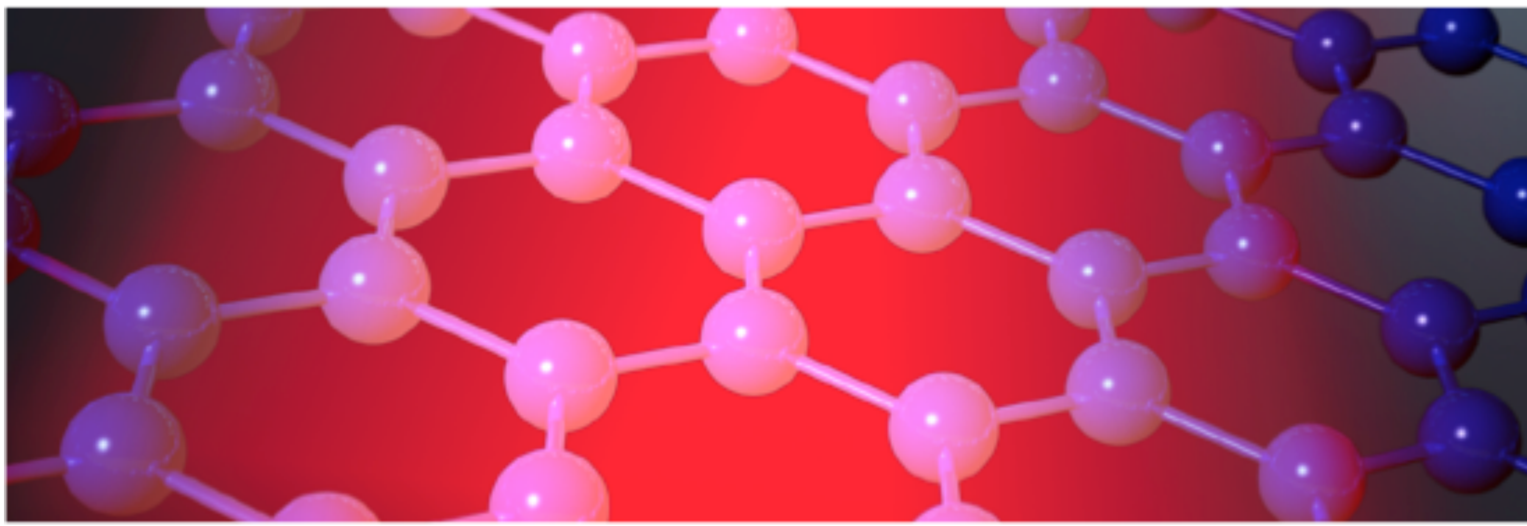
Graphene in Sensors Applications

Amaia Zurutuza
Scientific Director



Graphenea

Content

Graphenea

Important milestones

Geim & Novoselov publiish Science paper

Jesus de la Fuente writes first Business Case

First funding round closed $1,8 m

Graphenea founded

First Graphene produced in Graphenea

Moving to a larger laboratory

First commercial order

NOKIA Connecting People

SIGMA-ALDRICH

Sigma-Aldrich selects Graphenea as supplier

PHILIPS

Graphene Flasghip approved €1B 10 years project

REPSOL

Repsol Energy Ventures joins Graphenea €1 m

GRAPHENE FLAGSHIP

US branch opened

€1 m sales milestone

2.5M $ investment for scale up secured

Global Top 100 Ones to Watch

Capacity Expansion

20x times

2004 // **2008** | **2009** | **2010** | **2011** | **2012** | **2013** | **2014** | **2015** | **2016**

We are expanding our global presence

Graphenea

Graphenea sites

Research @ CIC nanogune (San Sebastian, Spain)

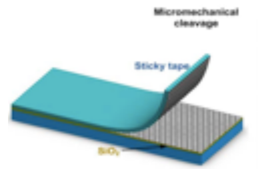
CVD & GO Production Lab @ Miramon Technology Park
(San Sebastian, Spain)

Graphenea

Graphene synthesis

Graphene Powder

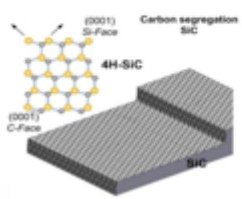
Micro-mechanical exfoliation



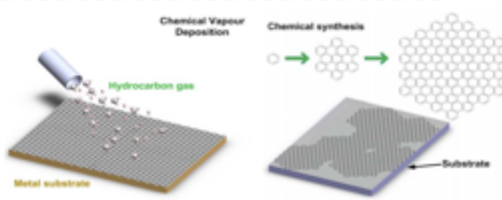
Liquid phase exfoliation (chemical)

Graphene Films

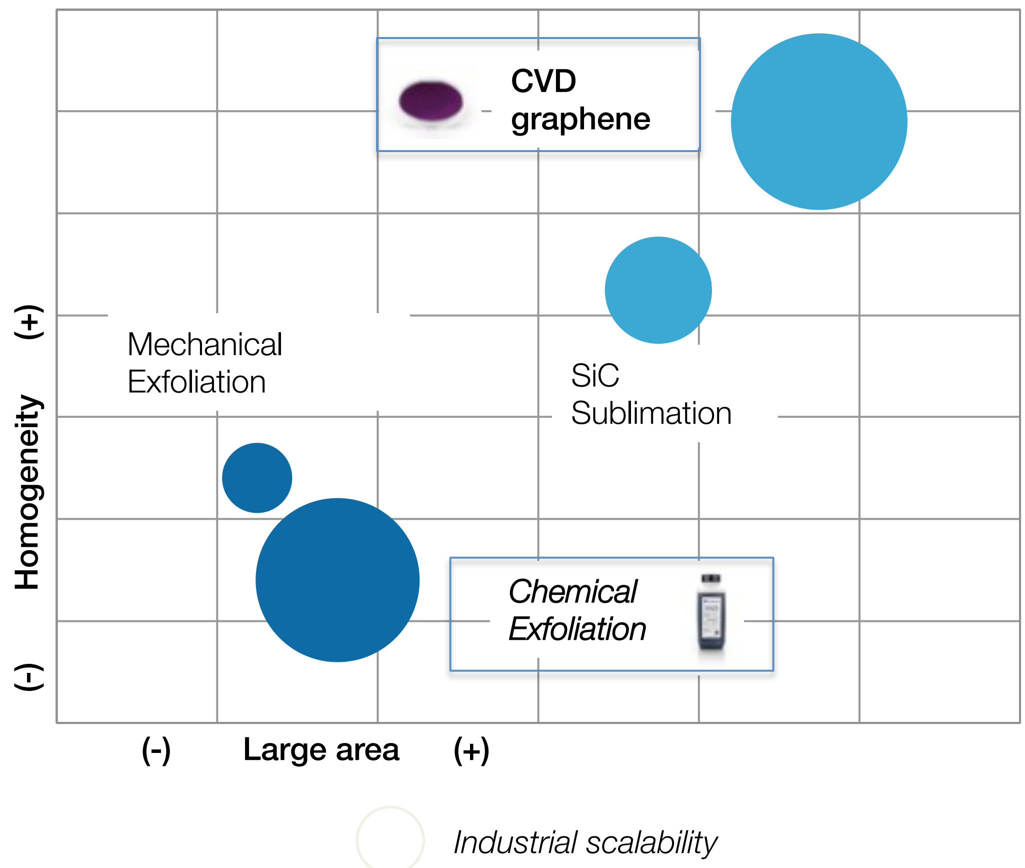
SiC Sublimation



CVD



Graphene synthesis technologies comparison



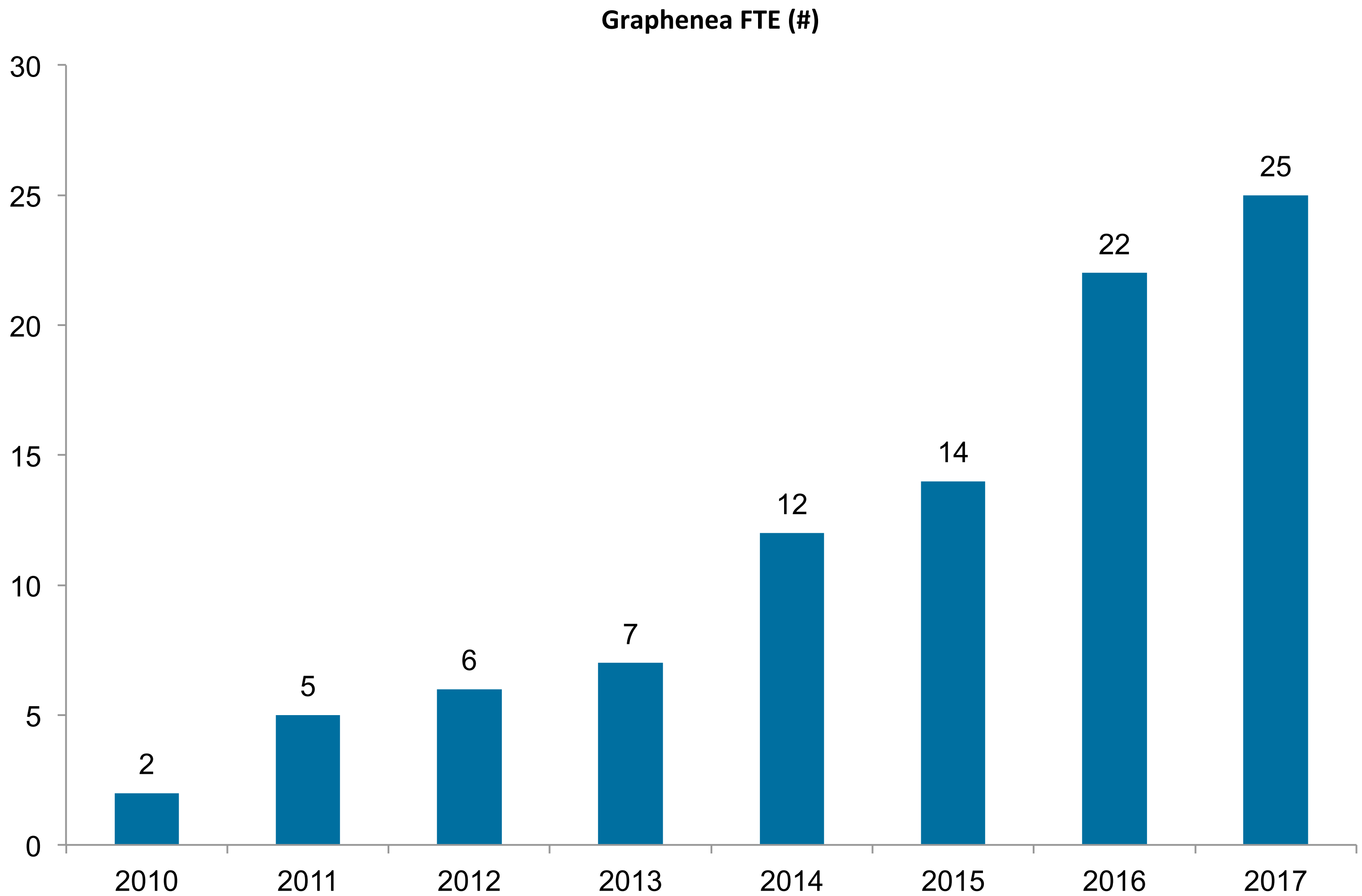
New facilities

- New 8” CVD system
- Cleanroom class ISO7
- GO pilot plant 1Tone/year

Clean room CVD graphene

GO Pilot plant

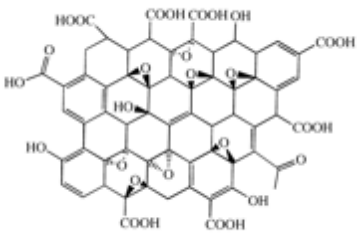
Large team



Source: Graphenea

Graphenea GO Product Range

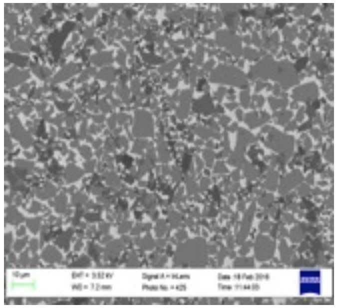
Graphene oxide



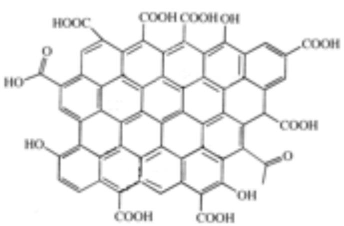
Form	Dispersion of graphene oxide sheets
Particle size	D90 29.05 - 32.9 µm
	D50 14.30 - 16.6 µm
	D10 5.90 - 6.63 µm
pH	2,2-2,5

Carbon	49-56%
Hydrogen	0-1%
Nitrogen	0-1%
Sulfur	2-4%
Oxygen	41-50%

SEM image



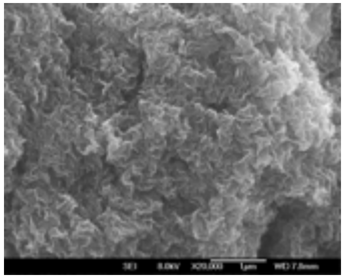
Reduced graphene oxide



Form	Powder
Electrical conductivity	≈ 667 S/m
BET surface area	422.69-499.85 m^2/g
Particle size (z-sizer in NMP at 0,1 mg/mL):	260-295nm
Density	1,91 g/cm^3

Carbon	77-87%
Hydrogen	0-1%
Nitrogen	0-1%
Sulfur	0%
Oxygen	13-22%

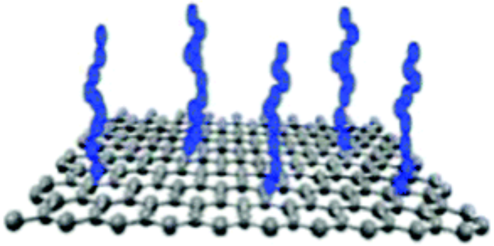
SEM image



Functionalized graphene oxide

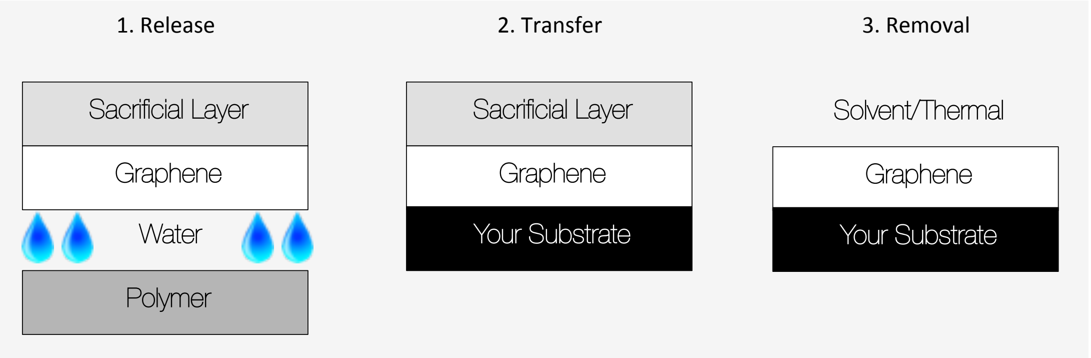
Customised functionalization:

- Compatibilisation with matrix



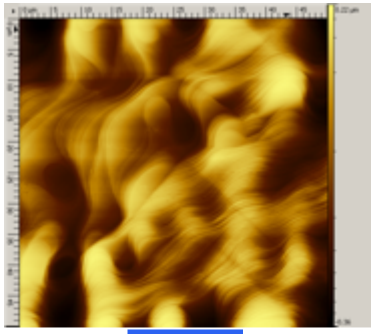
Graphenea CVD Product Range

Easy transfer graphene

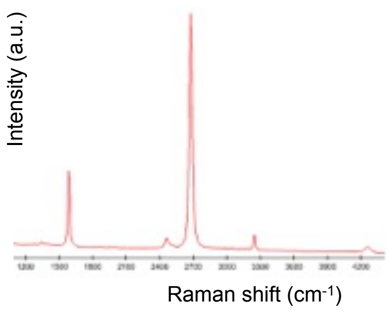


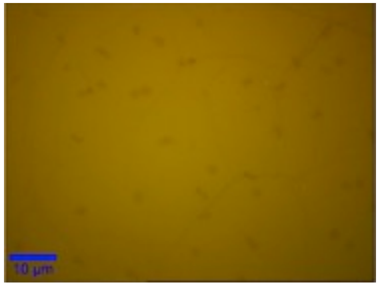
Graphene on different substrates

Graphene on Cu



G/Cu





$G/SiO_2/Si$

Graphenea CVD production capacity roadmap

Graphenea

2010-2012

PHASE 0
1 cm x 1 cm/2 hour

1,000 cm2/year

310 $/cm2

2013-2014

PHASE 1
4” wafer/ 2 hour

85,000 cm2/year
1,000 x 4” wafers/year)

5 $/cm2

2015-2016

PHASE 2
8” wafer/ 30 min

2,250,000 cm2/year
7,000 x 8” wafers/year

< 0.80 $/cm2

2017-…

PHASE 3
12” wafer/30 min
Roll-to-Roll 300 mm wide

+15,500,000 cm2/year

< 0.25 $/cm2

CMOS compatible

RESEARCH → DEVELOPMENT → COMMERCIAL

Graphene films

CVD Graphene

GROWTH

TRANSFER

INTEGRATION

Graphenea

GROWTH

Monolayer Graphene
Chemical Vapour Deposition (CVD)

Catalyst: Cu foil

- Current Capacity: 4’’ wafer
- Next: 8” wafer

❖ **Advantages:**

- Homogeneous growth
- >95% Monolayer
- Few defects
- Good properties
- Optimized transfer process

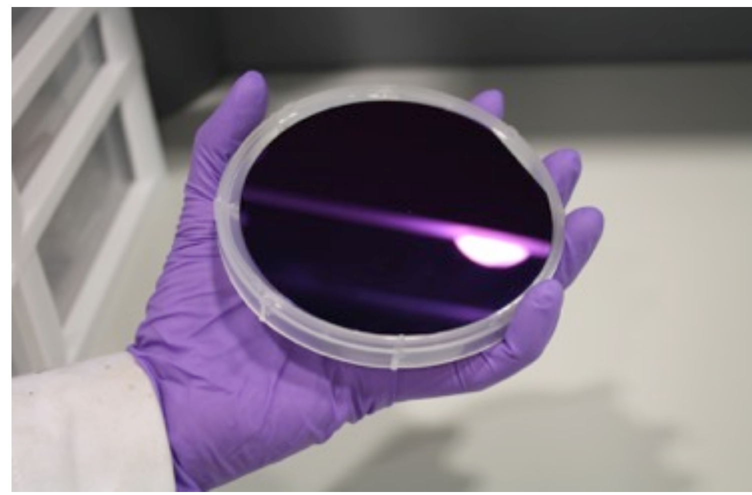
Nucleation — Coalescence — Continuous film

time

TRANSFER

CVD Graphene Transfer

Graphene on catalyst → Graphene onto the desire substrate



- The quality of the transfer and the substrate supporting graphene together with the quality of the interface between graphene and the substrate have large impacts on the properties of graphene and device performance

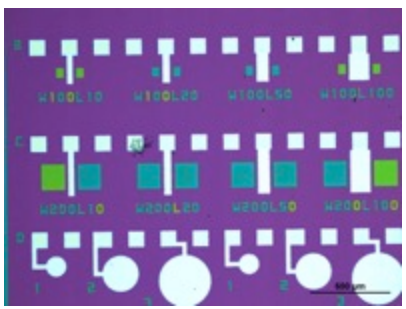
TRANSFER

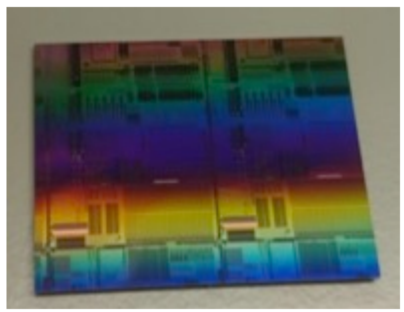
Graphenea

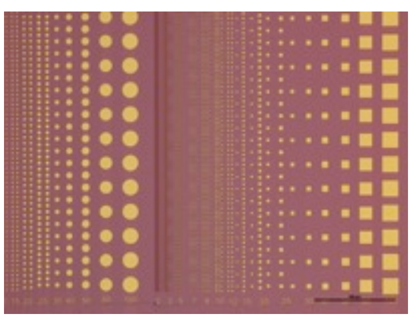
CVD Graphene Transfer

Importance of the substrate

The type of substrate will define the transfer process







- Structured substrates
- Perforated substrates: holes, cavities
- Water soluble substrates
- Number
- Size: $1x1mm^2$ up to 4”
- Shape: rectangular, circular..
- Type of Material: CaF_2, Si_3N_4, Al_2O_3..
- Roughness
- Hydrophobicity

TRANSFER

CVD Graphene Transfer

Graphenea

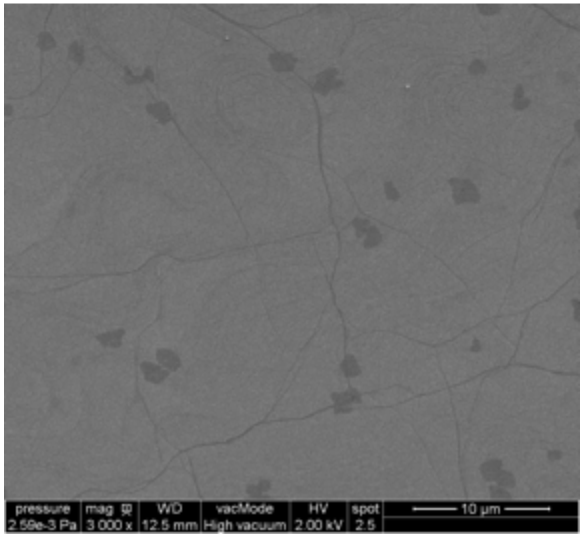
There is no standard process for all the substrates and applications

- Wet Transfer
- Dry Transfer
- Semi-dry Transfer

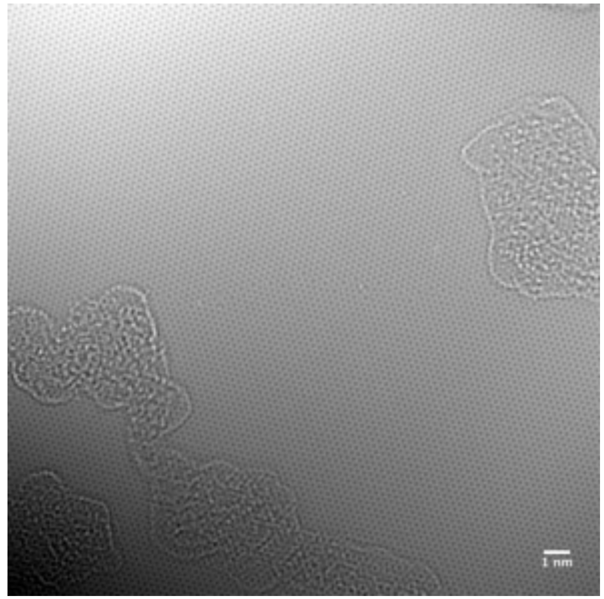
ANALYSIS

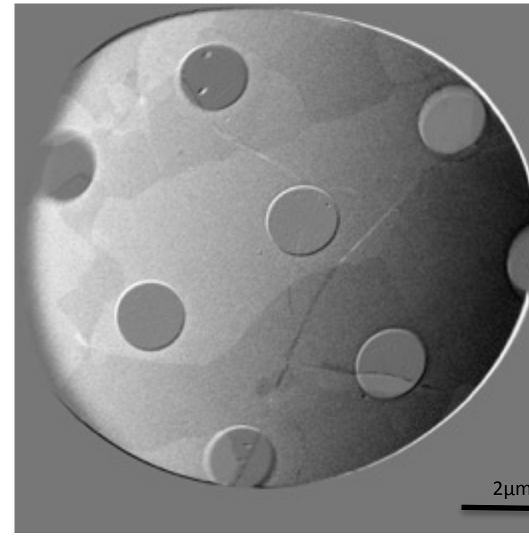
CVD Graphene characterisation

Scanning Electron Microscopy (SEM)

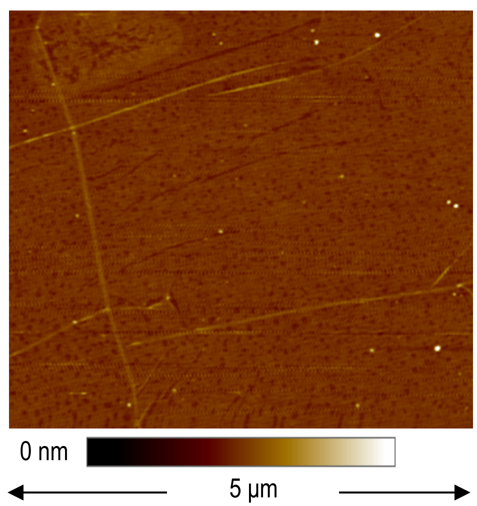


Transmission Electron Microscopy (TEM)

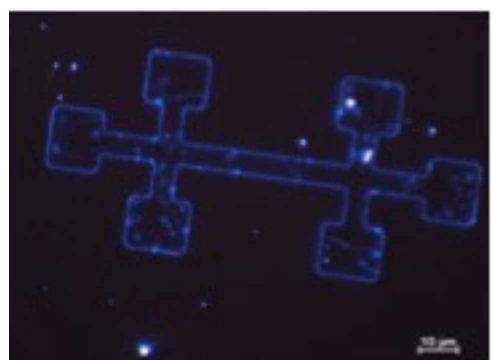


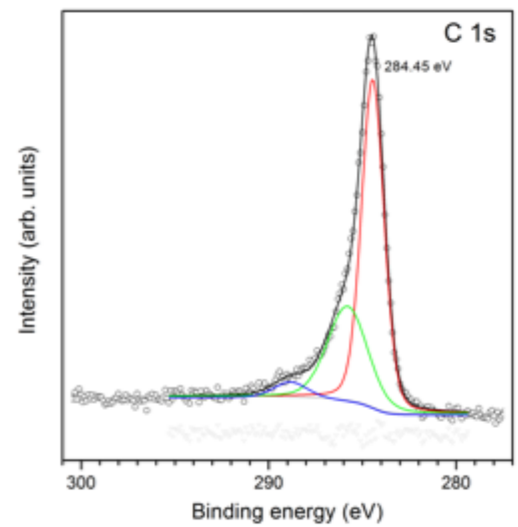


Atomic Force Microscopy



Electronic characterisation

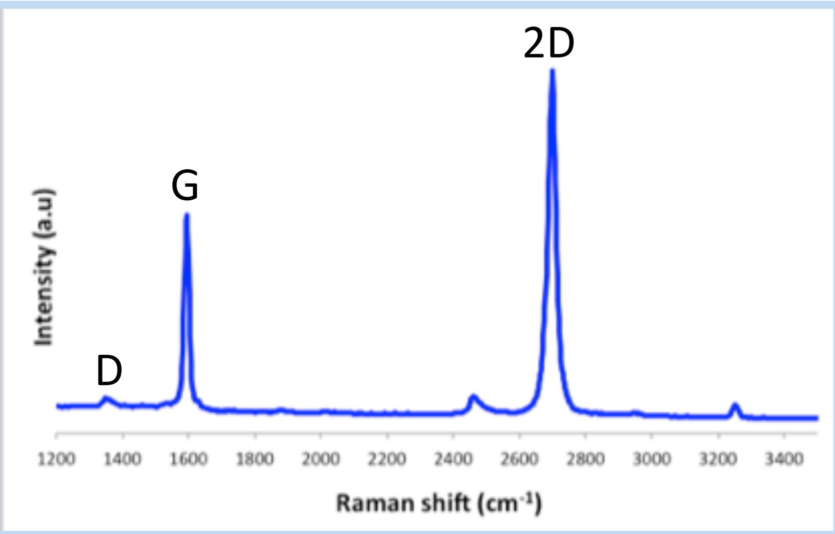


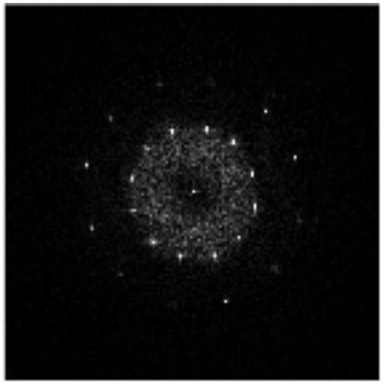


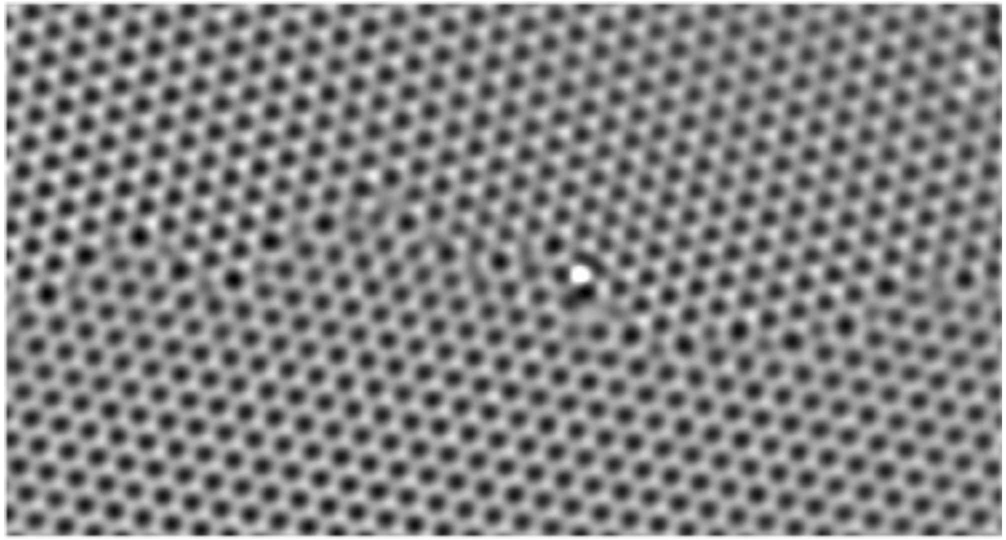
X-Ray Photoelectron Spectroscopy (XPS)

ANALYSIS

CVD Graphene characterisation







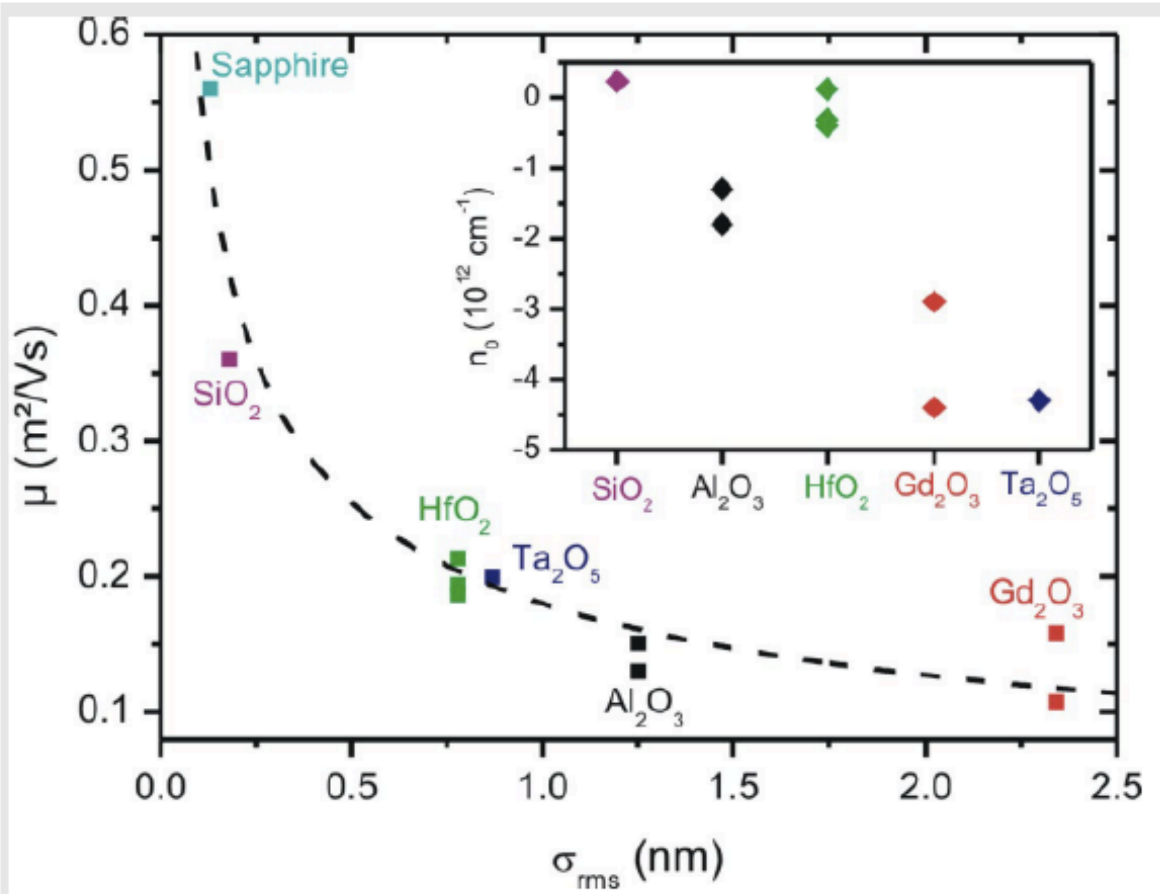
- ✓ Monolayer continuous films
- ✓ Polycrystalline: grain sizes up to 20μm

INTEGRATION

Graphenea

Substrate effect on Graphene

Electronic characterisation



Substrate influence on mobility

AMO

INTEGRATION

Encapsulation

Ambient air, organic solvents, chemicals, lithography resist

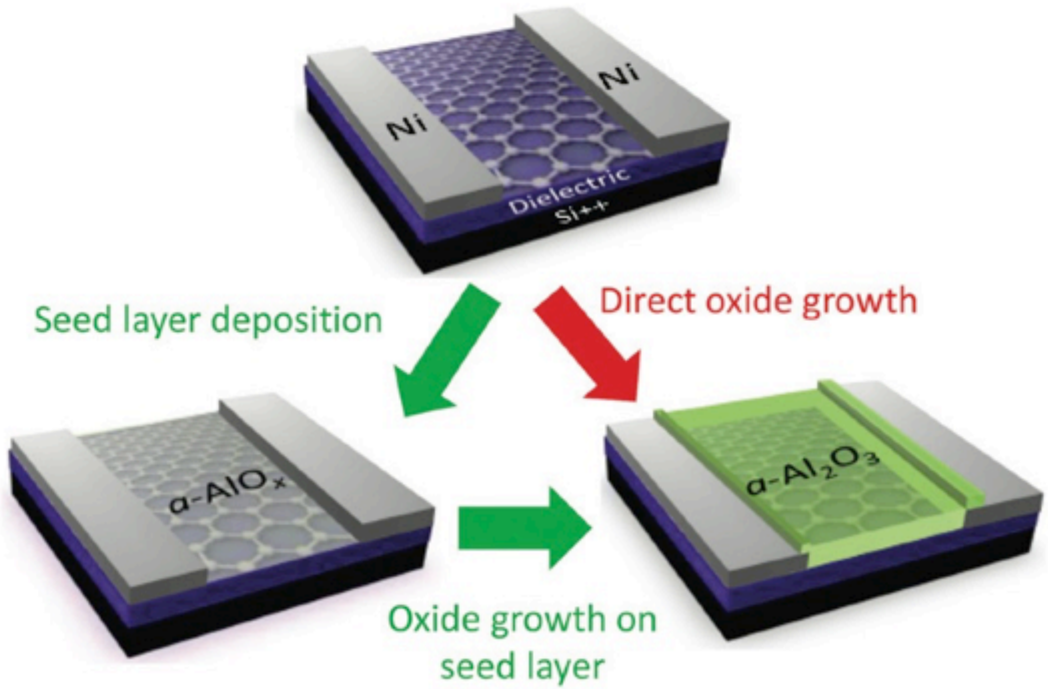
- ✓ Lead to graphene doping and hysteretic behaviour in DC characteristics of FETs

Encapsulation of graphene with Al_2O_3

*A.A. Asade et.al. Nanoscale **7**, 3558 (2015)*

INTEGRATION

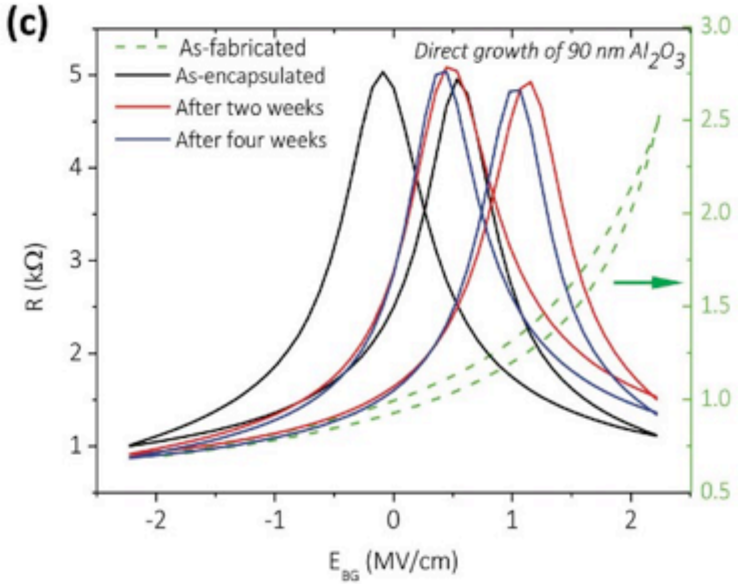
Encapsulation



- ✓ Direct deposition of Al_2O_3 by ALD
- ✓ Al seed layer growth by e-beam evaporation + Al_2O_3 by ALD

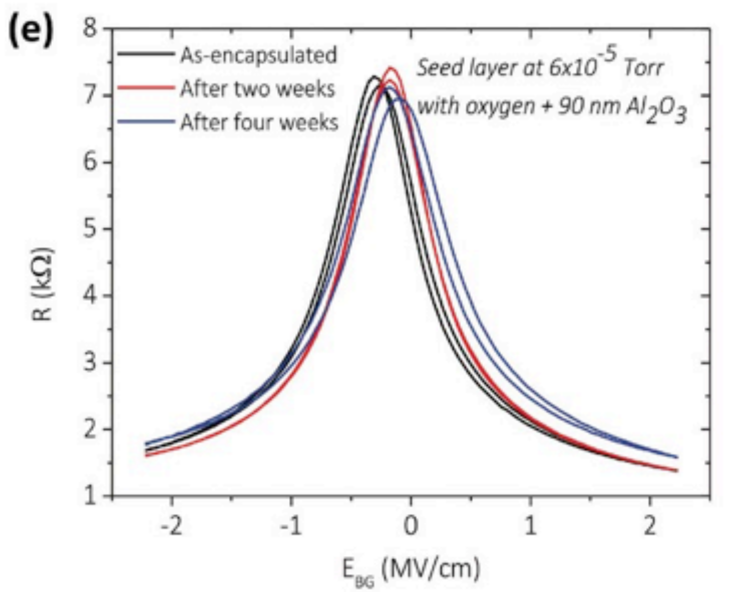
A.A. Asade et.al. Nanoscale ***7****, 3558 (2015)*

Encapsulation



Direct growth of Al_2O_3 by ALD

- ✓ Hysteresis
- ✓ Not stable over time



Al seed layer + Al_2O_3 by ALD

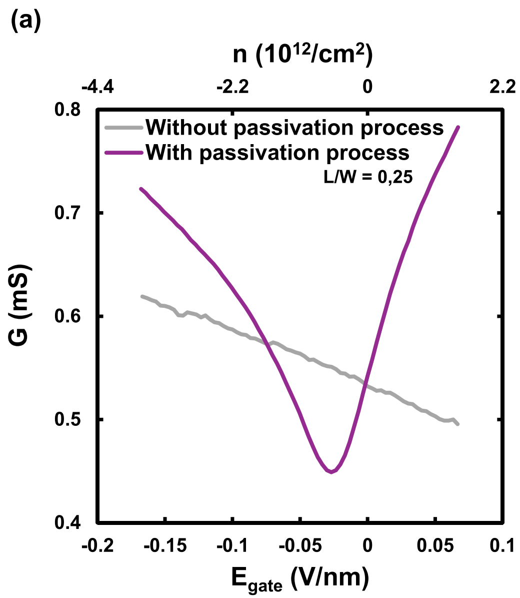
- ✓ No hysteresis
- ✓ Stable over time

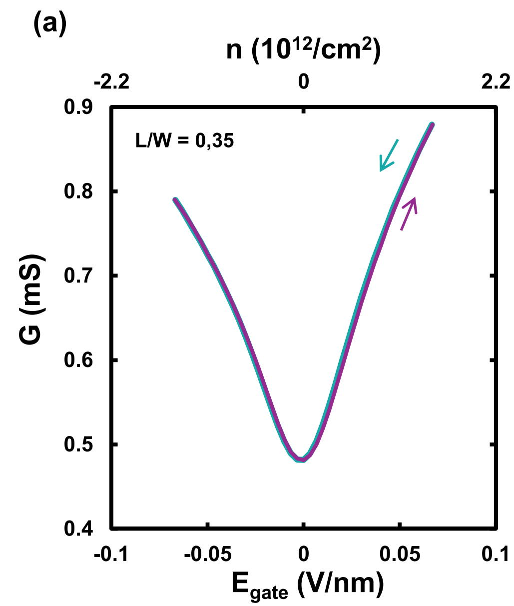
A.A. Asade et.al. Nanoscale ***7****, 3558 (2015)*

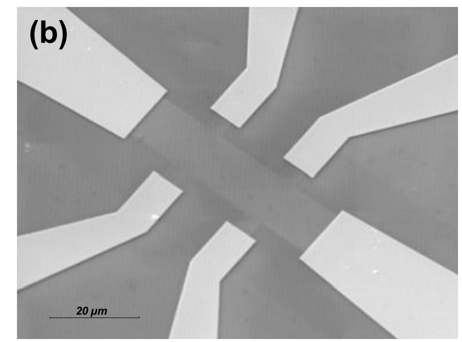
INTEGRATION

Graphene Integration

Statistical analysis of 500 GFETs





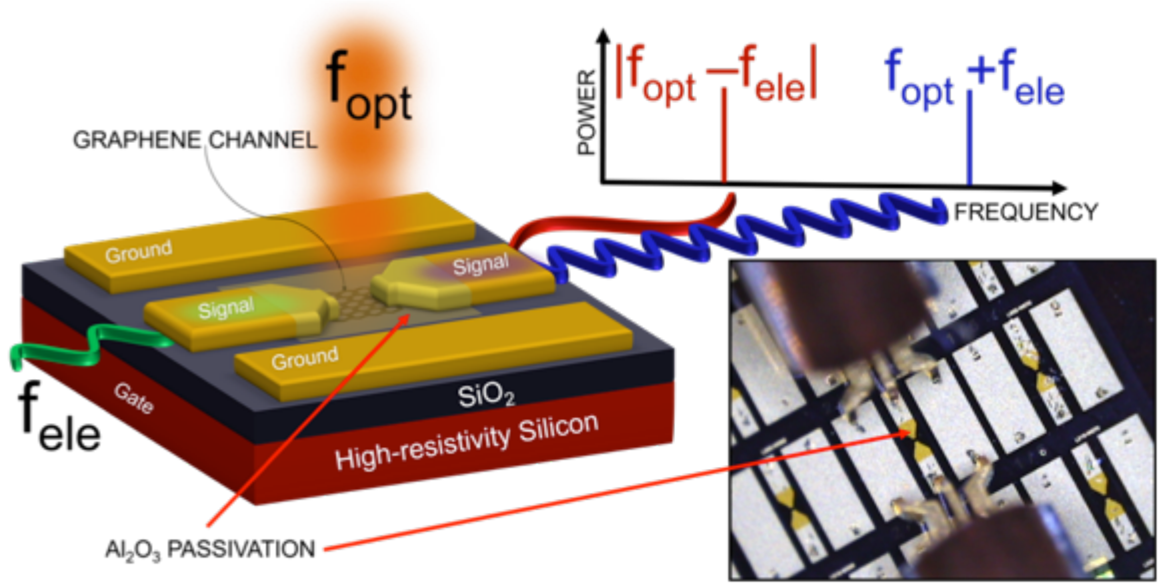


- Mobilities up to 6,900cm^2/Vs on passivated devices
- 75% of passivated transistors exhibited a conductance minimum and low hysteresis

S. Mzali e et.al. Appl. Phys. Lett. ***109****, 253110 (2016)*

INTEGRATION

Graphene optoelectronic mixer



- ✓ 30 GHz optoelectronic mixing
- ✓ Frequency down conversion to 100MHz

A. Montanaro et.al. Nano Lett. 16, 2988 (2016)

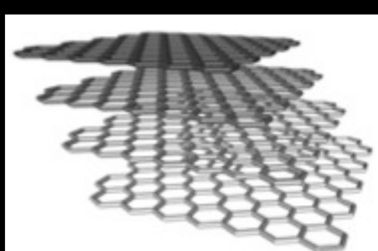
APPLICATIONS

Graphene Integration

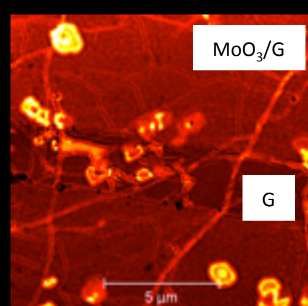
The application will define the graphene requirements

- Properties: Mobility, sheet resistance, transparency…
- Contamination limits: polymer residues, metal content
- Integration: Suspended, back-end, front-end..

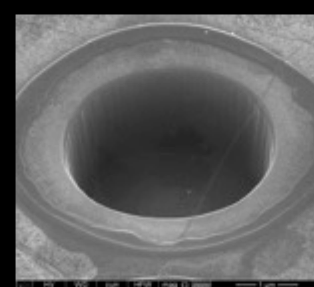
Multilayer samples Stacking



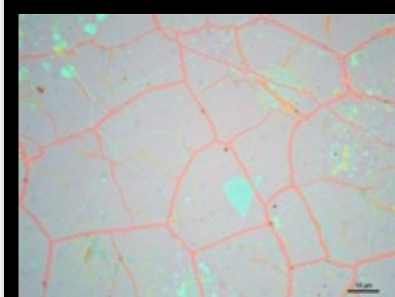
Doped Graphene



Suspended graphene



Encapsulation



APPLICATIONS

Graphenea

Graphene biosensors

Surface plasmon resonance (SPR) - real time detection & monitoring of biological binding processes at solid interfaces

- ✓ Conventional SPR nanomolar sensitivity
- ✓ Not sufficient for gene expression and cancer markers (femto to attomolar required)

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sensia

APPLICATIONS

Graphene biosensors

Point of care sensor for the detection of folic acid protein (FAP)

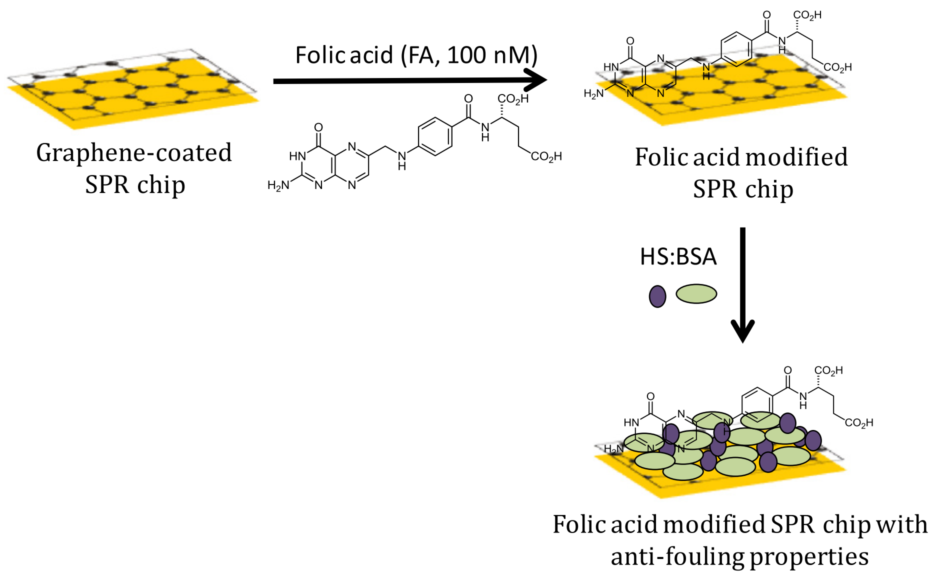
- ✓ FAP is associated with numerous malignancies and are over-expressed in many human epithelial-derived tumors
- ✓ Specific recognition of FAP based on the interaction between folic acid receptors integrated through π stacking on the graphene and the FAP analyte in serum

L. He et.al. Biosens. Bioelectron. (2016)

APPLICATIONS

Graphenea

Graphene biosensors



- ✓ FA immobilised onto graphene coated SPR chips by drop casting followed by dipping into mixture of HS and BSA (to prevent non-specific adsorption)
- ✓ Interaction with FAP by injecting FAP in HS (500fM)

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L. He et.al. Biosens. Bioelectron. (2016)

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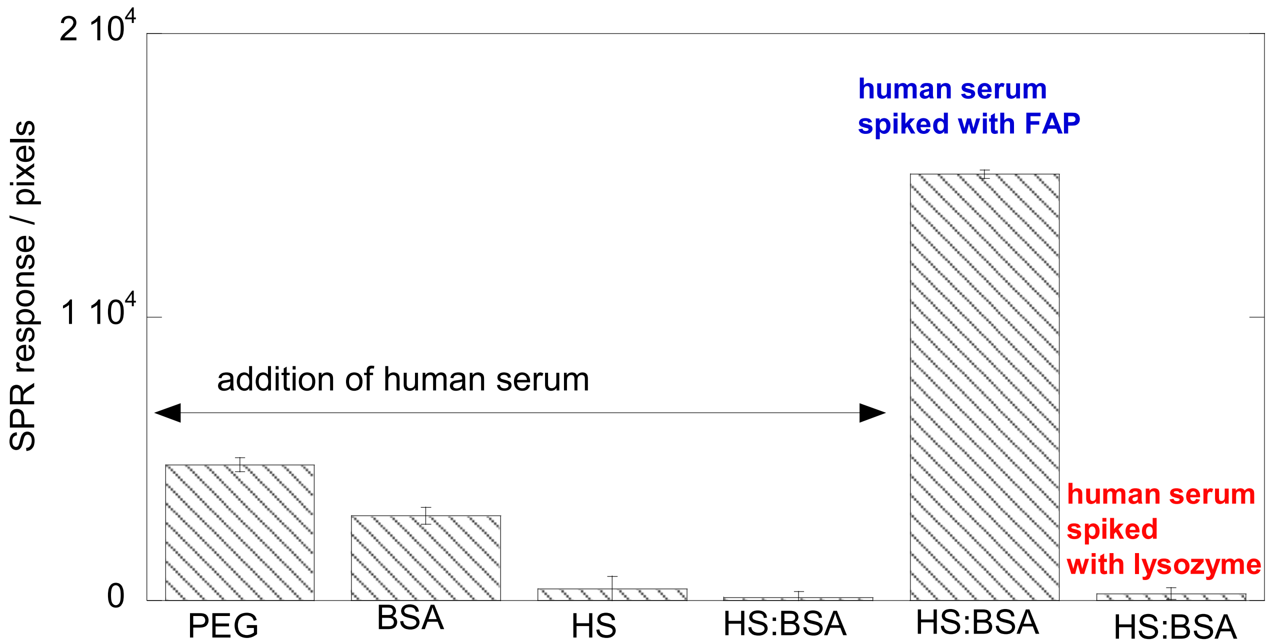
APPLICATIONS

Graphene biosensors



L. He et.al. Biosens. Bioelectron. (2016)

APPLICATIONS

Graphenea

Graphene biosensors

✓ Detection limit of FAP was ≈5fM

Methodes	Interface	LOD	Linear range	Reference
QCM	Au + folate/BSA + anti-FBP	50 pM	50 pM to 2 μM	Henne et al. (2006)
Fluorescence	Ag nanoclusters-coated DNA /SWCNTs	33 pg/mL	0.1–3 ng/mL	Jiang et al. (2015)
DPV	CNTs + surface tethered small molecules linked ssDNA	3 pM	3 pM to 1 nM	Wu et al. (2009)
DPV	Au/rGO-FA	1 pM	1–200 pM	He et al. (2016)
DPV	CuNPs-coated DNA/ magnetic graphene	7.8pg/mL	100–0.01 ng/mL	Zhao et al. (2015)
EIS	Au + FA-linked DNA	3 pM	10 pM to 500 nM	Wang et al. (2014)
CV	Graphene + peptide na-notube-FA	8 nM	8 nM to 13 μM	Castillo et al. (2013)
SPR	Graphene + Folic acid	5 fM	5–500 fM	This work

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L. He et.al. Biosens. Bioelectron. (2016)

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APPLICATIONS

Graphenea

Graphene biosensors

✓ Sensor suitable for biomedical analysis – required FAP concentrations in the low pM range

biomarker	LOD	Linear range	Ref.
p53	1.06 pM	1.06 pM to 53.2 nM	Wang et al. (2009)
Aβ(1-42)	3.5 pM	0.02–150 nM	Xia et al. (2010)
Aβ(1-40)	0.02–150 nM	3.3 pM	Xia et al. (2010)
C-reactive protein	5 fg/mL	5–5000 fg/mL	Vance and Sandros (2014)
Prostate-specific antigen	8.5–1100 pM	8.5 pM	Uludag and Tothill (2012)
Prostate-specific antigen	300 aM	300 aM to 30 fM	Krishnan et al. (2011)
FAP	5 fM	5–500 fM	This work

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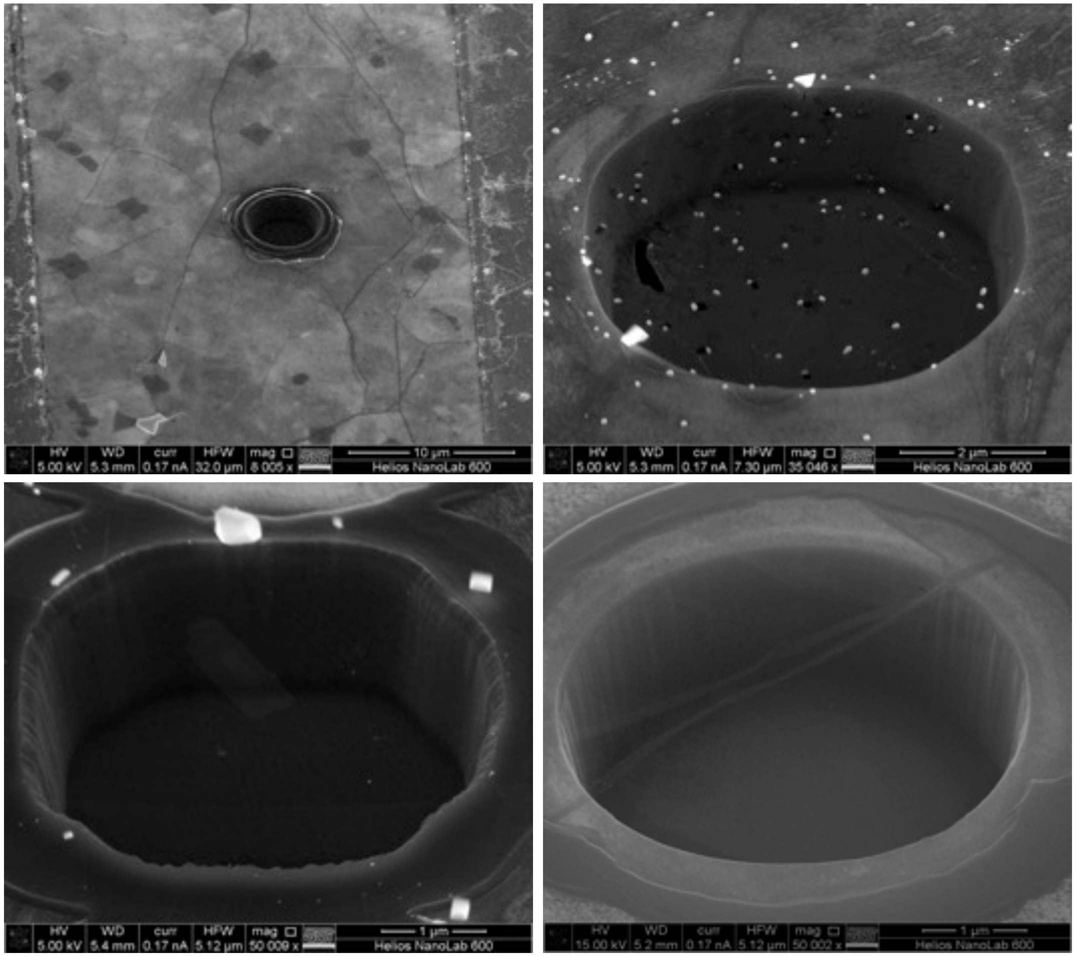
APPLICATIONS

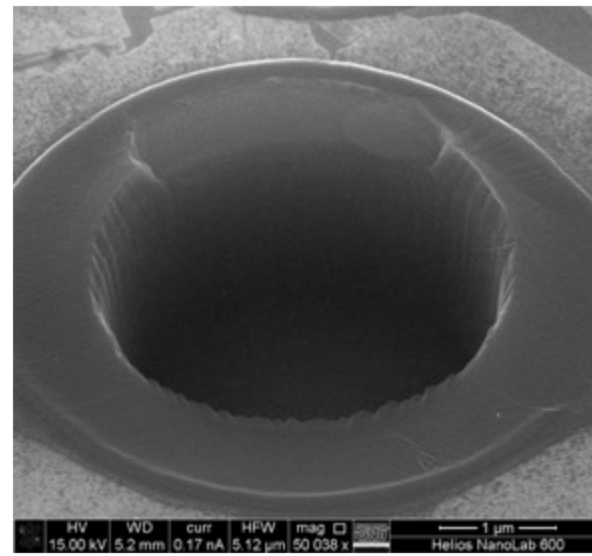
Graphenea

Graphene in NEMS/MEMS

Suspended graphene in pressure sensors

AMO





Courtesy of University of Siegen

EU Project: NanoGram Consortium

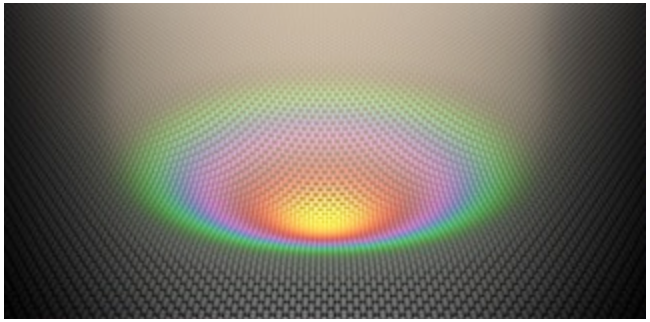
- Development of homogeneous and high quality CVD graphene

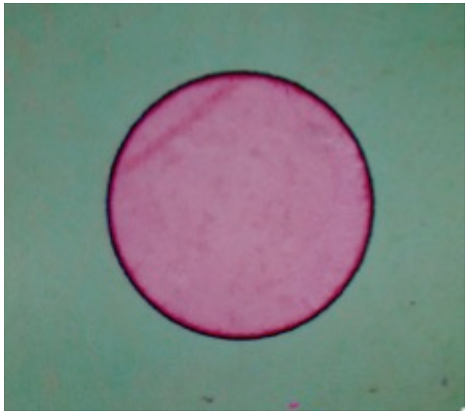
APPLICATIONS

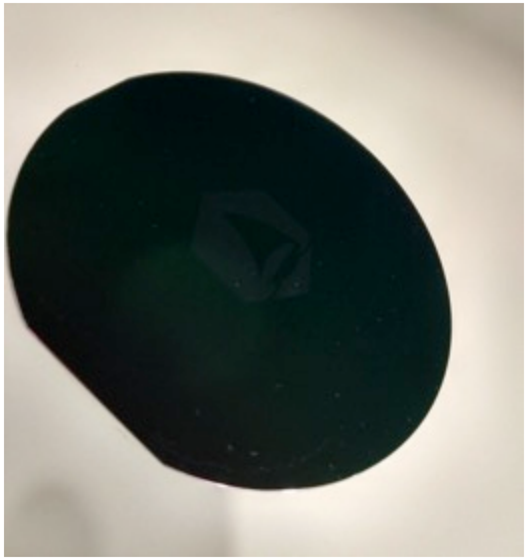
Graphene Interferometric Modulator Display (GIMOD)

TU Delft

Graphene for mechanical pixels







- Bilayer CVD Graphene suspended onto 50microns cavities that compose the Flagship logo

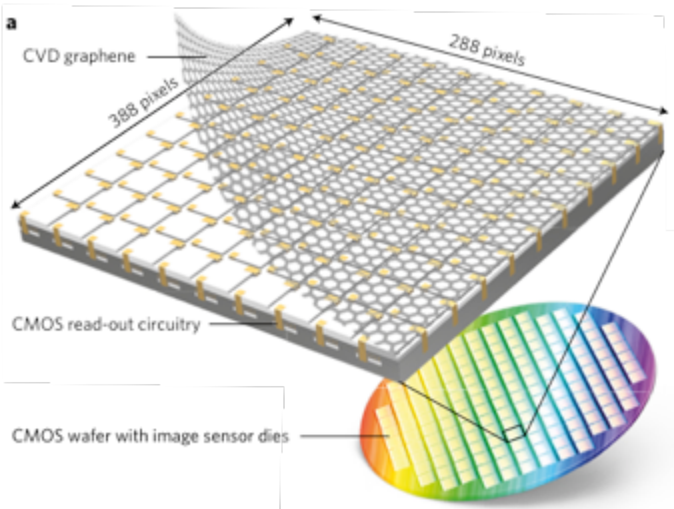
GRAPHENE FLAGSHIP

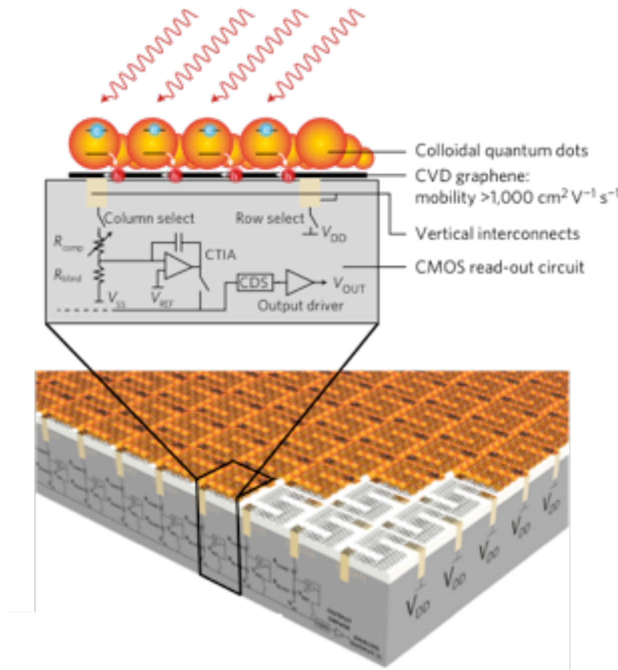
APPLICATIONS

Broadband image sensor array

Graphene-quantum dot photodetector array

- Monolithic integration of CMOS ROIC with graphene
- Graphene operates as a high mobility phototransistor
- QDs sensitising layer (PbS)
- Sensitive to UV, visible and IR light (300-2,000nm)





S. Goossens et.al. Nat. Photon. ***11****, 366 (2017)*

APPLICATIONS

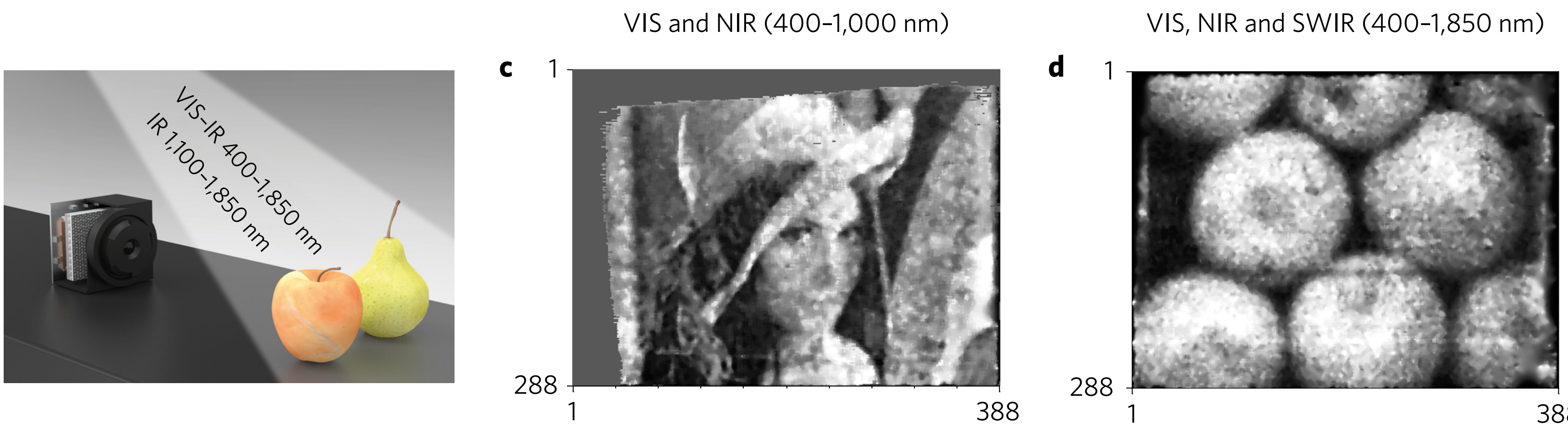
Graphenea

Broadband image sensor array

ICFO
The Institute of Photonic Sciences

Operates as digital camera

- Graphene-QD image sensor captures reflection images from objects illuminated by a light source (office illumination)



- 99.8% of pixels functional
- >95% pixels sensitive to irradiance corresponding to partial-moon and twilight conditions

GRAPHENE FLAGSHIP

S. Goossens et.al. Nat. Photon. ***11****, 366 (2017)*

APPLICATIONS

Graphenea

Ultra-sensitive and low-cost Graphene Quantum-Dot Photodetector

Non-invasive health monitoring applications

- ✓ Flexible and transparent
- ✓ Blood volume
- ✓ Heart rate
- ✓ Ultra-sensitive with a gain of 10^8 carriers per absorbed photon
- ✓ Sensitive to both visible and infrared light
- ✓ No cooling required

ICFO

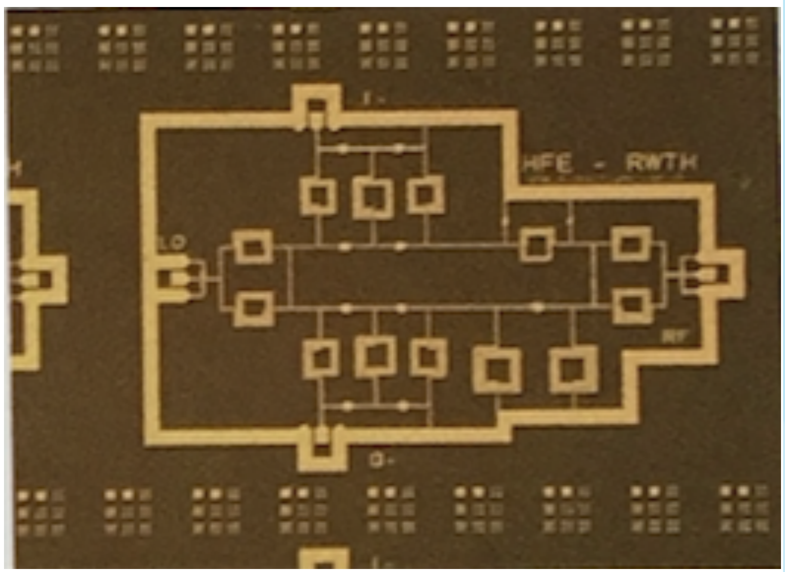
GRAPHENE FLAGSHIP

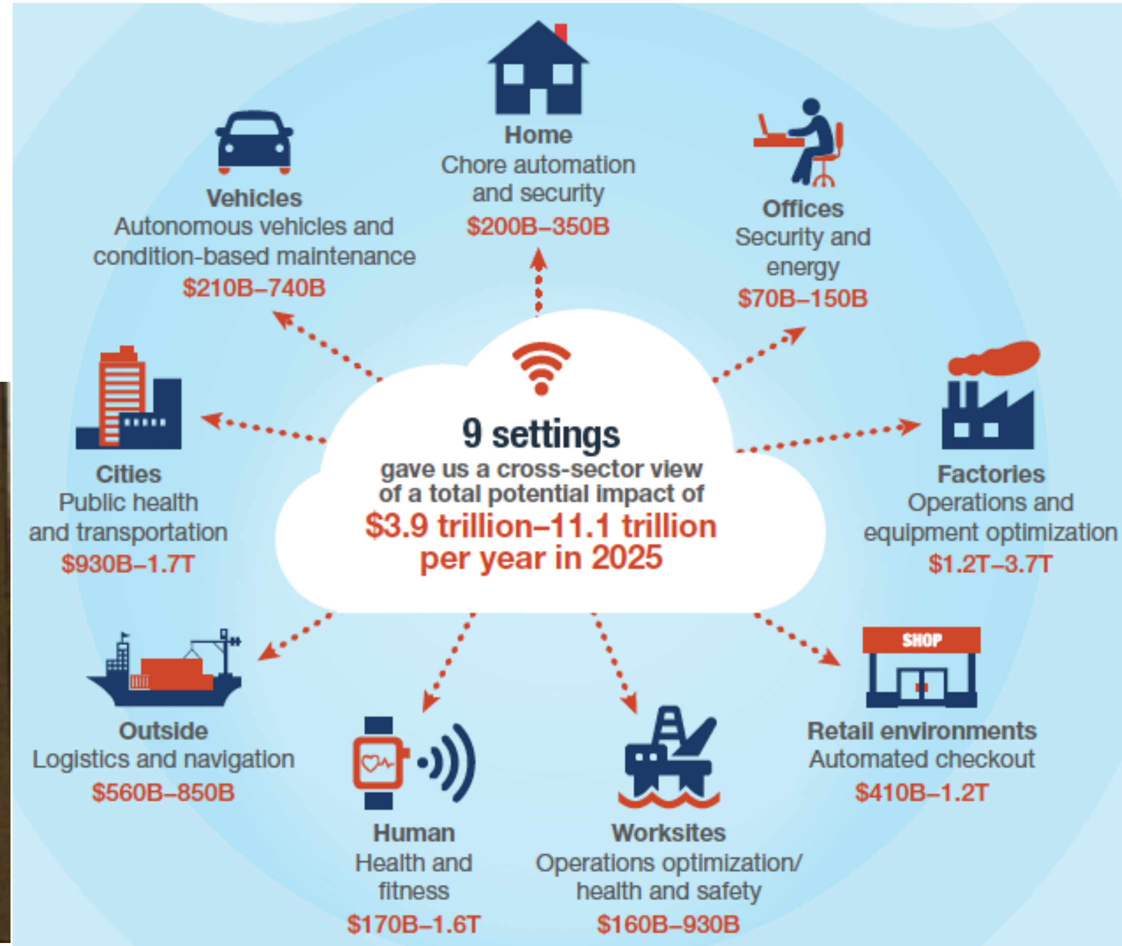
APPLICATIONS

Graphene flexible WiFi receiver

AMO

- 2.4 GHz receiver circuits on plastic
- Ideal for IoT and flexible electronics





Source: McKinsey

Graphenea

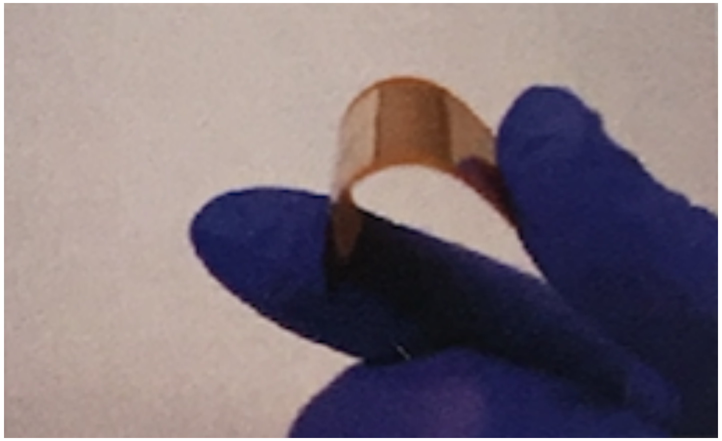
GRAPHENE FLAGSHIP

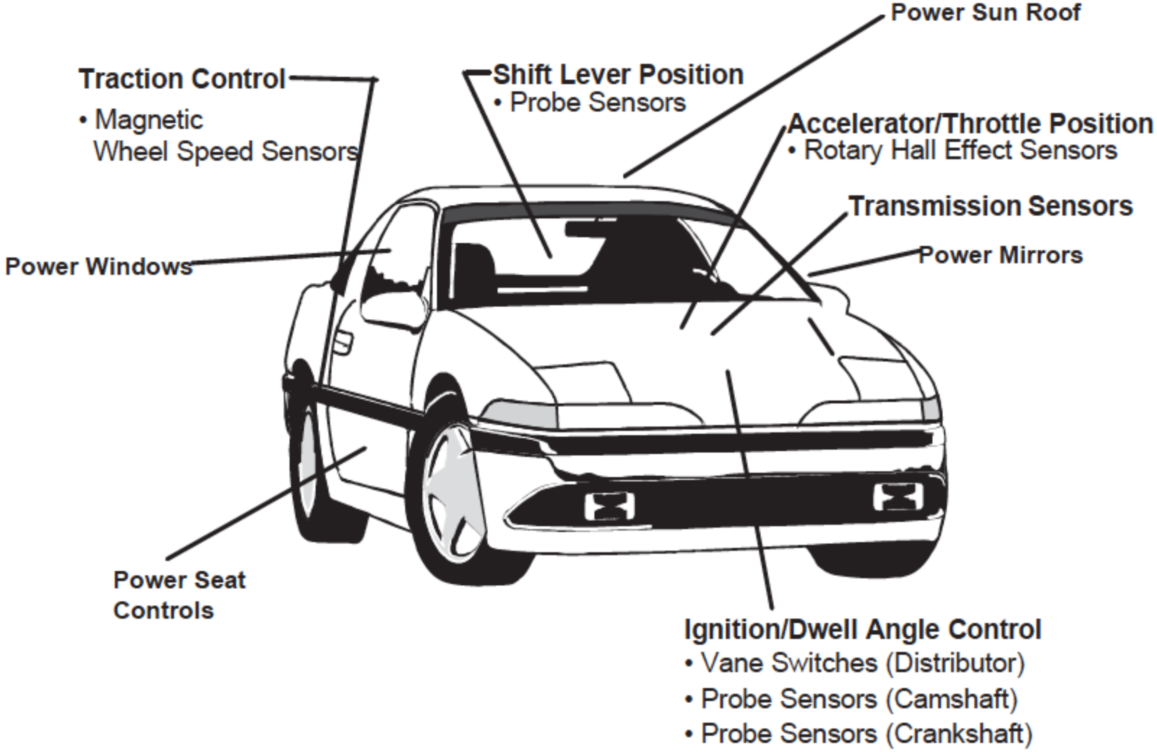
APPLICATIONS

Graphene flexible Hall sensor

AMO

- High sensitivity, linearity and flexibility
- The key factor determining sensitivity of Hall effect sensors is high electron mobility





Source: Honeywell

Challenges

It is necessary to develop a customised material depending on the application and provide an easy integration method in order to promote graphene into commercial applications

- Graphene Customisation
- Scale-up
- Integration

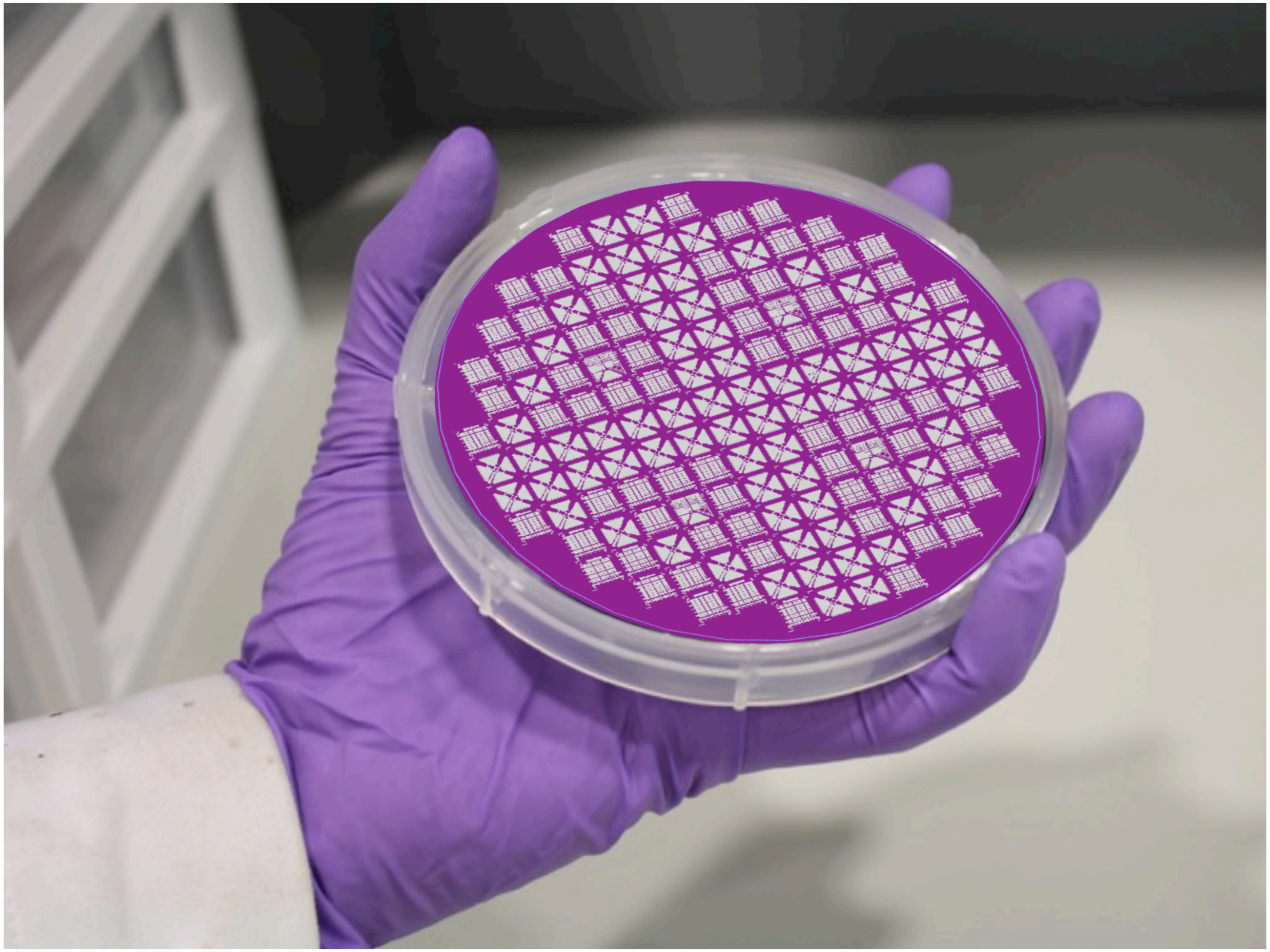
Integration Opportunities - GFET platform

Strategy to aid graphene integration into commercial products

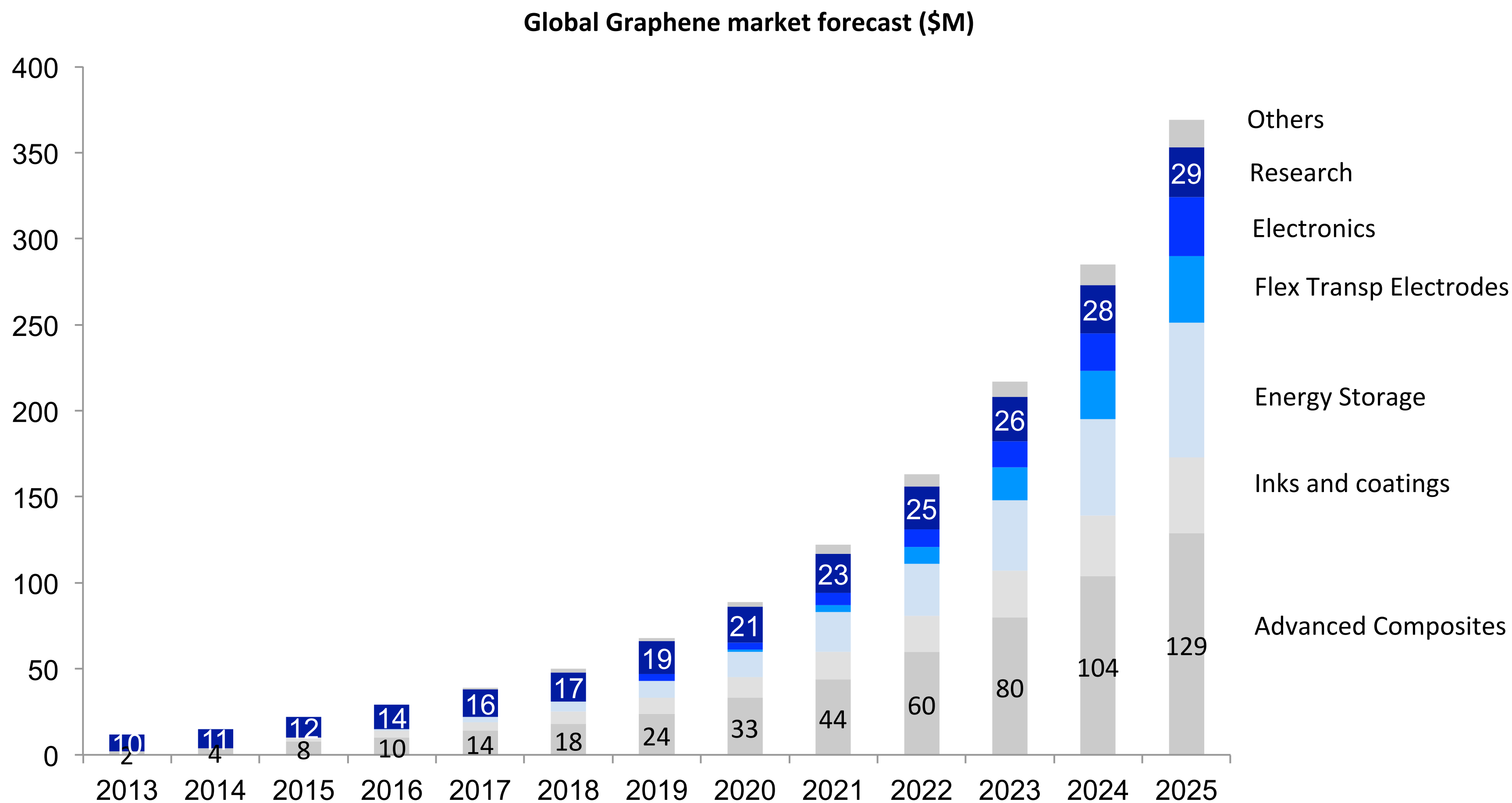
- Semiconductor industry not interested in few thousand wafers market – fill gap in value chain
- Commercialise GFET wafers
- Targeted markets: biosensors, sensors (photosensors), etc.

Graphenea

GFET platform

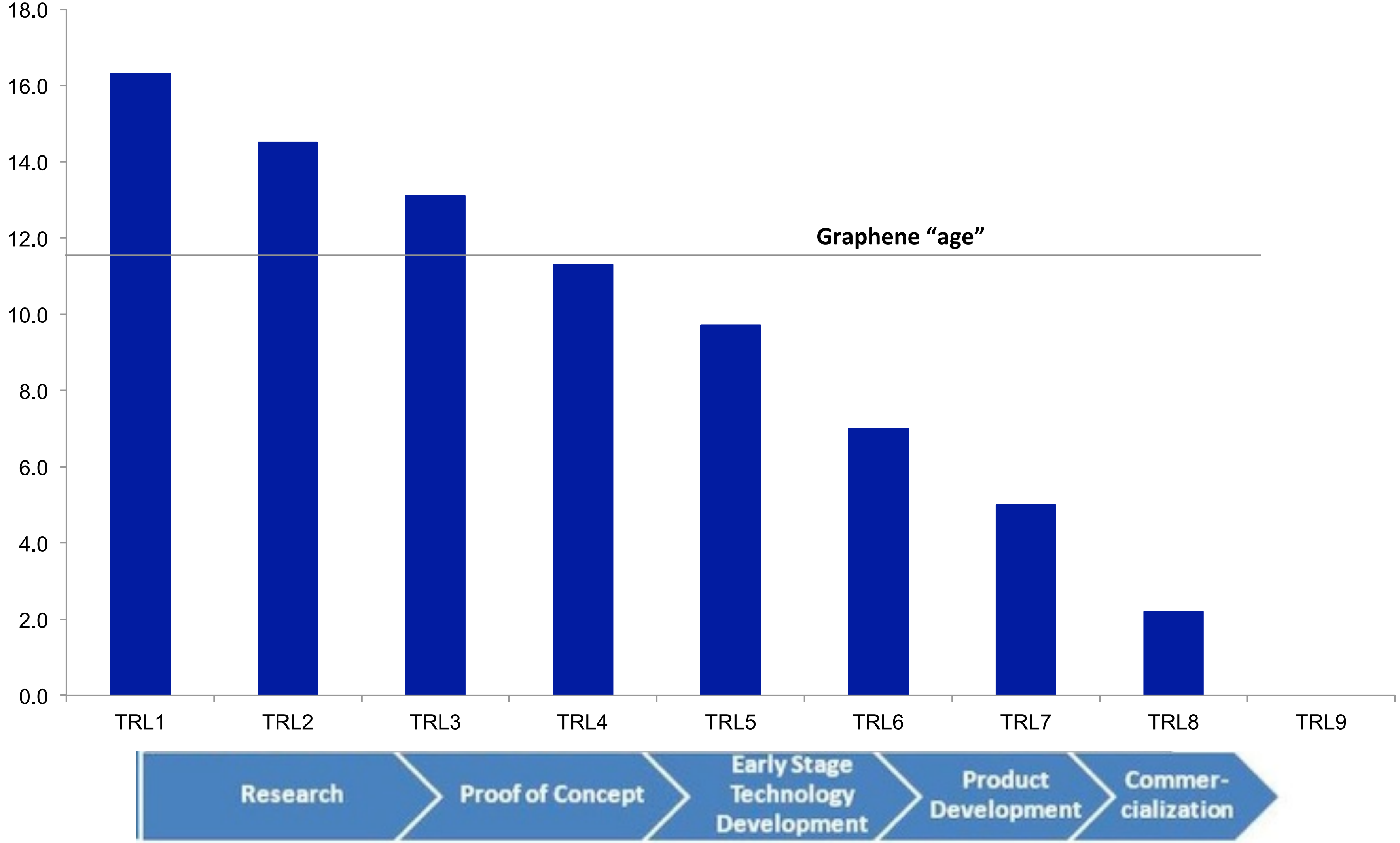


Graphene market is very small and driven by Research-related demand



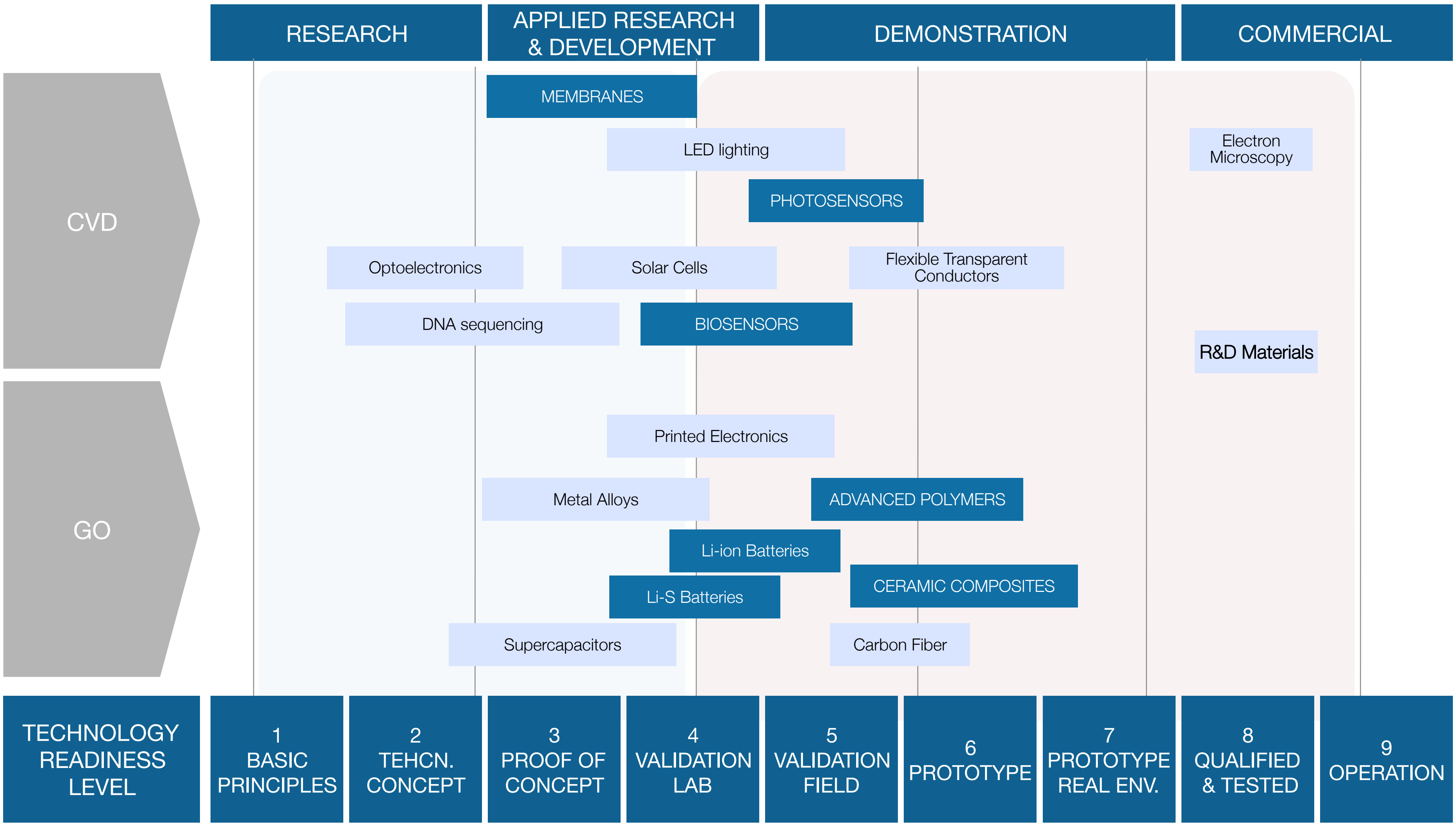
Source: Graphenea estimations

Time to market – Aerospace industry



Source: ESA

Each application requires a specific type and grade of graphene



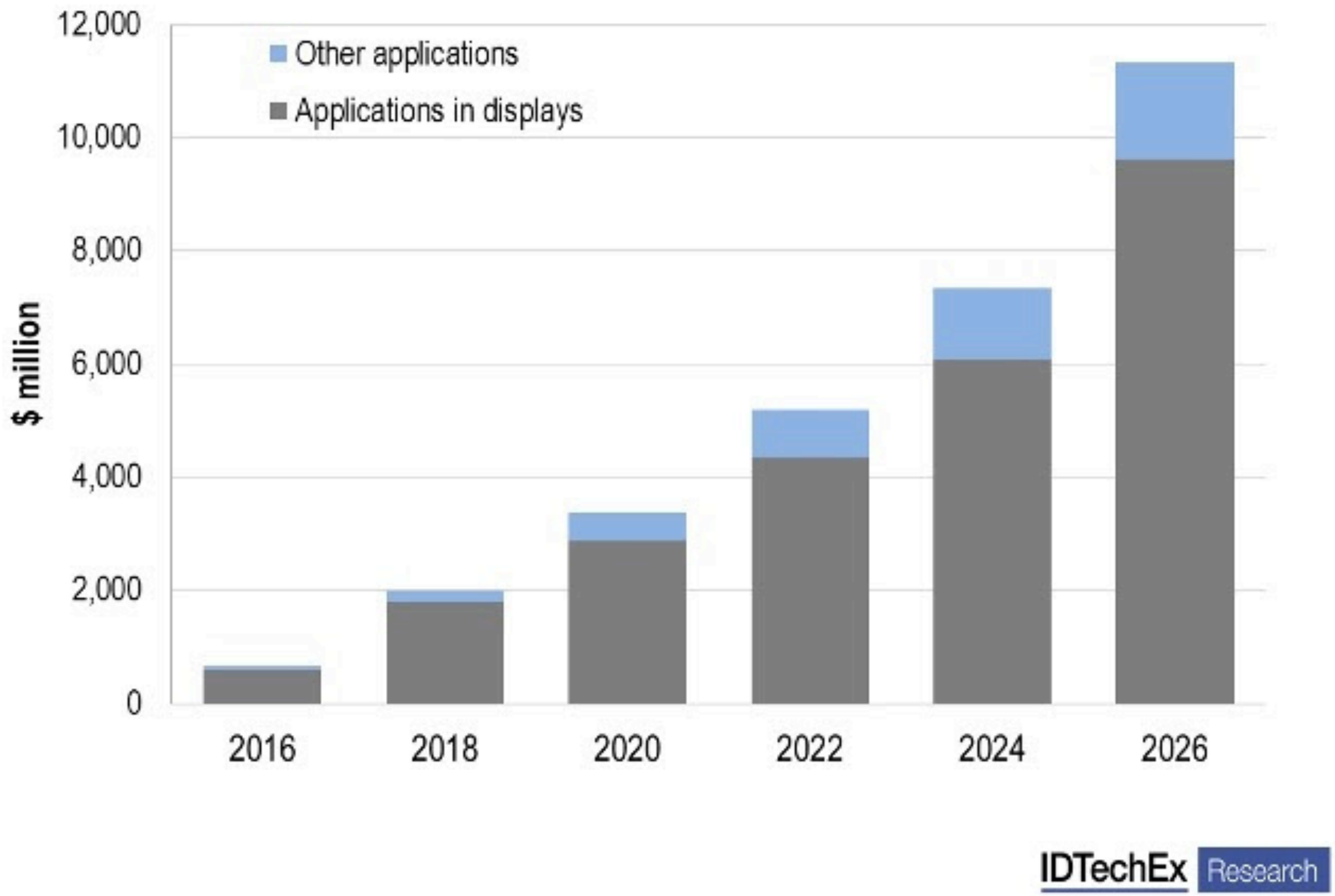
Illustrative TRL application map

Advanced materials that needed > 20 yrs

- ✓ Silicon
- ✓ Carbon fibre
- ✓ Fluorescent lamp
- ✓ Liquid crystals
- ✓ Kevlar
- ✓ PVC
- ✓ PE

Bell Labs 1947

Quantum dots - How things can change dramatically



Graphenea

Conclusions

- ✓ Customised graphene material is required for each specific application
- ✓ Many technological challenges still remain
- ✓ Many diverse multifunctional prototypes have been successfully fabricated
- ✓ We hope graphene will be a success story – similar to QDs