Massless Dirac Fermion in Borophene

Honeycomb structures of group IV elements can host massless Dirac fermions with nontrivial Berry phases. Their potential for electronic applications has attracted great interest and spurred a broad search for new Dirac materials especially in monolayer structures. We present a detailed investigation of the β_{12} sheet, which is a borophene structure that can form spontaneously on a Ag(111) surface. Our tight-binding analysis revealed that the lattice of the β_{12} sheet hosts Dirac cones, and each Dirac cone could be split by overlayer-substrate interactions. These unusual electronic structures were confirmed by angle-resolved photoemission spectroscopy and validated by first-principles calculations.

One of the promising routes for realizing novel two-dimensional materials is by tailoring or modifying the honeycomb lattice. An example is a monolayer boron sheet (i.e., borophene), which is realized by introducing periodic boron atoms in a honeycomb-like lattice. As boron has one less electron than carbon, the honeycomb structure is unstable, but the introduction of additional boron atoms in the honeycomb lattice can stabilize the structure by balancing out the two- and multicenter bonds. Depending on the arrangements of the extra boron atoms, various monolayer-boron structures have been proposed, such as α sheet and β sheet. Recently, several monolayer boron phases have been experimentally realized on Ag(111) [1-4]. For example, it was reported that there were a stable striped phase and a metastable homogeneous phase [1]. The striped phase was proposed to be a complete triangular lattice with anisotropic, out-of-plane buckling. In another study, a similar striped phase with a different rotation angle was observed [3]. This phase, named β_{12} sheet (**Fig. 1h**), has an essentially flat structure and interacts weakly with the Ag(111) substrate [3, 4]. However, there have been few experimental investigations on the electronic properties of monolayer boron.

We synthesized β_{12} borophene and studied its electronic structure by angle-resolved photoemission spectroscopy at BL-2A [5]. A schematic drawing of the Brillouin Zone (BZ) of Ag(111) with the three domain orientations is shown in **Fig. 1a**, together with the measured Fermi surface. The band structure from the boron layer shows one Fermi pocket centered at the S point of the β_{12} sheet and a pair of Fermi pockets centered at the $\bar{M}$ point of Ag(111), as indicated by the red and black arrows, respectively. The photoemission bands derived from the boron layer do not disperse with photon energy, which is in agreement with its two-dimensional characteristic.

The pair of Fermi pockets centered at the $\bar{M}$ point of Ag(111) is associated with Dirac cones. In **Fig. 1b**, we show constant energy contours (CECs) at different binding energies (E_B). With increasing binding energies, the Fermi pockets first shrink in size and then become points at E_B = –0.25 eV. Further increase of the binding energy leads to a pair of closed contours which touch each other at E_B = –0.68 eV. The pair of closed contours merges into one contour at higher binding energies. The measurements of cut 1 using *p* polarized light (**Fig. 1d**) reveal a Dirac cone as well as the bulk *sp* band of Ag(111). The Dirac point is located at approximately 0.25 eV below the Fermi level, in agreement with the evolution of the CECs in **Fig. 1b**. The linear dispersing bands extend to as deep as 2 eV. Within the first BZ of the β_{12} sheet, we observed two pairs of Dirac cones in total, as schematically illustrated in **Fig. 1g**.

The orbital contribution of the boron bands can be probed by switching the linear polarization of the incident light. The *s* polarized light primarily probes the in-plane p_x and p_y orbitals, while the *p* polarized light probes both the in-plane (p_x and p_y) and out-of-plane (p_z) orbitals. The band structures along cut 1 measured with *s* and *p* polarized light are shown in **Figs. 1c** and **1d**, respectively. The Dirac cone was not observed with the *s* polarized light, leaving only the bulk *sp* bands of Ag(111). This means that the Dirac cones originate from the p_z orbital of boron.

Recent successes in graphene science indicate that "borophene", as revealed by our work, is an interesting new field of research in physics and technology.

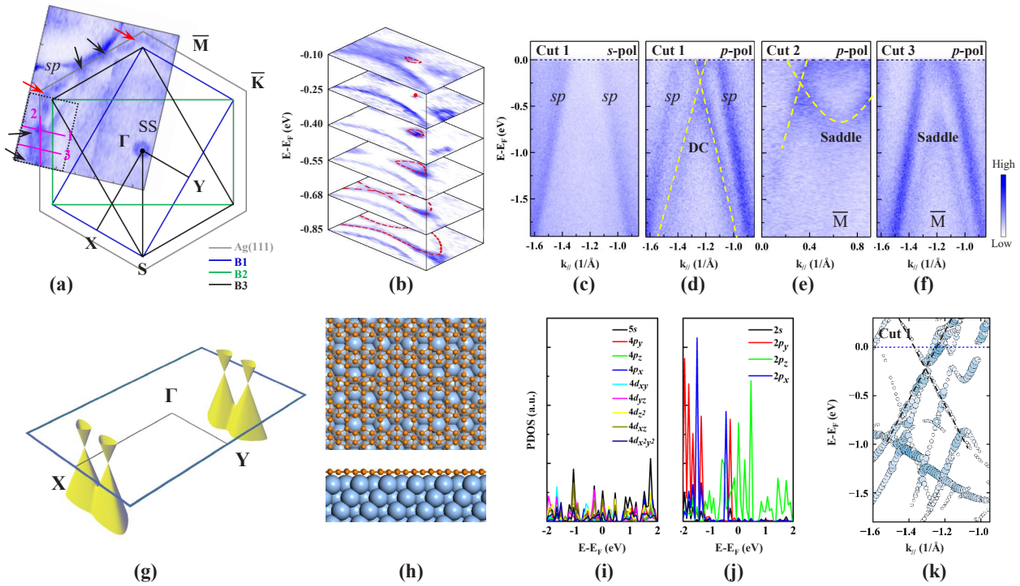

Figure 1: Band structures of the β_{12} sheet on Ag(111). **(a)** The Fermi surface of the β_{12} sheet on Ag(111). The black, green, and blue rectangles indicate the BZ of three equivalent domains; the gray hexagon indicates the BZ of Ag(111). The black and red arrows indicate the bands of the boron layer. The surface state (SS) and bulk *sp* band of Ag(111) are also observed because the coverage of boron is less than 1 ML. The pink lines indicate cuts 1–3 where the ARPES intensity plots in **(c)–(f)** were measured. **(b)** CECs derived from the second-derivative energy distribution curves measured in the black dotted rectangle in **(a)**. E_F in the figure corresponds to the Fermi level. All the data in **(a)** and **(b)** were measured with *p* polarized light. **(c)** ARPES intensity plot measured along cut 1 with *s* polarized light. **(d)–(f)** ARPES intensity plots measured with *p* polarized light along cut 1 to cut 3, respectively. The yellow dashed lines indicate the Dirac cones (DC). All the ARPES data in **(a)–(f)** were measured with a photon energy of 80 eV. **(g)** Schematic drawing of the Dirac cones according to our experimental results. **(h)** Relaxed structure model of the β_{12} sheet on Ag(111) from our first-principles calculations. The orange and blue balls indicate the B and Ag atoms, respectively. **(i)** and **(j)** Calculated partial DOS of B atoms and Ag atoms, respectively. **(k)** Calculated band structure along cut 1.

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