Transparent Conductive Oxides (TCOs)

Ecole Polytechnique Fédérale de Lausanne
PV-Lab

Transparent Conductive Oxides (TCOs)

- Materials that transmit light and conduct electrical current simultaneously.
- Application: transparent electrode in optoelectronic devices.

Display

Touch screens

TFTs

Lighting

OLEDs

Energy Harvesting

Low e-windows

Photovoltaics

F.-J. Haug

TCO application example: OLEDs

1. High electrical conductivity:

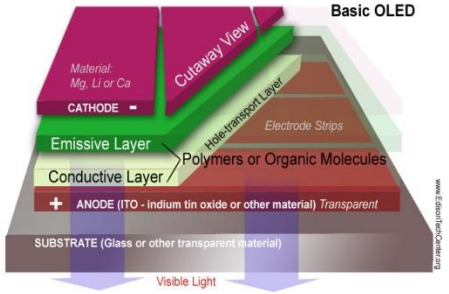
Cathode: Low work function for electron injection

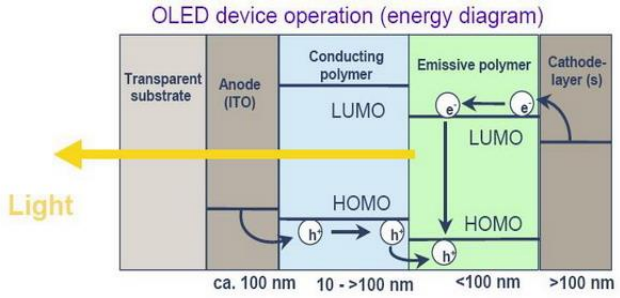
Anode: High work function for hole injection.

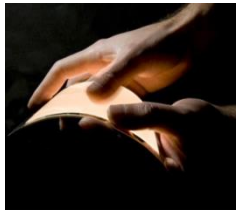
2. High optical transmittance in the visible range (for light extraction)

3. Low surface roughness (to avoid shunts through the thin organic layer)

4. Uniformity (layer thickness and R_{sh}) to ensure uniform luminosity.

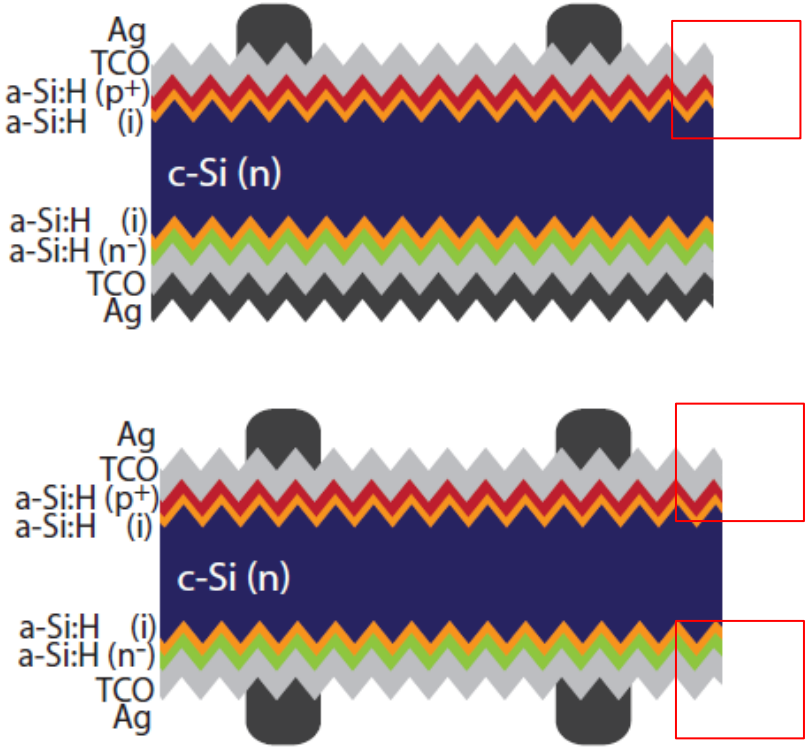






TCO application example: solar cells

Front TCO requirements in silicon heterojunction (SHJ) solar cells

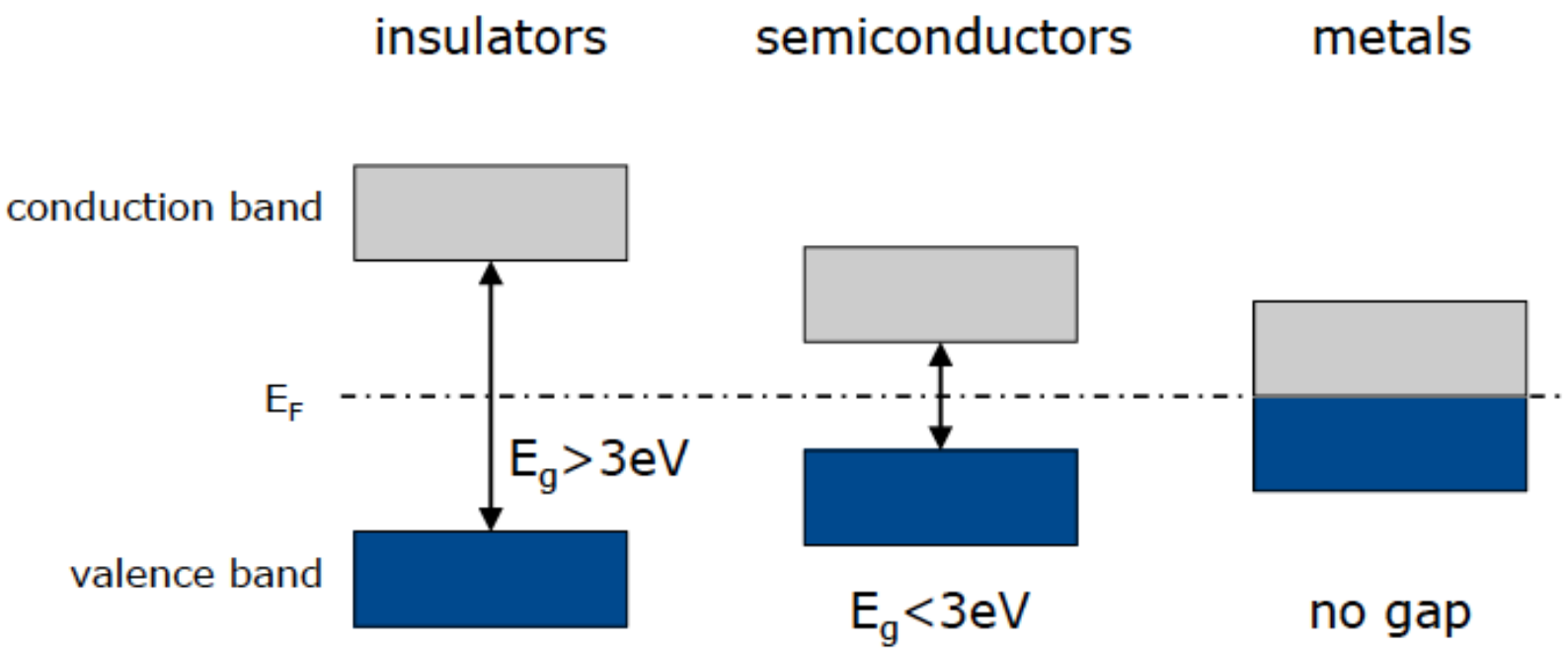


- High lateral electrical conductivity.
- Low optical absorption from the UV to the infrared (IR).

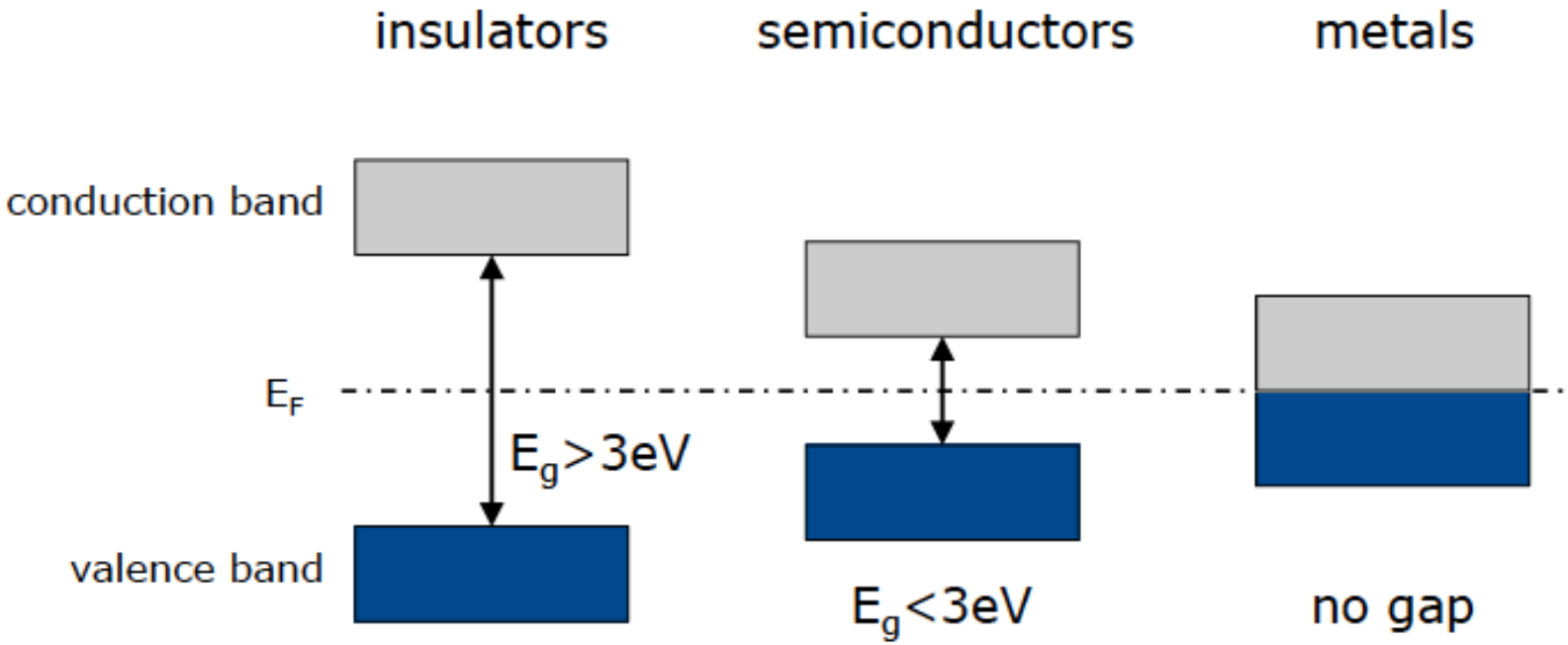
$$\uparrow \sigma = e n \mu \uparrow$$

- Low contact resistance with the adjacent layers.
- Appropriate refractive index for maximal light in-coupling.
- Deposition at low temperature (< 200 °C) and w/o damage to layers below

Semiconductors

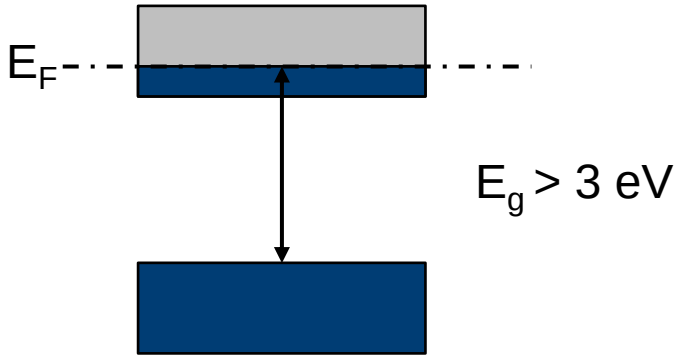


Semiconductors



Transparent Conductive Oxides (TCOs):

Degenerate semiconductors (CB resembles a metal)



Semiconductors

Transparent Conductive Oxides (TCOs):

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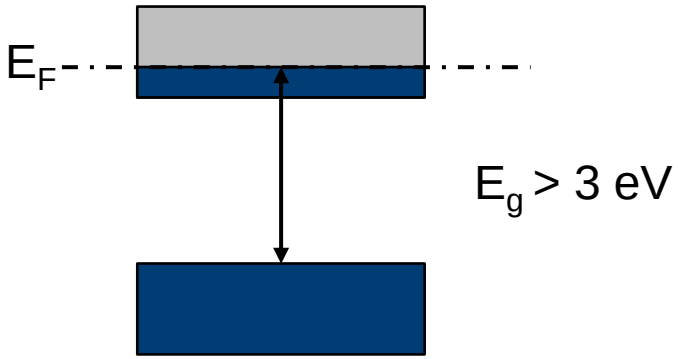
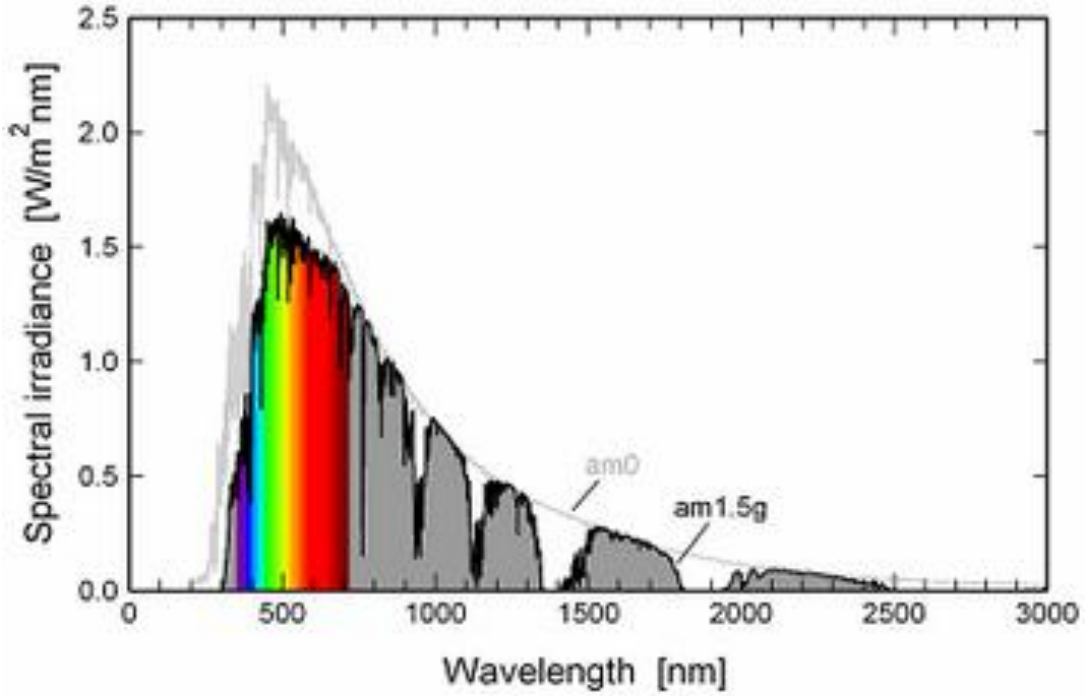




Transparent for wavelengths $\lambda < 1241[\mathrm{nm}]/E_g[\mathrm{eV}]$

Basic properties of TCOs

Transparency for visible light

=> Require semiconductor with bandgap > 3 eV
=> e.g. metal oxides

Key attribute of n-type TCOs: Highly dispersive conduction band (CB).

=> High mobility of the carries (electrons) due to their small effective mass m^*
remember: $m^* = (d^2E(k)/dk^2)^{-1}$

=> Large dispersion due to the low density of states $g(E)$
remember: $g(E)dE = \frac{8\sqrt{2}\pi {m_e^*}^{3/2}}{h^3}(E - E_C)^{1/2}dE$

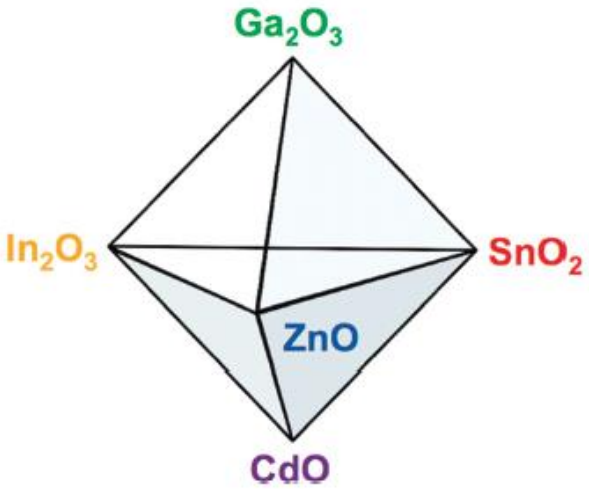
TCO material system

n-type TCOs
(electrons as majority carriers)

TCOs evolved from
individual (binary) oxides
to
multi-compound
and alloy mixtures

p-type TCOs:
Cu_2SrO_2, etc., difficult to achieve

Conventional TCO composition space



Ref. Pasquarelli *et al*. Chem. Soc. Rev **40**, 2011

TCO materials system: ‘conventional’ TCOs

Oxide	Dopants
In_2O_3	Sn^{4+} replacing In^{3} (**ITO**)
ZnO	Al^{3+} (**AZO**), Ga^{3+} (**GZO**)
	B^{3+} (**BZO**), replacing Zn^{2+}
SnO_2	F^{-1} replacing O^{-2} (**FTO**),
	Sb^{5+} replacing Sn^{4+}

Conventional TCO composition space

Ref. Pasquarelli *et al*. Chem. Soc. Rev **40**, 2011

TCO materials system: ‘conventional’ TCOs

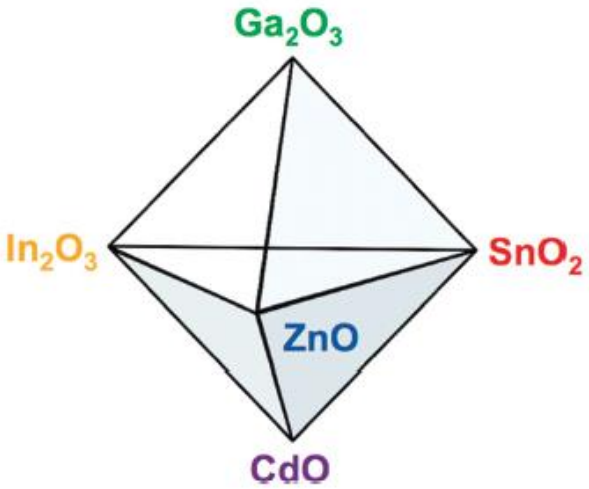
Oxide Dopants

In_2O_3 Sn^{4+} for In^3 (**ITO**)

Industry standard for optoelectr. applications

- ☑ Sputter-deposited: high-volume for large area coatings in rigid and plastic substrates
- ☑ Low thickness (~90nm) require to achieve good conductivity
- ☒ Indium: rare metal, expensive and limited in supply
- ☒ Brittle target materials

Conventional TCO composition space



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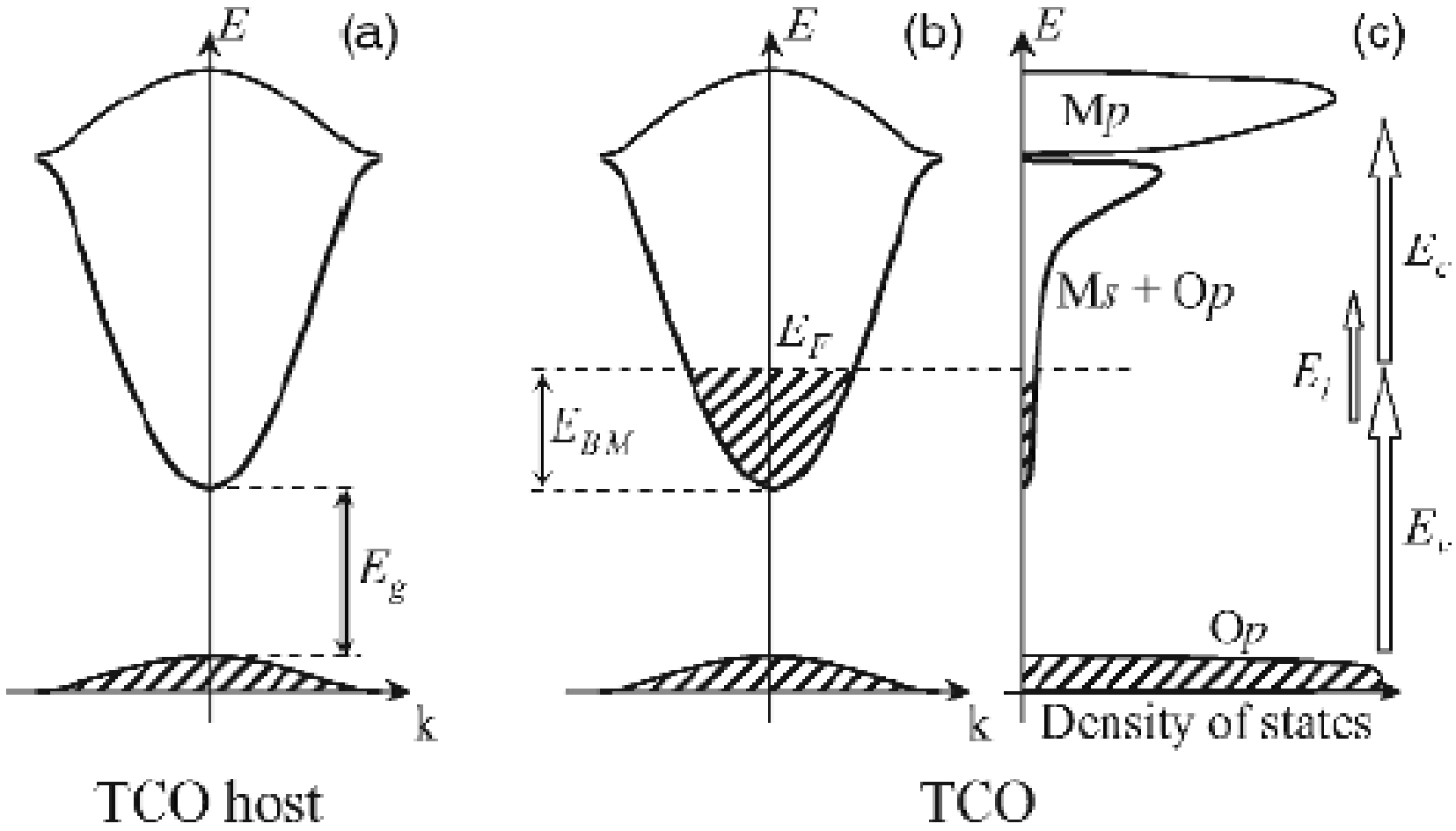
SnO_2	F^{-1} for O^{-2} , Sb^{5+} for Sn^{4+} (**FTO**)

- ☑ All n-type wide band gap semiconductors (> 3 eV)
- ☑ Earth-abundant materials
- ☑ Transparent in the VIS and NIR
- ☑ Conductive
- ☒ Polycrystalline nature (brittle, grain boundaries)

Basic properties of TCOs

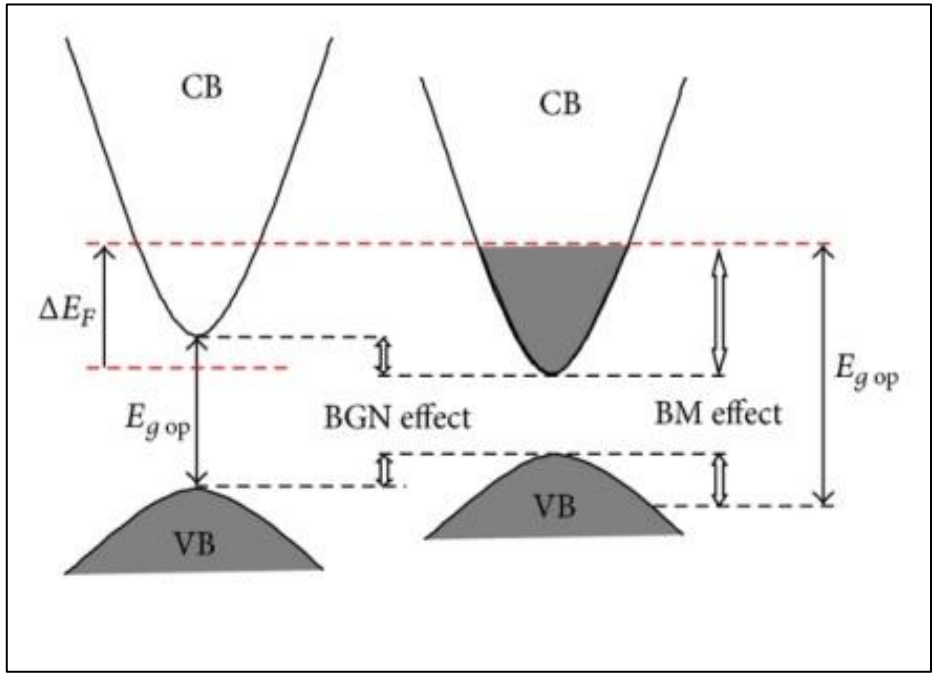


Ch. 1. Book. Transparent Electronics: From Synthesis to Applications Edited by Antonio Facchetti and Tobin J. Marks. 2010 John Wiley & Sons, Ltd

Basic UV-properties of TCOs

High energy dispersion of the conduction band facilitates degenerate doping with Fermi energy displacement up above the CBM:

=> broadening of the optical transparency, called Burstein Moss (BM) shift



E_F rises into CB, optical transitions must go “higher up”

$\Delta E_g^{opt} \sim + n^{2/3}$

(Burstein Moss shift)

Also: band gap narrowing (BGN) due to cohesive energy of free carriers

$\Delta E_g^{SC} \sim - n^{1/3}$

Electrical properties

Electrical conductivity

$$\sigma = en\mu$$

n = carrier concentration (cm^{-3})

μ = mobility (cm^2/Vs)

e = electron charge (1.6 $x10^{-19}$ C)

σ < 5000 S/cm

high temperature ITO

(for metals σ ~10^5 S/cm)

μ = 10 - 100 cm^2/Vs

(for Cu: μ ~ 60 cm^2/Vs,

>200 cm^2/Vs for CdO)

n = 10^{15} – 10^{21} cm^{-3}

(for metals: N ~ 10^{22} cm^{-3})

↑ with doping

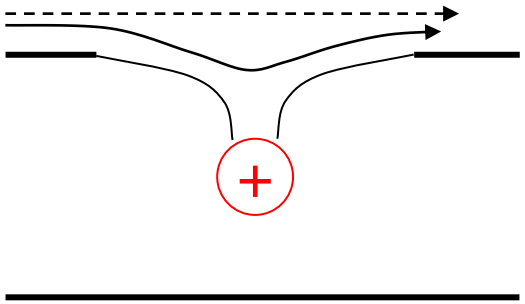
Experimentally accessible:

- mobility: material parameter, dependence on doping
- controllable, but very high doping can impair optical properties

Relation between μ and n

Impurity Scattering (intra-grain scattering)

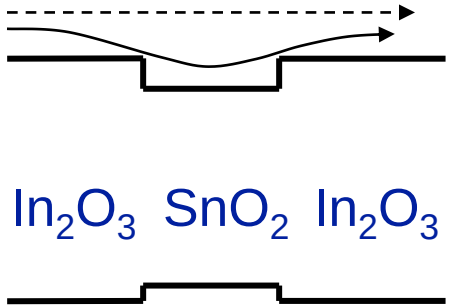
ionized impurity (dominating)



ionized dopants represent potential wells (~1/r)

higher doping:
=> more scattering sites
=> lower mobility

neutral impurity (illustrative)



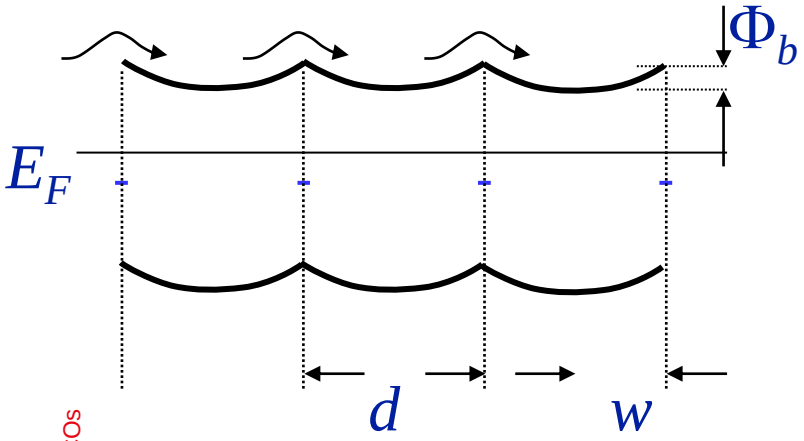
SnO_2 clusters can be imagined as square wells with different E_g

e.g. Ellmer, J. Phys. D, (2000)

Relation between μ and n

Grain Boundary Scattering (inter-grain scattering)

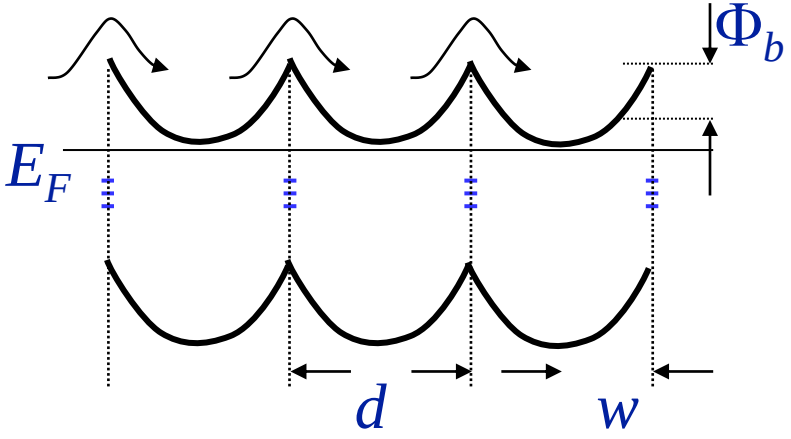
low doping



capture of free carries in surface states at boundaries:

=> depleted regions of GBs extend over full grain

intermediate doping

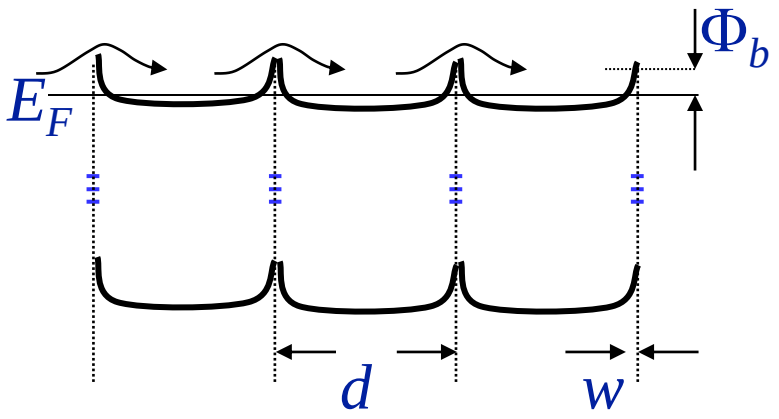


still full depletion,

but higher doping yields larger band bending

=> barrier increases with doping

high doping



all surface states filled,

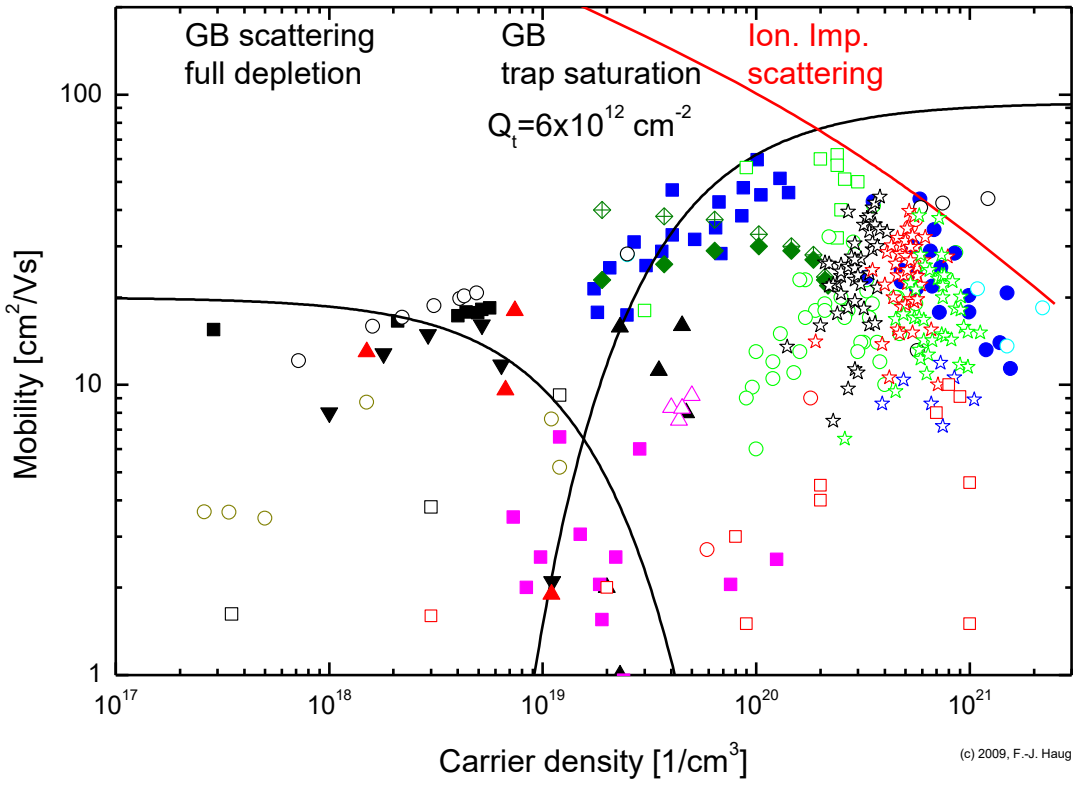
free carriers available within grains

=> barrier shrinks with doping

=> eventually tunnelling transport

Seto, J. Appl. Phys. (1975)

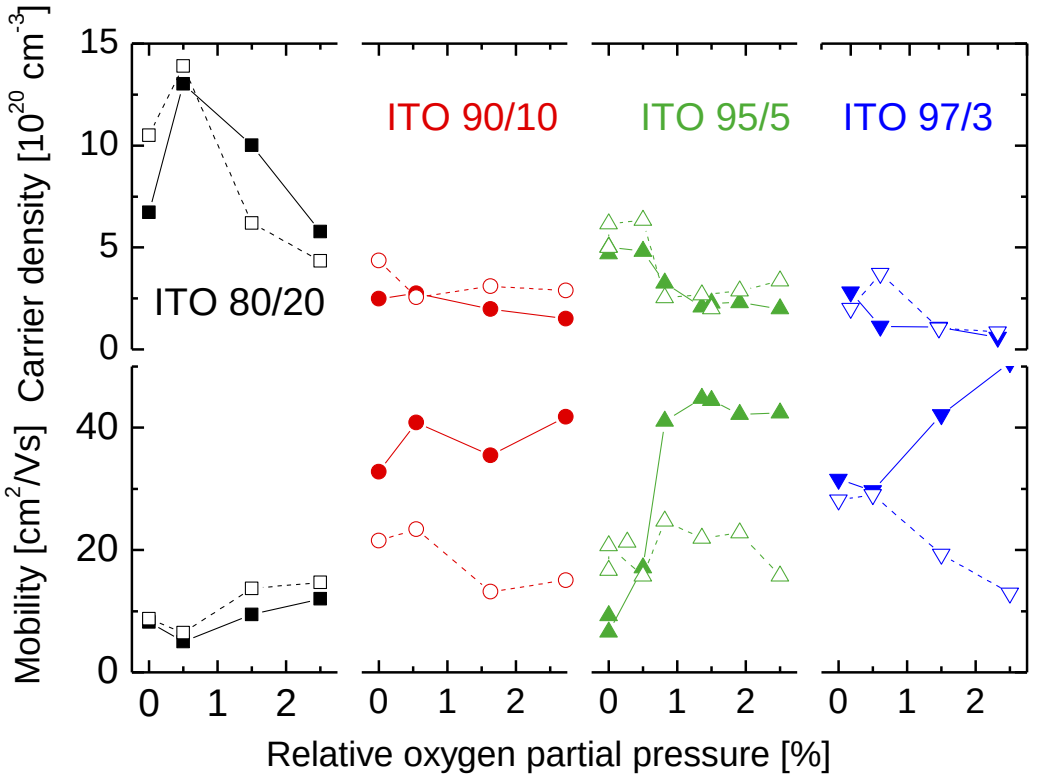
Example: ZnO and ZnO:Al



Global trend:

- transition between depleted/undepleted grain boundary regimes: ~10^{19} cm^{-3}
- higher doping: ionized impurity scattering above10^{20} cm^{-3}

ITO vs. composition and oxygen content



high carrier density:

- achieved by Sn doping or low oxygen content (V_O are donors)
- correlates with low mobility (impurity scattering)

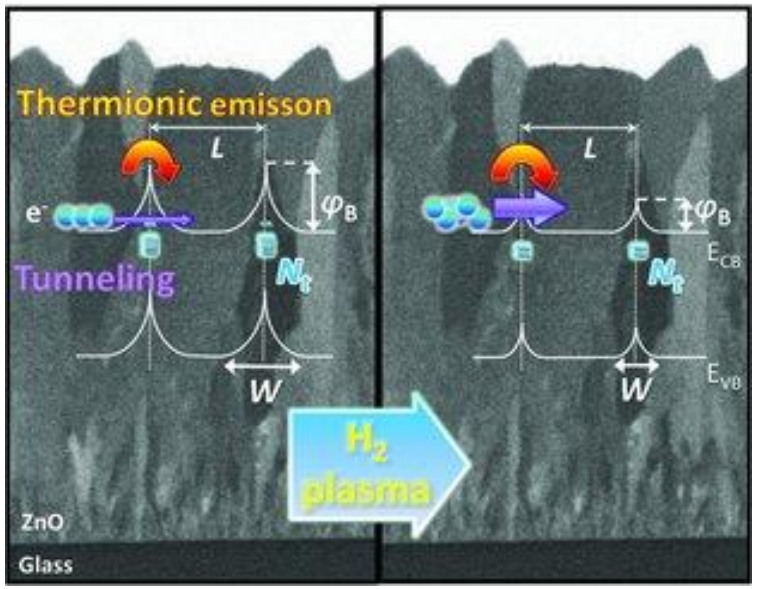
Polycrystalline vs. amorphous TCOs

Polycrystalline TCOs

Increase grain size

Passivation of GB

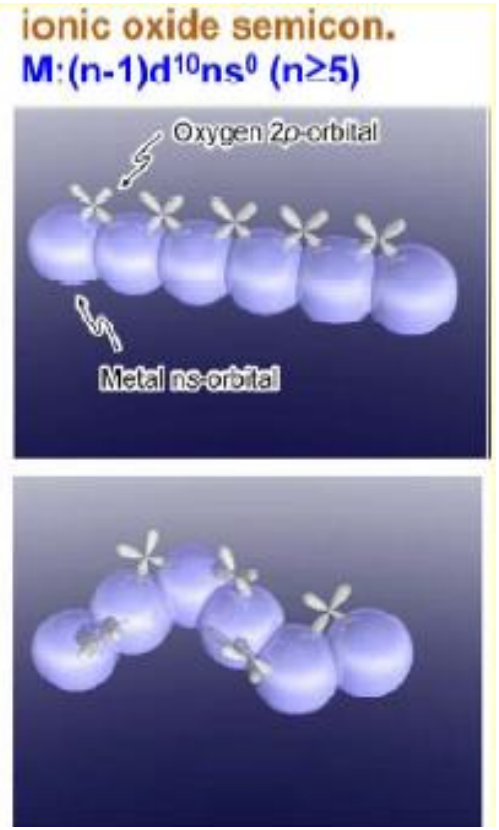
Ref. Ding *et al*. Adv.Func.Mat **23**, 2013



Amorphous TCOs

Increase overlap of s-orbitals of the metal ions

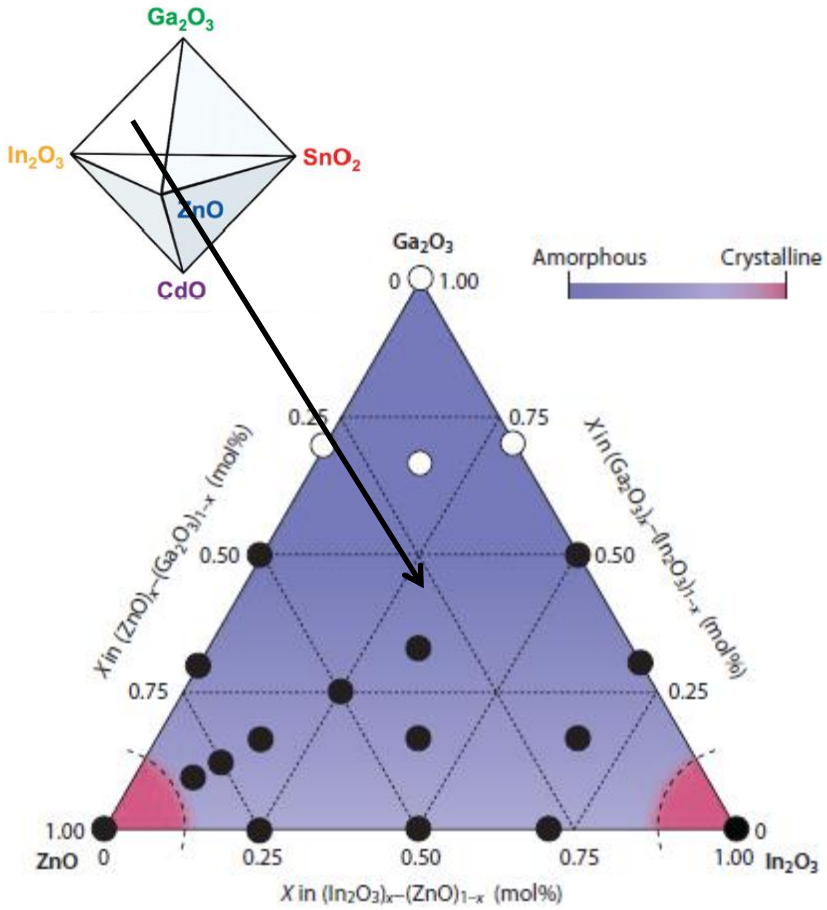
Ref. Hosono, J.Non Crystalline Sol. 352 (2006)



Applications

- TFT channel materials
- Low e coatings (purely optical)
- Carrier transport in solar cells

IGZO

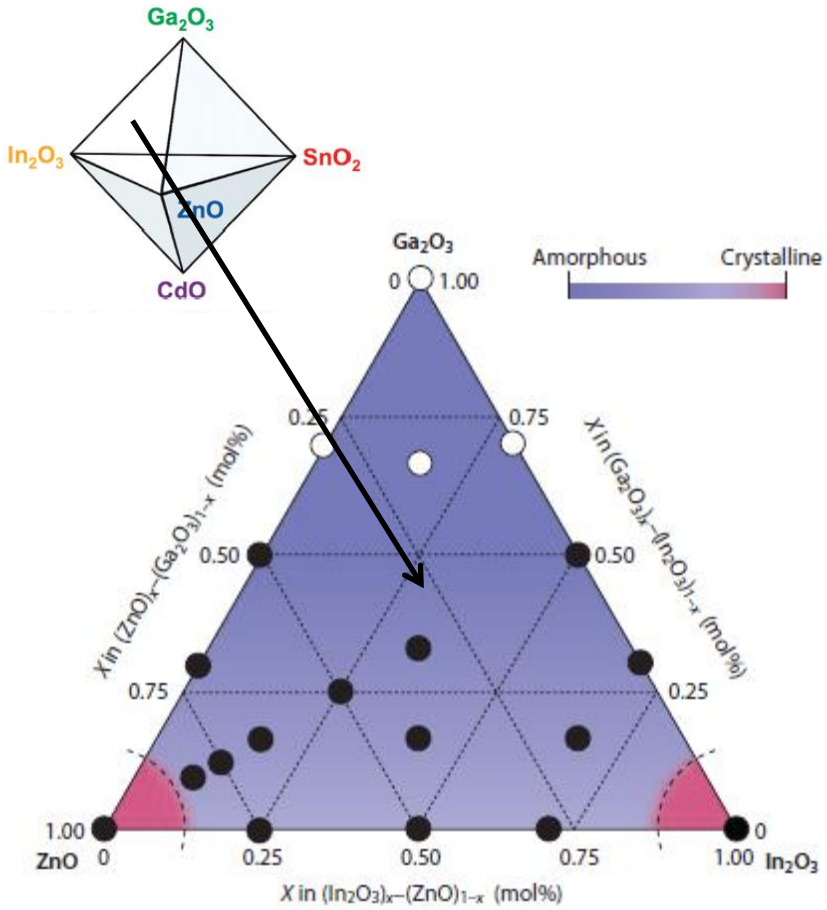


Multi-compound oxides

- ✓ amorphous materials. Very smooth surfaces (R_{RMS} < 0.5nm)
- ✓ low temperature deposition (as low as RT). Favorable for plastic substrates and flexible applications
- ✓ Comparable electrical and optical properties of crystalline TCOs.
- ✓ Mobility ~10cm^2/Vs (high compared to a-Si).

Alternative class: ZTO (Zn-Sn-O)

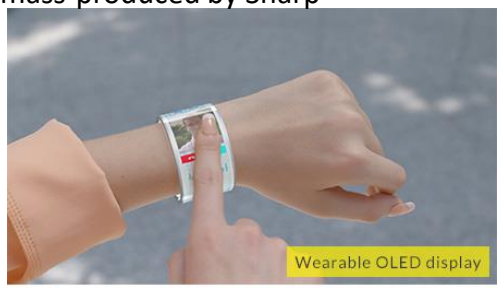
IGZO



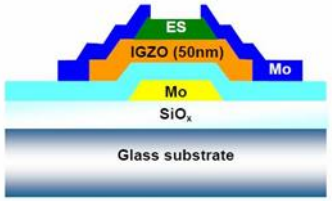
Ref. Kamiya et al. NPG Asia Mater **2** 2011
Ref. Pasquarelli *et al*. Chem. Soc. Rev **40**, 2011

In-Ga-Zn-O (IGZO)

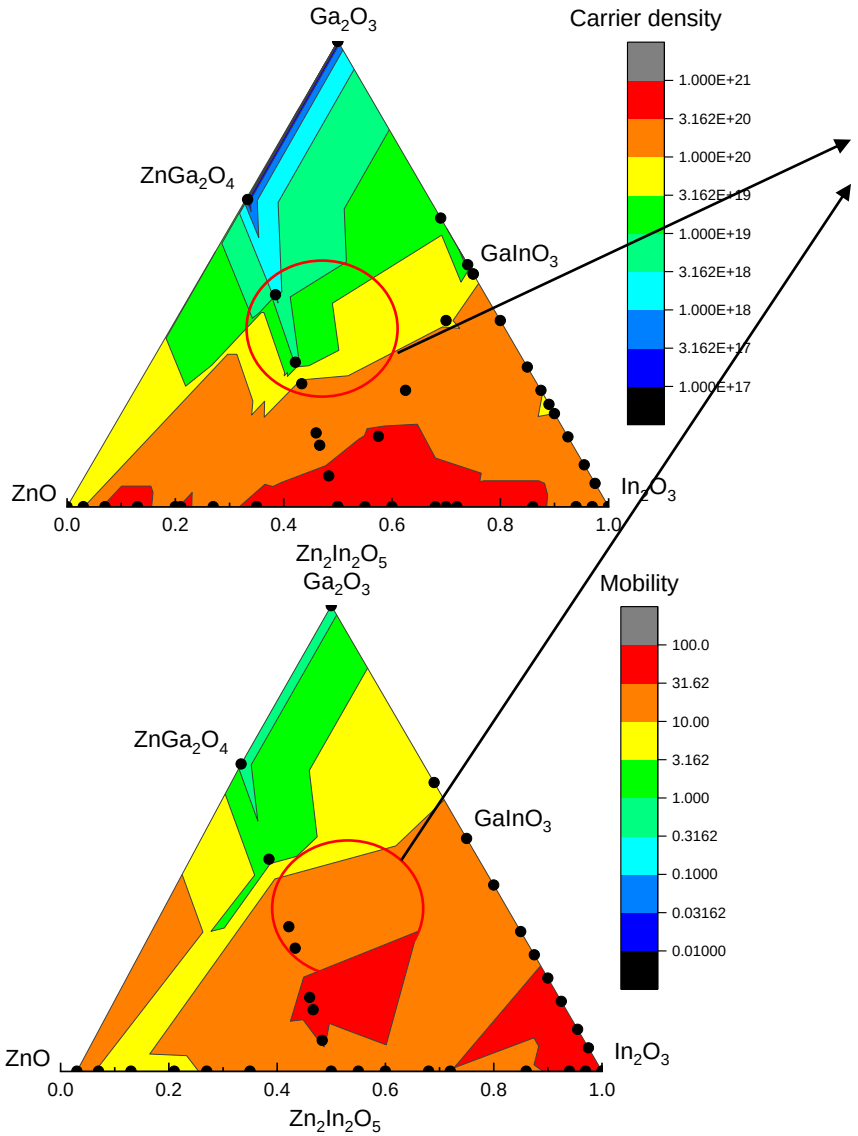
mass-produced by Sharp



Flexible AM-OLED

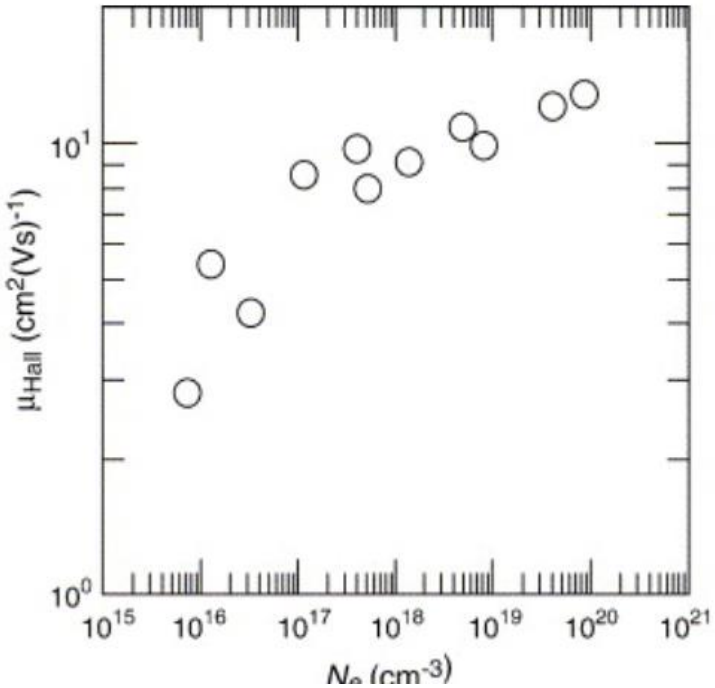


IGZO: n and μ vs. composition



Find composition with acceptable μ and
low intrinsic n (allow induced fields in TFT operation)

additional handle: play with oxygen content



$\mu(n)$: indicative of percolation/hopping

Minami, SCT (1999)

Takagi, TSF (2005)

Optical properties of free carriers – Drude model

$$\epsilon_m = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)}$$

$$= 1 - \frac{\omega_p^2 \tau^2}{1+\omega^2\tau^2} + i\frac{\omega_p^2\tau^2}{\omega\tau\cdot(1+\omega^2\tau^2)}$$

with plasma frequency $\omega_p = \sqrt{\frac{nq^2}{\epsilon_0 m^*}}$

asymptotic behaviour:

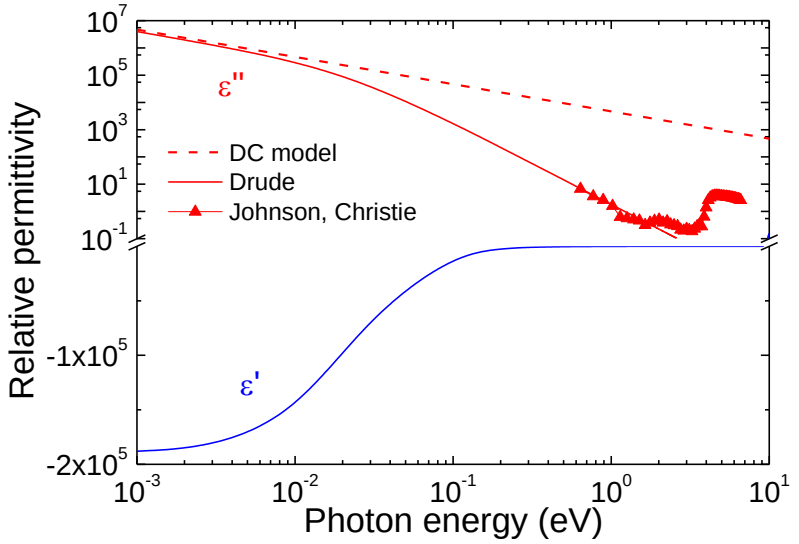
$\omega \to 0$:

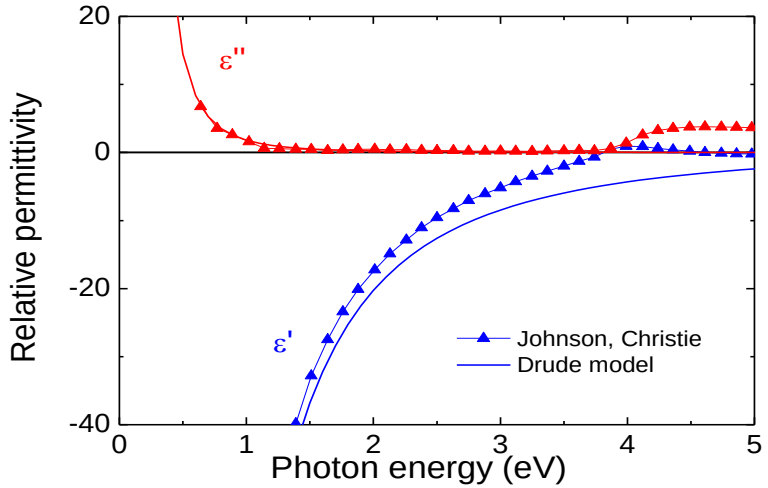
$$\epsilon_m \approx 1 - \omega_p^2\tau^2 + \frac{i\omega_p^2\tau}{\omega}$$

$\omega \gg \tau$:

$$\epsilon_m \approx 1 - \frac{\omega_p^2}{\omega^2}$$

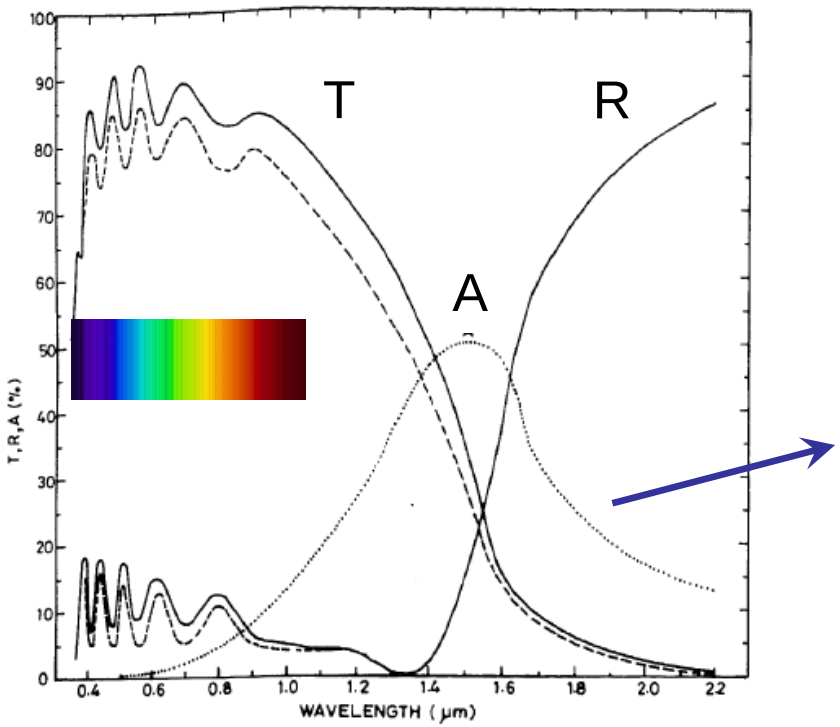
Example: Ag





IR properties of free carriers

In the NIR range:
=> reflective if $h\nu < \omega_p$
=> absorbing if $h\nu \approx \omega_p$ (*plasma frequency*)
=> transparent if $h\nu > \omega_p$



IR (heat) emission:

$$E = A_{FCA} \cdot E_{black\ body}$$

Different from glass, TCOs absorb little in the IR (high reflectivity)

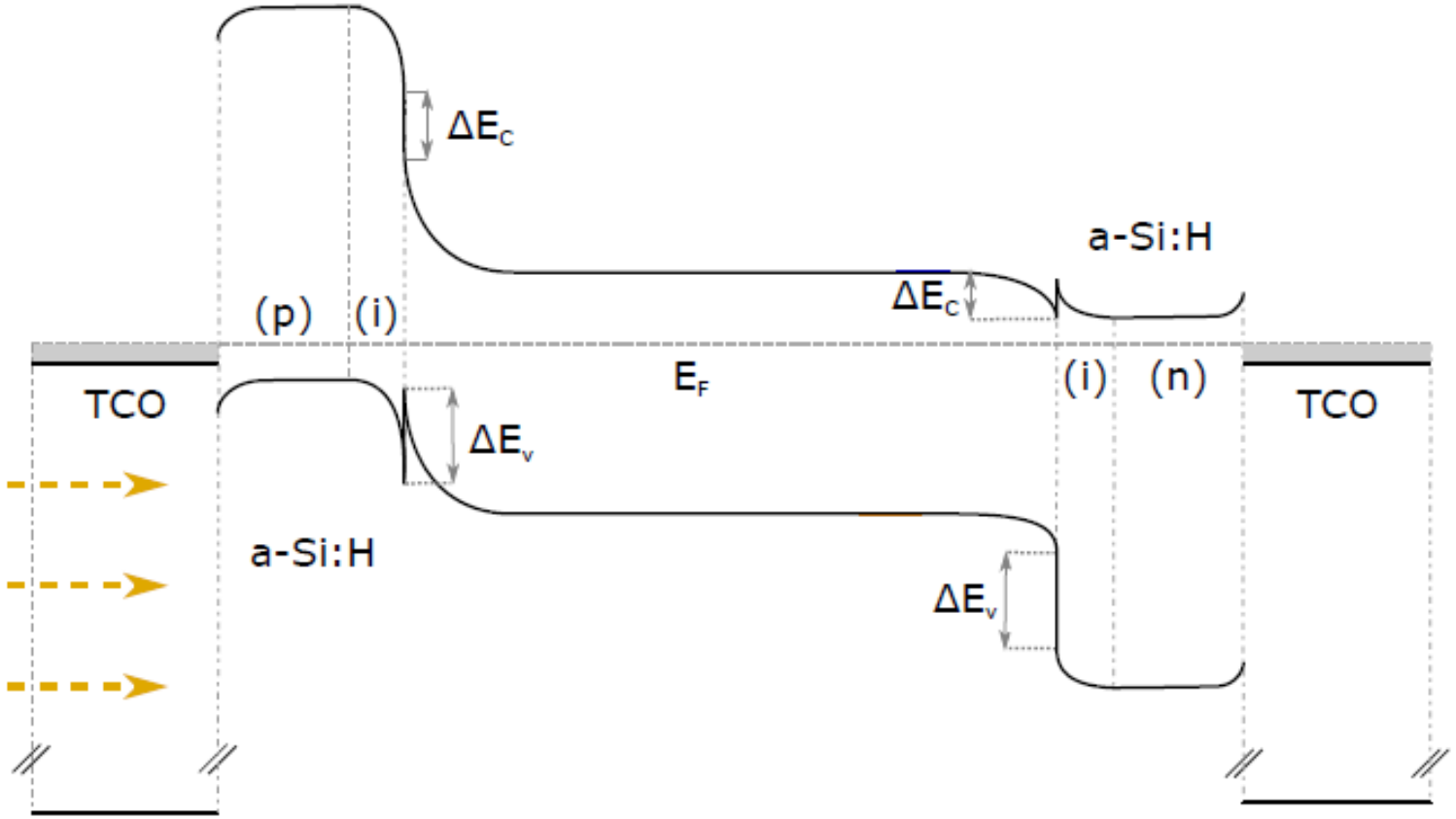
=> they are used as low-e coatings for insulating windows

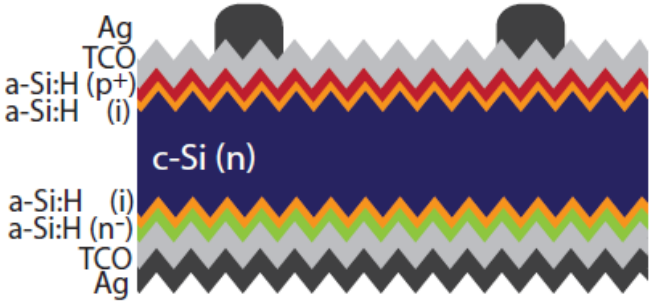
K. L. Chopra et al.,Thin Solid Films **102**, 1 (1983).

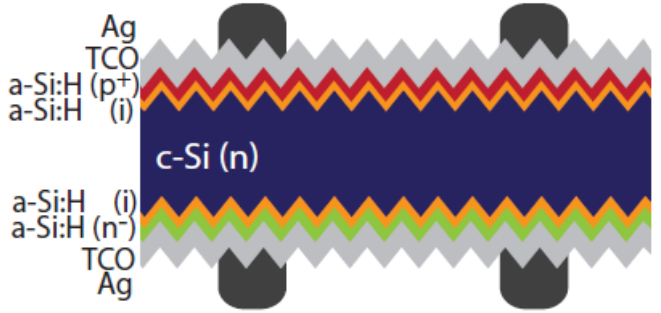
Carrier transport in solar cells

F.-J. Haug

example: silicon heterojunction solar cell (SHJ)





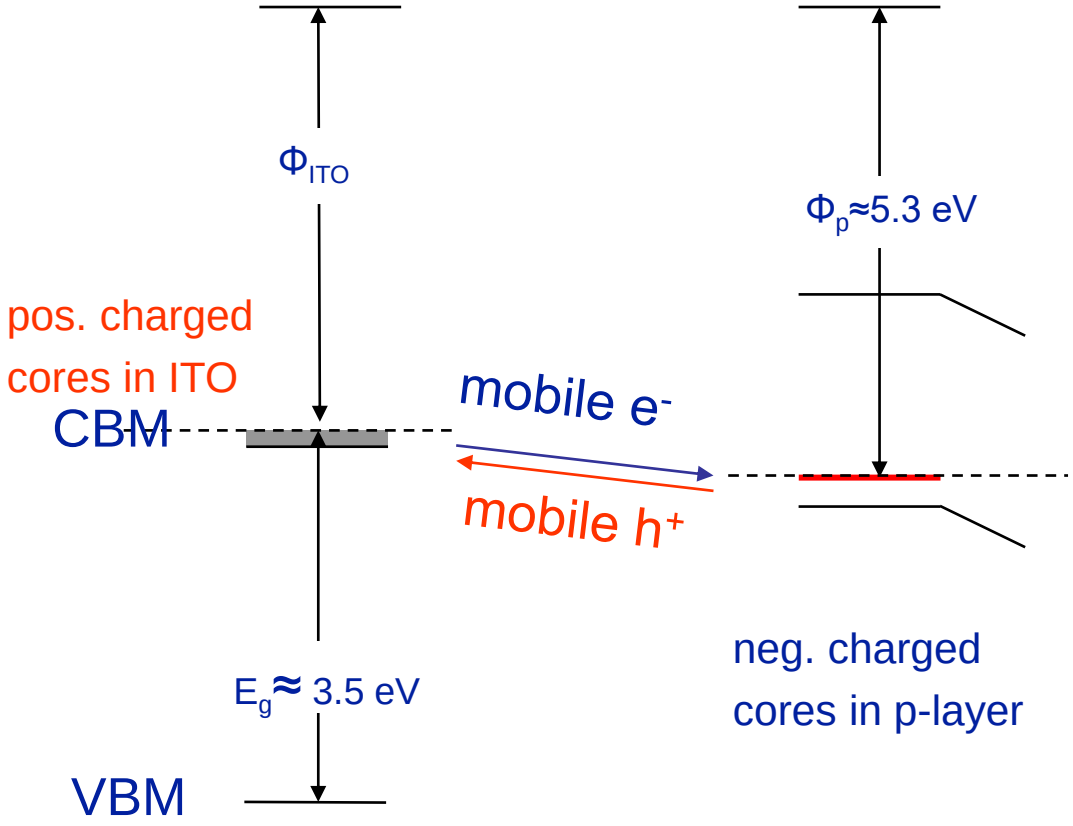


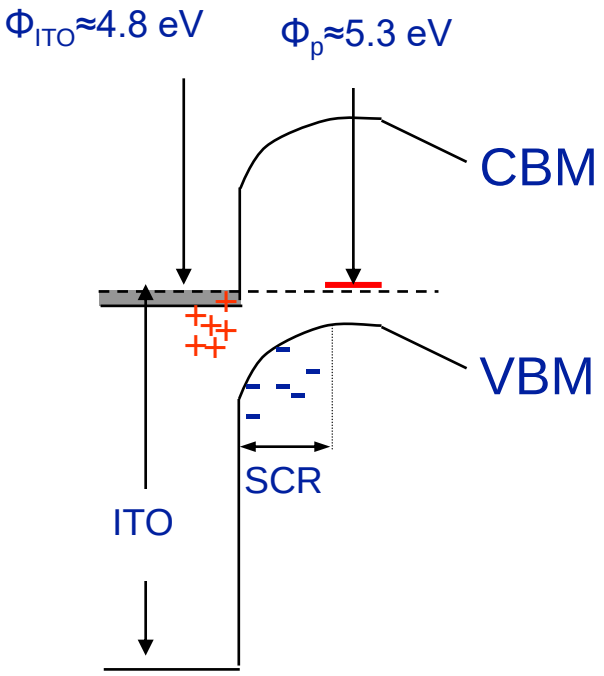
note: modern cells are bifacial, TCO at rear also needed for transport

TCO work function and Vbi

Junction between p-layer and TCO:

asymmetric p-n junction or Schottky junction (degenerate ITO)

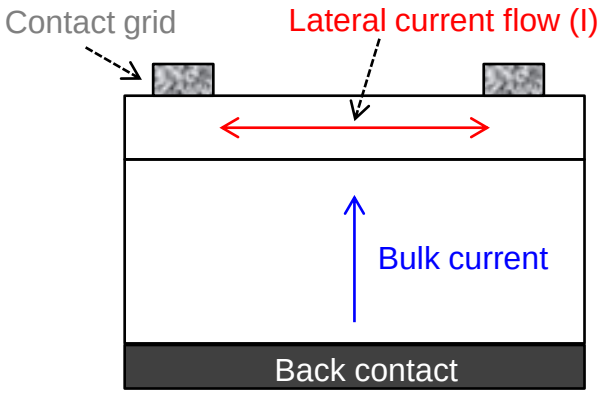




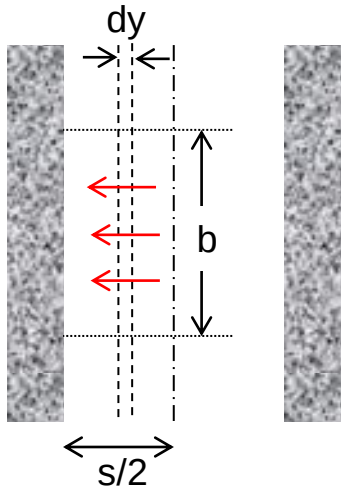
TCOs with metal grids

The R_{sh} of the TCO determines the minimum spacing (s) required between the grid lines of the top contact.

Side view



Top view



- Resistive power loss due to lateral current flow can be calculated.
- Incremental power loss in section *dy*:

$$dP = I^2 dR$$

with $dR = R_{sh} dy/b$

and $I = jby$,

j: current density of the device

- Total power loss:

$$P_{loss} = \int I^2 dR = \int j^2 b^2 y^2 R_{sh}/b \cdot dy$$

- At maximum power point, the generated power from the region under consideration is: $V_{mpp} j_{mpp} \cdot b \cdot S/2$

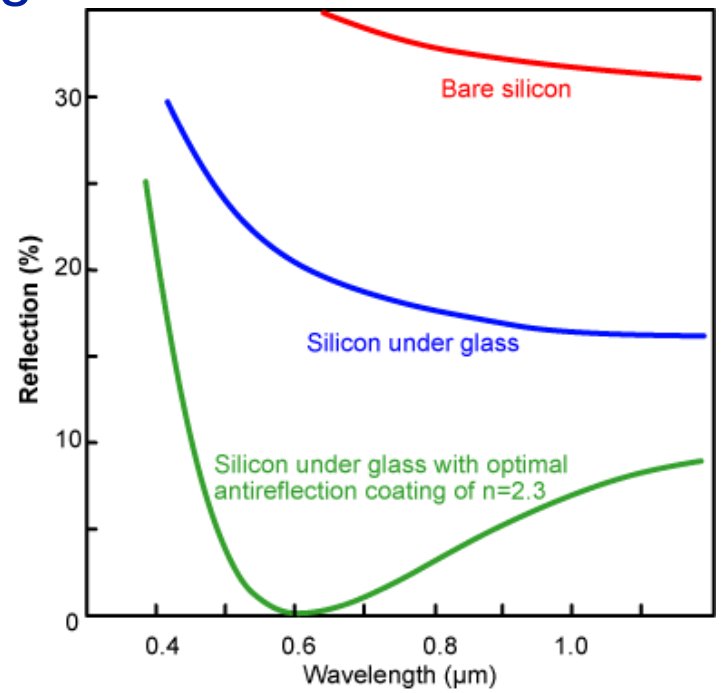
- Fractional power loss:

$$\frac{P_{loss}}{P_{mp}} = \frac{R_{sh}\, S^2\, J_{mpp}}{12\, V_{mpp}}$$

Second functionality: antireflection coating

- A bare silicon wafer has a surface reflection of over 30% in the visible range of the spectra.
- This reflection is reduced by applying an antireflection coating (ARC) to the surface or by texturing.

Example: comparison of surface reflection from a silicon solar cell, with and without antireflection coating.



Source: http://www.pveducation.org/pvcdrom/design/anti-reflection-coatings

Antireflection coating

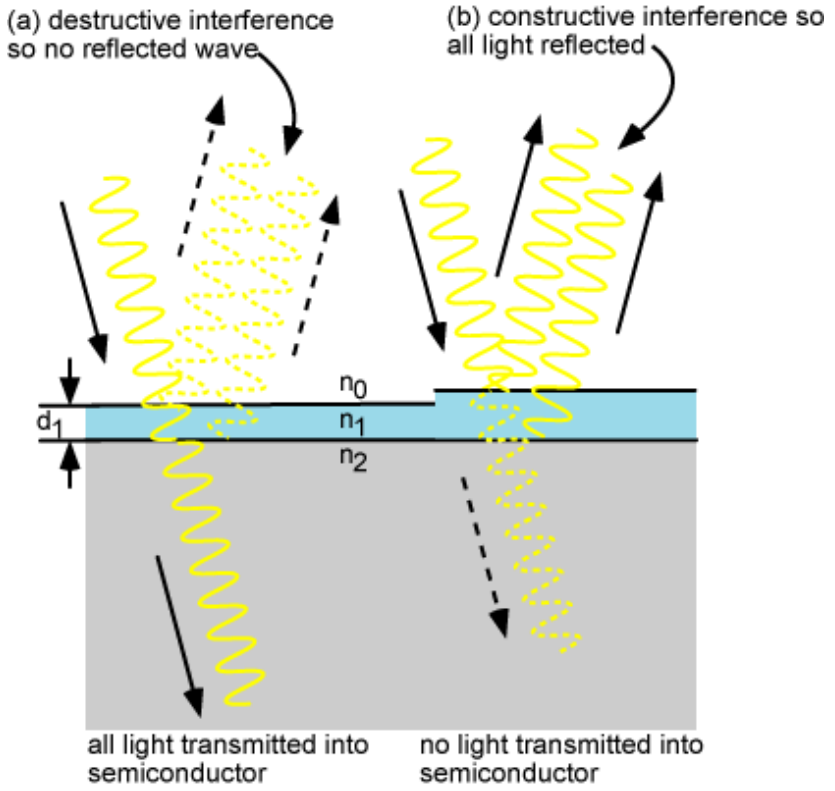
Principle of quarter wavelength antireflection coating:

Light reflected from the second interface arrives back at the first interface 180° out of phase with that reflected from the first interface, cancelling out.

Air or glass

Antireflection coating (ARC)

Silicon



Antireflection coating

Expression for the reflected intensity

- incidence from air ($n_1 = 1$), perpendicular $\theta = 0$, in cells on 54.7° facets
- ARC with index n_2 and thickness d_2
- infinite bulk (n_3), e.g. Si

$$R = \left|r_{123}^2\right| = \frac{r_{12}^2 + r_{23}^2 + 2r_{12}r_{23}\cos 2\gamma_2 d_2}{1 + r_{12}^2 r_{23}^2 + 2r_{12}r_{23}\cos 2\gamma_2 d_2}$$

The Fresnel coefficient at each interface given by: $r_{12} = \frac{\gamma_1 - \gamma_2}{\gamma_1 + \gamma_2}$ $r_{23} = \frac{\gamma_2 - \gamma_3}{\gamma_2 + \gamma_3}$

The propagation constant is given by: $\gamma_2 = k_0\sqrt{n_2^2 - n_1^2\sin^2\theta}$, for $\theta = 0$: $\gamma_i = n_i$

*Note: here n_1, n_2 assumed purely real (complex for real materials)

F.-J. Haug

Antireflection coating

For minimal reflectance at design wavelength λ_0 (incident from air):
chose the thickness d_2 of the ARC equal to one quarter of the effective wavelength λ_0/n_2:

$$d_2 = \frac{\lambda_0}{4n_2}$$

The minimum value is given by:

$$R_{min} = \left(\frac{n_2^2 - n_1 n_3}{n_2^2 + n_1 n_3}\right)^2$$

This is zero if n of the ARC is the geometric mean of the of the adjacent materials on either side:

$$n_2 = \sqrt{n_1 n_3}$$

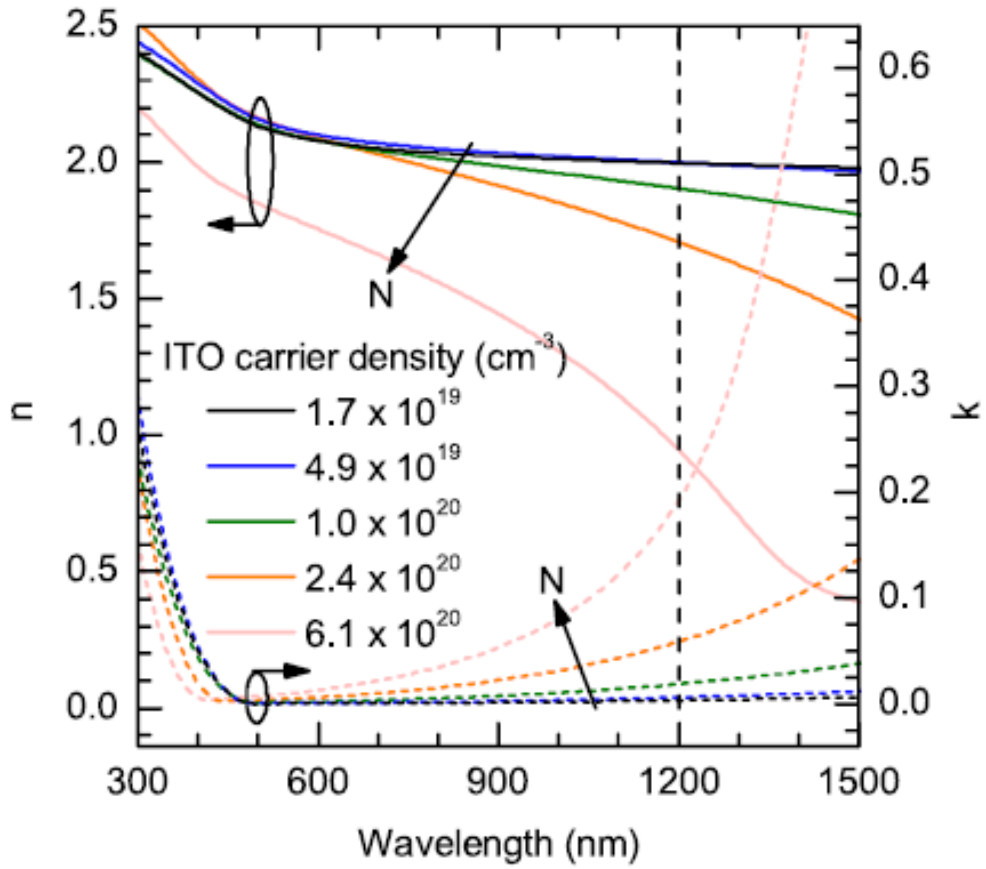
Question: for a silicon cell (n_{Si} = 3.8) in air, what is the optimum refractive index to achieve $R = 0$ at 600 nm? And what is the thickness the ARC should have?

Antireflection coating materials

Material	Refractive Index
MgF_2	1.3-1.4
SiO_2	1.4-1.5
Al_2O_3	1.8-1.9
ITO	1.9-2.2
Si_3N_4	~1.9
ZnS	2.3-2.4

Relation refractive index – carrier density in TCOs

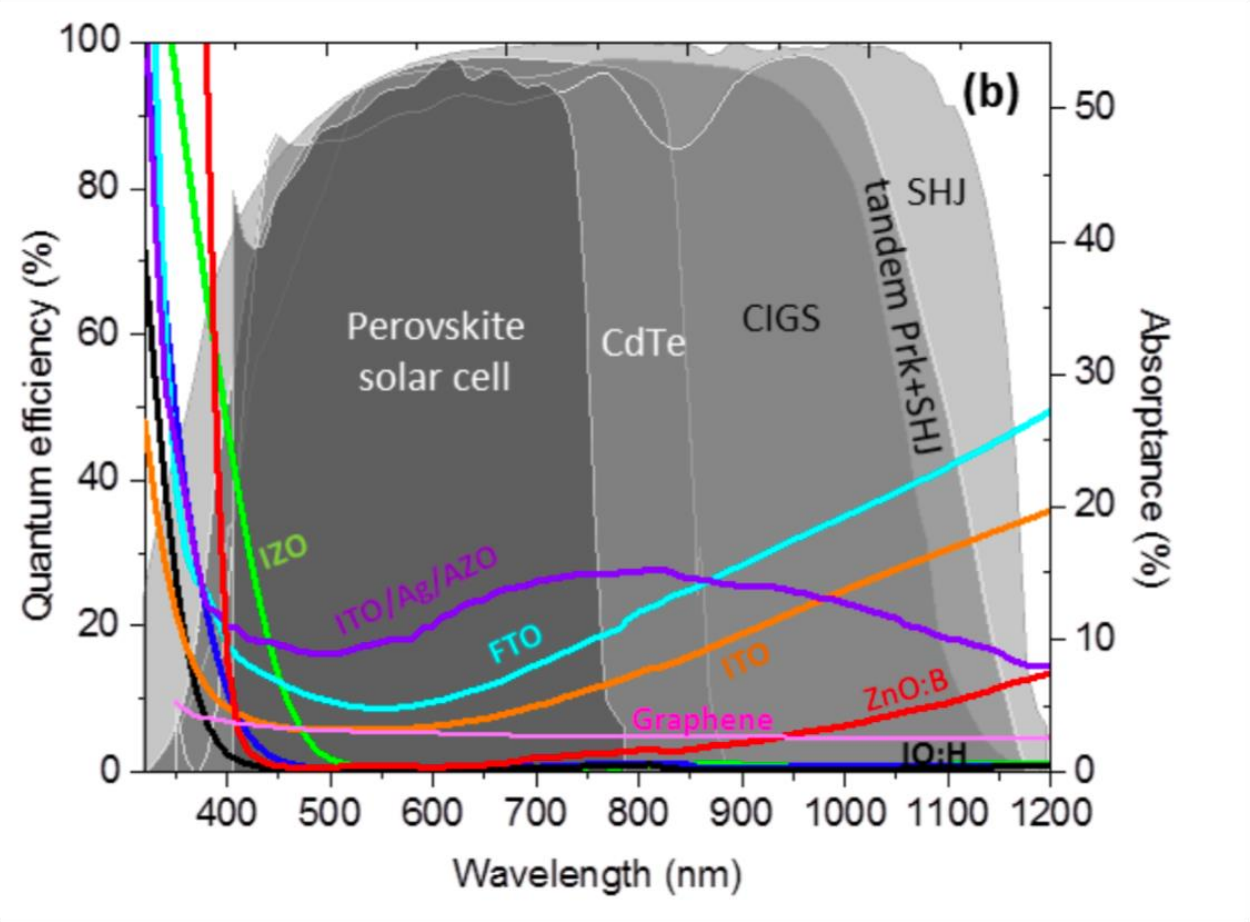
$$n_{ITO} = n + ik$$



High doping: reduced refractive index makes less efficient AR coatings

Holman et al. JAP 113 (2013)

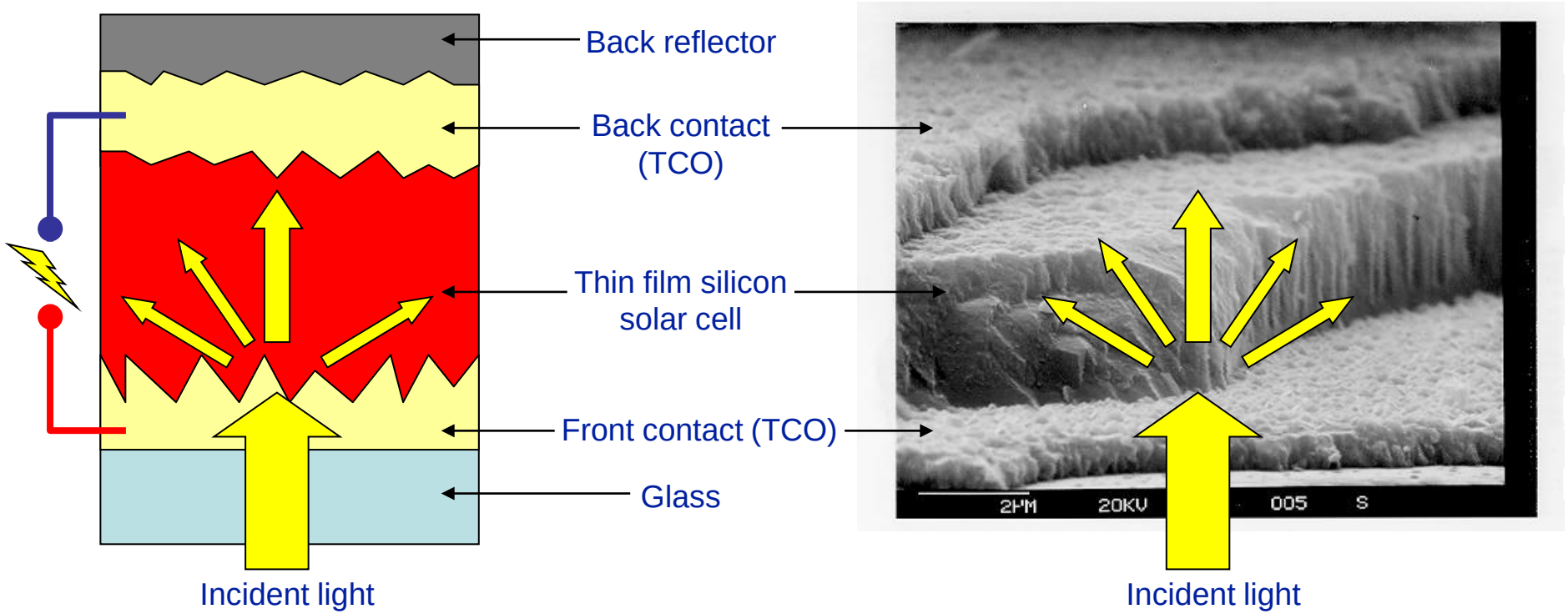
Parasitic absorption in TCOs



The control of the free carrier absorption (FCA) is important when used in cells that absorb >900 nm

Ref. Morales-Masis et al. *Adv. Electron. Mater.* 2017, 1600529. **DOI: 10.1002/aelm.201600529**

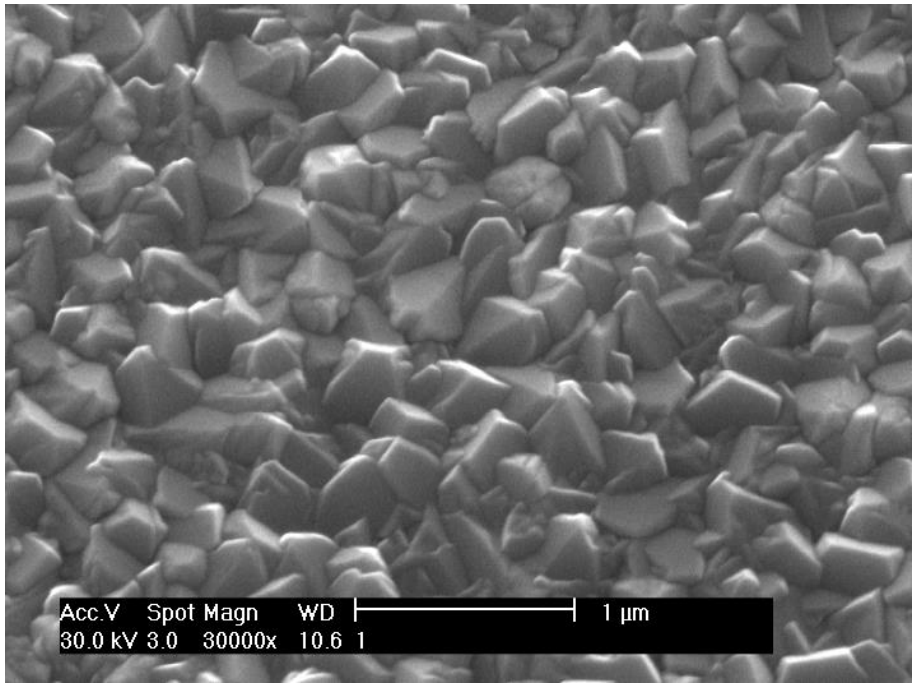
Third functionality: light scattering (in thin film solar cells)



TCO provides textured growth template for light scattering

for absorber thickness d: prolonged absorption path $d' = d / \cos\theta$

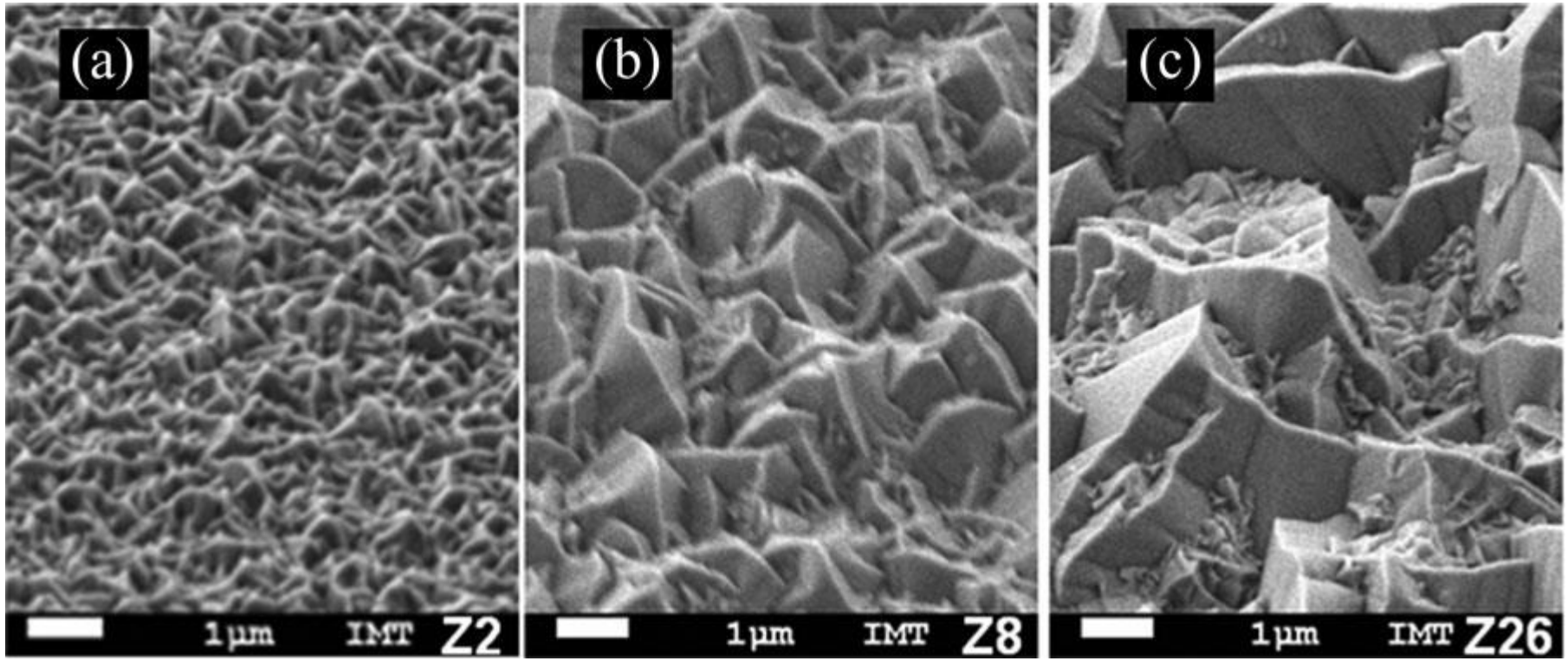
Examples of rough TCOs



Tin Oxide (SnO_2:F) deposited by AP-CVD

(industry and research standard, Asahi-U)

Adapt feature size to cell type, e.g. ZnO:B



2 µm thick ZnO
std. for scattering in a-Si
(550 – 750 nm)

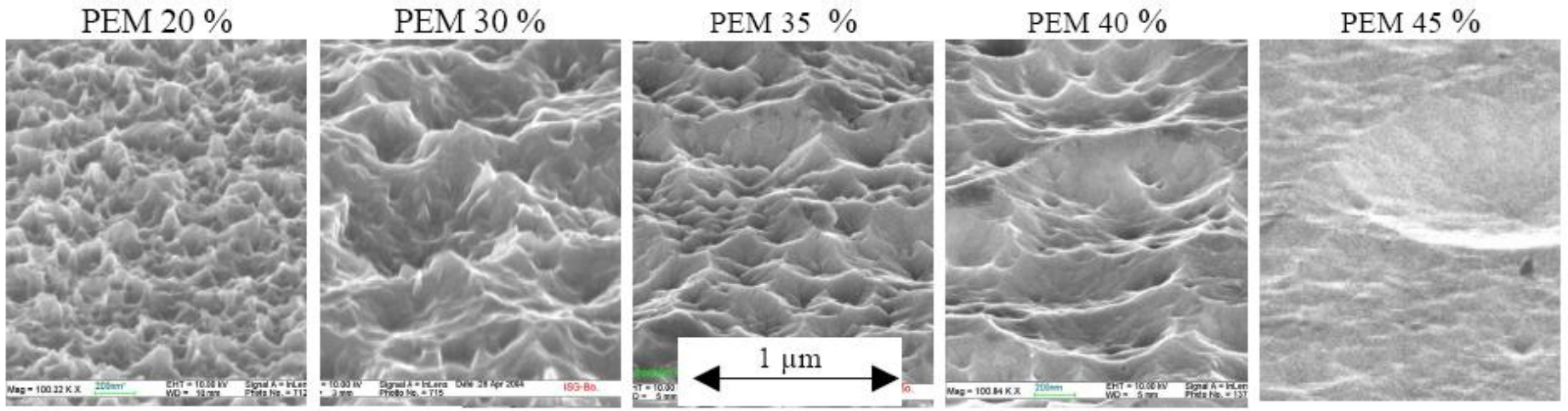
5 to 8 µm thick ZnO
used for scattering in µc-Si
(850 – 1050 nm)

26 µm thick ZnO
(test structure)

M. Boccard, JPV, (2012)

Texture by etching

Zinc Oxide (ZnO) deposited by sputtering and etched with diluted HCl

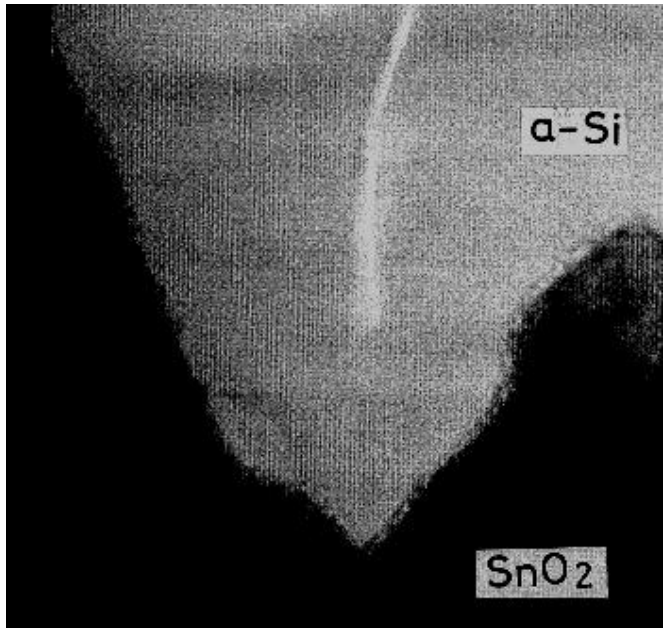


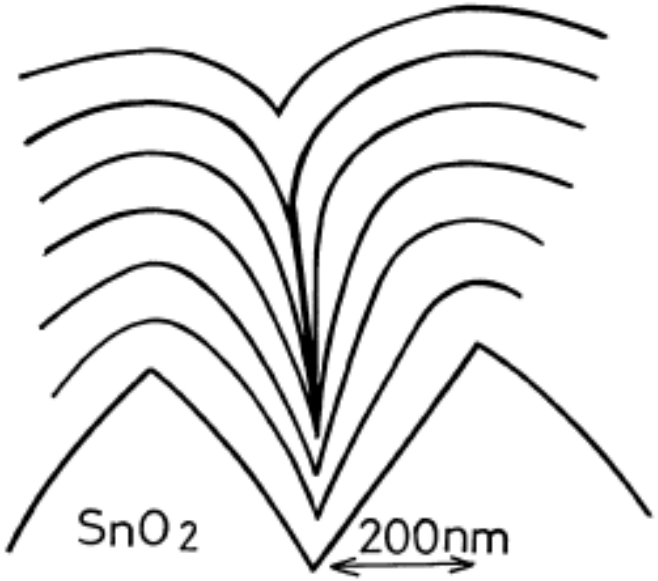
Morphology depends on sputtering conditions and etch time

*PEM: plasma emission of zinc; high PEM <=> low oxygen

J. Hüpkes, Dissertation (2005)

Word of caution: texture and growth





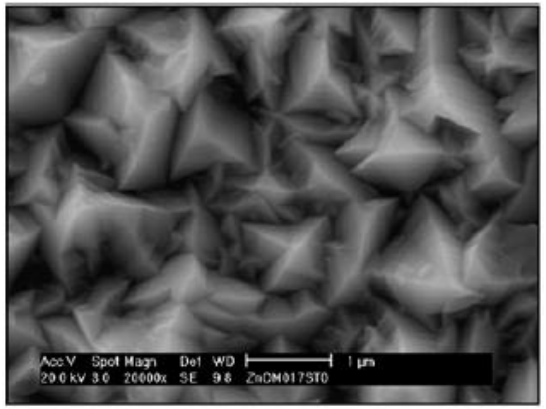
Extreme textures capture bad quality material above V-shaped valleys

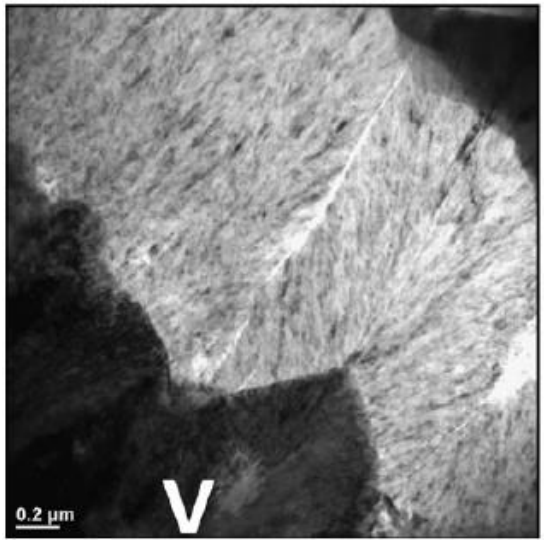
Avoid by using U-shape (c.f. Asahi-U texture)

Sakai et al. Jap. J. Appl. Phys. (1990)

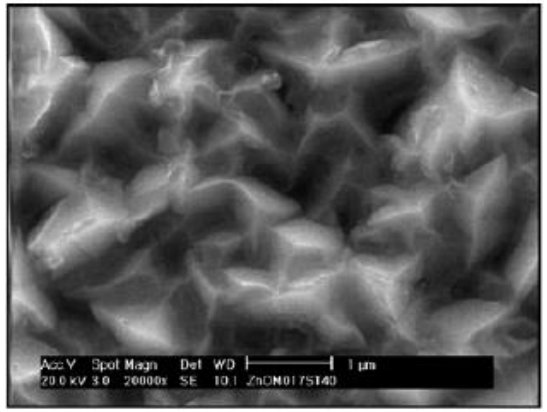
Additional Ar plasma treatment

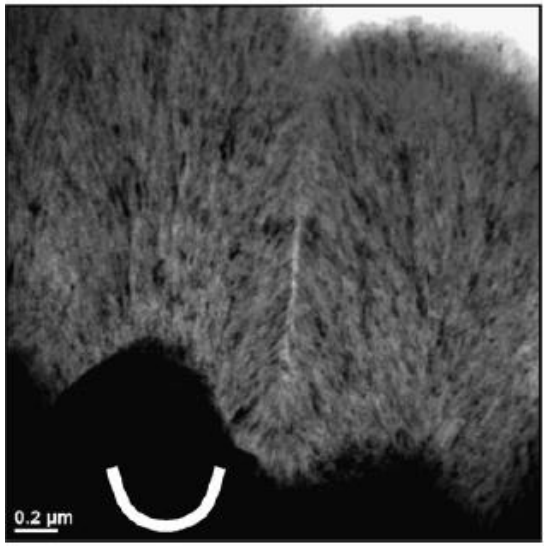
untreated





20 min Ar-plasma treated





Takeaways

- Transparency and conductivity
  => usually found in highly doped transition metal oxides

- Doping often related to oxygen vacancy
  => control by oxygen partial pressure during deposition (or anneal)

- Application driven
  - TFTs: field effect only accessible for low carrier density (addition of Ga)
  - low e coating: high carrier density for high IR reflection
  - solar cells: additional functions like ARC or light scattering