July 24 2013

Solar Cells

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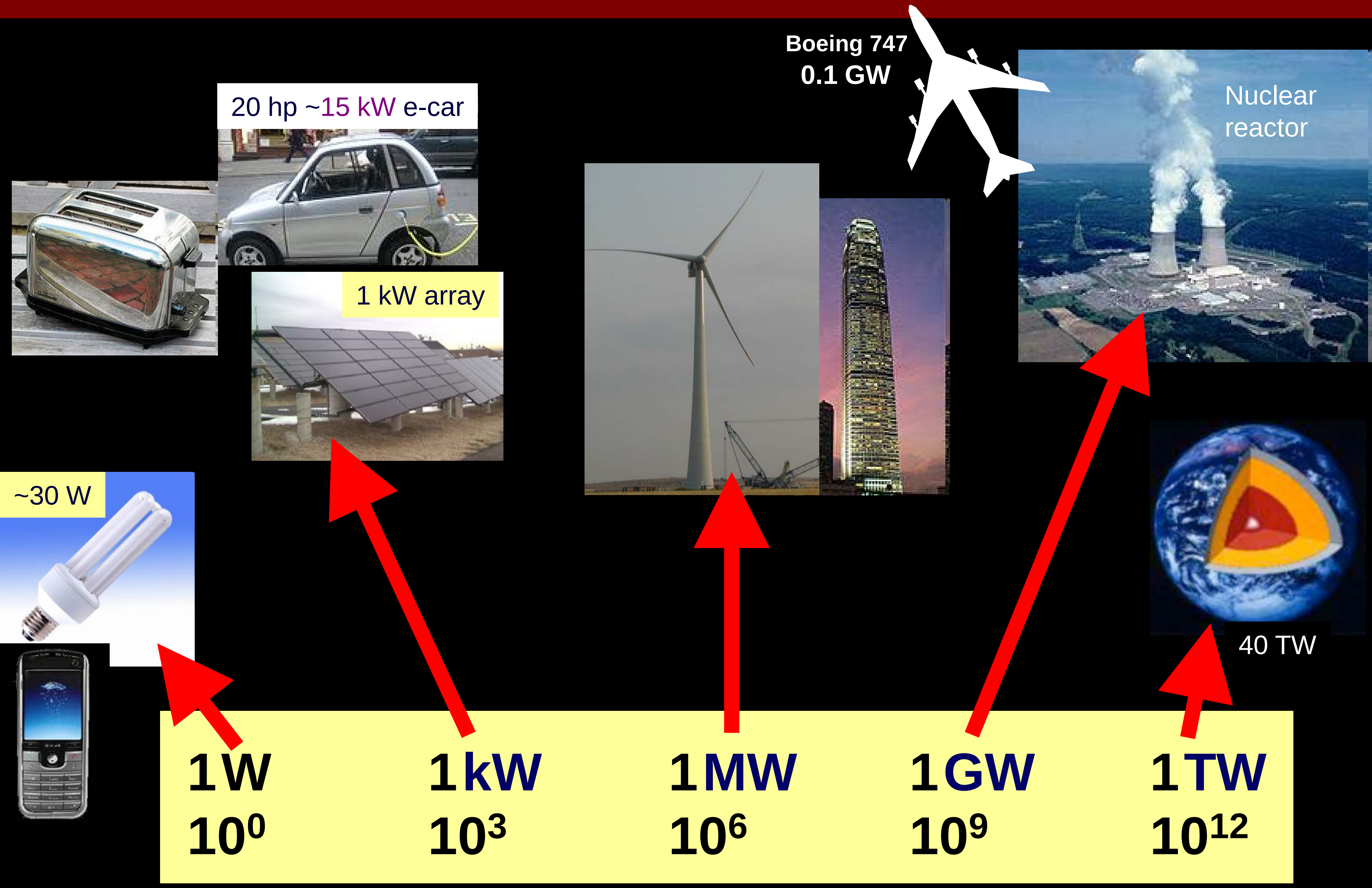
World Energy Consumption

	2012	2050
People:	**7** bil	**12** bil
Energy:	**15** TW	**30** TW

~3 kW / person

What is Watt ?

We will need ~**30 TW** in 2050



Can we use only nuclear power ??

We will need ~**30 TW** in 2050

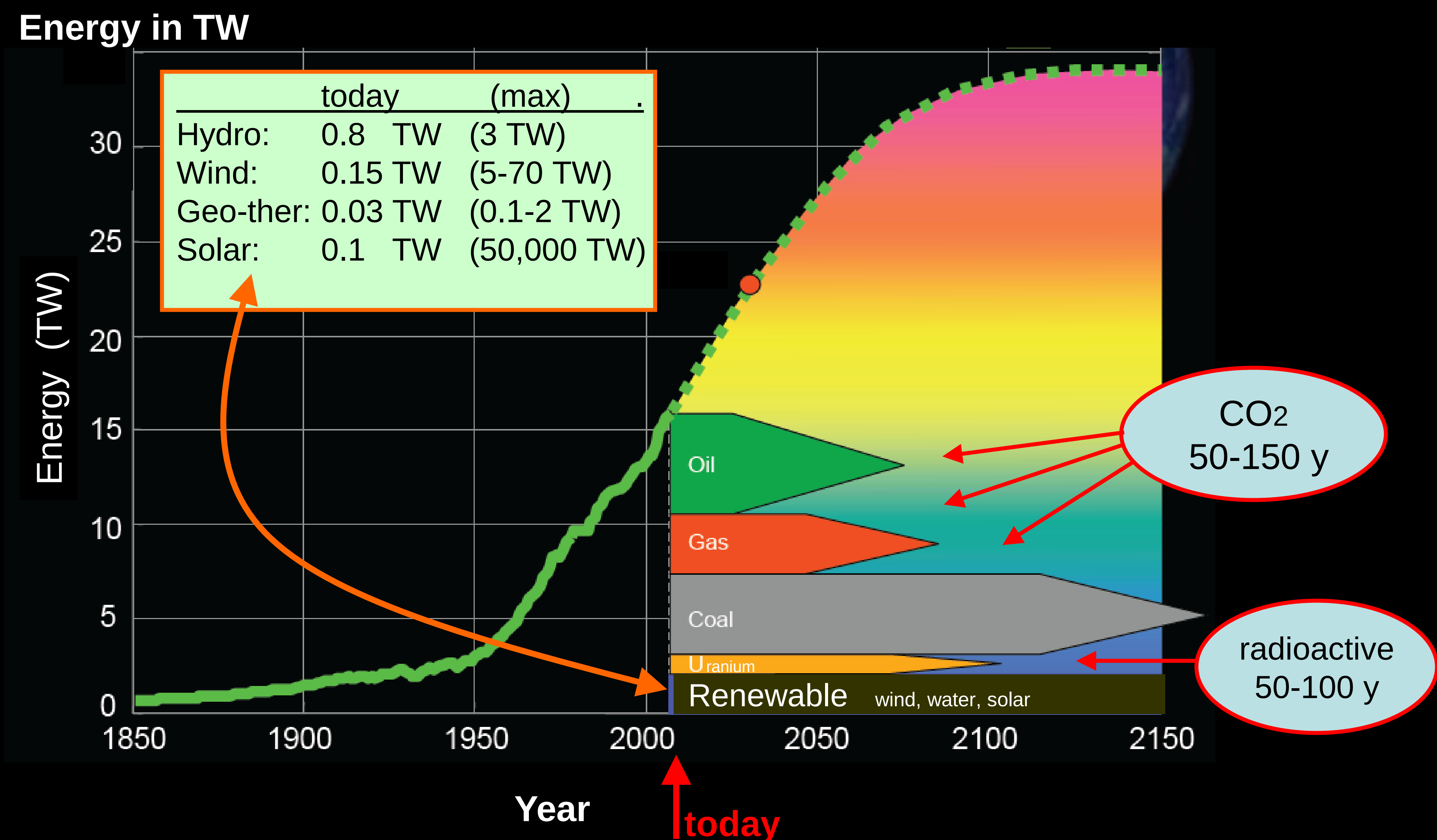
0ne reactor ~1 GW

~30,000 nuclear reactors
(today ~450 reactors)

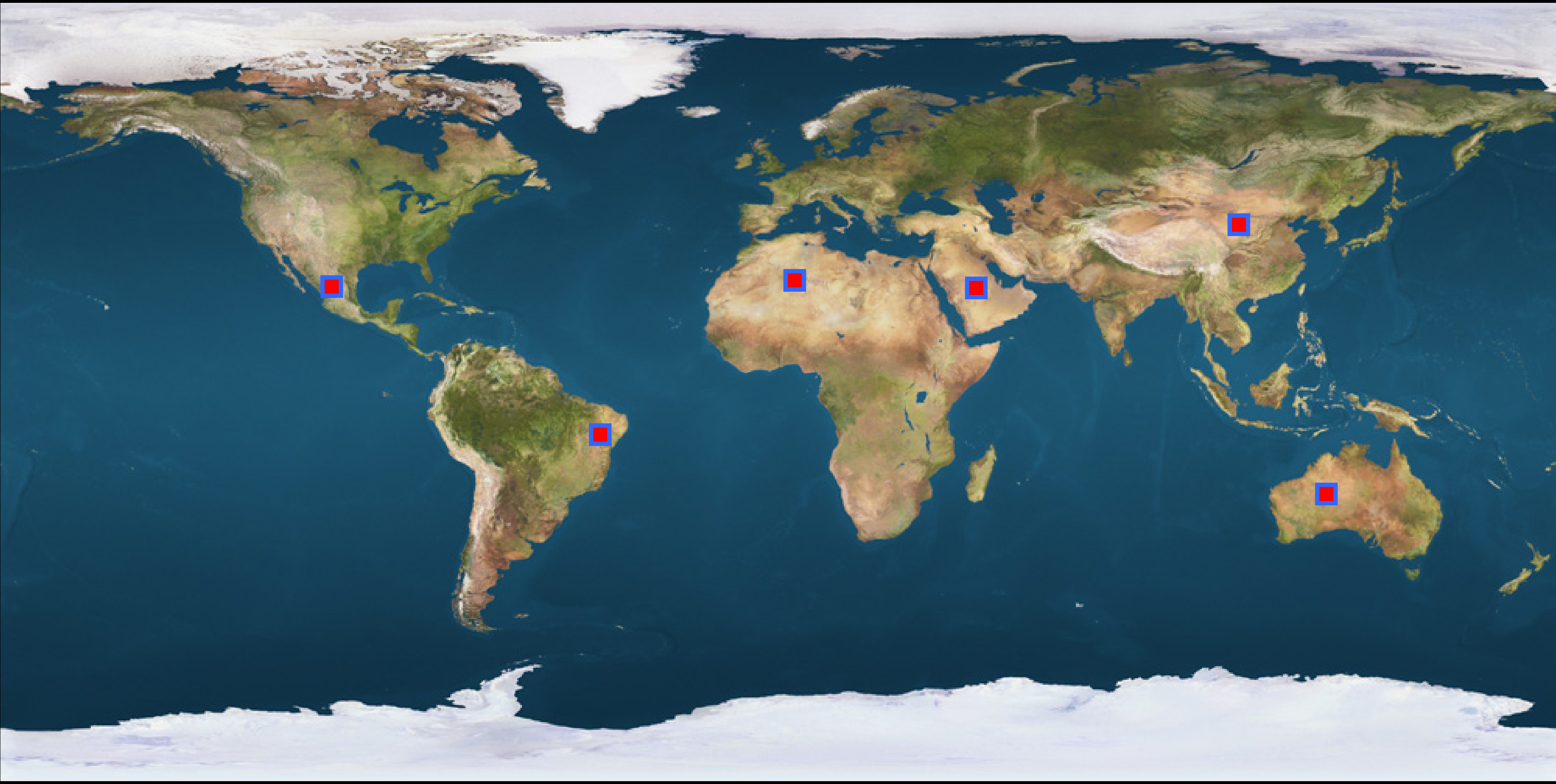
..... 2 new reactors every day over 40y !!

Different alternatives

We will need ~**30 TW** in 2050



Required land area



Six power plants can cover our need:
500 x 500 km^2 each
Problem is distribution, losses and starage

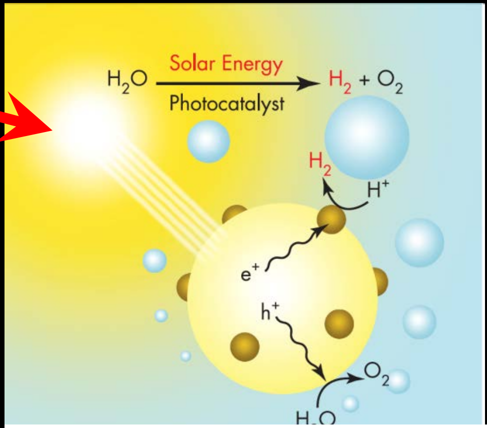
Average sunlight power:
~1 kW/m^2

3 types of solar-energy technologies

1. **Solar-thermal**
   heat water

Power tower in California: 10 MW Steam engine

2. **Solar-chemical**
   H_2 from split of water



mimic photo-catalyst reaction

3. **Solar-electricity**
   photovoltaics
   or solar cells

~5 kW roof top system

What will each person need in 2050 ?

Sunlight power: ~1 kW/m^2

Each person ~3 kW
that is, ~3 m^2 solar cell

In addition, we need
energy storage, ie, batteries !

3rd/4th Generation of Photovoltaic Cells

Low-cost and high-efficient solar-cell modules

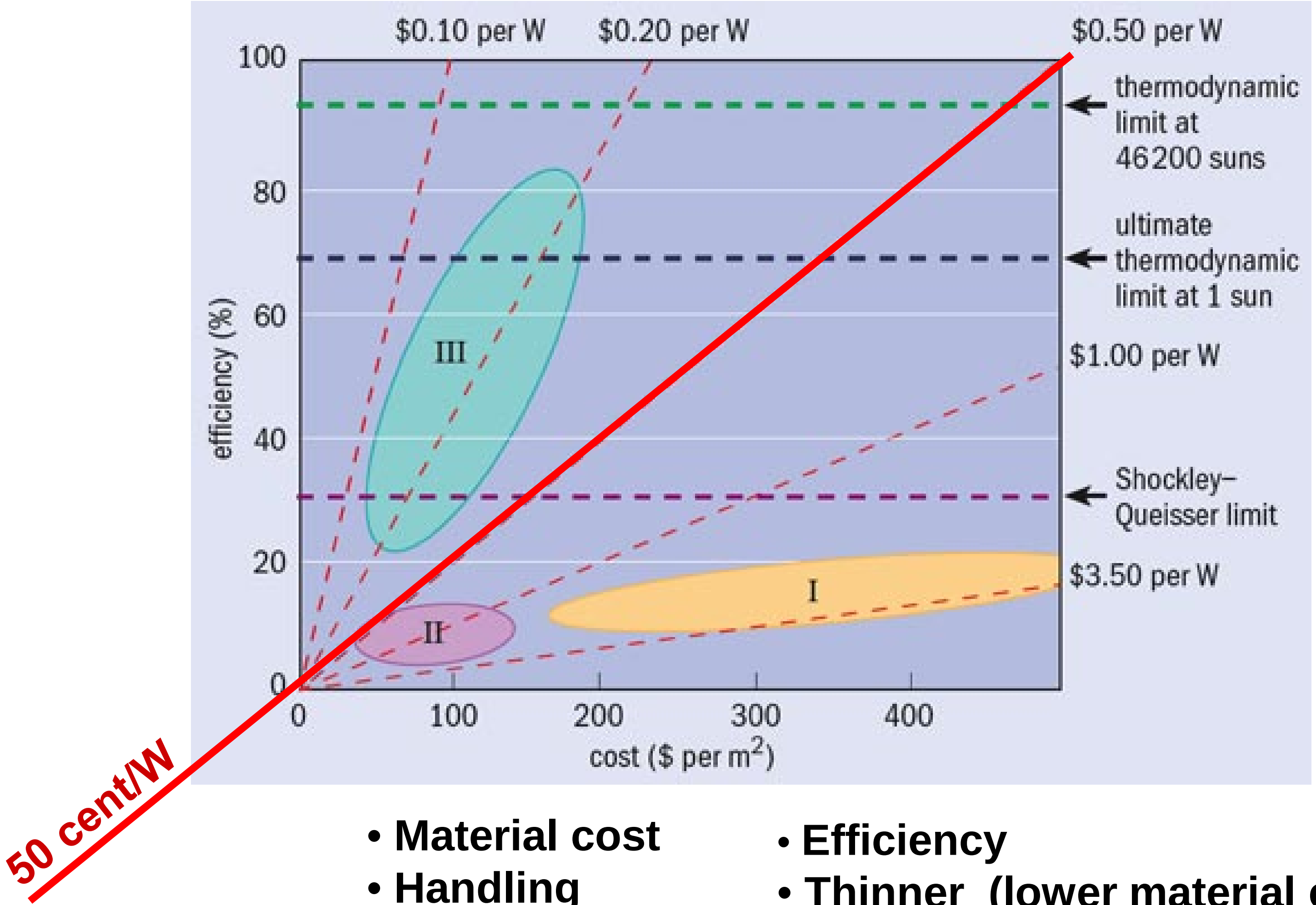
- High device efficiency: **n = output electric power / input sunlight**

- Low material costs
- Low degradation => Longer life-time of the solar cell panels
- Cost-efficient processing,manufacturing, development, handling
- Low installation costs

- Earth-abundant materials
- Non-toxic elements
- Environment friendly production

3rd generation solar cells

Martin Green, 3rd Generation PV, Springer-Verlag, Berlin, (2003).

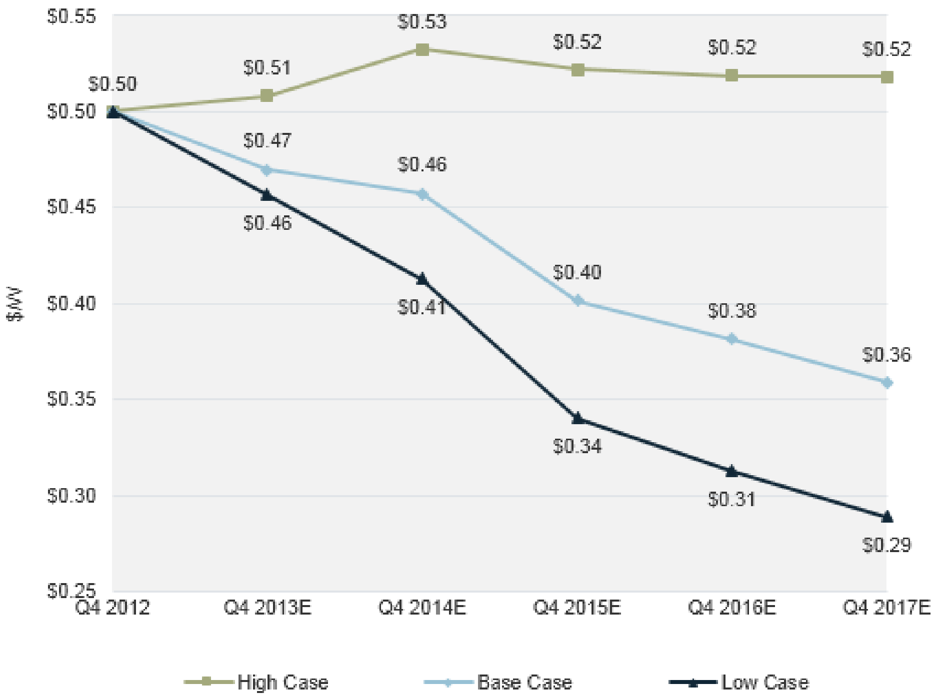


- Material cost
- Handling
- Processing
- Fabrication
- Packing
- Installation

- Efficiency
- Thinner (lower material costs)
- Crystal and device stability
  => better lifetime (cost to replace)

Module Cost Outlook: 36 cents/W in 2017

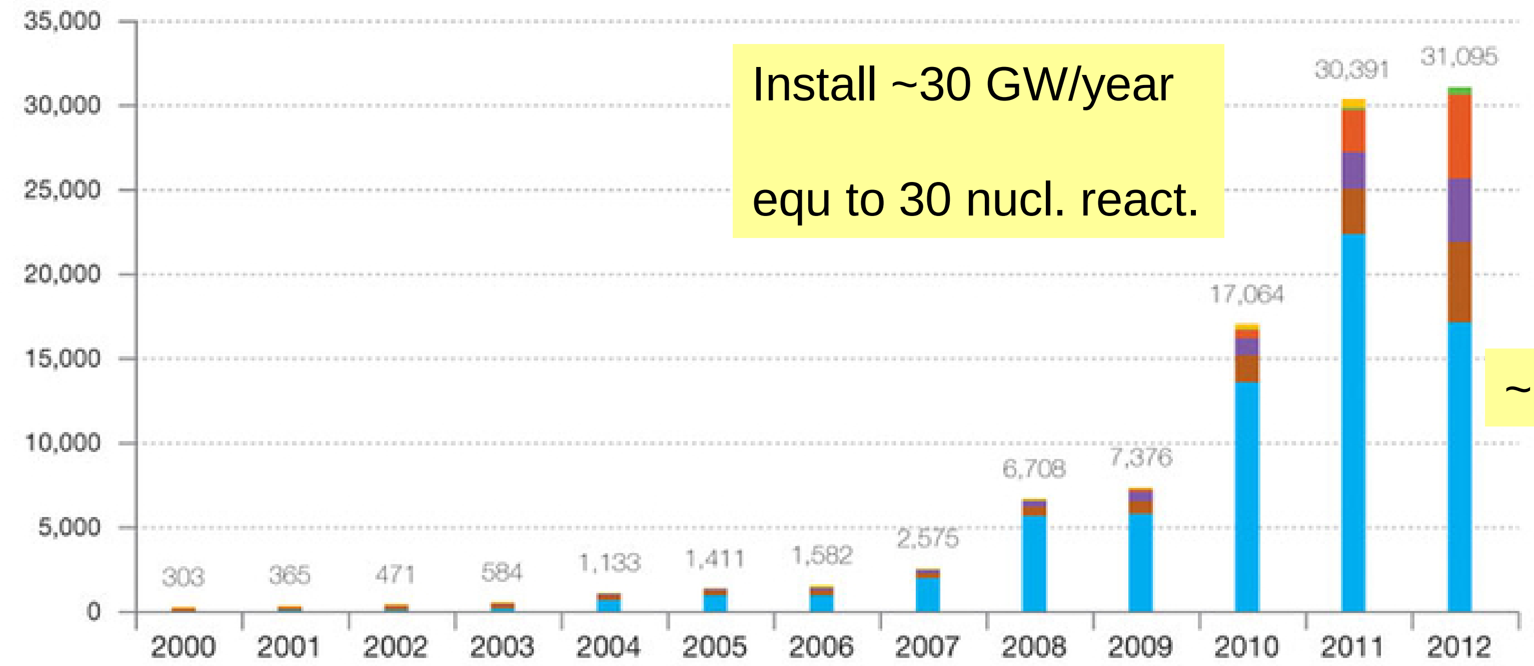
Cost $/Watt



GTM Research, June 2013
Source: *PV Technology and Cost Outlook, 2013-2017*

Primary Category	Secondary Category	Historical Trend (2009-2012)	Base Case Forecast (2013-2017)
Technology Parameters	Conversion Efficiency (Module)	Average increase of 0.2% absolute per year	0.2% annual increase through 2017 to 16.2%
	Wafer Thickness	180 micron (2009-2012)	Drops to 160 micron in 2015
	Kerf (Sawing) Loss	160 micron (2009-2011) to 145 micron (2012)	Drops to 120 micron in 2015
	Cell-to-Module Loss	Average annual increase of 0.1% absolute	Average annual increase of 0.1% absolute
Capital Equipment Cost	Capex per Watt (Ingot-to-Module)	Annualized decline of 21%	Flat from 2012-2014; increases by 21% in 2015 due to increased automation to counter labor rate
Consumables Pricing	Polysilicon	Dropped from $80/kg (Q4 2009) to $18/kg (Q1 2013) - annualized decline of ~40%	Increases to $22/kg by 2014 and then declines to $18/kg by 2017
	Metallization Paste	Increased from $700/kg in 2010 to $1900/kg in mid-2011, dropped to $1000/kg currently	Increases by 5% annually
	Other Consumables	~25-30% annualized decline (wafer), 15-25% decline (module)	Declines by 5% annually
Consumption Efficiency	Silicon	8% annualized decline to 5.3g/W by Q4 2012	6% annualized decline to 4.1g/W in 2017
	Electricity (Ingot)	4% annual average decline	1% annual average decline
	Wafer Slurry	3% annual average decline	17% reduction in 2015 with adoption of thinner sawing wire, flat thereafter (2% annualized decline)
	Silver	20% annual average decline	4% annual decline
Labor	Labor Rates	~10% annual increase	~10% annual increase
	Labor Intensity	3% annual decline due to increases in tool throughput and conversion efficiency	25% reduction from 2014-2015 due to increased automation
Manufacturing Scale	Plant Capacity	Increased by ~700 MW annually to 2.5 GW in 2012	Increase by 500 MW annually to 5 GW by 2017

Evolution of global PV annual installations 2000-2012 (MW)



Install ~30 GW/year

equ to 30 nucl. react.

~50% in Europe

	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
ROW	88	56	80	77	29	10	105	42	76	80	284	508	-*
MEA	n/a	n/a	n/a	n/a	1	n/a	n/a	1	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
China	19	5	19	10	10	8	10	20	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Americas	24	32	47	66	104	106	150	213	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
APAC	117	140	191	230	282	303	324	271	535	742	1,583	2,672	4,769
Europe	56	133	135	202	707	984	992	2,028	5,710	5,830	13,622	22,411	17,159
Total	303	365	471	584	1,133	1,411	1,582	2,575	6,708	7,376	17,064	30,391	31,095

We need 30 TW effect,
Thus ×25 more PV installation

* From 2012 onwards, these figures are directly integrated into those of the relevant regions.

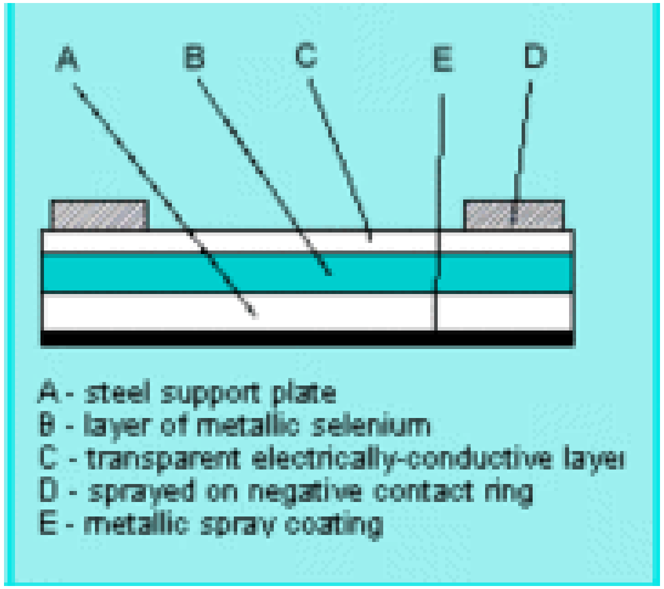
Source: EPIA, "Global Market Outlook for Photovoltaics 2013-2017", 2013

History

PV = Photo+voltaic = convert light to electricity

1839: A. E. Becquerel first recognized photovoltaic effect.

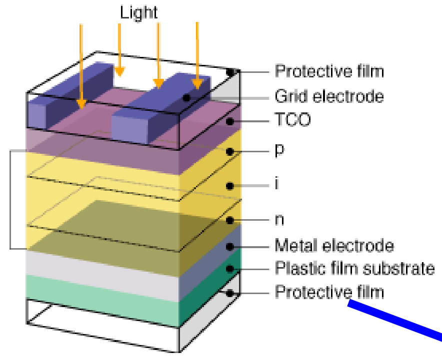
1883: First solar cell built, by Charles Fritts, gold-coated selenium.



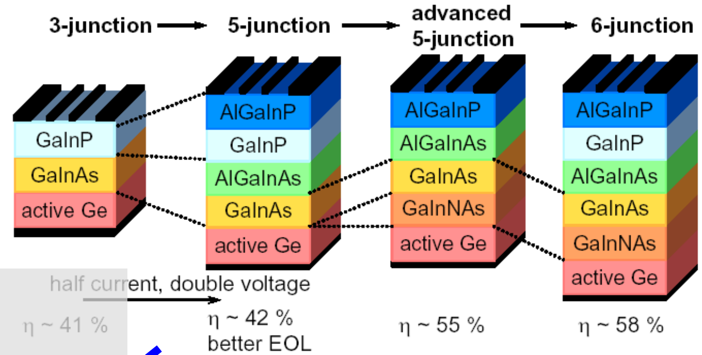
1941: First silicon-based solar cell demonstrated, by Russell Ohl (70y ago)

2013: Crystalline Si is dominating (80% market).

Future: More thin-film technologies ?



SANYO, Amorton

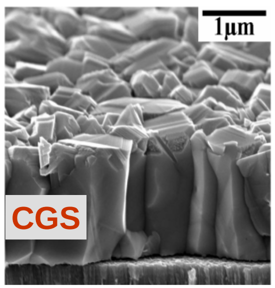


AW Bett ,Fraunhofer Inst, Freiburg

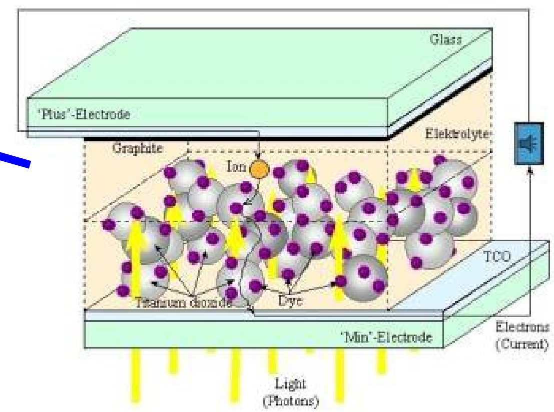
combinations of

1. crystalline Si (n ≈ 30%)
2. Thin-film solar cell (~20%)
3. Multi-junction solar cells (~40%)

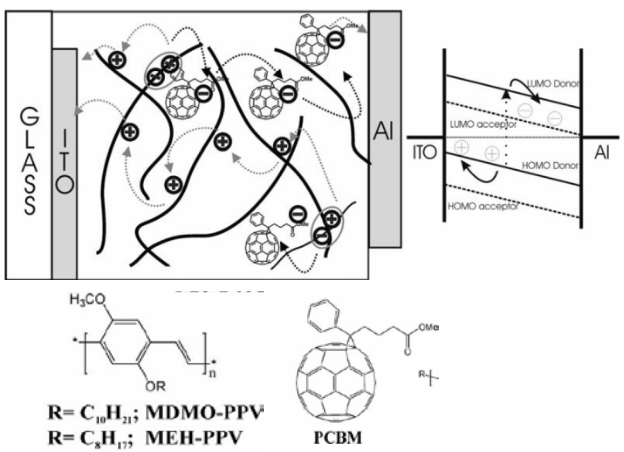
4. Dye-sensitized solar cells (~10%)
   Polymer solar cells
   Nanocrystal solar cells

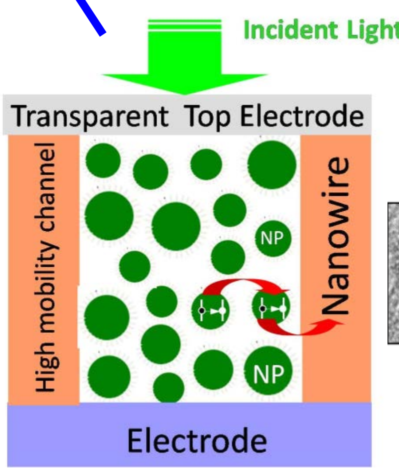


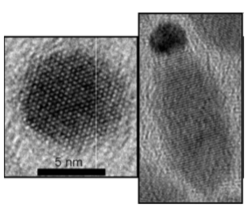
S. Schuler, *et al*. 29th IEEE PV Conf.(2002)



Man Solar, Petten



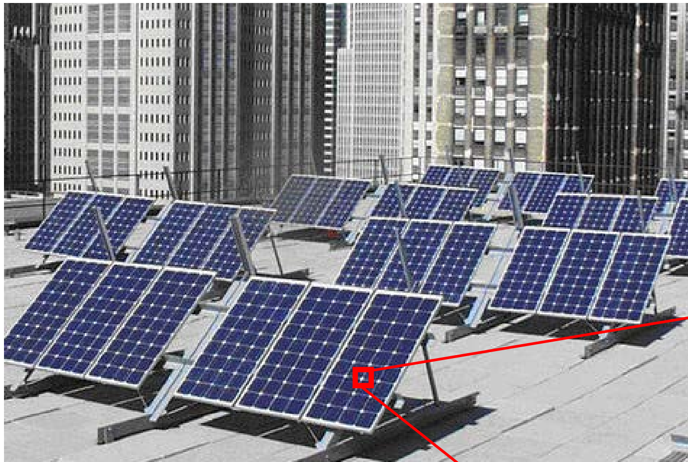


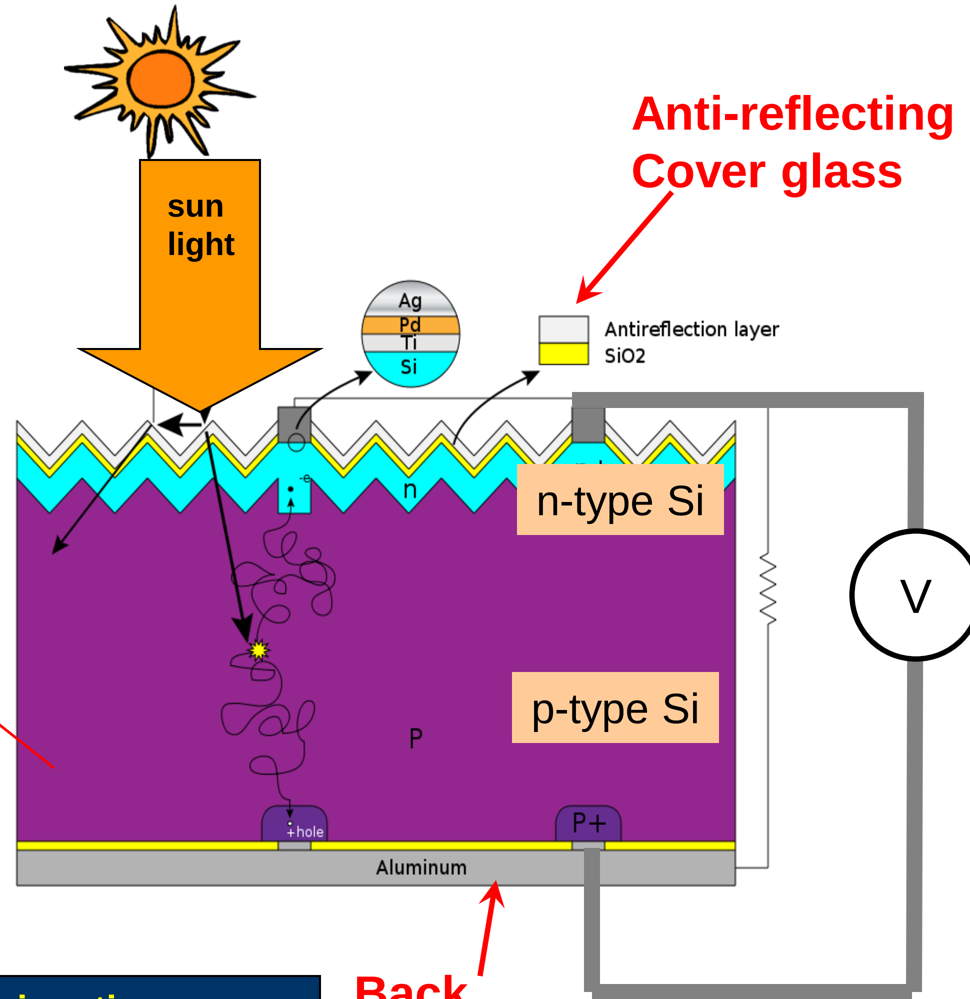


Nanostructure Materials & Devices Laboratory, USC

#1 Crystalline Si

~80% of solar cell market





Anti-reflecting & Cover glass

Back contact

200 µm

thick device

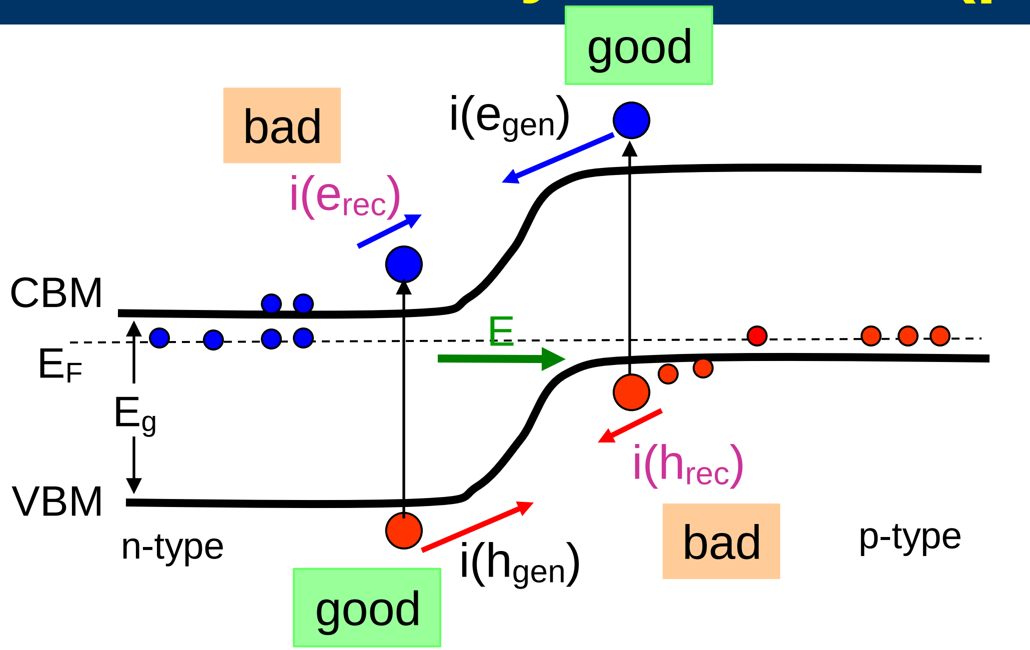
Sun light λ~0.5 µm
Hair ~75 µm

Si Eg ~ 1.1 eV

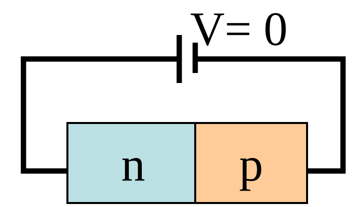
Transport via pn-junctions

- Good efficiency (25 %)
- Expensive since thick device

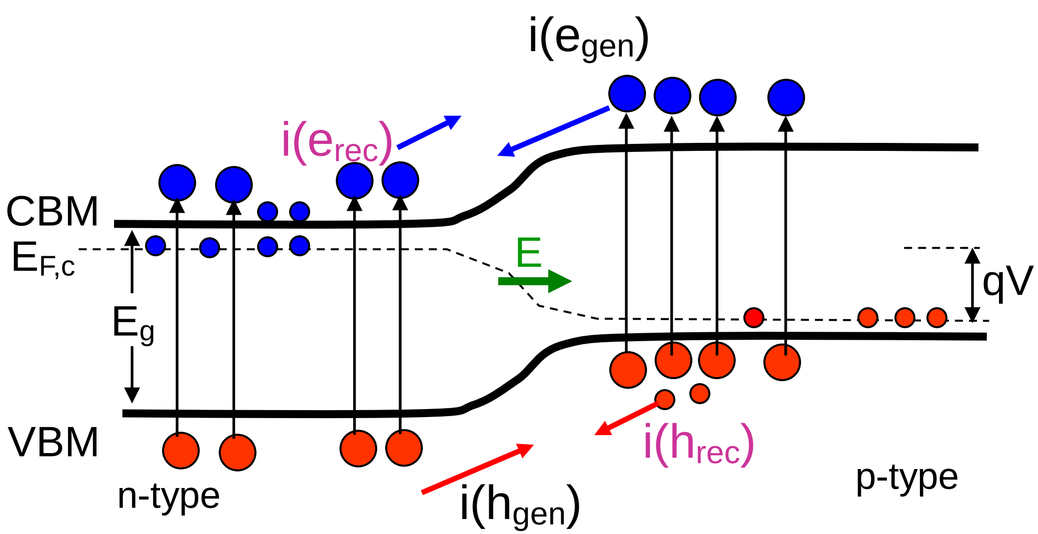
#1 Crystalline Si (pn-junction)



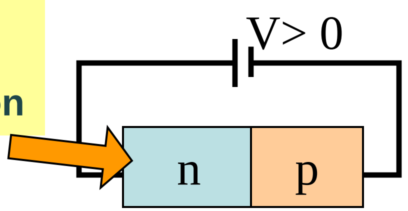
T >> 0
V = 0



$i(e_{gen})$ due to E-field
$i(e_{rec})$ due to entropy (dn/dx)



T >> 0
V > 0
illumination



$i(e_{gen})$ due to E-field
$i(e_{rec})$ due to entropy (dn/dx)
$i(e_{gen})$ from light absorption
P = V * I

#1 Crystalline Si

Two main problems with c-Si

1) 200 μm thick:
   Much material, and c-Si is costly to produce

2) band 1.1 eV
   Not optimized band gap

#2 Thin-film Si

a-Si (or a-Si:Hi); amorphous silicon,

Low processing temperature (lower cost)

Eg = 1.7 eV, better absorber => thinner cell (~1 μm thin)

But much less efficiency (~10%) compared to c-Si (~30%).

nc-Si (microcrystalline Si)

Low processing temperature, but Eg = 1.1 eV

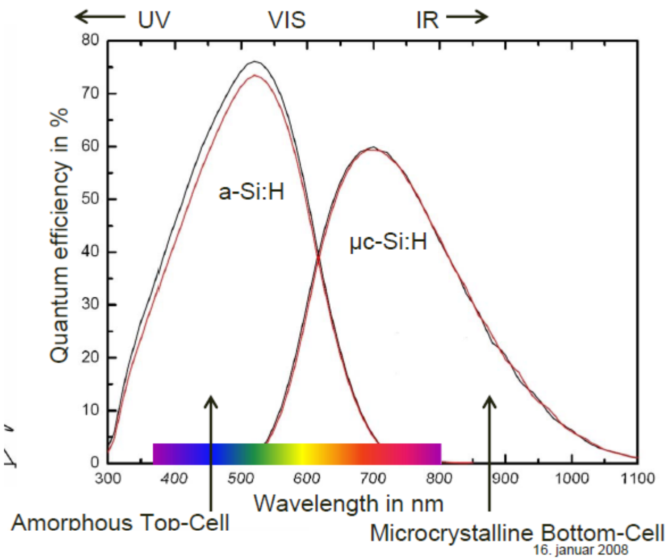
Improved material quality over a-Si

1.8 μm thin with 10.7% efficiency (EPFL Inst of Microengineering, Feb 2013)

a-Si + nc-Si; micromorphous

Eg = 1.1 and 1.7

=> broader abs. spectrum



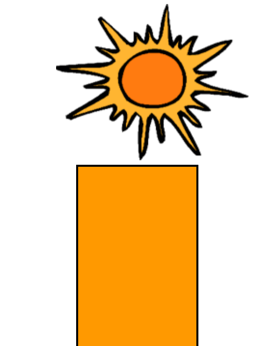
NorSun and Sunfilm; C: Rohr 2008

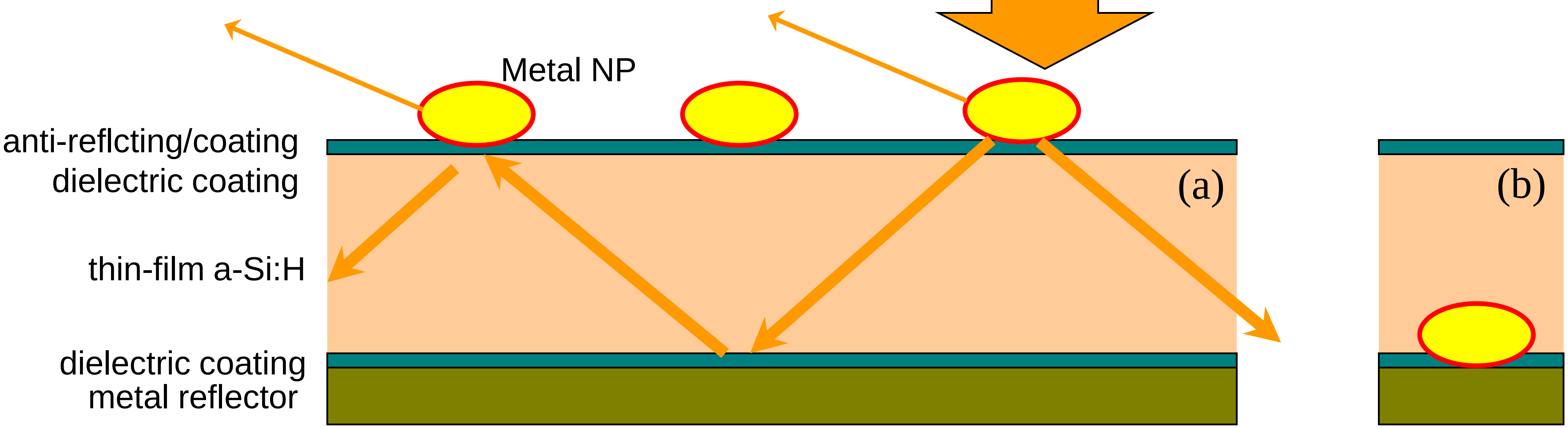
#1 Plasmonic solar cells (thin film)

a-Si, coated with metal nanoparticles

1-2 μm thick and ~20 nm metal NP

disadvantages are low absorption and heat generation

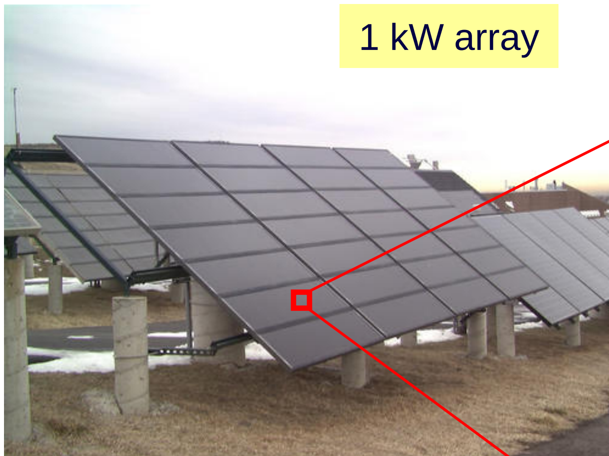




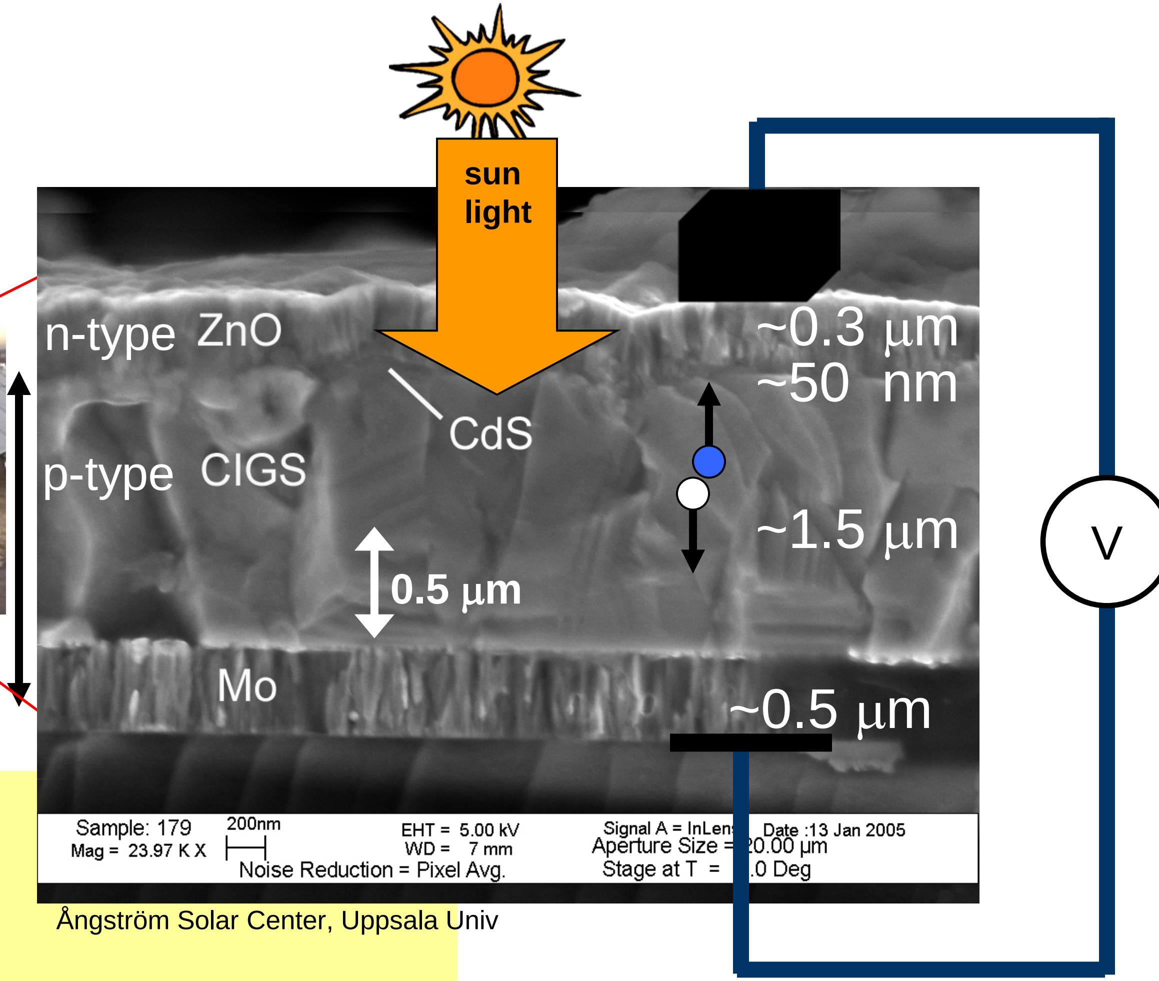
Light scatters through surface plasmon resonance, and get trapped inside a-Si layer. >90% of light can be trapped.

Surface plasmon = collective electron vibration

#2 Other thin-film pn-junction



NREL, USA



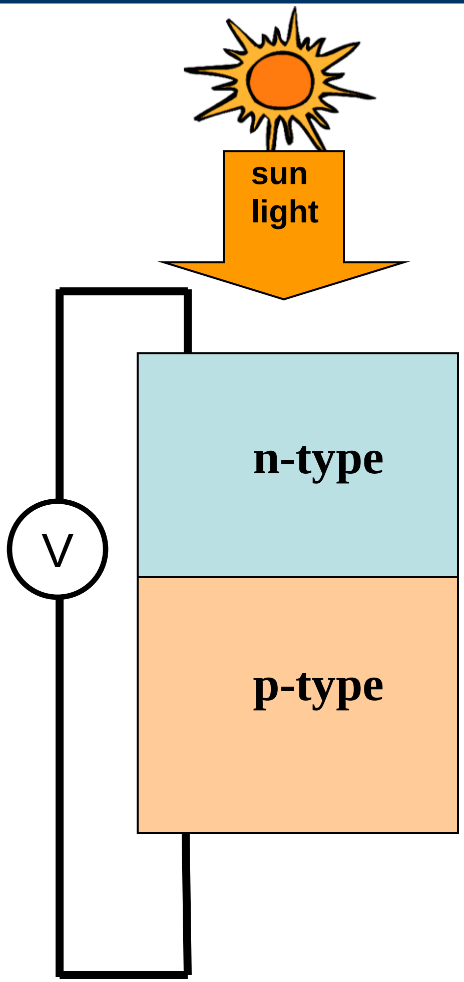
Ångström Solar Center, Uppsala Univ

a-Si Eg ~ 1.7 eV
CdTe (toxic) Eg ~ 1.5 eV
GaAs (expens) Eg ~ 1.5 eV
$CuIn_{1-x}Ga_xSe_2$ Eg ~ 1.3 eV
higher efficiency (20%) than thin-film a-Si (10%)
In is expensive; Se is toxic.
Cu_2ZnSnS_4 Eg ~ 1.5 eV

Transport via pn-junction

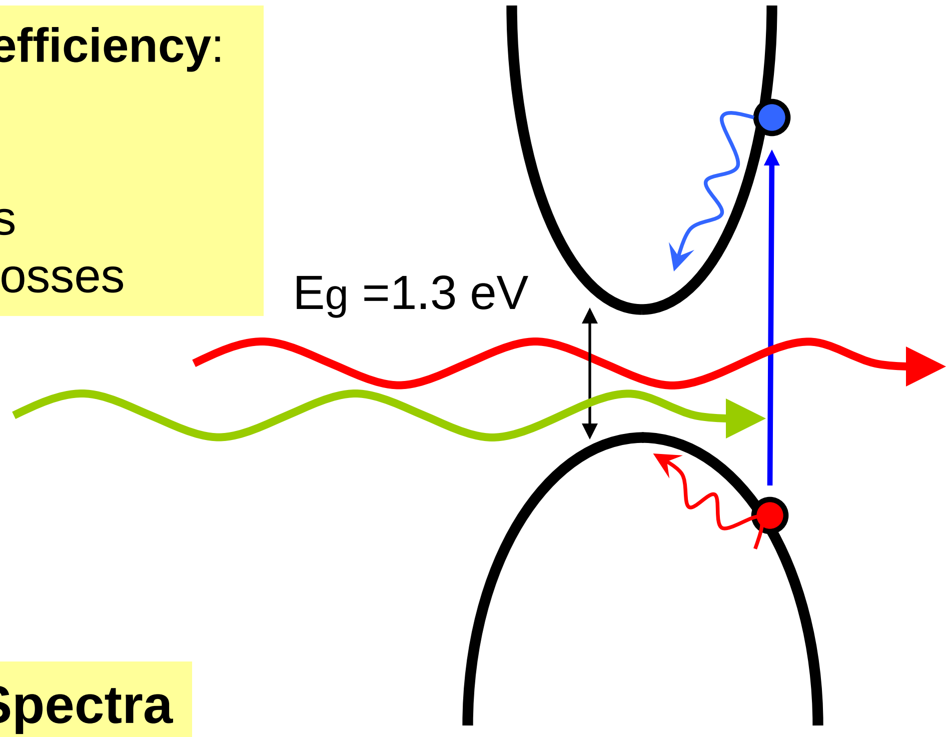
- Good efficiency (20 %)
- Medium expensive
- Long life-time

Two problems with traditional solar cells



Single-junction efficiency:
Theo. max ~31%

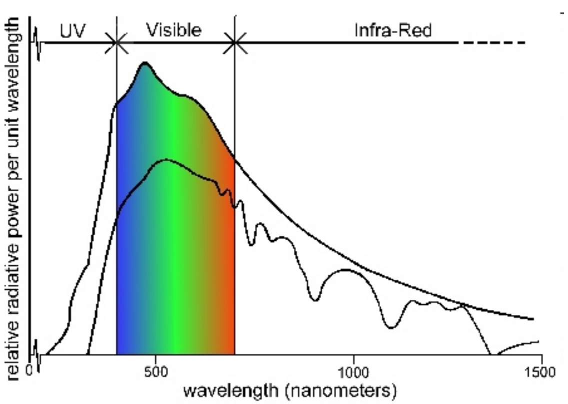
* Below-Eg losses
* Thermalization losses



Sunlight Spectra

~800 to 400 nm
~1.0 to 3.5 eV

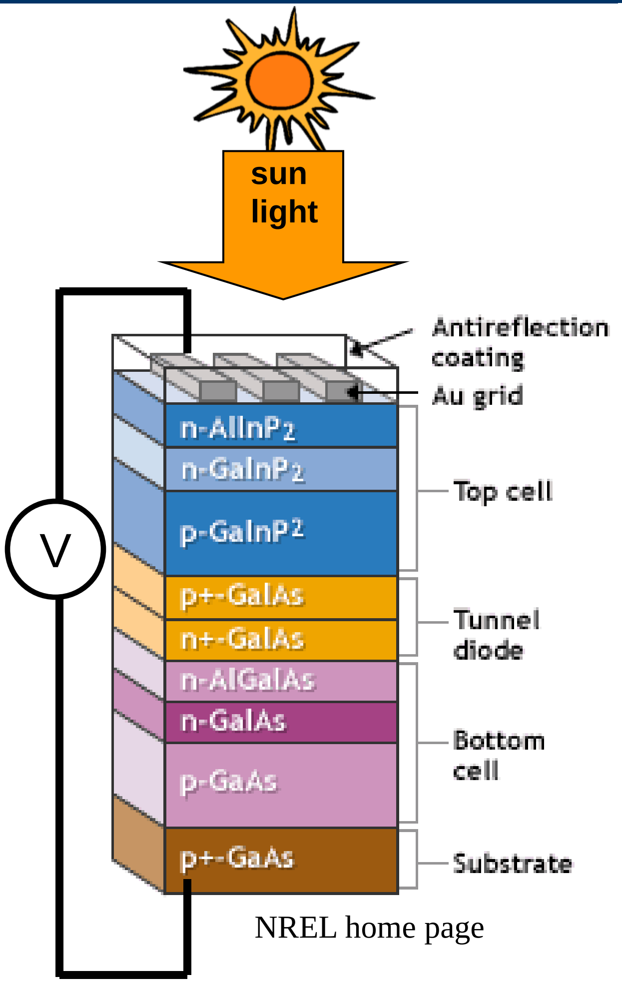
550 nm ~ 2.2 eV



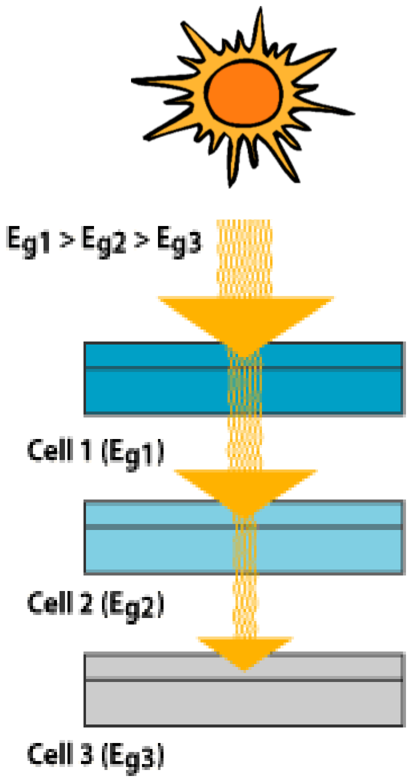
#3 Thin-film multi-junction (40%)

Ga-based 0.7< Eb < 2.0 eV

High efficiency, >50%
but expensive



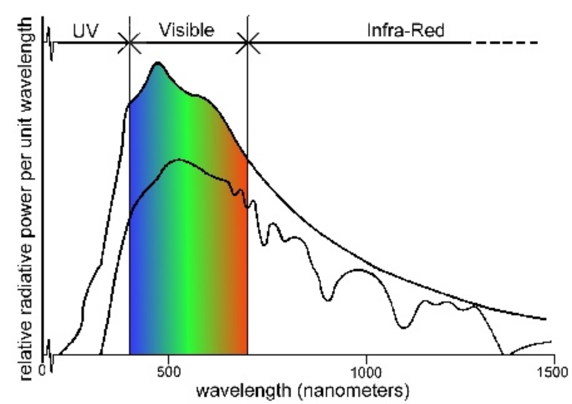
NREL home page



pn-junction **#1:** **E > 2.0 eV**

pn-junction **#2:** **E > 1.5 eV**

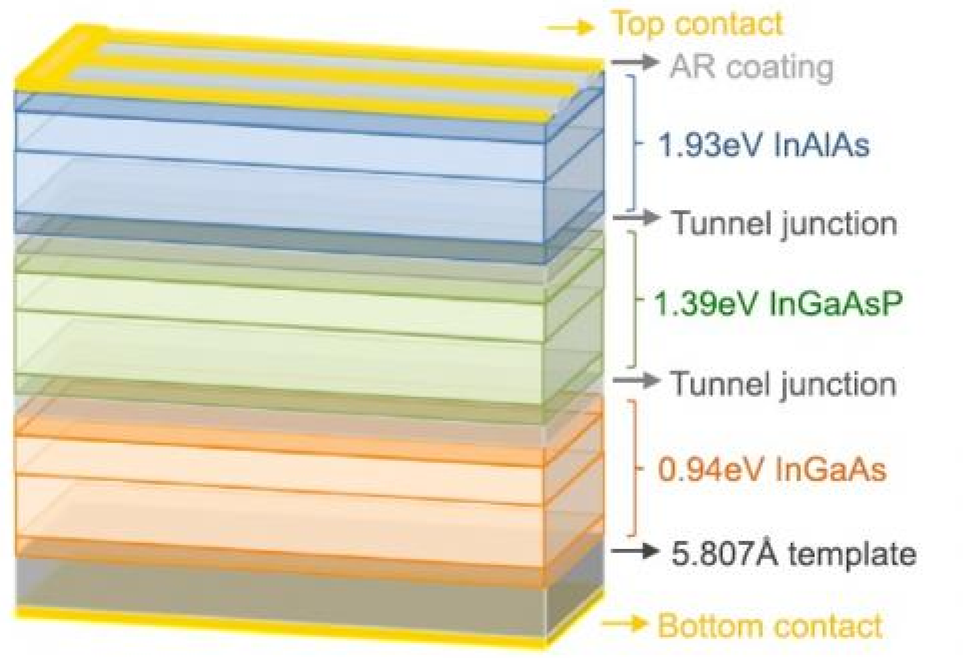
pn-junction **#3:** **E > 1.0 eV**



Transport via pn-junctions

- High efficiency (>50 %)
- Expensive
- Lattice matching

Multi-junction cell, InGaAs-based
52% efficiency in 2013 for 3-junction cell



Marina S. Leite, et al. APL, 102, 033901 (2013)

Theoretical limit

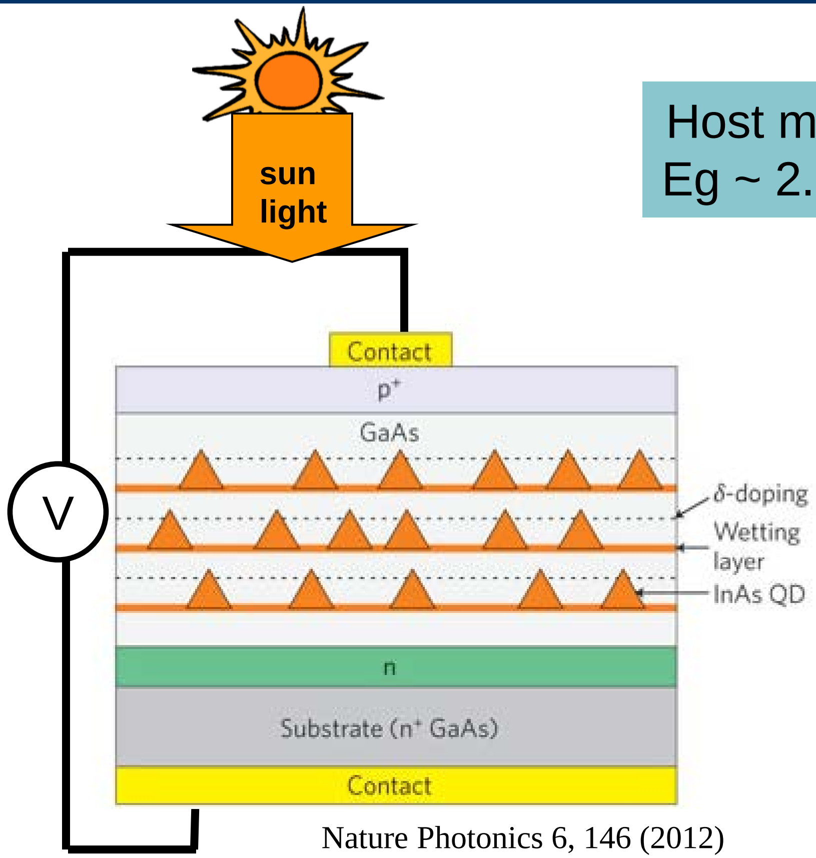
31 % for single junction.

50% for 2-junction,
56% for 3-junction,

86% for infinite-junction

Indium is expensive

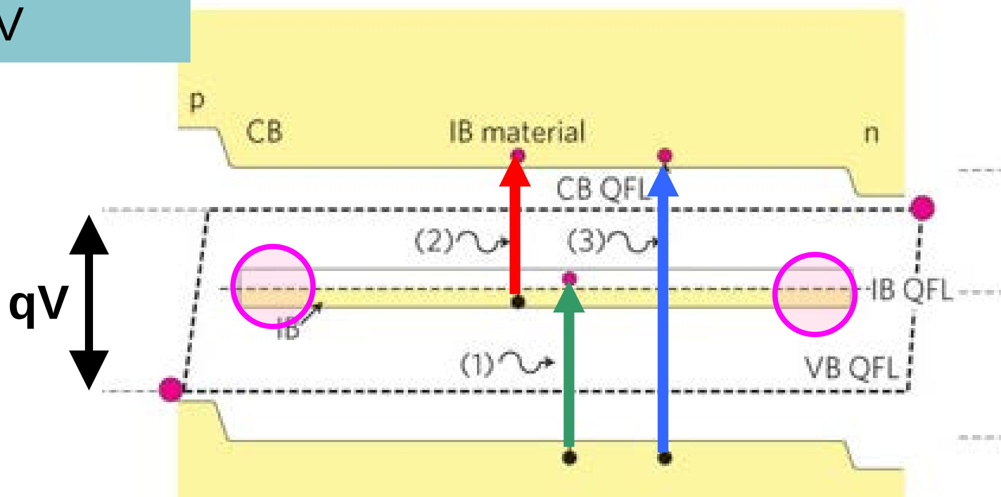
Thin-film intermediate band (future)



Nature Photonics 6, 146 (2012)

Host material with
Eg ~ 2.0 eV

Luque and Martí, PRL 78, 5014 (1997)

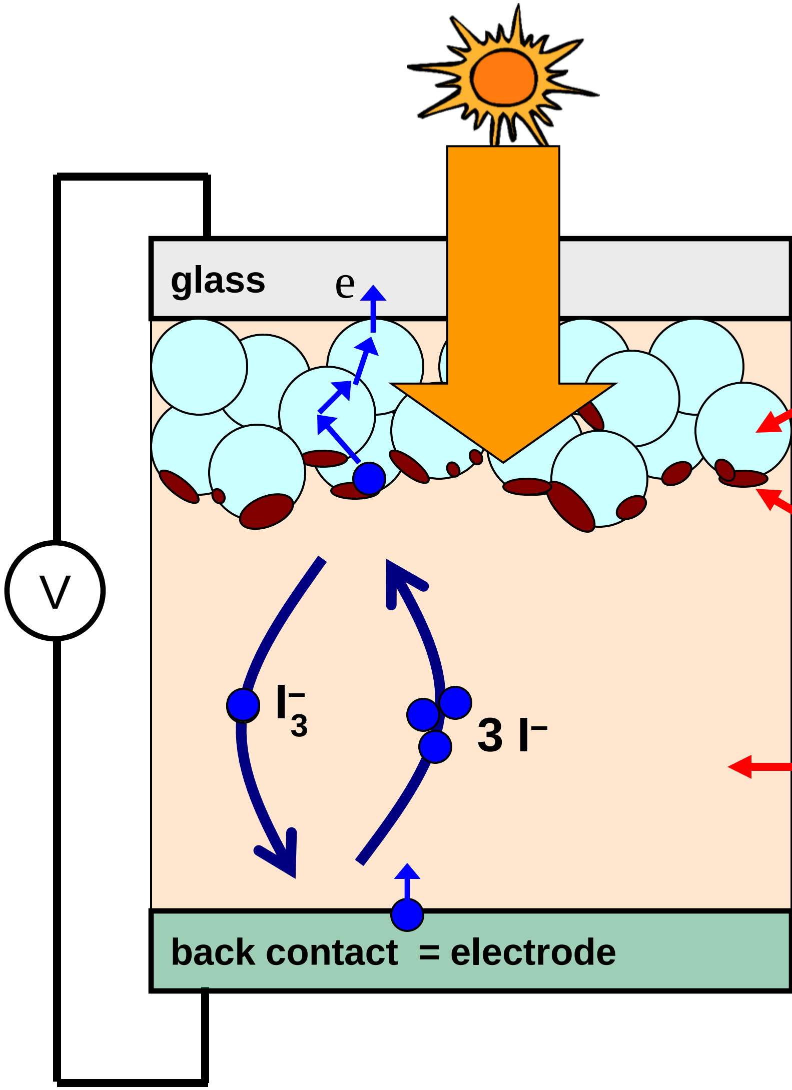


Single-junction, but IB helps absorbing different energies
Optimum: Eg = 0.7, 1.2, and 2.0 eV

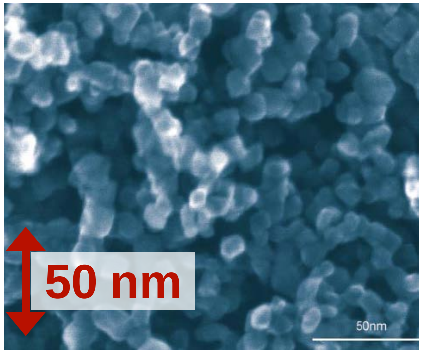
- n ~ 55% (theo), instead of ~31% for single gap cell
- low absorption in QD,
- Extra non-radiative recomb
- difficult to realize a half-filled band wi no tunneling, and ackummulation in IB
- Band (not defect level) to avoid SRH-recomb.

ZnTe:O
50% increase in power conversion efficiency
Wang et. al, APL 95, 011103 (2009)

#4. Dye-sensitized solar cell (O'Regan and Grätzel, 1991)



NP-TiO_2
transparent and good e^- conductor, through diffusion



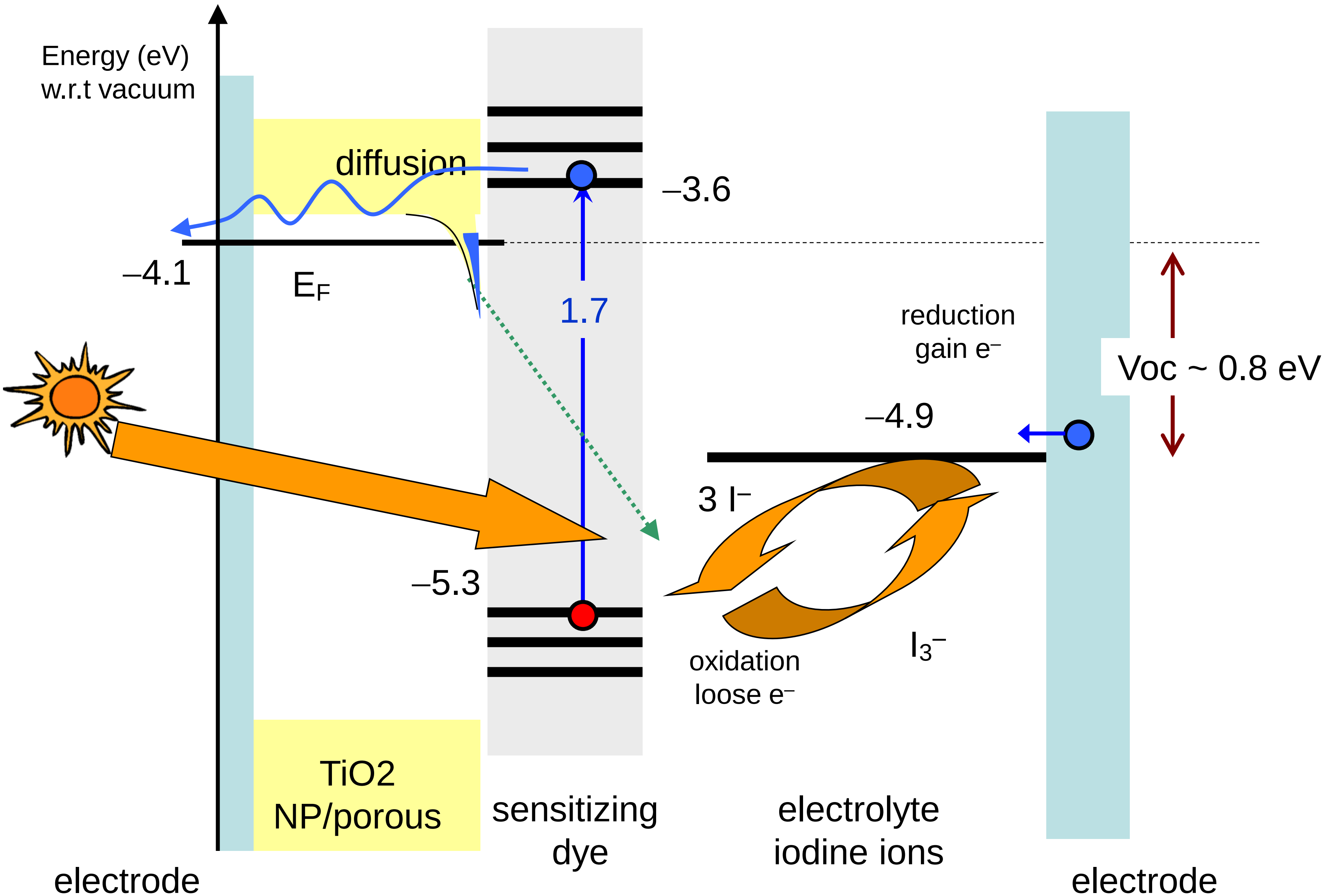
SEM: mesoporous anatase TiO_2
M. Grätzel, Nature, **414**, 338 (2001).

dye film (Ru-based)
good absorber

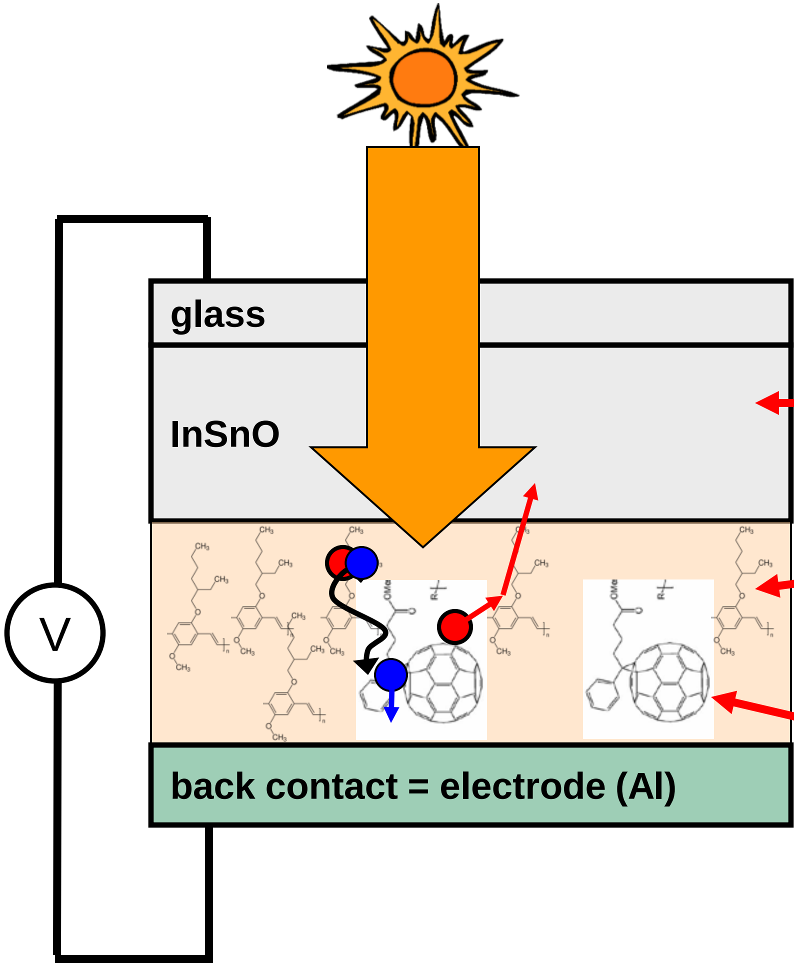
electrolyte
iodine ions

Transport via electrolyte

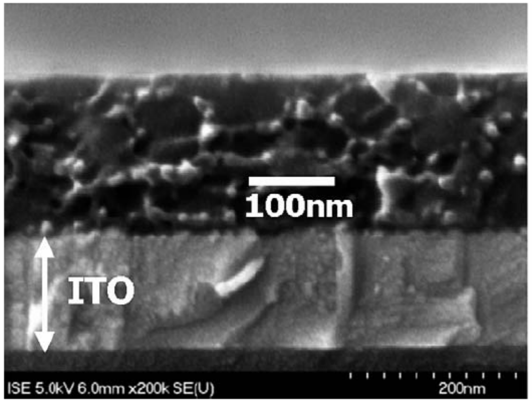
- Inexpensive,
- Slow diffusion in NP-TiO2
- Reasonable efficiency (15 %)
- Degradation and instability


Energy (eV)
w.r.t vacuum
diffusion
–3.6
–4.1
E_F
1.7
reduction
gain e⁻
Voc ~ 0.8 eV
–4.9
3 I⁻
–5.3
I_3^-
oxidation
loose e⁻
TiO2
NP/porous
sensitizing
dye
electrolyte
iodine ions
electrode
electrode

#4 Organic solar cells



ITO / TiO_2
transparent and
good e^- conductor



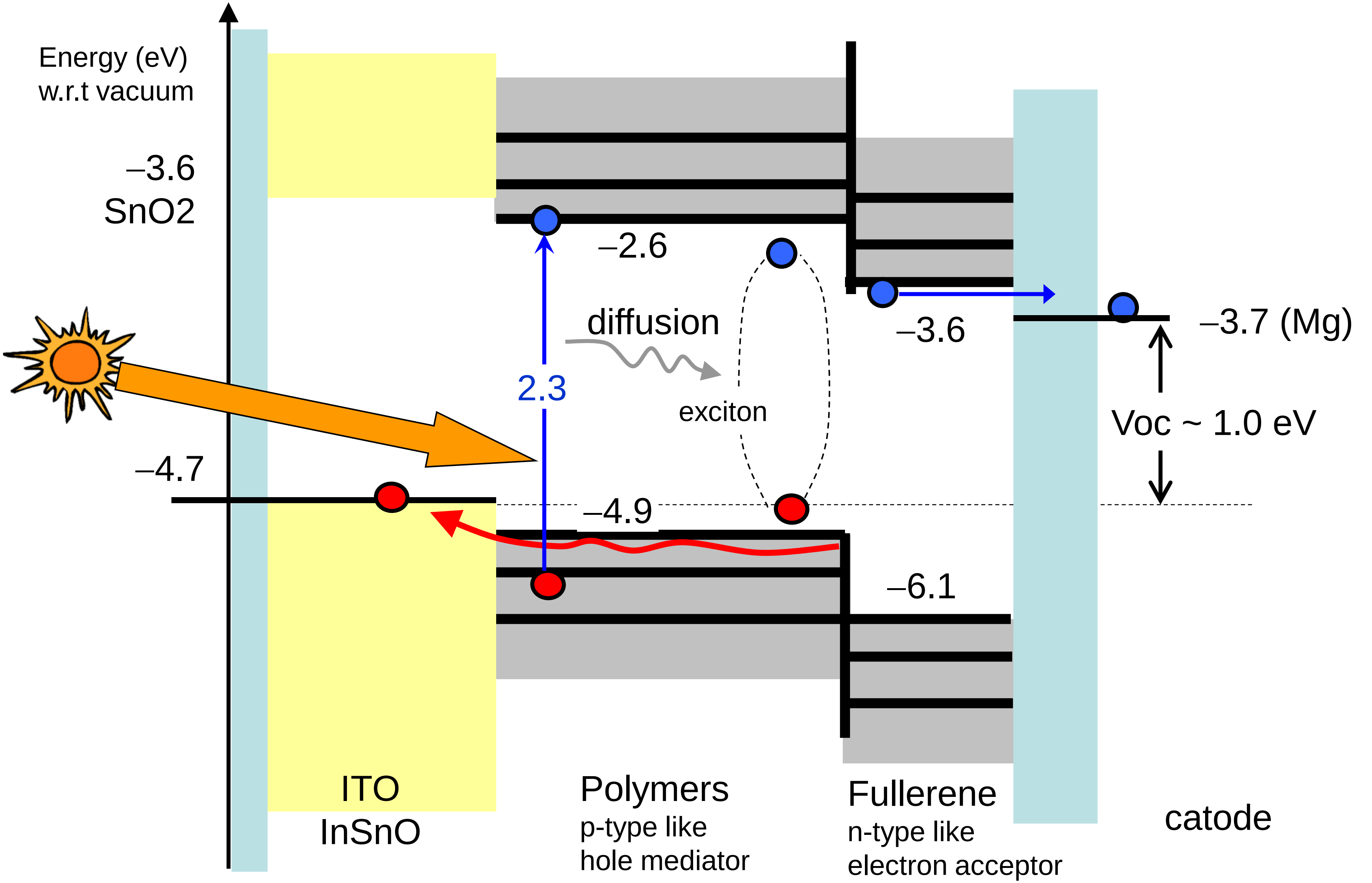
SEM images of MDMO-PPV/PCBM
Mozer, CR Chimie, **9**, 568 (2006).

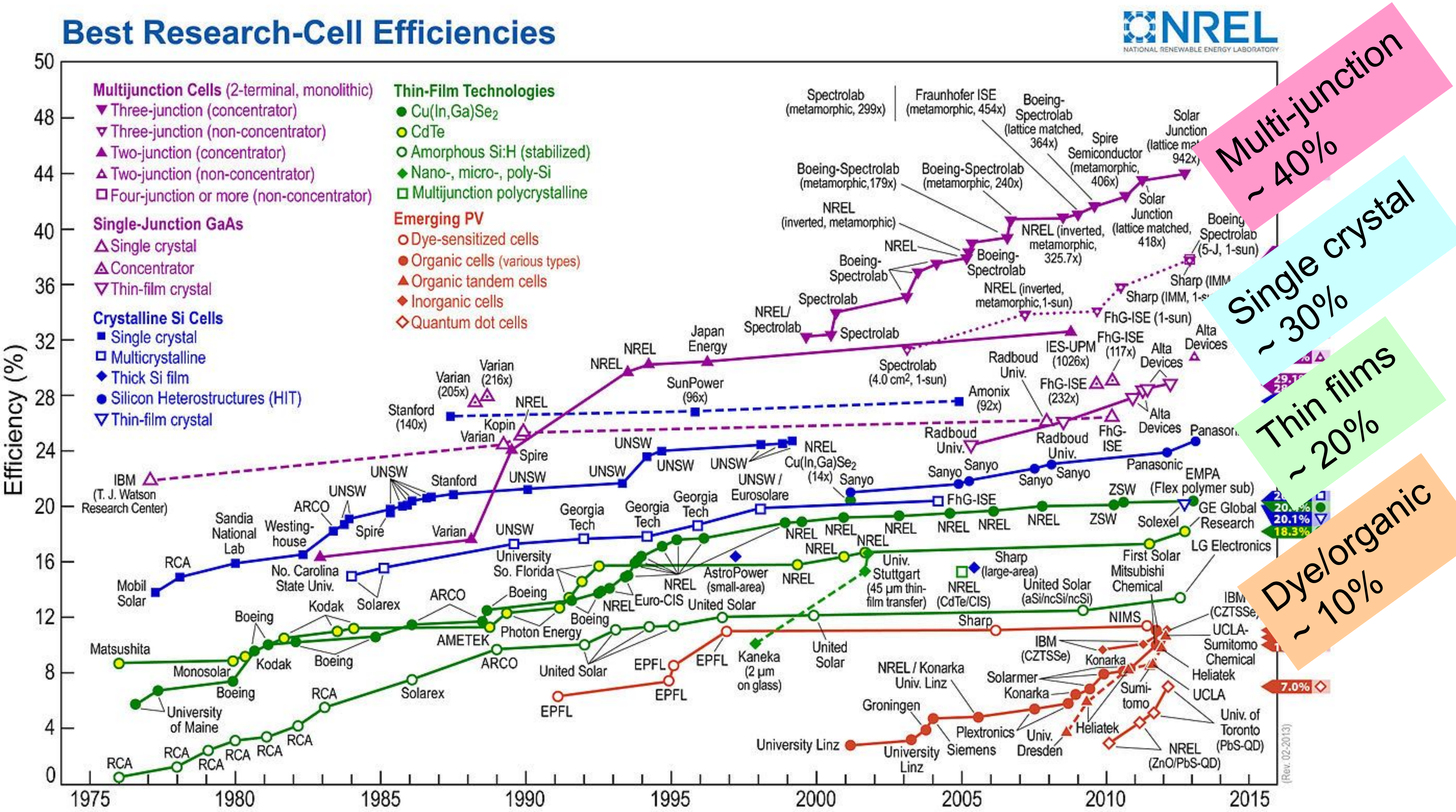
Polymers (donor)
Easy to vary gap 1-4 eV, good e-conductor;
Localizes e and h.
Absorb, confine, and transport e-h excitons

Fullerene (acceptor)
Dissocioation, good e-conductor

Transport via diffusion
e-h diffusion lenght ~10nm
(needs 100nm for absorption)

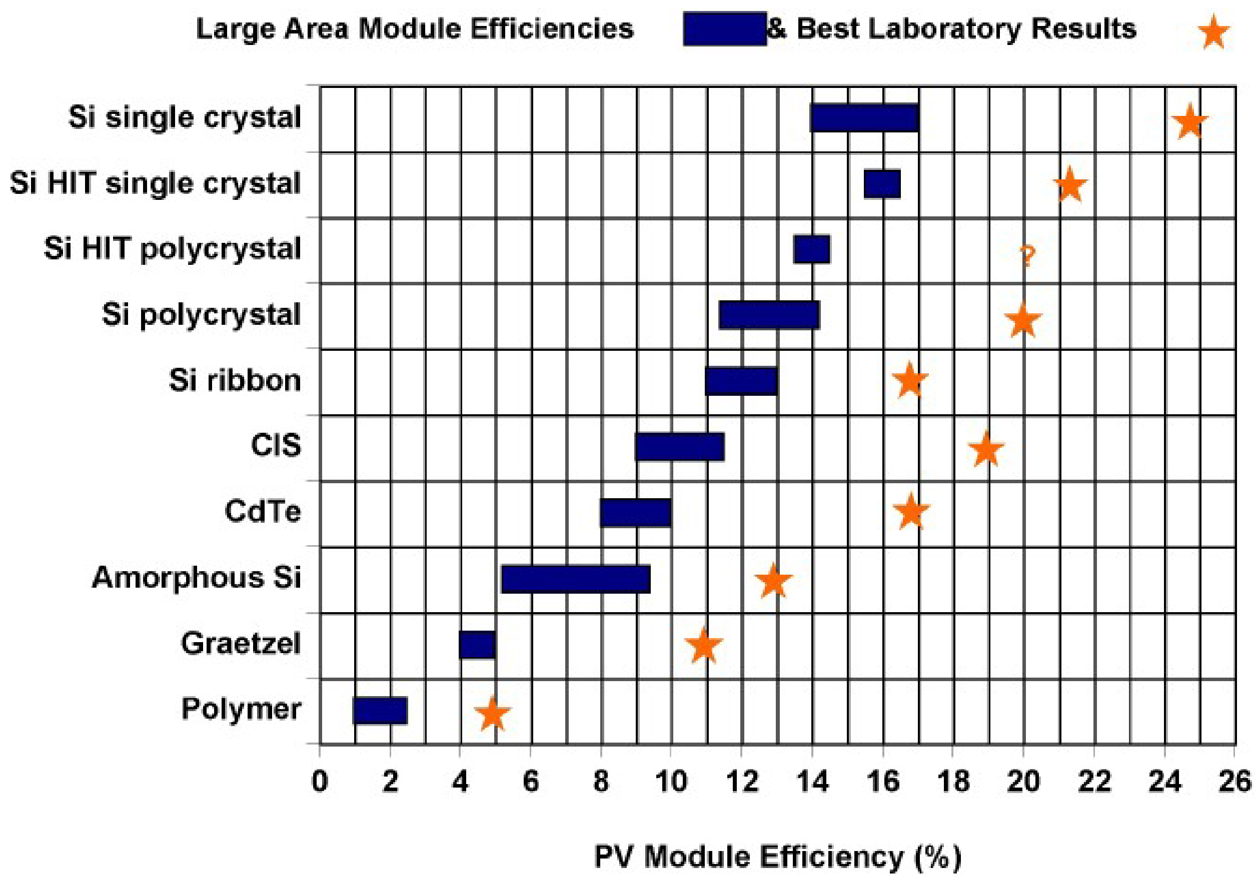
- Inexpensive
- Low efficiency (10 %)
- Degradation and instability


Energy (eV)
w.r.t vacuum
–3.6
SnO2
–2.6
diffusion
exciton
2.3
–3.6
–3.7 (Mg)
Voc ~ 1.0 eV
–4.7
–4.9
–6.1
ITO
InSnO
Polymers
p-type like
hole mediator
Fullerene
n-type like
electron acceptor
catode

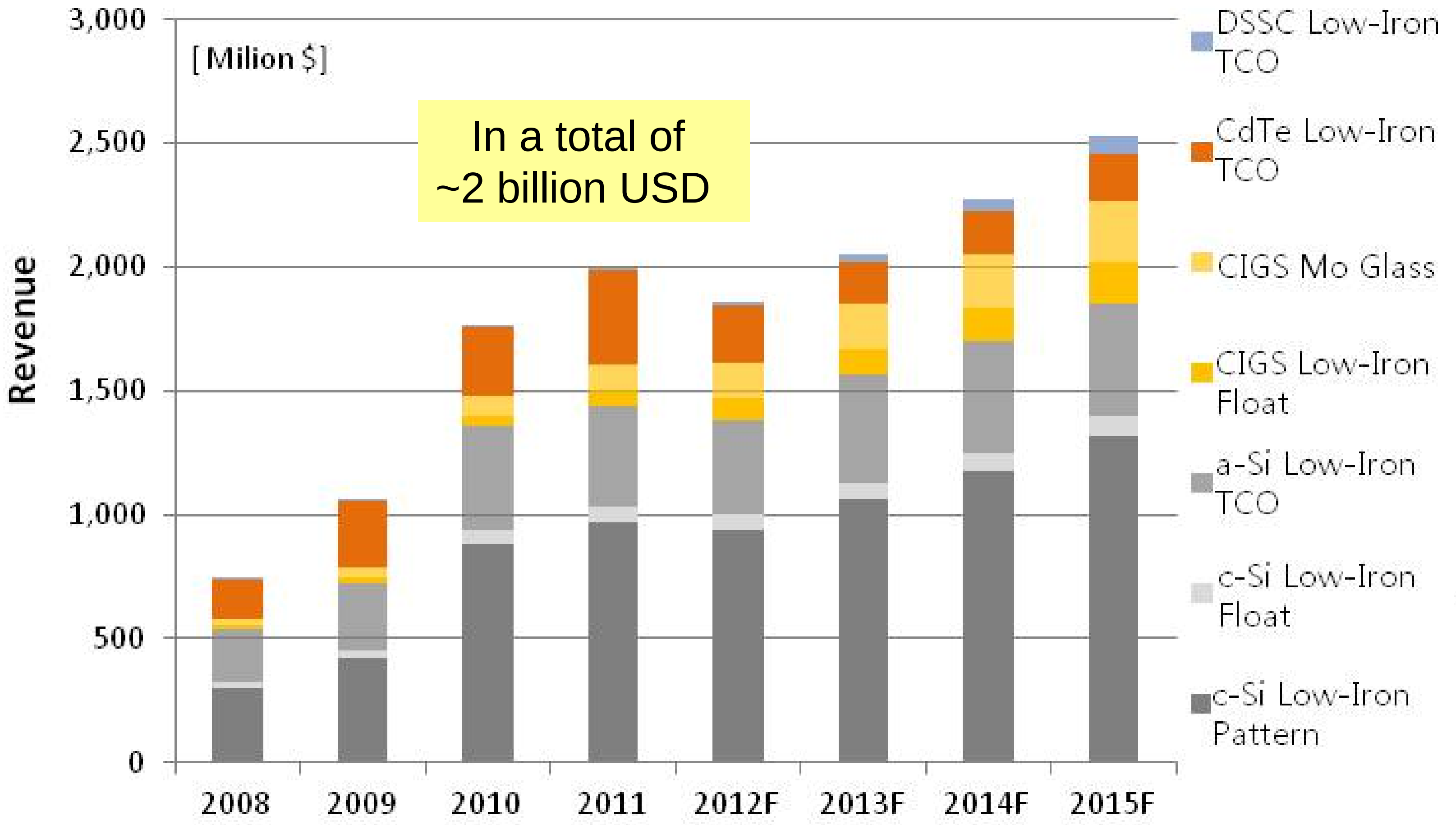


Best Research-Cell Efficiencies
NREL
NATIONAL RENEWABLE ENERGY LABORATORY
Efficiency (%)
Multijunction Cells (2-terminal, monolithic)
Three-junction (concentrator)
Three-junction (non-concentrator)
Two-junction (concentrator)
Two-junction (non-concentrator)
Four-junction or more (non-concentrator)
Single-Junction GaAs
Single crystal
Concentrator
Thin-film crystal
Crystalline Si Cells
Single crystal
Multicrystalline
Thick Si film
Silicon Heterostructures (HIT)
Thin-film crystal
Thin-Film Technologies
Cu(In,Ga)Se2
CdTe
Amorphous Si:H (stabilized)
Nano-, micro-, poly-Si
Multijunction polycrystalline
Emerging PV
Dye-sensitized cells
Organic cells (various types)
Organic tandem cells
Inorganic cells
Quantum dot cells
(Rev. 02-2013)
Multi-junction ~ 40%
Single crystal ~ 30%
Thin films ~ 20%
Dye/organic ~ 10%

Lab Results vs Module Efficiency



A. Saengprajak, Kasel Univ Press
also Wikepedia



Solar Cell Glass Market In-depth Analysis 2008-2015F, Feb 2013

Material Properties

What properties do we want (for most solar cells)?

- High absorption in $1.0 < h\nu < 3.5$ eV
- High carrier mobility
- High crystalline stability (long lifetime)

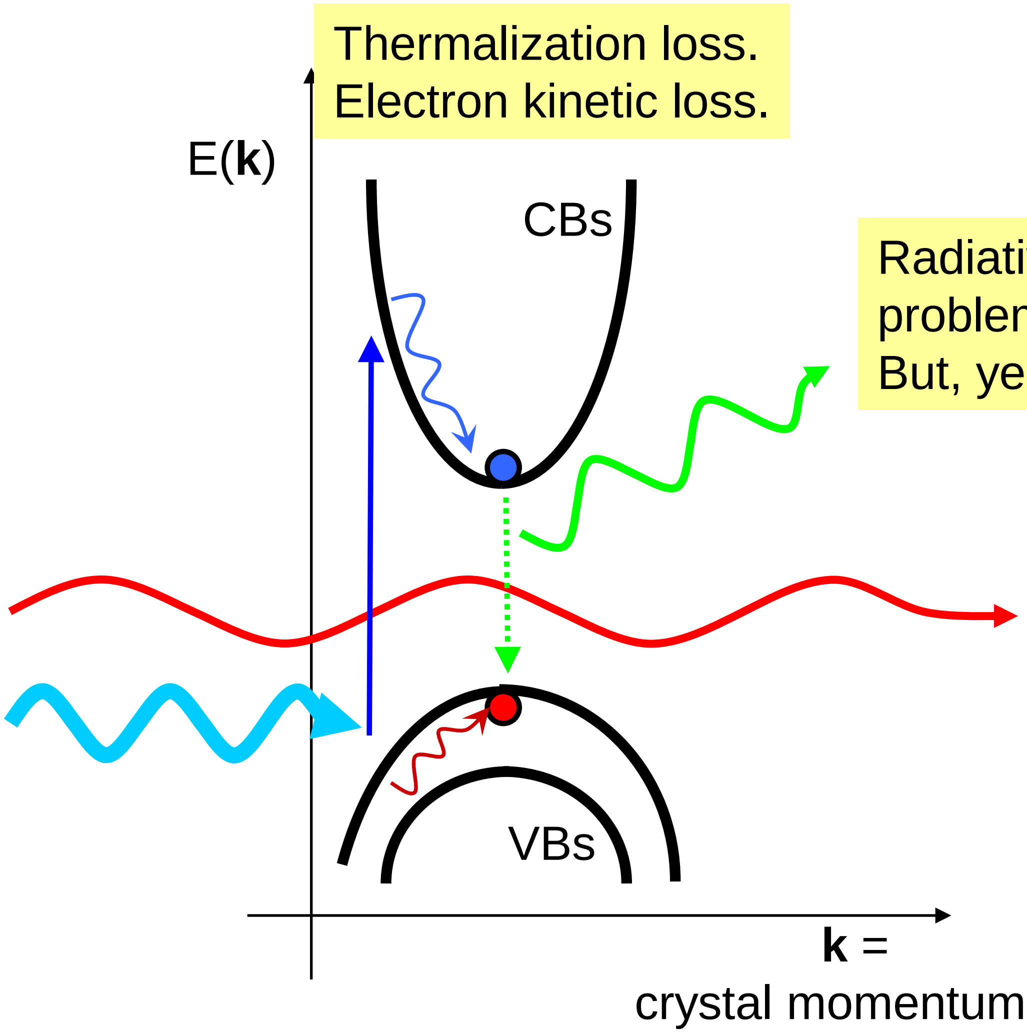
  No deep-level in-gap defects
- Dopability (n- and/or p-type)

- Control of complexes, nanostructures, etc

Material Properties: High absorption

Find mater with good Eg

Si:	**1.1 eV**
a-Si:	**1.7 eV**
GaAs:	**1.5 eV**
CdTe:	**1.7 eV**
$CuInGaSe_2$:	**1.0–1.7 eV**

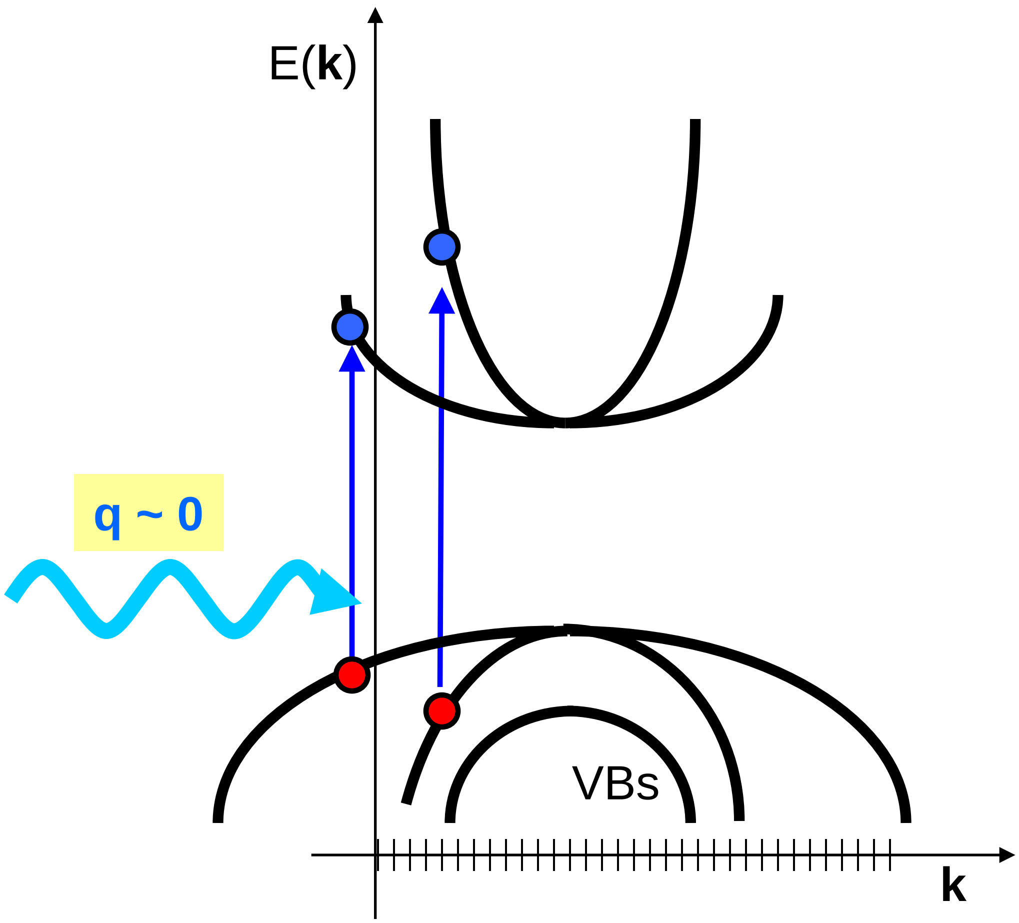


Radiative recombination is less problem. It can be absorbed again. But, yes, loss of energy.

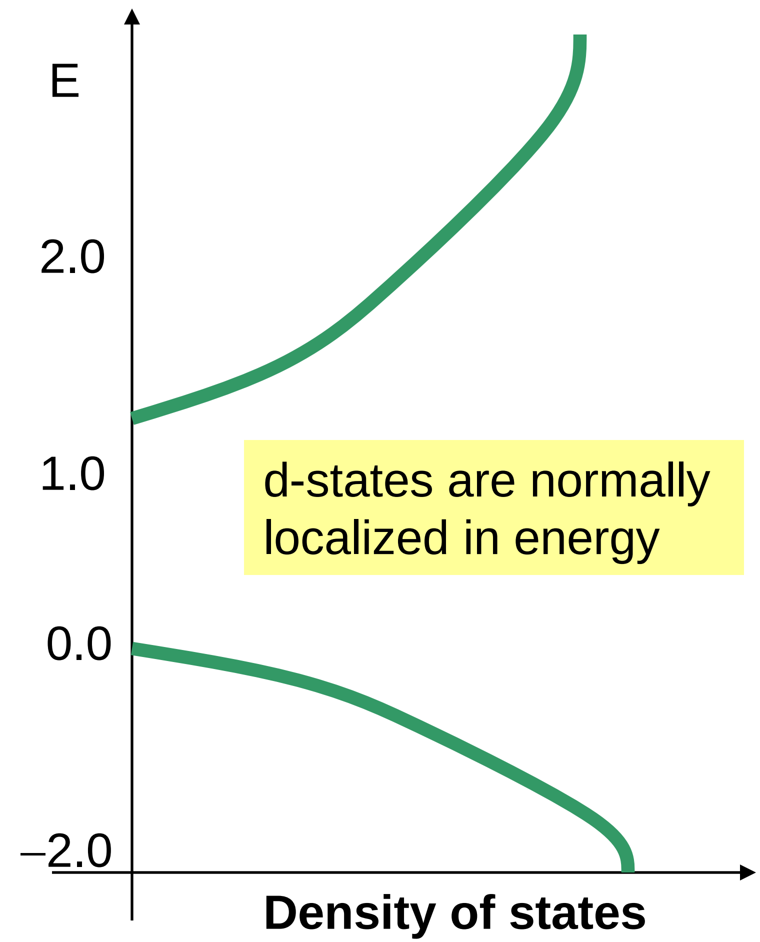
Below Eg loss for photons with hv < Eg

Material Properties: High absorption

* Direct band gaps (q ~ 0)
* Good having CBM/VBM a BZ edge instead of at Γ-point, => higher JDOS

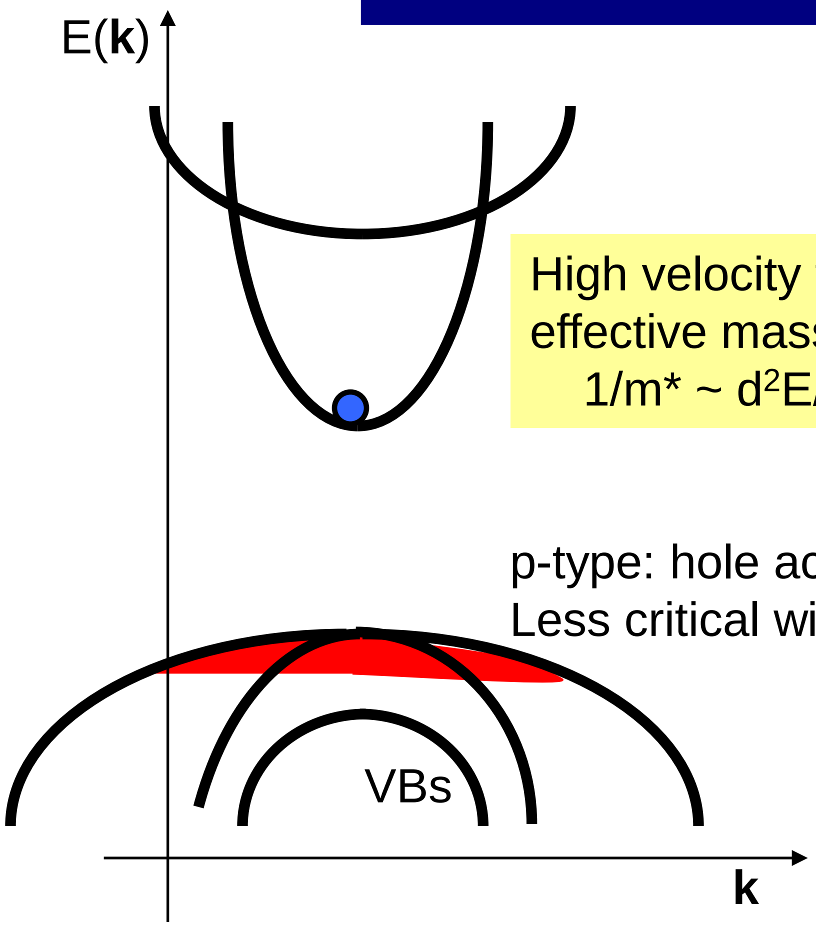


High joint DOS -2 < E < 3 eV
Many bands
Flat bands



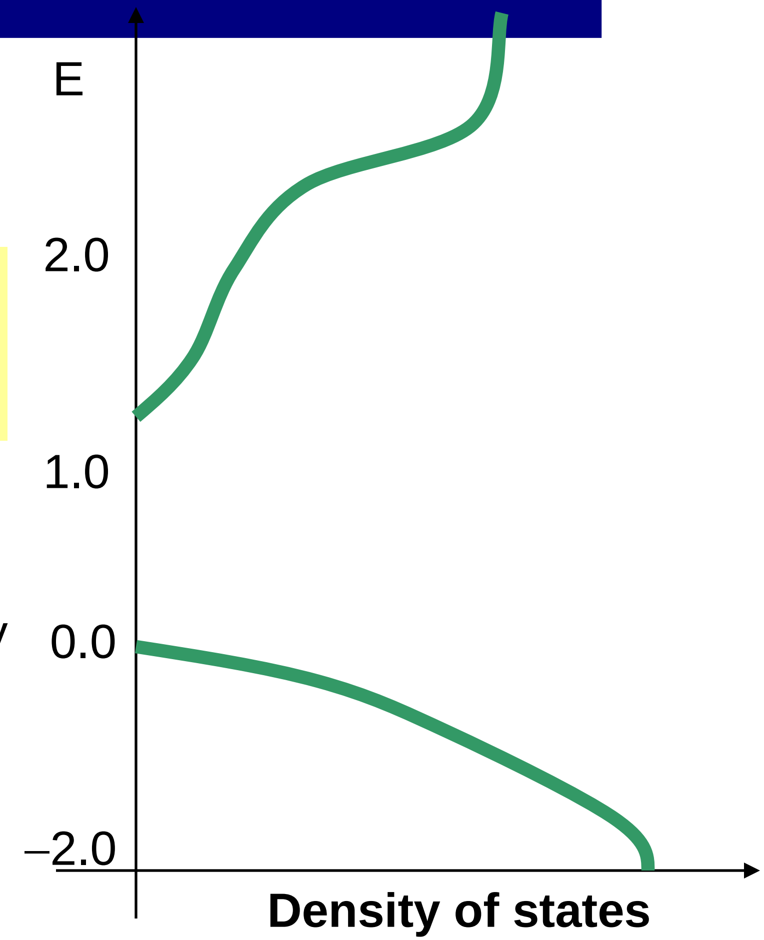
Material Properties: High mobility

Small mass for minority carrier
That is, for n-type:
  CB should have strong curvature (lower absorp)
  But OK with flat VBs



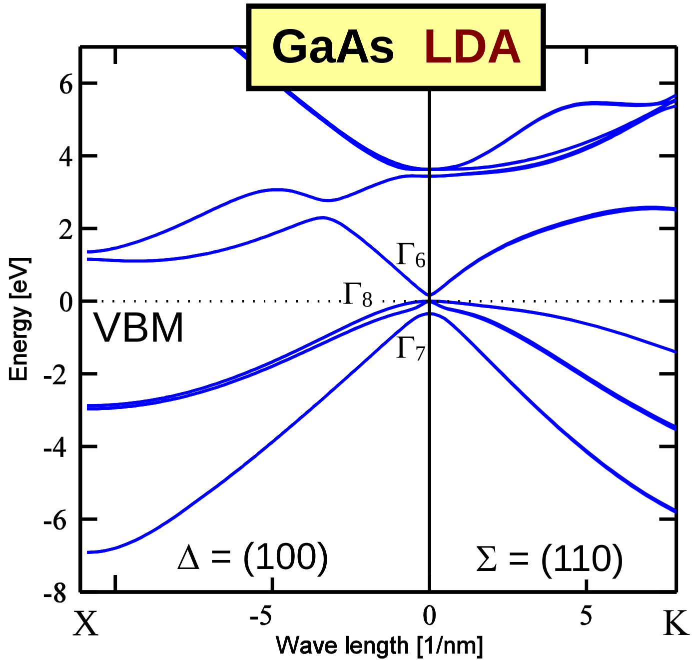
High velocity for small effective mass:
  $1/m^* \sim d^2E/dk^2$

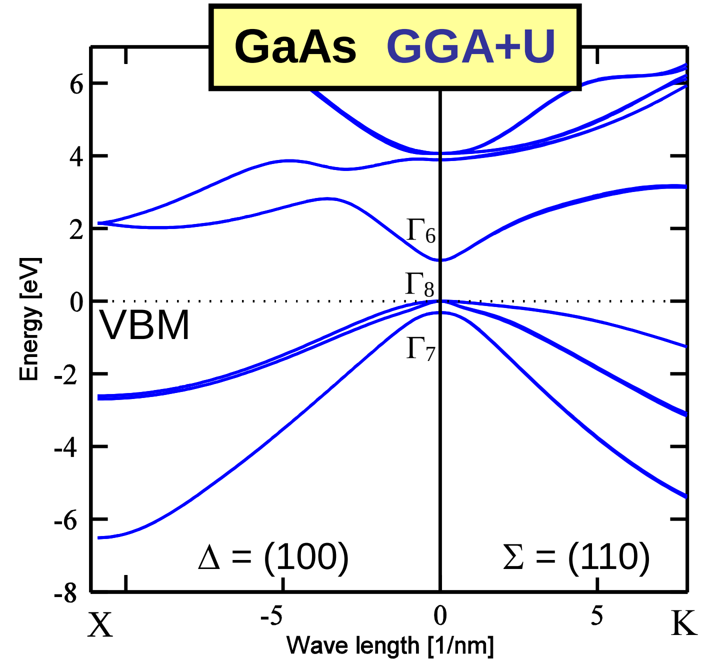
p-type: hole access
Less critical with mobility



LDA error of masses

Persson et al. Phys.Rev B **64**, 033201 (2001)





CB mass → m_{c1}; hh-mass → m_{hh}; lh-mass → m_{lh}; so-mass → m_{so}

GaAs LDA

	(100)	(110)	(111)
m_{c1} =	**0.01**	**0.01**	**0.01**
m_{hh} =	**0.32**	**0.56**	**0.77**
m_{lh} =	**0.01**	**0.02**	**0.02**
m_{so} =	**0.08**	**0.08**	**0.08**

GaAs GGA+U

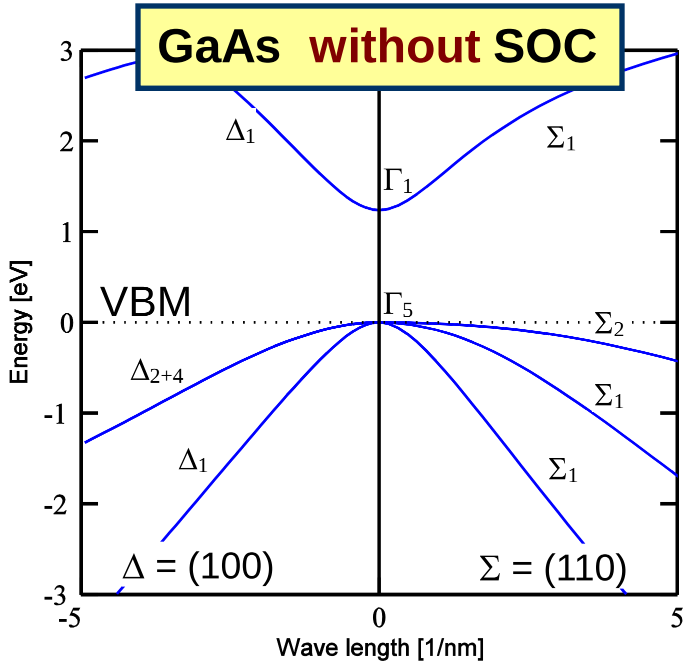
	(100)	(110)	(111)
m_{c1} =	**0.07**	**0.07**	**0.07**
m_{hh} =	**0.38**	**0.70**	**0.92**
m_{lh} =	**0.09**	**0.08**	**0.08**
m_{so} =	**0.18**	**0.18**	**0.18**

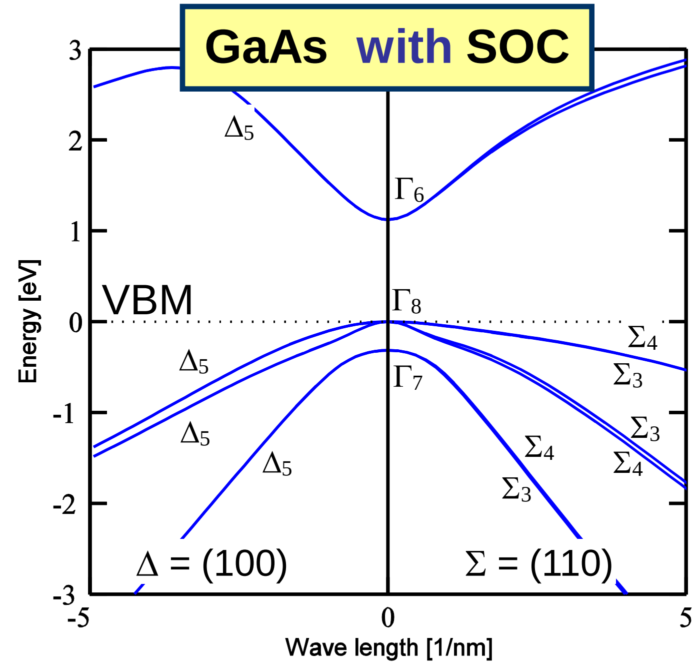
Expt data →

EXPT	(100)	(110)	(111)
m_{c1} =	**0.07**	**0.07**	**0.07**
m_{hh} =	**0.35**	**0.64**	**0.89**
m_{lh} =	**0.09**	**0.08**	**0.08**
m_{so} =	**0.17**	**0.17**	**0.17**

Hole masses depends on spin-orbit coupling (SOC)

Christensen, PRB 30, 5753 (1984); Persson et al, PRB. **64**, 033201 (2001); *ibid* **54**, 10257 (1996)





CB mass → m_{c1}; hh-mass → m_{hh}; lh-mass → m_{lh}; so-mass → m_{so}

Without SOC:

	(100)	(110)	(111)
m_{c1} =	0.07	0.07	0.07
m_{hh} =	0.41	2.70	0.94
m_{lh} =	0.41	0.41	0.94
m_{so} =	0.07	0.06	0.06

With SOC:

	(100)	(110)	(111)
m_{c1} =	0.07	0.07	0.07
m_{hh} =	0.38	0.70	0.92
m_{lh} =	0.09	0.08	0.08
m_{so} =	0.18	0.18	0.18

zb-AlN: $m_{hh}(\Gamma K) = -253.1 m_0 \Rightarrow +3.1 m_0$
J.Cryst Growth **231**, 397 (2001)

Material Properties: Defects

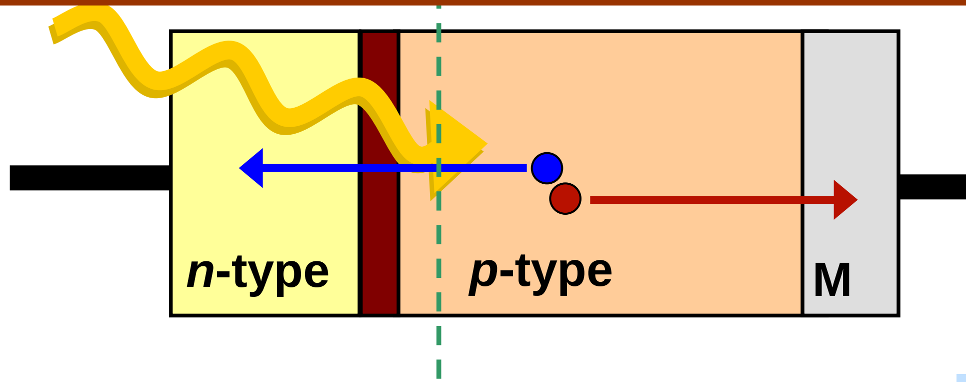
- Defect involves scattering, and recombinations

- Deep-level in-gap state are normally non-radiative, and transfer energy to heat.

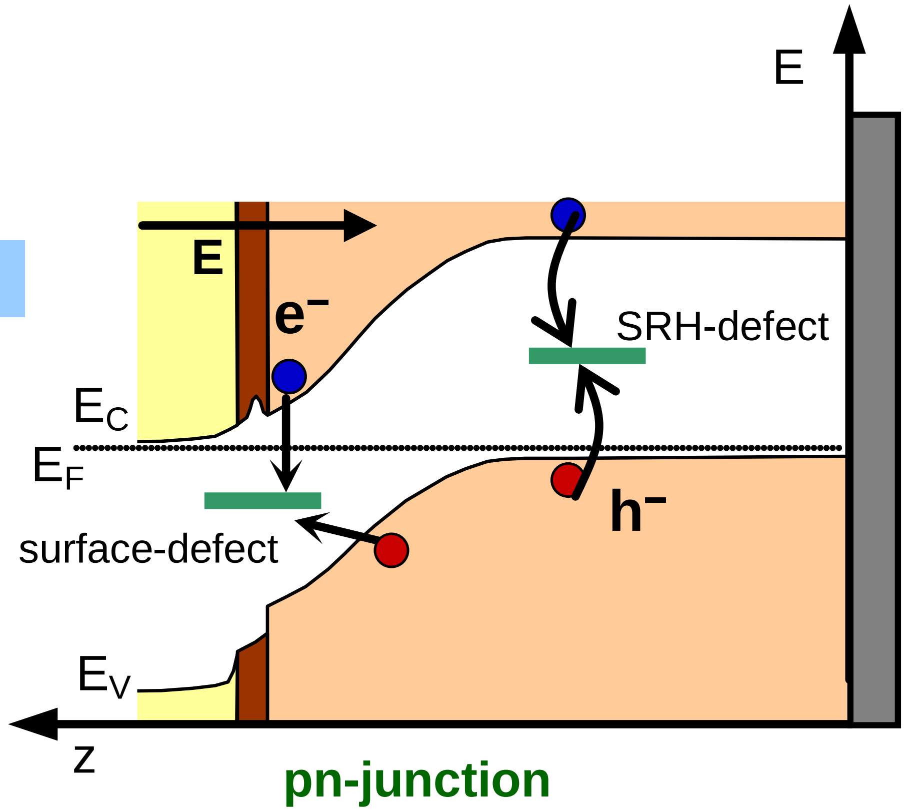
- Defects can diffuse, and form complexes, => degradation, especially at high operating temperature.

Material Properties: Defects

PV cell structure



Energyband diagram



Many type

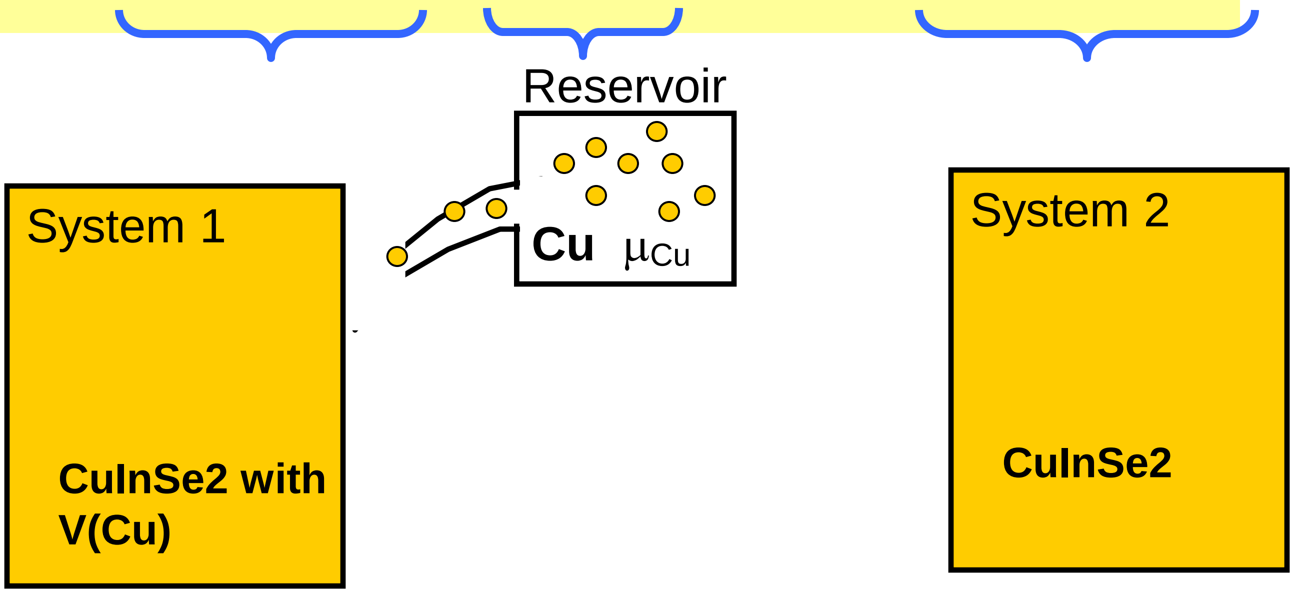
- Recombinations
- Auger,
- avalanche multiplication
- Zener breakdown

Scattering processes

- charged defects
- neutral defects
- carrier-carrier
- interfacial scatt
- deformation pot
- phonons, plasmons

Material Properties: Formation energies

$$dHf(V) = [\, E(V) - TS(V) + \mu_{Cu} \cdot N_{Cu} \,] - [E(0) - TS(0)]$$

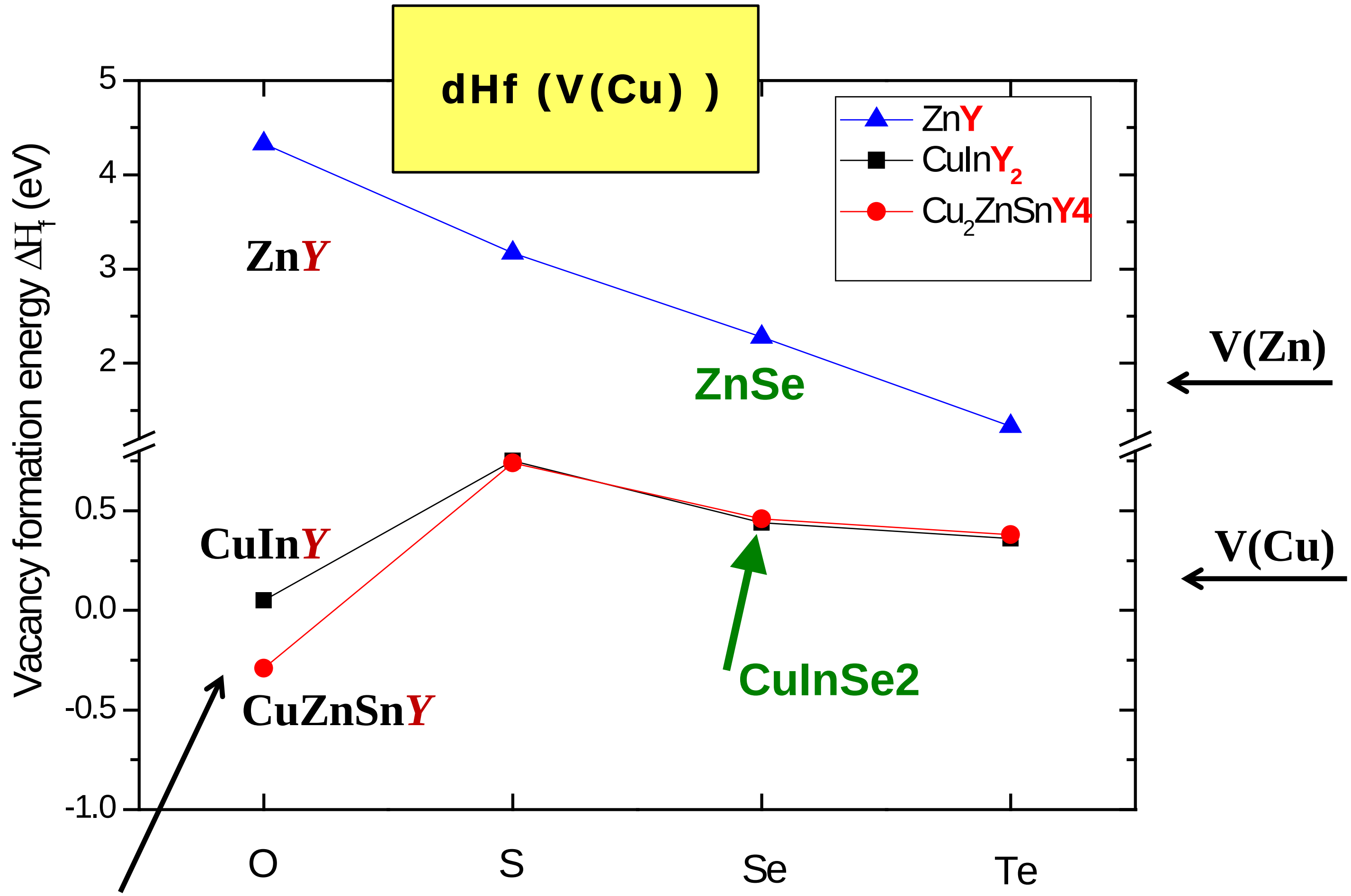


Set up two big supercells: one with V, and one without
Calculate total energies.
Calculate chemical potential for Cu.

Problem: What is chemical potential for Cu

Formation energy of V(Cu) for different anion-alloys

S-based alloys have higher dHf in Cu-compounds



May reflect the problem with
oxygen in chalcopyriten structure

Kumar, Zhao, and Persson. submitted

Material Properties: Dopability

Because V(Cu) has so low formation energy in CuInSe2, the defect is used as an acceptor in p-type CuInSe2.

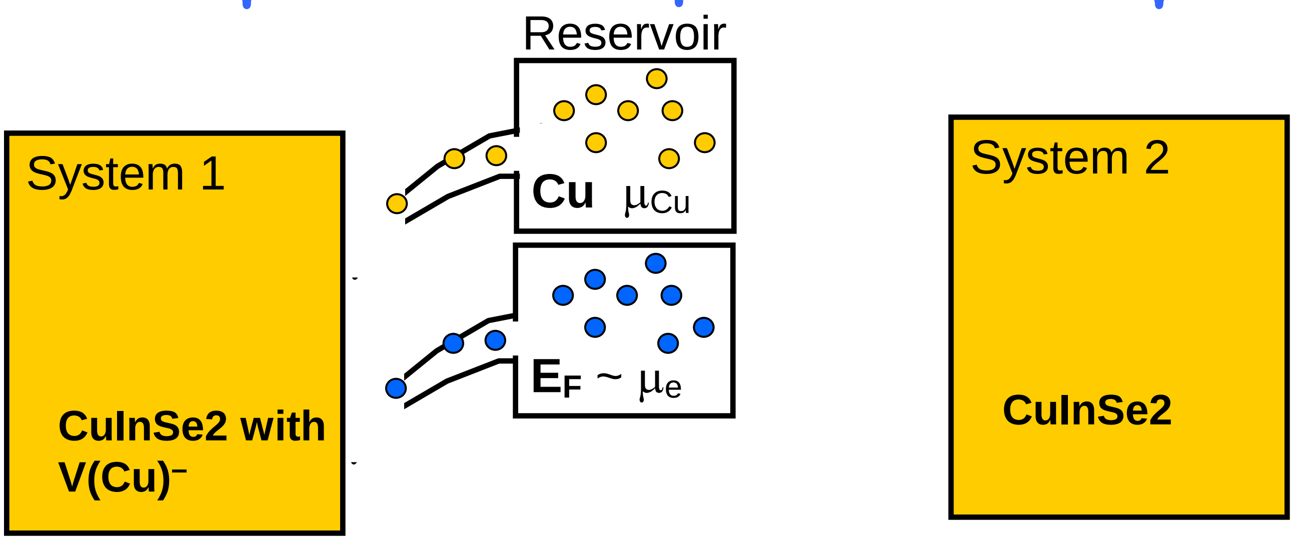
What is the ionization energy (= transition energy) of V(Cu) as acceptor.

That is, how much energy does it cost to ionize it ??

= how much energy to trap one electron at the acceptor ??

neutral $dHf(V) = [\, E(V) - TS(V) + \mu_{Cu} \cdot N_{Cu} \,] - [E(0) - TS(0)]$

charged $dHf(V;q) = [\, E(V;q) - TS(V) + \mu_{Cu} \cdot N_{Cu} + q \cdot E_F \,] - [E(0) - TS(0)]$



The transition energy can be defined as the Fermi energy for which dHf(V) = dHf(V;q)

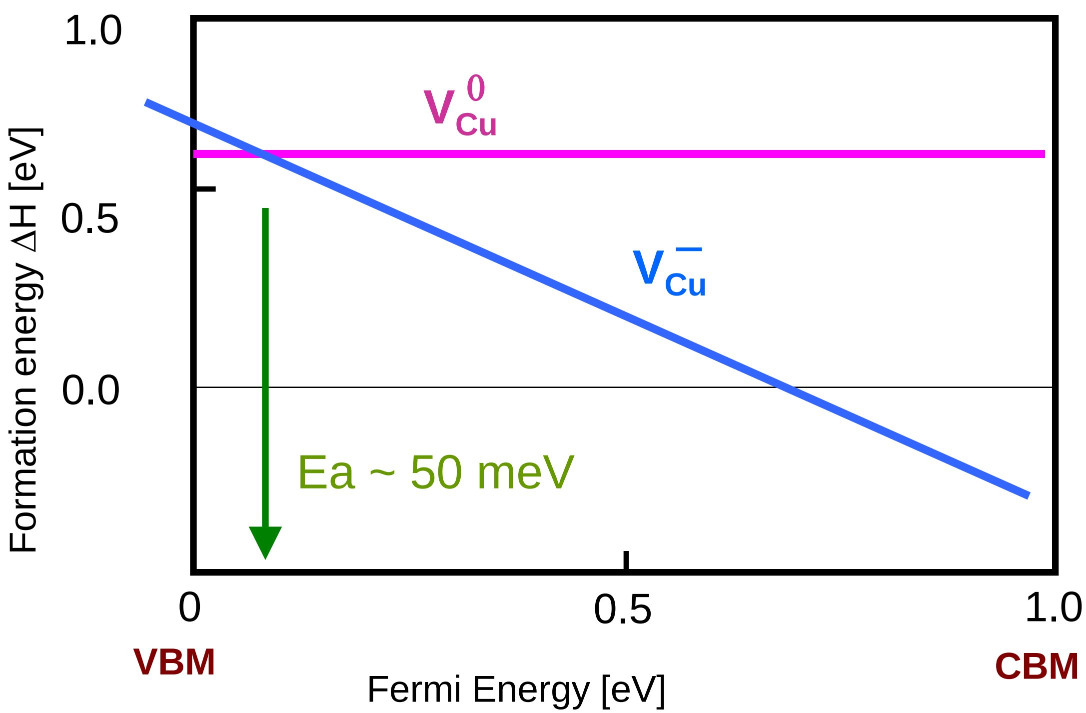
$0 = E(V;q) - E(V) + q \cdot E_F \quad \Rightarrow \quad E_F = [E(V) - E(V;q)] / q$

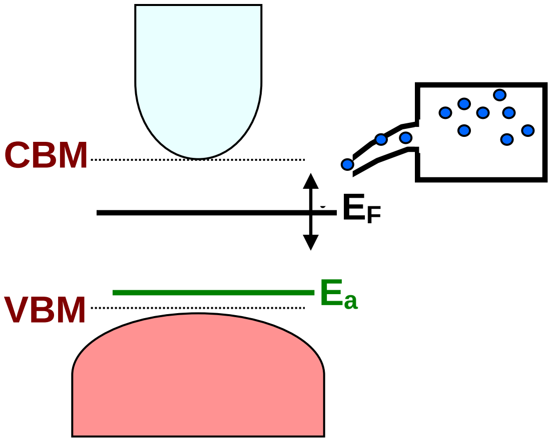
neutral

$$dHf(V) = [\, E(V) - TS(V) + \mu_{Cu} \cdot N_{Cu} \,] - [E(0) - TS(0)]$$

charged

$$dHf(V;q) = [\, E(V;q) - TS(V) + \mu_{Cu} \cdot N_{Cu} + q \cdot E_F \,] - [E(0) - TS(0)]$$





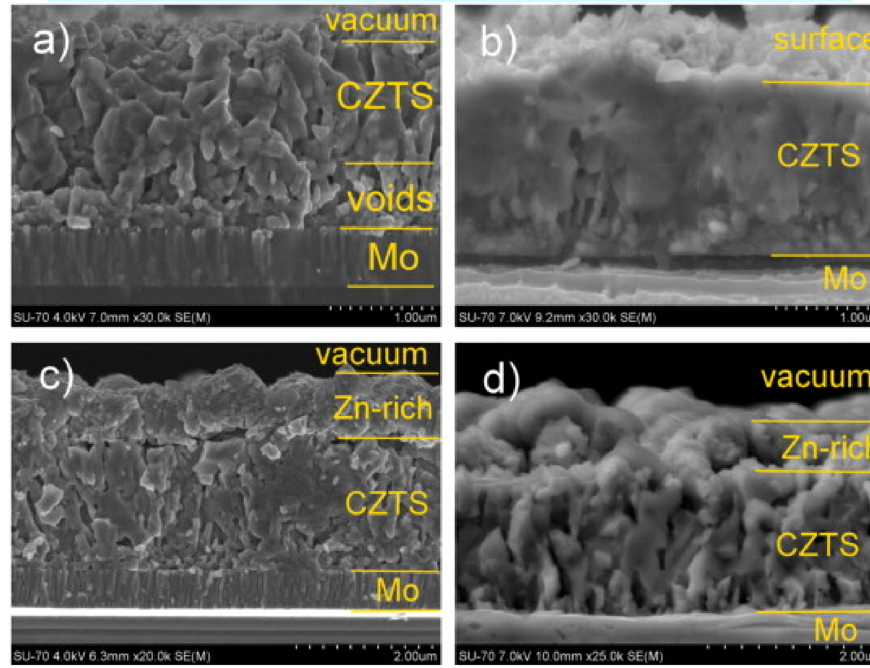
Cu(InGa)Se2 and Cu2ZnSn(S,Se)4

Cu(InGa)Se2 commercialized

NREL, USA

indium-free

Cu2ZnSn(S,Se)4 under developments

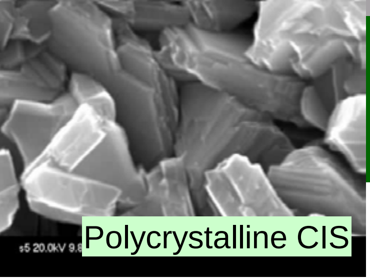


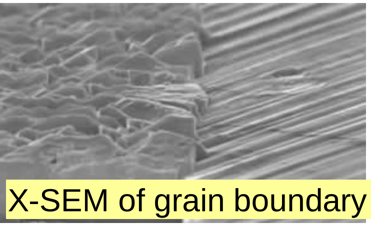
Salomé , et al. Solar Energy Mater & Solar Cells 95, 3482 (2011),

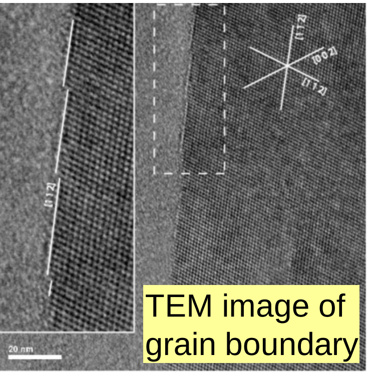
CISe = $CuInSe_2$
CGSe = $CuGaSe_2$
CIGSe = $CuIn_{1-x}Ga_xSe_2$

CZTS = Cu_2ZnSnS_4
CZTSe = $Cu_2ZnSnSe_4$
CZTSSe = $Cu_2ZnSn(S_{1-x}Se_x)_4$

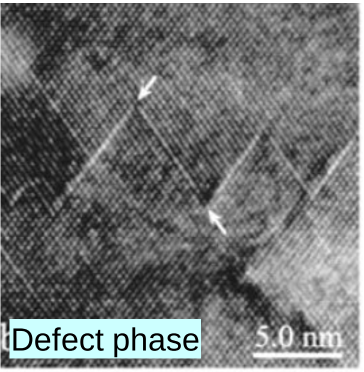
Puzzeling properties of CIGSe devices, different from Si, GaAs and CdTe devices





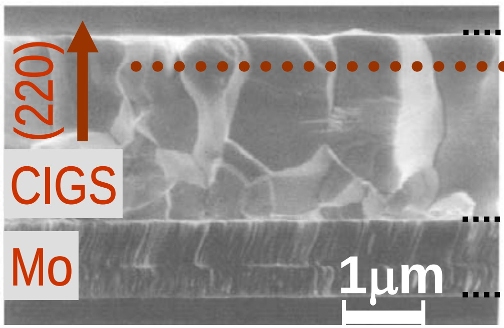


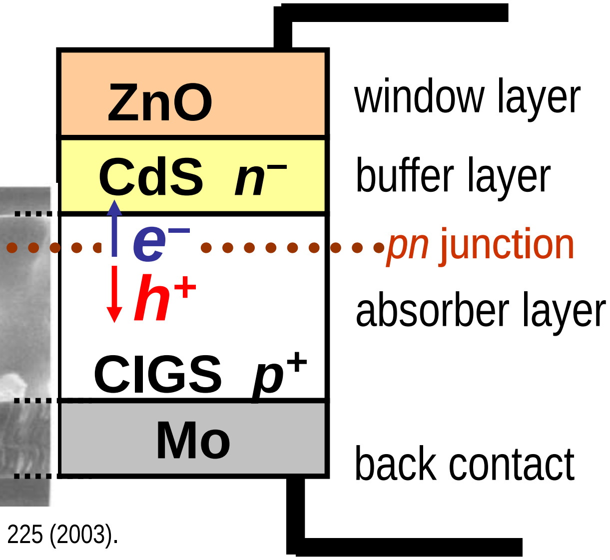
rockett.mse.uiuc.edu



Y. Yan, et.al, report, NREL/CP-520-33615 (2003)

Cross section SEM image





K. Ramanathan, *et al*. Prog. PV Res. Appl. 11, 225 (2003).

(1) Grain boundaries are harmless for the device !!!

(2) Best CIGS material is Cu-poor ($[V_{Cu}]$, $[In_{Cu}]$ ~ 1%) polycrystalline, non-stoichiometric, ODP (eg $CuIn_3Se_5$)

(3) Extremely Cu-poor at surface/interfaces !!!

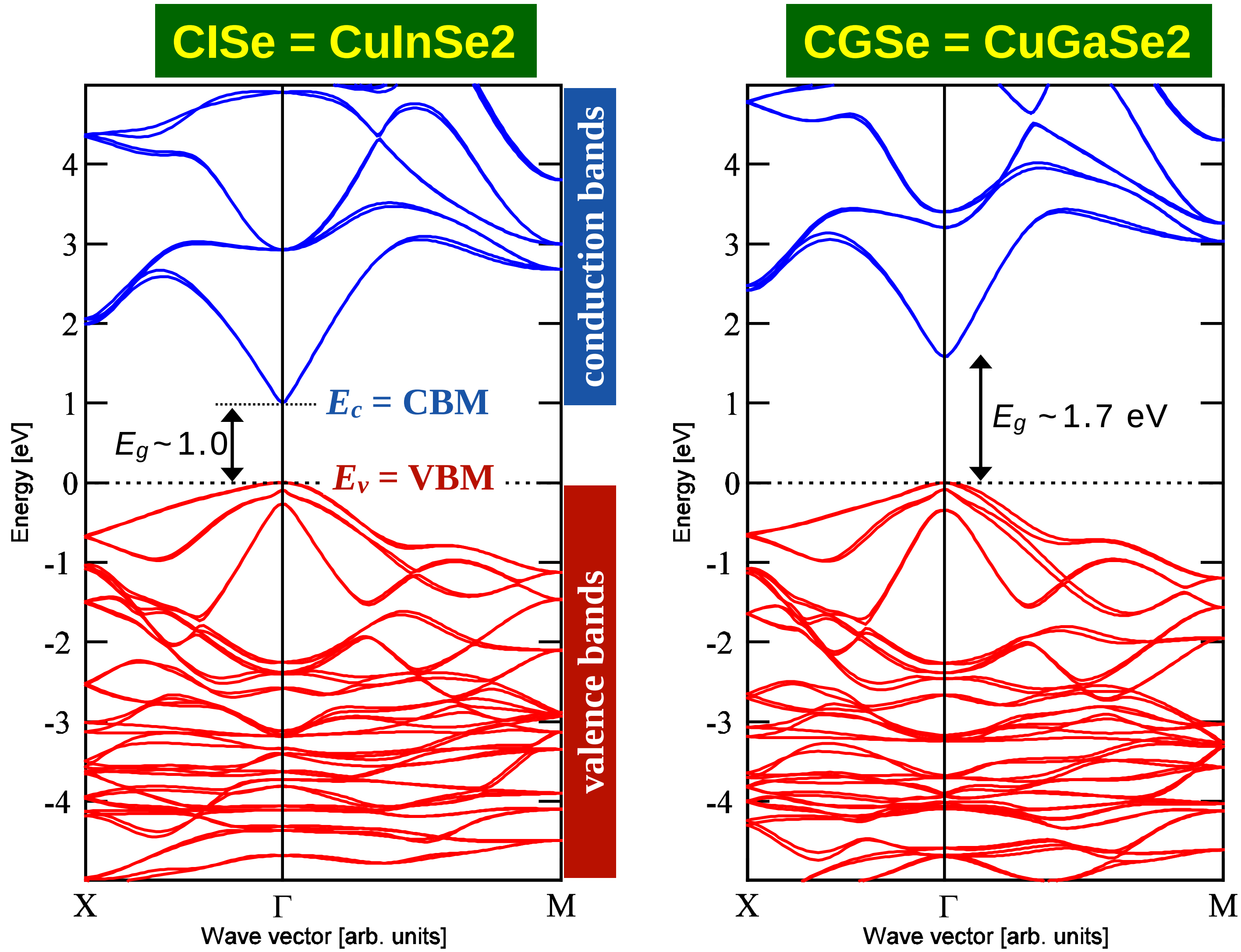
(4) CIGSe is typically *p*-type as grown !!!

(5) CISe can be *n*-type, but CGSe cannot !!!

(6) Na at grain-boundaries is good for the device !!!

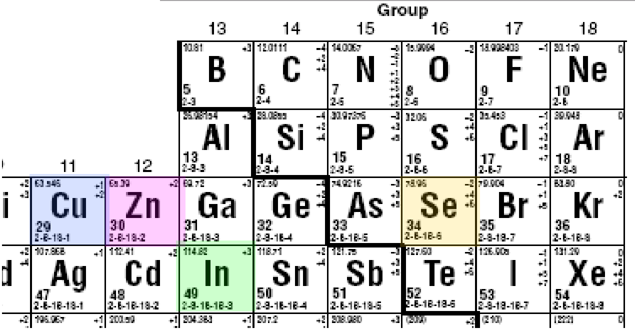
(7) Not better efficiency for high Ga content (x>0.30)

CISe and CGSe are direct band-gap semicond.



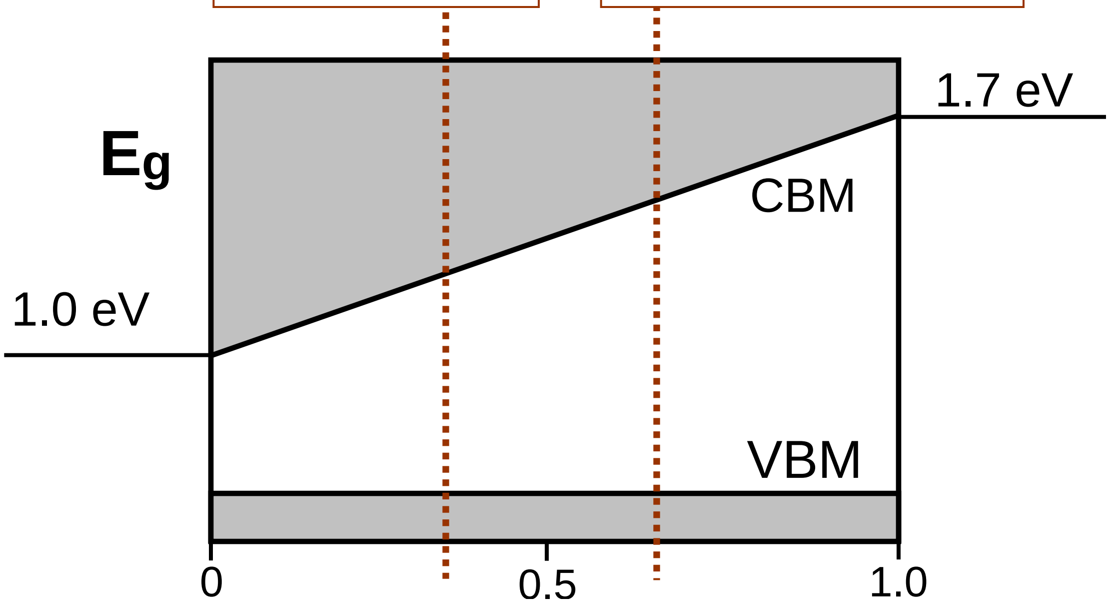
Solar cells need direct-gap materials because photons has q ~ 0

CIGSe band gap fits sun-light spectrum



Expt. best composition ~30% Ga

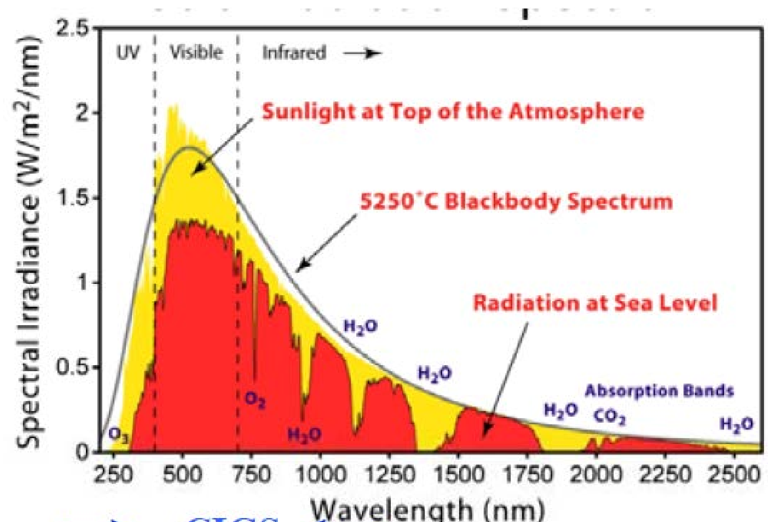
Best theoretical composition 50–60% Ga ??



$CuInSe_2$

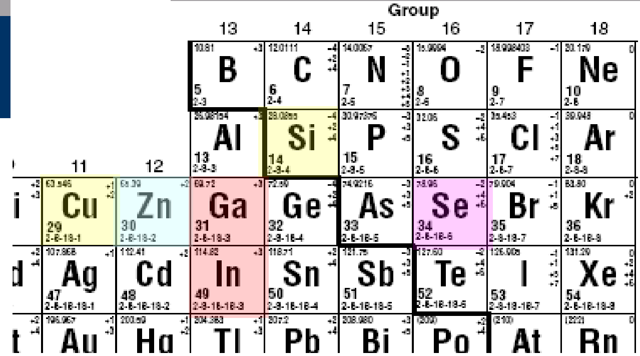
$CuGaSe_2$

$CuIn_{1-x}Ga_xSe_2$



sun-light spectrum

Why is not solar-cell efficiency increasing for $x > 30\%$???



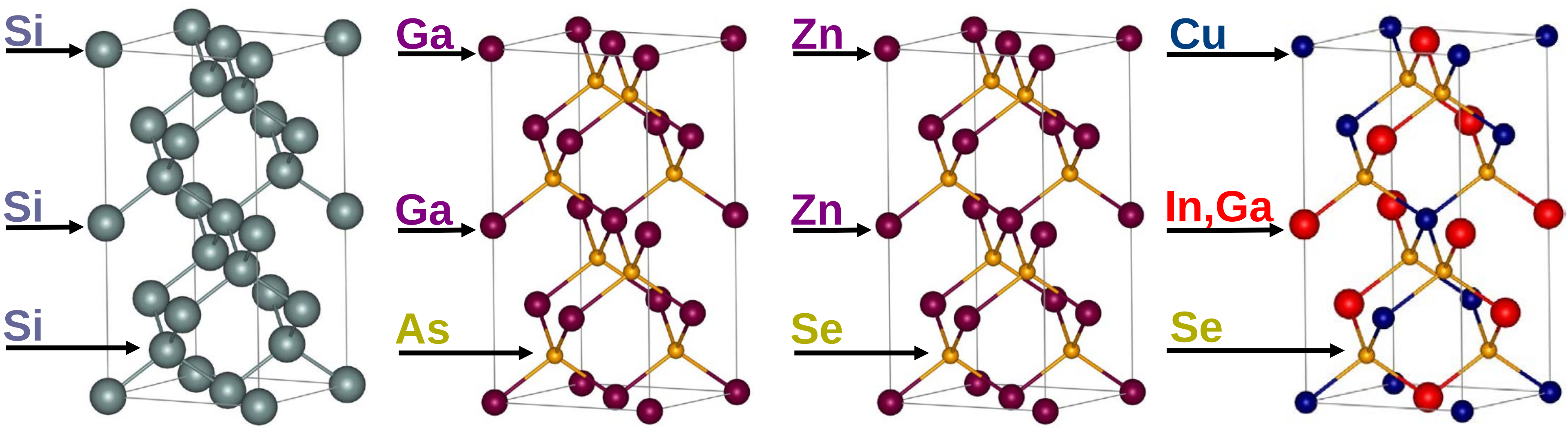
Ga
⇕

SiSi SiSi
4+4+4+4 =16

GaAs GaAs
3+5 +3+5 =16

ZnSe ZnSe
2+6 +2+6 =16

CuSe InSe
1+6 +3+6 =16



diamond structure
e.g. group IV
Si, Ge, C

zinc-blende struct.
e.g. III-V and II-VI
GaAs, ZnSe

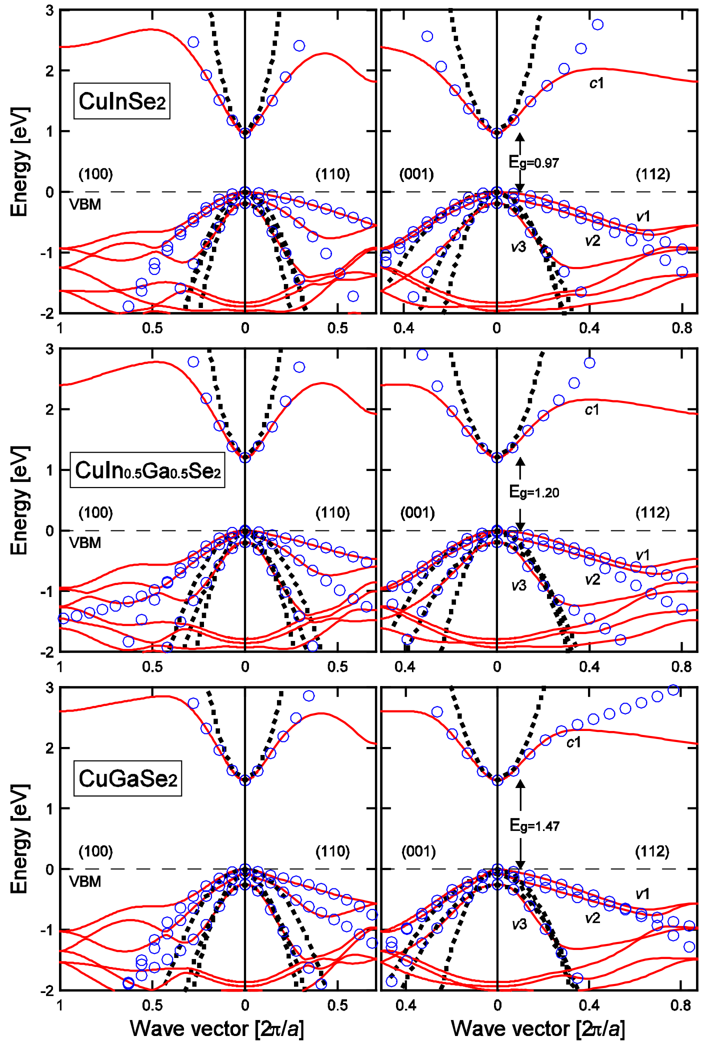
chalcopyrites
e.g. I-III-VI_2
$CuInSe_2$, $AuAlO_2$

Electronic band-edge structure

CuInSe2

CIGSe = CuIn0.5Ga0.5Se2

CuGaSe2

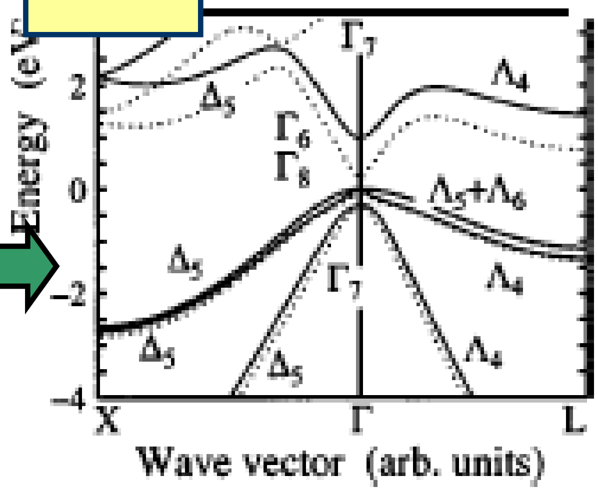


blue circles show fitted band structure

Chen and Persson, Thin Solid Films 519, 7503 (2011).

We are interested in details near CBM and V BM

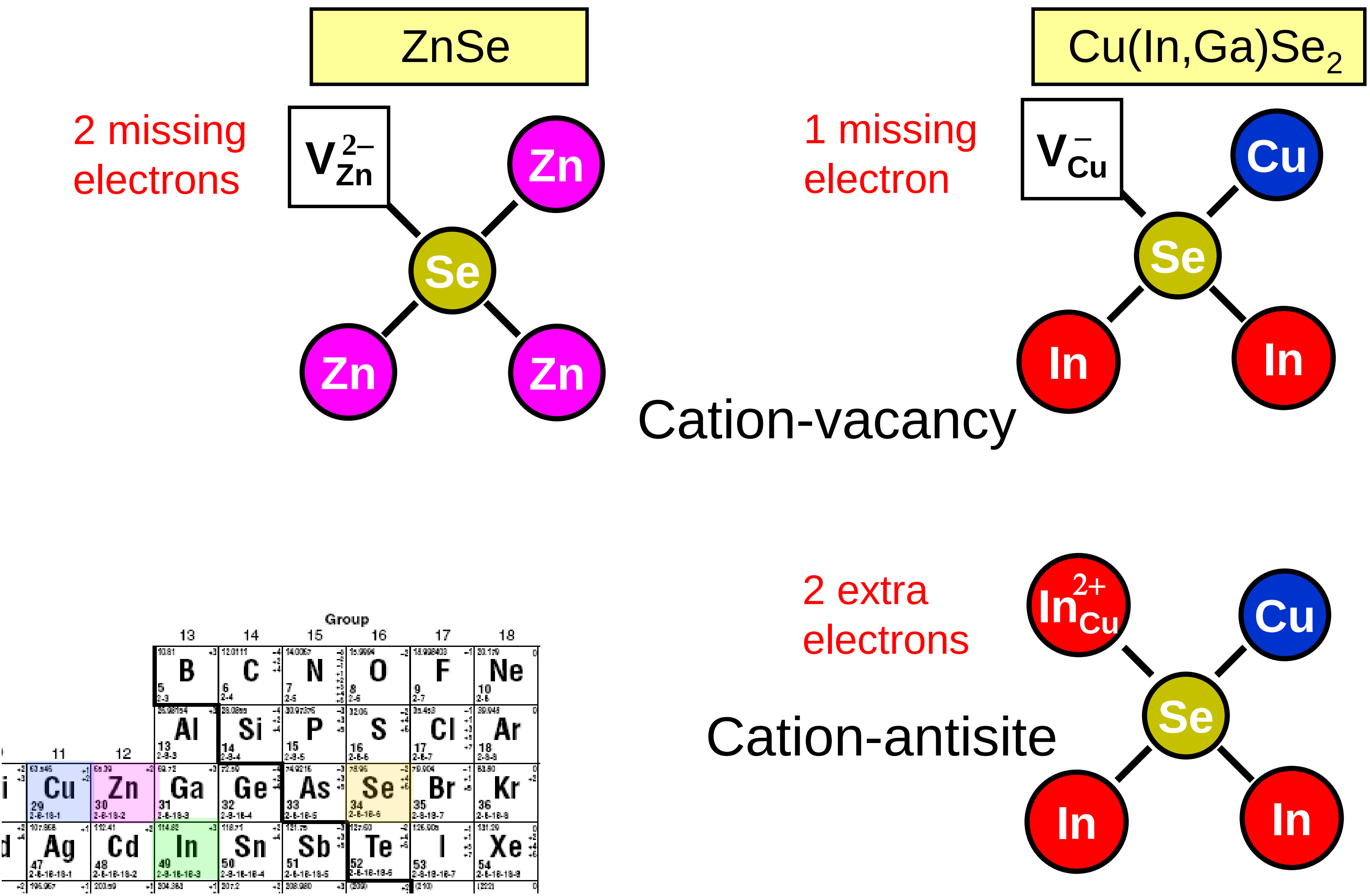
GaAs



Persson, et al PRB 033201 (2001)

Similar CB as GaAs (but more VBs)

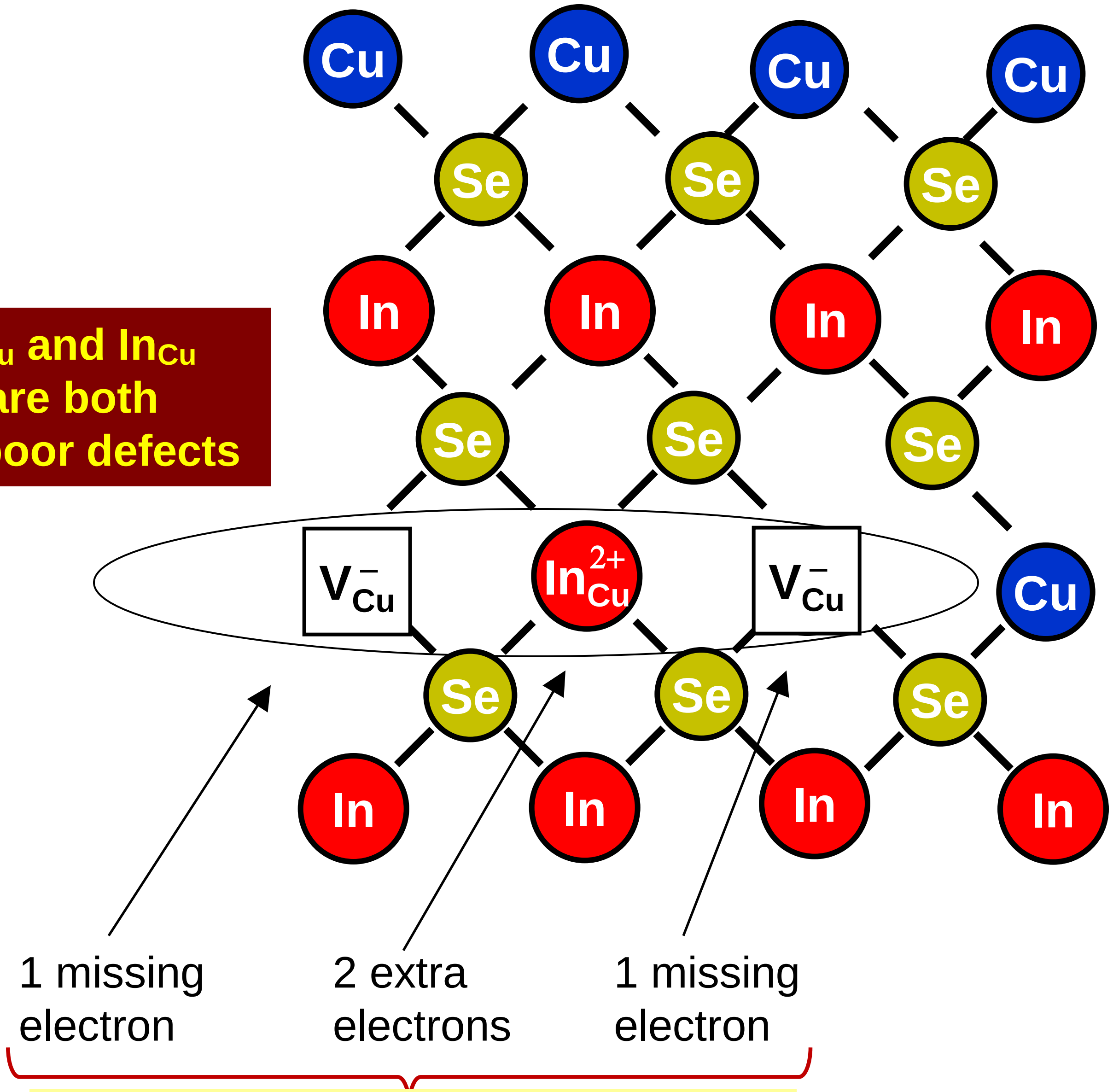
Easy to form cation vacancies and antisites



V_{Cu} and In_{Cu} have very low formation energies in CIGSe

Charge-neutral / isovalent defects $[2V_{Cu}+In_{Cu}]$

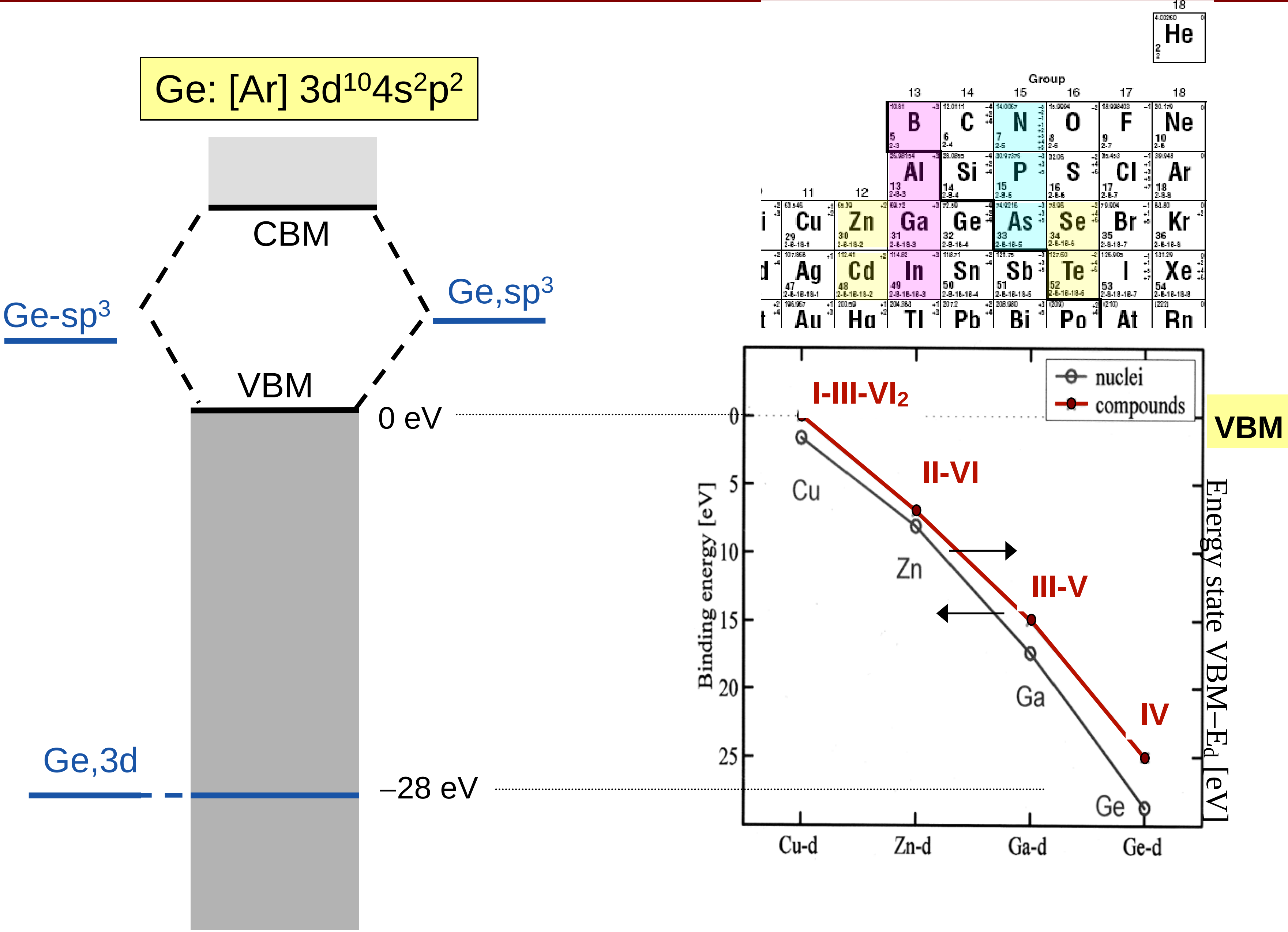
V_{Cu} and In_{Cu} are both Cu-poor defects



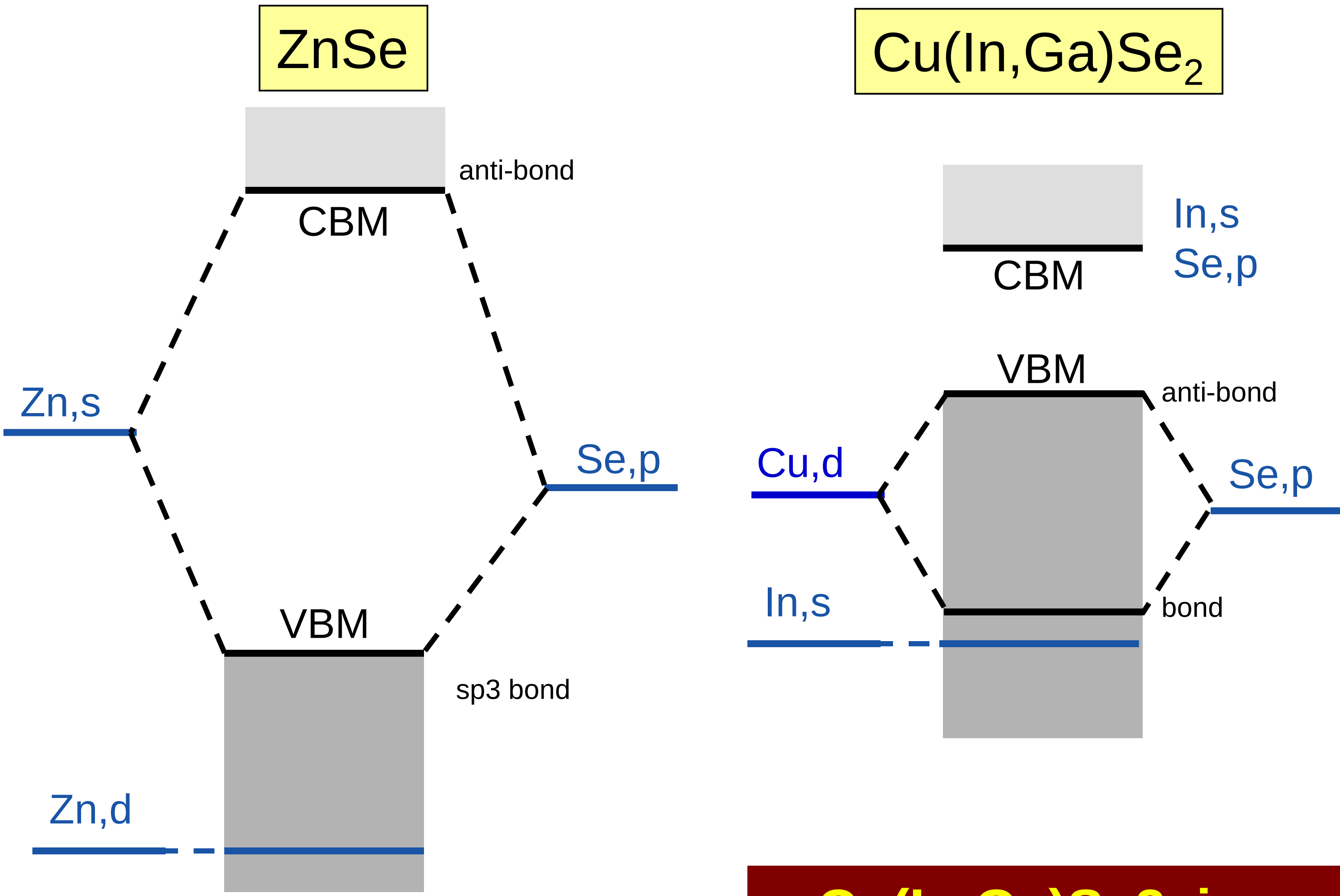
0 missing/extra electron, that is isovalent

$[2V_{Cu}+In_{Cu}]$ Charge-neutral defect !!

Trends in d-state energies



VBM of CIGS has strong d-character !!



Cu(In,Ga)Se2 is <u>very</u> <u>different</u> from ZnSe !!

Cation vacancy formation energies

CISe and CGSe

V_{Cu} **~ 0.7** $+ \Delta\mu_{Cu}$ [eV]

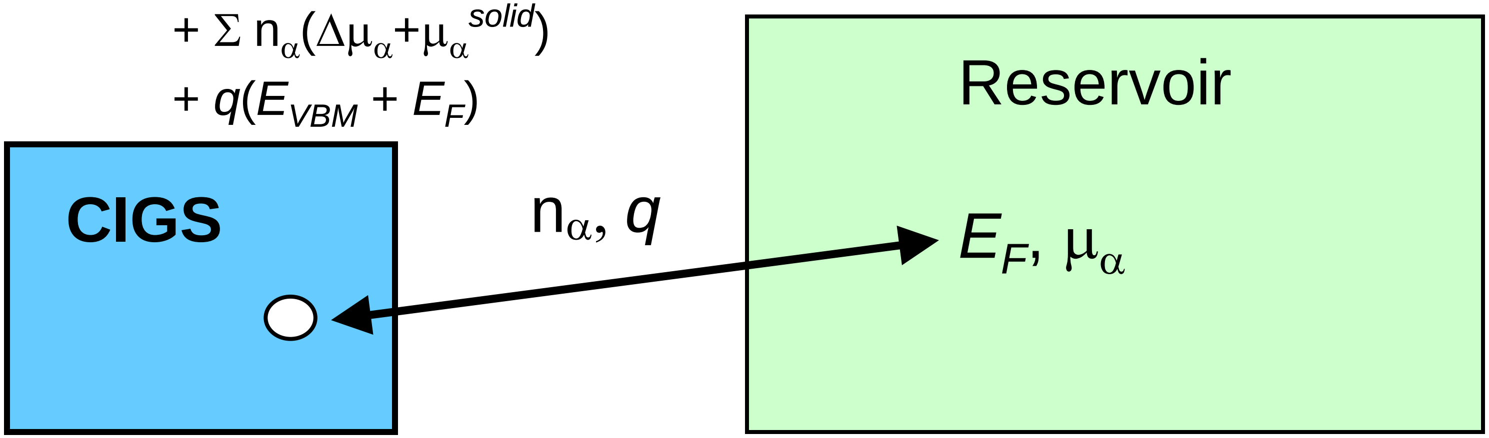
Persson, *et al*. PRB **72**, 035211 (2005)

ZnTe

V_{Zn} **~ 3** $+ \Delta\mu_{Zn}$ [eV]

Laks, *et al*. PRB **45**, 10965 (1992)
Cheocg, *et al*. PRB **51**, 10610 (1995)

$$\Delta H(\alpha,q) = E(\alpha,q) - E_{host} + \Sigma\, n_\alpha(\Delta\mu_\alpha + \mu_\alpha^{solid}) + q(E_{VBM} + E_F)$$

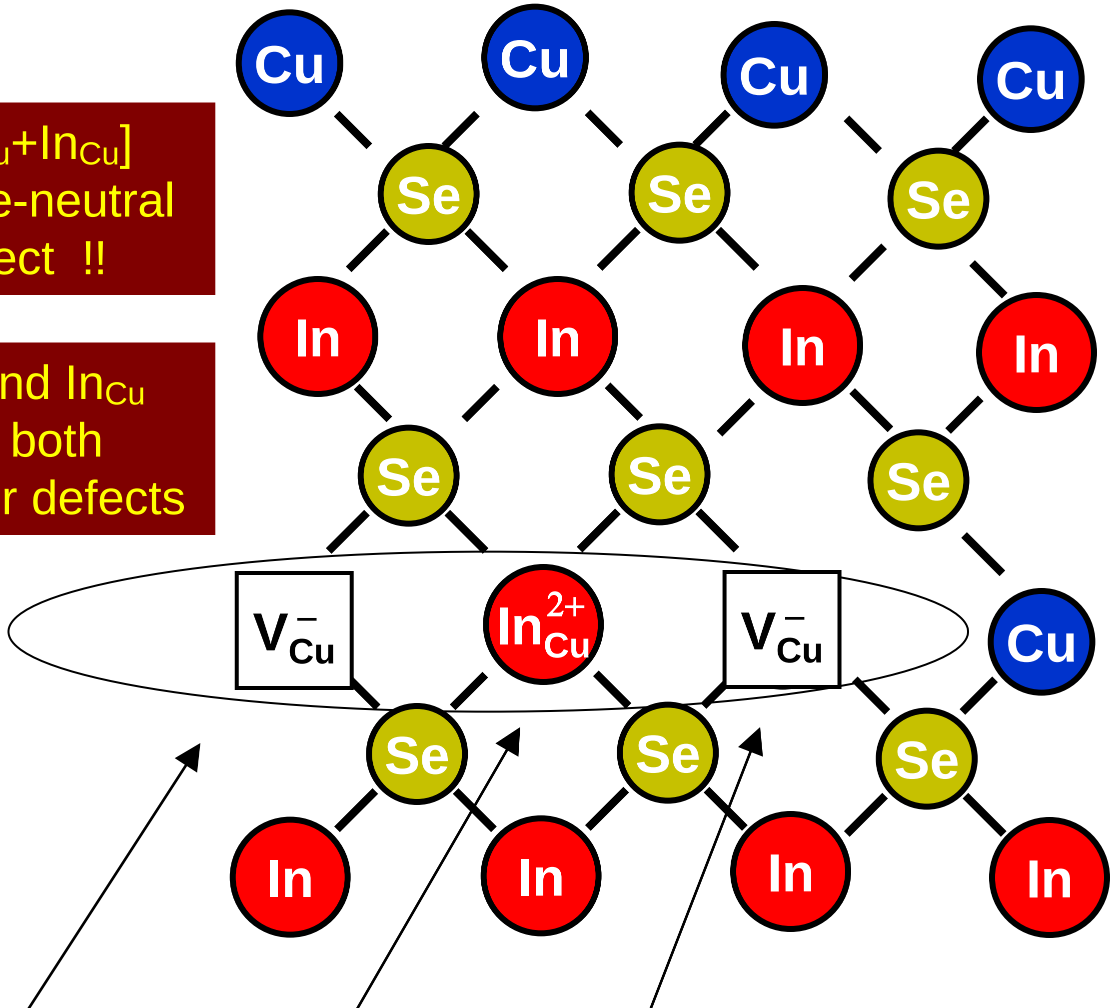


High quality CIGS is Cu-poor: 23.5 – 24.5 at.% (not 25%)

Charge-neutral complex $[2V_{Cu}+In_{Cu}]$

$[2V_{Cu}+In_{Cu}]$
Charge-neutral
defect !!

V_{Cu} and In_{Cu}
are both
Cu-poor defects

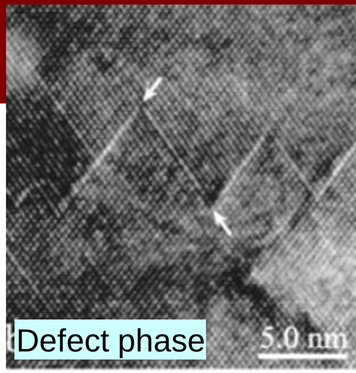


1 missing electron

2 extra electrons

1 missing electron

0 missing/extra electron, that is isovalent



Y. Yan, et.al, report, NREL/CP-520-33615 (2003)

$$CuInSe_2 + n\cdot[2V_{Cu}+In_{Cu}]^0$$
$$\Rightarrow Cu_1In_3Se_5$$
$$Cu_1In_5Se_8$$

Zhang et al. PRB 57, 9642 (1998).

Calculation $S = N_i\, e^{-\Delta H_f/k_BT}$
$\sim$ 1–5 % V_{Cu}

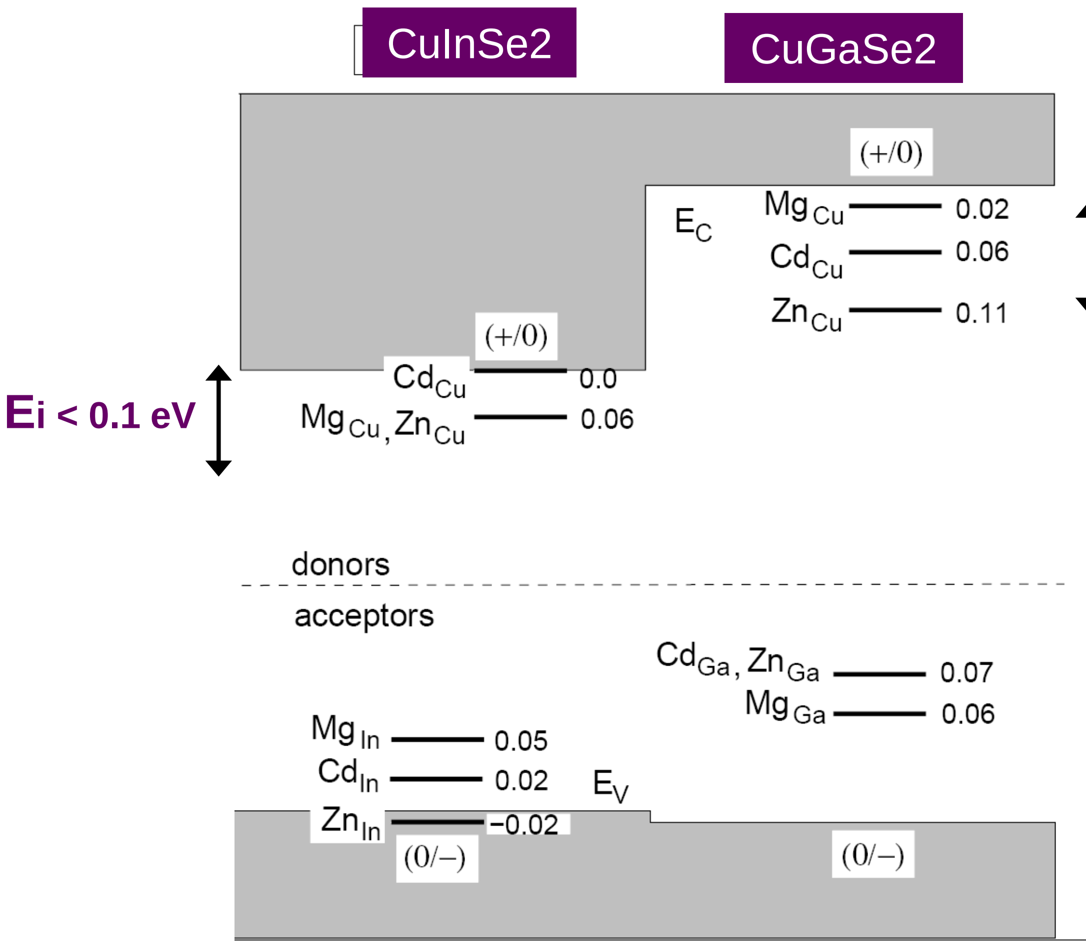
Cu-vacancies can

for example,
1) limit n-type doping

experimental observation:

$CuInSe_2$ be n-type, but not $CuGaSe_2$

Both CISe and CGSe have shallow donors !!!



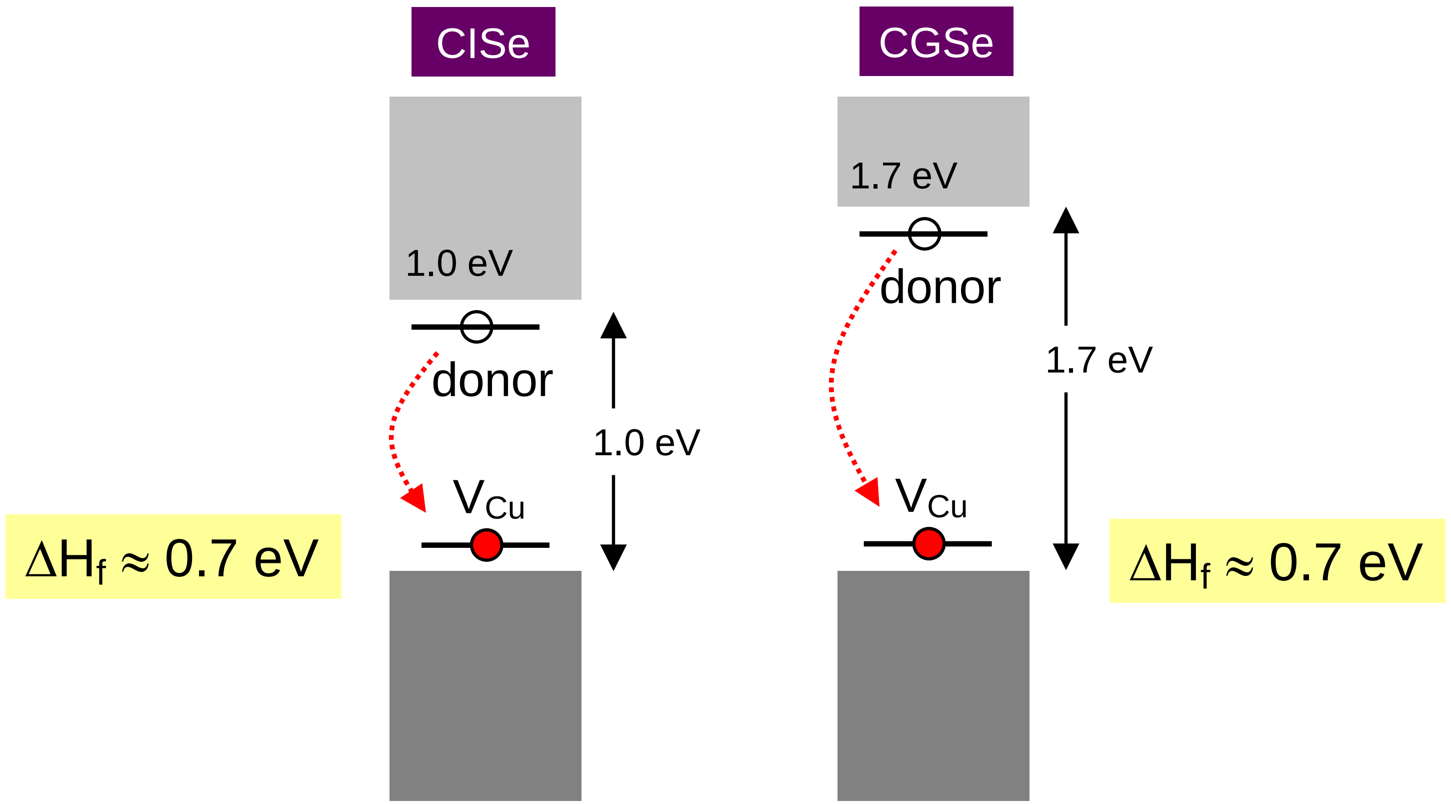
Ei < 0.1 eV

Formation energies of these donors are relatively small

The problem is not to create shallow donors

Persson, et al. PRB **72**, 035211 (2005)

Trying to n-type dope CGSe



simplified model

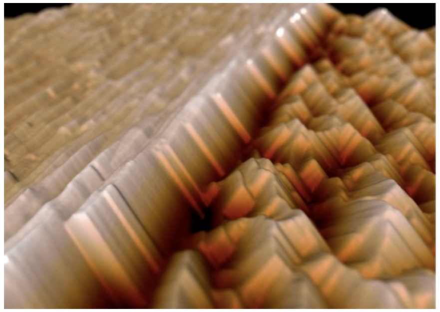
It costs ~0.7 eV to create V_{cu}

But V_{cu} -compensation, the system gains
~ 0.8 eV in CIS
~ 1.4 eV in CGS

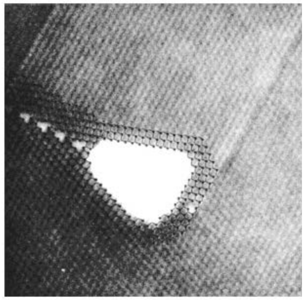
Cu-vacancies can

second example,
2) create hole barriers

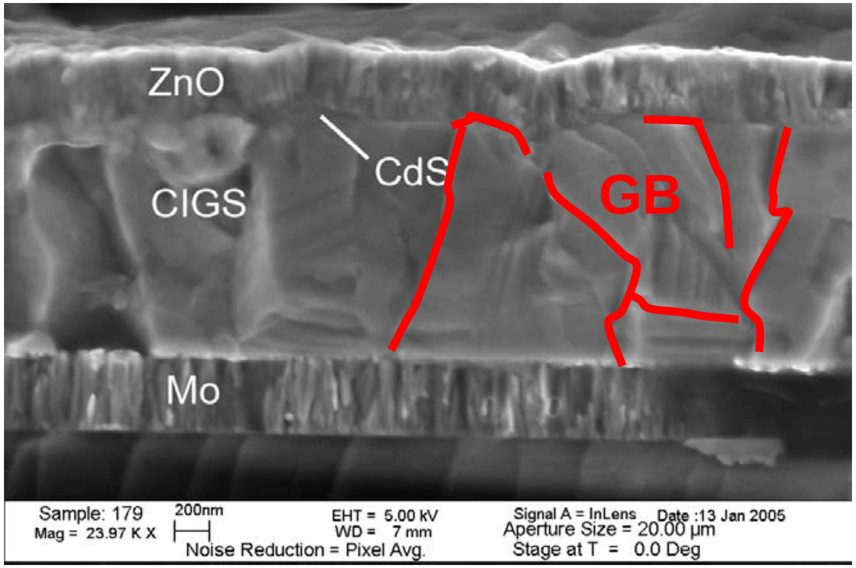
Modeling of GBs: GB are Cu poor

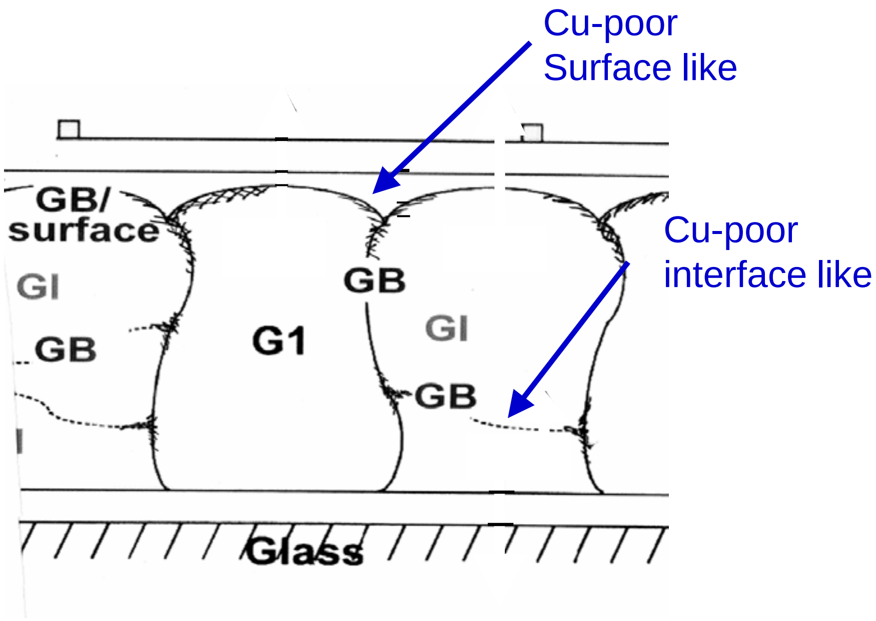


AFM grain boundaries in CISe
rockett.mse.uiuc.edu



nano-voids with (112)-surfaces
Lei, JAP 100, 073518 (2006)

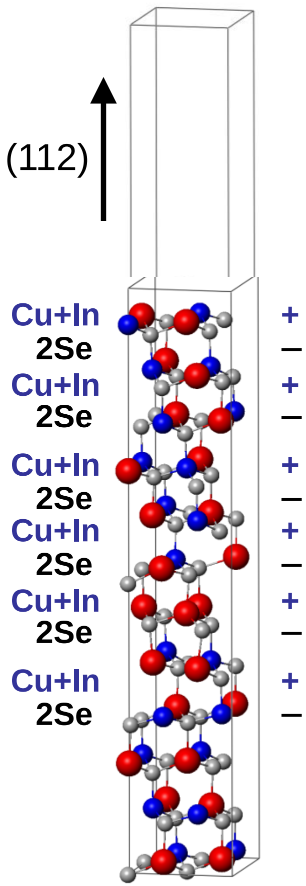




Why is GBs good/harmless for the device ?

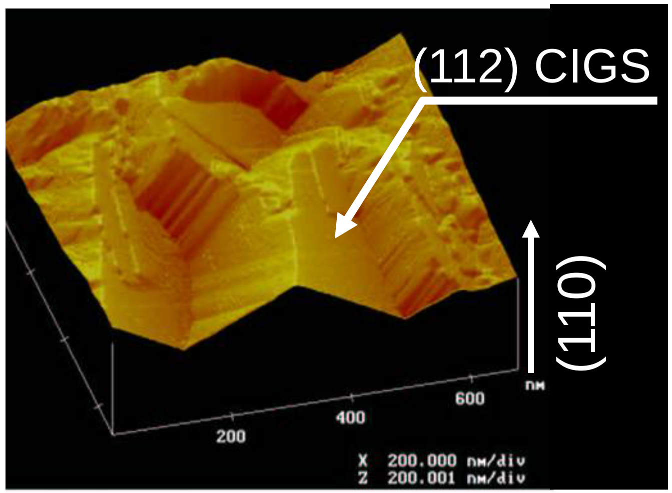
What is happening at GBs ?

Stable polar (112)-surface in CIGSe !!



Experimentally:

Liao and Rocket, 29th IEEE Conf. p. 515 (2002).

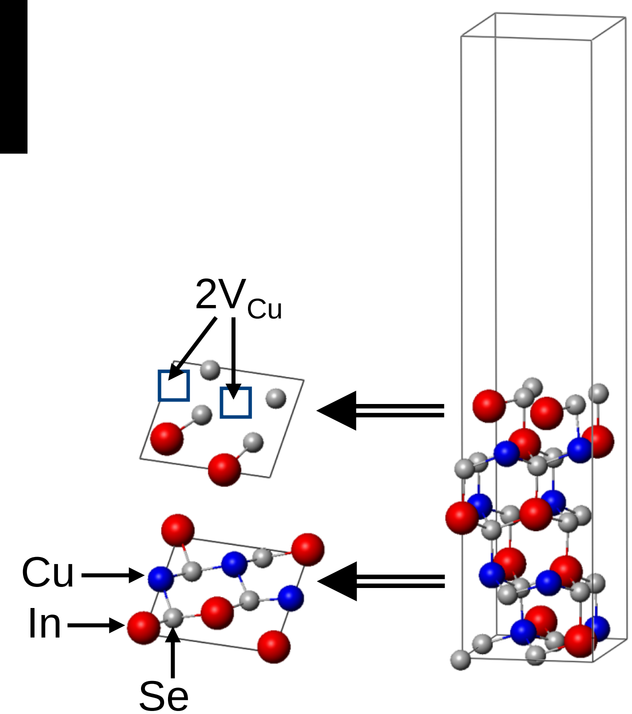


An atomic-force microscopy image of the urface of a (220)-oriented Cu(In,Ga)Se_2 epitaxial ayer grown on GaAs. The surface has ecomposed into two sets of polar (112) planes dentified by their crystallographic orientation).

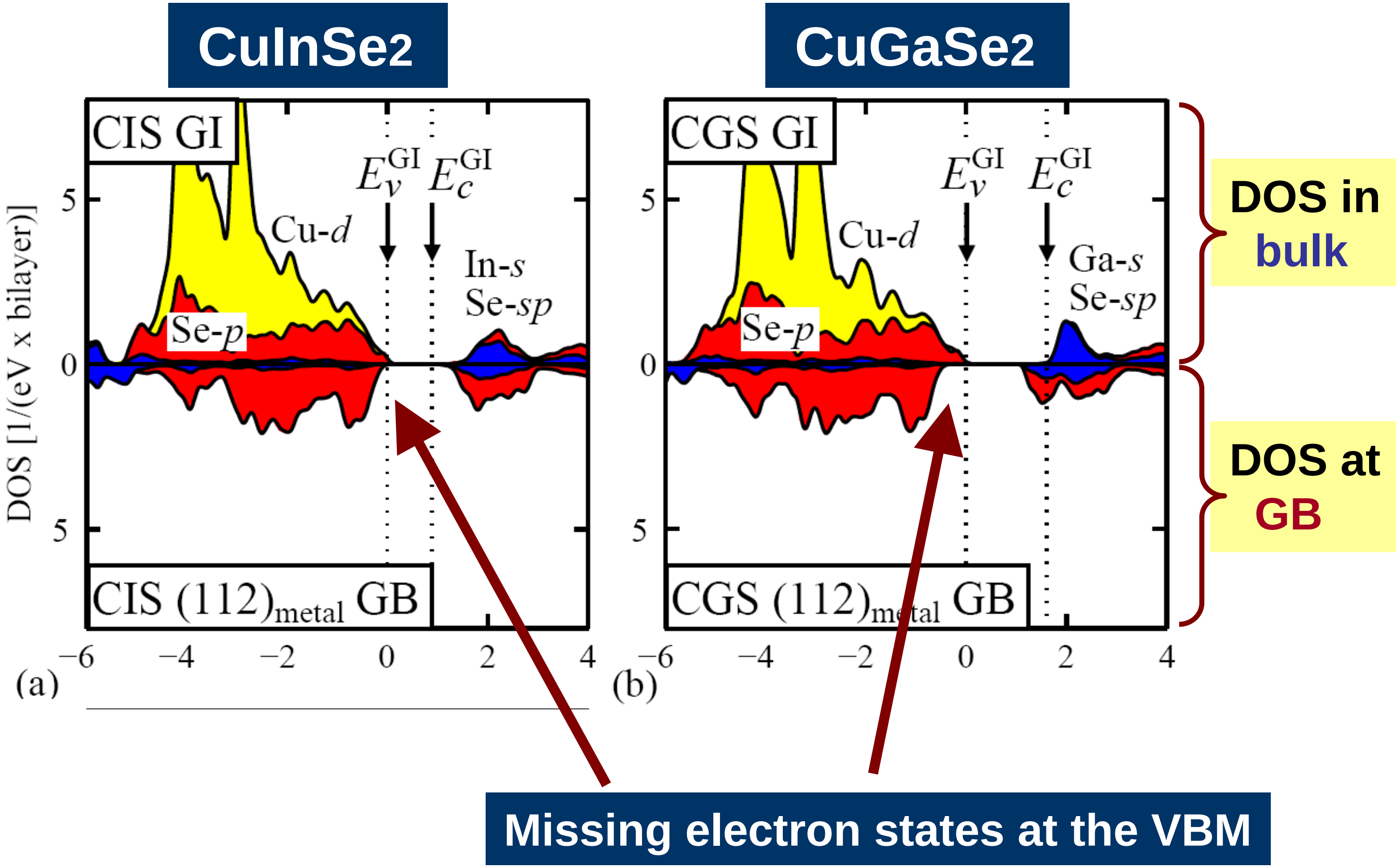
Theory:

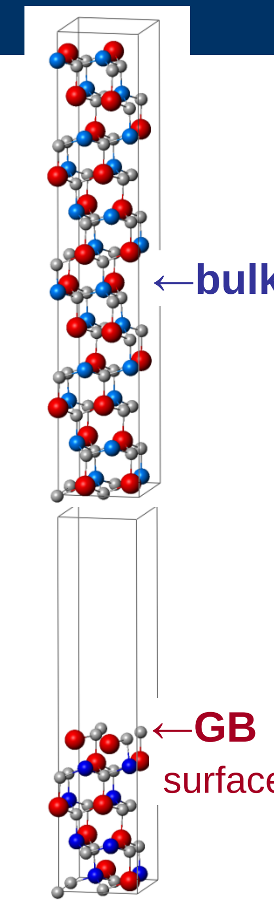
- In CIGSe: ***polar*** (112) is most stable
  it is energetically ‘cheap’ to create V_{cu}
  [Jaffe and Zunger, PRB 64, 241304 (2001)].

- (112) surface reconstruct by V_{Cu}.
  –(112) surface reconstruct by In_{Cu}.
  [Zhang and Wei, PRB 65, 081402 (2002)].



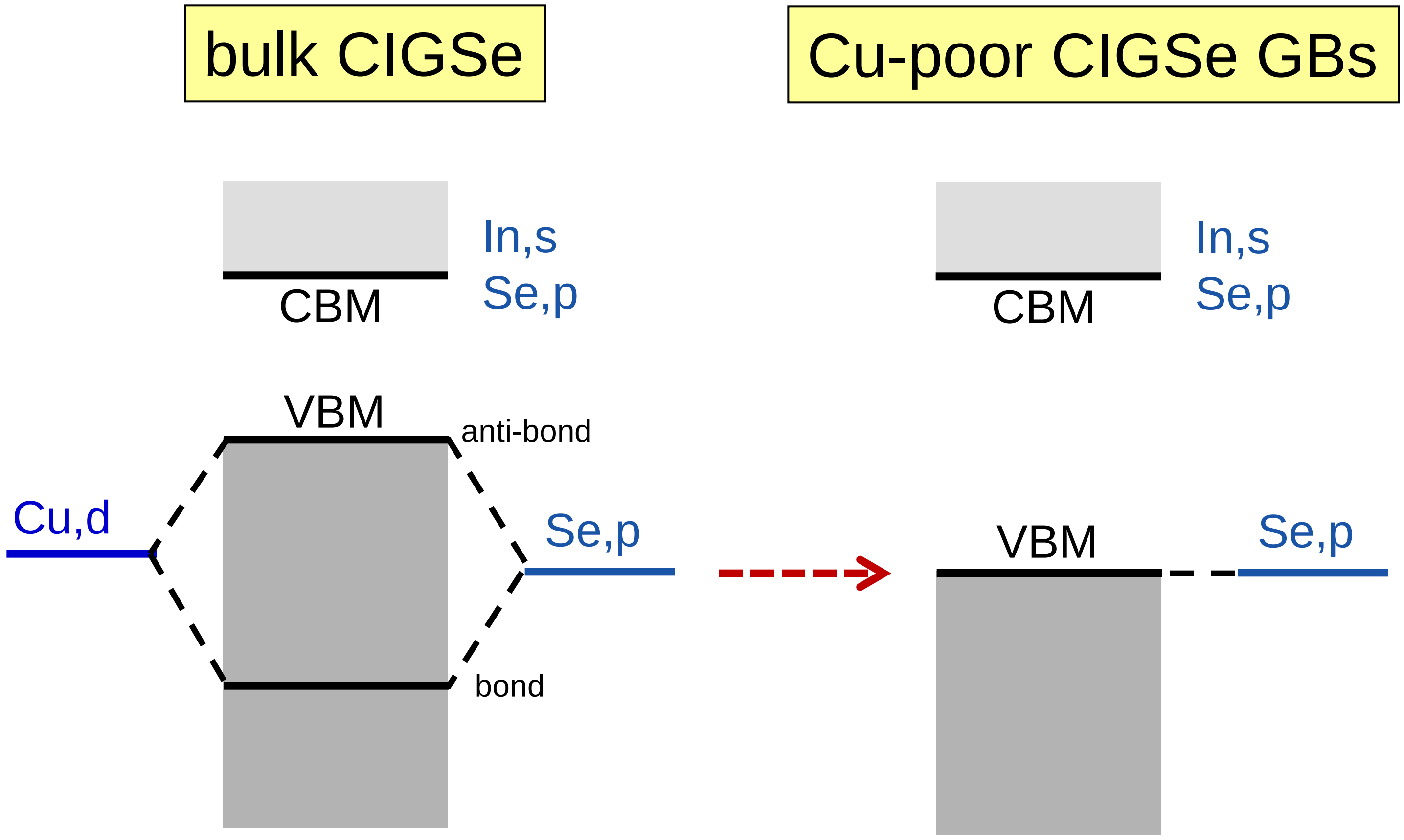
Hole barrier at the GBs





Persson, *et al*. APL **87**, 211904 (2005)

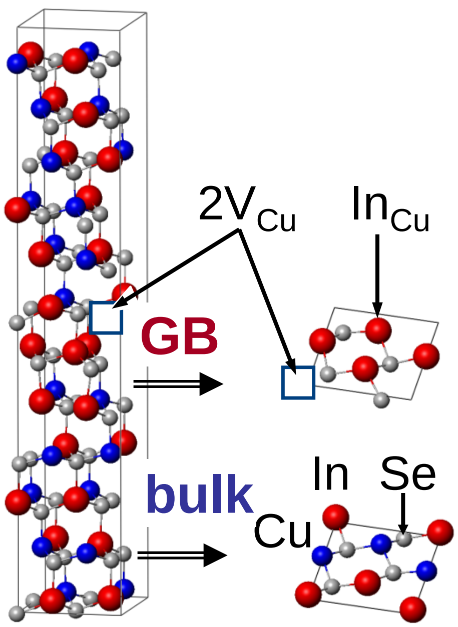
VBM of CIGS has strong d-character !!

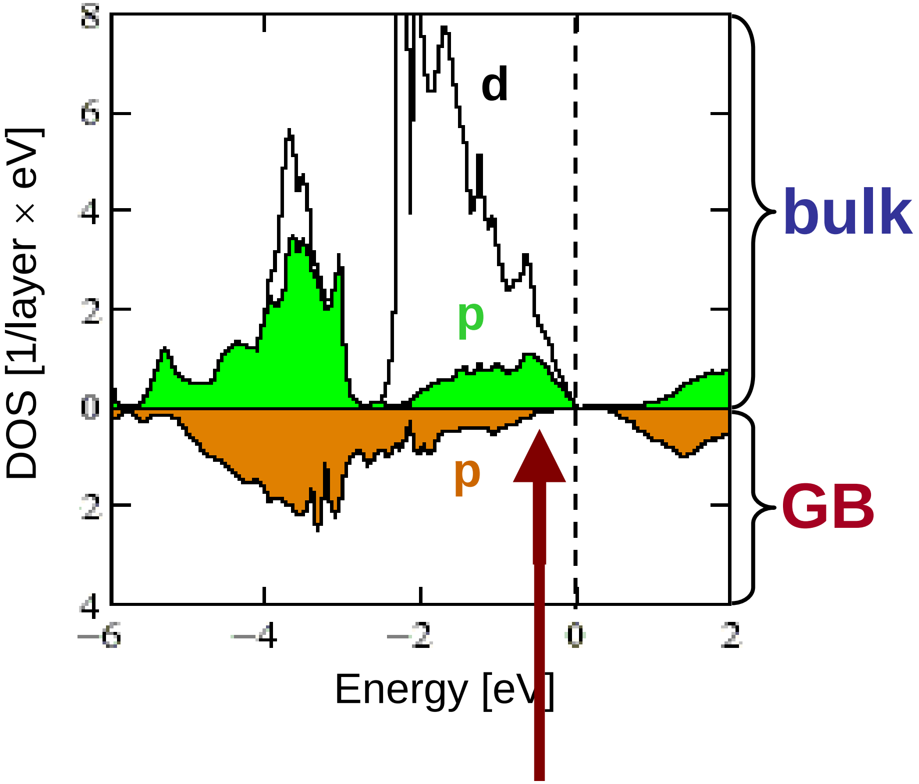


No Cu-d
⇒ lower VBM !!

[$2V_{Cu}+In_{Cu}$] at dislocations can also repel holes

CISe with $2V_{Cu}+In_{Cu}$

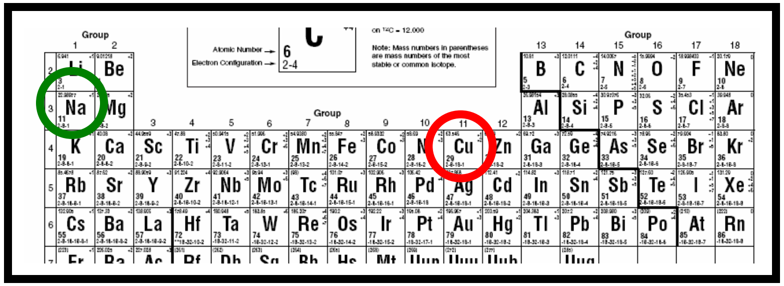




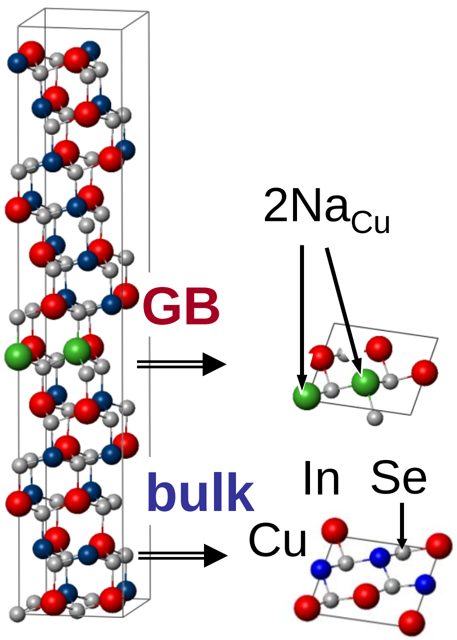
[$2V_{Cu}+In_{Cu}$] means Cu-poor region

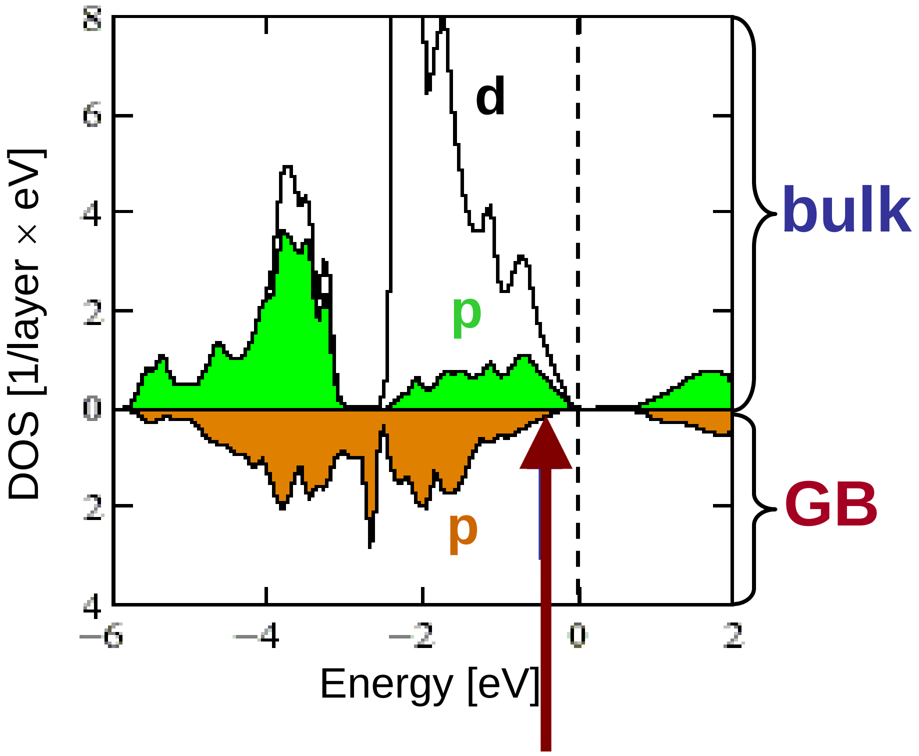
Persson, Zunger PRL **91**, 266401 (2003)

NaCu at dislocation interface can also repel holes



Cu: [Ar] $\mathbf{3d^{10}4s^1}$
Na: [Ne] $\mathbf{3s^1}$



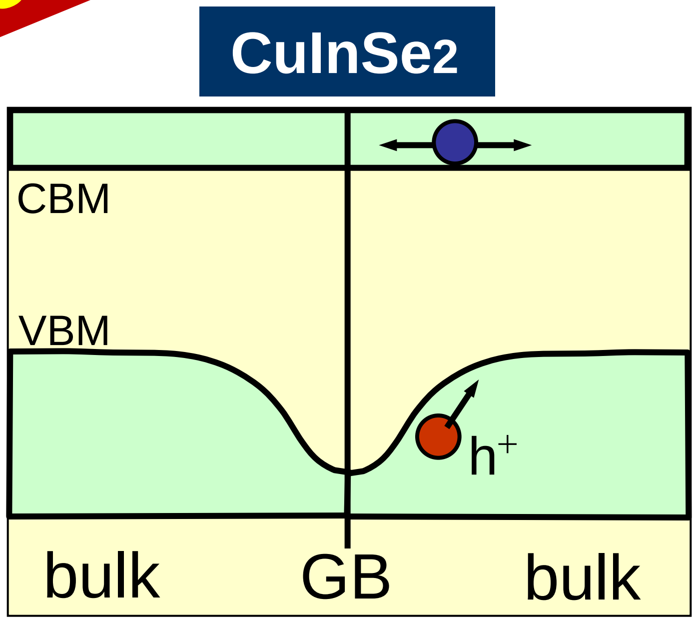


Na at GB lacks d-orbitals so it creates a hole barrier

PRL **91**, 266401 (2003)

Charged defects at GB (J.Y.W. Seto, JAP 46, 5247 (1975))

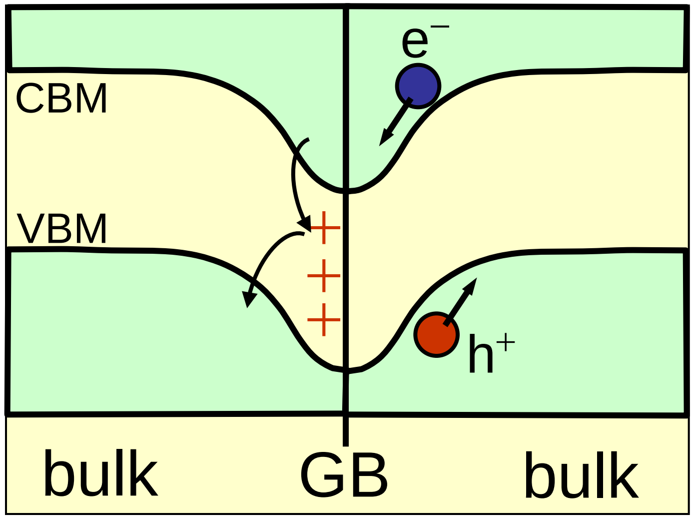
Good GB



Can we utilize this phenomena ?

Bad GB

case
ositively charged ions
Donors, e.g. V_{Se}^{++}



GB repels holes (majority), attracts electrons (minority)

Neutral GBs now observbed expt

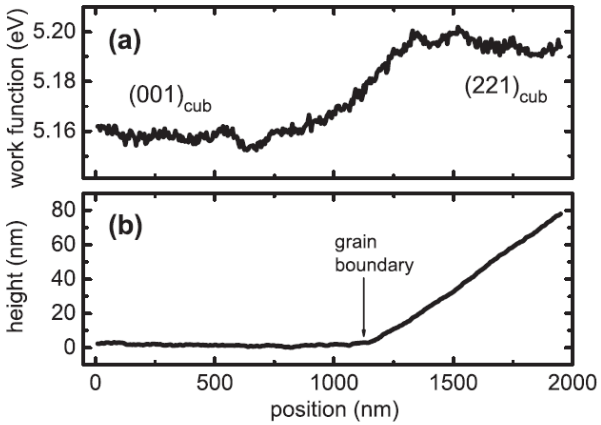
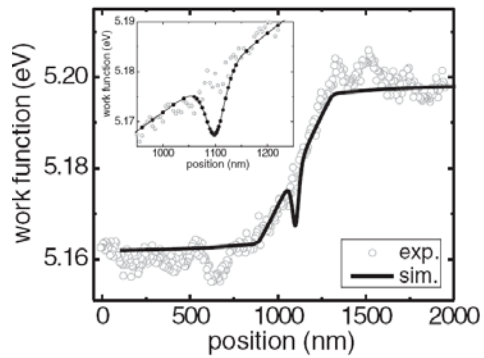


FIG. 3. KPFM line profile of the work function (a) and topography (b) across the grain boundary. The KPFM scan shows no indication of a space charge at the grain boundary.



'IG. 4. Simulation of the KPFM line profile (solid line) across he grain boundary assuming a 30 meV barrier at the grain oundary. The points show the comparison with the experimen- al data.

Siebentritt, et al, PRL 97,146601 (2006)

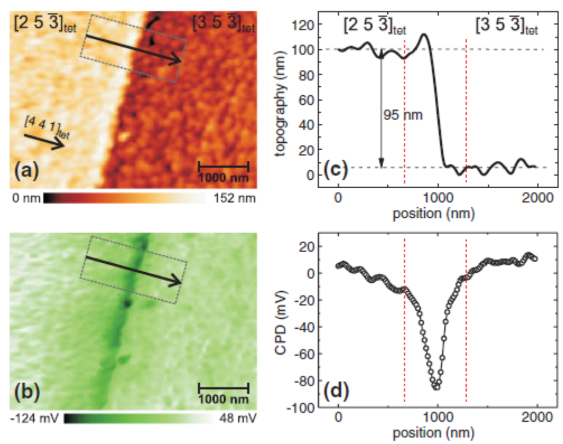


FIG. 1 (color online). KPFM measurement on the $CuGaSe_2$ bicrystal containing a $\Sigma 9$ grain boundary. (a) Topography and (b) CPD showing a dip along the GB. Averaged line profiles across the GB were extracted in the gray box indicated in the images for (c) topography and (d) CPD.

Hafenmeister, et al, PRL 104,196602 (2010)