The effect of magnetic fields on the microstructure of electroplated Co layers

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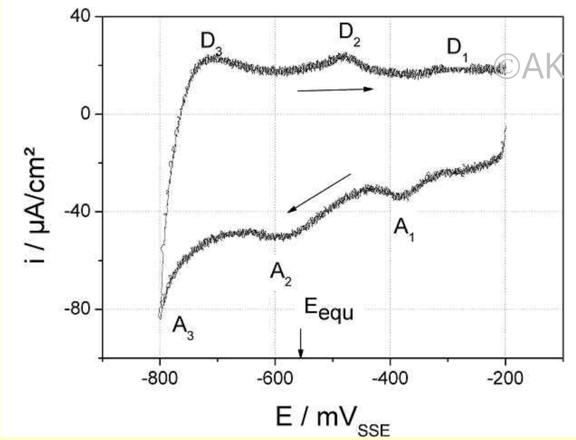
1 Nucleation of Co on Cu(100)

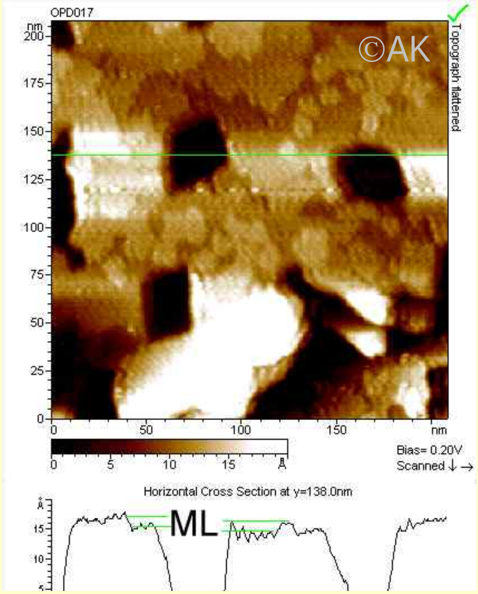
2 Influence of Magnetic fields on mass transport

3 Influence of Magnetic fields on Layer Structure

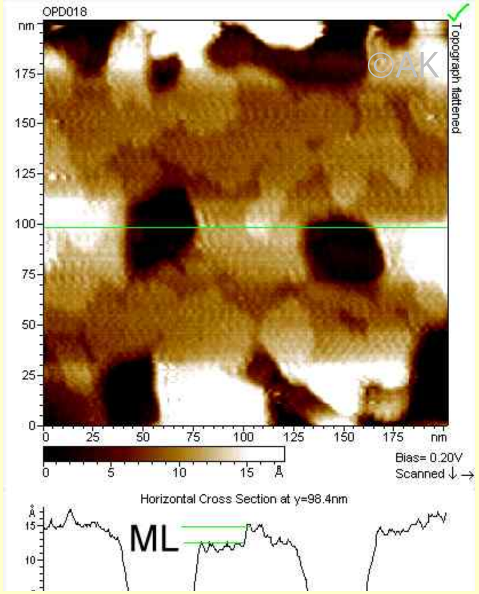
4 Summary

1 Nucleation of Co onto Cu(100)

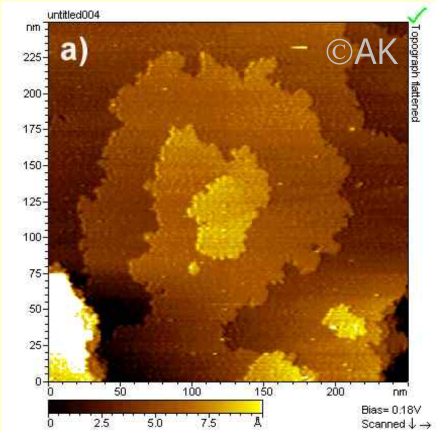




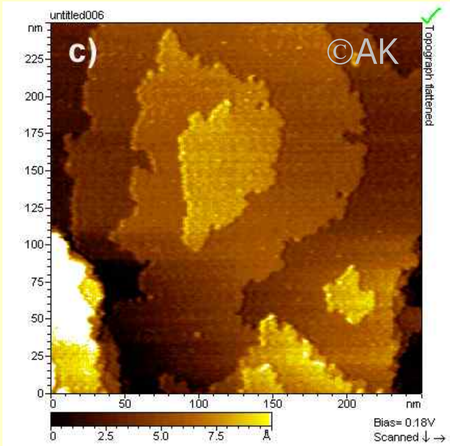
a) E= -200 mV$_{SSE}$, t= 0 s



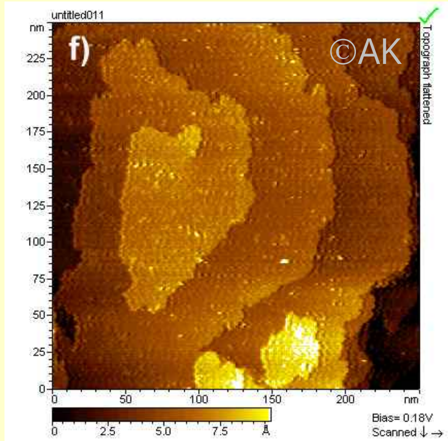
b) E= -400 mV$_{SSE}$, t= 90 s



a) E= -200 mV$_{SSE}$, t= 0 s

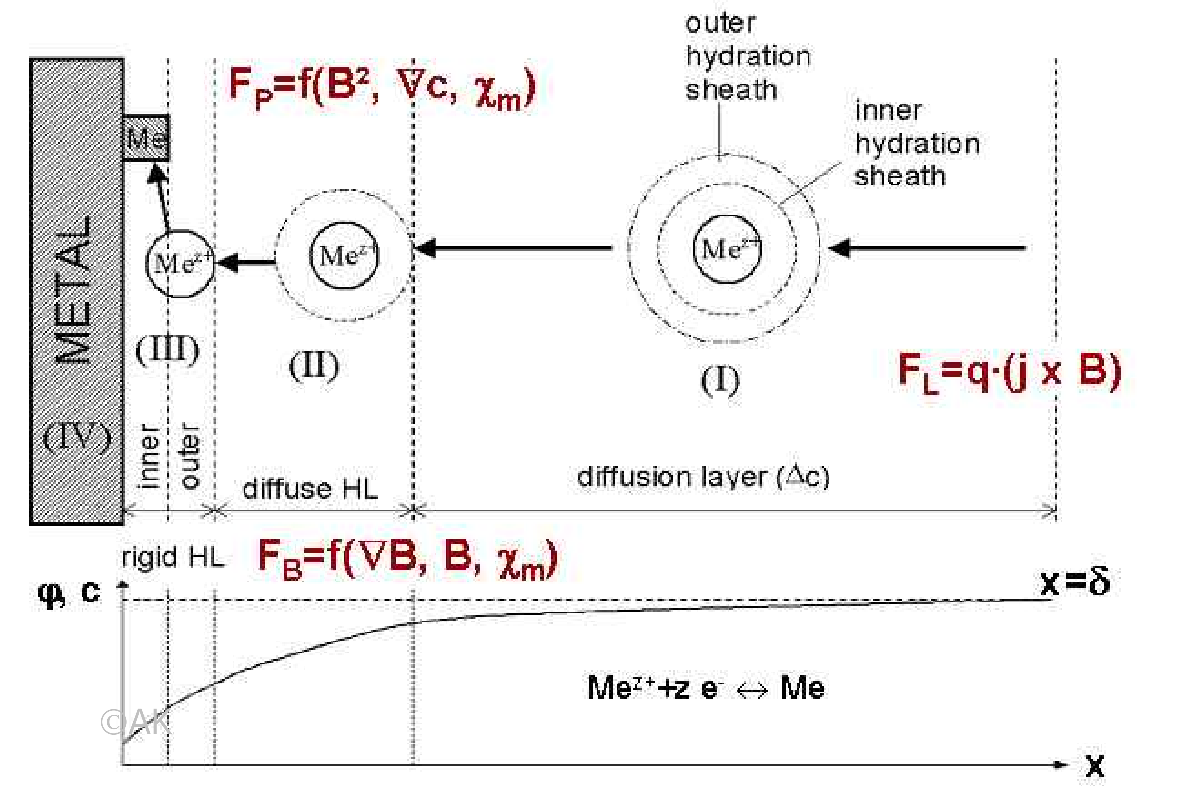


b) E= -400 mV$_{SSE}$, t= 170 s



c) E= -600 mV$_{SSE}$, , t= 600 s

2 Influence of a magnetic field on ion transport



- **Diffusion force:**
  à main driving force of the metal ions:

$$\vec{F}_D = -R \cdot T \cdot \vec{\nabla} c_{(x,t)}$$

- **Lorentzforce (MHD):**
  à B II surface: agitation reduces δ_D, ↑i_D:

$$\vec{F}_L = \vec{i} \times \vec{B}$$

$$\varepsilon_{mag} = \frac{\chi_m}{2\mu_0} \cdot B^2$$

- **Field gradient force:**
  à in inhomogeneous B

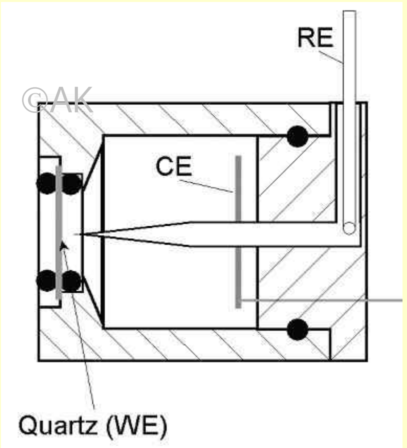
$$\vec{F}_{\nabla B} = \chi_m \cdot \frac{c \cdot B}{\mu_0} \cdot \vec{\nabla} B$$

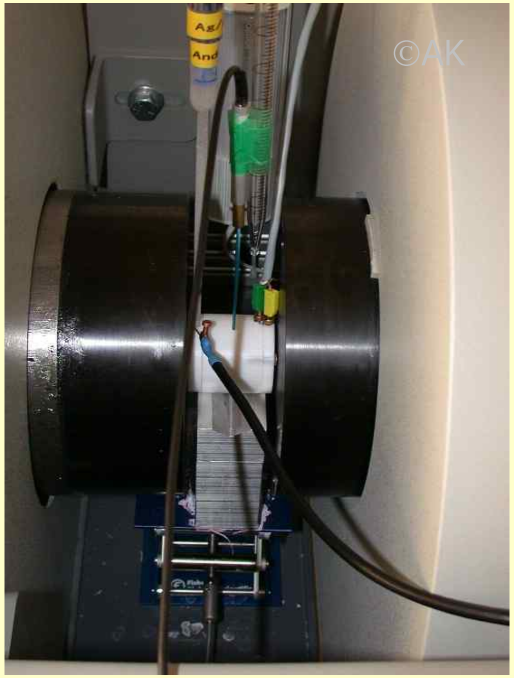
- **Paramagnetic ∇-force:**
  à in the diffusion layer (∇c)

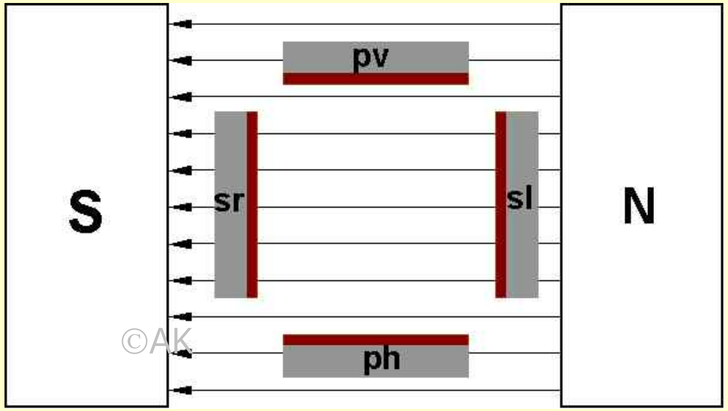
$$\vec{F}_p = \chi_m \cdot \frac{B^2}{2\mu_0} \cdot \vec{\nabla} c$$

	χ_m / m³/mol
Co^{2+}	$1 \cdot 10^8$
Cu^{2+}	$1{,}46 \cdot 10^7$

2 Experimental







- **QMB-Cell:**

B = 1.2T

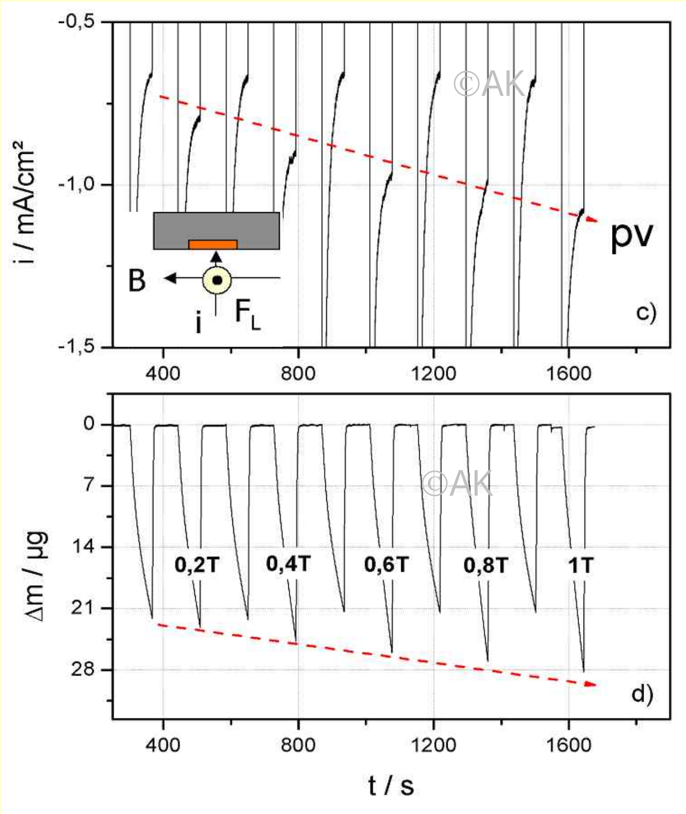
- simultaneous measurement of Δ**m** and **i**
- simple and constant geometry

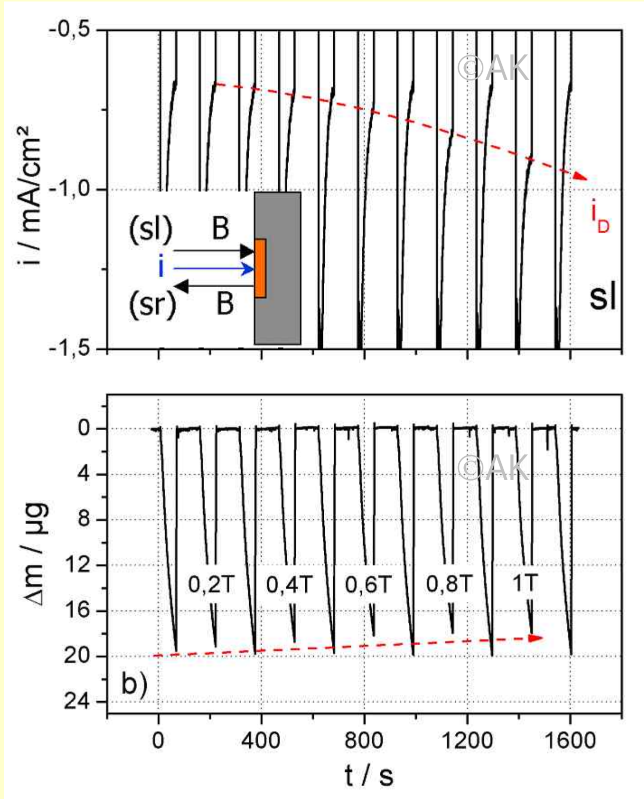
- **Four different magentic field to electrode configurations**

Electrolyte: 0.01M $CoSO_4$, 0.1M Na_2SO_4, pH3

2 Influence of magnetic fields on mass transport

B ⊥ I: E= -1V_{SSE}, t= 60s B || I:

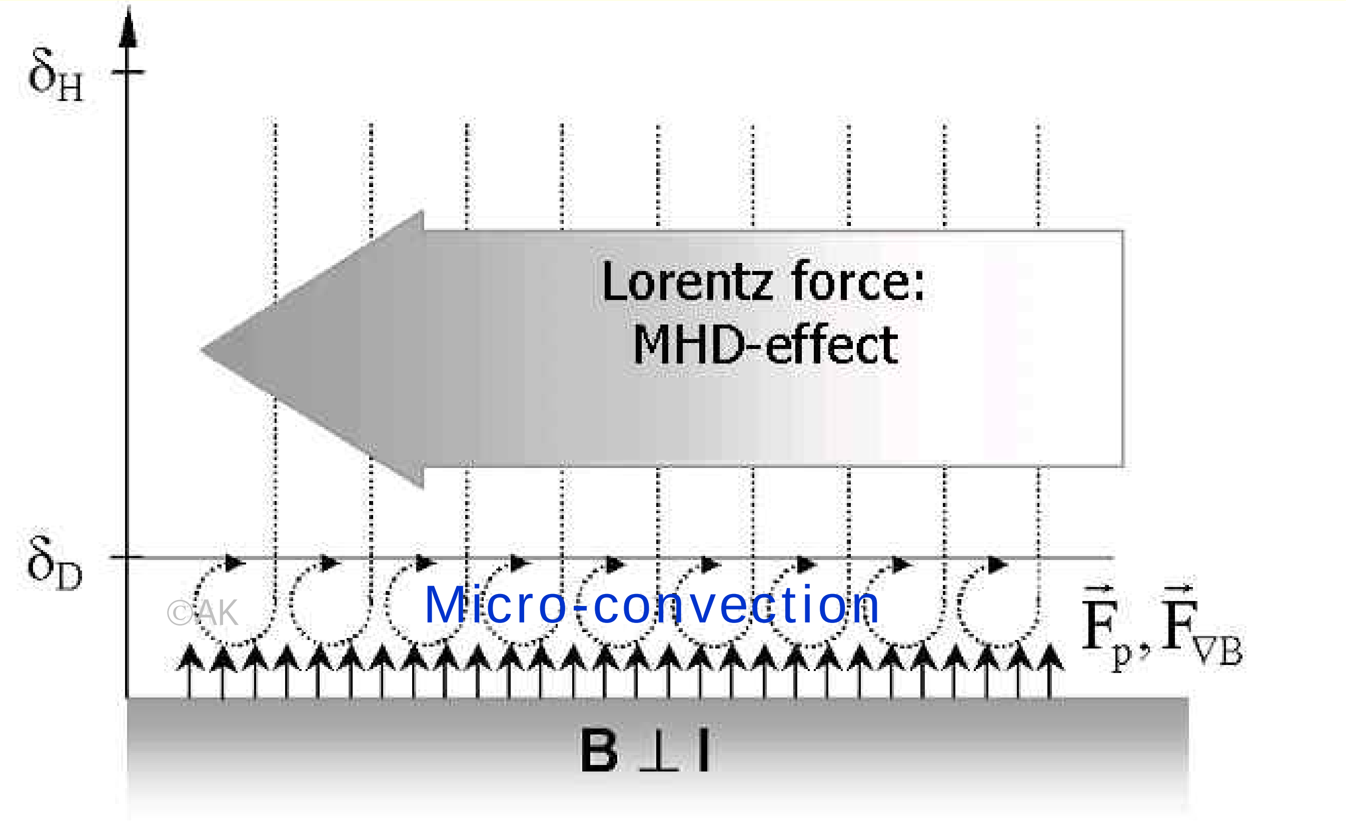




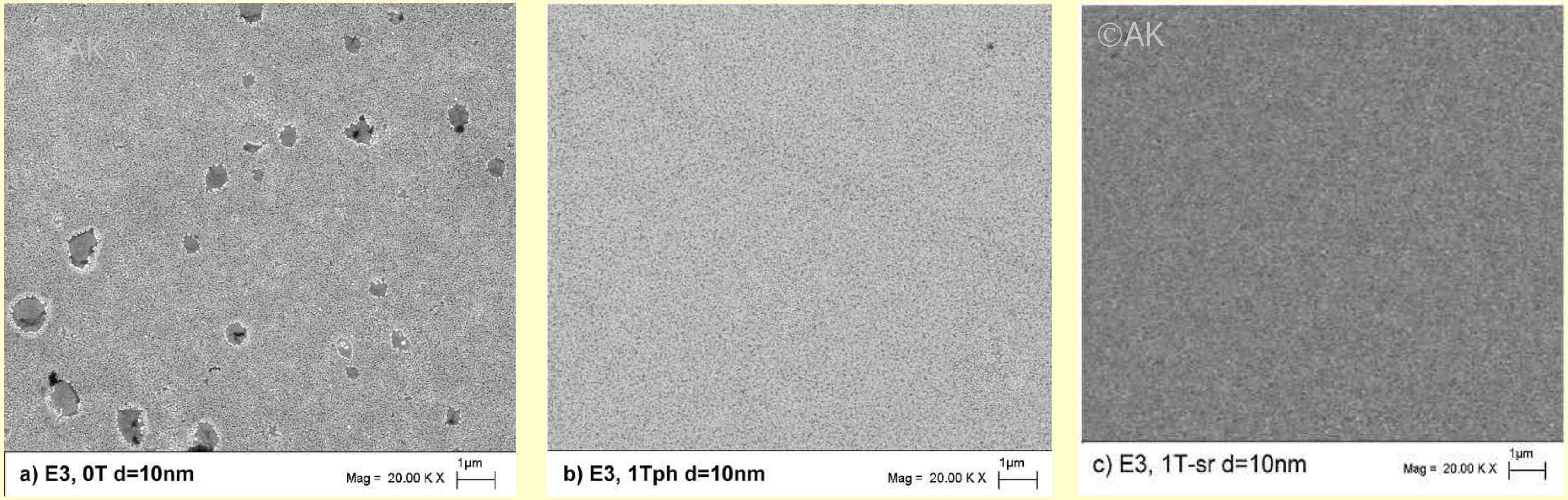
- u ↑IΔmI, Ii_DI~$B^{1/3}$ à MHD-effect
- u increasing current efficiency (especially for ↑η) à cobalt deposition stronger affected than hydrogen reaction

- u no F_L (because B II i)
- u ↓ IΔmI à decreasing deposition rate due to F_P (Co-ions away from electrode)[1]
- u ↑ IiI à B support the hydrogen reaction à decreasing current efficiency!

Magnetic induced convection - model



3 Influence of magnetic fields on morphology of Co-deposits

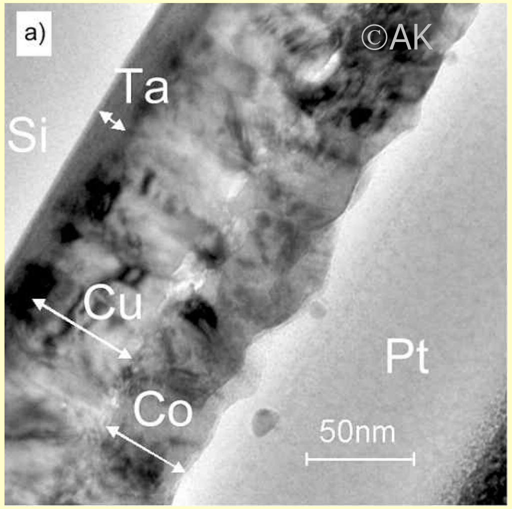


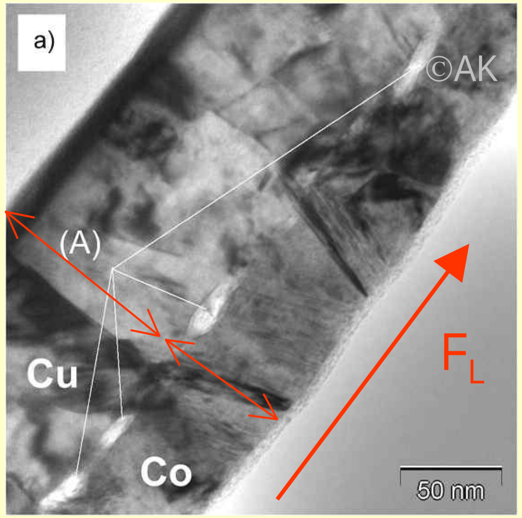
a) E3, 0T d=10nm
b) E3, 1Tph d=10nm
c) E3, 1T-sr d=10nm

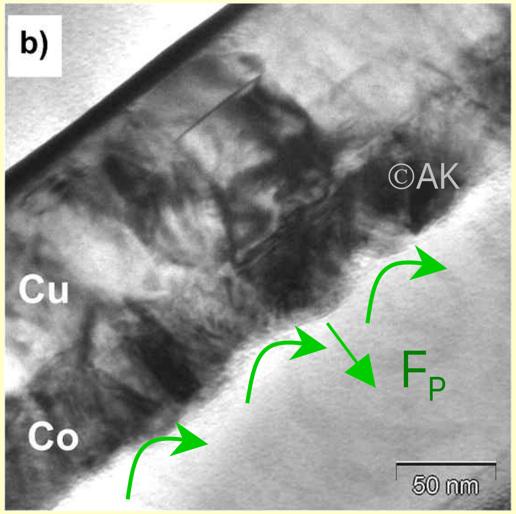
u **B=0T, E_3=-1100mV$_{SSE}$:**
holes appear due to adsorbed hydrogen; diameter <1µm à inside the diffusion layer (δ_D~100µm)

u **B=1T (independent on orientation), E_3=-1100mV$_{SSE}$:**
very smooth and closed layer, desorption of H_2 is supported by B due to diamagnetic effect of H_2 or magnetoconvection

Influence of magnetic fields on the microstructure of Co deposits







B=0:

- irregular growth
- high roughness
- reaction layer at the Co-Cu interface

B II surface:

- coherent growth
- fibre texture of Co-layer
- low roughness
- reaction layer at the Co-Cu interface

B ⊥ surface:

- disturbed microstructure
- fibre texture of Co-layer
- higher roughness than B II surface
- wavy surface

3 Effects of magnetic fields on crystallographic orientation and phase formation

Free surface energy:
(dominates texture)

Co	fcc(100)	fcc(111)	hcp(100)	hcp(002)
γ_{hkl} J/m^2	2,78	2,7	3,035	2,775

Magneto-crystalline anisotropy energy:

$$u_a = K_0 + K_1 \sin^2\theta + K_2 \sin^4\theta ...$$

hcp_{max}: (100)-(002) $u_a = 560\ kJ/m^3$

fcc_{max}: (111)-(100) $u_a = 16\ kJ/m^3$

Surface anisotropy energy:

$$\gamma_{hkl-uvw} = (\gamma_{hkl} - \gamma_{uvw}) \cdot \sin\theta$$

crystallographic orientation:

$$d \approx \gamma_{hkl-uvw} / u_a$$

$d_{fcc} > 4\ \mu m$ $d_{hcp} > 0{,}46\ \mu m$

Phase-formation:

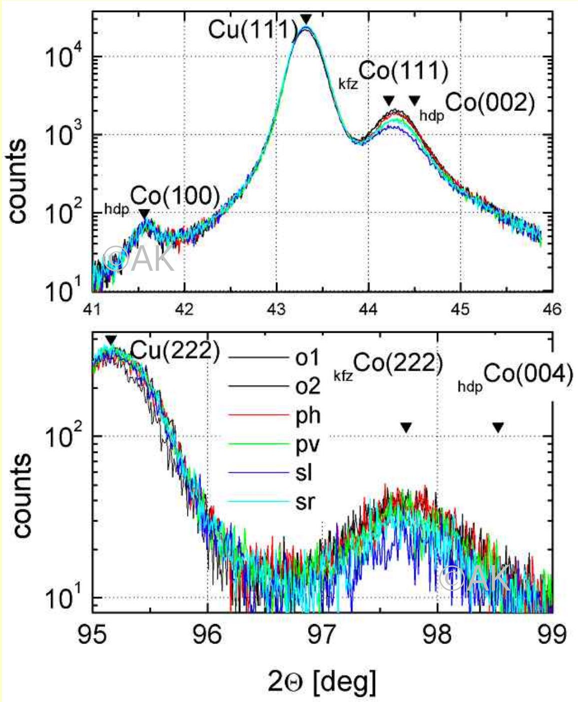
Stacking fault energy:
$\gamma = 25 mJ/m^2$

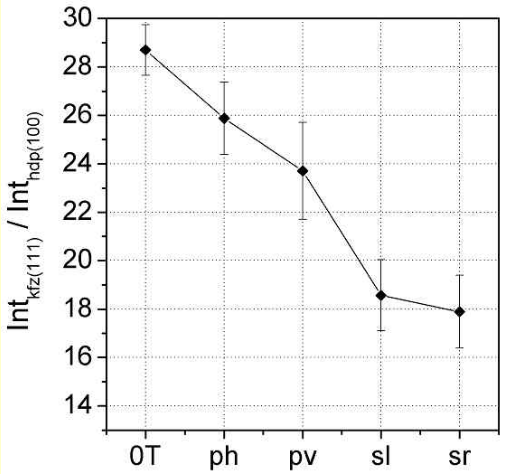
B=1T: $\mu_0 HM \approx 10^3\ kJ/m^3$

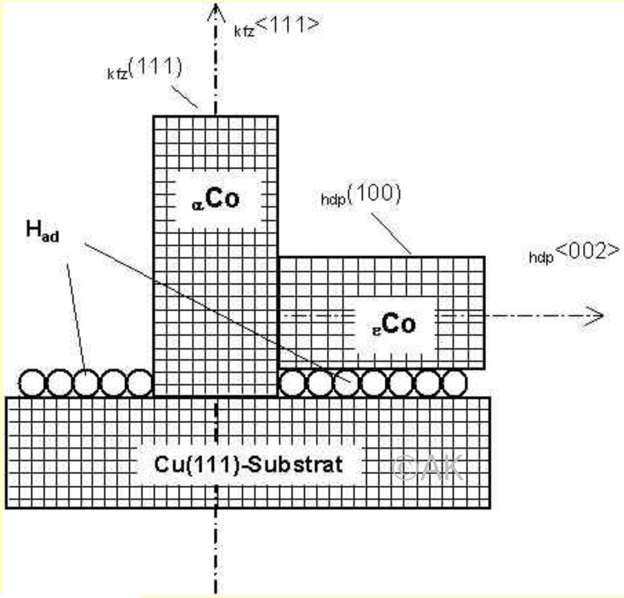
$d > 25\ nm$

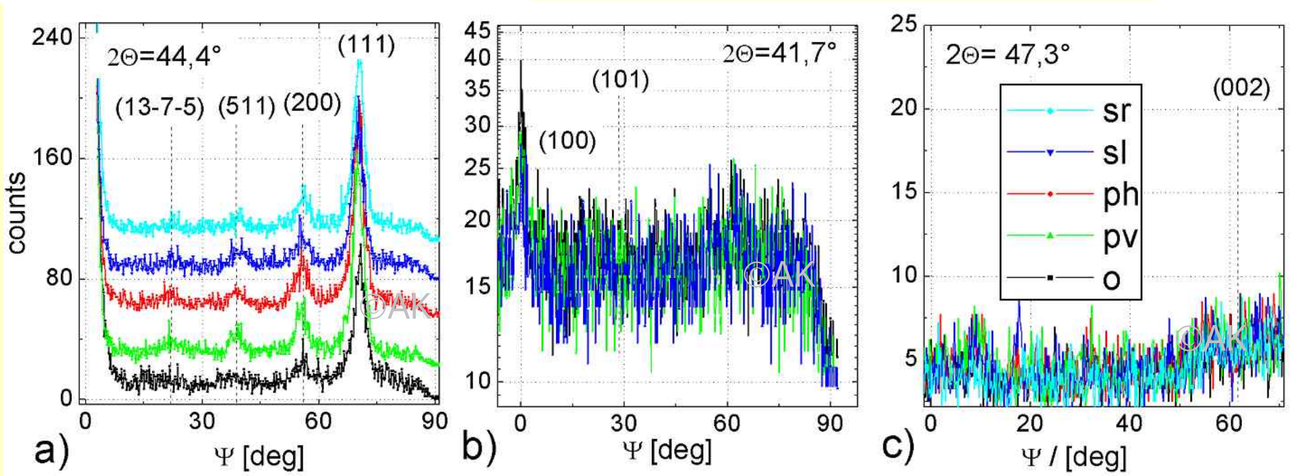
3 Growth model for Co on Cu(111)

E=-1V$_{SSE}$, d= 50nm









Summary

<u>Nucleation:</u>

- 2D- growth of Co onto Cu(100)

<u>Influence of B on ion transport:</u>

B *//* electrode:

- F_L à $\uparrow$i, Δm, efficiency
- Convection in the hydrodynamic layer: MHD-effect, laminar flow at the electrode (u=1,5 cm/s)

B $\perp$ electrode:

- F_P à $\uparrow$i but $\downarrow\Delta$m, $\downarrow$efficiency
- Magneto-convection in the diffusion layer

<u>Influence of B on microstructure and morphology:</u>

- hydrogen holes are reduced due to B
- more hcp-phase due to B
- less disturbed microstructure if B is parallel