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Instytut
Mikroelektroniki
i Fotoniki

Secondary Ion Mass Spectrometry

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31.05.2022

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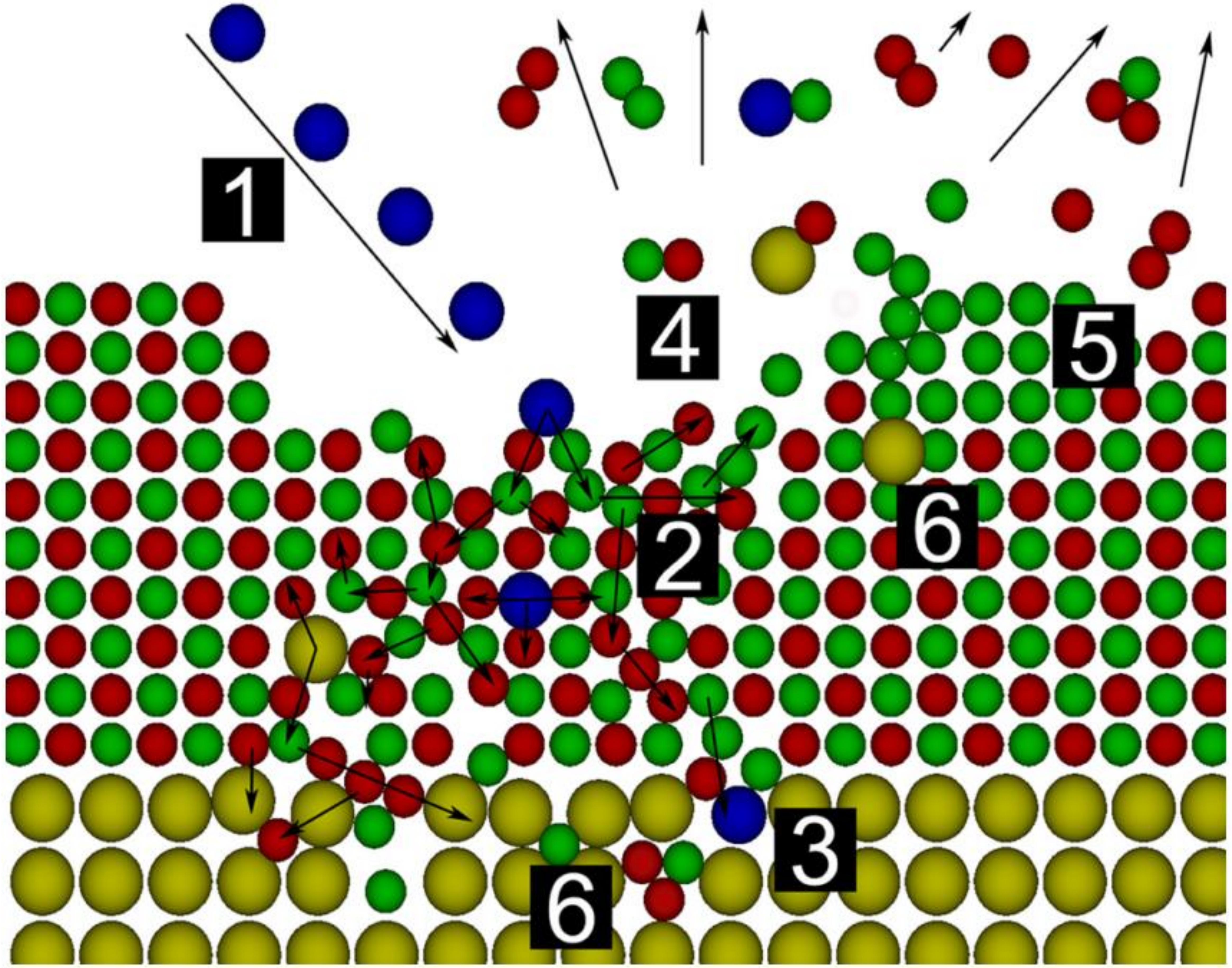
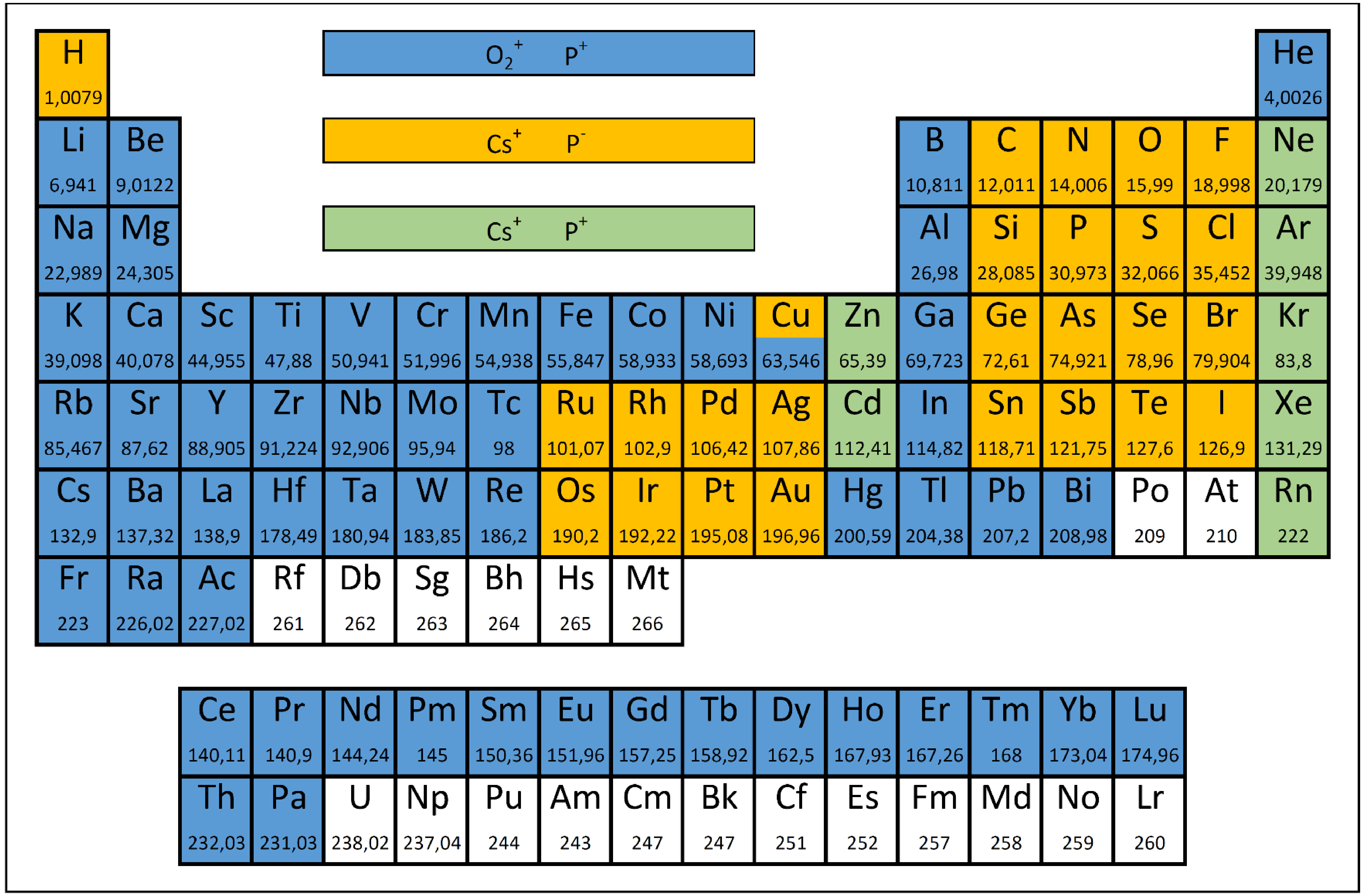
Fundamentals – Ion Bombardment



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

Fundamentals – two sources

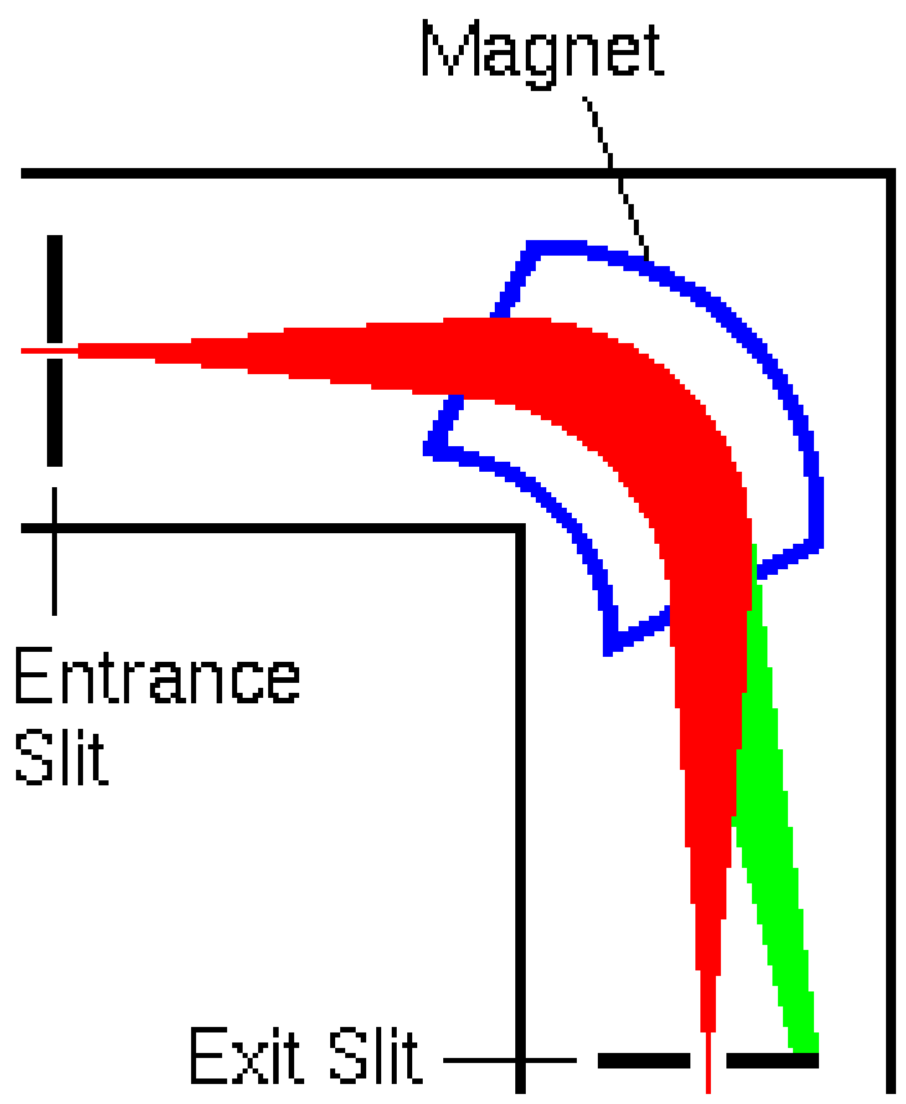


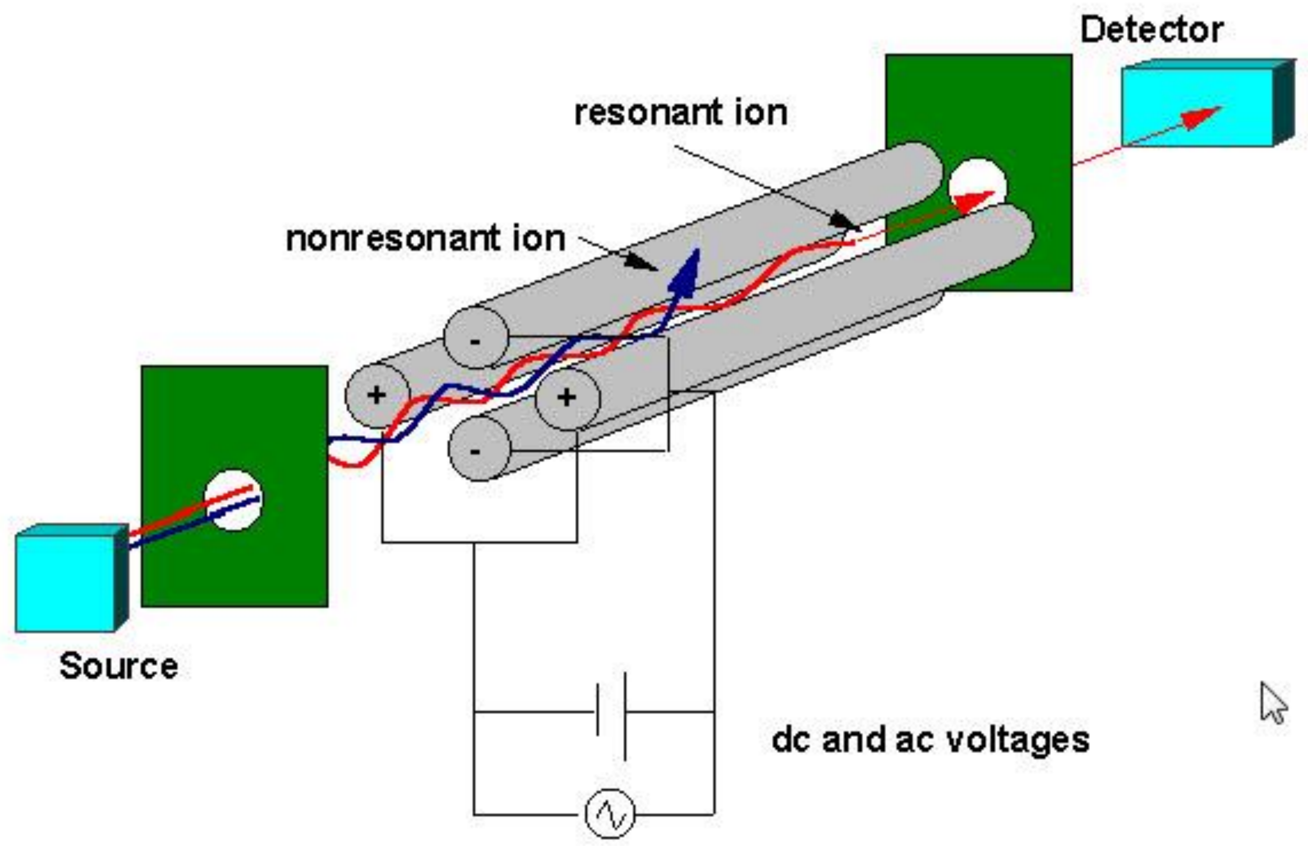
O_2^+ - electronegativity – formation of cations

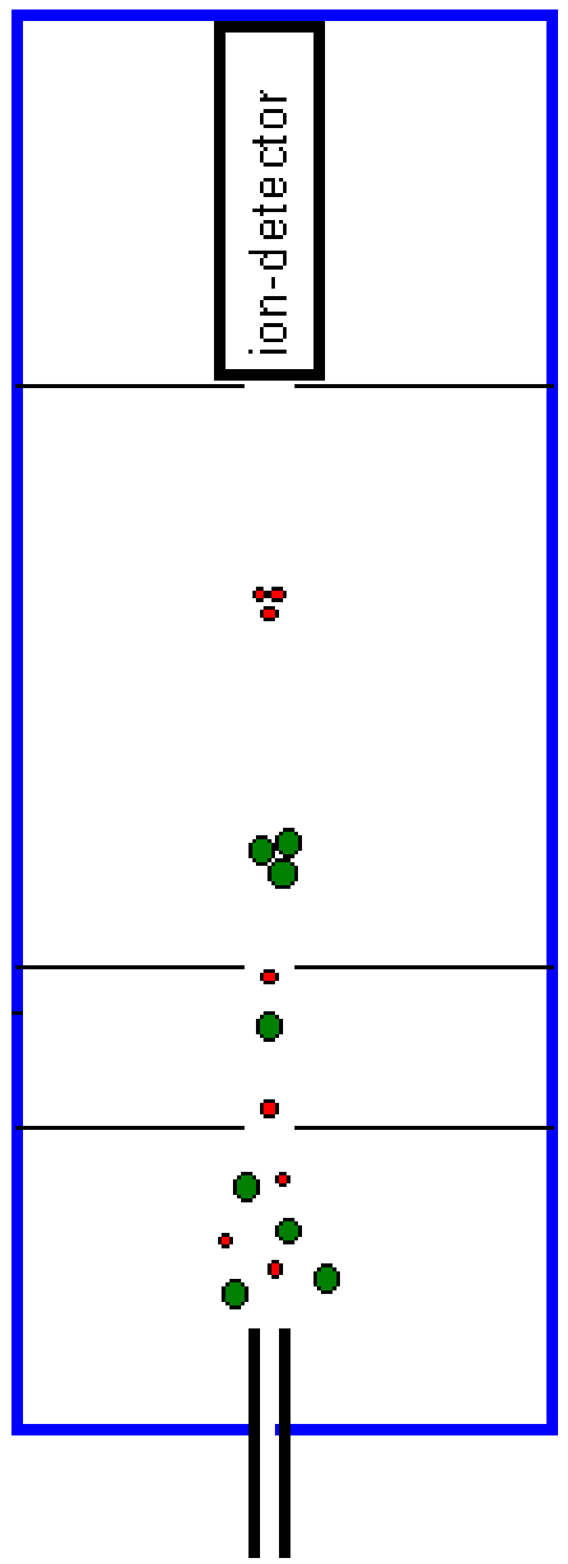
Cs^+ - decreases work function of electrons – formation of anions

Four order of magnitude difference!!!

Fundamentals – detectors





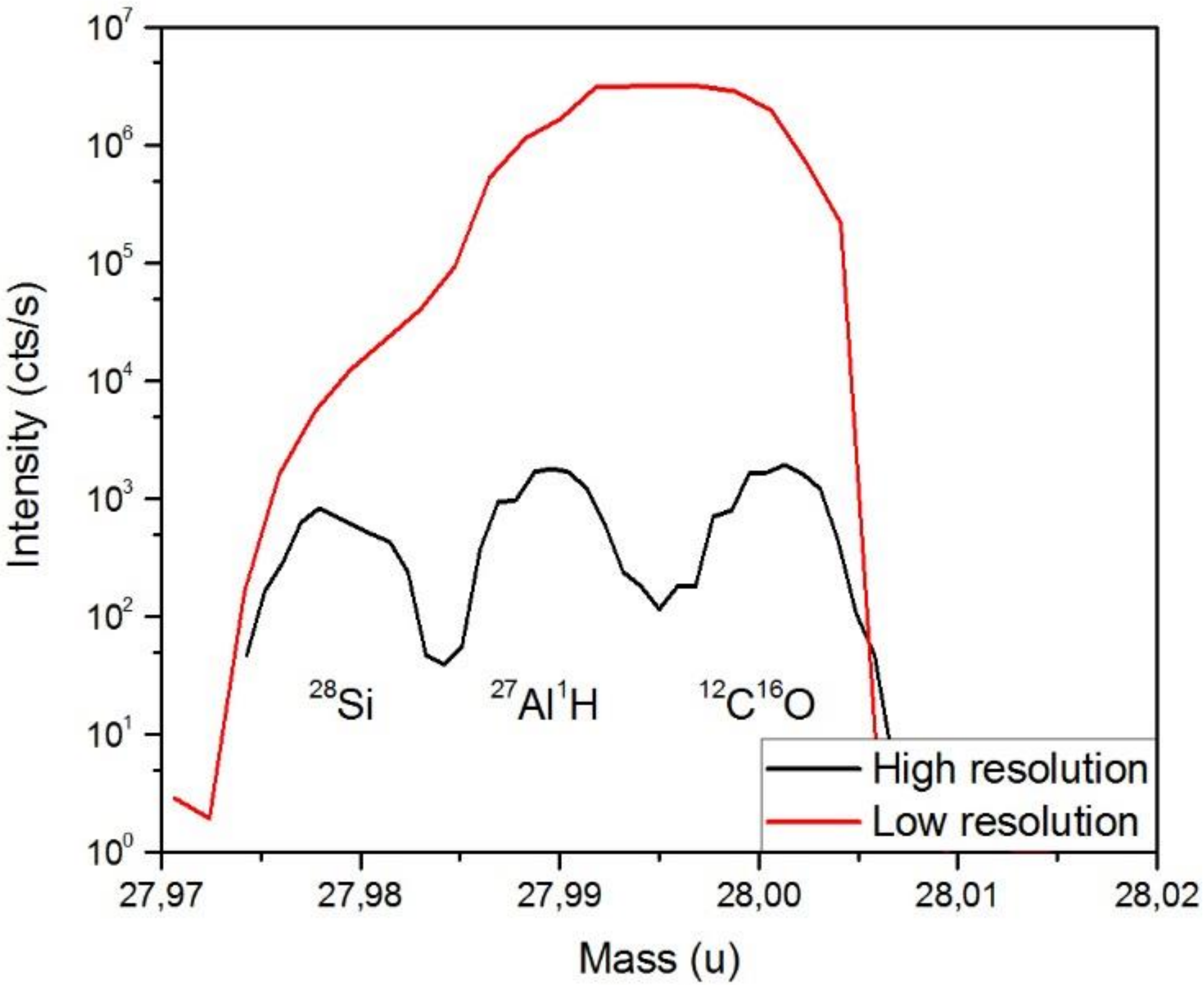


Magnetic sector
Best detection limits
Quantitative analysis

Quadrupole
Insulators

Time-of-Flight
Organic materials
Simultaneous
measurements

Fundamentals – mass interferences



Solutions

- High mass resolution
- Different isotopes
- Monoatomic ions

Lower sensitivity!

$MRP = m/\Delta m$

^{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

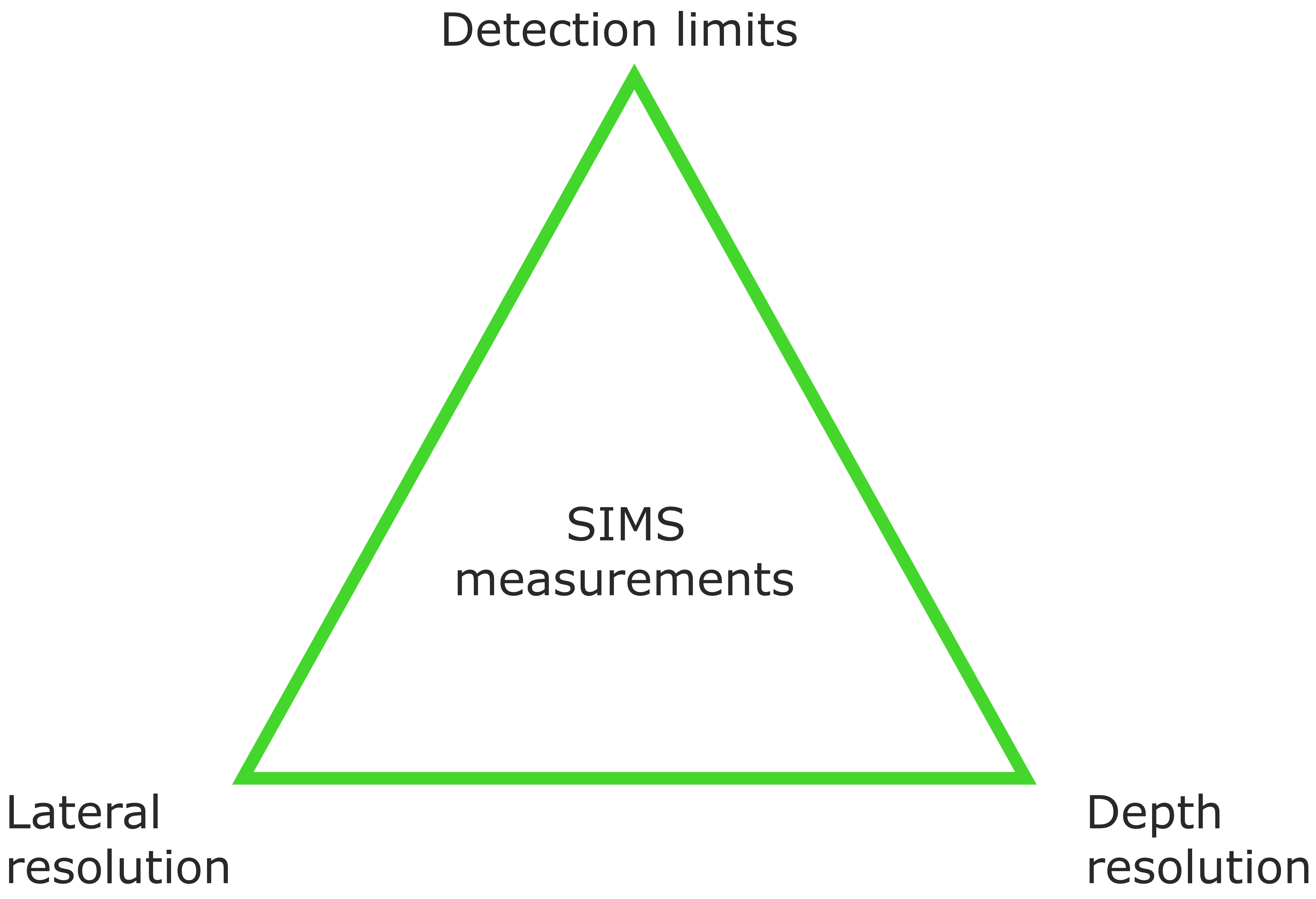
O_2^+ Primary Ion Beam Positive Ions		Cs^+ Primary Ion Beam Negative Ions		Cs^+ Primary Ion Beam Positive Ions (MCs^+)	
Element	DL (atoms/cm³)	Element	DL (atoms/cm³)	Element	DL (atoms/cm³)
He	5E+17	H	1E+17	Ar	1E+17*
Li	5E+12	B	1E+15	-	-
B	2E+13	C	1E+16	-	-
Na	5E+12	N	1E+15	-	-
Mg	5E+12	O	5E+16	-	-
Al	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



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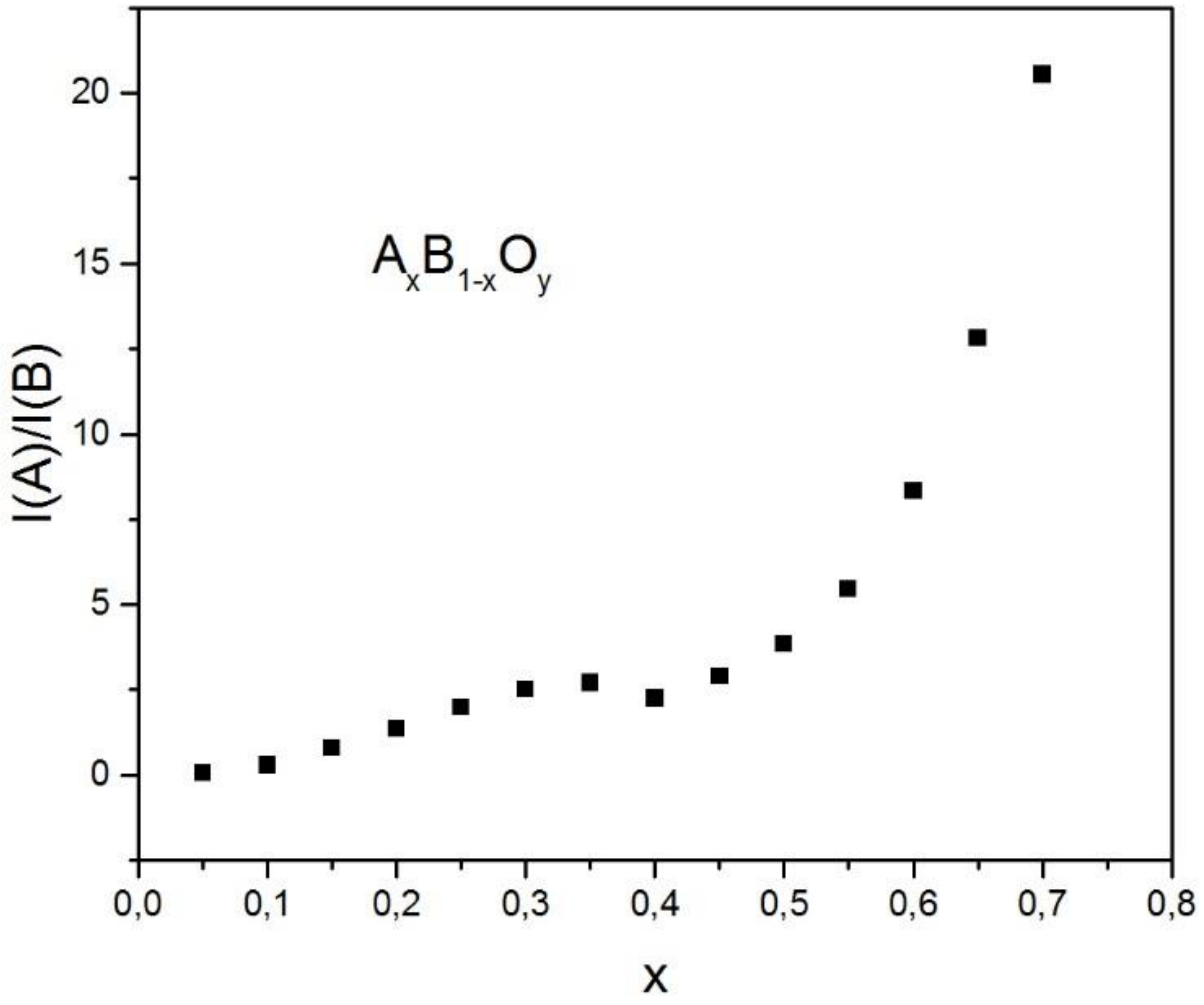
Quantitative analysis – basic equation

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

$I(A)$	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

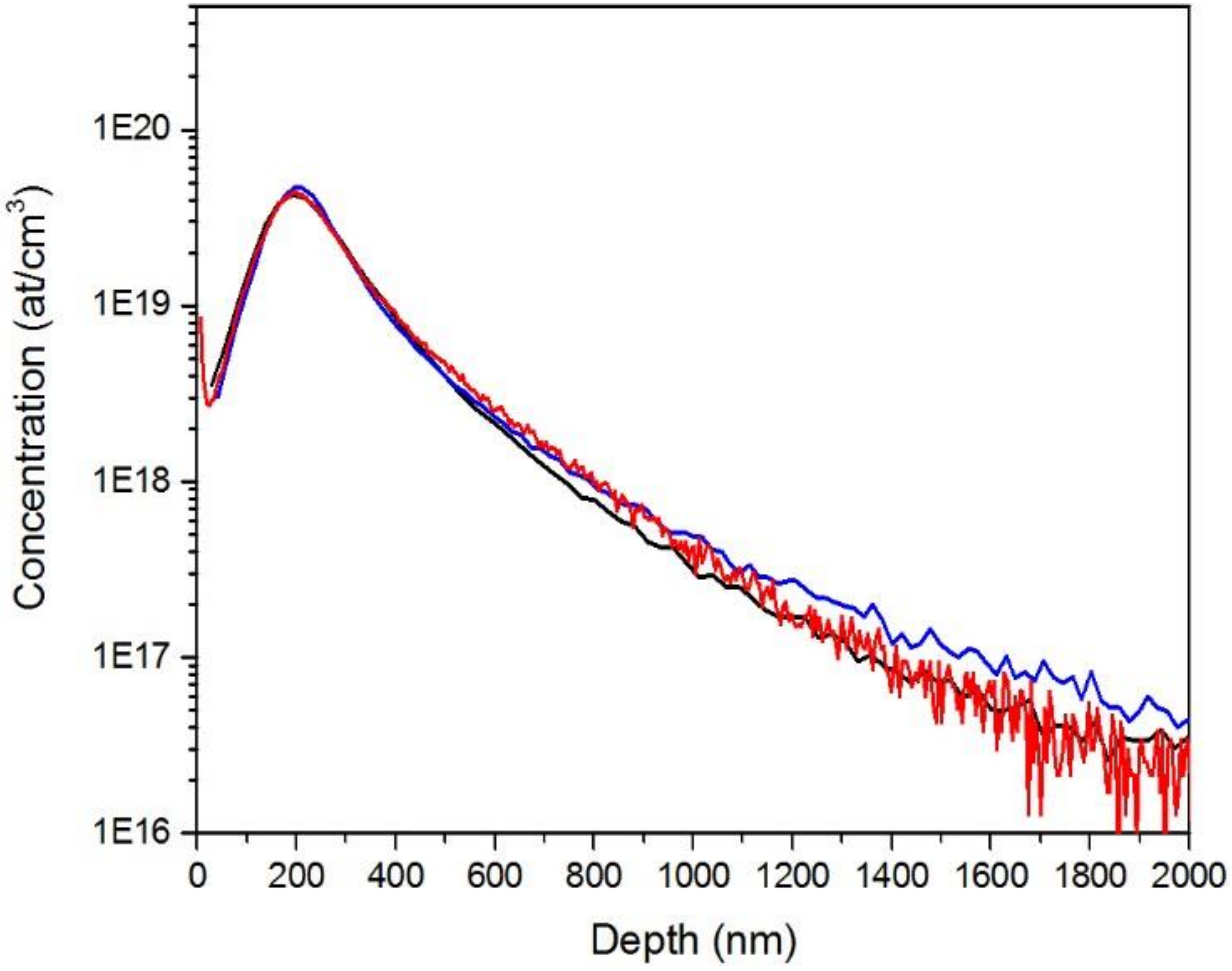
Quantitative analysis – elemental composition

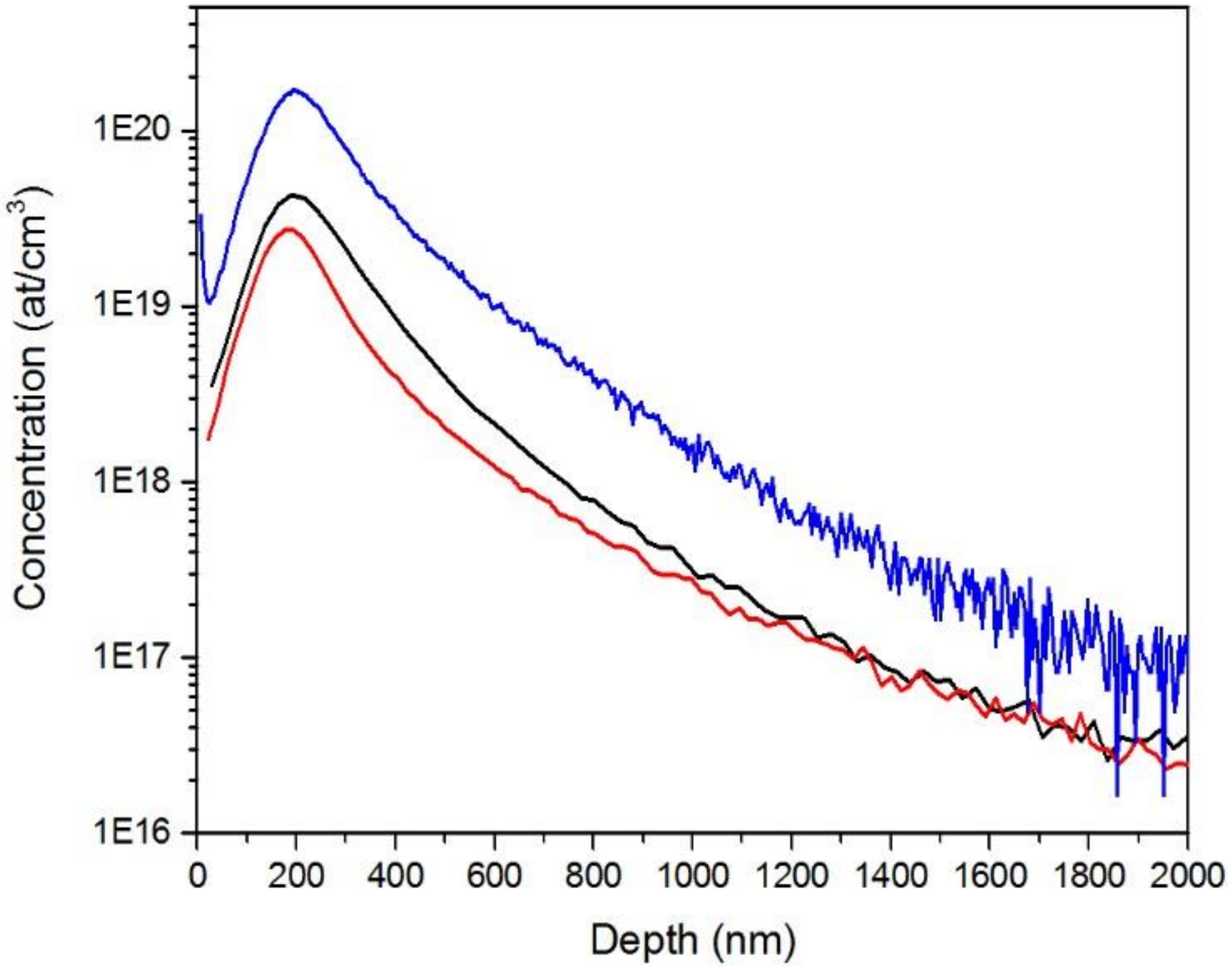


- Simple samples
- Complicated procedure
- Possible errors
- Identification: other techniques
- Depth profiles: good choice

Quantitative analysis – Dopants and contamination

Very precise measurements: $C(A) = RSF_A\, I(A) / I(M)$
RSF based on reference samples





Contents

Ultra Low Impact Energy SIMS (ULIE SIMS)

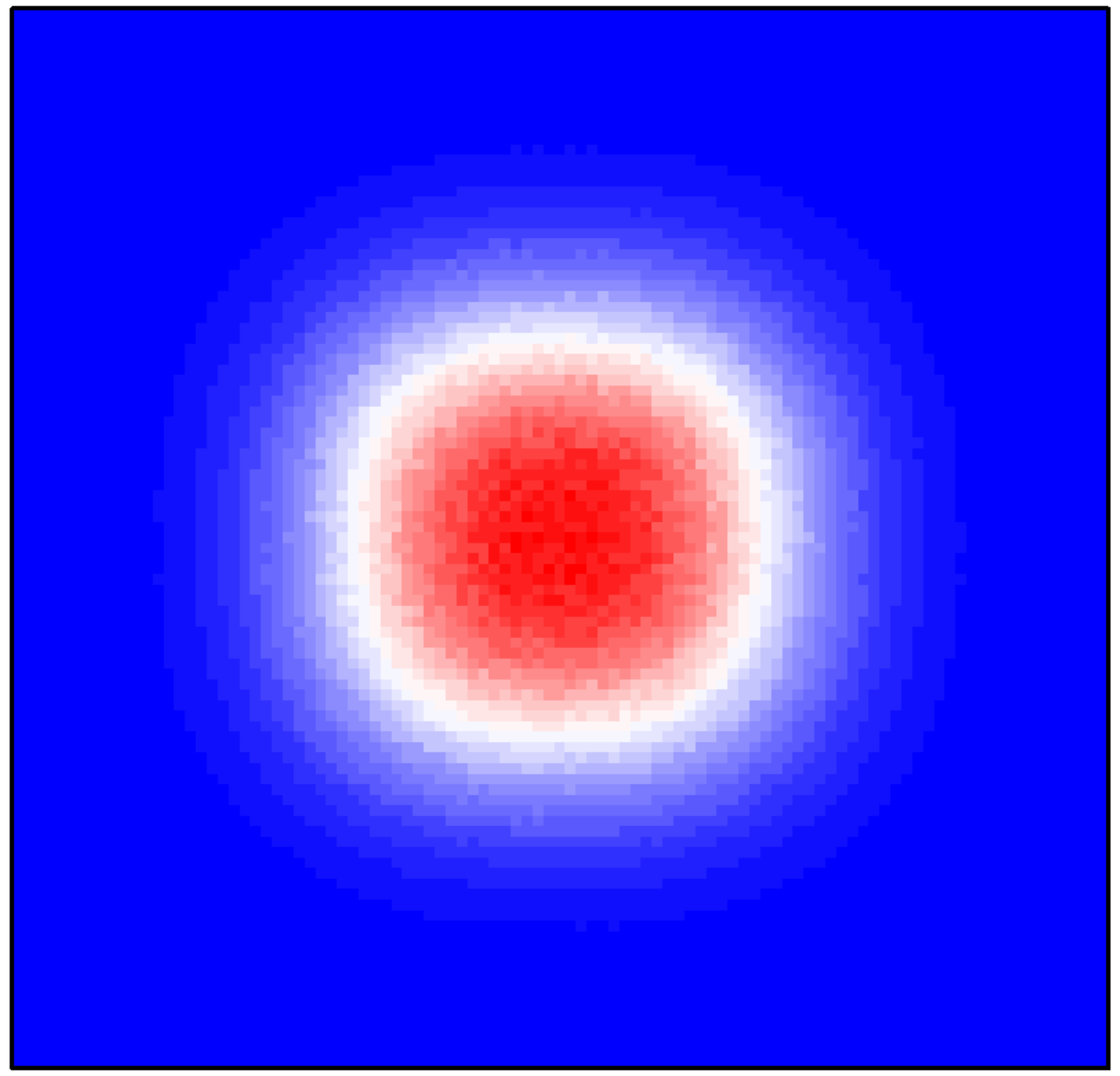
EXLIE (EXtreme Low Impact Energy) technology

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

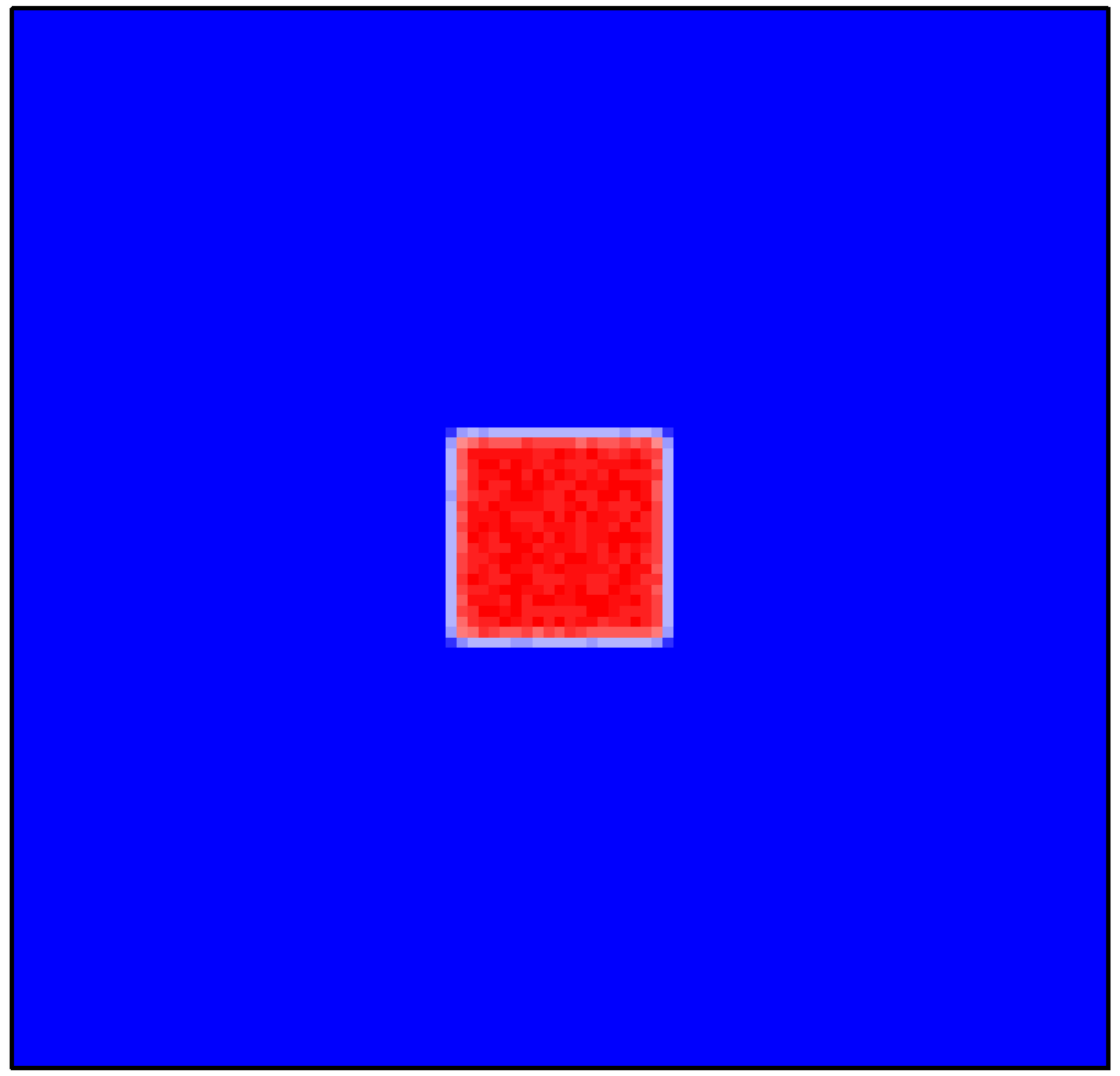
Beam shape

15 instruments!!!

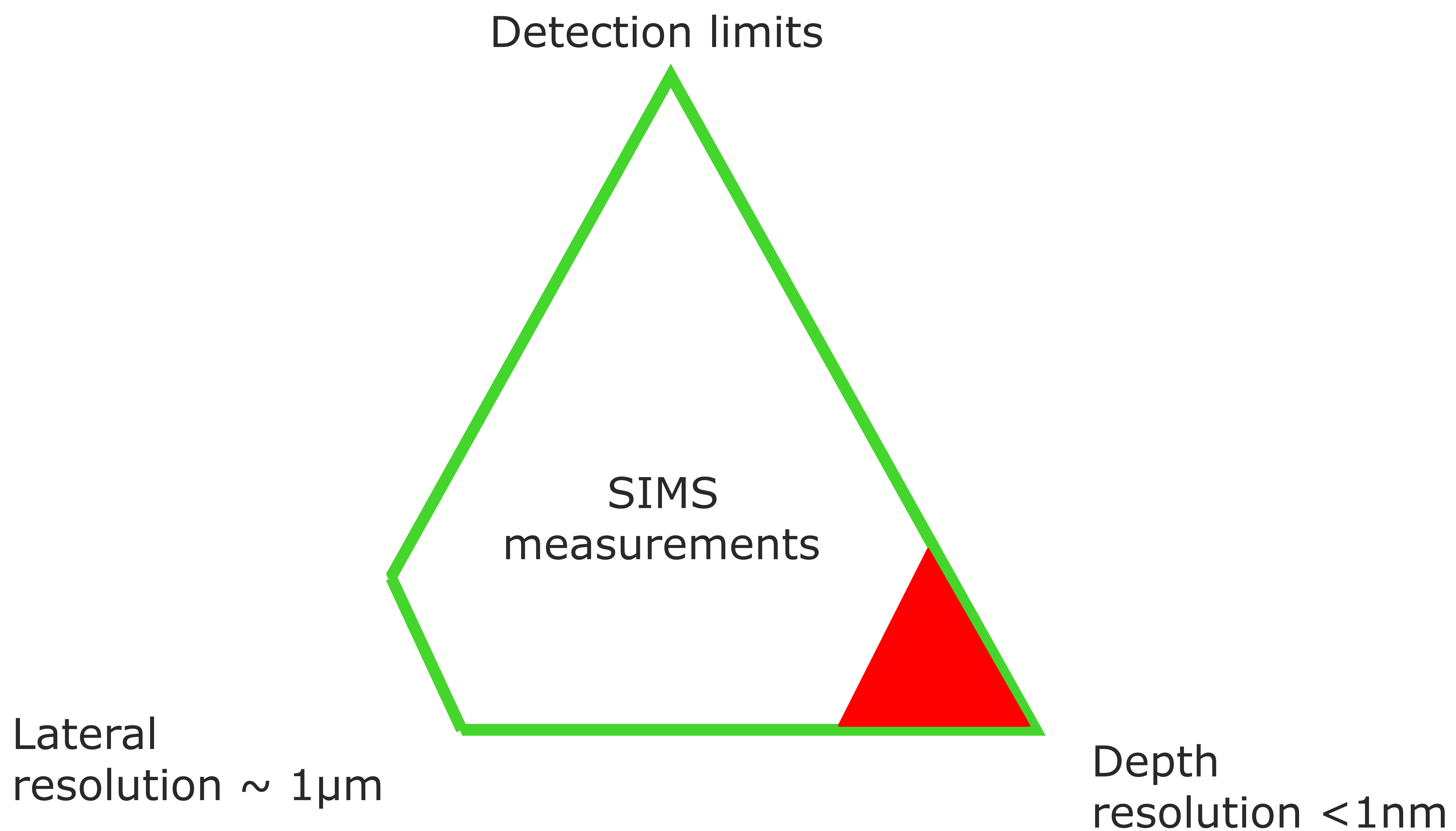
Typical Gaussian-shaped beam



Projected on square stencil



CAMECA IMS SC Ultra - limitations

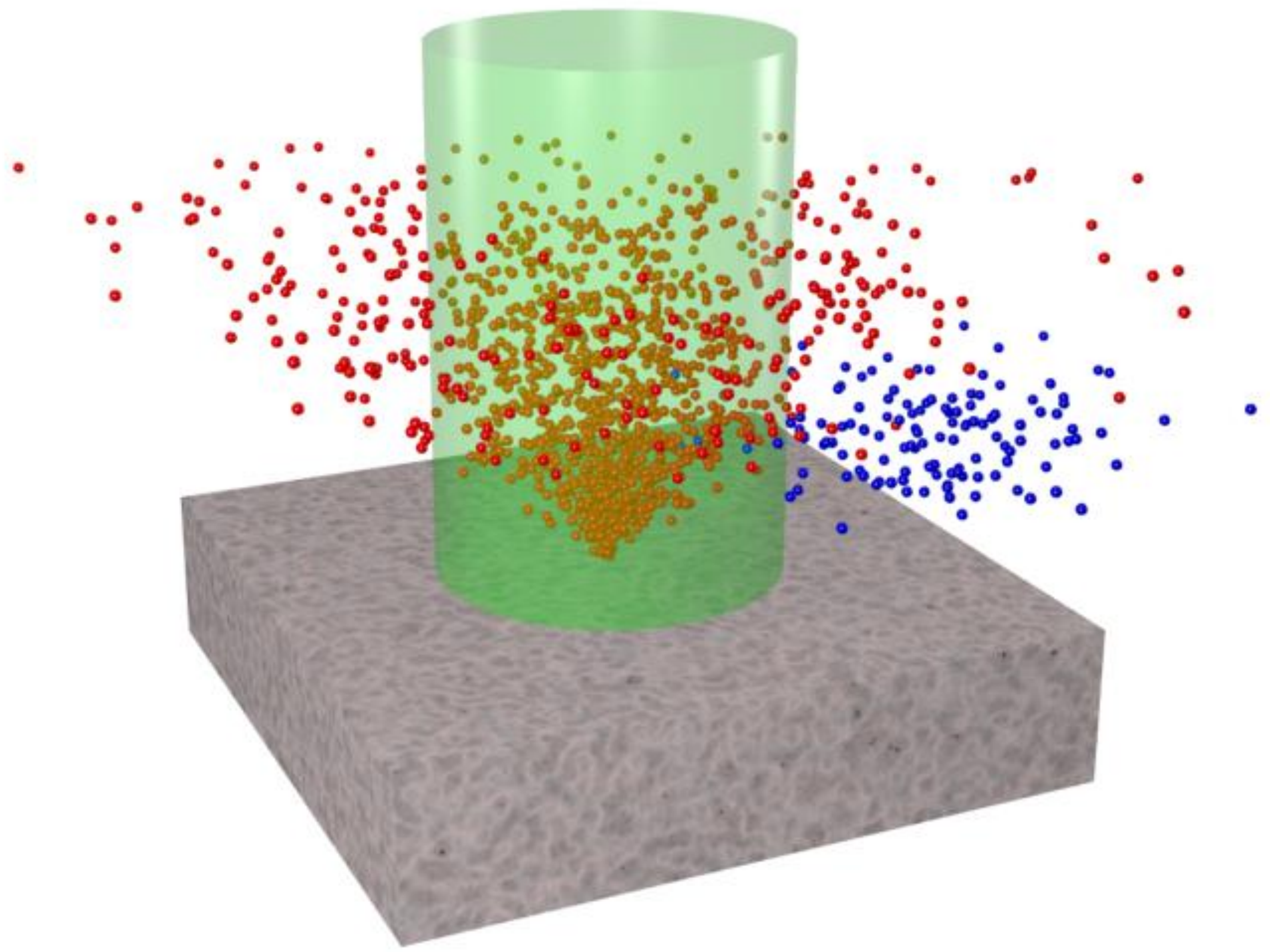


CAMECA IMS SC Ultra – dedicated procedures

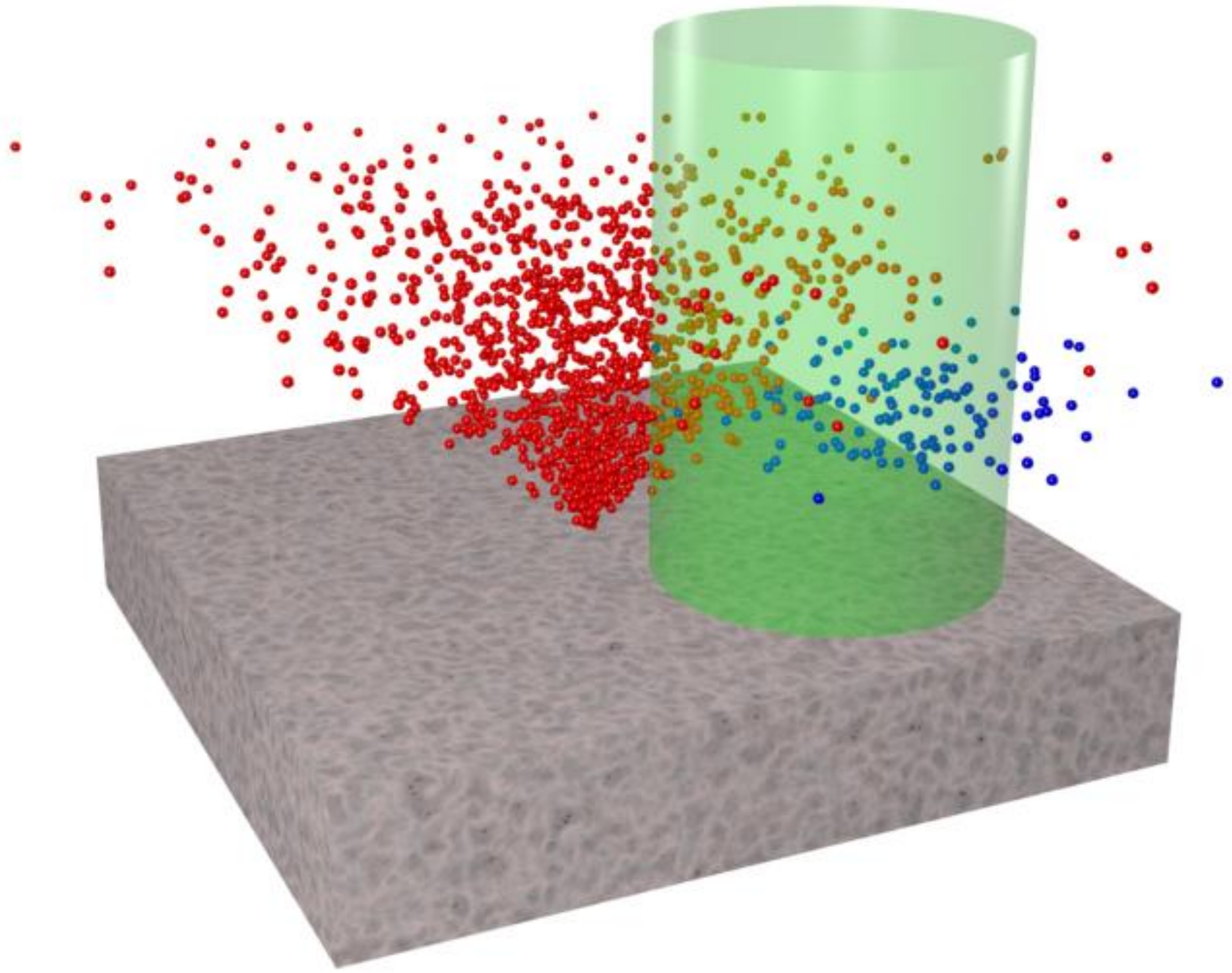
Type of procedures

- Standard/universal
- Dedicated

Standard



Dedicated



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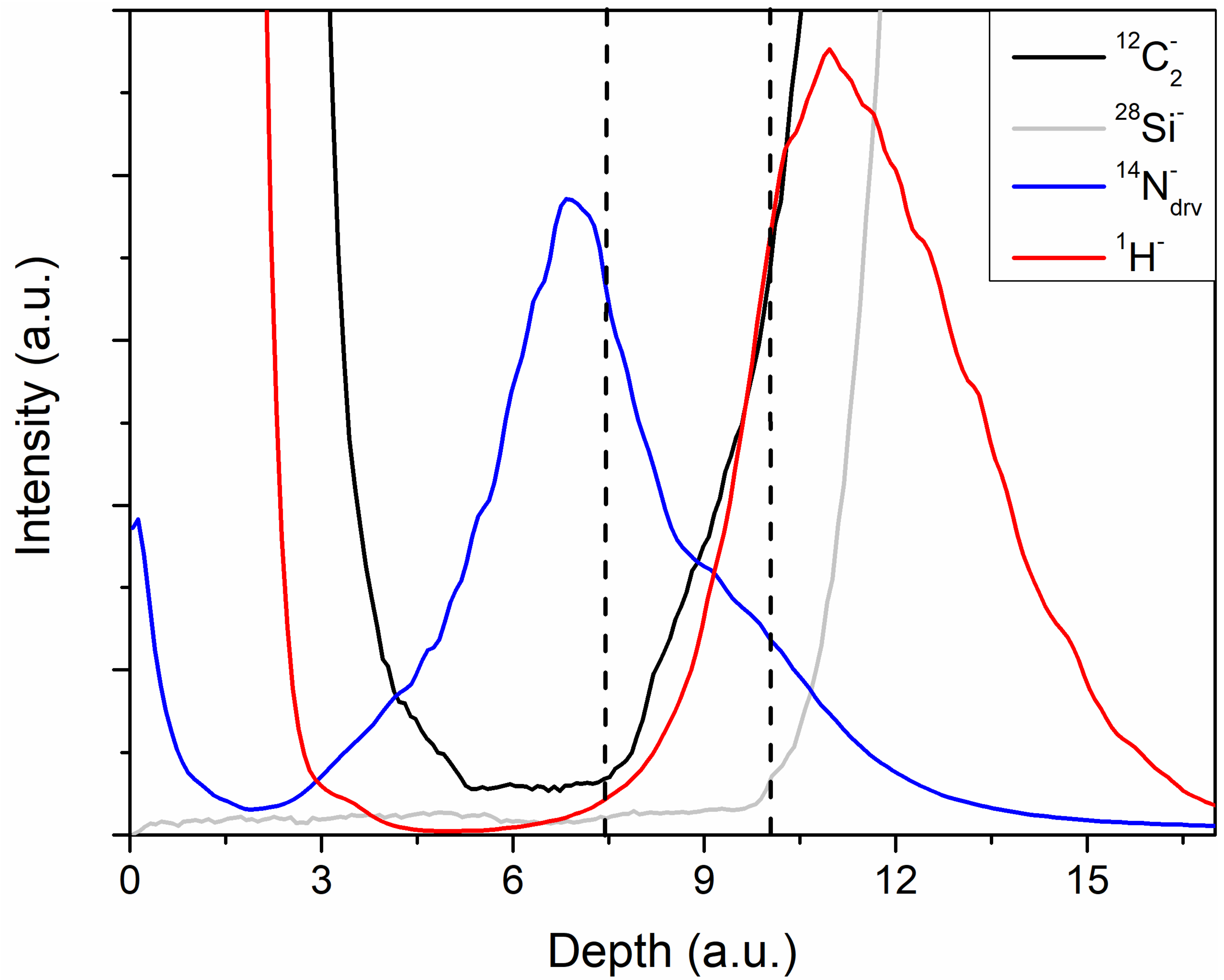
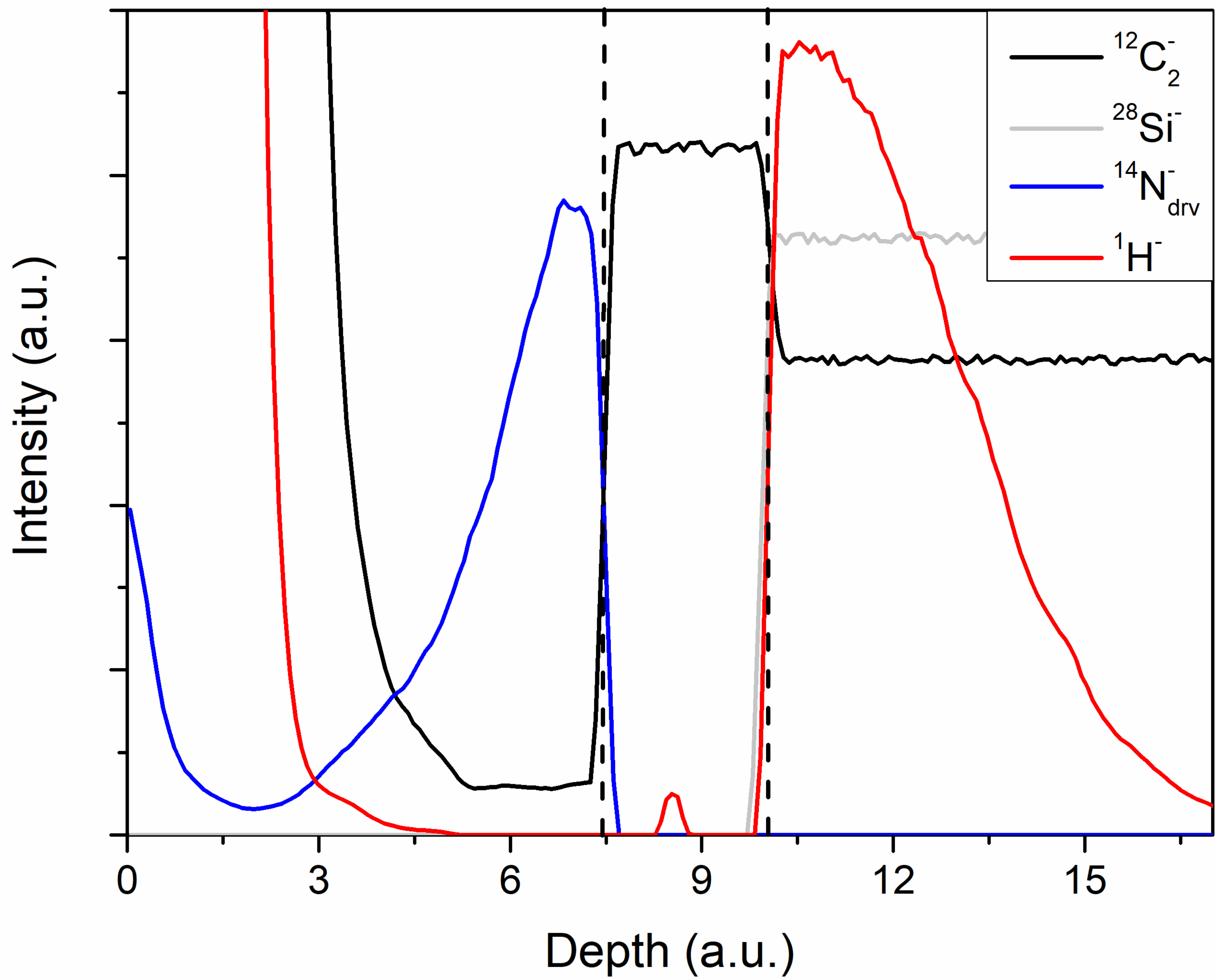
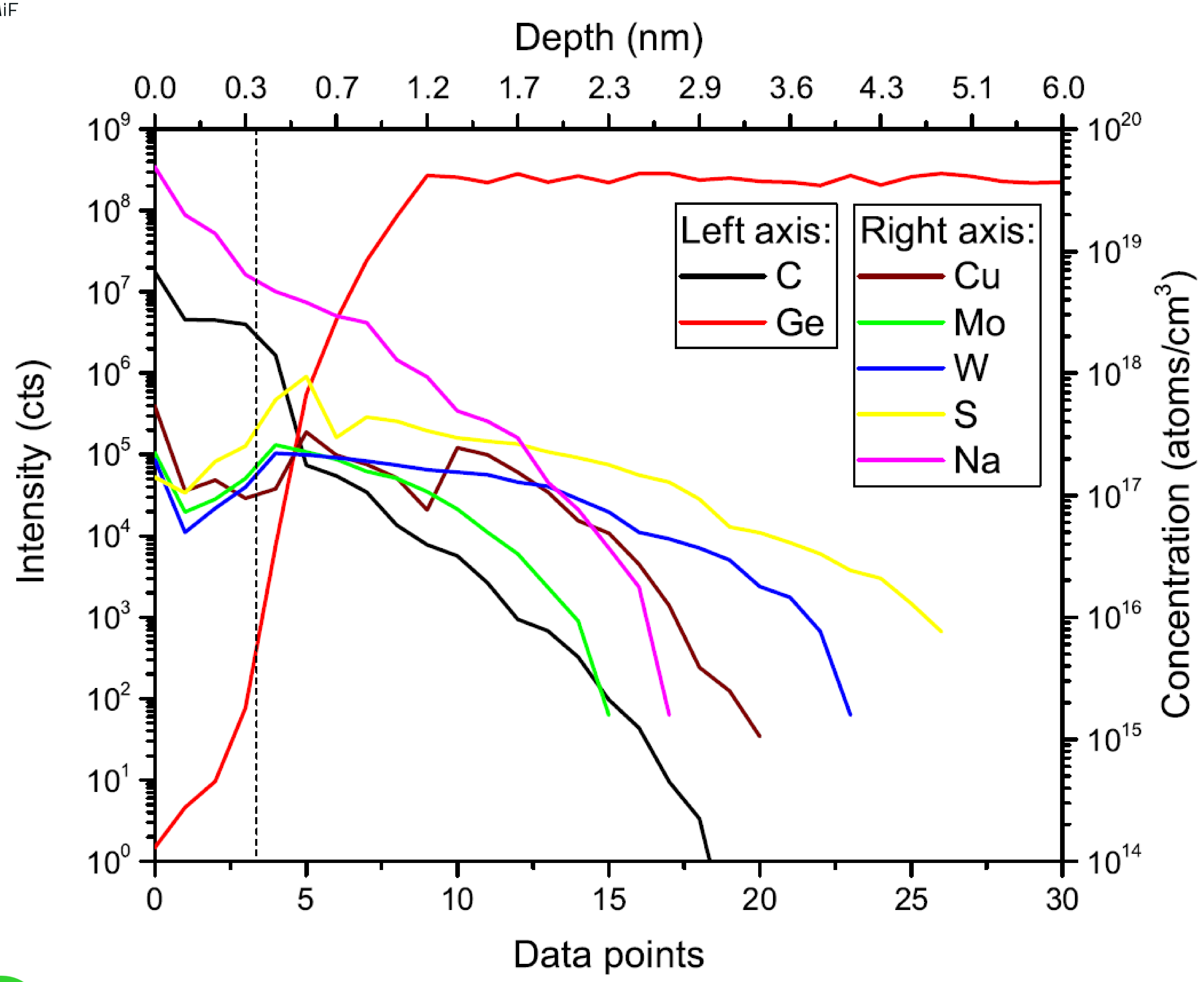
Graphene/SiC





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

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PROBLEMS AND POTENTIAL SOLUTIONS

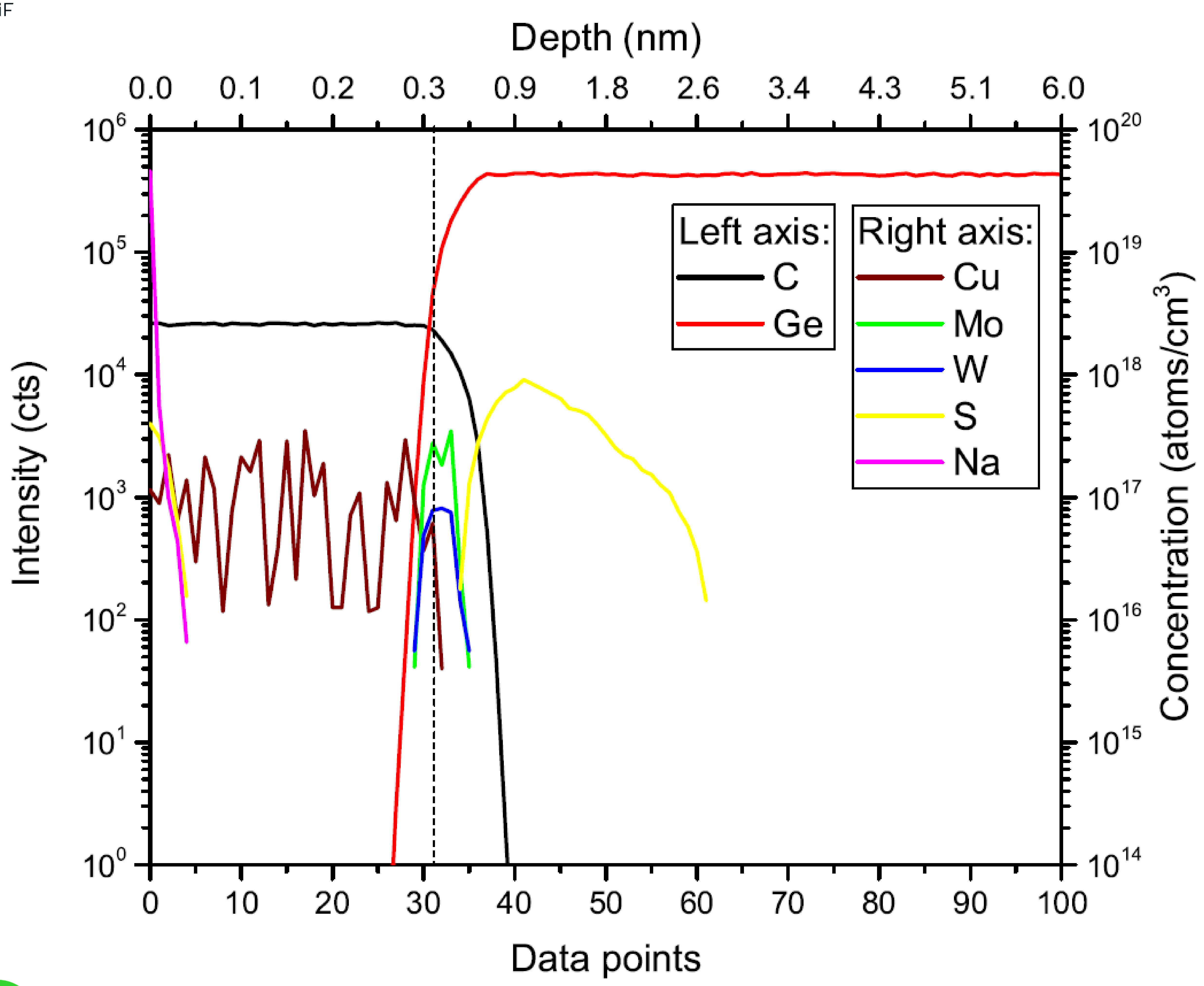
Problem	Potential solution	Resulting problems	Potential solution	Conclusion
Transition layer	Lower beam density	Signals intensity reduction	Higher integration time	Still a few data points per graphene
Ion mixing	Lower impact energy	Signals intensity reduction	Higher integration time	Still a few data 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)
45º	4 for graphene	Severe	Severe	Severe	5 minutes	0.2 – 1.5
75º	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

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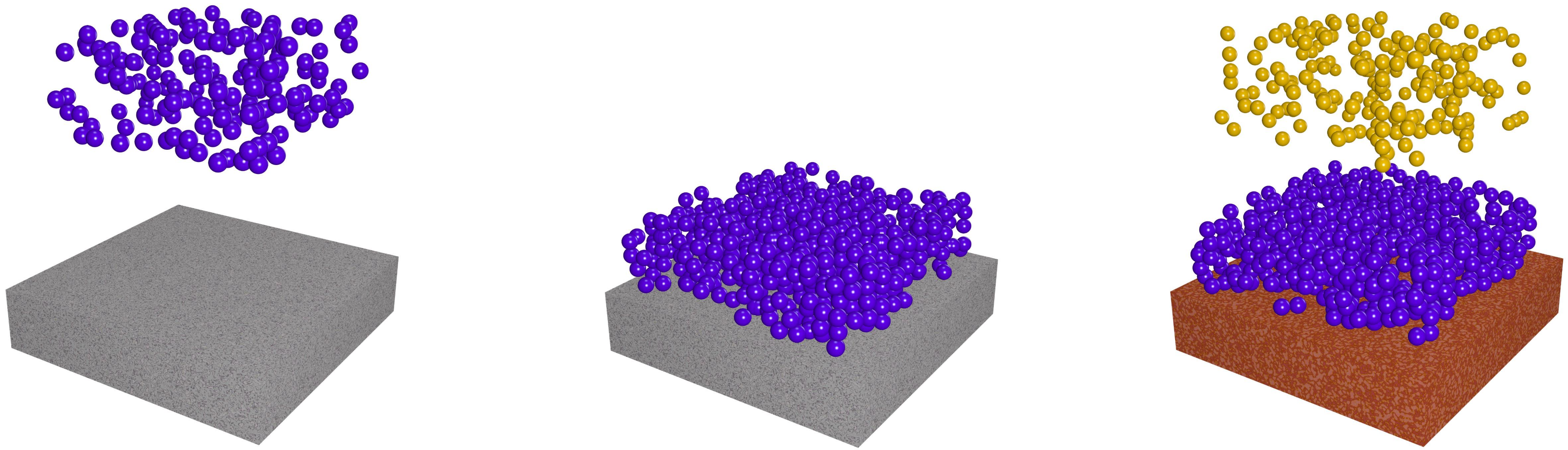
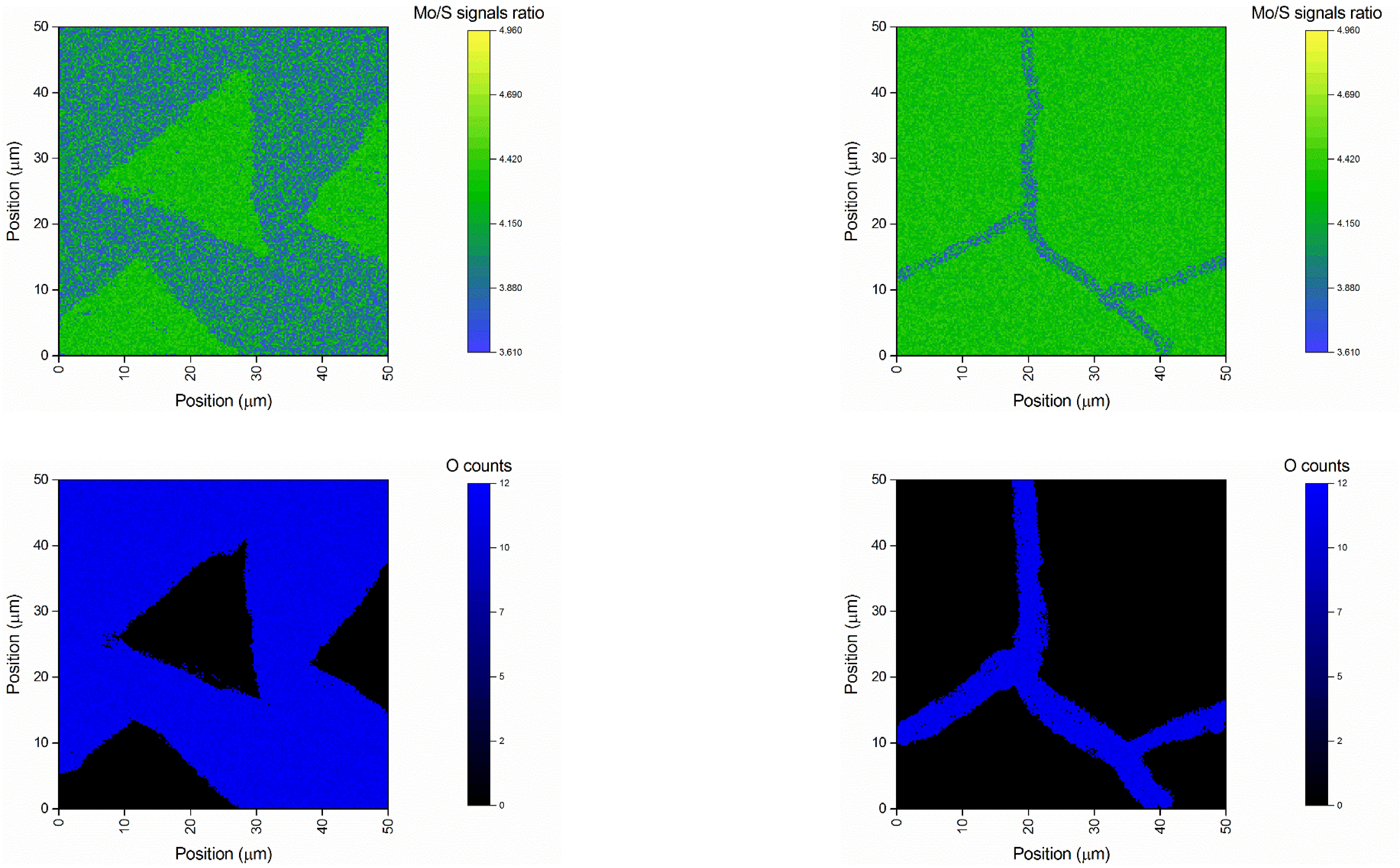


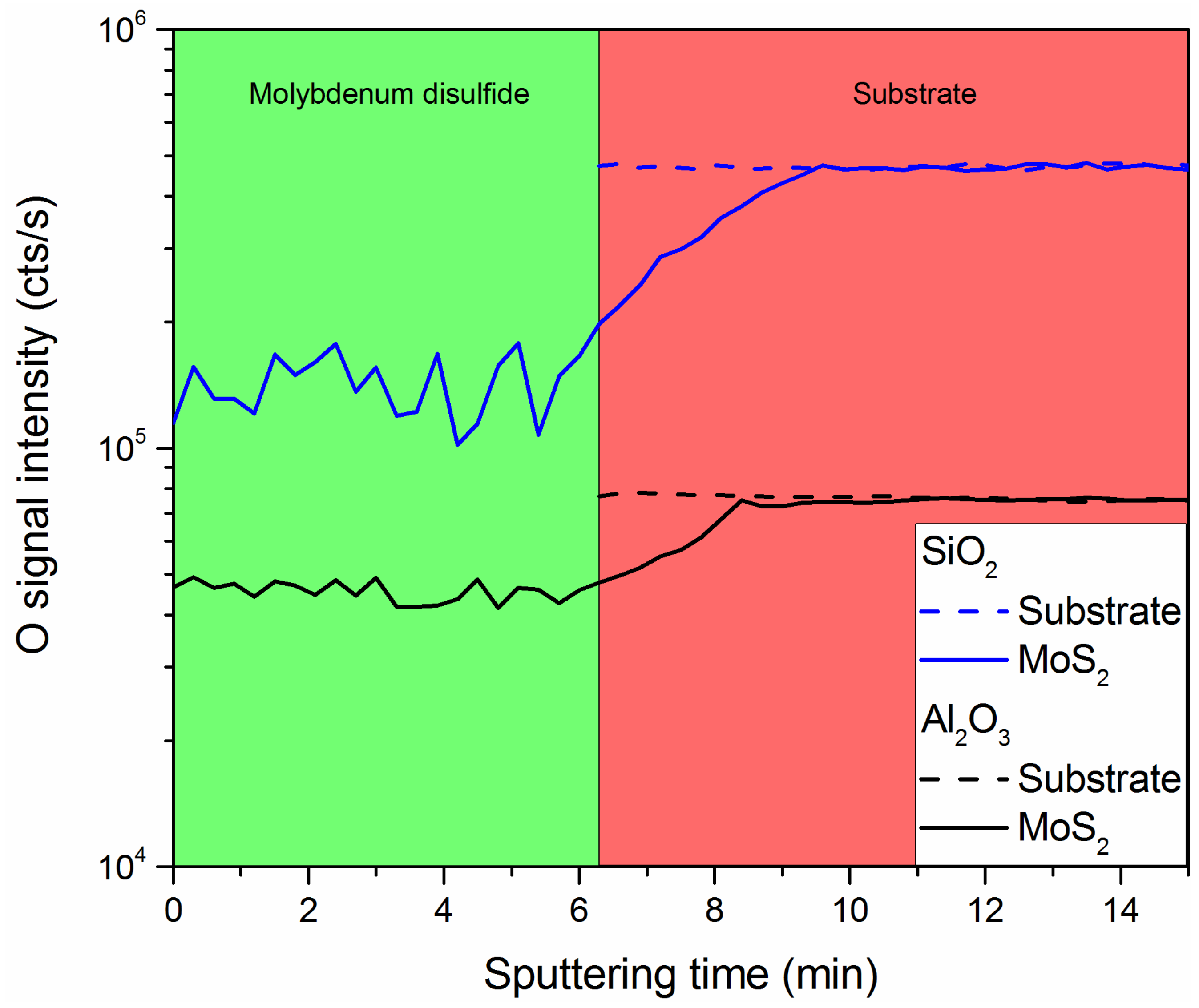
Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

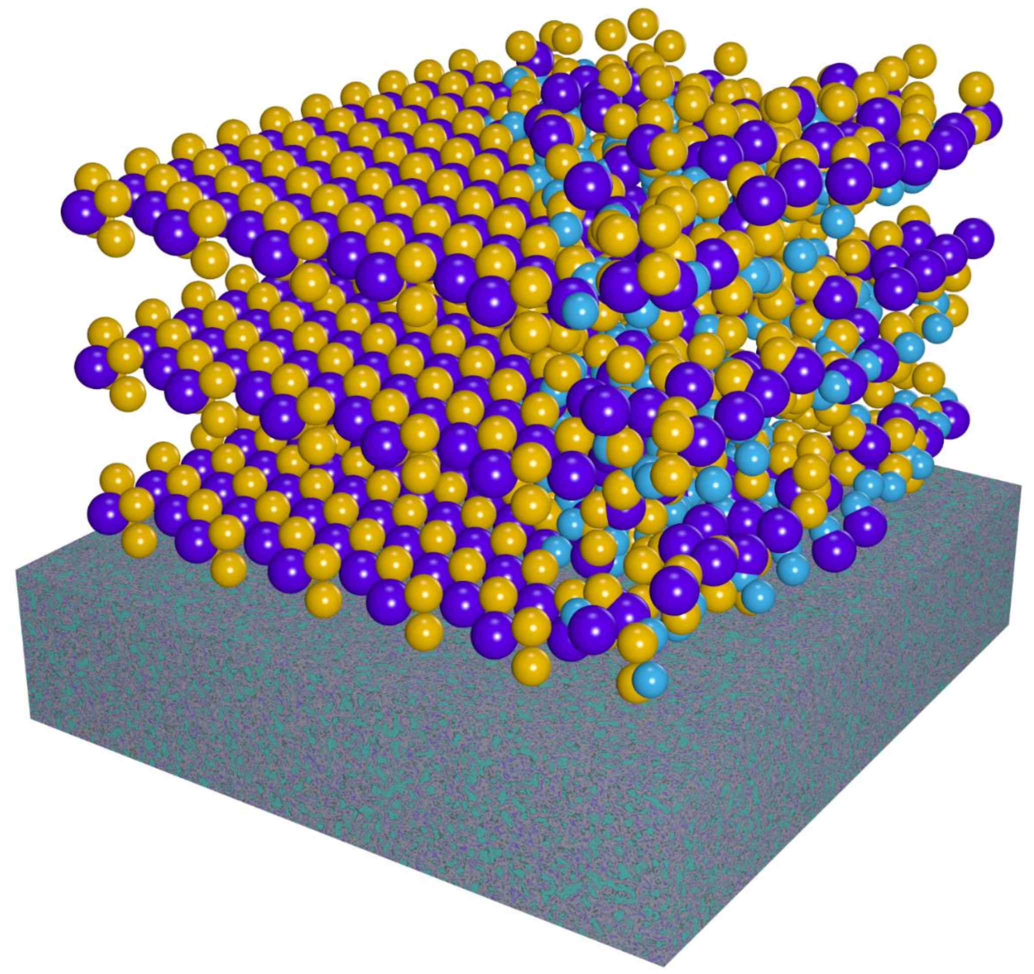
SiO_2 | Al_2O_3

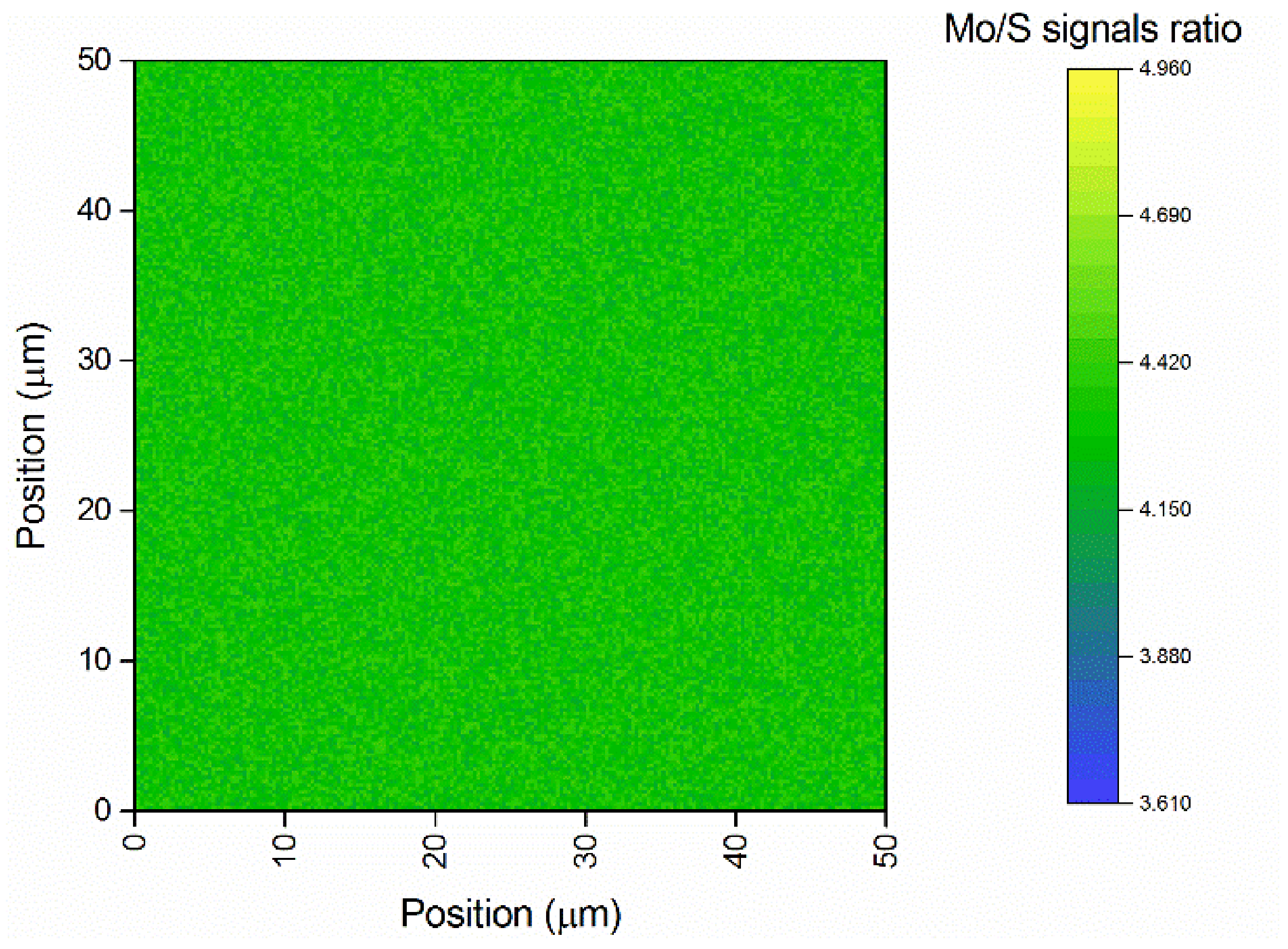


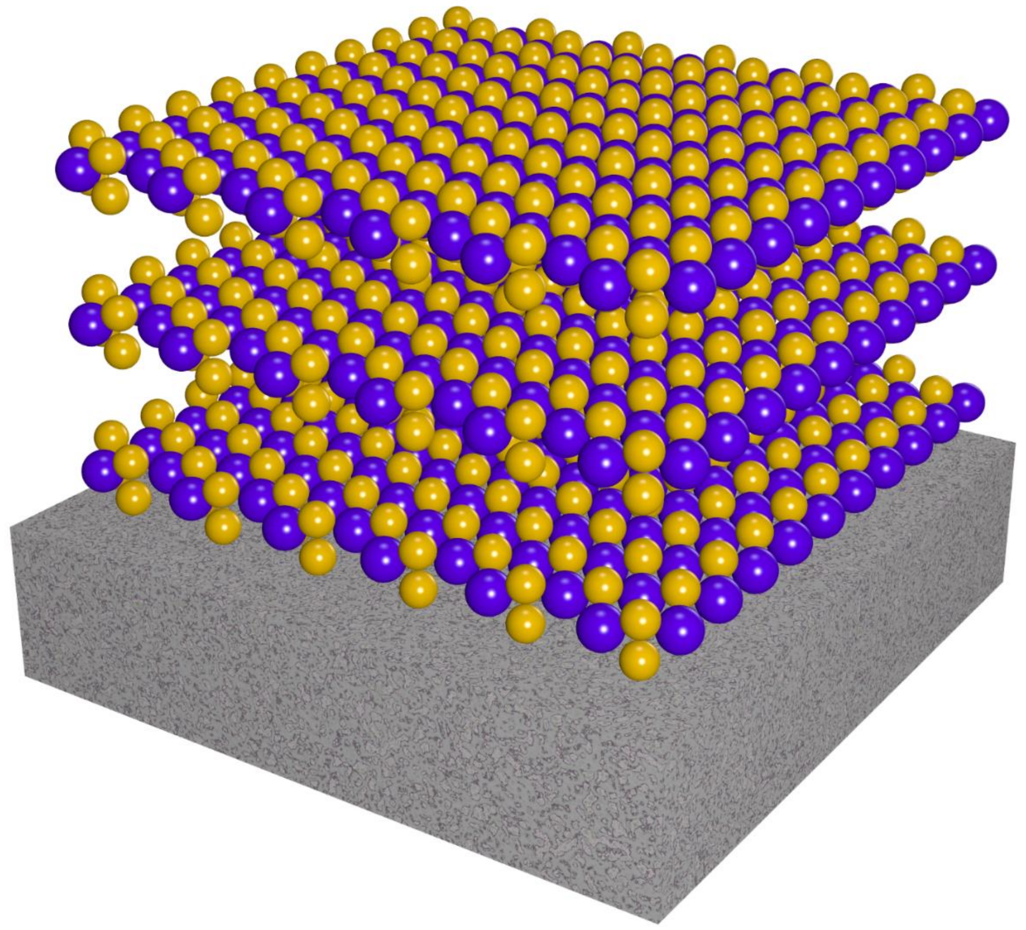
Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

Substrate type / procedure optimization



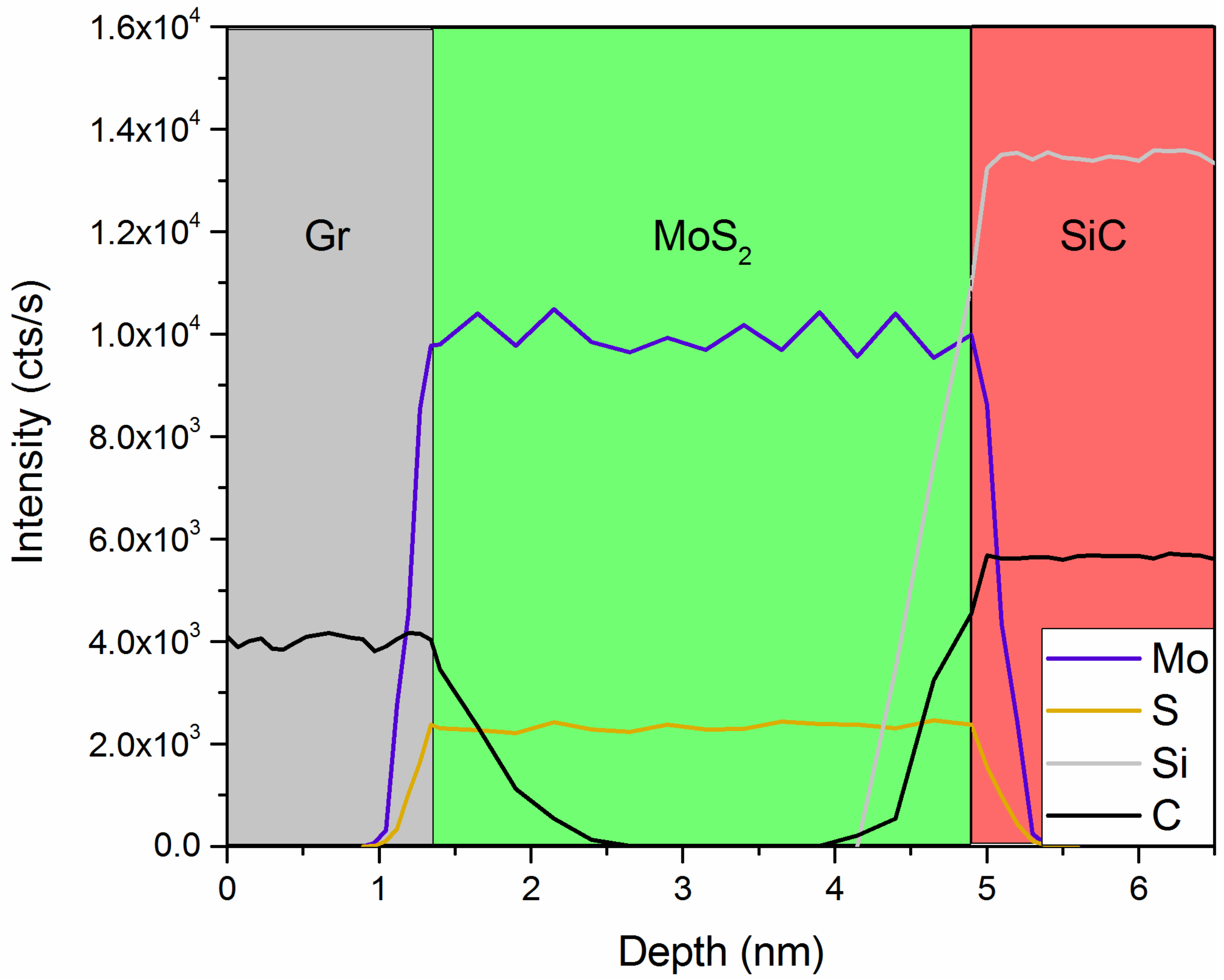


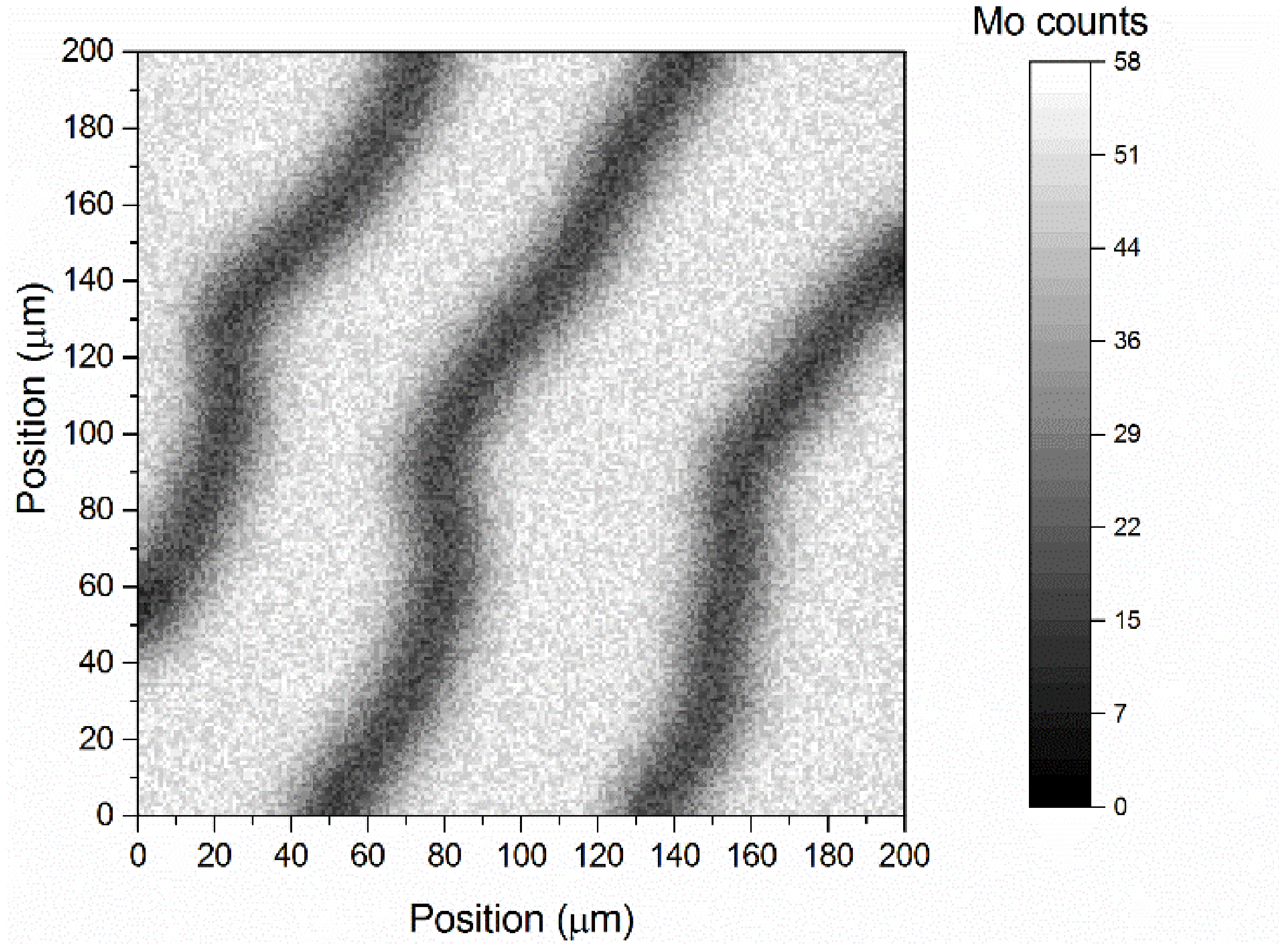


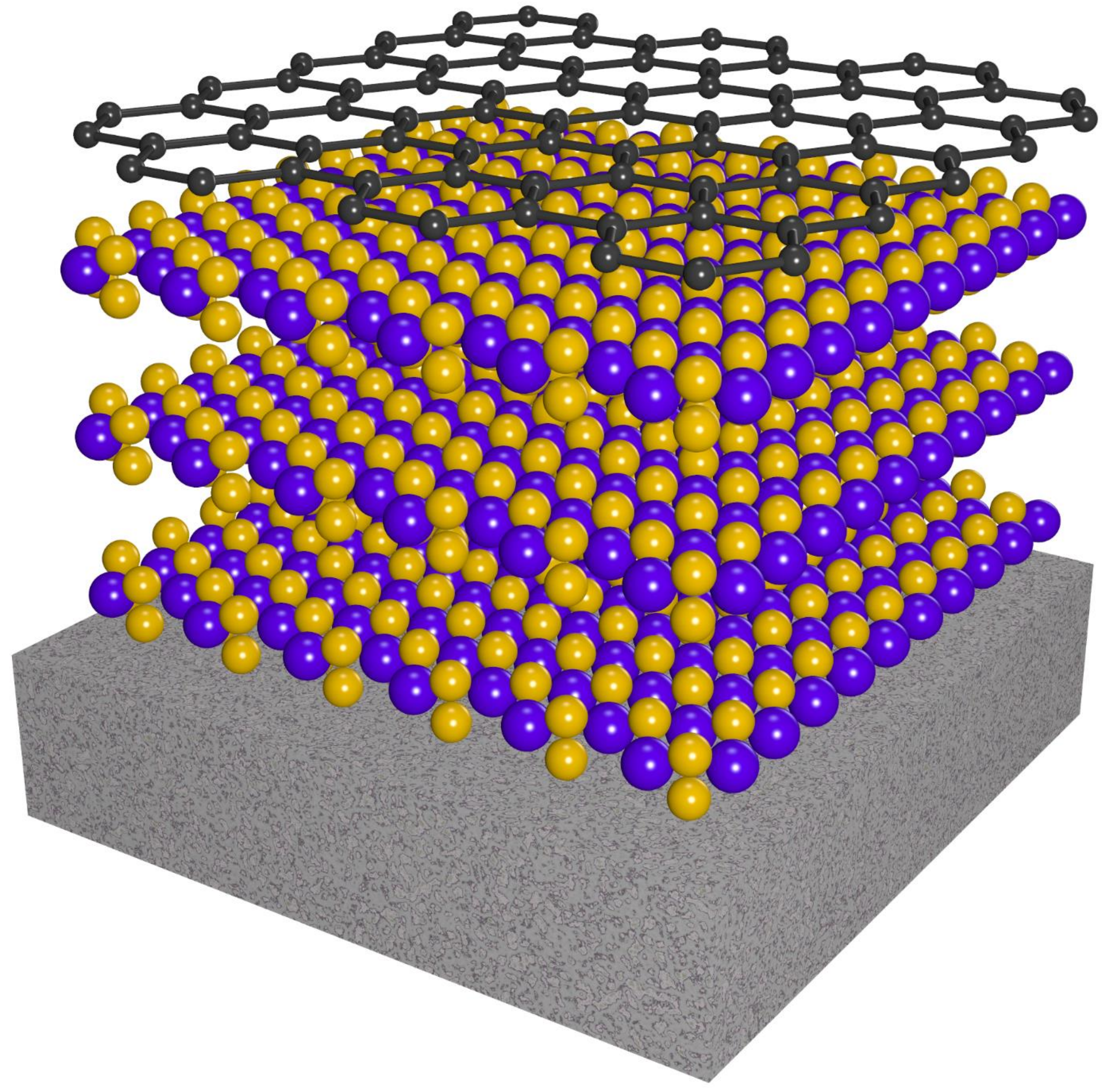


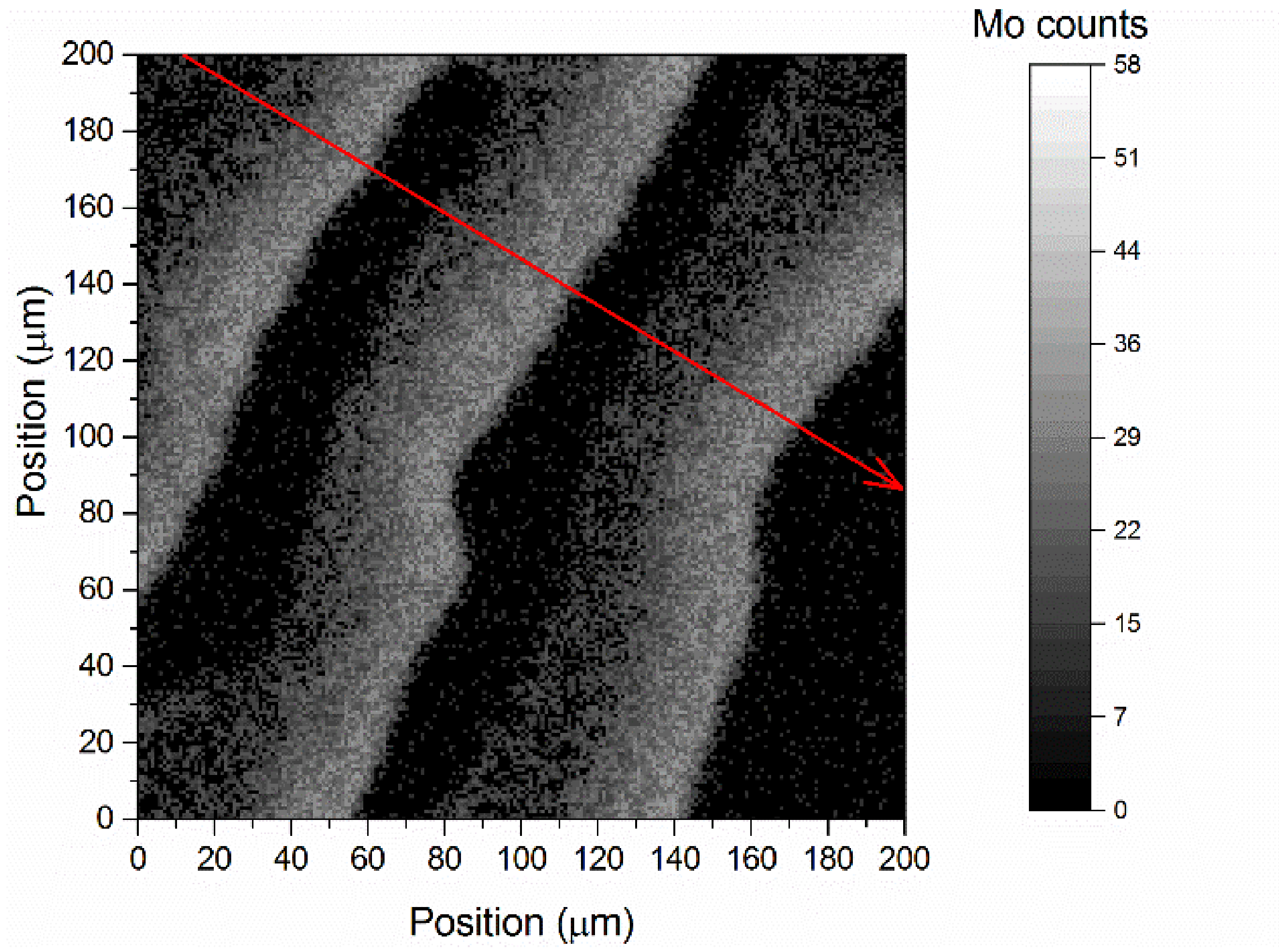
Physical Chemistry Chemical Physics **21**, 8837-8842 (2019)

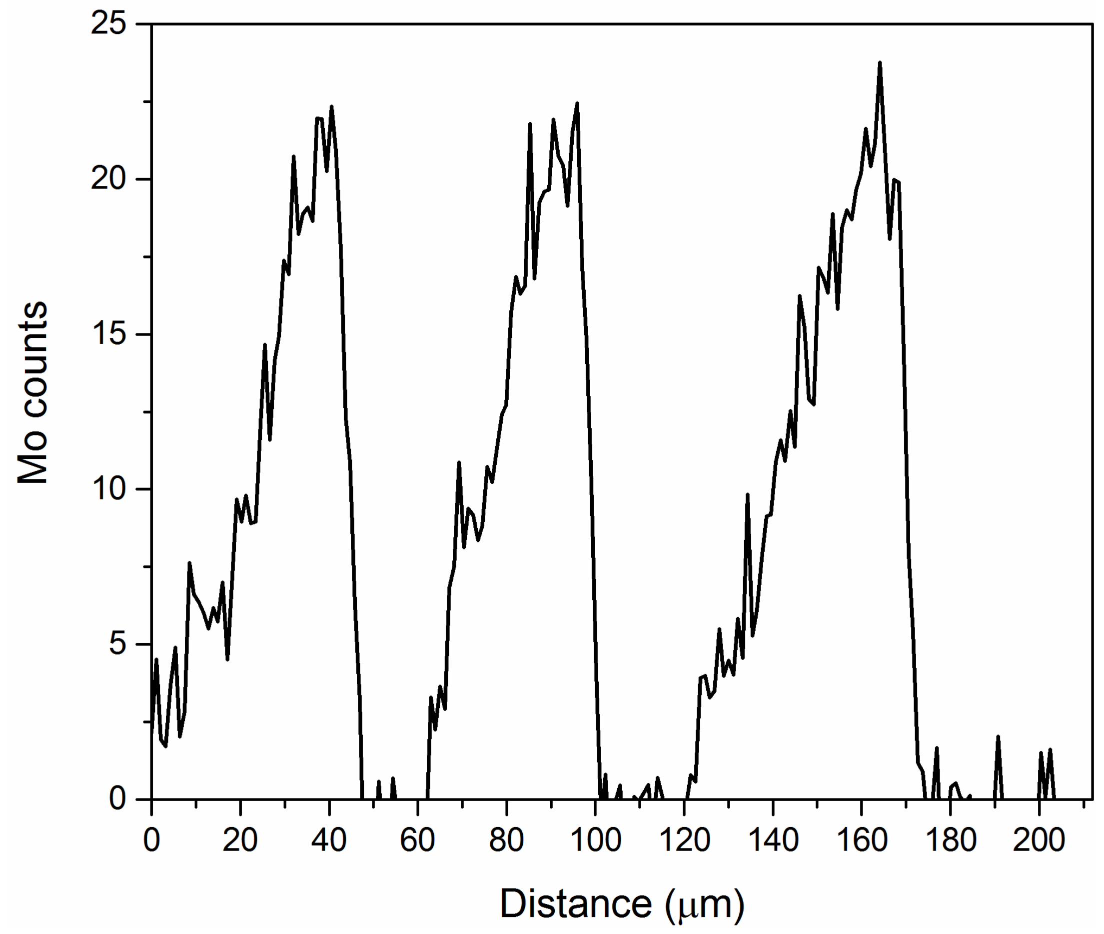
Graphene/SiC case





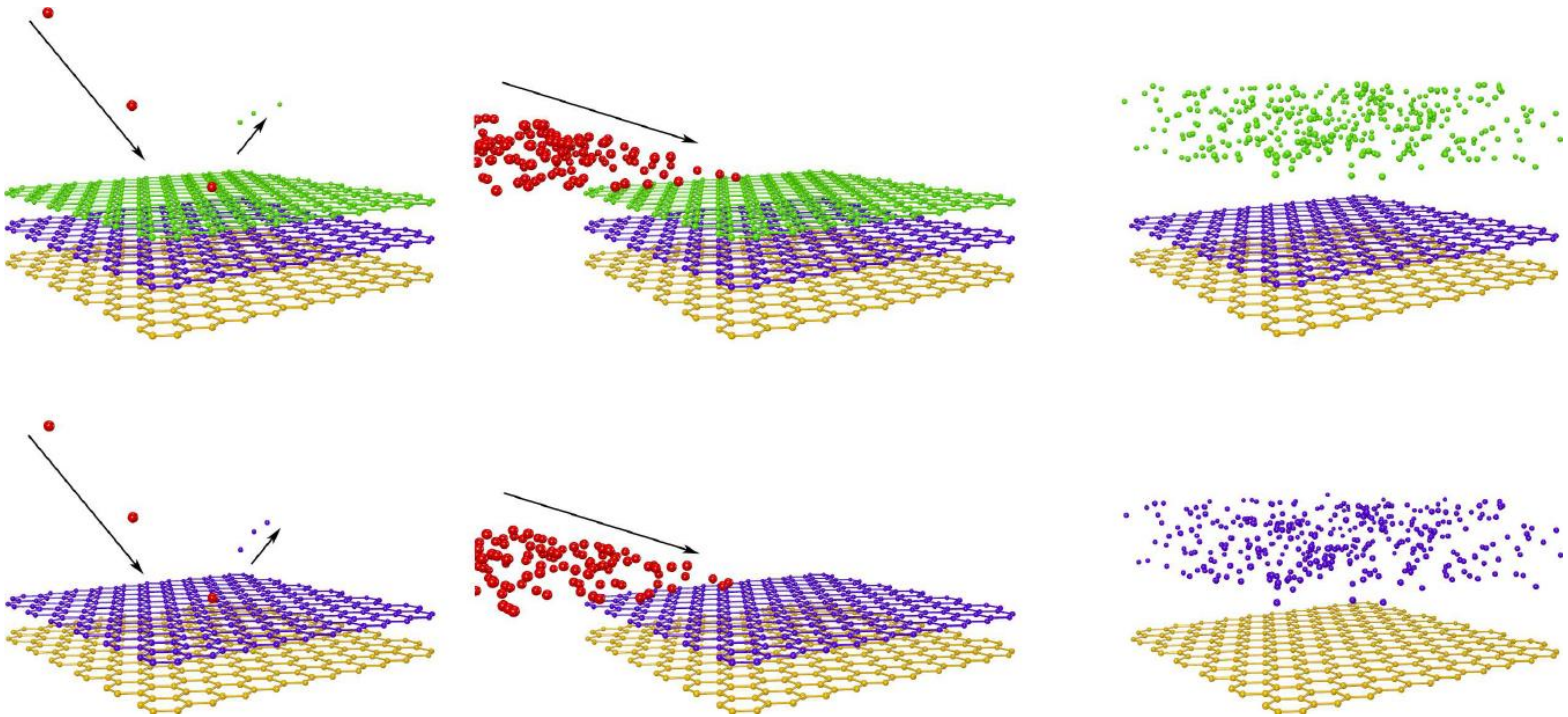






Physical Chemistry Chemical Physics **21**, 20641-20646 (2019)

Hexagonal boron nitride

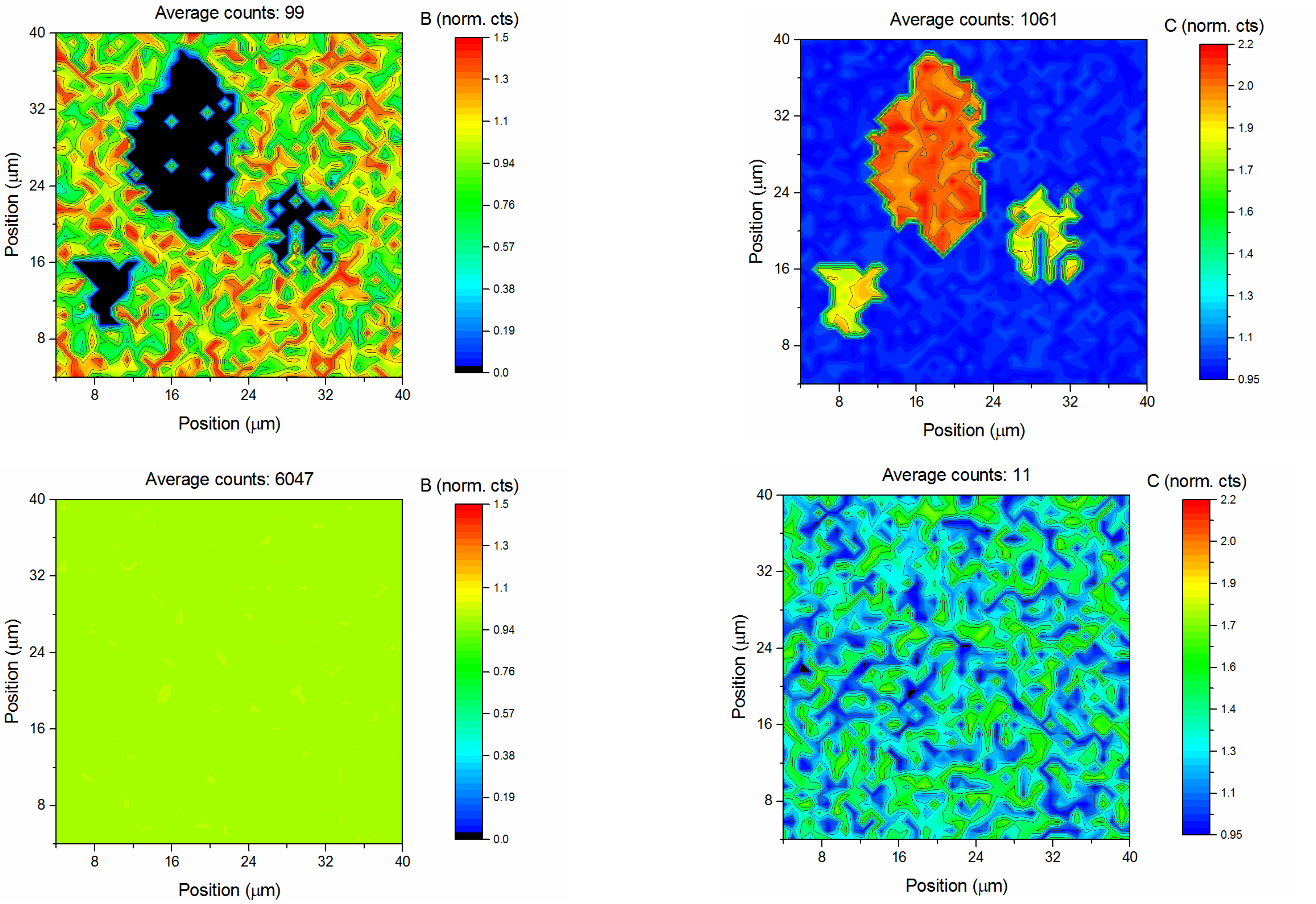


Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

Different carrier gas

Ar

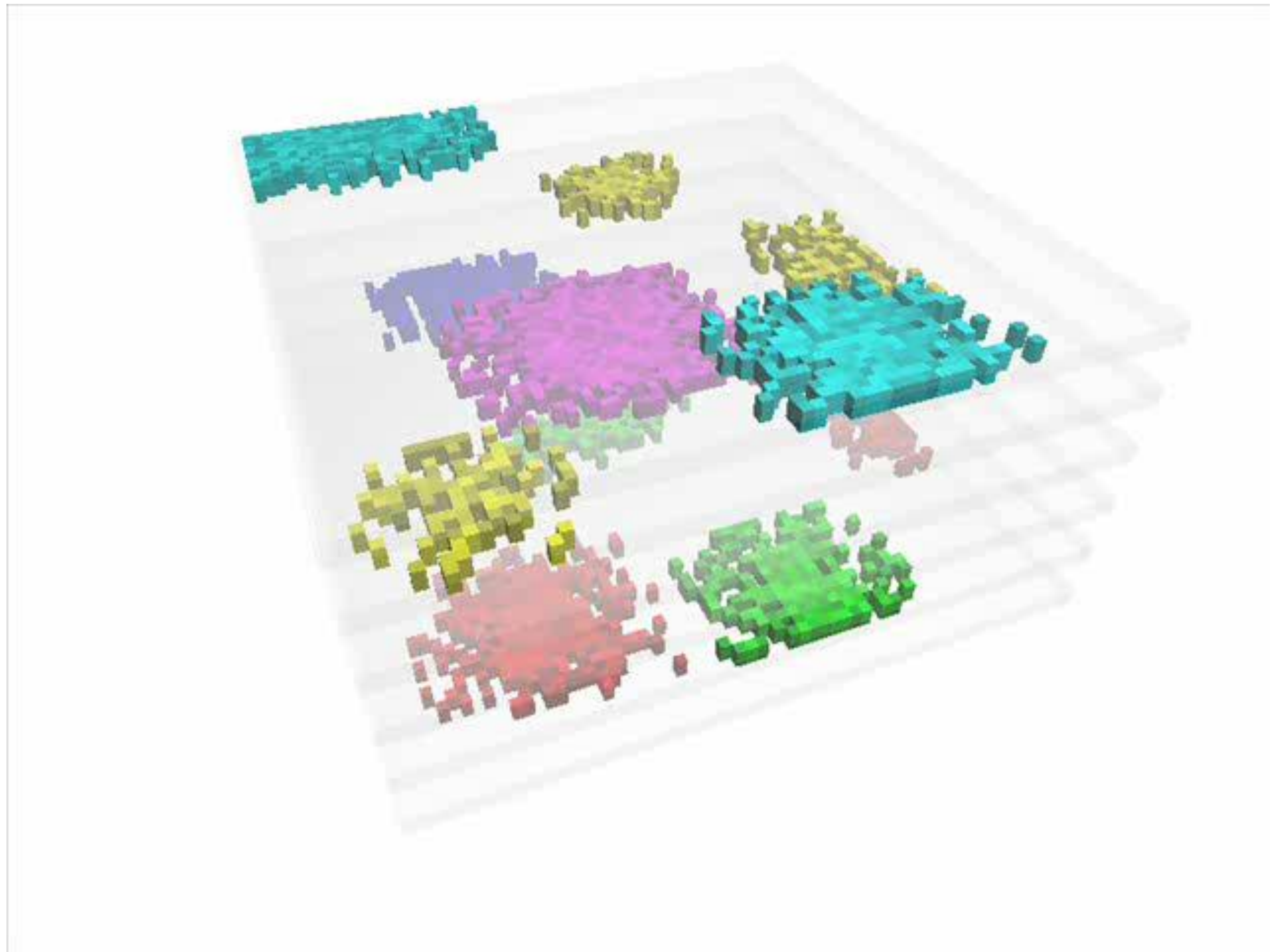
H_2



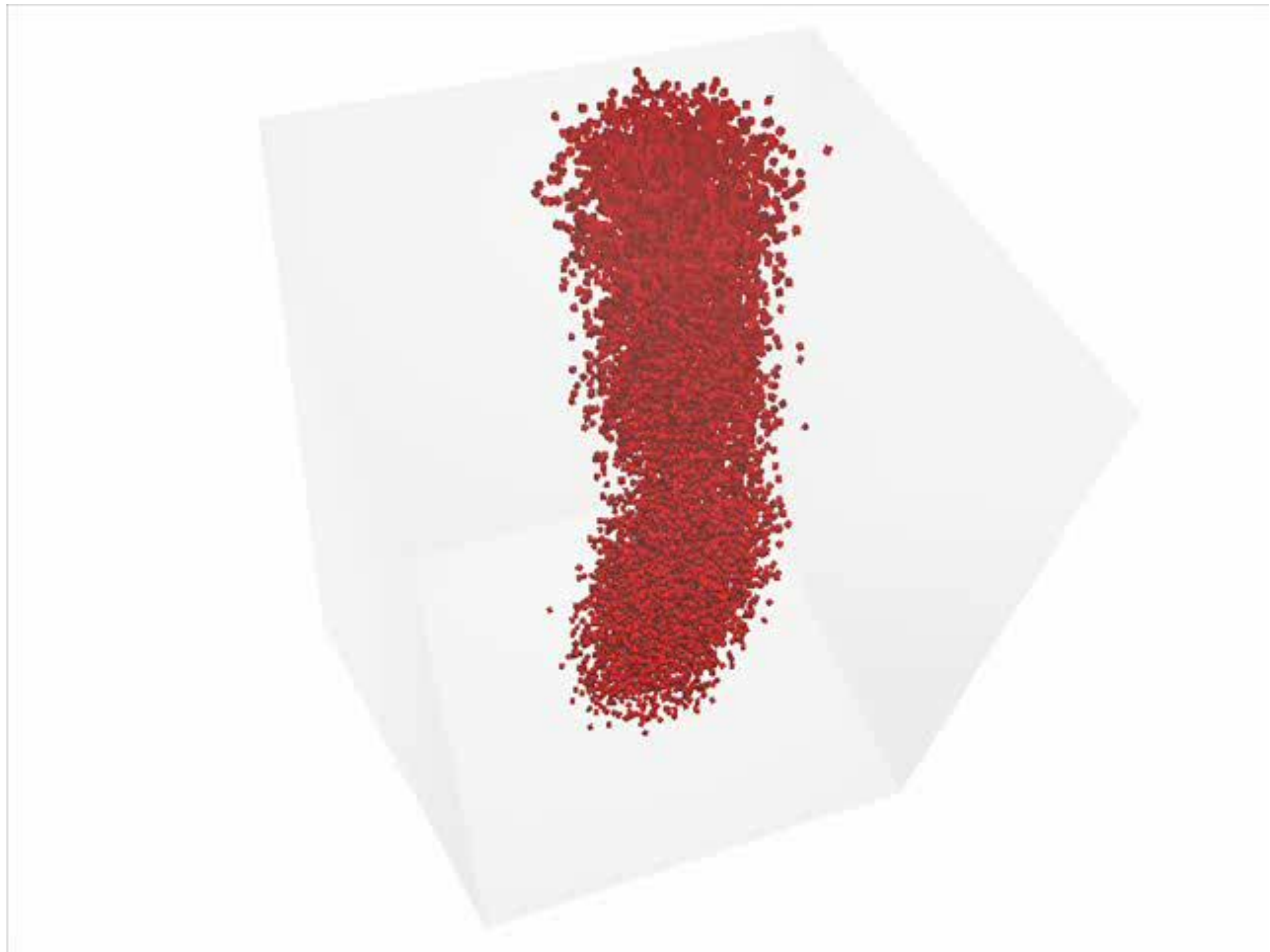
Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

Different reactor pressure

High

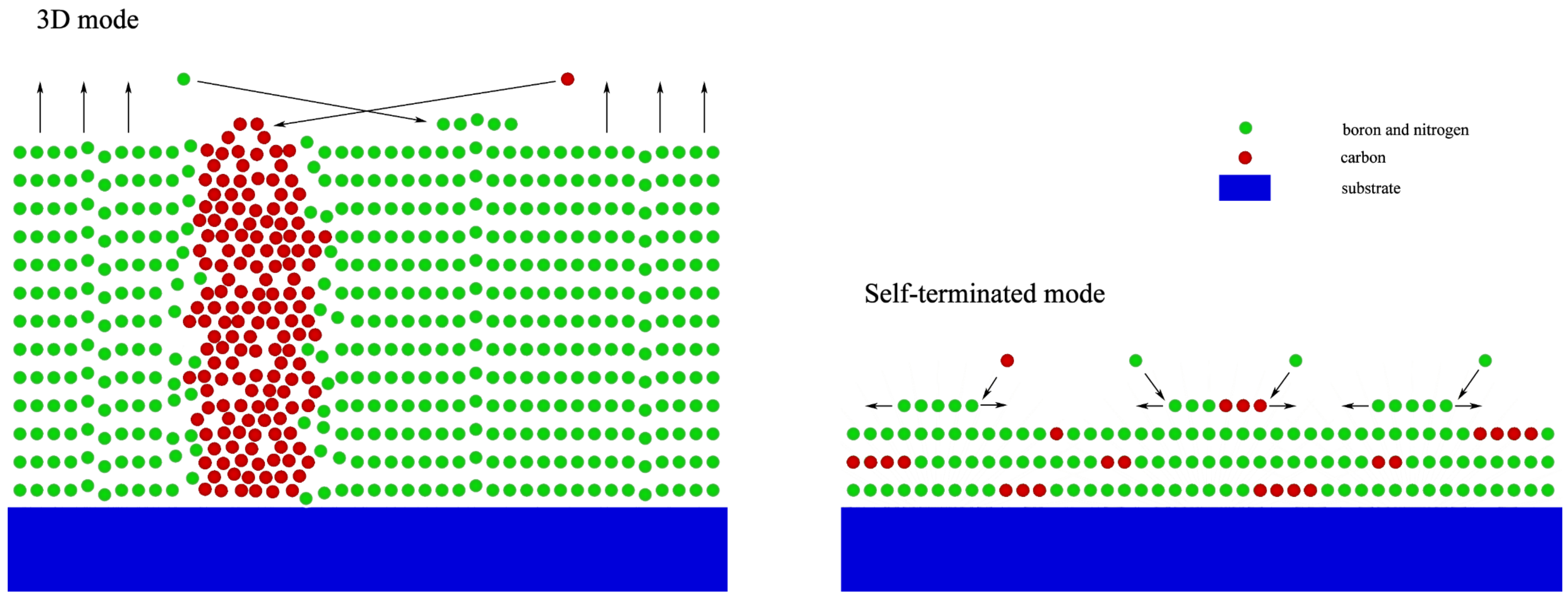


Low



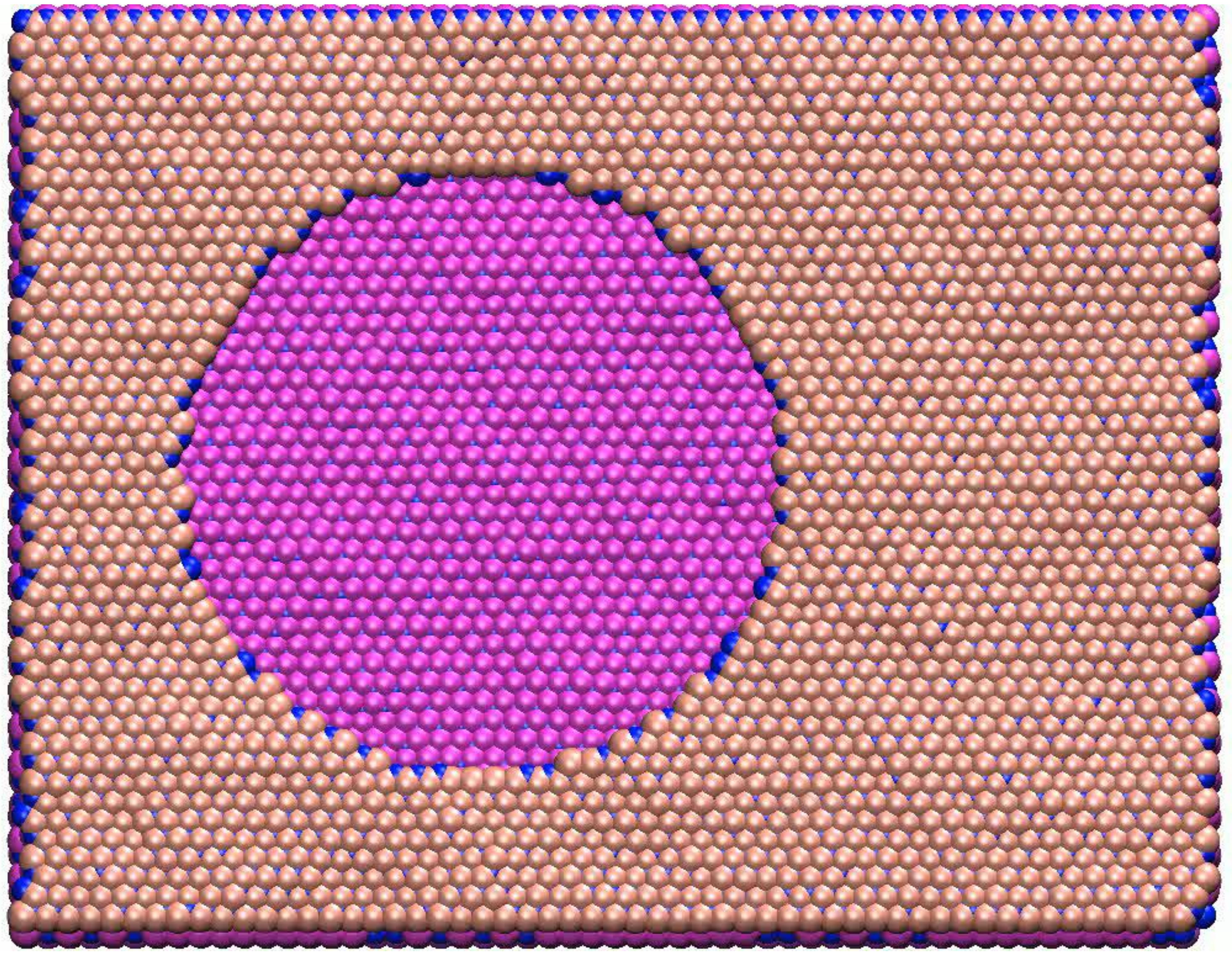
Journal of Analytical Atomic Spectrometry **34**, 848-853 (2019)

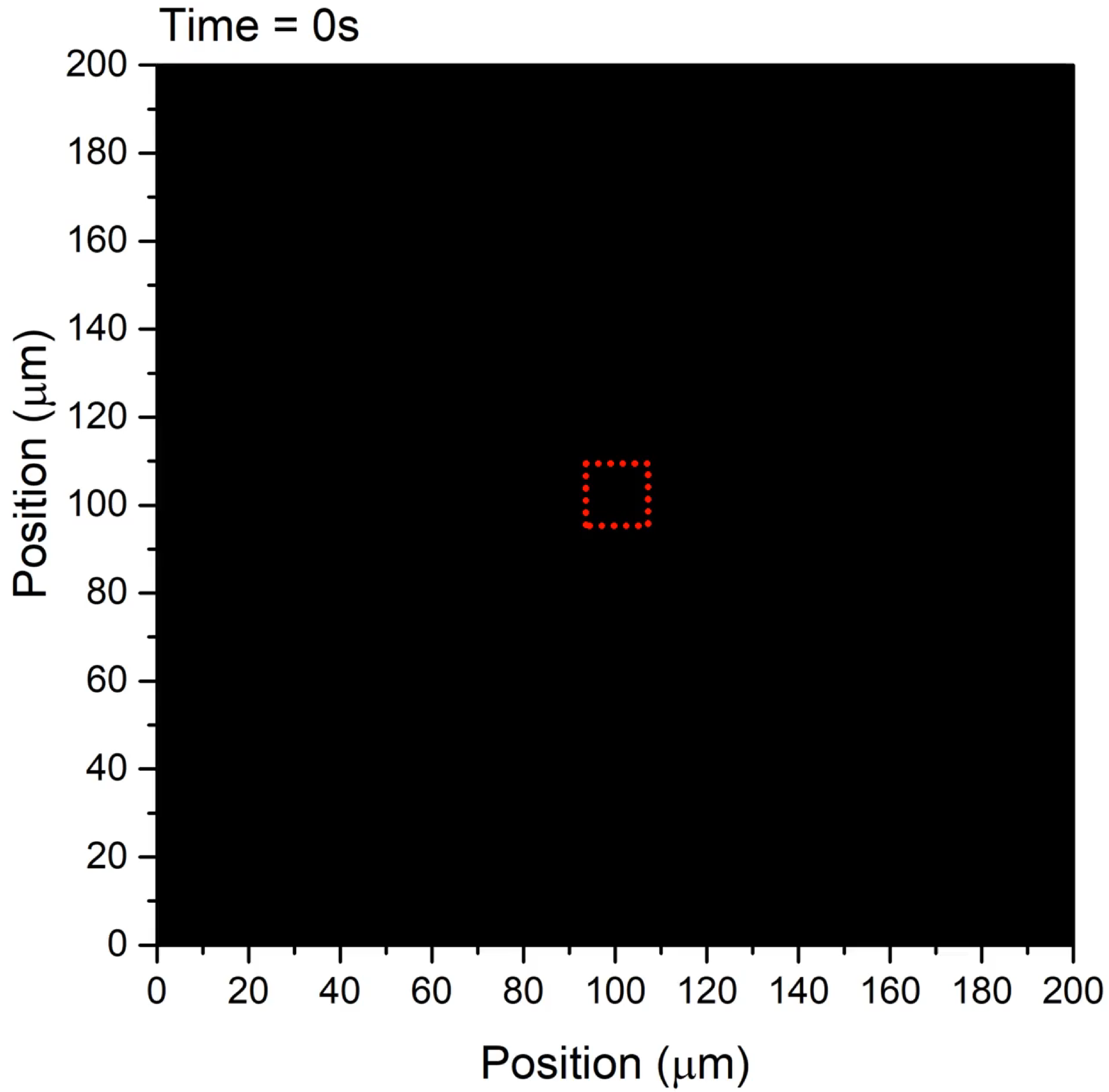
hBN - summary



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

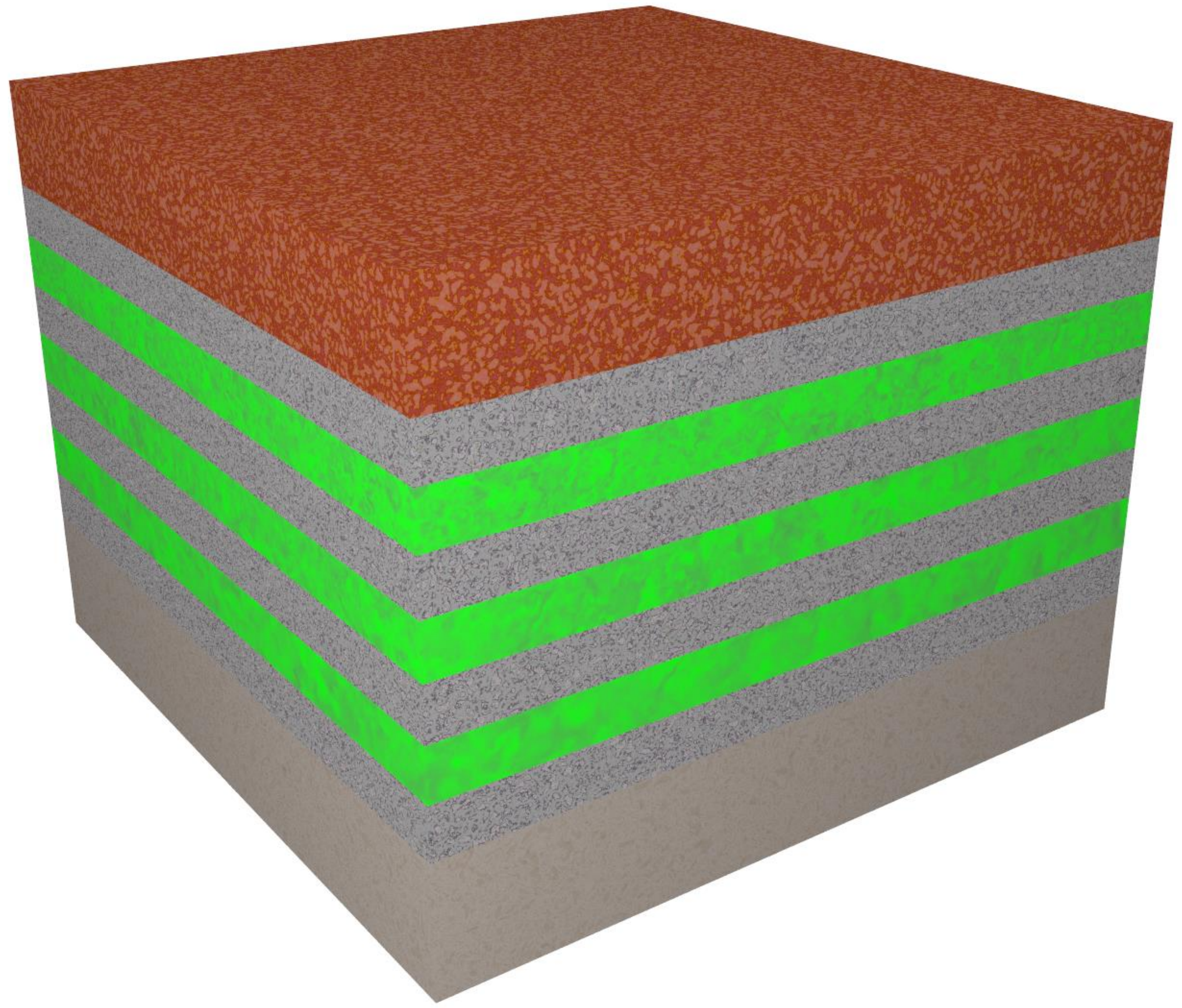
How does it work?





Measurement **179**, 109487 (2021)

InGaN QWs

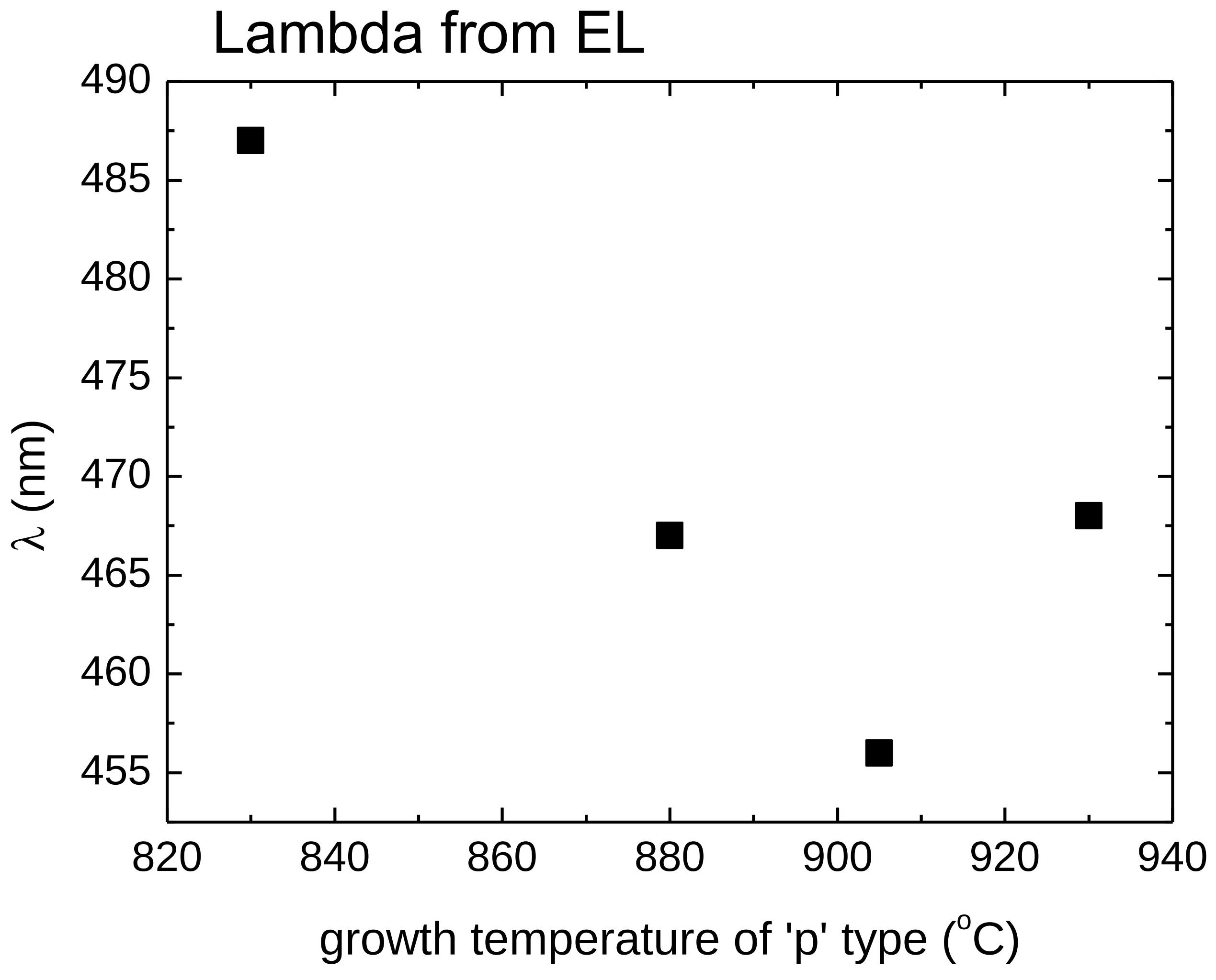


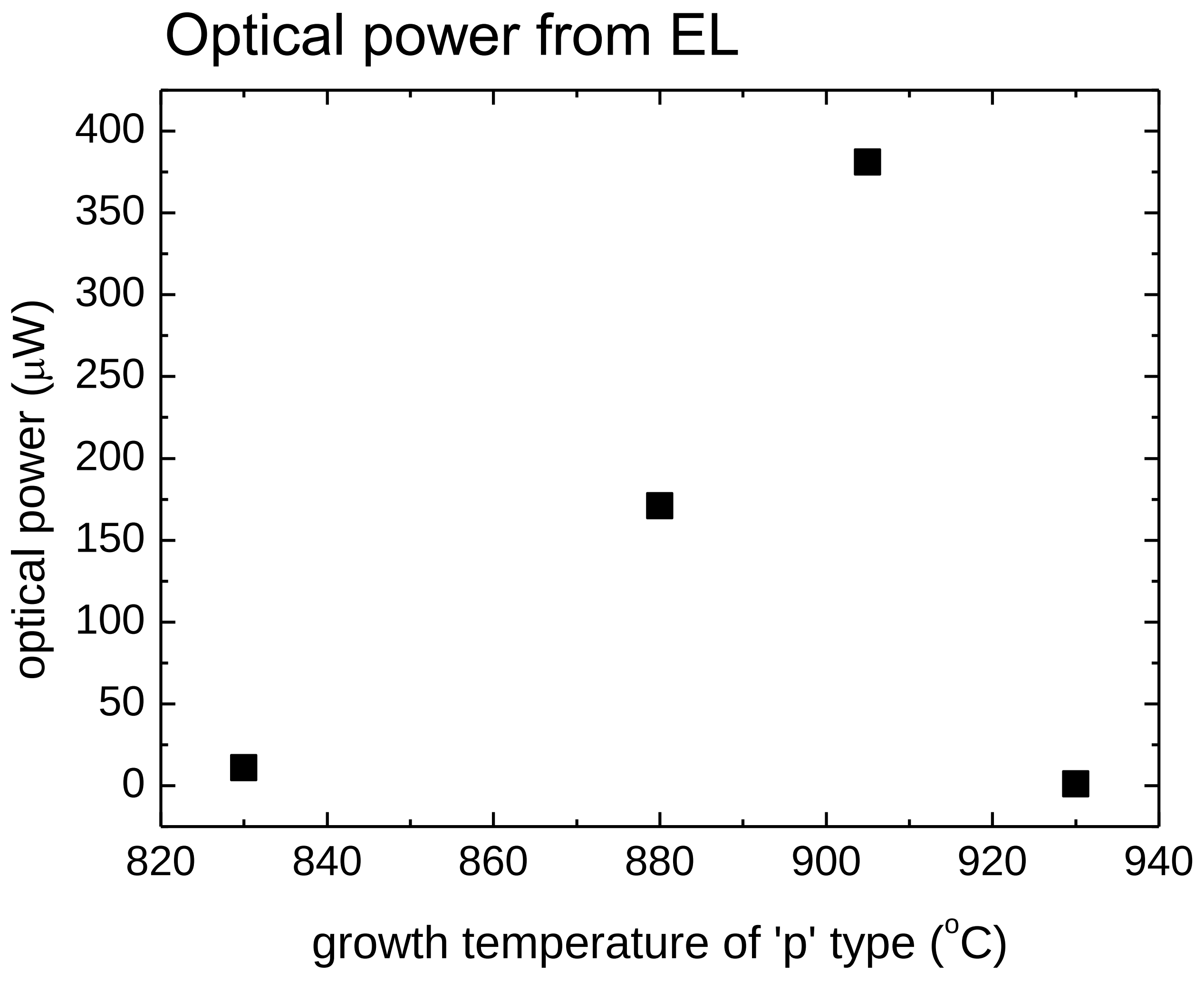
p-type GaN

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

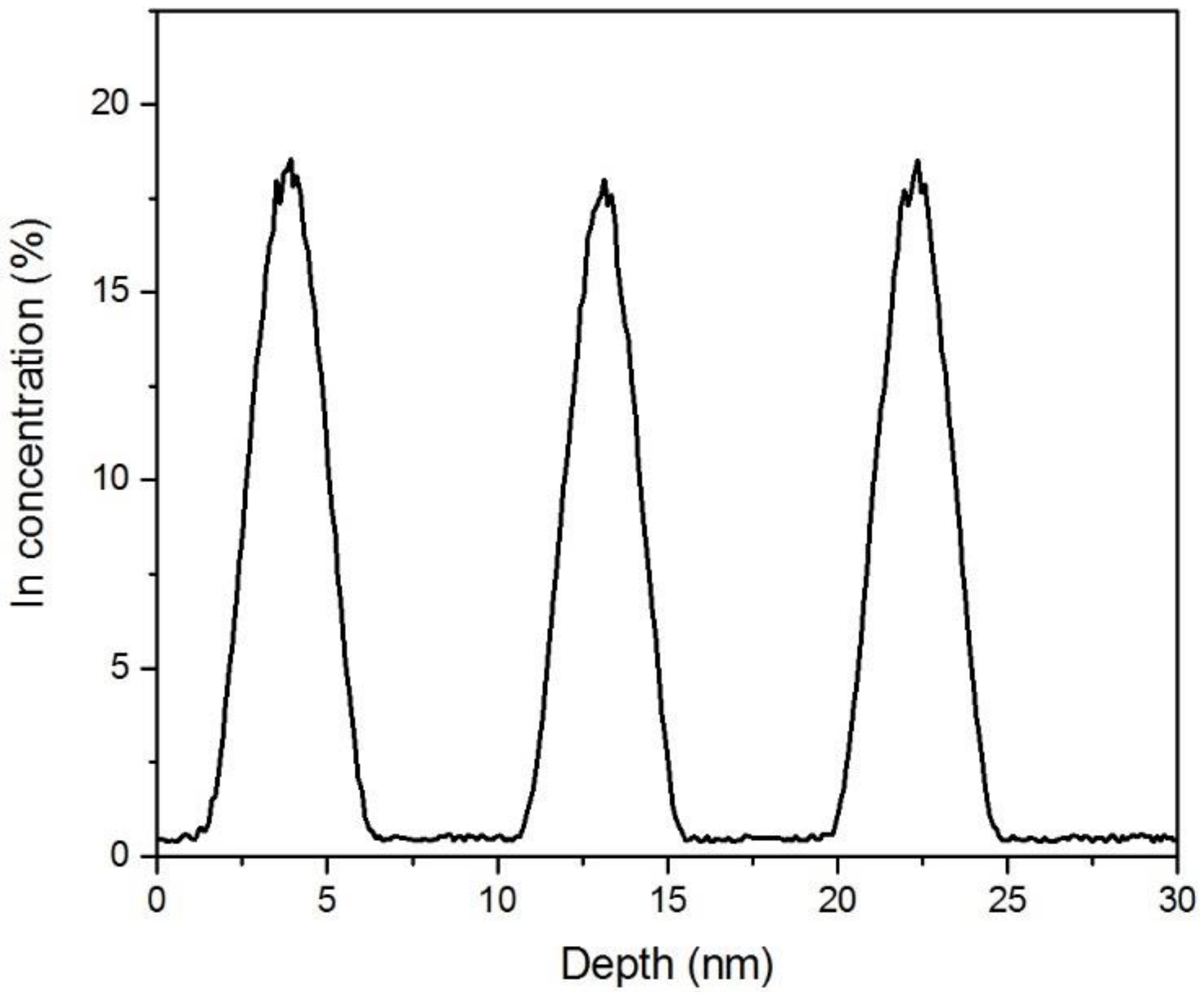
n-type GaN

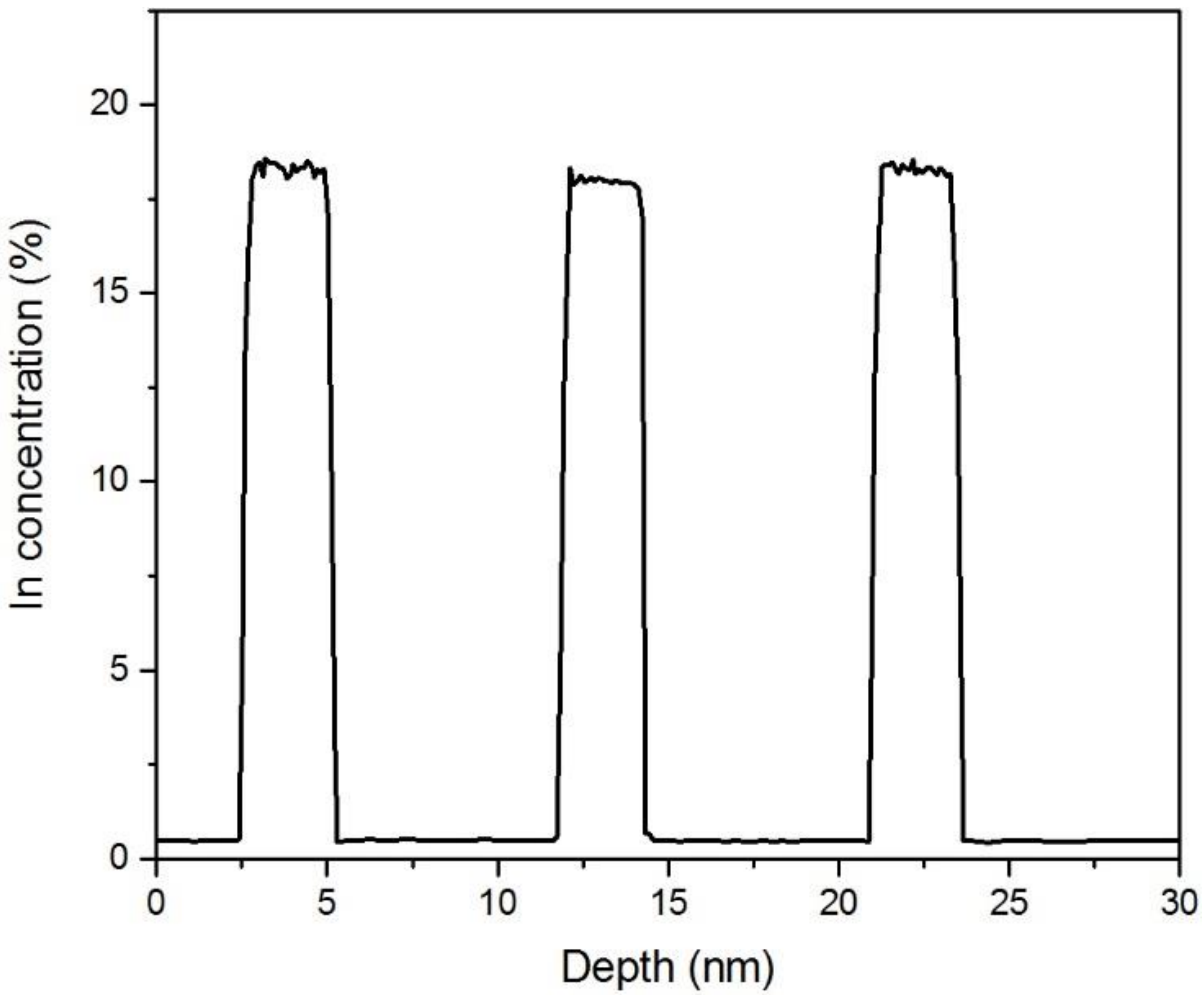
Lattice mismatch
Growth temperature differences



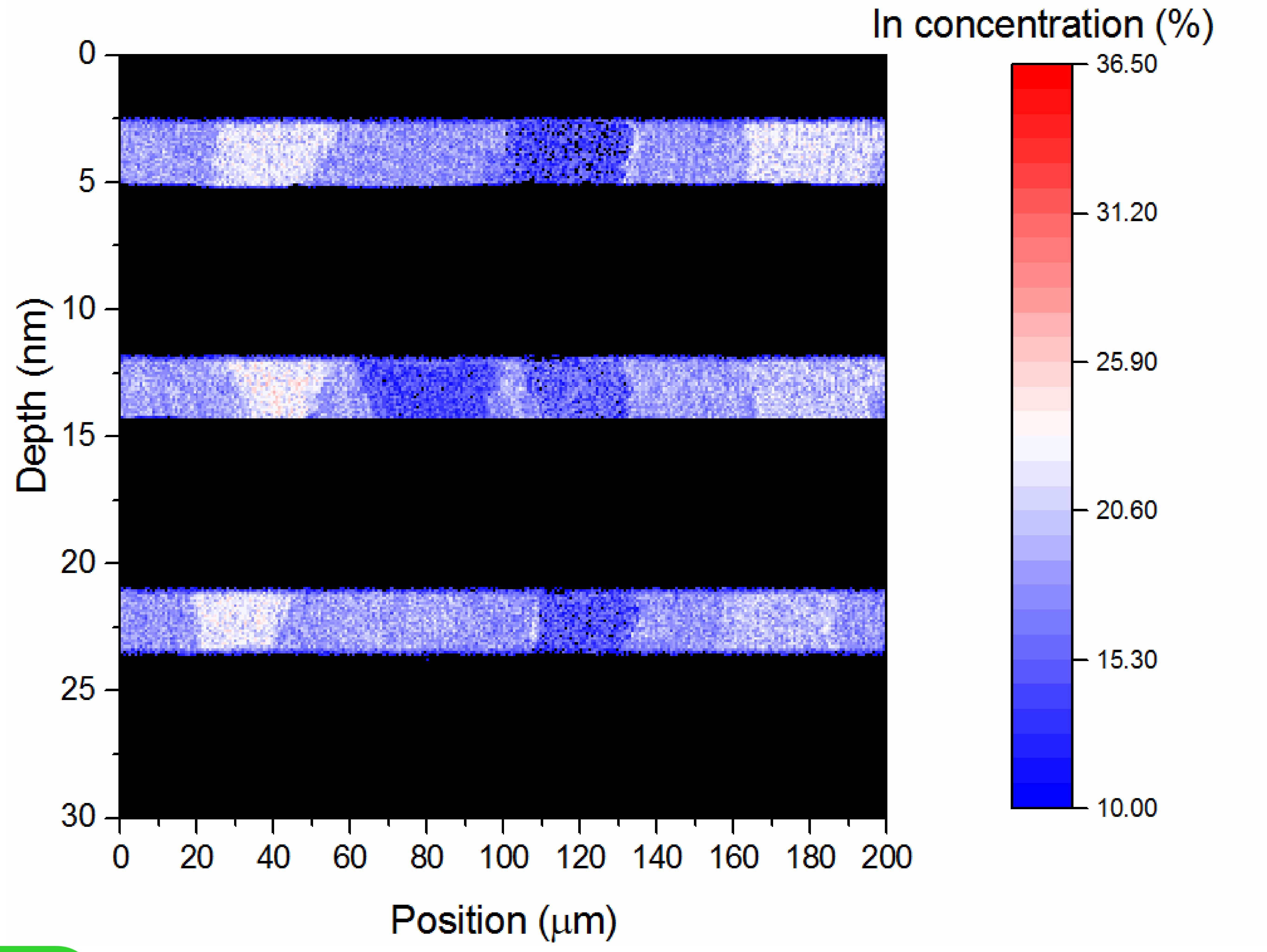


Standard SIMS vs ULIE-SIMS

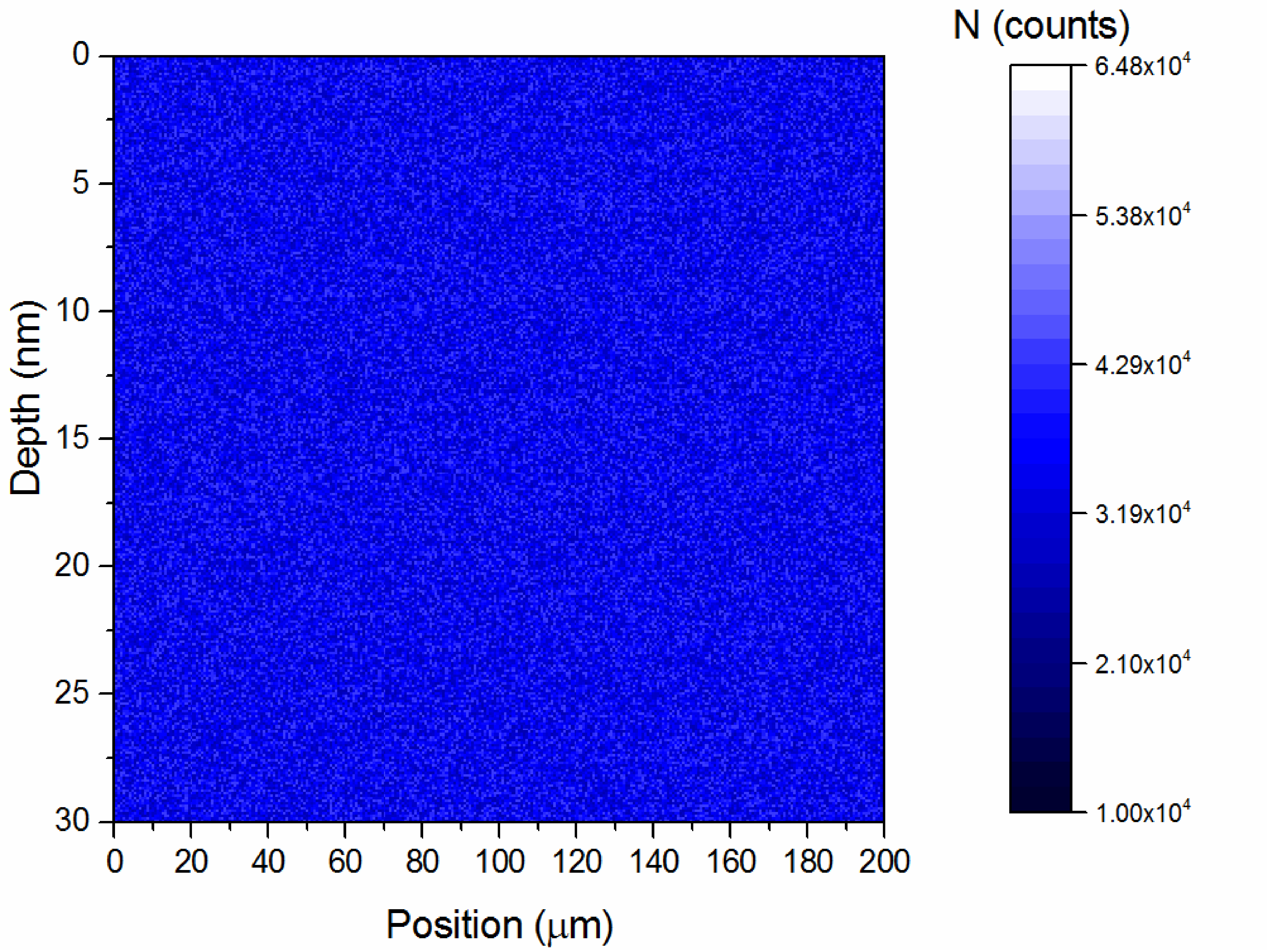




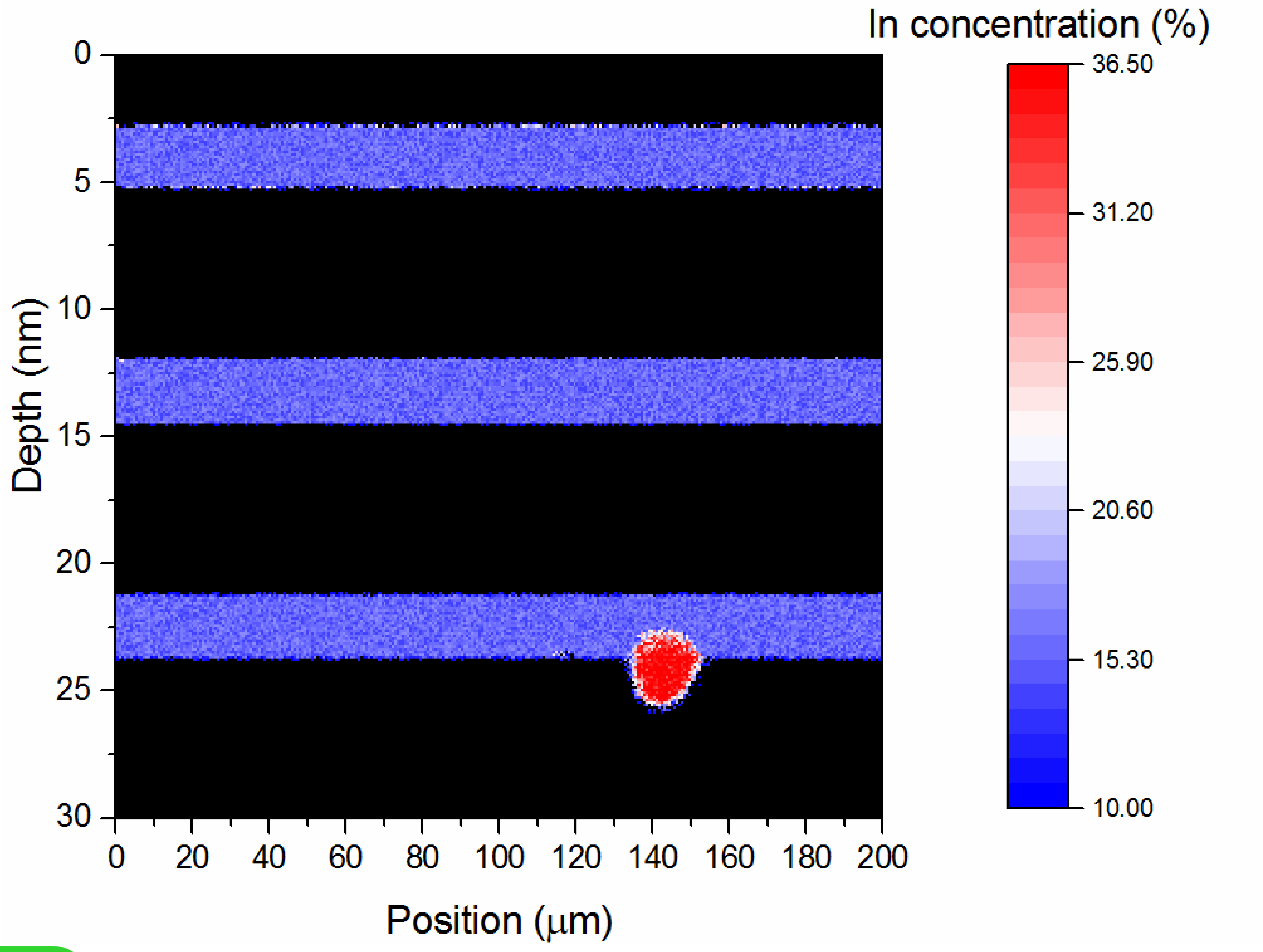
Growth temperature 830ºC



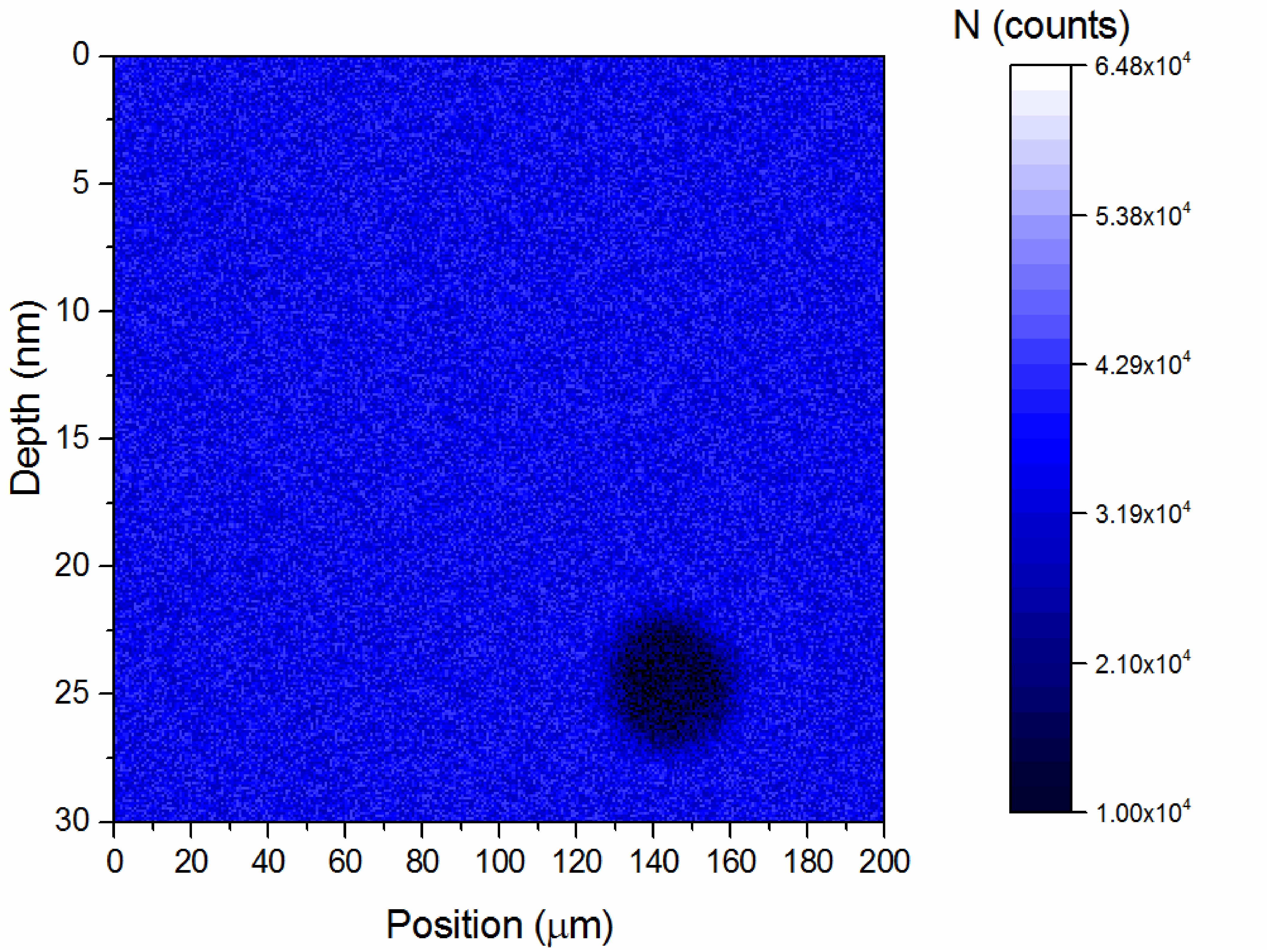
Please note the scale! Not TEM!



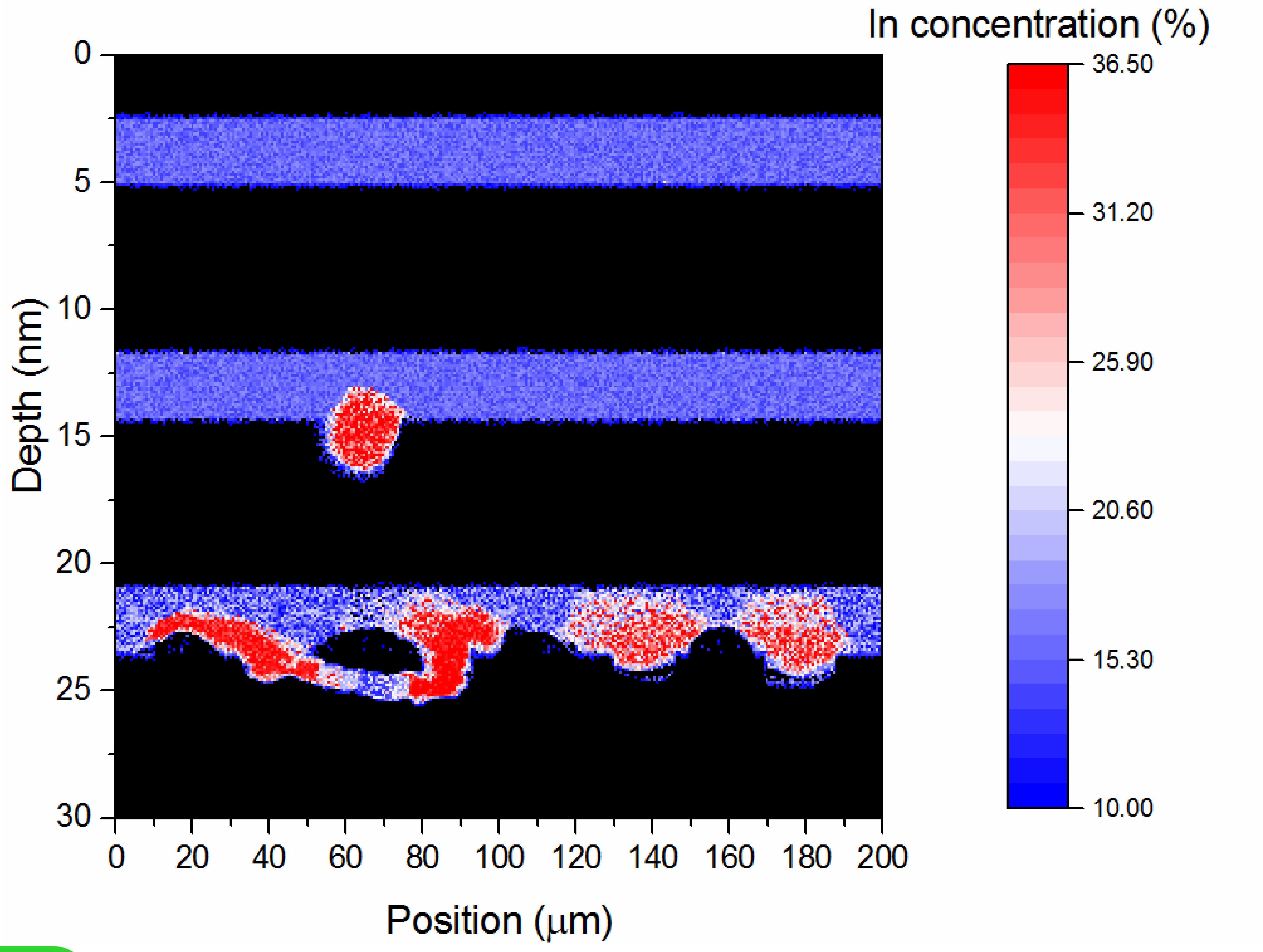
Growth temperature 905ºC



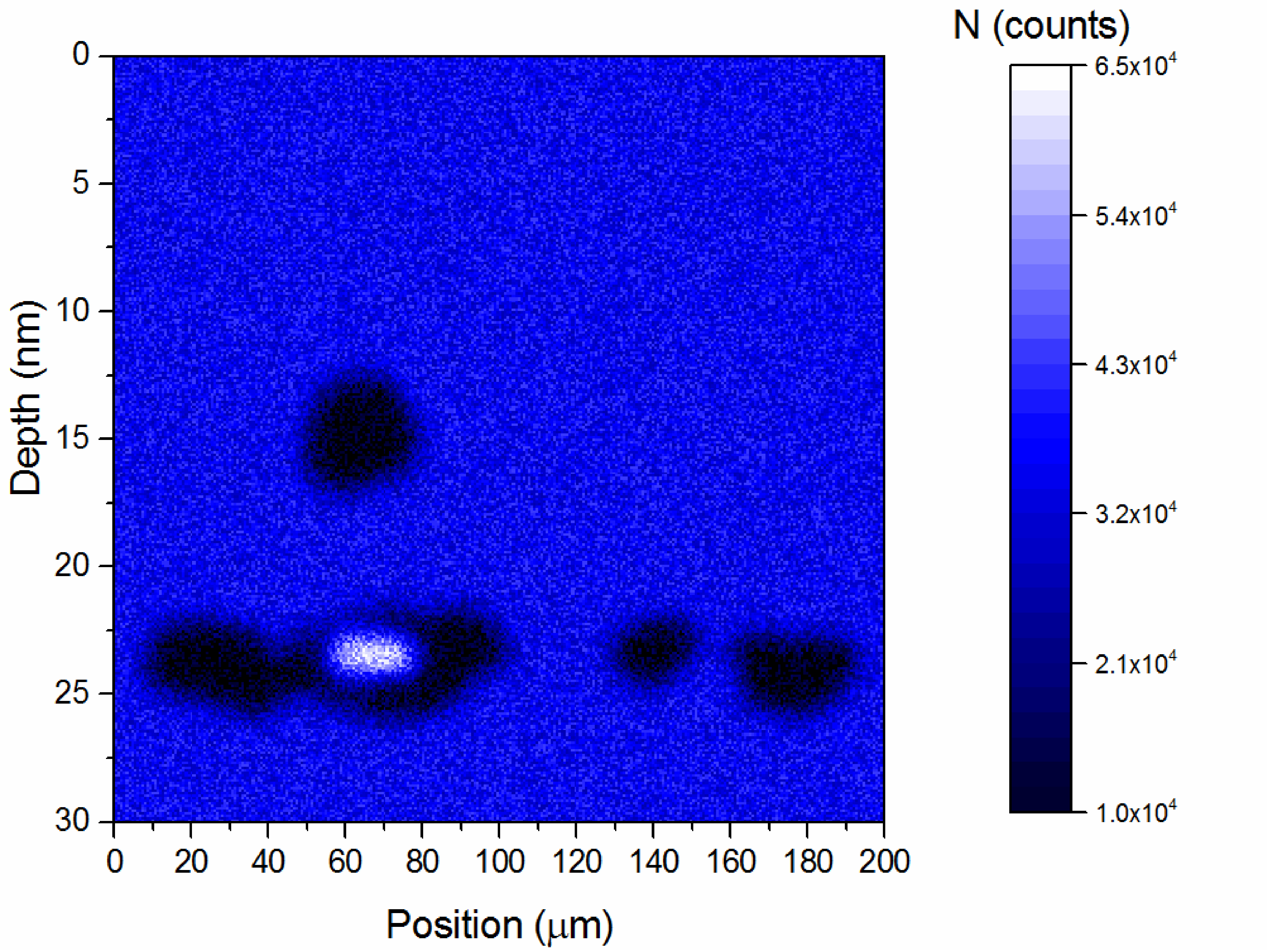
Please note the scale! Not TEM!



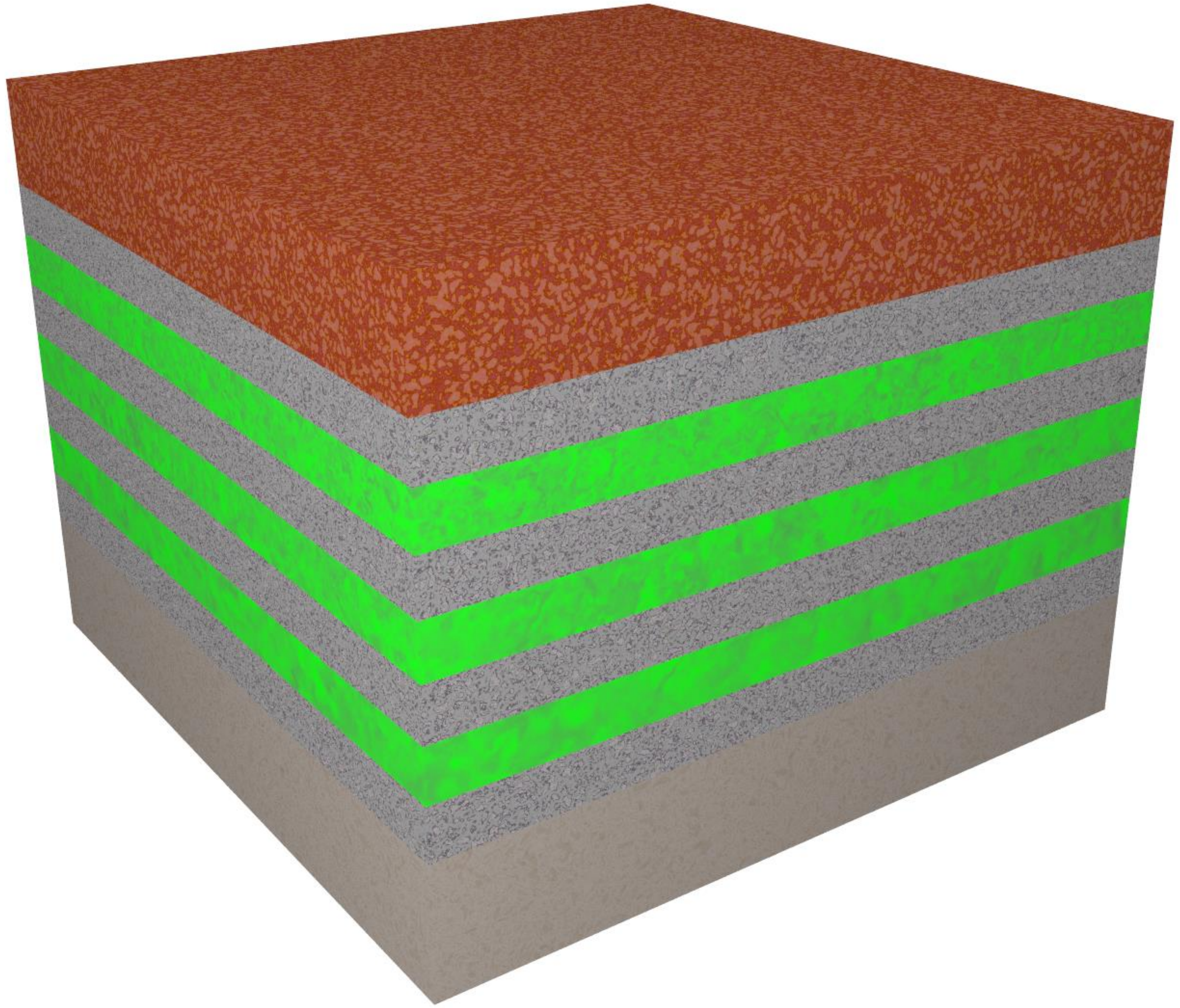
Growth temperature 930ºC



Please note the scale! Not TEM!



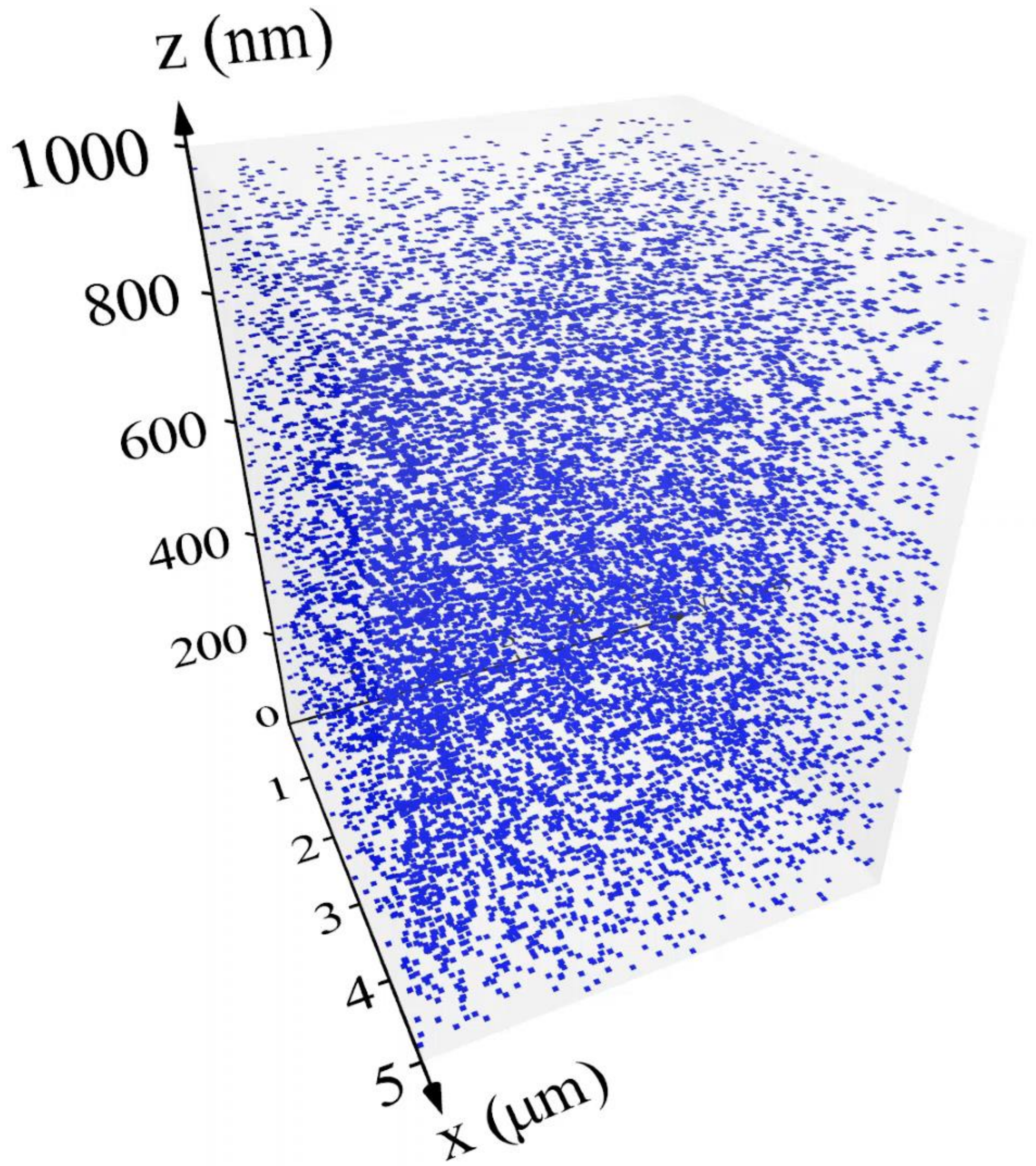
InGaN QWs – summary



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

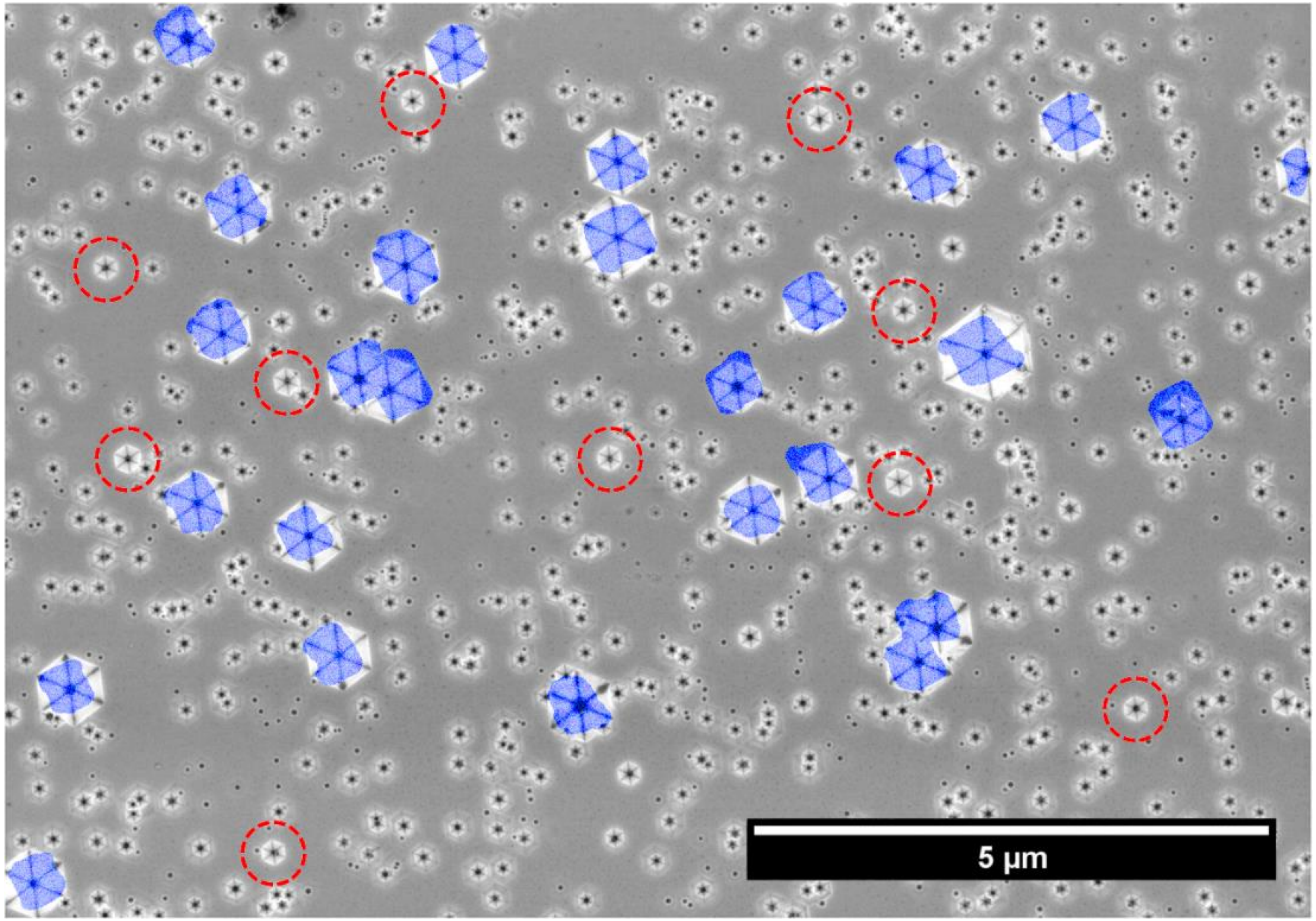
Oxygen in GaN

- Sophisticated procedure
- Background contribution
- Random



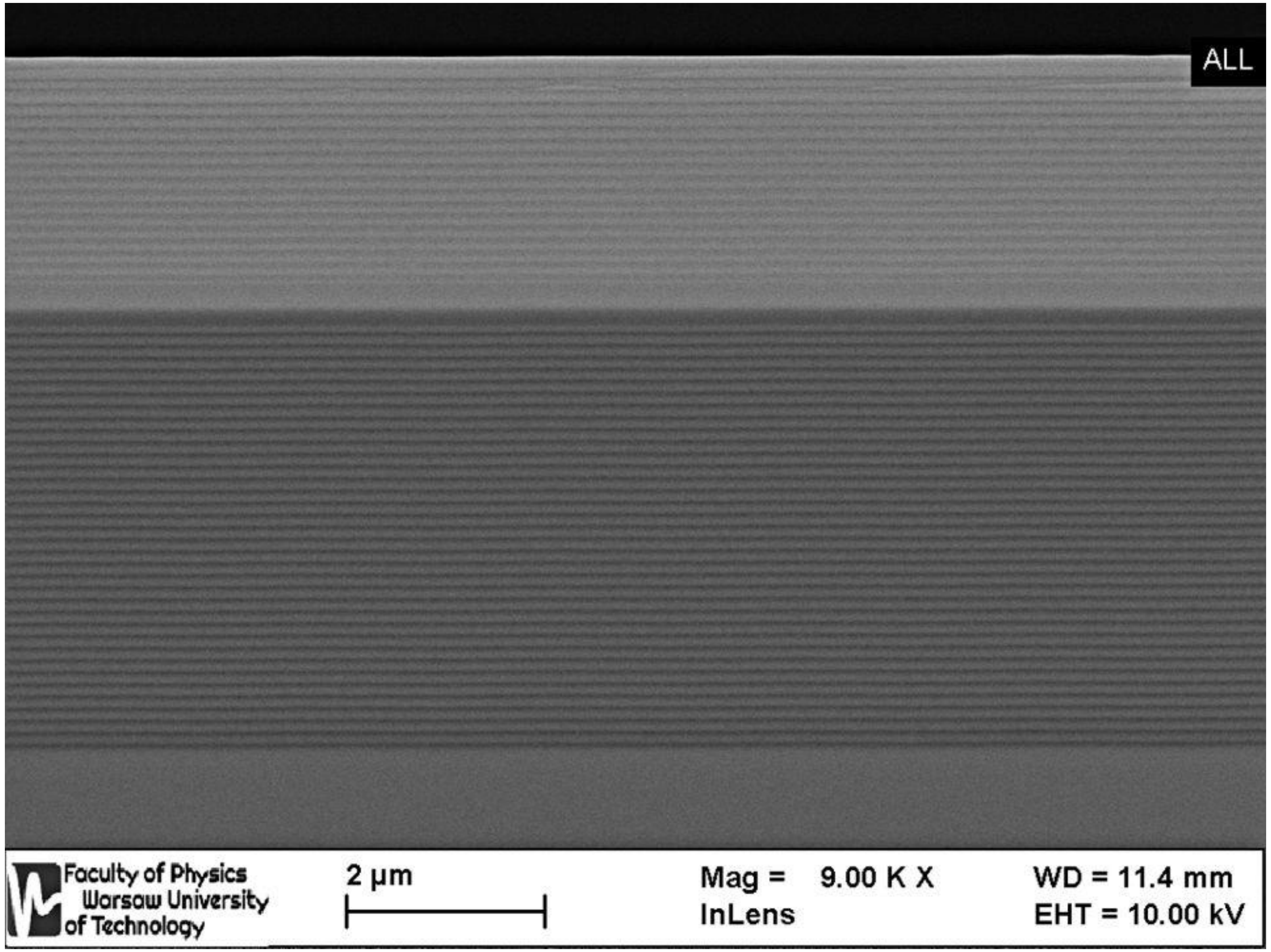
Chemical Communications 55, 11539-11542, 2019
Journal of Visualized Experiments 158, e61065, 2020

Oxygen in GaN



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

Vertical-cavity surface-emitting laser

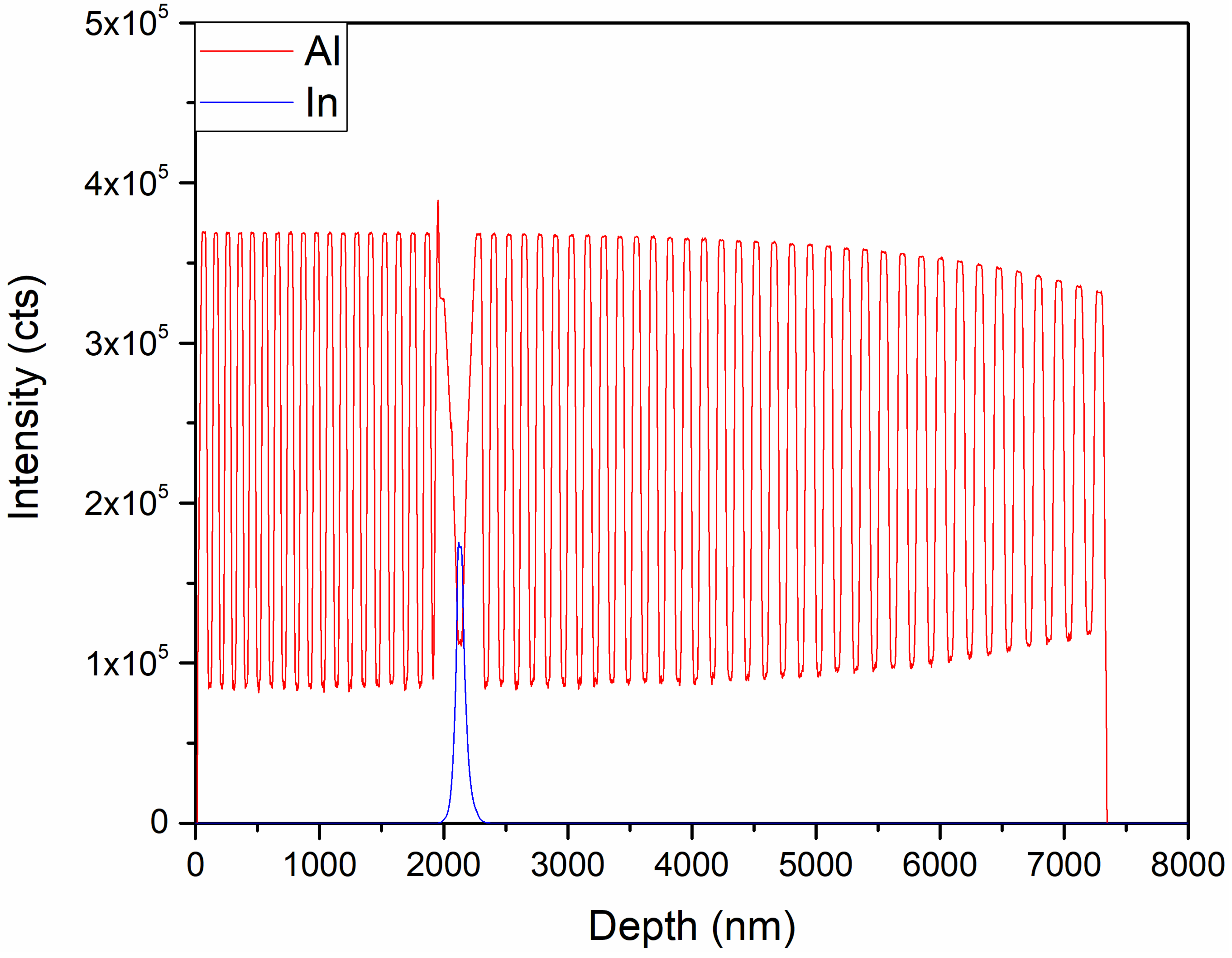


Remarks

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

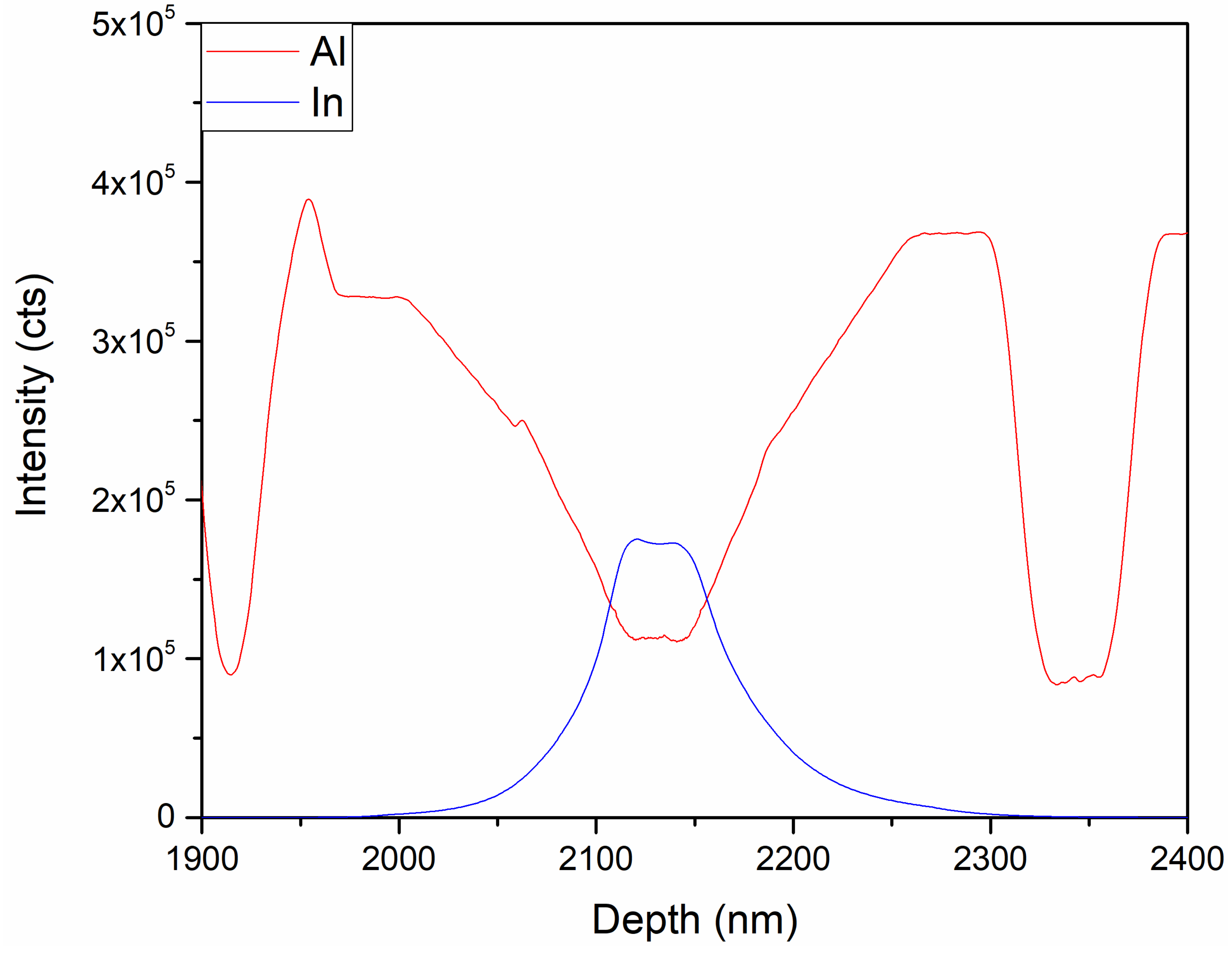
- Difficult sample for SIMS

Standard SIMS procedure



Remarks

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



Solution

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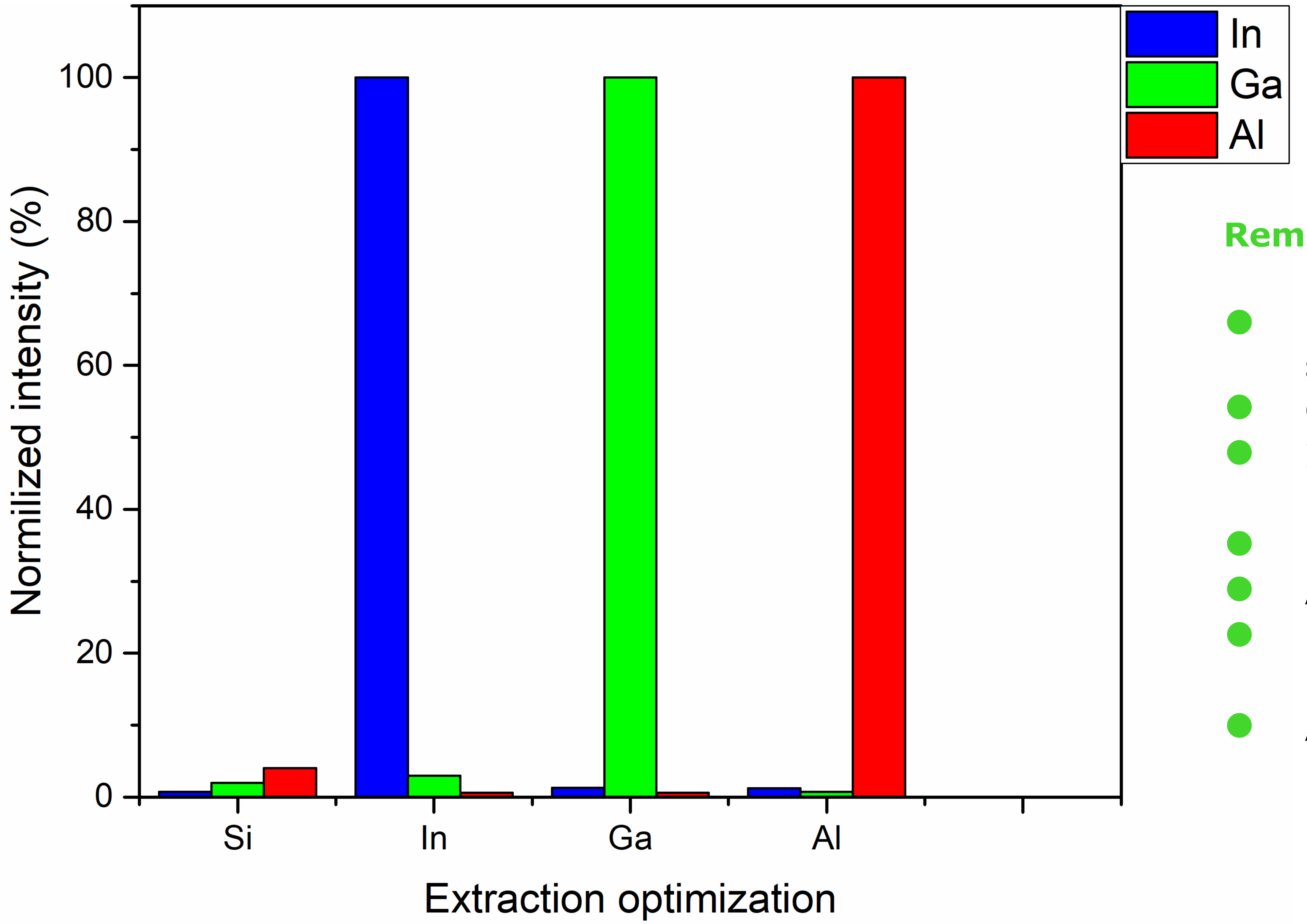
Optimization

- 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



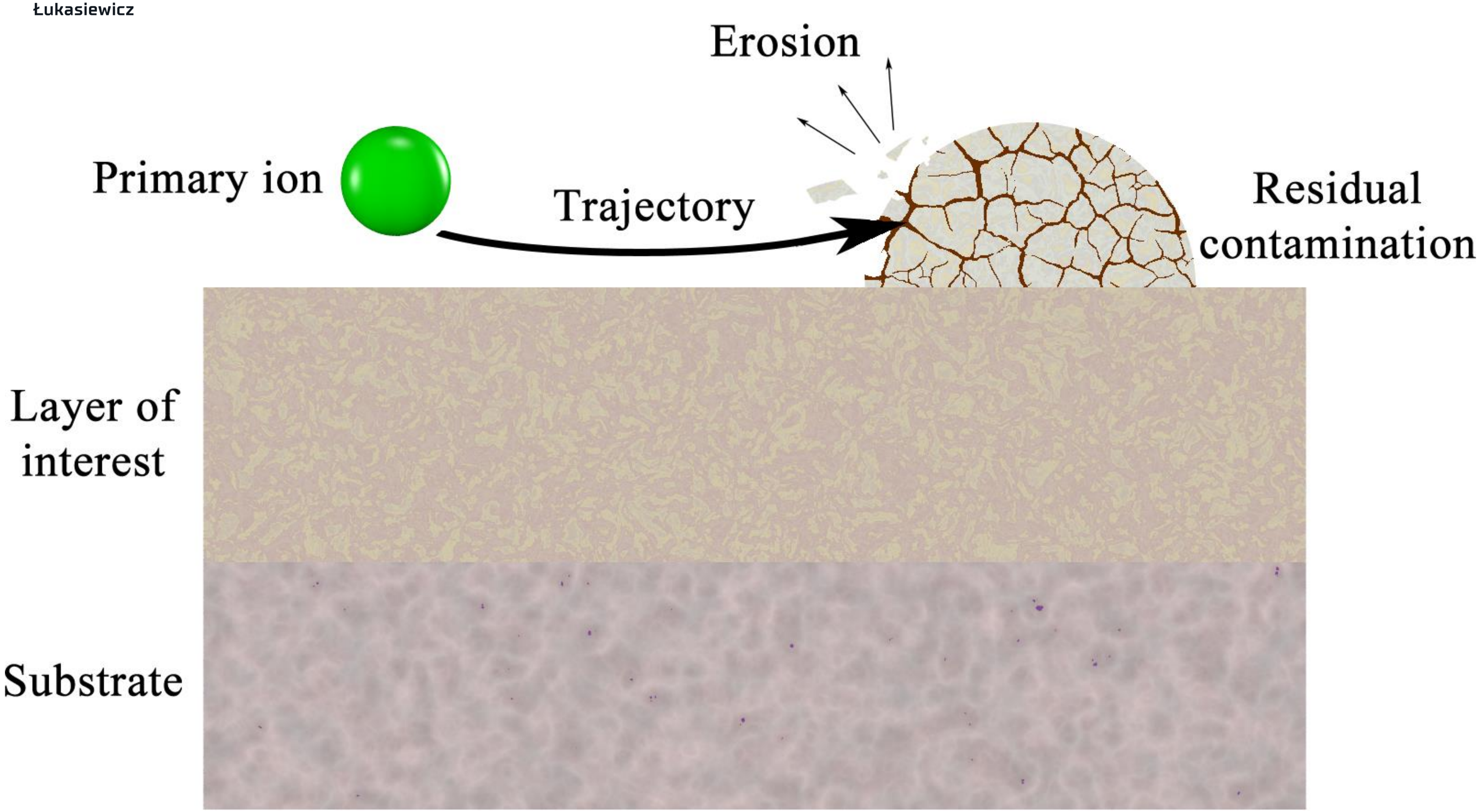
Remarks

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

- Energy
- Angle
- Polarity

- Additional steps

Ion polishing

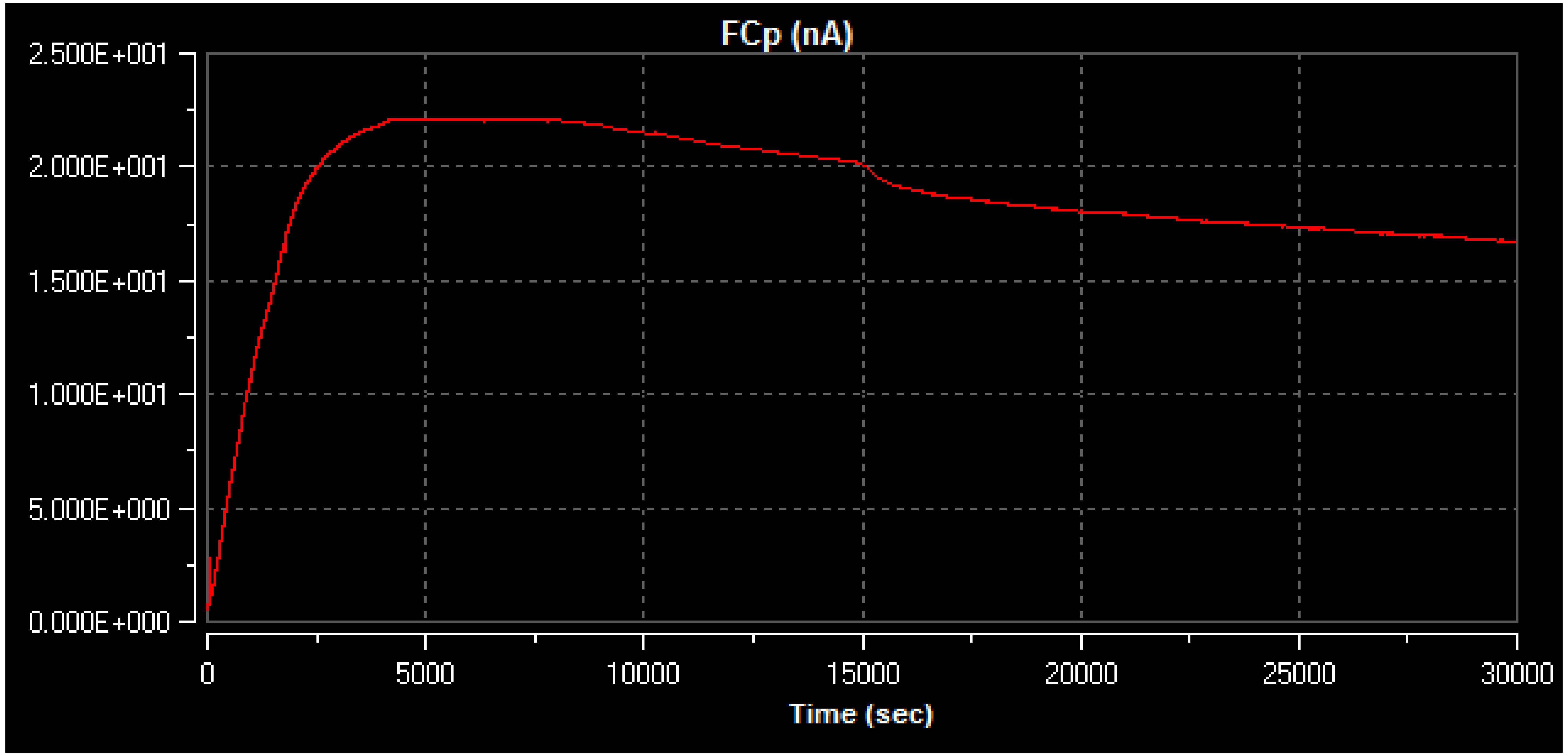


Idea

- 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

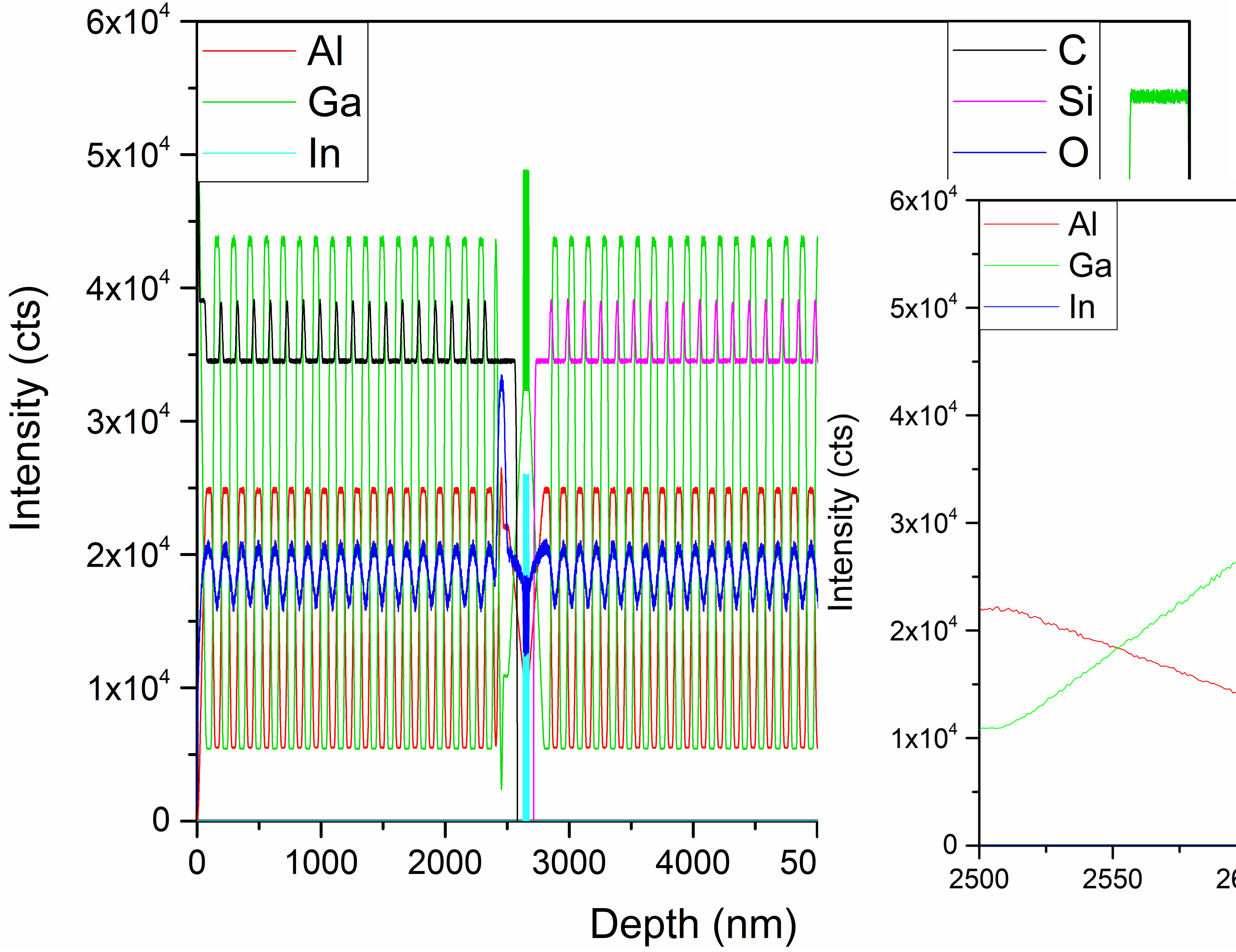
Primary beam service

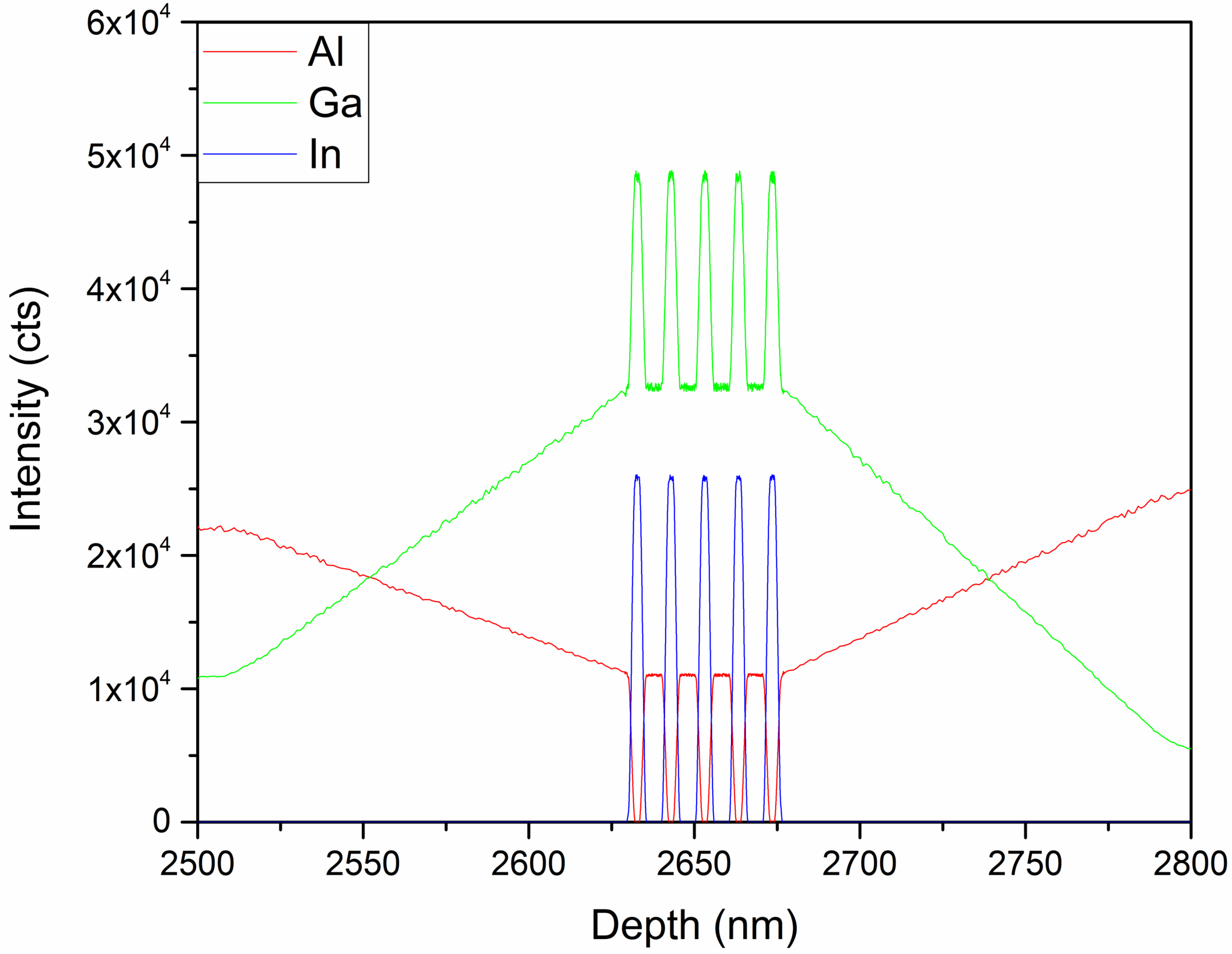


Idea

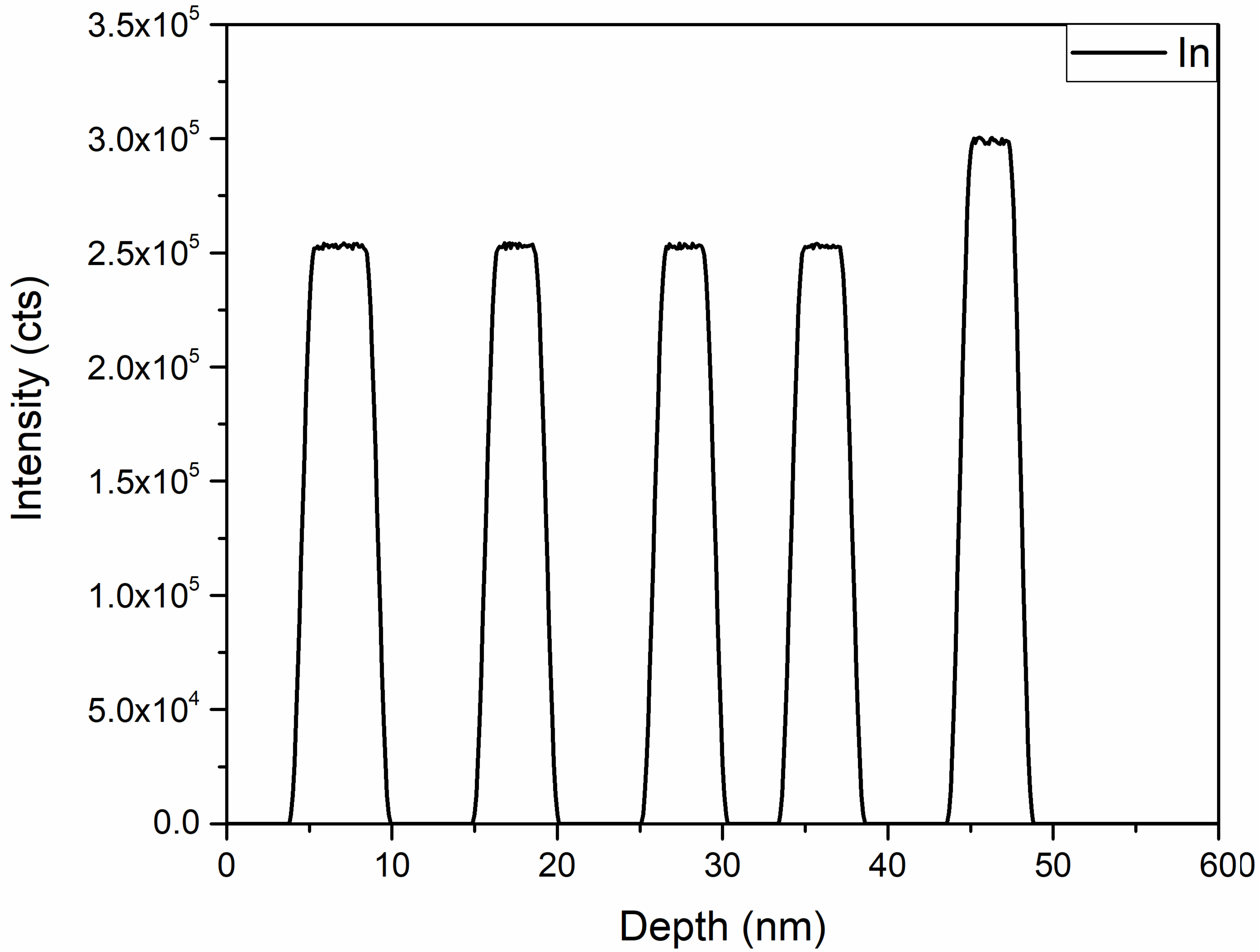
- Safe value (15 nA)
- Every 0.5 – 1 hour
- Fully automated

Final result

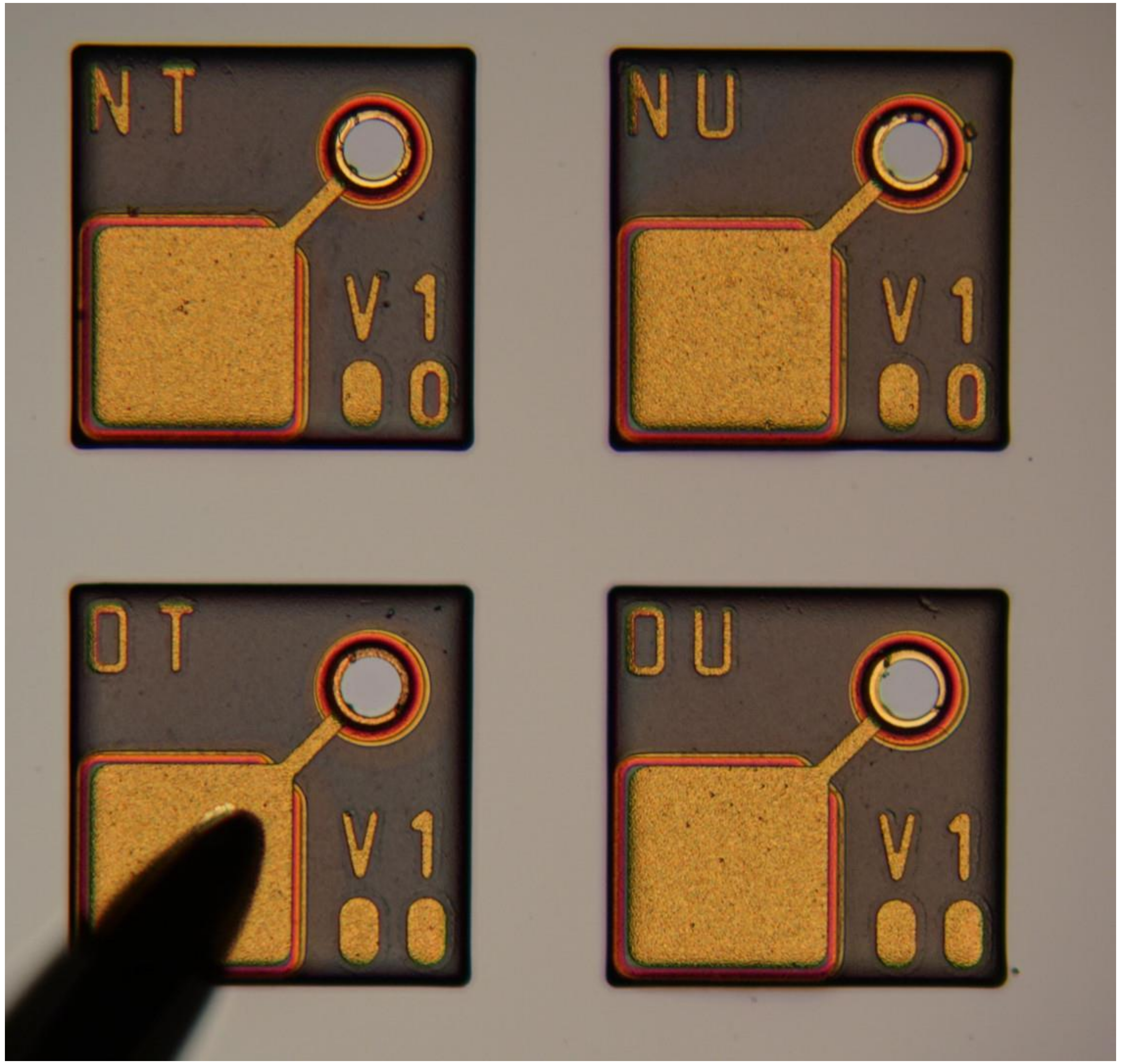


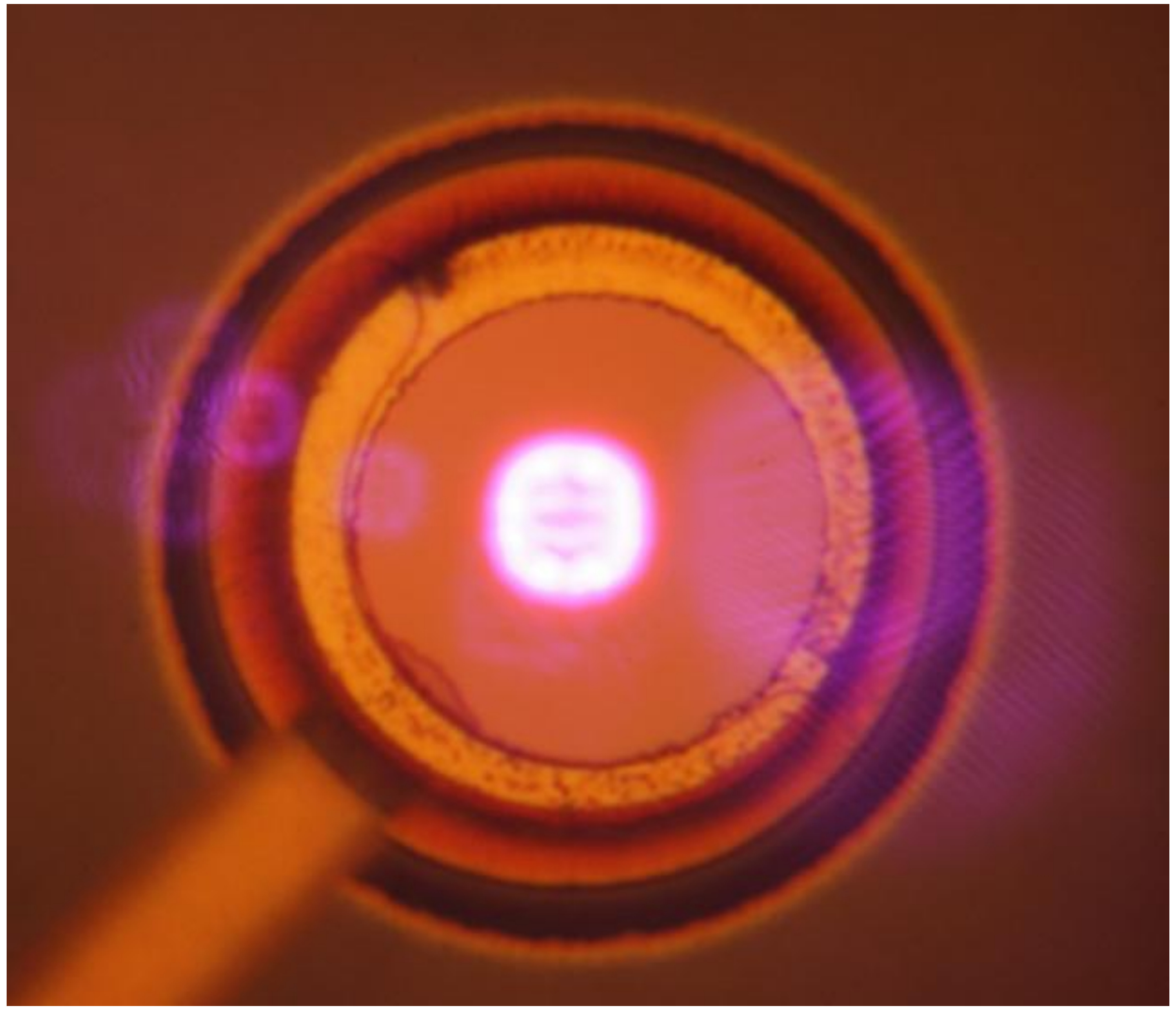


Impact energy modulataion – is it important?

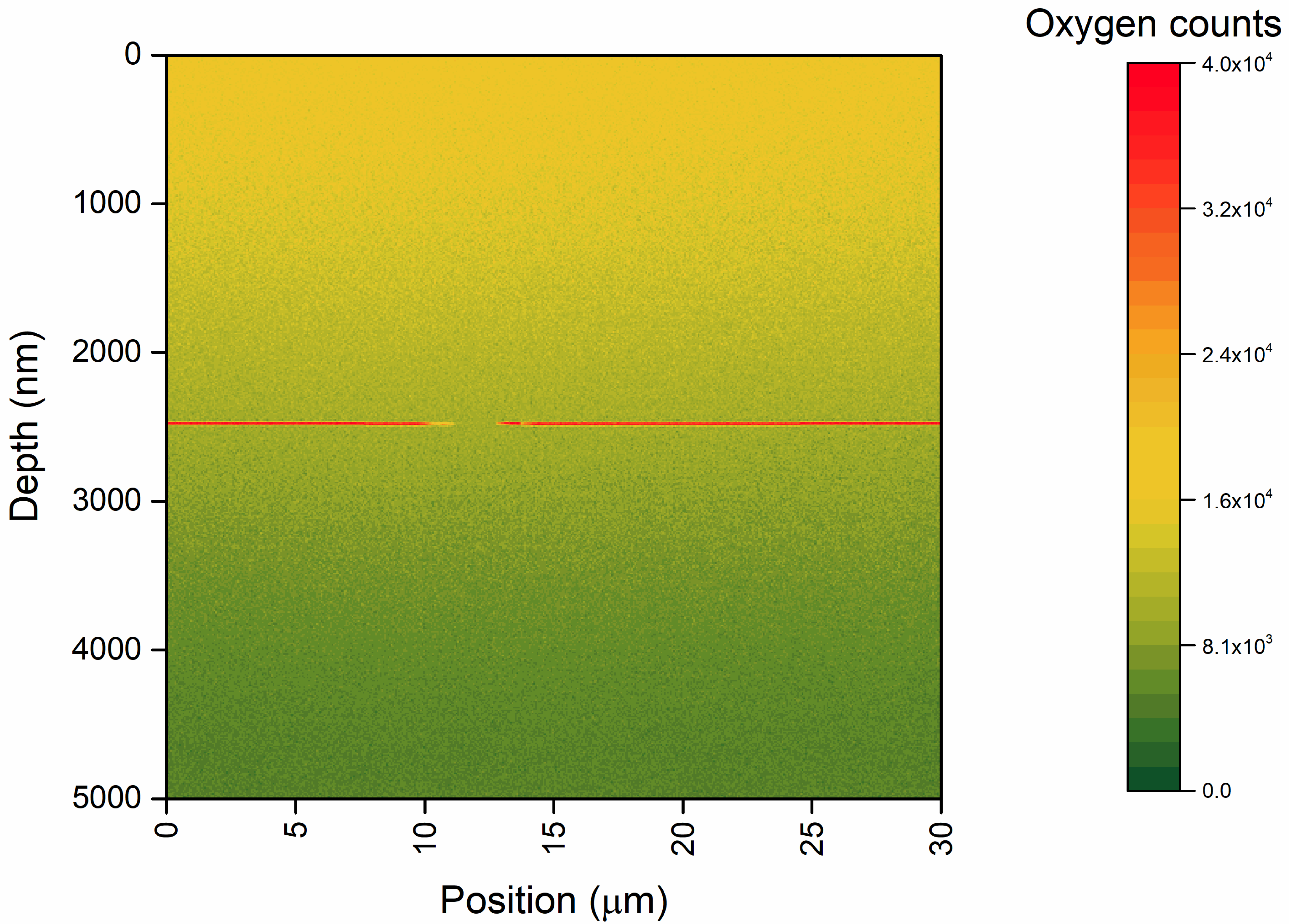


Aperture



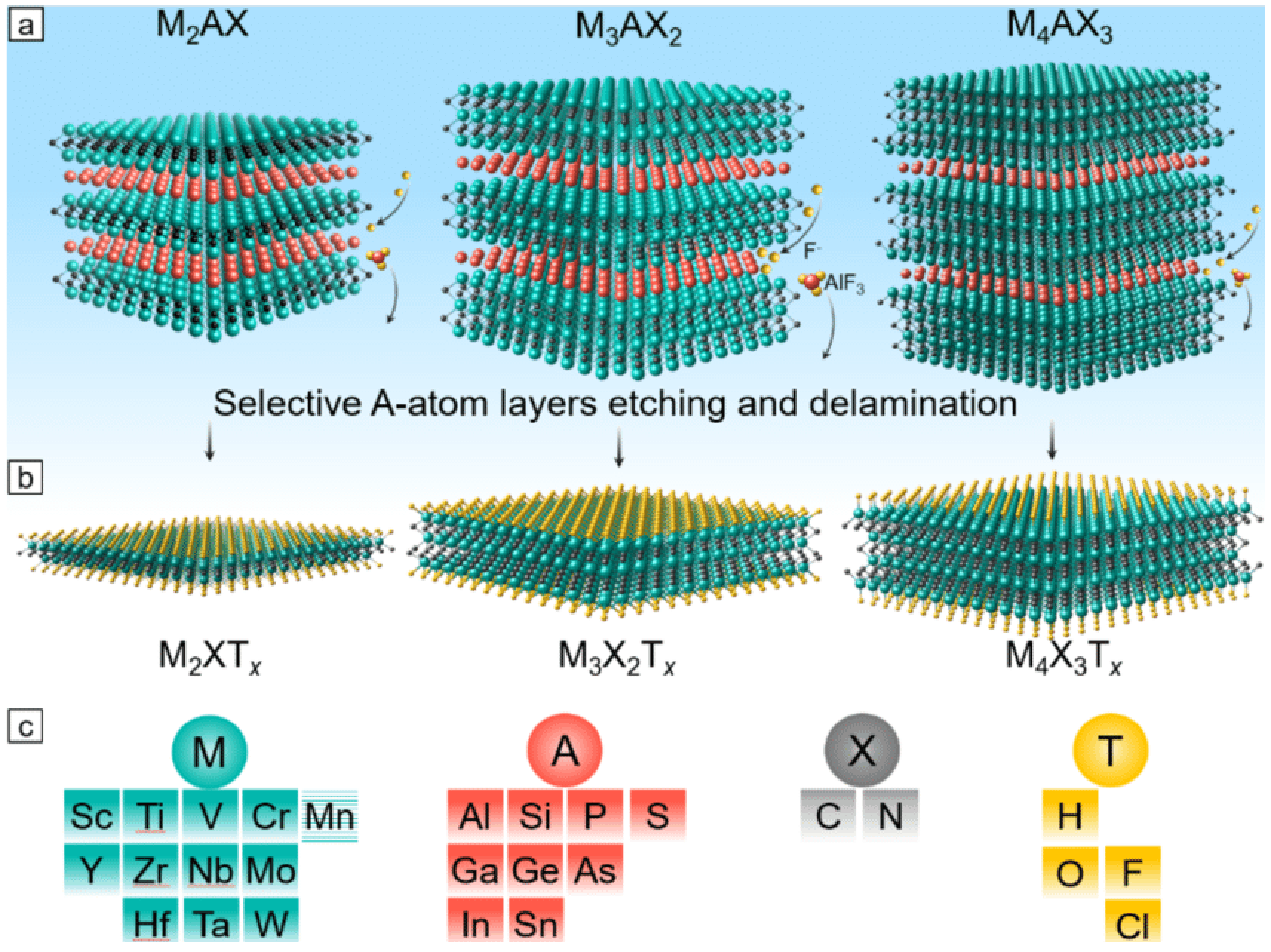


Aperture


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

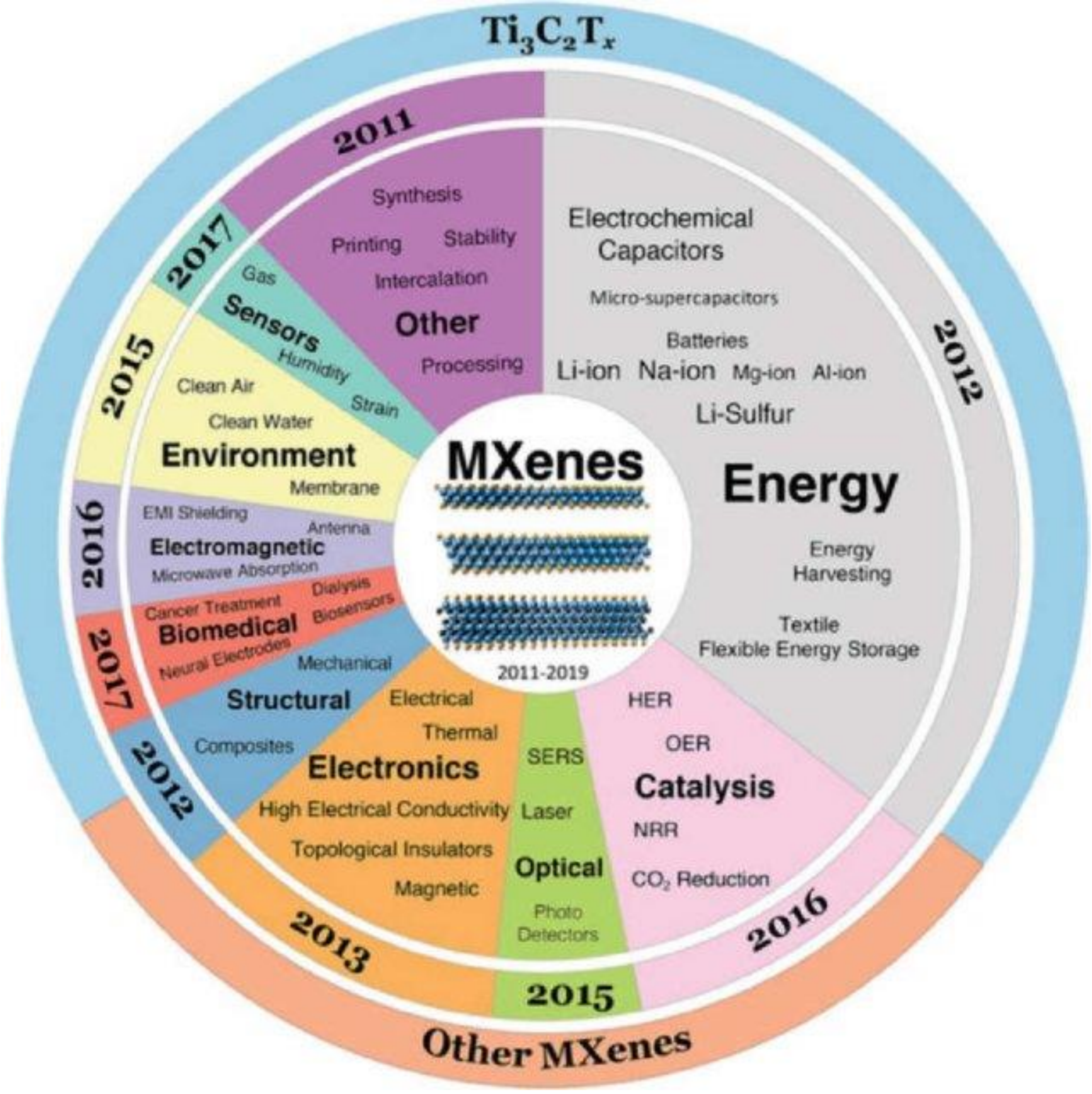
MAX / MXene samples

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



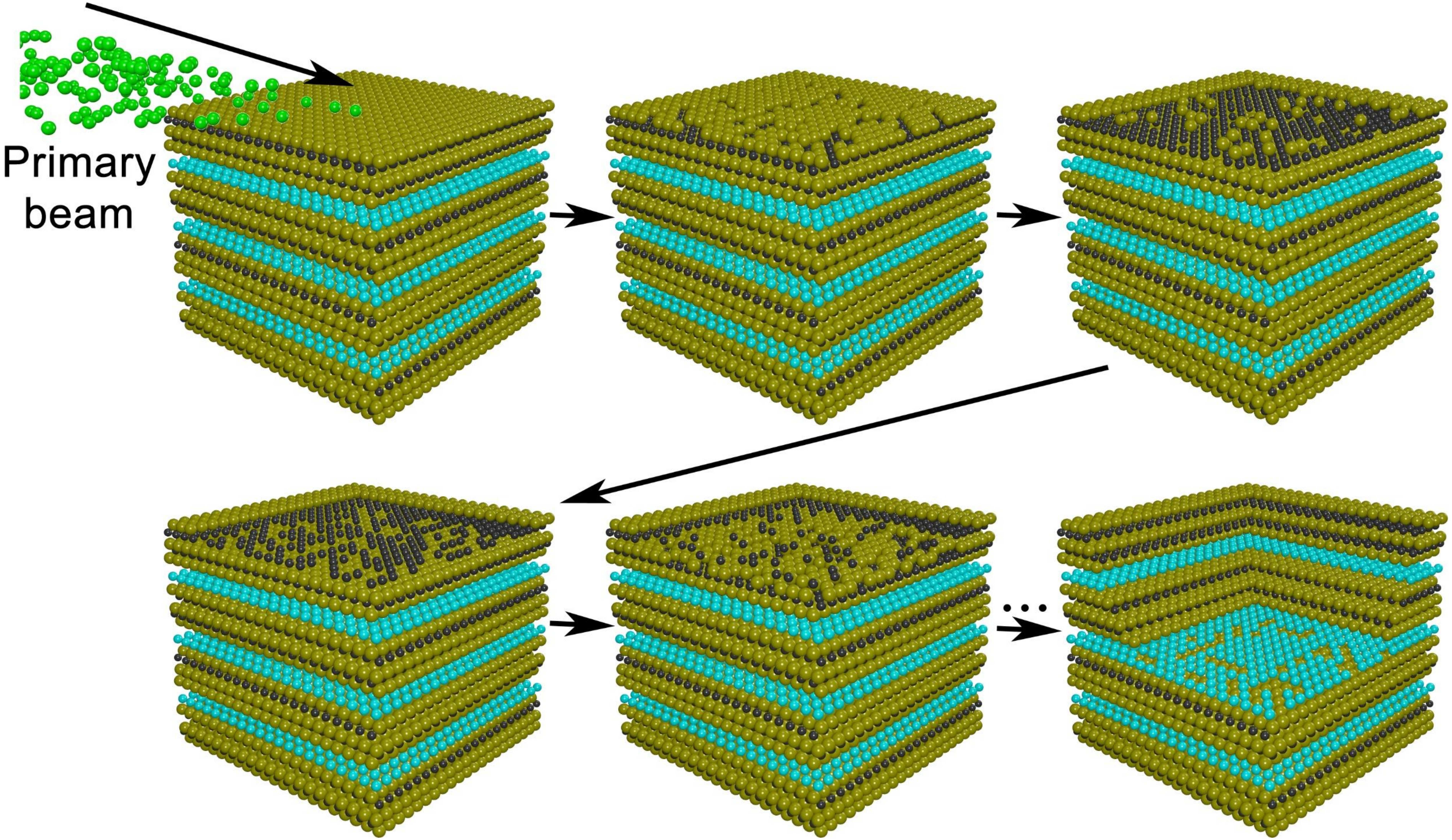
Hong, W. *et al.* *MRS Bulletin* **45,** 850–861 (2020).

Prof. Yury Gogotsi



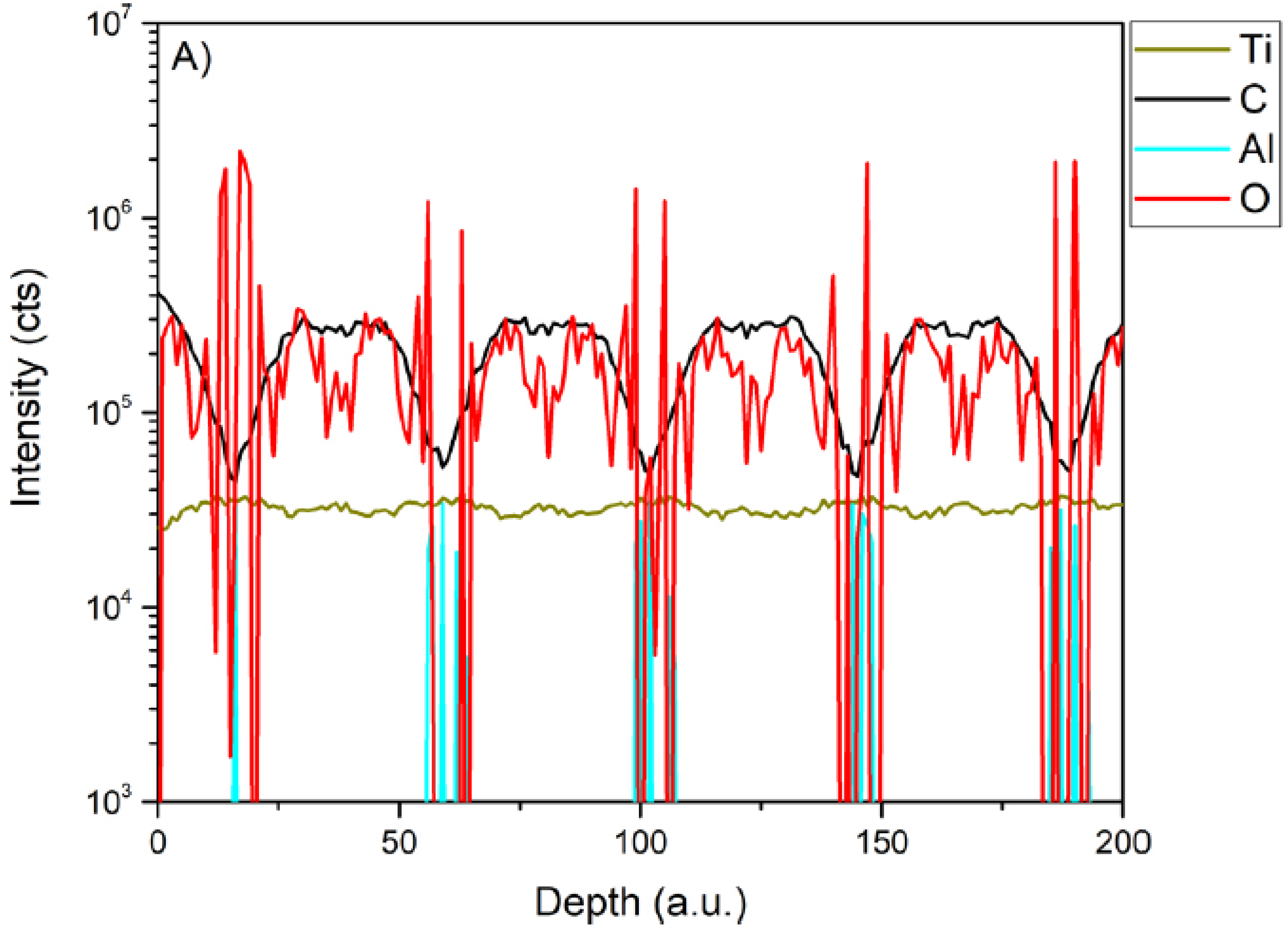
https://nano.materials.drexel.edu/research/synthesis-of-nanomaterials/mxenes/

How to make such measurements?



Supercycle

Standard cycle



Standard cycle

1. C – 2 s
2. O – 2 s
3. Al – 2 s
4. Ti – 2 s

Total: 8 s

Supercycle

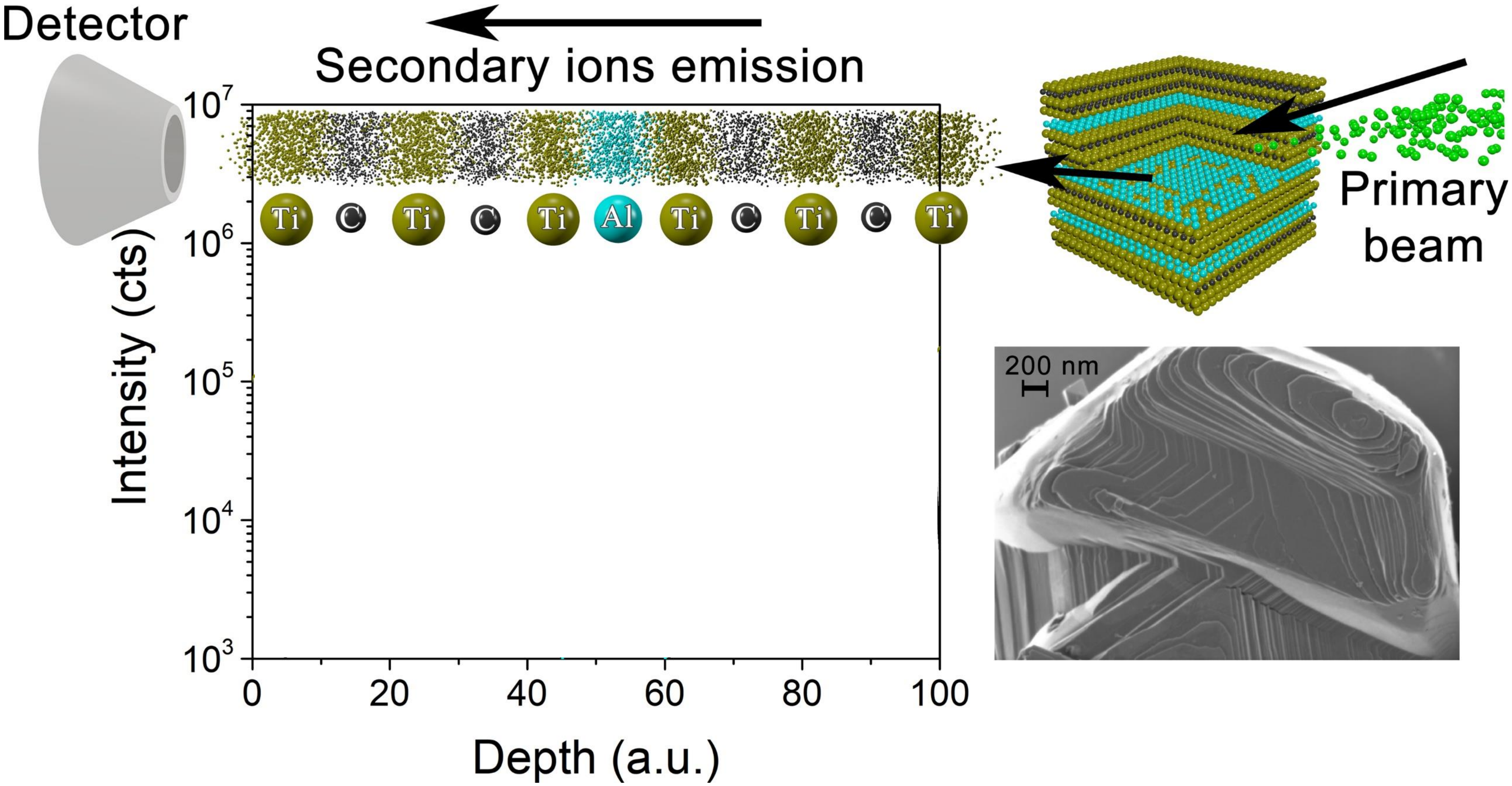
1. O – 0.4 s
2. C – 0.4 s
3. Al – 0.4 s
4. O – 0.4 s
5. Ti – 0.4 s
6. Al – 0.4 s

x5

Total: 12 s

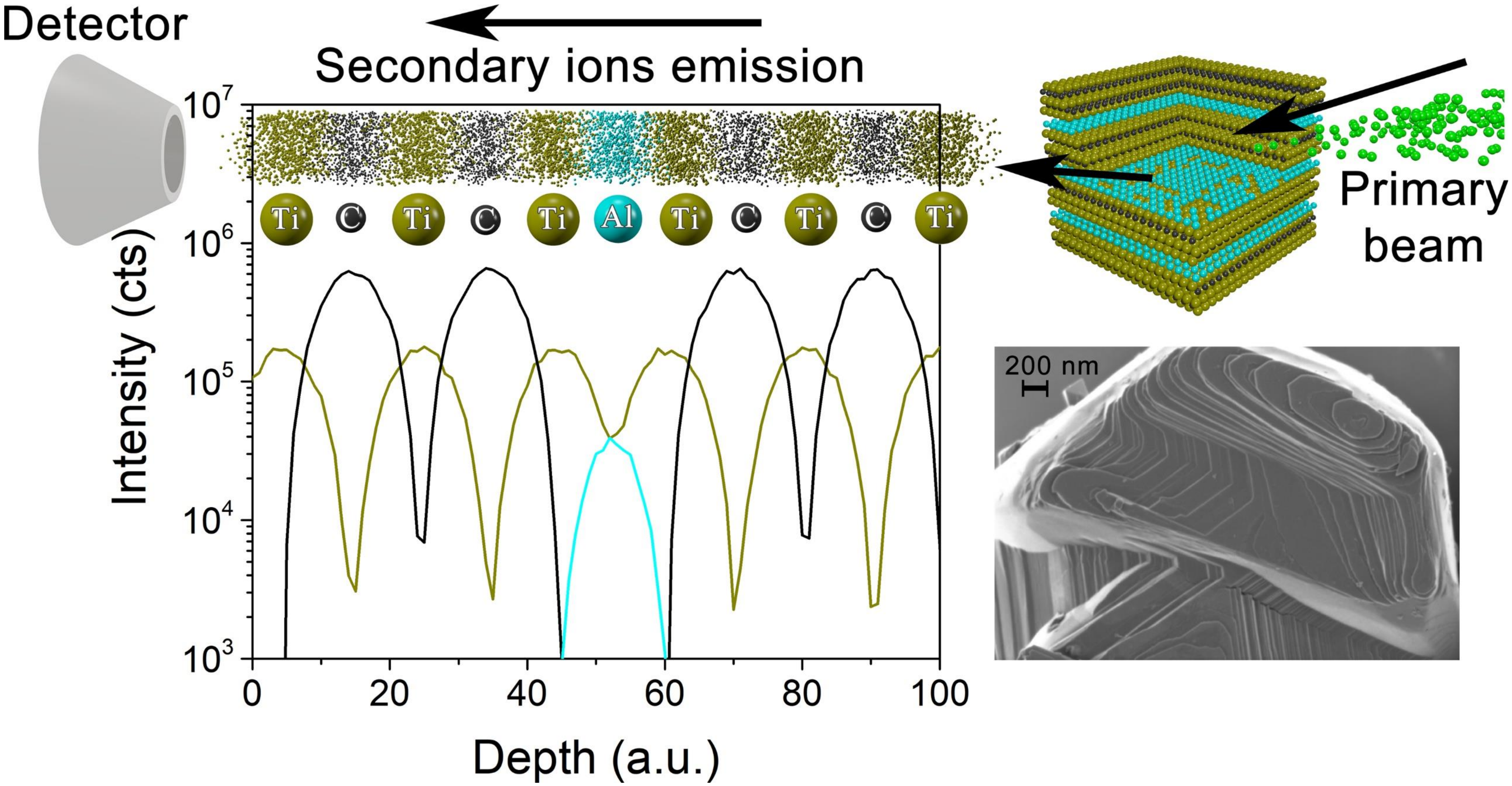
+ Beam positioning

A depth profile of Ti_3AlC_2 MAX phase

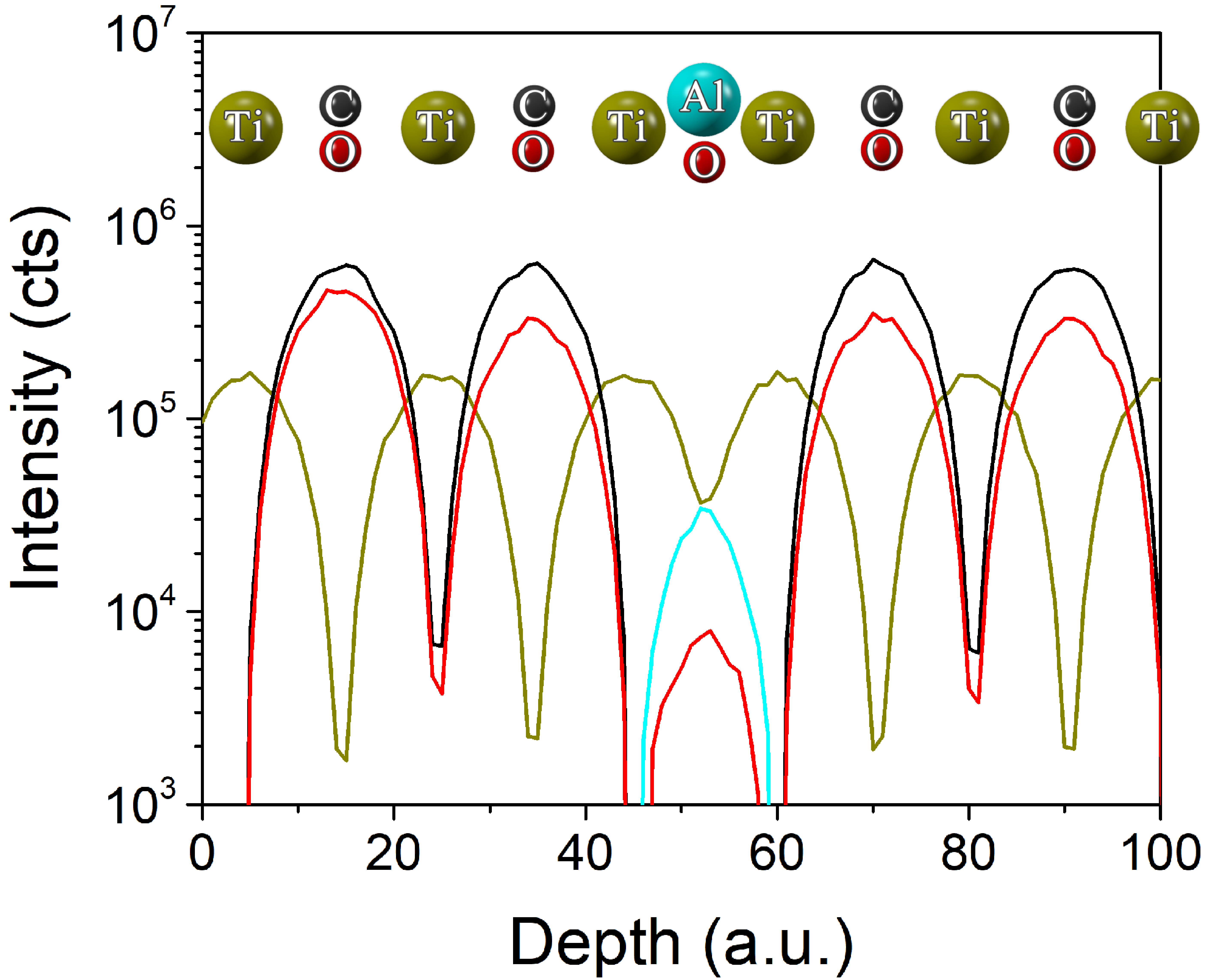


Łukasiewicz
IMiF

A depth profile of Ti_3AlC_2 MAX phase



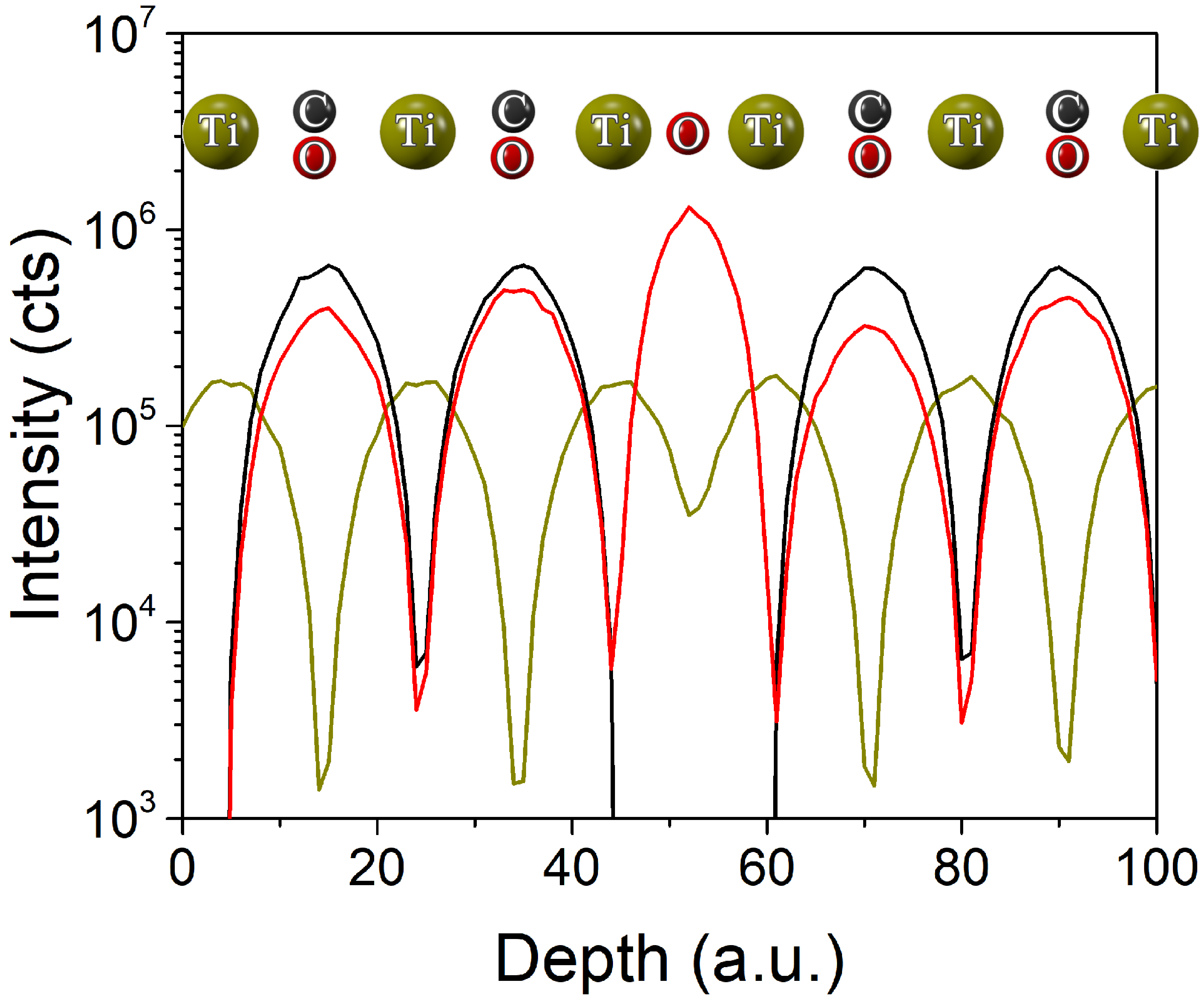
Carbides? Or oxycarbides?



Standard Ti_3AlC_2 MAX sample

- ~10-30% of oxygen in C site
- Residual oxygen in Al site

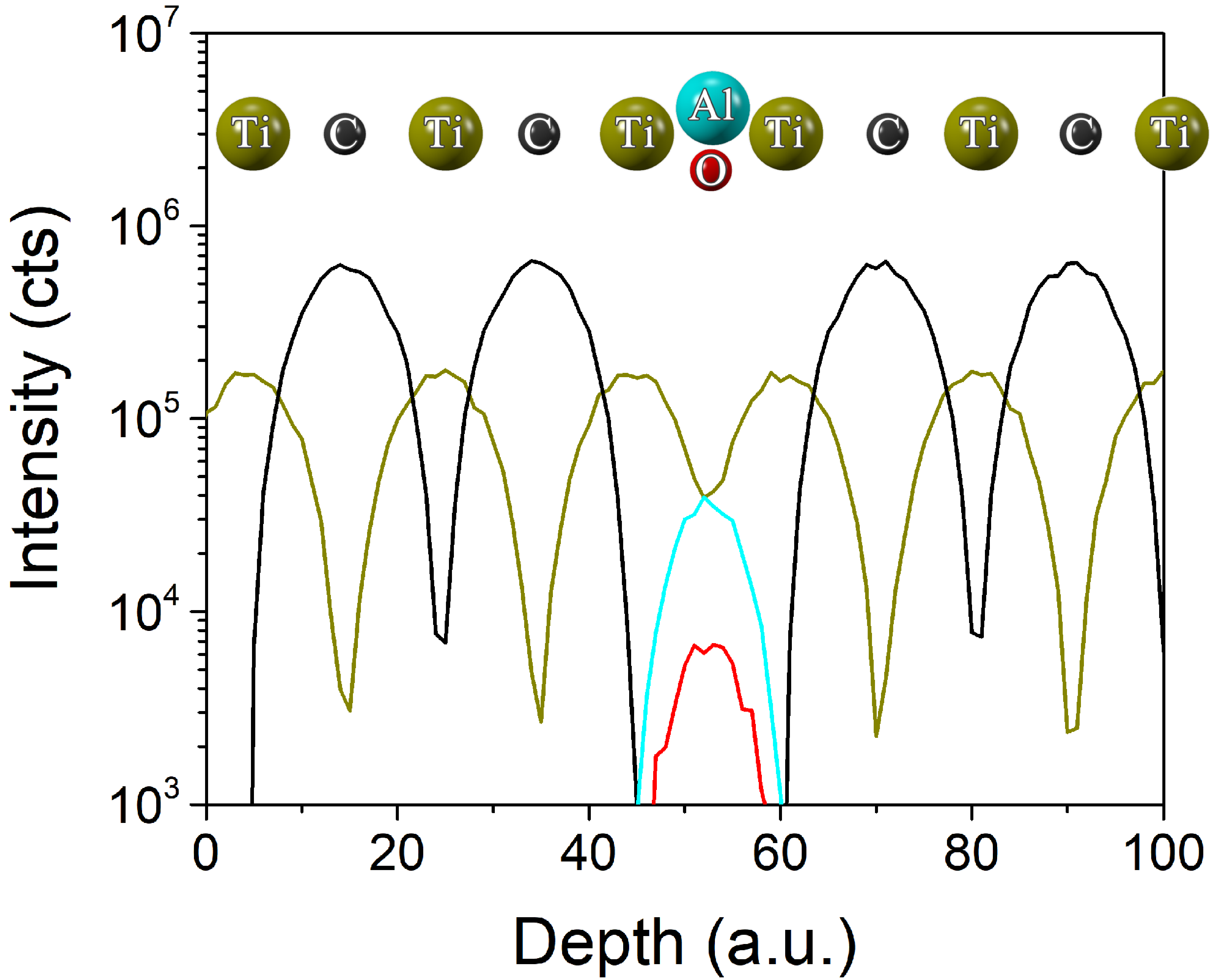
Carbides? Or oxycarbides?



Standard Ti_3C_2 MXene sample

- ~10-30% of oxygen in C site
- Oxygen in termination layers

Carbides? Or oxycarbides?

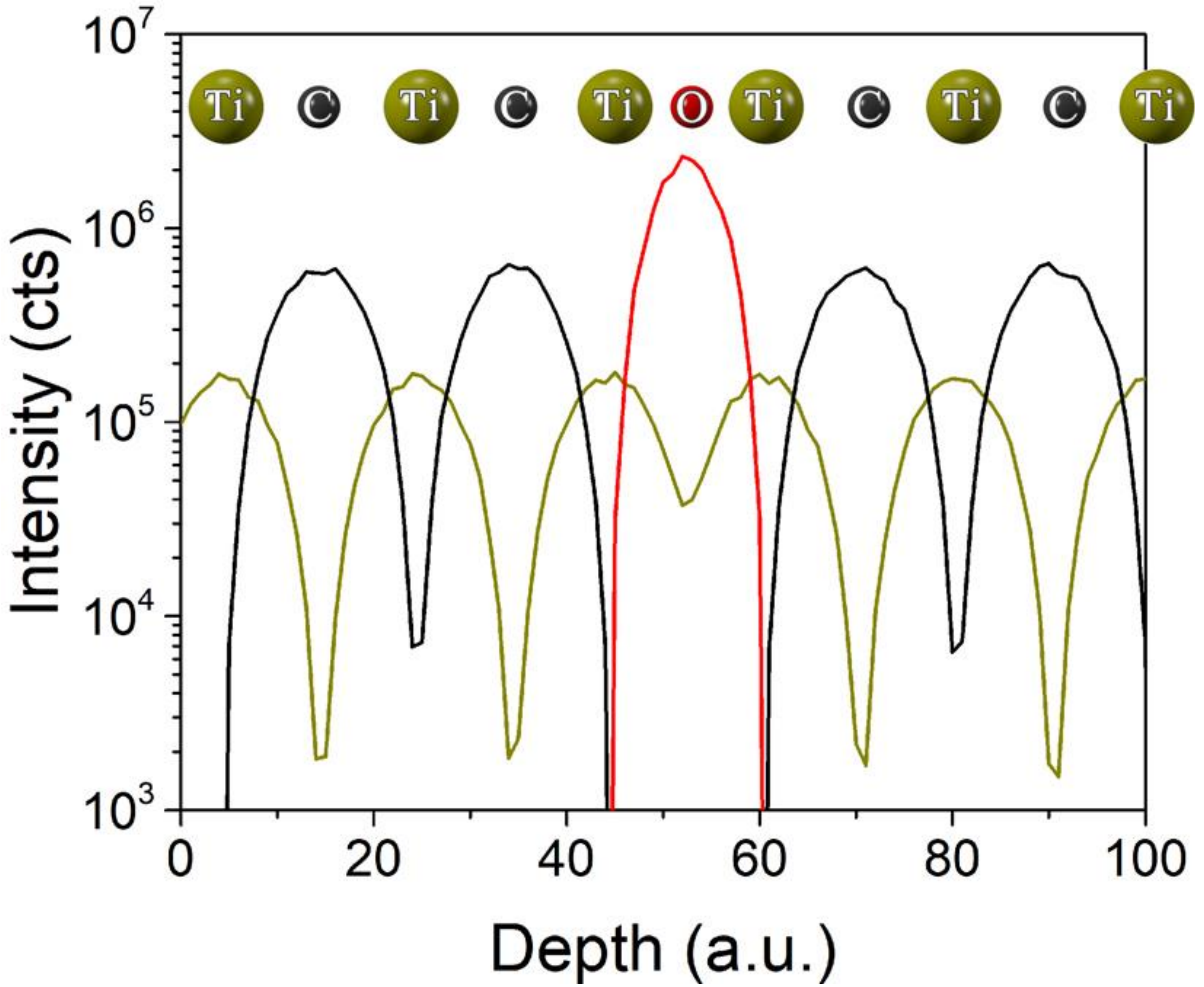


Modified Ti_3AlC_2 MAX sample

Mathis et al.
ACS Nano 2021, 15, 4, 6420–6429
DOI 10.1021/acsnano.0c08357

- No oxygen in C site
- Residual oxygen in Al site

Carbides? Or oxycarbides?

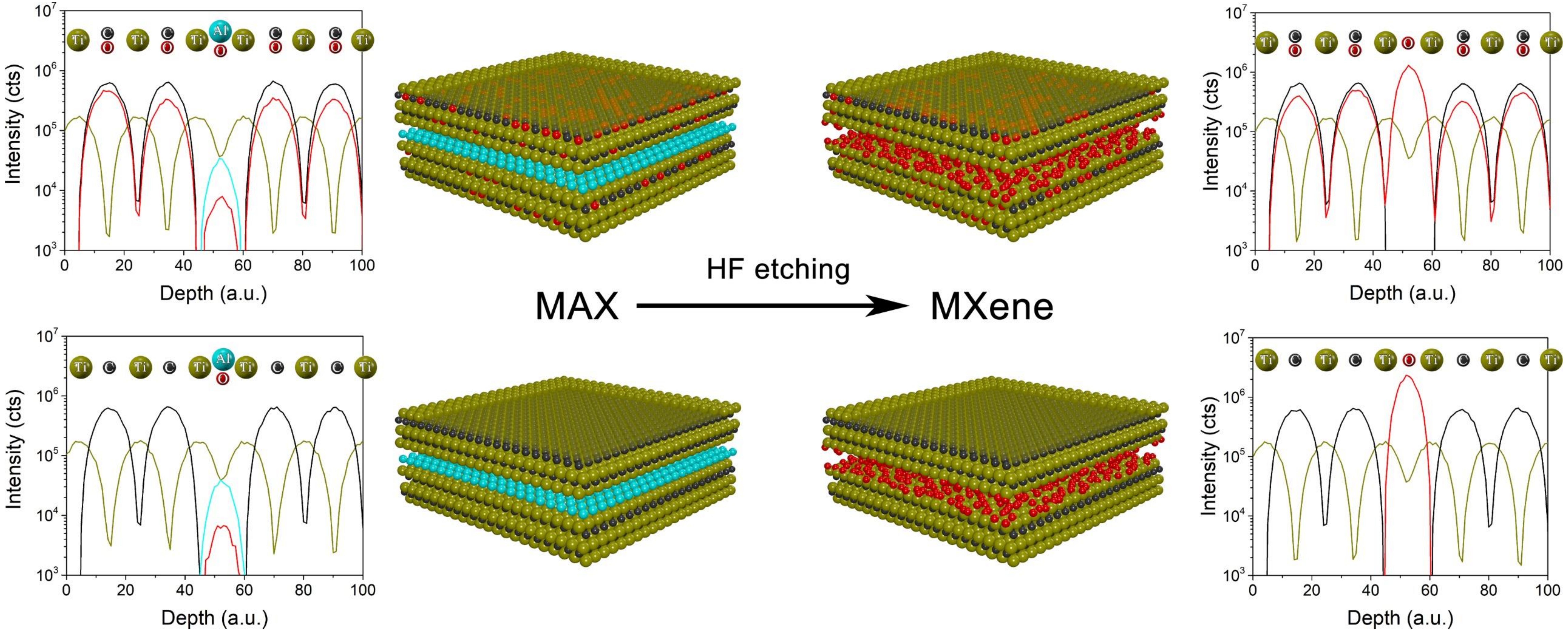


Modified Ti_3C_2 MXene sample

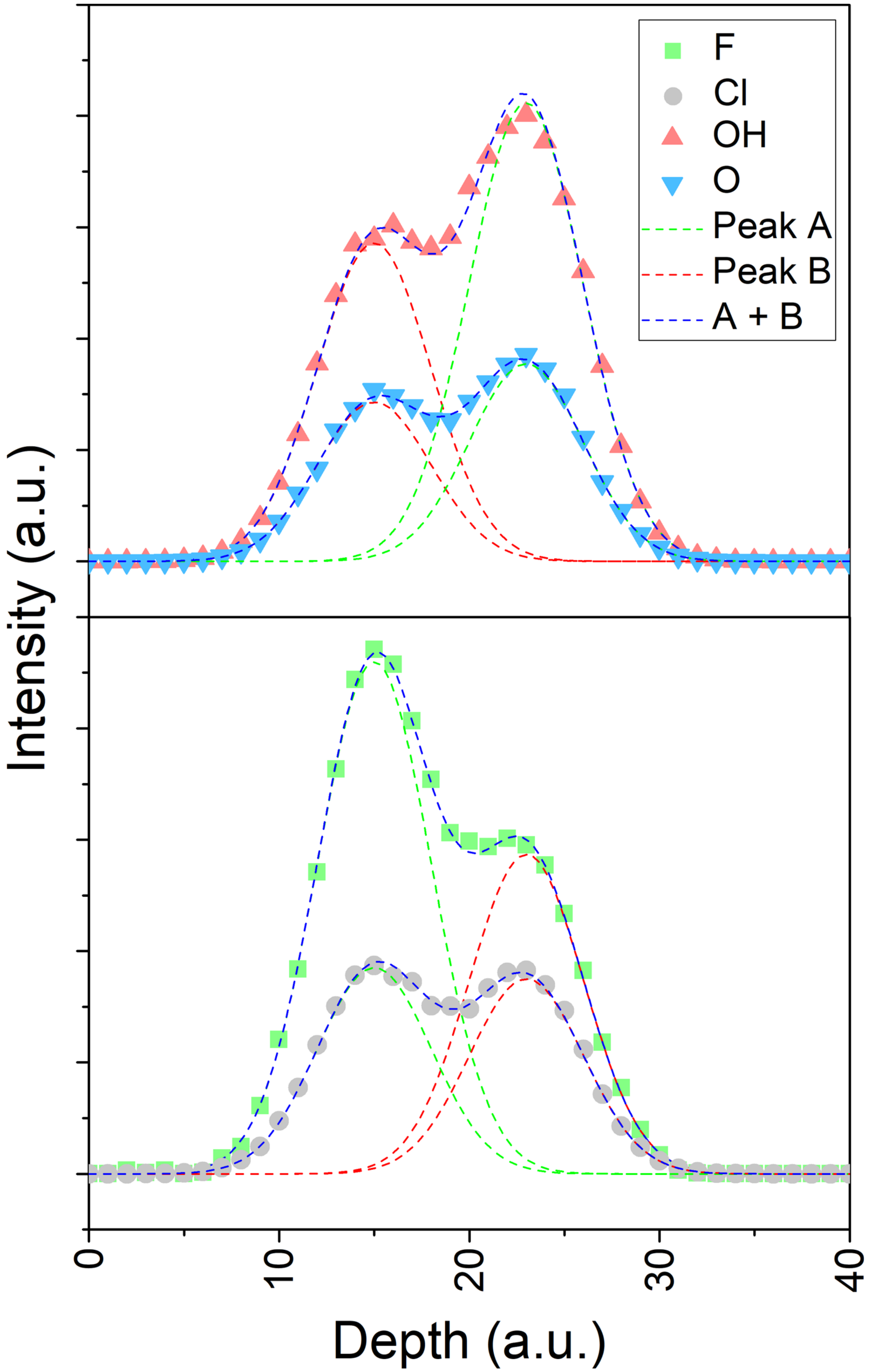
Mathis et al.
ACS Nano 2021, 15, 4, 6420–6429
DOI 10.1021/acsnano.0c08357

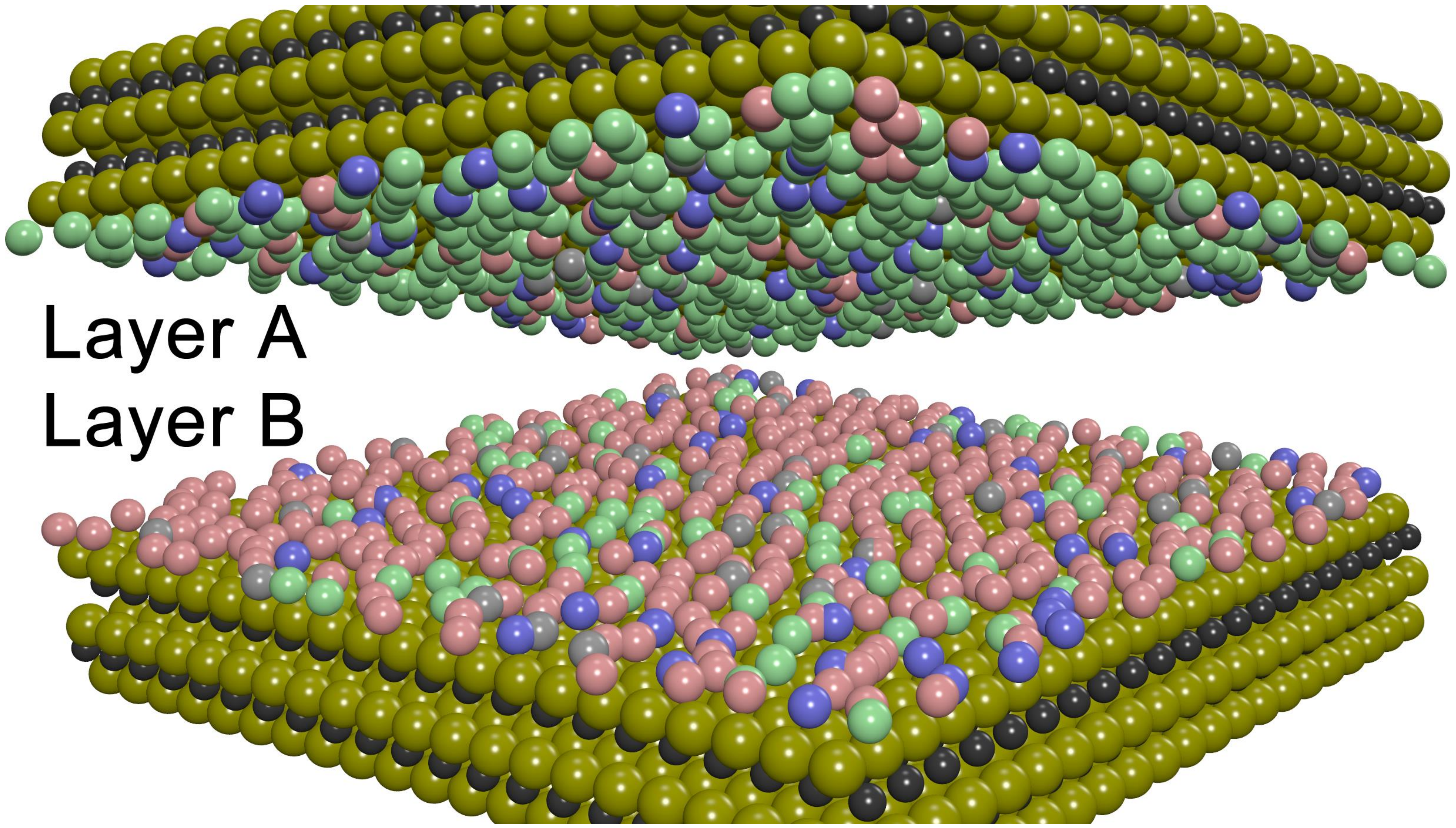
- No oxygen in C site
- Oxygen in termination layers

Carbides? Or oxycarbides? Summary

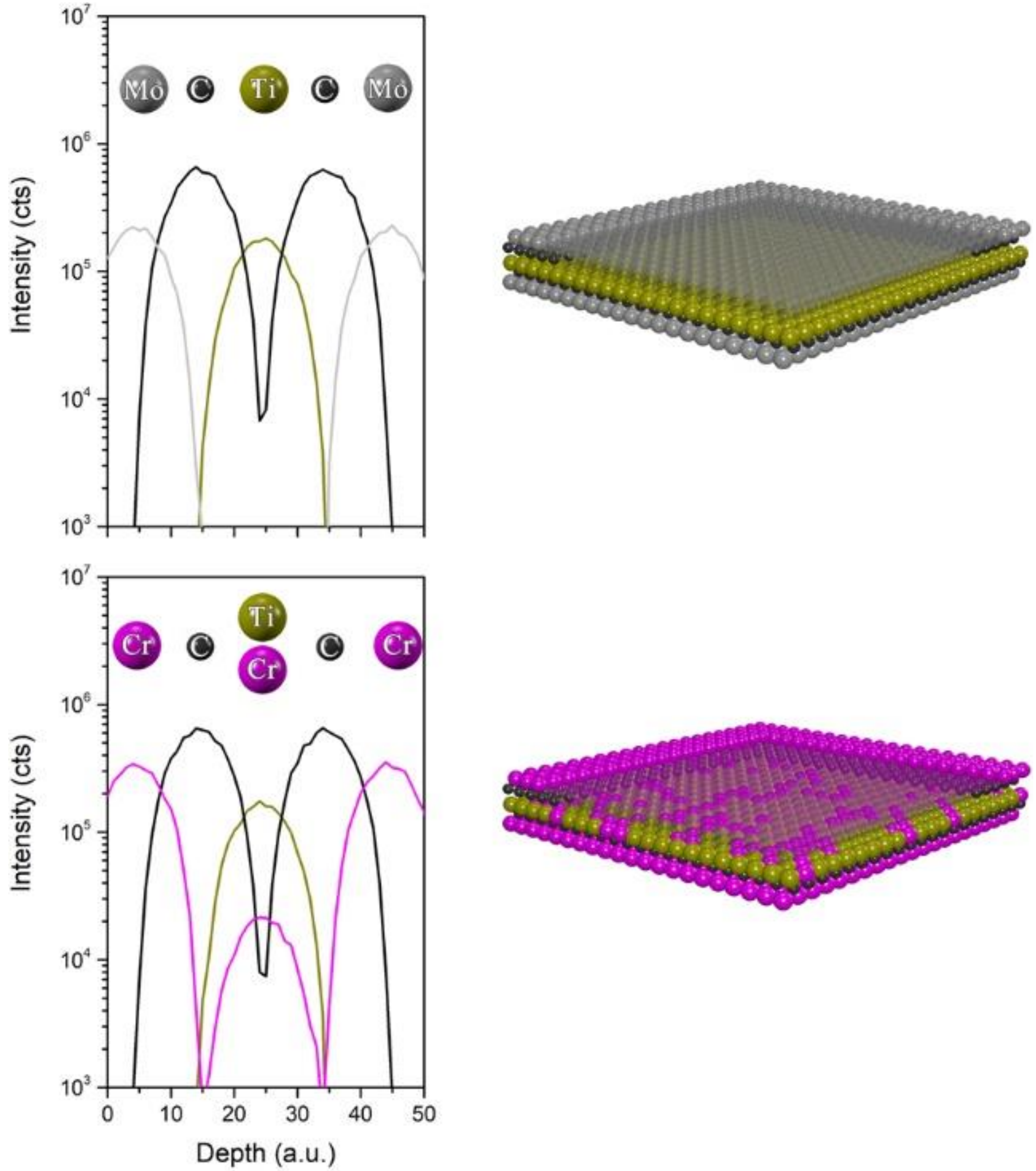


Termination layers



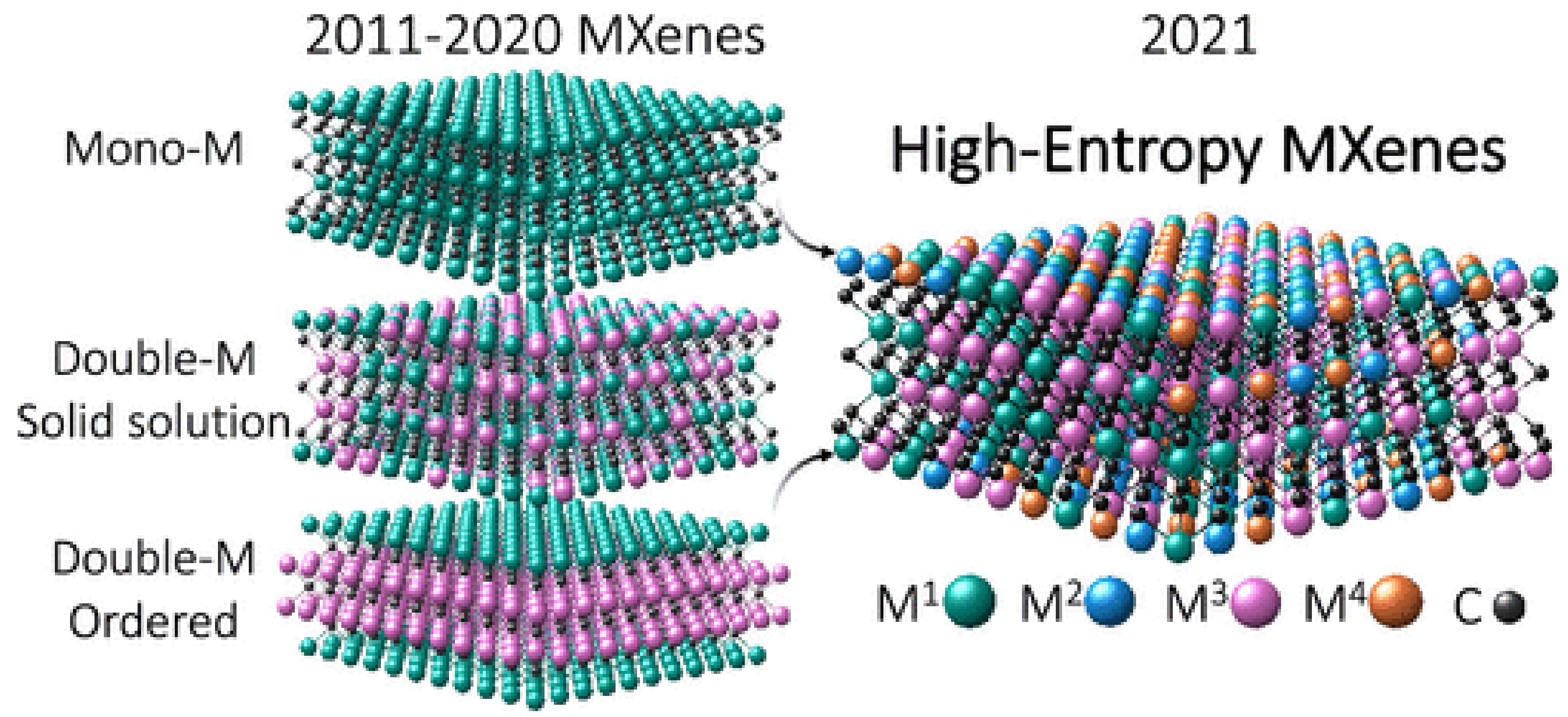


Out-of-plane ordered MAX and MXenes



Mo_2TiC_2 vs Cr_2TiC_2

- Perfect separation for Mo_2TiC_2
- Solid solution for Cr_2TiC_2
- Silmuations required!



Nemani et al.
ACS Nano 2021, 15, 8, 12815–12825

Contents

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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!)