Heating experiments in STEM-EDS

Bruker Nano Analytics, Berlin, Germany
Webinar, August 29, 2018

Presenters

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Global Product Manager TEM
Bruker Nano Analytics, Berlin, Germany

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DENSsolutions, Delft, Netherlands

Dr. Igor Németh

Application Scientist, EDS
Bruker Nano Analytics, Berlin, Germany

Outline

Part 1. (S)TEM sample holder optimization

Mauro Porcu, DENSsolutions

- In-situ applications
- The new heating Nano-chip
- Wildfire product family

Part 2. Heating experiments (EDS mapping study at elevated temperatures) - Igor Németh, Bruker Nano

- IR effects under control: low energy threshold, peak broadening
- Demonstrate elemental mapping results up to 1000° C for the first time in literature
- Autophase results

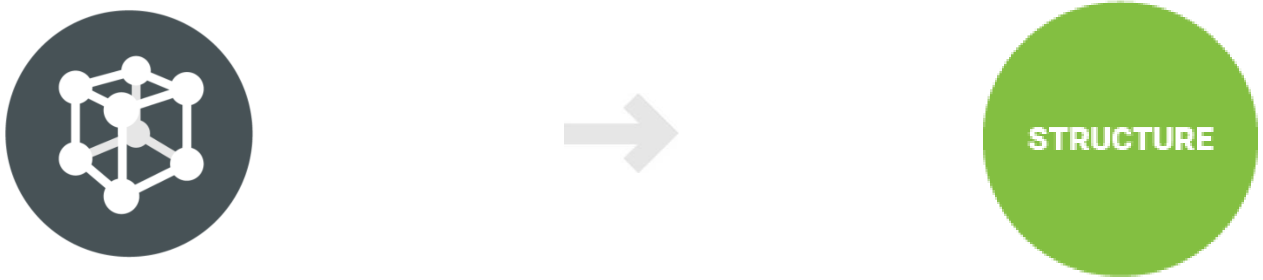
INNOVATIONS THAT MATTER

The Wildfire solution: superior in situ TEM heating

Mauro Porcu, Marketing Manager

The power of In Situ TEM

Traditional TEM



DENS solutions
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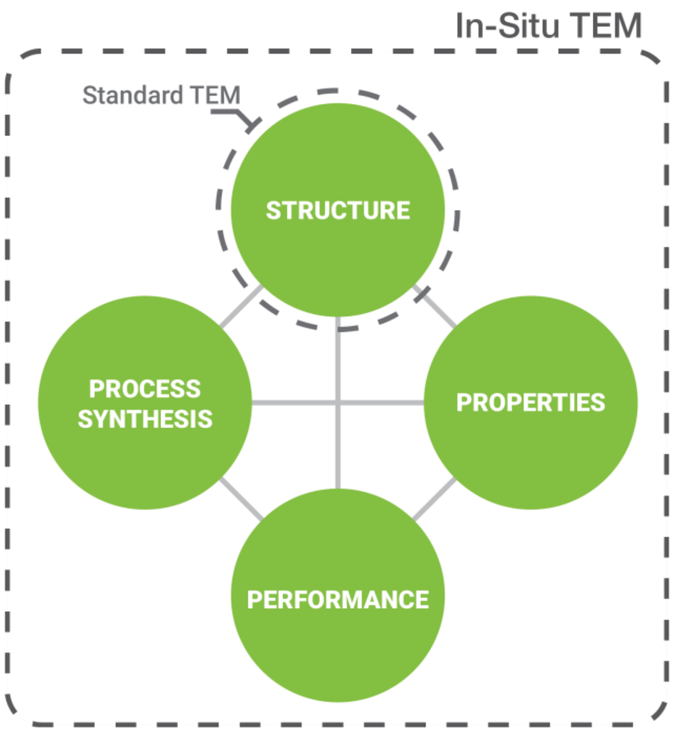
The power of In Situ TEM

In situ TEM



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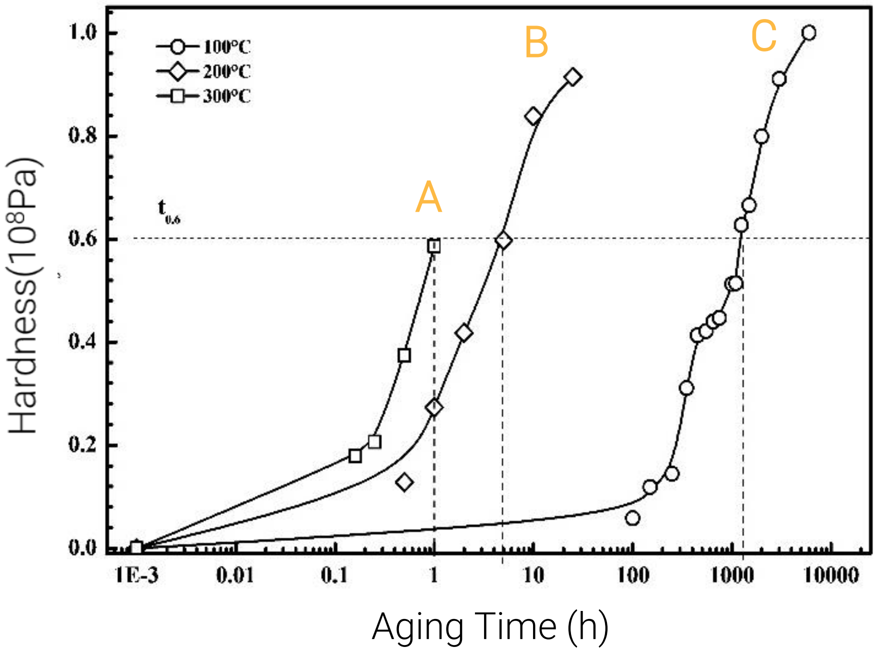
The benefit of in situ heating

Precipitation hardening of metal alloys

Challenges:

- Optimising heat treatments in the production process

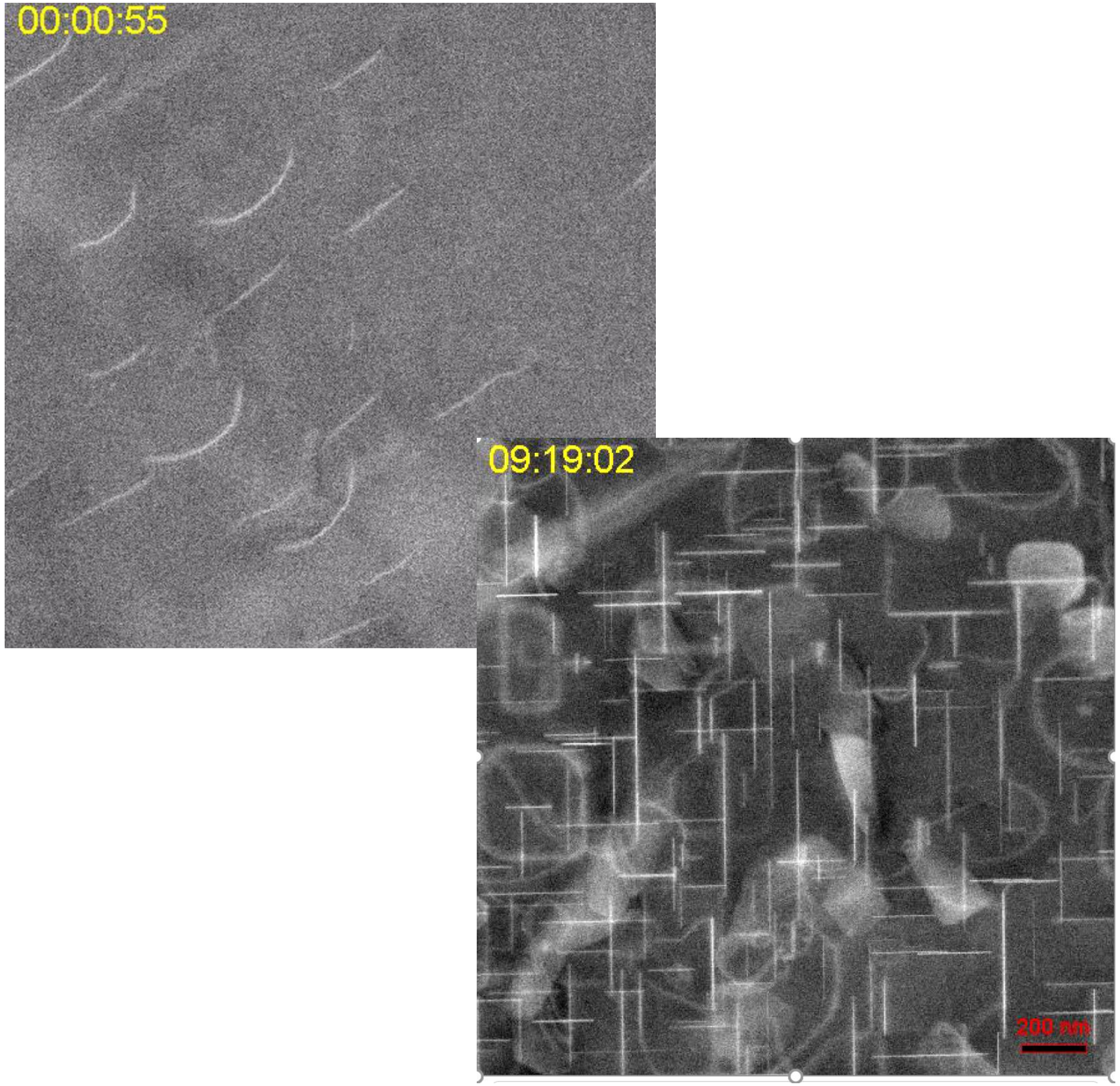
Process and Property relation



INNOVATIONS THAT MATTER

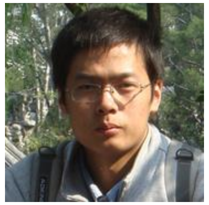
Correlate structure with properties

Precipitation hardening of metal alloys



Challenges: Optimising heat treatments in the production process

Researcher:
Dr. C. Liu



Double tilt Heating

Conditions: FIB lamella, 140 – 200 °C, 20 hours, HAADF STEM

Results: Mechanism of the morphological evolution of the precipitates in Al alloys

Liu, Chunhui, et al. Scientific reports 7 (2017).

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INNOVATIONS THAT MATTER

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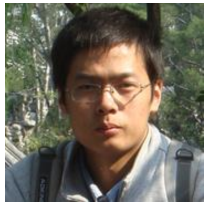

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Results: Mechanism of the morphological evolution of the precipitates in Al alloys

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"For this we used the MEMS based heating holder which allows precise control of the temperature, a very low specimen drift and high stability of the sample during heating."

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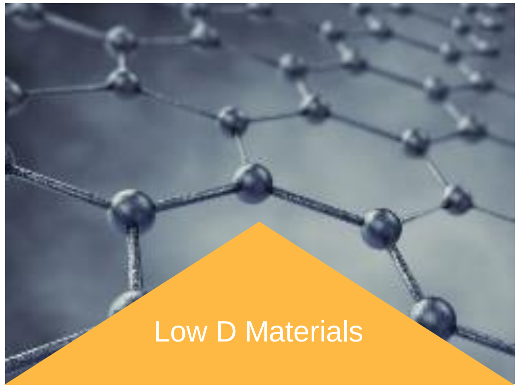
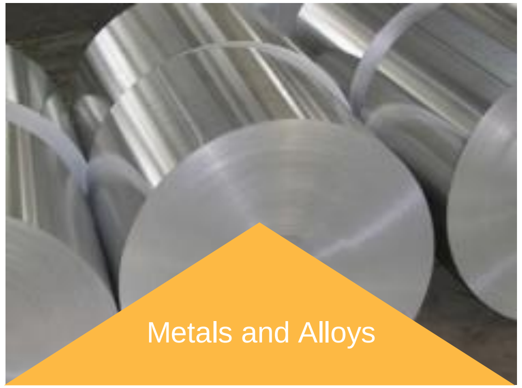
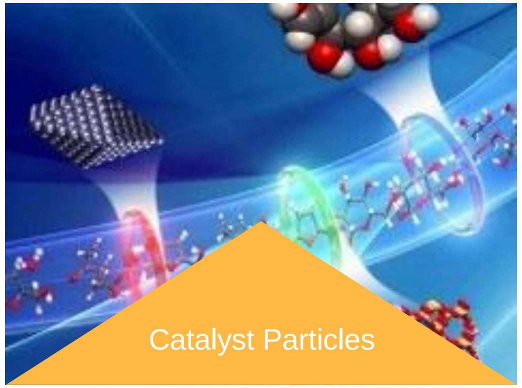
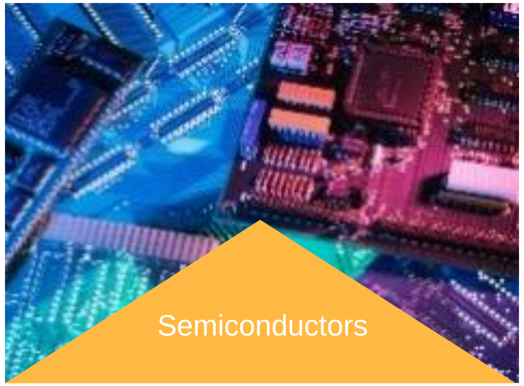
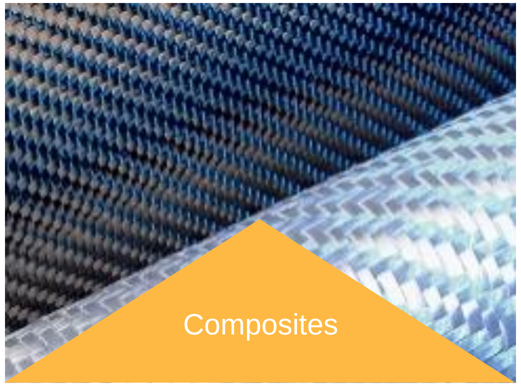
In situ heating applications

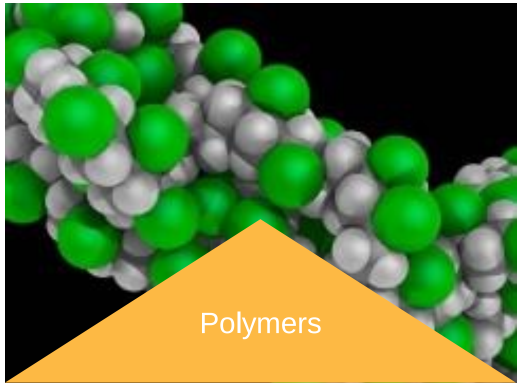












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The new heating Nano-Chip

Optimized heater's dimensions and shape
Improved stability, temperature uniformity and IR emission

Optimized for sample handling
Largest viewable area and optimum design to safely handle the most common types of samples

> 850 μm^2
Viewable area

+

Optimized
for different samples

→

Increased
success rate

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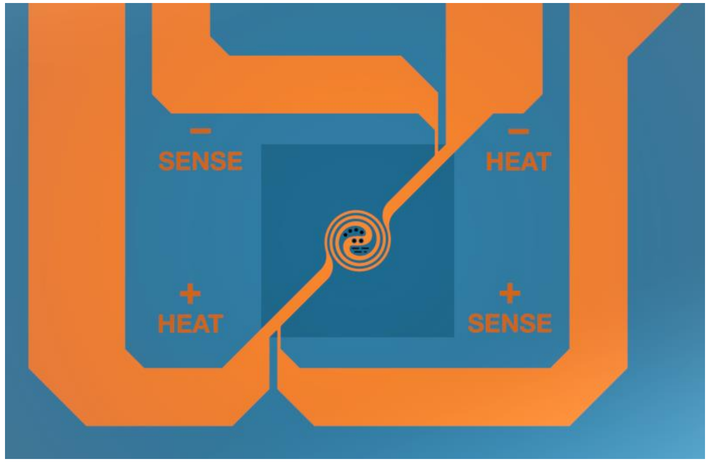
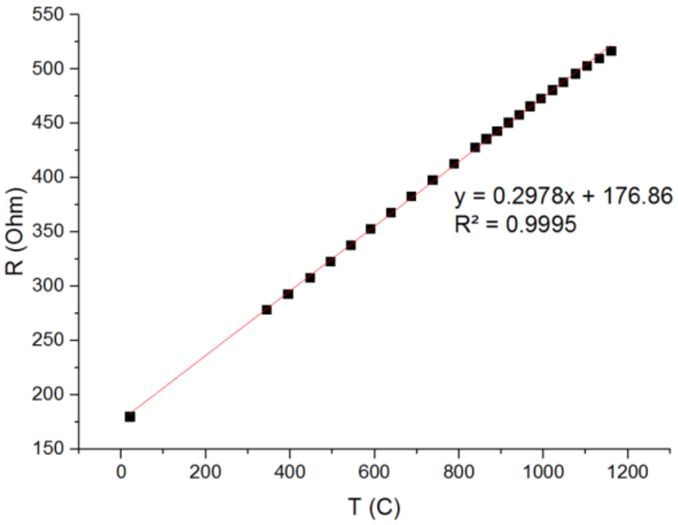
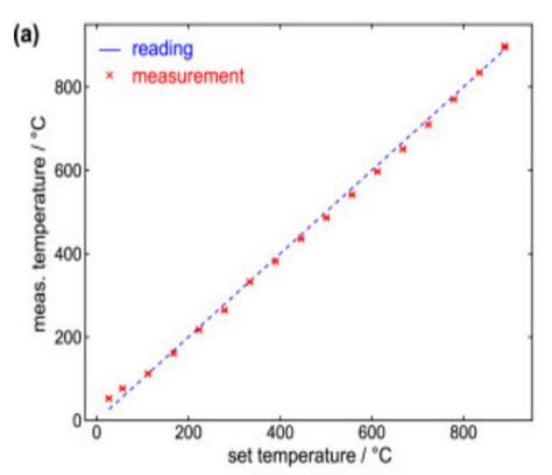
Results you trust

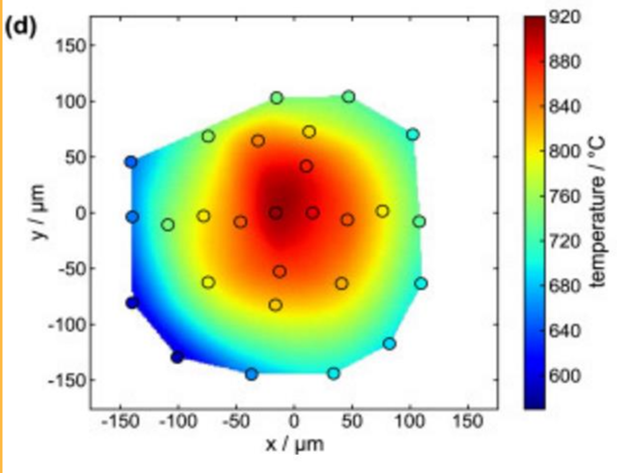
Local temperature measurements
Resistance as a temperature indicator



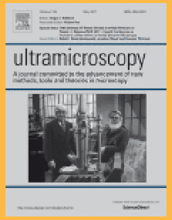


Temperature **accuracy** and **homogeneity proven by customers** by local measurements in TEM





The **local sample temperature** is measured in TEM by NB electron diffraction. Results indicate a high temperature uniformity with **deviations around 3%.**



Florian Niekiel, et al. Ultramicroscopy (2016).

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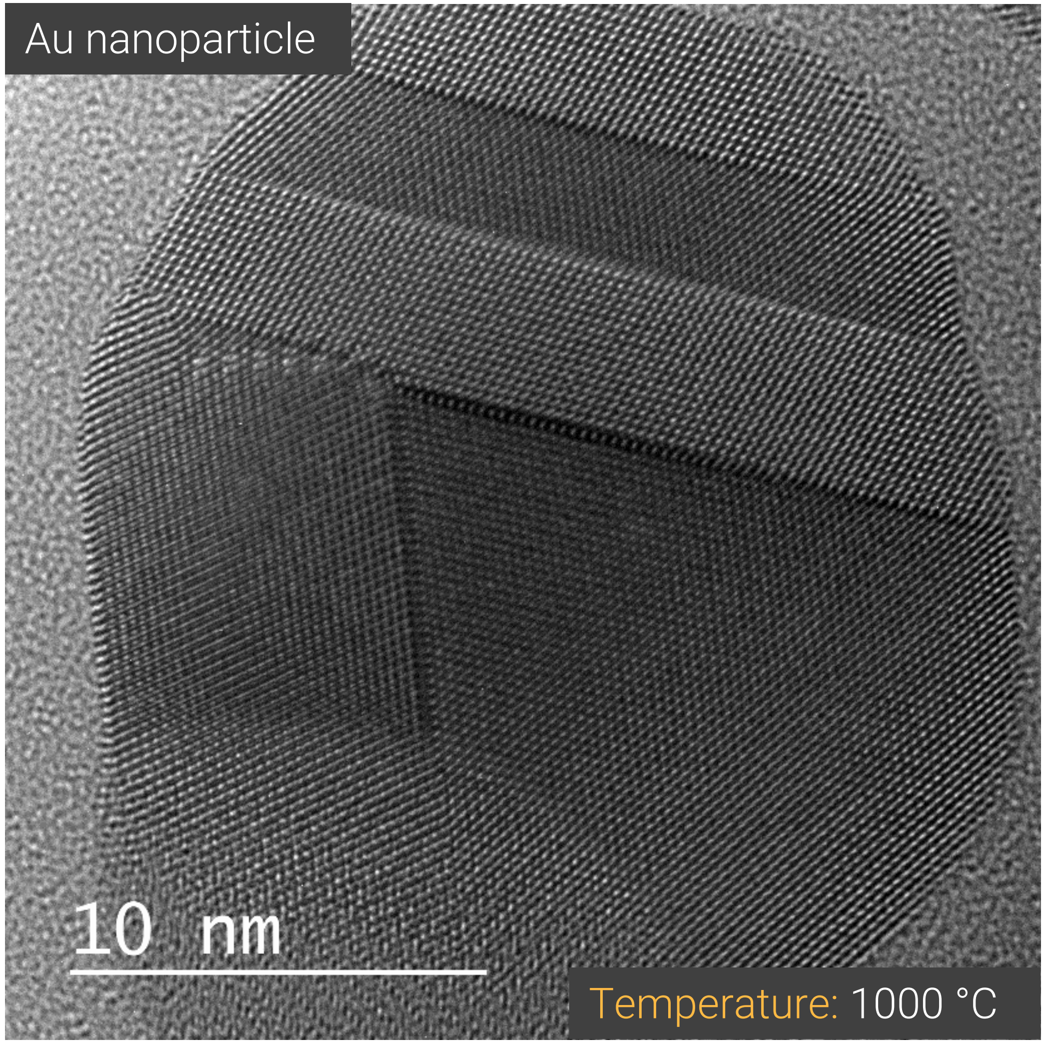
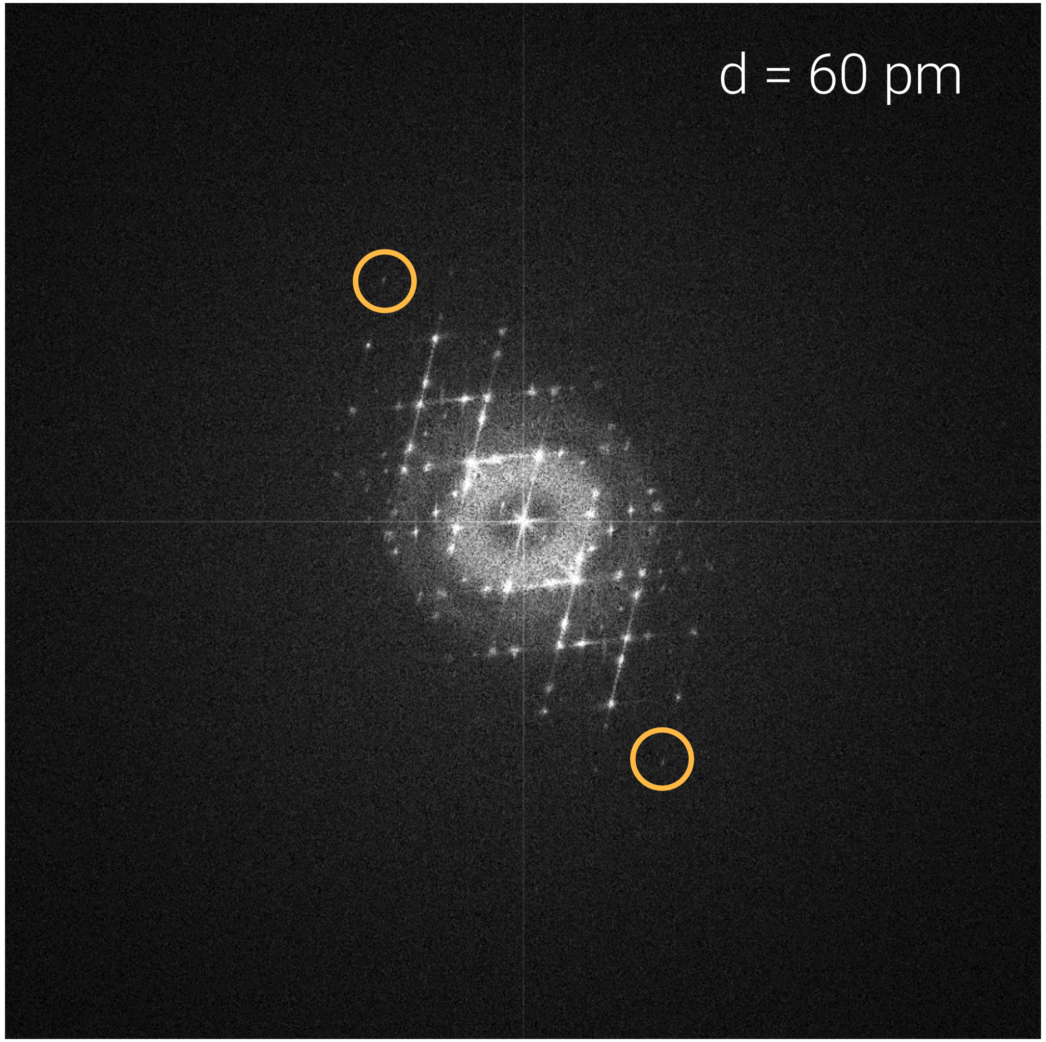
Full S/TEM performance guaranteed

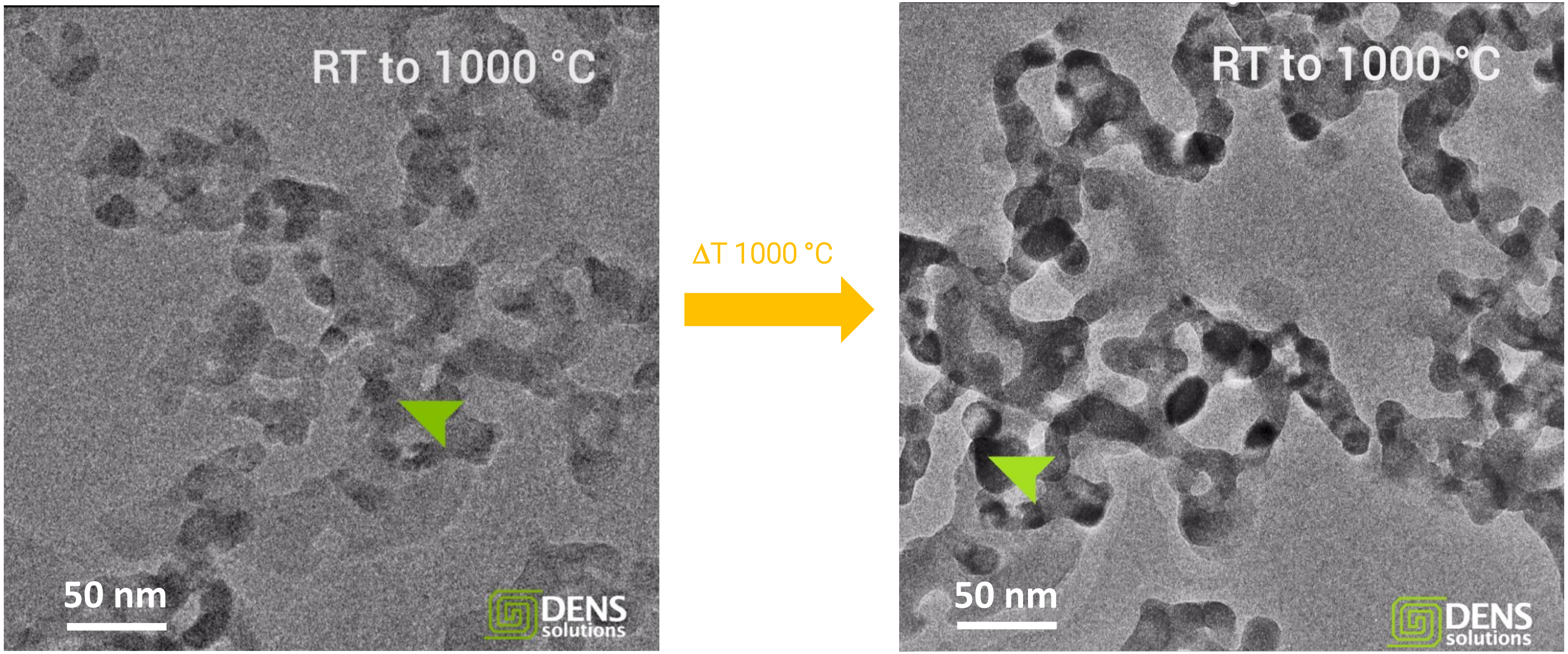
The best TEM performance in any environment





Never miss a thing

The highest sample stability in 3 dimensions



<200 nm	Displacement for ΔT 1000 °C	<0.3 nm/min	Drift rate at 1000 °C after <60 s

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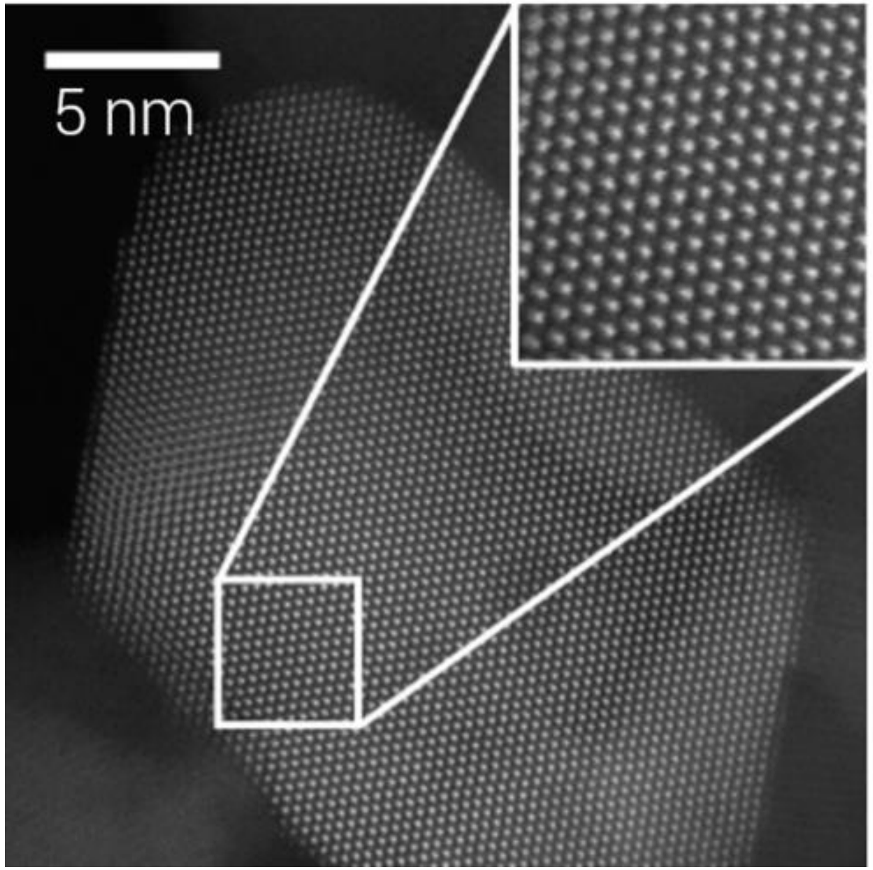
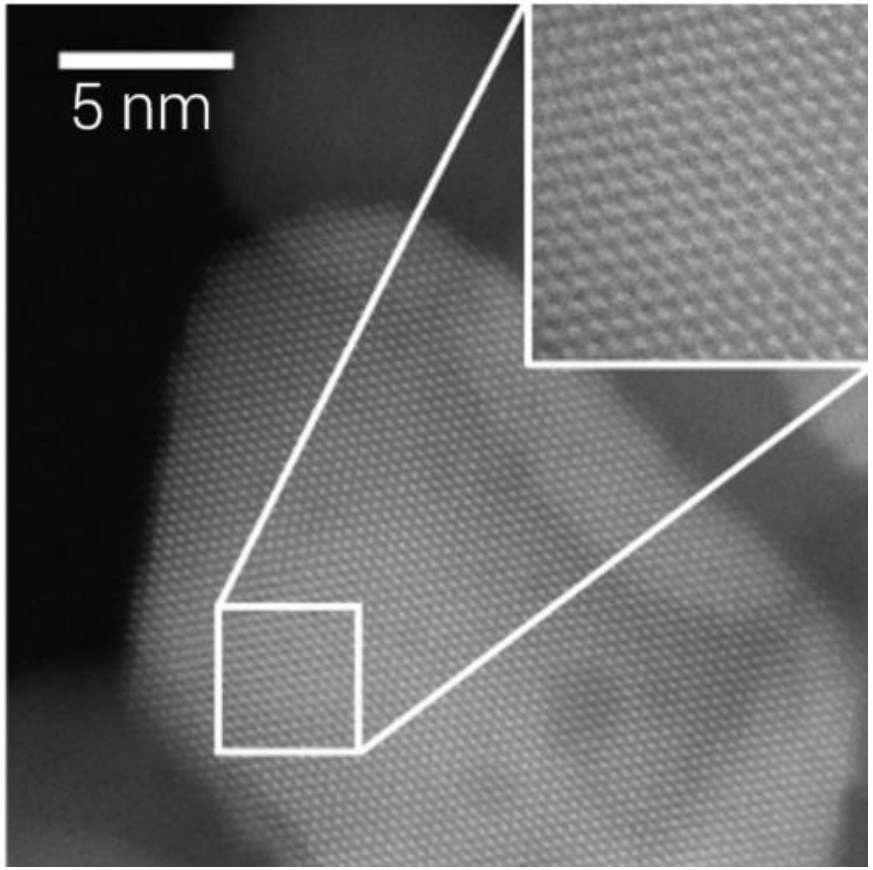
Less bulging: better resolution?

From RT to 750 °C, image refocused with FOCUS



NEW design



PREVIOUS design

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Fast results with more impact

Impulse, the next-gen in situ SW

impulse

Features:

- Synchronized control of all in situ stimuli
- Graphical profile builder
- Fully customizable UI

Benefits:

- Easily correlate all the in situ parameters
- Set up complex experiments with only few mouse clicks
- Monitor conveniently only the parameters that matter

http://denssolutions.com/impulse/

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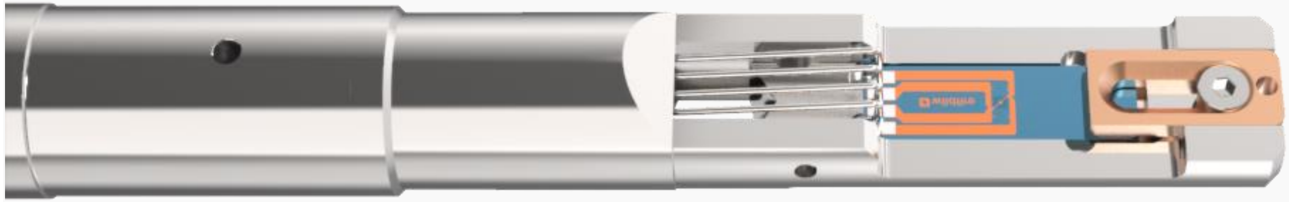
The complete Wildfire range

Our products

Thermo Scientific TEM



Wildfire H	Wildfire H+	Wildfire H+ 3D	Wildfire H+ DT
RT – 600 °C	RT – 1300 °C	RT – 1300 °C	RT – 1300 °C
±30 ° alpha tilt	±30° alpha tilt	±70° alpha tilt	±25° alpha and beta tilt

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The complete Wildfire range

Our products

JEOL TEM

Wildfire H	Wildfire H+	Wildfire H+ DT
RT – 600 °C	RT – 1300 °C	RT – 1300 °C
±20 ° alpha tilt	±20° alpha tilt	±20° alpha tilt ±15° beta tilt

DENS solutions
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Our products

Portfolio & focus

Materials Science

Micro Electronics

Chemistry

Life&materials Sciences

DENS solutions

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Thank you for your time

http://denssolutions.com/events/imc19/

Part 2. Heating experiments in STEM-EDS

Outline

- Demonstrate element mapping results at 1000° C for the first time
- Heating can cause sample drift and membrane bulging
- Infrared radiation disturbs X-ray detection
  - Effects of heat and IR-radiation on EDS signal detection:
    noise effects and peak broadening
- Elemental maps of Au/Pd nanoparticles
- Autophase results: tracking phase transition

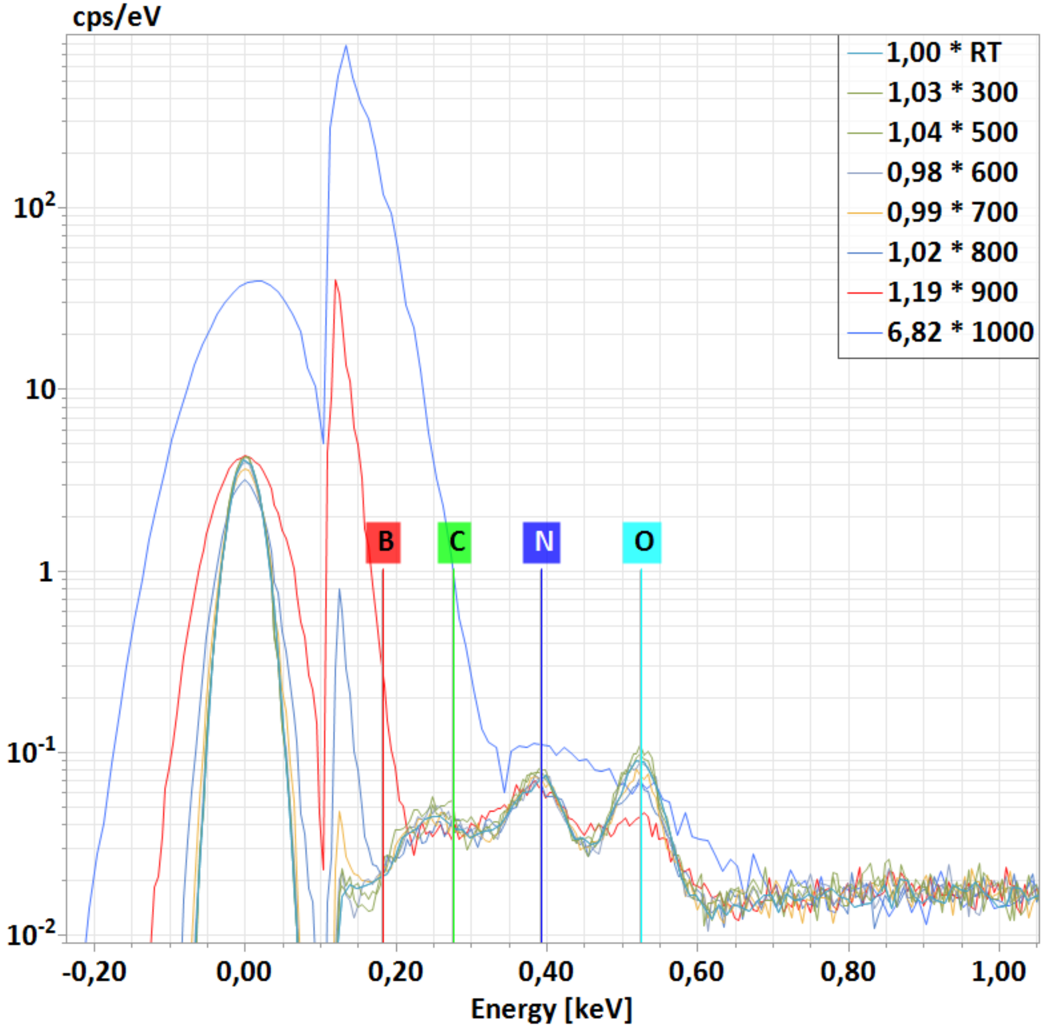
System parameters
EDS

System configuration	
Microscope type	JEOL JEM-2200FS, UHR polepiece, operated at 200kV
Detector type	Bruker X-Flash® 5030T, 30mm² active SDD chip size, 0.12 sr solid angle
SW configuration	Hypermap, drift correction, Autophase
SW options	online deconvolution – included in basic SW package
Sample holder	DENS Solutions, Wildfire in-situ heating sample holder

STEM located at the Humboldt University of Berlin, Institute of Physics

We thank **Dr. Holm Kirmse** (HUB) for operating the STEM and
Sander van Weperen (DENSsolutions) for operating the Wildfire system!

IR-radiation and heating affecting SDD



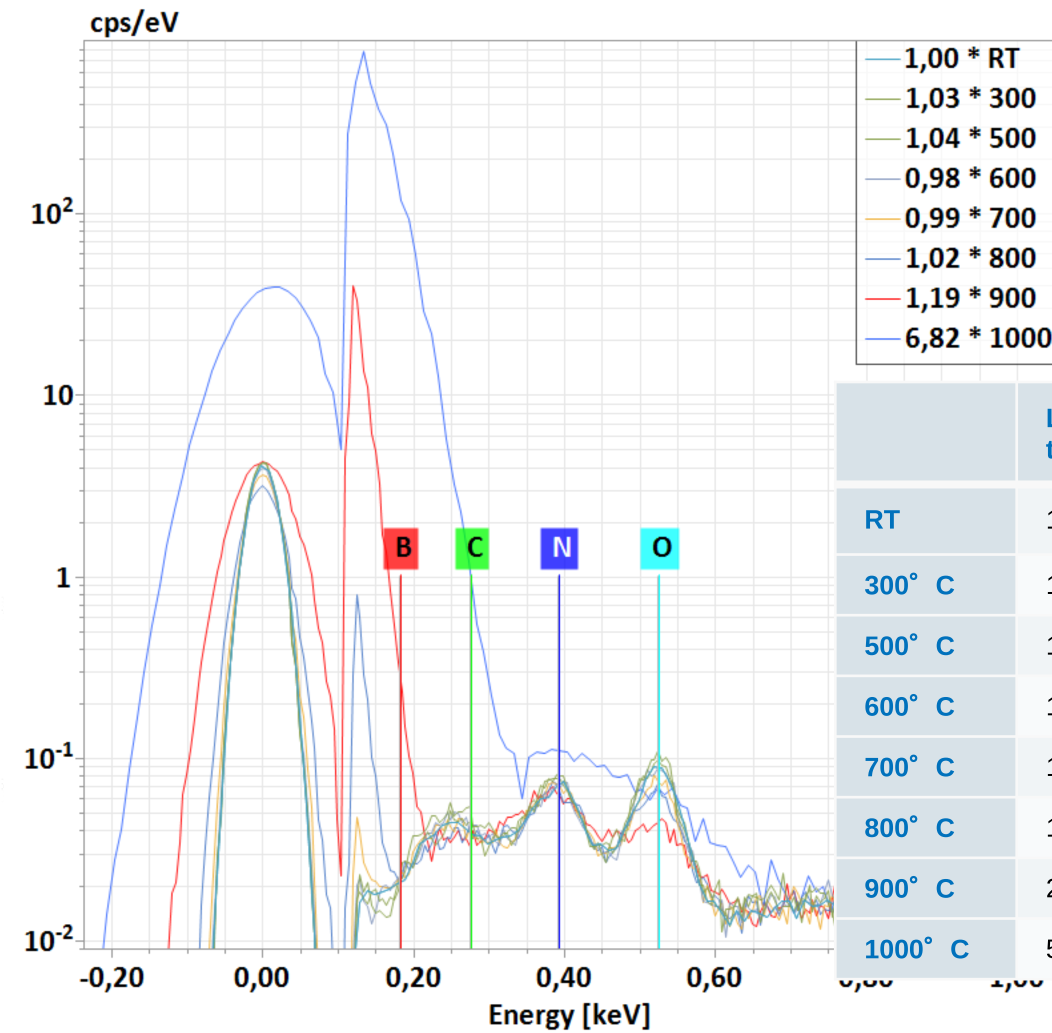
Effect of infrared radiation for X-ray detection with an SDD:

- **Noise effects:** the low energy region: detection of low kV X-rays is disturbed. Rising noise at low energies.

->low energy threshold for useful data interpretation

- **Peak broadening:** peak FWHM is increasing.

IR-radiation effect – low energy threshold

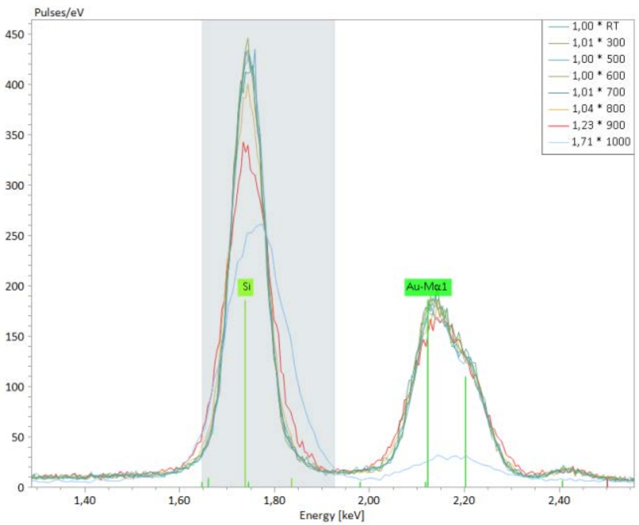


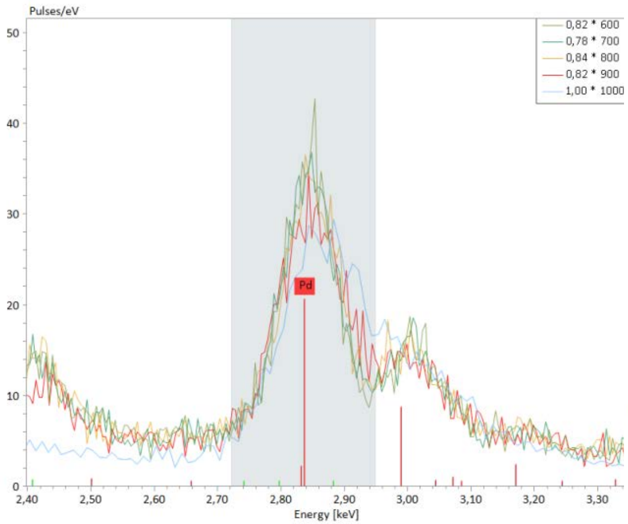
Low energy threshold: the minimal energy for useful data interpretation

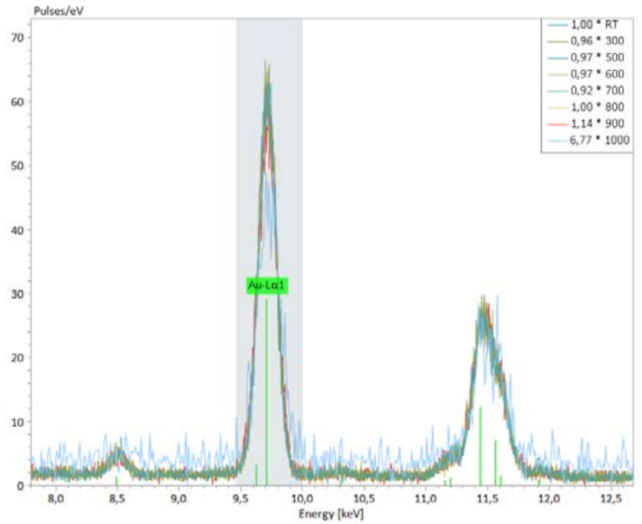
	Low energy threshold	Si K-peak FWHM	Pd Lα- peak FWHM	Au Lα- peak FWHM
RT	110 eV	79,4 eV	88,3 eV	169,2 eV
300° C	110 eV	80,6 eV	84,4 eV	167,6 eV
500° C	110 eV	79,6 eV	83,5 eV	167,7 eV
600° C	110 eV	79,6 eV	86,3 eV	168,1 eV
700° C	150 eV	82,5 eV	89,4 eV	169,3 eV
800° C	180 eV	91,3 eV	92,9 eV	172,0 eV
900° C	215 eV	110,6 eV	111,9 eV	188,7 eV
1000° C	500 eV	148,5 eV	182,4 eV	219,6 eV

IR-radiation effect – peak broadening

Si Kα (1,740 keV)	Pd Lα (2,837 keV)	Au Lα (9,704 keV)







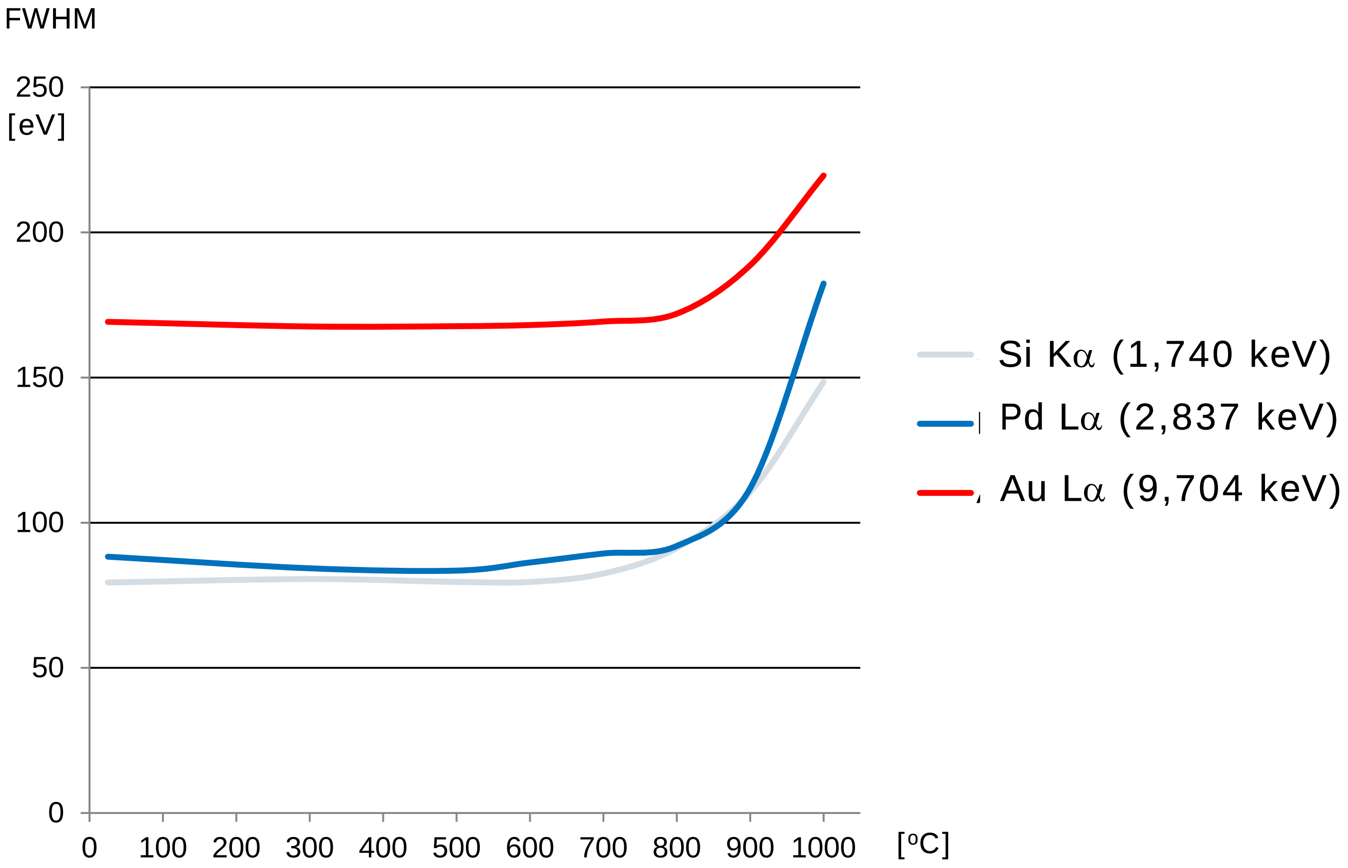
All		FWHM [eV
EDS	RT	79,4
EDS	300	80,6
EDS	500	79,6
EDS	600	79,6
EDS	700	82,5
EDS	800	91,3
EDS	900	110,6
EDS	1000	148,5

All		FWHM [e
EDS	RT	88,3
EDS	300	84,4
EDS	500	83,5
EDS	600	86,3
EDS	700	89,4
EDS	800	92,0
EDS	900	111,9
EDS	1000	182,4

All		FWHM [e
EDS	RT	169,2
EDS	300	167,6
EDS	500	167,7
EDS	600	168,1
EDS	700	169,3
EDS	800	172,0
EDS	900	188,7
EDS	1000	219,6

- Stronger peak broadening at lower energies
- Peaks are still significantly strong to use EDX signal for element mapping

IR-radiation effect – peak broadening



- Stronger peak broadening at lower energies
- Peaks are still significantly strong to use EDX signal for element mapping

Sample

Au/Pd sputtered on a silicon-nitride membrane.

Nominal layer thickness: 10nm

The Au/Pd material system is a good model system to demonstrate processes like

- dewetting, **element segregation** within nanoparticles
- nanoparticle **size and shape change**
- **evaporation of elements** (Au) due to melting temperature differences

Measurement parameters
EDS and STEM

Measurement parameters	
Map size	256 x 246 pixels
Pixel size	0.55 nm
Mapping time	15 minutes
Input count rate	220-260 cps
Drift correction	active

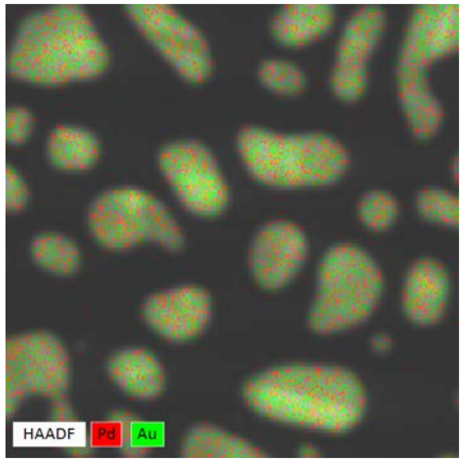
STEM-EDS geometry parameters	
Take off angle	22°
Solid angle	0.12 sr
Sample tilt	0°
Beam current	350pA
SDD window	Super Light Element Window (SLEW) AP3.3 (Moxtek)

Mapping at different temperatures

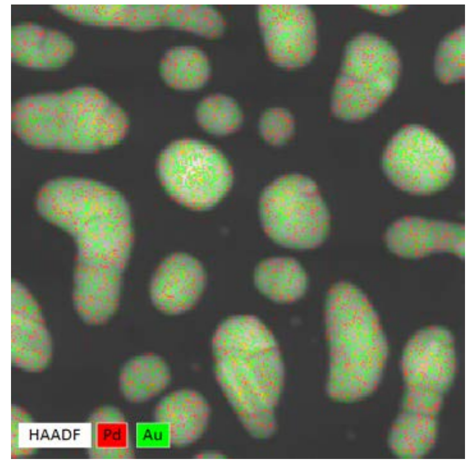
RT, 500, 600° C:
random sample areas

700-1000° C:
same sample area

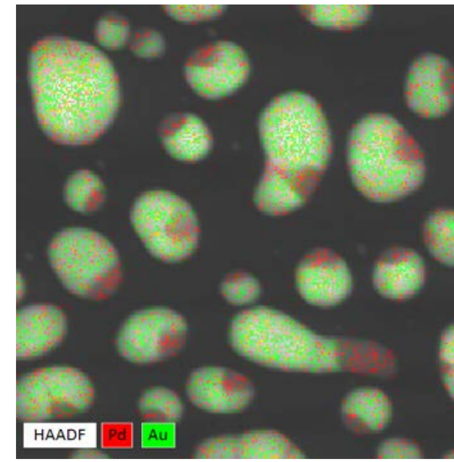
RT



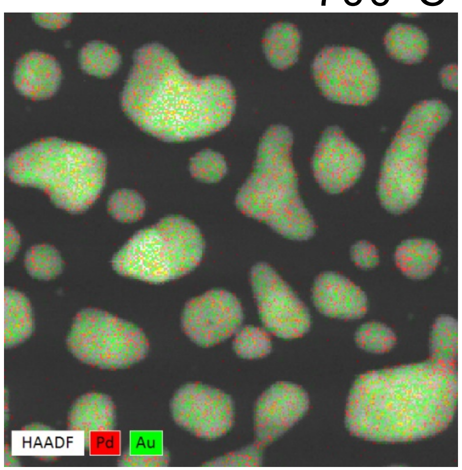
500°C



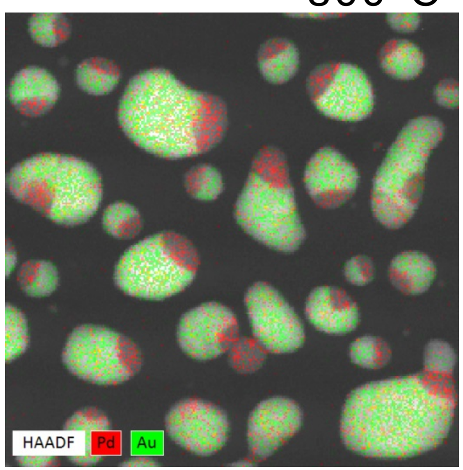
600°C



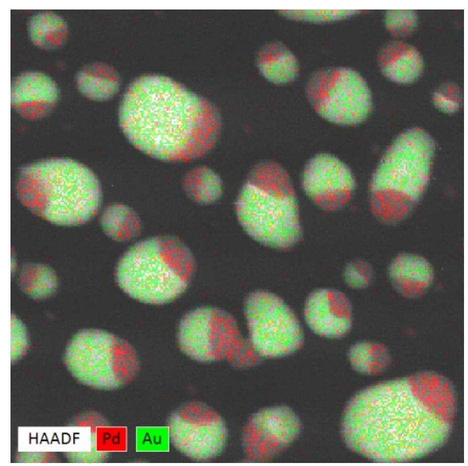
700°C



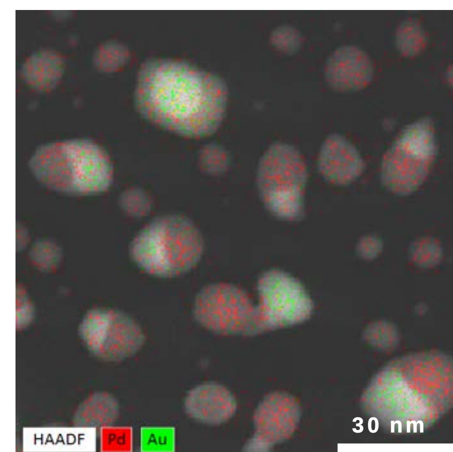
800°C



900°C

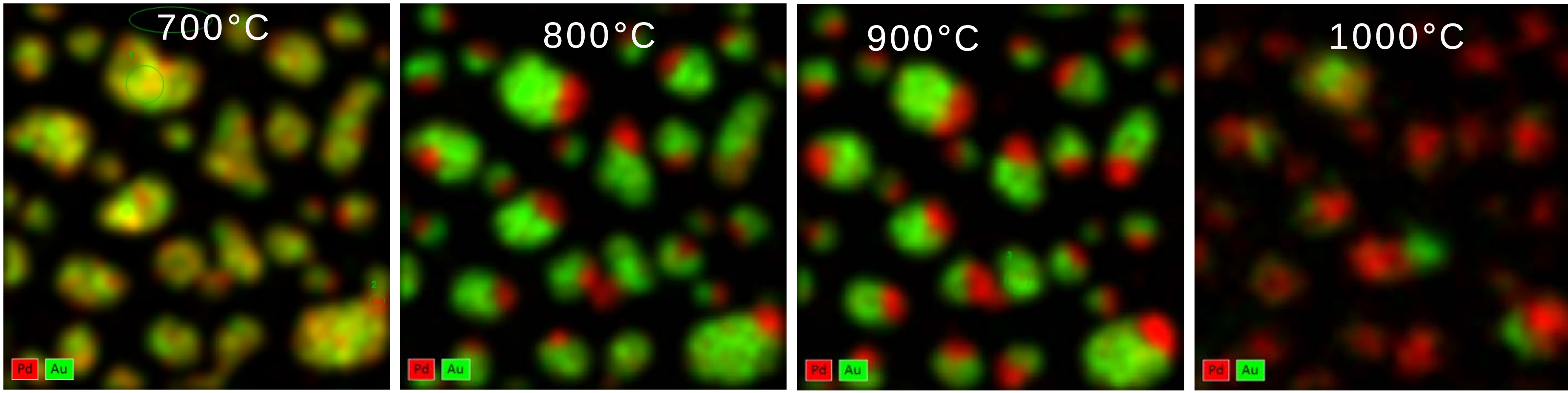


1000°C

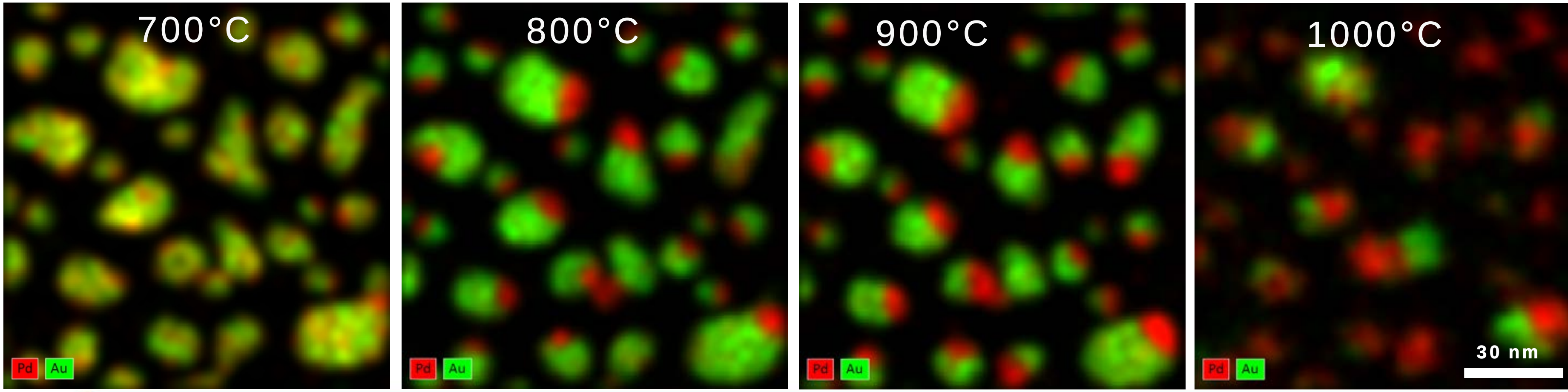


Maps with autofilter
Au M-lines (2,123kV) & Au L-lines (9,704kV)

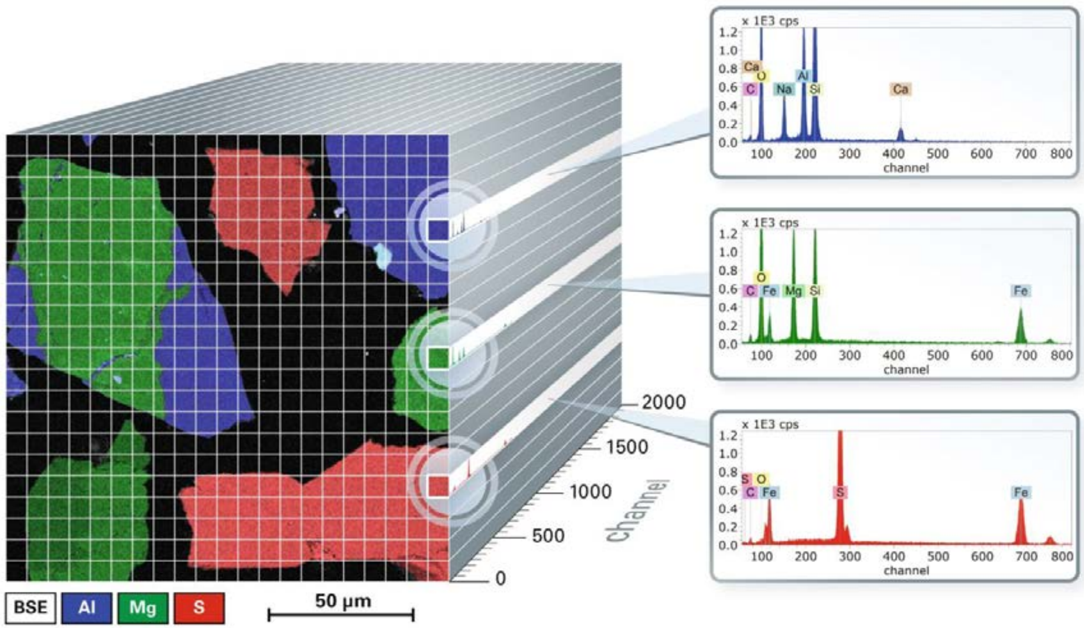
Au L-lines



Au M-lines



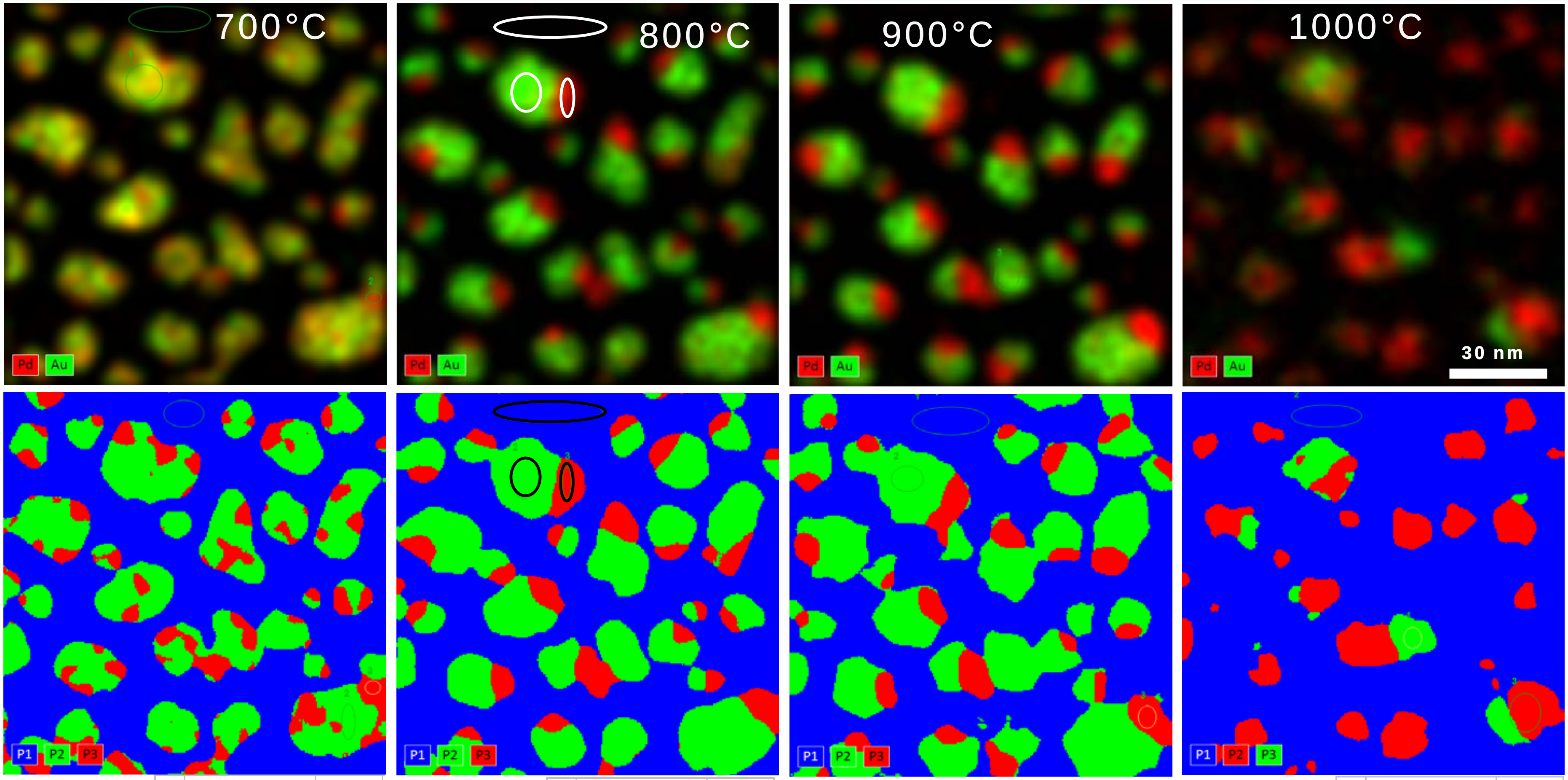
Autophase – find „similar“ areas in a map



Autophase workflow:

All spectra in a Hypermap can be described with as an n-dimensional data vector. Autophase uses different algorithms (like PCA) to identify and sort “similar” spectra within the map.

Autophase results



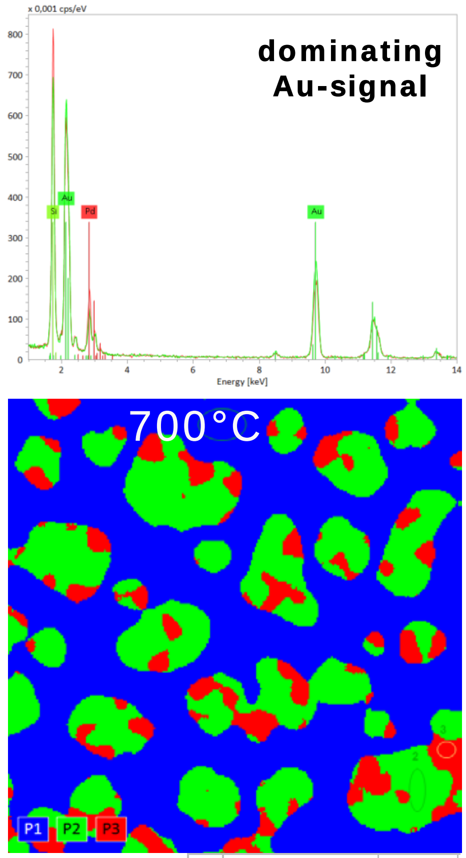
	Counts/Pixel		Area
■	P1		59,2 %
■	P2	Au	30,5 %
■	P3	Pd	10,3 %

	Counts/Pixel		Area
■	P1		58,1 %
■	P2	Au	32,2 %
■	P3	Pd	9,7 %

	Counts/Pixel		Area
■	P1		57,1 %
■	P2	Au	33,6 %
■	P3	Pd	9,3 %

	Counts/Pixel		Area
■	P1		82,6 %
■	P3	Pd	13,8 %
■	P2	Au	3,7 %

Autophase results
Phase changes



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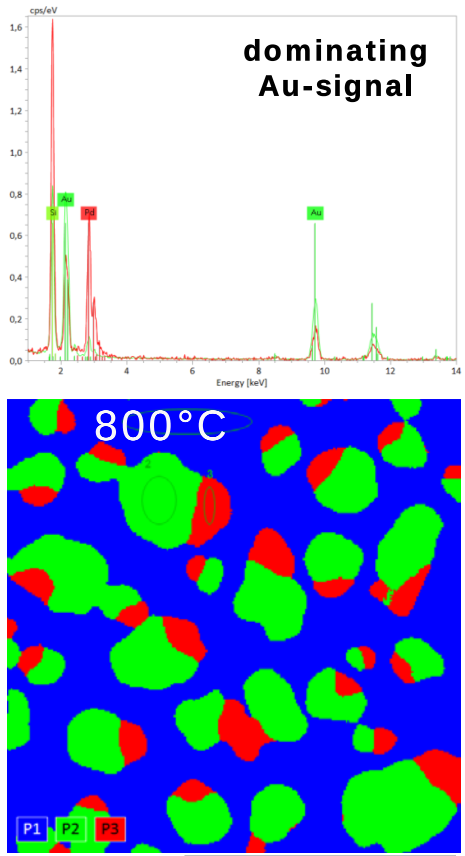

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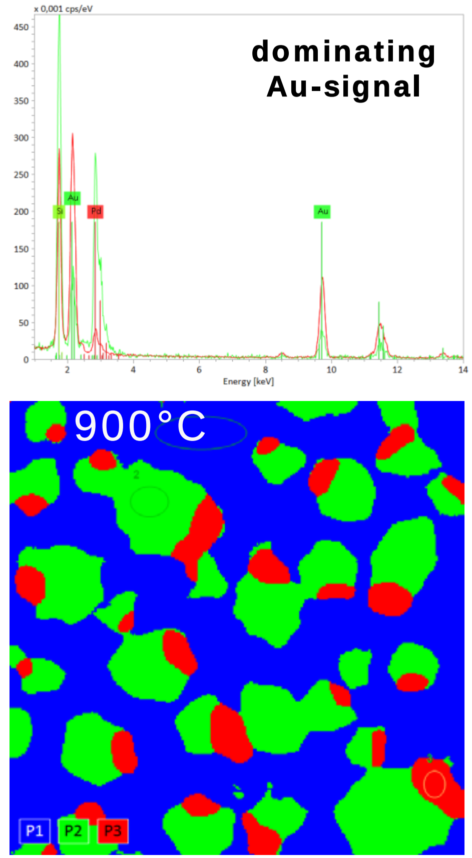

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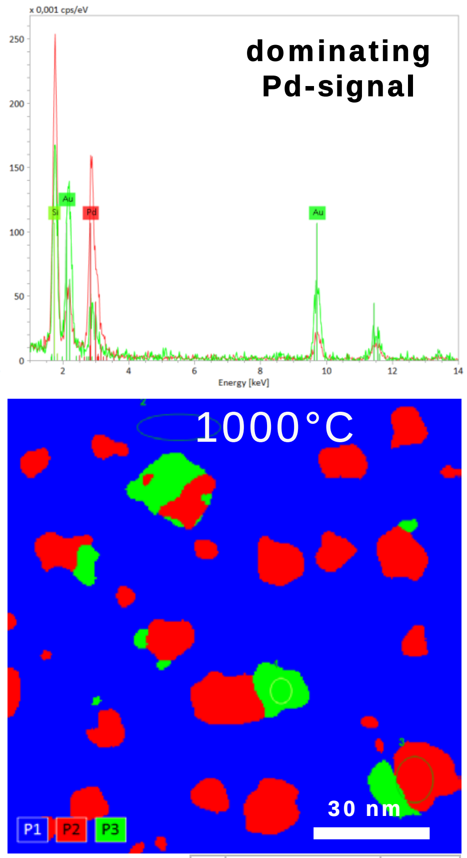

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■	P1		82,6 %
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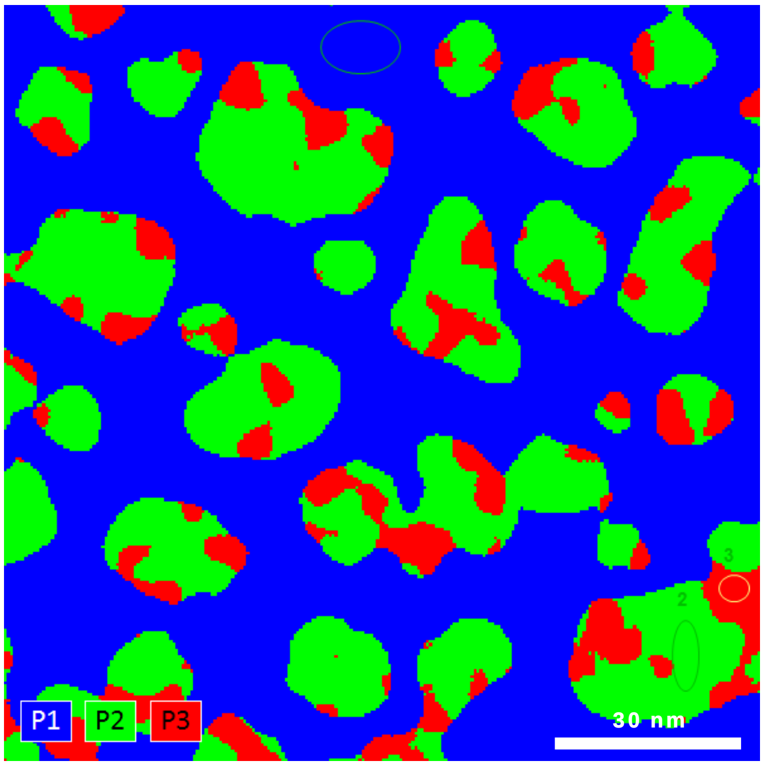
Autophase results
Phase changes

700°C



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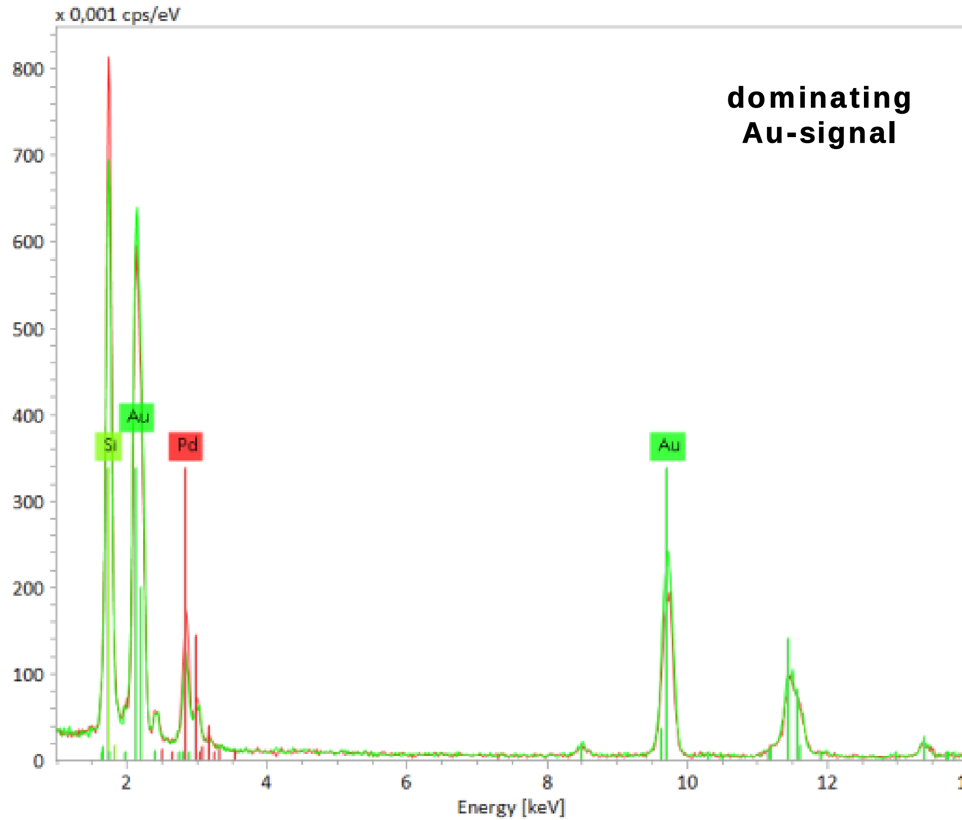
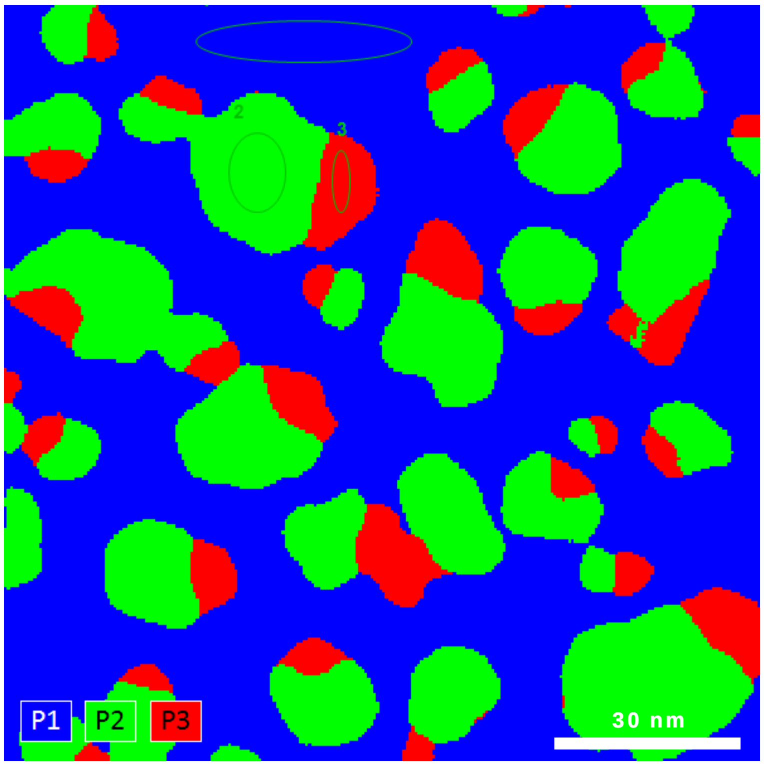


Autophase results
Phase changes

800°C



	Counts/Pixel		Area
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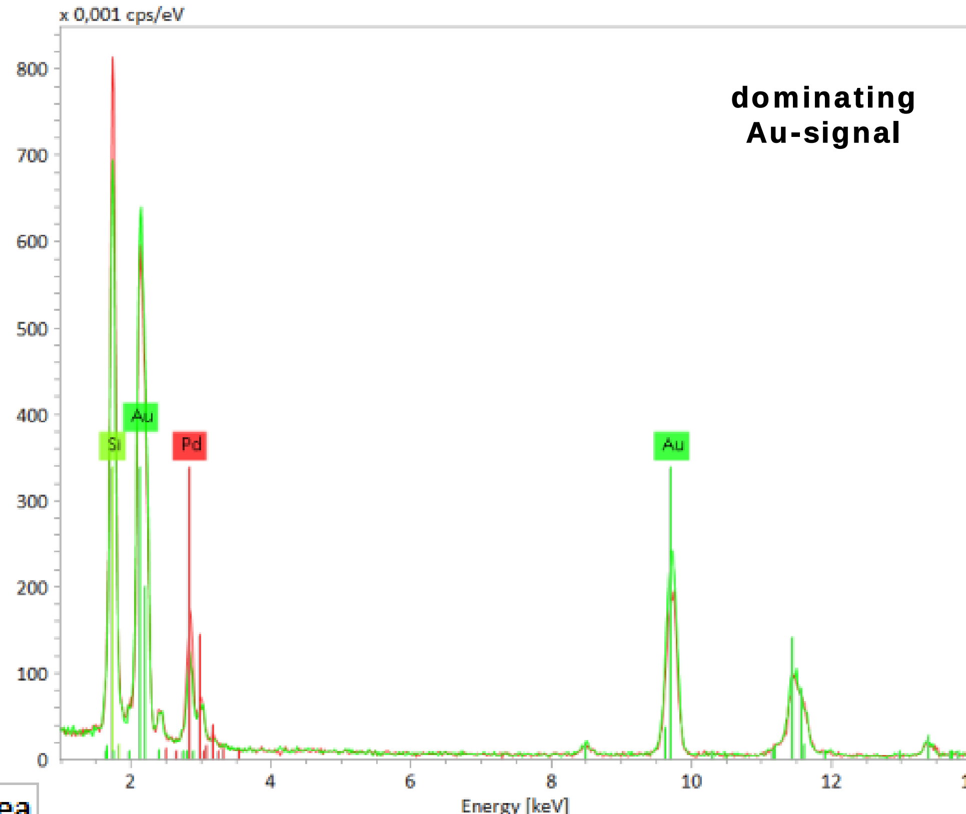
	P3	Pd	10,3 %

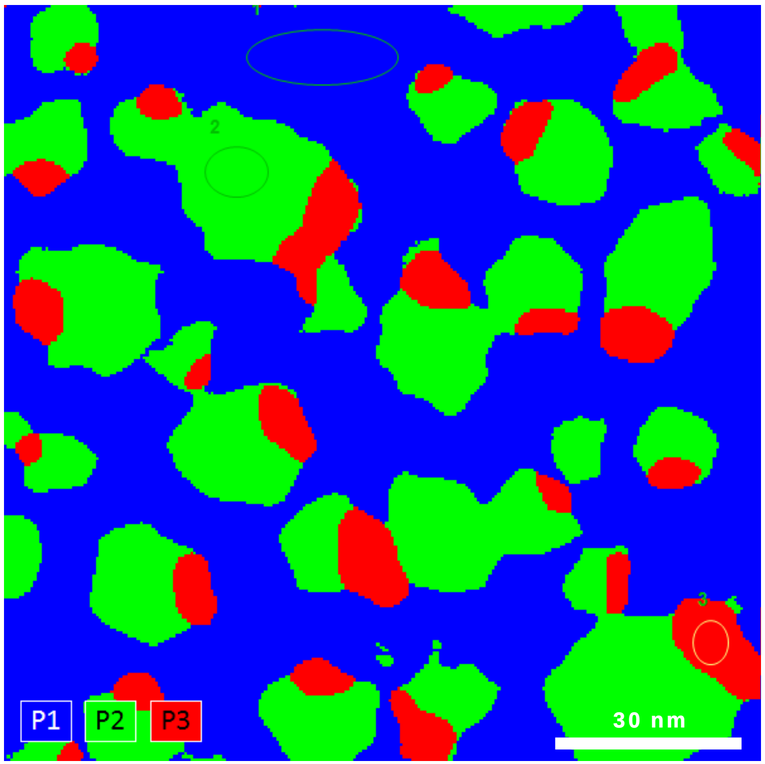
→

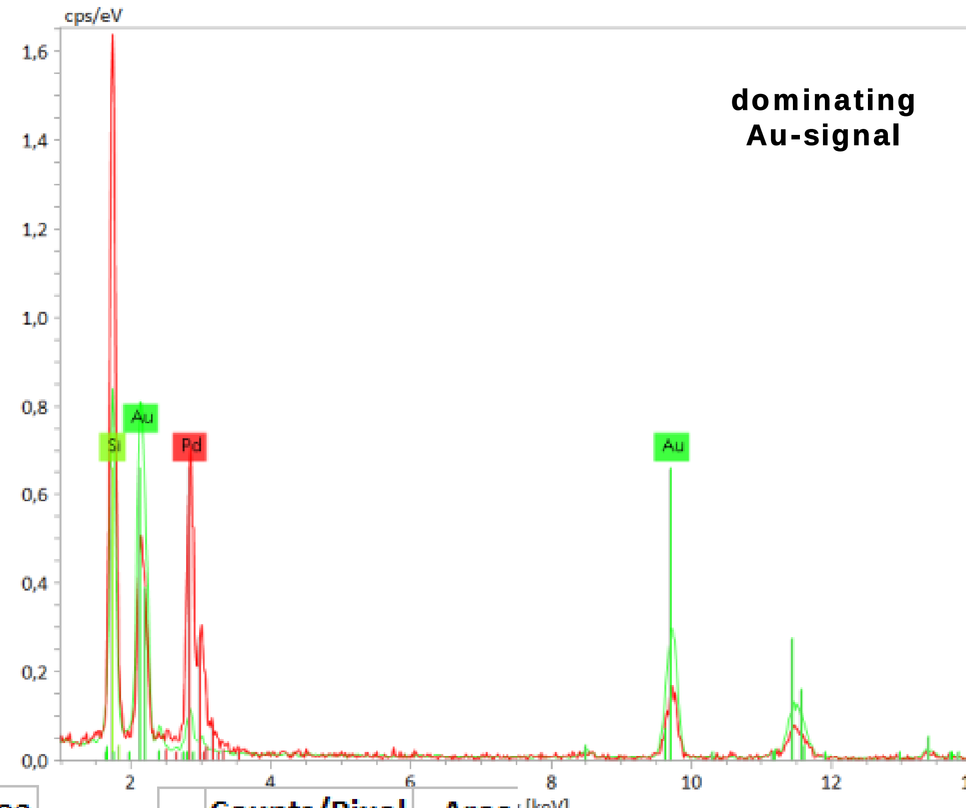
	Counts/Pixel		Area
	P1		58,1 %
	P2	Au	32,2 %
	P3	Pd	9,7 %



Autophase results
Phase changes

900°C





	Counts/Pixel		Area
■	P1		59,2 %
■	P2	Au	30,5 %
■	P3	Pd	10,3 %

→

	Counts/Pixel		Area
■	P1		58,1 %
■	P2	Au	32,2 %
■	P3	Pd	9,7 %

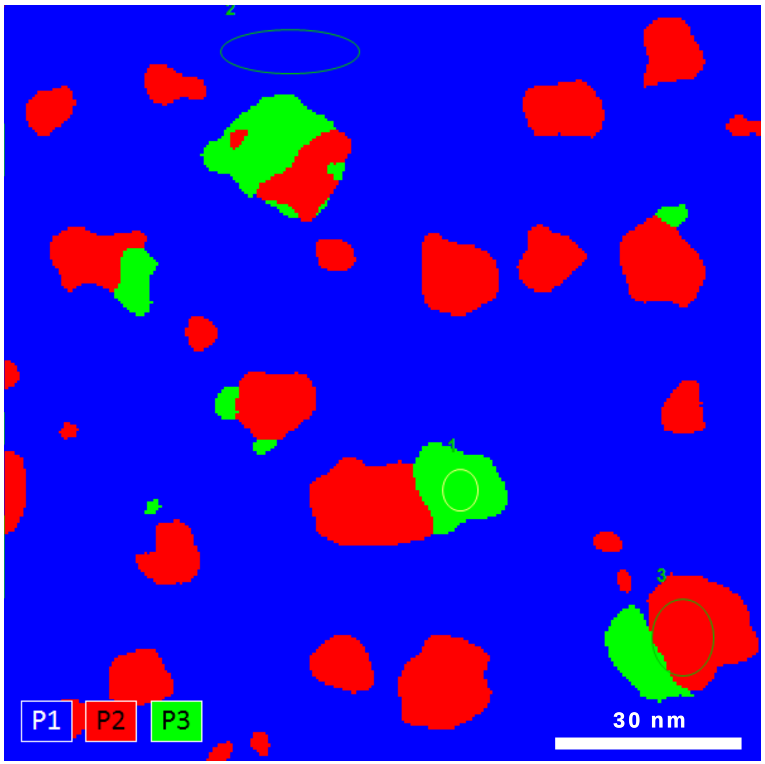
→

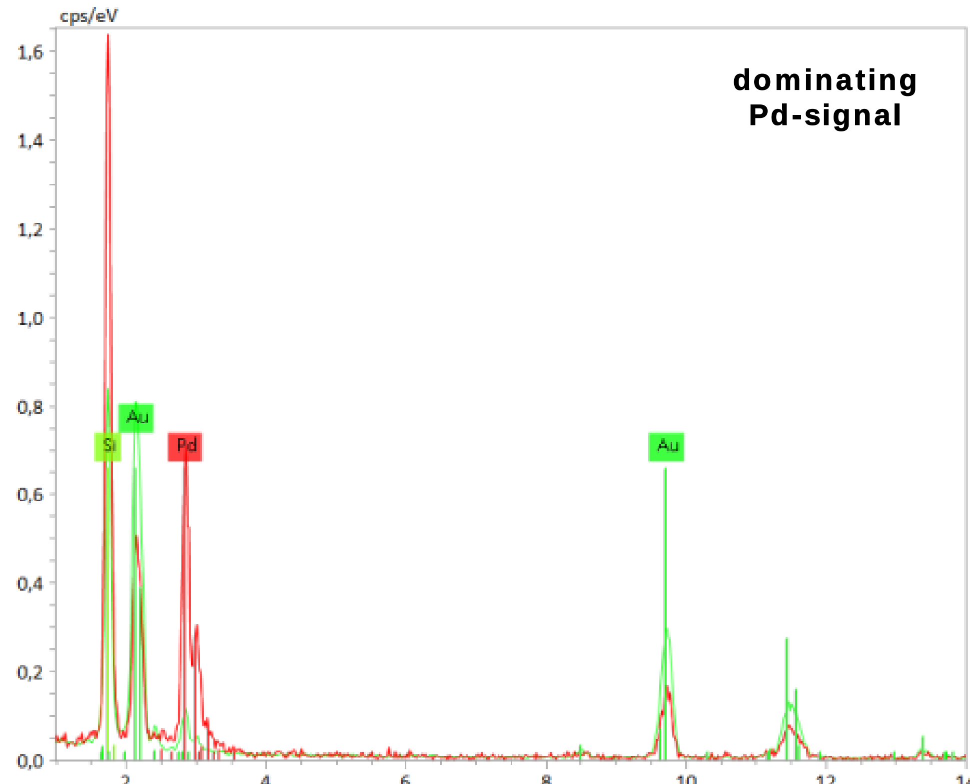
	Counts/Pixel		Area
■	P1		57,1 %
■	P2	Au	33,6 %
■	P3	Pd	9,3 %

Autophase results

Phase changes

1000°C





	Counts/Pixel		Area
■	P1		59,2 %
■	P2	Au	30,5 %
■	P3	Pd	10,3 %

→

	Counts/Pixel		Area
■	P1		58,1 %
■	P2	Au	32,2 %
■	P3	Pd	9,7 %

→

	Counts/Pixel		Area
■	P1		57,1 %
■	P2	Au	33,6 %
■	P3	Pd	9,3 %

→

	Counts/Pixel		Area
■	P1		82,6 %
■	P3	Pd	13,8 %
■	P2	Au	3,7 %

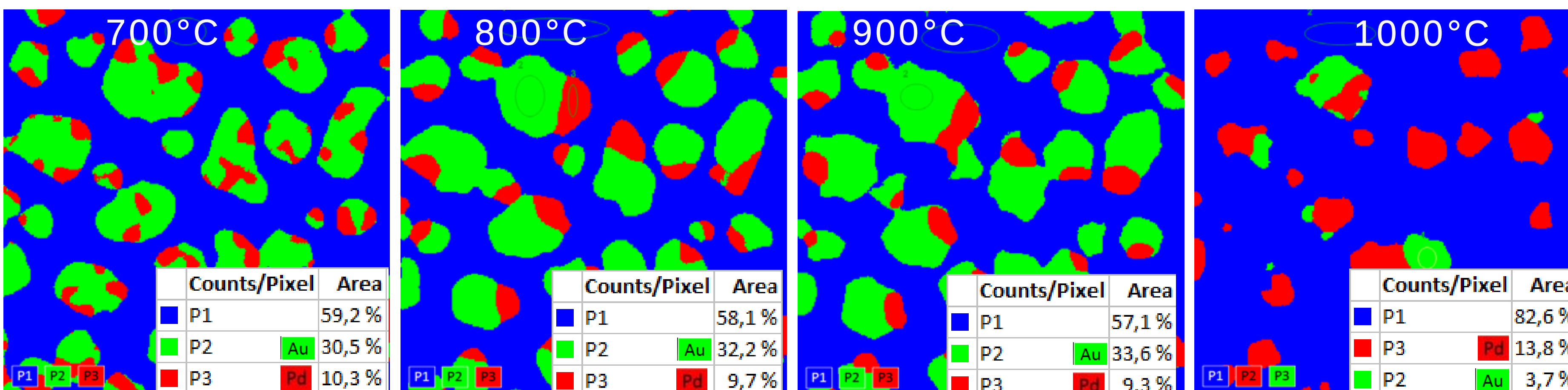
Autophase results

Phase changes

Au/Pd material system undergoes changes with increasing temperature:

- Ostwald ripening
- element segregation within nanoparticles: Au and Pd segregation
- shrinking of nanoparticles (material loss: individual particles decreasing)
- evaporation of elements (Au) due to melting temperature differences
- area coverage of Au is decreasing with increasing temperature

=>quantitatively measured using AutoPhase



Conclusions

- Demonstration and control of IR effect on EDS spectra using optimized in-situ sample holder
- Unprecedented in-situ heating study in STEM at temperatures up to 1000° C
- Esprit HyperMap and AutoPhase tool tracks phase transition of Au/Pt nanoparticles by measuring phase area coverage

Further information:

Advanced microheater for *in situ* transmission electron microscopy; enabling unexplored analytical studies and extreme spatial stability

Ultramicroscopy 192 (2018) 14–20

doi: 10.1016/j.ultramic.2018.05.005.

Q&A session

Please type in the questions you have
in the Q&A box and press ***Send*.**

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