Graphene-Metal Interactions
The case of mono- bi- and tri- graphene layers deposited on gold substrate studied by Scanning Tunneling Spectroscopy (STS) and Density Functional Theory (DFT)

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It is crucial for the future applications to understand the nanoscale electronic properties of graphene considered in terms of the electron local density of states (LDOS) on different substrates. This is because a substrate or deposited coating can considerably affect nanoscale electronic properties of graphene. Particularly, it has been proved theoretically using density functional theory (DFT) and van der Waals density functional (vdW-DF) calculations that the unique conical dispersion relation around K/K' points in graphene is preserved on (111) surfaces of Al, Cu, Ag, Pt, and Au [1-3]. However, this is accompanied with the change of position of the Dirac point (E_D) relative to the Fermi level (E_F) due to the presence of substrate (doping effect). This is especially important in the case of Au which is widely used in fabrication of metal-graphene contacts in graphene devices.

In the presentation we will show detailed scanning tunneling microscopy and spectroscopy (STM/STS) studies of graphene interactions with gold substrate. The obtained experimental results will be discussed in the frame of theoretical models. Mono-, bi- and tri- graphene layers (MG, BG, TG) were deposited on 8 nm of Au, with 0.5 nm Cr adhesion layer sputtered onto 100 nm SiO_2 (Graphene Industries, UK). This type of substrate enables to create a setup suitable for the STM/STS experiments without micro fabrication processes and studies of LDOS on multilayer graphene systems [4]. Identification of MG, BG and TG were carried out using optical microscopy (OM), Raman spectroscopy (RS) – (Renishaw InVia) and scanning electron microscopy (SEM) - (Vega Tescan). All the STM/STS experiments were carried out at room temperature in UHV condition using VT-STM/AFM microscope integrated with the XPS/UPS/AES/LEED/MULTIPROBE P system (Omicron GmbH).

The STM results show that the height of MG relative to Au substrate is close to 0.5 nm, the height of BG relative to MG varies from 0.30 nm up to 0.50 nm, while TG relative to BG gives the value 0.35-0.50 nm. The detailed STM topography of MG/Au border structure is presented in Fig.1a.The STM topographies for MG/BG/TG on Au at atomic resolution present triangular structure typical for graphite with the distance between atoms equals about 0.25 nm. We would like to emphasize that honeycomb lattice typical for unperturbed MG with the distance between atoms equal to 0.142 nm has never been observed.

The STS results prove that holes are donated by Au substrate to graphene which becomes p-type doped i.e. E_F is located below E_D. Particularly, E_D for MG is located in the range of 0.35 - 0.43 eV; for BG varies from 0.22 eV up to 0.30 eV, and for TG is close to 0.1- 0.15 eV. Estimated positions of the Dirac point show that the higher number of graphene layers the lower Fermi level shift is observed. Typical STS results for MG and TG are presented in Fig.1b,d and Fig.2b,c,d,e. Additionally the STS results show presence of energetic heterogeneity considered in terms of changes LDOS measured at different places on the surface. This is particularly well seen in the case of TG on Au – see Fig.2a,d.

Finally, graphene-gold interactions were studied using both local density approximation and van der Waals density functionals. In the LDOS profiles the Dirac points were clearly identified and compared with the positions of Dirac cones in the bandstructure. The theoretical results will be compared with experimental STM/STS data.

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References

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Figures

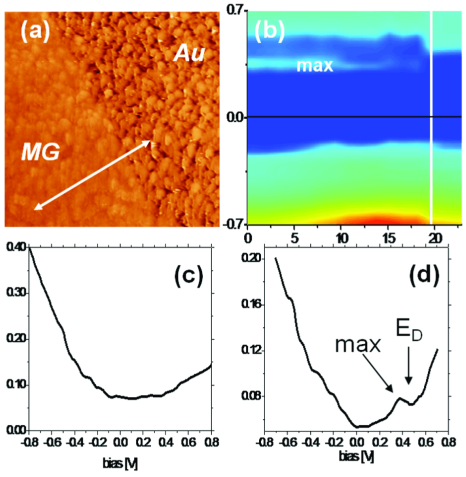

Fig.1

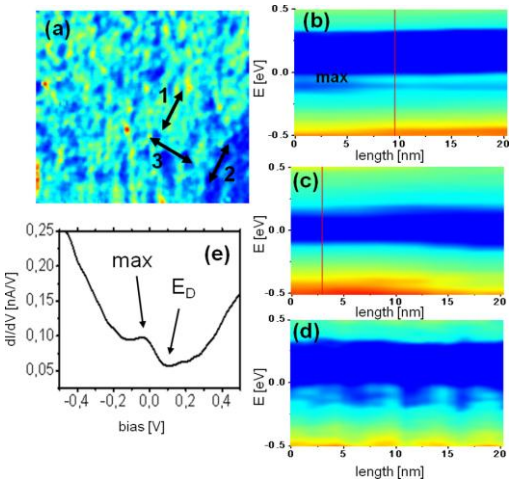

Fig.2

Fig.1 (a) 450 nm x 450 nm STM topography showing the details of MG and Au border line. (b) dI/dV (E, line) map recorded on MG/Au along arrow in figure (a). Colors: blue, green, red - low, intermediate, and high value of the LDOS, respectively. (c) dI/dV profile of Au. (d) Typical dI/dV profile of MG/Au.

Fig.2 (a) 200 nm x 200 nm dI/dV (E, x, y) map recorded at 0.05 eV on TG/Au. Colors: blue, green, red - low, intermediate, and high value of the LDOS, respectively.(b, c, d) dI/dV (E, line) maps recorded on different TG/Au regions denoted by #1, #2 and #3 lines on figure (a). (e) Typical dI/dV profile of TG/Au showing Dirac point.