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## Thermal stability of transport properties

Two-dimensional character Why graphene? Relatively high charge carriers mobility

Well-defined charge carriers concentration





Epitaxy: Chemical Vapor Deposition (CVD)

Carbon source: methane or propane

Substrate: 4H-SiC(0001) or 6H-SiC(0001)

Type: semi-insulating on-axis

Dimensions: 20 mm x 20 mm







dx.doi.org/10.1016/j.carbon.2015.06.032 dx.doi.org/10.1016/j.carbon.2016.01.093

Hydrogen intercalation: quasi-free-standing graphene

On 4H-SiC(0001): p = 1.2 E13 cm<sup>-2</sup>

On 6H-SiC(0001): p = 7.5 E12 cm<sup>-2</sup>



doi.org/10.1016/j.apsusc.2020.148668



Principle of operation: classical Hall effect

Configuration: van der Pauw

Active area: equal-arm cross 100 µm x 300 µm

Total dimensions: 1.4 mm x 1.4 mm



doi.org/10.1016/j.carbon.2018.07.049





Passivation: aluminum oxide

Process: atomic layer deposition

Precursors: TMA and DI

Purpose: environmental protection



doi.org/10.1016/j.physe.2022.115264





Mounting: custom holders or ceramic packages

Feed current: < 10 mA

Magnetic induction: 0.55 T

Temperatures: from liquid nitrogen to 500 °C



10.1109/TED.2019.2915632









doi.org/10.1016/j.physe.2021.114853







I4BAGS Webinar January 10, 2023



**I4**Bags

Double-carrier transport: holes in QFS graphene and thermally-activated electrons emitted in the bulk of the semi-insulating 6H-SiC(0001) and 4H-SiC(0001)





I4BAGS Webinar January 10, 2023



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Temperature T [°C]

Completed experiment in MARIA reactor: neutron fluence of 6.7 10E17 cm<sup>-2</sup>

Estimated defect density: 4 E10 cm<sup>-2</sup> (low cross-section)



doi.org/10.1016/j.apsusc.2022.152992 doi.org/10.3390/s22145258



Summary: Al2O3/QFS-graphene/SiC(0001)

### Competitive advantages:

- operates at elevated temperatures
- largely resistant to neutron irradiation

### **Potential application:**

- magnetic diagnostics in fusion reactors







### I4BAGS – Technical kick off meeting January 10<sup>th</sup> 2023







### Ion implantation for monitoring material properties in thin film solid state battery



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### Outline

- Presentation of Materia Nova
- Battery development
- Action Plans
- Equipment
- Collaborative activities



### **Presentation of Materia Nova**





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### **Battery developments at Materia Nova**

### Materia Nova : validator off innovative material and processing solution in thin film battery

Background and current activities:

- Li layer (up to 10 μm) deposited by PVD
- Deposition of thin film anode by PVD for low weight solid state batteries
- Characterization of materials thin films towards (semi-)battery systems



Cross-sectional topography of Li thin film by SEM

### 15x15 µm² TM-AFM of Li film



Impedance spectroscopy of solidstate devices



Li film on 5x5 cm<sup>2</sup> glass (left) and 10x10 cm<sup>2</sup> Cu substrates



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### Equipment for thin film deposition and ion implantation

## **Deposition methods**



Spectros<sup>™</sup>150 from K. J. Lesker Connected to a Glovebox Jacomex conditioned in inert atmosphere (Ar)

### 3 lab-scale ion implanter for:

Flat samples (up to 40x40cm<sup>2</sup>) Small 3d shape and powder (up to 100cm<sup>3</sup>) **2 semi-industrial ion implanter (lonics) for :** large dimensions (1.6x1.6 m<sup>2</sup>; R2R)





Magnetron sputtering and PECVD chambers To be equipped with ion gun for direct implantation





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### **Equipment for characterization of materials and devices**

### **Chemical analysis**

XPS (Omicron)





Raman spectrometer (Bruker Senterra)

# Topographical and electrical analysis



PEC Corp multichannel cell tester

Cell Tester. 10 Ch. 5A, 5V Incl LifeTest

PEC ACT0505 Table Top



Atomic Force Microscope with electric modules Low T to RT Hall effect characterization platform



### **Device conditionning**

MSK-115 Vacuum Sealing Machine Conditioned in inert atmosphere (Ar)





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### Low energy and low coast ion implantation activities at Materia Nova and Ionics

### **R&D** activities

Implanted species: all kind of gaseous atomic or molecular compound Operating environment: high vacuum (~10<sup>-5</sup> Torr) Energy range: 10 keV to 40 keV Dose (fluence): 10<sup>14</sup> cm<sup>-2</sup> to 10<sup>18</sup> cm<sup>-2</sup> Near surface implantation: up to 500 nm

Simple process → Industrialization

- Any solid materials: metals polymers glasses...
- Any shapes: flat powders small 3D objects, wire...
- No adherence issues

Monitoring mechanical properties

- Surface hardening
- Improved corrosion and HT oxidation resistance
- Wettability modification
- Adhesion improvement at interfaces
- Enhancing barrier properties (polymers)
- Doping and allowing (oxides, nitride...)



### Spin off from Materia Nova

Design, conception and fabrication of ion implanter Large dimension implantation equipment Versatile application: automotive, health...





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### Action plan at Materia Nova

### 2023 Graphite electrodes:

- Purchasing of graphite thick electrode
- Carbon thin film (50 nm) deposited by magnetron sputtering lon implantation
- Non-reactive implantation: Ne, Ar for monitoring vacancies in graphite
- Reactive implantation: N for doping

Morphological, chemical and electrical characterization

### Solid state electrolytes:

Materials and fabrication methods: Li-PEO (Wet X) and LIPON (PVD) Non-reactive ion implantation for monitoring ionic transport: Species: Ar, N, He, Ne Electrical characterization with impedance spectroscopy (Biologic, Modulab)

### 2024 Li electrode:

Deposition of Li layer ( $\mu$ m) and additional interfacial thin film (LiF, MoS<sub>2</sub>) Transfer issue to be solved to prevent contamination (C, N, and O) Ion implantation for monitoring stability upon cycling Non-reactive implantation of multilayer vs. Reactive implantation (H<sub>2</sub>S, CF<sub>4</sub>) of Li layer

### Characterization of layers in half cells: capacity & energy, (de)charging time, stability in cycling

MATERIA NOVA Materials R&D Center

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### **Collaborative actions**

### From Materia Nova to QWED:

- Fabrication on low loss substrate (quartz, borosilicate glass) of reference (thin) films (graphite, solid electrolyte, Li) ion implanted upon selected protocols to be sent to QWED
- Electrical characterization (determination of permittivity) of reference samples with microwave dielectric resonator
- Model supply to describe electrical properties and transport (electrons, ions) behavior First samples to be sent: ion implanted carbon and graphite thin films on quartz samples What are the maximum dimensions of the sample to be sent?

### From L-IMIF to Materia Nova

- Determination of ion implantation protocol for SiC/graphene reference structures and devices (sensors)
- Reference graphene/SiC reference structures to be sent to Materia Nova for ion implantation, then to be returned for comparative testing

What are the dimensions of the reference samples to be received





# Bridging the gaps between microwave modelling and materials measurements and between women and engineering

Malgorzata Celuch QWED Sp. z o.o., Poland







- 1. From research on Electromagnetic Modelling to its exploitation by QWED
- 2. QWED expanding into Material Measurements
- 3. Exploring the synergies between EM Modelling and Material Measurements
- 4. Validation of resonators in 5G/mmWave iNEMI project



# **25 years in a Nutshell**

presented annually at IEEE IMS Show

& design software, 3D & BOR 2D tools

**Electromagnetic simulation** 

based on 300+ publications by:

dr.M.Celuch, President of QWED



**R&D** projects

FP6 SOCOT – development and validation of an optimal methodology for overlay control in semiconductor industry, for the 32 nm technology node and beyond.



FP6 CHISMACOMB - development, modelling, and applications of chiral materials  $\rightarrow$  EM validation of mixing rules



PREZES RADY MINISTRÓW

届国际发明展览会

Eureka E! 2602 MICRODEFROST MODEL - innovative software-based product development tool for simulating and optimising heating and defrosting processes in microwave ovens



FP7 HIRF SE (High Intensity Radiated Field Synthetic Environment) - numerical modelling framework for aeronautic industry









**Consultancy & design services** based on EM expertise & tools team of 10+engineers, 4 PhDs, 2 Profs key areas: MW power appliances, customised resonators, antennas & feeds ERA-NET MNT NACOPAN – applications and modelling of nano-conductive polymer composites

NGAM2 – designing an industrial device for thermal bonding of bituminous surfaces with the aid of microwave heating

MMAMA (Microwave Microscopy for Advanced and Efficient Materials Analysis and Production) - EM modelling & characterisation for the development of high efficiency solar cells



MMAMA

NanoBat - developing a novel nanotechnology toolbox for quality testing of Li-ion and beyond Lithium batteries with the potential to redefine battery production in Europe and worldwide.

**ULTCC6G EPac** – development & application of novel M-ERA.NET ceramics for 5G & beyond

**I4BAGS** – modelling & characterisation of ionimplanted battery & graphene-enabled devices

3

# **Origins of QWED Computer Modelling**



10.01.2023

Fellow,

Certifies that

Fellow

## **QWED started 1997**

## celebrating 25 years



### Founders: A.Wieckowski, M.Sypniewski, M.Celuch, W.Gwarek



Prof. Jerzy Buzek awarding QWED team in 1998 Prime Minister of Poland 1997-2002 President of the European Parliament 2009-2012



### Dr. Malgorzata Celuch President since 2017. VP 1997-2017

- · 35 y experience in mathematical, 25 y in management
- Awards for excellence from e.g. Prime Minister of Poland, Rector of WarsawUnivTech



### Dr. Marzena Olszewska-Placha, VP for R&D

- 15 y of experience in simulation-based MHz to THZ design and consultancy
- 4 y experience in research management

### Prof. Wojciech Gwarek, President 1997-2017

 22 years of experience in simulation software development



 22 years of experience in simulation software development



### Dr. Andrzej Więckowski Senior in CAD

 48 years of experience in computer-aided electronic engineering and engineering software development



Senior in CAE 35 years of experience in engineering software development

and GHz measurements

people employed

consultants cooperating

50%

female



10.01.2023

# Origins of QWED Material Measurements

获奖证书

### since 1980s...

awarded research of Prof. Jerzy Krupka (IEEE Fellow) on dielectric resonators (best known: Split-Post Dielectric Resonator)







### ... by early 2000s:

QWED commercialises the SPDRs endorsement by Agilent / Keysight publication of standard IEC 61189-2-721:2015



Agilent Both IEEE IMS 2006, San Francisco, CA



MMA-2010, Warsaw PL co-organised by QWED & Warsaw Univ.Tech.

### 10.01.2023

## Current Work: Bridging Computer Modelling with Material Measurements



# Resonator methods – motivation and background (1)

**Resonance in practice:** given fixed strength of Signal(in), at resonance Signal (out) is strongest



## Resonator methods – motivation and background (2)

**Resonance in theory:** non-zero electromagnetic fields exist in isolated structures (no excitation). Field properties are well-defined and linked to material properties. E.g. for cylindrical cavities:





## Cylindrical resonator: single-mode versus multi-mode operation





Resonators are multimode devices.

Hence formally, material measurement can be performed at many frequencies in the same resonator.

However, some modes provide highest accuracy of material characterization. Some are difficult to excite.

Software provided with the resonator in compatible only with modes pre-selected by the vendor.

Software provided with the resonator in compatible only with modes pre-selected by the vendor.

Among the popularly available resonators, **BCDR and FPOR work as multi-modal**.



## Resonator methods – motivation and background (3) TE010 TM010





TE modes to measure in-plane component of Dk, Df

SCR, SPDR, FPOR

TM modes to measure out-of-plane component of Dk, Df BCDR

J.Krupka et al., "Complex permittivity of some ultralow loss dielectric crystals..", Meas. Sci. Technol. 10 (1999).

Full characterisation of anisotropic materials (like crystals) requires both measurements.



## Popular Dielectric Resonators by QWED

SPDRs for laminar dielectric materials typical units: 1.1 GHz -15 GHz



5 GHz SiPDR for resistive sheets



TE01 $\delta$  cavities, typically 1 – 10 GHz for bulk low-loss dielectrics

modified SiPDR for graphene





### 10.01.2023



# **Resonator methods considered in iNEMI 5G project**

Why we use resonant methods

**How these resonant methods work** 

Presentation will be illustrated with full-wave electromagnetic modeling with QuickWave<sup>™</sup> software by

Why these different methods may produce different results



what is vendor-specific, what is method-specific, and what other criteria may come into play

# **iNEMI 5G Round Robin Overview**



### Sample Material Requirements

- Stable, Low loss
- Low moisture absorption / temperature dependency
- Isotropic
- Good mechanical & handling properties

### **Techniques Included**

- Split Post Dielectric Resonator
- Split Cavity Resonator
- Fabry-Perot
- Balanced Circular Disk Resonator
- $\rightarrow$  Frequency Span : 10GHz 100GHz with overlaps

10 Sample Kits Created

- Sample sizes 35 mm x 45 mm, 90 mm x 90 mm
- circulated between 10 labs

- 1<sup>st</sup> Project Stage
- Precision Teflon
- Cyclo Olefin Polymer

**10 Laboratory Round Robin** 

### 2<sup>nd</sup> Project Stage

- Rexolite
- Fused Silica

### Industrial

• Automotive





### 10.01.2023

## **Split-Post Dielectric Resonator (SPDR) - basics**



- resonant mode with EM fields mostly confined in and between those ceramic posts
- $\rightarrow$  minimial losses in metal enclosure
- H-field is only vertical at the side wall of the enclosure → circumferential currents
- $\rightarrow$  no radiation through slot
- E-field tangential to SUT
- $\rightarrow$  air slots between SUT and posts have negligible effect
- easy SUT insertion through slot, no dismatling



- High measurement precision
- Easy to use
- Insensitive to many user errors
- Typically in-plane component of permittivity
- Typically extrapolated to 5G mmWaves
- Typical sample thicknesses less than 1 mm
- IEC 61189-2-721:2015
- https://www.qwed.com.pl/resonators\_spdr.html
- <u>https://www.keysight.com/us/en/assets/7018-01416/application-notes/5989-5384.pdf</u>



## **Split-Post Dielectric Resonator (SPDR) – modelling results**











## Split-Post Dielectric Resonator (SPDR) – operation (1)







## Split-Post Dielectric Resonator (SPDR) – operation (2)



For many practical materials, measuring only abs (S21) provides appropriate accuracy.

Keysight Option N1500A uses S21 (amplitude & phase) which helps enhance accuracy (under study in iNEMI project).

### 10.01.2023

## Fabry-Perot Open Resonator (FPOR) – basics..





- High measurement precision
- Can be sensitive to many user errors
- Uncertainty increases with increasing frequency
- Typically in-plane component of permittivity
- JIS R1660-2
- https://www.qwed.com.pl/resonators.html#ResonatorFPOR
- <u>https://www.keysight.com/main/editorial.jspx?cc=US&lc=eng&cke</u> y=2276755&nid=null&id=2276755



## Fabry-Perot Open Resonator (FPOR) - operation



1. Connect the FPOR to VNA and PC with control app.

PC app invoked and controlled measurement – fully automatic Total measurement time: 10min

5. Material parameters at consecutive frequencies (modes) are extracted automatically





Find modes of the empty resonator

2. Measure "empty FPOR" (resonant frequency and Q-factor at M..N modes)



3. Insert the sample into FPOR

4. Automatic procedure finds M..N modes of sample-loaded FPOR



## **Characterisation Results - Consistency**



### 3 labs, 3 techniques, 14 laboratory setups

Intel - SCR at 10 / 60 GHz and SPDR at 10/ 20 GHz, Keysight - SCR at 10 / 20 / 28 / 40 / 80 GHz QWED - SPDR at 10/15 GHz and FPOR over 10-110GHz.



### > 40GHz 2x increase in Df compared to 10GHz



(< 2% incl. outliers)

## Techniques colected in the completed industrial project

	Preferred t	Optional		
Technique	Split cylinder resonator (SCR)	Balanced-type circular disk resonator (BCDR)	Fabry-Perot open resonator (also called open cavity)	Split-post dielectric resonator (SPDR)
Sample dimensions	20 um ~ 300 um (best for 100 um), 34 mm x 45 mm > 20G	0.1 mm ~ 1 mm, Best for 0.2~0.5 mm, 50 mmΦ x 2 each	0.050 – 3 mm, min. diameter: 75 mm max diameter: 150 mm	max 0.6 mm, min. 15 mm x 15 mm max 40 mm x 40 mm @15G

Samples under test in Task 3: 35 mm x 45 mm

90 mm x 90 mm

thickness: 50, 125, 188 μm

Sample sizes compatible with both resonators



## 2D Imaging of Low-Loss Dielectric Materials

2D scanner designed with a modified 10 GHz SPDR



Finalist of the European Innovation Radar Prize 2021





<sup>for Research and Development</sup> 2D SPDR Imaging of HR- GaN for Light & Power M-ERA.NET Electronics Devices

Optical microscopy image at L-IMiF reveals morphology inhomogeneity in the central area:

- in qualitative terms only,
- attributed to non-uniformity of the growth,
- only the central part appears unuseful for making devices.



SPDR image:

- shows this whole GaN template unuseful,
- quantitative evaluation:
  - edge ring inherent to so-called edge effect,
  - ca.  $2 \cdot 10^4 \Omega$  cm in the centre (dark blue),
  - ca.  $5 \cdot 10^4 \Omega$  cm along the inner ring (light blue),
  - up to  $1.2 3 \cdot 10^5 \Omega cm$  across outer SUT's area (blue-green),
  - edge effect along the circumference.

## Modelling-Based Resolution Enhancement of Surface Images







raw image of sample resistivity (measured Q-Factor) image further deconvolved using SPDR field pattern pre-simulated in QuickWave



MATERIA NOVA OMATERIA.NET

Patterned PEDOT:PSS sample courtesy MateriaNova, Belgium



**2D SPDR scanner** 

## 2D Imaging of Conductive Films – Application to Graphene Anodes









- □ Scanning area: 50 mm x 75 mm (25 mm margin around SUT)
- Uniform scanning step: 2 mm
- 1014 measurement points
- $\Box$  Avr thickness of the deposited graphene anode layer: 0.130 mm  $\pm$  0.02 mm
- $\Box$  Non-uniformities in  $R_s$  map due to sample thickness variation
- $\Box$   $R_s$  extracted for average thickness value
- An absolute value of  $R_s$  can vary within uncertainty of  $\pm 15\%$
- $\Box$  Avr  $R_s$  of 19.3  $\Omega$ /sq. in exact agreement with point-wise 5GHz SiPDR device.



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more sophistocated design & calibration:

active sheet facing the DR head  $\rightarrow$  distance depends on the thickness of sample substrate

