

Black Phosphorus n-type Doping by Cu: A Microscopic Surface Investigation

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Black phosphorus (bP) has emerged as an interesting addition to the category of two-dimensional materials. Surface-science studies on this material are of great interest, but they are hampered by bP's high reactivity to oxygen and water, a major challenge to scanning tunneling microscopy (STM) experiments. Consequently, the large majority of these studies were performed by cleaving a bulk crystal in situ. We have developed a technique, which allows preparing clean exfoliated bP flakes for surface science studies, using epitaxial monolayer graphene as a conductive substrate for the exfoliation of the bP flakes.¹

Based on this approach, we study surface charge transfer doping of exfoliated black phosphorus flakes by copper using scanning tunneling microscopy and spectroscopy (STS) at room temperature.² The tunneling spectra reveal a gap in correspondence of Cu islands, which is attributed to Coulomb blockade phenomena. Moreover, using line spectroscopic measurements across small copper islands, we exploit the potential of the local investigation, showing that the n-type doping effect of copper on bP is short-ranged. These experimental results are substantiated by first-principles simulations, which quantify the role of cluster size for an effective n-type doping of bP and explain the Coulomb blockade by an electronic decoupling of the topmost bP layer from the underlying layers driven by the copper cluster. Our results provide novel understanding, difficult to retrieve by transport measurements, of the doping of bP by copper, which appears promising for the implementation of ultra-sharp p-n junctions in bP.

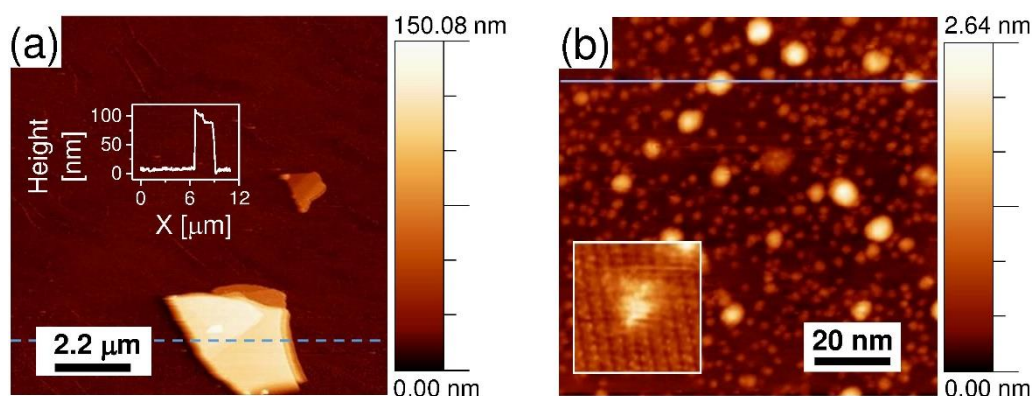


Figure 1. (a) $11 \mu\text{m} \times 11 \mu\text{m}$ STM image showing two bP flakes on a graphene substrate after 20 min of copper deposition. Scan parameters: $(-3.0 \text{ V}, 0.33 \text{ nA})$. Inset: height profile across the larger flake along the dashed blue line. (b) $100 \text{ nm} \times 100 \text{ nm}$ STM image on the larger flake, showing copper islands on bP. Inset: $5 \text{ nm} \times 5 \text{ nm}$ STM image obtained upon further zoom-in, showing a copper island on top of the atomically resolved bP surface. Scan parameters for both images: $(-1.0 \text{ V}, 0.33 \text{ nA})$.

1. Abhishek Kumar, F. Telesio, S. Forti, A. Al-Temimy, C. Coletti, M. Serrano-Ruiz, M. Caporali, M. Peruzzini, F. Beltram, and S. Heun: STM study of exfoliated few layer black phosphorus annealed in ultrahigh vacuum, *2D Mater.* 6 (2019) 015005.
2. Abhishek Kumar, Francesca Telesio, Deborah Prezzi, Claudia Cardoso, Alessandra Catellani, Stiven Forti, Camilla Coletti, Manuel Serrano-Ruiz, Maurizio Peruzzini, Fabio Beltram, and Stefan Heun: Black Phosphorus n-type doping by Cu: a microscopic surface investigation, *J. Phys. Chem. C* 125 (2021) 13477.