

STM studies of exfoliated black Phosphorus

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M. Peruzzini³, F. Beltram^{1,2}, S. Heun¹

¹NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, 56127 Pisa, Italy

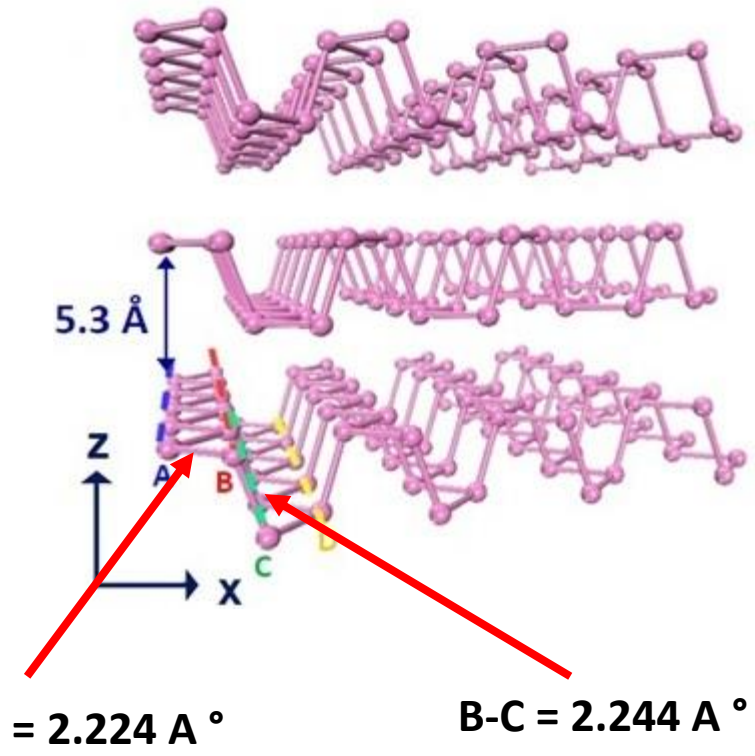
²Center for Nanotechnology Innovation @NEST, Istituto Italiano di Tecnologia, 56127 Pisa, Italy

³CNR-ICCOM, Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy

Introduction

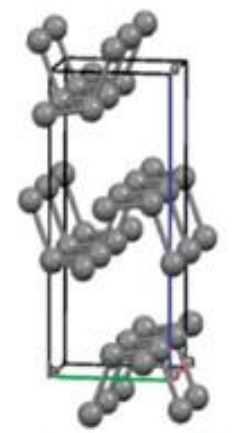
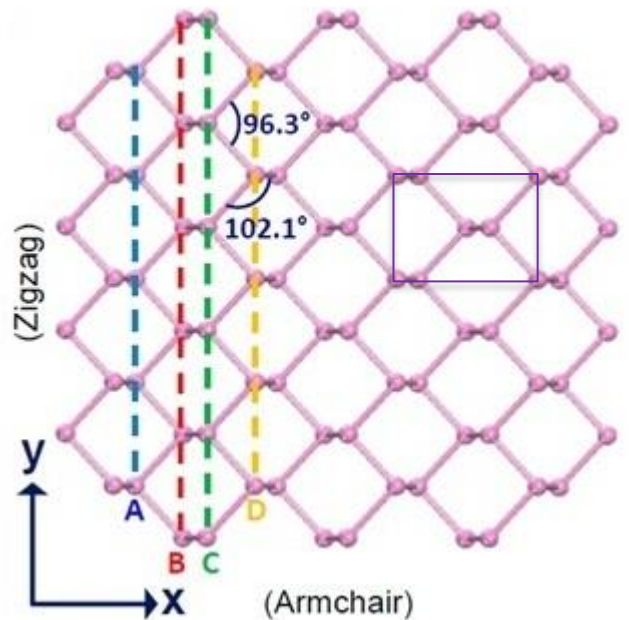
Black Phosphorous

- Puckered Layered material of elemental phosphorous
- Most stable allotrope of the phosphorus
- First successfully obtained from white P. (1.2 GPa & 200°C) by Bridgman in 1914



Phosphorene

- Single Layer of Black P
- Honeycomb network similar to Graphene.
- Exfoliated in 2014
- Armchair along X and Zig-Zag along Y



Orthorhombic Structure

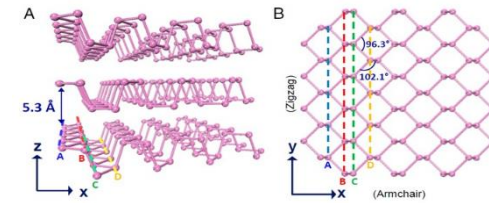
$a = 3.31 \text{ \AA}$

$b = 4.38 \text{ \AA}$

$c = 10.50 \text{ \AA}$

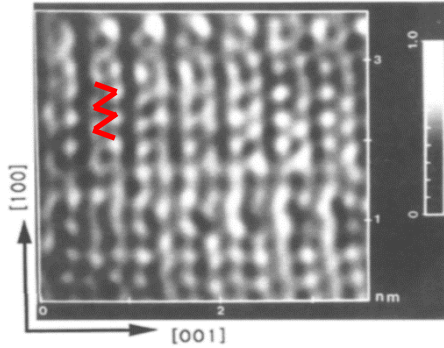
$\alpha = \beta = \gamma = 90^\circ$

STM works on black Phosphorus

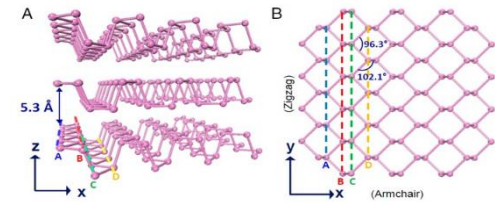


➤ Cleaved bP in air - (010) surface

S. L. Yau et. al. Chem, Phys, Lett, 1992, Vol-198, no.-3,4; page-383

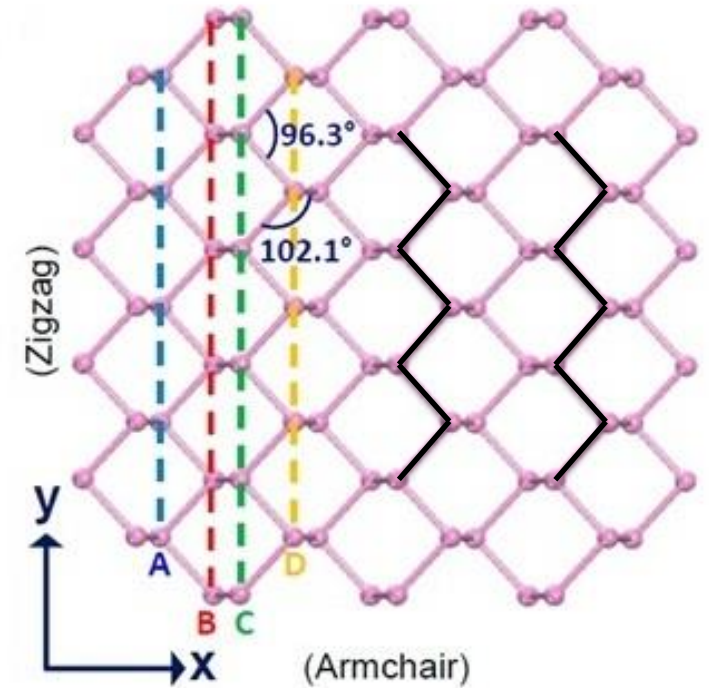
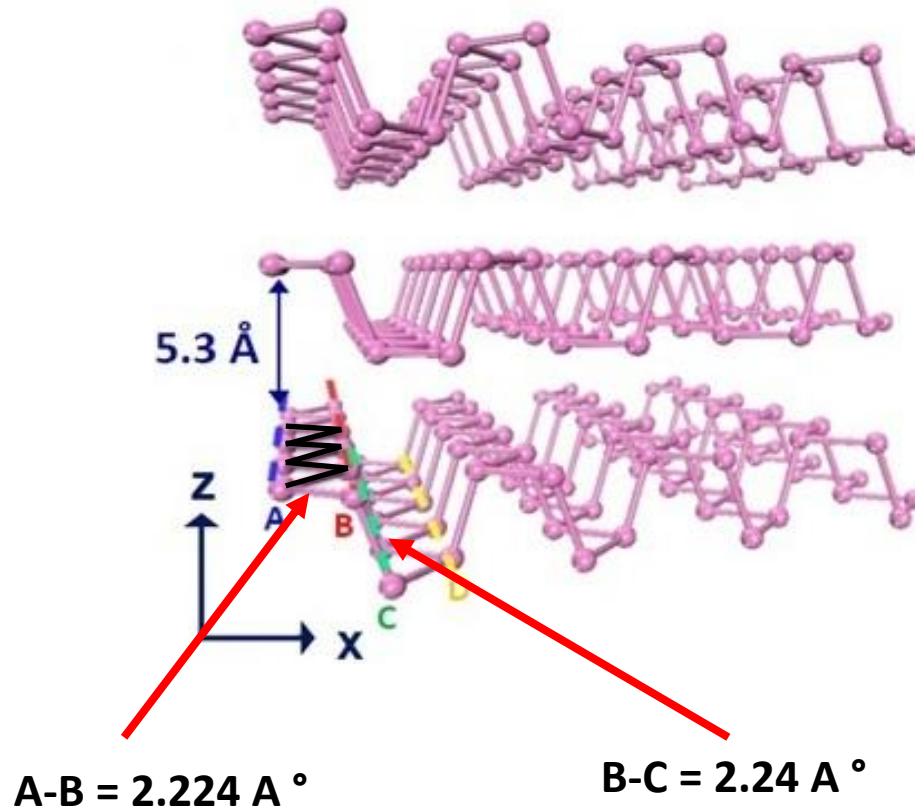
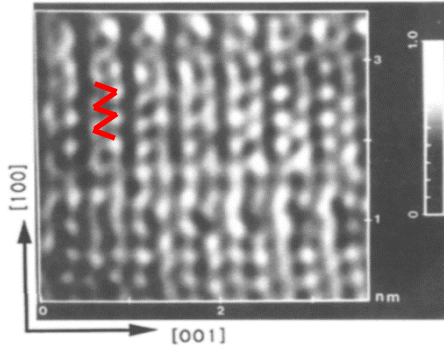


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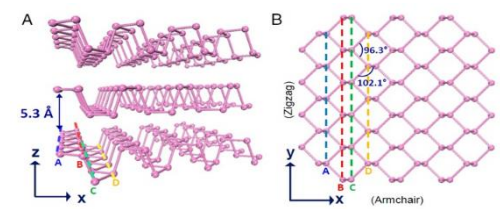


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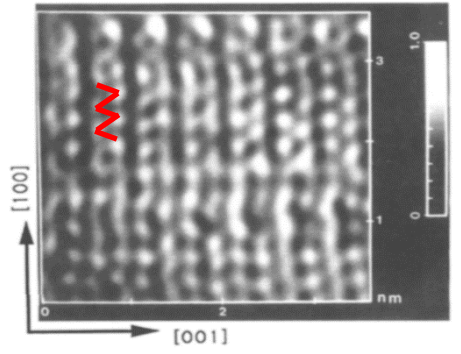


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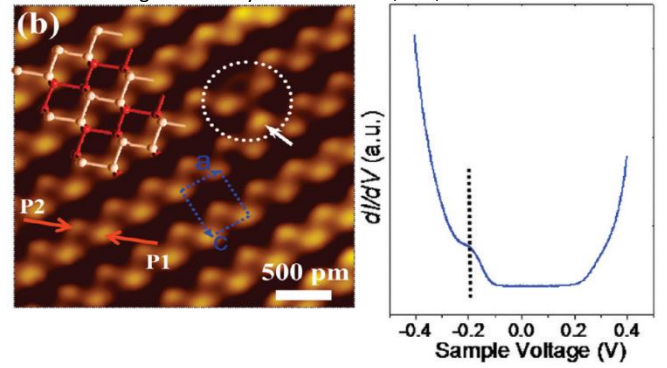
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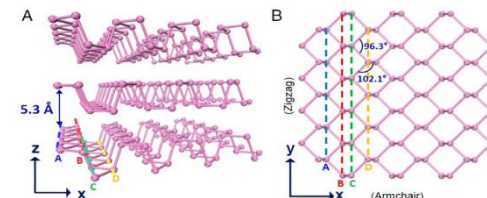
➤ Cleaved bP in dry N₂ – measured at 77K and 4.3K

- Band gap of 0.4 eV
- Peak at -0.17 V due to a surface state

C. D. Zhang et. al. J. Phys. Chem. C 2009, 113, 18823

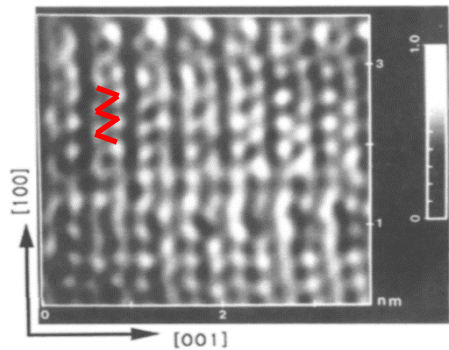


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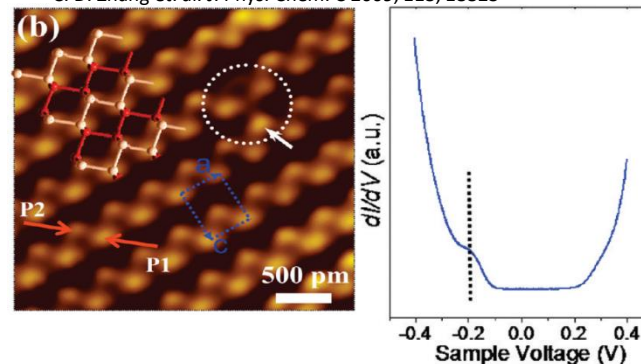
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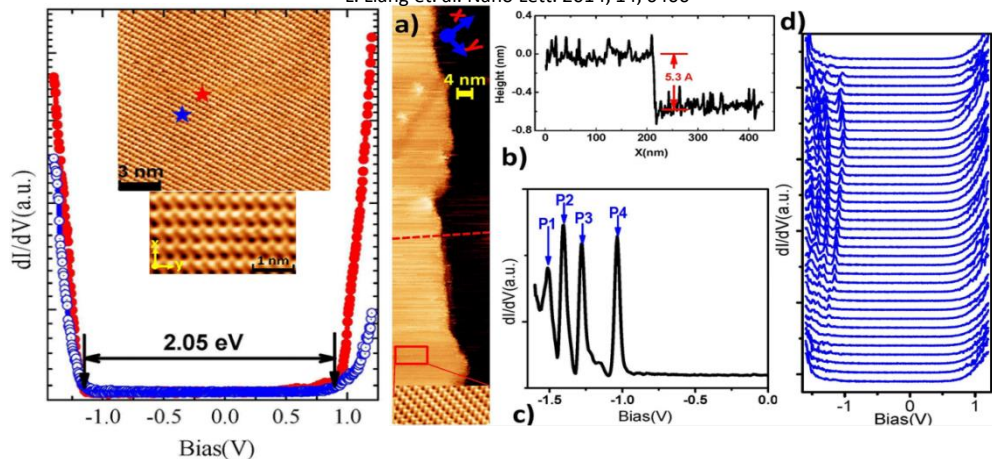
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➤ BP single crystal cleaved at RT in UHV – measured at 80K

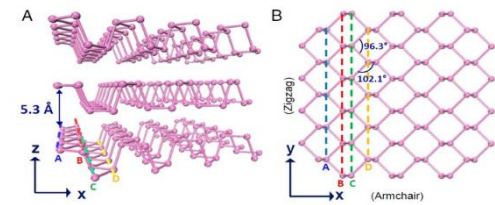
L. Liang et. al. Nano Lett. 2014, 14, 6400



Band gap of 2.05 eV

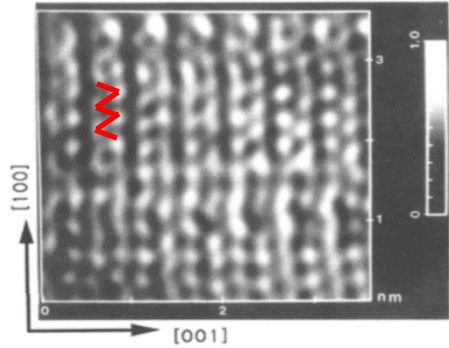
Edgestates

STM works on black Phosphorus



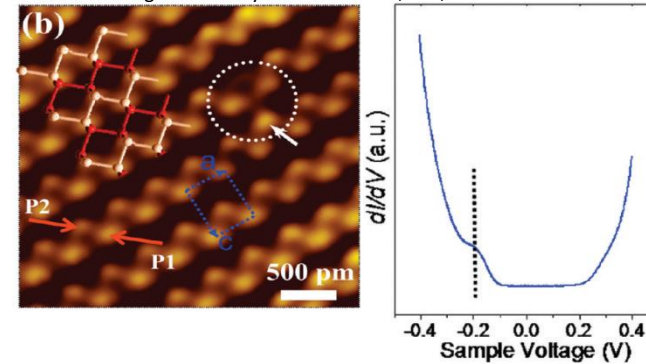
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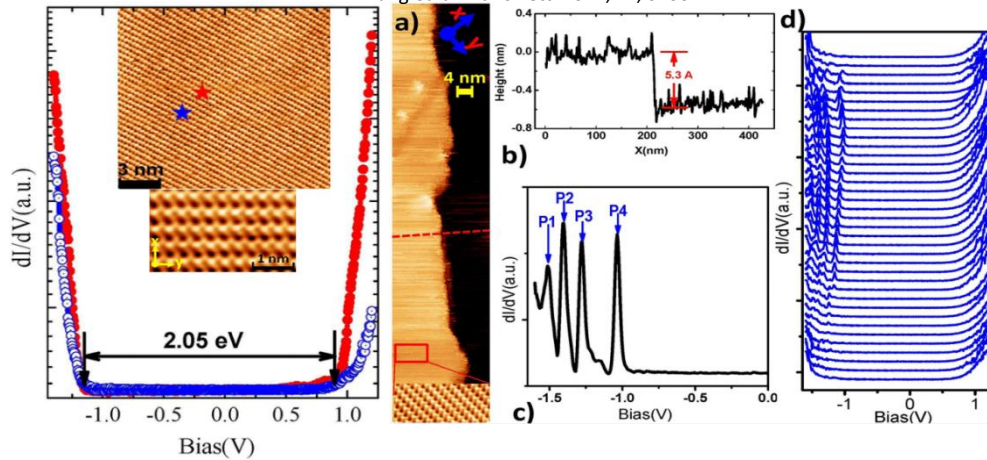
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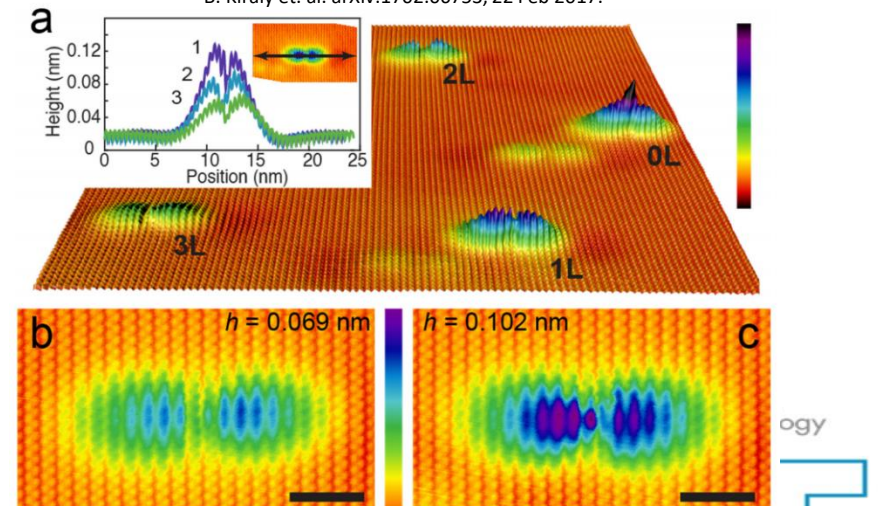


Band gap of 2.05 eV

Edgestates

➤ Single Vacancies in BP – measured at 4.6K

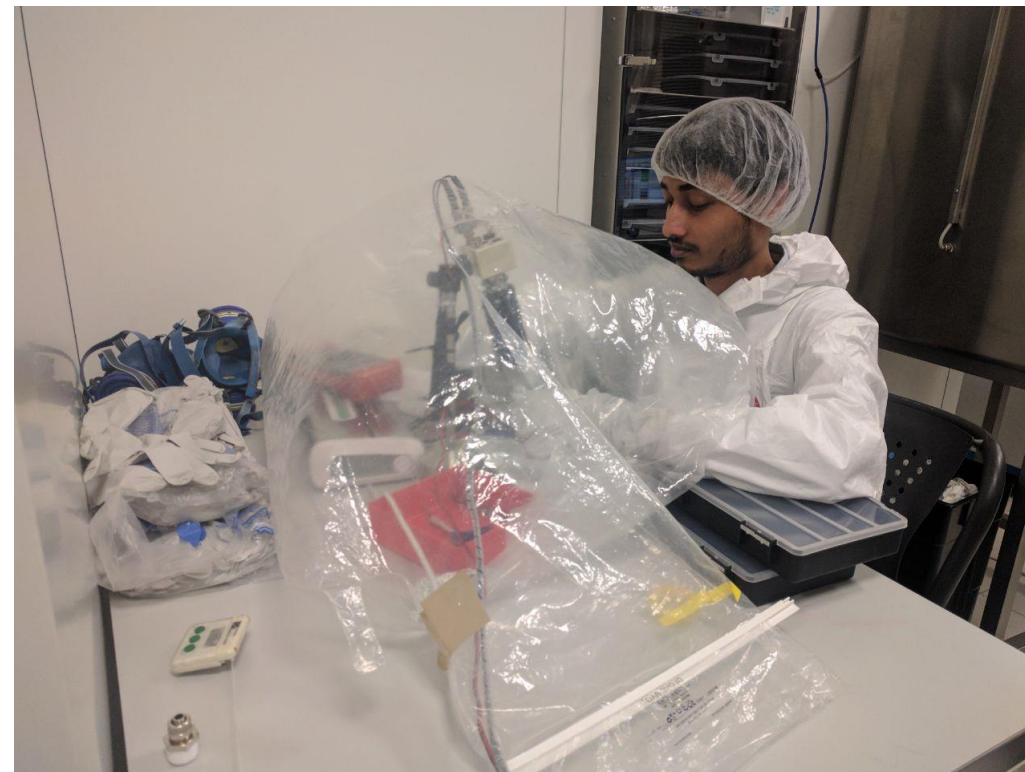
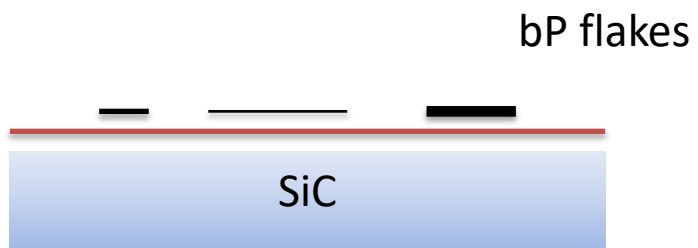
B. Kiraly et. al. arXiv:1702.06753, 22 Feb 2017.



Sample Preparation

- Monolayer epitaxial graphene on silicon carbide is used as the substrate
- bP exfoliation on the substrate and sample transfer to the STM is done inside a glove bag, with N_2 flowing through it – which provides inert atmosphere resulting in high sample quality

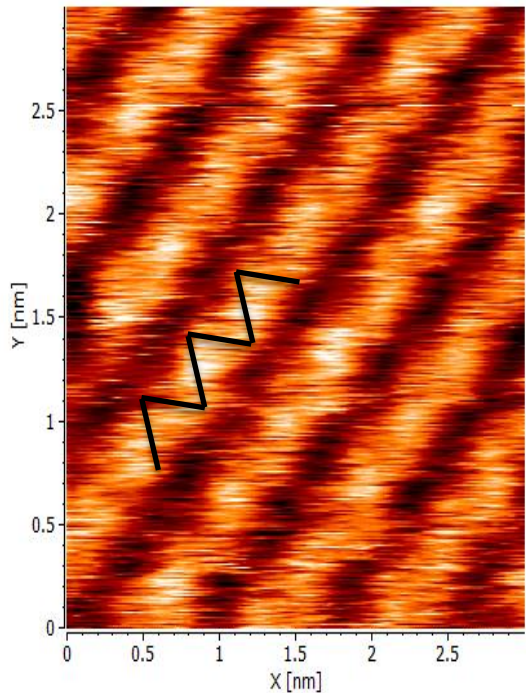
Graphene



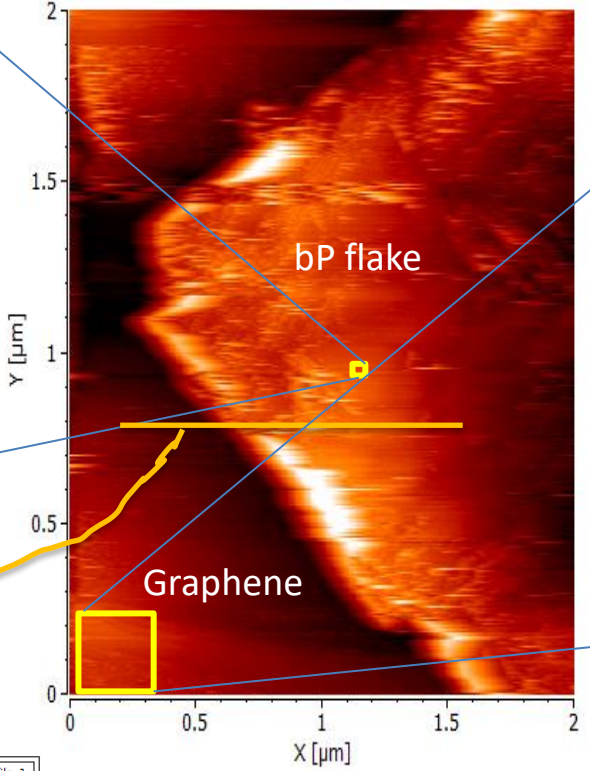


Clear identification of flakes and substrate

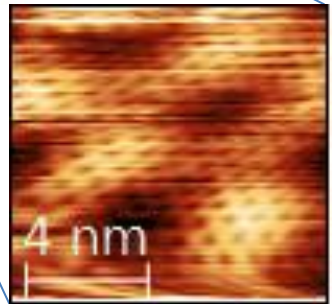
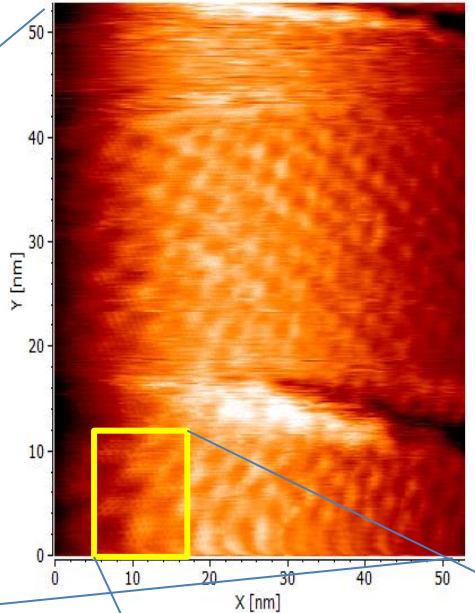
Z 33-1 (fwd-down)



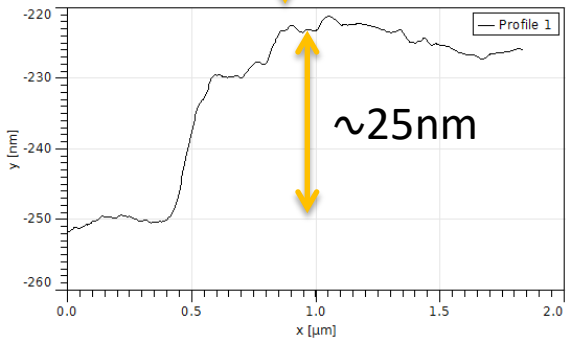
Z 55-1 (fwd-up)



Z 59-1 (fwd-up)



bP flake

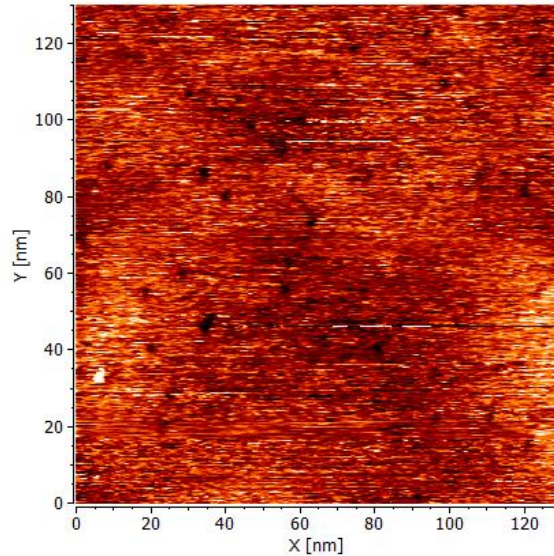


Typical Flake Dimensions
Area ~ 1 μm^2
Height ~ 30 nm

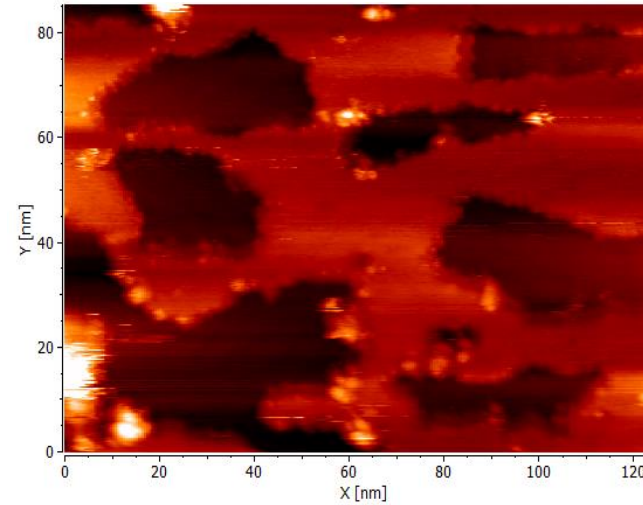
Annealing Experiments

- Sample annealed for 2 hours at temperatures in 50°C succession
- 300°C - 350°C – nice temperature for cleaning the surface – atomic resolution images
- 375°C - 400°C – formation of craters due to increased desorption of the Phosphorus atoms
- beyond 400°C – a sudden increase in the surface roughness
- 550°C – most of the flakes desorbed

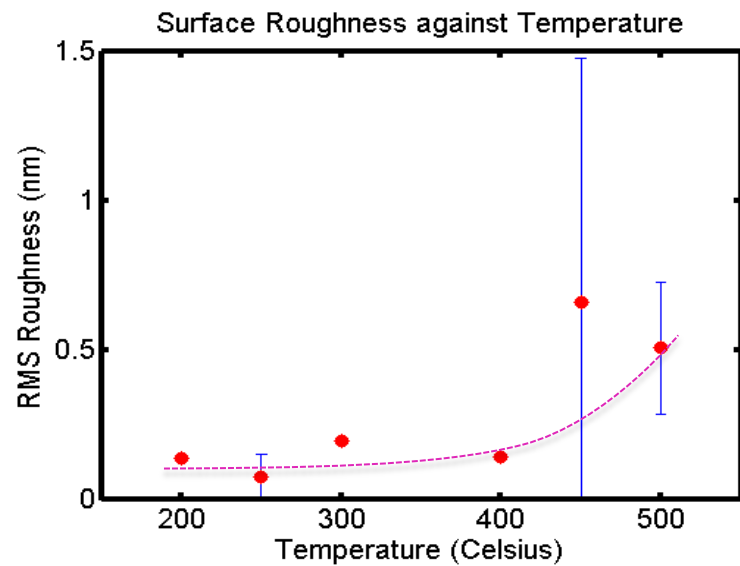
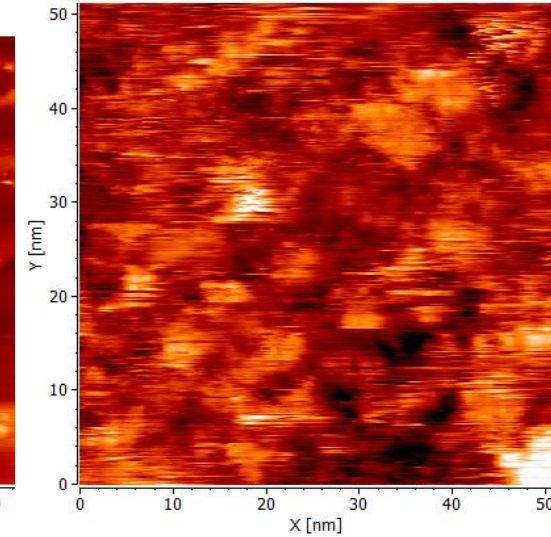
250°C, 2hrs



400°C, 10 min

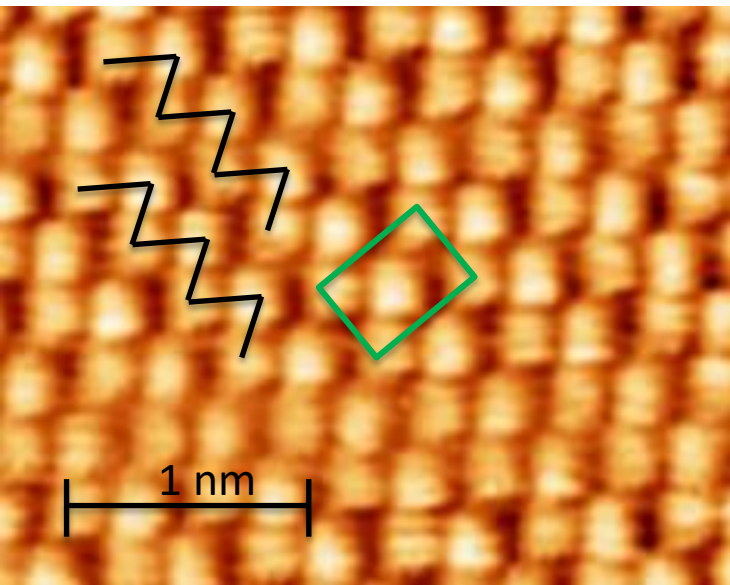
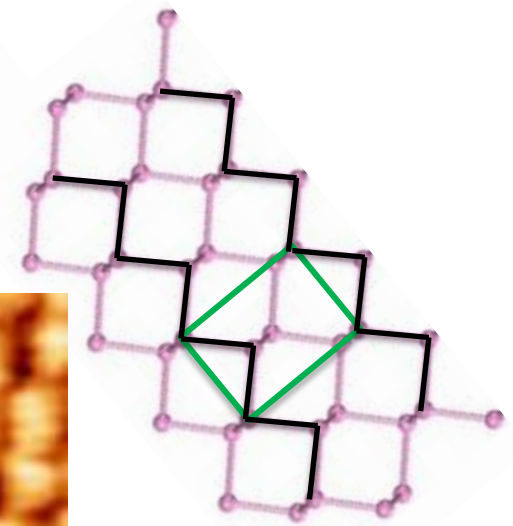


500°C, 2hrs



Atomic Resolution

Measured at RT
 $a = 3.25 \pm 0.04 \text{ \AA}$
 $c = 4.66 \pm 0.18 \text{ \AA}$



Measured parameters are in agreement to the reported and predicted values

TABLE 1: Measured Surface Lattice Constants and Theoretical Optimized Results Together with Previous Data of Bulk BP

reported by Morita ⁷	measured from STM images	theoretical optimized results
$a = 3.313 \text{ \AA}$	$a = 3.33 \text{ \AA}$	$a = 3.28 \text{ \AA}$
$b = 10.473 \text{ \AA}$		$b = 10.37 \text{ \AA}$
$c = 4.374 \text{ \AA}$	$c = 4.33 \text{ \AA}$	$c = 4.35 \text{ \AA}$
$d_1 = 2.222 \text{ \AA}, \alpha_1 = 96.5^\circ$		
$d_2 = 2.777 \text{ \AA}, \alpha_2 = 101.9^\circ$		

Morita, A et. al. Appl. Phys. A: Mater. Sci. Proc. 1986, 39, 227.

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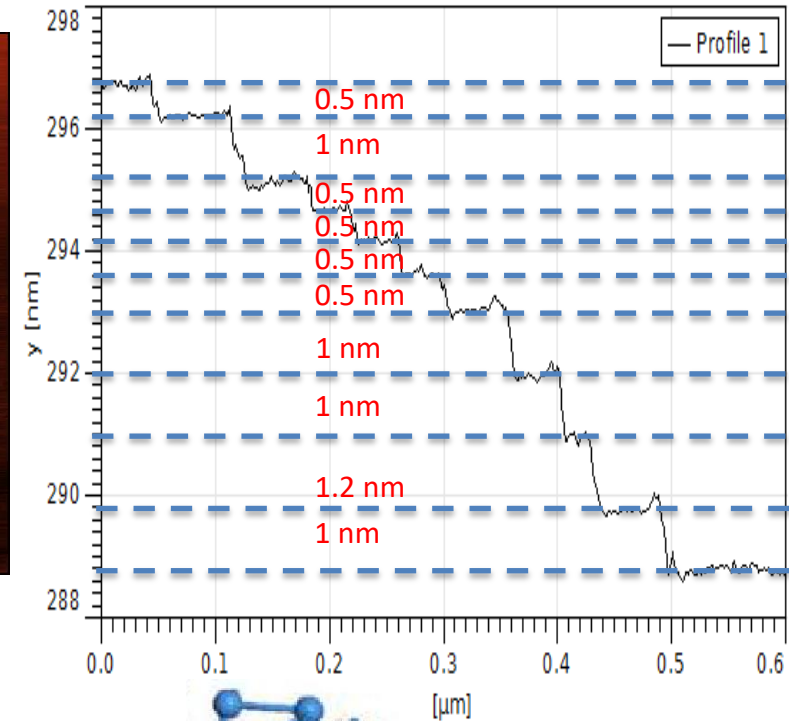
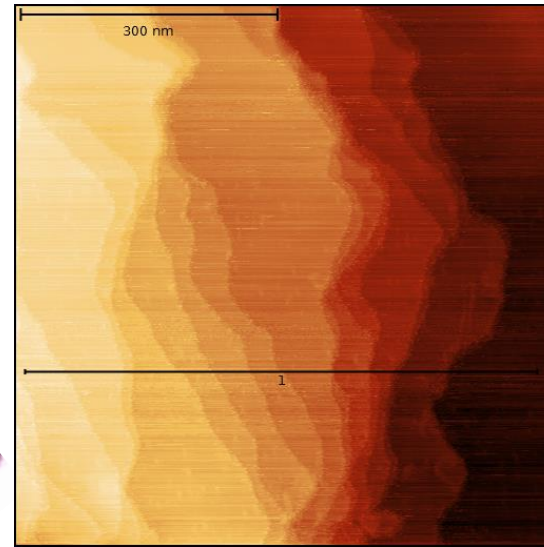
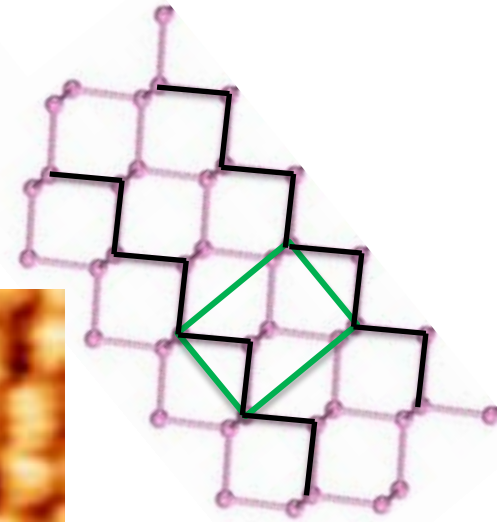
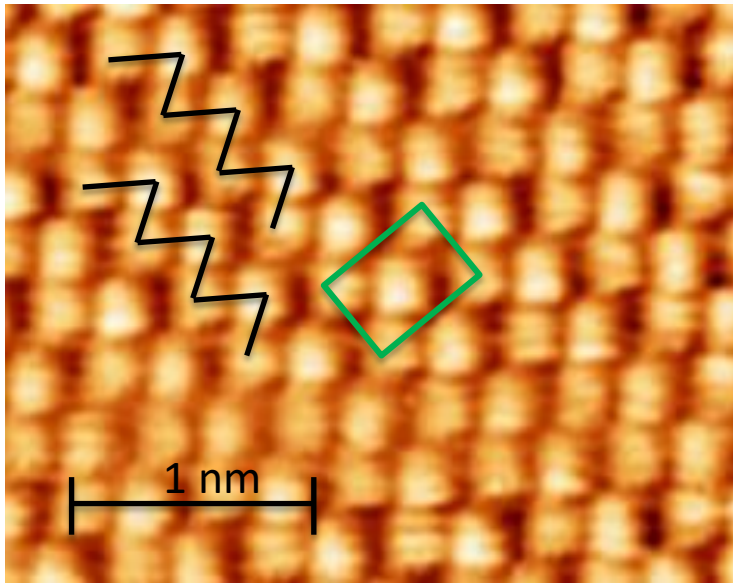
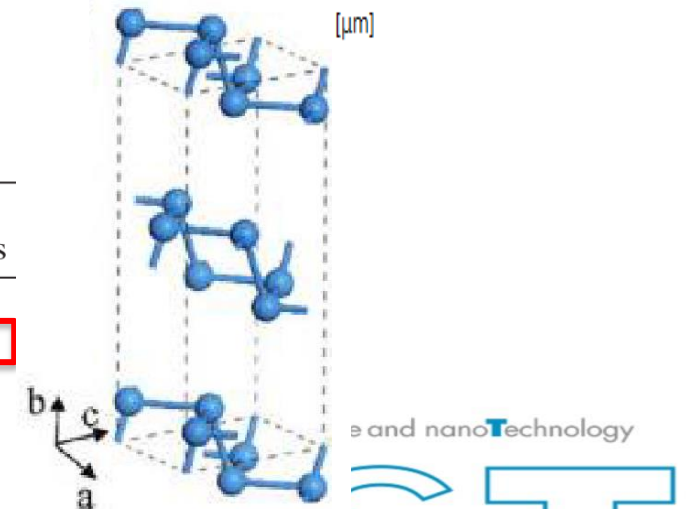


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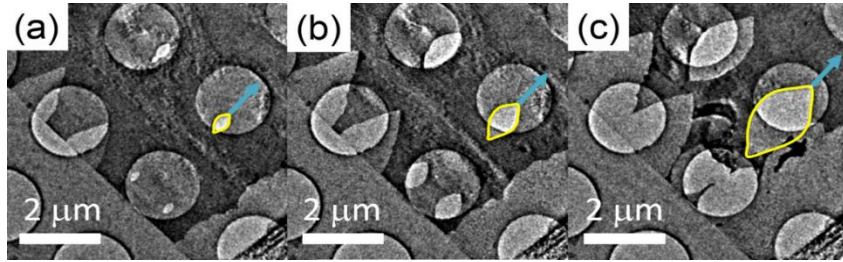
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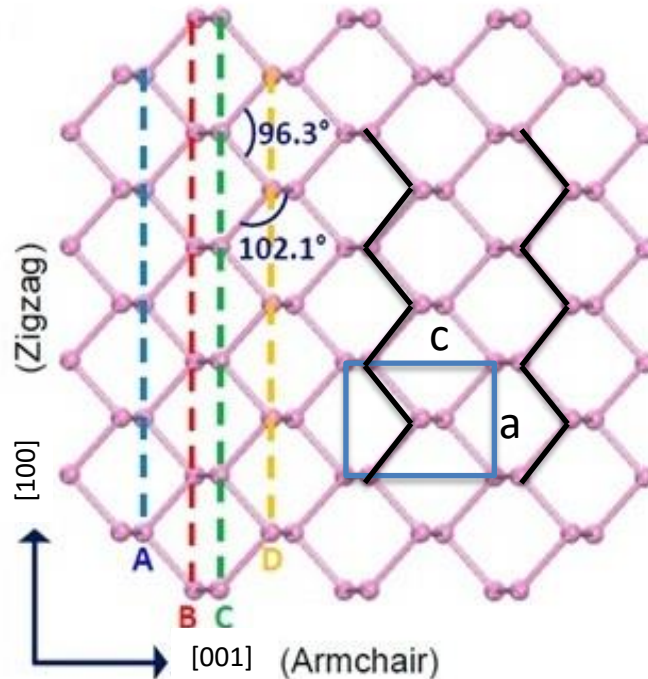
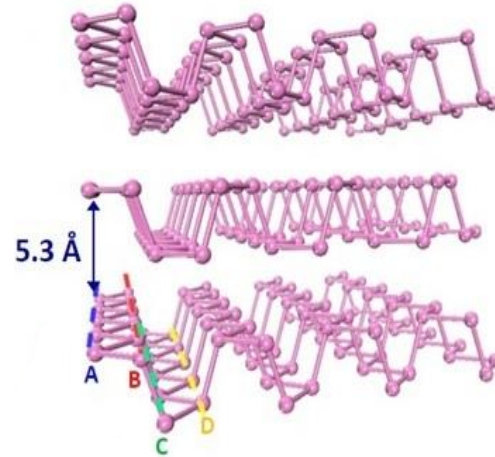
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bP desorption with annealing

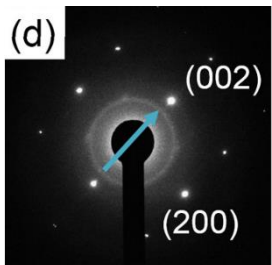
Xiaolong Liu et. al., J. Phys. Chem. Lett. 2015, 6, 773.



TEM image of eye shaped crack opening on heating bP flake at 400°C for 5, 8 and 12 min.

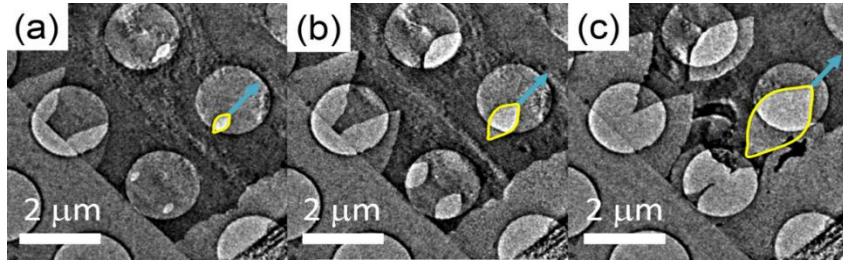


- decomposition of 2D BP is observed to occur at ~ 400 °C in vacuum, in contrast to the 550 °C bulk BP sublimation temperature
- This decomposition initiates via eye-shaped cracks along the [001] direction

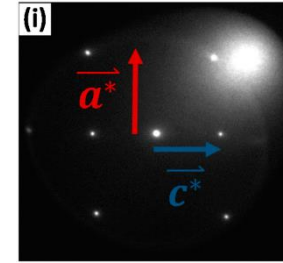
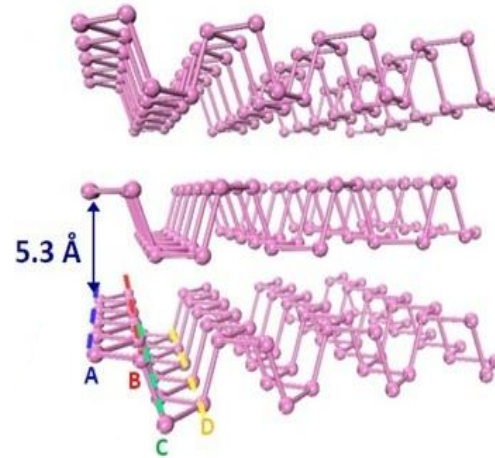


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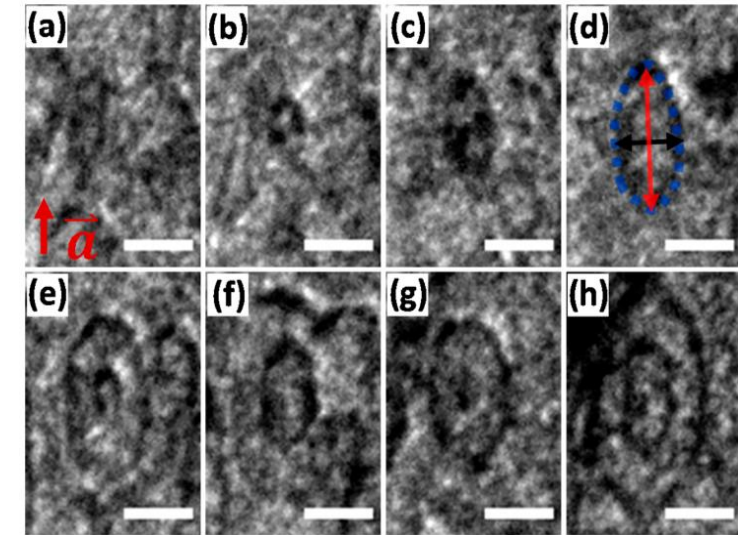
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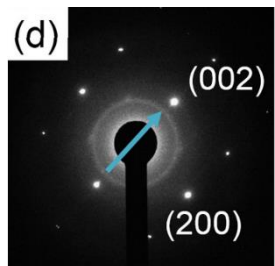
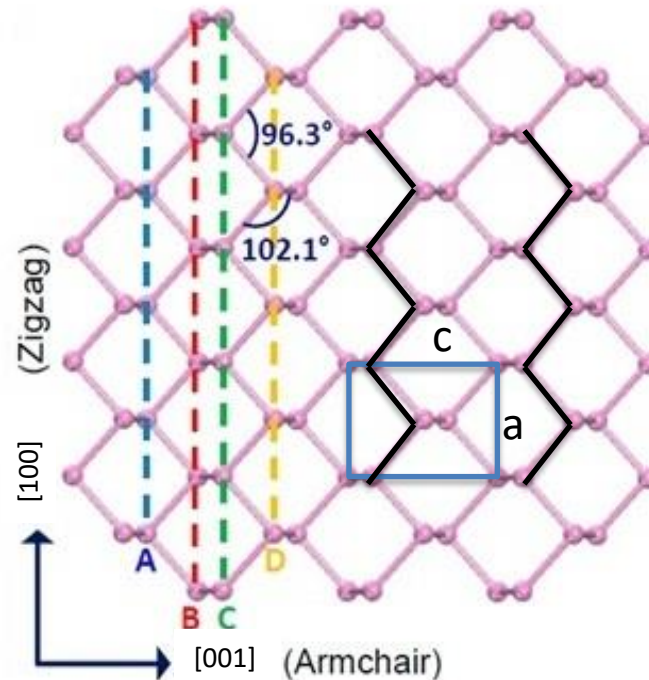


M. F. Deschenes et. al., J. Phys. Chem. Lett. 2016, 7, 1667.



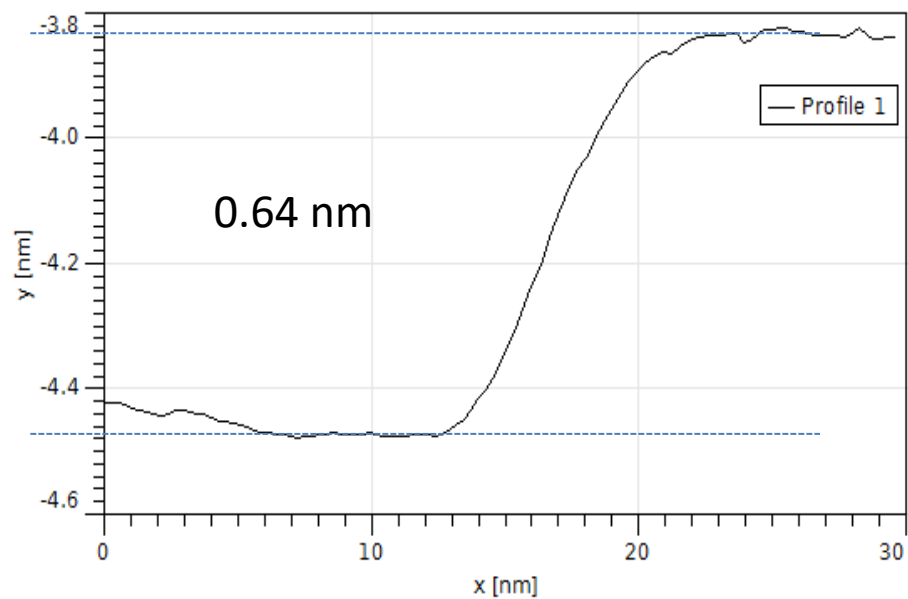
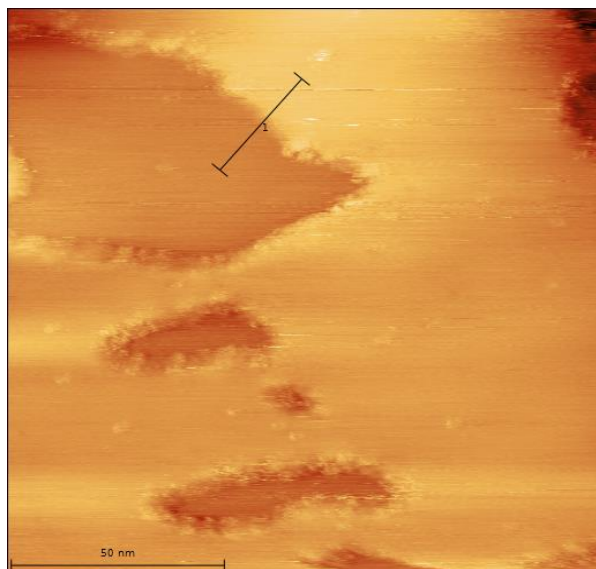
Bright-field LEEM snapshots of hole expansion during sublimation of exfoliated bP. Two seconds between each image from (a) to (h) recorded respectively at the following temperatures: 486 °C, 488 °C, 490 °C, 491 °C, 493 °C, 495 °C, 497 °C, and 499 °C.

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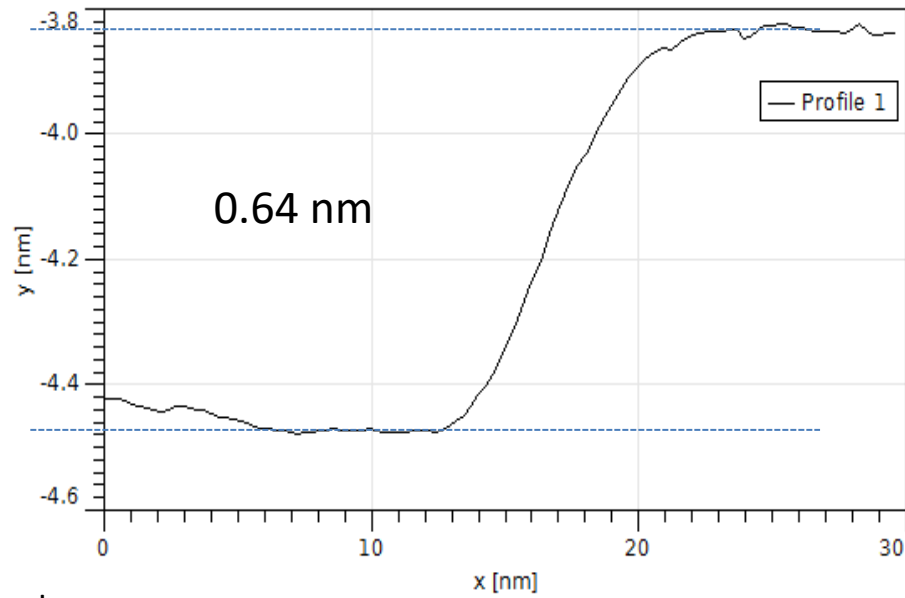
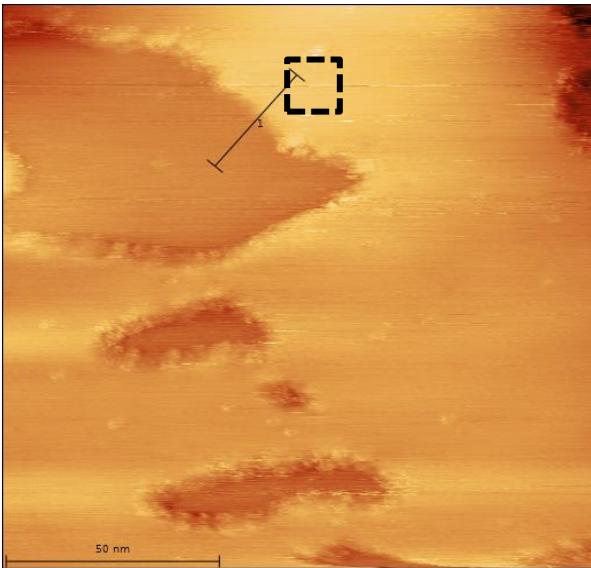


- Sublimation manifests itself above 375 ± 20 °C
- Faceted holes with the long axis aligned along the [100] direction, **in contrast to what was reported earlier**

bP craters alignment

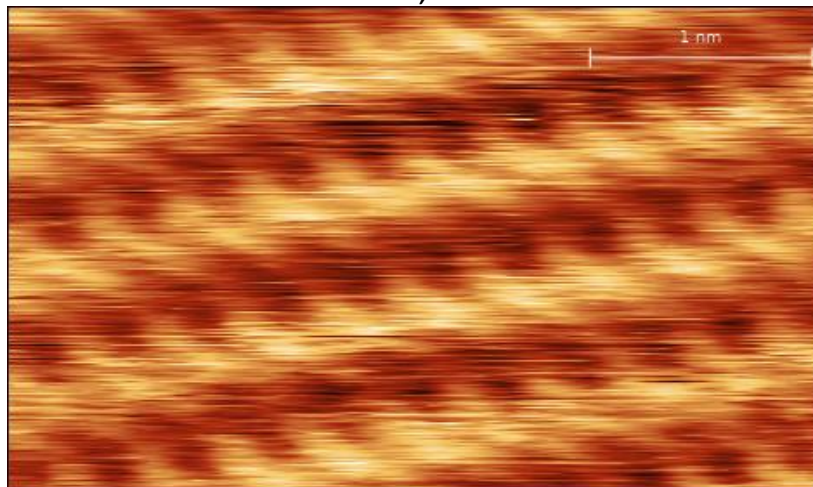


bP craters alignment

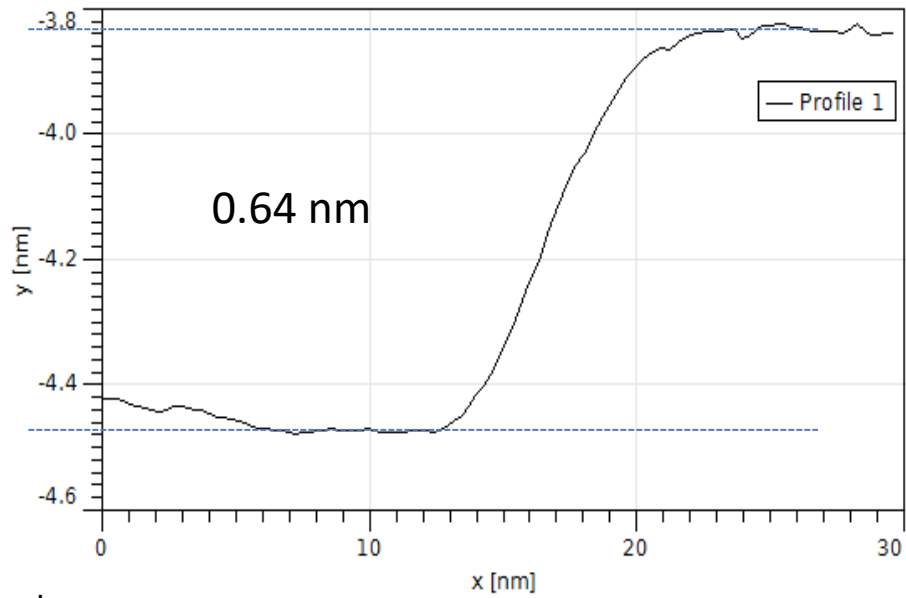
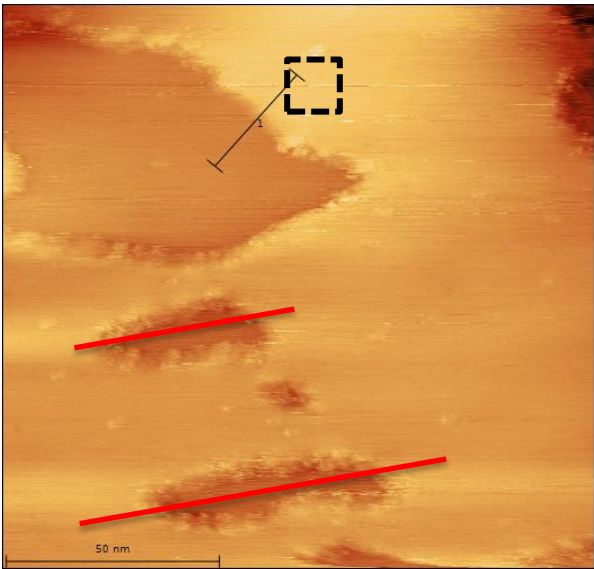


Measured Unit cell parameters

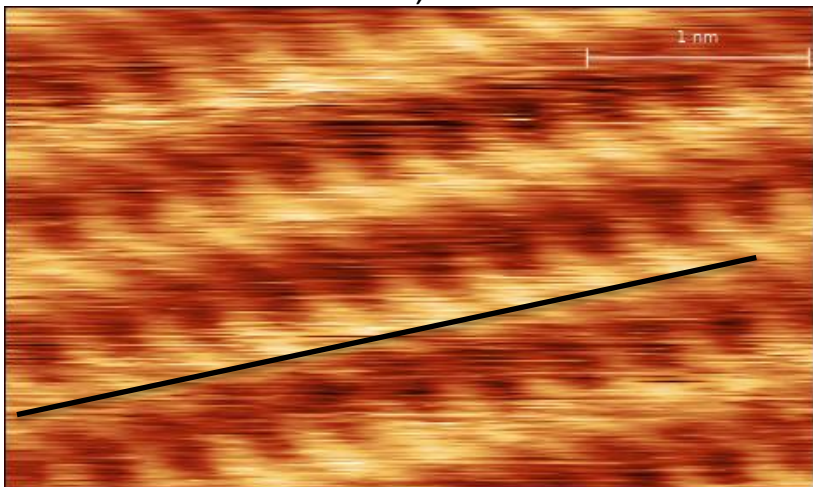
$A=0.367$ nm, $C=0.598$ nm



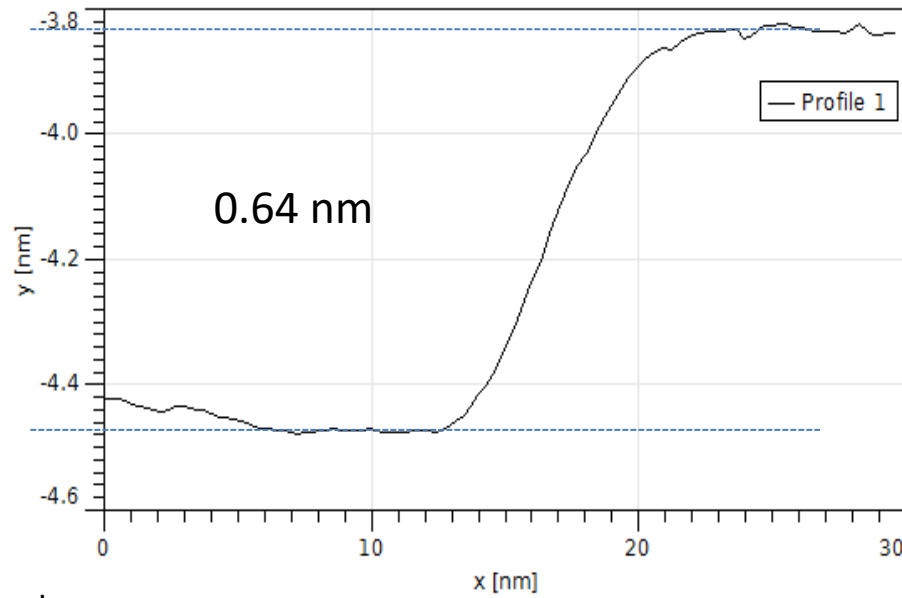
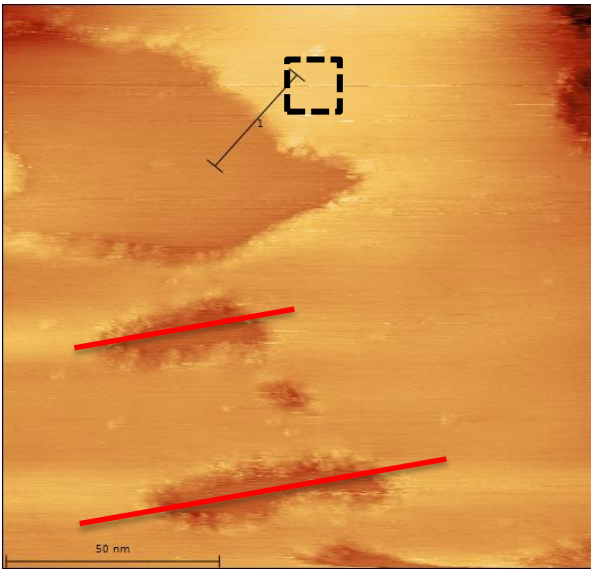
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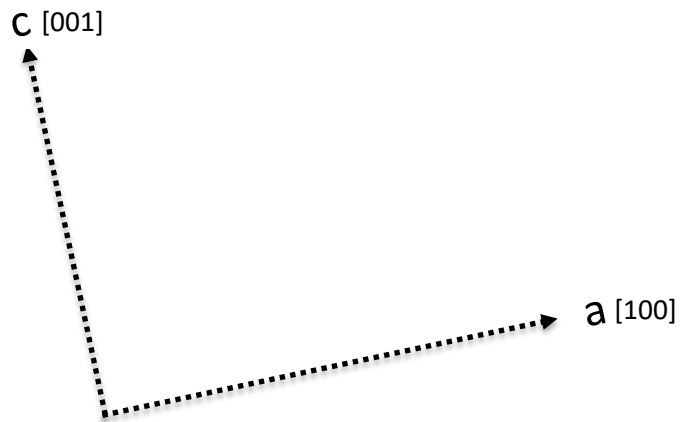
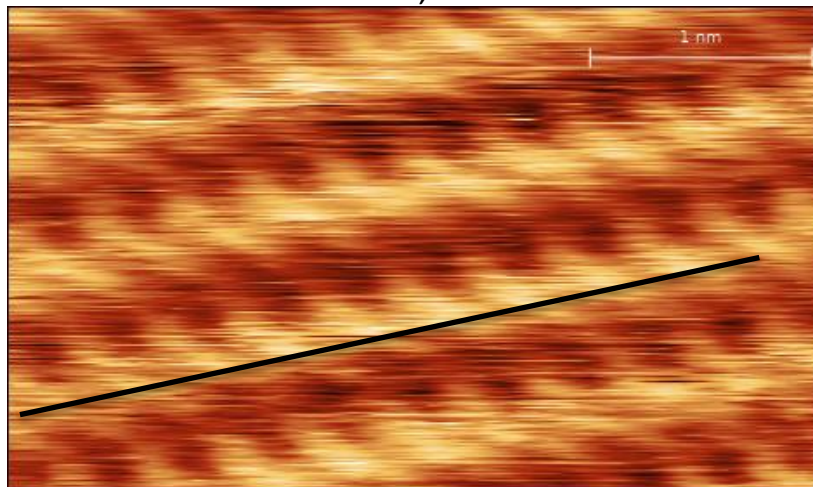
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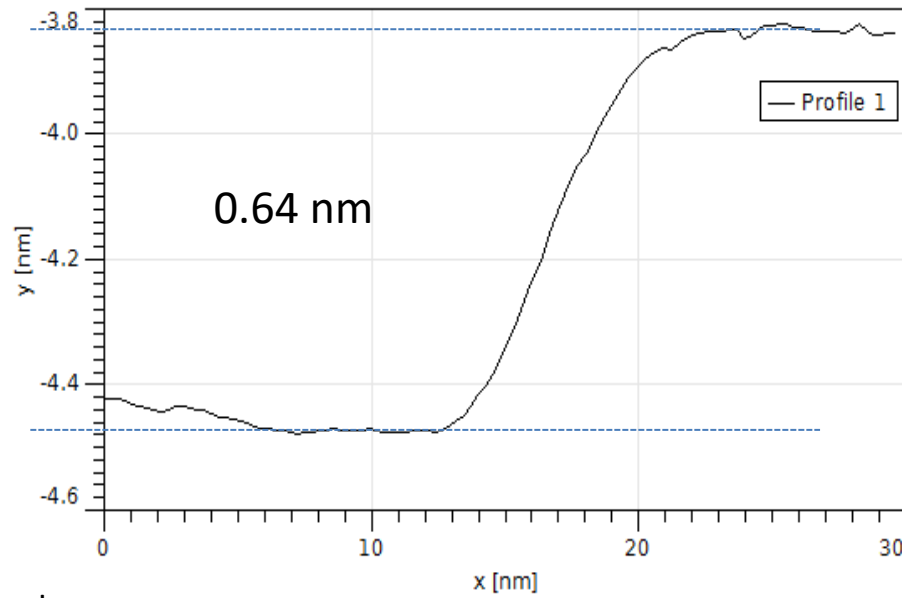
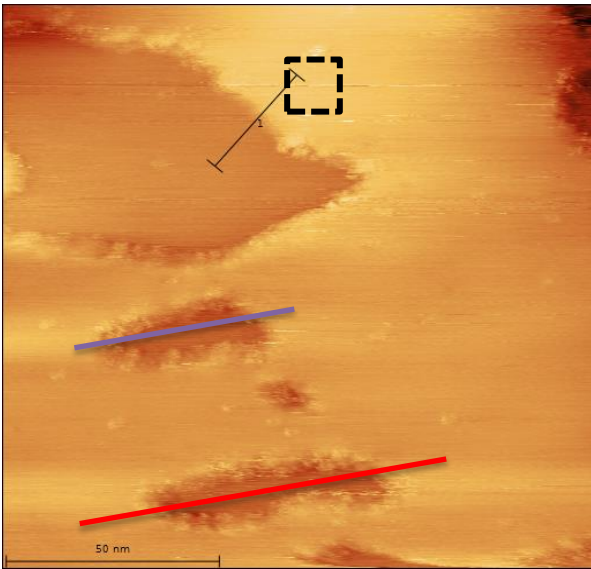
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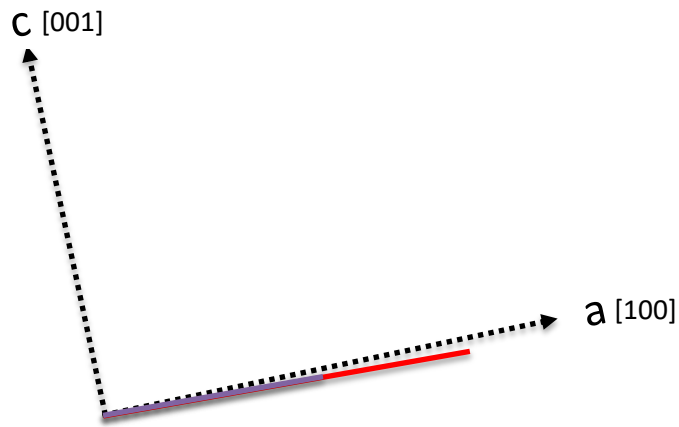
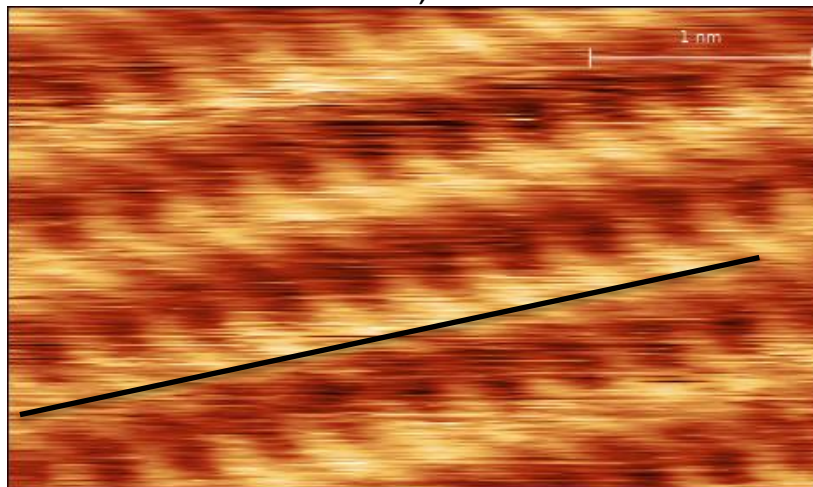
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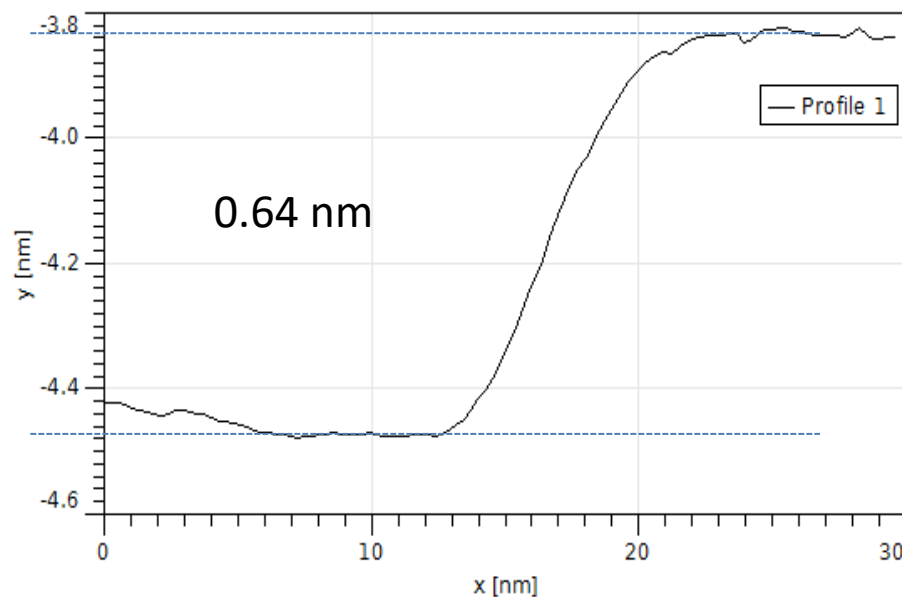
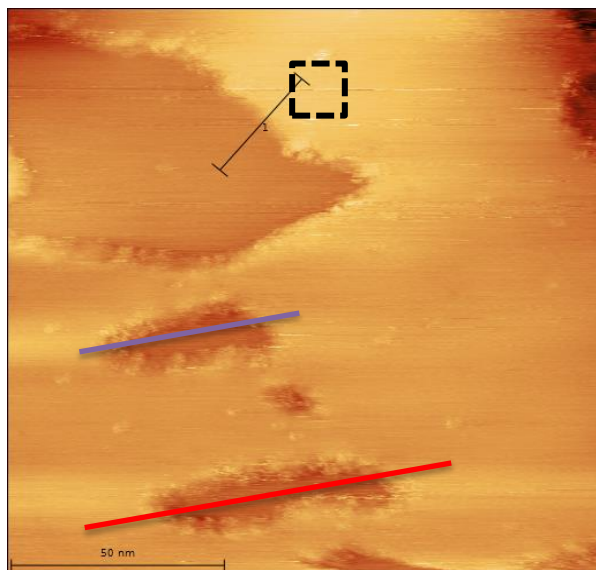
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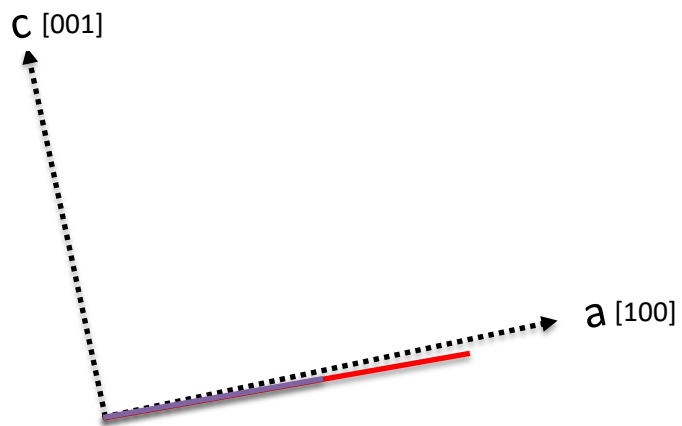
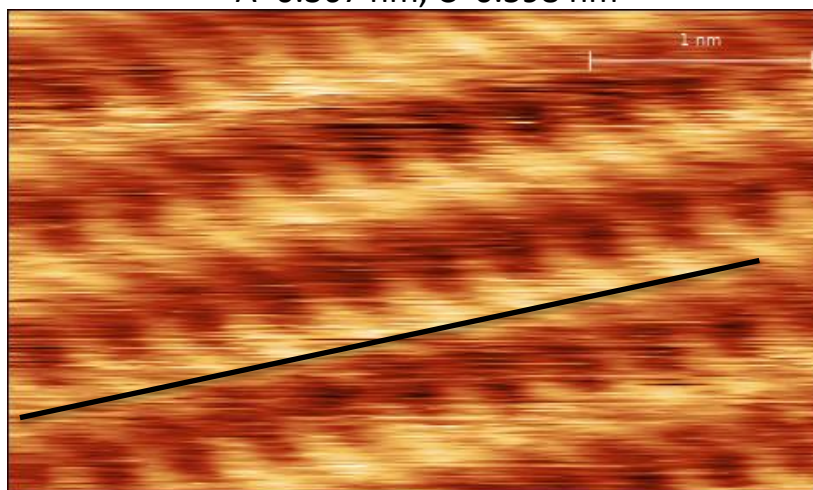
Measured Unit cell parameters
A=0.367 nm, C=0.598 nm



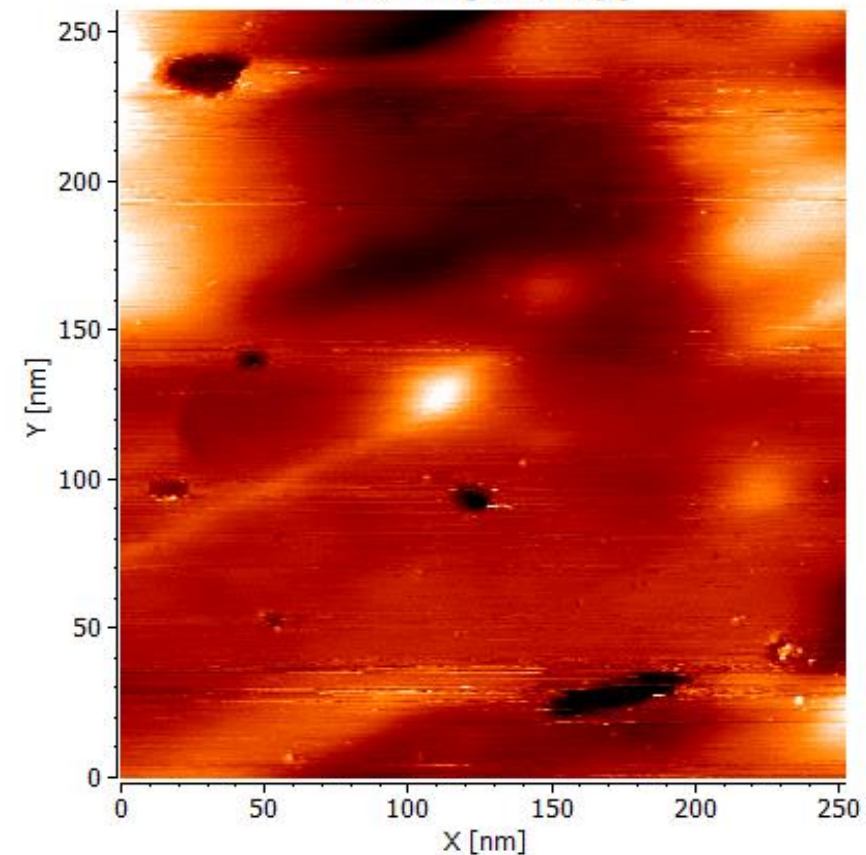
bP craters alignment



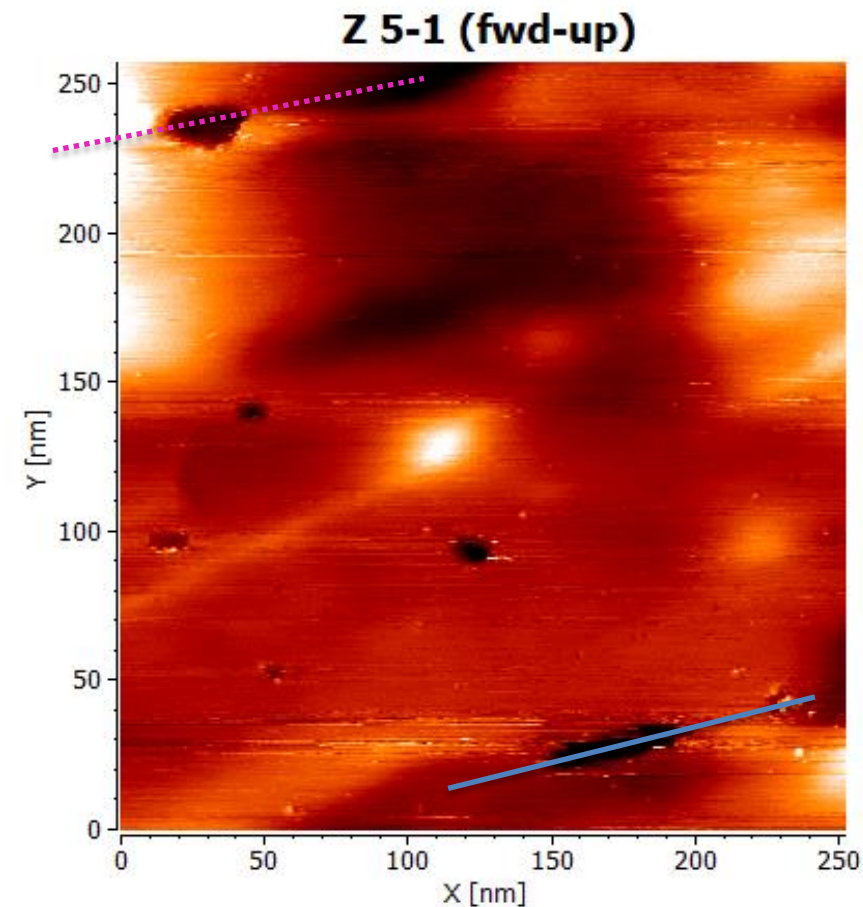
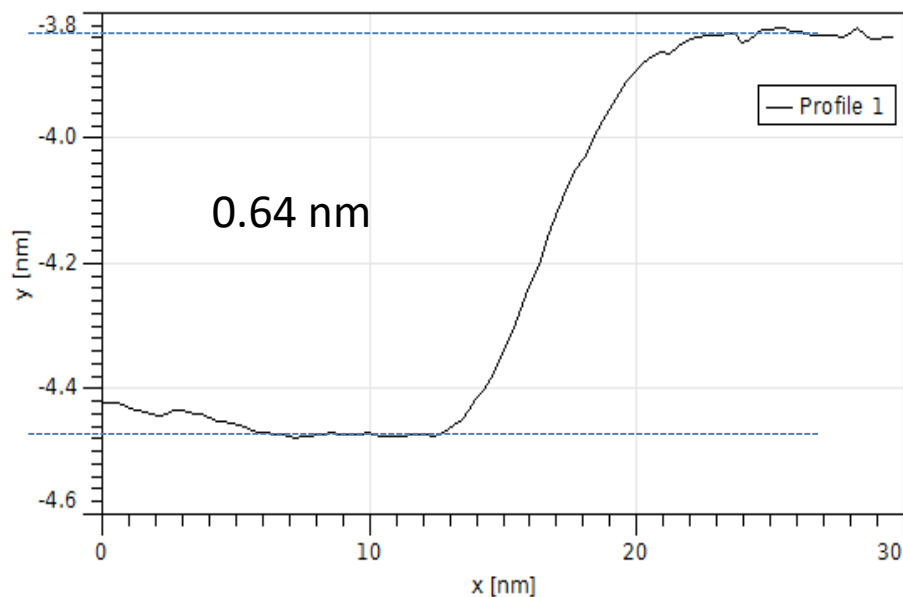
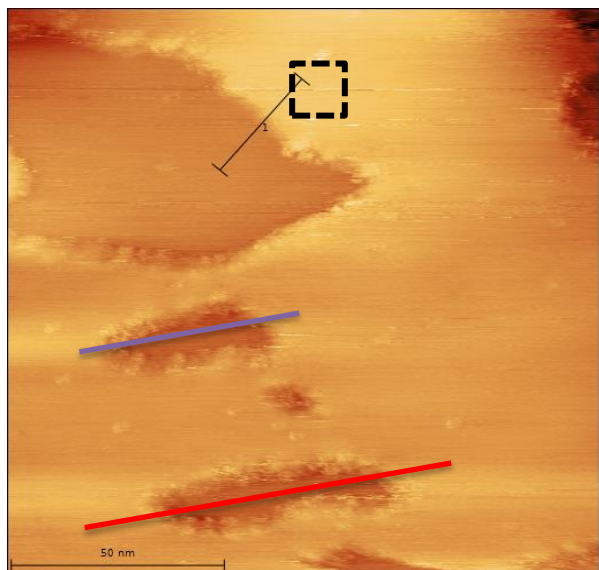
Measured Unit cell parameters
 $A=0.367$ nm, $C=0.598$ nm



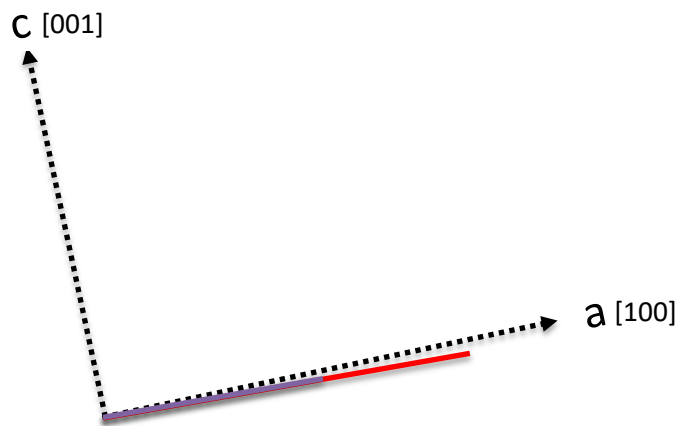
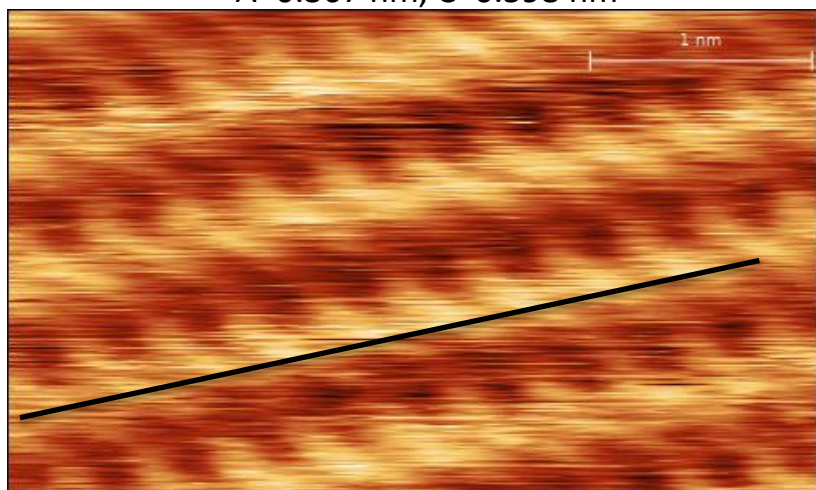
Z 5-1 (fwd-up)



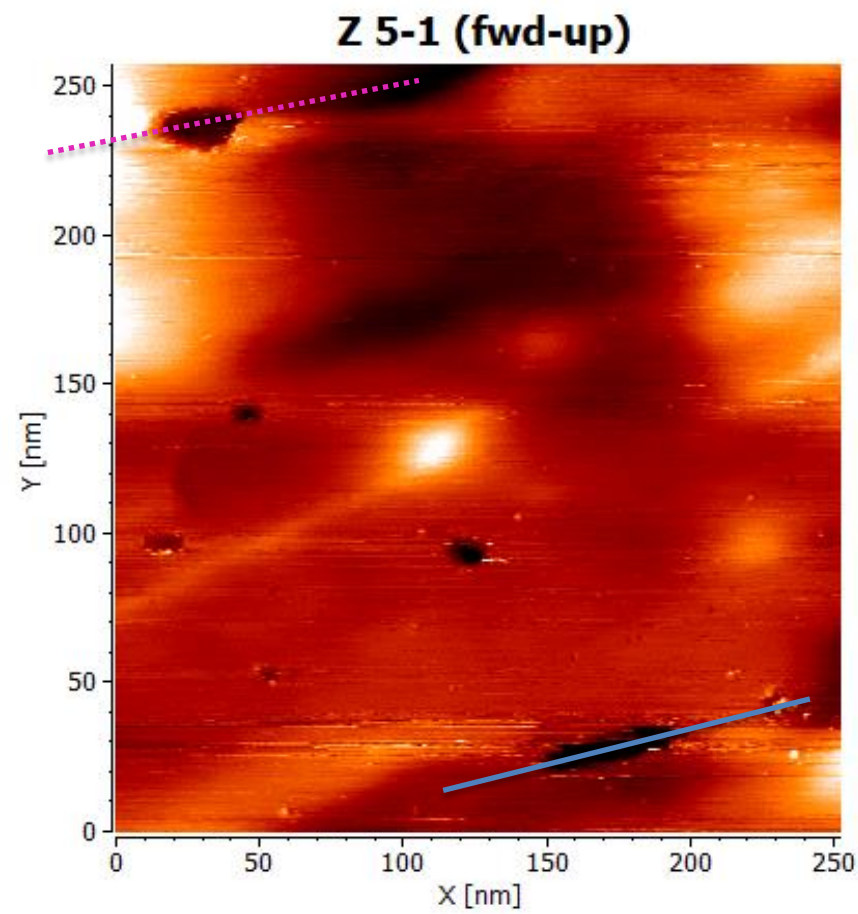
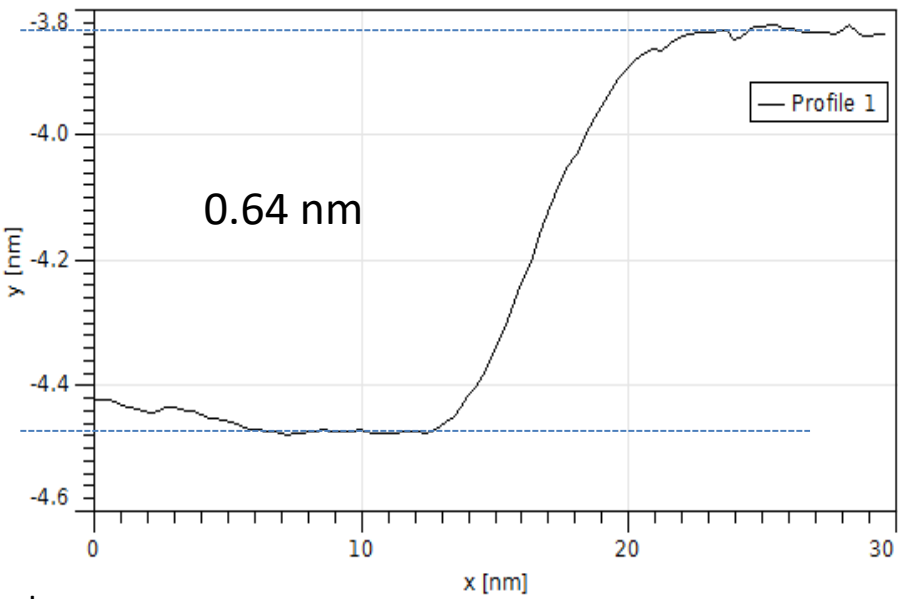
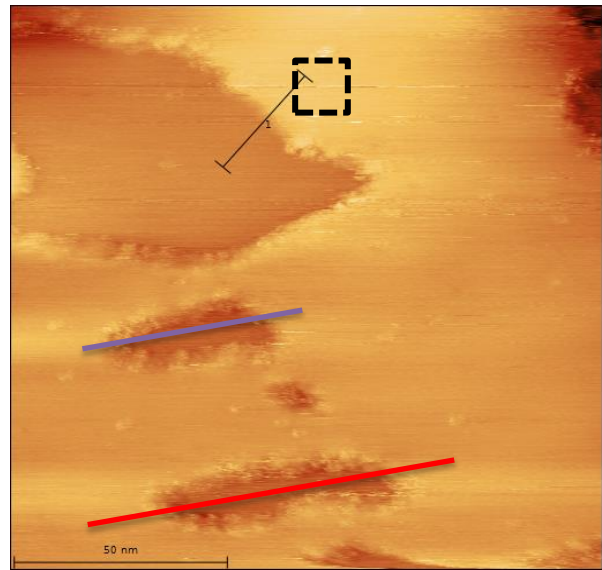
bP craters alignment



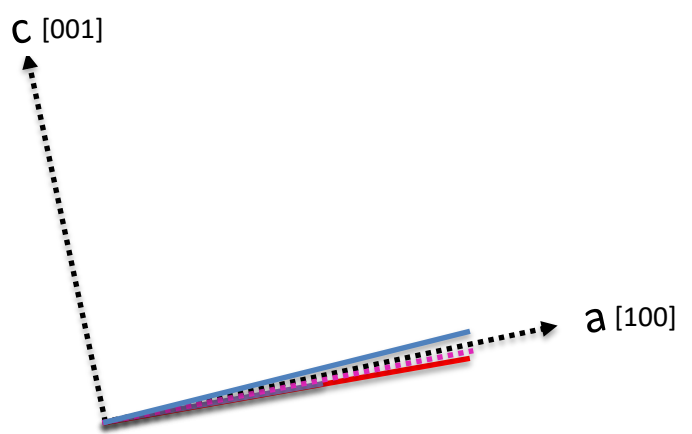
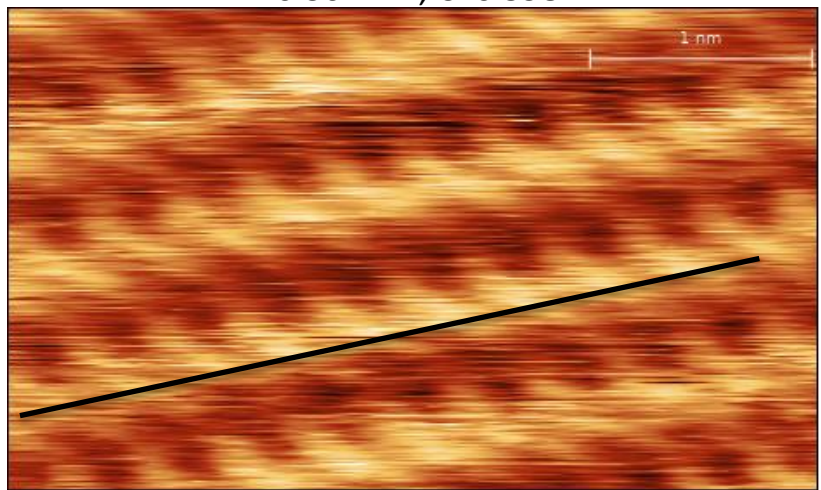
Measured Unit cell parameters
 $A=0.367$ nm, $C=0.598$ nm



bP craters alignment



Measured Unit cell parameters
A=0.367 nm, C=0.598 nm

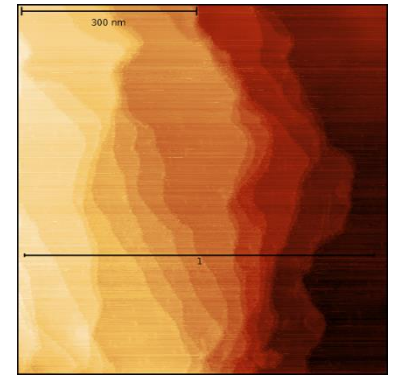
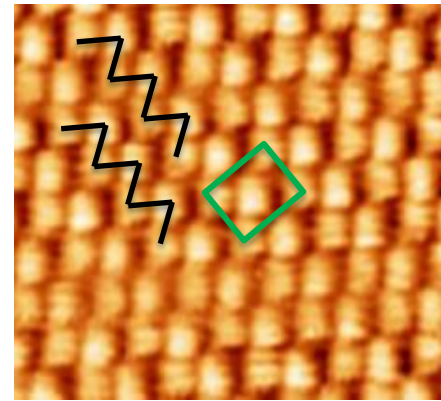


Conclusions

- First STM on exfoliated bP flakes

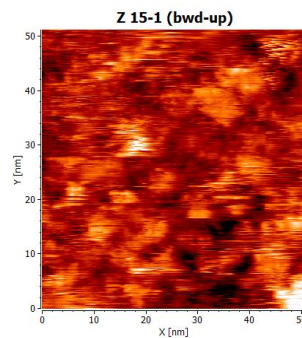
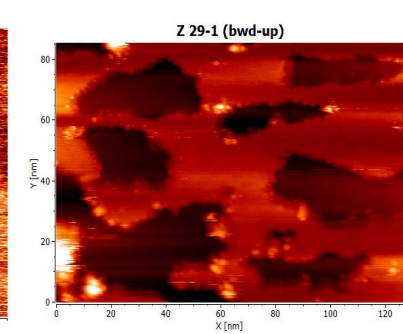
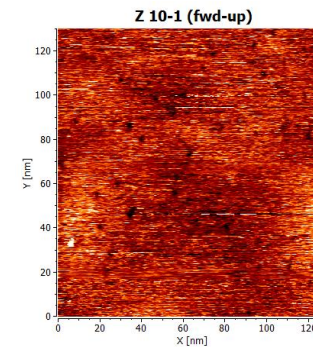
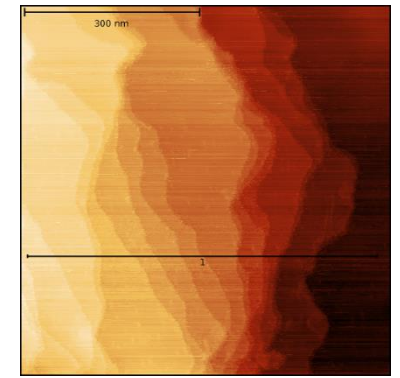
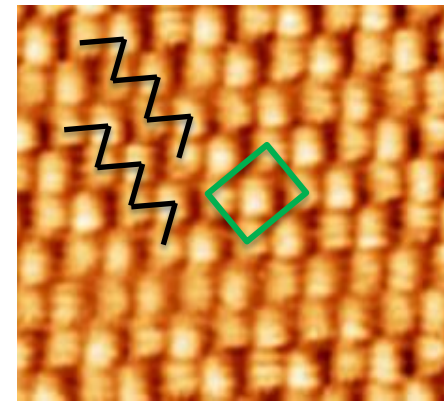
Conclusions

- First STM on exfoliated bP flakes
- Glove bag facilitates getting high quality samples



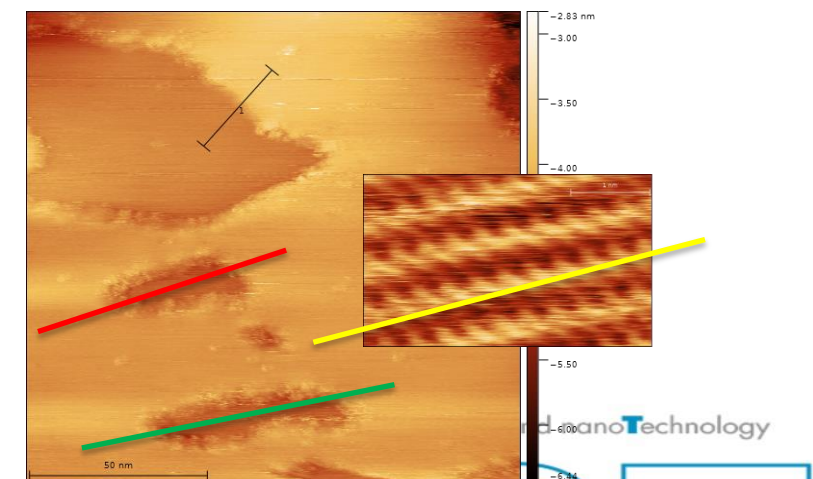
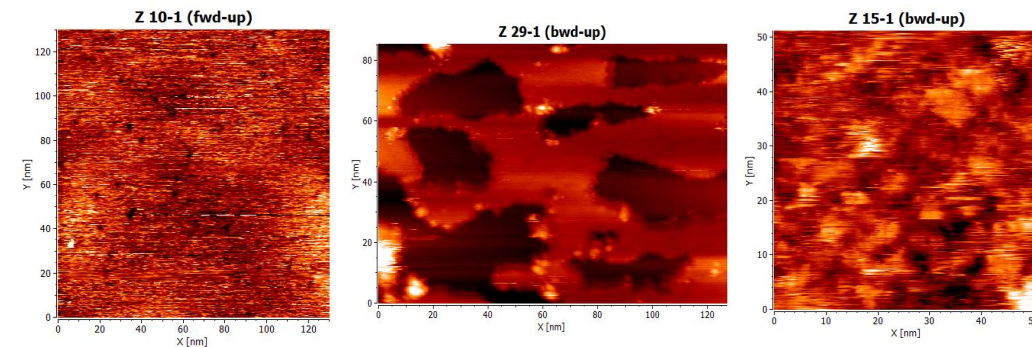
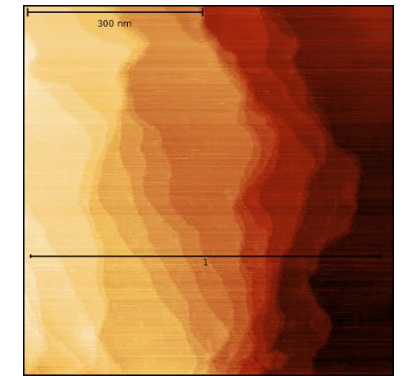
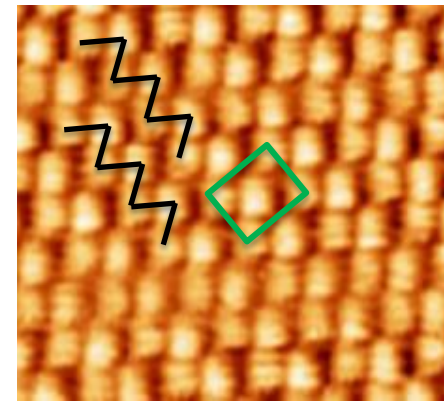
Conclusions

- First STM on exfoliated bP flakes
- Glove bag facilitates getting high quality samples
- Surface evolution with temperature



Conclusions

- First STM on exfoliated bP flakes
- Glove bag facilitates getting high quality samples
- Surface evolution with temperature
- Crater alignment to crystal lattice



Acknowledgement



SEED Project

PhosFun Project

Thank you for your attention