7 Basic Organic Electronic Devices

Table of Contents

7.1 Organic Field-Effect Transistors

Transistors

- transistors (derived from “transfer resistor”) are electronic switches or amplifiers

Transistor
- **Bipolar Junction Transistor (BJT, current controlled device)**
- **Field Effect Transistor (FET, voltage controlled device)**
  - **‘Classical’ FET**
  - **Thin Film Transistor (TFT)**

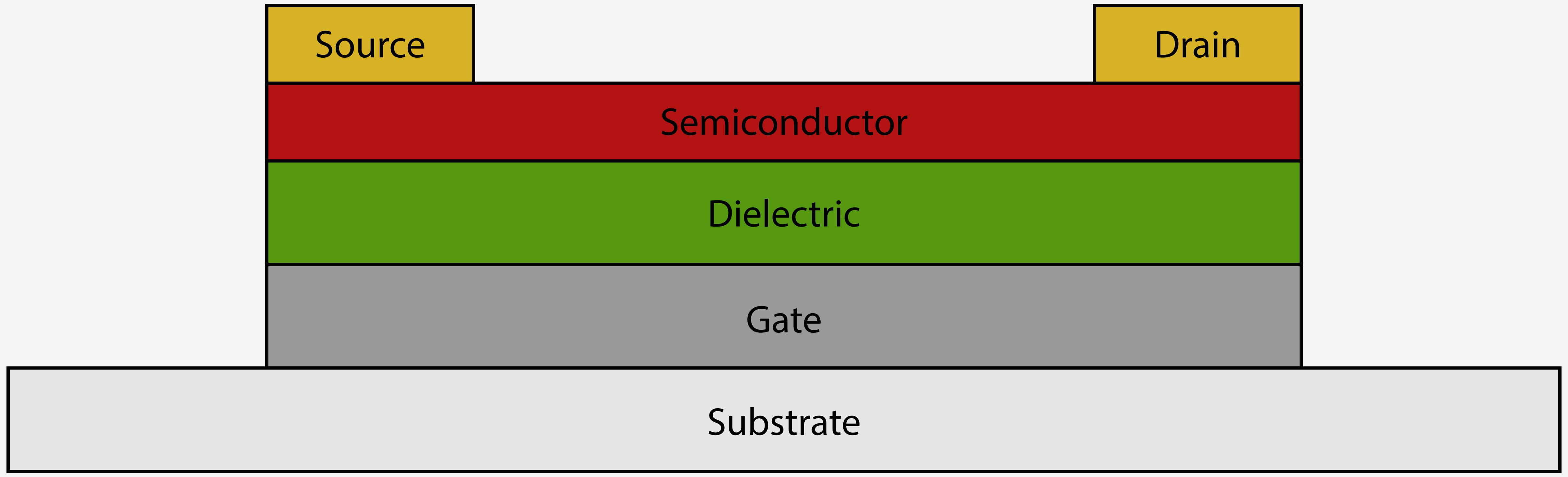
‘Classical’ FET
typically single-crystalline semiconductor
serves as substrate
logic circuits, computer processors

Thin Film Transistor (TFT)
all active components
deposited onto an insulating substrate
displays, RFID-tags

- **organic field-effect transistors (OFETs) are thin film transistors from organic semiconductors**

General Setup of a Thin Film Transistor

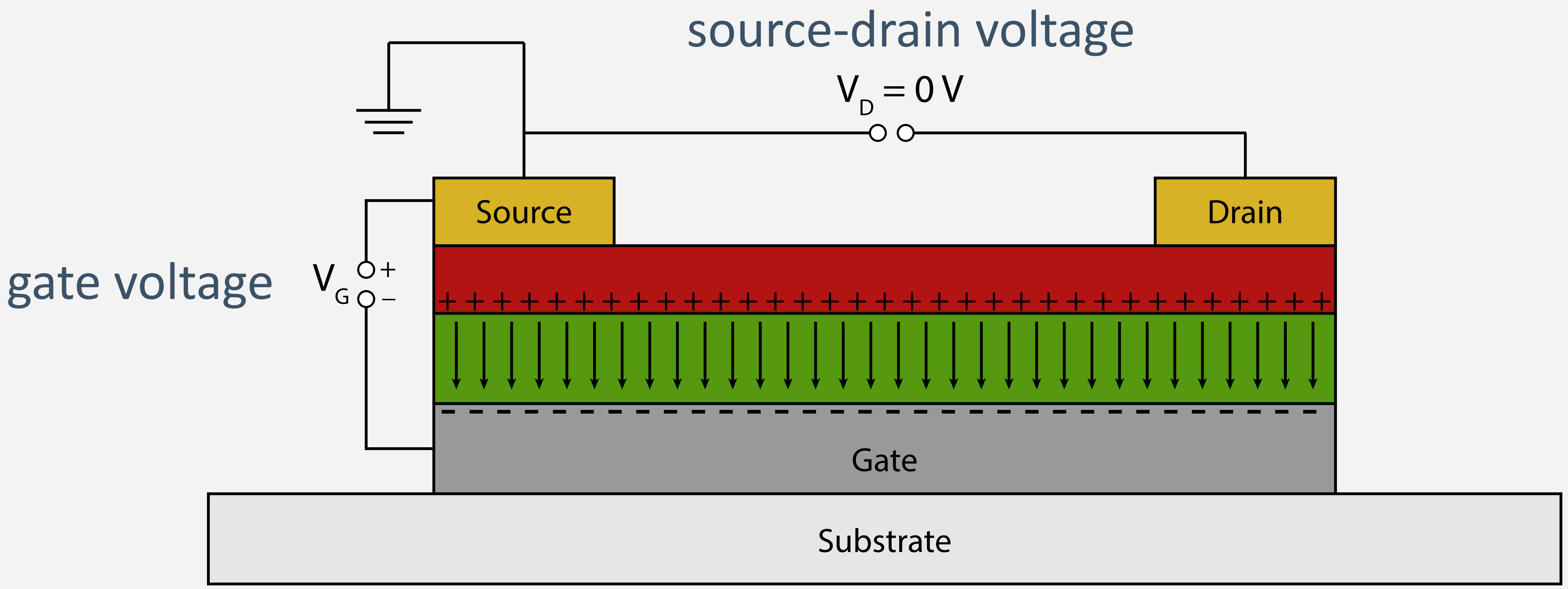
- all active layers are deposited as thin films onto a substrate (hence, thin film transistor, TFT)



- **three-terminal device: source, drain, and gate electrodes**
- gate electrode (voltage) is used to switch (on/off) a source-drain current
- source, drain, and gate electrodes typically made of Au, Ag, Al, ITO, PEDOT:PSS, etc.
- dielectric typically metal oxides (Al_2O_3, HfO_2, SiO_2) or organic insulators (PMMA, SAMs)

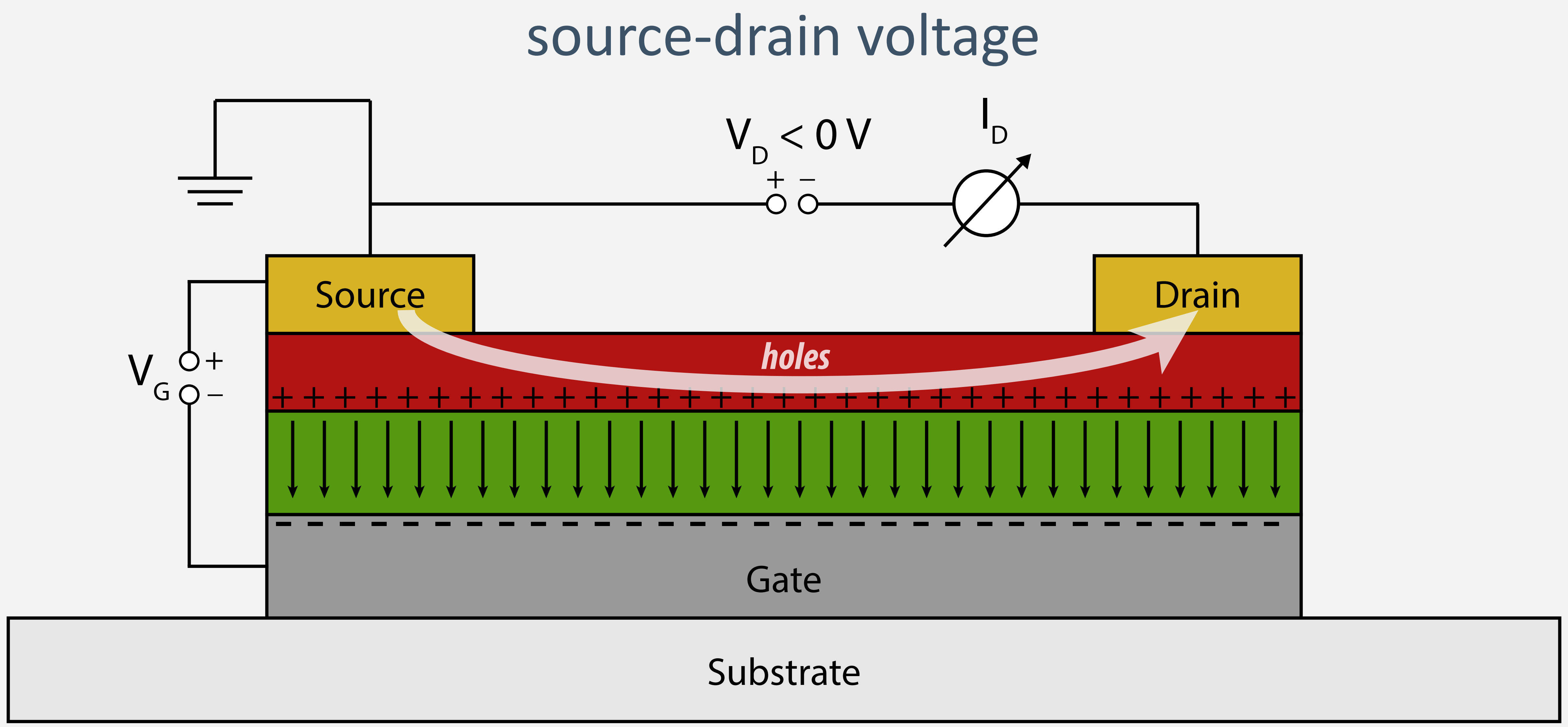
Working Principle of a Thin Film Transistor (TFT)

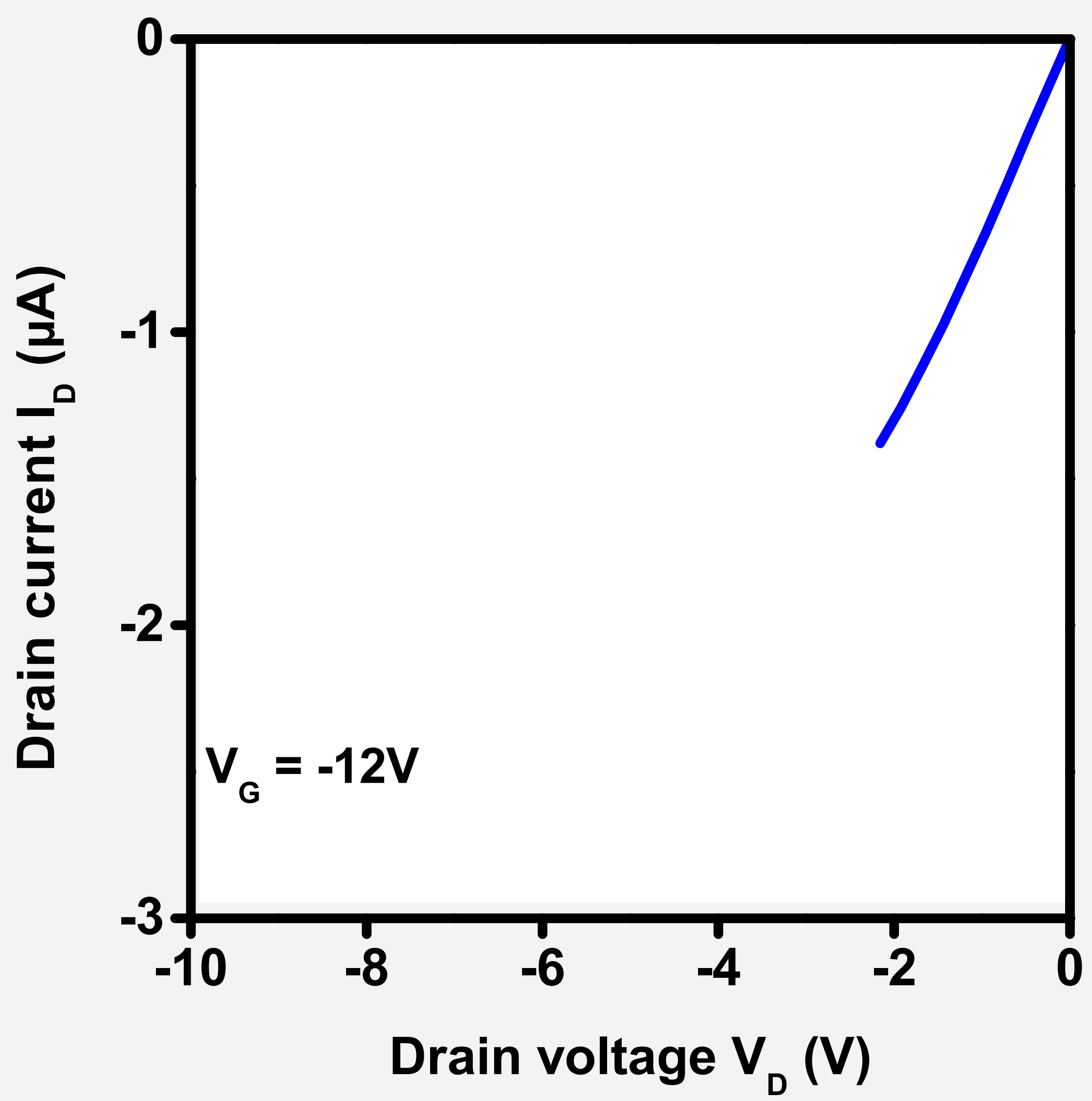
- electric charge per area $Q = C \cdot V_G$, typical value in on-state 10^{14} e/cm^2 or 1 e/nm^2
- capacitance per area $C = \varepsilon_0 \varepsilon_r / d$, vacuum permittivity $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m, dielectric constant (relative permittivity) ε_r of the gate dielectric, dielectric layer thickness *d*



- **V_G creates plate capacitor, charge accumulation at the semiconductor-dielectric interface**
- **organic semiconductor is doped by field effect (towards/beyond insulator-metal threshold)**
- **at V_D = 0 charge carriers are uniformly distributed over the whole semiconductor**

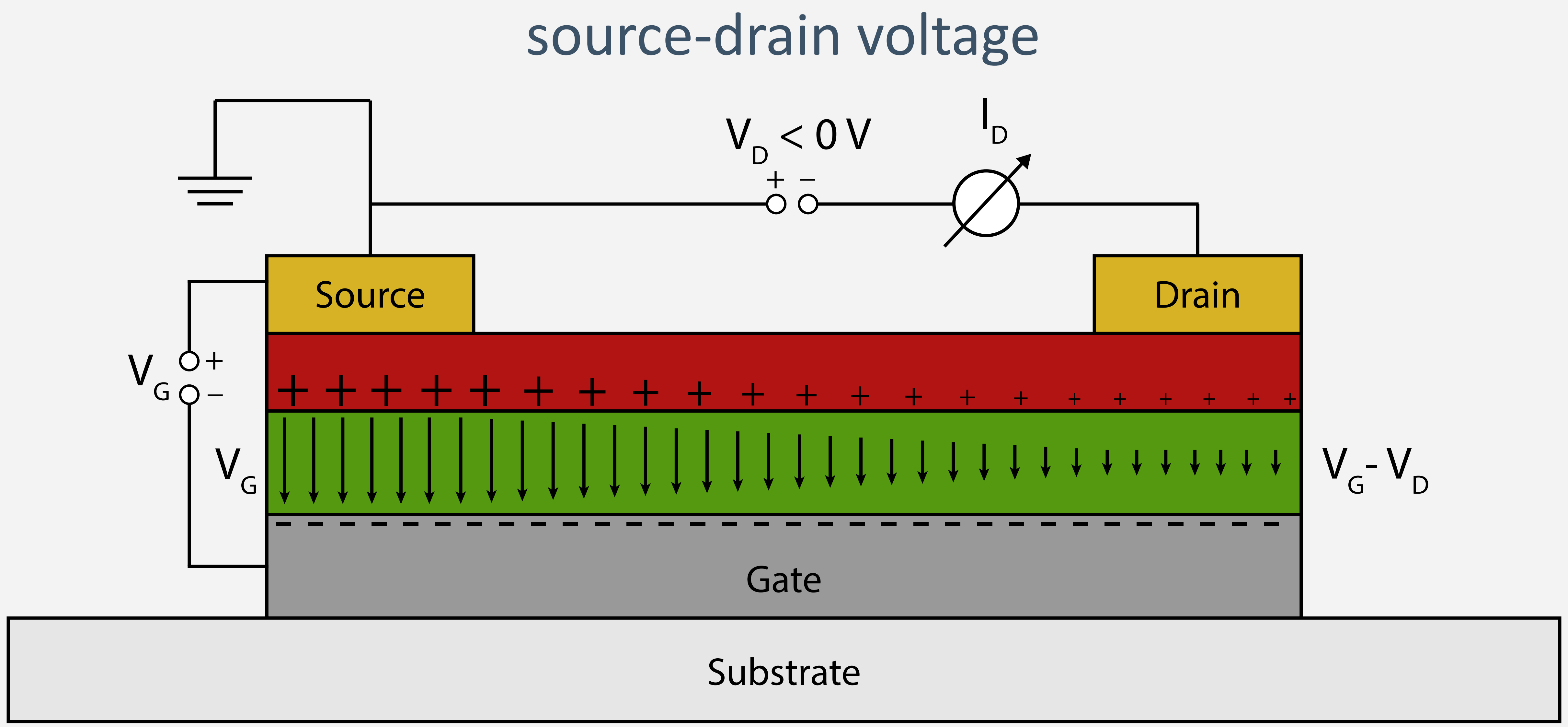
Response of an OFET in the Linear Regime

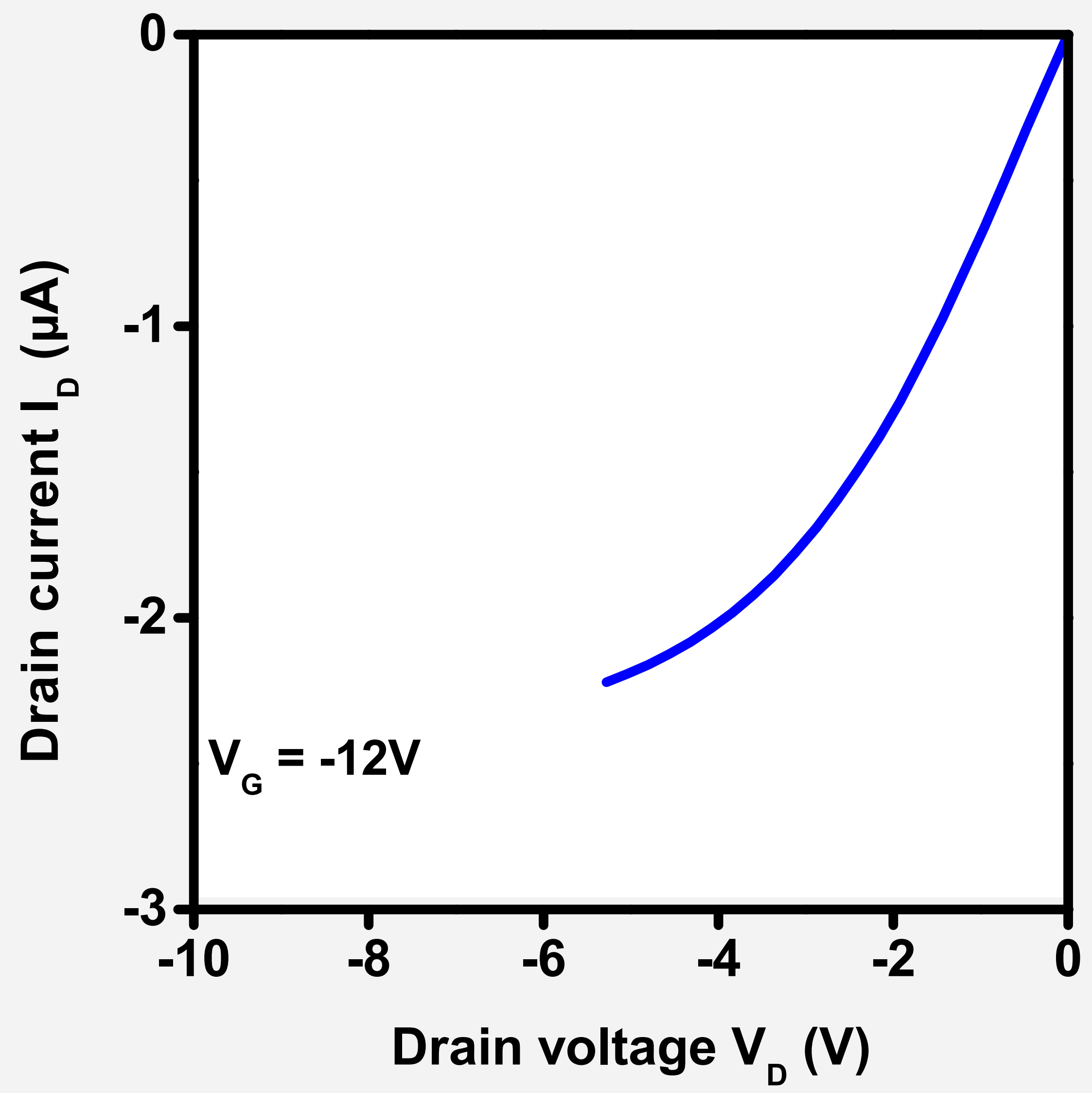




- applying V_D leads to charge flow between source and drain (drain current I_D)
- for $|V_D| \ll |V_G - V_{th}|$ charge carriers remain uniformly distributed over the whole channel
- initially Ohm beavior, linear increase of the drain current I_D with V_D (linear regime)
- critical is charge injection from the source/drain electrodes into bulk organic semiconductor

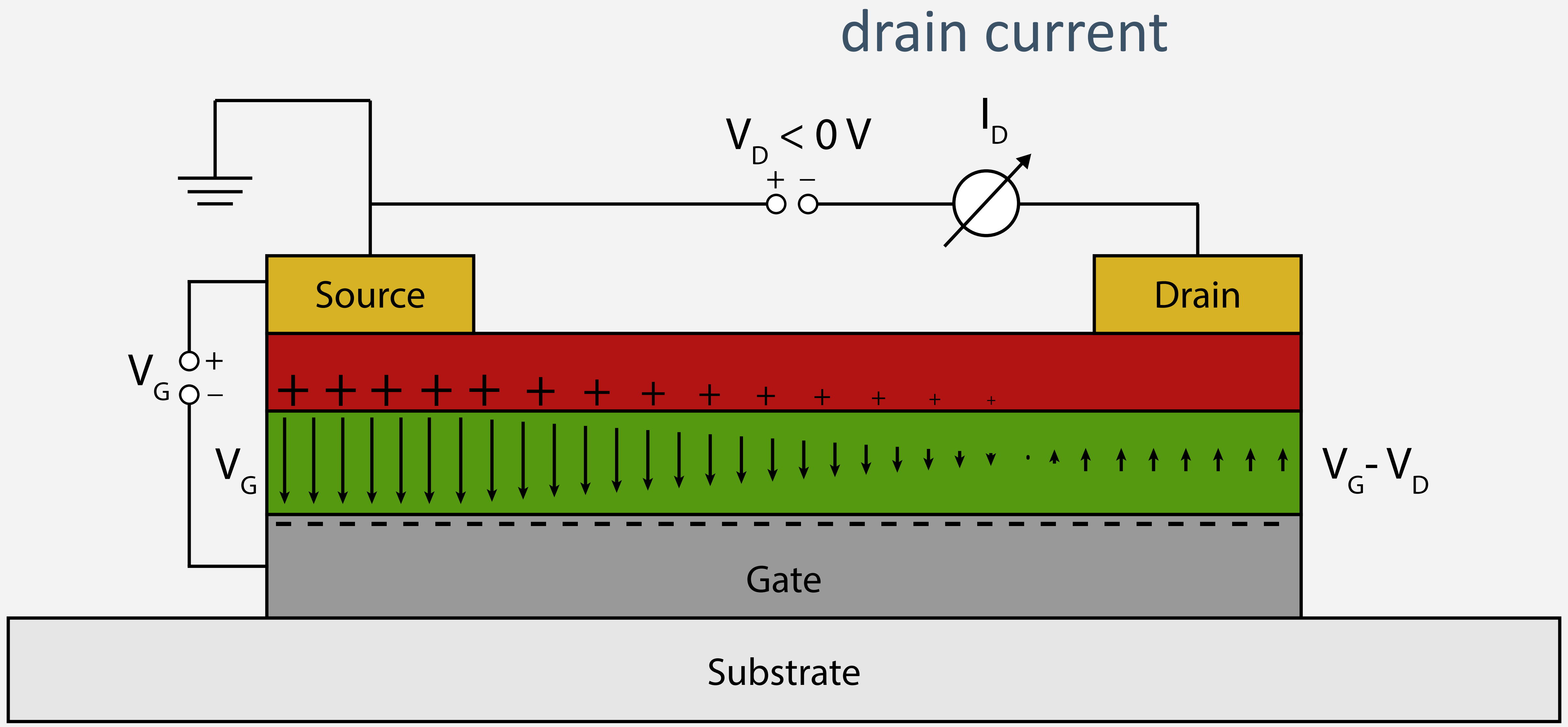
Response of an OFET in the Transition Regime

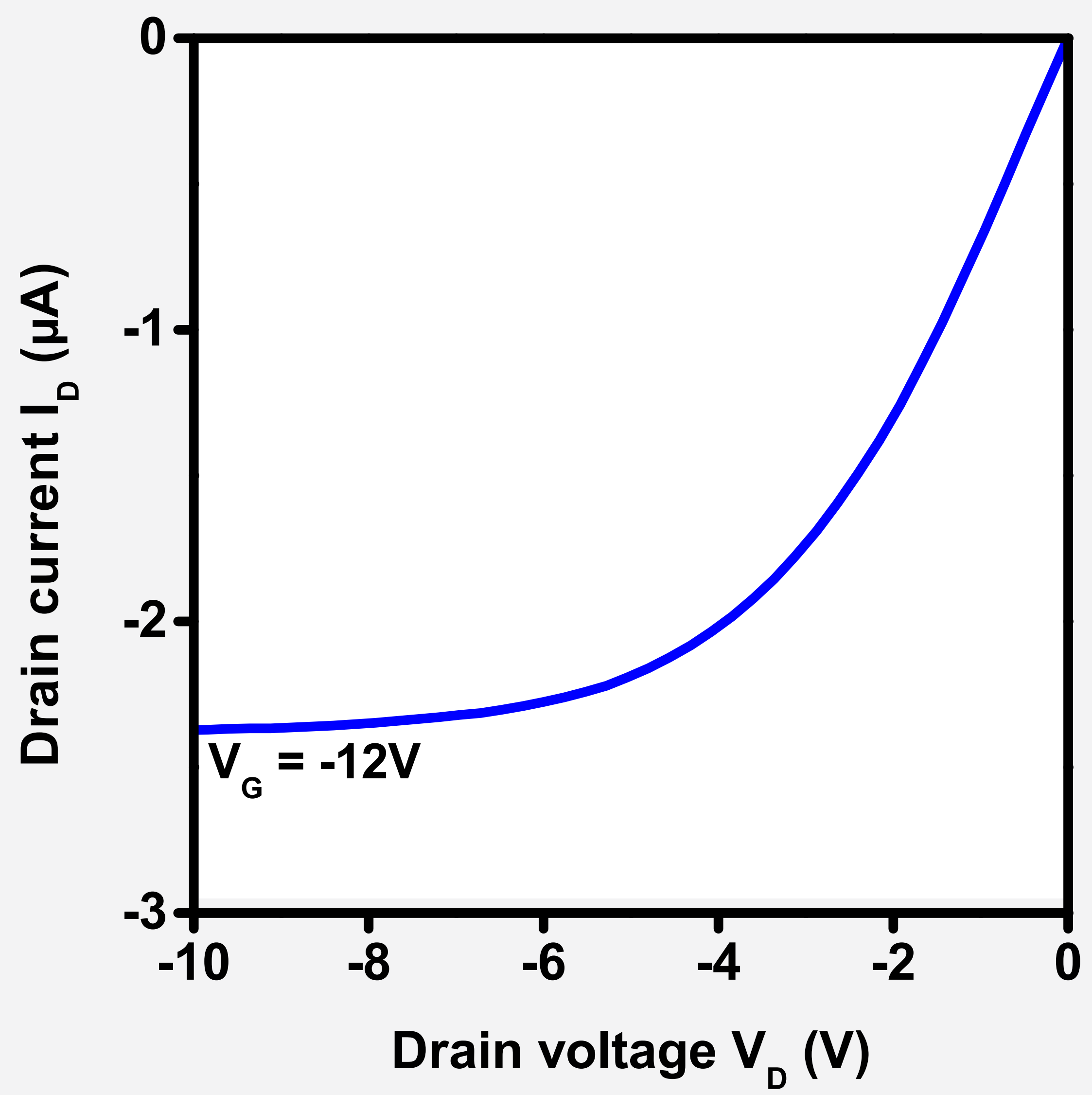




- at $|V_D| \approx |V_G - V_{th}|$ charge carrier distribution not uniform across channel anymore
- drain current I_D does not increase linearly with V_D (transition regime)

Response of an OFET in the Saturation Regime



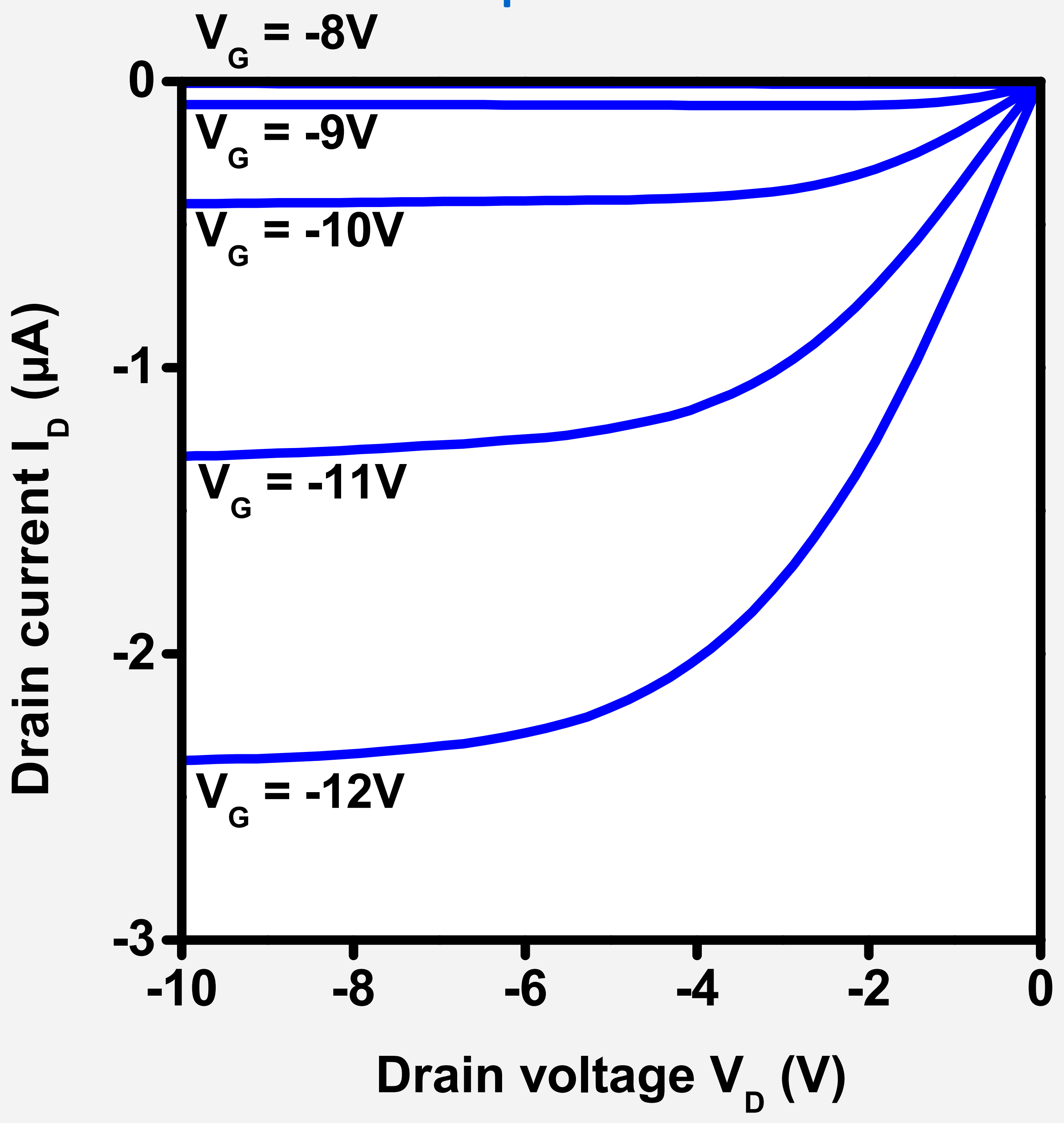


- at $|V_D| > |V_G - V_{th}|$ charge carrier distribution is highly unsymmetric over the channel
- drain current I_D saturates and does not increase with V_D (saturation regime)

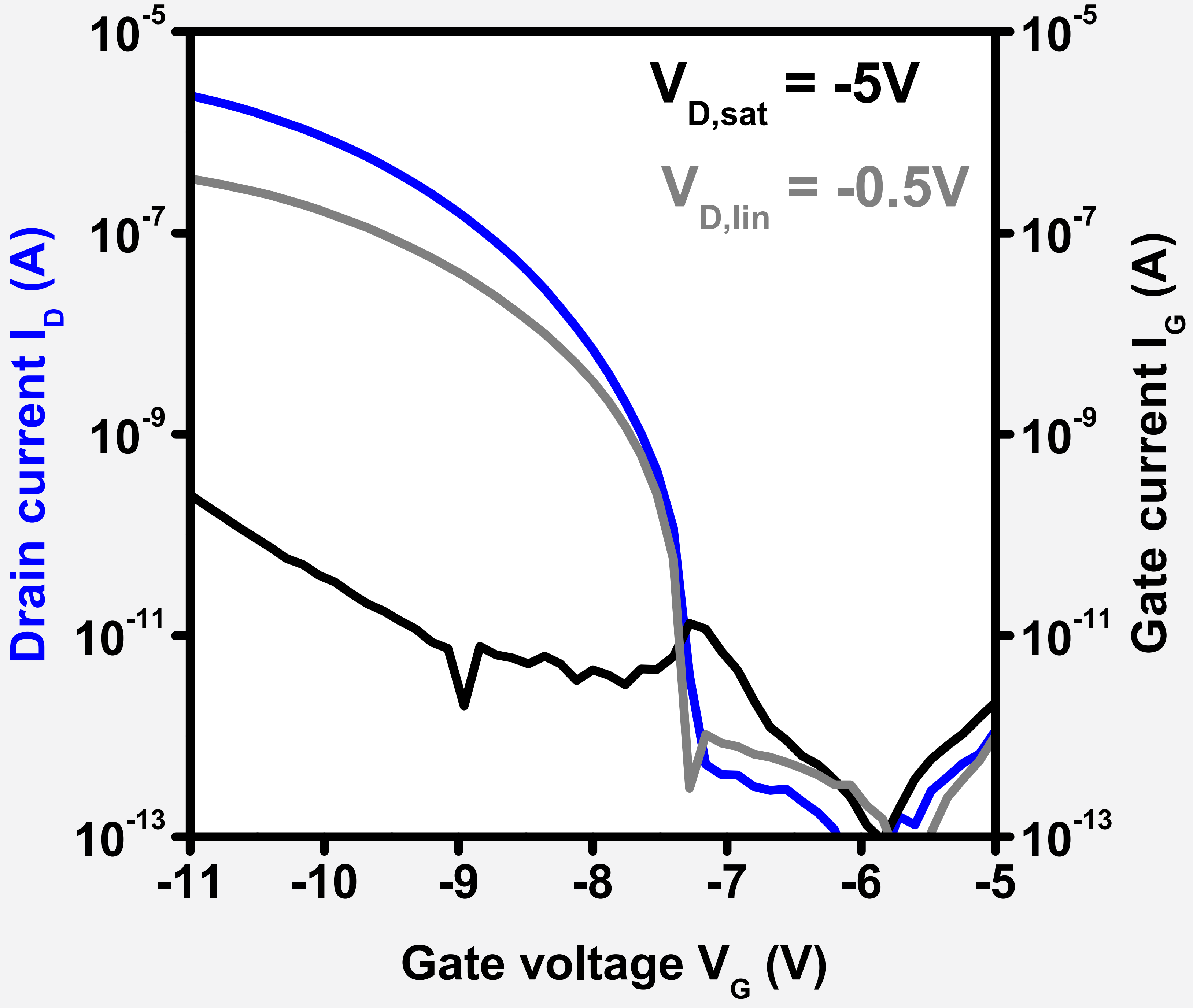
OFET Characterization

- as V_G and V_D can be varied, two different current-voltage characteristics can be recorded:

Output Curve



Transfer Curve

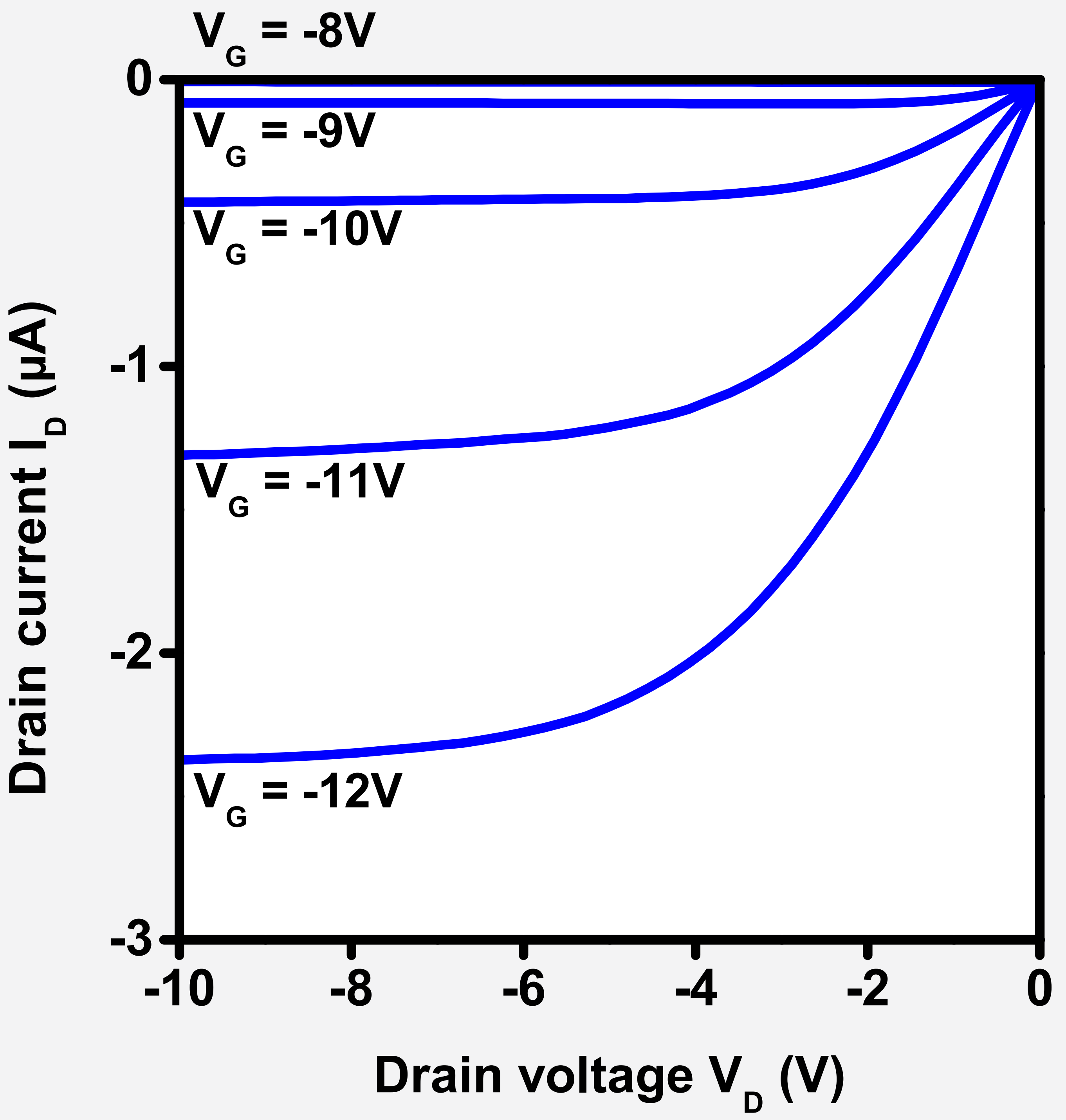


- **output characteristics from measuring I_D as a function of V_D, at a fixed V_G**
- **transfer characteristics from measuring I_D as a function of V_G, at a fixed V_D**
- **gate current I_G is unwanted “leakage current” through the gate dielectric**

OFET Characterization

- as V_G and V_D can be varied, two different current-voltage characteristics can be recorded:

Output Curve



- **linear regime at $|V_D| \ll |V_G - V_{th}|$**

$$I_{D,lin} = \frac{\mu \cdot C \cdot W}{L} \cdot \left((V_G - V_{th})V_D - \frac{V_D^2}{2} \right)$$

- **saturation regime at $|V_D| > |V_G - V_{th}|$**

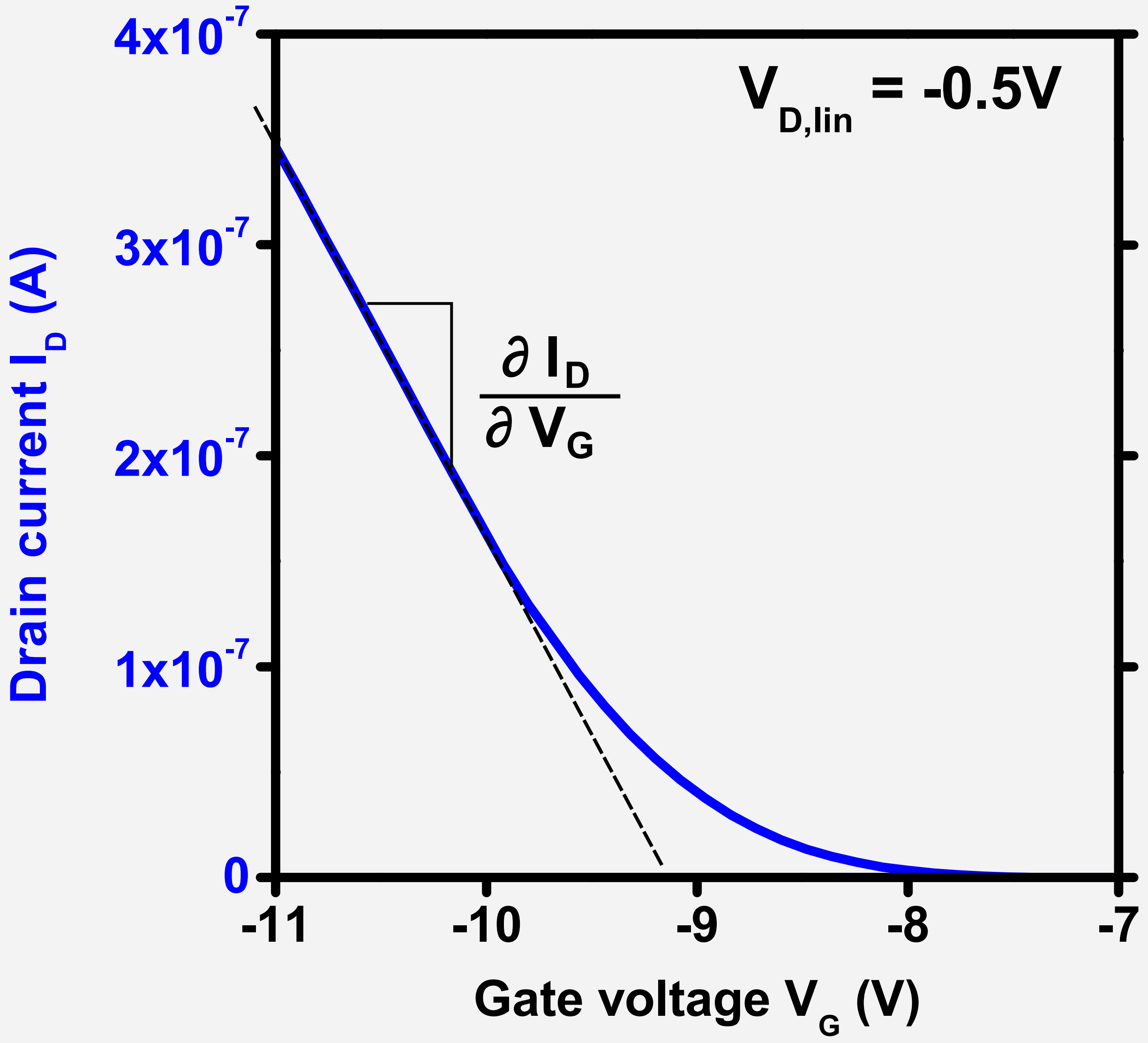
$$I_{D,sat} = \frac{\mu \cdot C \cdot W}{2L} \cdot (V_G - V_{th})^2$$

- **channel length *L* = distance between the source and drain electrodes**
- **channel width *W* lateral width of the source and drain electrodes**
- **capacitance per area *C*, charge carrier mobility *µ***

H. Klauk, *Chemical Society Reviews* **2010**, *39*, 2643.

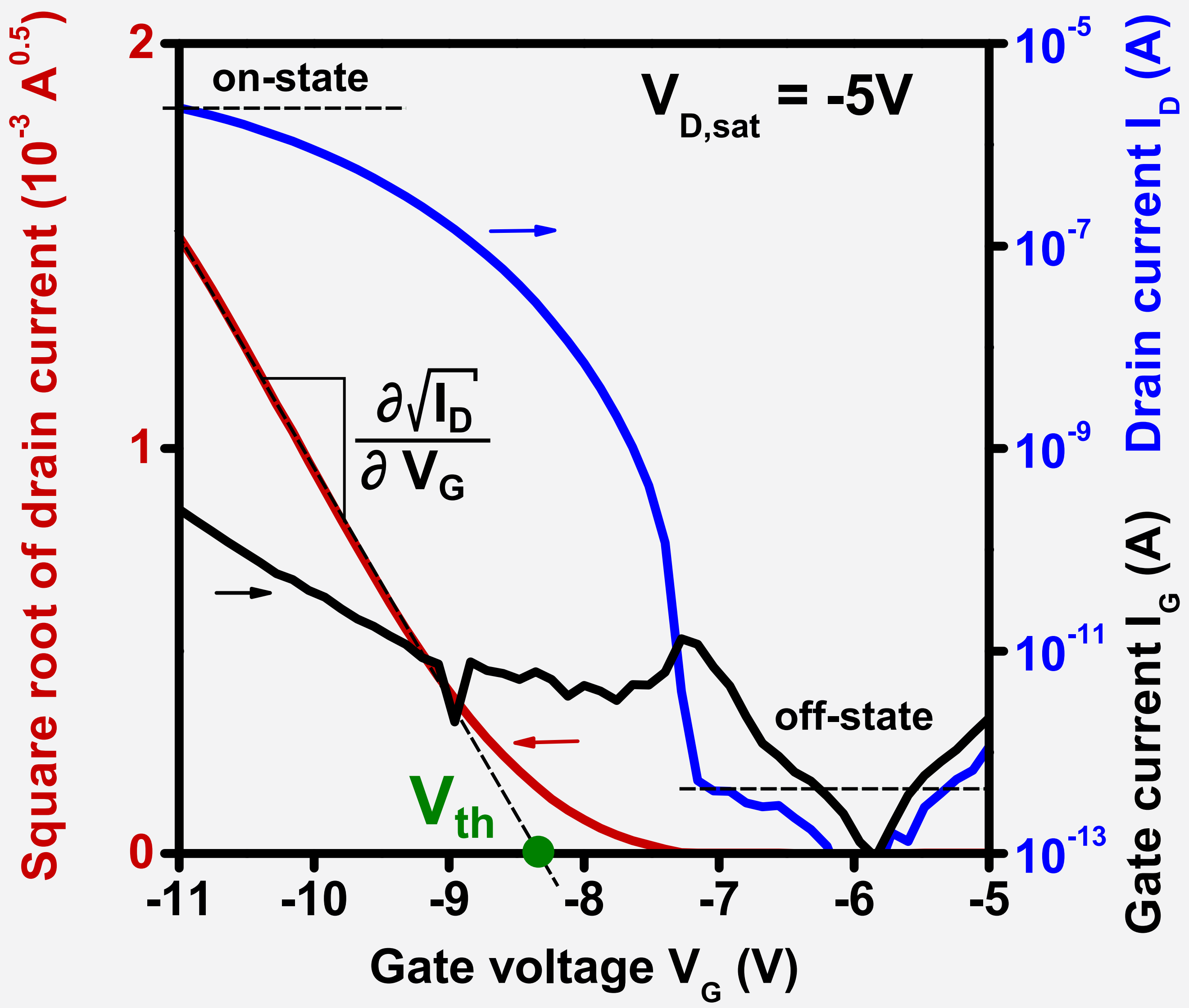
Parameters from Transfer Curves

- linear regime at $|V_D| < |V_G - V_{th}|$



$$\mu_{lin} = \frac{L}{C \cdot W \cdot V_D} \frac{\partial I_D}{\partial V_G}$$

- saturation regime at $|V_D| > |V_G - V_{th}|$

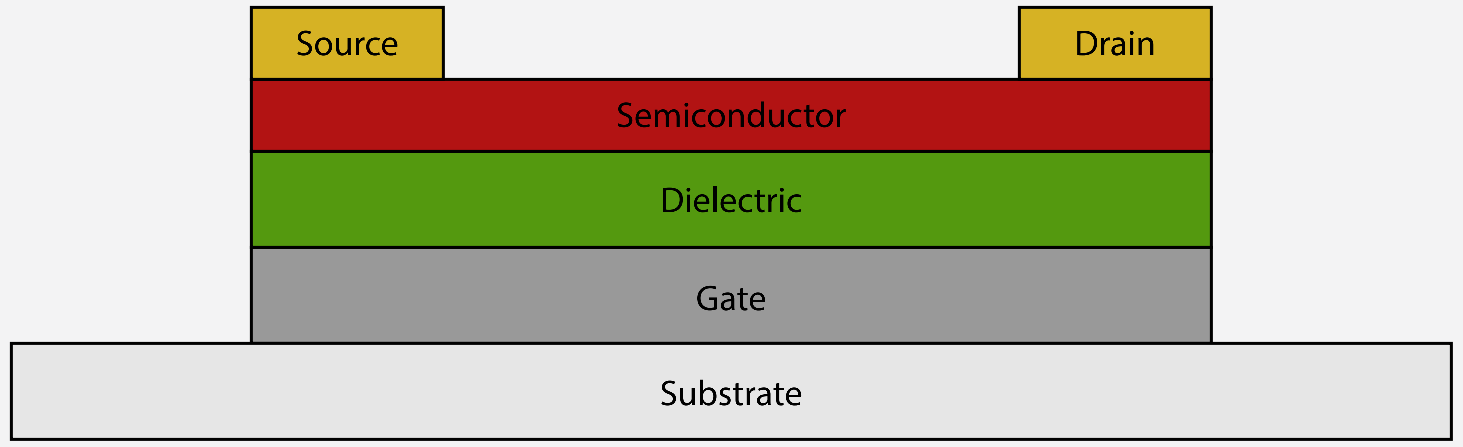


$$\mu_{sat} = \frac{2L}{C \cdot W} \left(\frac{\partial \sqrt{I_D}}{\partial V_G} \right)^2$$

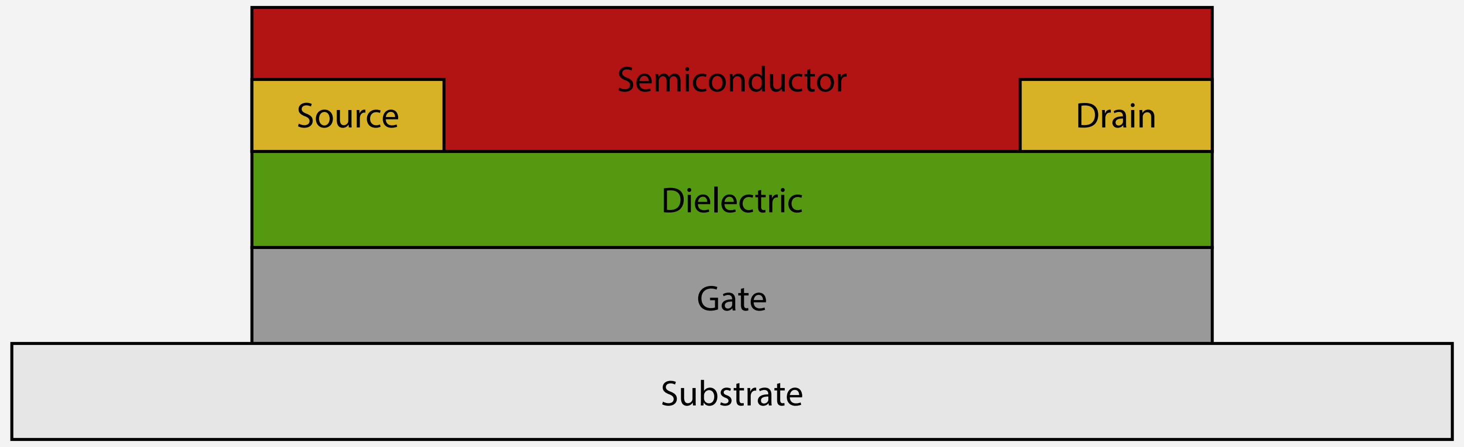
- on/off-ratio, drain current I_D in *on* versus *off* state, should ideally be $>10^6$
- charge carrier mobility μ, relevant for switching speed should be >1 cm^2 V^{-1} s^{-1}
- threshold voltage V_{th}, voltage required for switching; should be as low as possible
- gate current I_G (parasitic current, leakage current), should be on order of I_D in *off*-state

H. Klauk, *Chemical Society Reviews* **2010**, *39*, 2643.

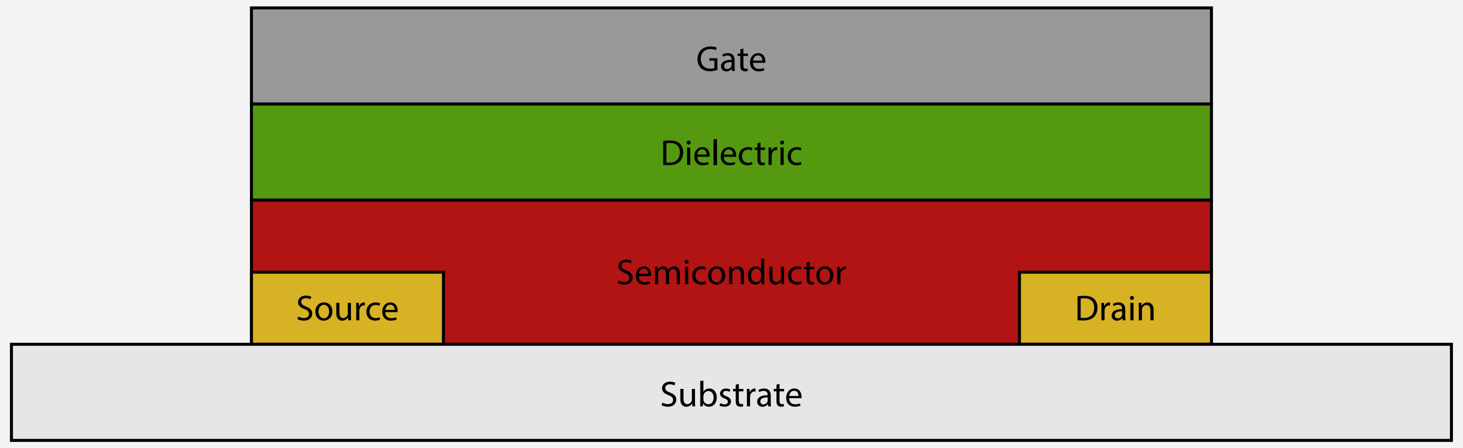
Device Geometries



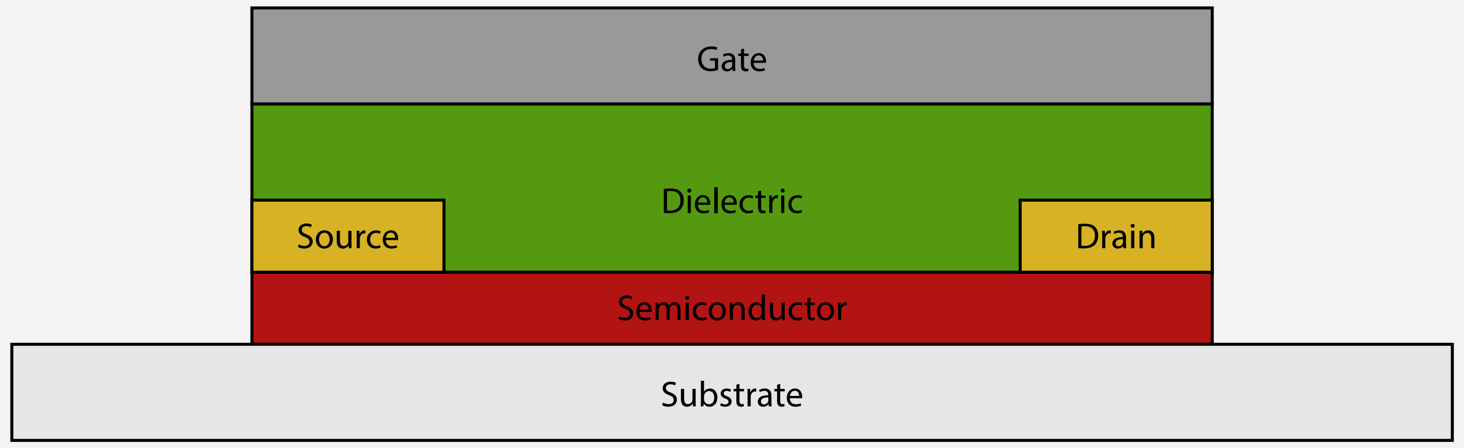
bottom gate, top contact
(staggered)



bottom gate, bottom contact
(coplanar)



top gate, bottom contact
(staggered)



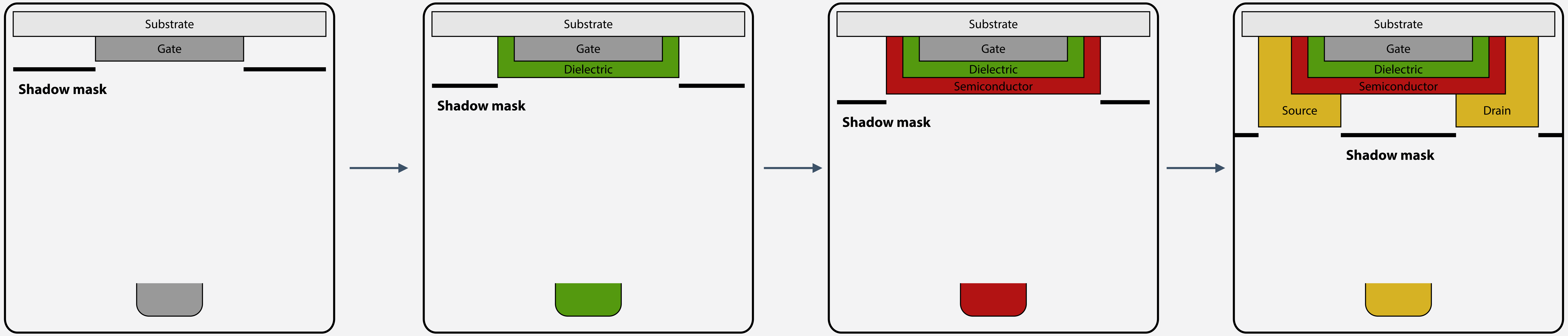
top gate, top contact
(coplanar)

- **bottom gate setups often used, because semiconductor deposition is one of the last steps**
- **often used in research: heavily doped Si wafer + SiO_2 layer (= gate electrode + dielectric)**
- **source/drain electrodes are often made of gold**

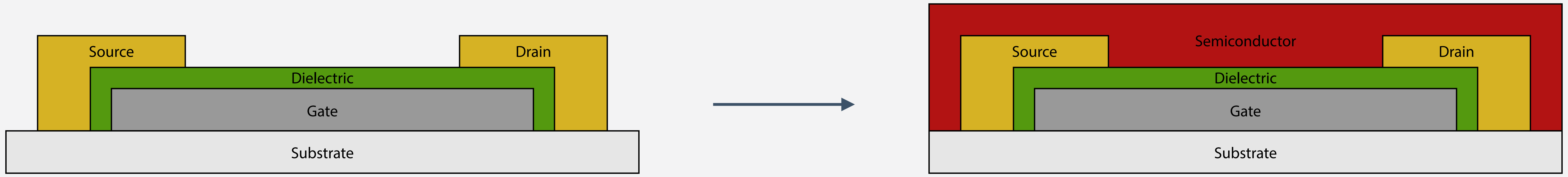
H. Klauk, *Chemical Society Reviews* **2010**, *39*, 2643.

Device Fabrication

Physical Vapor Deposition

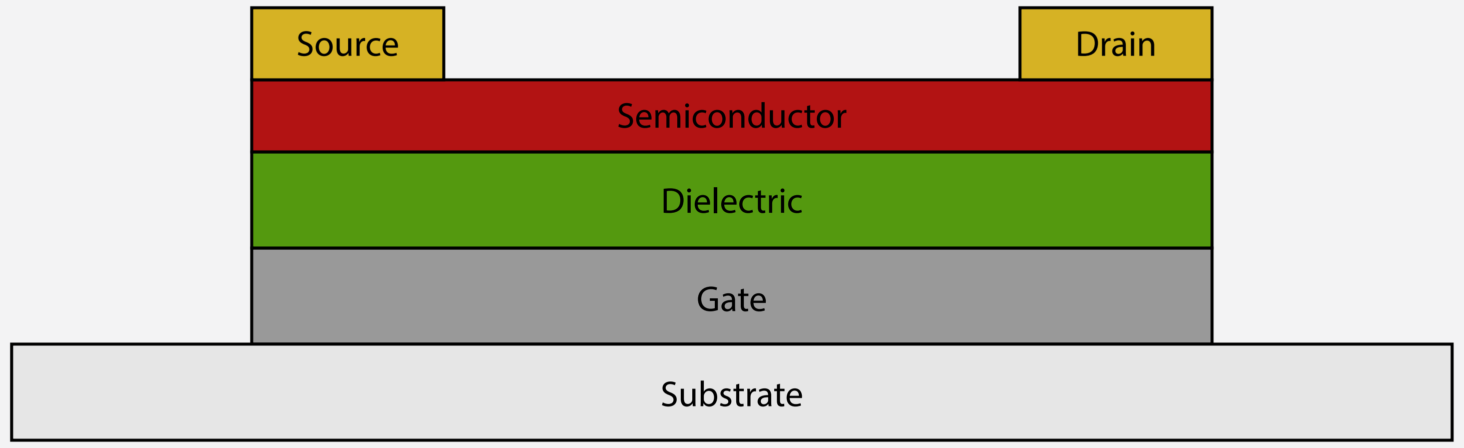


Solution Processing

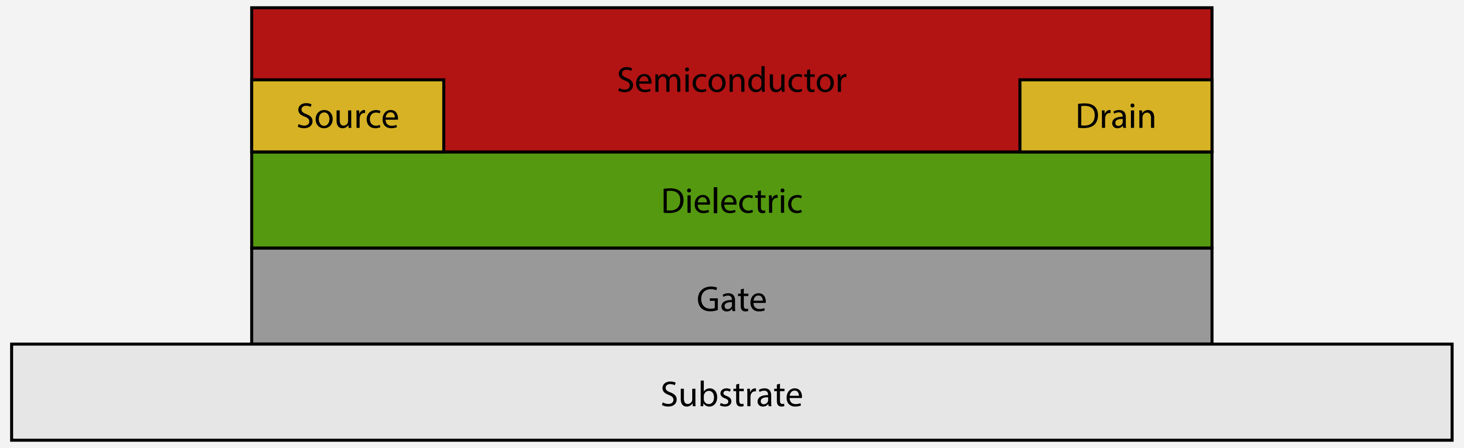


- semiconductor and electrodes can be deposited thermally: physical vapor deposition
- semiconductor can be deposited from solution (spin coating, drop casting, doctor blading…)
- annealing required after solution process to allow for better molecular arrangement
- patterning via shadow masking or lithography

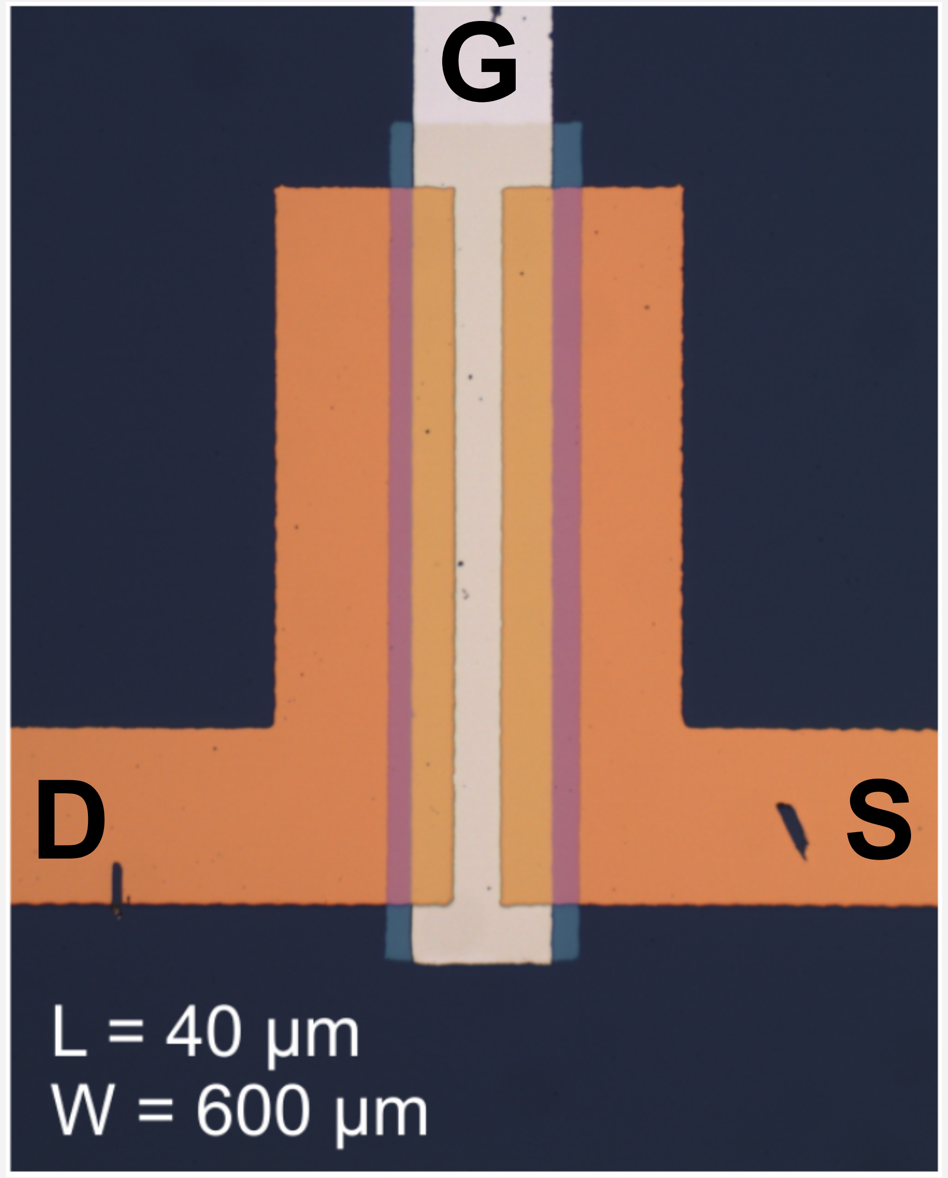
What Real Devices Look Like

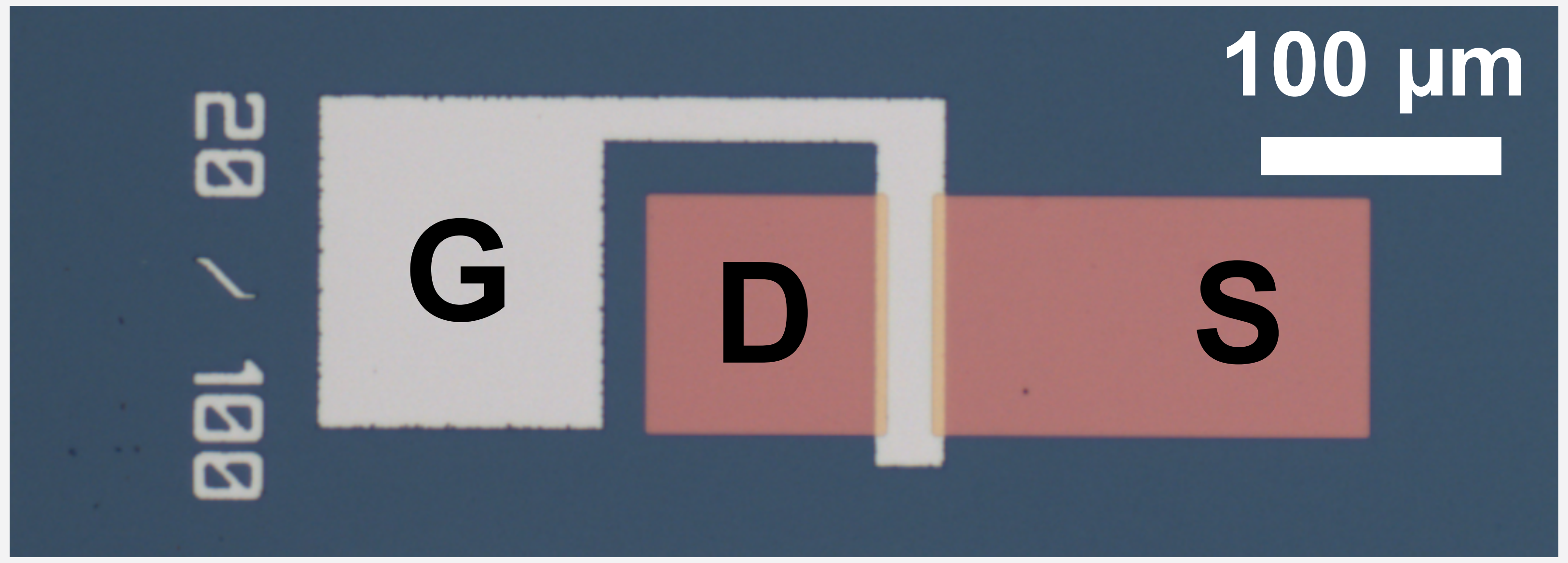


bottom gate, top contact
(staggered)



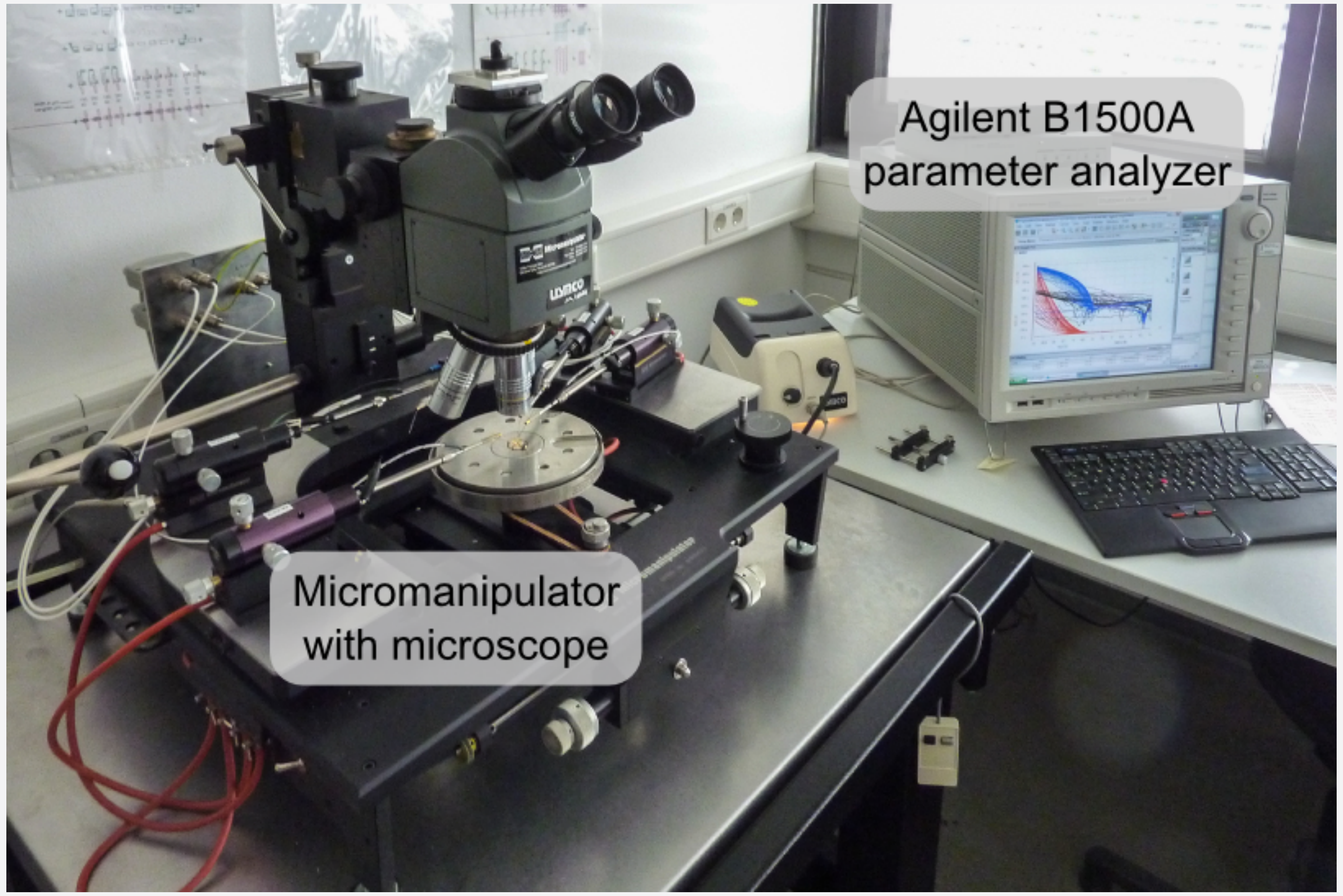
bottom gate, bottom contact
(coplanar)

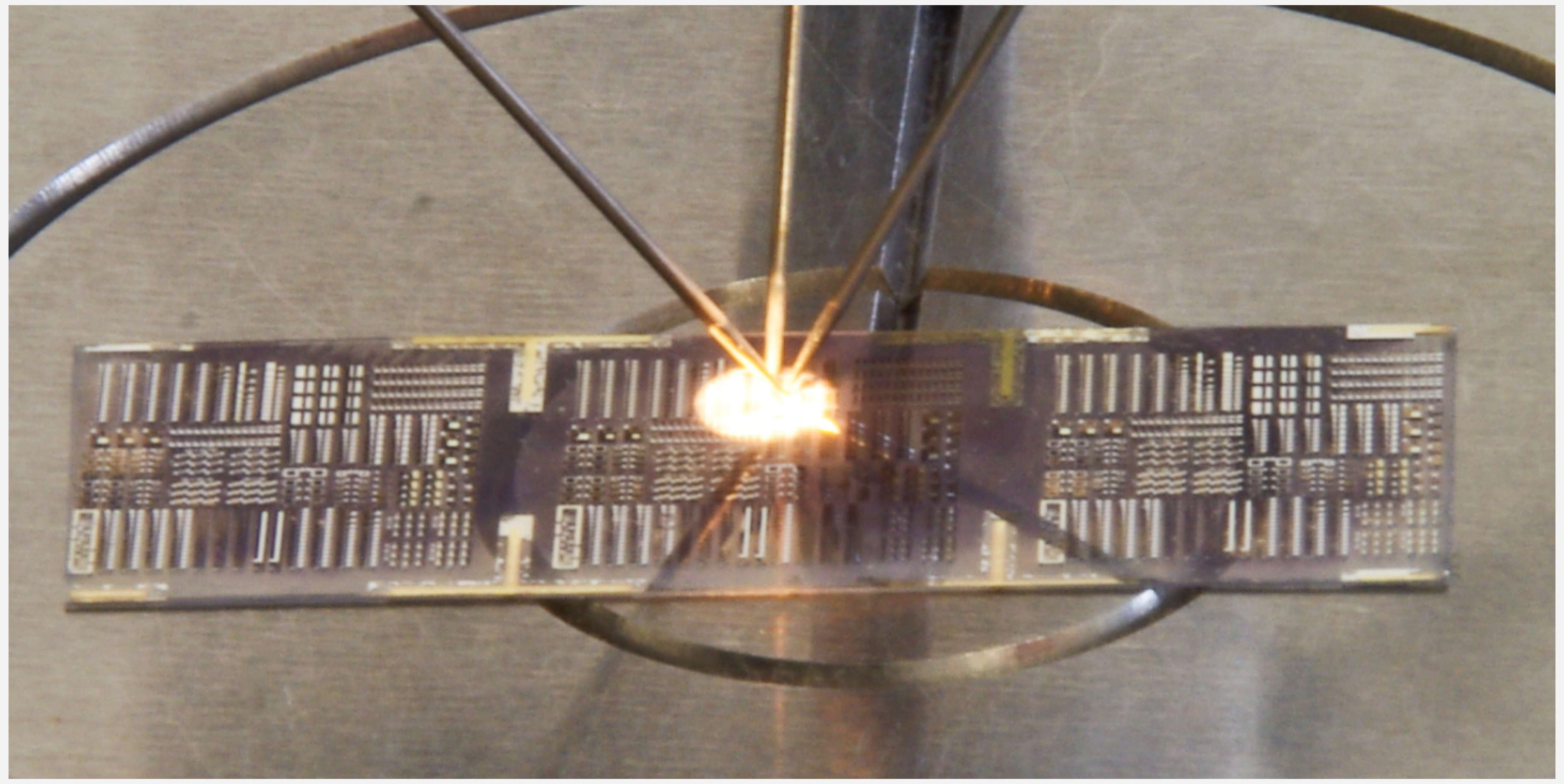




- **examples of OFETs with Al gate electrode, Al_2O_3 dielectric and gold electrodes**

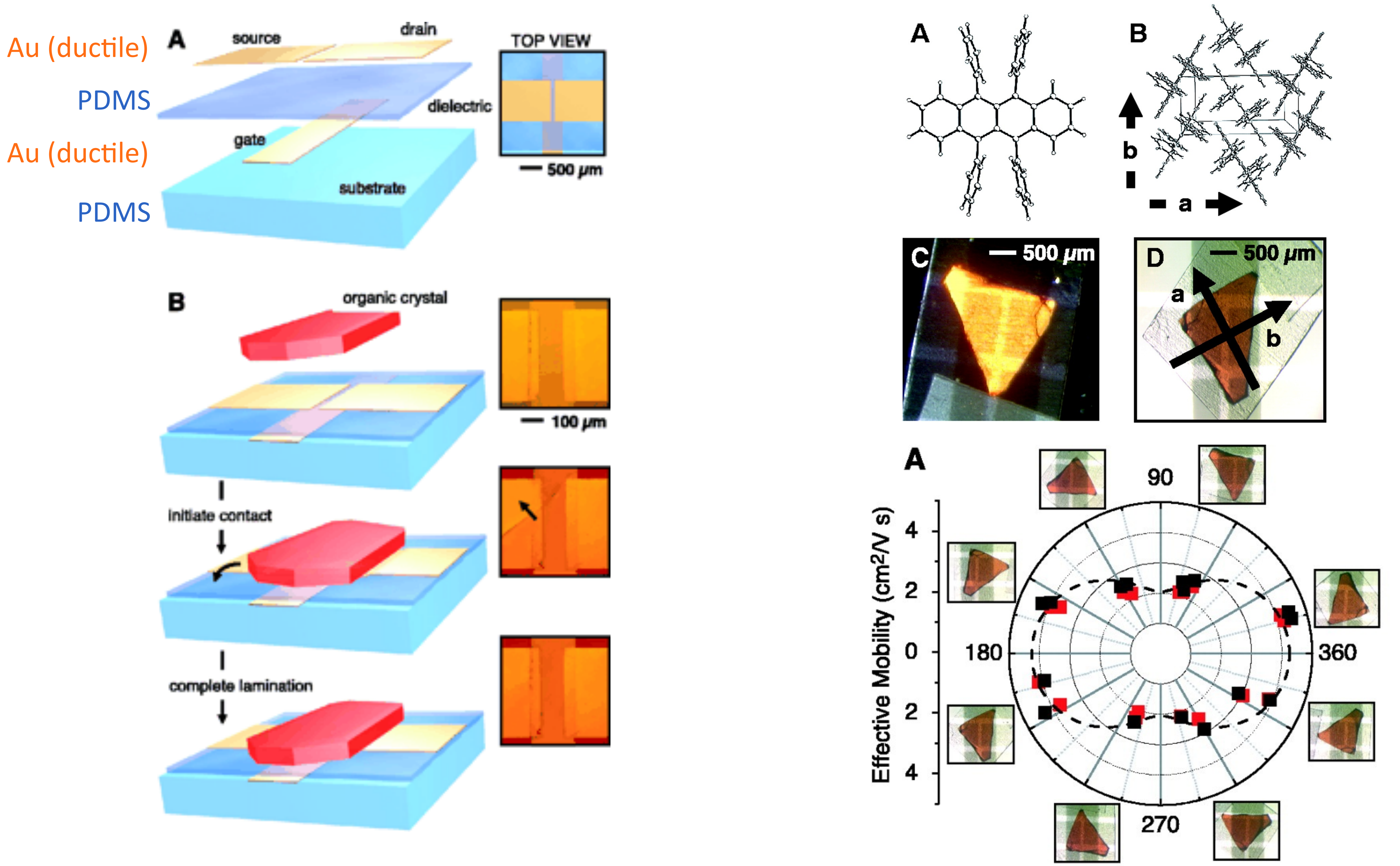
Device Characterisation Setup





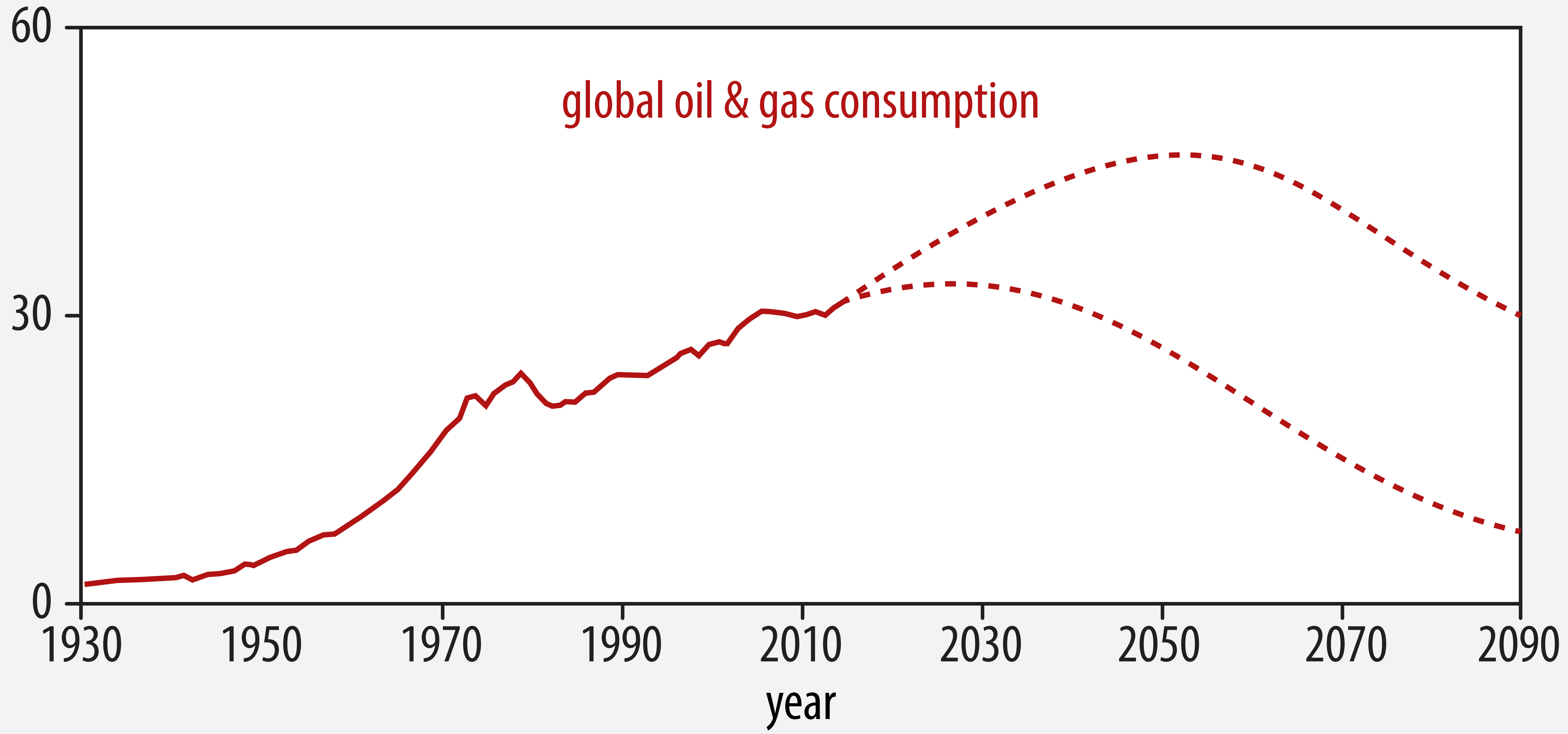
- electrodes are contacted with small needles, transfer and output characteristics are measured

Examples of OFET Research: Rubrene Single Crystal



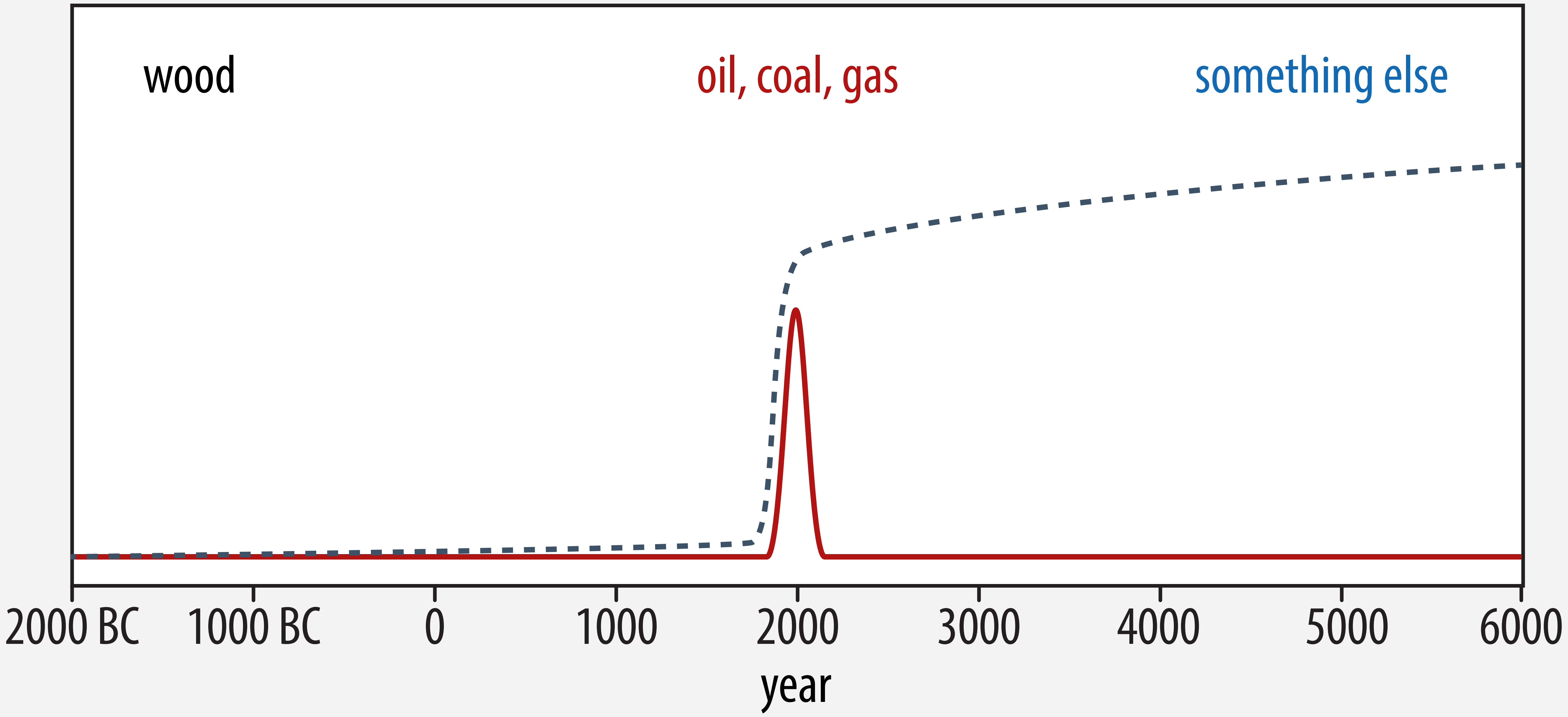
- flexible “stamp” device that can be reversibly stuck on rubrene single crystal
- anisotropy in mobility since anisotropy in crystal structure

7.2 Organic Photovoltaic Devices



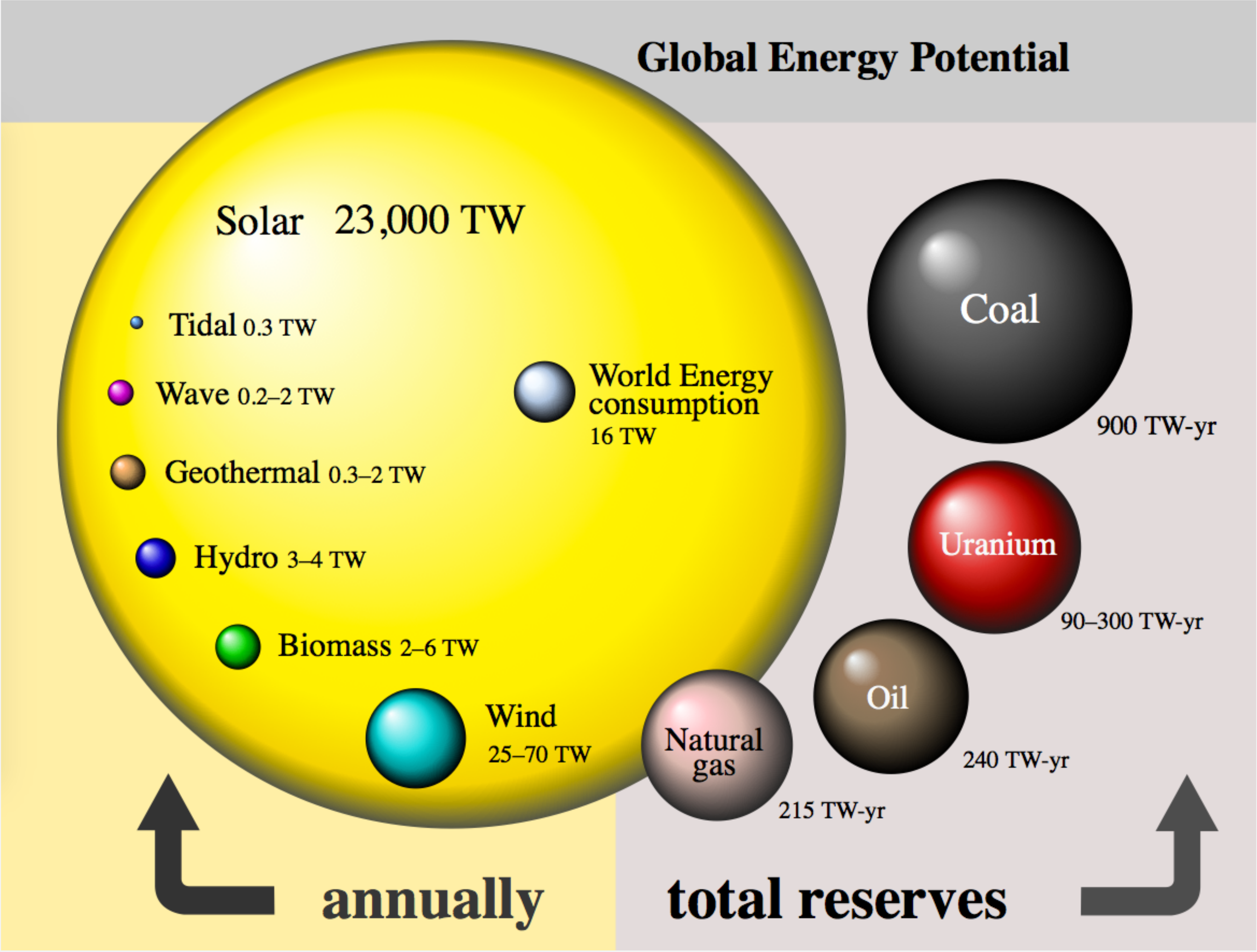
- **it is not a question if, just when will oil be replaced as our main source of energy**

Putting our Energy Consumption into Historic Perspective



- in a broader historic perspective, burning of fossil fuels was just a short (catastrophic) aberration

Energy Totally Available on Planet Earth

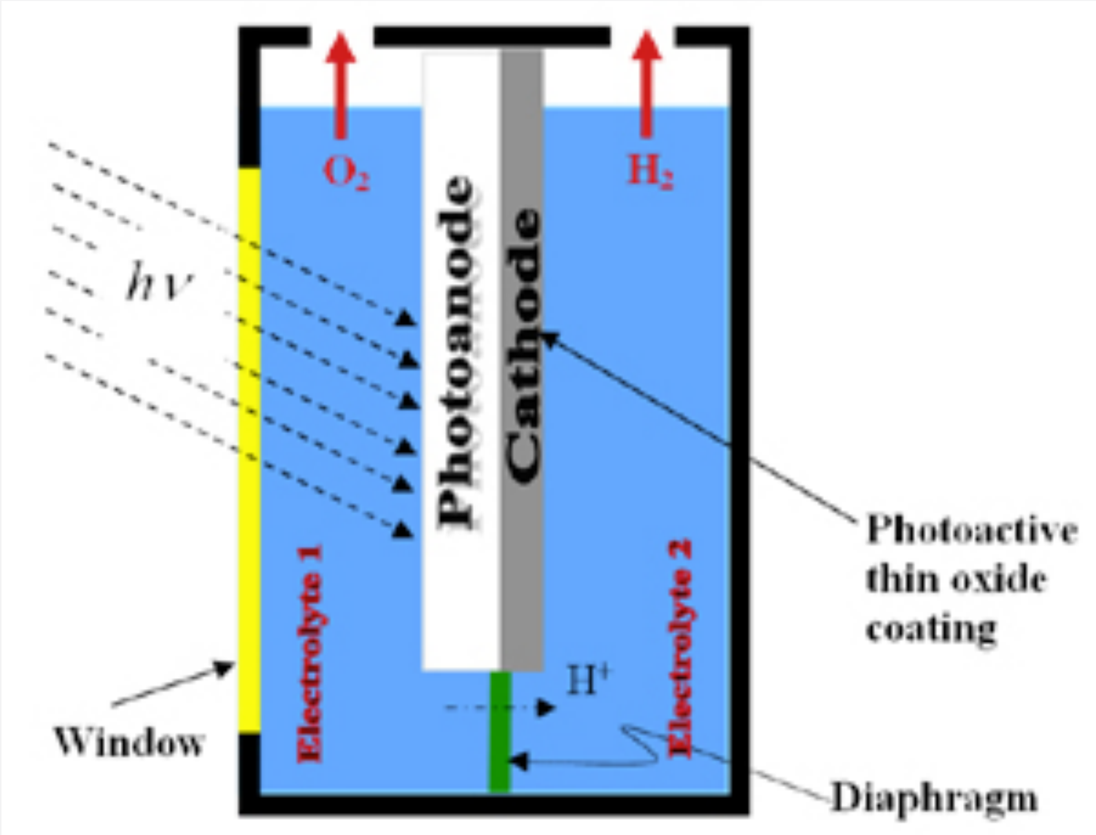


- solar energy has a the potential to supply the complete world energy consumption!

Solar Energy Conversion Methods

photothermal
solar power plant

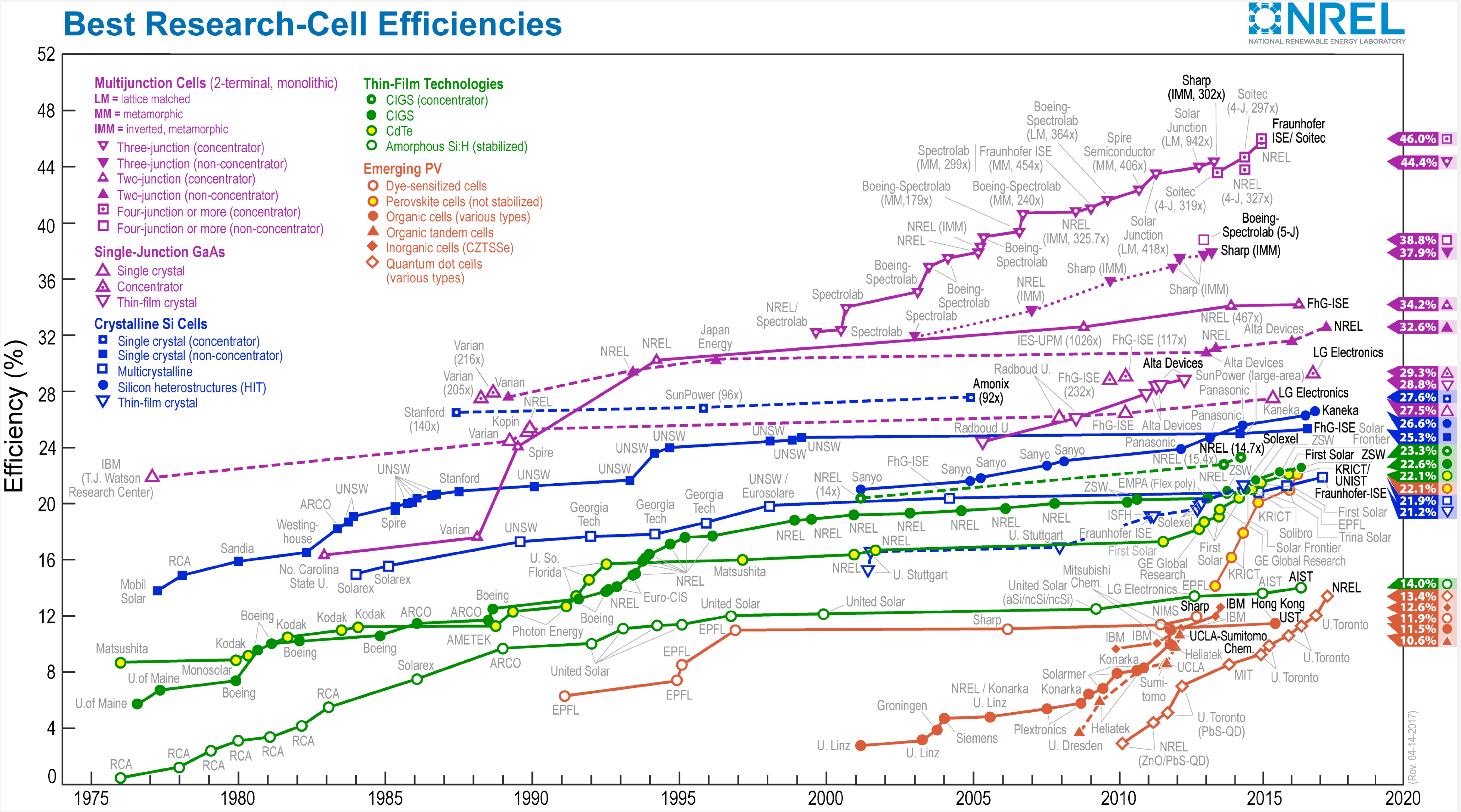
photochemical
artificial photosynthesis



photovoltaics
solar-electric conversion

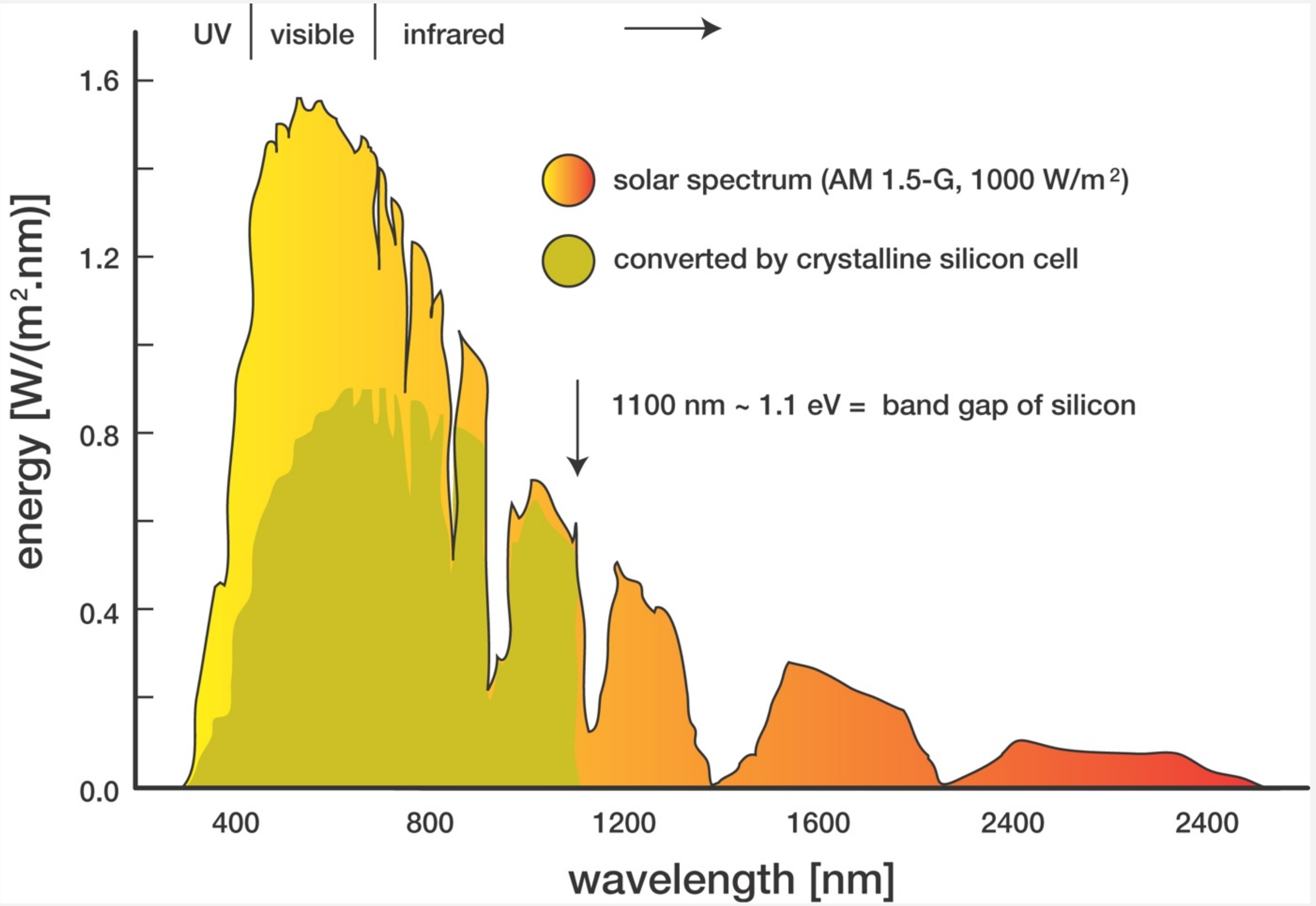
- **several possibilities for converting solar energy into usable forms of energy**
- **including "indirect" energy generation from wind or hydropower**
- **photovoltaics is the direct conversion of solar energy to electricity**

Solar cell efficiencies



Organic Solar Cells

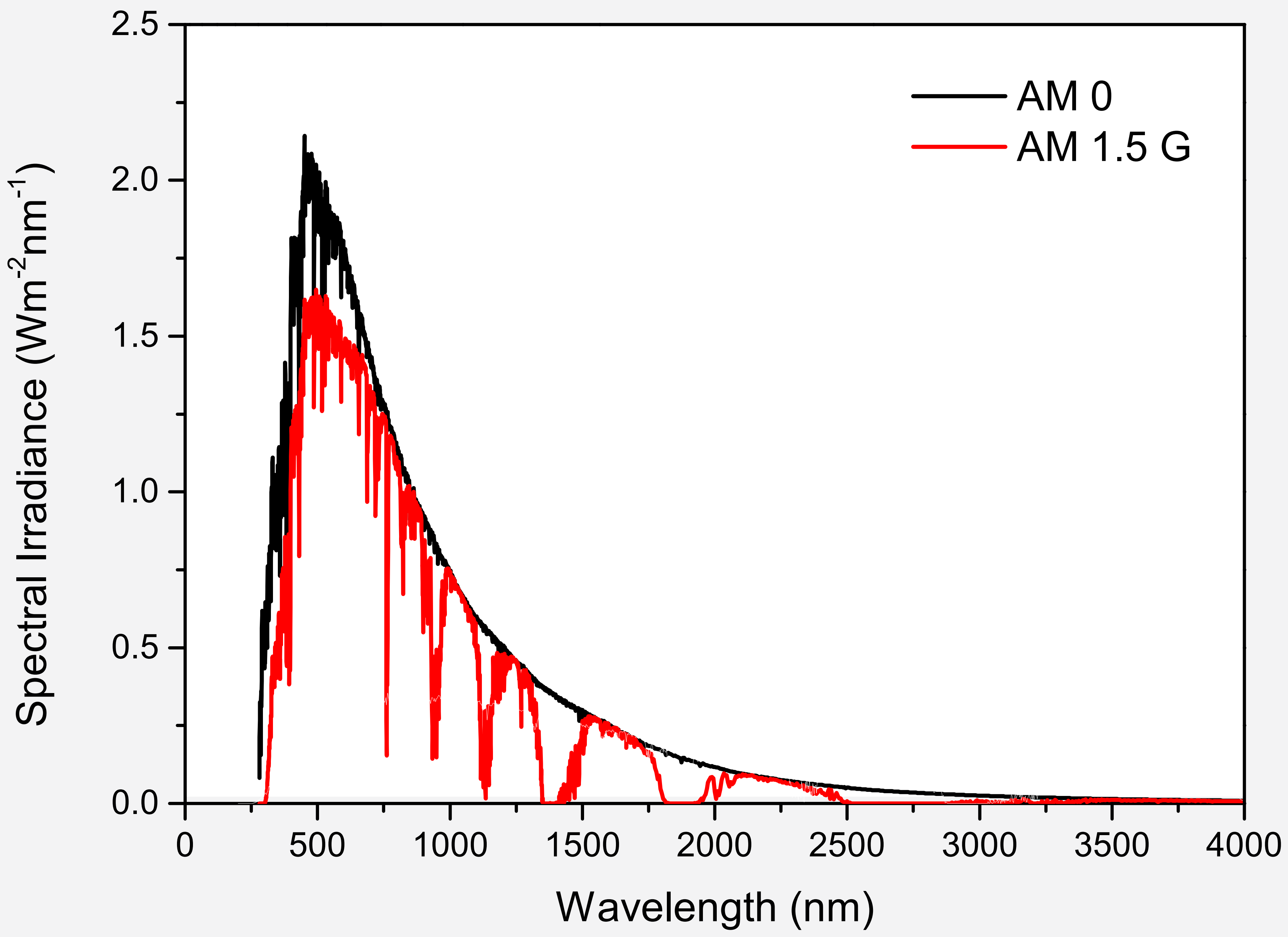
- total energy consumption $5 \cdot 10^{20}$ J/year in 2008; solar energy supply $4 \cdot 10^{24}$ J/year
- one hour of sun light ≥ overall annual global energy consumption

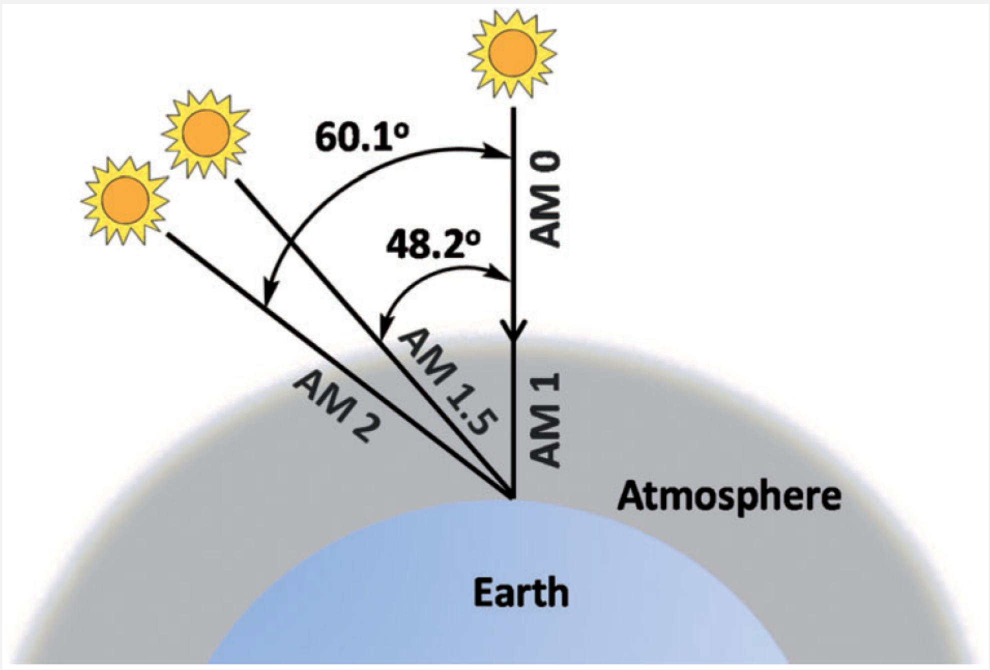


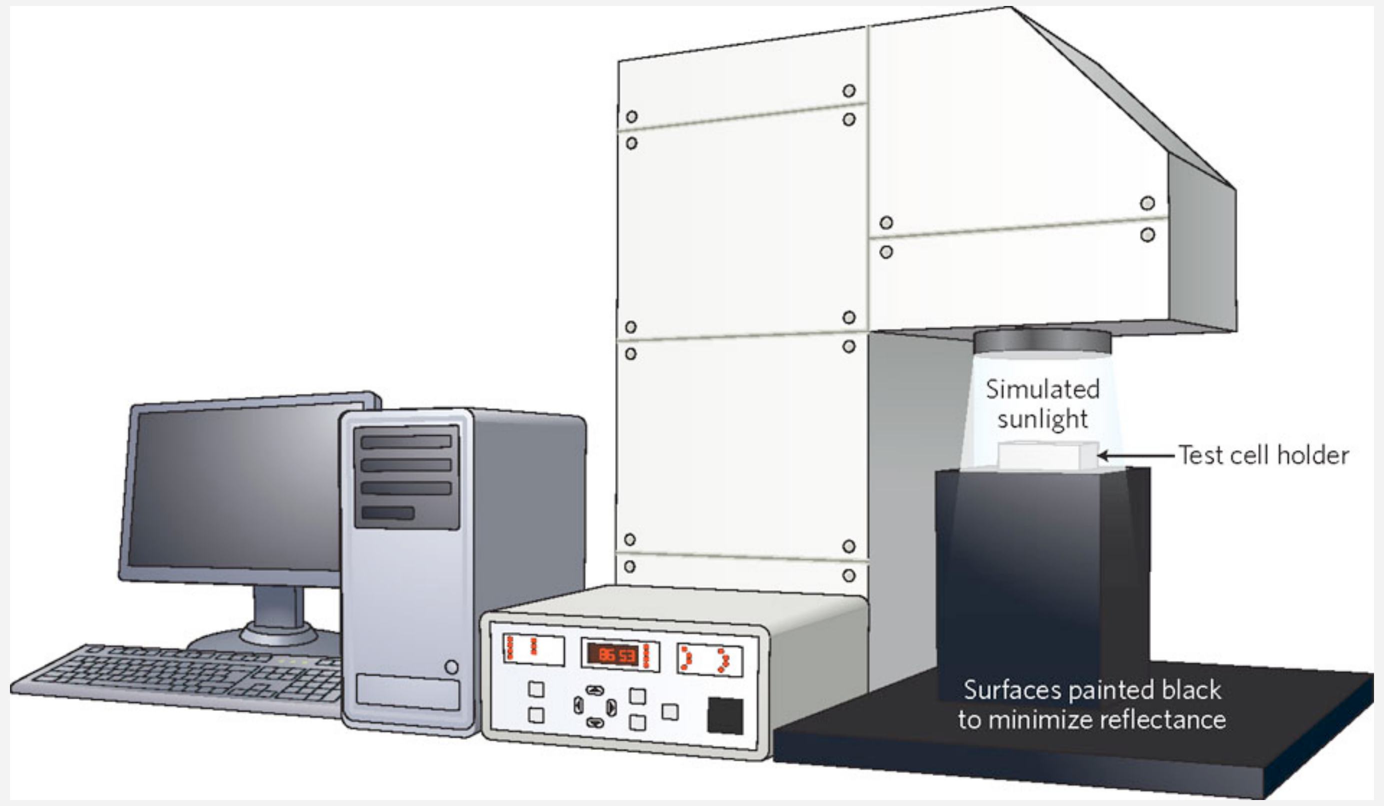
- **silicon-based photovoltaic modules are efficient but energetically & economically expensive**
- **organic photovoltaics may be inexpensive, energetically more favorable alternatives**

Solar Spectrum and Standardized Lighting Conditions

- solar cells need to be tested under standardized lighting conditions for comparibility







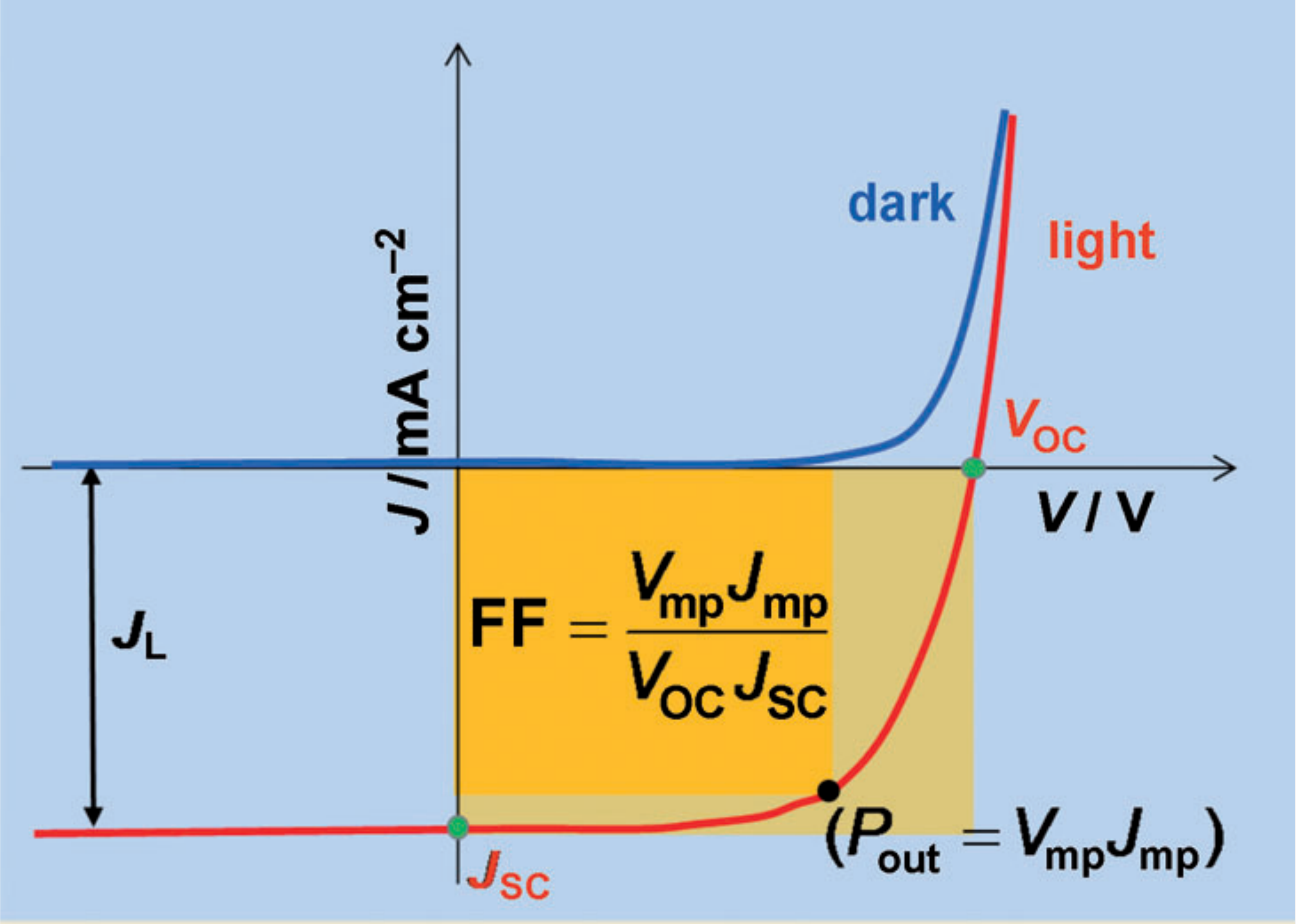
- **Xenon lamp plus filters as a light source matched to the (terrestrial) solar spectrum**
- **J-V curves are measured under AM 1.5 G solar spectrum (AM = air mass, G = global)**
- **AM 1.5 G spectrum represents the annual average solar irradiance at mid-latitudes (US)**

Bäuerle, *Angew. Chem. Int. Ed.* **2012**, 51, 2020; Snaith *Nat. Photon.* **2012**, 6, 337.

Device Characteristics

- J-V curve measured in dark (blue) and under illumination of AM 1.5 G solar spectrum (red)

- Characteristic parameters:
  - short circuit current J_{SC}
  - open circuit voltage V_{OC}
  - maximum power output P_{out}
  - fill factor FF
  - power conversion efficiency η

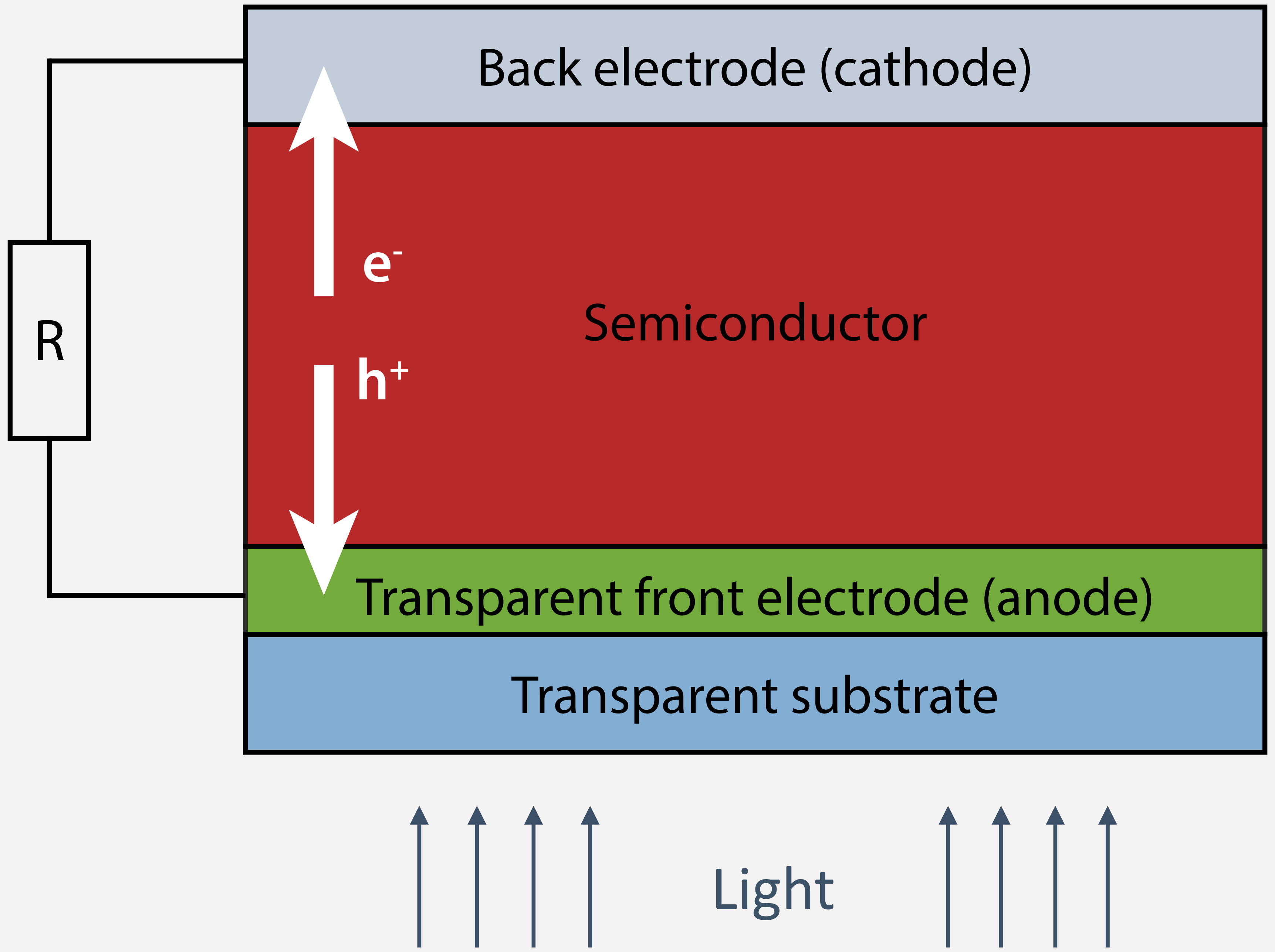


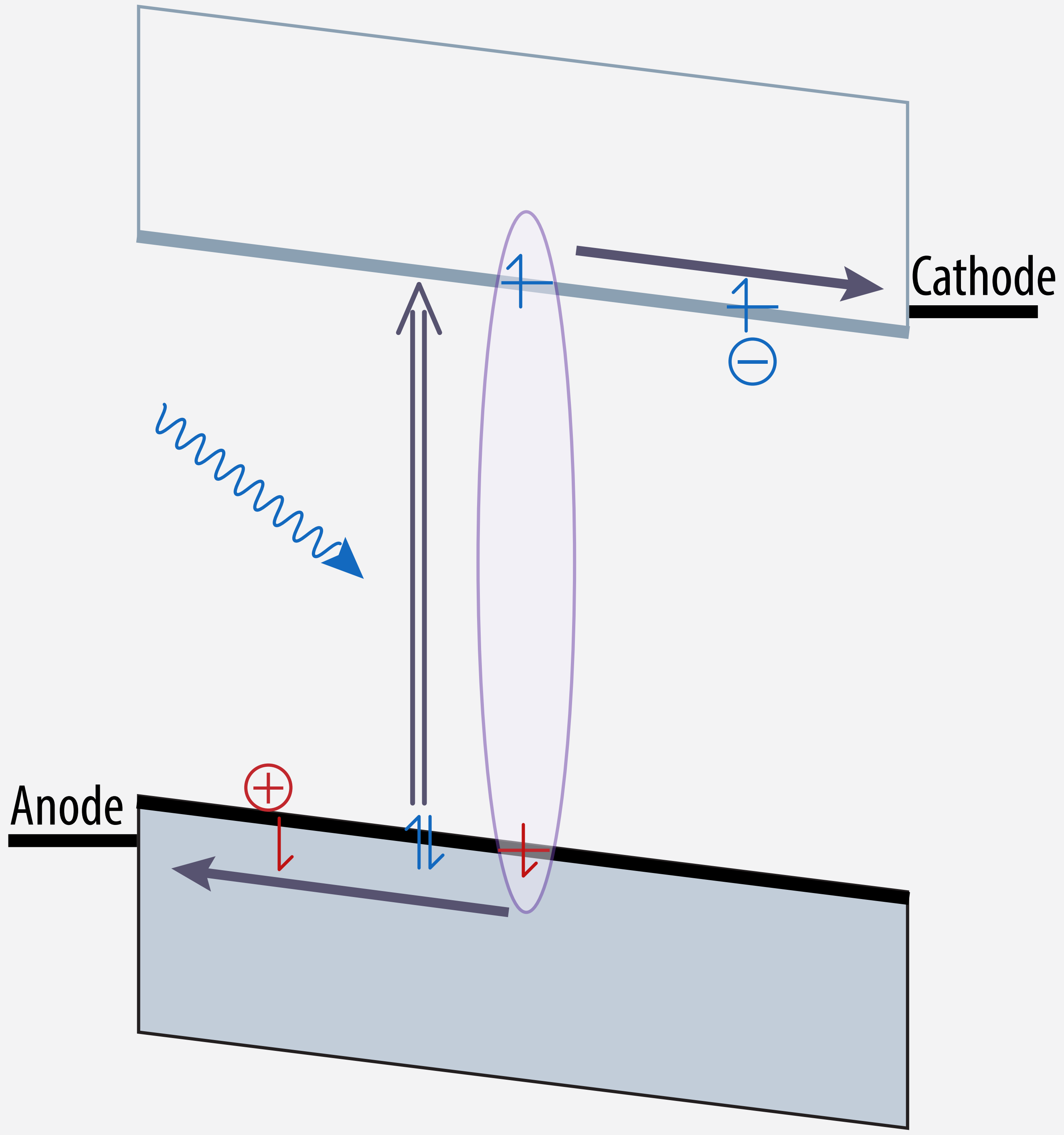
$$\eta = \frac{P_{out}}{P_{in}} = \frac{V_{mp}J_{mp}}{P_{in}} = \frac{V_{oc}J_{sc}FF}{P_{in}}$$

- **short circuit current J_{SC} is "maximum current" in the absence of a resistance / voltage**
- **open circuit voltage V_{OC} is "available potential" limited by E_{LUMO}(acceptor) – E_{HOMO}(donor)**
- ***J*$_{SC}$, *V*$_{OC}$, and *FF* must be large because maximum power output $P_{out} = J_{SC} \bullet V_{OC} \bullet$ FF**

Bäuerle et al., Angew. Chem. Int. Ed. 2012, 51, 2020.

General Setup and Working Principle of a Solar Cell





- light is absorbed in semiconductor layer
- an electron-hole pair is generated
- electron and hole are transported to separate electrodes and extracted

Difference Between Inorganic and Organic Materials

- **Coulomb force between two charge carriers:**

$$F = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_r r^2}$$

- **inorganic materials: high permittivity and weak electron-vibration coupling (fixed lattice)**

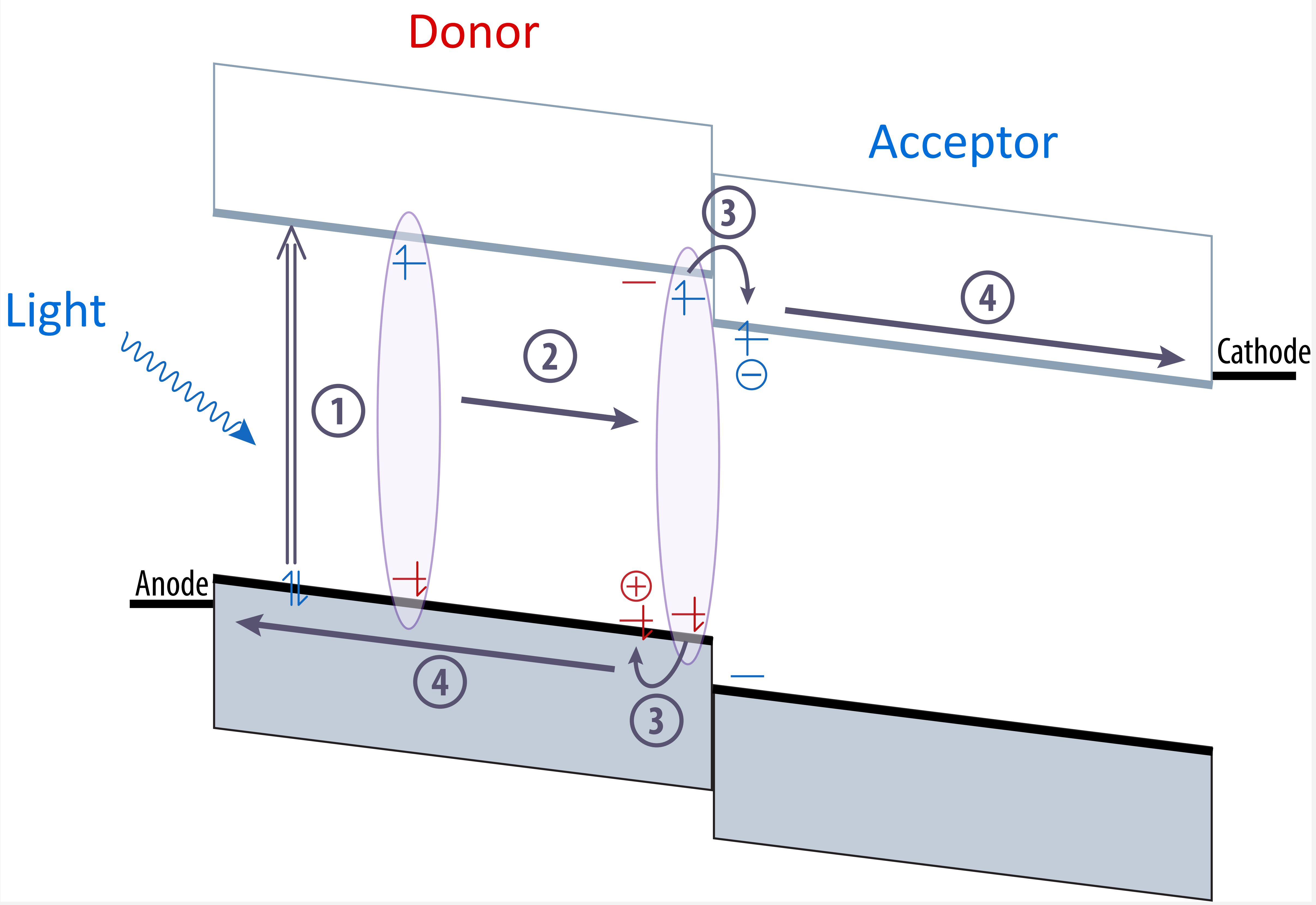
$\varepsilon_r \simeq 12$ light absorption results in separated charges

- **organic materials: low permittivity, strong electron-vibration coupling (geometric relaxation)**

$\varepsilon_r \simeq 2–3$ light absorption results in excitons (strongly bound e^-/h^+ pairs)

- **donor-acceptor (p-n) interface is required to separate charges in organic semiconductors!**

Mechanism for Charge Generation in Heterojunction Solar Cells



(1) light absorption, exciton formation

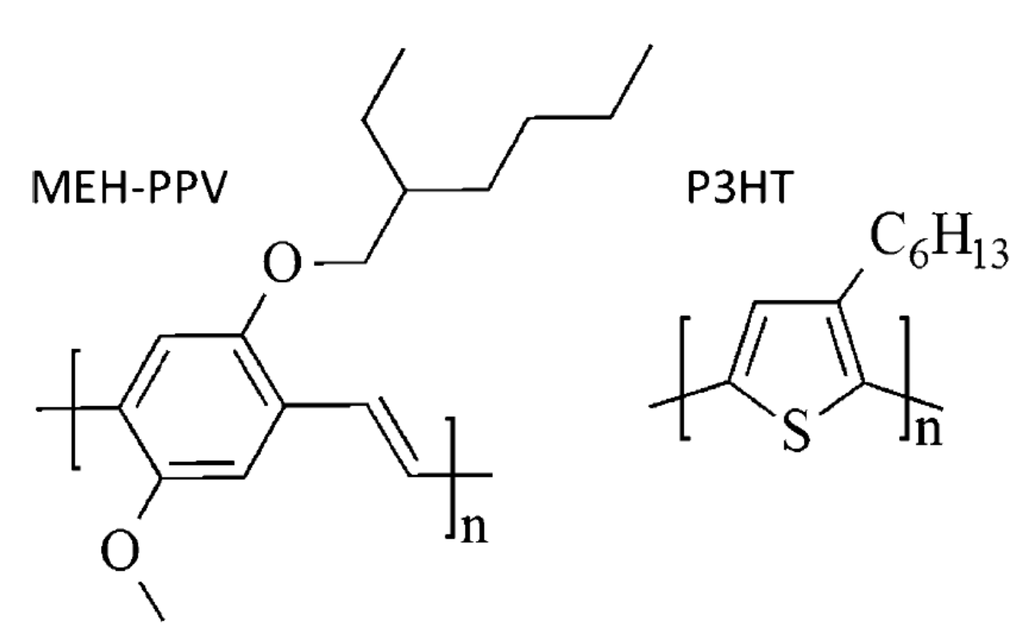
(2) exciton diffusion to interface (≃10 nm)

(3) charge separation

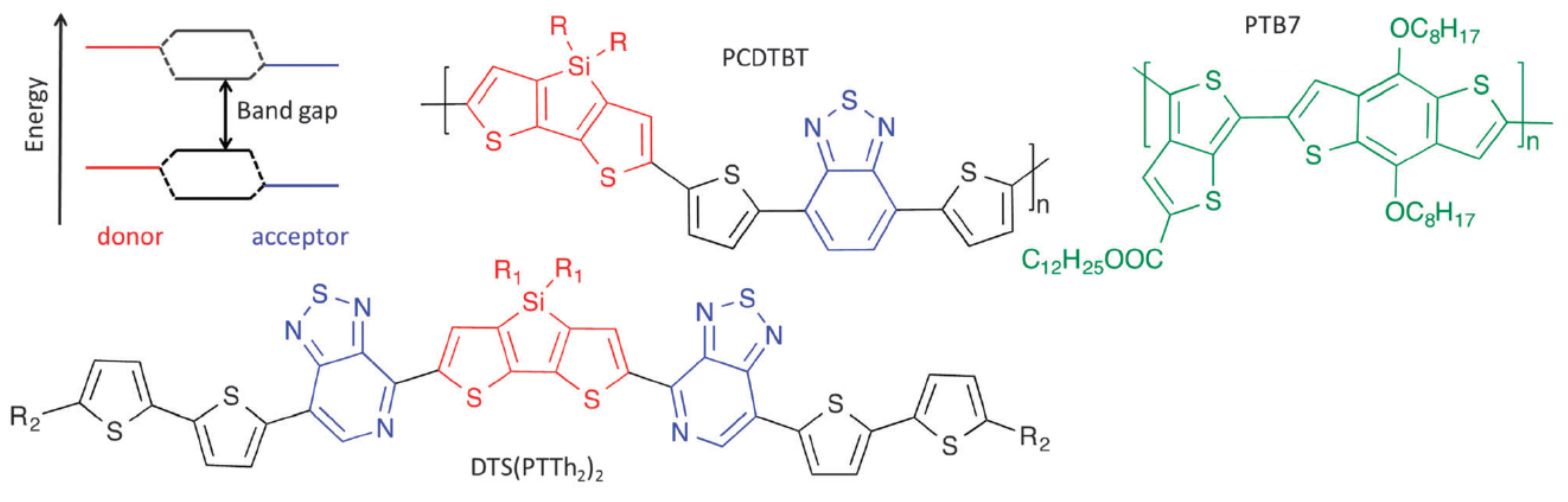
(4) charge migration to the electrodes

Typical Donor Materials

- classical polymer donor materials:



- low bandgap polymer donor materials:

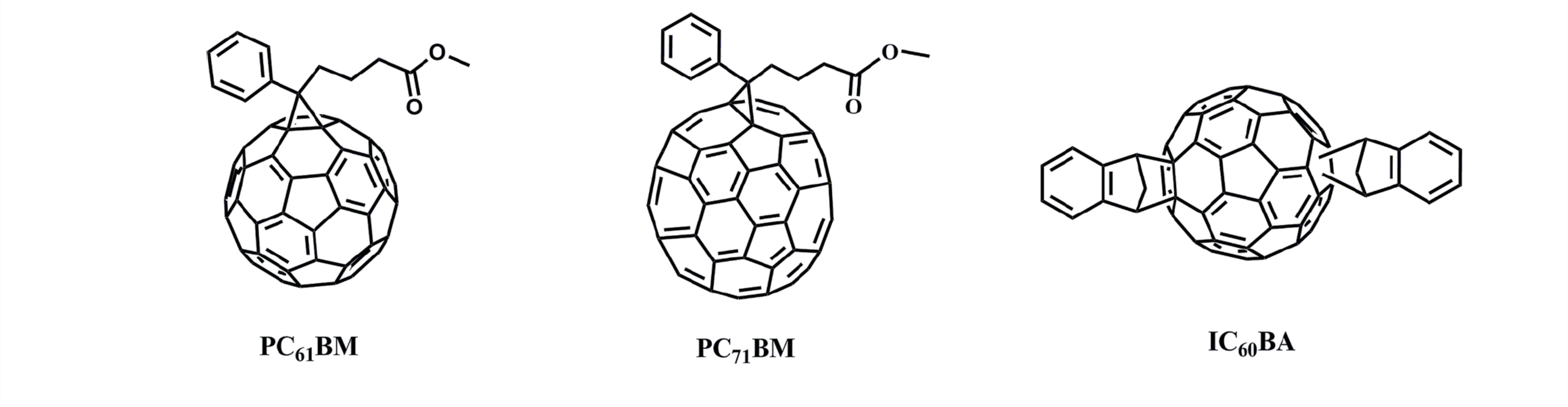


- **electron-rich (p type) organic semiconductors**

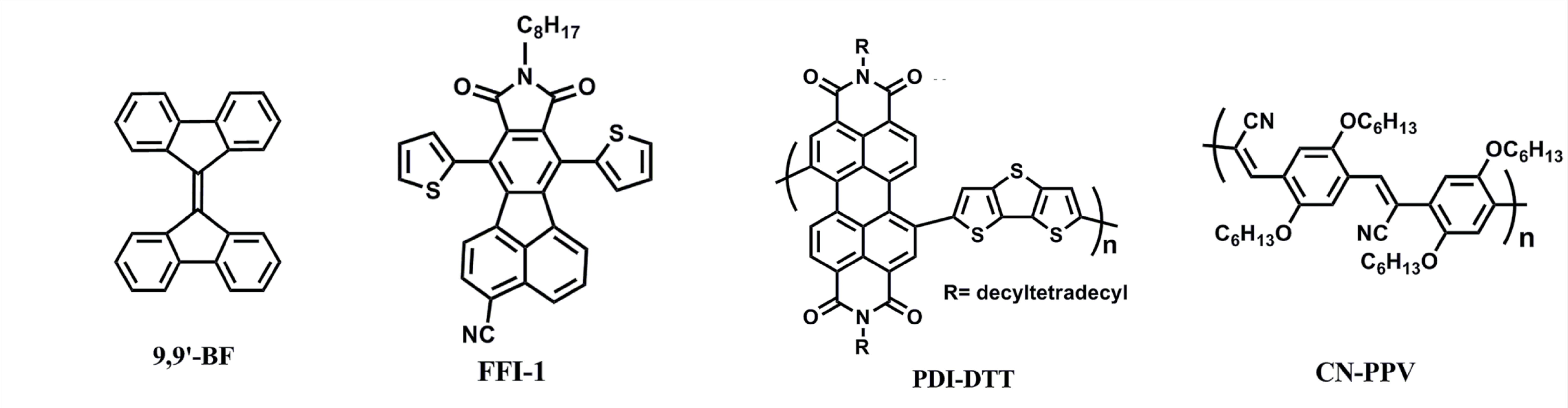
Mazzio & Luscombe, *Chem. Soc. Rev.* **2015**, *44*, 78.

Typical acceptor materials

- best results so far with fullerene derivatives

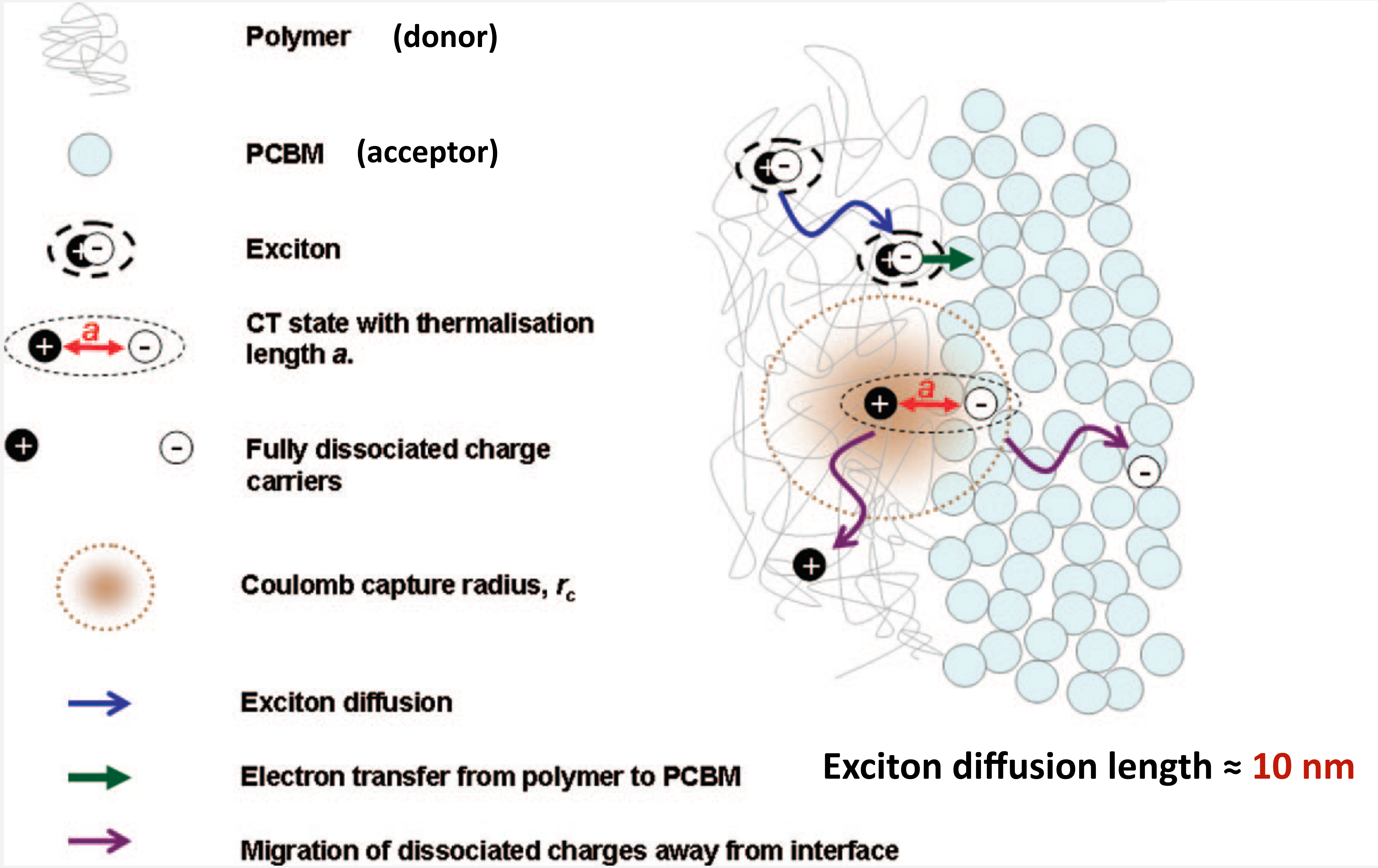


- other acceptor materials



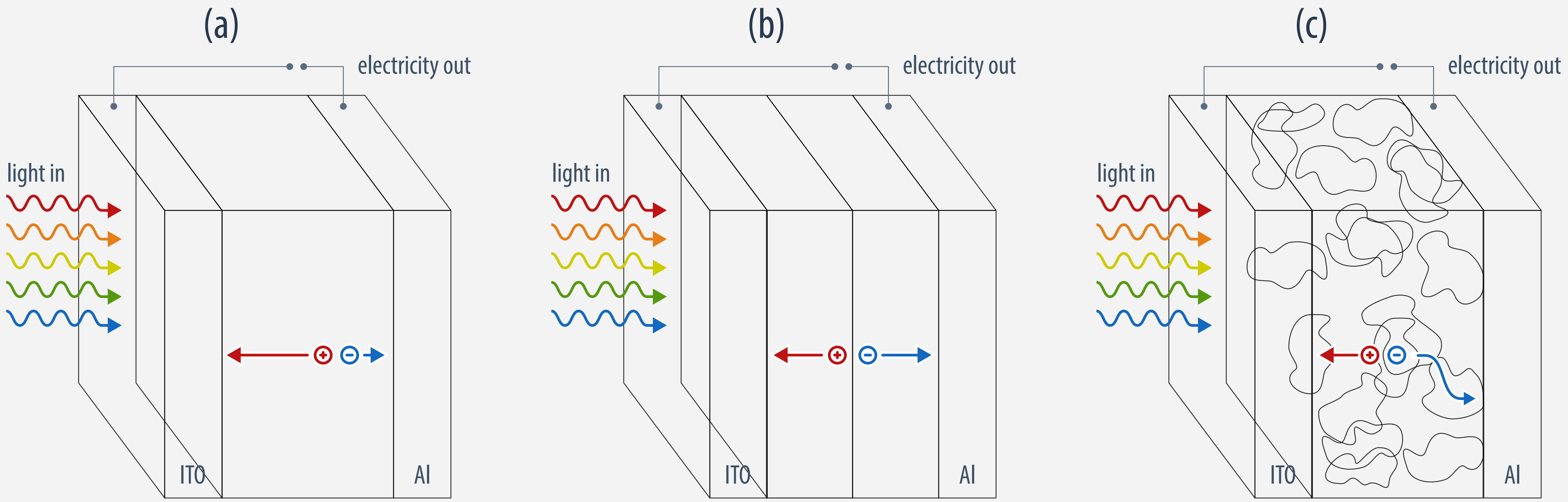
- **electron-poor (n-type) organic or polymer semiconductors**

Exciton Diffusion and Charge Separation



Exciton diffusion length ≈ 10 nm

Role of the Donor-Acceptor Microstructure



single layer

1st cell in 1978: 0.001%

bilayer

first in 1986: 1%

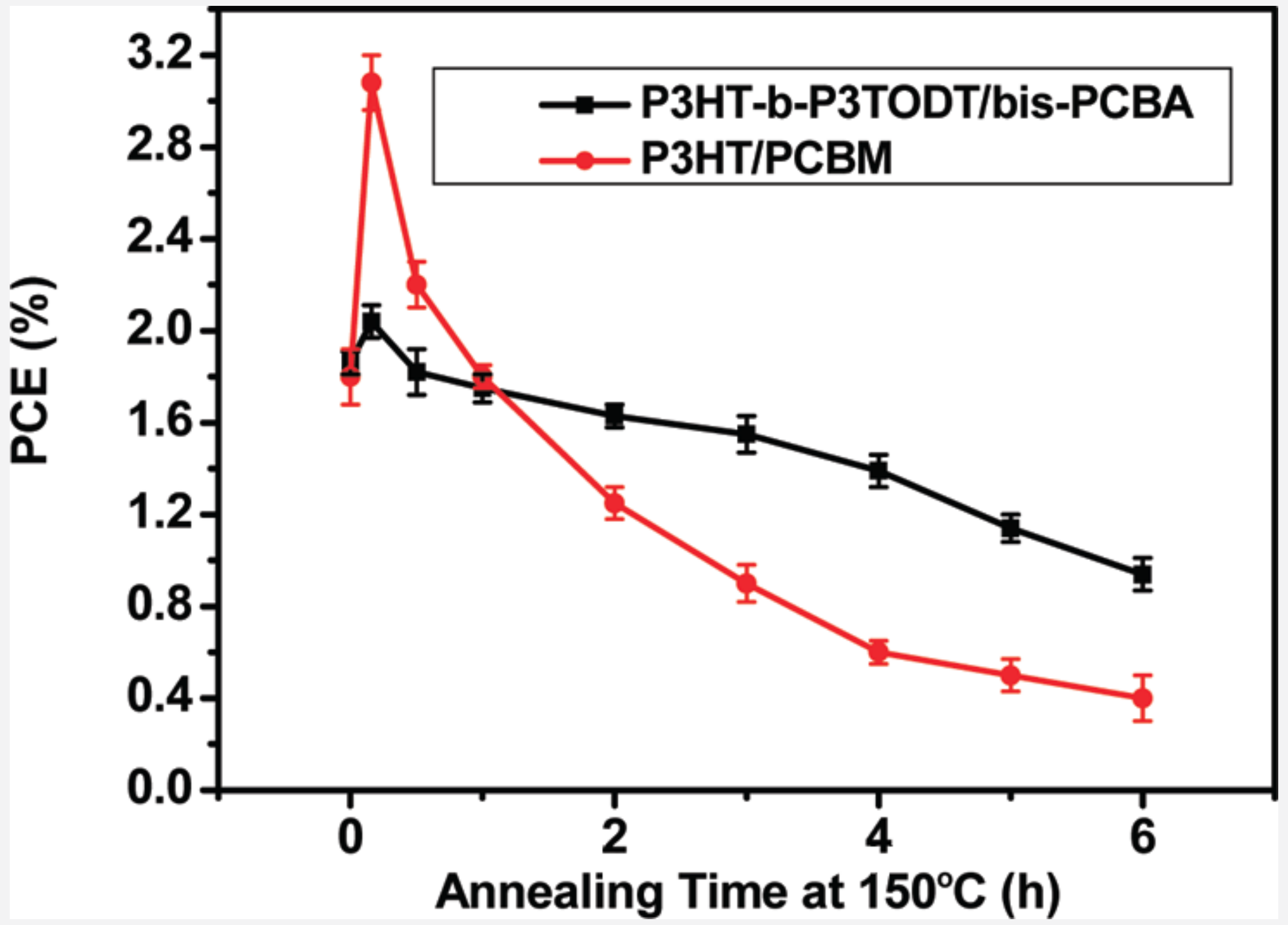
bulk heterojunction

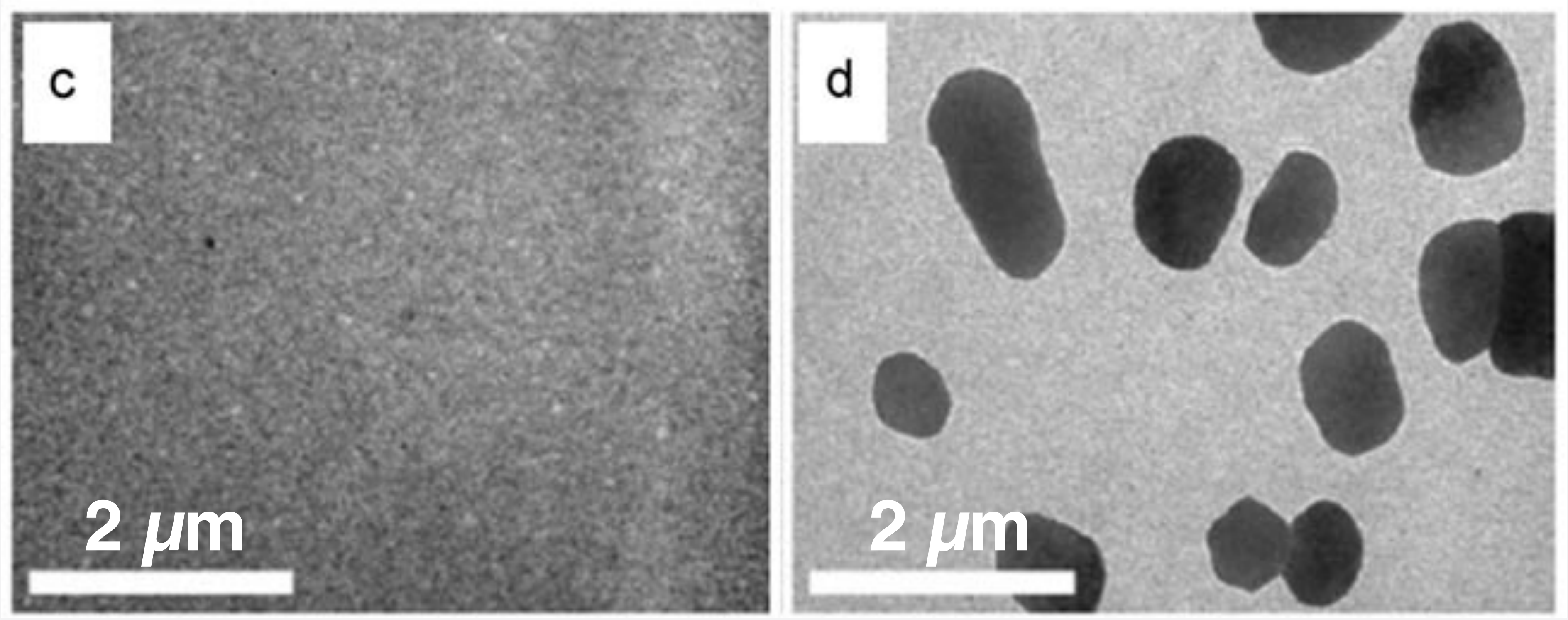
first in 1995

today: >10%

- **due to match with diffusion length of excitons and large interface, bulk heterojunctions yield so far best performance**

Inherent Problem with BHJs



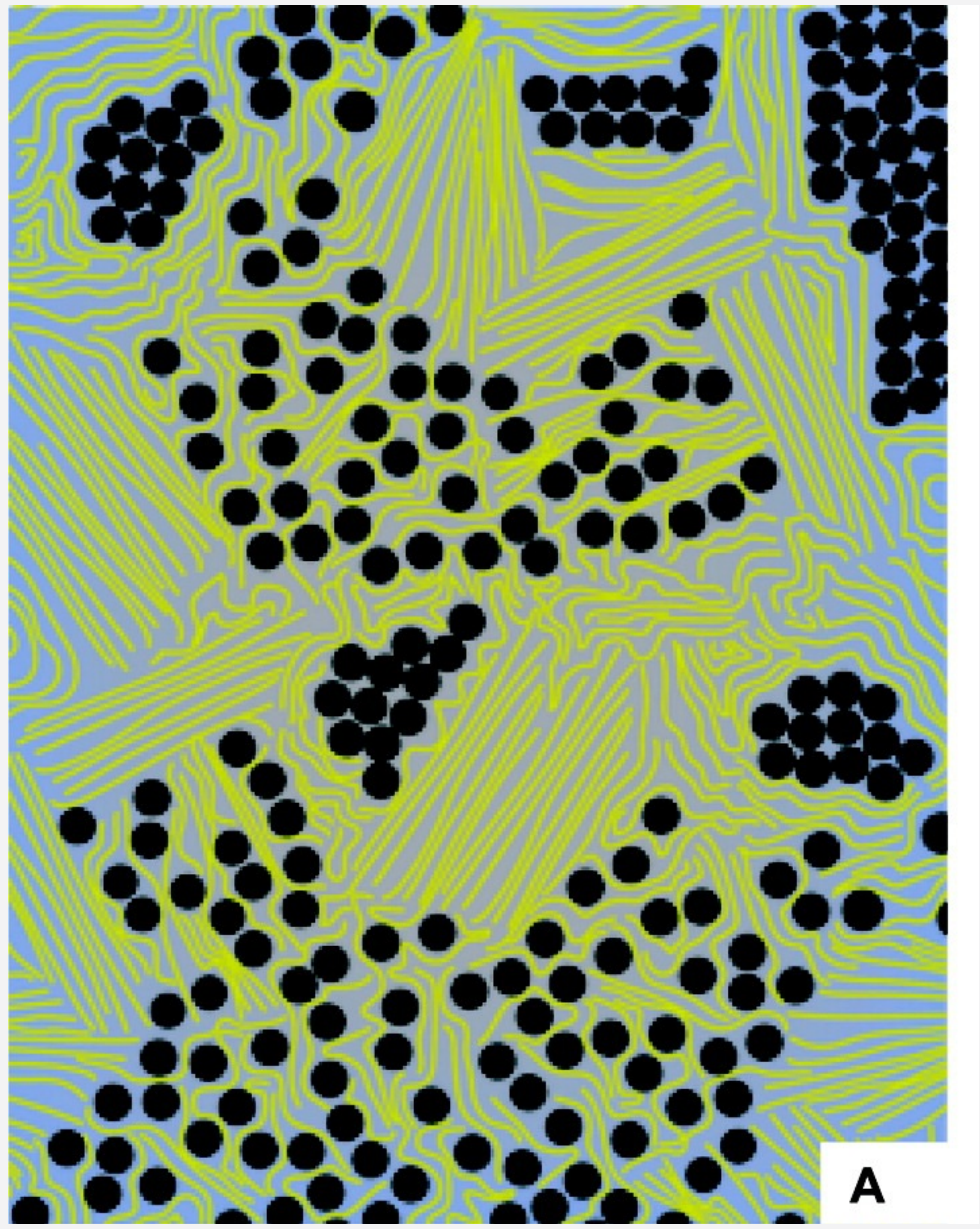


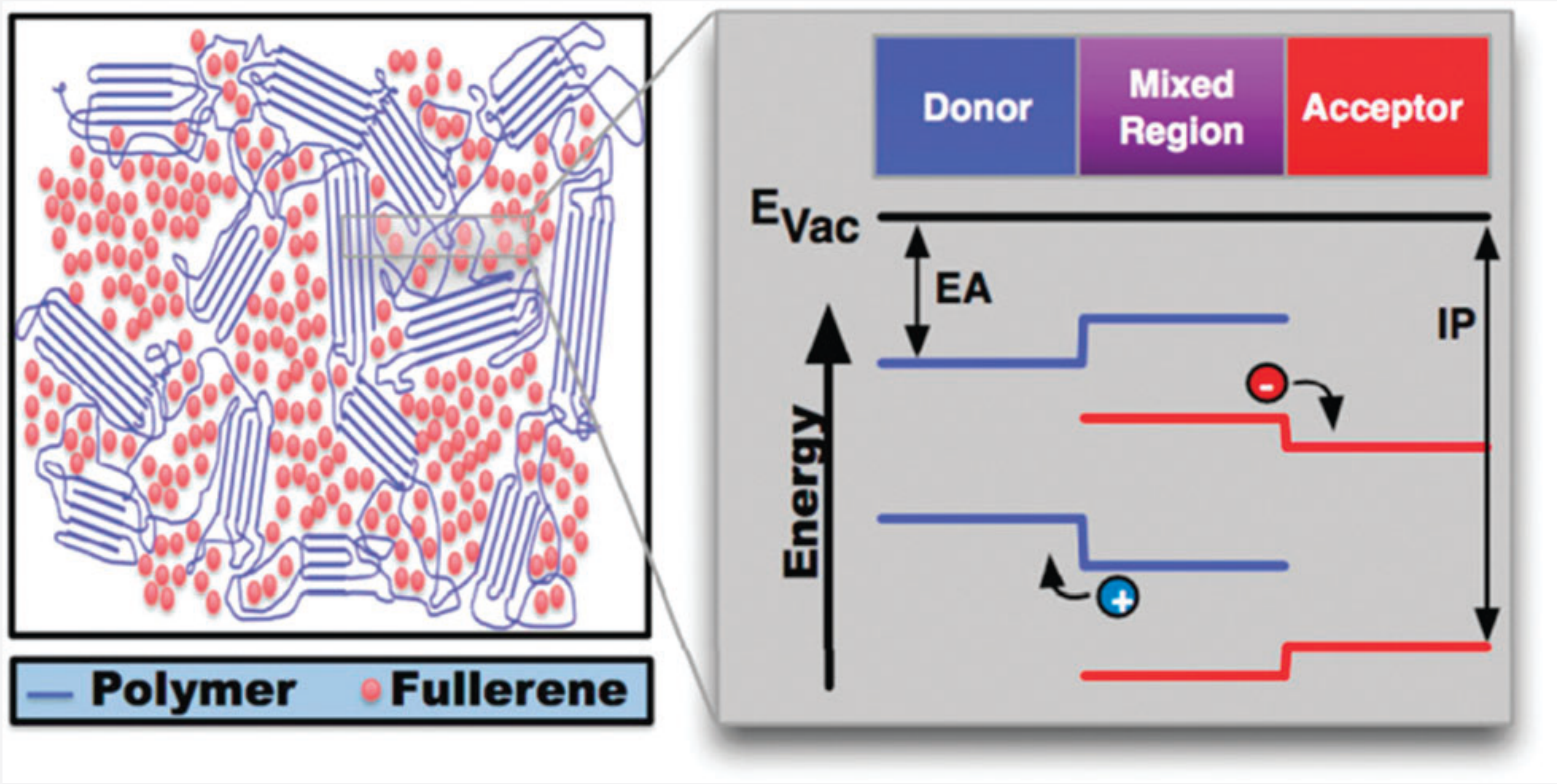
P3HT/PCBM 1:1 mix before / after 1h @140C̊

- **low but finite miscibility of the two materials**
  - miscible at high temperatures, but phase separation by spinodal decomposition upon cooling
  - spinodal decomposition is diffusion-limited process that results in bicontinuous structure
  - further cooling “freezes” the diffusion process, kinetically controlled microstructure
- **inherent problems from a kinetically controlled microstructure:**
  - morphology is hard to control
  - resulting morphology not thermodynamically stable (only metastable)

Watkins, *Chem. Mater.* **2012**, *24*, 622; Fréchet, *Angew. Chem. Int. Ed.* **2008**, *47*, 58

Mixed Phase in Bulk Heterojunction





- **PCBM is about 20% miscible in P3HT, resulting in a three-phase system:**
  - ultrafast charge separation occurs in mixed amorphous P3HT/PCBM phase
  - directed transport following chemical potential microgradients
  - ideally "arborescent structure" of crystalline P3HT and crystalline PCBM phases

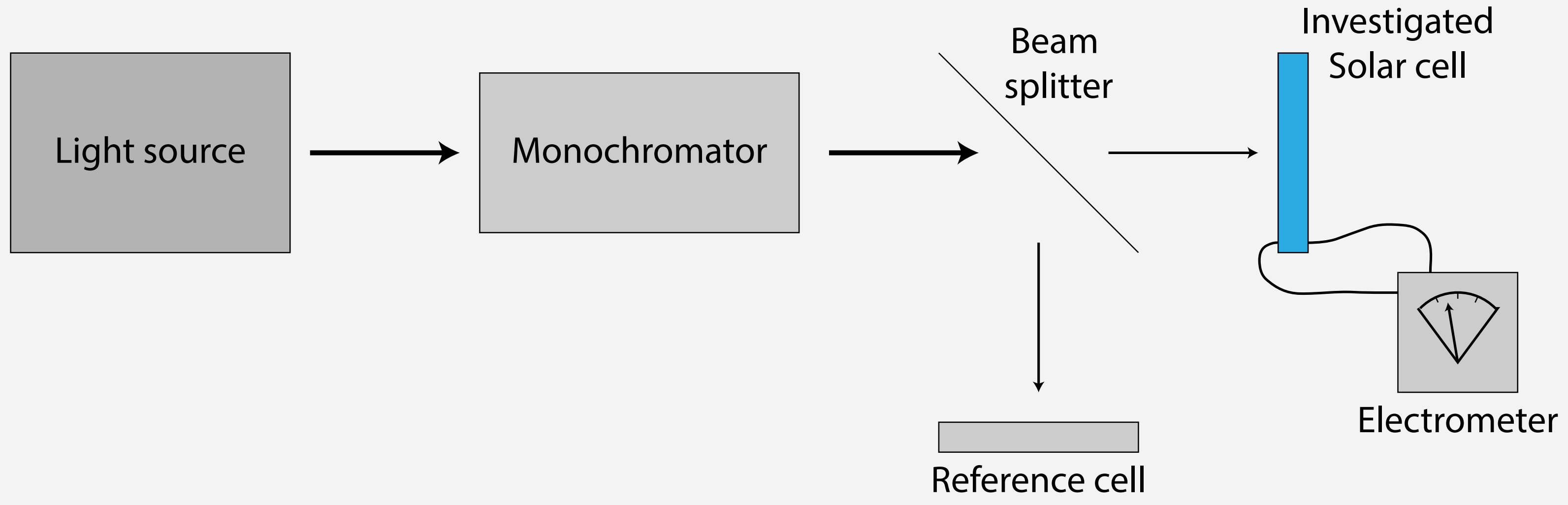
Yin & Dadmun, *ACS Nano* **2011**, *5*, 4756; Mazzio & Luscombe, *Chem. Soc. Rev.* **2015**, *44*, 78.

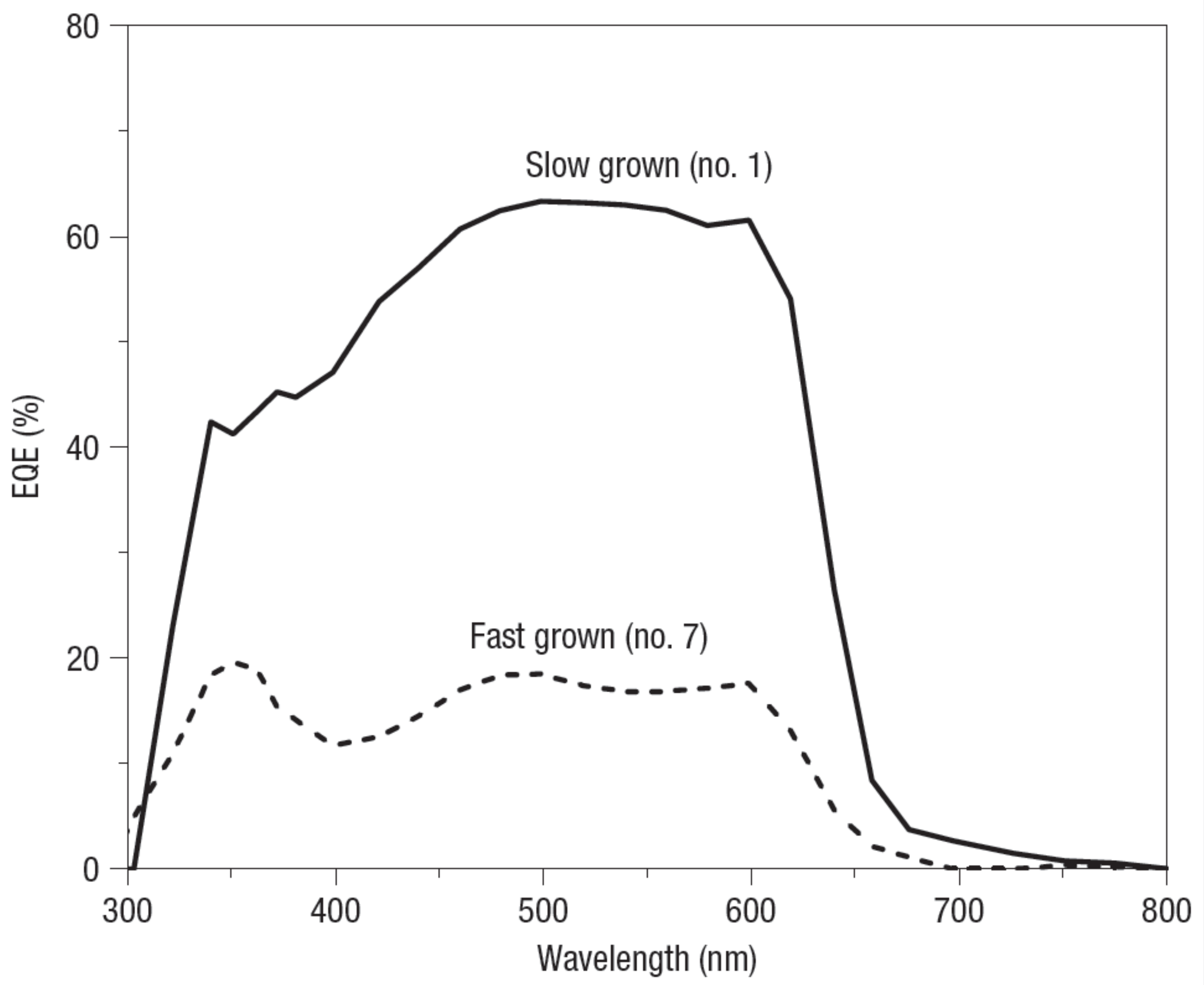
Quantum Efficiencies

- external quantum efficiency $EQE(\lambda)$: photogenerated charges per incident photons

$$EQE(\lambda) = \eta_{abs}(\lambda) \cdot \eta_{diff}(\lambda) \cdot \eta_{CT}(\lambda) \cdot \eta_{coll}(\lambda)$$

$\eta_{abs}(\lambda)$ photoabsorption efficiency
$\eta_{diff}(\lambda)$ exciton diffusion efficiency
$\eta_{CT}(\lambda)$ charge transfer efficiency
$\eta_{coll}(\lambda)$ charge collection efficiency

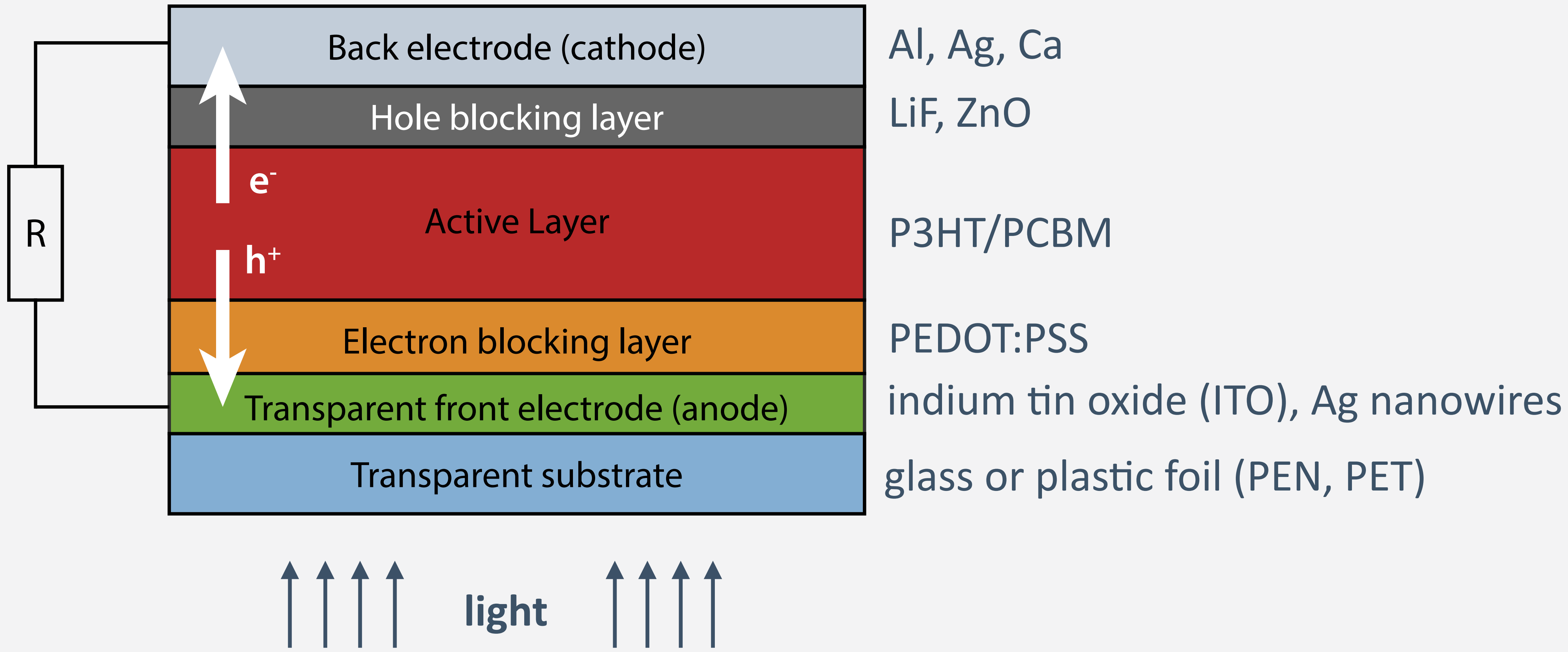


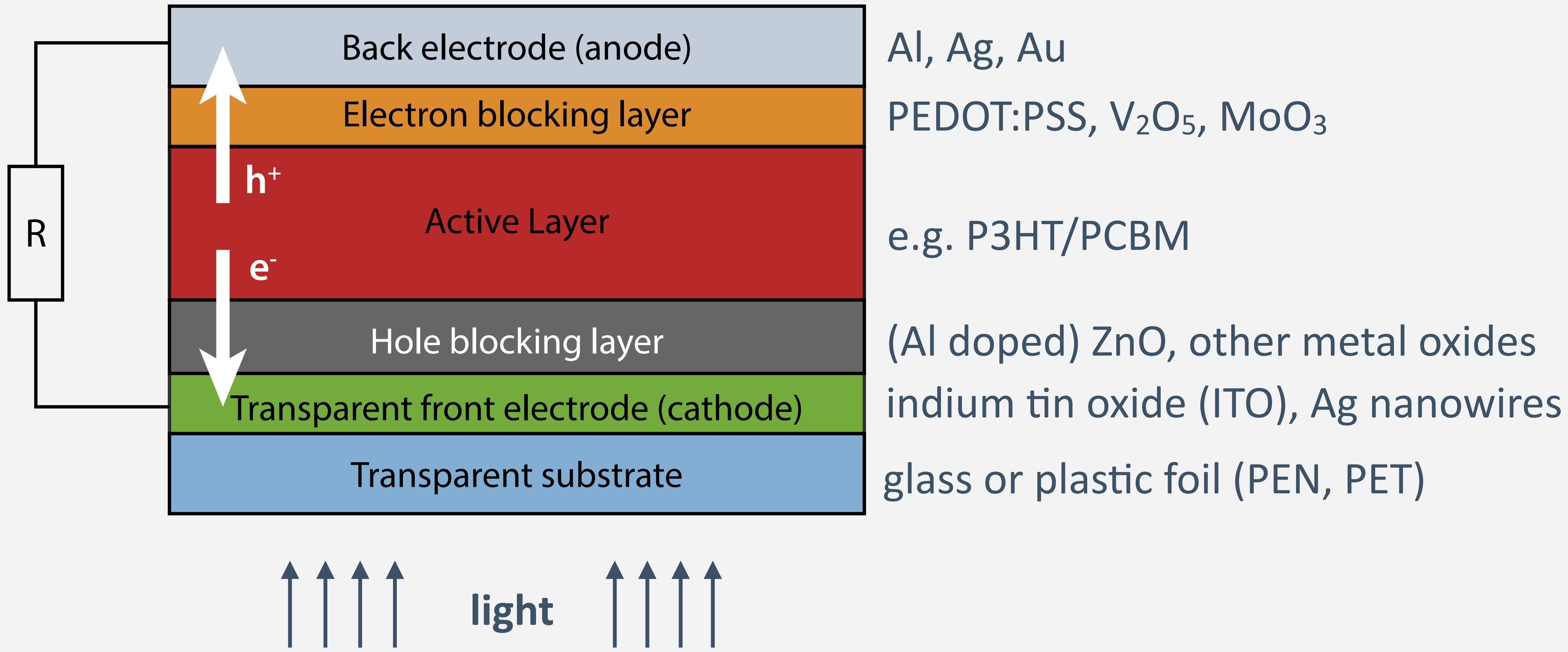


- **the EQE describes the overall efficiency of the four main photophysical processes**

Mazzio & Luscombe, *Chem. Soc. Rev.* **2015**, *44*, 78; Gang, *Nat. Mater.* **2005**, *4*, 864.

Normal and Inverted Device Structure

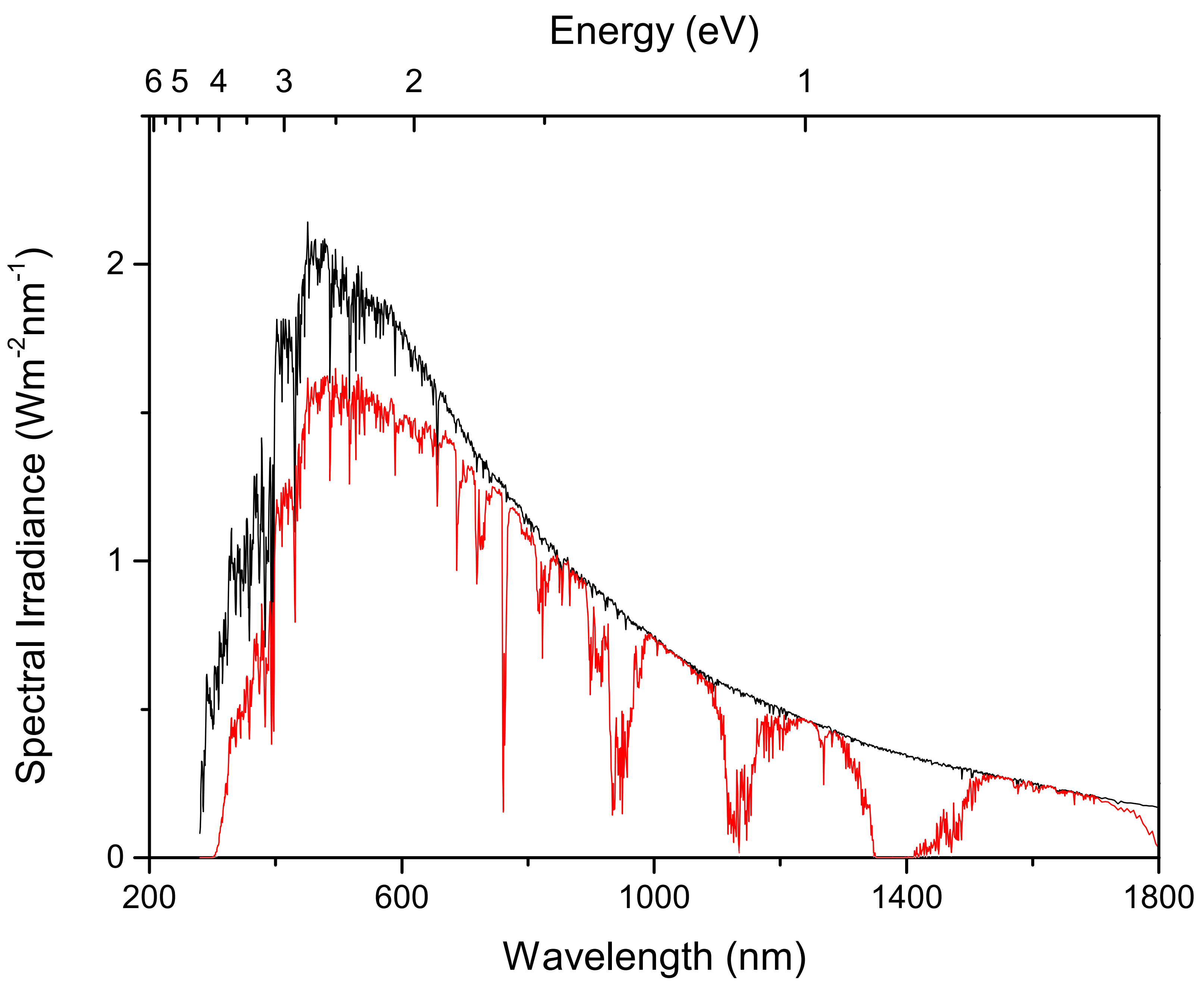


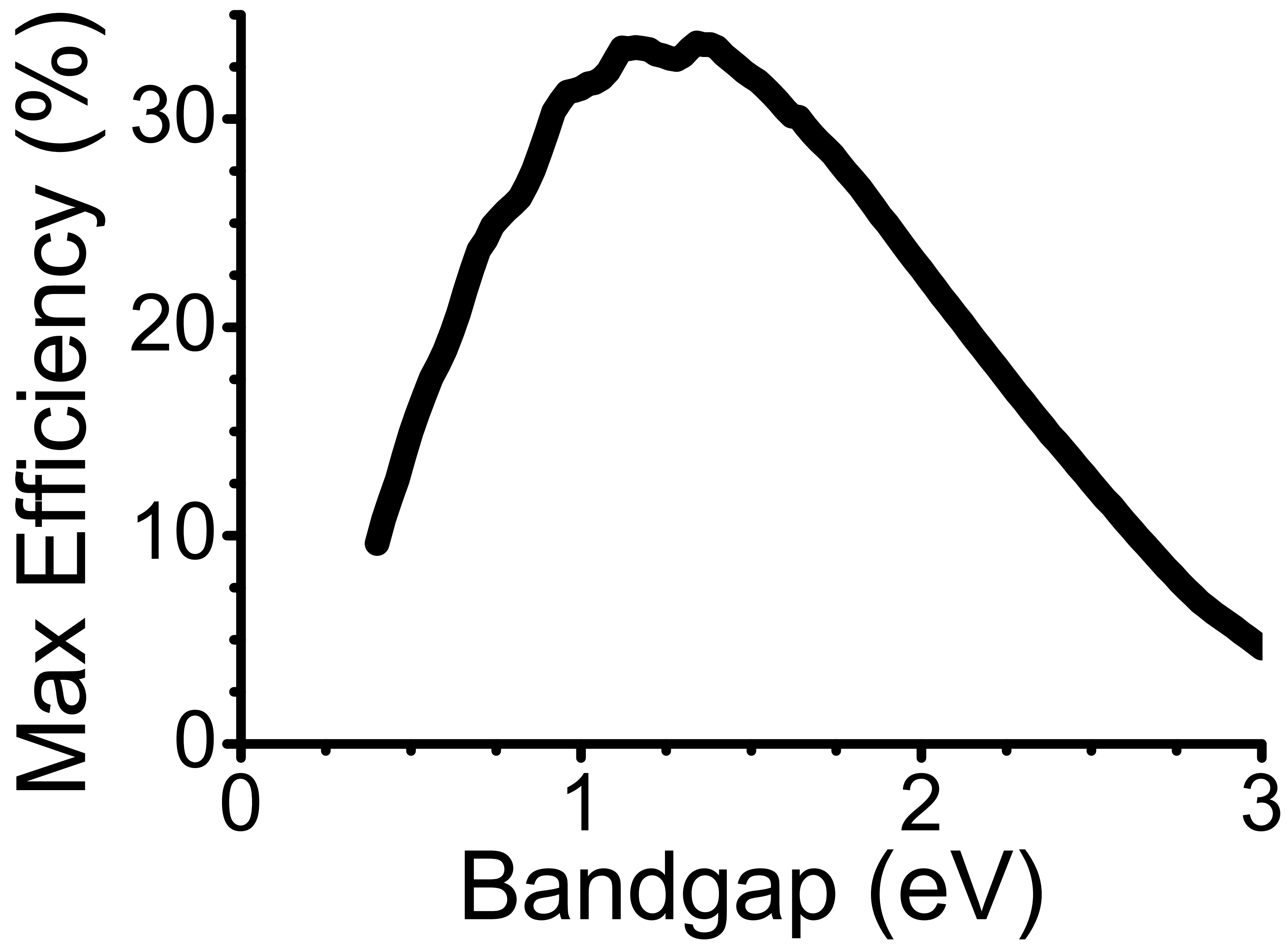


- **one electrode inevitably needs to be transparent!**
- **work functions of electrodes & blocking layers should match E_{LUMO}(acceptor), E_{HOMO}(donor)**
- **benefit of inverted device layout: no need for low work function metals as cathode**

Limits of Single Cell Devices

- Shockley-Queisser limit of power conversion efficiency for single cell



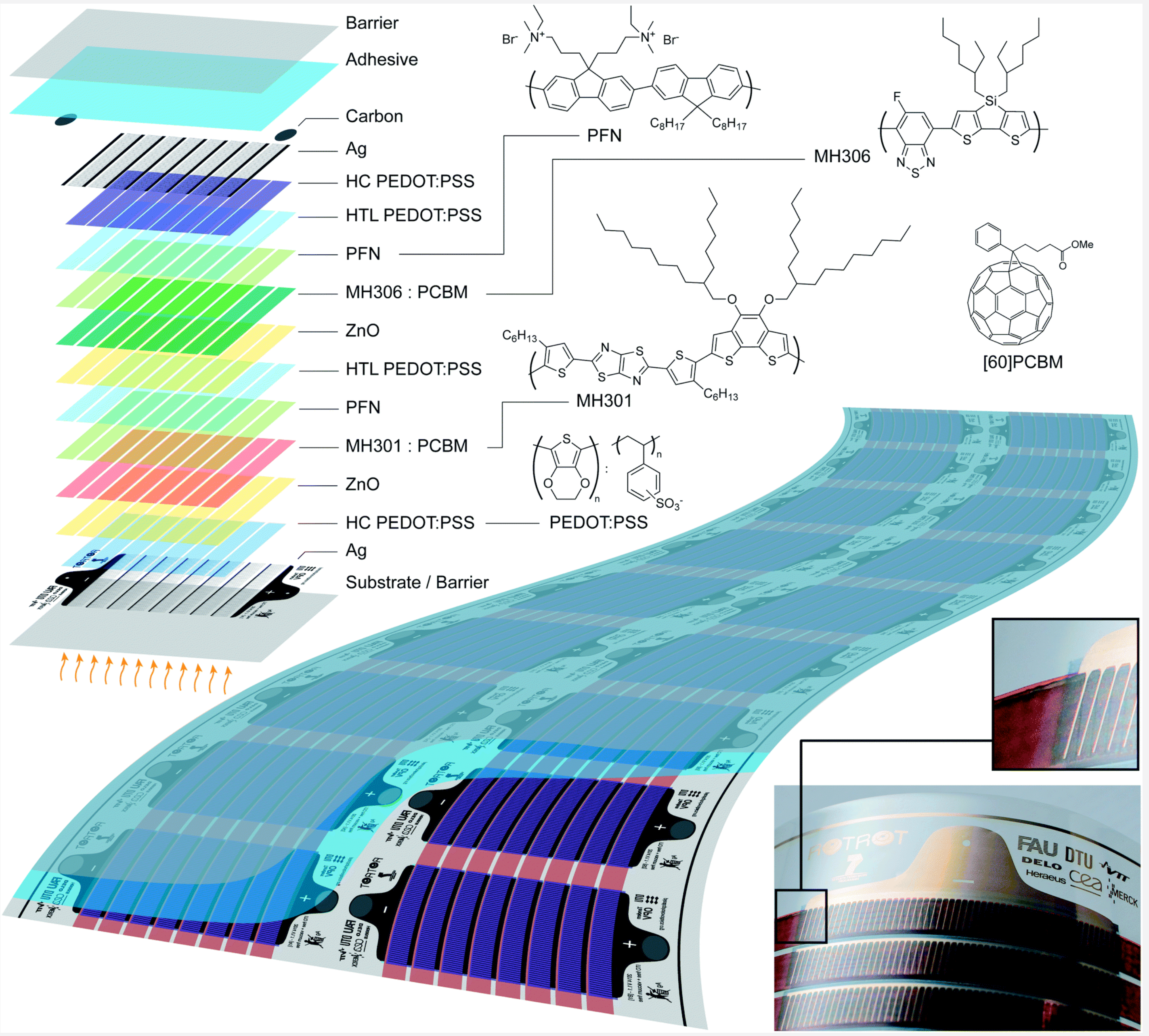


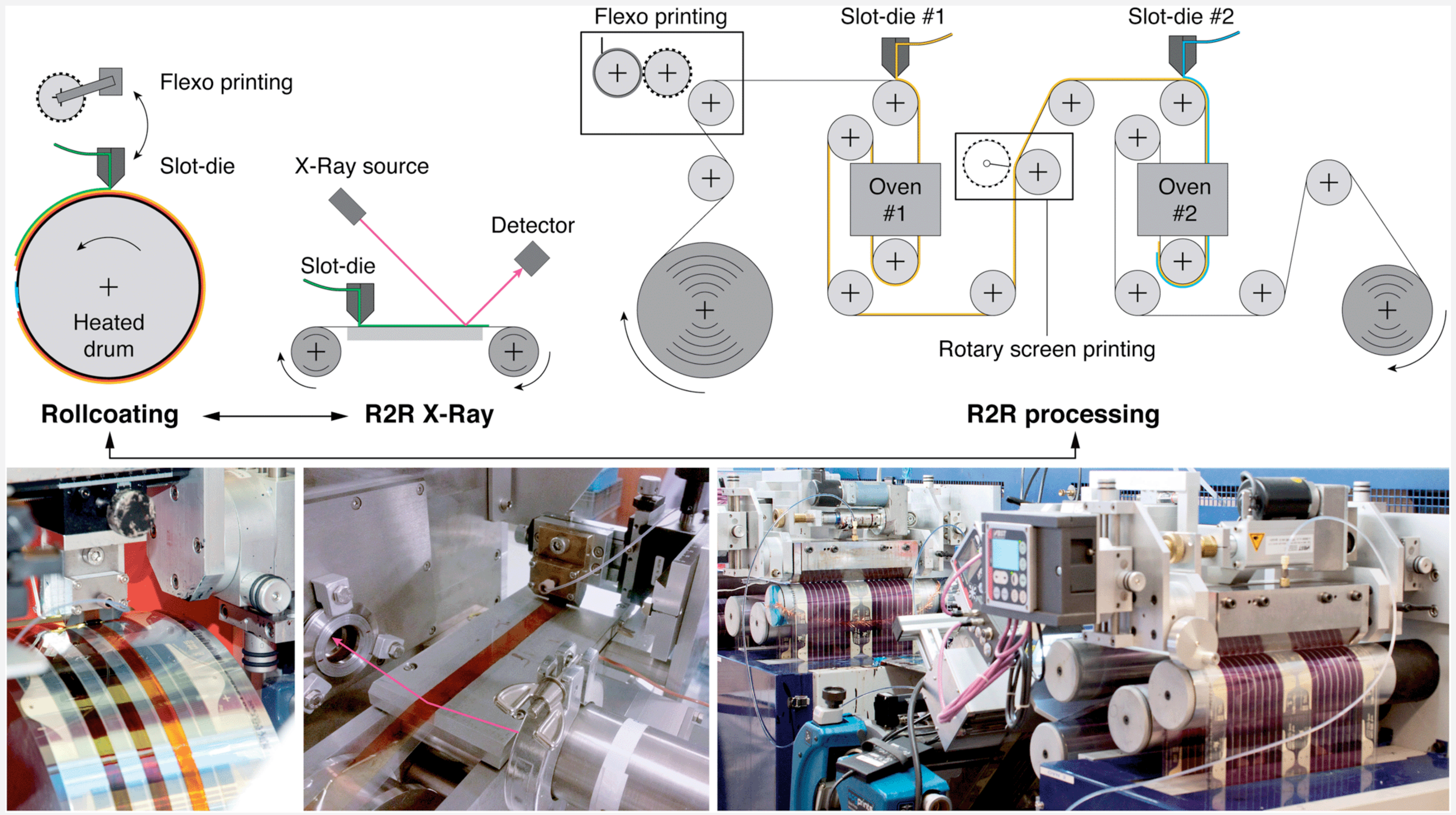
- **large bandgap mean higher usable potential (after thermal relaxation), but all photons below bandgap energy are wasted**
- **smaller band gap means that more photons can be absorbed (even at higher wavelengths), but all excess energy of photons with higher energy than band gap is wasted (due to "internal conversion")**

Shockley, Queisser, *J. Appl. Phys.* **1961**, *32*, 510.

Printing of Multilayer Polymer Solar Cells

- roll-to-roll solution process for organic solar cells





- **fully printed solar cells, even electrodes are printed**
- **solvent must not attack the underlying layers**

Vacuum Processing of Organic Solar Cells

- roll-to-roll vacuum process for organic solar cells

- **whole process in vacuum chamber**
- **no problems with dissolving the underlying layers**
- **vapor phase processing enables the fabrication of gradual interfaces**
- **accurate control over layer thickness and molecular composition**

http://m.eet.com/media/1167154/fraunhofer_fig1.jpg

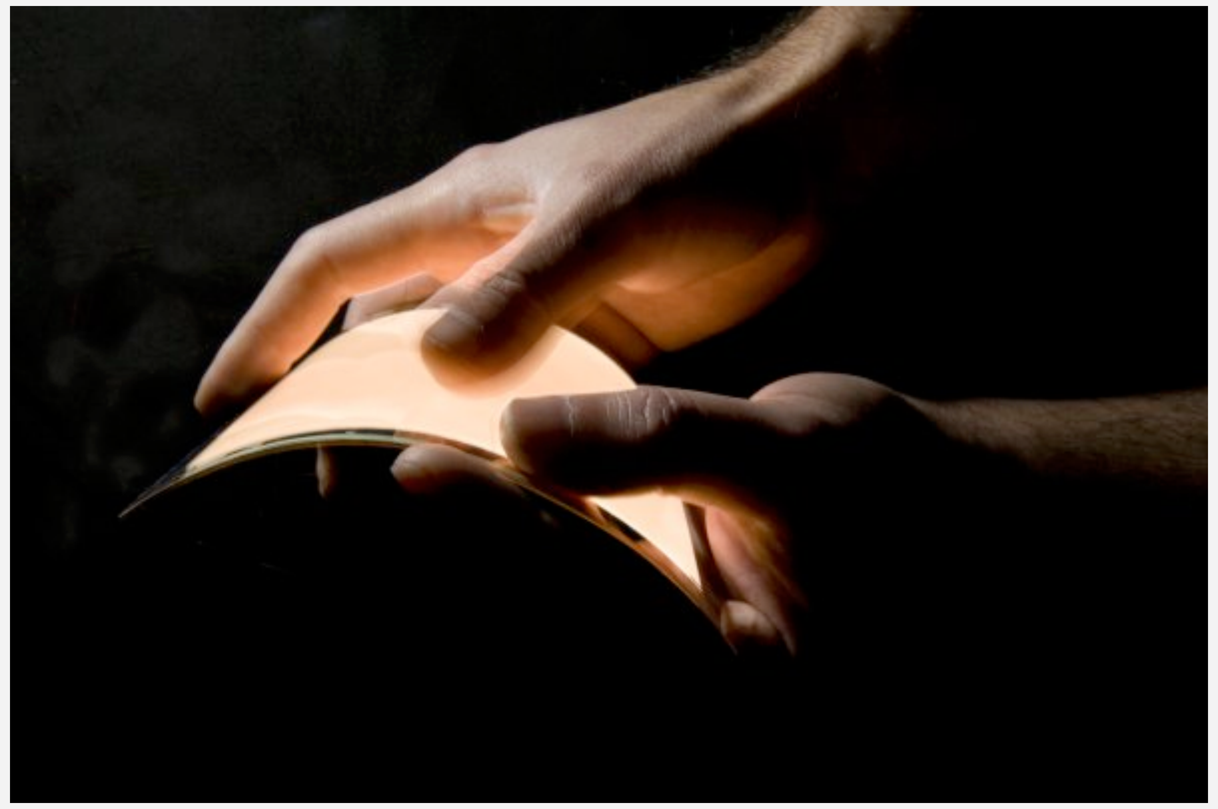
Literature

7.3 Organic Light-Emitting Diodes

Perspectives for Organic Light Emitting Diodes (OLEDs)

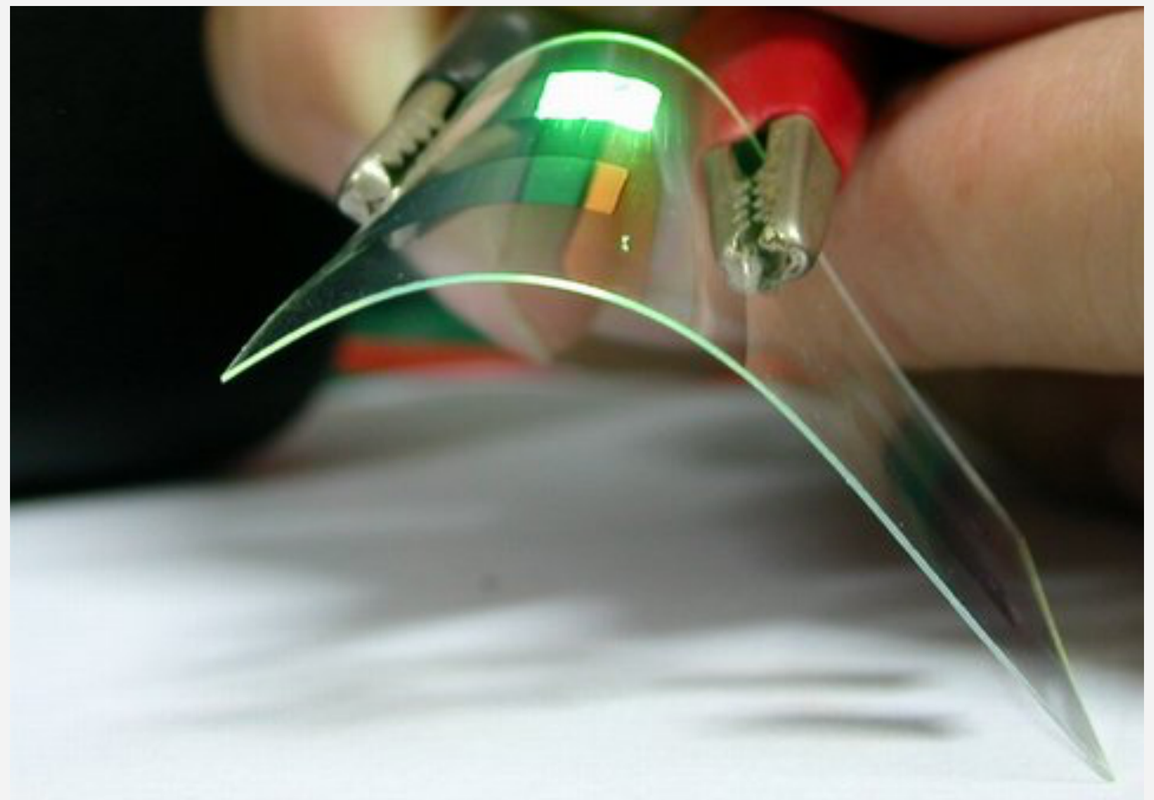
- two-terminal devices from organic semiconductors that emit light upon electric current
- used for displays and lighting devices

Lighting



Displays

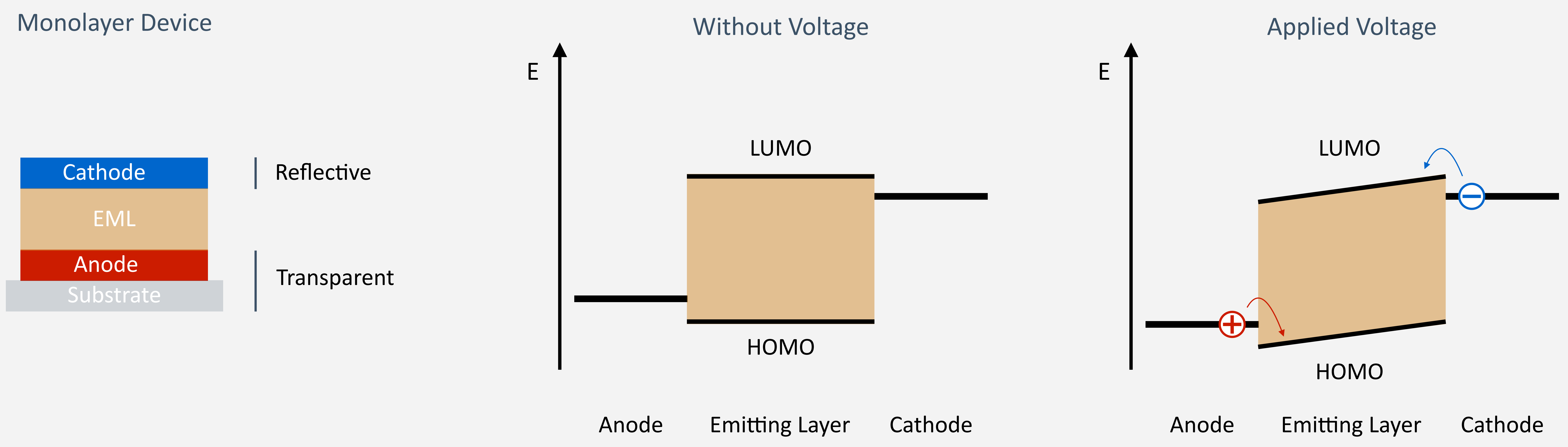
Transparent



- **low-cost, large-area processing, lightweight, ultrathin, flexible applications, high efficiencies**
- **challenges remain in terms of lifetime, color balance, and lower production costs**

Energy Diagram of a Monolayer Device

- organic light emitting diodes generate light by electrical excitation
- this can be achieved by sandwiching a suitable organic material between two electrodes

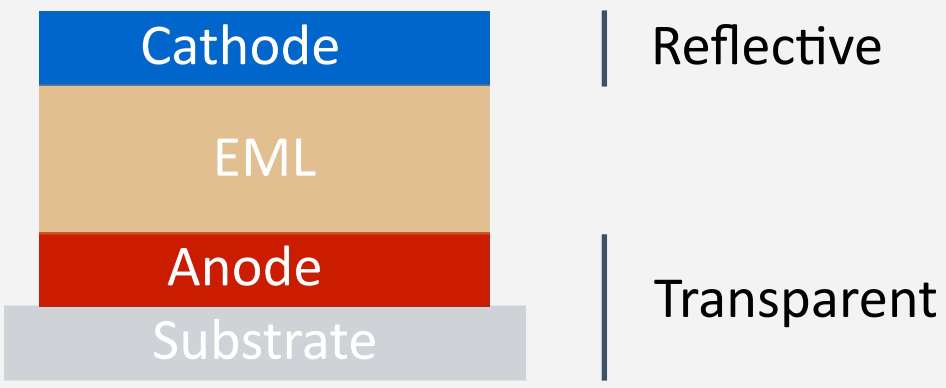


- **charge carriers can only be injected and moved if a voltage is applied between the electrodes**

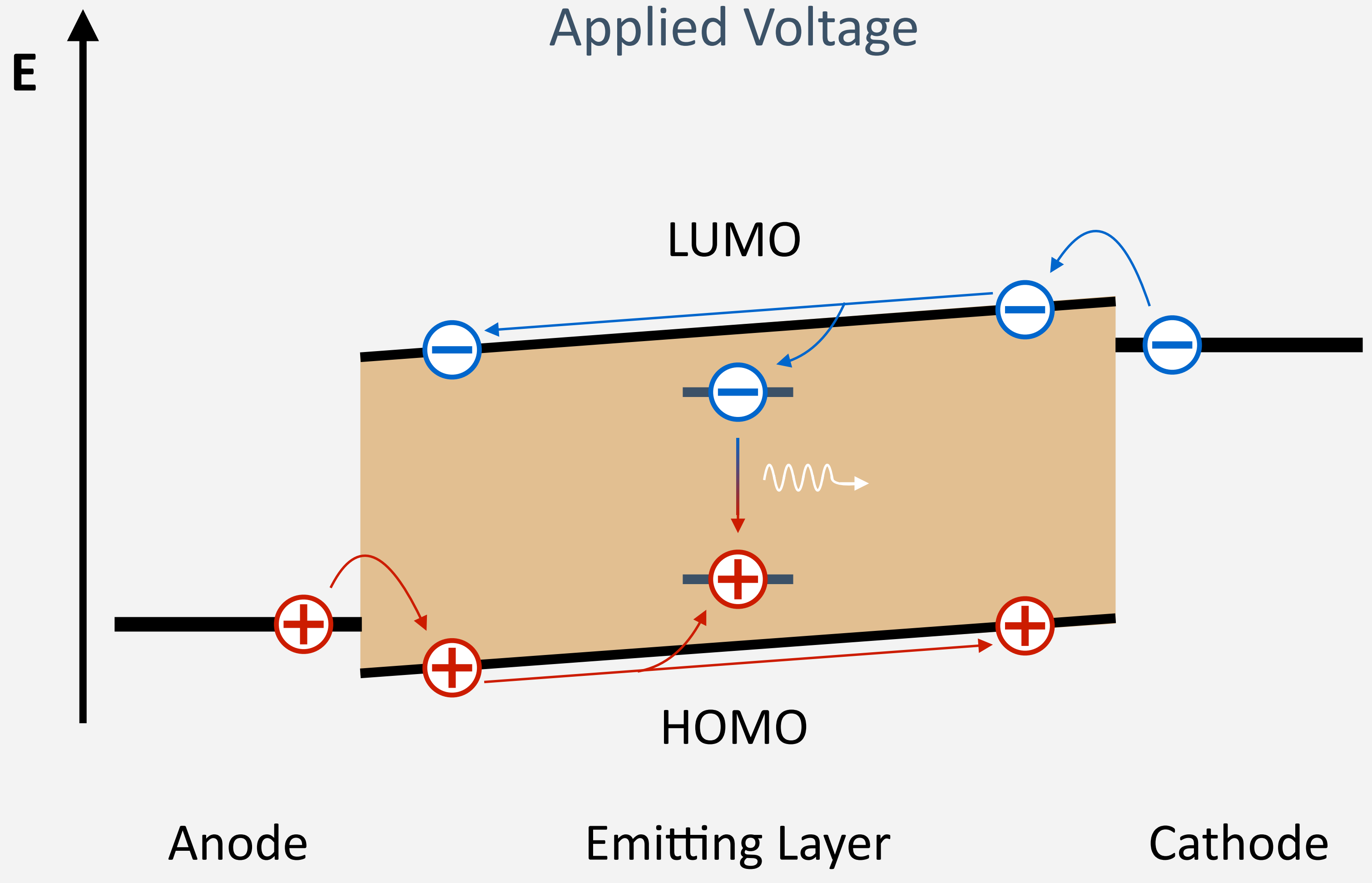
Basic Working Principle of OLEDs

- electroluminescence in organic solids requires for basic steps:

Monolayer Device



Applied Voltage

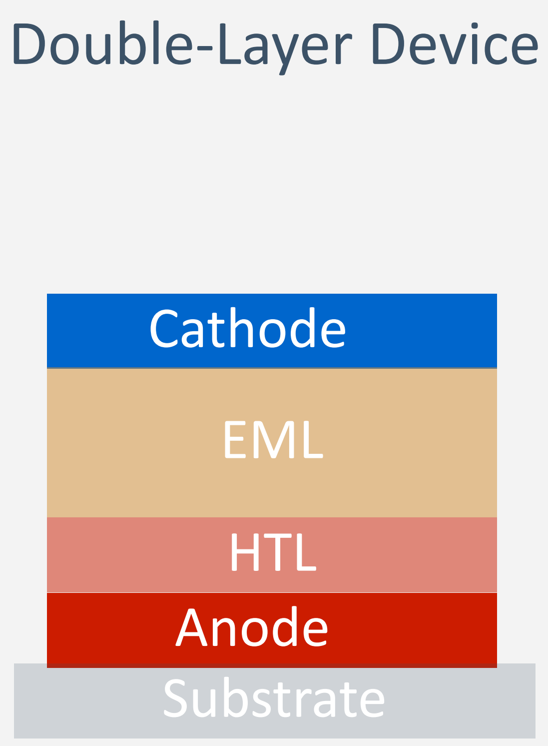


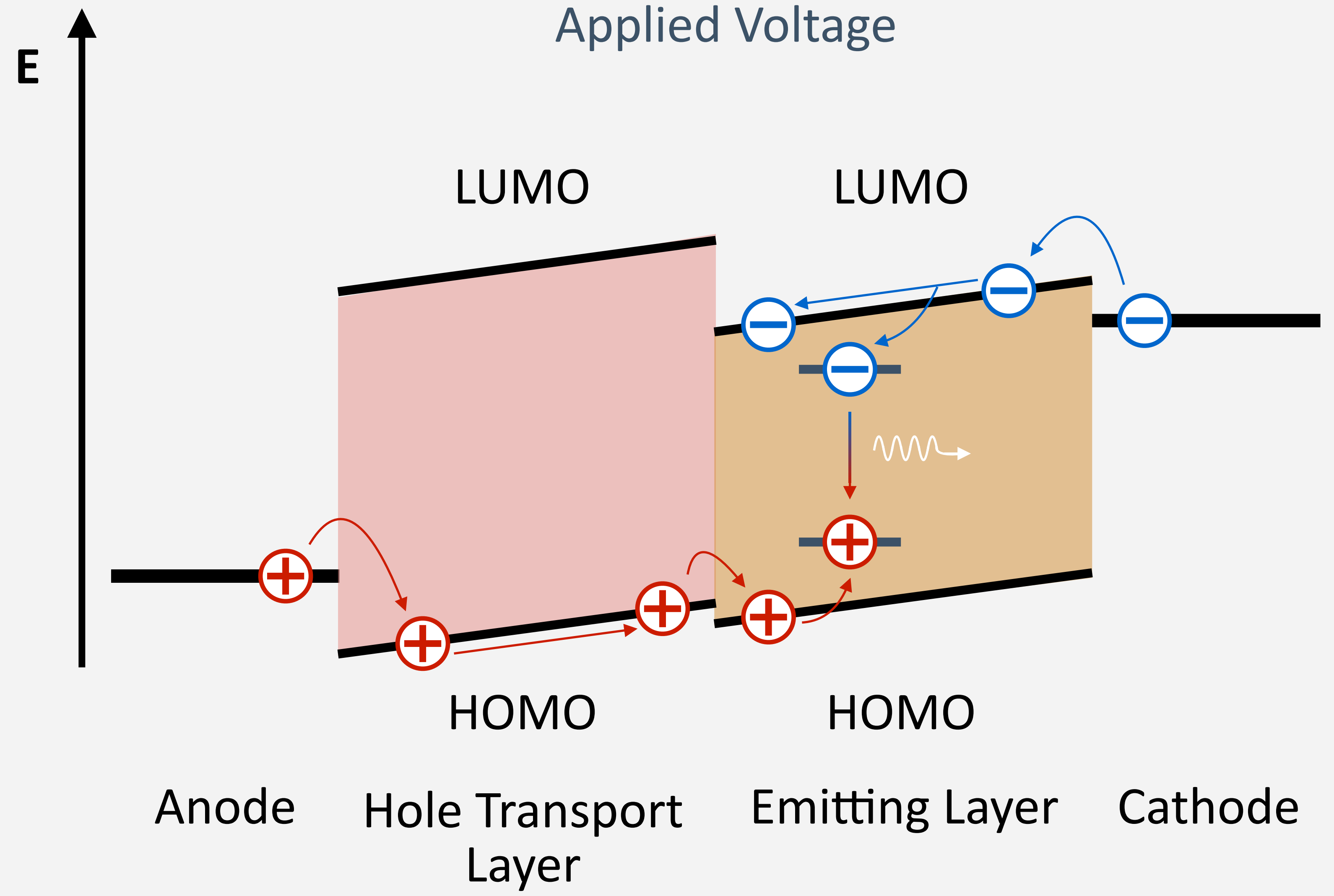
Basic Steps

1.) charge carrier injection
2.) charge carrier transport
3.) exciton formation
4.) radiative exciton decay

- **in a monolayer device all basic steps take place in the same organic layer**
- **low probability for exciton formation**

Energy Diagram of a Double-Layer Device

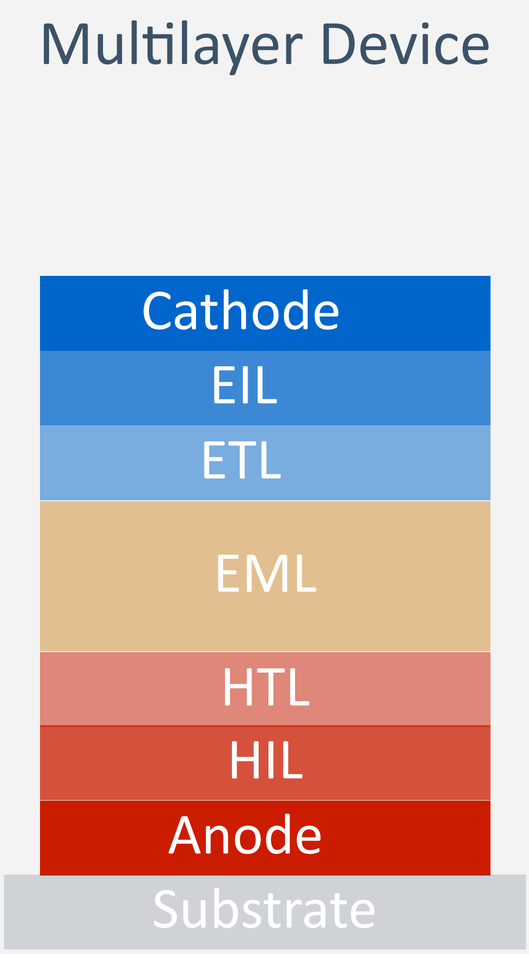


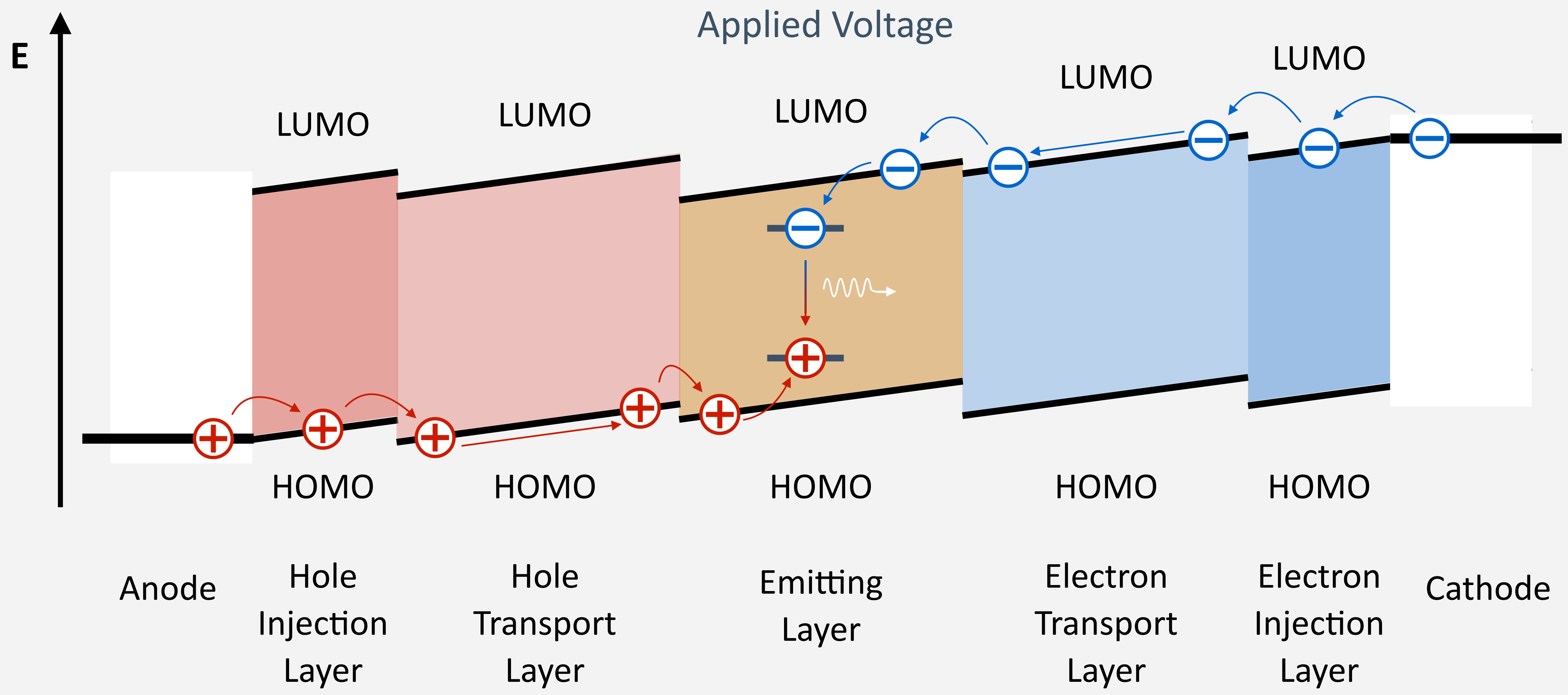


- **hole and electron transport** are **separated** in two **different layers**
- holes and electrons form **excitons** in a **confined** volume at one side of the interface

Energy Diagram of a Multilayer Device

- charge injection and transport as well as emission takes place in different layers
- each layer optimized for its specific function to maximize the overall performance



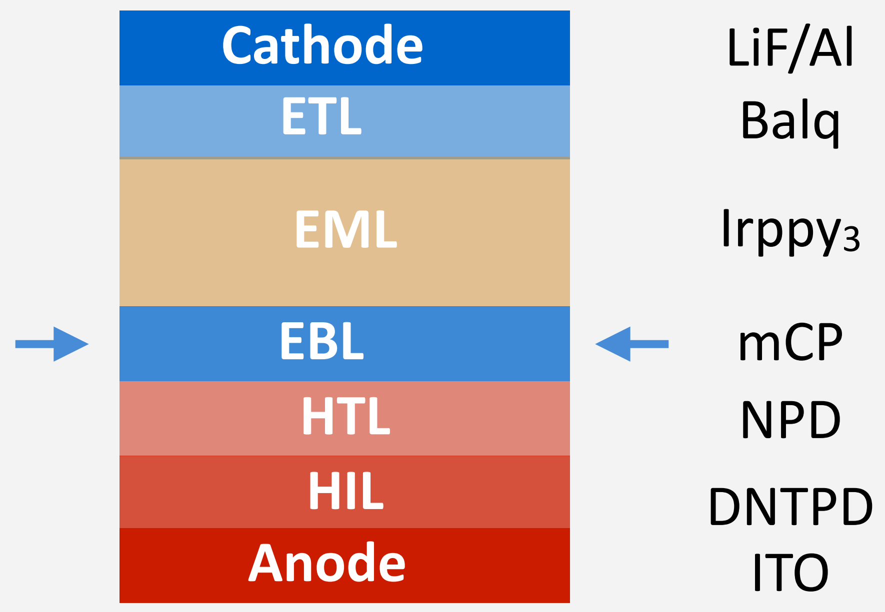


- **state of the art high performance OLEDs are based on a multilayer structure**

Impact of Electron Blocking Layer

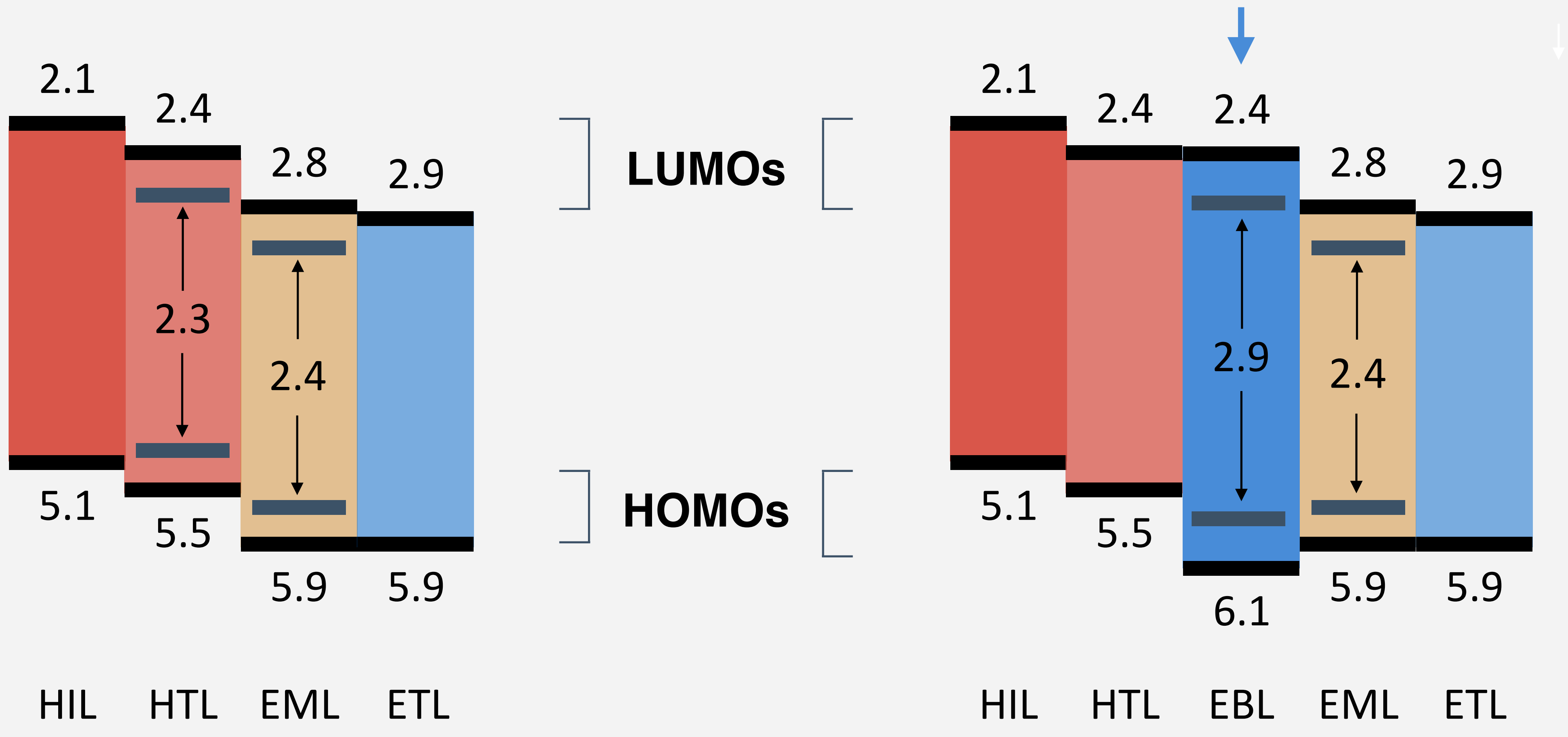
- charge **blocking layers increases** efficiency by confining the charges to the emission layer

Device Layout



Without Electron Blocking Layer

With mCP as Electron Blocking Layer



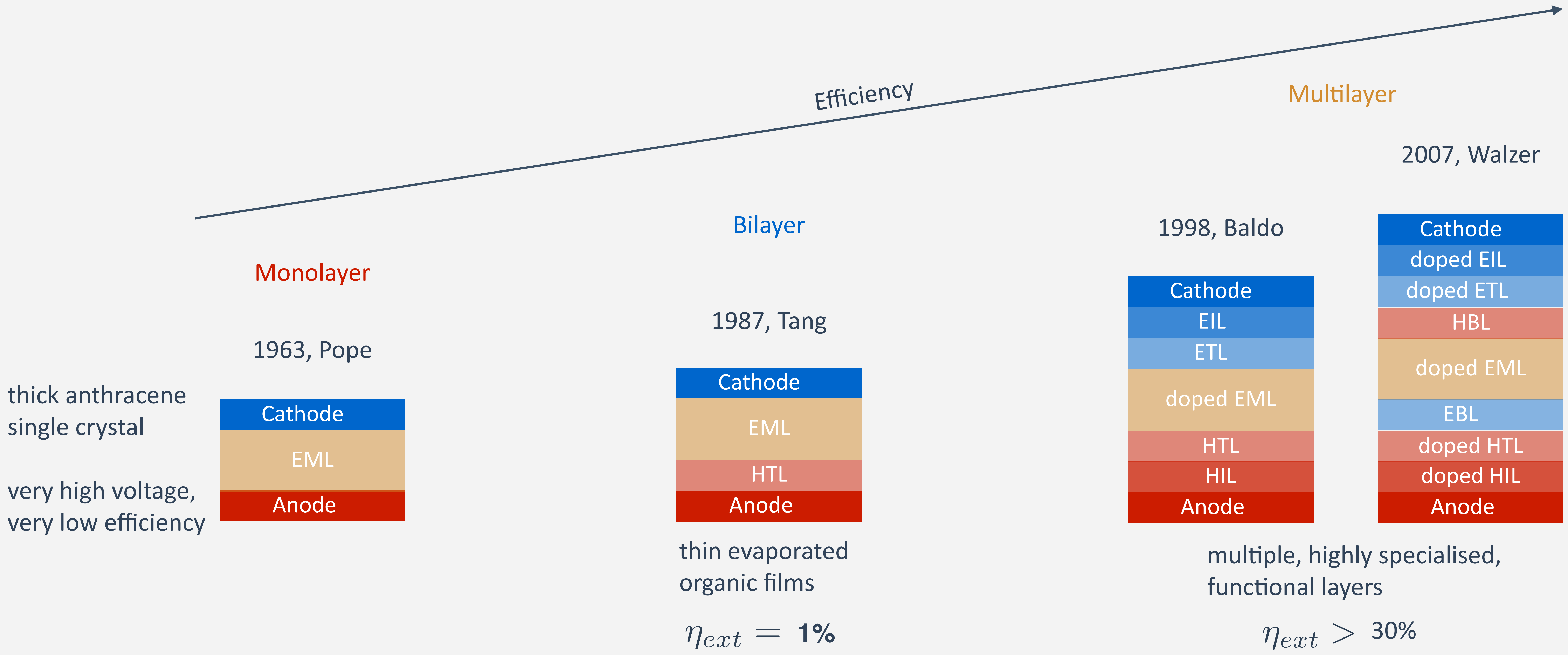
$\eta_{ext} =$ 3.4%

$\eta_{ext} =$ 14%

- **electron blocking layer increases the efficiency of a green OLED by more than three times**
- **intersystem crossing (ISC) is a non-radiative transition under spin inversion**
- **the much larger time scale of phosphorescence is caused by “spin-forbidden" relaxation**

From Mono- to Multilayer OLEDs

- to increase their efficiency OLEDs evolved from monolayer, to bilayer, into multilayer devices



- **low production cost, large area processing**
- **low temperature-solvent based manufacturing technique**

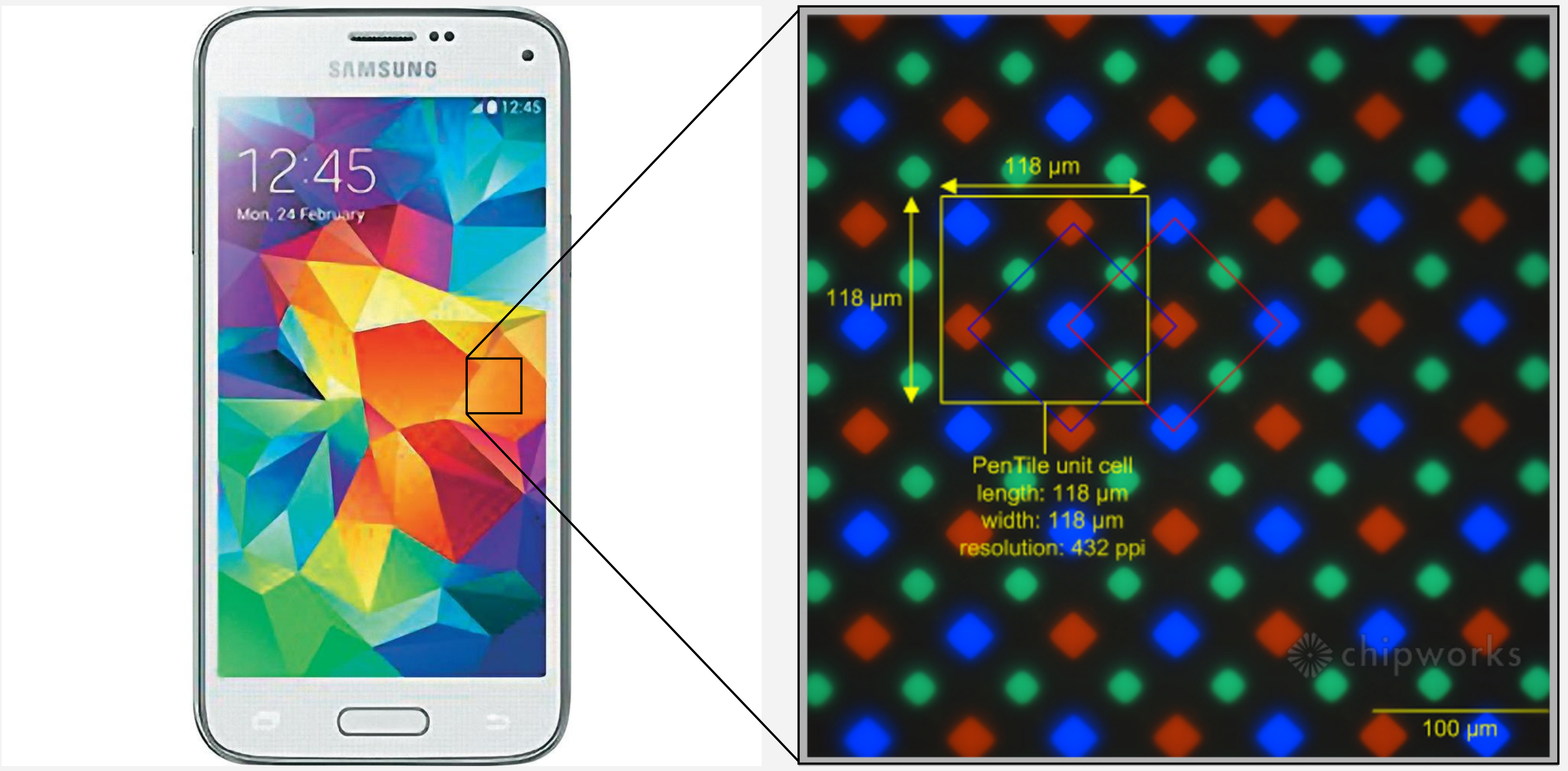
Pope, *J. Chem. Phys.* **1963**, *38*, 2042; Tang, *Appl. Phys. Lett.* **1987**, *51*, 913; Baldo, *Nature* **1998**, *395*, 151; Walzer, *Chem. Rev.* **2007**, *107*, 1233.

OLED Displays

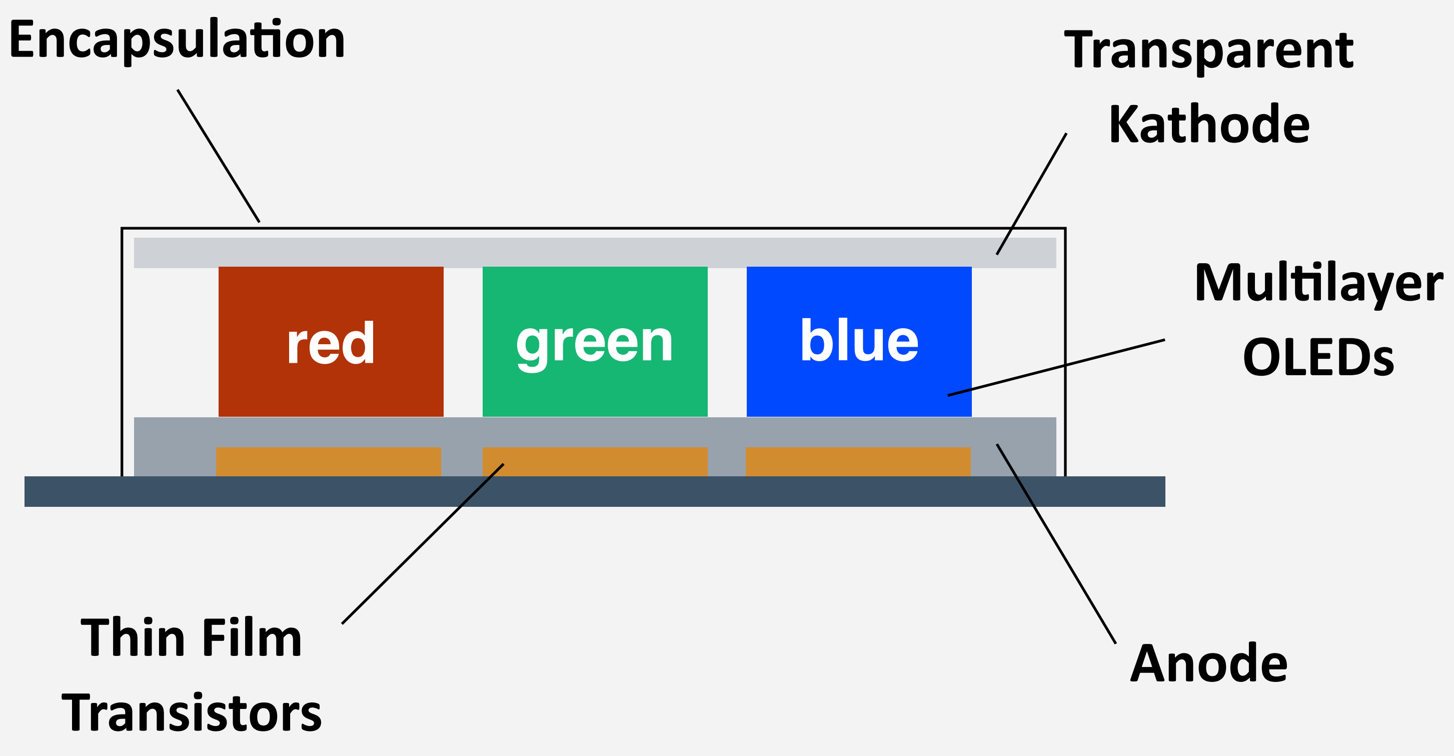
- OLEDs are already commercialized in the form of TV, laptop, and smartphone displays

Smartphone

Zoom-In on OLED Display



Basic Device Layout



- **individual OLEDs emit red, green and blue light together creating one colour-tunable pixel**
- **every single OLED is driven by its own thin-film transistor**
- **the whole device structure is encapsulated to ensure longterm stability**