Surface structure of Pyrite thin films on Si

- Raw
- Fitting
- Elemental sulfur
- Bulk sulfide (Fully coordinated, 1S, 3Fe)
- Surface sulfide (Lower coordinated 1S, 2Fe)
- Monosulfide

S\textsubscript{2p} KE=200eV

![Graph showing bond energies (eV) with peaks at various energies and labels for different sulfide structures.](image)
Advanced X-Ray Analysis Methods

XPS (Photoemission) → Binding Energy
(beamline 11.0.2, beamline 9.3.2)
XAS (Absorption) → Unoccupied Density of state (HOMO)
(beamline 11.0.1, beamline 10.3.2)
XES (Emission) → Occupied Density of state (LOMO)
(beamline 8.0.1)
All in one?

XPS, XAS, XES all in Beamline 11.0.2?
Purpose

• XPS & Electron Yield XAS
  ➢ Binding Energy, Density of State of Conduction Band
  ➢ Fermi Surface Determination: Valence Band Spectrum, or know BE element
  ➢ Band Gap
  ➢ Testing experiment on Si

• Electron Yield XES & XAS
  ➢ Density of State of Valence and Conduction Band
  ➢ Band Gap and Core Hole Effect

Chem. Mater. 2009, 21, 2568–2570
XPS

One Photon process: Photon in Electron out
**XPS Cartoon Mechanism**

**XPS**: $E_B = \hbar \nu - E_{\text{kin}} - \Phi_s$ For example, $E_B$ for $S2p_{3/2}$

- **Free electron level**
- **Vacuum level**
- **Fermi level**
- **Conduction band**
- **Valence band**

Incident X-ray $\hbar \nu$
Surface Sensitivity

• Electron Inelastic Mean Free Path

\[ E_{\text{kin}} = h\nu - E_B - \Phi_s \]

Photoelectron effect

Detector

Depth profile experiment and inelastic mean free path (IMFP)

Depth profile experiment

Synchrotron Light (various $h\nu$)

Detector

• Continuous
• Changeable

Photoelectrons with different kinetic energies come from different depth of the sample.
XES and XAS

Two Photons process: Photon in Photon out
**XES Cartoon Mechanism**

**XES**: (Photon in Photon out) Fluorescent photon created by electron decay from valence band to core level.
**XAS Cartoon Mechanism**

Free electron level

E_{kin}

Vacuum level

\( \Phi_s \)

Fermi level

\( E_B \)

Incident X-ray \( h\nu \)

Conduction band

Valence band

**XAS:** Electrons from core level to unoccupied conduction band, For example, \( A_1 \) for S_L edge

\( E_A = h\nu - h\nu_T \) For example
Limitation

• Traditional Measurement (Transmission)
  ➢ Signal-to-background ratios limited by thickness (~500Å)
  ➢ Radiation damage
  ➢ Reflection geometry experiment
  ➢ Surface Sensitive?!

• We can only collect electron not photon in beamline 11.0.2
Electron Yield

• Electron Yield or Secondary Electron
  ➢ Auger electron & Fluorescent Photon

- Photoelectron
- Auger electron
- Higher shell
- Incident X-ray hv
- Fluorescent Photon

\[ \text{Ev} \]
Electron Yield

• Auger electron yield dominate
  - For K shell excitation of low-Z atoms
  - For L shell excitation of all Z < 90
  - C, N, O, S, Si

**Electron Yield**

- **Detection Mode**
  - Auger Electron Yield (AEY)
  - Partial Electron Yield (PEY)
  - Total Electron Yield (TEY)

Stöhr, Joachim, NEXAFS Spectroscopy, Springer-Verlag 1996
Reviews:
XPS & Electron Yield XAS
Band Gap Determination
Fermi Surface Determination

• Testing Experiment on Si (band gap 1.11eV)

• Binding Energy calibration
  - Au $4f_{7/2} = 84.00$ eV
  - Ag $3d_{5/2} = 368.27$ eV
  - Cu $2p_{3/2} = 932.67$ eV

• Valence Band Spectrum

Take-home messages

• Band Gap Determination by XPS+XAS
  ➢ Fermi Surface Determination by Valence Band Spectrum
  ➢ Fermi Surface Determination by Binding Energy Calibration
  ➢ Testing Experiment on Si

• Band Gap Determination by Electron Yield XES+XAS
  ➢ Density of State Information of Valence band and Conduction band
  ➢ Core Hole Effect Analysis