Experimental Report

Proposal title: Strain, nanorippling, and commensurability of graphene on iridium: SXRD at the atomic scale and at the nanometer scale (super-crystallography)

Beamline: IF-INS

Number of shifts: 18

Local Contact: Gilles Renaud

Objective & expected results:
We planned to investigate the structure of graphene, an atomically thin layer of carbon atoms arranged into a honeycomb lattice, prepared by chemical vapour deposition on an iridium substrate. This model system, which can be prepared with high structural quality under ultra-high vacuum, is a playground for exploring the properties of quasi-freestanding graphene with the help of surface science techniques. It exhibits many of the features which make graphene such an interesting and rich system for basic research studies, including a complex structure resulting from the interaction with a substrate. Determining the nature of the epitaxy of graphene on its substrate, how this varies with sample temperature, and whether the thermal expansion coefficient of graphene on a substrate follows the behaviour predicted by theory, were the main objectives of our beamtime.

For this purpose we performed temperature-dependent grazing incidence X-ray scattering, exploring the structure in and out of the plane of the sample surface, in situ, in the same ultra-high vacuum environment where the samples were prepared.

Results and the conclusions of the study:

The experiments were especially successful and the results have been partly analysed thus far. Part of them have been published (Phys. Rev. B 86, 235439), another part of them is the matter of a second manuscript which will be submitted soon (F. Jean *et al*. "Commensurabilities and thermal expansion of graphene on iridium for different preparation conditions"). The last part of the results, dealing with the out-of-plane structure of graphene, will be analysed following the submission of this second manuscript.

We conducted grazing incidence X-ray scattering experiments in the plane of the sample surface [Ir(111)] and along crystal truncation rods of Ir(111) and of graphene rods. Graphene was prepared at various temperatures, using a methods which is well documented in the literature: (i) room temperature adsorption of ethylene on Ir(111), (ii) heating to 1473 or 1573 K, leading to the formation of graphene islands, and (iii) cracking of ethylene on the graphene-free regions at 1123, 1173, 1273 or 1373 K, until full coverage of graphene. The X-ray measurements were then performed at varying temperature, between 300 and 1100 K, upon increasing and decreasing temperature.

Here below we only discuss the results related to the X-ray measurements in the plane of the sample, which were the only one analysed thus far.

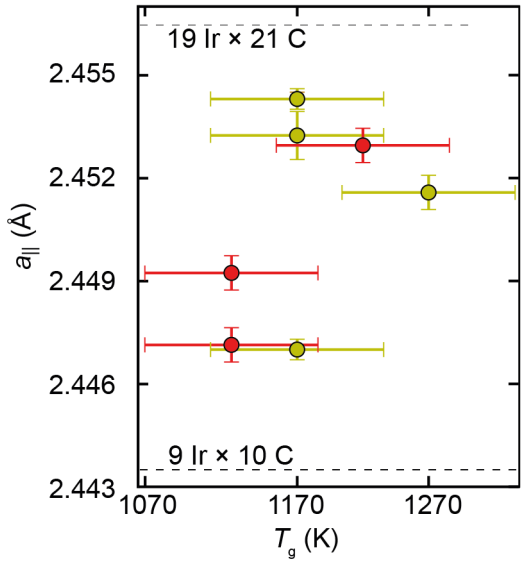

Fig. 1: *Room temperature lattice parameter in graphene on Ir(111), for different preparation temperatures. The commensurate phases between graphene and Ir(111) are marked with doted lines. Different colours indicate results obtained with different substrates [two Ir(111) single crystals were studied].*

Room temperature measurements (after growth) reveal that, depending on the preparation temperature, the lattice parameter in graphene vary by as much as 0.4% (Fig. 1). This shows that the growth temperature must be determined with great precision for determining which kind of epitaxy will graphene adopt on its substrate. The value of the lattice parameter does not however match with any commensurate structure with the substrate, at variance with the situation in another, related system, graphene/Ru(0001). This difference is interpreted as the result of a graphene-metal interaction which differs in strength from one system to the other. Actually, this should be correlated to another observation which we made on graphene/Ir(111): the graphene peaks have a certain width, which increases with the diffraction order, which points to a distribution of lattice parameters in graphene, with a typical lengthscale comparable to the width of the substrate terraces. Complementary electron diffraction measurements indicate that these spatial variations of the structure should be interpreted as follows: graphene adopts a series of commensurate structure with its substrate as a function of graphene coverage, and the mismatch in thermal expansion coefficient of graphene and Ir results in a partial loss of this commensurability. Those graphene regions which are close to the substrate edges, where the graphene-Ir is stronger, are pinned and forced to adopt a large ca. 5 nm commensurability, and discommensurations develop upon cool down in between two steps of the substrate.

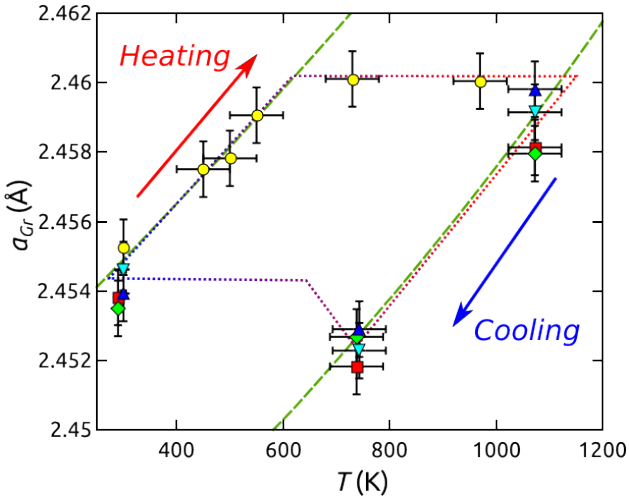

Fig. 2: *Lattice parameter in graphene on Ir(111) as a function of the sample temperature. Different colours indicate the results for different samples.*

Temperature-dependent measurements of the lattice parameter of graphene reveal a hysteresis (Fig. 2) related to the formation and suppression of linear delaminations, so-called wrinkles. These form and disappear in reason of the mismatch in thermal expansion coefficient between graphene and Ir. At high temperature, a commensurate phase with 9 Ir atoms matching 10 C rings is observed: upon cool down the graphene thermal expansion coefficient follows that of Ir, presumably in order to preserve this commensurability which maximizes the number of C-Ir bonds thus stabilizing the system. This holds until the lattice parameter stops decreasing, presumably due to the formation of the wrinkles, whose energetic cost must be smaller than the elastic energy to be paid in order for graphene to further follow the thermal contraction of Ir. We find that contrary to the predictions for isolated graphene, the thermal expansion of graphene on Ir is not negative, but rather positive and to a large extend governed by that of Ir.

Justification and comments about the use of beam time:

The experiments which we have been performing require extreme resolution in reciprocal space in order to make out distinct commensurabilities or incommensurability. The use of ultra-high vacuum for in situ preparation of the samples, together with high counting rates associated to the low scattering power of carbon, makes the experiments especially time consuming and require a large number of shifts. As X-ray scattering performed in these conditions is probably the only technique liable to provide such accurate measurement, the effort in these experiment are justified. A large number of shifts (here 18) are required for extensive and reliable characterizations.

Publication(s):

- N. Blanc, J. Coraux, C. Vo-Van, A. T. N'Diaye, O. Geaymond, G. Renaud. “Local deformations and incommensurability in high-quality graphene on a weakly interacting transition metal” Phys. Rev. B 86, 235439 (2013)

- N. Blanc, F. Jean, A. Krasheninnikov, G. Renaud, J. Coraux. “Strains induced by point defects in graphene on a metal”, submitted

- F. Jean, T. Zhou, N. Blanc, J. Coraux, G. Renaud. “Commensurabilities and thermal expansion of graphene on iridium for different preparation conditions”, in preparation