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Materials, devices and applications

Vincenzo Pecunia

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'Where were you when I laid the foundation of the Earth?'  $\label{eq:Job 38:4-(RSV)} \textit{Solution}$ 

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## **Preface**

The ability to sense light within a narrow wavelength range is an integral part of our visual perception, enabling us to distinguish a rich range of colours. An equivalent function in electronics is carried out by devices called narrowband photodetectors, which deliver an electric signal when interacting with light of a particular 'colour', i.e. light within a narrow wavelength window that falls in the visible, or the near-infrared, or the ultraviolet range. While in many ways mimicking our visual function (e.g. for digital photography), narrowband photodetectors have been developed over the years to address a very broad range of applications, including areas such as computer vision and chemical fingerprinting for biology, medicine, etc. Conventional semiconductors inherently lack 'colour' (i.e. narrowband) selectivity, hence a workaround has been devised to equip them with this capability: the use of input filters that block off all light except that of the target 'colour'. In spite of its technological success, this approach, however, is laden with challenges and limitations.

In recent years, organic semiconductors have emerged as a class of materials that can uniquely address the demands of narrowband photodetection. Indeed, manifold colours in nature result from  $\pi$ -conjugated molecular structures akin to those of organic semiconductors. Therefore, organic semiconductors with particular composition and structure can inherently and selectively respond to these same colours, precisely matching the scope of narrowband photodetection. In fact, this capability goes beyond the visible range and is also applicable to the ultraviolet and the nearinfrared ranges. In addition, organic semiconductors possess key processing advantages over conventional technologies, as they can be deposited over large areas (e.g. on flexible plastic foils) via simple and potentially low-cost methods (e.g. by printing and coating). All these attractive properties make organic semiconductors particularly well suited for the development of narrowband photodetectors and imagers that can be placed ubiquitously in the objects and environments of our daily lives—e.g. so as to function as smart sensors for emerging application areas. Going beyond the limitations of conventional semiconductors, organic semiconductors have consequently enabled a paradigmatic shift in narrowband photodetection technology. A rich research landscape has thus emerged, with manifold new materials, device configurations and narrowband strategies being explored.

This book arises from the need for a comprehensive and unified picture of the subject of narrowband organic photodetection. While a few review articles covering this area have appeared in scientific journals over the years, such works have placed emphasis on particular aspects and are specialistic in nature. Additionally, the relevant literature is particularly heterogeneous, not only because it presents a wide range of materials, narrowband strategies and descriptions thereof, but also because it provides performance figures in a way that may not allow a straightforward comparison between different works. Considering that by now narrowband organic photodetection builds on a vast body of literature and varied interdisciplinary knowledge, the need is thus manifest for a comprehensive and unified treatment of this topic. Addressing this very need, the present book in fact constitutes—to the

best of the author's knowledge—the first ever and most extensive monograph on the subject. For the sake of comprehensiveness, this book covers organic photodetectors with narrowband character in the visible, near-infrared and ultraviolet ranges. Aiming for a self-contained treatment, this book additionally covers the background of pertinent physical, material and device engineering aspects. In order to overcome the heterogeneity of the literature, this book presents a unified treatment of the narrowband strategies employed with organic semiconductors, and offers a contextualisation of the material innovations in terms of families of compounds and molecular design approaches. In the same direction, this book additionally offers a comprehensive and cross-sectional analysis of the literature, highlighting performance trends in relation to material and device physics aspects, and providing an extensive tabulated collection of performance data.

In regard to its structure, the present book takes the reader on a journey from the basic concepts to the latest scientific literature on narrowband organic photodetection, while covering the subject from several angles-materials, physical properties, device physics and engineering, and technological implications. The foundation layer (chapter 1) illustrates the motivation for an organic route to narrowband photodetection. It does so by surveying the wealth of relevant application areas and the properties that make organic semiconductors particularly attractive for such applications. The book then presents a discussion of the essentials of organic semiconductors and photodetectors thereof (chapter 2). This discussion identifies the key aspects underlying the capability of organic semiconductors to deliver narrowband photodetection. After presenting the physical mechanisms through which light in such materials is converted into an electric signal, the devices which implement this functionality are illustrated, along with the corresponding performance metrics. The specifics and significance of narrowband photodetection are then presented (chapter 3). This is coupled with a detailed treatment of the many narrowband strategies that have been pursued with organic semiconductors. The book finally delivers an in-depth analysis of the literature implementations of organic narrowband photodetectors and associated integration works. The discussion examines the numerous aspects involved: materials and processing (chapter 4); performance metrics and underlying trends (chapter 5); and integration schemes for specific applications (*chapter* 6).

The comprehensive and harmonised treatment of narrowband organic photodetection provided in this book is particularly relevant to researchers and technologists active in the area of photodetection and/or organic semiconductors. In view of its extensive survey of the literature, this book additionally serves as a useful reference text for experts and practitioners working in organic semiconductors, printed and flexible optoelectronics, and/or sensors and imaging devices. Finally, by covering both the basics and the latest trends in organic narrowband photodetection, this book is also relevant to physics, chemistry and engineering students and enthusiasts, especially those interested in organic semiconductors, optoelectronics and/or colour/imaging science.

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## Author biography

### Vincenzo Pecunia



Vincenzo Pecunia is a Principal Investigator and an Associate Professor at the Institute of Functional Nano & Soft Materials, Soochow University (China). He earned his Bachelor's and Master's in Electronics Engineering from Politecnico di Milano (Italy). Subsequently, he was at the Cavendish Laboratory of the University of Cambridge (UK) for over six years. There he obtained his PhD in Physics and also worked as a postdoctoral scientist.

His research has addressed the physics of printable optoelectronic materials—e.g. organic, perovskite and amorphous-metal-oxide semiconductors—and their application to optoelectronics. The Thin-Film Optoelectronics Group that he leads researches the charge transport physics and photoelectronic properties of solution-processed semiconductors, related optoelectronic devices (e.g. solar cells, photodetectors and thin-film transistors) and their application to large-area electronics. His research has led to numerous publications in top scientific journals. Additionally, drawing from his research experience, he has also lead-authored a monograph for Cambridge University Press titled Organic and Amorphous-Metal-Oxide Flexible Analogue Electronics.

## Abbreviations<sup>1</sup>

A Acceptor

AI Artificial Intelligence BHJ Bulk heterojunction

CCN Charge collection narrowing

CCNx Charge collection narrowing with gain

CFA Colour filter array

CIE Commission Internationale de l'Eclairage

c-Si Crystalline silicon CT Charge transfer

D Donor

D:A BHJ between a D and an A D|A PHJ between a D and an A DBR Distributed Bragg reflector

EA Electron affinity

EQE External quantum efficiency
ETL Electron-transport layer
FWHM Full width at half maximum
HOMO Highest occupied molecular orbital

HTL Hole transport layer InpF Input optical filtering IntF Internal filtering

IntF-1 Single-component internal filtering

IntF-1x Single-component internal filtering with gain

IOEF Internal optoelectronic filter

IoT Internet of Things
IP Ionisation potential
IQE Internal quantum efficiency
LDR Linear dynamic range

LUMO Lowest unoccupied molecular orbital MEMS Micro-electro-mechanical system

NBA Narrowband absorption

NBAx Narrowband absorption with gain

NEP Noise equivalent power

NIR Near infrared

NIRS Near-infrared spectroscopy

NP Nanoparticle NR Nanorod NW Nanowire

OLED Organic light emitting diode PCL Photoconversion layer PHJ Planar heterojunction PMT Photomultiplier tube

QD Quantum dot R2R Roll-to-roll

<sup>&</sup>lt;sup>1</sup> Abbreviations of chemical compounds referred to in the text are not listed here, as they follow the relevant journal papers or the dominant nomenclature in the literature.

RCResistor-capacitor Red-green-blue Root mean square RGB RMS

UV

Ultraviolet
Visible light communications
Microcavity VLC

μC μL Microlens

## **Symbols**

[adj]Spectral range adjacent to [targ]BNoise measurement bandwidthcSpeed of light in free space $C_p$ Photodetector capacitance

D Detectivity

 $D^*$  Specific detectivity E Electric field

 $E_B$  Exciton binding energy  $E_g^{(opt)}$  Optical bandgap  $EQE_p$  Peak EQE

fModulation frequency $f_{3dB}$ 3dB frequency/bandwidth $f_{RC}$ RC-limited 3dB frequency

 $f_{tr}$  Transit-time-limited 3dB frequency

 $FWHM_{\alpha}$ FWHM of  $\alpha(\lambda)$  $FWHM_{EQE}$ FWHM of  $EQE(\lambda)$  $FWHM_R$ FWHM of  $R(\lambda)$  $FWHM_{Voc}$ FWHM of  $V_{oc}(\lambda)$ 

G\* Photocurrent/photoconductive gain

hPlanck constant $h\nu$ Photon energy $i_{dark}$ Dark current $i_n$ Noise current

 $i_{n,RMS}$  RMS value of the noise current

*i*<sub>ph</sub> Photocurrent

 $i_{ph,max}$  Upper photocurrent limit of the LDR  $i_{ph,min}$  Lower photocurrent limit of the LDR

 $i_{tot}$  Total photodetector current  $J_{dark}$  Areal dark current density  $J_{ph}$  Areal photocurrent density

 $J_0$  Reverse-bias saturation current density

 $egin{array}{lll} K & LDR & prefactor \\ k_B & Boltzmann & constant \\ L & Interelectrode & distance \\ \end{array}$ 

 $l_{cav}$  Geometrical length of a resonance cavity

 $L_D$  Exciton diffusion length

m Resonance ordern Ideality factor

 $\hat{n}$  Average refractive index of a resonance cavity

 $NEP_{A,\sqrt{B}}$  Noise equivalent power per unit bandwidth and area

 $NEP_{\sqrt{B}}$  Noise equivalent power per unit bandwidth  $N_e$  Number of collected photocarriers per unit time

 $N_{gen}$  Number of photogenerated electron-hole pairs per unit time  $N_p$  Number of photons incident on a photodetector per unit time

 $PB_n$  Passband of the *nth* photodetector

 $P_{opt}$  Incident optical power

 $P_{opt,max}$  Upper power limit of the LDR  $P_{opt,min}$  Lower power limit of the LDR

q Elementary charge

R Responsivity  $R_L$  Load resistance  $R_p$  Peak responsivity

 $R_{PD}(\lambda)$  Unfiltered spectral responsivity in an InpF photodetector

 $R_s$  Series resistance

 $R_{sh}$  Parallel (shunt) resistance

 $S_{ct,ij}$  Spectral crosstalk between photodetectors i and j

 $S_{i_n,g-r}$  Generation-recombination-noise power spectral density

 $S_{i_n,shot}$  Shot-noise power spectral density  $S_{i_n,th}$  Thermal-noise power spectral density

 $S_n$  Noise power spectral density

 $S_{n,w}$  White-noise power spectral density  $S_{n,flicker}$  Flicker-noise power spectral density

 $S_{sct}$  Spectral self-crosstalk

 $SRR_R(\lambda_{p,R}, \lambda_{adi})$  Responsivity spectral rejection ratio

 $SRR_{EQE}(\lambda_{p,EQE}, \lambda_{adj})$  EQE spectral rejection ratio

S/N Signal to noise ratio T Absolute temperature [targ] Target spectral range

 $T_{if}(\lambda)$  Transmittance of input filter

 $t_{fall}^{(50)}$  50% fall time  $t_{fall}^{(10.90)}$  10%–90% fall time  $t_r^{(10.90)}$  10%–90% response time

 $t_r^{(50)}$  50% response time  $t_r^{(99.5)}$  99.5% response time  $t_{rise}^{(10.90)}$  10%–90% rise time  $t_{rise}^{(50)}$  50% rise time

 $t_{tr}$  Average carrier transit time

 $t_{tr,p}$  Electron transit time  $t_{tr,p}$  Hole transit time  $V_{BIAS}$  Applied voltage  $V_{oc}$  Open circuit voltage  $W_F^{(a)}$  Anode workfunction  $W_F^{(c)}$  Cathode workfunction  $\alpha$  Absorption coefficient

 $\hat{\alpha}$  Effective absorption coefficient

 $\hat{a}_{act}$  Effective absorption coefficient of the photoactive material

 $\alpha_p$  Peak absorption coefficient

 $\gamma$  Exponent of the power-law relationship between  $i_{ph}$  and  $P_{opt}$ 

 $\eta_{abs}$  Absorption efficiency  $\eta_{coll}$  Collection efficiency

 $\eta_{diff}^{(ex)}$  Exciton diffusion efficiency  $\eta_{diss}^{(ex)}$  Exciton dissociation efficiency

 $\eta_{extr}$  Extraction efficiency

 $\eta_{gen}$  Photocarrier generation efficiency  $\eta_{gen}^{(ex)}$  Exciton generation efficiency

 $\eta_{tr}$  Transport efficiency

 $\theta$  Internal angle of incidence

 $\lambda$  Wavelength

 $\lambda_{adj}$  Selected wavelength in [adj]  $\lambda_m$  Resonance wavelength  $\lambda_{onset}$  Absorption onset

 $\lambda_p$  Peak absorption wavelength  $\lambda_{p,EOE}$  EQE peak wavelength

 $\lambda_{p,R}$  Responsivity peak wavelength

 $\mu_n$  Electron mobility  $\mu_p$  Hole mobility

 $\Sigma$  Cross-sectional area of a photodiode

 $\tau$  Effective optical depth of the mirrors in a  $\mu$ C-based device

 $\tau_n$  Electron lifetime