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Instytut
Mikroelektroniki
i Fotoniki

Secondary Ion Mass Spectrometry

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31.05.2022

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Contents

1. Principles of SIMS
2. Basic applications
3. Quantitative analysis
4. CAMECA SC Ultra
5. Examples
6. Conclusions

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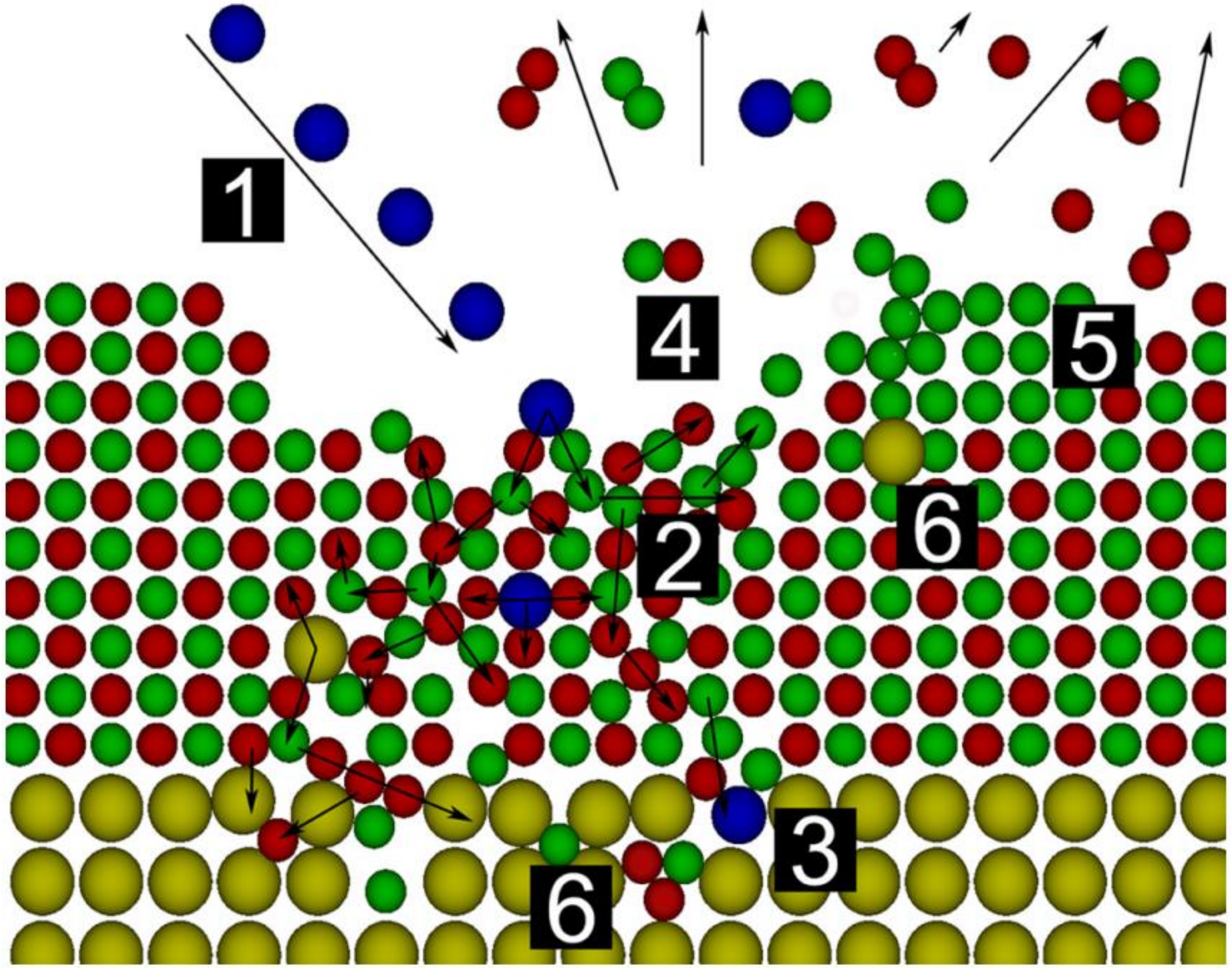
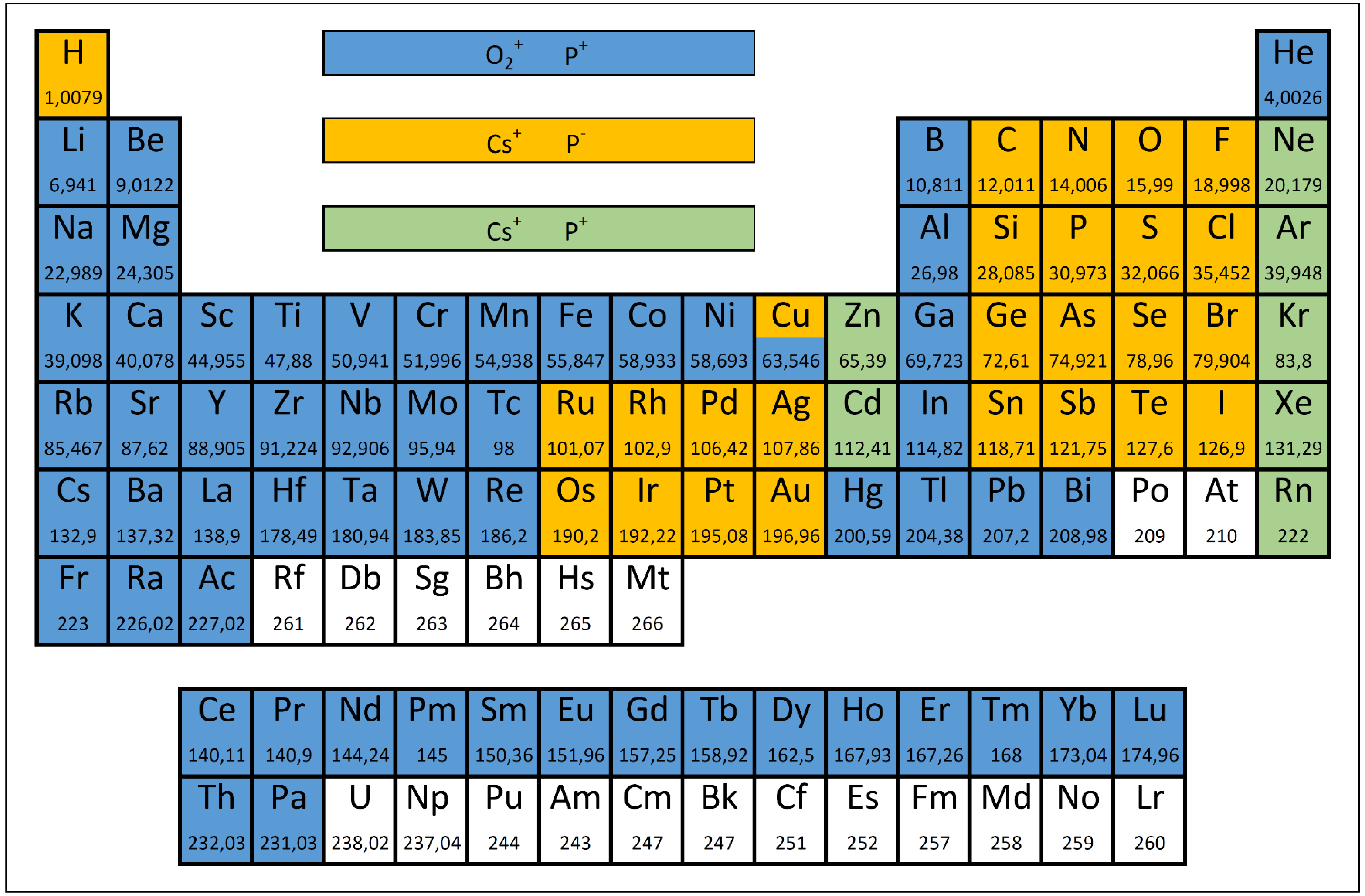
Fundamentals – Ion Bombardment



1. Primary beam
2. Collision cascade
3. Implantation
4. Sputtering and ionization
5. Preferential sputtering
6. Mixing

Fundamentals – two sources



🟦 O_2^+ P^+

🟨 Cs^+ P^-

🟩 Cs^+ P^+

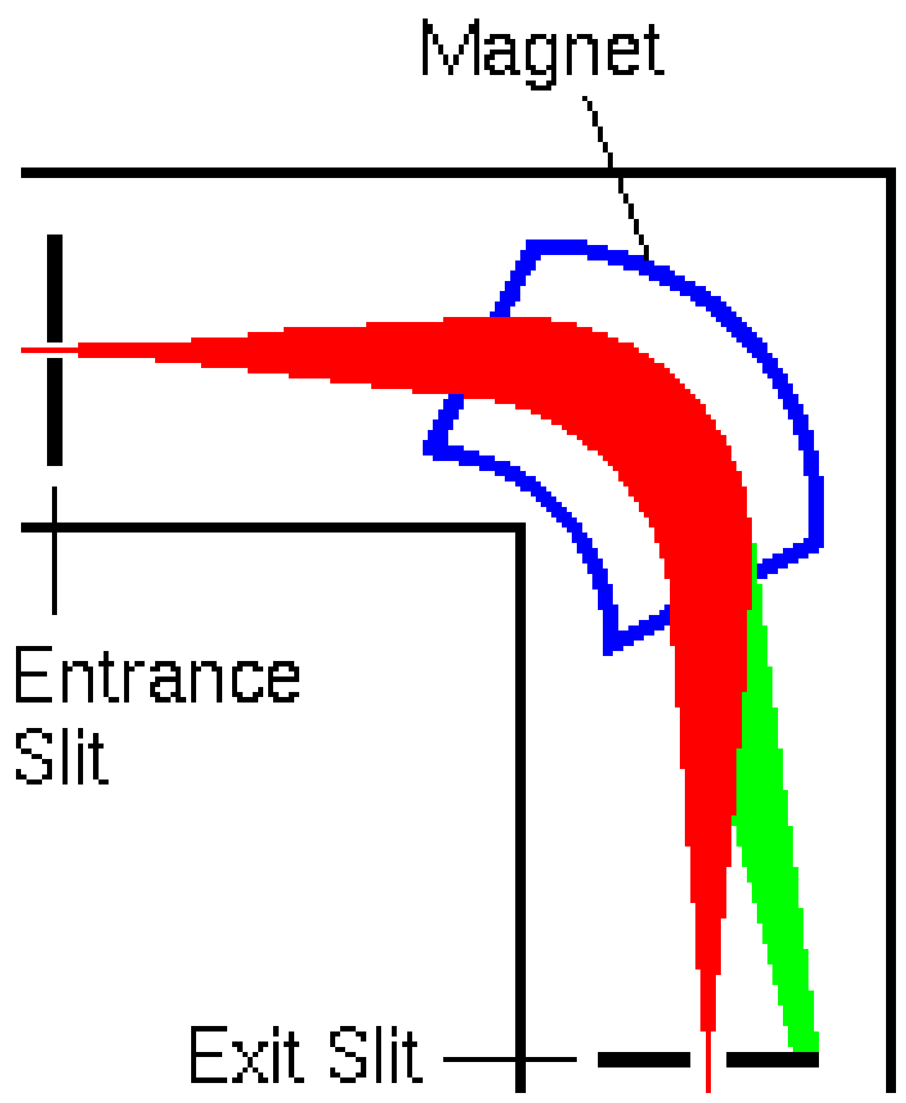
🟨 H 1,0079																	🟦 He 4,0026
🟦 Li 6,941	🟦 Be 9,0122											🟦 B 10,811	🟨 C 12,011	🟨 N 14,006	🟨 O 15,99	🟨 F 18,998	🟩 Ne 20,179
🟦 Na 22,989	🟦 Mg 24,305											🟦 Al 26,98	🟨 Si 28,085	🟨 P 30,973	🟨 S 32,066	🟨 Cl 35,452	🟩 Ar 39,948
🟦 K 39,098	🟦 Ca 40,078	🟦 Sc 44,955	🟦 Ti 47,88	🟦 V 50,941	🟦 Cr 51,996	🟦 Mn 54,938	🟦 Fe 55,847	🟦 Co 58,933	🟦 Ni 58,693	🟨 Cu 🟦 63,546	🟩 Zn 65,39	🟦 Ga 69,723	🟨 Ge 72,61	🟨 As 74,921	🟨 Se 78,96	🟨 Br 79,904	🟩 Kr 83,8
🟦 Rb 85,467	🟦 Sr 87,62	🟦 Y 88,905	🟦 Zr 91,224	🟦 Nb 92,906	🟦 Mo 95,94	🟦 Tc 98	🟨 Ru 101,07	🟨 Rh 102,9	🟨 Pd 106,42	🟨 Ag 107,86	🟩 Cd 112,41	🟦 In 114,82	🟨 Sn 118,71	🟨 Sb 121,75	🟨 Te 127,6	🟨 I 126,9	🟩 Xe 131,29
🟦 Cs 132,9	🟦 Ba 137,32	🟦 La 138,9	🟦 Hf 178,49	🟦 Ta 180,94	🟦 W 183,85	🟦 Re 186,2	🟨 Os 190,2	🟨 Ir 192,22	🟨 Pt 195,08	🟨 Au 196,96	🟦 Hg 200,59	🟦 Tl 204,38	🟦 Pb 207,2	🟦 Bi 208,98	Po 209	At 210	🟩 Rn 222
🟦 Fr 223	🟦 Ra 226,02	🟦 Ac 227,02	Rf 261	Db 262	Sg 263	Bh 264	Hs 265	Mt 266									
		🟦 Ce 140,11	🟦 Pr 140,9	🟦 Nd 144,24	🟦 Pm 145	🟦 Sm 150,36	🟦 Eu 151,96	🟦 Gd 157,25	🟦 Tb 158,92	🟦 Dy 162,5	🟦 Ho 167,93	🟦 Er 167,26	🟦 Tm 168	🟦 Yb 173,04	🟦 Lu 174,96		
		🟦 Th 232,03	🟦 Pa 231,03	U 238,02	Np 237,04	Pu 244	Am 243	Cm 247	Bk 247	Cf 251	Es 252	Fm 257	Md 258	No 259	Lr 260		

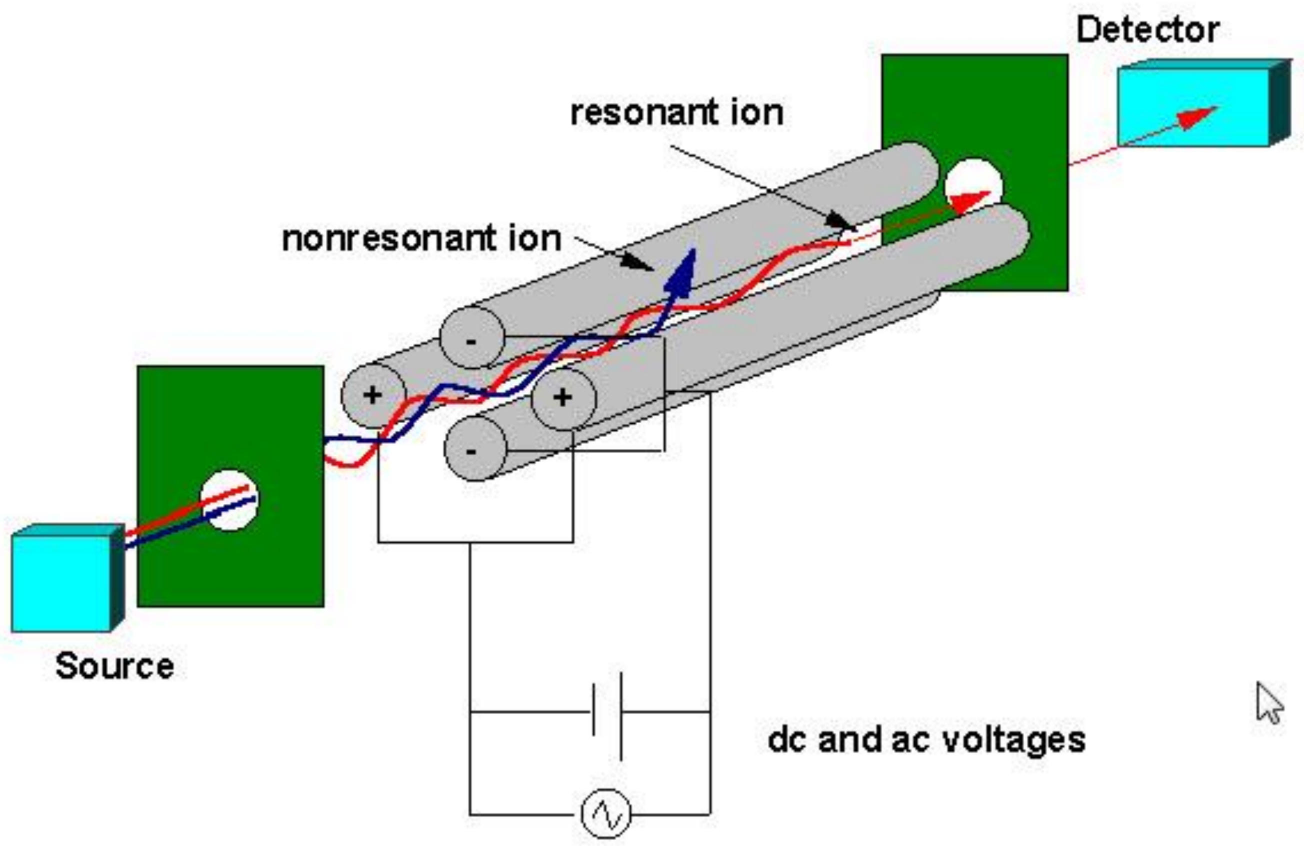
O_2^+ - electronegativity – formation of cations

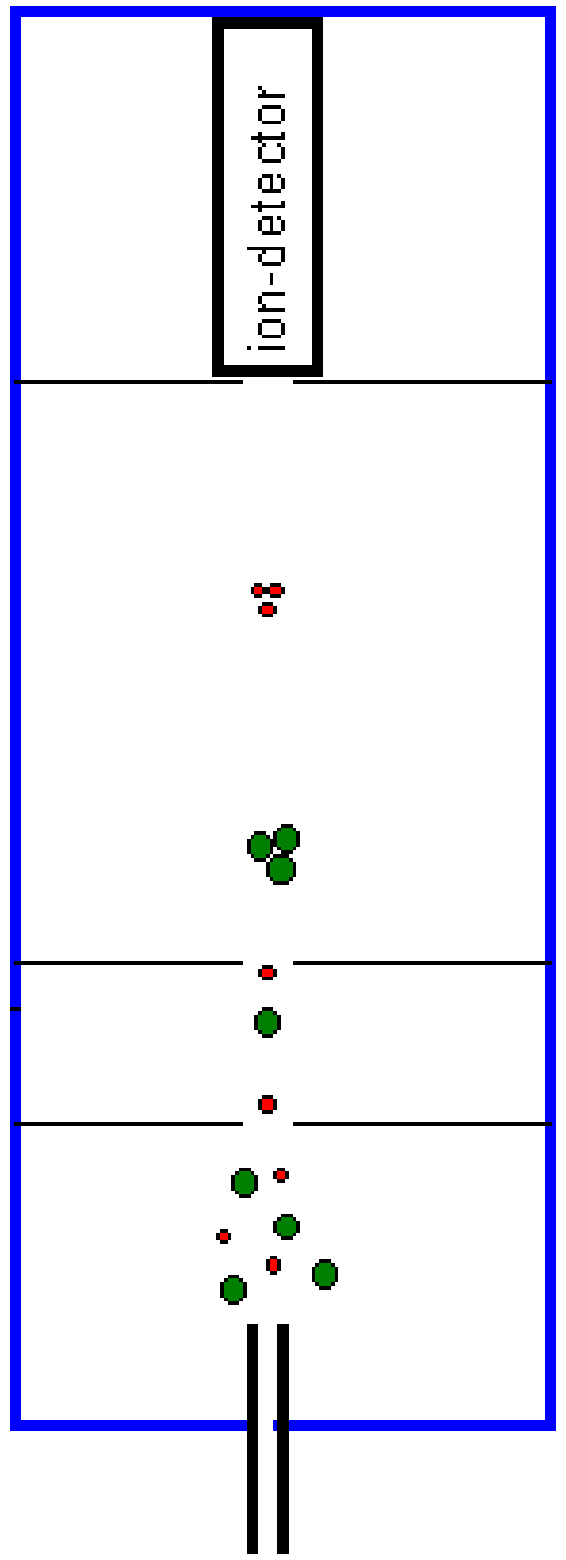
Cs^+ - decreases work function of electrons – formation of anions

Four order of magnitude difference!!!

Fundamentals – detectors





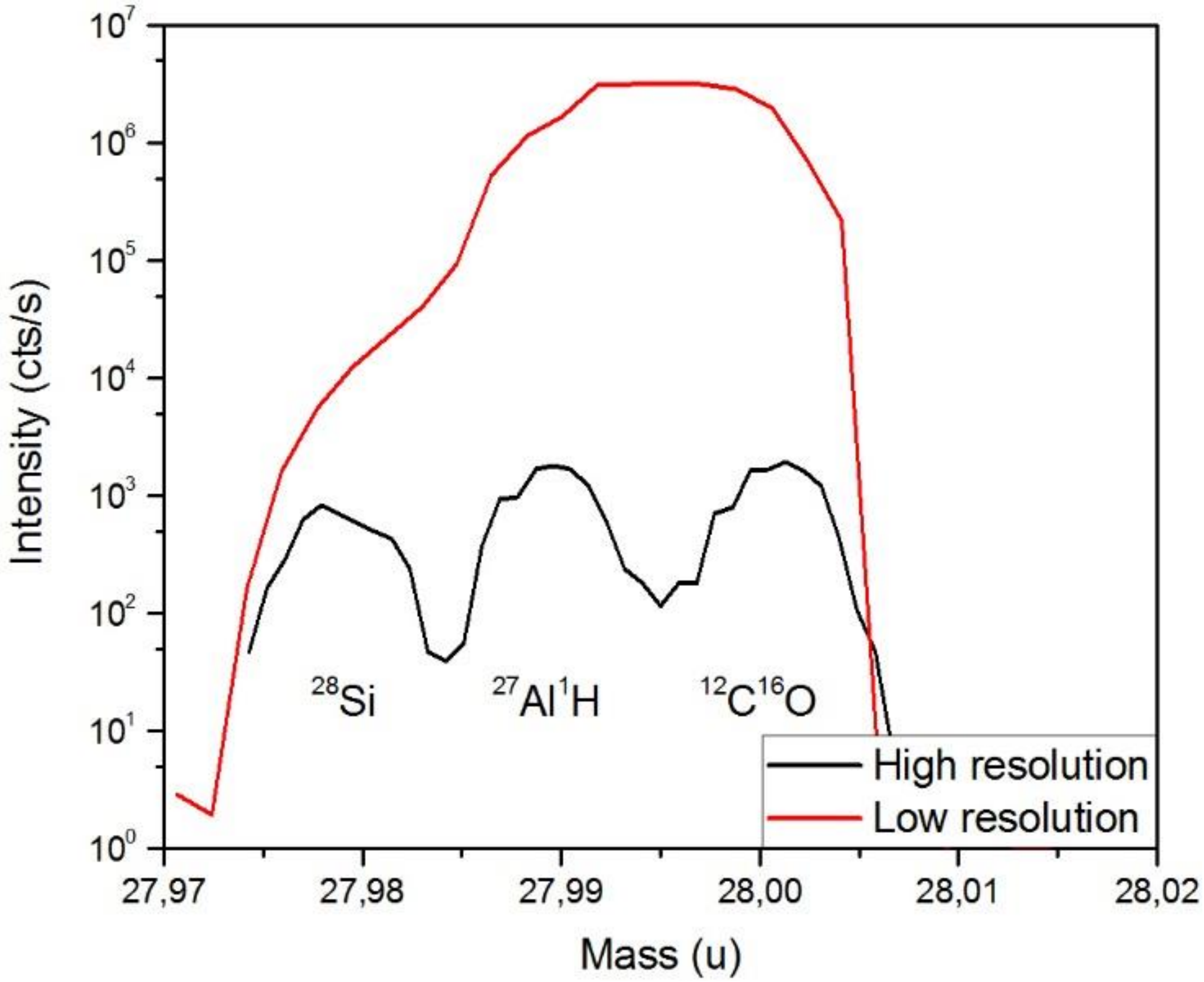


Magnetic sector
Best detection limits
Quantitative analysis

Quadrupole
Insulators

Time-of-Flight
Organic materials
Simultaneous measurements

Fundamentals – mass interferences



Solutions

- High mass resolution
- Different isotopes
- Monoatomic ions

Lower sensitivity!

MRP = m/Δm
^{28}Si – ^{12}C^{16}O MRP = 1246
^{28}Si – ^{27}Al^{1}H MRP = 2231
^{31}P – ^{30}Si^{1}H MRP = 3116
^{104}Ru – ^{104}Pd MRP = 74452

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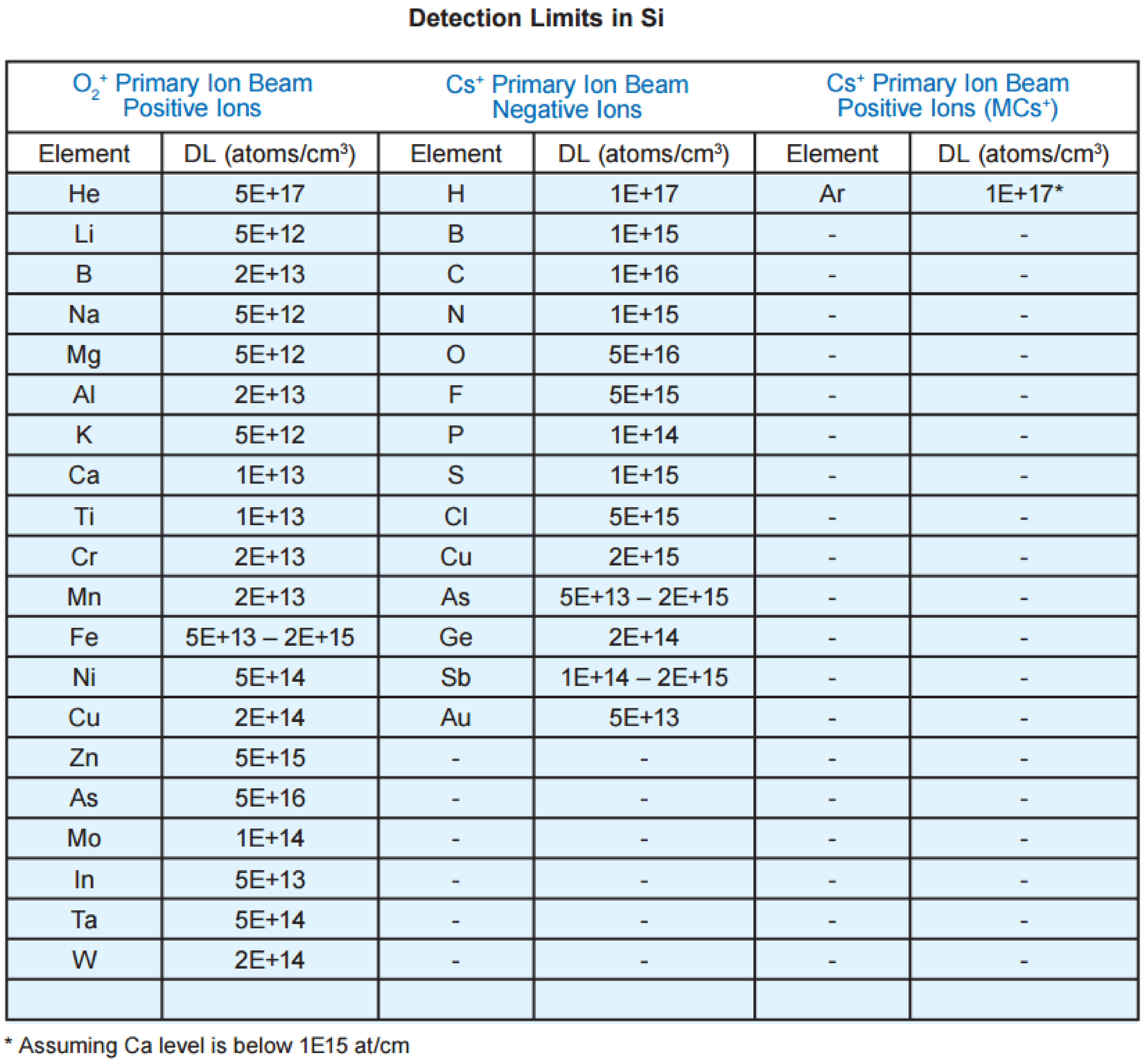
Basic applications



Detection Limits in Si

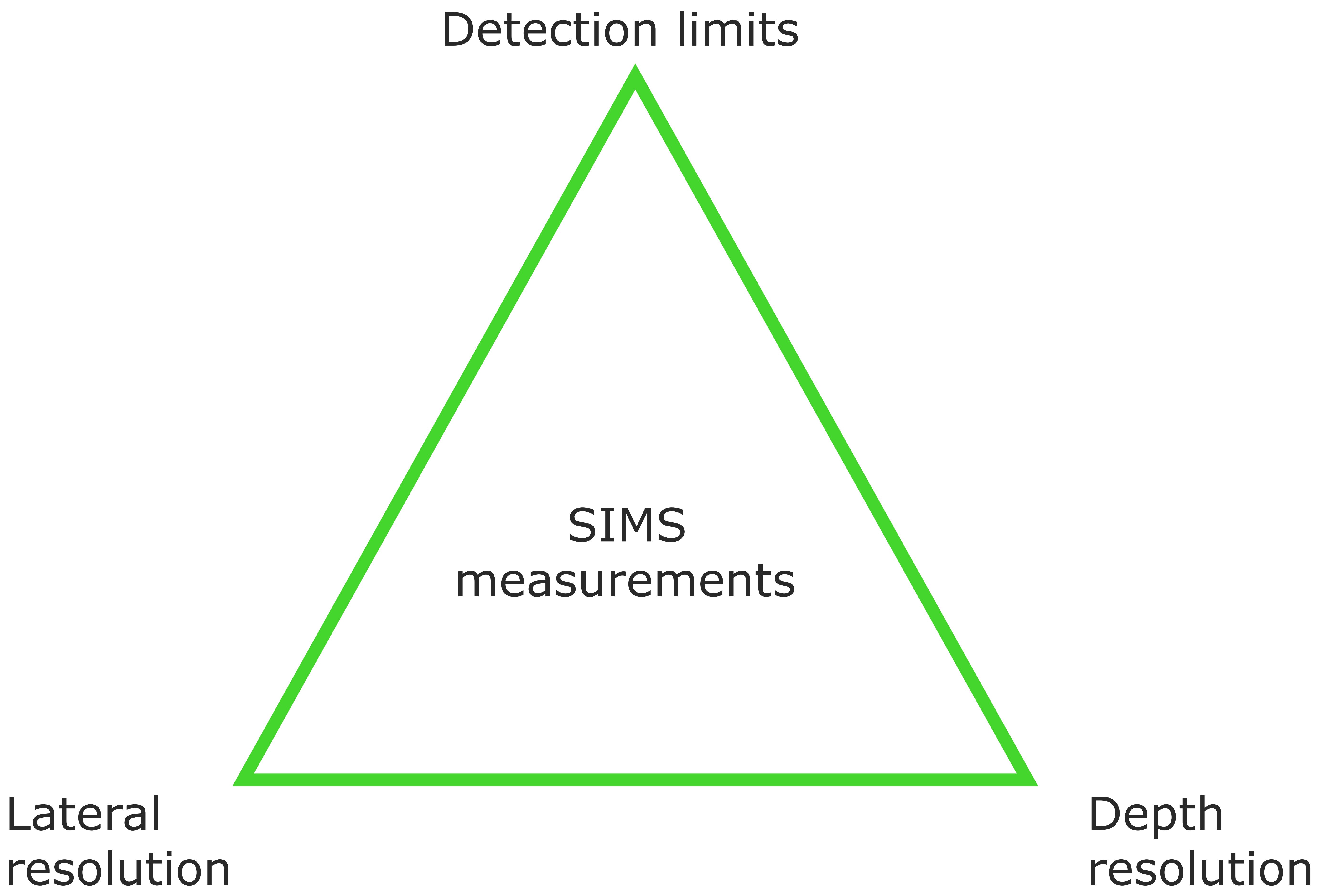
O_2^+ Primary Ion Beam Positive Ions		Cs^+ Primary Ion Beam Negative Ions		Cs^+ Primary Ion Beam Positive Ions (MCs^+)	
Element	DL (atoms/cm^3)	Element	DL (atoms/cm^3)	Element	DL (atoms/cm^3)
He	5E+17	H	1E+17	Ar	1E+17*
Li	5E+12	B	1E+15	-	-
B	2E+13	C	1E+16	-	-
Na	5E+12	N	1E+15	-	-
Mg	5E+12	O	5E+16	-	-
Al	2E+13	F	5E+15	-	-
K	5E+12	P	1E+14	-	-
Ca	1E+13	S	1E+15	-	-
Ti	1E+13	Cl	5E+15	-	-
Cr	2E+13	Cu	2E+15	-	-
Mn	2E+13	As	5E+13 – 2E+15	-	-
Fe	5E+13 – 2E+15	Ge	2E+14	-	-
Ni	5E+14	Sb	1E+14 – 2E+15	-	-
Cu	2E+14	Au	5E+13	-	-
Zn	5E+15	-	-	-	-
As	5E+16	-	-	-	-
Mo	1E+14	-	-	-	-
In	5E+13	-	-	-	-
Ta	5E+14	-	-	-	-
W	2E+14	-	-	-	-

* Assuming Ca level is below 1E15 at/cm

- Elemental composition
- No/minimal information about chemical state
- Depth profile
- Lateral analysis + 3D

- Stability of layers
- Diffusion
- Dopants and contamination

Basic applications - limitations



Detection limits

SIMS
measurements

Lateral
resolution

Depth
resolution

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Quantitative analysis – basic equation

$$I(A) = I_P\, Y(A)\, \alpha(A)\, c(A)\, \eta$$

$I(A)$	secondary ion current
I_P	primary ion current
$Y(A)$	partial sputter yield
$\alpha(A)$	ionization probability
$c(A)$	concentration
η	transmission and detection coefficient

Challenges
- Matrix effect
- High sensitivity on conditions

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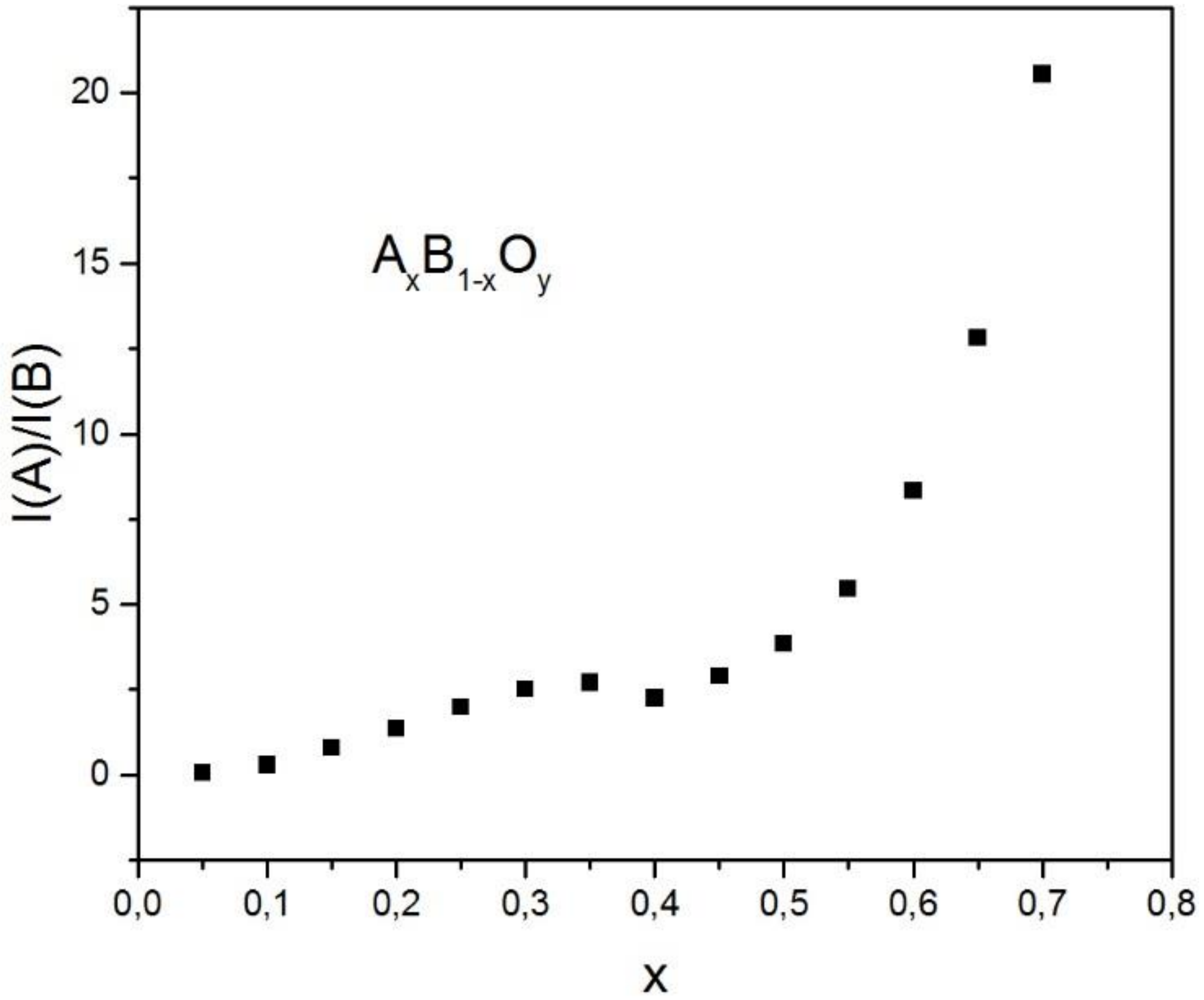
Quantitative analysis – elemental composition

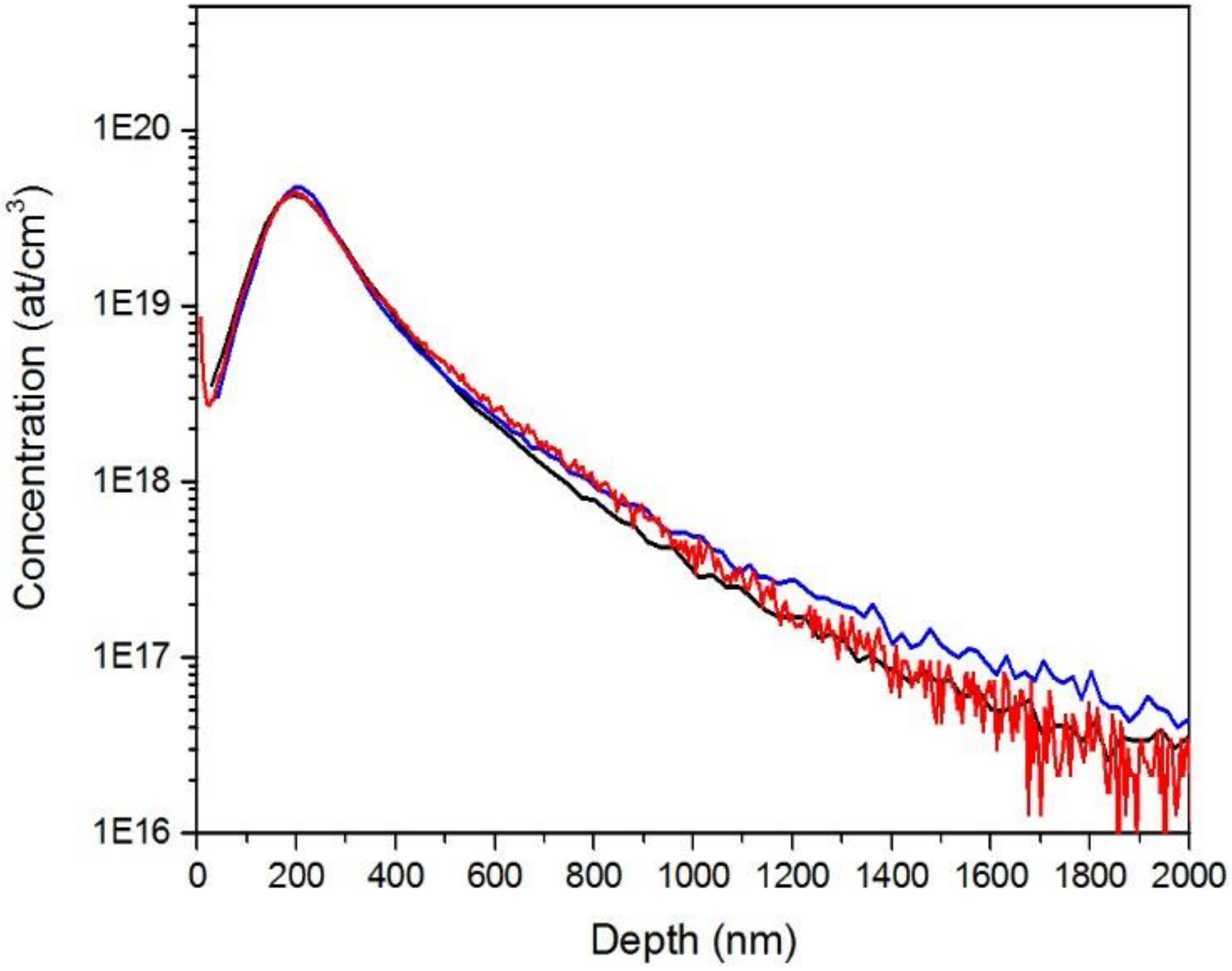


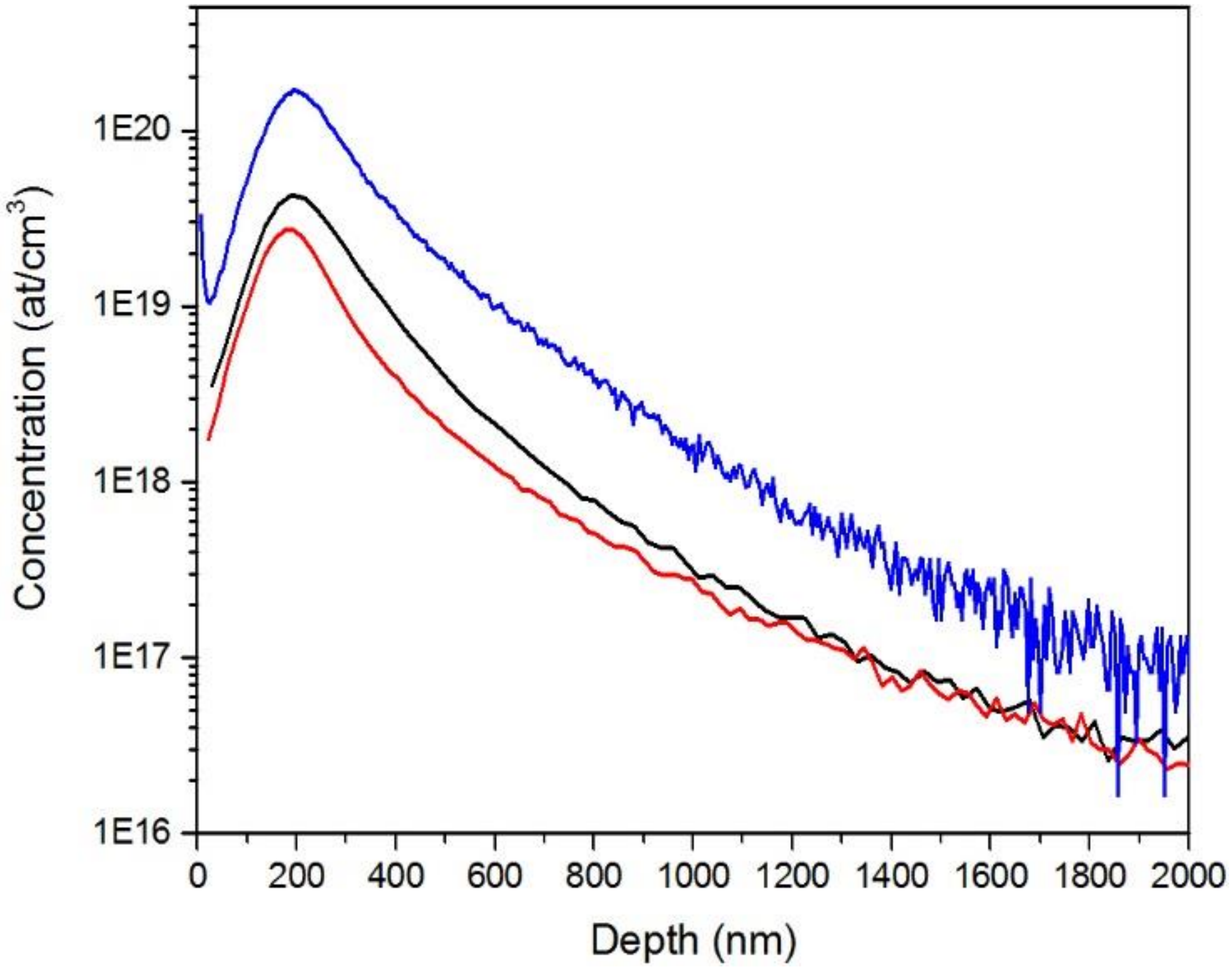
- Simple samples
- Complicated procedure
- Possible errors
- Identification: other techniques
- Depth profiles: good choice

Quantitative analysis – Dopants and contamination

Very precise measurements: $C(A) = RSF_A\, I(A) / I(M)$

RSF based on reference samples





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Ultra Low Impact Energy SIMS (ULIE SIMS)

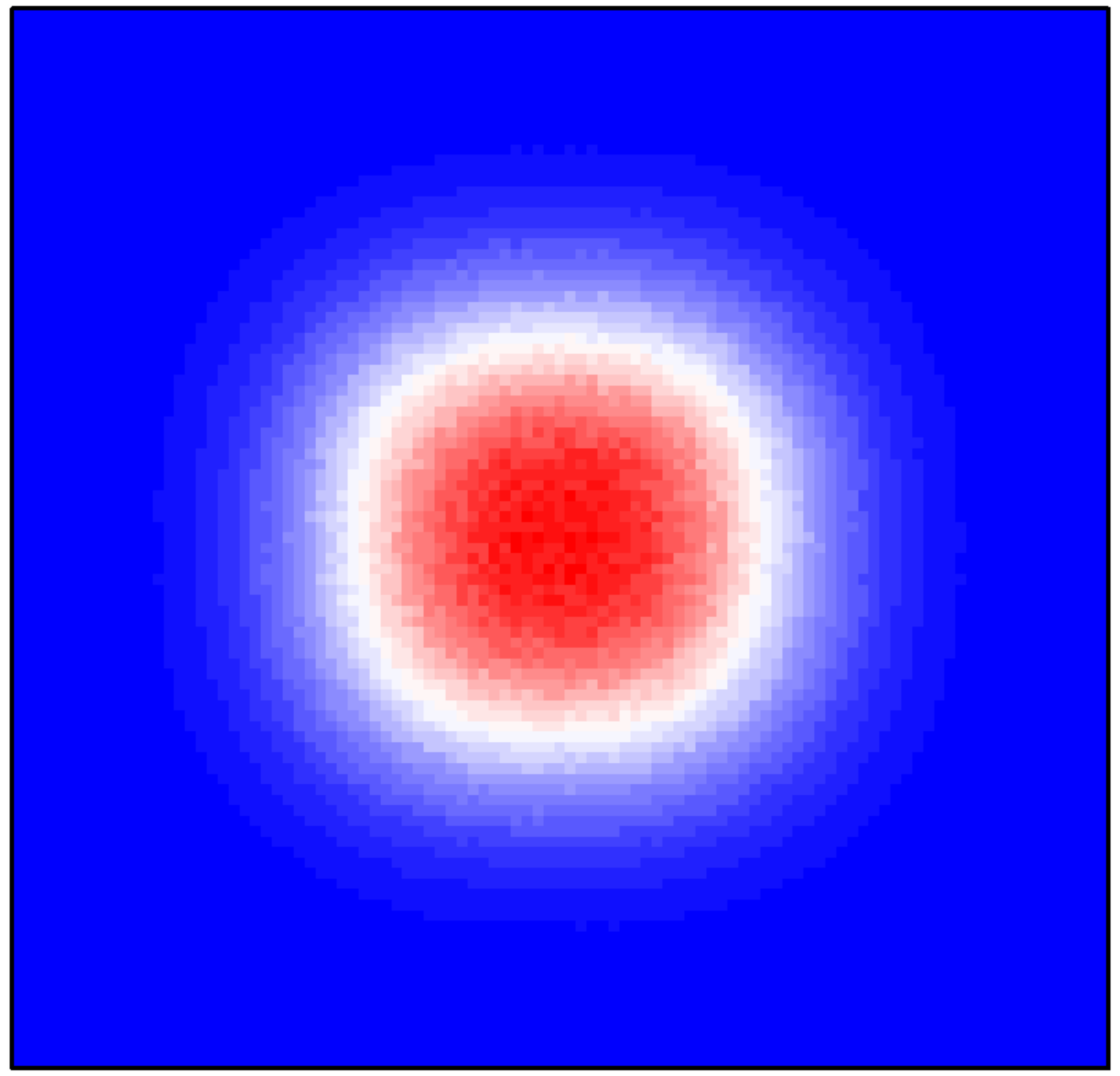
EXLIE (EXtreme Low Impact Energy) technology

- RF Plasma for oxygen column – down to 60 eV
- Floating voltage for cesium column – down to 90 eV

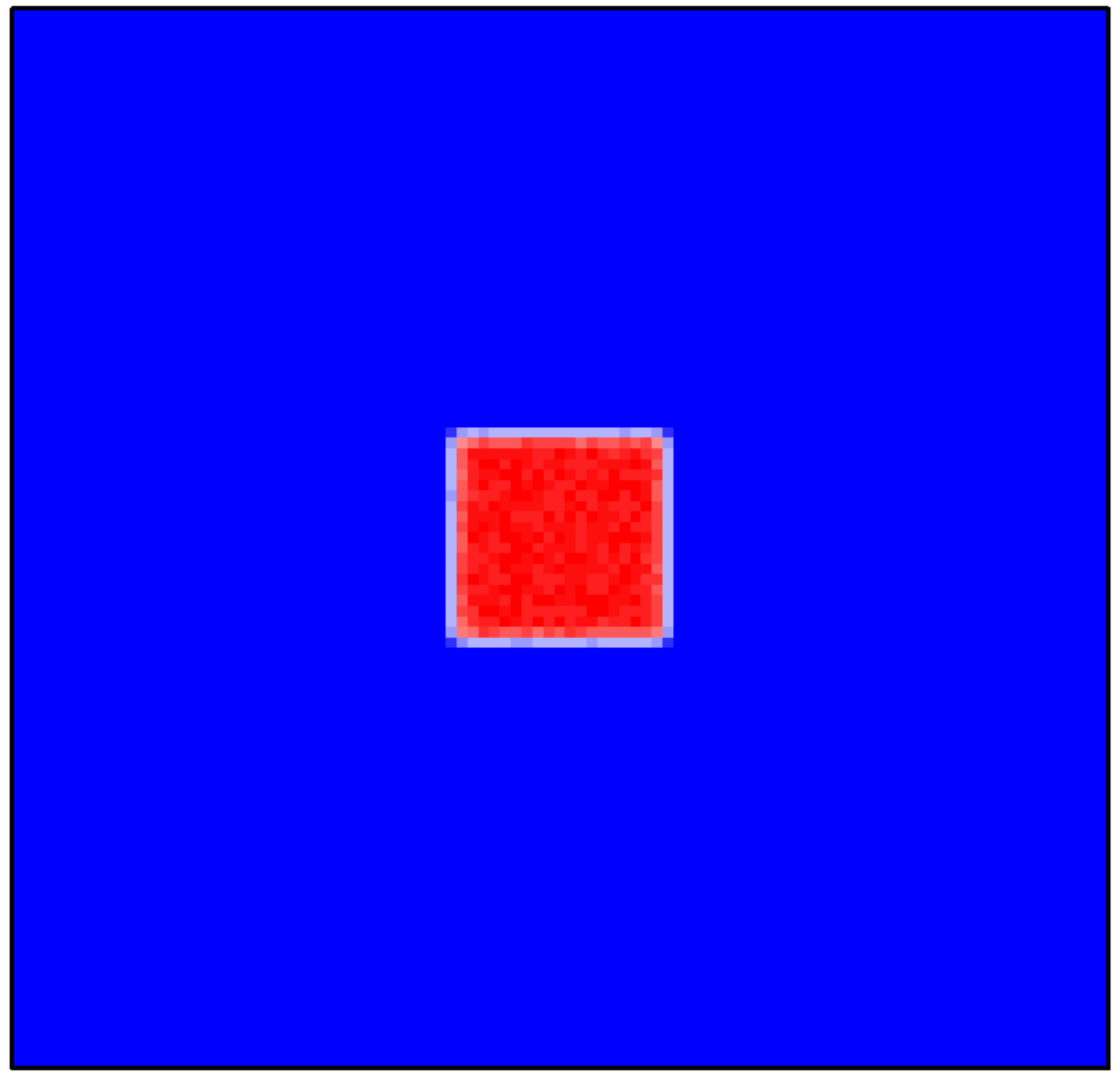
Beam shape

15 instruments!!!

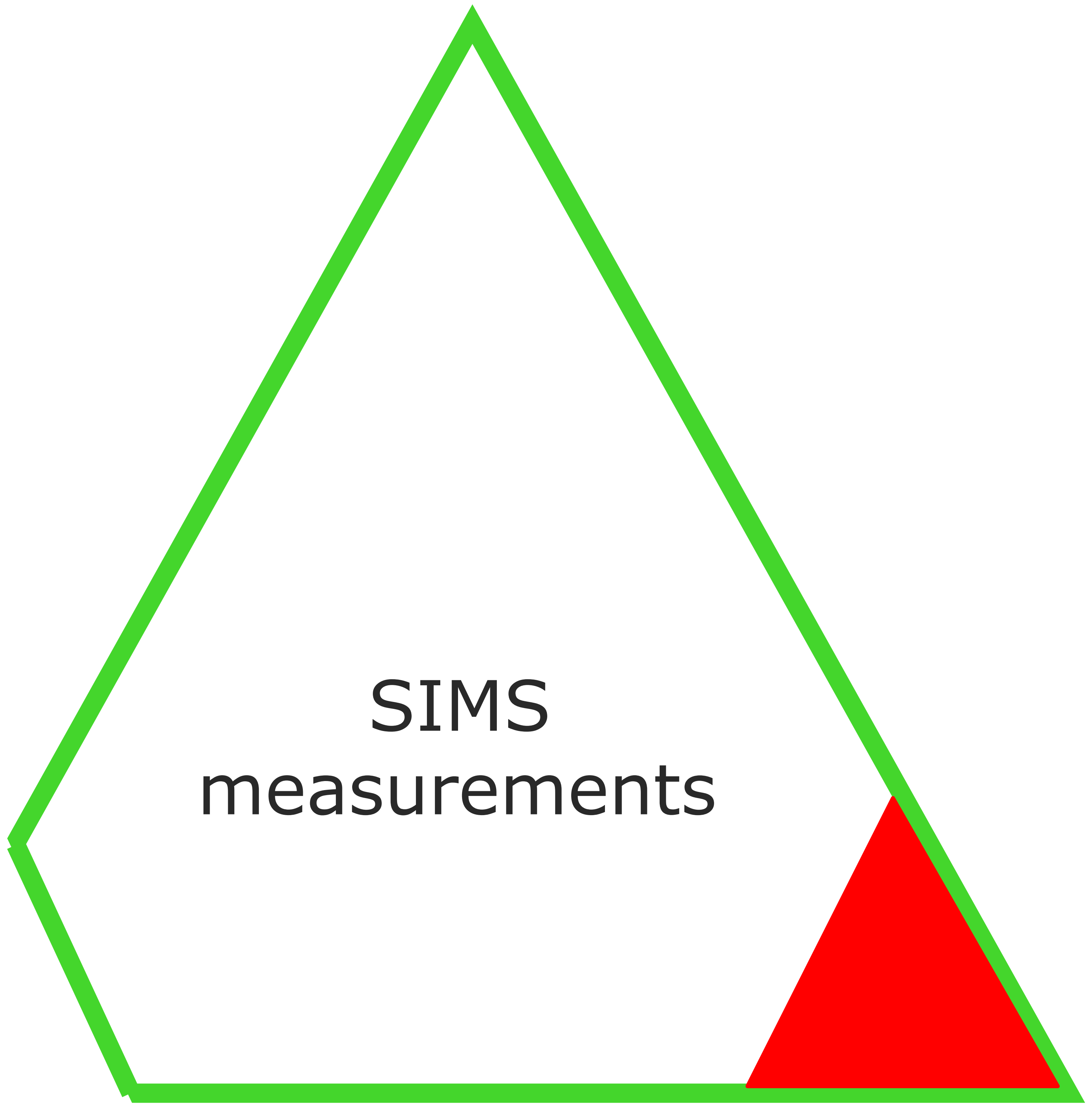
Typical Gaussian-shaped beam



Projected on square stencil



CAMECA IMS SC Ultra - limitations



Detection limits

SIMS measurements

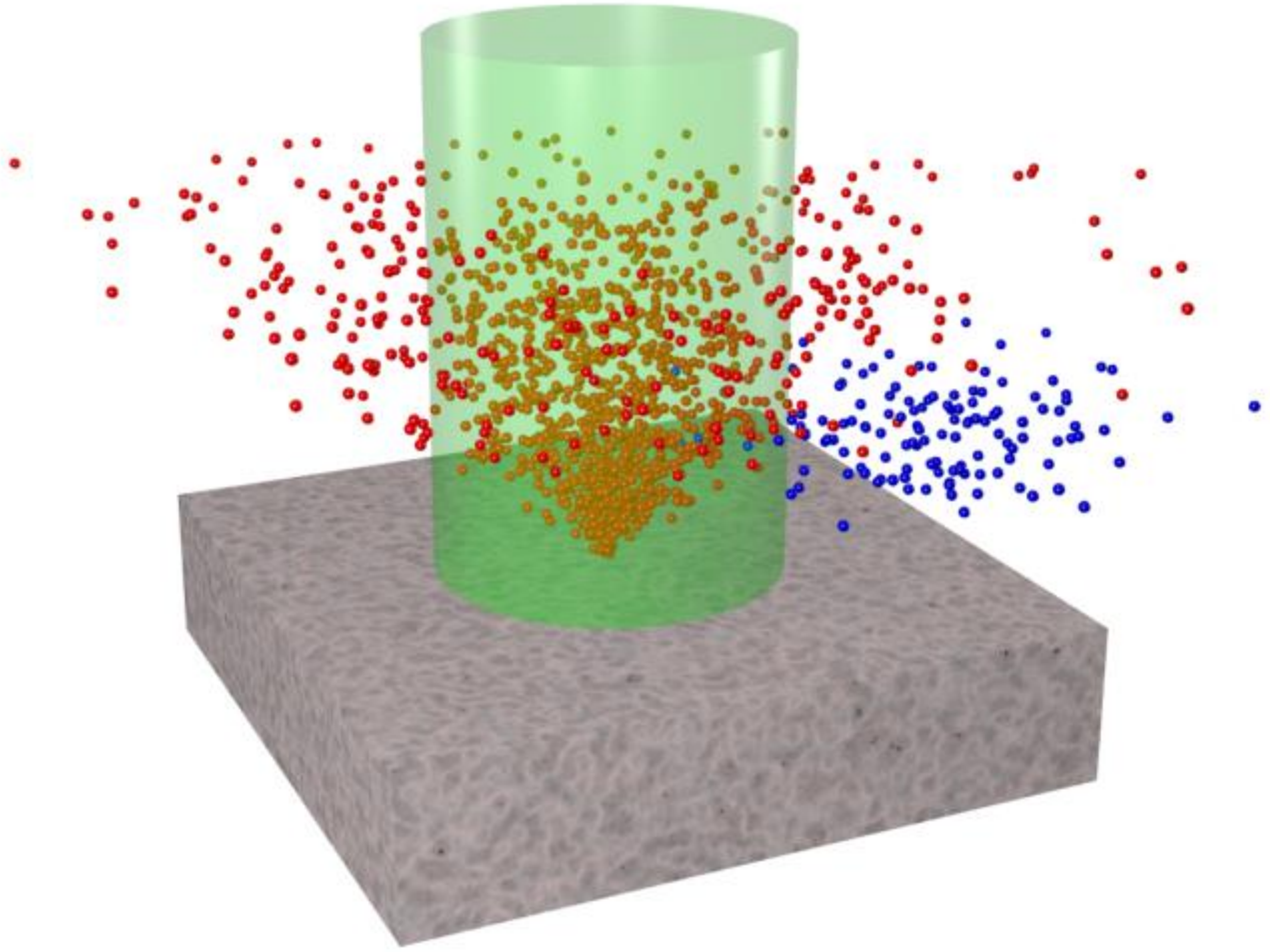
Lateral resolution ~ 1µm

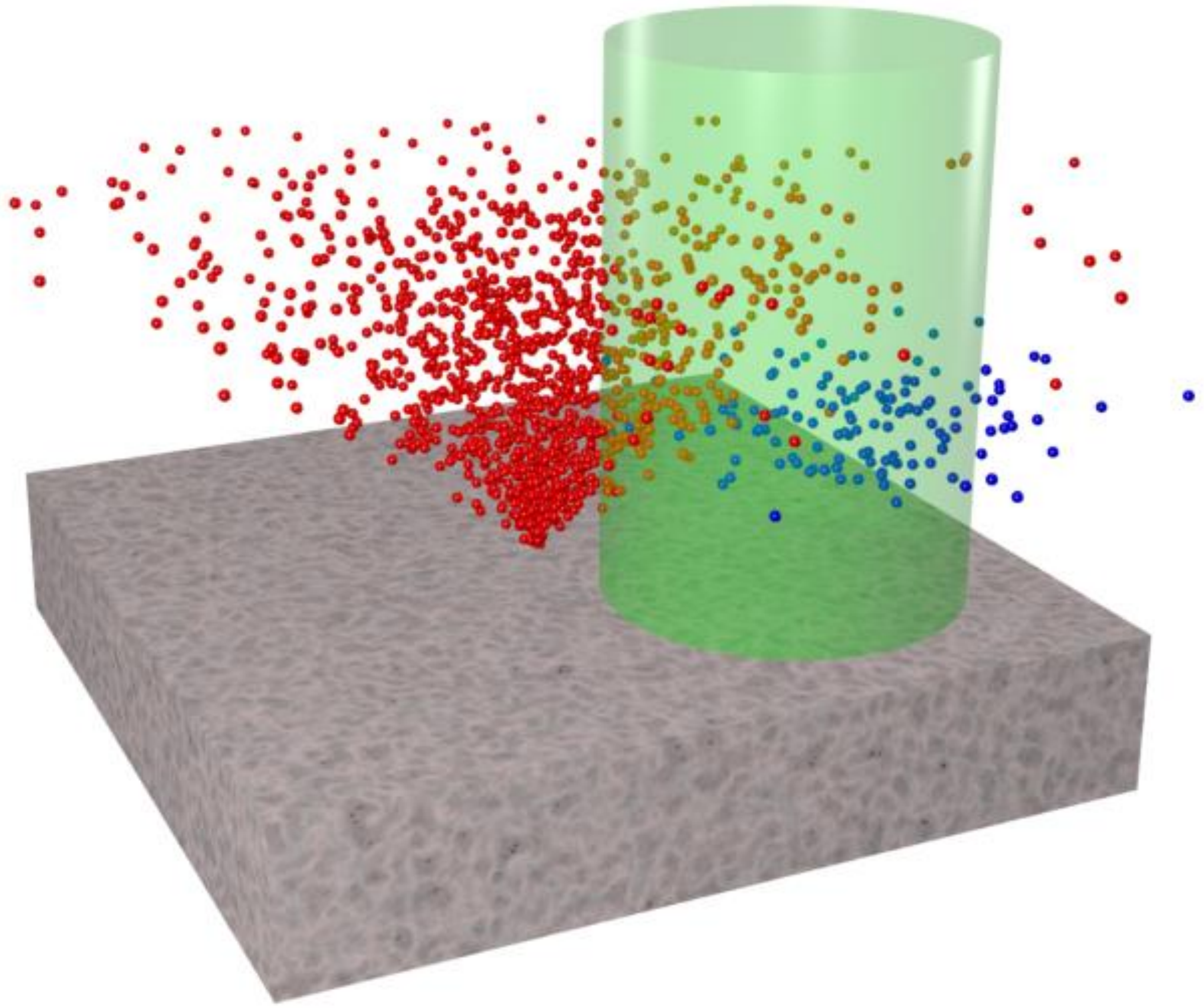
Depth resolution <1nm

CAMECA IMS SC Ultra – dedicated procedures

Type of procedures

- Standard/universal
- Dedicated


Standard


Dedicated

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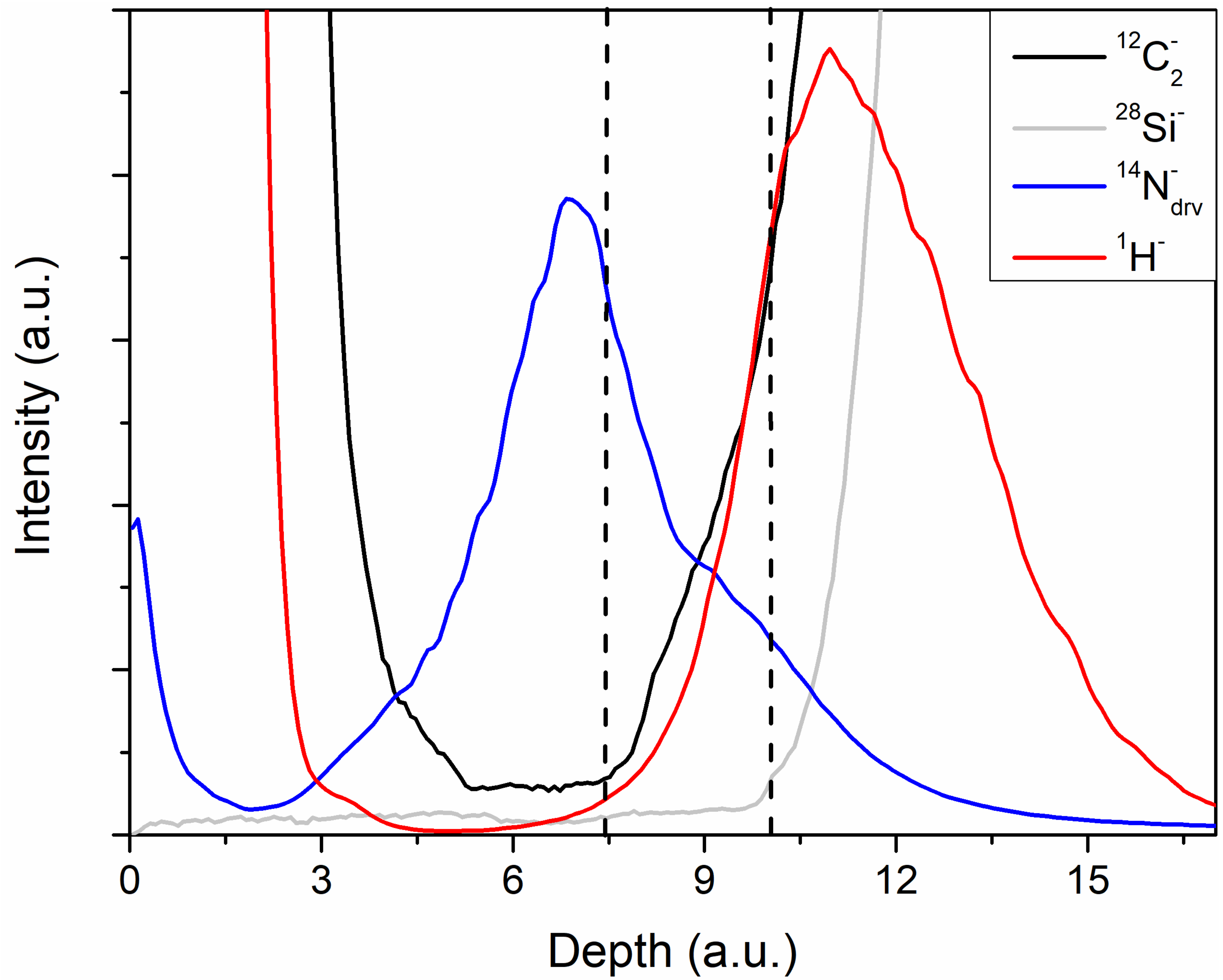
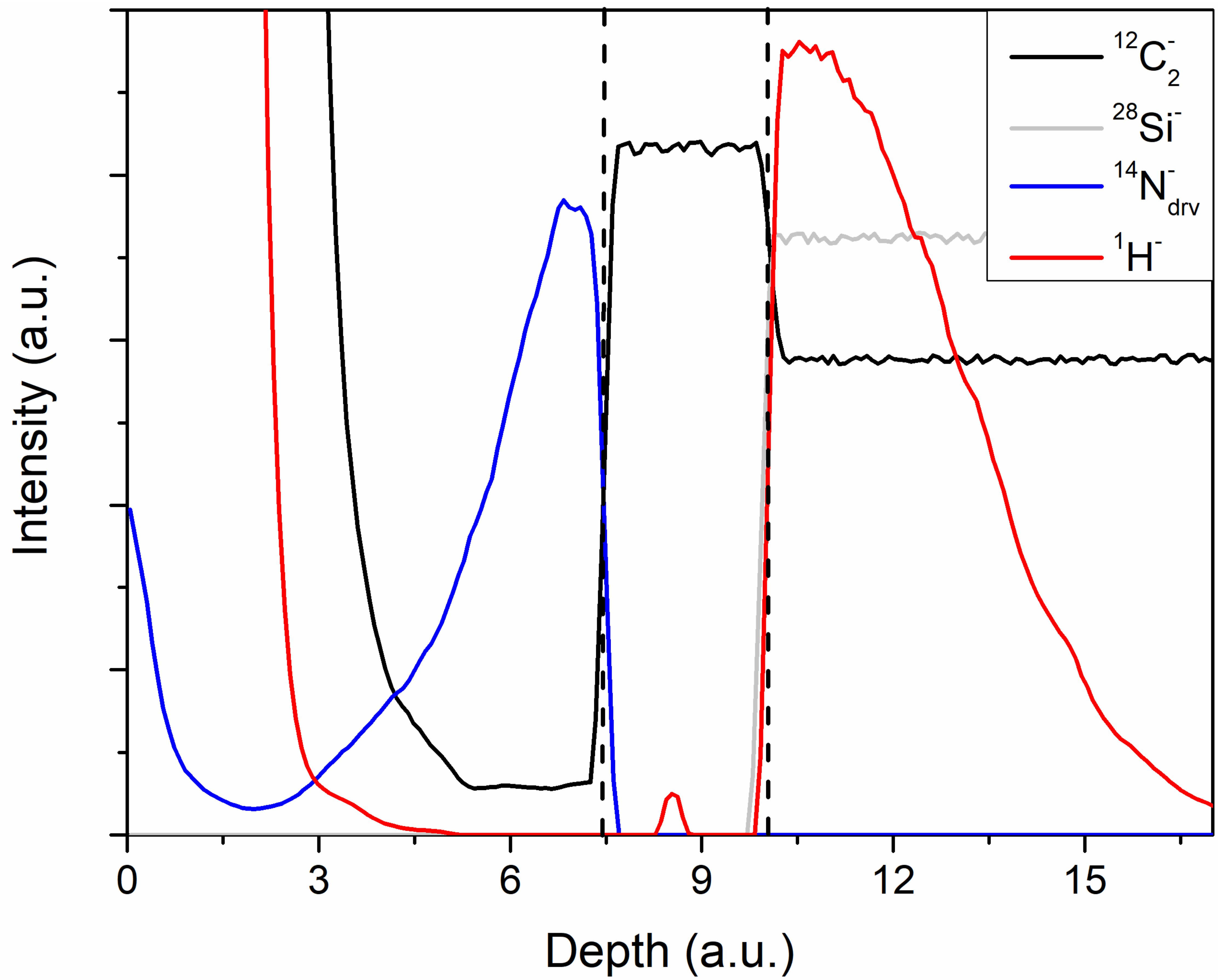
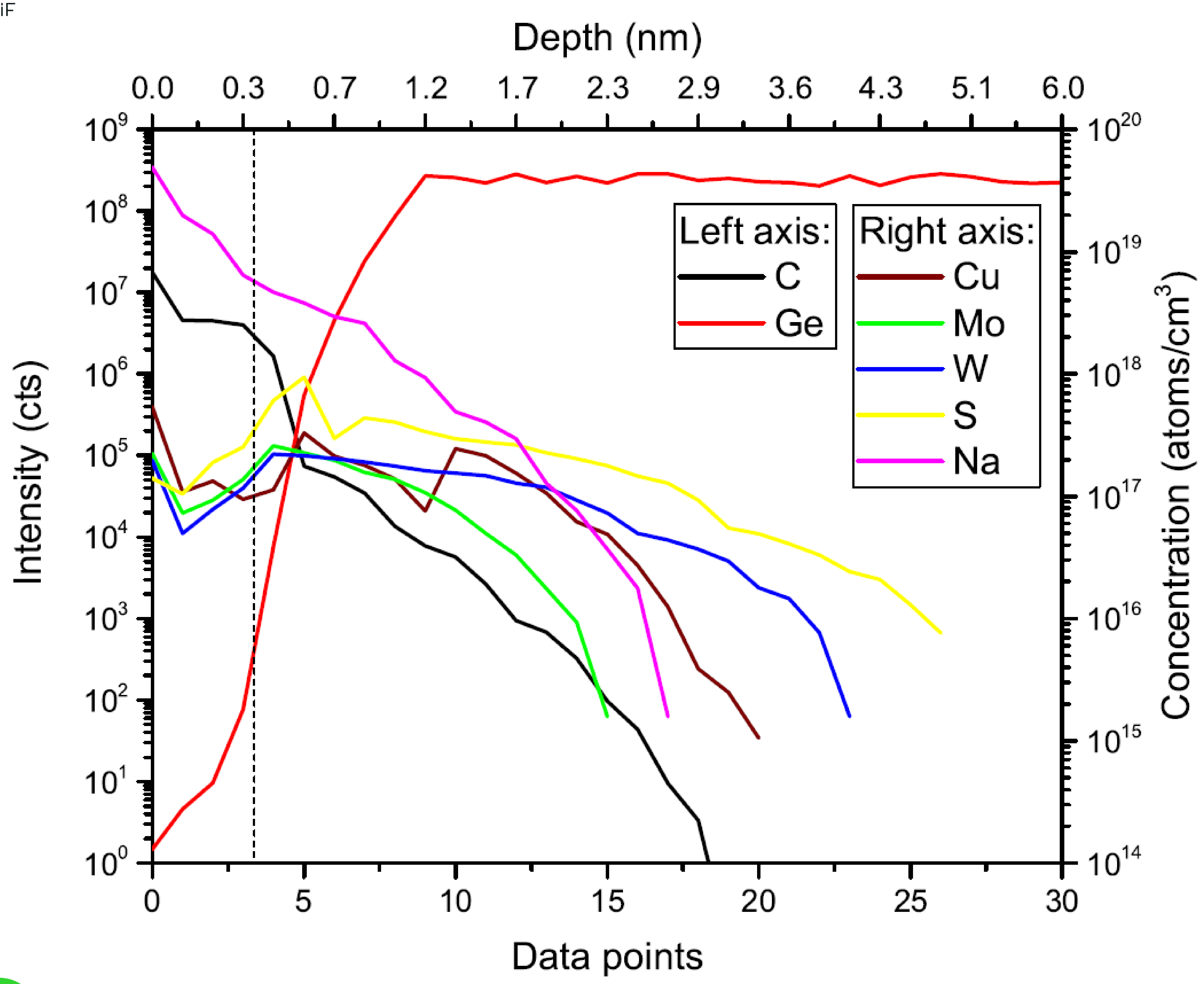
Graphene/SiC





Applied Physics Letters **109**, 011904 (2016)

How clean is Graphene?



Remarks

- 250 eV impact energy
- 45º incident angle

- Detection
- Localization?

Measurement **187**, 110308 (2022)

Solution

PROBLEMS AND POTENTIAL SOLUTIONS

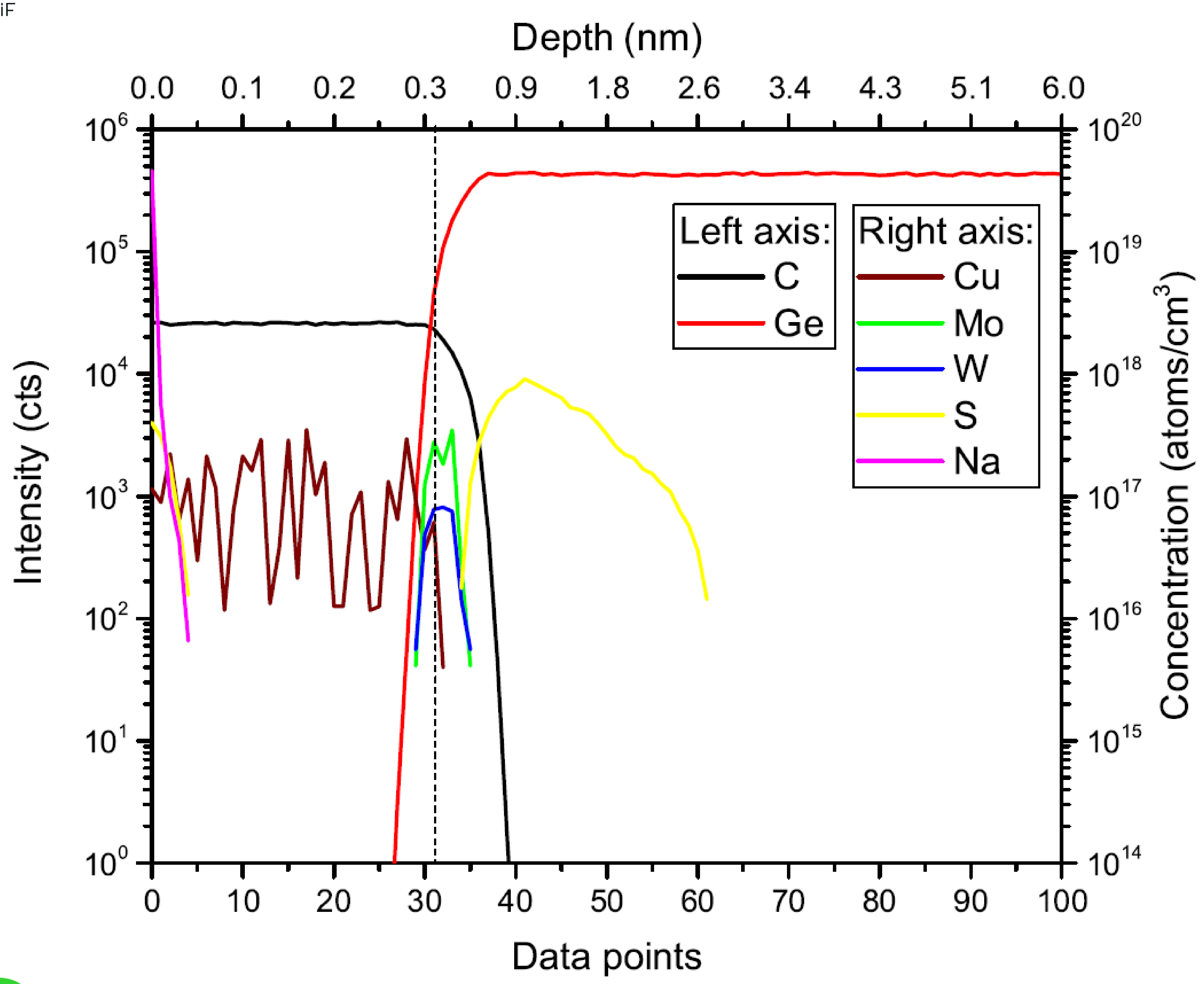
Problem	Potential solution	Resulting problems	Potential solution	Conclusion
Transition layer	Lower beam density	Signals intensity reduction	Higher integration time	Still a few data points per graphene
Ion mixing	Lower impact energy	Signals intensity reduction	Higher integration time	Still a few data points per graphene
Preferential sputtering	Higher impact energy	Bigger ion mixing	?	Not feasible

REALISTIC SOLUTION – HIGH INCIDENT ANGEL

Angle	Data points	Transition layer	Ion mixing	Preferential sputtering	Acquisition time	Detection limits (ppm)
45°	4 for graphene	Severe	Severe	Severe	5 minutes	0.2 – 1.5
75°	30 for graphene	Negligible	Negligible	Negligible	3 hours	0.8 – 2.9

Measurement **187**, 110308 (2022)

Enhanced procedure?



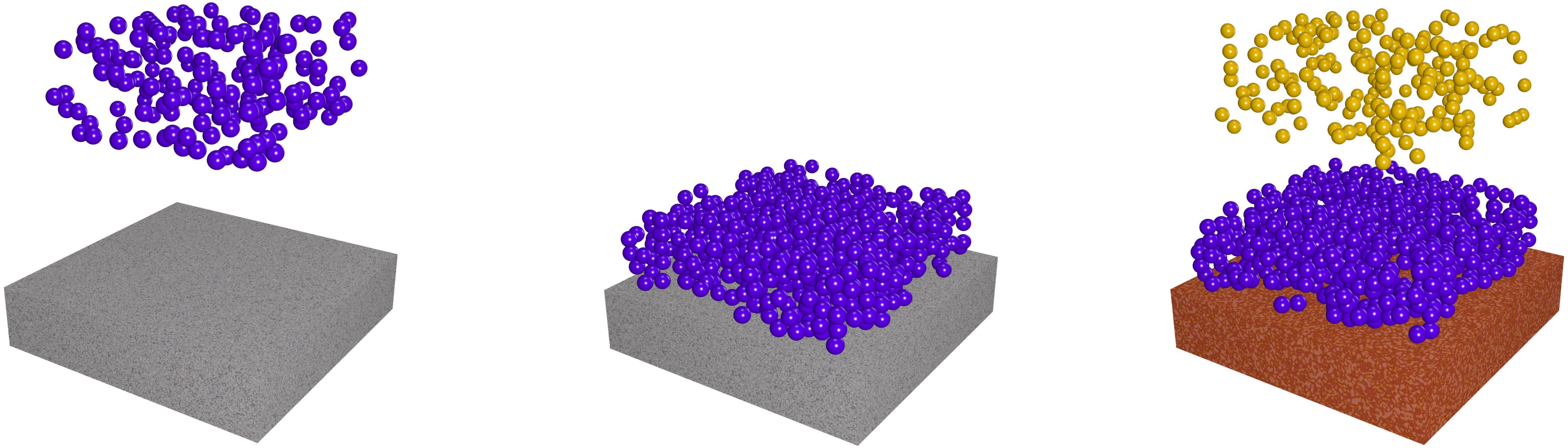
Remarks

- 250 eV impact energy
- 75° incident angle

- Detection
- Localization!

Measurement **187**, 110308 (2022)

Molybdenum disulfide



Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

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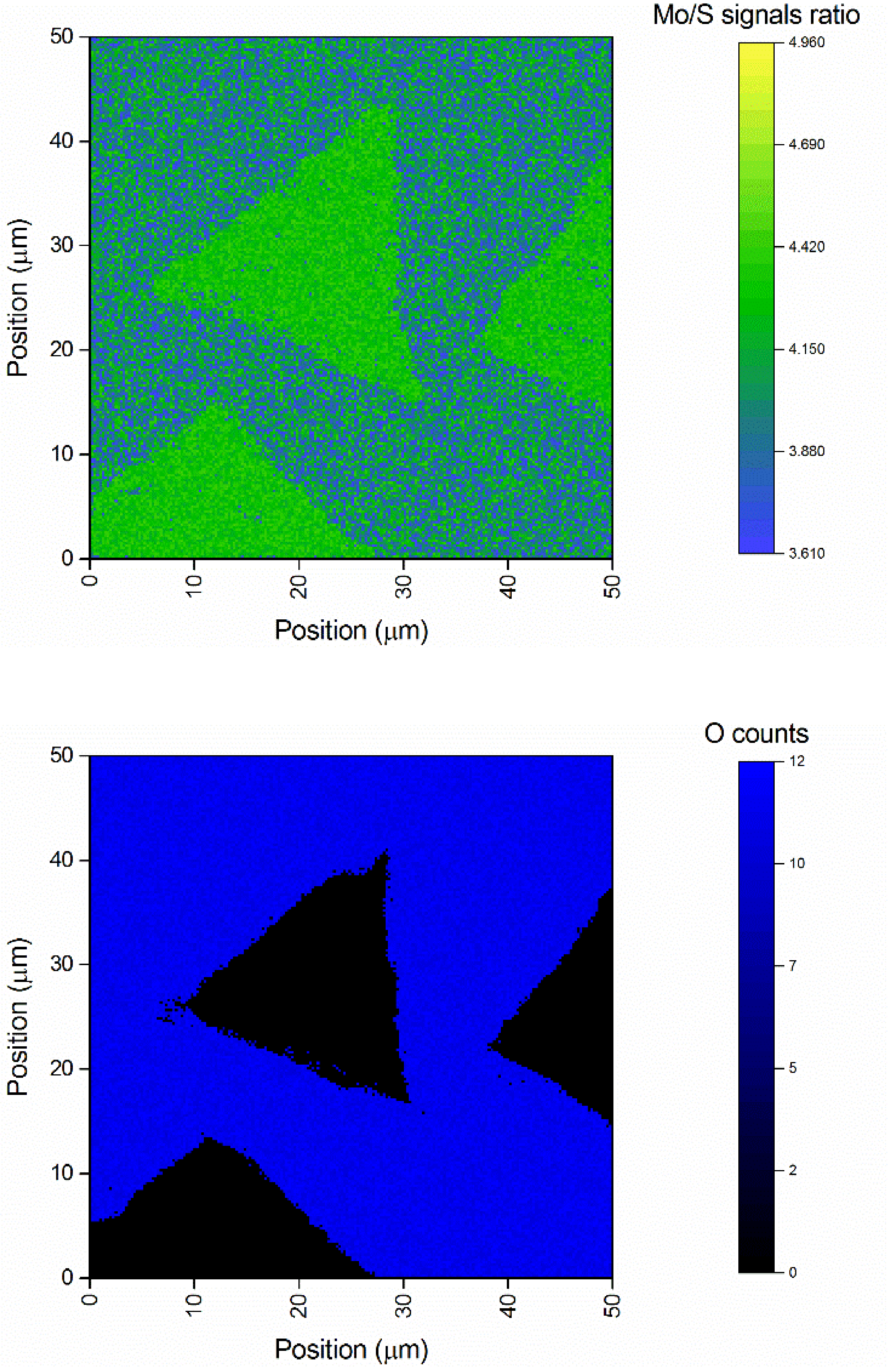
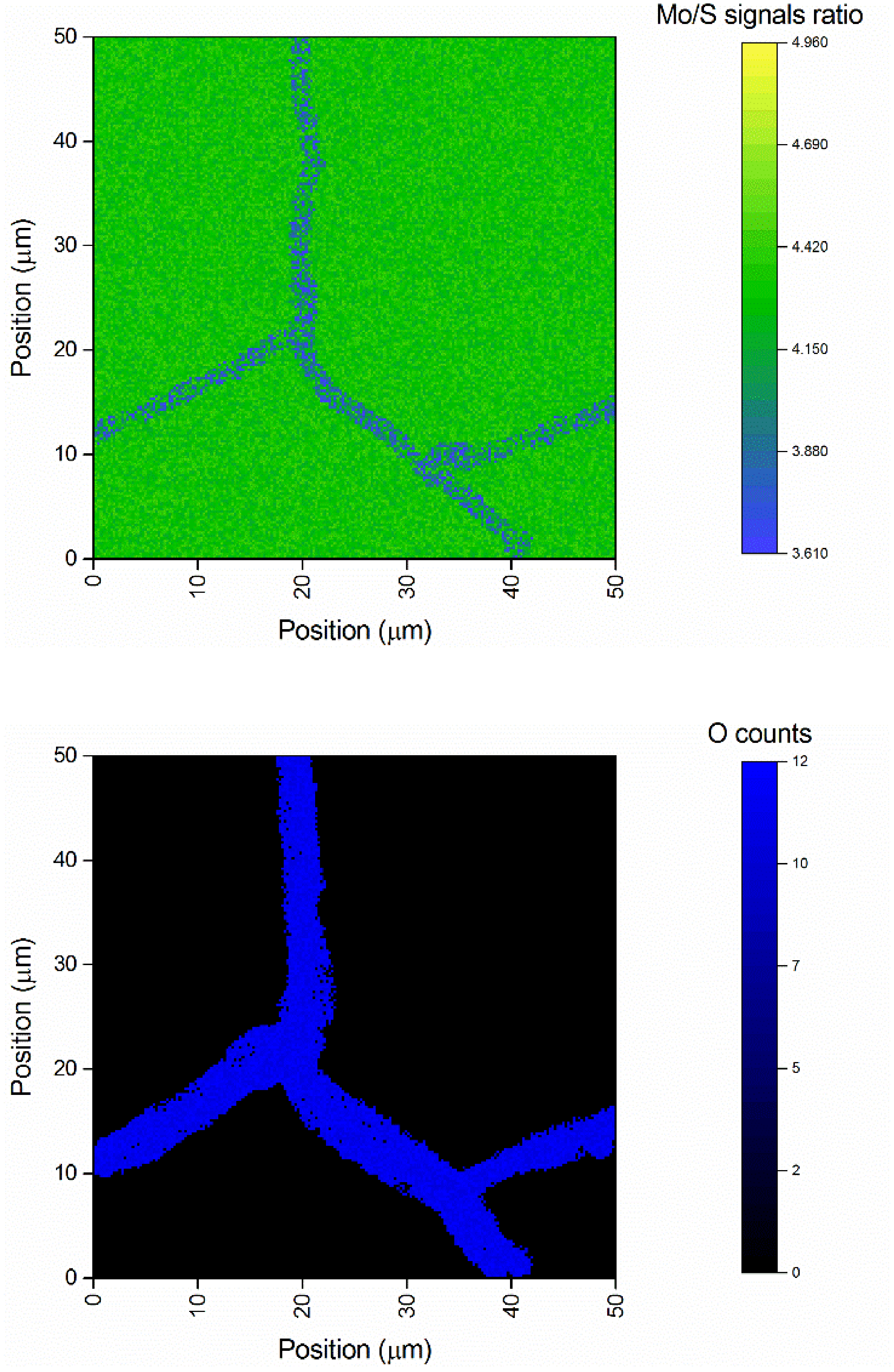
SiO_2

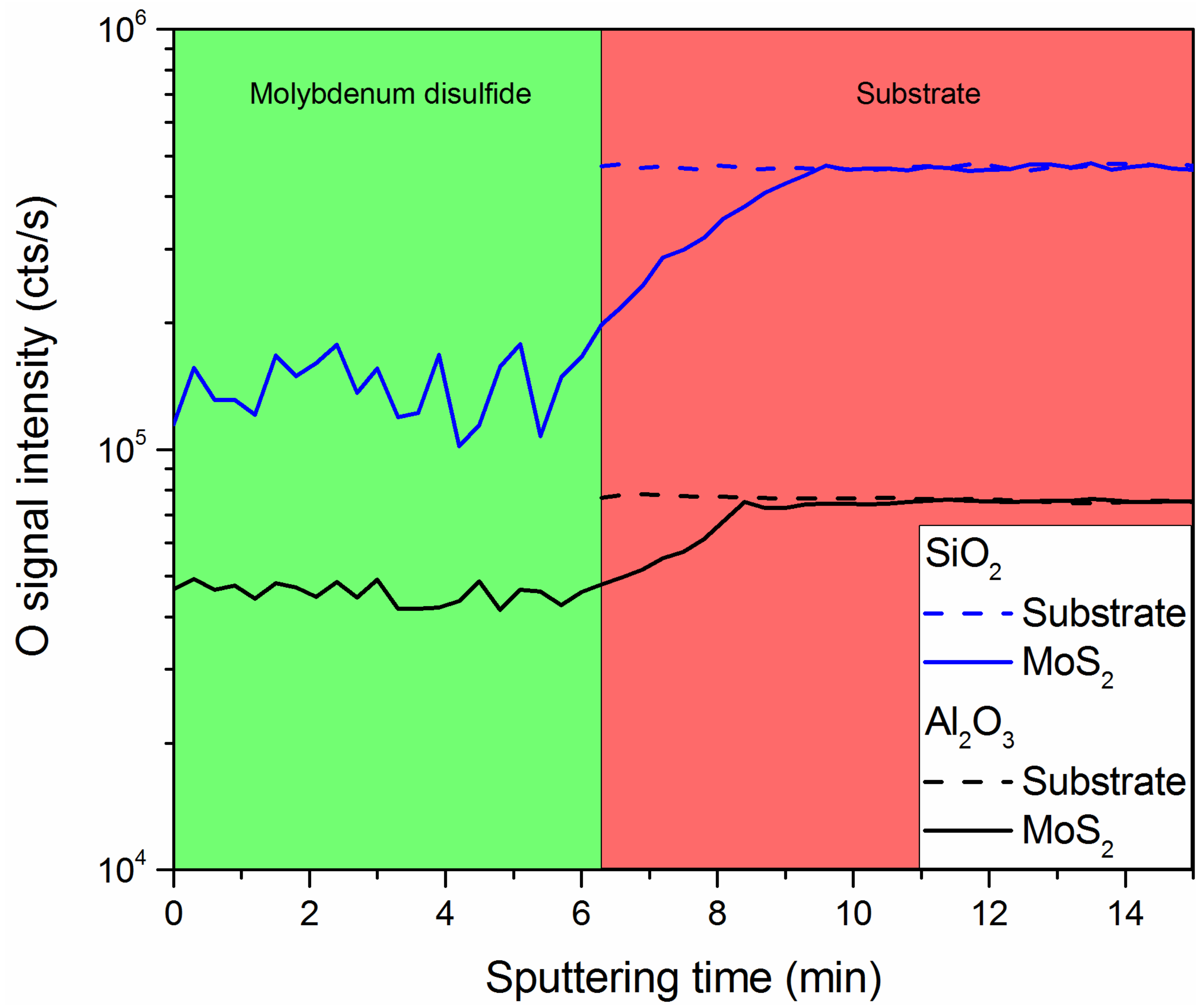


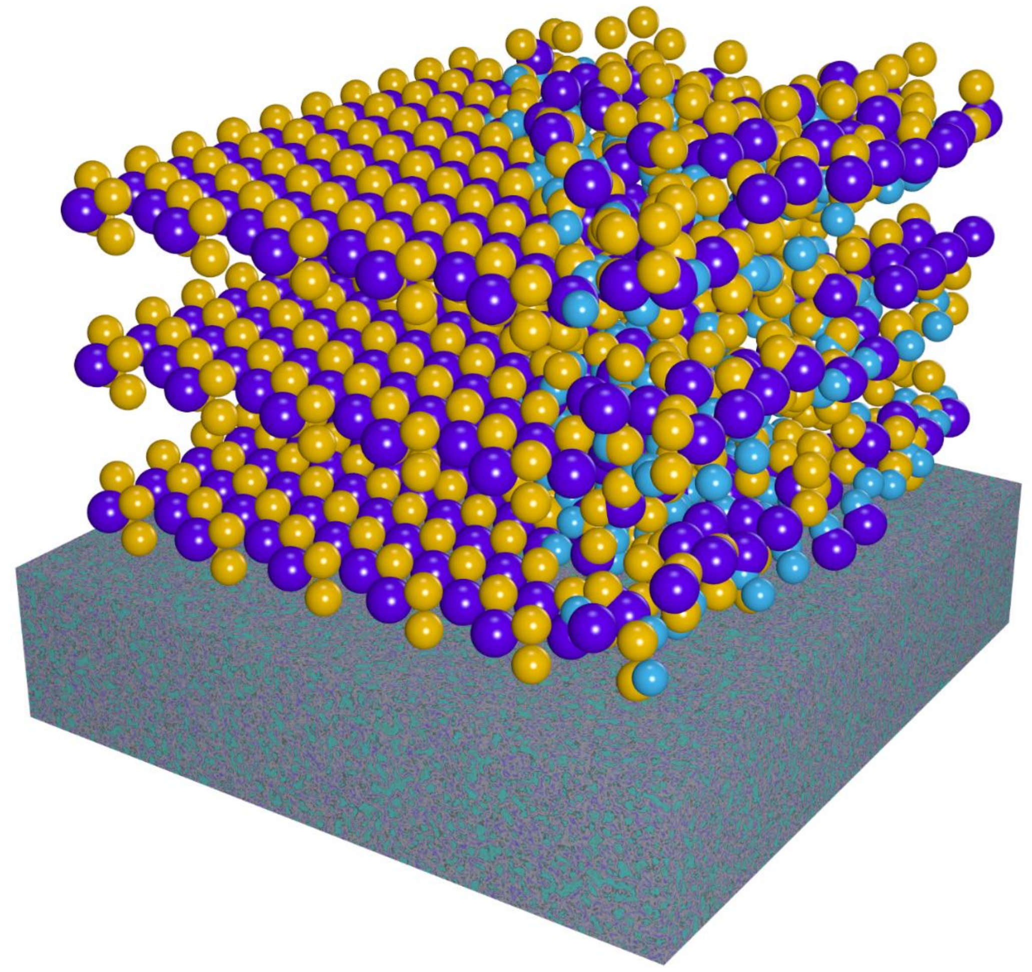
Al_2O_3

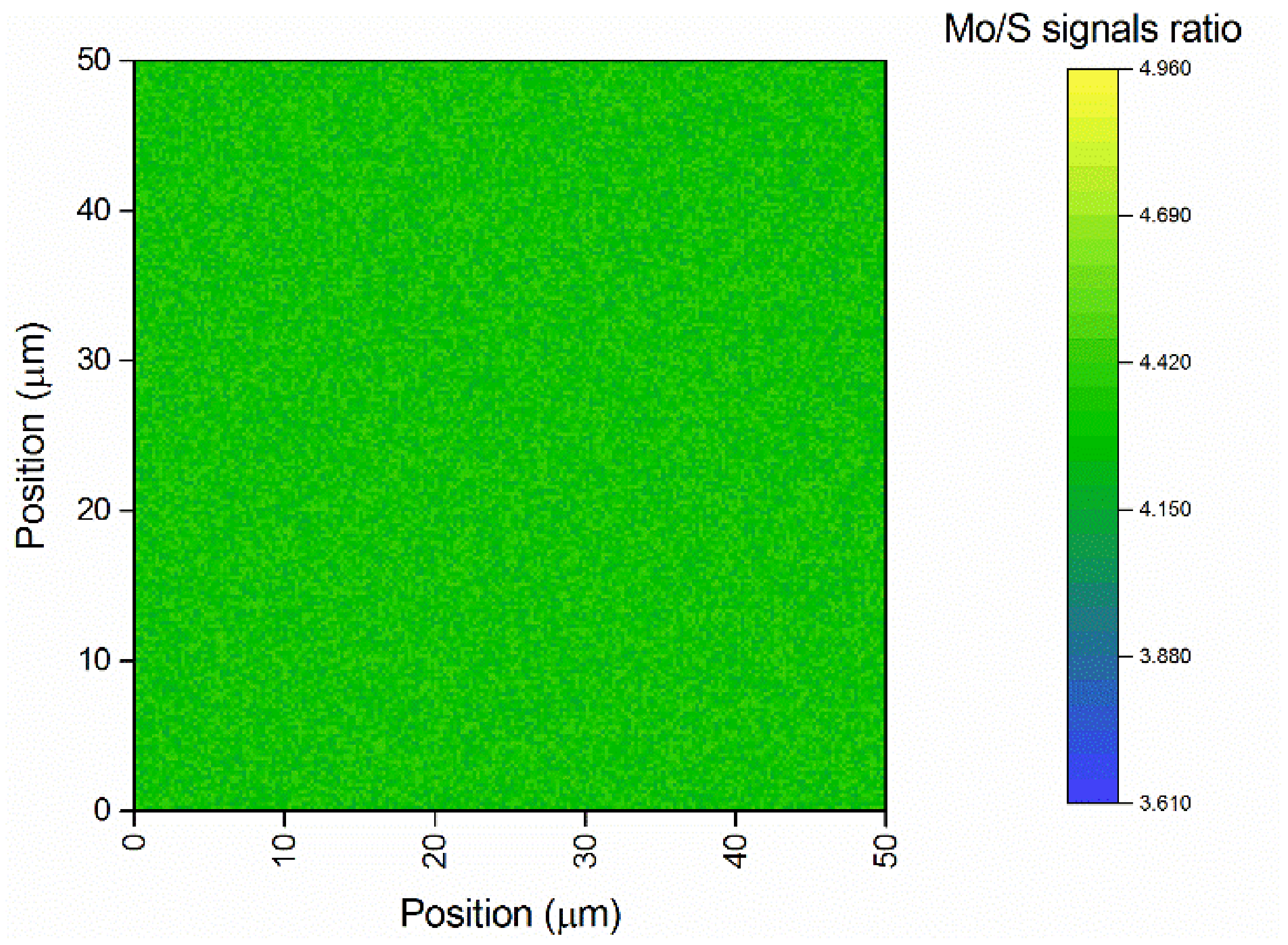


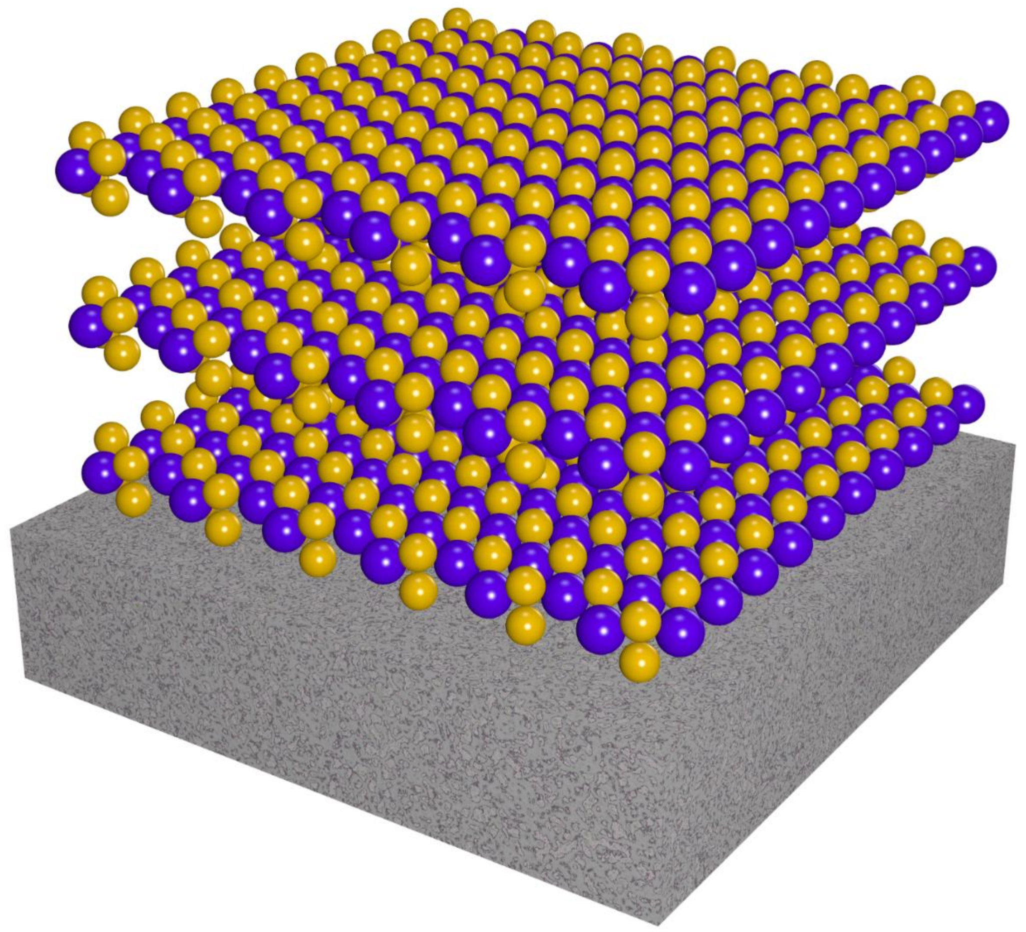
Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

Substrate type / procedure optimization



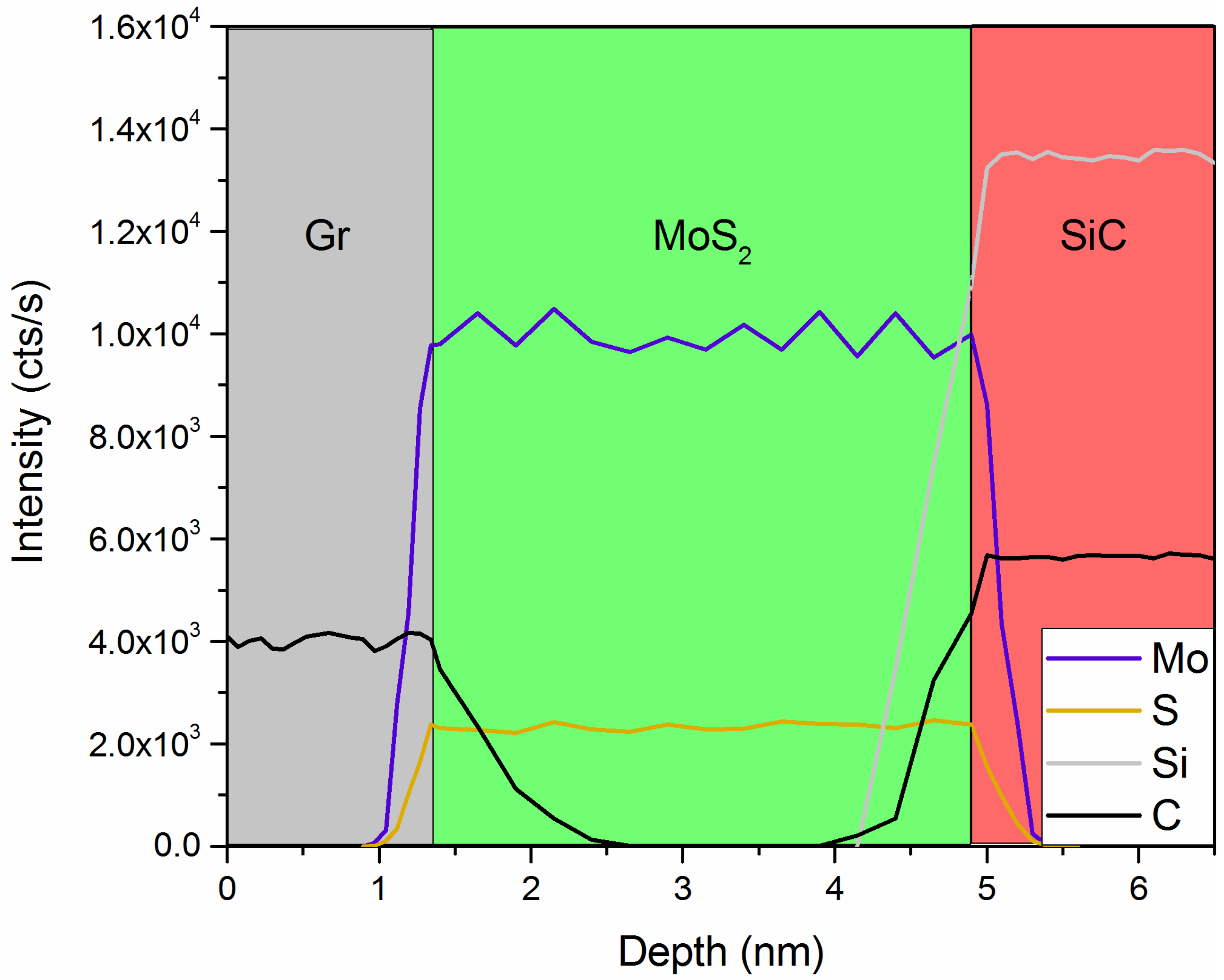


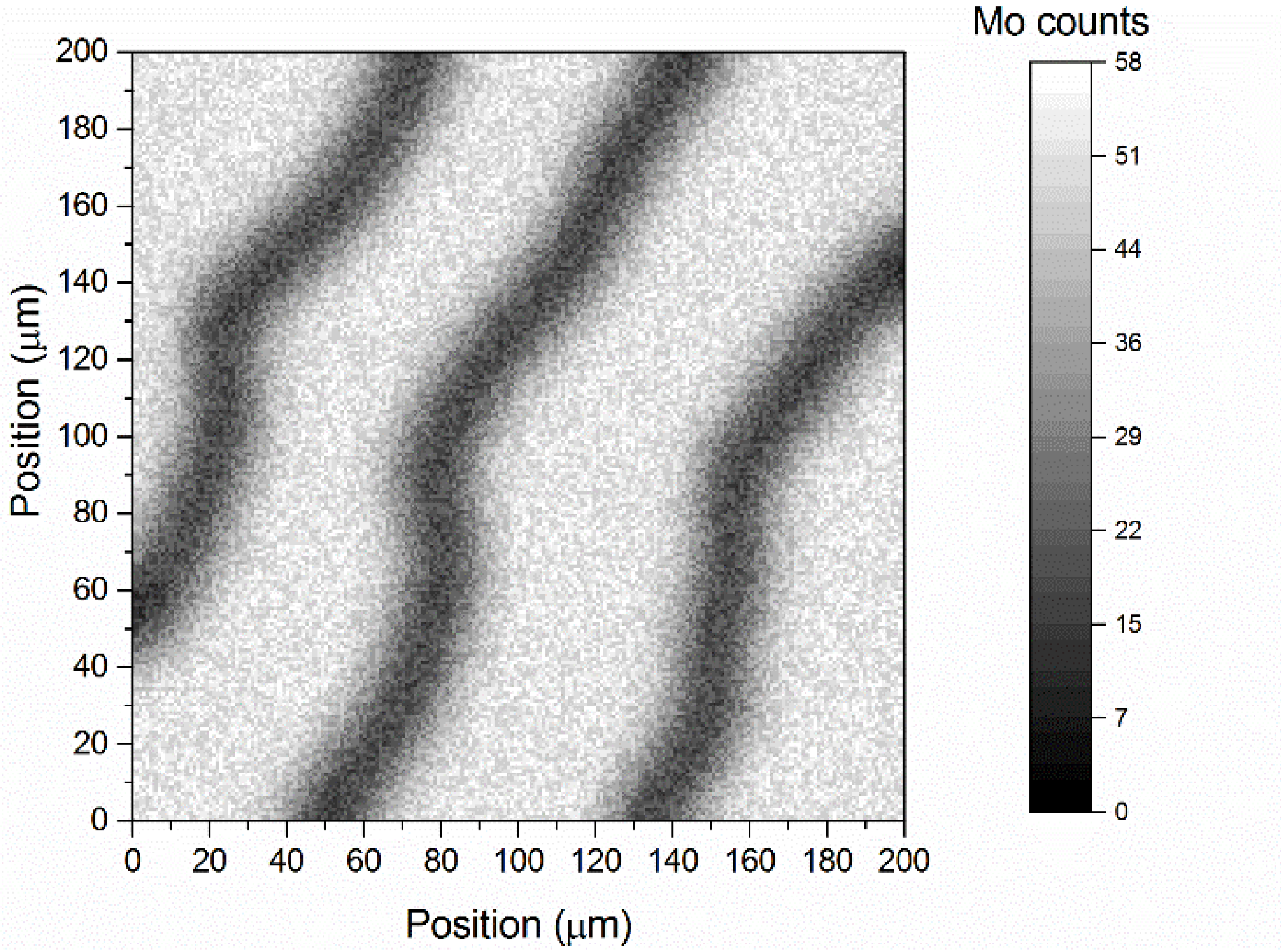


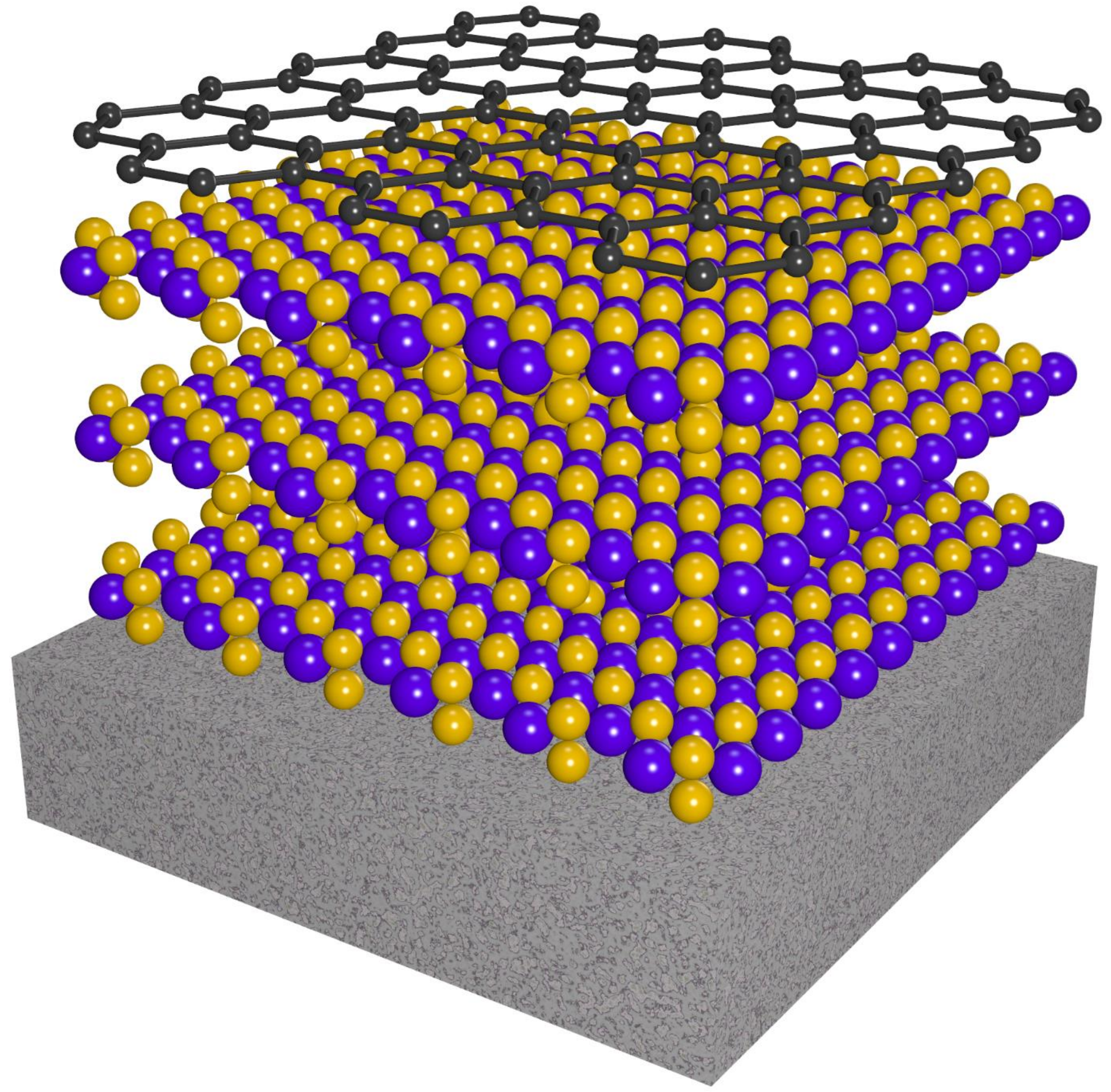


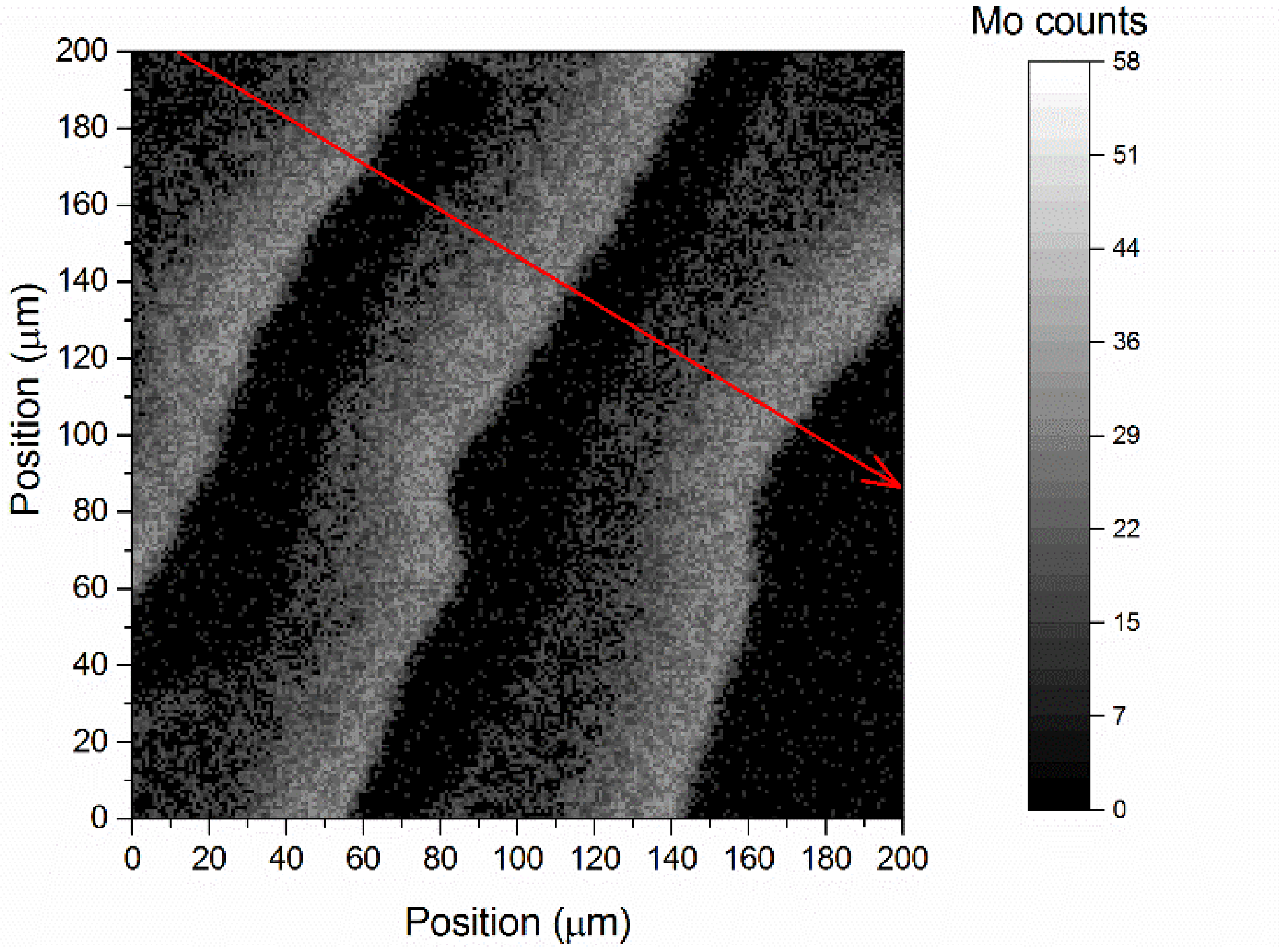
Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

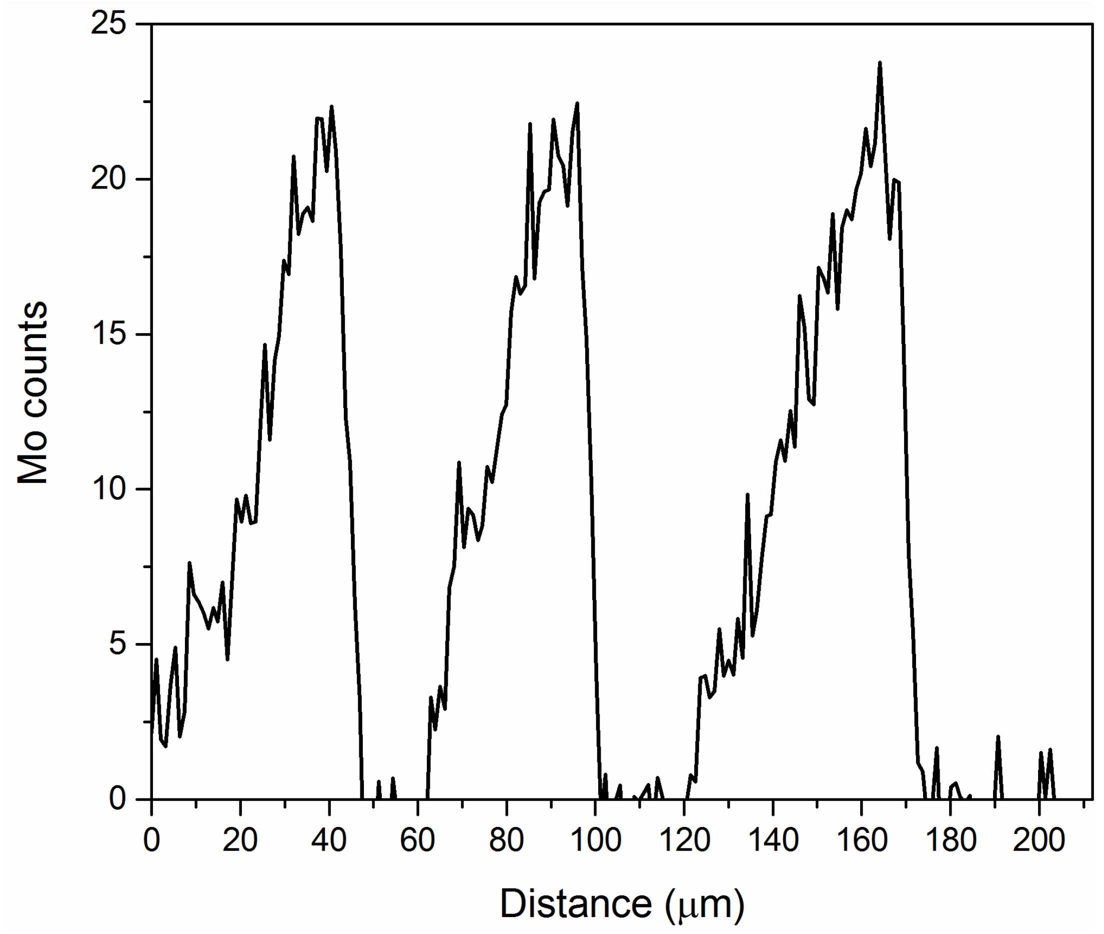
Graphene/SiC case





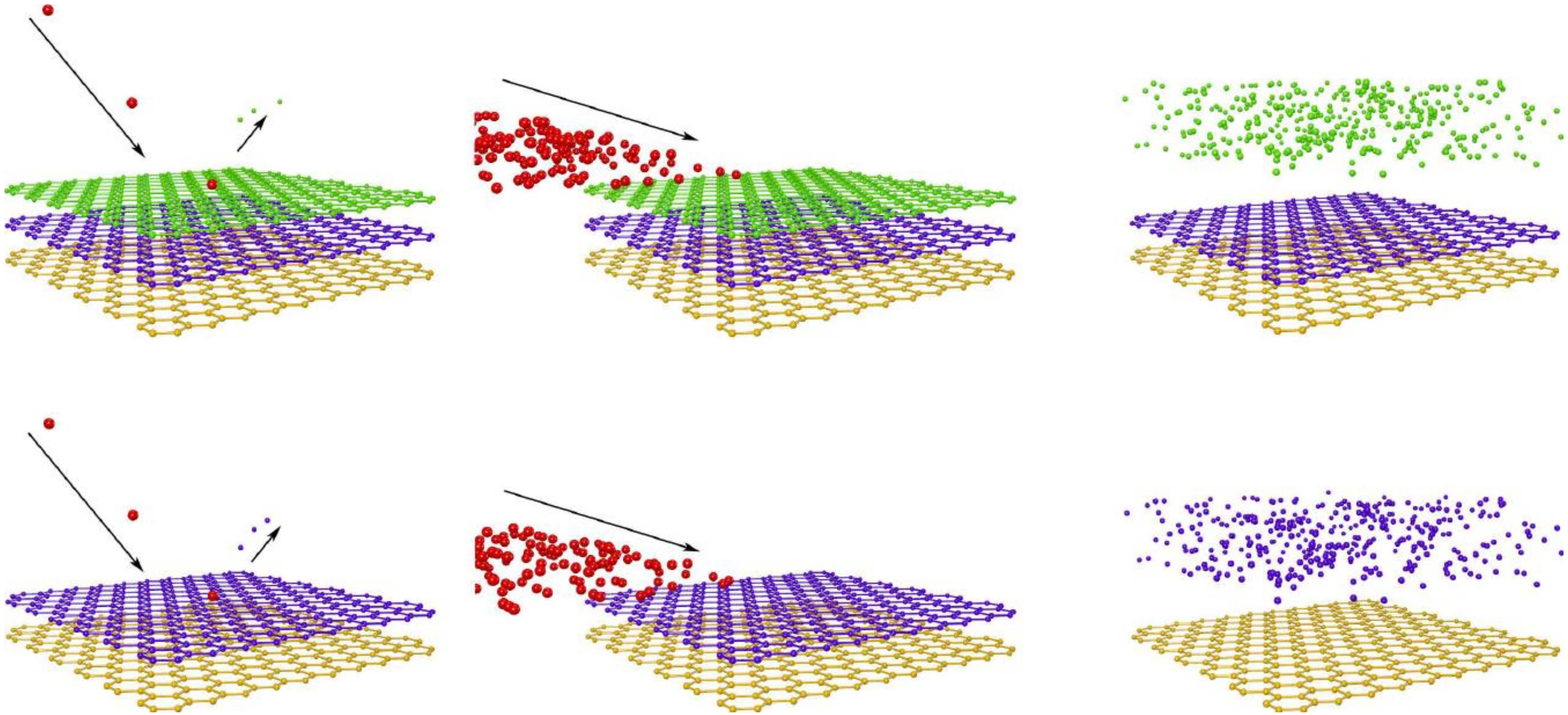






Physical Chemistry Chemical Physics **21**, 20641-20646 (2019)

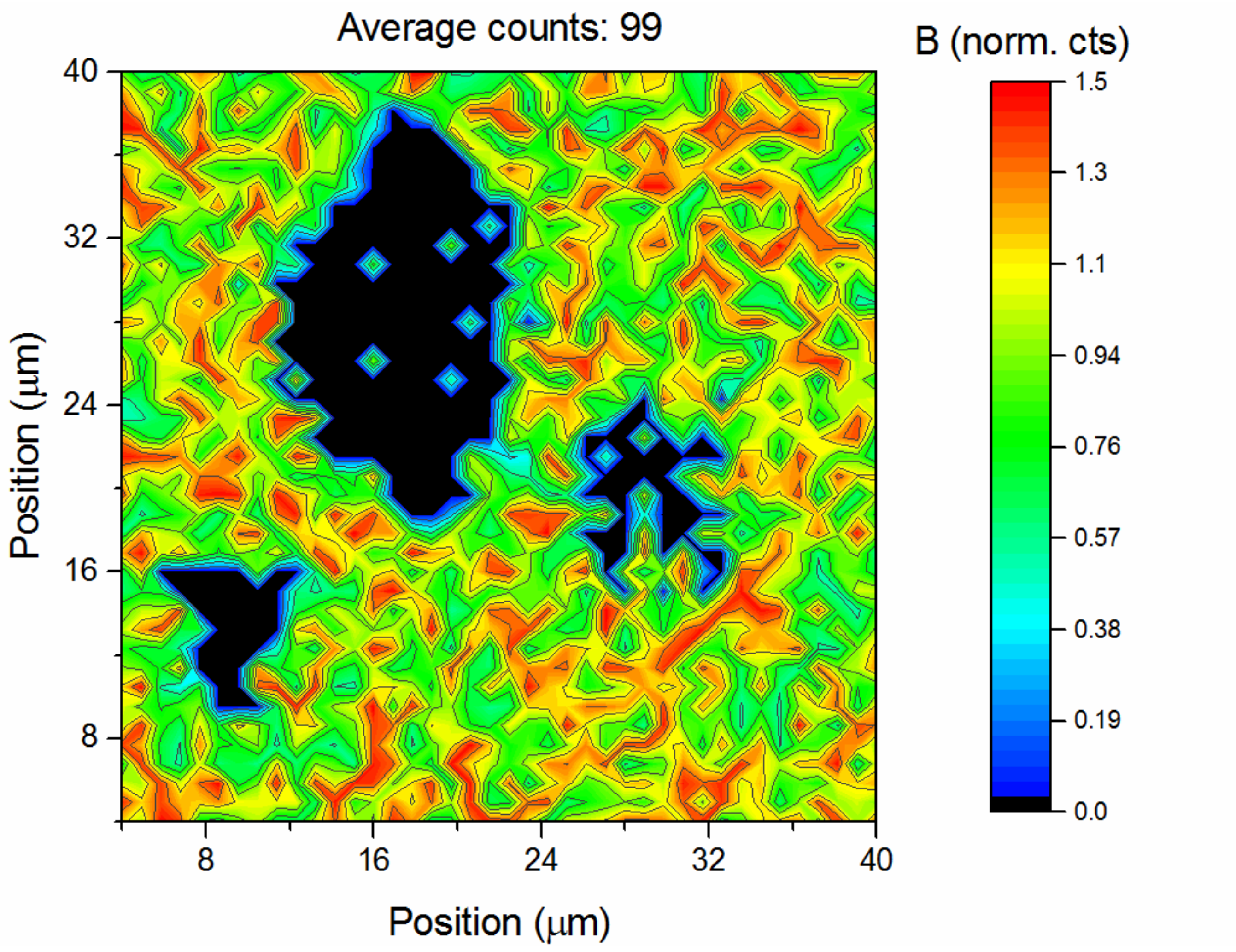
Hexagonal boron nitride

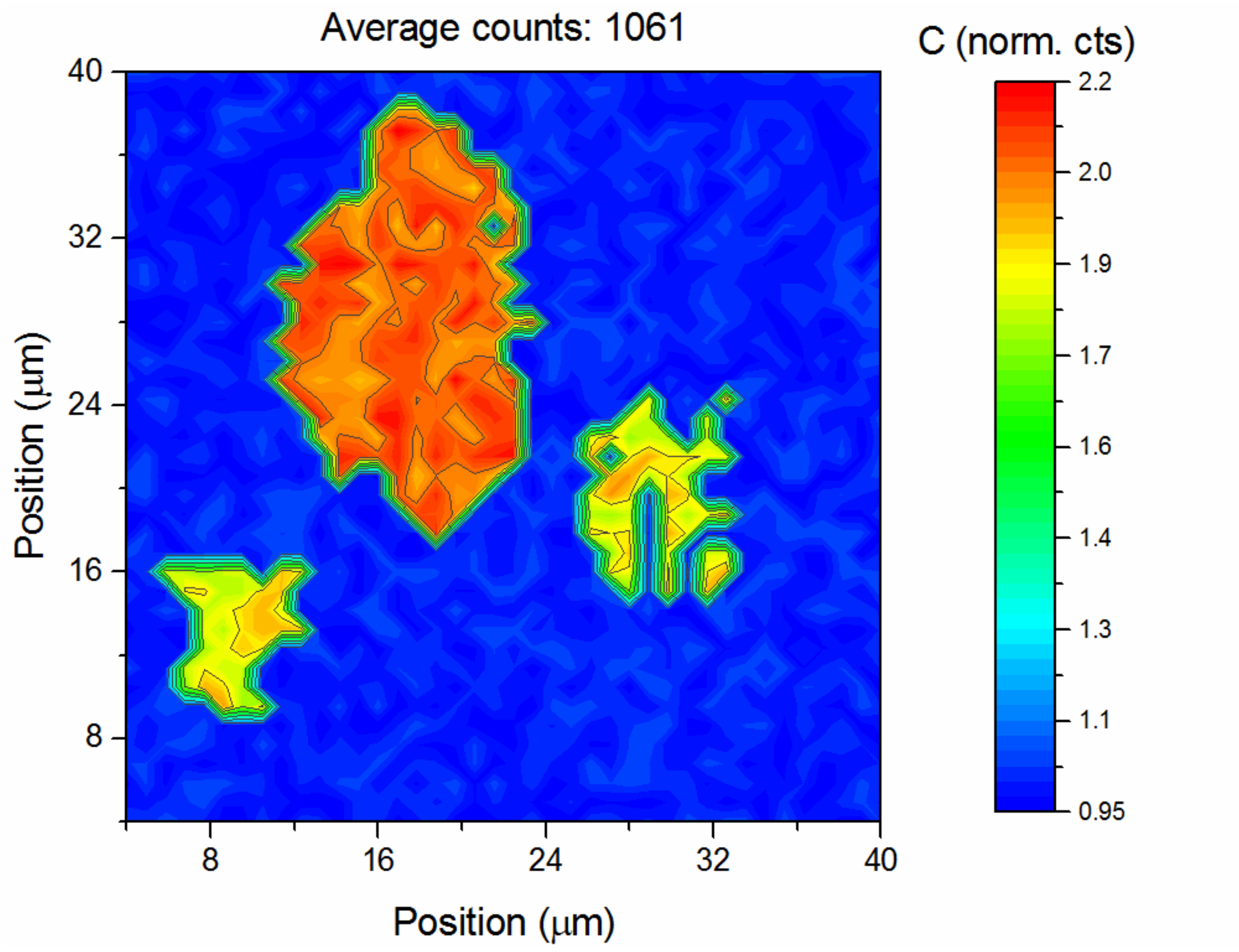


Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

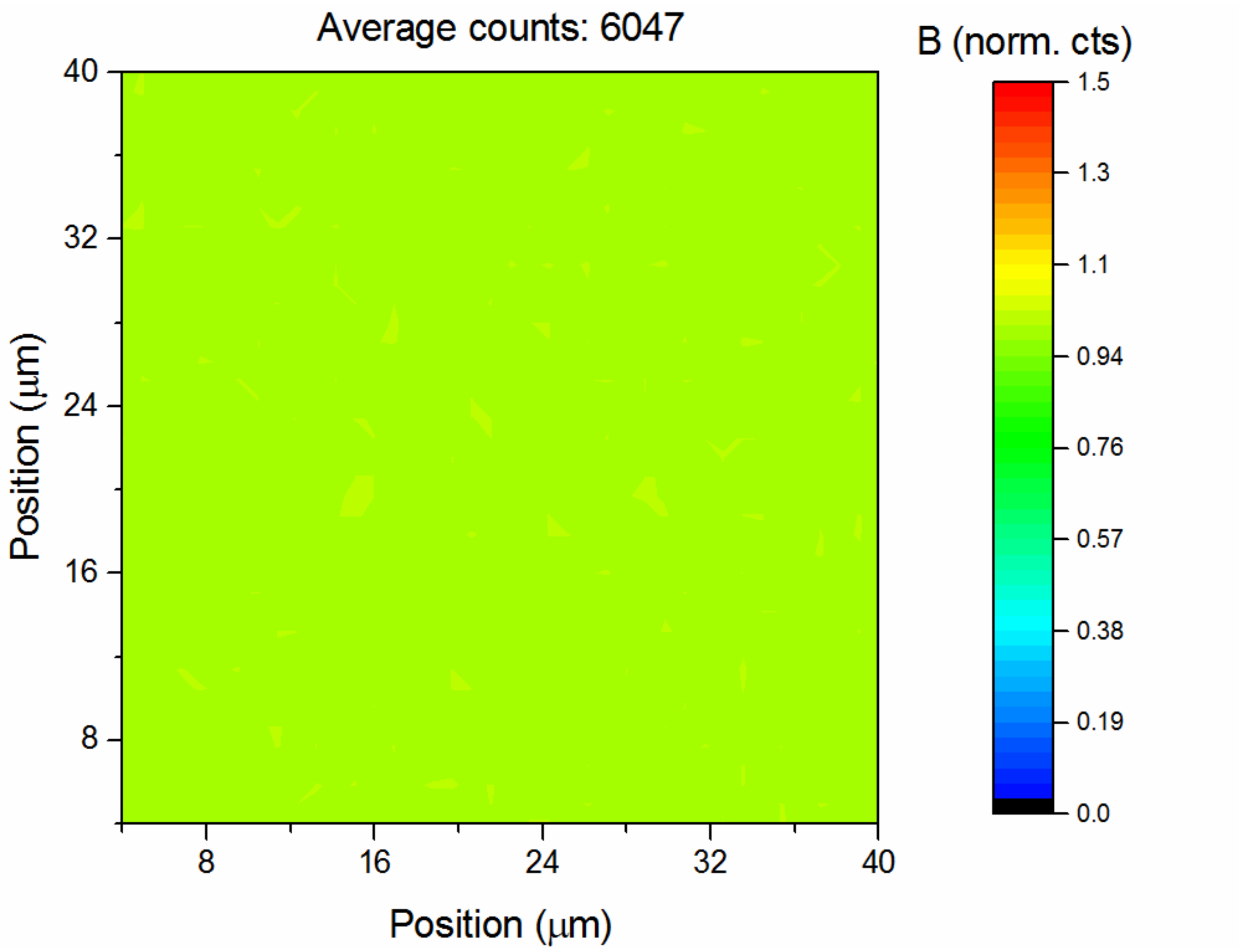
Different carrier gas

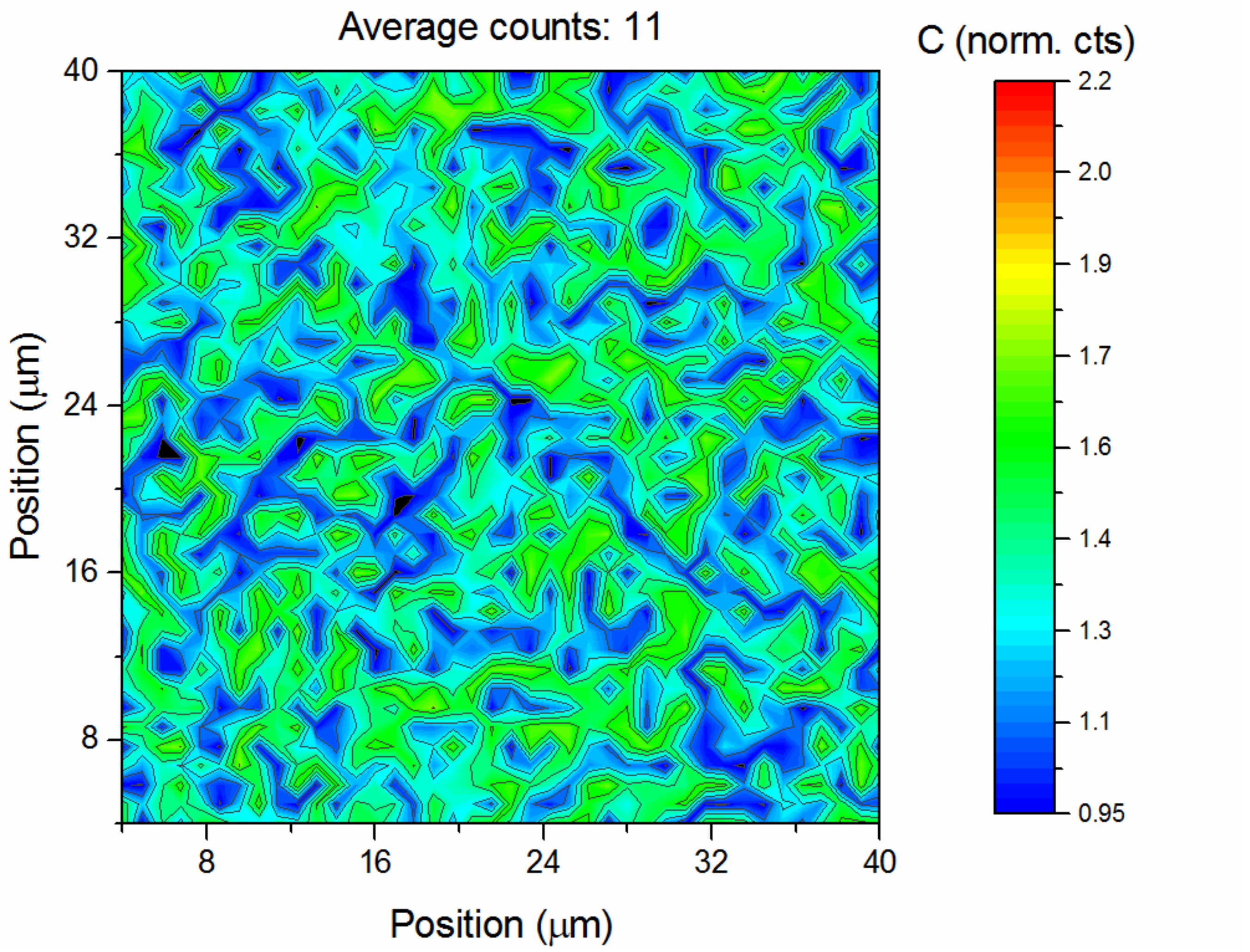
Ar





H_2





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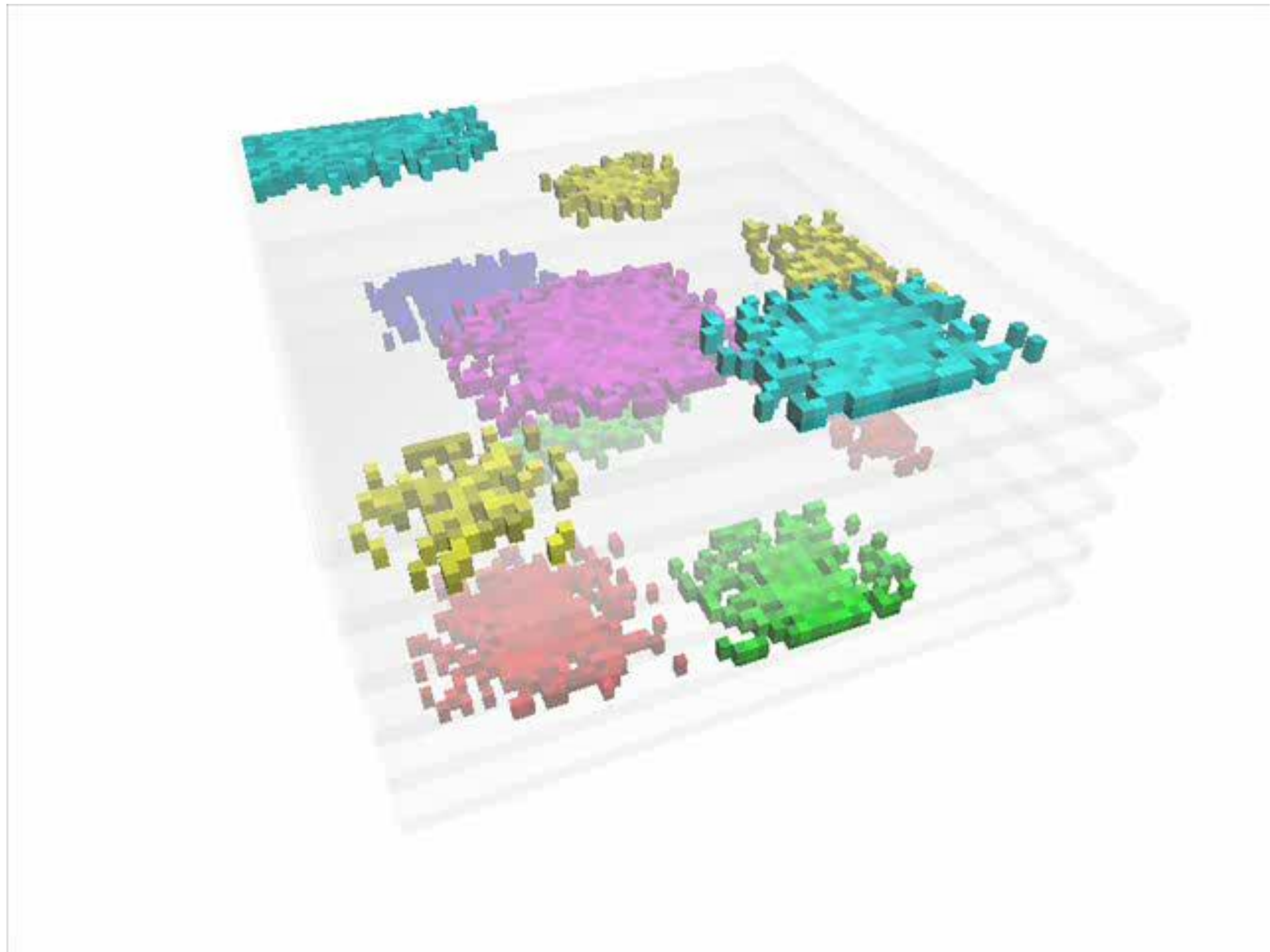
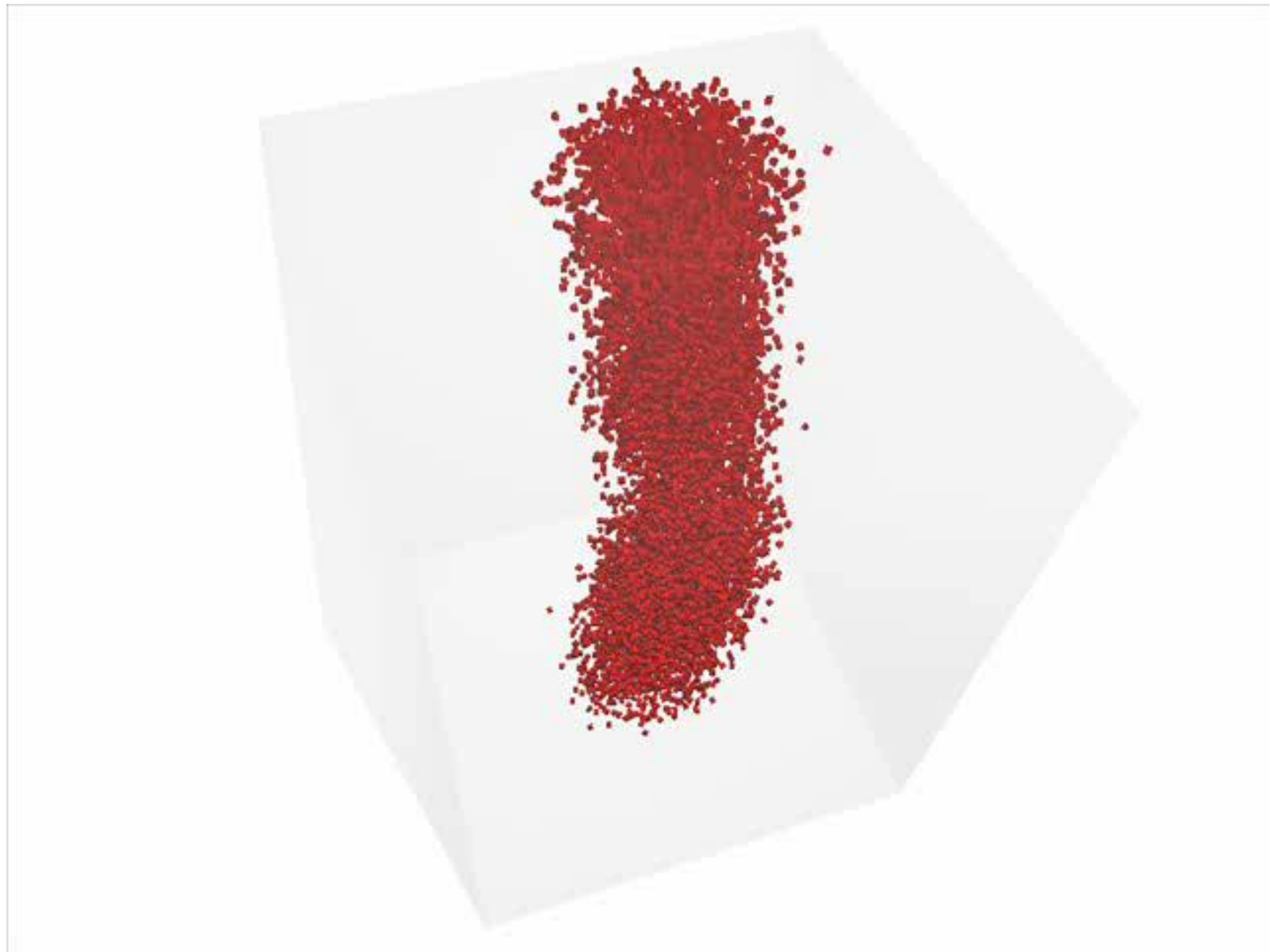
Different reactor pressure

High

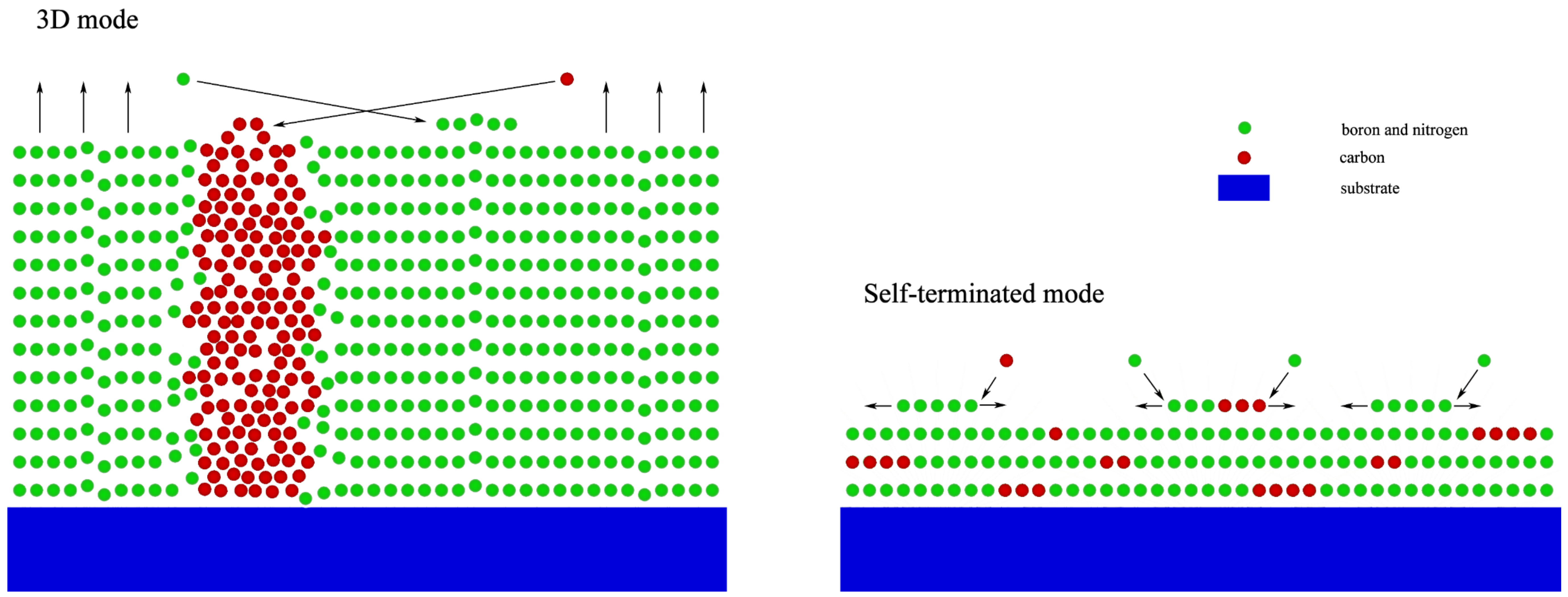


Low



Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

hBN - summary



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PAPER
Paweł Piotr Michałowski *et al.*
Secondary ion mass spectrometry investigation of carbon grain formation in boron nitride epitaxial layers with atomic depth resolution

Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

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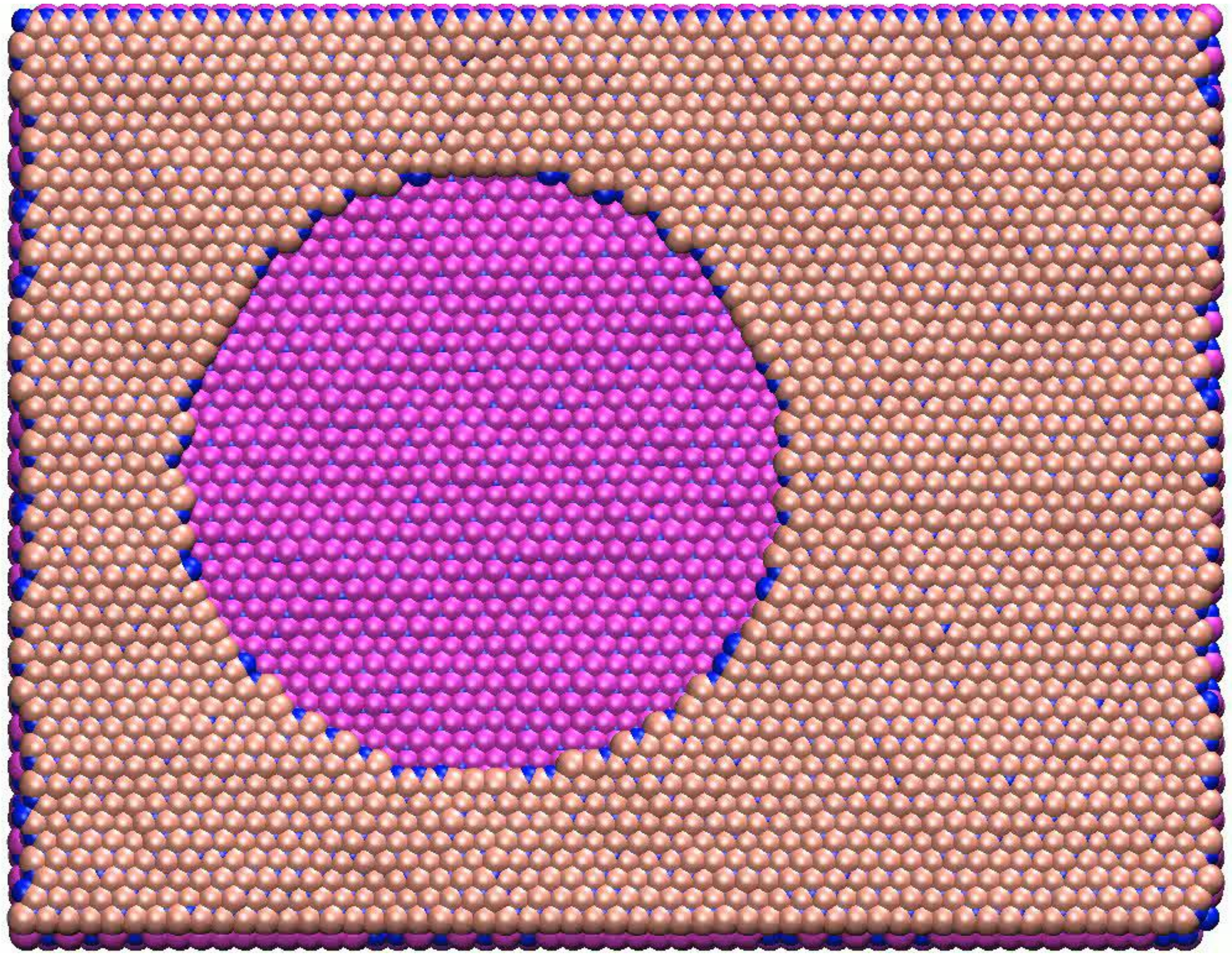
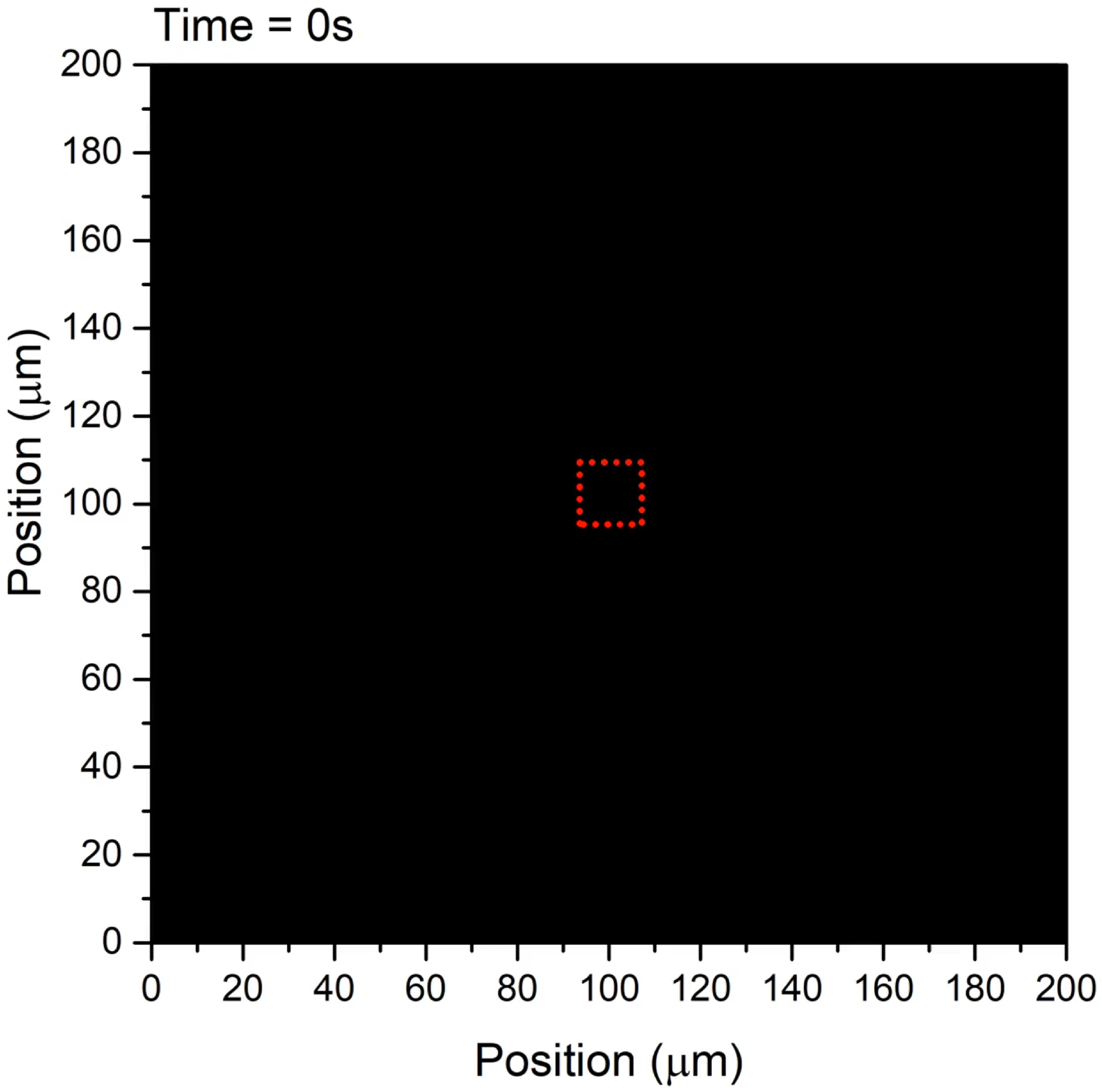
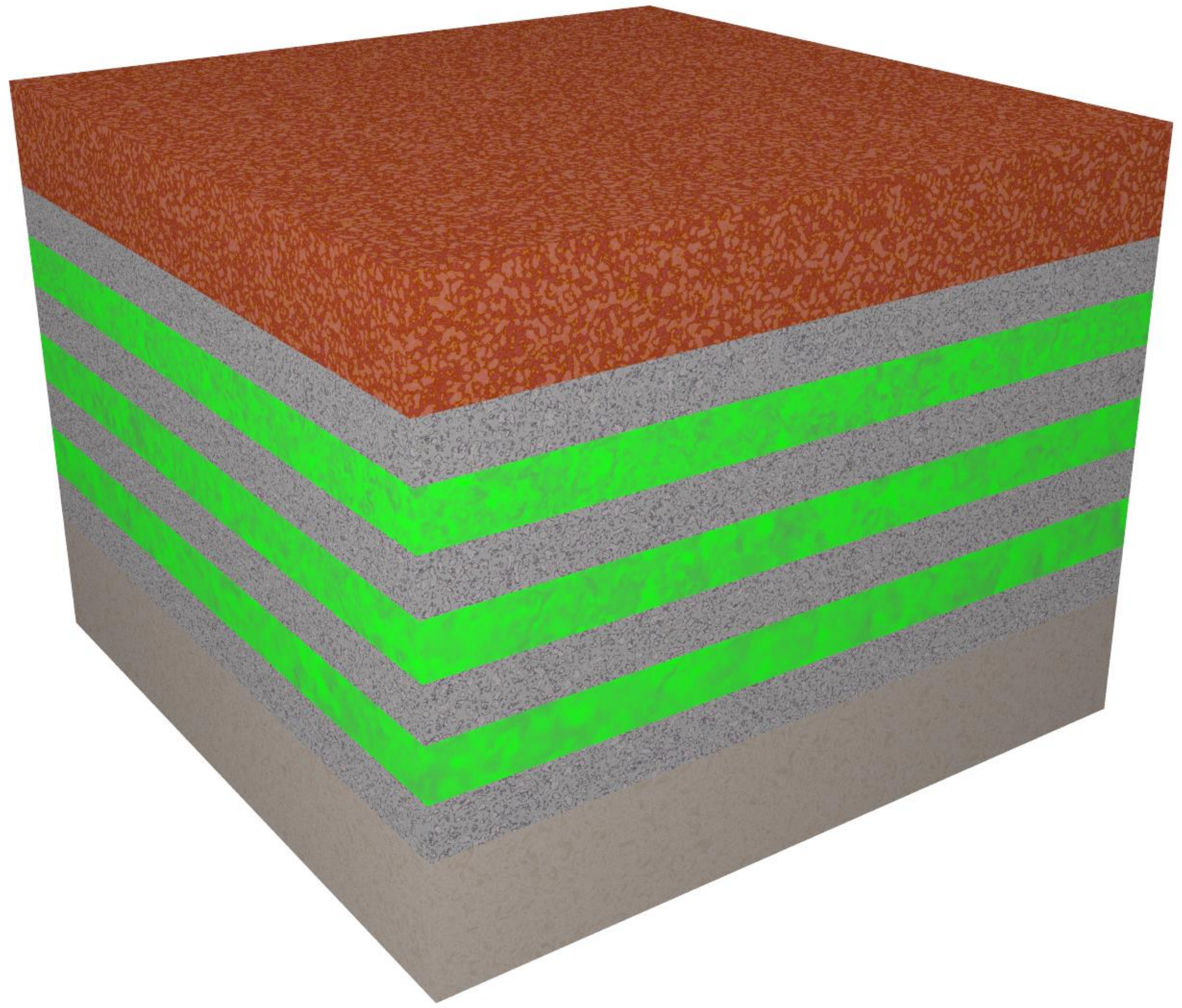
How does it work?





Measurement **179**, 109487 (2021)

InGaN QWs

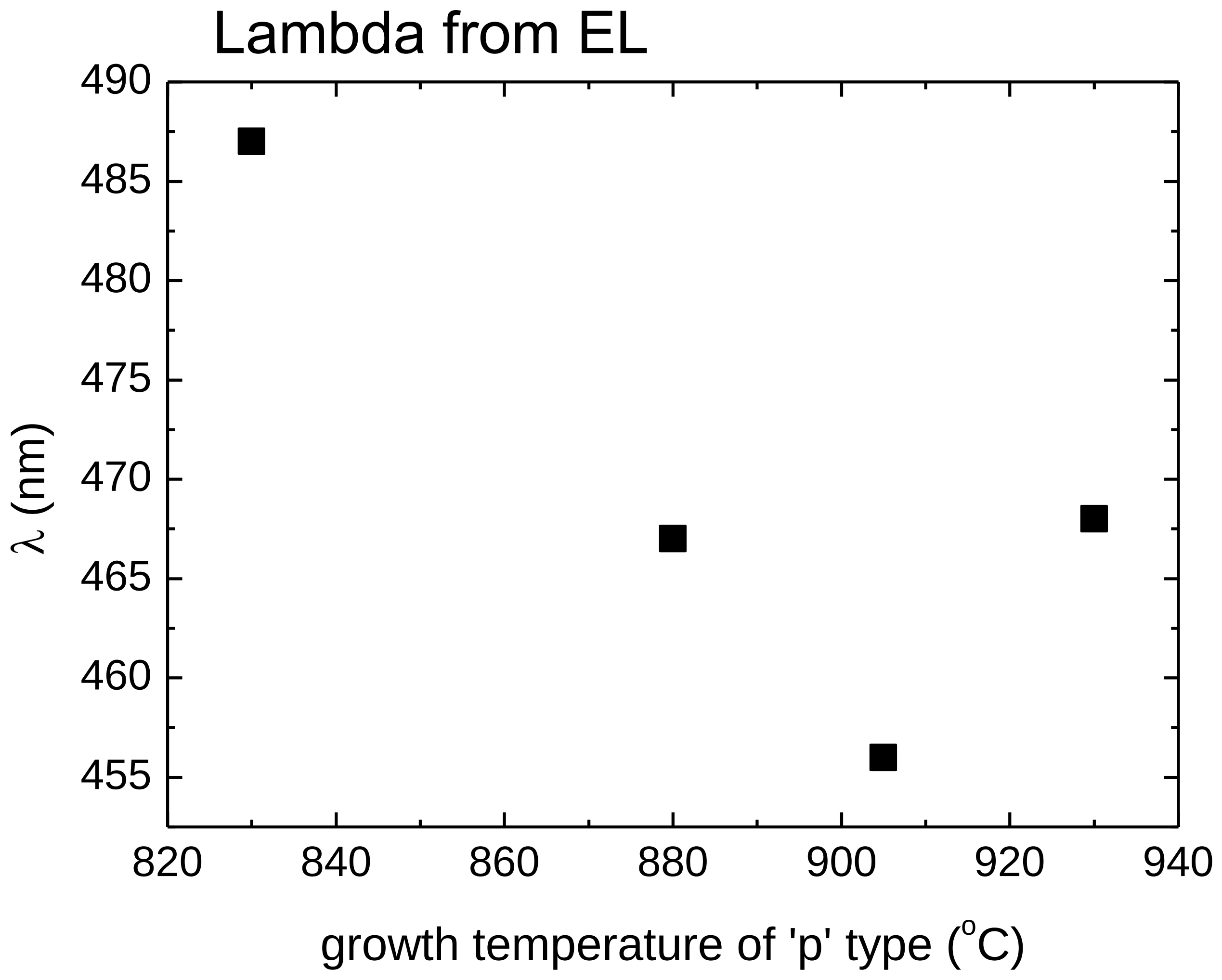


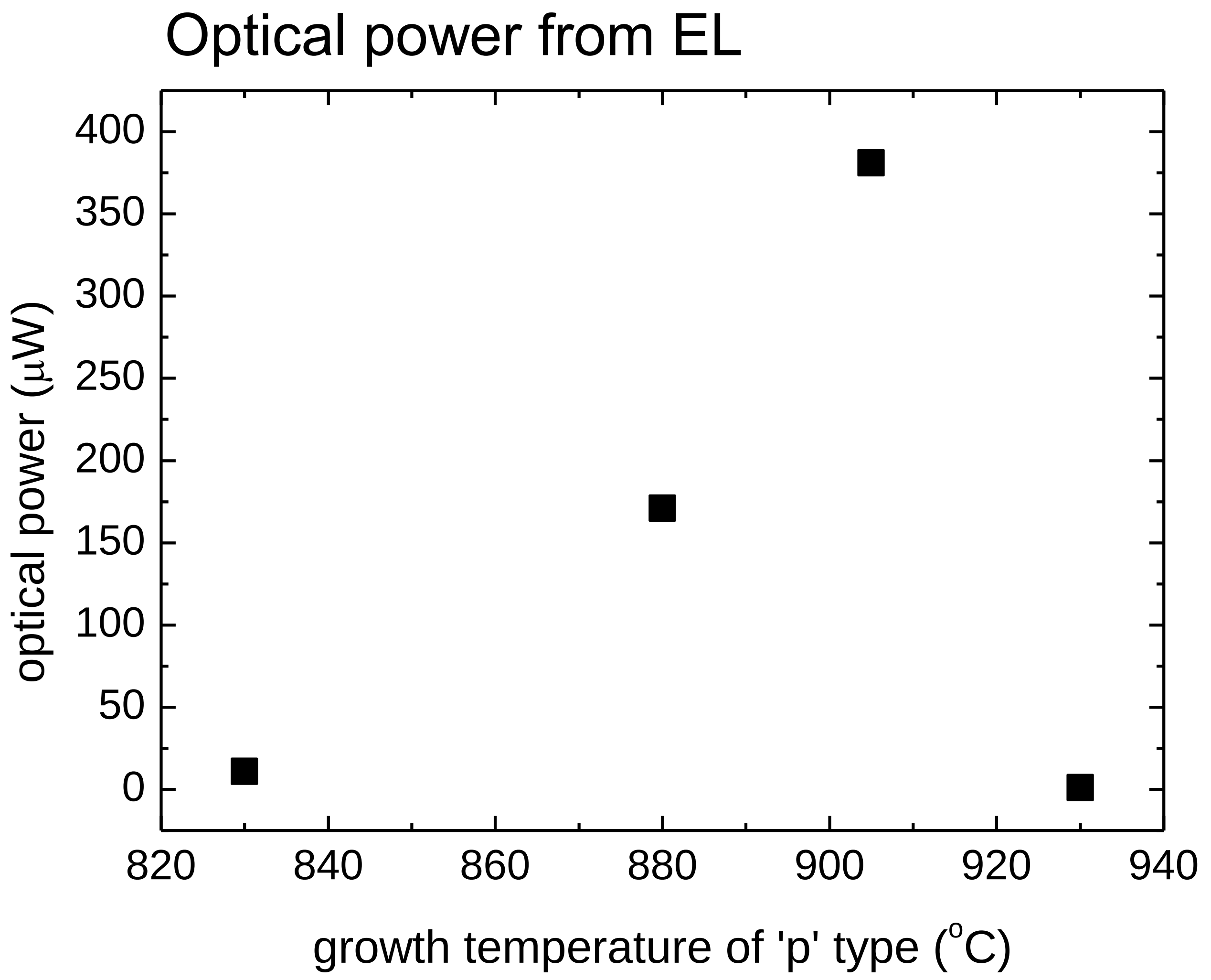
p-type GaN

QW InGaN (In 18%) 2.5nm
QB InGaN (In 0.5%) 7nm

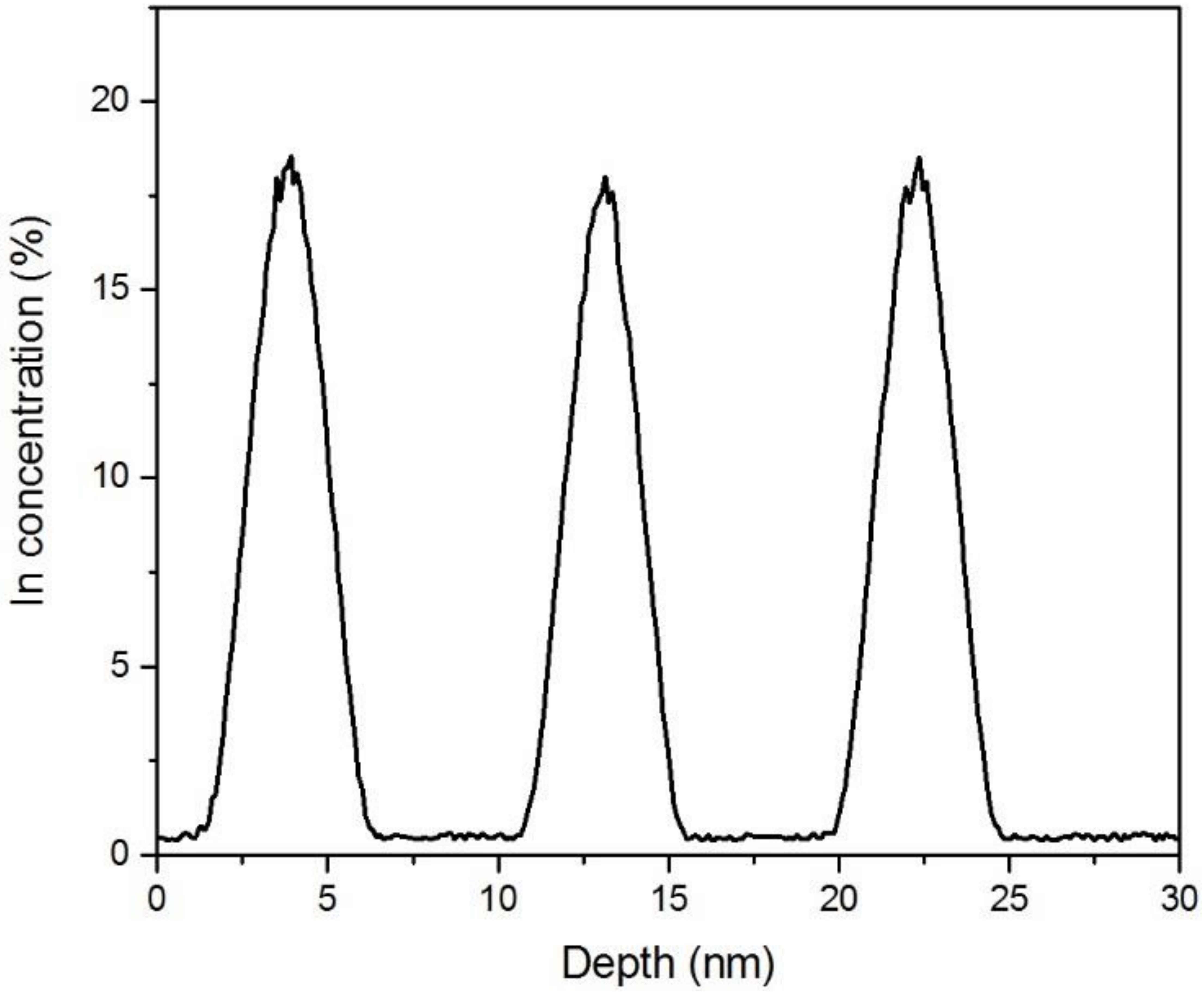
n-type GaN

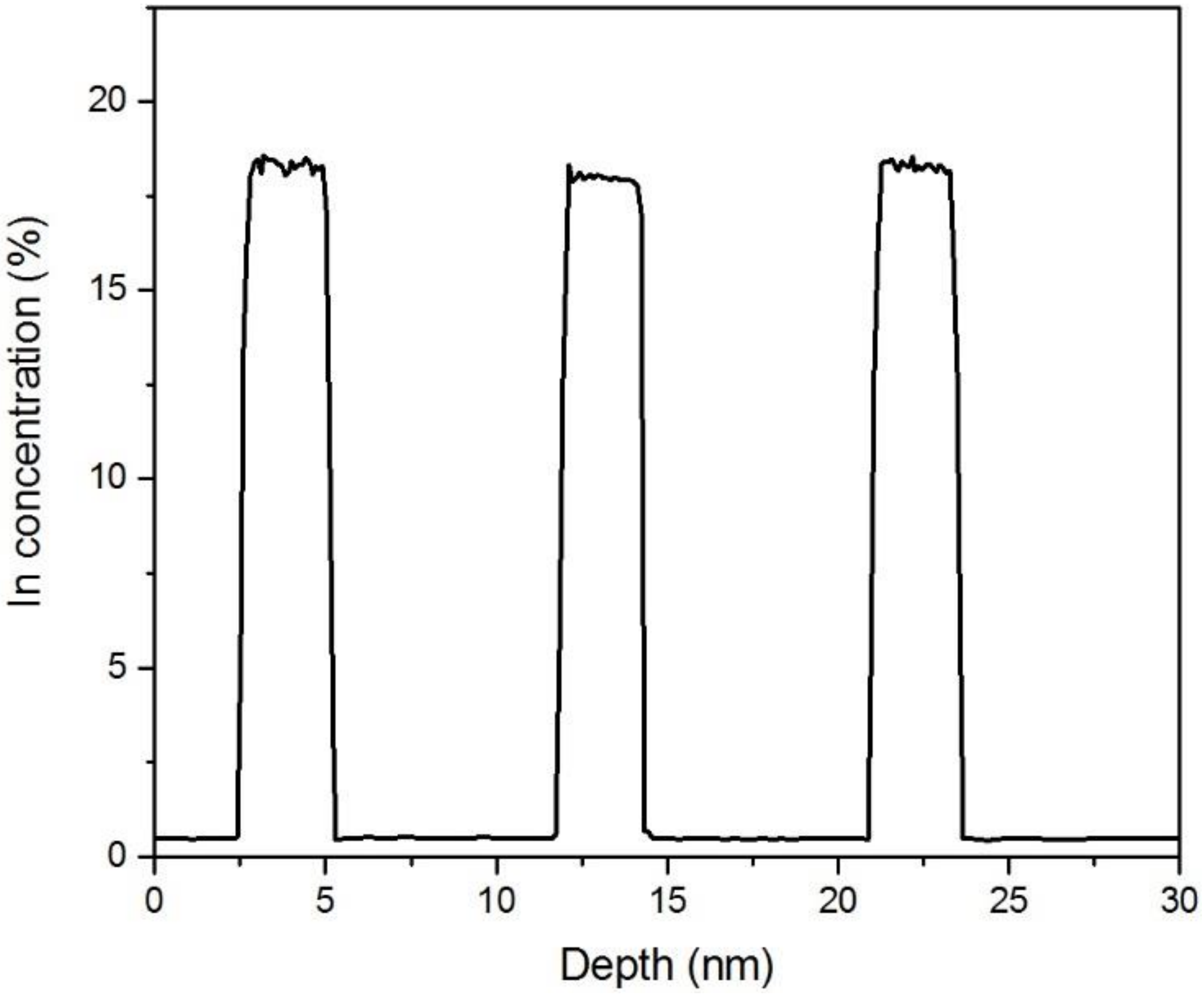
Lattice mismatch
Growth temperature differences



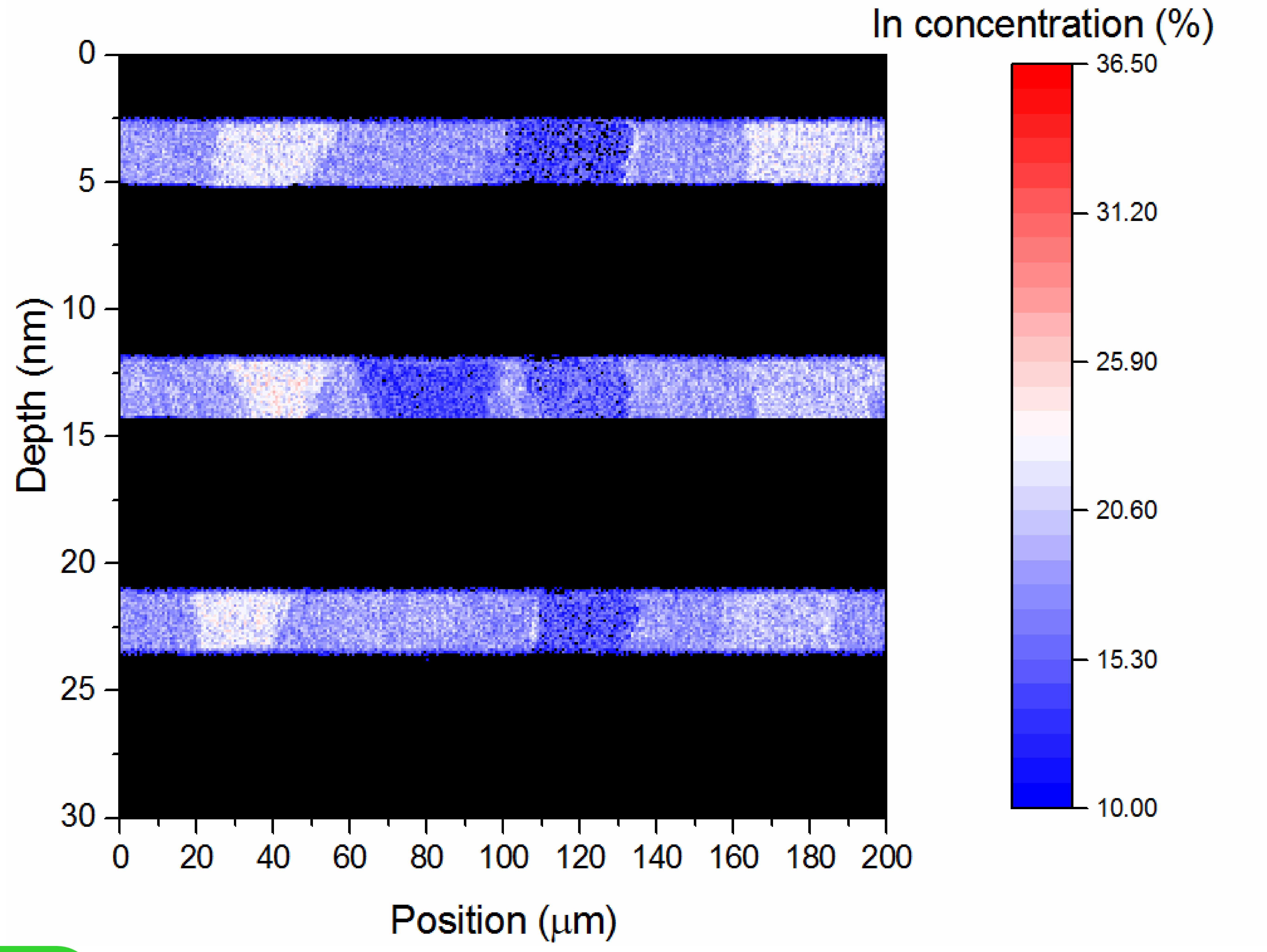


Standard SIMS vs ULIE-SIMS

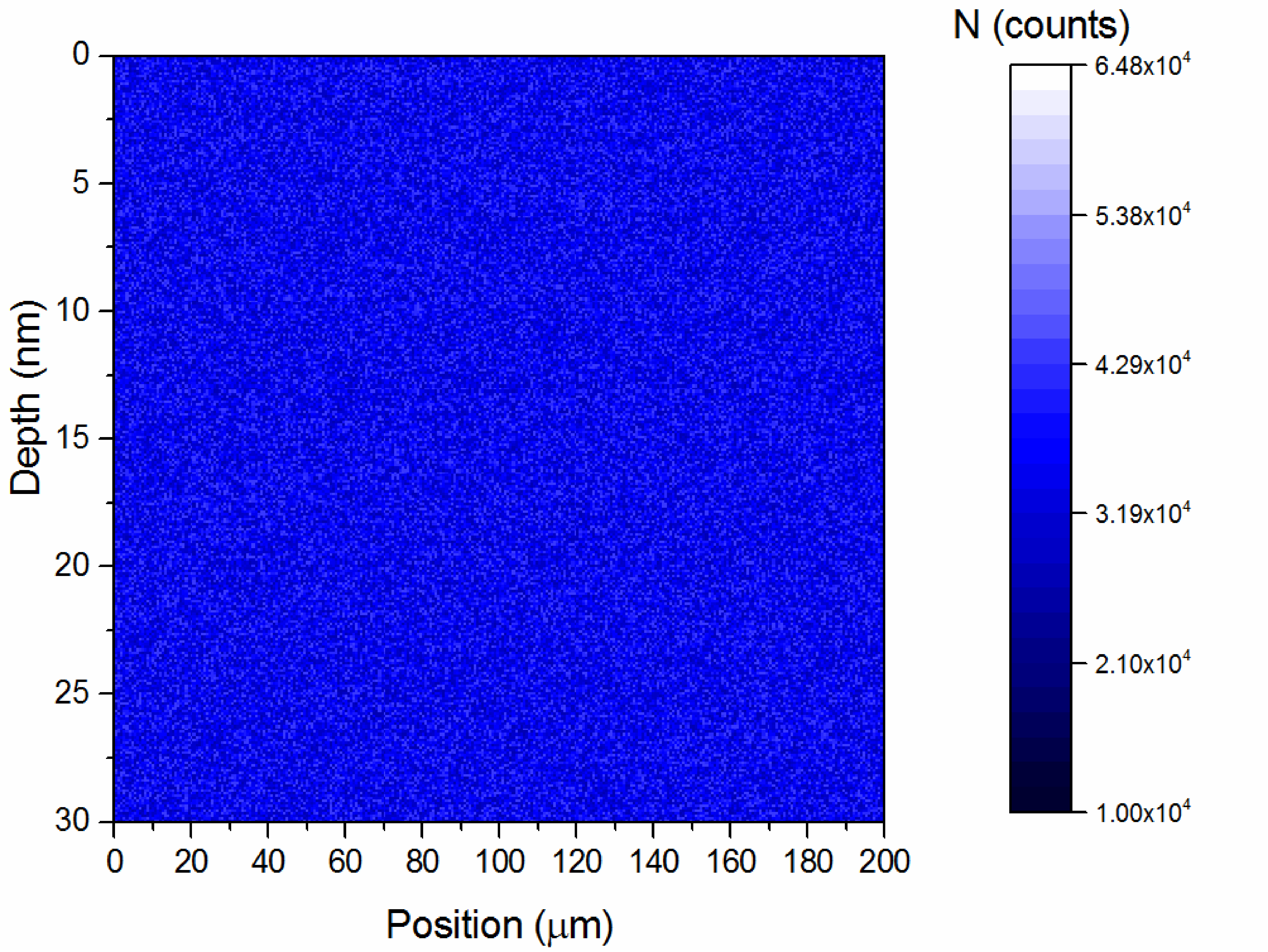




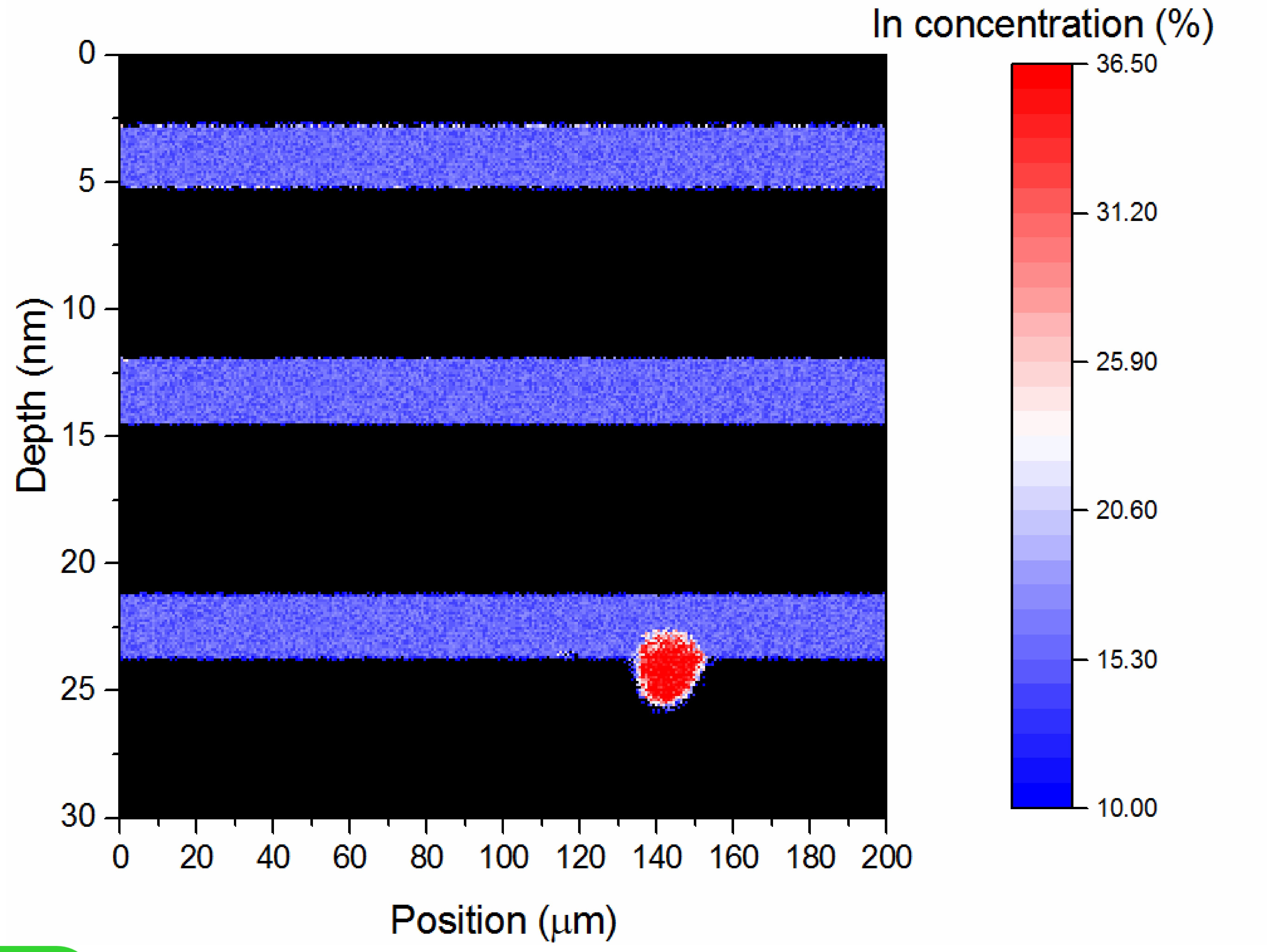
Growth temperature 830ºC



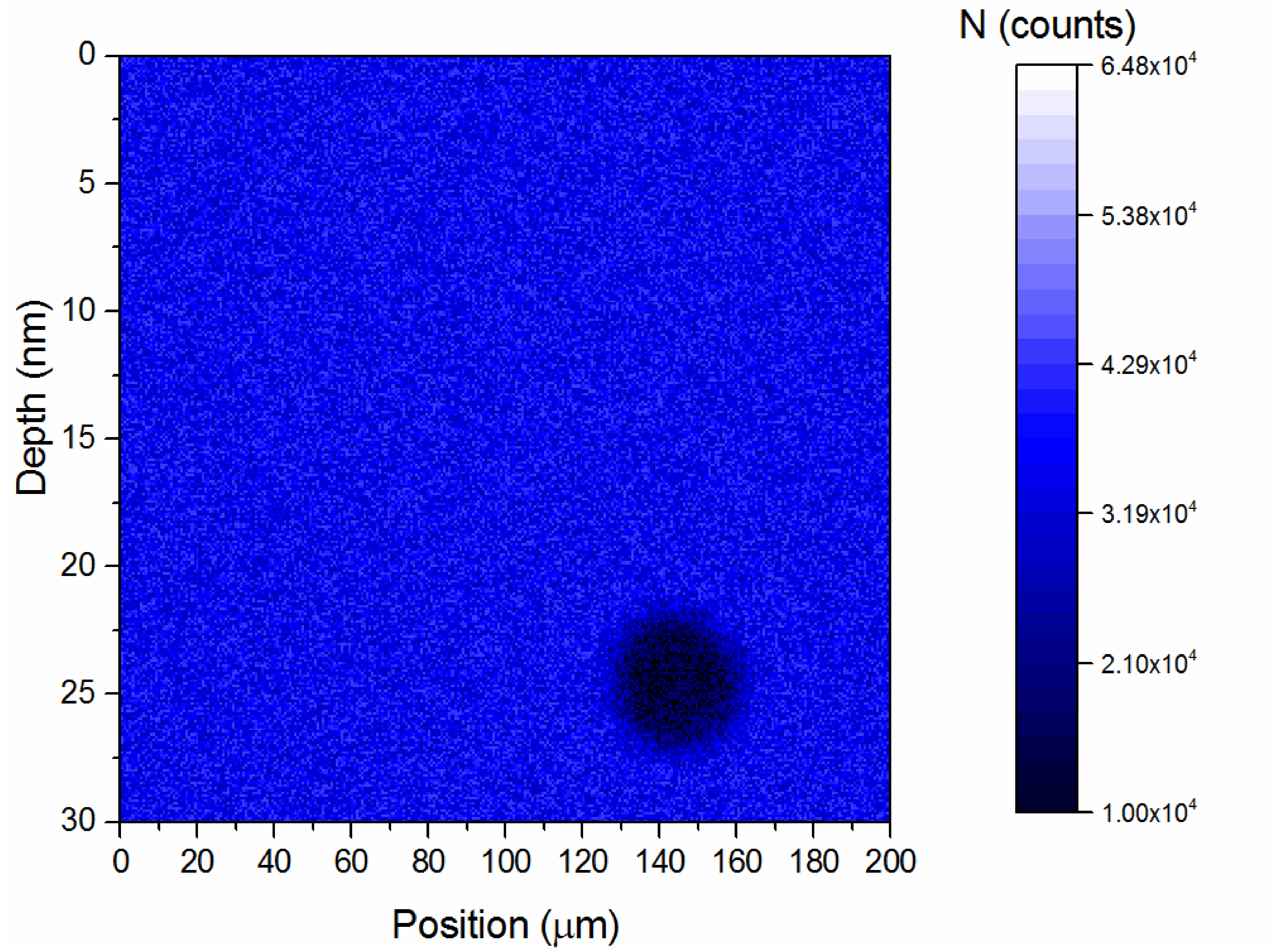
Please note the scale! Not TEM!



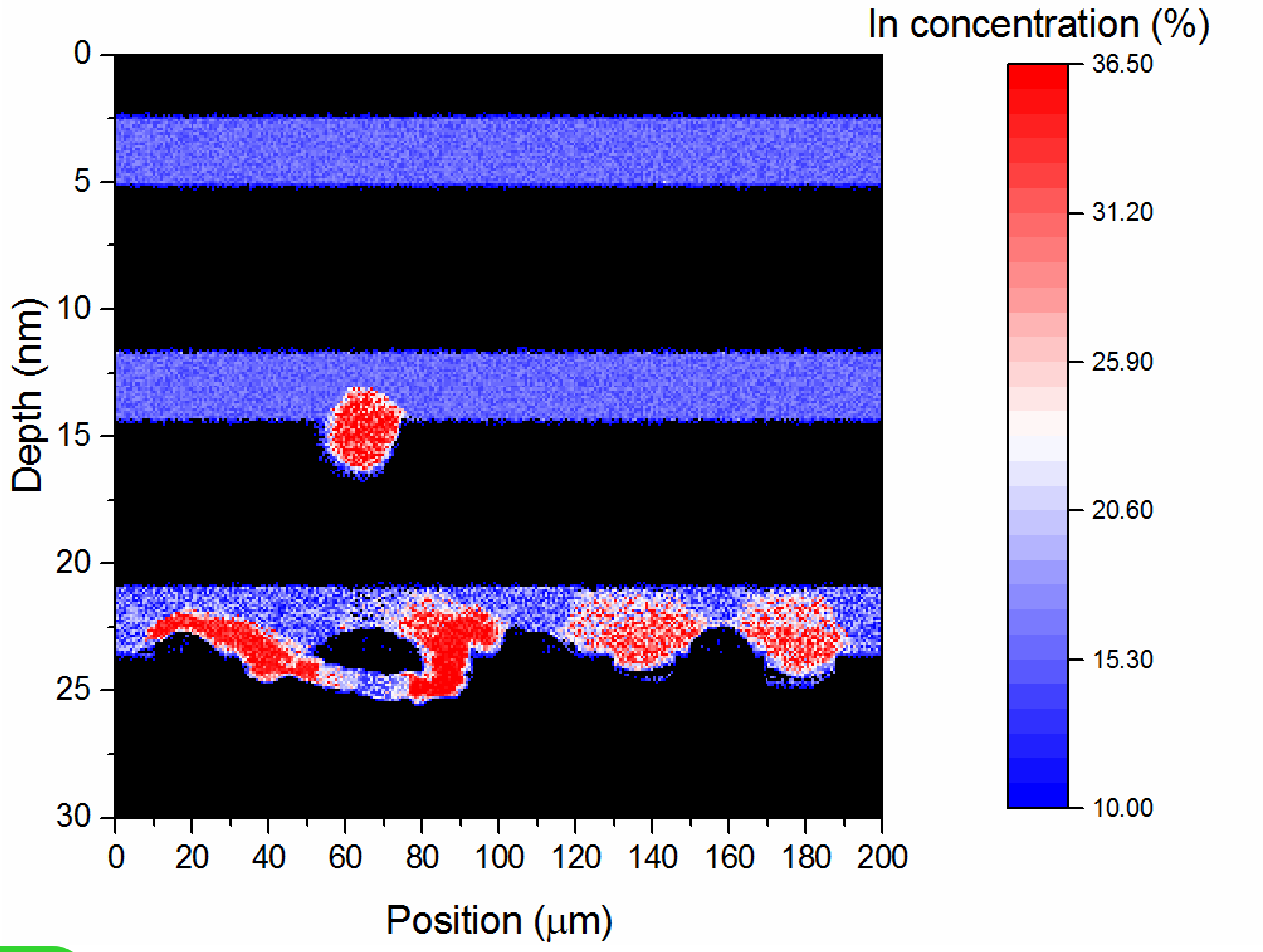
Growth temperature 905ºC



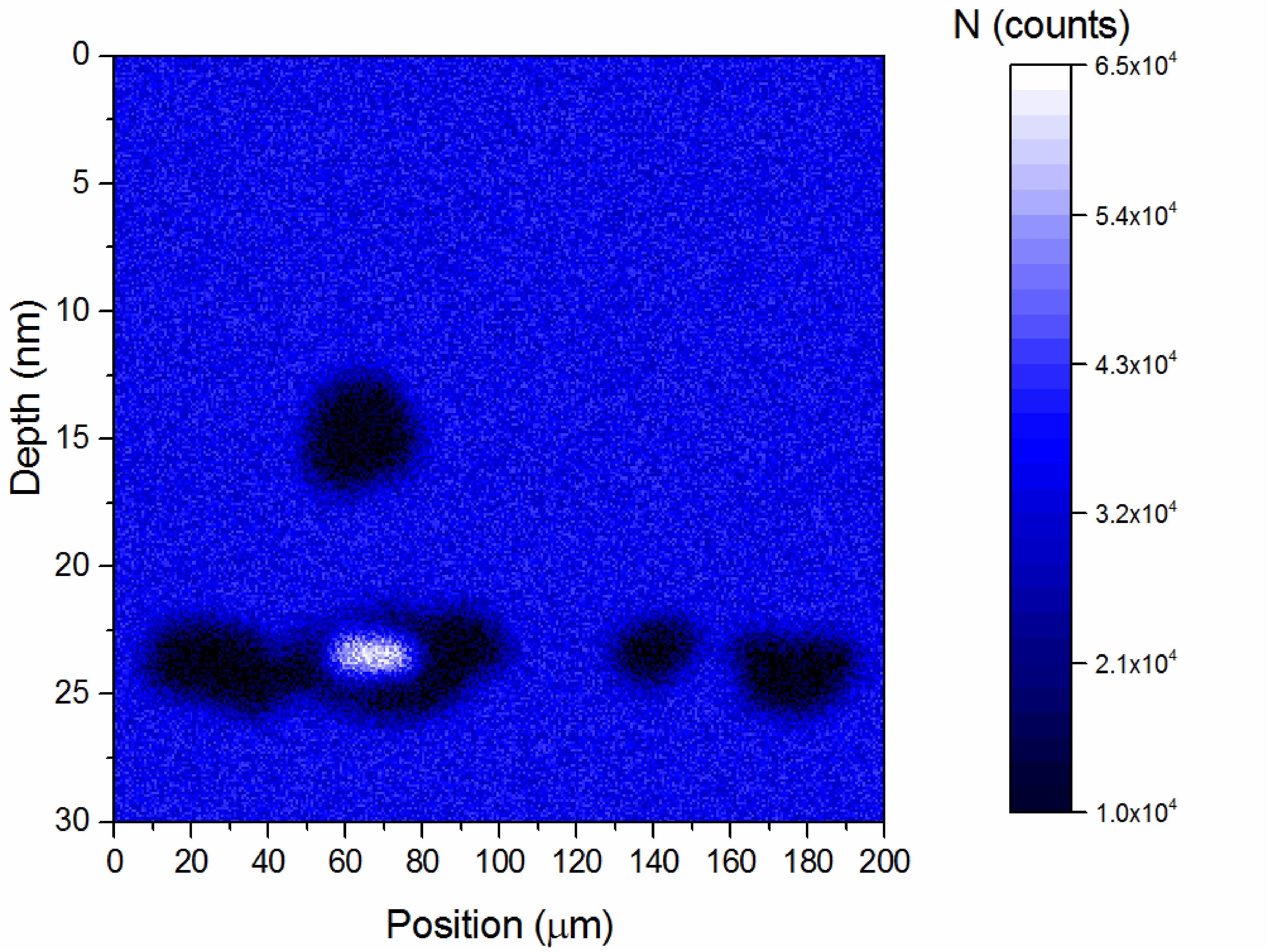
Please note the scale! Not TEM!



Growth temperature 930ºC



Please note the scale! Not TEM!



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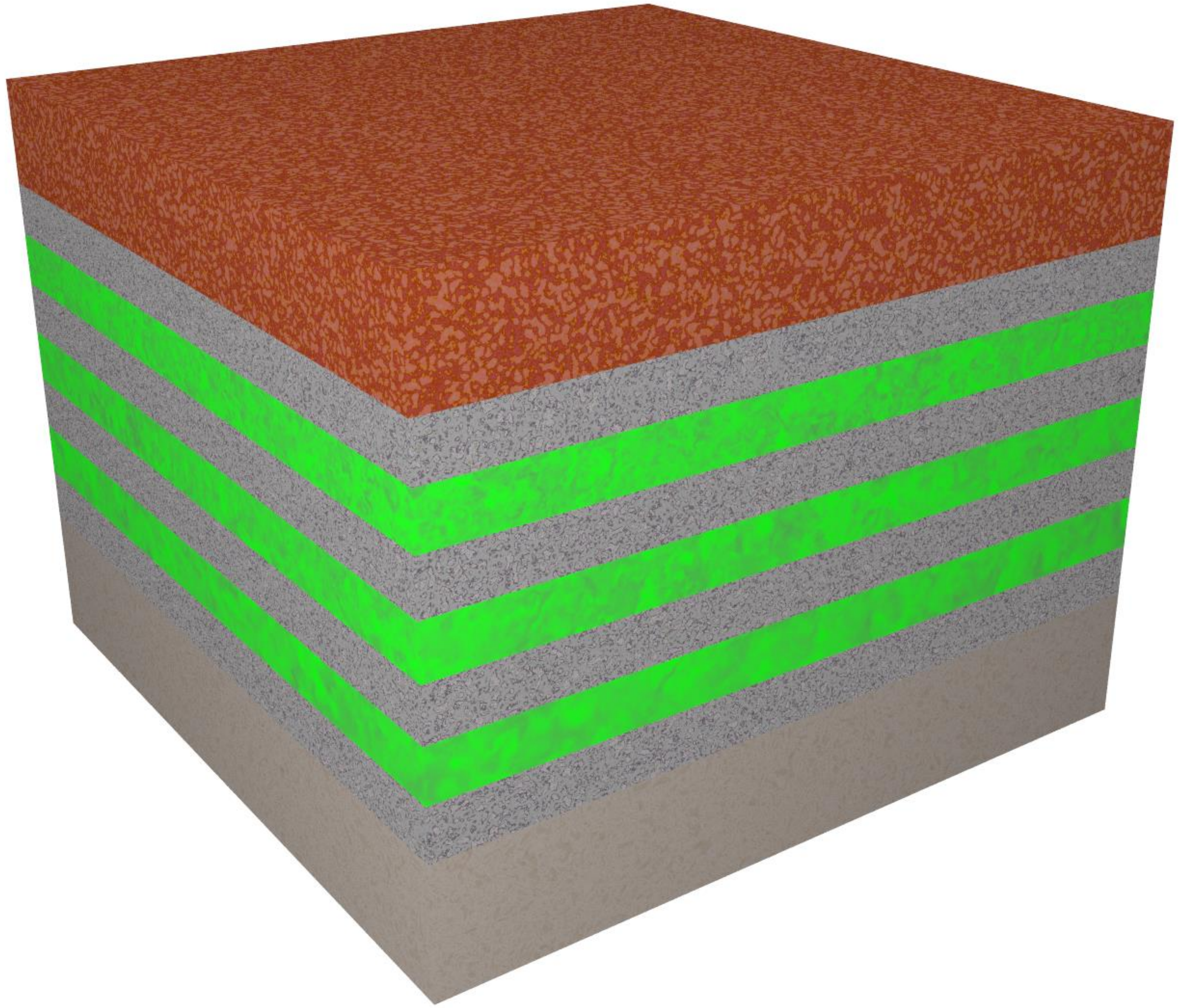
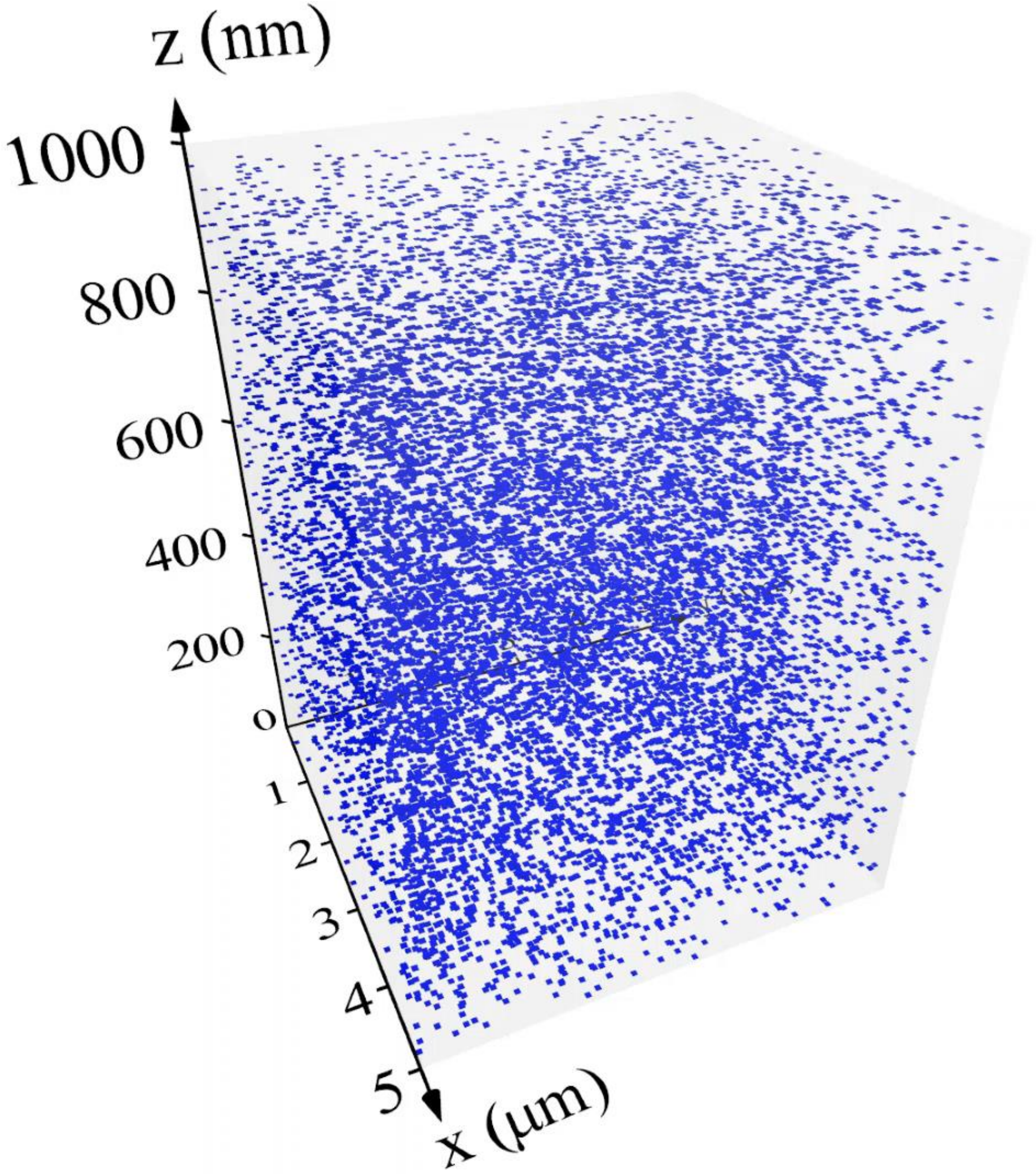
InGaN QWs – summary



- Microscopic fluctuations
- Metallic indium precipitation
- Nitrogen bubbles
- Only one interface!
- Vacancies out-diffusion

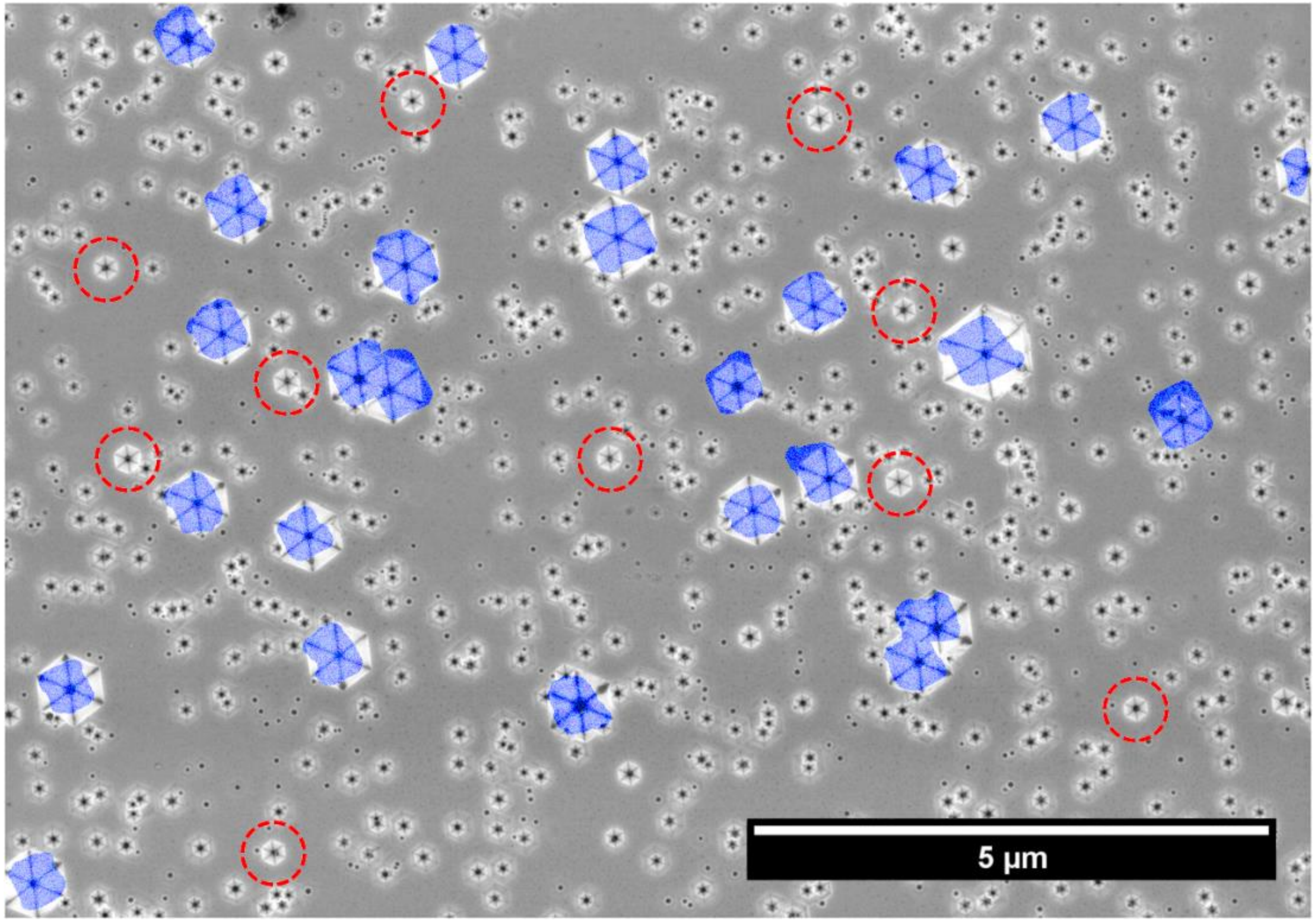
Oxygen in GaN

- Sophisticated procedure
- Background contribution
- Random



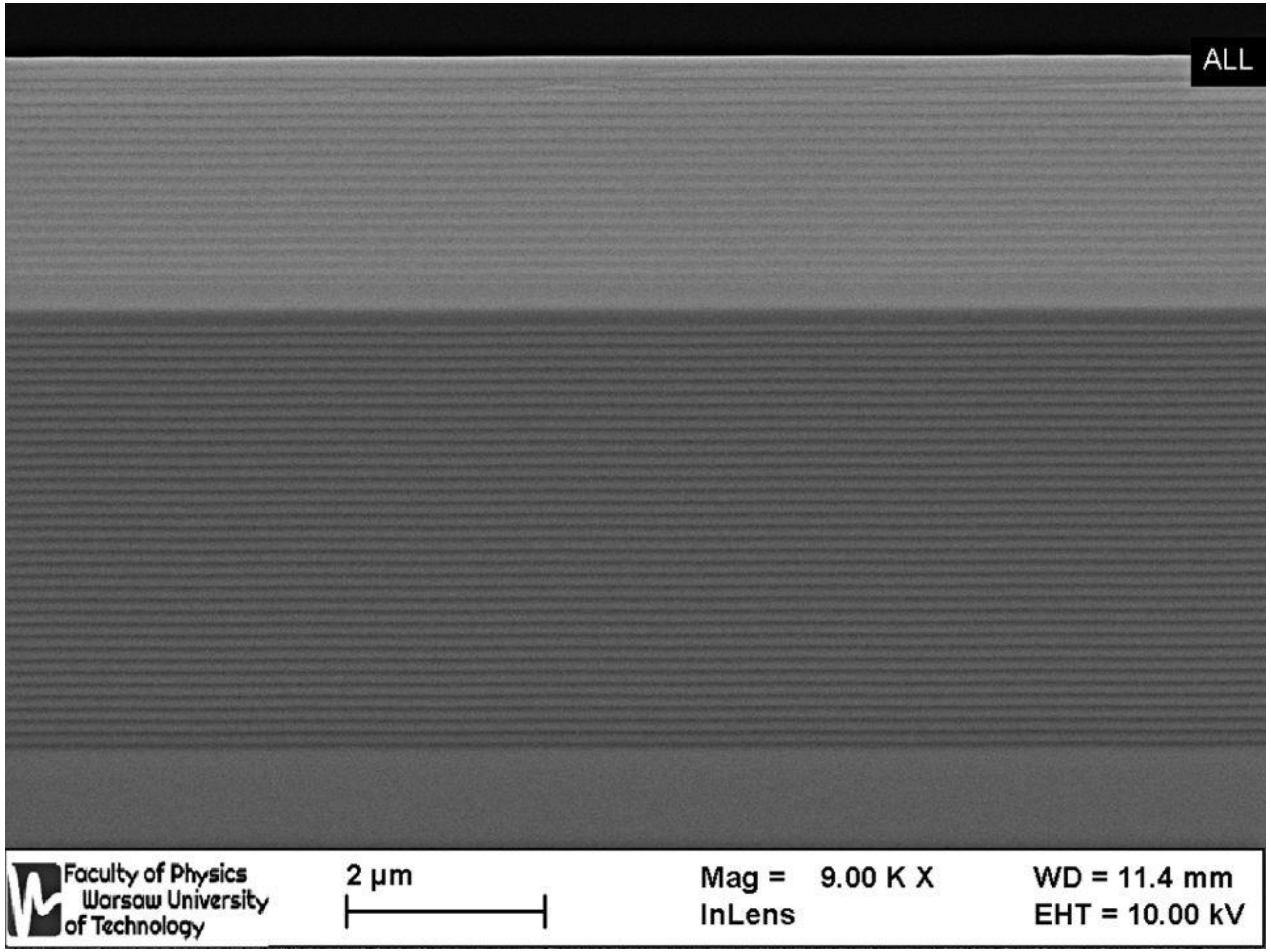
Chemical Communications 55, 11539-11542, 2019
Journal of Visualized Experiments 158, e61065, 2020

Oxygen in GaN



Chemical Communications 55, 11539-11542, 2019
Journal of Visualized Experiments 158, e61065, 2020

Vertical-cavity surface-emitting laser

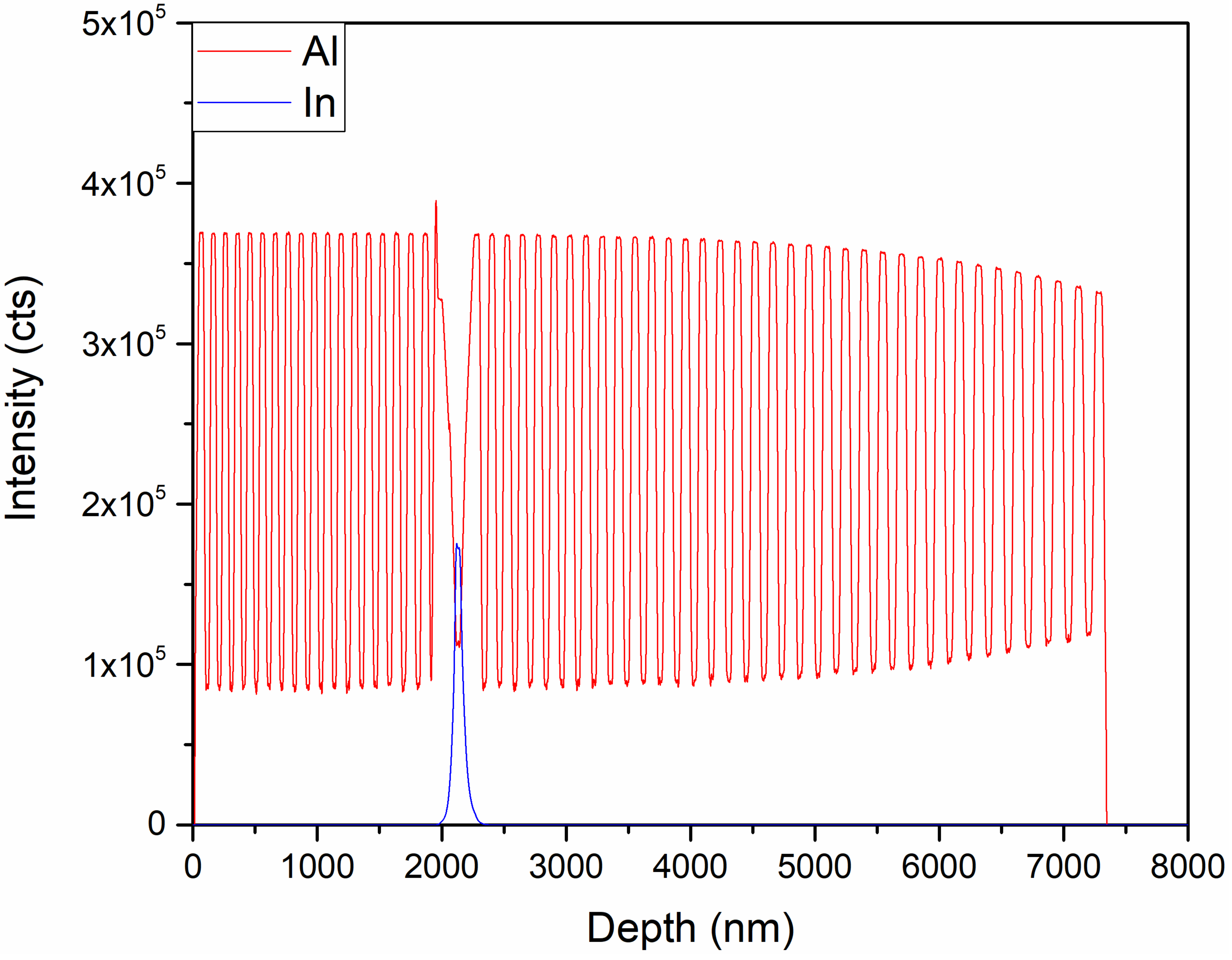


Remarks

- Hundreds of layers
- 3 nm thick QWs
- Oxidation aperture

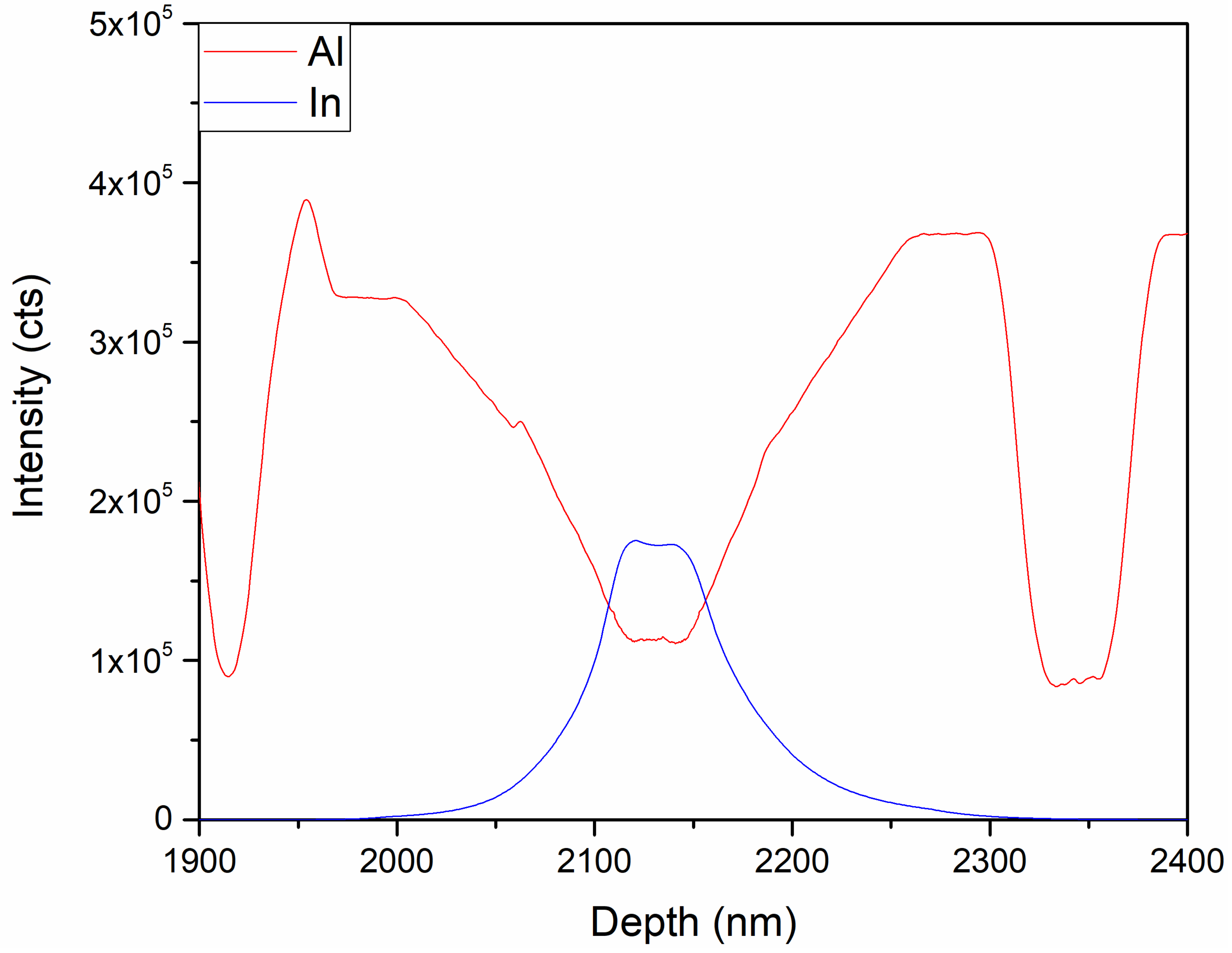
- Difficult sample for SIMS

Standard SIMS procedure



Remarks

- Cs$^+$, 1000 eV
- Mixing effect
- Crater roughness
- Primary beam deterioration
- Poor depth resolution



Solution

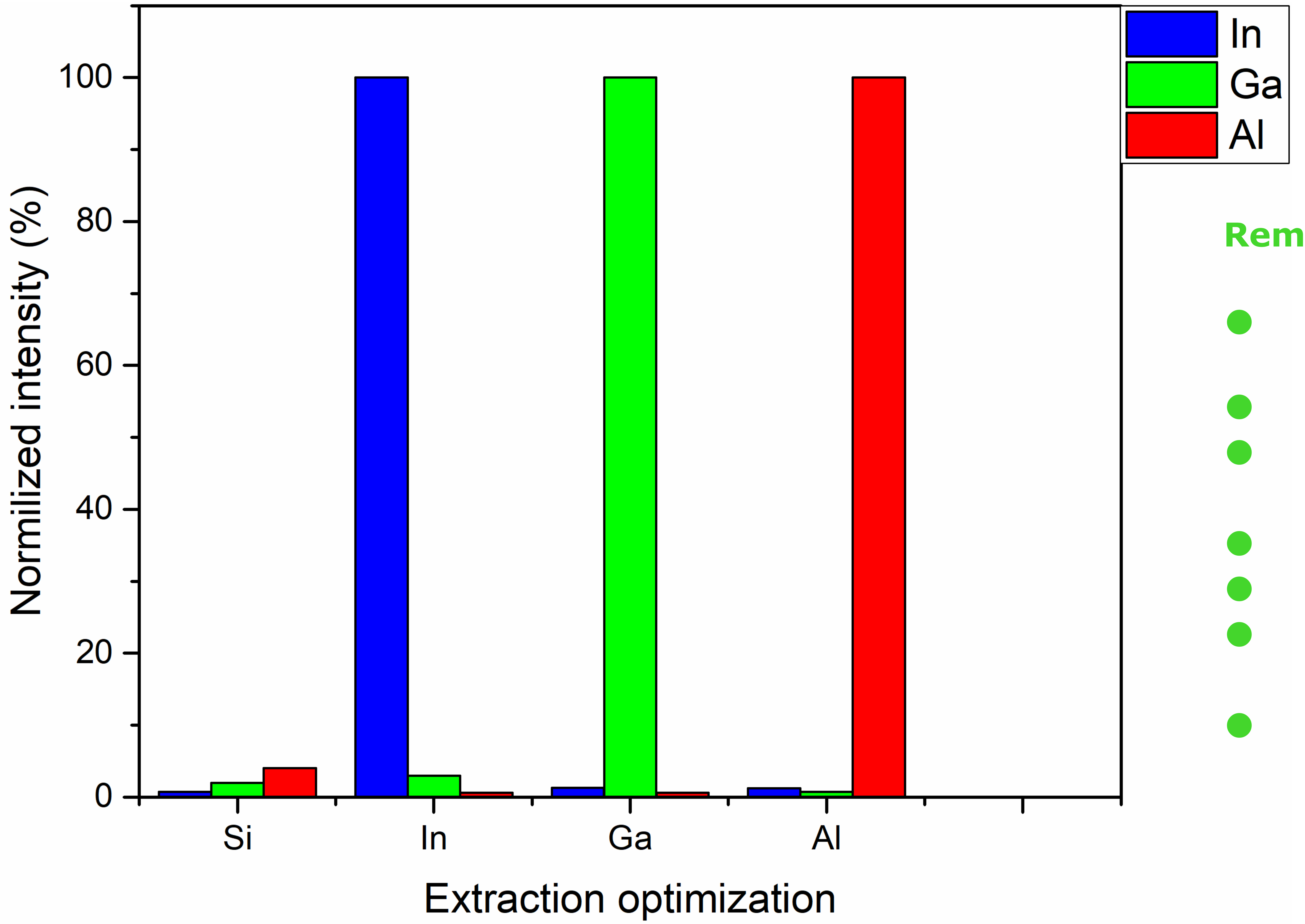
Optimization

- Mixing effect – lower impact energy -> Preferential sputtering and crater roughness
- Crater roughness – higher impact energy -> mixing effect
- Primary beam deterioration – higher beam density -> poor depth resolution
- Poor depth resolution – where to begin?
- Is it possible to optimize?

Paradigm shift

- Mixing effect – high incident angle
- Crater roughness – ion polishing
- Primary beam deterioration – beam service
- Poor depth resolution – impact energy modulation

500 eV, 69º incident angle – extraction parameters



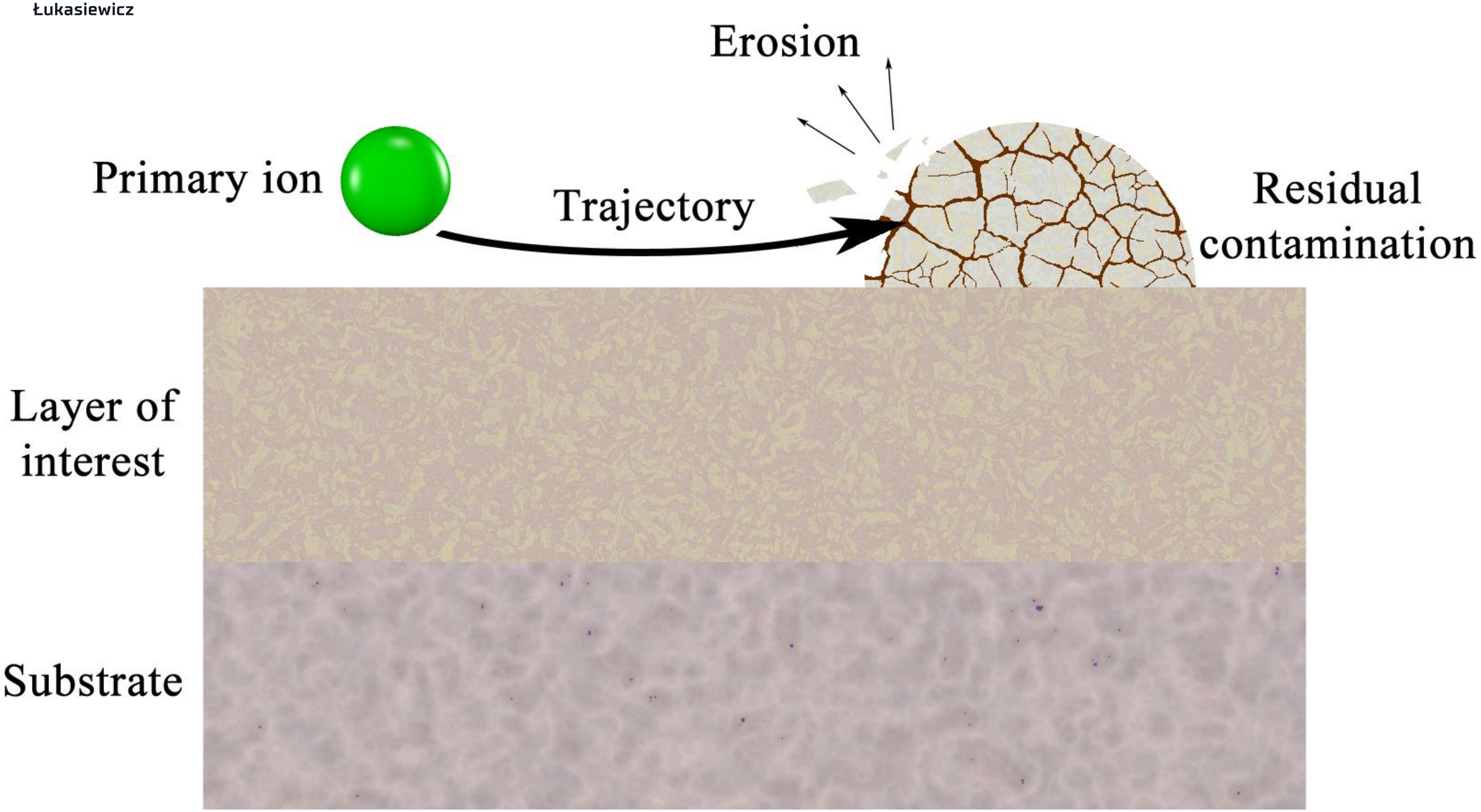
Remarks

- Not supported by software
- One point per file
- Interruptions so…

- Energy
- Angle
- Polarity

- Additional steps

Ion polishing

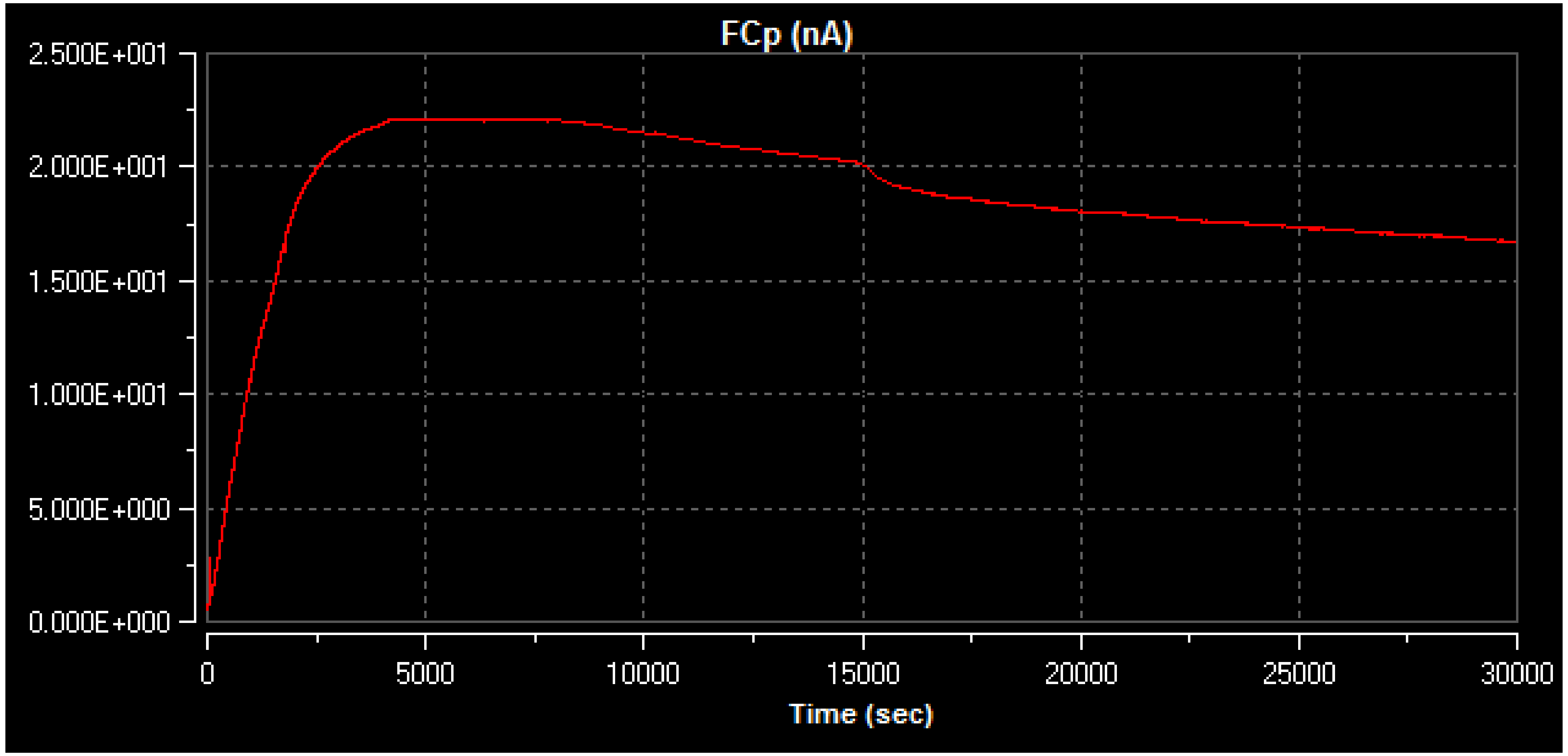


Idea

- High Energy (2-3 keV)
- High incident angle (75^o)
- 96.5% of p || to the surface!
- Offset voltage
- No damage to the surface
- Cleaning

- Every 0.5 – 1 hour
- Fully automated

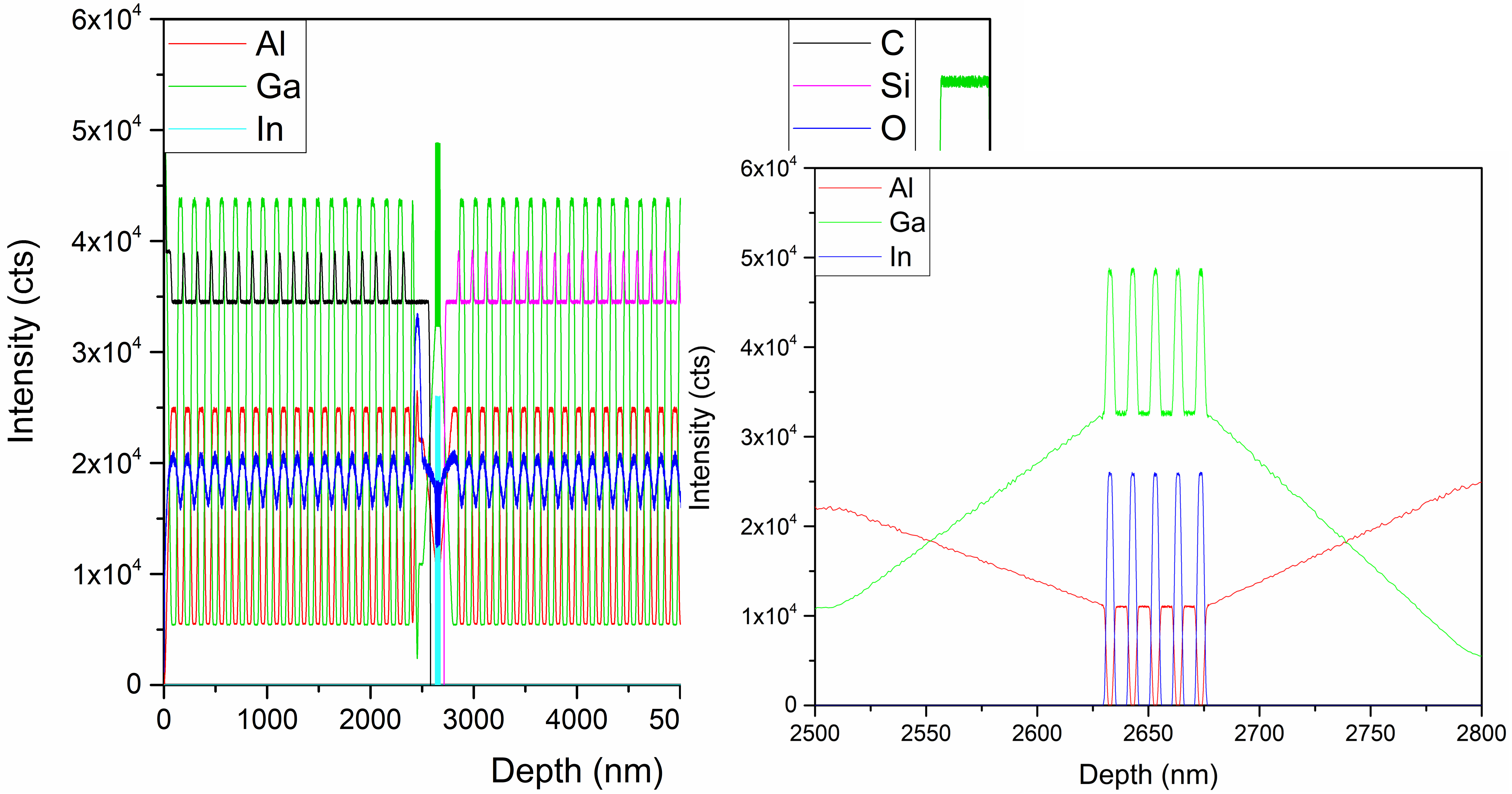
Primary beam service



Idea

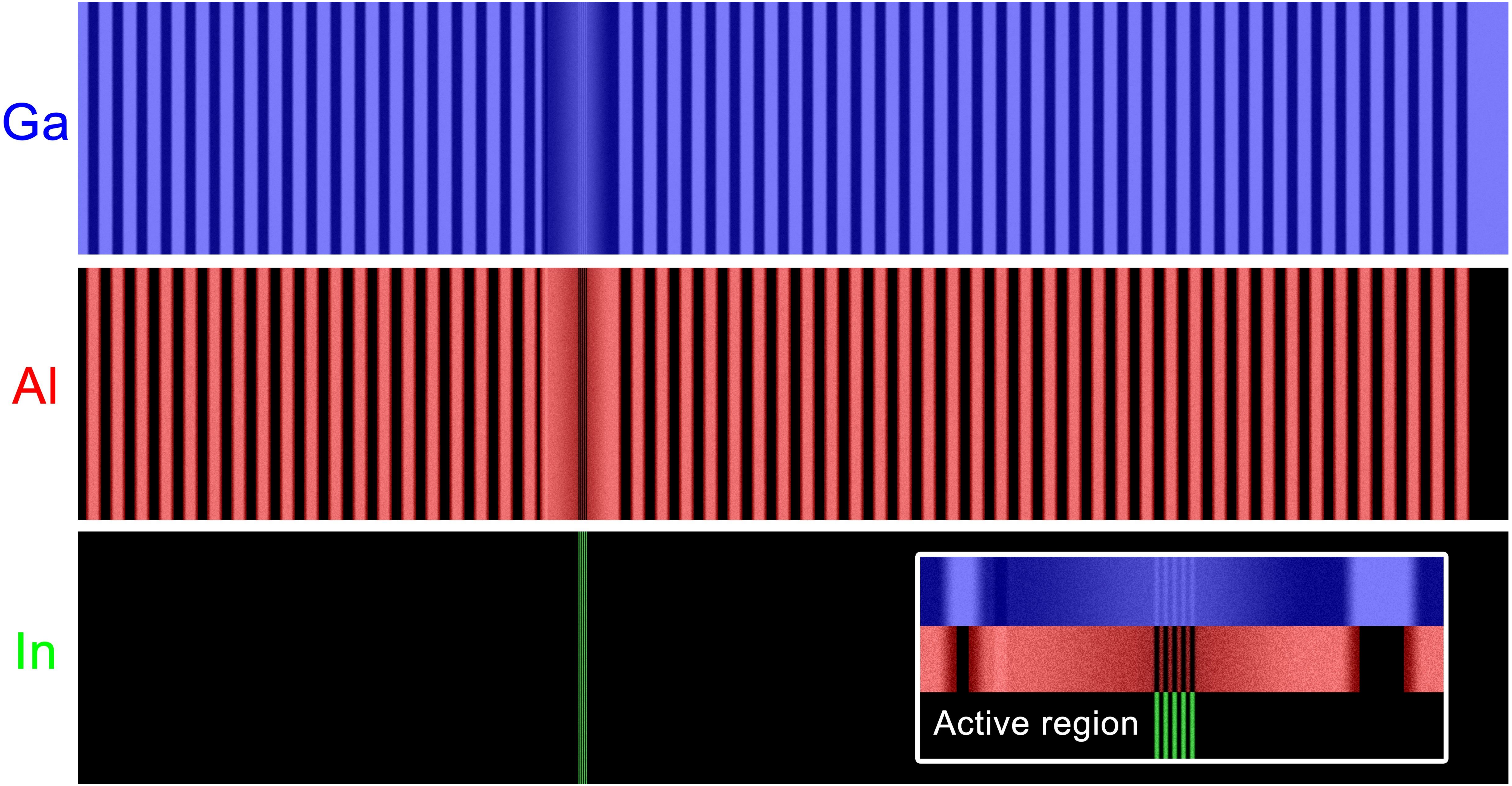
- Safe value (15 nA)
- Every 0.5 – 1 hour
- Fully automated

Final result

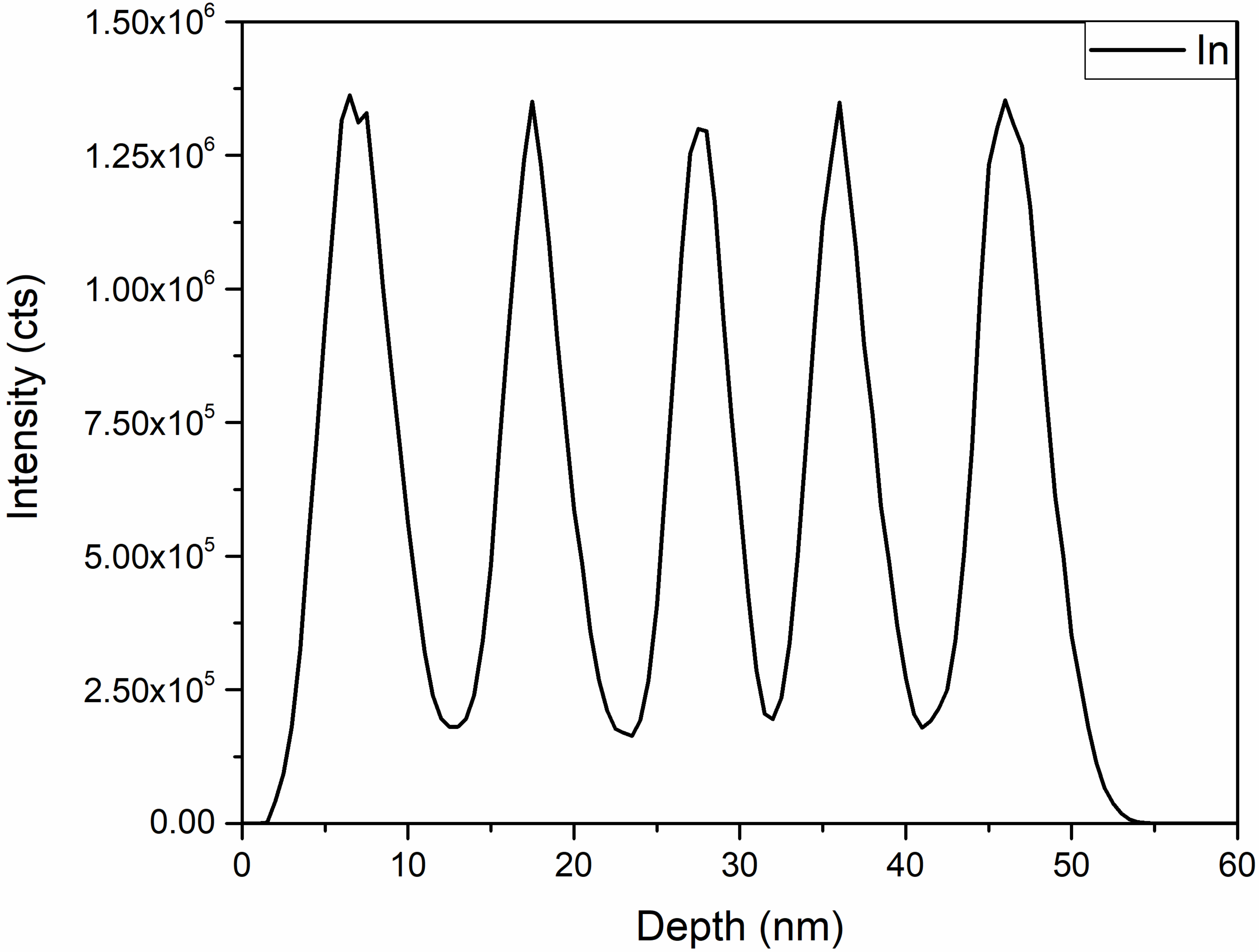


Science meets art

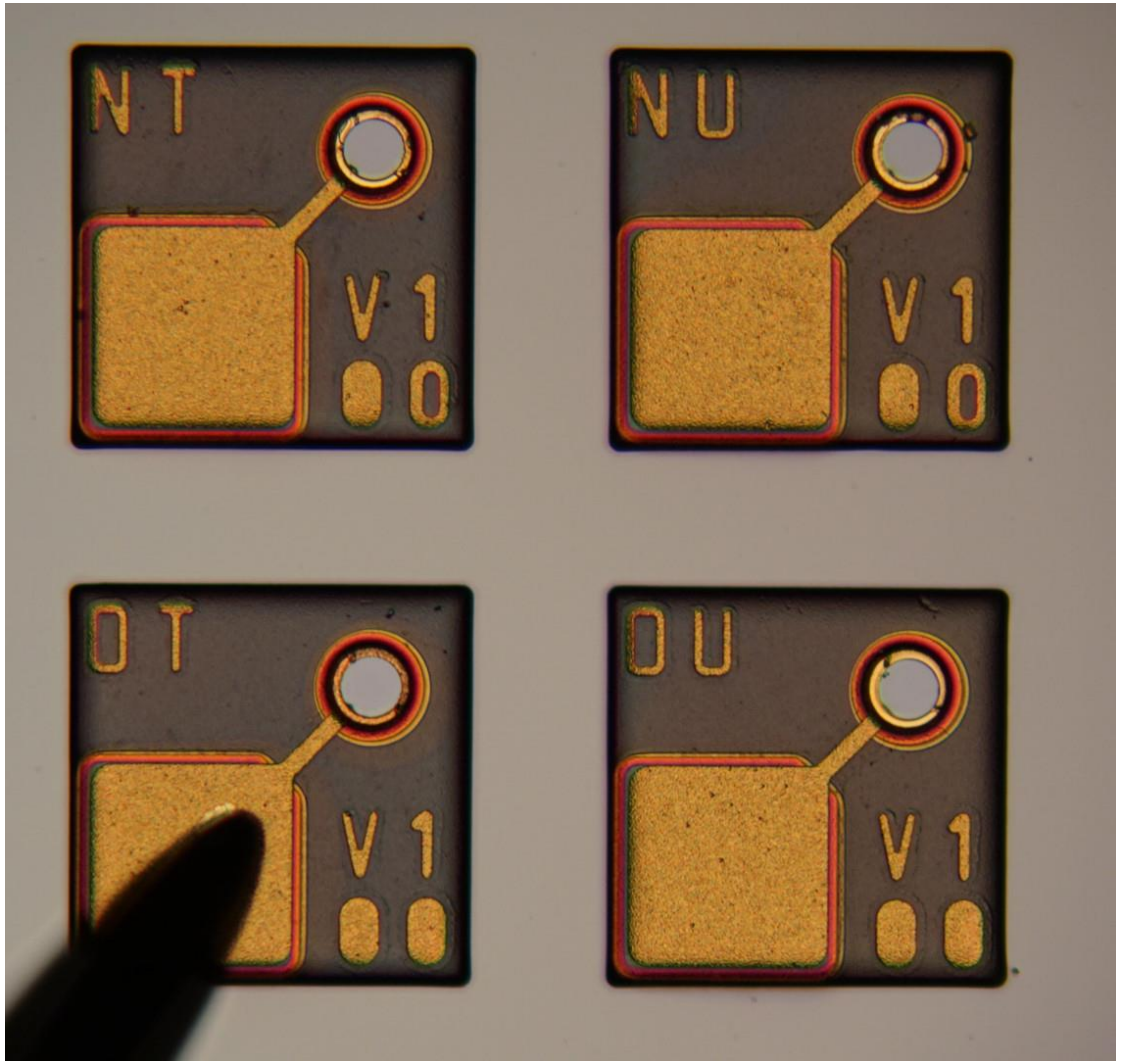
https://www.cameca.com/company/newsandevents/2023-calendar-competition/march

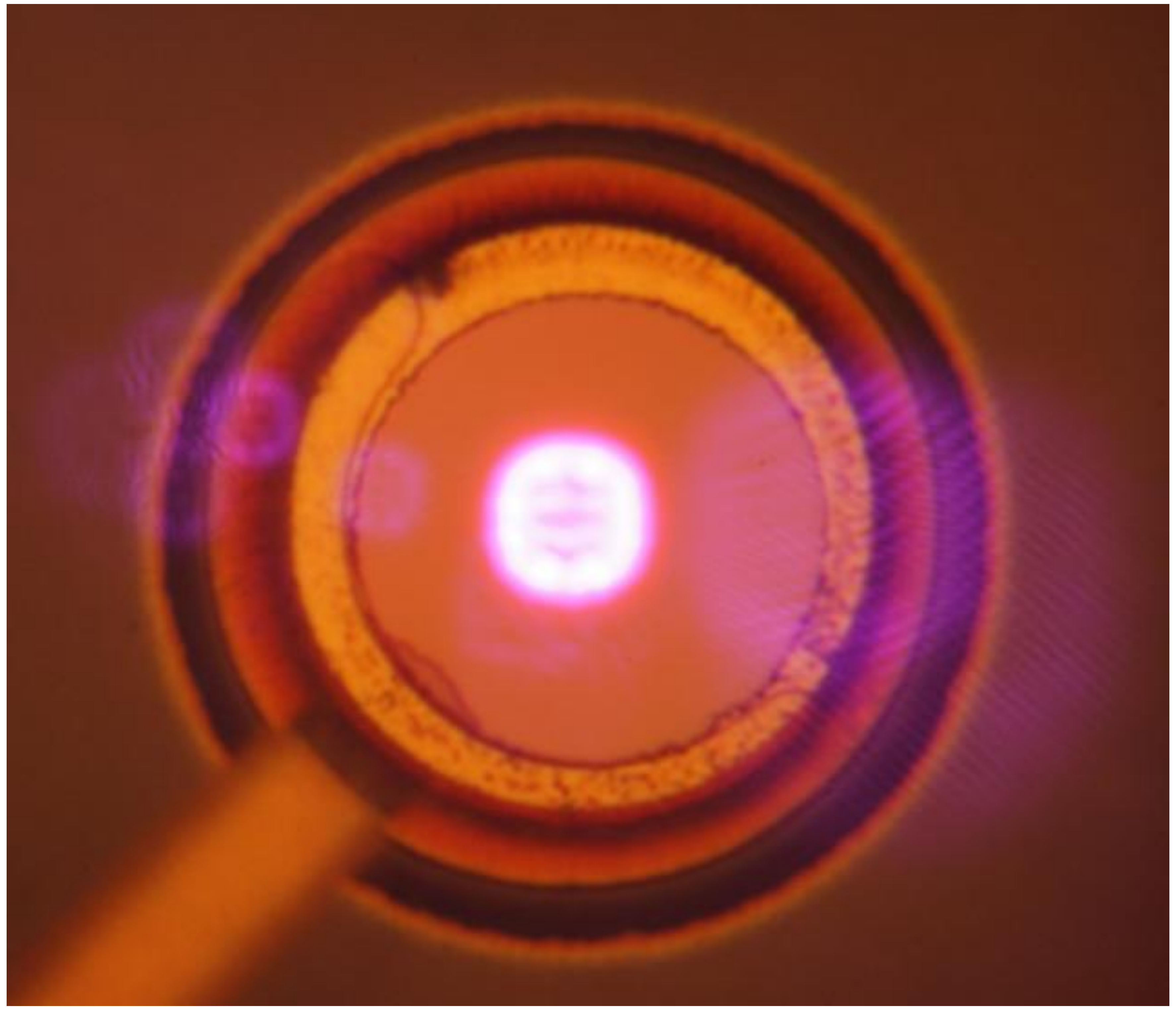


Impact energy modulataion – is it important?

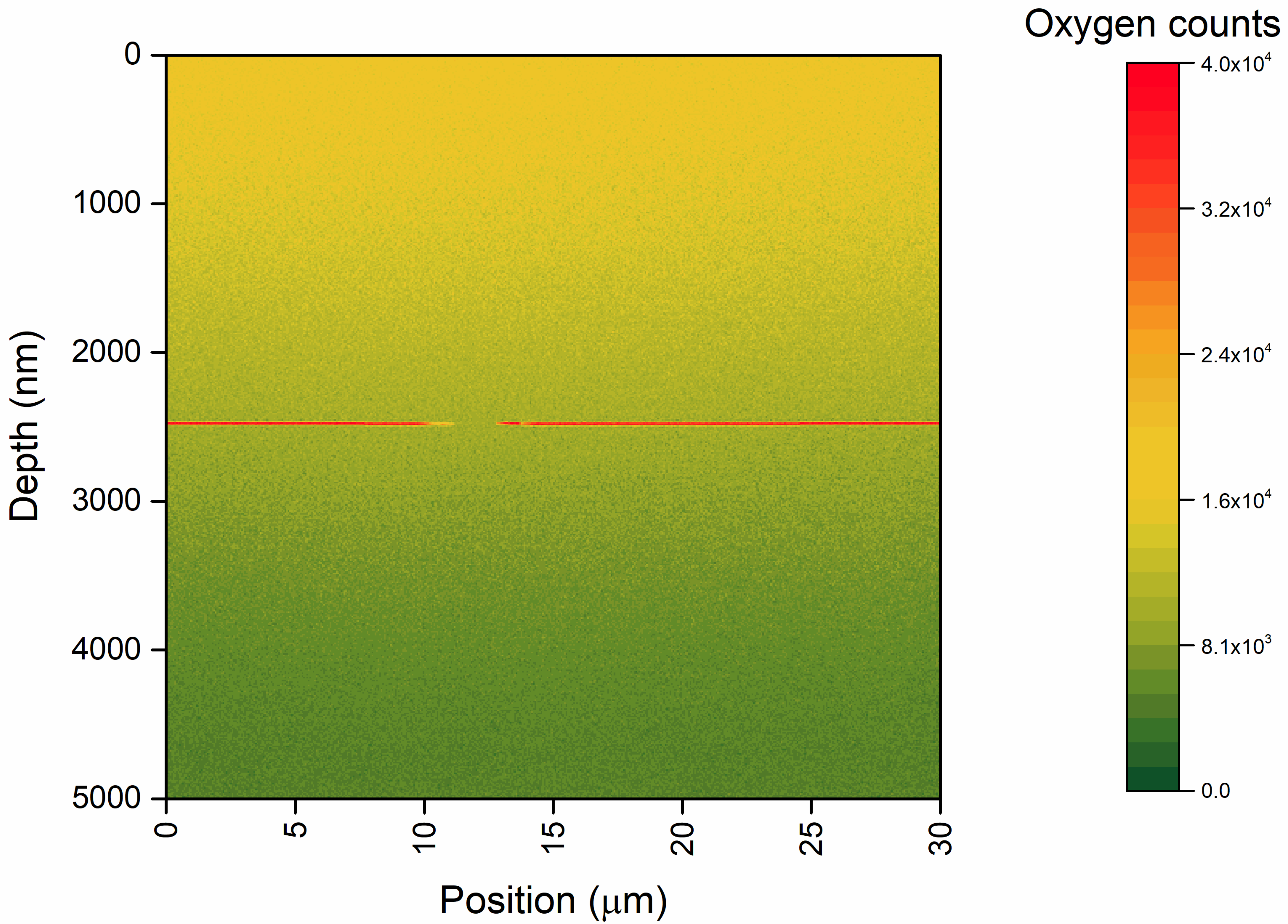


Aperture





Aperture


Oxygen counts
4.0x10^4
3.2x10^4
2.4x10^4
1.6x10^4
8.1x10^3
0.0
Depth (nm)
0
1000
2000
3000
4000
5000
Position (µm)
0
5
10
15
20
25
30

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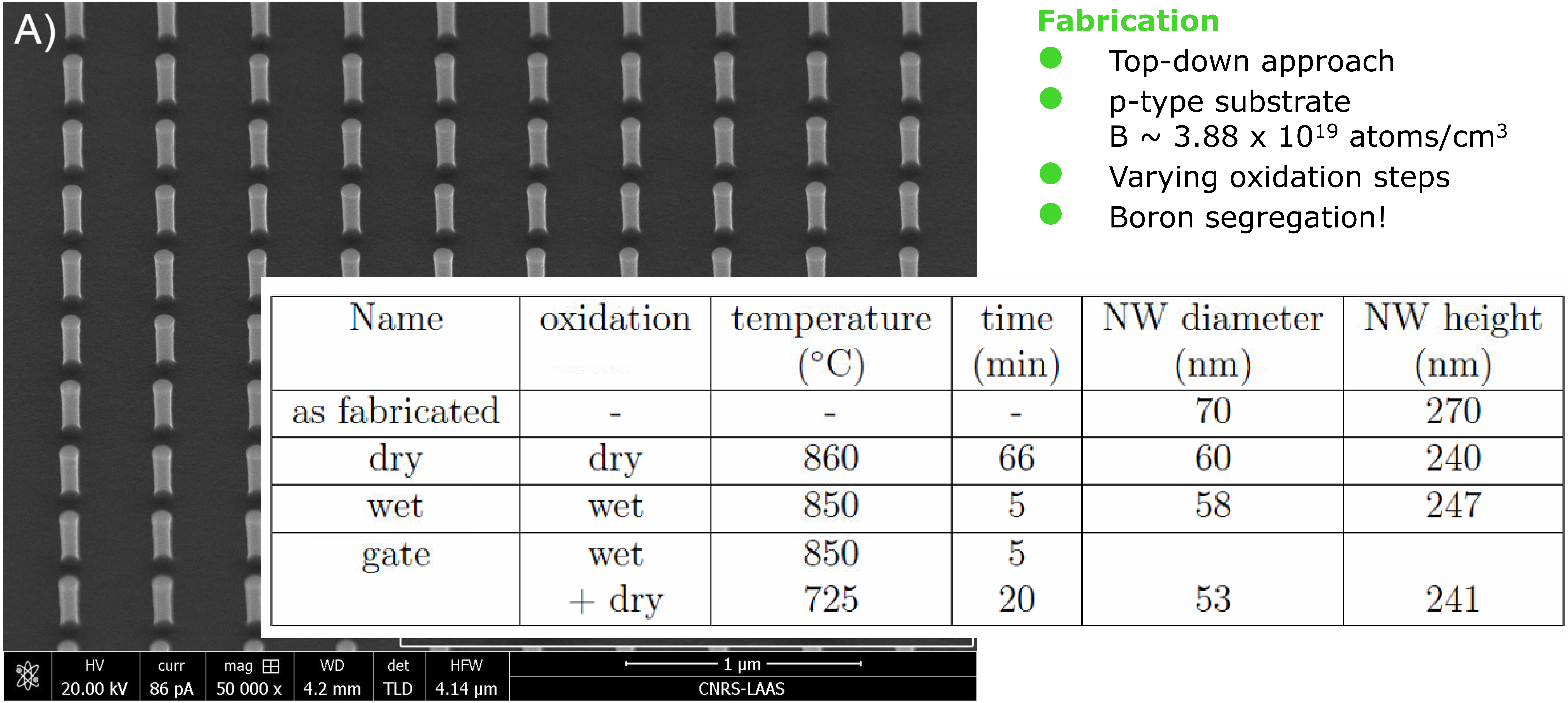
Array of nanowires



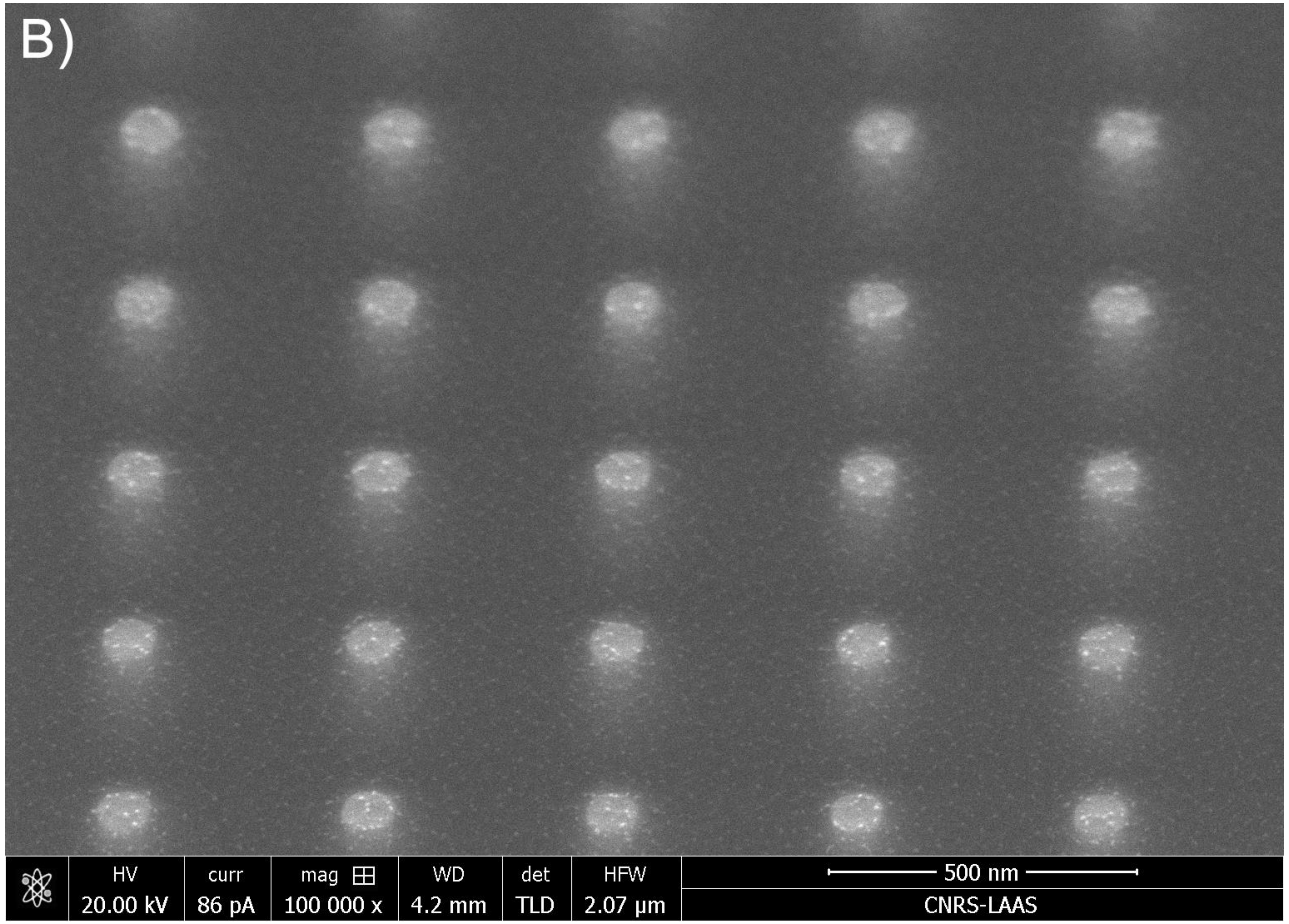
Name	oxidation	temperature (°C)	time (min)	NW diameter (nm)	NW height (nm)
as fabricated	-	-	-	70	270
dry	dry	860	66	60	240
wet	wet	850	5	58	247
gate	wet + dry	850 725	5 20	53	241

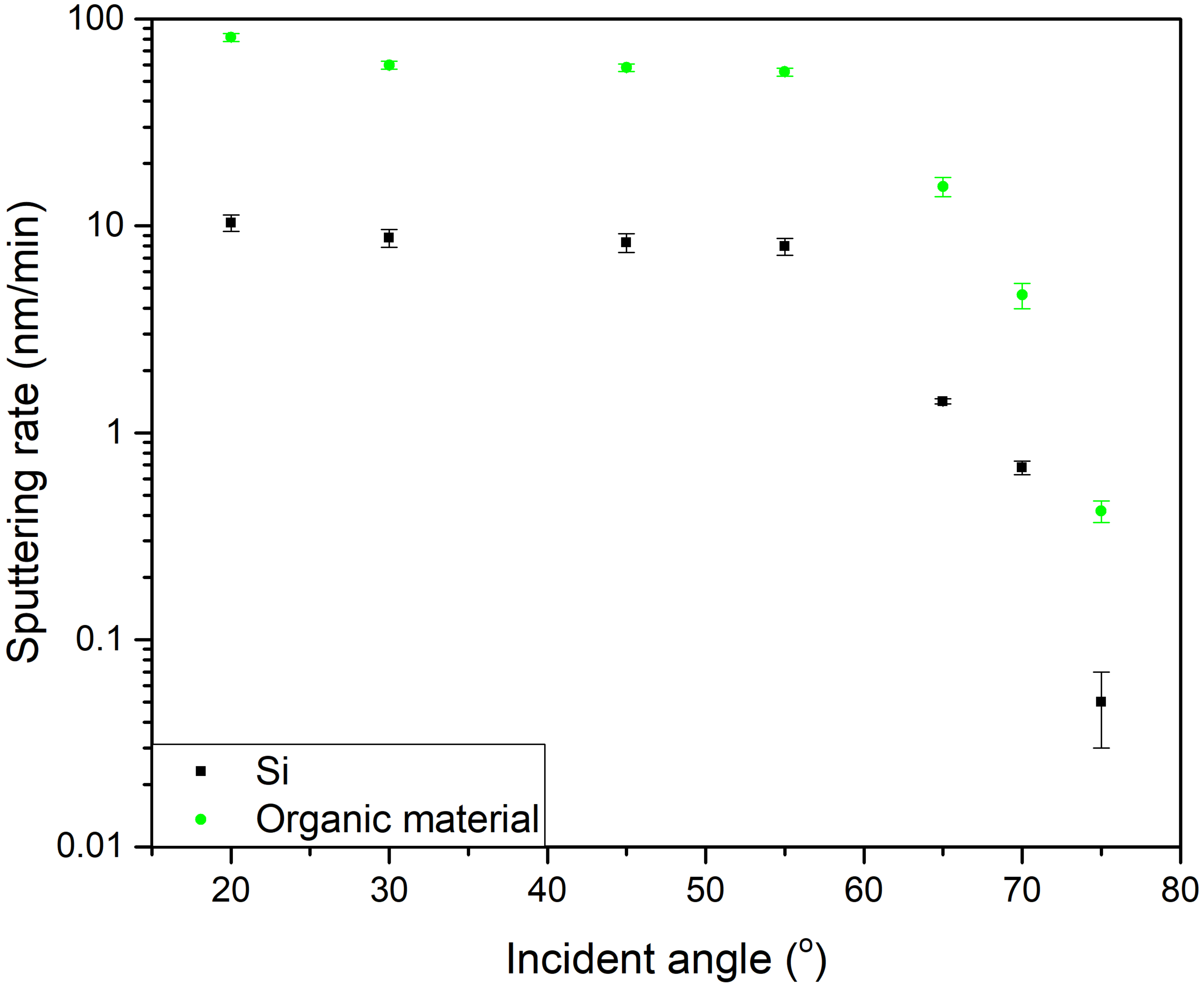
Fabrication

- Top-down approach
- p-type substrate
  B ~ 3.88 x 10^{19} atoms/cm^3
- Varying oxidation steps
- Boron segregation!

Measurement 211, 112630, 2023

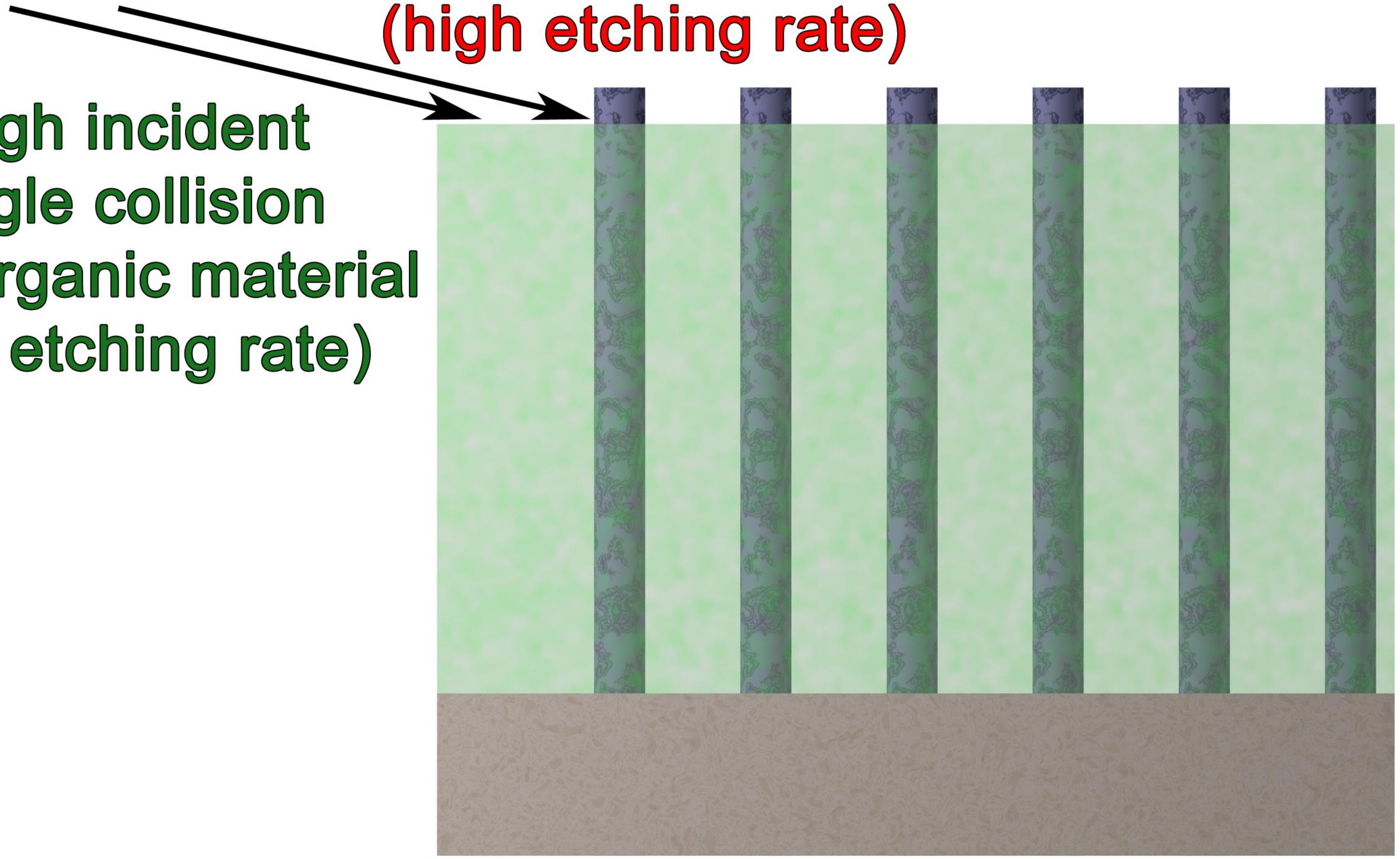
SIMS measurements on 3D structures





Measurement 211, 112630, 2023

SIMS measurements on 3D structures

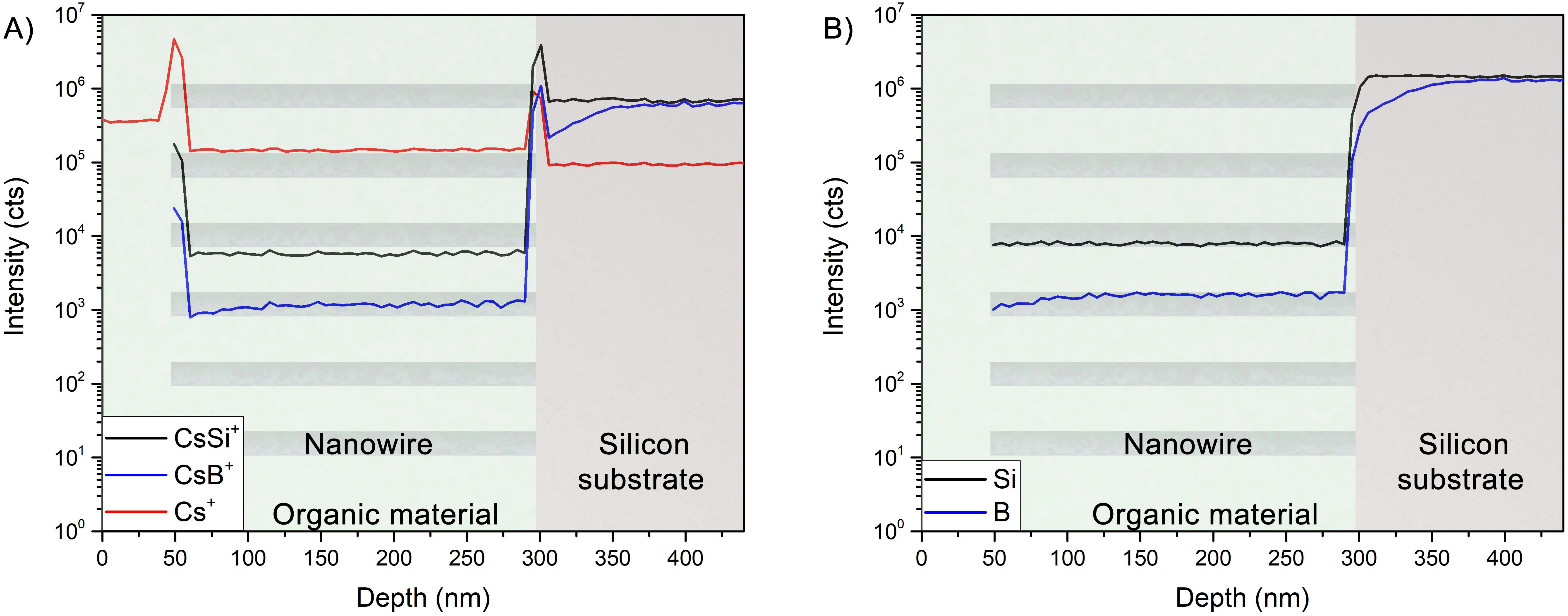


Low incident
angle collision
with silicon nanowire
(high etching rate)

High incident
angle collision
with organic material
(low etching rate)

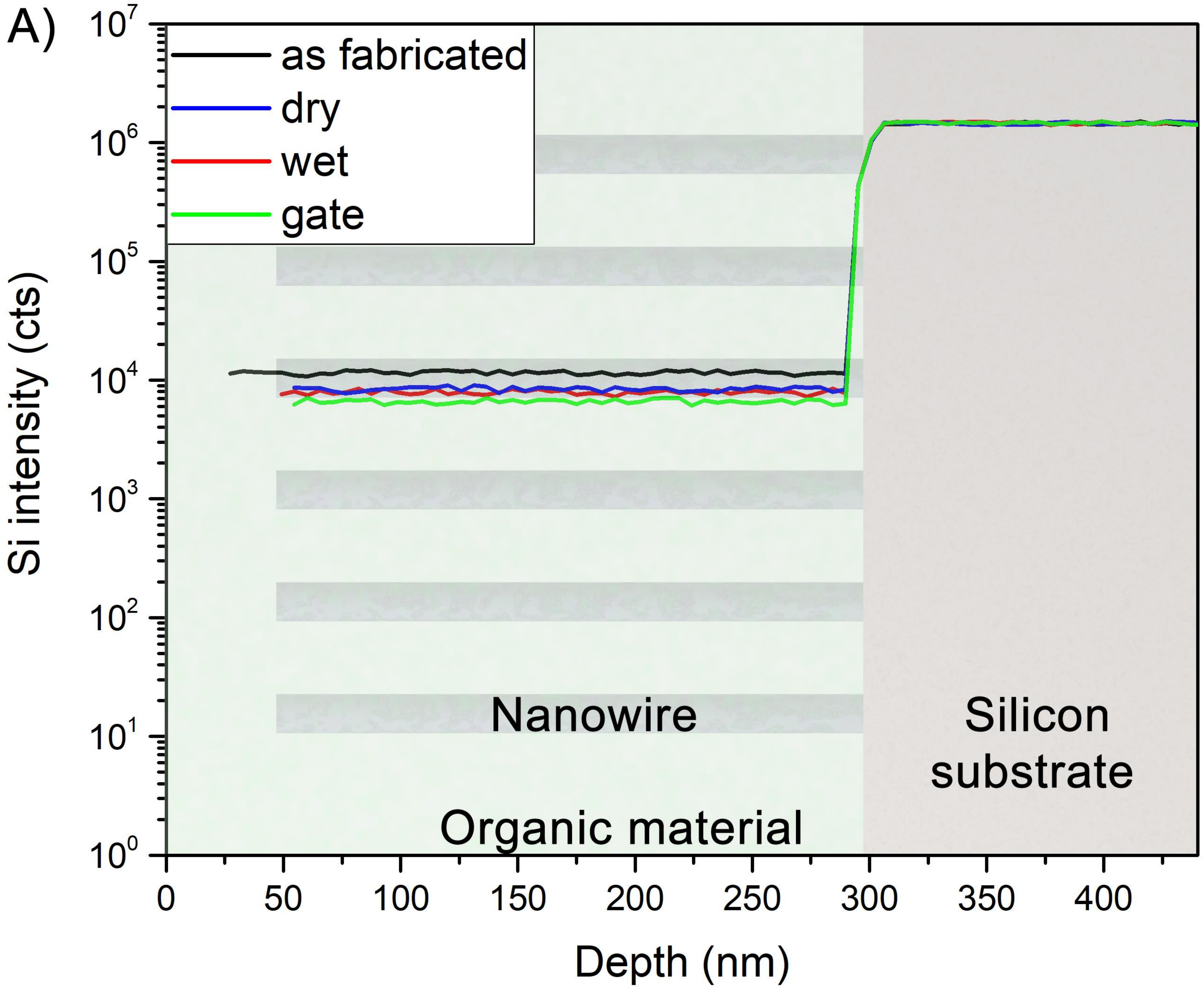
Measurement 211, 112630, 2023

Data analysis



Measurement 211, 112630, 2023

Silicon signal

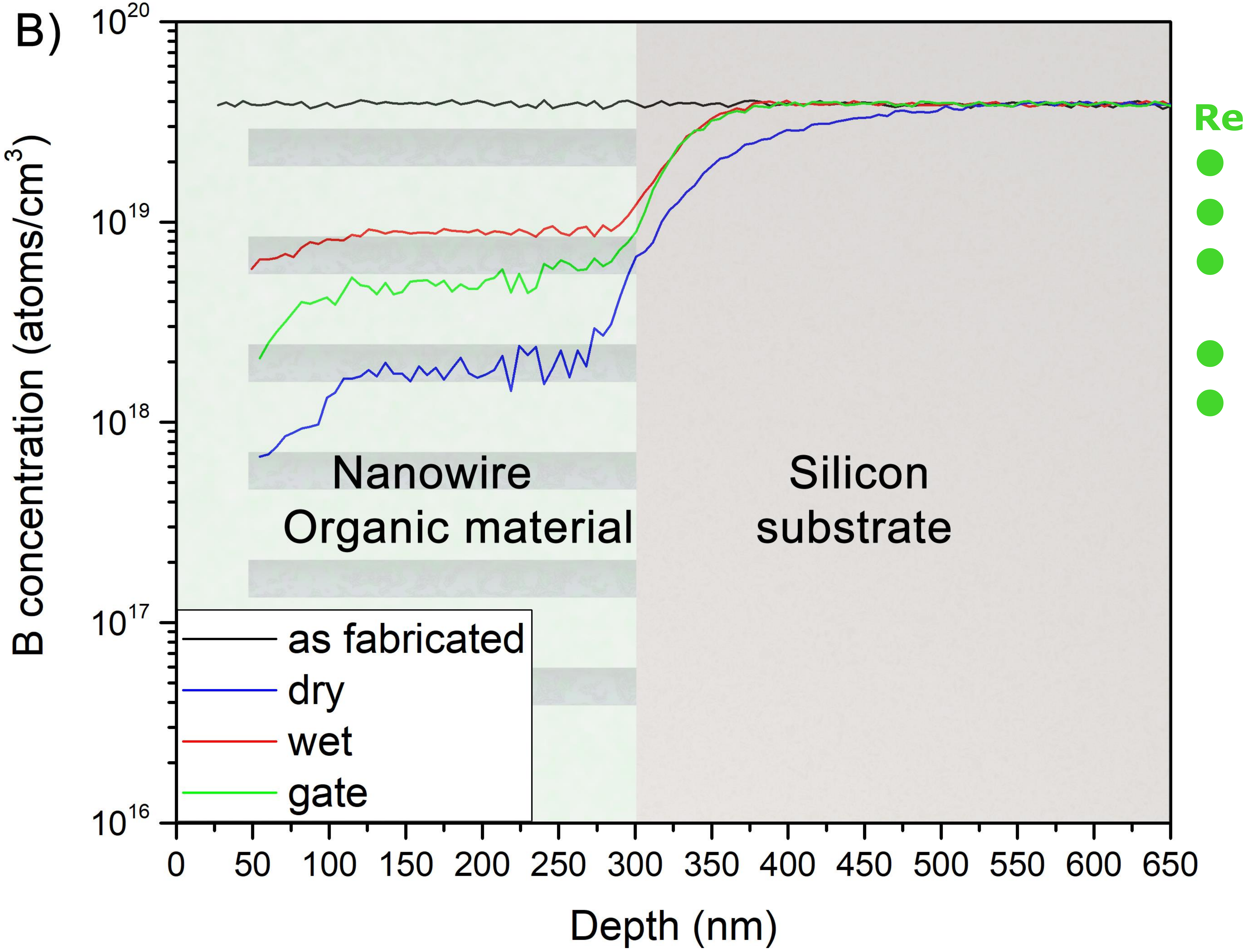


Remarks

- Intensity ~ d^2
- Very high quality
- As fabricated: 70.1±0.6 nm (70)
- Dry: 59.9±0.7 nm (60)
- Wet: 57.8±0.7 nm (58)
- Gate: 52.9±0.8 nm (53)

Measurement 211, 112630, 2023

Boron signal

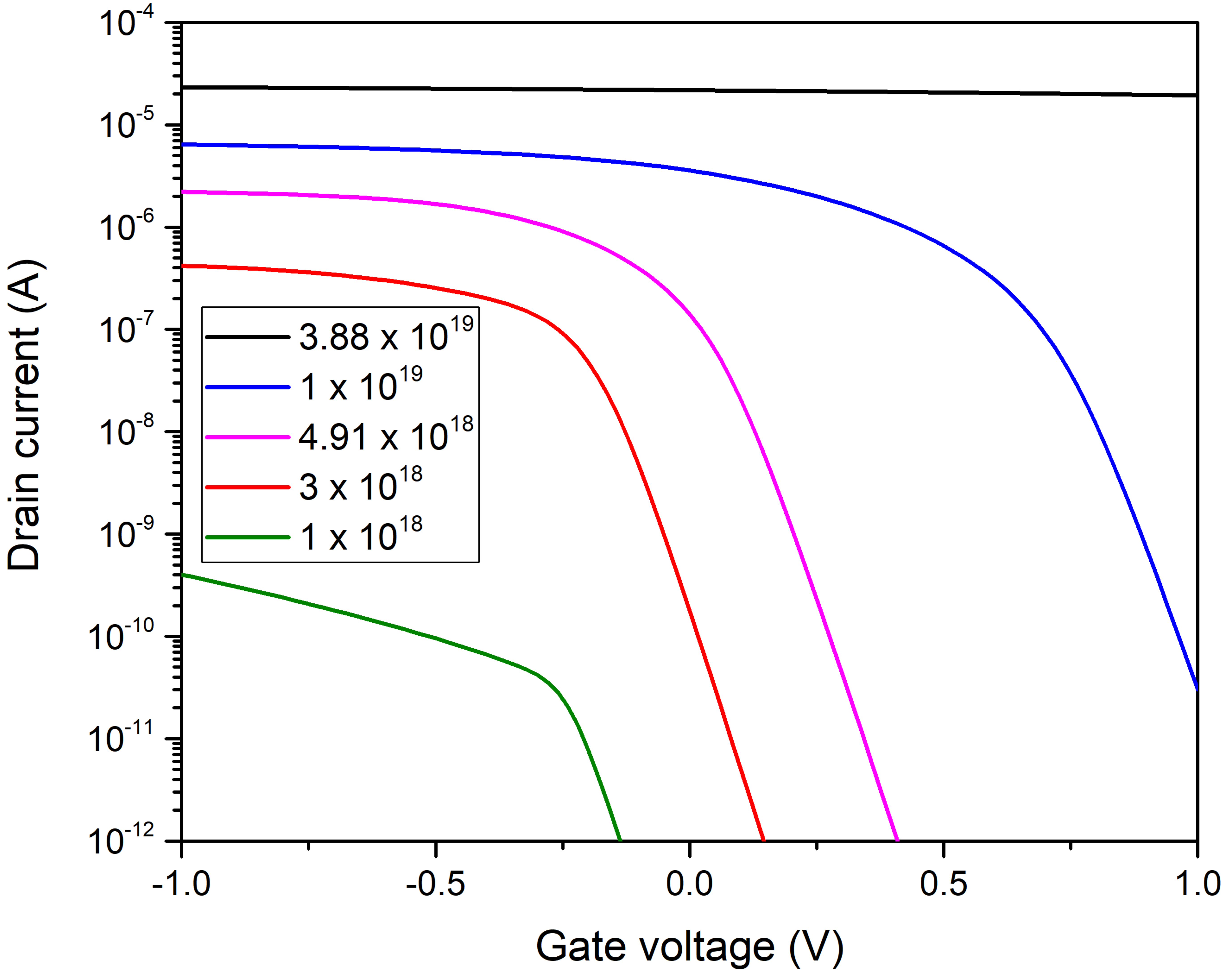


Remarks

- Clear depletion of boron
- Affects the substrate and NWs
- Depends strongly on oxidation time
- Good SNR (>8.3 dB)
- Detection limit
  5 x 10^{16} atoms/cm^3
  for array 1000 x 1000 NWs

Measurement 211, 112630, 2023

Gata-all-around nanowire field effect transistor



Remarks

- Not possible to switch off with the initial doping
- Small differences in doping Significant changes in operation!

Measurement 211, 112630, 2023

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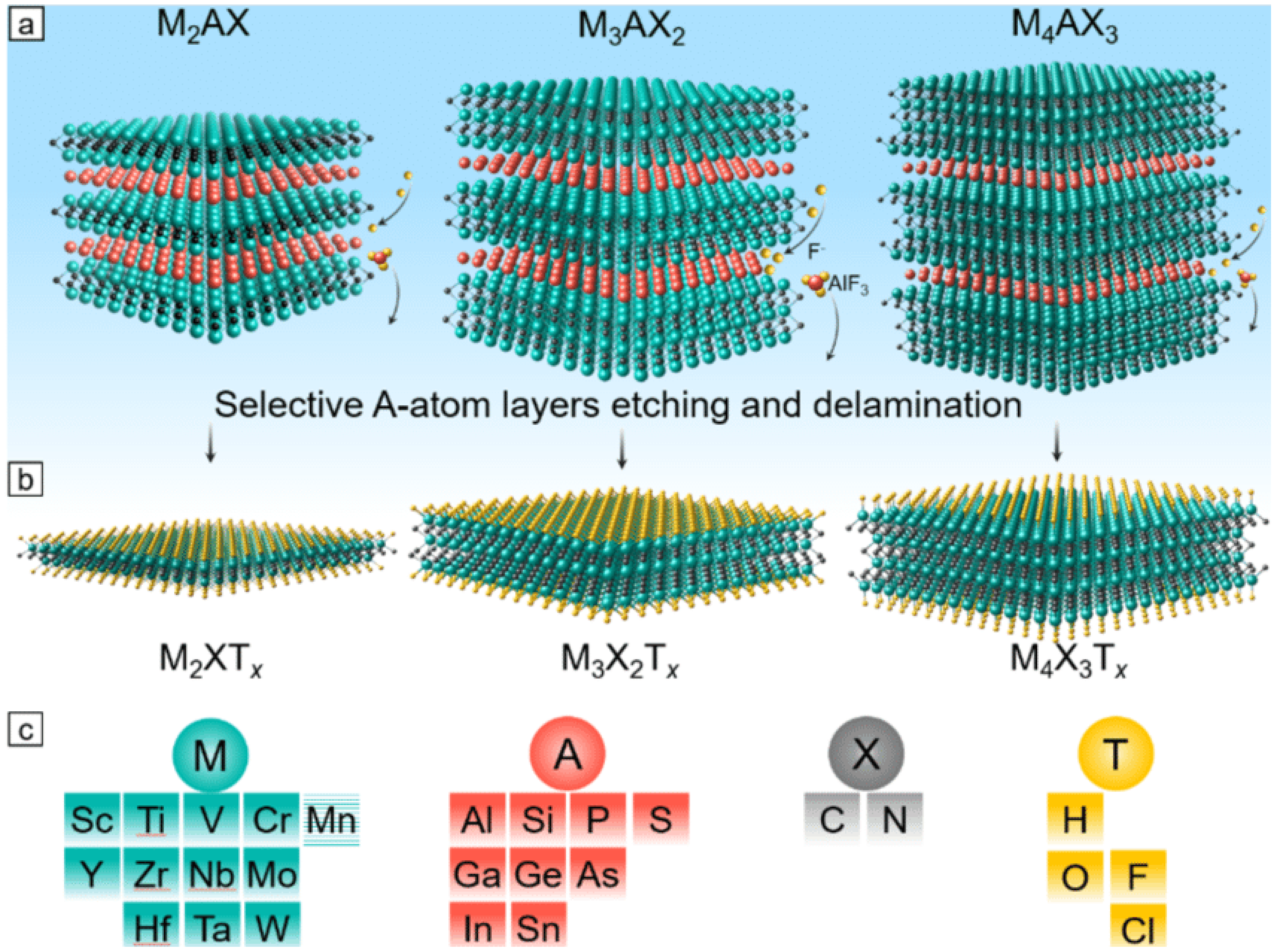
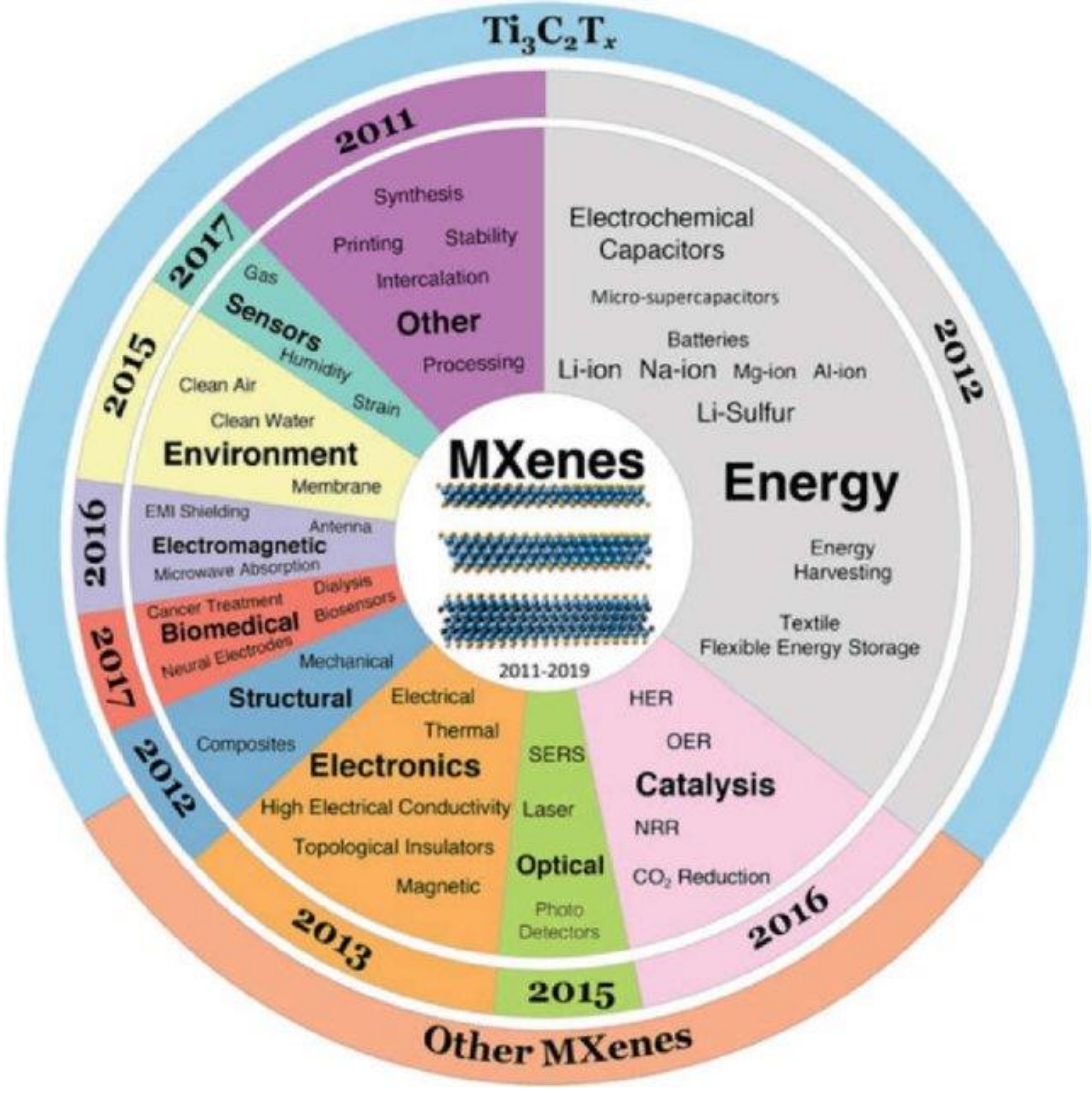
Graphene/SiC case

- MXenes: a new family of two-dimensional (2D) transition metal carbides, carbonitrides and nitrides
- Synthesized from a MAX phase



Hong, W. *et al. MRS Bulletin* **45,** 850–861 (2020).

Prof. Yury Gogotsi



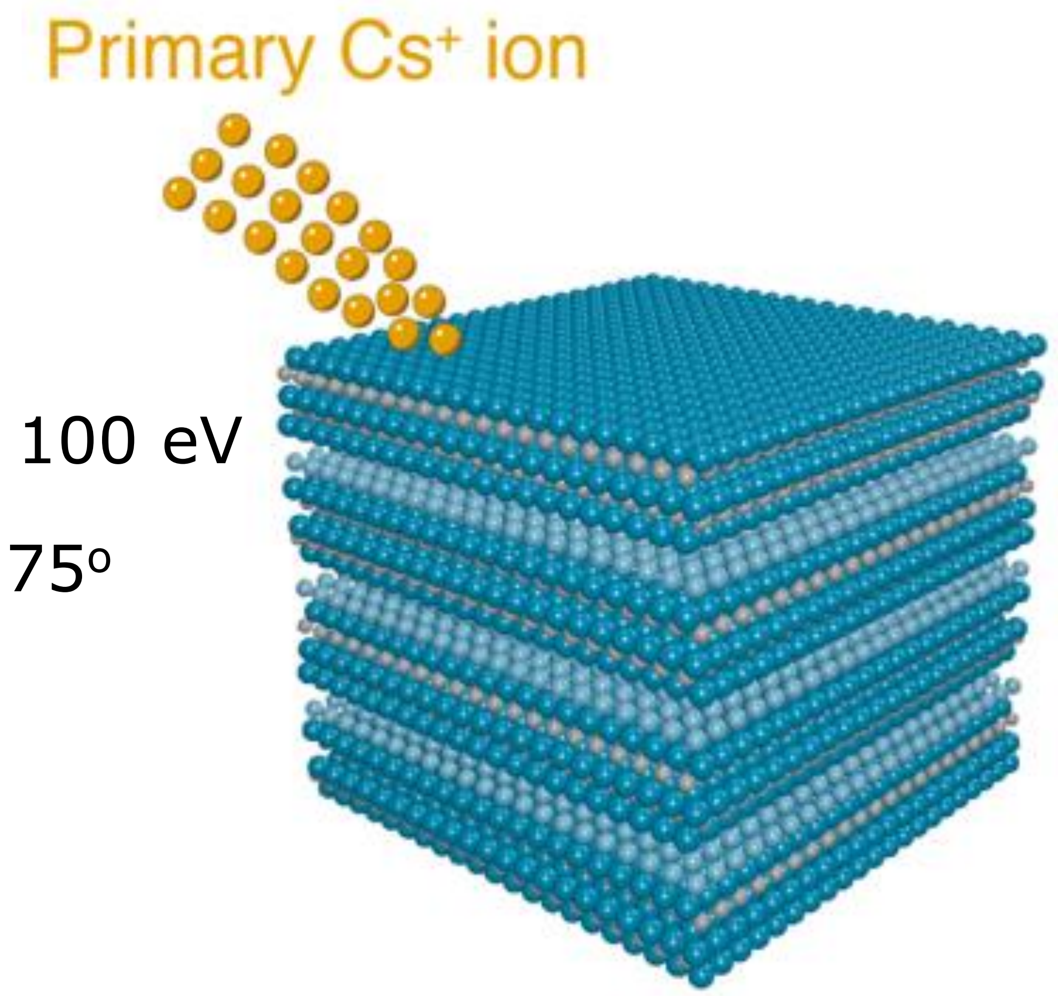
https://nano.materials.drexel.edu/research/synthesis-of-nanomaterials/mxenes/

How to measure MAX/MXene using SIMS? Ti_3AlC_2 case

https://www.nature.com/webcasts/event/secondary-ion-mass-spectrometry-characterization-of-max-and-mxene-samples/

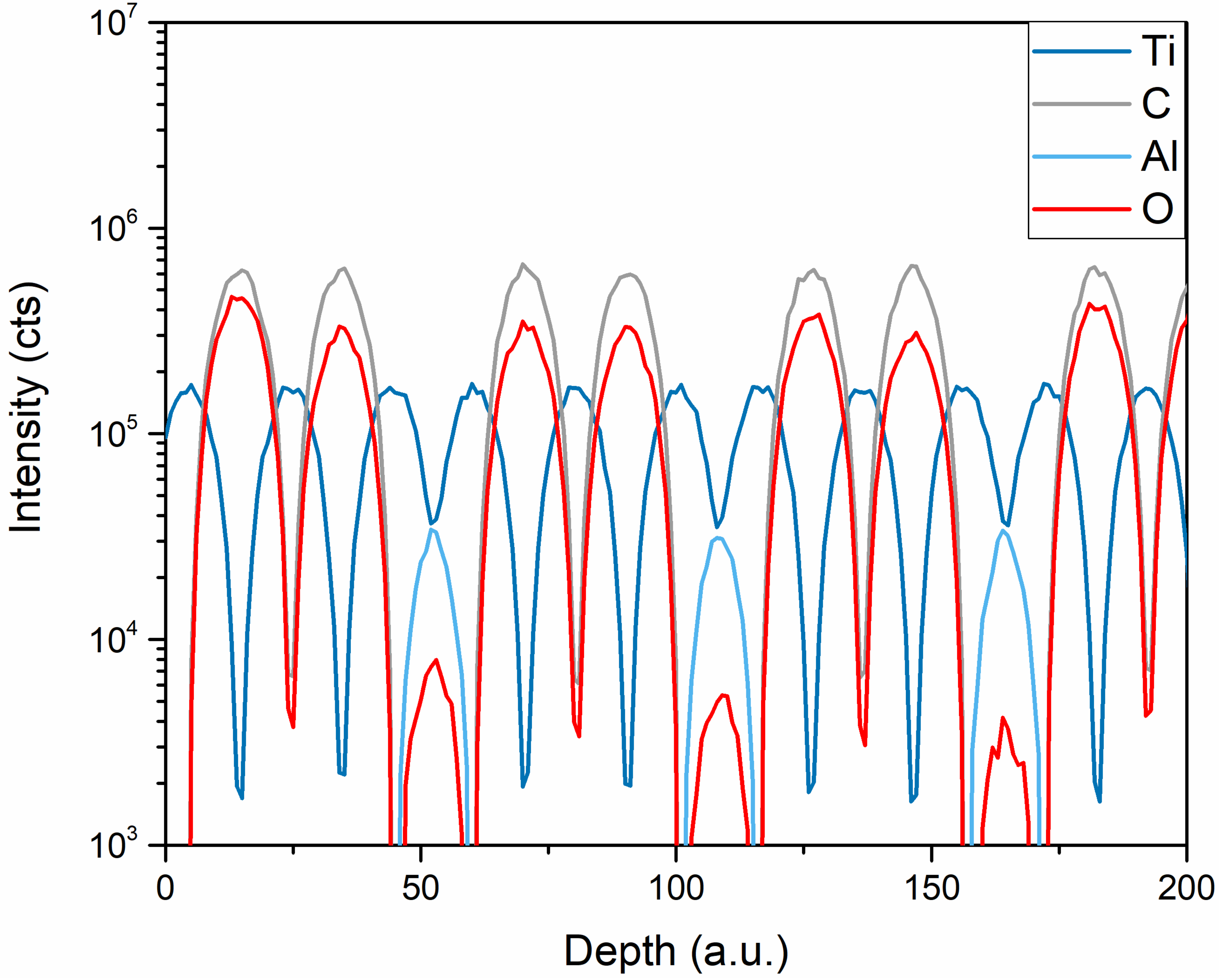
Impact energy 100 eV

Incident angle 75°



Nature Nanotechnology **17**, 1192 (2022)

Final result



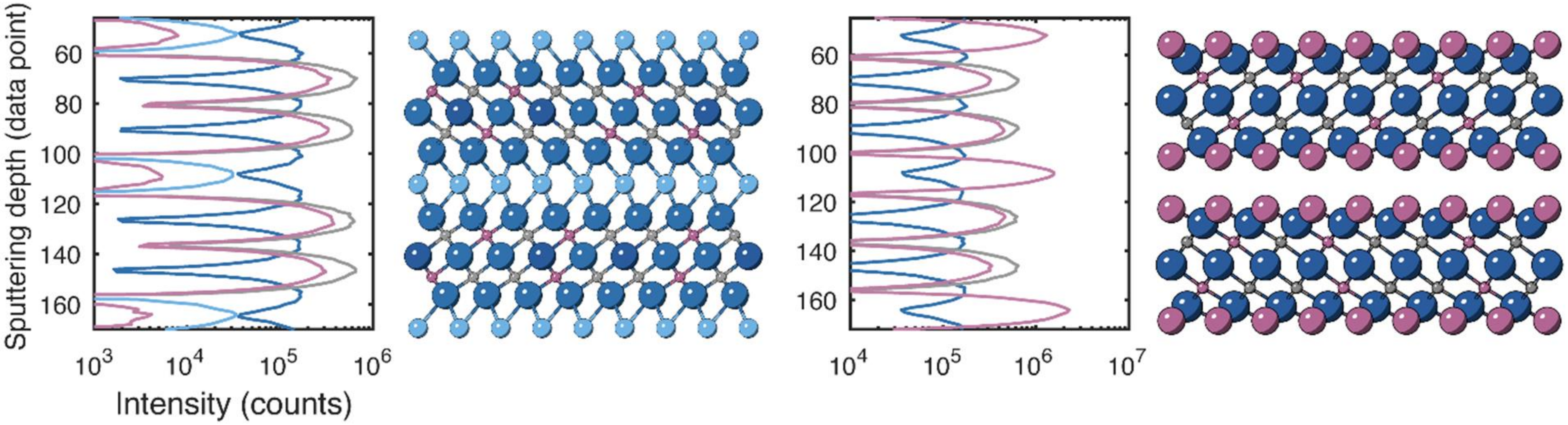
Nature Nanotechnology **17**, 1192 (2022)

Remarks

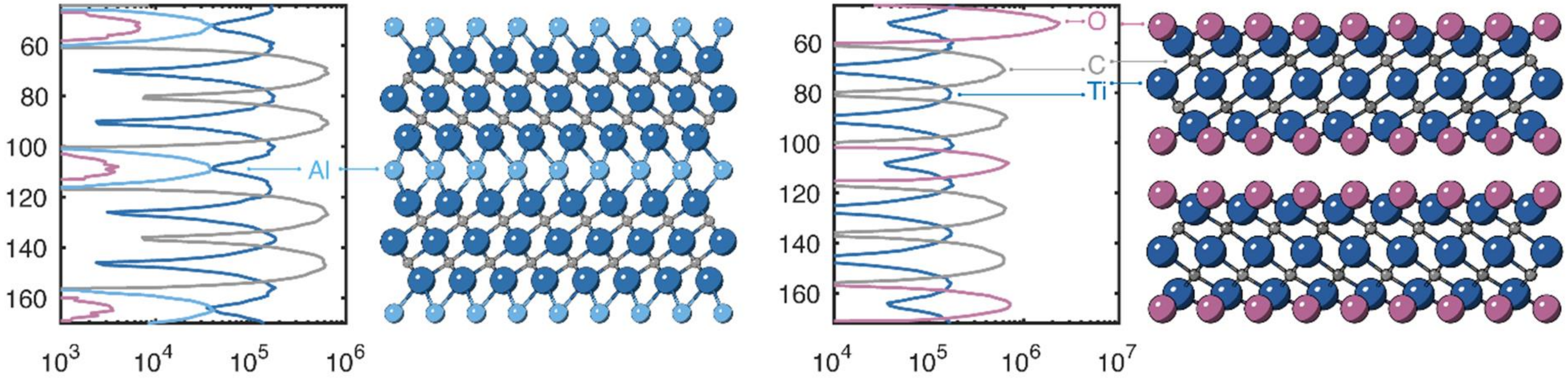
- Much better quality
- Atomic depth resolution!
- Fully reproducible
- Oxygen signal!!!

Carbides? Oxycarbides!

Conventional MAX/Mxene



Synthesis with Al excess – Mathis et al. ACS Nano 2021, 15, 4, 6420–6429



Nature Nanotechnology **17**, 1192 (2022)

Contents

1. Principles of SIMS

2. Basic applications

3. Quantitative analysis

4. CAMECA SC Ultra

5. Examples

6. Conclusions

Conclusions

- Powerful characterization technique
- Possibility of measurement artifacts
- Need to plan the experiment
- State-of-the-art instrument
- Dedicated procedures (time-consuming but worth it!)
- Superior depth resolution (even atomic!)

Thank you for your attention

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