Cathode lens spectro-microscopy of the graphene-metal interface: film-substrate interactions, buffer layers and trapped species

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The interest stimulated by the discovery of graphene's unique electronic properties has motivated a large number of studies aiming at the characterization of graphene epilayers on a variety of transition metals and SiC supports. On the experimental side, cathode lens microscopy with low energy electrons (LEEM) has been widely employed to study dynamical processes in such model systems [1,2]. These investigations delivered a wealth of information on film morphology and crystal structure, disclosing also the mechanisms of graphene nucleation and growth. The parallel use of synchrotron-based microscopy methods allowed researchers to map the interface chemistry and film electronic structure with nanometer resolution. In my talk, I will illustrate the present capabilities of energy-filtered photo-emission electron microscopy (XPEEM) applied to graphene research, focusing on the characterization of complex, laterally inhomogeneous, graphene-metal interfaces by means of laterally resolved photoelectron spectroscopy and microprobe angle resolved photoelectron spectroscopy (μ-ARPES).

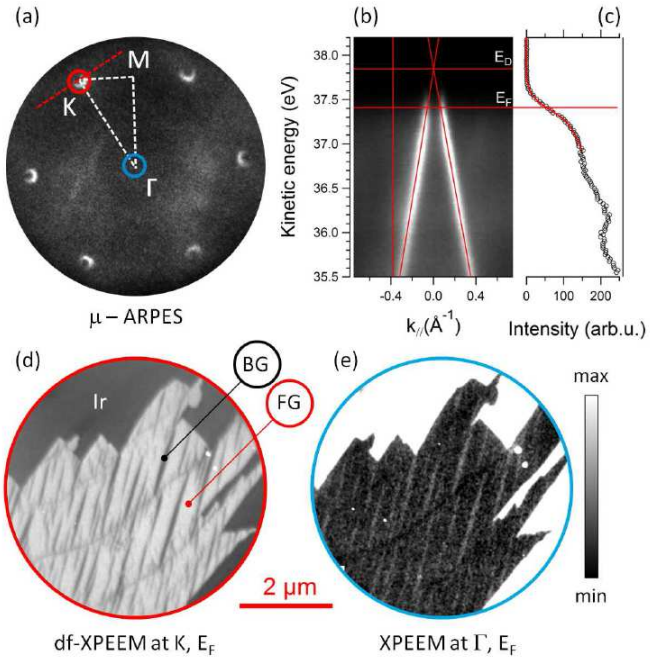

Figure 1: Microprobe ARPES map of flat graphene (FG) on Ir(100) and (b,c) cross section through one of the Dirac cones. (d) Dark-field PEEM image, obtained at the K point, demonstrating the higher DOS of FG with respect to that of BG; (e) inversion of contrast in the PEEM image at the Γ reveals hybridization with Ir states in BG. Reprinted with permission from [2].

In the past years, graphene on metals has evolved into a paradigm for understanding how the substrate interactions influence the electronic properties of two-dimensional sp^2-hybridized atomic networks. Nonetheless, the properties of graphene on crystal faces showing different symmetry than the threefold are still largely un-explored. In the first part of my presentation, I will focus on the unusual properties of graphene grown on a square lattice support, Ir(100) [3,4]. Here, distinct physic-sorbed and chemisorbed graphene phases are found to coexist below 500°C, characterized by flat and buckled morphology, respectively. Notably, the relative abundance of physisorbed and chemisorbed gra-phene can be tuned by simply varying the sample temperature. Such process is reversible and occurs via the formation and rupture of a small fraction of chemisorption bonds, which is found to profoundly

alter the local electronic structure, the graphene's density of states changing from semi-metal to metallic type (see Figure 1). Such behavior can be permanently modified by depositing Au atoms, which intercalate and organize into a buffer layer that restores graphene's free-standing behavior already at room temperature [5]. As I will show, graphene/Ni(111) provides yet another remarkable example of a model system where the electronic properties can be tuned by temperature. In this case, however, the reversible interposition of a buffer between graphene and the substrate is obtained "from below", through the formation or dissolution of a nickel-carbide layer at the interface between Ni and rotated graphene domains [6].

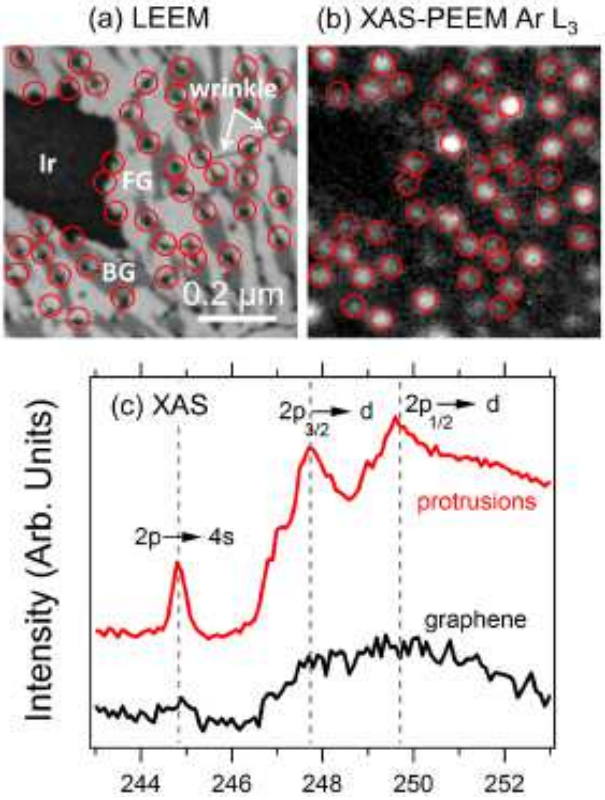

Figure 2: room temperature LEEM image of a graphene flake after Ar ion irradiation and subsequent annealing to 1050°C; the black dots correspond to Ar nanobubbles under graphene (b) XAS-PEEM image of the same region. The intensity of the resulting image is proportional to the Ar concentration, with the bright regions corresponding to Ar clusters. (c) Spectra obtained from inside and outside the spots in graphene.

The final part of my talk will be dedicated to the irradiation of graphene with low energy ions, reporting on the formation of Ar nanobubbles upon sample annealing [7]. Such structures display a lateral size up to tens of nanometers (see Figure 2) and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Most interestingly, ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion. Nanobubble ripening seems to be a general phenomenon, which can be exploited to "strain-engineer" the properties of graphene.

References:

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