# Device Architecture and Materials for Organic Light-Emitting Devices

Sarah Schols

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## Targeting High Current Densities and Control of the Triplet Concentration

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# Preface

This book is a reprint of the manuscript entitled "Device architecture and materials for organic light-emitting devices", that was submitted to the jury deciding on the achievement of my PhD at the Katholieke Universiteit Leuven in Belgium. It is the result of five years fascinating research at imec in Leuven, Belgium, between 2004 and 2009. Different people contributed to my work and I want to show gratitude to all of them. First, I would like to thank my two promoters, Prof. Paul Heremans (KUL/imec) and Prof. Robert Mertens (KUL/imec) who gave me the opportunity to start a PhD in an inspiring environment as imec. I am also very grateful to the other PhD jury members who took the time to carefully read my manuscript: Prof. Mark van der Auweraer (KUL), Prof. Jan Engelen (KUL), Prof. Henning Sirringhaus (University of Cambridge), Prof. Uli Lemmer (Universität Karlsruhe) and Prof. Adhemar Bultheel (KUL). My special thanks go to Andrey Kadashchuk for introducing me into the exciting world of spectroscopy and for the many scientific discussions, but of course also all other colleagues of the Polymer and Molecular Electronics group at imec with whom I worked together during my PhD are gratefully acknowledged. Besides, I would like to thank Thilo Stöferle (IBM Research Zurich), Tobias Plötzing (RWTH Aachen) and Thorsten Wahlbrink (AMO GmbH) for the nice collaboration. The FWO is acknowledged for the financial support. Finally, I warmly thank my family for their continuous support and interest in my work.

Sarah Schols

# Contents

# List of Symbols and Abbreviations

| | |
|---|---|
| $\alpha$ | (*Depending on context*) 1. Loss coefficient ($cm^{-1}$) 2. Absorption coefficient ($cm^{-1}$) |
| $\alpha_{photon}$ | Photon loss ($cm^{-1}$) |
| $A(\lambda)$ | Constant related to the cross-section for spontaneous emission |
| $c$ | (*Depending on context*) 1. Concentration (wt%) 2. Speed of light in free space ($299.79 \times 10^6$) (m/s) |
| $C_{ox}$ | Gate dielectric capacitance per unit area ($F/m^2$) |
| $\delta$ | Density ($g/cm^3$) |
| $\Delta E_T$ | Difference in triplet energy (eV) |
| $\Delta G^\circ$ | Gibbs free energy (kJ/mol) |
| $\Delta r$ | Nuclear displacement (Å) |
| $\Delta E_{ST}$ | Singlet-triplet splitting (eV) |
| $\varepsilon(\lambda)$ | Absorption spectrum |
| $\varepsilon_r$ | Relative dielectric constant |
| $\eta_{ext}$ | External quantum efficiency (%) |
| $\eta_{int}$ | Internal quantum efficiency (%) |
| $\eta_{coupling}$ | Out-coupling efficiency (%) |
| $E^\circ$ | Standard cell potential (V) |
| $E_{phot}$ | Average photon energy (eV) |
| $F$ | Faraday constant (≈96485) (J/(V mol)) |
| $f(\lambda)$ | Photoluminescence spectrum |
| $g$ | Gain coefficient ($cm^{-1}$) |
| $\gamma$ | Charge balance |
| $\Gamma$ | Optical confinement factor (%) |
| $h$ | Planck's constant ($\approx 6.626 \times 10^{-34}$) (Js) |
| $I$ | (*Depending on context*) 1. Light intensity ($W/cm^2$) 2. Current (A) |
| $I_{ds}$ | Drain to source current (A) |
| $I_p$ | Pumping intensity ($J/cm^2$) |
| $J$ | Current density ($A/cm^2$) |

| | |
|---|---|
| $k_{ET}^{F}$ | Förster energy transfer rate ($s^{-1}$) |
| $k_{ET}^{D}$ | Dexter energy transfer rate ($s^{-1}$) |
| $K$ | Constant proportional to the orbital overlap between host and guest |
| $\kappa$ | Polarization factor |
| $l$ | Distance traveled in the gain medium (cm) |
| $L$ | (*Depending on context*) 1. Sum of the van der Waals radii of host and guest (nm)<br>2. Transistor channel length (μm) |
| $L_{diff}$ | Exciton diffusion length (nm) |
| $\lambda$ | Wavelength (nm) |
| $\lambda_{Bragg}$ | Bragg wavelength (nm) |
| $\lambda_{exc}$ | Excitation wavelength (nm) |
| $\Lambda$ | Modulation periodicity of a DFB resonator (nm) |
| $m$ | DFB order number |
| $M$ | Molecular weight (g/mol) |
| $\mu$ | Mobility ($cm^2/Vs$) |
| $n$ | (*Depending on context*) 1. Index of refraction<br>2. Overall number of electrons exchanged between an oxidizing and reducing agent |
| $n_{eff}$ | Effective refractive index |
| $N_{exc}$ | Density of excited states ($cm^{-3}$) |
| $N_{th}$ | Exciton density at the laser threshold ($cm^{-3}$) |
| $N_A$ | Avogadro's constant ($\approx 6.022 \times 10^{23}$) ($mol^{-1}$) |
| $v_i$ | Vibrational energy level (eV) |
| $p$ | Pressure (torr) |
| $\phi_{PL}$ | Absolute photoluminescence efficiency (%) |
| $P_{meas}$ | Measured light power (W) |
| $P_{tot}$ | Total optical power (W) |
| $\Psi_{molecule}$ | Wavefunction of a molecule |
| $\Psi_{electronic}$ | Electronic component of the molecular wavefunction |
| $\Psi_{nuclear}$ | Nuclear component of the molecular wavefunction |
| $q$ | Elementary charge ($\approx 1.602 \times 10^{-19}$) (C) |
| $Q$ | Resonator quality factor |
| $R$ | Mean distance between host and guest (nm) |
| $R_0$ | Effective Förster radius (nm) |
| $r_{st}$ | Singlet/triplet ratio of excitons |
| $\rho$ | Average distance between dopant molecules (nm) |
| $S_i$ | Singlet exciton energy level (eV) |
| $S$ | Subthreshold slope (V/dec) |
| $\sigma_{RZ}$ | Exciton density per unit area in the recombination zone ($cm^{-2}$) |
| $\sigma_{SE}(\lambda)$ | Cross-section for stimulated emission ($cm^2$) |
| $\sigma_{TT}$ | Cross-section for triplet-triplet absorption ($cm^2$) |
| $T_i$ | Triplet exciton energy level (eV) |

| | |
|---|---|
| $T_{bake}$ | Baking temperature (°C) |
| $t$ | Thickness of the dielectric layer (nm) |
| $t_{del}$ | Time delay (s) |
| $\tau$ | Lifetime (s) |
| $\tau_r$ | Radiative lifetime (s) |
| $V_{ds}$ | Drain to source voltage (V) |
| $V_{gs}$ | Gate to source voltage (V) |
| $V_{on}$ | Onset voltage (V) |
| $V_{th}$ | Threshold voltage (V) |
| $W$ | Transistor channel width (μm) |
| AFM | Atomic force microscopy |
| Ag | Silver |
| Al | Aluminum |
| $Alq_3$ | Tris-(8-hydroxyquinoline) aluminum |
| ASE | Amplified spontaneous emission |
| AZO | Aluminum doped zinc oxide |
| BARC | Bottom anti reflection coating |
| $BCl_3$ | Boron trichloride |
| BSP-Me | 1,4-Bis(4-methylstyryl)benzene |
| $Btp_2Ir(acac)$ | Bis(2-(2'benzothienyl)pyridinato-N,$C^{3'}$)(acetylacetonate)-iridium(III) |
| CAMFR | Cavity modelling framework |
| CCD | Charge coupled device |
| $CH_2$ | Methylene |
| CNPPP | 2-[(6-cyano-6-methylheptyloxy)-1,4-phenylene] copolymer |
| COT | 1,3,5,7-cyclooctatetraene |
| Cr | Chromium |
| CW | Continuous-wave |
| $C_4F_8$ | Octafluorocyclobutane |
| DBR | distributed Bragg reflector |
| DCM | 4-(dicyanomethylene)-2-methyl-6-[(4-dimethylaninostyryl)-4H-pyran |
| $DCM_2$ | 4-(dicyanomethylene)-2-methyl-6-(julolindin-4-yl-vinyl)-4H-pyran |
| DF | Delayed fluorescence |
| DFB | Distributed feedback |
| DFH-4T | $\alpha$,$\omega$-diperfluorohexyl-quaterthiophene |
| DFHCO-4T | 5,5"'-diperfluorohexylcarbonyl-2,2':5',2":5",2"'-quaterthiophene |
| 2D | Two-dimensional |
| DOS | Density of states |
| EBL | Electron beam lithography |
| EL | Electroluminescence |
| ETL | Electron-transporting layer |
| Fe | Iron |

| | |
|---|---|
| FWHM | Full-width-half-maximum |
| $F_{16}$CuPc | Copper hexadecafluorophthalocyanine |
| He | Helium |
| HOMO | Highest occupied molecular orbital |
| HSQ | Hydrogen silsesquioxane |
| HTL | Hole-transporting layer |
| $H_2O$ | Water |
| IC | Internal conversion |
| ICP-RIE | Inductively coupled plasma reactive ion etching |
| IL | Interference lithography |
| ISC | Intersystem crossing |
| ITO | Indium tin oxide |
| LEOFET | Light-emitting organic field-effect transistor |
| LiF | Lithium fluoride |
| LPPP | Ladder-type poly(para-phenylene) |
| LUMO | Lowest unoccupied molecular orbital |
| MEH-PPV | Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene-vinylene) |
| MeLPPP | Methyl-substituted ladder-type poly(para-phenylene) |
| Mg | Magnesium |
| MTR | Multiple trapping and release model |
| $N_2$ | Nitrogen |
| OLED | Organic light-emitting diode |
| OMA | Optical multichannel analyzer |
| OMBD | Organic molecular beam deposition |
| OTFT | Organic thin film transistor |
| $O_2$ | Oxygen |
| P$\alpha$MS | Poly-$\alpha$-methylstyrene |
| PF | Prompt fluorescence |
| PF2/6 | Poly(9,9-di(ethylhexyl)fluorene) |
| Ph | Phosphorescence |
| PL | Photoluminescence |
| PMMA | Poly(methyl metacrylate) |
| PmPV-co-DOctOPV | Poly(*m*-phenylenevinylene-*co*-2,5-dioctoxy-p-phenylenevinylene) |
| PPV | Poly(phenylene vinylene) |
| PS | Polystyrene |
| PTAA | Poly(triarylamine) |
| PTCDA | 3,4,9,10 perylenetetracarboxylic dianhydride |
| PTCDI-$C_{13}H_{27}$ | N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide |
| SEM | Scanning electron microscopy |
| SEP | Standard electrode potential |
| SF | Superfluorescence |
| SHG | Second harmonic generation |
| $SiO_2$ | Silicon dioxide |

| | |
|---|---|
| SMU | Source-measure unit |
| spiro-SBCz | 2,7-bis[4-(N-carbazole)phenylvinyl]-9,9'-spirobifluorene |
| $Ta_2O_5$ | Tantalum pentoxide |
| TCO | Transparent conductive oxides |
| TE | Transverse electric |
| THF | Tetrahydrofuran |
| Ti | Titanium |
| $TiO_2$ | Titanium dioxide |
| TMAH | Tetramethylammonium hydroxide |
| TSL | Thermally stimulated luminescence |
| UV | Ultra violet |
| VR | Vibronic relaxation |
| Yb | Ytterbium |
| Zn | Zinc |