Probing hidden films with neutron reflectometry
contributors

experiments
Ursula Bengaard Hansen
Wolfgang Kreuzpaintner
Saumya Mukherjee
Birgit Wiedemann
Wolfgang Gruber
Harald Schmidt
Florian Strauß
Erwin Hüger
Artur Glavic
Bujar Jerliu
Sina Mayr
...

simulations
Emanouela Rantsiou
Tobias Panzner
Panos Korelis
Uwe Filges

ideas / discussions
Marité Cardenas
Rob Dalgliesh
Frédéric Ott
Phil Bentley
Bob Cubitt
Peter Böni
Uwe Stuhr
...

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• reflectometry
  general introduction
  the neutron

• neutron reflectometry
  the next generation

• experimental examples
  → Li diffusion in Si
  → in-situ film growth
  → strain-induced magnetism
  → in-operando Li battery

• the future
  → projects for Amor
  → instrumentation
  → conceptual challenges
features of **neutron reflectometry**

- depth-profile of chemical composition
- depth-profile of magnetic induction
- near surfaces: $\rightarrow 0.5 \, \mu m$
- flat samples: $\rightarrow 30 \, \text{Å}$
- sample sizes: $3 \, \text{mm}^2 \rightarrow 30 \, \text{cm}^2$
- measurement time: $1 \, \text{min} \rightarrow 1 \, \text{day}$
- high penetration depth: $\rightarrow 10 \, \text{cm}$

alternative / complementary to: XR, resonant x-ray techniques, SIMS, TEM, . . .
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**analogy to visible light**

*flat* surfaces partly reflect light → picture of the boot

some media also transmit light → ground below the water

parallel interfaces → colourful soap bubbles

\[
q_z = 2|k_0| \sin \omega
\]

|k| = \(2\pi/\lambda\)

\(n = \) index of refraction
reflected intensity of a multilayer

\[ R(q_z) \approx |\mathcal{F}[\rho(z)]_{q_z}|^2 \]

⇒ all phase information is lost
⇒ one way road:
⇒ calculation of \( R(q_z) \) using a model
  and
  comparison to measured curve(s)

real effects
to be taken into account:
– non-sharp interfaces
– inhomogeneous layers
– illumination of the sample
– resolution of the set-up \( \Delta \omega, \Delta \lambda \)
Simulated reflectivity of a surface

![Graph showing log10 [R(ω)] vs. ω/deg]

- Critical edge ⇒ $n_{\text{substrate}}$

- Snell’s law: $\frac{\cos \omega_i}{\cos \omega_{i+1}} = \frac{n_{i+1}}{n_i}$

- $\Rightarrow \cos \omega_c = n_1$
simulated reflectivity of a thin layer

\[ \log_{10}[R(\omega)] \]

amplitude \( \Rightarrow \Delta n_{\text{layer,substrate}} \)

minimum \( \Rightarrow d_{\text{layer}} \)
simulated reflectivity of a thick layer

\[ \log_{10}[R(\omega)] \]

amplitude \( \Rightarrow \Delta n_{\text{layer, substrate}} \)

minima \( \Rightarrow d_{\text{layer}} \)
simulated reflectivity of a periodic multilayer

\[ \log_{10}[R(\omega)] \]

maxima \( \Rightarrow d_{\text{bilayer}} \)

amplitudes \( \Rightarrow \Delta n_{\text{layers}} \)
\( \Rightarrow \Delta d_{\text{layers}} \)

minima \( \Rightarrow d_{\text{film}} \)
... with neutrons

- building unit of atomic nuclei
- \( \approx \) mass of a proton
  \( \Rightarrow \) collision with nuclei
- no charge
  \( \Rightarrow \) no interaction with electrons / charges
- spin 1/2
  \( \Rightarrow \) magnetic moment
  \( \Rightarrow \) interaction with magnetic fields
- De-Broglie wavelength \( \approx 1 \ldots 20\,\text{Å} \)
  \( \Rightarrow \) atomic / crystallographic dimensions
  \( \Rightarrow \) energy of phonons
- interaction with nuclei
  \( \Rightarrow random \) sensitivity across the PSE
  \( \Rightarrow \) isotope-sensitive
some numbers

probed depth \( 100 \, \text{nm} \rightarrow 1 \, \mu\text{m} \) (less for absorbers)

depth resolution \( 0.2 \, \text{nm} \rightarrow 400 \, \text{nm} \) strongly model dependent

\( t \) and \( \delta \) might be correlated

lateral coherence \( 1 \, \mu\text{m} \rightarrow 100 \, \mu\text{m} \) averaging laterally over all microstructures

penetration depth \( \rightarrow 10 \, \text{cm} \)
reflectometry

equipment
neutron reflectometer
e.g. Morpheus at SINQ

\[ q_z = \frac{4\pi}{\lambda} \sin \omega \]

angle-dispersive set-up
**equipment**

sample environment
e.g. cooling with a *closed cycle refrigerator* \(8 \text{ K} < T < 300 \text{ K}\)

application of an external magnetic field with *Helmholtz coils* \(-1000 \text{ Oe} < H < 1000 \text{ Oe}\)

*tilt- and translation stages* for alignment

*ω rotation stage*

*sample within sample-holder*
data acquisition

typical quantities:

angular range $0^\circ \ldots 10^\circ$

$\lambda$ range $3\,\text{Å} \ldots 15\,\text{Å}$

measurement time $10\,\text{min} \ldots 12\,\text{h}$

example:

Fe/Si multilayer on glass
polarised neutrons
1h per spin state
reflectometry

data acquisition and interpretation

reflectivity vs. $\omega / ^\circ$

reflectivity vs. $\omega / ^\circ$

reflectivity vs. $\omega / ^\circ$
data acquisition and interpretation

Fe/Si multilayer

interdiffusion leads to 5 Å thin magnetically dead Fe : Si layers
reflectometry

**typical scientific questions**

adsorption at ...

solid/water

growth mechanisms

air/water

diffusion

interface magnetism

exchange bias

... interfaces

multiferroics

spintronics
liquid/gas interface

compression of self-organising polyglycerol-ester films

model-system for foams used for stabilising food products e.g. yogurt

trough to investigate membranes at the liquid/air interface
reflectometry

liquid/gas interface
compression of self-organising polyglycerol-ester films

H$_2$O substituted by D$_2$O

⇒ strong contrast between solvent and film (essentially [CH$_2$]$_n$)
⇒ *high* critical edge

![Graph showing reflectivity against qz (Å$^{-1}$)]

C. Curschellas, IACIS, Sendai, 2012
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focusing reflectometry

specular reflectometry

\[ q_z = 4\pi \frac{\sin \theta}{\lambda} \]
focusing reflectometry

specular reflectometry

\[ k \propto \frac{1}{\lambda} \]

\[ \theta, \lambda \]

\[ \log_{10} R(q_z) \]

angle-dispersive
focusing reflectometry

specular reflectometry

angle-dispersive

energy-dispersive

$log_{10} R(q_z)$
focusing reflectometry

specular reflectometry

angle-dispersive

energy-dispersive

$k \propto 1/\lambda$

$\theta \theta$

$log(4\pi\sin(y\pi/180)/x)/log(10)$
focusing reflectometry

$\lambda$-dispersion by time-of-flight

$t \propto \lambda$

$\theta$

$x$

$\lambda$

$\theta$
focusing reflectometry

ω-dispersion by focusing
focusing reflectometry

the *Selene* guide

point-to-point focusing

with

2 subsequent elliptical reflectors

for

horizontal and vertical direction

*Selene* picture: ceiling painting in the Ny Carlsberg Glyptotek, København
focusing reflectometry

the Selene guide

light-field-diaphragm
control of footprint

uncorrected, inverted image

aperture defines divergence

image sample
focusing reflectometry

the *Selene* guide demonstrator on Amor@PSI

- total length $= 4\text{ m}$
- max spot size $\approx 2 \times 2\text{ mm}^2$
- divergence $\approx 1.8^\circ \times 1.8^\circ$
focusing reflectometry

the *Selene* guide demonstrator on Amor@PSI

- slit = virtual source
- polariser
- 1\textsuperscript{st} segment
- spin flipper
- 2\textsuperscript{nd} segment
- sample stage
- flight tube
- detector
- optical bench, 8 m long
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Li transport through thin silicon films

*in-situ* study in cooperation with E. Hüger, F. Strauß and H. Schmidt, TU Clausthal

technological motivation:

- Si layers can be used in Li batteries to prevent oxidation of the electrodes
- Si films can be used as electrodes in Li batteries

⇒ How fast does Li diffuse through thin amorphous Si films?
⇒ What is the solubility of Li in Si?
⇒ What is the influence of the Si:O:Li interface layer?

Li transport | the sample

multilayer structure using the different densities of $^6\text{Li}$ and $^7\text{Li}$
Li transport | experimental set-up

*in-situ* furnace

- $T \in [25^\circ C, 500^\circ C]$
- $\dot{T} = 50 \text{ Ks}^{-1}$ for heating
- $\dot{T} = 12 \text{ Ks}^{-1}$ for cooling

here: $T = 240^\circ C$

time-structure

- interval
  - (measurements at RT in between annealing periods)
- continuous measurement
Li transport | measurements

$^6\text{LiNbO}_3/\text{Si}/^7\text{LiNbO}_3/\text{Si}$ multilayer counting time 1.5 min

$\log_{10} I(\lambda, \theta)$

raw data

$\theta$ deg

$\lambda/\text{Å}$
Li transport | measurements & data reduction

raw data

$\theta \text{ deg}$

reference

$\rho \text{ deg}$

$R(\lambda, \theta)$

$\theta \text{ deg}$

$\lambda / \text{Å}$

$6\text{LiNbO}_3/\text{Si}/7\text{LiNbO}_3/\text{Si} \text{ multilayer}$

counting time 1.5 min

$\log_{10} I(\lambda, \theta)$

$m = 5 \text{ supermirror}$

quotient
Li transport | measurements & data reduction

$^6\text{LiNbO}_3/\text{Si}^/^7\text{LiNbO}_3/\text{Si}$ multilayer

counting time 1.5 min
Li transport | reflectivity curves

measurements on a $^6\text{Li}_3\text{NbO}_4/\text{Si}/^7\text{Li}_3\text{NbO}_4/\text{Si}$ multilayer

annealing at $T = 240^\circ C$

(a) ml is chemically stable

(b) Li contrast is vanishing

t = $0 \rightarrow 3$ min

18 $\rightarrow$ 24 min

558 $\rightarrow$ 570 min
quasi in-situ reflectometry during sample growth
sample: Si/Cu(50 nm)/Fe(0...20 layers)

by B. Wiedemann, S. Mayr, W. Kreuzpaintner, TU Munich
quasi in-situ reflectometry during sample growth

sample: Si/Cu(50 nm)/Fe(0…20 layers)

\[
\log_{10} R_{\uparrow\downarrow}(q_z)
\]

\[
\log_{10} R_{\uparrow\uparrow}(q_z)
\]

\[
\frac{R_{\uparrow\downarrow} - R_{\downarrow\downarrow}}{R_{\uparrow\uparrow} + R_{\downarrow\downarrow}}
\]

\(q_z/\text{Å}\)
strain-induced ferromagnetism

sample:
- LuMnO$_3$
- ferroelectric
- antiferromagnetic

film (20…50 nm) on YAlO$_3$ substrate:
- strained at interface
- induced ferromagnetism

⇒ manipulation of magnetic state
  by electric polarisation
strain-induced ferromagnetism

last week’s measurements:

\[ T = 10 \text{ K}, \quad H = 4 \text{ T}, \quad \rho = 10^{-10} \text{ bar} \]

\[
E = 0 \text{ kVmm}^{-1}
\]

\[
E = -2.5 \text{ kVmm}^{-1}
\]

\[
E = +2.5 \text{ kVmm}^{-1}
\]
In-operando investigation of mechanism in Si/Li batteries

CHARGING

DIS-CHARGING

Cu

Si

Li

Li$_4$Si

electrolyte

experiments
in-operando battery studies

Cu contact $\Rightarrow$ oscillations
Si electrode $\Rightarrow$ adds phase factor
Li in Si $\Rightarrow$ swelling
  $\Rightarrow$ phase shift
  $\Rightarrow$ density change
  $\Rightarrow$ contrast variation

time-resolution: 1...6 min
$\approx$ 400 measurements per cycle
$\approx$ 4000 measurements per beamtime
$\Rightarrow$ new data analysis strategy required
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projects for Amor

- smaller electrochemical cell
  - lower background
  - less absorption

- extension to fundamental research:
  - e.g. switching of FM by Li intercalation
    ⇒ low $T$ and high $H$ needed

- spin-analysis
  - switching of magnetic domains
Amor upgrade with *Selene* guide:

- *Selene* guide, 30 m
- total length $\approx 40$ m
- construction 2017
- commissioning 2020
- user operation 2020
- 1...2 orders of magnitude faster than Amor (now)
Estia at the ESS

Estia:
- Selene guide, 24 m
- total length $\approx 40$ m
- construction since 2015
- commissioning 2020
- user operation 2023
- 3...4 orders of magnitude faster than Amor (now)
the future

**concepts and software**
we are working on:

- better instrument control
- faster and reliable alignment
- automatising of data reduction
- new concepts of data interpretation

<table>
<thead>
<tr>
<th>Software</th>
<th>Time</th>
</tr>
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<tbody>
<tr>
<td>Amor</td>
<td>15 min</td>
</tr>
<tr>
<td>D17@ILL</td>
<td>6 min</td>
</tr>
<tr>
<td>Amor + prototype</td>
<td>&lt; 3 min</td>
</tr>
<tr>
<td>Amor with <em>Selene</em> guide</td>
<td>10 sec</td>
</tr>
<tr>
<td><em>Estia</em></td>
<td>&lt; 0.1 sec</td>
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Thank you!
reflectometry, in general
  J. Daillant, A. Gibaud: *X-ray and Neutron Reflectivity*

  U. Pietsch, V. Holý, T. Baumbach: *High-Resolution X-Ray Scattering*
  (Springer 2004)

... on magnetic systems
  F. Ott: *Neutron scattering on magnetic surfaces*
  C. R. Physique 8, 763-776 (2007)

focusing reflectometry
  J. Stahn, A. Glavic: *Focusing neutron reflectometry*
  N.I.M. A 821, 44-54 (2016)

this talk