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Smart Diaspora 2023

NANOMATERIALS ENABLING SMART ENERGY HARVESTING FOR NEXT-GENERATION INTERNET-OF-THINGS

Mircea Modreanu

Tyndall National Institute-University College Cork, Ireland

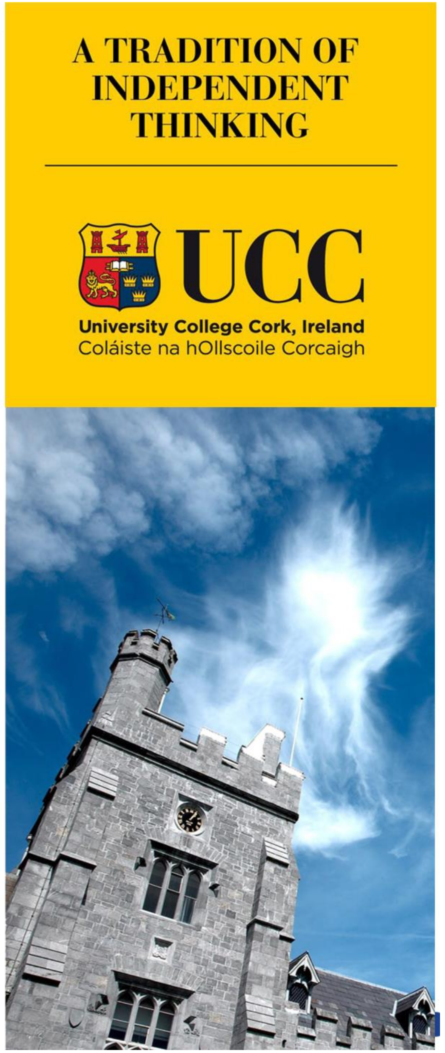
Outlook

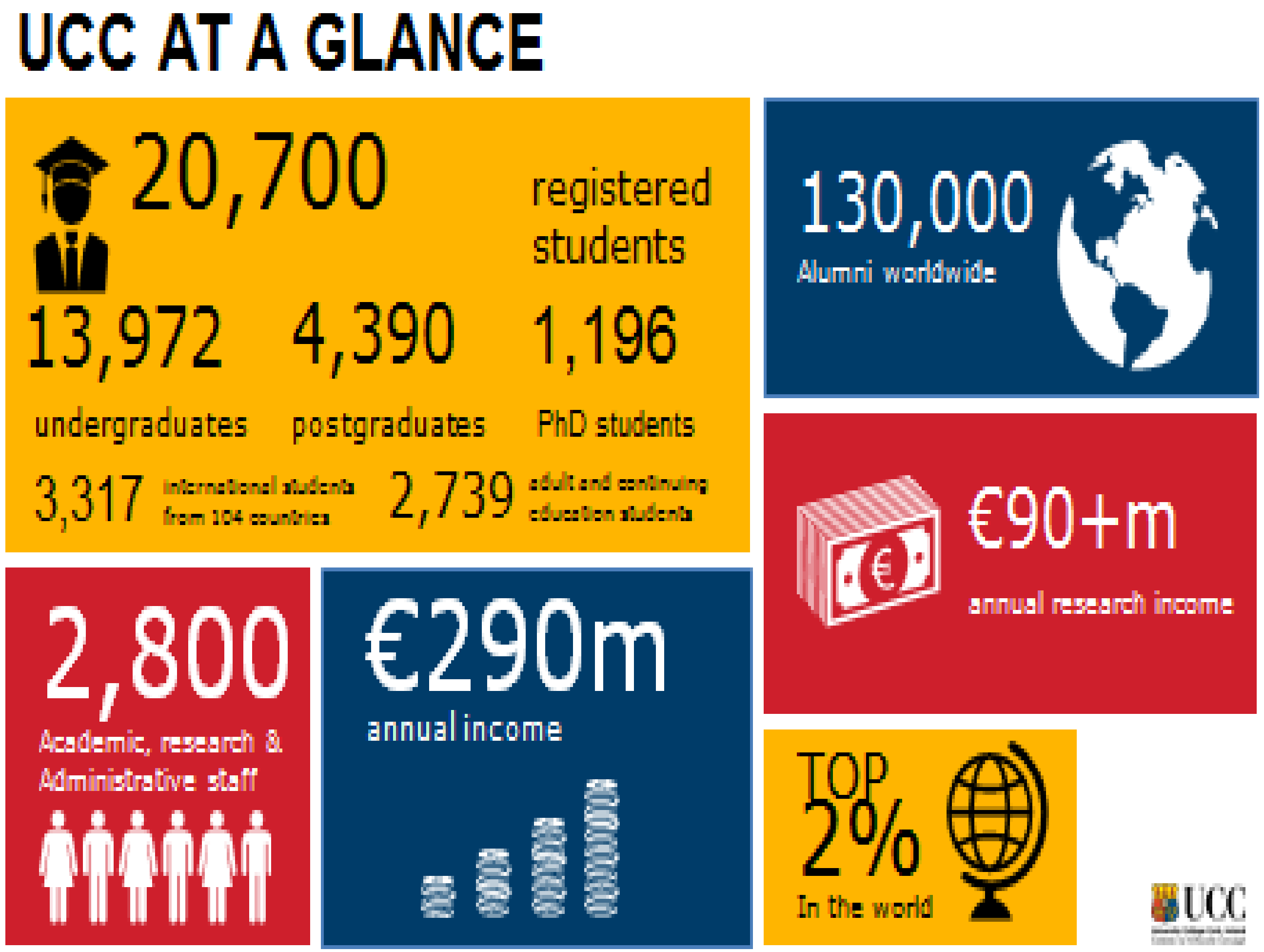
- Introduction:
  - Tyndall National Institute and University College Cork
- Smart Cities
  - The 4th Industrial Revolution-*European Concept*
  - Society 5.0- *Japanese concept*
- Internet of Things *future and stringent needs*
- The need for material research as trigger for new device architecture
- Smart Materials platform developed within an European Innovation Council project, NANO-EH
  - Nanoscale hafnium zirconium oxide ferroelectric
- NANO-EH's multi-source EM energy harvesting/energy storage platform integrated on Si substrate
- Conclusions

Tyndall National Institute and University College Cork

University College Cork – quick facts

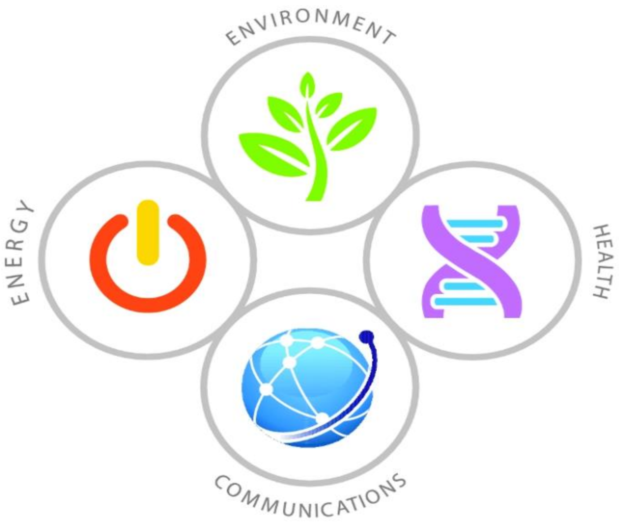
- Comprehensive university – Est. 1845
- Ranked in the Top 2% of universities worldwide
- Wide range of internationally recognised degrees
- Ireland's first five star university (*QS Stars*)
- 13 subject areas ranked in world's top 300 (QS)
- Sunday Times University of The Year 2016 and 2017
- First university in the world awarded the international green flag for environmental friendliness
- 84% of higher degree and diploma graduates are in employment or further study



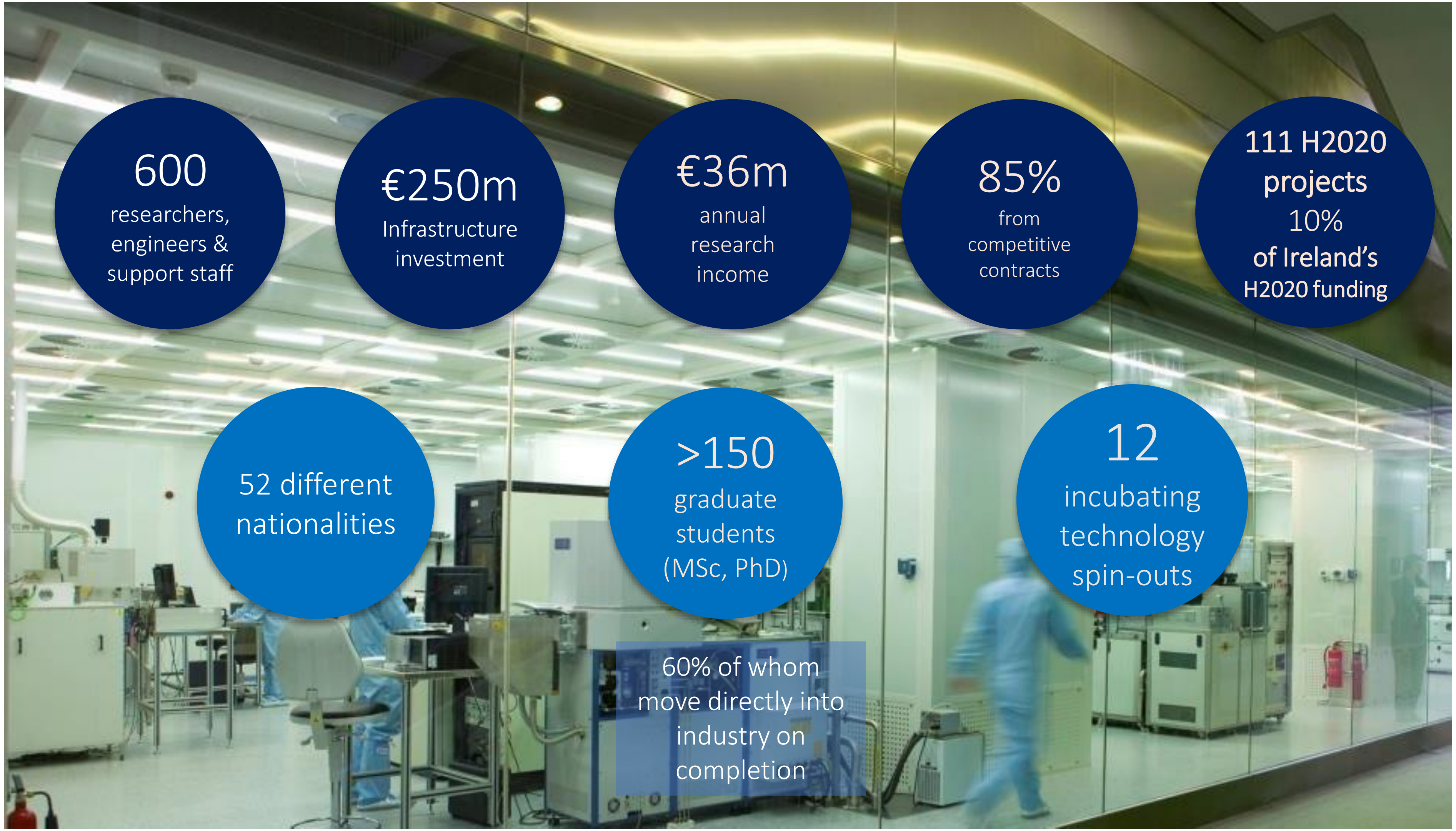

UCC AT A GLANCE
20,700
registered students
13,972
undergraduates
4,390
postgraduates
1,196
PhD students
3,317
international students from 104 countries
2,739
adult and continuing education students
130,000
Alumni worldwide
€90+m
annual research income
2,800
Academic, research & Administrative staff
€290m
annual income
TOP 2%
In the world
UCC

Tyndall National Institute in brief

- **Tyndall is Ireland's largest research institute. A leading European Research Centre in Integrated Information and Communications Technology hardware and systems**
- **Established in 2004, created from the National Microelectronics Research Centre (NMRC) – Est. 1982**
- **Host to:** iERC International Energy Research Centre; MCCI Microelectronic Circuits Centre Ireland; IPIC Bringing Photonics to Life; CONNECT Networks of the Future
- **Our Expertise:**
  - Smart Sensors & Systems
  - Optical Communication Systems
  - Mixed Signal & Analog Circuit Design
  - Microelectronic & Photonic Integration
  - Semiconductor Wafer Fabrication
  - Nano Materials & Device Processing



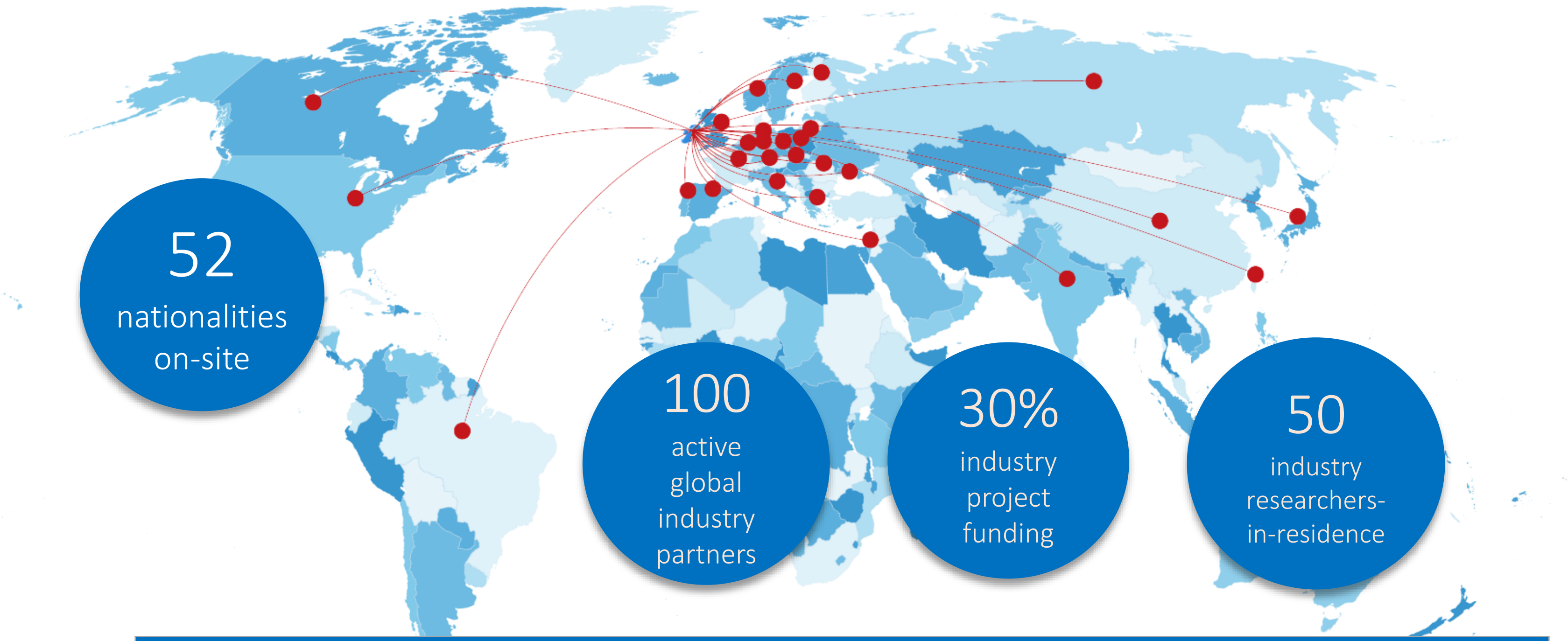
Tyndall National Institute at a glance
UCC and Ireland flagship Research Institute



Tyndall National Institute at a glance
UCC and Ireland flagship Research Institute

Deep technology research at the convergence of micro & nano-electronics, photonics and materials, involving chemists, physicists, engineers and manufacturing personnel

Tyndall Global industrial impact



Industrial partner recognition: 3 of 12 Intel *Global Outstanding Researcher Awards* have been awarded to Tyndall researchers

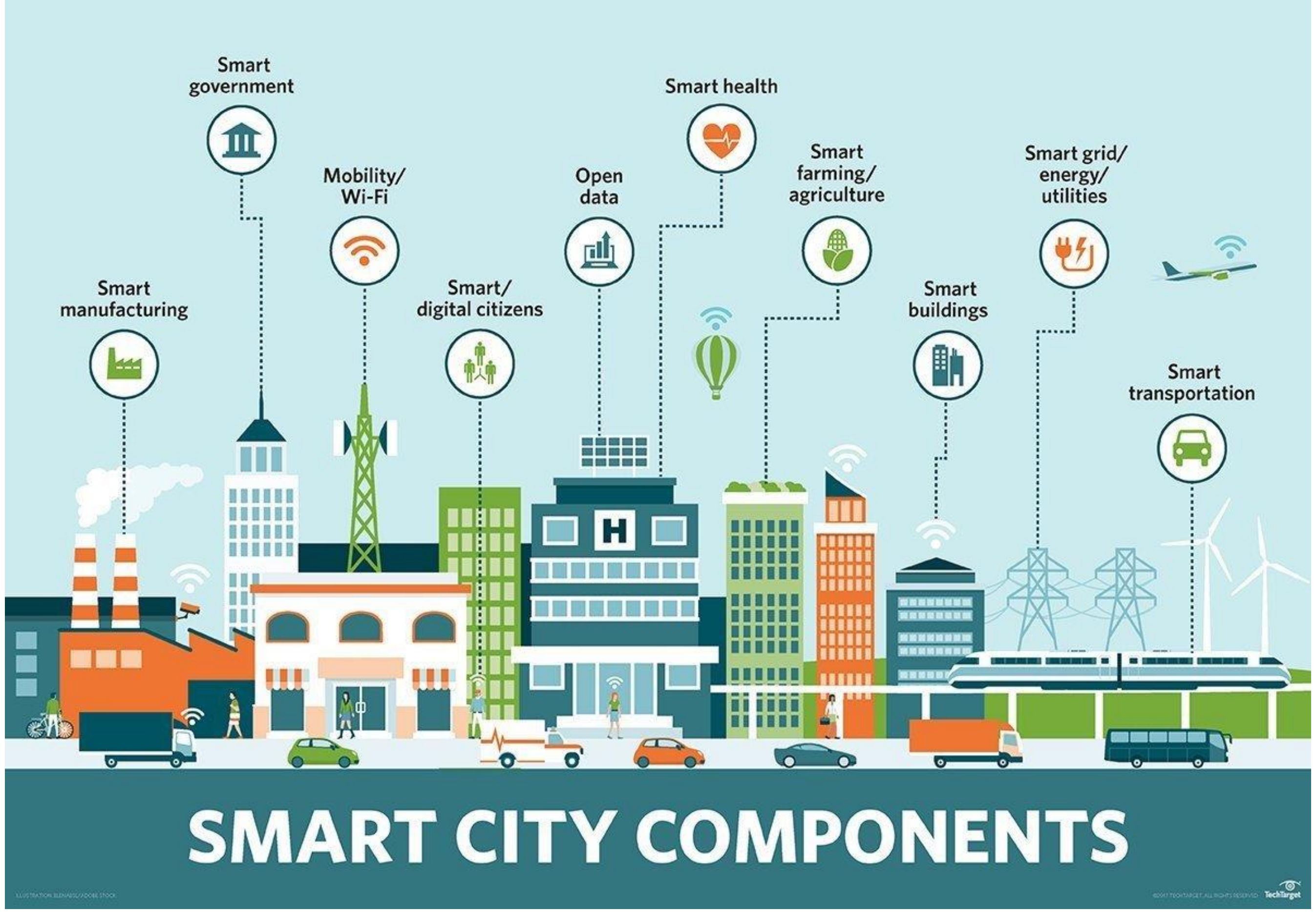
On-going-collaboration with Romanian's Academics@SMEs

Currently 4 EU projects, one ICT, one EIC FETProactive, one EIC FETOpen and one Twinning action

NANO components for electronic SMART wireless systems	NANOMATERIALS ENABLING SMART ENERGY HARVESTING FOR NEXT-GENERATION INTERNET-OF-THINGS	ACTIVE OPTICAL PHASE-CHANGE PLASMONIC TRANSDIMENSIONAL SYSTEMS ENABLING FEMTOJOULE AND FEMTOSECOND EXTREME BROADBAND ADAPTIVE RECONFIGURABLE DEVICES	NETWORKING CENTER FOR EXCELLENCE IN NANOELECTRONIC DEVICES FOR AIR MONITORING
NANOSMART	NanoEH	Phemtronics	NET4Air

Smart City of the future builds on *Internet of Things concept*

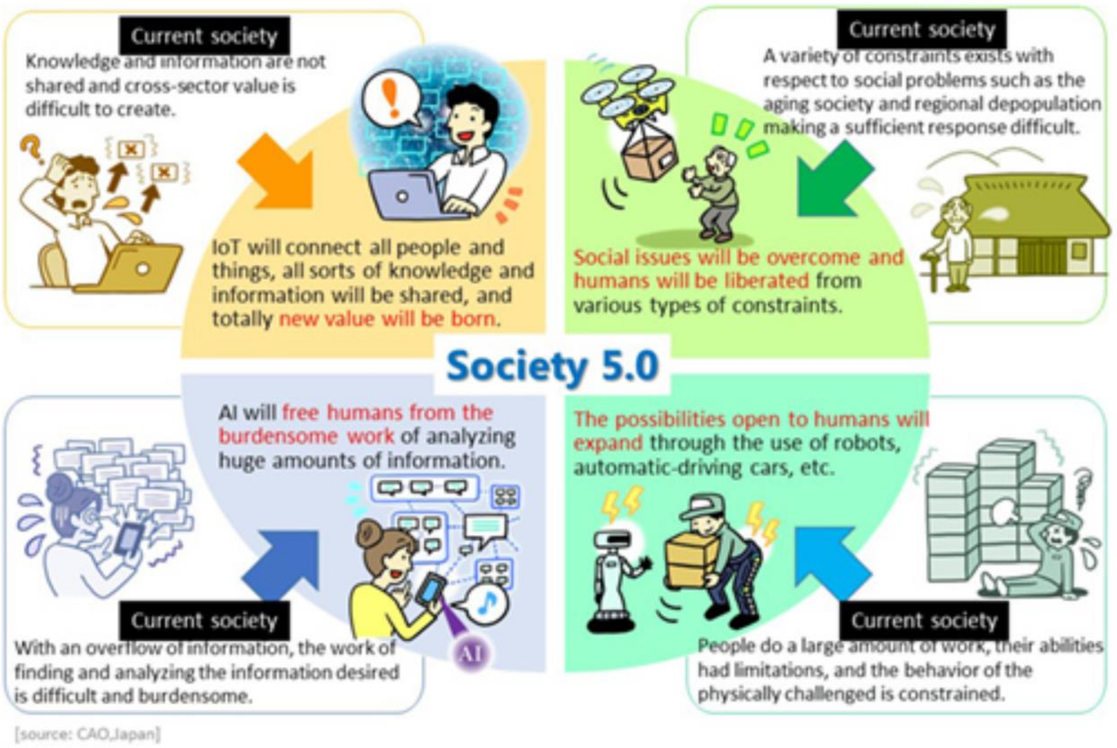
The 4th Industrial Revolution-European Concept



IoT describes the network of physical objects embedded with sensors, software, and other technologies for the purpose of connecting and exchanging data with other devices and systems over the internet

Smart City of the future builds on *Internet of Things concept*

Society 5.0- Japanese concept



Internet of Things future and stringent needs

The 4th Industrial Revolution

Next Gen Mobile Comm.
Emerging Connected-Health
Smart Farming
Smart Cities
builds on the

Internet-of-Things (IoT) paradigm

- **Scenario (2030) of having billions of interconnected autonomous mobile devices, with unprecedented processing power, storage capacity and access to knowledge**

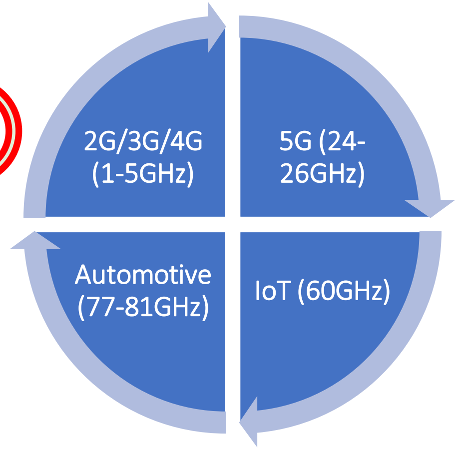
Billions interconnected of IoTs in networks need to be remotely deployed

- **IoTs maintenance may be either inconvenient or impossible(e.g. in 4IR)**

Key to successful deployment of future IoTs networks

IoT nodes operates maintenance-free over their whole predicted lifetime

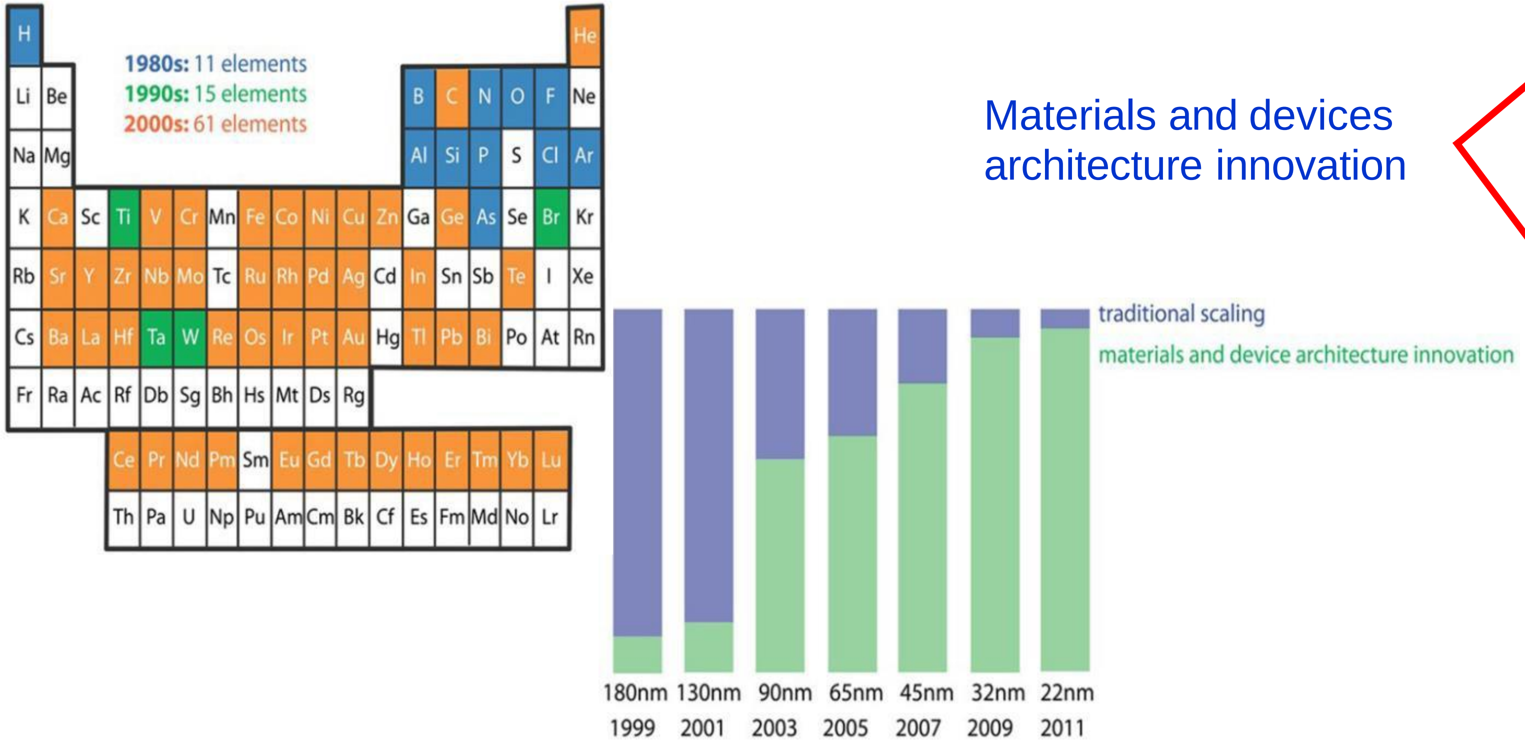
The *broadening of the wireless communication spectrum* in Europe makes the Radio frequency (RF) energy scavenging a highly desirable way forward for clean powering of the next-generation IoT.



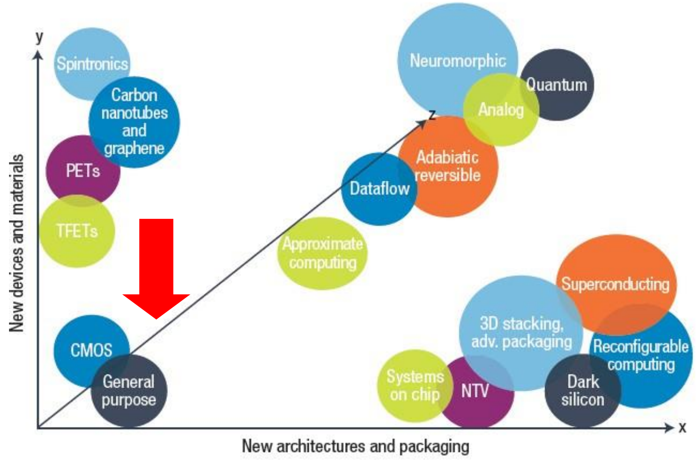
NANO-EH consortium aims to use RF energy scavenging a clean energy source for powering IoT

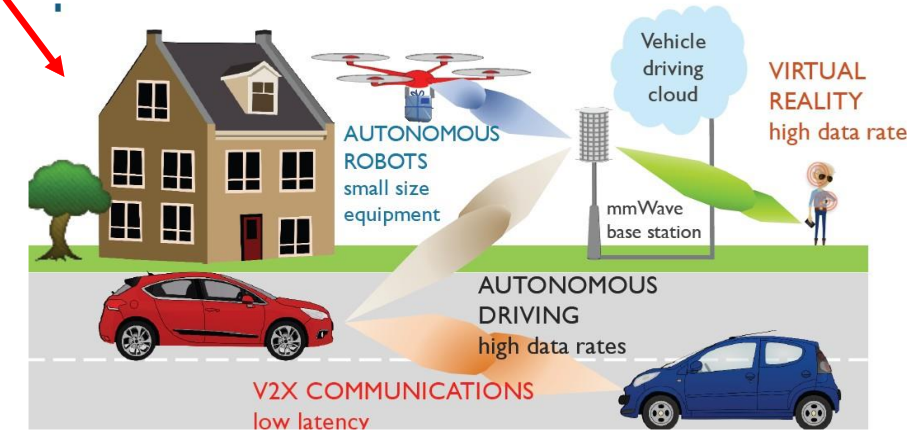
Emerging materials triggers device architecture innovation

The end of Moore's Law could be the best thing that has happened in computing since the beginning of Moore's Law," R. Stanley Williams, research scientist for HP Labs.
"Confronting the end of an epoch should enable a new era of creativity."
(Computing in Science & Engineering. IEEE CS and AIP – March/April 2017)



Materials and devices architecture innovation





Applied Physics Reviews 4, 011105 (2017)

Circuits reconfigurability and tunability for reconfigurable computing and communications such as 5G, 6G

- EU FUNDED UNDER EUROPEAN INNOVATION COUNCIL (EIC)

- FET Proactive project : emerging paradigms and communities call (FETPROACT-EIC-05-2019) in the subtopic “Breakthrough zero-emissions energy generation for full decarbonisation”.

- WWW.NANO-EH.EU

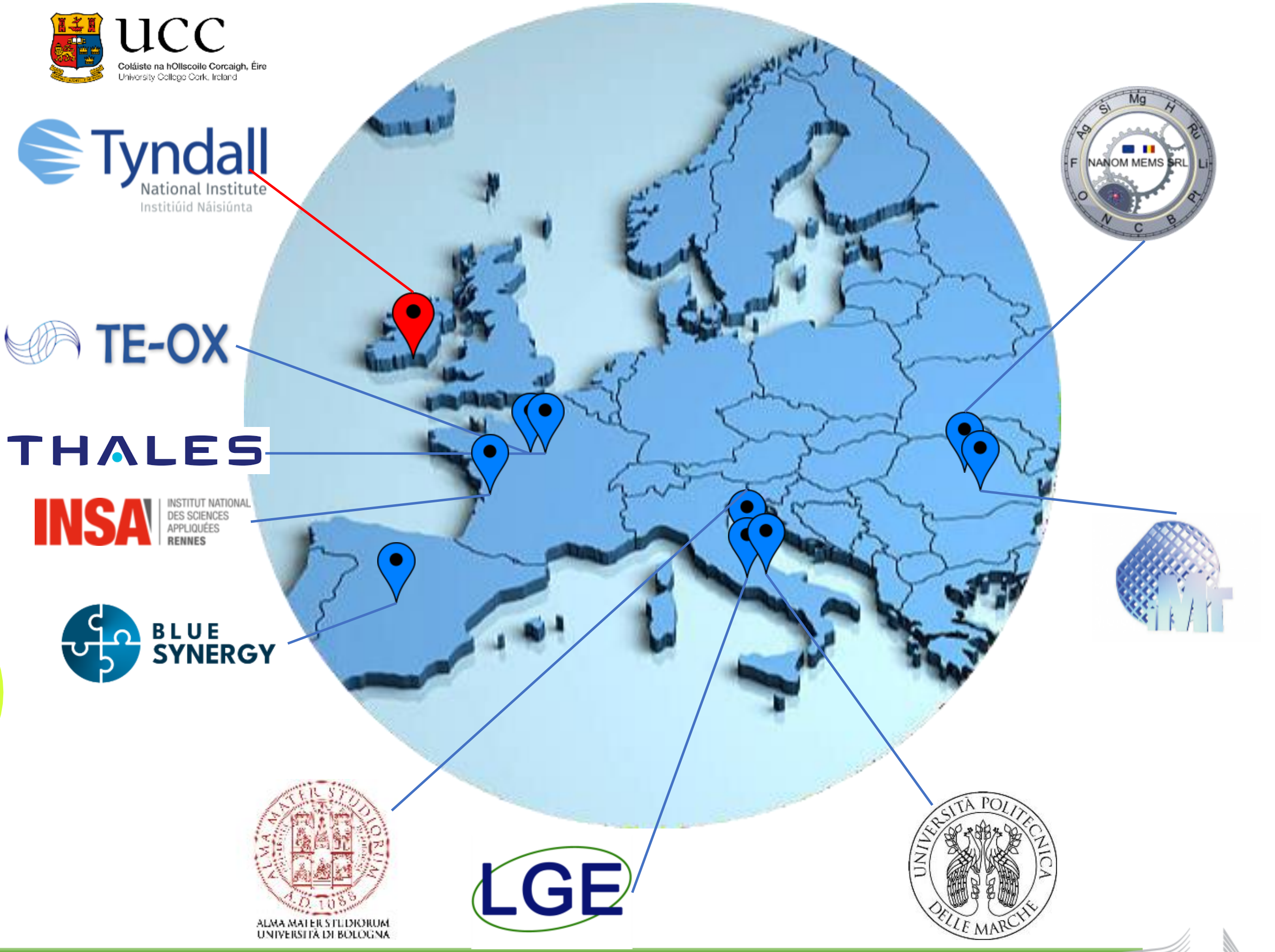
NANOMATERIALS ENABLING SMART ENERGY HARVESTING FOR NEXT-GENERATION INTERNET-OF-THINGS :NANO-EH

Duration:	42 months
Call identifier	H2020-EIC-FETPROACT-2019
Total Cost	3 929 360.00 €
Coordinator	Mircea Modreanu, UCC-TNI
Project website	www.nano-eh.eu

- Tyndall National Institute
- University of Bologna
- University Polytechnical delle Marche
- INSA Rennes
- IMT-Bucharest
- Thales
- TE-OX
- NANOM
- Luna Geber
- Blue Synergy

2 RDTs
2 University
1 Large Industry
4 SME

10 partners
5 countries



NANO-EH: OBJECTIVES

Hybrid integration of multi-source harvesters (RF, piezoelectric, heath, ambient light) on the same platform.

1. On-chip energy storage capabilities integration via high-performace supercapacitors.
2. On-demand energy harvesting: the appropriate source of energy harvesting selected according to the ambient availability, or a combination of the various sources.
3. Low cost, reliable, efficient and high-volume CMOS-compatible manufacturing processes on silicon.

5. Green technology approach: exploitation of non-toxic, easy materials recovery and recyclable materials for environment-friendly battery-less energy supply sub-systems/modules for IoT and WSNs

- NANO-EH address the fragmentation in the energy supply module for IoT market by proposing a platform compatible with Si planar technologies
- Key Benefits : lower cost, able to deliver large volume, easily deployable and widely accepted technological platform

NANO-EH: SMART MATERIALS PLATFORM

NANO-EH's exploits three classes of ***smart nanomaterials*** that are *non-toxic*, *lead- and rare earth-free :*

- One new class of energy harvesting/storage oxide nanomaterials: *Hafnium Zirconium Oxides* ($HfZrO_f$ *and* $HfZrO_d$)
- One new class of energy harvesting of *Two-Dimensional (2D)* nanomaterials: *2D* MoS_2
- One class of renewable bio-based piezoelectric nanomaterials, namely the *functionalised nanocellulose*
- Energy storage functionality will be built in via *high performance supercapacitors (HfZrO and* VO_2*(B) oxides)*

NANO-EH's has the ambition of covering the whole technological value chain:

Materials development → design and modelling of devices → devices fabrication and testing →integration of devices in demonstrators

1st Challenge
- Nanomaterials development at wafer scale

2nd Challenge
- Design with electromagnetic modelling tools of new energy harvesting and energy storage device architectures

3rd Challenge
- Fabrication, testing and benchmarking at both device and submodule level

Emerging nanoscale wide bandgap HfO_2 ferroelectrics

Why researching nanoscale HfO_2 (and others) ferroelectrics ?

Traditional ferroelectric (e.g. $BaTiO_3$ or PZT) cannot

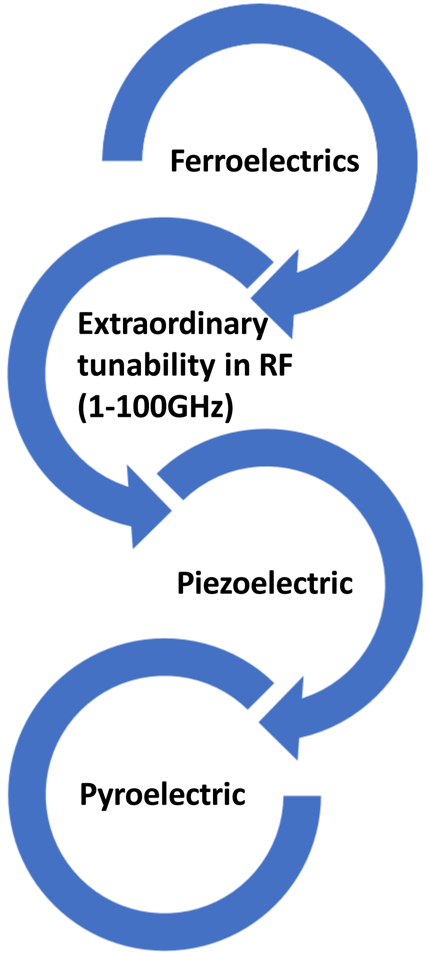
Be downscaled to a few nm	Requires high operation voltages	Not CMOS compatible

Emerging Hafnium oxides ferroelectrics

Can be downscaled to 1-2nm	Low operation voltages 1-3V	CMOS compatible

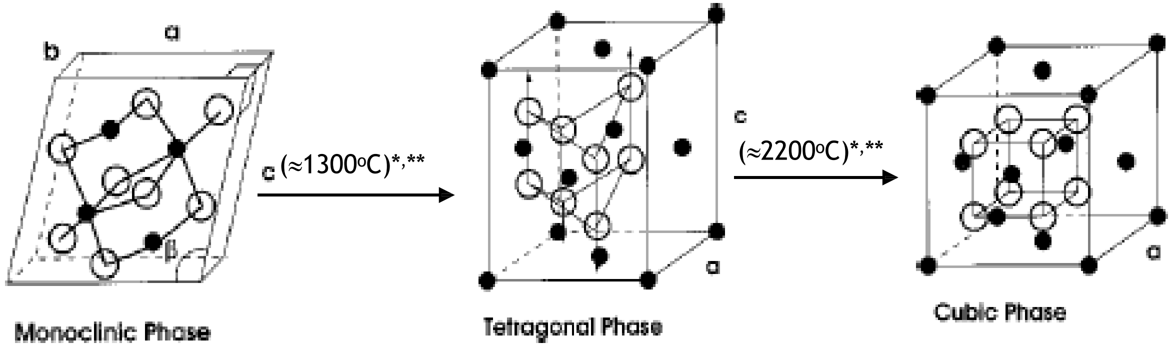
The rise of ferroelectrity at nanoscale

New devices architectures for CMOS FeFET, FERam	New devices architectures for high frequency devices (5G&6G) RF and Pyroelectric Harvesters and energy storages devices

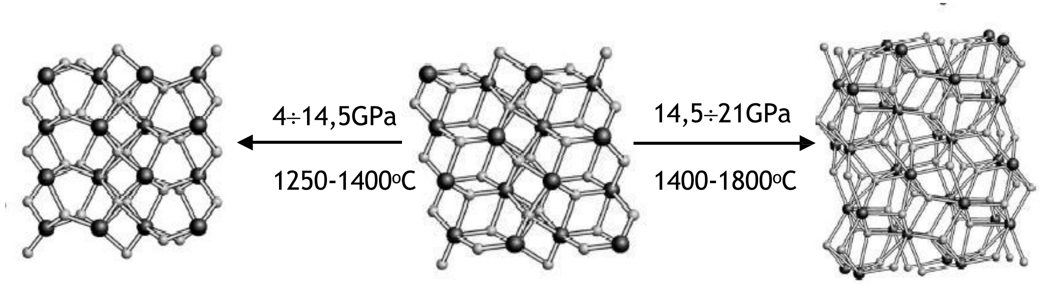


State-of the art knowledge of HfO_2 polymorphs about two decades ago

i) Ambient pressure and high temperature



ii) High pressure and high temperature



Orthorhombic-I phase*** Monoclinic phase** Orthorhombic-II phase***

Theory prediction: all HfO_2 polymorphs are dielectrics

Orthorhombic phases of HfO_2 stabilized at high pressure and high temperatures and only in bulk

No report of orthorhombic phases of HfO_2 reported in thin films until …2006 (*see next slide*)

*X.Zhao et al. al. Phys.Rev.B , 65, 233106 (2002); **J.M.Leger et al. Phys.Rev.B, 48, 93, (1993); ***J. Kang, et al. Phys.Rev.B 68, 054106 (2003)

Nanoscale HfO_2 ferroelectrics: first report of orthorhombic polar (o-III) phase

- The discovery of ferroelectricity in few nm HfO_2/HfZrO was a Big Surprise
- Traditional thinking (*20 years ago…)* →HfO_2 (HfZrO) is a dielectric irrespective crystalline polymorphs (***m***, ***o***, ***t*** or ***c)***

Orthorhombic polar (o-III) Raman fingerprint around 322cm-1

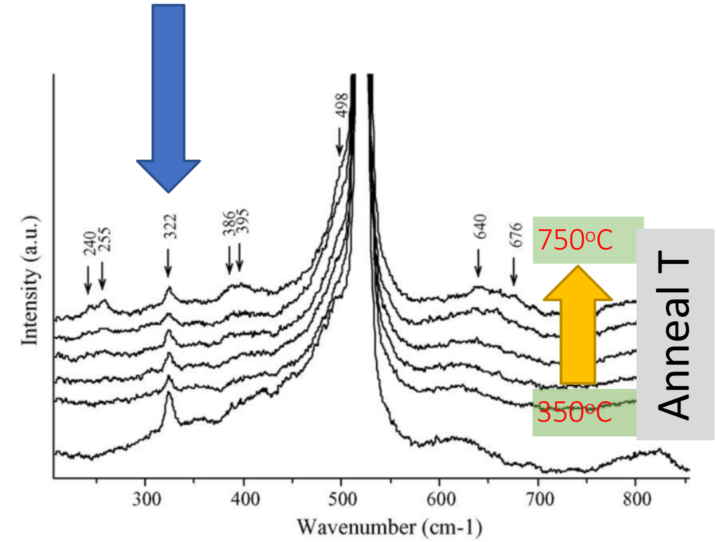


Fig. 4. Raman spectra recorded in 600 s at 325 nm on samples Hc1 (bottom) to Hc6 (top). The peak of Silicon is located at ~520 cm^{-1}. The peak at 322 cm^{-1} cannot be assigned to any known HfO_2 crystalline phase.

First report of HfO_2 Orthorhombic polar (o-III) : 2006

M. Modreanu et al. / Applied Surface Science 253 (2006) 328–334

First reported at EMRS Spring Meeting 2005 !

However, in 2006 HfO_2 Orthorhombic polar was not known

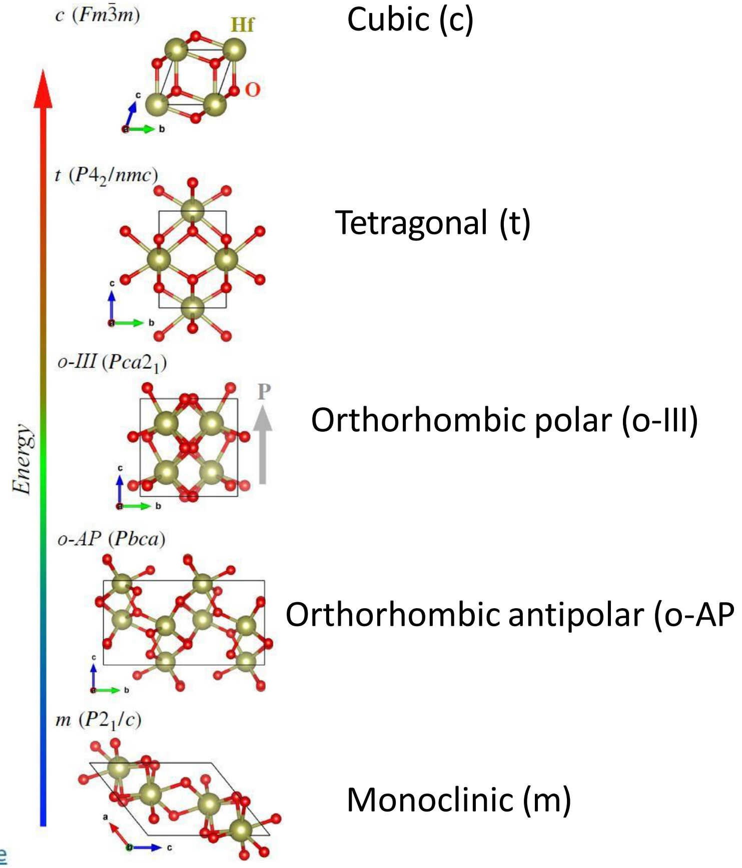
Raman phonon modes for Orthorhombic polar (o-III) : 2022

nature > npj quantum materials > articles > article

Article | Open Access | Published: 18 March 2022

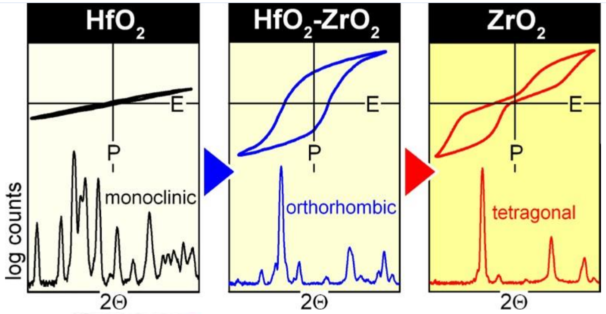
Vibrational fingerprints of ferroelectric HfO_2

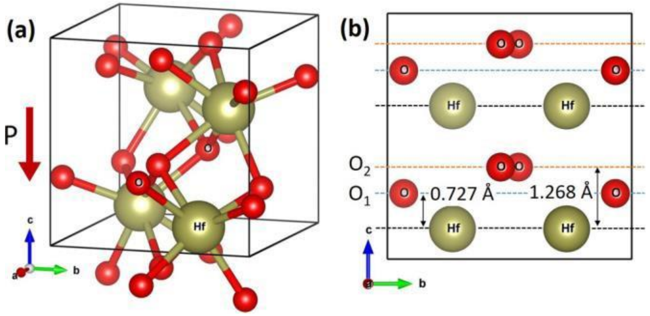
Shiyu Fan, Sobhit Singh, Xianghan Xu, Kiman Park, Yubo Qi, S. W. Cheong, David Vanderbilt, Karin M. Rabe



Ferroelectricity in hafnium oxide thin films

- T. S. Böscke, et al, Ferroelectricity in hafnium oxide thin films, Appl. Phys. Lett. 99, 102903 (2011);
- J. Müller, et al., Ferroelectricity in Simple Binary ZrO_2 and HfO_2, Nano Lett. 12, 4318-4323 (2012).





Strategy

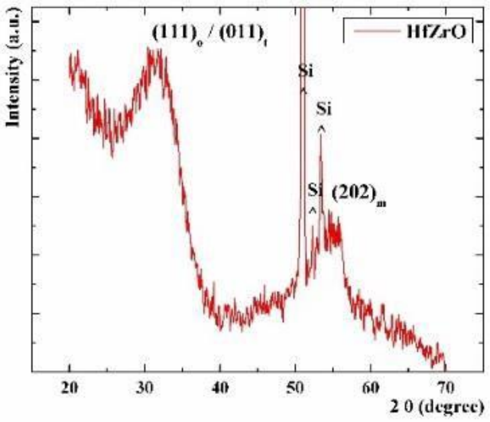
ALD HfO_2 (*undoped* or *doped*-Si, Al, Y, La) deposited between two TiN layers then a wake-up RTA around 450°C required to stabilize **orthorhombic polar (o-III)**

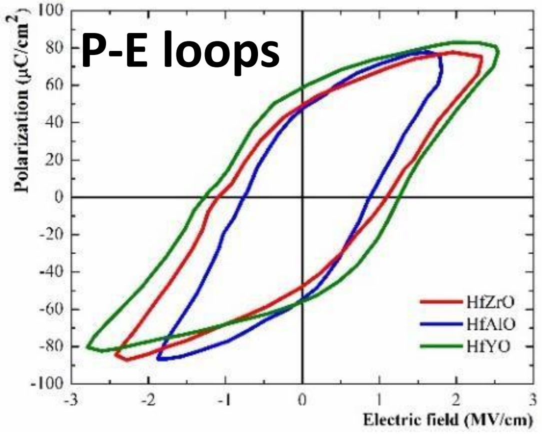
TiN
6-8nm HfO_2
TiN
Si

Many devices demonstrated
FeFET, FERAM, Supercaps
Typically, CMOS (<2 GHZ)

Our approach for hafnium oxide ferroelectrics

- Avoid confinement between two TiN layers
- Avoid wake-up annealing for stabilization of **orthorhombic polar**
- Direct ALD growth on HR Si using nanolaminate growth regime
- Ferroelectric 7nm-thick HfZrO, HfAlO and HfYO demonstrated
- Diffraction patterns consistent with a paracrystalline like-structure with a high degree of disorder introduced by the presence oxygen vacancies

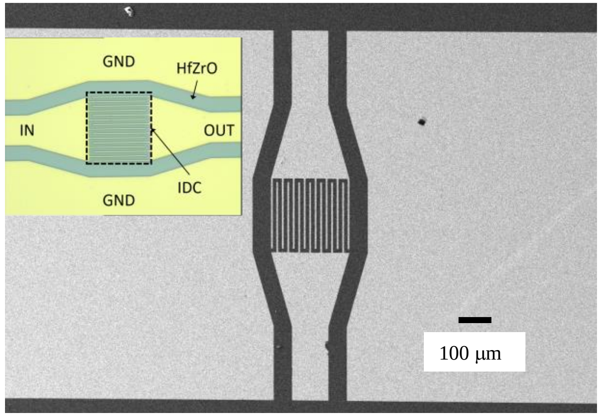


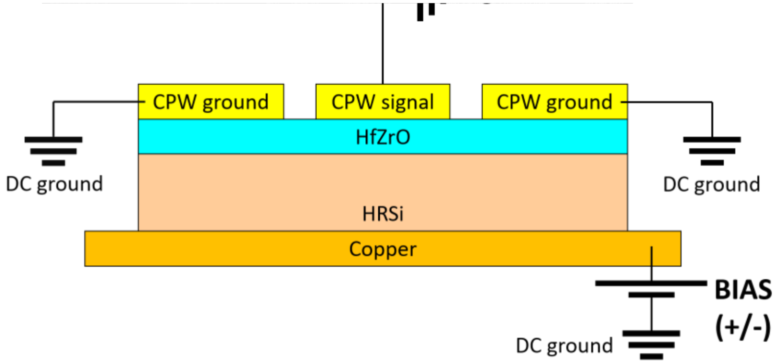


Film	HfZrO	HfAlO	HfYO
Coercive field E_c (MV/cm)	1.09	0.81	1.25
Remanent polarization P_r [μC/cm²]	48.5	50.5	56.5

Direct growth of HfO_2 ferroelectrics on High Resistivity Si opened the way for high-frequency application

HfZrO ferroelectrics: RF applications-*Phase shifters*





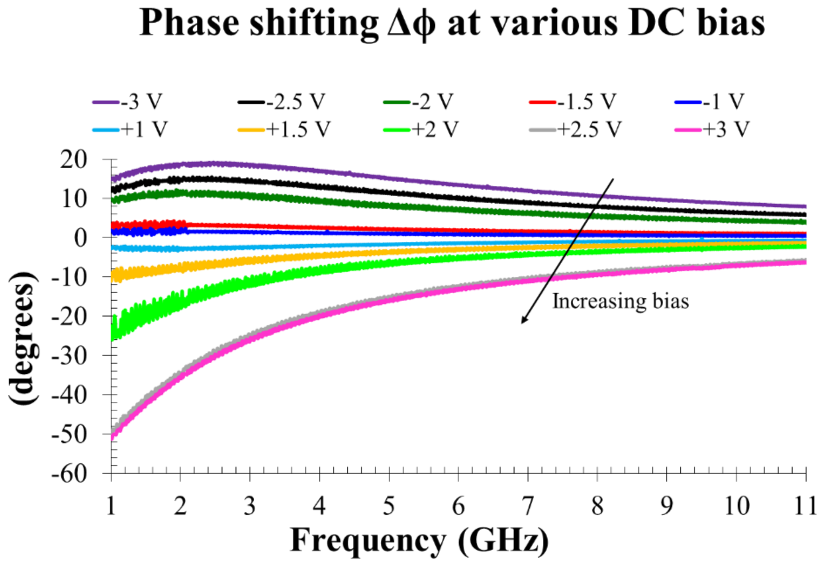
Nanotechnology 28 (2017) 38LT04 (5pp) https://doi.org/10.1088/1361-6528/aa8425

Letter

Very large phase shift of microwave signals in a 6 nm $Hf_xZr_{1-x}O_2$ ferroelectric at ±3 V

Mircea Dragoman[1], Mircea Modreanu[2], Ian M Povey[2], Sergiu Iordanescu[1], Martino Aldrigo[1], Cosmin Romanitan[1,3], Dan Vasilache[1], Adrian Dinescu[1] and Daniela Dragoman[3,4]

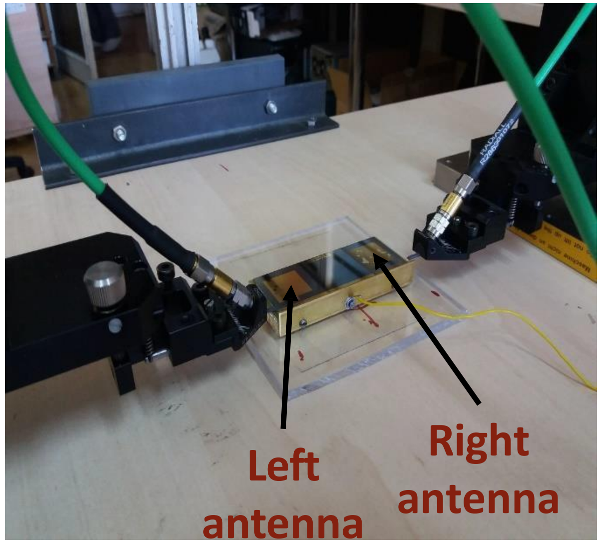
2017

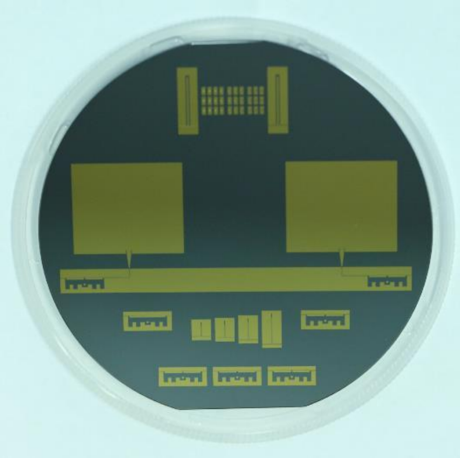


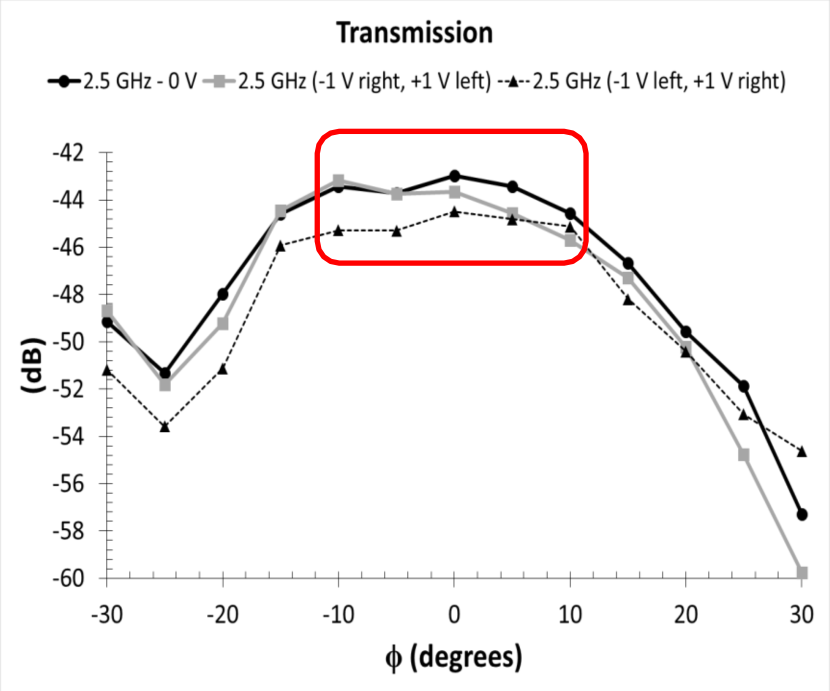
Frequency (GHz)	$\Delta\varphi_{-3V}$	$\Delta\varphi_{+3V}$	$\Delta\varphi_t$
1	14.99°	-51.24°	66.23°
2.45	18.92°	-30.87°	49.79°
5.5	14.20°	-14.56°	28.76°
10	8.78°	-6.86°	15.62°

Nanoscale HfZrO ferroelectrics: RF applications

Steering radiation beam of an antenna array (2 antennas) 25 ^{0} with ±1 V at 2.55 GHz







Antennas and propagation | Free Access

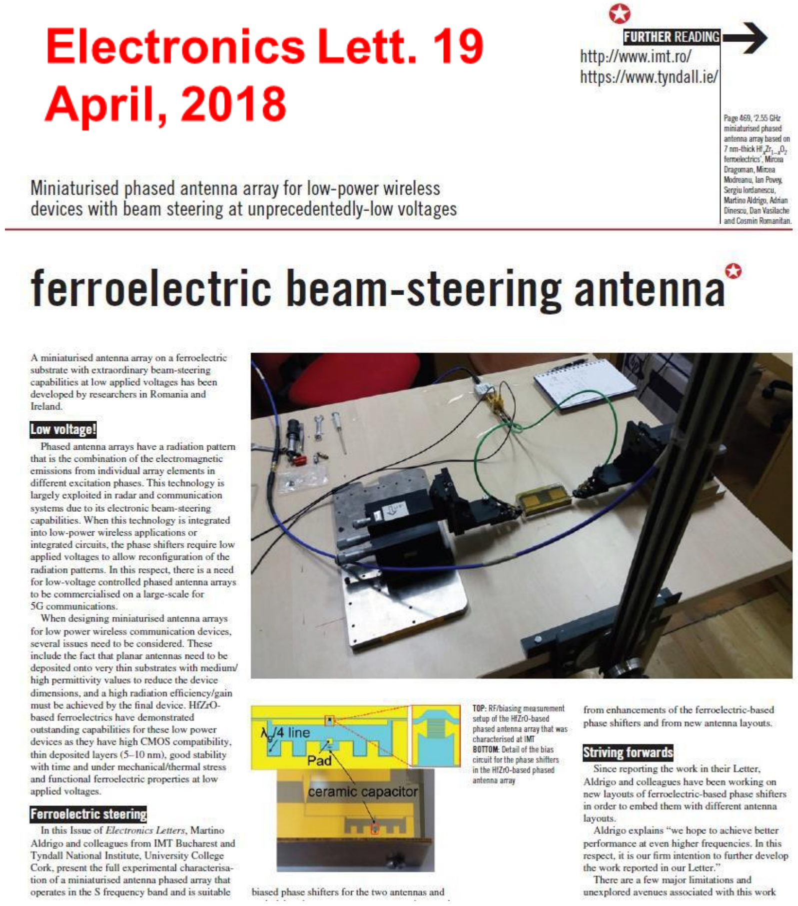
2.55 GHz miniaturised phased antenna array based on 7 nm-thick $Hf_xZr_{1-x}O_2$ ferroelectrics

M. Dragoman, M. Modreanu, I. Povey, S. Iordanescu, M. Aldrigo, A. Dinescu, D. Vasilache, C. Romanitan

First published: 01 April 2018 | https://doi.org/10.1049/el.2018.0111 | Citations: 8

2018

Electronics Lett. 19 April, 2018



FURTHER READING

http://www.imt.ro/
https://www.tyndall.ie/

Page 469, '2.55 GHz miniaturised phased antenna array based on 7 nm-thick $Hf_xZr_{1-x}O_2$ ferroelectrics', Mircea Dragoman, Mircea Modreanu, Ian Povey, Sergiu Iordanescu, Martino Aldrigo, Adrian Dinescu, Dan Vasilache and Cosmin Romanitan.

Miniaturised phased antenna array for low-power wireless devices with beam steering at unprecedentedly-low voltages

ferroelectric beam-steering antenna

A miniaturised antenna array on a ferroelectric substrate with extraordinary beam-steering capabilities at low applied voltages has been developed by researchers in Romania and Ireland.

Low voltage!

Phased antenna arrays have a radiation pattern that is the combination of the electromagnetic emissions from individual array elements in different excitation phases. This technology is largely exploited in radar and communication systems due to its electronic beam-steering capabilities. When this technology is integrated into low-power wireless applications or integrated circuits, the phase shifters require low applied voltages to allow reconfiguration of the radiation patterns. In this respect, there is a need for low-voltage controlled phased antenna arrays to be commercialised on a large-scale for 5G communications.

When designing miniaturised antenna arrays for low power wireless communication devices, several issues need to be considered. These include the fact that planar antennas need to be deposited onto very thin substrates with medium/high permittivity values to reduce the device dimensions, and a high radiation efficiency/gain must be achieved by the final device. HfZrO-based ferroelectrics have demonstrated outstanding capabilities for these low power devices as they have high CMOS compatibility, thin deposited layers (5–10 nm), good stability with time and under mechanical/thermal stress and functional ferroelectric properties at low applied voltages.

Ferroelectric steering

In this Issue of *Electronics Letters*, Martino Aldrigo and colleagues from IMT Bucharest and Tyndall National Institute, University College Cork, present the full experimental characterisation of a miniaturised antenna phased array that operates in the S frequency band and is suitable

biased phase shifters for the two antennas and

TOP: RF/biasing measurement setup of the HfZrO-based phased antenna array that was characterised at IMT
BOTTOM: Detail of the bias circuit for the phase shifters in the HfZrO-based phased antenna array

from enhancements of the ferroelectric-based phase shifters and from new antenna layouts.

Striving forwards

Since reporting the work in their Letter, Aldrigo and colleagues have been working on new layouts of ferroelectric-based phase shifters in order to embed them with different antenna layouts.

Aldrigo explains "we hope to achieve better performance at even higher frequencies. In this respect, it is our firm intention to further develop the work reported in our Letter."

There are a few major limitations and unexplored avenues associated with this work

Nanoscale HfZrO ferroelectrics: RF applications

FIRST MICROWAVE INTEGRATED CIRCUIT BASED ON HfZrO: graphene/HfZrO radio

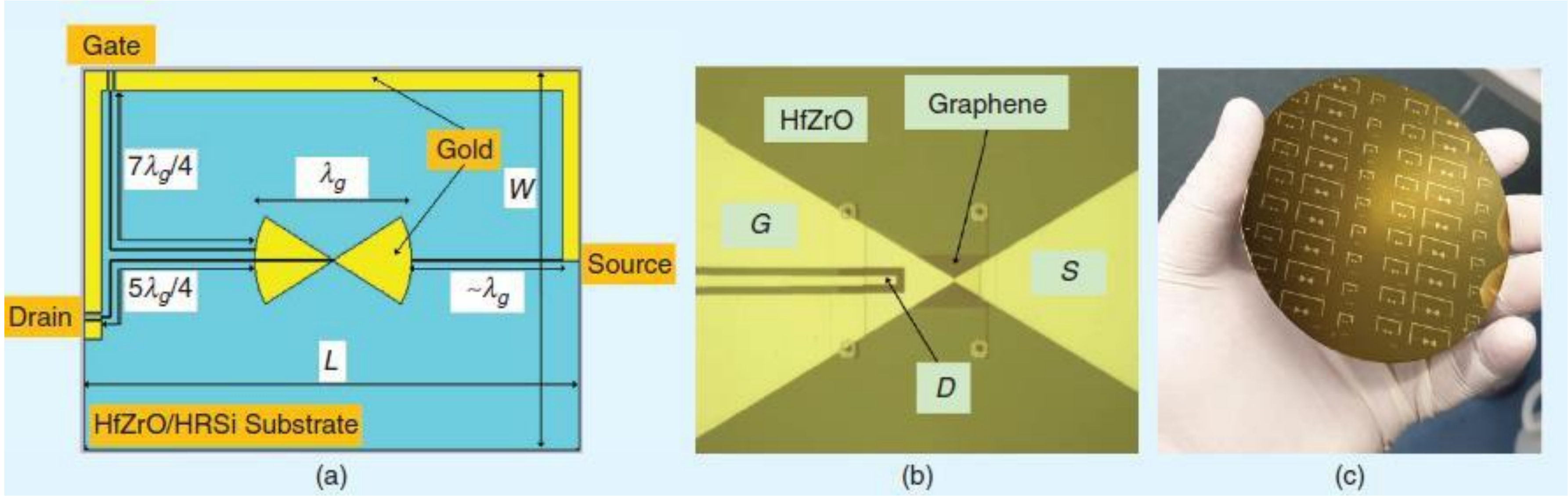
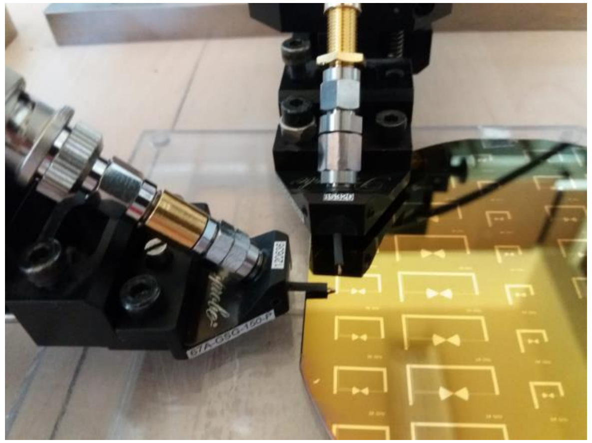


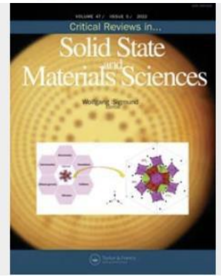
TABLE 4 The performance of the graphene/HfZrO FET microwave detector.

FREQUENCY (GHz)	V_G (V)	V_D (V)	DETECTED DC VOLTAGE (MV)
4	0	+0.02	12
4	0	−0.02	7.2
4	+2	+1.02	11.4
4	−2	−1.02	11
6	+2	+1.02	1.04
12	+2	+1.02	0.88



The Rise of Ferroelectricity at Nanoscale: Nanoelectronics is rediscovering the ferroelectricity

IEEE Nanotechnology Magazine (Volume: 15 , Issue: 5, October 2021)



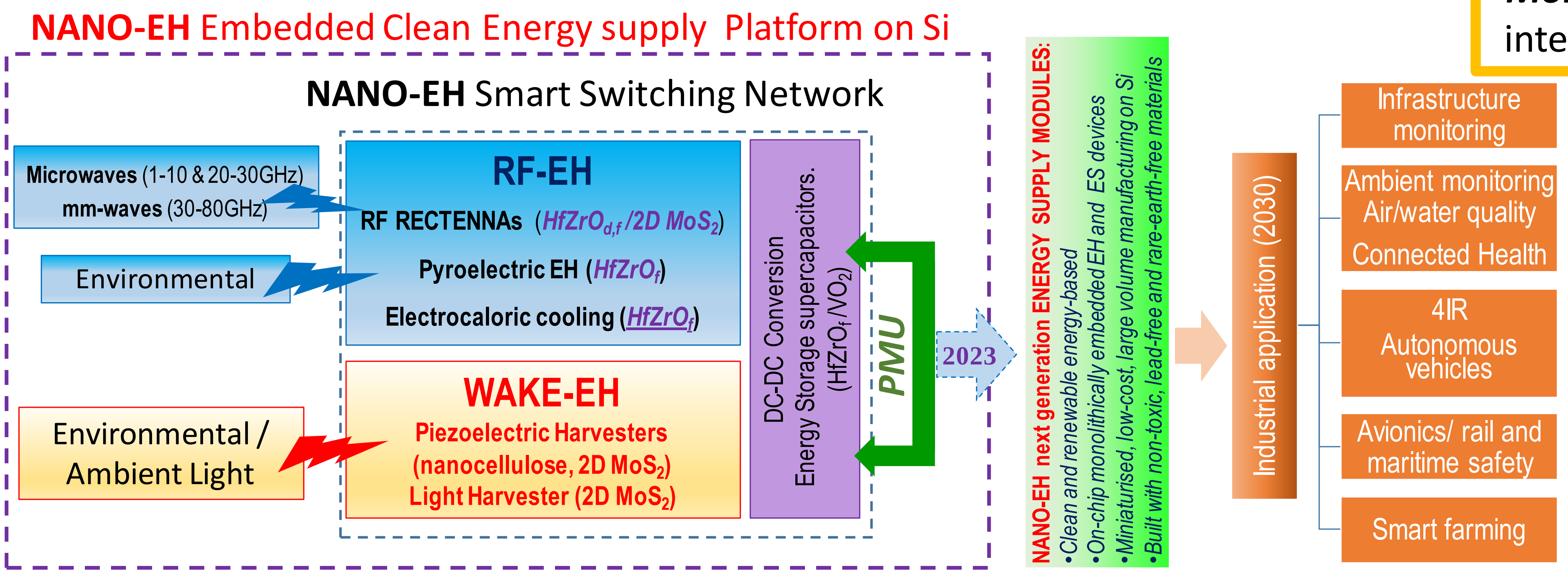
Review Critical Reviews in Solid State and Materials Sciences (2022)

Ferroelectrics at the nanoscale: materials and devices – a critical review

https://doi.org/10.1080/10408436.2022.2083579

NANO-EH's concept of a multi-source EM energy harvesting/energy storage platform integrated on Si substrate

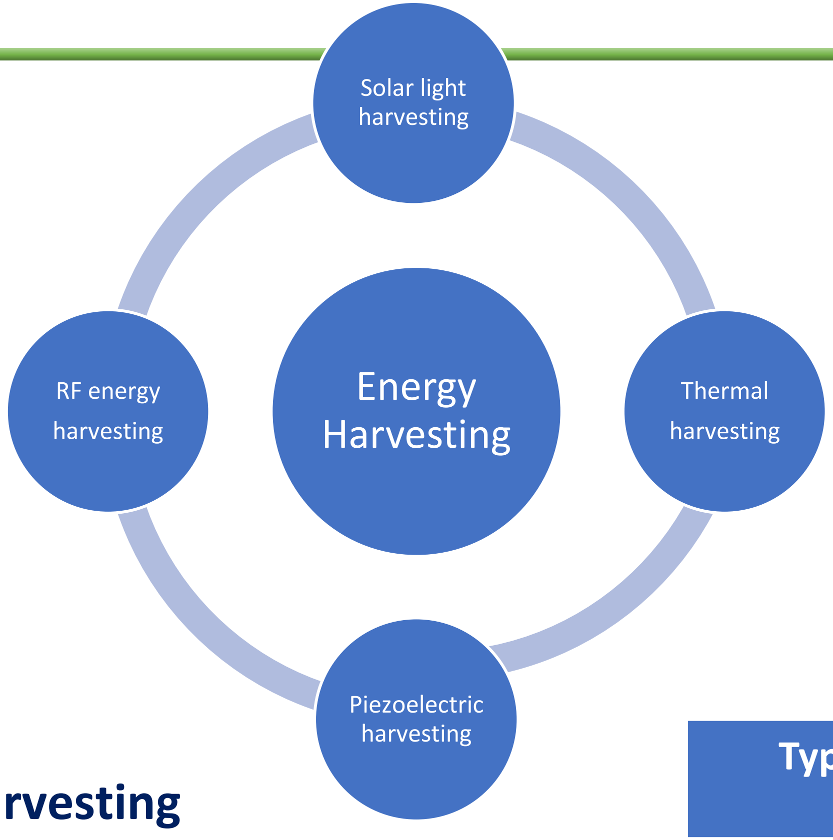
TARGET
Monolithic or ***hybrid***
integration on silicon



Need for design/simulation/modelling of different energy harvesters/energy storage devices and components

Multi-source Energy Harvesting

Gather energy from ambient environment and **convert it into** usable **electrical power**



Advantages

- Plentiful energy solution → Unlimited usage
- Readily available, anywhere, everywhere
- **Green and clean**

Importance of Energy Harvesting

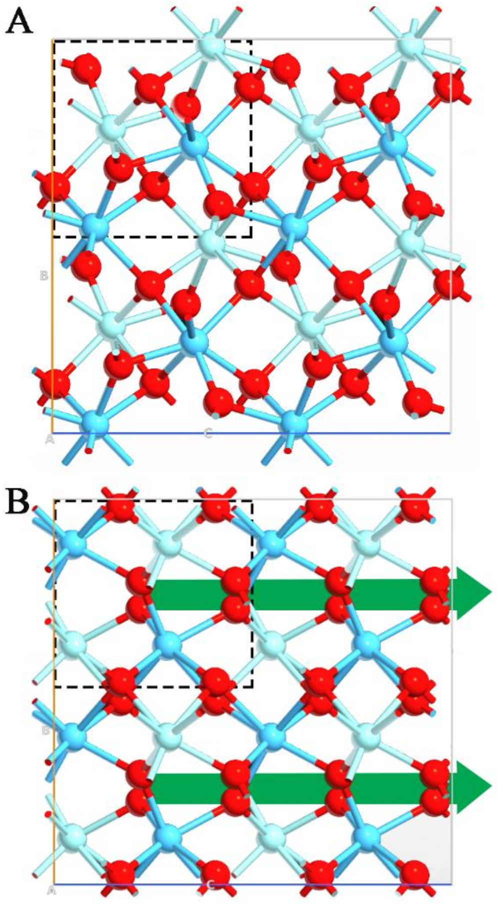
- Accelerated interest for powering ubiquitously deployed sensor networks and mobile electronic products
- To reduce dependency on batteries
- To conserve energy consumption and promote environmental friendliness

Typical energy harvester Output power	
RF	0,1 μW/cm^2
Piezo	1 nW/cm^2
Thermal	10 mW/cm^2
Solar	100 mW/cm^2

Typical energy harvester Voltages	
RF	0.01 mV
Piezo	0.1 ~ 0.4 V
Thermal	0.02 ~ 1 V
Solar	0.5 ~ 0.7 V

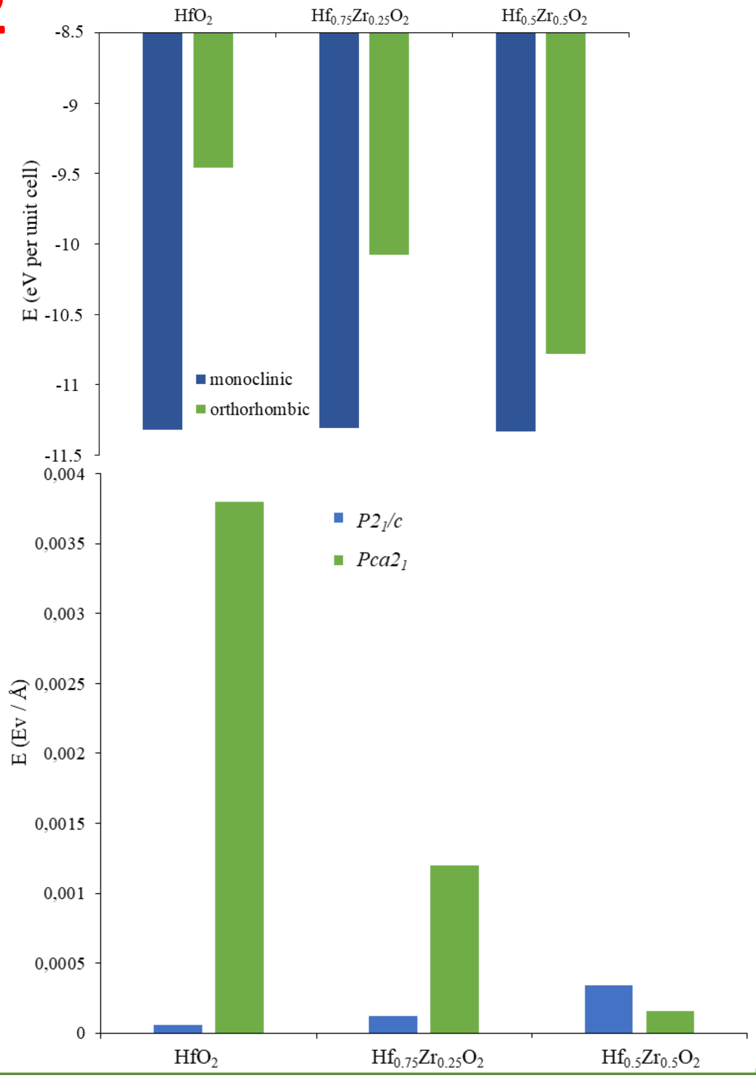
NANO-EH Atomistic to Mesoscale Modelling platform

1 Monoclinic HfZrO



Orthorombic HfZrO

2

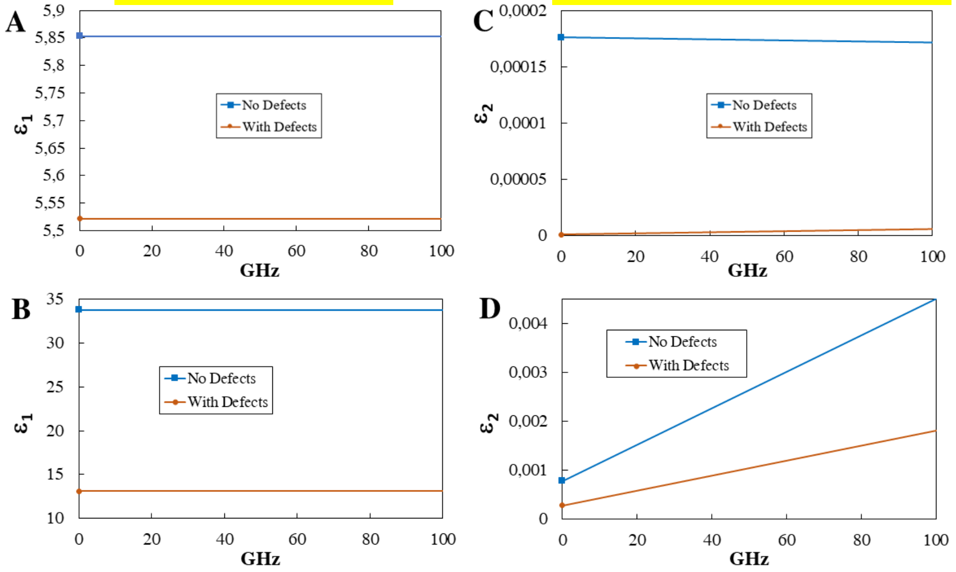


3

$Hf_xZr_yO_2$ systems	ε_1 at 0 GHz	ε_2 at 0 GHz
m-HfO_2	5.73	3.25×10^{-4}
m-$Hf_{0.75}Zr_{0.25}O_2$	5.02	3.26×10^{-4}
m-$Hf_{0.5}Zr_{0.5}O_2$	4.33	3.29×10^{-4}
o-HfO_2	5.88	3.02×10^{-6}
o-$Hf_{0.75}Zr_{0.25}O_2$	11.04	3.75×10^{-6}
o-$Hf_{0.5}Zr_{0.5}O_2$	36.06	4.01×10^{-6}

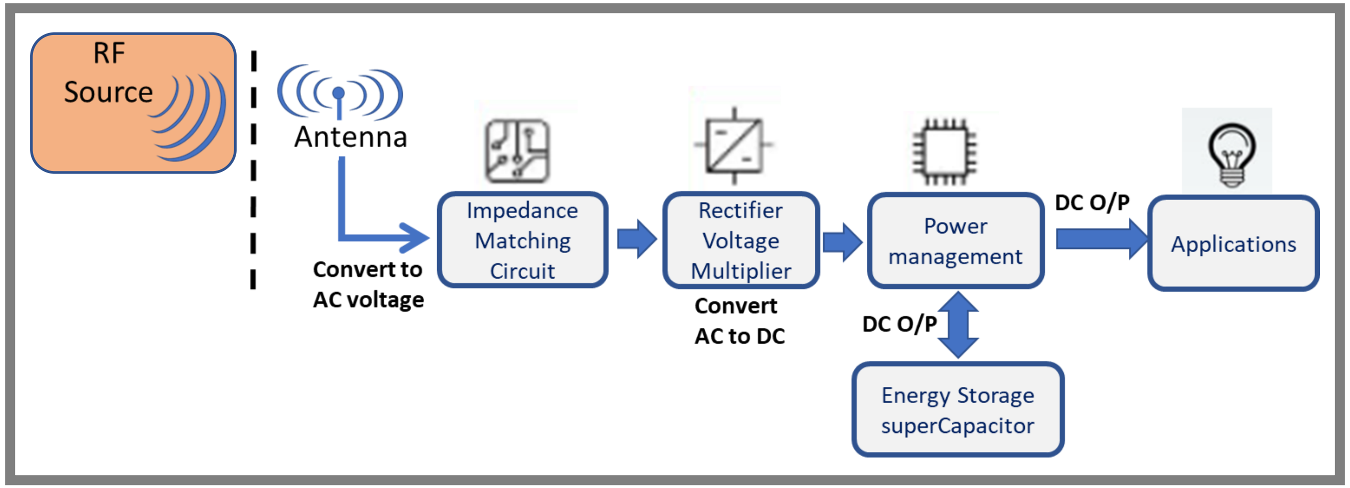
Real part, ε_1

Imaginary part, ε_2

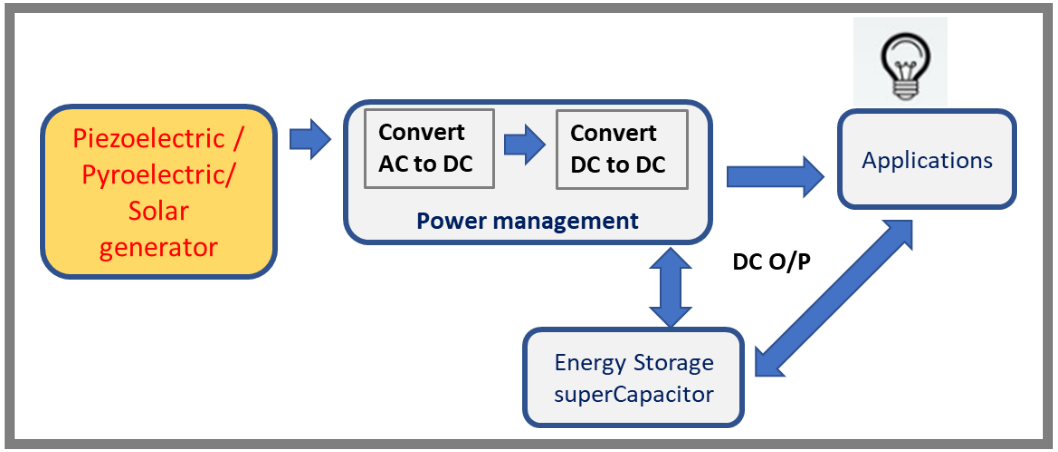


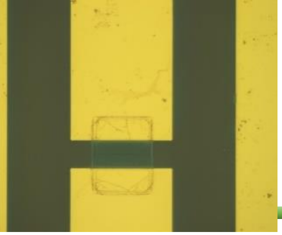
Multi-source Energy Harvesting

- RF harvester
  - Antenna
    - 2.45 GHz → 2G/3G/4G
    - 24-26 GHz → 5G
    - 60 GHz → IoT
  - MIM or SS diodes
  - DC circuitry
  - Power divider
  - Phase shifter



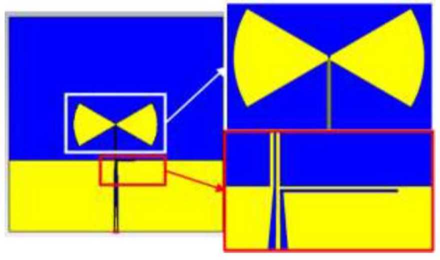
- Piezoelectric harvester
- Pyroelectric harvester
- Solar/light harvester
- Energy storage devices
  - Supercapacitors

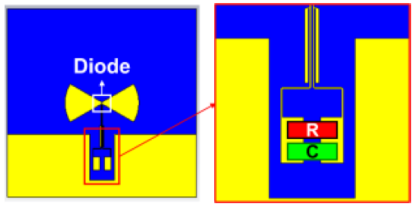




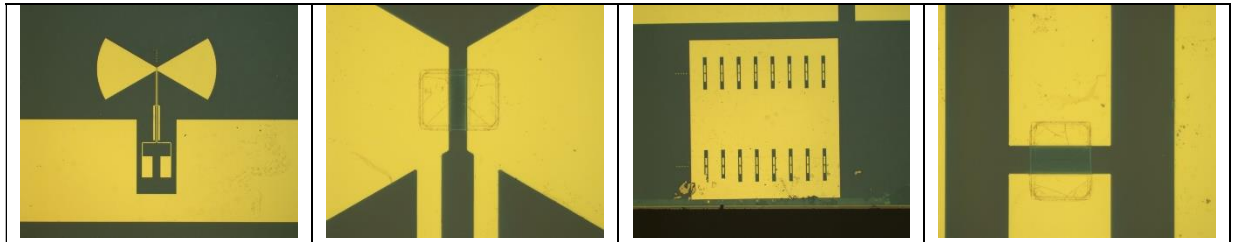
NANO-EH project highlights

Bow-tie antenna @ 24 GHz





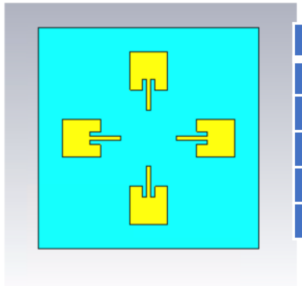
Performance indicator	Value
Resonance frequency	24 GHz
Radiation efficiency	90%
Gain	7.3 dBi



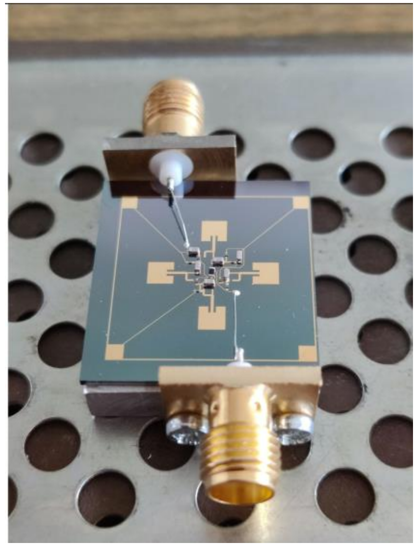
(a)	(b)	(c)	(d)

Optical pictures of the fabricated (a) 24-GHz bow-tie antennas; (b) detail of the gap of the antenna; (c) MoS_2-based SSDs in CPW technology; (d) detail of the diode's area in between a CPW signal line

Dual-polarized patch antenna array @ 24 GHz



Performance indicator	Value
Resonance frequency (Lego antenna)	24 GHz
Radiation efficiency (Lego antenna)	75%
Gain (Lego antenna)	4.5 dBi
Maximum conversion efficiency	43% at 14 dBm
Differential output voltage	6.7 V (on a 3.9 kΩ load)

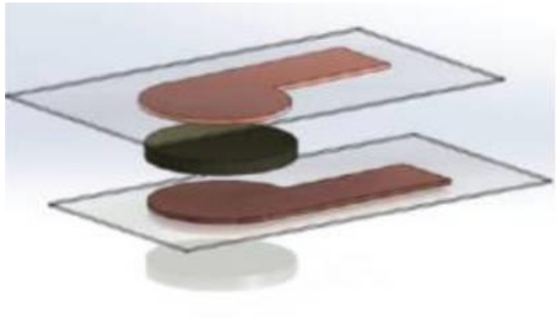


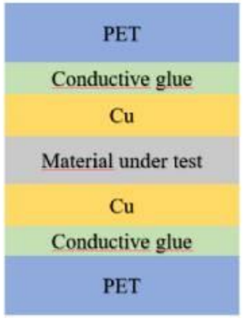
First proof-of-concept RF harvesters (24-27 GHz)

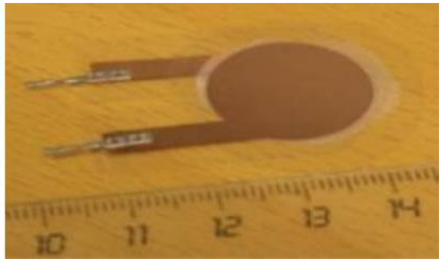
Realization of a mixed RF-piezo energy harvester

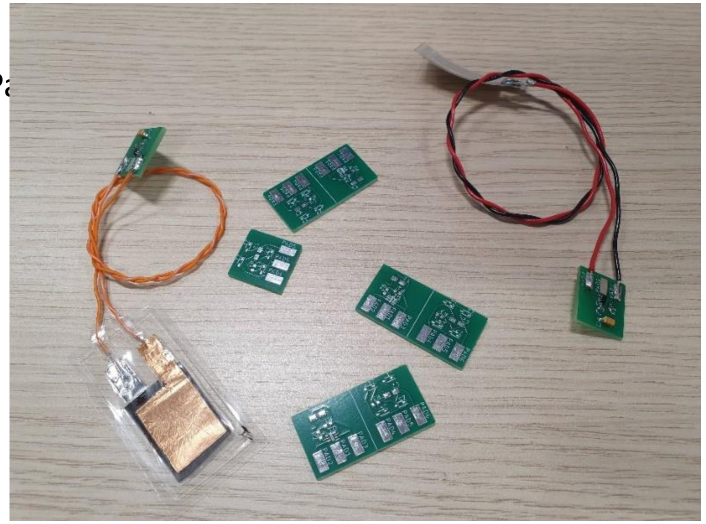
Goal: use of recyclable, bio-based, piezoelectric materials to design an innovative EH demonstrator capable of improving the RF-DC conversion efficiency of the RF-EH

- Key specifications for the demonstrator have been identified:
  - Substrate thickness: min. 100 µm
  - Substrate Young's modulus: min. 2 GPa
  - Dimensions: 20x30 mm
  - Frequency: 1-50 Hz
  - Thermal stability: up to 50°C
  - Open circuit peak voltage: > 100 mV
  - Vibrational input: max. 20 g.
  - Pressure input: max 500 N







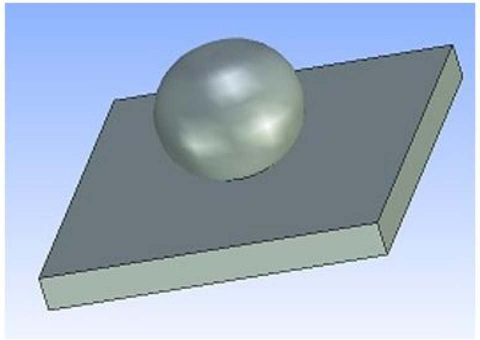


NANO-EH fabricated piezo-harvester

NANO-EH project highlights : Spherical solar cells

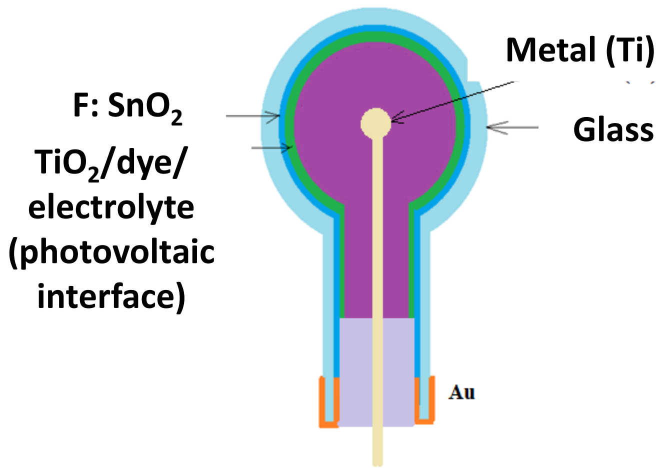
Advantages of spherical solar cells:

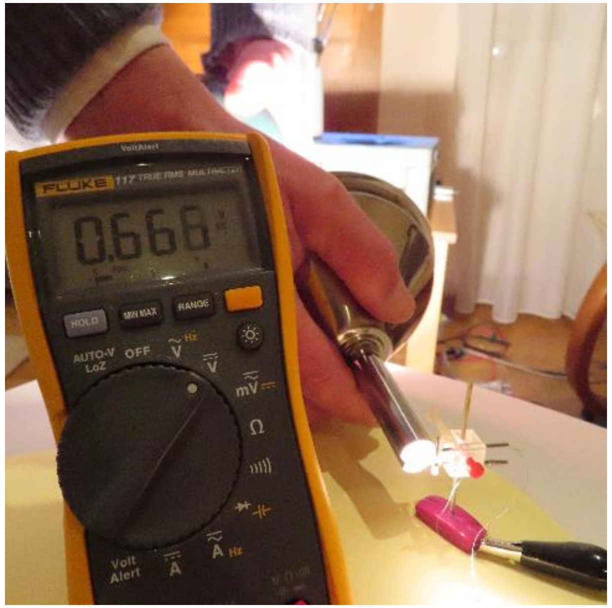
- Collect and harvest sunlight three-dimensionally
- The spherical shape offers a good protection of the active layers.
- Simple structure, cheap and suitable for mass production
- They can be made in a large variety of sizes, colors, and curvatures
- Dust accumulation is greatly diminished compared with planar solar cells.



Specifications required:

- **Conversion efficiency:** min 10%
- **V_{OC}:** min 0.7 V
- **Fill factor:** min. 0.6
- Dimension 2.5mmx8mm





Fabricated spherical solar cells in NANO-EH

Conclusions

- Internet of Things *future and stringent needs they need to be energy autonomous*
- *Need to address* the fragmentation in the energy supply module for IoT market (30 bilions/2030)
- European Innovation Council's NANO-EH proposes a low cost, reliable, efficient and high-volume CMOS-compatible manufacturing processes on silicon
- NANO-EH envisages a Green technology approach: exploitation of non-toxic, easy materials recovery and recyclable materials for environment-friendly battery-less energy supply sub-systems/modules for IoT and WSNs

- Please follow our progress on www.nano-eh.eu as well on LinkedIn and Twitter

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www.nano-eh.eu

Thank you very much for your attention !