STM Study of Exfoliated Few Layer Black Phosphorus Annealed in Ultrahigh Vacuum

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Abstract

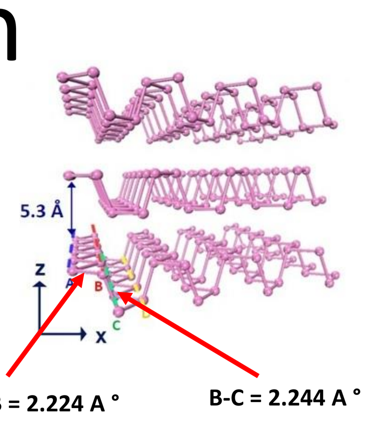
Black Phosphorus (bP) has emerged as an interesting addition to the category of two-dimensional materials. Surface-science studies on this material are of great interest, but they are hindered by bP's high reactivity to oxygen and water, a major challenge to scanning tunneling microscopy (STM) experiments. As a consequence, the large majority of these studies were realized by cleaving a bulk crystal in situ. 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 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, whether they align along the zig-zag or the armchair direction. Thanks to the atomic resolution provided by STM, we are able to identify the orientation of the crystal with respect to the craters: the long axis of the craters is aligned along the zig-zag direction of bP. This allows us to solve this controversy, and, moreover, to provide insight in the underlying desorption mechanism leading to crater formation.

Introduction

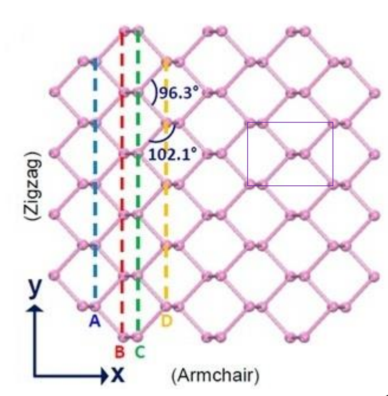
Black Phosphorus

- Puckered Layered material of elemental phosphorous – most stable allotrope
- First successfully obtained from white Phosphorus (1.2 GPa & 200°C) by Brigdman in 1914

P. W. Bridgman, J. Am. Chem. Soc., 1914, **36** (7), 1344.



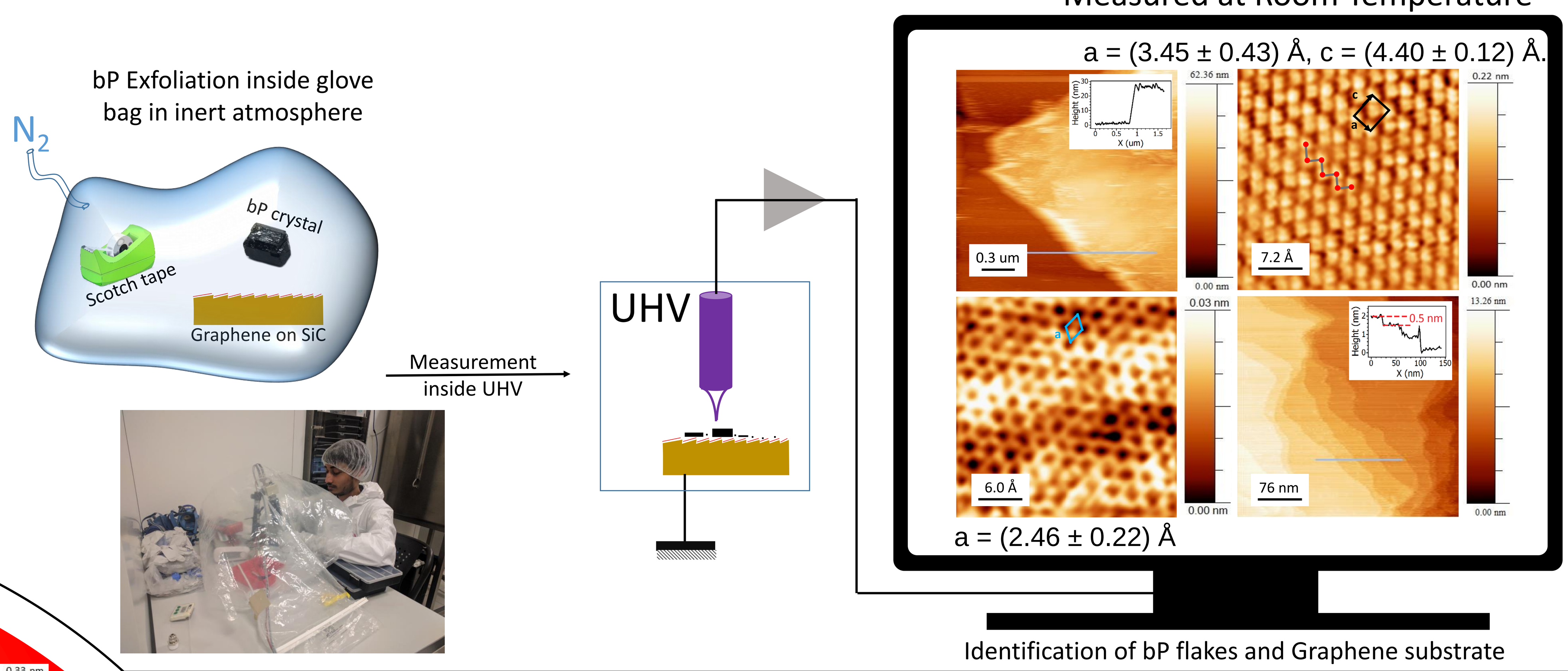
Phosphorene



- Single Layer of Black Phosphorus
- Honeycomb network similar to Graphene
- Exfoliated in 2014
- Armchair along X and Zig-Zag along Y
- Tunable bandgap ~ 0.3 – 2.0 eV

X. Ling et al., PNAS 2015, **112** (15), 4523.

Sample Preparation and STM



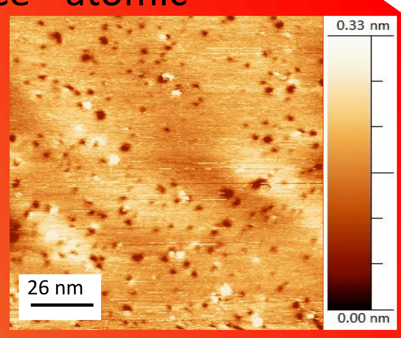
Annealing Experiment

Annealing Strategy

- Annealed in steps of 50 °C inside UHV chamber
- Measured by STM after each annealing step
- Starting temperature: 150 °C

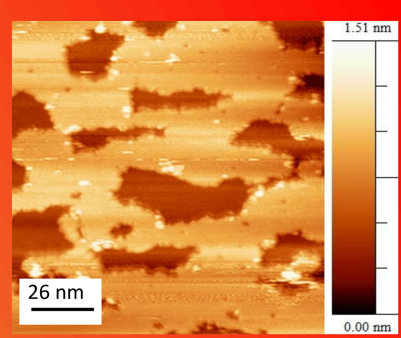
300 °C

- Clean surface - atomic resolution
- Some defects - dark and bright spots



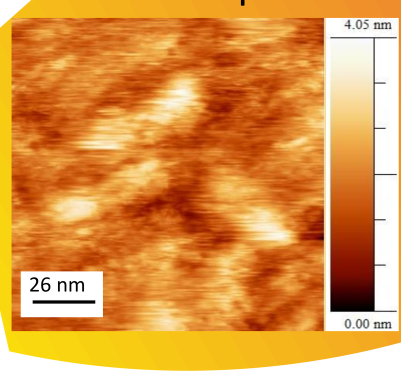
400 °C

- Phosphorus starts desorbing
- Formation of craters on the surface



500°C

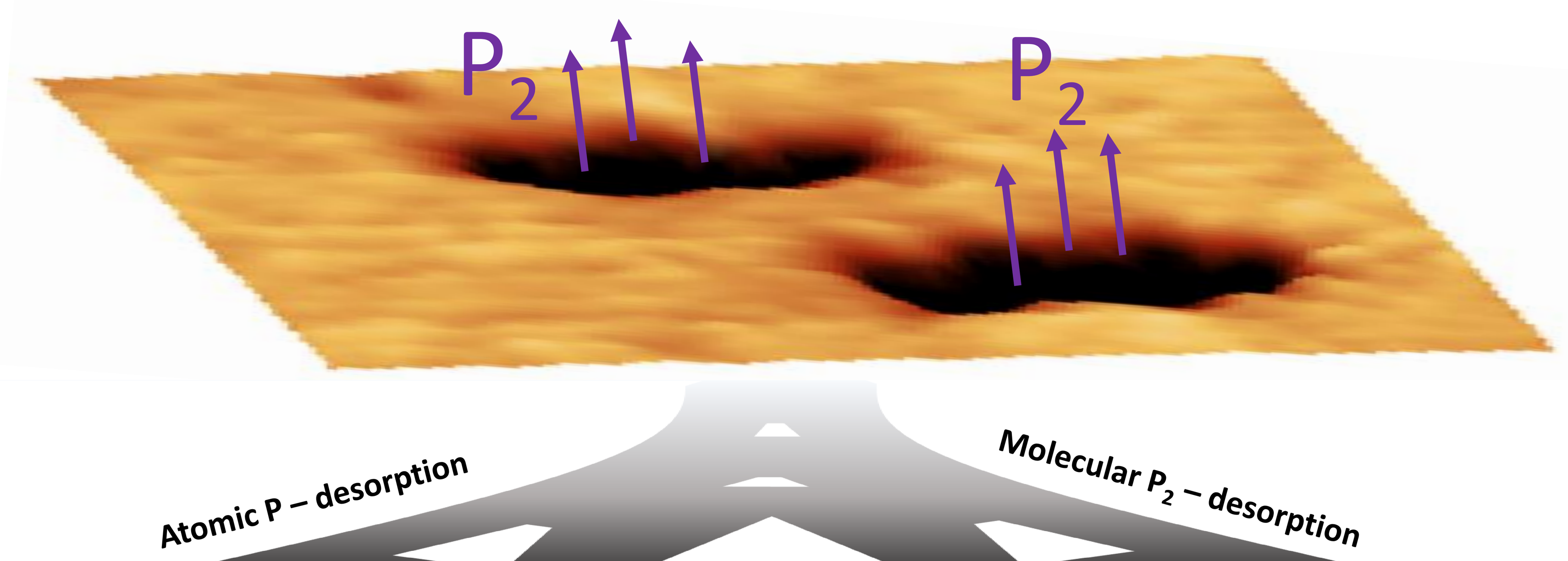
- Above sublimation temperature – higher desorption
- Surface becomes quite rough



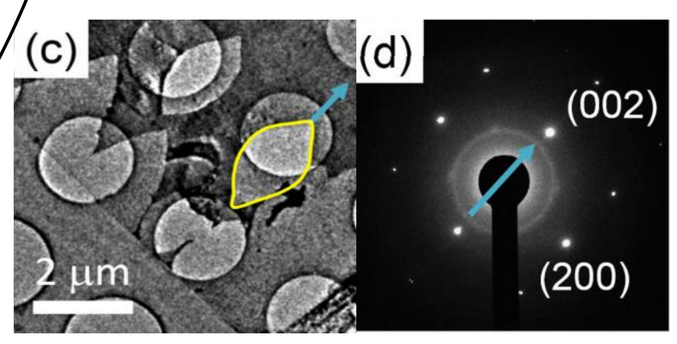
600 °C

- Much above than the sublimation temperature
- Most of the flakes desorbed Flake density decreased by more than one order of magnitude.

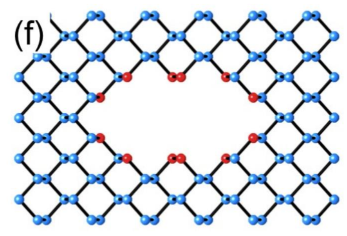
Phosphorus Desorption



Armchair



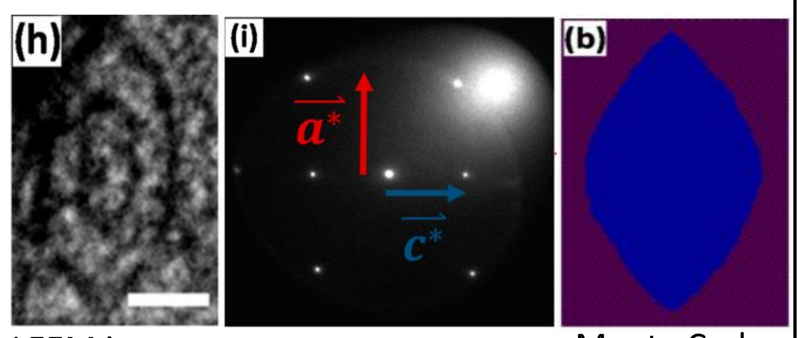
TEM image — Selected Area Diffraction (SAD) pattern



(f) Modelling by removal of P atoms - Preferential order of removal:
(a) Singly bonded P
Doubly bonded P
(b) Two A-B bonds
(c) One A-B, one B-C bond

Xiaolong Liu et. al., J. Phys. Chem. Lett. 2015, **6** (5), 773.

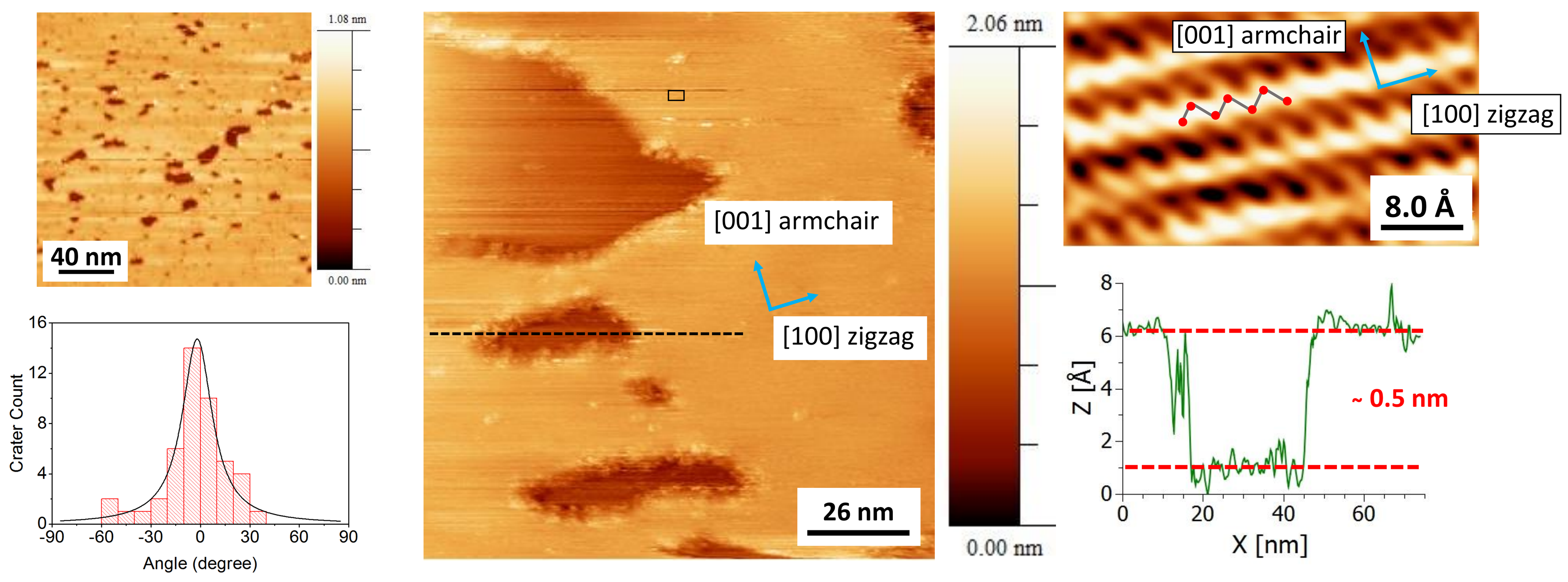
Zig-Zag



LEEM image (460 × 720 nm²) — LEED pattern — Monte Carlo simulation for P_2 desorption

M. F. Deschenes et. al., J. Phys. Chem. Lett. 2016, **7** (9), 1667.

Our measurement – craters aligned along zig-zag



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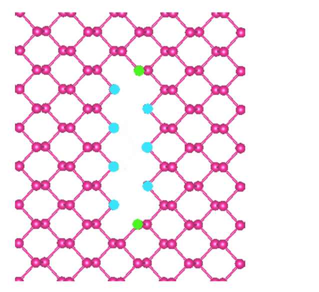


Typical Flakes

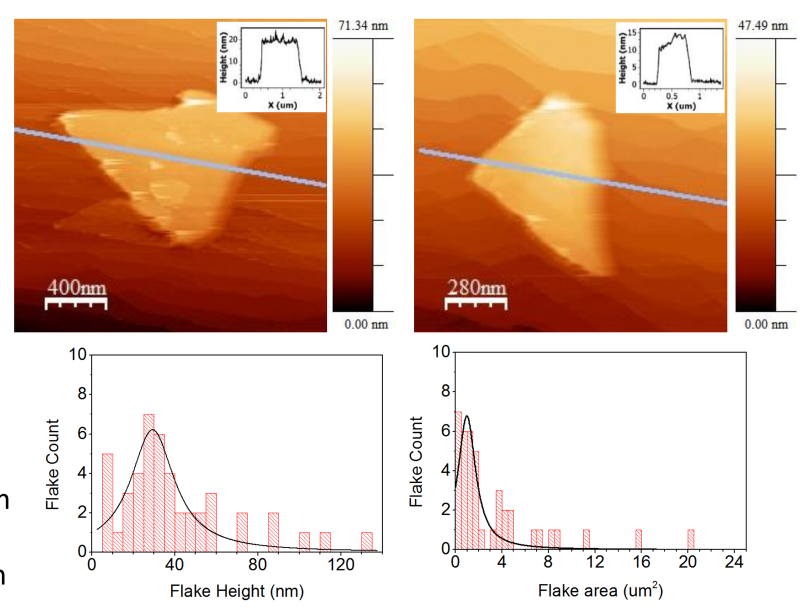
Average height - (37.5 ± 22.4) nm (from 42 flakes)

Average area - (2.7 ± 3.2) µm² (from 36 flakes)

Lorentzian fit of the histogram gives the nominal values for flakes:

height of (29.1 ± 1.6) nm with FWHM (25.8 ± 4.9) nm

area of (1.0 ± 0.1) µm² with FWHM of (1.7 ± 0.3) µm²



References

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A. Kumar et. al., 2018, submitted.

Conclusion and Acknowledgements

In summary, our study provides information on the annealing conditions (300 °C - 350 °C) yielding stable and clean bP flakes. It indicates the onset of sample modification (375 °C - 400 °C) by eye-shaped crater formation due to desorption and further degradation of the sample at higher temperatures (450 °C - 500 °C). Furthermore, we examined the craters' preferential long-axis alignment and assigned it to the crystallographic [100] (zigzag) direction. This supports molecular P_2 desorption as the dominating sublimation mechanism in these bP flakes. The present is the first surface morphological study of exfoliated few layer bP using STM and provides insight on surface behavior and its degradation with temperature. The latter properties are of much importance in view of the limitations on thermal processing of bP for any practical application of this material.

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