The BESSY HIKE Project

Mihaela Gorgoi
29 ID-Beamlines
25 DIP-Beamlines

IR to x-Ray (11 x-Ray Beamlines)

BESSY II
1.7 GeV
300 mA
16 straight sections

VUV
XUV:

4 lin. Undulators
6 ell. Undulators

x-Ray:

3 7T-WLS
1 7T-Wiggler
Photoemission Spectroscopy

- monochromatic photon beam ionises electrons from sample

- the kinetic energy \((E_{\text{kin}})\) of photoelectrons in vacuum outside sample is measured

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

binding energy of electrons in the sample

• core levels strongly localized, thus BE's give elemental identification
• chemical shifts give information on:
  - chemical environment of emitter atoms
  - oxidation / valence / bonding state
Why high kinetic energy?

Advantages

- Large Sampling Depth (Bulk sensitive)
- Less Surface Sensitive
- Non-destructive

Disadvantage

- Low photoionization cross sections

Typical samples:

- Bulk structures, multilayers, buried nano layers and interfaces

[Graph showing electron escape depths and kinetic energy]
Double-crystal monochromator:
angular range $5^\circ$ - $82^\circ$

Si (111) 1997 - 12000 eV
Si (422) 5639 - 12000 eV
Si (311) 4000 - 12000 eV

The resolution becomes very high at certain photon energies.
The HI KE Set-up

Motorized 5-axis sample manipulator:

Electron spectrometer: Scienta R4000 optimized for high kinetic energies up to 10 KeV

Motorized chamber stand

Load-lock for sample introduction & storage

KMC-1
The HIKE station at BESSY II

Chamber stand positioning accuracy within 2 μm!

Fermi level of Au(111)

Excitation energy: 2010 eV

Gaussian contribution = beamline resolution: ~ 0.22 eV

Analyzer: PE 200 / 0.3 mm slit 150 meV resolution
HI KE on Au: Depth Profiling with Fixed Monochromator Setting

- Si (111) 4 min.
  - Kinetic Energy / eV: 2002 eV
  - ΔE = 0.21 ± 0.01 eV

- Si (333) 40 min.
  - Kinetic Energy / eV: 6006 eV
  - ΔE = 0.050 ± 0.02 eV

- Si (444) 2 hours
  - Kinetic Energy / eV: 8008 eV
  - ΔE = 0.073 ± 0.02 eV

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F. Schäfers, M. Mertin, M. Gorgoi, BESSY Annual Report 2006, 211
Selected Results

• Metal multilayers - interdiffusion
• Organic and inorganic solar cells
• X-ray standing waves
• Ni 1s and satellites
Addressing interfacial quality in CuNi multilayers

- Grown by UHV-based dc magnetron sputtering
- Heating to a preset temperature
- 2010 eV excitation energy
- 0.26 eV overall resolution

What we observe as “one” core photoelectron line is in reality an envelope originating from a distribution of many chemically shifted core levels.

A calculation of the chemical shift therefore originates from many calculations (using DFT and other tricks).

Use a GAUSSIAN distribution of chemically inequivalent atoms around the interface, where the imperfection is described by the distribution width $\Gamma$. 
Results Summary

Interface Theoretical Model

Example: \( x = 5 \text{ ML} \)

- \( \Gamma \) describes the quality of the interface


➢ the experimentally determined shifts converge towards the theoretically predicted value of dilute alloy state.
Results: Cu 2p3/2 spectra of Ni$_5$Cu$_5$

2nd experiment – new samples with the same composition
Results: Binding energies of 2-peak-fit components in Ni$_5$Cu$_5$
The intensities of Cu 2p, Ni 2p core-levels relative to the intensity of Pt 4f core level from the cap.
Repeated heating results in alloying of the cap into the multilayer!
Cu 2p3/2 core-level spectra of Ni$_5$Cu$_5$ without Pt cap
Cu $2p_{3/2}$ core-level spectra of Ni$_5$Cu$_5$ without Pt cap

Similar to previous data for low - intermediate temperature anneal

Core level shift almost vanish for high temperatures?!
Intensities ratios of $\text{Ni}_5\text{Cu}_5$ without Pt cap

Cu enrichment of surface during repeated anneals at high temperatures
At 6 keV excitation energy the contribution from the outermost layers is further suppressed.

We recover the picture from the first published results.
Sample: polymer blend (1:1)

**F8DTBT**  

**PCBM**  

C60 cage

- At 2keV none of the shake-up features characteristic to the C60 cage are present.  
  **no surface presence of PCBM.**
- The presence of the shake-ups at 6keV indicates the segregation of PCBM to the inner layers of the film.

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Metal-Ligand Interaction in the Valence Electronic Structure of Ruthenium Complexes

- HOMO is determined as a function of ligands
- The splitting of the Ru 4d level into two peaks depends on the ligands.

HIKE on Inorganic Thin Film Solar Cells

Cu(In,Ga)Se$_2$ (CIGS) - Zn(O,S) - 15 nm buffer layer

Glass + Mo

Above approximately 5 keV excitation energy the absorber becomes visible!

Depth profiling of the device is possible!

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E.M.J. Johansson et al, BESSY annual report 2006, 508
Cu-Diffusion into In$_2$S$_3$-Cover Layer

Excitation energy: 4000 eV
Heating rate: 2 °C/min

Cu 2p$_{3/2}$

Cu(In,Ga)Se$_2$

20 nm In$_2$S$_3$

Countrate [kcts/s]

Kinetic Energy [eV]

Temperature [°C]

Standing wave formation in reflection from a surface, or single-crystal Bragg planes, or a multilayer mirror.
X-ray Standing Waves - SWEDGE

Probing Buried Interfaces: The Standing Wave-Wedge Method

X-ray Standing Waves

Multilayer Mirror

Buried Interface

Fe

Cr wedge

Scanned standing wave

Fixed phase

B4C

W

SiO2

Scanned sample

Si-wafer

~6.0 mm

~0.1 mm spot

MFe

Fe

θBragg

Photo-Electron
Or Soft X-ray

λSW (|E2|) = λx/2sinθinc
≈ dML

1st order Bragg:
λx = 2dMLsinθBragg

courtesy Chuck Fadley
HI KE on Ni Core Levels (6 eV satellite)

- Famous, „classical“ problem in condensed-matter physics:
- Enormous attention for several decades - many publications (sampling surface or bulk?)
- Correlation effects giving rise to the satellites in the Ni PES: surface plasmon vs. excitonic states

- Satellites are located at different energy w.r.t. the main 1s (2p) core level line
- Ni 1s measured for the first time!

- DFT calculation: 3d shake up
- Difference in core hole screening and localisation of 1s and 2p states
Bending magnet beamlines at third generation facilities provide attractive opportunities for HIKE

- ‘high’ flux **continuum** from soft to hard (2-12 keV)
- sometimes **crystal limited resolution** (~100 meV)
- resolution always < 1 eV

HIKE allows depth profiling of real devices, especially electronic properties of buried interfaces

- HIKE allows determination of core level energy shifts
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