The interior interfaces of a semiconductor/metal nanocomposite and their influence on its physical properties

P. Granitzer[1,2], K. Rumpf[1], P. Poelt[2], M. Albu[2], B. Chernev[2]

[1] *Institute of Physics, Karl Franzens University Graz*

[2] *Institute for Electron Microscopy, TU Graz*

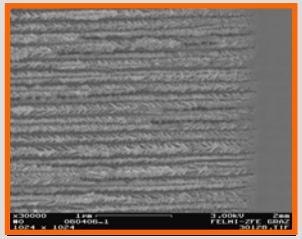
TNT2008 Trends in NanoTechnology Oviedo (Spain) September 01-05, 2008

Talk, TNT 2008, Oviedo, Spain

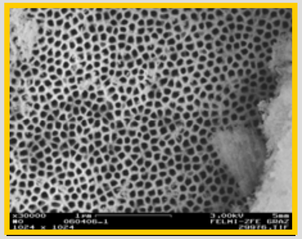
Outline

- **PS-Matrix**

  Fabrication of the PS matrix with a certain morphology



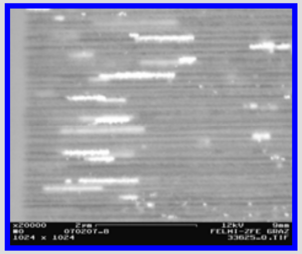
- **Structural characterization by SEM**



- **Nanocomposite system**

  Metal-filling – ferromagnetic nanostructures

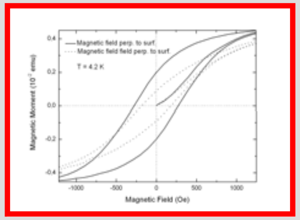
- **Specific physical properties due to nanostructuring**



- **Interface: Si/PS/metal**

  FTIR-investigations, Raman-spectroscopy

  Magnetic characterization



- **Outlook**
- **Conclusion**

Fabrication of the PS-matrix

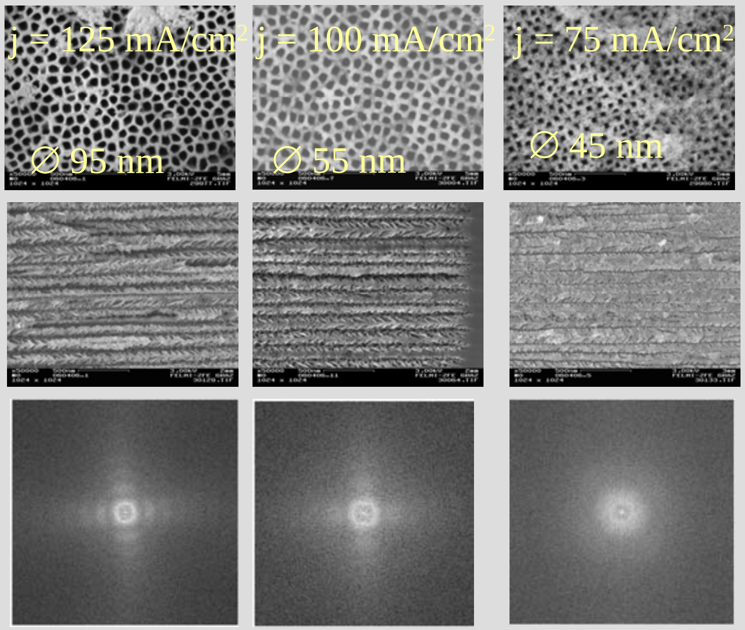
Aim: fabrication of mesoporous silicon templates by self-organization

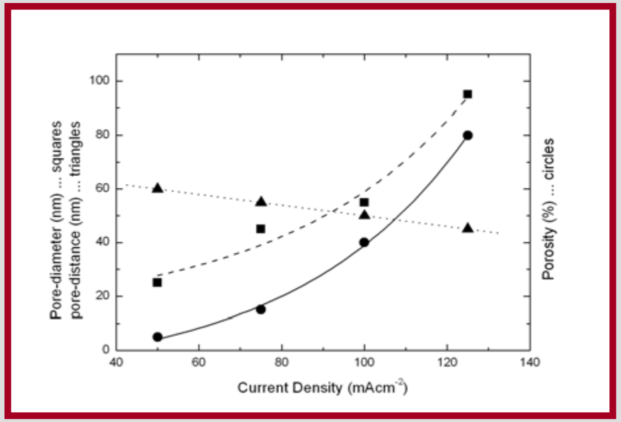
Desired properties: ***defined morphology with***:

oriented, separated pores

quasi-regular pore arrangemet

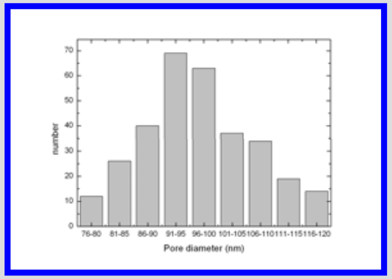
narrow pore-size distribution



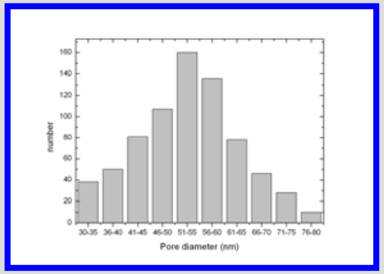


Decreasing current density ($j < 75\ mA/cm^2$) – more and more random pore distribution

$j = 125\ mA/cm^2$



$j = 100\ mA/cm^2$



Metal-deposition – ferromagnetic nanostructures

Metal-filling of the PS-template by electrochemical deposition

Typical used deposition parameters

Current density j [mA/cm^2]	Pulse duration t_{pulse} [s]
10	20
20	20
50	10
50	5

Used electrolytes
$NiCl_2$ – solution: 170 g/l $NiCl_2$ 40 g/l H_3BO_3
Watts-electrolyt: 45 g/l $NiCl_2$ 300 g/l $NiSO_4$ 45 g/l H_3BO_3
$CoSO_4$ – solution: 120 g/l NiCl2 30 g/l H3BO3

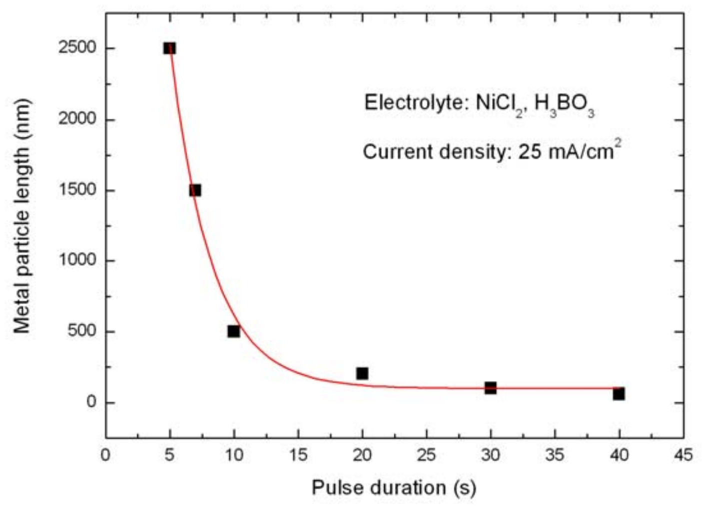
Metal filling of the channels depends on the process-parameters

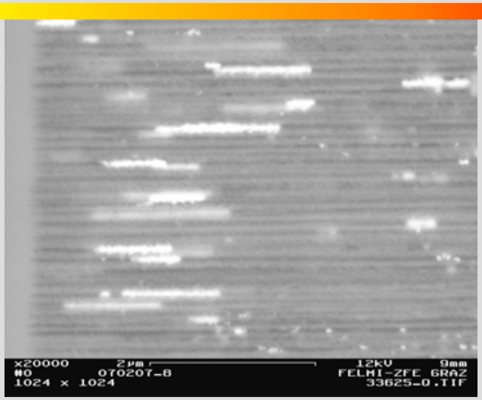
Various metals precipitate differently under similar deposition conditions

Structural characterization of the nanocomposite

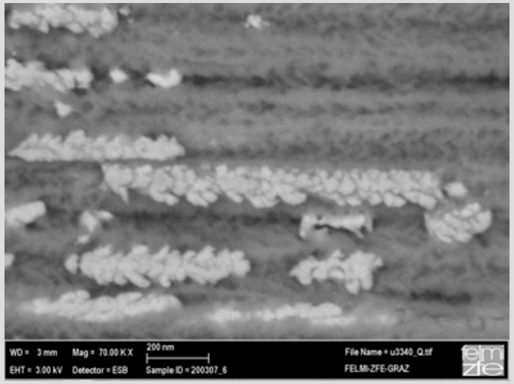
Precipitated Ni-stuctures

With decreasing pulse duration the elongation of the precipitated nanostructures increases



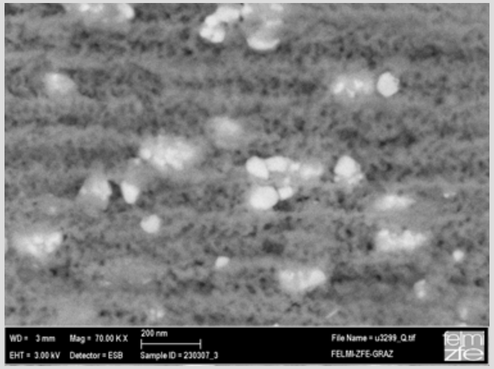


t_P = 5 s
l = 2 µm



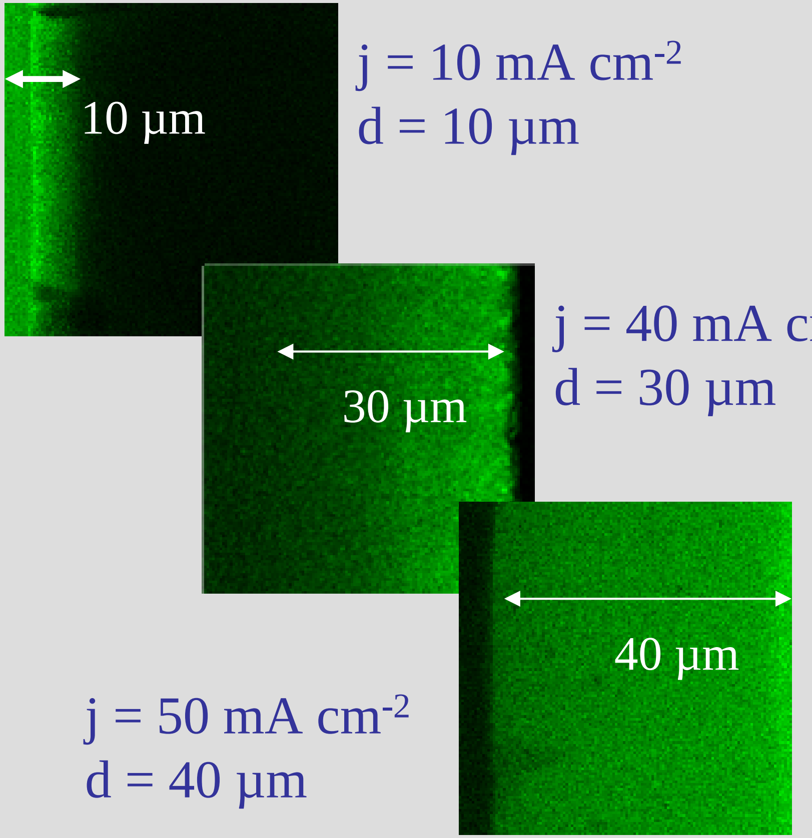
t_P = 10 s
l = 500 nm

t_P = 40 s
l = 60 nm



EDX spectroscopy - element distribution

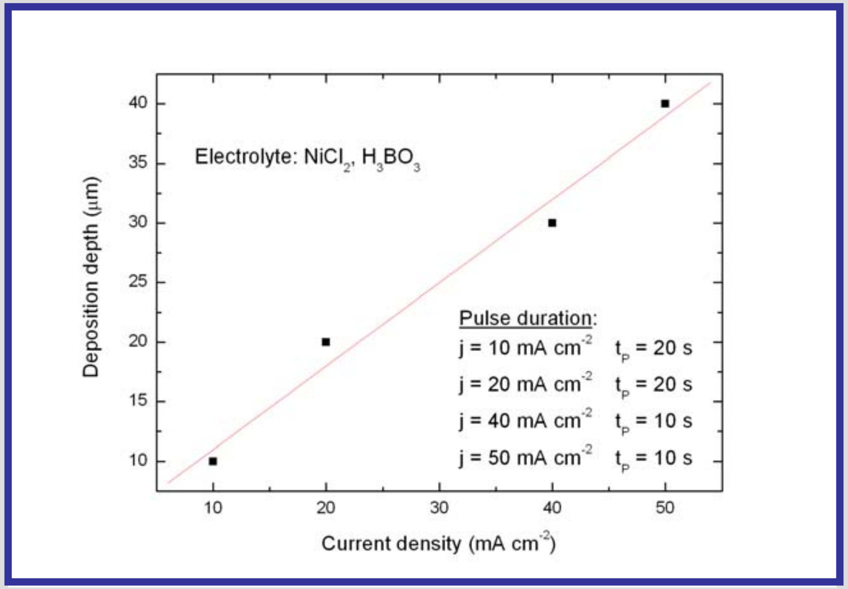
Spatial Ni-distributions



$j = 10\ mA\ cm^{-2}$
$d = 10\ \mu m$

$j = 40\ mA\ cm^{-2}$
$d = 30\ \mu m$

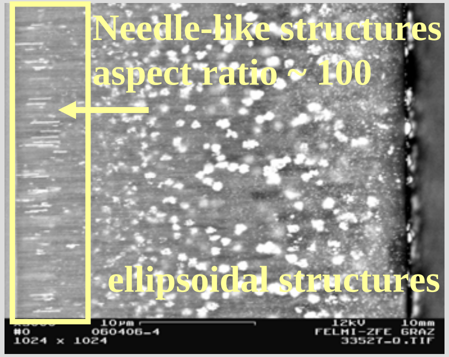
$j = 50\ mA\ cm^{-2}$
$d = 40\ \mu m$

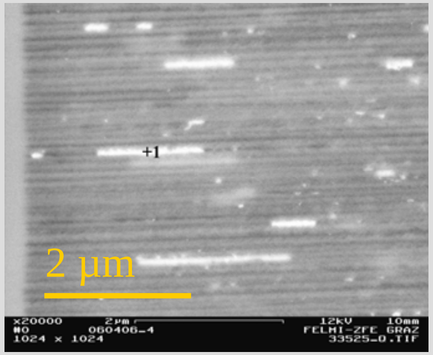


Realtion between current density and deposition depth

Embedded metal-structures

Embedded Ni-wires



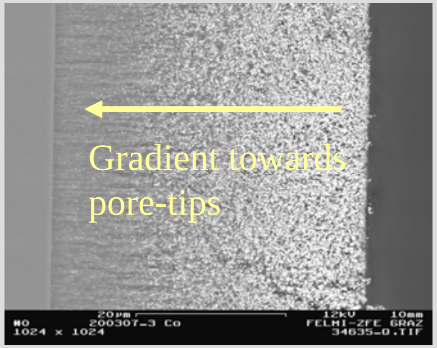


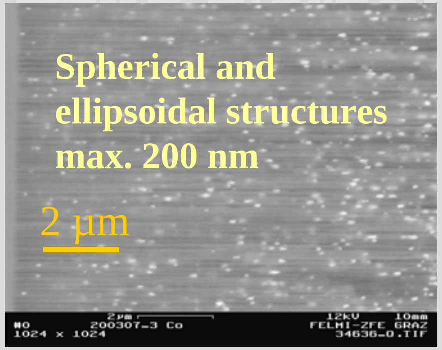
Deposited Ni within the pores shows a distribution between spherical and elongated particles.

Elongated Ni-particles with a length of about 2 µm and a diameter of 50 nm (**aspect ratio 40**).

PS-channels: aspect ratio ~ 1000

Embedded Co-particles

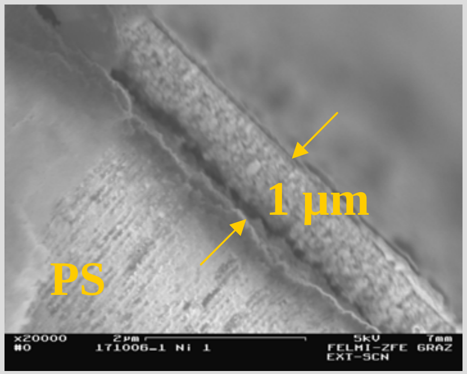




Gradient of the Co concen-tration with increasing pore length.

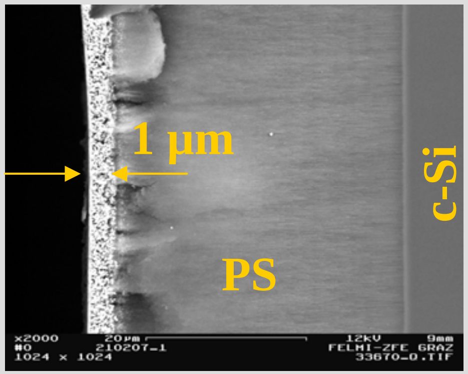
The size of the precipitated Co-particles is in the range of a few hunded nm. The filling is achieved down to the por tips.

Deposited Ni-layer



⇒ Of interest for coming transport measurements

Deposited Co-layer



Nanosystem – particles / wires

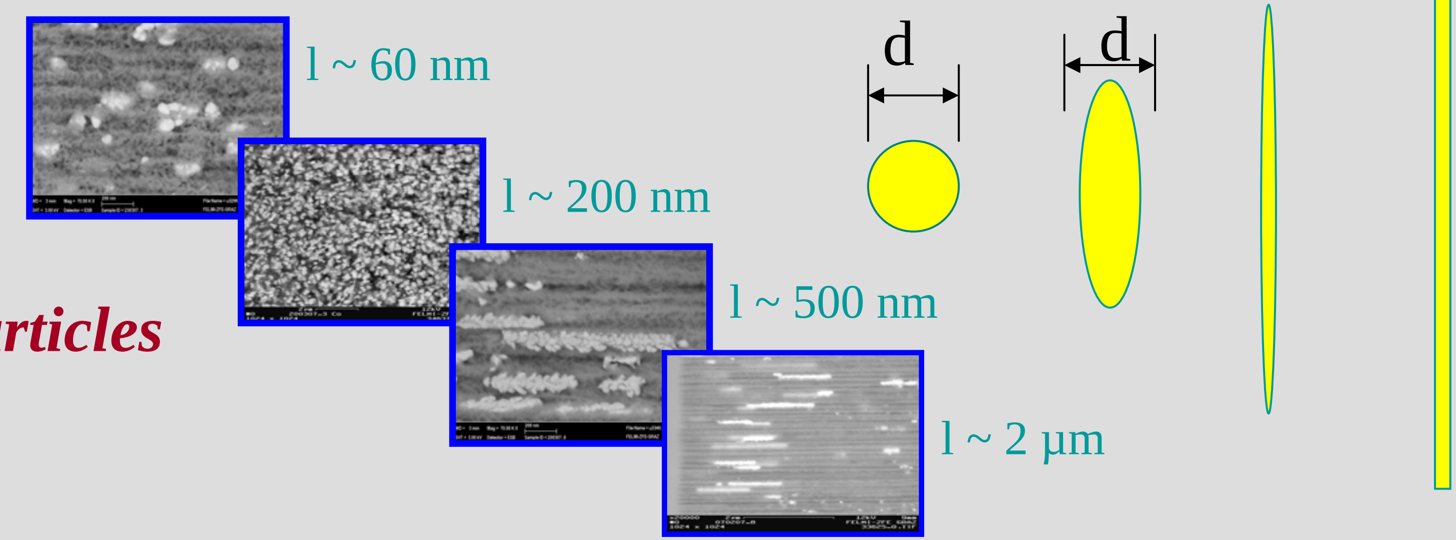
Ferromagnetic nanosystem with tailored metal structures:

Spheres

Ellipsoides

Elongated particles

Wires



Magnetic properties of such ferromagnetic nanoparticles mainly depend on their size and shape

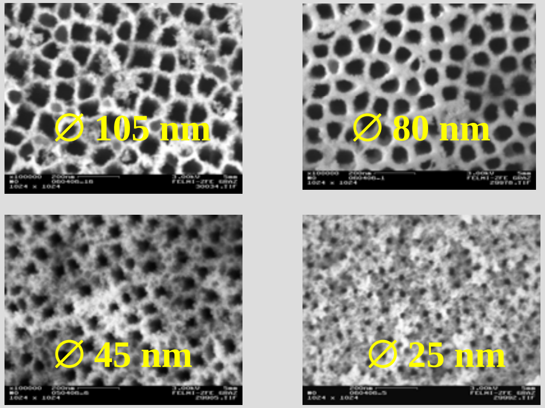
Properties of the whole system are determined by the distribution of the structures and their mutual arrangement

⇒ **Magnetic properties tunable by process parameters**

Distribution of the magnetic nanostructures

Modification of the PS-templates

⇒ **influence on the magnetic interactions**



⇒ Different interactions of the particles:

- Dipolar interaction
- Exchange interaction - RKKY-interaction
- Interaction by tunnelling through barriers

⇒ **Complex system with tunable properties**

Specific physical properties due to nanostructuring

- **Silicon ⇒ PS**: optical properties change due to QC-effects
  the properties are influenced by oxidation
  (L. Canham, Appl. Phys. Lett. 57, 1990, 1046)

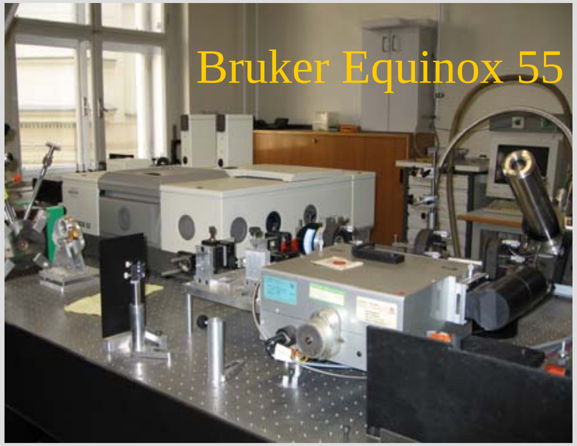
- **Metal nanostructures**: magnetic behaviour – change from
  multi domain to single domain behaviour
  oxidation of particles – exchange bias effect
  (if the metal-oxide is AFM)
  (J. Nogues, et al. Physics Reports 422, 2005, 65-117)

Knowledge about interface important

Interface

Optical characterization is carried out by FTIR-spectroscopy

FTIR-magnetometer: Bruker Equinox 55
Raman-spectroscopy



Structural characterization

SEM-, TEM-images

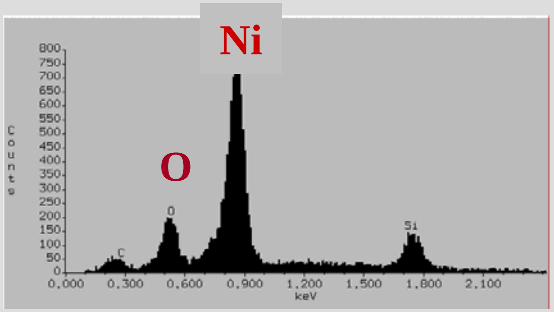
Magnetization measurements performed by SQUID-magnetometry

SQUID-magnetometer: Quantum Design MPMS XL7
Field range: ± 7 T
Temperature range: 1.7 K – 360 K
Resolution: $5 \cdot 10^{-9}$ emu

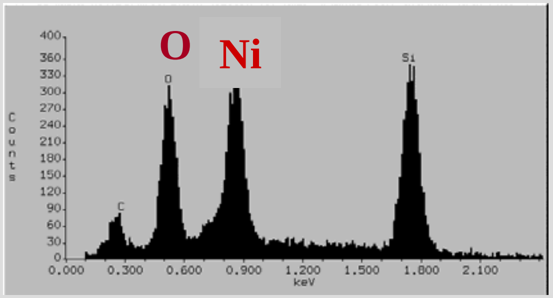
SEM – EDX spectroscopy

EDX-Spectroscopy

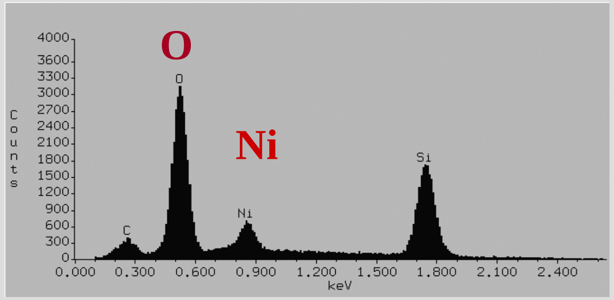
1



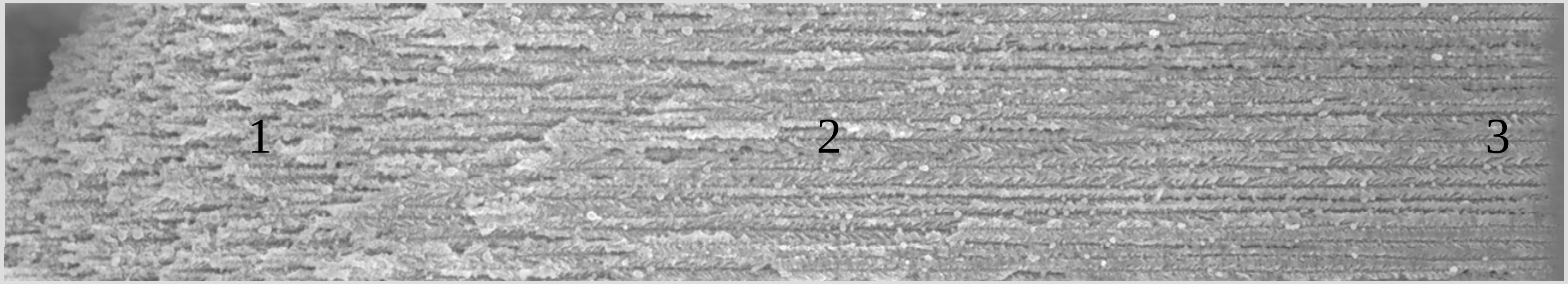
2



3



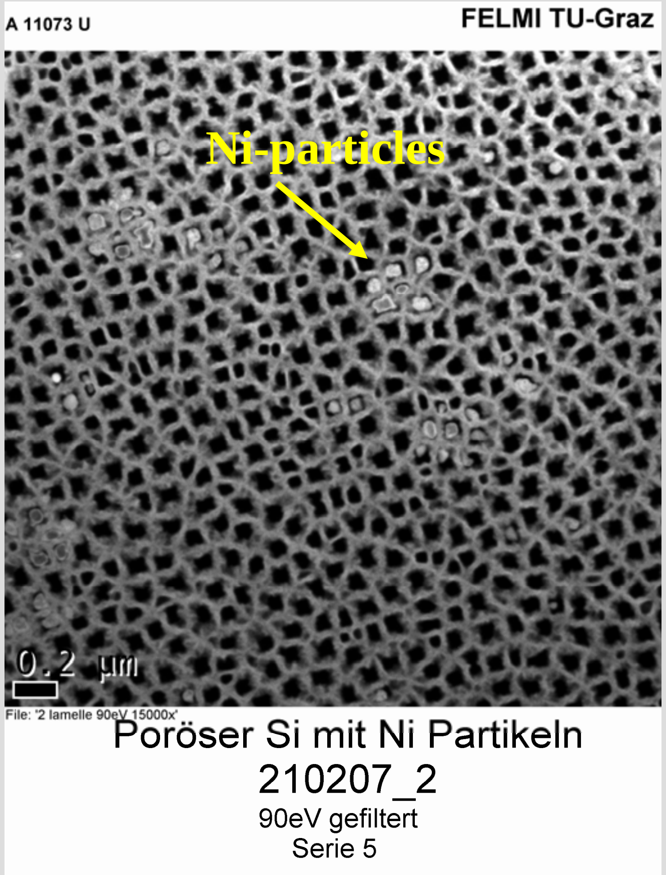
EDX-Spectra, 3keV



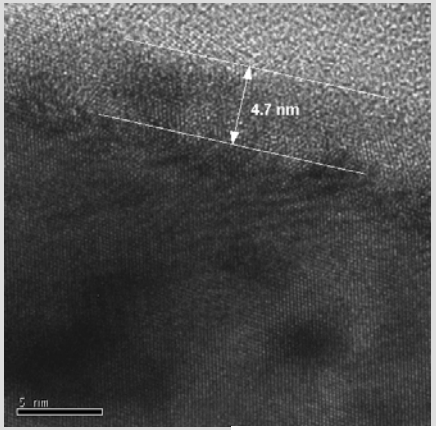
Ni-distribution is in good agreement with the pore length;
The estimated oxigen content is due to SiO_2

TEM-images of FIB cut sample

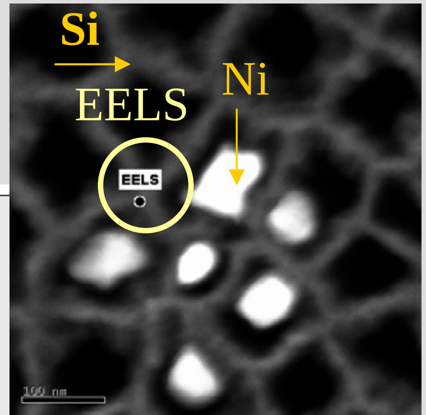
Ni-filled PS-specimen cut by FIB

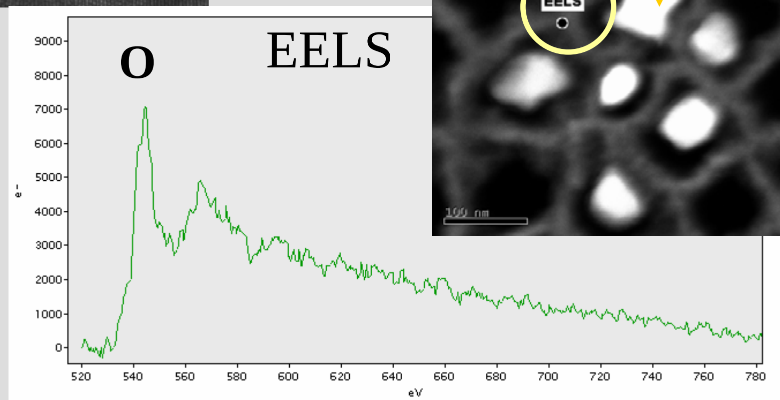


Top view-image showing the Ni-filled pores



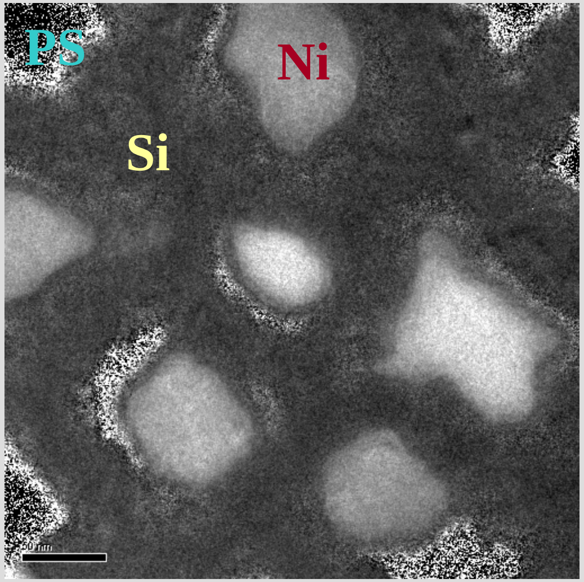
Interior surface of the PS-template



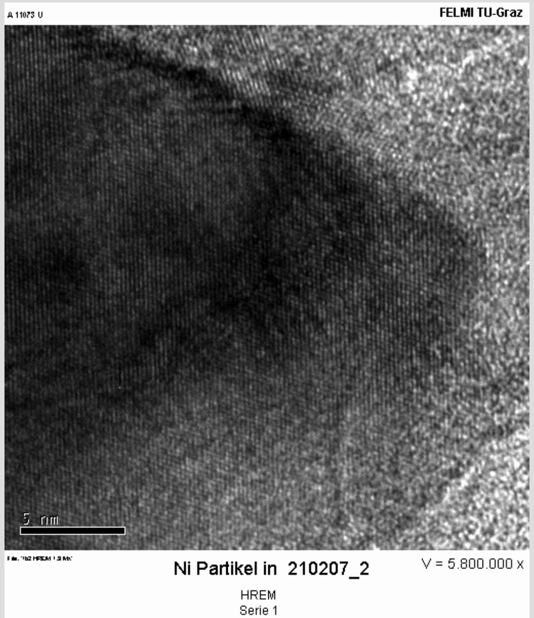


HRTEM – crystalline orientation

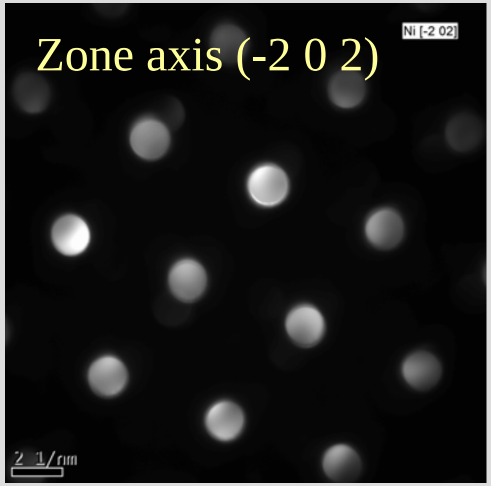
Ni-particles within pores



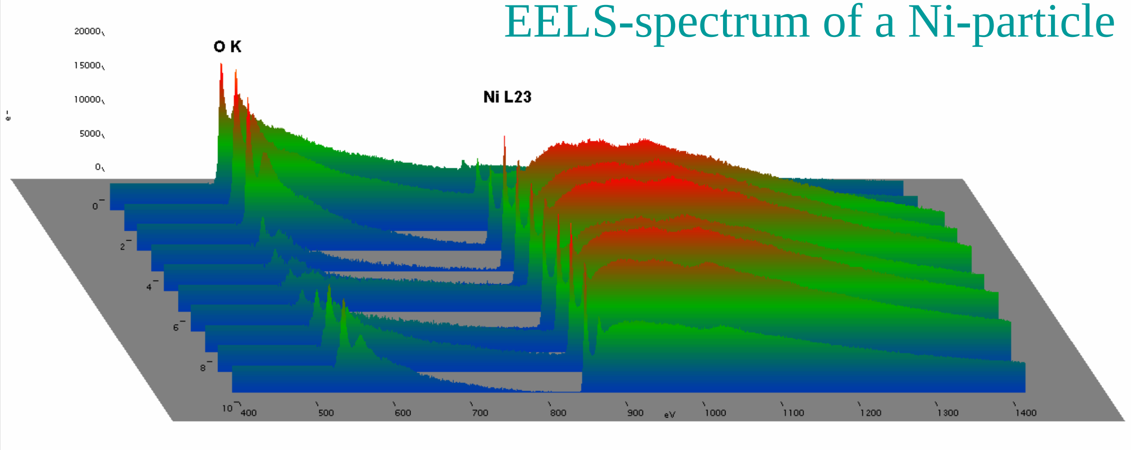
HRTEM of a Ni-particle



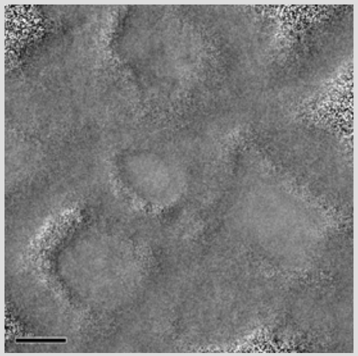
Crystalline orientation of a Ni-particle



EELS-spectrum of a Ni-particle



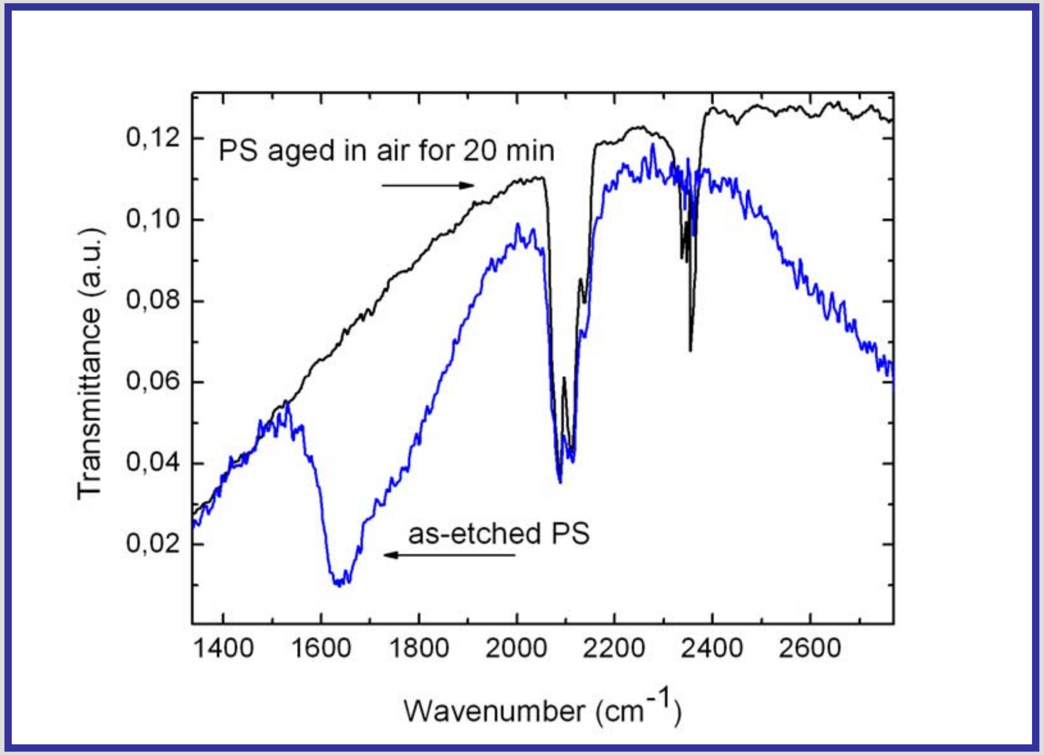
Oxide distribution



Optical behaviour

FTIR-investigations

Comparison between as-etched PS and aged PS



Si-H vibration modes:
2087 cm^{-1}: Si_2-Si-H_2 stretching mode
2115 cm^{-1}: Si_3-Si-H streching mode
2138 cm^{-1}: Si_2-Si-H streching mode

O-Si-H modes:
2250 cm^{-1}

Si-OH modes:
1635 cm^{-1}

FTIR-investigations of metal filled samples

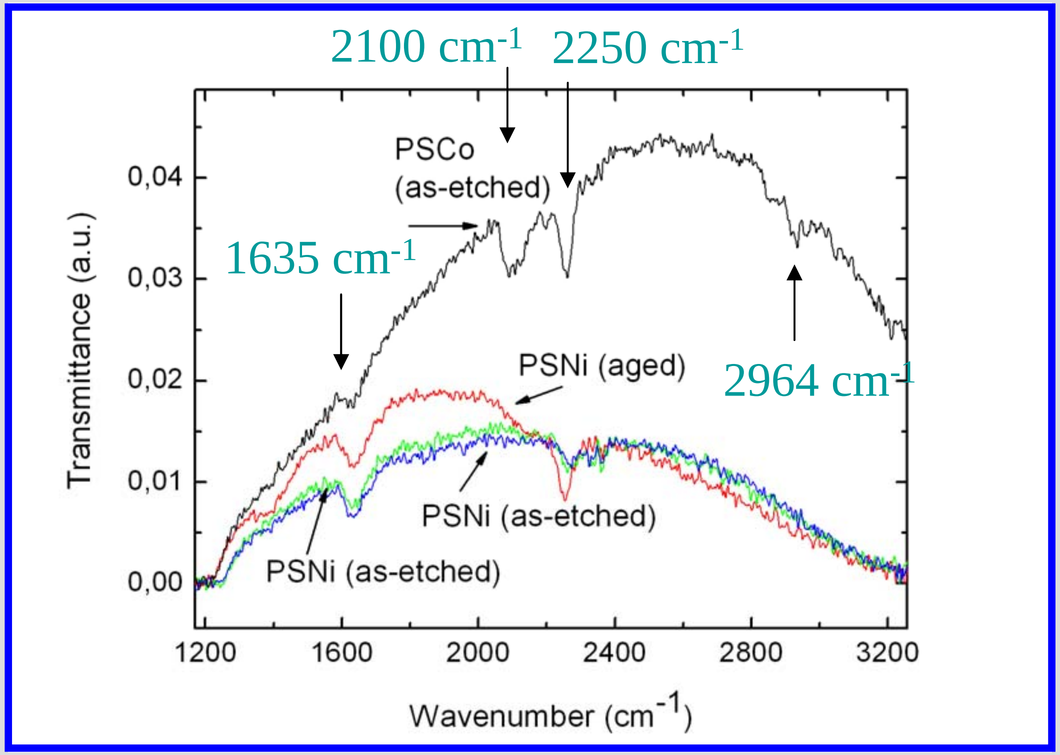
Comparison between Ni and Co filled specimens

2200 cm^{-1} and 2250 cm^{-1}:
O-Si-H modes

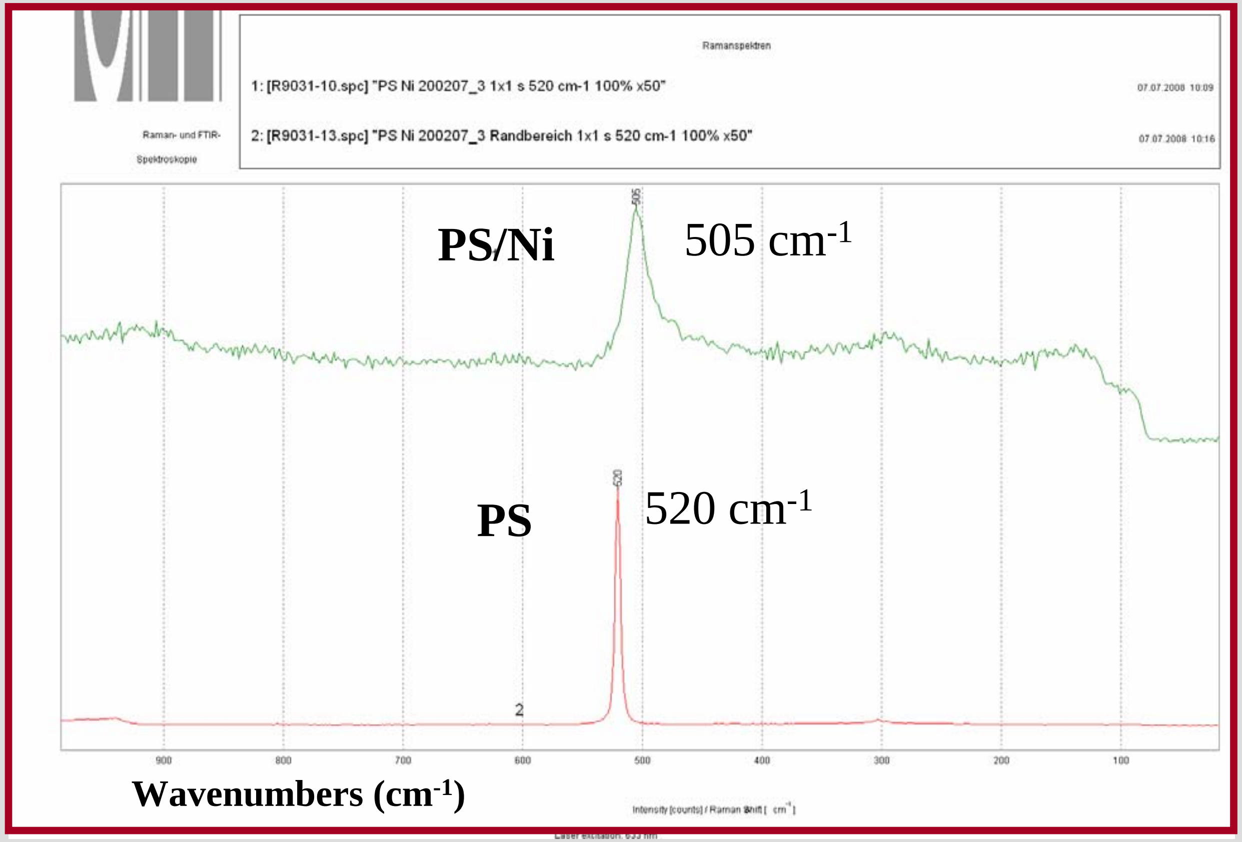
1635 cm^{-1}: Si-OH

Co-loaded sample:
~ 2100 cm^{-1}: SiH-modes
2964 cm^{-1}: SiO_x modifications

Ni-loaded sample:
1368 cm^{-1}. SiO_3

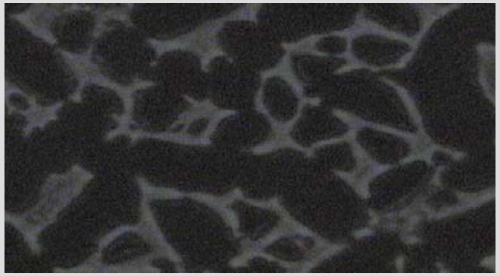


Comparison between bare PS and Ni-filled PS



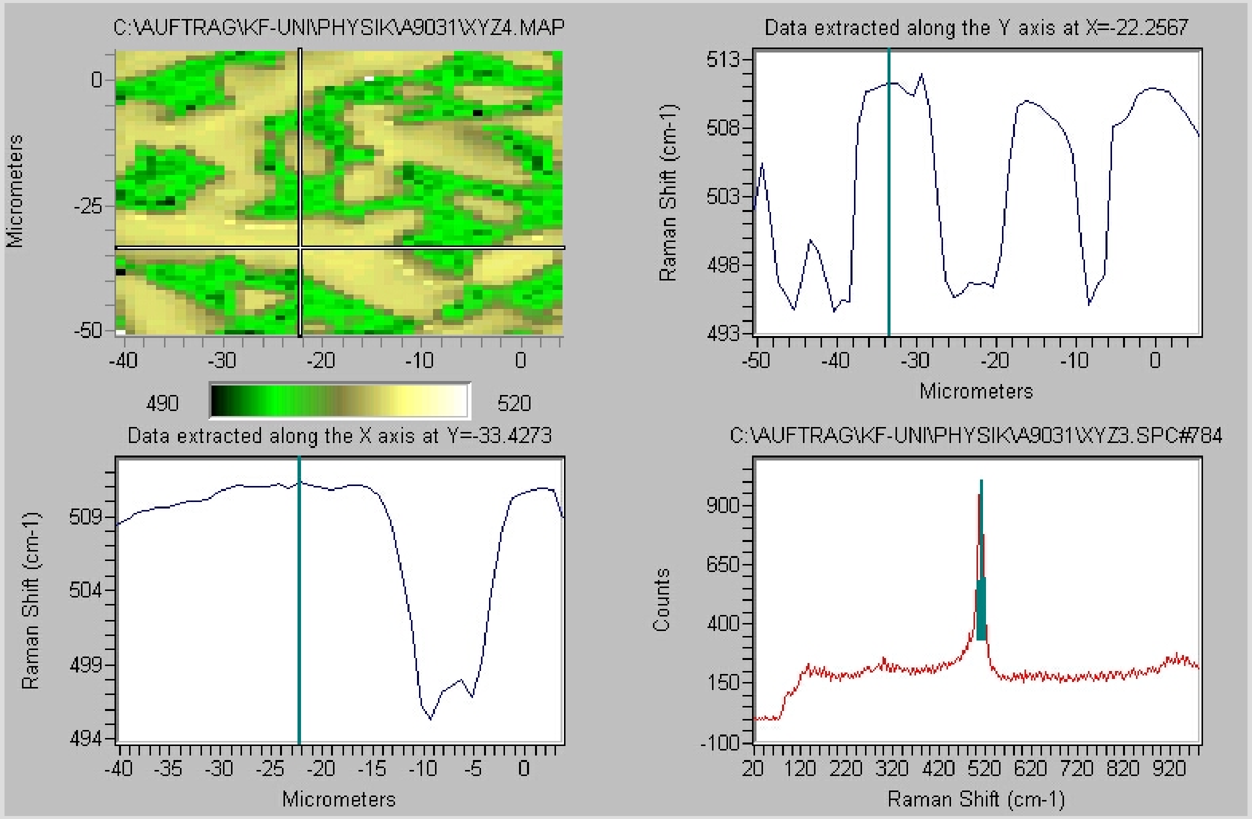
Shift of the Raman peak of PS/Ni to lower wavenumbers caused by stress

Raman-mapping

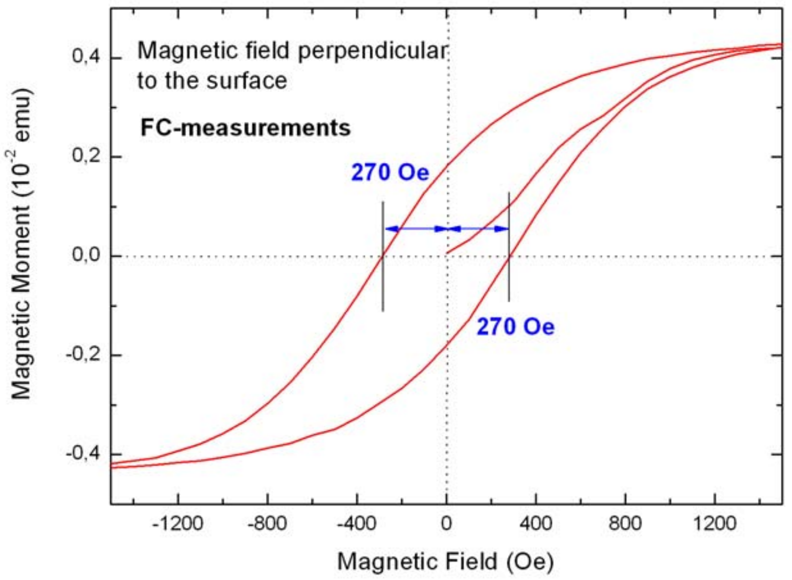


Micrograph of a PS/Ni sample

Raman mapping of the area shown beside:
Green: Ni-loaded regions – shift of the Raman peak due to higher stress
Yellow: silicon



Magnetization measurements



Proof of an oxide shell

Symmetrical coercivity (H_C = 270 Oe) obtained from field cooled measurements indicates that the metal particles are not covered by an antiferromagnetic oxide layer

Due to field cooled measurements exchange bias effects can be excluded.

Perspectives and ideas for future work

INSTITUTE OF PHYSICS MAGNETOMETRY PHOTONICS UNI GRAZ

- **Control of oxide growth during electrodeposition**

- **High quality oxide layer as tunnel barrier for spin-injection into silicon**

- **Transport measurements**
  (magnetic field parallel and perpendicular to the surface, respectively)

Conclusion

- Effective method to achieve a quasi-regular PS template in the meso-/macro porous regime without lithography.

- The oriented pores show a quite homogeneous pore distribution which shows a quadratic-like symmetry for special preparation conditions.

- This PS template is used for filling with a ferromagnetic metal to obtain 3-dim nanostructure arrays with tunable magnetic properties.

- This nanocomposite system gives rise to applications in sensor technology, magneto-optical devices but also to detect spin-injection into Si. Promising candidate for silicon based spintronic devices.

Coworkers

H. Krenn

K. Rumpf

P. Granitzer

P. Poelt

M. Albu

B. Chernev

Colaboration / Acknowledgements

TUG

nanolytics
Dr. K. Schilcher

THANK YOU FOR
YOUR ATTENTION !