Transparent Conductors
Part II

Prof. Tom Mason
Northwestern University
Materials Science & Engineering
Conclusions

• With the exception of ZnO, the best TCOs are high octahedral site density crystal structures
• They are n-type only
• The “basis” cations are In, Sn, Zn, Cd and Ga
• Their defect chemistries can be complicated (not just oxygen vacancies)
• Phase diagrams play an important role
• If you can make a comparable p-type TCO...
An Introduction to TCOs

- What About p-Type TCOs
- The Importance of Work Functions
- The What and How of Work Functions
- Surface Science Definitions
- Work Function “Myths”
- Manipulating Work Functions
- Motivation for New TCOs
- Amorphous TCOs
- What the Future Holds

Transparency
(> 80% through visible spectrum for typical 1 µm thin film)

Conductivity (> 10^3 S/cm)
What About p-Type TCOs?
The Strategy of Kawazoe et al.

- Delocalize O-2p levels at the VBM through enhanced covalency
  - Quasi-tetrahedral coordination of oxygen by cations
  - Linear coordination of cations
- Chose d^{10} cations with energy levels close to that of O-2p

Linear cation TCO family

“delafossite” AMO$_2$

- Alternating layers of octahedra and Cu in linear coordination
- Two stacking sequences: rhombohedral and hexagonal
- p-type!

Band structure of CuAlO$_2$

CuAlO$_2$ Single Crystal Electrical Results

- Band Conductor

- Relatively low, anisotropic mobilities
  - $ab$-plane: 3.0 cm$^2$ V$^{-1}$ s$^{-1}$
  - $c$-direction: 0.12 cm$^2$ V$^{-1}$ s$^{-1}$

- Tough to dope!

# Review of literature data for delafossites

<table>
<thead>
<tr>
<th></th>
<th>$\sigma$ (S/cm)</th>
<th>%T (visible)</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuYO$_2$:Ca$^{(1)}$</td>
<td>1.0</td>
<td>40-50 (250 nm)</td>
<td>3.5</td>
</tr>
<tr>
<td>CuScO$_2$ $^{(2)}$</td>
<td>15-30</td>
<td>40 (110 nm)</td>
<td></td>
</tr>
<tr>
<td>CuGaO$_2$ $^{(3)}$</td>
<td>$6.3 \times 10^{-2}$</td>
<td>80 (500 nm)</td>
<td>3.6</td>
</tr>
<tr>
<td>CuInO$_2$:Ca $^{(4)}$</td>
<td>$2.8 \times 10^{-3}$ (p)</td>
<td>3.9</td>
<td></td>
</tr>
<tr>
<td>CuInO$_2$:Sn $^{(5)}$</td>
<td>$3.8 \times 10^{-3}$ (n)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuAlO$_2$ $^{(5)}$</td>
<td>16</td>
<td>32-52 (120 nm)</td>
<td>3.6</td>
</tr>
</tbody>
</table>

A New Approach: Non-$d^{10}$ Cations
d^6 p-TCOs: Spinels

Normal II-III Spinels:

\[ \text{O}_n \text{ site (e.g., Rh, Cr, Co)} \]

\[ \text{A}^{+\text{II}} \text{B}_{2}^{+\text{III}} \text{O}_4 \]

\[ \text{T}_d \text{ site (e.g., Zn, Mg, Mn)} \]

Yellow: Tetrahedral (T_d)  Blue: Octahedral (O_h)

Vertices of each polyhedron are oxygen anions.

http://phy.bris.ac.uk
d⁶ p-TCOs: Spinels

Crystal field splitting gives rise to transparency.
Transmission Data for ZnM$_2$O$_4$
(M = Ir, Rh, Co)

### Electrical Data for $d^6$ Spinels

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\sigma$ (S/cm)</th>
<th>$E_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnIr$_2$O$_4$</td>
<td>3.39</td>
<td>2.97</td>
</tr>
<tr>
<td>ZnRh$_2$O$_4^{(1)}$</td>
<td>2.75</td>
<td>2.74</td>
</tr>
<tr>
<td>ZnCo$_2$O$_4^{(1)}$</td>
<td>0.39</td>
<td>2.26</td>
</tr>
<tr>
<td>ZnCo$_2$O$_4$:Mg$^{(2)}$ (bulk)</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

Low conductivities attributed to small hole mobilities!

---

Hall Effect: 17 T and 0.58 T
Hall mobility at room temperature

\[ R_{xy} = \frac{B}{p ed_{xy}} \]

\[ p = 1.4 \pm 0.3 \times 10^{20} \text{ cm}^{-3} \]
\[ \sigma = 4.0 \text{ S/cm} \]
\[ \mu = 0.18 \text{ cm}^2/\text{V.s} \]

ZnRh\(_2\)O\(_4\)

Zn-Co-O is a Good Hole Transport Layer (HTL) for OPV

In collaboration with A. Sigdel, N.E. Widjonarko and J.J. Berry – CIS:SEM EFRC

Performance comparable to PEDOT:PSS on the first try!
Back to n-Type TCOs:
The Importance of Work Functions
The Need for Ohmic Contacts

- TCOs play an integral role as electrically transparent contacts in solar cells.
- Device performance depends on Ohmic contacts with electrodes.
- Contact type depends on band alignment between layers.

Organic Photovoltaic (OPV)

- Anode (TCO)
- Active Layer (organic)
- Cathode

Photons
What is the Work Function?
How is it Measured?
Photoelectron Spectroscopy

$$E_{BE} = h\nu_{\text{source}} - E_{\text{kinetic}} - \Phi_{\text{analyzer}}$$
XPS Survey Spectra

[Graph showing different spectra for Reduction, Oxidation, and As-Deposited states, with peaks labeled for In MNN, Zn 2p, O KLL, Sn 3p, In 3p, O 1s, Sn 3d, In 3d, In & Sn 4p, and In & Sn 4s]
UV Photoelectron Spectroscopy

$WF = h\nu - SEC$

Valence Band Offset

$E_F$

$E_{vac}$
In Situ Photoelectron Spectroscopy

Technical University of Darmstadt (Darmstadt, Germany)
Kelvin Probe WF Measurements

Kelvin Probe Method

Under ambient conditions!
Zn-In-Sn-O System

\[ \text{In}(2-2x)\text{Sn}_x\text{Zn}_x\text{O}_3 \]

\[ x = 0-0.40 \ (\text{ZITO}) \]

\[ \text{In}_2\text{O}_3(\text{ZnO})_k \]

\[ \text{T} = 1275 \ ^\circ \text{C} \]

Zn-In-Sn-O System

$\text{In}_{2-2x}\text{Sn}_x\text{Zn}_x\text{O}_3$

$x = 0-0.40$ (ZITO)

$\text{In}_2\text{O}_3(\text{ZnO})_k$

$T = 1275 \, ^\circ\text{C}$

Comparison of KP and UPS

![Graph showing comparison of KP and UPS with different k values.](chart.png)
Some Surface Science Definitions
Some Basic Definitions

- $E_{\text{vac}} = \text{vacuum level}$
- $E_F = \text{Fermi level}$
- $E_{\text{CBM}} = \text{conduction band minimum}$
- $E_{\text{VBM}} = \text{valence band maximum}$
- $E_{g0} = \text{fundamental band gap}$
- $\Delta E_g = \text{Burstein-Moss shift}$
- $I_p = \text{ionization potential}$
- $(E_F - E_{\text{VBM}}) = \text{Fermi level position}$
- $WF = \text{work function (}\Phi\text{)}$
Debunking Work Function Myths
TCO Work Function Myths

• Every material has a unique work function

• The work function of a given oxide’s surface is a constant

• The only way to change the work function of an oxide surface is “extrinsically” (e.g., by surface adsorbates)*

Manipulating Work Functions
How to Modify Work Function?

- Two ways:
  - Shift the Fermi level position
    \[(E_F - E_{VBM})\]
    can change independently with doping
  - Change the Ionization potential
    \[(E_{vac} - E_{VBM})\]
    can change independently with surface dipole changes (assuming \(E_g\) is constant)
Ionization Potential Plots

\[ I_p = (E_F - E_{VBM}) + WF(\Phi) \Rightarrow WF(\Phi) = I_p - (E_F - E_{VBM}) \]
Changing Fermi Level Position

Burstein-Moss Shift (ITO)

\[ \text{IP} = (E_F - E_{VB}) + \text{WF} \]

ITO Defect Chemistry

\[ \log [ (2\text{Sn}_{\text{In}} \cdot \text{O}_i^{-})^x ] \]

\[ \log pO_2 \]

\[ n = 2[V_O^{-}] \]
\[ n = [\text{Sn}_{\text{In}}^{-}] \]
\[ n = [\text{Sn}_{\text{In}}^\cdot] \]
How to Modify Work Function?

- Two ways:
  - Shift the Fermi level position
    \((E_F - E_{VBM})\)
    can change independently with doping
  - Change the Ionization potential
    \((E_{vac} - E_{VBM})\)
    can change independently with surface dipole changes (assuming \(E_g\) is constant)

\(\text{EF Shifts (In}_2\text{O}_3)\)

\(\text{Vacuum} \uparrow \text{Vacuum} \uparrow \text{EF} \uparrow \text{CB} \uparrow \text{Sn defect band} \uparrow \text{EF} \uparrow \text{VB} \)
## Surface Orientation Effects

### Silver

<table>
<thead>
<tr>
<th>Surface</th>
<th>Work Function</th>
<th>Polycrystalline Work Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (111)</td>
<td>4.74 eV</td>
<td></td>
</tr>
<tr>
<td>Ag (100)</td>
<td>4.64 eV</td>
<td></td>
</tr>
<tr>
<td>Ag (110)</td>
<td>4.52 eV</td>
<td></td>
</tr>
<tr>
<td>Au(poly)</td>
<td>4.26 eV</td>
<td></td>
</tr>
</tbody>
</table>

### Gold

<table>
<thead>
<tr>
<th>Surface</th>
<th>Work Function</th>
<th>Polycrystalline Work Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au (111)</td>
<td>5.31 eV</td>
<td></td>
</tr>
<tr>
<td>Au (100)</td>
<td>5.47 eV</td>
<td></td>
</tr>
<tr>
<td>Au (110)</td>
<td>5.37 eV</td>
<td></td>
</tr>
<tr>
<td>Au(poly)</td>
<td>5.10 eV</td>
<td></td>
</tr>
</tbody>
</table>

Note: close-packed surfaces have high work functions; polycrystalline specimens represent averages with low-work function orientations.

ZnO-Surface Orientations

ZnO has polar and non-polar surface terminations

Red = ZnO
Blue = Al:ZnO

ZnO:Al Defect Chemistry

\[ n = [\text{Al}_{Zn}^\cdot] \]

\[ 2[V_{Zn}'''] = [\text{Al}_{Zn}^\cdot] \]

\[ \log[pO_2] \]

\[ \log[\cdot] \]

\[ [V_{Zn}'''] \]

\[ +1/2 \]

\[ -1/4 \]

S. Lany, A. Zunger, PRL, 98, 045501 (2007)
SnO$_2$ Surface Terminations

(110) Surface

(a)

(b)

(c)

Red = SnO$_2$

Blue = Sb:SnO$_2$

Green = Bulk Sb:SnO$_2$

SnO$_2$:Sb Defect Chemistry

\[ n = 2[V_{O}^{\cdots}] \]
\[ n = [\text{Sb}_{\text{Sn}}^{\cdot}] \]

\[ \log n \]

\[ \log pO_2 \]

ATO
TCO Work Function Truths

- The WF of an oxide surface decreases linearly as Fermi level increases (if IP remains constant).
- The IP (WF) of an oxide surface can be changed by dipole modifications—surface orientation, surface termination, surface stoichiometry—(if Fermi level remains constant).
- We can therefore change oxide surface work functions both “intrinsically” and “extrinsically”.*

Motivation for New TCOs
Why Do We Need New TCOs?

• Why do people use ITO?
  – Available
  – Good TCO (up to 10,000 S/cm conductivity, good transparency)

• Drawbacks to ITO
  – COST
    • In costs are volatile
  – STABILITY
    • ITO is etched by common barrier layer PEDOT:PSS
  – WORK FUNCTION
    • ITO work function is generally < 5eV
The Importance of TCOs in OPVs

- TCOs play an integral role as electrically transparent contacts in solar cells.
- Device performance depends on Ohmic contacts with electrodes.
- Contact type depends on band alignment between layers.

Organic Photovoltaic (OPV)

- Anode (TCO)
- Active Layer (organic)
- Cathode

Photons

The diagram illustrates the process of converting sunlight into electricity in an organic photovoltaic (OPV) device. Photons enter the active layer, which contains the organic material, and are converted into electrical energy. This energy is then transferred to the anode (TCO) and cathode, allowing the device to function as a solar cell.
TCOs in Traditional/Inverted Cells

Traditional Polarity

- Al
- Cathode interlayer
- Blend
- PEDOT:PSS
- ITO
- Glass

Want high work function: > 5eV
Want low work function: < 4eV
Both: Want high Fermi level (high conductivity)

Inverted Polarity

- Ag
- PEDOT:PSS
- Blend
- Metal oxide e.g. ZnO
- ITO
- Glass
The Zn-In-Sn-O System

$T = 1275 \, ^\circ C$

$\text{In}_2\text{O}_3(\text{ZnO})_k$

$\text{InO}_{1.5}$

$\text{Zn}_2\text{SnO}_4$

$\text{ZnO}$

$\text{SnO}_2$
ZITO (Zn,Sn co-substituted ITO) Surfaces

![Graph showing the relationship between work function [eV] and \(E_F-E_{VB}[eV]\) with lines corresponding to IP=7.0 eV, IP=7.7 eV, and IP=8.1 eV.]

Two-Step Processing
C-ZITO Bulk Structure: Bixbyite

\[ \text{In}_2\text{O}_3 \]

bixbyite = fluorite with \( \frac{1}{4} \) of the anions missing

Two different cation positions

Structural oxygen interstitial positions

Blue = oxygen
Yellow = indium

• High $\mu_O$ can produce a high $\text{In}_2\text{O}_3$ work function on a peroxidized (100) surface)

• Polycrystalline materials will exhibit inhomogeneous surface work functions: “hot spots,” “cold spots”

M.V. Hohmann et al., J. Phys.: Condens. Matter 23 (2011) 334203
Predicted Ionization Potentials

- Ionization potentials –
  - Vary little on (111) and (110) surfaces
  - Vary greatly on (100) surface
    - Metallic termination = low ionization potential
    - Oxide termination = high ionization potential

M.V. Hohmann et al., J. Phys.: Condens. Matter 23 (2011) 334203
In$_2$O$_3$ Surfaces

\[ \text{work function [eV]} \]

\[ (E_F - E_{VBM}) [\text{eV}] \]

\[ \text{In}_2\text{O}_3 \]

\[ I_P = 8.1 \text{ eV} \]

\[ I_P = 7.6 \text{ eV} \]

\[ I_P = 7.0 \text{ eV} \]
Two-Step Processing
Parallelogram Plots

• **Left side:**
  Fundamental Band-gap

• **Right side:**
  maximum Burstein-Moss shift

• **Top and bottom:**
  achievable ionization potential ranges

- ITO: Tin-doped In$_2$O$_3$
- ZITO: Zn,Sn-doped In$_2$O$_3$
- ATO: Sb-doped SnO$_2$
- AZO: Al-doped ZnO
- IZO: In$_2$O$_3$(ZnO)$_k$

Amorphous TCOs
Advantages of Amorphous TCOs

• Easier, cheaper processing
  – Low temperature
  – Flexible substrates
  – Better etching characteristics

• Smoother surfaces

• Wide composition range
  – Minimization of toxic/expensive elements

• No hot/cold spots
Amorphous ZITO TCOs

$T = 1275 \, ^\circ\text{C}$

$\text{InO}_{1.5}$

$\text{ITO}$

$\text{In}_{(2-2x)}\text{Sn}_x\text{Zn}_x\text{O}_3$

$x = 0-0.40$ (ZITO)

$\text{In}_{2}\text{O}_3(\text{ZnO})_k$

$\text{ZnO}$

$\text{SnO}_2$

Why a-TCOs Have Good Properties

- Conventional Semiconductor (silicon)
  - Crystalline
  - Amorphous

- Traditional TCO (indium oxide)
  - Crystalline
  - Amorphous

Pulsed Laser Deposited a-ZITO Films

- **mobility (cm²/V·s)**
  - 50
  - 40
  - 30
  - 20
  - 10
  - 0

- **Carrier Conc. (cm⁻³)**
  - $10^{21}$
  - $10^{20}$
  - $10^{19}$
  - $10^{18}$
  - $10^{17}$
  - $10^{16}$

- **Conductivity (S/cm)**
  - 1600
  - 1200
  - 800
  - 400
  - 0

- **PO₂ (mTorr)**
  - 0
  - 2
  - 4
  - 6
  - 8
  - 10
  - 12
  - 14
  - 16
  - 18

- **Deposition Temperature**
  - 25°C
  - 200°C
  - 400°C

- **In₂O₃: No cosubstitution**
- **ZITO-30: 30 at.% cosubstituted**
- **ZITO-50: 50 at.% cosubstituted**
- **ZITO-70: 70 at.% cosubstituted**
How a-ZITO Compares

Red symbols: a-ZITO

$E_F - E_{VBM}$ (UPS) [eV]

D. E. Proffit et al., Thin Solid Films (submitted)
Ashby Plot of TCO Properties

Rs (Ω/sq)

Work function (eV)

log (Rs (Ω/sq))

ATO: Sb-doped SnO₂
ITO: Sn-doped In₂O₃
AZO: Al-doped ZnO
CNT: Carbon nanotube
ZITO: Zn,Sn codoped In₂O₃
What the Future Holds
Pulsed Laser Deposited a-ZITO Films

- **In$_2$O$_3$**: No cosubstitution
- **ZITO-30**: 30 at.% cosubstituted
- **ZITO-50**: 50 at.% cosubstituted
- **ZITO-70**: 70 at.% cosubstituted
Application of ZITO TCO & TOS for FETs

TCO ZITO-30 used for Gate, Source & Drain
TOS ZITO-30 used for Channel Layer

On plastic substrate to form all amorphous, flexible, transparent FET

ZITO Films Grown at Room Temperature by PLD
Conclusions

• TCO work functions can be modified “intrinsically” through:
  – Fermi level shifts (via donor doping—defect chemistry plays a vital role!)
  – Surface dipole modifications by:
    • Changing surface orientations (e.g., Al-doped ZnO)
    • Altering surface terminations (e.g., Sb-doped SnO₂)
    • By changing surface stoichiometry (e.g., peroxidation, Sn-doped In₂O₃ or ITO, Zn,Sn-cosubstituted In₂O₃ or ZITO)
Conclusions (cont’d)

• Work function vs. Fermi level “parallelogram plots” allow comparison of candidate TCOs for OPV applications
  – AZO (Al-doped ZnO) or alternatives (Ga-doped ZnO) are best for low work function applications, e.g., in inverted OPV designs
  – ZITO (Zn-In-Sn-O) or ATO (Sb-doped SnO$_2$) and alternatives (FTO, F-doped SnO$_2$) are best for high work function applications, e.g., in traditional OPV designs

• Amorphous TCOs exhibit work functions and Fermi levels comparable to their crystalline counterparts (e.g., ZITO)

• An emerging “frontier” for TCOs is as Amorphous Oxide Semiconductors (AOSs)