

Elettra Sincrotrone Trieste

Chemical and magnetic imaging with x-ray photoemission electron microscopy (XPEEM)

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Why do we need photoelectron microscopy?



- To combine SPECTROSCOPY and MICROSCOPY to characterise the structural, chemical and magnetic properties of surfaces, interfaces and thin films
- Applications in diverse fields such as surface science, catalysis, material science, magnetism but also geology, soil sciences, biology and medicine.

Surface Science



DOI: 10.1103/PhysRevLett.86.5088

Magnetism



DOI: 10.1103/PhysRevLett.87.247201

Biology



PRL 98, 268102 (2007)

9/22/2015

Outline



- Synchrotron radiation and x-ray spectro-microscopy: basics
- Cathode lens microscopy: methods
- Applications
 - Chemical imaging of micro- structured materials
 - Graphene research.
 - Biology
 - Magnetism
 - Time-resolved XPEEM

Why does PEEM need synchrotron radiation?



- High intensity of SR makes measurements faster
- Tuneability very broad and continuous spectral range from IR to hard X-Rays
- Narrow angular collimation
- Coherence!
- High degree of polarization
- Pulsed time structure of SR This adds time resolution to photoelectron spectroscopy!
- Quantitative control on SR parameters allows spectroscopy:
 - Absorption Spectroscopy (XAS and variants)
 - Photoemission Spectroscopies (XPS, UPS, ARPES, ARUPS)

$$J = f(hv, \varepsilon, \Theta, \Phi; E_{kin}^{e}, \sigma, \theta_{e}, \varphi_{e})$$

Cathode lens microscopy methods

PEEM, LEEM, SPELEEM, AC-PEEM/LEEM

PEEM basics





- Direct imaging, parallel detection
- Lateral resolution determined by electron optics: with AC, few nm possible
- Elemental sensitivity (XAS)
- Spectroscopic ability (energy filter)
- P_{max} < 5·10⁻⁵ mbar

PEEM is a full-field technique. The microscope images a restricted portion of the specimen area illuminated by x-ray beam. Photoemitted electrons are collected at the same time by the optics setup, which produces a magnified image of the surface. The key element of the microscope is the objective lens, also known as cathode or immersion lens, of which the sample is part

Cathode lens operation principle

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



Example for E = 20000 eV: E₀ 2 eV 200 eV α for α_0 = 45° 0.4° 4.5°



3. The aberrations of the objective lens and the contrast aperture size determine the lateral resolution

$$d = \sqrt{d_{SP}^{2} + d_{CH}^{2} + d_{D}^{2}}$$



The different types of PEEM measurements





Simple PEEM instruments

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PEEM instrments with energy filter: NanoESCA



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Different contrast mechanisms are available for strucutre characterization

SURFACE STRUCTURE



FILM THICKNESS



STEP MORPHOLOGY





quantum size contrast

geometric phase contrast



SPELEEM = LEEM + PEEM





Applications:

characterization of materials at microscopic level, magnetic imaging of micro-structures Imaging of dynamical processes A. Locatelli, L. Aballe, T.O. Menteş, M. Kiskinova, E. Bauer, Surf. Interface Anal. 38, 1554-1557 (2006)

T. O. Menteş, G. Zamborlini, A. Sala, A. Locatelli; Beilstein J. Nanotechnol. 5, 1873–1886 (2014)

SPELEEM many methods analysis



angular resolution

transfer width: 0.01 Å⁻¹

LEEM : 10 nm

XPEEM: 25 nm

XPEEM: 0.3 eV



Performance:lateral resolution in imaging:10nm (LEEM)30 nm (XPEEM)30 nm (XPEEM)energy resolution:0.3 eV (0.1 eV muXPS)

Key feature: <u>multi-method</u> instrument to the study of surfaces and interfaces offering *imaging* and *diffraction* techniques.

Probe:*low energy e-* (0-500 eV) \leftrightarrow structure sensitivity
soft X-rays (50-1000 eV) \leftrightarrow chemical state, magnetic
state, electronic struct.

Applications:characterization of materials at microscopic levelmagnetic imaging of microstrucutresdynamical processes

Correction of spherical and chromatic aberrations





The SMART AC microscope: calculation



d

with

 α^{5}

 $\Delta E \alpha^2$

 $+ \Delta E^2 \alpha$

 $1/\alpha$



D. Preikszas, H. Rose, J. Electr. Micr. 1 (1997) 1 Th. Schmidt, D. Preikszas, H. Rose et al., Surf.Rev.Lett 9 (2002) 223

First results of the SMART microscope @BESSY

Atomic steps on Au(111), LEEM 16 eV, FoV = 444 nm x 444 nm (18.09.06)



Courtesy of Th. Schmidt et al.; 5th Int. Conf. LEEM/PEEM, Himeji, 15.-19. Oct. 2006

Lateral resolution limitations: space charge

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Ni/W(100) hv = 181 eV



photocurrent estimate for SPELEEM@Elettra; Au/W(110)

- 440 bunches
 - rev. frequency: 1.157 MHz bunch length: 42 ps (2GeV)
- 1 10¹³ ph./s on sample =
 - = 20000 ph./bunch
- Total photoionization yield: about 2% photons result in a photoemission event
- I peak ≈ 400 e⁻/ 42 ps
 - ≈ 1.5µA vs 20 nA (LEEM)
- 13 pA/ μ m² versus 20 nA/ μ m²
- 1. Image blur can be observed with SR but only under very high photon fluxes. Must Keep into account in beamline design. No space charge in LEEM
- 2. Both the lateral and energy resolution are strongly degraded by Boersch and Loeffler effects occurring in the first part of optical path.

Chemical imaging applications

PEEM, LEEM, SPELEEM, AC-PEEM/LEEM

Au/TiO₂(110): controlling growth by vacancies





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94 96 98 Kinetic energy (eV)

100

102

Creation of ordered oxygen vacancies

9/22/2015

Surface Oxygen on Ag : *e-beam "Lithography"*



Full oxidation of Ag using NO₂ does not occur:

 $NO_2 \rightarrow NO_{ad} + O_{ad}$

Instead: e-beam (60 eV) stimulated desorption of NO_{ad} works at RT!



S. Günther et al., App. Phys. Lett. 93, 233117 (2008).

Low T: NO_{ad} stays, prevents oxidation.

High T: NO_{ad} desorbs, but Ag₂O unstable.

LEED reveals path towards Ag₂O under e-beam



S. Günther et al., Chem. Phys. Chem. 2010.

Surface Oxygen on Ag : photon-beam "Lithography"





MEM 28 µm x 350 µm; after 130 L NO₂;



(c) $t = 540 \text{ s}, p(NO_2) = 2.5 \times 10^{-7} \text{ mbar}, 67 \text{ L } NO_2.$

S. Günther et al., Chem. Phys. Chem. 2010.

Thickness dependent reactivity in Mg





L. Aballe et al., Phys. Rev. Lett. 93, 196103 (2004)

Oxidation of Mg film and QWR





FACTS

- Strong variations in the oxidation extent are correleted to thickness and to the density of states at E_F
- XPEEM is a powerful technique for correlating chemistry and electronic structure information

SIGNIFICANCE OF THE EXPERIMENTS

- ✓ Control on film thickness enables modifying the molecule-surface interaction
- ✓ Theoretical explanation: Decay length of QWS into vacuum is critical: it reproduces peak of reactivity in experimental data. See Binggeli and M. Altarelli, Phys.Rev.Lett. 96, 036805 (2005)

L. Aballe et al., Phys. Rev. Lett. 93, 196103 (2004)

Spatio-temporal patterns in surface chemical reactions



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VOLUME 65, NUMBER 24

PHYSICAL REVIEW LETTERS

10 DECEMBER 1990

Spatiotemporal Concentration Patterns in a Surface Reaction: Propagating and Standing Waves, Rotating Spirals, and Turbulence

> S. Jakubith, H. H. Rotermund, W. Engel, A. von Oertzen, and G. Ertl Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany (Received 25 June 1990)



Belousov-Zabatinski reaction (solution of, acidified bromate, malonic acid, ceric salt) Pattern formation in surface chemical reactions oscillatory oxidation of carbon monoxide on a Pt(110) surface standing fronts rotating spirals

Jakubith et al., PRL 65, 3013 (1990)

See also: W. Engel, et al., Ultramicroscopy 36, 148–153 (1991).

Reaction diffusion patterns: NO+H₂ /Rh(110)





9/22/2015

Reaction diffusion patterns: NO+H₂ /Rh(110)





LEEM, micro-LEED

Th. Schmidt *et al.,* Chem. Phys. Lett. 318, 549 (2000)



Reactive phase-separation processes





The complexity of the metal-graphene interface

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- Understand and control the fundamental interactions occurring at the interface
- verify the properties (crystal quality, stoichiometry, electronic structure) at the mesoscale!

XPEEM studies of graphene

- Effect of substrate' symmetry
 - The complex structure of g/lr(100)
- Buffers
 - Au Intercalation
 - Carbides in graphene on Ni(111)
- Irradiation/implantation
 - Low energy N+ ion irradiation of g/lr(111)
 - Irradiation with noble gases of g/Ir(100)

High temperatrue graphene growth on Ir(100)



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LEEM imaging

microprobe-LEED: Ir



microprobe-LEED: graphene



T > 800 C;P= $2 \cdot 10^{-8}$ mbar ethylene

Reversible graphene phase transformation



Upon cooling a distinct graphene phase nucleates forming dark stripes



1 µm

The stripes disappear when annealing the sample to high temperature.



Fov 4 μm , S.V. 13 eV

22/09/2015

Graphene/Ir(100): strucutre of FG and BG





Buckled graphene unit cell by ab-initio





Buckled graphene shows regular one-dimensional ripples with periodicity of 2.1nm.

Electronic structure: graphene doping



what is the <u>difference in electronic structure</u> between FG and BG? do they both show the same Dirac-like dispersion?

Diffraction Imaging



Different character of FG and BG





Decoupling graphene from substrate:

- Intercalated Au/g/Ir(100)
 - Switchable formation of carbides in g/Ni(111)

Tuning the interaction by Au intercalation





Identifying crystal grains in graphene/Ni(111)



Formation/dissolution of carbides under rg/Ni(111)





Different electron reflectivity explains change of contrast



All movies: LEEM FoV 6 um, electron energy: 11 eV

temperatures below 340°C

Coupling-decoupling is revealed by μ -ARPES



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Ion irradiation of graphene:

- Ar nanobubbles ripening under graphene

Morphology of Ar⁺ irradiated graphene/Ir(100)





Evolution upon annealing: STM and $\mu\text{-XPS}$



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^{22/09/20}IFradiation with 0.1keV Ar⁺ 150 s and 5 min annealing; The XPS data were acquired at RT

LEEM & XPEEM formation of Ar nanobubbles



LEEM movie 12 eV





NB formation for g/Ne/Ir(100)



100 eV Ne+ ion irradiation was followed by 5 min annealing to 650 °C and subsequent cooling to RT

bright-field LEEM 12 eV



dark-field LEEM BG phase



0.5 µm

0.5 µm

- Wrinkles surround the larger particles
- At RT, bubbles have a polygonal shape → solid?

XPEEM imaging Ne 2p



- 0.5 µm
- elemental composition below graphene!
- XPS from individual particles
- Shift to high BE for large clusters

XAS-PEEM applications to biosciences

biomineralization

Applications of XAS in biology: biomineralization





- Bio-mineralization resulting from microbal activity
- X-PEEM images of (A) non mineralized fibrils from the cloudy water above the biofilm (scale bar, 5 um)
- (B) mineralized filaments and a sheath from the biofilm (scale bar, 1 um); (bottom)
- X-PEEM Fe L-edge XANES spectra of the FeOOH mineralized looped filament shown in (B), compared with iron oxyhydroxide standards, arranged (bottom to top) in order of decreasing crystallinity.

P.U.P.A Gilbert *et al. (ALS group), Science* **303** 1656-1658, 2004.

Nano-scale architecture of Nacre





5μm

$$I(\vartheta, \theta, T) = a + b(3\cos^2\vartheta - 1)\langle Q_{zz}\rangle + c(3\cos^2\theta - 1)\langle M^2\rangle_T + d\sum_{i,j}\langle \hat{s}_i \cdot \hat{s}_j\rangle_T$$

Contrast is observed between adjacent individual nacre tablets, arising because different tablets have different crystal orientations with respect to the radiation's polarization vector.

The 290.3 eV peak corresponds to the C $1s \rightarrow Pi^*$ transition of the CO bond. Synchrotron radiation is linearly polarized in the orbit plane. Under such illumination, the

intensity of the peak depends on the crystallographic orientation of each nacre tablet with respect to the polarization. This was the first observation of x-ray linear dichroism in a bio-mineral.

R.A. Metzler *et al., Phys.Rev.Lett.* **98**, 268102 (2007)

Magnetic imaging

XMCD and XMLD PEEM

1. 1.40

Magnetic imaging: XMCD



Circular Dichroism - Ferromagnets



X-ray magnetic circular dichroism (XMCD) is the dependence of <u>x-ray absorption</u> on the relative orientation of the local magnetization and the polarization vector of the circularly polarized light

✓ Element sensitive technique

✓ Secondary imaging with PEEM determine large probing depth (10 nm), buried interfaces.

MnAs/GaA



Magnetic domain imaging

At resonance, the secondary electron yield is proportional to the dot product between the magnetization direction and the photon helicity vector, which is parallel or anti-parallel to the beam propagation direction

XMCD principles





- We **PROBE** 3d elements by exciting 2p into unfilled 3d states
- •Dominant channel: $2p \rightarrow 3d$
- •White line intensity of the L3 and L2 resonances with the number N of empty d states (holes).

- By using circularly polarized radiation, the angular momentum of the photon can be transferred in part to the spin through the spinorbit coupling. Photoelectrons with opposite spins are created in the cases of left and right handed polarization. Spin polarization is opposite also for p_{3/2} (L₃) and p_{1/2} (L2) levels.
- The spin-split valence shell is thus a detector for the spin of the excited photoelectron. The size of the dichroism effect scales like cosθ, where θ is the angle between the photon spin and the magnetization direction.
- Refs: IBM. J. Res. Develop. 42, 73 (1998) and J. Magn. Magn. Mater. 200, 470 (1999).

Image algebra



The size of the dichroism effect scales like $\cos\theta$, where θ is the angle between the photon spin and the magnetization direction. Hence the maximum dichroism effect (typically 20%) is observed if the photon spin and the magnetization directions are parallel and anti-parallel. Sum rules allows measuring orbital and spin moments



Examples of XMCD-PEEM applications



MAGNETIC STATE using XMCD &

Co nanodots on Si-Ge



Co - L₃ edge

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

patterned XMLD structures



1.6 um

pulse injection



M. Klaeui et al, PRL , PRB 2003 - 2010

domain wall motion induced by spin currents



Laufemberg et al, APL 88, 232507(2006).

Examples of XMCD-PEEM applications



nano-magnetism of (Ga,Fe)N films

Fe L3 edge (chemical) Fe L3 edge (XMCD)



Magnetization in NiPd nanostructures



I Kowalik, D. Arvanitis, M.A. Niño et al., in preparation

J.-Y. Chauleau, Phys. Rev. B 84, 094416 (2011)

Magnetic imaging basics: XMLD



Linear Dichroism - Antiferromagnets In the presence of spin order the spin-orbit coupling leads to preferential charge order aFeO. relative to the spin direction, which is exploited to determine the spin axis in ntensit antiferromagnetic systems. \checkmark Element sensitive technique ✓ Secondary imaging with PEEM determine large probing depth (10 nm), buried 720 722 724 interfaces. Photon Energy (eV

✓ Applied in AFM systems (oxides such as NiO)

Absorption intensity at resonance $I(\vartheta, \theta, T) = a + b(3\cos^2\vartheta - 1)\langle Q_{zz}\rangle$

+
$$c(3\cos^2\theta - 1)\langle M^2 \rangle_T$$
 + $d\sum_{i,j}\langle \hat{s}_i \cdot \hat{s}_j \rangle_T$

1st term: quadrupole moment, i.e.electronic charge (not magnetic!)

 2^{nd} term determines XMLD effect; θ is the angle between E and magnetic axis A; XMLD max for E || A;



Linear vertical and linear horizontal polarization of the photon beam

Applications of XMCD and XMLD



Co layer

Direct observation of the alignment of ferromagnetic spins by antiferromagnetic spins

F. Nolting*, A. Scholl*, J. Stöhr†, J. W. Seo‡§, J. Fompeyrine§, H. Siegwart§, J.-P. Locquet§, S. Anders*, J. Lüning†, E. E. Fullerton†, M. F. Toney†, M. R. Scheinfein|| & H. A. Padmore*

Nature, 405 (2000), 767.

ferromagnet/antiferromagnet Co/LaFeO3 bilayer interface exchange coupling between the two materials

LaFeO₃ layer **XMLD Fe L₃**



DW imaging in magnetic wires





S. Da Col et al., Phys. Rev. B89, 180405(R) (2014)

Limited probing depth of XMCD: MnAs/GaAs



Experiment: Straight walls; Head to head domains



Simulation: Cross sectional cut: diamond state

R. Engel-Herbert et al, J. Magn. Magn. Mater. 305, (2006) 457

Adding the time domain to PEEM

TR-PEEM methods

1. 1.11

Time-resolved PEEM: the stroboscopic approach



Stroboscopic experiments combine high lateral resolution of PEEM with high time resolution, taking advantage of pulsed nature of synchrotron radiation



Detector gating for time-resolved XMCD PEEM





Multi-bunch image 32 images per helicity Image exposure 4 s Acquisition time: 5':18"





Single bunch image 24 images per helicity Image exposure 20 s Acquisition time: 17':40"





Current-induced motion of magnetic domain walls in Permalloy (Fe20Ni80) nanostripes, through the spintransfer torque (STT) effect. Our measurements reveal clear eformations of the domain wall shape

J. Vogel, A. Locatelli et al., in preparation

Time resolved XMCD-PEEM: applications



- Switching processes (magnetisation reversal) in magnetic elements (in spin valves, tunnel junction)
 - Nucleation, DW propagation or both?
 - Effect of surface topography, morphology crystalline structure etc.
 - Domain dynamics in Landau flux closure structures.
- response of vortices, domains, domain walls in Landau closure domains in the precessional regime
- Stroboscopic technique:
 - <u>only reversible processes can be studied by pump probe</u>
 <u>experiments</u>
 - Measurements are quantitative

Magnetic excitations in LFC structures



Quantitative Analysis of Magnetic Excitations in Landau Flux-Closure Structures Using Synchrotron-Radiation Microscopy

J. Raabe,^{1,*} C. Quitmann,¹ C. H. Back,² F. Nolting,¹ S. Johnson,¹ and C. Buehler¹

The time dependent magnetization is described by the phenomenological Landau-Lifshitz-Gilbert equation

$$\frac{d}{dt}\vec{M} = -\gamma_0\vec{M}\times\vec{H}_{\rm eff} + \frac{\alpha}{M}\left(\vec{M}\times\frac{d}{dt}\vec{M}\right).$$

The first term describes the precession of the magnetization \vec{M} about the total effective field \vec{H}_{eff} . The second term describes the relaxation back into the equilibrium state using the dimensionless damping parameter α .





Summary



- XPEEM is a versatile full-field imaging technique. Combined with SR it allows us to implement laterally resolved versions of the most popular x-ray spectroscopies taking advantage of high flux of 3rd generation SR light sources.
- In particular, XAS-PEEM combines element sensitivity with chemical sensitivity (e.g. valence), and, more importantly, magnetic sensitivity. Magnetic imaging has been the most successful application of PEEM (next tutorial lecture!).
- XPEEM or energy-filtered PEEM adds true chemical sensitivity to PEEM. Modern instruments allow to combine chemistry with electronic structure using ARUPS.
- XPEEM can be complemented by LEEM, which adds structure sensitivity and capability to monitor dynamic processes.
- Lateral resolution will approach the nm range as AC instruments become available. Limitations due to space charge are not yet clear
- Novel application field are being approached, such as biology, geology and earth sciences. HAXPES will increase our capabilities to probe buried structures (bulk).

Review work



Reviews and topical papers on x-ray spectromicroscopy and XPEEM

- S. Guenther, B. Kaulich, L.Gregoratti, M. Kiskinova, Prog. Surf. Sci. 70, 187–260 (2002).
- E. Bauer, Ultramicroscopy **119**, 18–23 (2012).
- E. Bauer, J. Electron. Spectrosc. Relat. Phenom. (2012): http://dx.doi.org/10.1016/j.elspec.2012.08.001
- G. Margaritondo, J. Electron. Spectrosc. Relat. Phenom. 178–179, 273–291 (2010).
- A. Locatelli, E. Bauer, J. Phys.: Condens. Matter 20, 093002 (2008).
- G. Schönhense *et al.,* in *"Adv. Imaging Electron Phys.",* vol. **142**, Elsevier, Amsterdam, P. Hawkes (Ed.), 2006, pp. 159–323.
- G. Schönhense, J. Electron. Spectrosc. Relat. Phenom. 137–140, 769 (2004).
- C.M. Schneider, G. Schönhense, *Rep. Prog. Phys.* 65, R1785–R1839 (2002).
- W. Kuch, in *"Magnetism: A Synchrotron Radiation Approach"*, Springer, Berlin, E. Beaurepaire et al. (Eds.), 2006, pp. 275–320.
- J. Feng, A. Scholl, in P.W. Hawkes, "Science of Microscopy", Springer, New York, J.C.H. Spence (Eds.), 2007, pp. 657–695.
- E. Bauer and Th. Schmidt, in *"High Resolution Imaging and Spectroscopy of Ma-terials"*, Springer, Berlin, Heidelberg, F. Ernst and M. Ruehle (Eds.), 2002, pp. 363-390.
- E. Bauer, J. Electron Spectrosc. Relat. Phenom. **114-116**, 976-987 (2002).
- E. Bauer, J. Phys.: Condens. Matter 13, 11391-11405 (2001).

Credits & Acknowledgments



Thank you for attention!

T. Onur Menteş

Giovanni Zamborlini

Alessandro Sala

Theory group at ICTP (Trieste)

Nataŝa Stojić Nadia Binggeli Mighfar Imam Chen Wang STM group at IOM-CNR TASC laboratory

Laerte Patera Cristina Africh Giovanni Comelli