

Graphene-semiconductor interfaces

Electronic structure of graphene on Ge substrates with different interlayers

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In Short

- Electronic structure of graphene
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- Doping of graphene on Ge
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Graphene, a single layer of carbon atoms arranged in a honeycomb lattice, which demonstrates many fascinating properties and attracts enormous attention in science and technology [1,2]. Its unique electronic structure in the vicinity of the Fermi level (E_F) opens wide perspectives for industrial application, like fabrication of touch screens (as a replacement for indium tin-oxide), gas sensors, high-speed transistors, etc. However, despite the recent success in studies of the fundamental properties of graphene, free-standing as well as on the different supporting substrates, and demonstration of some graphene-based devices prototypes, there is “a lack of a killer app” on the market [3].

The implementation of graphene in semiconducting technology requires precise knowledge about the graphene-semiconductor interface. In our work the structure and electronic properties of the graphene/Ge(110) interface are investigated on the local (nm) and macro (from μm to mm) scales via a combination of different microscopic and spectroscopic surface science techniques accompanied by density functional theory (DFT) calculations.

The ordering and structure of the graphene/Ge(110) interface on the nm-scale was investigated by means of STM at different bias voltages (Fig. 1). Such experiments allow the discrimination between graphene and Ge(110) contributions in the imaging and the identification of the relative alignment of atoms in the graphene layer and the Ge(110) substrate: the arm-chair edge of graphene is parallel to Ge $\langle 1\bar{1}0 \rangle$. One can clearly see that experimentally obtained STM images of graphene/Ge(110) demonstrate pronounced areas of high electron density, which are imaged as bright patches. Variation of the bias voltage between $\pm 0.1\text{ V}$ and $\pm 1.0\text{ V}$ allows one to assign them to agglomerations of the impurities,

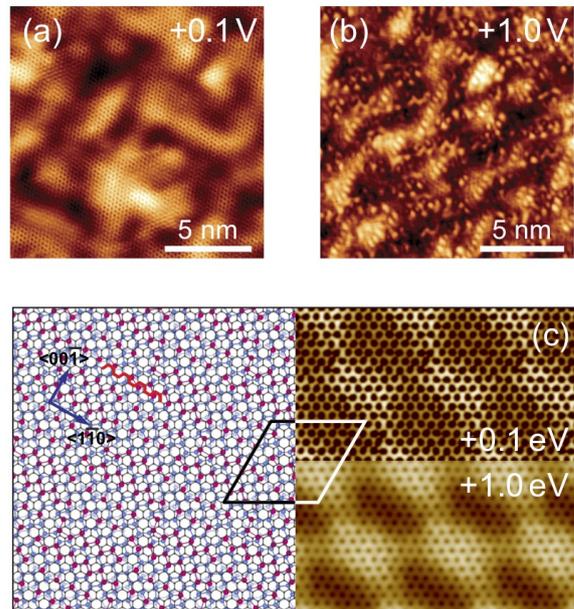


Figure 1: (a, b) STM images of graphene/Ge(110) at different bias voltages. (c) Structural model and the respective simulated STM image for gr/Sb/Ge(110) interface. Black, blue, and red spheres are C, Ge, and Sb atoms, respectively.

which segregate at the graphene/Ge(110) interface and contribute strongly to the imaging contrast. For the present samples, these impurities can be Sb atoms, which segregate during the sample preparation routine (sample sputtering and high-temperature annealing). Therefore, in our DFT studies we considered graphene adsorbed on both pristine Ge(110) surface and Ge(110) with Sb-defects.

According to the band structure calculations, for the clean graphene/Ge(110) interface, without the inclusion of any dopants, graphene is p -doped with the position of the Dirac point at $E_D - E_F = +195\text{ meV}$ (see panel (b) of Fig. 2), which is consistent with the previously published results for graphene grown on the Ge(001)/Si(001) epilayer. Generally, the band structure of graphene with the considered graphene/Ge interface resembles one of the free-standing graphene layers, but just shifted upwards due to doping and without any indication of orbital overlap of the valence band states of graphene and the substrate.

In order to reproduce the experimentally observed doping level of graphene on Ge(110) (see panel (d) of Fig. 2), we based our next model for this interface on our STM results, which clearly indicate the presence of a large amount of defects (probably dopant atoms) at the graphene/Ge(110) inter-

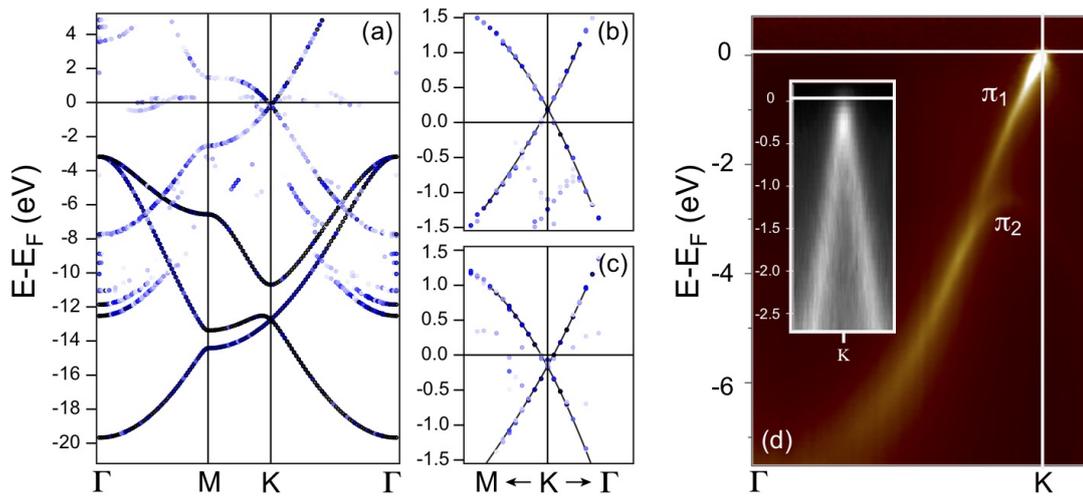


Figure 2: (a-c) Calculated electron energy dispersion of the graphene-derived π and σ valence band states along the main directions of the hexagonal Brillouin zone for the graphene/Ge(110) system with Sb dopants placed at the interface. (b) The zoomed image of the energy dispersion of the graphene π states in the vicinity of the K-point for the clean graphene/Ge(110) interface (graphene is p-doped). (c) The zoomed image of the energy dispersion of the graphene π states in the vicinity of the K-point from (a) (graphene is n-doped). (d) ARPES intensity map presented along the Γ -K direction of the graphene-derived Brillouin zone.

face. Several models of the graphene/Ge(110) interface with the inclusion of Sb dopants were considered: (i) clean interface, (ii) Sb atoms inside the Ge slab, and (iii) different concentrations of Sb atoms at the graphene/Ge interface. One of such equilibrium structures, when Sb atoms were initially placed directly under the carbon atoms (within the $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with respect to the graphene lattice) with a concentration of 27 Sb atoms per (9×9) graphene supercell, and the respective simulated STM images are displayed in Figure 1 (c). The resulting band structure of this system unfolded on the original (1×1) unit cell of graphene, i. e. presenting the weight of the π and σ states, is shown in Figure 2 (a) with the respective zoom around the K-point in Figure 2 (c). From these results we conclude that graphene is n-doped in this system with a position of the Dirac point of $E_D - E_F = -170$ meV, which is in rather good agreement with the experimental ARPES and STS data [4].

Despite the fairly good agreement with the experiment [4], it was recently revealed that the reason for the experimental observations can be a Ge(110) (6×2) reconstruction stabilised by the presence of epitaxial graphene [5,6], rather than the Sb-impurities. Thus, the areas of high electron density imaged as bright patches in STM can be due to the Ge-adatoms carrying dangling bonds. These adatoms may also be responsible to the n-doping of graphene. Therefore, now we intend to reconsider our data and perform the calculations for the reconstructed Ge(110). As a further extension we will consider intercalation of different species (H, Au, Pb, Ca) underneath graphene on Ge(110). The choice

of interlayers has the following reasoning: Au ($d^{10}s^1$, heavy metal) and Pb (s^2p^2 , heavy metal) may enhance the spin-orbit interaction in graphene; Ca may lead to superconductivity [7]. Intercalation of H can yield transformation from the (6×2) phase back to the (1×1) phase [5]. The results of these studies will be used for the understanding and interpretation of the experimental data obtained by our colleagues in Konstanz and Frankfurt/Oder.

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More Information

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Project Partners

University of Konstanz, AG Rüdiger/Fonin

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