

Electronic structure of graphene/Ge systems with tailored interfaces

Band structure engineering of 2D materials

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In Short

- Electronic structure of graphene
- Graphene-semiconductor systems with different interlayers
- Mutual effect of exchange and spin-orbit coupling interactions on the graphene band structure
- Spintronics

Spintronics is a field of science whose history goes back to the theoretical work of Rashba on spin-orbit effects in non-centrosymmetric crystals [1] and to the experimental work of Tedrow and Meservey on tunnelling in ferromagnet/superconductor junctions [2], devoted to the electron spin and its influence on the transport properties of various materials and interfaces [3]. Progress in this field led to the discovery of the giant magnetoresistance effect in metallic multilayer structures, which was followed by the creation of the spin-valve sensor, which allows for a significant increase in the density of data storage devices. On the other hand, the creation of the field-effect transistor (FET), in which the channel conductivity is controlled by an external electric field, and which is currently the basic building block in semiconductor technology, prompted the idea of creating a spin-FET device for two-dimensional (2D) electron gas semiconductors, where the channel spin conductivity also depends on the electric field via the Rashba effect.

Discovery of the unique properties of the truly 2D material graphene (gr) immediately places it in the forefront of spintronics research [4] with the ultimate goal of manipulating the spin by an external electric field. In fact, being made by a light element such as carbon, graphene presents an intrinsic weak spin-orbit interaction, while its enhancement is expected to pave the way to a multitude of exotic phenomena, such as quantum spin Hall effect and possible applications as spin injectors or spin filters.

Various methods were proposed to induce or/and enhance the spin-orbit interaction in graphene. One of the most used approaches has been by proximity with metallic compounds. In such a case two main mechanisms can be at work: the Rashba effect and an induced spin-orbit interaction by direct hybridisation of the graphene π states with the valence band

states of the metal. The resulting spin splitting is expected to present a different configuration depending on the leading mechanism: a constant energy separation as a function of the wave vector in the vicinity of the Dirac point of the graphene π states in the case of Rashba splitting (Fig. 1), while an energy- and momentum-dependent splitting for the graphene π states, with strong reduction when approaching the Fermi energy (E_F), in the case of direct hybridisation of the valence band states of graphene and metal[5].

In order to take a further step towards real applications, the integration of graphene into the existing complementary metal-oxides-semiconductor (CMOS) technology must be resolved. All integration methods that have been used until now are based on the transfer of synthesised graphene layers onto the semiconductor material, which greatly complicates the control of the graphene-semiconductor interface and leads to parasitic effects in the device operation, which cannot be acceptable in semiconductor technology. Therefore, the search for new graphene synthesis methods directly on semiconductor surfaces was very active in the last decade and led to the recent discovery of graphene synthesis on the catalytically active semiconducting Ge substrates of different orientations [6].

Further modification of the graphene/Ge interface can be performed via intercalation of different species under graphene, that can be considered as an effective way to tailor electronic properties of these systems. As it was proposed in our theoretical work [7] and later confirmed experimentally [8], intercalation of Mn in the gr/Ge interfaces leads to formation of a thin layer of Mn_5Ge_3 at the interface (Fig. 2a,b). Mn_5Ge_3 demonstrates very strong exchange splitting of the valence band states with the magnetic moment of Mn atoms of $3.11 \mu_B$. Also,

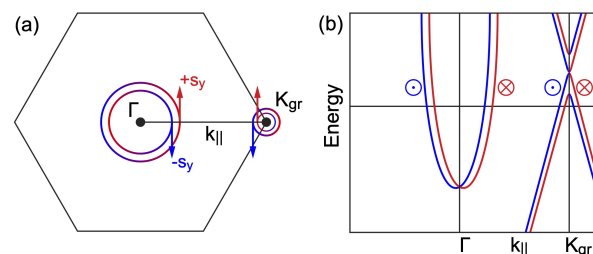


Figure 1: Example of the simplified band structure for the graphene/metal systems displaying: (a) the constant energy cut and (b) the respective $E(k_{||})$ plots for the Rashba-split surface state of metallic substrate (around the Γ point) and graphene-derived π states (around the K_{gr} point).

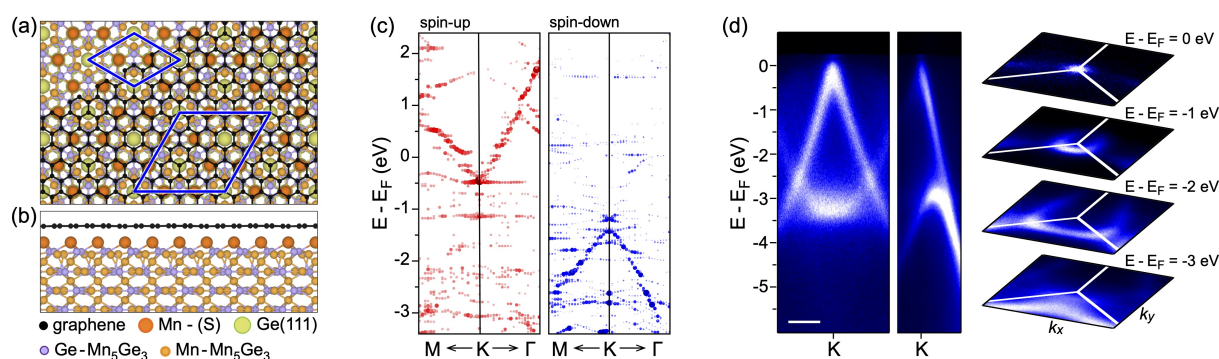


Figure 2: (a,b) Top and side views of the crystallographic structure of $gr\text{-Mn}_5\text{Ge}_3/\text{Ge}(111)$. Blue rhombuses mark unit cells of $(\sqrt{3} \times \sqrt{3}) R30^\circ\text{-Mn}_5\text{Ge}_3(0001)$ and $(5 \times 5)\text{-gr/Mn}_5\text{Ge}_3(0001)$. The side view in (b) is taken for the view direction perpendicular to the main diagonal of the big rhombus in (a). (c) Spin-resolved band structure obtained after unfolding procedure and presented around the K point of the (1×1) graphene-derived Brillouin zone for the $(5 \times 5)\text{-gr-Mn}_5\text{Ge}_3(0001)$ system [7]. (d) ARPES intensity maps along $\pi\Gamma\text{K}/\Gamma\text{K}$ directions of the hexagonal Brillouin zone and stacks of constant energy intensity maps for $gr/\text{Mn}_5\text{Ge}_3/\text{Ge}(110)$ [8].

this material demonstrates a relatively large spin polarisation of $42 \pm 5\%$. The contact of graphene with this ferromagnetic substrate yields spin polarisation of its π states. Despite the small distance between graphene and Mn_5Ge_3 causing the strong interaction at interfaces, the linear band dispersion around the Fermi level for the carriers in graphene is preserved (Fig. 2c,d). Yet, due to the effect of the spin-conservation during hybridisation of the valence band states at the graphene/ Mn_5Ge_3 interface, only spin-up electrons of graphene at the K point and at E_F conserve the Dirac-electron-like character and for the spin-down electrons the band gap is found at E_F (Fig. 2c). Thus, Mn_5Ge_3 can be considered as an efficient spin injector fully compatible with CMOS technology and the complete heterostructure as a potential building block for spintronic devices.

In the next project period we plan to explore the potential of controlled tailoring the graphene/Ge and graphene/ Mn_5Ge_3 interfaces by intercalation with atoms of heavy materials with the goal to induce strong spin-orbit and exchange interaction in graphene. The simultaneous presence of both exchange and spin-orbit interactions is expected to lead to non-trivial electronic properties and it is expected to give access to novel quantum phases in the graphene layer. At the same time, the carbon driven magnetic properties will be addressed to elucidate the role of the interface electronic hybridisation in the system magnetic behaviour. Large-scale DFT calculations of the studied systems will give understanding of induced effects via calculation of the band structure, charge transfers at the interface, and spin topology of the electronic bands of graphene. In order to contribute to a deeper understanding of electronic structure of graphene-semiconductor systems with different interlayers the research in the framework of the present proposal will be performed in close collaboration between theory and experiment.

Our joint studies will allow us to understand the underlying mechanisms that lead the systems under consideration to induced spin-orbit and/or exchange interactions and will allow us to draw conclusions on the perspectives to use obtained interfaces in future nanoelectronics and spintronics.

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More Information

- [1] E. I. Rashba, V. I. Sheka, *Fiz. Tverd. Tela* **2**, 162 (1959).
- [2] P. M. Tedrow, R. Meservey, *Phys. Rev. Lett.* **26**, 192 (1971). doi:10.1103/physrevlett.26.192
- [3] S. A. Wolf *et al.*, *Science* **294**, 1488 (2001). doi:10.1126/science.1065389
- [4] G. Zhang *et al.*, *Appl. Phys. Rev.* **11**, 021308 (2024). doi:10.1063/5.0191362
- [5] E. Voloshina, Y. Dedkov, *Adv. Theory Simul.* **1**, 1800063 (2018) doi:10.1002/adts.201800063
- [6] Y. Dedkov, E. Voloshina, *Nanoscale* **12**, 11416 (2020) doi:10.1039/d0nr00185f
- [7] E. Voloshina, Y. Dedkov, *J. Phys. Chem. Lett.* **10**, 3212 (2019). doi:10.1021/acs.jpcllett.9b00893
- [8] Y. Dedkov *et al.*, *ACS Appl. Mater. Interfaces* **15**, 26190 (2023). doi:10.1021/acsami.3c03553

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DFG Subject Area

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