DESY Summer Student Lectures

Solid State Physics and Nanoscience @ DESY

Andreas Stierle DESY NanoLab Centre for X-Ray and Nano Science CXNS Deutsches Elektronen Synchrotron (DESY) and University of Hamburg, Physics Department





Solid State Physics and Nanoscience @ DESY

Scattering with coherent X-rays (G. Grübel)

X-ray Physics and Nanoscience (A. Stierle)

X-ray Crystallography and Imaging (E. Weckert, I. Vartaniants)

Magnetism and Coherent Phenomena

(R. Röhlsberger)

X-ray Nanoscience and X-ray Optics (C. Schroer)

Soft X-ray Spectroscopy of Quantum Materials (Kai Rossnagel)

High-Resolution X-Ray Analytics & Physics of Materials (Patrick Huber)

Complex liquids and glasses Ultrafast magnetization dynamics

Catalytic Reactions on Nanomaterials Nanoscale Phenomena **Oxide Surfaces and Interfaces**

Coherent diffraction from individual semiconductor nanostructures

Magnetism and magnetic dynamics Fundamentals of resonant light-matter interaction at x-ray energies

X-ray imaging: ptychography Hard X-ray microscopy X-Ray tomography

Spectroscopy of electron dynamics at surfaces and interfaces

https://photon-science.desy.de/research/research_teams/index_eng.html

Correlation structure / composition with functionality Watch structure formation: In-situ / operando x-ray diffraction experiments









DESY Site – Campus Bahrenfeld Andreas Stierle | Solid State Physics and Nanoscience | 4.8. 2022| Page 3



DESY NanoLab Mission

Providing on-site methods for nanoscience complementary to DESY photon science techniques at PETRA III(IV) and FLASH

- nano characterization techniques (atomic scale structure, chemistry and magnetism)
- nano structuring techniques
- nano synthesis techniques

















Overview DESY NanoLab Techniques

Spectroscopy & Growth (H. Noei)

- UHV sample preparation
 chambers with LEED / AES
- XPS, FT-IR, STM

X-ray diffraction (V. Vonk)

- Reflectometer
- Six circle diffractometer
- Sample Environments

Microscopy & Structuring (T. Keller)

- AFM, STM, optical
- SEM + FIB + EBSD + EDX (tomography)
- Lithography (CHyN)
- Scanning Auger Microscope (2021)

Magnetic Characterization (C. Strohm)

- Physical properties measurement system
- Kerr Microscope

Electrochemistry (L. Jacobse)

- Dedicated chemistry lab
- Potentiostats
- Induction oven / gases
- Solid / liquid FT-IR (FAU Erlangen)





Introduction

Today's nanotechnology is based on surfaces and interfaces and materials in reduced dimensions

Semiconductor integrated circuits Topological materials, graphene, vdW materials

Magnetic sensors (GMR, TMR) Quantum computers

Heterogeneous Catalysis Energy harvesting and conversion Energy storage











The Nanoworld





 $1 \text{ nm} = 10^{-9} \text{ m}$ is with respect to 1 m as







In the "Dwarf" World the Rules are Changed



bulk material

Nanoparticle

Physical und chemical properties of materials are changed in reduced dimensions



In the "Dwarf" World the Rules are Changed

Example: Melting of Gold Nanoparticles



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In the "Dwarf" World the Rules are Changed



Atoms with reduced coordination:

- 1: on facets
- 2: at edges
- 3: at corners

Relation surface / volume no of atoms

$$\frac{N_o}{N_V} = \frac{3a}{D}$$

Typical Values for spherical particles

 $D = 3 \text{ nm}: N_s/N_v = 0.25$

 $D = 2 \text{ nm}: N_S/N_V = 0.375$

$$D = 1 \text{ nm}: N_S/N_V = 0.75$$

Reduced dimensions: quantum mechanical effects box potential for electrons



Real Catalysts: The Nanoworld Comes Into Play

"real" catalyst

Pd SiO₂ 50 nm

A. K. Datye, Topics in Catalysis 13, 131 (2000)

Only surface atoms are "active"



Goal: smaller particles stabilized on an oxide support

Surface area comparison for 1 kg Pd (expensive !)

Sphere diameter	No of spheres	Surface area
54 mm	1	0.01 m ²
1 mm	159337	0.5 m ²
1 μm	1.58x10 ¹⁴	498 m ²
3 nm	5.85x10 ²¹	1.67x10 ⁵ m ²

23 soccer fields !



Introduction

Characterization on the atomic scale desired

- x-rays: λ=0.1 0.01 nm
- non-destructive probe
- sample charging not important (oxides !)
- in-situ measurements (high T, high gas pressure, UHV, electro-magnetic fields, in contact with liquids, .) or during their formation (growth)
- probing statistical information, single objects with nanobeams
- allow studying functionality and microscopic structure of the surface / interface / nano-object in the same experiment !





X-Ray Diffraction Techniques for Structural Characterization in Reduced Dimensions

- X-ray reflectivity
- Grazing incidence x-ray diffraction
- (GI) small angle scattering
- Surface x-ray diffraction
- Nanoparticle structural analysis
- Coherent diffraction imaging
- (Extended X-ray absorption Fine Structure (EXAFS) (see talk from Christian Schroer)



X-rays: electro-magnetic waves

Fulfill boundary conditions at interfaces

Maxwell's equations are applied Snell's law:



 $\cos \alpha_i = n \cos \alpha_t$

For x-rays: refractive index n<1 in matter

Consequence: total external reflection occurs !



$$n = 1 - \delta - i\beta$$

$$\delta = \frac{\lambda^2 r_e \rho_e}{2\pi}$$

$$\beta = \frac{\lambda \mu}{4\pi}$$

refractive index

 $\begin{array}{l} r_e: \mbox{classical electron radius} \\ (2.82x10^{-15}\mbox{ m}) \\ \rho_e: \mbox{total electron density} \\ \mu: \mbox{linear mass absorption} \\ \mbox{coefficient} \end{array}$

$$\alpha_c = \sqrt{2\delta} = \lambda \sqrt{\frac{r_e \rho_e}{2\pi}}$$

critical angle for total external reflection



Quantitative description: Fresnel's formulas $(sin(\alpha) < <1)$

$$T_F = \left| \frac{2\alpha_i}{\alpha_i + \alpha_t} \right|^2 \quad R_F = \left| \frac{\alpha_i - \alpha_t}{\alpha_i + \alpha_t} \right|^2$$

Transmitted (reflected) amplitudes





More complicated case: layered structures



Generalized reflectivity: Parratt formalism

L. G. Parratt, Phys. Rev. 95, 359 (1954)



Example: reflectivity of a Cr film before and after oxidation





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Influence of roughness:





Height fluctuations at an interface

- σ: root mean square roughness
 from specular reflectivity
- ξ: characteristic length to find same height on the surface from off-specular scattering, Qx,y≠0, not discussed here



Example: reflectivity from a Si block







X-Ray Reflectivity from VUV mirrors











L. Tamam, et. al., J. Phys. Chem. Lett.1 (2010) 1041



High Energy X-Ray Reflectivity: deeply buried interface



V. Vonk et al., Langmuir 33, 814 (2017).



Pt-Rh Nanoparticles under CO Oxidation Conditions



X-Ray Reflectivity Results





Reaction Induced Sintering Mechanism



Non-classical Ostwald ripening:



U. Hejral, P. Müller, O. Balmes, D. Pontoni, A. Stierle Nature Communications 7, 10964 (2016).

Coverage Determination for Nanoparticles

PdRh nanoparticles on MgAl₂O₄







Height: 6 nm Coverage: 36%

P. Müller, et al., Phys. Chem. Chem. Phys. 16, 13866 (2014)



Summary x-ray reflectivity:

Obtainable Parameters (with sub-nm resolution)

- layer thicknesses
- statistical information on interfacial roughness
- layer density profiles
- limited to stratified media, flat substrate
- independent of crystalline state



Remember: total external reflection induces evanescent wave traveling parallel to the surface.



q': scattering vector inside material



Example: evanescent Bragg scattering



evanescent Bragg scattering law

H. Dosch, Springer Tracts in Mod. Phys. (Springer), Berlin, 1992, p. 126.



Example: surface melting of Al(110)



H. Dosch, Physica B 198 78 (1994)



Example: oxidation of Nb(110)



101911 (2008)



Summary grazing incidence x-ray diffraction:

Obtainable Parameters (with nm resolution)

 all structural parameters and chemical composition with variable information depth, e.g. lattice and order parameters, crystallinity, mosaicity, interstitials,...



Grazing incidence small angle scattering (GISAXS)



D. Franz, A. Stierle, et al, Phys. Rev. B 93, 045426 (2016)



Grazing incidence small angle scattering (GISAXS)



J. Oleander, et al., Phys. Rev. B B 76, 075409 (2007) D. Carbone et al., J. Phys. Cond. Matt. 21 224007 (2009)



Summary GISAXS

Obtainable Parameters (with nm resolution)

- average nanoparticle / nanostructure size, distance, shape
- lateral morphological information
- independent of crystalline state










Influence of roughness:



 β model: occupation of layer n: β^n



Experimental realization:





Oxidation of CoGa(100): Previous Results from LEED and STM



LEED: (2x1) superstructure

Oxidation at 2x10⁻⁷ mbar, 1260 s at 720 K



320 x 320 Å²

R. Franchy, Surf. Sci. Rep. 38 (2000) 195-294







Fit: red line (DFT model: green line)



Starting point: monoclinic Ga₂O₃

Oxidation conditions: 500°C , p(O₂)= 5x10⁻⁷ mbar

A. Vlad, et al., Phys. Rev. B 81, 115402 (2010)







2D diffraction pattern of growing Ga oxide layer

A. Stierle, et al., New Journal of Physics 9, 331 (2007)



In-situ Studies of Chemically Active Nanomaterials

Method: In-situ high energy x-ray reciprocal space mapping (E=85 keV)



P07 PETRAIII



In-situ Studies of Chemically Active Nanomaterials

X-ray movie of Rh(111) surface during CO Oxidation (P07, PETRA III)

2D Detector 40 cm x 40 cm

RA Kollaboration E. Lundgren, J. Gustaton, U. Hejral, A. Stierle



Summary surface x-ray diffraction

fit: kinematical diffraction theory

parameters:

overlayer structure+registry, thickness,

relaxations, roughness

Structure of ultrasmall nanoparticles

near surface composition

thermal vibrations

In-situ observation of surface processes





Surface Sensitive X-ray Diffraction

Surface Sensitive X-Ray Diffraction Methods

Andreas Stierle, University of Siegen, Germany; Elias Vlieg, Radboud University Nijmegen, The Netherlands

1 Introduction

Since the first demonstration in 1912 [1], X-ray diffraction (XRD) has become the dominant technique to determine the bulk structure of crystals. In fact, many crystals are grown with the sole purpose of determining the structure of their building blocks. This is especially relevant for

A. Stierle, E. Vlieg, in *Modern Diffraction Methods*, edited by E. J. Mittemeijer and U. Welzel, Wiley VHC Weinheim, 2012.



Nanoparticle Structural Analysis



q= $4\pi/\lambda$ sin (θ): scattering vector





epitaxial film diffraction

- Surface information lost for powder diffraction
- Small particles produce wide peaks in reciprocal space



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Interference function for single crystalline film

Our Approach: Epitaxial Nanoparticles

Model system: epitaxial nanoparticles supported by oxide single crystals



Pd, Rh, Pt/MgO(100) PtRh, PdRh /MgAl₂O₄(100) cube-on-cube epitaxy

FEI Nova Nano, E= 1 keV HRTEM, ARM 1.2 MeV

Sample preparation by MBE growth at T=400°C Size distribution: 30-60%



Shape Change of Pd and Rh Nanoparticles on MgO(100)

High resolution reciprocal space mapping

Experimental set-up at BM32, ESRF



UHV surface x-ray diffraction and GISAXS chamber

G. Renaud, et al. Nuc. Inst. Meth. B 95, 422 (1995)





Shape Change of Pd and Rh Nanoparticles on MgO(100)

Particle Size & Shape Variation:



N. Kasper, et al., Surf. Sci. 600, 2860 (2006)

Shape Change of Rh Nanoparticles on MgO(100)

Clean Rh nanoparticles SXRD reciprocal space maps at T=600 K





Fit Results: NP=31±1, NT=20±1, NB=5±1 NE=3±1

average diameter: 8.3 nm average height: 4.8 nm





Shape Change of Rh Nanoparticles on MgO(100)

Oxidation at T=600 K, p(O₂)=3x10⁻⁵ mbar





Shape Change of Rh Nanoparticles on MgO(100)



Ex-Situ Cross-Section TEM Characterization



HR-TEM MPI IS (MPI-MF) Stuttgart

N.Y. Jin-Phillipp, et al., Surf. Sci. 603, 2551 (2009)



Pd on MgO(100): Overview Mesh Scan



P. Nolte, et al., Nano Letters 11, 4505 (2011)



Pd Nanoparticles on MgO(100) SXRD Reciprocal Space Maps at T=570 K





Pd Nanoparticles on MgO(100) Reversibility of Shape Change at 570 K

Linescans at L=0.8



n i

PtRh Nanoparticles under Operando CO Oxidation

PHYSICAL REVIEW LETTERS 120, 126101 (2018)

Identification of a Catalytically Highly Active Surface Phase for CO Oxidation over PtRh Nanoparticles under Operando Reaction Conditions

U. Hejral,^{1,2,3,†} D. Franz,^{1,2} S. Volkov,^{1,2} S. Francoual,¹ J. Strempfer,¹ and A. Stierle^{1,2,*} ¹Deutsches Elektronen-Synchrotron DESY. 22603 Hamburg. Germany



Time Resolved High Energy X-ray Diffraction (80 keV)



Rh nanoparticle oxidation





Atomic Structure of Ultra-small Nanoparticles (< 2 nm)

Nanoparticles: Pt, Ir, Pd(Ir), Fe(Ir), Au(Ir), Rh Support: graphene



Ultrasmall Particles Supported by Graphene

Ir nanoparticle superlattice enhanced x-ray diffraction



Features of map:

- (0 1) CTR,(0 1) SR
- (0 2 0) Bragg-Peak
- superstructure rods
- oscillation of rods (crystalline NP, well defined height)



(0KL) map – clean sample

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Ultrasmall Particles Supported by Graphene



Ultrasmall Particles Supported by Graphene

- SXRD together with graphene moire templated growth is a possible route of metal cluster structure analysis
- Gas adsorption experiments (suitable metals, reactions)
- Alloy nanoparticles in confinement

Magnetism



D. Franz, S. Runte, C. Busse, S. Schumacher, T. Gerber, T. Michely, M. Mantilla, V. Kilic, J. Zegenhagen, A. Stierle, Phys. Rev. Lett. 110, 065503 (2013). S. Billinge, Nature 495, 453 (2013) PhD work Dirk Franz

Pair Distribution Function Analysis



Cleveland, et al. Phys. Rev. Lett. 79, 1873 (1997)

Single crystal XRD from 3D nanoparticle lattices



Thiol stabilized Au nanoparticles grown into a single crystal

Jadzinsky, et al. Science 318, 430 (2007)



Nanoparticle Structural Analysis

Summary nanoparticle structural analysis

- Atomic structure of nanoparticles: size, shape
- Model systems needed to address nanoparticle surface
- Analysis complicated by broad Bragg reflections, random particle orientation and size distribution
- Protein crystallography approach allows to get atomic scale information
- EXAFS: local structure, chemically sensitive





Single particle diffraction with coherent x-ray beam

M. A. Pfeifer, et al., Nature 442, 63 (2006).



M. Abuin, et al., ACS Applied Nanomaterials 2,8, 4818 (2019)







Structure and strain





Coherent Diffraction X-Ray Imaging under Reaction Conditions



Y. Y. Kim, T. F. Keller, T. J. Gonvalves, M. Abuin, H, Runge, L. Gelisio, J. Carnis, V. Vonk, P. N. Plessow, I. A. Vartaniants, A. Stierle, Science Advances, Vol 7, 40 (2021)
Coherent Diffraction X-Ray Imaging under Reaction Conditions



