Haute résolution en basse tension, pression variable, EDS, WDS, EBSD et TKD - Présentation du système avec des exemples

Andrea Campos

CP2M

Centre Pluridisciplinaire
de Microscopie électronique
et de Microanalyse

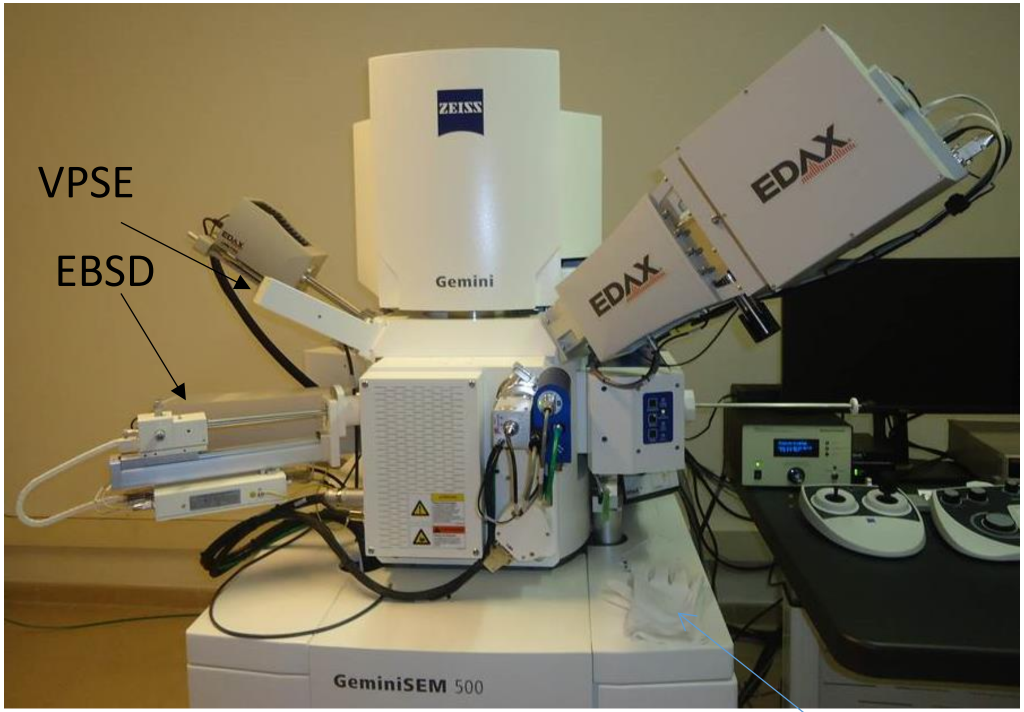
* Aix-Marseille University-CNRS

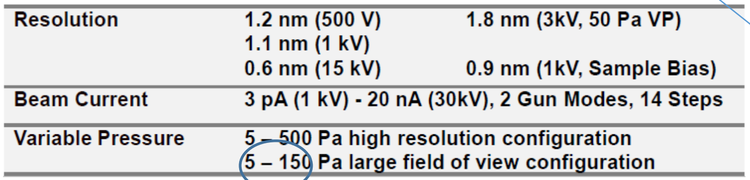
Sommaire

Maintenant Gemini 560
Resolution : 0.5 nm @ 15 kV
0.8 nm @ 1 kV

Février 2015

MEB ZEISS Gemini 500 20 nA

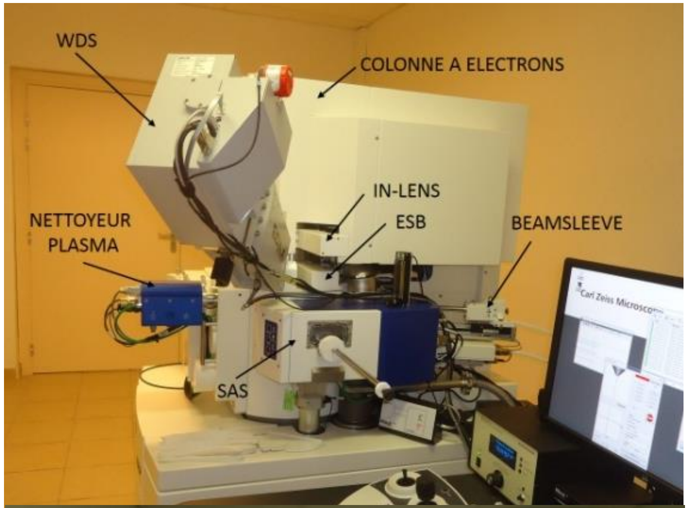




Resolution	1.2 nm (500 V) 1.1 nm (1 kV) 0.6 nm (15 kV)	1.8 nm (3kV, 50 Pa VP) 0.9 nm (1kV, Sample Bias)
Beam Current	3 pA (1 kV) - 20 nA (30kV), 2 Gun Modes, 14 Steps	
Variable Pressure	5 – 500 Pa high resolution configuration 5 – 150 Pa large field of view configuration	

1.8 nm à 30 Pa et 3 kV

Notre configuration



EBSD – EDAX HIKARI SUPER

Mais comment on peut définir la résolution?

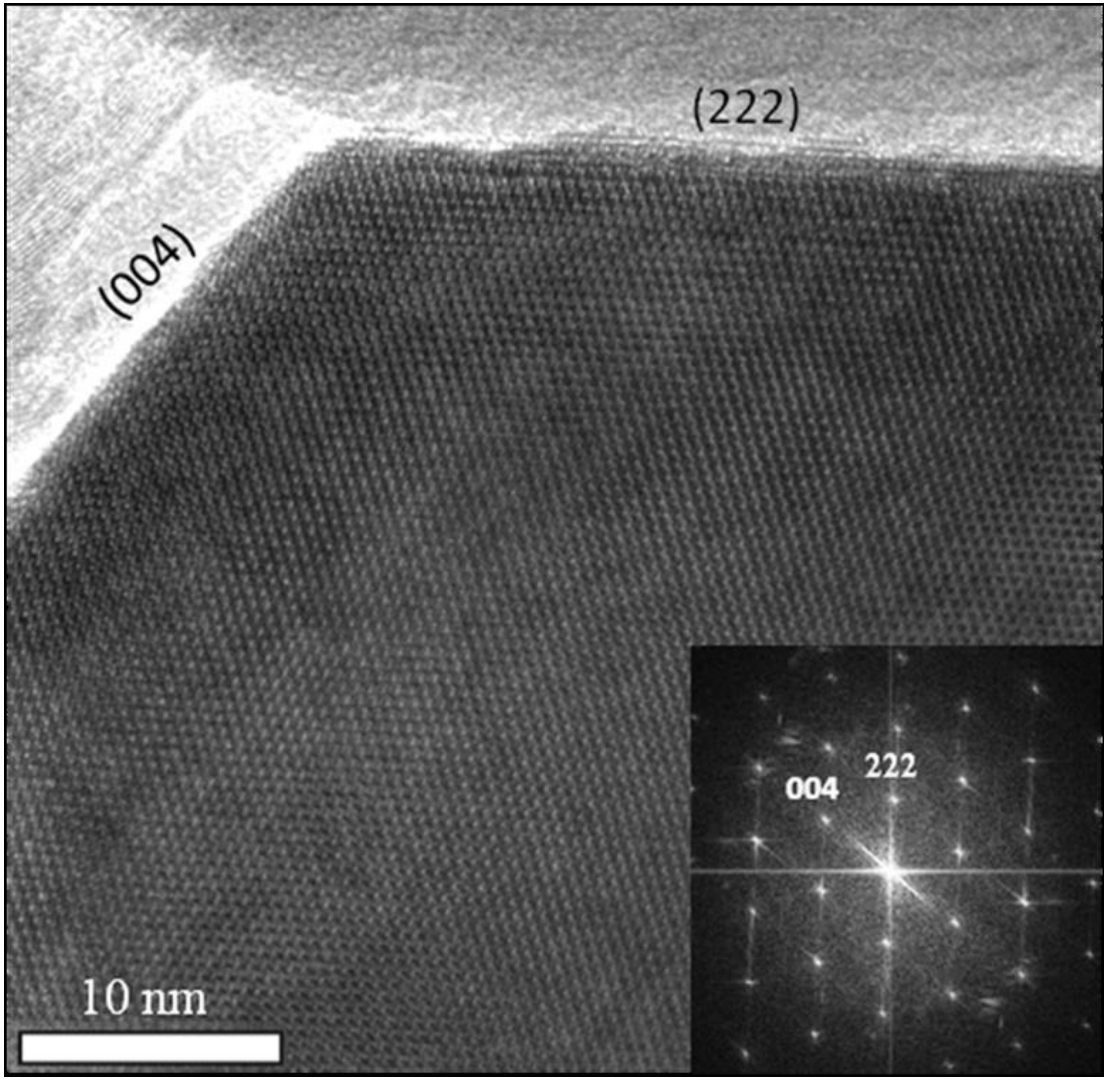
ISO 22493:2008(fr)
Analyse par microfaisceaux — Microscopie électronique à balayage — Vocabulaire

7.2
résolution d'image
écartement minimal auquel deux détails de l'image peuvent être reconnus comme distincts et séparés

Résolution = capacité de distinguer deux objets proches mais distincts

Mais comment on peut mésurer la résolution?

En TEM: image de contraste de phase – échelle atomique – physique des interférences



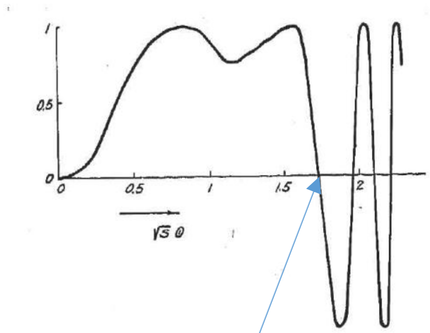


FIG. 4. The function $\sin(3s\Theta^2 - s^2\Theta^4)$, describing the phase shift in case of optimum contrast.

VOLUME 20, JANUARY, 1949

Phase contrast transfer function at Scherzer focus

$$\Delta f_{Scherzer} = -1{,}2\sqrt{C_S \lambda}$$

$$u_{res}(Scherzer) = 0{,}6\lambda^{3/4} C_S^{1/4}$$

Mais comment on peut mésurer la résolution?

En SEM:

La résolution établie en calculant la en examinant le profil de ligne des changements d'intensité du signal à travers le bord (**edge**) d'une particule d'or

Each of these methods is subjective in nature. Determining what constitutes as the particle's edge will differ from person to person based on individual interpretation or how each person comes to observe the edge of a particle. When conducting the line profile technique, the distance for the signal transition is deemed to be related to probe diameter.

JEOL uses the conventional protocol and measures at the 84th and 16th percentile of the transition (1 sigma value). This is not true for all manufacturers and values of 75th/25th and 65th/35th percentile have been declared by other vendors. As illustrated in Table 1, this causes lower reported values of resolution even from the same edge profile in an image. Evidently, it is not easy to compare resolution specifications today between different manufacturers.

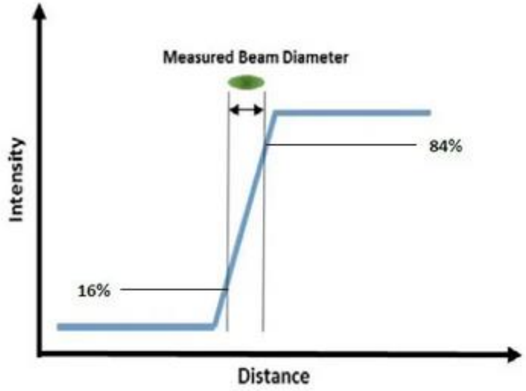
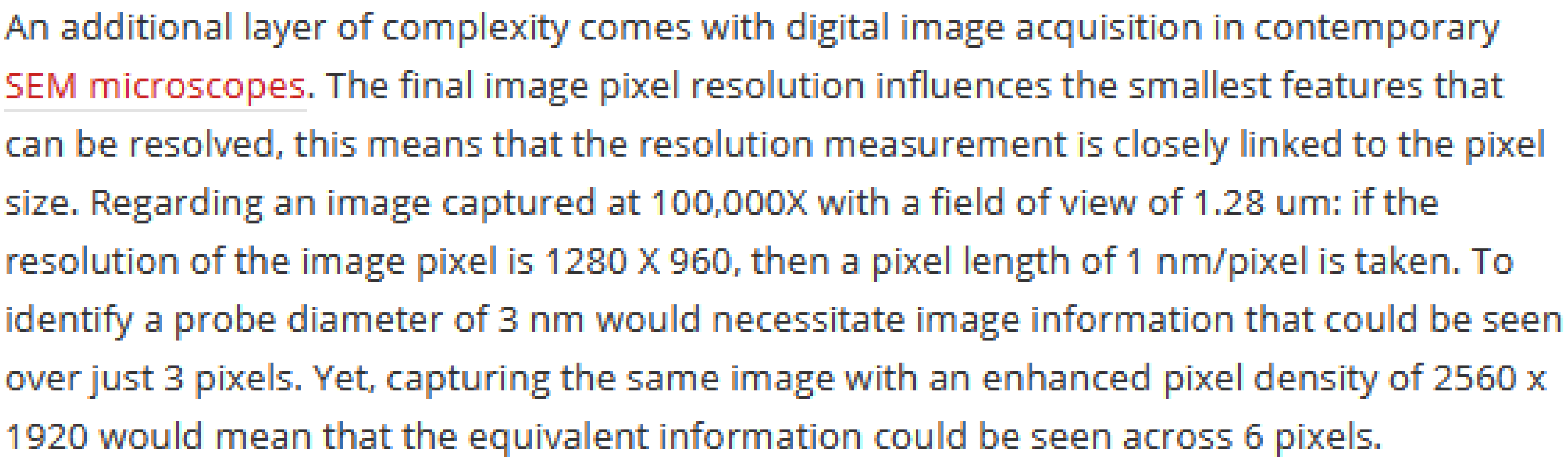


Figure 2. *Line Profile Method for SEM Resolution. Image Credit: JEOL USA, Inc.*

Table 1. Example showing the resolution determined from the same edge profile using three different percentiles to calculate the beam diameter. Source: JEOL USA, Inc.

	84%	75%	65%
Beam diameter (resolution)	1.4 nm	1.1 nm	0.6 nm

https://www.azom.com/article.aspx?ArticleID=19693



An additional layer of complexity comes with digital image acquisition in contemporary SEM microscopes. The final image pixel resolution influences the smallest features that can be resolved, this means that the resolution measurement is closely linked to the pixel size. Regarding an image captured at 100,000X with a field of view of 1.28 um: if the resolution of the image pixel is 1280 X 960, then a pixel length of 1 nm/pixel is taken. To identify a probe diameter of 3 nm would necessitate image information that could be seen over just 3 pixels. Yet, capturing the same image with an enhanced pixel density of 2560 x 1920 would mean that the equivalent information could be seen across 6 pixels.

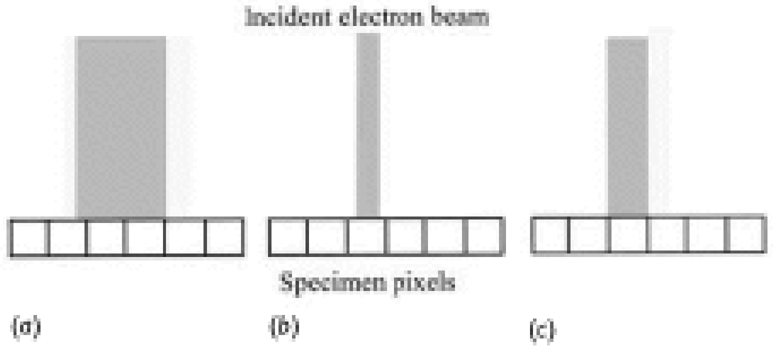
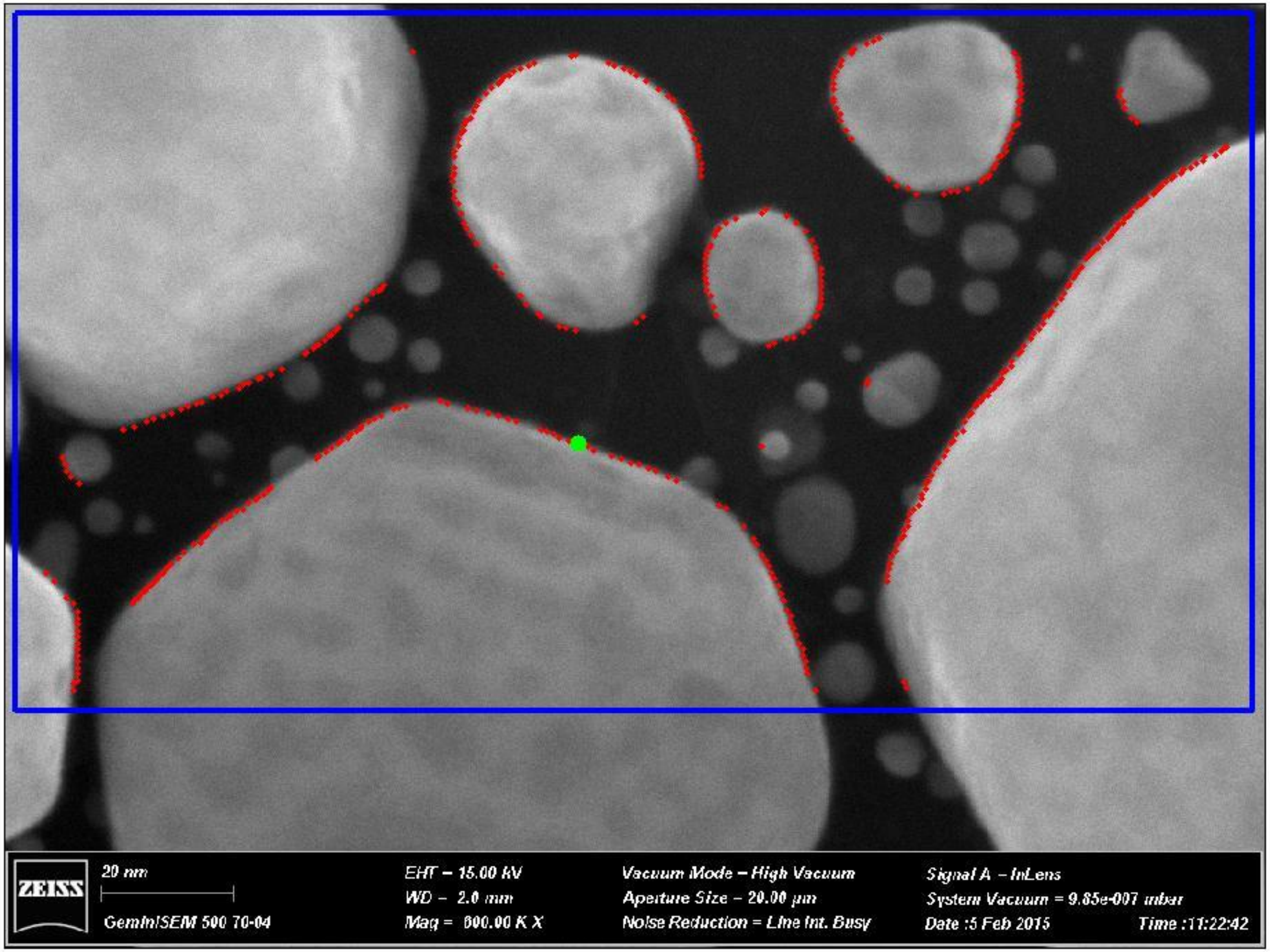


Figure 5.13 The relationship between the electron beam diameter and the size of the specimen pixels.

En pratique: Si la **taille de sonde** est plus grande que la **taille du pixel**, ce n’est plus la peine d’augmenter le grandissement

https://www.azom.com/article.aspx?ArticleID=19693

E:\Final Acceptance GeminiSEM500-70-04\Res_1500V_05.tif



PATE V4.00.05
17-June-2014

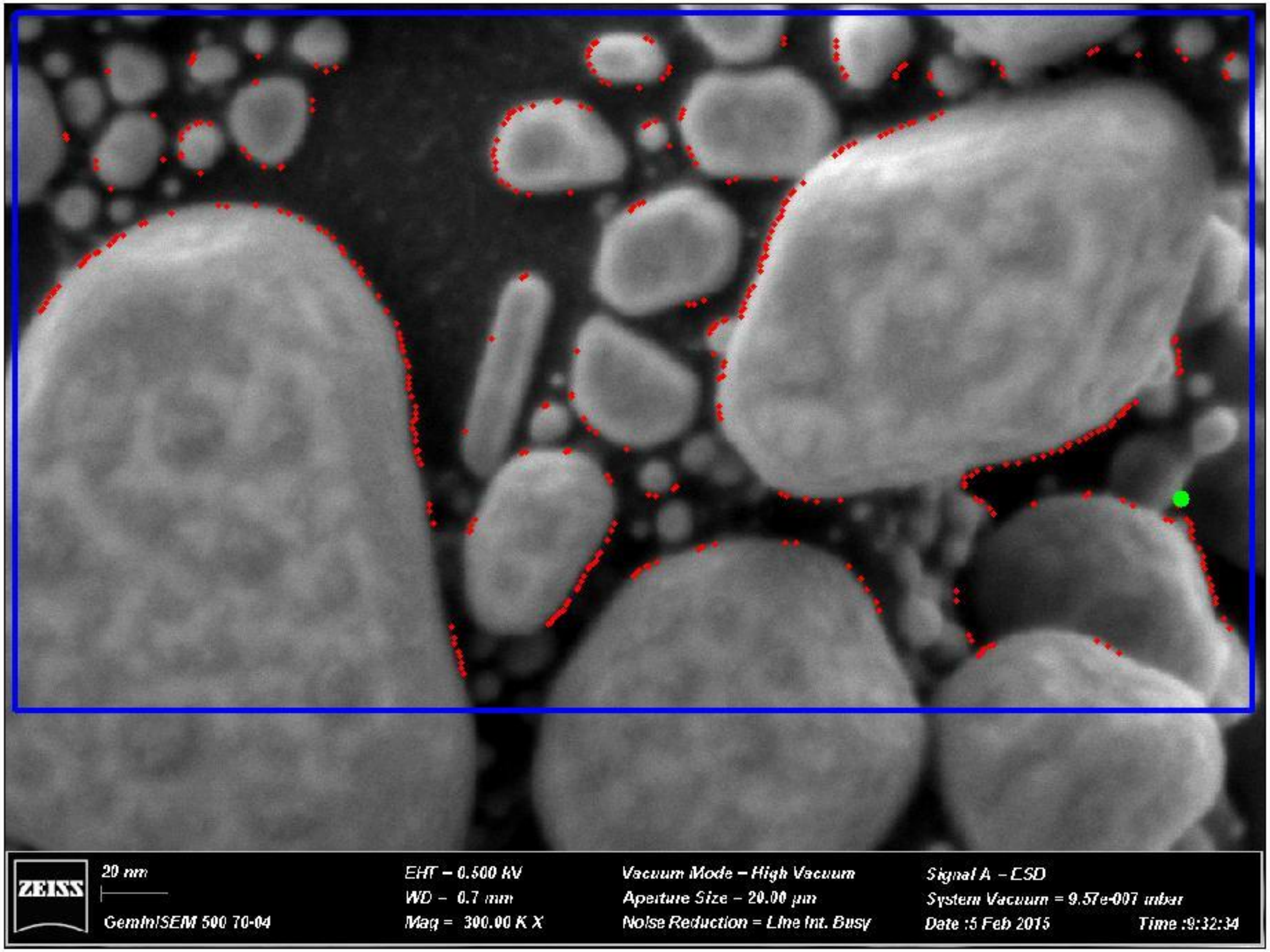
Results:

Resolution = 0.4 ± 0.03 nm
434 edges evaluated
S/N ratio = 107.2

Details:

Pixelsize = 0.186 nm
Mode = Resolution 25/75

C:\Users\y5rse\Desktop\Service Einsätze\Marseille\Final Acceptance GeminiSEM500-70-04\Res_500V_05.tif



ZEISS

20 nm

GeminiSEM 500 70-04

EHT = 0.500 kV
WD = 0.7 mm
Mag = 300.00 K X

Vacuum Mode = High Vacuum
Aperture Size = 20.00 µm
Noise Reduction = Line Int. Busy

Signal A = ESD
System Vacuum = 9.57e-007 mbar
Date :5 Feb 2015
Time :9:32:34

ZEISS

PATE V4.00.05
17-June-2014

Results:

Resolution = 1.0 ± 0.10 nm
382 edges evaluated
S/N ratio = 119.7

Details:

Pixelsize = 0.372 nm
Mode = Resolution 25/75

Paramètres de réglage pour l’imagerie MEB:influence sur la qualité des images

- Tension d’accélération des électrons
- contraste et brightness
- wobble et astigmatisme
- Grandissement
- Distance de travail
- diaphragme et courant de sonde
- Dwell-time (temps d’acquisition par pixel)
- images numériques

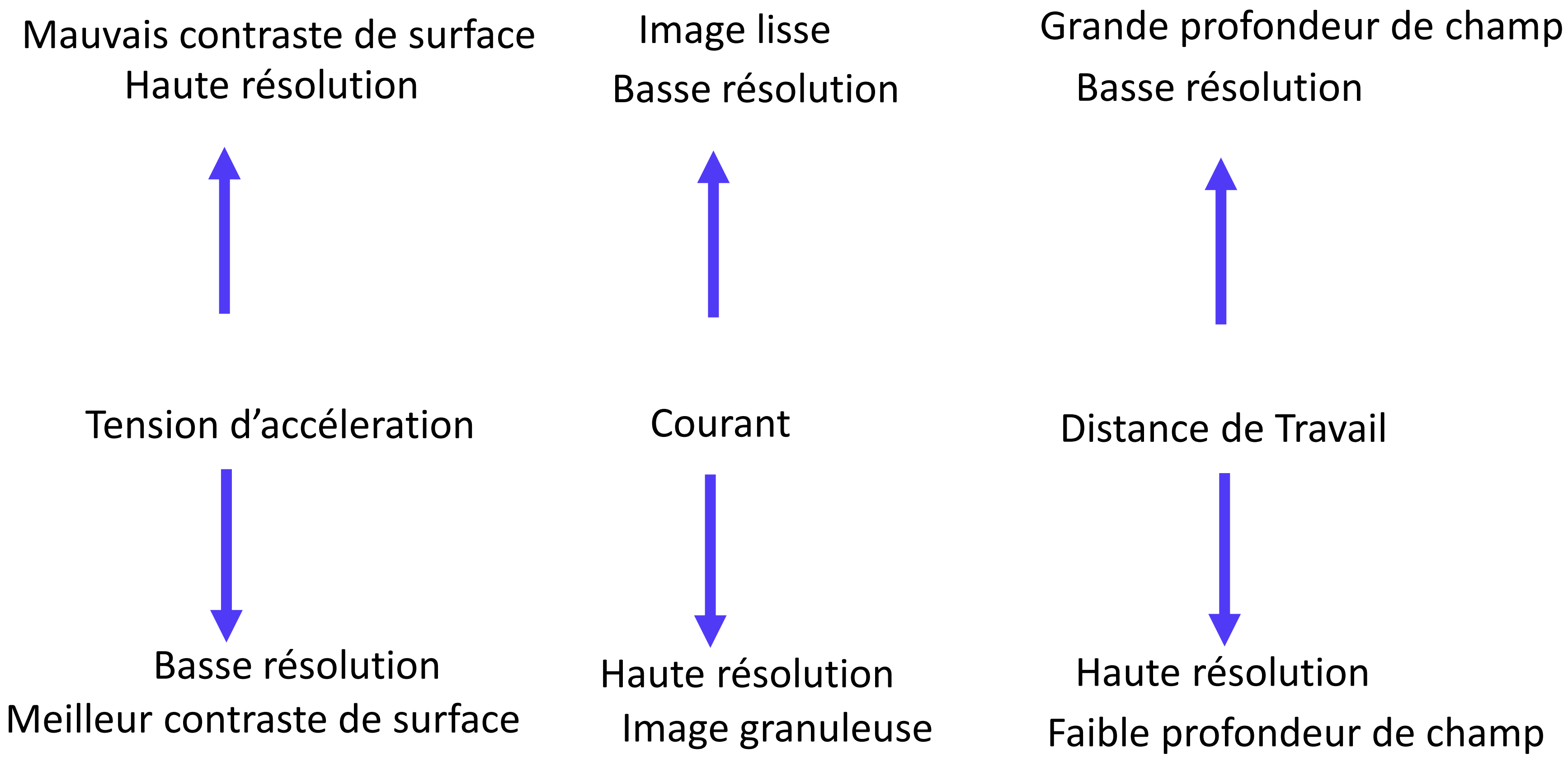
Résolution

- Plus la tension est élevée, plus la taille de sonde sur l'échantillon est petite parce que:

- les lentilles électromagnétiques à haute énergie ont moins d'aberrations, la brilliance de la source augmente (meilleur rapport signal/bruit) et le faisceau est moins dévié de sa position nominale par les champs magnétiques parasites.

- Une petite taille de sonde (meilleure résolution) fournit un courant plus faible, donc un rapport **signal/bruit** plus faible.
- Ce problème peut être contourné avec un temps d'acquisition plus long mais la résolution peut se dégrader avec les effets de charge et contamination

- **La résolution dépend du compromis entre la taille et le courant de sonde**
  - Et ensuite elle dépend de la taille choisie pour l'image (en pixels)



Mauvais contraste de surface
Haute résolution

Tension d’accéleration

Basse résolution
Meilleur contraste de surface

Image lisse
Basse résolution

Courant

Haute résolution
Image granuleuse

Grande profondeur de champ
Basse résolution

Distance de Travail

Haute résolution
Faible profondeur de champ

Conclusion: Les paramètres de réglage sont interconnectés et à chaque changement il faut reajuster de sorte à obtenir l’image avec la meilleure netteté possible

Pourquoi utiliser la basse tension (low kV)?

Example

Sample 2: Si nanopillars Top view

Équipe μten IM2NP Aix-Marseille

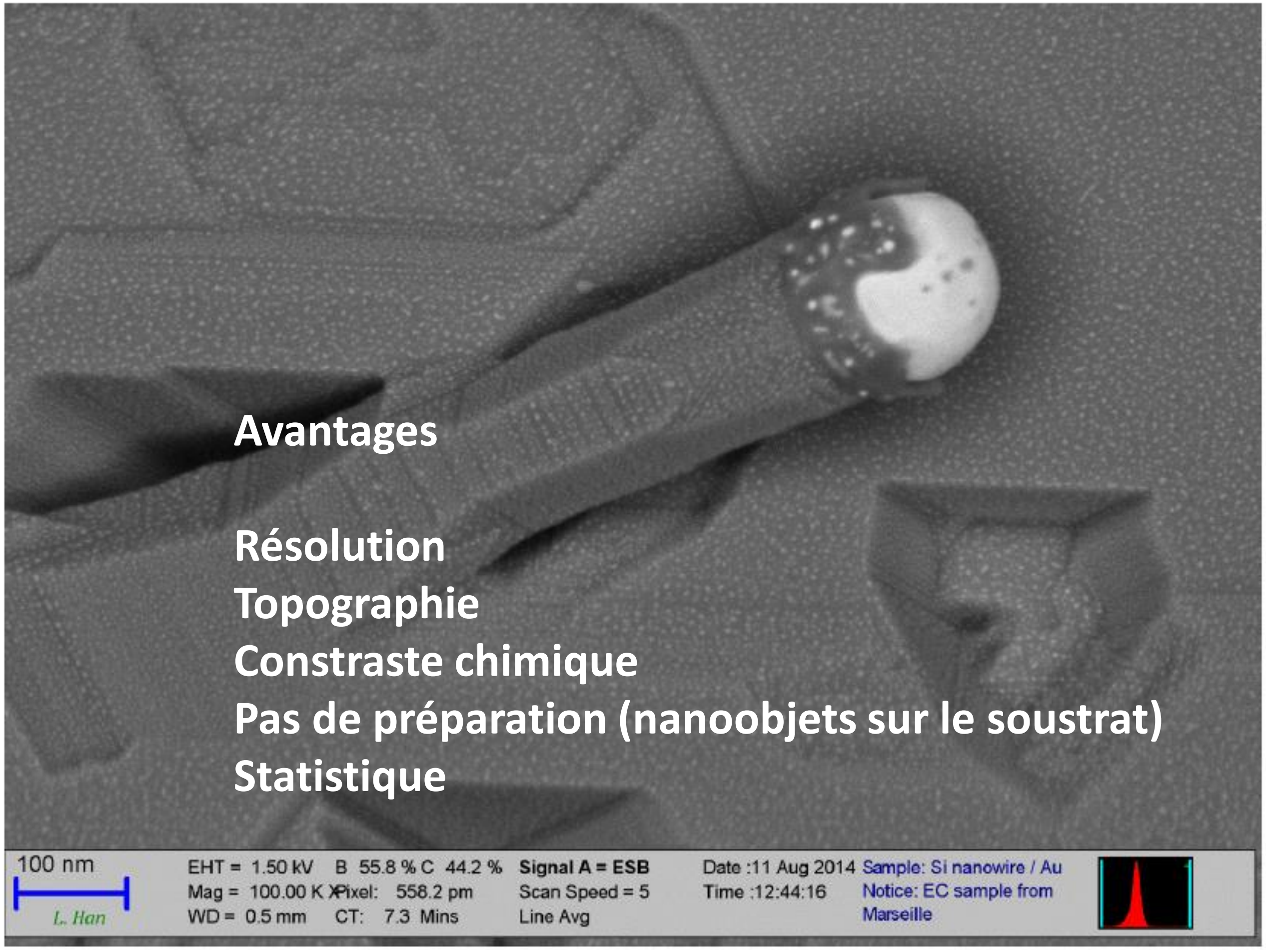
EHT 1.5 kV, InLens

Facets of the pillar is clearly visible.

Fine structure on surface revealed.

Infos avant obtenues via HRTEM et Tomographie TEM

Sample 2: Si nanopillars Top view



Avantages

Résolution
Topographie
Constraste chimique
Pas de préparation (nanoobjets sur le soustrat)
Statistique

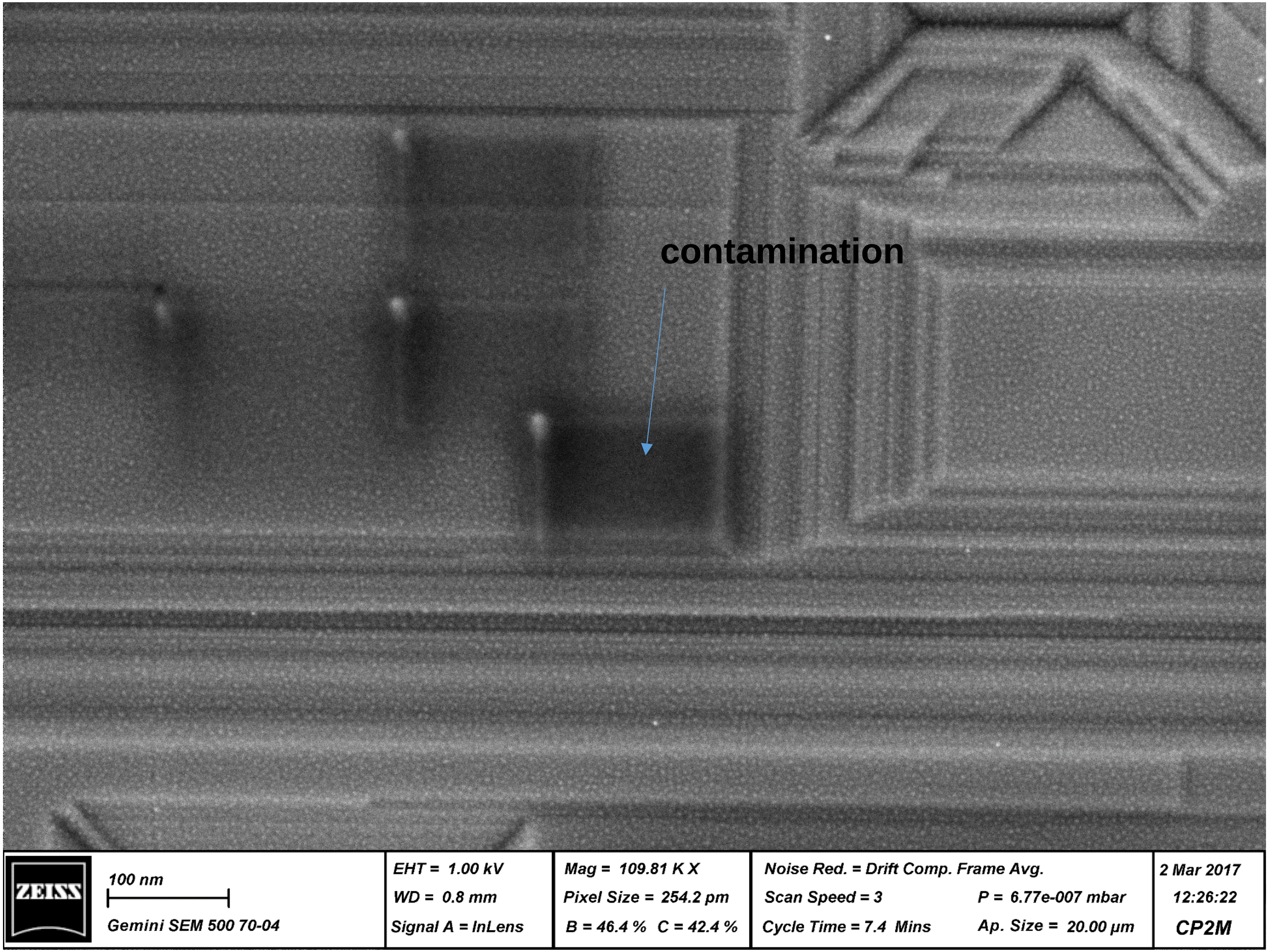
EHT = 1.50 kV   B 55.8 % C 44.2 %   Signal A = ESB   Date :11 Aug 2014   Sample: Si nanowire / Au
Mag = 100.00 K X   Pixel: 558.2 pm   Scan Speed = 5   Time :12:44:16   Notice: EC sample from Marseille
WD = 0.5 mm   CT: 7.3 Mins   Line Avg

EHT 1.5 kV, EsB

Material contrast

Metallic particle on top of the pillar + small metallic nanoparticles on surface.

Mais à basse tension on a aussi des problèmes…


contamination

Gemini SEM 500 70-04

EHT = 1.00 kV
WD = 0.8 mm
Signal A = InLens

Mag = 109.81 K X
Pixel Size = 254.2 pm
B = 46.4 % C = 42.4 %

Noise Red. = Drift Comp. Frame Avg.
Scan Speed = 3
Cycle Time = 7.4 Mins
P = 6.77e-007 mbar
Ap. Size = 20.00 µm

2 Mar 2017
12:26:22
CP2M

Après un coup de **Plasma cleaner** interne – échelle de « TEM »

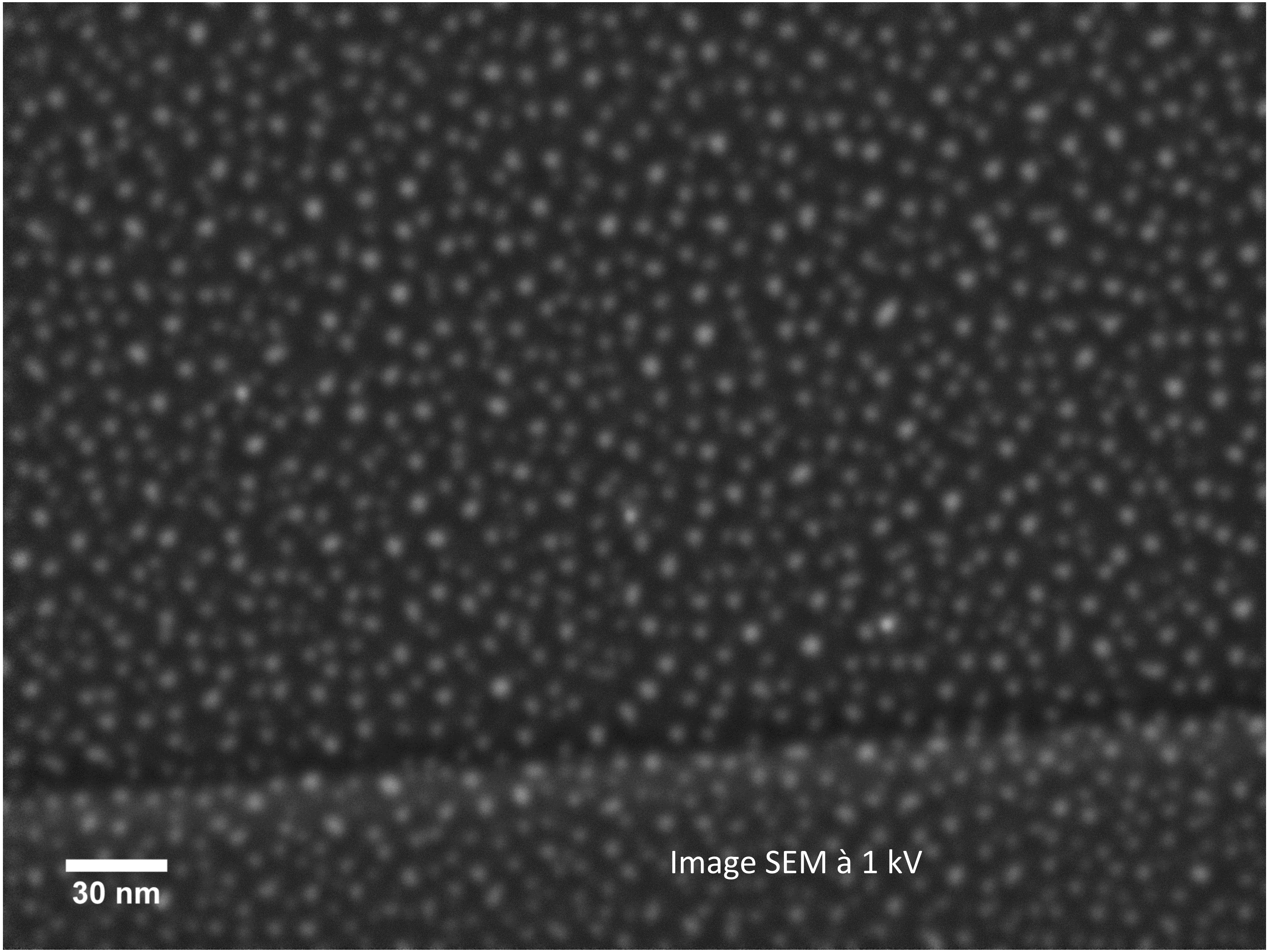
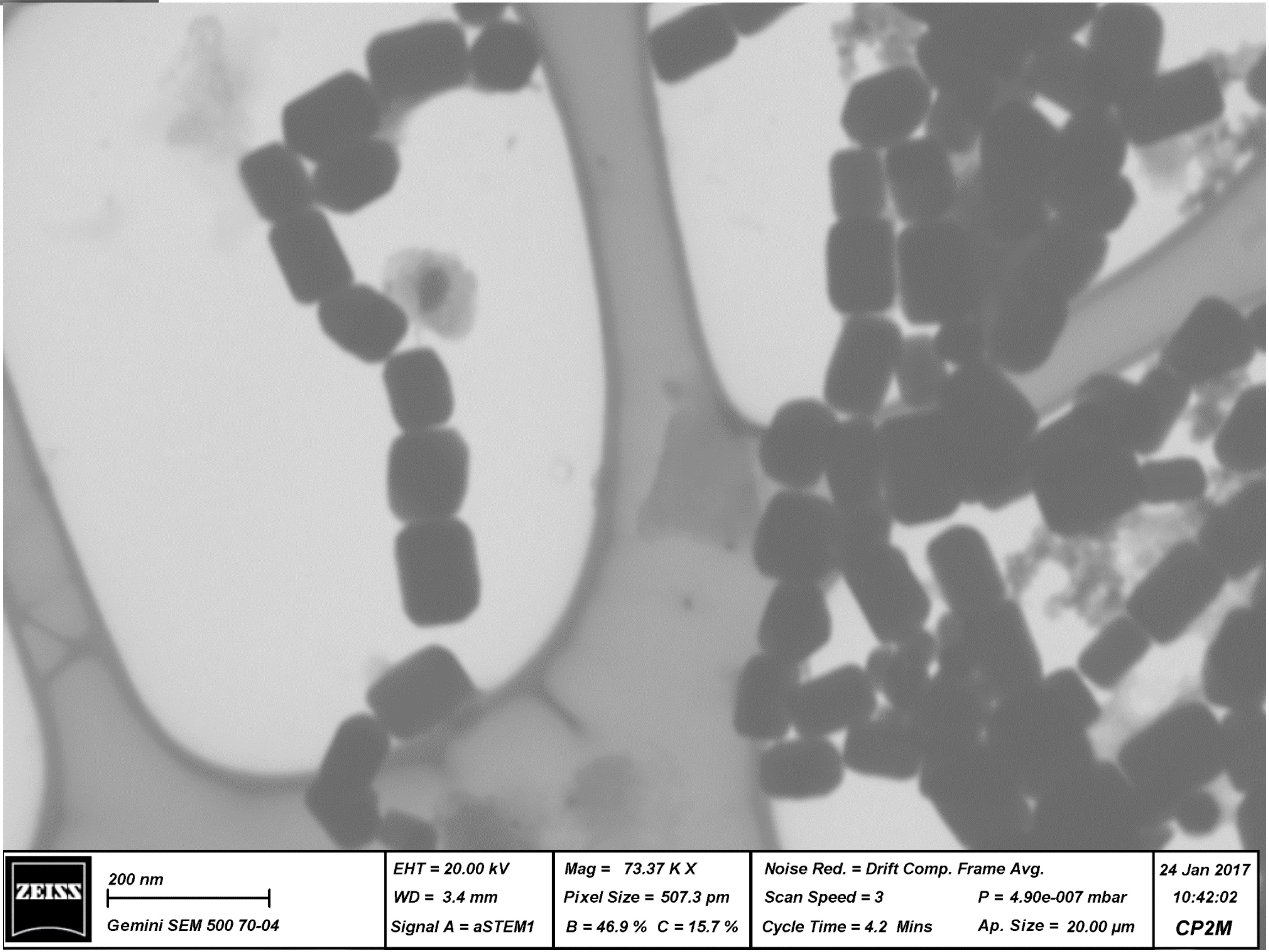
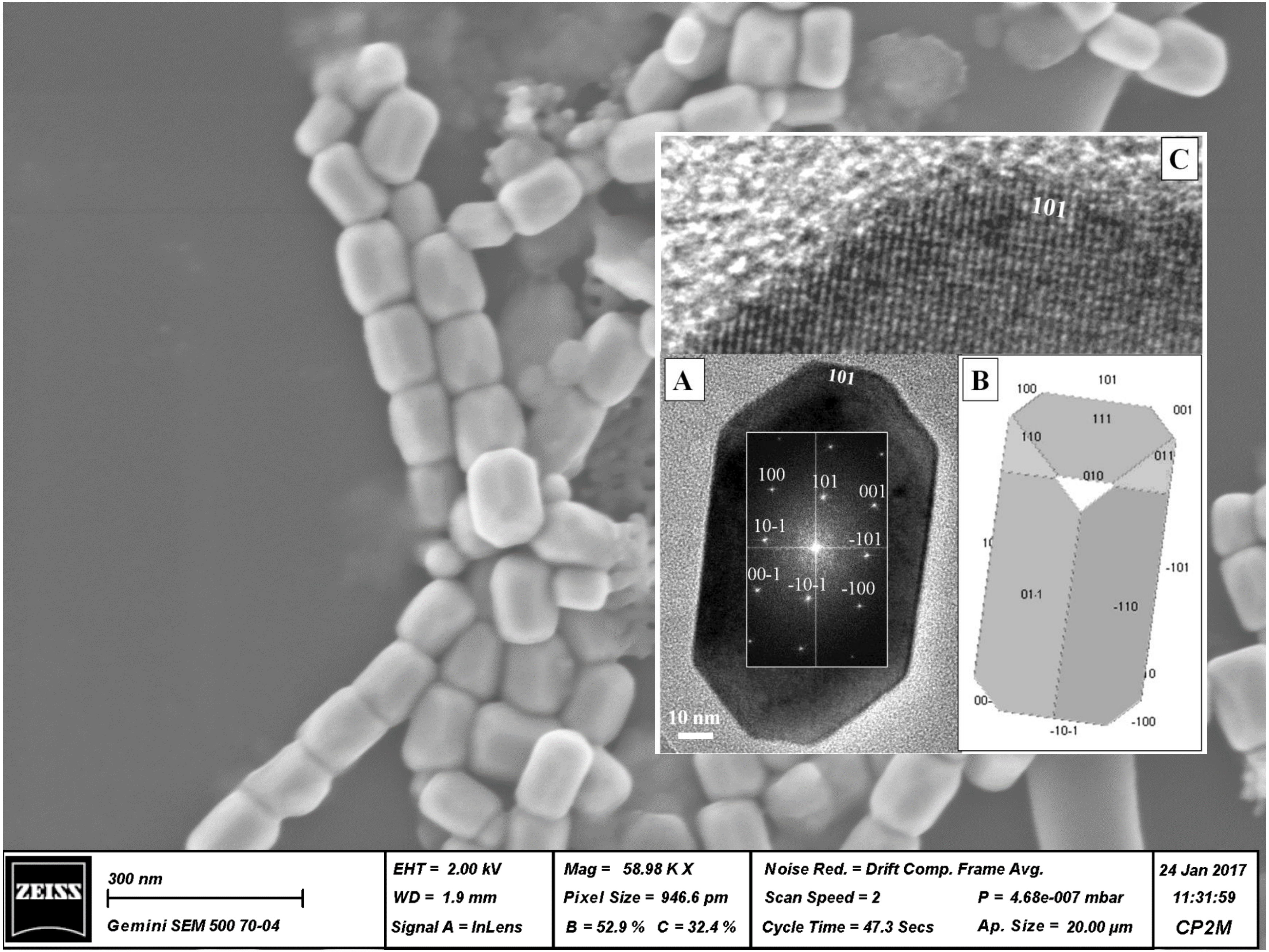


Image SEM à 1 kV

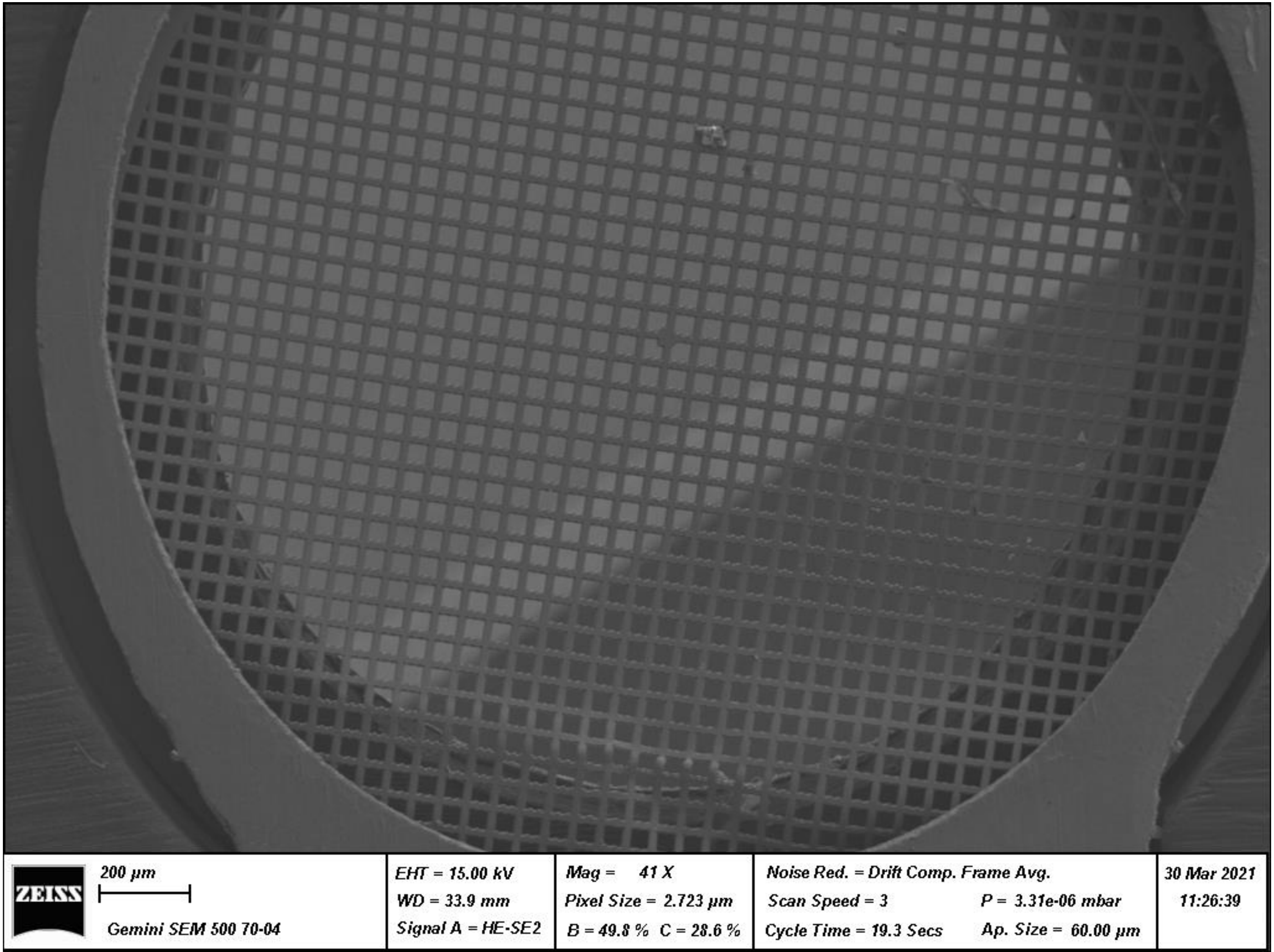
Example STEM

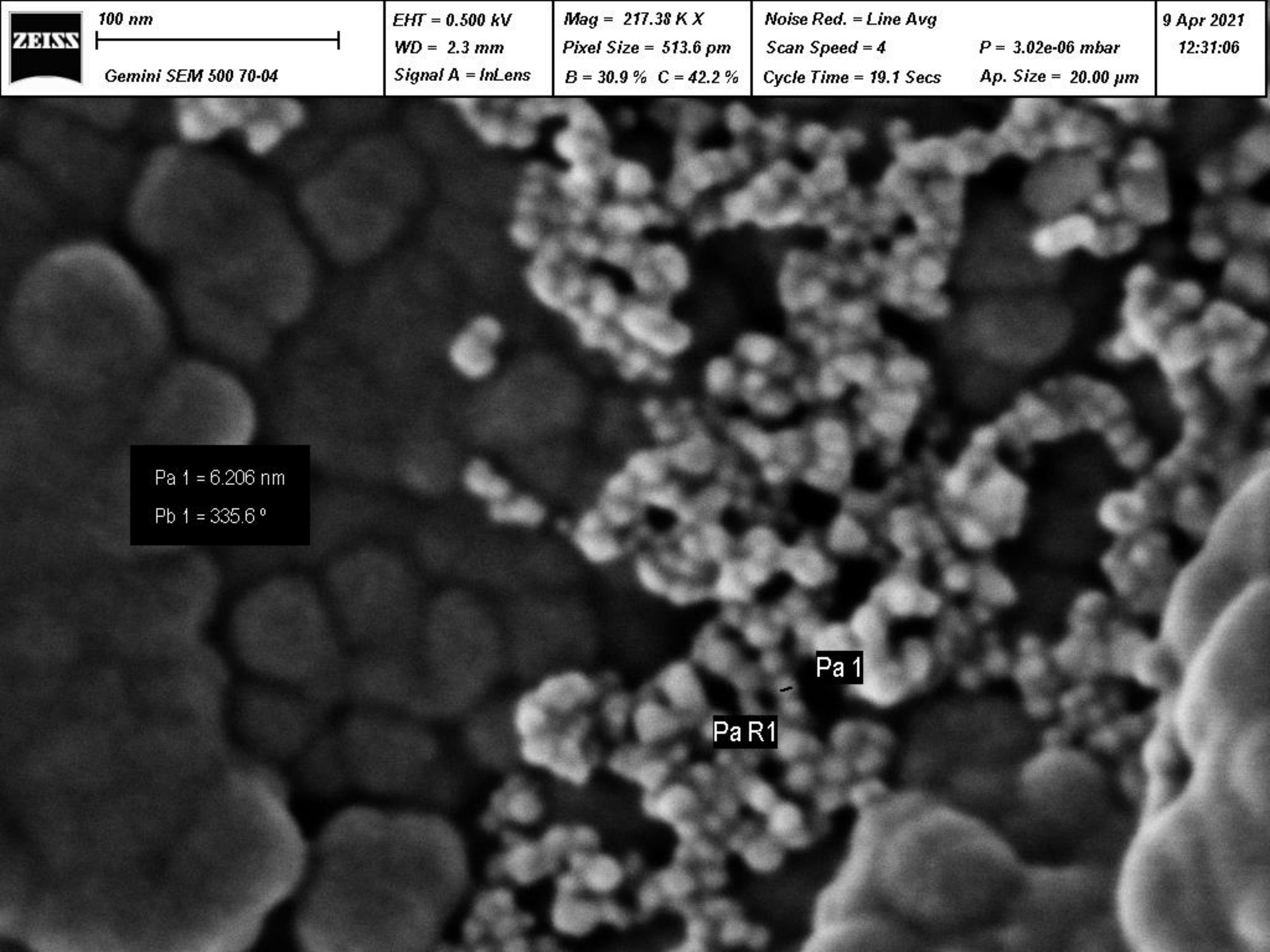


In lens: topographie et confirmation de l'information TEM



Nanoparticules visibles sur la grille




ZEISS
100 nm
Gemini SEM 500 70-04
EHT = 0.500 kV
WD = 2.3 mm
Signal A = InLens
Mag = 217.38 K X
Pixel Size = 513.6 pm
B = 30.9 % C = 42.2 %
Noise Red. = Line Avg
Scan Speed = 4
Cycle Time = 19.1 Secs
P = 3.02e-06 mbar
Ap. Size = 20.00 µm
9 Apr 2021
12:31:06
Pa 1 = 6.206 nm
Pb 1 = 335.6 °
Pa 1
Pa R1

Example

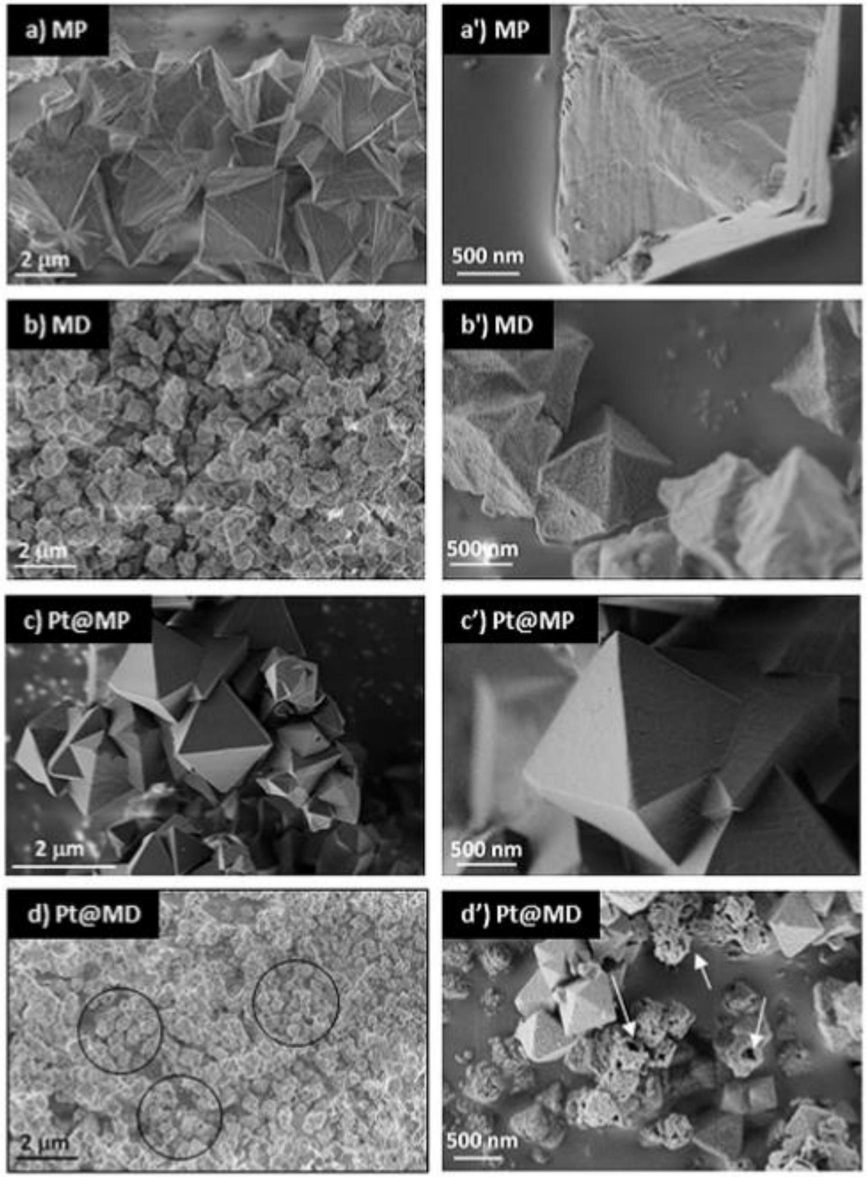


Figure 1. SEM images of the different synthetized samples: MP (a,a'); MD (b,b'); Pt@MP (c,c'); Pt@MD (d,d'). In Figure d) and d'), the circles and the arrows indicates the holes created in the MOF-808 crystals.

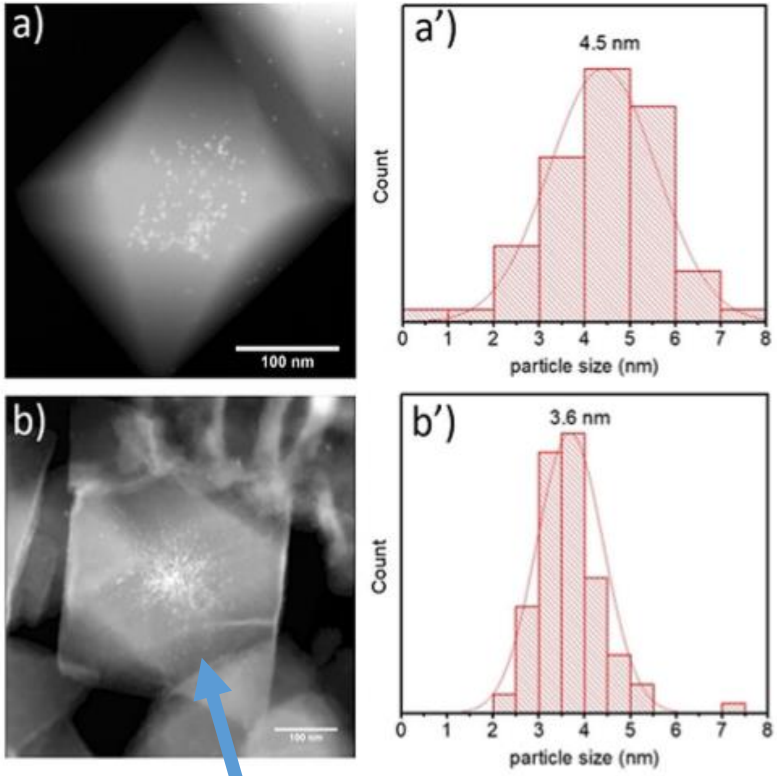
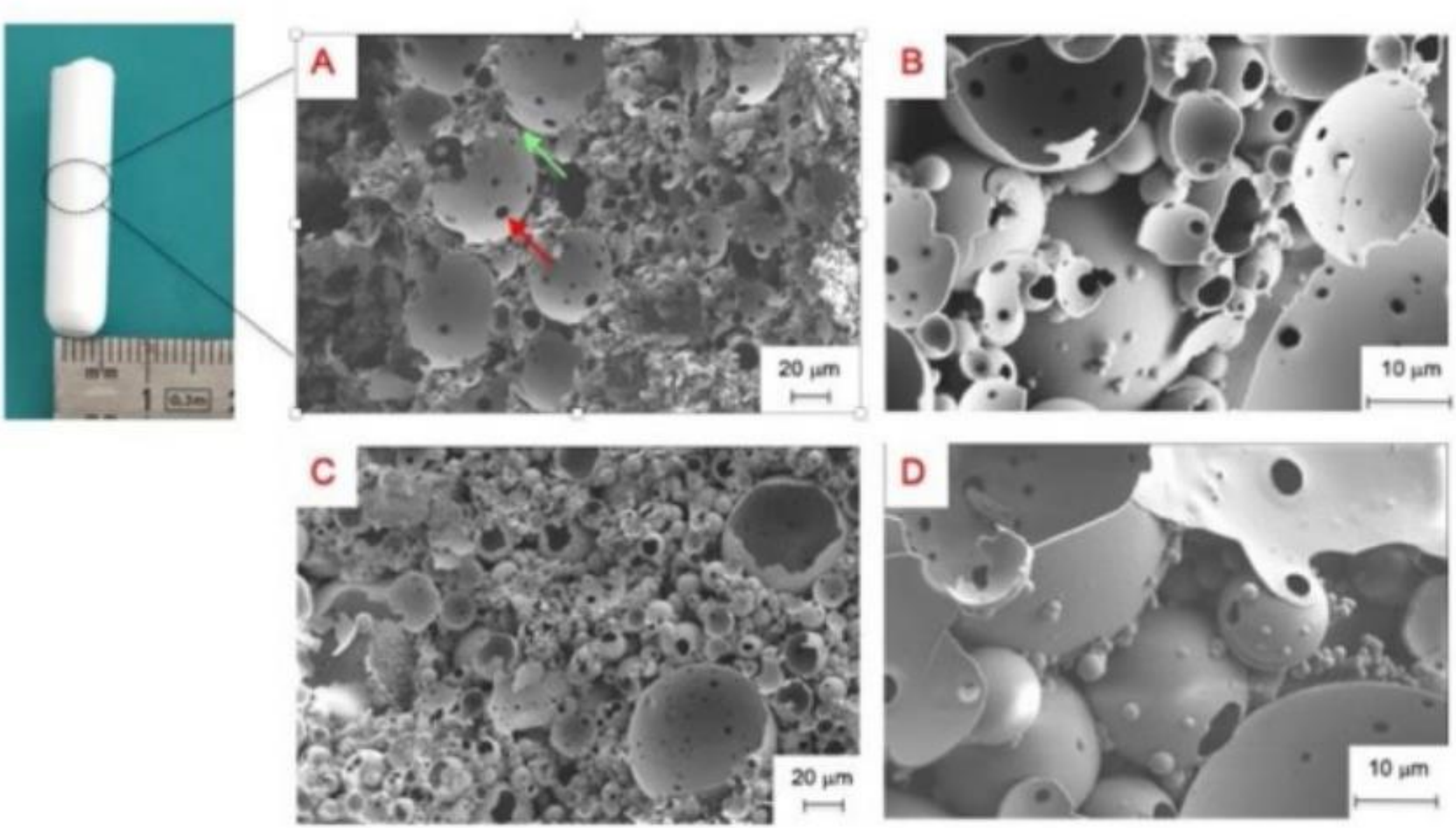


Figure 2. STEM images of Pt@MP (a) and Pt@MD (b) samples. The white dots located in the centre of the crystal indicate the presence of Pt-NPs. Pt particle size distributions are given by the histograms for Pt@MP (a') and for Pt@MD (b'). The distribution was made over 100 particles.

TEM: Particules dedans ou sur la surface??
Avec SEM, topographie

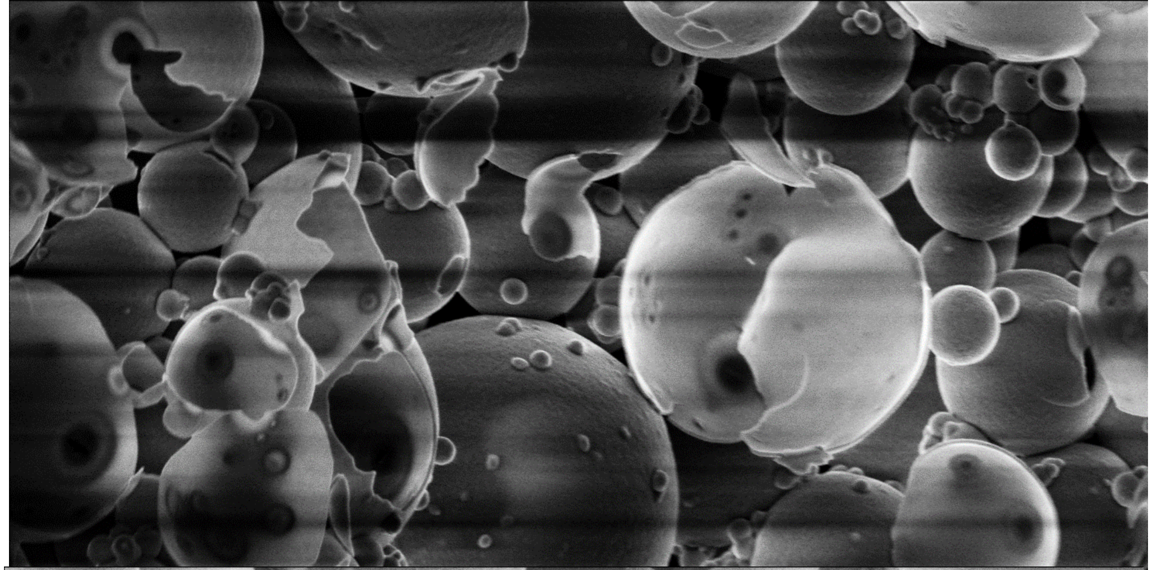
Chem. Eur. J. 2021, 27, 1-12

Example

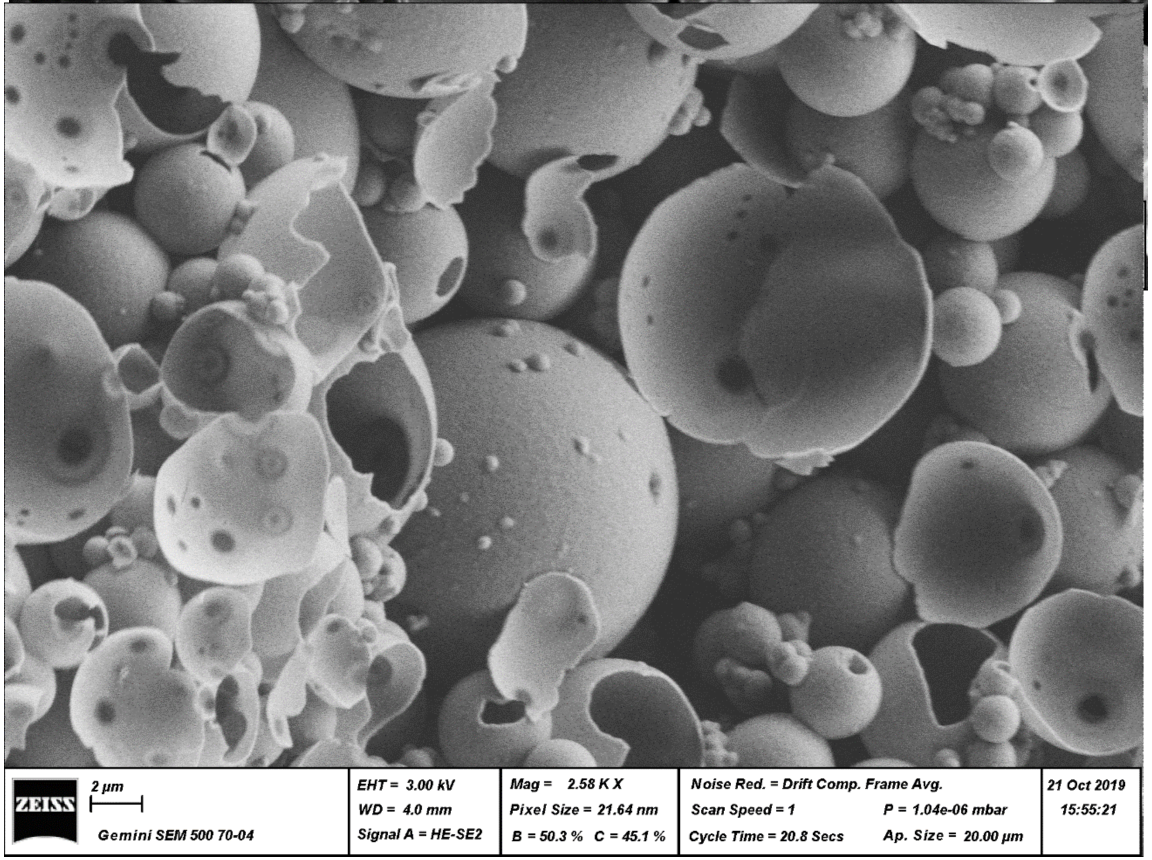


Biotechnology Reports 31, 2021 e00645

Images avec détecteur SE Latéral
Moins d’effets de charge



In-lens



Gemini SEM 500 70-04

EHT = 3.00 kV
WD = 4.0 mm
Signal A = HE-SE2

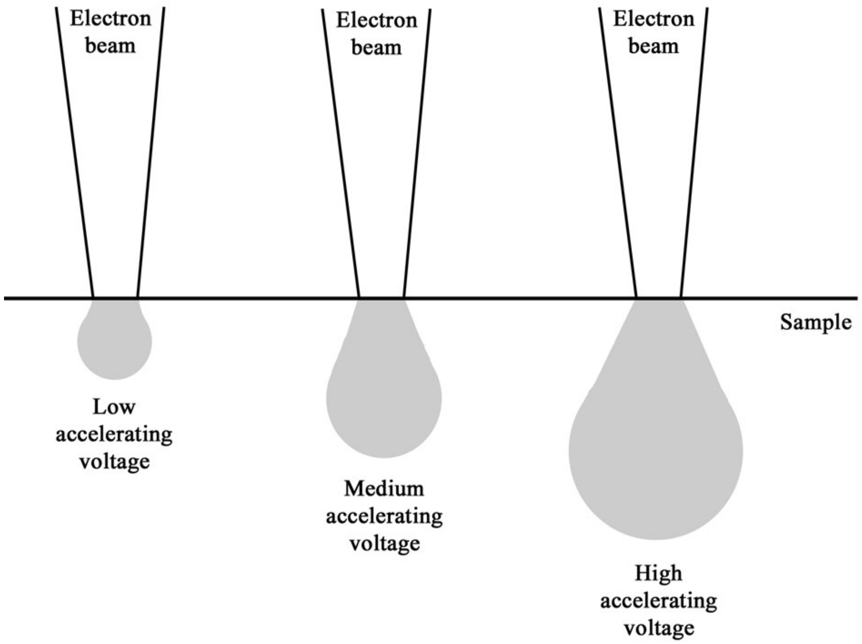
Mag = 2.58 K X
Pixel Size = 21.64 nm
B = 50.3 % C = 45.1 %

Noise Red. = Drift Comp. Frame Avg.
Scan Speed = 1
P = 1.04e-06 mbar
Cycle Time = 20.8 Secs
Ap. Size = 20.00 µm

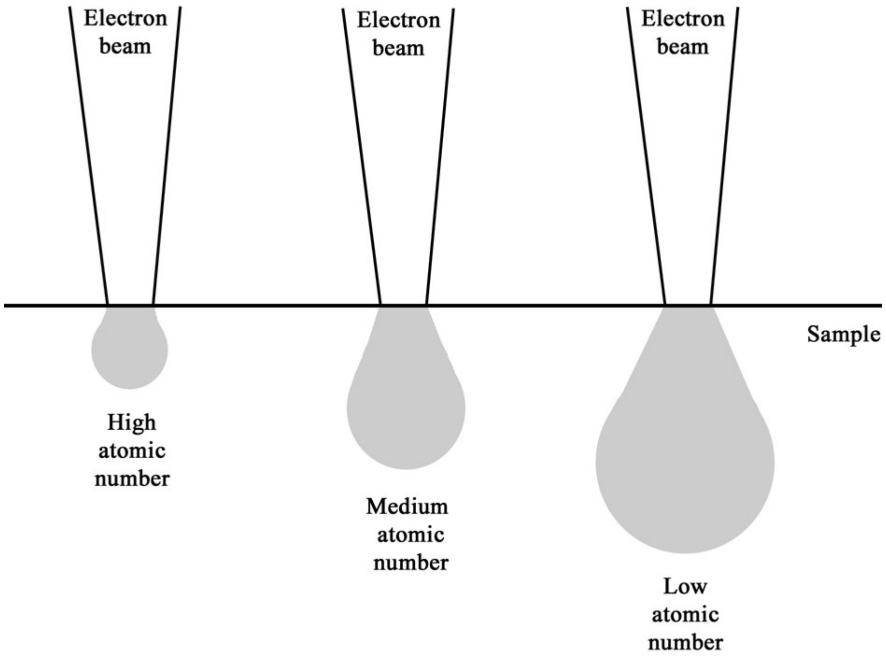
21 Oct 2019
15:55:21

HE-SE

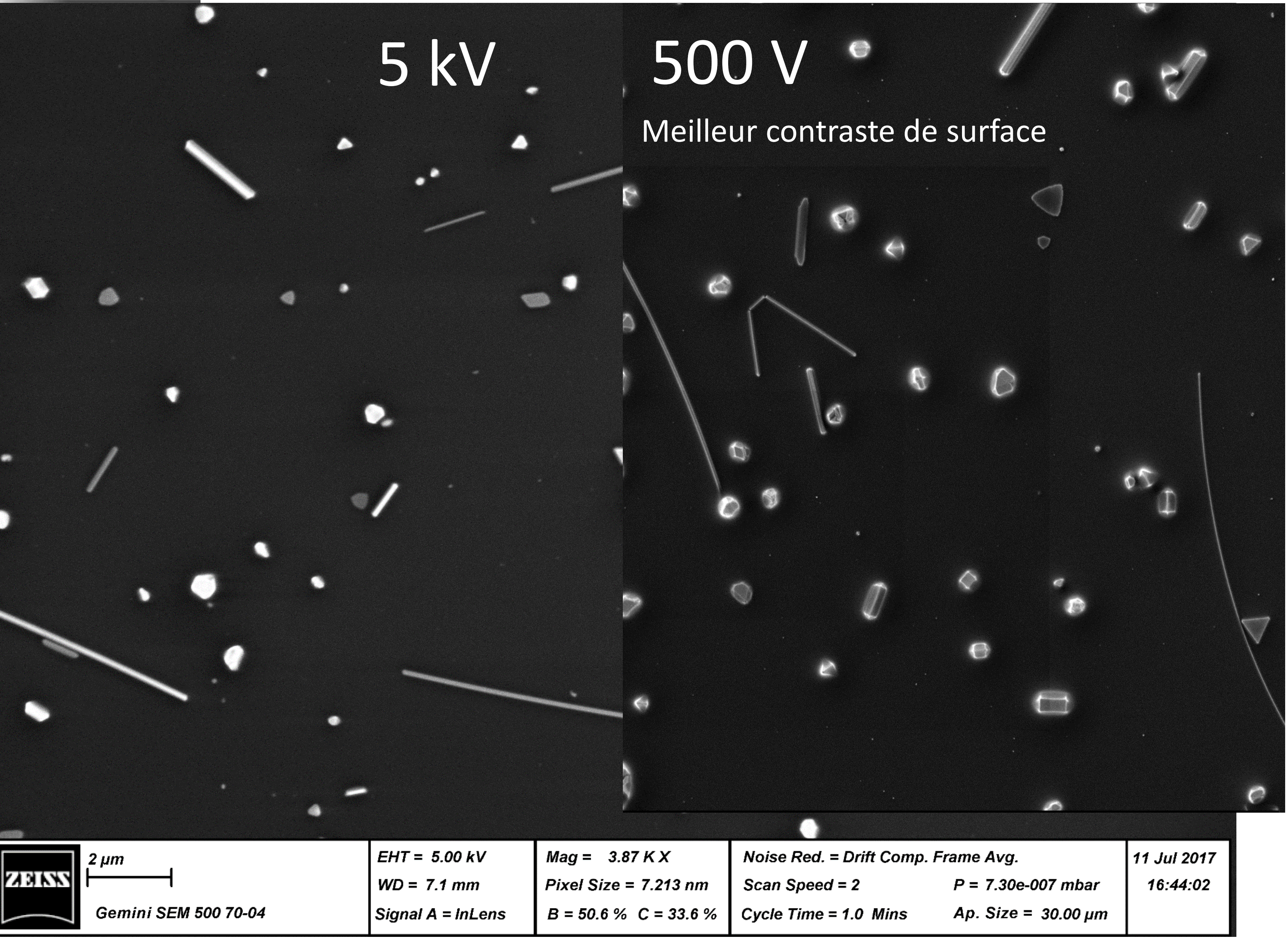
Influence de la tension d’accélération



Influence de la nature de l’échantillon



Example – collaboration avec le CEREGE



5 kV

500 V

Meilleur contraste de surface

Gemini SEM 500 70-04

EHT = 5.00 kV
WD = 7.1 mm
Signal A = InLens

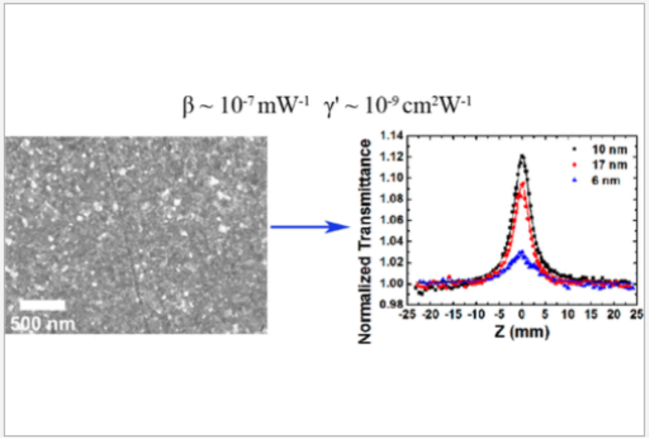
Mag = 3.87 K X
Pixel Size = 7.213 nm
B = 50.6 % C = 33.6 %

Noise Red. = Drift Comp. Frame Avg.
Scan Speed = 2
Cycle Time = 1.0 Mins
P = 7.30e-007 mbar
Ap. Size = 30.00 µm

11 Jul 2017
16:44:02

Example *ACS Appl. Nano Mater.* 2020, 3, 8, 7963–7972

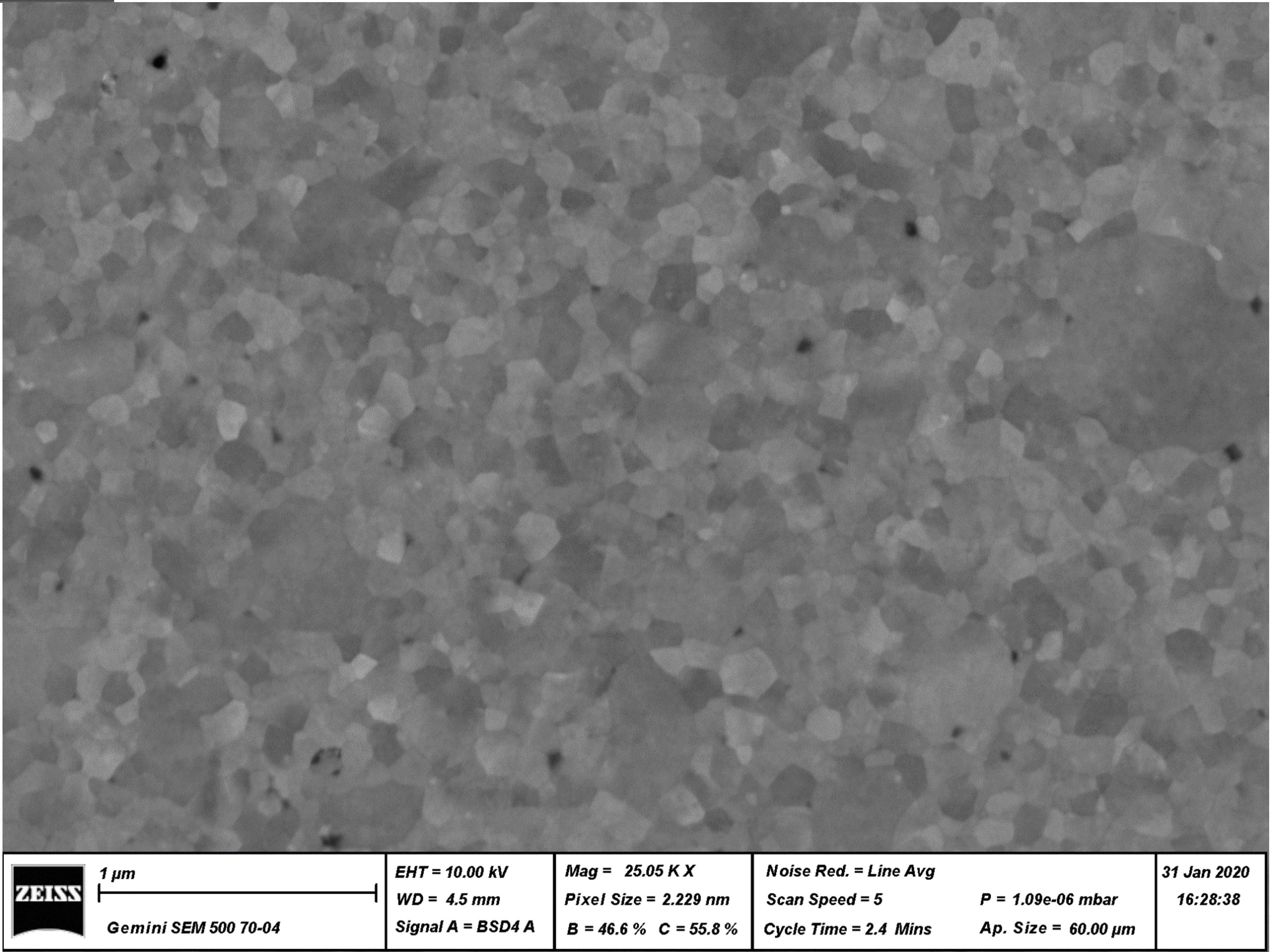
Abstract



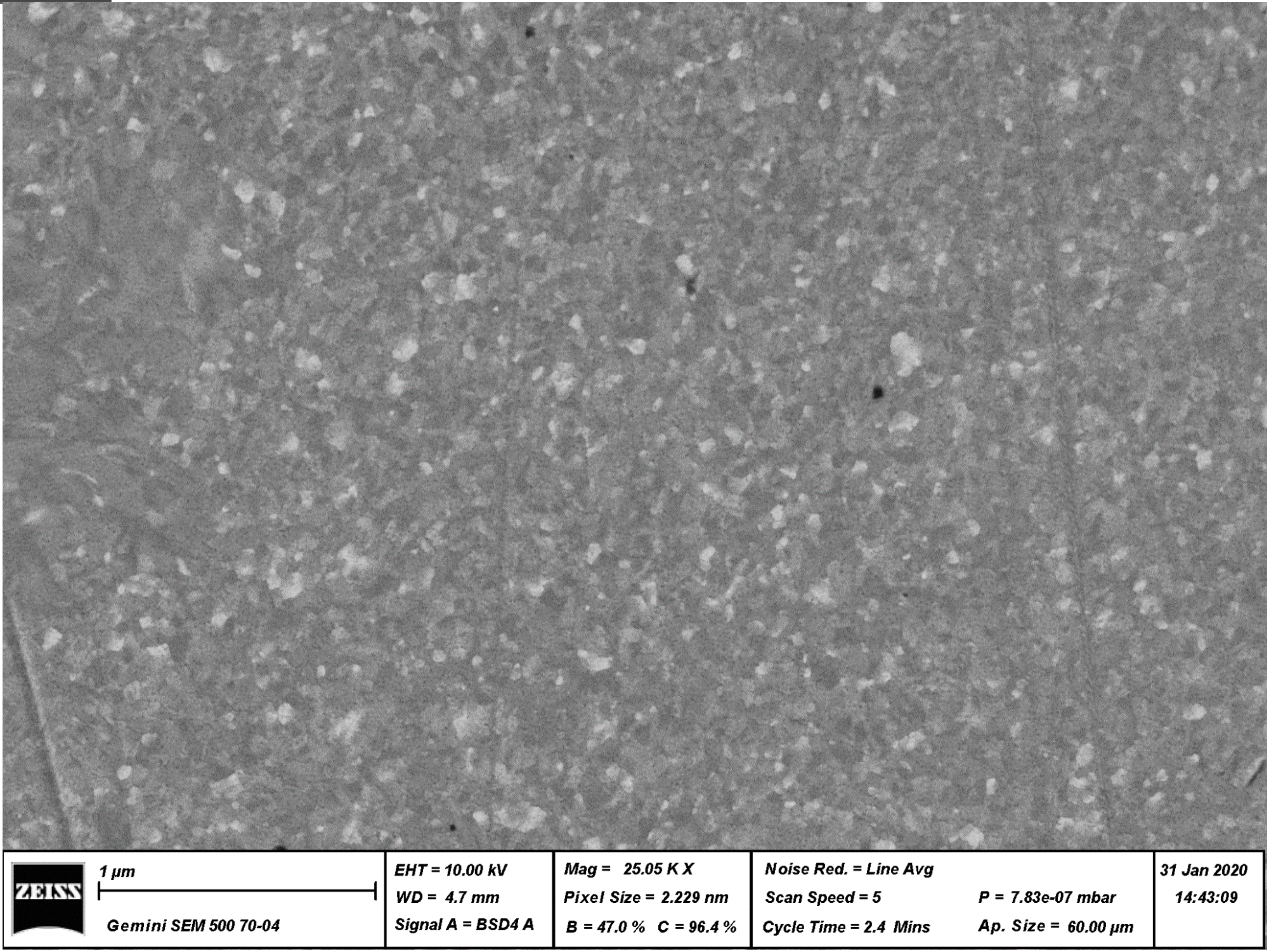
2D materials are currently very promising candidates for various photonic applications. Optimizing their optical nonlinearities requires a thorough adjustment of several properties including the film thickness. In this work thin Sb_2Te_3 layers with different thicknesses (ranging from 2.5 to 50 nm) are prepared by the electron beam deposition technique, and then they are properly annealed in order to achieve significant third order nonlinearities. The film structure and morphology are extensively studied by means of X-ray diffraction, scanning electron microscopy, transmission electron microscopy and energy-dispersive X-ray spectroscopy. The presence of nanocrystals with sizes highly depending on the film thickness has been observed. Optical studies are carried out by Vis–NIR spectrophotometric studies. Finally, a thickness dependent study of the ultrafast third order nonlinear optical properties of the Sb_2Te_3 thin films is performed. This study is carried out by means of the Z-scan technique, employing 400 fs laser pulses at 1030 nm. The observed optical nonlinearities are very high, compared with those of state-of-the-art nonlinear optical materials. Moreover they are highly dependent on the thickness of the layers. The findings demonstrate the importance of a fine adjustment of the Sb_2Te_3 thickness in order to enhance its nonlinear optical efficiency. They are expected to be of significant importance for mode-locking of laser systems and super-resolved direct laser writing.

Centre Pluridisciplinaire de Microscopie électronique et de Microanalyse

Échantillon 2nm SiO2/30 nm Sb2Te3/verre



Échantillon 2nm SiO2/10 nm Sb2Te3/verre



Gemini SEM 500 70-04

EHT = 10.00 kV
WD = 4.7 mm
Signal A = BSD4 A

Mag = 25.05 K X
Pixel Size = 2.229 nm
B = 47.0 % C = 96.4 %

Noise Red. = Line Avg
Scan Speed = 5
Cycle Time = 2.4 Mins

P = 7.83e-07 mbar
Ap. Size = 60.00 µm

31 Jan 2020
14:43:09

Low kV: visualisation du graphène

Nanomaterials **2022**, *12*, 1914 7 of 14

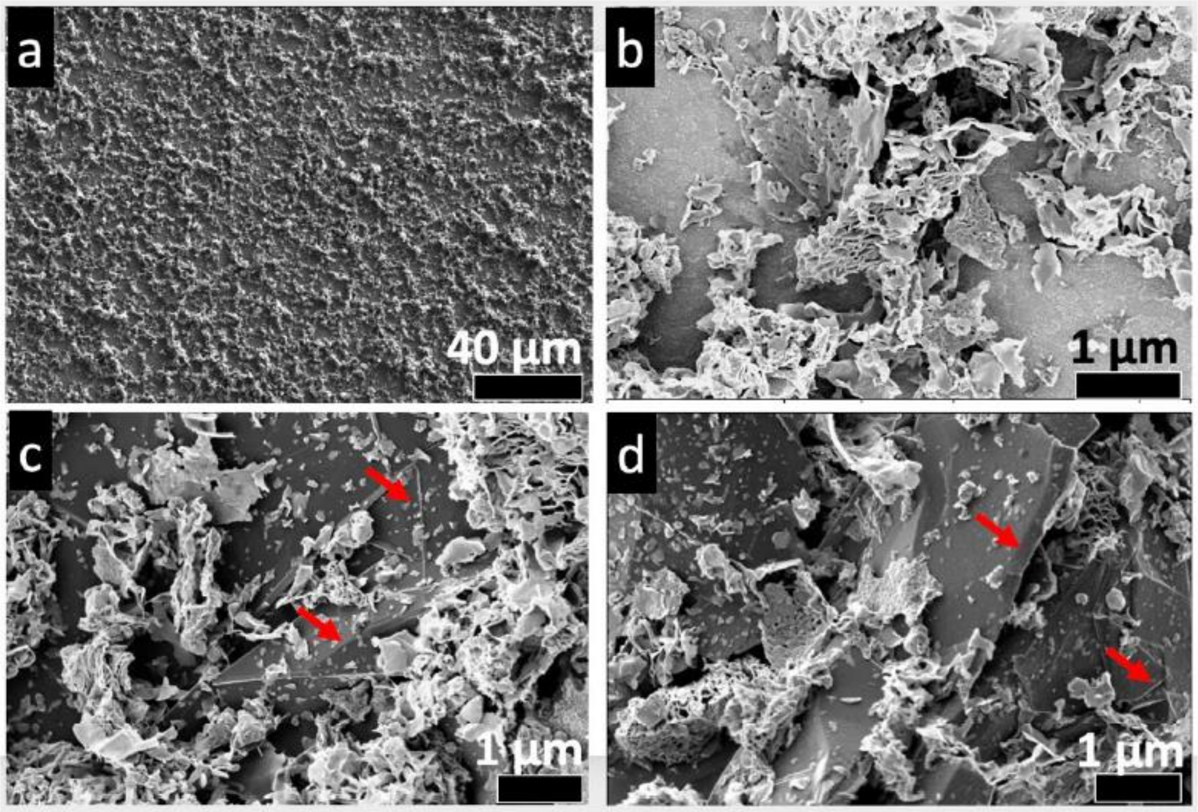
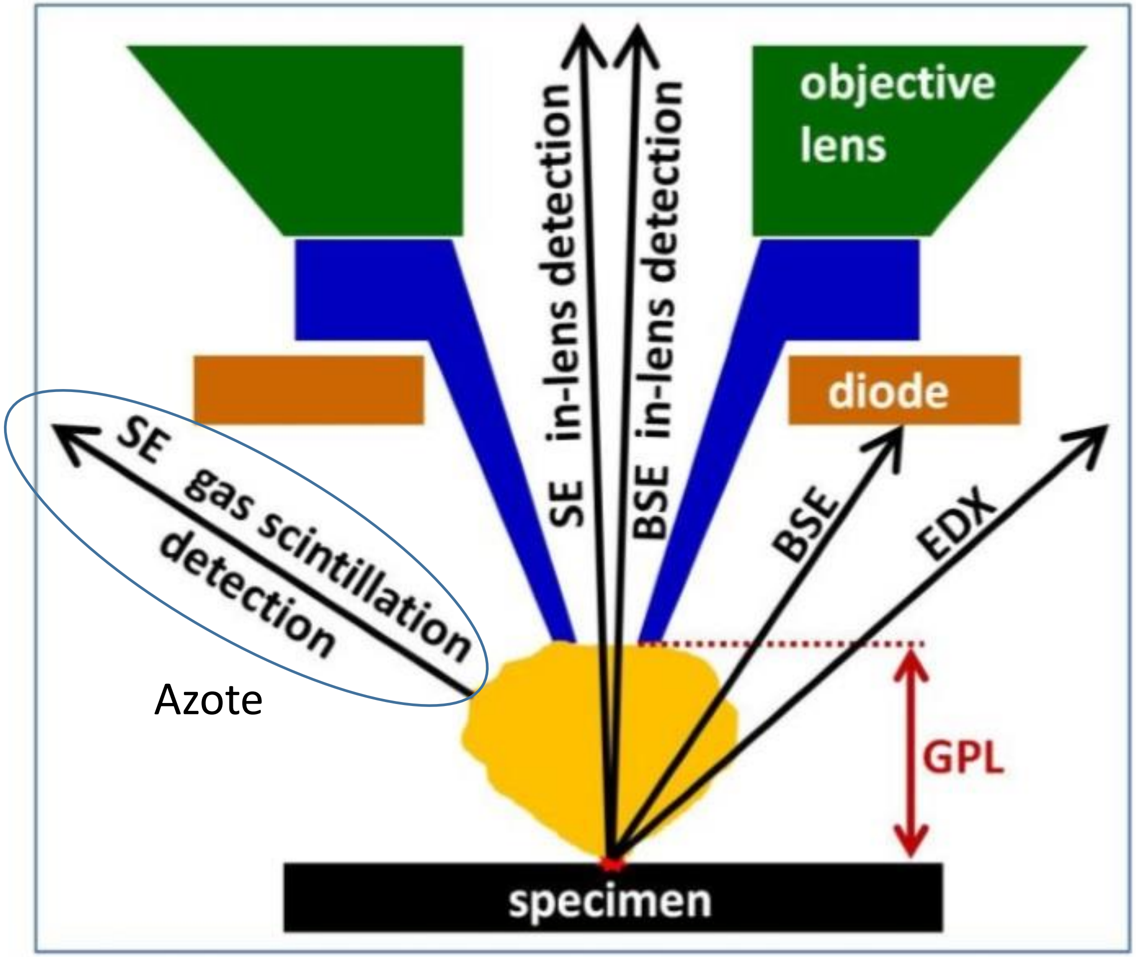


Figure 7. Low kV SEM micrographs: (**a**) typical general view for all samples; (**b**) zoom-in on neat WS$_2$ nanosheets; (**c**) zoom-in on WS$_2$: 0.5 wt% sample; and (**d**) zoom-in on WS$_2$: 1 wt% sample. Red arrows identify the graphene platelets on grapahene@WS$_2$ samples.
]

Pression Variable dans le SEM: Une façon simple d'éviter les effets de charge sur l'échantillon

L`ionisation dans le gaz produit un flux positif d'ions qui migrent vers la surface et la neutralisent

Un détecteur de scintillation du gaz peut être utilisé pour l'imagerie SE



DETECTEUR
VPSE

Azote

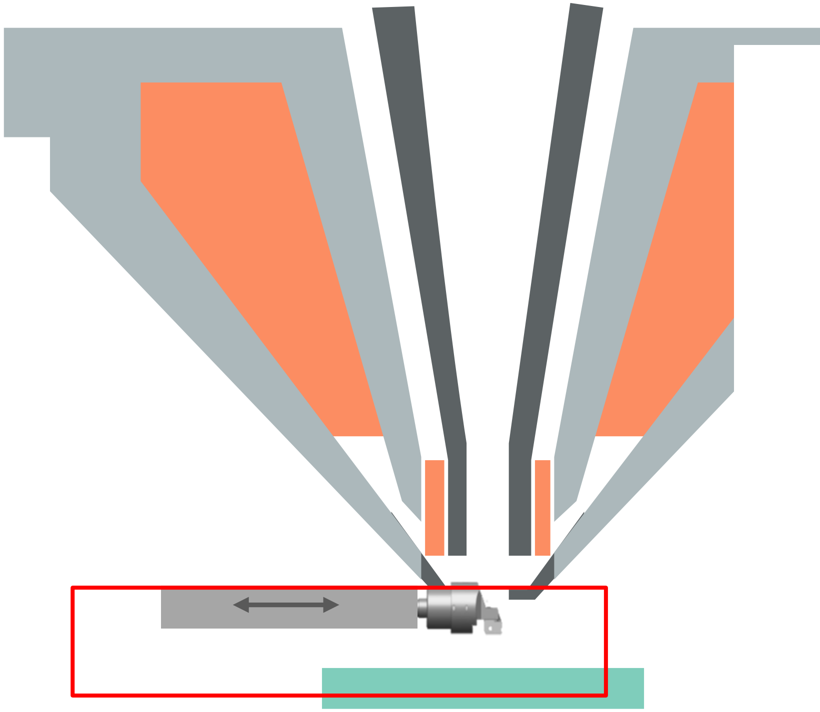
Option

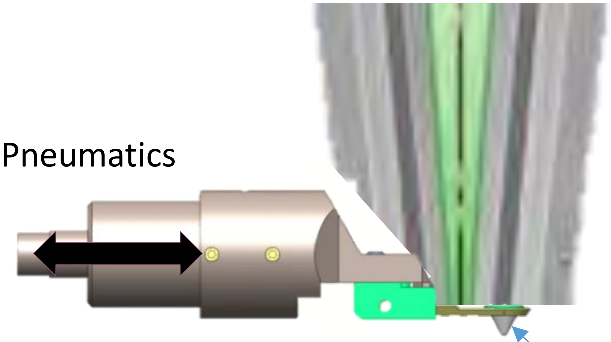
NanoVP – The Technology Behind

Source: Fang, ZEISS

- In NanoVP mode a differential pumping aperture can be inserted below the objective lens.
- This greatly reduces the path length of the incident beam in the gas thus reducing beam broadening.
- Best imaging performance

  up to 150 Pa, **full in lens detection**, outstanding resolution (1.8 nm at 3kV, 30 Pa), reduced field of view (350µm)
- In order to enable chamber BSD detection in VP mode a one channel BSD detector, which is integrated in the beam sleeve pneumatics, is available.

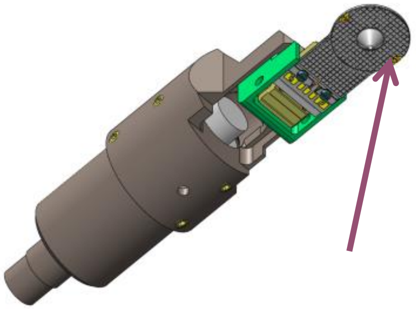




Pneumatics

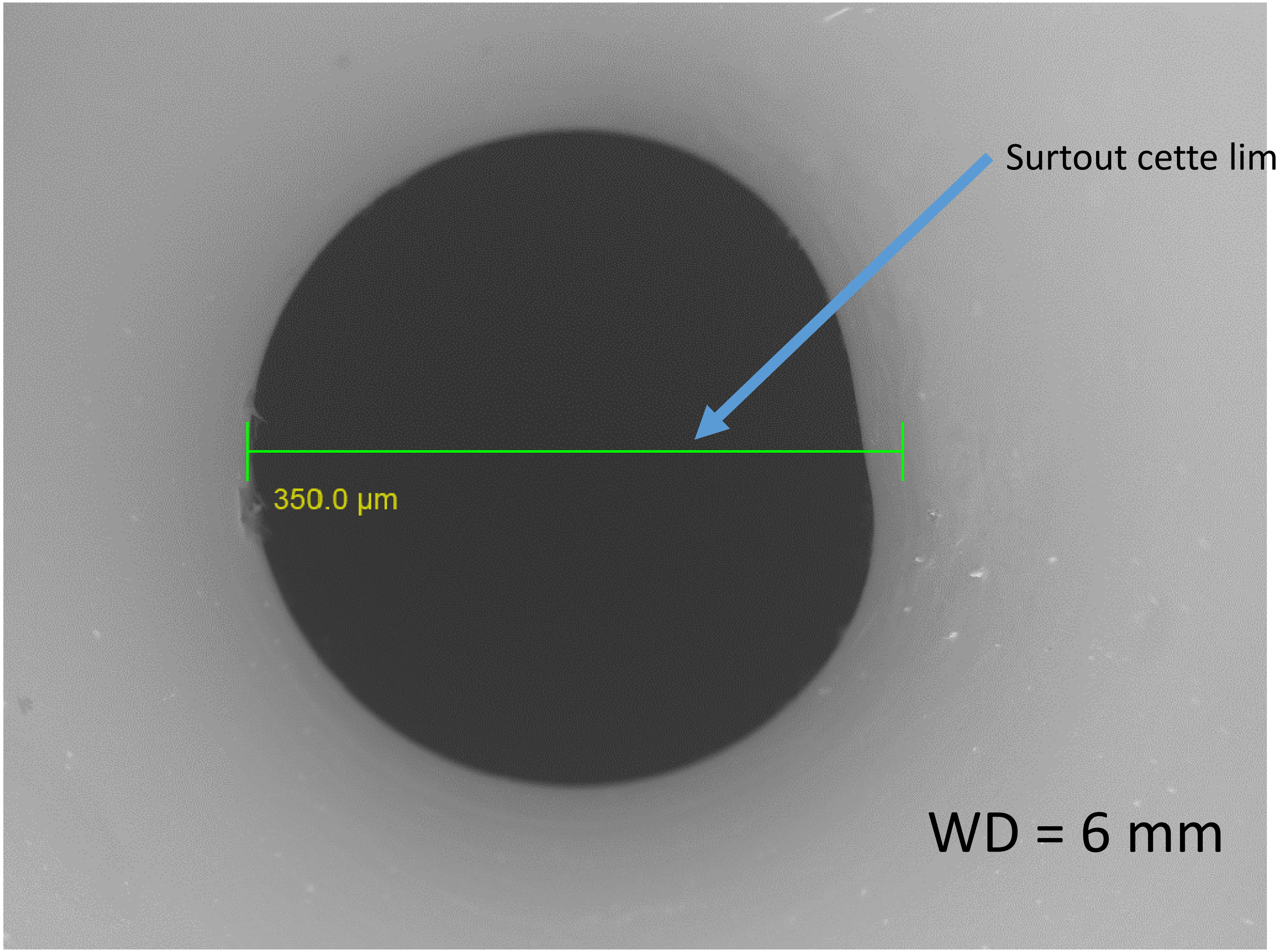
Beamsleeve

Detecteurs VPSE + INLENS + VP BSD



BSD - 5 segments diode

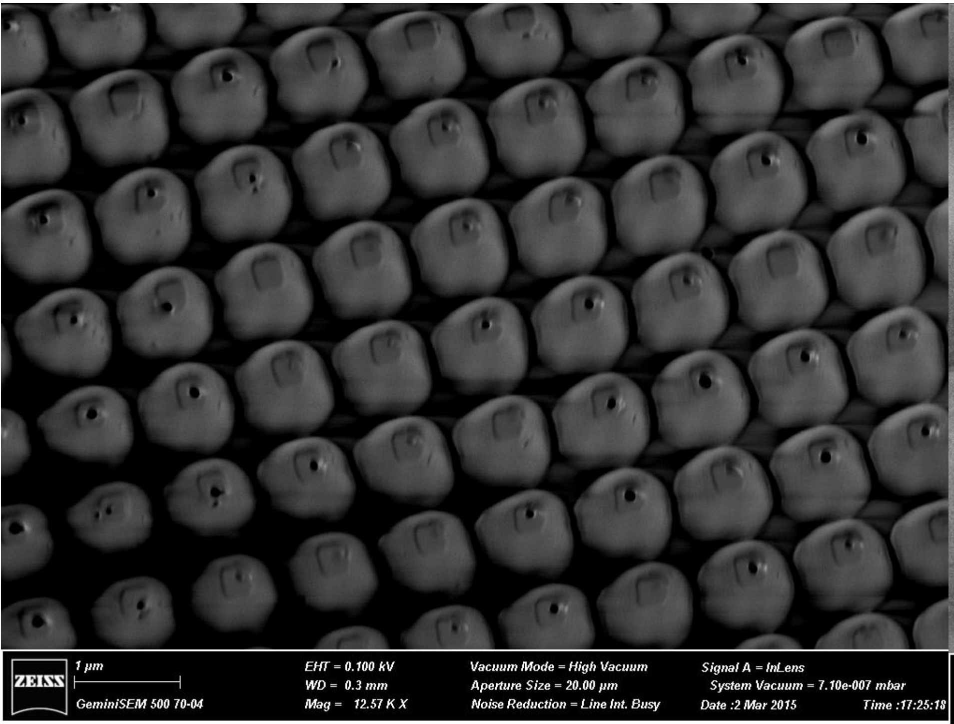
BEAMSLEEVE (CONE)



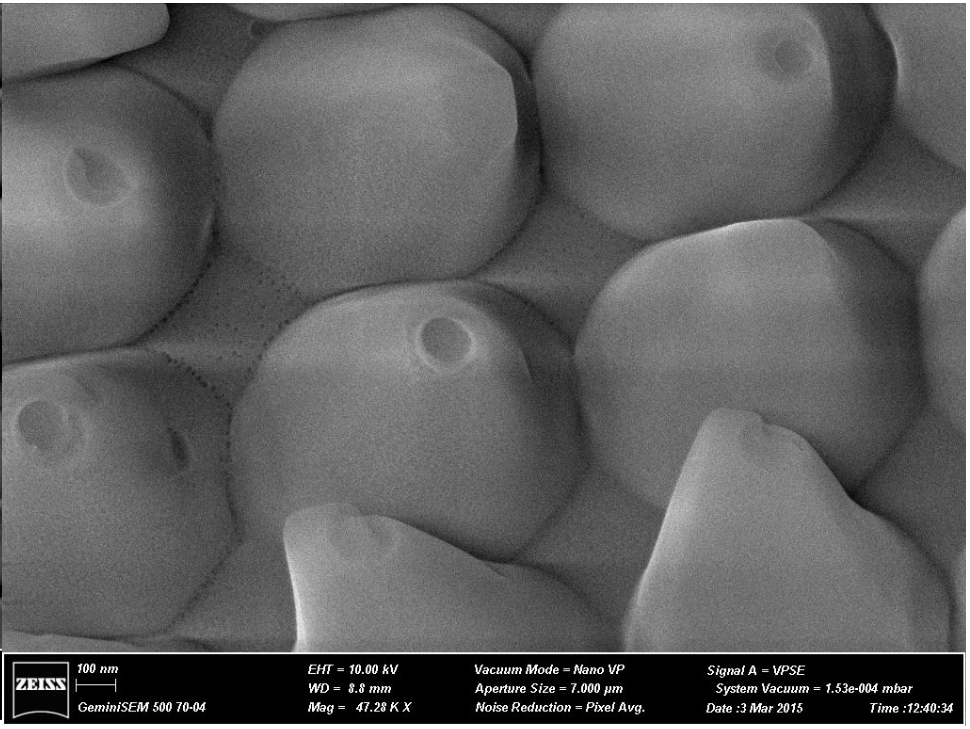
Surtout cette limitation

WD = 6 mm

Exemple – polymère



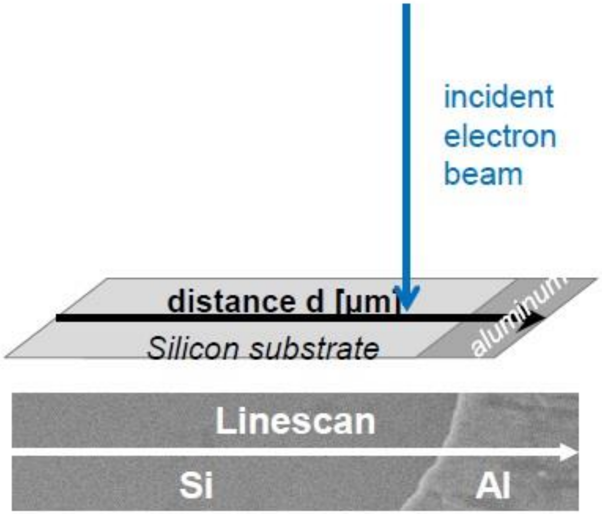
ZEISS 1 µm GeminiSEM 500 70-04
EHT = 0.100 kV
WD = 0.3 mm
Mag = 12.57 K X
Vacuum Mode = High Vacuum
Aperture Size = 20.00 µm
Noise Reduction = Line Int. Busy
Signal A = InLens
System Vacuum = 7.10e-007 mbar
Date :2 Mar 2015
Time :17:25:18



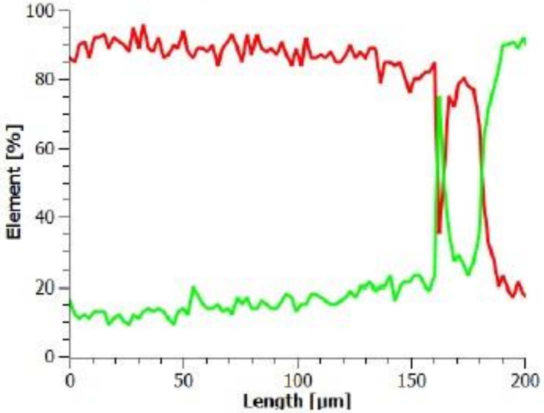
ZEISS 100 nm GeminiSEM 500 70-04
EHT = 10.00 kV
WD = 8.8 mm
Mag = 47.28 K X
Vacuum Mode = Nano VP
Aperture Size = 7.000 µm
Noise Reduction = Pixel Avg.
Signal A = VPSE
System Vacuum = 1.53e-004 mbar
Date :3 Mar 2015
Time :12:40:34

il y a des limites pour la pression variable NanoVP
EHT min 3 kV et WD min 8 mm
Les images en HV sont toujours plus résolues
MAIS…pour l’EDS et l’EBSD on a besoin des tensions plus élevées
C’est possible avec NANOVP

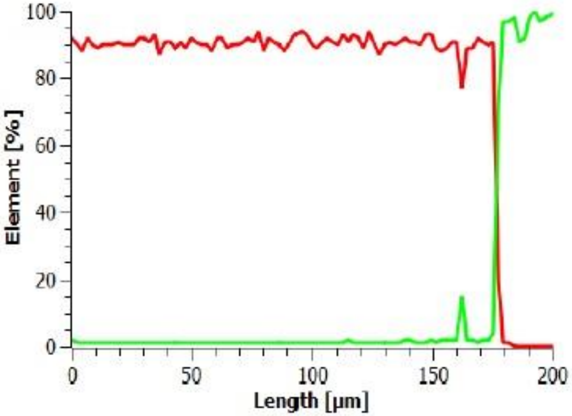
EDS analysis in VP mode



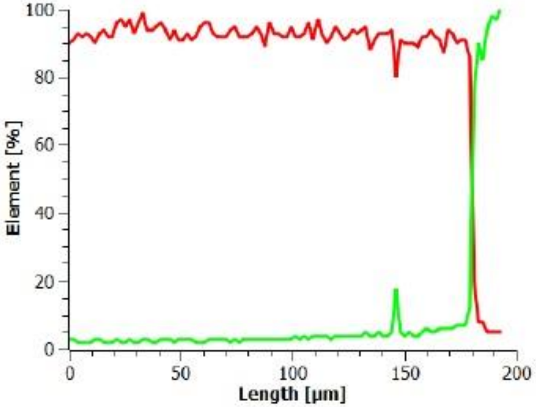
Normal VP 30 Pa



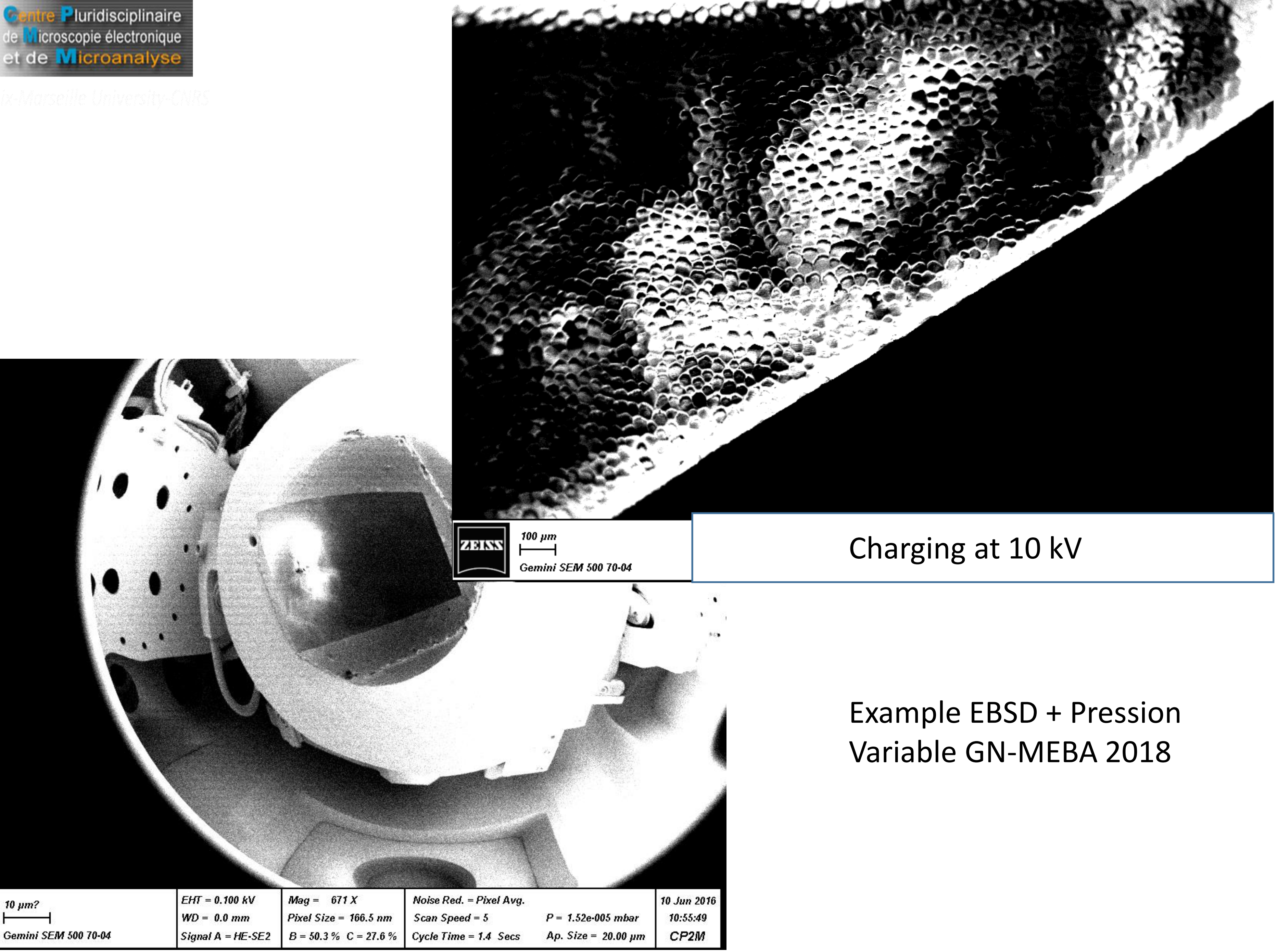
High Vaccum



NanoVP 30 Pa



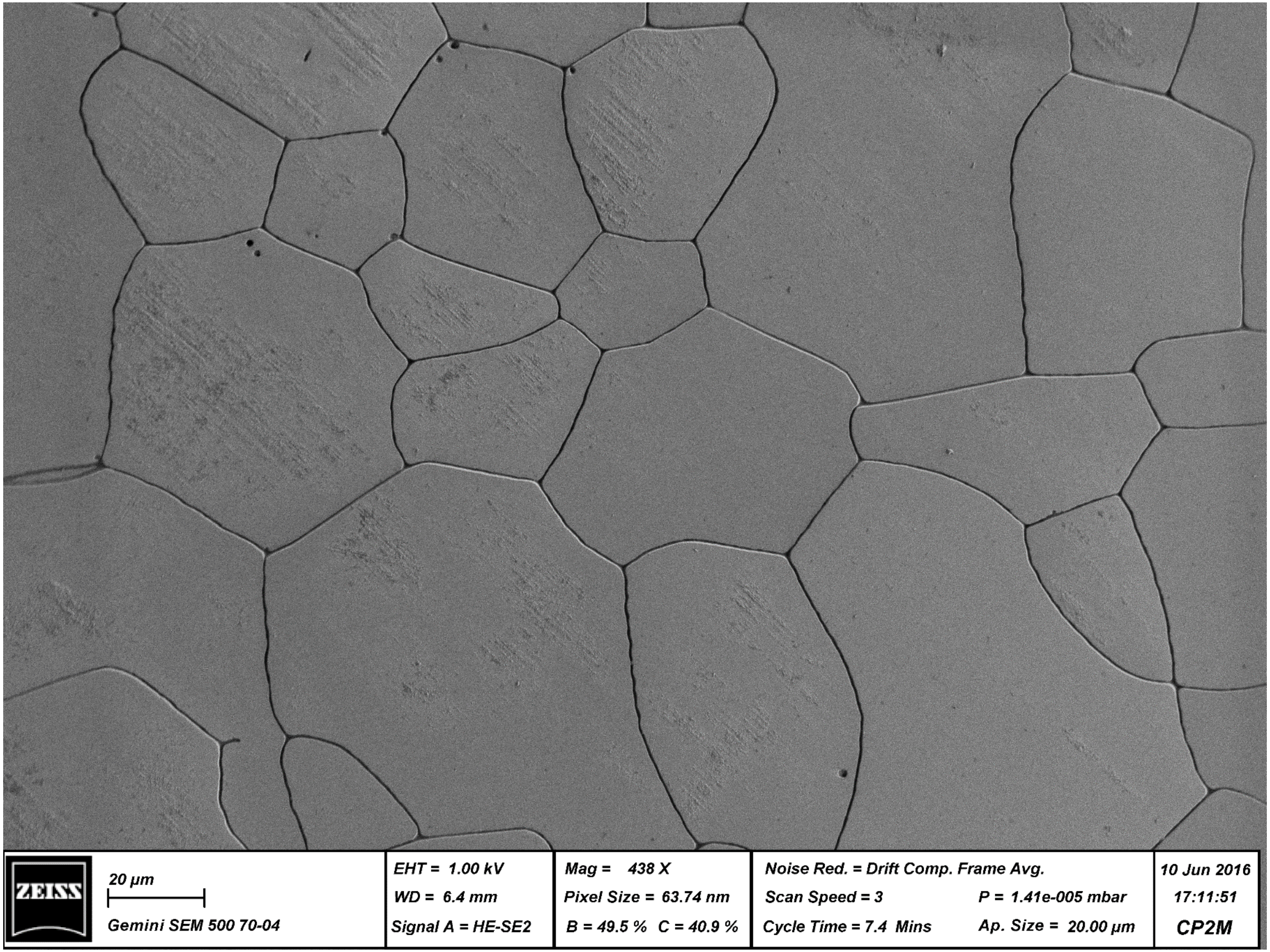
- Normal VP mode does not combine well with EDS analysis. The skirt effect creates a highly delocalized elemental signal.
- By controlling BGPL in NanoVP mode, spreading of EDS signal is largely reduced.
- High resolution EDS is possible on insulate samples with NanoVP.



Charging at 10 kV

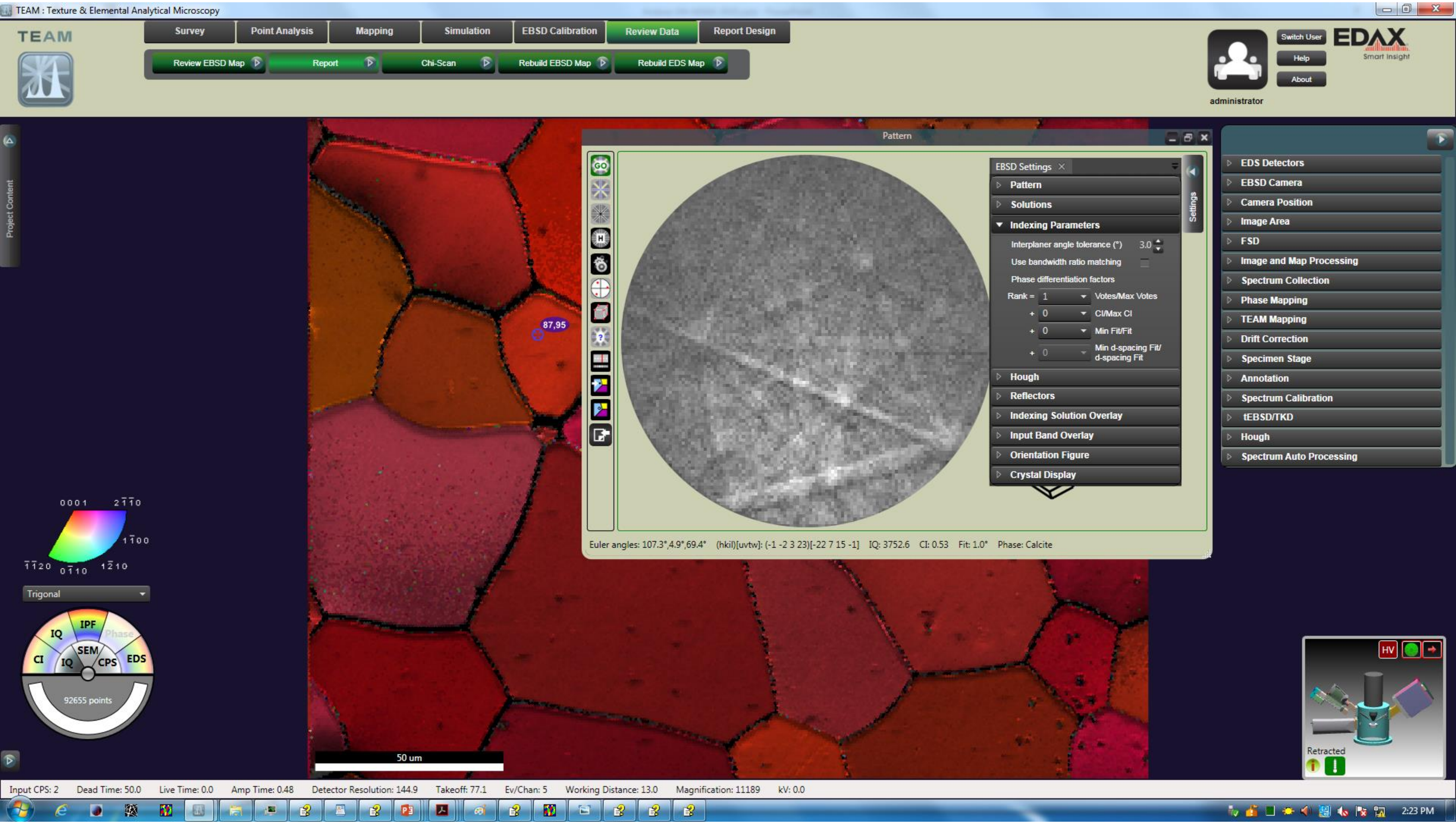
Example EBSD + Pression Variable GN-MEBA 2018

Low kV, pas de problème de charge



Centre Pluridisciplinaire
de Microscopie électronique
et de Microanalyse
ix-Marseille University-CNRS

Mode nano VP (avec beamsleeve) - 30 Pa – 15 kV



Interplaner angle tolerance (°) 3.0

Use bandwidth ratio matching ☐

Phase differentiation factors

Rank = 1 Votes/Max Votes
+ 0 CI/Max CI
+ 0 Min Fit/Fit
+ 0 Min d-spacing Fit/ d-spacing Fit

Euler angles: 107.3°,4.9°,69.4° (hkil)[uvtw]: (-1 -2 3 23)[-22 7 15 -1] IQ: 3752.6 CI: 0.53 Fit: 1.0° Phase: Calcite

Input CPS: 2 Dead Time: 50.0 Live Time: 0.0 Amp Time: 0.48 Detector Resolution: 144.9 Takeoff: 77.1 Ev/Chan: 5 Working Distance: 13.0 Magnification: 11189 kV: 0.0

Acta Materialia 223 (2022) 117491

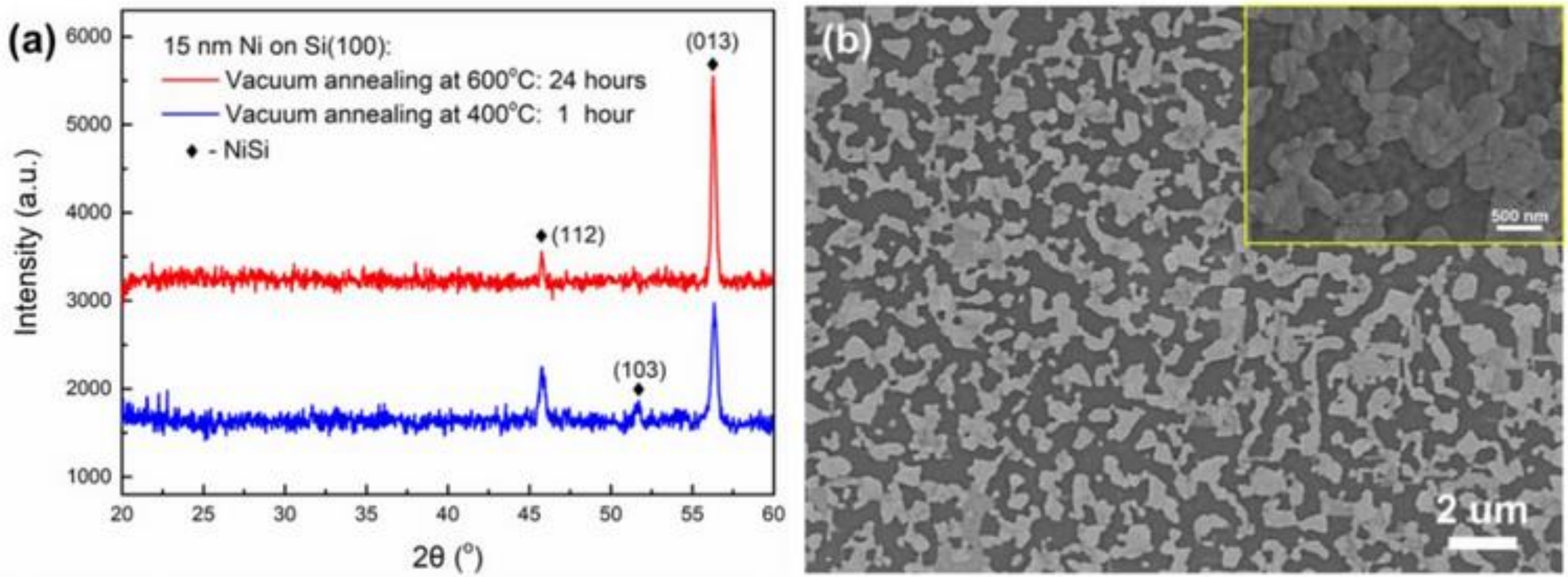


Fig.4 (a) XRD scan at room temperature and (b) Low kV SEM images for 15nm Ni on Si(100) substrate with annealing 24 h at 600 °C. The illustration in (b) shows the surface morphology of NiSi.

Centre Pluridisciplinaire de Microscopie électronique et de Microanalyse

jeudi 20 mai 2021 22:11

And, there is a question from the coauthor -----------: EBSD mapping for is really impressive and (for us at least !) strongly unusual! Did you use a specific procedure?

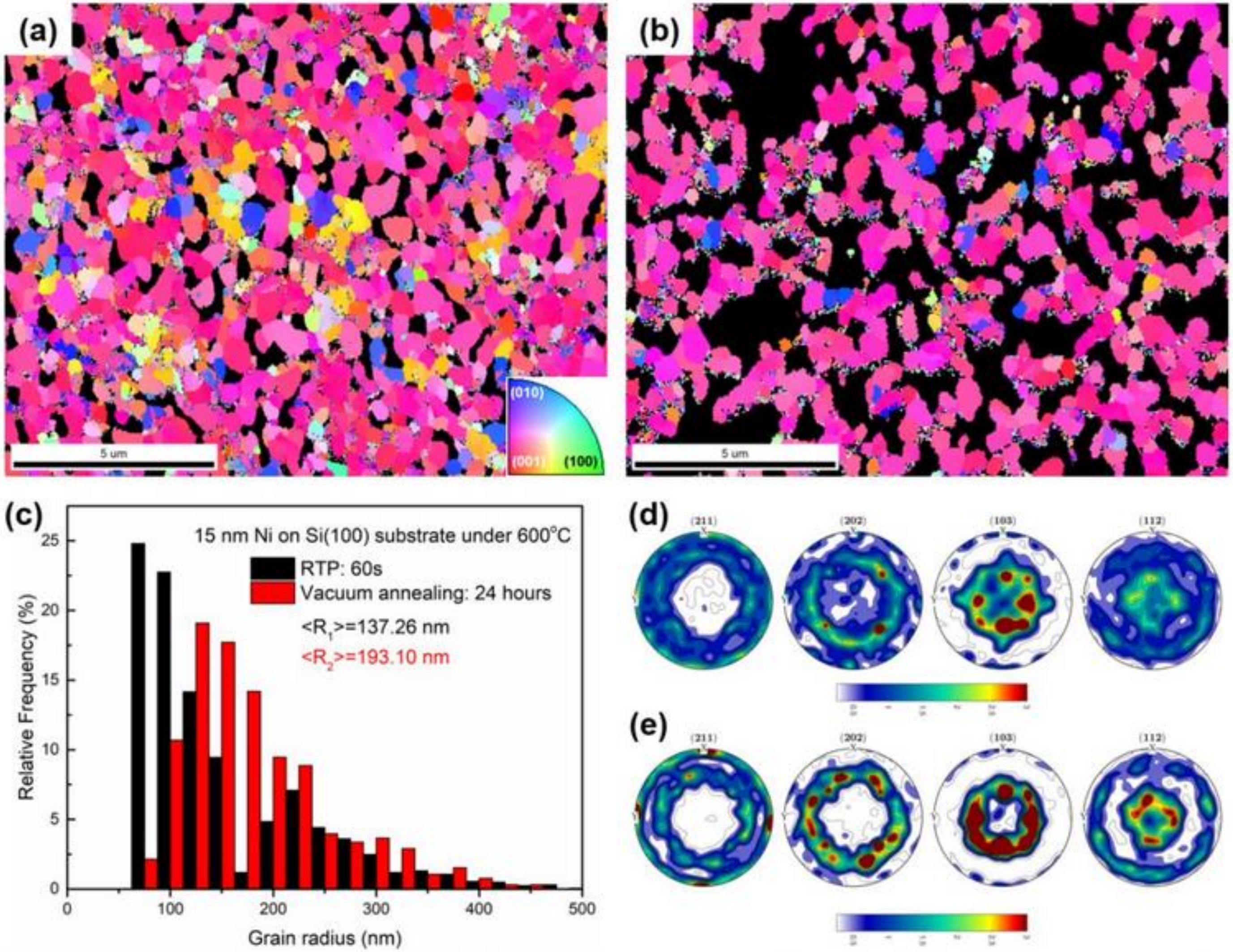


Fig.5 EBSD orientation maps and pole figures for 15nm Ni film on Si(100) substrate: (a) RTP at 600°C for 60s and (b) vacuum annealing 24 hours at 600°C, (c) grain size distribution, pole figures for 15nm Ni film on Si(100) substrate: (d) RTP at 600°C for 60s, (e) vacuum annealing 24 hours at 600°C.

12 kV

Beaucoup de Patience

OIM

Correlated TKD/EDS - TEM - APT analysis on selected interfaces of $CoSi_2$ thin films

Ultramicroscopy 206 **(2019)** 112807

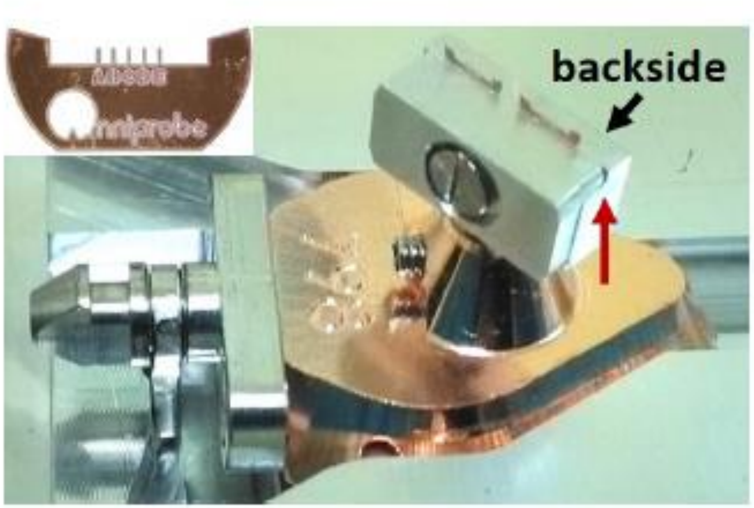


Figure 1: Modified SEM-TEM grid holder for FIB preparation of samples on TEM grids (Cu TEM-5-post half grids, top left), TKD and APT analysis. The backside is diminished to be suitable for TKD analysis. The step facilitates transfer and alignment of the grids. The stub is thinned to fit in the conventional APT holder.

Ultramicroscopy 206 **(2019)** 112807

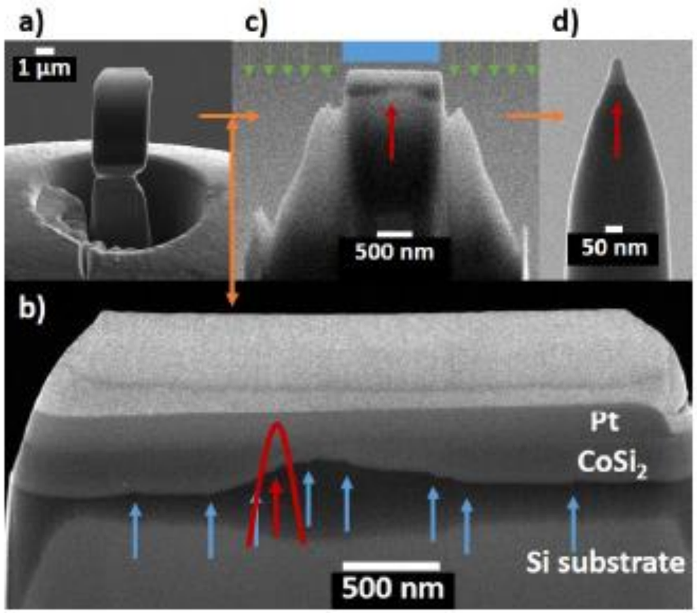
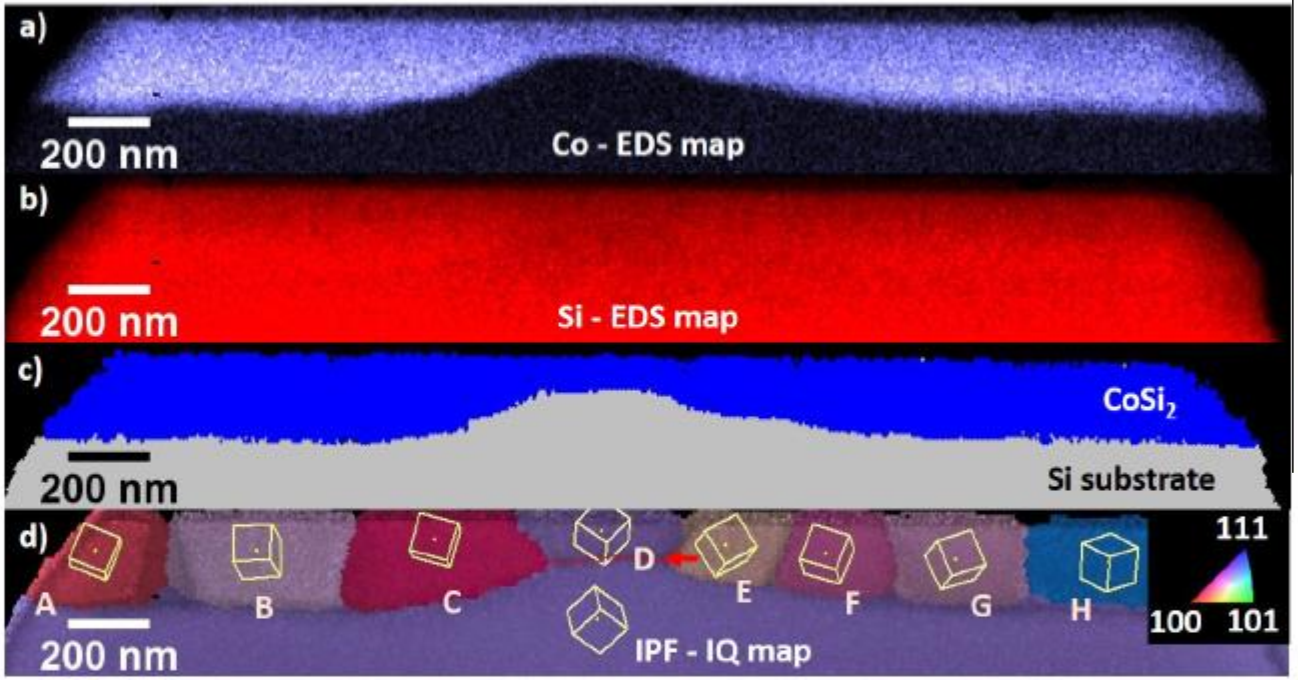
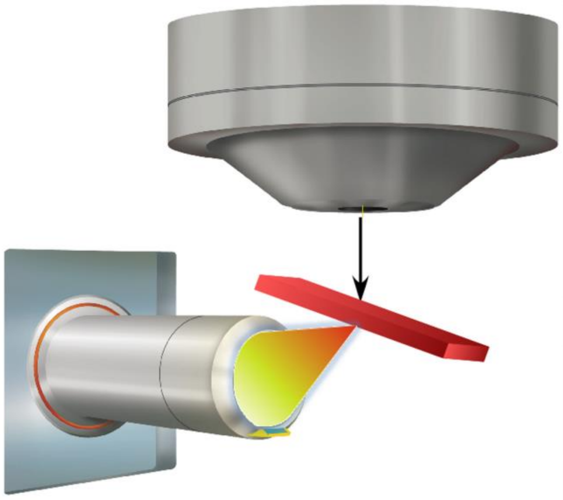
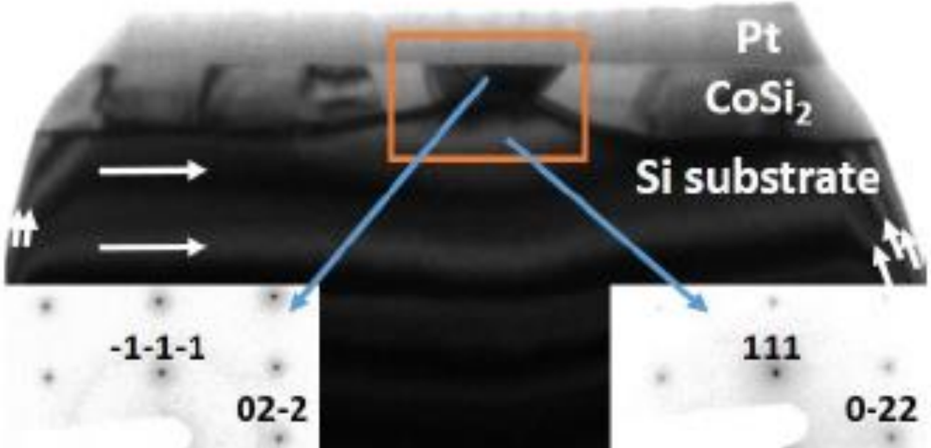


Figure 5: SEM sideview on sample before and during annular milling. a) Sample after TEM analysis. b) Indications from the interface (red arrow and blue arrows) can be used to place the annular mask arround the ROI by measuring the distances to the borders. c) Milling pattern (green arrows milling region) with the center on the ROI (red arrow). Reducing the inner radius of the pattern allows to control the position of the ROI. d) Final tip for APT analysis including ROI.

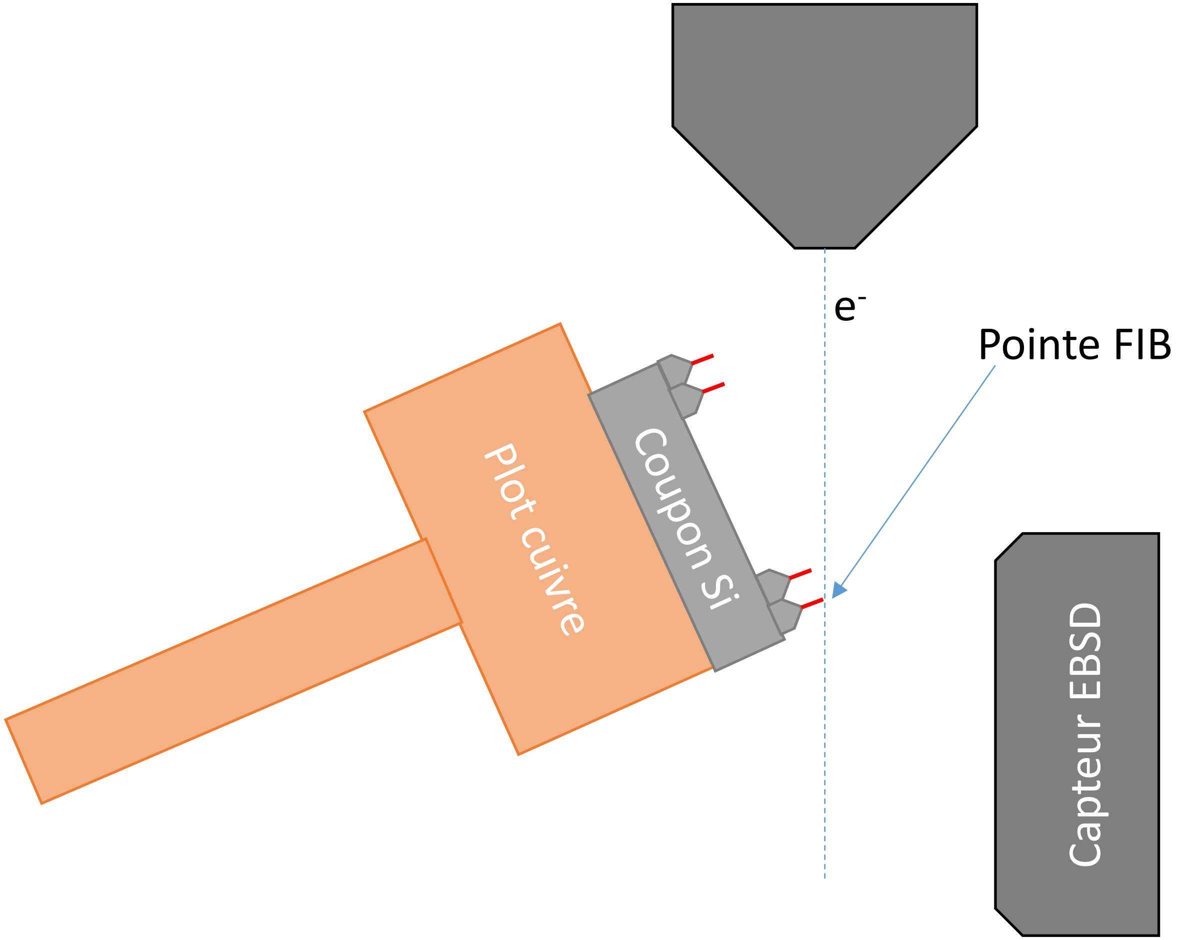
TKD

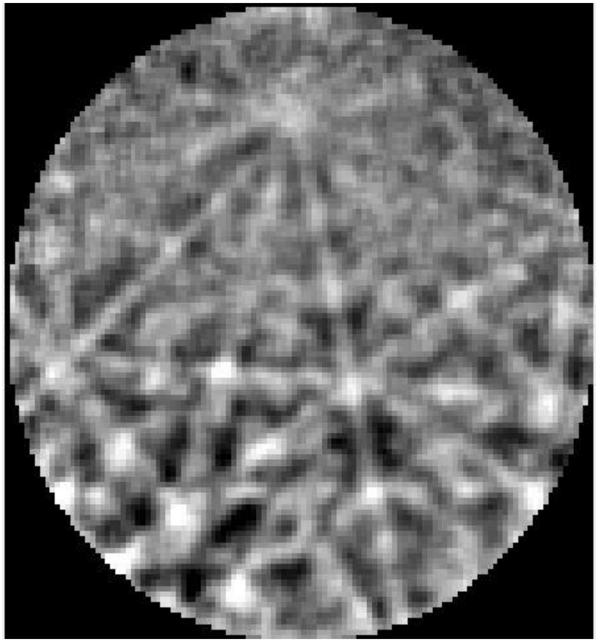

a)
200 nm
Co - EDS map
b)
200 nm
Si - EDS map
c)
$CoSi_2$
200 nm
Si substrate
d)
A
B
C
D
E
F
G
H
111
100
101
200 nm
IPF - IQ map




Pt
$CoSi_2$
Si substrate
-1-1-1
02-2
111
0-22

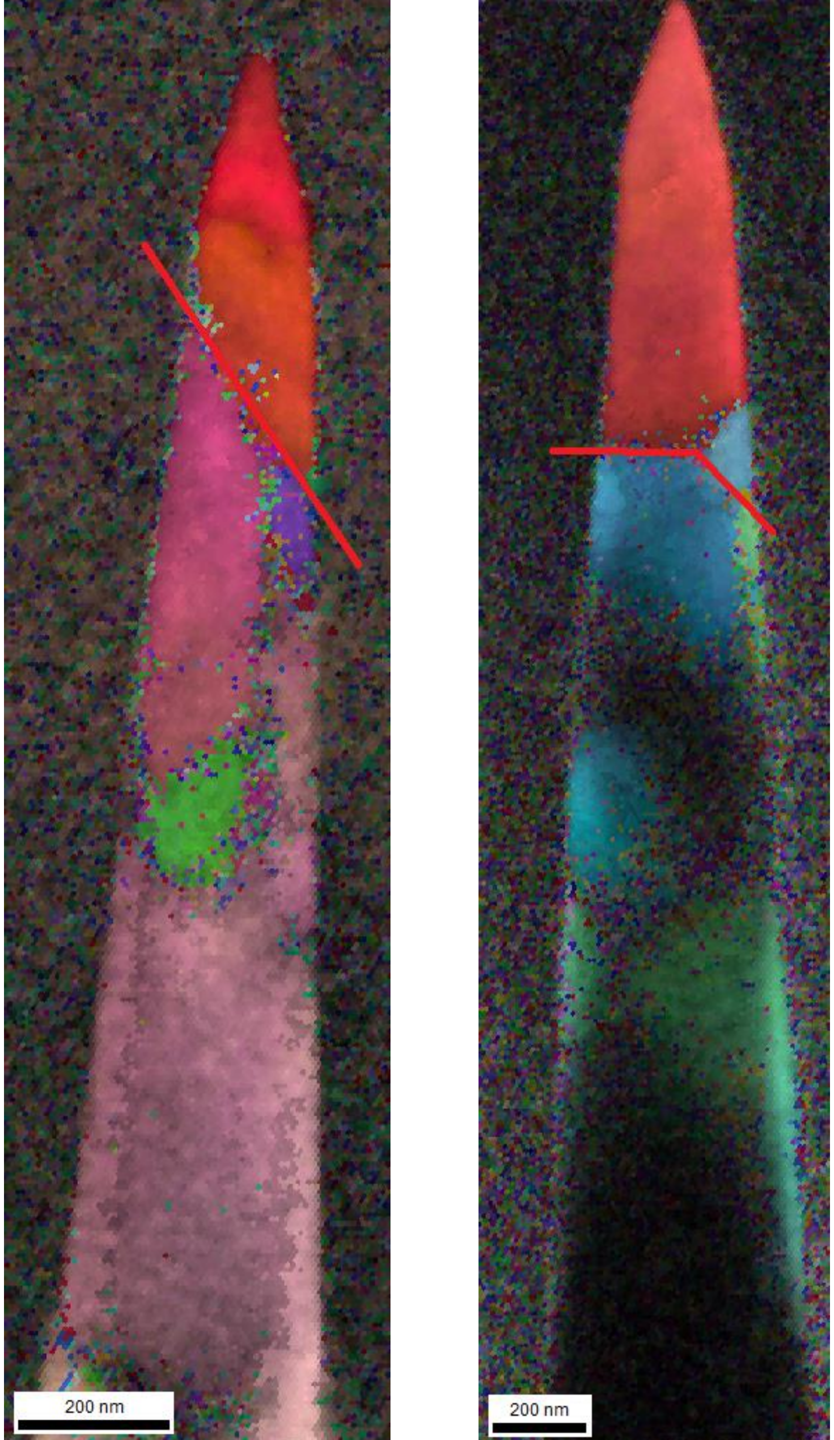
Sonde atomique et TKD





1 min d'acquisition

Examples pointes
Pierre Douguet
IM2NP



Potential of Ligand-Promoted Dissolution at Mild pH for the 2 Selective Recovery of Rare Earth Elements in Bauxite Residues

ACS Sustainable Chem. Eng. 2022, 10, 21, 6942–6951

ACS Sustainable Chemistry & Engineering pubs.acs.org/journal/ascecg Research Article

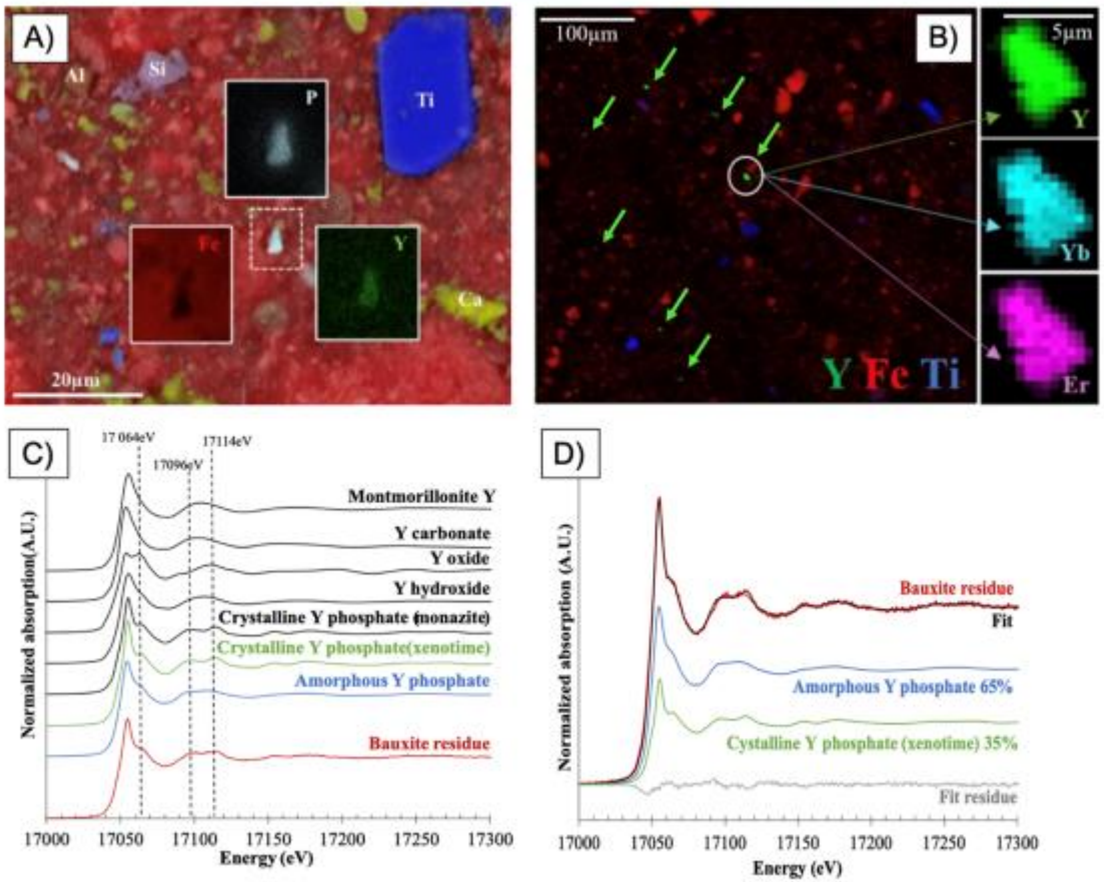
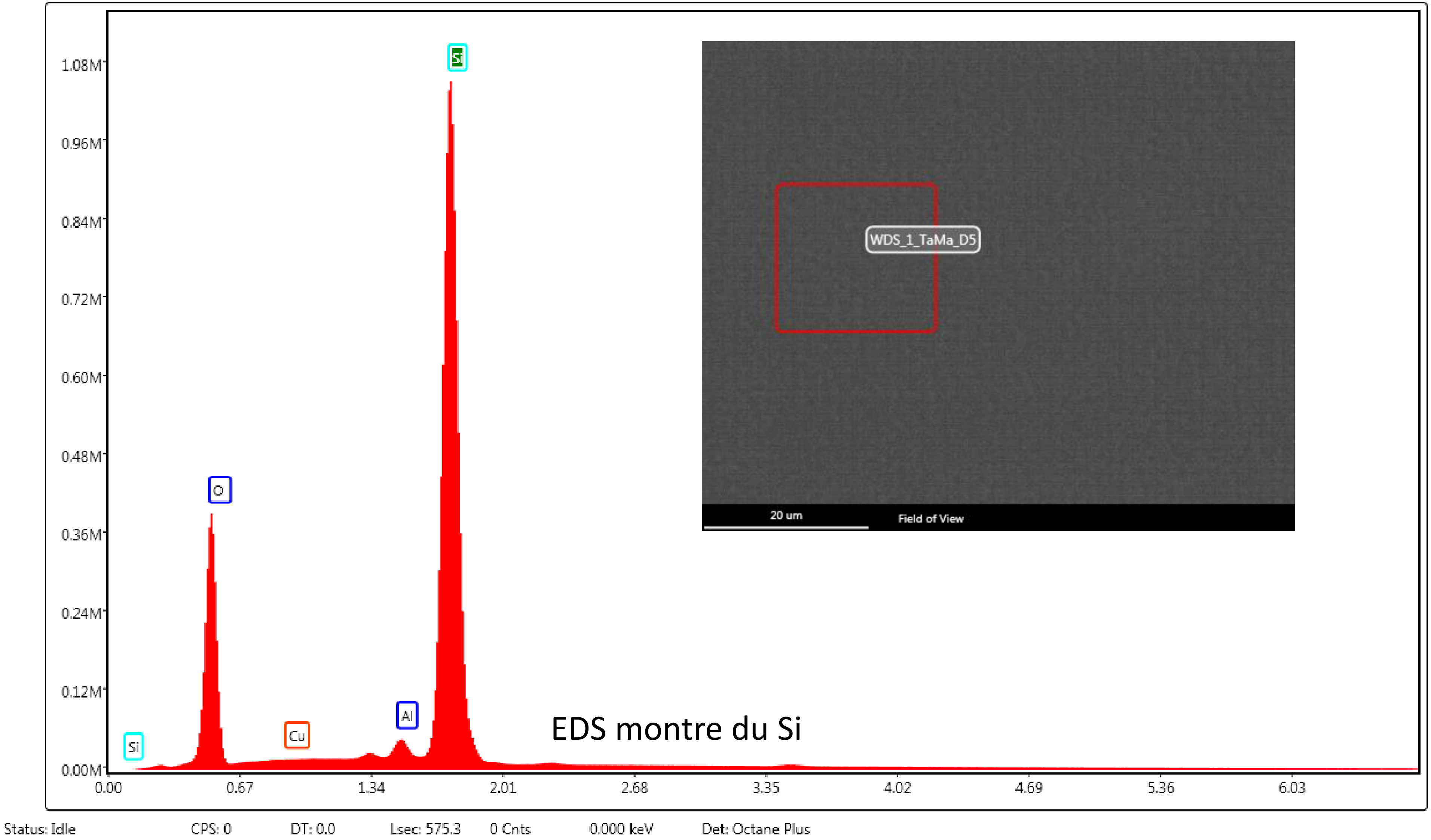


Figure 1. (A) Combined elemental map obtained by SEM−EDX showing the spatial correlation between Al, Si, Ti, Fe, Ca, Y, and P in the BR sample (30 kV, pixel = 71.11 nm). (B) Combined elemental map obtained by nano-XRF showing the distribution of Fe, Ti, Y Yb, and Er in the BR sample (1 px = 1 μm for the large image, 1 px = 400 nm for small images). (C) Bulk XANES spectra of BR and model compounds at the Y K-edge and (D) LCF performed with Athena software (*R*-factor = 0.0009) (right).

Collaboration avec le CEREGE

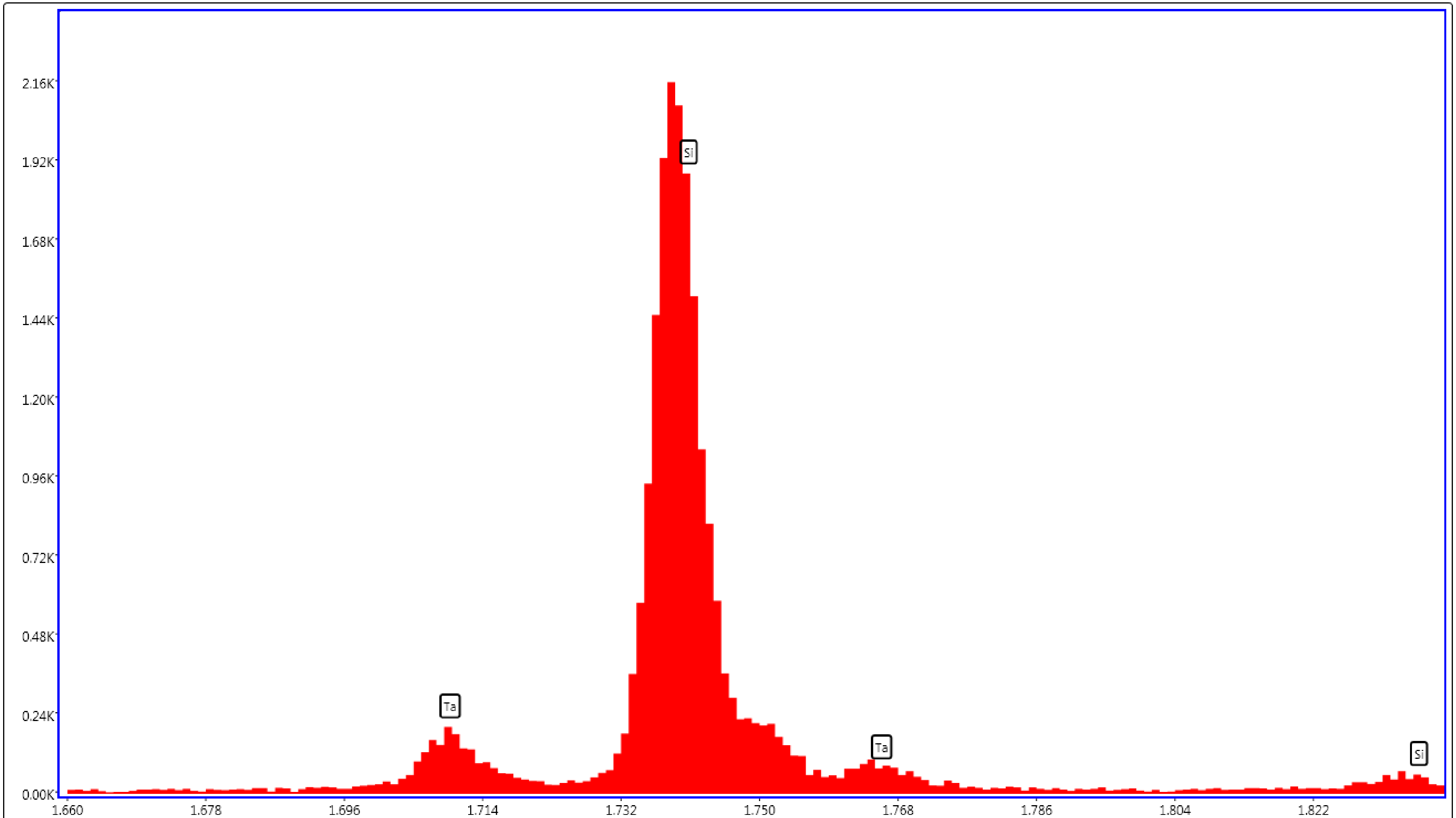
Atteia, Aix-Marseille Université



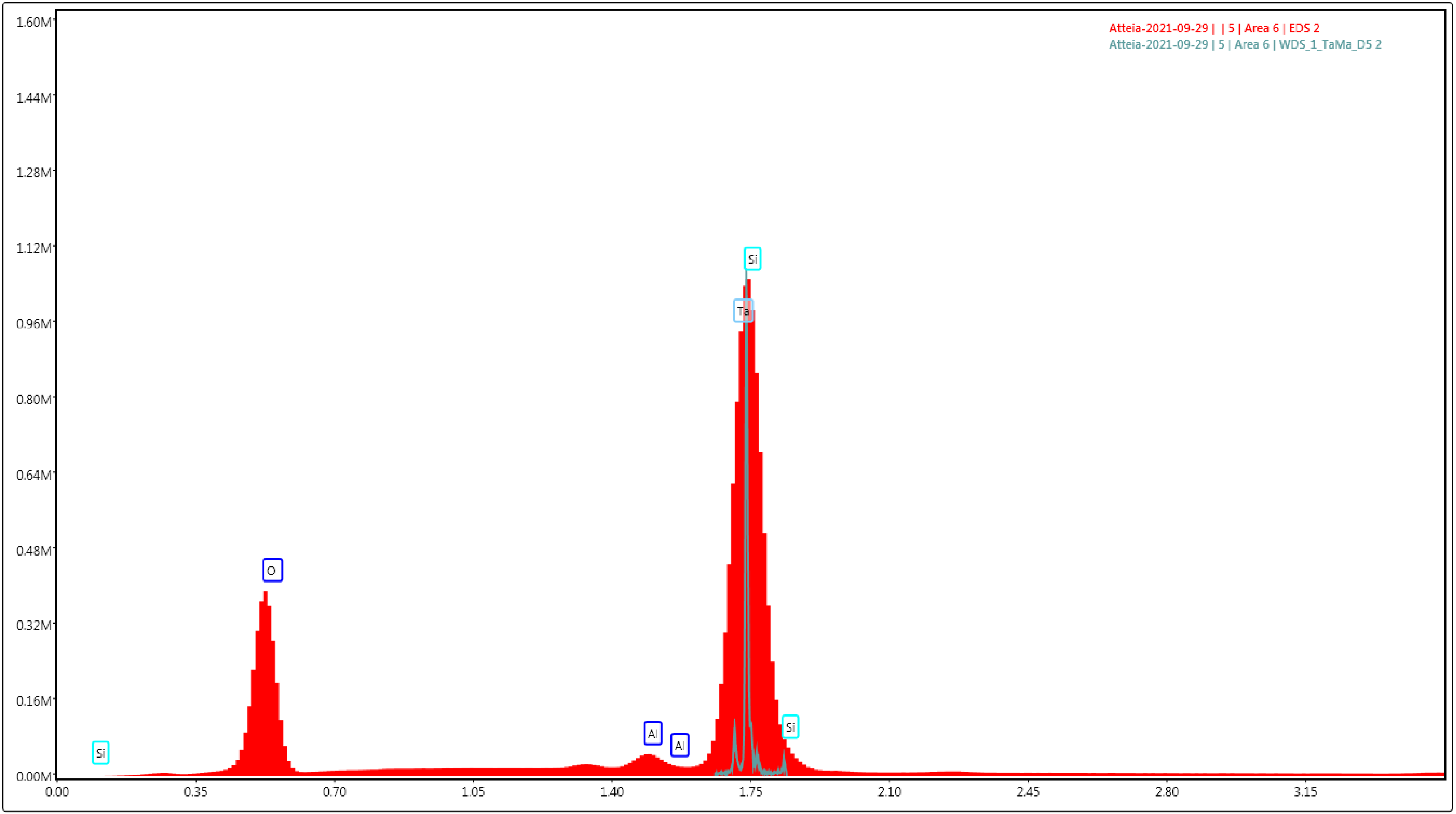
Status: Idle CPS: 0 DT: 0.0 Lsec: 575.3 0 Cnts 0.000 keV Det: Octane Plus

EDS montre du Si

WDS montre la présence de Si et Ta



WDS + EDS



Status: Idle CPS: 1 DT: 0.0 Lsec: 1.0 0 Cnts 0.000 keV Det: Apollo XF

CONCLUSION

Avec un système doté de 7 détecteurs pour l'imagerie et 3 détecteurs de techniques analytiques, il est possible de caractériser une vaste gamme de matériaux en synergie avec d'autres techniques comme TEM, DRX, AFM, RAMAN.

Imagerie	
HE-SE2 In-Lens	Électrons secondaires
VPSE	Photons (détection indirecte des électrons secondaires)
BSD BSE VPBSD	Électrons rétrodiffusés
aSTEM	Électrons transmis

Analytique

EDS

WDS

EBSD (tkd)

Perspectives: upgrade de programmes, détecteurs; modules in-situ