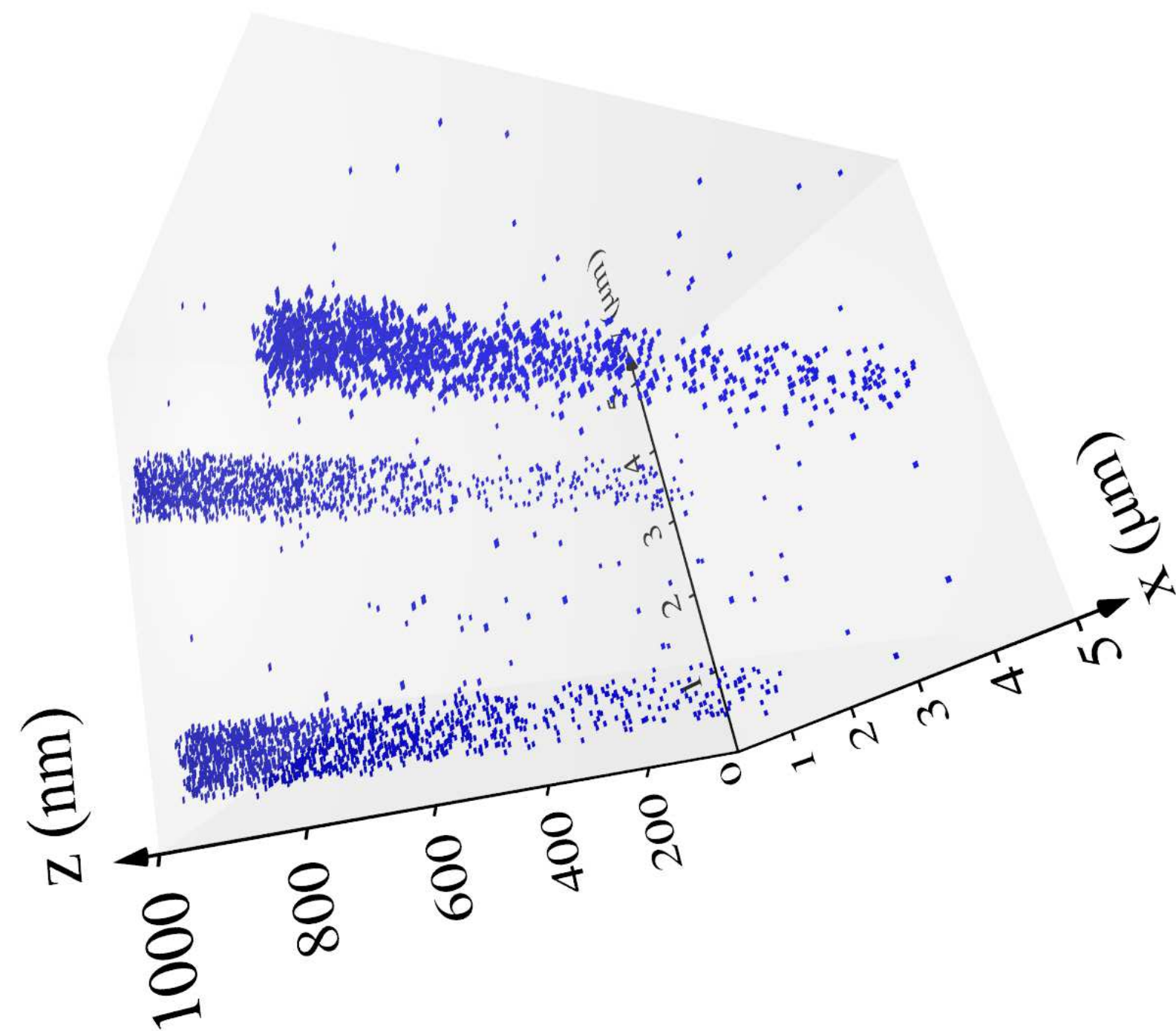
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Figure 7.mp4

Supplemental Figure 1

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Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Heating plate with ceramic top plate	IKA - Werke GmbH	3644200	for defect selective etching; yellow MAG HP 7
Hydrochloric acid (HCl) solution 35-38%	Chempur	115752837	for etchant removal; pure p.a.; CAS: 7647-01-0
Magnesium oxide (MgO)	Chempur	116140200	for eutectic solid etchant prepration; pure p.a.; CAS: 1309-48-4
Potassium hydroxide (KOH)	POCH S.A.	746800113	for eutectic solid etchant prepration; pure p.a.; CAS: 1310-58-3
Sodium hydroxide (NaOH)	POCH S.A.	810925112	for eutectic solid etchant prepration; pure p.a.; CAS: 1310-73-2
Secondary ion mass spectrometer	CAMECA	IMS SC Ultra	
Scanning electron microscope	Hitachi	SU8230	

Dear Editor and Reviewers,

We are very thankful for your comments about the protocol. We followed your suggestions and we believe that it helped us to increase the quality of our work.

Let me point by point discuss the changes:

Editorial comments:

1. Some reviewer comments have not been fully addressed (see below); note that other readers may have similar concerns. Please provide the information/explanations requested, or at least explanations in the manuscript for why these concerns are not relevant.
2. Reviewer 1 points:
a. Please provide information on the lateral resolution and *measured* size of the beam.

Lateral resolution for such experiments is predetermined by the size of a beam (sentence added to 3.1.1.). For spot size measurements user manual was cited (reference #15)

b. Please provide the pixel size.

Raster and analysis are provided along with spatial resolution (3.1.3)

c. 3.3.3: What depth do you reach here?

(It's now point 3.3.4) It is not of crucial importance as the test can be done on any other blank wafer and the depth will vary a lot depending on a material. Please note that in this point no depth profile is obtained but an image.

d. 4.5: More information on how the superposition is done may be helpful.

Suitable information about image editor softawe with layers support was added

3. Reviewer 2 points:
a. Please provide more information why 'it can be assumed that each point of the sample has the same probability to adsorb these atoms.'

A more clear explanation is included in the introduction

b. 3.3.1: More information on this procedure may be helpful.

This point is now expanded and even though reading the source material is beneficial it is possible to perform it without any knowledge about it

4. Summary, Abstract, Introduction: The protocol is generally introduced in a roundabout way in these sections ('the method allows', etc.) and it is not clear what exactly is done in the protocol from reading these sections. A sentence or two saying what the protocol is (e.g., 'here, we present a method to…') would be helpful.

Sections have been modified accordingly

5. The GaN surface is not in the Table of Materials, nor is other information available for how to obtain it.

The experiment can be performed on any GaN sample so it wouldn't be good to point a specific type of samples. Furthermore similar measurements can be done for other materials and/or dopant/contamination atoms and thus we decided to not include any information about the sample in the Table of Materials. In point 1.2.1 we mentioned which samples we used with a proper citation (publication and electronic supplementary information contain many details about growth process)

6. 3.3.2: Do you mean 50 µm × 50 µm and 35 µm × 35 µm here?

Raster and analysis area are now presented in point 3.1.3.

7. Results: It may be best to show an example of 'random distribution of oxygen counts' as a figure.

Figure 8 presents such a result. Additionally Figure 9 presents a typical result obtained with an unstable beam.

8. Please provide a legend for Figure 7.

Done

9. Figure 2: How well does the line fit (e.g., R-squared)? Also, 'numer' is a typo.

Corrected. R2 provided in point 3.3.3

Sincerely,

Paweł Piotr Michałowski

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