

Elettra Sincrotrone Trieste

# Basic concepts for LEEM, XPEEM and applications

Andrea Locatelli

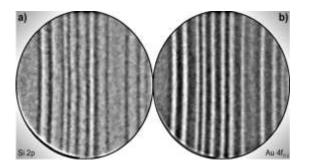
Andrea.locatelli@elettra.eu

## Why do we need photoelectron microscopy?



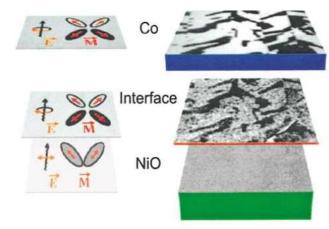
- To combine SPECTROSCOPY and MICROSCOPY to characterise the structural, chemical and magnetic properties of surfaces, interfaces and thin films
- Applications in diverse fields such as surface science, catalysis, material science, magnetism but also geology, soil sciences, biology and medicine.

Surface Science



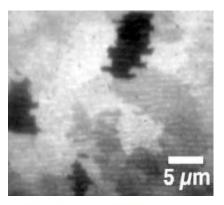
DOI: 10.1103/PhysRevLett.86.5088

Magnetism



DOI: 10.1103/PhysRevLett.87.247201

Biology



PRL 98, 268102 (2007)

4/19/2016

#### 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)

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

## Outline

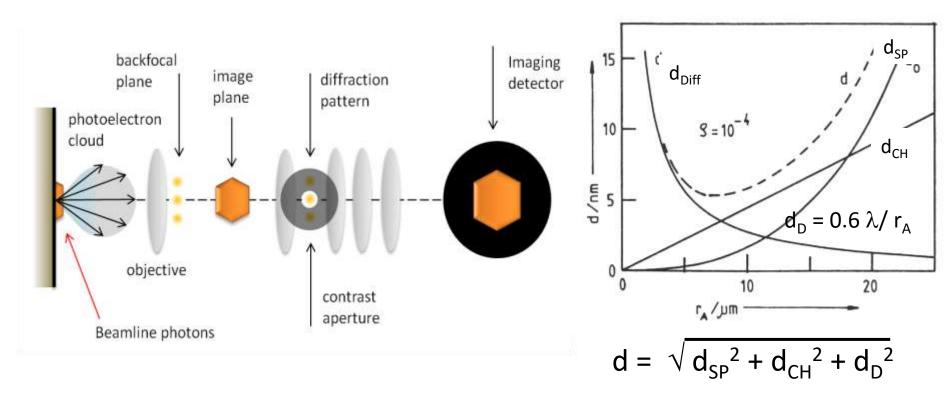
- Synchrotron radiation and x-ray spectro-microscopy: basics
- Cathode lens microscopy: methods
- Applications
  - Chemical imaging of micro-structured materials
  - Graphene research.
  - Magnetism
  - Time-resolved XPEEM

## **Cathode lens microscopy methods**

#### PEEM, LEEM, SPELEEM, AC-PEEM/LEEM

## **PEEM basics**

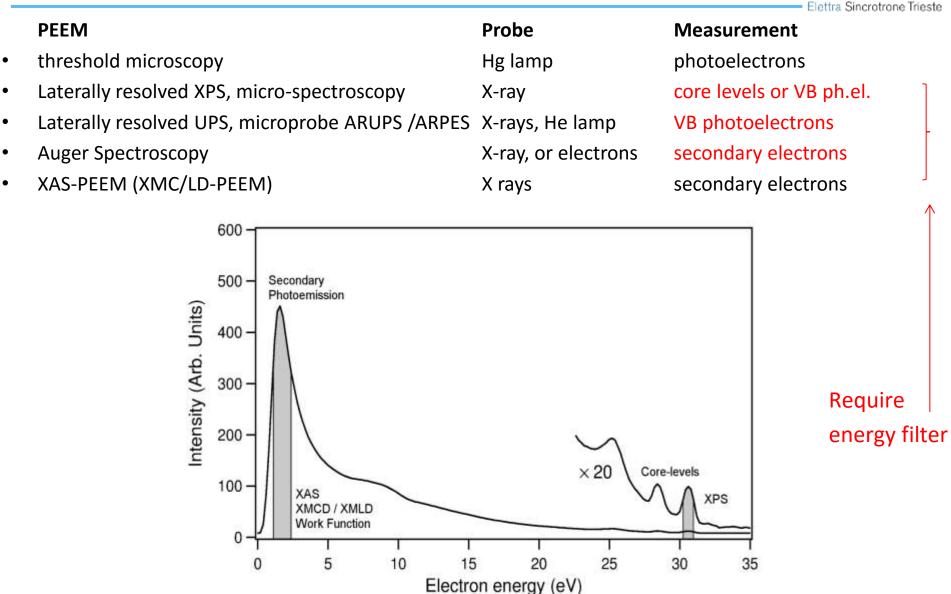




PEEM is a full-field technique. The microscope images a restricted portion of the specimen area illuminated by x-ray beam. Photoemitted electrons are collected at the same time by the optics setup, which produces a magnified image of the surface. The key element of the microscope is the objective lens,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

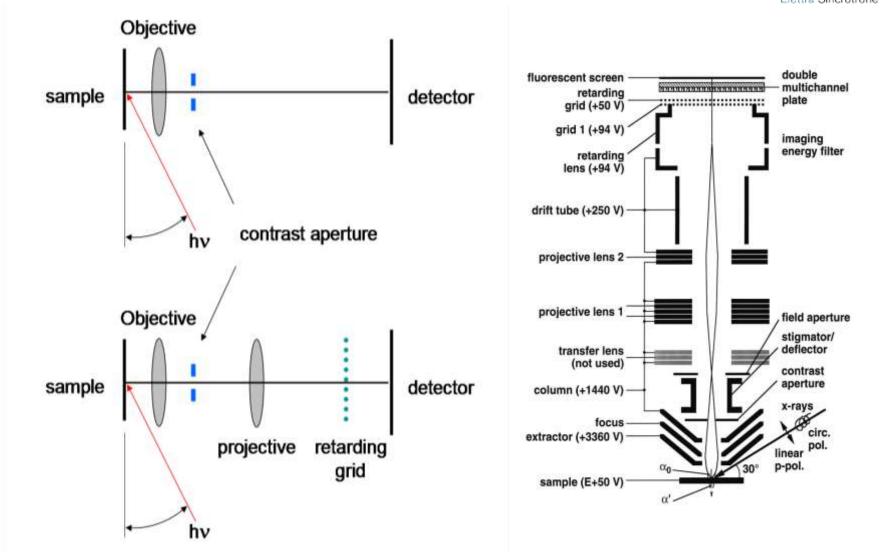
## The different types of PEEM measurements





## **Simple PEEM instruments**

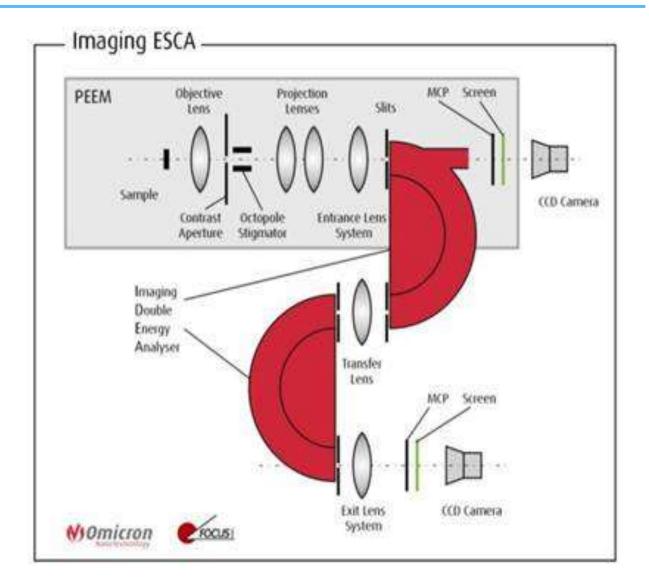
Elettra Sincrotrone Trieste



#### **PEEM instrments with energy filter: NanoESCA**

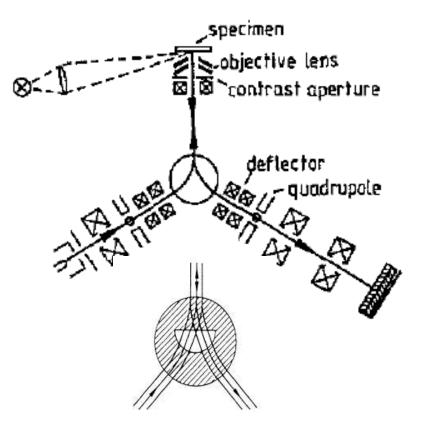


Elettra Sincrotrone Trieste



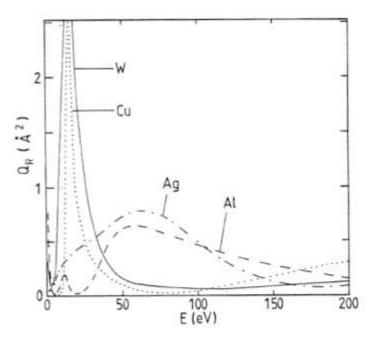
## Low energy electron microscopy (LEEM)





- LEEM probes surfaces with low energy electrons, using the elastically backscattered beam for imaging.
- Direct imaging and diffraction imaging modes

#### **Backscattering cross section**



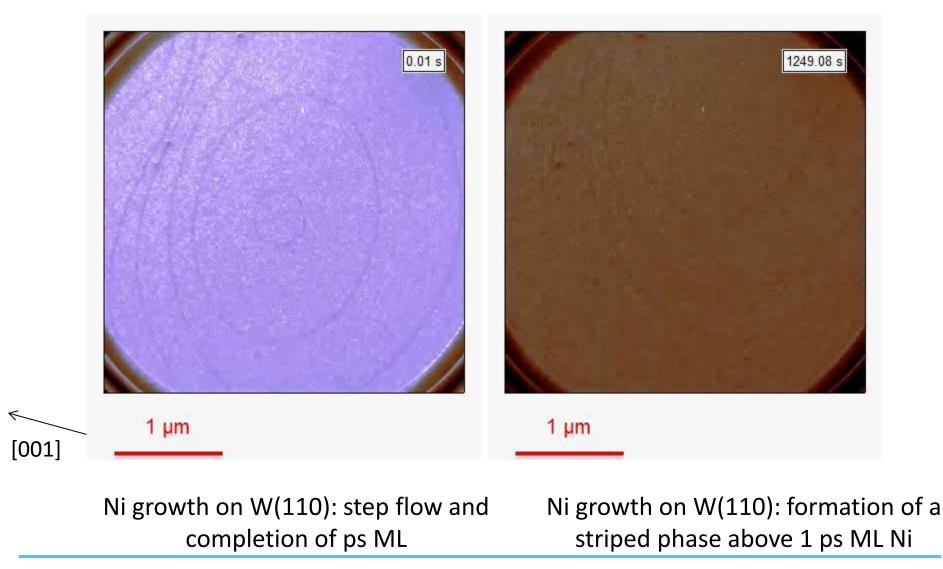
E. Bauer, Rep. Prog. Phys. 57 (1994) 895-938.

- High structure sensitivity
- High surface sensitivity
- Video rate: reconstructions, growth, step dynamics, self-organization

#### Imaging dynamic processes in LEEM



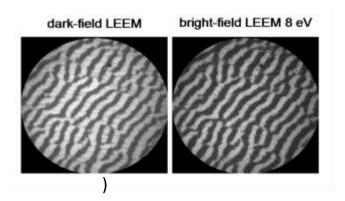
#### 540 < T < 750 C



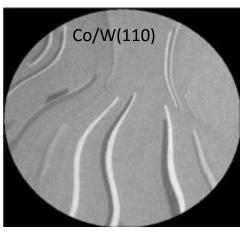


Different contrast mechanisms are available for strucutre characterization

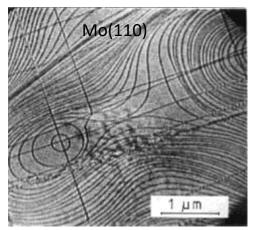
#### SURFACE STRUCTURE



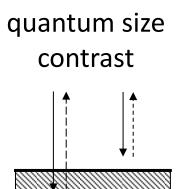
#### FILM THICKNESS



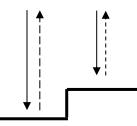
#### STEP MORPHOLOGY



diffraction contrast sample (h,j) (0,0) objective aperture

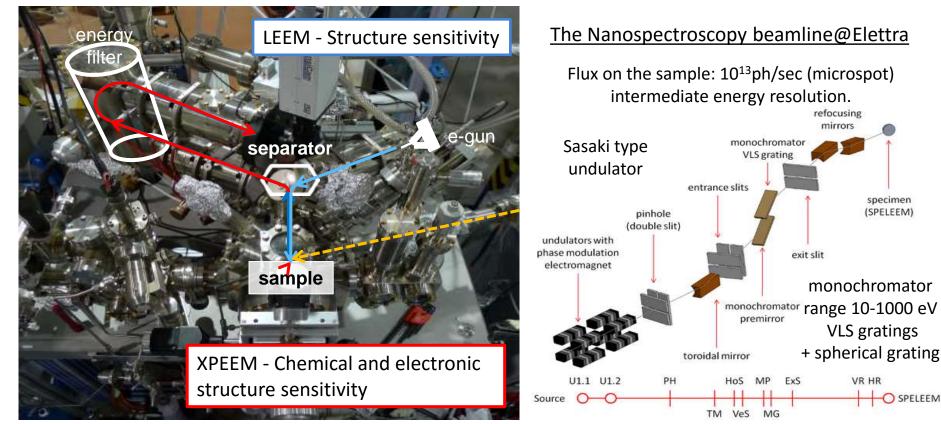


geometric phase contrast



#### **SPELEEM = LEEM + PEEM**



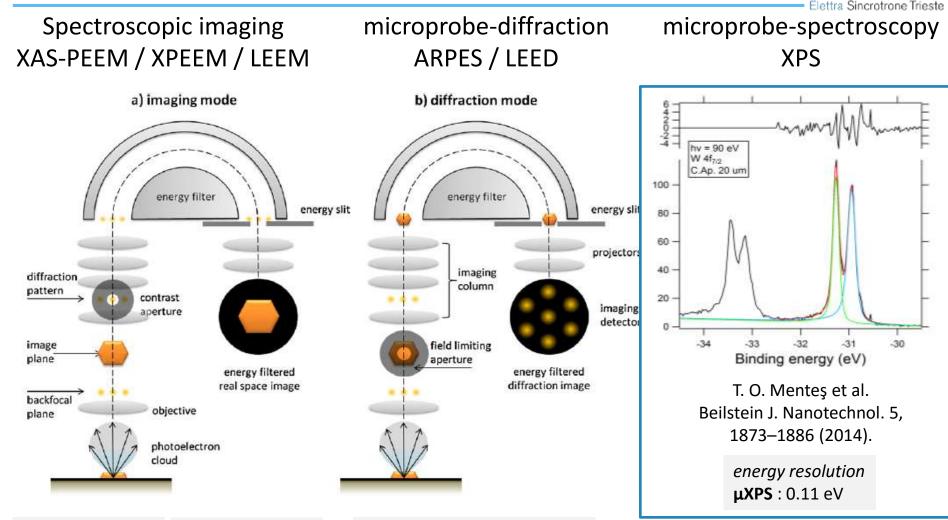


#### **Applications**:

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**



spatial resolution LEEM : 10 nm XPEEM : 25 nm *energy resolution* **XPEEM** : 0.3 eV

Limited: to 2 microns in dia. angular resolution transfer width: 0.01 Å<sup>-1</sup>



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

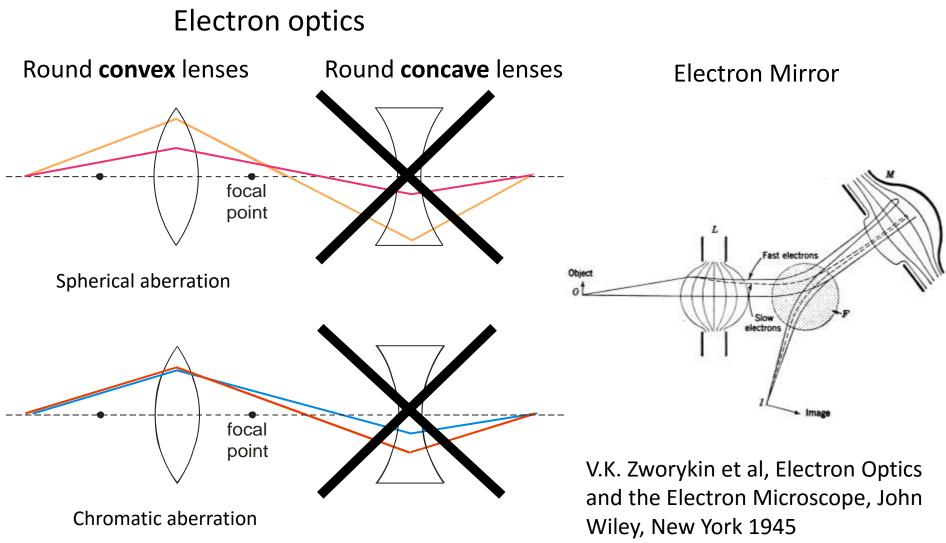
**Key feature**: <u>multi-method</u> instrument to the study of surfaces and interfaces offering *imaging* and *diffraction* techniques.

Probe:low energy e- (0-500 eV)  $\leftrightarrow$  structure sensitivity<br/>soft X-rays (50-1000 eV)  $\leftrightarrow$  chemical state, magnetic<br/>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

correction

 $\alpha^{5}$ 

 $\Delta E \alpha^2$ 

 $+ \Delta E^2 \alpha$ 

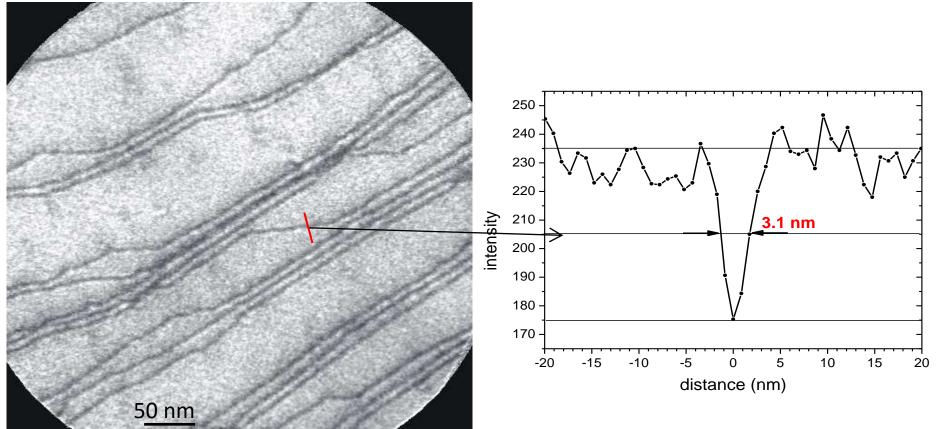
 $1/\alpha$ 

Simultaneous improvement in Transmission and Resolution!!! transmission 1E-4 1E-3 0.01 0.1 α **Resolution limit** without resolution limit d (nm) correction corrected  $\alpha^3 + \dots$ Spherical Chromatic  $\Delta E \alpha + \dots$ Diffraction  $1/\alpha$ 1 TITI 10 100 1000 acceptance angle  $\alpha$  (mrad)

> 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)

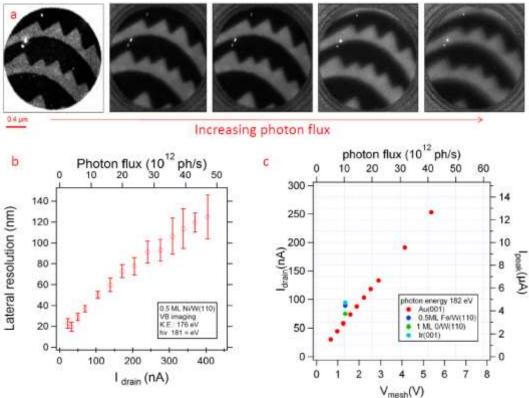


Courtesy of Th. Schmidt et al.; 5th Int. Conf. LEEM/PEEM, Himeji, 15.-19. Oct. 2006

## Lateral resolution limitations: space charge

Elettra Sincrotrone Trieste

#### 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 10<sup>13</sup> ph./s on sample =
  - = 20000 ph./bunch
- Total photoionization yield: about 2% photons result in a photoemission event
- I peak ≈ 400 e<sup>-</sup>/ 42 ps

#### ≈ 1.5µA vs 20 nA (LEEM)

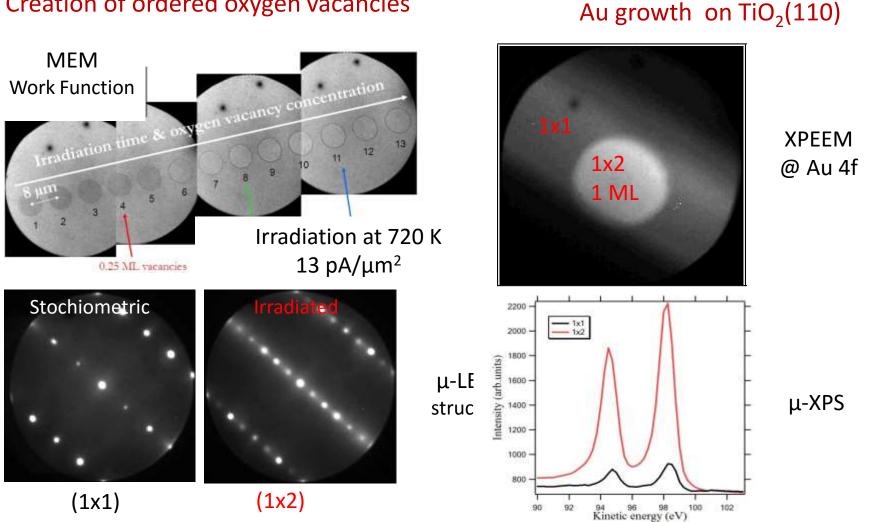
- 13 pA/ $\mu$ m<sup>2</sup> versus 20 nA/ $\mu$ m<sup>2</sup>
- 1. Image blur can be observed with SR but only under very high photon fluxes. Must Keep into account in beamline design. No space charge in LEEM
- 2. Both the lateral and energy resolution are strongly degraded by Boersch and Loeffler effects occurring in the first part of optical path.

## **Chemical imaging applications**

#### PEEM, LEEM, SPELEEM, AC-PEEM/LEEM

### Au/TiO<sub>2</sub>(110): controlling growth by vacancies





#### Creation of ordered oxygen vacancies

4/19/2016

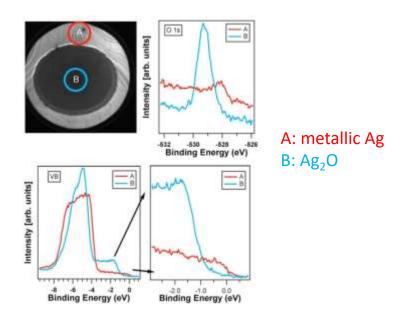
#### Surface Oxygen on Ag : *e-beam "Lithography"*



Full oxidation of Ag using NO<sub>2</sub> does not occur:

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

Instead: e-beam (60 eV) stimulated desorption of NO<sub>ad</sub> works at RT!

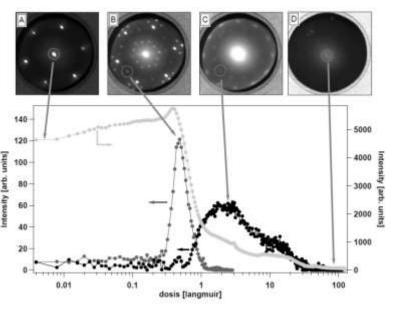


S. Günther et al., App. Phys. Lett. 93, 233117 (2008).

Low T: NO<sub>ad</sub> stays, prevents oxidation.

High T: NO<sub>ad</sub> desorbs, but Ag<sub>2</sub>O unstable.

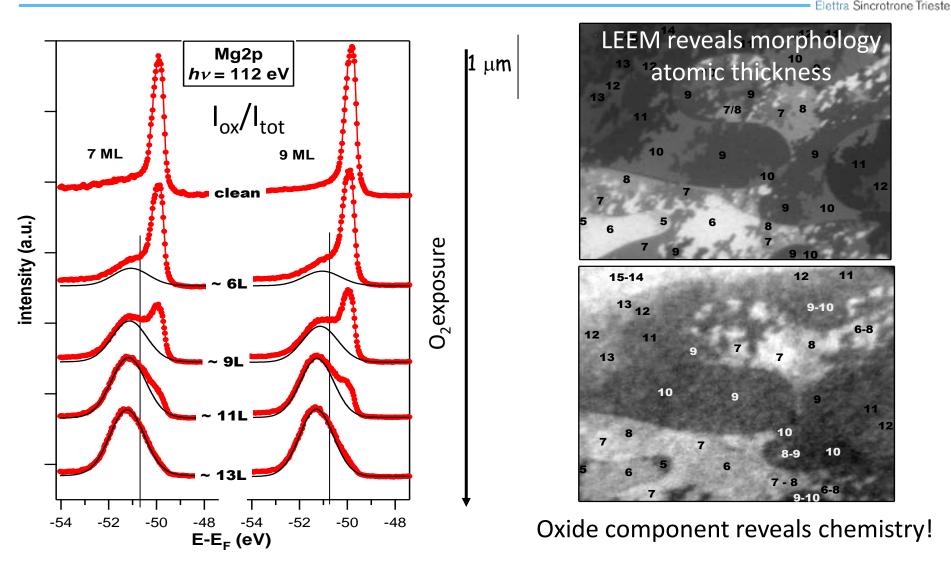
LEED reveals path towards Ag<sub>2</sub>O under e-beam



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

## **Thickness dependent reactivity in Mg**

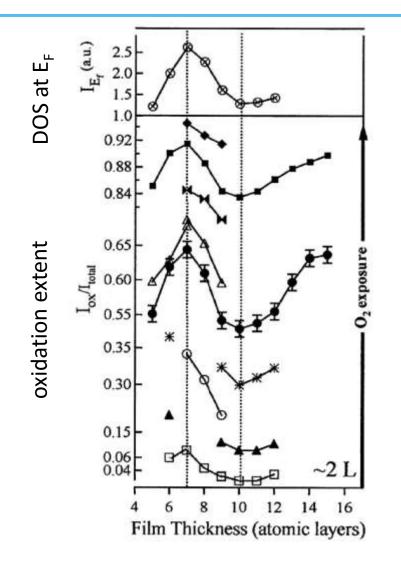




L. Aballe et al., Phys. Rev. Lett. 93, 196103 (2004)

## **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<sub>F</sub>
- XPEEM is a powerful technique for correlating chemistry and electronic structure information

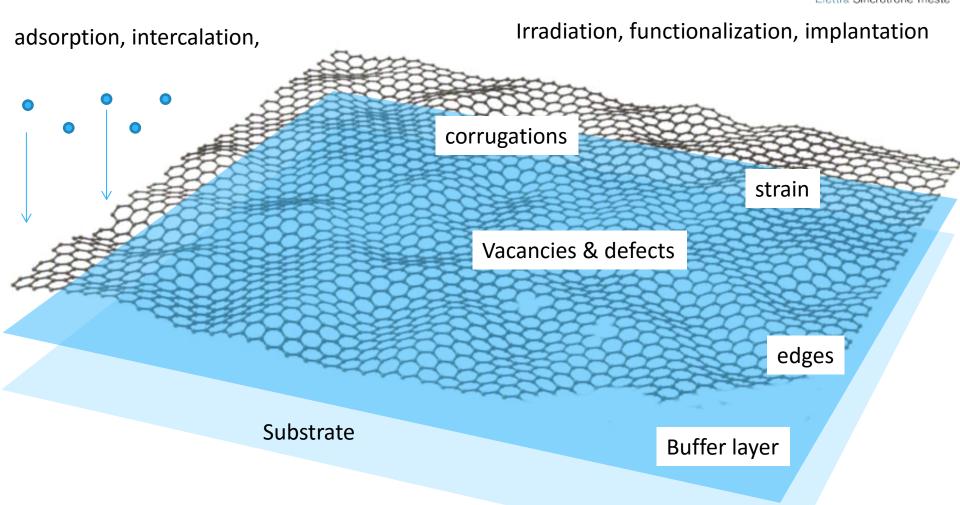
SIGNIFICANCE OF THE EXPERIMENTS

- ✓ 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)

#### **XPEEM studies of the metal-graphene interface**

Elettra Sincrotrone Trieste

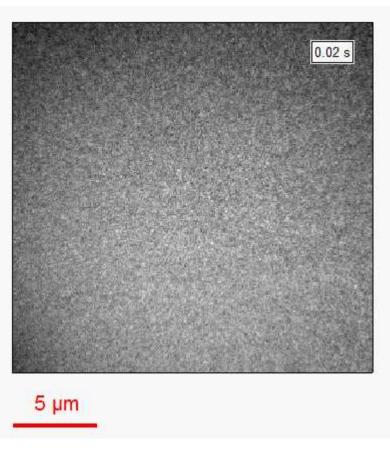


- Understand and control the fundamental interactions occurring at the interface
- verify the properties (crystal quality, stoichiometry, electronic structure) at the mesoscale!

#### High temperatrue graphene growth on Ir(100)

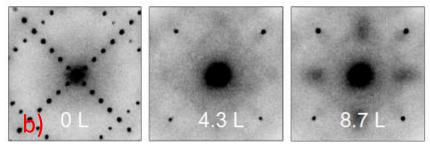


Elettra Sincrotrone Trieste

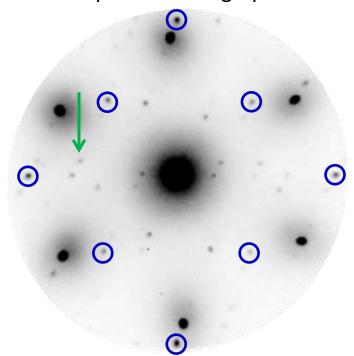


#### LEEM imaging

#### microprobe-LEED: Ir



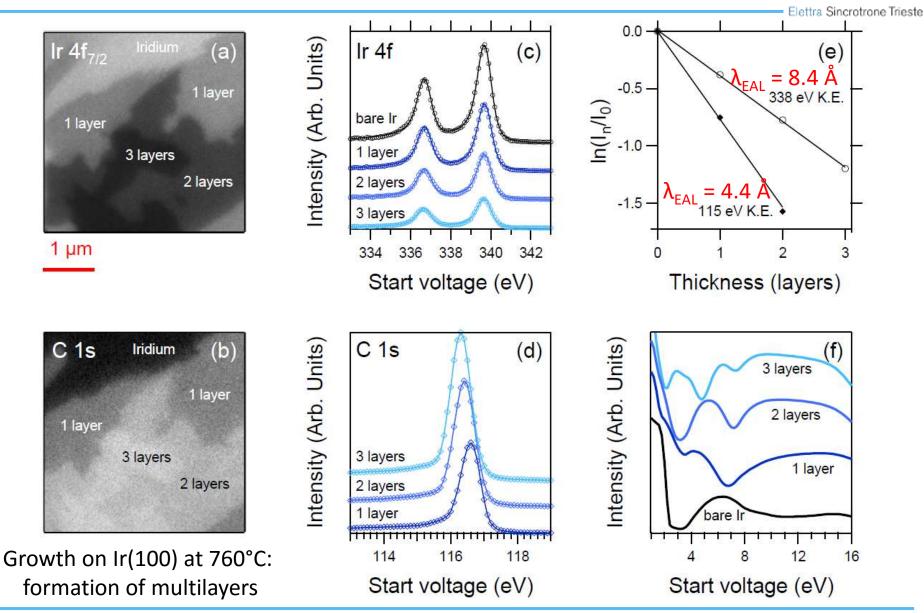
#### microprobe-LEED: graphene



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

## **Graphene thickness determination**

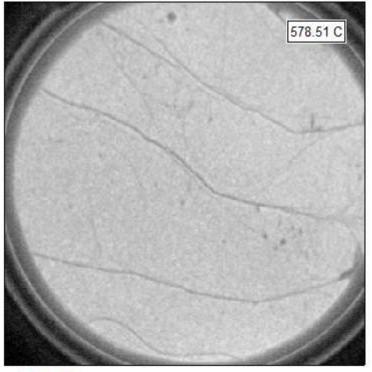




## **Reversible graphene phase transformation**

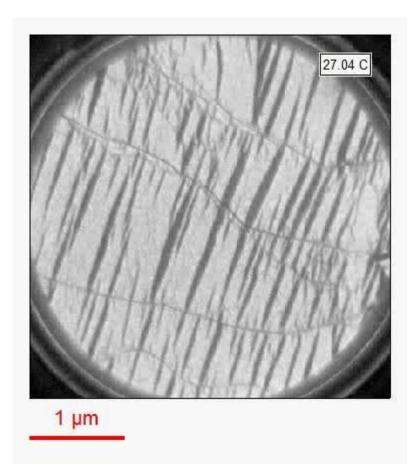


# Upon cooling a new graphene phase nucleates (dark stripes)



1 µm

# The stripes disappear upon annealing to high temperature.

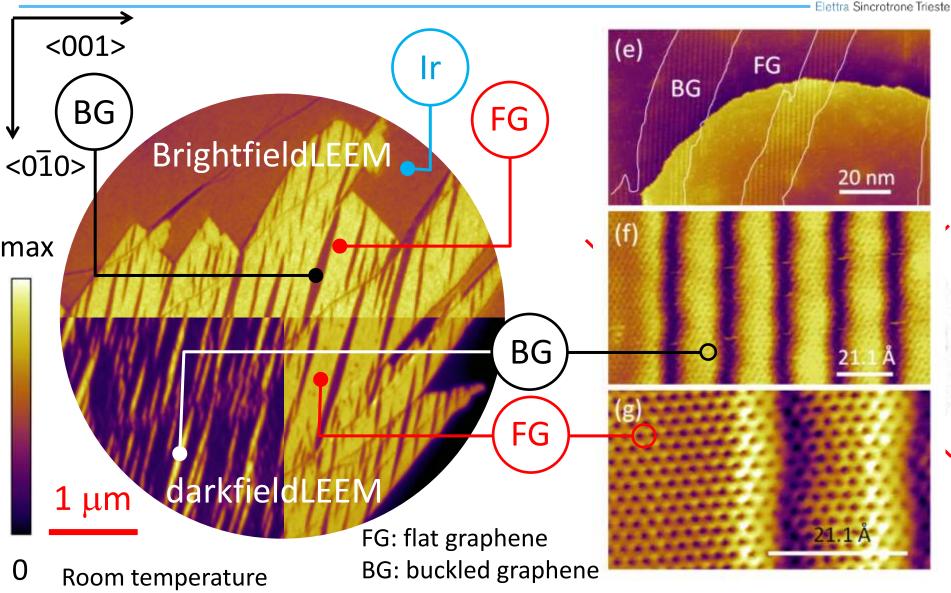


#### LEEM, Fov 4 $\mu$ m, S.V. 13 eV

19/04/2016

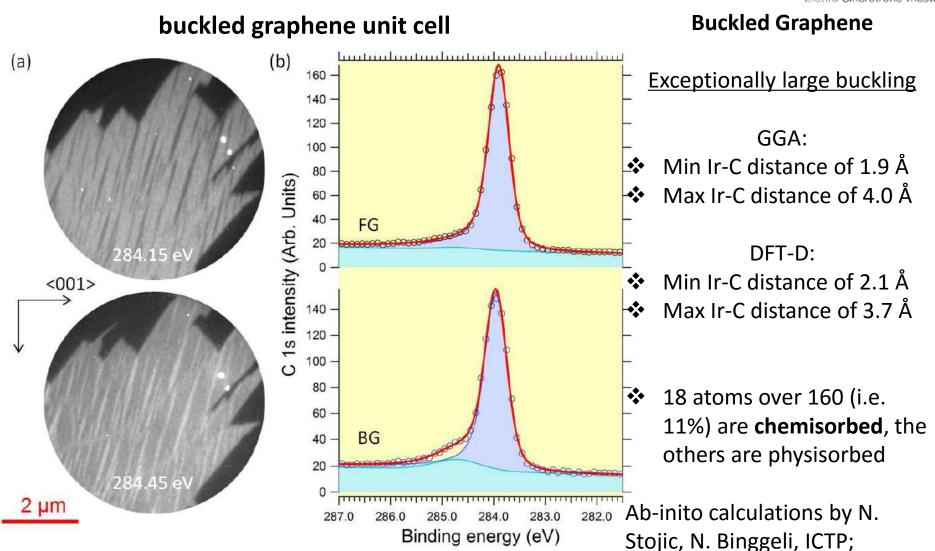
## Graphene/Ir(100): strucutre of FG and BG





## Buckled graphene unit cell by ab-initio

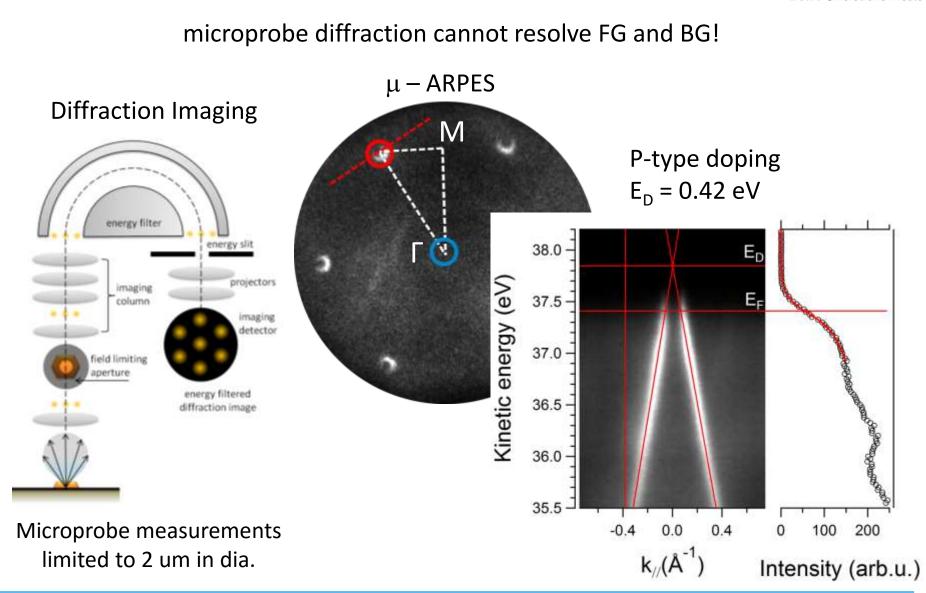




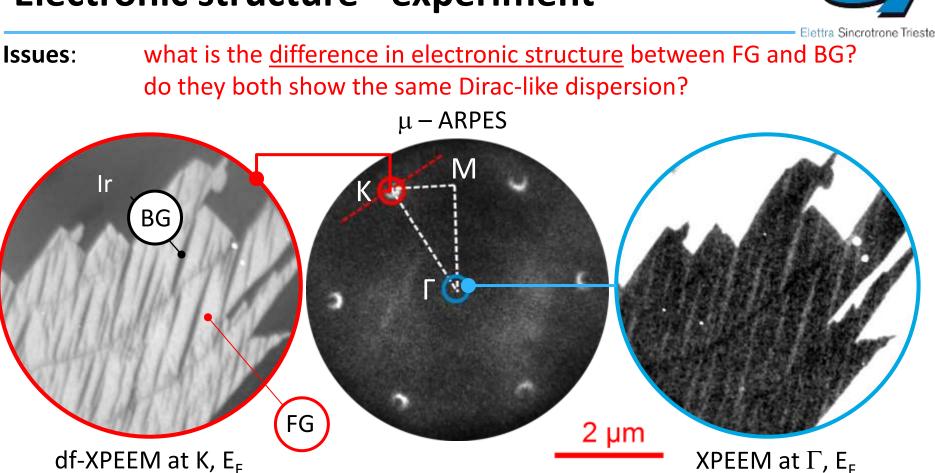
Buckled graphene shows regular one-dimensional ripples with periodicity of 2.1nm.

## **Electronic structure: graphene doping**





## **Electronic structure - experiment**

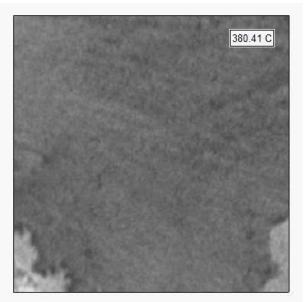


- the mission from the π band at K allows quantifying local DOS of FG and BG phases.
- DF-PEEM images at E<sub>F</sub> clearly indicate that **only FG** shows high DOS at K.
- ↔ much reduced DOS and contrast inversion at  $\Gamma \rightarrow$  BG hybridization and metallicity.
- Microprobe-ARPES data are thus representative of the FG phase, not the BG one!

#### Carbides formation/dissolution under rot. Graphene/Ni(111)

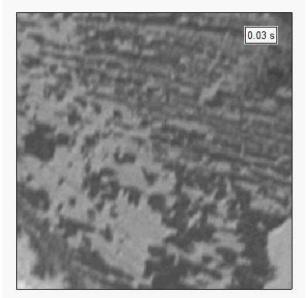


#### 1: carbide nucleation



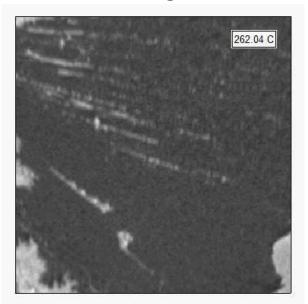
1 µm

2: carbide growth



1 µm

3: carbide growth



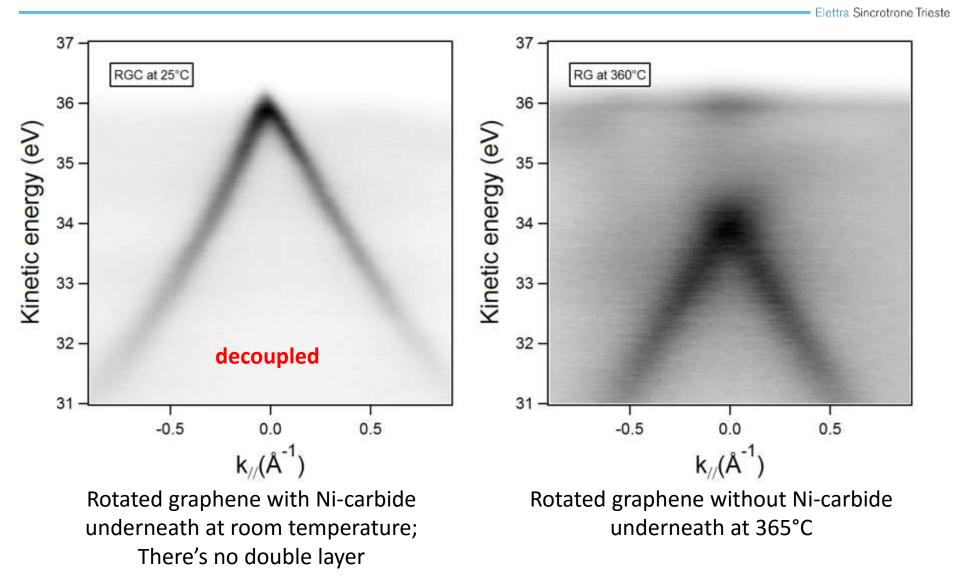
1 µm

The Ni-carbide nucleates under rotated graphene, T < 340°C Patera et al., ACS Nano 7, 7901 (2013) A uniform layer of Nicarbide is formed below graphene in about two hours

The carbide is dissolved into the bulk at about 360°C. The process is repeatable!

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

### Electronic structure is by $\mu$ -ARPES



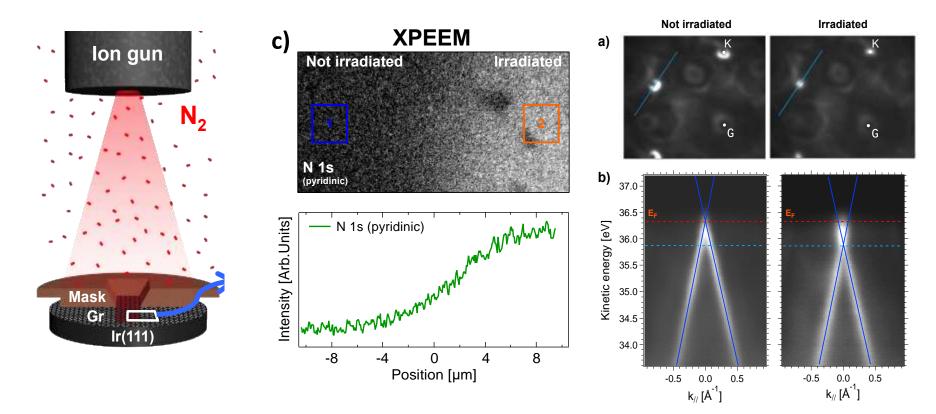
#### Ion irradiation of graphene:

- Substitutional implantation:
  - Local doping by low energy ion irradiation
  - Ar nanobubbles ripening under graphene
    - Strain engineering! [C. Lee et al., Science 321, 385 (2008)]
  - Anvil cells (high pressure) [Xuan Lim et al., Nat. Comm. 4, 1556 (2013)
  - Exhotic magnetic properties [N. Levy et al. Science 329, 544 (2010)]

#### 2D heterojunction by low energy N<sub>2</sub><sup>+</sup> irradiation



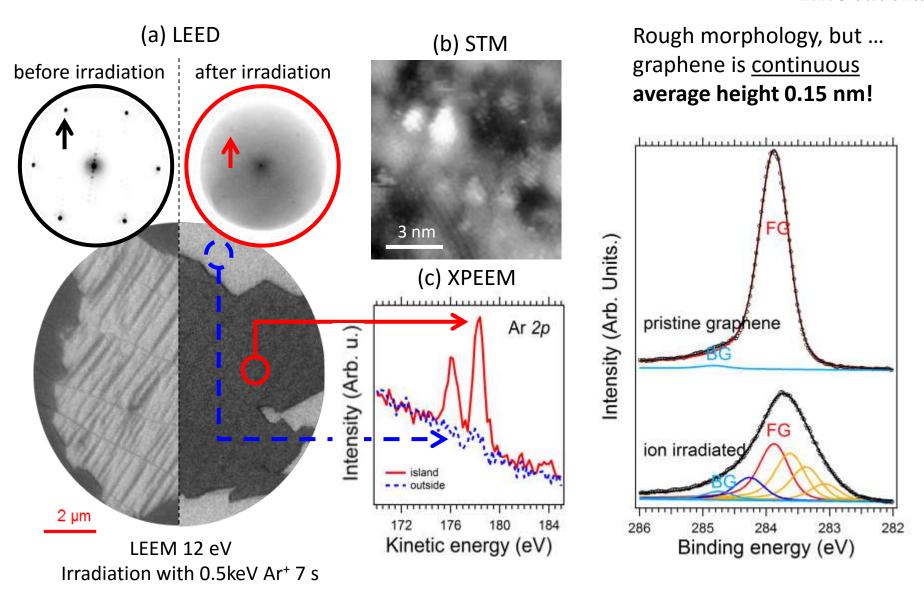
Elettra Sincrotrone Trieste



- Small damage to graphene lattice;
- Thermal stability: graphitic: stable above 700°C; pyridinic stable up to 400°C;
- Boundary also stable upon annealing (no migration/loss)
- $\clubsuit$  Negative doping  $\rightarrow$  formation of doping patterns

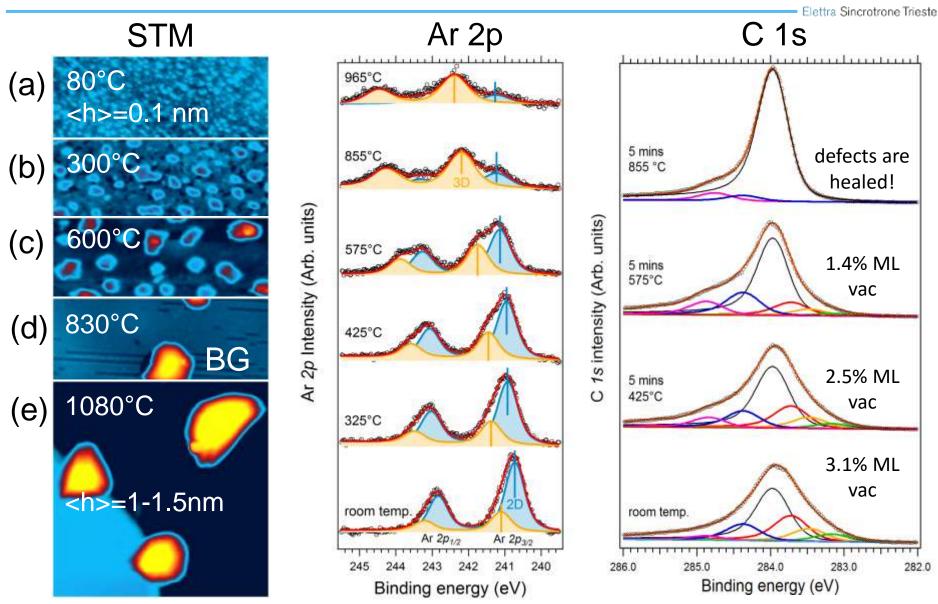
## Morphology of Ar<sup>+</sup> irradiated graphene/Ir(100)





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



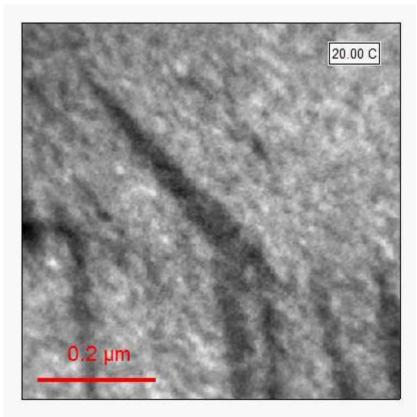


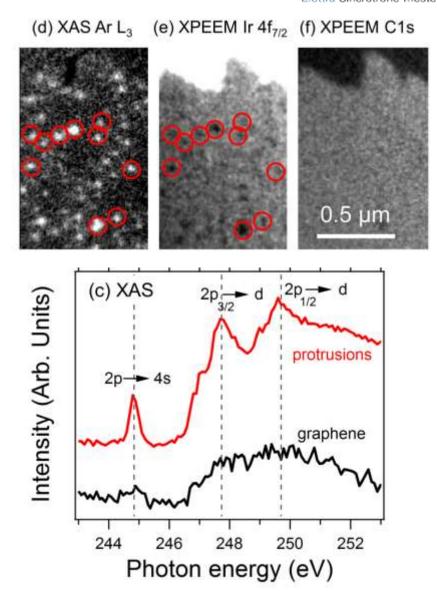
<sup>19/04/20</sup>If radiation with 0.1keV Ar<sup>+</sup> 150 s and 5 min annealing; The XPS data were acquired at RT

## **LEEM & XPEEM formation of Ar nanobubbles**



LEEM movie 12 eV



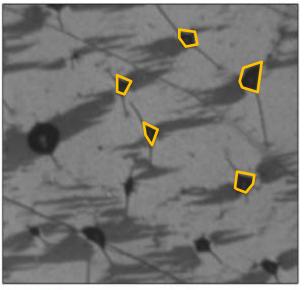


# NB formation for g/Ne/Ir(100)



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

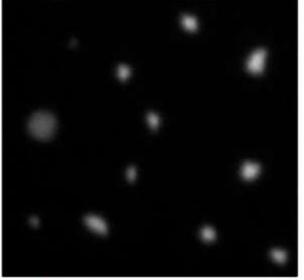


0.5 µm

0.5 µm

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

XPEEM imaging Ne 2p



- elemental composition below graphene!
- XPS from individual particles

0.5 µm

• Shift to high BE for large clusters

# Magnetic imaging

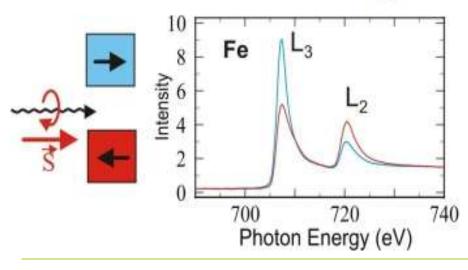
## XMCD and XMLD PEEM

1. 1.40

# Magnetic imaging: XMCD



### **Circular Dichroism - Ferromagnets**

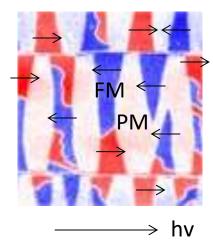


X-ray magnetic circular dichroism (XMCD) is the dependence of <u>x-ray absorption</u> on the relative orientation of the local magnetization and the polarization vector of the circularly polarized light

✓ Element sensitive technique

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

### MnAs/GaAs

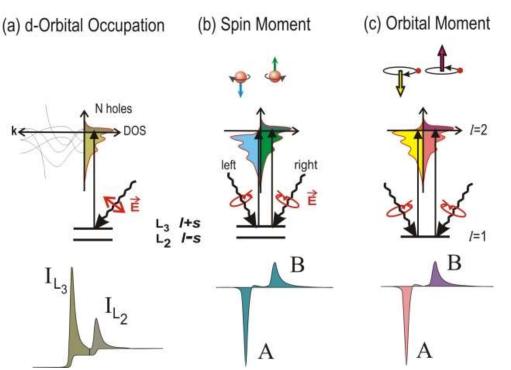


### Magnetic domain imaging

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





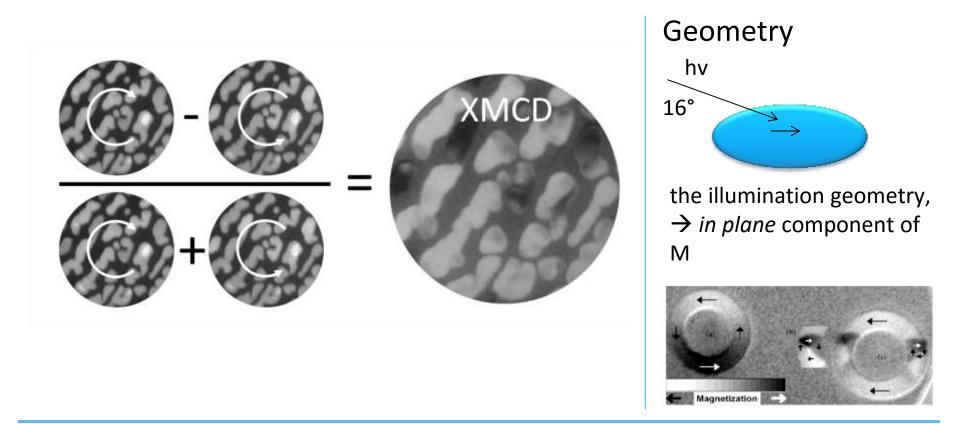
- We **PROBE** 3d elements by exciting 2p into unfilled 3d states
- •Dominant channel:  $2p \rightarrow 3d$
- •White line intensity of the L3 and L2 resonances with the number N of empty d states (holes).

- 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<sub>3/2</sub> (L<sub>3</sub>) and p<sub>1/2</sub> (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).

# XMCD image algebra

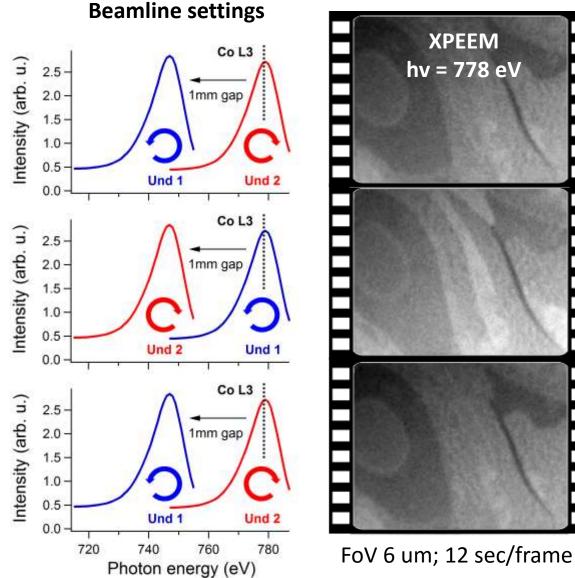


The size of the dichroism effect scales like cos $\theta$ , where  $\theta$  is the angle between the photon spin and the magnetization direction. Hence the maximum dichroism effect (typically 20%) is observed if the photon spin and the magnetization directions are parallel and anti-parallel. Sum rules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

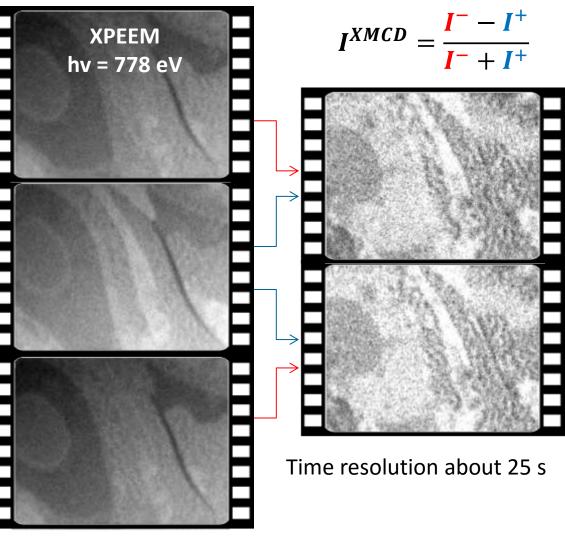


# **XMCD** movies

Elettra Sincrotrone Trieste



19/04/2016

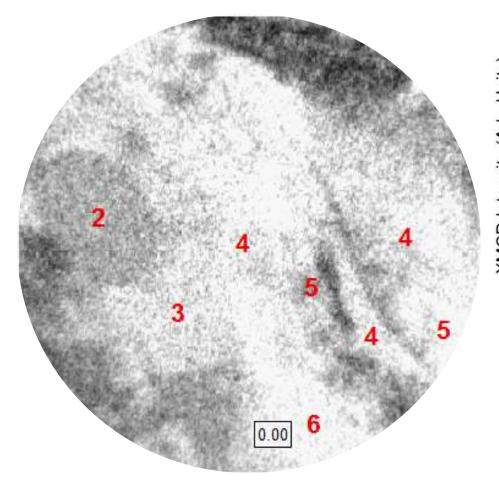


### Event Name, Name Surname; otherwise leave blank and use for references

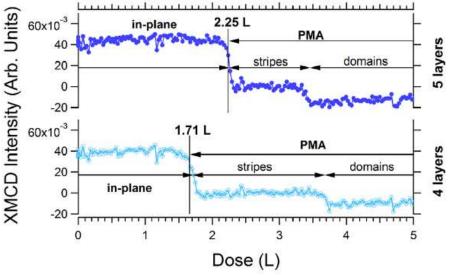
## XMCD movie of a spin reorientation transition



### XMCD movie @ Co L<sub>3</sub> edge in P<sub>CO</sub>=2·10<sup>-9</sup> mbar; frame acquisition 12 s, FoV 6 $\mu$ m



### 4 atomic layers Co more reactive than 5 & 3



Different layers have different period Unstable domain structure Period changes with CO dose

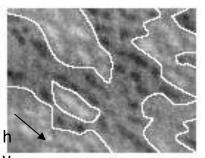
# **Examples of XMCD-PEEM applications**



## MAGNETIC STATE using XMCD &

XMLD

### Co nanodots on Si-Ge



Co - L<sub>3</sub> edge

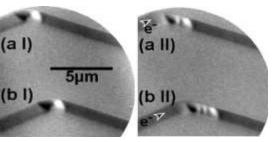
A. Mulders et al,Phys. Rev. B 71,214422 (2005).

structures

patterned

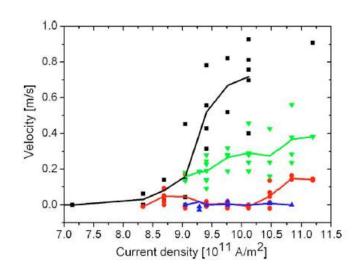
1.6 μm

pulse injection



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

# domain wall motion induced by spin currents



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

# Magnetic imaging basics: XMLD



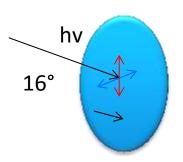
#### Linear Dichroism - Antiferromagnets In the presence of spin order the spin-orbit coupling leads to preferential charge order aFeO. relative to the spin direction, which is exploited to determine the spin axis in ntensit antiferromagnetic systems. ✓ Element sensitive technique ✓ Secondary imaging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

<u>Absorption intensity at resonance</u>  $I(\vartheta, \theta, T) = a + b(3\cos^2\vartheta - 1)\langle Q_{77}\rangle$ 

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

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

 $2^{nd}$  term determines XMLD effect;  $\Theta$  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

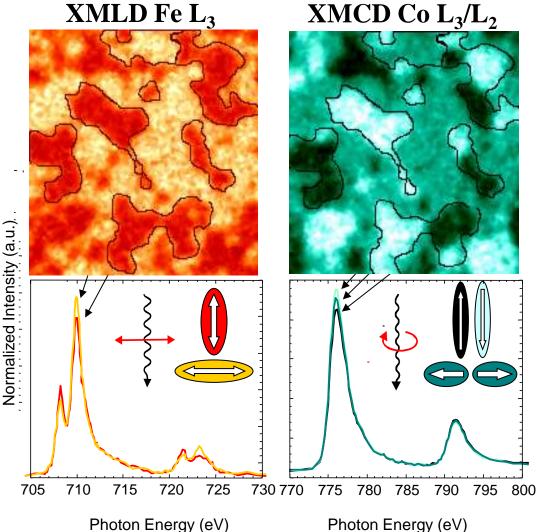
### Direct observation of the alignment of ferromagnetic spins by antiferromagnetic spins

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\*

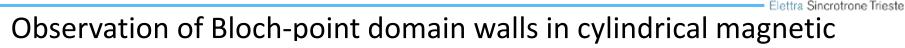
Nature, 405 (2000), 767.

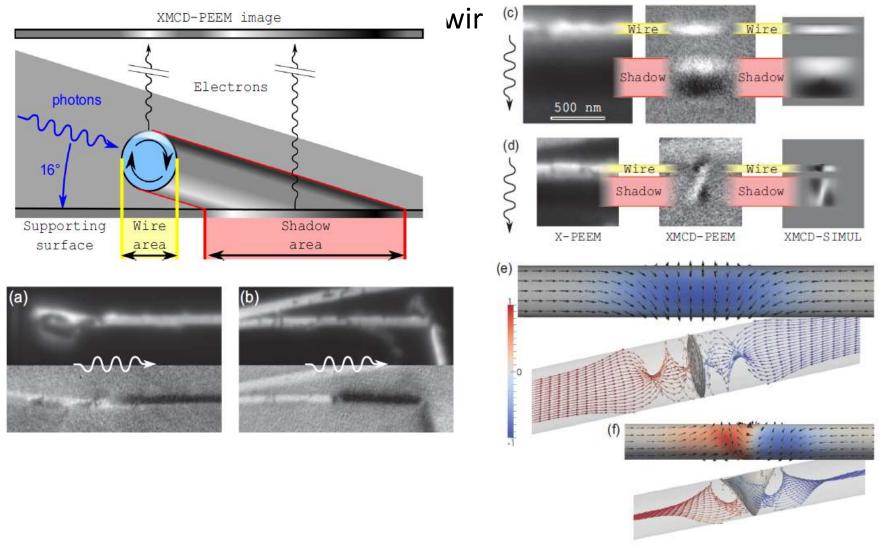
ferromagnet/antiferromagnet Co/LaFeO3 bilayer interface exchange coupling between the two materials

### LaFeO<sub>3</sub> layer **XMLD Fe L<sub>3</sub>**



# DW imaging in magnetic wires



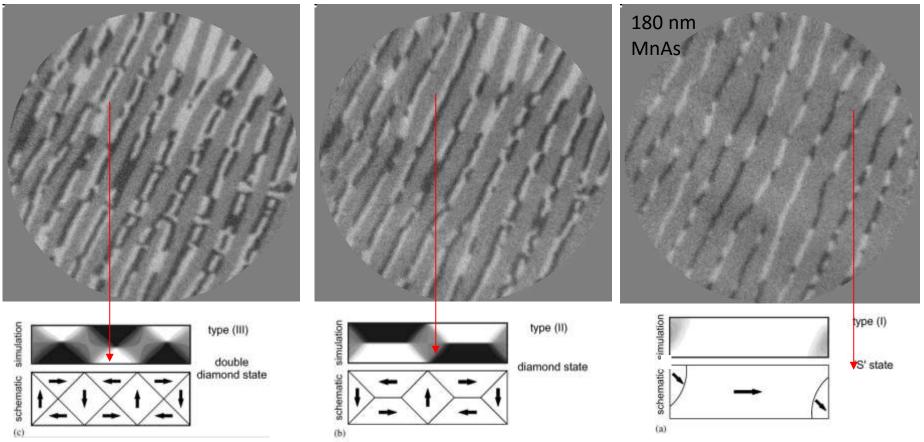


S. Da Col et al., Phys. Rev. B89, 180405(R) (2014)

## 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

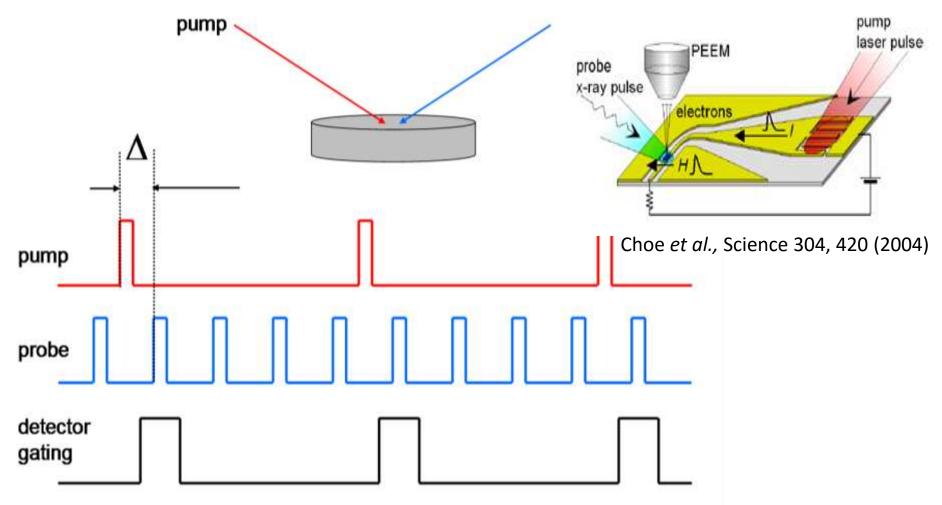
### **TR-PEEM** methods

1. 1.11

## Time-resolved PEEM: the stroboscopic approach

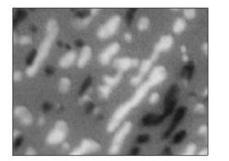


Stroboscopic experiments combine high lateral resolution of PEEM with high time resolution, taking advantage of pulsed nature of synchrotron radiation

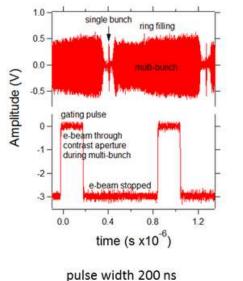


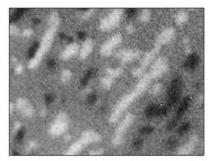
## **Detector gating for time-resolved XMCD PEEM**



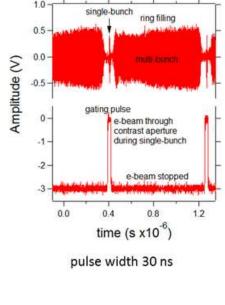


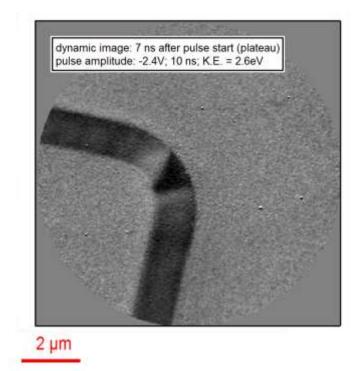
Multi-bunch image 32 images per helicity Image exposure 4 s Acquisition time: 5':18"





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

## **Magnetic excitations in LFC structures**



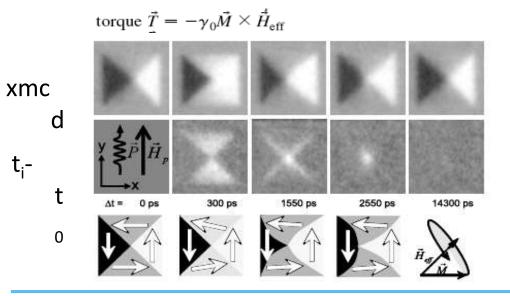
### Quantitative Analysis of Magnetic Excitations in Landau Flux-Closure Structures Using Synchrotron-Radiation Microscopy

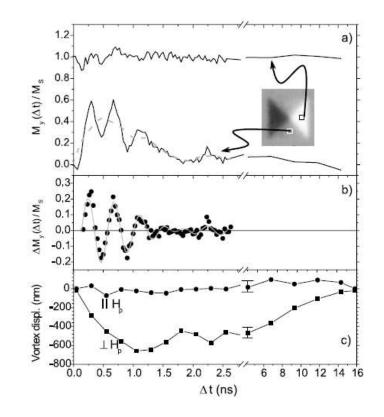
J. Raabe,<sup>1,\*</sup> C. Quitmann,<sup>1</sup> C. H. Back,<sup>2</sup> F. Nolting,<sup>1</sup> S. Johnson,<sup>1</sup> and C. Buehler<sup>1</sup>

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  $\vec{H}_{\text{eff}}$ . The second term describes the relaxation back into the equilibrium state using the dimensionless damping parameter  $\alpha$ .





### 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 3<sup>rd</sup> 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).