



characterization of 2D materials growth

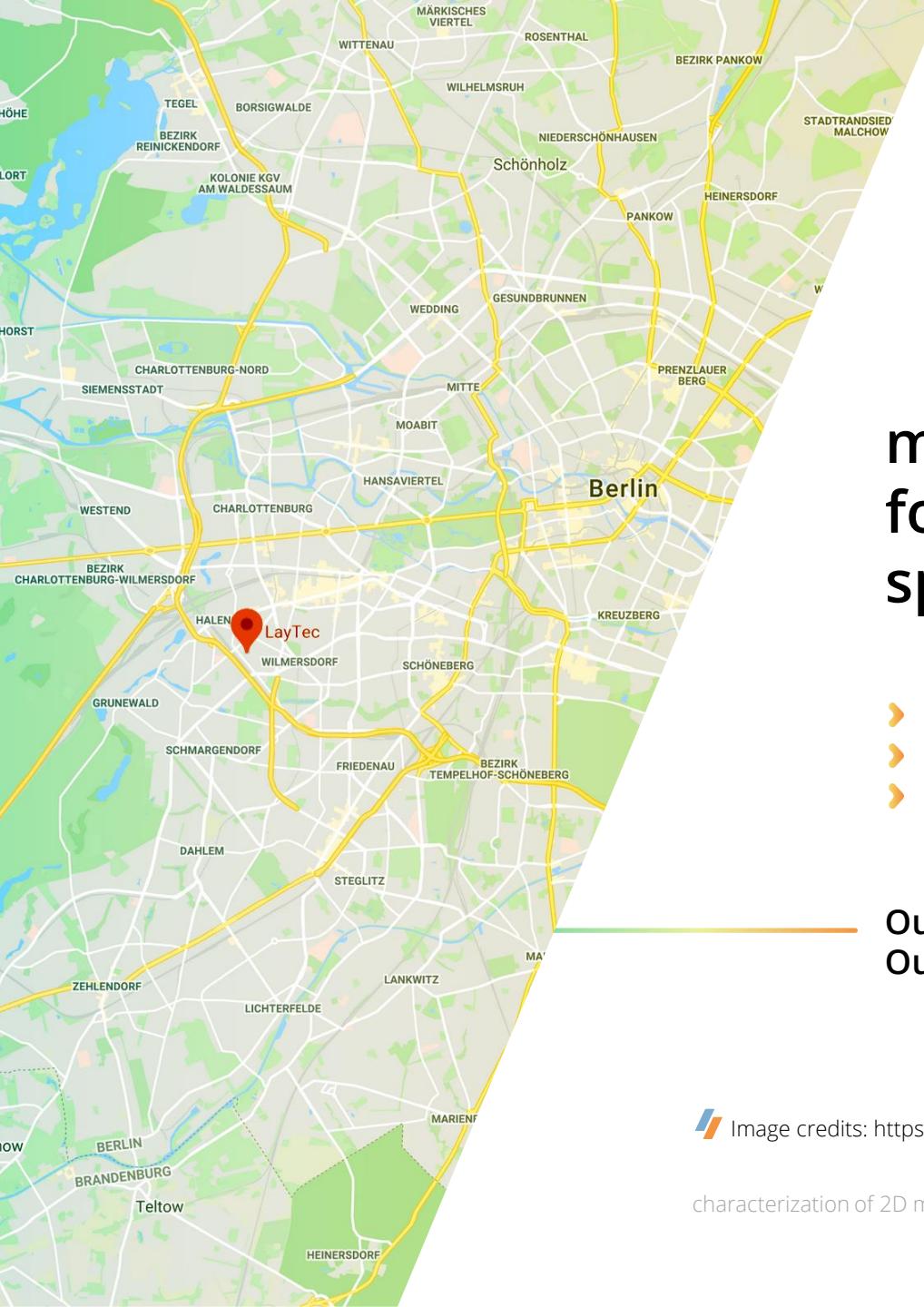
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LayTec AG, Seesener Str. 10-13, 10719 Berlin, Germany

Ben Conran, Dr. Clifford McAleese, Dr. Xiaochen Wang

AIXTRON Ltd, Buckingway Business Park, Anderson Road,
Swavesey, Cambridge CB24 4FQ, UK





metrology company founded 1999 in Berlin spin-off of TU Berlin

- 22 years old
- 70 employees
- 2500 systems sold
- operating worldwide
- member of Nynomic group

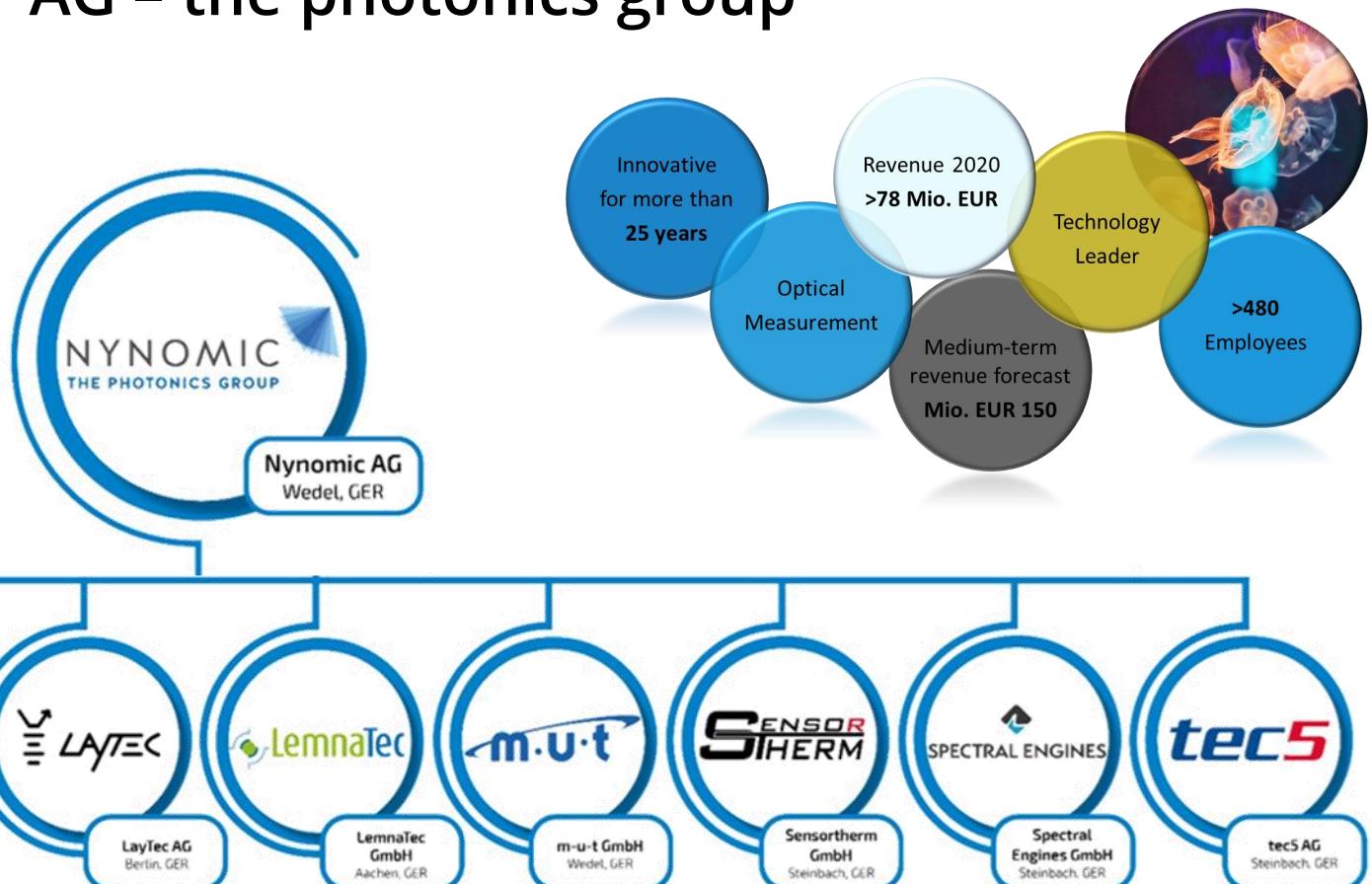
Our business: Process-integrated optical metrology
Our markets: Semiconductor and thin-film industry & academia
incl. lighting, laser, PV, glass coating ...

 Image credits: <https://www.google.de/maps>

characterization of 2D materials growth | LayTec AG | marcello.binetti@laytec.de

LayTec is a member of Nynomic AG – the photonics group

A growing number of companies, acquired strategically and all dedicated to permanent, non-contact and non-destructive optical measurement technology



Integrated metrology for various industries and markets

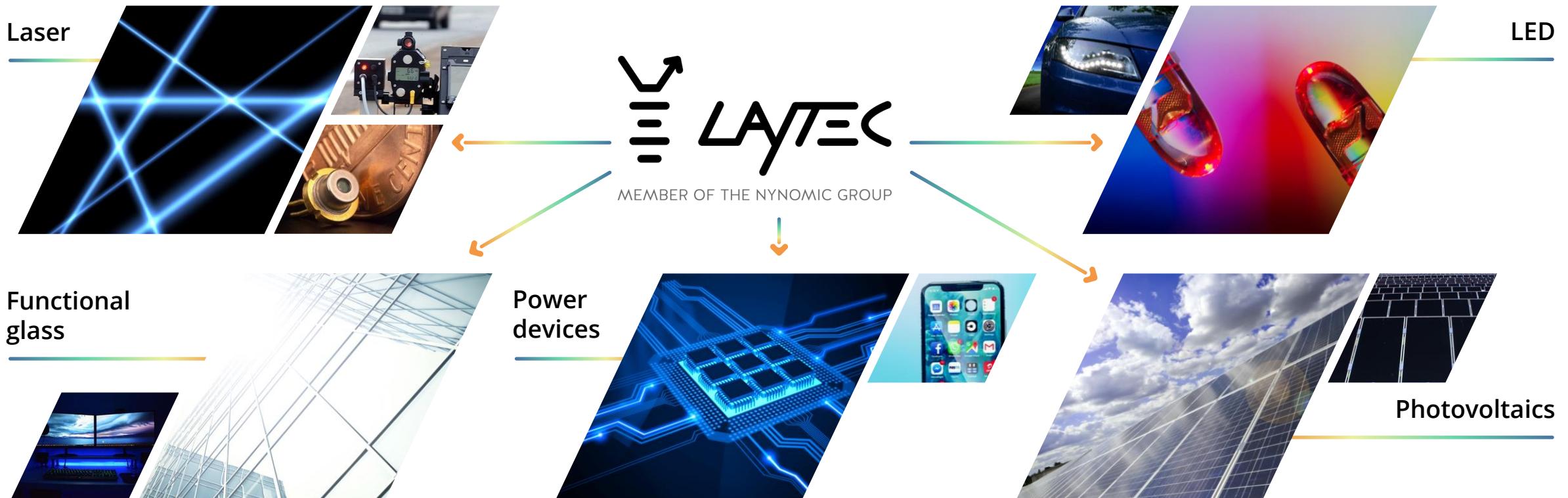


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Integrated metrology for various industries and markets

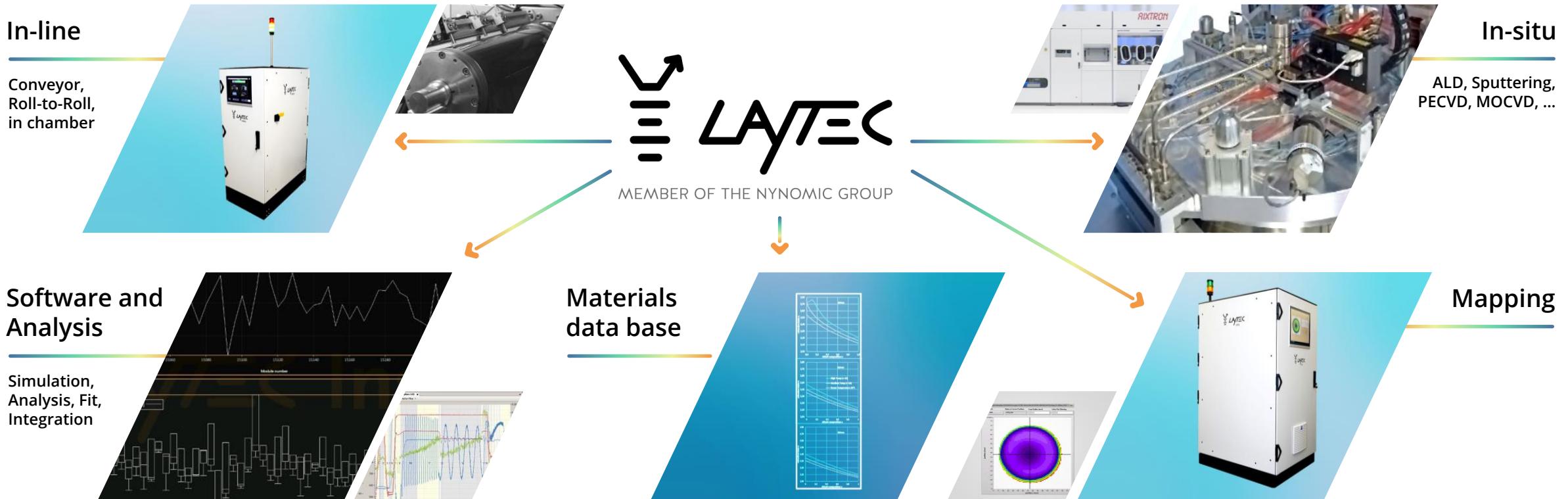


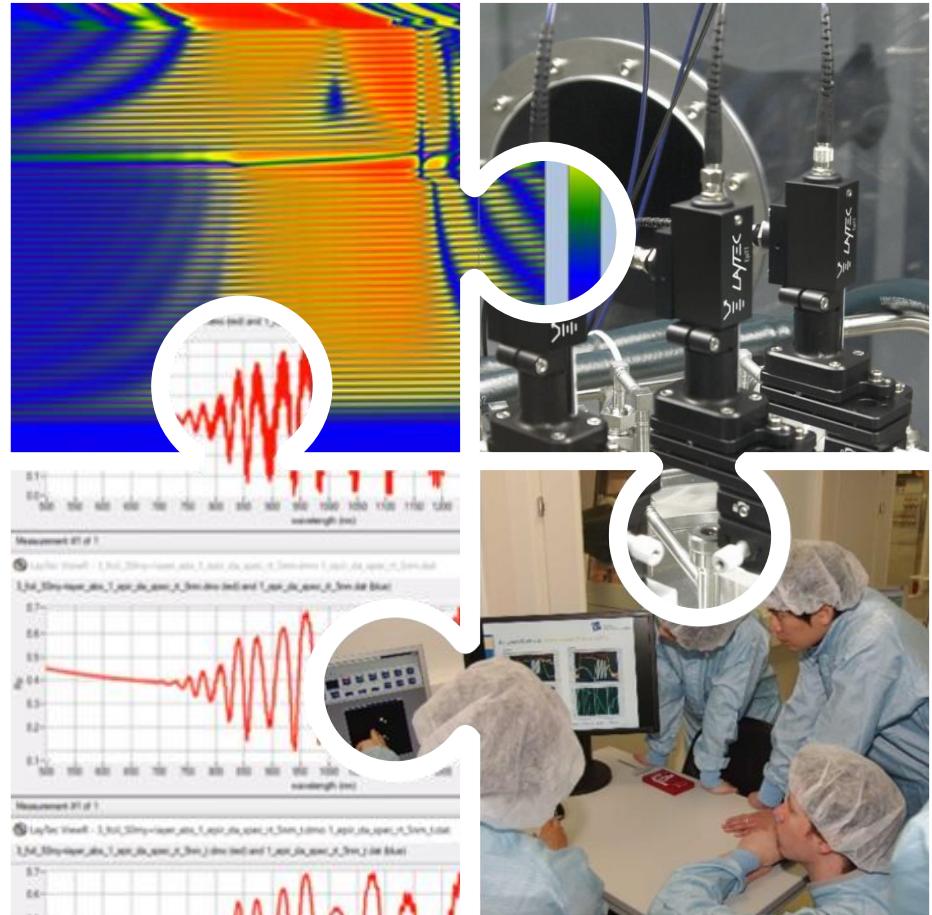
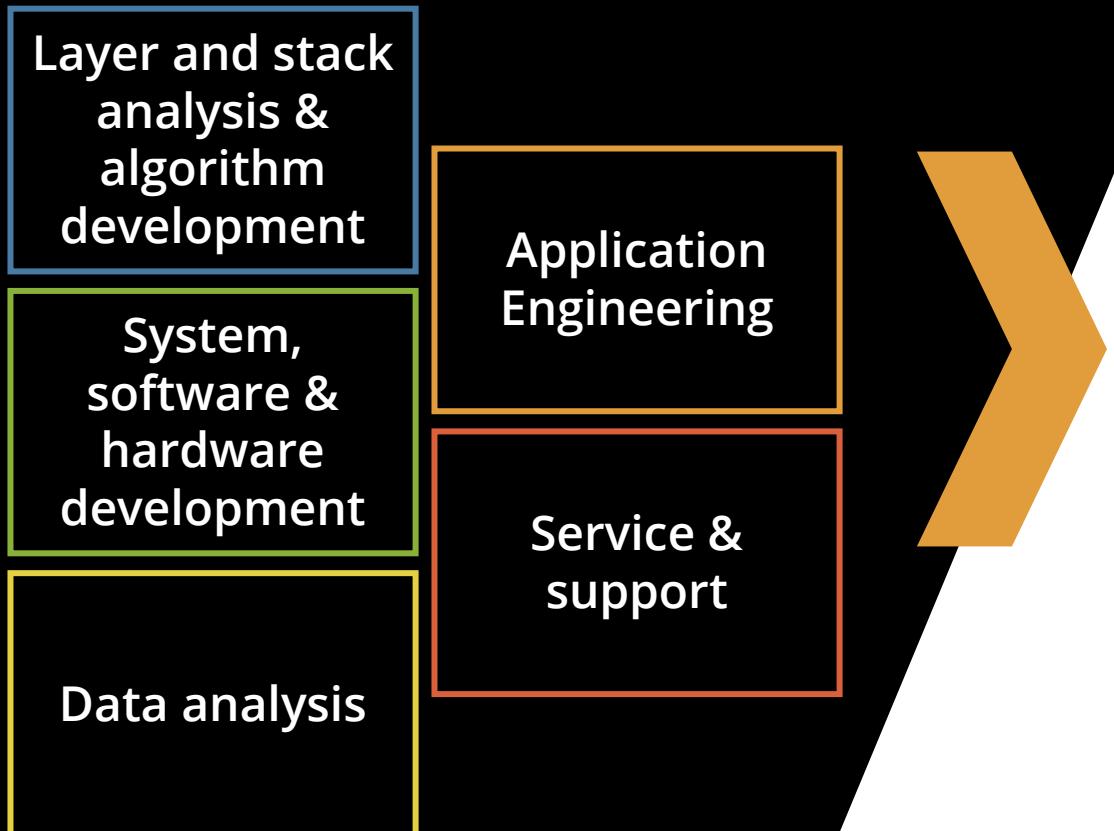
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In-situ metrology within manufacturing chain, e.g. LED

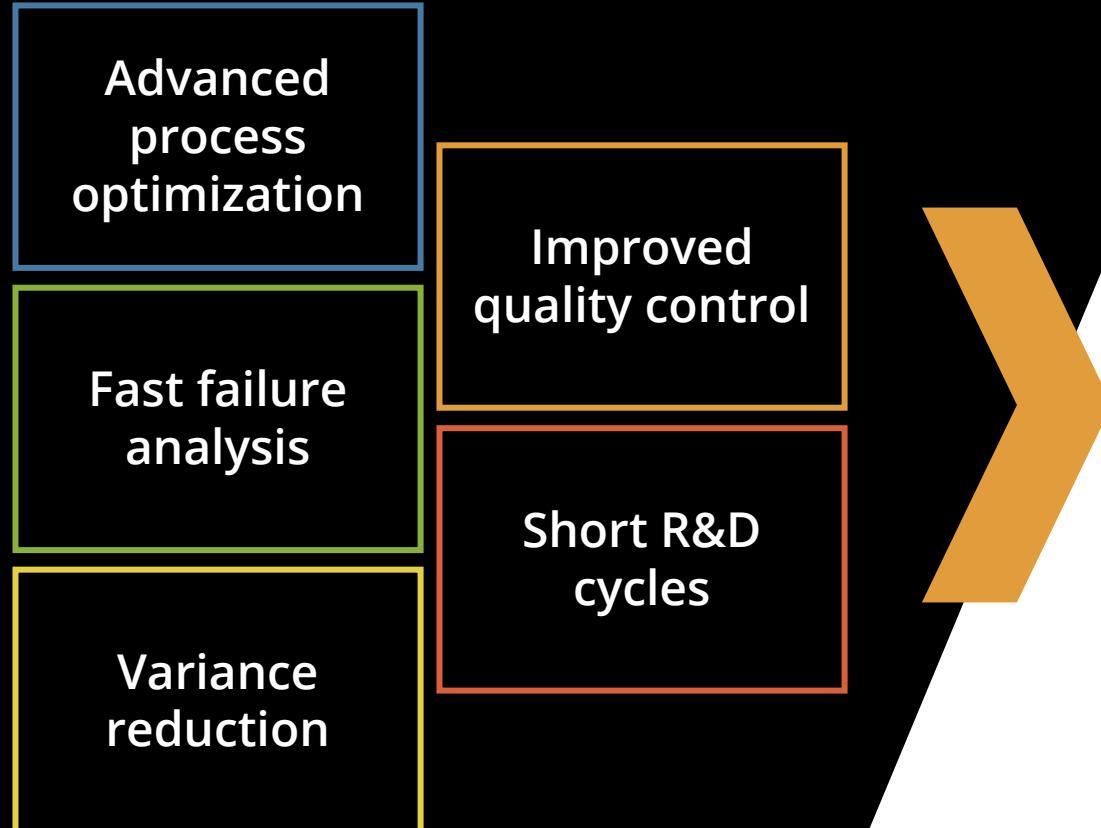


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The one-stop-shop for integrated metrology



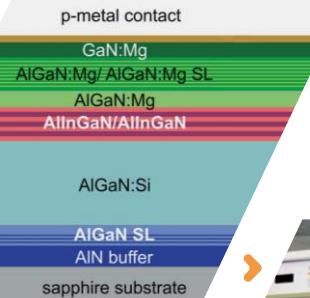
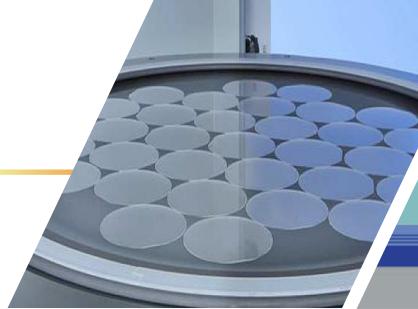
Customer's benefits:



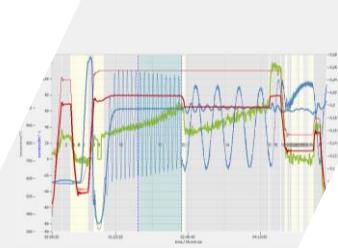
We make the related global industries more effective, more productive and less consuming of energy and resources!

In-situ metrology for compound semiconductor deposition processes

substrate
wafers + recipe
for layer stack



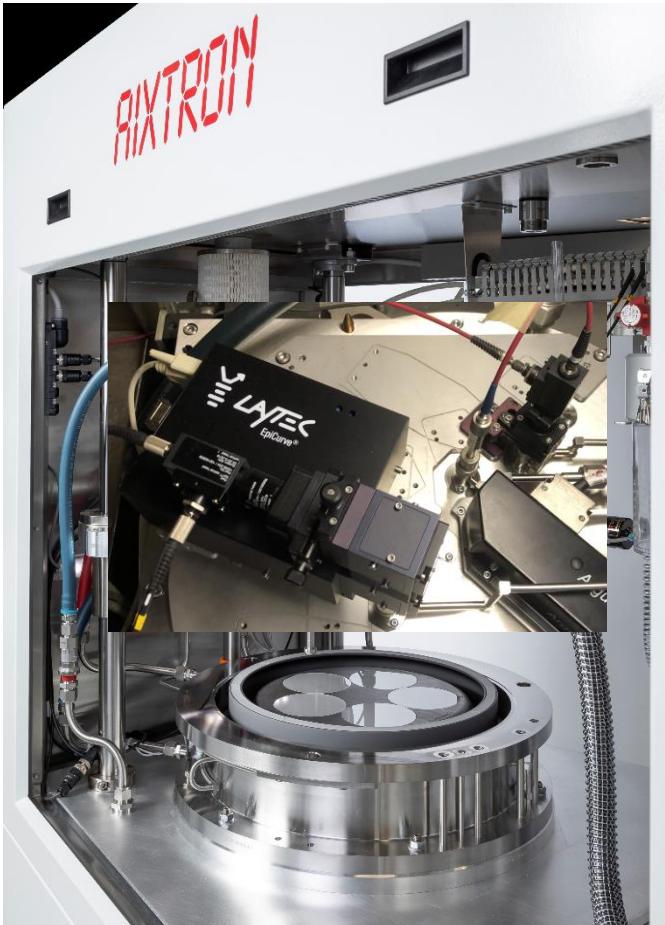
In-situ data for
process control
= monitoring and
control of key growth
parameters and layer
properties



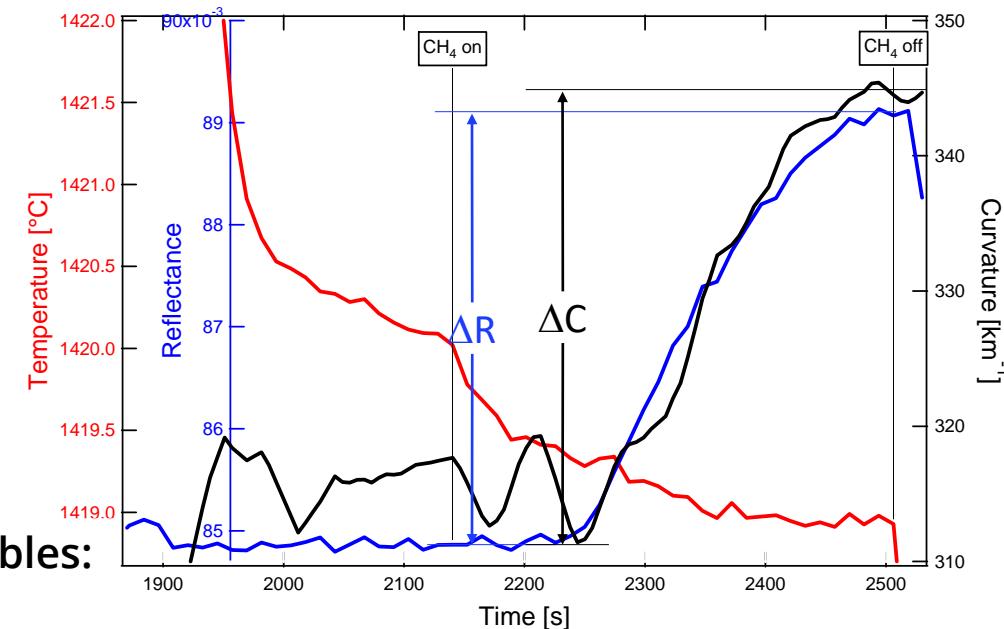
Measurement of

- wafer and pocket temperature
- layer thickness
- growth rate
- wafer curvature
- ternary composition
- surface morphology
- on-wafer uniformity
- ...

LayTec EpiCurve® TT on RAXTRON CCS MOCVD Reactor



Graphene/Sapphire



in-situ measurables:

Emissivity corrected
IR pyrometry (ECP)

Reflectance (R)

- Substrate back-side temperature ($T_{growth} \sim 1400 \text{ }^{\circ}\text{C}$)
- Precise process information: induction period (~100 s, depending on deposition parameters), R is function of coverage (θ)

Wafer bow (C)

- Substrate front-side temperature

Graphene – CVD deposition: 1st ML (in-situ reflectance, R405nm)

in-situ

$R_{405\text{nm}}$ allows measuring coverage (θ)

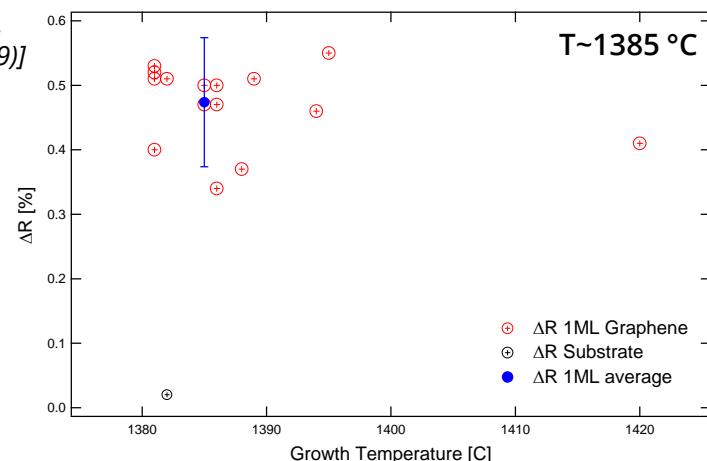
$$\frac{\delta R}{\delta t} \rightarrow 0 \text{ for } \theta(1^{\text{st}} \text{ML}) \rightarrow 1$$

Exp. result:

$$\Delta R(1\text{ML})_{405\text{nm}} = 0.5\% \pm 0.1\%$$

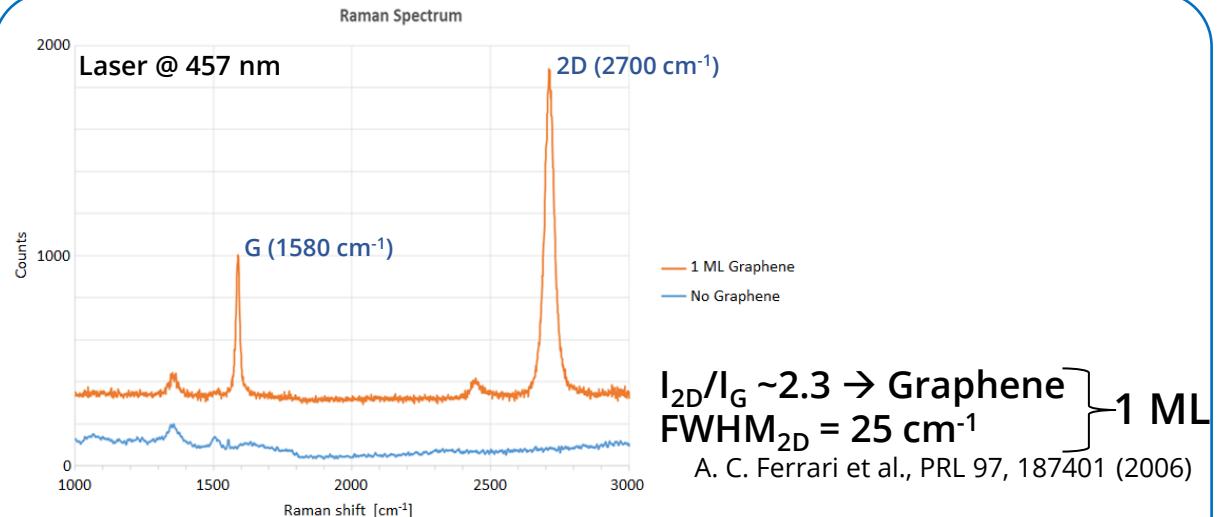
@High Temp:
interaction C-O-Al →
→ Gr/Sapphire bond

[Dou, Z., Chen, Z., Li, N. et al.
Nat Commun 10, 5013 (2019)]



Exp. data by
RIXTON

Raman spectroscopy & simulation



$I_{2\text{D}}/I_{\text{G}} \sim 2.3 \rightarrow \text{Graphene}$
 $\text{FWHM}_{2\text{D}} = 25 \text{ cm}^{-1}$

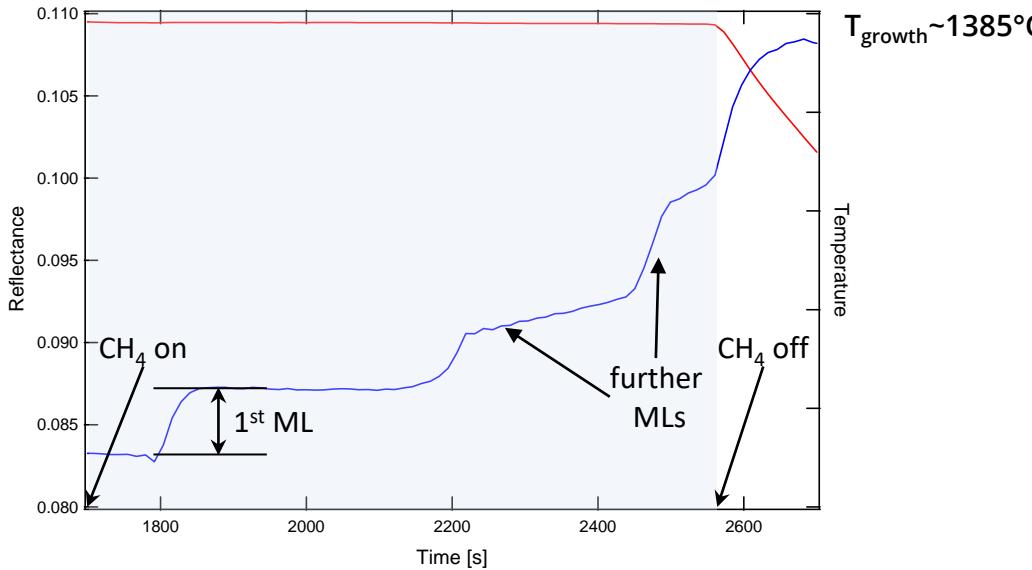
A. C. Ferrari et al., PRL 97, 187401 (2006)

Analysis (RT): $\Delta R(1 \text{ ML})_{405 \text{ nm}} = 0.63\%$

- 1 ML ~0.335 nm [Dresselhaus M. S. et al., *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, CA, 1996; p 965]
- n&k for exfoliated graphene at room temperature [Song, B et al., Appl. Surf. Sci. 439 (2018) 1079–1087]
- Sapphire optical constants (@HT) [LayTec database]

Graphene – CVD deposition: further monolayers

in-situ analysis, during deposition:



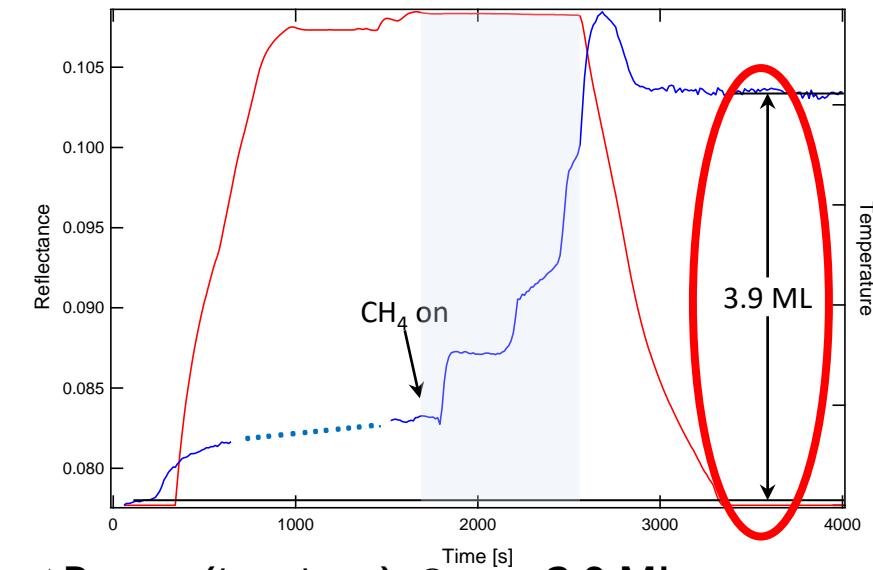
CH_4 pressure: stepwise increase to deposit 3 ML

ML ≥ 2 : difficult control for single ML deposition

- different C-species

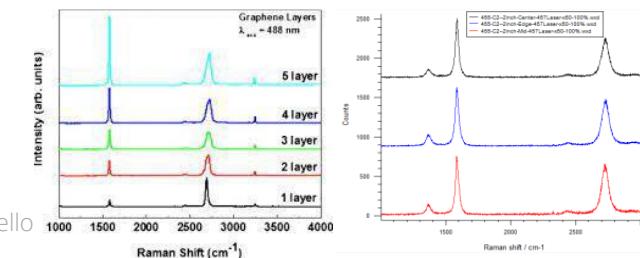
Exp. data by
RIXTRON

in-situ analysis, post deposition:



$\Delta R_{405 \text{ nm}} (t_{\text{end}} - t_{\text{start}})$: $\Theta_{\text{end}} = 3.9 \text{ ML}$ expected: 3 ML

Excess reflectivity: Amorphous carbon (Raman)



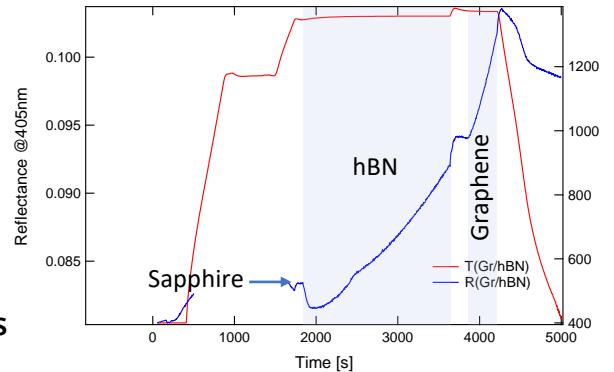
Heterostructure: Graphene/hBN/sapphire (in-situ reflectance, R405nm)

in-situ

R405: hBN decouples Gr/sapphire

hBN:
nucleation
coalescence (1 ML)
further MLs

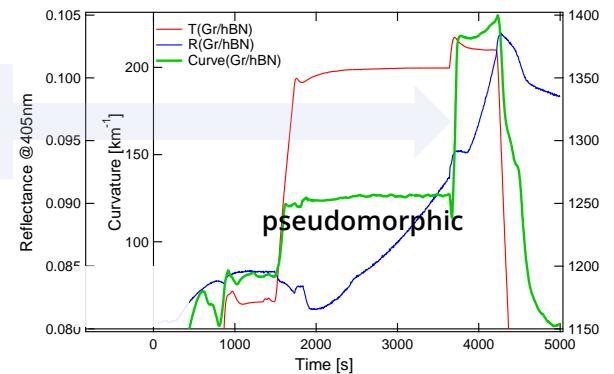
1 ML Graphene/hBN:
 $\Delta R(1 \text{ ML})_{405 \text{ nm}} = 0.007 \pm 0.001$
 similar to exfoliated samples



Curvature: ΔT through sapph.* + $\Delta\alpha$ (sapp/BN) + $\Delta\varepsilon$ (Gr)

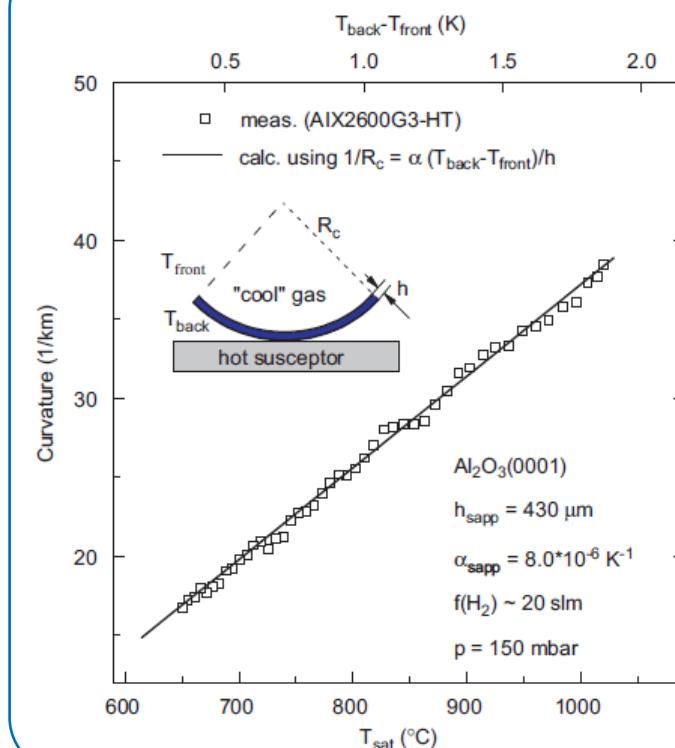
$$\alpha_{\text{sapp.}} = 5.5 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$$

$$\alpha_{\text{BN}} = 1.2 \cdot 10^{-6} \text{ } ^\circ\text{C}^{-1}$$



Exp. data by
RIEYTRON

*thermal cycling of bare sapphire wafers:



$$T_{\text{front-side}} = T_{\text{ECP pocket}} + \Delta C * h/\alpha$$

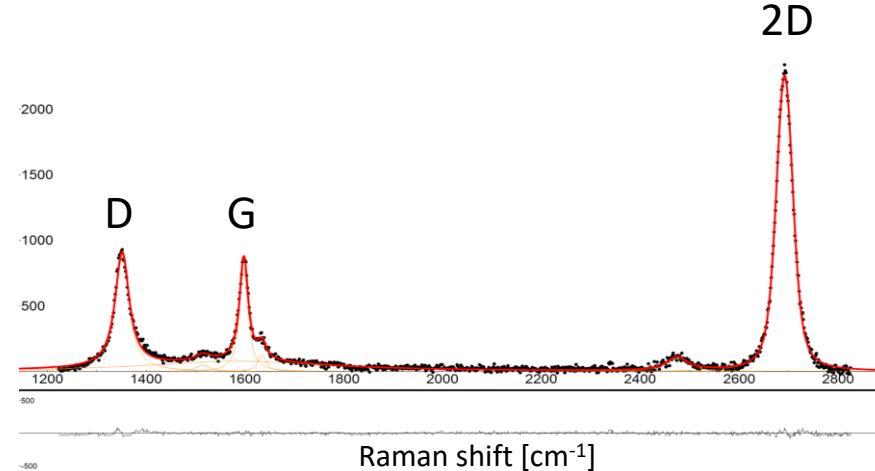
h = wafer thickness
 α = sapphire th.
 exp.ansion coefficient

[F. Brunner et al., J. Crystal Growth 289 (2007) 202]

Raman integration in EPIX – LayTec's mapping system



Raman + WLR
LayTec's Prototype Demonstrator



Measured parameters:	
ν	Peak position
$\Delta\omega$	Bandwidth
I	Intensity
$A(I, \Delta\omega)$	Integrated peak intensity

Laser:
Wavelength: 532 nm
Linewidth: <5 cm⁻¹
Spot diameter: ~30 μm
Power: <80 kW/cm²

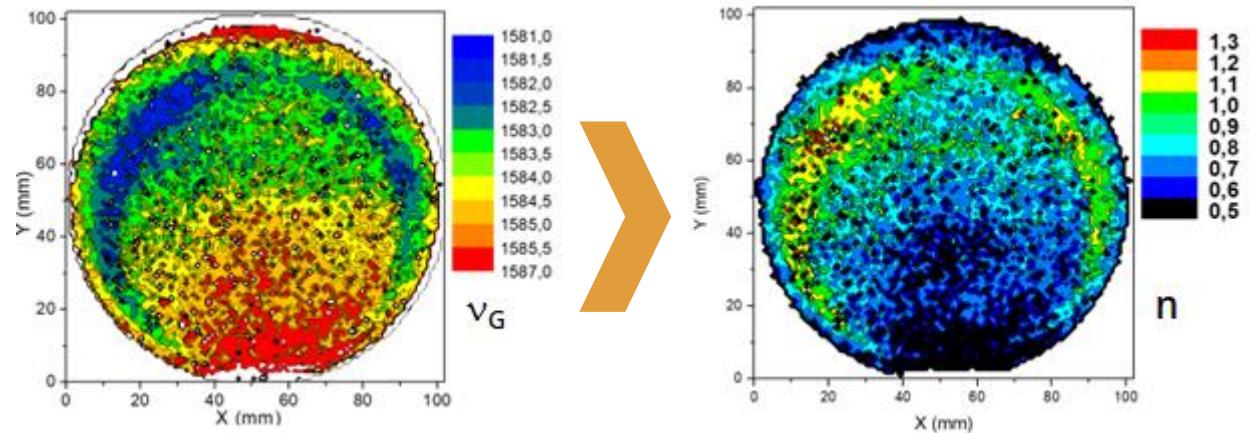
Spectrometer:
Spectral res.: 6.5 cm⁻¹
Acq. rate: 0.3 Hz

Measurables:
MLs: I_{2D}/I_G , ν_G
Strain, Defects: $\Delta\omega$, ν
 E_F : A_G/A_{2D}

Raman maps - Graphene monolayers (empirical)

- ▶ **n:** number of graphene monolayers
- ▶ **v:** G-peak position
- ▶ *v*-values vary around average values for an unperturbed single monolayer
- ▶ **Graphene-Sapphire interaction:** $\Delta v = 5 \text{ cm}^{-1}$

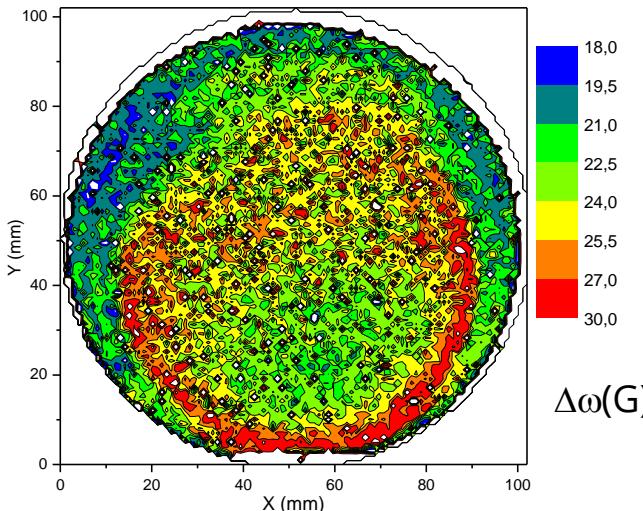
$$n = \left(\frac{11}{v + \Delta v - 1581,6 \text{ cm}^{-1}} \right)^{1/1,6}$$



I. Calizo et al., The effect of substrates on the Raman spectrum of graphene: Graphene- on-sapphire and graphene-on-glass, Appl. Phys. Lett. 91, 201904 (2007); <https://doi.org/10.1063/1.2805024>

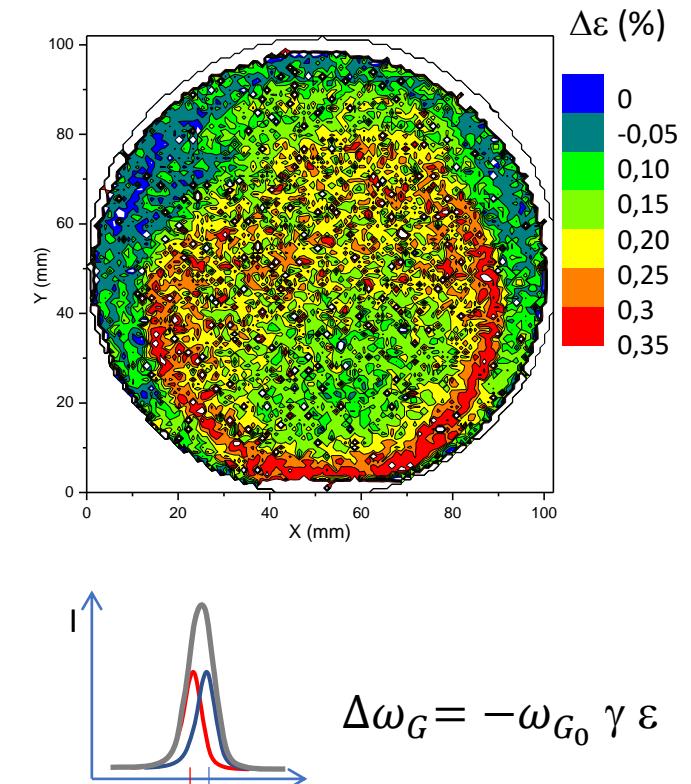
Samples by
RIXTRON

Raman maps - local stress



- ▶ Non-polarized Raman measurements
- ▶ $\Delta\omega$ -values vary around average values for an unperturbed single monolayer

- ▶ $\Delta\omega$ radial symmetry → stress radial symmetry
 - ▶ Considering:
 - ▶ $\alpha_{\text{Graphene}} < 0$
 - ▶ $\alpha_{\text{Sapphire}} > 0$
 - ▶ **wafer curvature**
Approximate wafer distortion profile
- LayTec EpiCurve measurement
- ▶ $\Delta\omega$ distribution results from a uniaxial strain, with radial symmetry

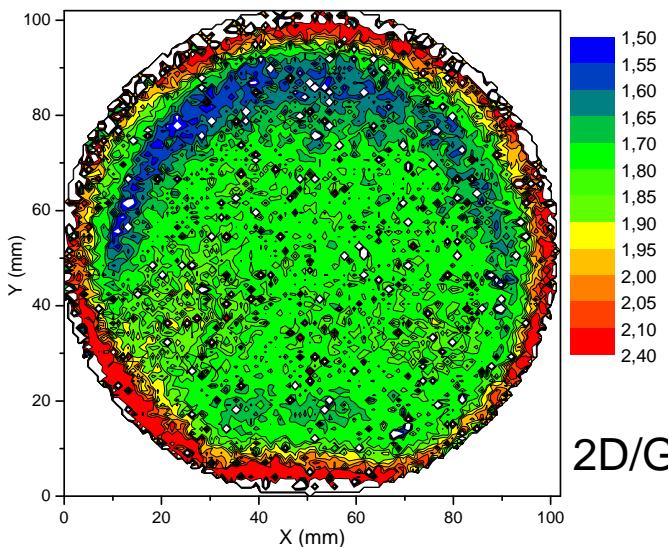


$$\Delta\omega_G = -\omega_{G_0} \gamma \epsilon \quad \text{for } \gamma=2$$

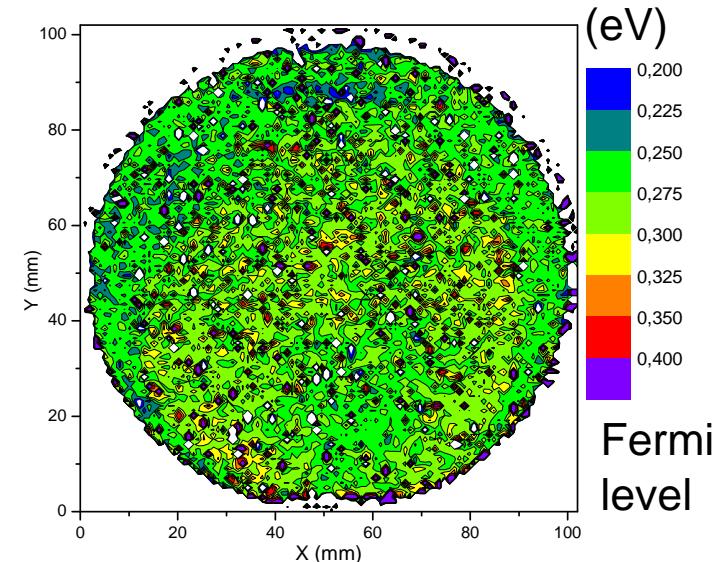
▶ 6 cm^{-1} broadening → $\epsilon = \underline{\sim 0.3 \% \text{ stress}}$

Samples by
RIXTRON

Raman maps – local Fermi level & doping



$$|E_F| = 0,9 \cdot \sqrt{\frac{A(G)}{A(2D)}} - 0,23$$



► **$A(I, \Delta\omega)$: Integrated peak intensity**

W.-J. Zhao et al., Intercalation of Few-Layer Graphite Flakes with FeCl₃: Raman Determination of Fermi Level, Layer by Layer Decoupling, and Stability, J. Am. Chem. Soc., 2011, 133, 5941–5946, <https://pubs.acs.org/doi/10.1021/ja110939a>

A. Das et al., Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor, Nat. Nanotechnol., 2008, 3, 210–215, <https://doi.org/10.1038/nnano.2008.67>

Samples by
RIIXTRON

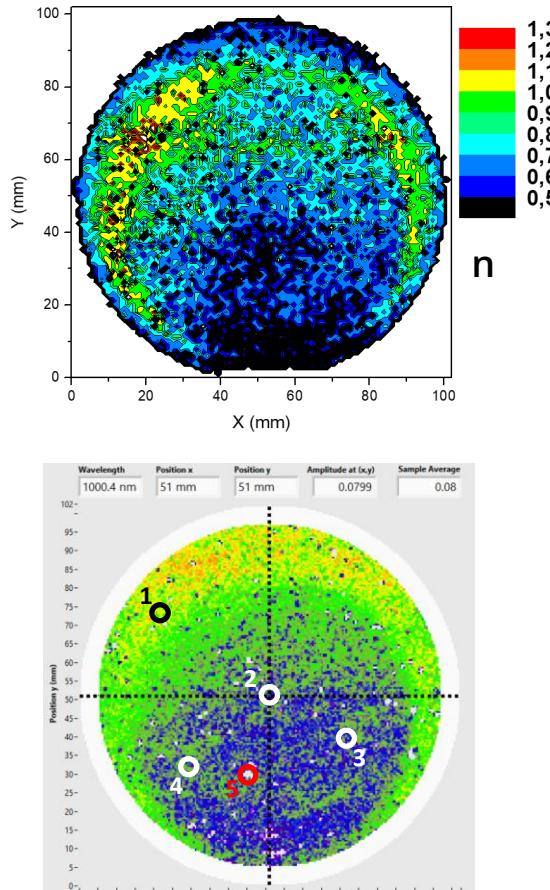
MEMBER OF THE NYNOMIC GROUP

White Light Reflectometry (WLR)

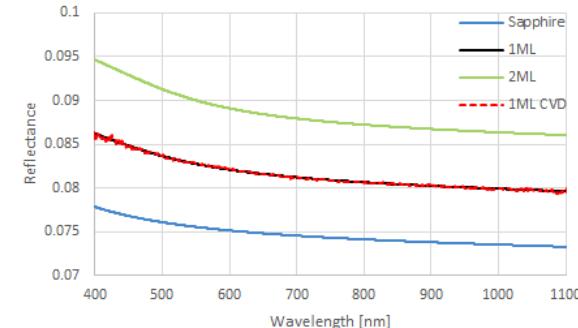


Raman + WLR
LayTec's Prototype Demonstrator

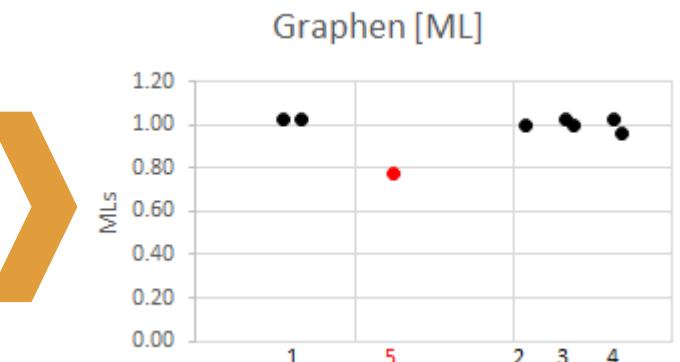
Samples by
RIEGLER



- ▶ High T Gr/Sapph interaction
 - ▶ C-O-Al bond (stronger than VdW)
 - ▶ [Dou, Z., Chen, Z., Li, N. et al. Nat Commun 10, 5013 (2019)]
- ▶ Reflectance vs Wavelength (nm) for Sapphire, 1ML, 2ML, and 1ML CVD samples.
- ▶ "Training" WLR with Raman results



- ▶ Fast measurement: 10Hz
- ▶ Spot diameter: 300µm



- ▶ layer number,
- ▶ uniformity,
- ▶ defects

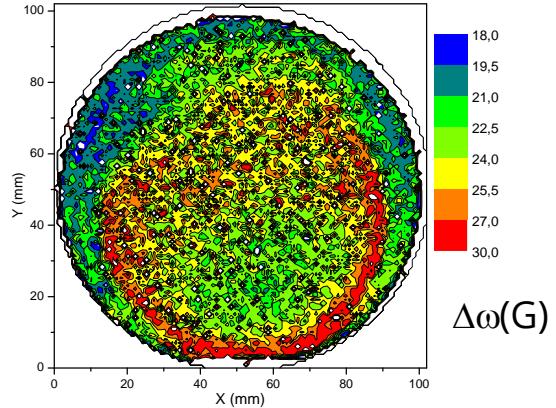
White Light Reflectometry (WLR)



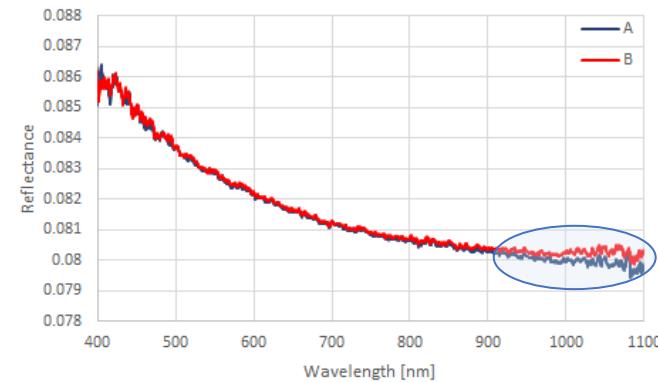
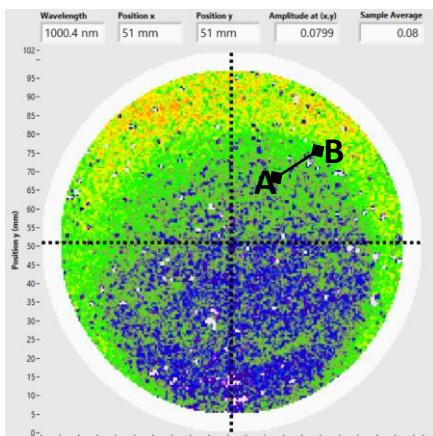
Raman + WLR

LayTec's Prototype
DemonstratorSamples by
RIELE

- $\Delta\omega(G)$ measures film stress



- WLR: similar symmetry



- NIR reflectance enables fast assessment of film stress at $10^2 \mu\text{m}$ scale

Thanks to ...



:
Prof. Costas Galiotis, Dr. Anastasios Manikas

RIXTRON:

UK: Ben van Well, Alex Jouvray
Oliver Whear

D: Simonas Krotkus, Sergej Pasko

LAYTEC:

Kolja Haberland, Thomas Zettler



German Federal Ministry of Education
and Research partial funding through:

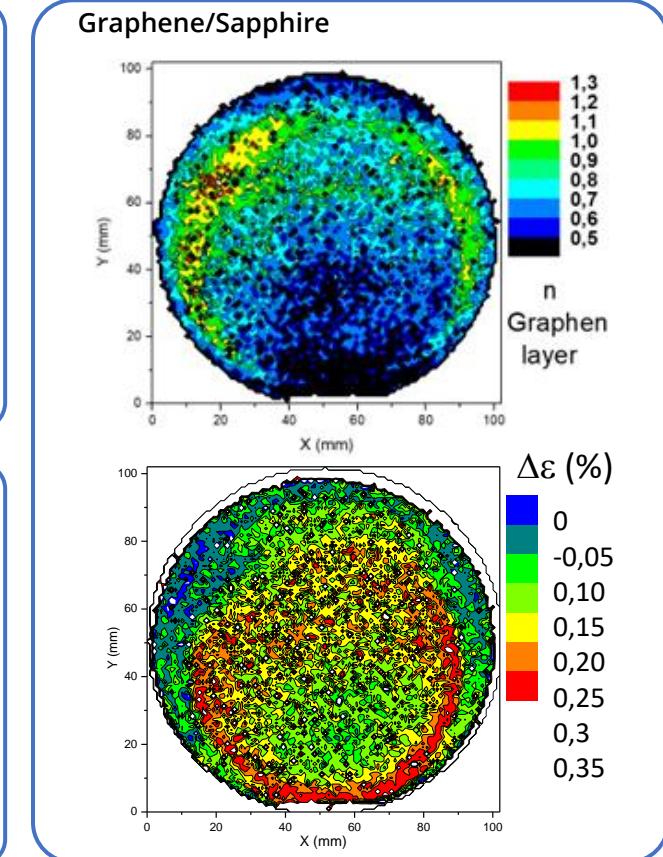
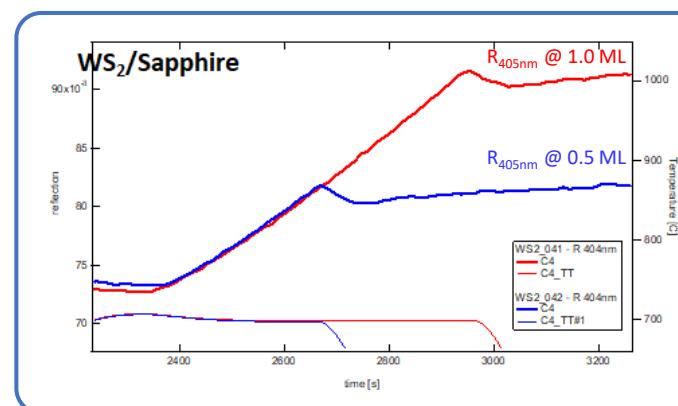
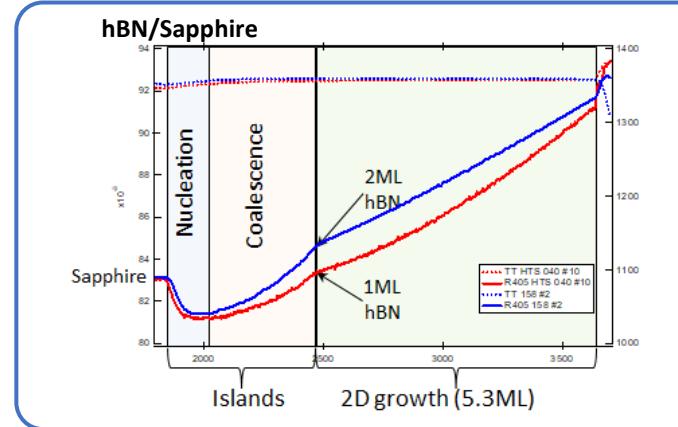
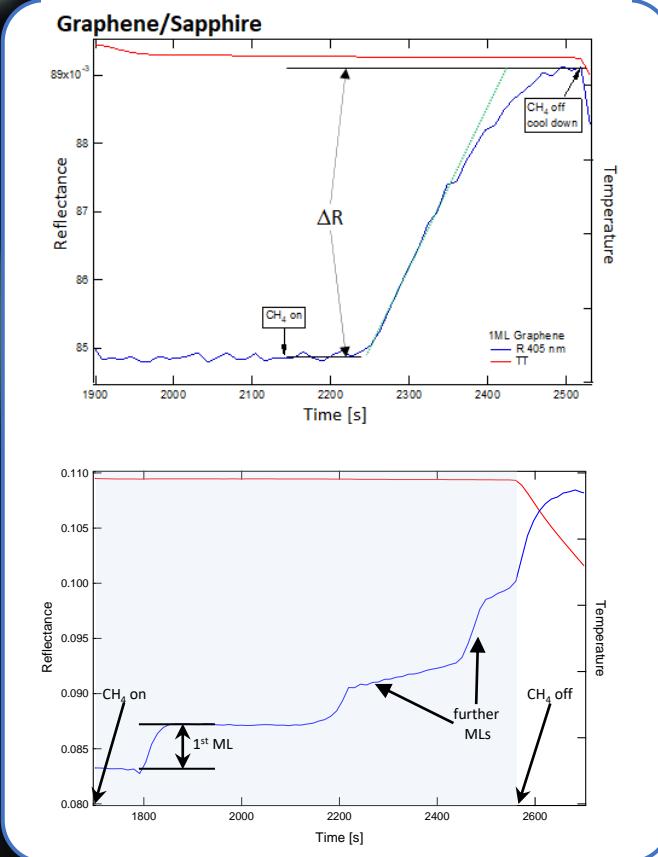


GIMMIK – Grant 03XP0210F
Graphene processing on 200mm
wafers for microelectronic applications

...all of you for your attention!

in a nutshell...

LayTec metrology enables comprehensive process optimization and control of 2D material epitaxy





Knowledge is key

www.laytec.de