Nanoprobes in Materials Science, Physics & Chemistry

Week 2

Rainer H. Fink 莱纳·芬克教授 博士
Friedrich-Alexander University
Erlangen-Nürnberg
Physical Chemistry 2 (surface & interface science)

rainer.fink@fau.de www.raifi.de

FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG

FRIEDRICH-ALEXANDER
UNIVERSITÄT
ERLANGEN-NÜRNBERG

- **Introduction and Motivation**
  - Length scales, physical properties, quantization effects
  - Nano-objects, "bottom-up" / "top-down" approach
- **Optical methods**
  - Visible light microscopy (VLM)
  - Confocal laser-scanning microscopy(CLSM)
  - Scanning near-field optical microscopy (SNOM)
- **Scanning probes**
  - Scanning-tunneling microscopy / -spectroscopy
  - Scanning-force microscopy
  - Other scanning probe techniques
- **Electron probes**
  - Field-electron- / field-ion-microscopy (FEM / FIM)
  - Electron microscopy (SEM, TEM, SAM, LEEM, PEEM)
- **Ion probes**
  - He Ion Microscopy / FIB / AtomProbe Tomography
- **X-ray techniques**
  - Basics (Synchrotron radiation, Photoelectron spectr., x-ray absorption, x-ray fluorescence)
  - X-ray microscopy using soft and hard x-rays
  - Small-angle x-ray scattering (SAXS) – compare to neutrons

Electron microscopy

EMITTED ELECTRONS:

- Field electron microscopy (FEM)
- Field ion microscopy (FIM)
- Photo electron emission microscopy (PEEM)

INCIDENT ELECTRONS:

- Scanning-electron microscopy (SEM, SAM, ...)
- Transmission electron microscopy (TEM)
- Low-energy electron microscopy (LEEM)

Electron Microscopy

$$E = \hbar\omega, p = \hbar k = {}^{h}/_{\lambda}$$

$$E_k = \frac{1}{2}mv^2 = eU, |\vec{p}| = mv$$

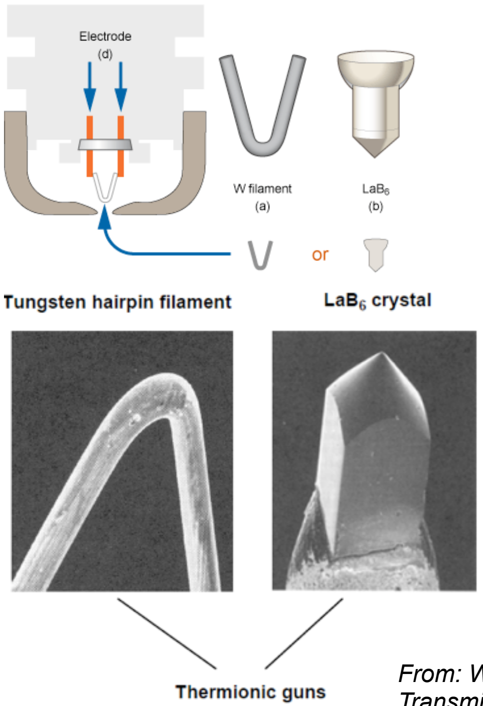
$$\lambda_{vac} = \frac{h}{\sqrt{2meU}}, \lambda_{med} = \frac{h}{\sqrt{2m(eU - E_p)}}$$

$$n = \frac{\lambda_{vac}}{\lambda_{med}} = \sqrt{1 - \frac{E_p}{eU}}$$

U/V	v/c	λ/nm
10^{-1}	$6.3\ 10^{-4}$	3.9
1	$2.0\ 10^{-3}$	1.2
10^{1}	$6.3\ 10^{-3}$	$3.9\ 10^{-1}$
10^{2}	$2.0\ 10^{-2}$	$1.2\ 10^{-1}$
10^{4}	0.19	$1.2\ 10^{-2}$
10^{6}	0.94	$8.7\ 10^{-4}$

Significantly shorter wavelength compared to visible light will offer better resolution !

Creating electrons, e.g., by thermal emission



Thermal emission according to **Richardson law**:

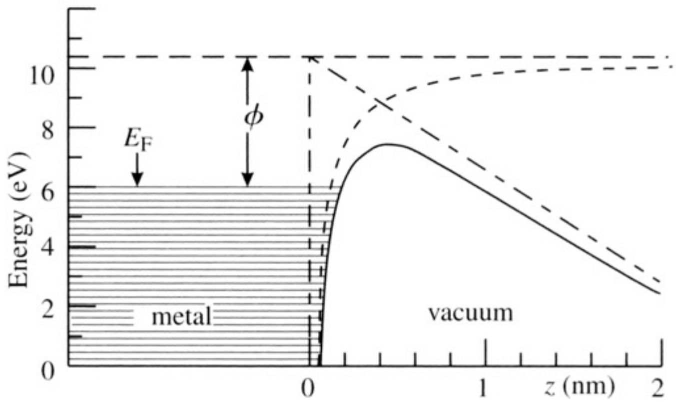
Emission current density $j = A\,T^2 \exp(-\Phi / k_B T)$

A is a material constant, e.g. $A_W = 120\ \mathrm{A/(cm\ K)^2}$ $\Phi_W = 4.5$ eV

Sharp tip spot-welded to the hairpin filament incrfeases j by a factor of 4

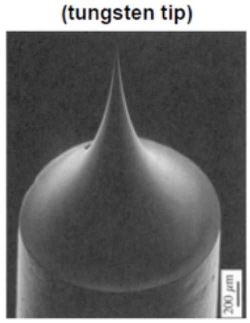
From: Williams/Carter
Transmission electron microscopy

Creating electrons, e.g., by cold field emission



$$J(T) = AE^2 \exp\left(-B\phi^{3/2} / E\right)$$

Field emission source
(tungsten tip)

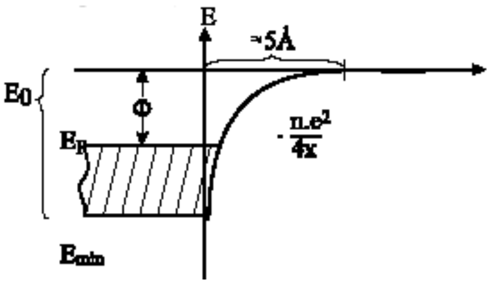


From: Williams/Carter Transmission electron microscopy

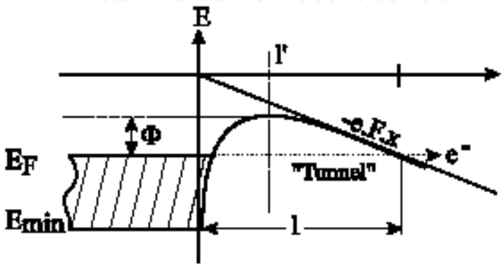
Fowler/Nordheim equation (1928) describes current density J emitted by a filament under a high electric field, where plot of $\log(J/E^2)$ vs. $1/E$ gives straight line.

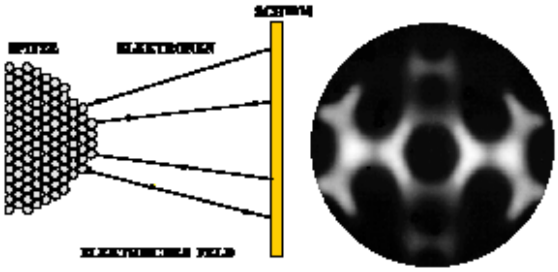
Field electron microscopy (FEM)

1D electrostatic potential at a metal surface without field

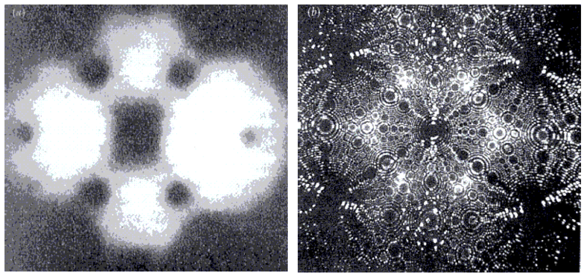


... with external electric field





FEM scheme

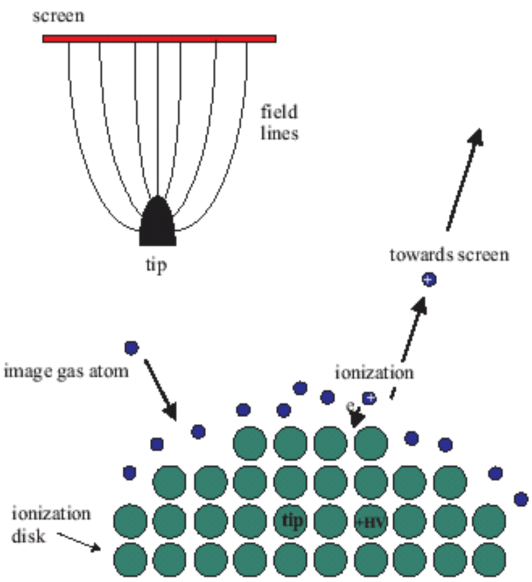


Δx = 2-3 nm

348

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

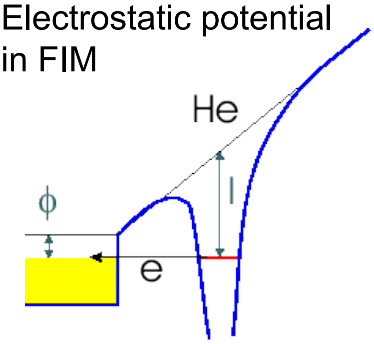
Field Ion Microscopy (FIM)

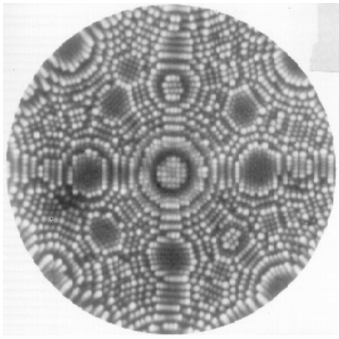


E. Müller, Univ. Erlangen, 1950's

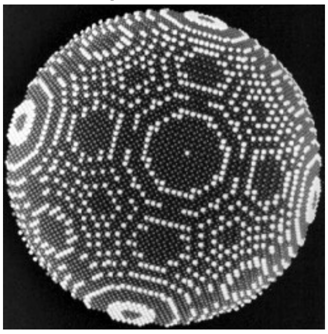
Field ion microscopy (FIM)

Electrostatic potential in FIM

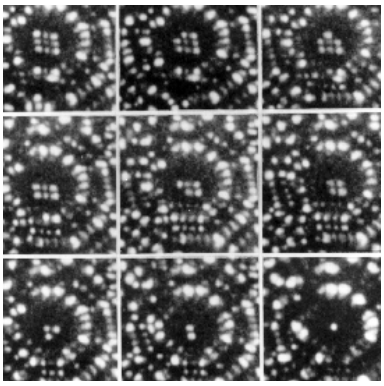




Experiment



Simulation



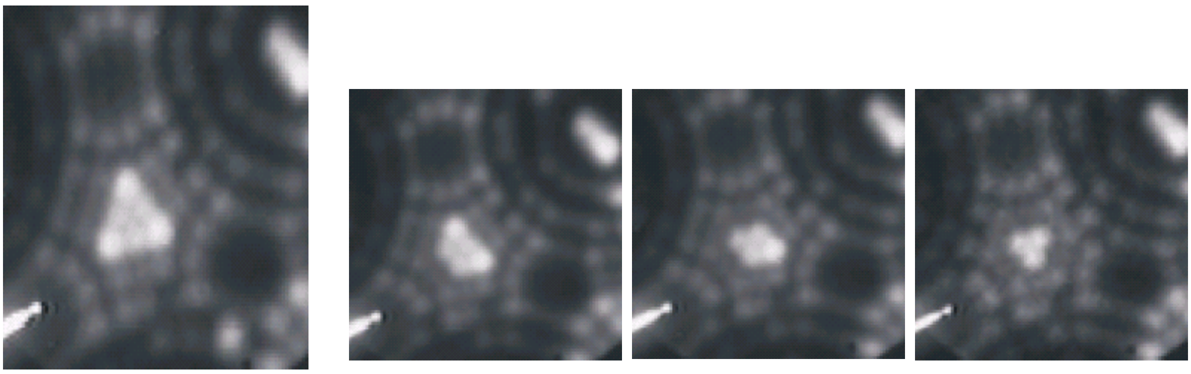
Removal of individual atoms from FIM tip

Due to the higher mass of the gas atoms (compared to electrons) and thus smaller Brownian motion, the resolution in FIM is higher than in FEM

Δx = 0.1 nm

350

Atomic manipulations in FIM: W(111) tip



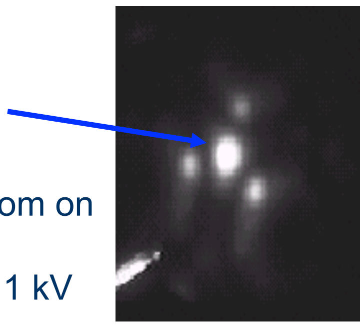
Imaging at 5.0 kV

Manipulating at 6.0 kV

<u>In addition:</u>

Field desorption

Field evaporation



Single Au atom on W(111) tip imaged at 2.1 kV

Electron microscopy

EMITTED ELECTRONS:

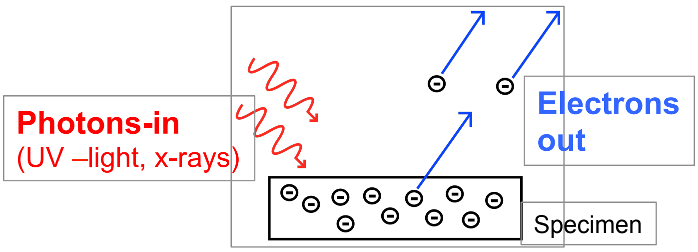
- Field electron microscopy (FEM)
- Field ion microscopy (FIM)
- Photo electron emission microscopy (PEEM)

INCIDENT ELECTRONS:

- Scanning-electron microscopy (SEM, SAM)
- Transmission electron microscopy (TEM)
- Low-energy electron microscopy (LEEM)

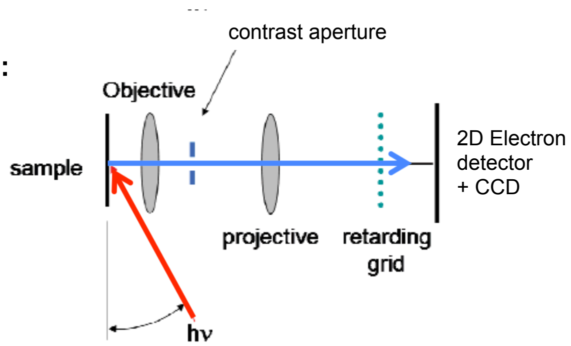
PEEM = Photo Electron Emission Microscopy

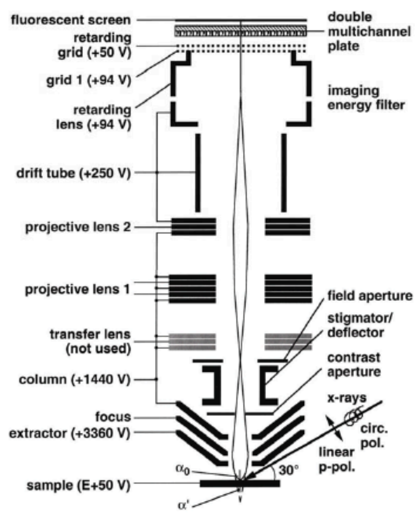
Concept: Photoelectric Effect (Einstein, 1905)



Requirement: light energy > work function

Setup:



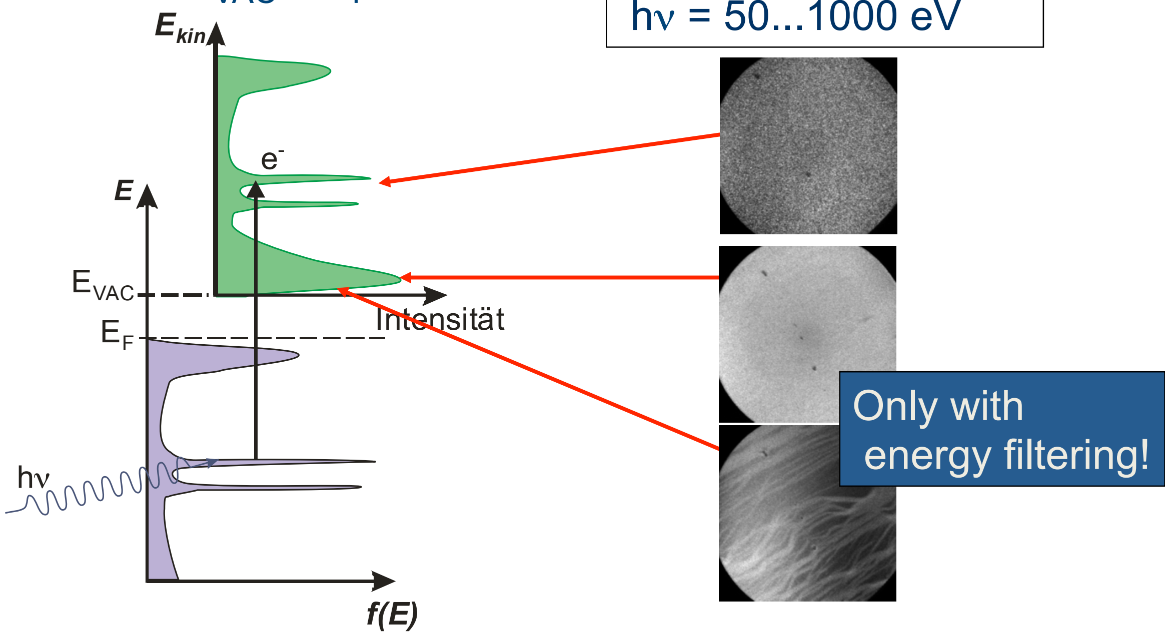


Focus PEEM with high pass filter

Principle of PEEM/XPEEM

$h\nu >> (E_{VAC} - E_F)$

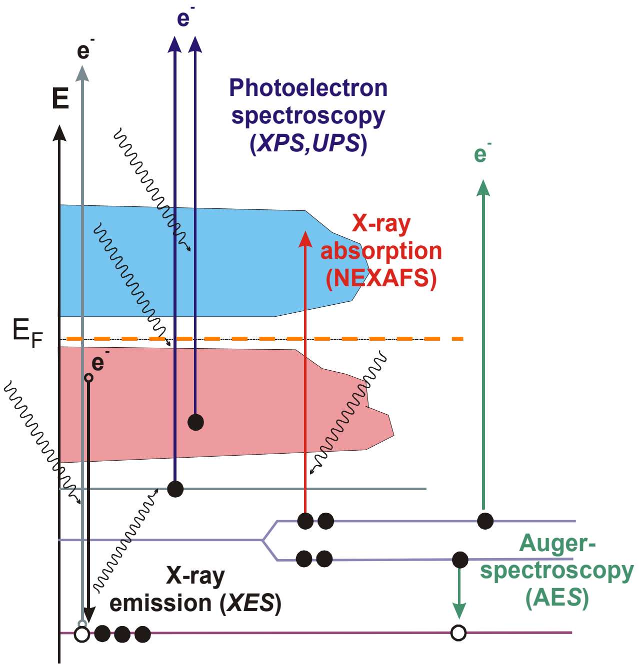
Synchrotron radiation:
$h\nu$ = 50...1000 eV



Appendix: Core-level electron spectroscopies

FAU FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

Example: p-type semiconductor DOS



Energy dispersive **electron detection** (i.e. inelastic mean free path is limited)

→ **surface sensitive**

(PES, NEXAFS, AES)

Energy dispersive **photon detection** (i.e., higher penetration depth)

→ **bulk sensitive**

(XES)

NEXAFS = Near-Edge X-Ray Absorption Fine Structure

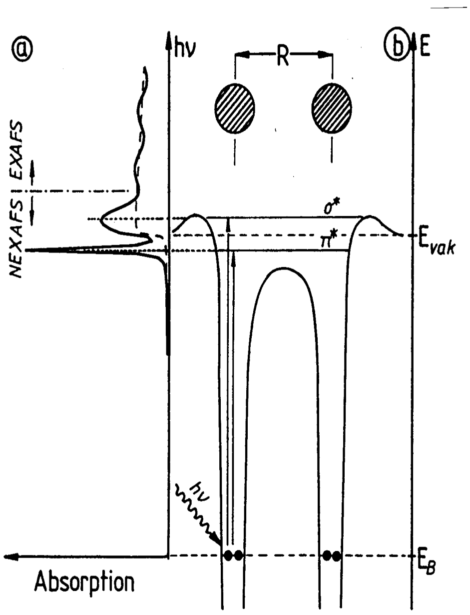
core excitation into unoccupied molecular
orbitals (π*-resonances) [LUMO]
and into delocalized states (σ*-resonances

local chemical probe
→ *chemical bonds*

polarization dependence *(dichroism)*
→ molecular orientation

$$W_{if} \propto |< f \,|\, \boldsymbol{p}\cdot\boldsymbol{e} \,|\, i >|^2 \cdot \rho\,(f)$$

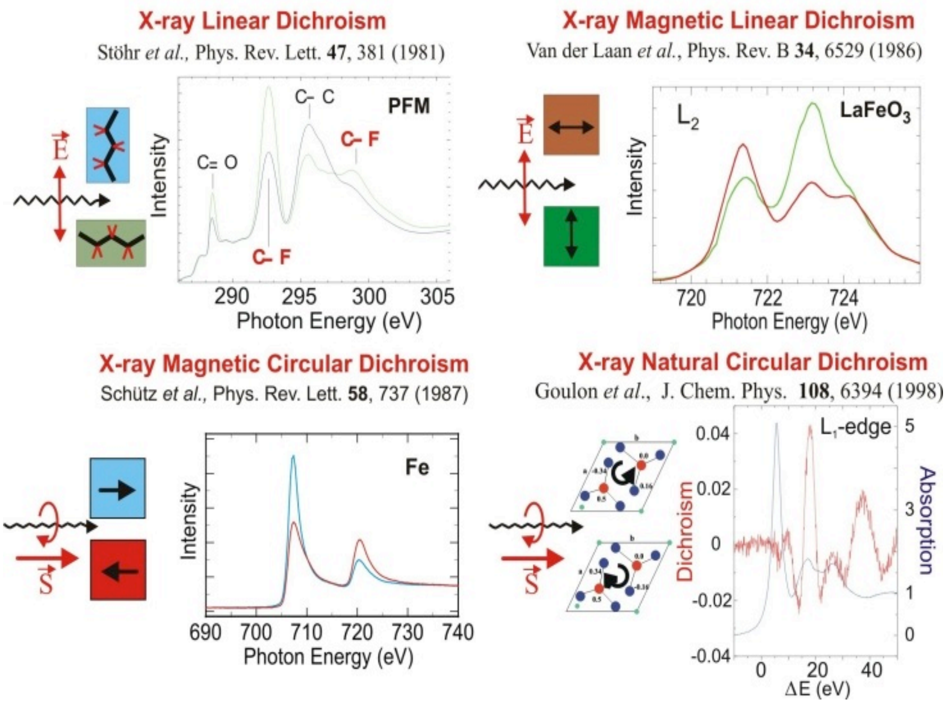
strong — no absorption



many distinct resonances → model calculations

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

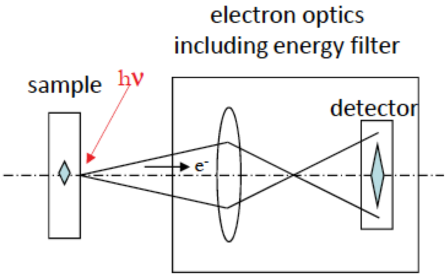
Polarization effects in NEXAFS



Taken from: J. Stöhr, Stanford

Method characteristics (PEEM / XPEEM)

X-ray photo emission electron microscopy (XPEEM)



- Direct imaging, parallel detection
- Dynamic processes ok!
- Lateral resolution is determined by electron optics (10-50 nm); with aberration correction: few nm will be possible.
- Requires smooth sample morphology.
- Combination with LEEM/LEED
- Spectroscopic PEEM! Intermediate spectroscopic ability(200 meV).
- Diffraction imaging possible.
- Sensitive in plane magnetisation!
- Vacuum better than $1 \cdot 10^{-5}$ mbar

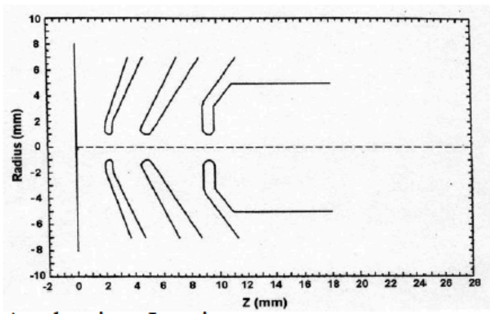
Cathode lens in PEEM (LEEM)

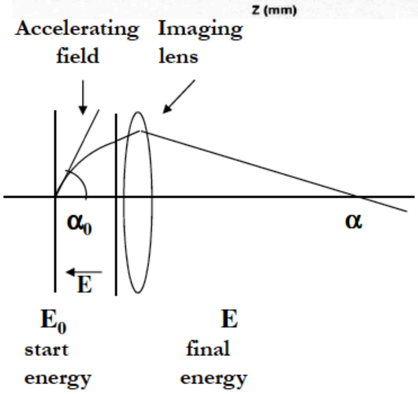
1. In emission microscopy θ (emission angle) is large. Electron lenses can accept only small θ because of large chromatic and spherical aberrations
2. Solution of problem: accelerate electrons to high energy before lens → Immersion objective lens or cathode lens

$$n \sin\theta = \text{const}$$
$$n \sim \sqrt{E}$$
$$\theta \rightarrow \alpha$$
$$\sin\alpha / \sin\alpha_0 = \sqrt{E_0/E}$$

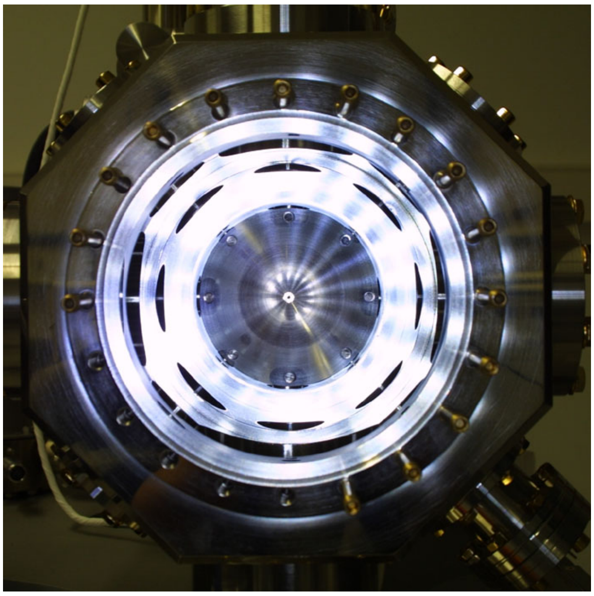
Example for E = 20000 eV:

E_0	2 eV	200 eV
α for $\alpha_0 = 45°$	0.4°	4.5°





Magnetic Lenses



Objective Lens of new S-PEEM in Essen

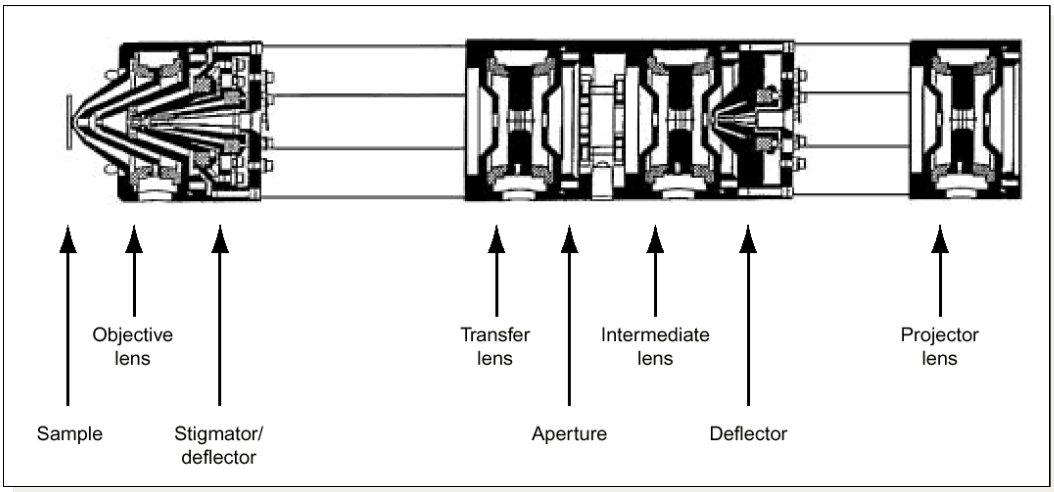
- **As Lenses for Optics**
  - Focal Length

$$\frac{1}{f} = \frac{e}{8m_e U}\int_{-\infty}^{\infty} B_z^2 dz$$

- **A Few Differences**
  - Image Rotation
  - Only Convex Lenses

Courtesy of F. Meyer-zu-Heringsdorf, Univ. Essen-Duisburg www.leem-user.de

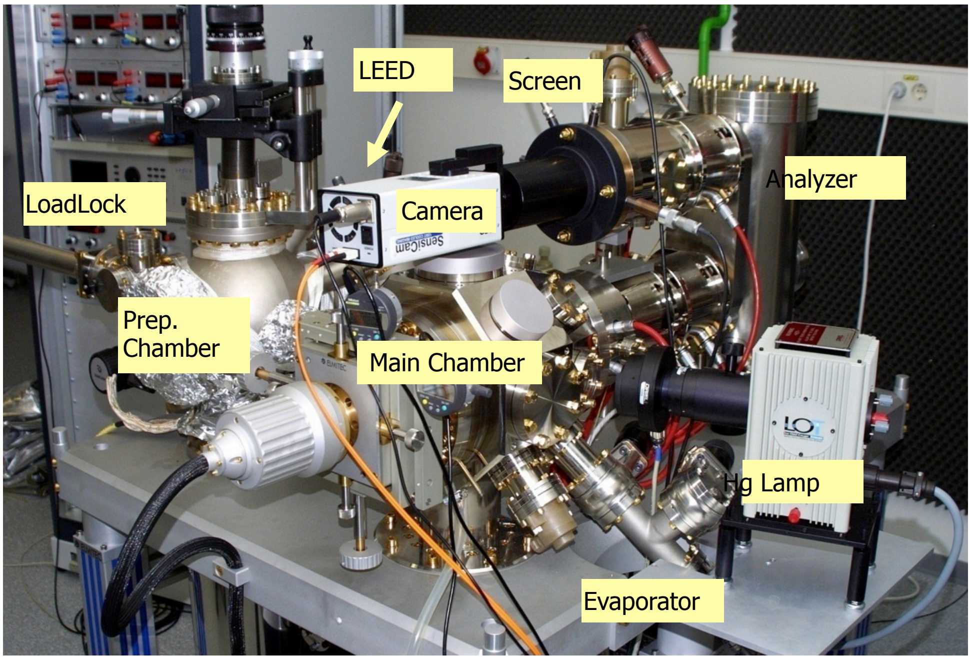
PEEM2, ALS Berkeley, USA (J. Stöhr, S. Anders et al)



Only electrostatic lenses !

from the endstation datasheet BL 7.3.1., ALS, Berkeley, USA, J. Stöhr et al

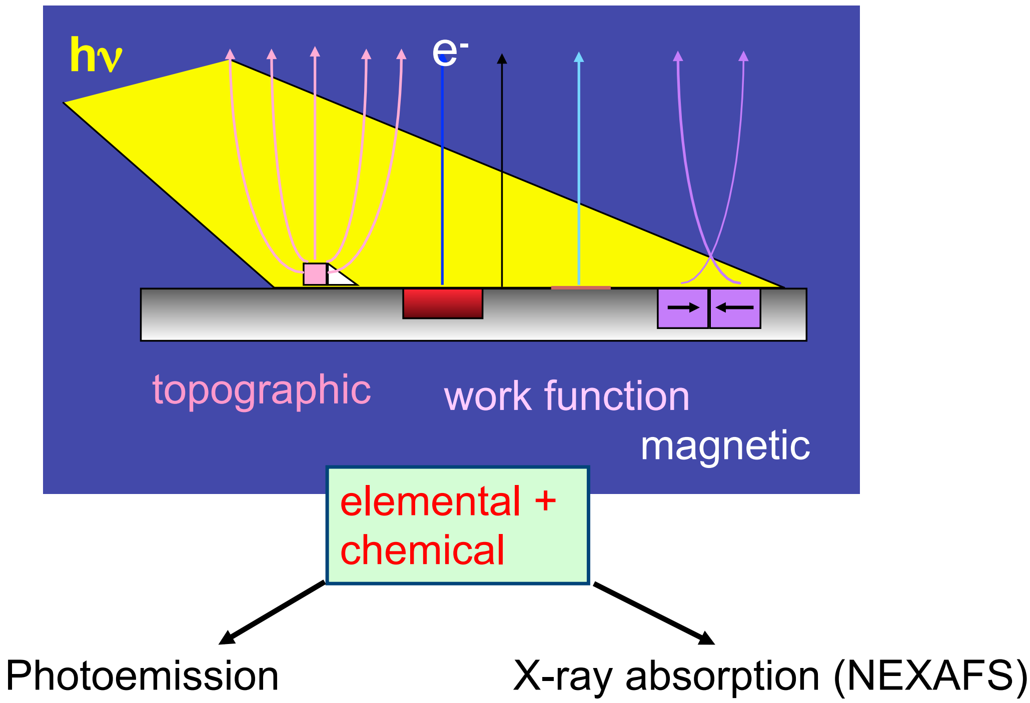
Spectroscopic PEEM (ELMITEC PEEM-III)



http://www.physik.uni-essen.de/SFB616

- Energy Analyzer
- LN2 Sample Cooling
- Preparation Chamber
- LEED, Auger

PEEM contrast mechanisms



Sample requirements for XPEEM

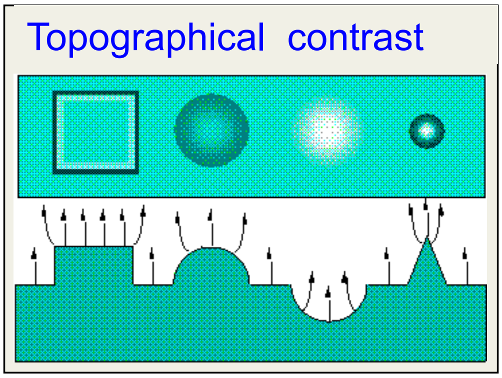
conducting samples (avoids charging !)

conducting substrates

surface roughness crucial

sample size > 8 mm diameter

sample in ultrahigh-vacuum

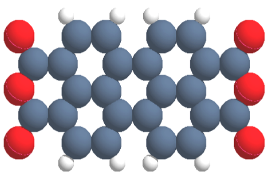


CRUCIAL: extreme high photon flux density → sample degradation

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

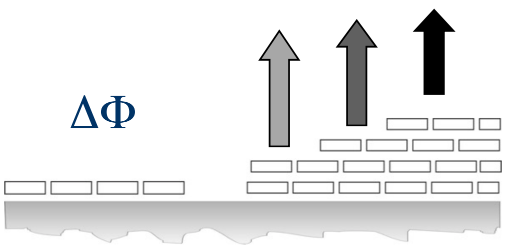
ORGANIC EPITAXY : layer-by-layer growth (1)

PTCDA/Ag(111)

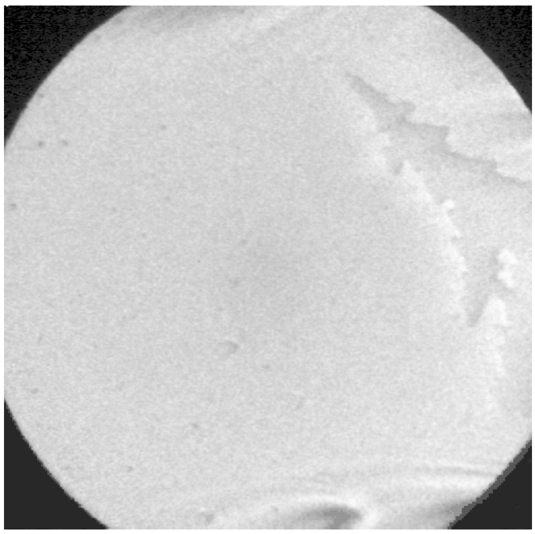


Deposition at **420 K** **(0.2 ML/min.)**

PEEM-contrast



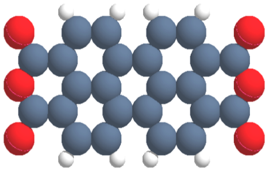
UV-PEEM: field of view 27 µm



Exp.: Th.Schmidt, H. Marchetto, R.F.

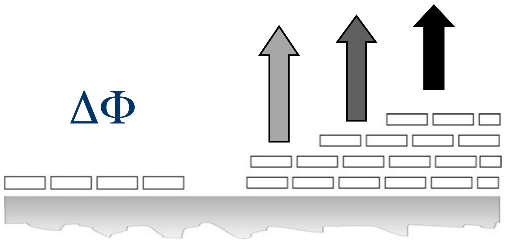
ORGANIC EPITAXY : layer-by-layer growth (2)

PTCDA/Ag(111)

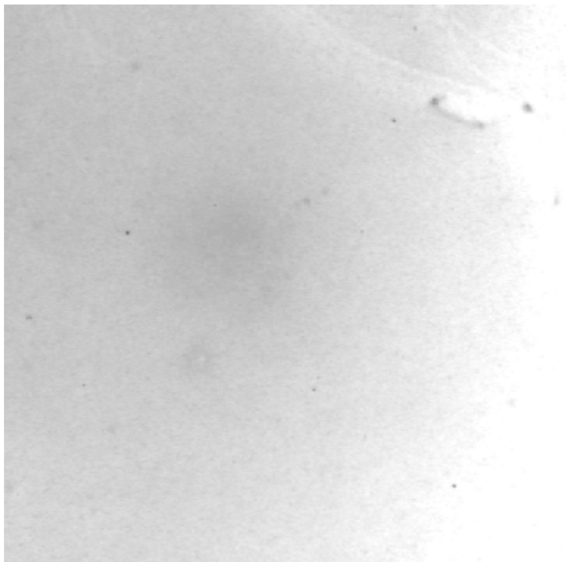


Deposition at **room temperature**
(0.2 ML/min.)

PEEM-contrast

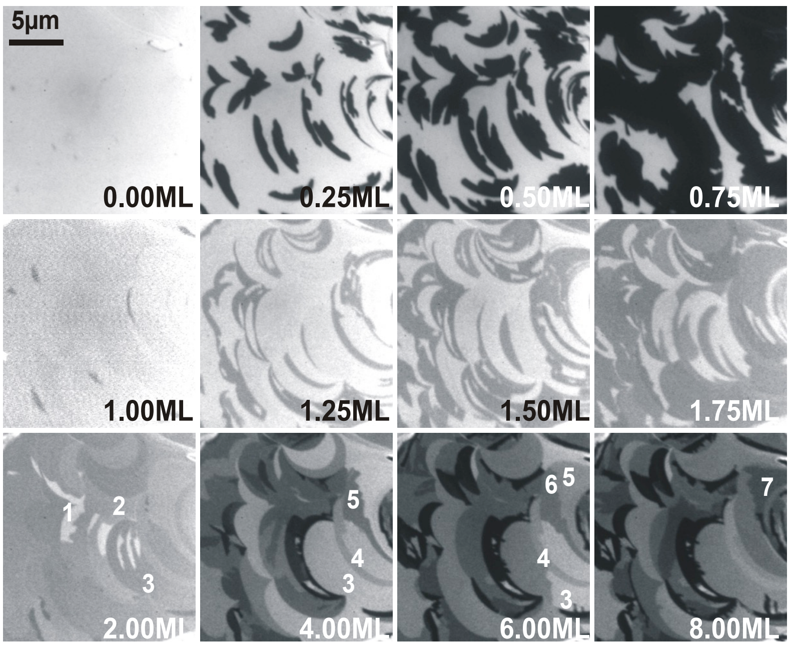


UV-PEEM: field of view 27 µm

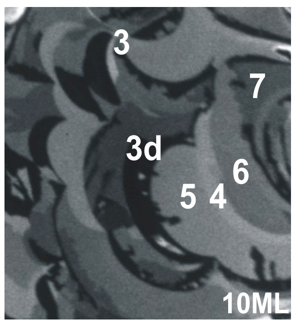


Exp.: Th.Schmidt, H. Marchetto, R.F.

PTCDA - epitaxial growth - PEEM

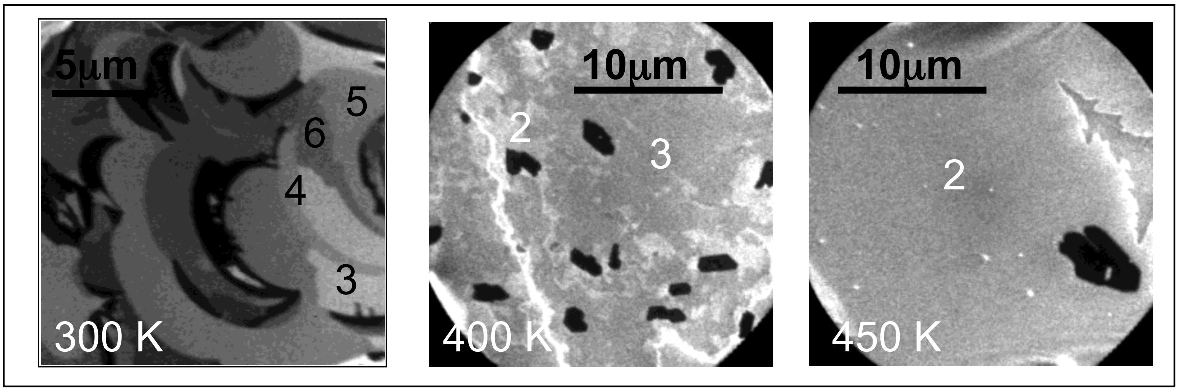


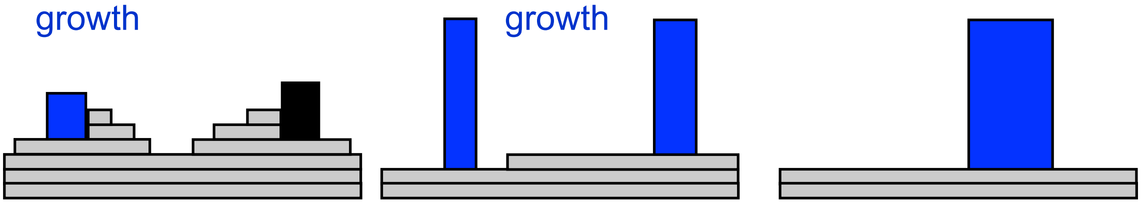
Frame szize: 17 x 17 µm²



1ML 2ML 3ML 4ML 5ML 6ML 7ML 3d

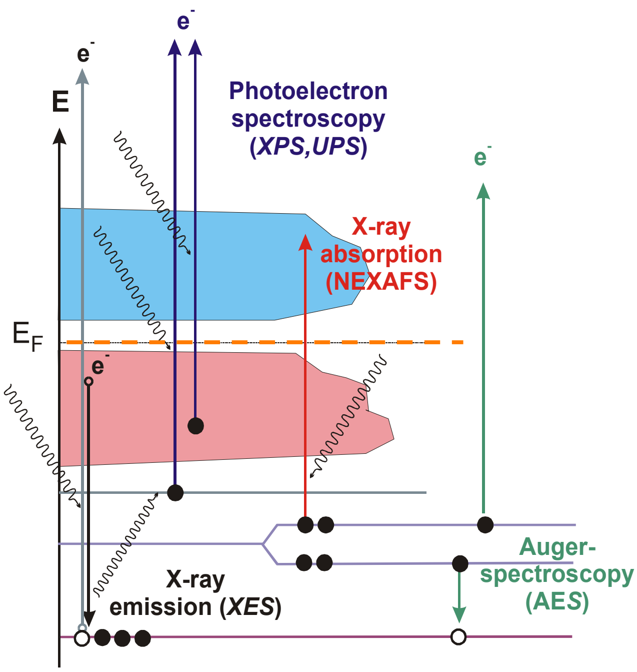
Temperature dependence of growth





Appendix: Core-level electron spectroscopies

Example: p-type semiconductor DOS



Energy dispersive **electron detection** (i.e. inelastic mean free path is limited)

→ **surface sensitive**

(PES, NEXAFS, AES)

Energy dispersive **photon detection** (i.e., higher penetration depth)

→ **bulk sensitive**

(XES)

NEXAFS = Near-Edge X-Ray Absorption Fine Structure

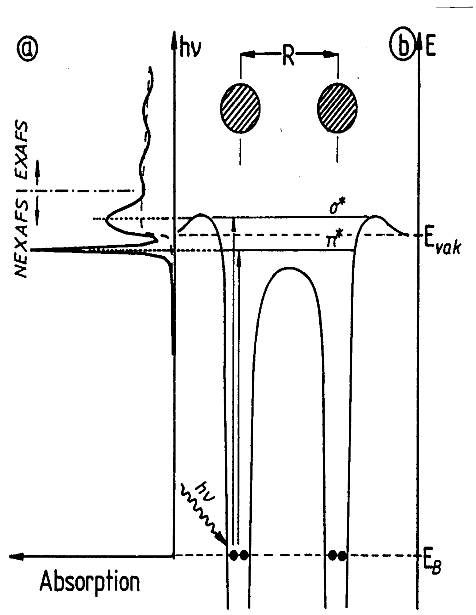
core excitation into unoccupied molecular
orbitals (π*-resonances) [LUMO]
and into delocalized states (σ*-resonances

local chemical probe
→ *chemical bonds*

polarization dependence *(dichroism)*
→ molecular orientation

$W_{if} \propto |\langle f \,|\, \boldsymbol{p}\cdot\boldsymbol{e} \,|\, i \rangle|^2 \cdot \rho\,(f)$

strong   no absorption



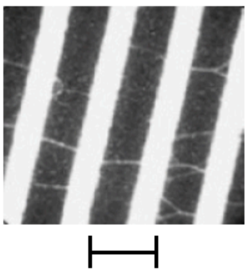
many distinct resonances → model calculations

370

Properties accessible in XPEEM

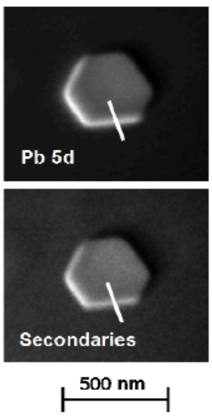
ELEMENTAL COMPOSITION & CHEMICAL STATE

C1s image of SWCN



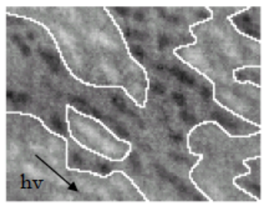
S. Suzuki et al, J. El. Spec Rel. Phenom. 357-360, 144 (2005)

Pb on W110



MAGNETIC STATE using XMCD

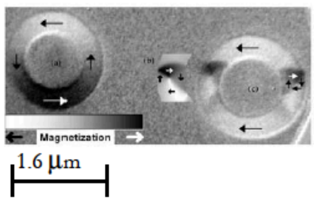
Co nanodots on Si-Ge



Co - L_3 edge

A. Mulders et al, Phys. Rev. B 71, 214422 (2005).

patterned structures

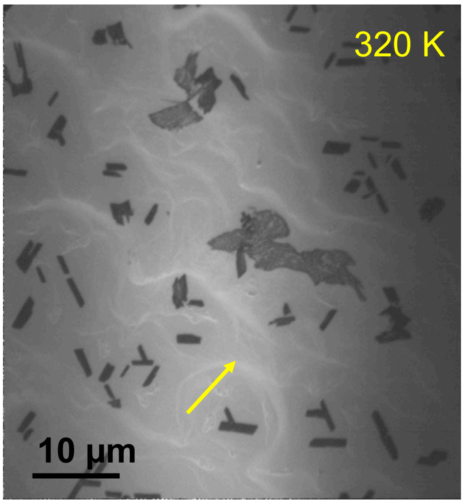


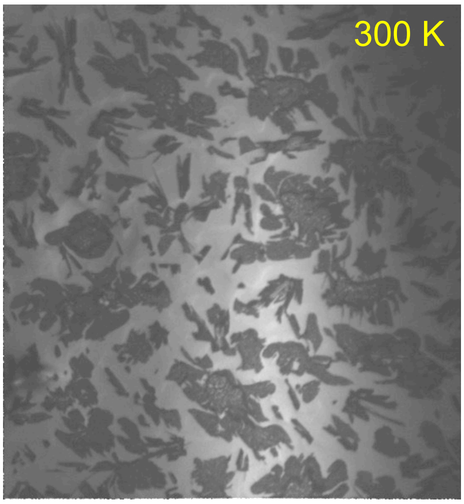
M. Klaeui et al, Phys. Rev. B 68, 134426 (2003).

Taken from A. Locatelli (ELETTRA)

Film morphology - **XPEEM**

NTCDA/Ag(111):





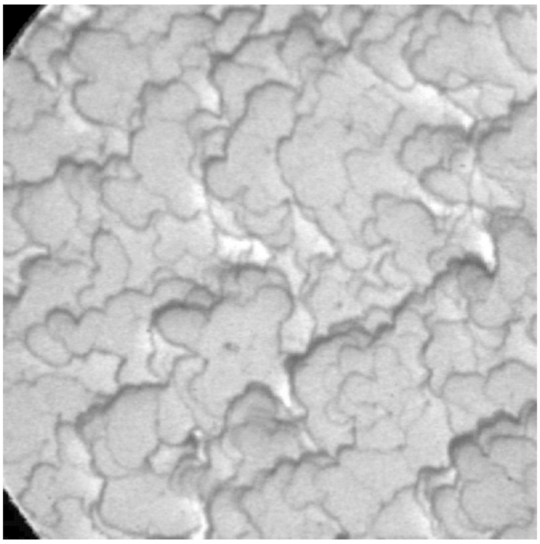
Stranski-Krastanov growth mode (layer-plus-island)

320 K: NTCDA crystallites (upright standing molecules)

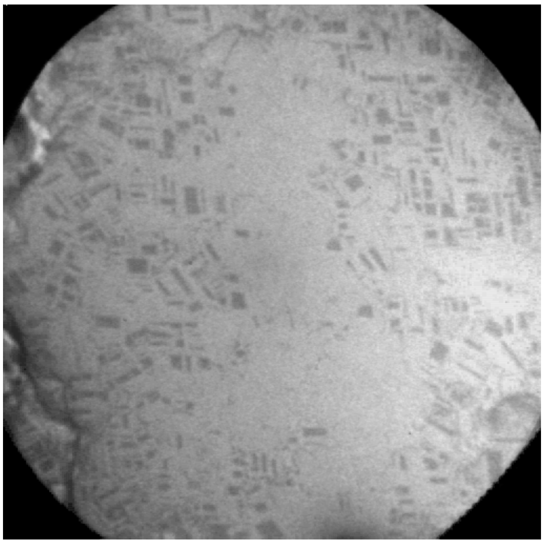
300 K: dendritic growth, different island morphology

NTCDA/Ag(111) - in-situ growth (UV-PEEM)

Adsorption



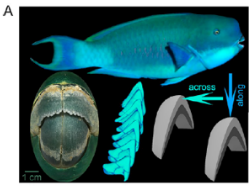
Desorption (thermal annealing)

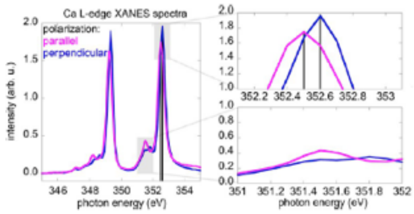


Photoelectron emission contrast partly due to molecular reorientation: **modification of the surface dipole**

Experiments: Thomas Schmidt

Biominerals in parrotfish teeth





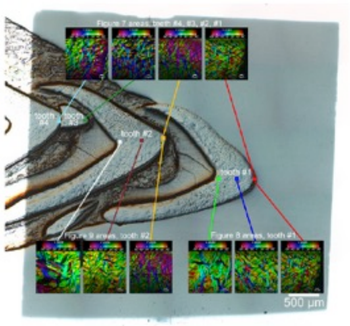


Figure 6. VLM micrograph of embedded and polished parrotfish teeth. The colored squares the 60 μm × 60 μm areas where the PIC maps of Figures 7–9 were acquired.

Nanocrystal orientation from polarization depen-dent imaging contrast (PIC, linear abs. dichroism)

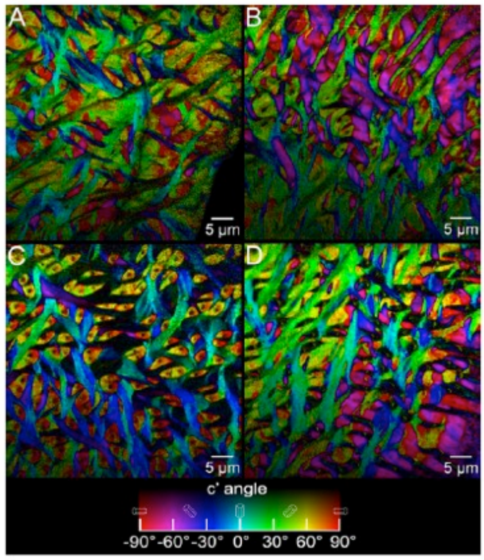
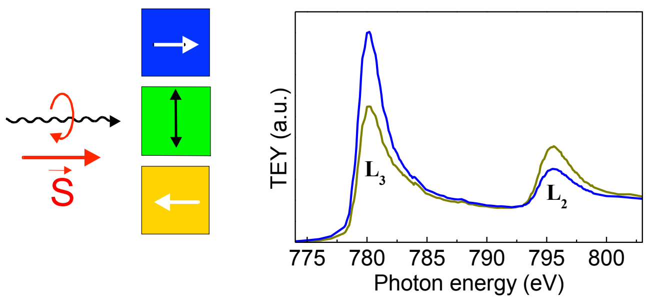


Figure 7. PIC maps showing different fluorapatite crystal sizes and orientations at the biting tips of teeth #1–4 as labeled in Figure 6. Two μm-wide fibers, made of 100 nm wide FAP crystals, are interwoven. The crystal orientations, shown schematically by prisms in the color bar, are as seen in projection perpendicular to the X-ray beam, which comes in from the right, at 30° from the surface.

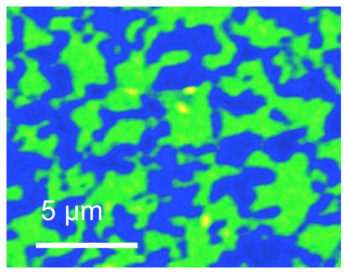
M.A. Marcus et al., ACS Nano 2017, 11, 11856

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG

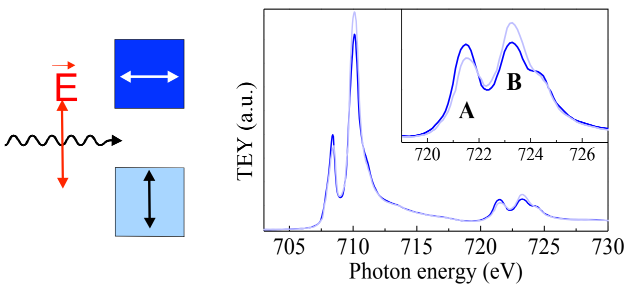
XMCD (X-ray Magnetic Circular Dichroism)



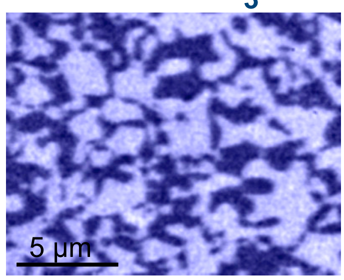
Co



XMLD (X-ray Magnetic Linear Dichroism)

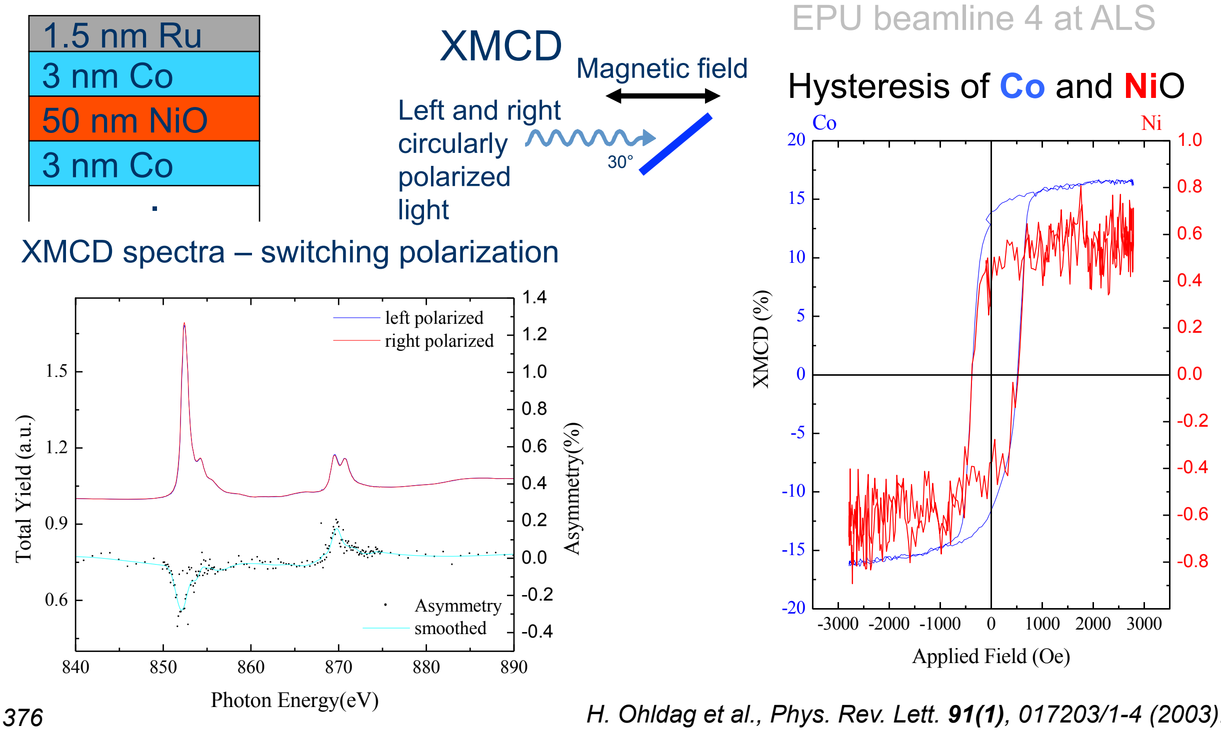


$LaFeO_3$



J. Stöhr et al. Science 1993 *A. Scholl et al. Science 2000* *F. Nolting et al. Nature 2000*

Exchange biased Co/NiO multilayer



H. Ohldag et al., Phys. Rev. Lett. **91(1)**, 017203/1-4 (2003).

(X)PEEM: Good points, bad points

- Surface inspection
  Chemical composition info available
- Large areas accessible
- In-situ observations
- Informative 3d images
- Aberration correction already available ! (later)

- Only used on conducting samples
- Sample in vacuum
- Edge effects cause image distortions
- Possibility of beam damage due to high photon intensities