Experimental report on proposal HC-1440 (mp Dr. Nikolay VINOGRADOV), ID03

“In situ study of the formation and structural evolution of graphene/Fe systems”

The growth of high structural quality graphene on metal surfaces by chemical vapor deposition (CVD) is an extensively studied process, since it is considered to be most industry-compatible. Amongst the other suitable substrates for CVD growth of graphene the (110) face of iron was reported recently [1]. Compared to the other substrates used for CVD growth of graphene, Fe(110) has a number of advantages, which are low cost of iron and high degree of structural perfectness of graphene/Fe(110). The essential drawbacks of using iron substrate are high reactivity of iron, its propensity to carbide formation and extremely high solubility and diffusion rate of carbon in iron. In particular, the latter can lead to a segregation of carbon from iron sub-surface region or dissolution of graphene in iron during the CVD reaction and deteriorate the structural quality of the resultant graphene overlayer significantly.

Therefore, the aims of the experiment were: firstly, to study the thermal stability of graphene layer on iron. We focused on observing graphene dissolution in iron at elevated temperatures and on the possibility for graphene segregation from the iron substrate, in the CVD conditions and in the ultra-high vacuum (UHV). Secondly, it was shown, that graphene/Fe(110) forms a very particular 17/18 x 7/6 superstructure (17x7 in graphene unit cell vectors, or 18x6 in Fe(110) unit cell vectors) [1]. The scanning tunneling microscopy (STM) and the density functional theory (DFT) studies, performed in Ref. 1, have revealed a strong corrugation of graphene layer. However, despite the qualitative agreement of the STM and the DFT data in Ref. 1, the exact structure and the corrugation amplitude of the graphene overlayer in graphene/Fe(110) are still to be confirmed. Therefore, we intended to clarify the graphene/Fe(110) structure using surface X-ray diffraction (SXRD) proven efficient for determination of graphene/Ru(0001) structure [2,3].

Two graphene/Fe(110) samples were prepared independently in a standalone UHV system (base pressure 5×10^{-10} mbar), according to the recipe reported [1]. W(110) single-crystal substrates were cleaned by cycles of flashing to ~1800°C and oxygen treatment at ~1200°C and oxygen partial pressure of 1×10^{-6} mbar. The cleanliness of the substrates was verified by low-energy electron diffraction and X-ray photoelectron spectroscopy apparatus mounted on the chamber. Then, around 150 monolayers of iron were deposited on the substrate by electron bombardment of an iron rod, at room temperature, followed by annealing to 500°C. The precise thickness of the iron film was determined post-factum using the SXRD data. Then the samples were annealed to ~600°C and 1-2×10^{-6} mbar of ethylene (C_2H_4) were introduced in the chamber, followed by cooling the sample to 500°C in 10 min. The quality of the resultant samples was controlled by LEED and XPS,

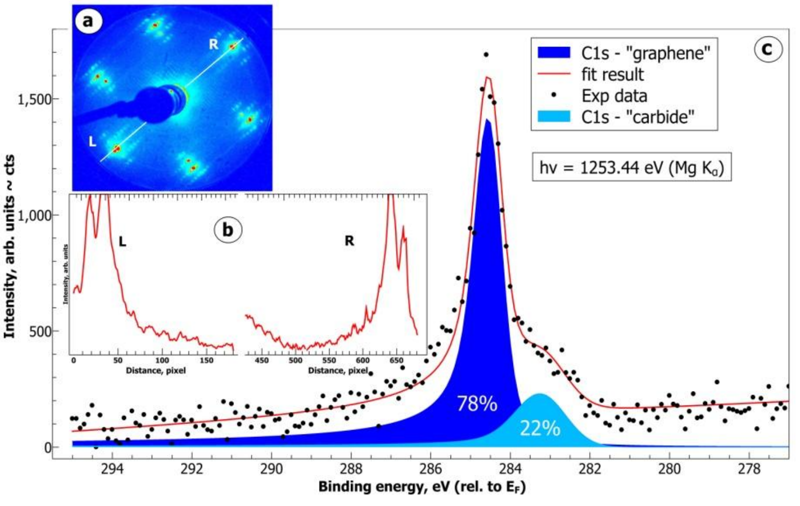

Fig. 1
Main panel (c): XPS study of graphene/Fe/W(110) sample. In white are shown contributions from “graphene” and “carbide” phases, derived from the fit. Insets: (a) – LEED pattern from graphene/Fe/W(110), electron energy is 76 eV; (b) – intensity profile in (a) along the white line.

as shown in Fig. 1. The samples were then transferred to the diffractometer vacuum chamber (base pressure 1x10^{-10} mbar) using a portable vacuum chamber (base pressure 3x10^{-9} mbar). No further treatment was performed prior to the SXRD measurements of these pristine samples.

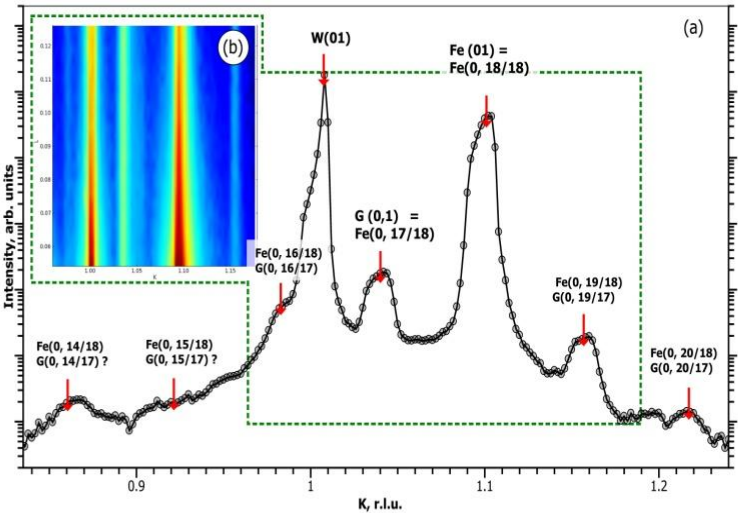

Fig. 2
(a) K-scan (in the chosen frame scan along [1-1 0] crystallographic direction) of pristine graphene/Fe/W(110). Inset (b) is a projection of enframed-green scan area on the H-axis of the reciprocal lattice, with clearly visible CTRs.

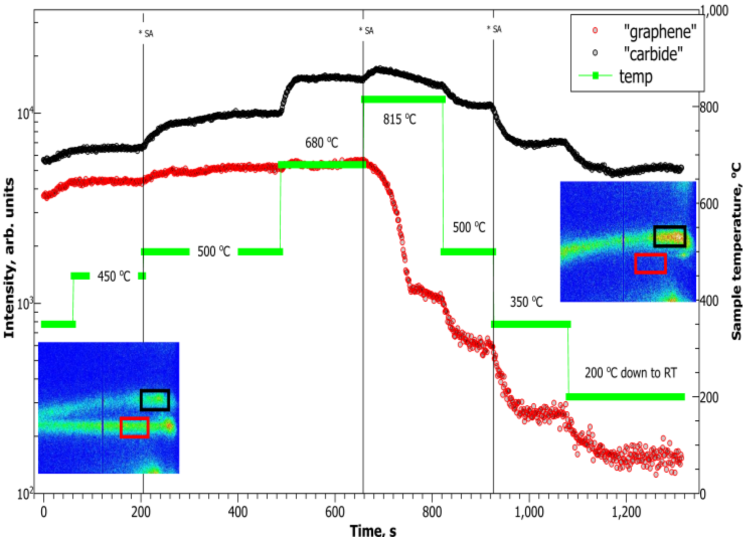

Fig. 3
The intensity variation of Fe carbide-related powder ring (black) and graphene (0,1) CTR (red) upon annealing of C-saturated Fe film in UHV. The insets in left and right of the Figure are the detector images in the beginning and in the end of the process, respectively.

From the analysis of the intensity oscillations in the measured specular (0, 0) crystal truncation rod (CTR) the thicknesses of the Fe films was determined as (164±1)ML and (150±1)ML, respectively. Both samples were extensively characterized by SXRD, and the positions of the principal reflexes (W, Fe) as those of the satellite peaks (graphene, graphene/Fe superstructure) were determined, as shown, e.g. in Fig. 2. The thermal stability of the sample and the evolution of its structure were assessed by measuring a set of CTRs for W, Fe, and graphene, after each annealing step. The process of graphene dissolution and graphene-to-carbide transformation was monitored in situ, by recording diffraction intensity in the proximity of graphene (0,1) CTR, as demonstrated in Fig. 3. The drastic intensity interplay of the observed features, attributed to graphene (0,1) CTR and Fe carbide powder ring was observed at 800 °C, in both UHV and presence of ethylene. This was interpreted as graphene dissolution and formation of Fe carbide grains.

The structure factors were obtained from the recorded diffraction intensities using two independent approaches: the explicit integration of the detector images with corresponding corrections, and integration of the intensities in the reciprocal space. Information on the actual graphene corrugation structure and related to it Fe lattice perturbation, alloying on the Fe/W(110) interface, as well as evaluation of the carbide phases, will be obtained through a detailed data analysis which is in progress. The latter is hindered by the structural complexity and fast evolution of the system under investigation.

References:

[1] N.A. Vinogradov, A.A. Zakharov, V. Kocevski *et al.,* Phys. Rev. Lett. **109**, 026101 (2012)
[2] D. Martoccia, M. Björck, C.M. Schlepütz *et al.,* New J. Phys. **12**, 043028 (2010)
[3] D. Martoccia, P.R. Wilmott, T. Brugger *et al.,* Phys. Rev. Lett. **101**, 126102 (2008)