
TAILORING THE ELECTRONIC STRUCTURE OF EPITAXIAL GRAPHENE ON SiC(0001): TRANSFER DOPING AND HYDROGEN INTERCALATION

**C. Coletti^{a*}, C. Riedl^a, K. V. Emtsev^a
S. Forti^b, A. A. Zakharov^b and U. Starke^a**

^aMax-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart, Germany

^bMAX-Lab, Lund University, S-22100 Lund, Sweden

*Corresponding author: *c.coletti@fkf.mpg.de*

With its unconventional two-dimensional electron gas properties and exceptional thermal, optical and mechanical characteristics, graphene holds great potential for a wide variety of technological applications. Possibly the successor of silicon in the post Moores law era, graphene could be as well used in spintronics, quantum computing and in state-of-the-art gas-and bio-sensors. Among the different techniques presently used to obtain graphene, thermal decomposition of silicon carbide (SiC) is the one that, by offering the possibility of growing large area graphene directly on semi-insulating substrates [1], might likely yield towards a future of carbon-based electronics. However, a hurdle might sensibly limit the prospects of graphene on SiC(0001): as-grown epitaxial graphene is electron doped which, in terms of electronic band structure, translates into a measurable displacement of the crossing point of the π -bands (Dirac point) below the Fermi level (see Figure 1, left hand side). Clearly, this intrinsic electron doping badly agrees with conventional circuit design.

In this work the electronic, chemical, morphological and structural properties of epitaxial graphene on SiC(0001) will be first introduced by using angle resolved photoemission spectroscopy (ARPES), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), low energy electron microscopy (LEEM) and low energy electron diffraction (LEED). Subsequently, two effective and practical solutions which allow one to overcome the intrinsic n-type doping and to successfully tailor the band structure of epitaxial graphene will be presented.

The first solution consists in non-covalently functionalizing graphene with a strong electron acceptor molecule. We show that by deposition of tetrafluorotetracyanoquinodimethane (F4-TCNQ) onto the epitaxial graphene layers the n-type doping can be progressively compensated [2]. By applying a complete molecular layer charge neutrality can be achieved (see Figure 1). XPS core level analysis and valence band investigations are used to provide a structural characterization of this charge transfer complex and show that the electrons are removed from the graphene layers via the cyano groups of the molecules. When applied on bilayer graphene, F4-TCNQ not only renders the layers semiconducting thanks to the full compensation of the excess negative charged carriers but also increases the band-gap size to more than double of its initial value. The F4-TCNQ doping effect is stable in air and temperature resistant. Moreover, the molecular layer can even be applied via wet chemistry leading to a comparable doping effect. Thus F4-TCNQ deposition on epitaxial graphene represents a technologically robust band structure engineering technique promising for

future electronic applications.

The alternative and extremely elegant solution that will be discussed and that solves the doping problem by aiming directly at the cause is hydrogen intercalation [3]. The intrinsic electron doping originates from the strong coupling between graphene and SiC and is embodied by the existence of an interface layer. This layer, also known as graphene buffer-layer or zerolayer, although presenting carbon atoms arranged in a graphene-like honeycomb structure, does not display the electronic properties of graphene. This is because circa 30% of its carbon atoms are bound to the silicon atoms of the SiC(0001) surface. Annealing a buffer-layer at high temperatures in a hydrogen atmosphere causes the hydrogen atoms to migrate through the carbon layer and to passivate the silicon atoms of the SiC(0001) surface. As a result the buffer-layer, now decoupled from the substrate, fully displays graphene properties (see Figure 2). Hydrogen intercalation of a graphene buffer-layer yields to a quasi-free standing graphene monolayer that is charge neutral within a few milli-electronvolt. In a more general way, the intercalation process transforms (n)-layer graphene into ($n + 1$)-layer quasi-free standing graphene even for large values of n . Hydrogen intercalation is stable to air exposure and up to 700°C. Thanks to this method, large area, charge neutral, quasi-free standing mono-, bi- and trilayer graphene can be obtained and their structural and electronic properties studied. Hydrogen intercalation underneath epitaxial graphene deserves primary attention as, by ultimately decoupling the graphene layers from the substrate, might represent a promising route towards a future of graphene based electronics. This research was supported by the Alexander von Humboldt Foundation [4].

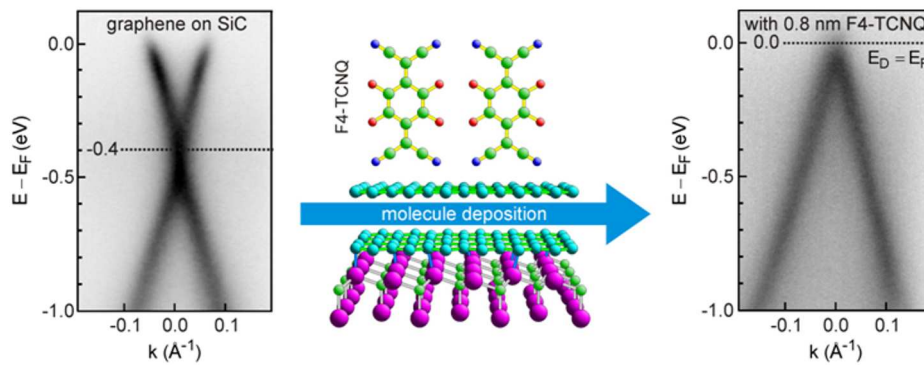


Figure 1: Effect of F4-TCNQ on the band structure of monolayer graphene. Dispersion of the π -bands measured with ARPES perpendicular to the ΓK direction of the graphene Brillouin zone before (left hand side) and after (right hand side) deposition of F4-TCNQ.

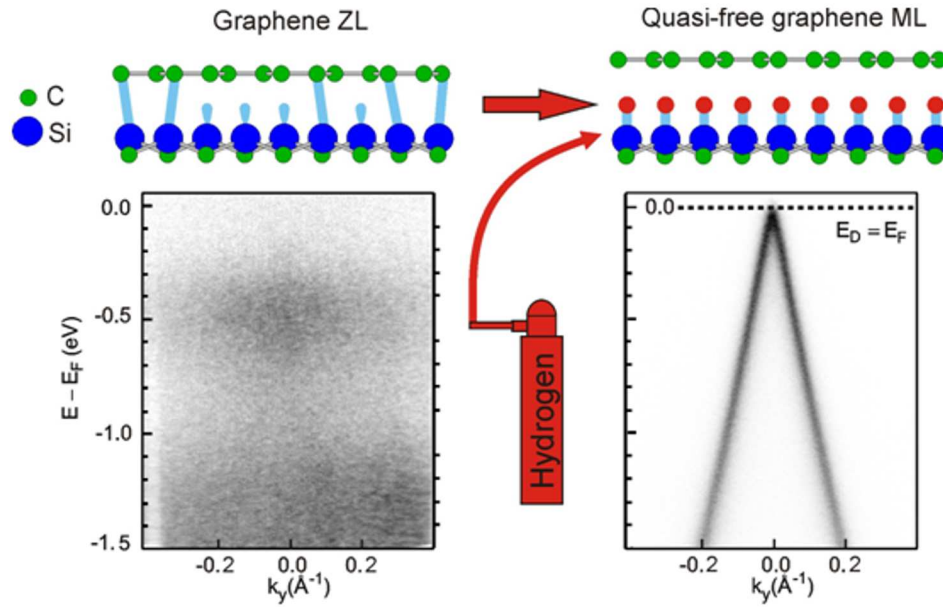


Figure 2: Effect of hydrogen intercalation on the band structure of a graphene zerolayer. Electron dispersion measured with ARPES perpendicular to the ΓK direction of the graphene Brillouin zone before (left hand side) and after (right hand side) annealing in a hydrogen atmosphere.

References

- [1] K.V. Emtsev, A. Bostwick, K. Horn, *et al.*, Nature Materials, 8 (2009) 203-207.
- [2] C. Coletti, C. Riedl *et al.*, Physical Review B, 81 (2010) 235401.
- [3] C. Riedl, C. Coletti *et al.*, Phys. Rev. Lett., 103 (2009) 246804.
- [4] C.C. acknowledges the "Alexander von Humboldt Fellowship for Postdoctoral Researchers" for financial support.