STM Study of Exfoliated Few Layer Black Phosphorus Annealing in Ultrahigh Vacuum (Oral contribution)

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After its exfoliation in 2014, black Phosphorus (bP) has emerged as a very interesting new member in the family of two-dimensional (2D) materials, due to its unique properties like layer-number-driven band-gap tunability and in-plane anisotropy. Surface-science studies on this material are of great interest for the bP community, but they are hindered by its high reactivity to oxygen and water, a major challenge to scanning tunneling microscopy experiments. As a consequence, the large majority of these studies have so far been realized by cleaving a bulk crystal in situ under vacuum[1-3]. Here we present a study of surface modification on exfoliated bP flakes upon subsequent annealing steps, up to 550 °C, well above the sublimation temperature. In particular, our attention is focused on the temperature range around 375 °C - 400 °C, when sublimation starts, and a controlled desorption from the surface occurs with the formation of characteristic well-aligned craters. There is an open debate in the literature about the crystallographic orientation of these craters, i.e. whether they align along the zig-zag[4] or the armchair[5] direction. Thanks to the atomic resolution provided by scanning tunneling microscopy, we are able, with a direct measurement, to identify the crystallographic orientation of the crystal with respect to the craters, and thus, their alignment: the long axis of the craters is aligned along the [100] (zig-zag) direction of bP. This allows us to solve this controversy, and, moreover, to provide insight in the desorption mechanism, since different mechanisms (namely P or P_2 desorption) lead to different orientations of the craters.

References:

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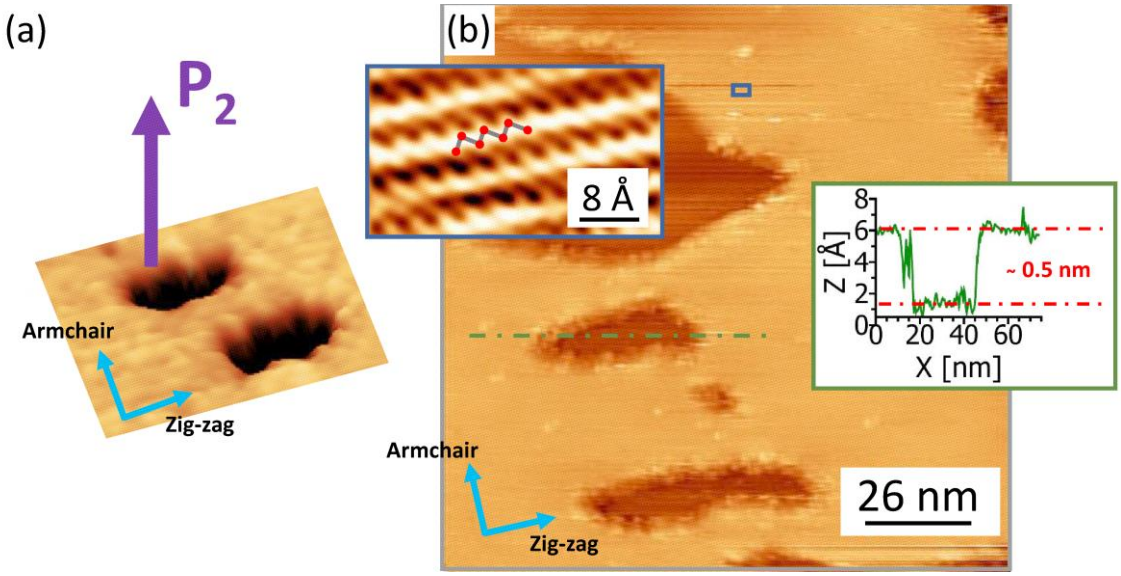

Fig 1. (a) Illustration of sublimation of phosphorus dimers from bP surface, forming craters with long axis parallel to [100] zig-zag crystallographic direction. (b) RT STM data showing atomically resolved images of bP surface near monolayer deep craters, providing crystallographic direction for crater orientation and underlying desorption mechanism.