Printed organic photodetectors for large area detection on conformable substrates

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Photodetecting devices

« Conventional » inorganic photodetectors

1. Photomultiplier tubes
2. Si photodiode (p-n; p-i-n)
3. Phototransistor
4. Pyroelectric photodetector
5. Photoresistor
6. Charge-Coupled Device (CCD)
7. Bolometer

Organic photodetectors

- Phototransistors

- Photoresistors

- CCD

- Photodiodes
  *G. Yu et al, Science 270, 1789 (1995)*
Organic vs inorganic: complementary technologies

**Inorganic**
- High performances,
- Robust and reliable devices,
- Well established technologies and industrial context,

**but...**
- Needs for cost effective tools,
- Long development cycles,
- Low versatility (difficulties for exotic integration).

**Organic**
- Ease for large surface integration,
- Use of flexible plastic substrates,
- Compatibility with high throughput printing tools,
- Short development cycles,
- Well adapted for non standard designs,
- Ease of hybridization on existing technologies,

**but...**
- Lower performances (still under improvement),
- Industrial field under construction.
π-conjugated organic materials

Unique properties:
- Electrical properties of semiconductors and conductors (if doped),
- High absorption coefficients of organic materials,
- Mechanical properties of polymers,
- Ease of process of polymers.
Light harvesting: the role of excitons

Excitons = **bound** hole/electron pairs

<table>
<thead>
<tr>
<th></th>
<th>Permittivity</th>
<th>Exciton type</th>
<th>Exciton binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Si</td>
<td>12</td>
<td>Wannier-Mott (c)</td>
<td>&lt;0.05eV</td>
</tr>
<tr>
<td>Organic materials</td>
<td>3-4</td>
<td>Frenkel (a) or Charge-Transfer (b)</td>
<td>0.1-1eV</td>
</tr>
</tbody>
</table>

Strong exciton delocalization
EQE>80%

Strong exciton localization
EQE<1%

« Organic devices can not copy inorganic photodiodes structures »

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Combination of Donor and Acceptor material


\[ \eta_{EQE} = \eta_{abs} \cdot \eta_{ED} \cdot \eta_{CT} \cdot \eta_{CC} \]
Planar heterojunction vs bulk heterojunction

Typical exciton diffusion length in conjugated polymers: $L_d \approx 10\text{nm}$ (Optimum domains length $\approx 2L_d$)

Bilayer heterojunction
Poorly efficient devices
EQE$\approx 1\%$

Bulk heterojunction
Highly efficient devices
EQE$\approx 50$-$100\%$

R.H. Friend et al., Nature 1995, 376, 498
A.J. Heeger et al., Science 1995, 270, 1789
Visualisation of the bulk heterojunction

Transmission Electron Microscopy (TEM)

A.J. Heeger et al., Nano Lett. 2009, 9, 230
Quantum Efficiency (1/2)

\[ IQE = \frac{J_{bias}/q}{P_{abs} \lambda / hc} \]

\( P_{abs} \) absorbed light

\[ EQE \text{ or } IPCE = \frac{J_{bias}/q}{P_0 \lambda / hc} \]

\( P_0 \) incident light

A.J. Heeger et al, Nat. Photonics 3 (2009), 297
Quantum Efficiency (2/2)

“Major impact of materials and blend morphology”

Y. Kim et al., Nat. Mater., 2006, 5, 197

Regioregular P3HT

Amorphous P3HT

Reverse dark current

- Topological defects (pinholes, spikes, dusts),
- Injection from electrodes: barrier height,
- Gap states (thermal generation, tunneling current),
- Unintentional doping,
- Morphology (material percolation),
- Ground state charge transfer.

Charge generation through gap states

Defects (scratch) revealed by Dark Lock In Thermography

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Reverse dark current: impact of contact barrier height

Others figures of merit

Photocurrent linearity

- Low light intensity $\Rightarrow$ Photocurrent mainly limited by traps,
- High light intensity $\Rightarrow$ photocurrent limited by Langevin recombination.

Response time

- Organic slower than Si
- Rooms for optimizations

Data taken from Benjamin Bouthinon PhD (CEA/IMEP)

Ref Si photodiode $\sim 50$ ns

J. Huang et al., Chapter 6, Organic Electronics in Sensors and biotechnology
Mechanical strain: organic vs inorganic photodiodes on plastic substrate

“Failure limits of organic photodiodes exceed those of a-Si:H under tension and compression strains”

T.N Ng et al., Adv. Mater. 2009, 21, 1855
Organic layer for photoconversion

Vacuum evaporation (small molecules)

Solution-process (small molecules/polymers)

« Infinity of solutions offered by organic chemical synthesis and chemical designs »
Donors polymers: Band Gap tuning

1st strategy: Planarizing the polymer backbone

Gap~2eV

aromatic

quinoid

Gap~1eV

2nd strategy: Push-Pull: combination of electron-deficient and electron-rich units


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Tuning the absorption of polymers

410 nm (3.0 eV)

1100 nm (1.1 eV)

Mario Leclerc et al., Polym. Chem., 2010, 1, 127

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Photodetection in the near-infrared

Max light harvesting near 1100nm, due to currently available materials.

Polymer (tunable band gap)

Acceptor molecule (« almost frozen »)

Driving force for charge separation

LUMO

HOMO

Optical gap

External Quantum Efficiency (%)

Wavelength (nm)

Photoconversion layer A

Photoconversion layer B

Photoconversion layer C

400 600 800 1000 1200

0

10

20

30

40

50

60

70

LUMO

HOMO

LUMO

HOMO
Acceptors: Fulleren derivatives

- Good solubility,
- Good electron mobility,
- Low lying LUMO (well matched with conventional polymeric semiconductors),
- Good miscibility with polymers,
- Low absorption in the visible.

“Current best material choice for organic bulk-heterojunction systems”

Examples of some fulleren derivatives

- Bis-[60]PCBM
- Tris-[60]PCBM
- Bis-indene
- [70]PCBM

References:
- H.W. Kroto et al., Nature 1985, 318, 162
Printing: « the » disruptive technology?

Graphic art printing techniques well adapted for organic macroelectronic:
- Thicknesses of printed layer<100nm,
- Good layer homogeneity,
- Micrometric resolution and alignment,
- Sheet to sheet or roll to roll.

(1) Screen-printing
(2) Inkjet
(3) Spray-coating
(4) Slot-die
(5) Inkjet (lab tool)
(6) Local spray coating
(7) Gravure printing

Images taken from CEA

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Some challenges about printing

**Wetting**

\( \gamma_{\text{substrate}} > \gamma_{\text{ink}} \)

**Edge effect (coffee stain)**

Film is thicker at the edge than in the middle

**Inks formulation**

**Resolutions (line/space)**

Decreasing spacing

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Printed OPD devices on large area (Gen1)

Fully printed OPD devices (>1000/sheet)

Custom printed OPD designs
Organic photodetectors on Active matrix

- Fully solution-processed and flexible visible imager (OTFT + OPD),
- Collaboration between CEA/ISORG/plastic Logic (Flexi Award 2014),
- Demo substrate size: 50x50mm,
- 96x96 pixels,
- Pixel size = 175µm,
- Pixels spacing = 200µm (<30µm for next demo),
- Process compatible with large area.
ISORG (Image Sensor ORGanic)

- 21 employees,
- Technological developments supported by CEA,
- Manufacturing plants by mid 2016,
- Customized discrete OPD and imager designs on large area, rigid and flexible substrates,
- Fields of applications: medical, industrial, scientific, security, consumer...
- Contact: laurent.jamet@isorg.fr
- Website: www.isorg.fr
Conclusions

- Organic photodetectors have gained in maturity in the last ten years, and are now on the way to be commercialized,

- Organic photodetectors take unique advantages of organic materials (opto-electronic properties and processability),

- Photoconversion from UV up to the near infrared,

- Organic photodetectors are compatible with large area and flexible substrates, and could be hybridized on many existing inorganic technologies.
Thank you for your attention