New Concepts and Materials for Solar Energy Conversion

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http://emat-solar.lbl.gov/

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The Energy Challenge

- With a projected global population of 12 billion by 2050 coupled with moderate economic growth, the total global power consumption is estimated to be ~28 TW.

Current global use is ~13 TW.

- To cap CO_2 at 550 ppm (twice the pre-industrial level), most of this additional energy needs to come from carbon-free sources.
- A comprehensive approach is required to address this difficult and complex issue facing humankind.

Solar Energy Potential

- Theoretical: 1.2×10^5 TW solar energy potential

  (1.76×10^5 TW striking Earth; 0.30 Global mean)

  - Energy in 1 hr of sunlight $\leftrightarrow$ 14 TW for a year

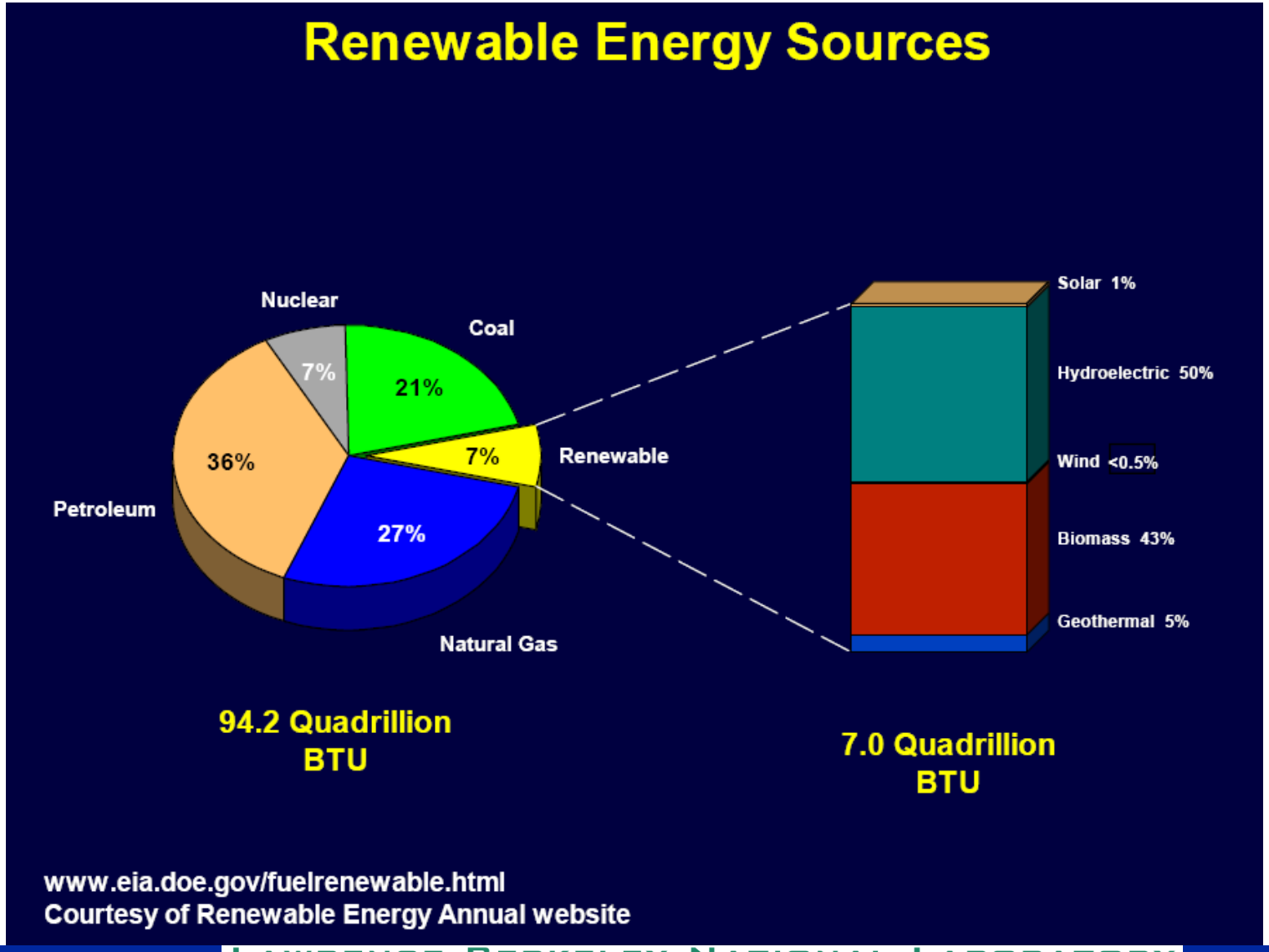
- Practical: $\approx$ 600 TW solar energy potential

  (50 TW - 1500 TW depending on land fraction etc.; WEA 2000)

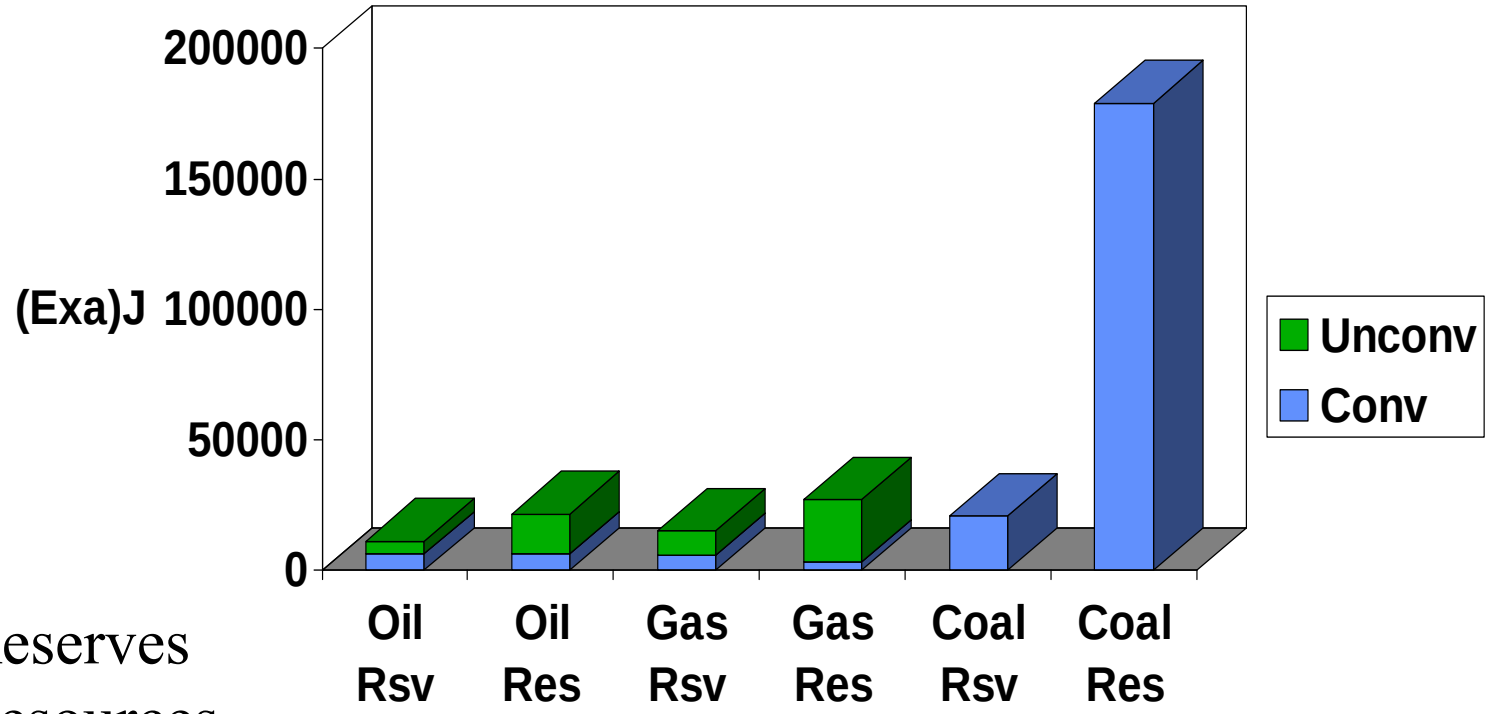
  Onshore electricity generation potential of $\approx$60 TW (10% conversion efficiency):

- *Photosynthesis*: 90 TW

Energy Production by Source



Energy Reserves and Resources



Rsv=Reserves
Res=Resources

There is a growing consensus that continued use of carbon based fuels for energy production will irreversibly change planets climate

Energy dilemma

Fossil fuels

Abundant, inexpensive energy resource base

Potentially destructive to environment and survival of humankind

Renewable Energy Sources

Safe and environmentally friendly

Still relatively expensive, cumbersome technology

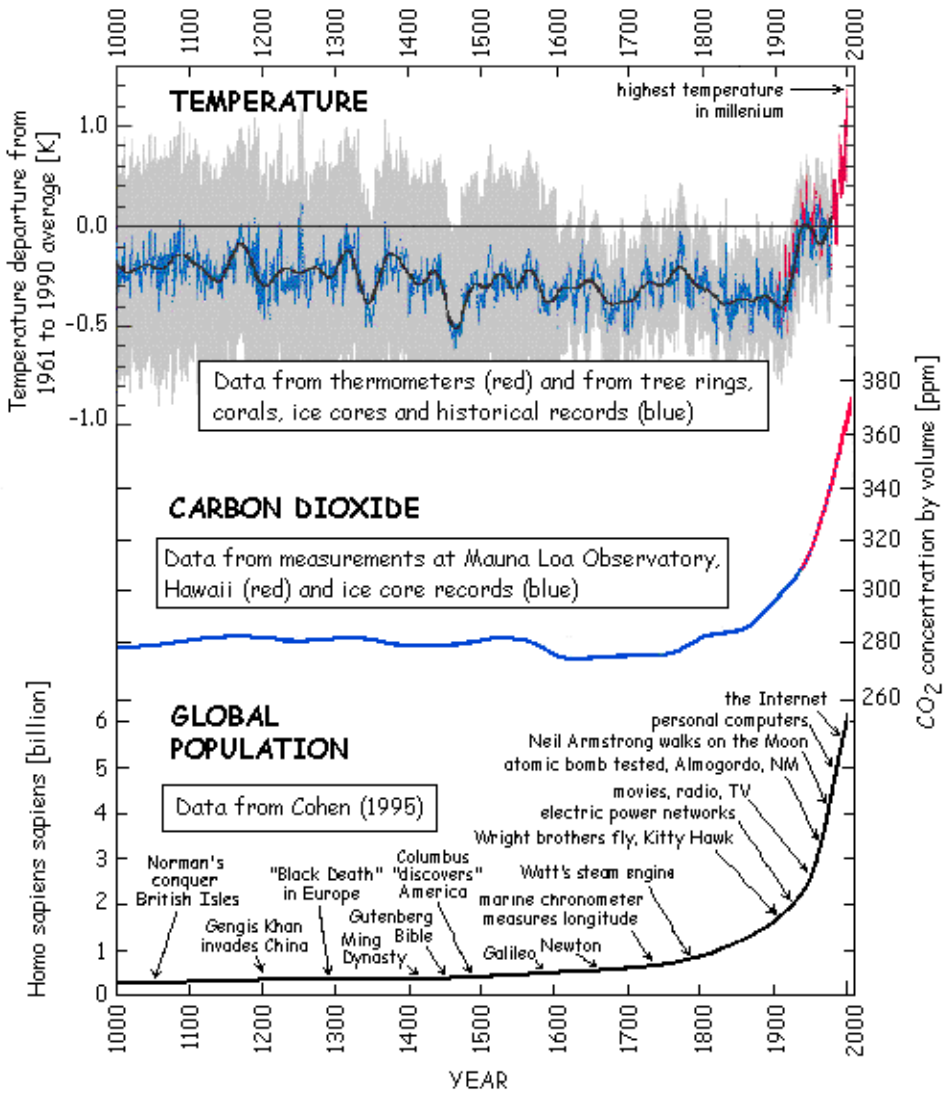
Needs major scientific/technological/cost breakthroughs

Why should one work on renewable energy?

To Save Humankind

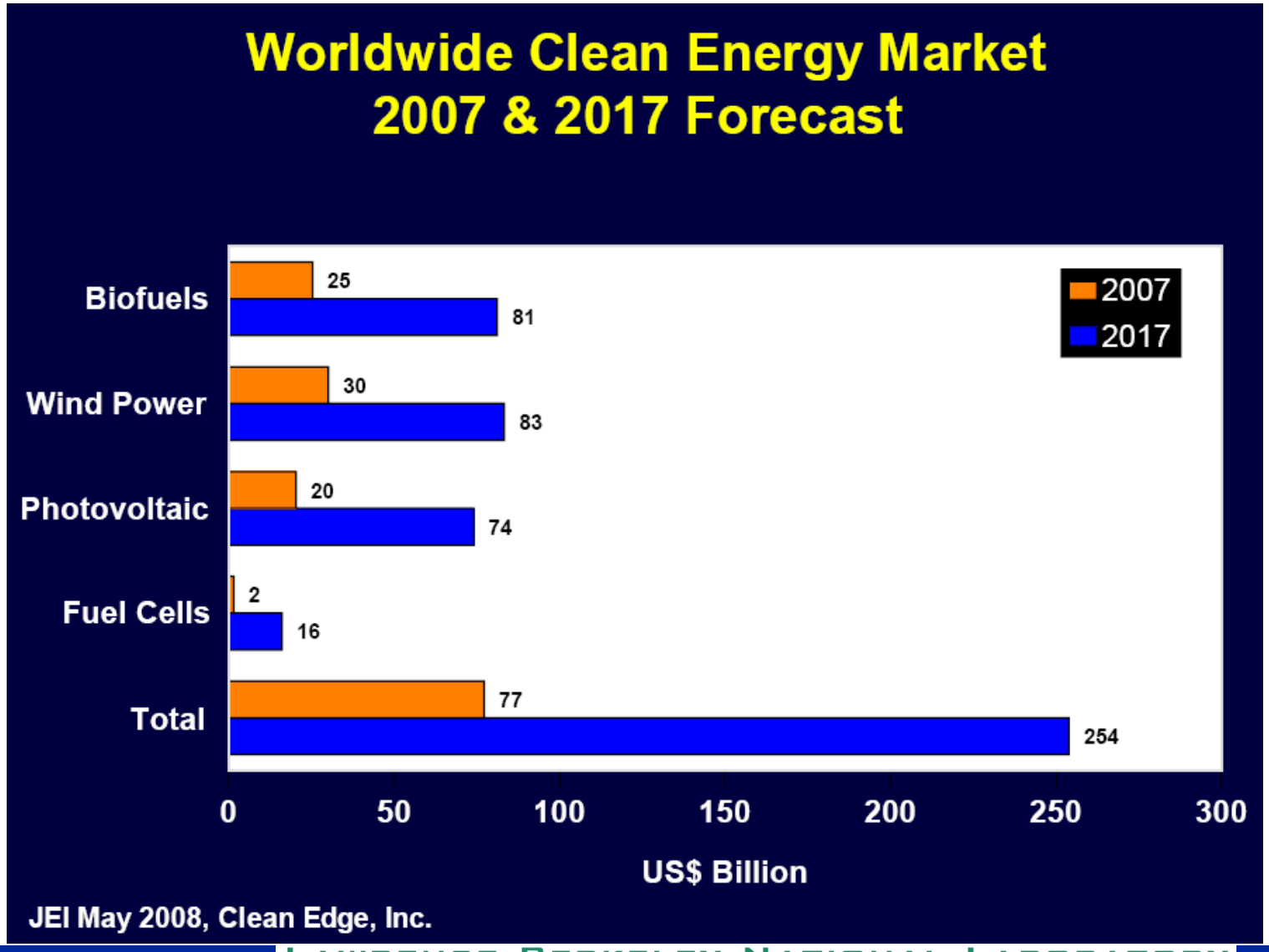
Global Warming and CO_2 Emission

Over the 20th century, human population quadrupled and energy consumption increased sixteenfold. Near the end of the last century, a critical threshold was crossed, and warming from the fossil fuel greenhouse became a dominant factor in climate change.



Hoffert, DOE workshop

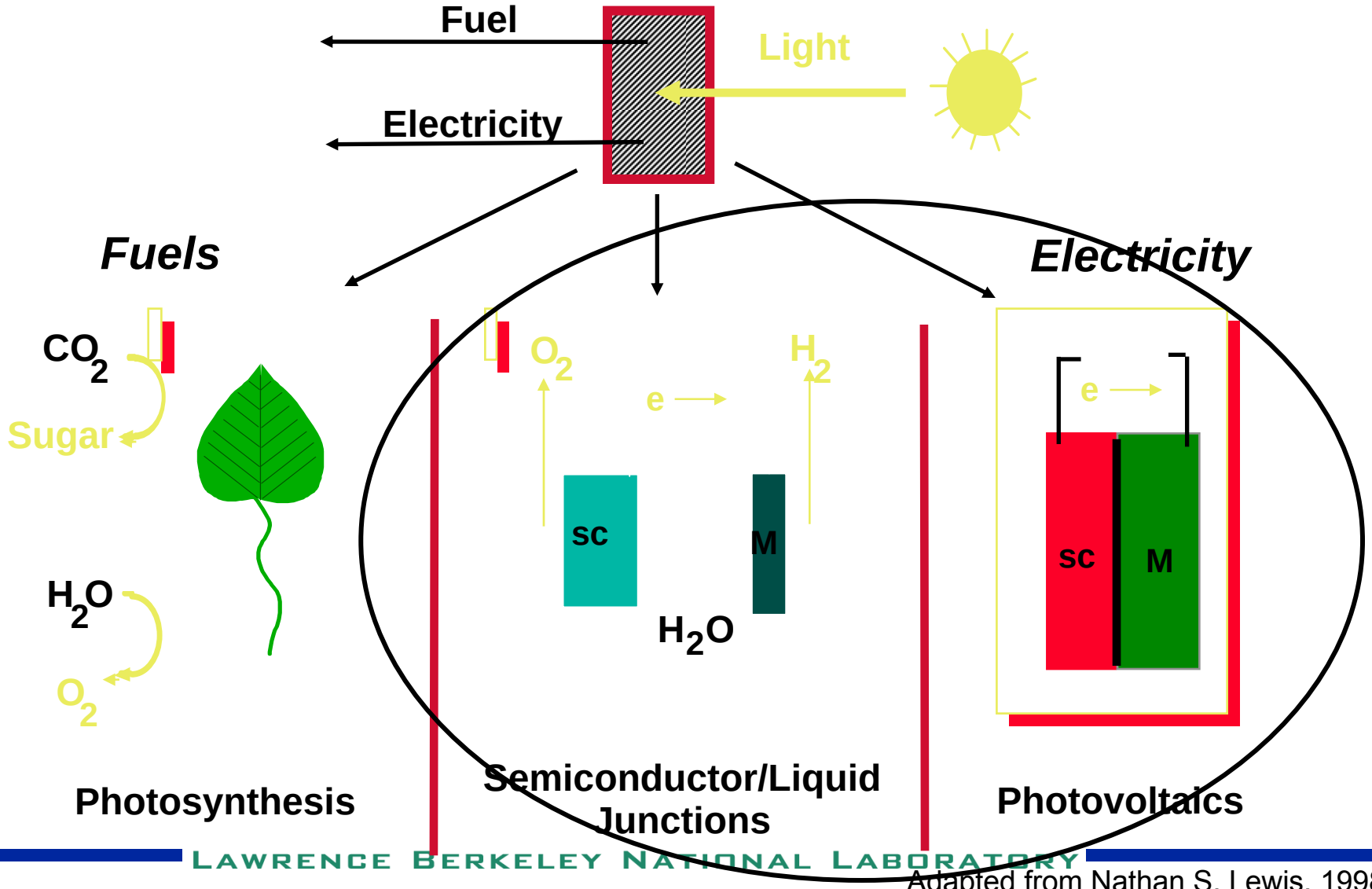
To make money



To do exciting multidisciplinary science

Intersection of physics, chemistry and material science

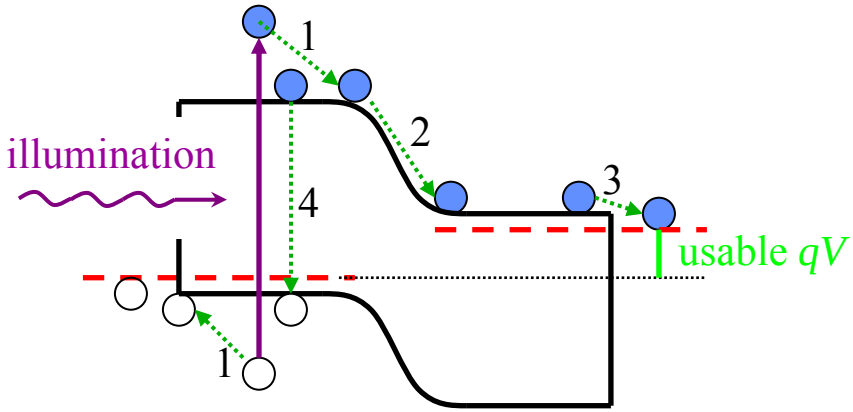
Solar Energy Utilization

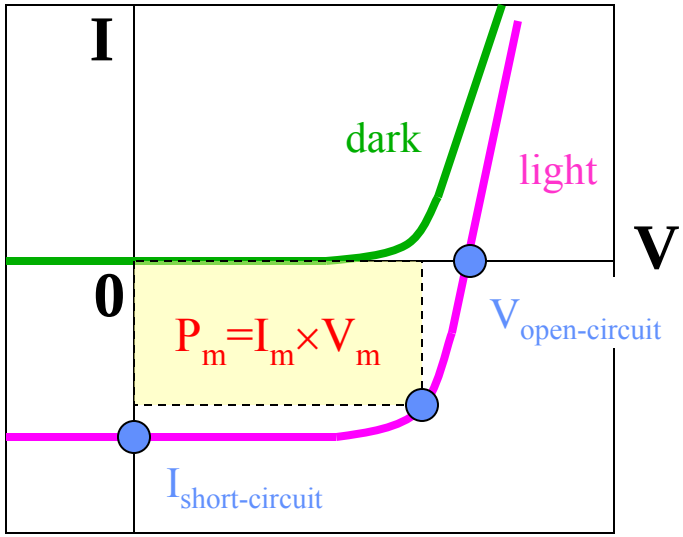


Adapted from Nathan S. Lewis, 1998

Fundamentals of Photovoltaics (single p/n junction)

1. **Thermalization loss**
2. **Junction loss**
3. **Contact loss**
4. **Recombination loss**



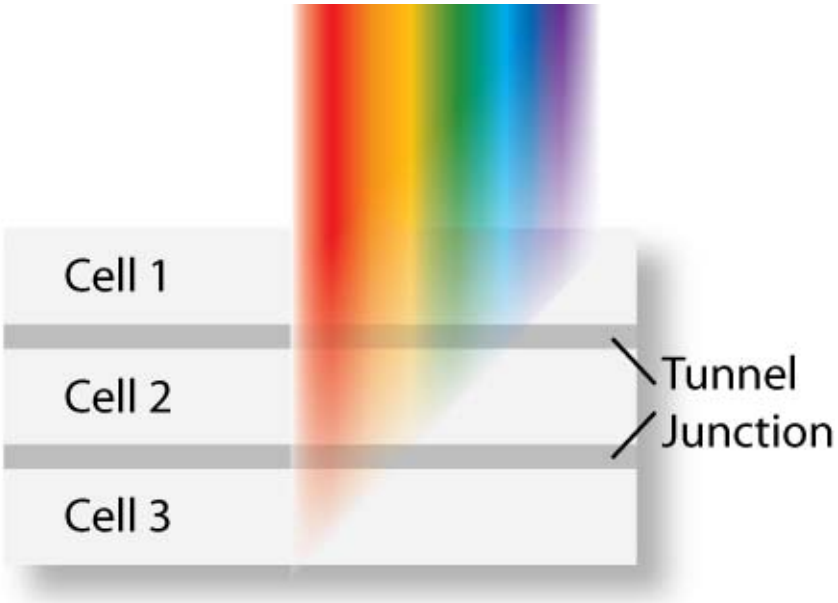


- **Dark and light I-V curves**
- **$V_{open\text{-}circuit}$**
- **$I_{short\text{-}circuit}$**
- **Maximum power P_m**
- **Fill factor (squareness)**

  $FF=P_m/(V_{open\text{-}circuit}\times I_{short\text{-}circuit})$

How to improve the power conversion efficiency?

multijunction

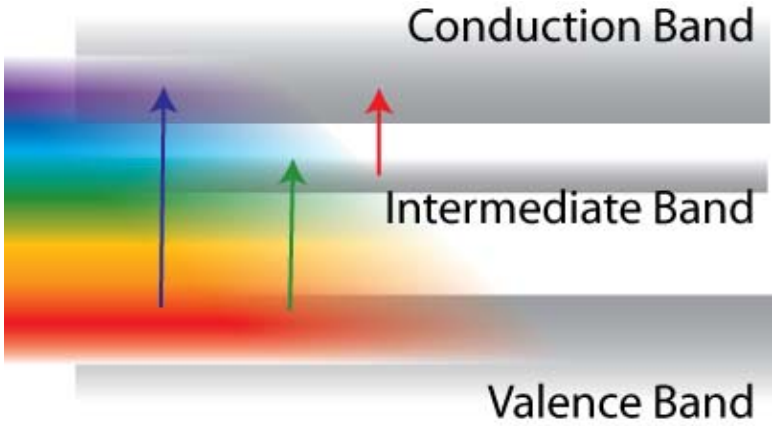


Each of the cells efficiently converts photons from a narrow energy range.

Band gaps are selected for optimum coverage of the solar energy spectrum.

Strict materials requirements
Complex, expensive technology

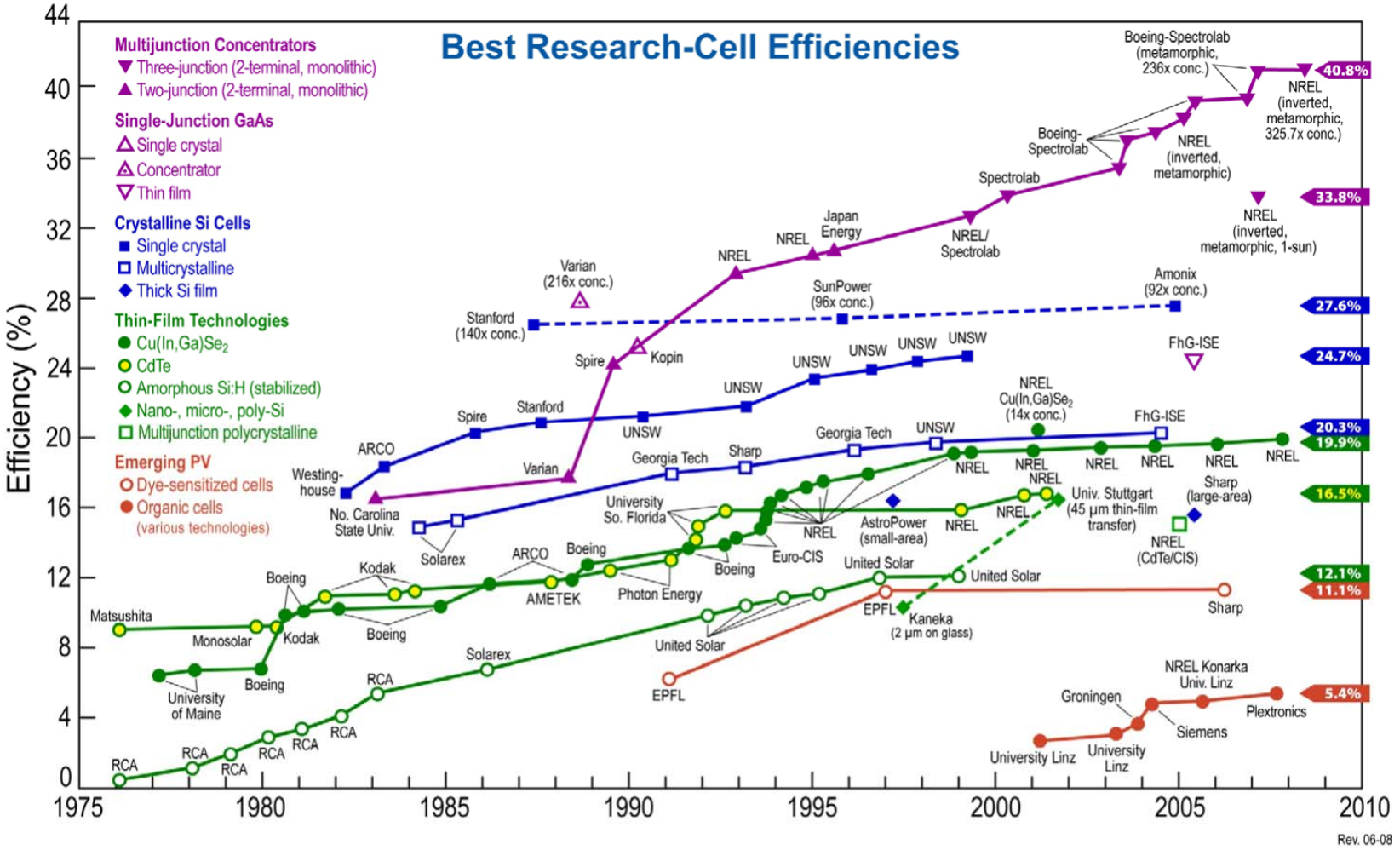
multiband



The intermediate band serves as a "stepping stone" to transfer electrons from the valence to conduction band.

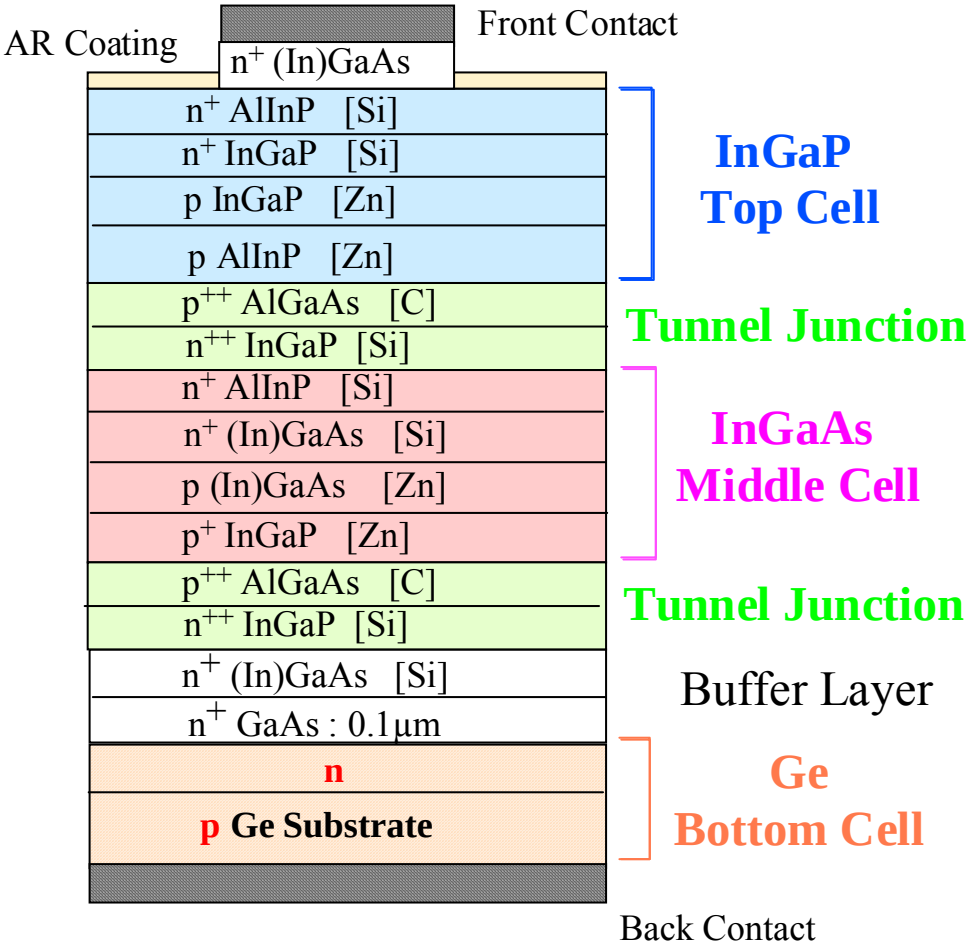
Photons from broad energy range are absorbed and participate in generation of current.

Best Research-Cell Efficiencies



Current record - 43.5%

Three-Junction Solar Cells

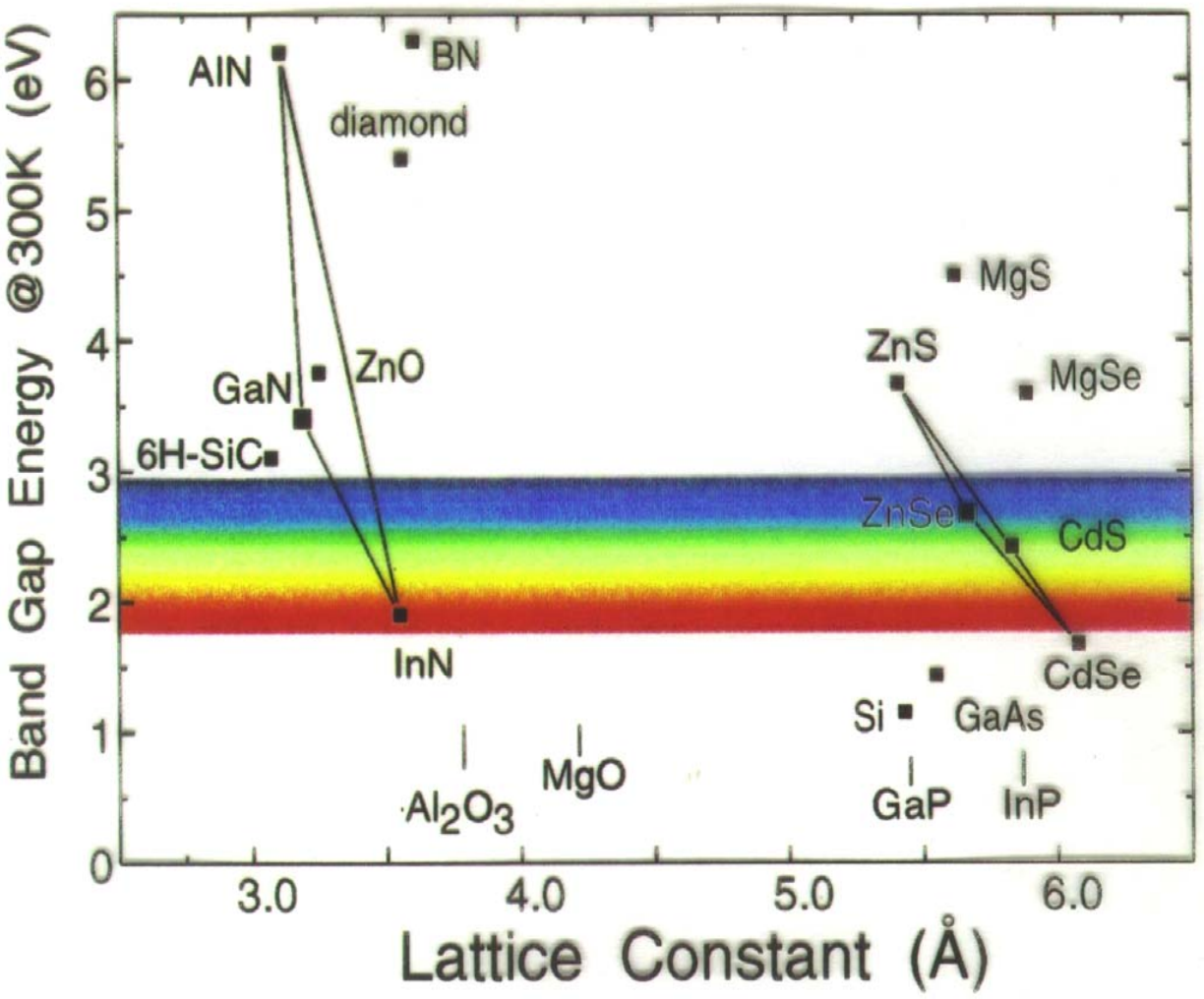


- **Efficiencies up to 41%**
- **Six different elements**
- **Three different dopants**
- **Practically used: 3-junction cells**
- **Research: 4 to 5 junctions**

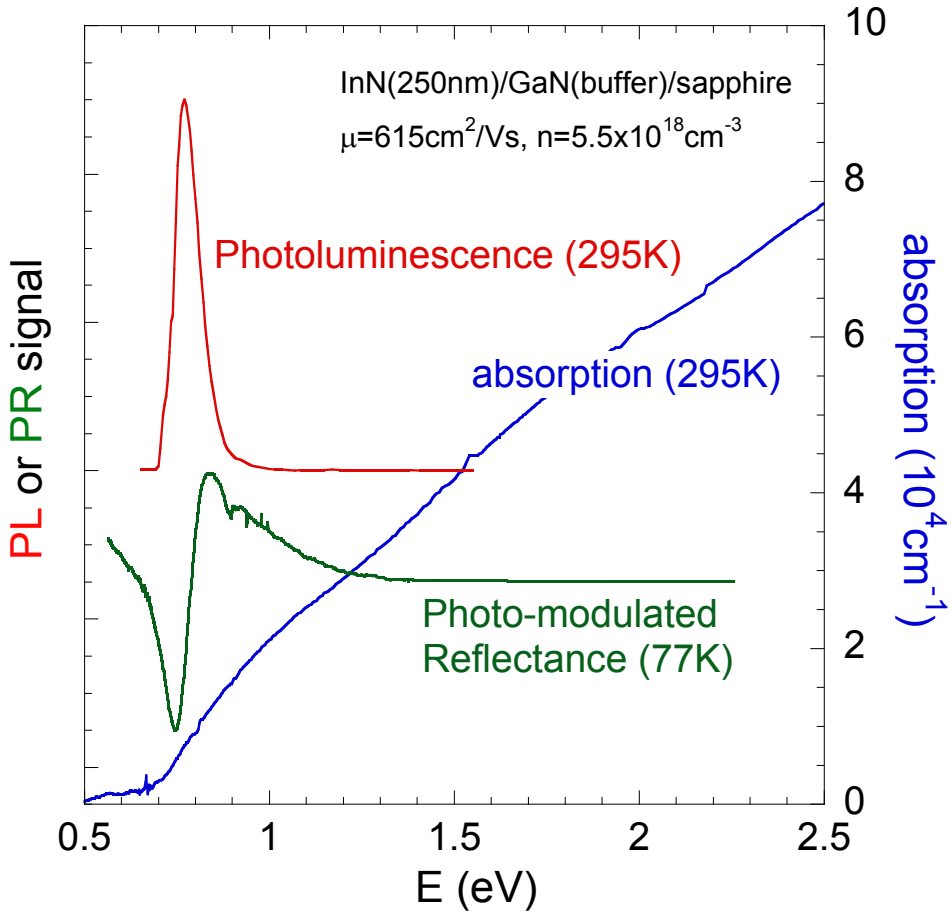
Yamaguchi et. al., 2003 Space Power Workshop

Could this be simplified?

Group III-Nitrides before 2002

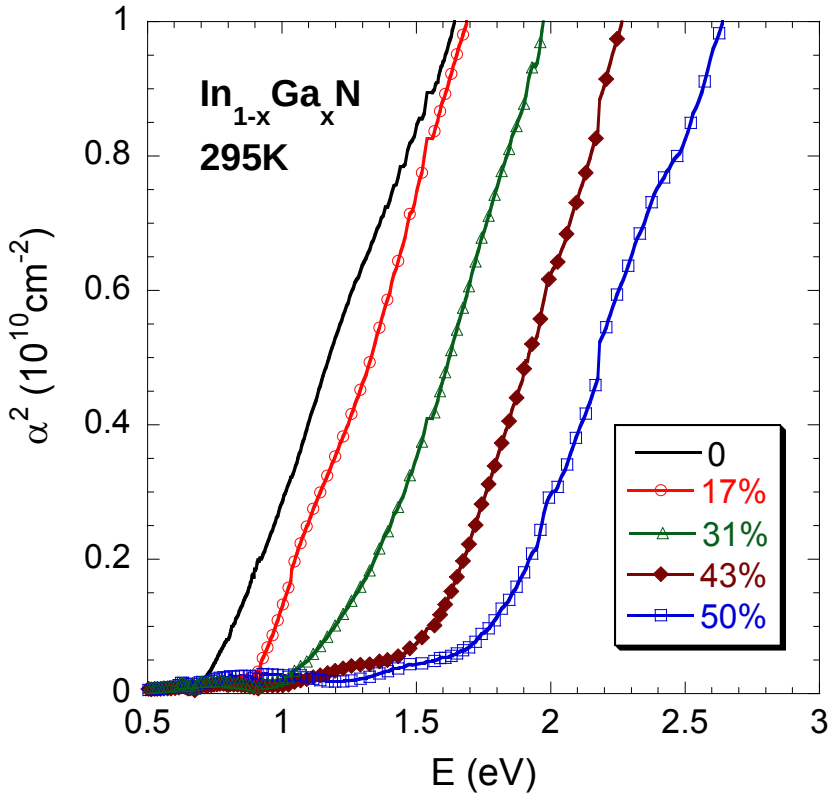


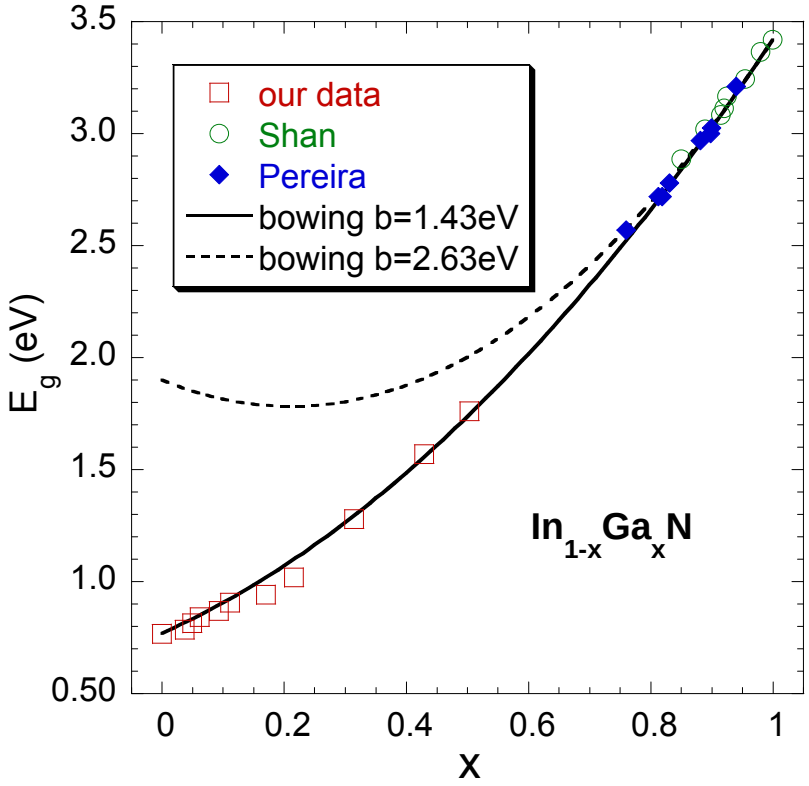
Fundamental Bandgap of Wurtzite InN



- **MBE-grown high-quality InN**
- **All characteristic band gap features lie near 0.7 eV**
- **No energy gap is observed around 2 eV**

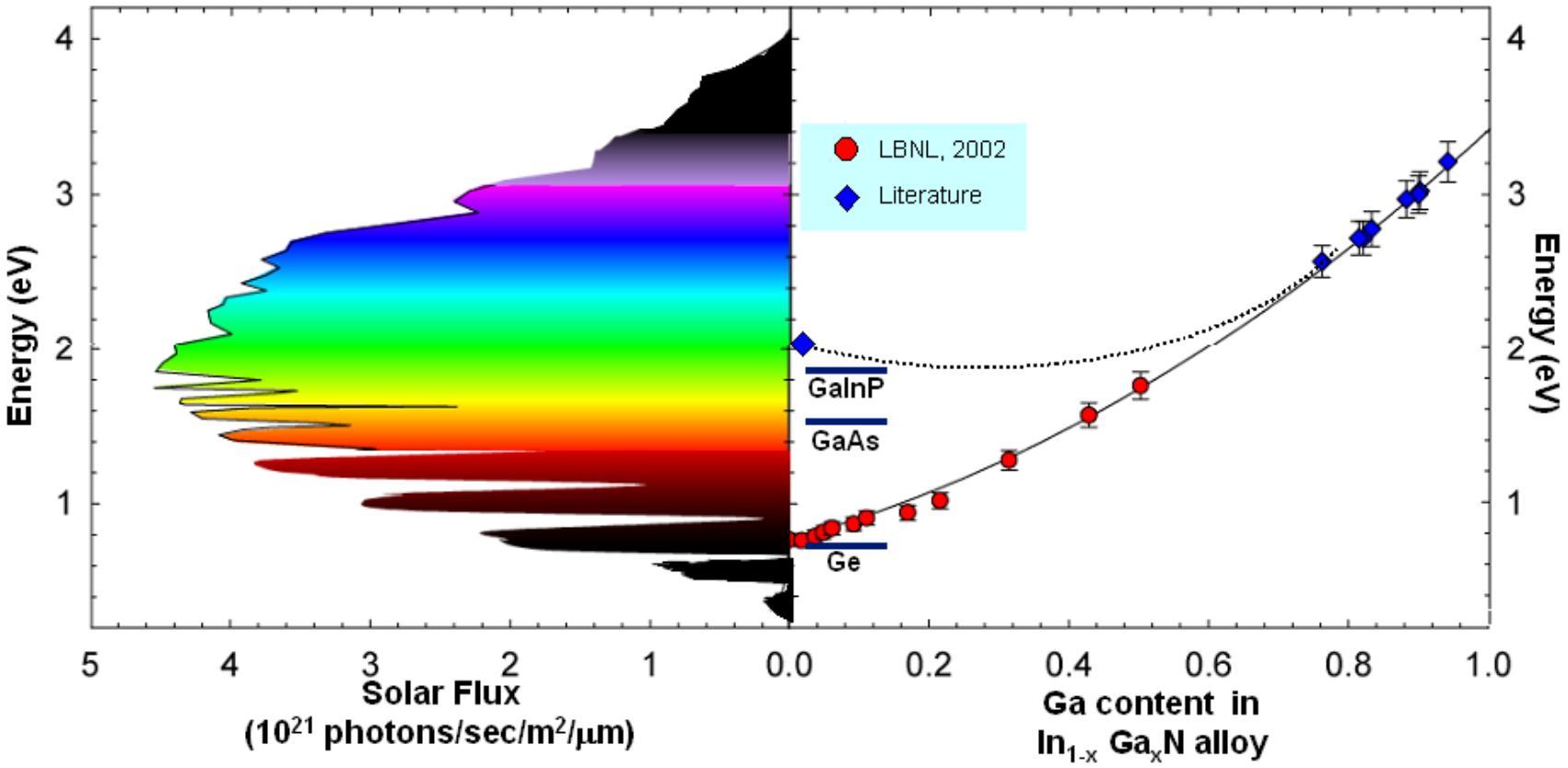
$In_{1-x}Ga_xN$ Alloys





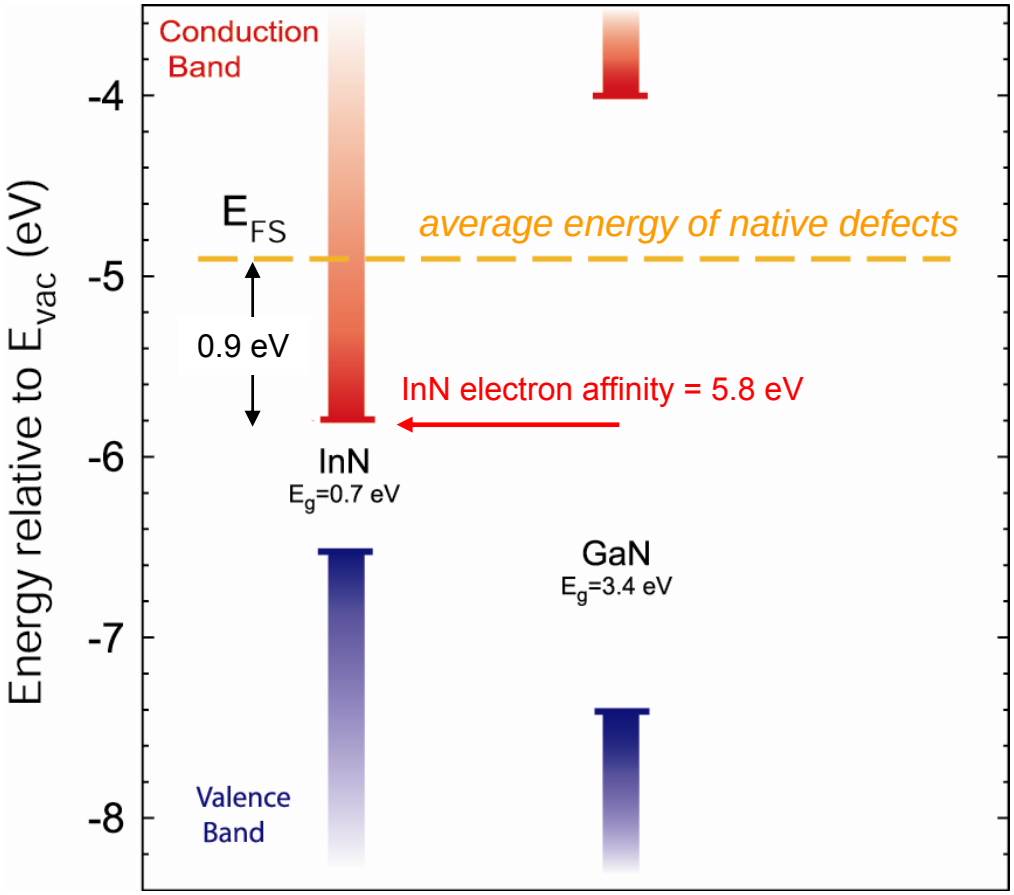
- Small bowing parameter in $In_{1-x}Ga_xN$: b = 1.43 eV
- The bandgap of this ternary system ranges from the infrared to the ultraviolet region!

Full solar spectrum nitrides



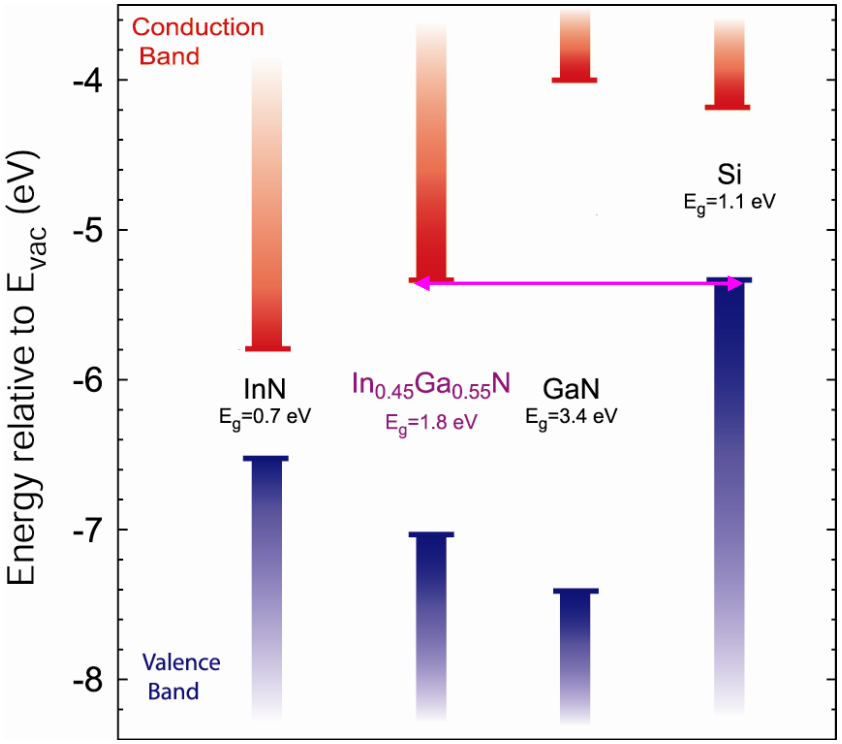
- The direct energy gap of $In_{1-x}Ga_xN$ covers most of the solar spectrum

What is unusual about InN?



- **InN has electron affinity of 5.8 eV, larger than any other semiconductor**
- **Extreme propensity for native n-type conduction and surface electron accumulation for InN and In-rich $In_xGa_{1-x}N$**

Integration of InGaN with Si

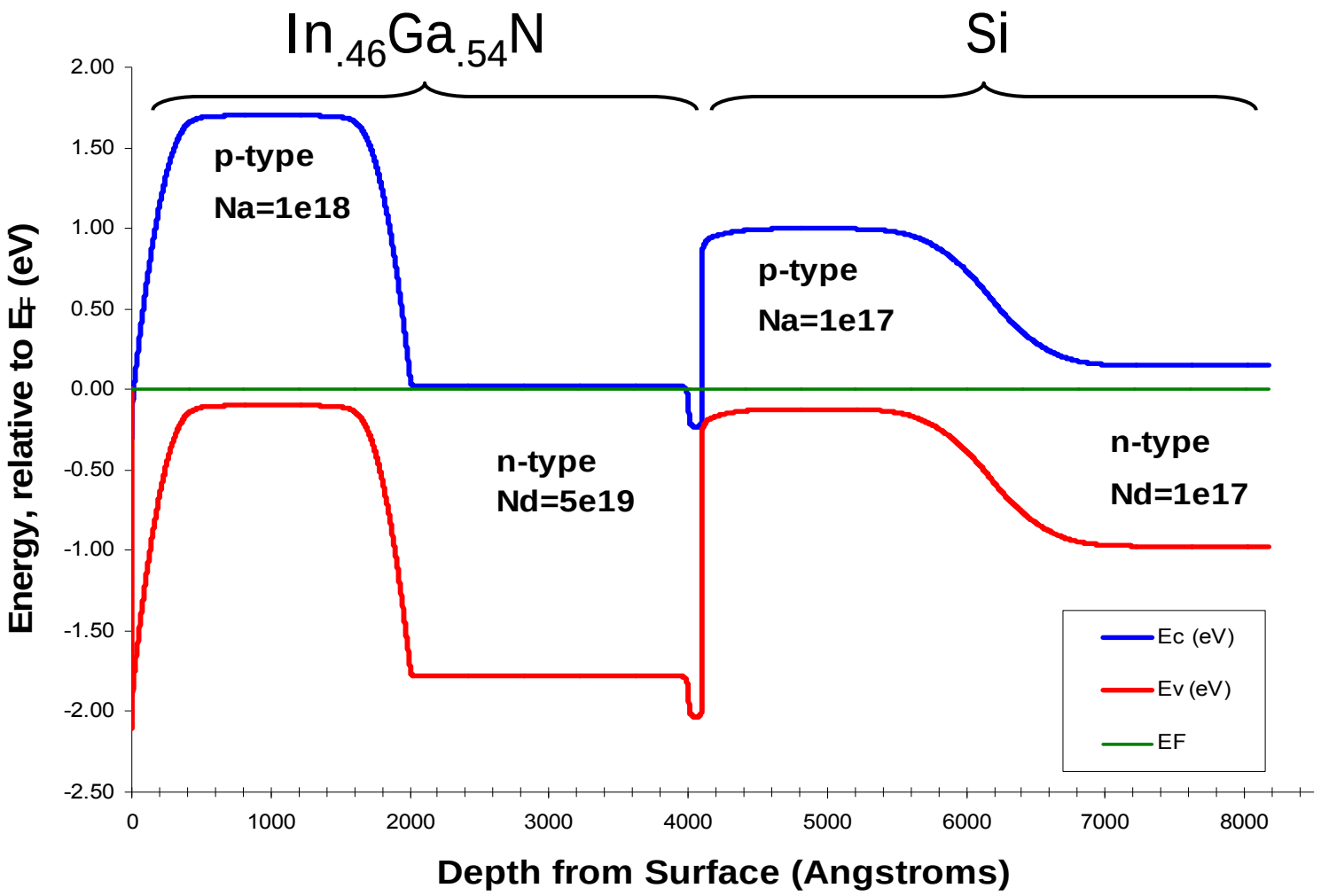


E_g ~ 1.7-1.8 eV

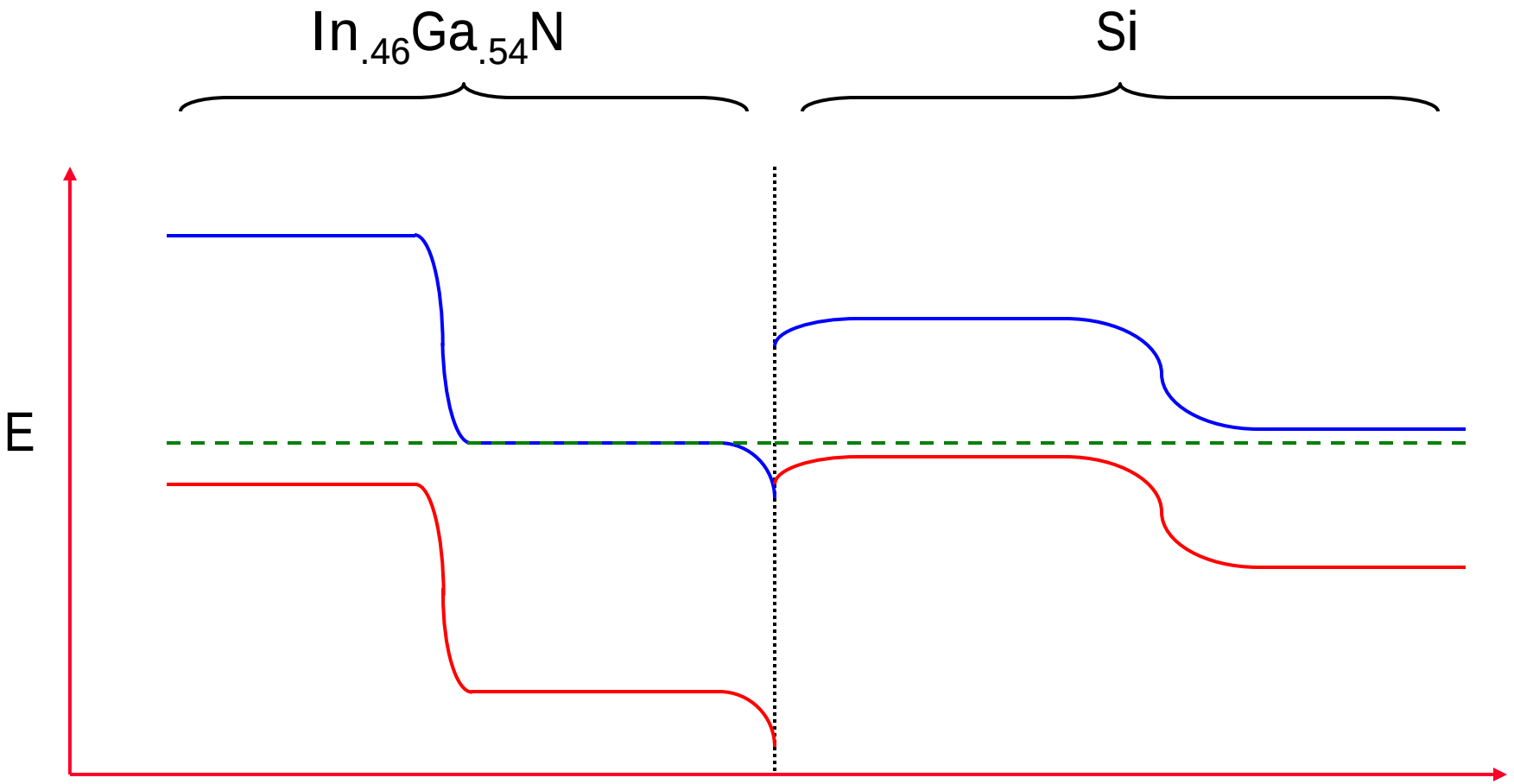
No barrier for e-h recombination

E_g = 1.1 eV

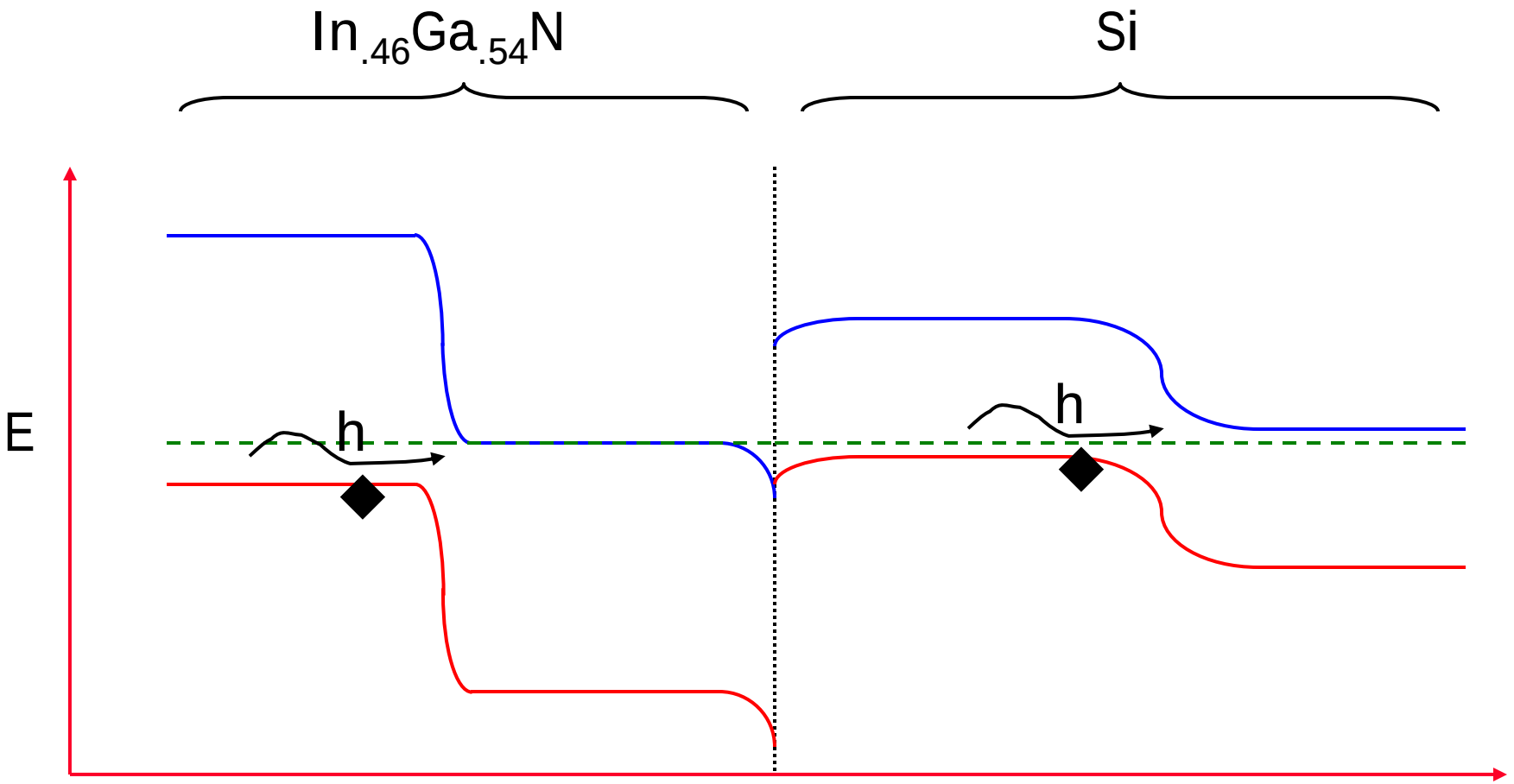
Band diagram of $In_{.46}Ga_{.54}N/Si$



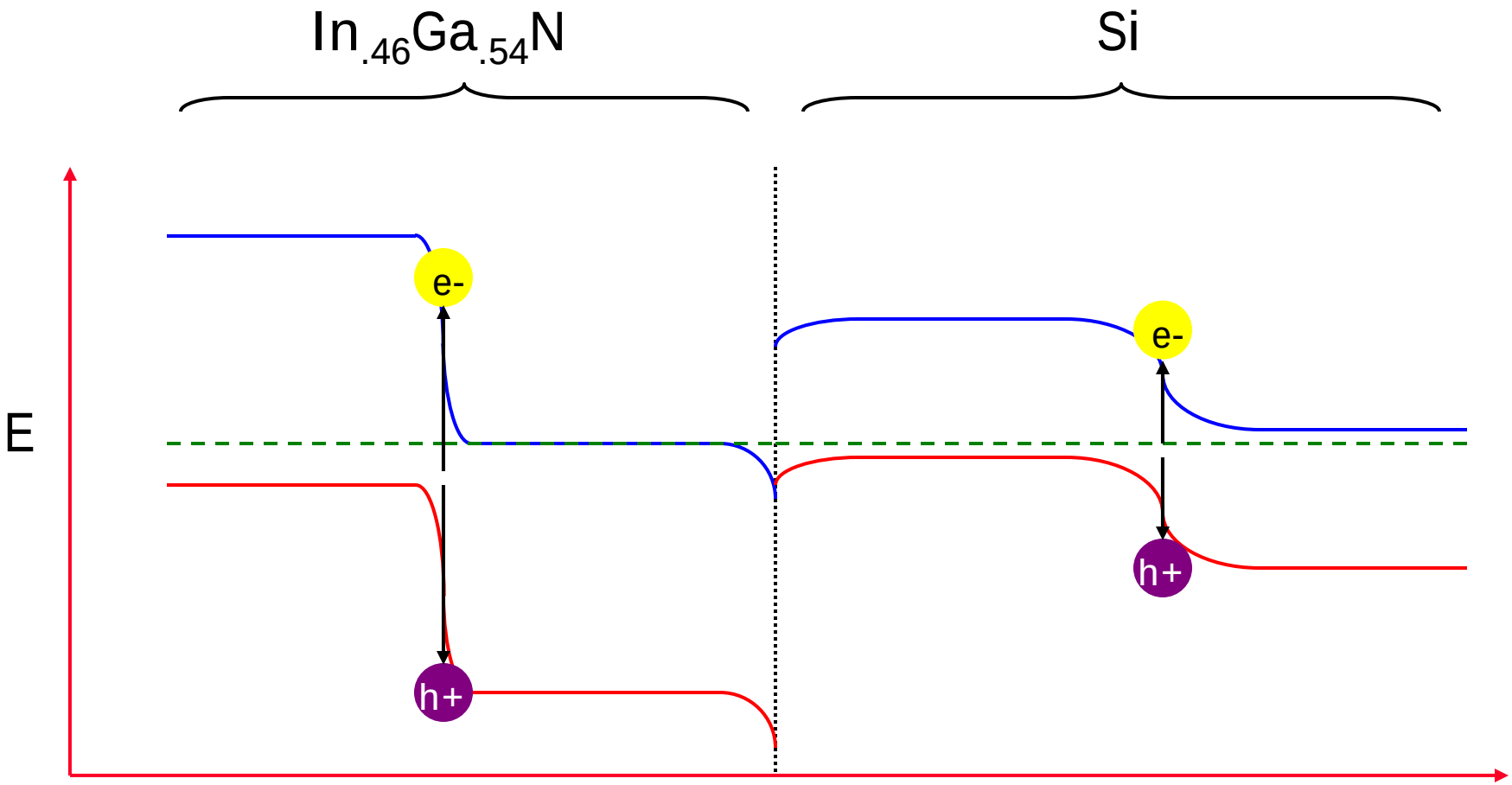
Two-junction hybrid solar cell



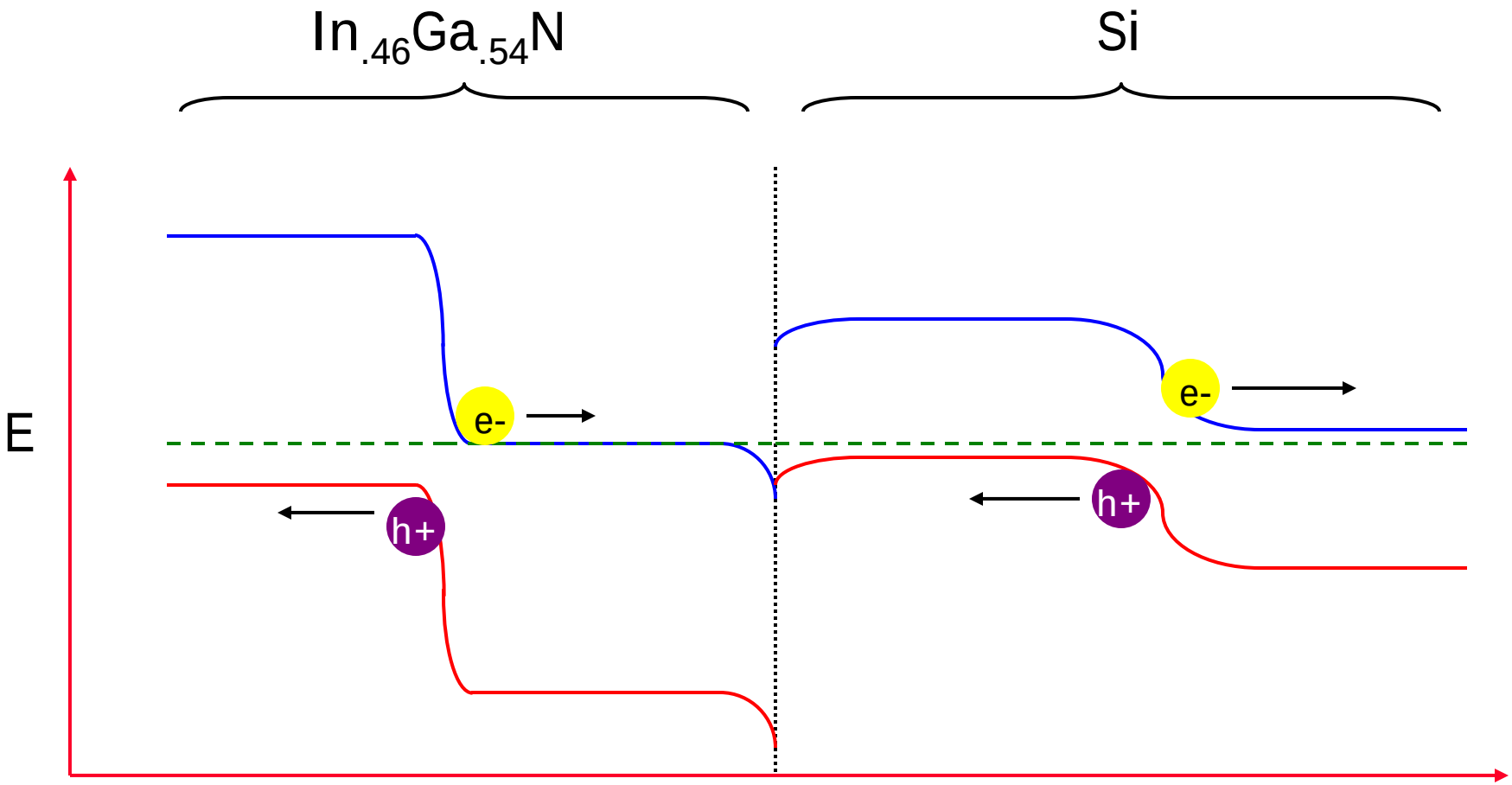
Two-junction hybrid solar cell



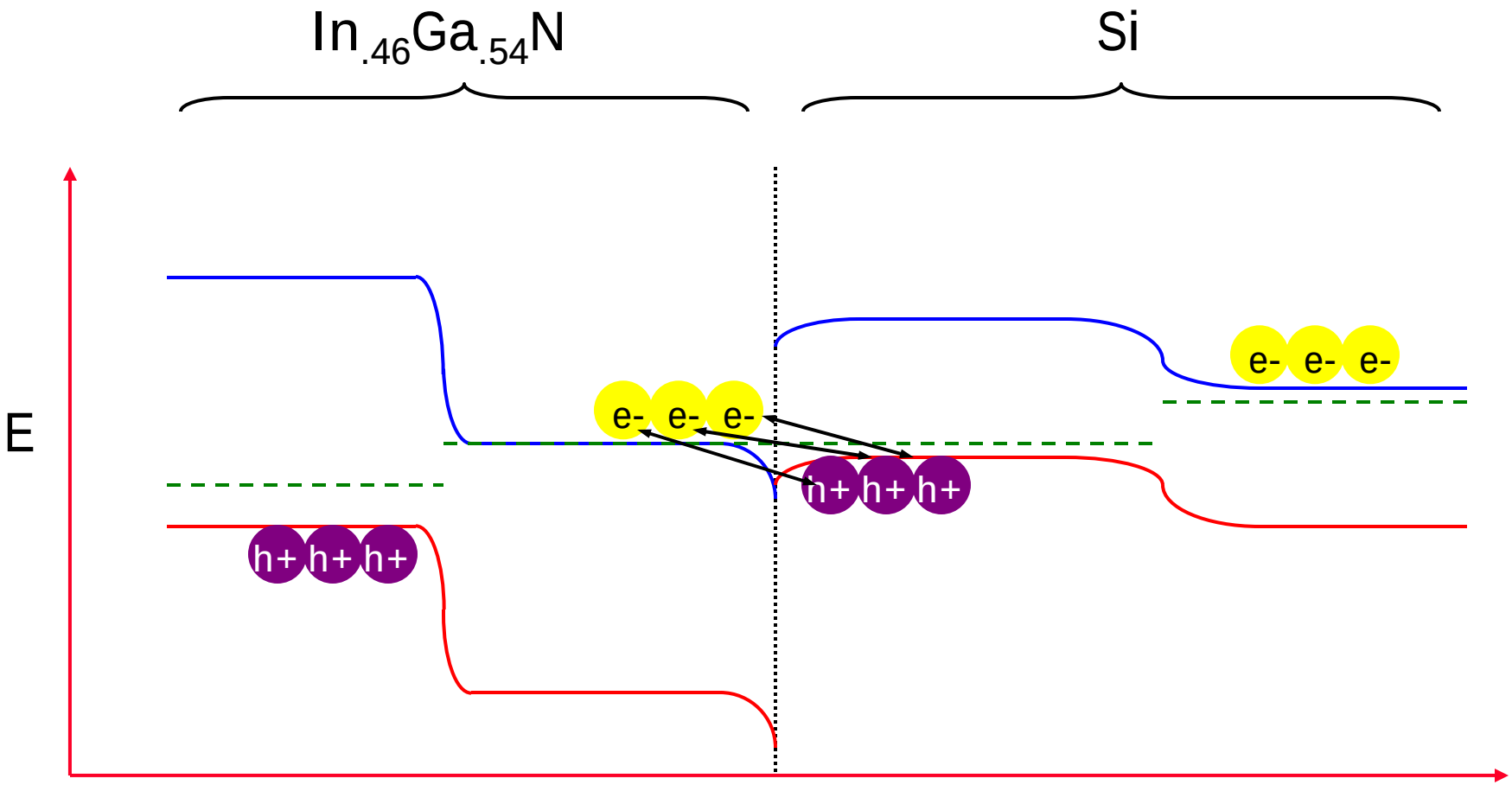
Two-junction solar cell



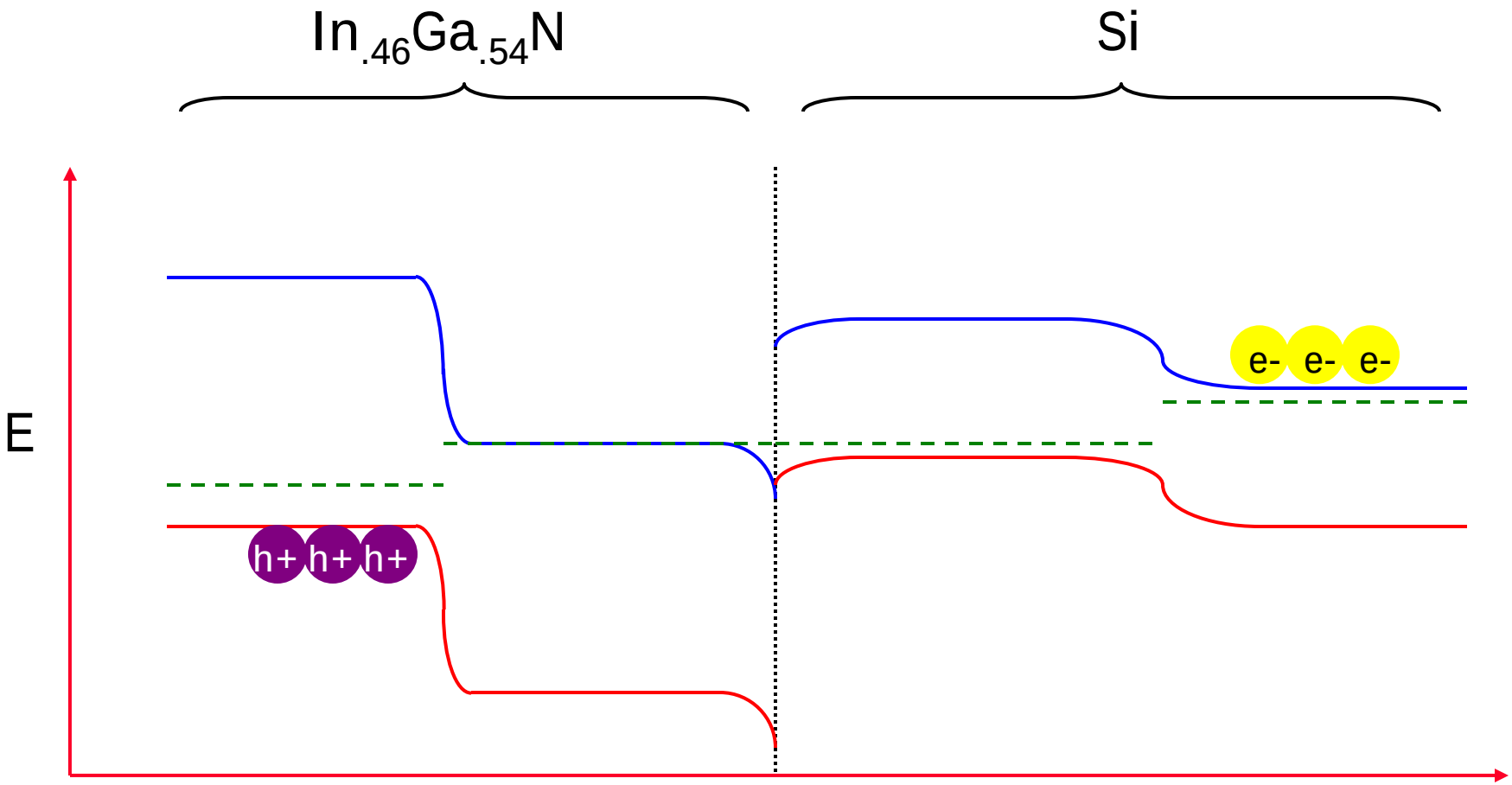
Two-junction hybrid solar cell



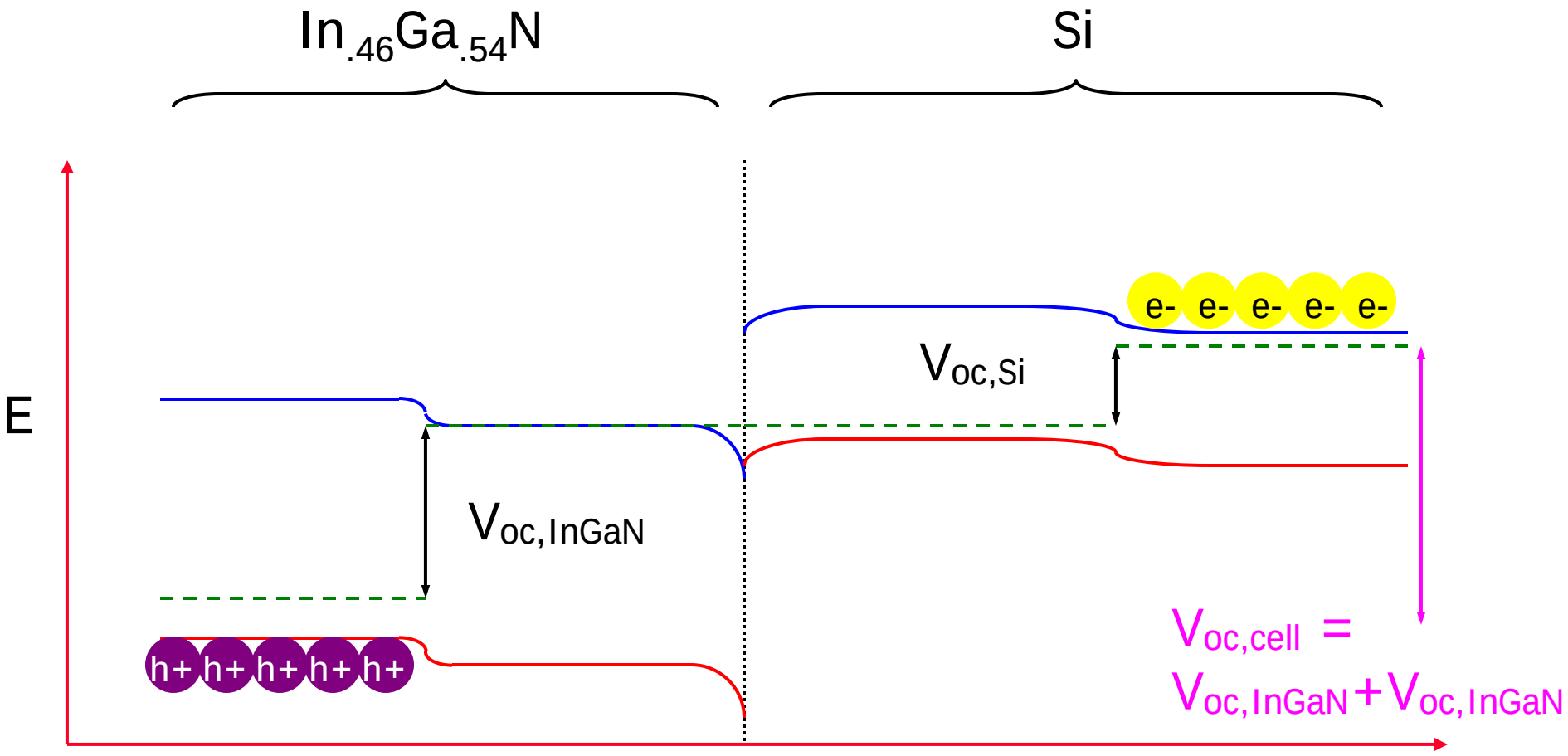
Two-junction hybrid solar cell



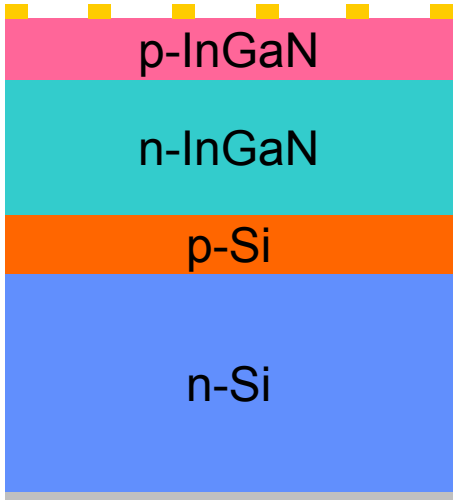
Two-junction hybrid solar cell



Two-junction hybrid solar cell

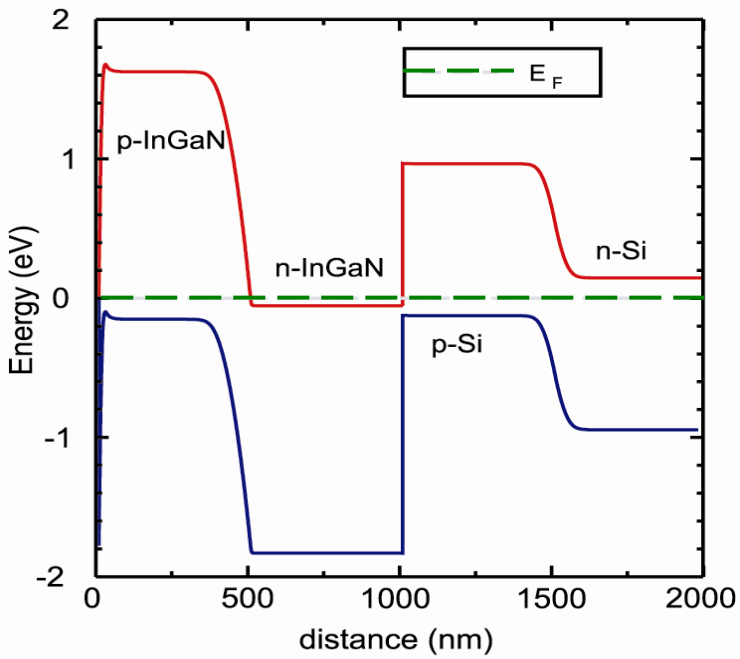


InGaN/Si tandem



No barrier for e-h recombination

InGaN-Si tandem



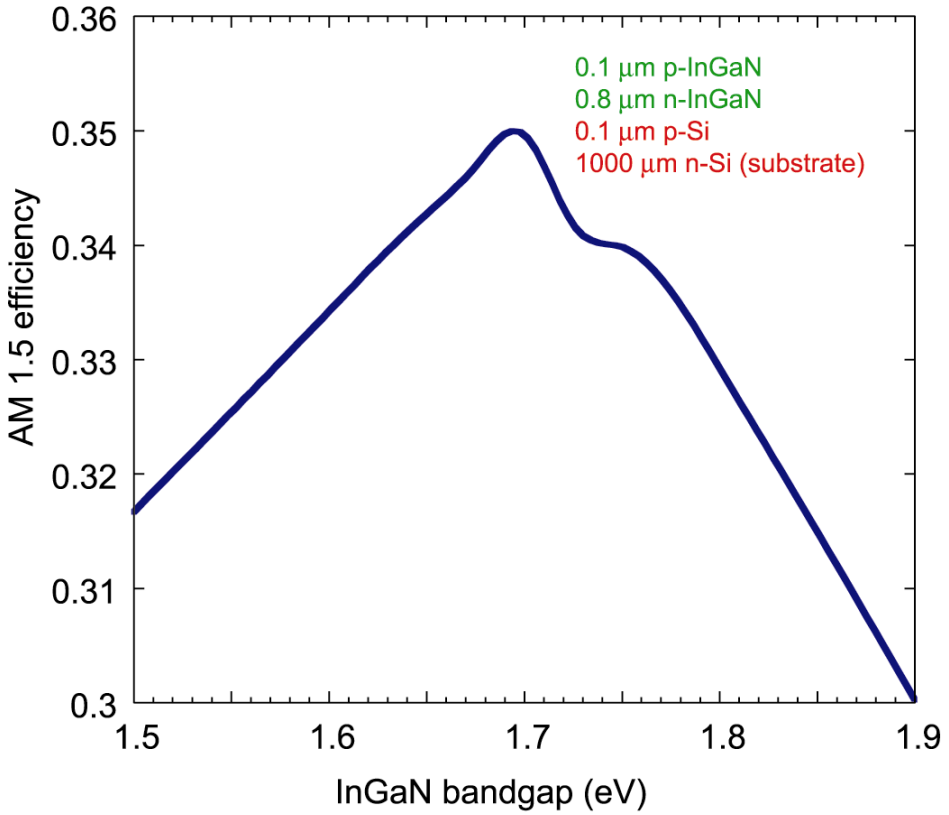
- Optimum top cell bandgap for a dual junction tandem solar cell with a Si bottom cell: 1.7~1.8 eV
- Thermodynamic efficiency limits (1x sun AM1.5G) Si single junction: 29%, with additional top cell: 42.5%

Adding InGaN top cell boosts a 20% efficient Si cell into more than 30% efficient tandem cell !

No tunnel junction needed

InGaN/Si MJ efficiency estimates

Calculated 300 K AM1.5 direct efficiency of a 2J InGaN/Si tandem solar cell.



Assumed InGaN parameters

$\mu_e = 300\ cm^2\ V^{-1}\ s^{-1}$

$\mu_h = 50\ cm^2\ V^{-1}\ s^{-1}$

$m_e = 0.07m_0$

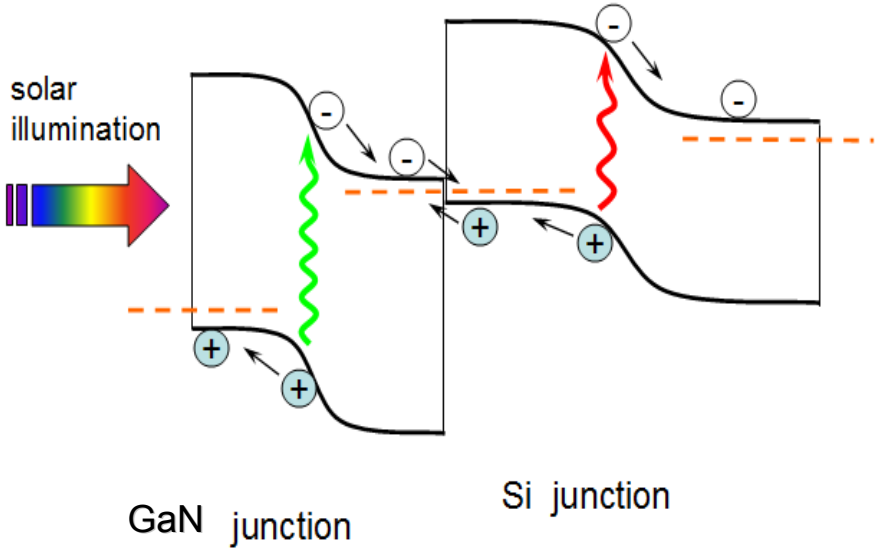
$m_h = 0.7m_0$

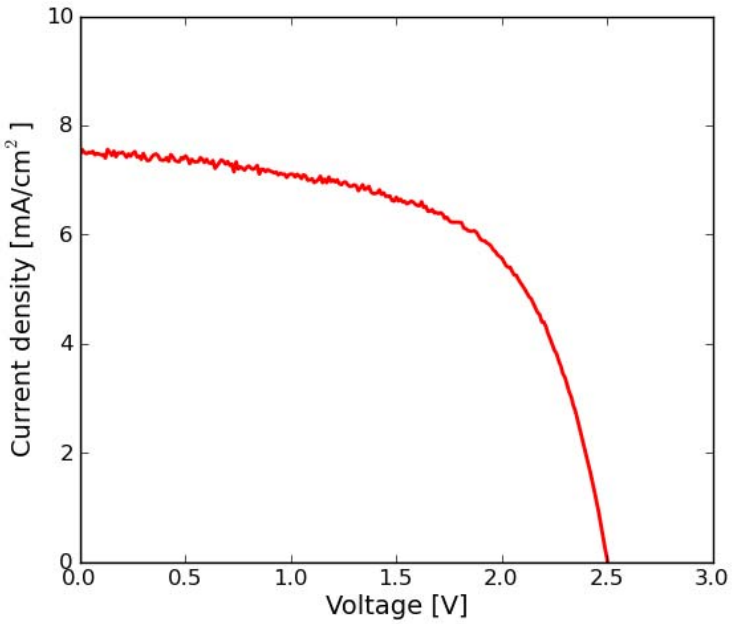
The surface recombination velocities assumed to be zero.

The maximum efficiency is 35% using InGaN with a bandgap of 1.7 eV ($In_{0.5}Ga_{0.5}N$).

GaN-Si tandem cell

GaN/Si hybrid tandem





Not current matching !
Top cell greatly restricts the current
Eg = 3.4 eV → max. Jsc= 0.6 mA/cm^2
(1 sun, 100% QE)

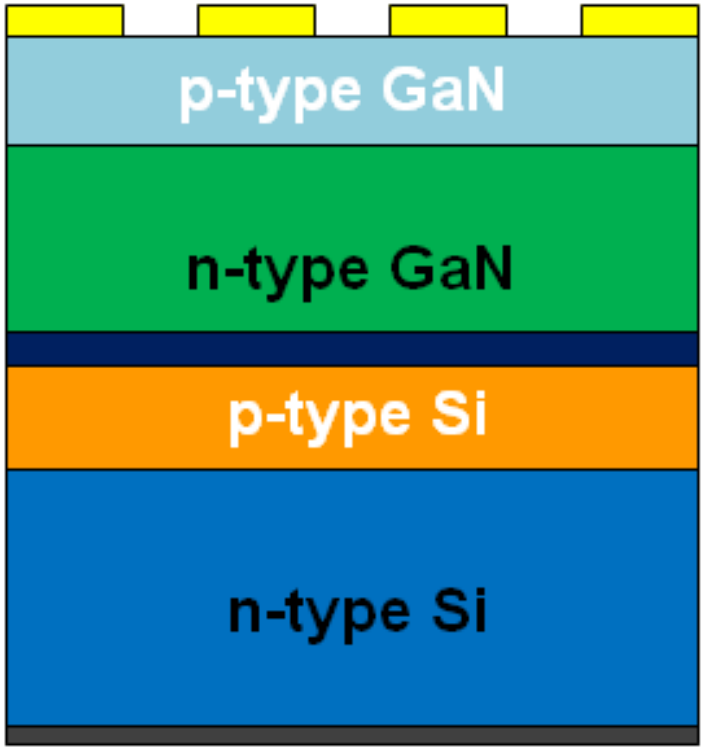
Illumination: 1x AM1.5G plus 325 nm HeCd laser
Voc= 2.5 V, Jsc= 7.5 mA/cm2 , fill factor = 61%

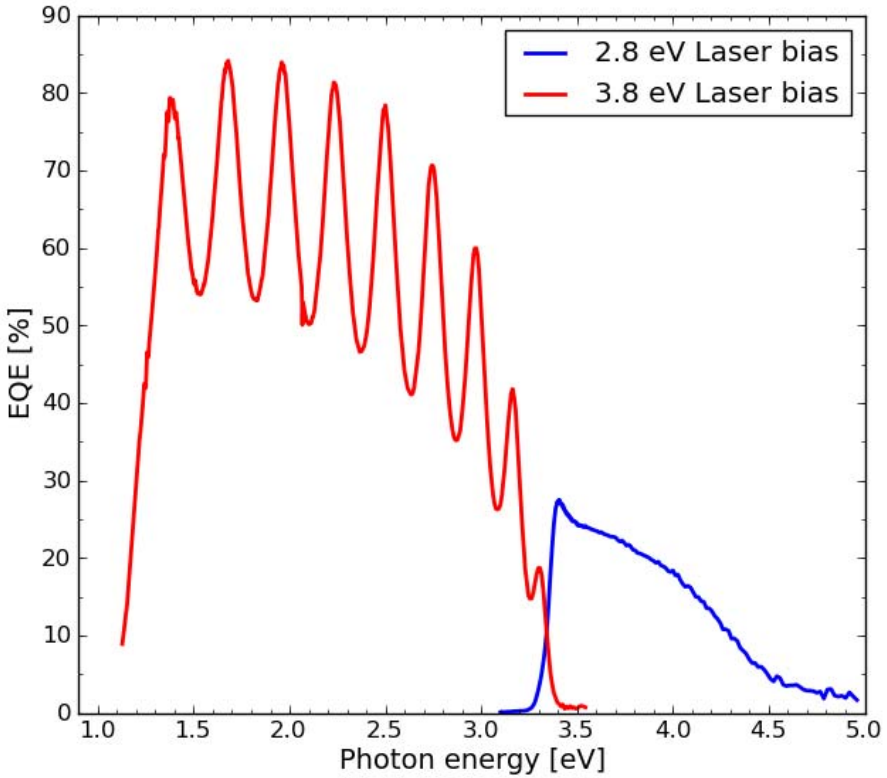
Demonstration of GaN-Si tandem
(developed with funding by RSLE)

RoseStreet Labs

W. Walukiewicz, K.M. Yu, J. Wu, U.S. Patent No. 7,217,882, "Broad spectrum solar cell," (issued May 15, 2007).
W. Walukiewicz, J.W. Ager, K.M. Yu, Patent Application No. PCT/US2008/004572,"Low-resistance Tunnel Junctions for High Efficiency Tandem Solar Cells."
W. Walukiewicz, J.W. Ager III, K.M. Yu, Patent Application No. PCT/US2008/067398, "Single p-n Junction Tandem Photovoltaic Device."

External Quantum Efficiency

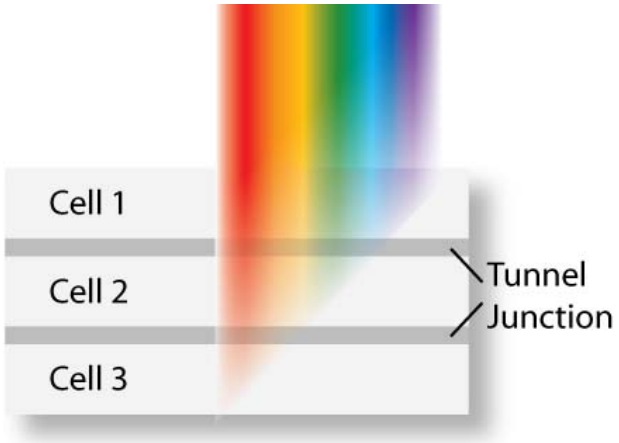




Clear evidence for tandem PV action

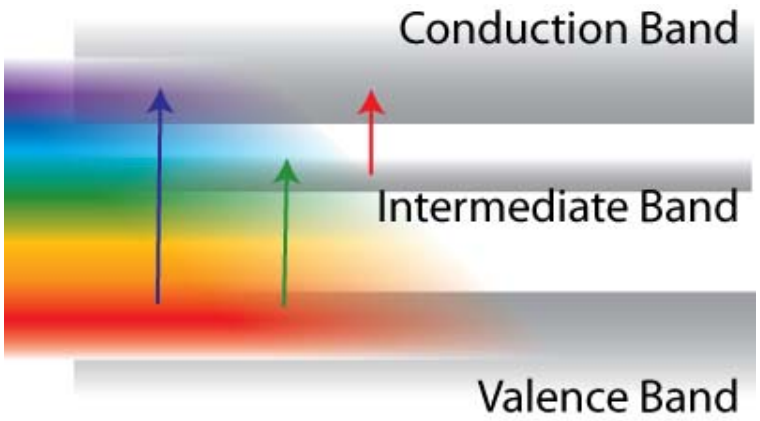
Intermediate band solar cells

Multi-junction solar cell



Each cell converts photons from a narrow energy range.
Band gaps are selected for optimum coverage of the solar spectrum
Strict materials requirements
Complex, expensive technology

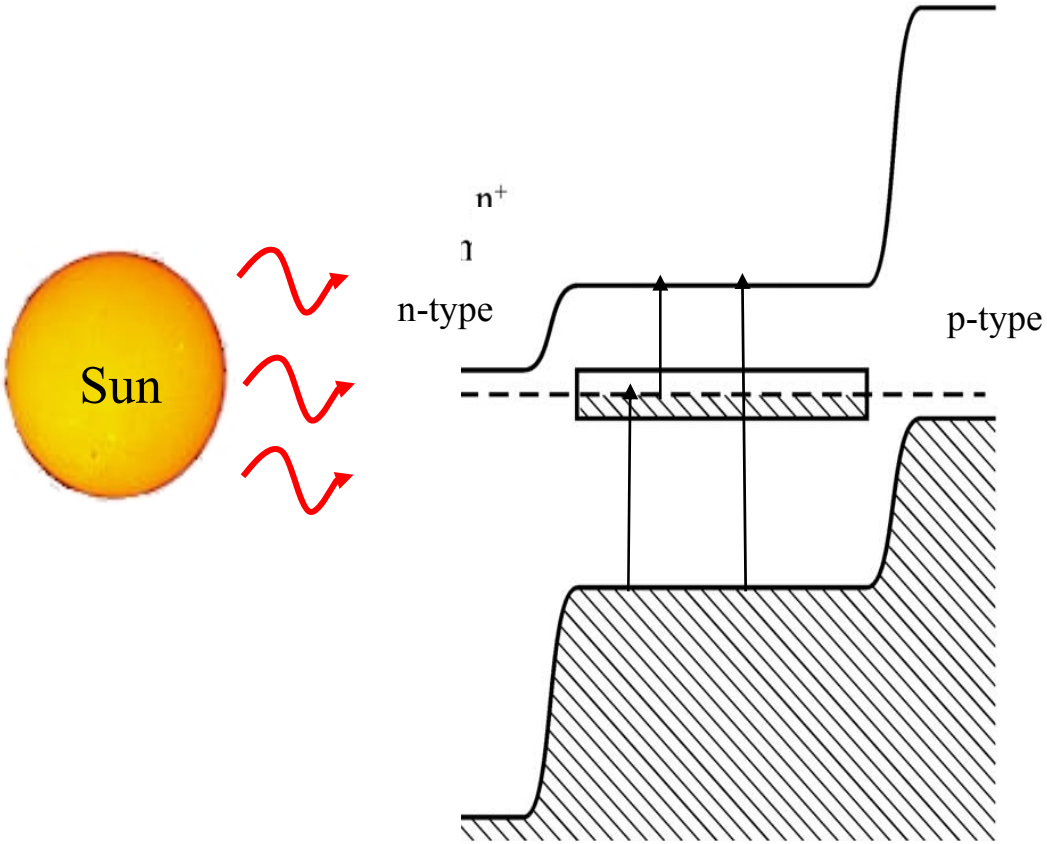
Intermediate band solar cells



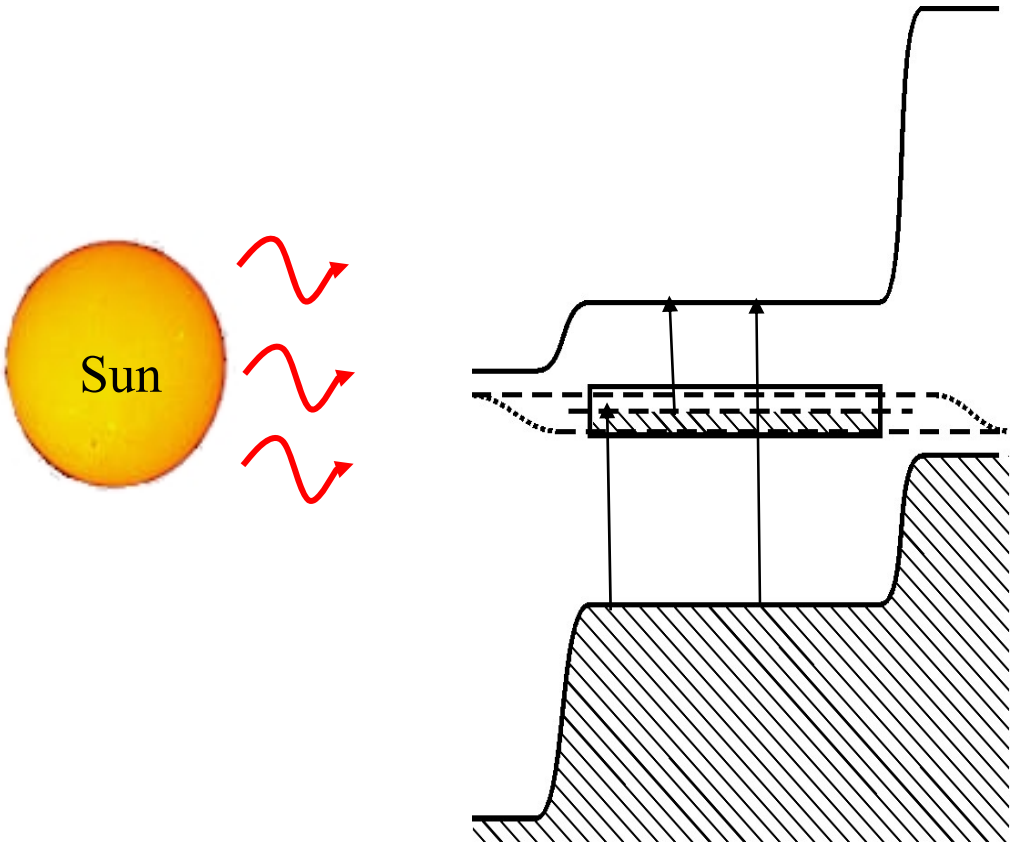
The intermediate band serves as a "stepping stone" to transfer electrons from the valence to conduction band.

Photons from broad energy range are absorbed and participate in generation of current.

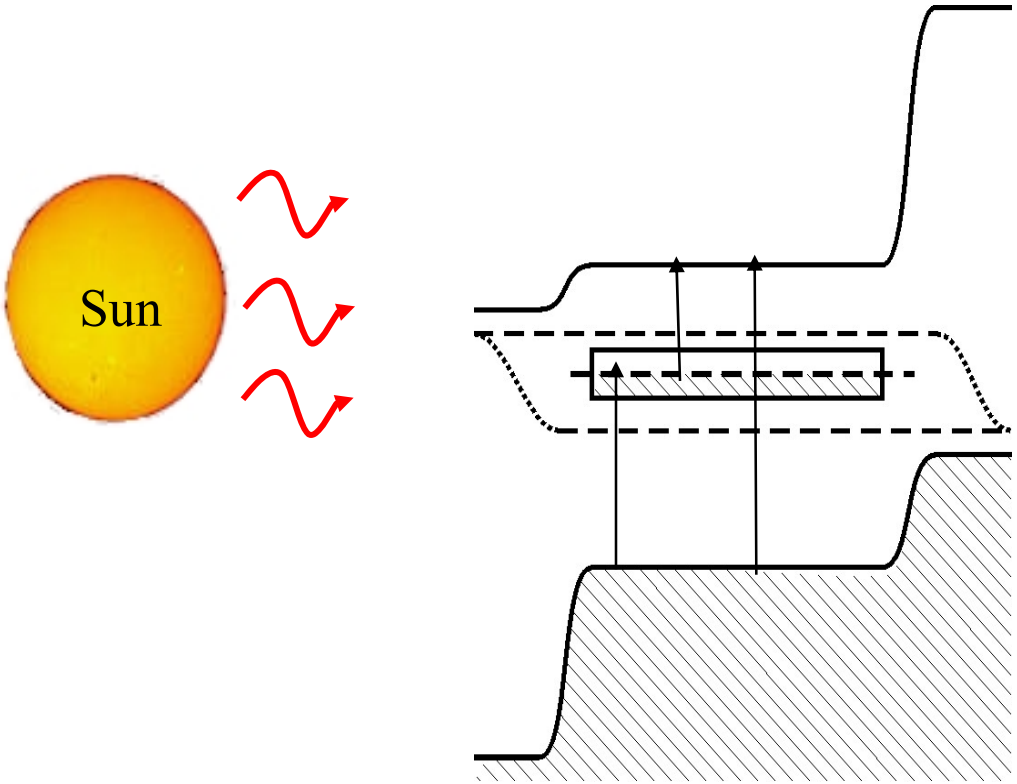
Intermediate band cell



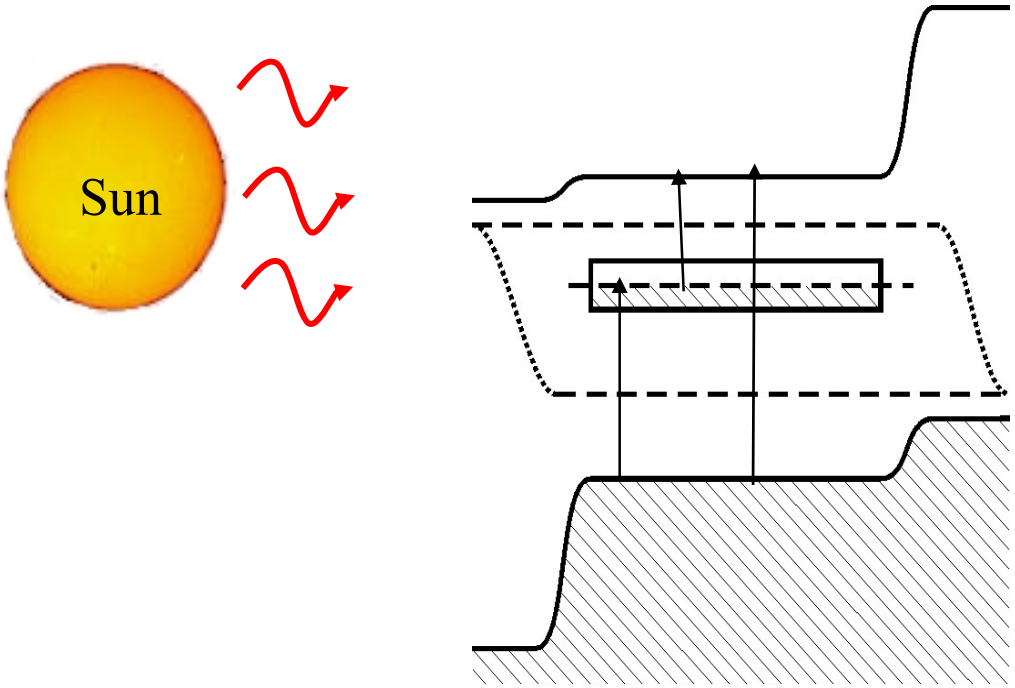
Intermediate band cell



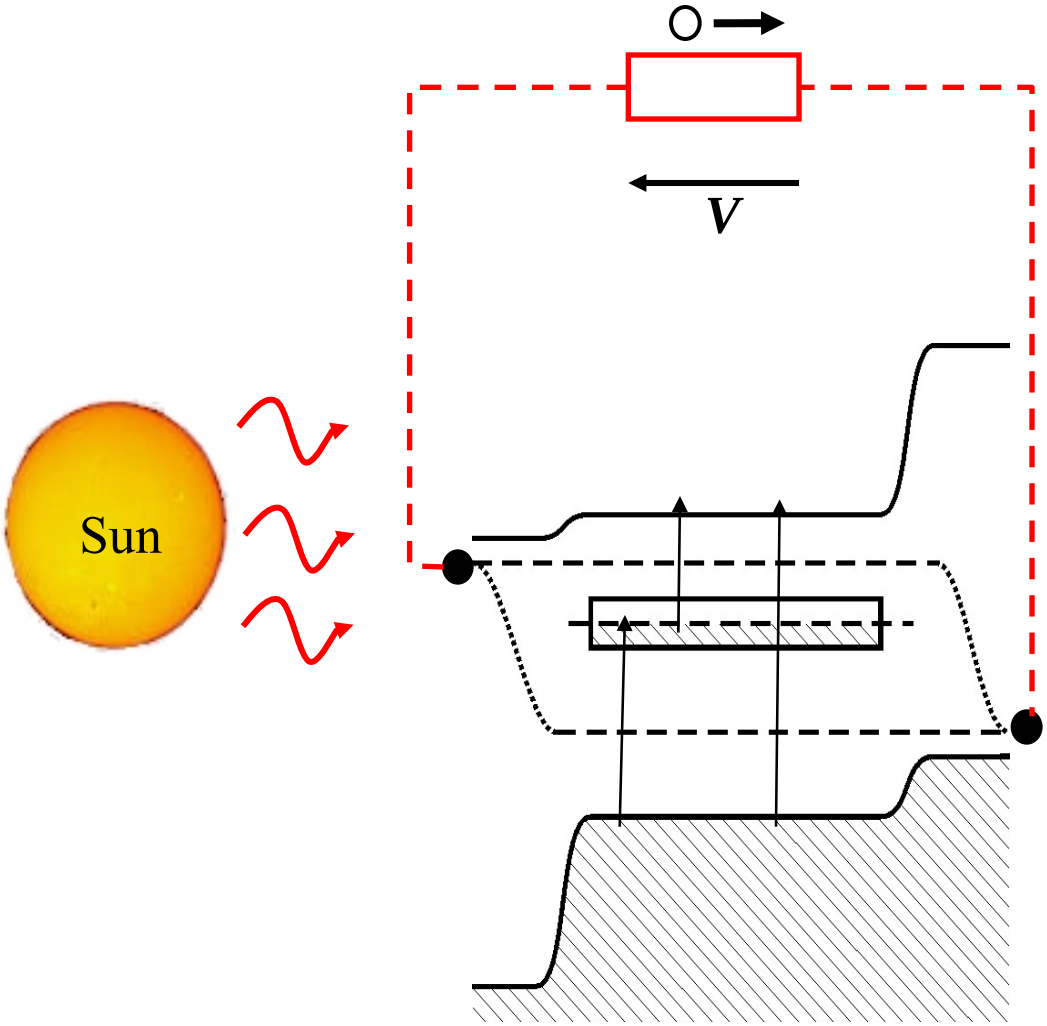
Intermediate band cell



Intermediate band cell



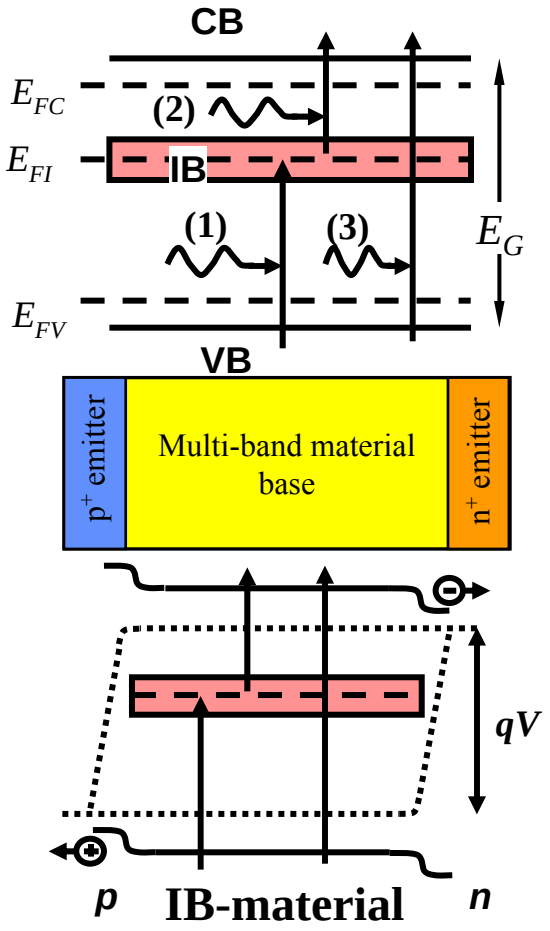
Intermediate band cell



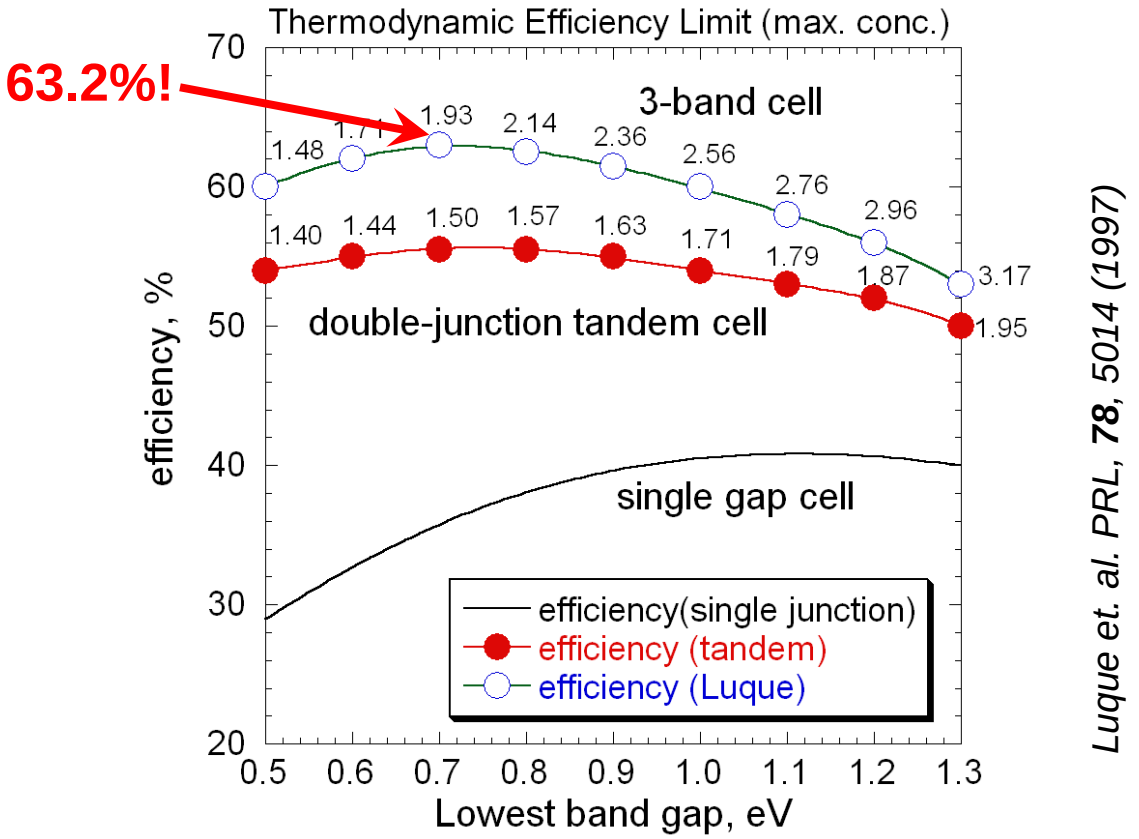
The intermediate band cell acts as a up-converter for low energy photons

Two small energy photons produce single electron-hole pair contributing to large V_{oc}

Intermediate Band Solar Cells (IBSCs)



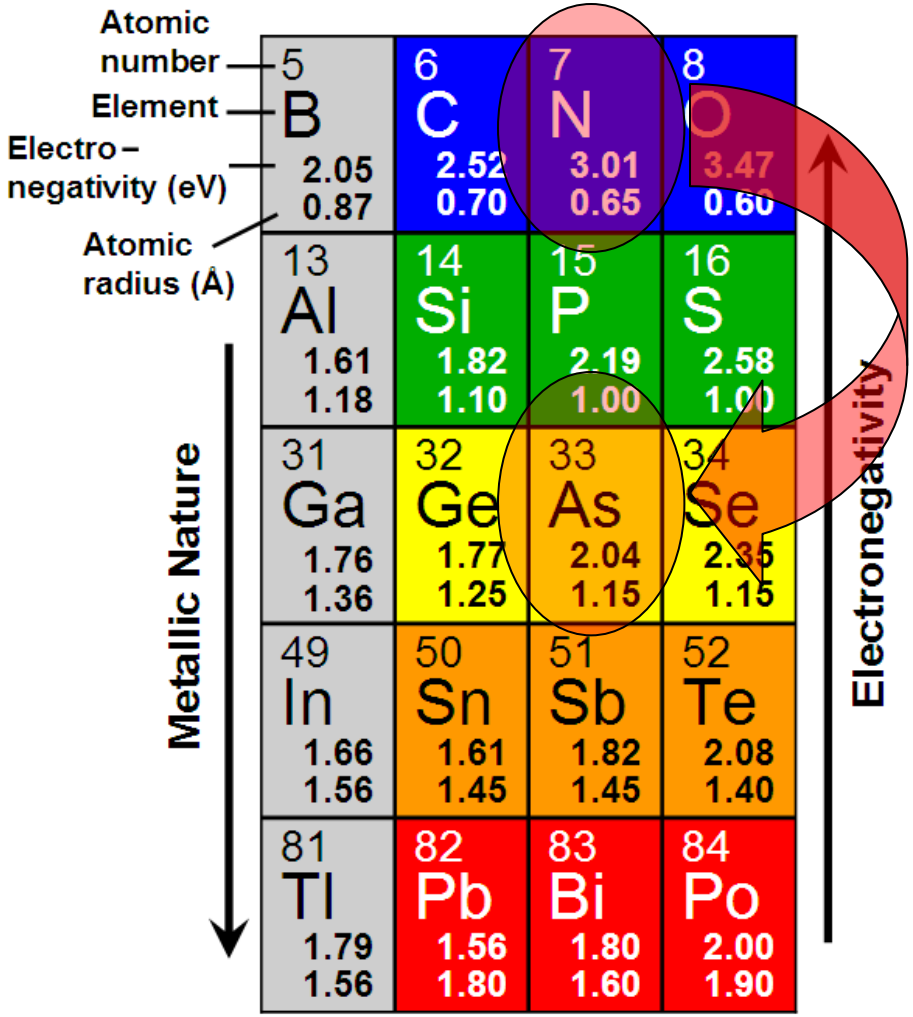
Concept first proposed in early 1960's <u>but no practical demonstrations</u>



*Luque et. al. PRL, **78**, 5014 (1997)*

- Simple, one junction design
- Higher efficiency limits
- No material suitable for IBSC
- QD arrays used to demonstrate IB transition

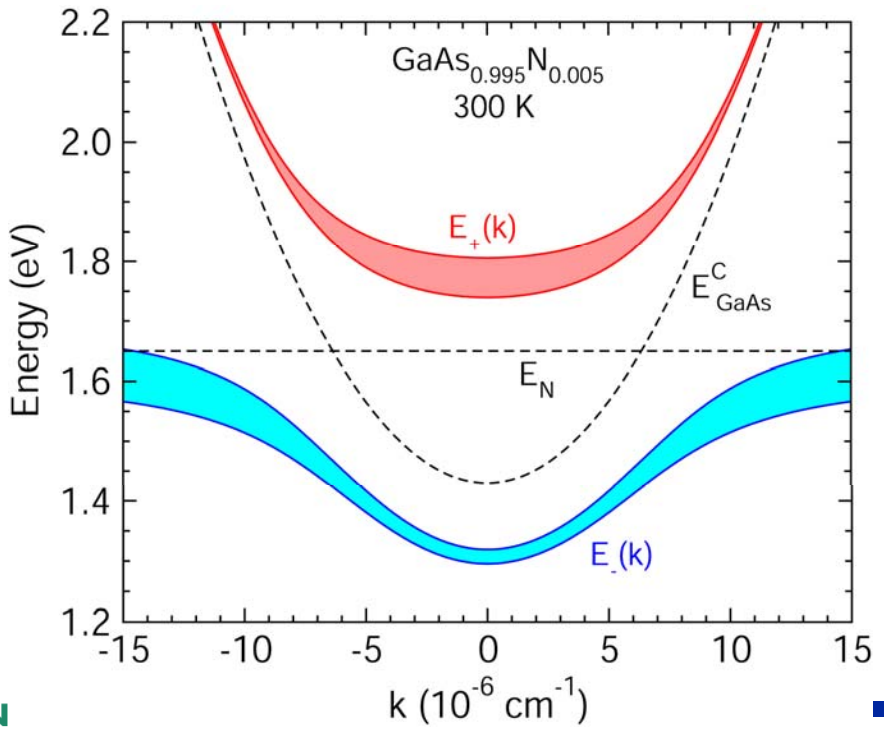
Engineering *Electronic Band Structure* for Solar Energy Applications



- Alloying materials with distinctly different electronegativites and/or atomic radii, e.g.

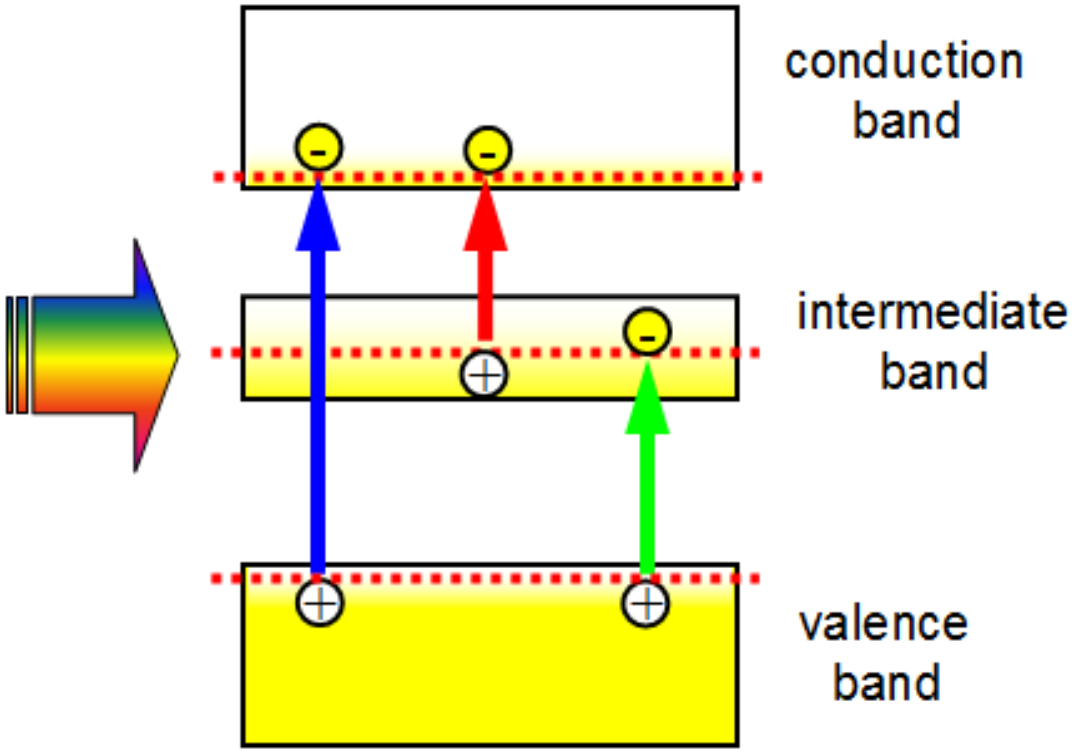
  $III\text{-}N_x\text{-}V_{1-x;}$ $II\text{-}O_x\text{-}VI_{1-x}$

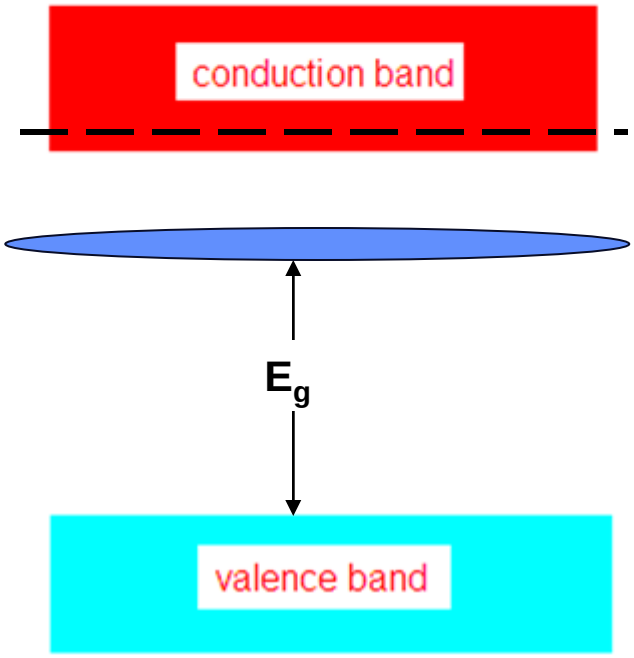
- *Band edges are strongly affected by anticrossing interaction between localized and extended states*
- *Such highly mismatched alloys (HMAs) are difficult to synthesize*



Highly Mismatched Alloys: conduction band anticrossing

A highly mismatched alloy (HMA) is formed when anions are partially replaced with distinctly different isovalent elements



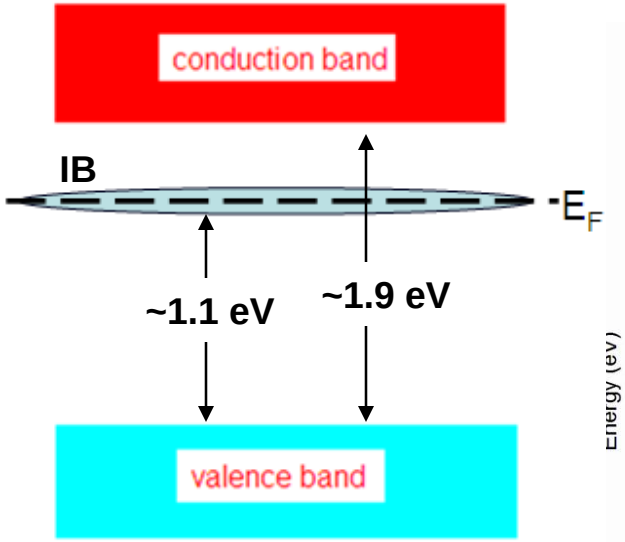


- **Drastic decrease in bandgap with N incorporation**
- **Changes in transport properties due to modified conduction band**
- **Formation of an intermediate band**

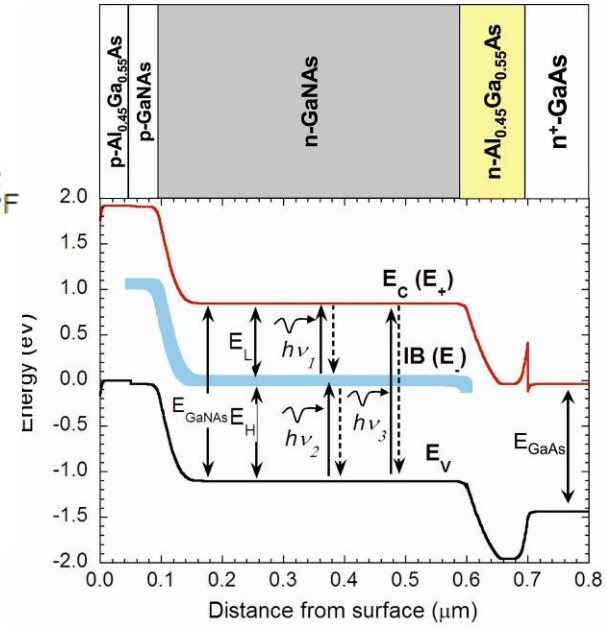
Conduction band anticrossing
e.g. As-rich GaNAs, Te-rich ZnOTe

Multiband in Dilute Nitride HMA

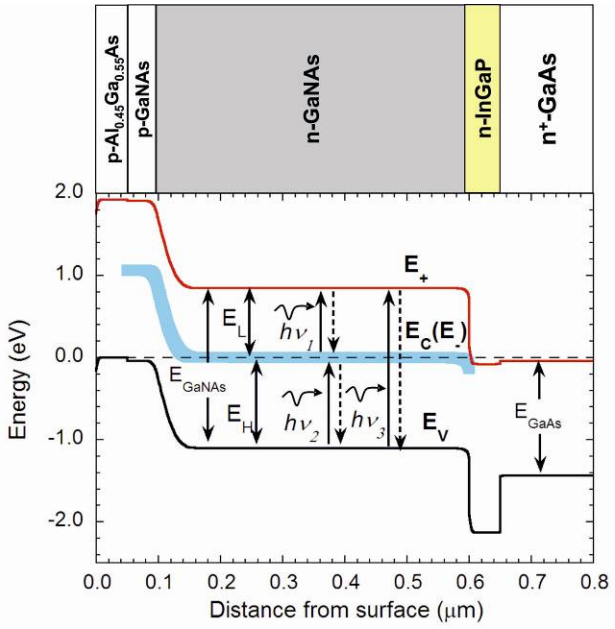
Dilute nitride HMA (GaN_xAs_{1-x}, x~0.02)



Blocked intermediate band (BIB)



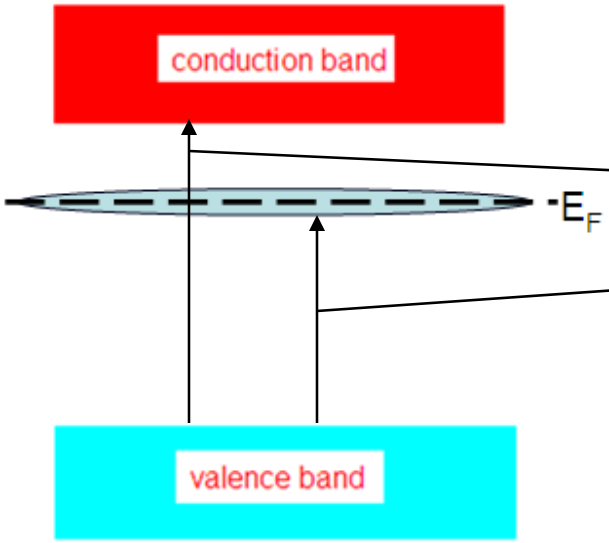
Unblocked intermediate band (UIB)

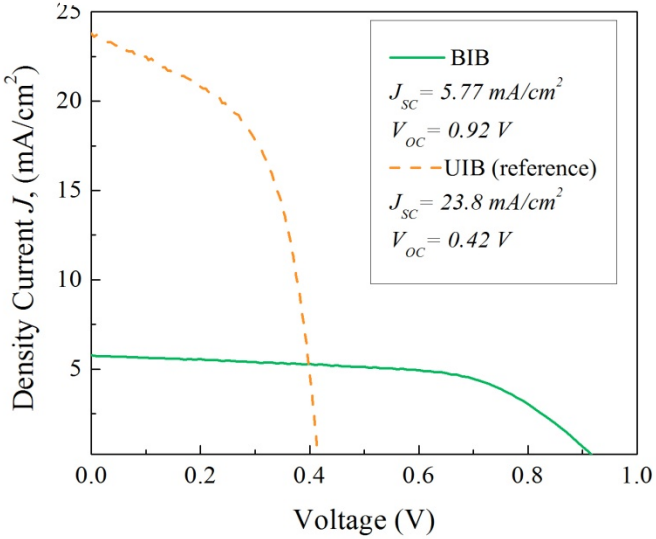


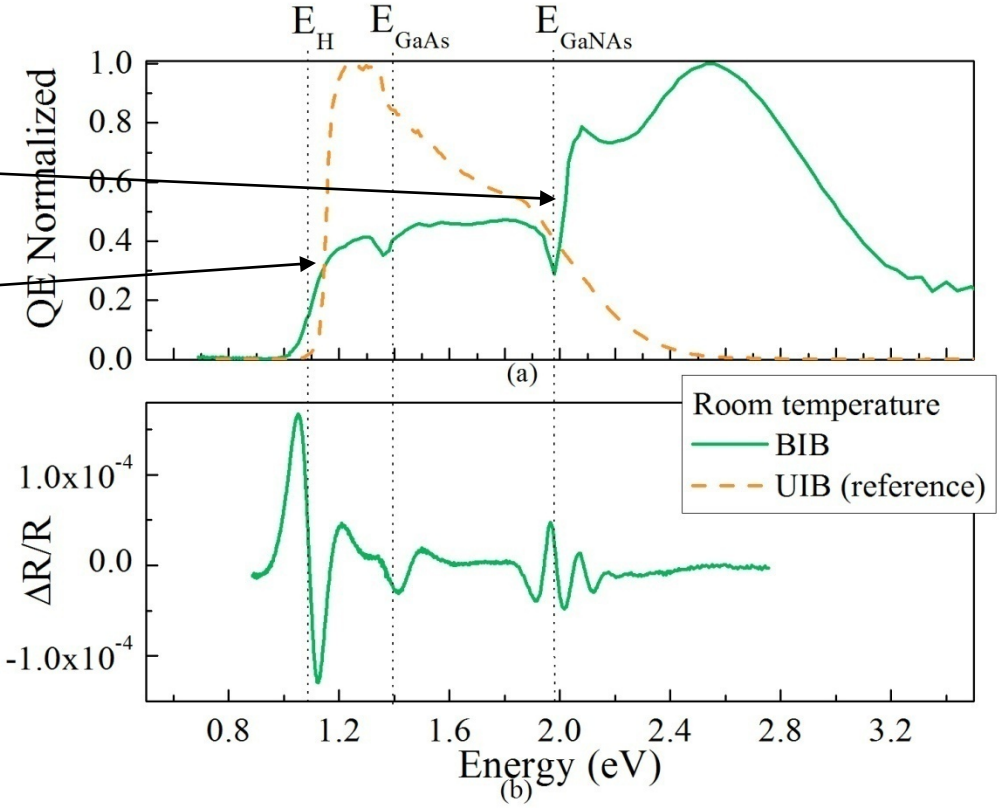
- BIB-AlGaAs blocking layers to isolate the IB from the charge collecting contacts
- UIB- no blocking layers, IB acts as the conduction band

Nair. López, L.. A. Reichertz, K. M. Yu, K.Campman, and W. Walukiewicz, Phys. Rev. Lett. 106, 028701 (2011).

Dilute Nitride HMA IBSC



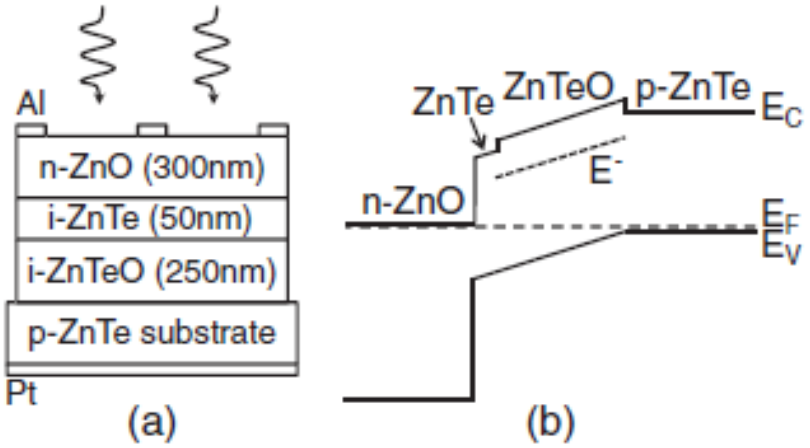


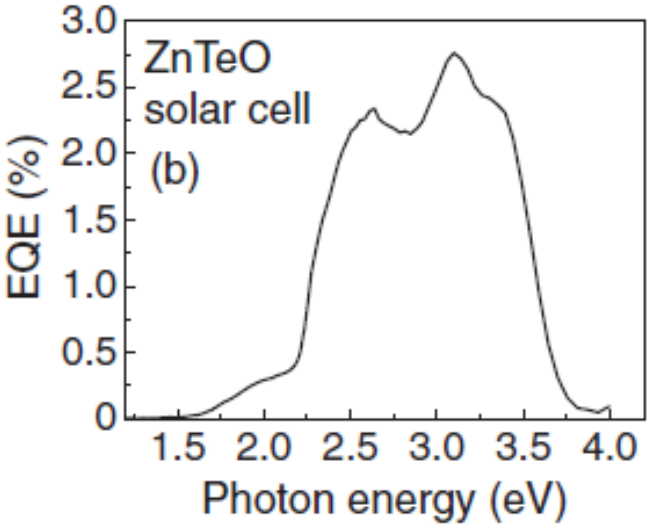


Demonstrates the principle of IBSC with a three band dilute nitride material.

Issues: optimize N concentration
more efficient carrier collection
doping level in absorber layer

ZnOTe Based Intermediate Band Solar Cell





ZnOTe synthesized using O implantation followed by pulsed laser melting

External Quantum Efficiency clearly shows a photocurrent with excitations to the intermediate band

T. Tanaka et. al., Jpn. J. Appl. Phys**. 50** (2011) 082304

Band Anticrossing in HMAs

- **Localized level above CBE and interaction with CB**
  - ⇨ **GaAs(N), ZnSe(O), CdTe(O)**

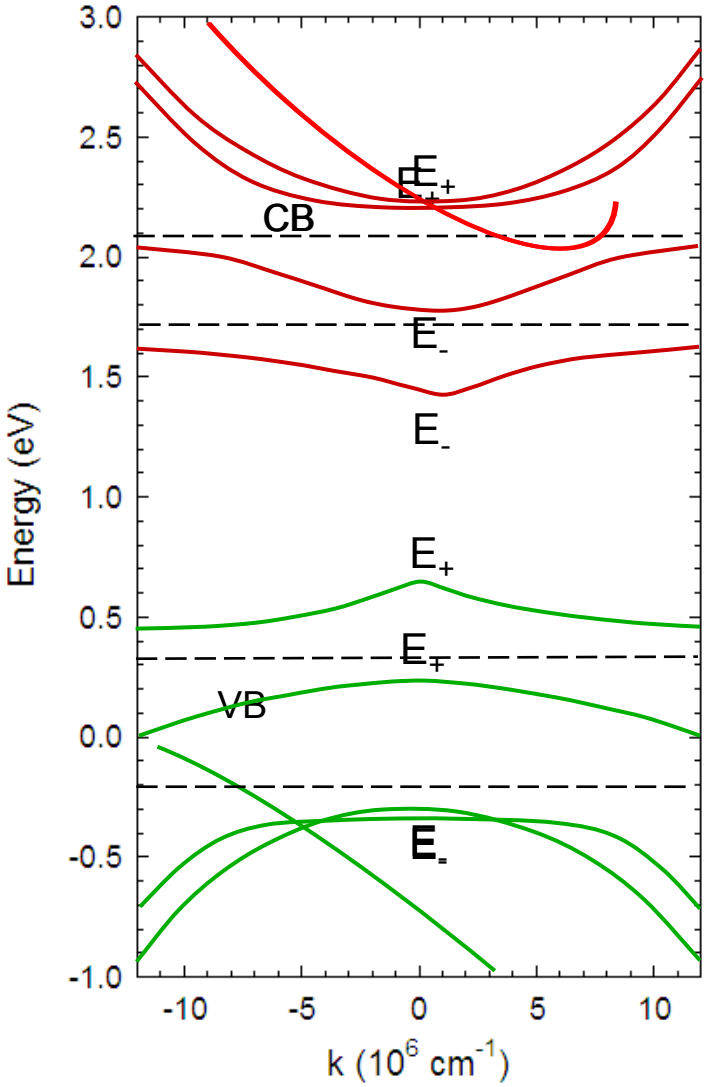
  W. Shan et al. Phys. Rev. Lett. 82, 1221 (1999).
- **Localized level below CBE and interaction with CB**
  - ⇨ **GaAsP(N), ZnTe(O)**

  K. M. Yu et al., Phys. Rev. Lett. 91, 246203 (2003).
- **Localized level above VBE and interaction with VB**
  - ⇨ **GaN(As), ZnSe(Te), ZnS(Te), GaN(Bi)**

  ***A. Levander, et. al. Appl. Phys. Lett.* 97, 141919 (2010)**

  K. M. Yu, et al. Appl.Phys. Lett. 97, 101906 (2010)
- **Localized level below VBE and interaction with VB**
  - ⇨ **GaAs(Bi), GaAs(Sb), Ge(Sn)**

  K. Alberi at al., Appl. Phys. Lett., 91, 051909 (2007).



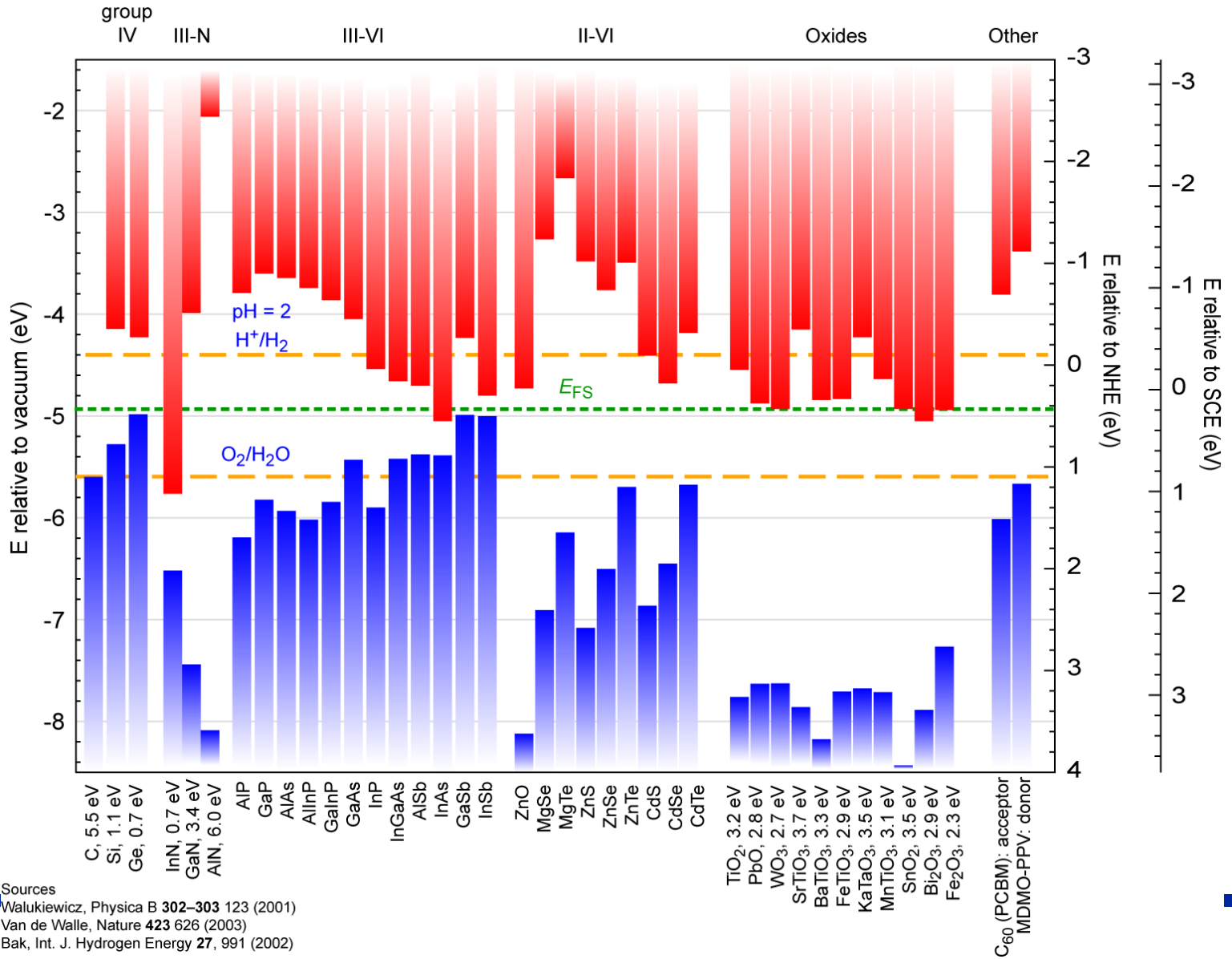
Photoelectrochemical Cells (PECs)

$$2h\nu + H_2O \rightarrow H_2(g) + \tfrac{1}{2} O_2(g)$$

Material requirements

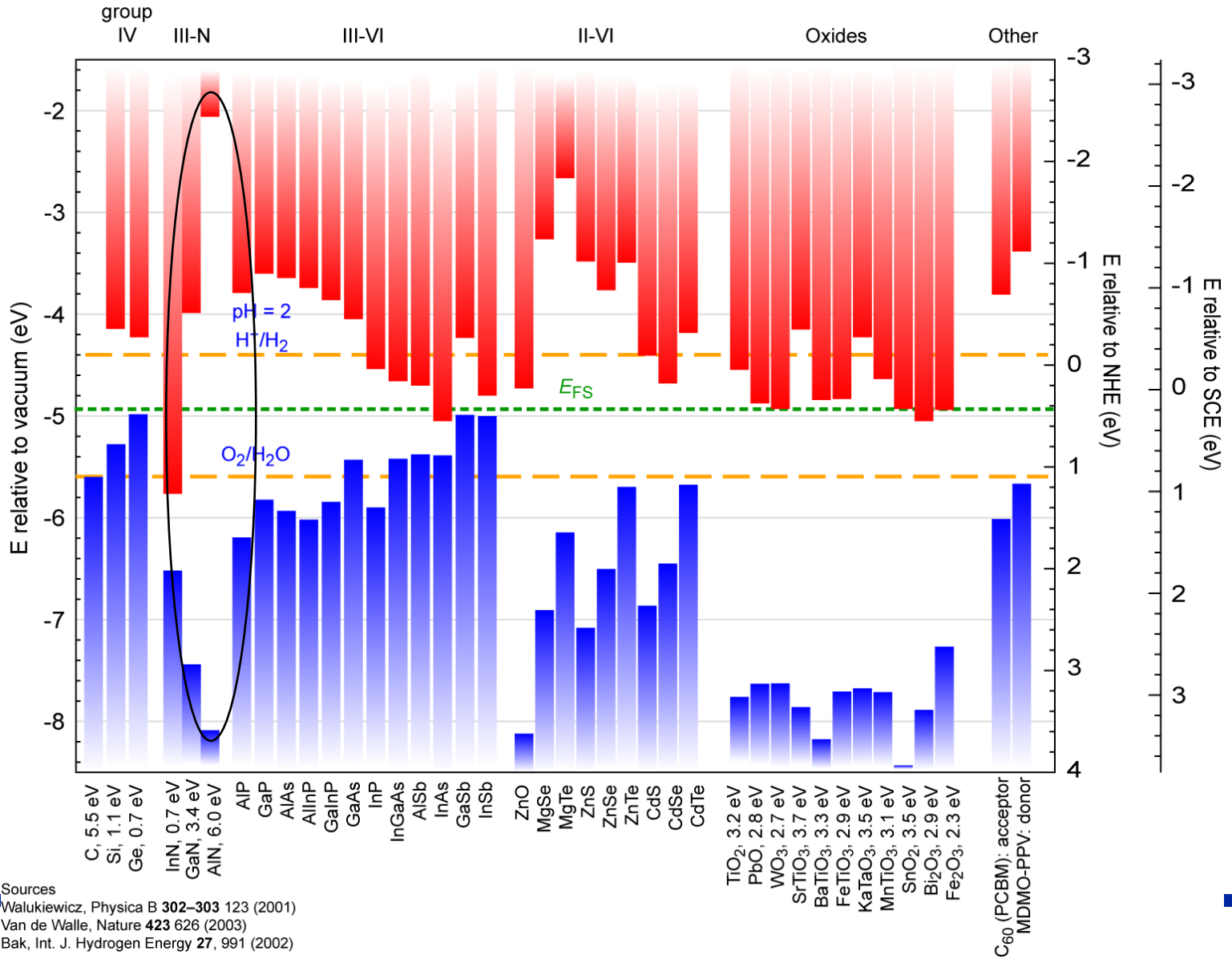
- **Band gap must be at least 1.8-2.0 eV but small enough to absorb most sunlight**
- **Band edges must straddle Redox potentials**
- **Fast charge transfer**
- **Stable in aqueous solution**

Semiconductors for PECs



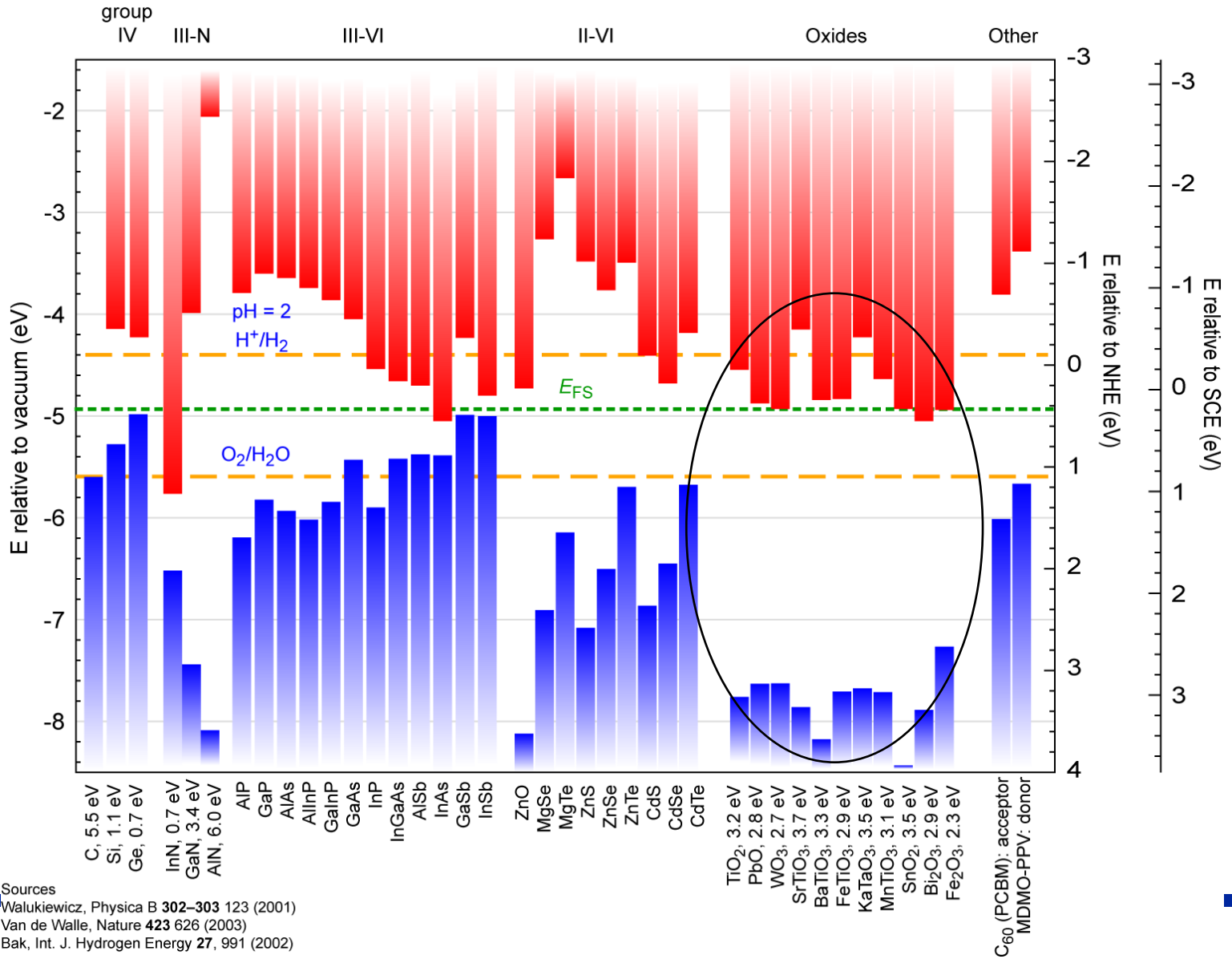
Sources
Walukiewicz, Physica B **302–303** 123 (2001)
Van de Walle, Nature **423** 626 (2003)
Bak, Int. J. Hydrogen Energy **27**, 991 (2002)

Semiconductors for PECs: III-nitrides



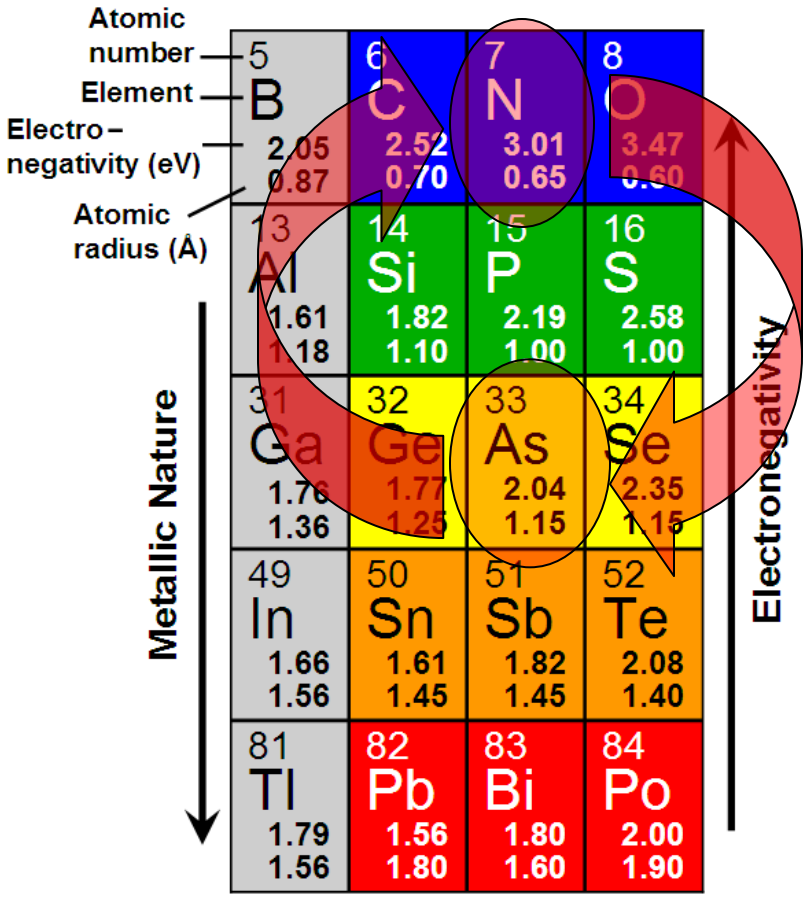
Sources
Walukiewicz, Physica B **302–303** 123 (2001)
Van de Walle, Nature **423** 626 (2003)
Bak, Int. J. Hydrogen Energy **27**, 991 (2002)

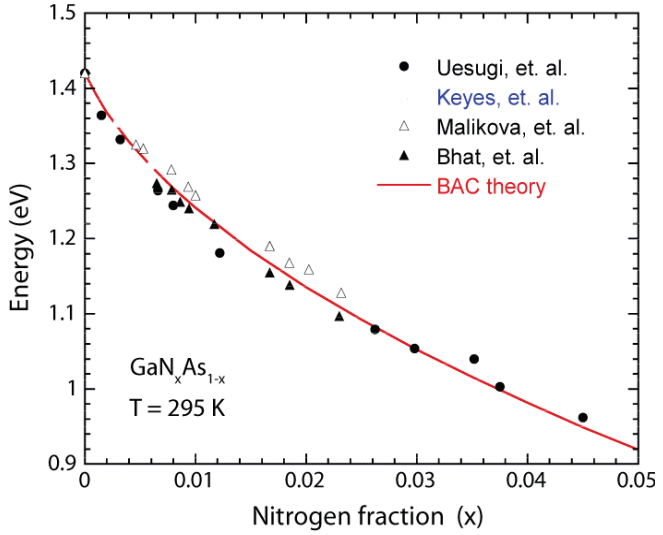
Semiconductors for PECs: oxides

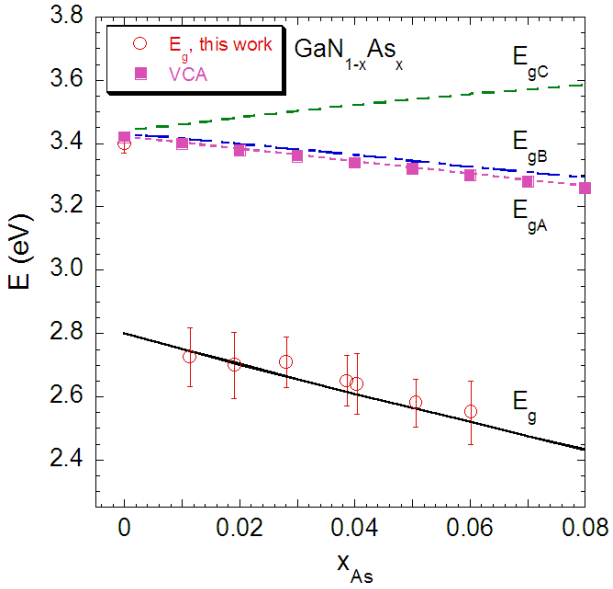


Sources
Walukiewicz, Physica B **302–303** 123 (2001)
Van de Walle, Nature **423** 626 (2003)
Bak, Int. J. Hydrogen Energy **27**, 991 (2002)

Band Structure Engineering: GaNAs

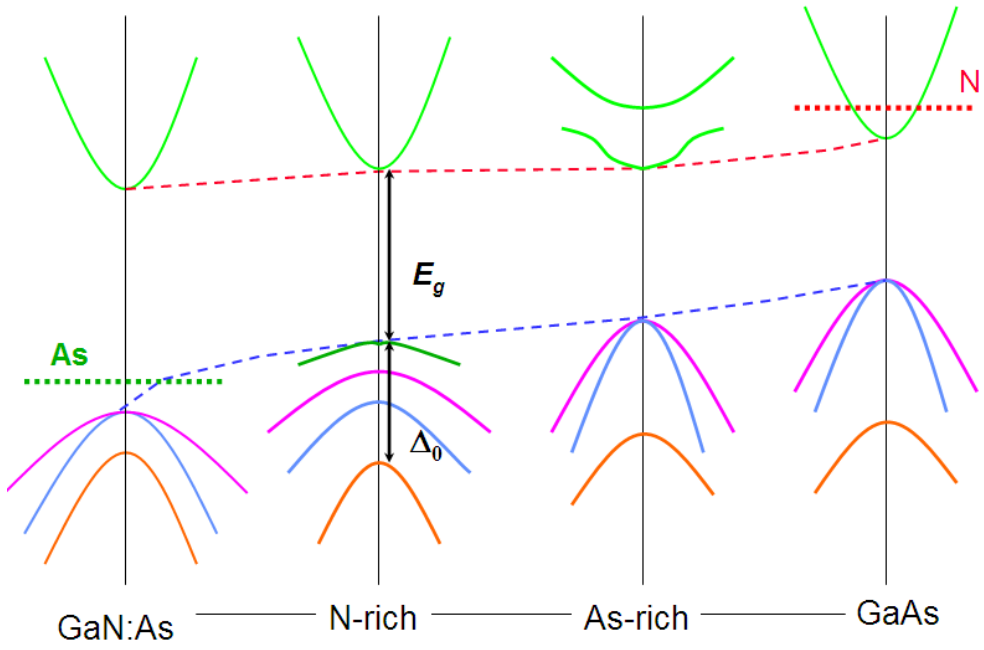


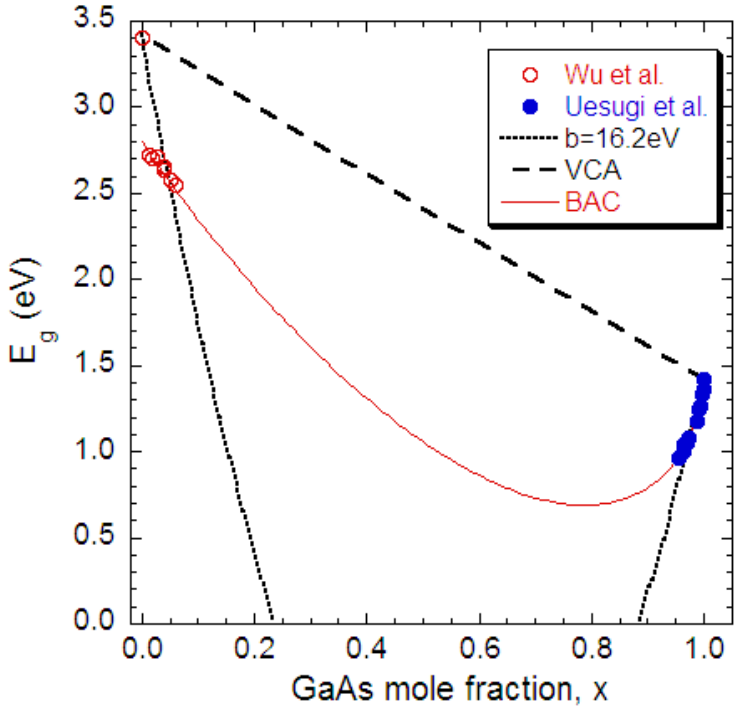




- Alloying materials with distinctly different electronegativites and/or atomic radii
- *Band edges are strongly affected by anticrossing interaction between localized and extended states*

$GaN_{1-x}As_x$ alloys over the whole composition range



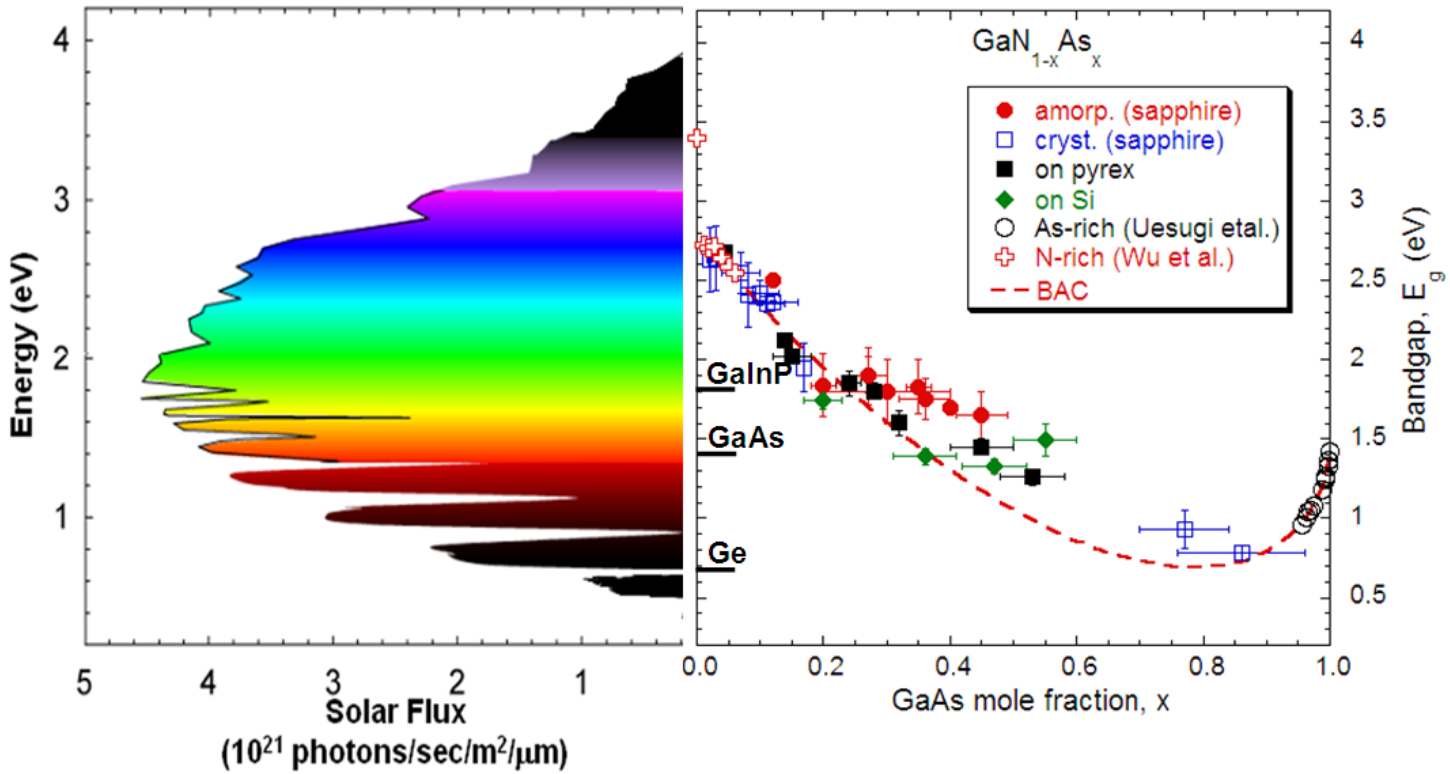


Interpolation of BAC of alloys with a limited composition range:

- Bandgap reaches a minimum at x~0.8 with a minimum band gap of 0.7 eV
- Drastically different from values predicted by virtual crystal approximation or using a single-bowing-parameter fitting.

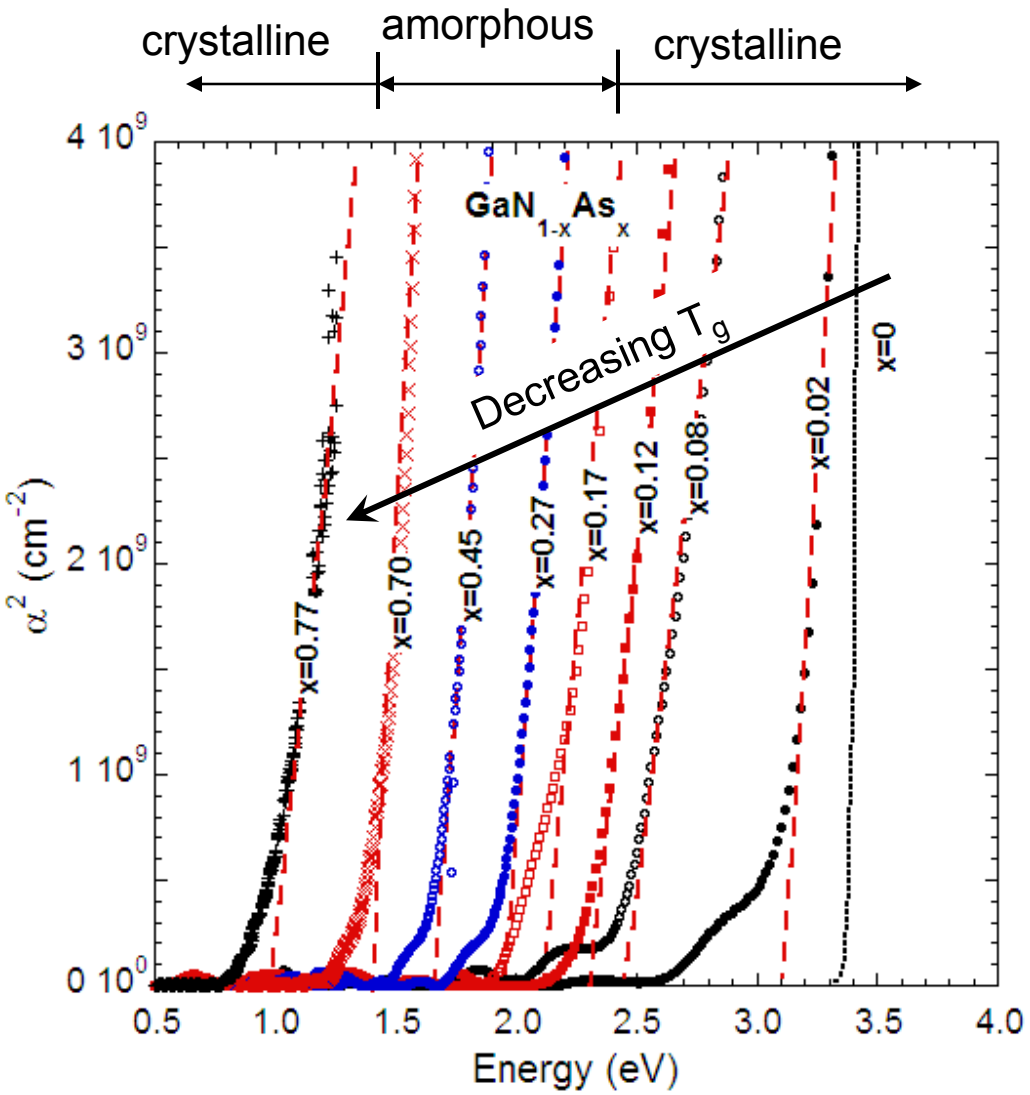
Growth of $GaN_{1-x}As_x$ alloys with large composition is challenging due to the miscibility gap for the Ga-N-As system

Band Gap: Composition Dependence



- Band gap of GaNAs covers most of the solar spectrum
- Films deposited on different substrates follow the same trend
- Experimental data follow the trend of the BAC interpolation.
- Amorphous alloys (0.15<x<0.8) can be utilized for low cost solar cell applications
- Can these materials be doped?

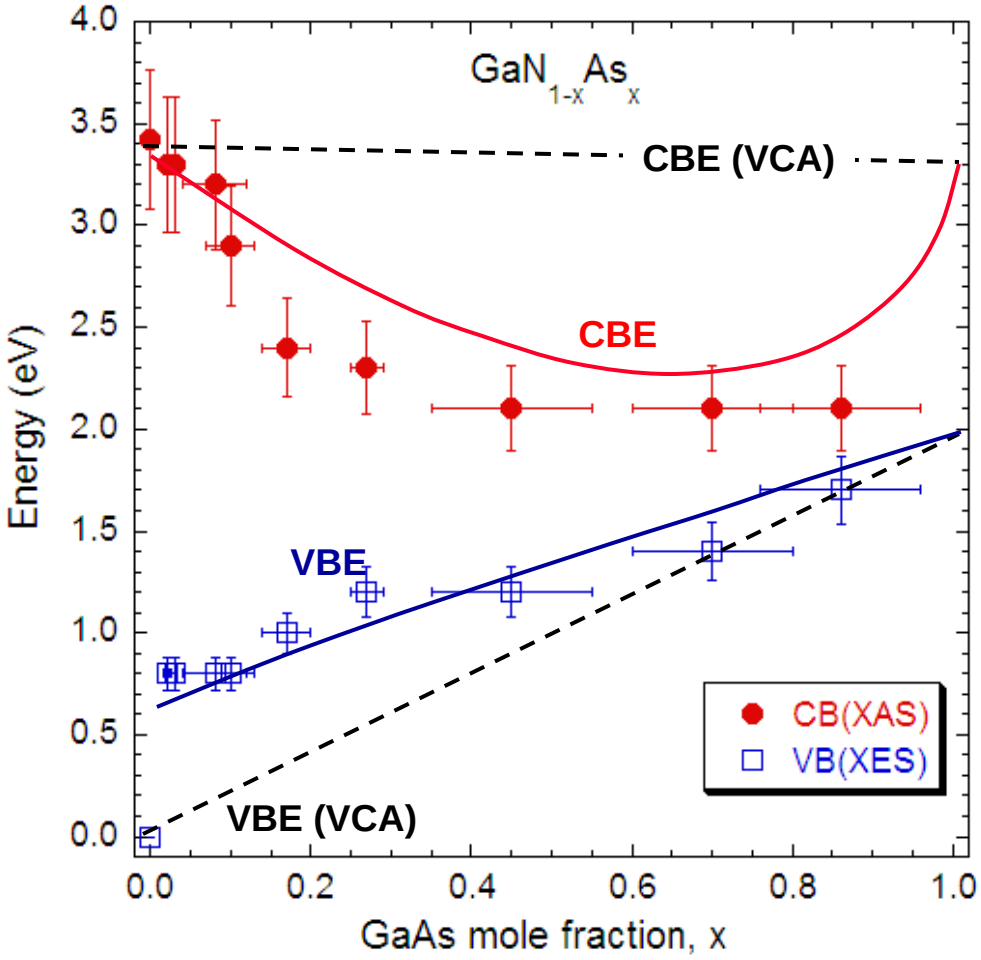
Strong Optical Absorption



- Sharp absorption edges
- Band gap decreases with As content
- the monotonic shift of absorption edge suggests random alloys with no phase separation
- All light absorbed by a thin film.

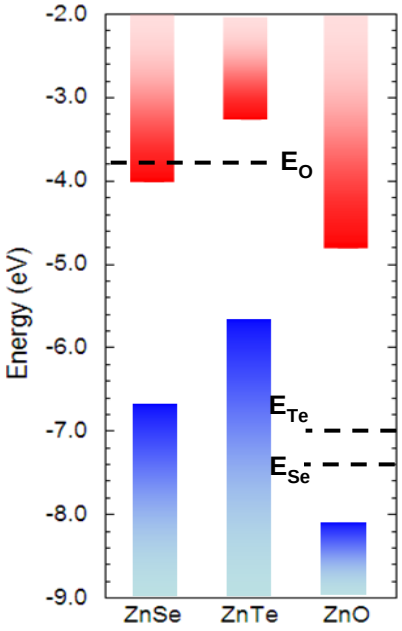
Conduction and valence band bowing

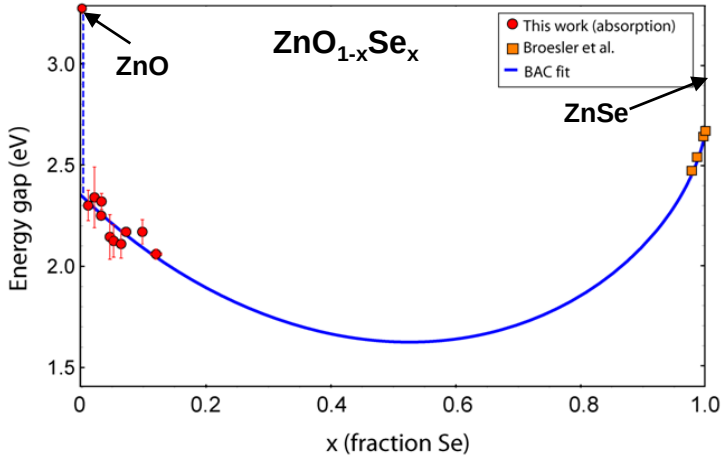
Soft x-ray absorption (CB) and emission (VB) spectroscopy

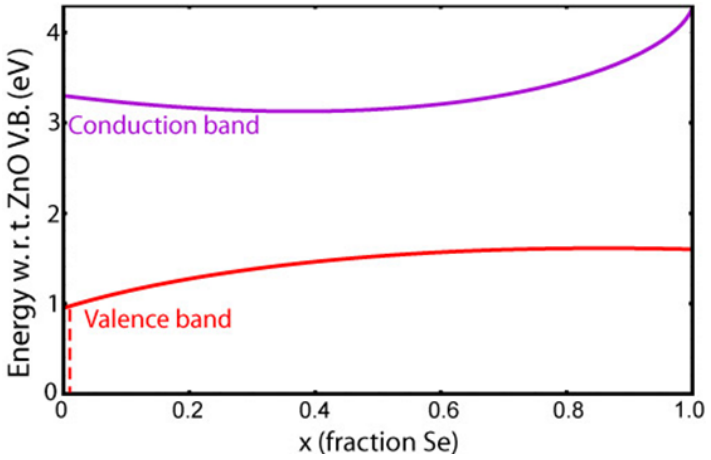


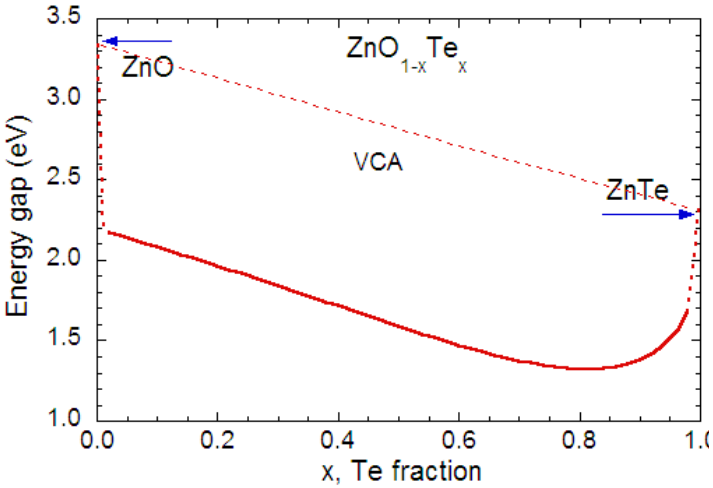
- E_g reduction due to movements of both CB and VB edges
- CB and VB shifts in crystalline/amorphous GaNAs alloys follows the trend of the BAC model

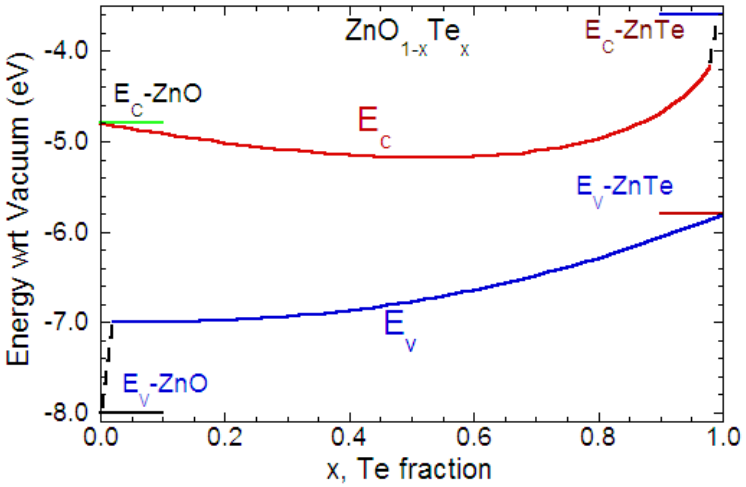
Highly Mismatched Oxides







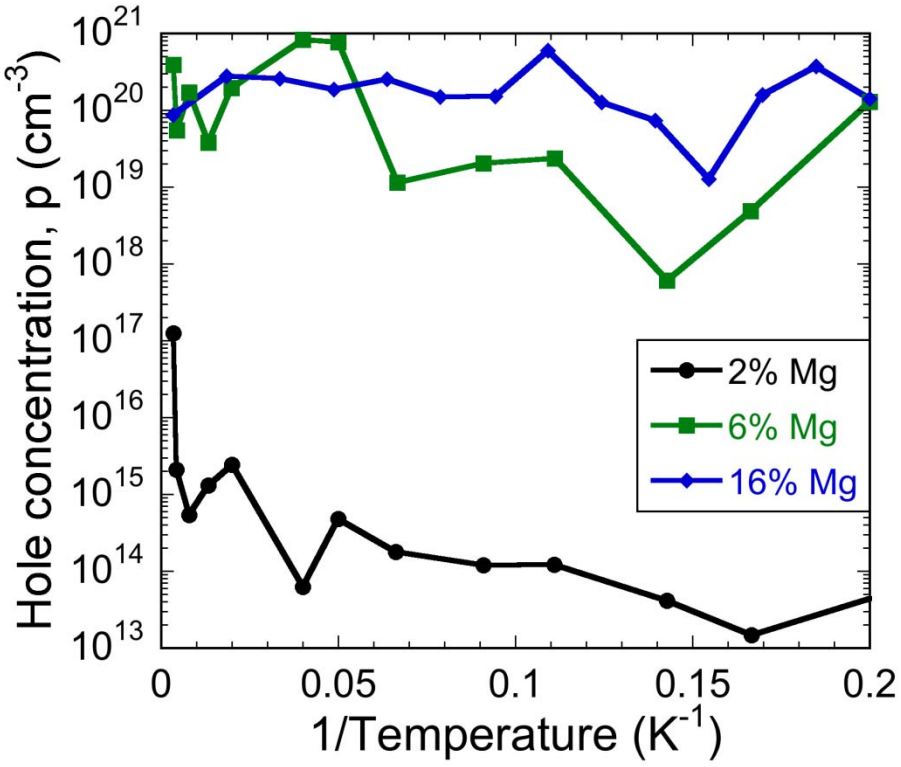


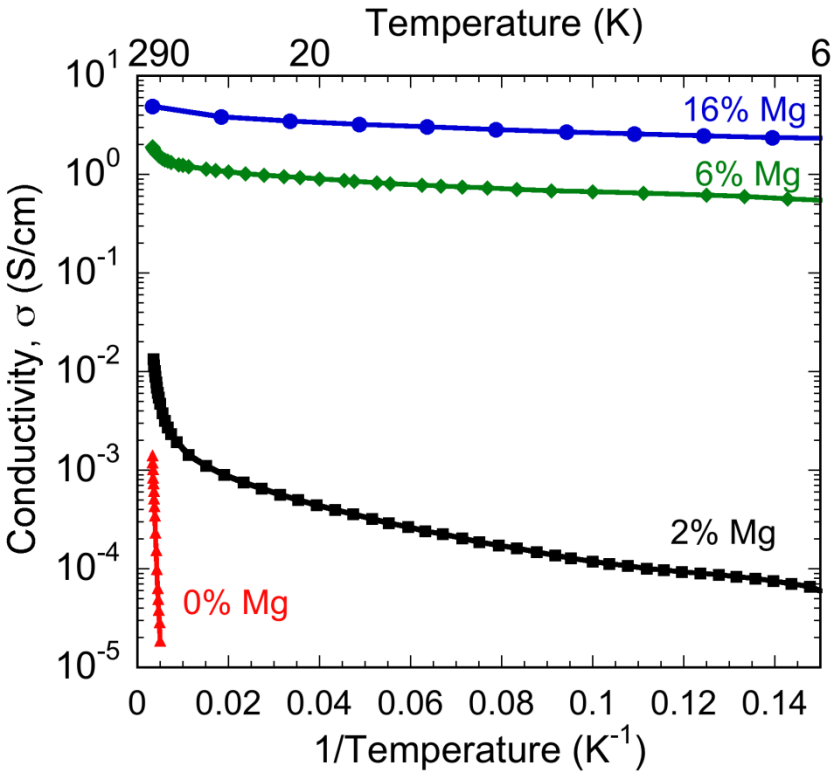


Summary

- New solar concepts are developed based on the progress in understanding of the electronic structure of complex semiconductor systems
- Highly mismatched semiconductor alloys allow for electronic band structure engineering through an independent control of the conduction and the valence band offsets.
- Better understanding of the properties of surfaces and interfaces of the dissimilar materials essential for the new concepts of high efficiency solar and photoelectrochemical cells.

Extremely High Hole Concentration





Controlled heavy p-type doping of amorphous GaAs could have significant consequences for the whole group III-nitride based semiconductor industry