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Understanding and optimizing surfaces and interfaces in energy conversion devices

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Understanding and Optimizing Surfaces and Interfaces in Energy Conversion Devices

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The Group at UNLV
Collaborations

On almost everything:
O. Fuchs, E. Umbach + group, Experimentelle Physik II, Universität Würzburg
J.D. Denlinger, Advanced Light Source, Berkeley

Solar Cells:
F. Karg + group, Avancis, Munich
Ch.-H. Fischer, M.-Ch. Lux-Steiner + the CISSY-Team, Hahn-Meitner-Institut, Berlin
NREL, U Central Florida/FSEC, IEC Delaware, U Toledo, UC Berkeley, Miasolé, Global Solar

Biointerfaces and liquids:
Y. Zubavichus, M. Zharnikov, M. Grunze, Universität Heidelberg
M. Odelius, L.G.M. Pettersson, A. Nilsson + group, Stockholm University/Stanford

Hydrogen:
NREL, Argonne Nat‘l Lab, U Hawaii, Altairnano, UC Santa Barbara, UTC

LEDs:
Linda Sapochak, Pacific Northwest Nat‘l Lab
Ted Moustakas, Kevin Smith, Boston University
Outline

- Group concept
- Why interfaces and surfaces?
- Electronic structure
- Soft X-ray spectroscopies
- Interfaces and surface treatments in Cu(In,Ga)(S,Se)$_2$ thin film solar cells
Use/develop combination of sophisticated surface and interface spectroscopies (the „tool chest“)
Bring tool chest into applied communities and „dig in deep“

Examples:
- Thin film solar cells (organic and inorganic)
- Nuclear fuel
- Hydrogen production
  - High-temperature electrolysis
  - Photoelectrochemistry
- Hydrogen storage in nanomaterials
- Hydrogen consumption (fuel cells)
- Bio-interfaces
Interfaces determine our lives
Interfaces determine our lives
Example: **Electrodes, Surfaces, and Interfaces for Photoelectrochemical Hydrogen Production**

E. Miller et al.
IJHE 28, 615 (2003)
Fig. 4. Structure of encapsulated triple-junction photoelectrode using (a) a-Si:Ge ; (b) CIGS.
Why care about the „Electronic Structure“?

- Is crucially important for electronic transport
- Gives insight into chemical bonding
- Determines the interaction of matter with light
- Allows determination of elemental composition at a surface/interface
What is an „Electronic Structure“?

• Atoms contain electrons

• Each electron is described by a set of „quantum numbers“ (Example: $n = 1$, $l = 0$, $m_l = 0$, $m_s = \frac{1}{2}$)

• Electrons with different quantum numbers ($n$ and $l$) have different „binding energies“

• The binding energies are unique for different elements and also for different chemical environments of a particular element

• The electrons with the smallest binding energy are called „valence electrons“ and form the „valence band“

• The lowest „states“ that are unoccupied form the „conduction band“
Electronic Structure of CdS

- Conduction Band
- Upper Valence Band
- Cd 4d
- S 3s
- S 2p\textsubscript{3/2}
- S 2p\textsubscript{1/2} Core Levels
Basic principle of X-ray emission: example CdS

\[ \begin{align*}
\text{Cd 4d} & \quad \text{S 2p}^{1/2} \\
\text{S 3s} & \quad \text{2p}^{1/2} \\
\text{h} \nu &= 162.7 \text{eV} \\
\text{h} \nu &= 208 \text{ eV}
\end{align*} \]

Normalized Intensity

Emission Energy (eV)

Vacuum Level

Conduction Band

Fermi Energy

Upper Valence Band

Valence Band

XES

S 3s\rightarrow 2p^{3/2}

Cd 4d\rightarrow S 2p^{3/2}

h\nu =162.7\text{eV}

UVB

h\nu =208 \text{ eV}

S 3s\rightarrow 2p^{1/2}

Cd 4d\rightarrow S 2p^{1/2}

Normalized Intensity
Basic principle of X-ray emission: example CdS
Methods I: Soft X-ray Spectroscopies

- Photoelectron-Spectroscopy (PES)
- X-Ray Emission Spectroscopy (XES)
- Auger-Electron-Spectroscopy (AES)
- X-ray Absorption Spectroscopy (XAS)
Methods II: Inverse Photoemission (IPES) 
Spectroscopy of unoccupied states

• "Time-reversed" process of PES: 
  – Excitation with electrons 
  – Detection with UV-photons

• 2 modes: 
  – Variation of electron energy, 
    fixed $h\nu$ (our case) 
  – Fixed electron energy, 
    $h\nu$-spectrometer

• Determination of the 
  conduction band minimum!
Combining UPS and IPES

- Investigates the entire electronic structure (valence and conduction band)
- Allows the determination of electronic surface band gaps
- Allows the determination of the Fermi energy position within the band gap
Methods

• **Photoelectron Spectroscopy (XPS, UPS, PES):**
  Chemical Environment, Valence Band and VB Offset (Surface)

• **X-ray excited Auger Electron Spectroscopy (XAES):**
  Chemical Environment (Surface)

• **Inverse Photoemission (IPES):**
  Conduction Band and CB Offset (Surface)

• **X-ray Emission Spectroscopy (XES):**
  Chemical Environment, Valence Band (Bulk, Buried Interface)

• **X-ray absorption Spectroscopy (XAS = NEXAFS = XANES)**
  Chemical Environment, Conduction Band (Bulk, Buried Interface)

• **Scanning Probe Microscopy and Spectroscopy**
  Morphology, Valence and Conduction Band (Surface)

• **Electronic Band Gap Combinations:**
  IPES+UPS (surface), XES+XAS (bulk), STS (surface)
Instruments

- At UNLV
  - XPS, UPS, XAES in two systems
  - Inverse Photoemission (IPES)
  - Ion sputtering, e-beam evaporation (metals), Knudsen cells (organic), LEED
  - Solar Simulator, UV-Vis
  - Variable-temperature SPM (STM, AFM, STS, KPFM; 50 – 650K)

- At ALS
  - XES, XAS, RIXS @ Beamline 8.0 – SXF endstation

- “At Würzburg“ (ALS):
  - High-resolution, high-transmission XES spectrometer
  - Liquid flow-through cell

- “At Hahn-Meitner-Institut, Berlin“ (BESSY):
  - CISSY endstation
Surface and Interface Science at UNLV

XPS, UPS, Auger

Analysis

Glovebox

Distribution

Preparation

Scanning Probe Microscope

IPES
Interfaces in Cu(In,Ga)(S,Se)$_2$ solar cells
Why Cu(In,Ga)(S,Se)$_2$ for solar cells?

- **High absorption coefficient**
- **Band gap 1.0-1.5 eV**
- **Thin film cells**
- **High efficiency (19.5%)**
- **Standard techniques, low material input**
- **Very cost-effective**
Cu(In,Ga)(S,Se)$_2$ in action:
Congress Center Salzburg 40 kWp
Sample preparation ("the RTP process")

- Sputter deposition of Mo layer on sodalime glass
- Sputter deposition of elemental layers of Cu, In, and Ga
- Evaporation of Se (and S)
- Thermal Processing (550 °C)
- Chemical bath deposition of CdS
- Deposition of ZnO electrode

![Diagram of sample preparation](image)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td></td>
</tr>
<tr>
<td>CdS (20 nm)</td>
<td></td>
</tr>
<tr>
<td>Cu(In,Ga)(S,Se)₂ (2µm)</td>
<td></td>
</tr>
<tr>
<td>Mo (2µm)</td>
<td></td>
</tr>
<tr>
<td>Na-lime glass (2 mm)</td>
<td></td>
</tr>
</tbody>
</table>
Real CIGSSe: an orthodontist’s nightmare

Intermixing at the CdS/CdSe interface (XES)

- Chemical bond between Cd and S
- Cd-S bond is absent for thin overlayer
  → diffusion of S into the CIGS film

APL 74, 1451 (1999)
Intermixing at the CdS/CISe interface (PES)

- detectable Se signal for thick CdS layers
  → Se segregation
- detectable In signal for (less) thick layers
  → In segregation

APL 74, 1451 (1999)
What is the effect of „spikes“ and „cliffs“ in the conduction band?
A brief history of valence band offsets

Valence Band Offset (eV)

- single crystal CIS + PVD-CdS
- thin film CIS + PVD-CdS
- thin film CIS + CBD-CdS
- theory
- our value

Year

A brief history of conduction band offsets

Conduction Band Offset (eV)

- Single crystal C1Se + PVD-CdS
- Thin film C1Se + PVD-CdS
- Thin film C1Se + CBD-CdS
- Theory
- Our value

Year

Band gap of CIGSe solar cell absorber

- Problem: real system with ex-situ preparation ⇒ Adsorbates!
- Ansatz: mild Ar\(^+\)-Sputtering (500 eV, 1 \(\mu\)A/cm\(^2\))
- Band gap at surface is bigger than expected: 1.3 - 1.4 eV instead of 1.0 eV!
- Explanation: Absorber is very In-rich and Cu-poor at the surface ⇒ IPE surface phase!
20 nm CBD-CdS/CIGSe

- Band gap (2.2 eV) is smaller than expected (2.4 eV)!
- Reason: CdS-film contains Se and In! ⇒ band gap reduction (e.g. CdSe: 1.7 eV)
- Estimate of conduction band offset: CISe: $E_{LM} = 0.6$ eV
  CdS: $E_{LM} = 0.4$ eV
  ⇒ 'CBO' = -0.2 eV (Cliff !)
  (± changes in the band bending)

APL 79, 4482 (2001)
CdS/CIGSe: band edge alignment

- CBO varies systematically around 0.0 eV
  ⇒ real CdS/CIGSe-interface: no Spike!
- Reason for variation: Intermixing!

CuInSe$_2$ surface

\begin{align*}
\text{CBM} & \quad \text{E}_F \quad 1.4 \ (\pm 0.15) \text{ eV} \\
\text{VBM} & \quad \text{EF} \quad 1.4 \ (\pm 0.15) \text{ eV}
\end{align*}

Thin CdS on CuInSe$_2$

\begin{align*}
\text{CBO} &= 0.0 \ (\pm 0.2) \text{ eV} \\
\text{VBO} &= 0.8 \ (\pm 0.2) \text{ eV}
\end{align*}

CdS surface (on CuInSe$_2$)

\begin{align*}
\text{CBM} & \quad \text{E}_F \quad 2.2 \ (\pm 0.15) \text{ eV} \\
\text{VBM} & \quad \text{EF} \quad 2.2 \ (\pm 0.15) \text{ eV}
\end{align*}

APL 79, 4482 (2001)
The CdS/CuInS$_2$ interface

- Why do CuInS$_2$ cells not perform up to expectations ($\eta < 13\%$)?

- Open-circuit voltage is too low!

- There is a cliff in the conduction band! → Modify interface
What does the Cd-treatment do on CuIn(S,Se)$_2$? (step 1)

- Alternative buffer layers (e.g., ZnO) often need Cd-treatment for high efficiency
- Current thinking: no CdS-film is grown
- Here: Auger spectroscopy shows:
  - Cd compound is deposited (thin)
  - Two different chemical species (conc. dep.)

APL 82, 571 (2003)
What does the Cd-treatment do? (step 2)

Photoemission analysis:

- Coverage as a function of Cd-concentration is
  - "instantaneous"
  - constant for each species
- Peak position:
  - 1: sulfide or selenide?
  - 2: oxyhydride!

APL 82, 571 (2003)
What does the Cd-treatment do? (step 3)

X-ray emission analysis:

- Formation of S-Cd bonds
- Breaking of S-Cu bonds
What does the Cd-treatment do on CuGaSe$_2$?

Form a monolayer of CdSe!

APL 86, 222107 (2005)
XES of the H$_2$O/CIGSSe interface

1 $\mu$m Polyimide
1.3 $\mu$m H$_2$O
1.3 $\mu$m Al
Cu(In,Ga)(S,Se)$_2$
Mo
soda-lime glass

$\nu_{\text{excitation}}$

$\nu_{\text{emission}}$

Summary

Soft x-ray spectroscopy allows the investigation of

- Surfaces and buried interfaces
  - Atom-specific and chemically sensitive
  - Variety of effects: reactions, intermixing, impurities, ...
  - Electronic structure

- A variety of novel fields of application
  - „Conventional“, organic, biological, wet, ...
  - Liquid-solid interfaces!
  - Energy conversion devices
  - Hydrogen-producing, -storing, and –consuming devices

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