Grazing incidence EXAFS

Outline

• Walk through history

• Surface EXAFS

• Grazing incidence and the total reflection of X-rays
  ▪ the penetration depth
  ▪ anomalous dispersion
  ▪ the x-ray standing wave field
  ▪ self-absorption effects

• Example:

  Characterization of ultra shallow junctions by GI-XAS

Excursion to BL6-2 and TXM-XANES
XAS  XAFS  \( \mu \text{XAS} \)

EXAFS  X-ray Absorption

SEXAFS  ReflEXAFS

XANES  NEXAFS
‘Der Kürze halber möchte ich den Ausdruck "Strahlen" und zwar zur Unterscheidung von anderen den Namen "X-Strahlen" gebrauchen.’

To shorten I shall use the designation "rays", and to differentiate it from the other ones, the naming "X-rays".

The first soft X-ray K-absorption spectrum measured with a synchrotron radiation source

The first hard X-ray K-absorption spectrum measured with a SR source

SCOPUS search for publications, June 24th 2011:

- ‘X-rays’ OR ‘Röntgenstrahlen’
- ‘X-ray absorption’
- ‘Synchrotron radiation’

1913:
- Bohr
- Moseley
- de Broglie
- Herweg

1920:
- Fricke, Hertz
- de Broglie (2)
- Bergenregen
- Kossel

1969:
- Sayers, Lytle, Stern

Total: 33,253

Search in TITLE, ABSTRACT, KEYWORDS for:
“synchrotron radiation"
“For dilute impurities or adsorbed species on a surface, the ability to isolate the absorption signal of the atom of interest by using fluorescence or Auger detection greatly enhances the sensitivity of the technique to the structure of interest.”

[...]

“As in fluorescence work, each atom is characterized by specific Auger energies.”
Figure a: [Stöhr 96]
Schematic diagram of a photon absorption process resulting in a photoelectron and a core hole. The hole is filled:
- radiatively -> emission of fluorescent photon
- non-radiatively -> emission of an Auger electron

Eisenberger & Kincaid, 1978
Lee, 1976
Citrin, 1977 & 1978
Stöhr, 1978

Figure a: [Stöhr 96]
Schematic diagram of a photon absorption process resulting in a photoelectron and a core hole. The hole is filled:
- radiatively -> emission of fluorescent photon
- non-radiatively -> emission of an Auger electron

Fig. 5.6. (a) Photoabsorption and electron production in a sample consisting of substrate atoms B and an adsorbate layer A. Only electrons created within a depth \( L \) from the surface contribute to the measured electron yield signal. Electrons originating from layer A constitute the NEXAFS signal; those from layer B give rise to unwanted background. (b) Electron mean free path in solids as a function of the electron kinetic energy above the Fermi level. The shaded area represents the distribution typically found for different materials [5.26, 27]
Figure a: [Stöhr 96]
Schematic diagram of a photon absorption process resulting in a photoelectron and a core hole. The hole is filled
- radiatively -> emission of fluorescent photon
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The fractions of the radiative and non-radiative decay rates are called Auger yield $\omega_a$ and fluorescence yield $\omega_f$ and satisfy the sum rule: $\omega_a + \omega_f = 1$
Auger yield and fluorescence yield are a function of atomic number $Z$.

Can we make it surface sensitive?

Table 1: [Lagarde 01]
Qualities (top) and pitfalls (bottom) of the different detection methods

Figure above: [Stöhr 96]
a) Fluorescence yields as a function of atomic number $Z$
b) Fluorescence yields for the K-shell excitation of low $Z$ atoms
LETTER TO THE EDITOR

Yes, we can (in theory, 1980)...

EXAFS and surface EXAFS from measurements of x-ray reflectivity†

R Fox and S J Gurman

and experiment (1981):
The extended x-ray absorption fine structure in the reflectivity at the K edge of Cu

G Martens and P Rabe
Institut für Experimentalphysik, Universität Kiel, D-2300 Kiel 1, West Germany

1980

A.H. Compton,
The Total Reflection of X-rays,
Philosophical Magazine 45 (1923) 1121-1132.
reprinted in:

L.G. Parrat,
Surface Studies of Solids by Total Reflection of X-Rays
Physical Review, Vol 95, 2, 1954

Fig. 1. Experimental arrangement for the x-ray total reflection method of studying smooth solid surfaces.
Total (external) reflection of X-rays

Sketch of optical paths of incident, reflected and transmitted beams at the interface of two media. The refraction index of medium 1 (usually vacuum or air) is larger that that of medium 2 (the reflector material).

The penetration depth $Z_p$ is defined as the distance measured normal to the samples surface where the intensity of the penetrating (here the refracted) beam is reduced by a factor of $e$

Snell's law: \[ \frac{n_{\text{medium 1}}}{n_{\text{medium 2}}} = \frac{\cos \varphi_T}{\cos \varphi_I} \]

Complex refraction index $n$:

\[ n \text{ (x-ray range ) } = 1 - \delta - i\beta \]

\[ \delta \sim 10^{-6} \quad \beta \sim 10^{-8} \]

\[ \varphi \text{ critical } = \sqrt{\frac{2}{\delta}} \]

\[ \varphi \text{ critical } \]

(Si, 17.5 keV) \( \approx 0.1^\circ \approx 1.75 \text{ mrad} \)

(Si, 500 eV) \( = 3.7^\circ \approx 64.6 \text{ mrad} \)

\[ n = 1 - N_A \frac{r_0 \lambda^2}{2\pi} \frac{\rho}{A} (f_1 + if_2) \]

‘Absorption’ term: \( \beta = N_A \frac{r_0 \lambda^2}{2\pi} \frac{\rho}{A} f_2 = \frac{\lambda \rho}{4\pi} \tau \)

\[ \mu(E) = \tau(E) + \sigma_{\text{coh}}(E) + \sigma_{\text{incoh}}(E) \]

\[ Z_p = \frac{1}{\mu(E)} \varphi_T \]

\[ I(x) = I_0 e^{-\mu(E)x} \quad \text{... Beer-Lambert’s law} \]
Total (external) reflection of X-rays

Penetration depth as a function of incident angle:
(calculated for Si substrate, 17.4 keV x-ray energy)

Idea to measure XAFS:
\[ I_r + I_{\text{absorb}} = I_0 \quad \Leftrightarrow \quad 1 - \frac{I_r}{I_0} \propto \mu(E) \]

But: the penetration depth \( Z_p \) is also a function of energy, \( z_p = f(\phi, E) \), because \( f_1, f_2 \) are functions of energy

The penetration depth:
\[ Z_p = \frac{1}{\mu(E)} \phi_r \]

Snell's law:
\[ \frac{n_{\text{medium}1}}{n_{\text{medium}2}} = \frac{\cos \phi_r}{\cos \phi_1} \]

Figure 1
Comparison between the 1/e penetration lengths in a series of bulk elements in normal and total reflection conditions. The calculations were performed at an angle \( \phi = 0.8 \phi_c \) and at an energy 100 eV above the relative K absorption edges to simulate the beam penetration in a typical EXAFS energy range. Values are around tens of \( \mu \)m in the former case and a few nm in the latter case, with a drop of roughly four orders of magnitude when working in total reflection.
**Total (external) reflection of X-rays**

Penetration depth into substrate (e.g., Si) as a function of incident angle and energy

- **Critical angle of TR**

Exciting energy: 5 – 25keV
Angle of incidence: 0 – 9 mrad
Penetration depth in log scale
Total (external) reflection of X-rays
Penetration depth into substrate (e.g. Si) as a function of incident angle and energy
Example: Arsenic EXAFS, typical range of energy (~1keV): 11800 – 12800 eV
Total (external) reflection of X-rays
Penetration depth into substrate (e.g. Si) as a function of incident angle and energy

Anomalous dispersion:
Penetration depth = f (β, δ, angle of incidence, τ)
τ, β = f (f₂)
δ (Dispersion), critical angle of TR = f (f₁)
f₁, f₂ ... atomic scattering factors
Total (external) reflection of X-rays

Anomalous dispersion:
Penetration depth = f (β, δ, angle of incidence, τ)
τ, β = f (f₂)
δ (Dispersion), φₜₐₖ = f (f₁)
f₁, f₂ ... atomic scattering factors

δ oscillations are 90° out of phase with normal EXAFS
=> distortion results in reduced amplitude & phase shift.

Challenges in ReflEXAFS/GI-EXAFS if element of interest forms the reflecting layer(s):
1) for φ₁ ≈ φₜₐₖ the edge is large, but strongly distorted by the anomalous dispersion effect
2) The absolute value of the reflectivity is unknown because of the roughness of the surface of the sample, together with the beam divergence which gives an overall slope to the reflectivity

Good news:
-) The distortions are small/negligible for ultra-thin layers (e.g. several atomic layers thickness) [Jiang 98]

Correction method(s) available:
-) Knowledge of δ, β over a long data range (Kramers-Kronig calculations) [Poumellec 89]
-) Derive an accurate model of the reflectivity from the sample. This can be done by fitting the angular dependence of the reflectivity to obtain the depth dependent density profile. [Heald 92]
J. A. del Cueto and N. J. Shevchik,
*EXAFS of ultra thin layers of Cu*

Figure 1. Experimental arrangement for obtaining EXAFS data on thin films. The angular divergence of the x-ray beam is $\Delta \theta$, the scattering angle is $2\theta$, and the angle of incidence of the x-rays upon the thin film of thickness $t$ is $\phi$. The detector subtends a solid angle $d\Omega_0$ with respect to a point on the sample.

L.G. Parrat,
*Surface Studies of Solids by Total Reflection of X-Rays*
Physical Review, Vol 95, 2, 1954

Fig. 1. Experimental arrangement for the x-ray total reflection method of studying smooth solid surfaces.

S.M. Heald, E. Keller, E.A. Stern,
*Fluorescence Detection of Surface EXAFS*
Physics Letters, 103A, 1984
• excellent S/N ratios
• wide applicability to surface and near surface systems
• detection of trace elements on surfaces

The possibilities for fluorescence detection of surface EXAFS are studied using thin films of gold on various substrates. For glancing incidence angles it is found that excellent signal to noise ratios can be obtained even for submonolayer films, demonstrating that the technique should have wide applicability to surface and near surface systems. In many cases the signal to noise is superior to electron detection techniques, and its sensitivity suggests the method may also be useful for detection of trace elements on surfaces.

Plus (for total reflection):
Interference of incident and reflected beam causes a standing wave field above the reflectors surface.

adapted from [Bedzyk 89]
Total (external) reflection of X-rays

\[ n \text{ (x-ray range)} = 1 - \delta - i\beta \]

\[ \delta \sim 10^{-6} \quad \beta \sim 10^{-6} \]

\[ \phi \text{ critical} = \sqrt{2}\delta \]

Characteristic shapes due the angular dependence of the fluorescence radiation for three different cases of atomic locations:

The interference of incident and reflected beam causes a standing wave field above the reflectors surface.

Intensity distribution in substrate as a function of incident angle and depth:

Si substrate, photon energy: 12.5keV
The x-ray standing wave (XSW) field

Challenge:
Influence of a finite coherence of the incident X-rays: => the number of nodes and antinodes in the intersection volume of the incident and reflected beam becomes limited.

But:
the high flux and natural collimation of a SR source allows small slits (typically <100 μm) and monochromators with high spectral resolution (Δλ/λ~10^-4), dramatically reducing spatial and energy divergence, which, in turn, increases the longitudinal and transversal coherence lengths

Fig. 5. 3D simulation of XSW in vacuum for a photon energy of 15 keV above a Si substrate for angles of incidence from 0.01° to 0.2° (left axis) and positions from 20 nm below to 120 nm above the surface (right axis). Intensity below the surface is decreasing exponentially with depth, above the surface oscillations occur with a maximum intensity of 4h₀.
Advantages of GI geometry

- background reduction in fluorescence spectra
- small distance sample ↔ detector (∼1mm) ⇒ large solid angle
- angle dependence of fluorescence signal ⇒ depth dependent information

Fluorescence spectra

Angle profile
The self absorption effect in TXRF XAS

Sample (droplet) size becomes thickness, i.e. path that the primary beam crosses

⇒ Large or highly concentrated samples: penetration depth of incident beam < sample size
The self absorption effect in TXRF XAS

- Large or concentrated samples: penetration depth < sample size
- An increased absorption coefficient of an XAFS oscillation will decrease the penetration depth (and vice versa) and therefore the illuminated volume
- The XAFS oscillations are attenuated or may disappear
The self absorption effect in TXRF XAS

Series of different total amounts of Arsenic on sample carriers

Damping of the XANES oscillations can be correlated to the mass of Arsenic

[Meirer 08]
The self absorption effect – comparison of GI and GE setup

Minimized path length of the incident beam through the sample
⇒ Normal incidence-grazing-exit geometry (GE-setup) should not suffer from self-absorption effects in XAFS analysis but delivers equivalent information (optical reciprocity theorem [Becker 83])

- Lightweight SDDs allow rotating the whole detector-slit system
- Center of rotation on reflector surface

Distance sample ↔ Detector: 40mm
Slit-width: 40µm

[Meirer 09]
The self absorption effect – comparison of GI and GE setup

- GE setup suffers minimally from self-absorption effects
- Shows lower sensitivity than GI-setup
  ⇒ difficult to apply to XAFS analysis of trace amounts (few nanograms) of samples

[Meirer 09]
References:


