



# Epitaxially grown photoabsorbers for efficient solar fuels production



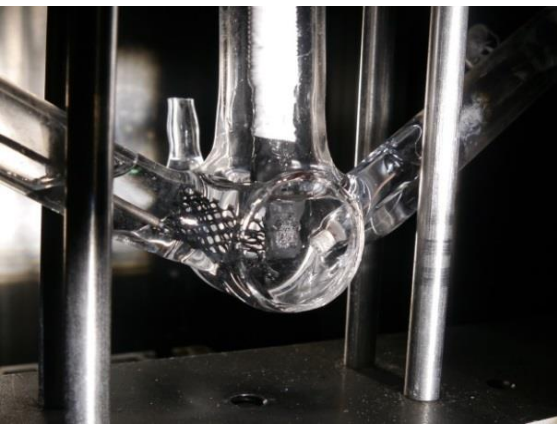
**Thomas Hannappel**

**Ilmenau University of Technology**  
*Fundamentals of Energy Materials*

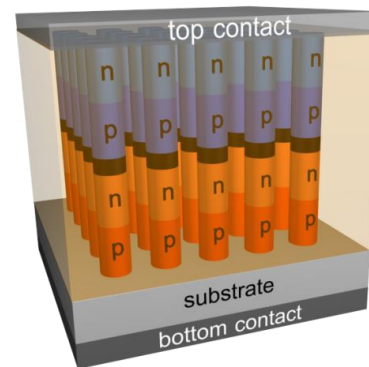
A. Paszuk<sup>1</sup>, P. Kleinschmidt<sup>1</sup>, M. Nandy<sup>1</sup>, D. Ostheimer<sup>1</sup>, M.A. Zare Pour<sup>1</sup>, M.M. May<sup>1,3,5</sup>, W.-H. Cheng<sup>2</sup>, M.H. Richter<sup>2</sup>, H. Atwater<sup>2</sup>, J. Ohlmann<sup>4</sup>, D. Lackner<sup>4</sup>, F. Dimroth<sup>4</sup>



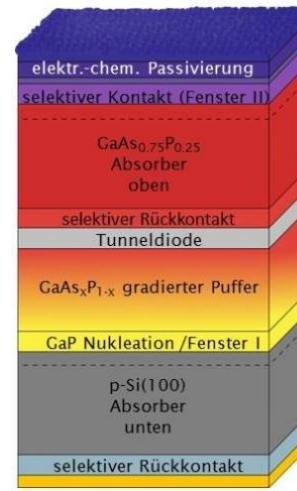
1: TU Ilmenau; 2: CalTech/JCAP; 3: HZB; 4: FhG-ISE; 5: Ulm U



Fraunhofer Institut Solare Energiesysteme



tandems





# Epitaxially grown photoabsorbers for efficient solar fuels production



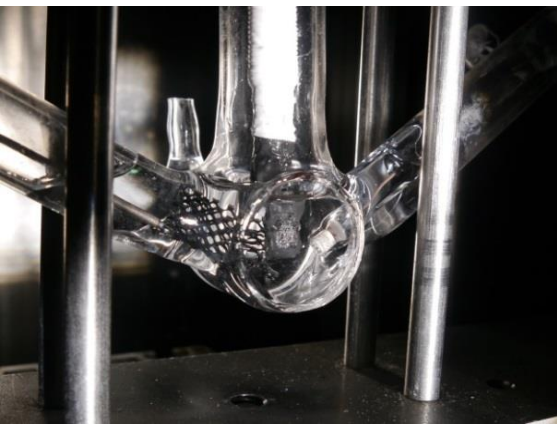
**Thomas Hannappel**

**Ilmenau University of Technology**  
*Fundamentals of Energy Materials*

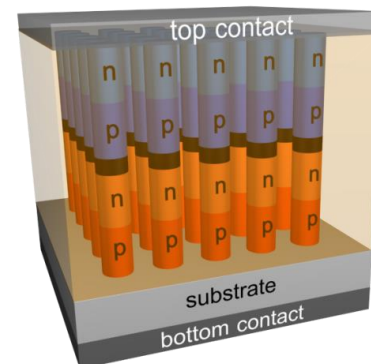
A. Paszuk<sup>1</sup>, P. Kleinschmidt<sup>1</sup>, M. Nandy<sup>1</sup>, D. Ostheimer<sup>1</sup>, M.A. Zare Pour<sup>1</sup>, M.M. May<sup>1,3,5</sup>, W.-H. Cheng<sup>2</sup>, M.H. Richter<sup>2</sup>, H. Atwater<sup>2</sup>, J. Ohlmann<sup>4</sup>, D. Lackner<sup>4</sup>, F. Dimroth<sup>4</sup>



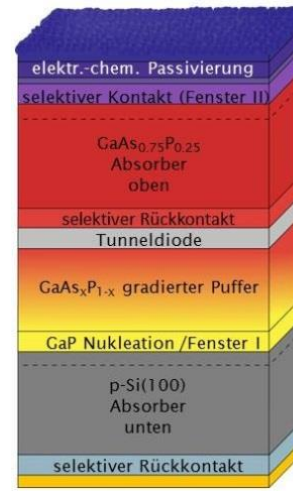
1: TU Ilmenau; 2: CalTech/JCAP; 3: HZB; 4: FhG-ISE; 5: Ulm U



Fraunhofer Institut Solare Energiesysteme



tandems

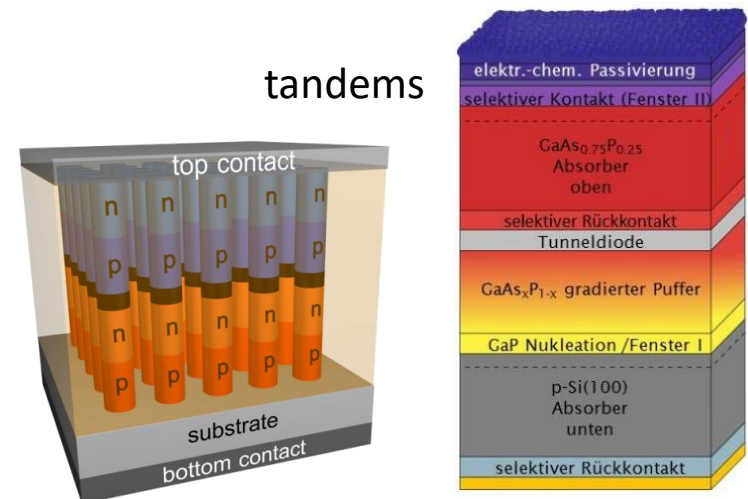
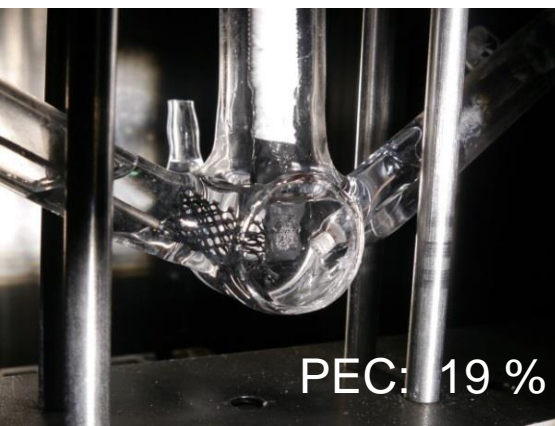




## Outline



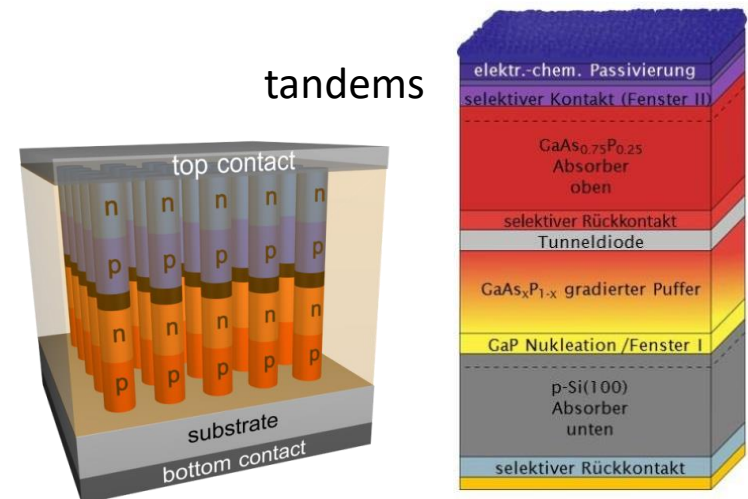
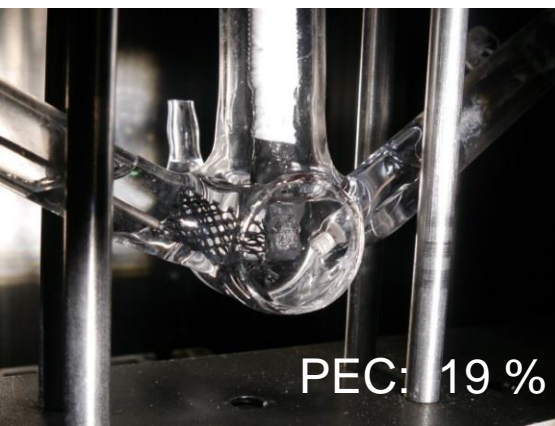
- Prerequisites for **efficient** absorber materials for direct **water splitting**
  - **Can we exceed the detailed balance limit of efficiency?**
  - Absorber, diffusion lengths, charge separation
- Current state of III-V on Si(100) growth: **Costs** ↓
- Interfacial control: ***In situ* spectroscopy**



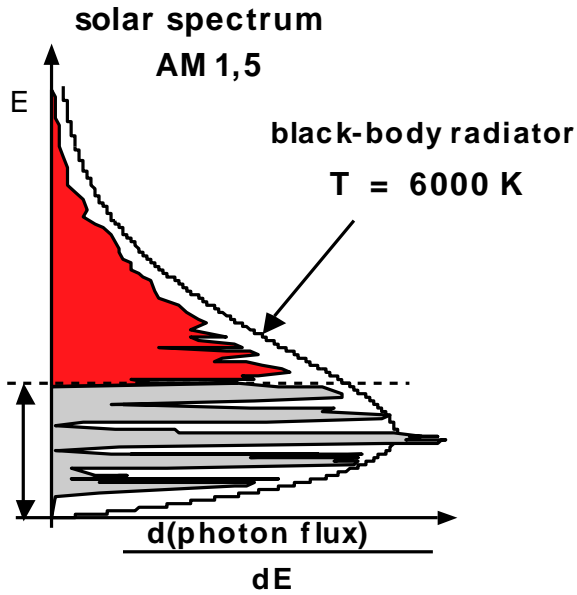


## Outline

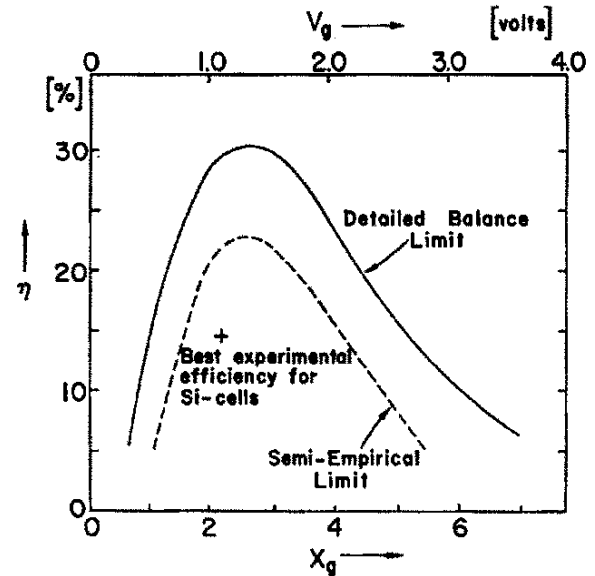
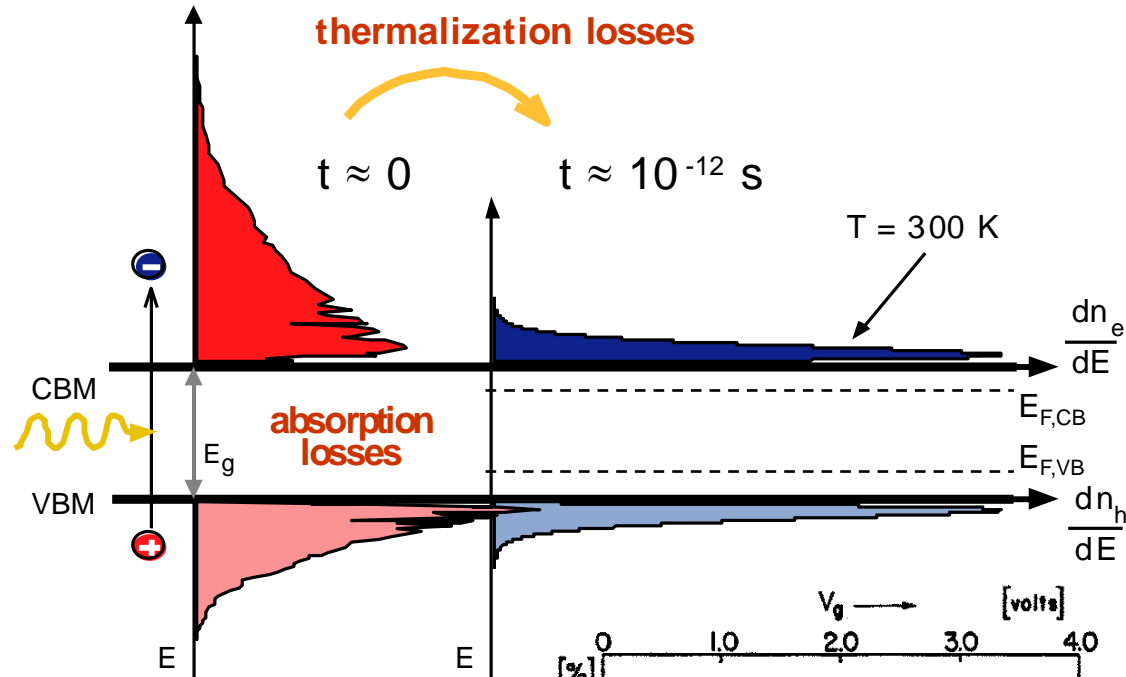
- Prerequisites for efficient absorber materials for direct water splitting
  - **Can we exceed the detailed balance limit of efficiency?**
    - Absorber, diffusion lengths, charge separation
- Current state of III-V on Si(100) growth: Costs↓
- Interfacial control: *In situ* spectroscopy



# Inherent losses in a 'normal' photo absorber



P. Würfel



Can we exceed the detailed balance limit of efficiency ?

**No!**

thermodynamic limits :

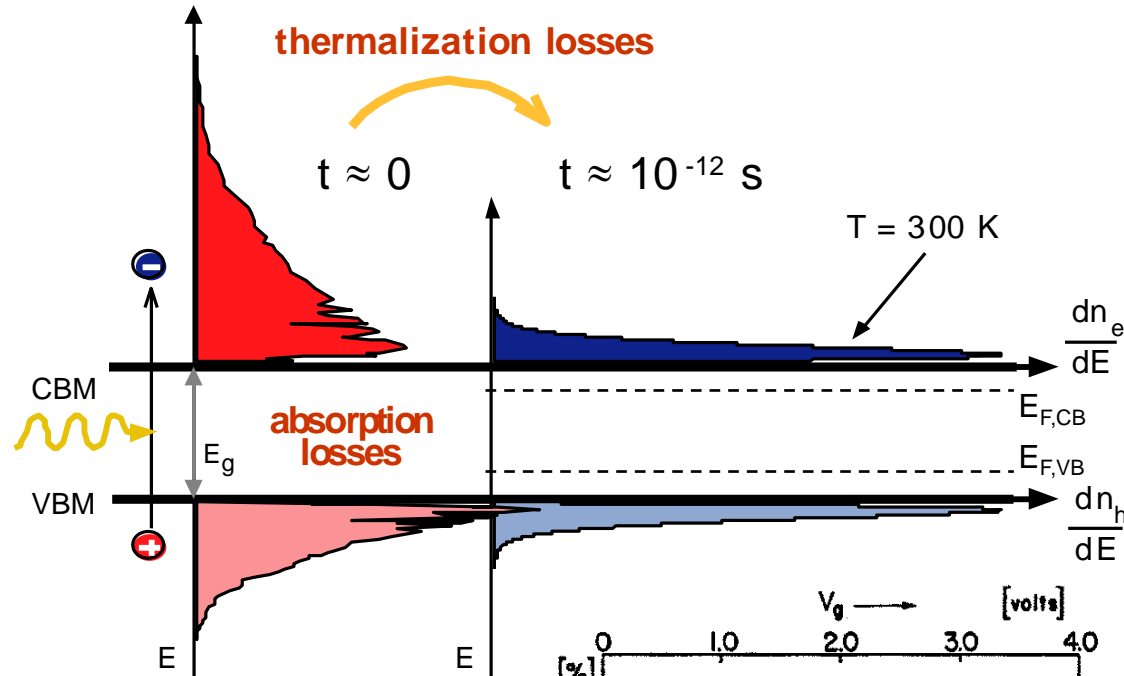
- only 1 absorber
- ~ 30 % (1 sun),
- ~ 45 % (max. concentration)

th

# The detailed balance principle

But we might improve constraints, which are:

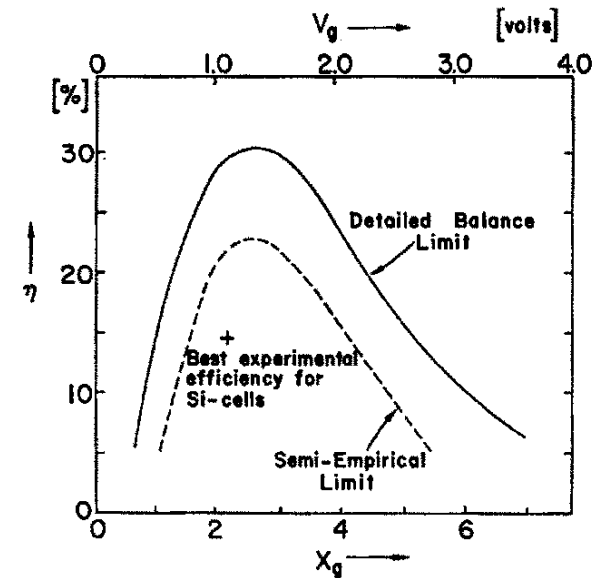
1.  $T_{\text{Sun}} = 6000 \text{ K}$
2.  $T_{\text{Earth}} = 300 \text{ K}$
3. only radiative recombination
4. only 1 absorber
5. complete absorption of photons above band gap
6. 1 e-h pair / incident photon: QY 100%
7. ultrafast thermalization
- { 8. complete conversion of free energy }



thermodynamic limits :

only 1 absorber  
 ~ 30 % (1 sun),  
 ~ 45 % (max. concentration)

optimum system  
 ~ 66% (1 sun)  
 ~ 86% (max. concentration)

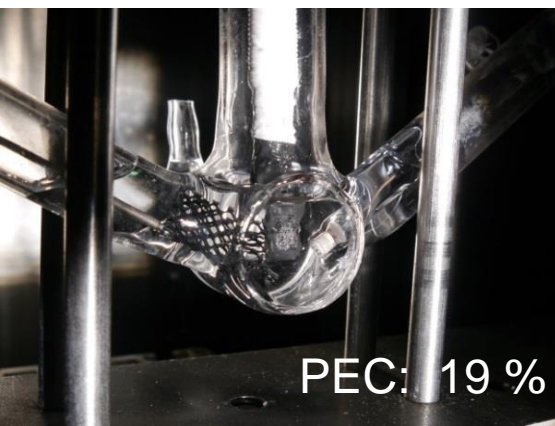




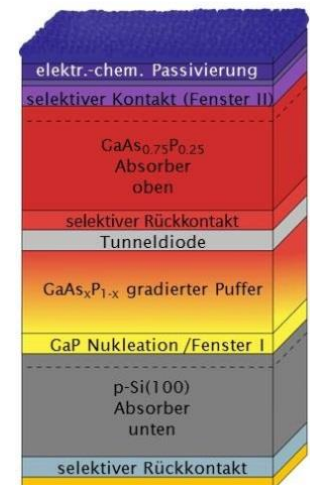
## Outline



- Prerequisites for **efficient** absorber materials for direct **water splitting**
  - Can we exceed the Shockley-Queisser-Limit?
  - **Absorber, diffusion lengths, charge separation**
- Current state of III-V on Si(100) growth: Costs↓
- Interfacial control: *In situ* spectroscopy



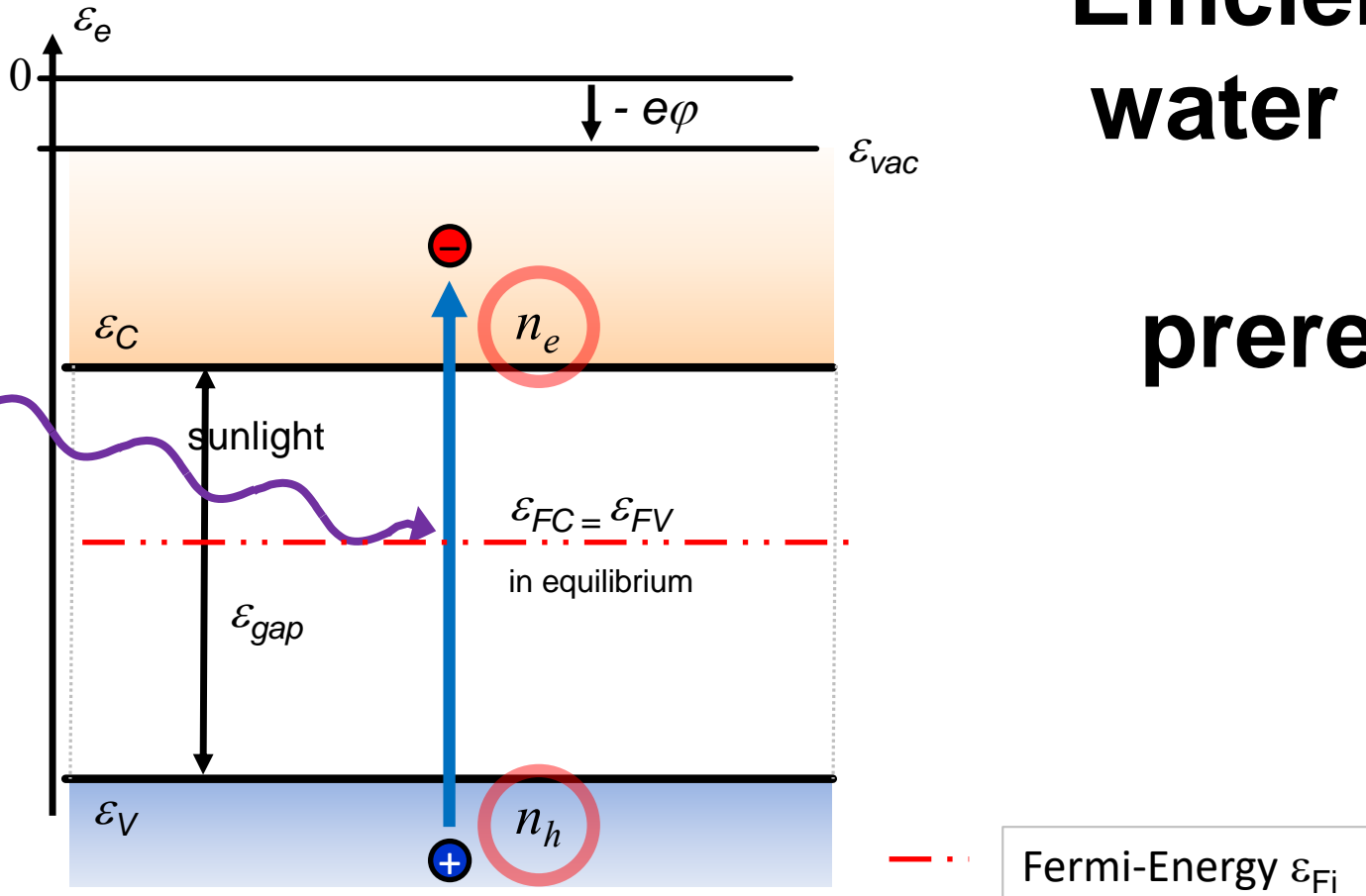
tandems



# Considering the integrated functionality

Requirements for semiconductor device structure

I) Production of appropriate chemical potentials for  $e^-$  in CB and VB (voltage)

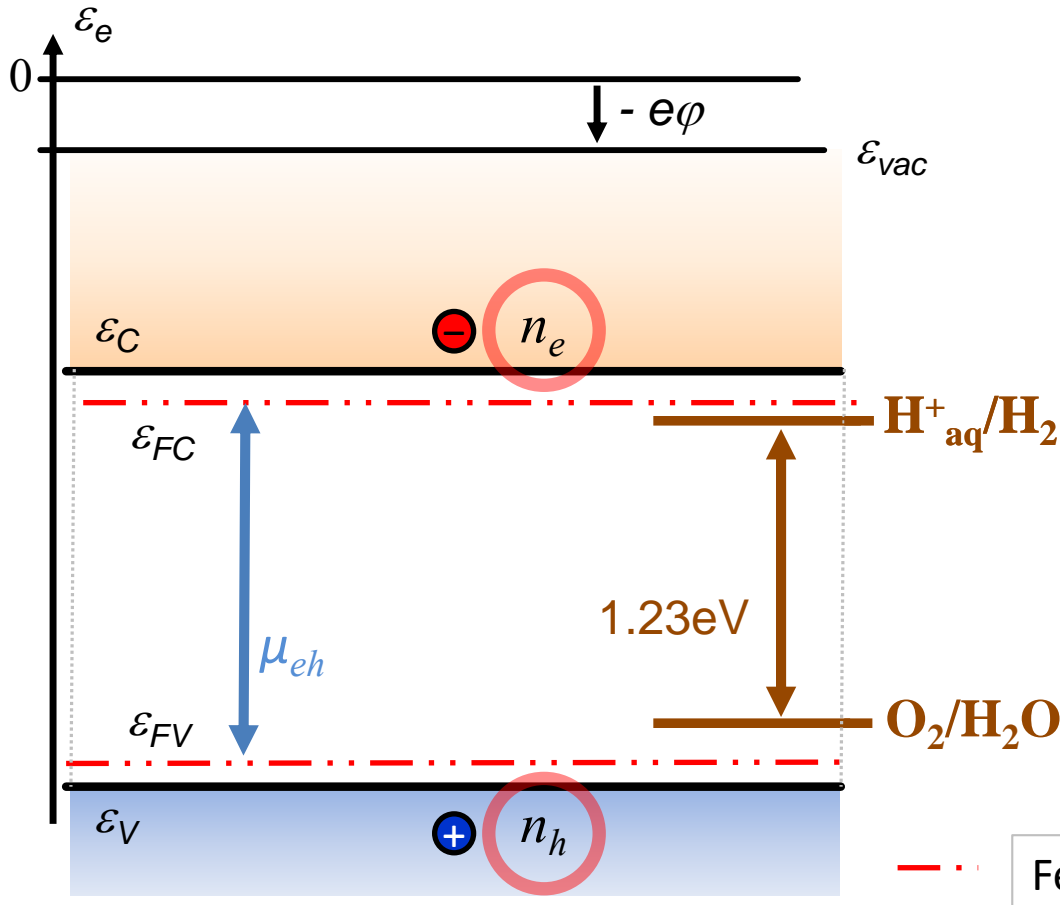


## Efficient direct water splitting - prerequisites

# Considering the integrated functionality

## Requirements for semiconductor device structure

I) Production of **appropriate chemical potentials for  $e^-$**  in CB and VB (voltage)



Chemical potential  $\mu_i$  of electrons  $\mu_e$  and holes  $\mu_h$

$$\mu_i = \mu_{i,0} + kT \ln \left( \frac{n_i}{N_i} \right)$$

for electrons:  $\mu_e - e \varphi = \epsilon_{FC}$

for holes:  $\mu_h + e \varphi = -\epsilon_{FV}$

under illumination

$$\mu_e + \mu_h = \epsilon_{FC} - \epsilon_{FV} > 0$$

--- Fermi-Energy  $\epsilon_{Fi}$

# Considering the integrated functionality

Dynamics: continuity of electrons and holes in steady-state

$$\frac{\partial n_e}{\partial t} = G_{eh} - R_{eh} - \text{div } j_e = 0$$

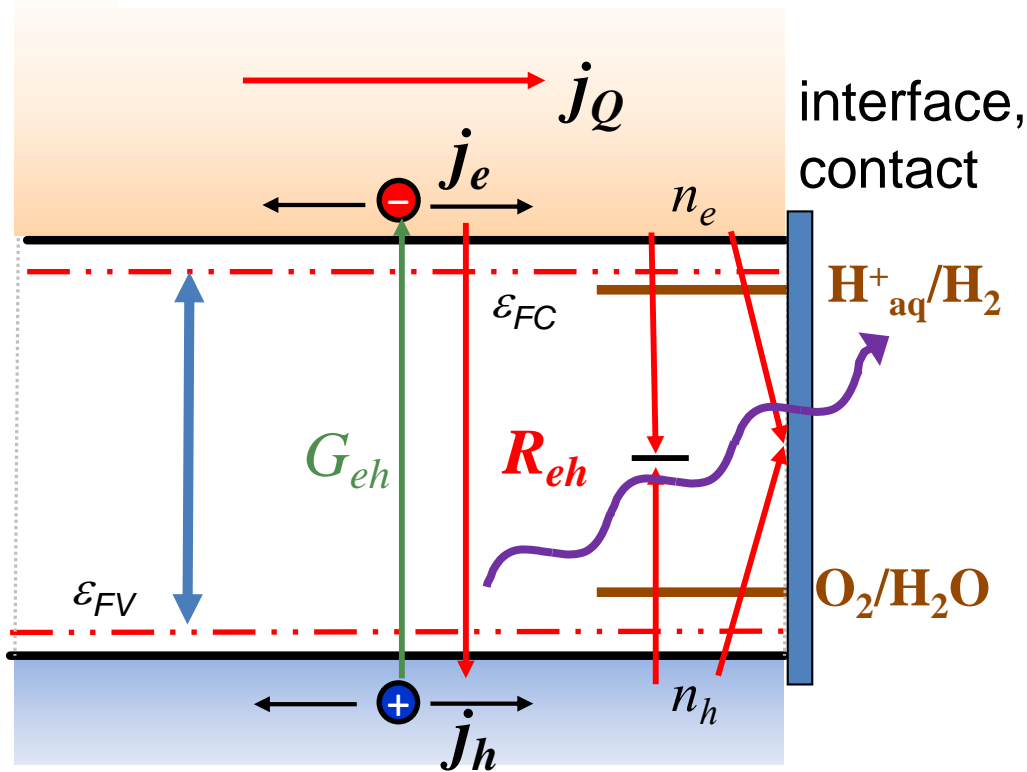
$$\frac{\partial n_h}{\partial t} = G_{eh} - R_{eh} - \text{div } j_h = 0$$

I) Production of **appropriate chemical potentials** in CB and VB (voltage)

$$j_Q = e(j_h - j_e)$$

integrated over cell volume:

$$j_Q = -e(G_{eh,tot} - R_{eh,tot})$$



see also: P. Würfel  
Physics of solar cells

# Considering the integrated functionality

**Dynamics:** continuity of electrons and holes in steady-state

$$\frac{\partial n_e}{\partial t} = G_{eh} - R_{eh} - \text{div } j_e = 0$$

$$\frac{\partial n_h}{\partial t} = G_{eh} - R_{eh} - \text{div } j_h = 0$$

I) Production of **appropriate chemical potentials** in CB and VB (voltage)

$$j_Q = e(j_h - j_e)$$

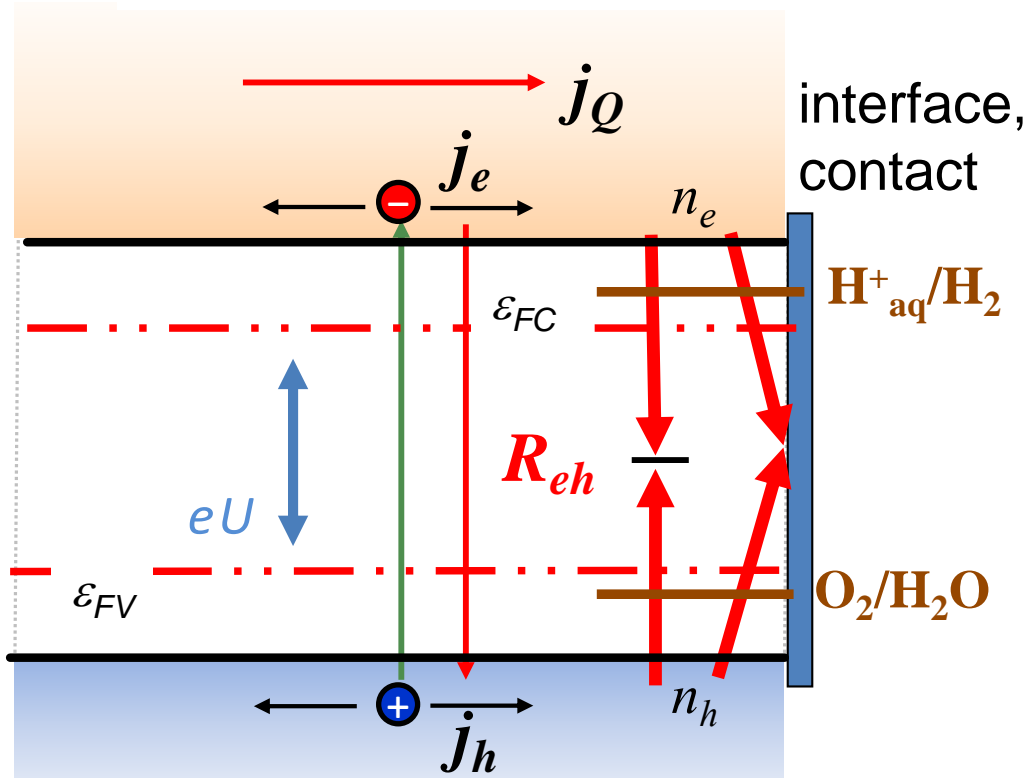
integrated over cell volume:

$$j_Q = -e(G_{eh,tot} - R_{eh,tot})$$

$$\mu_i = \mu_{i,0} + kT \ln \left( \frac{n_i}{N_i} \right)$$

Fermi-level splitting ( $\sim$  voltage)

$$\varepsilon_{FC} - \varepsilon_{FV} = \mu_e + \mu_h$$

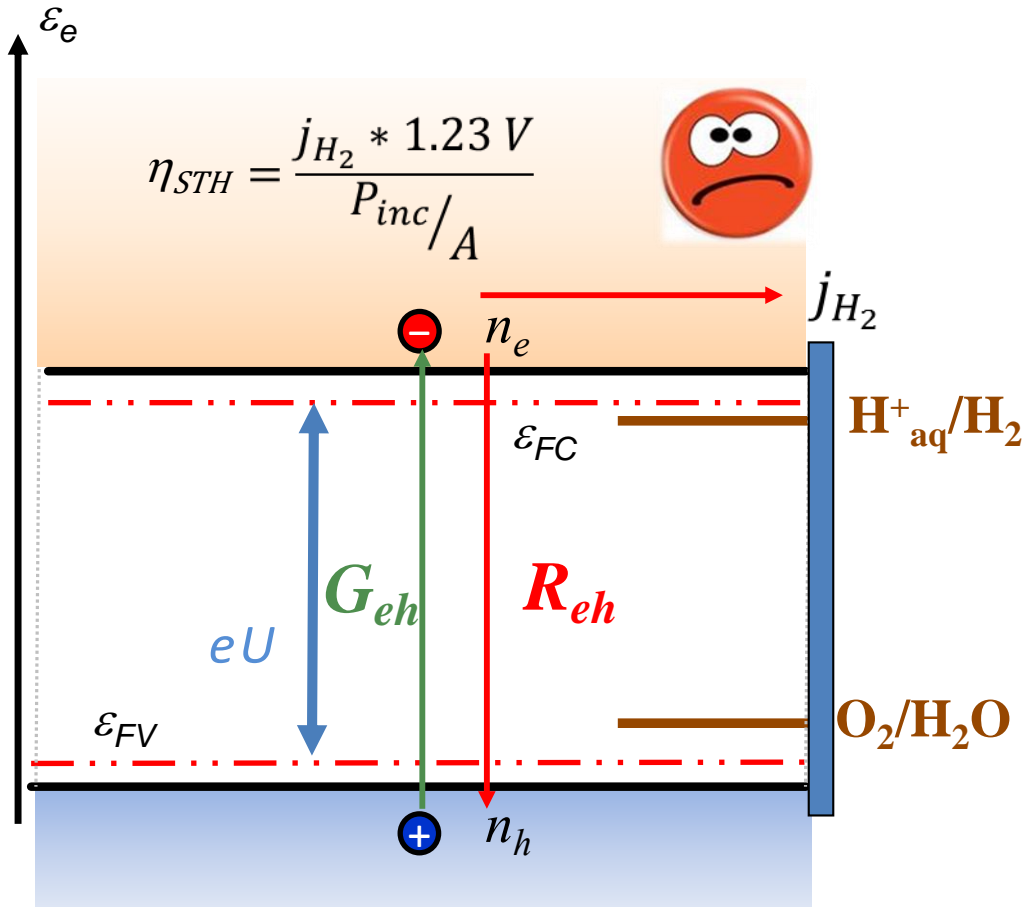


see also: P. Würfel  
Physics of solar cells

# Considering the integrated functionality

For bias-free solar water-splitting

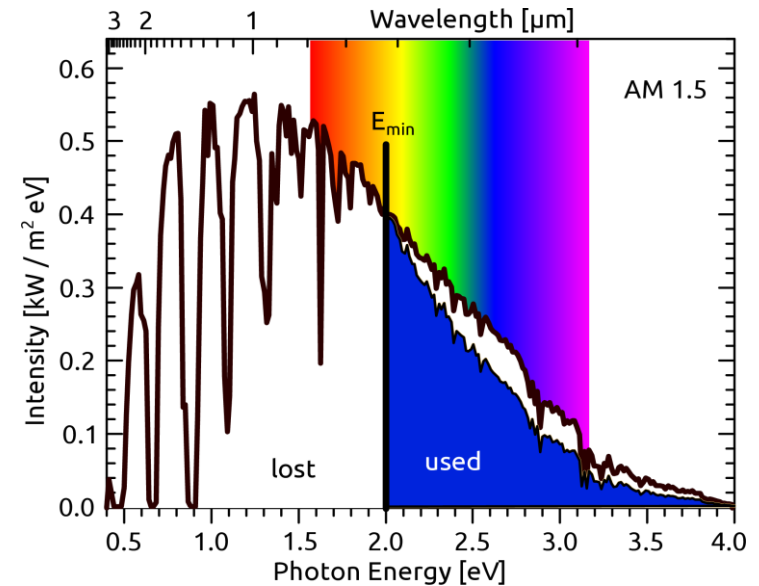
band gap > 2.0 eV mandatory



I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

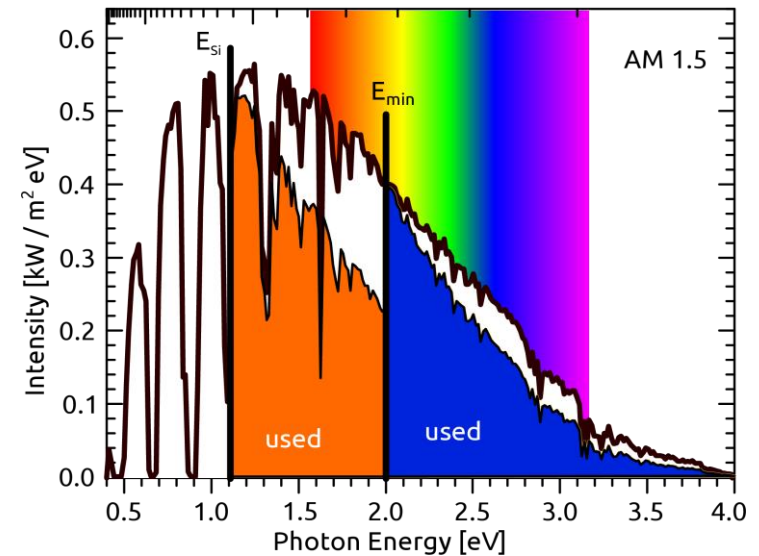
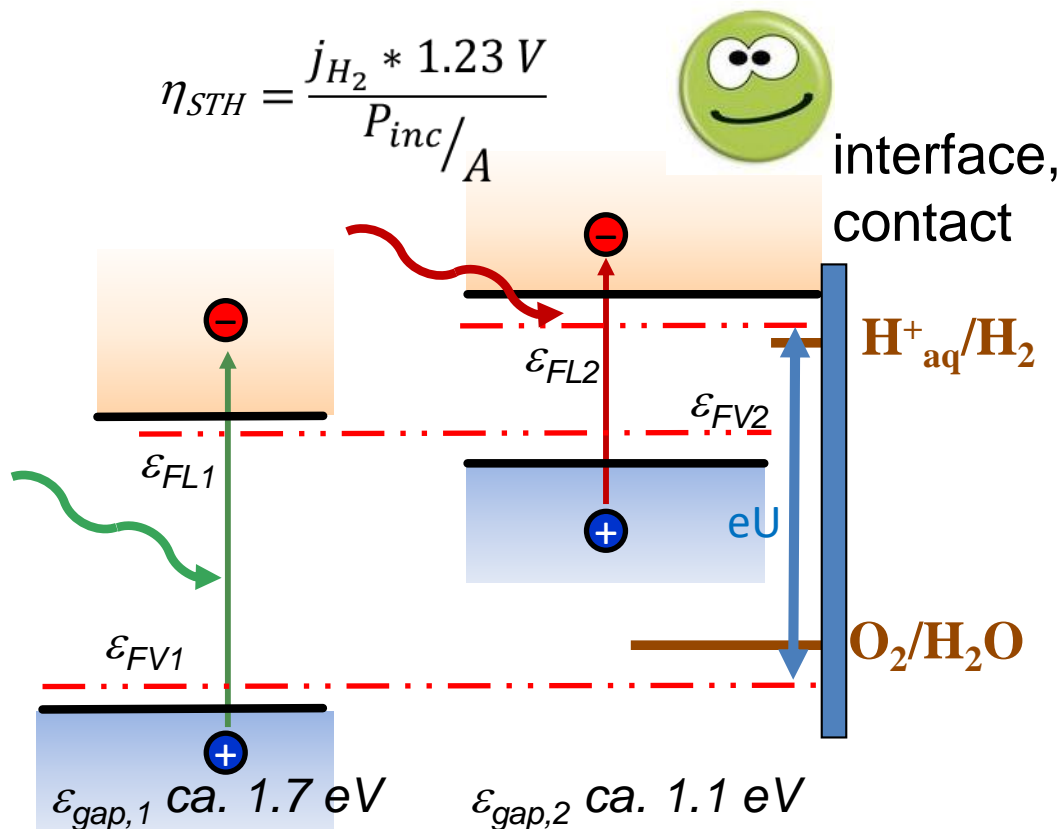
Even in **ideal case sun light exploitation insufficient** with only one absorber



# Principle of efficient solar energy conversion

Efficient bias-free solar  
watersplitting –  
**tandem** mandatory

- I) Production of **appropriate chemical potentials** in CB and VB (voltage)
- II) Exploitation of the **sun light**



# Principle of efficient solar energy conversion

## Diffusion length

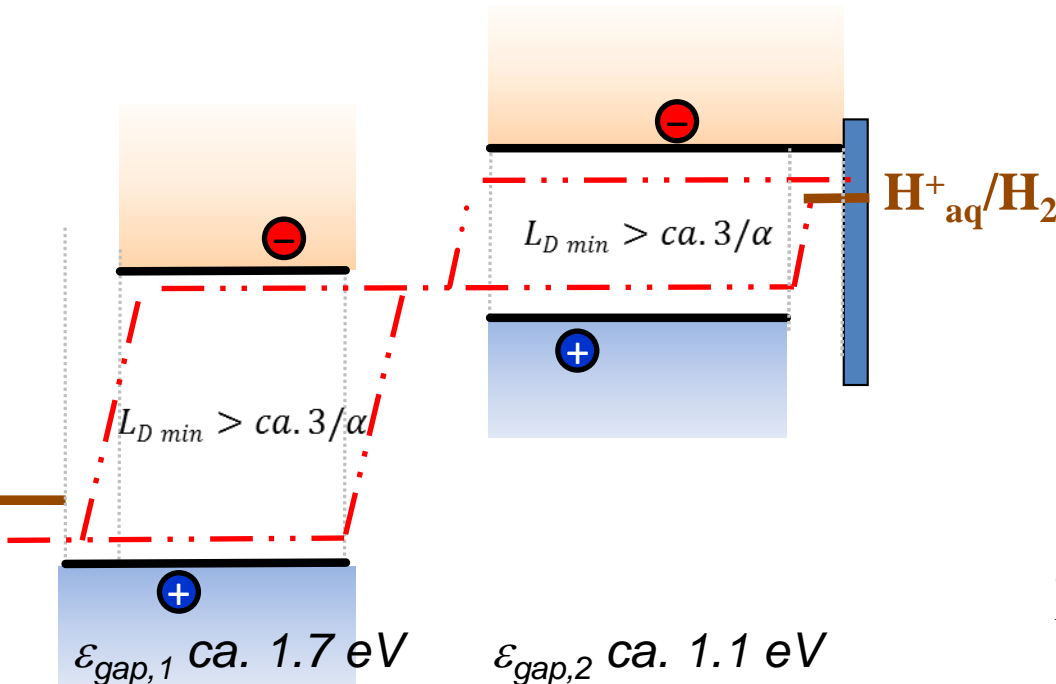
$$L_{D \min} > ca. 3/\alpha$$

## indispensable

I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation  
high **mobility**, low non-rad. **recombination**



Diffusion length  $L_{D \min}$

$$L_{D \min} = \sqrt{\tau_{\min} D_{\min}}$$

Einstein-Smoluchowski equation

$$D = \frac{k_B T}{e} \mu^b$$

$\mu^b$ : mobility

$D$ : diffusion coefficient

$\alpha$ : absorption coefficient

$\tau_{\min}$ : minority

charge carrier life

time

# Principle of efficient solar energy conversion

Charge selective contacts:  
indispensible

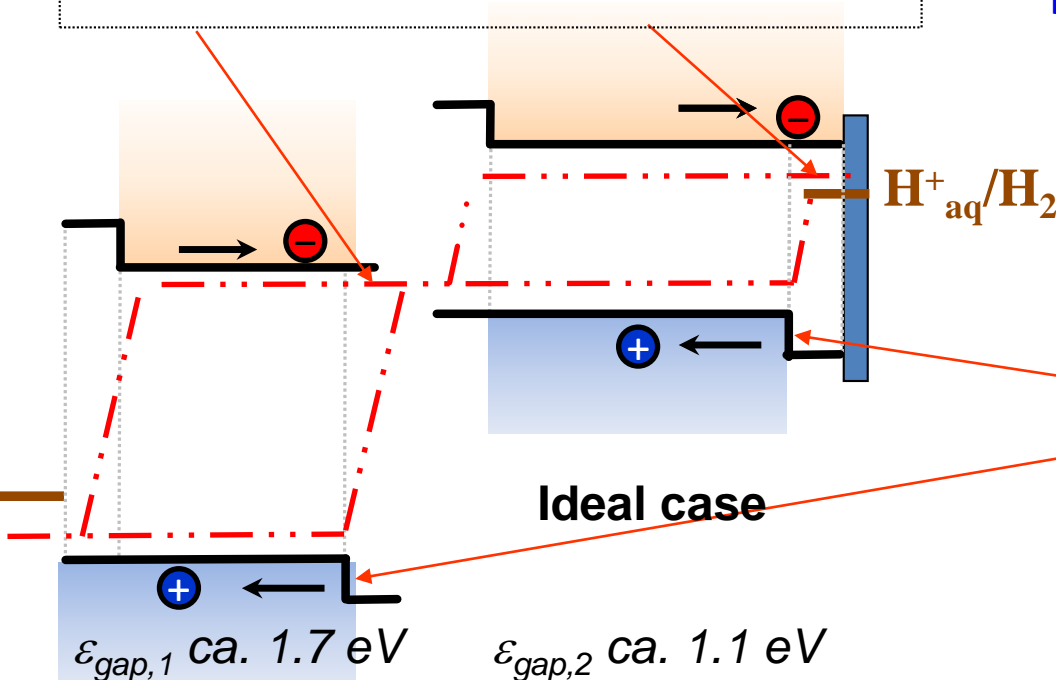
for electrons e.g. high conductivity for electrons, little conductivity for holes (low concentration) - **mandatory**

I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation high mobility, low non-rad. recombination

IV) **Charge separation**: photovoltage -> transformation of energy

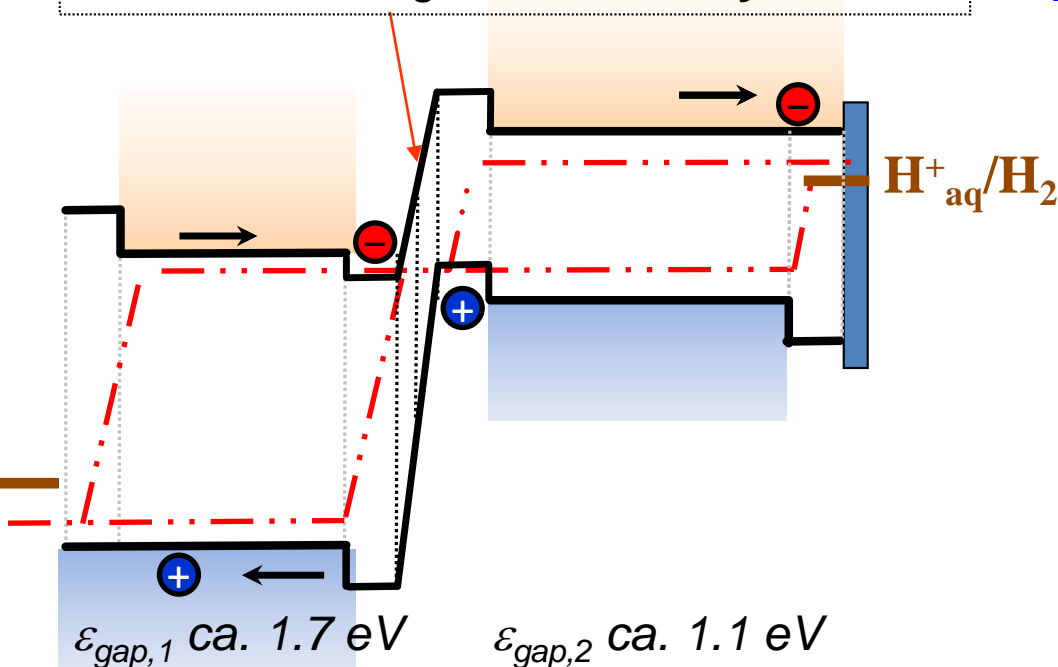


Valence band-offset and increase of band gap energy prevent higher hole concentrations

# Principle of efficient solar energy conversion

Charge transport, charge separation: **Ideal case**

**Tunnel junction** / recombination layer:  
Quantum mechanical tunneling with QE  
ca. 1; isoenergetic eh-recombination –  
current matching - **mandatory**



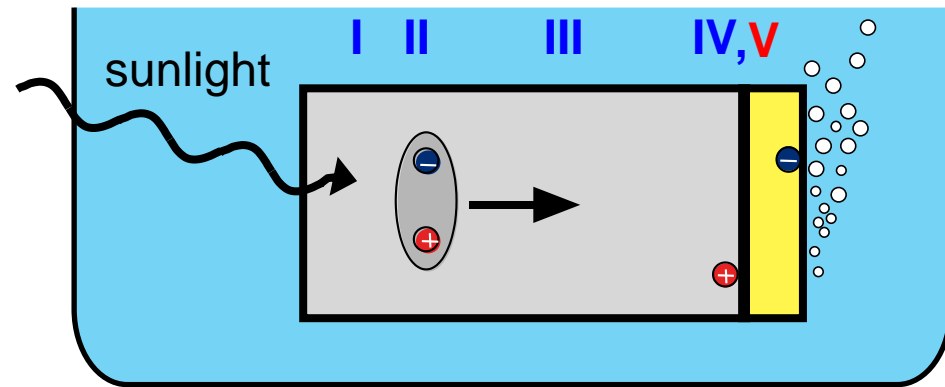
I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation  
high mobility, low non-rad. recombination

IV) **Charge separation**: photovoltage ->  
transformation of energy

# Specific requirements for water splitting



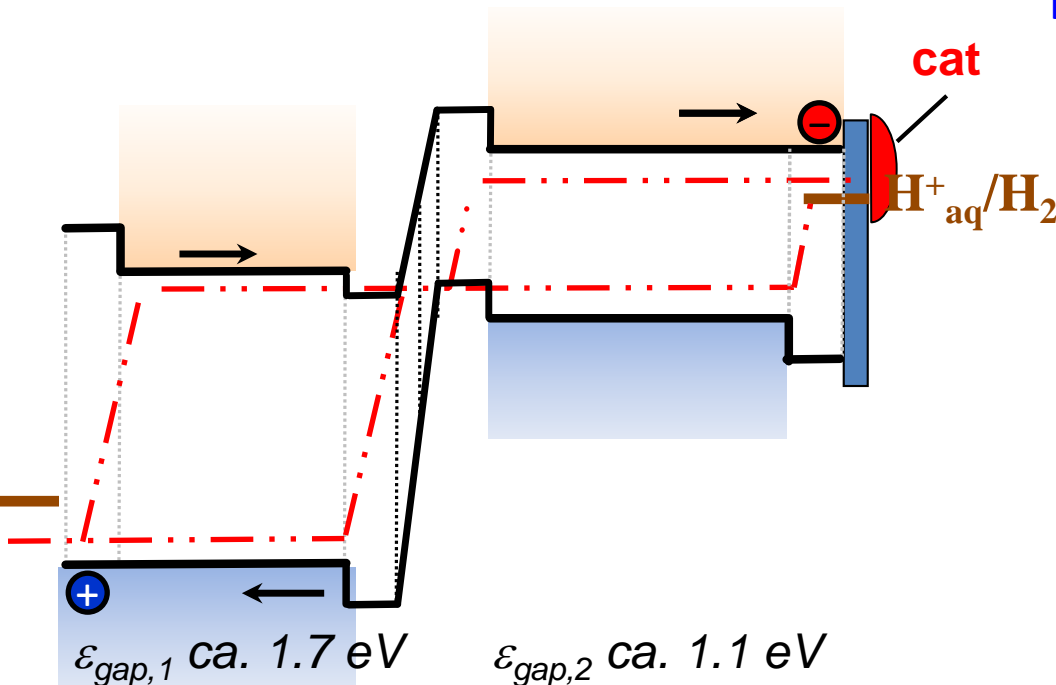
I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

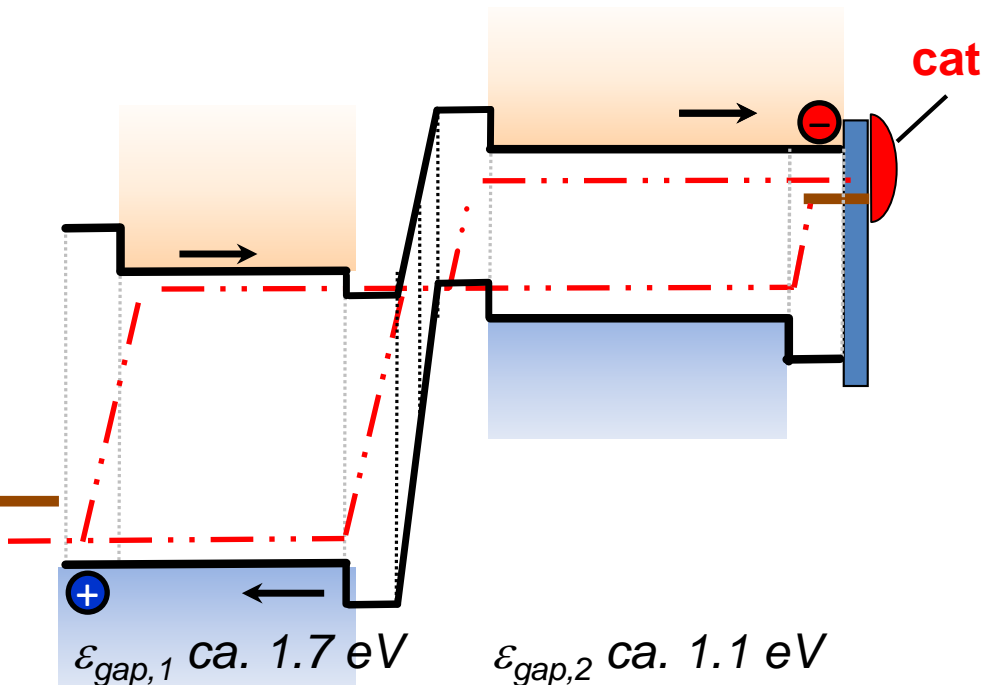
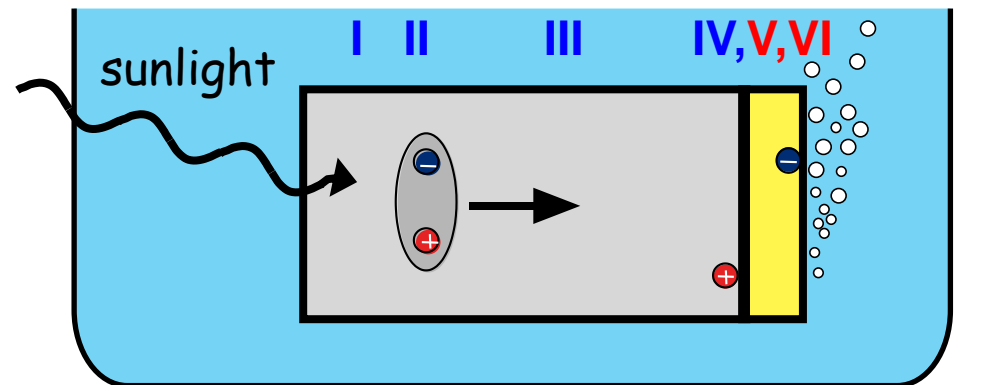
III) Spatial **transport** of electronic excitation  
high mobility, low non-rad. recombination

IV) **Charge separation**: photovoltage ->  
transformation of energy

V) **High catalytic activity**  
sufficiently low overpotentials



# Specific requirements for water splitting



I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation  
high mobility, low non-rad. recombination

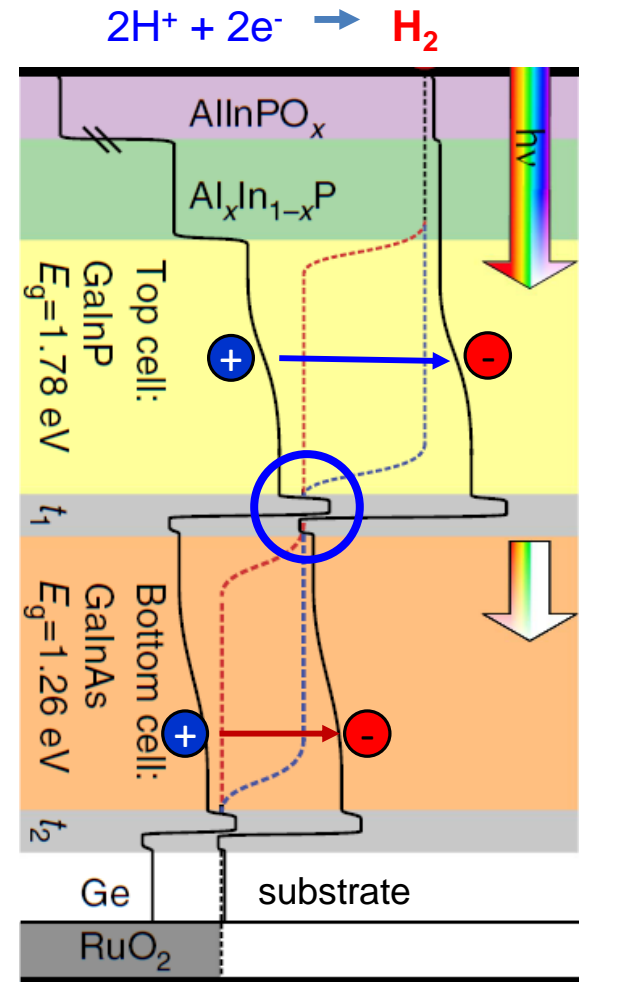
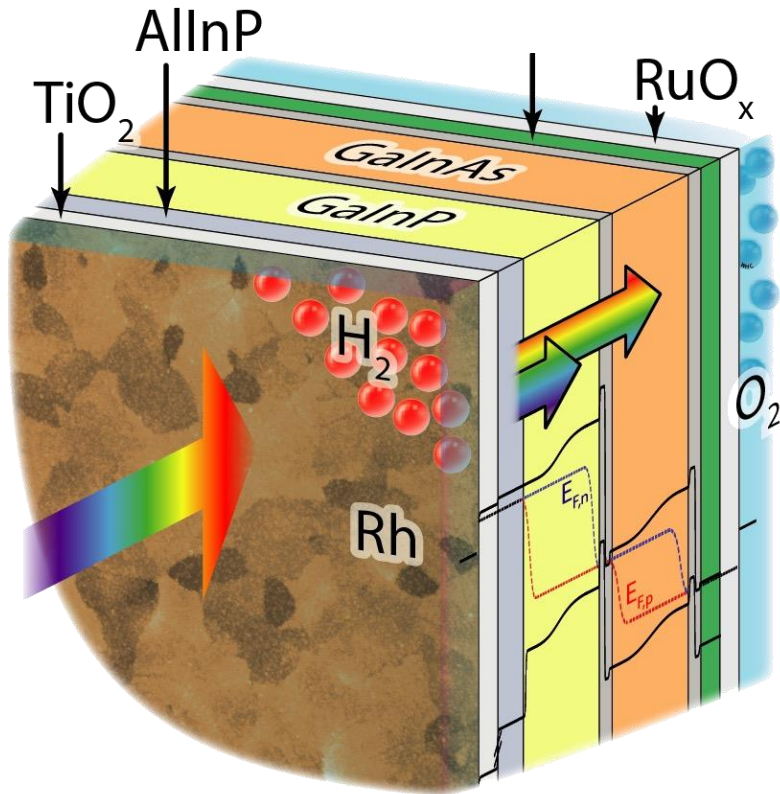
IV) **Charge separation**: photovoltage  $\rightarrow$   
transformation of energy

V) High **catalytic activity**  
sufficiently low overpotentials

VI) High **photochemical stability**:  
corrosion-resistant and/or surface  
passivation

# Potential efficiencies of tandems for water-splitting

- Bias-free solar water splitting requires voltage > ca. 1.7 eV
- Above that: maximisation of the current
- Two junction cells for efficiency optimum

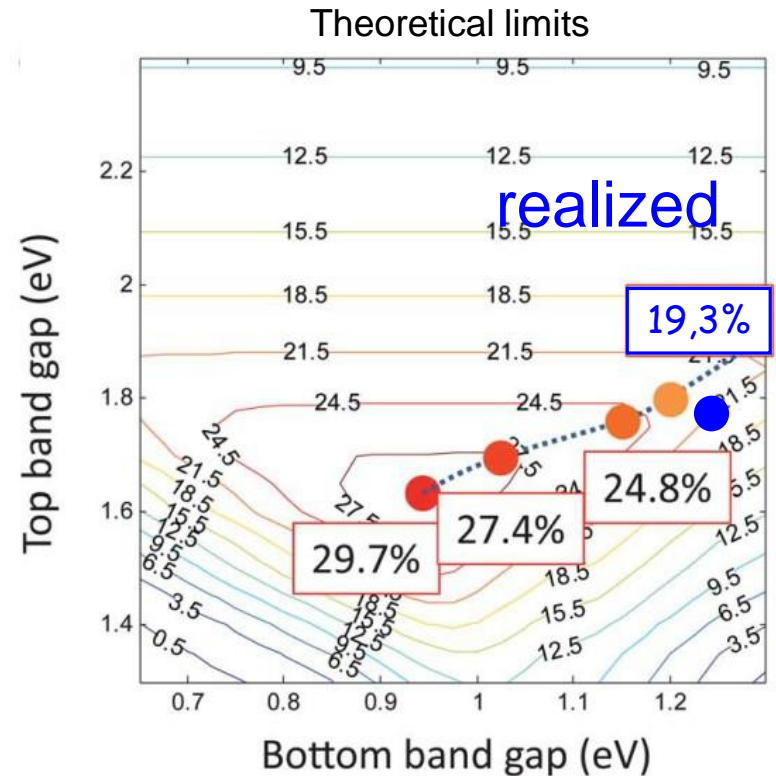
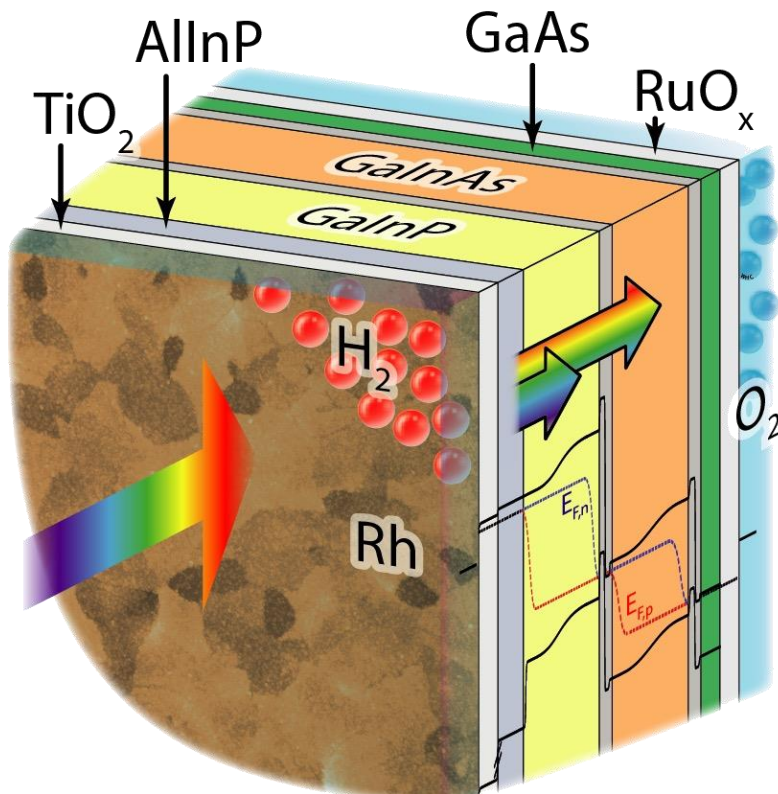


Solar to hydrogen  $\eta = \frac{j_H \times 1.23 \text{ V}}{P_{in}/A} = 19,3 \%$



# Potential efficiencies of tandems for water-splitting

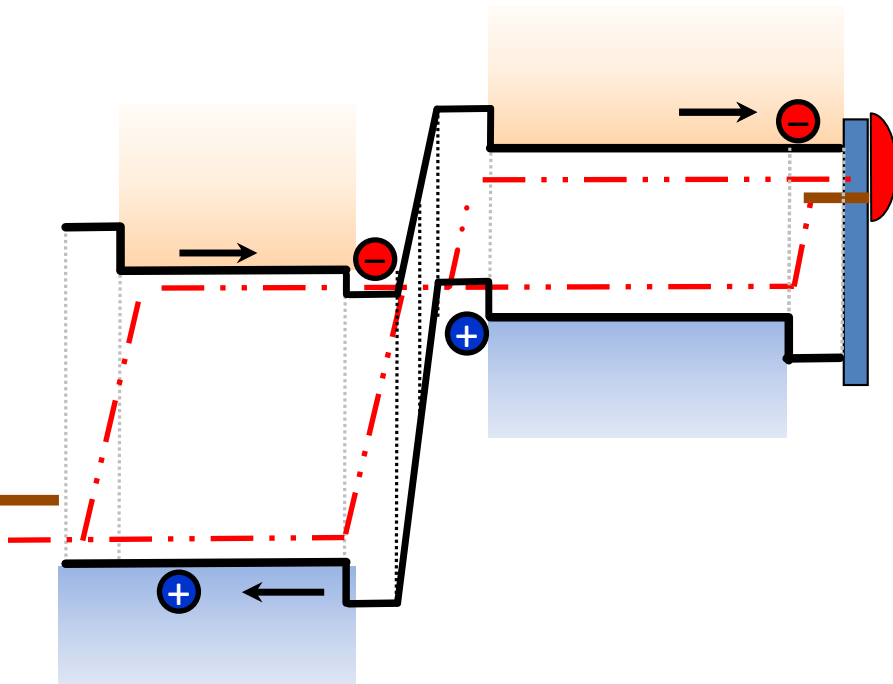
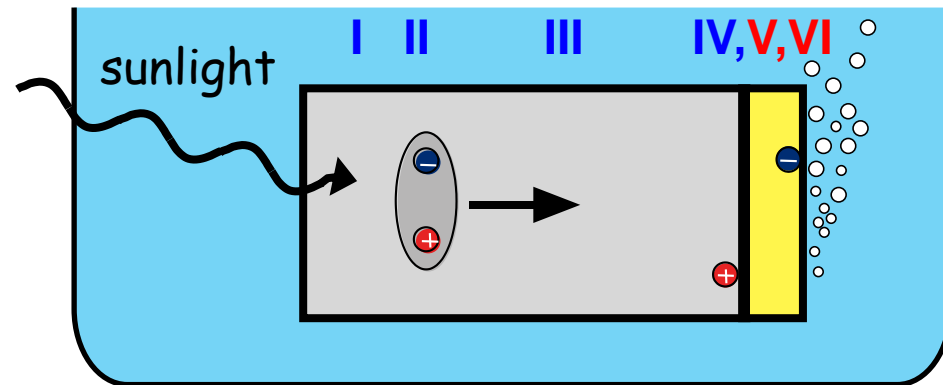
- Bias-free solar water splitting requires voltage > ca. 1.7 eV
  - Beyond that: maximisation of the current
    - Two junction cells for efficiency optimum



Solar to hydrogen  $\eta = \frac{j \times 1.23 \text{ V}}{P_{\text{in}}/A} = 19,3 \%$

S. Hu et al. *Energy Environ. Sci.* **6**:2984, 2013.

# Specific requirements for water splitting



I) Production of **appropriate chemical potentials** in CB and VB (voltage)

II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation  
high mobility, low non-rad. recombination

IV) **Charge separation**: photovoltage ->  
transformation of energy

V) High **catalytic activity**  
sufficiently low overpotentials

VI) High **photochemical stability**:  
corrosion-resistant and/or surface  
passivation

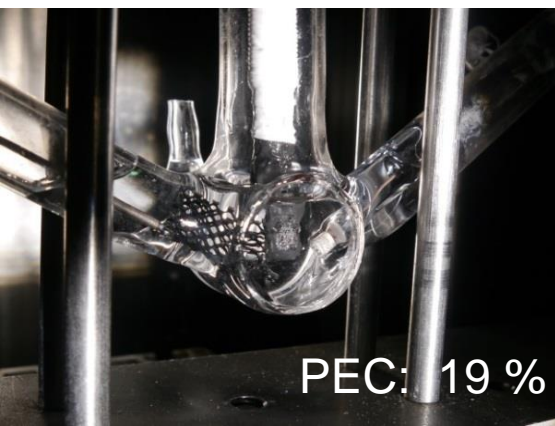
VII) **Costs**



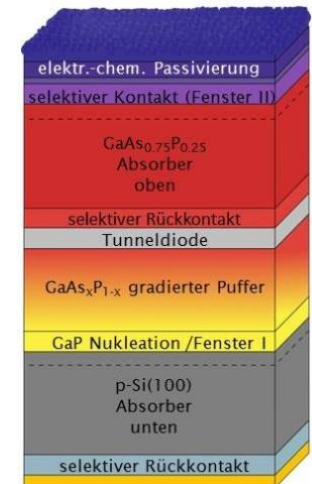
## Outline



- Prerequisites for efficient absorber materials for direct water splitting
  - Can we exceed the Shockley-Queisser-Limit?
  - Absorber, diffusion lengths, charge separation
- **Current state of III-V on Si(100) growth: Costs↓**
- Interfacial control: *In situ* spectroscopy



tandems



# State-of-the-art Multi Junction Cells

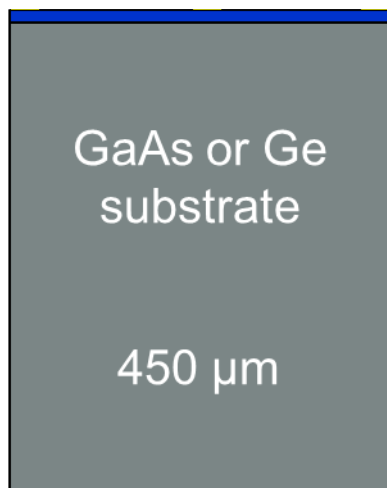
## Industrial Standard



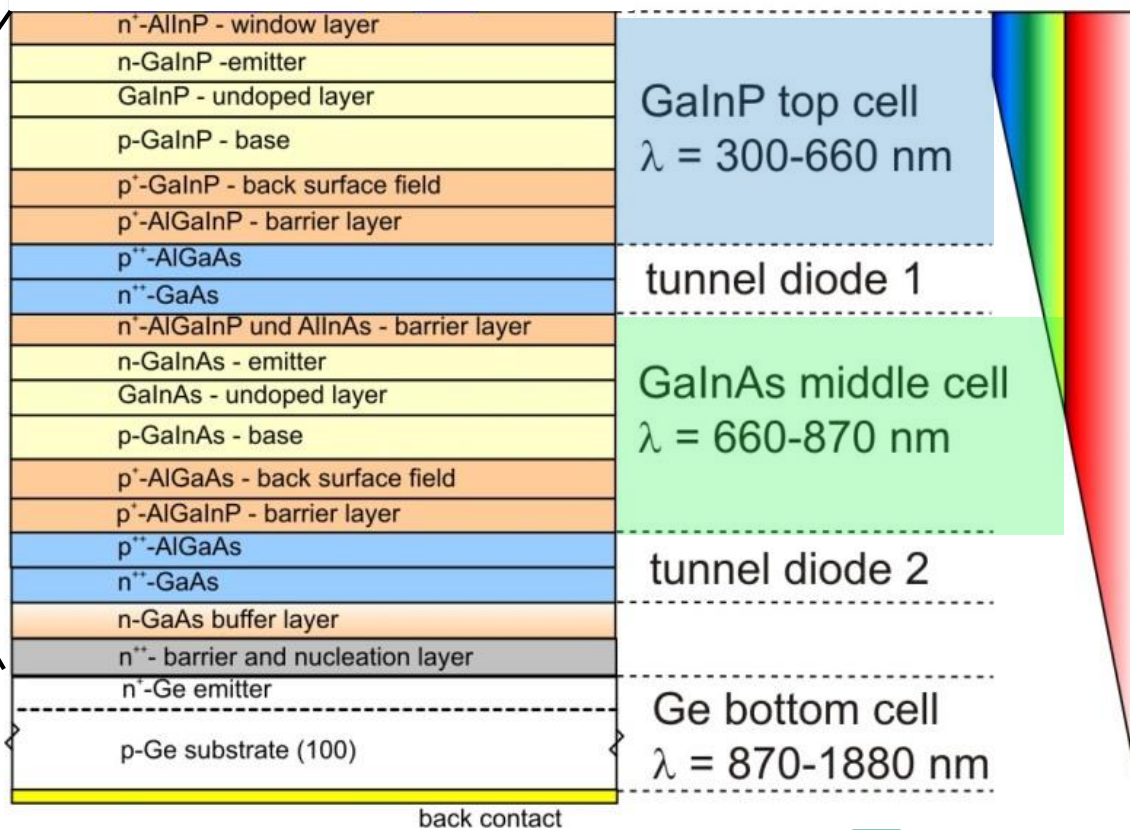
Only upper ~10  $\mu\text{m}$  of solar cell active



Exchange of substrate can lead to significant savings



Grown with MOVPE technology



Courtesy: F. Dimroth Fraunhofer ISE

**Costs**

Cell Cost [\$/Watt]

Cost advantages on module level

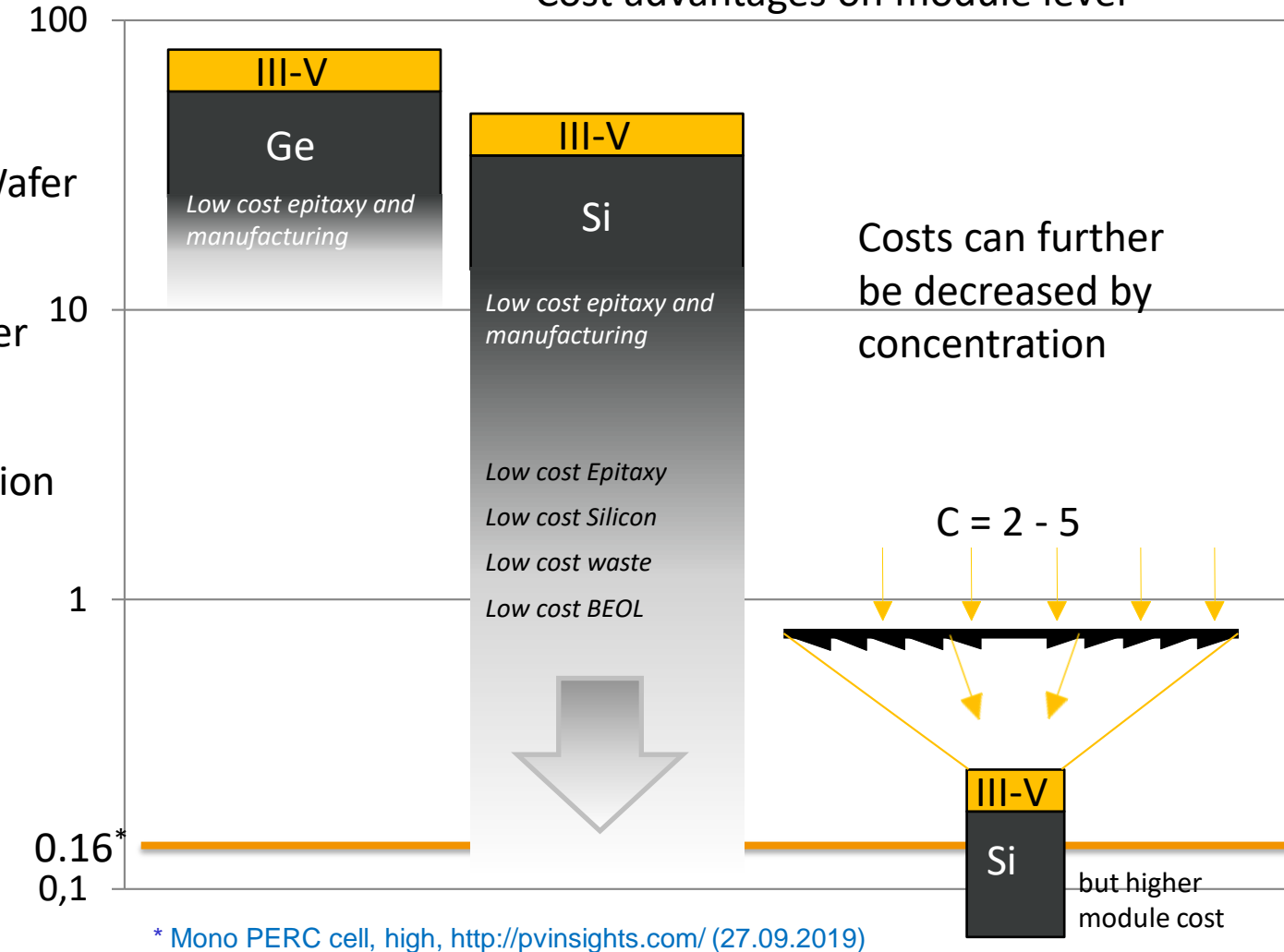
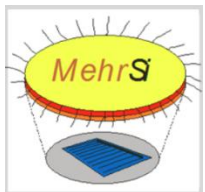
Ge Substrate ~100 €/6" Wafer



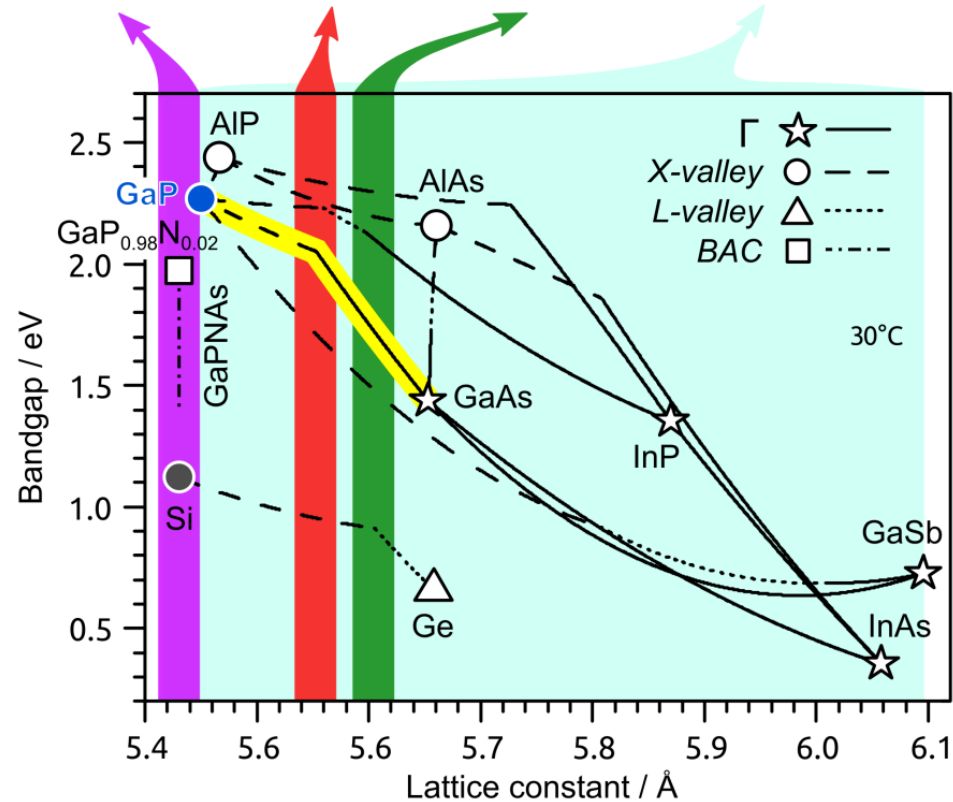
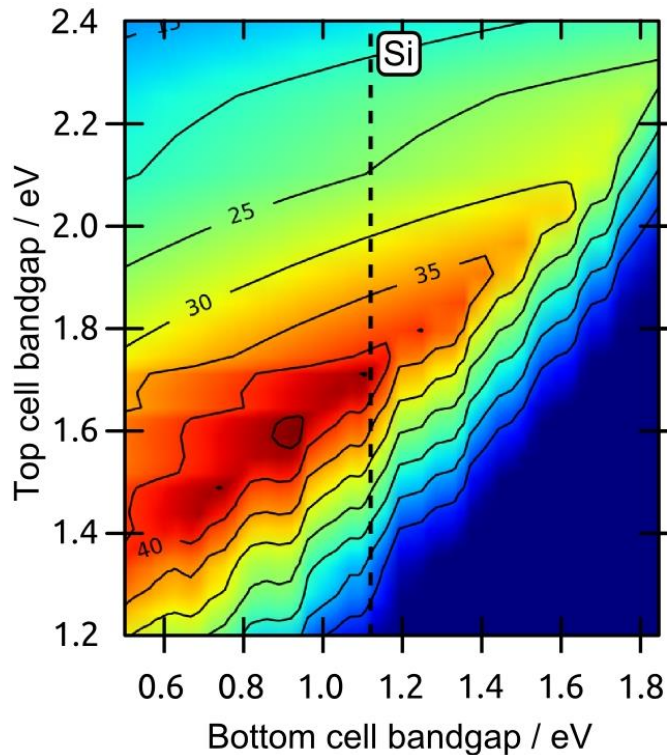
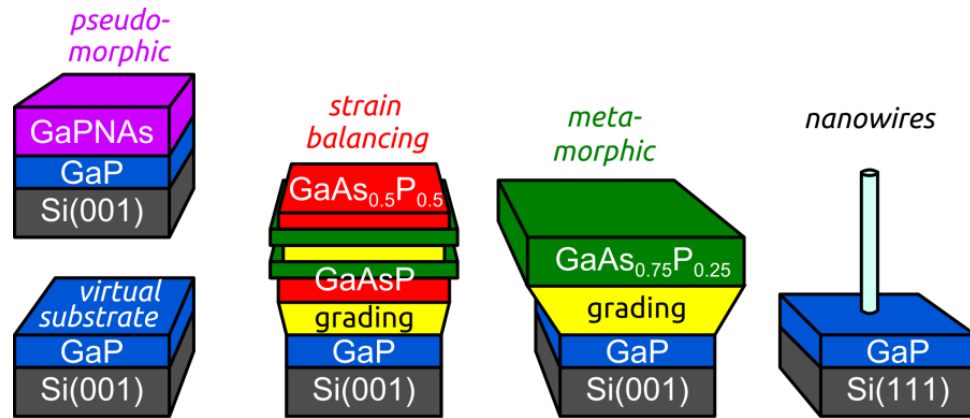
Si polished < 50 €/6" Wafer



Si etched in mass production  
~0.3 €/6" Wafer

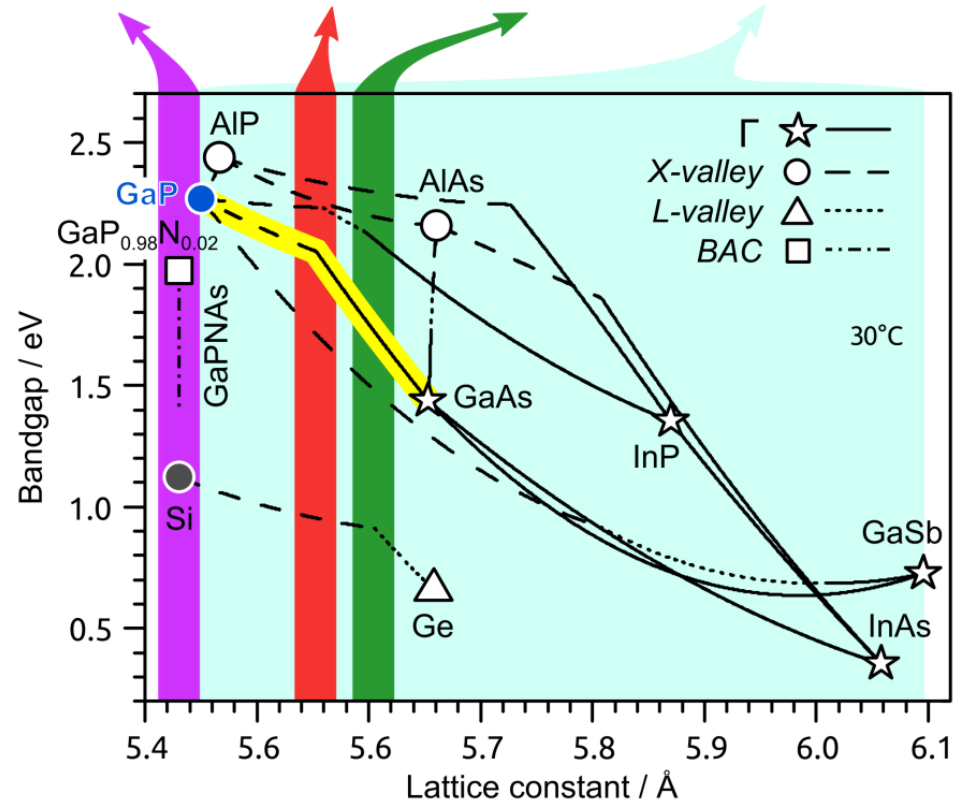
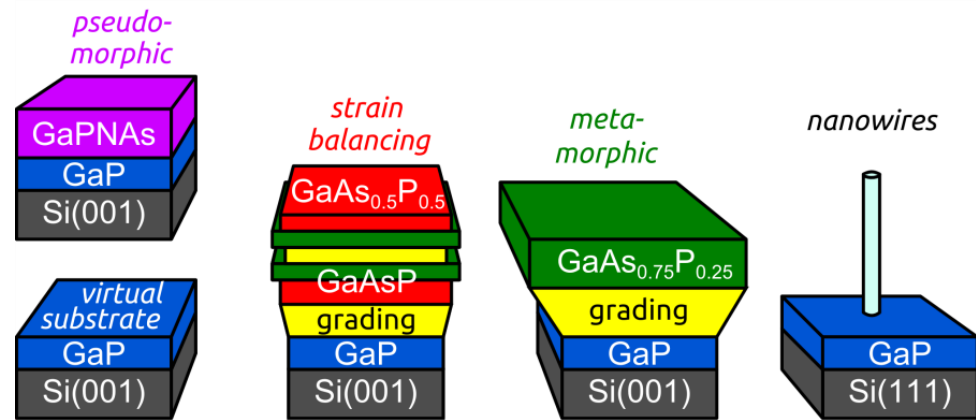


# Integration of III-V materials with silicon substrates



© O.Supplie, T.H. et al., *Adv. Mater. Interfaces* **4**:1601118, 2017; calc. with YaSoFo by MM. May, bitbucket.org/YaSoFo/yasofo.

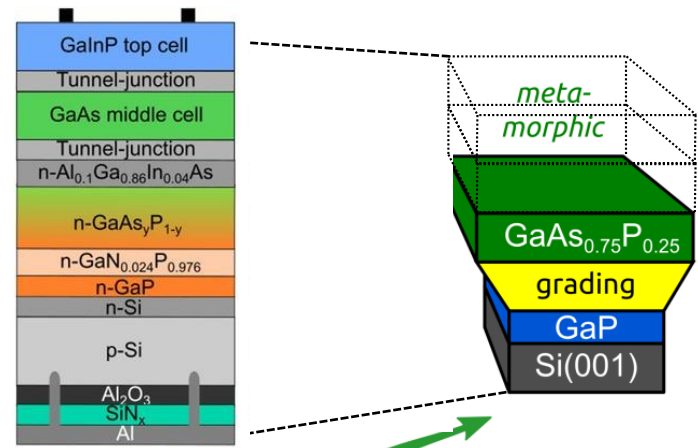
# How to reduce the defect density at the III-V/Si heterointerface?



# III-V-on-Si multijunction solar cell

Highest solar conversion efficiency for III-V/Si tandem cell

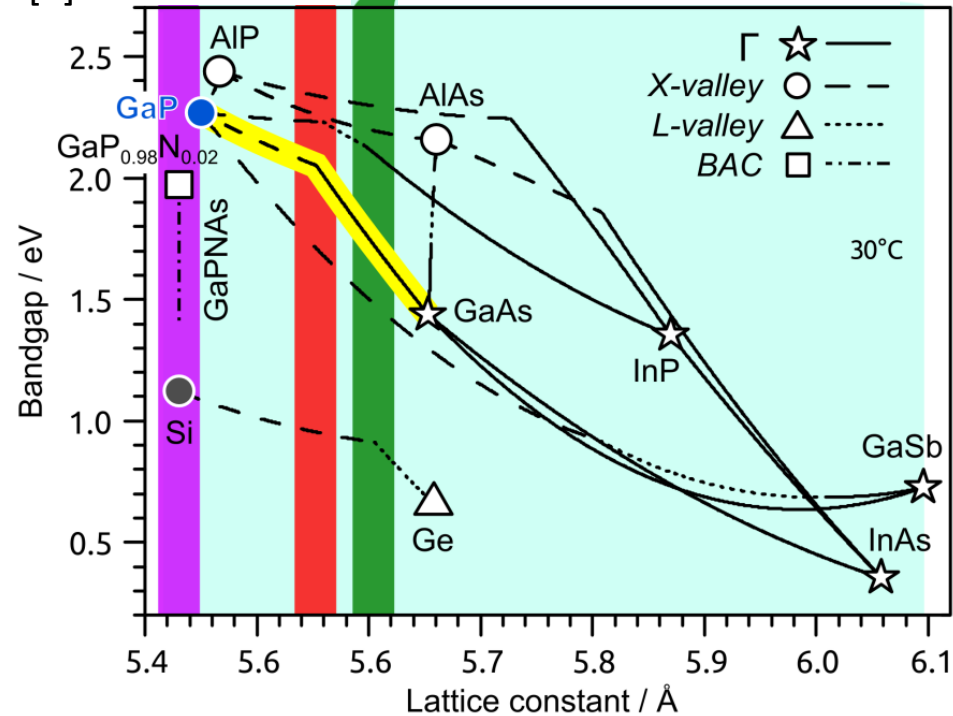
→ **25.9%** with GaInP/GaAs/Si [1]



From [3] GaInP/GaAs/Si

How to reduce the defect density at the III-V/Si heterointerface?

Pulsed nucleation [2]:  
Introduction of **AlGaP/Si** [4]



[1] M. Feifel *et al.*, Sol. RRL 2021, 2000763 (001), 1–7.

[2] K. Volz *et al.*, J. Cryst. Growth 315 (2011) 37.

[3] M. Feifel *et al.*, Sol. RRL 3 (2019) 1900313.

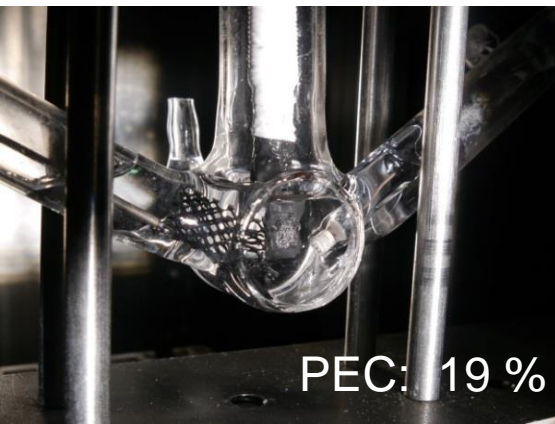
[4] M. Nandy *et al.*, submitted



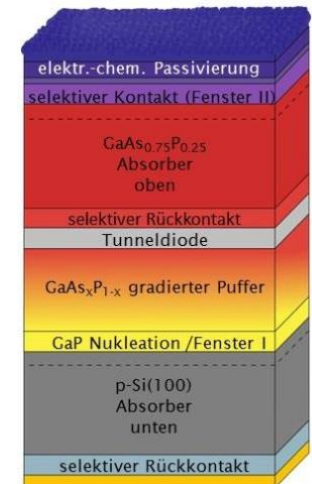
## Outline



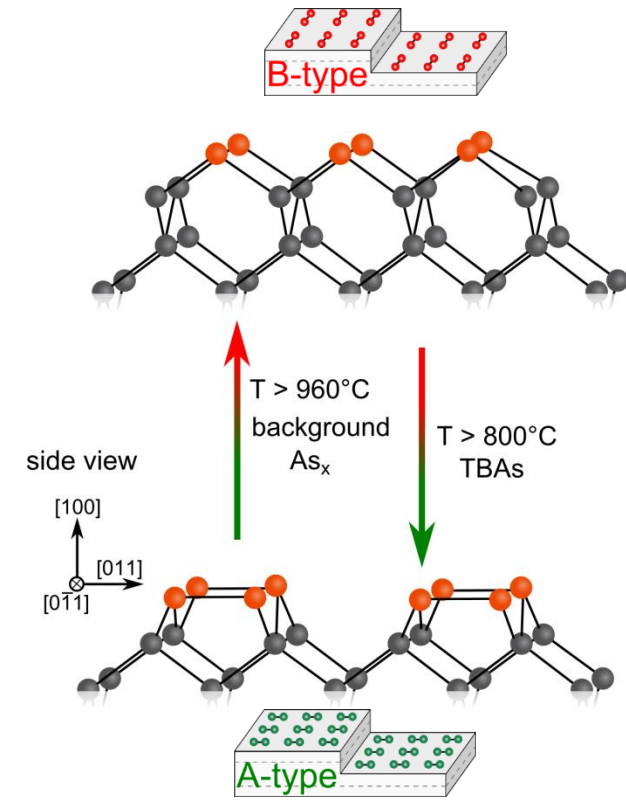
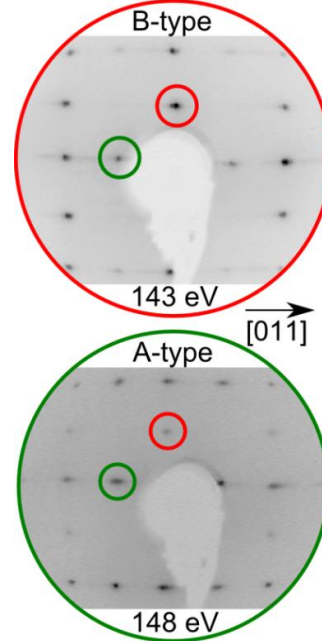
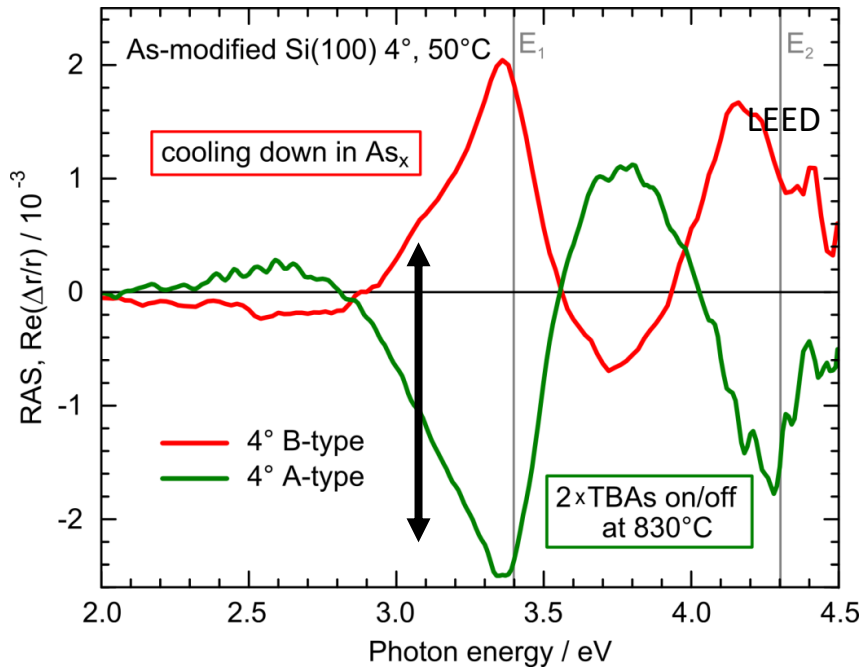
- Prerequisites for efficient absorber materials for direct water splitting
  - Can we exceed the Shockley-Queisser-Limit?
  - Absorber, diffusion lengths, charge separation
- Current state of III-V on Si(100) growth: Costs↓
- **Interfacial control: *In situ* spectroscopy**



tandems



# Impact on Arsen-precursor on GaP/Si(100) nucleation



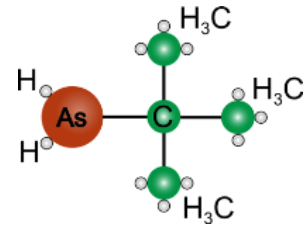
source of As:

**As<sub>4</sub> clusters (background)**



**tertiarybutylarsine (TBAs)**

(AsH<sub>3</sub>, AsH<sub>2</sub>, AsH, As, As<sub>2</sub>)



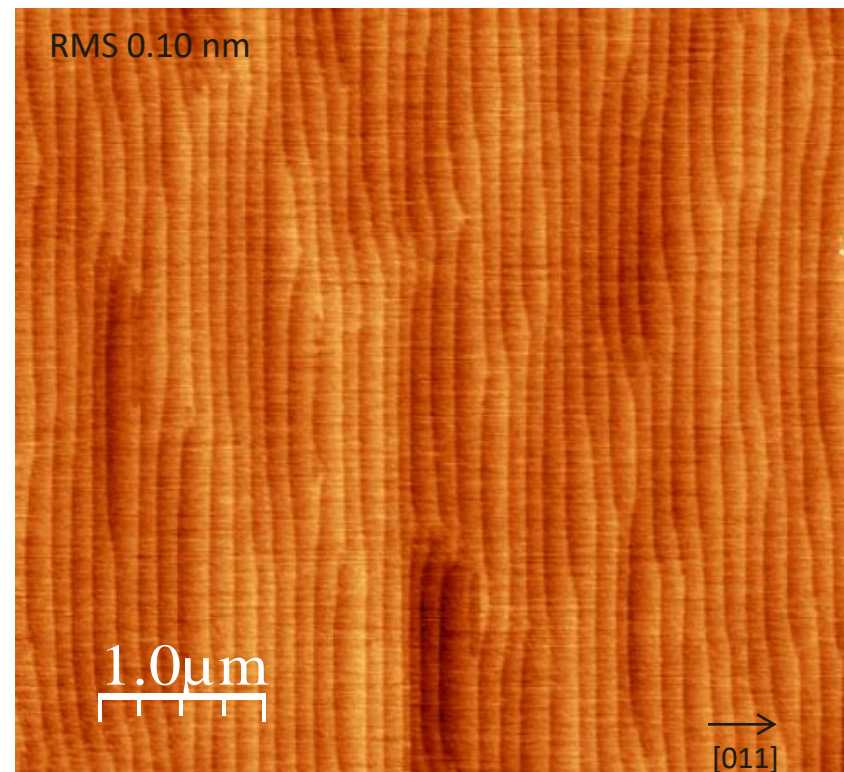
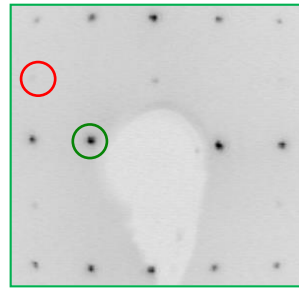
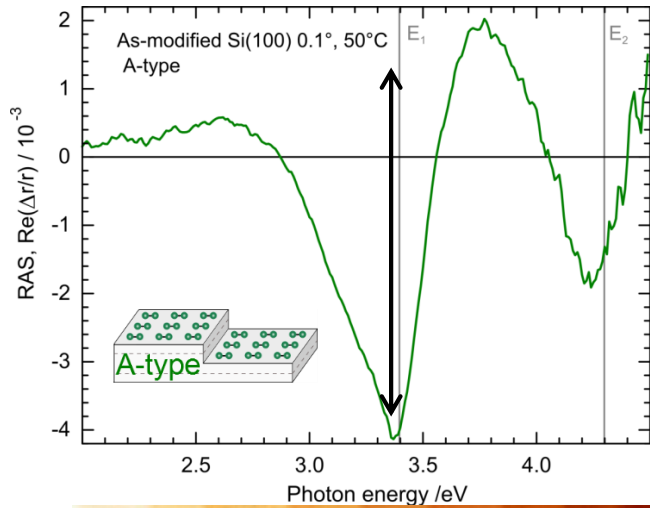
*In situ control* of the prevalent majority  
(1×2) or (2×1) domain

vicinal Si(100) substrates: **As<sub>4</sub> → B-type (2×1)**    **TBAs → A-type (1×2)**

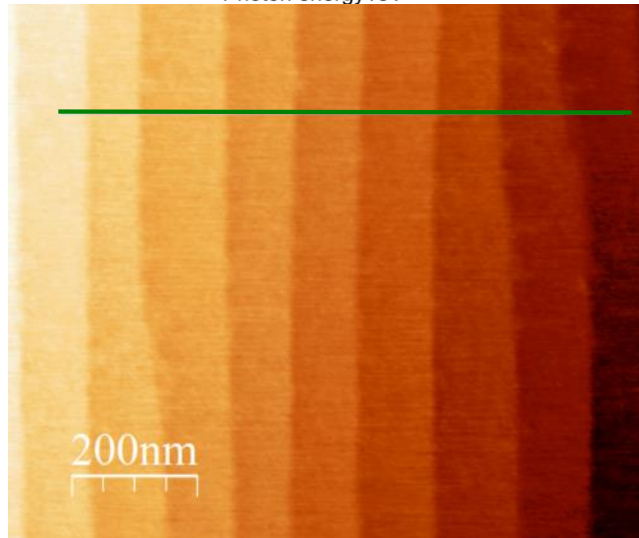
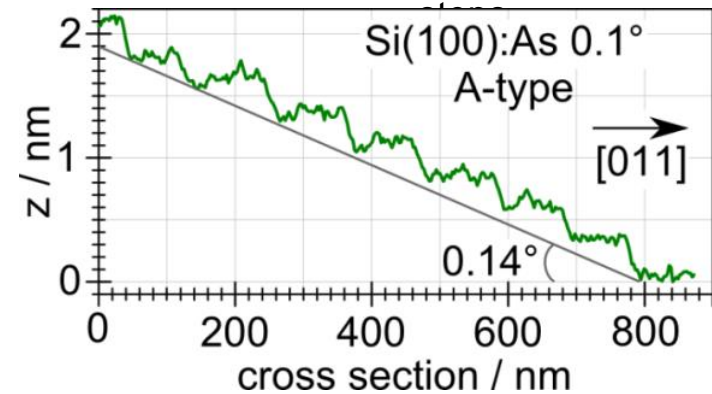
\*also for Si(100) 2°, 6°

A. Paszuk *et al.*, Appl Surf Sci. 462 (2018) 1002  
 O. Supplie, *et al.*, APL Mater. 3 (2015) 126110.1  
 T. Hannappel *et al.*, J. Cryst. Growth 272 (2004) 24

# Impact on Arsen-precursor on GaP/Si(100) nucleation



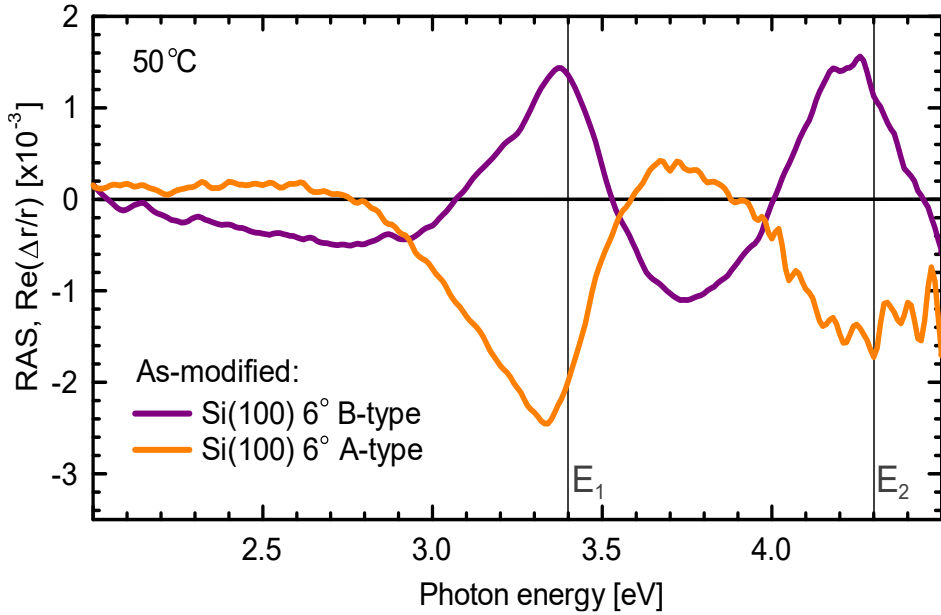
Atomically flat, single domain Si(100):As-(1 × 2) surfaces with well ordered, regular double-layer



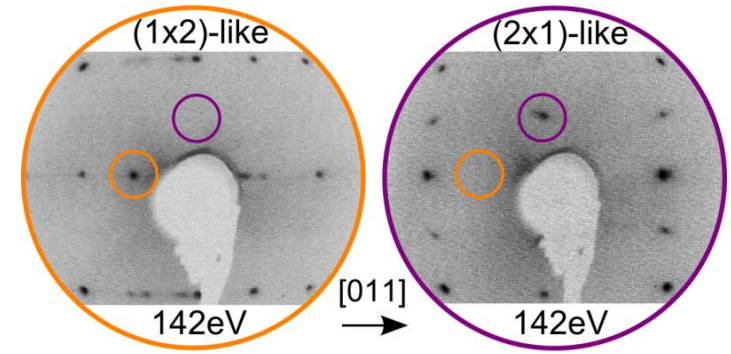
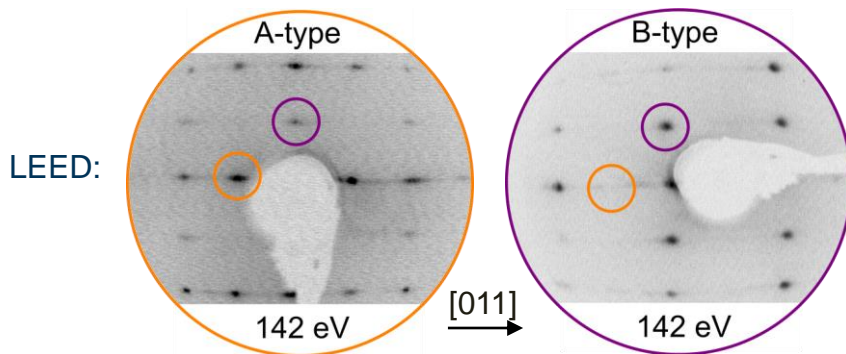
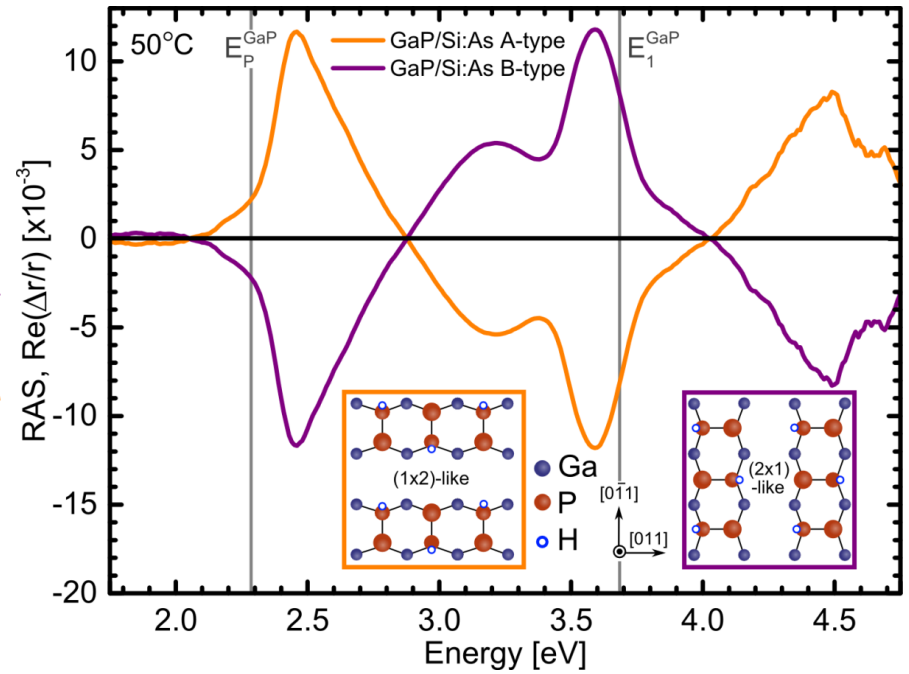
Low offcut Si(100) substrates:  $\text{As}_4 \rightarrow \text{A-type } (1 \times 2)$

# Control over the GaP(100) sublattice orientation

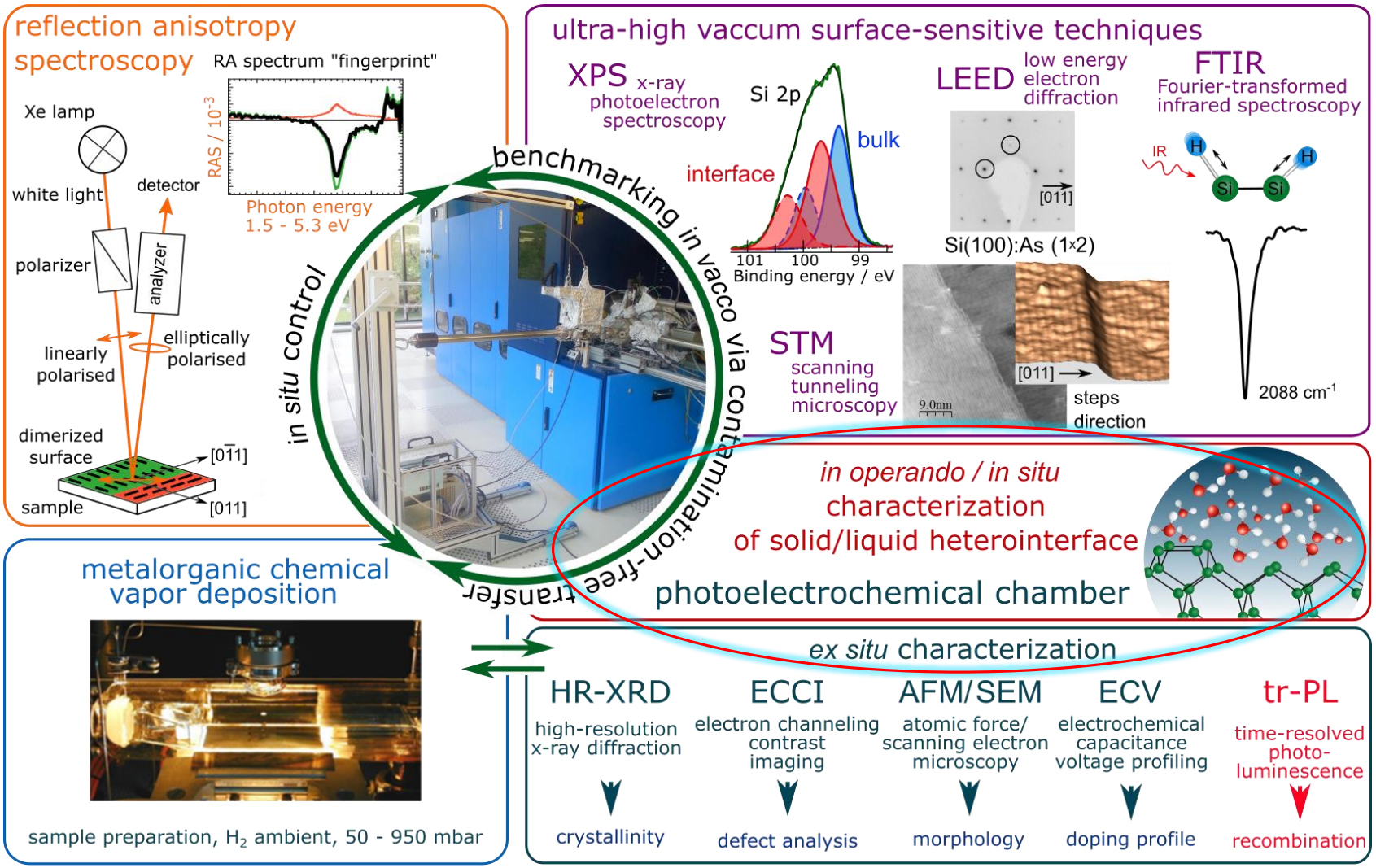
## A-type and B-type Si(100):As



## P-rich GaP/Si(100):As



# Experimental set-up

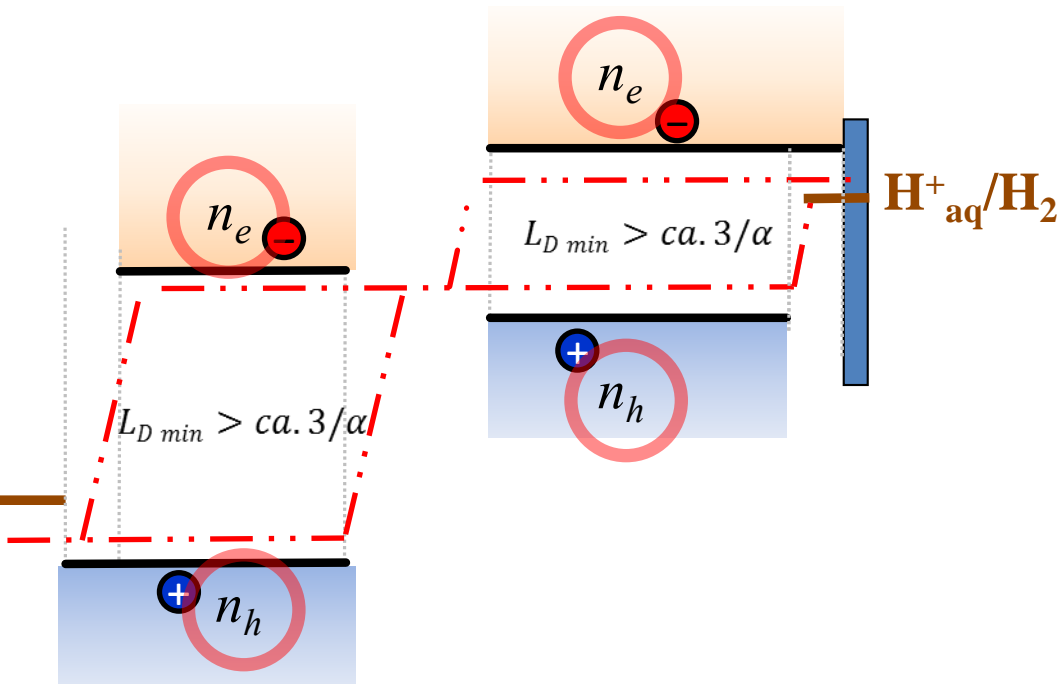


Method: D.E. Aspnes et al., Phys. Rev. Lett. 54 (1985) 1956; J. Vac. Sci. Technol. A 6 (1988) 1327  
 Review: P. Weightman et al., Rep. Prog. Phys. 68 (2005) 1251  
 T. Hannappel et al., Rev. Sci. Instrum. 75 (2004) 1296

# Summary

$$\mu_i = \mu_{i,0} + kT \ln \left( \frac{n_i}{N_i} \right)$$

$$\mu_e + \mu_h = \varepsilon_{FC} - \varepsilon_{FV} > 0$$



I) Production of **appropriate chemical potentials** in CB and VB (voltage)

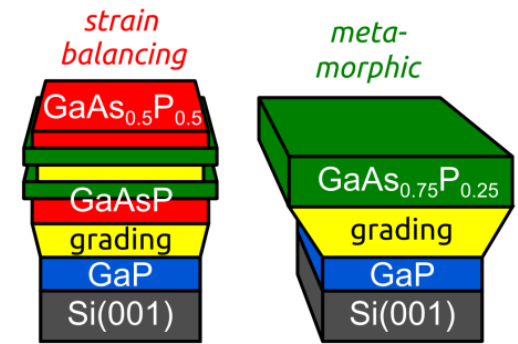
II) Exploitation of the **sun light**

III) Spatial **transport** of electronic excitation  
high **mobility**, low non-rad. **recombination**

IV) **Charge separation**: photovoltage -> transformation of energy

**Might be realized with epitaxial materials, e.g. with III-V on Si**

**Research needed to control interfacial reactions**



**Helmholtz-Zentrum Berlin:**

Roel van de Krol,  
Rainer Eichberger, Klaus Schwarzburg



**Academy of Sciences of the Czech Republic:**

Oleksandr Romanyuk



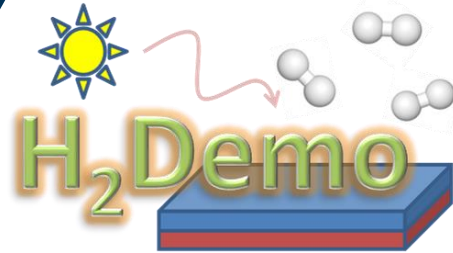
**Tokyo University:**

Masakazu Sugiyama, Kim Boram



**Azur Space Solar Power GmbH:**

Thomas Bergunde, Kristof Möller



Bundesministerium  
für Bildung  
und Forschung

**TU Darmstadt:**

Wolfram Jaegermann, Jan Philipp Hofmann



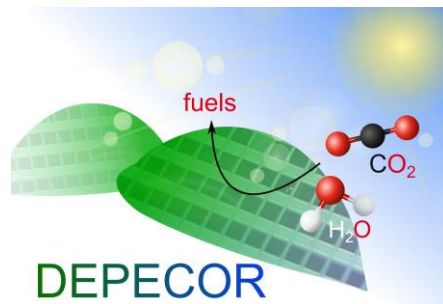
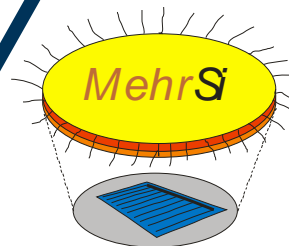
**TU München:**

Ian Sharp



**Uni Paderborn:**

Wolf Gero Schmidt



**Marburg University:**

Kerstin Volz, Andreas Beyer

**Evonik:**

Frank Menzel



**BASF:**

Sigmar Bräuninger



**Projects:**

- PAK 981/1,
- FR 4025/2-1
- HA 3096/10-1
- HA 3096/12-1
- HA 3096/14-1
- HA 3096/16-1

