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Electronic structure of graphene on Ni surfaces with different orientation

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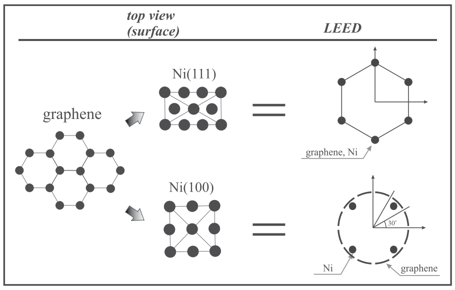
HIGHLIGHTS

- Graphene on Ni(111) is well-ordered, whereas on Ni(100) – multi-domain.
- Graphene on Ni(111) and Ni(100) is strongly bonded with substrate.
- Intercalation of Au atoms restores the linearity in dispersion and makes graphene quasi-free on both Ni(100) and Ni(111).

GRAPHICAL ABSTRACT



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ABSTRACT

An experimental study of the graphene, synthesized by propylene cracking on Ni surfaces with different orientation: (100) and (111), using angle-resolved photoemission, has been performed. It has been shown that graphene on Ni(111) had a perfect lateral structure due to consistency of their lattices, whereas graphene/Ni(100) consisted of a lot of domains. For both systems electronic structure was quite similar and demonstrated a strong bonding of graphene to the underlying Ni surface. After Au intercalation the electronic structure of graphene in both systems was shifted to the Fermi level and became linear in the vicinity of the **K** point of the Brillouin zone.

1. Introduction

Graphene and graphene-based systems remain one of the most attractive fields for scientists even ten years after the first publications [1]. Its unique electronic properties are due to massless Dirac fermions – the charge carriers that exhibit linear dispersion at the corners of the surface Brillouin zone (SBZ) of graphene which are denoted as **K** and **K**$'$ points. Cones of π and π^* states of graphene touch each other only in one point and this point is exactly at the Fermi level in freestanding graphene. Linear character of the π band in the vicinity of **K** and **K**$'$ points leads to such properties as ultra-high mobility of charge carriers and zero effective mass of the Dirac fermions [1–3]. However the contact with a substrate can significantly distort the electronic structure of graphene. Resulting distortions depend on the strength of chemical interaction between graphene and the substrate, on symmetry properties of the

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interface between them and on electronic structure of the substrate. As a result, charge doping, energy gap between the Dirac cones of π and π* states or a distortion of linearity in the dispersion of graphene π states may occur. Avoid-crossing effects may lead to an appearance of local band gaps in the dispersion of the π states [4–10].

There are a lot of methods for graphene synthesis, such as thermal graphitization of the surface of silicon carbide [11,12], cracking of carbonaceous gases on the surface of single-crystals and single-crystal films of transition metals [10,13–16] and segregation of carbon atoms through Ni film [17,18]. The second method is advantageous as the cracking reaction is a catalytic one and it goes on only till the formation of one graphene monolayer. However, despite the perfect crystalline quality of graphene obtained by these methods, the substrate strongly influences the graphene electronic structure. In some systems (graphene on the surface of Ni, Co, etc.) this results in a significant shift of graphene π and σ states and a distortion of the linearity of dispersion of π states [14,19]; in other cases [20] it may lead to a shift of the Fermi level and a partial filling of unoccupied π* states. Intercalation of different metals underneath a monolayer graphene (MG) can significantly reduce its interaction with a substrate and restore the electronic structure similar to the one characteristic of the quasi-freestanding graphene [9,19]. For instance, intercalation of Au underneath graphene on Ni(111) removes the energy shift of valence graphene states and restores the linear character of π states in the region of **K** point of the SBZ [19,21]. Intercalation of other metals, Ag and Cu, also blocks the strong covalent interaction of graphene with Ni substrate and restores the linearity of π states [9,13,22,23]. However small energy shift of the Dirac point (the point of graphene π and π* states crossing) towards high binding energies remains in these systems and a band gap is still visible.

Our recent investigations [9,24] showed that graphene synthesized on Ni(111) by cracking of propylene with subsequent intercalation of Au underneath the synthesized graphene monolayer is characterized by features of the electronic structure characteristic of quasifreestanding graphene.

The aim of this work is to compare the electronic structure of a graphene monolayer synthesized on different crystal surfaces of Ni: Ni(111) and Ni(100), – with subsequent intercalation of Au.

2. Experimental details

The experimental studies were performed on the Russian-German beamline (RGBL) at BESSY-II synchrotron center (Helmholtz-Zentrum, Berlin) and on the Research modular platform Nanolab at the Resource Center “Physical Methods of Surface Investigation” (RC PMSI) of Research park of Saint Petersburg State University.

Electronic structure after the synthesis was performed using angle resolved photoemission spectroscopy (ARPES). Information about the crystalline structure was obtained using Low Energy Electron Diffraction (LEED).

All measurements were performed *in situ*, the base pressure in the analytical chamber during experiments was maintained at a level of 2×10^{-10} mbar. The spectra of valence states were measured at a photon energy $h\upsilon = 40–62$ eV at room temperature with hemispherical electron energy analyzers (Scienta R4000, SPECS Phoibos 150).

The Ni(111) substrate was prepared as a Ni film on top of a W(110) single-crystal. W(110) surface was initially prepared in accordance to standard procedure which includes repeated annealing of the W surface in oxygen (partial pressure of 5×10^{-8} mbar, 1250 °C) and subsequent flashing to high temperature (1650–1800 °C) in UHV conditions. High quality Ni(111) film was afterwards prepared by deposition of ~100 Å of Ni on W(110) at room temperature with the deposition rate of 1–1.5 Å/min. The thickness was calibrated by a quartz microbalance. The graphene monolayer was synthesized on Ni(111) by cracking of propylene (C_3H_6) at a partial pressure 1×10^{-6} mbar and the sample held at the temperature of 500 °C for 5 min [14,25].

Single-crystal Ni(100) was used as a second sample for graphene synthesis. Clean Ni surface was obtained after repeated cycles of annealing in O_2 and flash-heating. The quality of Ni(100) surface was examined by LEED. Graphene was synthesized by propylene cracking: at a pressure of 3×10^{-6} mbar the sample was heated up to $T = 570$ °C for 15 min with subsequent annealing at the same temperature in UHV.

Intercalation of Au atoms underneath the graphene on Ni(111) and Ni(100) was provided by thermal annealing of the system with an Au monolayer deposited upon the graphene at a temperature ~400 °C for 5 and 15 min correspondingly [26].

3. Results and discussion

Synthesis of graphene on Ni(100) is harder than for Ni(111) due to differences in crystal lattices, that leads to the increasing of the temperature and exposure time of the process. Dispersion of obtained MG/Ni(100) along the **ΓK** direction of the SBZ is presented in Fig. 1a. The π states of graphene are localized close to the SBZ **Γ** point, at binding energies of ~10 eV. As the parallel component of the momentum ($k_{||}$) increases in the **ΓK** direction, the π states shift towards lower binding energies. At $k_{||}$ ~1.7 $Å^{-1}$, which corresponds to the **K** point of the SBZ, the π states' binding energy reaches its minimum of ~2 eV. The Ni *d* states appear at 2 eV from the Fermi level.

Fig. 1b presents the dispersion of graphene synthesized by propylene cracking on the surface of a thin Ni(111) layer which was deposited on W(110). The π states of graphene close to the SBZ **Γ** point are localized at energies of ~10 eV. The Ni *d* states at 2 eV and the graphene $\sigma_{2,3}$ states, which have a binding energy of ~5 eV close to the **Γ** point, are also visible. The π states of graphene have the binding energy ~2 eV at the **K** point of the SBZ.

In both systems graphene π and σ bands are shifted by ~2 eV towards high binding energies in comparison with quasi-freestanding graphene or single-crystal graphite [19]. This indicates the strong interaction of the formed graphene with nickel substrates. The binding energy of π states of graphene on different Ni surfaces in the **Γ** point of the SBZ differs by 0.2 eV, as can be seen on Fig. 1c. We also cannot see graphene π* states that means the existence of a large gap between π and π* zones of graphene caused by the influence of the Ni substrate. Graphene π states reach Ni 3*d* states in the region of ~2 eV in the vicinity of the **K** point of the SBZ. The strong interaction causes hybridization and the π states lose the linear character characteristic to quasifreestanding graphene.

LEED pattern of graphene on the Ni(100) surface represents a segmented ring structure of apparent 12-fold symmetry concentric with the (0,0) reflection of the Ni(100) substrate [27] (Fig. 2a). These “rings” around the main reflex spots correspond to the multi-domain graphene on single-crystal of Ni(100). Similar diffraction pattern was observed for MG/Cu(100) system [28]. The other reflexes correspond to the nickel carbide interface MG/Ni(100). The graphene layer and the Ni(111) film have the same lattice parameters, so the LEED pattern of graphene on Ni(111) surface (Fig. 2b) is a hexagon with sharp intense reflexes.

However, the LEED pattern is strongly changed after the gold intercalation underneath graphene. For MG/Au/Ni(111) system (see Fig. 3b) additional reflexes appear around the main reflexes (in the vertexes of hexagon) corresponding to graphene. It evidences the formation of the superstructure (p(9 × 9)). The crystal structure of