Introduction to passivated contacts

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Passivated Contact Workshop
Eindhoven, 31.1.2018

Carrier selective contacts for c-Si solar cells

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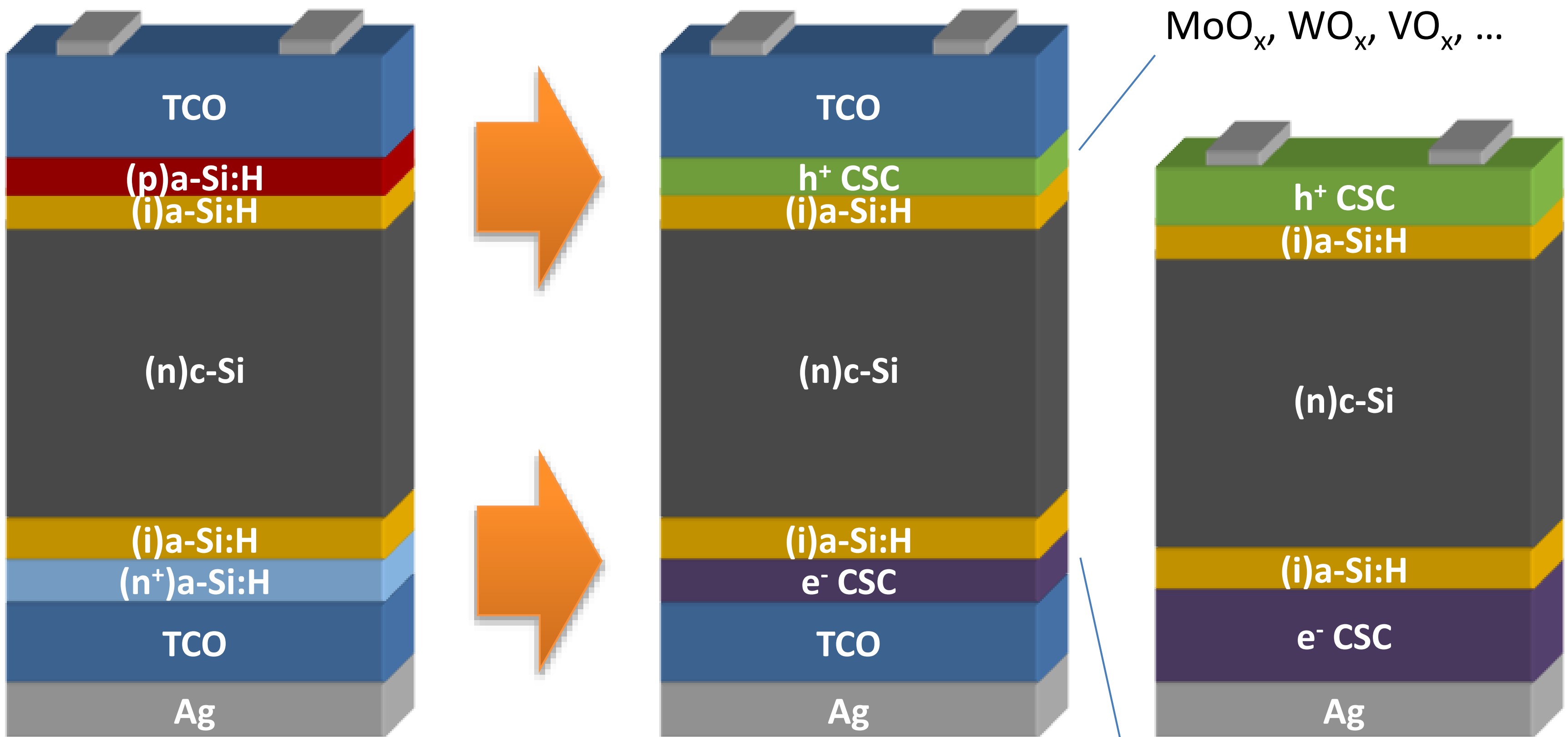
"classical" a-Si:H/c-Si heterojunction solar cell

CSC- based solar cells



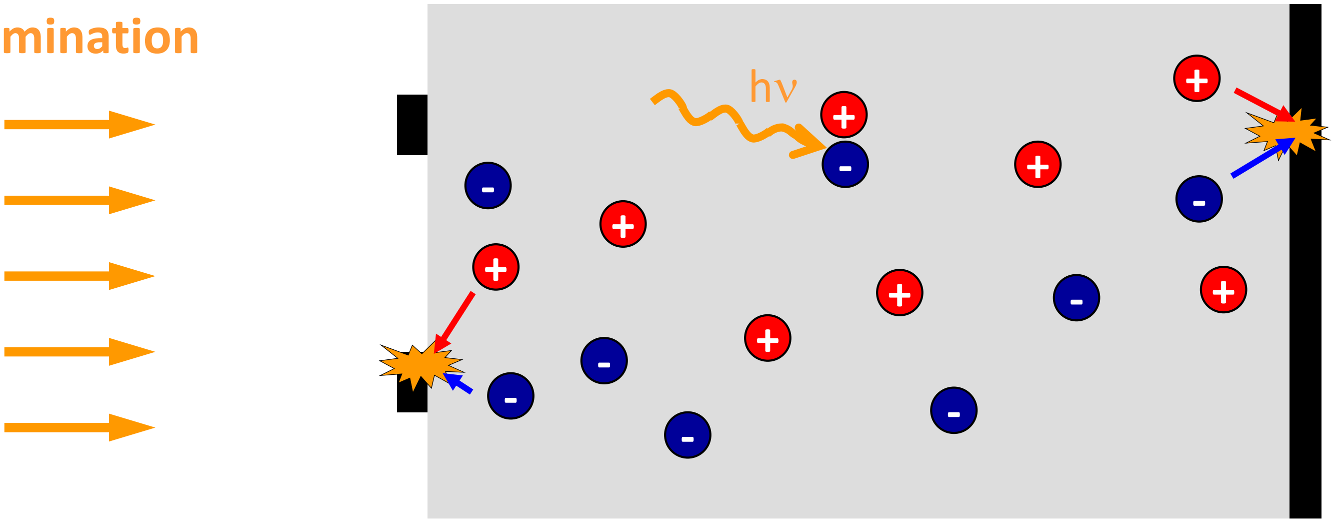
TiO_2, MgF_2, …

Replace doped layers by "carrier selective" layers

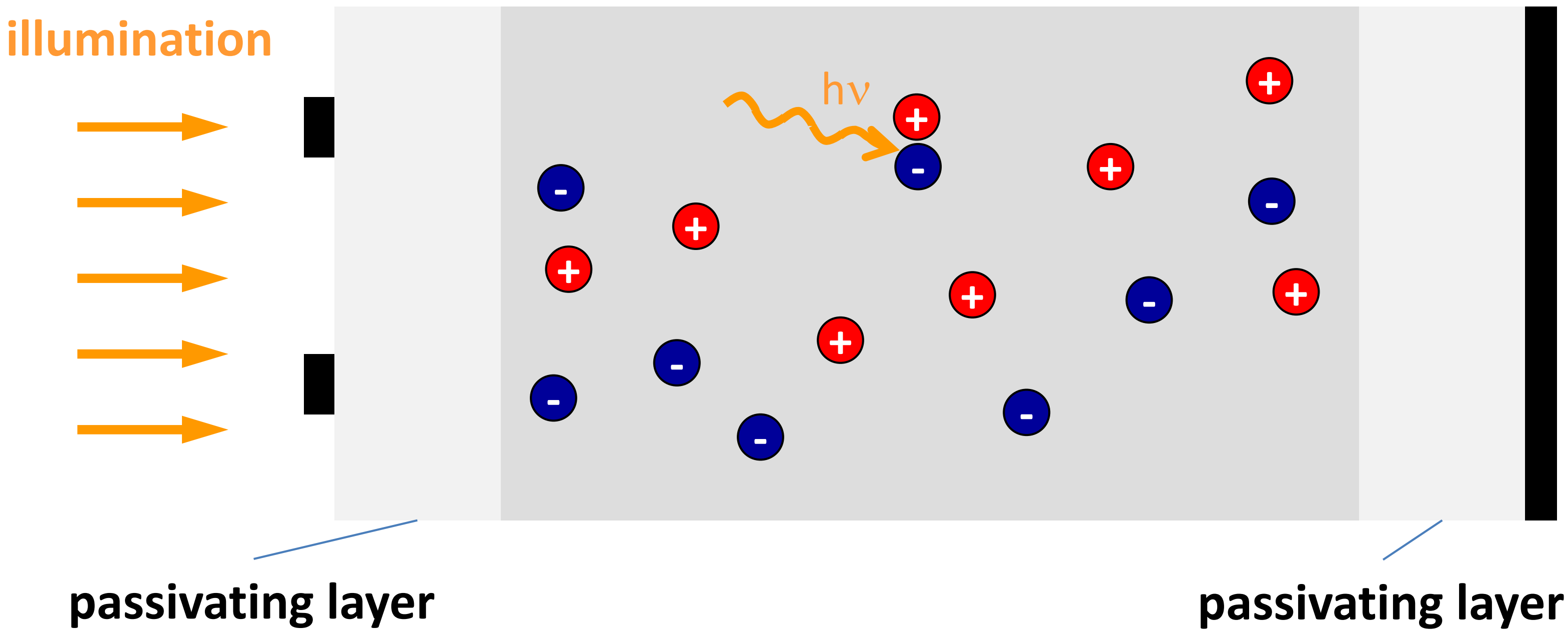
- → Highly transparent front contact
- → Might also replace TCOs if sheet resistivity is low enough (front), optics OK
- → Even omit passivating layers (a-Si:H, SiO_2)?

Passivating contacts

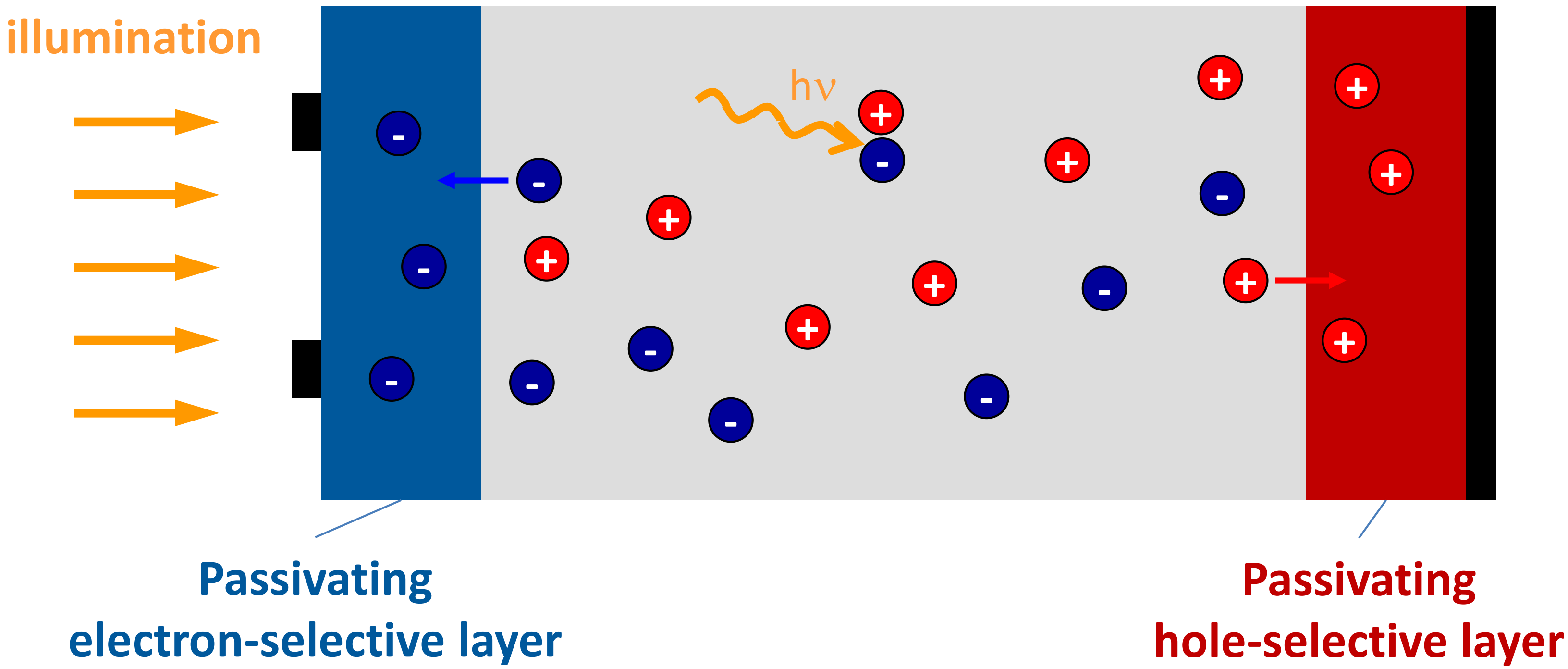
illumination



Passivating contacts

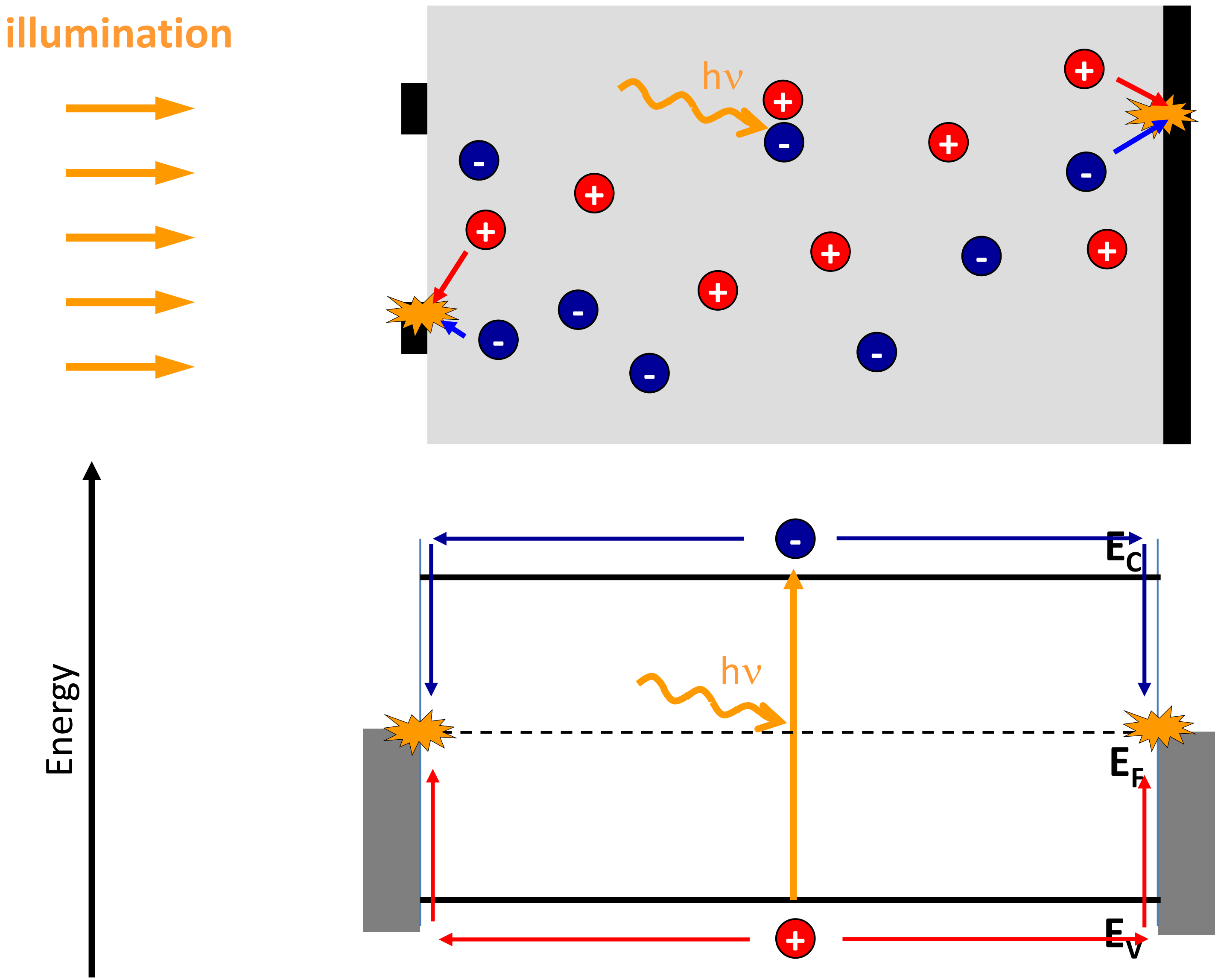


Passivating contacts selective



- What is a carrier-selective passivating contact (CSC)?
- “Classic” CSCs in silicon: amorphous/crystalline silicon heterojunctions
- Novel CSC example: IWO_x/c-Si – band line-up

Non-passivating, ohmic contacts



Non-passivating, ohmic contacts

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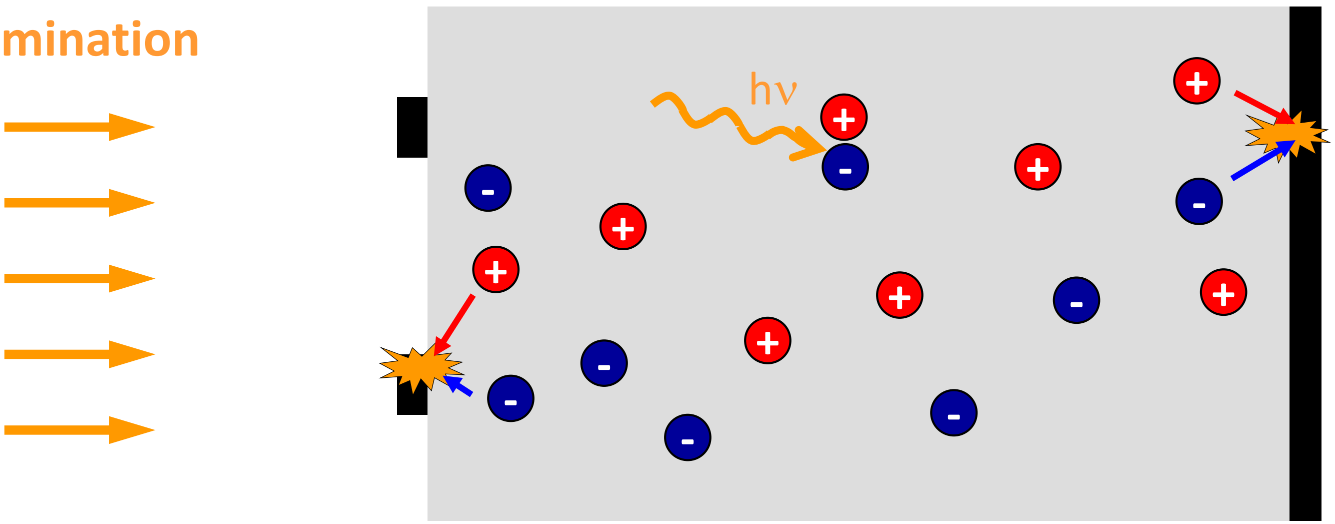
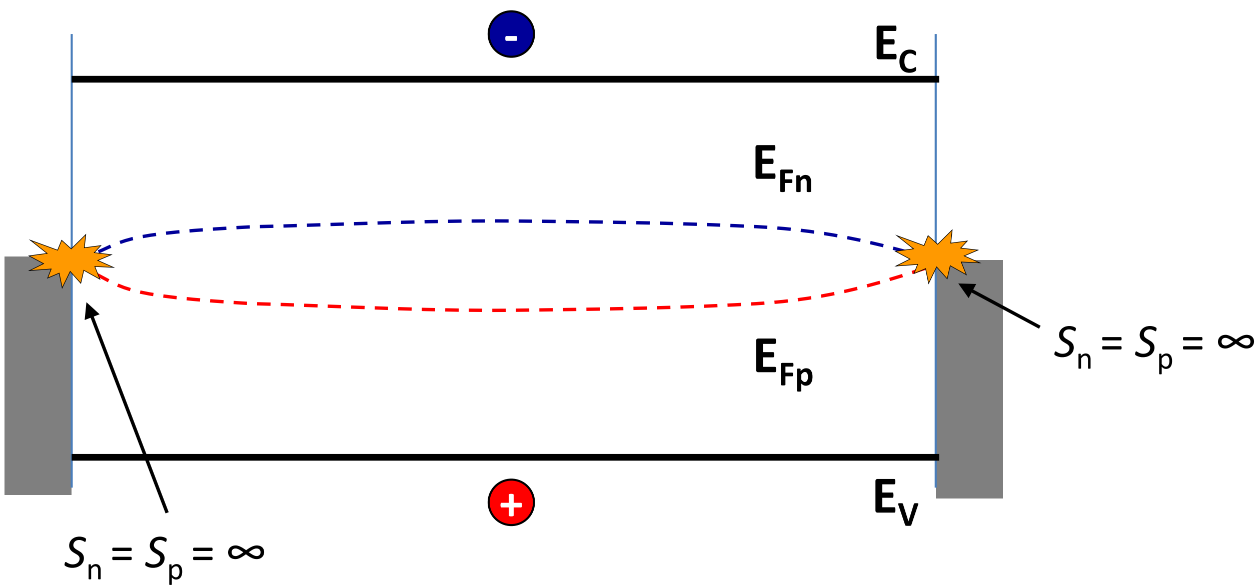


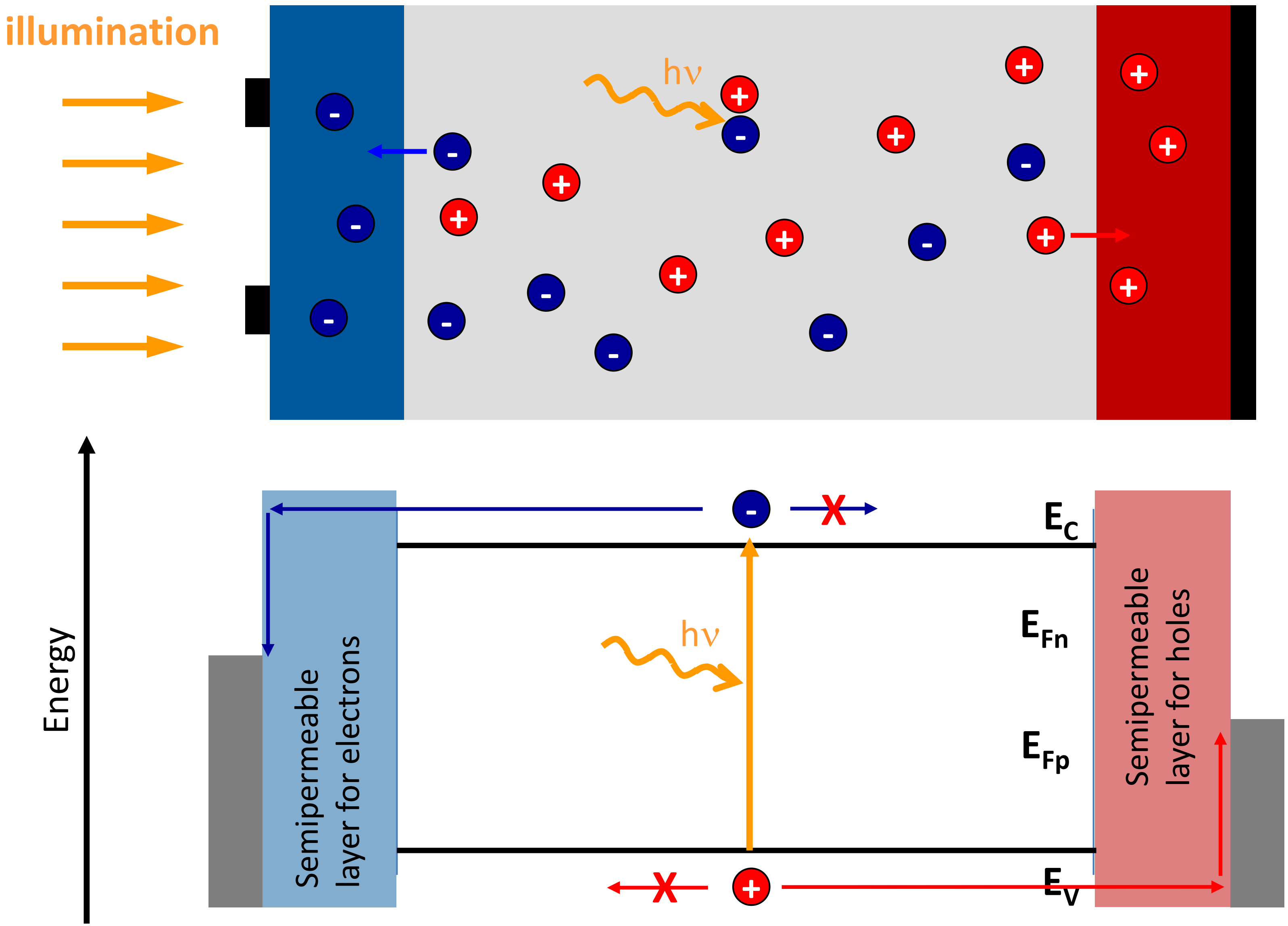
Surface recombination velocities S_n, S_p:

$$S_n = D_n \frac{dn}{dt}\Big|_s \;/\; (n - n_0)_s$$

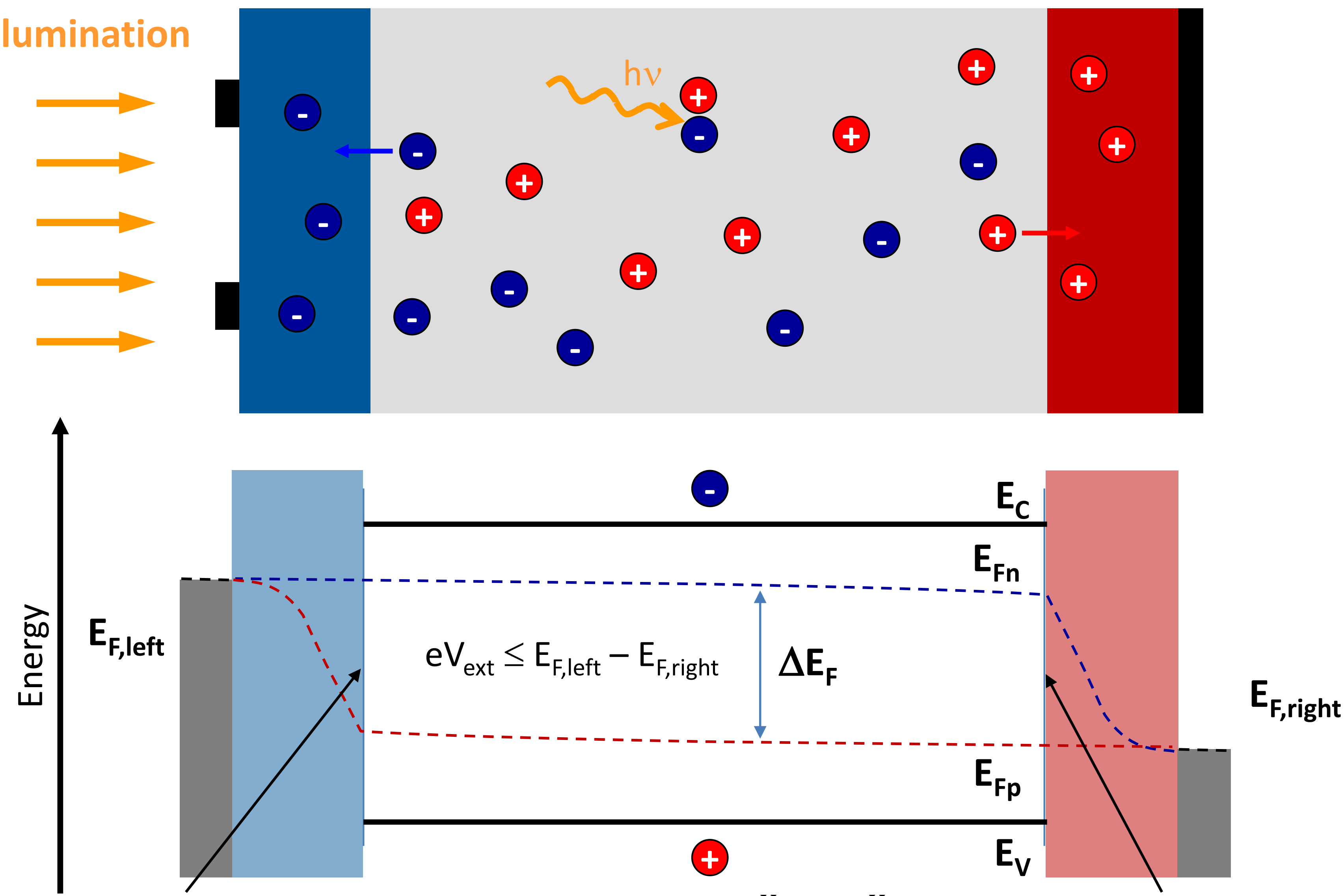
$$S_p = \underbrace{D_p \frac{dp}{dt}\Big|_s}_{U_s} \;/\; \underbrace{(p - p_0)_s}_{\Delta p_s}$$



Passivating carrier-selective contacts

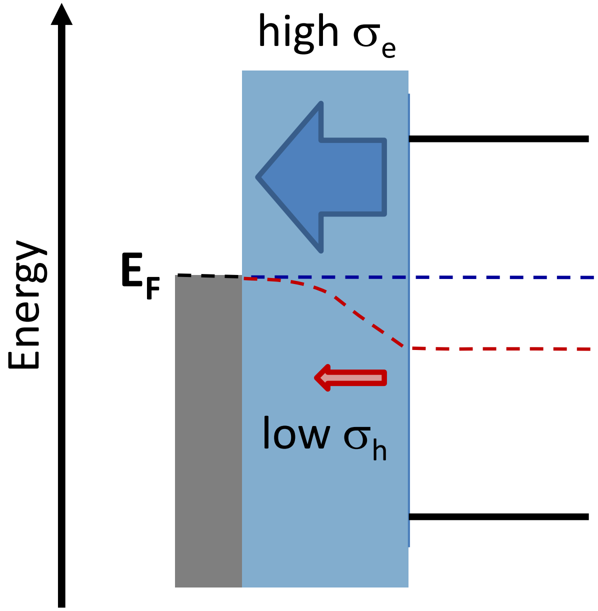


Passivating carrier-selective contacts



$S_{p,eff} << S_p$ Effective SRV: $S_{eff} = \frac{U_S}{\Delta n_{IF}} \ll \frac{U_S}{\Delta n_S}$ $S_{n,eff} << S_n$

What are our options to achieve carrier selectivity?



Charge current of electrons:

$$j_e = \frac{\sigma_e}{e} \text{grad } E_{f,n}$$

Charge current of holes:

$$j_h = \frac{\sigma_h}{e} \text{grad } E_{f,p}$$

Würfel *et al.*, IEEE J. Photovolt **5** (2015) 461

→ Change current flow towards contact by *changing carrier type's conductivity* $\sigma_i = \pm e n_i \mu_i$ i.e., change

- **carrier concentration** ($E_{Fp} - E_V$, $E_{Fn} - E_C$)
  - **doping** → "classical" p/n junctions
  - **band offsets** → "novel" CSCs
- (carrier mobility μ)

What are our options to achieve carrier selectivity?

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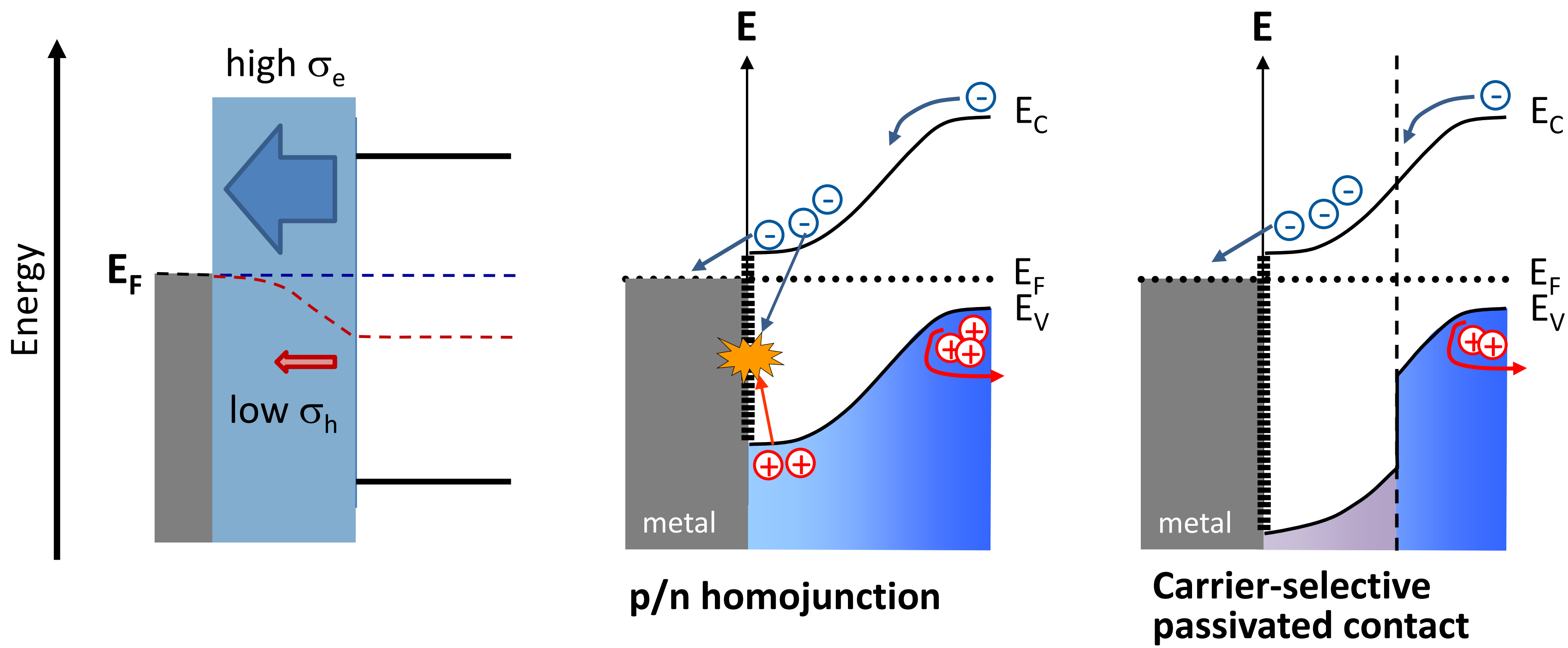

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Silicon-homo- and heterojunction solar cells

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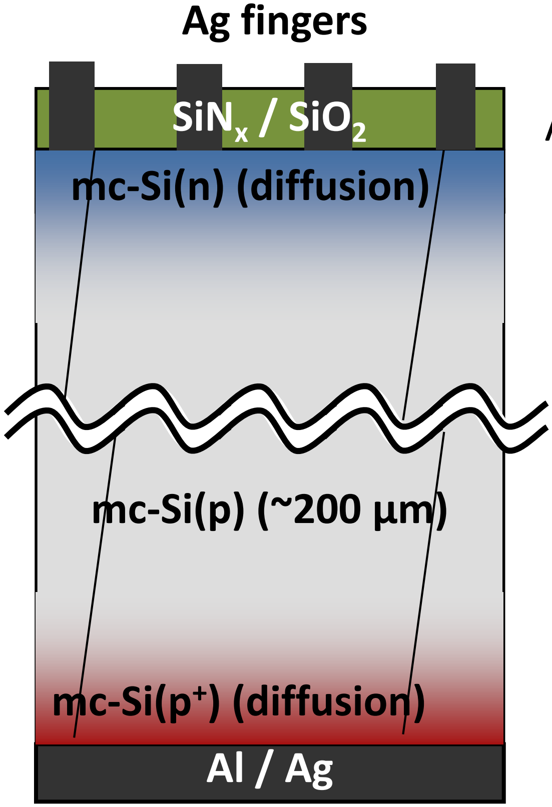
standard diffused junction

a-Si:H/c-Si heterojunction
the "prototypical" CSC cell…



function

front contact

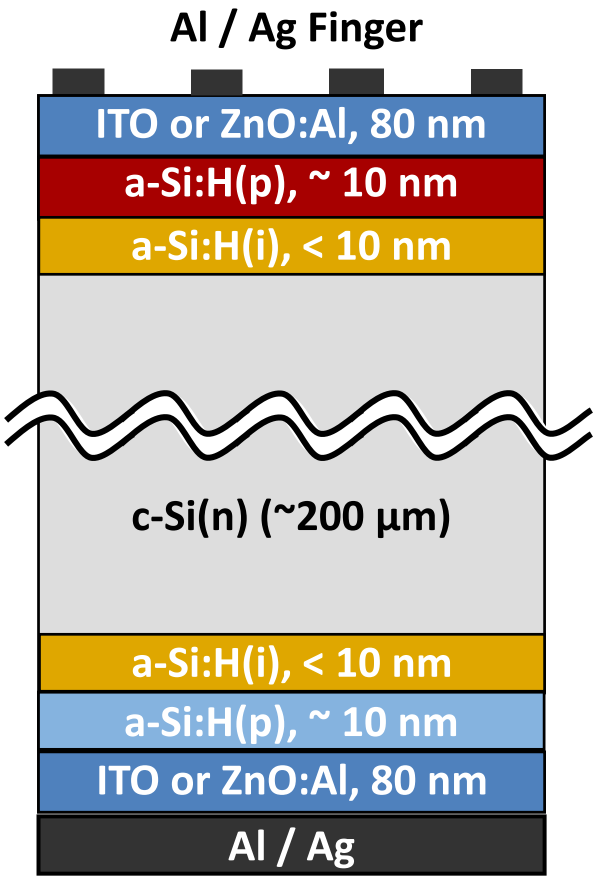
AR coating + TCO

emitter

base (absorber)

back surface field

rear contact

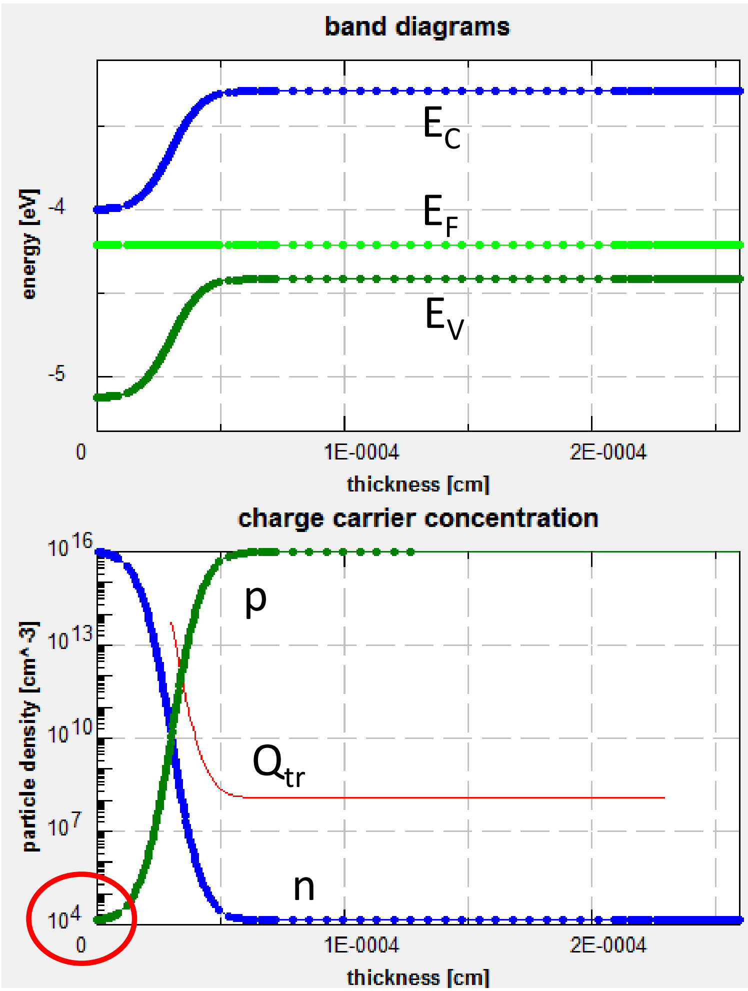


p/n homo- *vs.* heterojunction

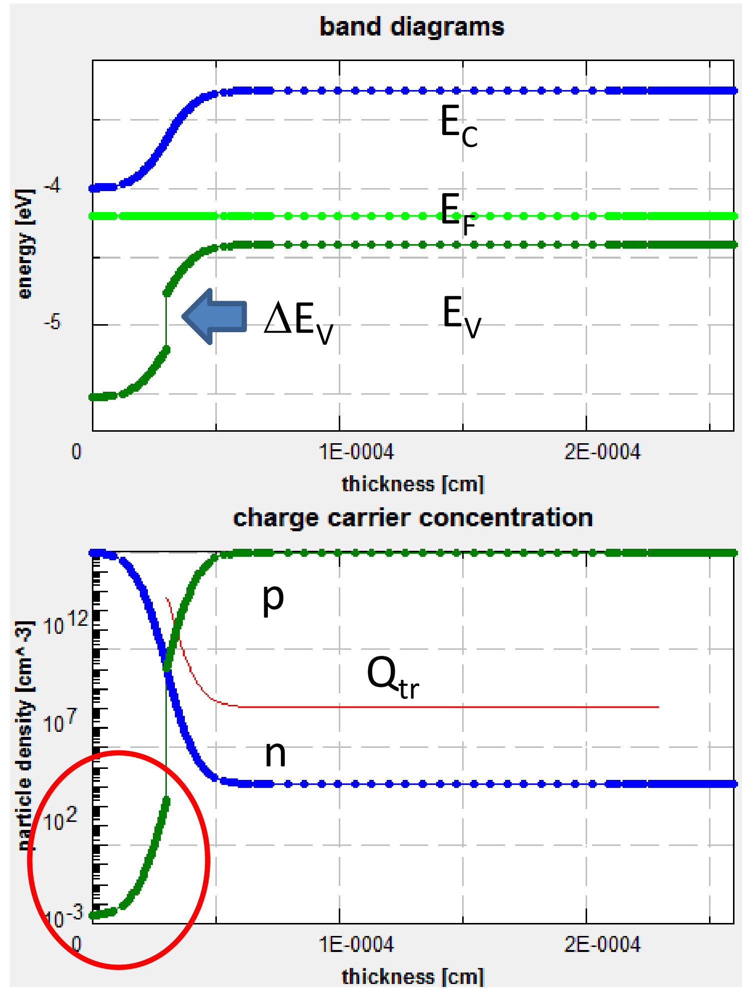
c-Si, N_D,N_A = 10^{16}/cm³, 10µm absorber; HJ: ΔE_V = 0.4eV, unchanged optics

in the dark, V_{ext} = 0

homojunction



heterojunction



Heterojunction: 10^7 times lower hole density at (n) contact → improved carrier selectivity?

p/n homo- *vs.* heterojunction

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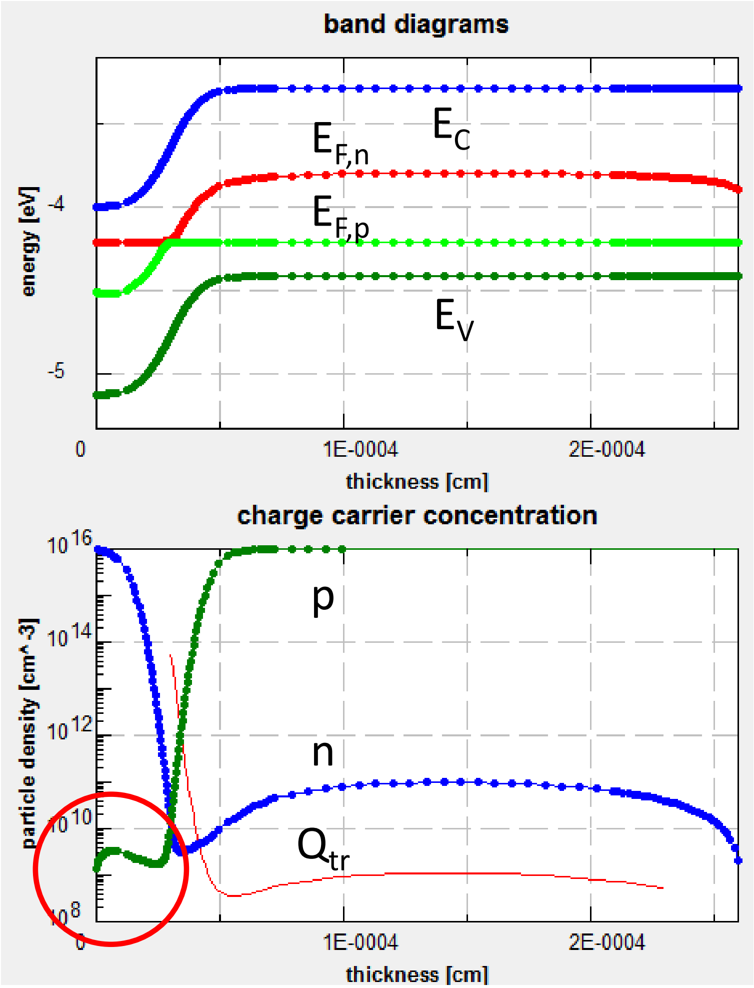
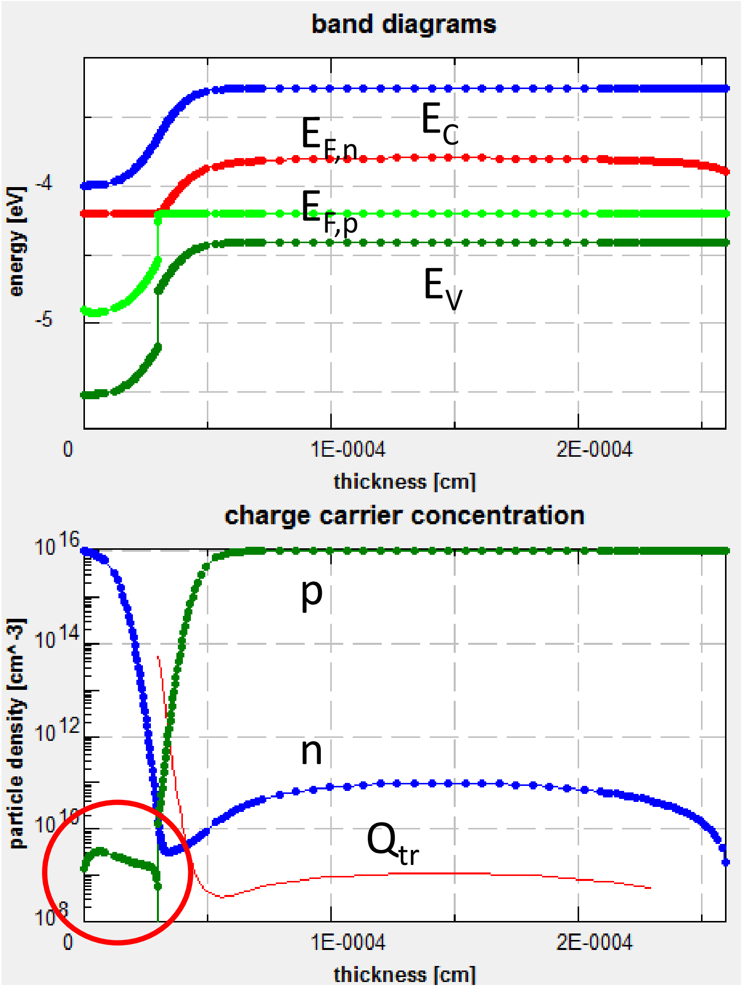
AM1.5 illumination, V_{ext} = 0

homojunction



heterojunction



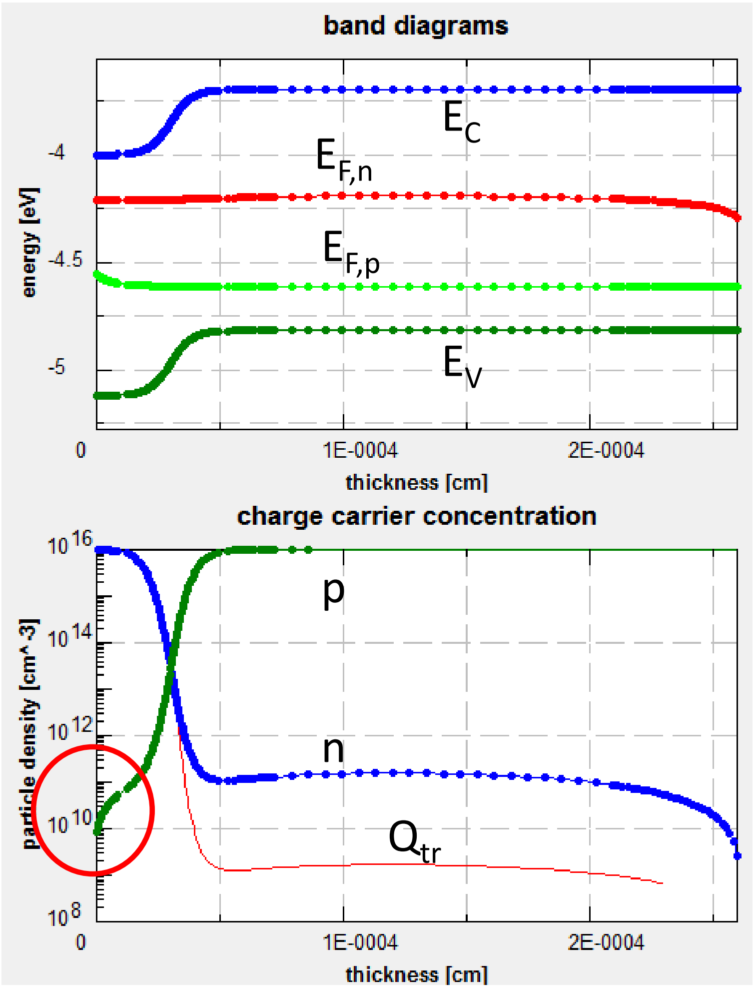
AFORS - HET v2.4.

Illuminated, at j_{sc}: p @ junction strongly increased, but still lower in HET

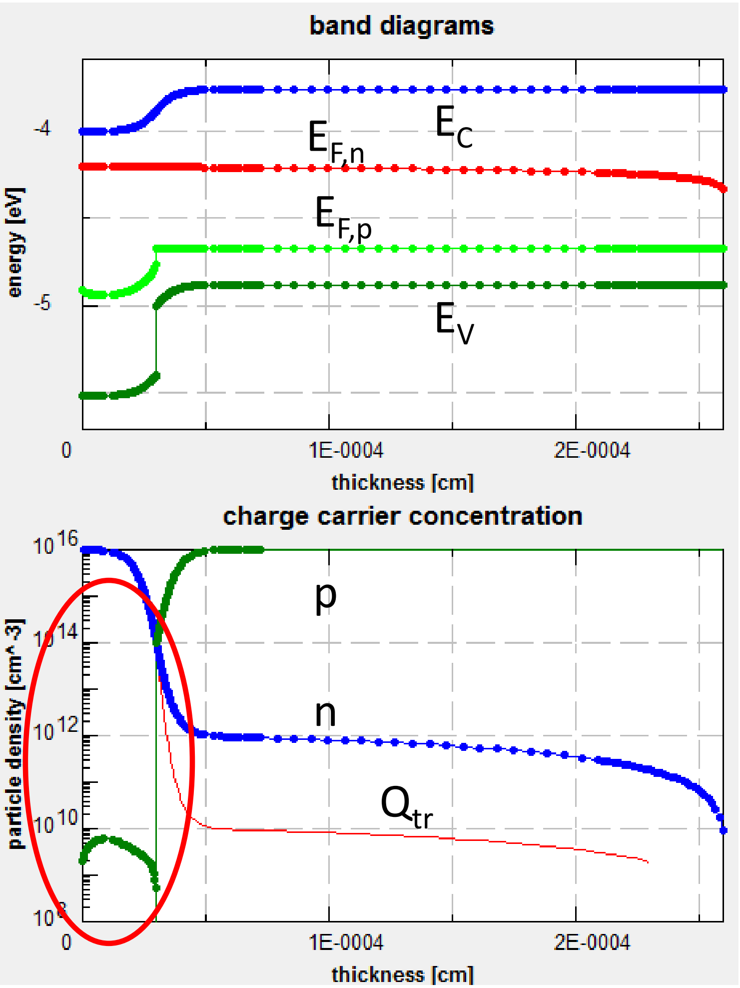
p/n homo- *vs.* heterojunction

AM1.5 illumination, $V_{ext} = V_{oc}$

homojunction



heterojunction



Illuminated, at V_{oc}: p “left of” heterointerface ~10^5 times lower than in homojunction!

Comparison of simulated I-V curves

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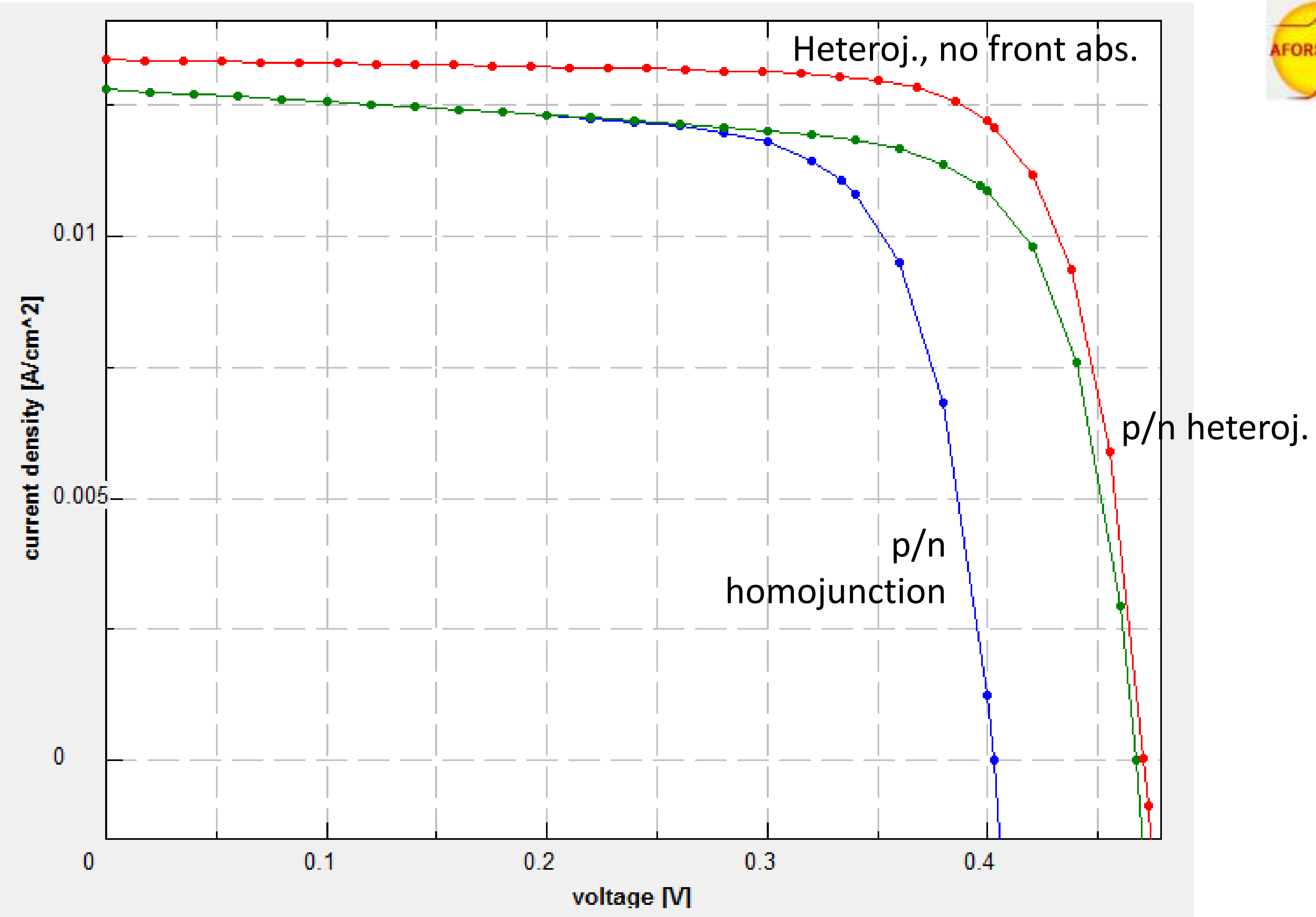
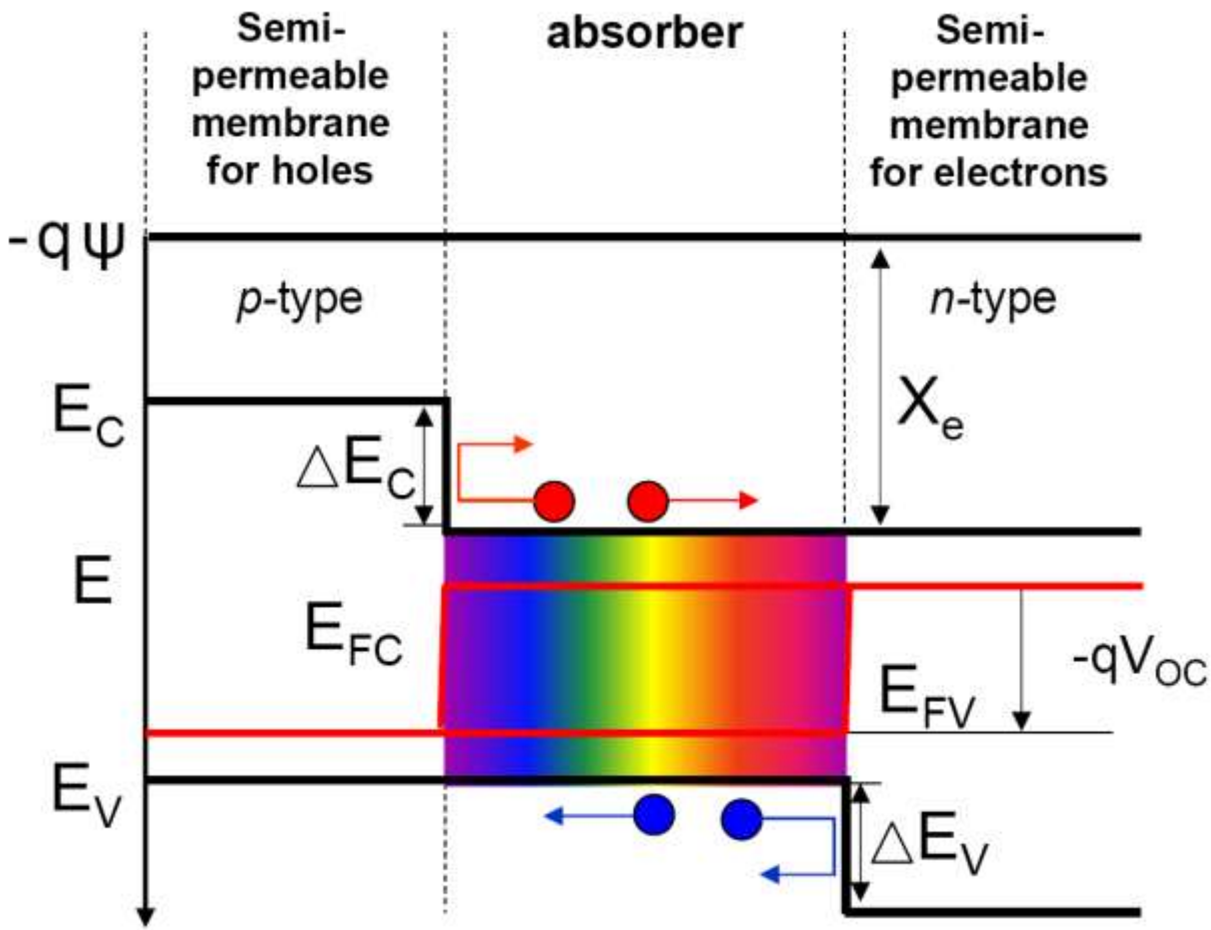


Solar cell with ideal (hetero-)contacts

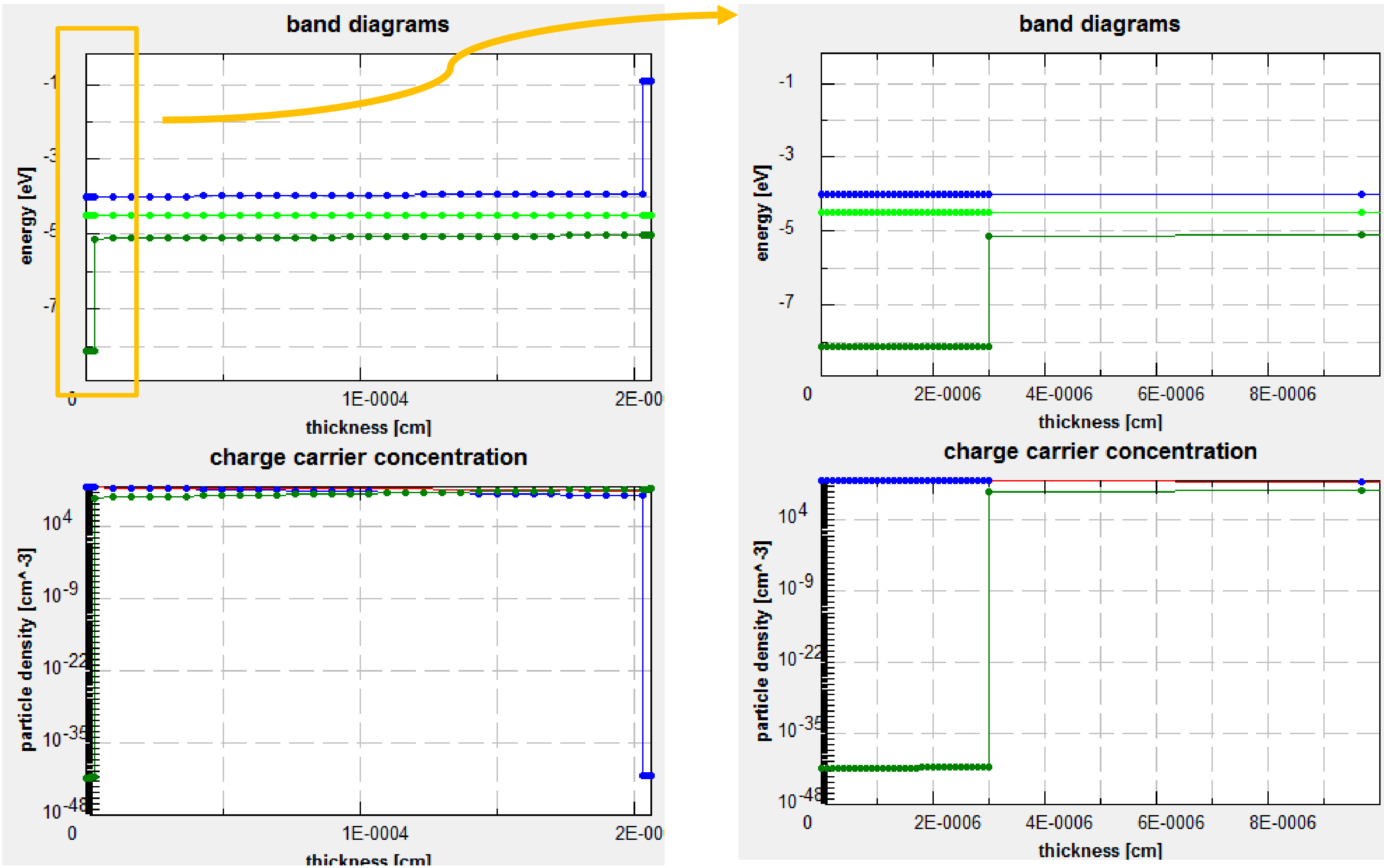


source: Zeman, Zhang, in: van Sark/Korte/Roca: Physics and Tech. of aSi/cSi Heterostructure cells

(almost) ideal carrier-selective contacts

(c-Si, $\Delta E_{V,front} = \Delta E_{C,rear}$ = 3eV, $N_A, N_D = 10^{11}/cm^3$, 2µm absorber, 30nm contacts)

in the dark, $V_{ext} = 0$



Very high carrier selectivity: $(n_s/p_s)_{Front} = (p_s/n_s)_{Back} > 10^{50}$

(almost) ideal carrier-selective contacts

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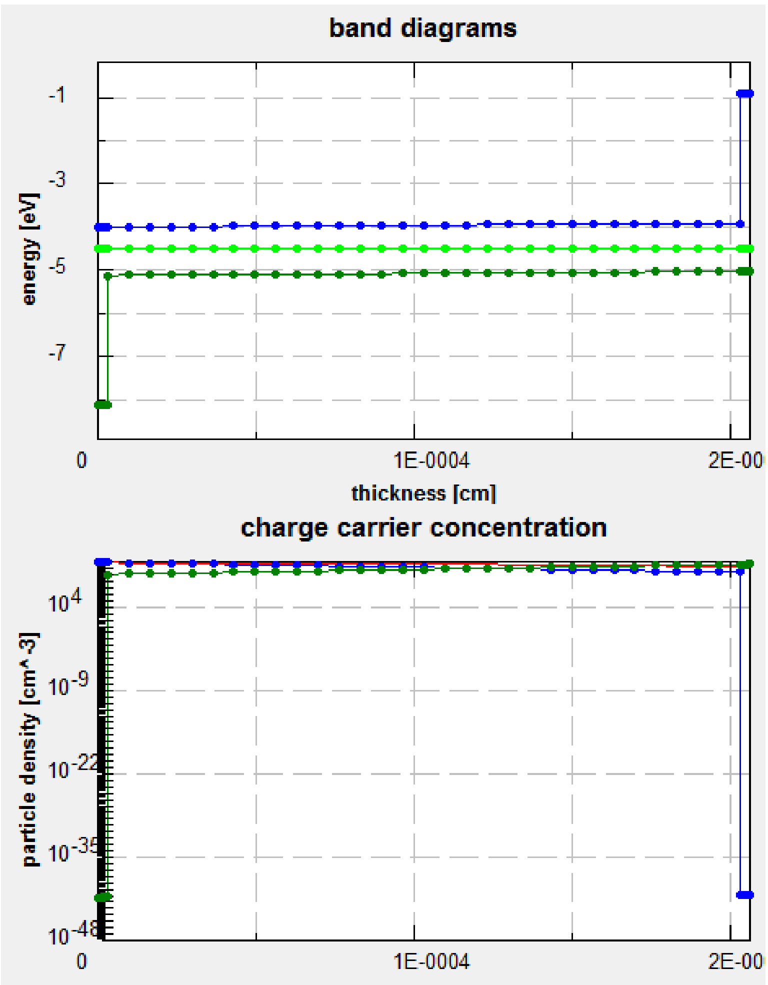

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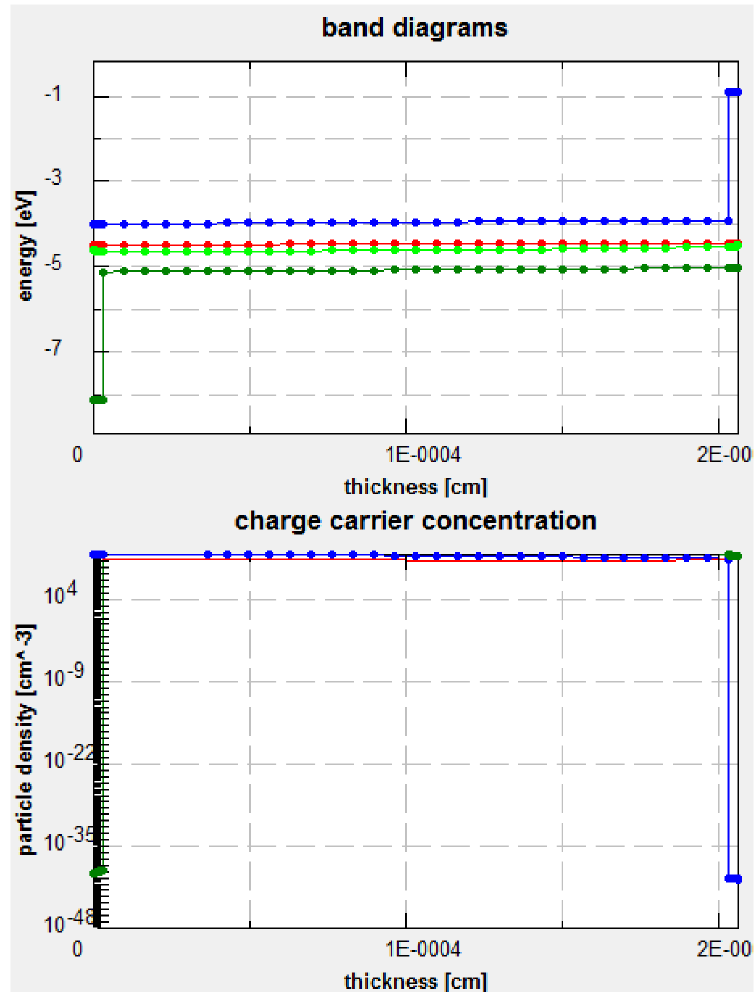

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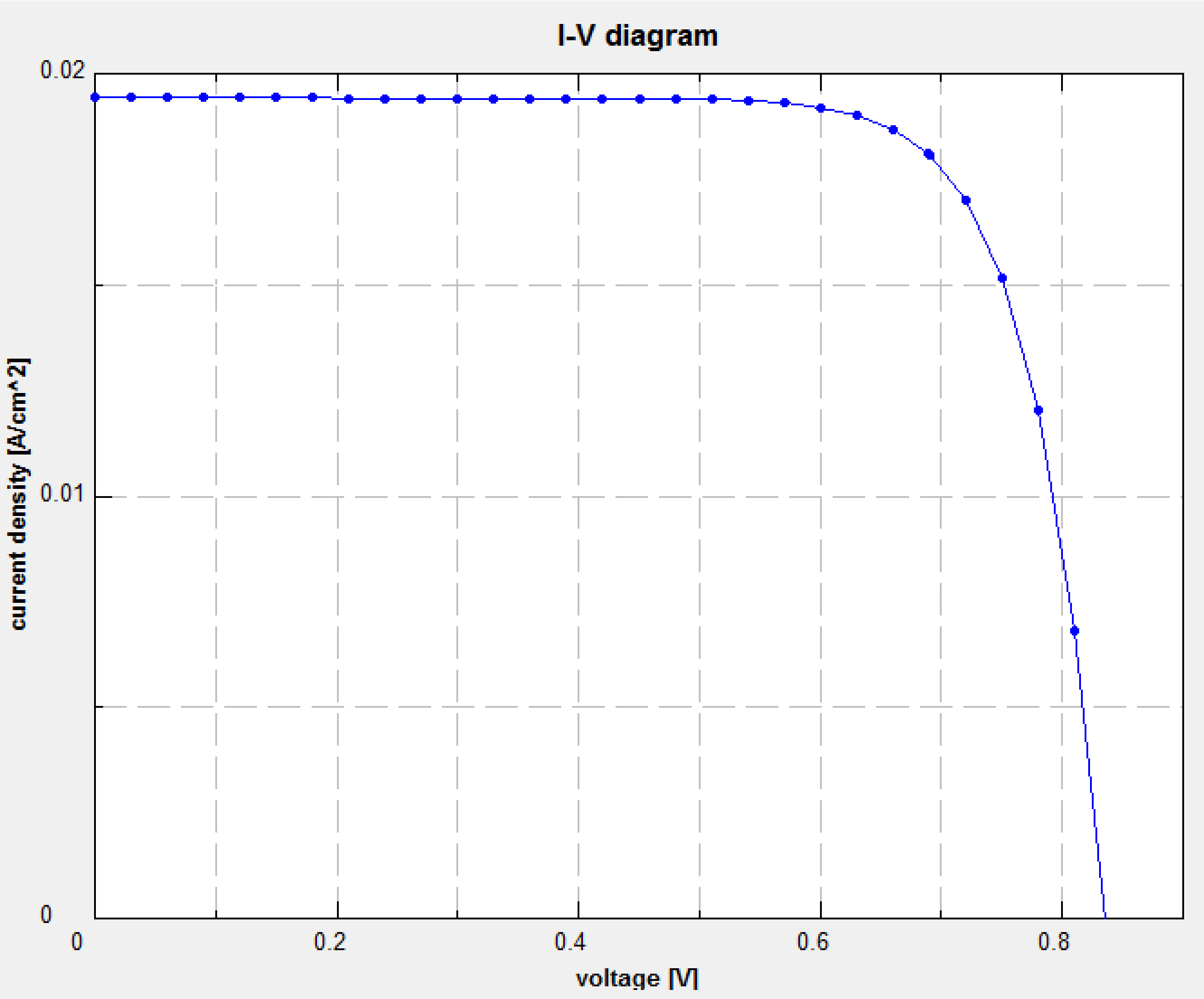
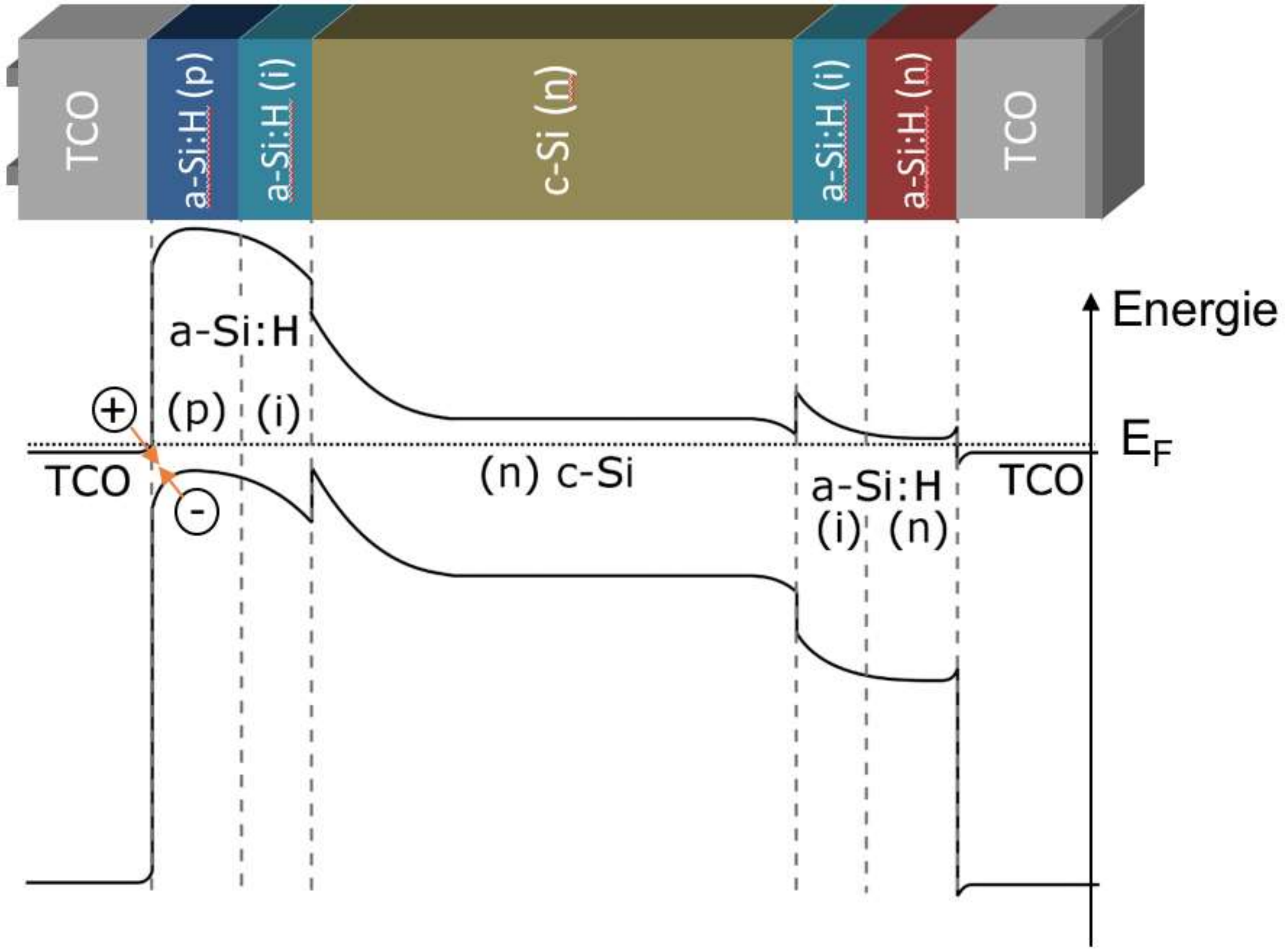
(almost) ideal carrier-selective contacts



Voc = 836mV, FF = 76.7%, jsc = 19.4mA/cm² (only 2µm c-Si absorber!)

Amorphous/crystalline silicon heterojunction solar cell



influence of interface defects and fixed charge on cell V_{oc} - simulation study

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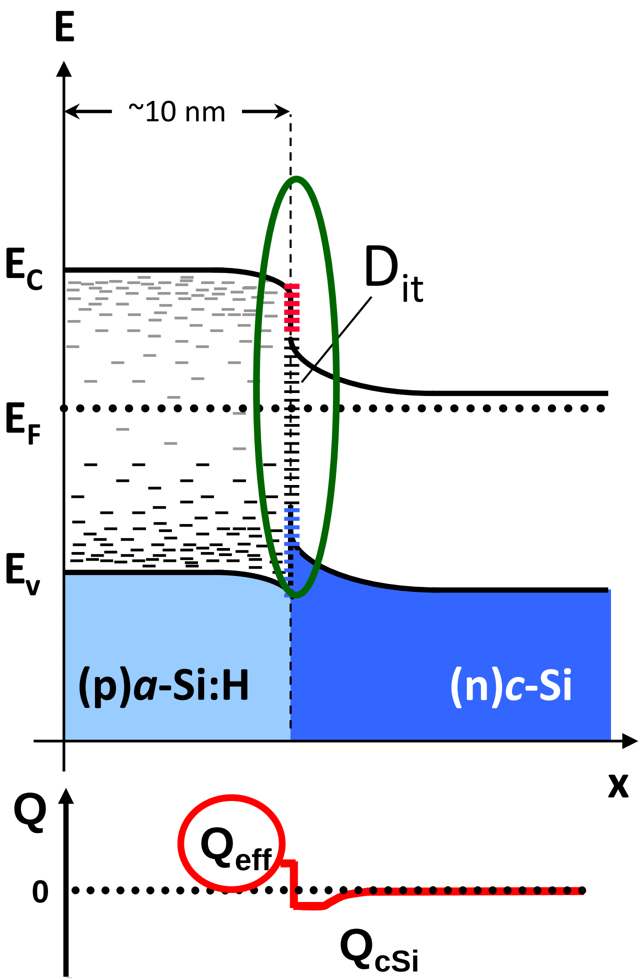
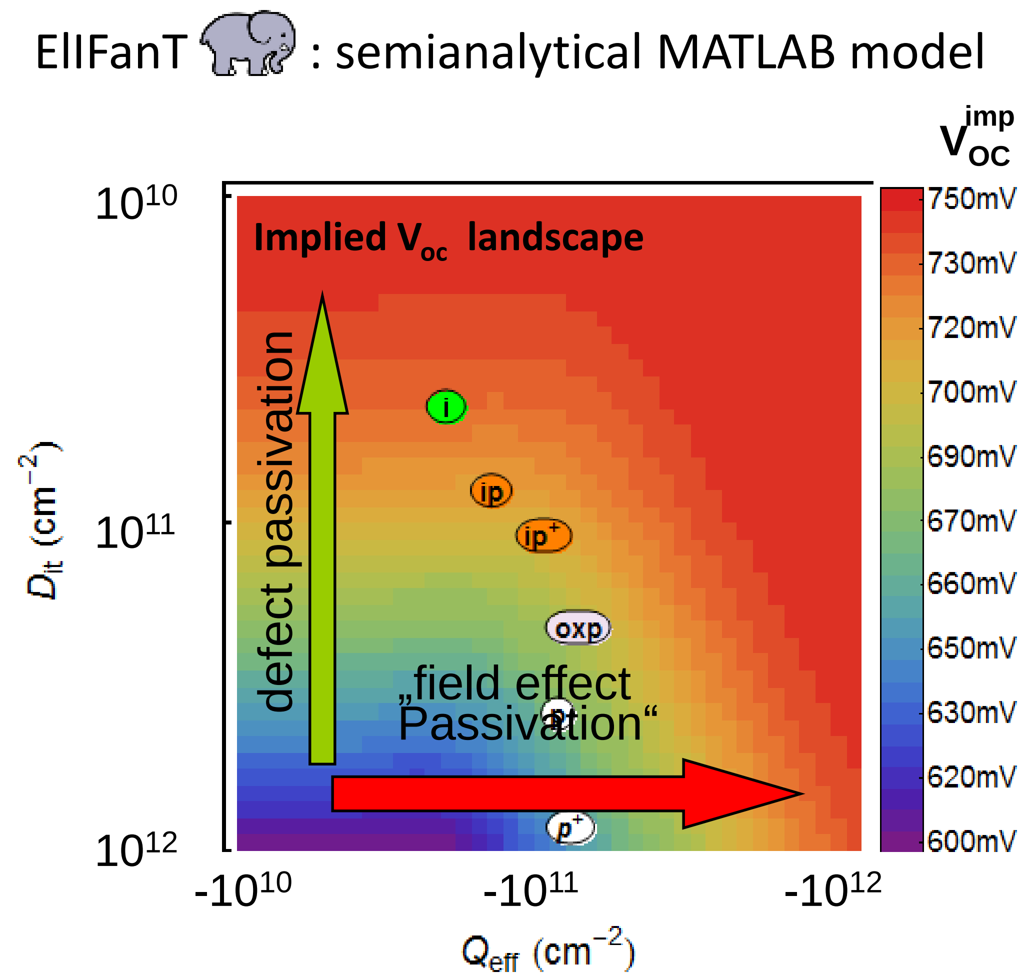


charge Q_{eff} in a-Si:H → band bending



- strong influence of interface recombination at front (and rear) side
- **D_{it} < 10^{10} cm^{-2} → IF recombination plays no role in cell**

C. Leendertz *et al.*, APL **98** (2011) 202108
R. Rößler, C. Leendertz *et al.*, JAP **113** (2013) 144513

Impact of i/p stack parameters on implied V_{oc}

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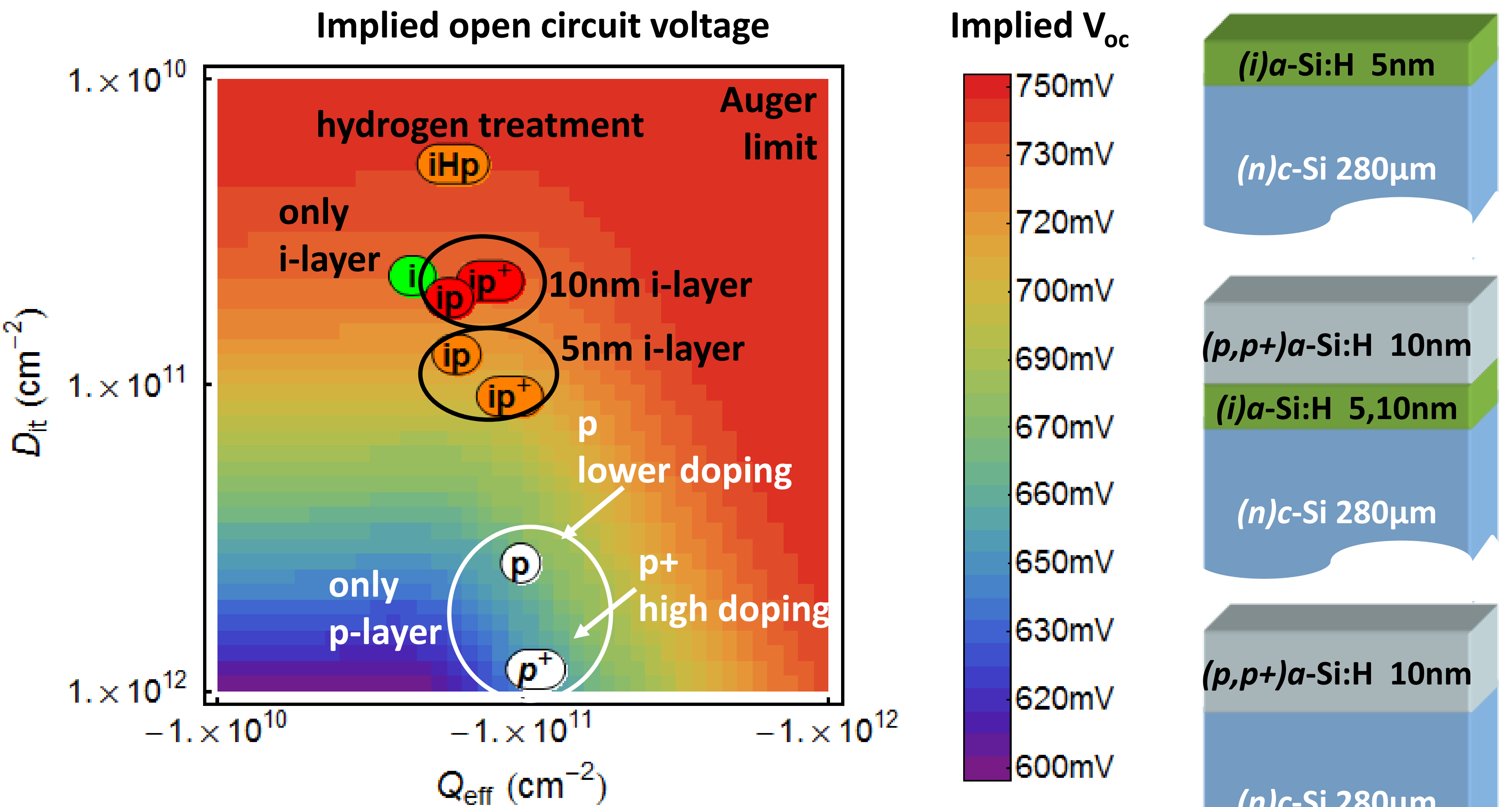

- D_{it} increases with doping of a-Si:H, decreases with a-Si:H layer thickness[1]
- V_{oc} is mainly governed by D_{it}; Q_{eff} has minor influence
- State of the art layers stacks close to the Auger limit

[1]S. de Wolf & M. Kondo, J. Appl. Phys., **105**, (2009)

R. Rößler, C. Leendertz *et al.*, JAP **113** (2013) 144513

Passivating carrier selective contacts

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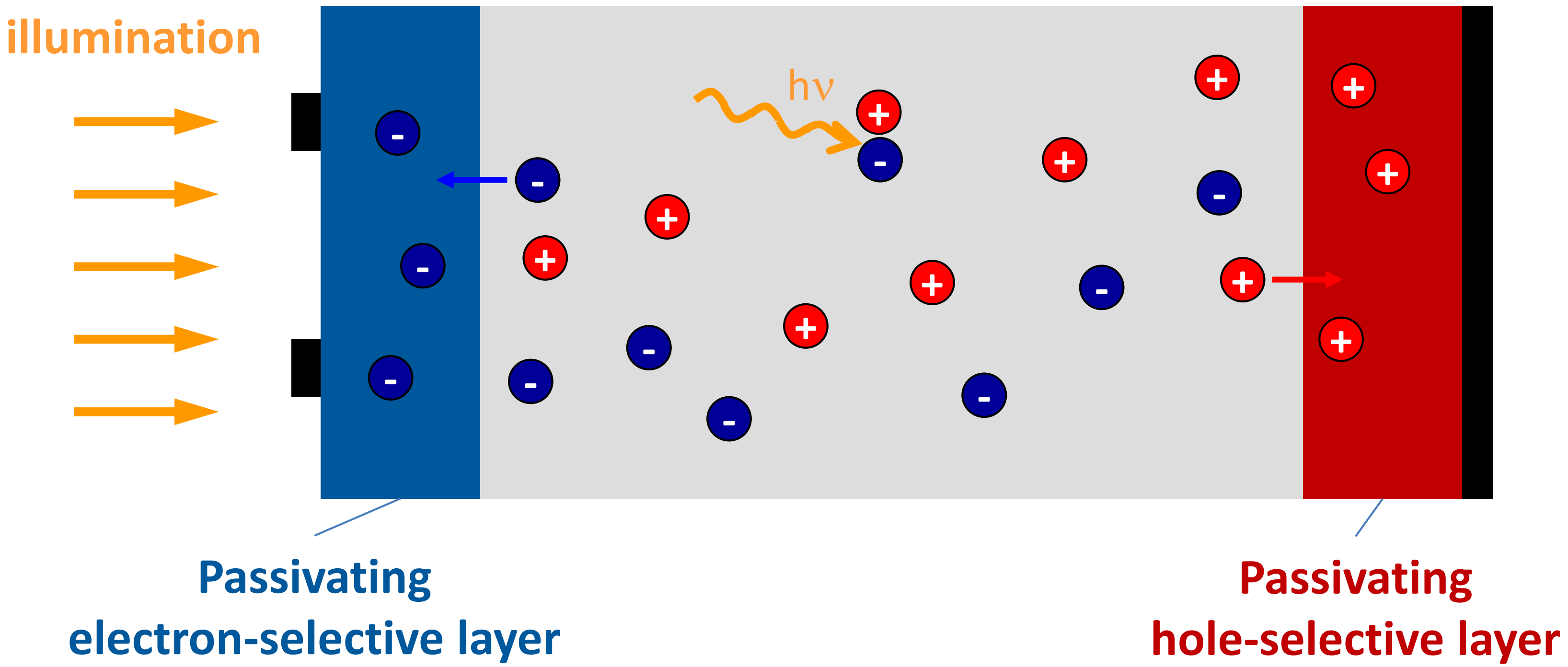

Key parameters of Carrier Selective Contacts

- Suitable energy band alignment
- Passivation (or non-existence) of interface defects
- Optical transparency
- (high electronic conductivity)

Passivating carrier selective contacts

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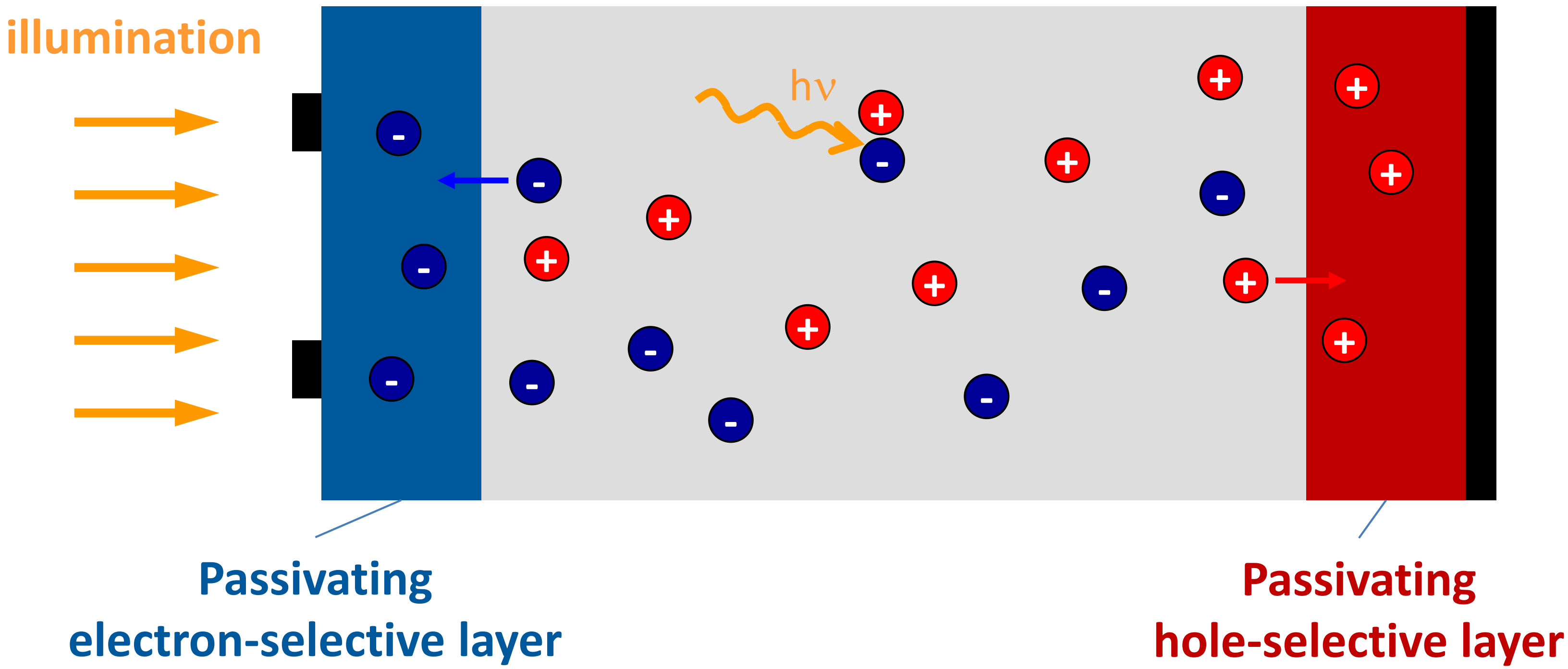

- What is a carrier-selective passivating contact (CSC)?
- “Classic” CSCs in silicon: amorphous/crystalline silicon heterojunctions
- Novel CSC example: IWO_x/c-Si – band line-up

Carrier selective contacts for c-Si solar cells

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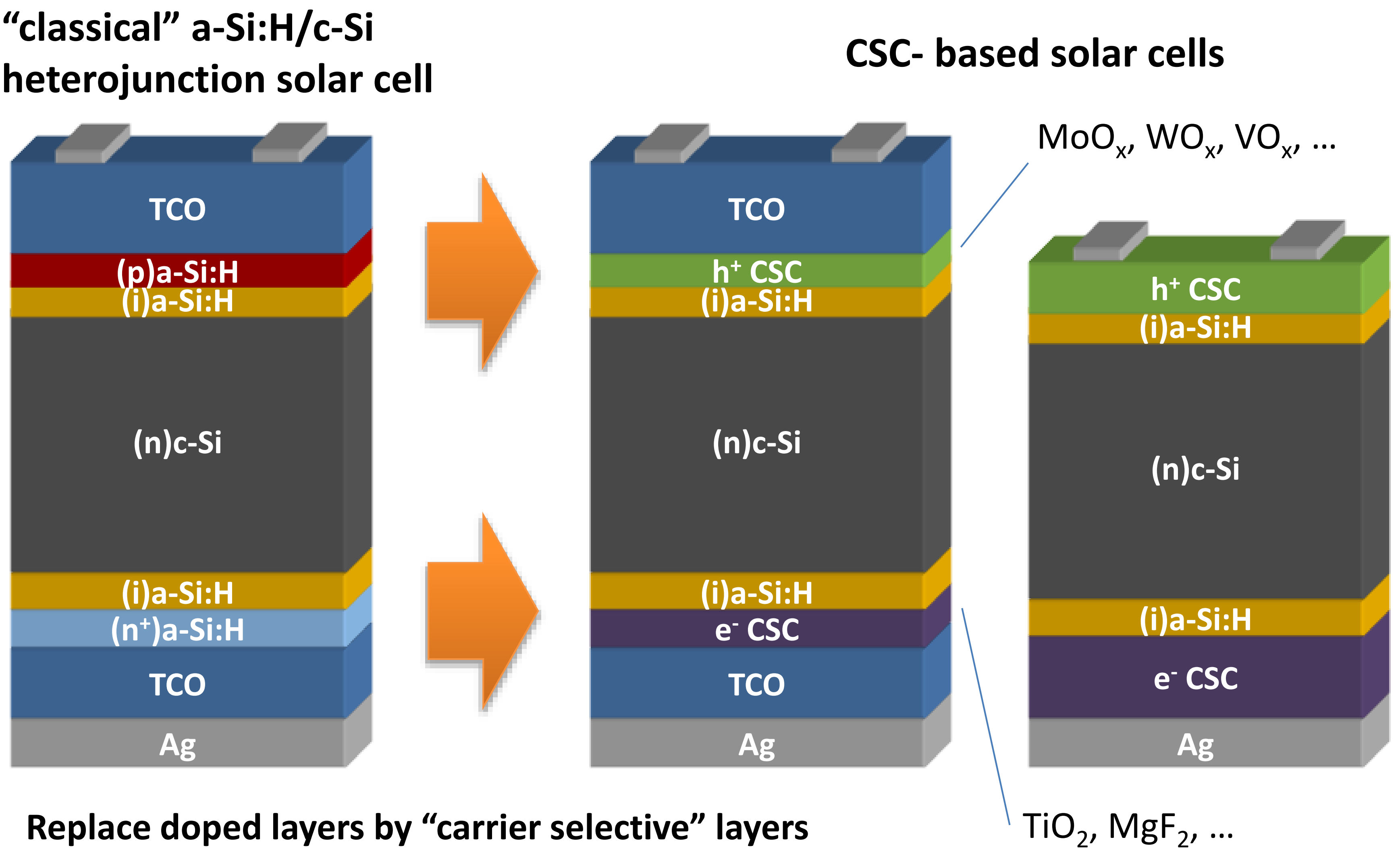

Replace doped layers by "carrier selective" layers

→ Highly transparent front contact

→ Might also replace TCOs if sheet resistivity is low enough (front), optics OK

→ Even omit passivating layers (a-Si:H, SiO_2)?

Work functions for selective contacts on Si

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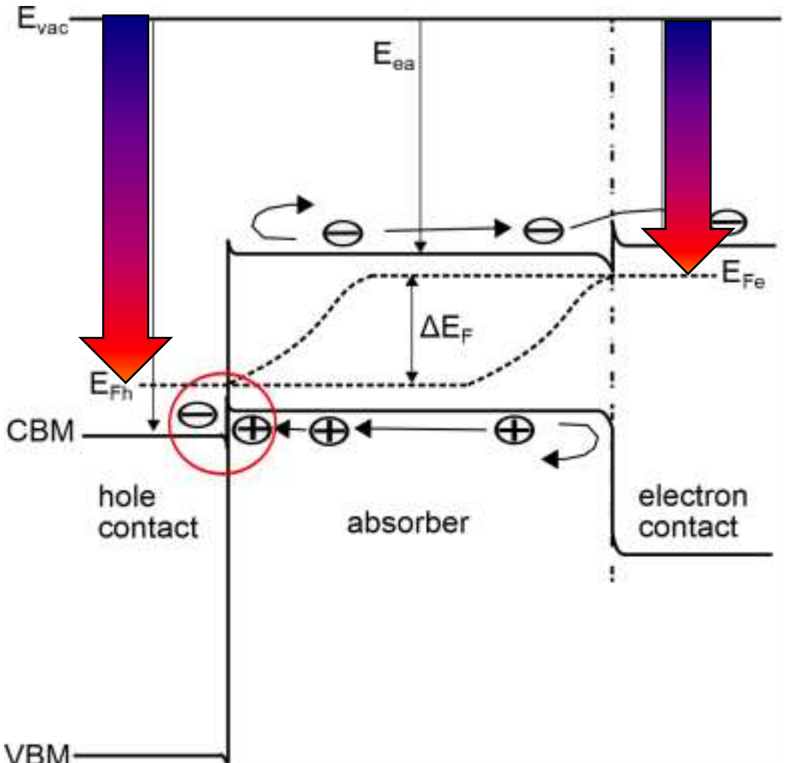
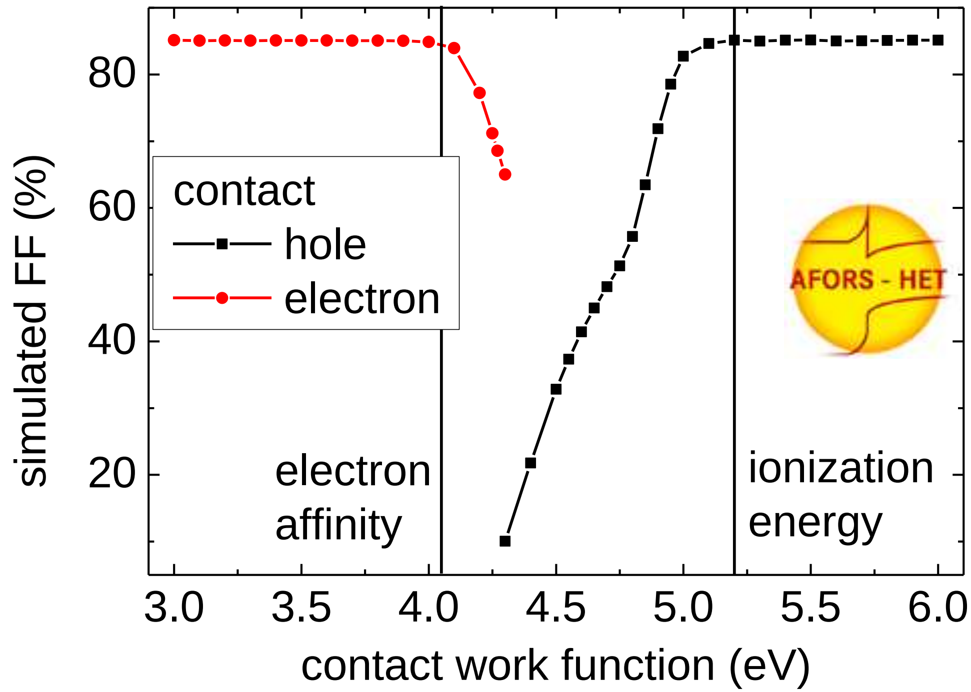
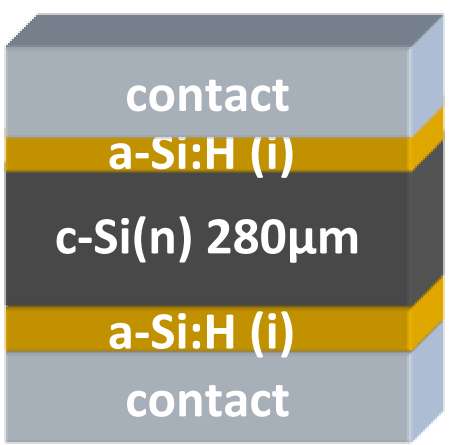


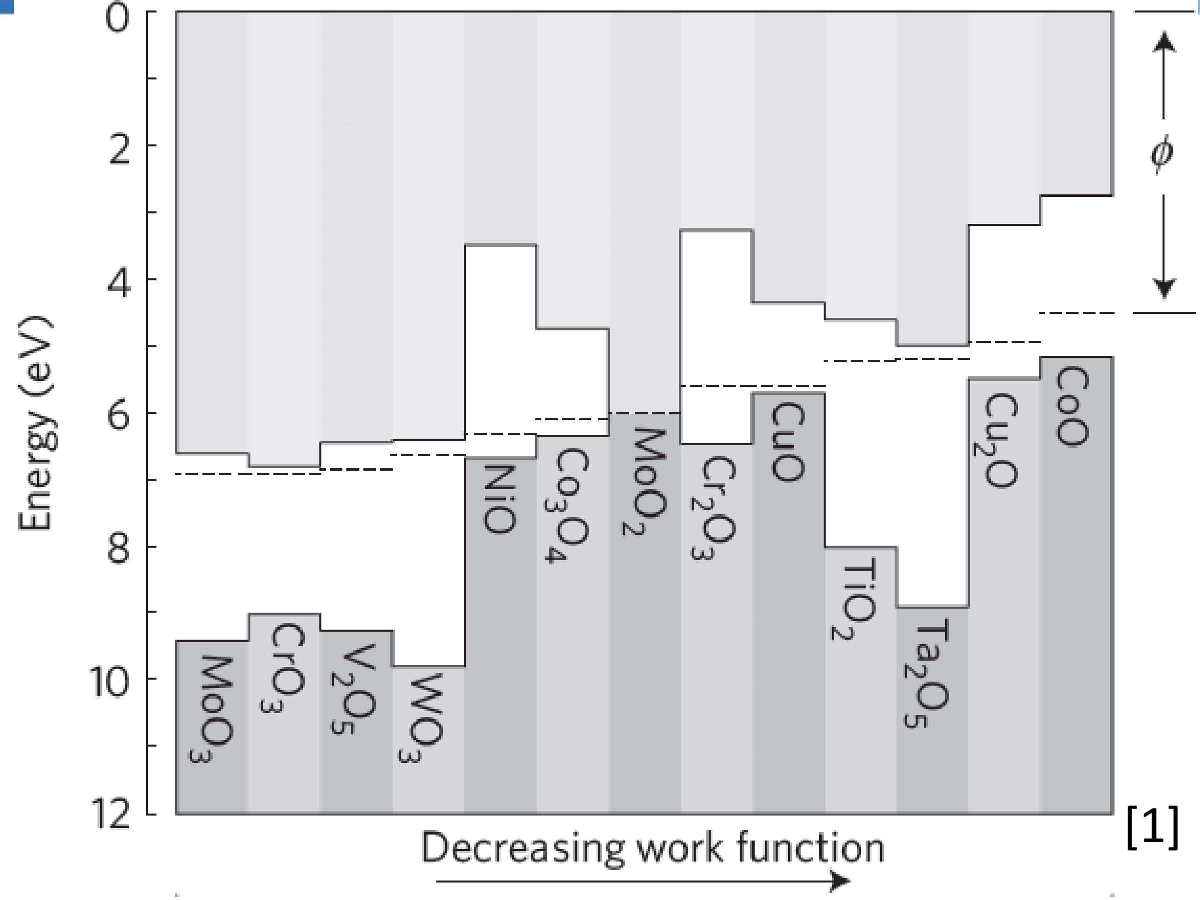




- **<u>electron contact:</u> work function $\phi_{ETM} < \phi_{cSi}$**
  in (n)cSi with e^- accumulation up to degeneration:
  ϕ_{cSi} = electron affinity χ_{cSi} → $\phi_{ETM} < \chi_{cSi}$

- **<u>hole contact:</u> work function $\phi_{HTM} > \phi_{cSi}$**
  in (n)cSi with h^+ inversion layer up to degeneration:
  ϕ_{cSi} = ionization potential I^*_{cSi} → $\phi_{HTM} > I^*_{cSi}$

High work function contact materials



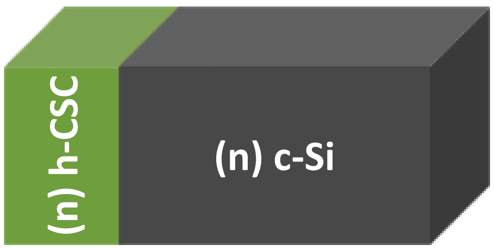
[1]

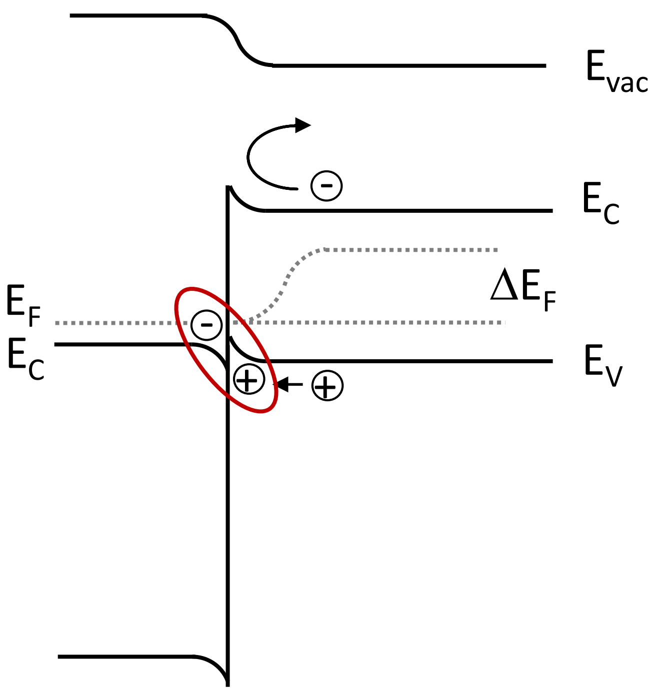
- organic photovoltaic community → MoO_x, WO_x, V_2O_5 [1]
- SHJ/c-Si solar cells with MoO_x[2,3], WO_x,[4] V_2O_5 [5]

[1] M. T. Greiner et al., Nature Mater. 11 (2012) 76-81
[2] C. Battaglia et al. Nano Lett. 14 (2014) 967-71 & Appl. Phys. Lett. 104 (2014) 113902
[3] J. Geissbühler et al. Appl. Phys. Lett. 107 (2015) 081601
[4] M. Bivour et al. Sol. En. Mat. Sol. Cells 142 (2015) 34-41
[5] L. G. Gerling et al. Sol. En. Mat. Sol. Cells 145 (2016) 109-15

Carrier selective *tunnel-recombination* hole contact

→ Compare to the TCO/(p)a-Si:H contact in SHJ



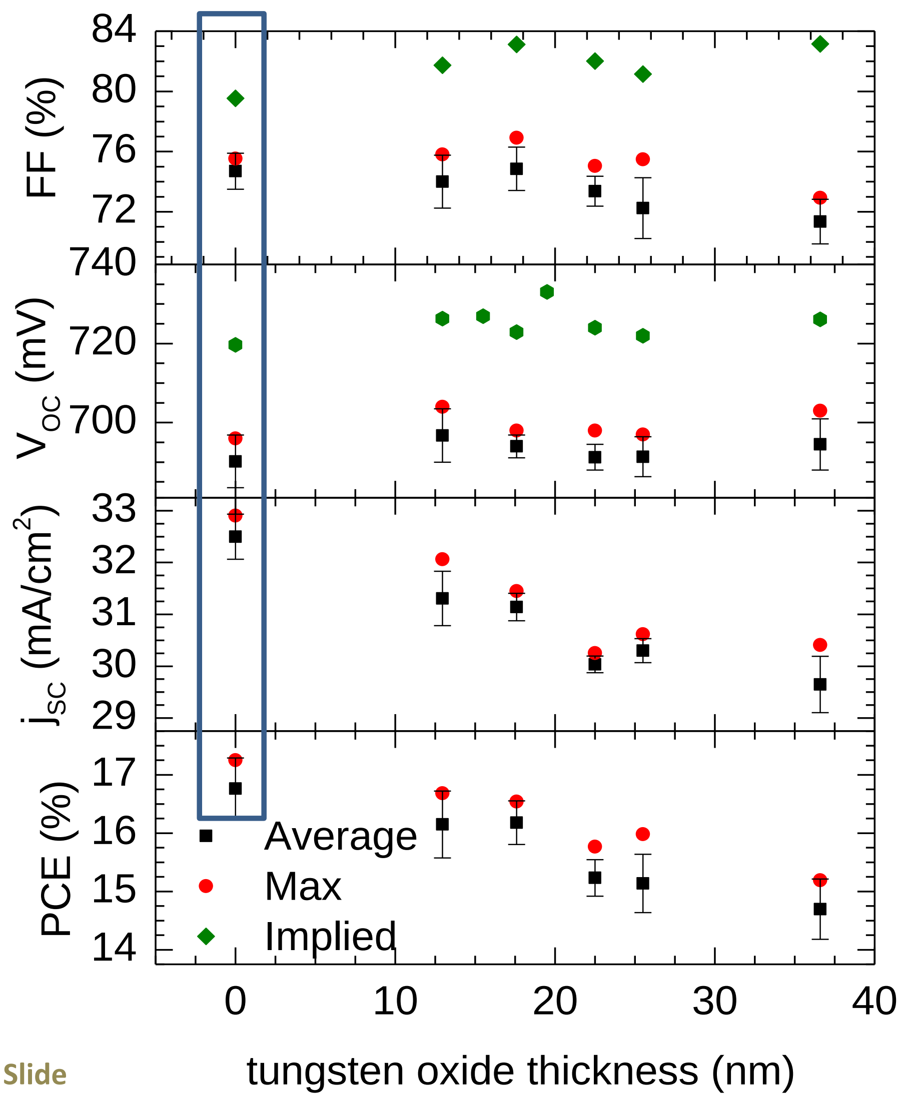


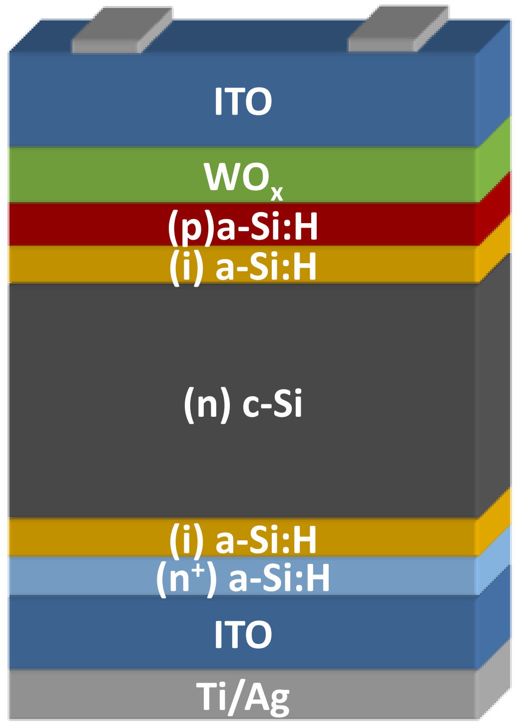
WO_x:

- n-type, high work function
- High stability (→ electrochromics, catalysis)

[1] M. T. Greiner et al., *Nature Mater.* **11,** 76-81 (2012)

WO_x thickness variation and solar cells





- Cells w/ WO_x: FF limited by series resistance
- Best FF at 20 nm tungsten oxide

Mews *et al.*, IEEE JPV **7** (2017) 1209

Indium tungsten oxide

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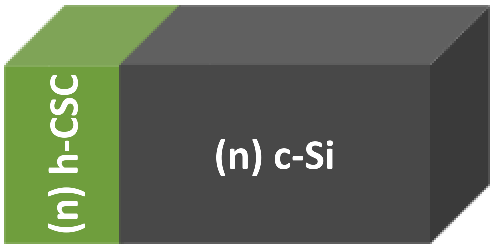
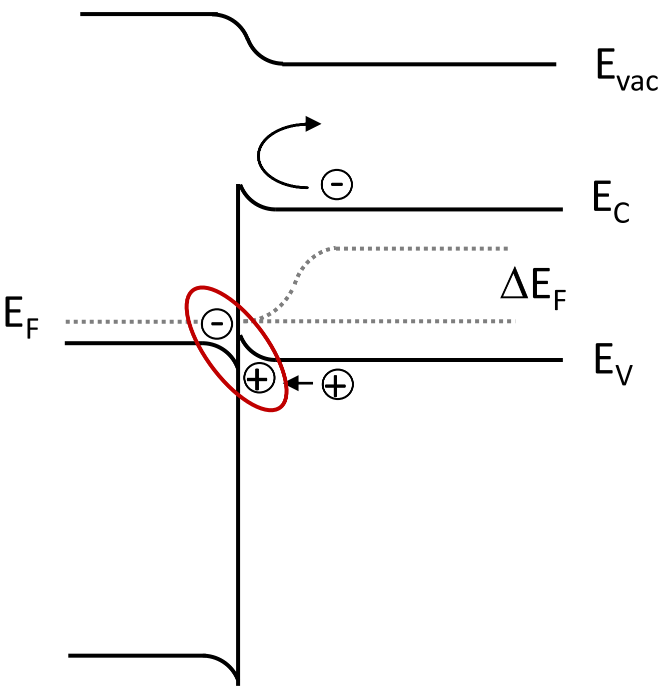
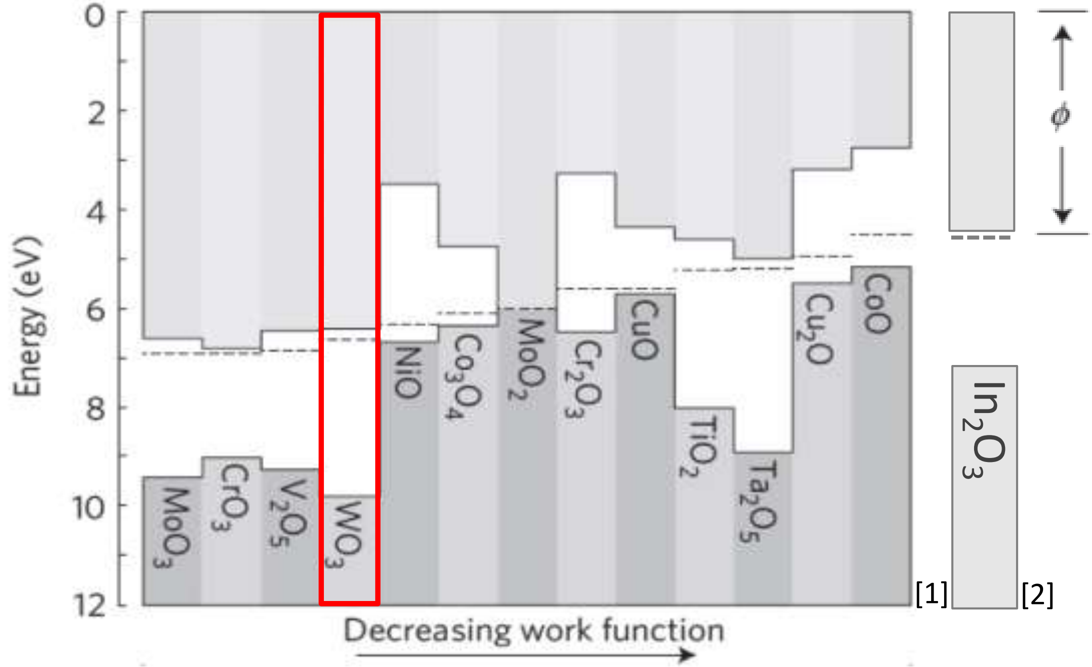
Carrier selective *tunnel-recombination* hole contact







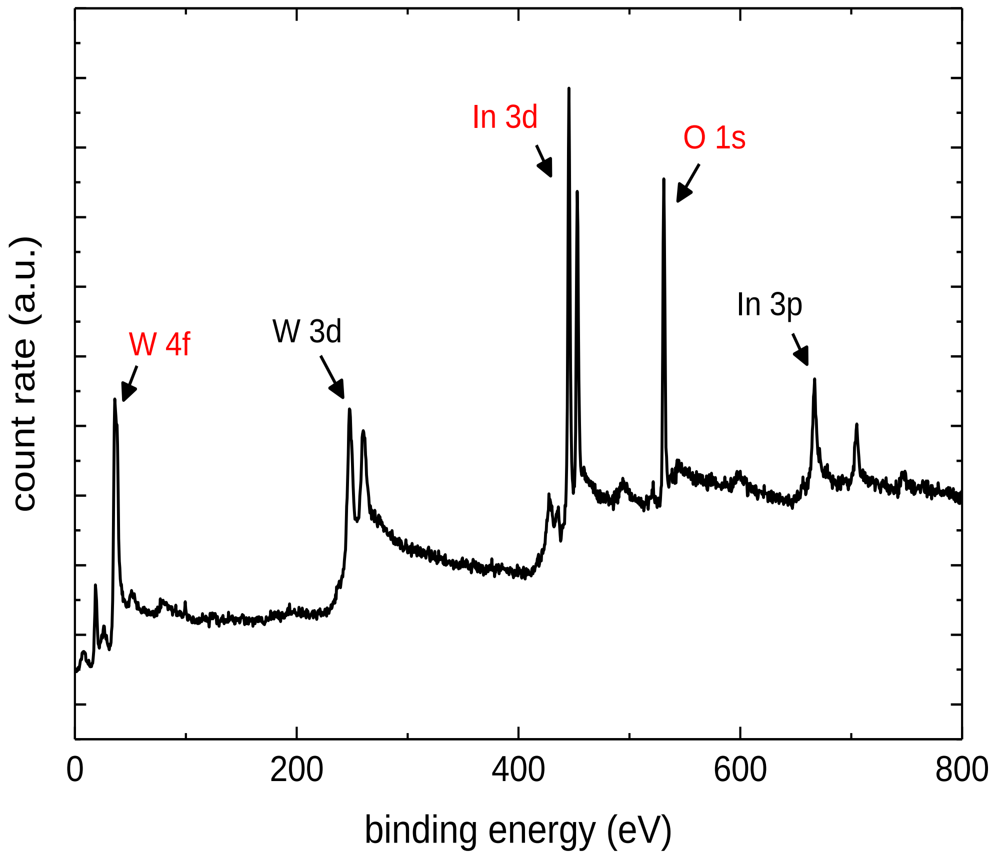
	WO_3	In_2O_3
High work function	✓	X
High conductivity	X	✓

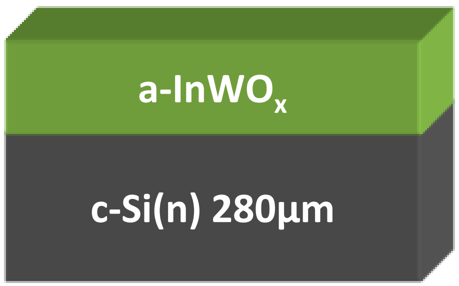
→ Find trade-off in indium tungsten oxide alloy?

[1] M. T. Greiner et al., *Nature Mater.* **11,** 76-81 (2012)
[2] Klein, A. et al., Materials, **3**, 4892 (2010)

XPS core level spectroscopy

W 4f, In $3d_{3/2}$ & O 1s core levels



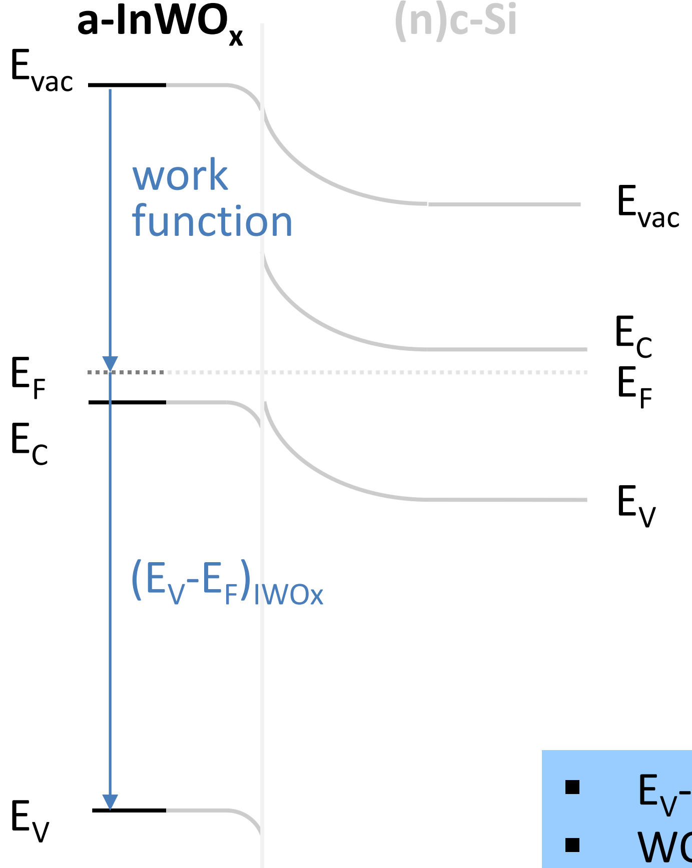


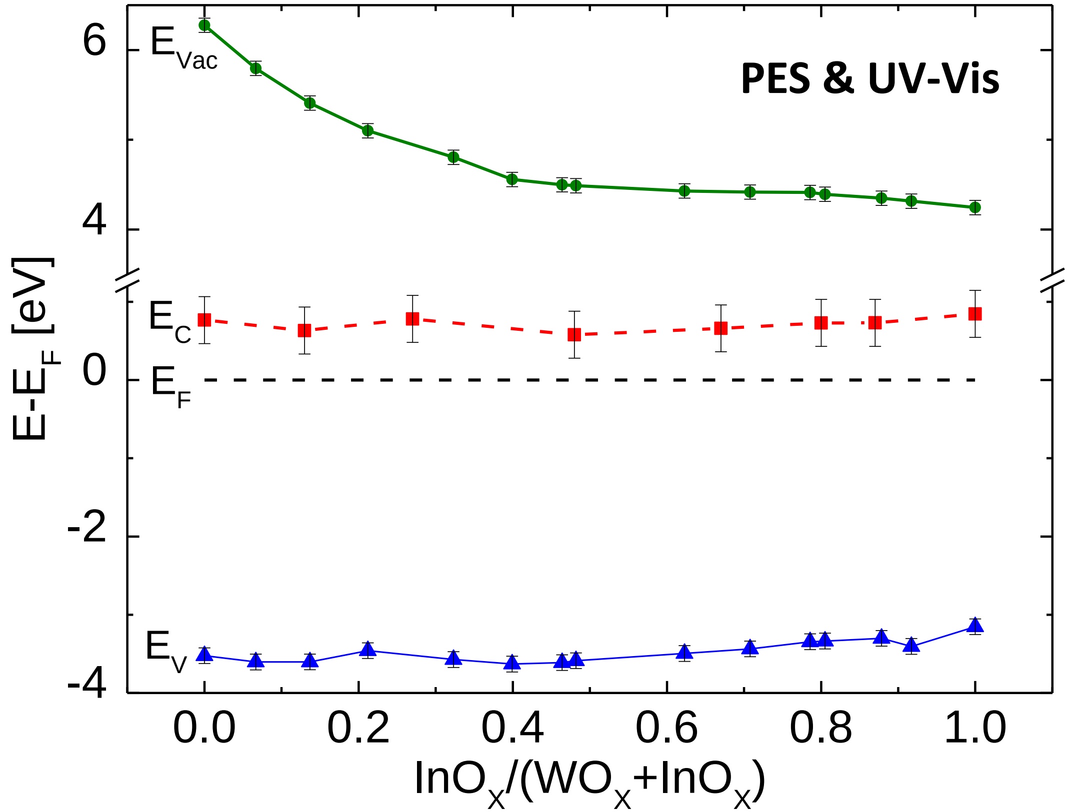
- HF dip
- load into MBE (p ~ 10^{-9} mbar)
- thermal co-evap. of WO_x + InO_x
- no intentional heating
  → **amorphous IWO_x**
- **in-system** photoelectron spectroscopy

Menzel *et al.*, Appl. Phys. Lett. **112** (2018) 011602

$InWO_x$/c-Si band diagram

In the dark, at equilibrium





- E_V-E_F = 3.2…3.6eV
- WO_x → InO_x: E_g = 4.3…4.0eV (Tauc, direct, allowed) *
- a-$InWO_x$ probably *not* degenerately doped

* WO_x: E_g ~ 2.6…3.5eV (Granqvist, Sol.En.Mat. 2000);
In_2O_3: $E_{g,direct}$ ~3.6eV (Liu, JAP, 2008)

Menzel *et al.*, Appl. Phys. Lett. **112** (2018) 011602

InWO$_x$/c-Si band diagram

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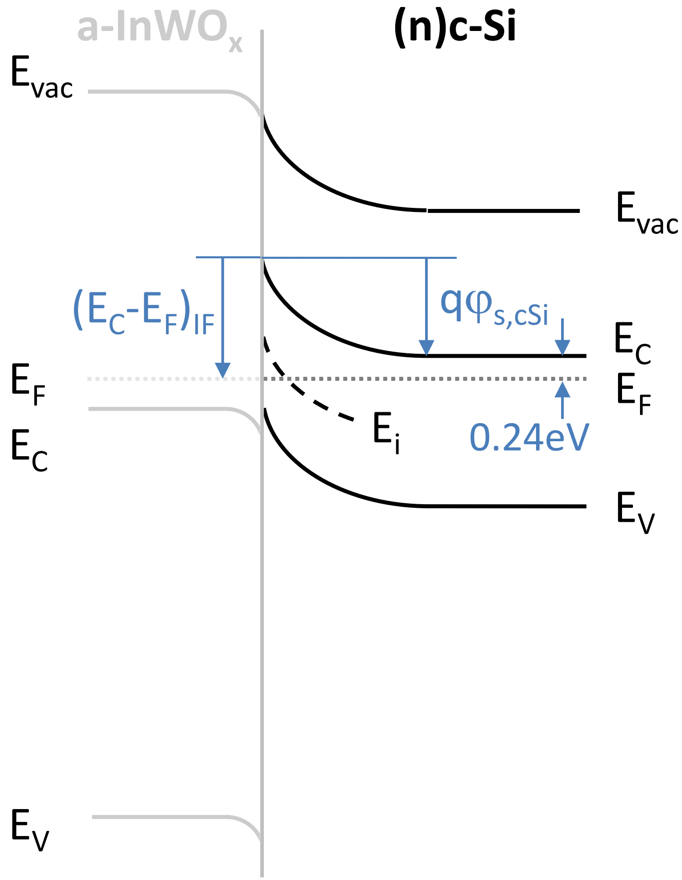
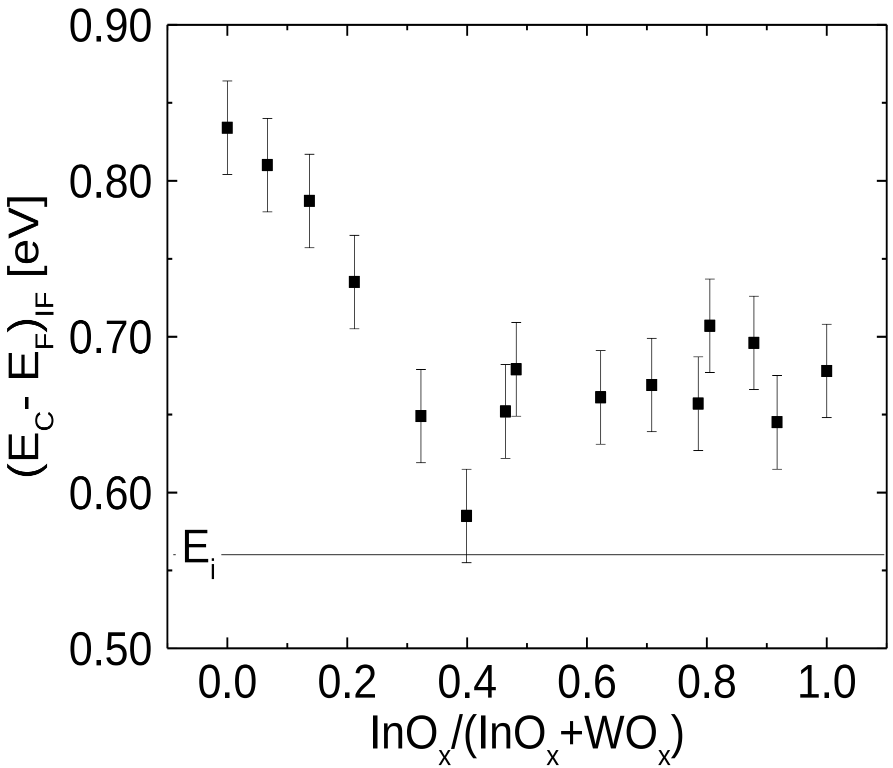


Barrier for electrons:
$(E_C-E_F)_{bulk} + q\varphi_{s,cSi}$ from surface photovoltage



- Inversion (accumulation of holes) for all stoichiometries

Menzel *et al.*, Appl. Phys. Lett. **112** (2018) 011602

$InWO_x$/c-Si band diagram

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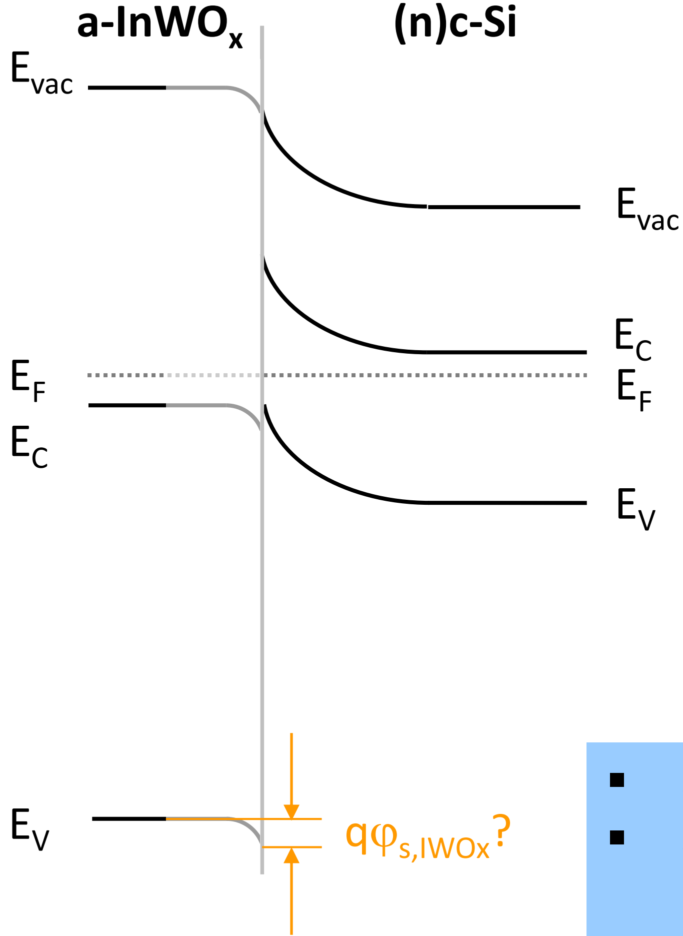
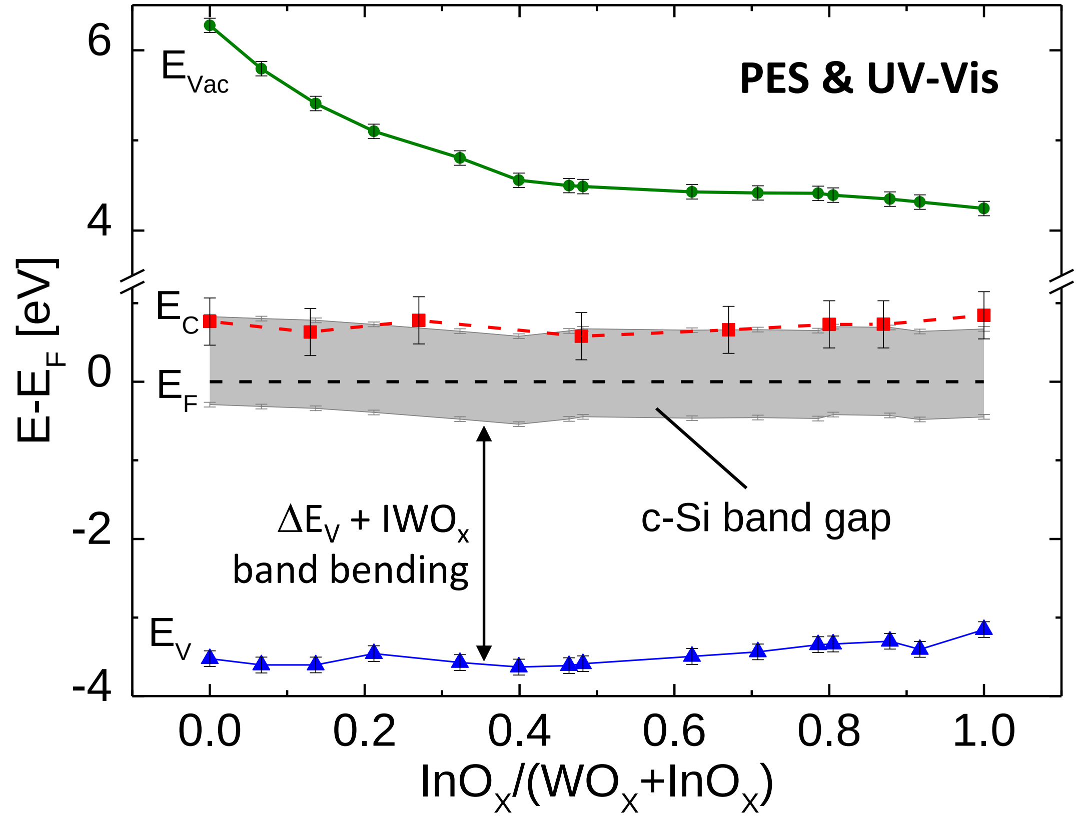
In the dark, at equilibrium





- a-IWOx/c-Si: staggered (type II) heterojunction
- a-WO_x → a-InO_x:
  - ΔE_V = 3.3…2.7 eV*
  - $\Delta E_C \approx 0$ eV

  } + band bending $q\varphi_{s,IWOx}$

* *Theory:* bcc-In_2O_3 ΔE_V = 3.2eV (Höffling, APL, 2010) *Exp.:* a-InOx, photoinjection: ΔE_V = 2.6eV (Schmidt, 2007)

Menzel *et al.*, APL (2018)

$InWO_x$/c-Si band diagram

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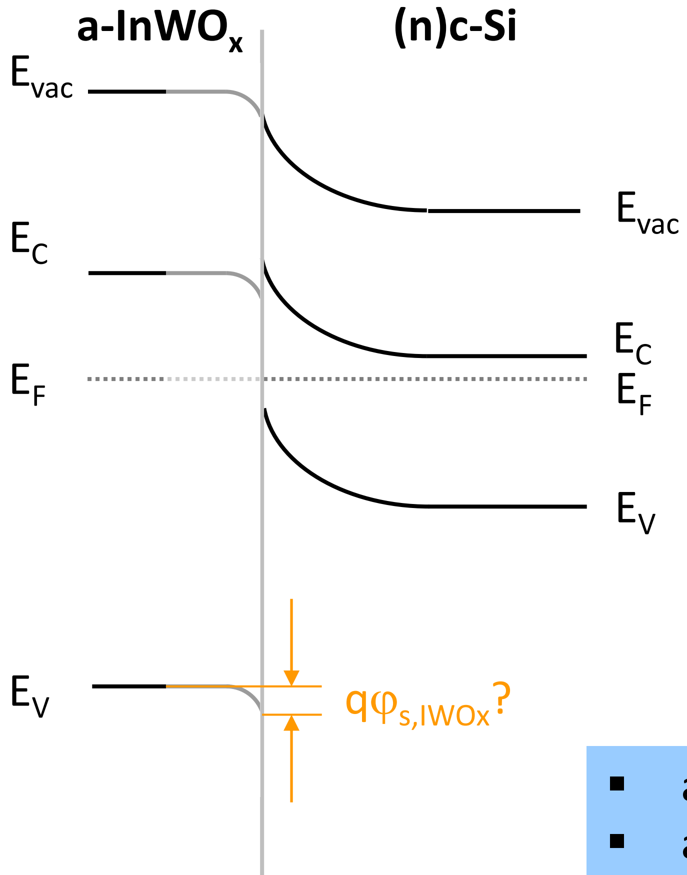

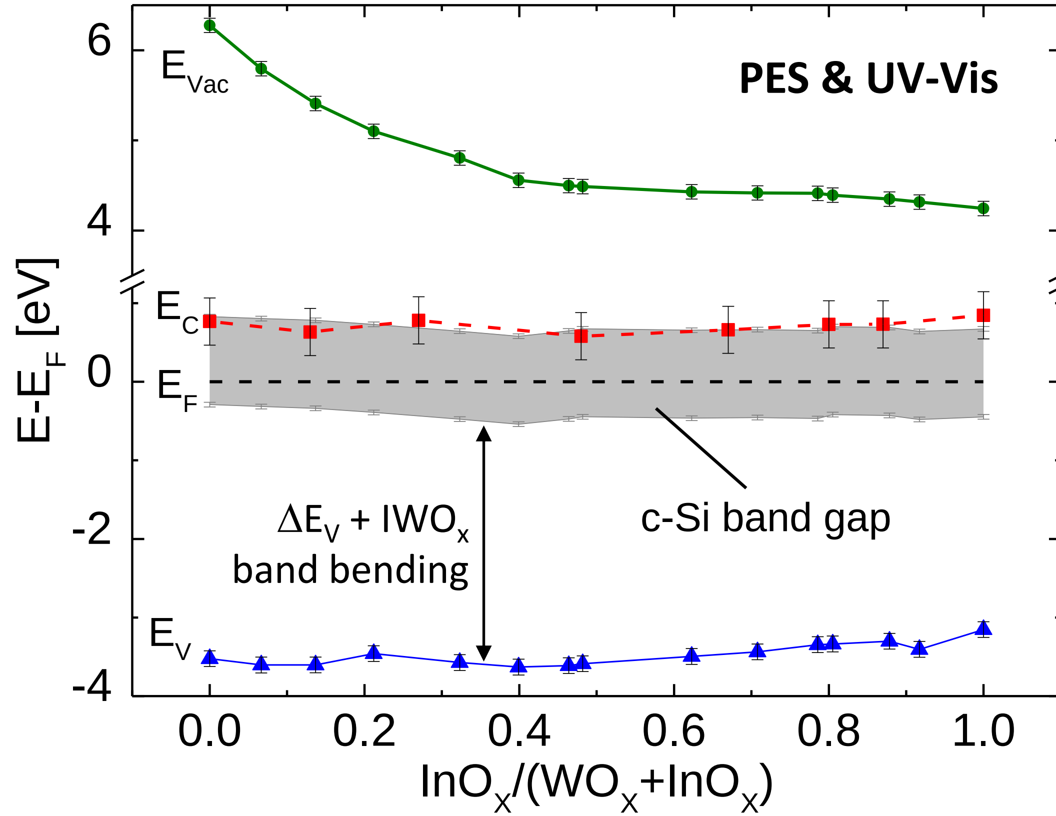

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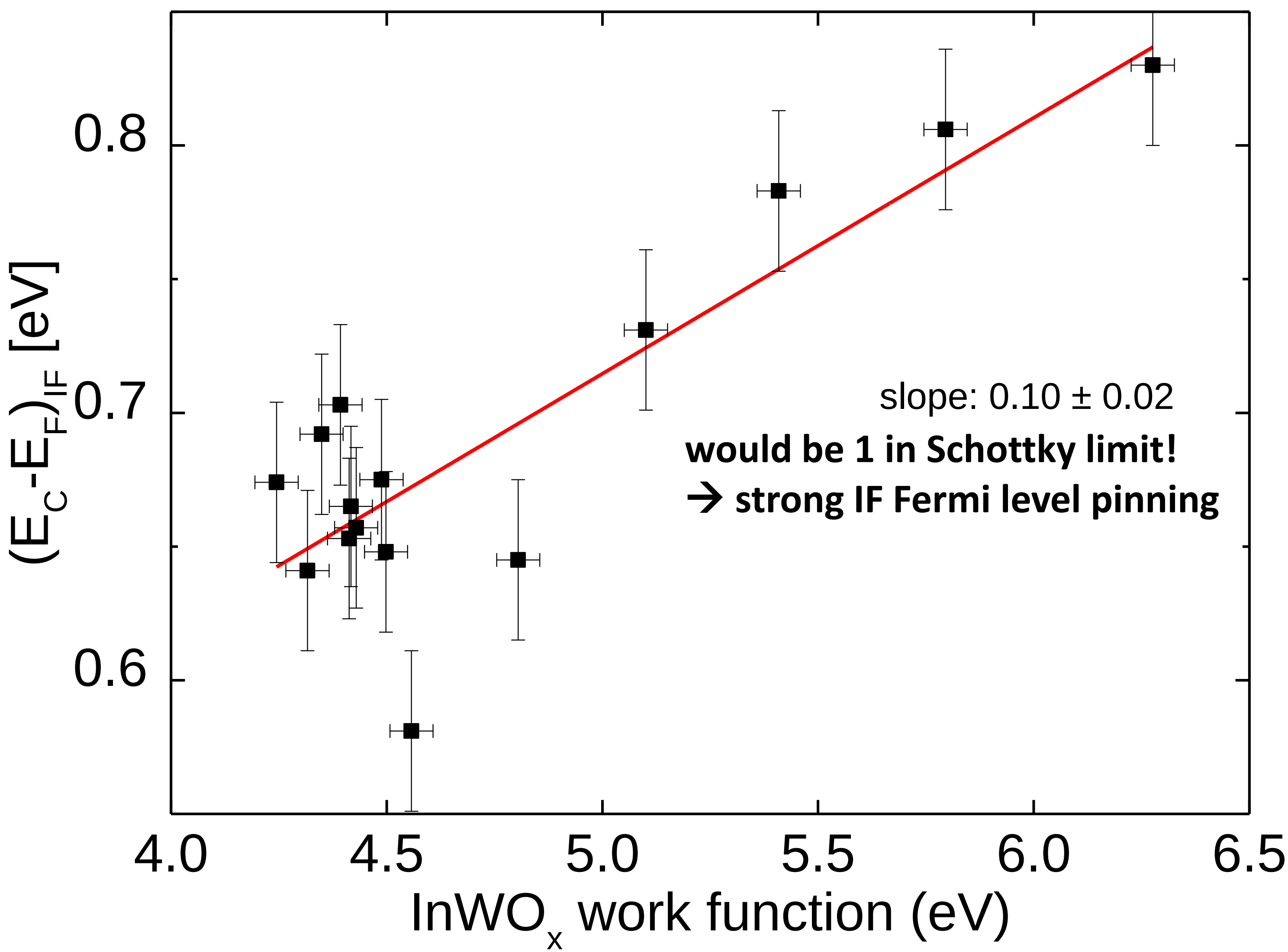
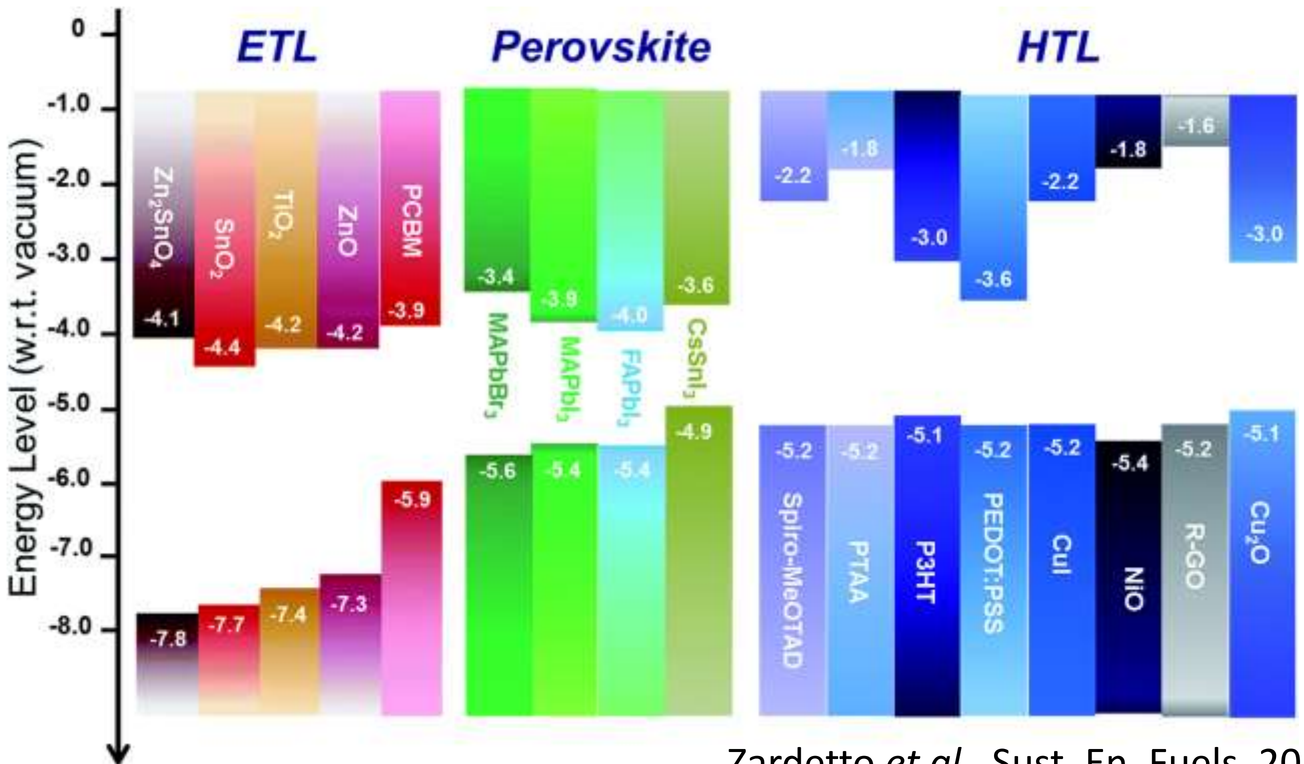
Menzel *et al.*, APL (2018)

Interface Fermi level pinning



Band line-ups in organic and perovskite-PV



Zardetto *et al.*, Sust. En. Fuels, 2017, 1, 30-55

Band line-up considerations in OPV and perovskites(?)

- **"Anderson's rule":** $\Delta E_C = \chi_A - \chi_B$, $\Delta E_V = I^*_A - I^*_B$
- **Schottky limit:** no interface defects – no Fermi level pinning

Usually not true for anorganic heterojunctions!

(but theories exist: charge neutrality levels, …)

e.g. Mönch, Electron. Prop. of Semicond. Interf., Springer (2004)

Summary

Passivating carrier-selective contacts

Basic requirements

- Passivation (or non-existence) of interface defects
- Energy band alignment: aligned band edges *vs.* barriers
- Optical transparency
- (high electronic conductivity)

"Classical" example for CSCs: Si heterojunction cells

- well-passivated interfaces $\rightarrow$ low recombination $\rightarrow$ V_{oc} >700mV

Novel carrier-selective contacts

- From OPV & microelectronics community: MoO_x, WO_x, V_2O_5, …

Example: Thermally evaporated $InWO_x$

- $InWO_x$/(n)c-Si IF inverted for all stoichiometries
- c-Si band bending > 0.5 eV for $InO_x/InWO_x$ = 0…20%
- Type II heterojunction, ΔE_V = 3.3…2.7 eV, ΔE_C ~ 0eV ($\pm$ $InWO_x$ b.b.)

Literature

HZB Helmholtz Zentrum Berlin

Textbooks & monographs

- P. Würfel, *Physics of Solar Cells*. New York, NY, USA: Wiley (2009)
- W. Mönch, Electron. Prop. of Semiconductor Interfaces, Springer (2004)

Carrier selective contacts & band line-up

- U. Würfel et al.: Charge Carrier Separation in Solar Cells. IEEE J. Photovolt **5** (2015) 461
- J. Melskens et al: Concepts and Prospects of Passivating Contacts for Crystalline Silicon Solar Cells. Proc. 42nd IEEE Photovoltaic Specialist Conference (PVSC), IEEE, 2015
- J. Tersoff: Theory of semiconductor heterojunctions: The role of quantum dipoles. Phys. Rev. B, **30** (1984) 4874
- A. Klein et al.: Transparent Conducting Oxides for Photovoltaics: Manipulation of Fermi Level, Work Function and Energy Band Alignment. Materials **3** (2010) 4892-4914

Numerical simulations of heterojunctions

- AFORS-HET, https://www.helmholtz-berlin.de/forschung/oe/ee/si-pv/projekte/asicsi/afors-het/index_en.html

Thank You

HZB Helmholtz Zentrum Berlin

"a-Si:H/c-Si heterojunction team" (current & former members):

H. Angermann, E. Conrad, J. Haschke, K. Jacob, C. Klimm, **C. Leendertz**, Th. Lußky, L. Mazzarella, **D. Menzel**, **M. Mews**, N. Mingirulli, M. Muske, R. Rößler, M. Schmidt, T. Schulze, C. Stang, R. Stangl, M. Wittig

…and all colleagues at HZB Inst. Silizium-Photovoltaik, PVcomB, Young Investigator Groups Albrecht & Unger

Financial Support:

HERCULES – EU FP7 project no. 608498

NEXTBASE - EU H2020 project no. 727523

HERA – German BMWi project

PersiST – German BMWi project