

Electronic structure and imaging contrast of graphene moire on metals: combined STM/AFM/Kelvin-probe and DFT studies

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Graphene layer on metal surfaces have been attracting the attention of scientists since several decades, starting from middle of the 60s, when catalytic properties of the close-packed surfaces of transition metals were in the focus of the surface science research [1,2]. The recent demonstration of the fascinating electronic properties of the free-standing graphene renewed the interest in the graphene/metal systems, which are considered as the main and the most perspective way for the large-scale preparation of high-quality graphene layers with controllable properties. For this purpose single-crystalline as well as polycrystalline substrates of $3d - 5d$ metals can be used. One of the particularly exciting questions concerning the graphene/metal interface is the origin of the bonding mechanism in such systems [2-4]. This graphene-metal puzzle is valid for both cases: graphene adsorption on metallic surfaces as well as for the opposite situation of the metal deposition on the free-standing or substrate-supported graphene. In the last case the close-packed surfaces of $4d$ and $5d$ metals are often used as substrates. A graphene layer prepared on such surfaces, i. e. Ru(0001), Rh(111), Ir(111), or Pt(111), forms so-called moire structures due to the relatively large lattice mismatch between graphene and metal substrates. As a consequence of the lattice mismatch the interaction strength between graphene and the metallic substrate is spatially modulated leading to the spatially periodic electronic structure. Such lateral graphene superlattices are known to exhibit selective adsorption for organic molecules or metal clusters. Especially, the adsorption of different metals - Ir, Ru, Au, or Pt - on graphene/Ir(111) has been intensively studied showing a preferential nucleation around the so-called FCC or HCP high-symmetry positions within the moire unit cell [5], which was explained via local sp^2 to sp^3 rehybridization of carbon atoms with the bond formation between graphene and the cluster. However, a fully consistent description of the local electronic structure of graphene/Ir(111), the observed imaging contrast in scanning probe experiments and the bonding mechanism of molecules or clusters on it is still lacking, motivating the present research. Here we present the systematic studies of a graphene layer on different lattice mismatched surfaces [Ru(0001), Rh(111), and Ir(111)] with the focus

on the graphene/Ir(111) system [6]. This research was performed via a combination of the density functional theory (DFT) calculations, low-energy electron diffraction, angle-resolved photoelectron spectroscopy (ARPES), and scanning tunneling and atomic force microscopy (STM and AFM) as well as Kelvin-probe techniques. The microscopy experiments were performed in constant current / constant frequency shift (CC/CFS) and constant height (CH) modes (combination of SPECS SPM Aarhus 150 and KolibriSensor). ARPES data clearly demonstrate a free-standing-like character of the electronic states of graphene in this system. Our further results obtained via combination of DFT calculations and scanning probe microscopy imaging allow to discriminate the topographic and electronic contributions in these measurements and to explain the observed contrast features. We found that in STM imaging the electronic contribution is prevailing compared to the topographic one and the inversion of the contrast can be assigned to the particular features in the electronic structure of graphene on Ir(111). Contrast changes observed in constant height AFM measurements are analyzed on the basis of the energy, force, and frequency shift curves, obtained in DFT calculations, reflecting the interaction of the W-tip with the surface and are attributed to the difference in the height and the different interaction strength for high-symmetry sites within the moire unit cell of graphene on Ir(111). The presented findings are of general importance for the understanding of the properties of the lattice-mismatched graphene/metal systems especially with regard to possible applications as templates for molecules or clusters.

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