Interface properties of ferroelectric Schottky barriers studied by soft X-ray absorption spectroscopy

Hermann Kohlstedt

Institut für Festkörperforschung,
Forschungszentrum Jülich, Germany
Outline

1. Why spectroscopy of devices under bias?
2. Introduction to X-ray absorption spectroscopy
3. A modified total electron yield mode
4. Results
5. Summary
Magnetic effects at the interface between non-magnetic oxides

A. BRINKMAN1*, M. HUIJBERG1, M. VAN ZALK1, J. HUIJBERG1, U. ZEITLER2, J. C. MAAN2, W. G. VAN DER WIEL3, G. RIJNDERS1, D. H. A. BLANK1 AND H. HILGENKAMP1

1Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands
2High Field Magnet Laboratory, Institute for Molecules and Materials, Radboud University Nijmegen, 6525 ED Nijmegen, The Netherlands
3Strategic Research Orientation NanoElectronics, MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

*Present address: Physics Department, University of California, Berkeley, California 94720, USA
*E-mail: a.brinkman@utwente.nl

LaAlO3/SrTiO3
Orbital Reconstruction and Covalent Bonding at an Oxide Interface

Schematic showing the interface between two metal oxide compounds being illuminated by x-rays from a synchrotron, yielding detailed information about the shape, and thus occupation and degeneracy, of electronic orbitals near the interface.
Interface Devices: Examples

Predicted Magnetoelastic Effect in Fe/BaTiO$_3$ Multilayers: Ferroelectric Control of Magnetism

Chun-Gang Duan, S. S. Jaswal, and E. Y. Tsymbal

FIG. 4 (color online). Minority-spin charge density (in arbitrary units) at the Fe/BaTiO$_3$ interface for two opposite polarizations in BaTiO$_3$. The charge density is calculated in the...
Ionic Screening


Why spectroscopy of devices under bias?

(Often) independently performed investigations:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Insulator</th>
<th>Metal</th>
</tr>
</thead>
</table>

a) Electrical device characteristics
   I-V Curve, C-V curve, etc.

b) Structure and Electronic structure: HRTEM, TEM EELS

b) Surface sensitive methods
   (XPS, AES, AFM, STM - without top electrode)

Try to correlate a), b) and c)

AIM: Device and interface studies under realistic boundary conditions
(A working device real time and in-situ)
Previous Investigations

Electric-Field-Induced Ionic Displacement and Redistribution of Bonding Electrons in LiNbO$_3$ and LiTaO$_3$ Revealed by Modulation X-ray Diffraction

**Hard X-rays**

by S. Fujimoto

Fig. 2. Schematic view of the experimental setup.

**Volume information**
Previous Investigations

Electric-field induced electron density response of GaAs and ZnSe

J. Stahn, et al.

Hard X-rays

Volume information
Previous Investigations

XPS: X-ray photo emission spectroscopy

New Method for Determination of Energy Distribution of Surface States in the Semiconductor Band Gap: XPS Measurements under Bias

Hikaru Kobayashi et al.

Interface information

but extremely thin top electrodes required: 2 nm – 3 nm

Fig. 2. XPS spectra in the In(3d5/2) region for the [ca. 30 Å-thick Pt/|ca. 25 Å-thick oxide/p-InP(1 0 0)] MIS diodes measured under following effective biases: (a) 0 V; (b) −0.94 V (reverse bias); (c) 0.78 V (forward bias). The inset shows the XPS spectrum in the P(2p) region measured under a zero bias.
Electronic Structure under Bias

- Top electrode thickness (characteristic length scales)
- Transport current
- Probe depth for photons: 100 nm
- Probe depth for electrons: 2-5 nm
Electronic Structure under Bias

- Which information we get?
- What’s the probe width?
- What’s the probe depth?
- Is the electric behavior with and without the photon beam different?
- Is the experiment non-destructive?
- How relevant are the results for the device without the photon beam on?
- …
X-ray Absorption Spectroscopy
Two fairly distinct synchrotron camps

Structure

Argonne National Lab

Hard X-rays:
Where are the atoms?

\[ E(\text{photon}) = \frac{hc}{\lambda_{ph}} \]
\[ \lambda_{ph} = 1 \text{ Å} \]
\[ E(\text{photon}) = 12.4 \text{ keV} \]

Electronic Structure

Advanced Light Source/Berkeley

Soft X-rays:
What are the electrons doing as they migrate between the atoms?

\[ E(\text{electron}) = \frac{h^2}{2m\lambda_{el}^2} \]
\[ \lambda_{el} = 1 \text{ Å} \]
\[ E(\text{electron}) = 150 \text{ eV} \]
\[ 100 \text{ eV up to } 2 \text{ keV} \]
Incident x-ray

Vary Energy

Sample

Transmitted x-rays
X-ray Absorption Cross-section for several Elements

\[ I = I_0 \exp (-\mu t) \]

\[ \mu \approx \frac{\rho Z^4}{AE^3} \]

1) Monotone regime: Raleigh and Compton scattering
2) Absorption edge
3) Oscillations just above edge
X-ray Absorption Spectroscopy: An Example - Pt L_{III}

X-ray absorption near edge spectroscopy

Extended x-ray absorption fine structure

Absorption coefficient (a.u.)

Energy (keV)

XANES

EXAFS

$E < E_0$

$E = E_0 + 10 - 50$ eV

$E = E_0 + 50 - 1000$ eV

Edge

Pre-edge
Multiple scattering

Single scattering

Atom A

$\lambda$ large

$E = E_x - E_0$

$|k| = \frac{2\pi}{\lambda} \sqrt{\frac{8\pi^2 m (E_x - E_0)}{h^2}} = \sqrt{0.2624 \cdot E}$

Atom B (neighbour)

$\lambda$ small

$5A < \lambda < 10A$
The ALS mostly produces ultraviolet light and soft x rays which have just the right energies to explore many of the atomic properties of matter.
Example: Insulator

**Density of States: DOS**

- Unoccupied Valence Band
- Occupied Valence Band
- Core level (e.g. Ti, O, C)

- Incoming Photon from Synchrotron
- Electron

**Soft X-Ray Spectroscopy: Introduction**

Core Ionization and Decay Processes

Decay Mechanisms

- Auger electron
- XES (elastic)
- XES (inelastic)
- RIXS
- DOS

Core ionization Auger emission X-ray fluorescence

\[ I_{\text{Auger}} \approx 100 - 1000 \times I_{\text{Fluores}} \]
Incident x-ray

Sample

Transmitted x-rays
Scattered x-ray

Incident x-ray

Transmitted x-rays

Sample

Fluorescence
Fluorescence x-rays

Photoelectrons
XAS Measurements: 3 Methods

Transmission

Bulk properties

Total Electron Yield: TEY

Total Fluorescence Yield: TFY

Surface properties

(only “conductor”)

Bulk properties

(conductor and insulator)

\[ I_t = I_0 e^{-\mu d} \]

\[ \mu = -\frac{1}{d} \ln \left( \frac{I_t}{I_0} \right) \]
X-ray absorption by emission

Absorption Spectrum

XAS

unoccupied CB

E\_Fermi

occupied VB

Core level

Photon Energy

DOS

E

XAS

„Absorption“ Spectrum maps DOS

!! Detected by emission (decay) process!!
X-ray Absorption and Emission Process: Schematic

Example: C\textsubscript{60}

\begin{align*}
h\nu & \quad \text{Photon Energy (eV)} \\
E\textsubscript{F} & \\
C \ 1s &
\end{align*}
XAS by using Fluorescence: TFY

Incident x-ray beam from synchrotron

Fluorescence and scattered x-rays

Filter

Preferred in case of thick samples or thin film devices
Total Electron Yield: TEY

- Chamber wall
- Auger electrons
- E photon
- Escape depth: (max) 5nm

TEY vs. $h\nu$

XAS can be surface sensitive!
Comparison: Total Electron Yield / Total Fluorescence Yield

Synchrotron radiation, soft-x-ray spectroscopy and nanomaterials
Characteristic Length Scales

Total electron yield (TEY)
Probe depth < 5 nm

Total fluorescence yield (TFY)
Probe depth 100 nm

TEY: surface sensitive
TFY: Bulk sensitive

Surface layer
Bulk atoms
Features of Absorption Spectroscopy with soft- and hard x-rays

- Site sensitive, i.e. element specific
- Chemical environment
- Inter-atomic distance
- Number and type of neighbors
- Bulk sensitive
- No long range order required
- (Vacuum not required)

Typical applications:

Amorphous solids and ceramics, liquids, e.g. solutions of ionic compounds or gels (not possible by x-ray diffraction), biomolecules, homogenous and heterogeneous catalysis

Synchrotron is the right choice:
High brilliant x-ray source - tune able - monochromatic – polarized
Beam line 8
Advanced Light Source
Example:

Crystal field splitting in TiO$_2$
Energy Diagram for a Metal Ion in an octaedral Ligand Field

Energy Diagram:

- **d-Orbitals**
  - $z^2$, $x^2 - y^2$

- **Spheric Ligand Field**

- **Isolated ion**

- **Ion in octaedral field**

- **Energy Levels**:
  - $\Delta_0 = 10Dq_0$
  - $\Delta_0 = \frac{3}{5}$
  - $\Delta_0 = \frac{2}{5}$

- **Orbitals**:
  - $e_g$
  - $t_{2g}$
Ti- Crystalfield Splitting

$d_z^2$  
d$_{xy}$

$d_{x^2 - y^2}$  
d$_{xz}$

e$_g$

t$_{2g}$

Orbitals on the axis

Orbitals in between the axis
Crystal Field of Ti-Oxide

\[ \Delta_0 = 10Dq_0 \]

Ti XAS of SrTiO$_3$

V. R. Mastelaro et al.
Different Structures of TiO$_2$

J.P.Crocombette and F. Jollet


E. Stoyanov, F.Langenerhorst, and G. Steinle-Neumann
American Mineralogist, 92, 577 (2007).
The effect of valence state and site geometry on Ti L$_{3,2}$ and O K electron energy-loss spectra of TixOy phases

The SXAS is sensitive to the local environment of Ti.
Can distinguish between anatase, rutile and brookite (even without long range order!!)
FIG. 2. Low energy region of Ti $L_{3,2}$-edge XANES spectra of $t$Pb$_{1-x}$La$_x$TiO$_3$ compounds.

Standard XAS Set-up for TFY and TEY

Jonathan’s and Wanli’s beam line 8

TFY mode

Neutralization current

I_{neut}

TEY mode
TFY and TEY on the bare Ferroelectric PZT

![Graph showing TEY and TFY data for bare Ferroelectric PZT with peaks at L3 and L2 edges.](image)

- **L3**
- **L2**
- **t2g**
- **eg**

The graph displays data for photon energy (eV) ranging from 450 to 480 eV, with TEY and TFY values in arbitrary units (a.u.). The Ti L₃,₂ edges are highlighted.
Ferroelectric Capacitor under Soft X-ray Irradiation
Ferroelectric Materials

$\text{PVDF}$

Polyvinylidene fluoride: $[\text{C}_2\text{H}_2\text{F}_2]_n$

$\text{BaZr}_x\text{Ti}_{1-x}\text{O}_3$

$\text{BaTiO}_3$

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$

$\text{BaTiO}_3$

$\text{PVDF}$
Ferroelectric Hysteresis

$P_r = +/- (10 - 80) \, \mu C/cm^2$

$E_c = 50 - 300 \, kV/cm^2$

Thin Film Capacitor: $t = 100 \, nm$

$V_C = 0.5 \, V - 2 \, V$

Comparison:

1 electron/per surface atom:

$10^{15}/cm^2 \times 1.6 \times 10^{-19} \, C = 160 \, \mu C/cm^2$

strong interface effects expected!!
$P$ vs. $V$ loop

Initial loop

Polarization ($\mu$C/cm$^2$)

Voltage (V)

Pt/PbZr$_{0.3}$Ti$_{0.7}$O$_3$/Pt
PZT 111 orientation

Modified TEY Mode

Chamber/Ground

50 nm Pt top

180 nm PZT (Ferroelectric)

Pt bottom

$A_{top}$

$A_{bot}$

$V_{Bias}$
Sample Holder and Ferroelectric Cap: Beam line 8

Cu sample holder

Top electrode

Connection to top electrode

Connection to Bottom electrode

Beam shape

1 cm
XAS of the Ferroelectric Capacitor

After +4V pulse

Base line current

1

+ $P_r$ top

$E_D$

Pt

PZT

- - - - - - - - - -

Pt

2

average

$-P_r$ top

3

After -4V pulse

4

Bottom current

+ $P_r$ bot

Photon Energy (eV)
Modified TEY Mode

No photons out-
Pt top too thick

soft X-rays \( hf \)

\[ \text{Electrons (from Pt)} \]

50 nm Pt top

180 nm PZT (Ferroelectric)

Pt bottom

1: External photo electric effect (Pt)
Modified TEY Mode

1: external photo electric effect (Pt)
2: Inner photo electric effect-electron-hole pair generation ($E_{\text{photon}} \approx 100 \times E_g$)
3: Inner photo electric effect-core hole excitation process (local)

No photons out-Pt top too thick

Neutralization current $I_{\text{neut}}$

Electrons (from Pt)

180 nm PZT (Ferroelectric)

Pt bottom

50 nm Pt top

soft X-rays hf

1

3

2

Chamber/Ground

$A_{\text{top}}$

$A_{\text{bot}}$

$I_{\text{top}}$

$I_{\text{bot}}$

$I_{\text{photo}}(+/\text{-}P_r)$

$V_{\text{bias}}$
Electrons and holes are separated due to the depolarization field. This results in an photo current in the external circuit.
External and inner Photo Electric Effect

Base line current

10

1.6

n (nA)

3 - Pr bottom average

0.8

Top and Bottom Current (nA)

450 455 460 465 470 475 480

Photon Energy (eV)
Example: PIN Photodiode (Solar Cell)

R. Paul
Optoelektronische Bauelemente
Teubner Studienskripten

Photo current due to build-in field

Ferroelectric solar cell??
Photon flux $P = P(x,y,z) = \text{const.} \neq 0$ and $\Phi_1 = \Phi_2$.
Photon flux $P = P(x,y,z) = \text{const.} \neq 0$ and $\Phi_1 \neq \Phi_2$
Photon flux $P = P(x,y,z) = 0$ and $\Phi_1 = \Phi_2$ or $\Phi_1 \neq \Phi_2$
D: Photon flux $P = P(z) = P_0 \exp(-\mu z)$ and $\Phi_1 = \Phi_2$
Photon flux $P = P(z) = P_0 \exp(-\mu z)$ and $\Phi_1 \neq \Phi_2$
Inner Potential is more complicated

(a)

Current base line

Top and Bottom Current (nA)

Δ$I_{\text{top}}(+P_r)$

$I_{\text{top}}(+P_r)$

$L_2$

$L_3$

average

Δ$I_{\text{top}}(-P_r)$

$I_{\text{top}}(-P_r)$

$I_{\text{bot}}(+P_r)$

$I_{\text{bot}}(-P_r)$

Top and Bottom Current (nA)

Photon Energy (eV)

Photon Energy (eV)

Photon flux

(c)

$E_{C}(+P_r)$

$E_{C}$

$E_F$

$E_V$

$e\phi$

Pt

Top

PZT

$+P_r$

Pt

Bot

p-type PZT

hf
A Dielectric (non-ferroelectric) Capacitor

- Ferroelectric: PZT
- Metal
- Dielectric: SrTiO$_3$
- Metal
XAS on a non-ferroelectric SrTiO$_3$ Capacitor

Pt/SrTiO$_3$(180nm)/Pt

CSD: Th. Schneller, RWTH Aachen
Comparison of $-P_r$ and $+P_r$ spectra after 30 hours irradiation and O K-edge experiment.
$P$ vs. $E$ loops

Initial loop

After 10 hours

30 hours and O K-edge experiments
Photo Catalytic Reactions: Pt-TiO$_2$

May be present in our ferroelectric Caps after 30 hours of high flux, high energy irradiation and an internal electric field

Possible Experiments
Ferroelectric-Caps and Fatigue

Initial TEY spectra

Spectra after fatigue cycles
TEY set-up for Resistive Switching Devices

Photon source

Radiation on entire top electrode

Current transport only through filaments

SRO/PZT/Pt
J. Rodriguez-Contreras
PhD Thesis 2003, Cologne

TEY spectra will contain information from the filament interfaces
In situ study of electrochemical processes by SXES

J. Guo - ALS Beam Line 8

Discharging

Charging

SR

Li+ conducting electrolyte

LiMO

Cu electrode

Li+ acceptor

Al electrode

SXES

SR

Li ion acceptor

Al electrode

SXES
PEEM on biased capacitors: Photon-in - Electron-out Experiment

Photon source

2 nm top electrode (a technical challenge)

Ferroelectric

PEEM microscope

BL 7: PEEM II
Andreas Scholl
Andrew Doran

P vs. E analyzer

Interface sensitive