European Commission

MMAMA

www.mmama.eu

PROBING (DI)ELECTRIC PROPERTIES OF ORGANIC PHOTOVOLTAIC NANOSTRUCTURES WITH NEAR-FIELD SCANNING MICROWAVE MICROSCOPY

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Session: Characterization of Nanomaterials
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MICROWAVE MICROSCOPY FOR ADVANCED AND EFFICIENT MATERIALS ANALYSIS AND PRODUCTION

Outline

- The MMAMA project:
  - ✓ Main topics
  - ✓ Consortium
  - ✓ Objectives
- Case study: probing (di)electric properties of organic semiconductors with Scanning Microwave Microscopy (SMM)
  - ✓ Challenges and experimental protocol
  - ✓ Results and analysis
  - ✓ Perspectives

MMAMA is supported through the Horizon H2020 Programme (grant agreement n°761036)

MMAMA Project: 2017-2020

Microwave Microscopy for Advanced and Efficient Materials Analysis and Production

Main topics

- Development of Scanning Microwave Microscopy (SMM) technology towards high performance and capabilities.
- Establishing electromagnetic 3D models and software modules for advanced materials
- Validation of high frequency characterization technology of novel reference materials and structures for alternative and sustainable energy
- Demonstration of multi-scale microwave imaging technologies for pilot scale production
- Development of standard operating procedures and open innovation environment

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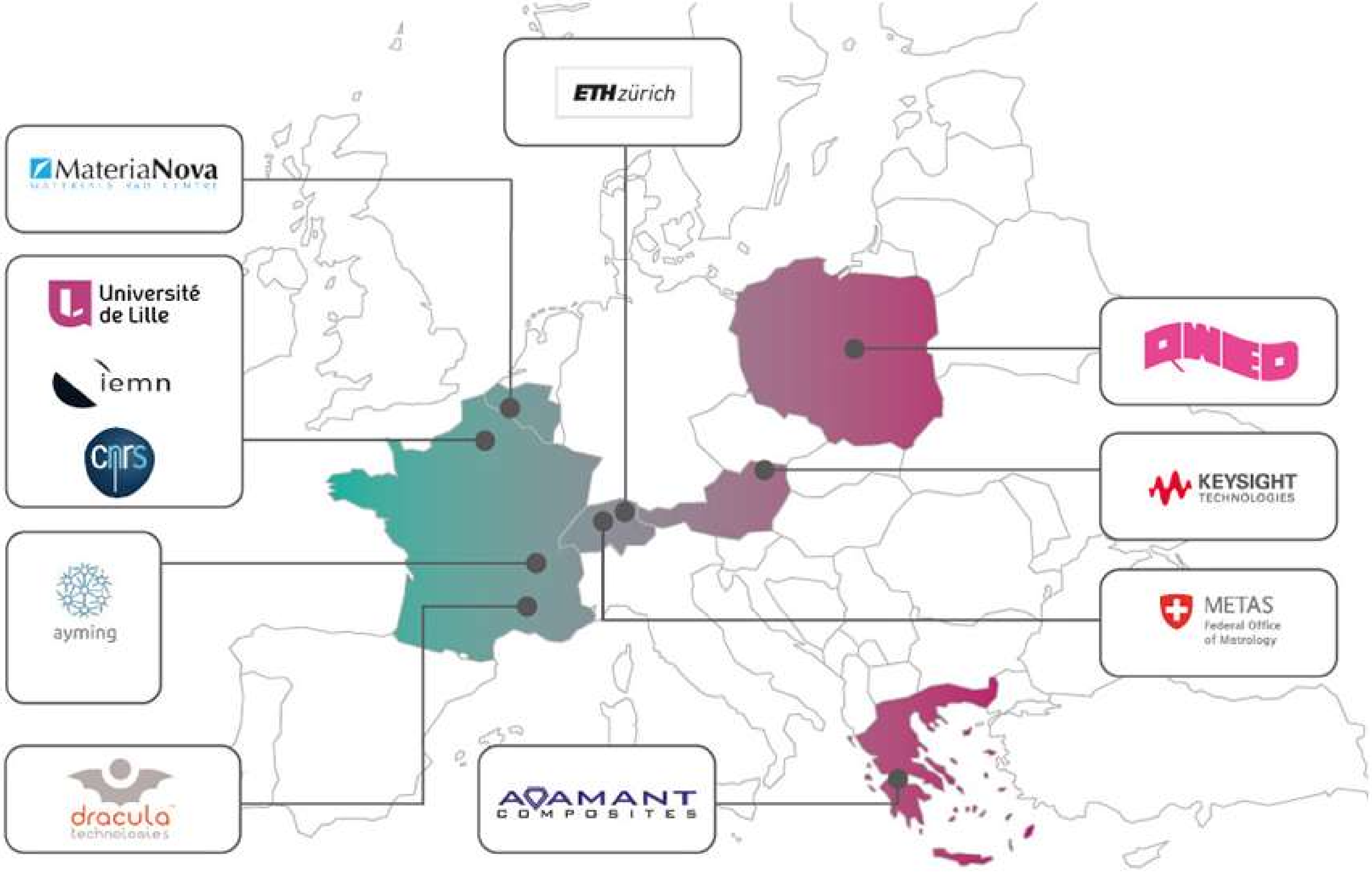
MMAMA- Consortium



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MMAMA- Consortium

Technology development
iemn

Product development
KEYSIGHT TECHNOLOGIES

Validation
MateriaNova
MATERIALS R&D CENTRE

Demonstration
dracula technologies
ADAMANT COMPOSITES

Modeling and open platform
QWED
ETH zürich

Standardization
METAS
Federal Office of Metrology

Dissemination and exploitation
ayming | business performance consulting

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MMAMA- Instrumentation

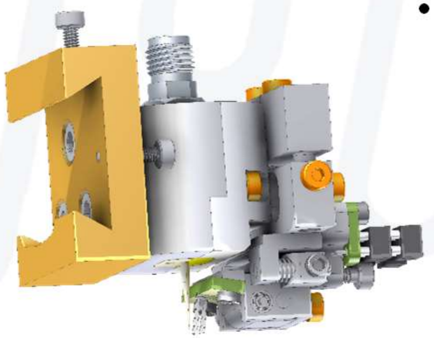
Highly performing Scanning Microwave Microscopy:

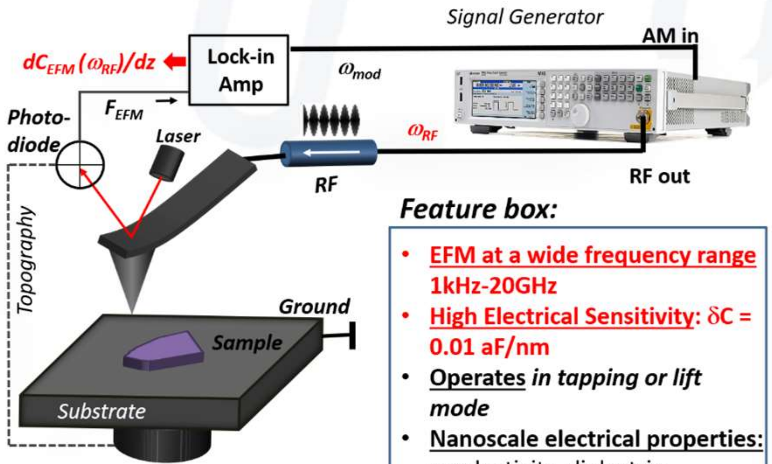
- Electrical resolution of 10 nm (or more) wide material features
- Bandwidth (frequency range) from DC to 100 GHz
- Multiple microwave probes geometries
- Embedded in SEM environment

iemn

KEYSIGHT TECHNOLOGIES

METAS





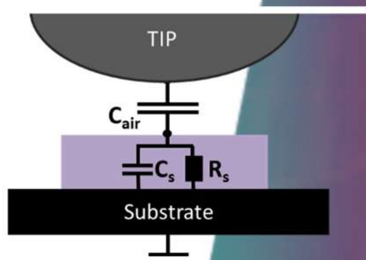
Feature box:

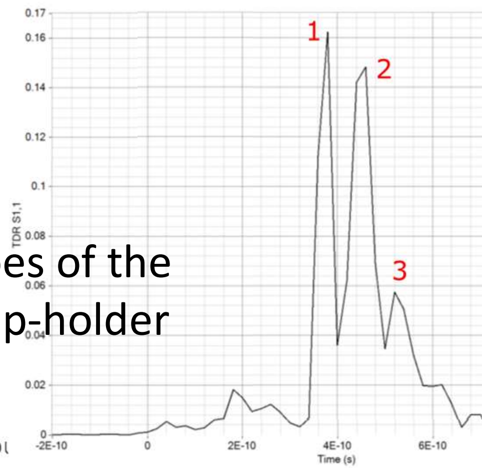
- **EFM at a wide frequency range 1kHz-20GHz**
- **High Electrical Sensitivity: δC = 0.01 aF/nm**
- ***Operates in tapping or lift mode***
- **Nanoscale electrical properties:** conductivity, dielectric permitivity, dopant density, loss, etc

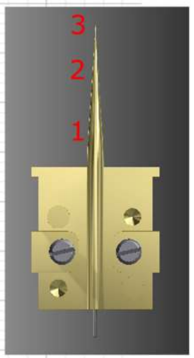
Measures |Z(C, G, f)|, Absolute Impedance

$$F_{es}(\omega_{RF}, Ca_{ir}, Cs, Rs) =$$

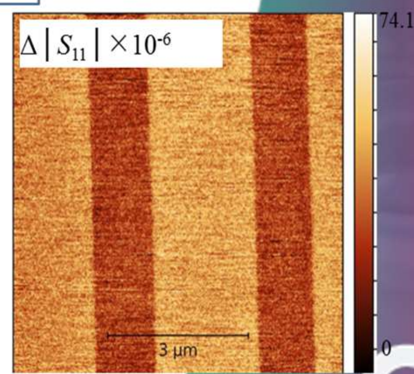
$$½\, dC/dz^{*}\,(\omega_{RF}, Ca_{ir}, Cs, Rs)\,V_{RF}^{2}$$







First prototypes of the coaxial tip / tip-holder



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MMAMA- EM Measurements and Modelling

ETH

Portable dielectric resonator for large-scale analysis of (semi-)conducting materials and structures

Simulation technology for SMM and other microwave materials characterization

- Modelling large aspect ratio geometrical systems
- Wide frequency range
- Coupling EM Field solver with semiconductor physics

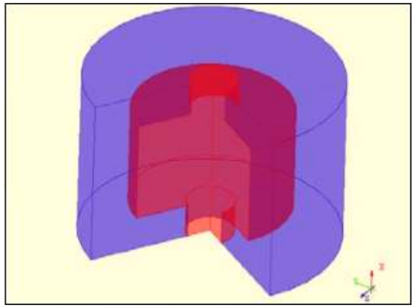
QWED

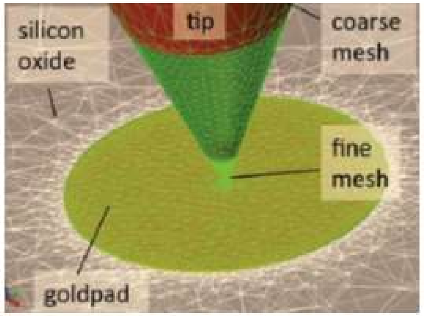
KEYSIGHT TECHNOLOGIES

Preliminary results:

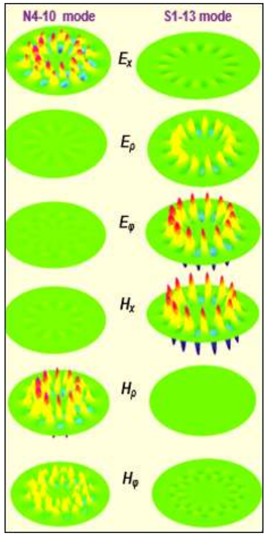
Sample - original sample (rectangular sample on film),
Measurement – direct scanning result
(dissolved, due to finite head of SPDR),
Solution - pattern after resolution improvement
Wiener - pattern after noise filtering

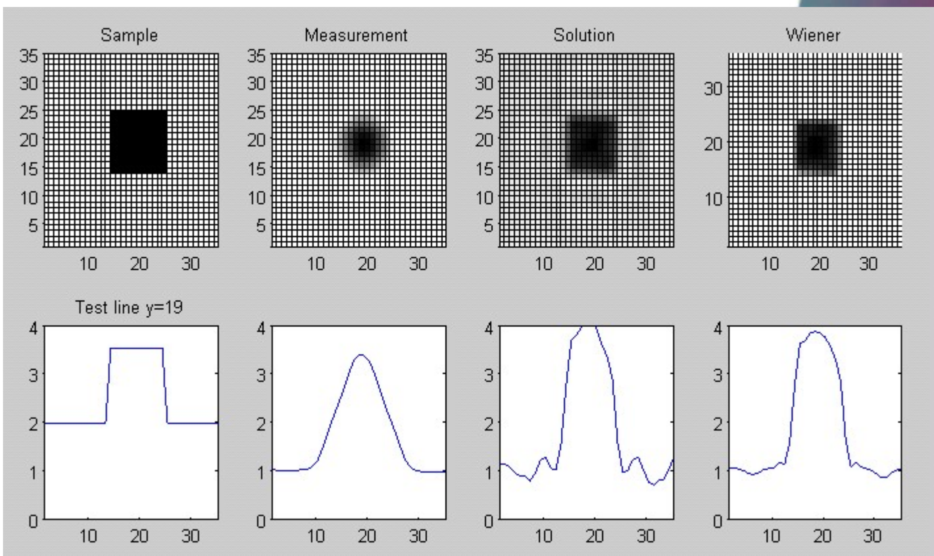
Example cases modelled:
dielectric resonator
and SMM tip





Example fields
of whispering
gallery modes





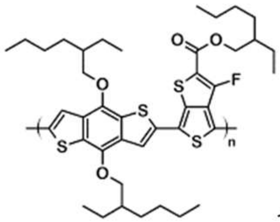
MMAMA- Materials and Devices

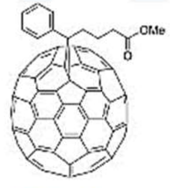
Advanced and novel components:

- Organic hetero-structures for solar technologies (OPV)
- Composite structures for energy applications (batteries)
  - ➔ Validation of SMM characterization protocols: σ and ε
  - ➔ Fabrication of standard calibration samples

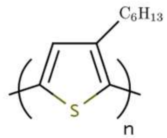
Correlation with well established characterization methods
Macroscale vs Nanoscale (AFM, C-AFM and KPFM)

PBDB-T

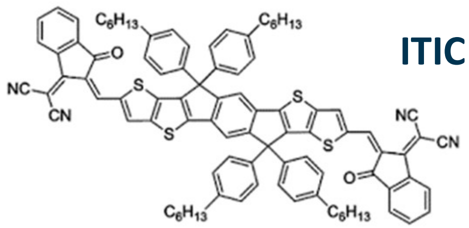




$PC_{70}BM$

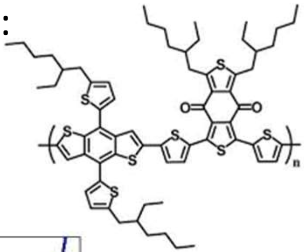


P3HT

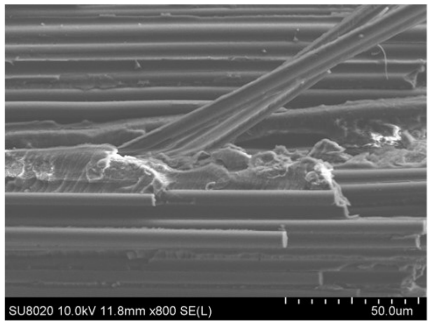


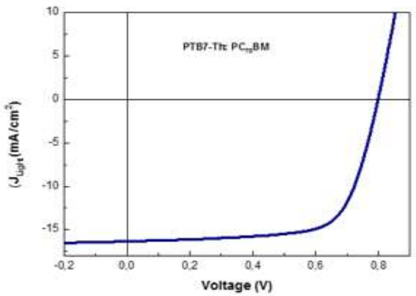
ITIC

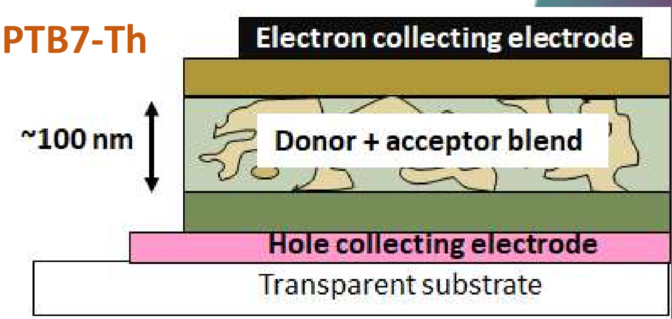
Frequency modulated SMM measurements:
3D imaging of impedance properties of reference samples for PV, batteries, ultracapacitors and ion-implanted surfaces



PTB7-Th







9.34 %

S. Ben Dkhil et al. **Adv. Energ. Mater.** (2016), 1600290/1-10

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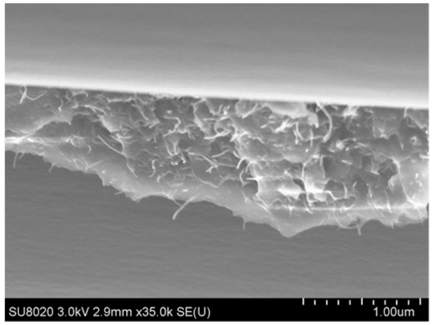
MMAMA- Industrial applications

Integration of macro-scale microwave techniques into industrial sheet-to-sheet and roll-to-roll processes.

ADAMANT COMPOSITES

- Nano-enabled prepregs for composites with tailored properties
- Graphene based electrodes for batteries and supercapacitors



In line characterization of:

- Nanomorphology
- Homogeneity
- Conductivity

dracula technologies

Flexible PV by inkjet printing
Sheet to sheet pilot line

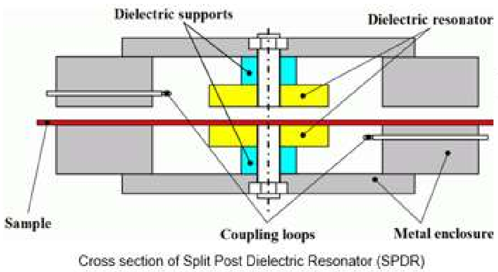
Microwave characterization techniques

KEYSIGHT TECHNOLOGIES

Probe kit

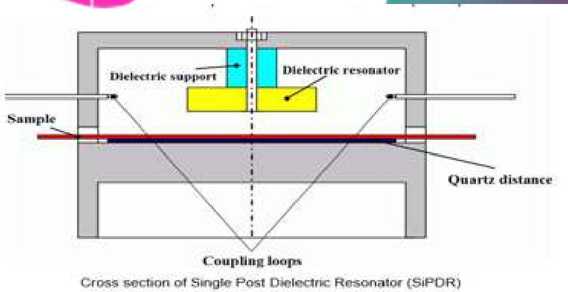
Impedance measurement

SPDR



QWED

SiPDR



MMAMA- open access environment

METAS

Creation of a common Open Innovation Environment (OIE) with NMBP projects for interaction with:

- Project partners
- Project stakeholders

Implementation of Metadata for SMM:

- Findable, Accessible, Interoperable and Re-usable Data
- Integration in open source file (Gwyddion)

Pre-normative metrology:

- MW methods: SMM, coaxial probe and dielectric resonator
- Standard operating procedures (SOPs) compatible with industrial partner and stakeholder specifications

ayming

MMAMA is supported through the Horizon H2020 Programme (grant agreement n°761036)

Case study: Probing electrical properties of organic semiconductors with SMM

1st challenge:
To evidence the sensitivity of SMM detection methods on organic semiconductors for PV applications

Berweger et al., Nano Letters 2017, 17, 1796−1801
Lai et al, Nature Communications, 2017 8: 2230

Mapping of S11 on photoactive thin films:

- Standard microscopy approach: the probe uses the microwave both as a perturbation and for detection
- Output: novel but mainly descriptive – significant scan induce artefacts and low signal variations

Seki et al., Appl. Phys. Lett. 110, 153303 (2017)

Carrier accumulation in a biased MI-organic conductor structure embedded in dielectric resonator:

- Perturbation in the resonating frequency (interferometric response) of the resonator (SMM detection unit)
- Direct evidence of sensitivity of microwave to variations of electrical properties – pending scanning issue

2nd challenge:
To determine impedance out of S11 variations
To extract electrical (σ and p/n), dielectric (ε) properties

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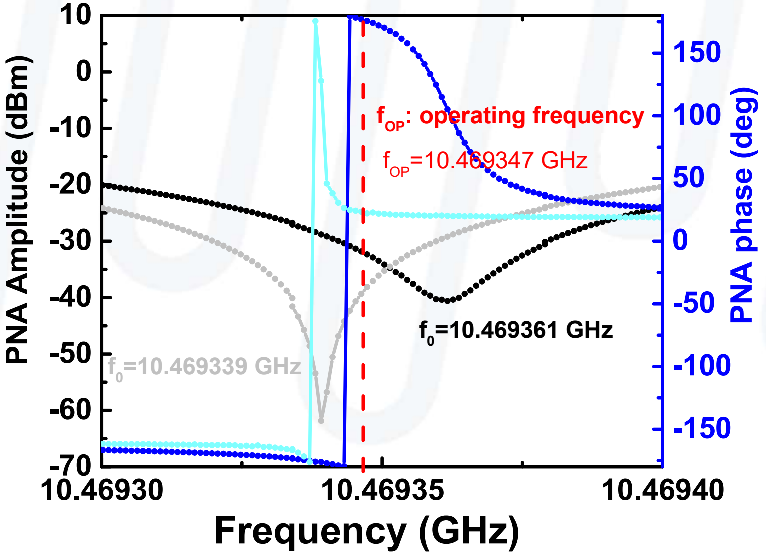
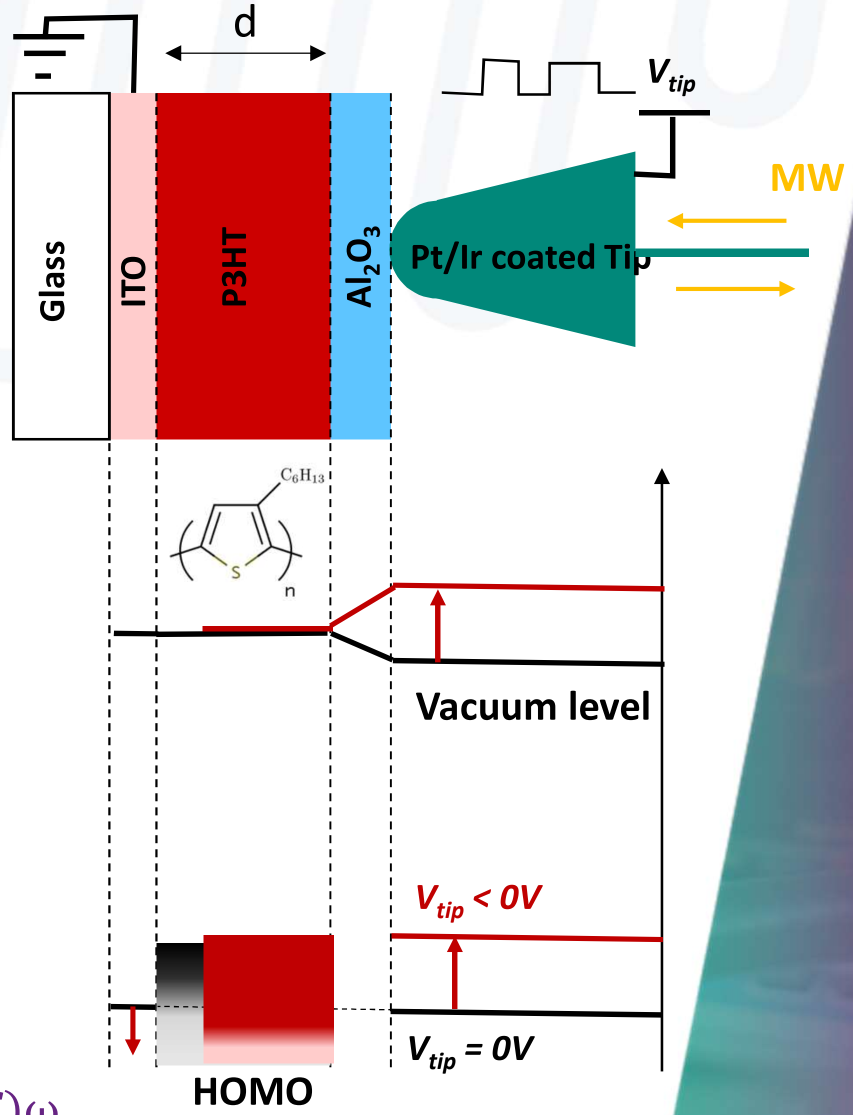
Case study: Probing electrical properties of organic semiconductors with SMM

Interferometric response



Protocol



Capacitive effect: Frequency shift
Conductive effect: Amplitude variations

$$S11 = AZ_C(Y_1 - Y) = AZ_C\Delta Y$$

S: Reflection coefficient (no unit)
A: Interferometric calibration parameter (no unit)
Y_1: Admittance when S=0
Y: Admittance of the sample

All of them are complex parameters

$$\Delta Y = Re\,(\Delta Y) + j\,Im\,(\Delta Y) \neq \Delta G + j(\Delta C)\omega$$

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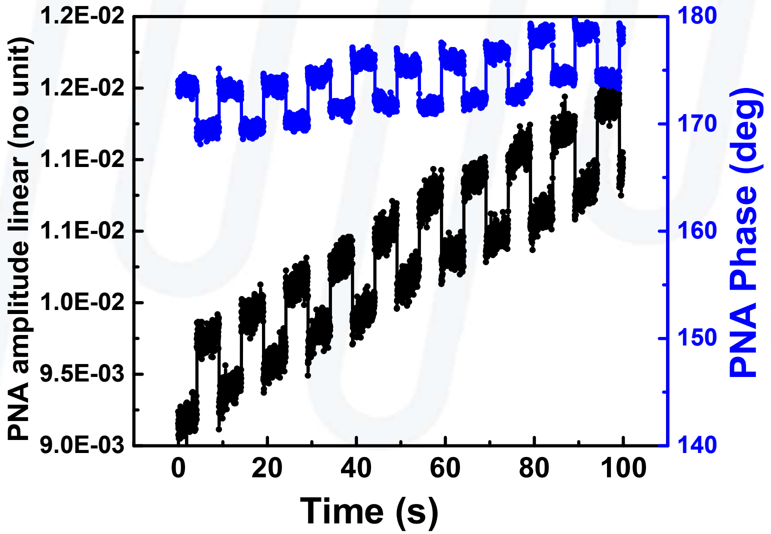
Probing electrical properties of organic semiconductors with SMM

Results

Signal response to step bias variations
Sensitivity to carrier density variations in the material

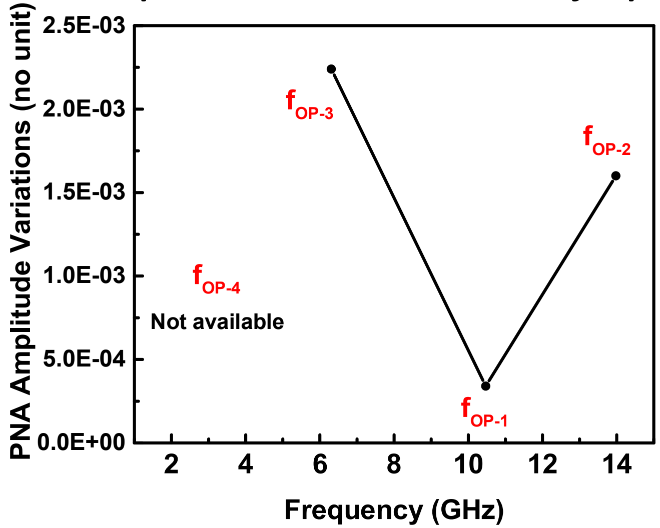


Conductive and capacitive effects mixed in both Amplitude and Phase signals
Yet to be outcoupled

Electrical properties: σ vs. ρ, μ, n vs. p

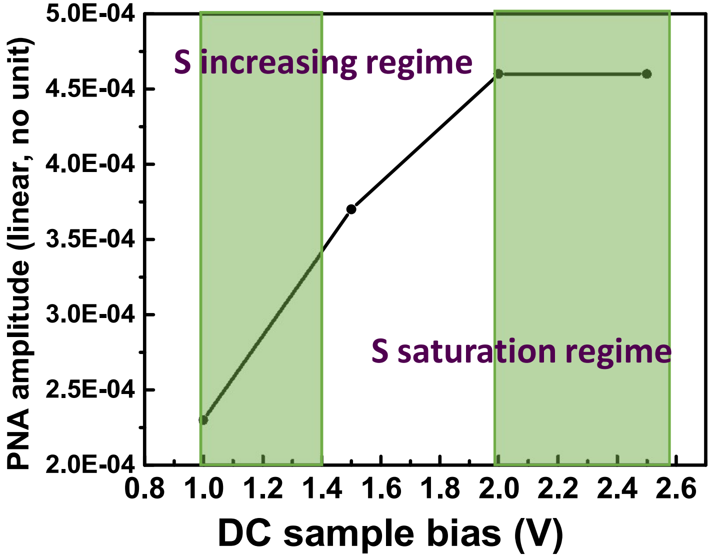
Dielectric properties: ε

PNA amplitude with the microwave frequency



Attempts to delineate depth profiling

PNA amplitude with the DC bias



Correlation of the regimes with both conductive (charge injection) and capacitive (space charge region) effects

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Probing electrical properties of organic semiconductors with SMM

Perspectives

Probing materials:

- **Reproducibility** of the as-observed results
- Determination of **(di)-electric properties**
- **Modelling** the interferometrical based SMM detection system
- **Comparing** with standard (di)electric characterization methods
- Validation of the **SMM protocol** with PTB7-Th and PBDB-T

Probing photoactive structures:

- Application of the probing protocol with **SMM mapping mode**
- **Carrier profiling** with materials and across interface
- Determination of **SMM spatial resolution** in test structures
- Protocol modification with **light excitation** instead of bias to electrically characterize photovoltaic mechanisms
- Validation of experimental **protocols** on **OPV industrial products**

감사합니다
THANK YOU

M6 meeting, 16th May 2018 at METAS, Switzerland

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