



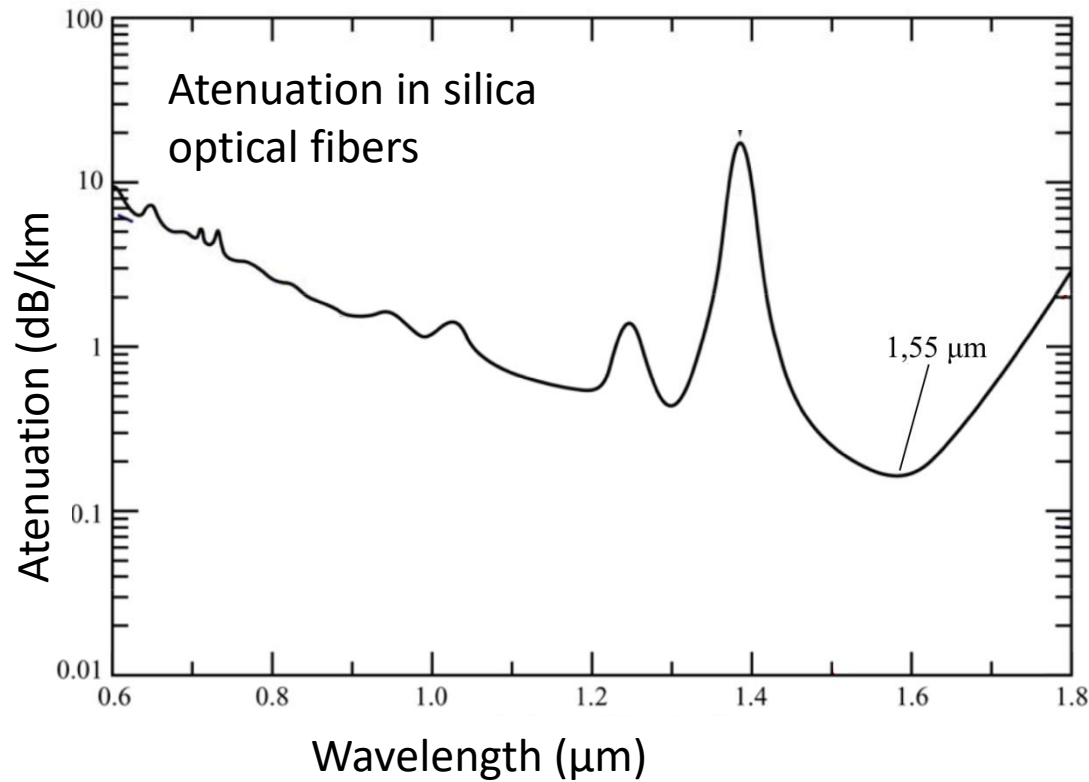
# NIR laser light sensors based on nanosilicon/organic semiconductor junctions for telecom applications

**Vedran Đerek<sup>1</sup>, Eric Daniel Głowacki<sup>2</sup>, Mateusz Bednorz<sup>2</sup>,  
Niyazi Serdar Sariciftci<sup>2</sup>, Mile Ivanda<sup>1</sup>**

<sup>1</sup> *Center of Excellence for Advanced Materials and Sensing Devicesn (CEMS),  
Ruđer Bošković Institute, Bijenička c. 54, 10000 Zagreb, Croatia*

<sup>2</sup> *Johannes Kepler University Linz, Linz Institute for Organic Solar Cells (LIOS) /  
Institute of Physical Chemistry, Altenbergerstraße 69, 4040 Linz, Austria*

# Motivation



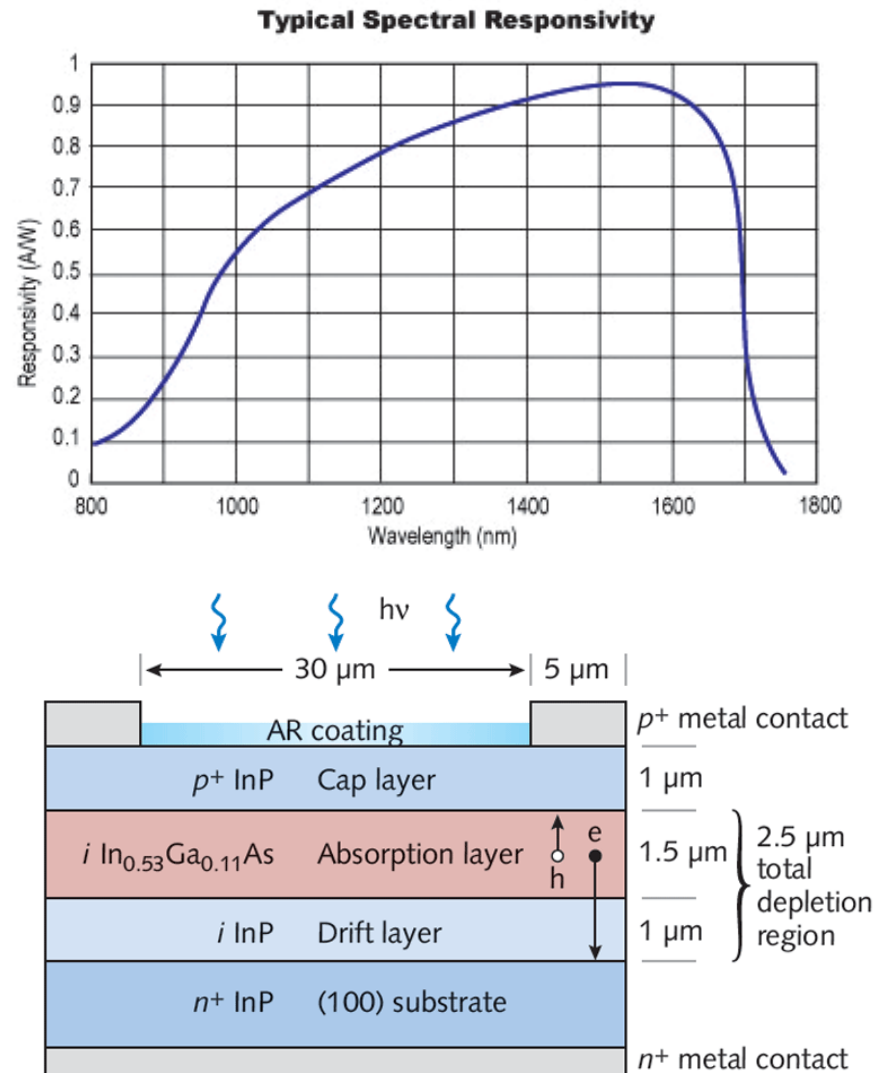
**Fiber Optics Market worth \$3.0 Billion by 2019**

The report "**Fiber Optics Market** by Application (Telecom & Broadband, Utilities, Oil & Gas, Private Data Networks, Military/Aerospace, Cable Television & Others) - Global Trends & Forecasts to 2019 " defines and segments the global fiber optics market with an analysis and forecast by region and application by value.

\*marketsandmarkets.com, September 2014, Report Code: CH 2695

# State of the art – InGaAs photodiode

- Tunable band-gap
  - GaAs (1.42 eV) to InAs (0.34 eV)
- Typical range 900nm to 1700nm
- 1.3 micron and 1.55 micron sensitivity
- High Responsivity
- Both Small Area (High Speed) and Large Area
- Not Si CMOS compatible
- Expensive (MBE)
- Toxic precursors



[\\*http://goo.gl/hz2Q6Q](http://goo.gl/hz2Q6Q)  
<http://goo.gl/W7f1rl>  
<http://goo.gl/H89sZG>

# Silicon/organic hybrid heterojunction



- Silicon (p-type)
- Organic semiconductor (n-type)

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- Organic semiconductor (n-type)

## Silicon

- well- developed Si CMOS technology

if micro/nano structured:

- large surface area
- light trapping
- nano-scale phenomena

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## Organic semiconductor thin films

- electronics with carbon-based materials
- chemically **tunable electronic properties**
- easy and cheap processing
- low environmental impact
- low material usage

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**Hybrid electronics**

integrating advantages of organics with silicon-based electronics - **going beyond Si**

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integrating advantages of organics with silicon-based electronics - **going beyond Si**

**+ advantages of nanostructuring of Silicon**



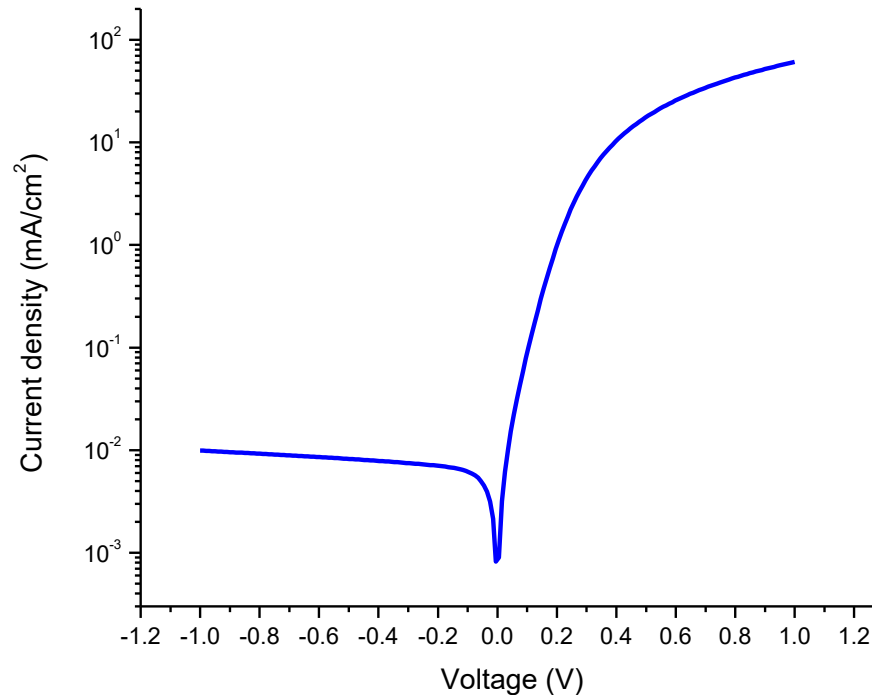
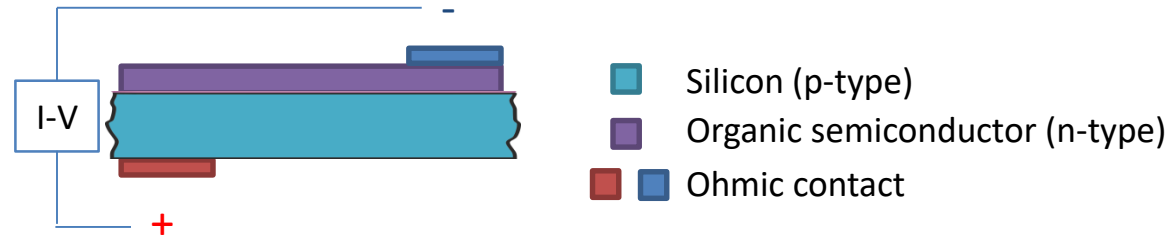
# Si/organic hybrid heterojunction electronic devices

Example: diode



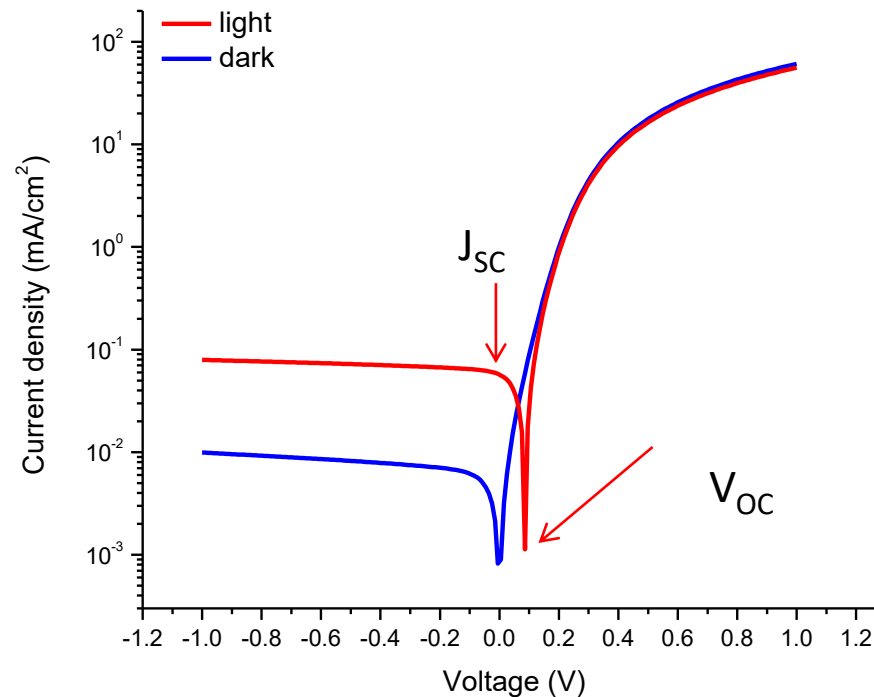
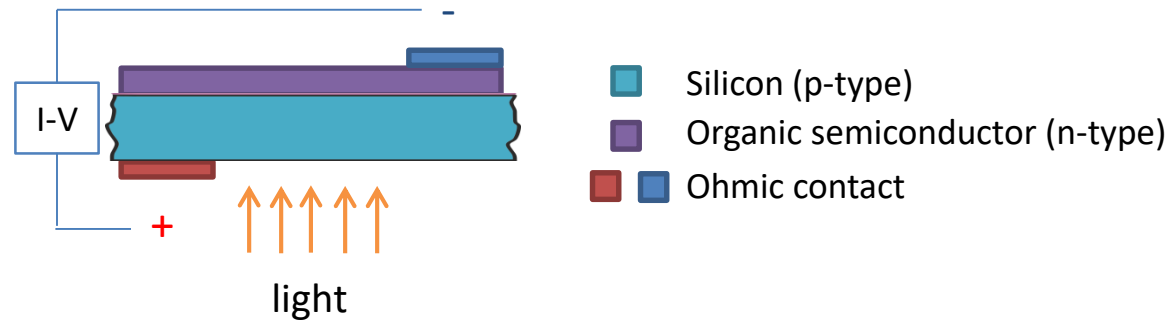
# Si/organic hybrid heterojunction electronic devices

Example: diode

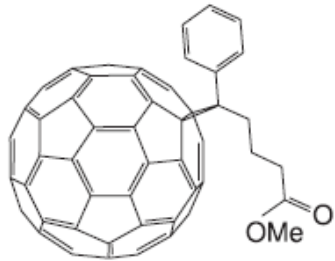


# Si/organic hybrid heterojunction electronic devices

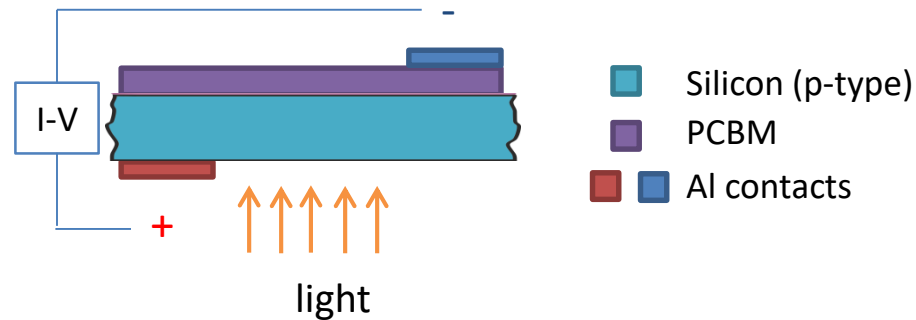
Example: photo-diode



# Si/PCBM photodiode



PCBM - Phenyl-C61-butyric  
acid methyl ester



- G. Matt et. al., LIOS, 2004-2009\*
- Si/Fullerene derivative (PCBM)
- Solution processed
  - Low device yield
  - LN<sub>2</sub> cooled

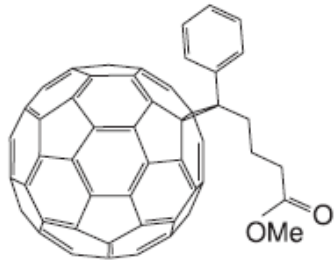
\*Sensing Infrared Light with an Organic/Inorganic Hetero-junction

G. Matt, T. Fromherz, G. Goncalves, C. Lungenschmied, D. Meissner, N.S. Sariciftci

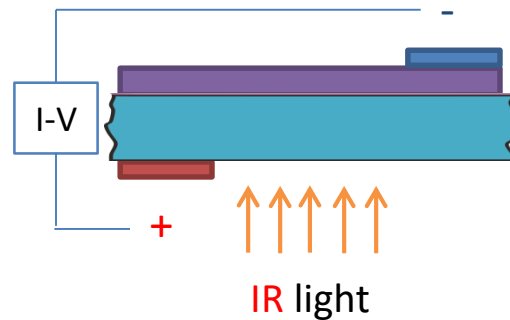
Interface Controlled Organic Thin Films, Springer Proceedings in Physics, Vol 129 (2009), 153

# Si/PCBM photodiode

Responsivity:  $10^{-6}$  A/W (room temperature, 1550 nm/0.8 eV)



PCBM - Phenyl-C61-butyric acid methyl ester



Silicon (p-type)  
 PCBM  
 Al contacts

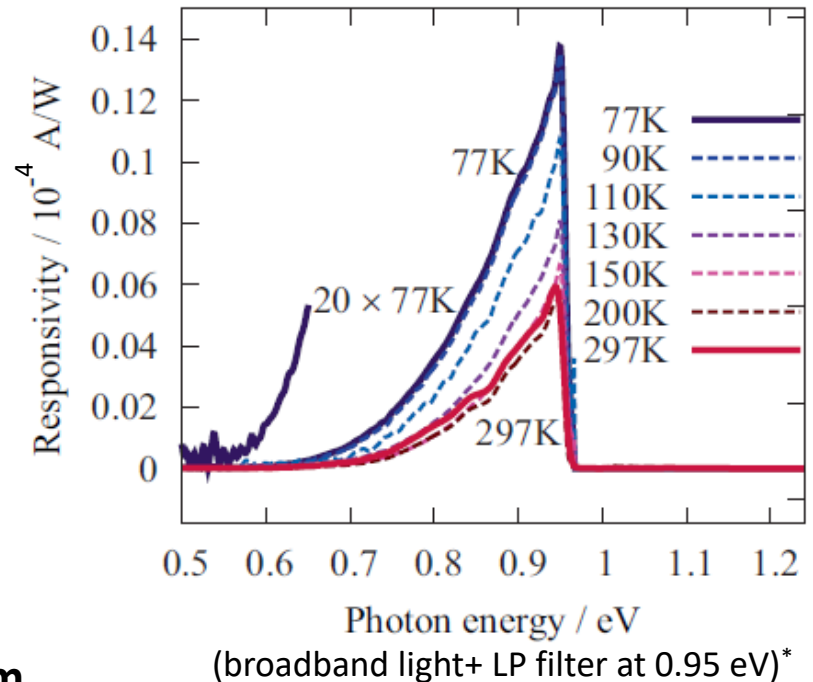
- G. Matt et. al., LIOS, 2004-2009\*
- Si/Fullerene derivative (PCBM)
- Solution processed
  - Low device yield
  - LN<sub>2</sub> cooled

Si: 1.1 eV  
PCBM: 2.4 eV

**Sub-bandgap photo current generation**

→ going beyond silicon ✓

→ possible important applications – telecom

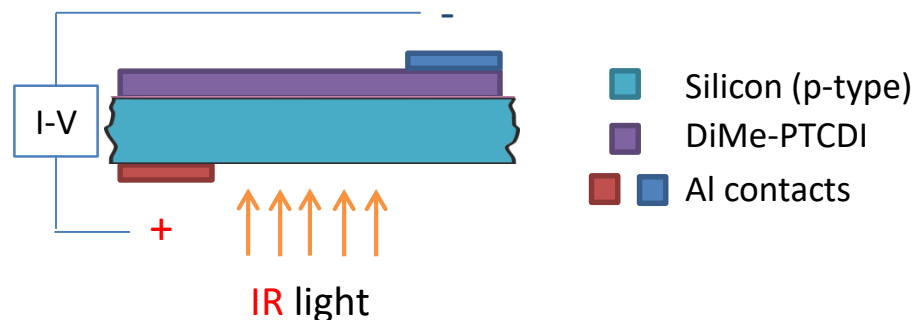
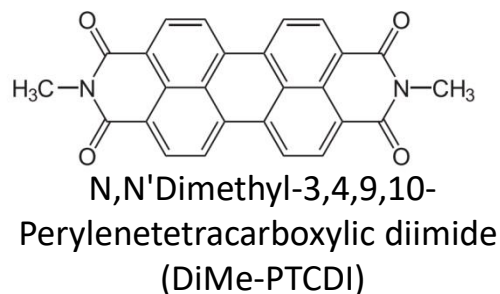


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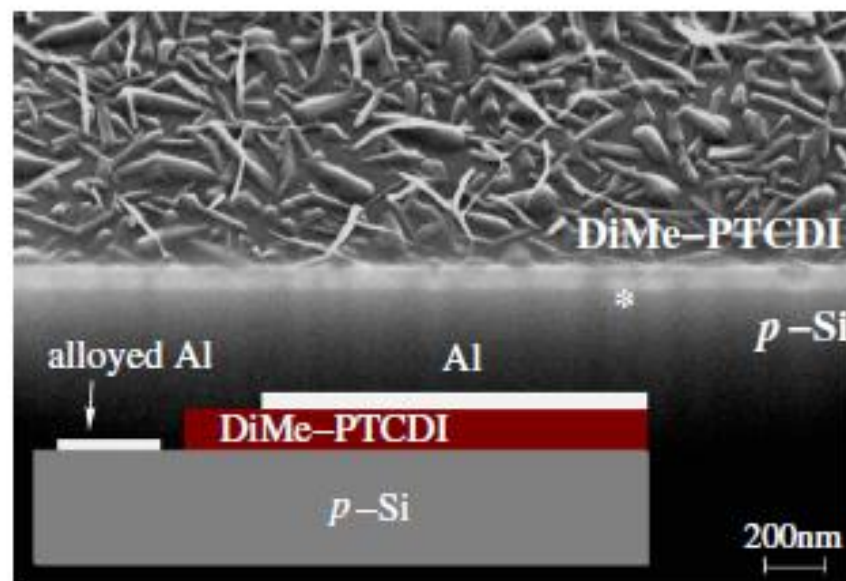
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Interface Controlled Organic Thin Films, Springer Proceedings in Physics, Vol 129 (2009), 153

# Si/DiMe-PTCDI photodiode

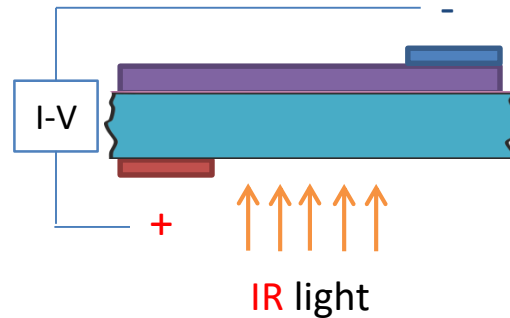
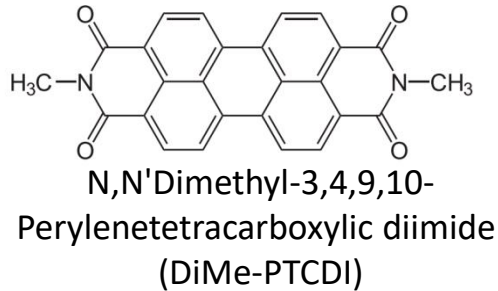


- Improvement by vacuum deposition of organic films (hot-wall epitaxy)
- Si/PCBM, Indigo, Tyrian Purple, DiMe-PTCDI



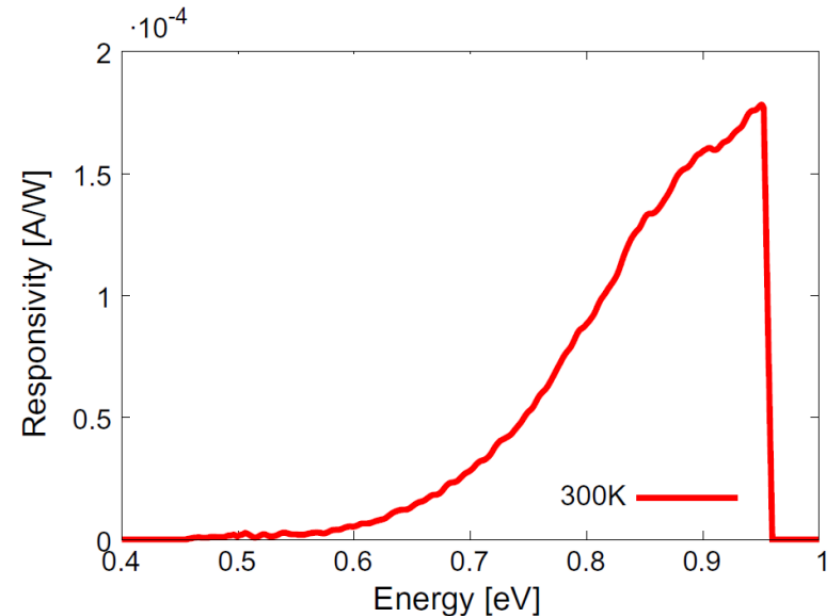
# Si/DiMe-PTCDI photodiode

Responsivity:  $10^{-4}$  A/W (room temperature, 1550 nm/0.8 eV)



■ Silicon (p-type)  
■ DiMe-PTCDI  
■ Al contacts

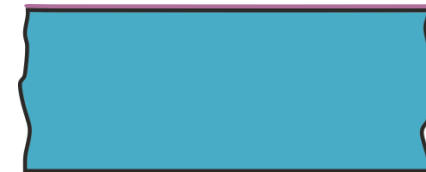
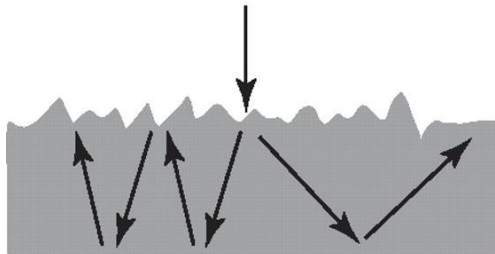
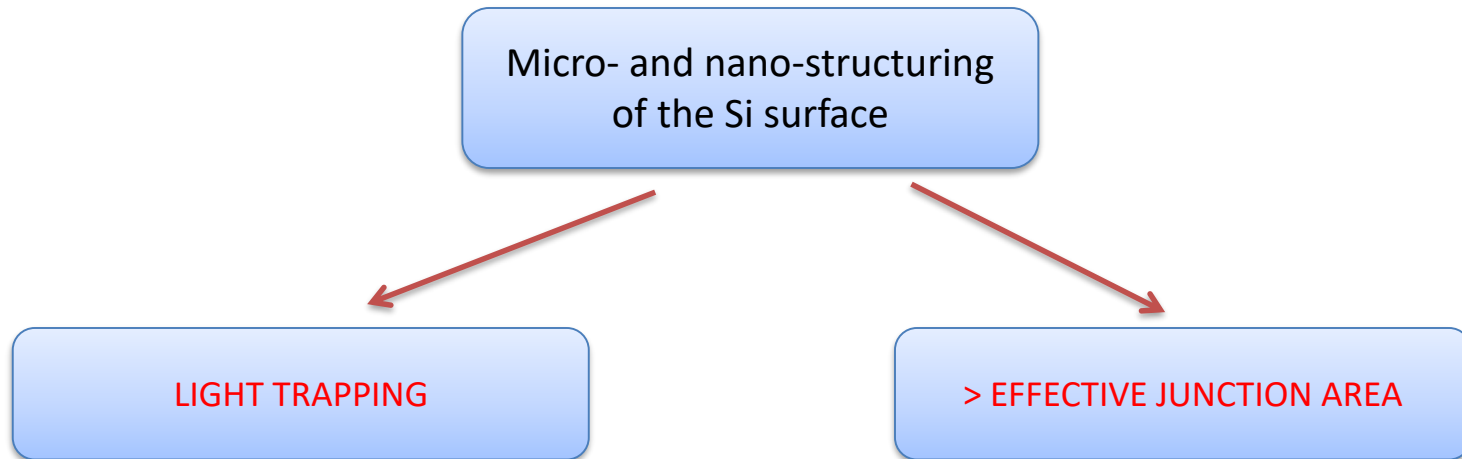
- Improvement by vacuum deposition of organic films (hot-wall epitaxy)
- Si/PCBM, Indigo, Tyrian Purple, DiMe-PTCDI
- Room-temperature diodes
- Device yield close to 100%
- >20-fold improved responsivity over 1<sup>st</sup> gen (0.2 mA/W at 300 K)



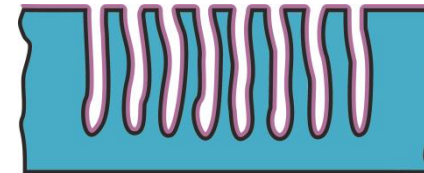
**Optimization of the organic layer**

→ approaching the limits of commercial usability ✓ (broadband light+ LP filter at 0.95 eV)

# Optimization of Si in hybrid heterojunction



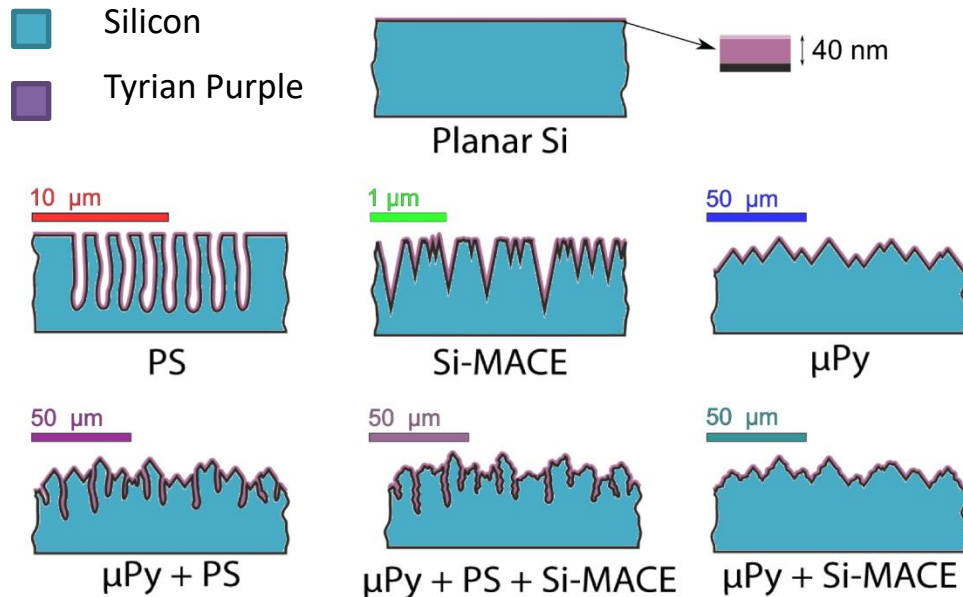
vs.





# Micro- and nano-structuring of the Si surface

- methods of wet chemistry -

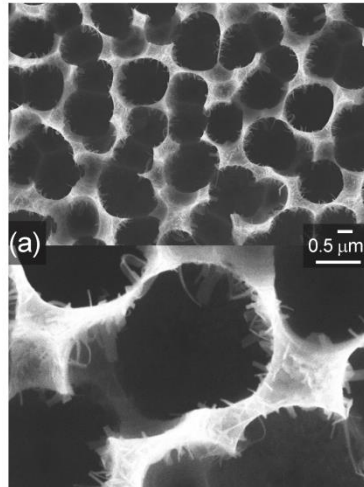


- Porous Si by anodisation in HF
- Silicon metal assisted chemical etching
- Si micropylramids by anisotropic KOH/IPA etch of (100) Si
- Hierarchical structures
  - Micropylramids+porous Si
  - Micropylramids+porous Si+MACE
  - Micropylramids+MACE

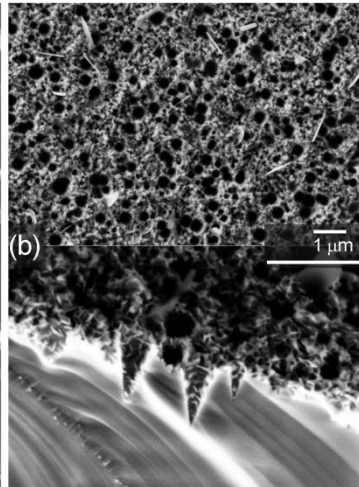
**Both micro- and nano-scaled features**

# Micro- and nano-structuring of Si surface

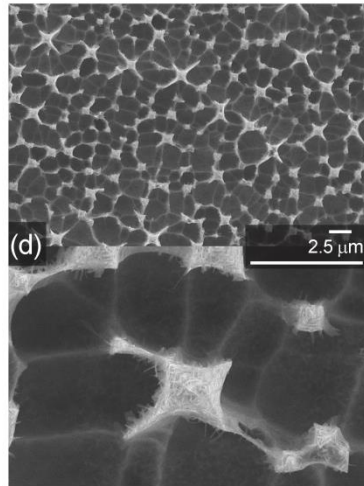
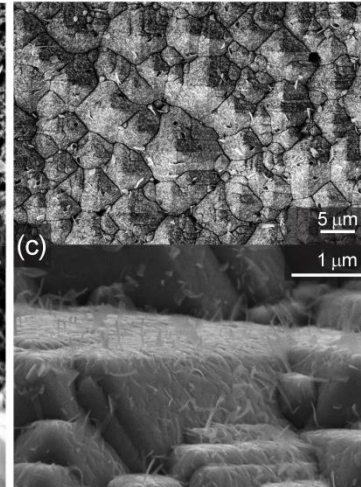
Porous Silicon



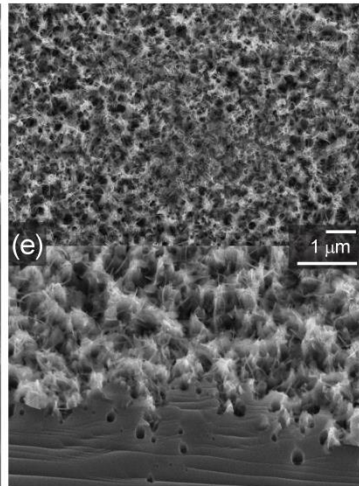
Si MACE



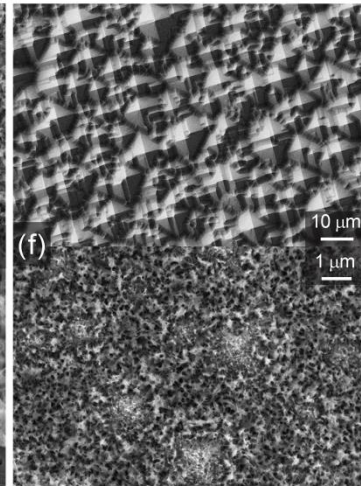
Si micropylramids



Micropylramids+PS

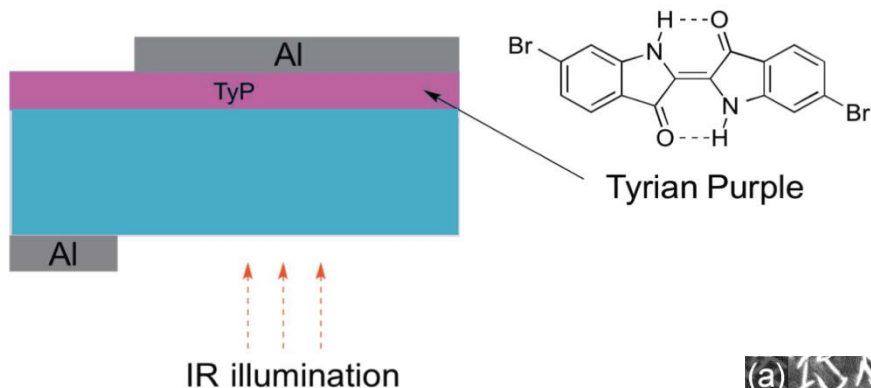


Micropylramids+MACE

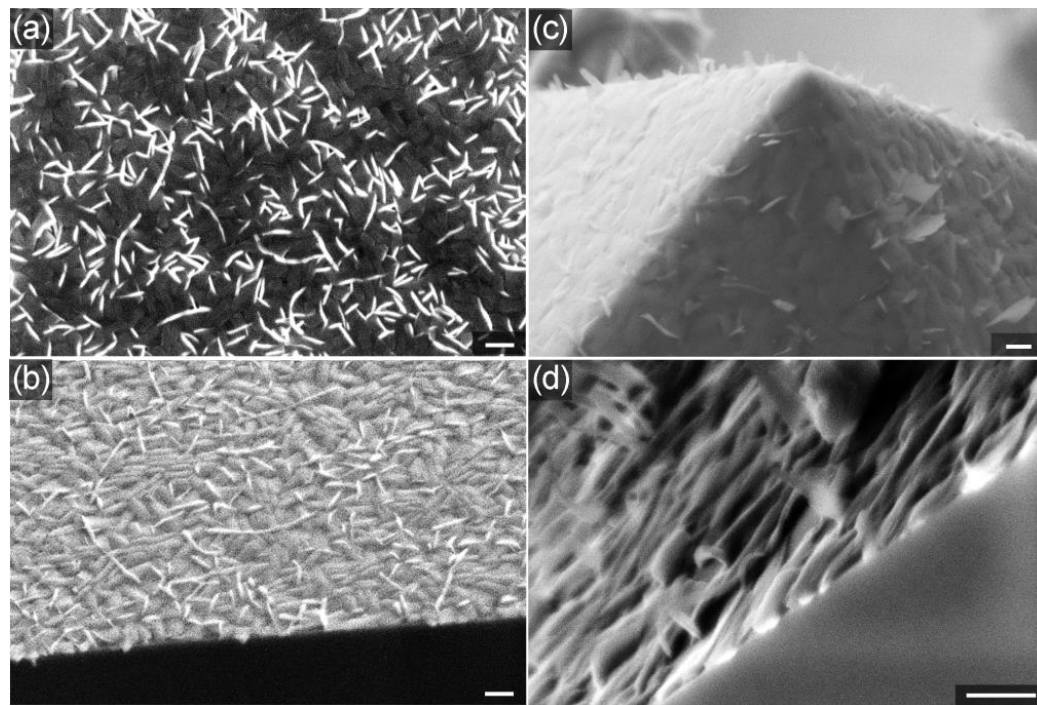
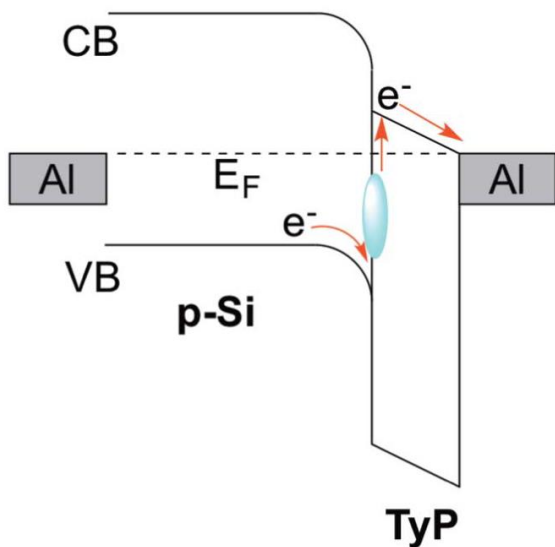


Micropylramids+MACE  
+ Porous Si

# Structured Si/Tyrian Purple photodiode

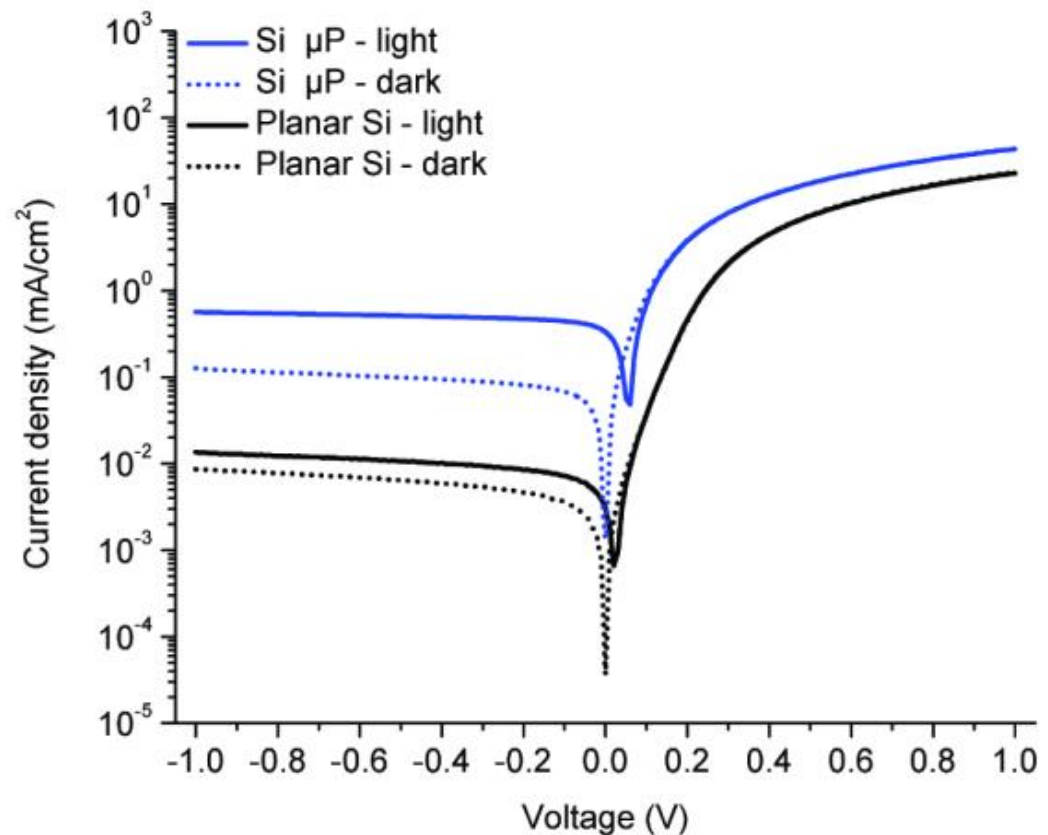


- 6,6'-dibromoindigo – Tyrian Purple
- Hydrogen-bonded pigment
- n-type organic semiconductor
- Thin films by hot-wall epitaxy



# Structured Si/Tyrian Purple photodiode

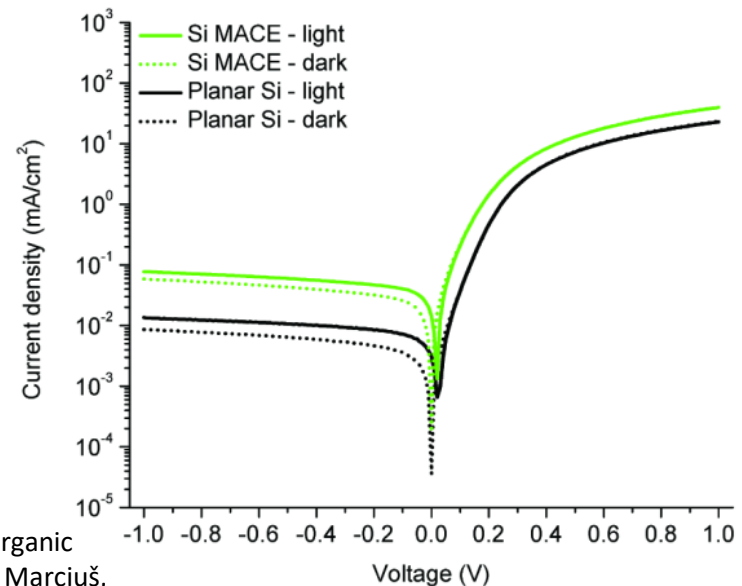
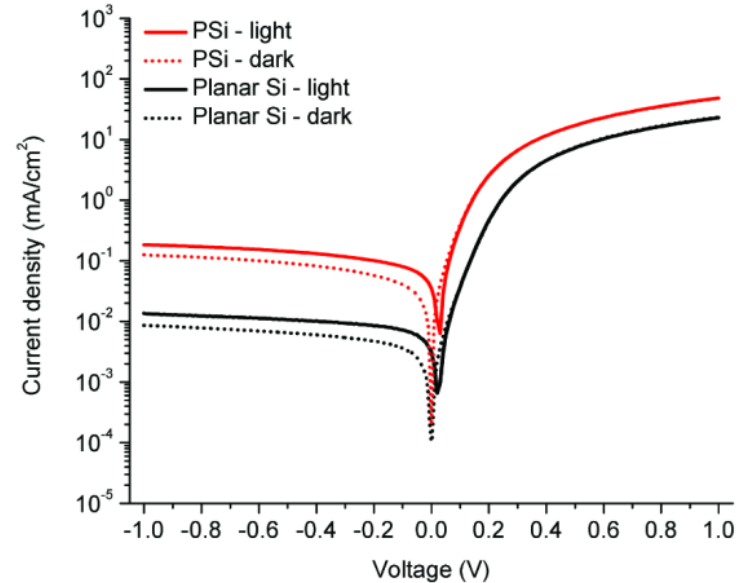
- Up to **700-fold** increase in short-circuit photocurrent over planar diodes
- Highest responsivity:  
**silicon micropylramids/TyP**
- Responsivity: **4 mA/W** at 1,55  $\mu\text{m}$  (room temperature, -1 V biased)
  - ~100-fold increase over gen 2
  - ~1000-fold increase over gen 1
- InGaAs: max 1A/W



light = 1,48  $\mu\text{m}$  laser diode (200 mW/cm<sup>2</sup>)

# Structured Si/Tyrian Purple photodiode

- Up to **700-fold** increase in short-circuit photocurrent over planar diodes
- Highest responsivity:  
**silicon micropyramids/TyP**
- Improvement for all methods of structuring

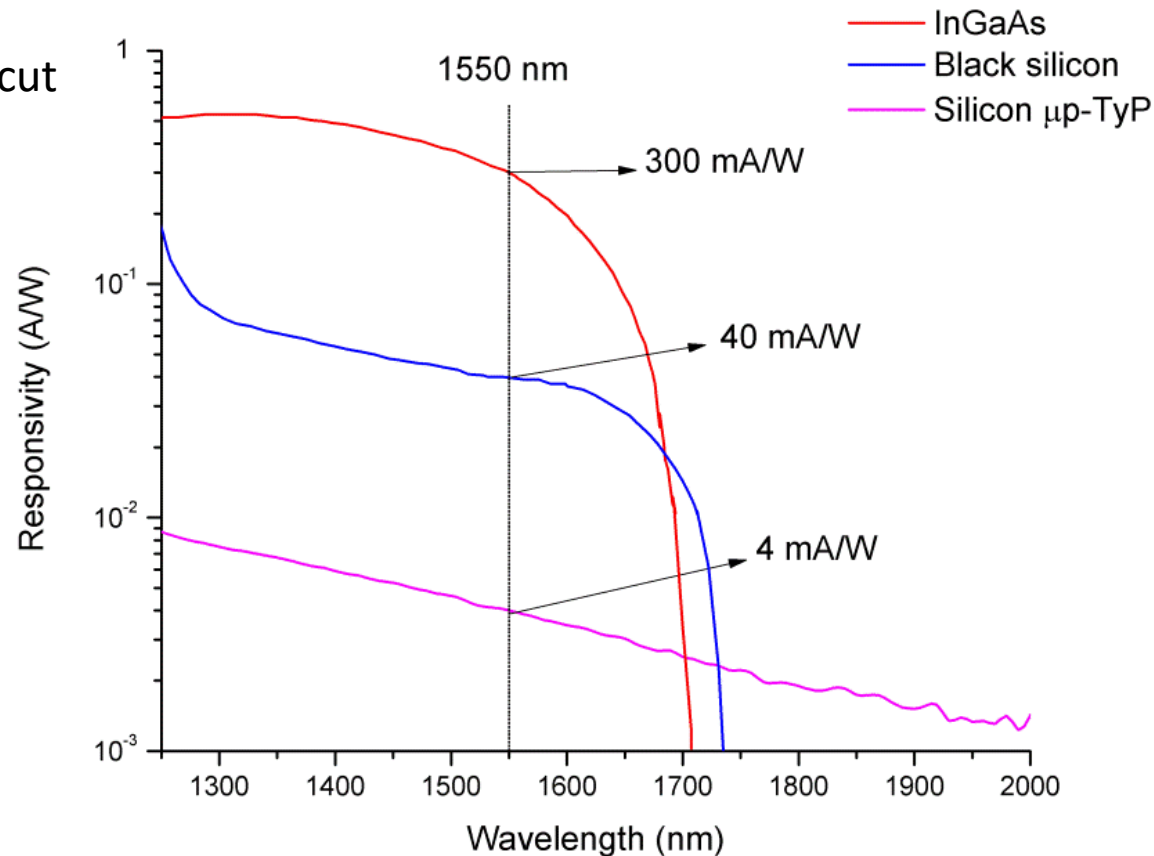


Enhanced near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors, V. Đerek, E. D. Głowacki, M. Sytnyk, W. Heiss, M. Marciaś, M. Ristić, M. Ivanda, and N. S. Sariciftci, Appl. Phys. Lett. 107, 083302 (2015)

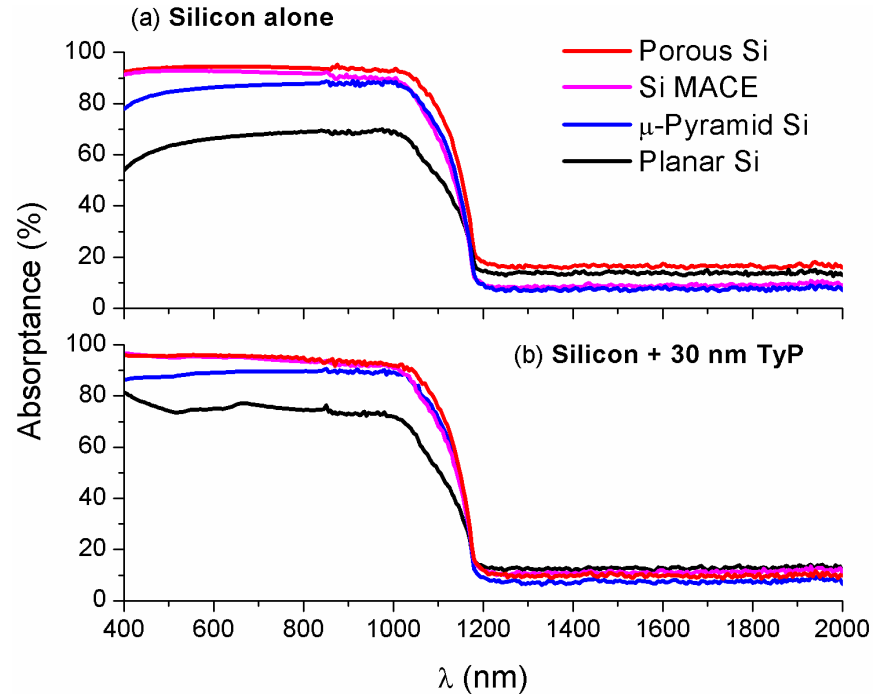


# Structured Si/Tyrian Purple photodiode

- Up to **700-fold** increase in short-circuit photocurrent over planar diodes
- Highest responsivity:  
**silicon micropyramids/TyP**
- Lower responsivity than competing technologies (black Si, InGaAs)
- But, broader response and plenty of space for improvement!

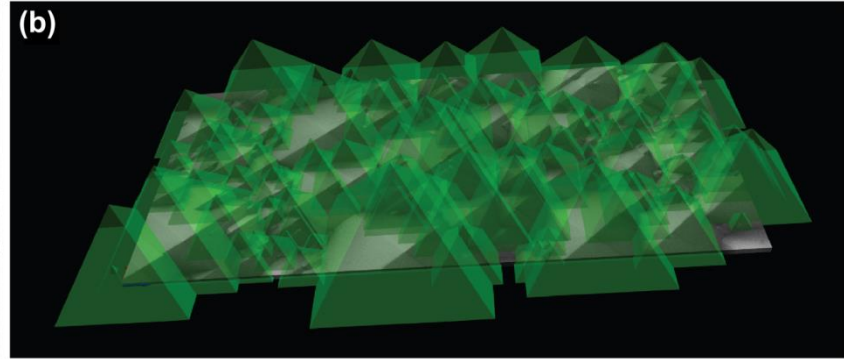
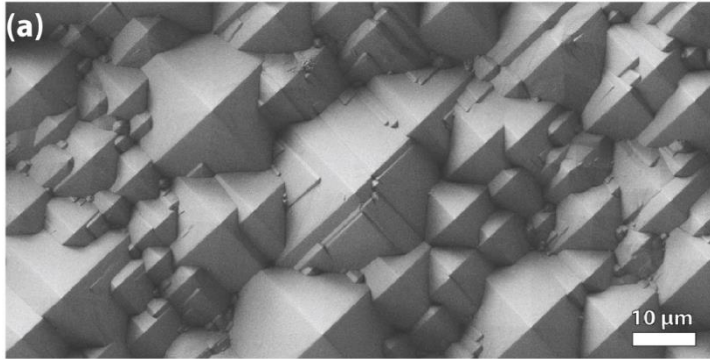


# Mechanisms of improvement



Light trapping – ruled out

# Mechanisms of improvement



- 3D model of the  $\mu$ -pyramid structured surface based on the SEM image
- Surface area: 1.55 times that of the planar sample
- $J_{\text{SC}} > 100$  times of the planar sample
- Other structuring methods give larger surface areas, but the microp pyramid samples give the highest improvement in photocurrent
- Increase of junction surface **ruled out as mechanism of improvement**



# Overview

- Silicon / organic semiconductor heterojunction – NIR photodetector
  - Origin of the effect –type II heterojunction and/or surface mid-gap states
- Micro/nano structuring increases the photoresponsivity **~100 fold**
  - Origin of the effect – not increase of surface area nor light trapping
  - Electric field effects?
- Responsivity – already interesting for telecom industry
- Work in progress

# Team

- Dr. Eric D. Głowacki (LIOS)
- Dr. Mateusz Bednorz (LIOS)
- o.Univ. Prof. Mag. Dr. DDr. h.c. Niyazi Serdar Sariciftci (LIOS)
- Dr. Mile Ivanda (IRB)

Special thanks to:

- Dr. Gebhard Matt (former LIOS)

LIOS team:

- M. Sytnyk, M. Scharber, P. Stadler, M. White, M. Havlicek, D. Apaydin, L. Leonat, C. Enengl, S. Enengl, P. Denk, G. Kalab...

IRB-CEMS team:

- D. Ristić, L. Mikac, H. Gebavi, M. Kosović, M. Marciuš, M. Ristić, S. Musić, T. Janči, V. Đurina

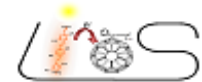
## We are grateful for the funding of this work:

Support by the Austrian Science Fund, FWF, within the Wittgenstein Prize of N. S. Sariciftci Solare Energie Umwandlung Z222-N19 and the Translational Research Project TRP 294-N19 “Indigo: From ancient dye to modern high-performance organic electronics circuits”

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This work was partially funded by the Croatian Science Foundation under the Project No. IP-2014- 09-7046



# Publications

SPRINGER PROCEEDINGS IN PHYSICS 129

## Sensing Infrared Light With an Organic/Inorganic Hetero-Junction

Gebhard J. Matt<sup>1</sup>, Thomas Fromherz<sup>1</sup>, Guillaume Goncalves<sup>2</sup>, Christoph Lungenschmied<sup>3</sup>, Dieter Meissner<sup>4</sup> and Serdar N. Sariciftci<sup>4</sup>

Phys. Status Solidi B 247, Nos. 11–12, 3043–3046 (2010) / DOI 10.1002/pssb.201000200



## Fullerene sensitized silicon for near- to mid-infrared light detection

G. J. Matt<sup>1</sup>, T. Fromherz<sup>1</sup>, M. Bednorz<sup>1</sup>, H. Neugebauer<sup>2</sup>, N. S. Sariciftci<sup>2</sup>, and G. Bauer<sup>a,1</sup>

JOURNAL OF APPLIED PHYSICS 112, 114508 (2012)



## Electrical properties of pSi/[6,6] phenyl-C61 butyric acid methyl ester/Al hybrid heterojunctions: Experimental and theoretical evaluation of diode operation

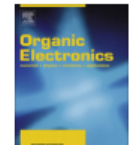
Mateusz Bednorz,<sup>1,a)</sup> Thomas Fromherz,<sup>1</sup> Gebhard J. Matt,<sup>2</sup> Christoph J. Brabec,<sup>2</sup> Markus Scharber,<sup>3</sup> and N. Serdar Sariciftci<sup>3</sup>



Contents lists available at SciVerse ScienceDirect

## Organic Electronics

journal homepage: [www.elsevier.com/locate/orgel](http://www.elsevier.com/locate/orgel)



## Silicon/organic hybrid heterojunction infrared photodetector operating in the telecom regime



Mateusz Bednorz<sup>a</sup>, Gebhard J. Matt<sup>b,\*</sup>, Eric D. Głowacki<sup>c</sup>, Thomas Fromherz<sup>a</sup>, Christoph J. Brabec<sup>b</sup>, Markus C. Scharber<sup>d</sup>, Helmut Sitter<sup>a</sup>, N. Serdar Sariciftci<sup>c</sup>

APPLIED PHYSICS LETTERS 107, 083302 (2015)

## Enhanced near-infrared response of nano- and microstructured silicon/organic hybrid photodetectors

Vedran Đerek,<sup>1</sup> Eric Daniel Głowacki,<sup>2,a)</sup> Mykhailo Sytnyk,<sup>3</sup> Wolfgang Heiss,<sup>3</sup> Marijan Marciuš,<sup>1</sup> Mira Ristić,<sup>1</sup> Mile Ivanda,<sup>1,a)</sup> and Niyazi Serdar Sariciftci<sup>2</sup>



Thank you for your kind attention!

