10 Tera-bits-per-square-inch arrays of self-organized, single crystalline 1D nanomagnets

T. Blon [1], N. Liakakos[1,2], C. Achkar[1], B. Cormary[1], R. P. Tan[1], G. Chaboussant[3], F. Ott[3], B. Warot-Fonrose[2], E. Snoeck[2], B. Chaudret[1], M. Respaud[1], K. Soulantica[1]

[1]*Laboratoire de Physique et Chimie des Nano-objets (LPCNO), Toulouse*

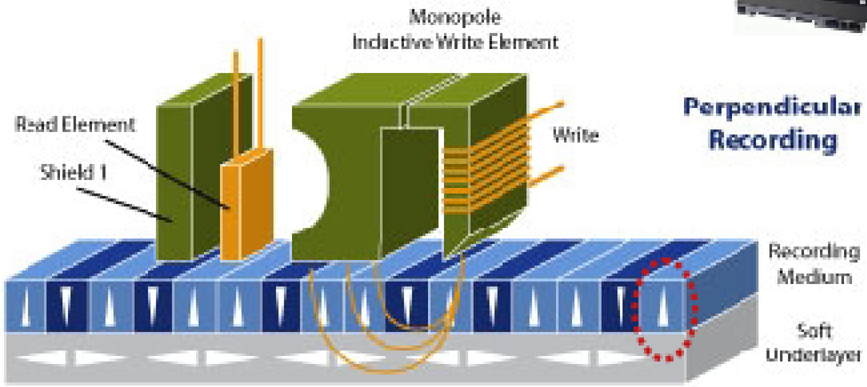
[2] *CEMES-CNRS, Toulouse*

[3] *Laboratoire Léon Brillouin, Gif sur Yvette*

Context: magnetic recording

Interest of ultra-high density nanomagnet arrays

Actual technology of Hard Disk Drives:
perpendicular magnetic recording (PMR)



Magnetic element of volume V
and magnetic anisotropy K

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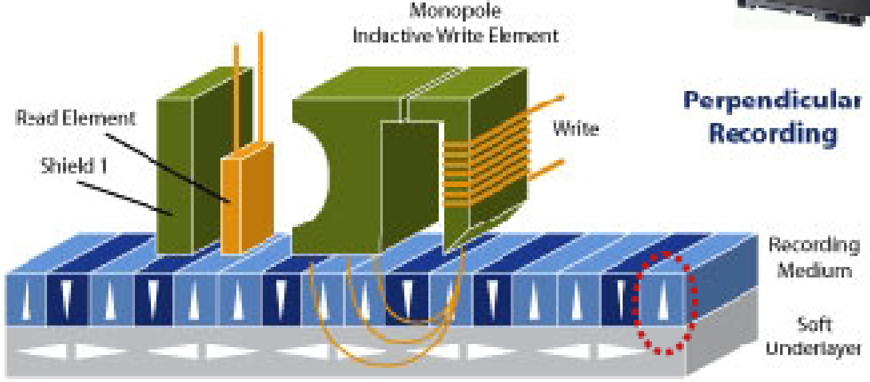

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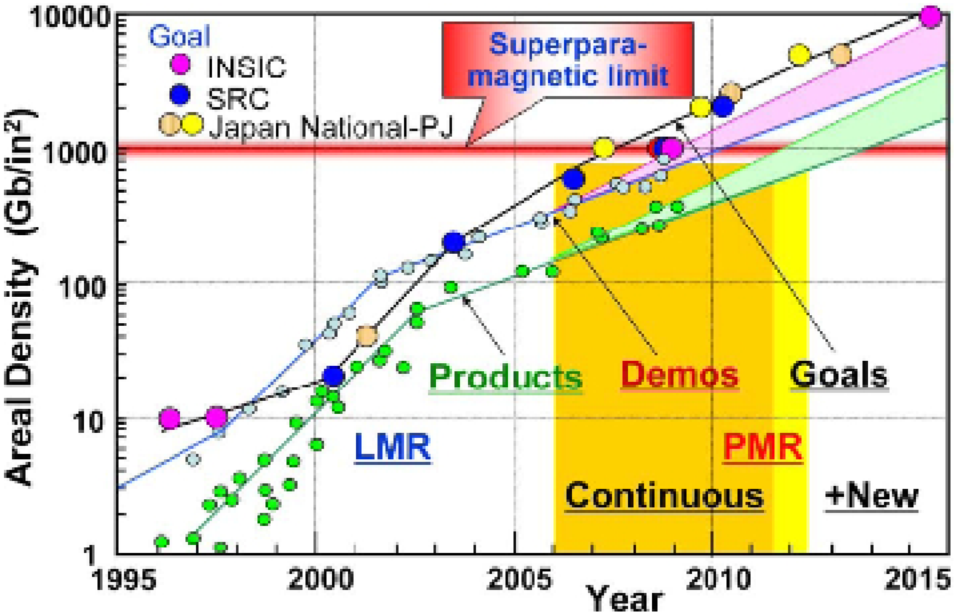
Interest of ultra-high density nanomagnets arrays

Areal density and R&D targets



Limitation of the actual technology: superparamagnetic limit

Relaxation time: $\tau = \tau_0 \cdot \exp(KV/k_BT)$ + Magnetic relaxation time > 10 years ⇨ High KV product are required ($KV \approx 40\ k_BT$)

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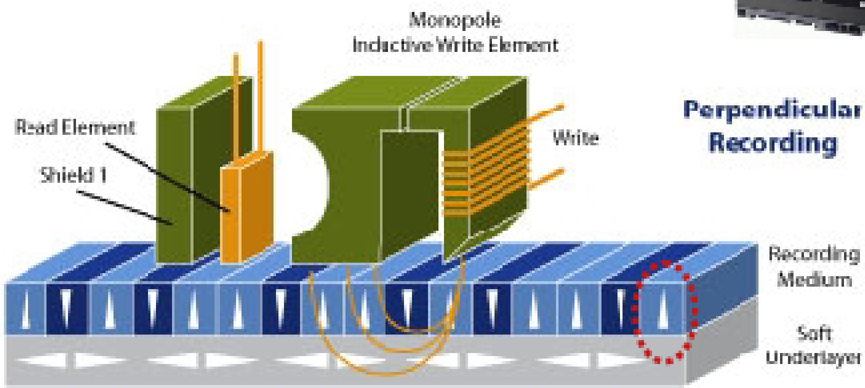

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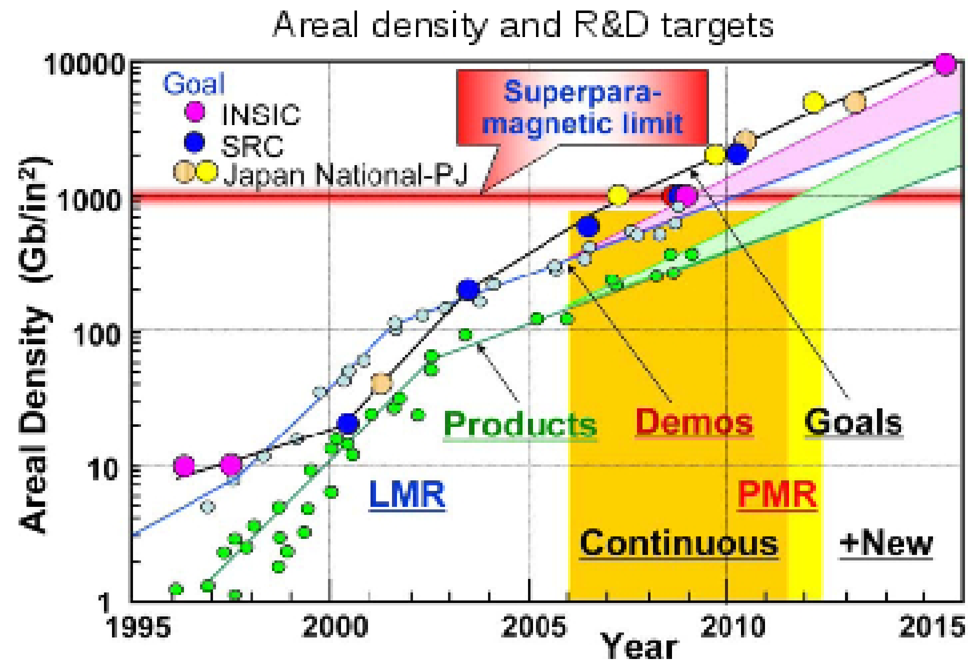

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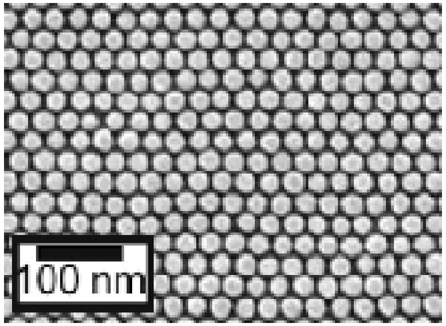
Relaxation time: $\tau = \tau_0 \cdot \exp(KV/k_B T)$ + Magnetic relaxation time > 10 years ⇨ High KV product are required ($KV \approx 40\ k_B T$)

Alternative technology: Bit Patterned media (BPM)



Demo : 1 Tbits/in²

CoCrPt PVD film deposited on a diblock copolymer template

T.R. Albrecht *et al.* *IEEE Trans. Mag.* 49(2) 773 (2013)

Context: Solution synthesis of Co NWs

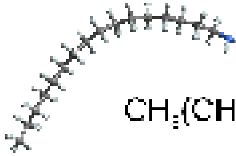
Decomposition of an organo-metallic precursor

Cobalt precursor: $Co[N(SiMe_3)_2]_2$

Organic ligands

+

Hexadecylamine (**HDA**)

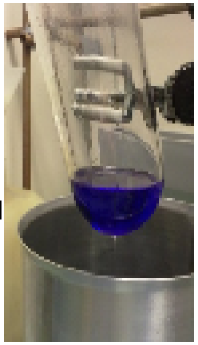


$CH_3(CH_2)_{15}NH_2$

+

Lauric Acid (**LA**)

$CH_3(CH_2)_{10}COOH$

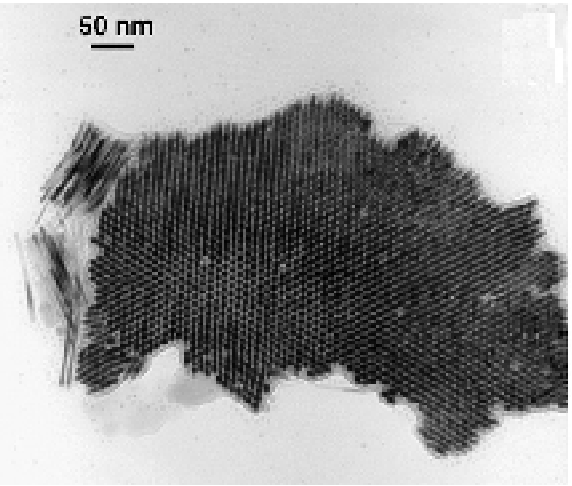


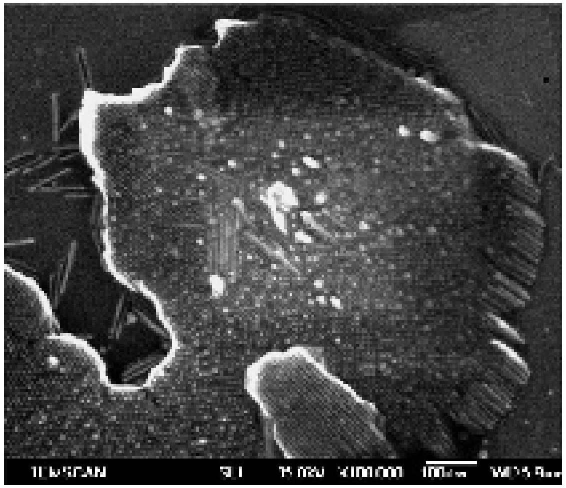
dissolved in dry anisole under 3bar of H_2

F. Wetz et al., Mater. Sci. Eng. C, 27, 1162 (2007)
K. Soulantica et al., Appl. Phys. Lett. 95, 152504 (2009)

Context: Solution synthesis of Co NWs

SEM and TEM after 48 hours





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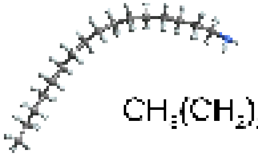

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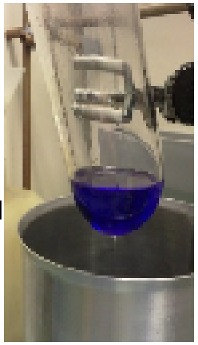

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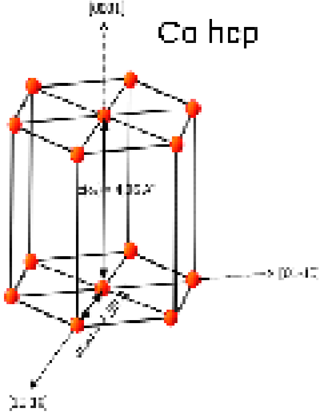
Single crystalline Co nanowires

- Length : 40 - 100 nm
- Diameter: 5 - 6 nm
- Single crystalline Co hcp



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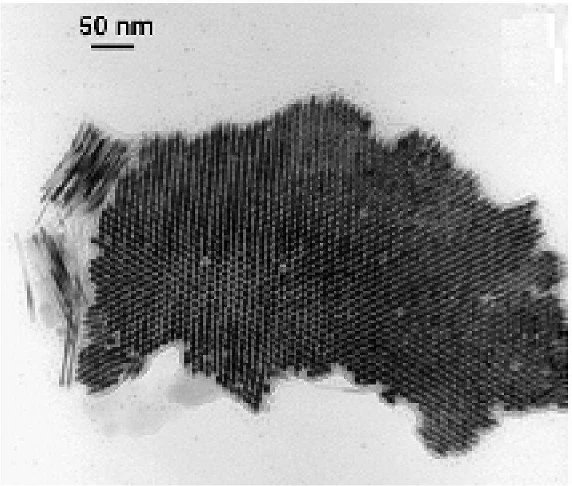

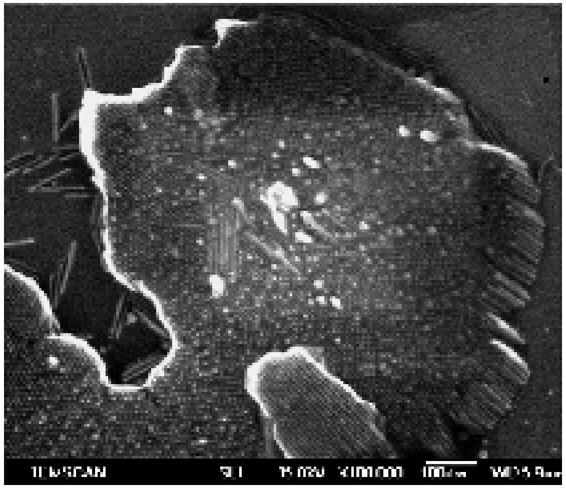

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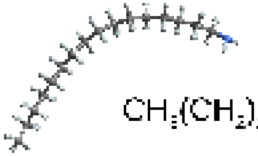

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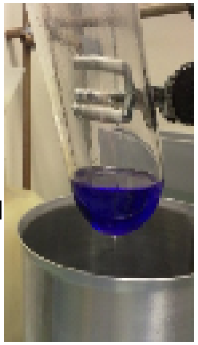

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Lauric Acid (**LA**)

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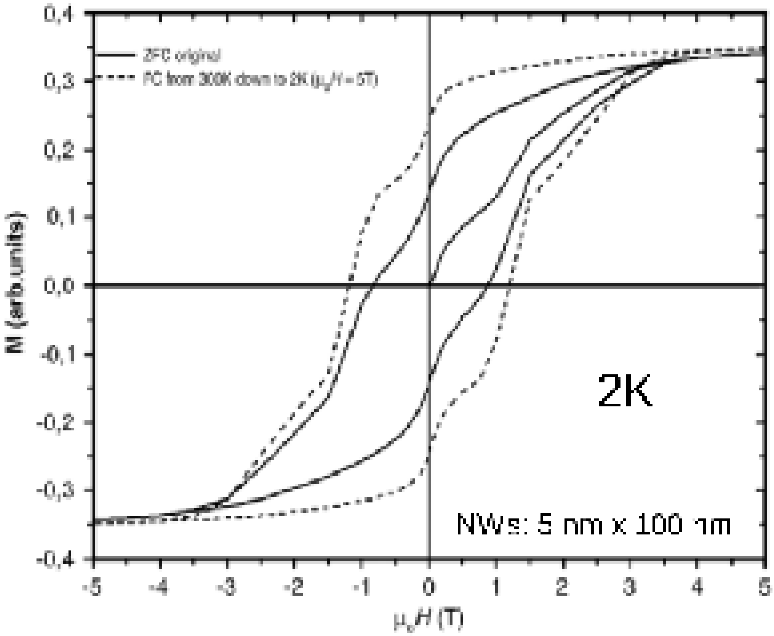
dissolved in dry anisole under 3bar of H_2



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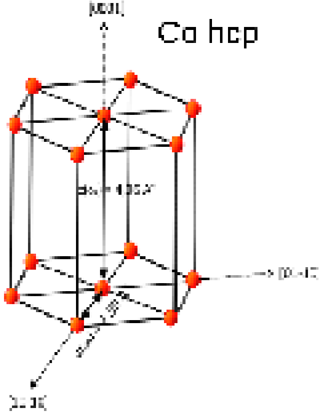

- $\mu_0 H_c$ @ 2K = 1.2T

=> Effective anisotropy K_{eff} = 8.10⁵ J/m³

vs theory: K_{eff} = *Kshape* + *Kmc* = 11 .10⁵ J/m³

F. Wetz et al., Mater. Sci. Eng. C, 27, 1162 (2007)
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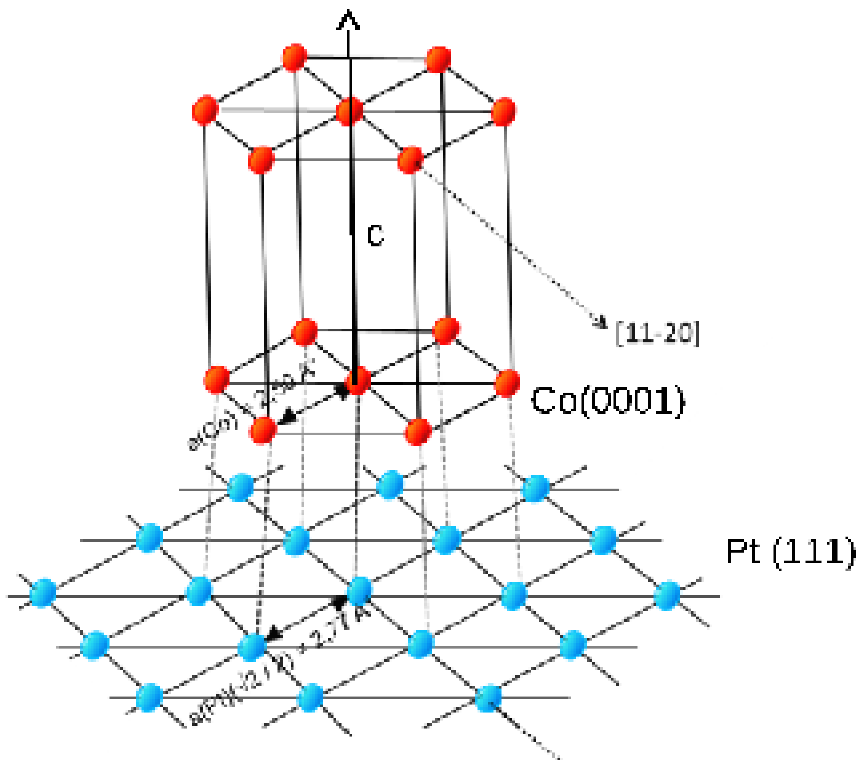
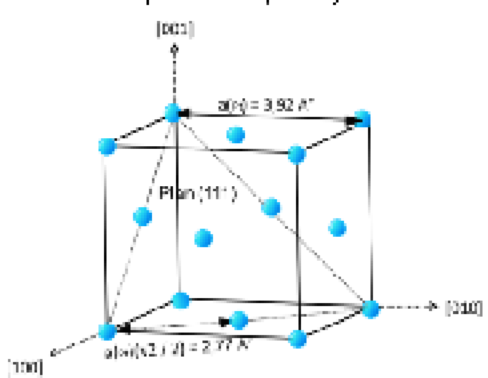
How to organize Co NWs on a surface?

State of the art of Co(0001) film growth

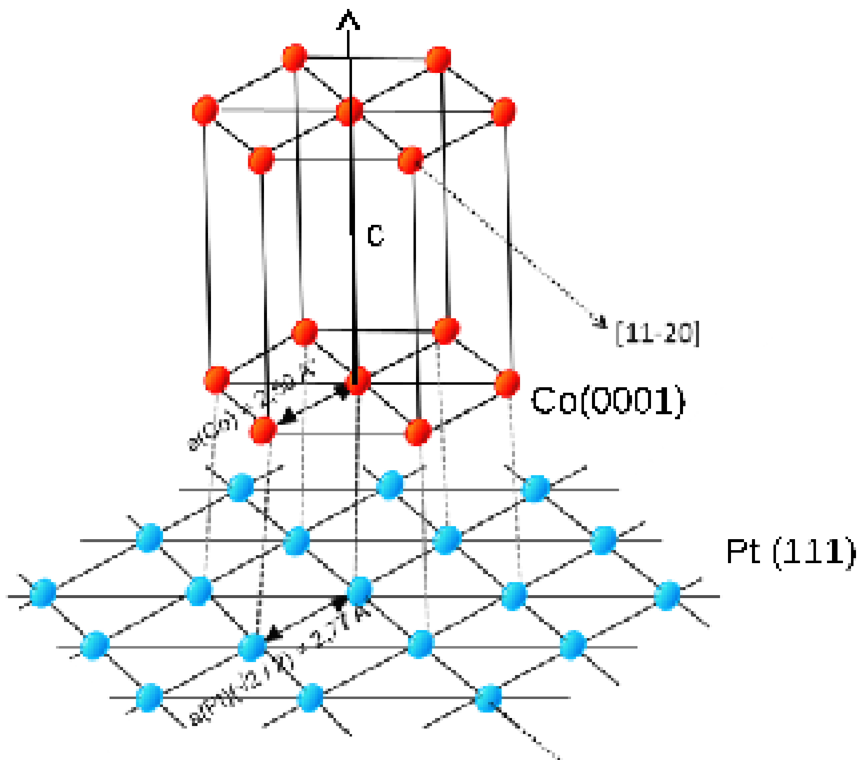


P. Grütter, U.T. Durig, Phys Rev B. ***49*** *2021 (1994).*
J. Thiele Surf. Sci. **384**, 120-128 (1997)



How to organize Co NWs on substrates?

State of the art of Co(0001) film growth



P. Grütter, U.T. Dürig, Phys Rev B. 49 2021 (1994).
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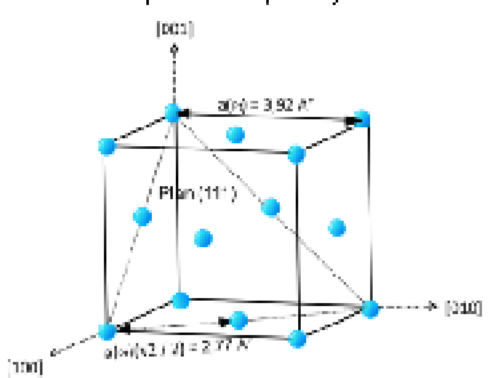
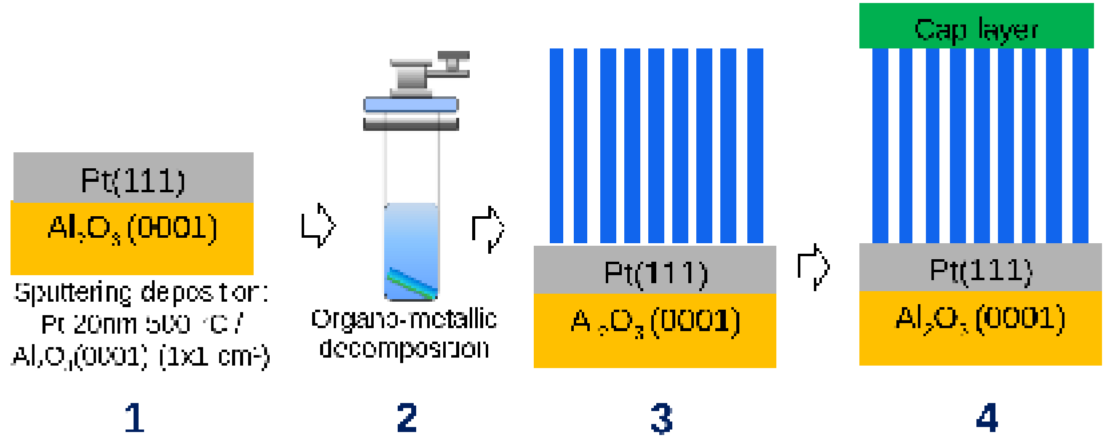


Process



Set-up

Glove Box

Ar atmosphere
(without H_2O and O_2)

Spin coating, dip coating, hot plate, electrical measurements, optical microscope

Thin Film deposition chamber

DC and RF sputtering, evaporation, reactive plasma, annealing

Co NWs / Pt(111)

Conditions 1

Co/LA/HDA=1/1.2/1.2 ; 100°C, 3 bars of H_2, 4.5 days of reaction

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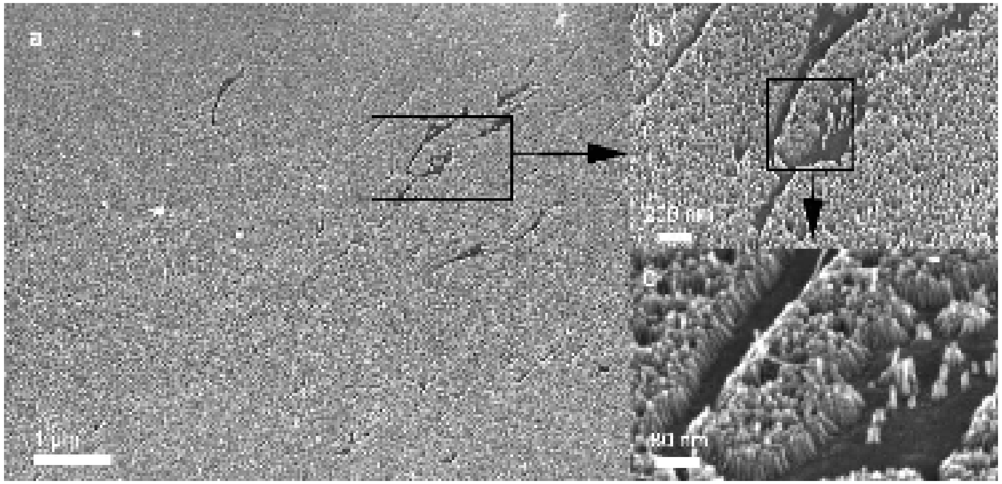
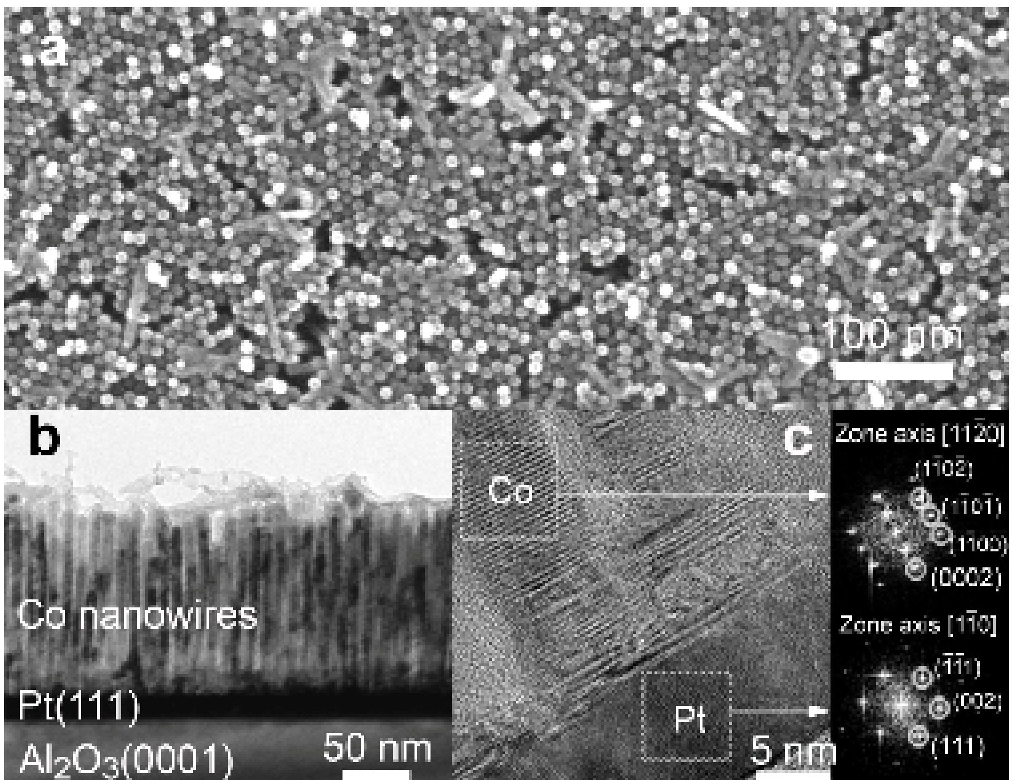
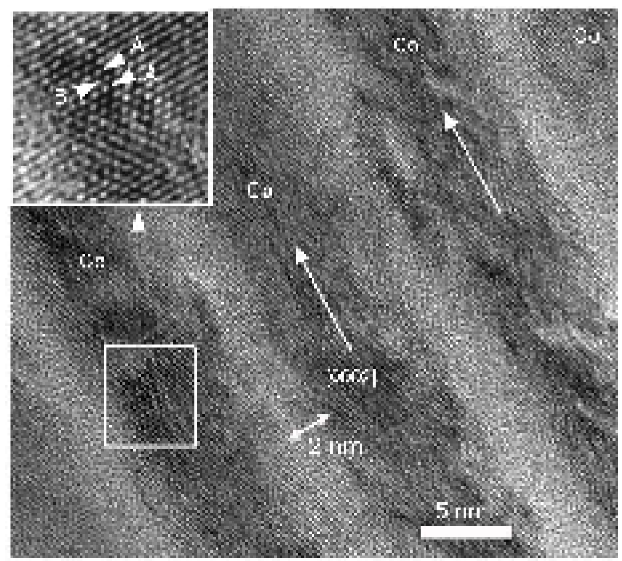


- 8 nm in diameter
- 150 nm in length
- 2 nm inter-NWs distance
- single-crystalline Co hcp
- epitaxial Co NW growth:

Co(0001) [11-20] // Pt(111) [2-20]

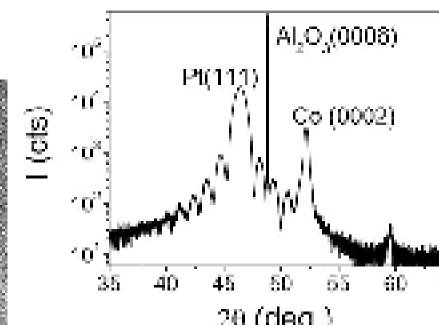


Electron microscopy

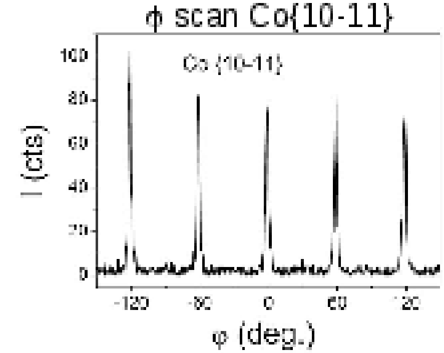


XRD

Symmetric θ-2θ scan



φ scan Co{10-11}

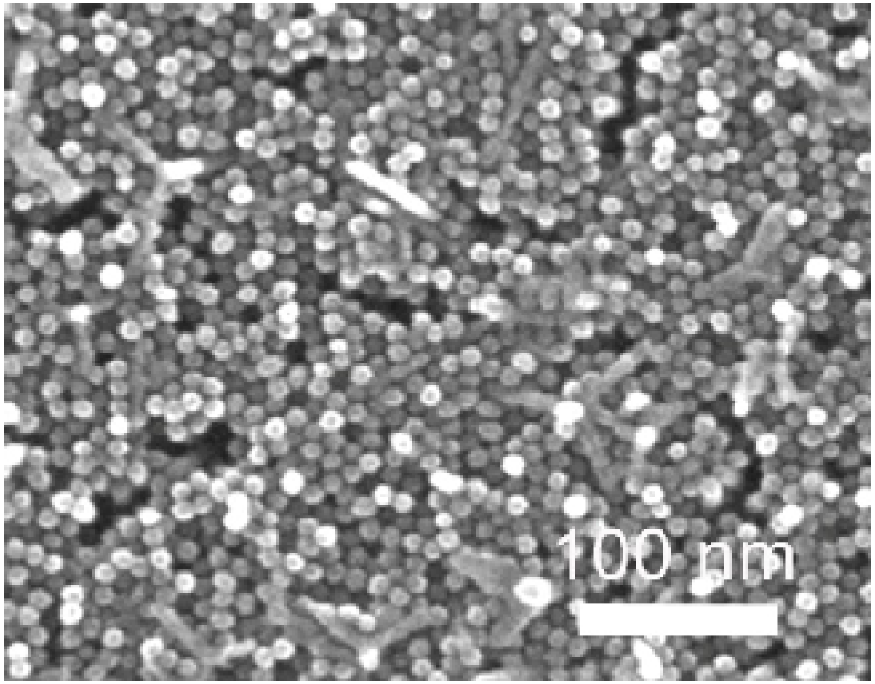


French Patent 10.00405 (2011),
PCT WO2011/095731

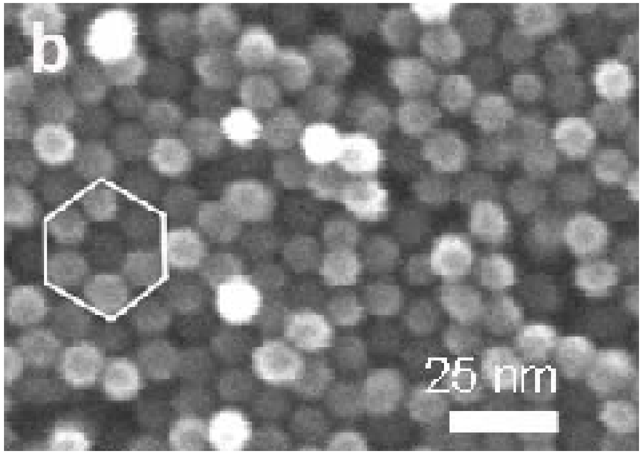
Co NWs / Pt(111): 7 T-wires/in² arrays

Conditions 1

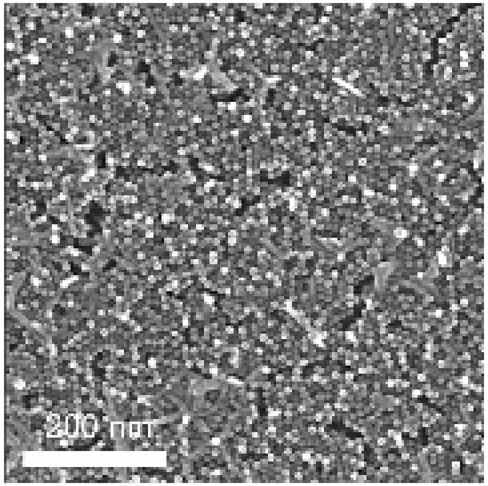
Co/LA/HDA=1/1.2/1.2 ; 100°C, 3 bars of H_2, 4.5 days of reaction



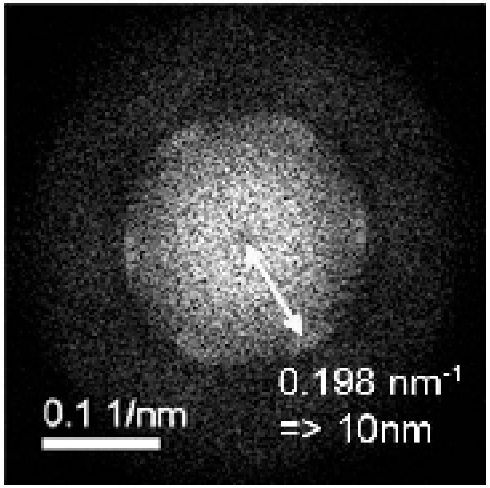
SEM micrographs



SEM micrograph



FFT



⇒ hexagonal array with a 10 nm periodicity

⇒ **7×10^{12} NWs/in²**

7 T-wires/in² Co NW arrays

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Conditions 2

Co/LA/HDA=1/2/2 ; 150°C, 3 bars of H_2, 24h of reaction

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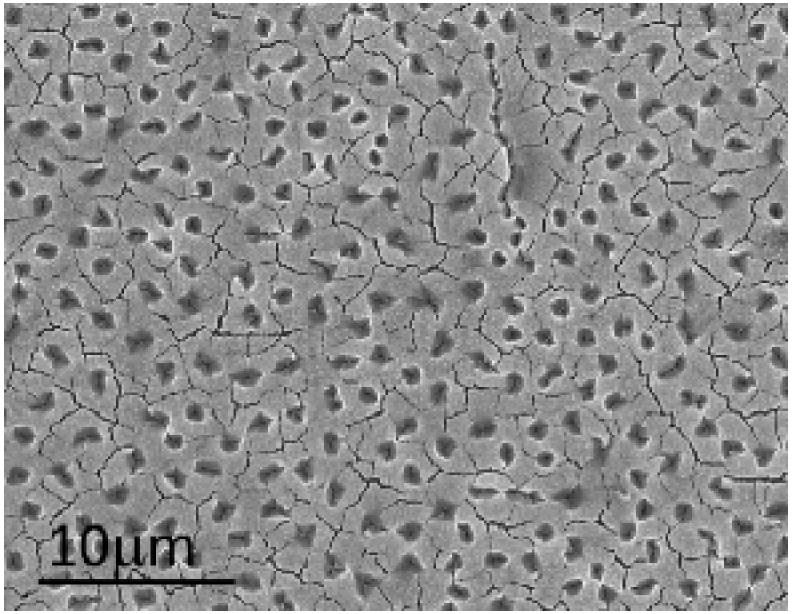

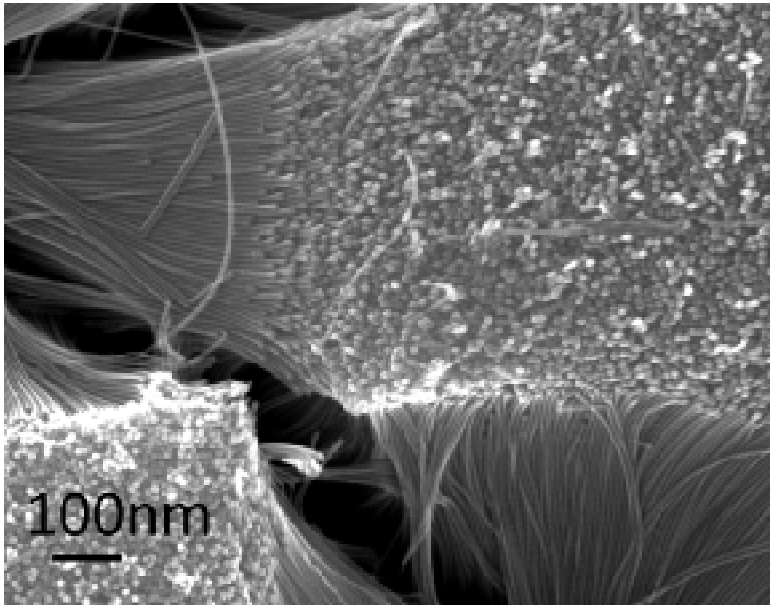

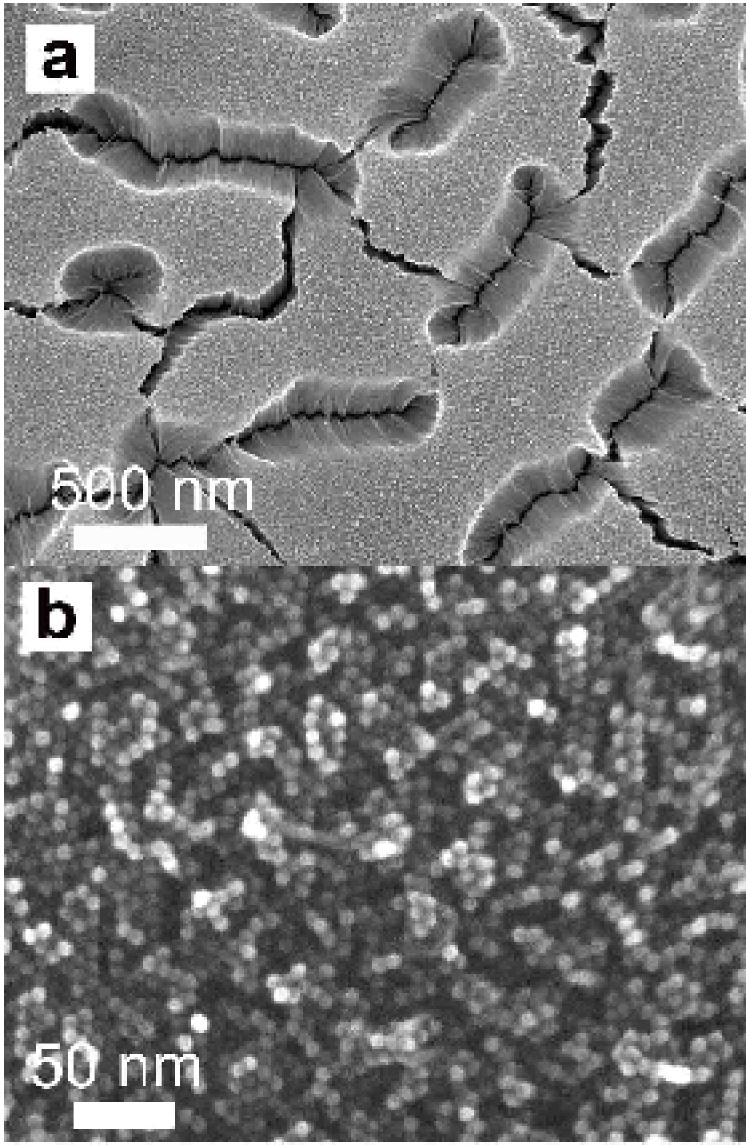

Co NWs / Pt(111)

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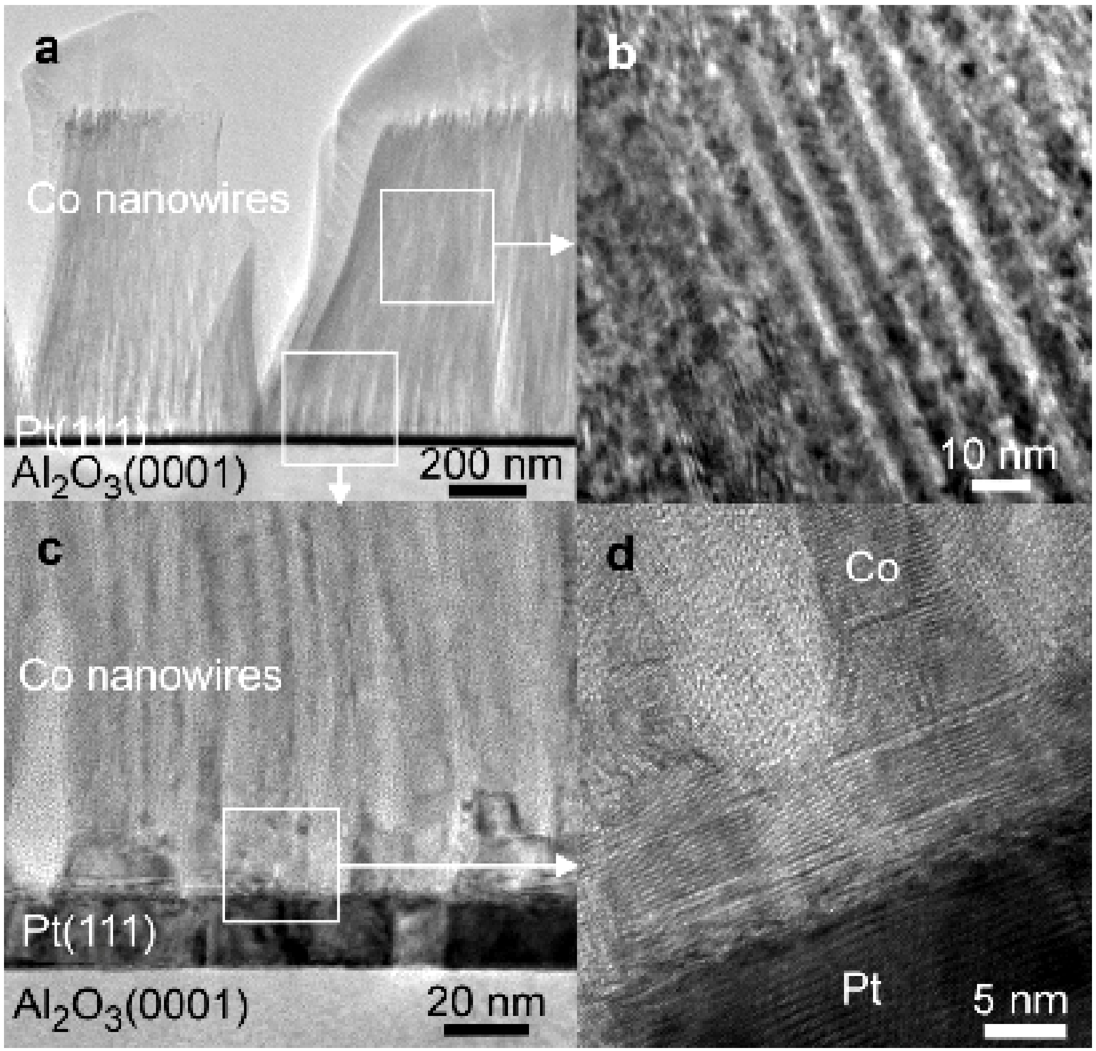
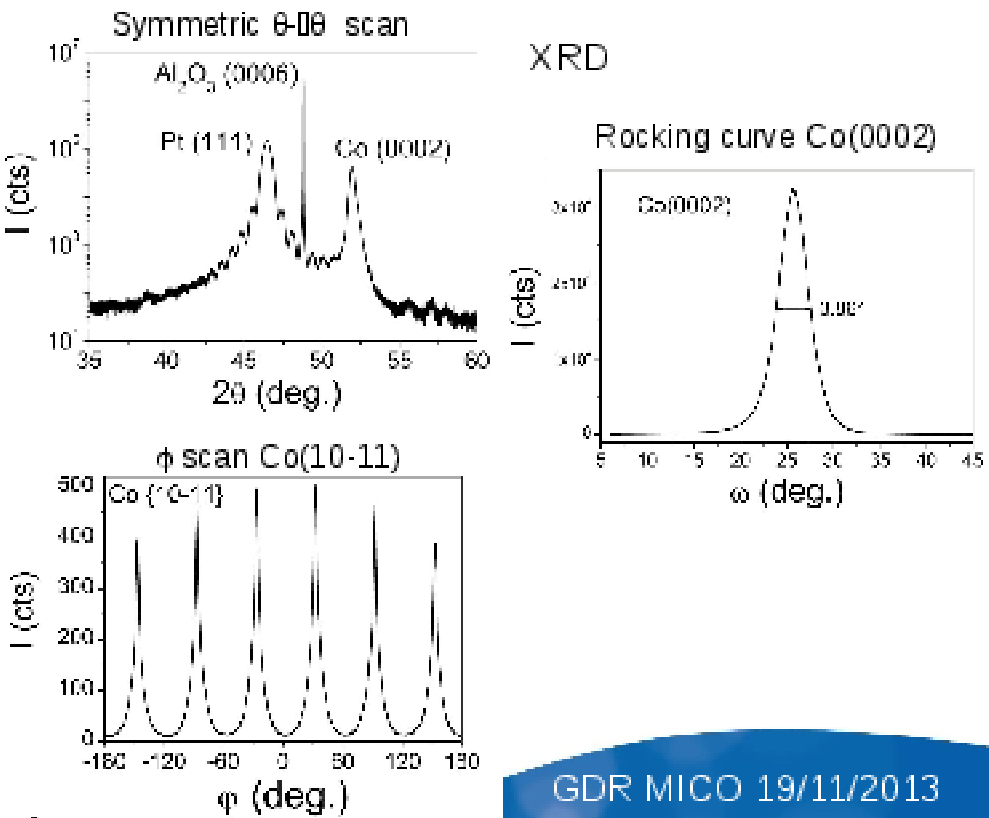
TEM micrographs



- 5-6 nm in diameter
- 960 nm in length
- 2 nm inter-NWs distance
- single-crystalline Co hcp
- epitaxial Co NW growth:
Co(0001) [11-20] // Pt(111) [2-20]
- Low dispersion of the NW axis: ±2°

XRD



Co NWs / Pt(111): 10 T-wires/in² arrays

Conditions 2
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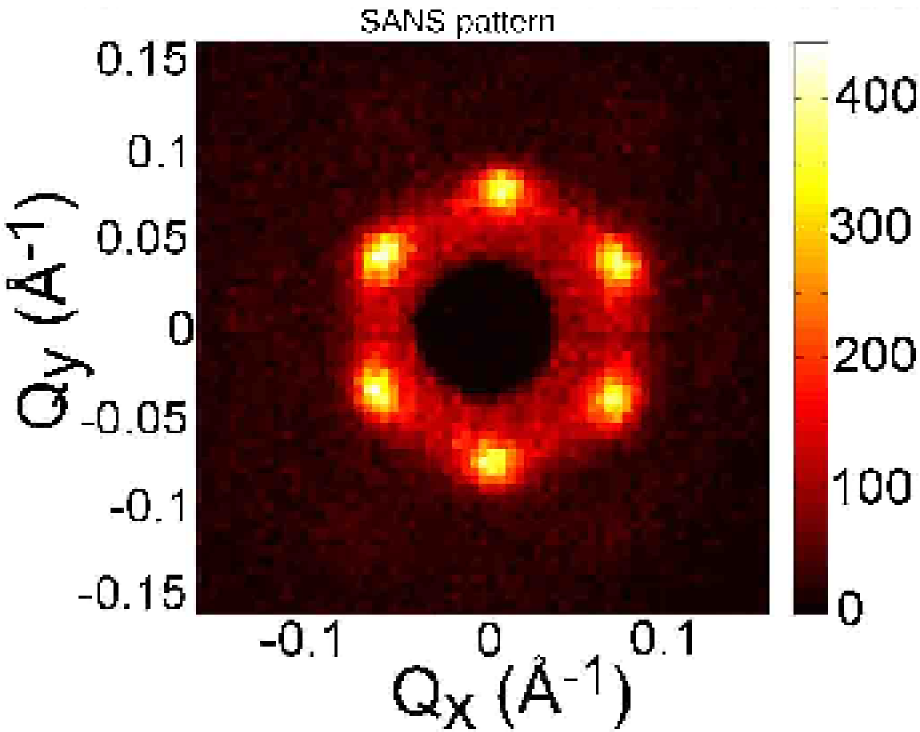
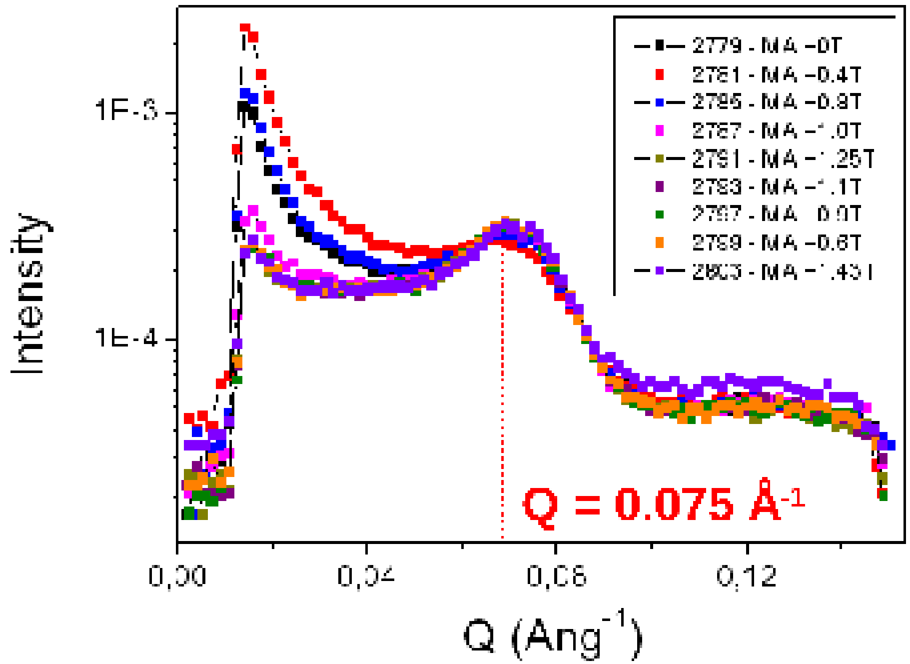
Small angle neutron scattering (SANS)

PAXY spectrometer at the Laboratoire Léon Brillouin / Orphée, Saclay, France



Integration circulaire de l'intensité diffusée



Array periodicity : $P = 2\pi / Q =$ **8.4 nm**

- **density : 10.3×10^{12} NWs/in²**
- packing fraction $P = 0.38$

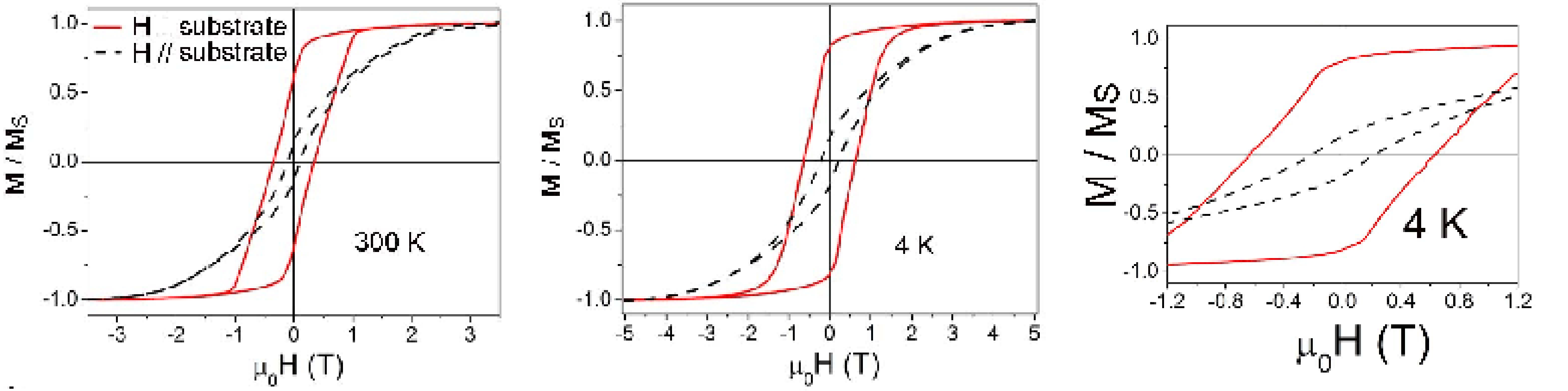
Collaboration: F. Ott, G. Chaboussant, LLB-CEA

10 T-wires/in² Co NW arrays

Co NWs / Pt(111):
10 T-wires/in² arrays

Conditions 2
Co/LA/HDA=1/2/2 ; 150°C, 3 bars of H_2, 24h of reaction

Hysteresis loops (VSM)



• <u>300K</u> : $\mu_0 Hc^{\perp}$ = 0.35 T and $Mr/Ms^{\perp}$ = 0.61
$\mu_0 Hc^{//}$ = 0.10 T and $Mr/Ms^{//}$ = 0.14

• no exchange bias after FC (5T 300K -> 4K)
=> no Co oxidation

<u>4K</u>: $\mu_0 Hc^{\perp}$ = 0.62 T and $Mr/Ms^{\perp}$ = 0.81
$\mu_0 Hc^{//}$ = 0.21 T and $Mr/Ms^{//}$ = 0.17

Co NWs / Pt(111): 10 T-wires/in² arrays

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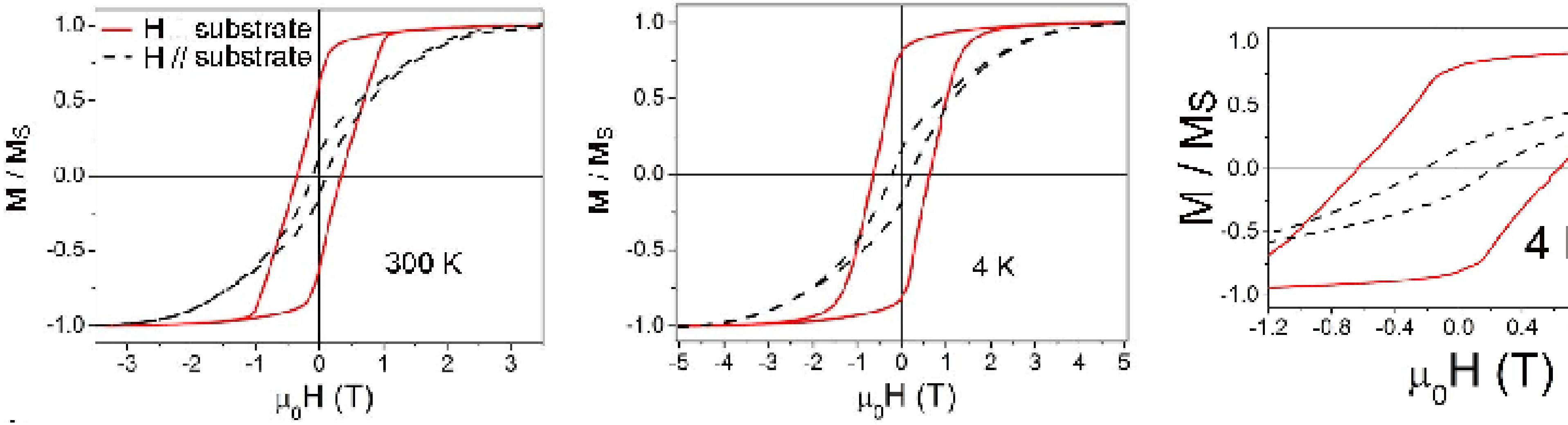

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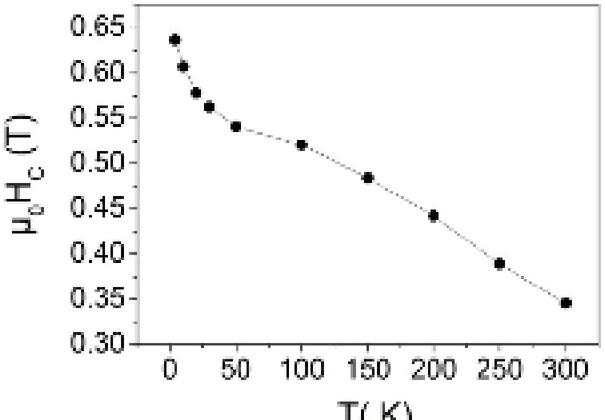

Impossibility to fit the data with the Sharrock formula :

$$H_C = H_0\left[1-\left(\frac{\ln(t/\tau_0)k_BT}{K(T)V}\right)^{1/m}\right]$$

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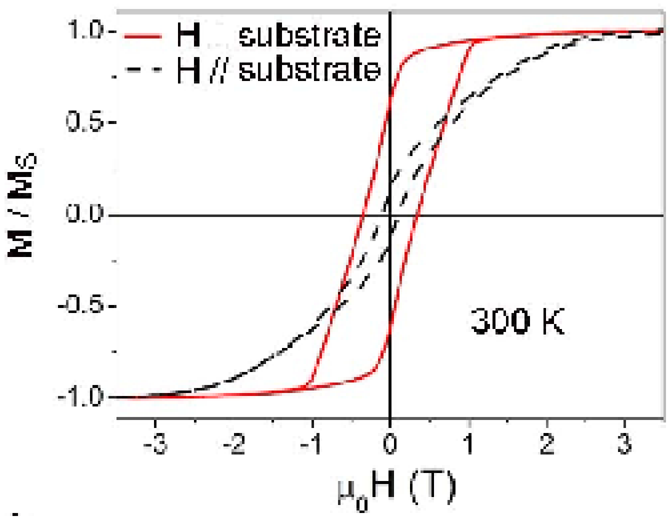

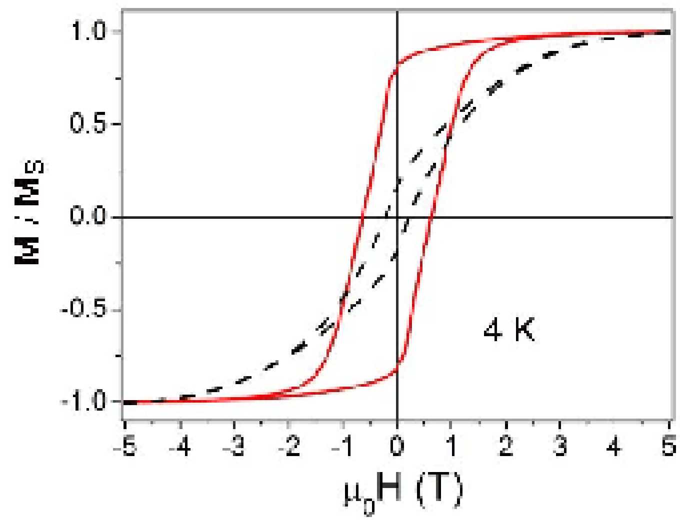

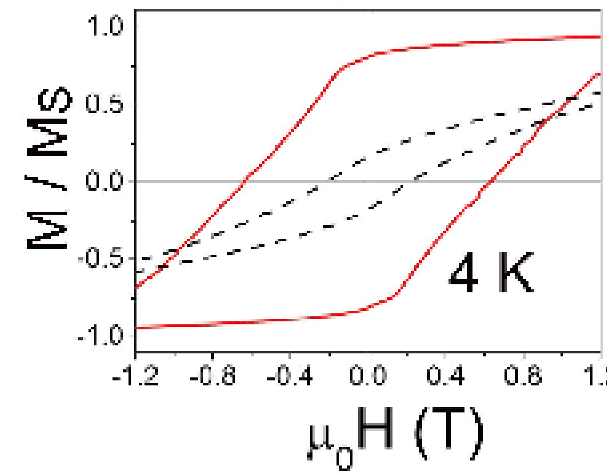

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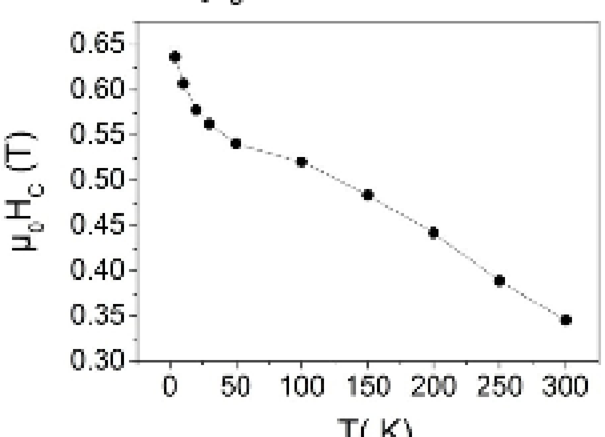

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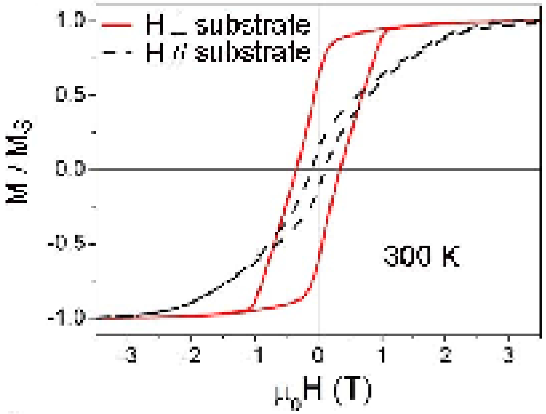
- no exchange bias after FC (5T 300K -> 4K)
  => no Co oxidation

- saturation magnetization: 7.1×10^{-3} emu.
  using bulk Ms => P = 0.42

- slope of hysteresis loop at Hc: $\left(\frac{dM}{dH}\right)_{Hc} \approx 1/P$
  => P = 0.40

Co NWs / Pt(111): 10 T-wires/in^2 arrays



- Measured perpendicular magnetic anisotropy (300 K):

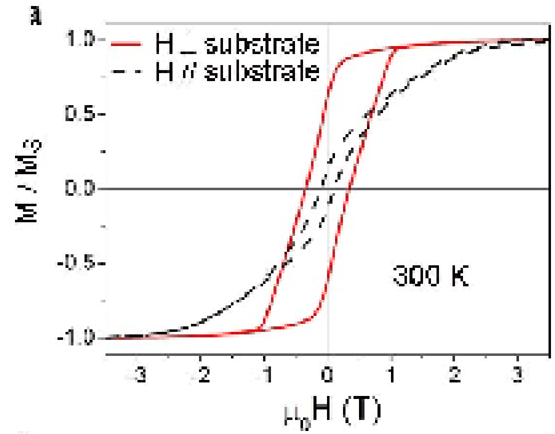
$$K_{eff} = 9.3 \;\; 10^5 \text{ J/m}^3$$

- Theoretical magnetic anisotropy:

$$K_{eff} = K_{mc} + \frac{\mu_0 M_S^2}{4}(1 - 3P) = 4.5 \times 10^5 J/m^3$$

⇨ Difference between exp. and expected anisotropies: dipolar interactions

Co NWs / Pt(111):
10 T-wires/in² arrays



- Measured perpendicular magnetic anisotropy (300 K):

$$K_{eff} = 9.3 \quad 10^5 \text{ J/m}^3$$

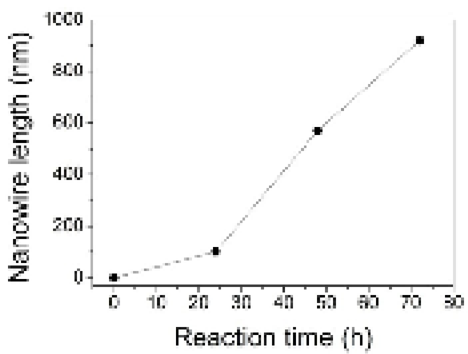
- Theoretical magnetic anisotropy:

$$K_{eff} = K_{mc} + \frac{\mu_0 M_S^2}{4}(1 - 3P) = 4.5 \times 10^5 J/m^3$$

⇨ Difference between exp. and expected anisotropies: dipolar interactions

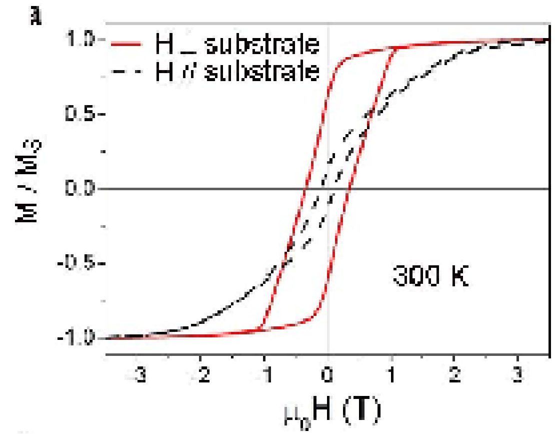
- $K_{eff}V \approx 4000 \times k_B T$ (using T=350K, a typical magnetic media working temperature)

⇨ Possibility to reduce the nanowire volume V



Nanowire length measured by TEM as a function of the reaction time (Co/LA/HDA ratio : 1/2/2, 110°C).

Co NWs / Pt(111): 10 T-wires/in² arrays



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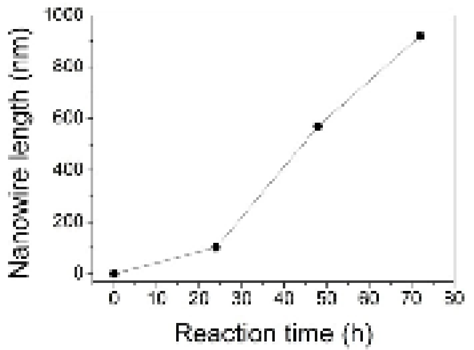
- $K_{eff}V \approx 4000\times k_B T$ (using T=350K, a typical magnetic media working temperature)

⇨ Possibility to reduce the nanowire volume *V*

- ***Magnetic media requirements***
  - *very low surface roughness*
  - *protection of the active layer with an adequate protective layer*

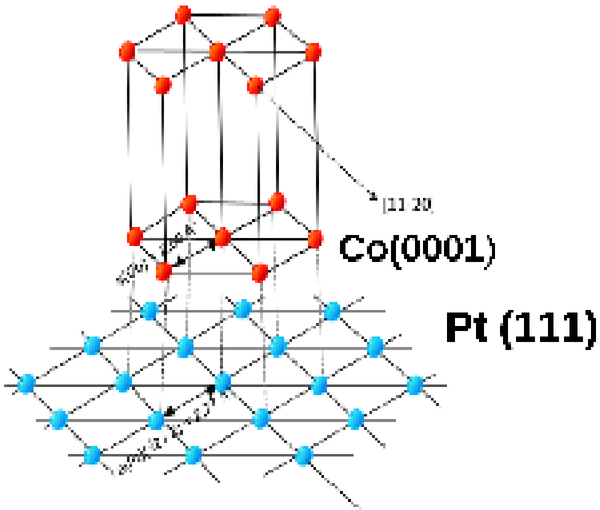
- ***Read/write process:***
  - Read/write methods are proposed for 10Tbits/in² (shingled writing and two-dimensional readback and signal processing)
  - bundles of several NWs => several Tbits/in² media



Nanowire length measured by TEM as a function of the reaction time (Co/LA/HDA ratio : 1/2/2, 110°C).

Influence of the film surface symmetry
Co NW / Pt(001)

Co(0001) NW growth on a 6-fold symmetry surface



Influence of the film surface symmetry
Co NW / Pt(001)

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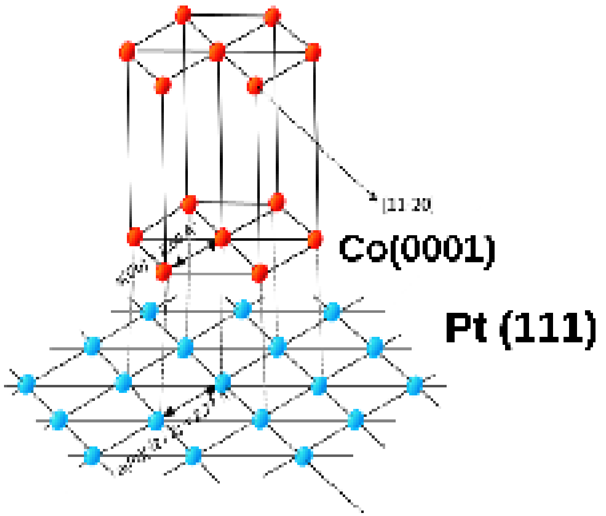
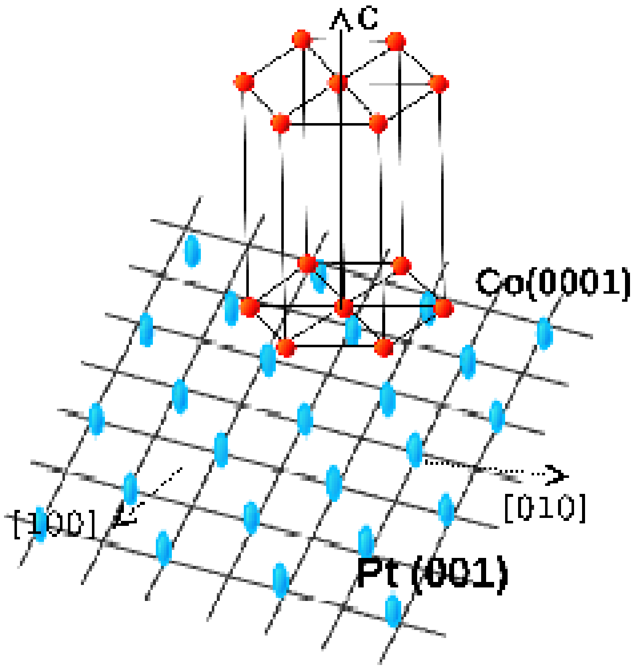
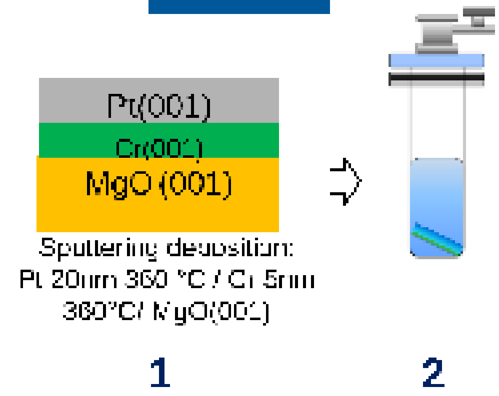


Co(0001) NW growth on a 4-fold symmetry surface ?



Process



Influence of the film surface symmetry
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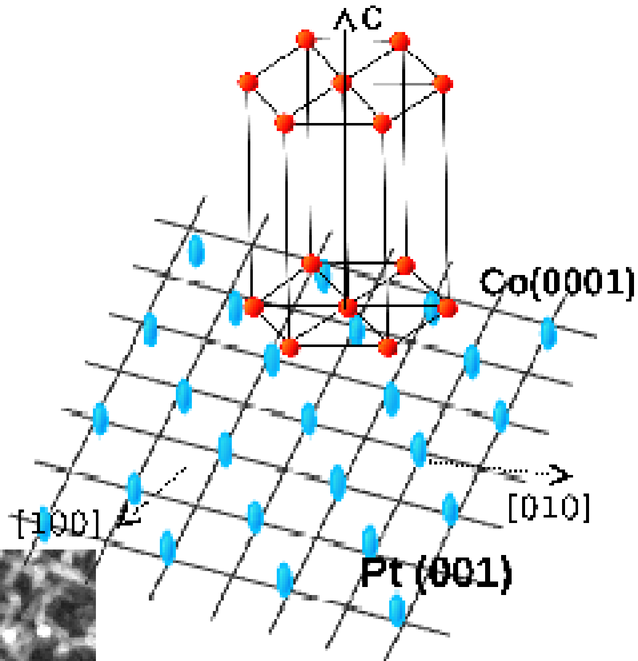
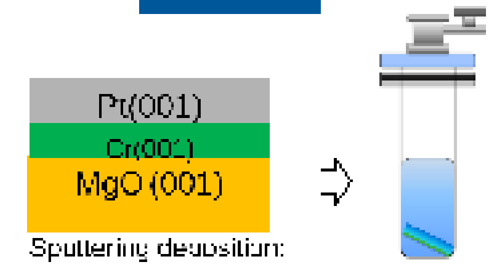


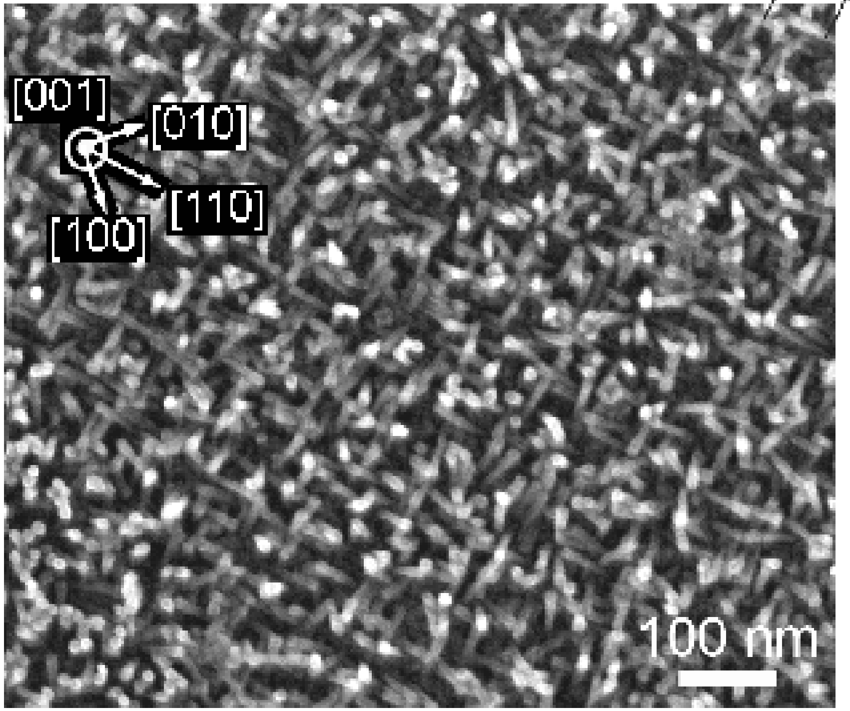
Process



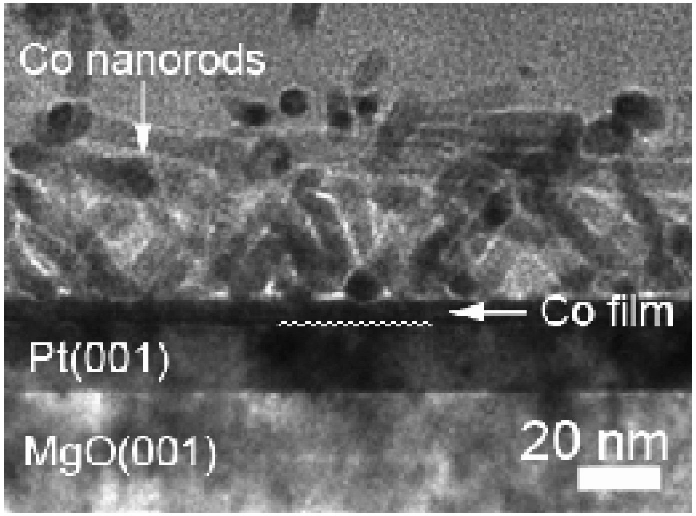
Sputtering deposition:
Pt 20nm 360 °C / Cr 5nm
360°C/ MgO(001)

1

2



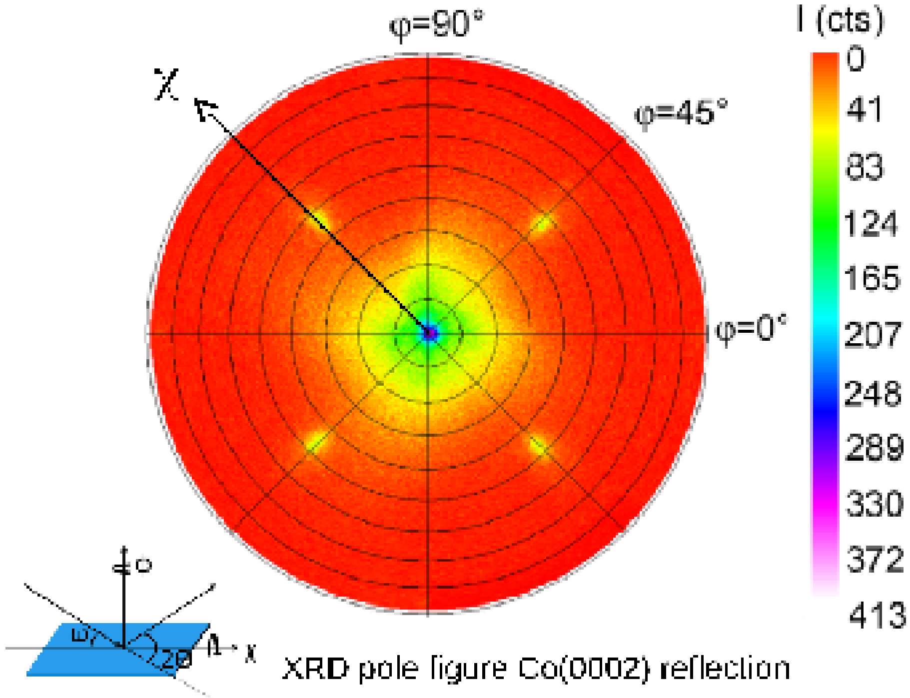
SEM



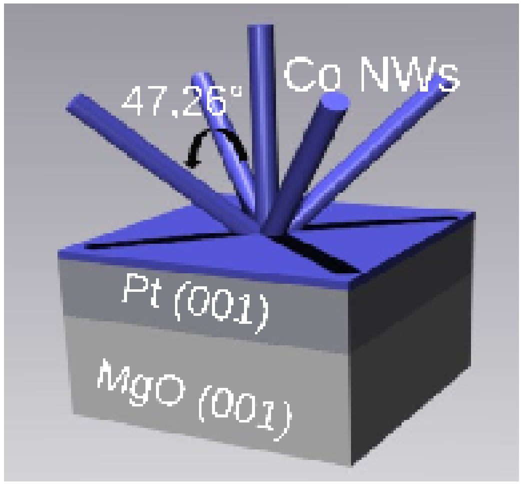
TEM

Tilted growth of Co nanowires on Pt(001)

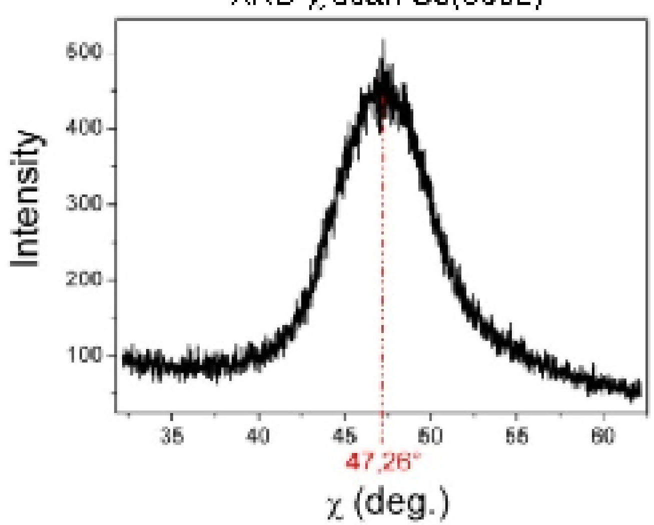
Influence of the film surface symmetry
Co NW / Pt(001)



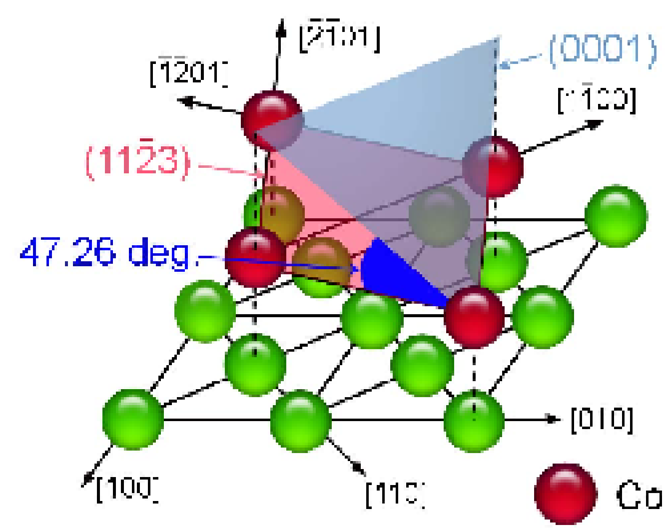
XRD pole figure Co(0002) reflection



XRD χ scan Co(0002)

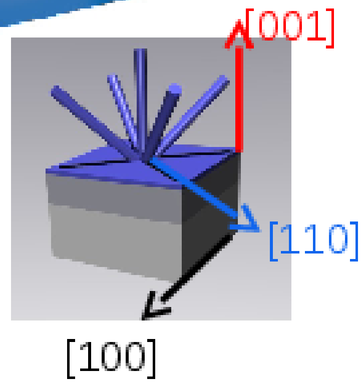


Hypothesis: Co (11-23) // Pt(001)

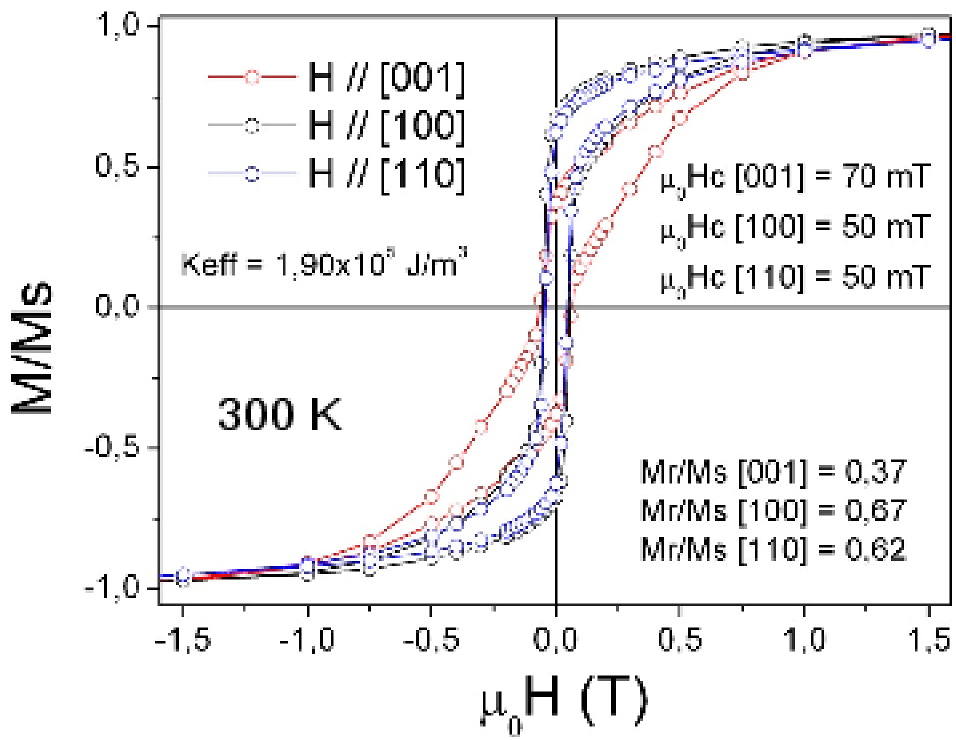


Co(11$\bar{2}$3) / Pt(001)

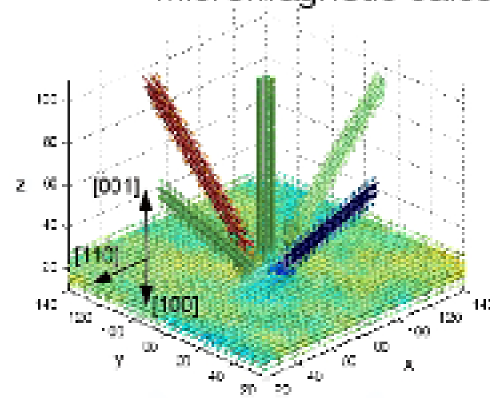
Influence of the film surface symmetry
Co NW / Pt(001)



Hysteresis loops (SQUID)



Micromagnetic calculation (OOMMF code)



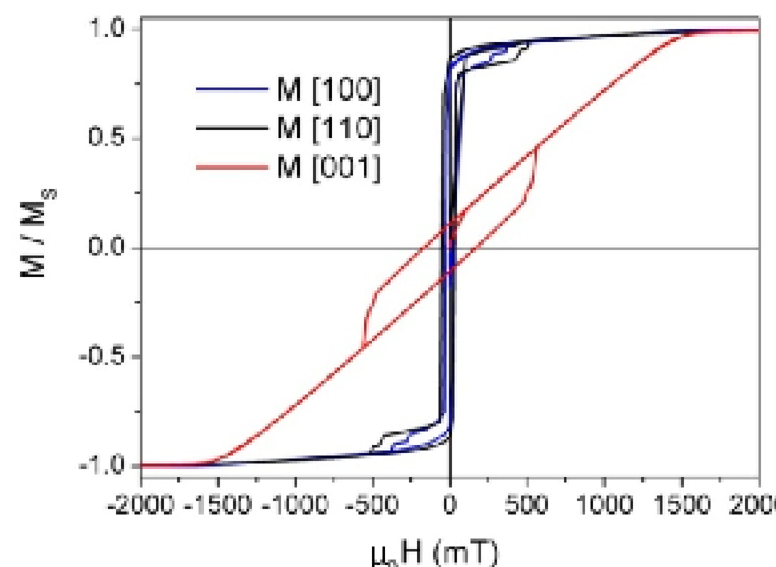
Cell size: 4*4*4 nm^3

Kmc = 5,3.10^5 J/m^3

Ms = 1,37.10^6 A/m

A = 1,3.10^{-11} J/m

α = 0,5



OOMMF code; Donahue M. J. and Porter D. G. 1999 *OOMMF User's Guide, Version 1.0, Interagency Report* NISTIR 6376, National Institute of Standards and Technology, Gaithersburg, MD. version 1.2a3

Localization of the Co NW growth

- Co NW growth does not occur on bare Al_2O_3

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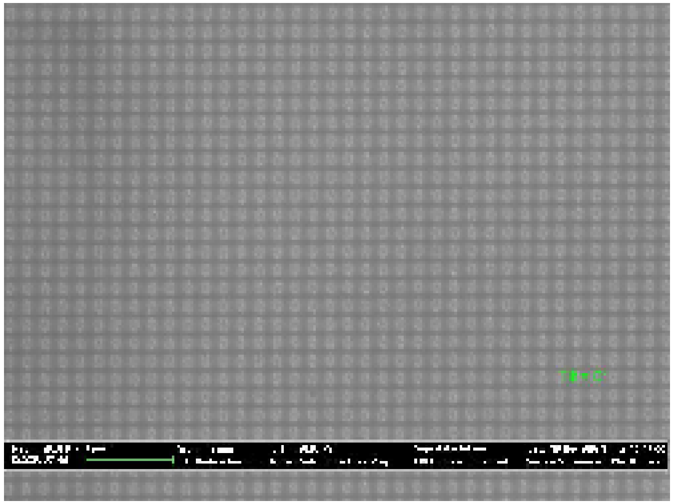
  ⇨ Co NW growth on predefined positions :

FIB patterned Pt(111) films: 100 x 100 nm² islands



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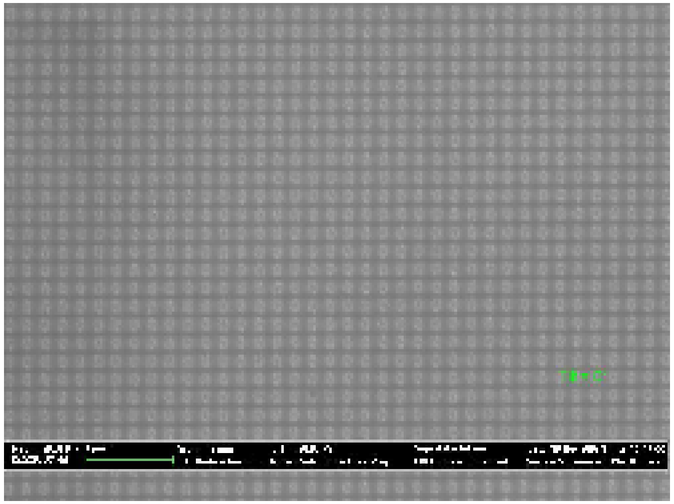
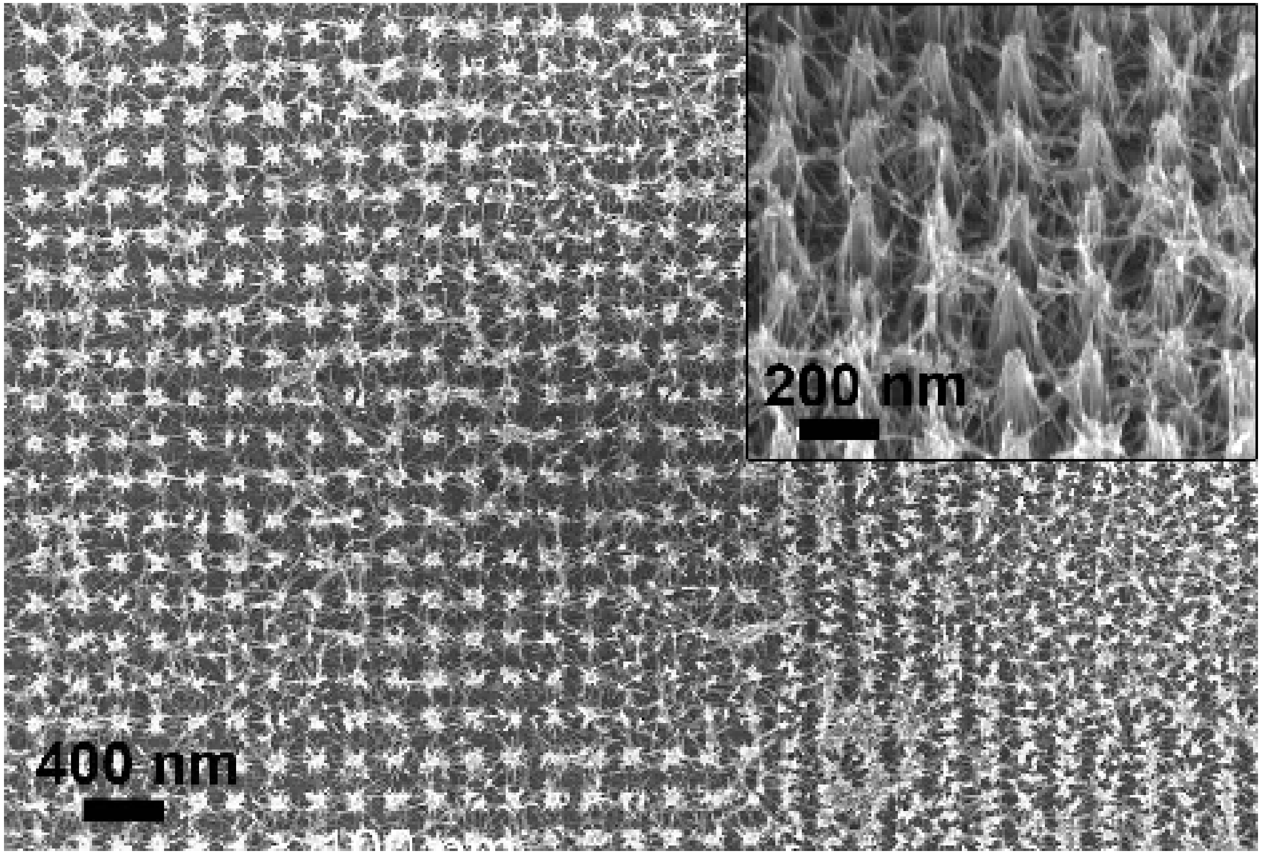


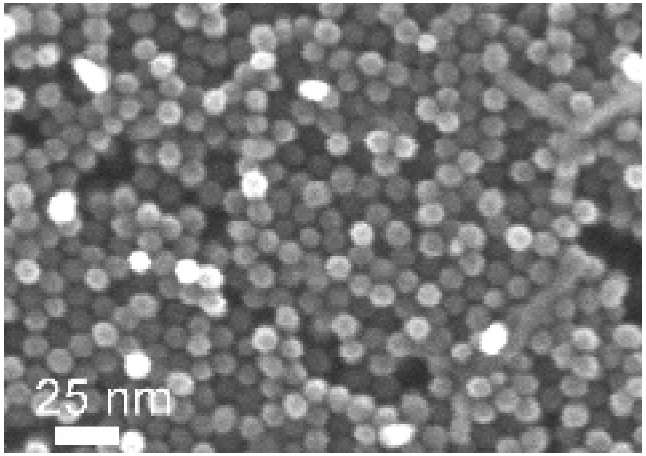
Co NWs grown on a FIB patterned Pt(111) film



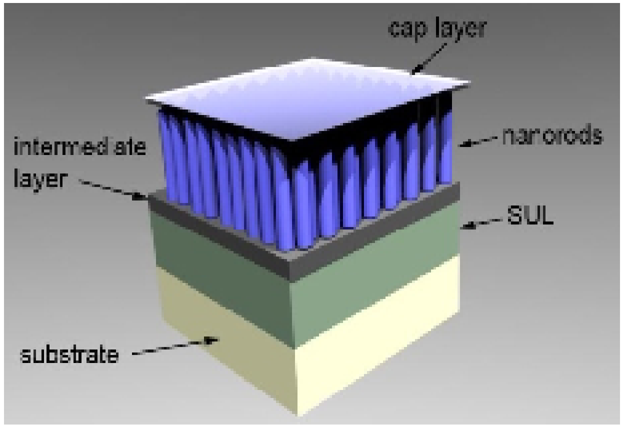
10 Tera-bits-per-square-inch arrays of self-organized, single crystalline 1D nanomagnets

- Nanowire arrays of ultra-high densities on large 2D surfaces (1 cm^2)
- Diameter < 10nm
- Single crystalline 1D nanomagnets ferromagnétiques => high perpendicular anisotropy
- Low cost and scalable process

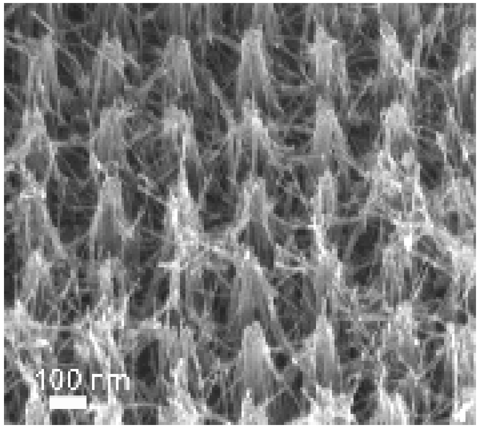
Understanding of the growth mechanism



Promising technology for future magnetic media



New bottom-up method for nano-object self-organization



10 Tera-bits-per-square-inch arrays of self-organized, single crystalline 1D nanomagnets

T. Blon [1], N. Liakakos[1,2], C. Achkar[1], B. Cormary[1], R. P. Tan[1], G. Chaboussant[3], F. Ott[3], B. Warot-Fonrose[2], E. Snoeck[2], B. Chaudret[1], [1] M. Respaud[1], K. Soulantica[1]

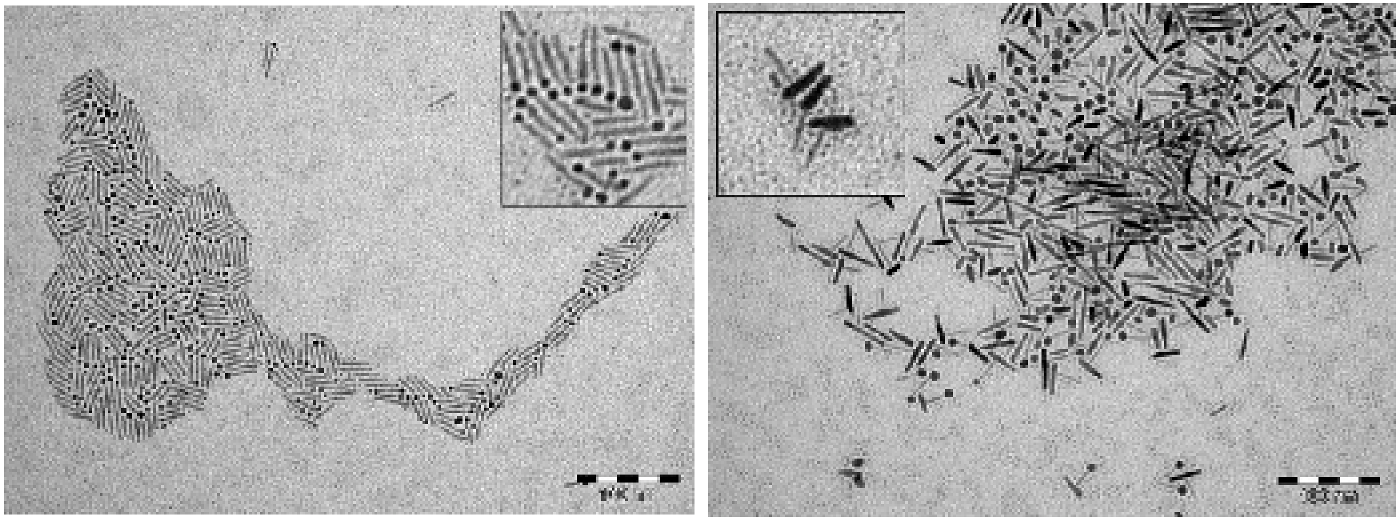
[1]*Laboratoire de Physique et Chimie des Nano-objets (LPCNO), Toulouse*

[2] *CEMES-CNRS, Toulouse*

[3] *Laboratoire Léon Brillouin, Gif sur Yvette*

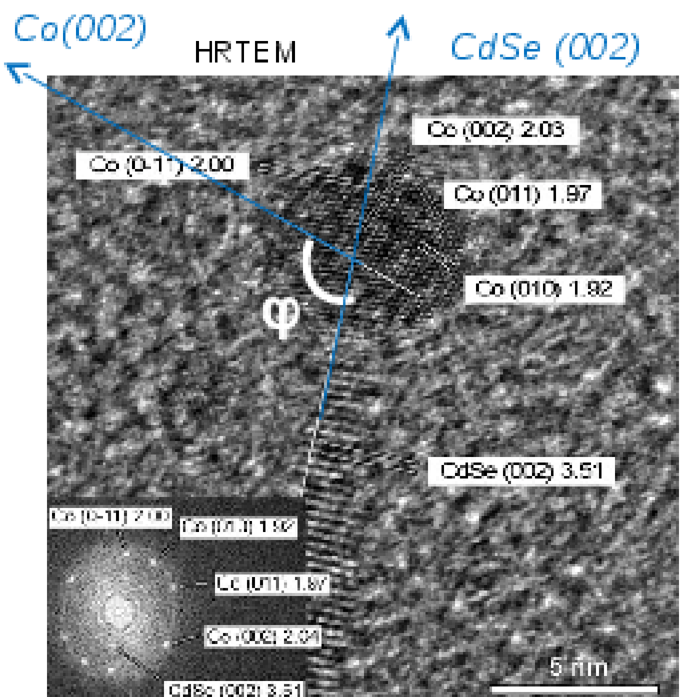
Context: Successive organo-metallic decompositions

TEM



Conditions 1 Conditions 2

HRTEM



Sequential decomposition of organo-metallic precursors

- 1- decomposition of CdSe precursor and formation of the CdSe nanorods
- 2- decomposition of Co precursor: $[Co(\eta_4\text{-}C_8H_{12})\text{-}(\eta_3\text{-}C_8H_{13})]$
- +HDA+LA

under H_2 pressure for 24h

4 defined φ angles between Co and CdSe NRS

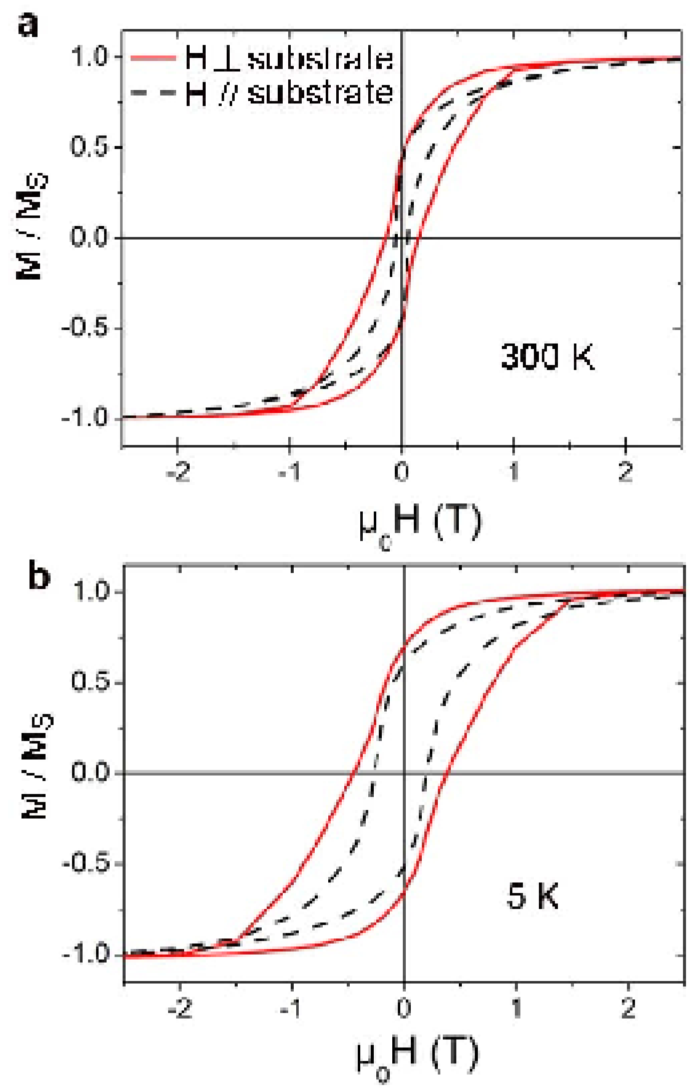
112±3°, 135±3°
6±3°, 99±3°

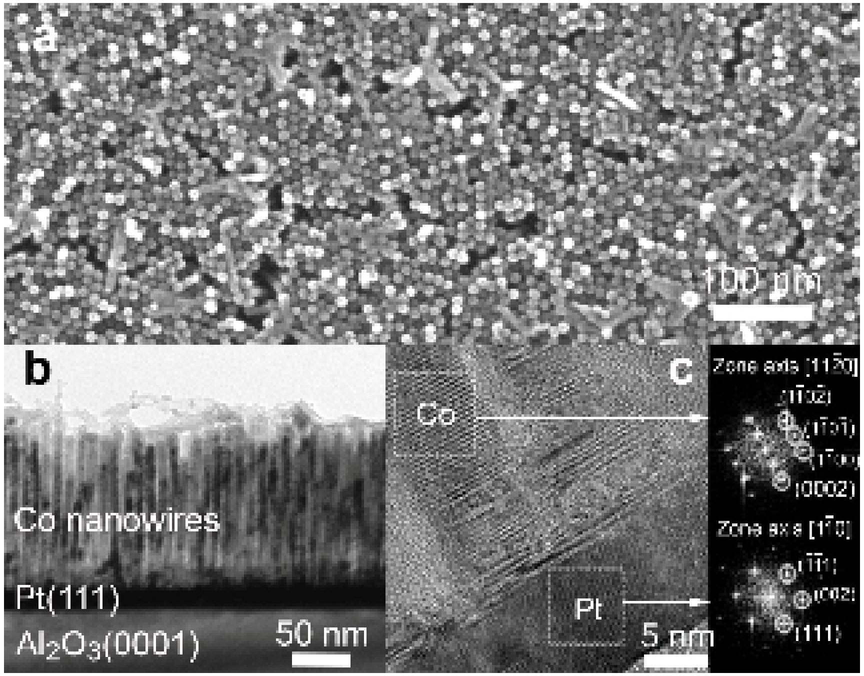
Epitaxial growth of Co on nano-objects

Maynadié *et al. Angew. Chem. Int. Ed.* *1814 48 (2009)*

Co NWs / Pt(111): 7 T-wires/in² arrays

Magnetic properties of the 7 T-wire/in² array (SQUID)





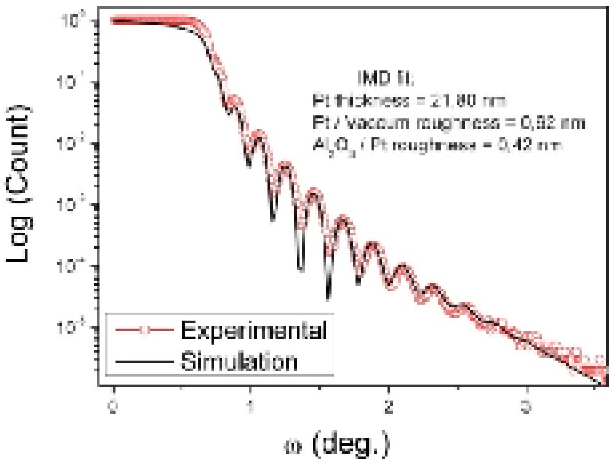
300K : $\mu_0 Hc^{\perp}$ = 147 mT ; $Mr/Ms^{\perp}$ = 0.46
$\mu_0 Hc^{//}$ = 57 mT ; $Mr/Ms^{//}$ = 0.43

5K: $\mu_0 Hc^{\perp}$ = 417 mT ; $Mr/Ms^{\perp}$ = 0.7; $\mu_0 H_{EB}$ = -35mT
$\mu_0 Hc^{//}$ = 234 mT ; $Mr/Ms^{//}$= 0.6 ; $\mu_0 H_{EB}$ = -35mT

Pt film growth

X-ray reflectivity (XRR)

X-ray diffraction (XRD)

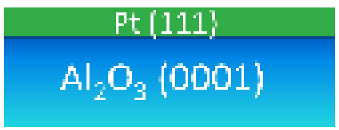


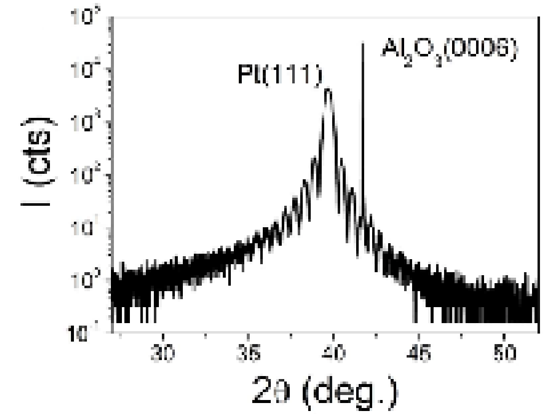
Pt (111) (20 nm) / Al_2O_3 (0001)

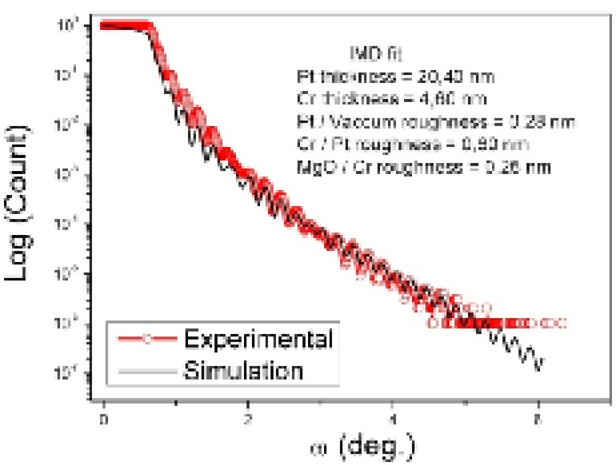
Al_2O_3 : recuit à 750°C / 30 min

Pt: 500°C (2,90 nm/min)

1*1 cm²







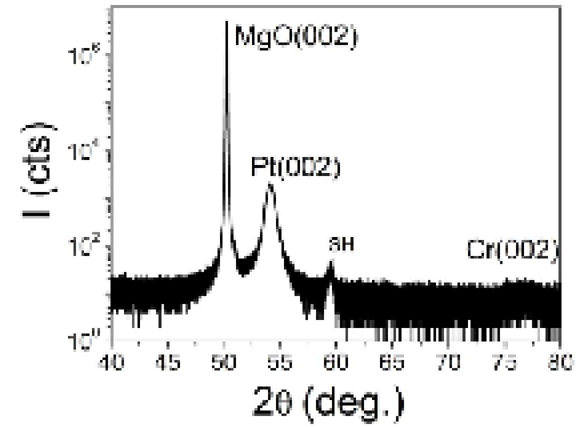
Pt (001) (20nm) / Cr (5nm) / MgO (001)

MgO: recuit à 750°C / 30 min

Cr: evaporée at 360°C (0,15 nm/sec)

Pt: 360°C (2,90 nm/min)

1*1 cm²

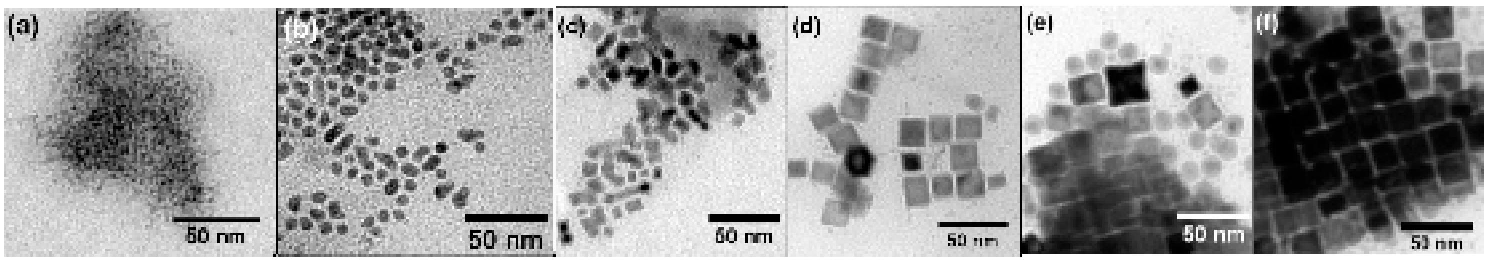


Extension of the method

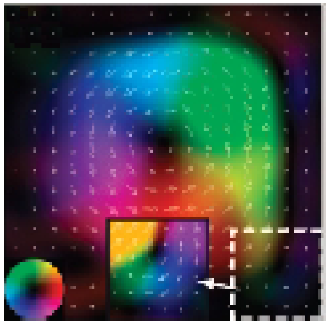
Iron Nanoparticles on Pt films

Homogeneous nucleation

$\{Fe[N(SiMe_3)_2]_2\}_2$ + HDA + PA (Palmitic Acid $CH_3(CH_2)_{14}COOH$)



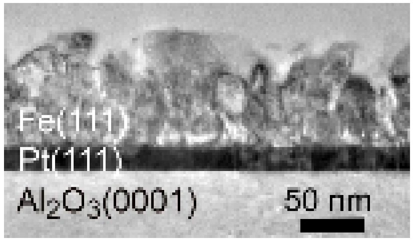
30 mn | 2 hr | 6 hr | 12 hr | 25 hr | 48 hr

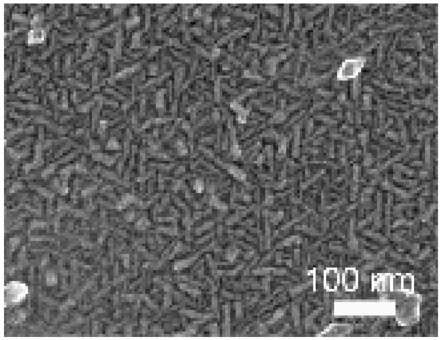


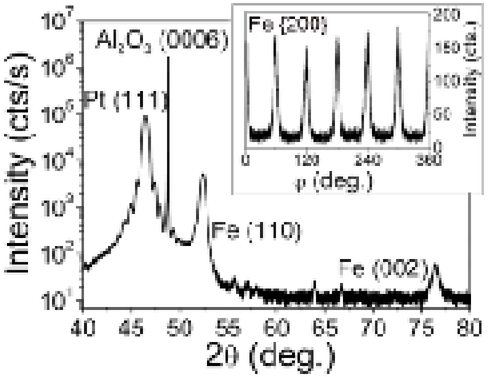
Induction mapping

Fe / Pt (111) 20nm / Al_2O_3 (0001)

Epitaxial growth
Fe (110) // Pt (111)

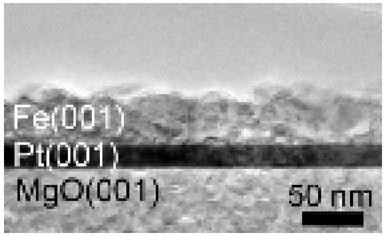


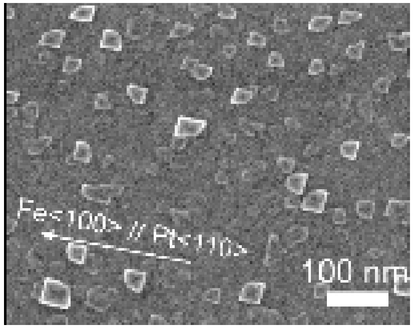


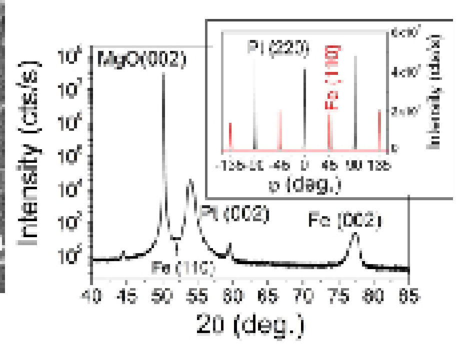


Fe / Pt(001) 20nm / MgO(001)

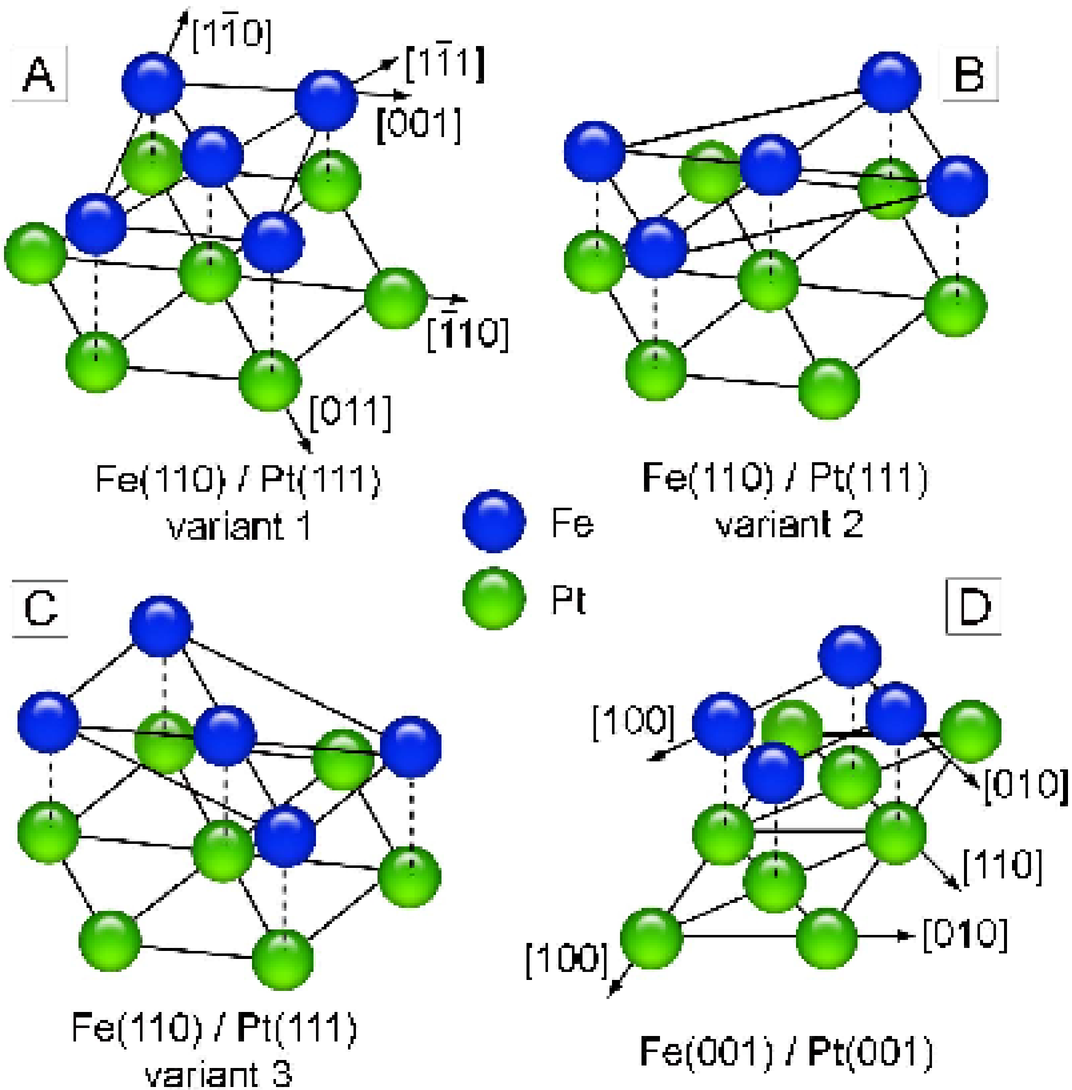
Epitaxial growth
Fe (001)[110] // Pt (001)[010]



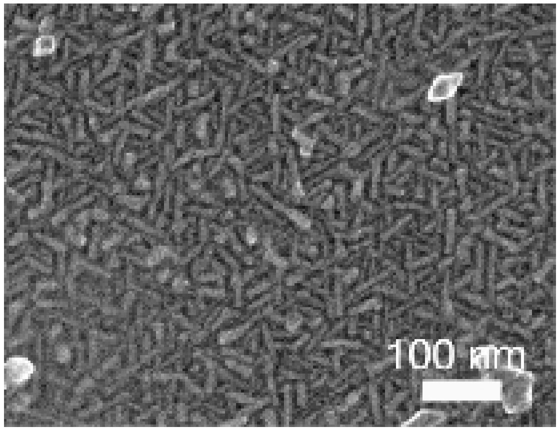




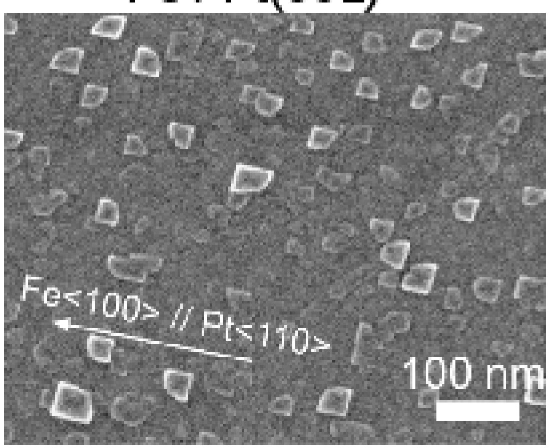
Fe / Pt films



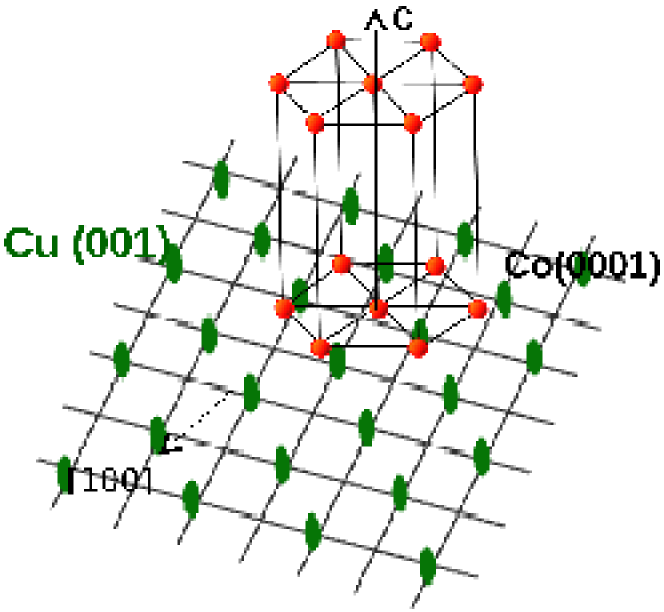
Fe / Pt(111)



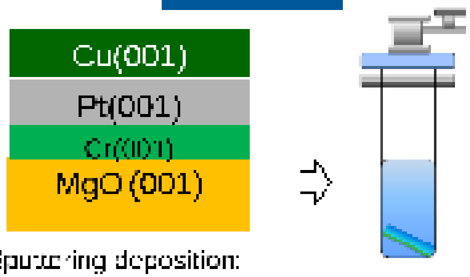
Fe / Pt(001)



Influence of the film surface symmetry
Co NW / Cu(001)

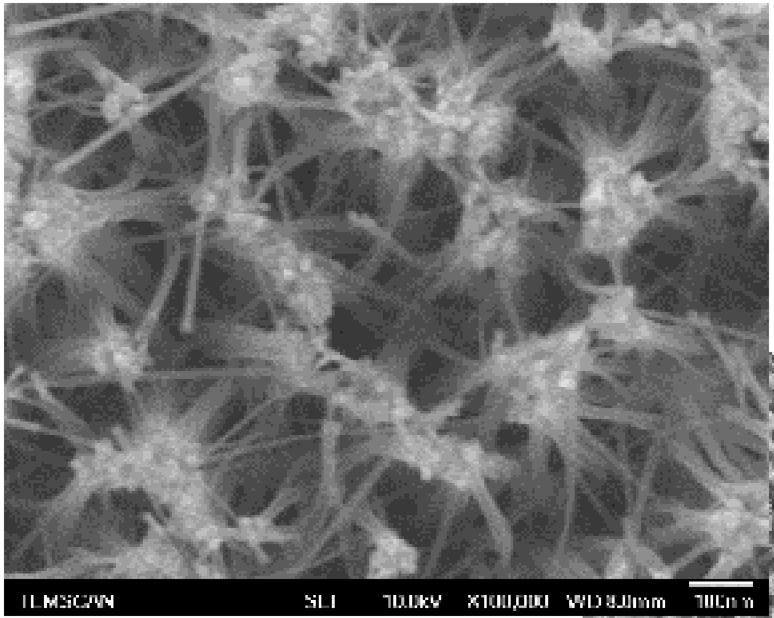


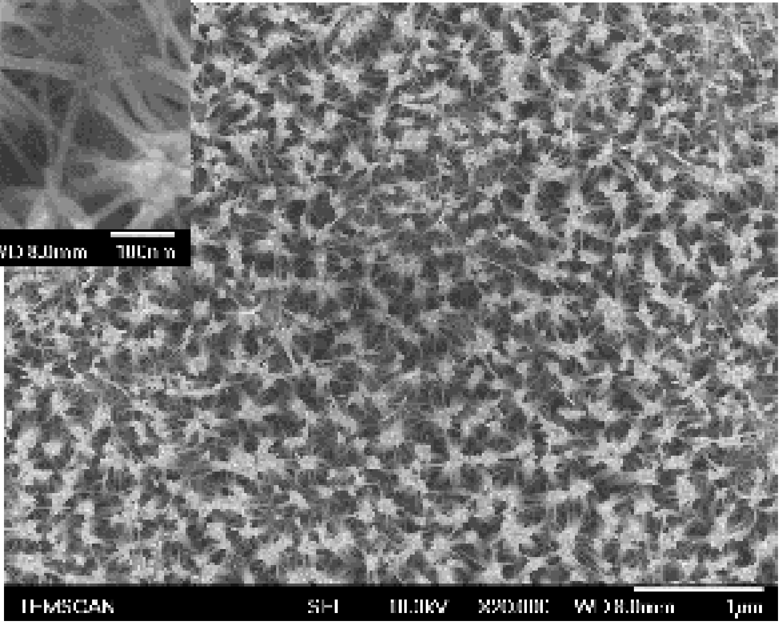
Process

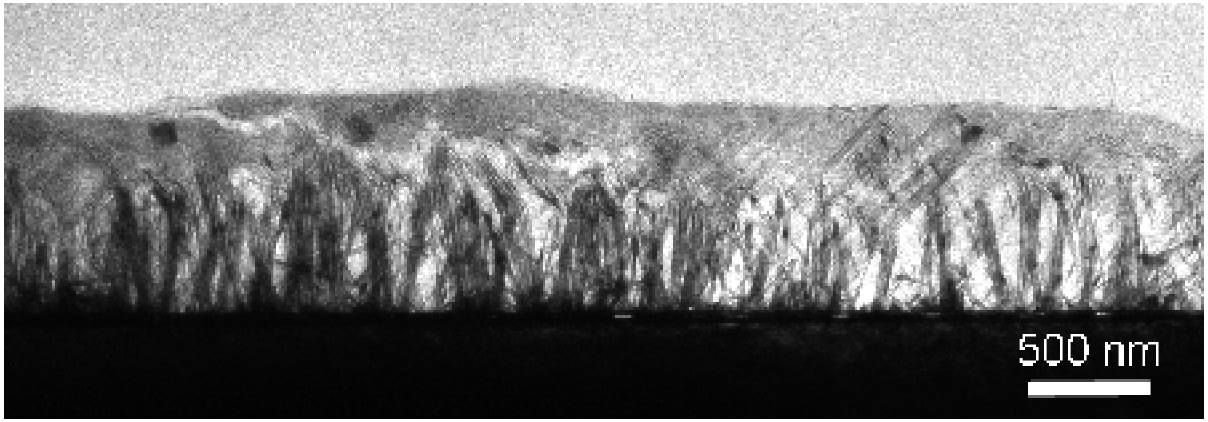


Sputtering deposition:
Cu 20nm 300°C/ Pt 20nm 300 °C / Cr 5nm 300°C/ MgO(001)

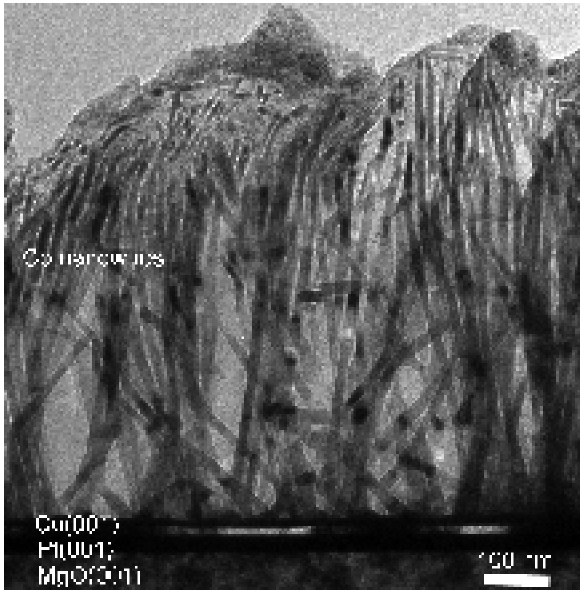
1 2

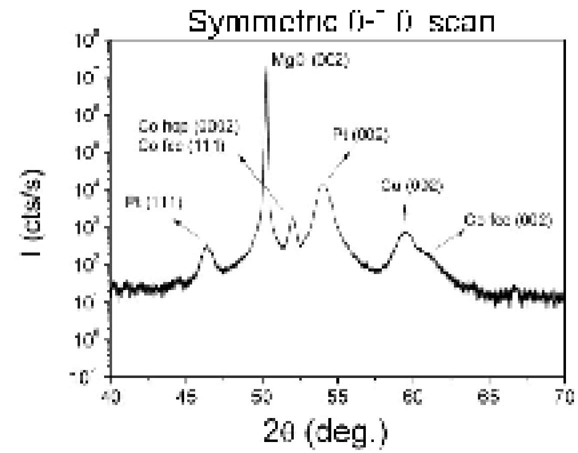


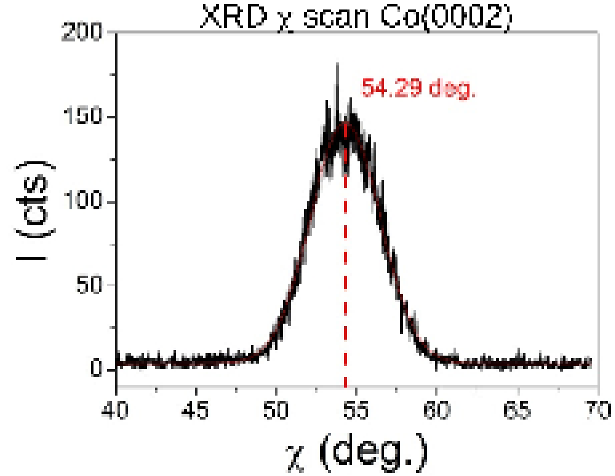


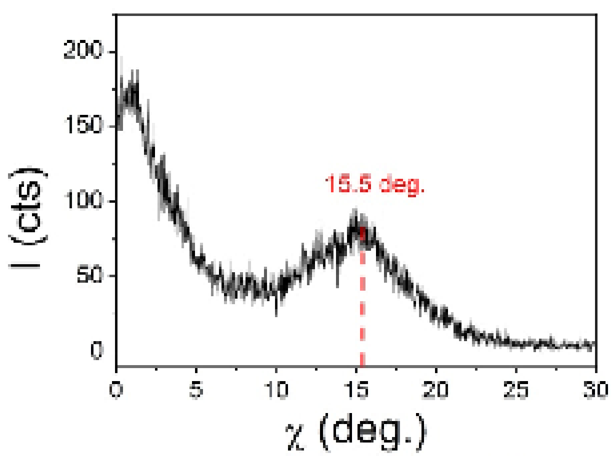


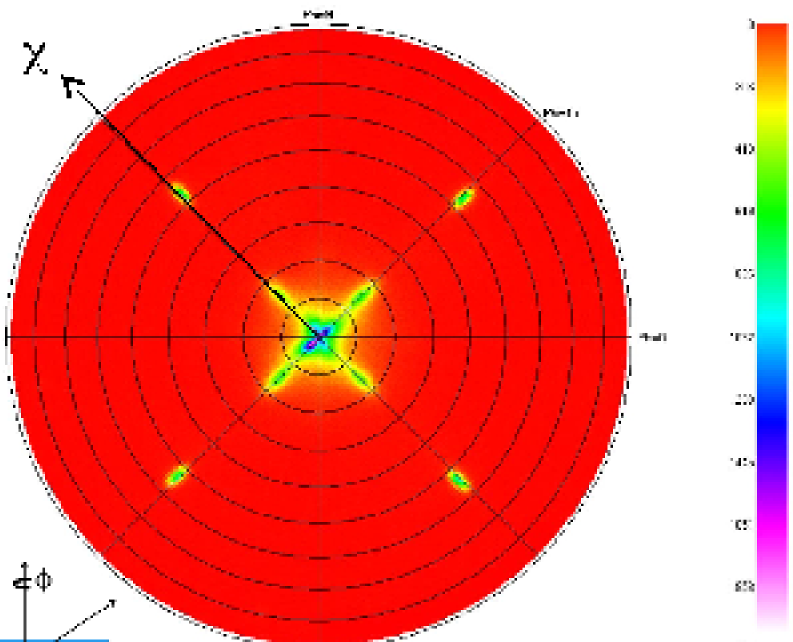
Influence of the film surface symmetry
Co NW / Cu(001)

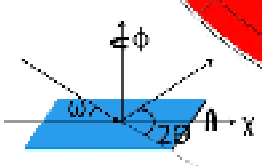








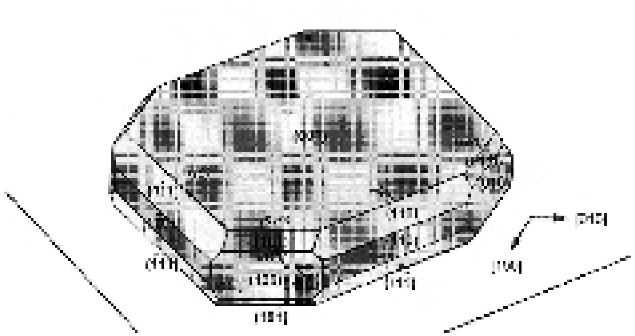


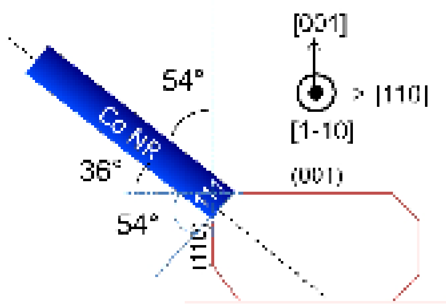


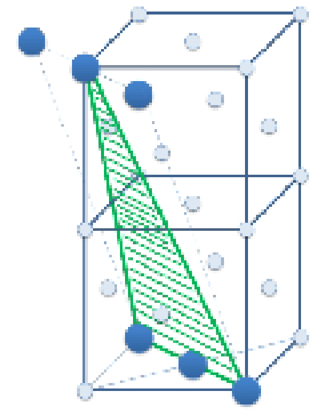
XRD pole figure Co(0002) reflection

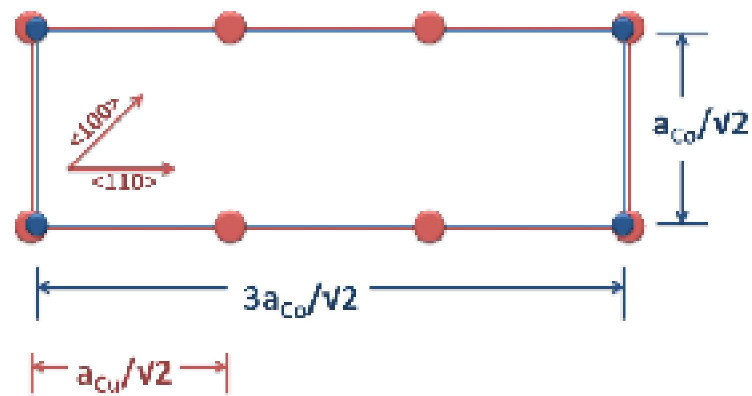
Hyptothesis: 3D growth of Co / Cu(001)

Co NW grown at 15°from the substrate normal

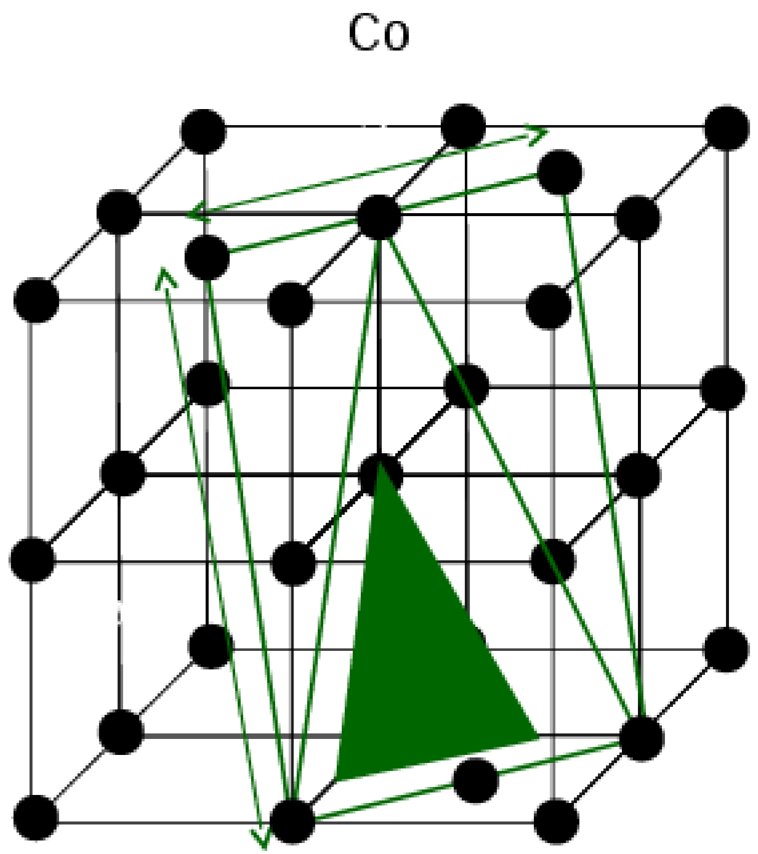


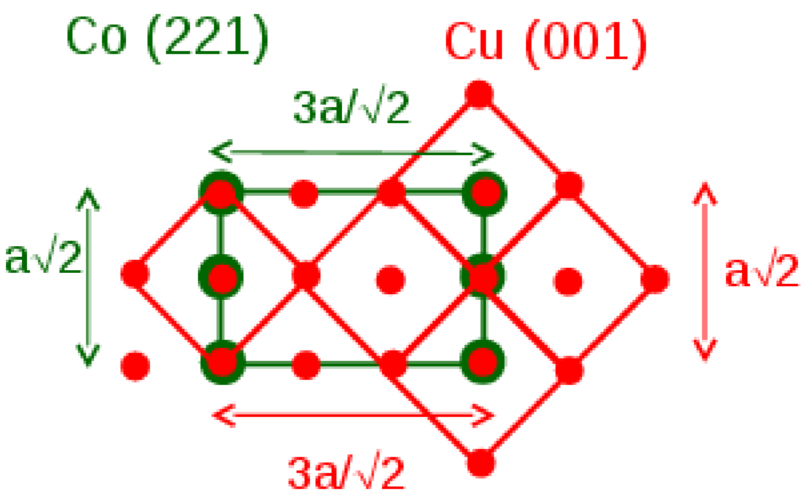






Co NW / Cu(001)





Misfit Co/Cu: - 1.93%