Interfacial engineering of the graphene band structure

Band structure engineering of 2D materials

E. Voloshina, B. Paulus, *Institut für Chemie und Biochemie, Freie Universität Berlin*

In Short

- Electronic structure of graphene

- Graphene-substrate interaction

- Induced magnetic moment in graphene

- Spintronics

Two-dimensional (2D) materials are atomically thin crystalline solids with very large lateral dimensions as compared to their thickness. Currently, hundreds of 2D materials are known. They are classified under broad categories of elements, metallic compounds, nonmetallic compounds, organics, and salts. These 2D materials have a wide range of electronic properties, such as metals, semimetals, semiconductors, insulators, and superconductors and exhibit great potential for many applications. However, there are some limitations to the applicability of 2D materials in various fields, and to overcome these, various strategies are being developed to tune their band structures [1].

The ongoing revolution of 2D materials begins with experiments on graphene, the first 2D material to be isolated. It is composed of a single atomic layer arranged in a 2D honeycomb lattice (Fig. 1a). C-atoms in graphene are sp^2 hybridised (Fig. 1b). Each atom in a graphene sheet is connected to its three nearest neighbours by σ bonds and contributes an electron to a conduction band that spans the entire sheet. This conduction band (π-band) makes graphene a semimetal (zero-gap semiconductor, see Fig. 1c) with unusual electronic properties that are best described by massless relativistic particle theory [2]. The unusual properties of graphene make it a promising material for building electronic and spintronic devices and simultaneously are its drawback, which limit applications of graphene [3].

Different techniques aiming of inducing desired novel properties in the graphene layer were proposed. In this context, interface effects between graphene and other materials have proven to be an efficient way for graphene band structure manipulation and theoretical calculations were shown to be effective for predicting novel properties of the interfaces once compared to experiments.

Among the graphene-based interfaces, special attention is paid to the graphene/ferromagnet (FM)

systems due to their perspectives for spintronic applications [4]. The overlap of the electronic states at the interface between graphene and FM materials allows to observe the induced spin polarisation of the graphene π states that was confirmed in a series of spectroscopic experiments for graphene/Ni(111) and graphene/Co(0001), and this effect can be used for an effective spin injection and manipulation in graphene. However, as a consequence of the strong interaction at the graphene/FM interface, graphene loses its free-standing character and the carriers in the vicinity of the Fermi level (E_F) cannot be described as massless Dirac particles. It is possible to decouple graphene from the underlying FM material via intercalation of different species, giving a route to restore the free-standing character of graphene despite losing the possibility of the induced spin polarisation in a graphene layer.

In order to induce spin-degeneracy in graphene while keeping the Dirac-electron-like character of its carriers, we proposed a new graphene/FM interface, namely, graphene/Mn_5Ge_3 (Fig. 2a,b). This system can be easily fabricated by means of intercalation of Mn in the graphene/Ge(111) interface [5]. Our systematic large-scale density functional theory calculations for this interface demonstrate that graphene
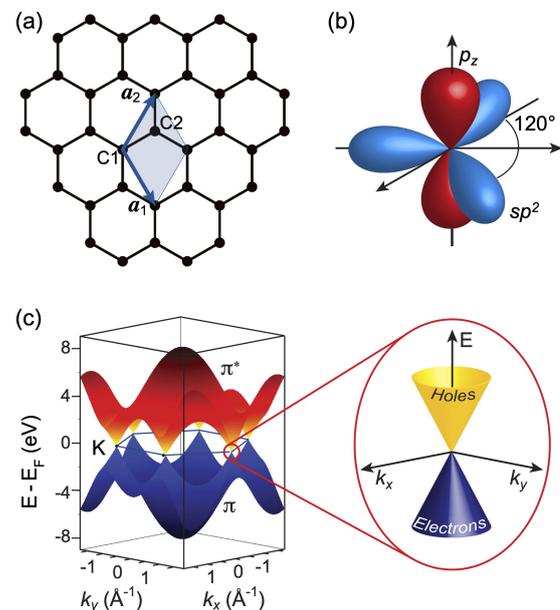

Figure 1: *(a) Lattice structure of graphene. Blue arrows indicate the lattice vectors. The shaded area indicates the unit cell with two carbon atoms: C1 and C2. (b) sp^2 hybridisation of carbon atoms. (c) 3D representation of the electronic band structure of monolayer graphene as obtained with tight-binding approach. A zoomed inset shows the Dirac cone.*
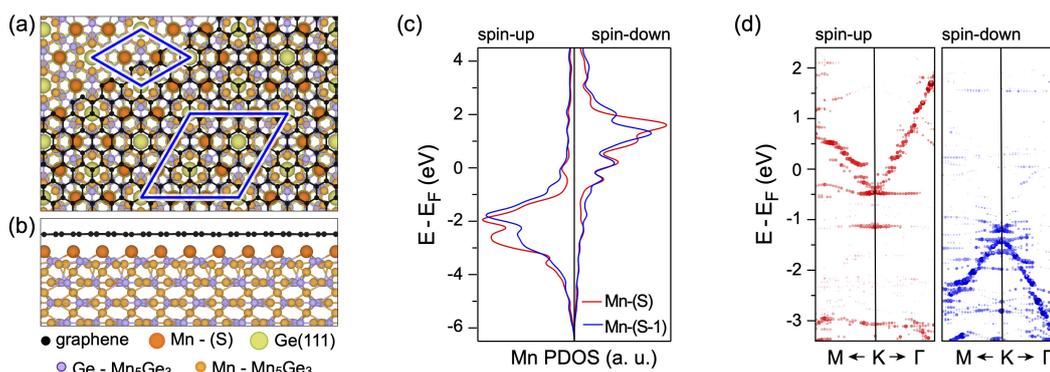
Figure 2: *(a,b) Top and side views of the crystallographic structure of graphene/Mn$_5$Ge$_3$(0001)/Ge(111). Blue rhombuses mark unit cells of $(3 \times 3)R30°$-Mn$_5$Ge$_3$(0001) and (5×5)-graphene/Mn$_5$Ge$_3$(0001). (c) Spin-resolved Mn-atom projected density of states for the clean Mn$_5$Ge$_3$(0001) surface. (d) Spin-resolved band structure obtained after unfolding procedure and presented around the K point of the (1×1) graphene-derived Brillouin zone for the (5×5)-gr/Mn$_5$Ge$_3$(0001) system for spin-up and spin-down channels.*

is relatively strongly bonded to the FM Mn$_5$Ge$_3$ substrate (see Fig. 2c) that leads to the substantial exchange splitting of the graphene π states. It is found that the effect of the spin-conservation during hybridisation of the graphene π and Mn $3d$ valence band states leads to the appearance of the large band gaps in the energy dispersion of the graphene π states for both spin channels. The combination of all factors leads to the observation of only spin-up electrons of graphene at the K point and at E_F which conserve the Dirac-electron-like character (Fig. 2d). At the same time, for the spin-down electrons the band gap is found at E_F. This unique feature of the studied interface can lead to its application in spintronics.

The present project is devoted to studying the electronic and magnetic properties of 2D materials and search for a route to tune their properties to meet requirements of specific applications. In the first funding period we plan to perform realistic large-scale density functional theory calculations for the graphene/M$_4$N(111) interfaces (M: Fe, Mn, Cr), which have not been studied so far neither in theory nor in experiment. Given their simple

compositions and crystal structures (Fig. 3a), transition metal nitrides display remarkably rich behaviour (e. g. Fig. 3b) and can be seen as promising candidates for utilisation in spintronic devices. When acting as a substrate, transition metal nitrides are expected to induce new properties in the graphene overlayer. The graphene itself can also modify the properties of the underlying material. Our calculations will allow to trace all changes in the electronic structure of graphene as well as of the substrate and to study the spin topology of the electronic states in the vicinity of the Fermi energy. All studies will be performed in close collaboration with experimental research group.

More Information

[1] K. Khan *et al., J. Mater. Chem. C* **8**, 387 (2019). doi:10.1039/C9TC04187G

[2] A. H. C. Neto *et al., Rev. Mod. Phys.* **81**, 109 (2009). doi:10.1103/RevModPhys.81.109

[3] K. A. Madurani *et al., ECS J. Solid State Sci. Technol.* **9**, 093013 (2020). doi:10.1149/2162-8777/abbb6f

[4] V. M. Karpan *et al., Phys. Rev. Lett.* **99**, 176602 (2007). doi:10.1103/physrevlett.99.176602

[5] E. Voloshina, Y. Dedkov, *J. Phys. Chem. Lett.* **10**, 3212 (2019). doi:10.1021/acs.jpclett.9b00893
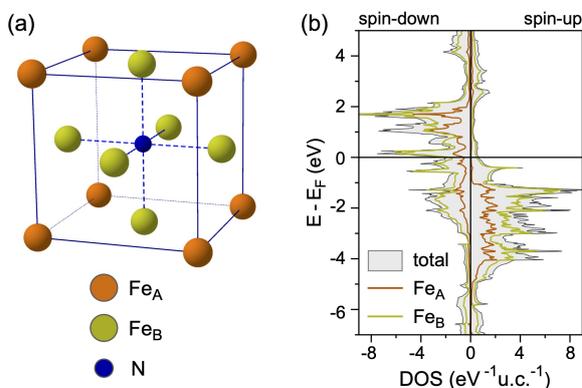
Figure 3: *Lattice structure (a) and density of states (b) of bulk Fe$_4$N.*

Project Partners

Prof. Y. Dedkov, CoE ENSEMBLE3, Poland

DFG Subject Area

327-02