



	Experiment title: Growth kinetics of graphene from C ₆₀ investigated by grazing incidence XRD and anti-Bragg specular reflectivity	Experiment number: 25-02-935
Beamline: BM25 Spline	Date of experiment: from: 09.05.2018 to: 16.05.2018	Date of report:
Shifts: 21	Local contact(s): Juan Rubio Zuazo	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Gonzalo Santoro ^{*1} , Jon Azpeitia ^{*1} , Shun Yu ^{*2} , María Francisca López ¹ , José Ángel Martín-Gago ¹ , Carmen Munuera ¹ . ¹ <i>Instituto de Ciencia de Materiales de Madrid (ICMM), Consejo superior de Investigaciones Científicas (CSIC), c/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain.</i> ² <i>Department of Material and Environmental Chemistry (MMK), Stockholm University, Svante Arrhenius väg 16 C, 106 91 Stockholm, Sweden.</i>		

Report:

The proposed experiments considered performing Surface X-ray Diffraction during the growth of graphene using C₆₀ as precursors in ultra-high vacuum (UHV) conditions. The experiment design was based on our paper Azpeitia *et al. Carbon*, 119 (2017) 535, in which we have demonstrated the propitiousness of this method for graphene growth on Cu foils. In addition, the C₆₀ precursor fits neatly with the quality demands of graphene for applications since C₆₀ is only comprised of carbon; thus, no elemental impurities are incorporated in graphene.

Nevertheless, though the graphene growth method has been already established by us, there are still some unknown phenomena concerning the growth kinetics which we tried to elucidate during our beamtime. In detail, DFT simulations suggest both the creation of vacancies at the Cu(111) and Cu(100) surfaces by the C₆₀ deposition (in a similar way as it occurs for the Pt(111) surface – see: Felici *et al. Nat. Mater.*, 4 (2005), 688) as well as an interaction of graphene with the underlying Cu surface. This last interaction leads to changes in the surface atomic positions. For these experiments we planned to perform the C₆₀ deposition with the substrate at 1100 K since it is known that this increases the graphene quality. Additionally, it is believed that, when the growth of graphene is through the deposition of C₆₀ on the surface at room temperature plus a subsequent annealing at 1100K, only one monolayer of C₆₀ remains adsorbed on the surface and that is the Cu catalytic activity on this monolayer which is responsible for graphene growth. Therefore, in our proposal we aimed at elucidating, on the one hand, the changes on the Cu(111) and Cu(100) surfaces *in situ* while growing graphene and, on the other hand, to follow the C₆₀ adsorption and desorption kinetics (by following the specular intensity at the anti-Bragg geometry of the C₆₀(111) peak) and to correlate it with the graphene surface (11) diffraction peak.

Although, we could measure the crystal truncation rods of the bare substrates – see Figure 1 for some exemplary results of Cu (111) –, we have faced several problems during the beamtime. First, the increased substrate to evaporator distance of the C60 evaporator in the UHV chamber at Spline (around 400 mm) in comparison to the distance we use in our labs (around 100 mm) diminished tremendously the deposition rate. Thus, we had to perform a minimum of 4 hour deposition whilst in our lab it only takes 30 min. We were following the deposition of C60 through the so-called growth oscillations in anti-Bragg geometry (see Fig. 2, left) and in 4 hours not even 5 monolayers of C60 were deposited. This implied that for the graphene growth at a substrate temperature of 1100K – which we checked by LEED (Fig 2., right) – we had to keep the Cu surface at 1100 K for 4 hours, which resulted in diminishing the surface quality so that the CTRs could not be measured after graphene growth (4 hours at 1100 K was simply too much). Additionally, the power supply used at the beamline for sample heating was damaged by a current peak (we kept the power supply at 4.1 A during the complete deposition but at some moment the 8A fuses were blown); thus, we were forced to use the same power supply for substrate heating and C60 evaporation. This resulted in just trying to perform the second part of the proposal, namely, C60 adsorption/desorption kinetics by depositing on the substrate at room temperature, for which we used a Cu(100) single crystal.

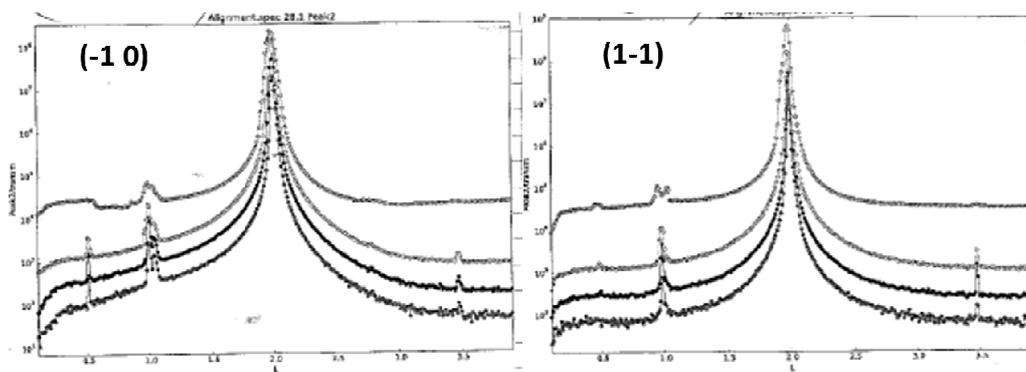


Figure 1. Exemplary results of the measured CTRs for Cu(111).

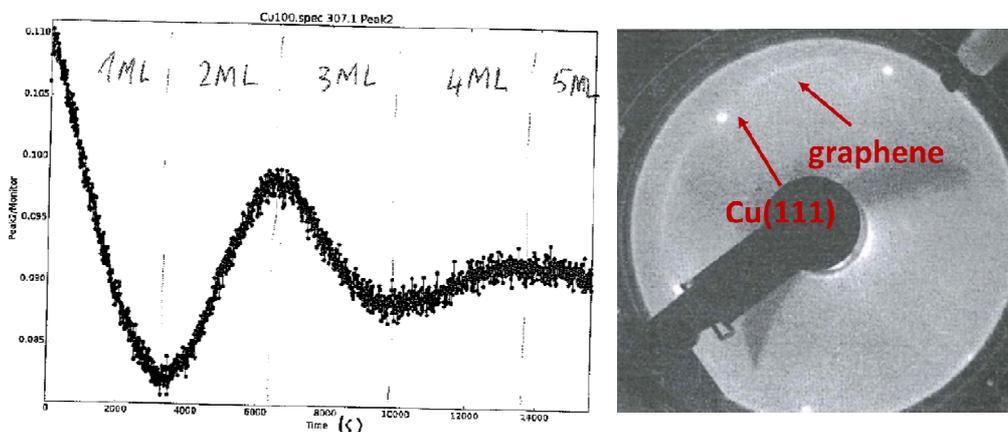


Figure 2. (left) C60 growth oscillations at the anti-Bragg geometry of the C60(111) peak. (right) LEED of graphene on Cu(111).

We were able to follow the C60 adsorption in real time but the desorption was too fast to be followed with the photon flux at BM25. This could have been somehow measured if a slow temperature ramp could have been applied to the substrate, but a PID temperature controller is not available at the beamline for sample heating. Moreover, in this case, we didn't succeed in growing graphene in the few shifts that were left before the beamtime was over.

Overall, the beamtime has not been successful due to the technical problems experienced both from our side (a closer evaporator-to-substrate distance was mandatory although we oversighted this) and from the beamline (there were no replacement fuses for the power supply). Anyway, the beamline support has been very good and we acknowledge the beamline staff help during the experiments.