GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO
10 ANNIVERSARY
Graphene online 2020
October 19-23

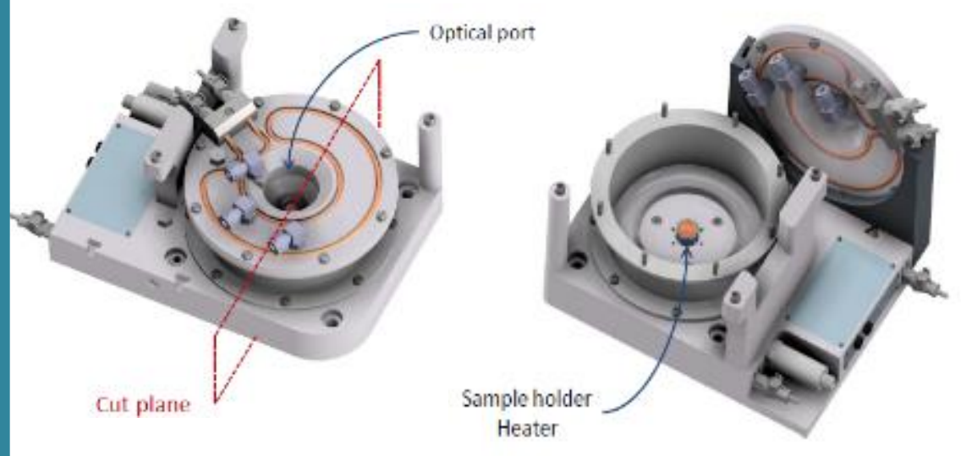
Growing perfect graphene on a liquid metal

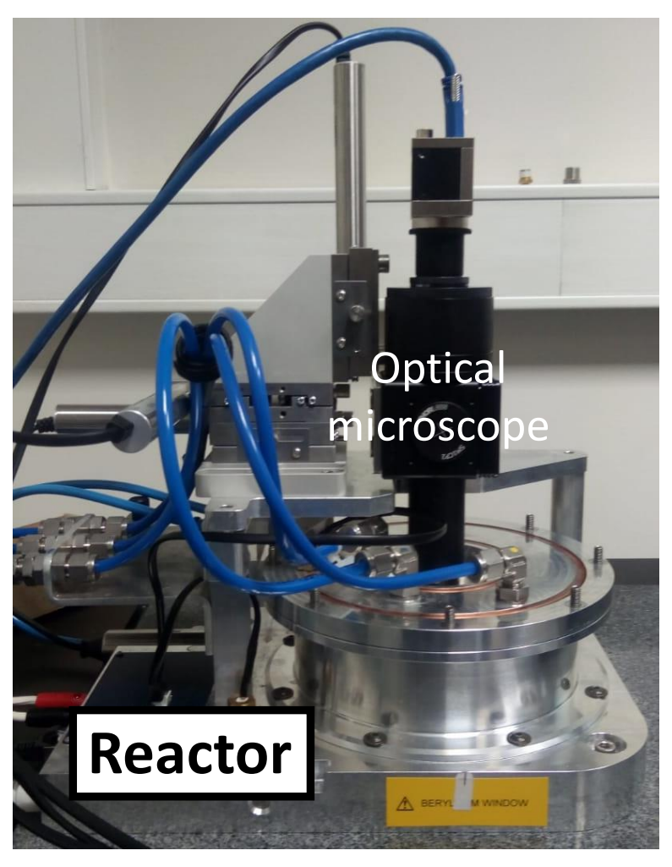
from self-organized flakes to the single layer

F. La Porta[1], M. Jankowski[2], A. Saedi[3], A.Manikas[4],M. De Voogd[5], C. Galitios[4],G. Van Baarle[5], K. Reuter[6], I. Groot[3], G. Renaud[2] and O.Konovalov[1]

[1] European Synchrotron Radiation Facility– 71 Avenue des Martyrs, 38000 Grenoble, France
[2] Univ. Grenoble Alpes, CEA, IRIG/MEM/NRS 38000 Grenoble, France
[3] Universiteit Leiden – Rapenburg 70, 2311 EZ Leiden, Netherlands
[4] FORTH – Stadiou Street, Platani, Patra 265 04, Greece
[5] LPM – Kenauweg 21, 2331 BA Leiden,The Netherlands
[6] TUM – Arcisstraße 21, 80333 München, Germany

In order to produce large-area single-layer graphene with the CVD method, the surface of the metal catalyzer must be homogeneous and smooth[1]. The graphene, as a matter of fact, nucleates on the defects, steps, and impurities. The use of the liquid phase can overcome these limitations and guarantee a uniform flat substrate[2]. Furthermore, the graphene crystals can float on the surface and self-align[3]. However, the study of such systems required the cooling at RT and, therefore, the re-solidification of the samples, altering the surface significantly. Furthermore, in this way, information on the dynamic of the growth was lost entirely. In order to fill this gap, a reactor was projected for the in-situ characterization with the simultaneous combination of x-ray scattering techniques and optical microscopy[4]. The synchrotron light provides atomic information, while the optical microscope is a perfect tool for monitoring the growth. A large area of high-quality graphene was created in the laboratory with high reproducibility. The growths were done on liquid copper at 1400K and 200 mbar.

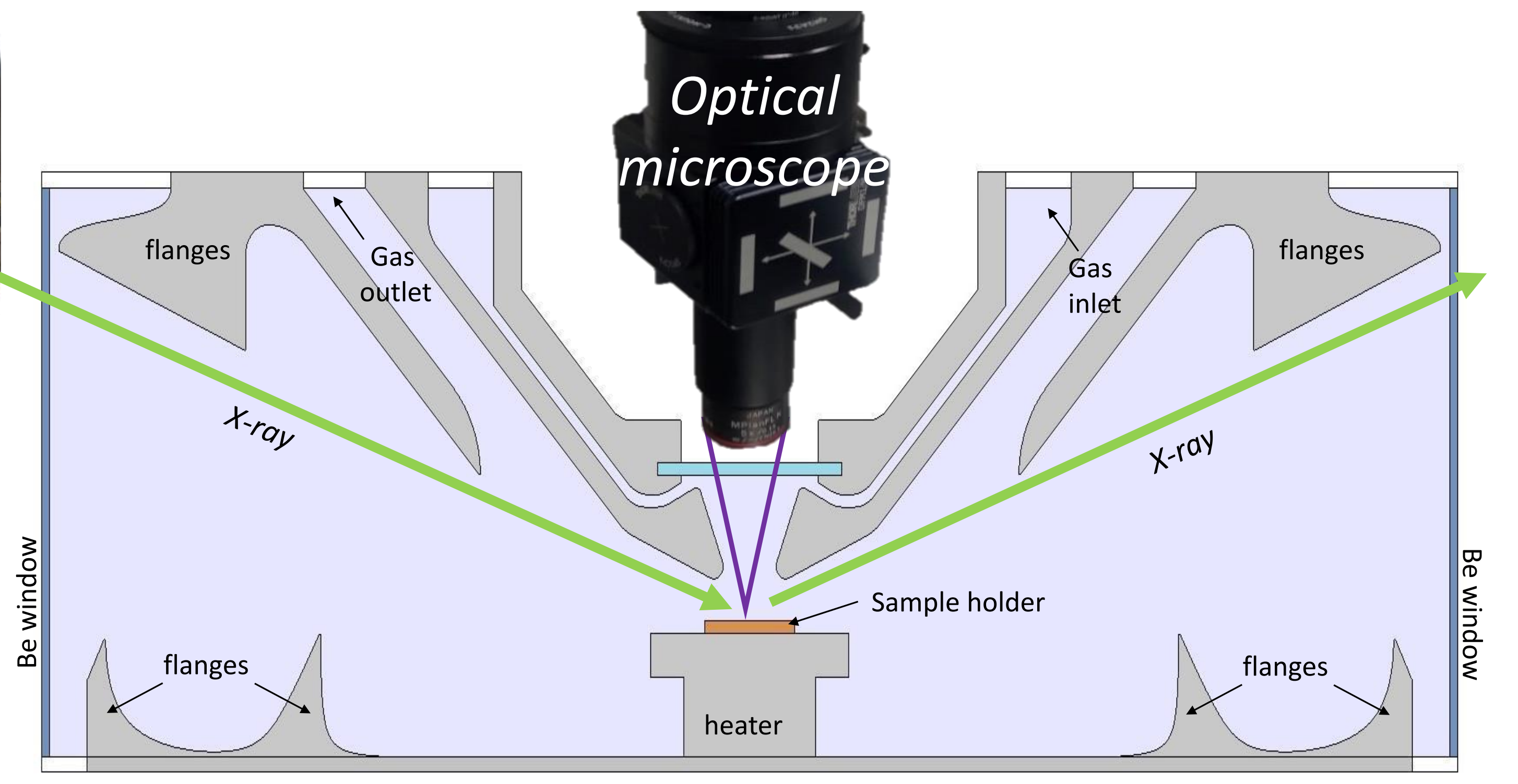




CVD reactor

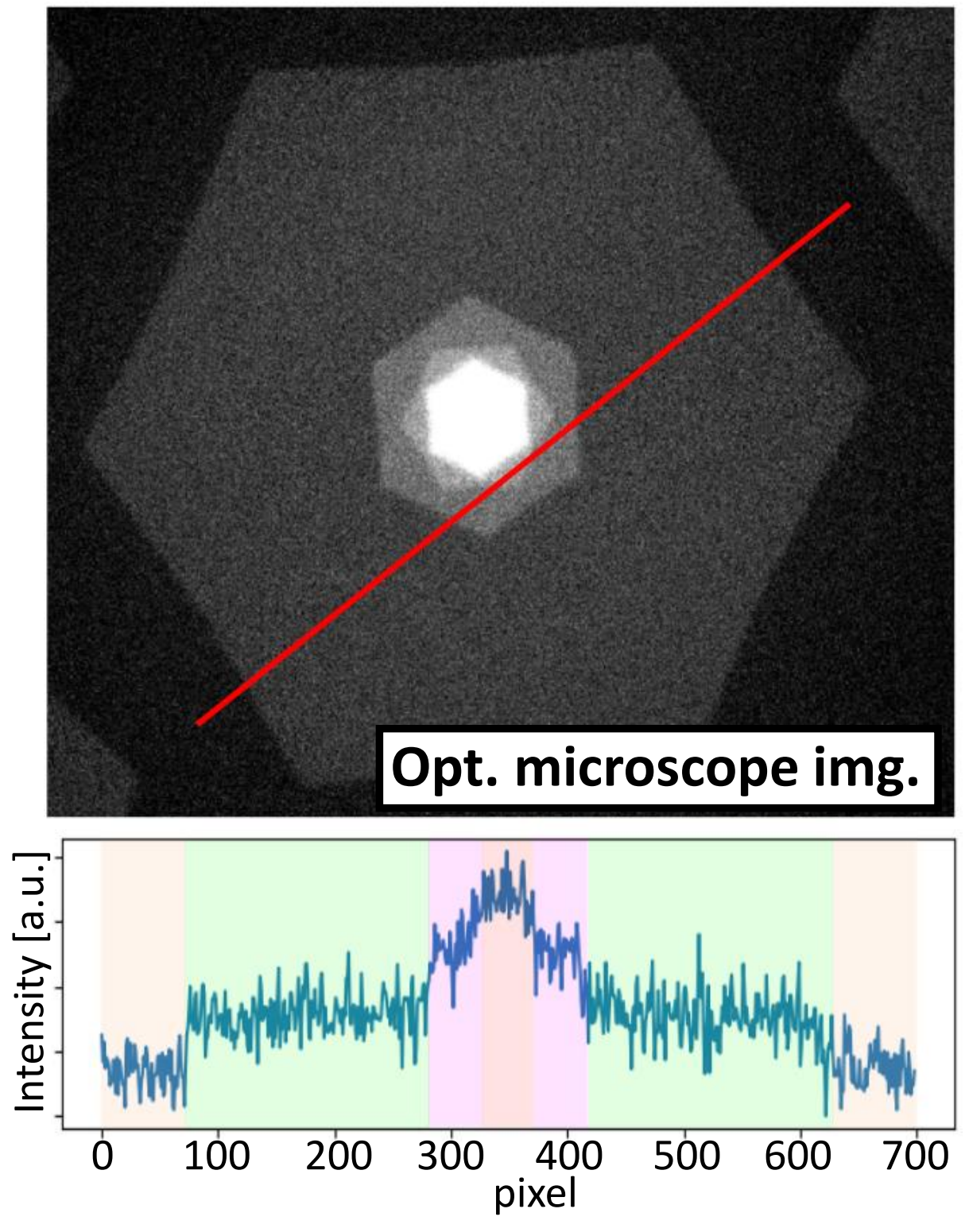
The synchrotron

The scattering factor of the carbon is low, while the one of Cu is high. In order to detect the graphene diffraction signal, the high brilliance source of the synchrotron is needed.



The optical microscope

At 1400K, the liquid copper and the graphene emit light due to the black body radiation. The different emissivity between the two materials is enough to discern them. The intensity of the graphene scale with the number of layers[5].

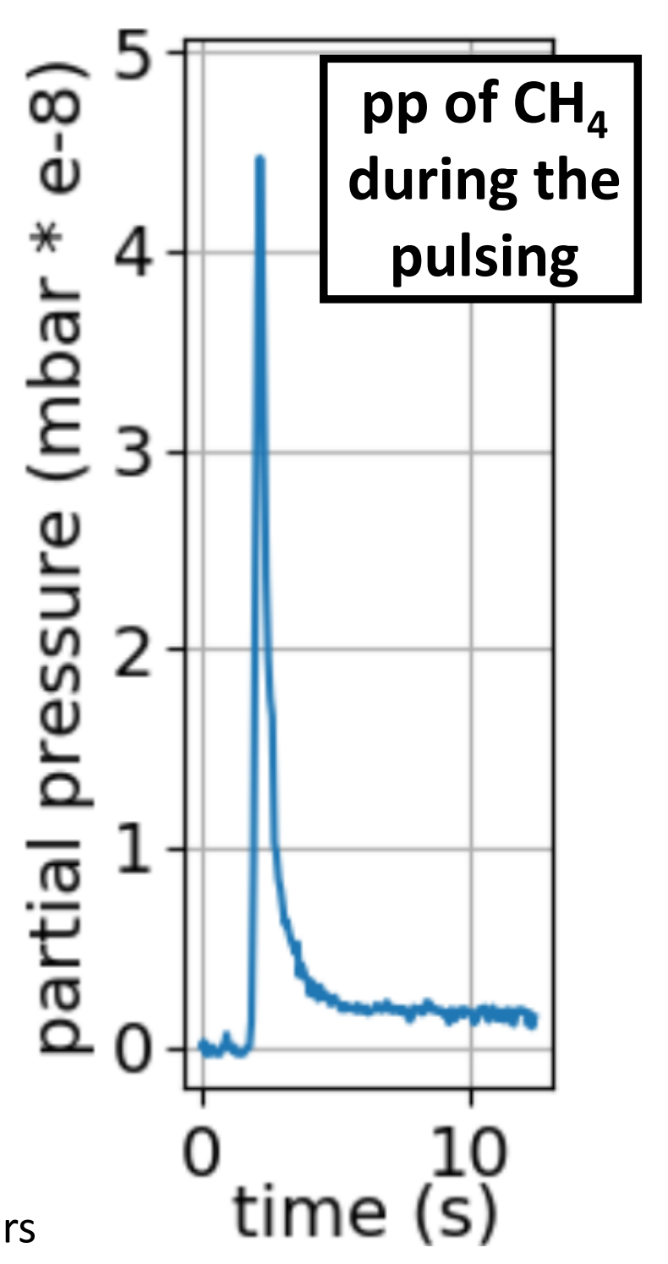


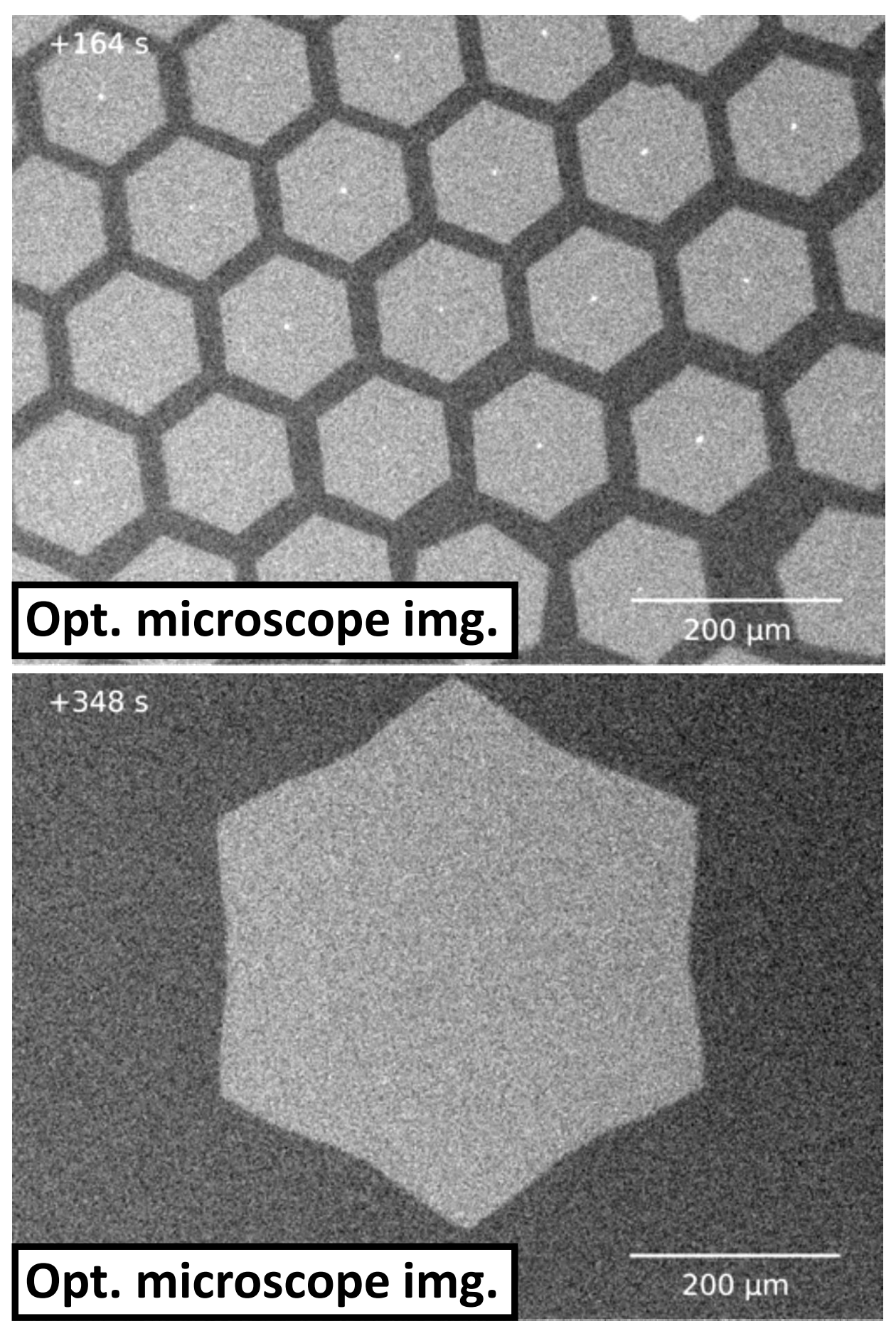
Observing the graphene

Control on the nucleation

The initial partial pressure of the methane precursor influences the nucleation density. To control the nucleation, therefore, the CH4 concentration was pulsed for ~1s, and later decrease to a constant value. If the carbon concentration is ~10 higher then the steady-state of the growth (as shown in figure), many atomically thick graphene crystals grow and later self-align and merge. If the pulsing is avoided, a unique graphene crystal with a large size, up to 2mm, can be produced*.

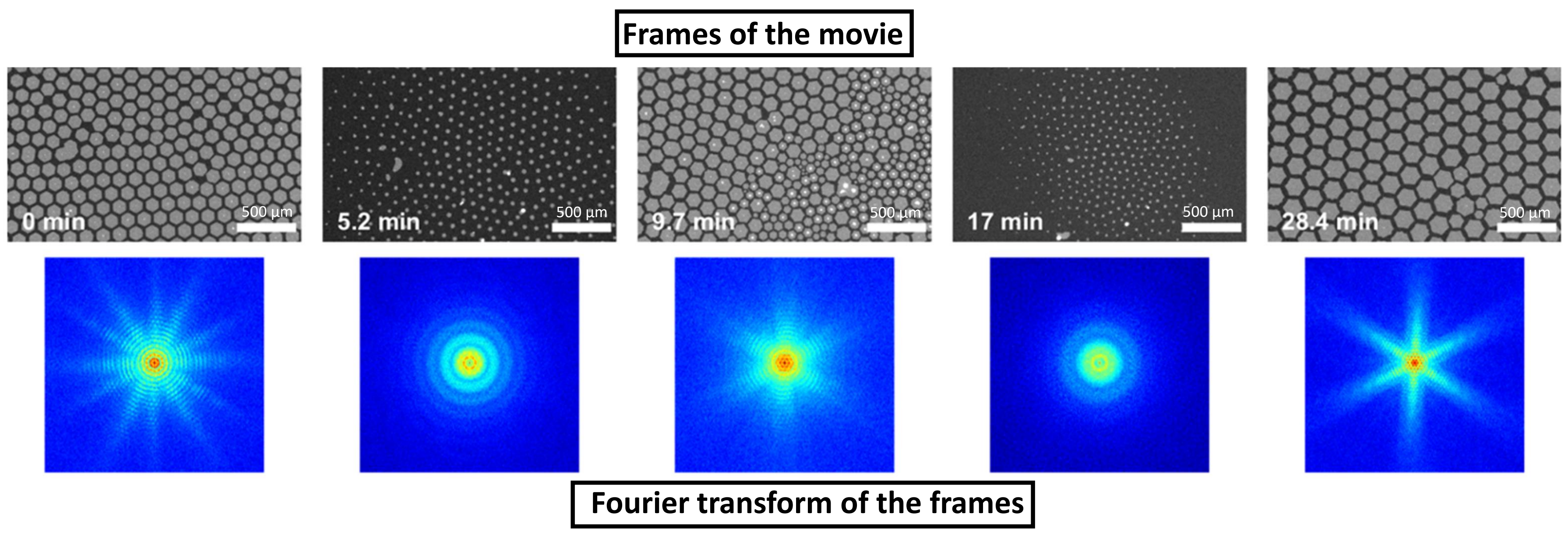
*distance between two opposite corners





Control of the growth

Real-time monitoring allows having a feedback on the status of the growth. The carbon precursor concertation could be varied anytime to alter the condition. In the example below, cycles of growing and etching were alternated in order to increase the periodicity of the self-alignment.

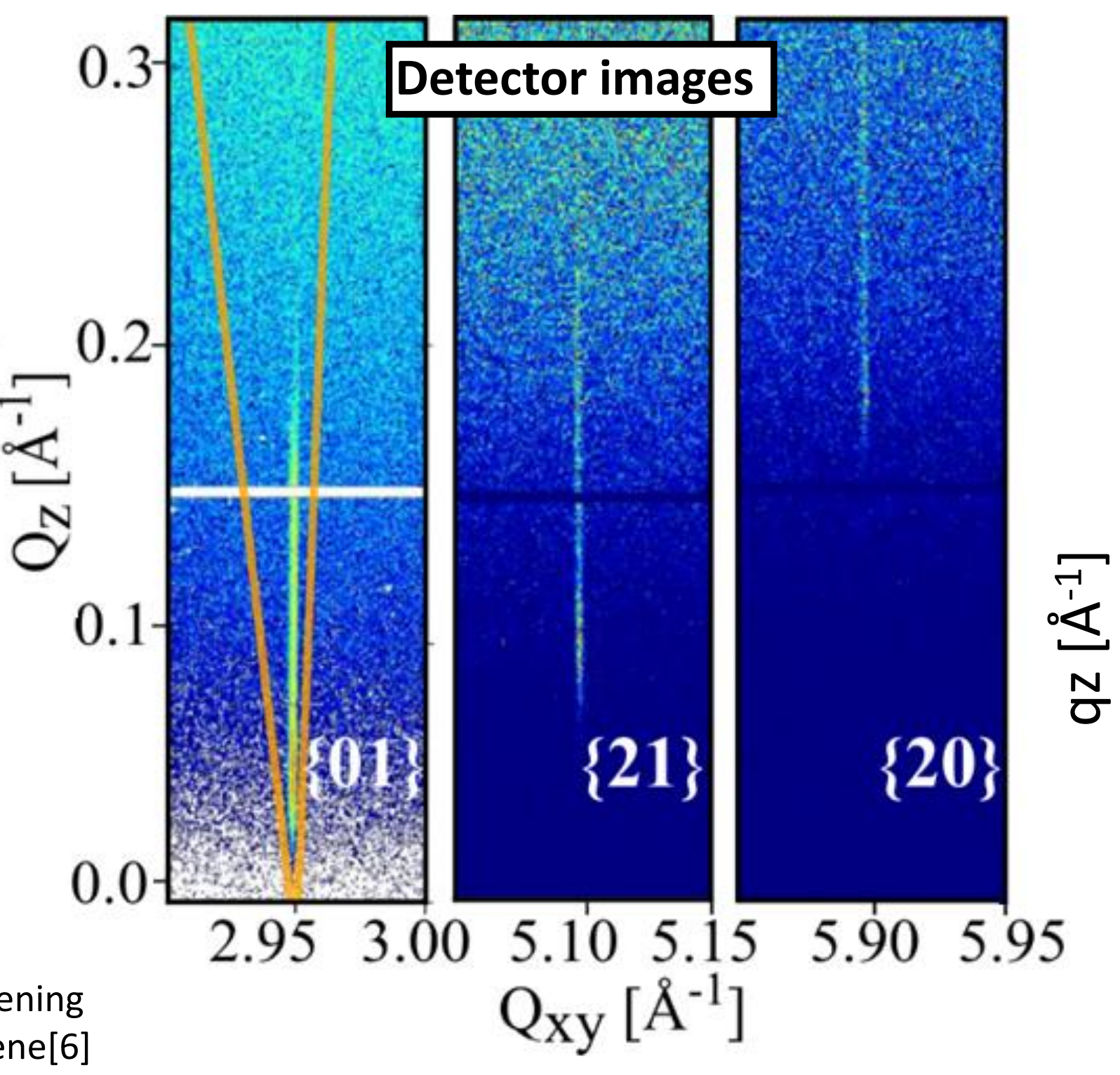


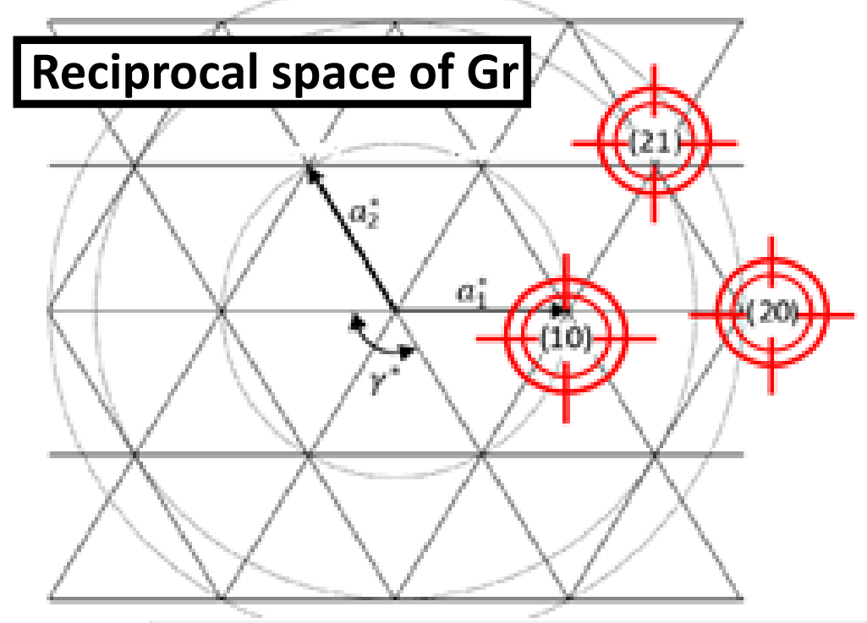
Information from the atoms

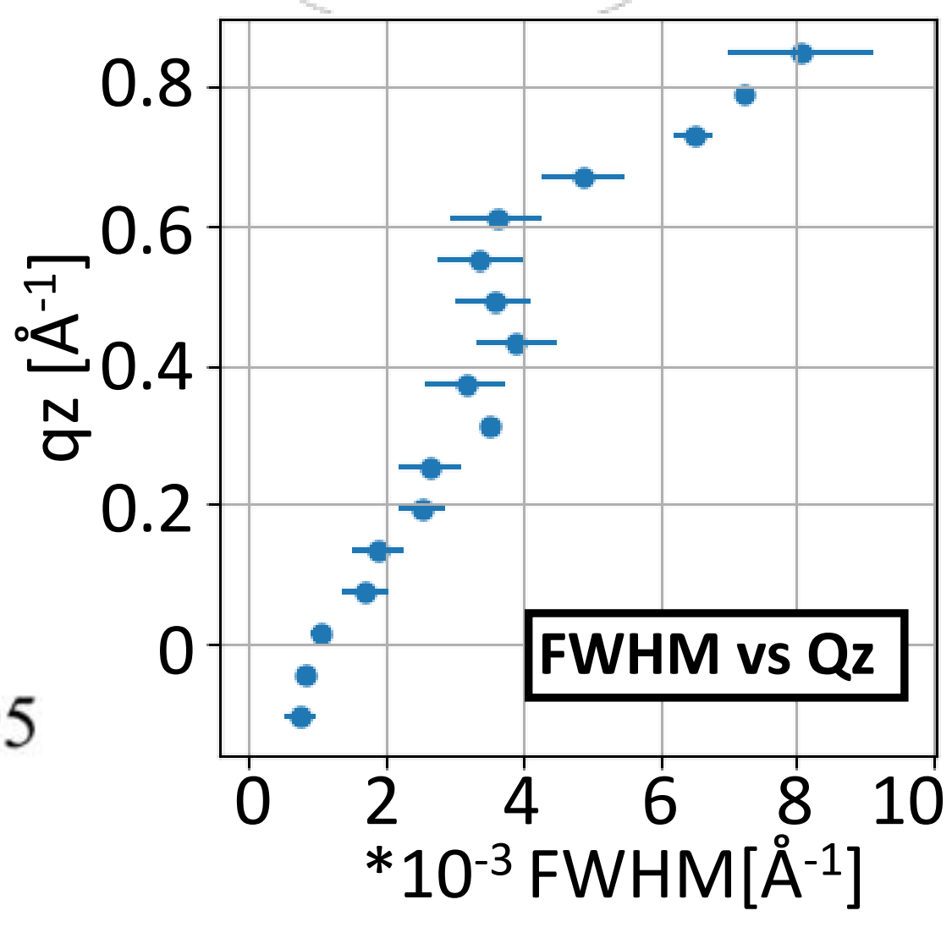
In-plane atomic-order

The GIXD technique was used to detect the diffraction signal of the graphene lattice. The lattice parameter was calculated to 2.4603 ± 0.0005 Å. The low broadening of the Bragg rod intensity with the q_z increase (lower than the one of free standing graphene**) suggests that the graphene is extremely flat on the surface of the metal.

**The orange lines in {01} are the broadening of the signal for the free standing graphene[6]





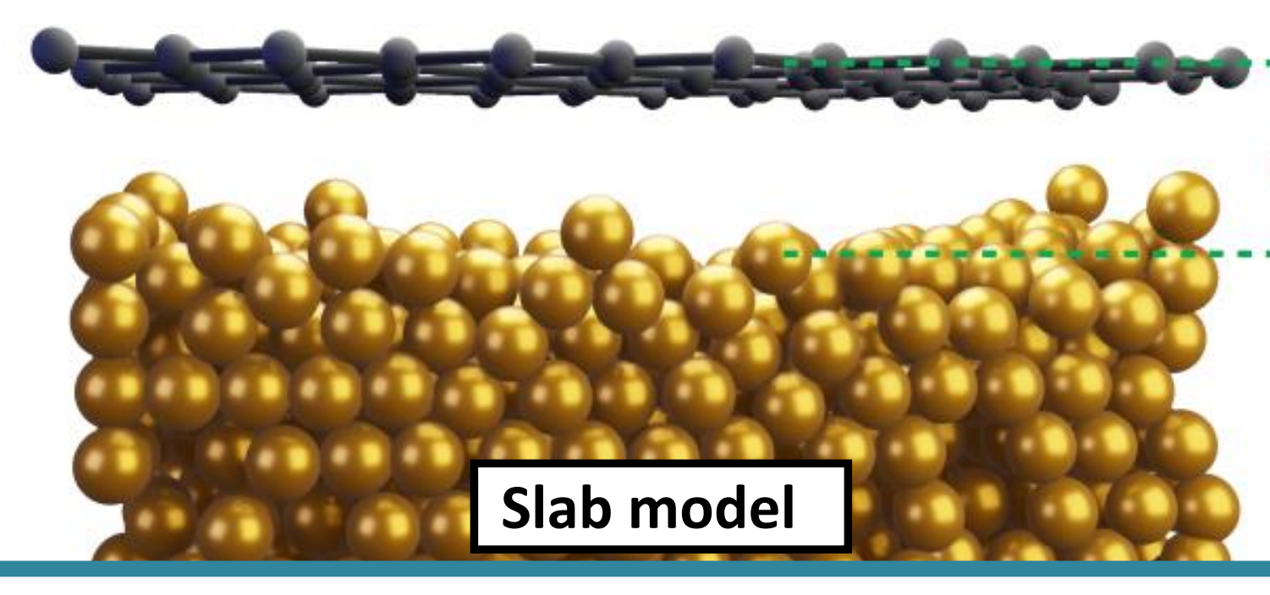


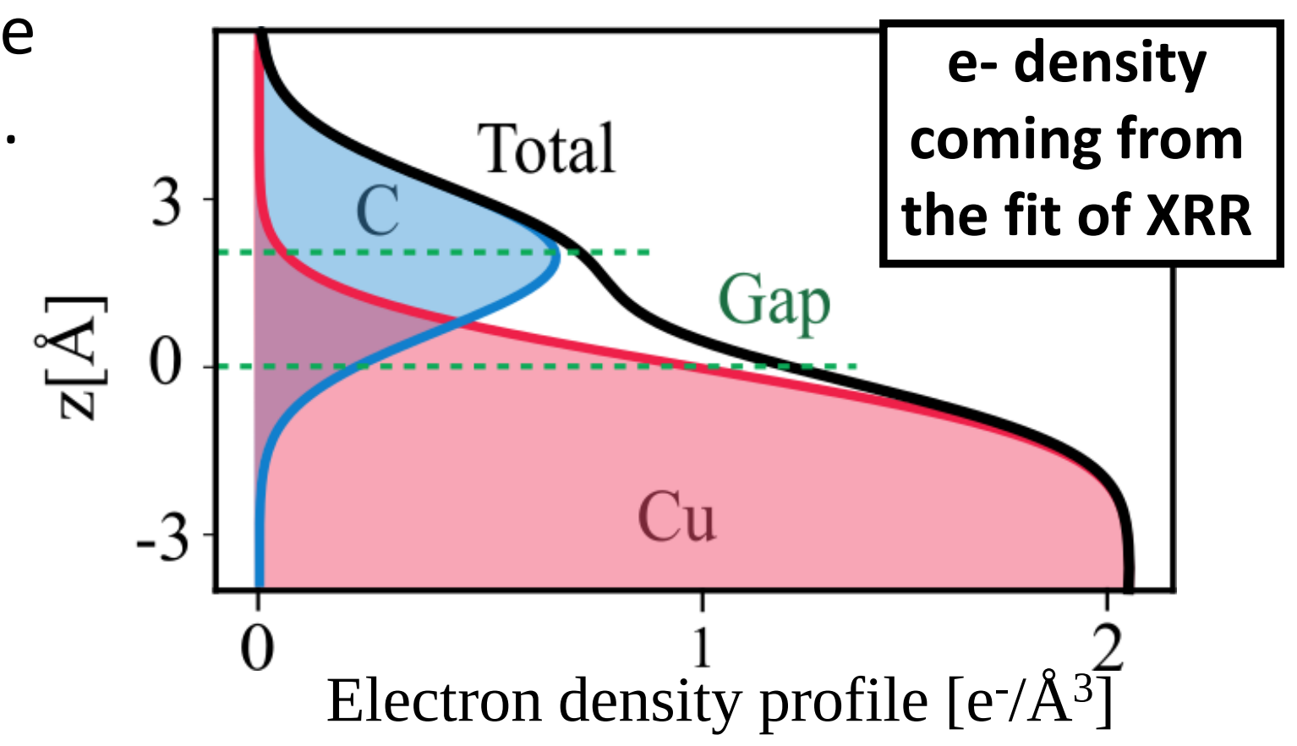
Out of plane electron density

The x-ray reflectivity technique allows measuring the electron density perpendicular to the surface plane. The data were fit with the slab model shown in the figure. In this model, every layer is an error function, the σ of the function gives the roughness. The parameters and the results of the fit are:

Gap	Cu roughness	C roughness
1.89 Å	1.06 Å	1.28 Å

From the value of the Gap, it is possible to derive the Cu-C average distance (Van der Waals gap) of 3.24 Å.





Conclusions

For the first time, the CVD growth of graphene on liquid metal was characterized *in-situ* with X-rays and optical techniques

The optical microscope is a cheap and powerful tool to control the growth

The x-ray techniques prove that the grown graphene is atomically thick and it is flat on the liquid

CONTACT PERSON

E-mail	francesco.la-porta@esrf.fr
Linkedin	linkedin.com/in/francescolaporta
Research gate	https://www.researchgate.net/profile/Francesco_La_Porta

REFERENCES

[1] Seah, C. M., Chai, S. P., & Mohamed, A. R. (2014). Mechanisms of graphene growth by chemical vapour deposition on transition metals. *Carbon*, *70*, 1-21.

[2] Liu, J., & Fu, L. (2019). Controllable growth of graphene on liquid surfaces. *Advanced Materials*, *31*(9), 1800690

[3] Cingolani, J. S., Deimel, M., Köcher, S., Scheurer, C., Reuter, K., & Andersen, M. (2020). Interface between graphene and liquid Cu from molecular dynamics simulations. *The Journal of Chemical Physics*, *153*(7), 074702.

[4] Saedi, M., de Voogd, J. M., Sjardin, A., Manikas, A., Galiotis, C., Jankowski, M., ... & Groot, I. M. N. (2020). Development of a reactor for the in situ monitoring of 2D materials growth on liquid metal catalysts, using synchrotron x-ray scattering, Raman spectroscopy, and optical microscopy. *Review of Scientific Instruments*, *91*(1), 013907.

[5] Terasawa, T. O., & Saiki, K. (2015). Radiation-mode optical microscopy on the growth of graphene. *Nature communications*, *6*(1), 1-6.

[6] Meyer, J. C., Geim, A. K., Katsnelson, M. I., Novoselov, K. S., Booth, T. J., & Roth, S. (2007). The structure of suspended graphene sheets. *Nature*, *446*(7131)

Graphene online 2020