Electronic and geometric structure of graphene/SiC(0001) decoupled by lithium intercalation

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The interaction between graphene and adsorbed or intercalated alkali metal atoms has received considerable attention in recent years, not only because of obvious analogies to the well-known graphite intercalation compounds, but also because the interaction may be used to induce a considerable "chemical doping", and deposition with subsequent intercalation can bring this doping to extreme values. Apart from doping effects, the intercalation process is also an interesting method for the decoupling of graphene from substrates, as in the case of the SiC(0001) surface with the so-called buffer layer on top, corresponding to the $(6\sqrt{3}\times6\sqrt{3})R30^{o}$ reconstruction. In the present work, we have investigated the lithium intercalation in between the carbon buffer layer and the silicon-terminated face of silicon carbide, i.e., SiC(0001), since the interaction of graphene with lithium attracts special attention for fundamental and technological reasons, related to the fabrication of Li-based batteries and a predicted superconducting phase [1].

Low energy electron diffraction (LEED) and core level photoemission spectroscopy results show that graphene formation already occurs at room temperature, and that the interface morphology is improved after thermal annealing. Our Angle-resolved photoemission spectroscopy (ARPES) results (Figure 1a) show that the resulting graphene layer is strongly n-type doped. In spite of the fact that the resulting graphene layer is decoupled by lithium intercalation, we find that a persistent interaction with the substrate imposes a superperiodicity on the graphene band structure that modulates the π band intensity and gives rise to quasi-(2x2) π replica bands, marked "F1" and "F2" in the Figure. Through a comparison of the ARPES-derived band structure with density functional theory calculations (Figure 1c), we are able to assign the observed bands to SiC-derived states and interface-related ones. Based on this assignment and the excellent agreement between theory and experimental bands, we are able identify the site that the intercalated lithium occupies: it is the T4 site in the topmost SiC layer [2].

References

[1] G. Profeta et al., Nat. Phys., 8 (2012) 131.
[2] F. Bisti et al., Phys. Rev. B, 91 (2015) 245411.

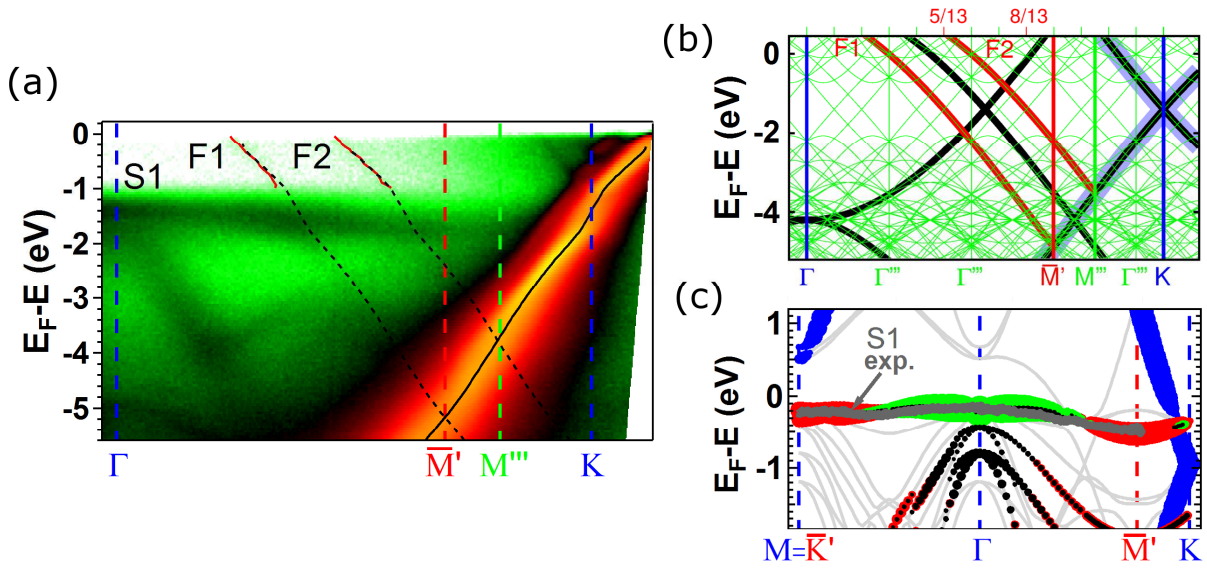

Figure 1: **(a)** ARPES photoemission image, showing the graphene π-band (black line) and the the quasi-(2x2) π replica bands ("F1" and "F2") (red lines) induced by the superperiodicity. **(b)** Tight-binding band structures of graphene in a (1 × 1) unit cell (light blue curves), along the Γ-K directions, folded onto the (2 × 2) (black) and (13 × 13) (green) ones, providing an assignment of the "F1" and "F2" features in terms of umklapp bands. **(c)** DFT band structures for the system with Li occupying the T4 sites. The band structures are weighted by the projecting factor on three different states bases: atomic Li states in SiC (1 × 1) (green dots), atomic Si states in SiC (1 × 1) (red dots), and atomic C states in SiC (1 × 1) and in graphene (1 × 1) (black and blue dots, respectively, with weight values divided by 2 for clarity). The dark gray line in **(c)** represents the experimental data of the "S1" feature shifted by 1.22 eV to lower binding energy.