N. Wyrsch

Photodetectors: Photodiodes and photoconductors

Devices and Applications

- Photodiodes
  - Solar cells
  - Particle detectors (X, α, β, γ)
  - Flat panel imagers (a-Si:H)
  - Photodiodes (micro-systems)
  - Position detectors
  - Spatial modulators (optical valves)
  - Bio-chips
  - Smart windows
  - …..

- Photoconductors
  - Xerography
  - Flat panel imagers (a-Se)
  - ……

Macro-electronic devices and applications

Thin-film device type

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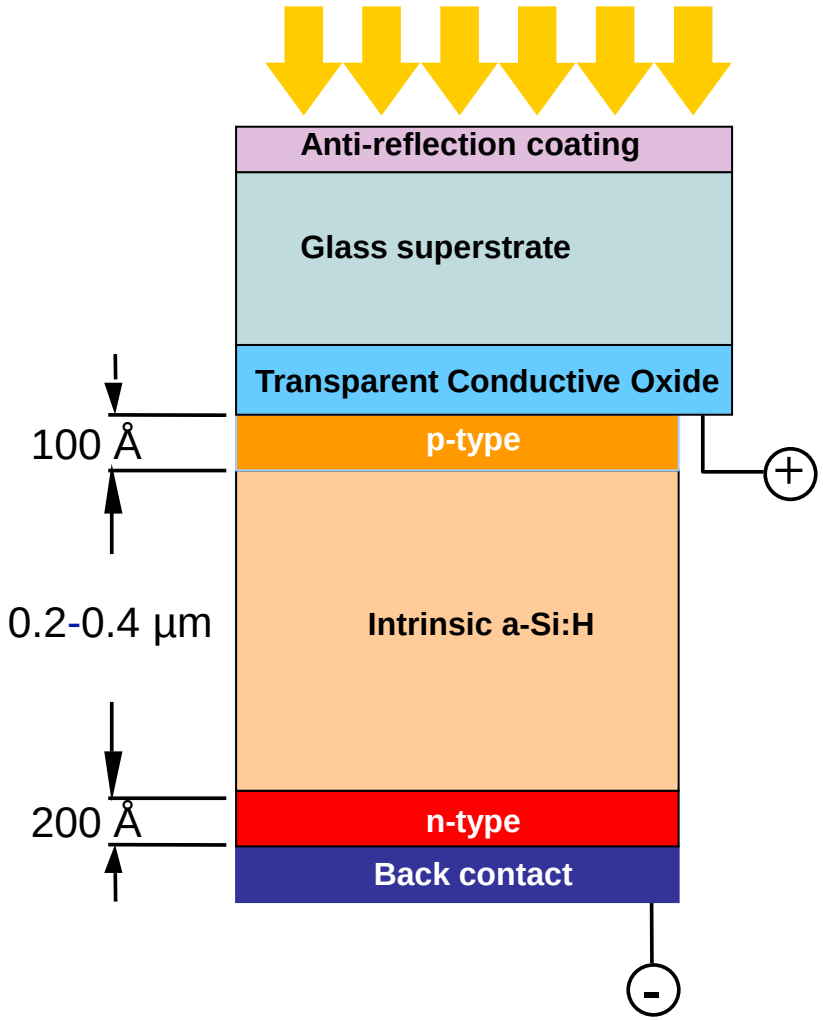
- Photodiodes
  - Internal junction or selective contacts needed
  - Controlled by the collection of carriers
  - p-n or junction, p-i-n junction Schottky diode
  - High linearity (in case of p-i-n)
  - Low dark current
  - Transverse carrier transport

- Photoconductors
  - Using ohmic or injecting contacts
  - Controlled by photoconductivity (lifetime)
  - Simple device structure (usually absorber and contact layers)
  - Limited linearity
  - Possibly high dark (leakage) current
  - Lateral or transverse carrier transport

p-i-n solar cell (for disordered semiconductors)



- p-i-n structure necessary for disordered semiconductors
  - N_{db} very high in doped layers (dead layers)
  - → Doped layers only serve for electric field build-up through the intrinsic layer
  - The intrinsic layer is the only active layer
- Light enters the cell through the p-layer (“window layer”)

Thin-film Solar cells vs Photodetectors (diodes)

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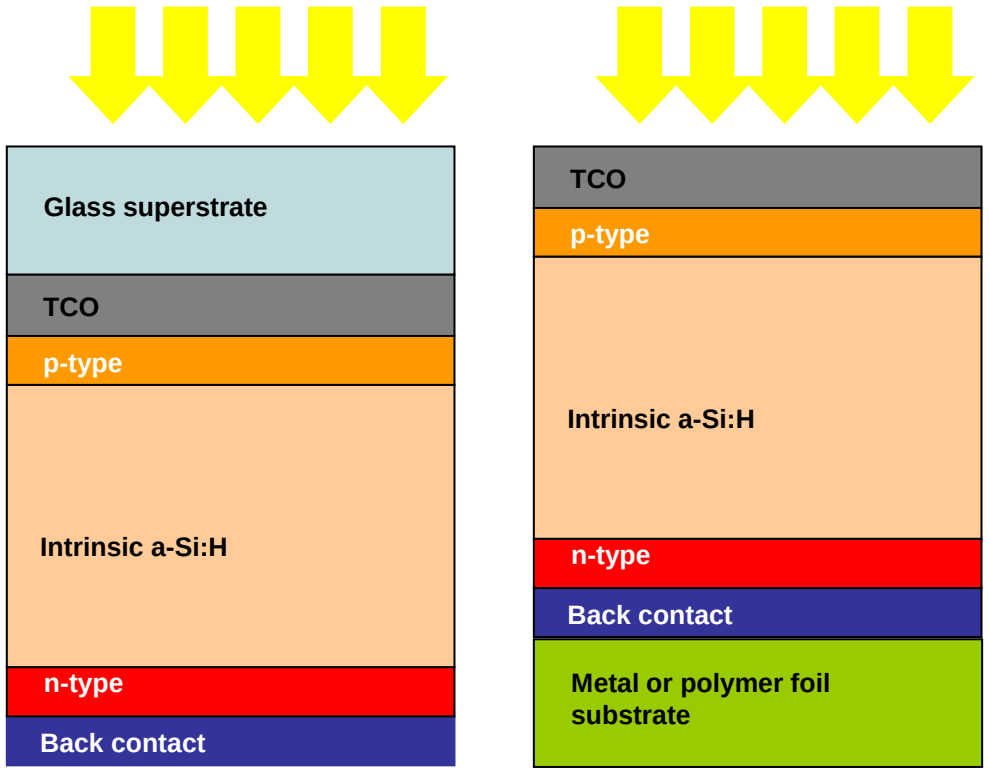
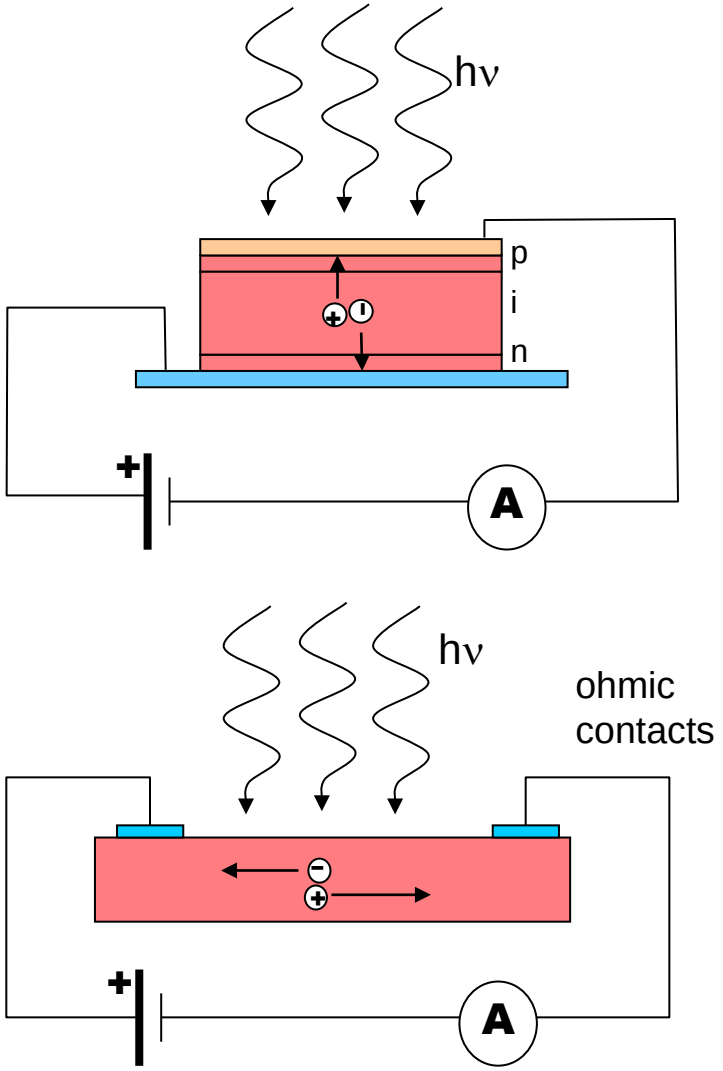


p-i-n configuration

n-i-p configuration

- Solar cells (Si based)
  - Self-polarisation (direct)
  - Thickness : 0.2-0.4 µm
  - Light-trapping scheme with rough TCO and rough back reflector
  - Current determined by efficiency of light trapping scheme
  - Very sensitive to SWE
  - p-i-n or n-i-p structure
- Photodiodes (Si based)
  - reverse polarization
  - Intrinsic layer can be thick (external field assisted collection) : 0.5-20 µm
  - Current determined by thickness
  - Less sensitive to SWE
  - p-i-n or n-i-p structure

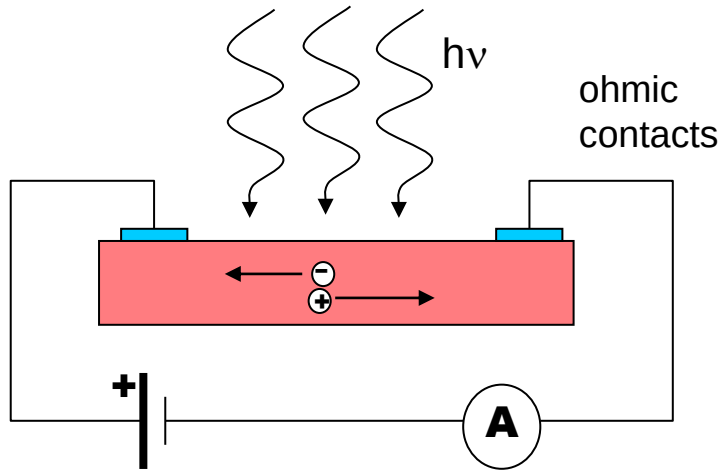
Photoconductivity

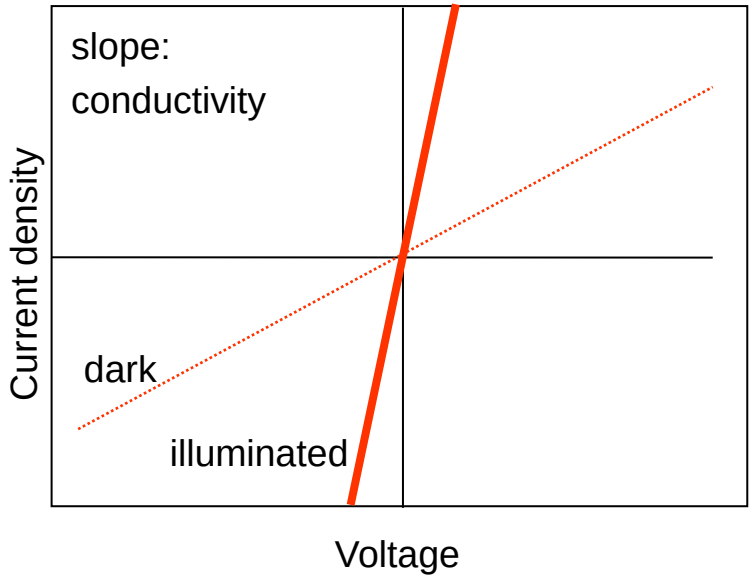


Two types of photoconductivity:

- **primary** photoconductivity**:**
  - given by the collection of photogenerated carriers
  - takes place in devices with **blocking** contacts (photodiodes, solar cells): in **photodetectors** or **optoelectronic detectors**.
- **secondary** photoconductivity**:**
  - given by the increase of the conductivity of an illuminated **intrinsic layers**
  - takes place in devices with **ohmic contacts: photoconductors**.

Secondary photoconductivity





- "Regular" conductivity
- Under steady state illumination:

  $\sigma_{tot} = \sigma_{photo} + \sigma_{dark}$

  with $\sigma_{photo} = e\,(\mu_n\, n_f + \mu_p\, p_f)$

  where $\mu_{n,p}$ are band mobilities and n_f, p_f are photogenerated free carriers densities.
- From recombination model in steady-state (G=R):

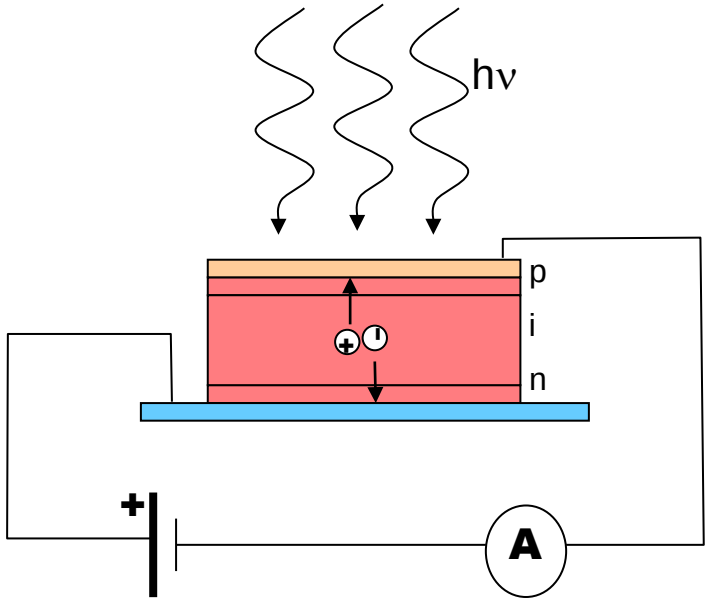
  $\sigma_{photo} = e\,G\,(\mu_n\tau_n + \mu_p\tau_p)$

  where $\tau_{n,p}$ are free carrier recombination times (in SRH model for doped SC: carrier recombination time=carrier lifetime!)
- Low defect density ⇒ large photoconductivity

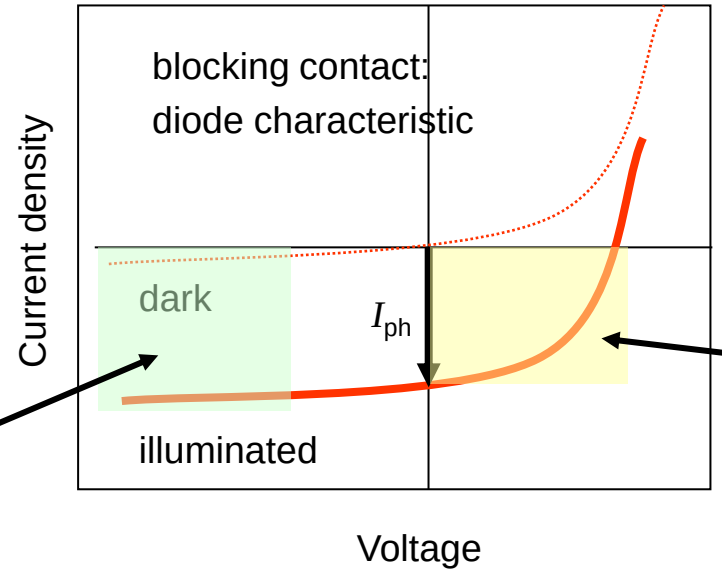
Secondary photoconductivity (2)

- For “best” photoconductor: $\sigma_{ph} \gg \sigma_{dark}$
  - Low σ_{dark}
    - high bandgap
    - Small σ_0
    - Intrinsic semiconductors (no impurities)
  - High σ_{ph}
    - High optical absorption (direct bandgap, disordered semiconductors)
    - $E_{gap} < E_{photon} = h\nu$
  - **The gap is the most important parameter !**

Primary photoconductivity: blocking contacts



- given by the collection of photo-generated carriers
- $I_{ph}=Ge\eta$ with η : quantum efficiency, $\eta \rightarrow 1$ (a-Si:H cells)
- Operation in reverse conditions for best linearity (external field assisted collection)



Operation conditions for a photodiode

Operation conditions for a solar cell

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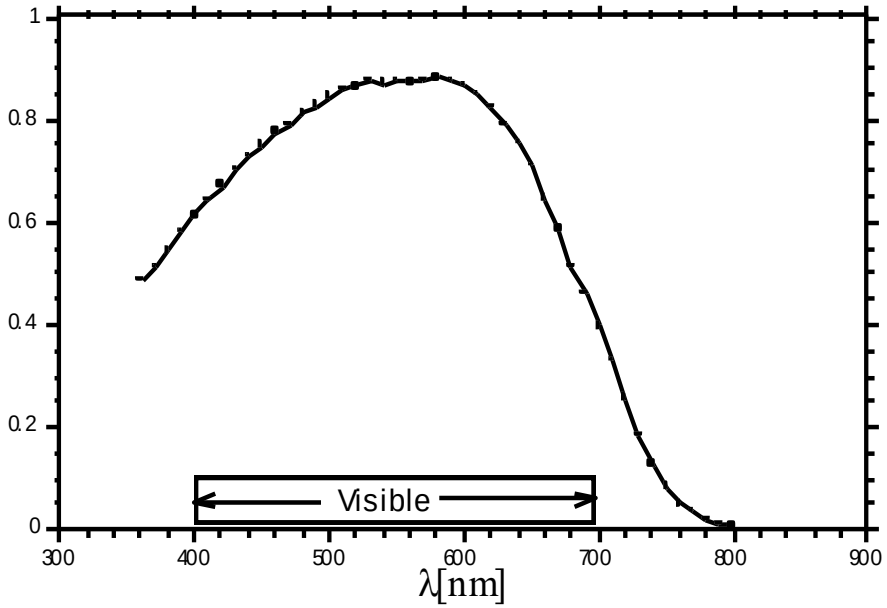
Requirements and device choice

- Doped layers or hetero-junction must be available for photodiodes
- Low leakage current
  - Blocking contacts for photodiodes
  - High gap material
- Suitable bandgap
  - High absorption in spectral range
  - High photocurrent
- Material stability
  - Temperature
  - Radiation
  - Chemical stability
- Material/device processing
- Compatibility with substrate
  - Adhesion
  - Thermal expension coefficient
  - Chemical stability
- Cost

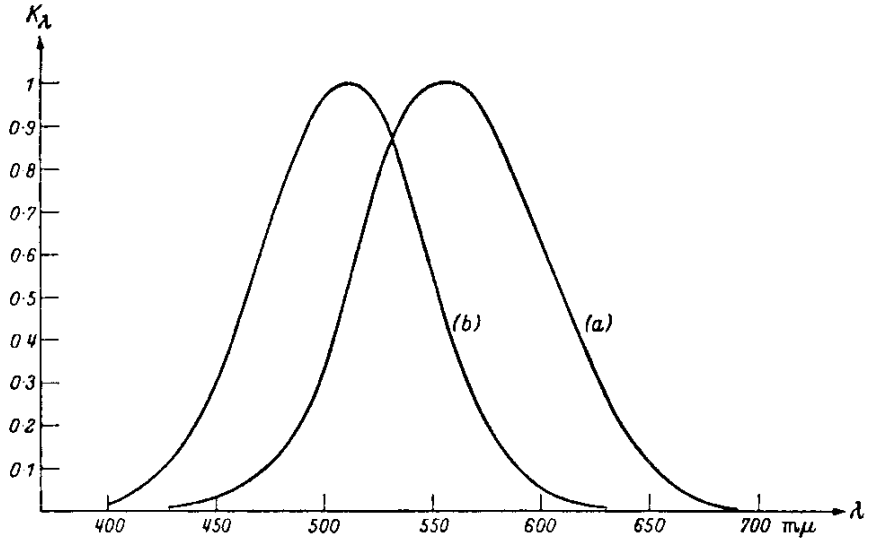
« Macro- » materials for photodiodes

- a-Si:H, μc-Si:H, a-Si based alloys (solar cells & sensors)
  - $Si_{1-x}C_x$, $Si_{1-x}Ge_x$ alloys
- Chalcopyrites (solar cells)
  - CIS ($CuInSe_2$, $CuInS_2$)
  - CIGS ($CuInGaSe_2$)
- Kesterites (solar cells, In free)
  - $CuZnSn(S,Se)_2$
- CdTe (solar cells, radiation hard diodes)
- Transparent conductive oxides (UV sensors)
  - ZnO, …
- Diamond like carbon
  (radiation, chemically, mechanically hard diodes)
- Organic materials (photodiodes, OLED)
  - Many…..
- Perovskytes
  - $CH_3NH_3PbI_{3-x}Cl_x$, ….

Spectral sensitivity



spectral response of a typical 0.5 µm thick a-Si:H p-i-n diode (at -3 V).



spectral sensitivity of the human eye for (a) daylight and (b) night vision

- a-Si:H spectral sensitivity matches human eye sensitivity !

→ a-Si:H photodiodes used e.g. for display illumination control

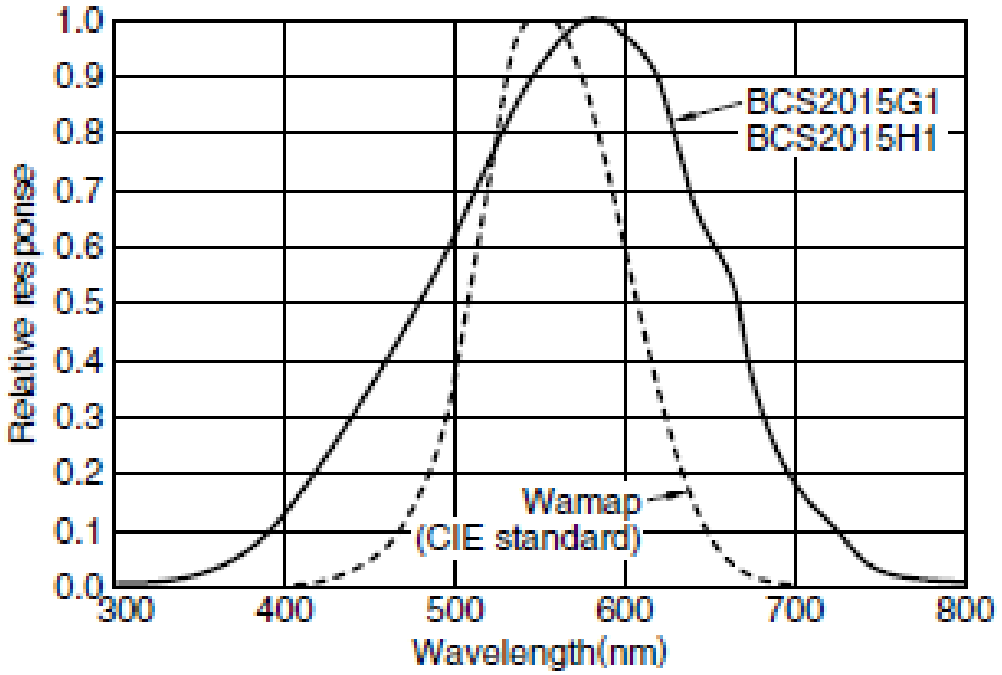
- Spectral sensitivity tuning by alloying Si with C, Ge, (O, N, …)

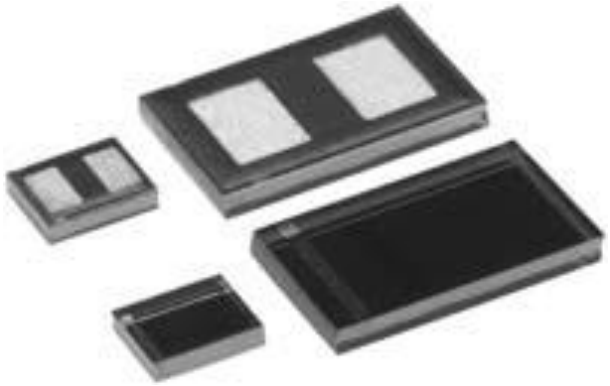
Commercial exemple

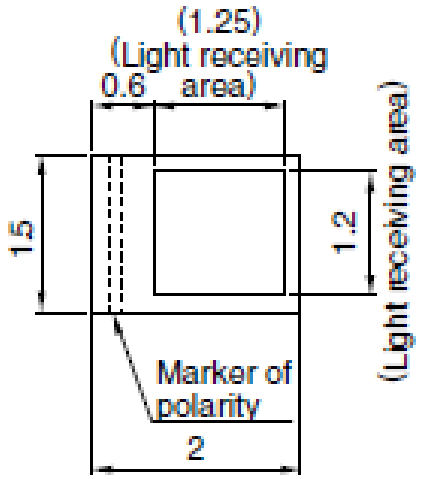
TDK

APPLICATIONS

- Brightness adjustment of LCD, CRT
- Camera AE sensor (Replace for CdS cell.)
- Lighting control

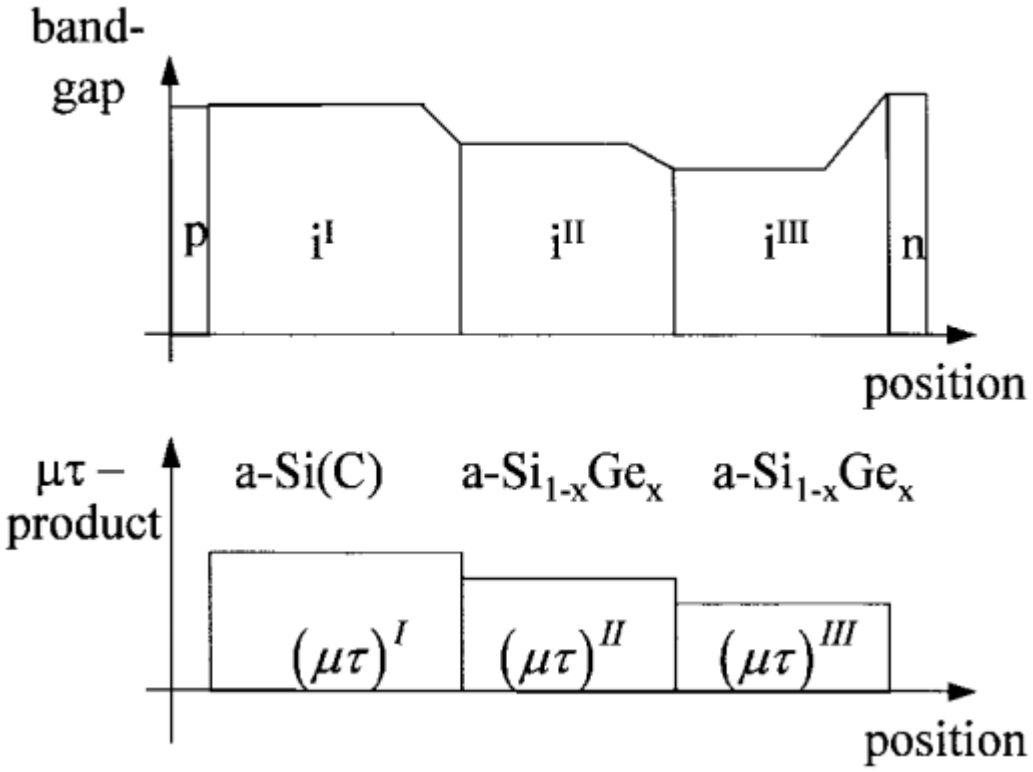




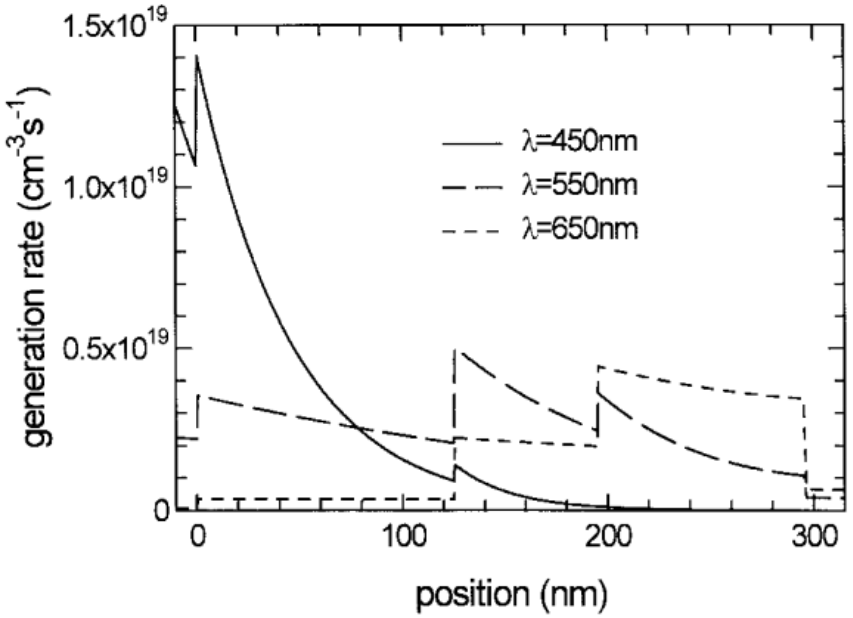


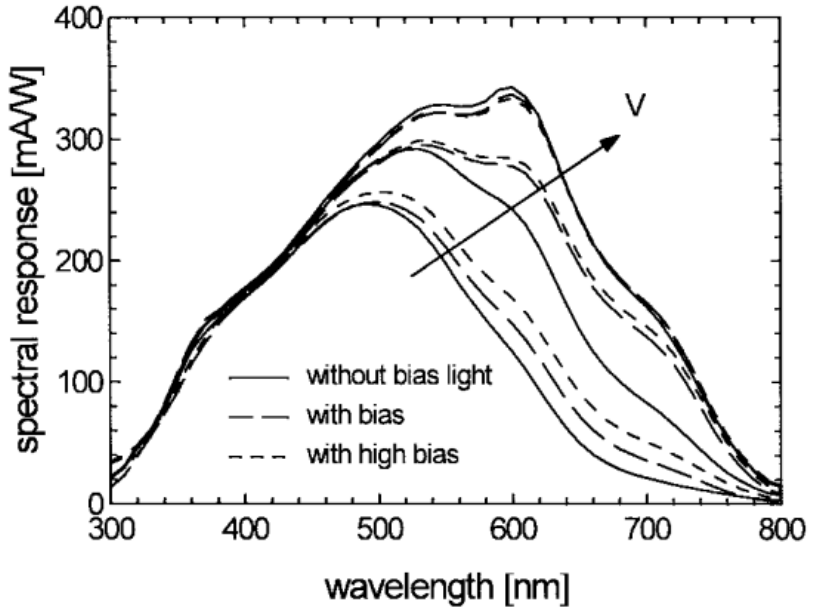
Color detectors

- Using bias voltage dependant spectral sensitivity (various device configurations possible)
- Detection without color filters



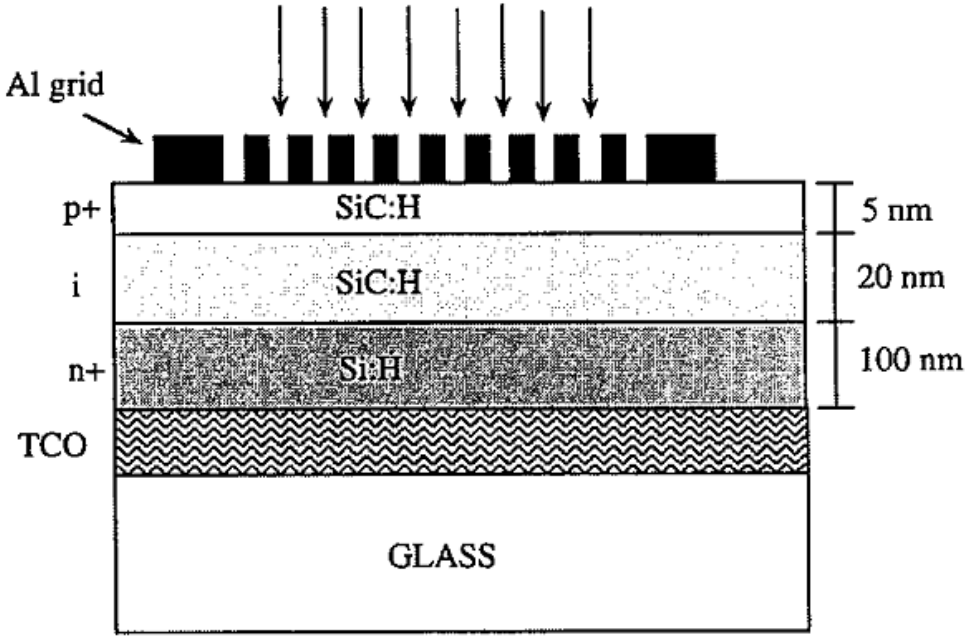
J. Zimmer et al., IEEE Trans. on El. Dev. 46 (1999)884

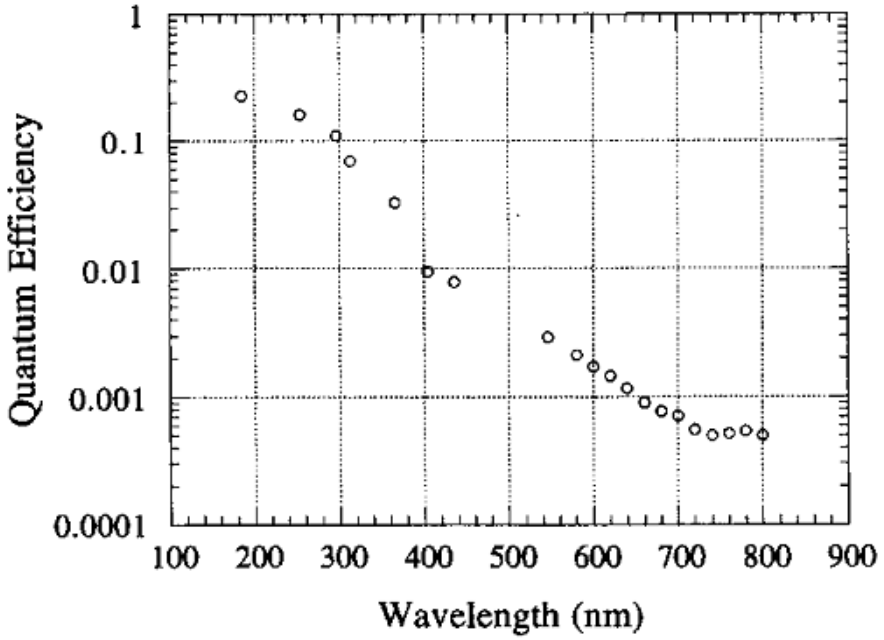




UV sensors requirements

- UV light → short penetration depths
- Illumination outside of contact area





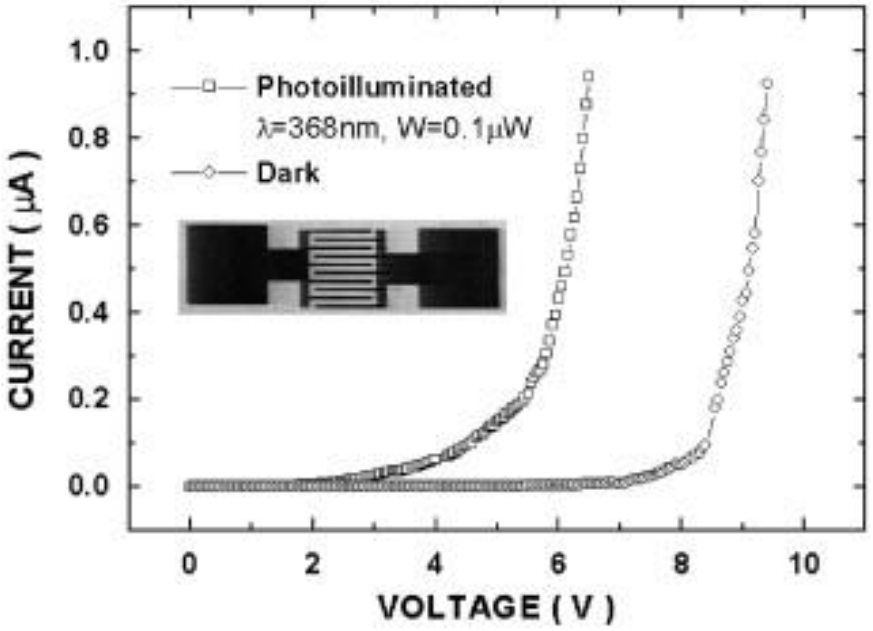
G. De Cesare et al., J. of Non-Cryst. Sol. 198-200 (1996) (2011)

- Other solutions: diode with high bandgap semiconductors

UV sensors

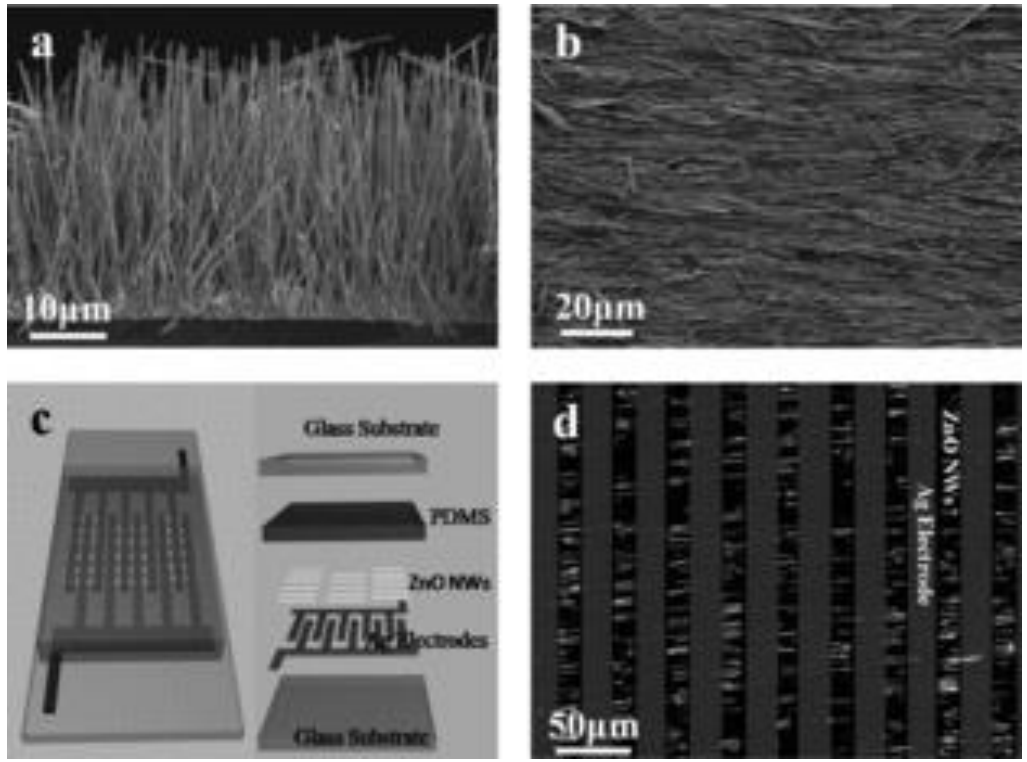
- UV sensor, visible light blind → High bandgap semiconductors

ZnO based detectors
(Schottky diodes, photodiodes)



S. Liang et al., J. of Cryst. Growth 225 (2001)

ZnO NW based detectors
(photodetectors)



S. Bai et al., Adv. Funct. Mat. 21 (2011)

Origin of ternary semiconductors

Elemental semiconductors:

IV: C, **Si**, **Ge**, β-Sn

			Si	P	S
Cu	Zn	Ga	Ge	As	Se
	Cd	In		Sb	Te

Iso-electronic compounds:

III-V (GaAs, InP, InSb, …)

II-VI (ZnS, ZnSe, CdTe, …)

Iso-electronic replacement of II:

I-III-VI: $CuInSe_2$ (1.04 eV), $CuGaSe_2$ (1.7 eV), $CuInS_2$ (1.5 eV)

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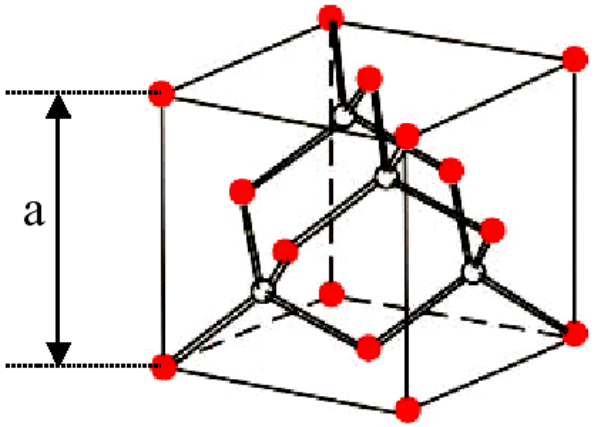
Crystallographic properties

Diamond stucture (element semiconductors: Ge and Si)

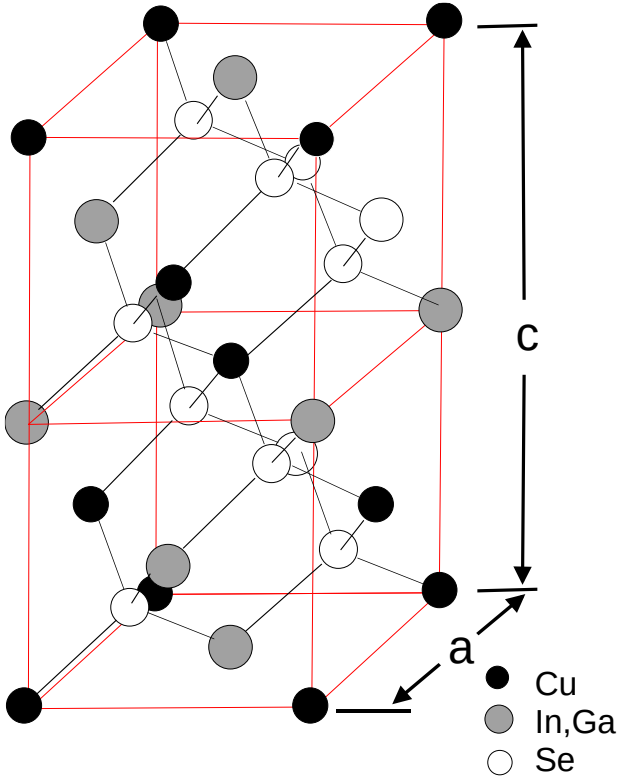
Zincblende (optoelectronic materials: GaAs, InP, GaN)



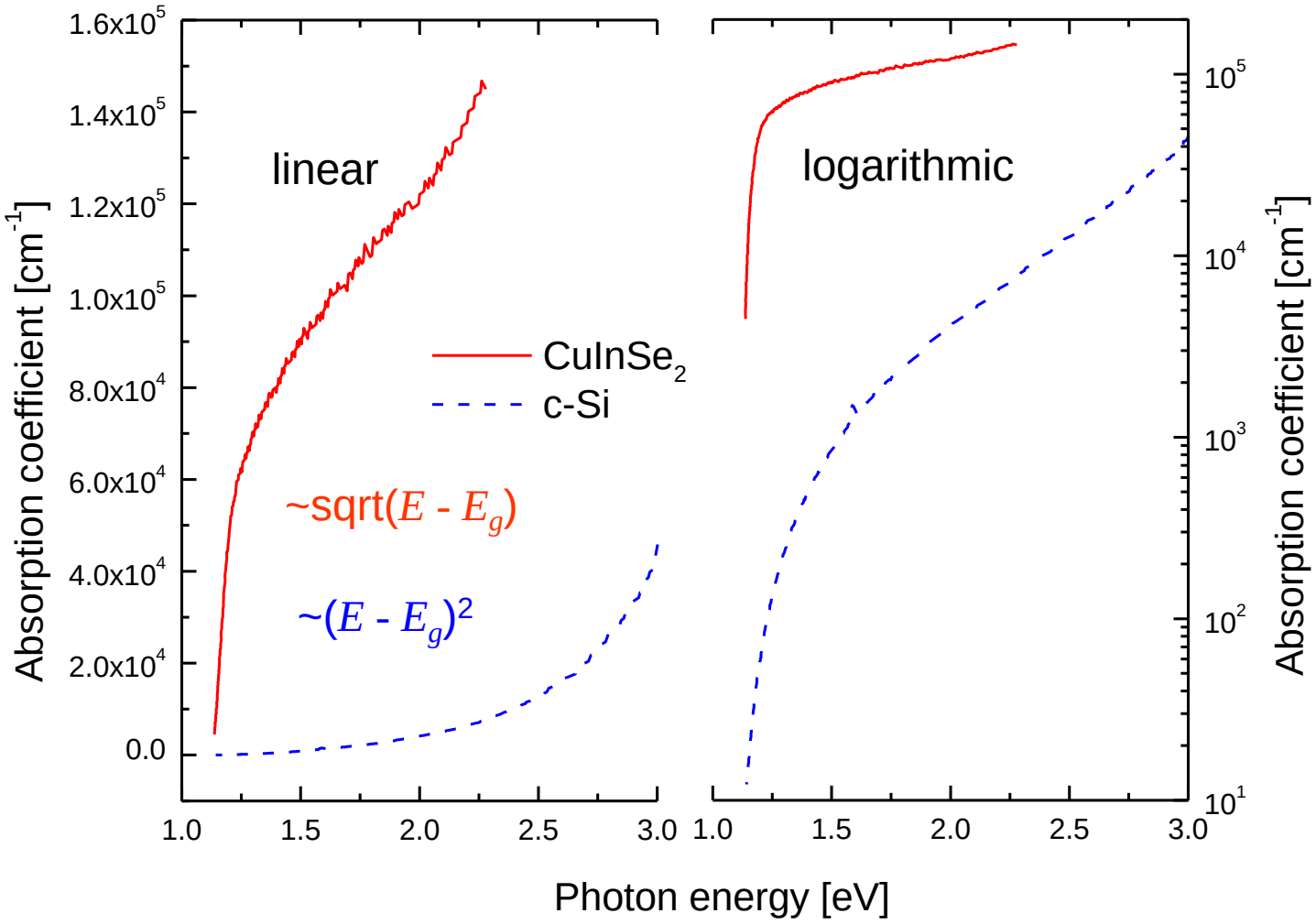
Photovoltaic materials:

CdTe (Zincblende)

$CuInSe_2$ (Chalcopyrite, tetragonal)



Spectral absorption

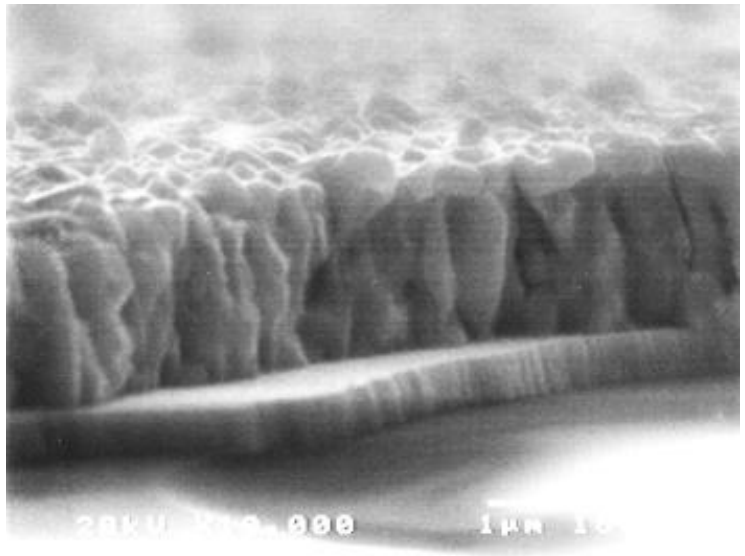


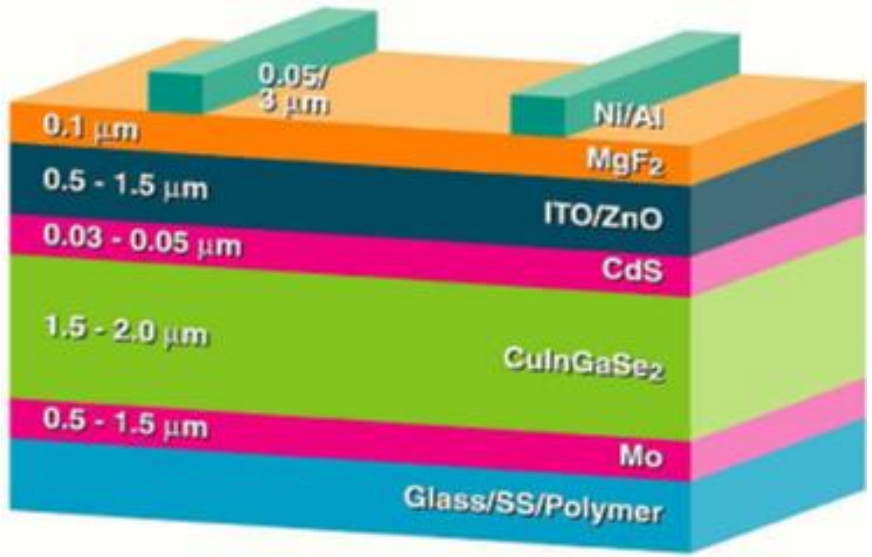
Direct band gap ($CuInSe_2$)

Indirect band gap (c-Si)
(additional phonon required)

$Cu(In,Ga)Se_2$ solar cells (or photodiodes)

- Heterojunction between p-type $Cu(InGa)Se_2$ and n-type CdS
- Bandgap of CuInSe: 1.0 eV, 1.15 eV for $Cu(InGa)Se_2$
- Best lab efficiency : 23.6% (Evolar, 2023),
  20.4% (EMPA on flexible substrate, 2013)
- Deposition on flexible substrates (Mo foil, PI, SS)
- Monolithic interconnection of cells in modules





Hetero-junction formation

Formation of p-n junction

- Historically: also front contact with doped CdS (no window layer)

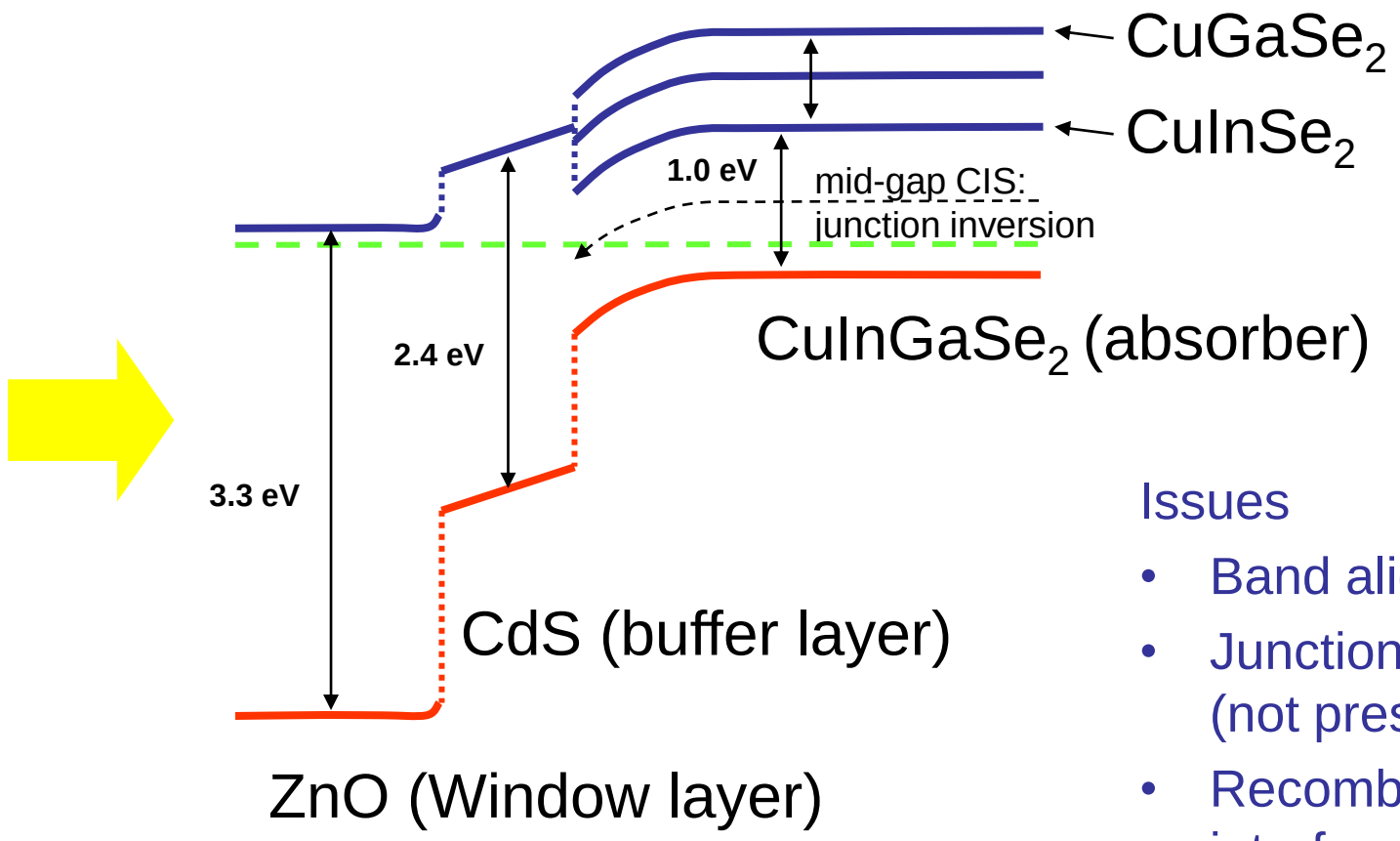
- Standard: deposition of CdS in chemical bath (CBD)
  - $Cd(Ac)_2$, $(H_2N)_2CS$ (Thiourea), NH_3 (pH control)
  - precipitation of CdS (nano-particles in solution, film growth on surfaces)

- Alternatives:
  - $In(OH)_xS_y$, ZnSe, ZnS (CBD process)
  - ZnS, ZnSe: (evaporation)
  - In_2O_3: atomic layer deposition (ALD)
  - Cd, Zn: (partial electrolyte treatment, diffusion of Cd beneficial for junction formation)

CIGS fabrication

- Fabrication:
  - Several possibilities for absorber deposition
    - Co-evaporation: several stages to adjust stochiometry
    - Sequential: sputtering of precursors (Cu and In) followed by selenization (thermal process in H_2Se atmosphere)
    - Non-vacuum techniques (electrodeposition, not possible for Mo)
  - Temperatures > 450 °C necessary for optimum efficiency (≈ 350 °C used for cell on PI + RTA)
  - Na necessary for best absorber growth and morphology, supplied by substrate (glass) or added during process
  - CdS usually deposited by chemical bath (deposition by CVD also possible)

Band diagram



Issues

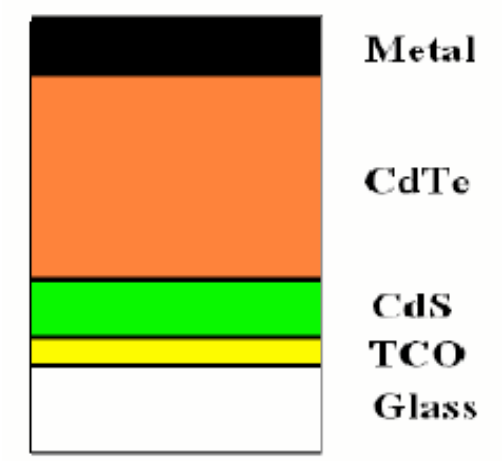
- Band alignement
- Junction inversion for CIS (not present for CIGS)
- Recombination at CdS/absorber interface

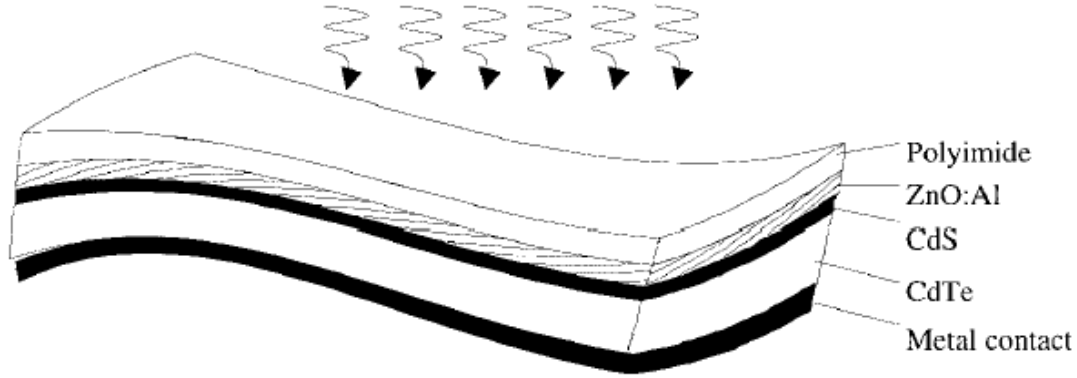
CIGS issues

- Issues
  - Stability (sensitive to humidity)
  - Cost (scale-up, In)
  - In availability (In is a byproduct of Zn extraction)
- Research topics
  - Buffer/window layer
  - Alternative back contact
  - Superstrate cells
  - Cd free cell (avoid CdS)
  - In free absorber: iso-electronic replacement of III by II-IV, e.g. Zn-Sn
    $\rightarrow$ Quaternary $Cu_2ZnSnSe_4$ compounds (Kesterites)
  - Ultra-thin absorber: 100 - 200 nm should be sufficient (direct gap)
  - Non-vacuum process
  - Wide gap absorber (for better single junction, for tandem configuration)
  - Flexible cells, nanoparticles, inks (Daystar, Nanosolar,…)
  - Micro-concentration

CdTe

- Heterojunction between p-type CdTe and n-type CdS
- Bandgap of CdTe : 1.45 eV
- Best lab efficiency = 22.6% (First Solar, 2024)
- Deposition on flexible substrates possible (spin coated polyimide), lower efficiency (best efficiency 13.8% by EMPA, 2011)
- Monolithic interconnection of cells in modules
- Very high radiation hardness (see also next lecture)





CdTe fabrication and issues

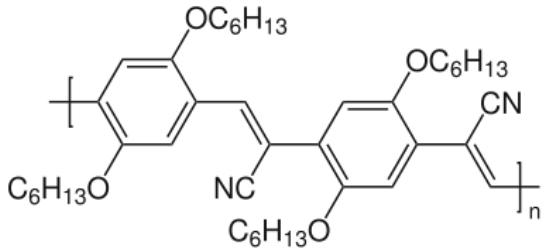
- Fabrication:
  - Deposition of
    - CdS using chemical bath technique (CVD also possible)
    - CdTe using close space vacuum sublimation.
      other possibilities: sputtering, electrodeposition, MOCVD, etc.
  - Deposition or annealing at relatively high temperature ≥ 400°C
- Issues
  - CdTe inert, Cd in production cycle could be an issue,
    Cd content is a legal issue !
- Research topics
  - Thinner cells
  - Absorber morphology
  - Substrate configuration

Organic materials

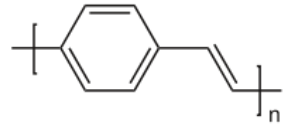
- Thousands of materials
- Small molecules or polymers

- p-type material with low mobility
- Tuneable light sensitivity
- Solution processing possible (spin-coating, printing)

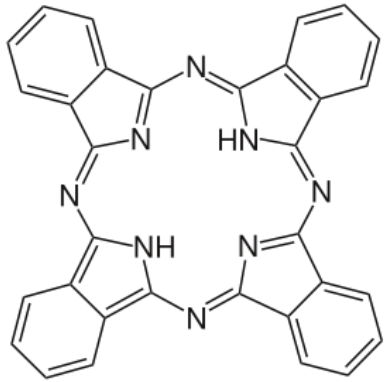
- Flexible devices
- Stability issues (UV, humidity,…)



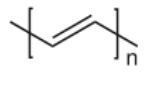
CN-PPV



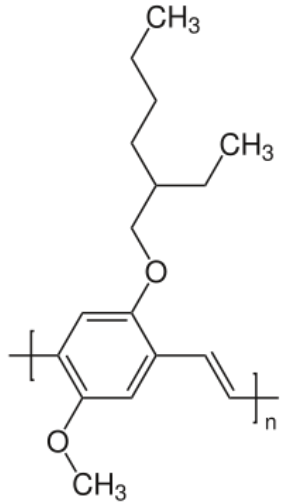
poly(phenylene vinylene) (PPV)



phthalocyanine

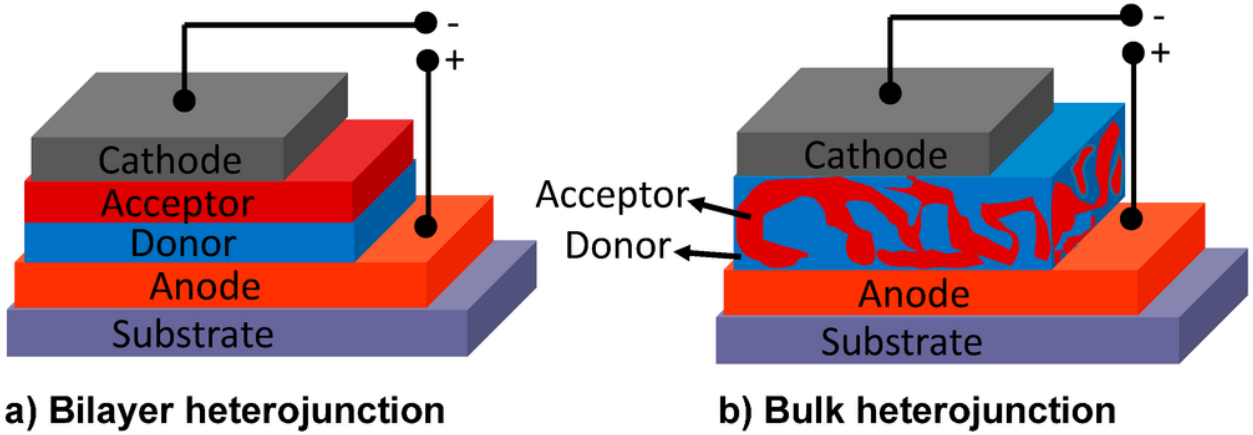


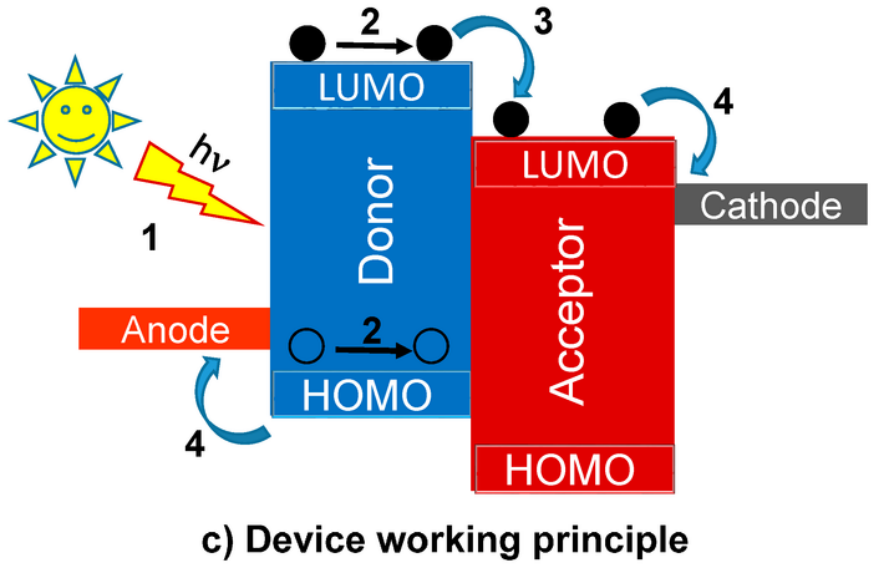
polyacetylene



MEH-PPV

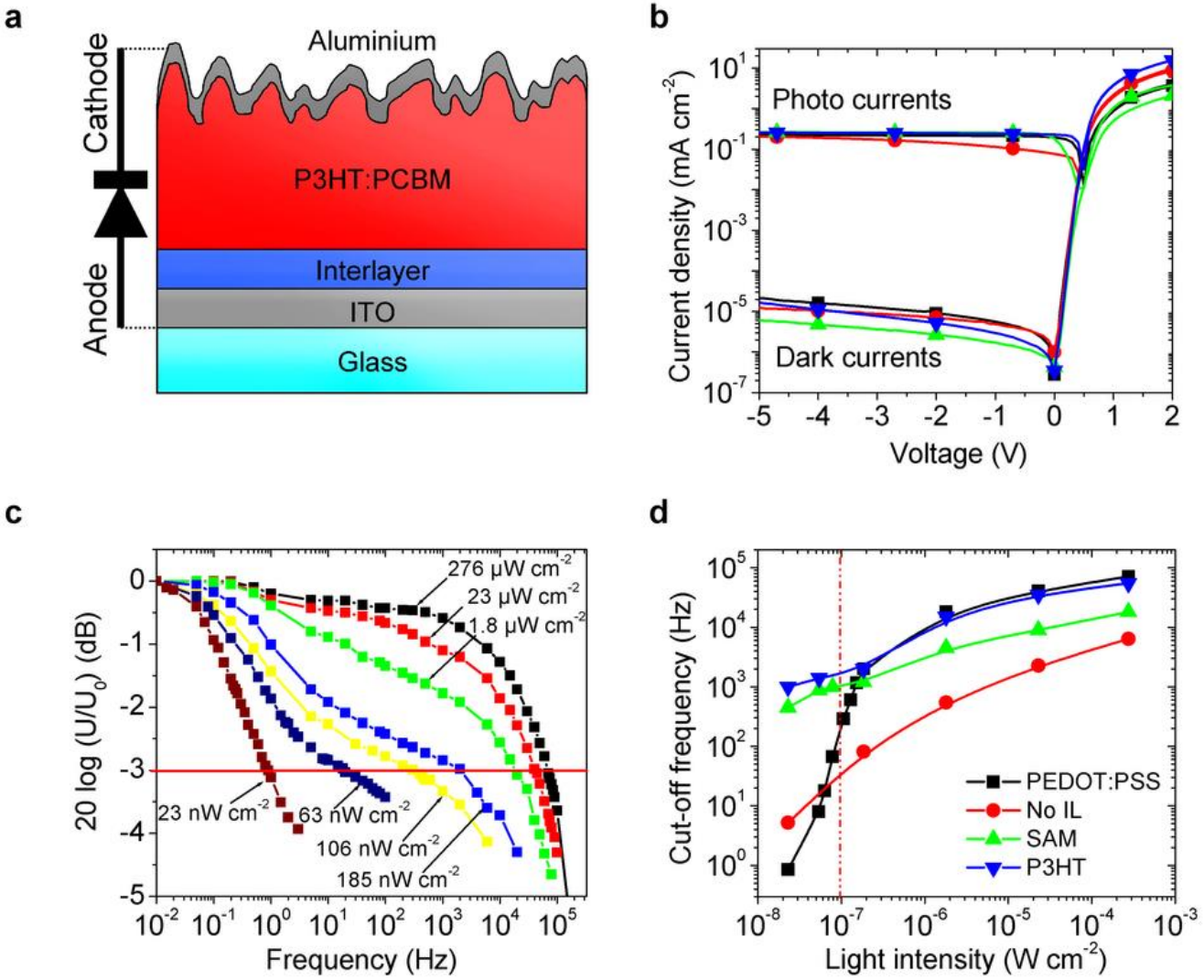
Organic photodiode structure





P. Kumaresan et al., Polymers 6 (2014)

Organic photodiode



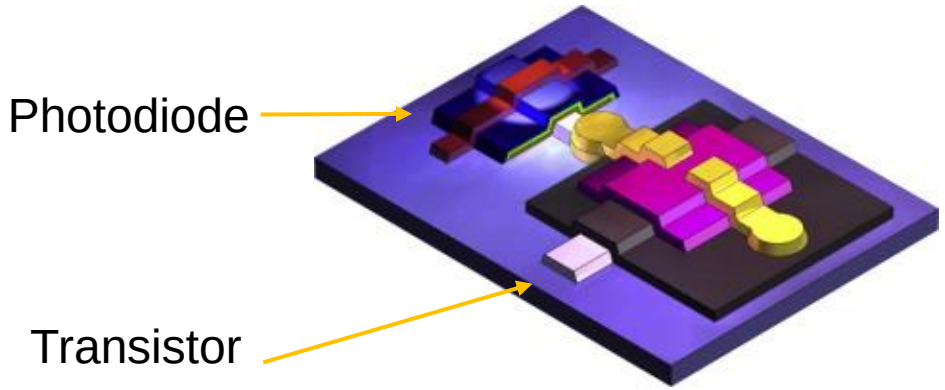
- Bulk heterojunction with P3HT:PCBM blend
- P3HT : donnor
- PCBM : acceptor (fullerene derivative)

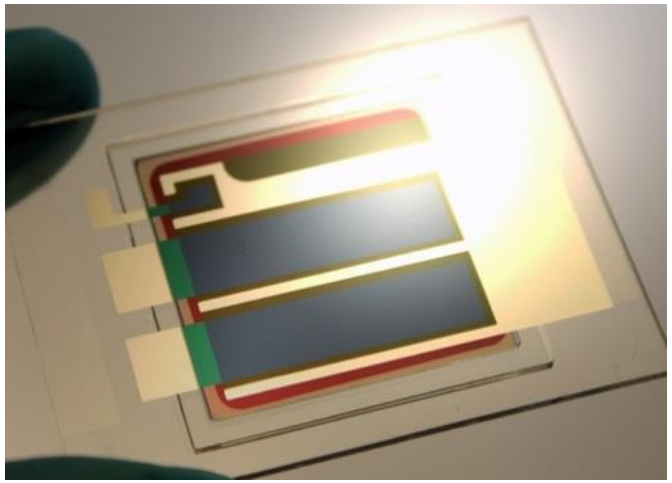
- Interlayer : «hole transport layer» (HTL)

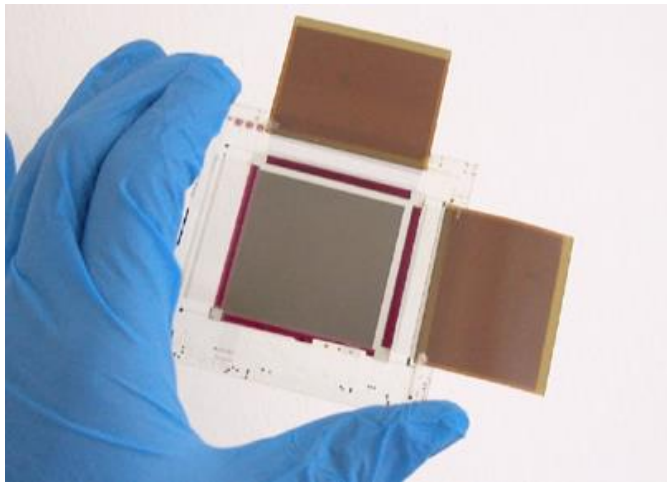
F. Arca et al.,
Scientific Reports 3 (2013)

Organic photodiodes

- Solar cells: 19.2% (SJTU, 2023, single), 14.2% (tandem devices, ICCAS, 2019),
- Straightforward tuning of spectral sensitivity
  - Infrared organic photodiodes (Siemens)
  - Transparent cells (in the visible)
- Integrated organic passive pixel sensor



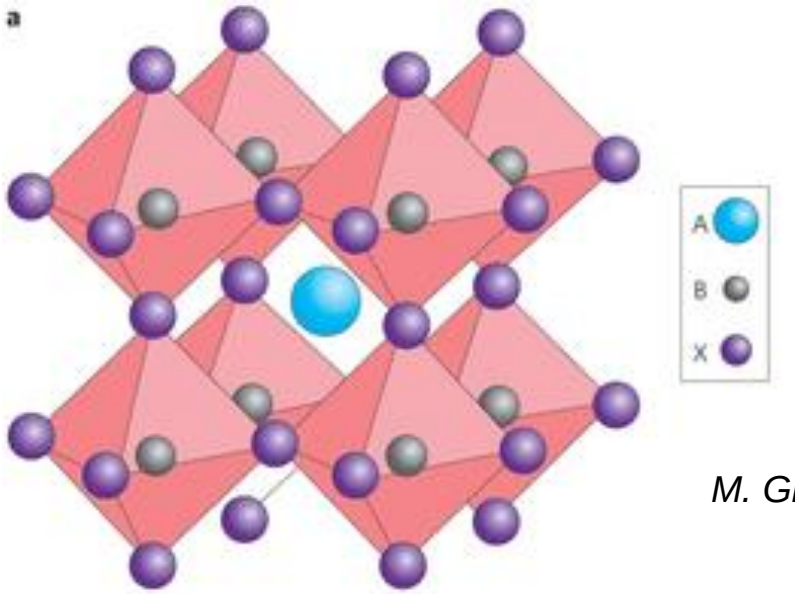




X. Tong et al. Organic Electronics 12 (2012)

Perovskites

- Cristallographic form named from Russian mineralogist L. A. Perovski
- Discovered in 1839
- General form ABX_3, *A,B* : cations, *X* : anion, *A* bigger than *B*
- Cubic cell

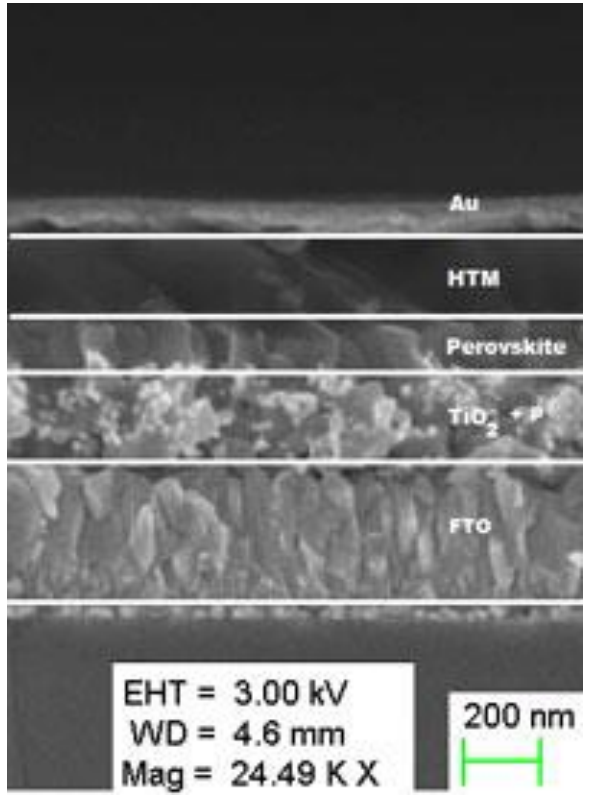


M. Green at al. Nature Photonics (2014)

- Crystallographic structure of various common oxides ($CaTiO_3$, $SrTiO_3$, $BaTiO_3$, $PbZrO_3$,…)

Perovskites

- High interest fo solar cells (lab developments) since 2009
- Pioneered by M. Greatzel (EPFL) using
  lead iodide perovskite
  ($CH_3NH_3PbI_3$, Methylammonium Lead Iodide-MALI)
  - Structure:
    Au / P3HT / $CH_3NH_3PbI_3$ /
    TiO_2 / ITO / Glass
- Best efficiency: 26.1% (NUUT, 2023, small area)
  Higher stability with hybrid/mixed perovskites:
  $CH_3NH_3PbI_{3-x}Cl_x$
- Issues : stability (short/long term, interfaces, contacts
  oxygen, moisture, temperature), usage of Pb, hole conducting layer
- Lead free perovkites solar cells with much lower efficiency
- Large effort to develop a top cell on c-Si for tandem device !
  Best efficiency: 33.9.0% (Longi, 2023)
- Interest as x-ray sensing material (heavy elements!)

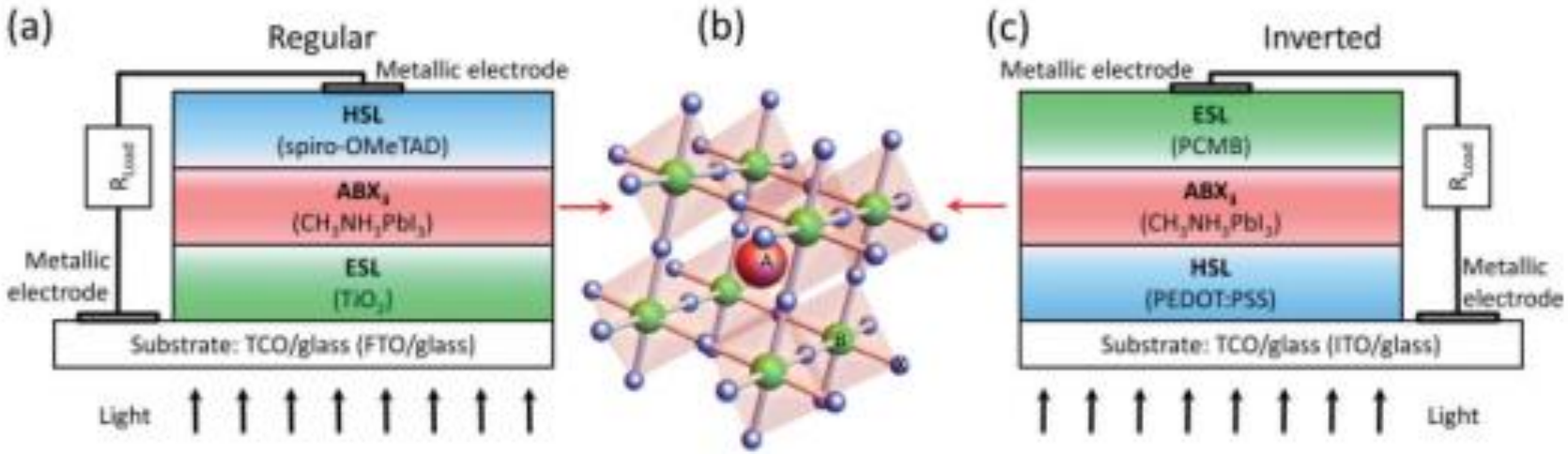


Perovskite materials

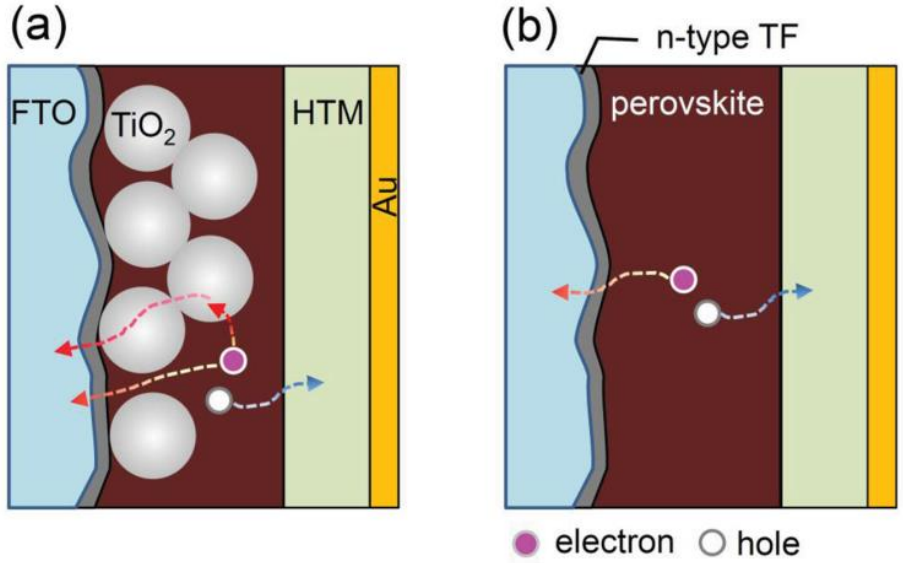
- Base materials (ABX_3)
  - A: CH_3NH_3 (MA), $HC(NH_2)_2$ (FA), PEA ($C_6H_5(CH_2)_2$)
  - B: Pb, Sn
  - X: Cl, Br, I
- Best materials
  - $CH_3NH_3PbI_3$, Methylammonium Lead Iodide ($MAPbI_3$ or MALI)
    $E_g \approx 1.7$ eV (direct-indirect, *Hutter et al., Nature Mat. 16 (2016)*)
  - $H_2NCHNH_2PbI_3$, Formamidinium Lead Iodide ($FAPbI_c$ or FALI),
    $E_g \leq 1.55$ eV
- Material modification (for higher stability and E_g tuning)
  - Replacement (small fraction) of I by Br or Cl
  - Replacement (small fraction) of FA by Cs
  - Hybrids/mixed perovskites

Qin et al., J. of Semiconductors 38 (2017)
Zhao et al., Nature Comm. 9 (2018)

Perovskite based devices



Lopez-Varo et al., Adv. Energy Mat. (2018)

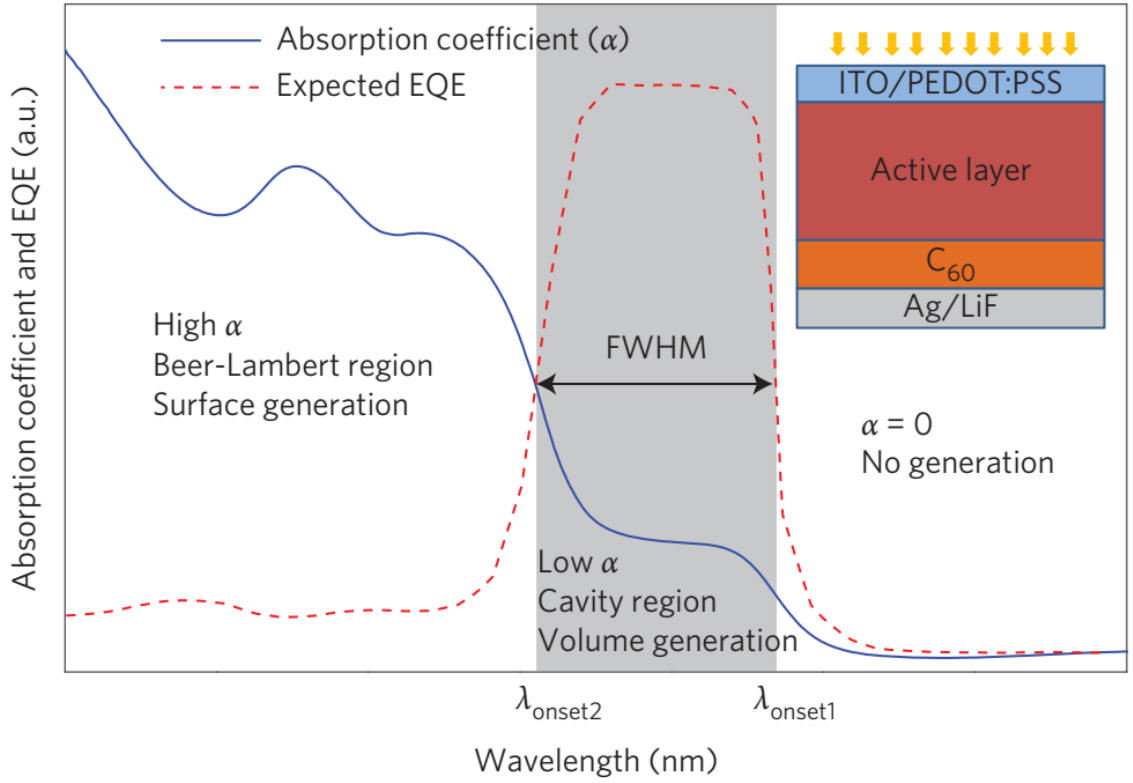


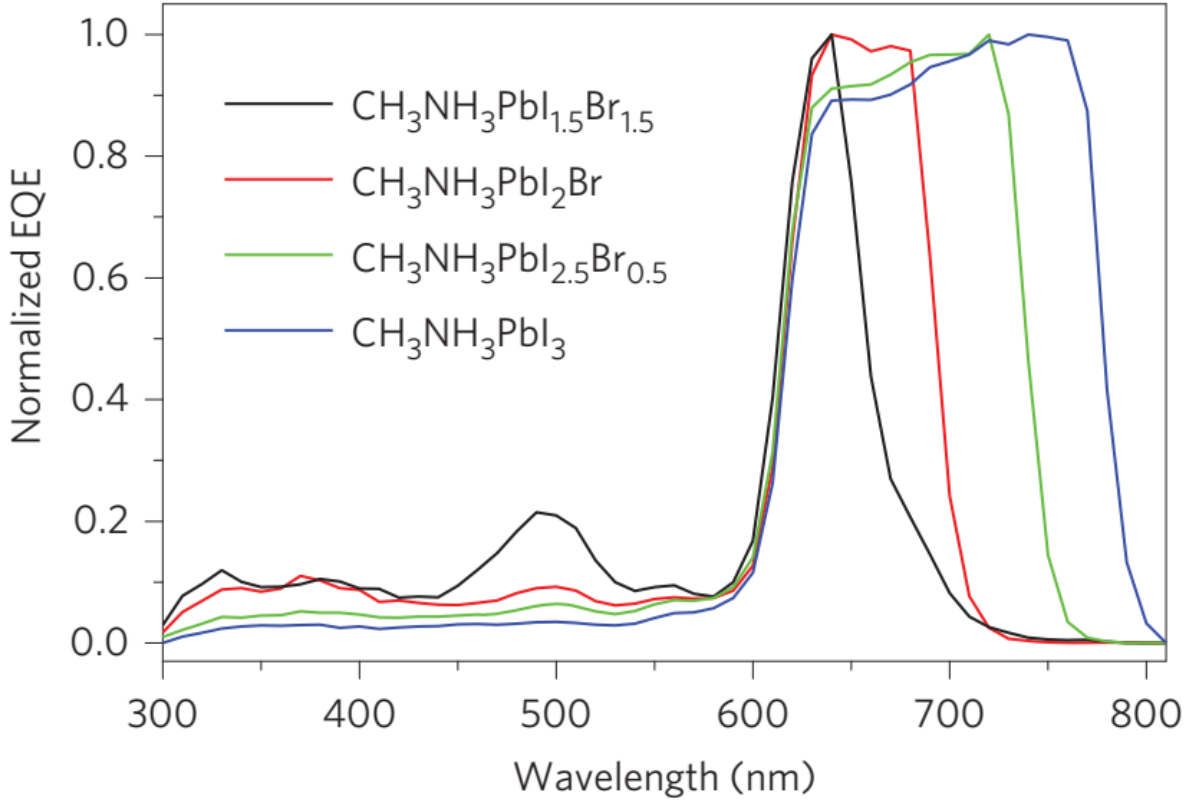
H.S. Jung, N.-G. Park, Small 11 (2015)

- Various (critical) choices for
  - HSL (Hole Selective Contact
  - ESL (Electron Selective contact
- n-i-p or p-i-n configuration

Perovskite based photodetectors

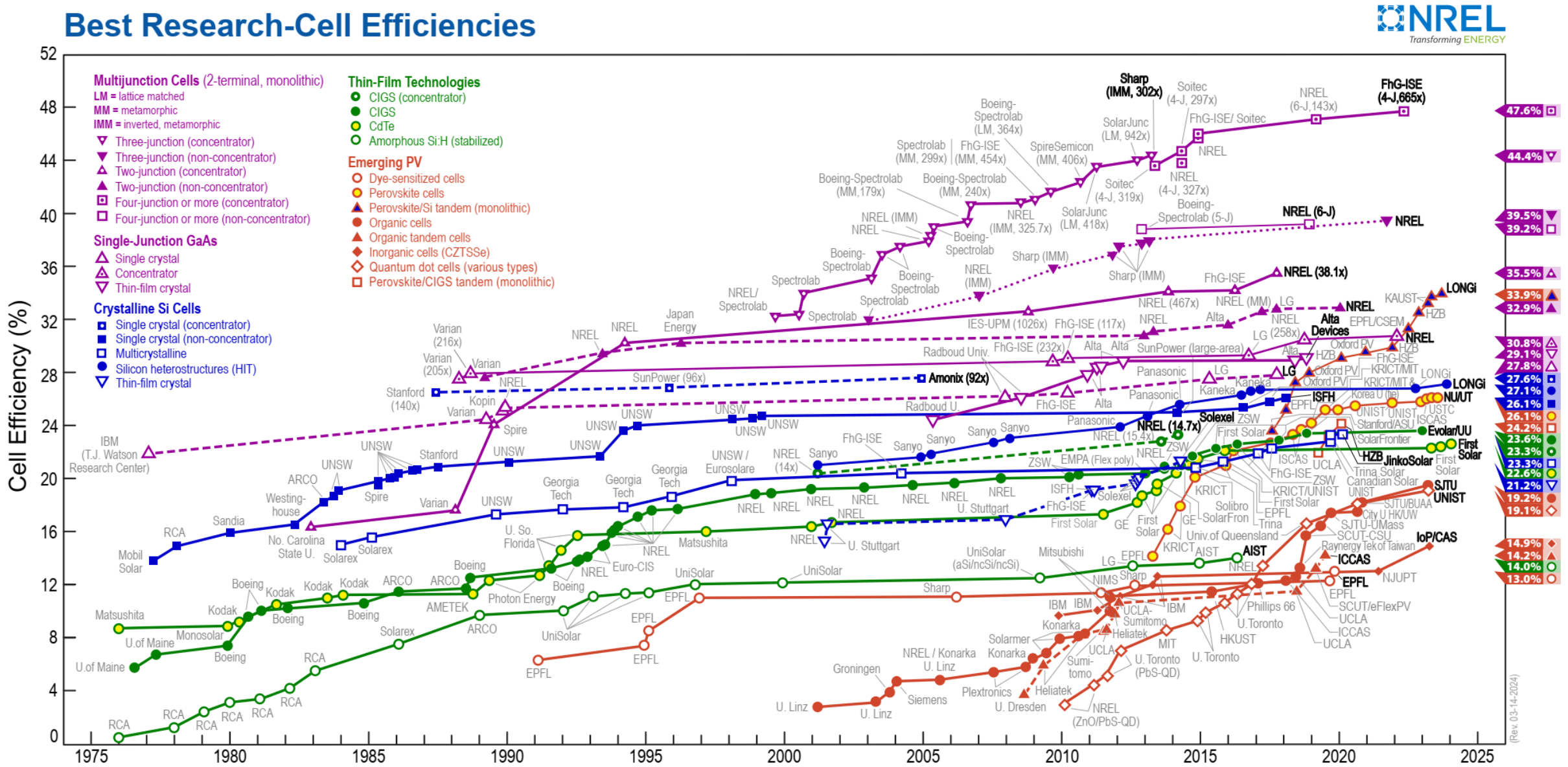
- Exemple of narrow bandgap detectors





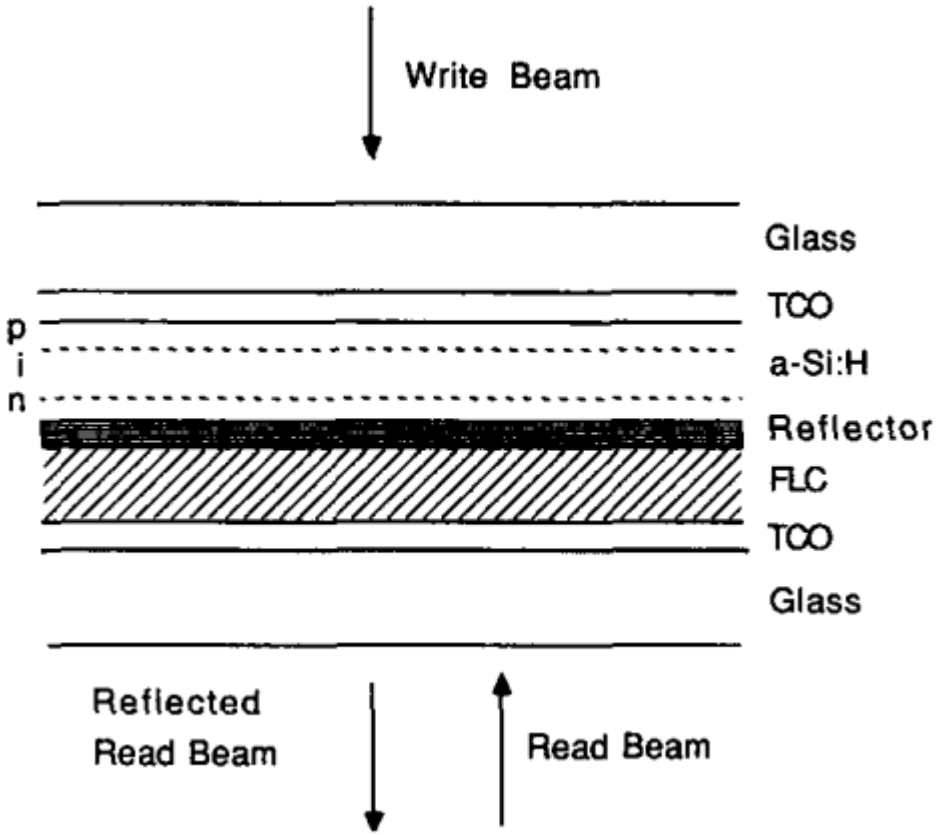
Q. Lin et al., Nature Photonics 9 (2015) 687.

Best solar cells



NREL, https://www.nrel.gov/pv/cell-efficiency.html

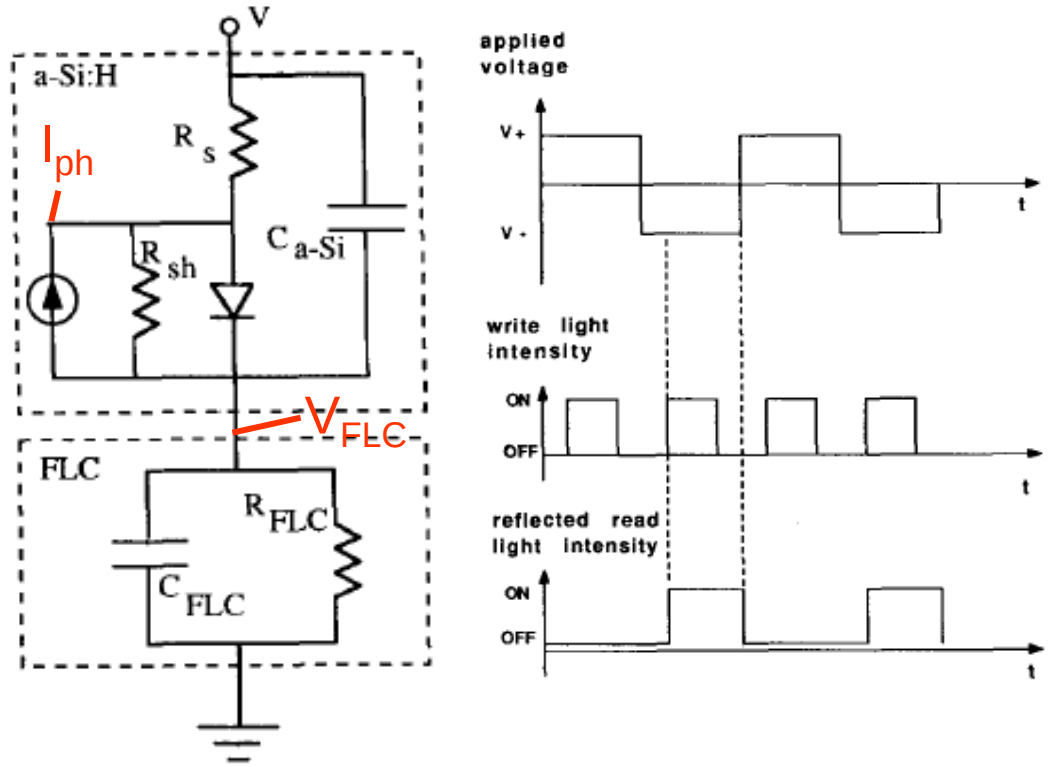
OASLM: Optically Addressed Spatial Light Modulator



- Applications
  - Spatial distribution of light amplifier
  - Image projection (amplification)
  - Spatial filtering
  - Light valves
  - Optical computing
- Principle
  - Liquid crystal cell (FLC : Ferro Liquid crystal) driven by a (p-i-n) solar cell

Li et al., IEEE Trans. On Elect. Dev. 36 (1989) 2959

OASLM operation



Li et al., IEEE Trans. On Elect. Dev. 36 (1989) 2959

Operations

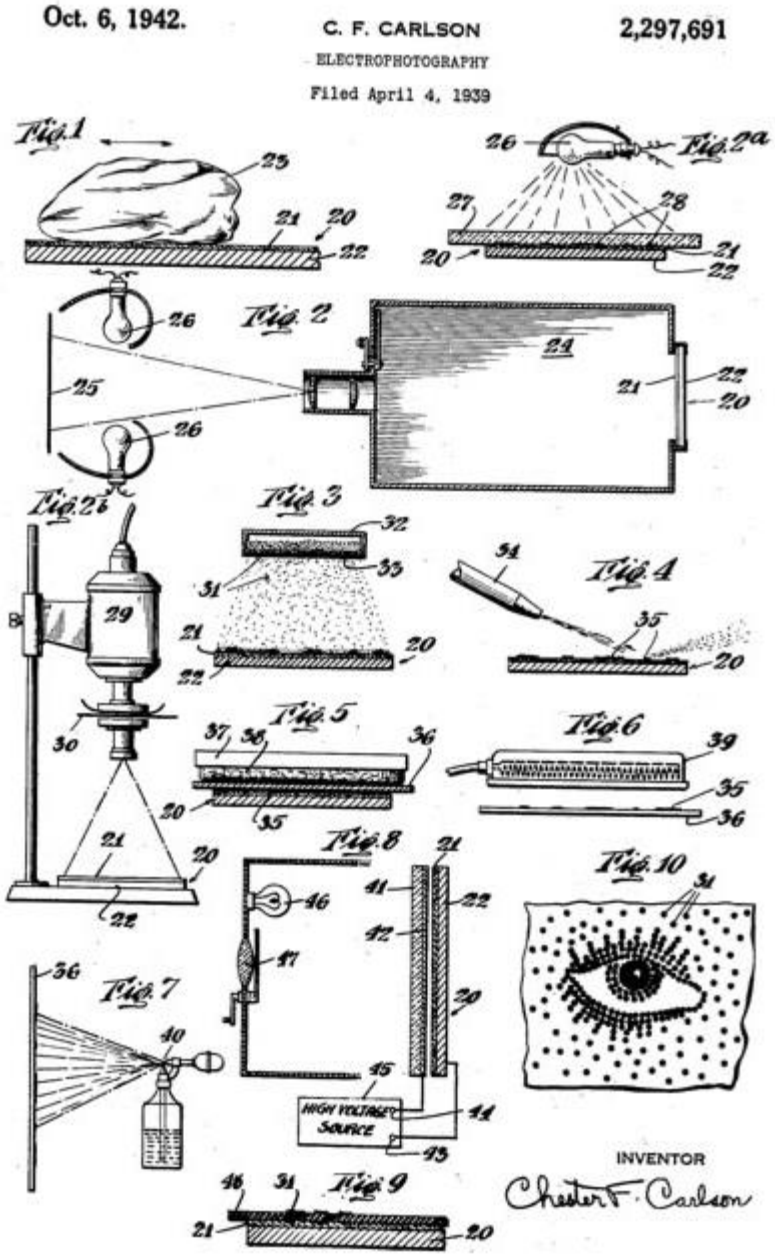
1. V>0 (forward bias)
   - Reset
   - $V_{FLC} > 0 \rightarrow$ OFF
2. V<0 (reverse bias)
   a) Write light ON
      - $I_{ph} > 0$
      - $V_{FLC} < 0 \rightarrow$ ON
   b) Write light OFF
      - $I_{ph} = 0$
      - V_{FLC} unchanged
      - State unchanged

States

- ON : light reflected
- OFF : light absorbed

Xerography

- Xerography or electro-photography
- First application of amorphous semiconductors!
- Discovered in 1938 by Chester Carlson in Astoria (NY)
- Patented in 1942 (US Patent 2,297,691)
- "xerography" comes from the Greek language and means *dry writing*.
- Principle used in copy machines & laser printers.



First copier, first laser printers

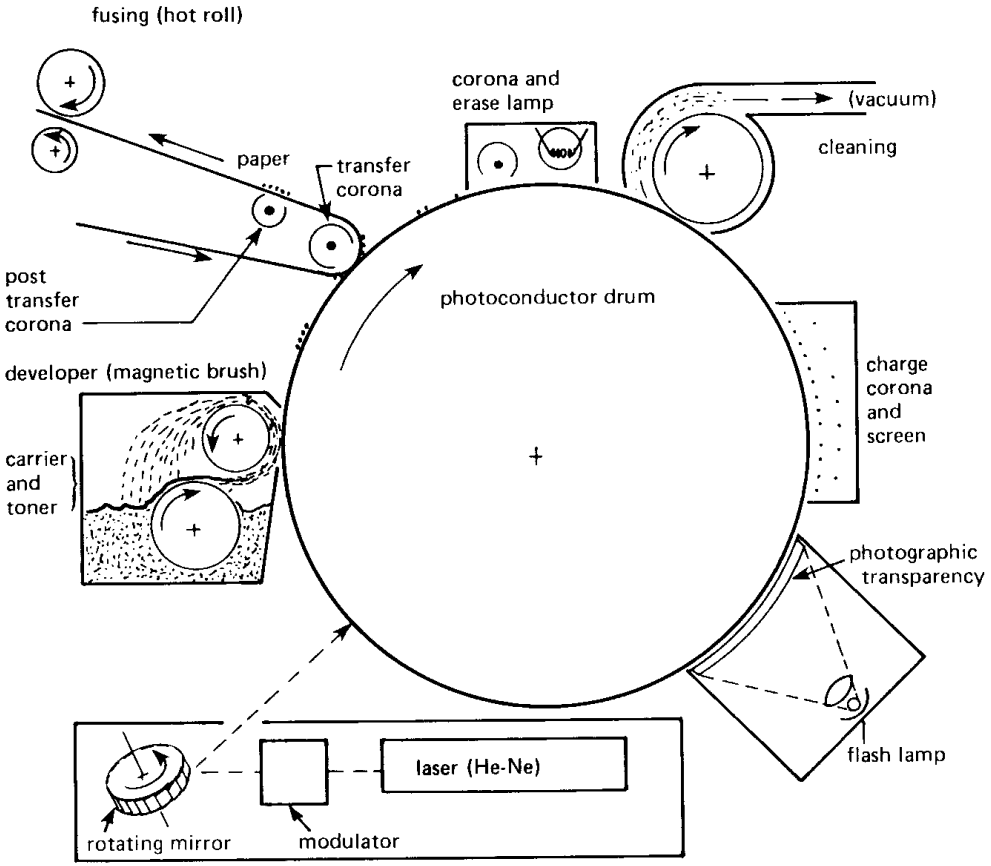
The first copier
XEROX's « Model A » , 1949

First laser printer prototype Xerox, 1969

IBM 3800
1975

The first commercial (office) laser printer
Xerox 9700, 1977

Principle

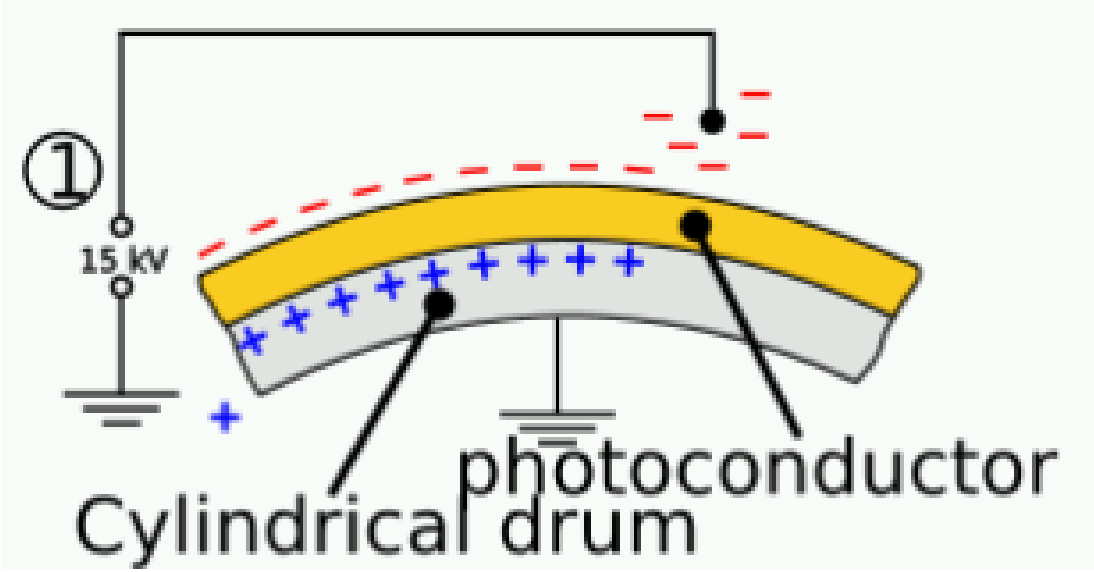


Williams, 1984

1. **Corona** discharge
   surface charging of the photo-conductor
2. **Exposure**
   charge neutralization as a function of the image to reproduce
3. **Development**
   reproduction on photoconductor with the help of colored polymer (toner)
4. **Transfer**
   of the image (toner) on paper
5. **Fusion**
   fixation of the image by fusion of the polymer
6. **Cleaning**
   of the surface of the photoconductor

The corona discharge and the exposure, are semiconductor dependent !

Principle and required properties

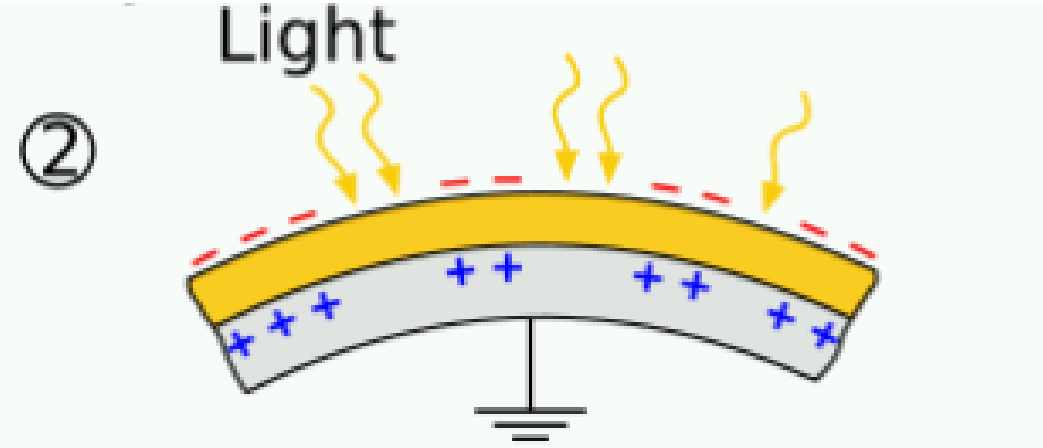


Wikipedia

Corona discharge

- High electrical strength
- High charge trap density
- Low dark conductivity (especially lateral conductivity)

Principle and required properties (2)

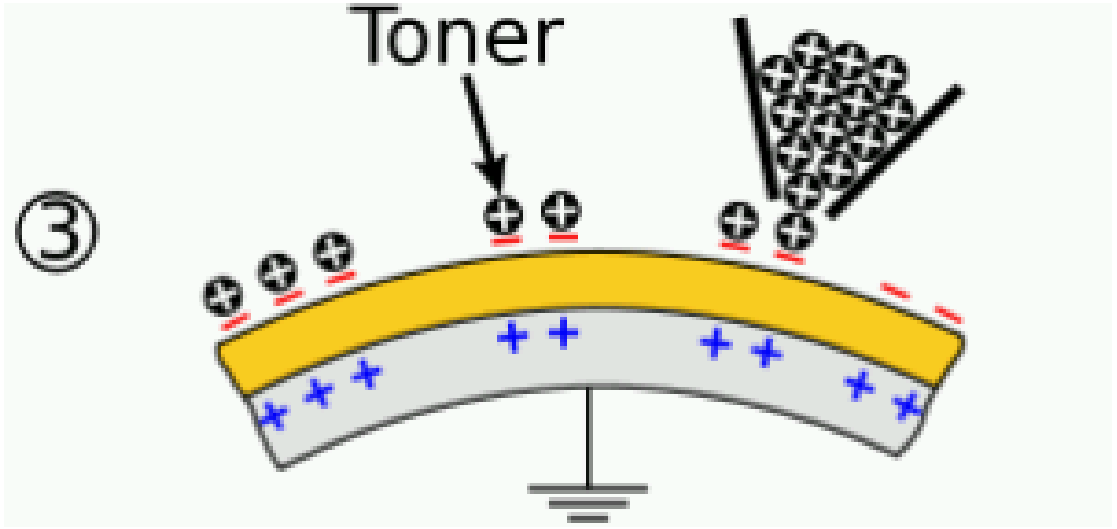


Wikipedia

Exposure

- High photoconductivity (for light wavelength used for exposure)
- High conductivity (for at least one type of carrier), property can be supplied by a separate layer (charge transport layer)

Principle and required properties (3)

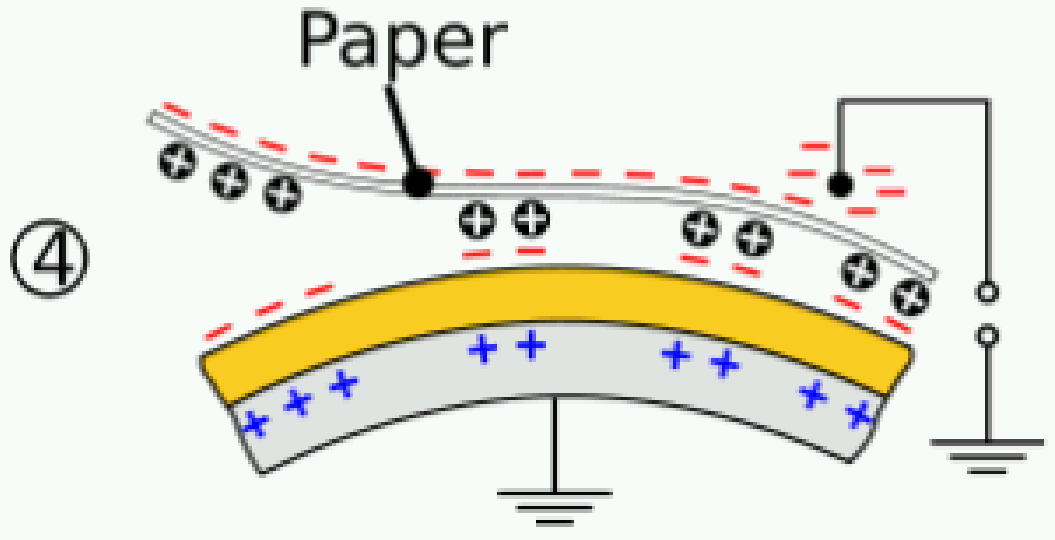


Wikipedia

Development

- Challenging step for good image (toner handling)
- Low surface conductivity (see also charging) to avoid image smearing
- Smooth surface

Principle and required properties (4)



Wikipedia

Transfer and cleaning

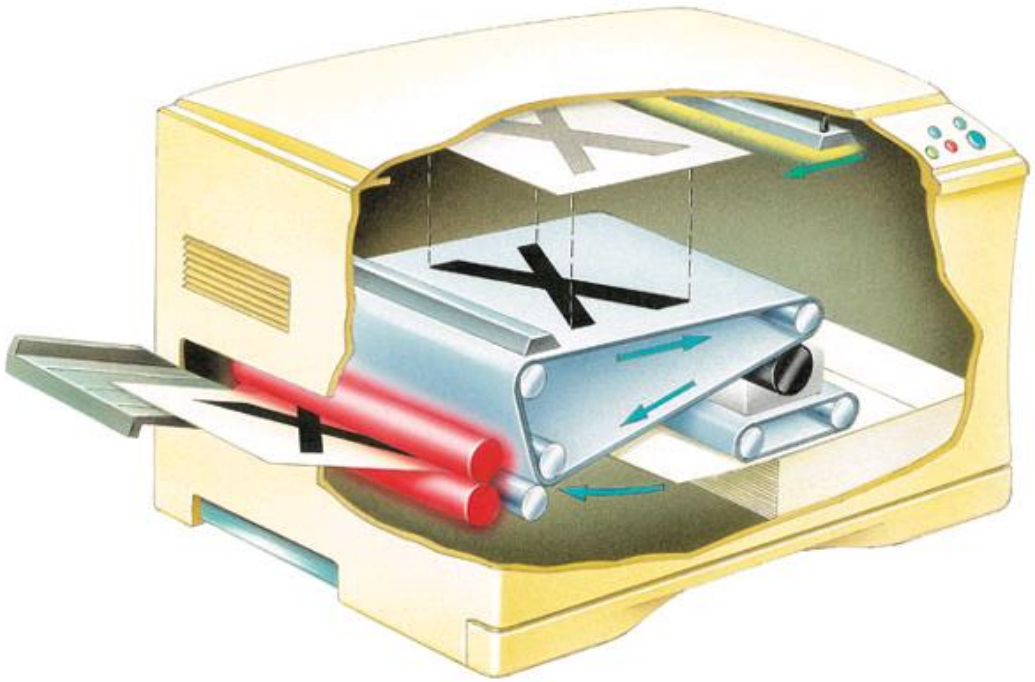
- High mechanical strength (especially surface strength)
- Smooth surface

Summary of photoconductor properties

- Ideal properties :
  1. Large surface trap density, density should be deep in energy
  2. No charge injection from the conductive substrate to the photoreceptor
  3. Should appear as a isolator in the dark and an efficient photoconductor under light

- **Necessary properties:**
  - keep a high density of charges on the photoconductor charges (a very high voltage is present between the surface and ground, >600 V)
  - high quantum efficiency for the electron-hole pair conversion
  - sufficient drift mobility for at least one type of carriers (electrons or holes)
  - mechanically stable, durable (physically and chemically), high surface hardness
  - low cost

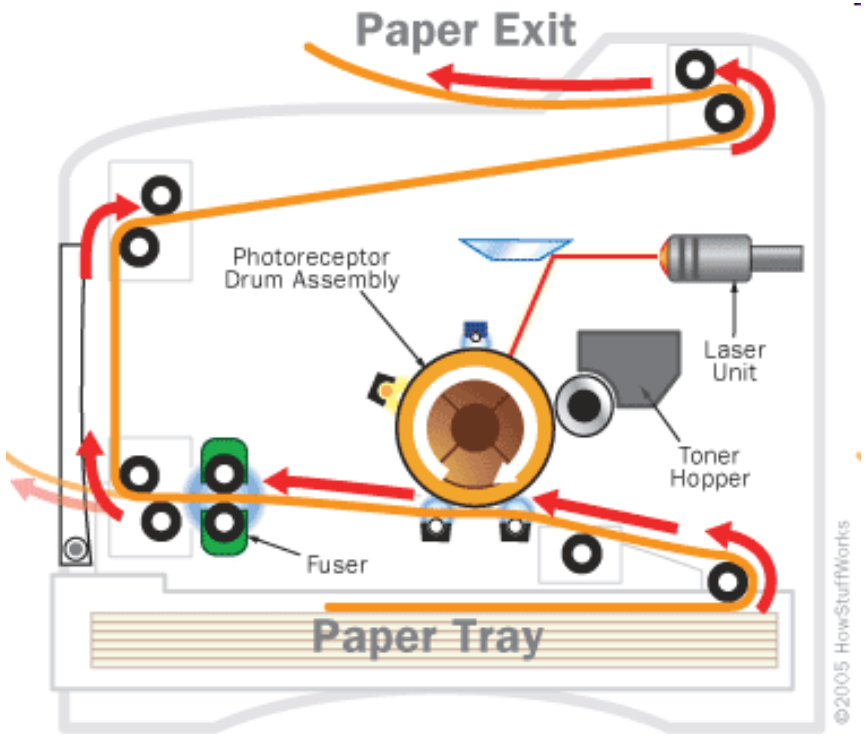
Copier

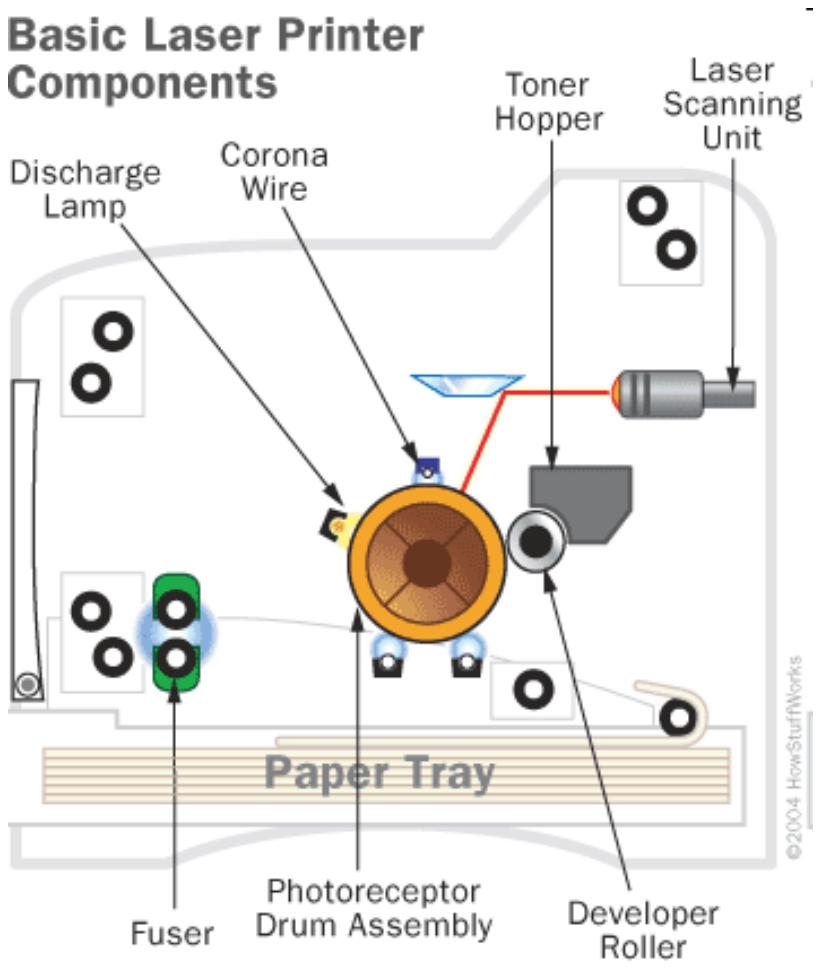


Photoreceptor (photoconductor)
deposited on a

- Drum
- Belt or ribbon
  (preferred design)
  - Advantage: permits the exposure of planar
    surfaces in one shot (copy of the image with one
    light flash without scanning).

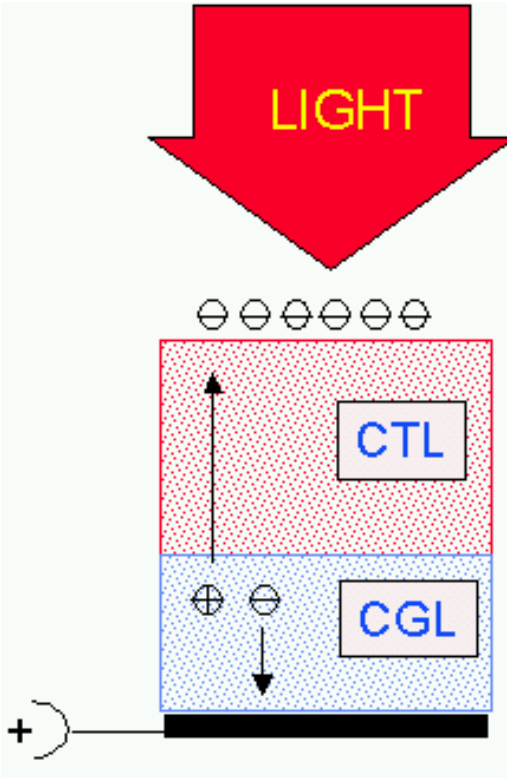
Laser printer





Photoreceptor structure

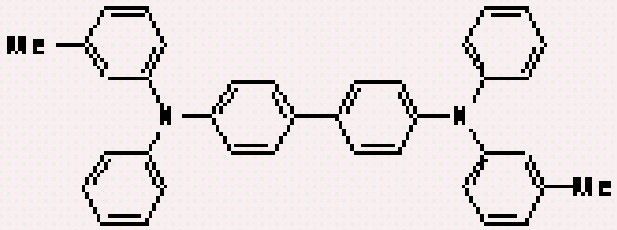
- Mono-layer
- Bi-layer
  - CTL : Charge transport layer
  - PGL : Photogeneration layer
    or CGL : charge generation layer
- Tri-layer
  - CTL : Charge transport layer
  - PGL : Photogeneration layer
    or CGL : charge generation layer
  - OL : Overlayer (protection and charge trap layer)



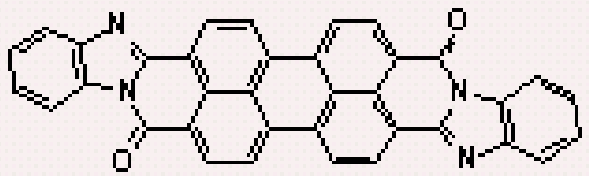
- Bi- or tri-layers photoreceptors enable obtaining all required properties by a combination of layers with specific functions and material properties

Materials for Xerography

- a-Se
- a-Si:H
- CdS, CdSe
- Se-Te based alloys: a-$Se_{1-x}Te_x$
- Se-As based alloys: a-As_2Se_3
- Multi-layer :
  Al / Se riched CTL / Se-Te PGL / Se-As OL
- Organic photoreceptors
  - Poly(N-vinylcarbazole) (PVK),
    2,3,7-trinitro-9-fluorenone (TNF)
    (first introduced in copier, IBM, 1970)
  - Many materials for PGL including dyes,
    fullerenes and CTL (hole transport)



Charge Transport Material ST 16/1



Charge Generation Material ST 2

a-Se, a-As_2Se_3

Table 9.1 Physical Properties of a-Se and a-As_2Se_3

Property	a-Se	a-As_2Se_3
Density, g · cm^{-3}	4.29	4.55
Glass transformation temperature (DSC at 5°C/min)	50°C	~180°C
Crystallization temperature (DSC at 5°C/min)	100°C	~300°C
Melting temperature, °C	218	~360
Microhardness (Vickers hardness number kgf/mm^2)	40	~150
"Photoconduction band gap" (eV)	2.5	1.8
Wavelength for unity photosensitivity, nm	500	720
Dark resistivity (Ω · cm)	10^{14}	10^{12}
Hole drift mobility, $cm^2/V \cdot s$ (F is the electric field in V · cm^{-1})	0.16	~$2 \times 10^{-10} F$
Electron drift mobility, $cm^2/V \cdot s$	7×10^{-3}	—
Quantum efficiency	Field dependent	Field dependent
Xerographic dark discharge	Depletion discharge	Depletion discharge

Sources: Barisova (1981, Ch. 1), Kasap and Juhasz (1987), Lutz (1987), Lutz and Reimer (1982), Scharfe (1984).