Black Phosphorus: Pristine and doped surface investigations using Scanning Tunneling Microscopy

Exfoliated black phosphorus (bP) attracted great interest after its first realization in 2014 for its interesting properties such as a band gap tunable with layer number and electrical and optical properties anisotropic in plane. However, surface studies on this material have been hampered because of its high reactivity with oxygen and water. We developed a protocol to study the surface of exfoliated bP by Scanning Tunneling Microscopy (STM). After achieving atomic resolution, we applied this protocol to controlled desorption experiments and studied the anisotropic craters that form on the surface with annealing close to desorption temperature.

Within the Cnr Nano SEED project 2017 SURPHOS we developed a procedure to exfoliate bP and mount the samples under nitrogen atmosphere in a glove bag on the sample holder for STM measurements. As a conducting flat substrate suitable for this technique, we use graphene on silicon carbide. That allows us to avoid any fabrication step and therefore to minimize environmental contamination of the samples. With this method, we obtain high quality samples, as demonstrated by the atomic resolution obtained on the bP flakes, shown in Fig. 1.
We study the modification of the surface upon annealing up to 550 °C. In particular, our attention is focused on the temperature range 375 °C–400 °C, when sublimation starts, and a controlled desorption from the surface occurs alongside with the formation of characteristic well-aligned craters. There is an open debate in the literature whether the crystallographic orientation of these craters is along the zigzag or the armchair direction [X. Liu et al., J. Phys. Chem. Lett. 6, 773 (2015); M. Fortin-Deschènes et al., J. Phys. Chem. Lett. 7, 1667 (2016)]. Thanks to the atomic resolution provided by STM, we are able solve the controversy, stating that the craters are one monolayer deep and identifying the orientation of the craters with respect to the bP crystal: the long axis of the craters is aligned along the zigzag direction of bP, as shown in Fig. 2 [1].
We also evaporated sub-monolayer copper in situ onto these exfoliated bP samples. From transport measurements, copper is known to n-dope bP [S. P. Koenig et al, Nano Lett. 16, 2145 (2016)] but no study of the microscopic mechanism has been performed so far. We investigate the samples by STM and scanning tunneling spectroscopy (STS). We observe an n-type doping of bP due to Cu islands as well as a band gap opening. Ab initio simulations complement the experimental observations.
Further activities on bP at Cnr Nano regard the study of longitudinal magneto transport at very high fields (in collaboration with McGill University Montreal) and the characterization of nanocomposites in which bP flakes are embedded in a polymeric matrix [2,3] (in collaboration with Cnr Iccom). This activity is part of the ERC Advanced grant PHOSFUN.

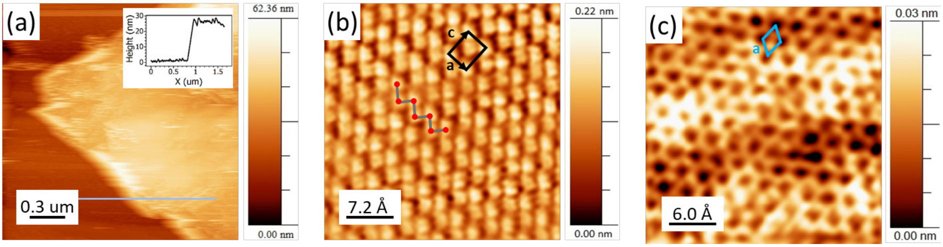

Fig. 1
STM images identifying bP flakes and graphene substrate. (a) STM image showing on the right a bP flake ~25 nm high above the graphene substrate on the left. The inset shows the height profile across the line shown in the STM image. Scan size: 2μm × 2 μm, imaging parameters: (0.7 V, 300 pA). Annealing conditions: 200 °C, 2 h. (b) Atomic resolution image obtained on bP at room temperature showing the zigzag pattern with unit cell parameters a = (3.45 ± 0.43) Å and c = (4.40 ± 0.12) Å. Scan size: 3.6 nm × 3.6 nm, imaging parameters: (0.7 V, 25 pA). Annealing conditions: 400 °C, 10 min. (c) Atomic resolution image on graphene. Unit cell indicated. Scan size: 3 nm × 3 nm, imaging parameters: (0.1 V, 157 pA). Annealing conditions: 450 °C, 2 h.

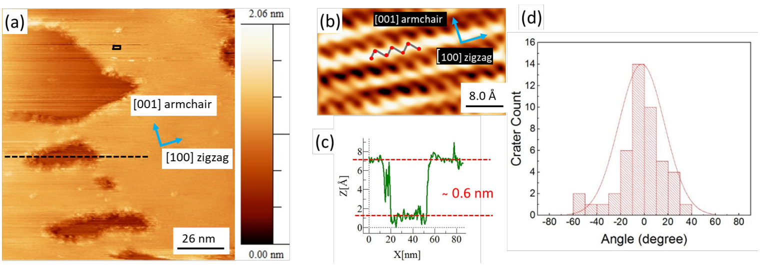

Fig. 2
Crystallographic direction of crater alignment. (a) STM image of a 130 nm × 130 nm scan area, showing aligned craters on bP after annealing at 400 °C for 2 h; scanning parameters: (1.2 V, 100 pA). (b) Atomic resolution image obtained after zooming into the region marked in (a), providing information of the crystallographic directions of the bP flake; scanning parameters: (1.2 V, 100 pA). (c) Height profile across the crater along the dashed line in (a), showing ~0.5 nm step height, compatible with monolayer desorption. (d) Histogram showing the distribution of crater angle orientation in one of the areas measured after annealing at 375 °C, 10 min. 0° corresponds to the horizontal axis in the image.

Contact persons

Francesca Telesio (francesca.telesio@nano.cnr.it)
Stefan Heun (stefan.heun@nano.cnr.it)

References

[1] STM study of exfoliated few layer black phosphorus annealed in ultrahigh vacuum. A. Kumar, F. Telesio, S. Forti, A. Al-Temimy, C. Coletti, M. Serrano Ruiz, M. Caporali, M. Peruzzini, F. Beltram, and S. Heun. 2D Mater. 6, 015005 (2019).
[2] Polymer-Based Black Phosphorus (bP) Hybrid Materials by in Situ Radical Polymerization: An Effective Tool to Exfoliate bP and Stabilize bP Nanoflakes. E. Passaglia, F. Cicogna, F. Costantino, S. Coiai, S. Legnaioli, G. Lorenzetti, S. Borsacchi, M. Geppi, F. Telesio, S. Heun, A. Ienco, M. Serrano-Ruiz, and M. Peruzzini. Chem. Mater. 30, 2036 (2018).
[3] Hybrid nanocomposites of 2D black phosphorus nanosheets encapsulated in PMMA polymer material: New platforms for advanced device fabrication. F. Telesio, E. Passaglia, F. Cicogna, F. Costantino, M. Serrano-Ruiz, M. Peruzzini, and S. Heun. Nanotechnology 29, 295601 (2018).