

Interfacial engineering of the graphene band structure

Electronic properties of the interface between 2D materials and functional alloys

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In Short

- Electronic structure of graphene
- Graphene-substrate interaction
- Intercalation of Pd and Co
- Metal alloy formation
- Mutual effect of exchange and spin-orbit coupling interactions on the graphene band structure

Graphene band structure engineering is currently one of the most important and competitive research fields with the ultimate goal of inducing desired novel properties in the graphene layer preserving its extraordinary electrons mobility. 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. Conversely, the graphene itself can modify the electronic properties of the underlying substrate. Astonishing examples are the graphene induced magnetic properties on ferromagnetic thin film on which the stability of the magnetisation is strongly enhanced. The aim of this project is to investigate, for the first time, theoretically and experimentally the interface effects between graphene and high spin-orbit coupled magnetic materials in order to elucidate the role of simultaneous exchange and spin-orbit interactions on the graphene band structure. Both interactions have been, so far, mainly studied in separate ways showing that spin-orbit coupling can lift the graphene spin degeneracy without inducing magnetic moment, while a net magnetisation can be induced in carbon atoms by direct exchange interaction. The simultaneous presence of both exchange and spin-orbit interactions will therefore 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 on the system magnetic behaviour. This understanding will open a new route to modify the magnetic properties in carbon/ferromagnetic hybrids by interface effects. The mutual presence of high spin-orbit coupled material and the graphene interface can lead to ultra-stable

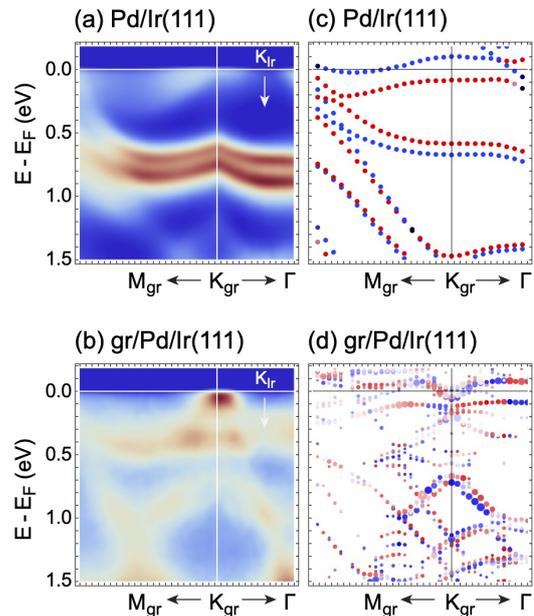


Figure 1: ARPES intensity maps for (a) Pd/Ir(111) and (b) gr/Pd/Ir(111). Calculated spin-resolved band structures of (c) Pd/Ir(111) and (d) gr/Pd/Ir(111).

magnetic thin film, which could be exploited as model systems for magnetic storage devices.

Using density functional theory (DFT) calculations and angle-resolved photoemission spectroscopy (ARPES) we investigated the modification of the electronic structure of graphene (gr) initially adsorbed on Ir(111) via intercalation of one monolayer Pd. We reveal that for the gr/Pd/Ir(111) intercalated system, a spin splitting of graphene π states higher than 200 meV is present near the graphene K point (Figure 1). This spin separation arises from the hybridisation of the graphene valence band states with spin-polarised quantum well states of a single Pd layer on Ir(111). Our results demonstrate that the proposed approach on the tailoring of the dimensionality of heavy materials interfaced with a graphene layer might lead to a giant spin-orbit splitting of the graphene valence band states. Further details can be found in Ref. [1].

Intercalation of other materials into the graphene-substrate interface may lead to formation of ordered surface alloys with interesting properties [2,3]. Our recently published work is devoted to the study of the structural and electronic properties of graphene on the surface and subsurface Co_xIr_y alloy - the system obtained by means of intercalation of Co in graphene/Ir(111) [4]. The analysis of stability suggests that at low Co concentration, the Co_xIr_y alloy prefers to exist on the subsurface underneath

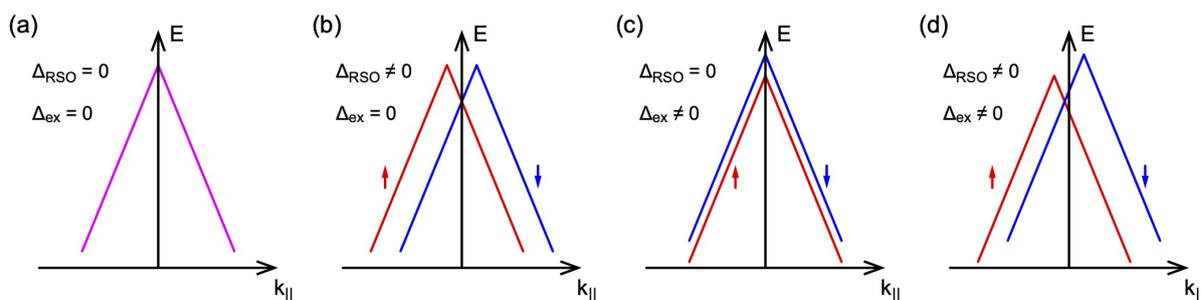


Figure 2: Schematic representation of the energy dispersion of graphene Dirac cone (a) with Rashba spin-orbit interactions (b), ferromagnetic exchange (c), Rashba and ferromagnetic exchange (d). Arrows indicate the electrons spin polarisation.

the graphene/Ir(111) interface bilayer to interact indirectly with the graphene layer; whereas at high Co concentration, Co_xIr_y alloy tends to segregate to the surface, thereby directly bonding with the graphene monolayer. This depends on the balance between the deformation of graphene and the interaction of graphene with the substrate. Our band structure calculations shows that the strong interaction of graphene with Co atoms destroys the Dirac cone; the formation of a subsurface Co_xIr_y alloy weakens the interaction between graphene and substrate and thereby makes the graphene layer more quasi freestanding with weak p doping. The results of our DFT calculations are supported by ARPES measurements, which demonstrate that, when graphene is lying on a Co monolayer on Ir(111), the Dirac cone vanishes. The formation of subsurface Co_xIr_y alloy restores the presence of the Dirac cone at the Fermi level. Still, the graphene π band in the vicinity of the K point is spin-polarised. Further details can be found in Ref. [4].

Within this proposal we plan to investigate bimetallic graphene stacked system composed of a graphene layer, HM layer and a ferromagnetic (FM) thin film. Both kind of interactions (graphene-FM and graphene-HM) have been, so far, studied in separate ways, showing that spin-orbit coupling can, in principle, change the Dirac cones structure from the one of pristine graphene (sketched in Figure 2 a) to spin-orbit split cones (Figure 2 b), while a net magnetisation can be induced in carbon atoms by direct exchange interaction (Figure 2 c). The combination of these two effects could then enable to realise both spin polarisation and spin-orbit splitting in the graphene band structure while keeping intact the dispersion of the Dirac cones (Figure 2 d).

The main objective driving this project is to study the mutual effect of exchange and spin-orbit coupling interactions on the graphene band structure. Being magnetically polarisable (such as Pt or Pd), the HM material will acquire a magnetic moment through its interface with the underlying magnetic film while conserving its natural high spin-orbit coupling. Via its in-

terface with the HM element, the graphene layer will therefore experience, at the same time, exchange and spin-orbit interactions. With the chosen system, we will be able to study the effect on the graphene band structure of simultaneous exchange and spin-orbit interactions, while keeping intact, as much as possible, the pristine electron linear dispersion of graphene. It is expected, that the mutual coexistence of exchange and spin-orbit interactions in the graphene layer will open the access to new physical phases such as topological quantum spin Hall effect and quantum anomalous Hall effect. Moreover, the insertion of the HM element in between graphene and the FM material provides a new degree of freedom, which can be exploited to modify the overall magnetic properties. Depending on how the coupling between electrons of the three constituents will behave one can expect, beside the enhancement of the magnetic anisotropy energy, even non-trivial spin textures. Here three alternative scenarios concerning the magnetic properties are possible: (i) the graphene/HM interface still induces a strong perpendicular magnetic anisotropy (PMA) thus creating a stacked system with extremely stable magnetisation direction up to several nanometers; (ii) no changes of the magnetic anisotropy energy; (iii) reduction of the PMA through the graphene/HM interface.

Our findings will be compared with the experimental results obtained in the QuantumSpecs Group, ESPCI Paris (Dr. S. Vlaic).

More Information

- [1] T. Vincent *et al.*, *J. Phys. Chem. Lett.* **11**, 1594 (2020).
- [2] E. Voloshina and Y. Dedkov, *J. Phys. Chem. Lett.* **10**, 3212 (2019).
- [3] E. Voloshina, B. Paulus, and Y. Dedkov, *J. Phys. Chem. Lett.* **12**, 19 (2021).
- [4] K. Wang *et al.*, *Carbon* **183**, 251 (2021).

Project Partners

ESPCI Paris, QuantumSpecs Group