Survey of Materials

Semiconductors

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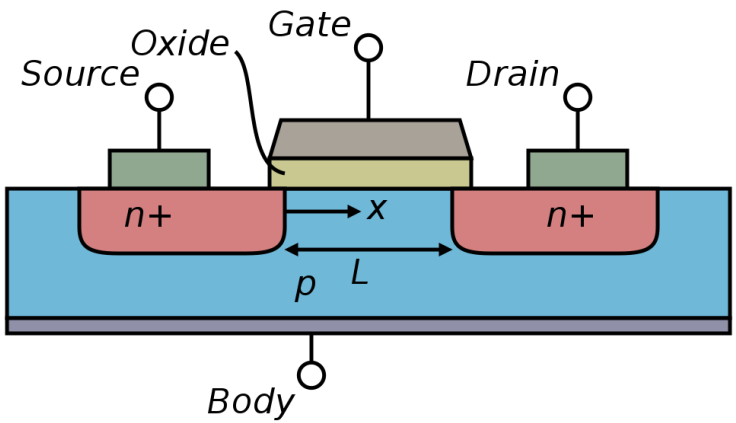
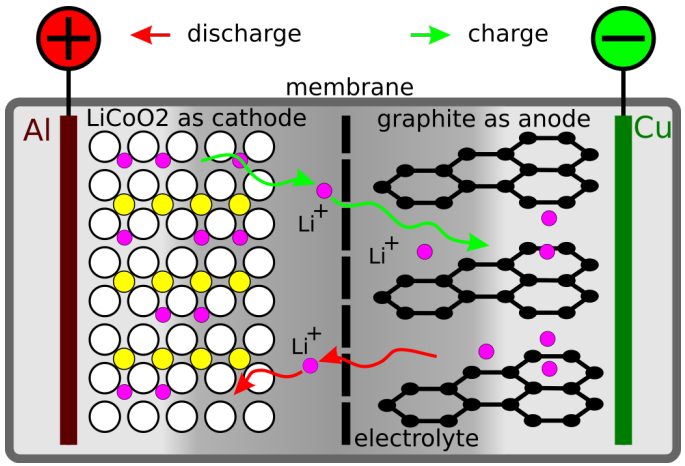
Outline

- Introduction: definition and classification
- Key properties
- Applications: solar cells and field-effect transistors
- Classical semiconductors (1 slide)
- Perovskites (1 slide)
- Pnictides and chalcogenides (4 slides + optional slides)
- See separate lecture on organic semiconductors

What is semiconductor: a functional electronic material

- Metals – passive electronic components (wires, electrodes)
- Insulators – passive electronic components (insulators)
- Semiconductors – active electronic components (device core)





Electronic devices: transistors, light emitters, solar cells, sensors – any device generating or transforming electronic current

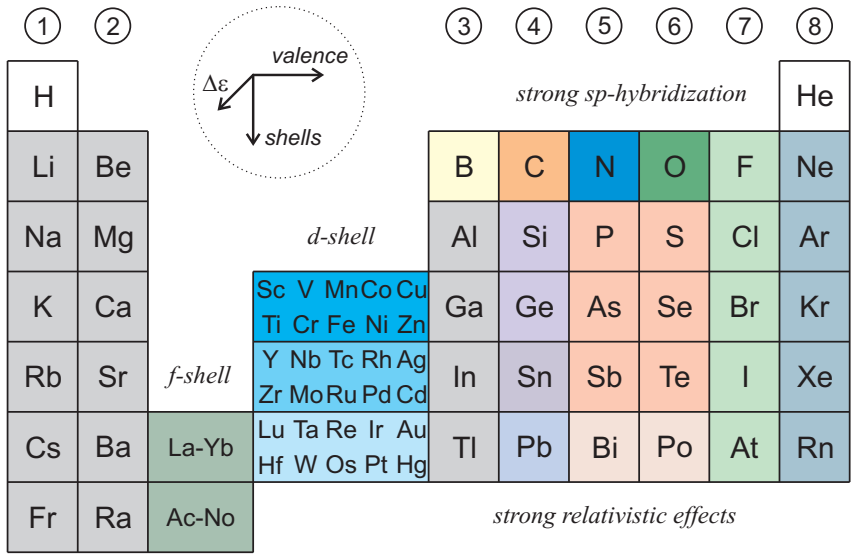
Passive electronic components in devices with electronic-ionic current, such as cathode/anode in rechargeable metal-ion batteries

What is semiconductor: definition by bandgap/conductivity

bandgap	class	electronic conductivity
several eV	insulators	no current because of self-localization
few eV	semiconductors	conductivity is easy to modulate
close to zero	semimetals	overlapping bands $\Longrightarrow$ similar to doped semiconductors
close to zero	strongly correlated	charge density fluctuations can close/open pseudogap
negative	simple metals	invariable conductivity due to large density of states at Fermi-level

Classes of semiconductors

Participating electrons: *sp*, *p*, *spd* (inorganic), π, πd (organic)



- (*sp*) "Classical" semiconductors – Si, GaAs, ZnS, CIGS
- (*sp*) Ionic "average-valence-4" semiconductors – $CsPbI_3$
- (*sp*) Electron-rich semiconductors – P, As, Se, AsSe, GeSbTe
- (*sp*) Electron-poor semiconductors – B
- (*spd*) Transition metal oxides, halides,. . . – TiO_2, MoO_x, $SrTiO_3$
- (π) π-conjugated (organic) semiconductors – graphene, molecules
- (πd) Metal-organic frameworks

Key functional properties of semiconductors

$$\text{Current density} \quad j = \mu \cdot n \cdot e\mathcal{E}$$

- high charge carrier mobility
- controllable charge carrier concentration

Factors influencing mobility

Current density	$j = \mu \cdot n \cdot e\mathcal{E}$
Mobility	$v = \mu\mathcal{E}$
Zero-field mobility	$\mu = \frac{e}{T} D$

Free charge carriers	**Localized charge carriers**
Drude formula	Hopping
$\mu = \frac{e\,\tau_{\text{scattering}}}{m_{\text{effective}}}$	$\mu = \frac{2\pi e}{\hbar} f \cdot (aV)^2 \frac{J}{T}$

* Purely electronic and electron-phonon interaction terms are factorized

Scattering (or localization) mechanisms:

- dynamic lattice defects (phonons, intramolecular vibrations)
- extrinsic disorder: from lattice defects to mesoscopic inhomogeneity (grain boundaries, interfaces)
- carrier-carrier interaction

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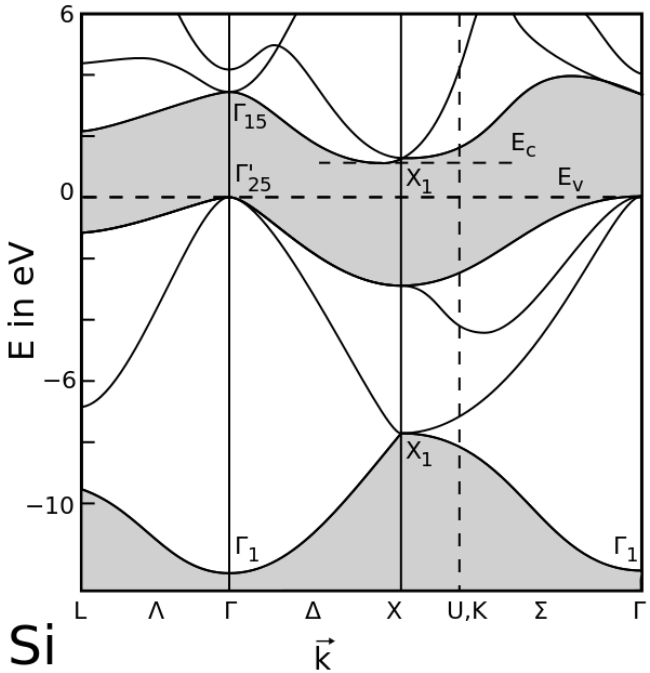
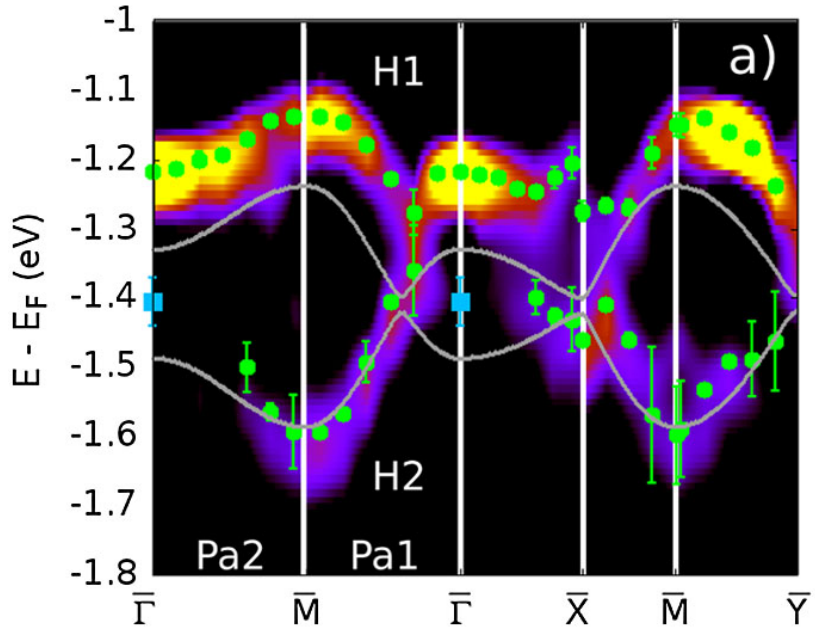
f is lattice form-factor, a is lattice spacing, V is electronic inter-site coupling, aV is hopping amplitude, J is spectral overlap

Need high bandwidth and low effective mass



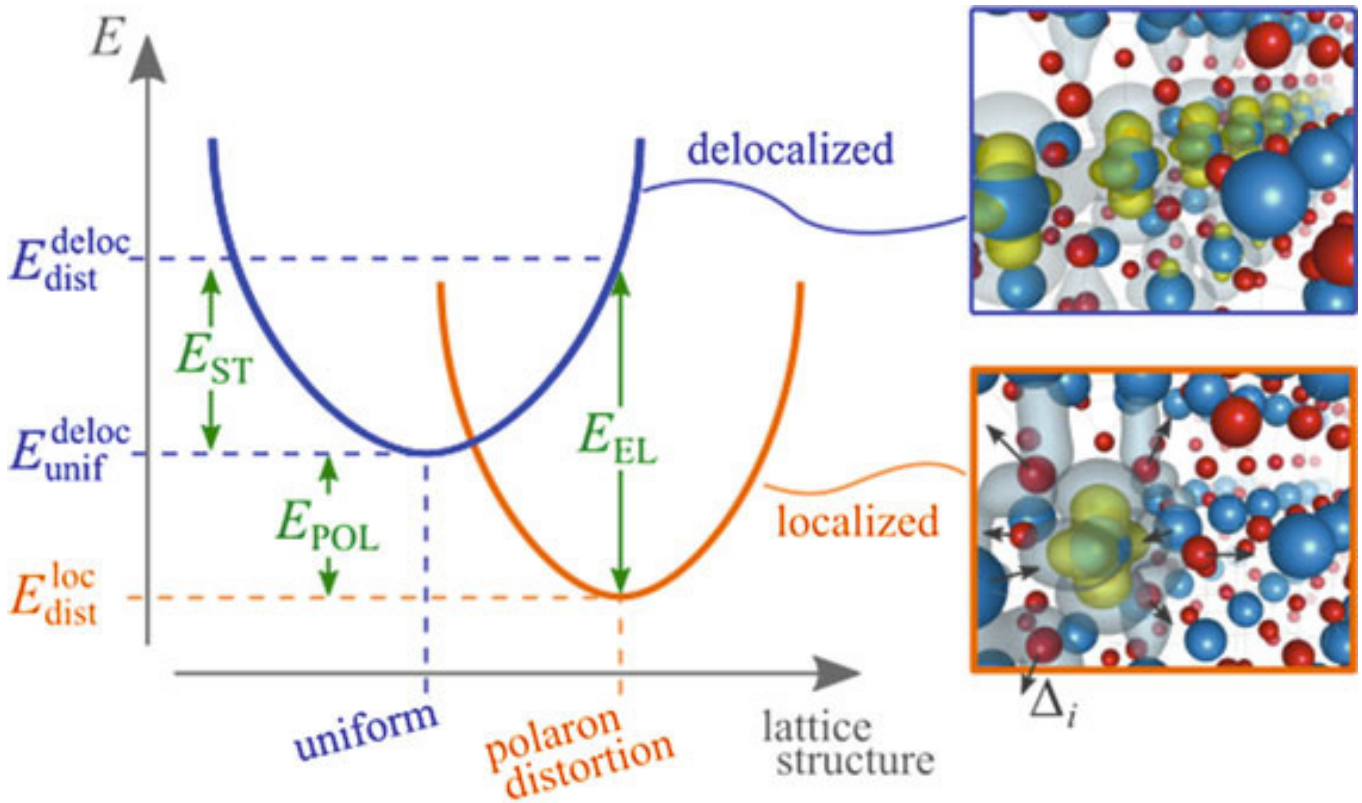


weak e-p interaction
$\Longrightarrow$ free charge carriers
scattered by phonons

strong e-p interaction
$\Longrightarrow$ mobile or
localized polarons

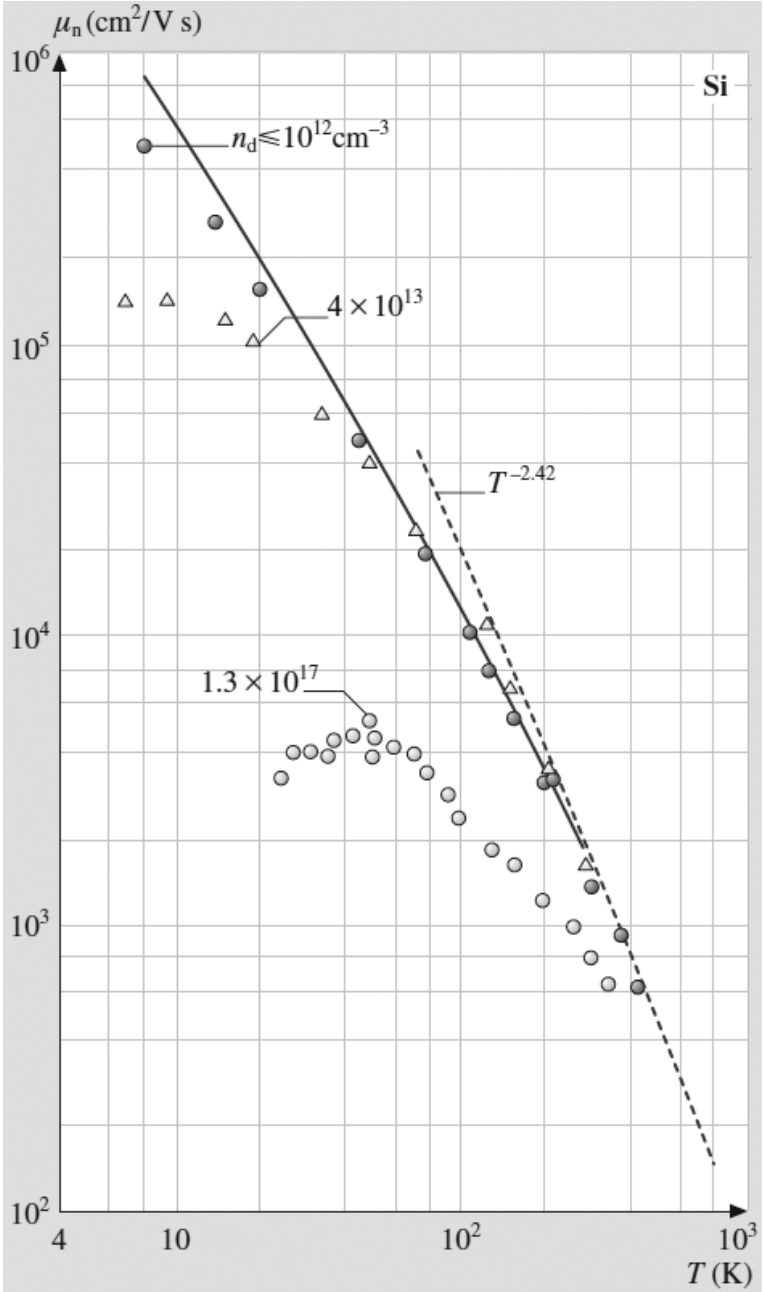
Polarons and localization

Free charge carriers – large polarons – mobile small polarons – localized charge carriers



M Reticcioli *et al*, Small Polarons in Transition Metal Oxides (Springer, 2020)

Scattering by phonons strongly depends on temperature



Room temperature mobility in different semiconductors

material	$\mu_n \left(\frac{\text{cm}^2}{\text{V}\cdot\text{s}}\right)$	$\mu_p \left(\frac{\text{cm}^2}{\text{V}\cdot\text{s}}\right)$
AlGaAs/GaAs 2DEG at low T	10^7	
graphene at low T	10^5	
InAs	10^4	
Ge	3800	1800
GaAs	3000	400
diamond	2000	2000
monocrystalline Si	1400	400
polycrystalline Si	100	
ZnS	100	40
best organic crystals	10	10
amorphous Si	1	
best organic polymers		0.1
solid electrolytes, water	10^{-3}	10^{-3}

Changing charge carrier concentration

- charge carrier injection
- doping (intentional and unintentional)
- photoexcitation
- field effect

Doping

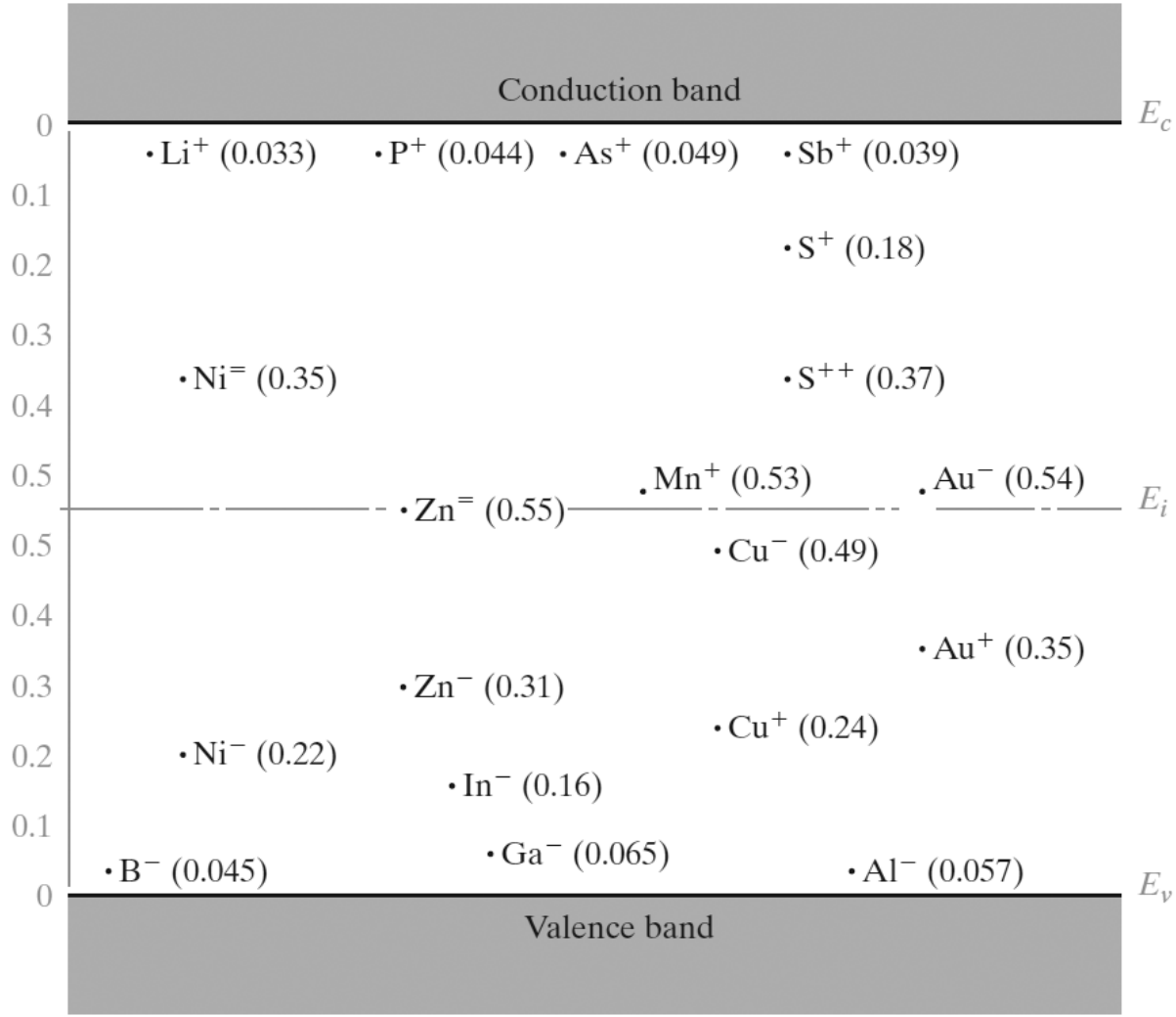
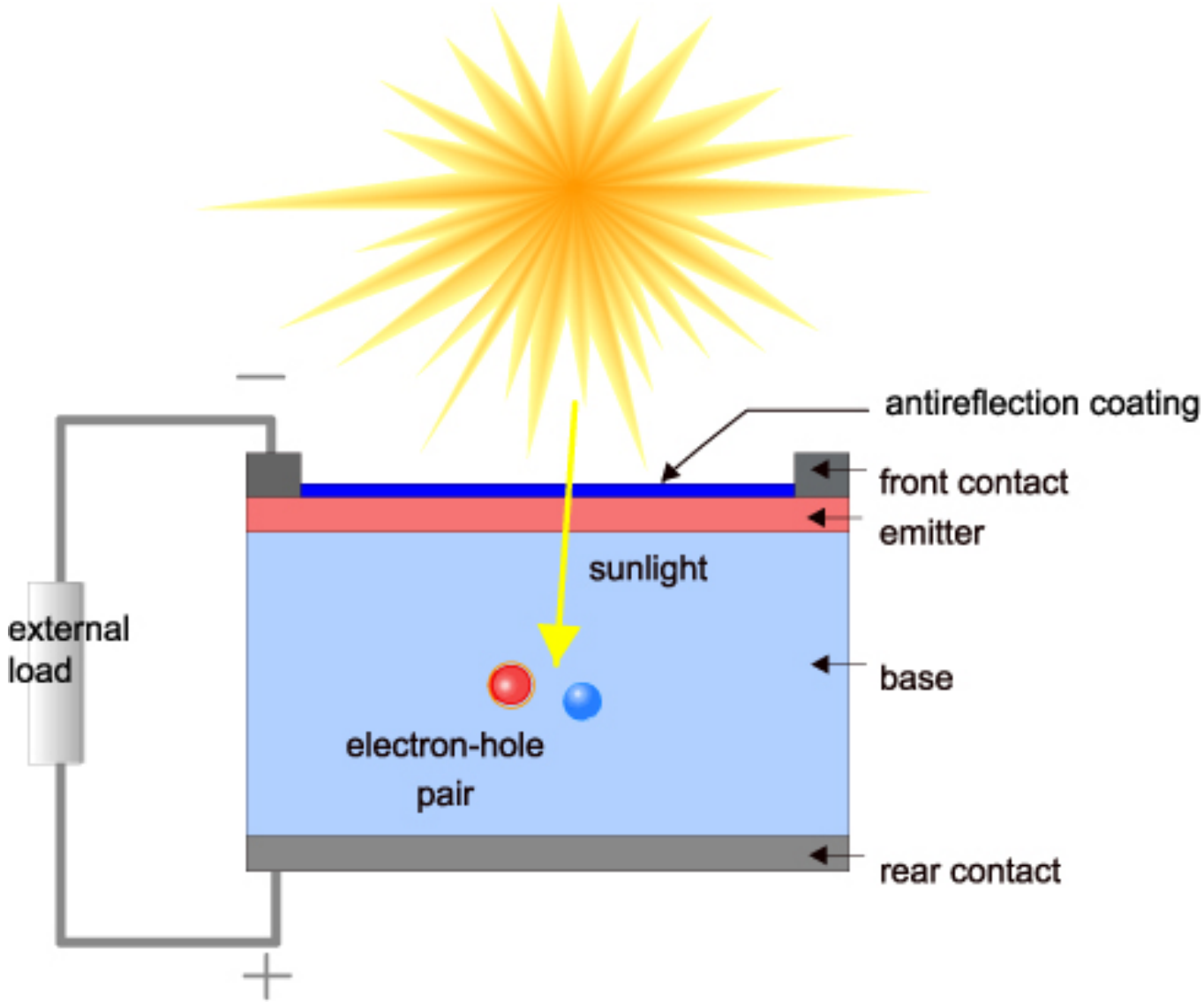


Figure 4–9
Energy levels of impurities in Si. The energies are measured from the nearest band edge (E_v or E_c); donor levels are designated by a plus sign and acceptors by a minus sign.

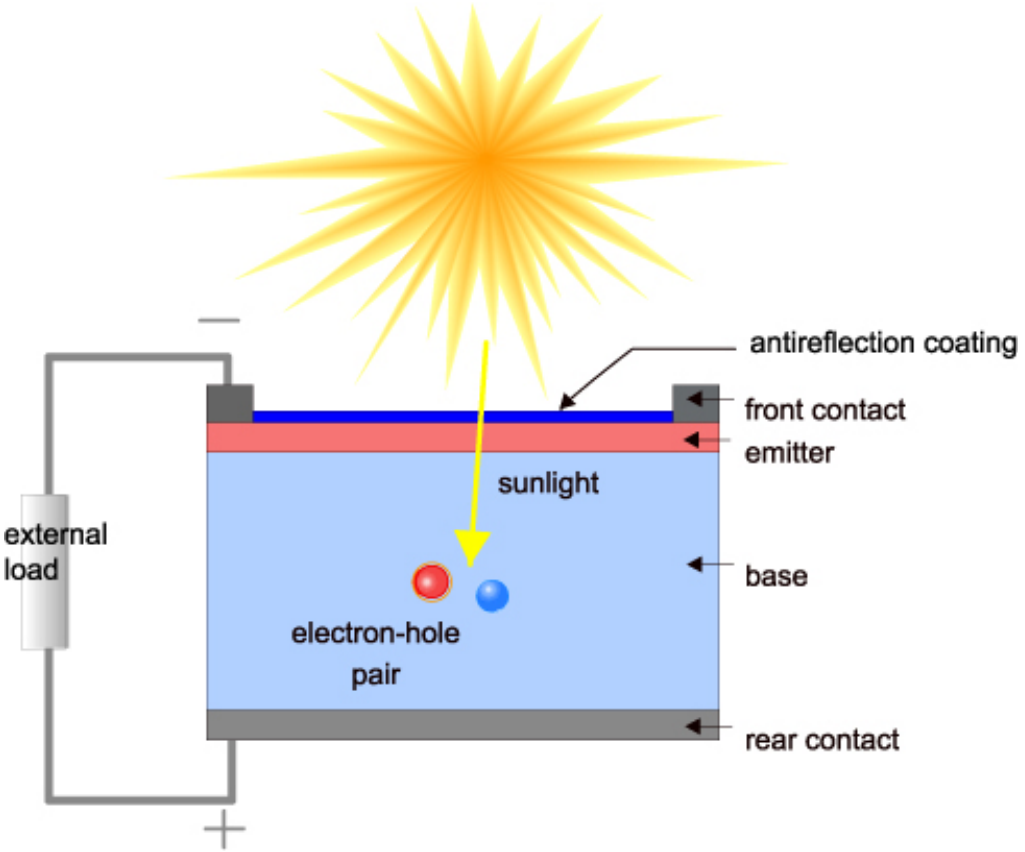
[4]References: S. M. Sze and J. C. Irvin, "Resistivity, Mobility, and Impurity Levels in GaAs, Ge and Si at 300 K," *Solid State Electronics,* vol. 11, pp. 599–602 (June 1968); E. Schibli and A. G. Milnes, "Deep Impurities in Silicon," *Materials Science and Engineering,* vol. 2, pp. 173–180 (1967).

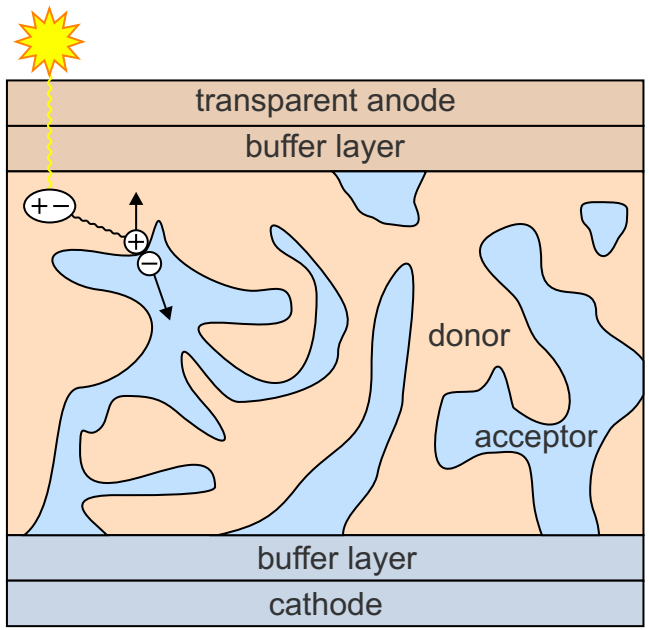
Photoexcitation



Either bound (Frenkel exciton) or free (or Wannier–Mott exciton) electron and holes depending on dielectric constant

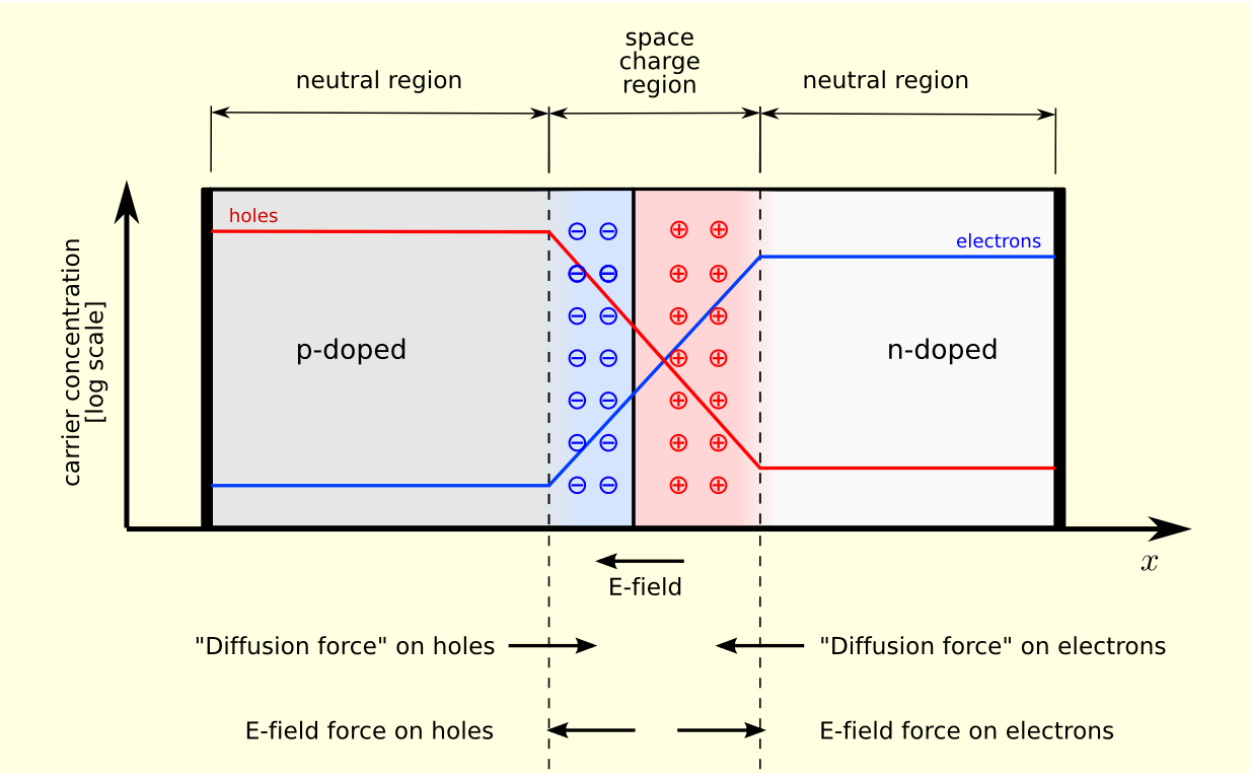
Photovoltaic effect and solar cells

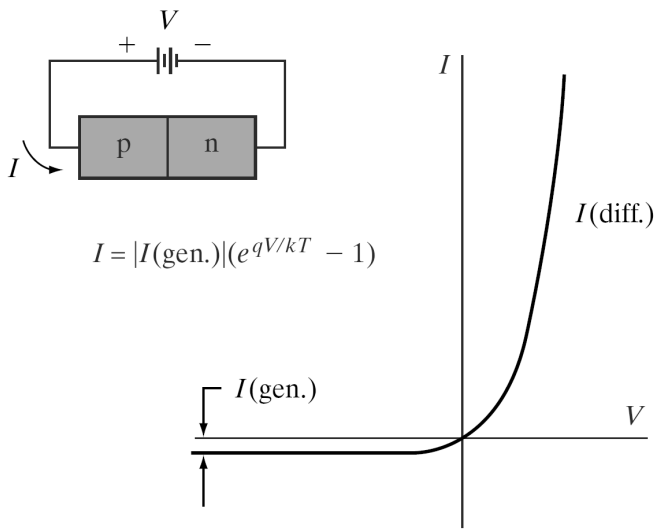




Challenge:
Efficient charge separation at full light absorption and high voltage

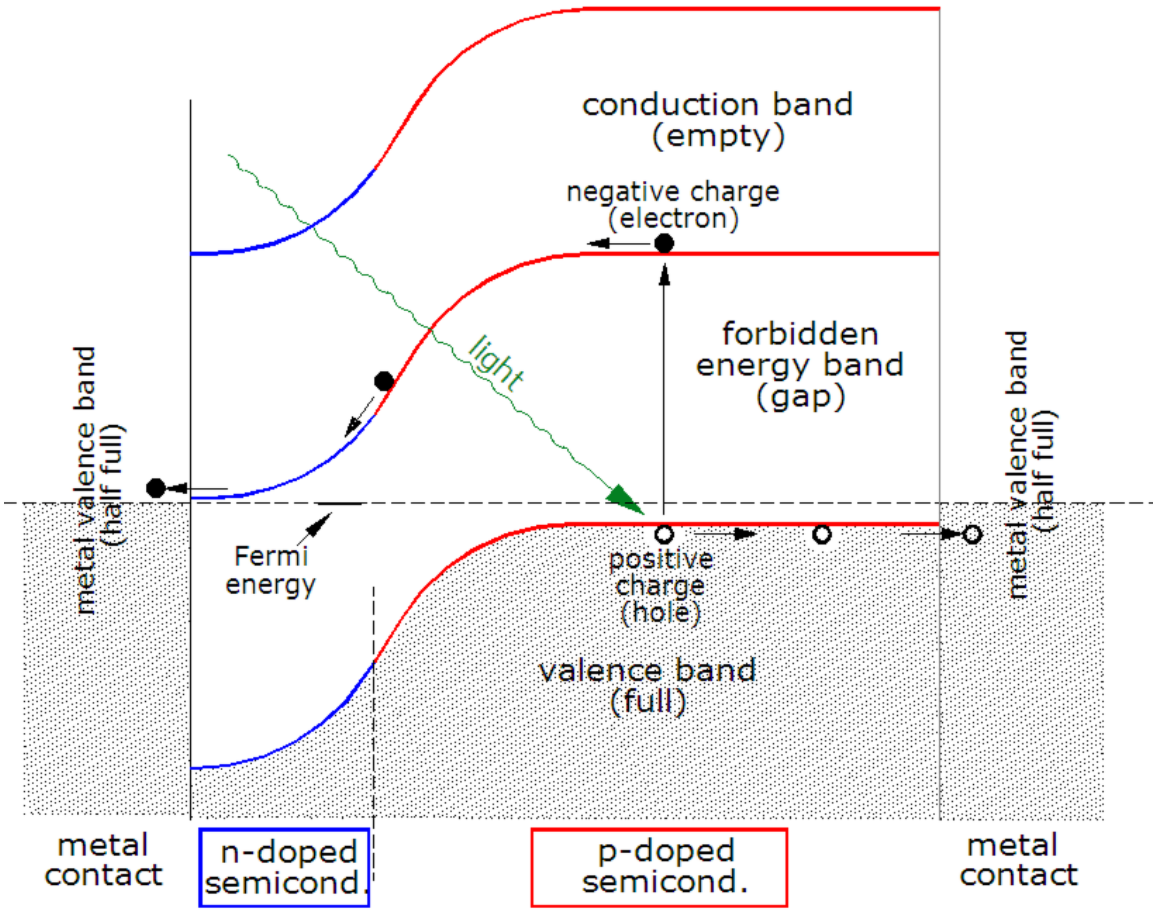
p-n junction and Shockley diode equation

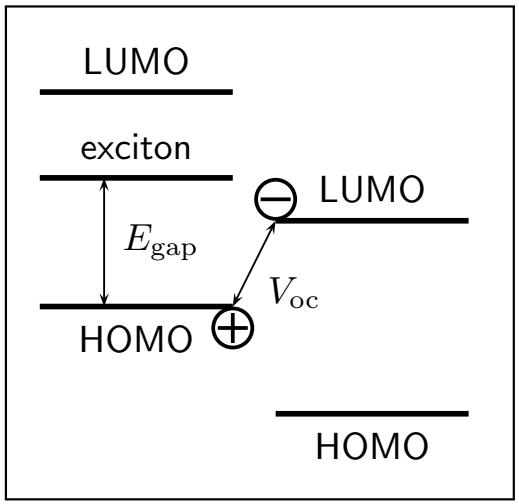




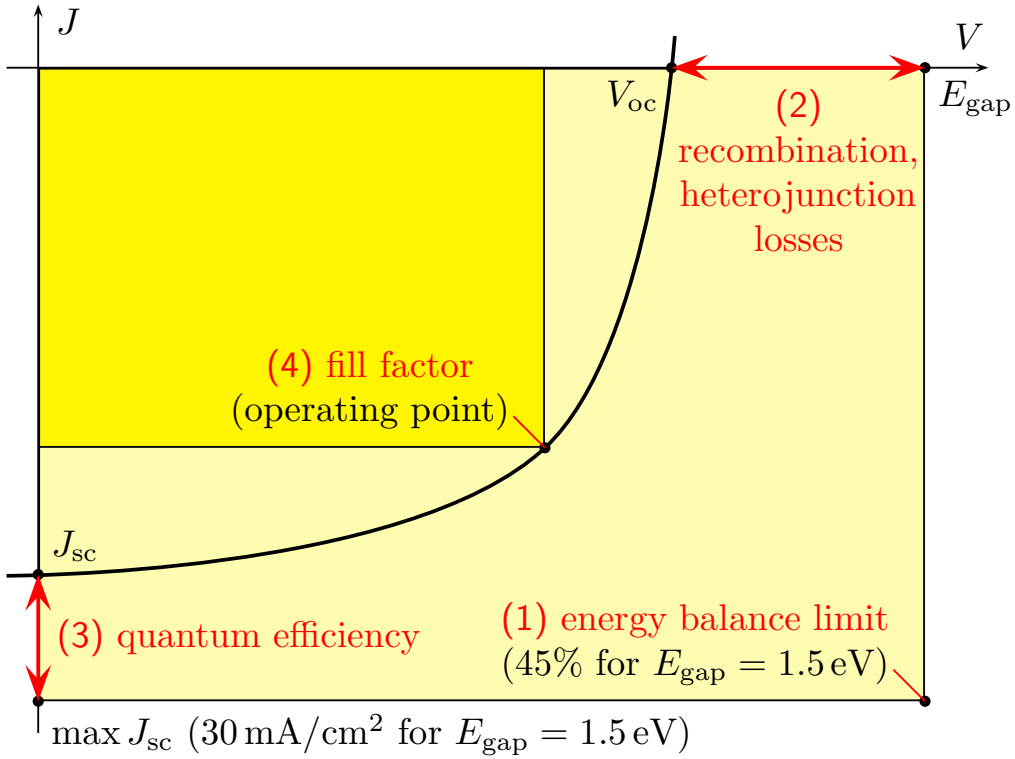
Wikipedia, Streetman2016

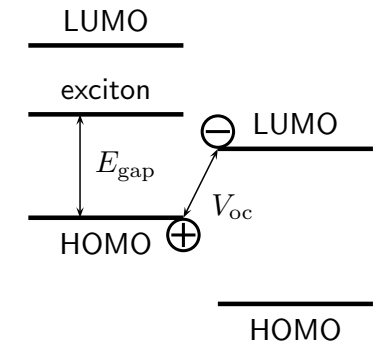
Photovoltaic effect: p-n junction and heterojunction

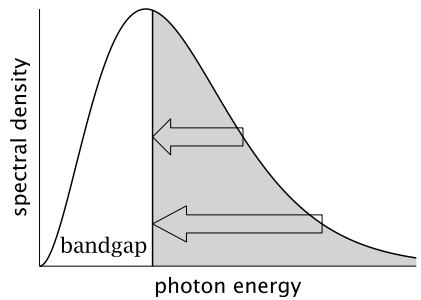




Power conversion efficiency (PCE): main factors



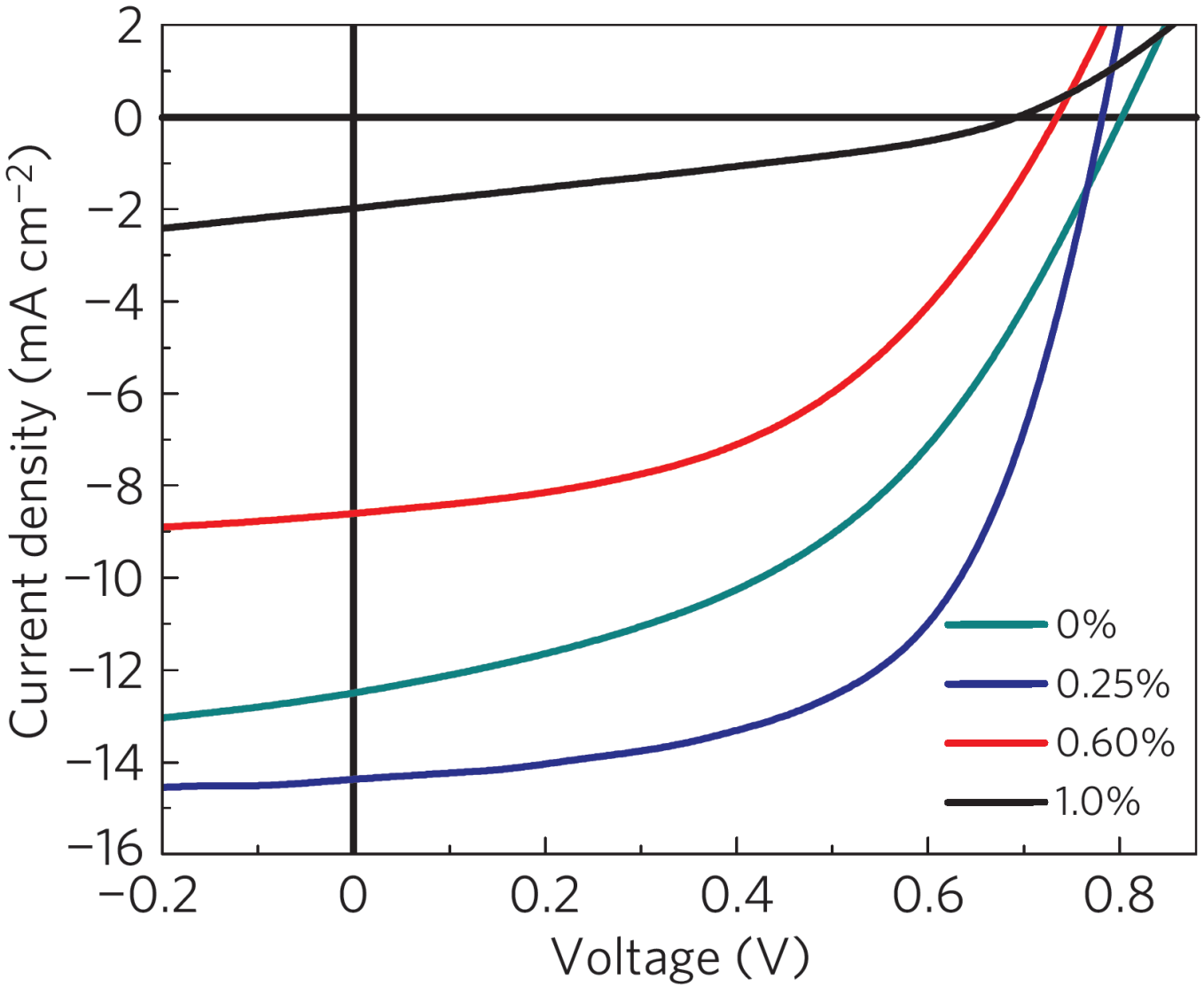




$$\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}} \equiv \eta_{abs}(E_g) \times \frac{eV_{oc}}{E_g} \times \frac{J_{sc}}{J_{sc}^{max}(E_g)} \times FF$$

V_{oc} – open-circuit voltage, J_{sc} – short-circuit current, E_g – bandgap

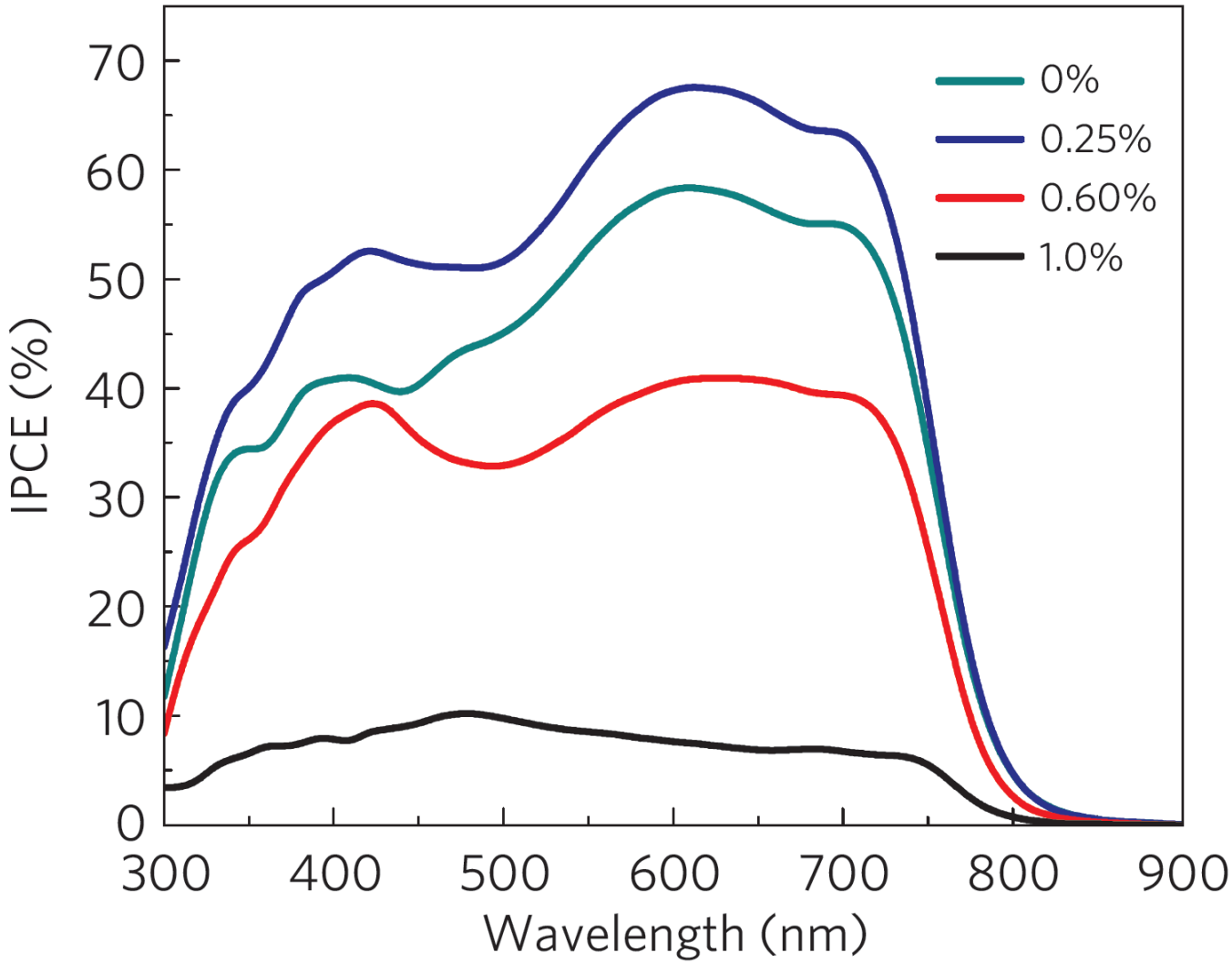
Power conversion efficiency: Fill factor



Nature Mater 11, 44 (2012)

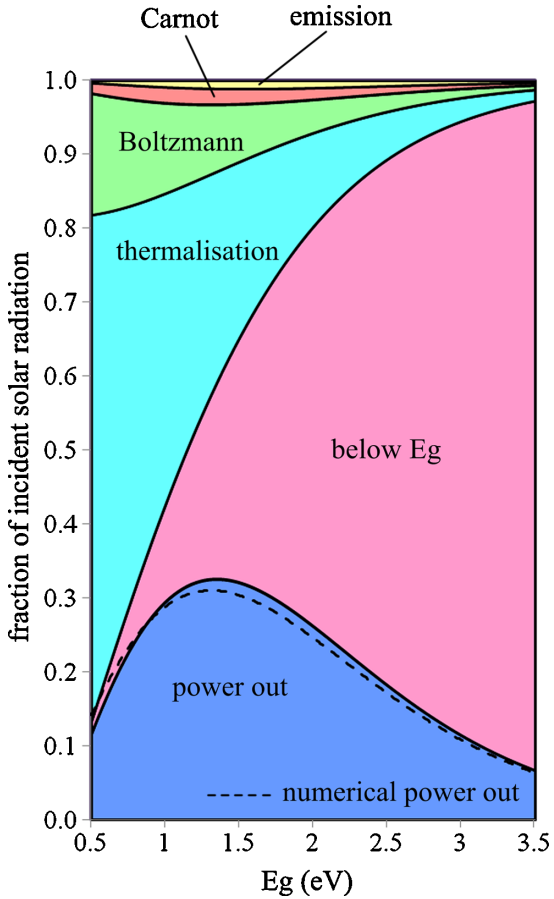
Power conversion efficiency: Quantum efficiency

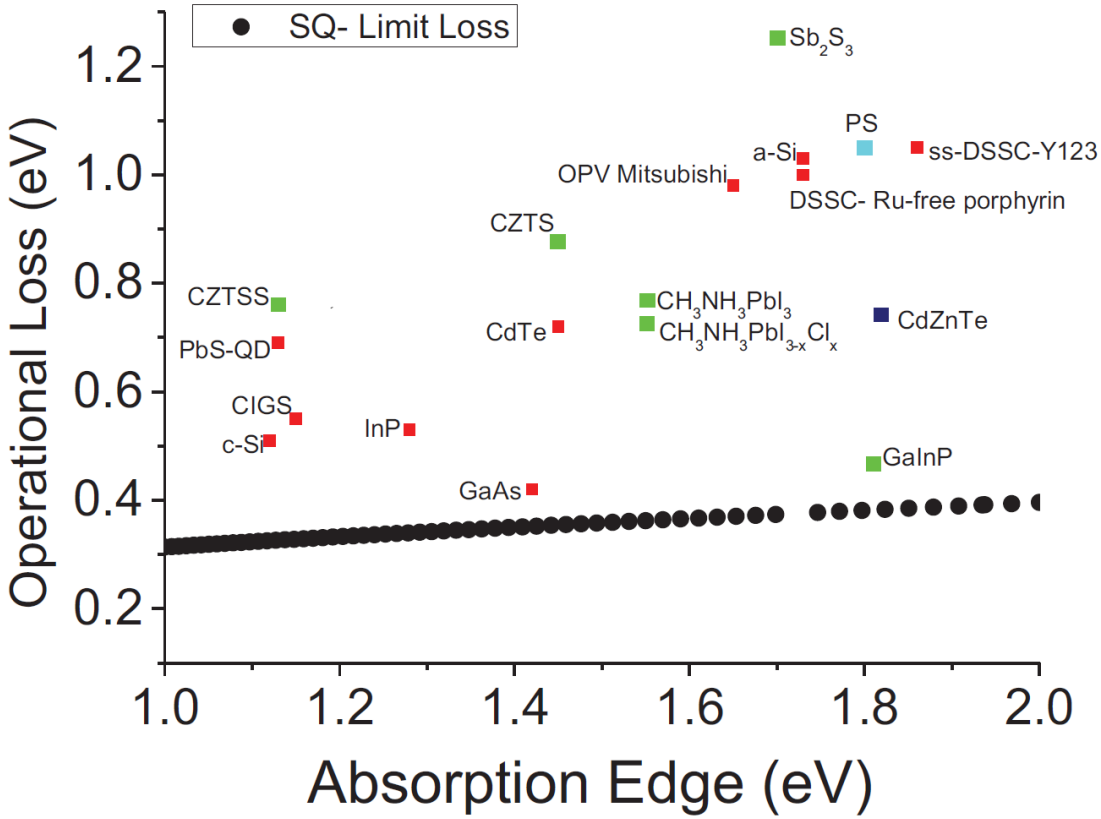
(IPCE = Incident Photon to Current Efficiency)



Nature Mater 11, 44 (2012)

Power conversion efficiency: Shockley–Queisser limit





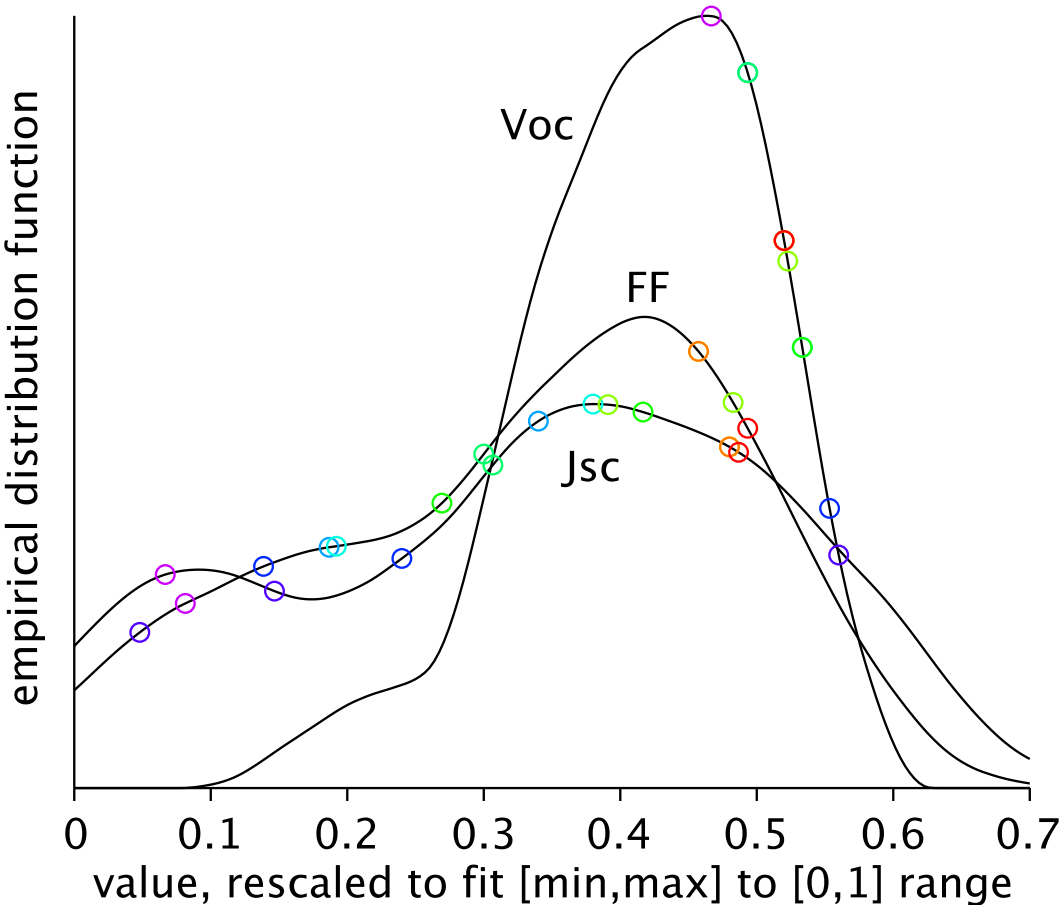
$$eV_{\mathrm{oc}} = E_{\mathrm{g}}\left(1 - \frac{T}{T_{\mathrm{in}}}\right) - kT \ln \frac{\Omega_{\mathrm{out}}}{\Omega_{\mathrm{in}}} + kT \ln \frac{\gamma(E_{\mathrm{g}}, T_{\mathrm{in}})}{\gamma(E_{\mathrm{g}}, T)} + kT \ln \eta_{\mathrm{lum}}$$

Ref.: J App Phys 32, 510 (1961), Adv Mater 26, 1622 (2014),
Prog Photovolt Res Appl 19, 286 (2011)

Power conversion efficiency: examples

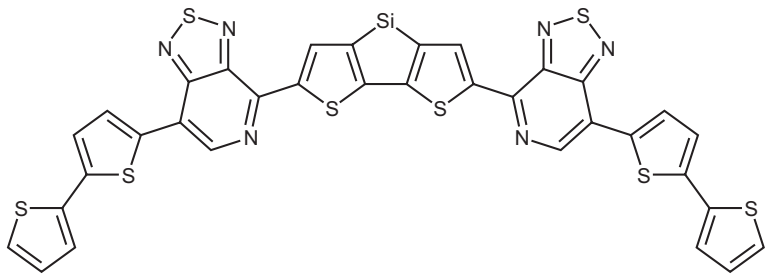
		OPV	Si	GaAs
Energy balance limit, $\eta_{\mathrm{abs}}(E_{\mathrm{g}})$		0.5	0.49	0.45
Recombination losses, $eV_{\mathrm{oc}}/E_{\mathrm{g}}$	$\times$	0.6	0.63	0.79
Quantum efficiency, $J_{\mathrm{sc}}/J_{\mathrm{sc}}^{\mathrm{max}}(E_{\mathrm{g}})$	$\times$	0.6	0.97	0.93
Fill Factor, $\max JV/J_{\mathrm{sc}}V_{\mathrm{oc}}$	$\times$	0.8	0.83	0.87
Power conversion efficiency	$=$	14%	25%	29%

Distribution of V_{oc}, J_{sc}, FF

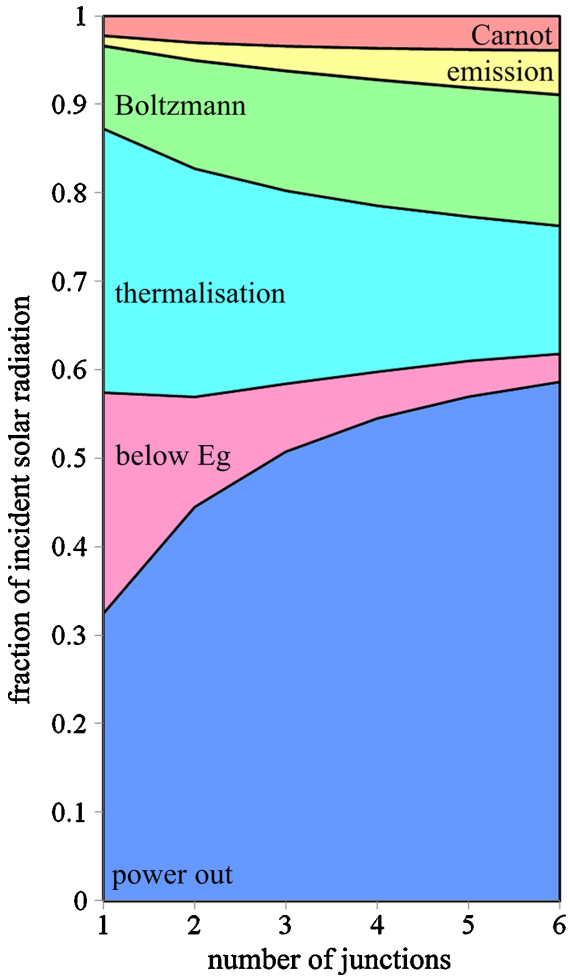


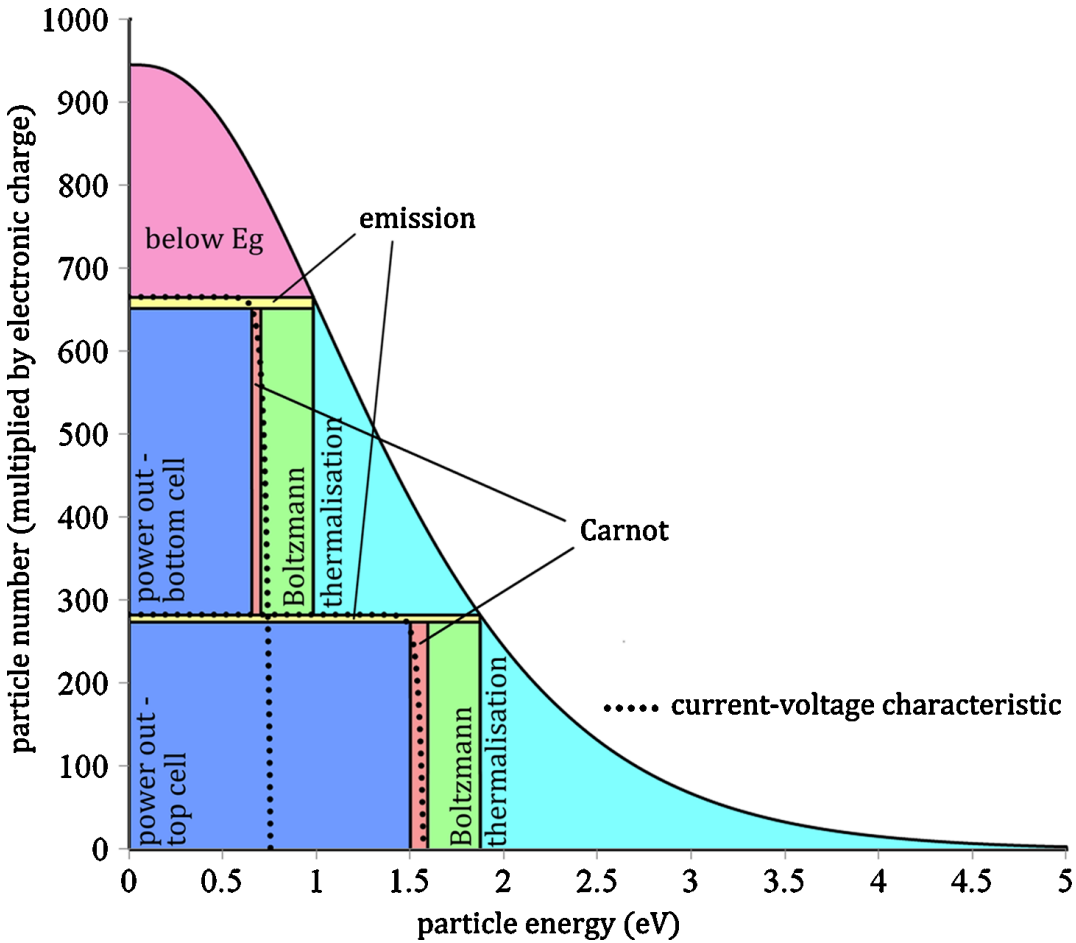
– Empirical distribution over 67 OPVs is provided by J. McClean (Clean Energy Project) http://cleanenergy.harvard.edu

◦ Dots correspond to refinement of one system, up to 7% PCE (Nature Mater 11, 44 (2012) JACS 134, 16597 (2012))



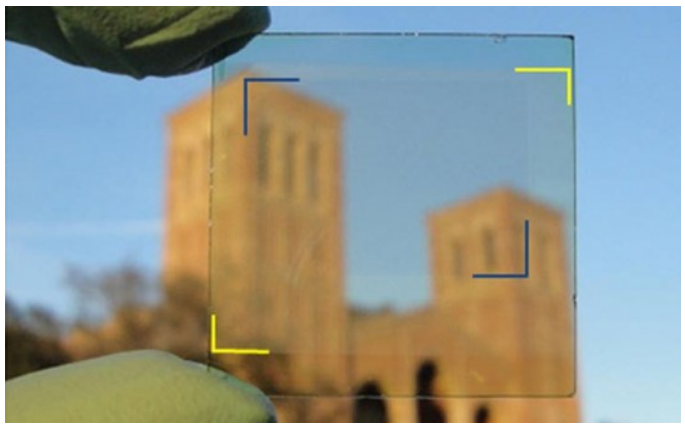
Multijunction cells

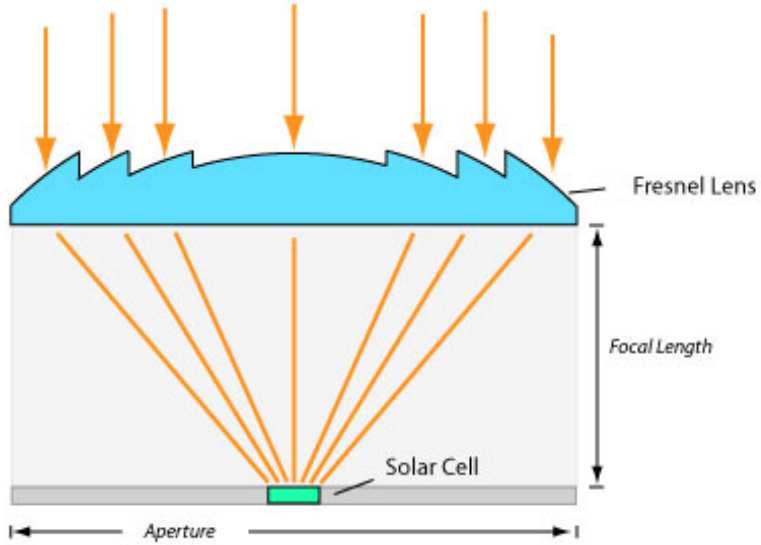


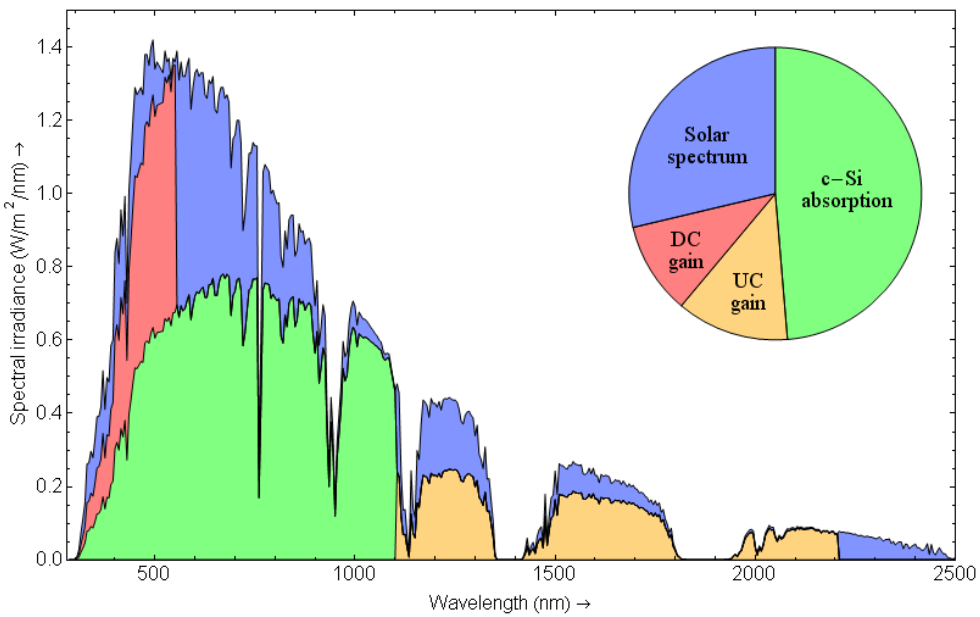


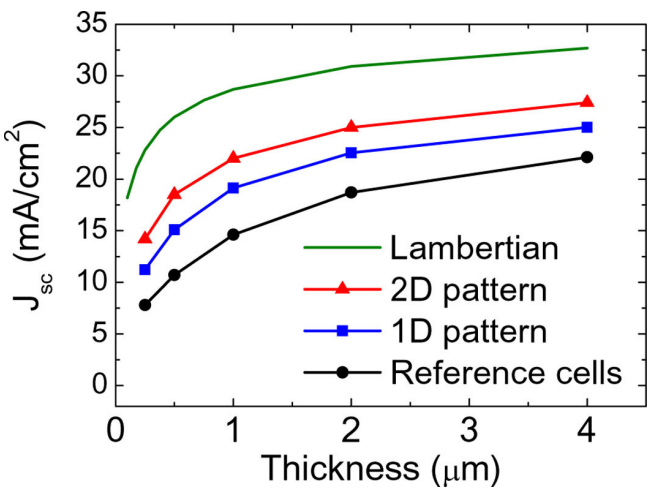
Technology: other tricks

(transparent, concentrated, up-down conversion, improved optics)

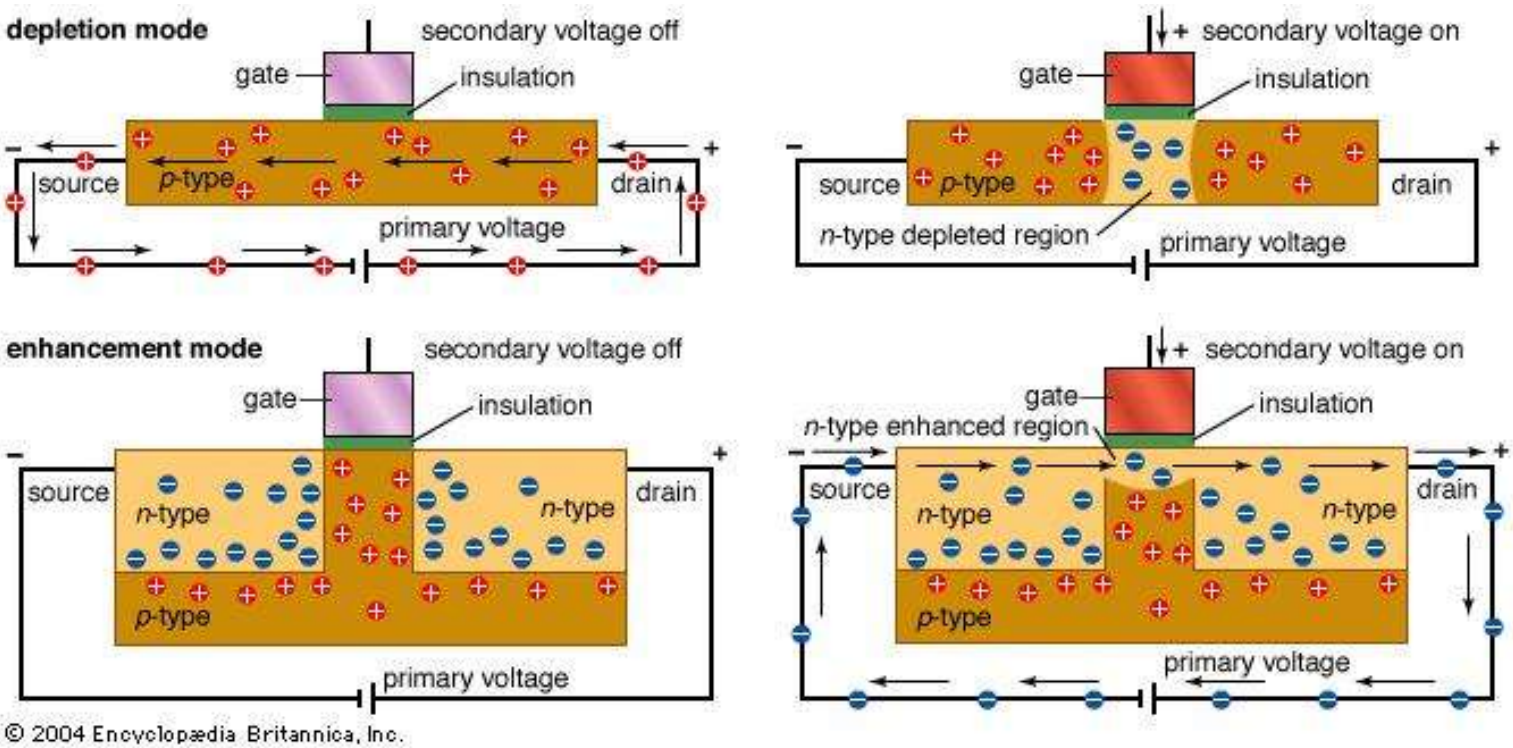






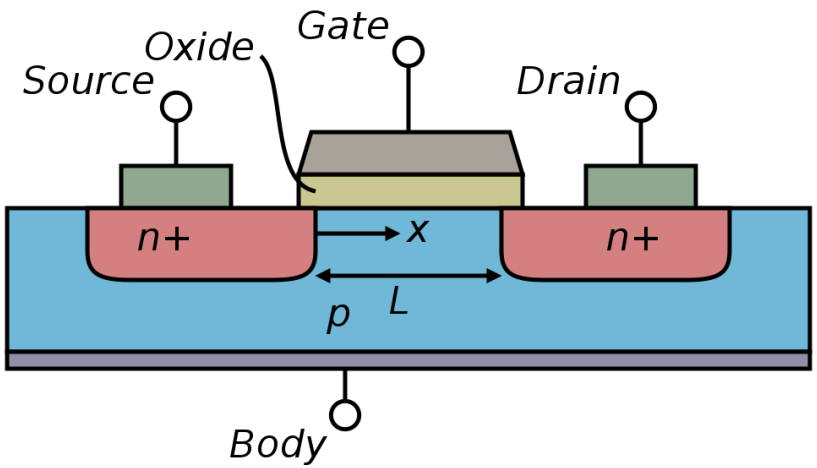


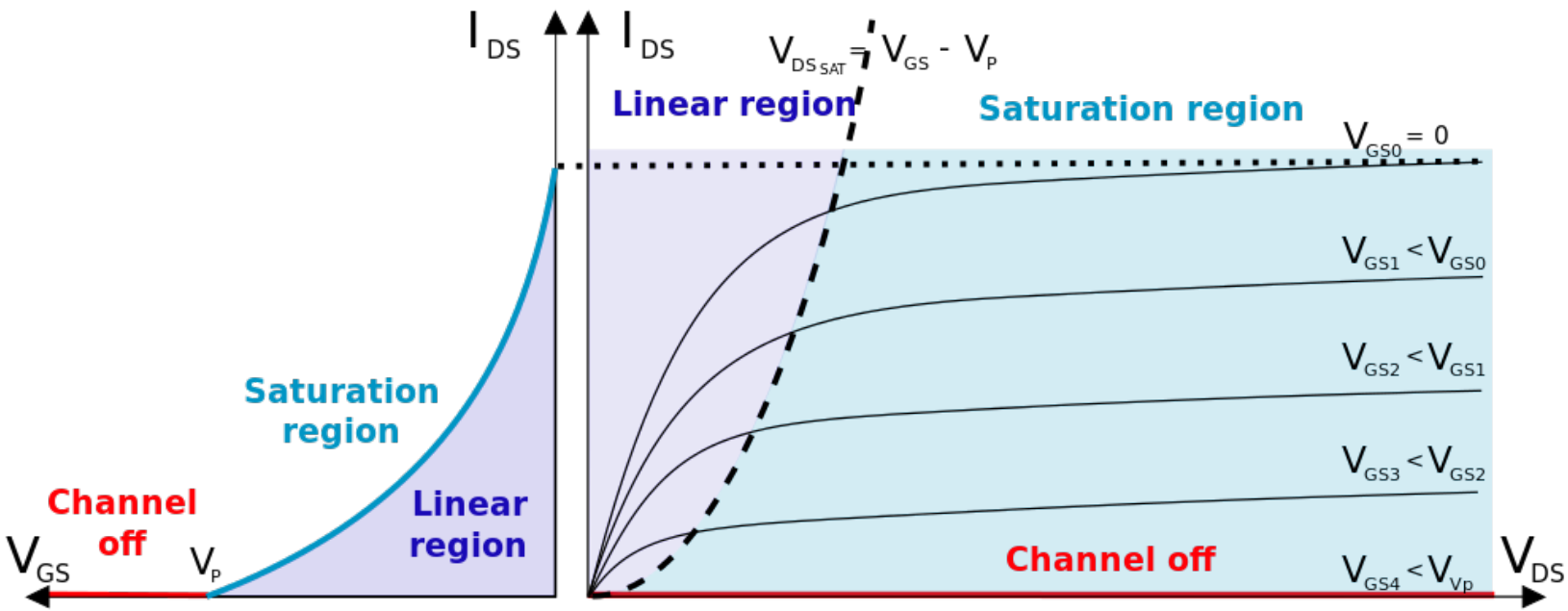
Field effect



Field effect transistor

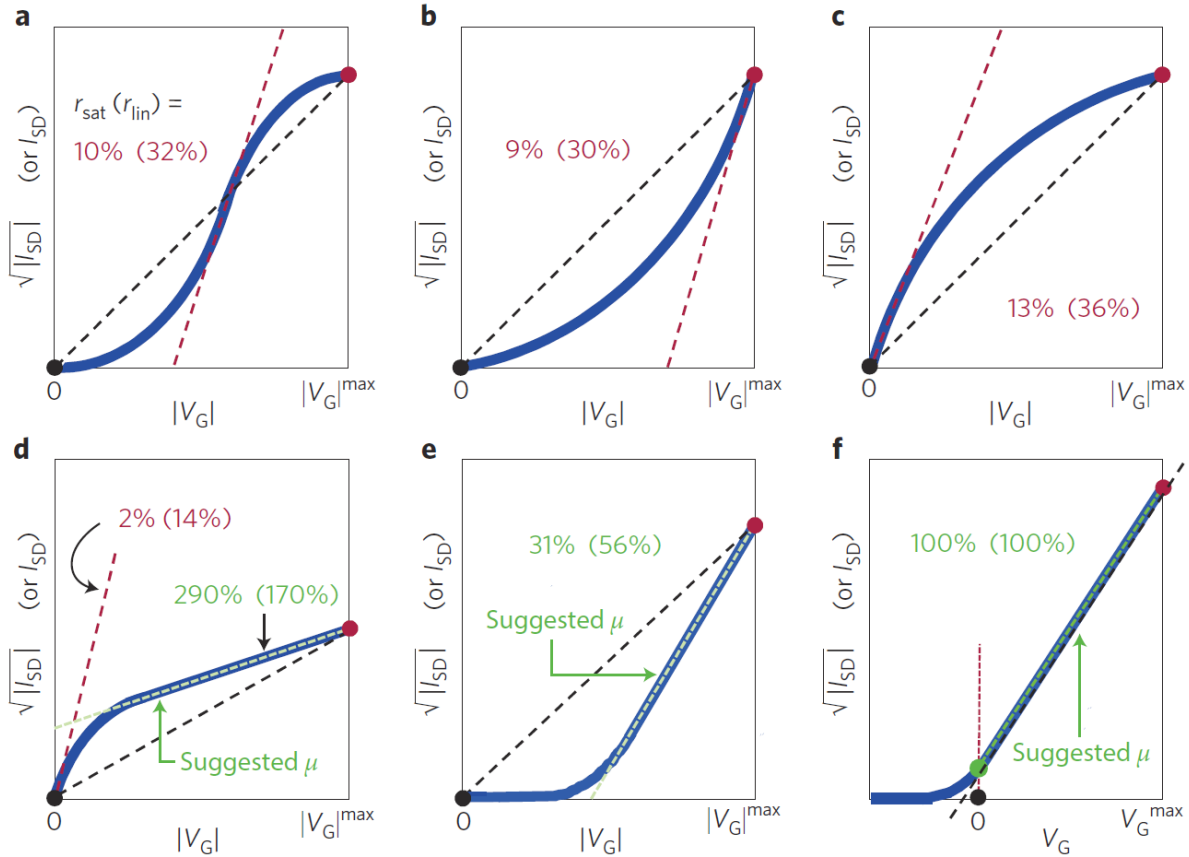
(depletion mode)





Field effect transistor: measuring mobility

H H Choi, K Cho, C D Frisbie, H Sirringhaus, V Podzorov, Nat Mater 17, 2 (2018) – pdf



In linear regime $\mu = \frac{L/W}{CV_{SD}} \frac{dI_{SD}}{dV_G}$, where L/W is channel form-factor (length/width) and C is gate-channel capacitance per unit area[1]

[1] Should be measured, if not possible, estimate as $\epsilon\epsilon_0/d$

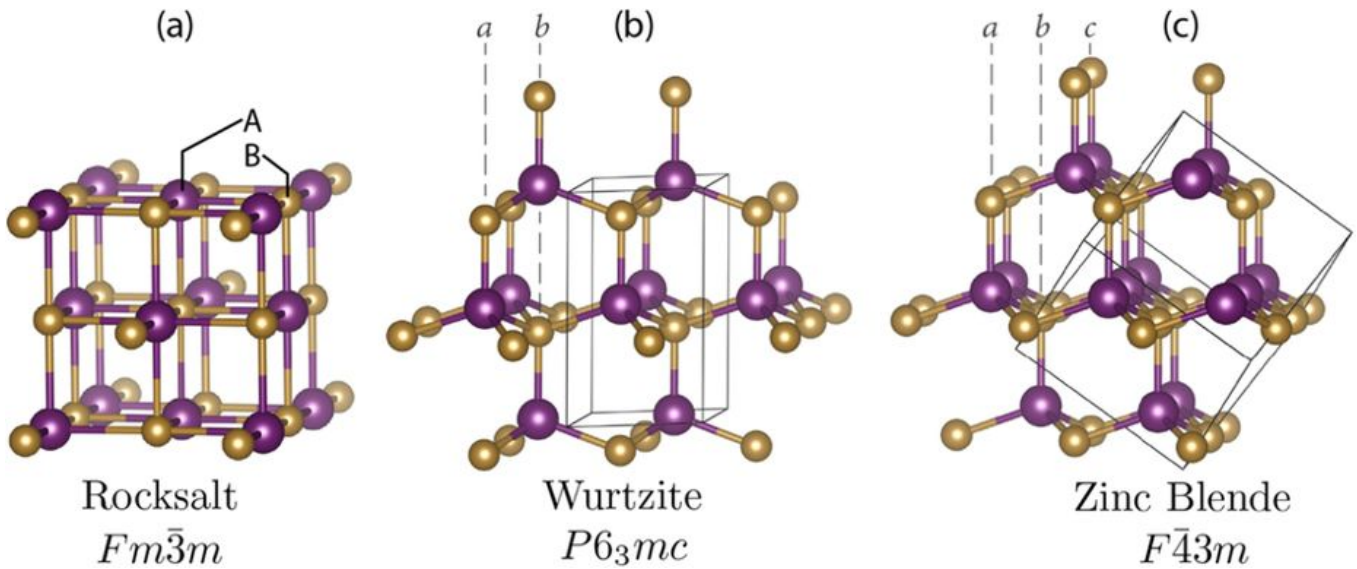
Other functional properties of semiconductors

- high charge carrier mobility
- controllable charge carrier concentration
- FET: high saturation velocity
- FET: high on/off ratio
- Solar/PD: strong light absorption (high IPCE)
- LED: efficient light emission (high EQE)
- Solar/LED: right bandgap (or use dopants)

"Classical" semiconductors

Average valence 4 compounds:

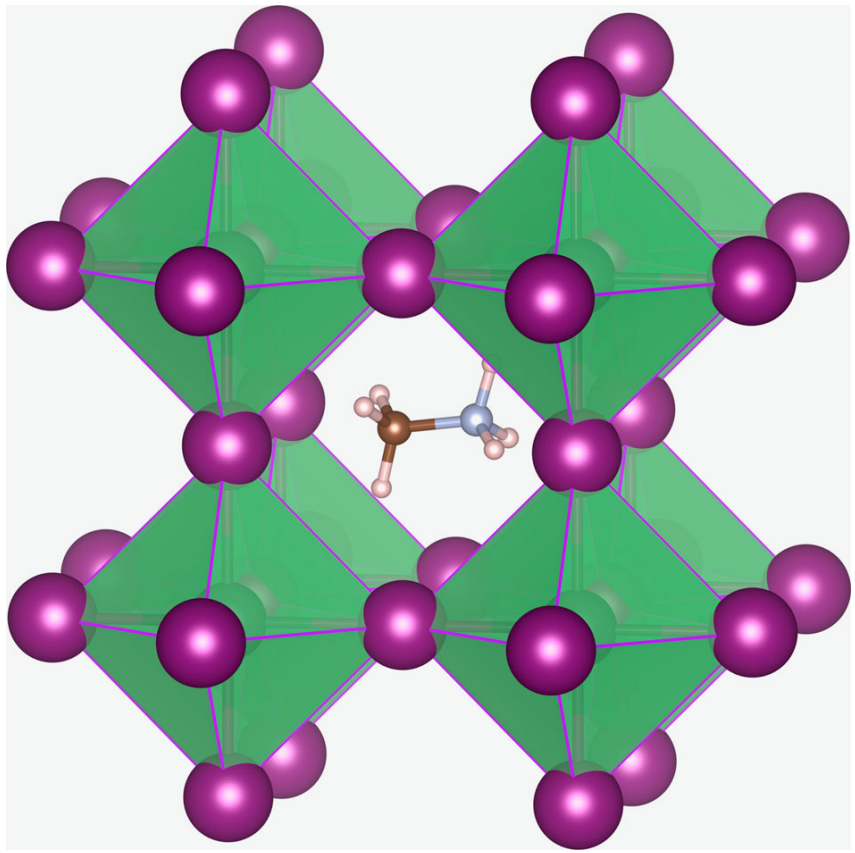
- IV (Si)
- III+V (GaAs)
- II+VI (ZnS)
- I+VII (AgI)
- II+IV+V ($CdSnAs_2$)
- I+III+VI (CIGS=$CuIn_{1-x}Ga_xSe_2$)



- Prefer mostly tetrahedral lattices: zincblende or wurtzite
- Wide-gap ionic compounds might form rocksalt lattice
- Also heterostructures and nanostructures

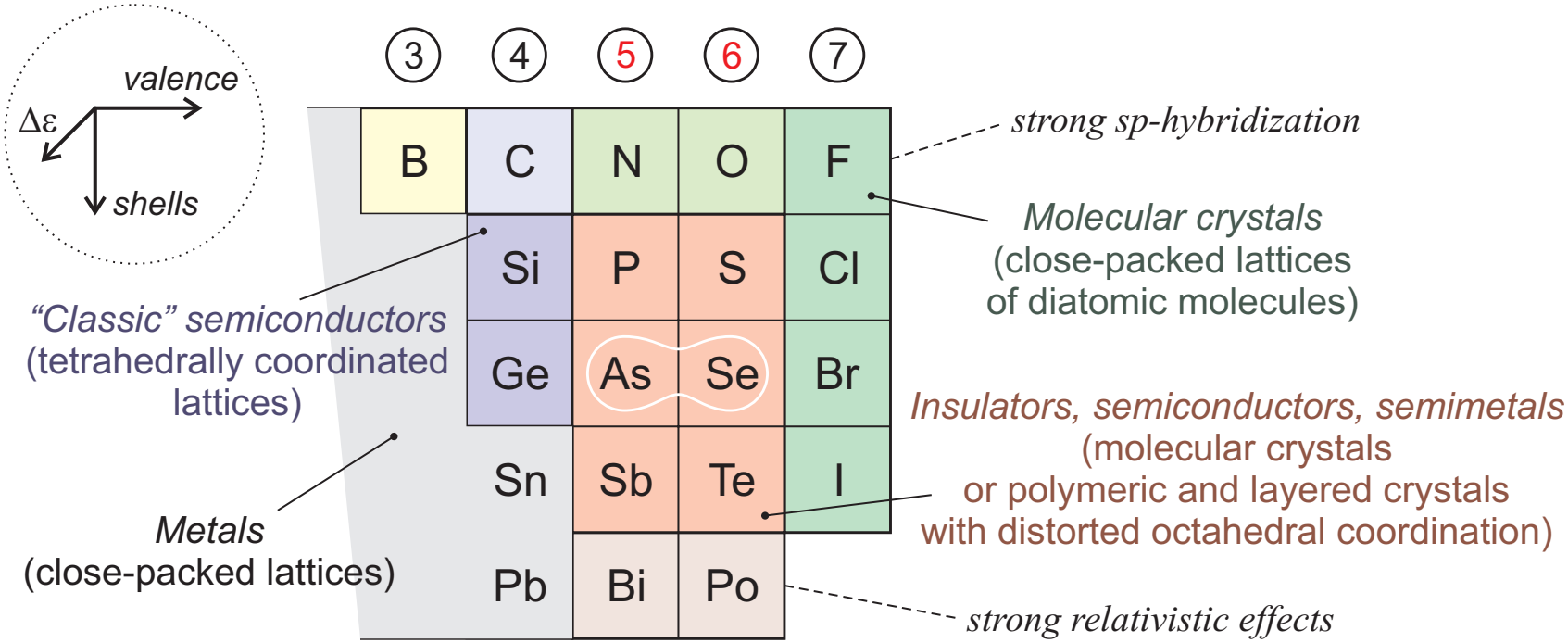
Ionic "average-valence-4" semiconductors

Semiconducting halide perovskites: I+II+VII or ABX3



Ionic $\Longrightarrow$ solution processable

Pnictide and chalcogenide semiconductors



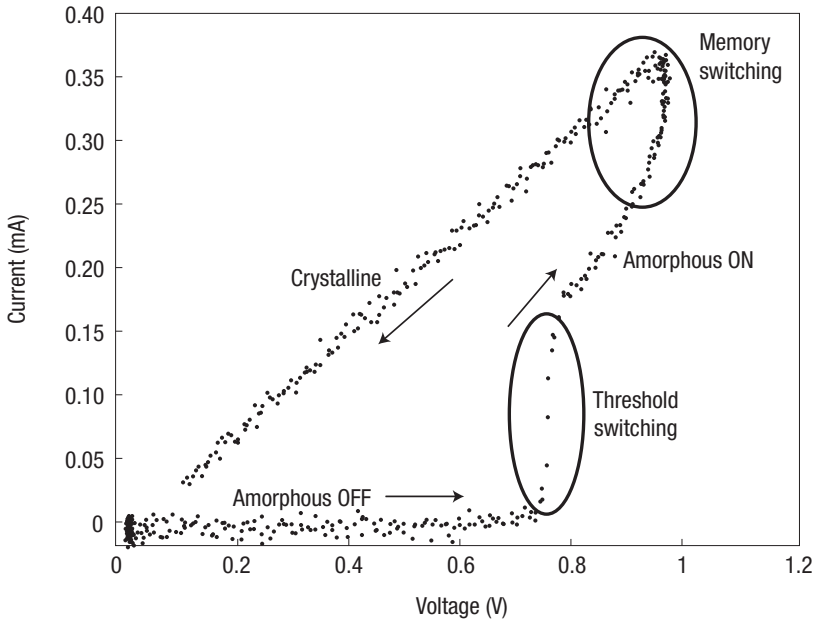
- Pnictogens: P, As, Sb
- Chalcogens: S, Se, Te
- Average valence 5-6
- Not in the class: transition metal pnictides and chalcogenides

Key properties

- Polymorphism with high contrast in electronic properties:
  crystalline As is metal, amorphous As is insulator
- Photo- and current-induced reversible structural changes:
  phase change memory alloys
- Low covalent connectivity (2-3), strong noncovalent bonding
  1D, 2D, and "sandwich" structures, nonstoichiometric alloys

Application: Phase change memory

Polymorphism with high contrast in electronic properties
+ fast transition between the two phases

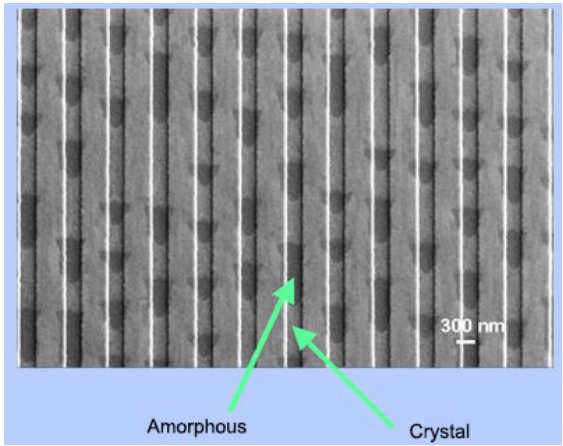


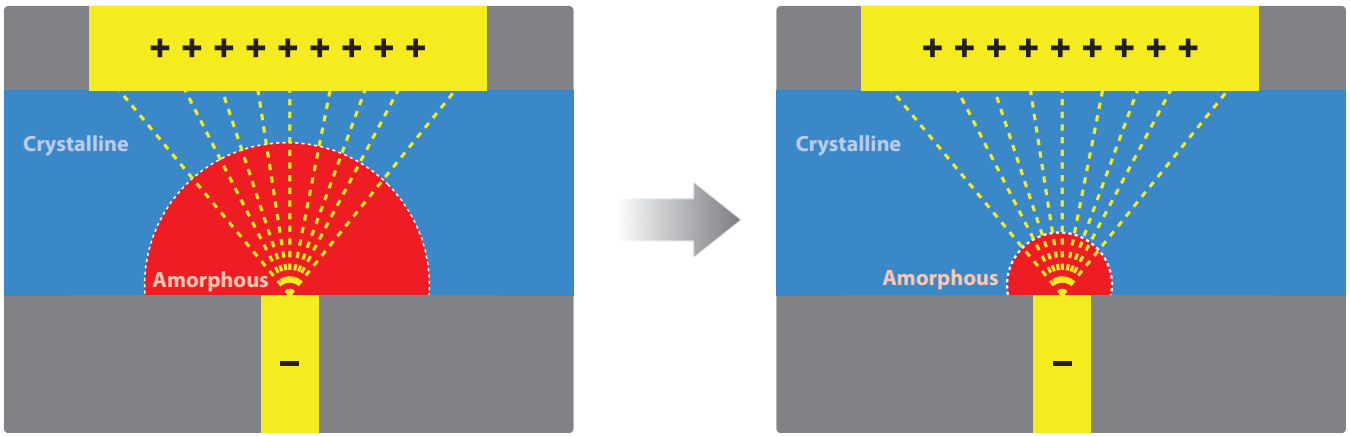
Nature Mater 6, 824 (2007)

$Ge_2Sb_2Te_5$

- DVD-RAM and DVD-RW
- PCM or PRAM
  non-volatile random-access memory

Phase change memory: historical perspective





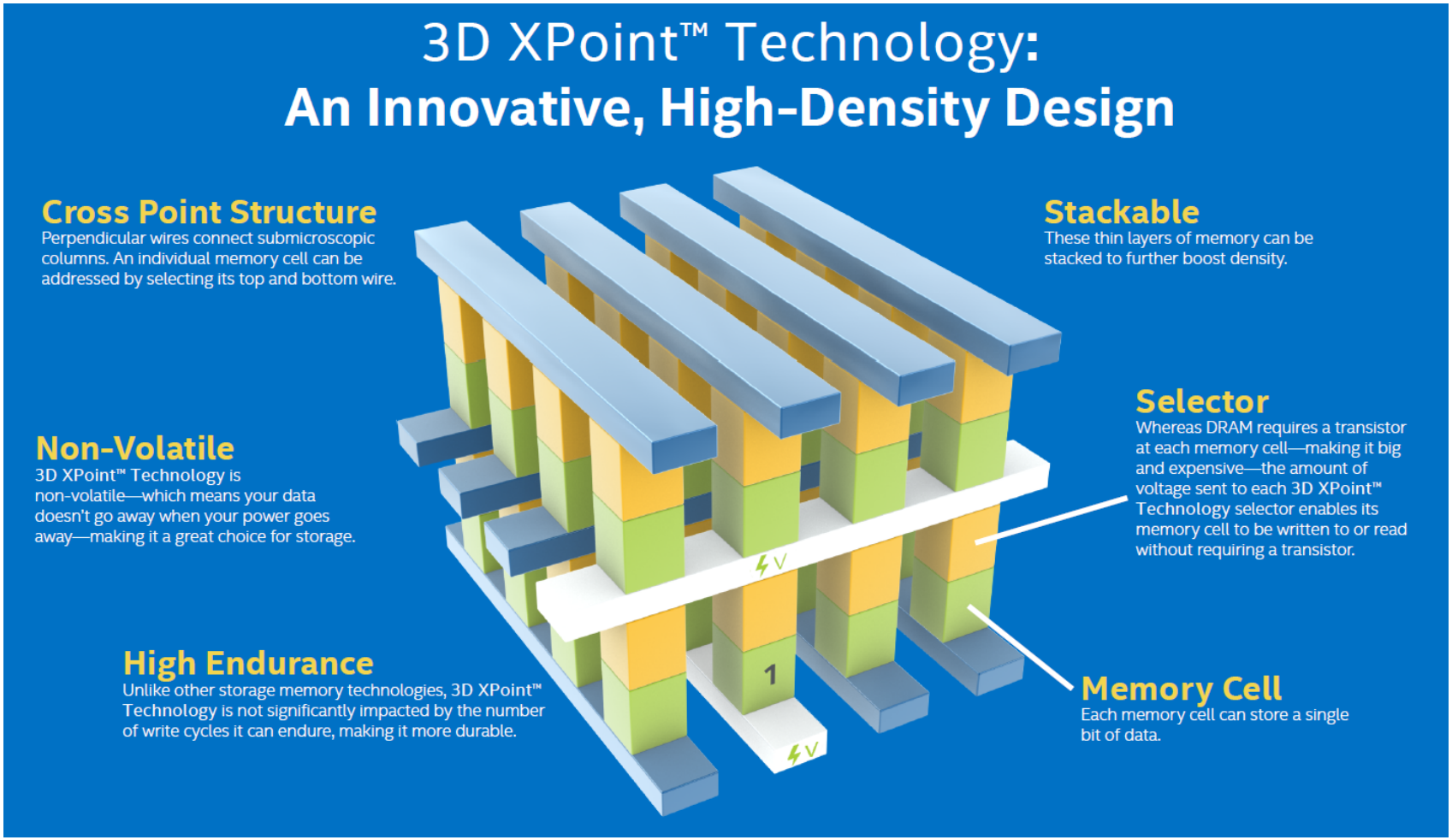
Phase change memory (PCM, PRAM) – 60-year evolution:

1) research $\Longrightarrow$ reviews 1955, patent 1966, DVD 1997

2) research $\Longrightarrow$ reviews 2000s, PRAM prototypes 2005

Phase change memory: engineering perspective

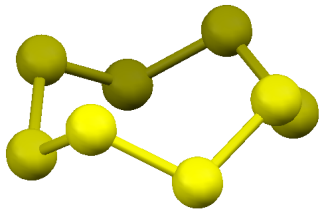
3D XPoint non-volatile memory (2015)



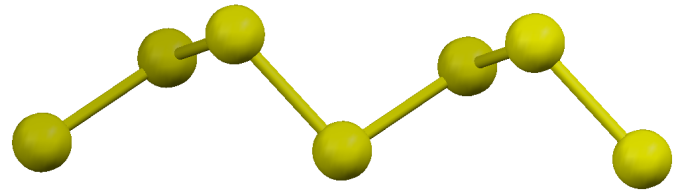
Examples and applications summary

- $Ge_2Sb_2Te_5$ and AgInSbTe – phase-change materials
- materials for "3D carving" for photonics and optoelectronics
- Se was commonly used as photoconductor in photocopiers
- Bi_2Te_3 – one of the best performing thermoelectrics
  (strictly speaking not in the class)

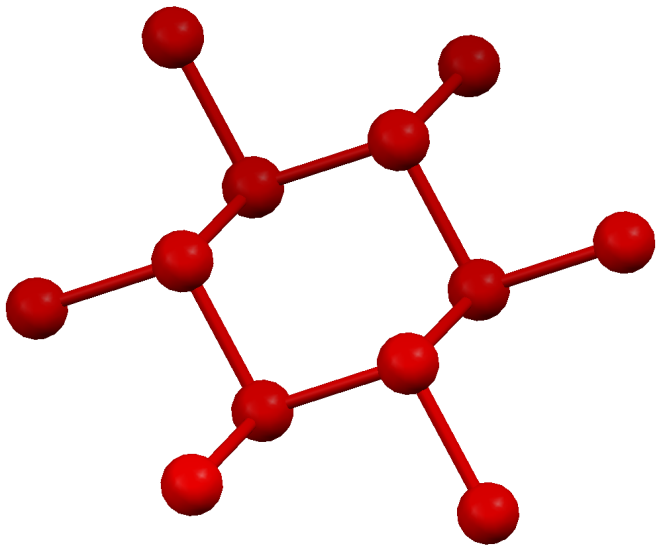
Structure: diversity and polymorphism



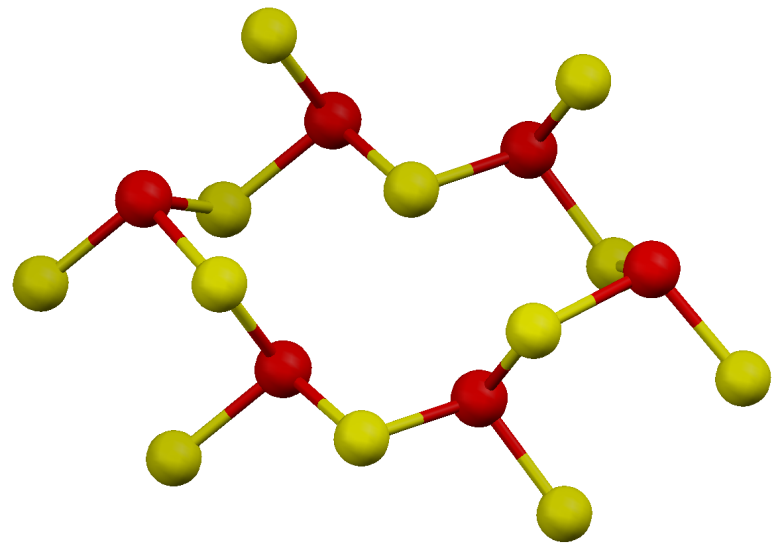
α-S
(molecular crystal)



Se, Te, high-pressure S
(polymeric crystal)



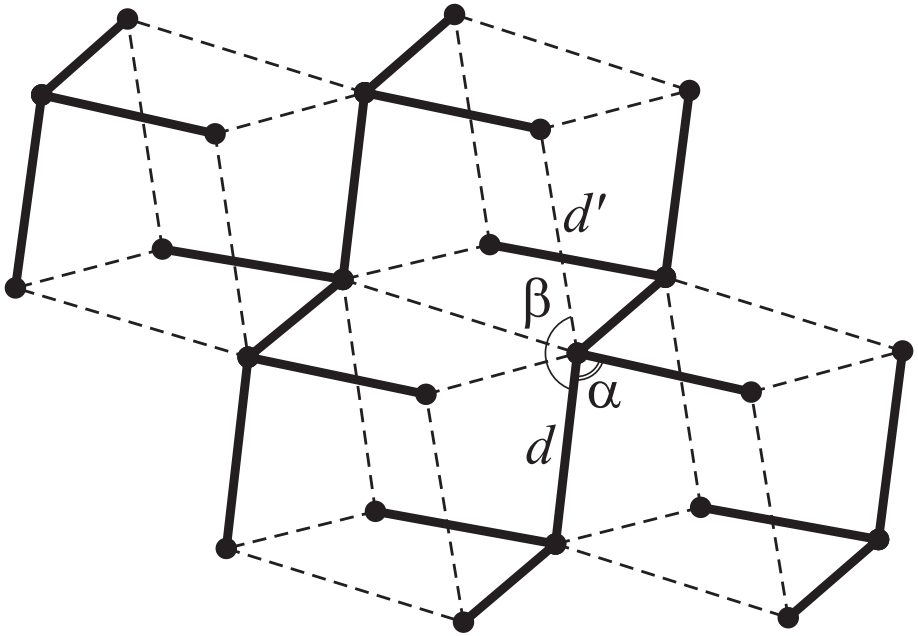
As, Sb, Bi, high-pressure P
(layered crystal)

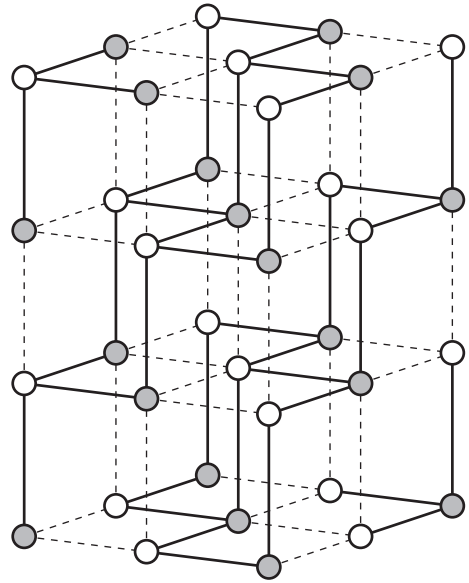


As_2S_3
(layered crystal)

Is there a common structural motif?

Structural motif: distorted octahedral coordination





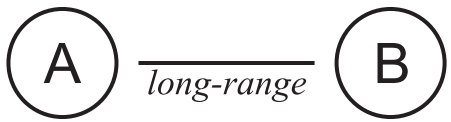
GeTe, rhombohedral As

- Right-angled geometry: $90^\circ \lesssim \alpha < 109^\circ$
- Secondary $pp\sigma$ bonding: $d'_{\mathrm{AB}} < r_{\mathrm{A}}^{\mathrm{vdW}} + r_{\mathrm{B}}^{\mathrm{vdW}}$
- Can be called "back-bonding": $\beta > 160^\circ$
- Trans-influence: $d_{\mathrm{AB}} > r_{\mathrm{A}}^{\mathrm{cov}} + r_{\mathrm{B}}^{\mathrm{cov}}$

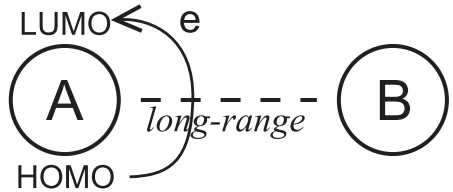
But

- some bonds may be missing for elements of group VI and VII
- competing tetrahedral coordination for elements of group IV

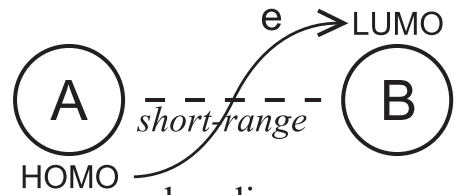
What is secondary bonding?



electrostatic



polarization,
induced dipole



bonding:
covalent if open-shell,
secondary if closed-shell

$$E_{\text{bind}} = \Delta E_{\text{nuc}} + \langle AB|H_{\text{int}}|AB\rangle + \sum_{\text{exc}} \frac{\langle AB|H_{\text{int}}|A^{\text{exc}}B^{\text{exc}}\rangle^2}{E_{\text{A}} + E_{\text{B}} - E_{\text{A}}^{\text{exc}} - E_{\text{B}}^{\text{exc}}} + \sum_{\pm\text{states}} \frac{\langle AB|H_{\text{int}}|A^{\pm}B^{\mp}\rangle^2}{E_{\text{A}} + E_{\text{B}} - E_{\text{A}}^{\pm} - E_{\text{B}}^{\mp}}$$

$$\Longrightarrow \quad E_{\text{sec.bond}} = \frac{2t_{12}^2}{E_1^{\text{ion}} - E_2^{\text{aff}}} \equiv \frac{E_1^{\text{ion}} - E_2^{\text{aff}}}{2} \times \langle \text{bond-order} \rangle$$

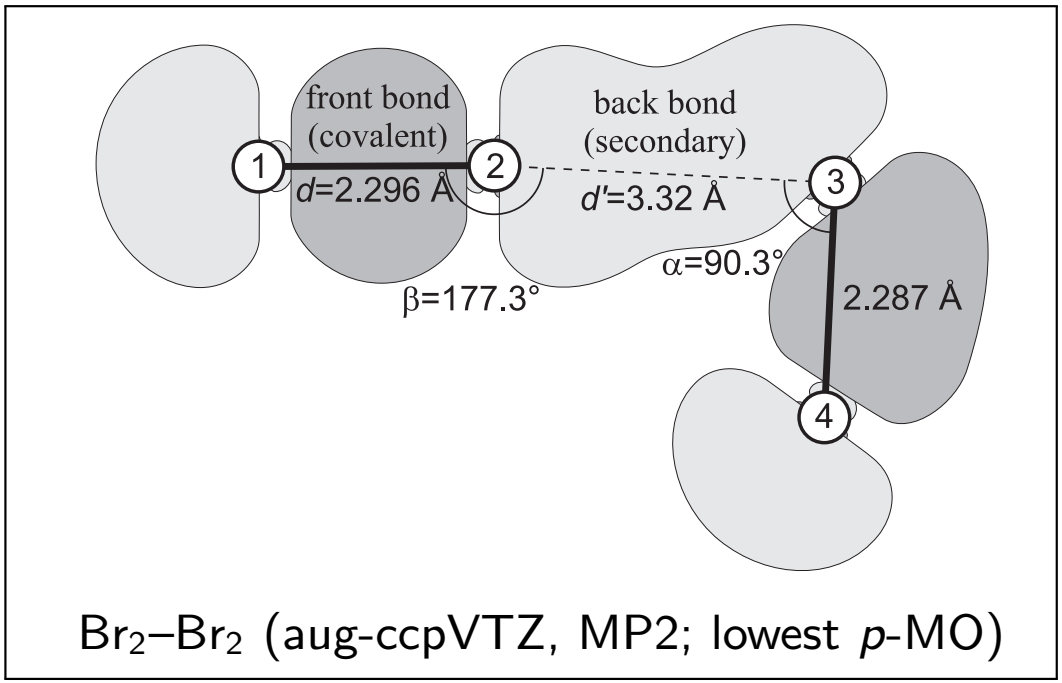
Examples of secondary bonding

Structural signatures of secondary bonding:

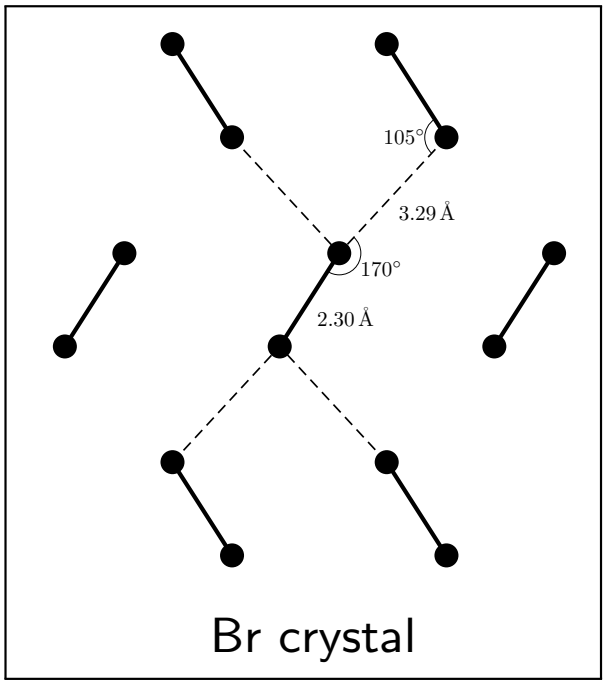
- Orbital overlap: $d'_{AB} < r_A^{vdW} + r_B^{vdW}$
- Trans-influence: $d_{AB} > r_A^{cov} + r_B^{cov}$
- Alignment with respect to the covalent bond

		donor	acceptor	t'	$E^{ion} - E^{aff}$
backbonding	α-As	$pp\sigma$	$pp\sigma^*$	$t'_{pp\sigma}$	$2t_{pp\sigma}$
backbonding	Br_2-Br_2	$pp\sigma$	p-LP	$t'_{pp\sigma}$	$t_{pp\sigma}$
π-conjugation	poly-CH	$pp\pi$	$pp\pi^*$	$t'_{pp\pi}$	$2t_{pp\pi}$
π-backbonding	$Cr(CO)_6$	$pp\pi$	d	$t'_{pp\pi}$	$t_{pp\pi} + \Delta\varepsilon_{pd}$
	Be_2	s	p	t_{sp}	$\Delta\varepsilon_{sp}$
hydrogen bond	H-A	s	A		
halogen bond	F-D	D	p		

Examples of secondary bonding: halogen molecules



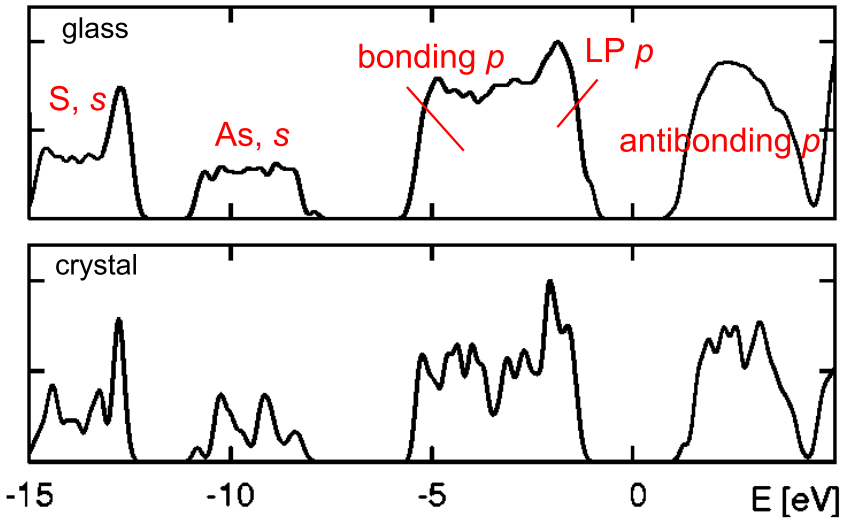
Br_2–Br_2 (aug-ccpVTZ, MP2; lowest *p*-MO)



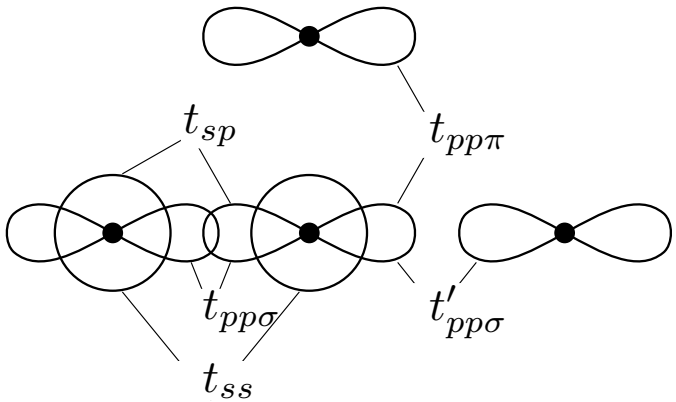
Br crystal

- Right-angled coordination: $\alpha \approx 90°$
- Secondary bonding: $d' < 2r_{\text{vdW}}$ and $\beta \approx 180°$
- Trans-influence: $d > 2r_{\text{cov}}$ (left molecule is elongated)
- Dimer and crystal have principally the same geometry

Electronic structure: degeneracy of the covalent network



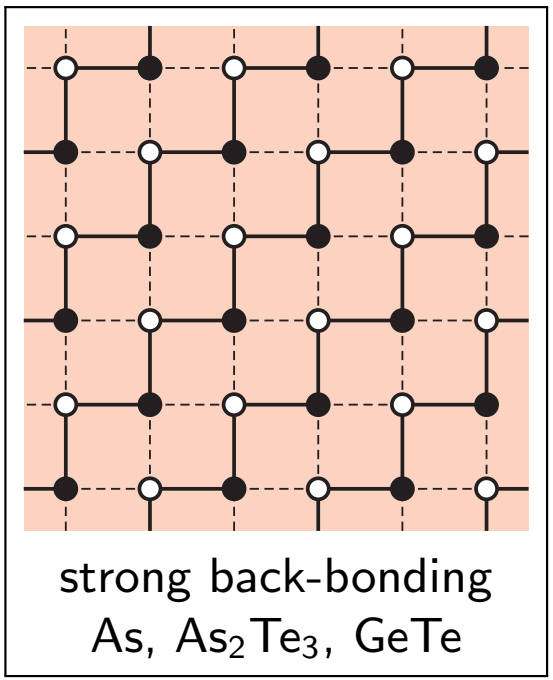
EDOS for As_2S_3 (Simdyankin, Elliott, 2004)



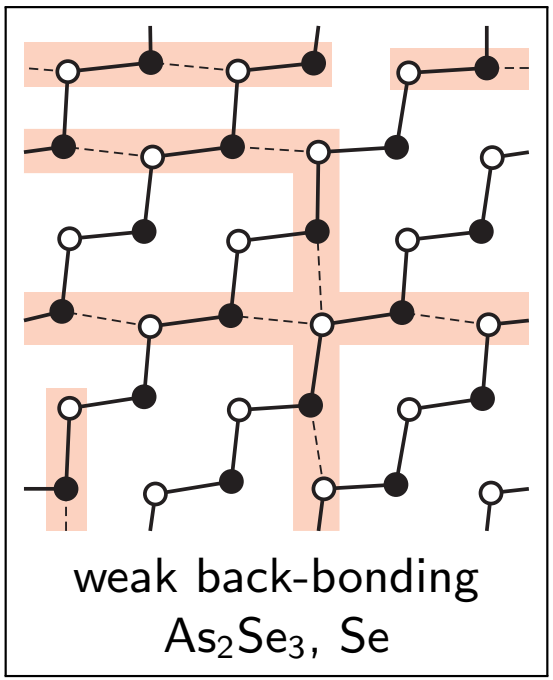
Transfer integrals

- *s*-orbitals do not contribute to bonding
  — it is the network of $pp\sigma$-bonds ($pp\sigma$-network)
- $pp\sigma$-bonds themselves do not form 3D solid
  — the structure is determined by the balance of
  - secondary bonding $t'^2_{pp\sigma}/2t_{pp\sigma}$
  - hybridization or *sp*-interaction $t^2_{sp}/(\varepsilon_p - \varepsilon_s - t_{pp\sigma})$
  - $pp\pi$-interaction (usually small) $t^2_{pp\pi}/2t_{pp\sigma}$

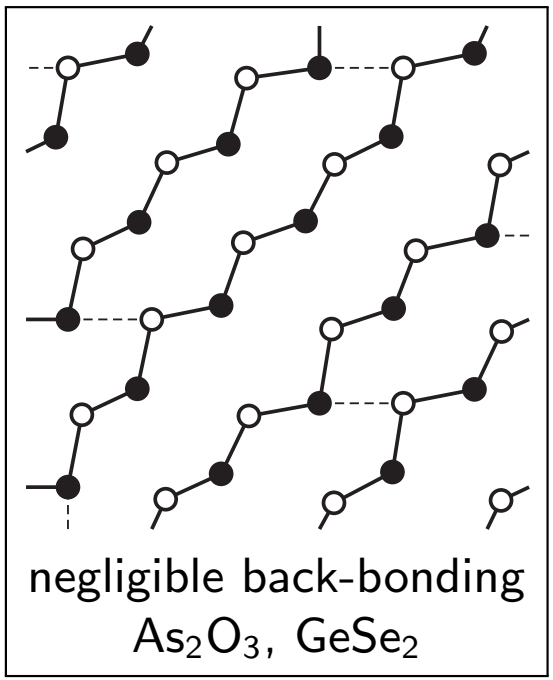
Structure: three classes of $pp\sigma$-networks



strong back-bonding
As, As_2Te_3, GeTe



weak back-bonding
As_2Se_3, Se

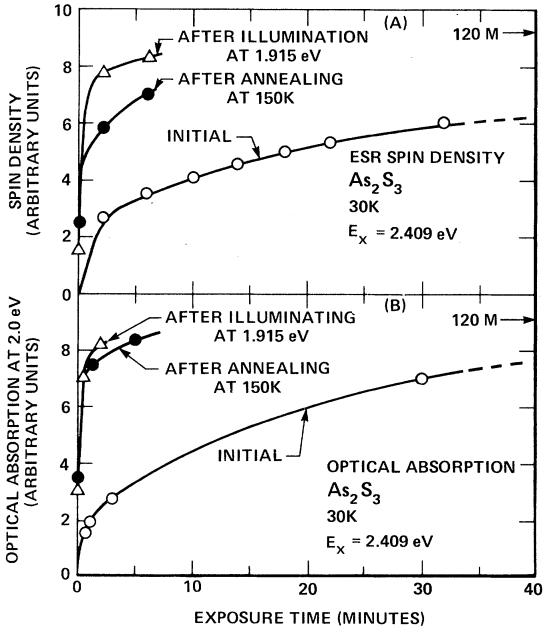


negligible back-bonding
As_2O_3, $GeSe_2$

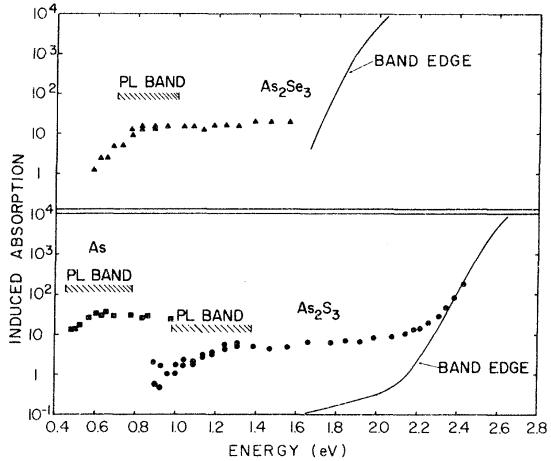
How to get this picture: Project Fock matrix onto valence p-orbitals and mark all the resulting elements $\gtrsim 0.5 t_{pp\sigma}$

Photoinduced phenomena: experiment

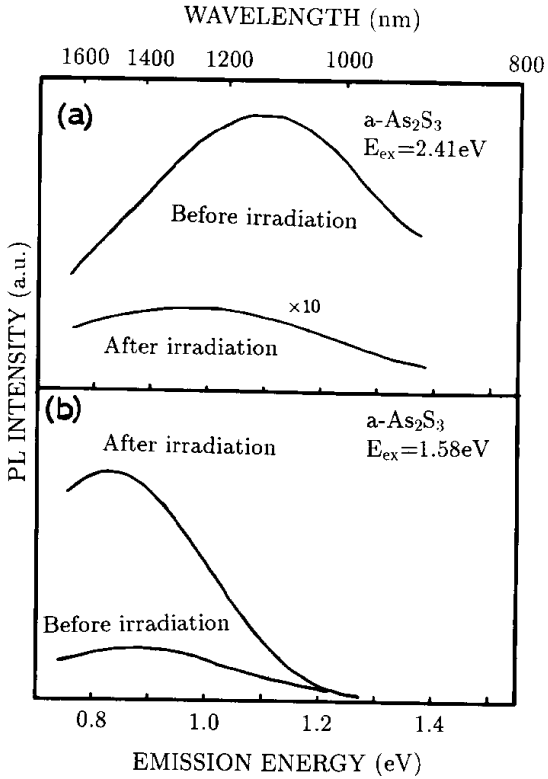
ESR and subgap absorption
Phys Rev Lett 44, 803 (1980)



Midgap absorption
Phys Rev B 15, 2278 (1977)

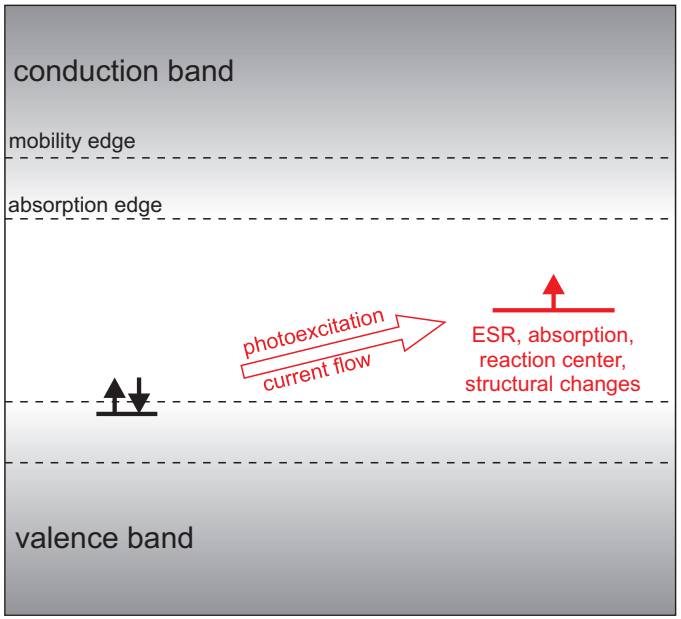


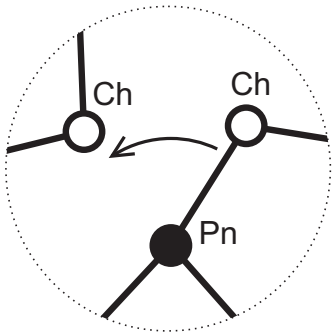
New PL after bandgap irradiation
J Non-Cryst Solids 114, 88 (1989)

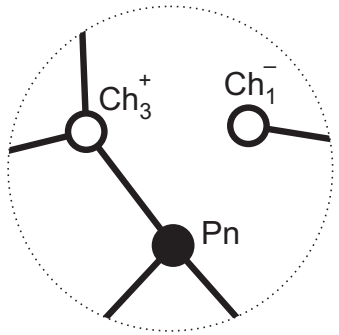


- 5% volume expansion [J Optoelectronics Adv Mater 8, 2058 (2006)]

Photoinduced phenomena: theory







1. Midgap states originate from coordination defects whose ground state is charged (Street, Mott, 1975)
2. They pair up into positively charged overcoordinated atom and negatively charged undercoordinated – VAP (Kastner, Adler, Fritzsche, 1976; Pollard, Joannopoulos, 1979)
3. Defects can move and be created by bond switching, which is the underlying mechanism for photoinduced phenomena

What is the microscopic mechanism for such an efficient bond switching?

Challenges

- Find better materials for phase change memory
- Improve device architecture for phase change memory
- How to drive structural changes nonthermally
- Lack of microscopic description of photoinduced changes
- Lack of quantitative prediction of photoinduced changes
- Limited use of pnictides and chalcogenides

Research at Skoltech

Theory:

- Vasili Perebeinos (now at Buffalo U) – classical semiconductors
- Xavier Gonze (also at UCLouvain) – classical semiconductors
- Sergei Tretiak (also at LANL) – perovskites, organic, quantum dots
- Sergey Levchenko – oxides
- Andriy Zhugayevych – organic, pnictides/chalcogenides

Experiment:

- Keith Stevenson – organic, perovskites
- Pavel Troshin (now at IPCP RAS) – organic, perovskites
- Albert Nasibulin – carbon nanotubes
- CPQM CREI – photonics and optoelectronics

Resources

- Wikipedia
- Callister chapter 18.(1-15)
- Ashcroft chapters 28-29
- Kittel chapter 8
- Textbooks (see Topical references on semiconductors)
- Perovskites: References
- Pnictides/chalcogenides: References
- Organic: References
  - Separate lecture here
  - Separate course in Term 3
  - A Koehler, H Bassler, Electronic Processes in Organic Semiconductors: An Introduction (Wiley, 2015) *in library*
  - Albert Nasibulin's lecture on carbon nanotubes in Canvas