High efficiency silicon heterojunction solar cells: From conventional concepts to a 3rd generation bi-triplet exciton generating hybrid device

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SPREE/UNSW Seminar 12/11/2015

Where I come from…

Berlin City

Helmholtz Center Berlin

EMIL

Energy **M**aterials **I**n-Situ **L**ab

HZB Helmholtz Zentrum Berlin EMIL

Valence band offset and hole transport in c-Si/a-SiO_x heterojunction solar cells

Cooperation:

Institut for Silicon Photovoltaics (HZB)

Lars Korte

Mathias Mews

…many more people involved

Financial support:

Bundesministerium für Bildung und Forschung

"SISSY" project

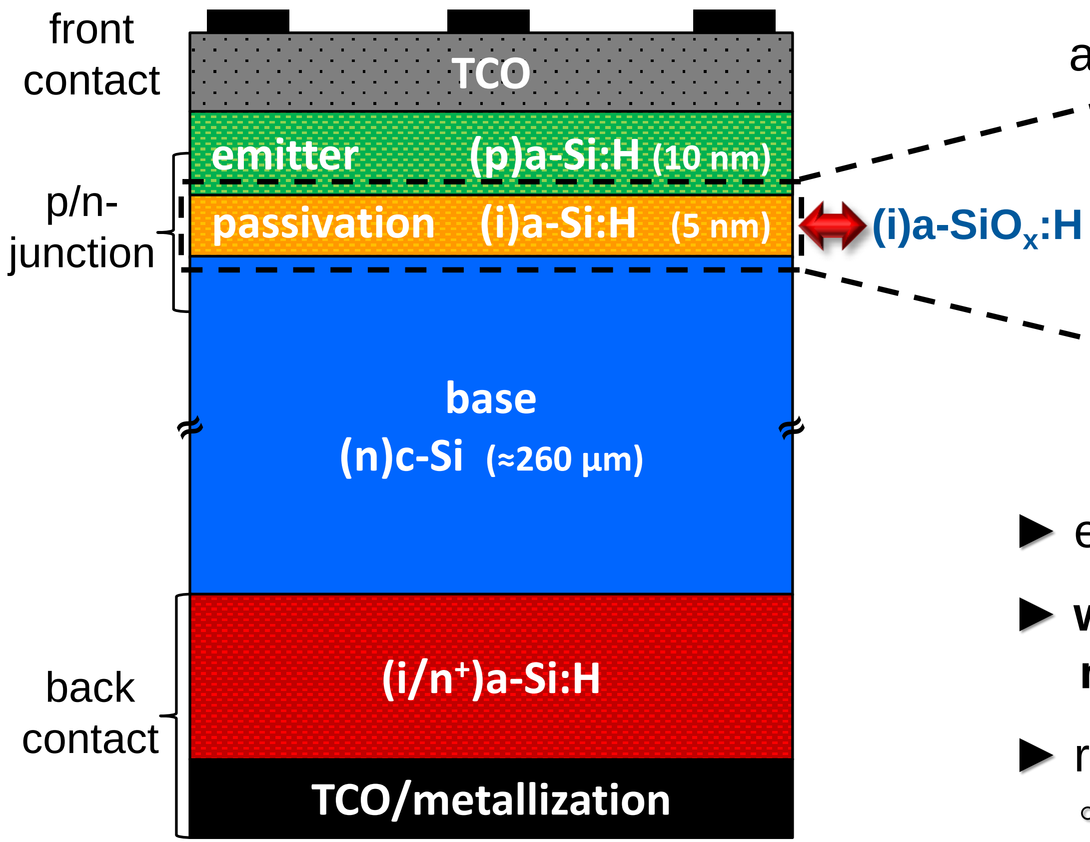
Grant No. 03SF0403

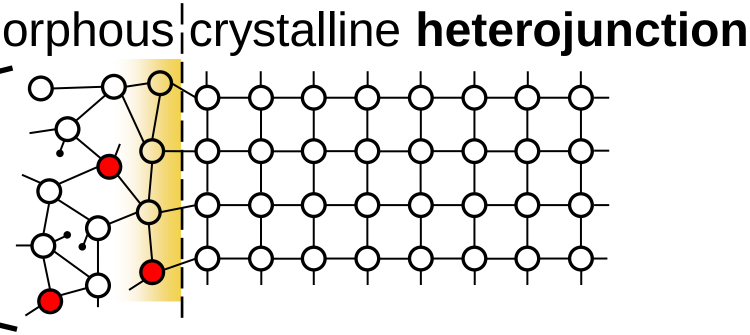
European Commission

HERCULES

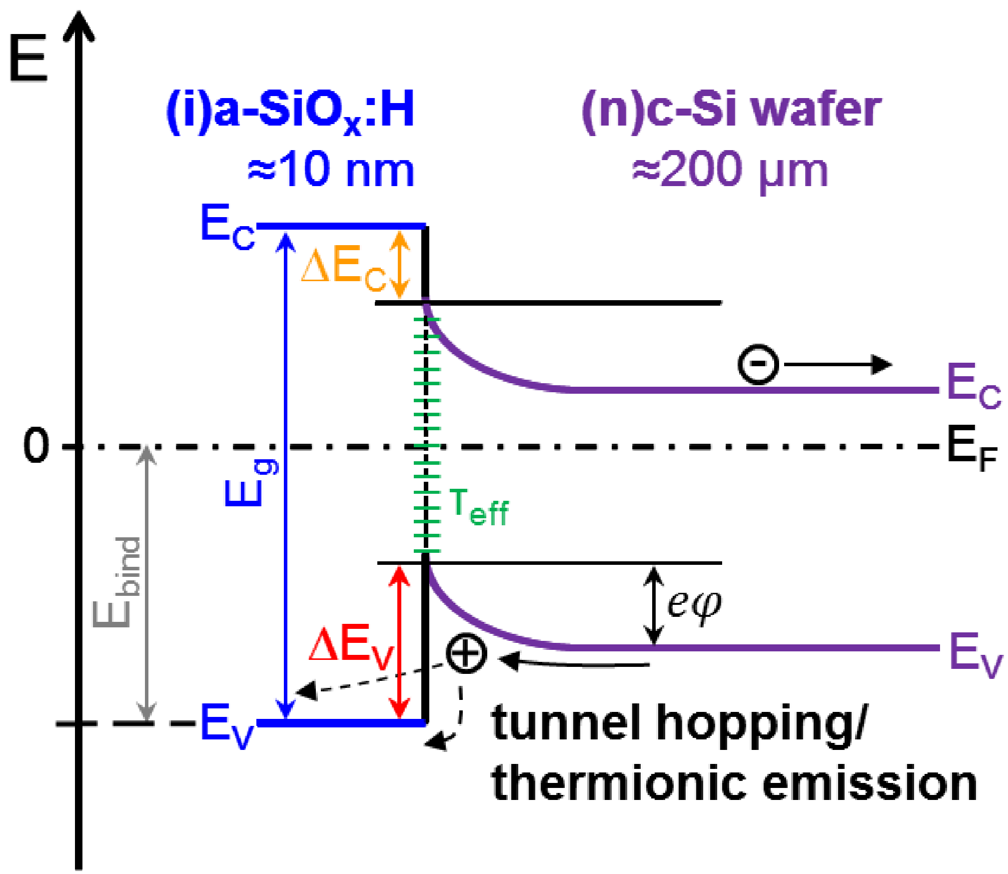
Grant No. 608498

SHJ solar cell
(Silicon Heterojunction)



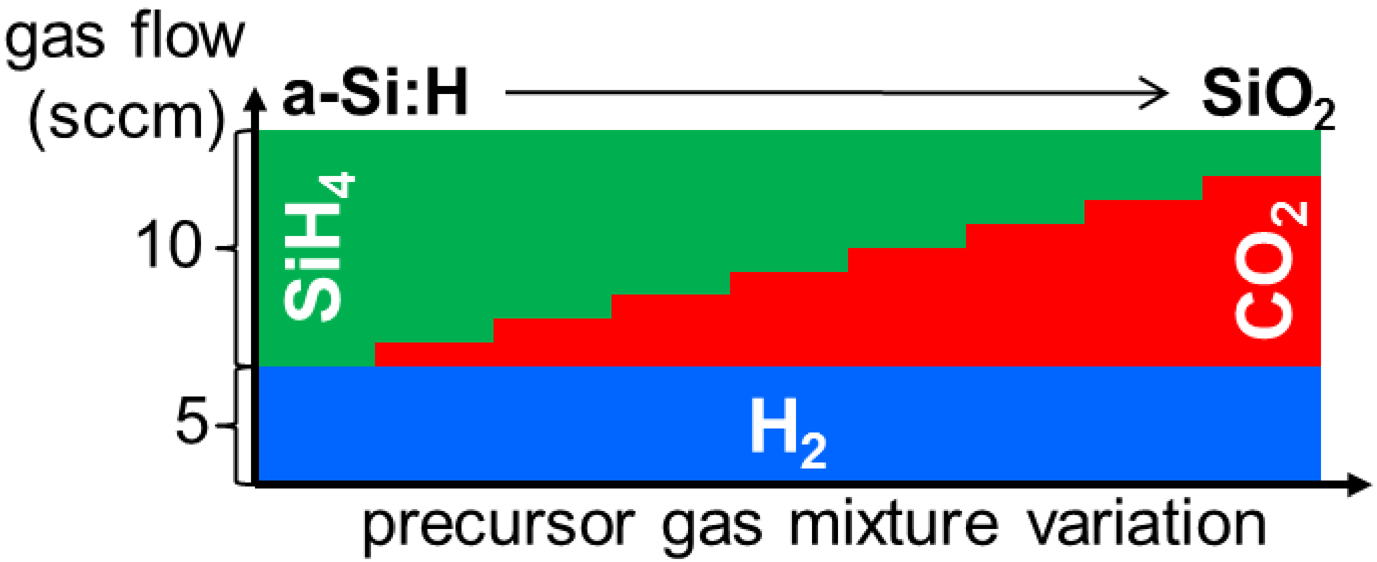


- ▶ excellently passivated contacts
- ▶ **world record** for Si based PV:
  η = 25.6%/ 22.5% (Panasonic, 2014/2015)
- ▶ reduce parasitic absorption
  - wide band gap materials
  - band offset modification

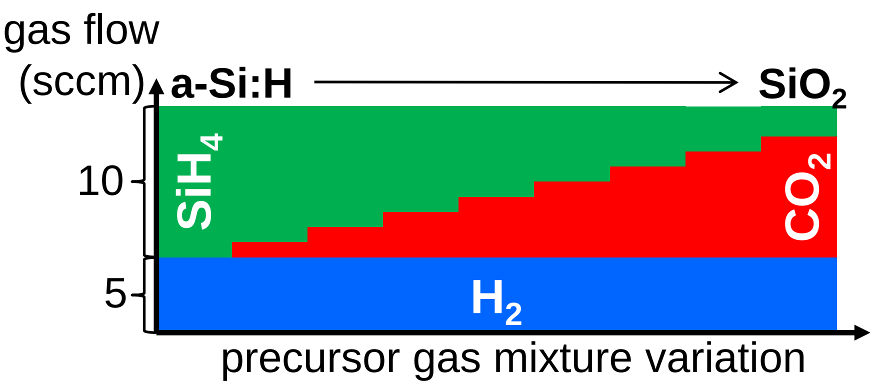


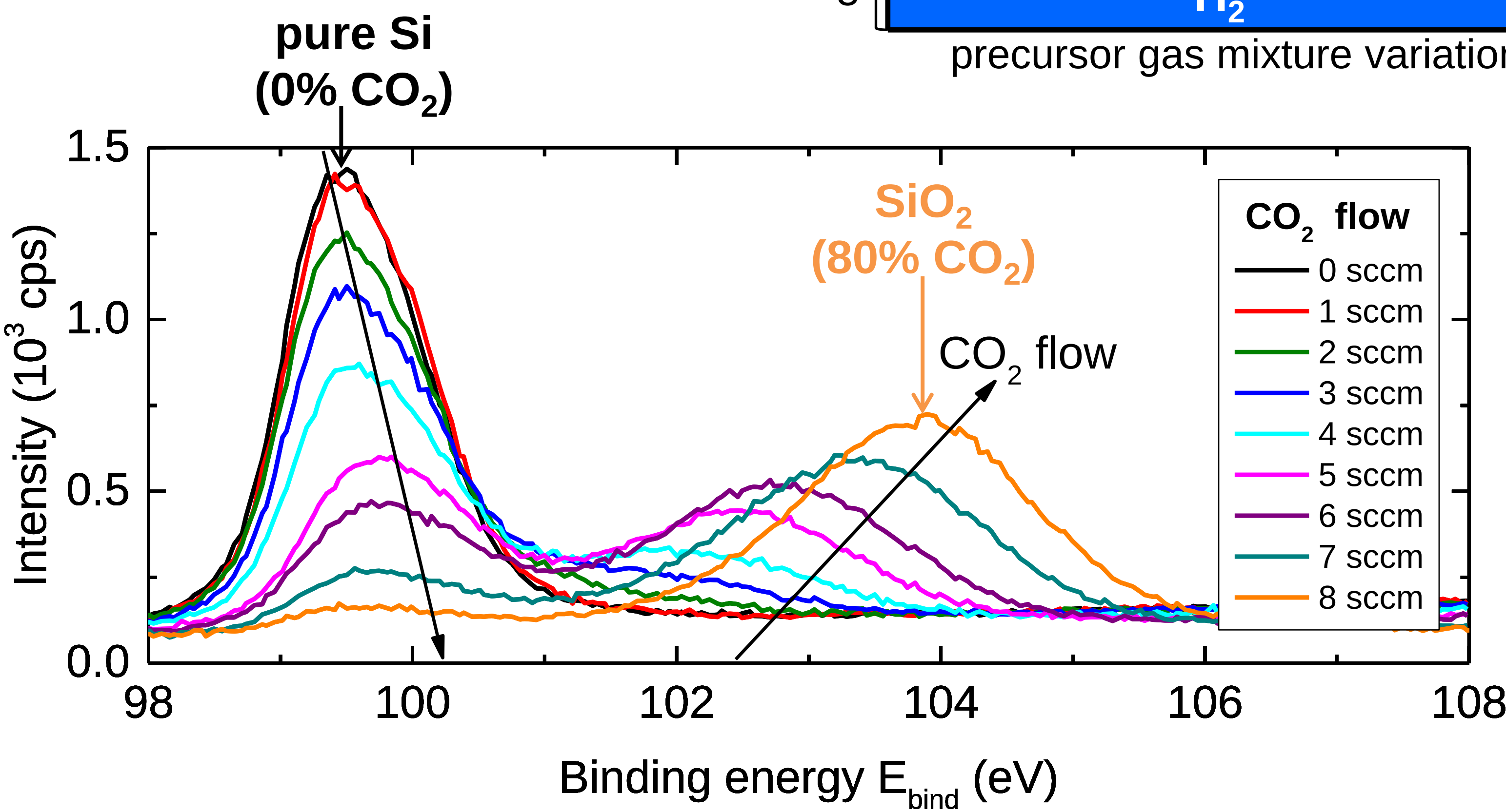
- **heterojunction parameter**
  - optical band gap E_g
  - band offsets ΔE_V, ΔE_C
  - surface passivation τ_{eff}
- **FOCUS** on ΔE_V of
  - **a-SiO$_x$:H/c-Si** heterointerface
  - **hole transport** mechanism

- **PECVD** layer deposition (**P**lasma **E**nhanced **C**hemical **V**apour **D**eposition)
  - varying precursor gas mixtures
  - change of *stoichiometry x* in a-SiO_x layers



- **X**-ray **P**hotoelectron **S**pectroscopy
- Si 2p peak

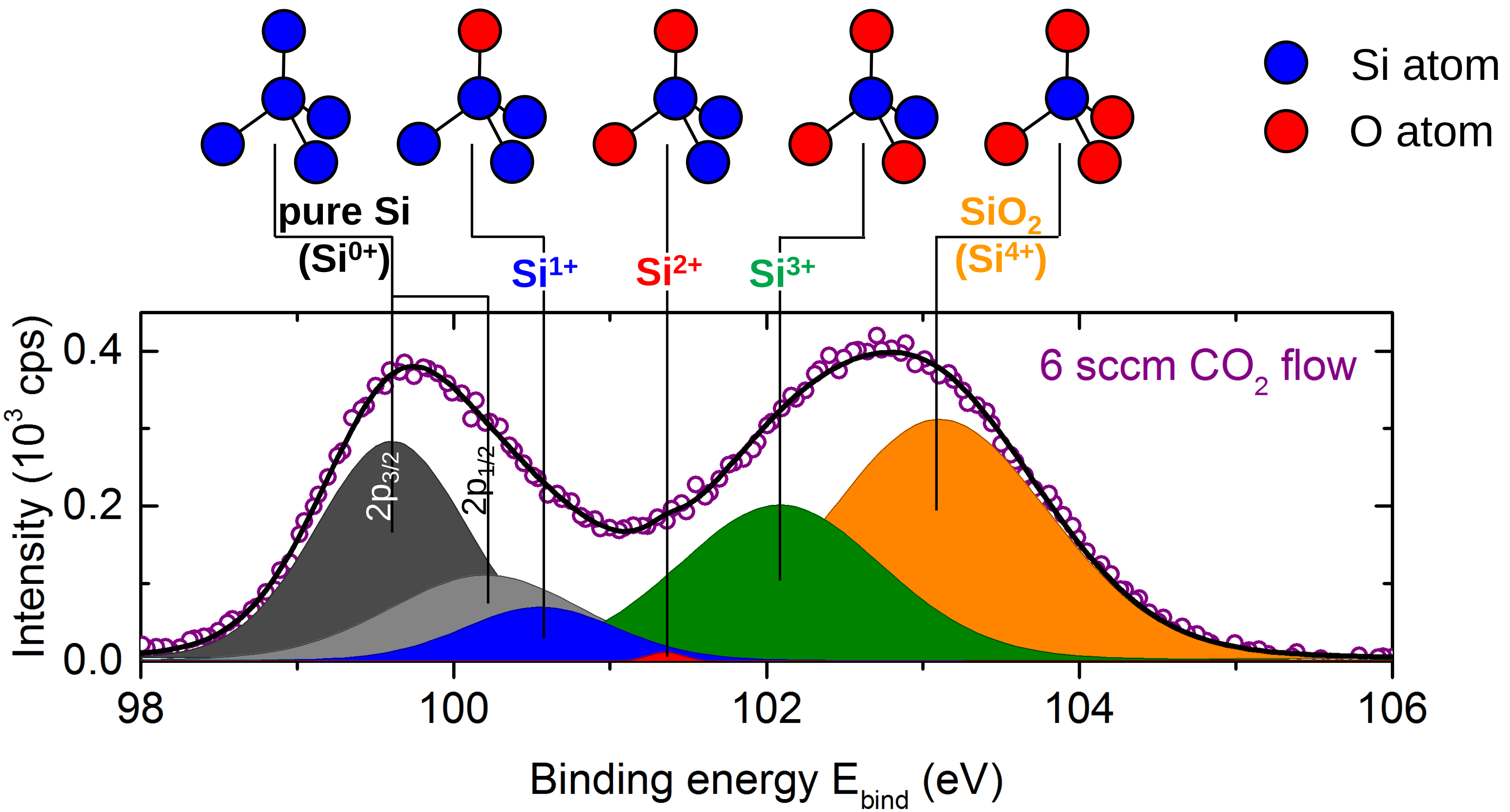




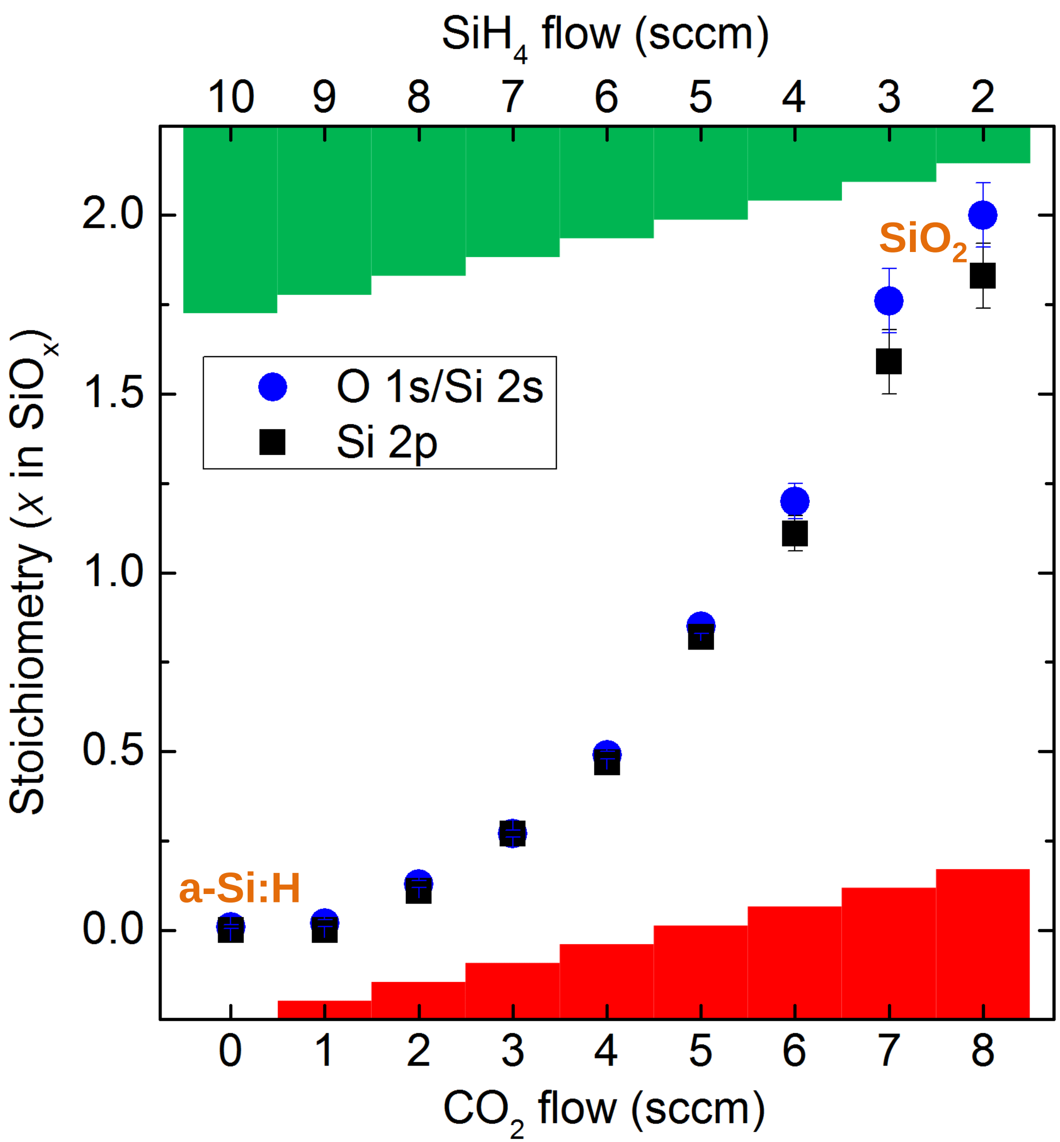
M. Liebhaber *et al.*, APL **106**, 031601 (2015)

Stoichiometry (XPS)

- chem. shift of core level peak depends on oxidation states
- peak intensity ratios ↔ oxygen concentration



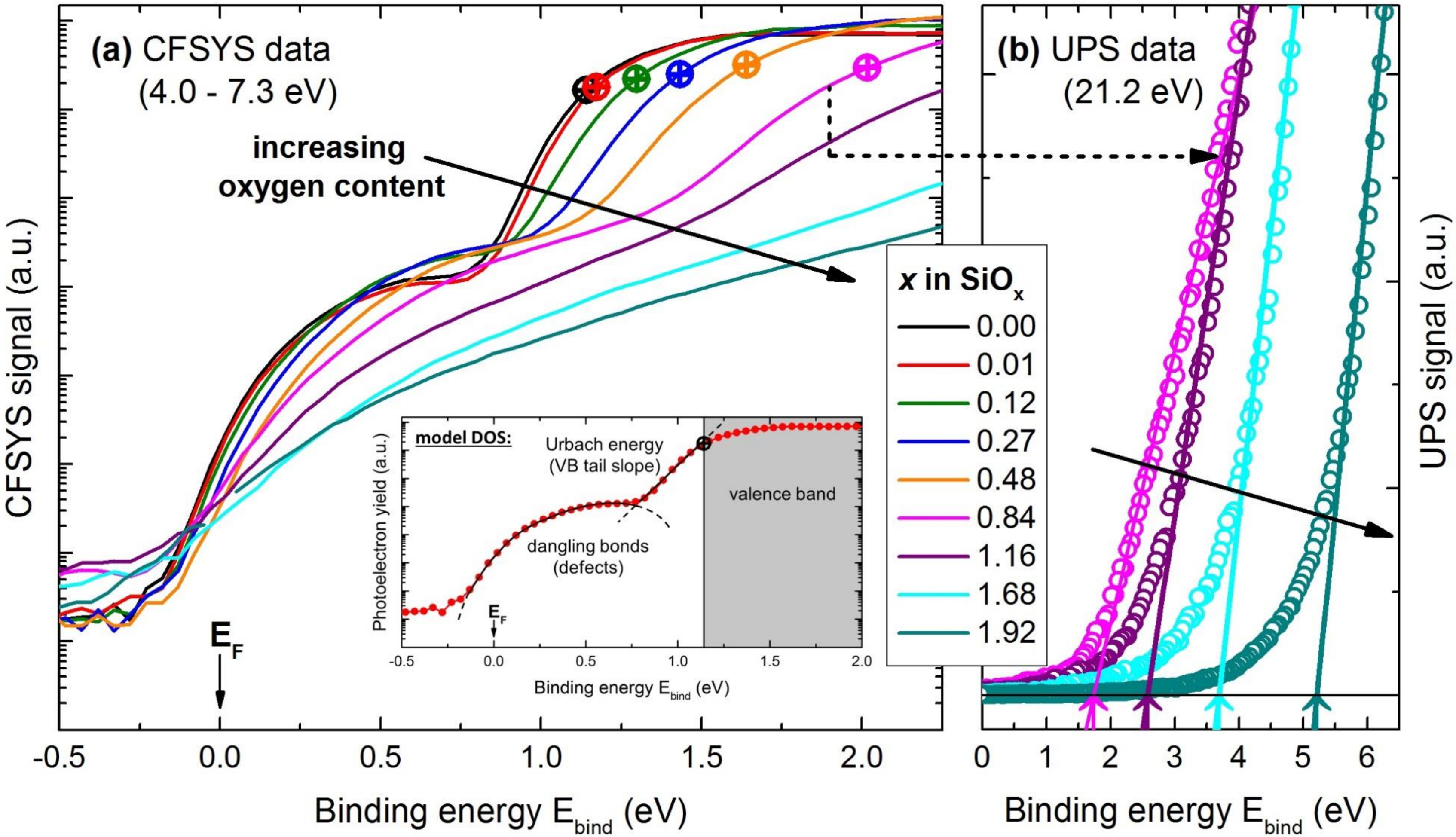
M. Liebhaber *et al.*, APL **106**, 031601 (2015)



- cross-check with other peaks
- **conversion:**
  SiH_4/CO_2 ratio → oxygen conc.
- non linear dependency of stoichiometry on gas phase composition

M. Liebhaber *et al.*, APL **106**, 031601 (2015)

- **U**ltraviolet **P**hotoelectron **S**pectroscopy
- obtain valence band position relative to E_F

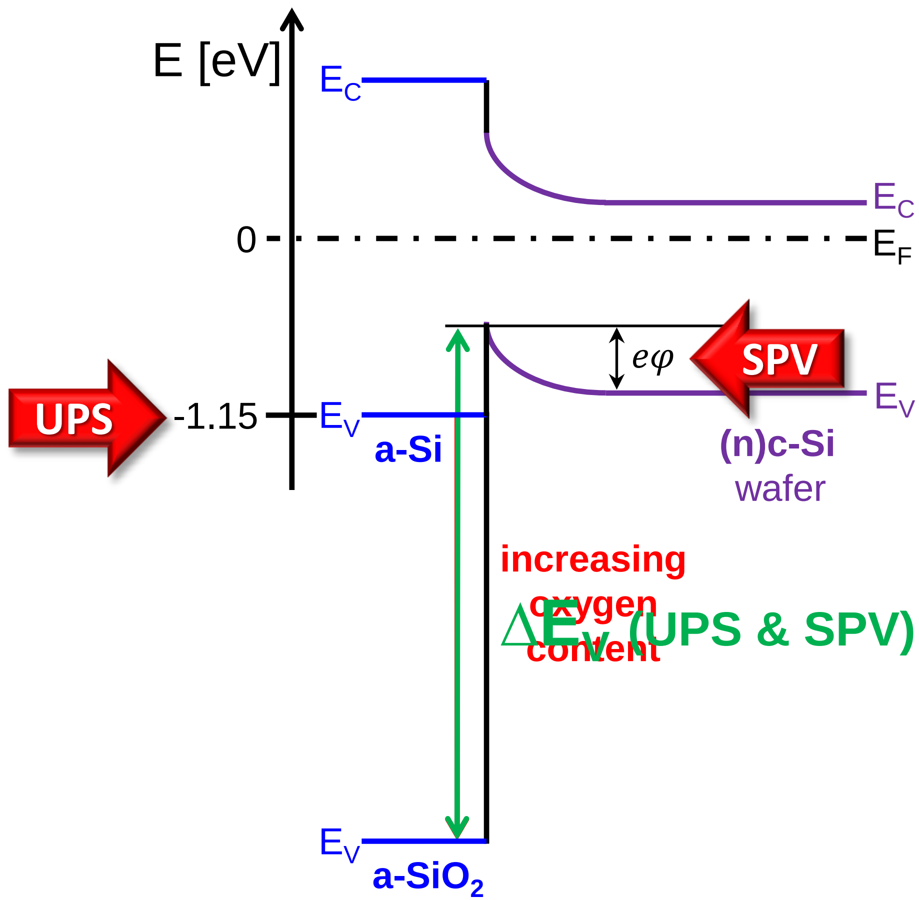


[1] L. Korte *et al.*, JAP **109**, 063714 (2011)
M. Liebhaber *et al.*, APL **106**, 031601 (2015)

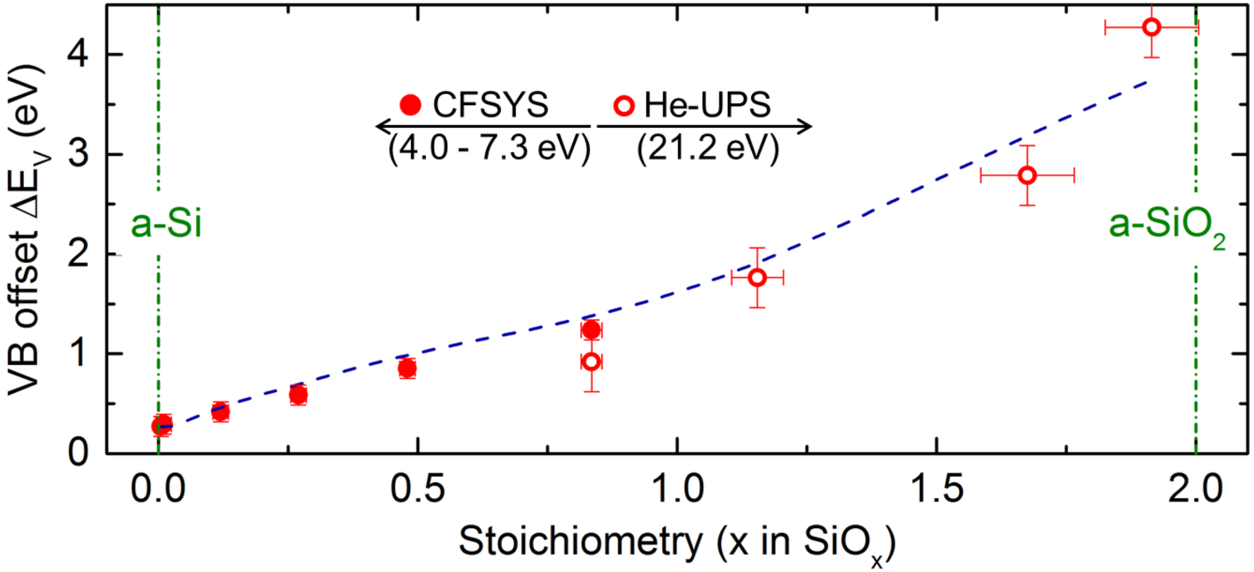
Valence band offset ΔE_V (UPS & SPV)

- **UPS:** valence band position (relative to E_F)
- **SPV:** band bending **≤ 150 meV**

Ultraviolet **P**hotoelectron **S**pectroscopy
Surface **P**hoto**V**oltage



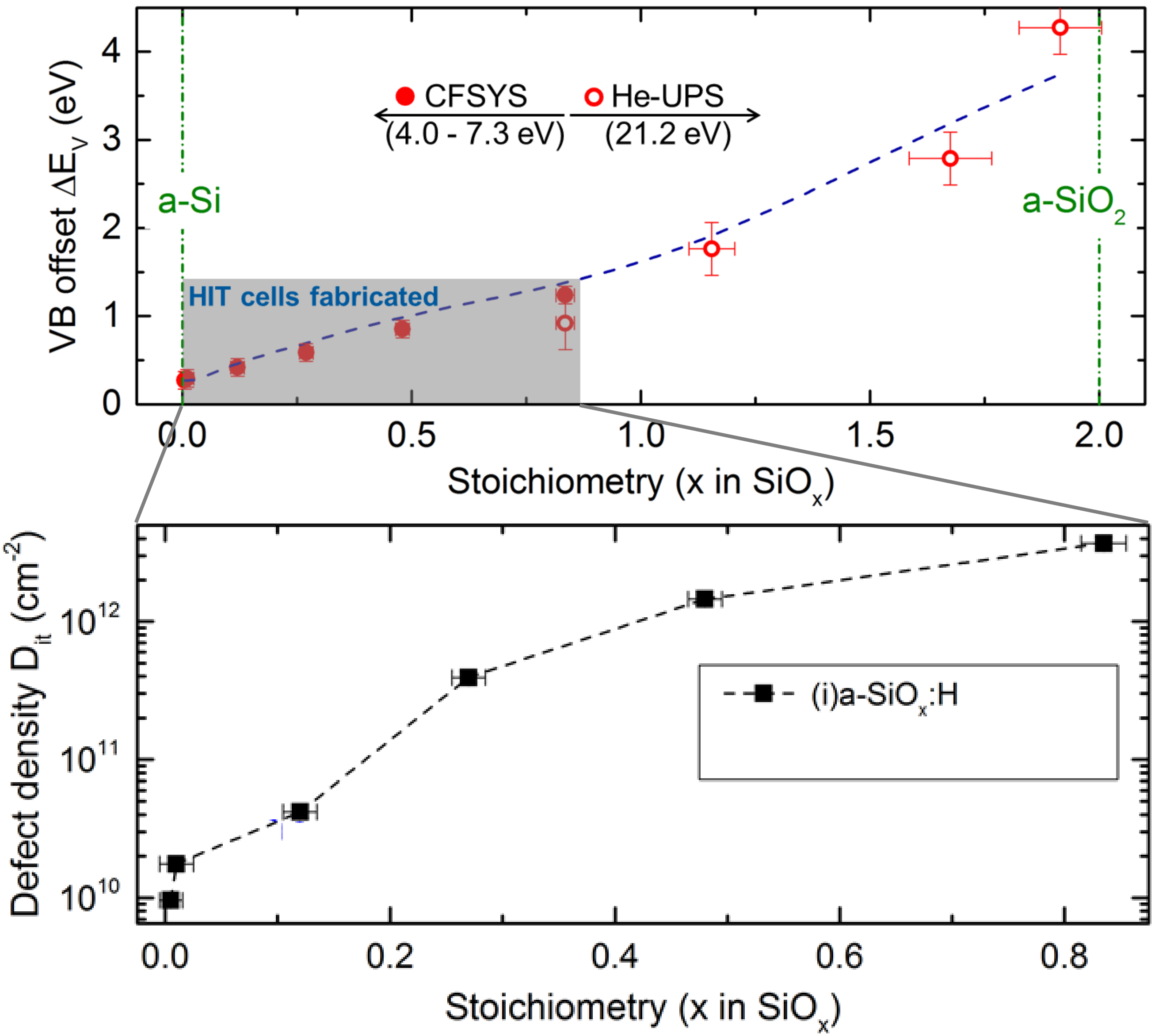
Valence band offset ΔE_V



- ► dependency of ΔE_V on stoichiometry
- ► direct correlation of ΔE_V on cell performance

M. Liebhaber *et al*., APL **106**, 031601 (2015)

a-SiO$_x$ passivation layers in SHJ solar cells

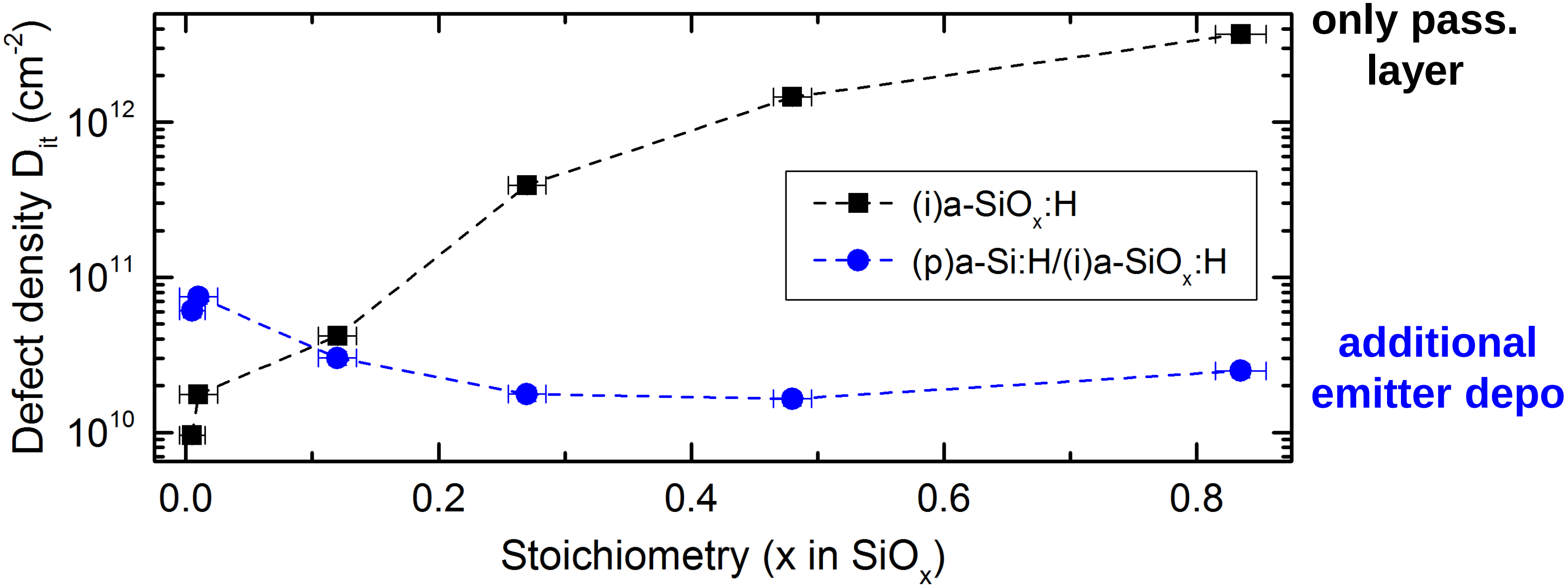


only pass. layer

M. Liebhaber *et al.*, APL **106**, 031601 (2015); M. Mews, M. Liebhaber *et al.*, APL **107**, 013902 (2015)

a-SiO_x passivation layers in SHJ solar cells

- increasing D_{it} for rising oxygen concentration
  - but decrease drastically after emitter deposition
  - similar passivation quality as standard interface
- dangling bonds at the SHJ are saturated by hydrogen during additional plasma process (emitter deposition)



M. Liebhaber *et al.*, APL **106**, 031601 (2015); M. Mews, M. Liebhaber *et al.*, APL **107**, 013902 (2015)

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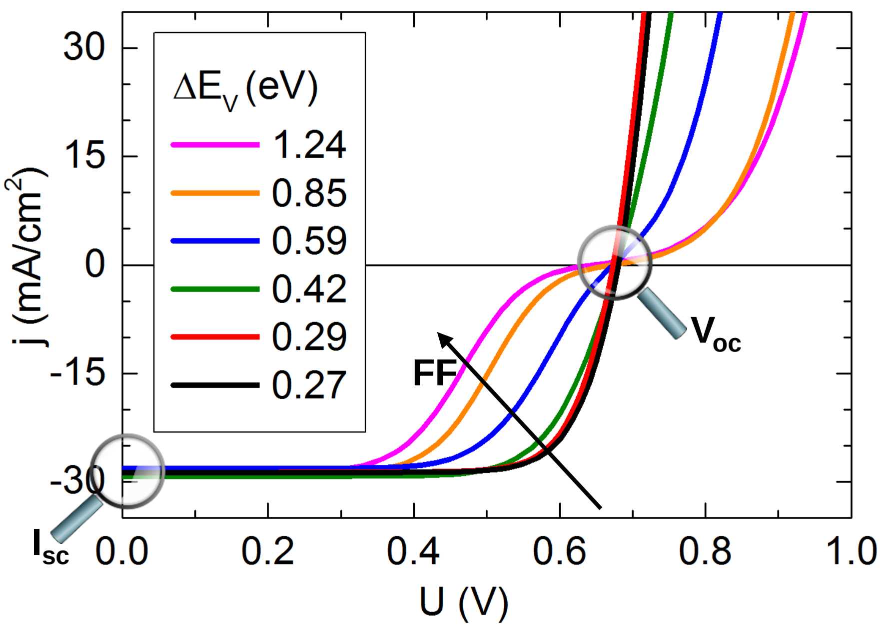
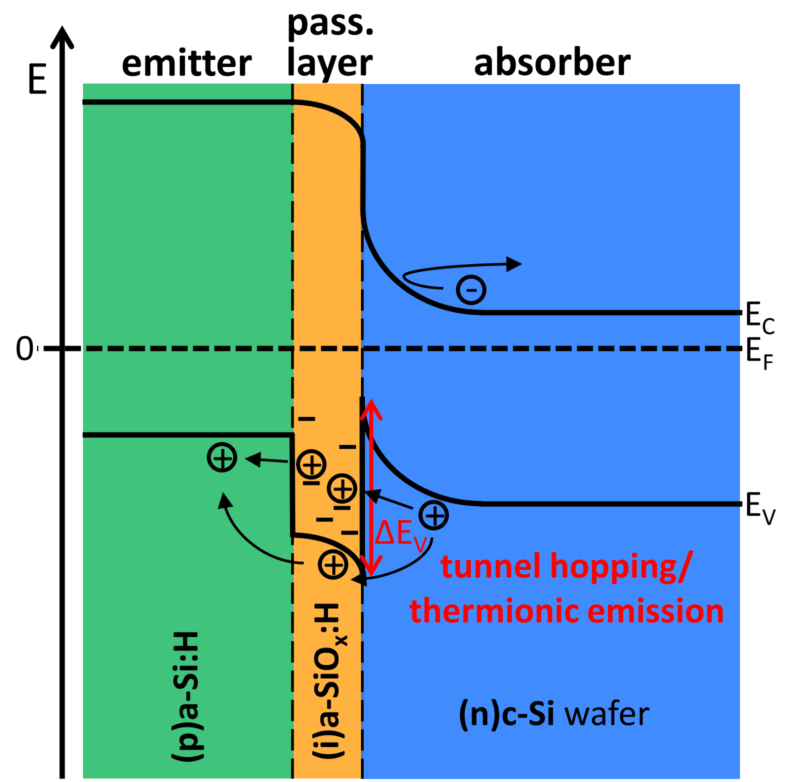




► solar cell parameter

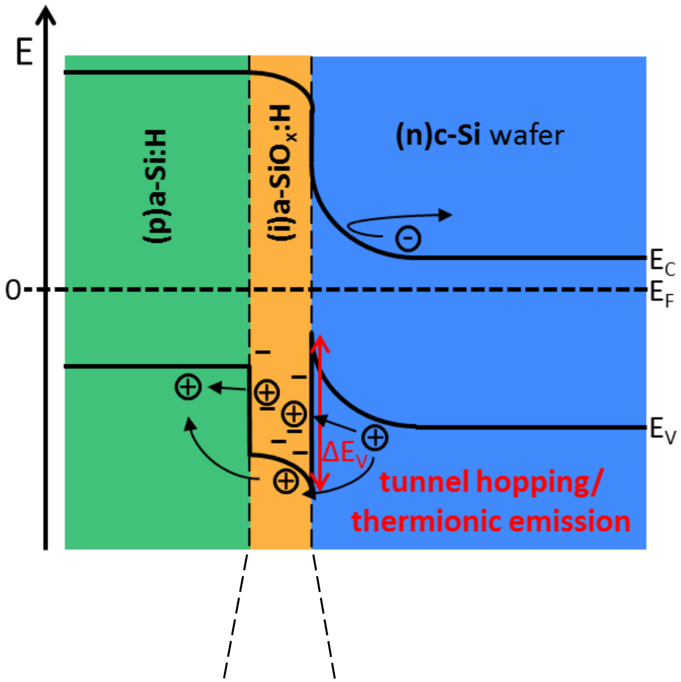
- surface passivation (→ V_{oc})
  - OK
- widening of band gap (→ I_{sc})
  - thin layer (small effect expected)
- band offsets (→ FF)
  - transport barrier

► hole transport mechanism

- transport barrier reflected in **FF**
  - **thermionic emission** (for small ΔE_V)
  - **tunnel hopping** through tail states (additional for higher ΔE_V [1])

[1] A. Kanevce *et al.*, JAP **105**, 094507 (2009)
M. Mews, M. Liebhaber *et al.*, APL **107**, 013902 (2015)

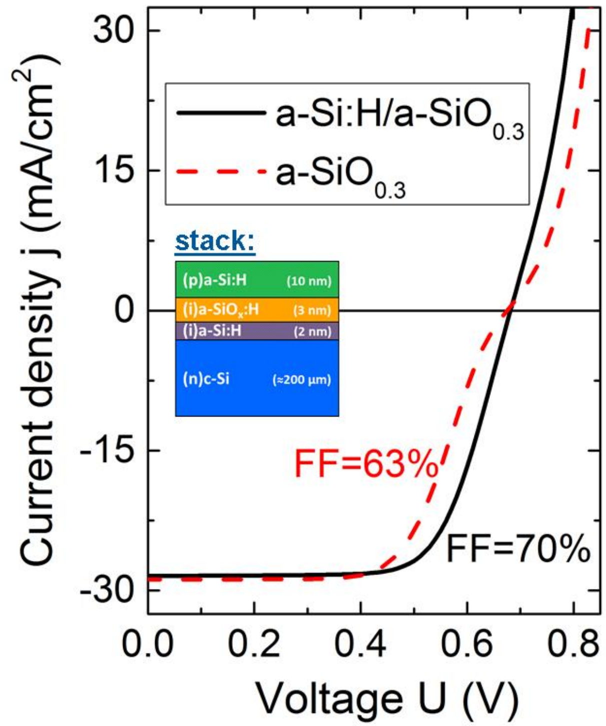
SHJ cell with stacked passivation layer



single layer split into layer stack

$\Delta E_{V,a\text{-}Si:H}$ = 270 meV

$\Delta E_{V,a\text{-}SiO0.3:H}$ = 585 meV



► **"staircase" of valence band offsets**
- **improved FF** for HIT cell with **stacked passivation layers**

► **promising concept:** combination of
- moderate band gap passivation layer
- high band gap hole contact layer

M. Mews, M. Liebhaber *et al.*, APL **107**, 013902 (2015)

Conclusion

► growth of **(i)a-SiO_x:H** thin films (PECVD)
- **stoichiometry** (XPS)
- Δ**E_V** (UPS/SPV)
- sufficient **passivation**

► implemented into **SHJ** cells (low *x*-regime)
- **FF** directly **linked to ΔE_V**
- discussion of **hole transport mechanism** (thermionic emission vs. tunnel hopping)

general challenge: transport limitation due to band offset induced by the high band gap of a-SiO_x

possible solution: band gap "staircase" also in combination with high band gap emitter

M. Liebhaber *et al.*, APL **106**, 031601 (2015); M. Mews, M. Liebhaber *et al.*, APL **107**, 013902 (2015)

Tetracene/c-Si hybrid solar cell
– multi-exciton generation via singlet fission –

THE UNIVERSITY OF NEW SOUTH WALES

June/July ´15

DAAD
Deutscher Akademischer Austausch Dienst
German Academic Exchange Service
Project-ID 57140921

Cooperation

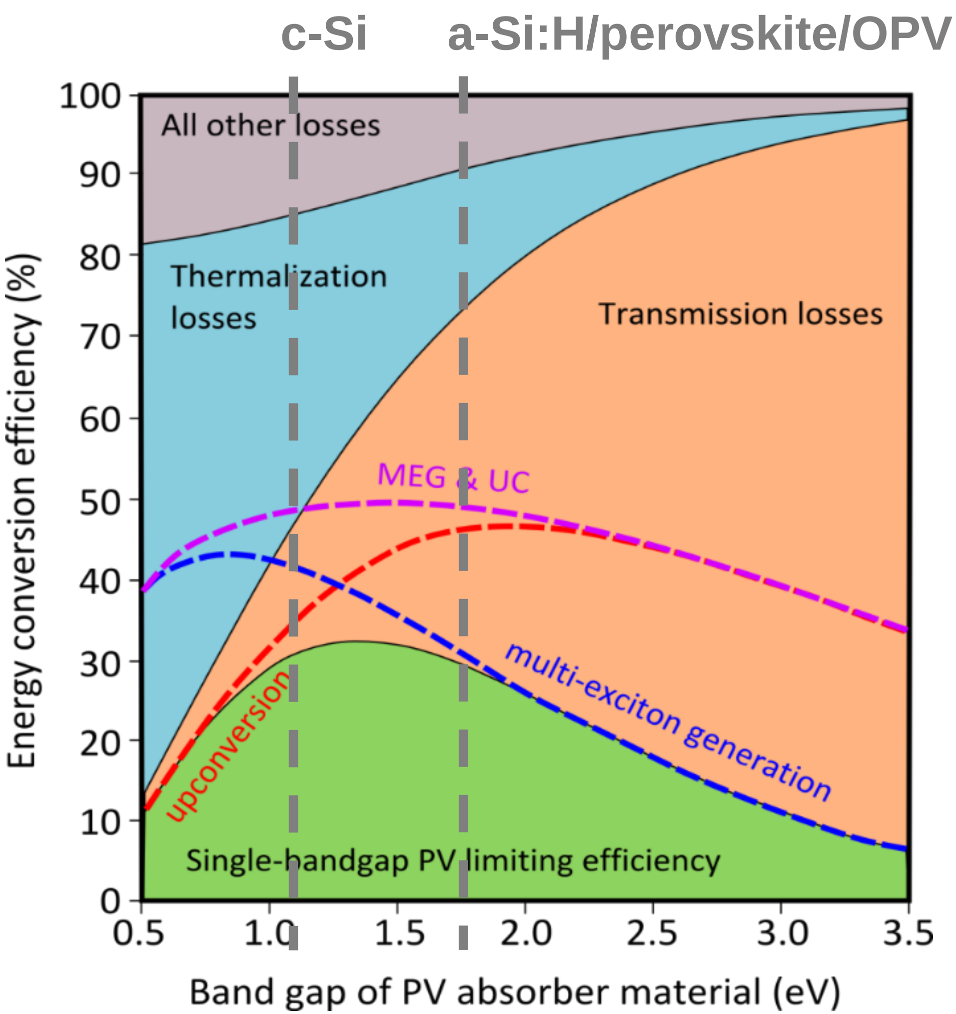
HZB Helmholtz Zentrum Berlin EMIL

March ´15

November ´15

…many more people involved

Motivation



UC: TTA, Er-Yb,…

MEG: Si nanocrystals, SF…

adapted from: L. C. Hirst and N. J. Ekins-Daukes, PIP **19**, 286 (2011)

MEG via Singlet Fission (SF): 1 photon → 2 e^--h^+ pairs

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► first observed in anthracene in 1965 by S. Singh *et al.*

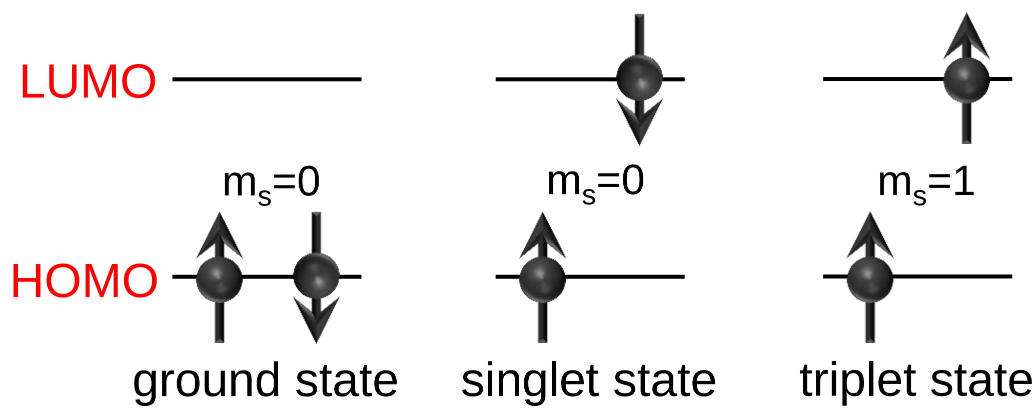
THE JOURNAL OF CHEMICAL PHYSICS VOLUME 42, NUMBER 1 1 JANUARY 1965

Laser Generation of Excitons and Fluorescence in Anthracene Crystals*

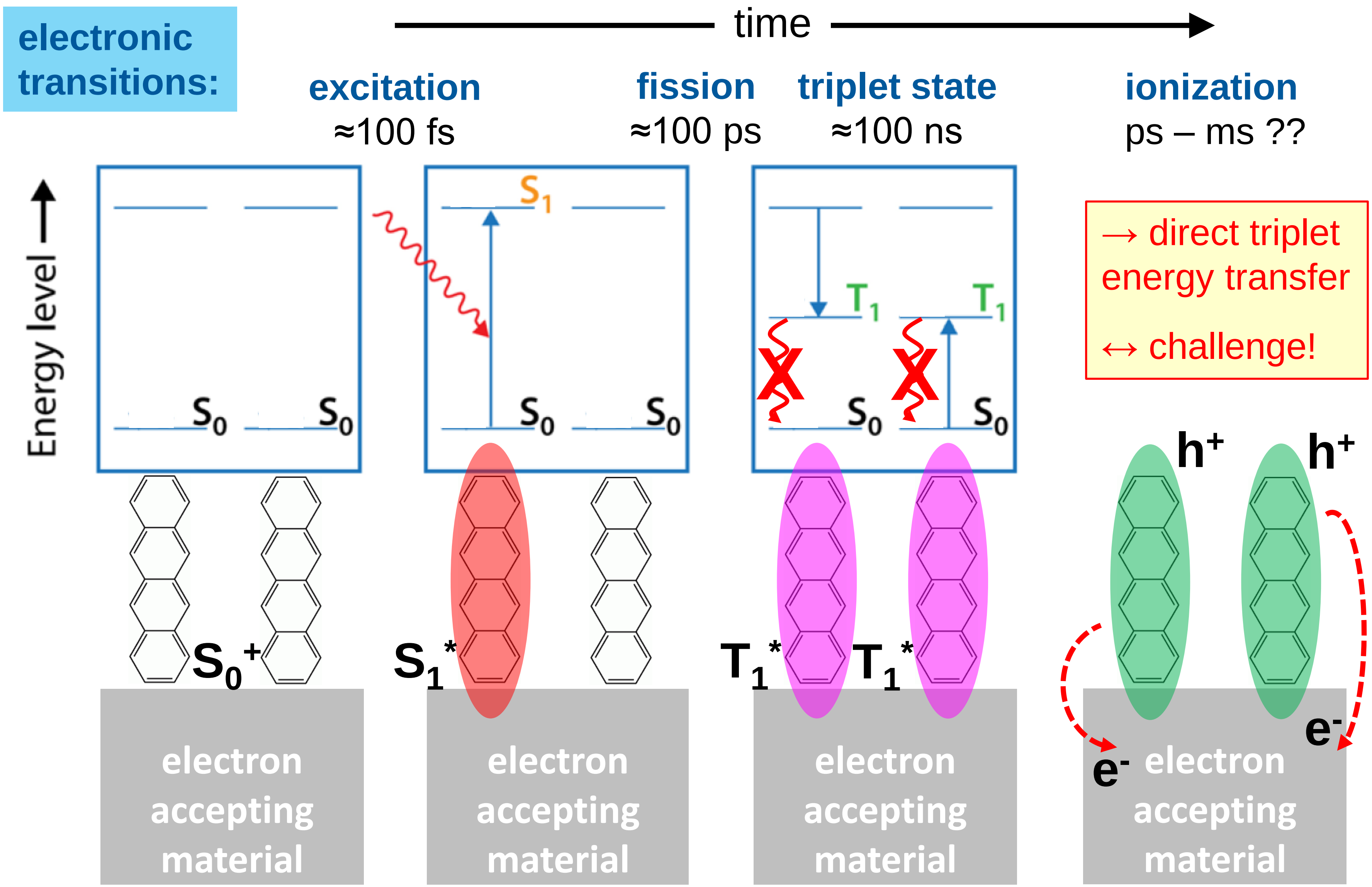
S. SINGH,† W. J. JONES,‡ W. SIEBRAND, B. P. STOICHEFF,§ AND W. G. SCHNEIDER
National Research Council of Canada, Ottawa
(Received 21 August 1964)

- ► organic chromophore in excited singlet state
- ► shares its excitation energy with a neighboring ground-state chromophore
- ► both are converted into correlated triplet excited states

molecular states of interest:

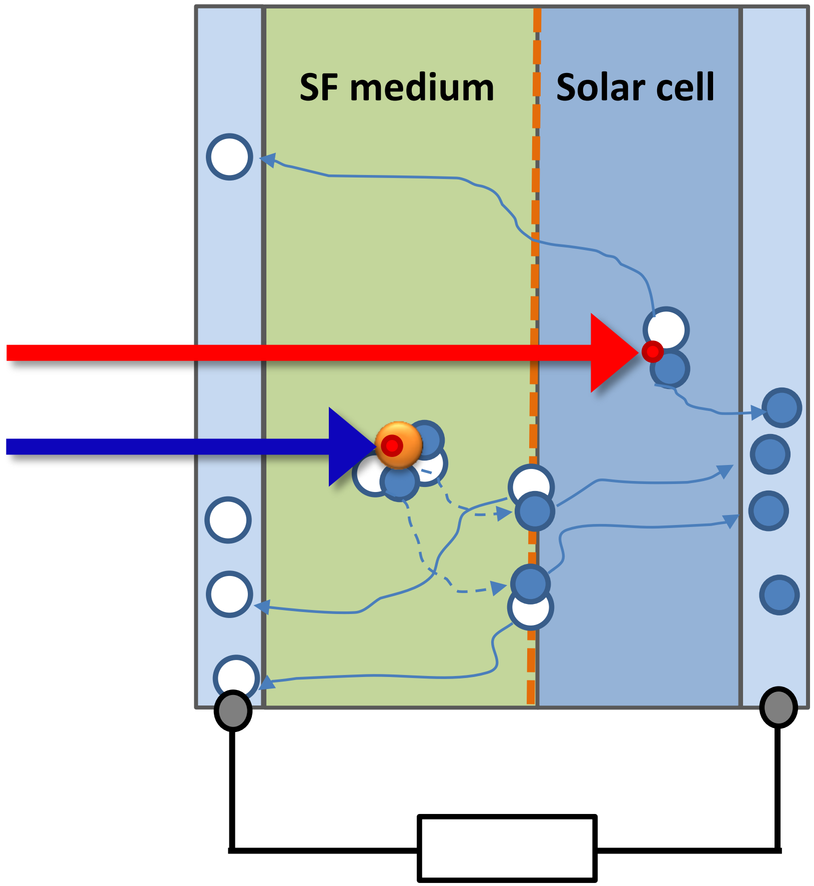


MEG via Singlet Fission (SF): 1 photon → 2 e^--h^+ pairs



J. J. Burdett *et al.*, J. Chem. Phys. **133**, 144506 (2010)

MEG device



Prerequisite:

- ▶ triplet exciton diffusion length longer than thickness SF medium
- ▶ geminate triplet exciton pair dissociation at hybrid interface

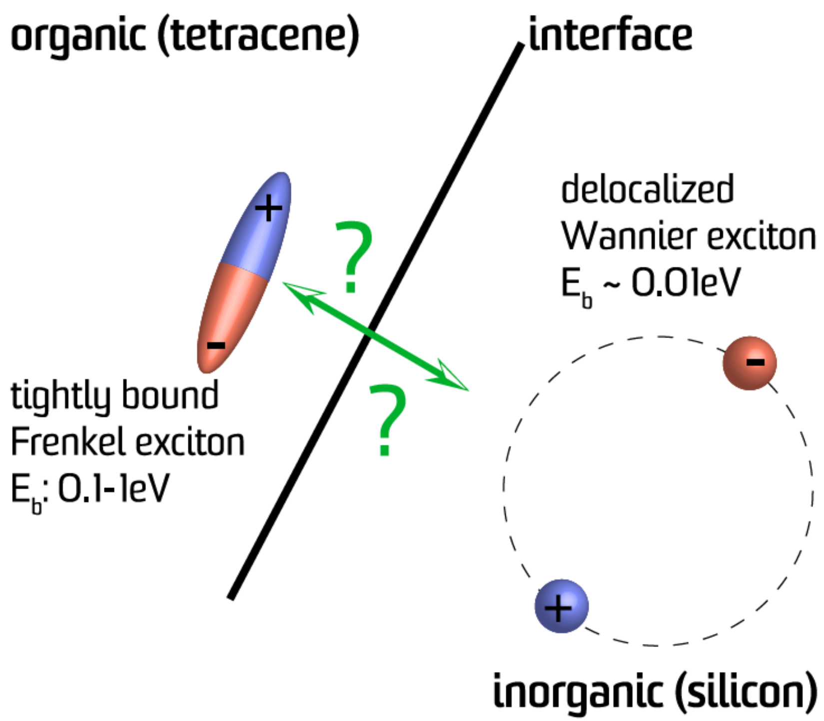
absorption

Exciton/
electron-hole-pair

MEG event

Exciton migration
carrier migration

How do we harvest triplets?

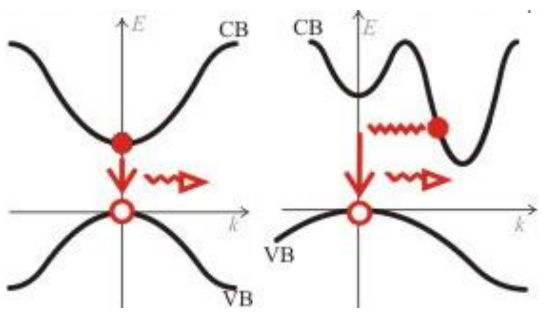


1. Charge transfer state
direct electron transfer with the hole on the organic & the electron on the inorganic material

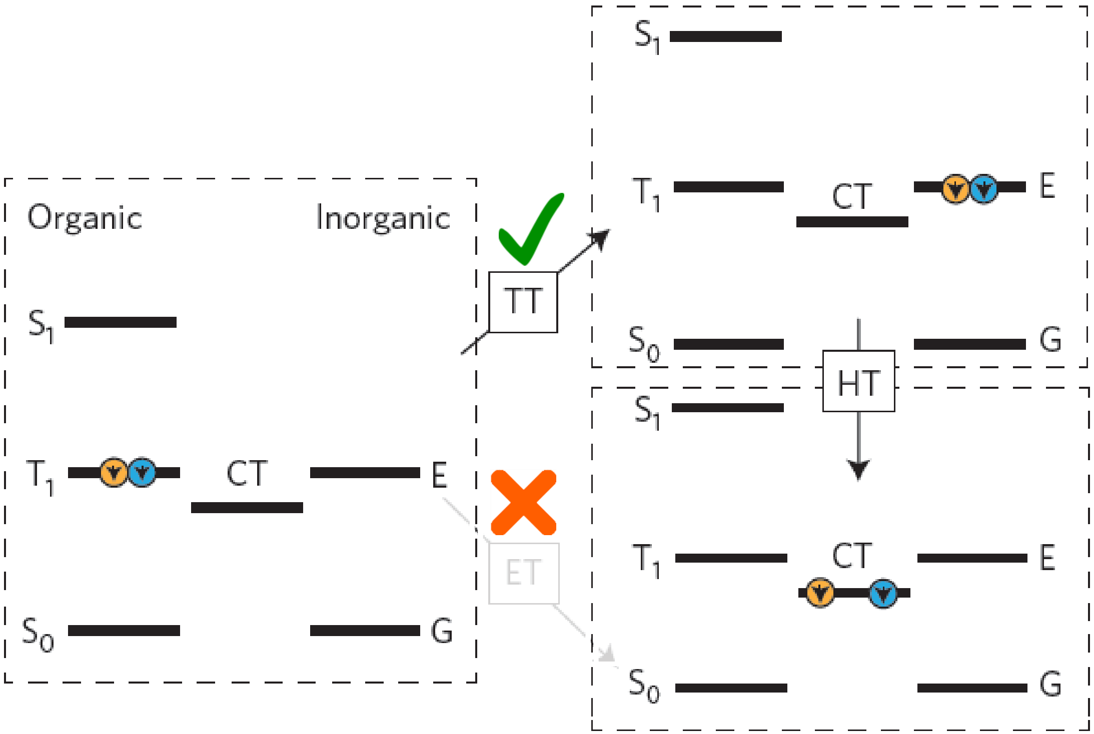
2. Förster type transition
- non-radiative transfer mechanism (long range)
- dipole transition ↔ spin forbidden for triplets

3. Dexter type transfer
- charges/triplets move
- wave function overlap (short range)

Challenges
- momentum conservation & localization effect
  → direct vs. indirect semiconductors
- loose spin correlation
  → easier in heavy atoms (spin-orbit coupling)



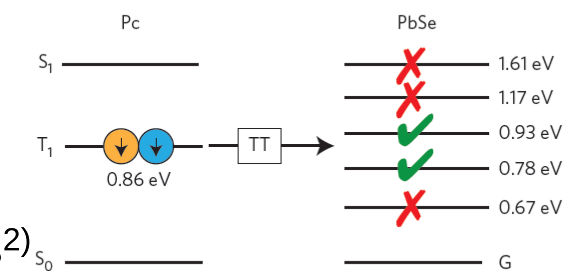
Charge transfer mechanisms (nanocrystals)



triplet transfer (TT) **"dexter type"**
followed by
hole transfer (HT) back

direct electron transfer (ET)
via charge transfer state (CT)

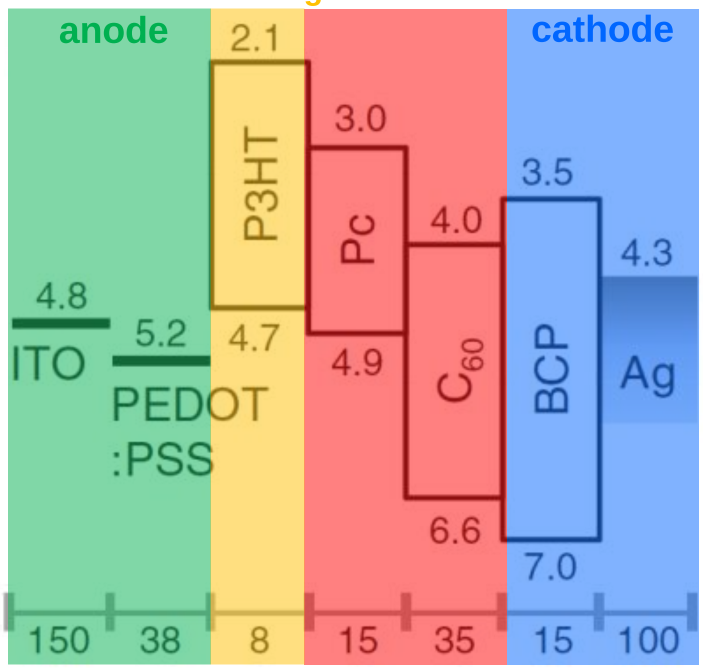
- ▶ transient optical absorption measurements ↔ dynamics[1)]
- ▶ efficient transfer only at resonance ↔ size of NCs[1)]
- ▶ exponential dependency of transfer efficiency ↔ NC ligands[2)]



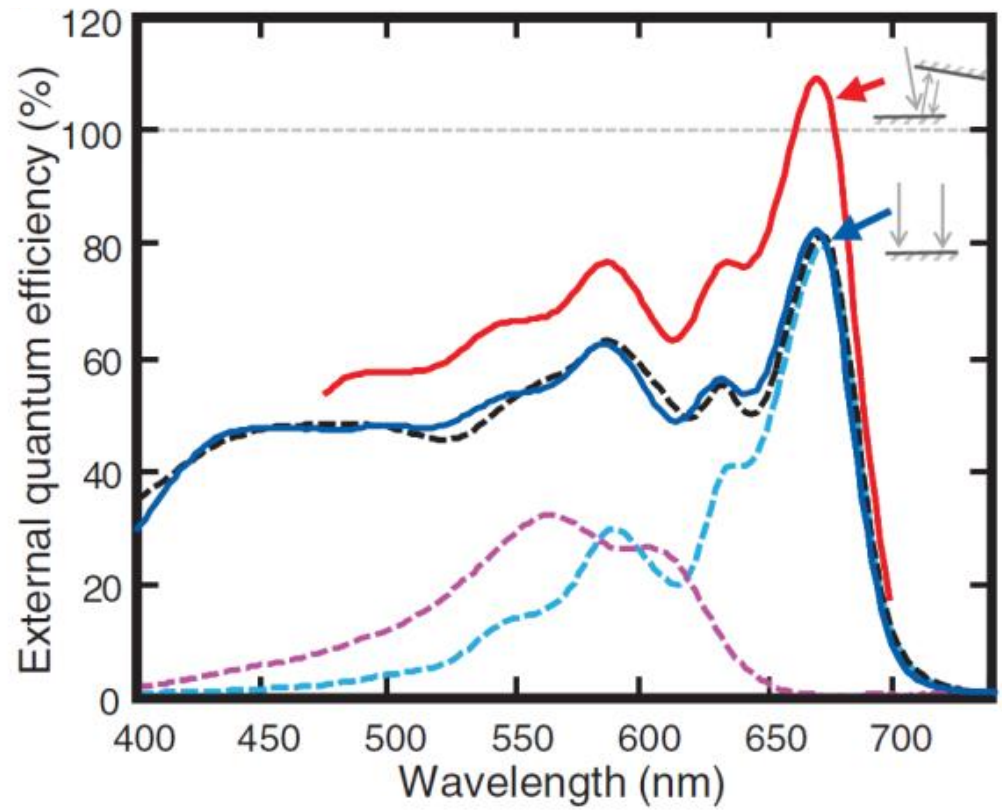
[1)] M. Tabachnyk *et al.*, Nature mat. **13**, 1033 (2014)
[2)] N. J. Thompson *et al.*, Nature mat. **13**, 1039 (2014)

Successful harvesting of triplet excitons

Singlet fission & triplet dissociation



EQE > 100% !!!



Side note: **Tc/C_{60}** proved by

T. C. Wu *et al.*, APL **104**, 193901 (2014)

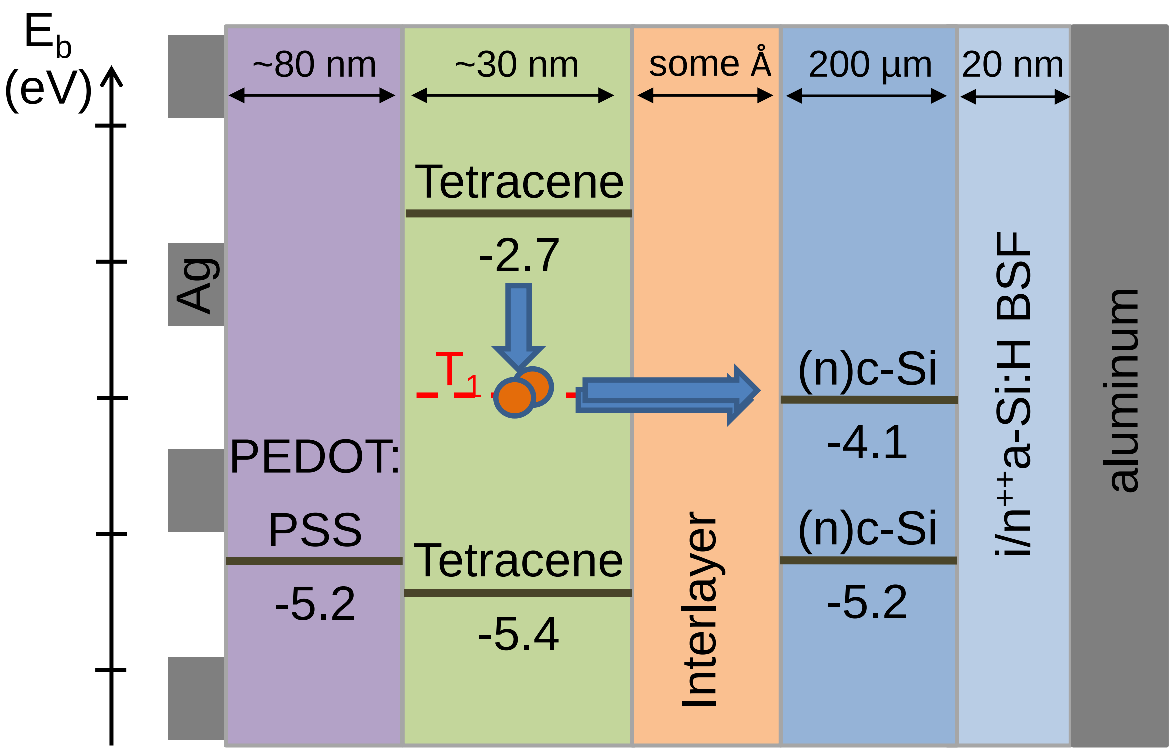
D. N. Congreve *et al.*, Science **340**, 334 (2013)

Tetracene/c-Si hybrid cells

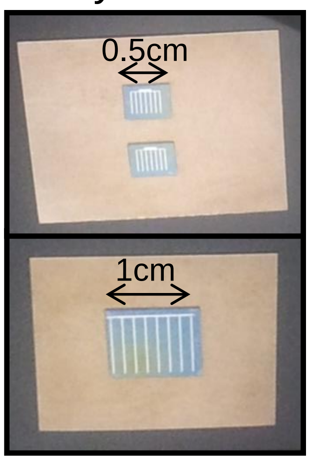
► **correct energy (band) alignment important**

motivation for c-silicon:

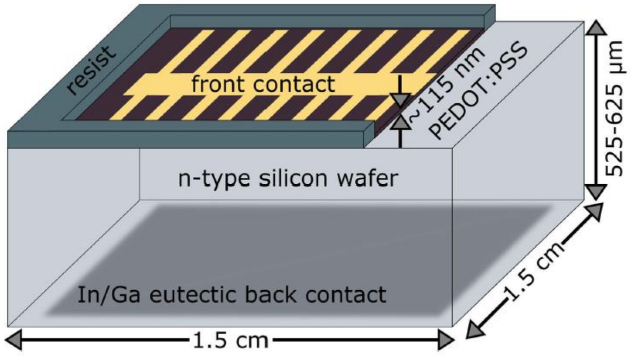
- **replace pentacene by higher band gap SF material**
- **proof of charge separation of triplets at hybrid interface**

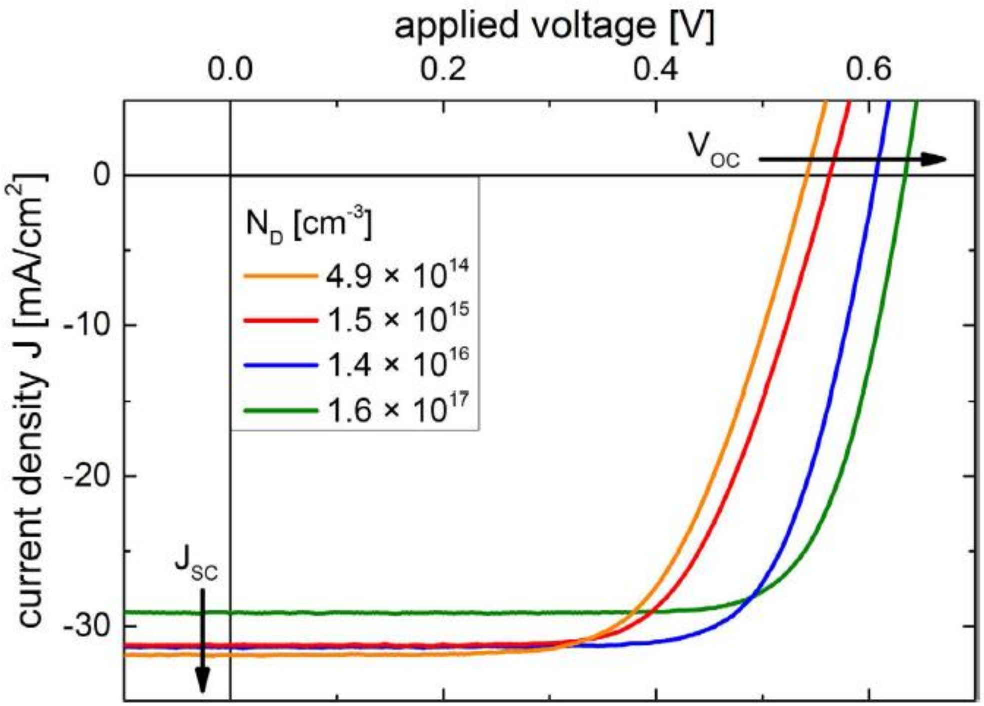


photograph of hybrid cells



PEDOT:PSS/c-Si hybrid front contact

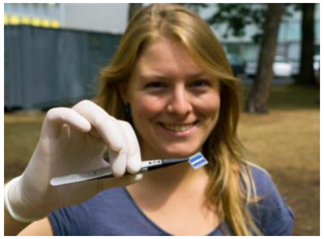




► ≈14 % hybrid cell

- optimized front contact
- planar, w/o antireflection, “simple” back contact

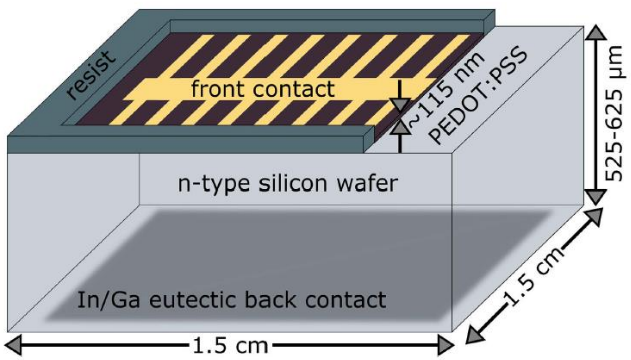
► PEDOT:PSS forms a hybrid heterojunction with (n)c-Si
→ described by p^+n-heterojunction
(in lit. commonly assumed as Schottky junction)

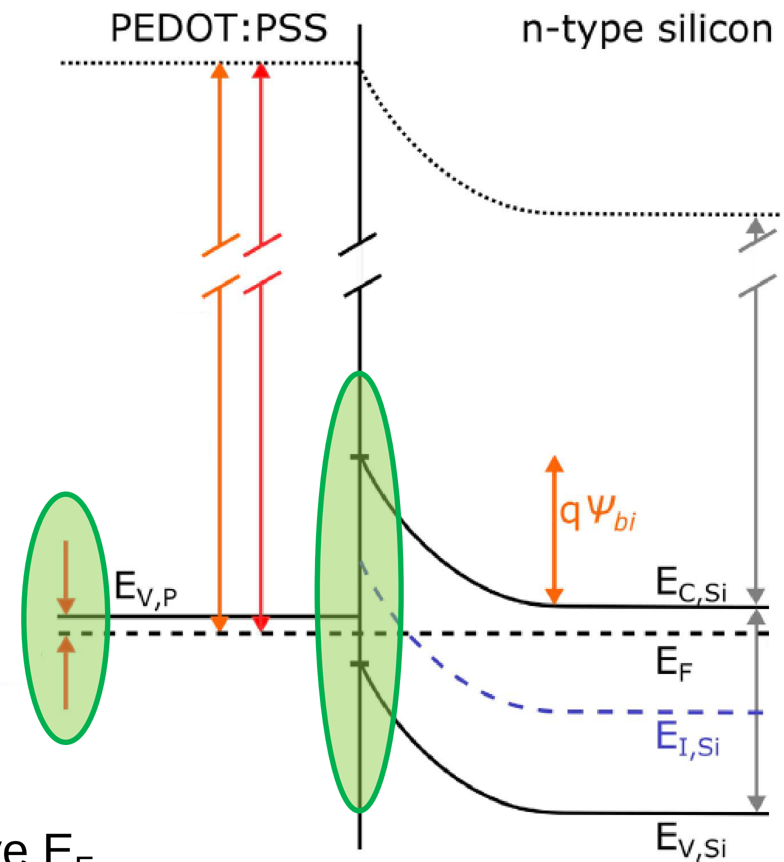


Sara Jäckle

S. Jäckle, M. Liebhaber *et al.*, Sci. Rep. **5**, 13008 (2015)

PEDOT:PSS/c-Si hybrid front contact





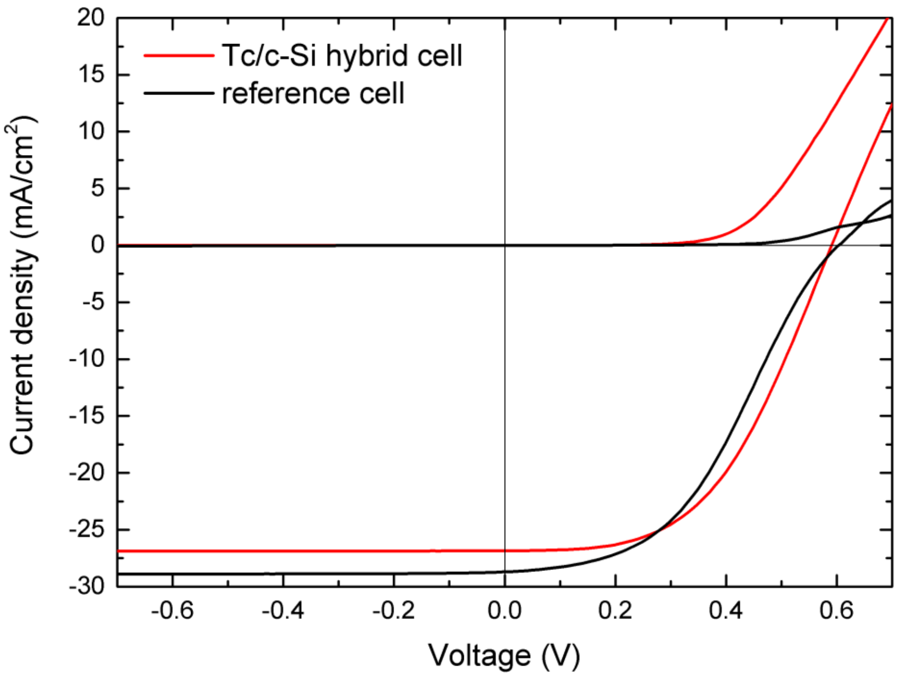
► highly p-doped polymer

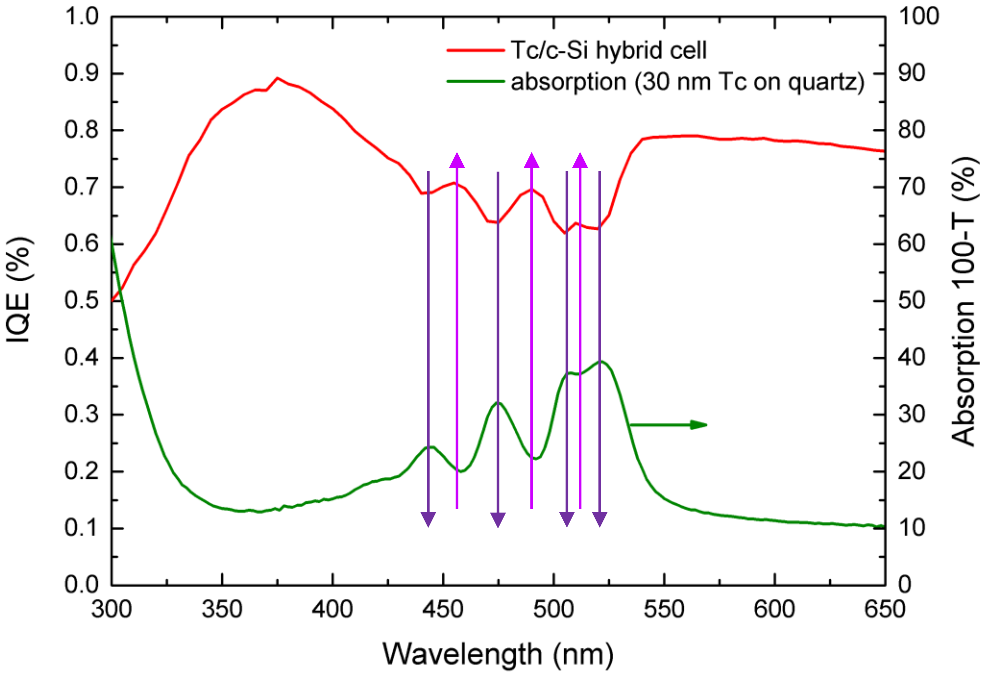
- filled (valence) states at E_F
- valence band edge $E_{V,P}$ ≈ 80 meV above E_F

► strong inversion of Si at the surface

→ intrinsic Fermi level $E_{I,Si}$ crosses E_F (n-doped Si)

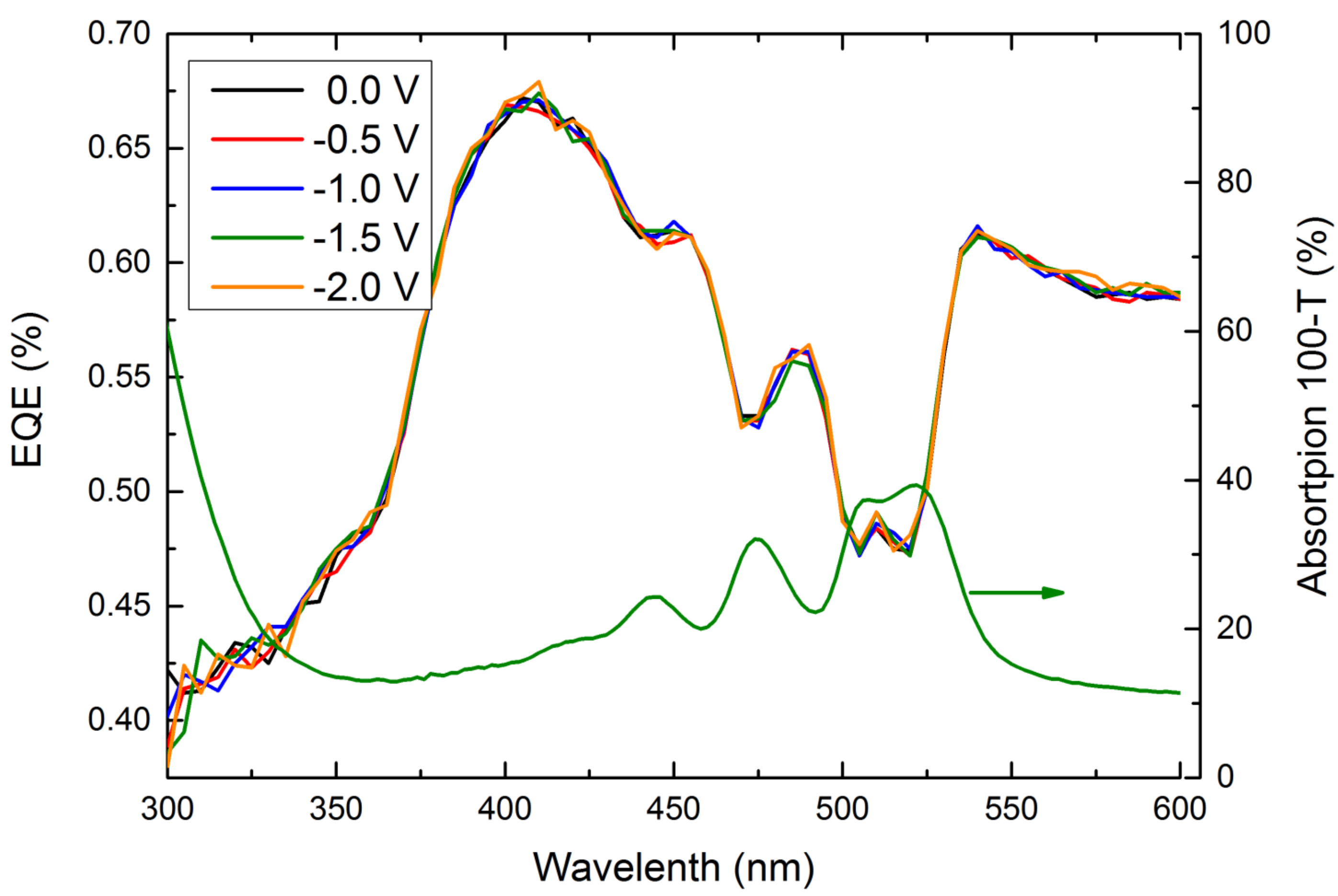
S. Jäckle, M. Liebhaber *et al.*, Sci. Rep. **5**, 13008 (2015)





► absorption spectra reflected in IQE

► “filter effect” of Tc in IQE, no exciton dissociation

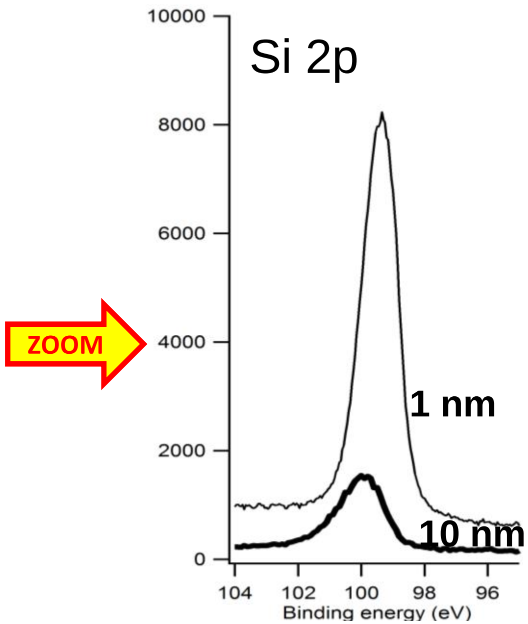


► no field assisted exciton separation

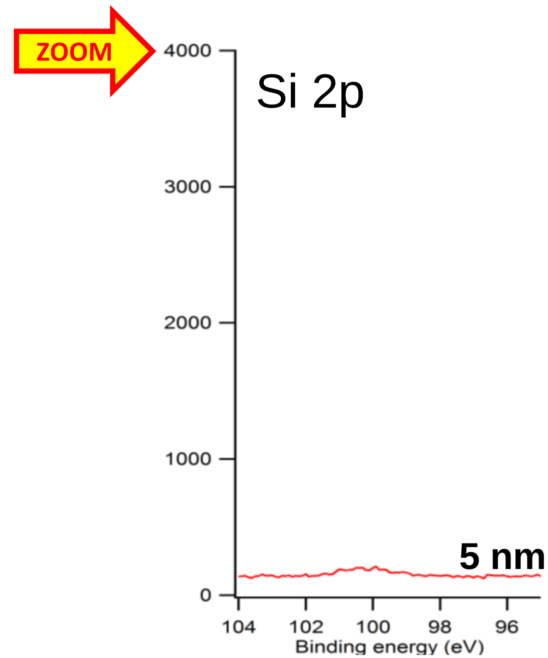
► indirect band gap a problem? → phonon assistance? temperature, a-Si:H…

Tetracene film morphology – XPS

1 nm & 10 nm Tetracene/c-Si
► **island growth**



5 nm Pd-Porphyrin/c-Si
► **no island growth**



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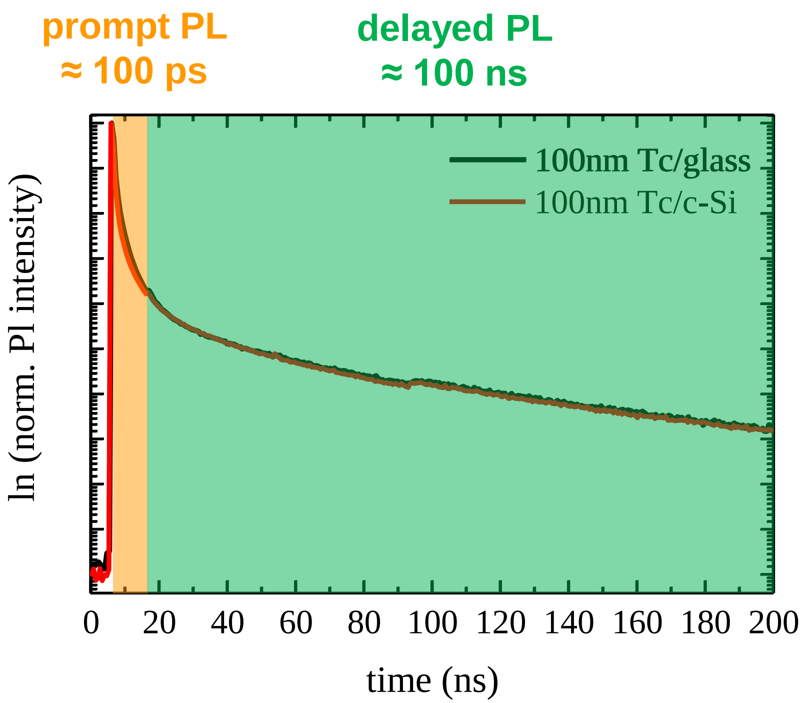
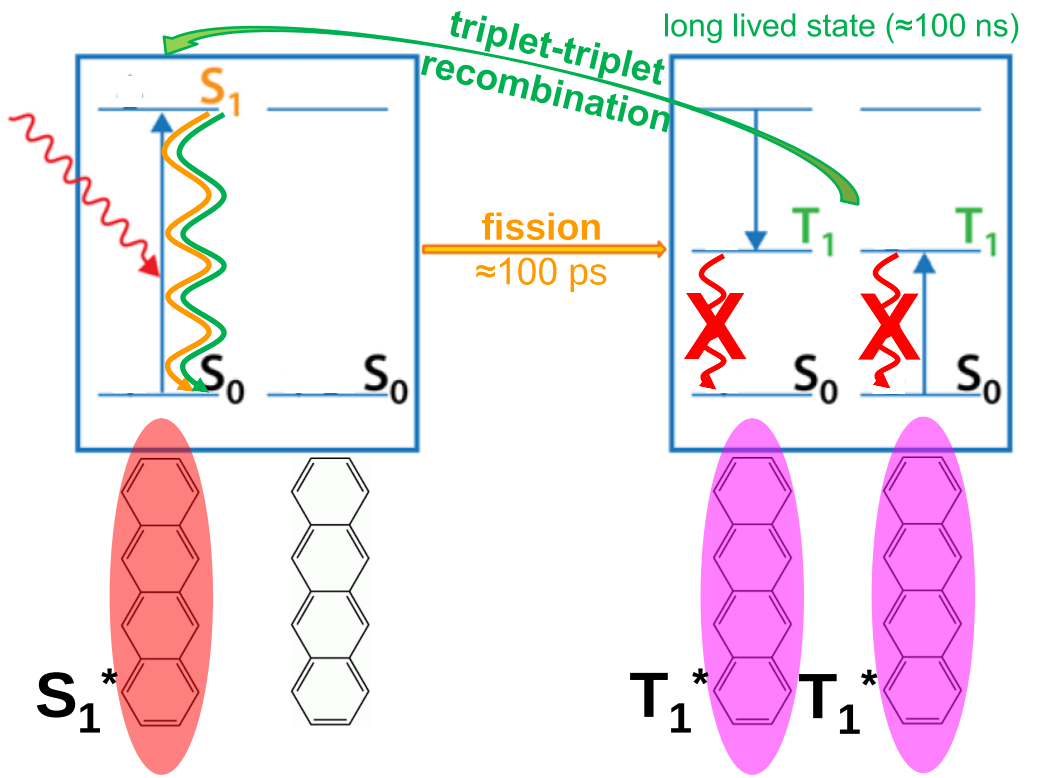
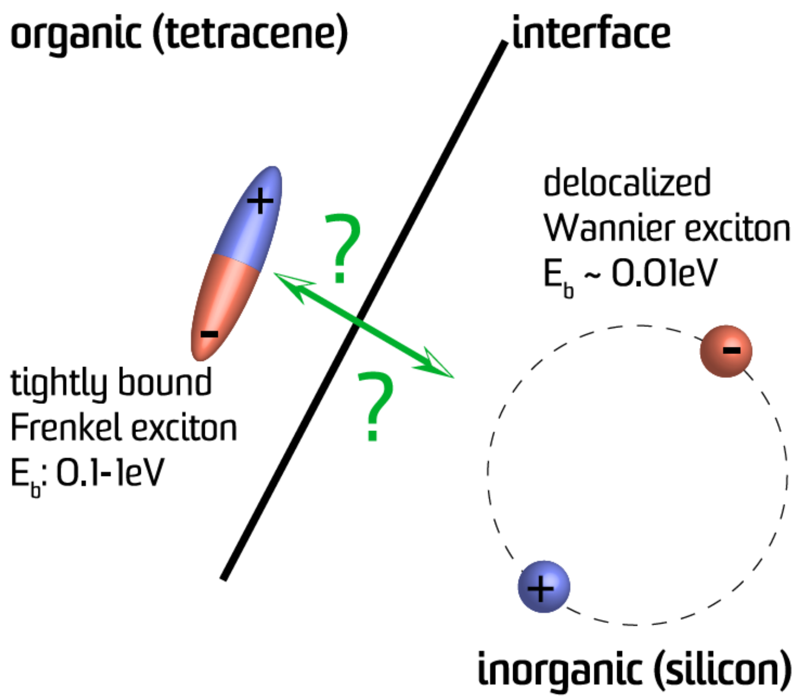




- ► first preliminary results: no differences in thickness & substrate variation
- ► triplets generated and long lived (≈100 ns)
- ► singlet fission in Tc layers (also on c-Si) but no injection ↔ in accordance to EQE

Challenges & open questions



1. Can correlated triplet excitons be transferred across a silicon interface?
2. How long do the triplets generated upon singlet fission remain geminate?
3. Which interlayers could help to dissociate triplet excitons?

Conclusion & Outlook

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► overcome fundamental thermalization loss

- MEG ("spectral downconversion") via singlet fission

ultrafast PL measurements:

- polycrystalline Tc thin layers show SF (glass & c-Si substrates)
- no differences in triplet lifetime observed → no exciton dissociation

hybrid devices:

- hybrid device works, but Tc layers act as filter
- so far no hint for exciton dissociation & charge injection (EQE)

► search and implementation of organic intermediate layer

- 1st step: charge separation at organic/organic interface works (shown in literature)
- 2nd step: injection of separated charges into c-Si
- correct band line-up!

► charge seperation at Pb-Nanocrystals works ↔ put on c-Si (Cambridge, MIT…)

Thank you…

especially I would like to thank:

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… and all colleagues at HZB:
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- Institute for Nanospectroscopy
- PVcomB

collaboration: UNSW THE UNIVERSITY OF NEW SOUTH WALES; Berlin Joint EPR Laboratory BeJEL

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"SISSY" project

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European Commission

HERCULES

Grant No. 608498

DAAD Deutscher Akademischer Austausch Dienst German Academic Exchange Service

Project-ID 57140921

Thank you for your attention!

Questions & discussion

M. Liebhaber

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Helmholtz Center Berlin
Institue for Nanospectroscopy
Energy Materials In-Situ Lab