Surface properties of black Phosphorus investigated by scanning tunneling microscopy

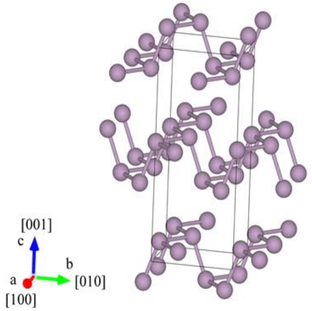
Francesca Telesio

October 29, 2018

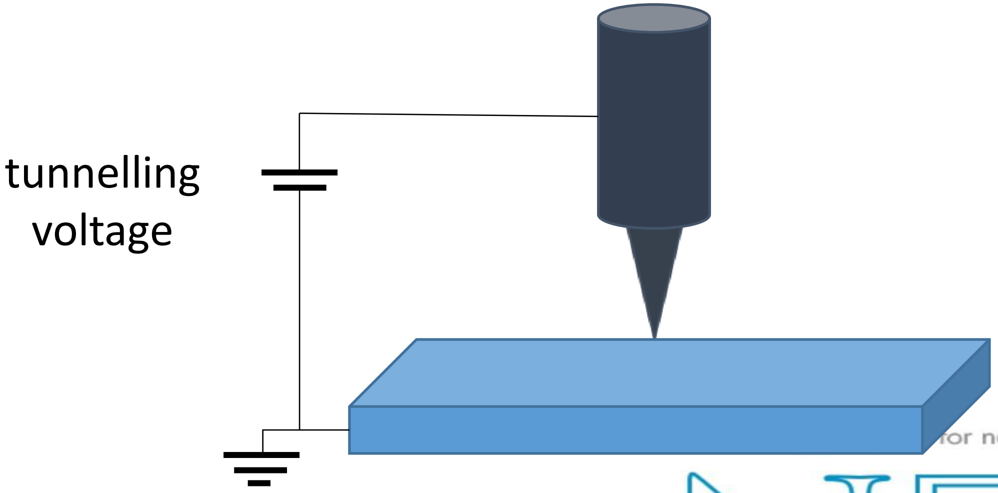
CNR-NANO Meeting, Pisa, Italy

National Enterprise for nanoScience and nanoTechnology

NEST

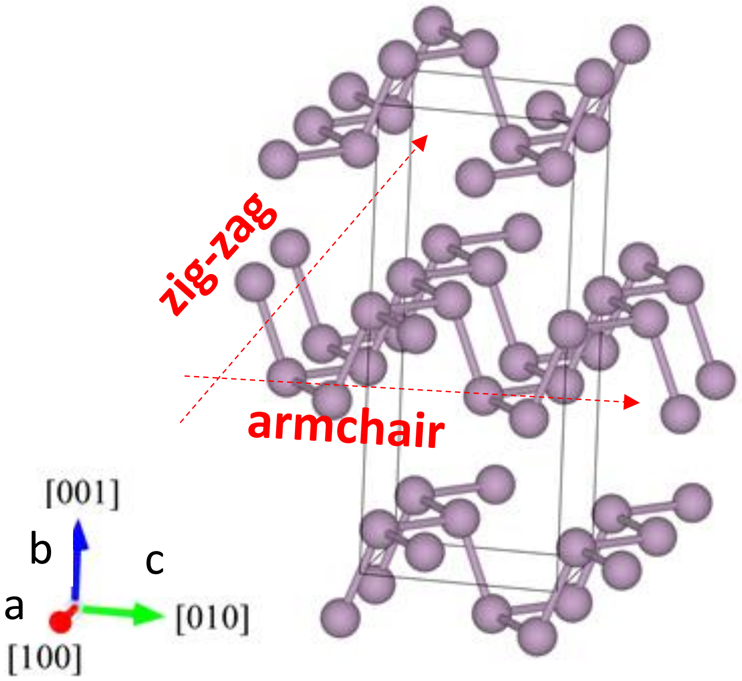


***Sur**face properties of black **Phos**phorus investigated by scanning tunneling microscopy*



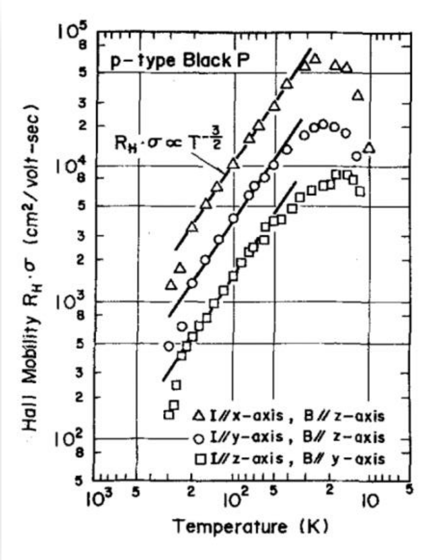
for nanoScience and nanoTechnology

What is black phosphorus?



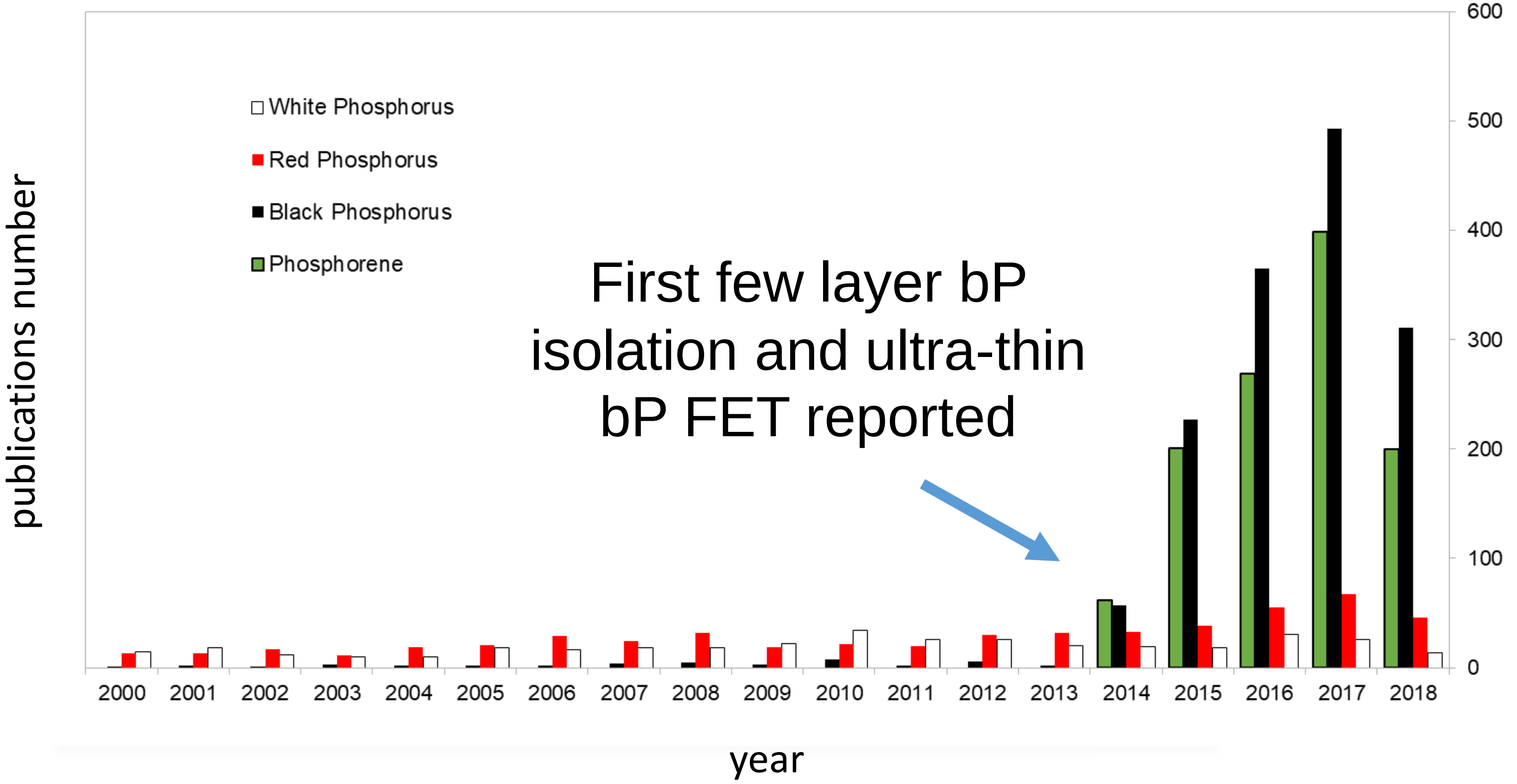
Cell parameters
a=3.3164 Å
b=10.484 Å
c=4.3793 Å

- ✓In 1914 first successful synthesis (Bridgman) and in 2007 synthesis at room pressure (Lange, Nilges)
- ✓p-type semiconductor: 0.3eV direct band gap and high hole mobility (64,000 cm^2/Vs @ 20 K)
- ✓1983 (Narita): n-type doping by Te



A. Morita, Appl. Phys. A 39 (1986); Lange et al. Inorg. Chem., 46 , 4028, (2007)

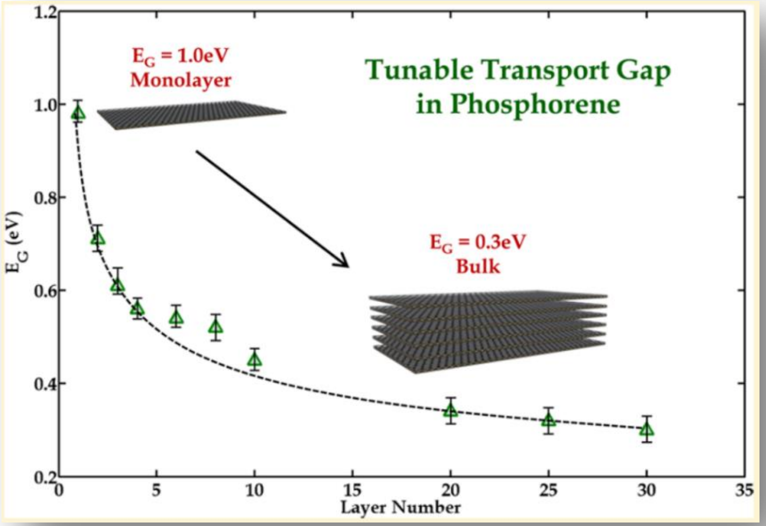
The Renaissance of Black Phosphorus



www.scopus.com

The renaissance of black phosphorus

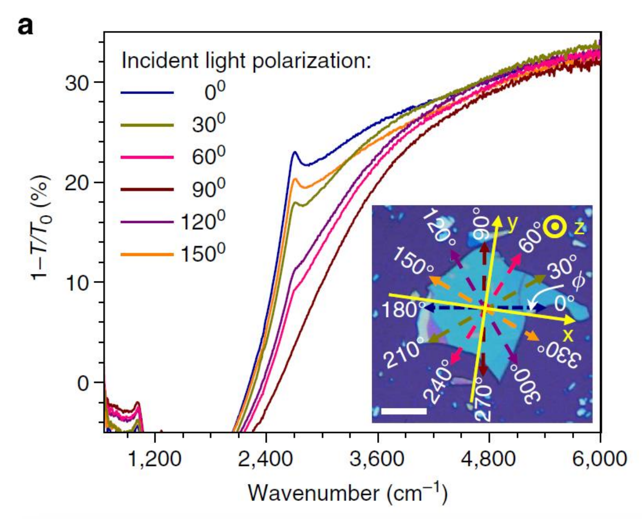
✓Direct band-gap tunable with layer number

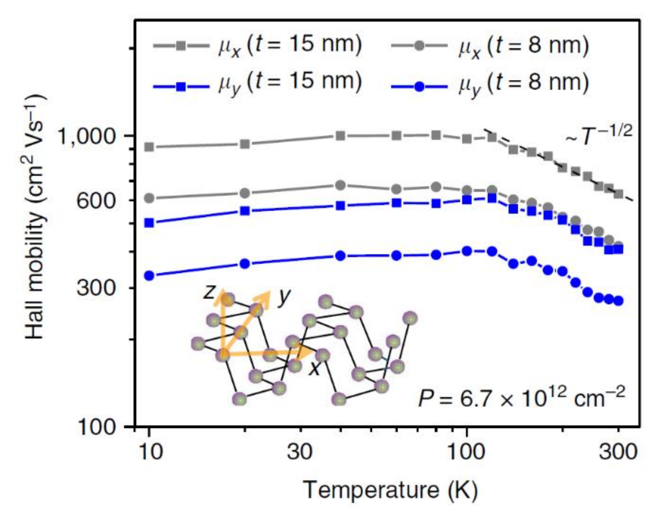


S. Das et al., Nano Lett. 14 (2014)

The renaissance of black phosphorus

- ✓Direct band-gap tunable with layer number
- ✓In-plane anisotropy of optical and electrical and thermal transport properties



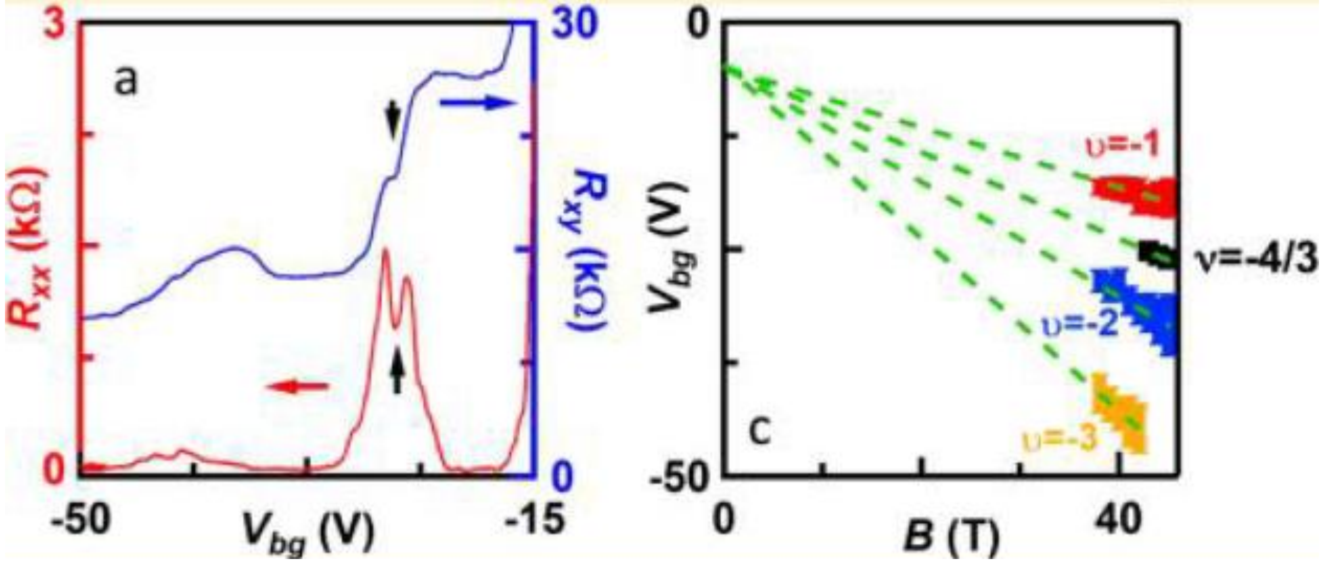


F. Xia et al., Nat. Comm. 5 (2014)

National Enterprise for nanoScience and nanoTechnology

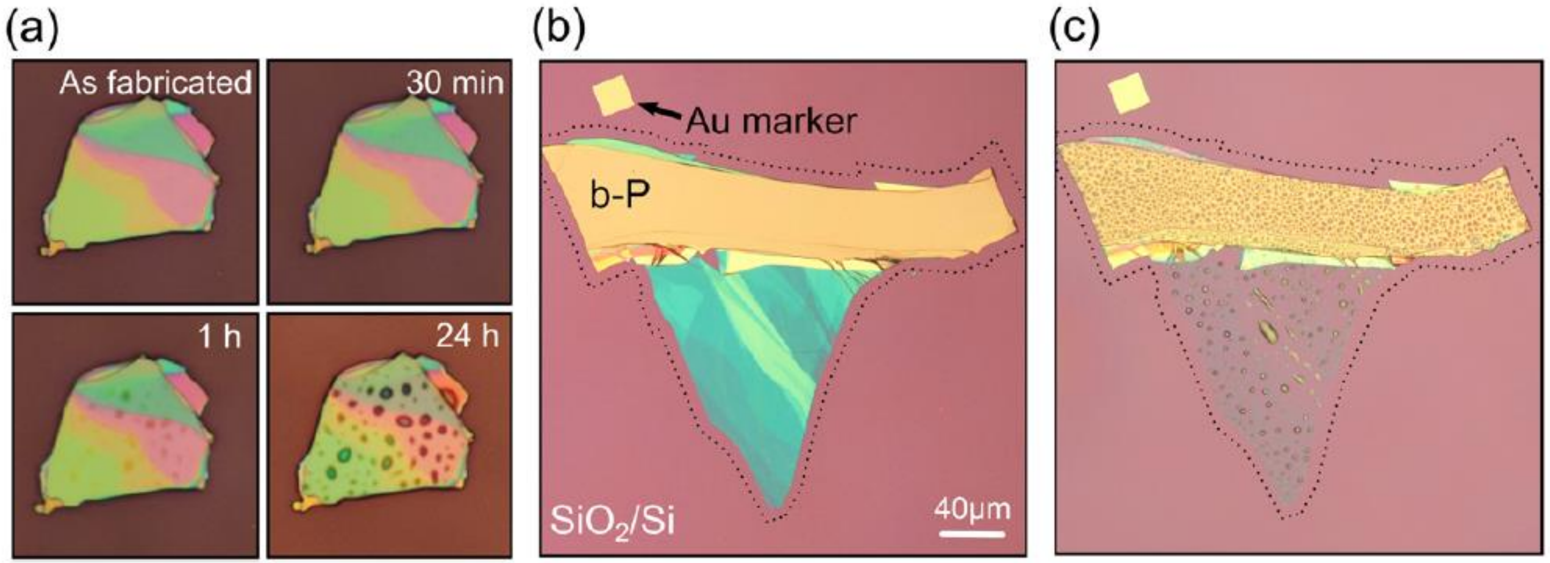
The renaissance of black phosphorus

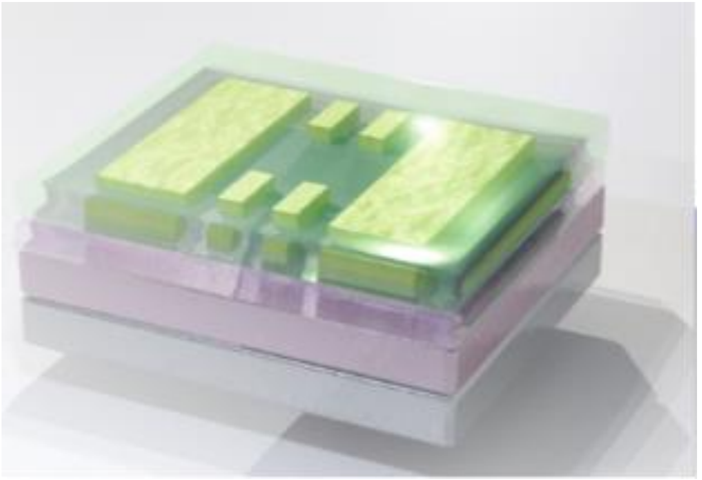
- ✓Direct band-gap tunable with layer number
- ✓In-plane anisotropy of optical and electrical and thermal transport properties
- ✓Fractional quantum Hall effect



J. Yang et al., Nato Lett (2018)

... but, black Phosphorus high reactivity





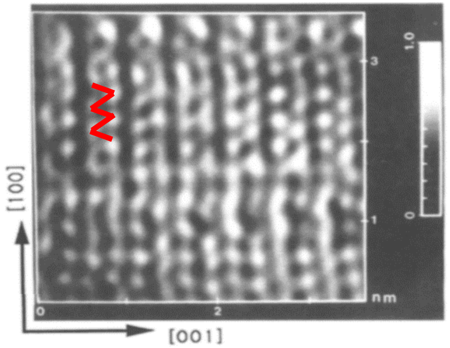
- Combined effect of light, oxygen and water
- Degradation is faster on thinner flakes
- A coating is needed to protect the bP devices... But it prevents the study of the surface!

National Enterprise for nanoScience and nanoTechnology

STM works on black Phosphorus

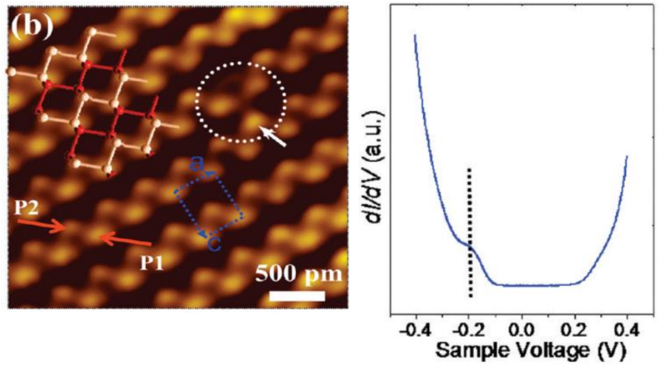
- Cleaved bP in air - (010) surface

S. L. Yau et. al. Chem, Phys, Lett, 198(1998),3,4;383

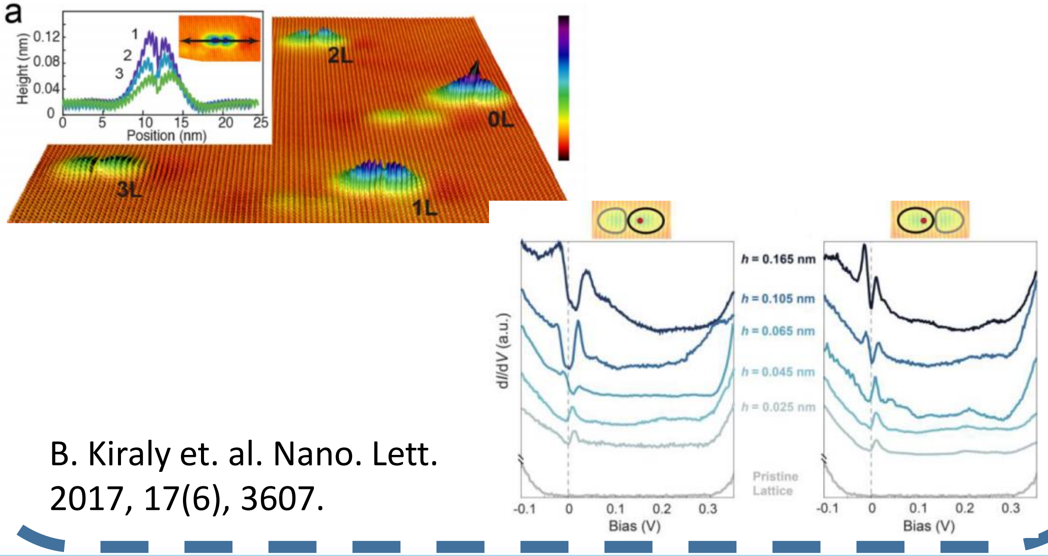


- Cleaved bP in dry N2 – measured at 77K and 4.3K
  - Band gap of 0.4 eV
  - Peak at -0.17 V due to a surface state

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

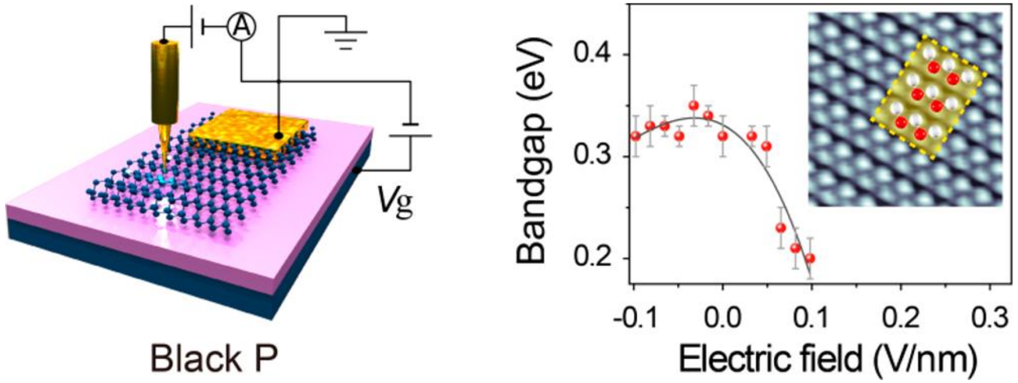


- Single Vacancies in BP – measured at 4.6K



B. Kiraly et. al. Nano. Lett. 2017, 17(6), 3607.

- Giant Stark effect
  - Measured at 77K and at 4.2K



Y. Liu et al, Nano Lett., 2017, 17, 1970

SEED project goals:

1. Study of the pristine exfoliated bP surface by STM

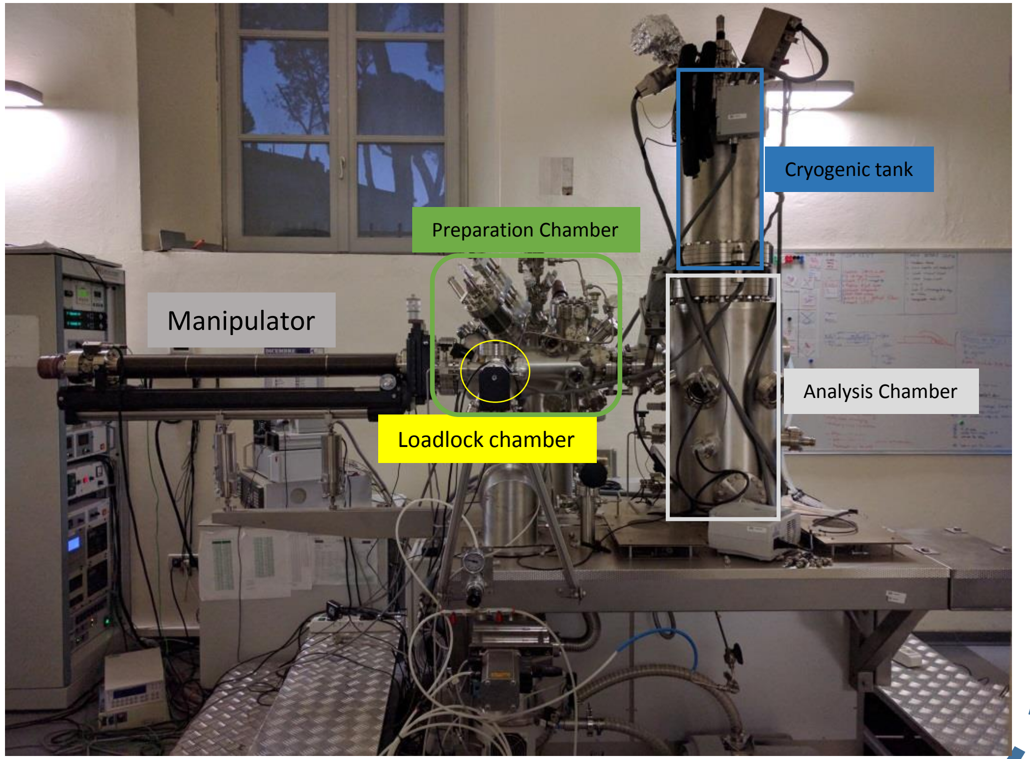
2. Study of defects on the surface

3. Surface functionalization, with particular focus on doping

Our approach

Sample preparation under protected atmosphere

Characterization by Scanning Tunnelling Microscopy



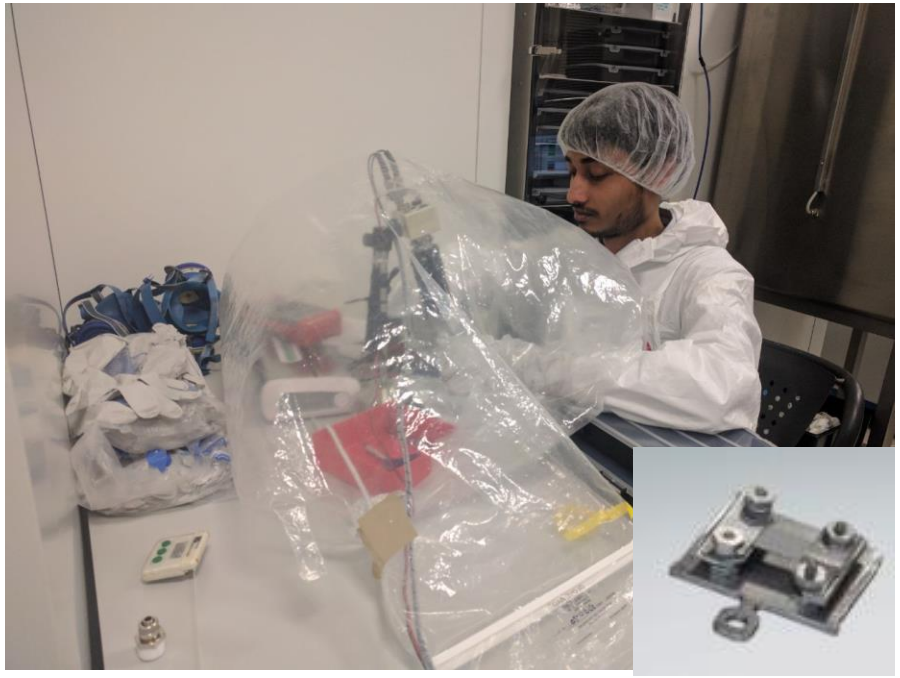
Modeling:
DFT Calculations performed at the scientific calculus center of CNR-NANO S3 and UNIMORE

National Enterprise for nanoScience and nanoTechnology

Sample preparation

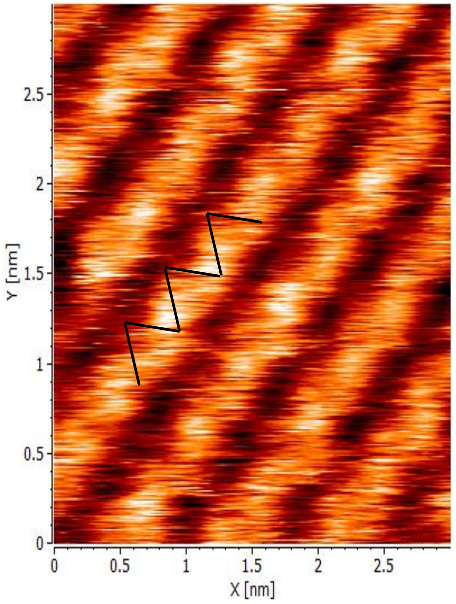
STM measurements need a flat, conducting substrate.

Epitaxial graphene on SiC

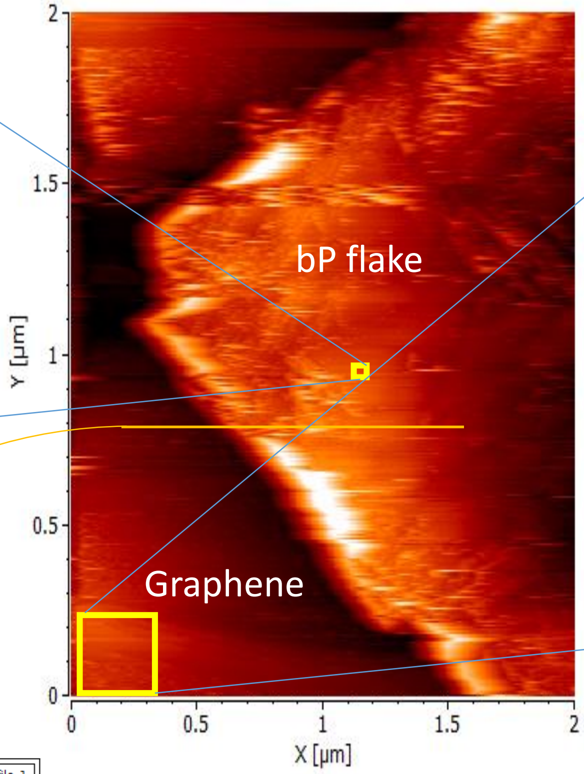


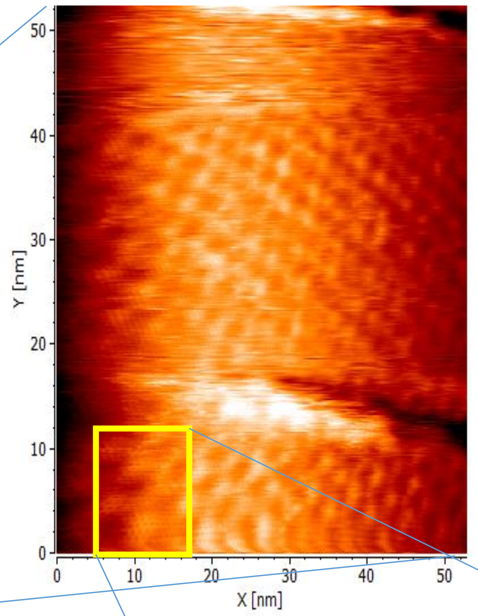
To prevent bP degradation a nitrogen-pressurized glove bag is used.

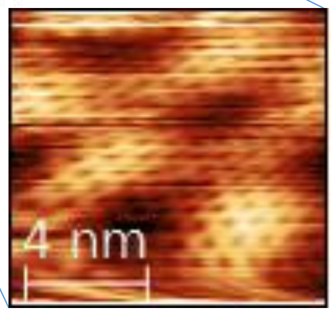
Clear identification of flakes and substrate

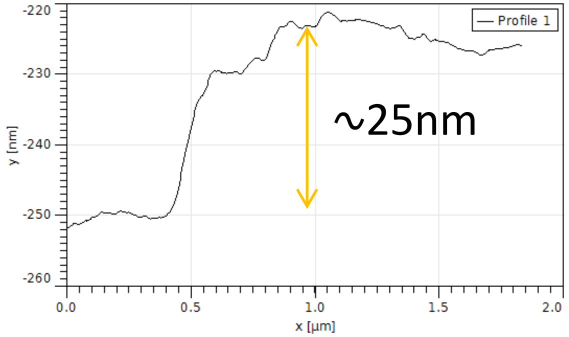


bP flake







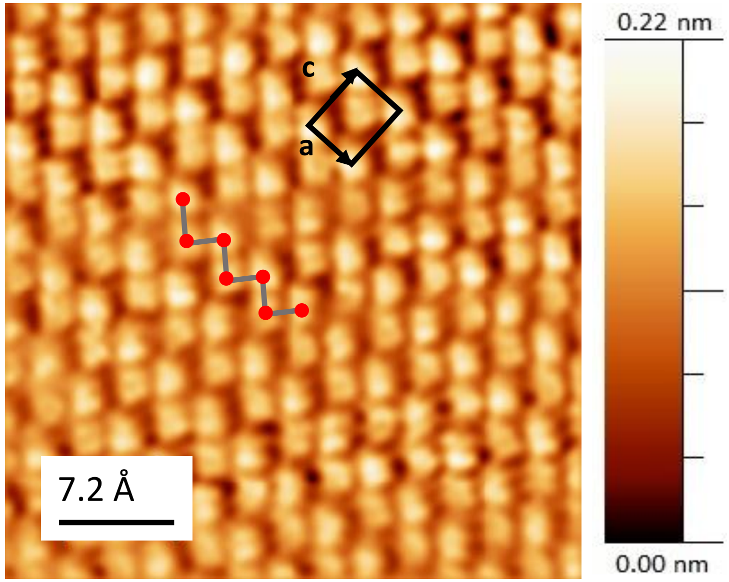


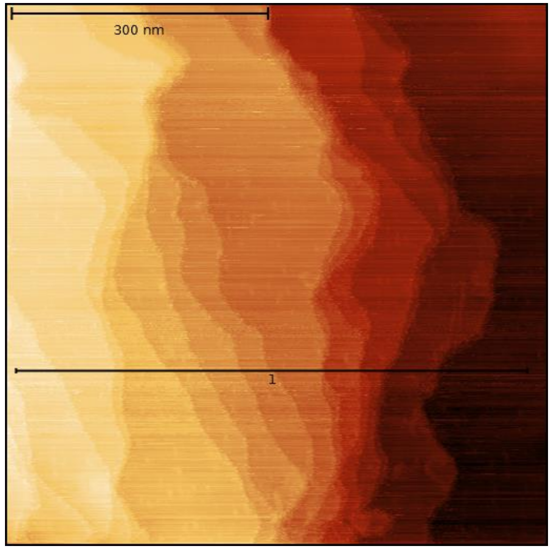
<u>Typical Flake Dimensions</u>

Area ~ 1 μm^2

Height ~ 30 nm

Atomic Resolution on bP flakes





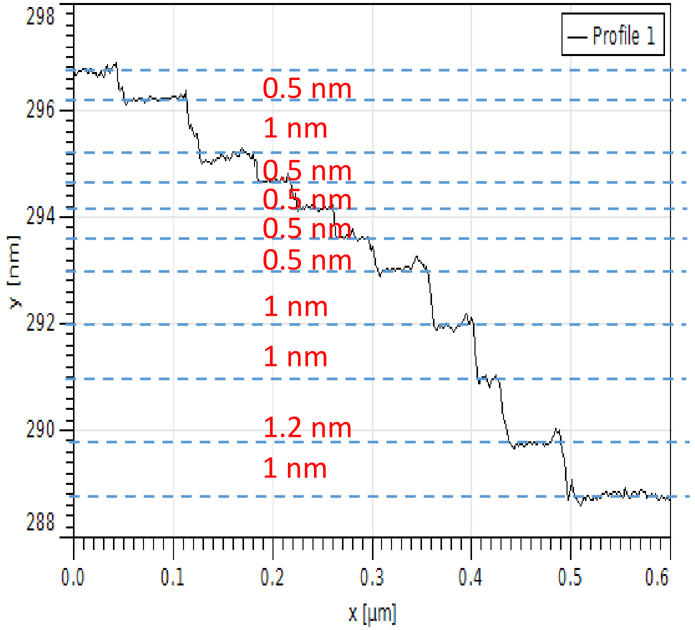


TABLE 1: Measured Surface Lattice Constants and Theoretical Optimized Results Together with Previous Data of Bulk BP

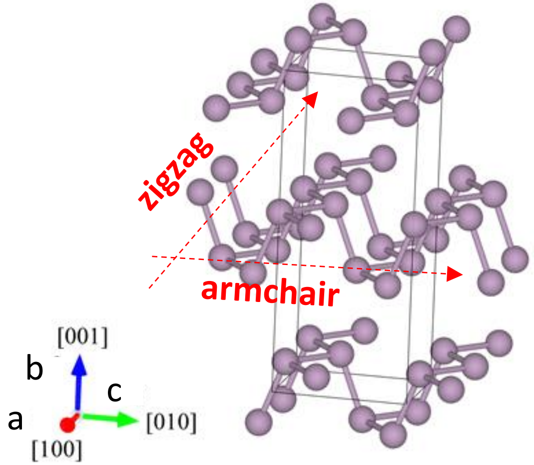
reported by Morita[7]	measured from STM images	theoretical optimized results
$a = 3.313$ Å	$a = 3.33$ Å	$a = 3.28$ Å
$b = 10.473$ Å		$b = 10.37$ Å
$c = 4.374$ Å	$c = 4.33$ Å	$c = 4.35$ Å
$d_1 = 2.222$ Å, $\alpha_1 = 96.5°$		
$d_2 = 2.777$ Å, $\alpha_2 = 101.9°$		

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

<u>Measured at RT</u>

a = (3.45 ± 0.43) Å

c = (4.40 ± 0.12) Å



Measured parameters are in agreement with the reported and predicted values

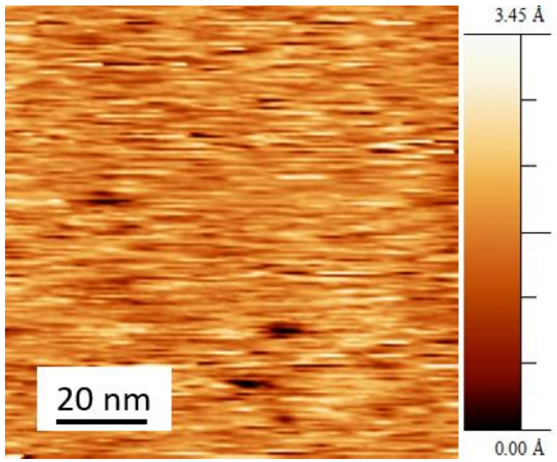
Annealing Study

200°C

300°C

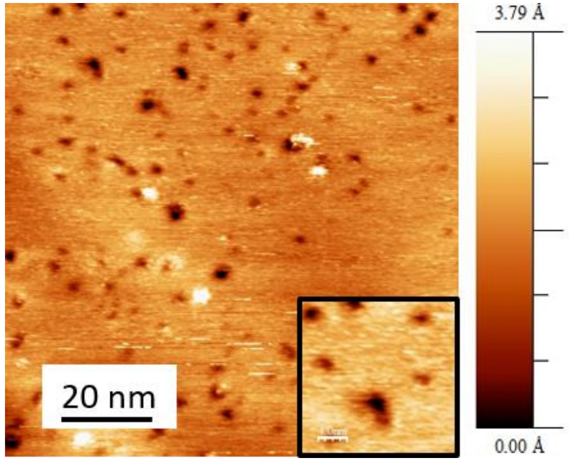
400°C

500°C



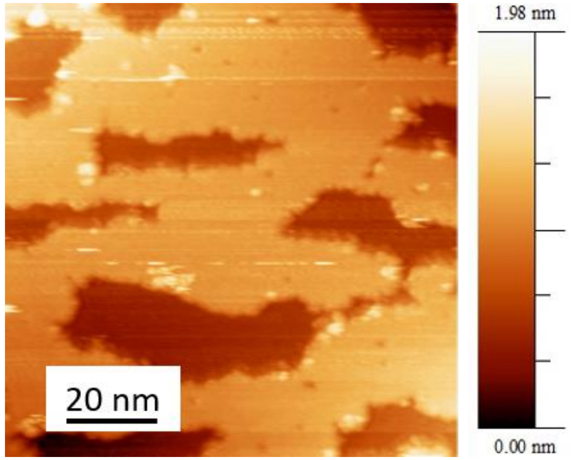
Annealing Study

200°C → 300°C → 400°C → 500°C



Annealing Study

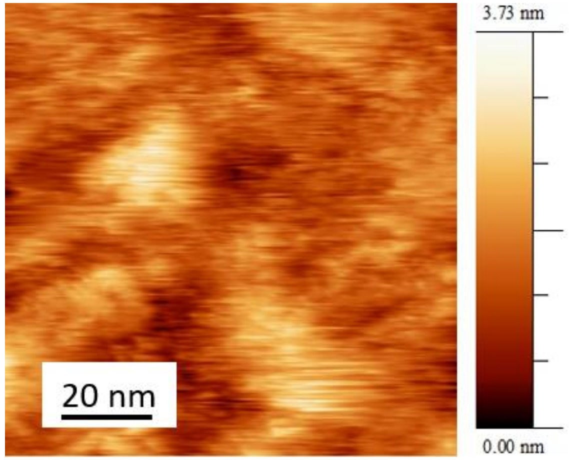
200°C → 300°C → **400°C** → 500°C



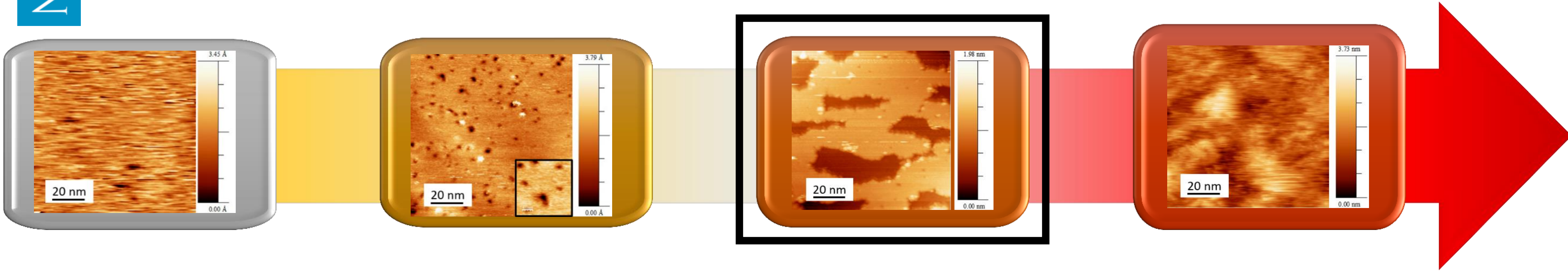
National Enterprise for nanoScience and nanoTechnology

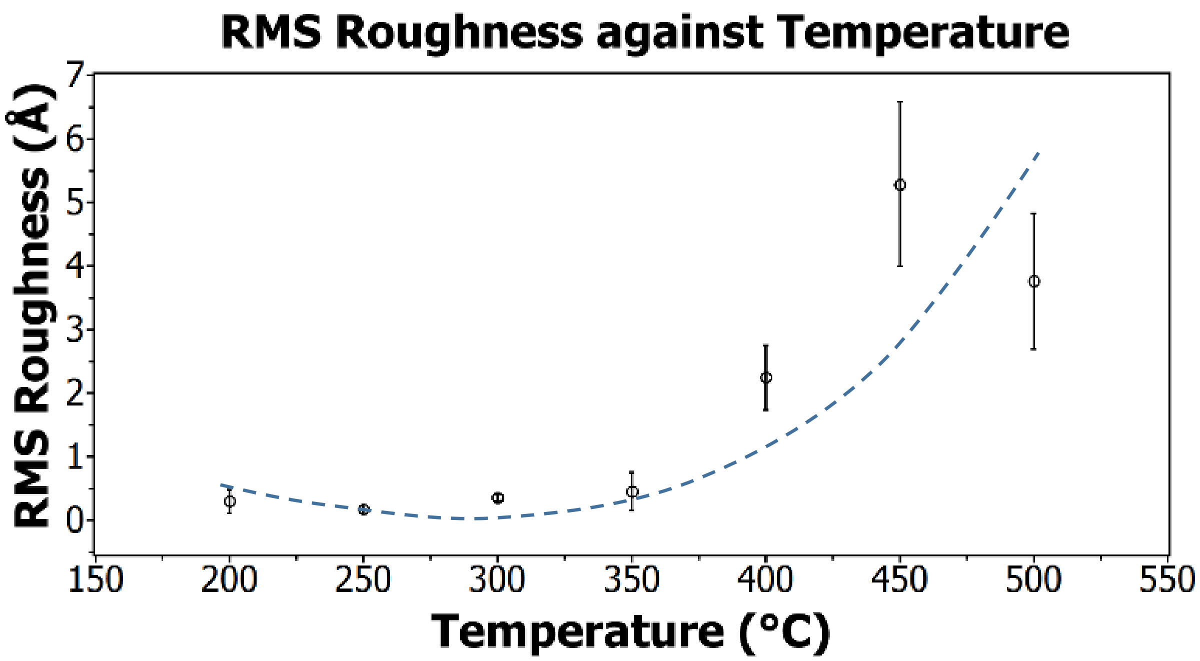
Annealing Study

200°C → 300°C → 400°C → **500°C**



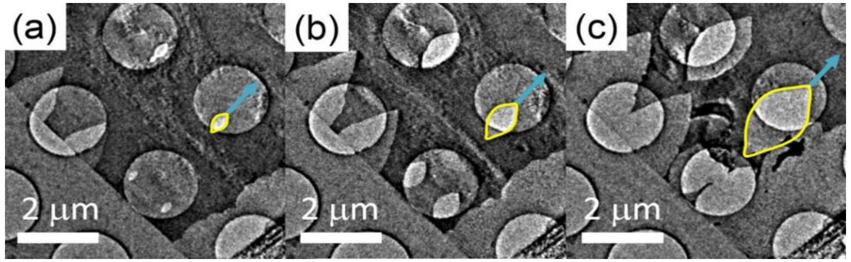
Annealing Study





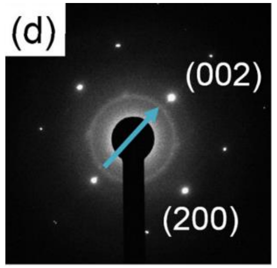
bP desorption with annealing: controlled sublimation regime

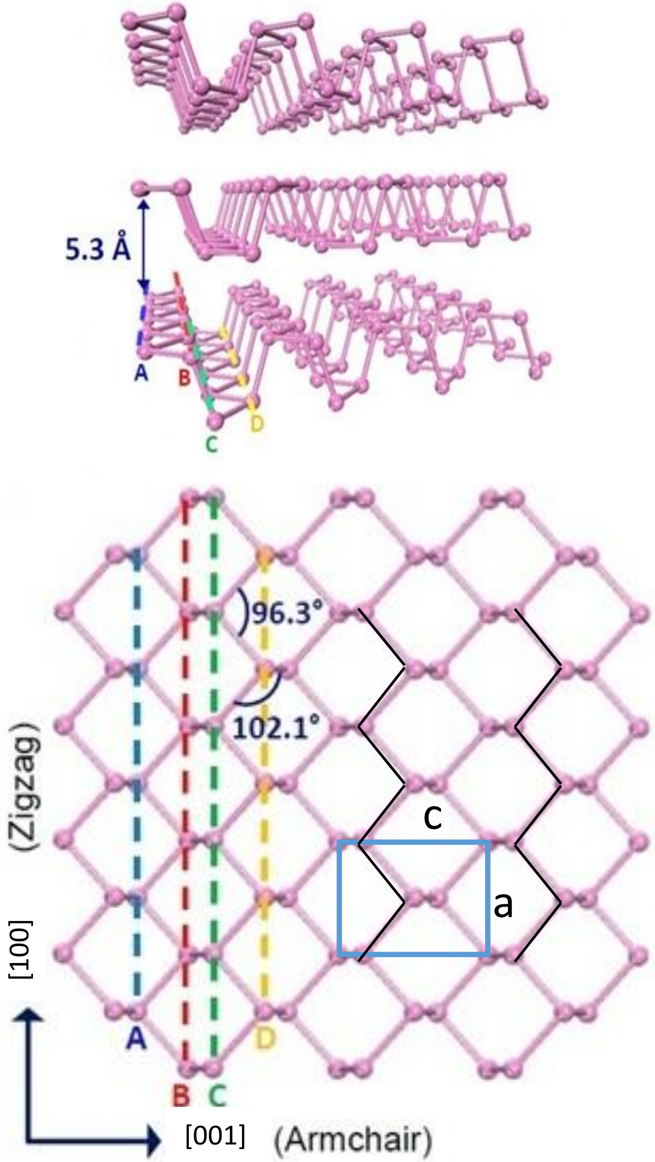
Xiaolong Liu et. al., J. Phys. Chem. Lett. 2015, 6, 773.



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

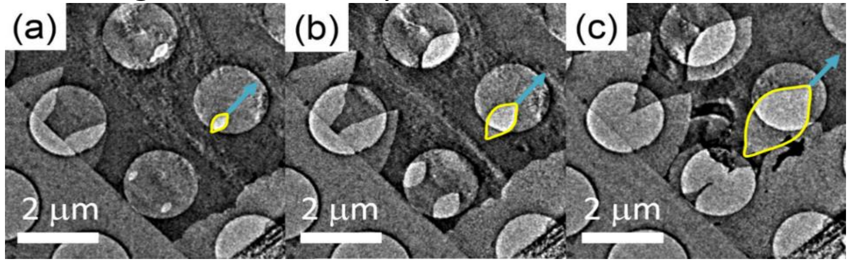
- decomposition of 2D BP is observed to occur at ~400 °C in vacuum, in contrast to the 550 °C bulk BP sublimation temperature
- This decomposition initiates via eye-shaped cracks along the [001] direction





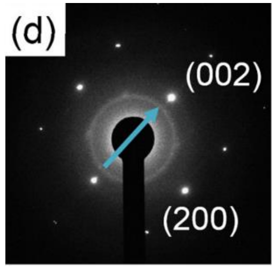
bP desorption with annealing: controlled sublimation regime

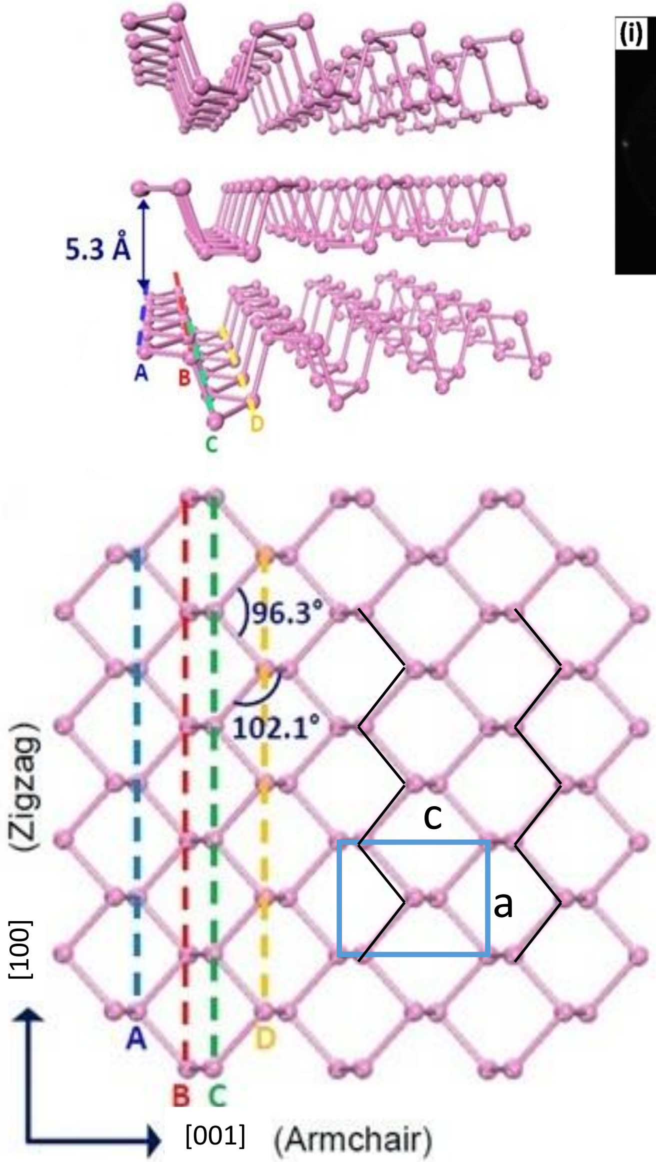
Xiaolong Liu et. al., J. Phys. Chem. Lett. 2015, 6, 773.

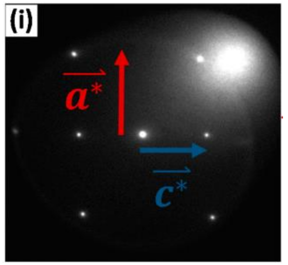


TEM image of eye shaped crack opening on heating bP flake at 400°C for 5, 8 and 12 min.

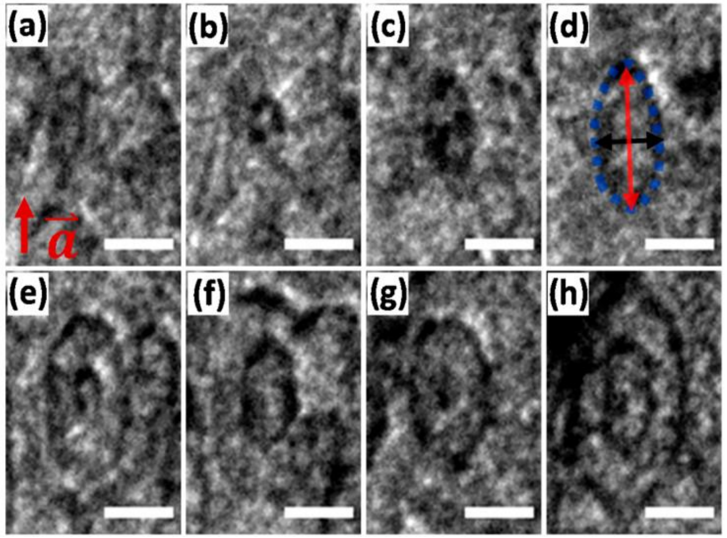
- decomposition of 2D BP is observed to occur at ~400 °C in vacuum, in contrast to the 550 °C bulk BP sublimation temperature
- This decomposition initiates via eye-shaped cracks along the [001] direction







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



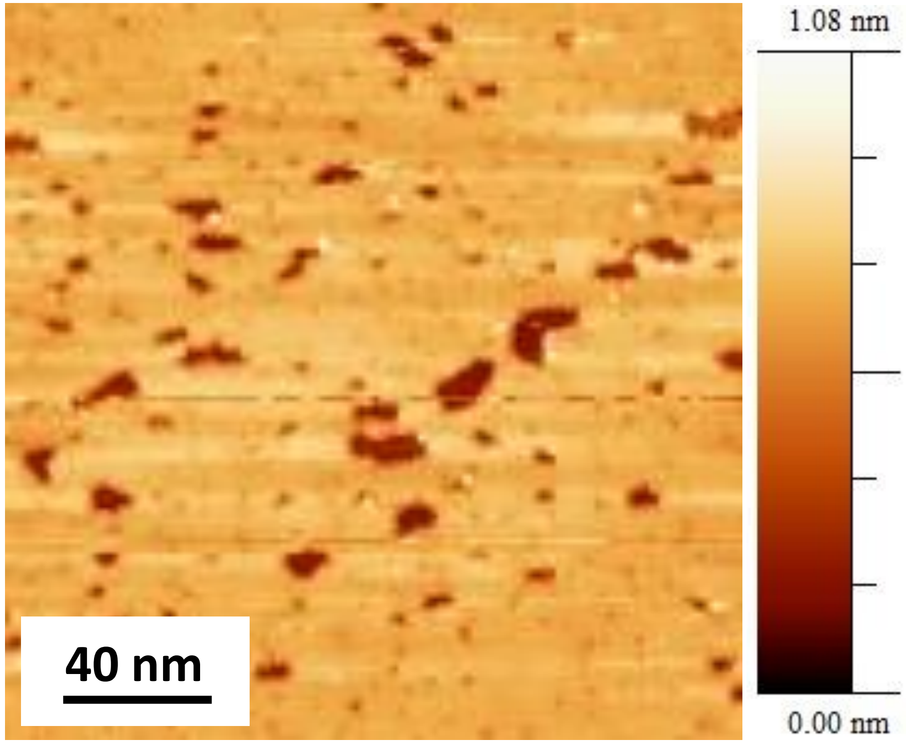
Bright-field LEEM snapshots of hole expansion during sublimation of exfoliated bP. Two seconds between each image from (a) to (h) recorded respectively at the following temperatures: 486 °C, 488 °C, 490 °C, 491 °C, 493 °C, 495 °C, 497 °C, and 499 °C.

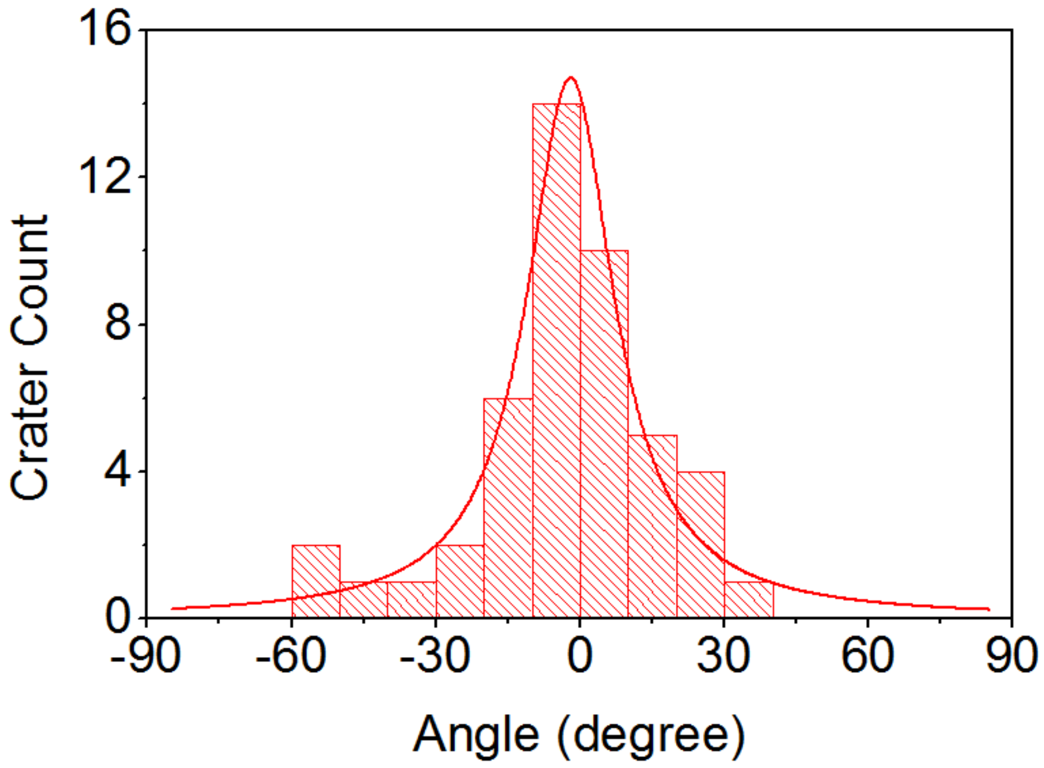
- Sublimation manifests itself above 375 ± 20 °C
- Faceted holes with the long axis aligned along the [100] direction, in contrast with what was reported earlier

National Enterprise for nanoScience and nanoTechnology

bP desorption with annealing: controlled sublimation regime

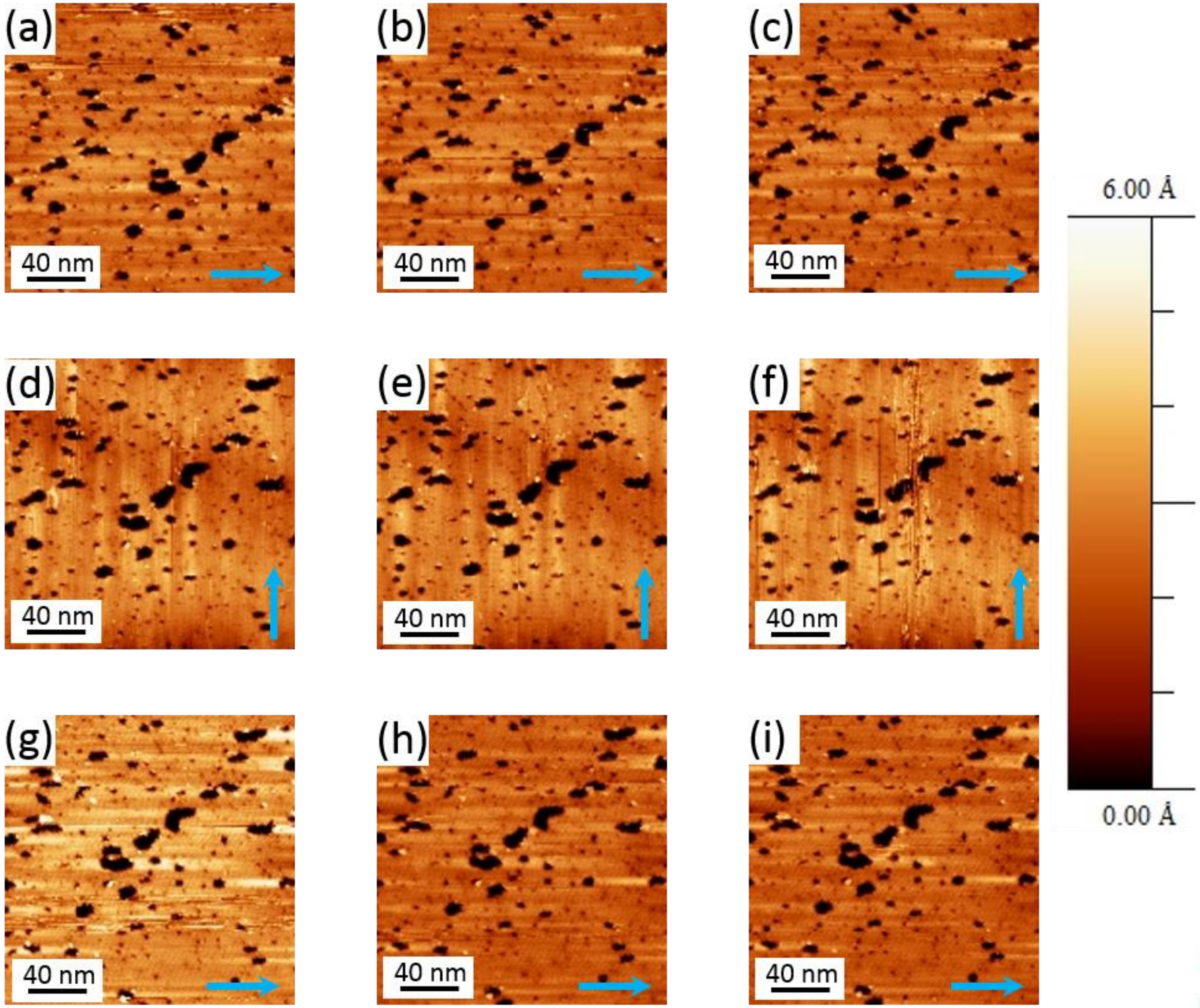
Our results:





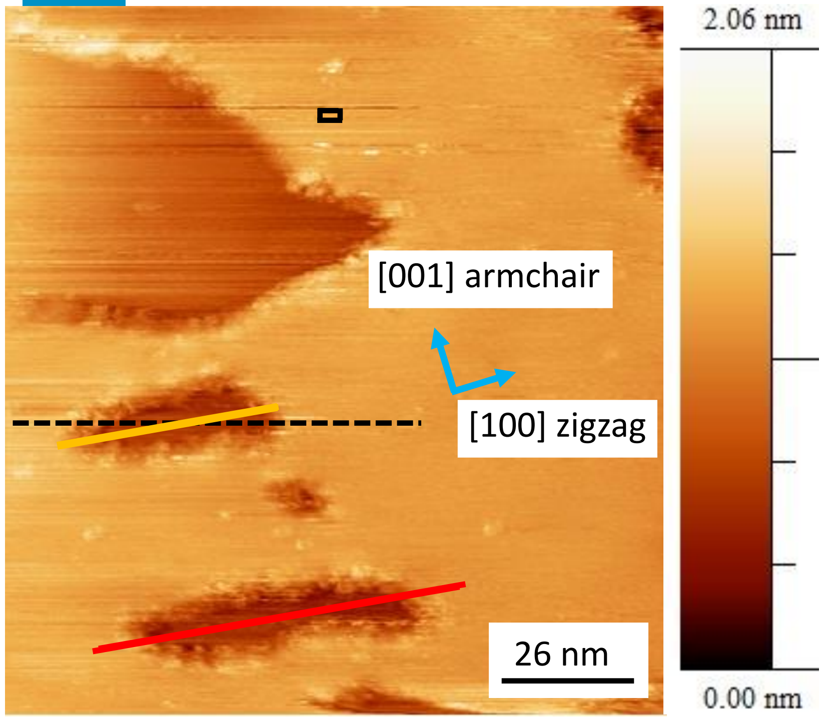
All the craters are aligned along one direction, with no crater oriented perpendicularly.

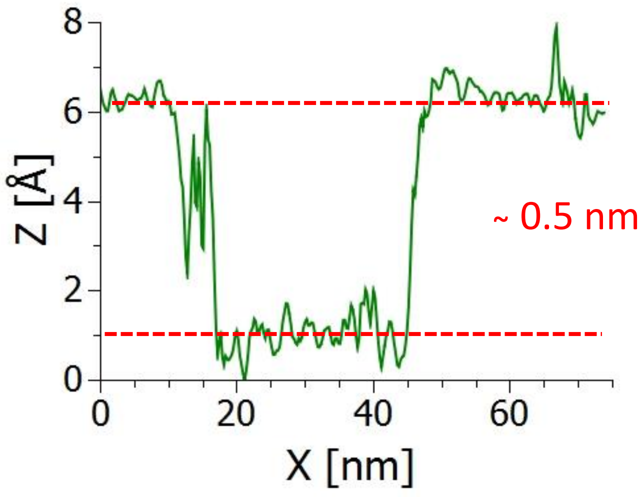
bP craters alignment: it is not a tip induced effect

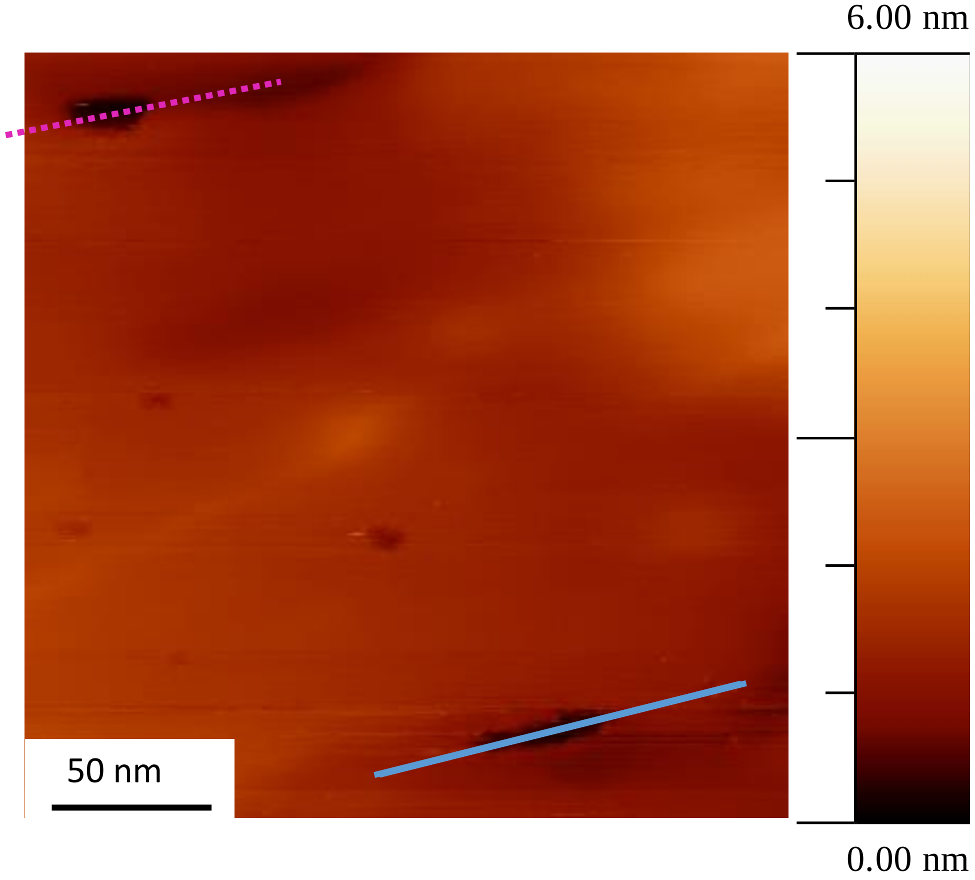


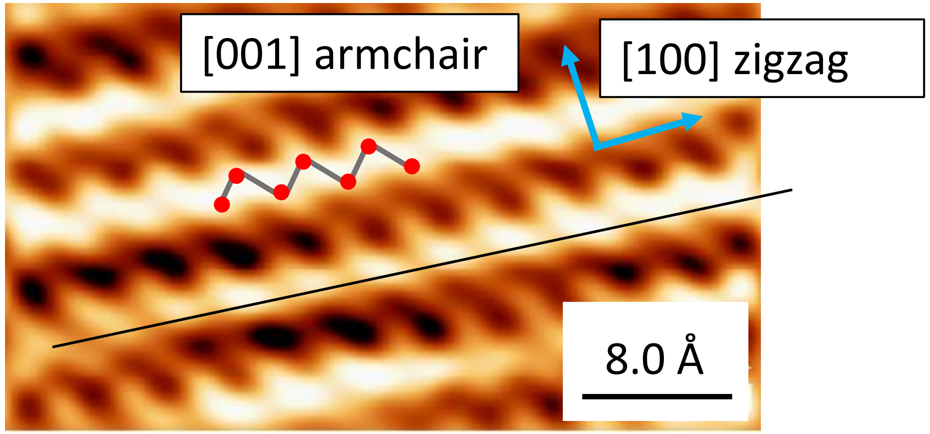
National Enterprise for nanoScience and nanoTechnology

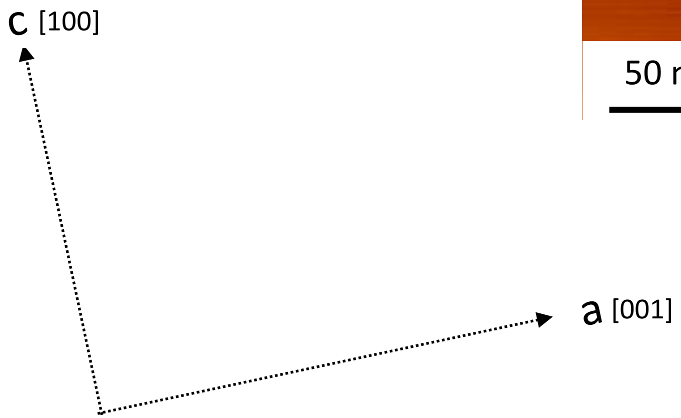
bP craters alignment





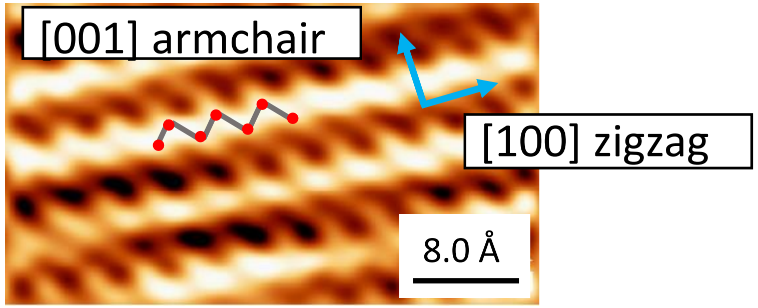


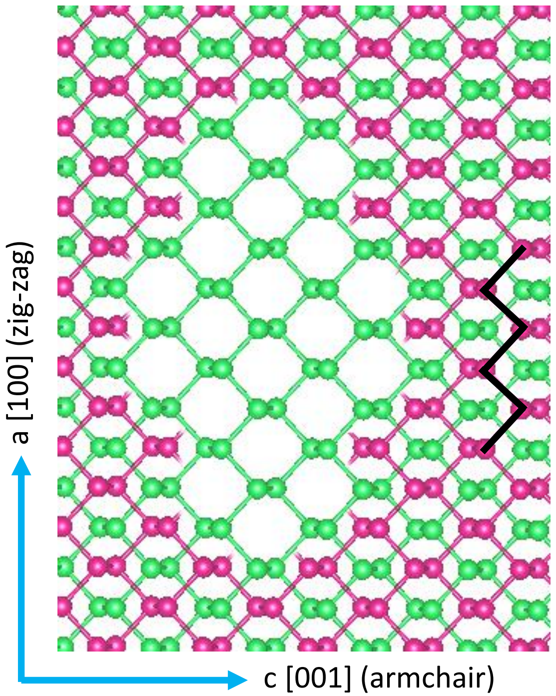




National Enterprise for nanoScience and nanoTechnology

bP craters alignment





Consistent with the result of Fortin-Deschenes et. al. paper

Gives a very clear evidence to settle the debate

IOPscience Journals Books Publishing Support Login Search IOPscie

2D Materials

PAPER • OPEN ACCESS

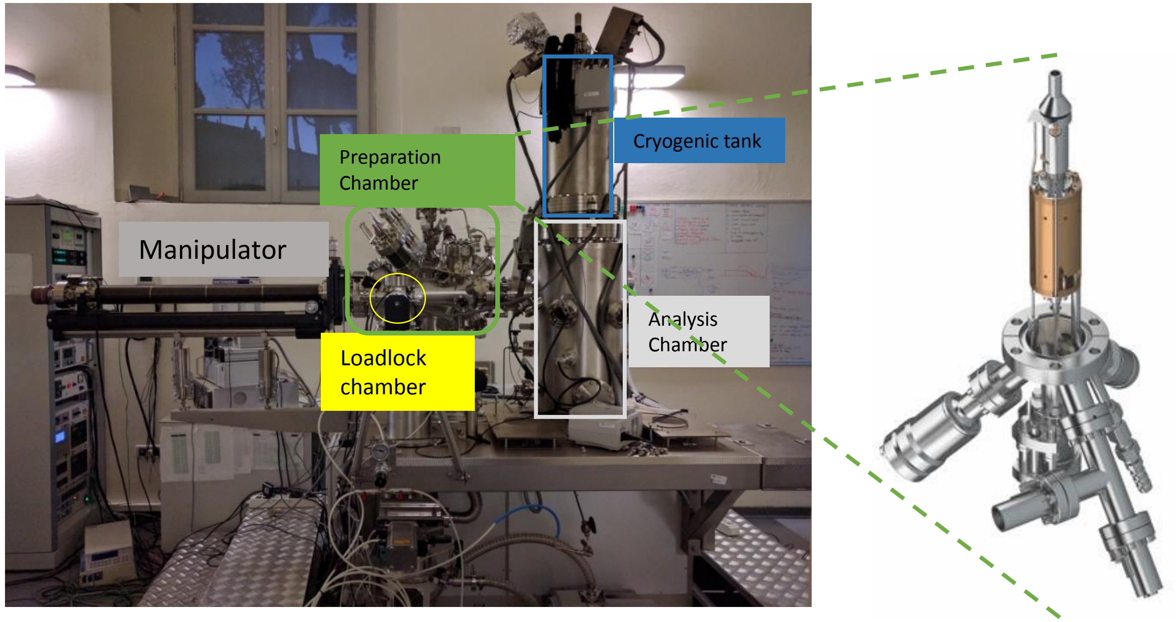
STM study of exfoliated few layer black phosphorus annealed in ultrahigh vacuum

Abhishek Kumar[1], F Telesio[1], S Forti[2], A Al-Temimy[2], C Coletti[2], M Serrano-Ruiz[3], M Caporali[3], M Peruzzini[3], F Beltram[1] and S Heun[1]

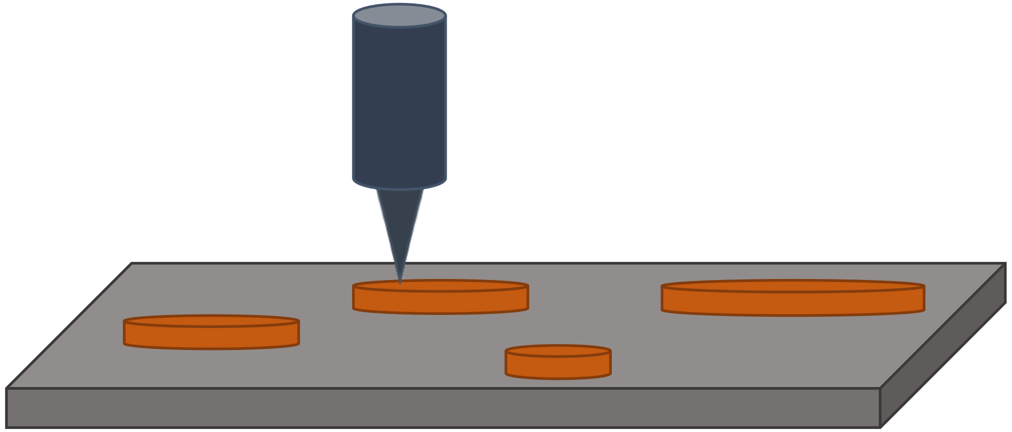
Published 22 October 2018 • © 2018 IOP Publishing Ltd

2D Materials, Volume 6, Number 1

Functionalization: study of transfer doping from metal islands



1. Study of the pristine bP sample
2. Sub-monolayer metal evaporation in the STM prep-chamber without breaking vacuum
3. Study of the functionalized sample

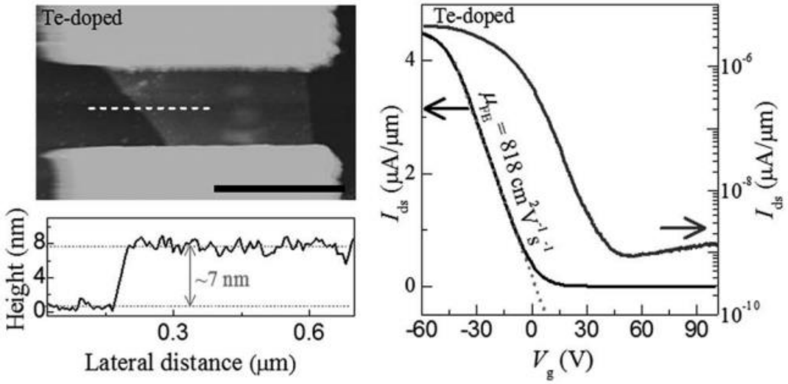


- ❑ Study of metallic islands morphology at different coverage
- ❑ Study of doping through Scanning Tunnelling Spectroscopy
  - ❑ Feedback is switched off
  - ❑ dI/dV $\propto$ LDOS

National Enterprise for nanoScience and nanoTechnology

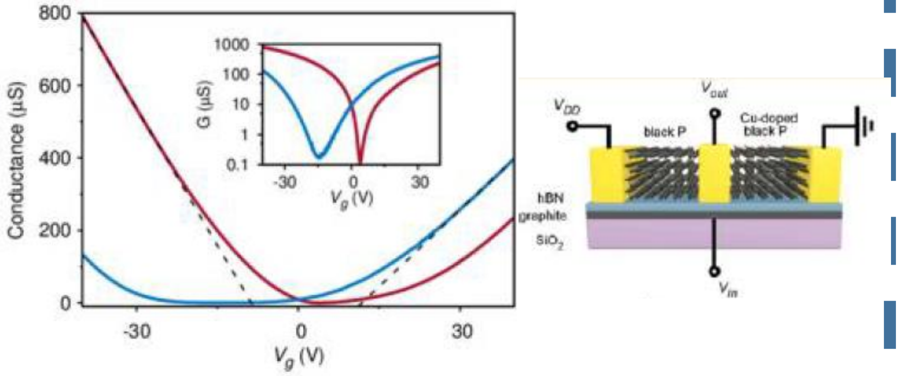
Functionalization: study of transfer doping from metal islands

➢ Te doping



B. Yang et. al. Adv. Mater., 2016, 28, 9408.

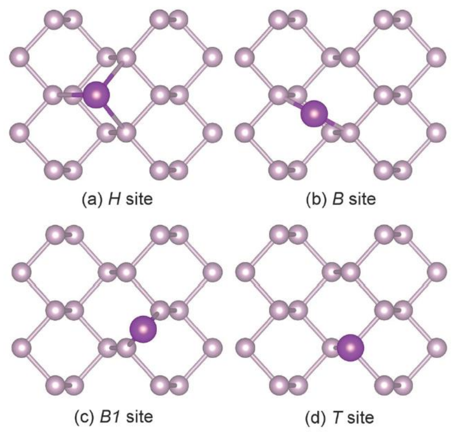
➢ Cu doping



Koening S. P., Nano Lett. 2016, 16, 2145.

➢ modeling

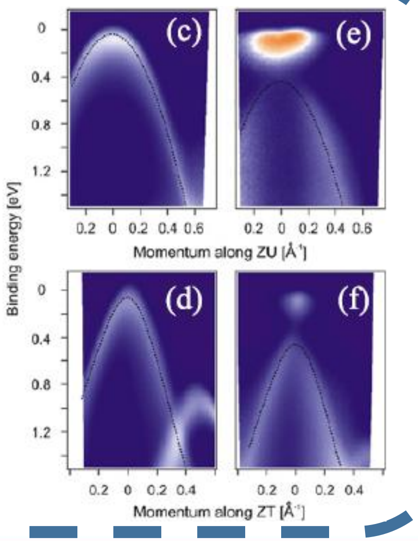
Adsorption of metal adatoms on phosphorene



Calculation of structural and magnetic properties for Li, Na, K, Cu, Ag, Au, Pd, Pt, Ti, V, Cr, Mn, Fe, Co, Ni, Si, Ge, P, H, O

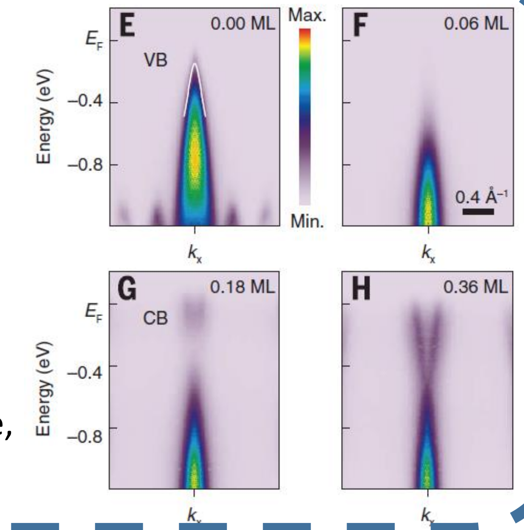
V. V. Kulish et al., Phys.Chem.Chem.Phys., 2015, 17, 992

➢ Li doping



A. Sanna et al, 2D Materials, 2016, 3, 205031 .

➢ K doping



J. Kim et al, Science, 2015, 349, 6249

W doping

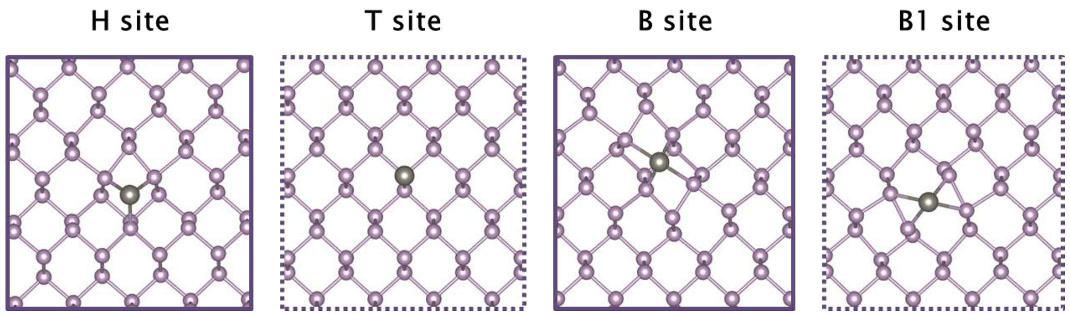
✓Tungsten was expected to strongly dope bP , similarly to Mo [2]

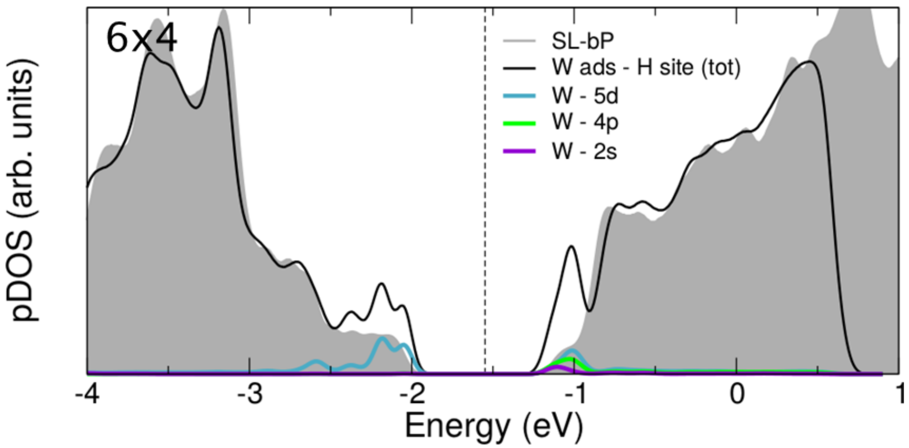
x It VERY hard to evaporate

… that is why evaporator crucibles are usually made by tungsten

x Modeling of W by DFT is not trivial since it's a very heavy atom, so a careful evaluation of pseudopotentials is needed.

… while we were trying to solve technical issues arose by evaporating tungsten…





...careful DFT calculations revaled that W did not have any significant doping effect on bP

[2] A. Ienco et al., Dalton Trans., 2018, accepted

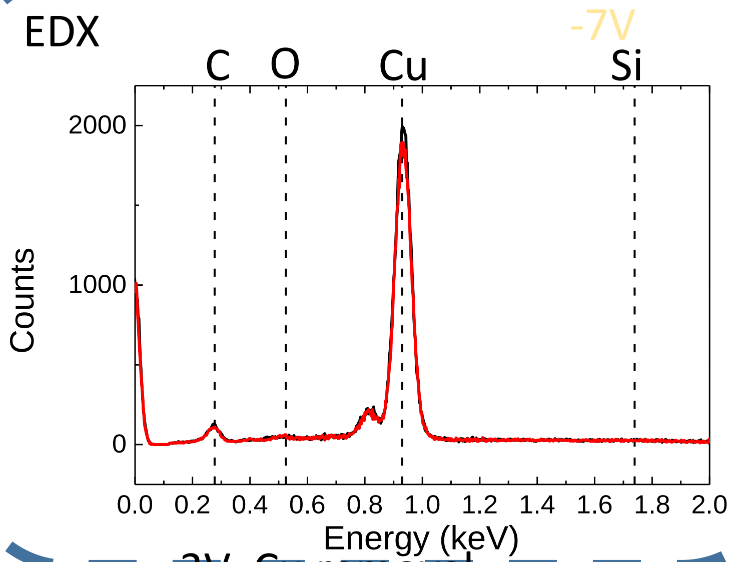
Cu doping

- ✓ Copper n-dope bP [1]
- ✓ It's much easier to evaporate
- ✓ In our team there is experience in Cu modeling by DFT

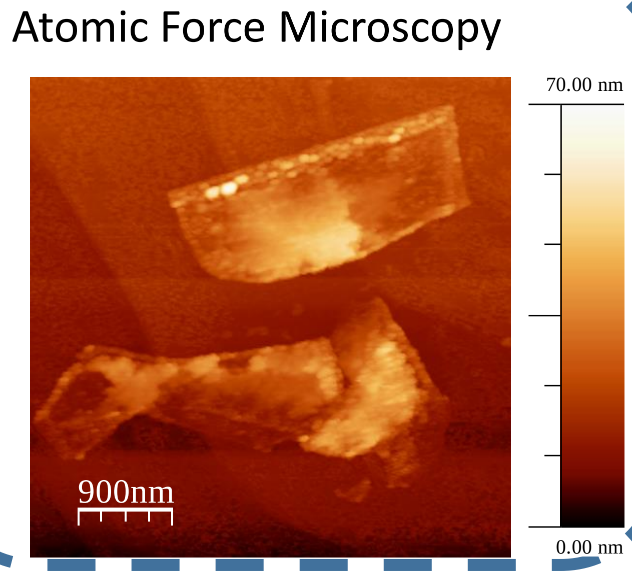
- Preliminary Characterization

First STM measurements

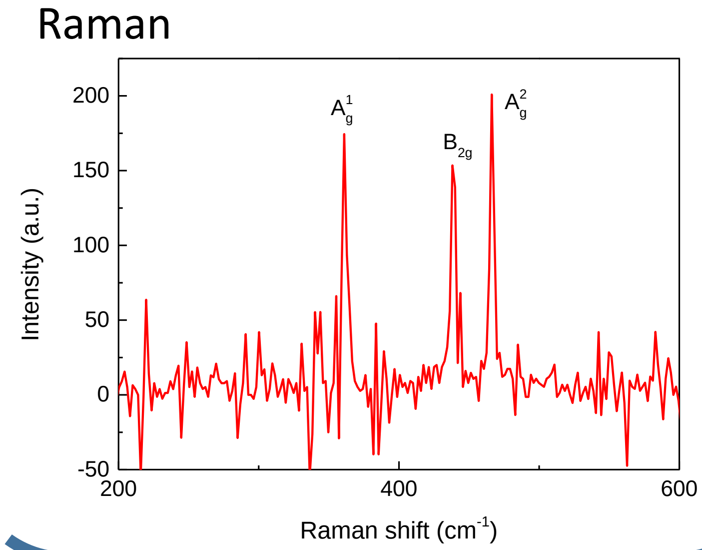
...Work in progress!



3V: Cu removal



ditic
tior
r Cu
nage



[1] Koening S. P., Nano Lett. 2016, 16, 2145

Conclusions

1. Study of the pristine exfoliated bP surface by STM
   - ✓ Low cost reliable method to obtain clean exfoliated bP flakes and good imaging of the pristine surface

2. Study of defects on the surface
   - ✓ Annealing of exfoliated bP flakes, focusing on the controlled sublimation regime
   - ✓ Preferential craters orientation, along the zigzag direction and solution of an existing debate

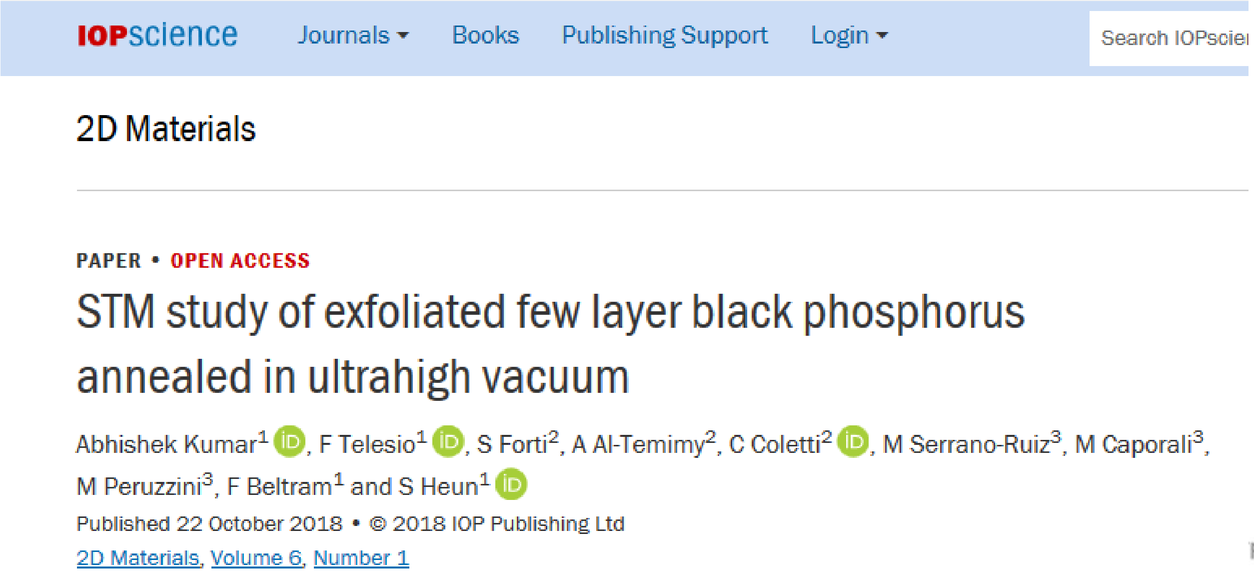
3. Surface functionalization, with particular focus on doping
   - ❑ The doping work is ongoing, both on the experimental and modeling sides

Outcomes and dissemination

- Oral presentation: “Phosphorene and 2D Companions” a national workshop held in Rome in May 2017

- Poster presentation: “SPM - International conference on Novel 2D materials explored via scanning probe microscopy and spectroscopy” in San Sebastian, Spain, in June 2018

- ✓ This project lead to a publication: Abhishek Kumar *et al* 2019 *2D Mater.* **6** 015005


IOPscience Journals Books Publishing Support Login Search IOPscie

2D Materials

PAPER • OPEN ACCESS

STM study of exfoliated few layer black phosphorus annealed in ultrahigh vacuum

Abhishek Kumar[1], F Telesio[1], S Forti[2], A Al-Temimy[2], C Coletti[2], M Serrano-Ruiz[3], M Caporali[3], M Peruzzini[3], F Beltram[1] and S Heun[1]

Published 22 October 2018 • © 2018 IOP Publishing Ltd

2D Materials, Volume 6, Number 1

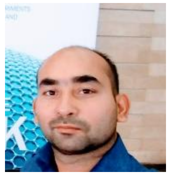

A. Kumar


S.Heun


D. Prezzi


A. Al-Temimy


S. Forti


N. Mishra


C. Coletti


M. Caporali


M. Serrano-Ruiz


M. Peruzzini

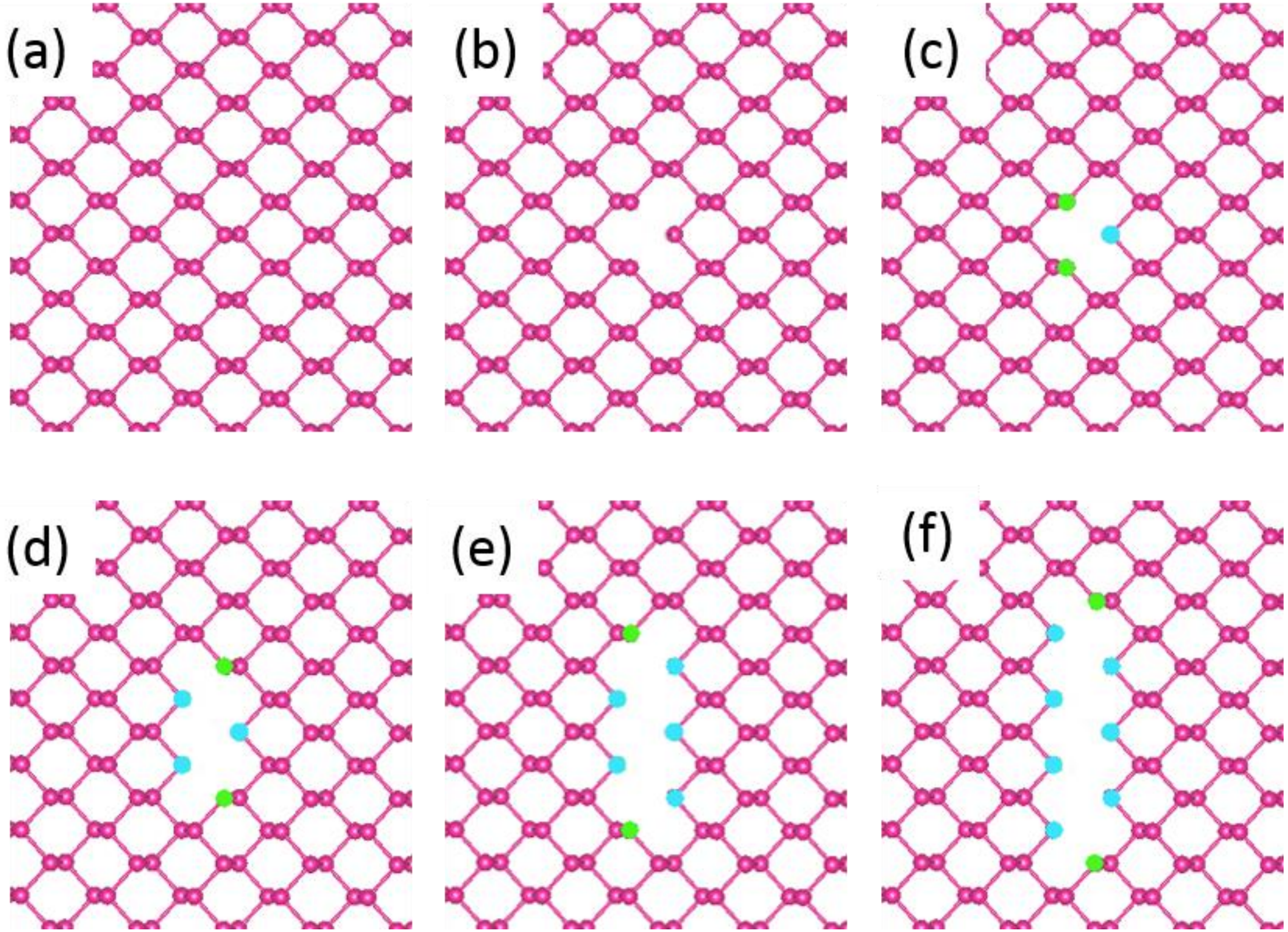
*SEED Project : **Surface** properties of black **Phosphorus** investigated by scanning tunneling microscopy*

*“**Phosphorene functionalization**: a new platform for advanced multifunctional materials”*

Thank you for your attention!

National Enterprise for nanoScience and nanoTechnology

Modeling of bP sublimation



In plane bond: 2.22Å
Out of plane bond: 2.24Å

Simple model in which:

- First desorb the atoms with just one bond
- Then the ones with one in plane and one out of plane bond
- Then the ones with two in plane bonds

National Enterprise for nanoScience and nanoTechnology

Modeling in Deschenes et al.

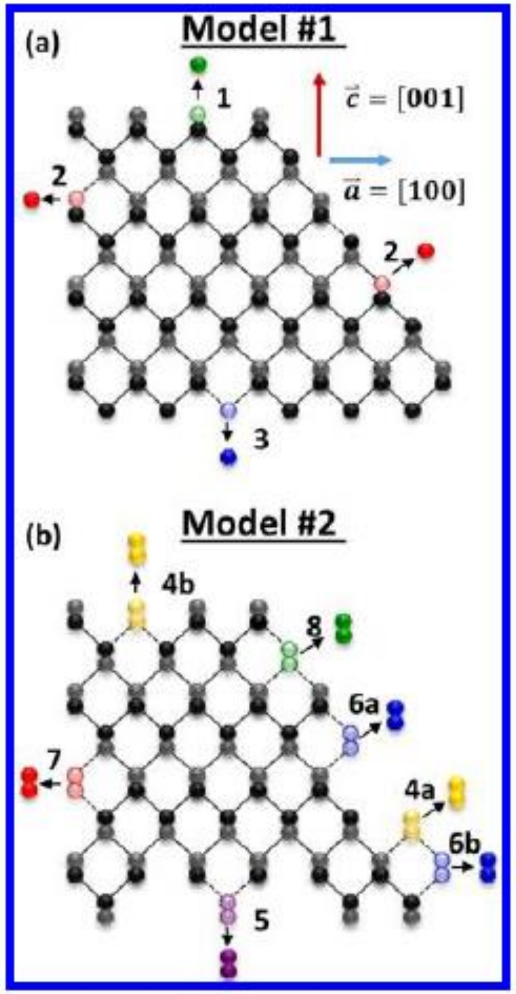
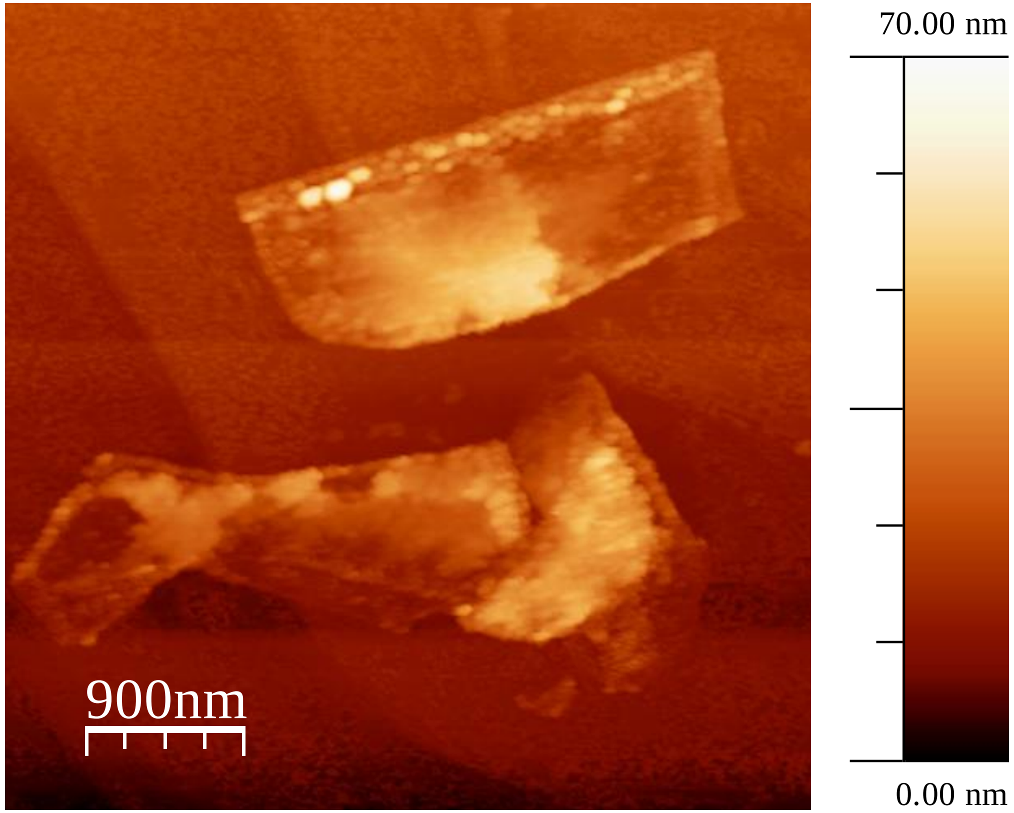


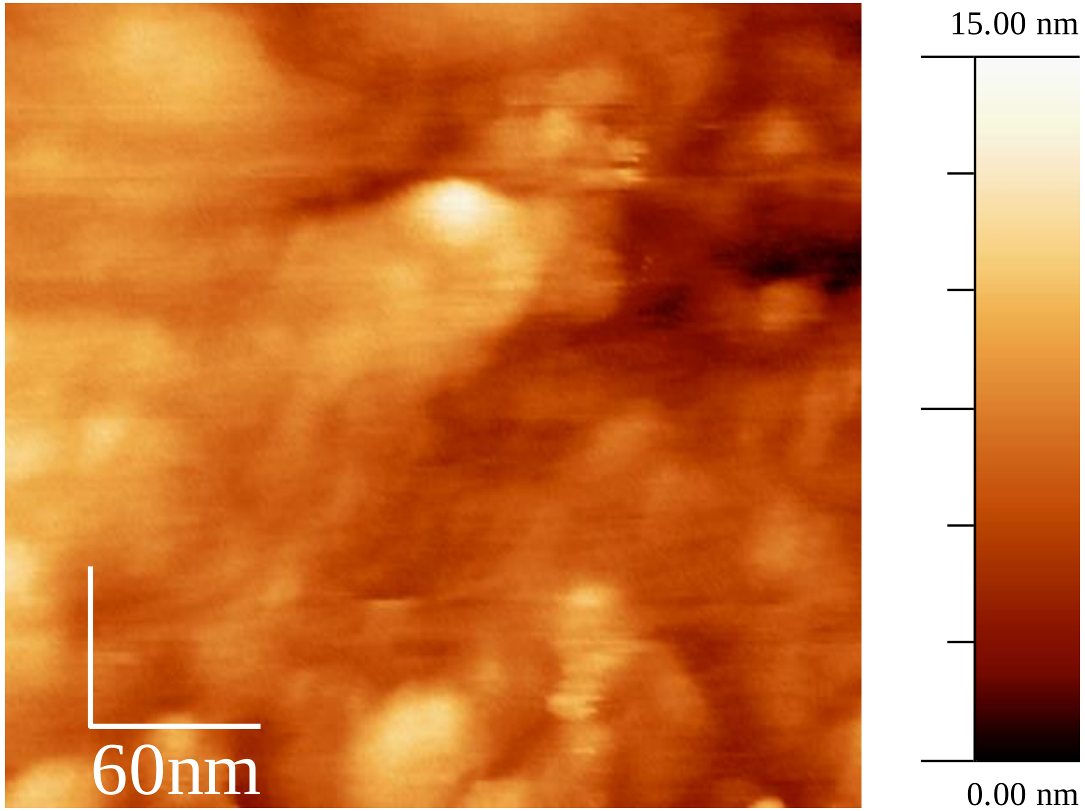
Table 1. Calculated DFT and Fitted KMC Energies for Different Sublimation Processes[a]

	model #1		model #2	
	ΔE (DFT)	E_a (KMC fit)	ΔE (DFT)	E_a (KMC fit)
process #1	2.32 eV	≪ 1.62 eV		
process #2	3.43 eV	1.57 eV		
process #3	4.02 eV	1.62 eV		
process #4a			1.69 eV	1.61 eV
process #5			1.04 eV	1.04 eV
process #6a			1.69 eV	1.41 eV
process #7			2.30 eV	1.59 eV
process #8			N/A	1.66 eV

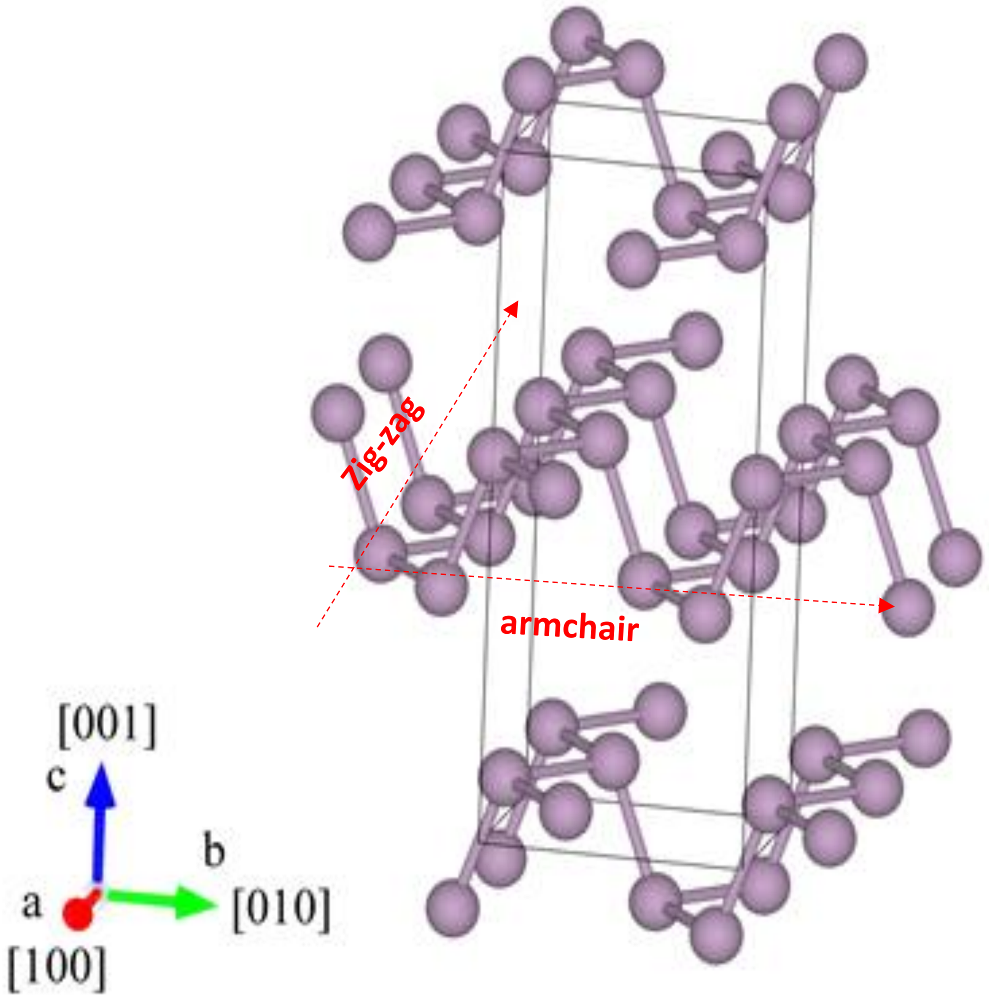
[a]For each model, the left column represents the energy calculated using eq 1 or (2) on the modeled PNRs. The right column represents the fitted KMC activation energies. For M1, an ellipse is fitted on the hole every n^2 iteration to track the hole expansion dynamics. For M2, only the extremity of the holes are followed. The fitted KMC values allow to reproduce the long to short axis ratio of 1.8 and the 21.5 nm/s velocity measured at 495°C within 1% error. For shape optimization, 245 000 atoms are sublimated and 10 simulations are averaged. For velocity calculations, 40 000 atoms are sublimated and 1000 simulations are averaged.

Further preliminary characterization: AFM on Graphene/bP/Cu





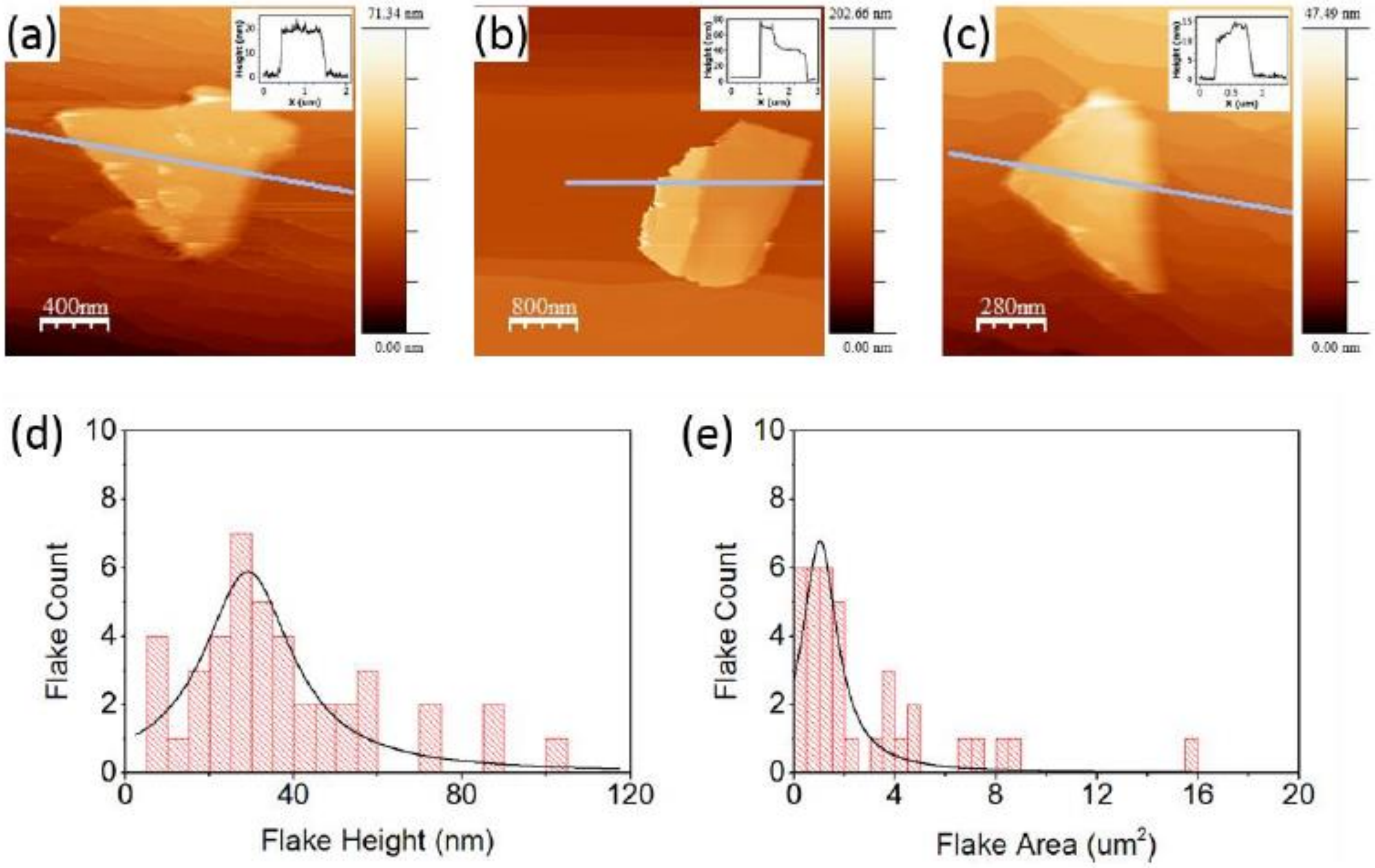
Black phosphorus



Cell parameters
a=3.13Å
b=10.47Å
c=4.37Å

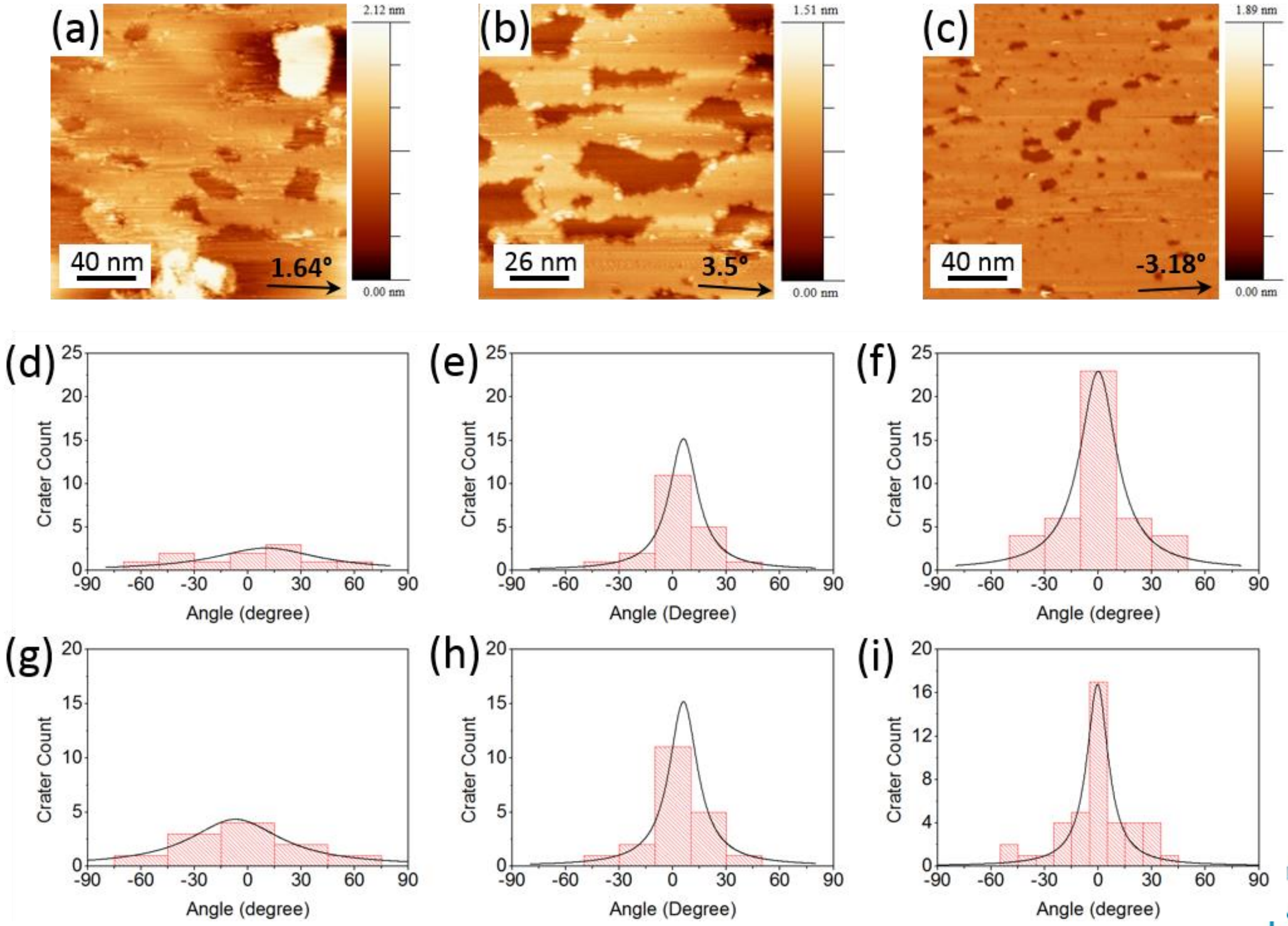
A. Morita, Appl. Phys. A 39 (1986) 227

Flakes size and thickness

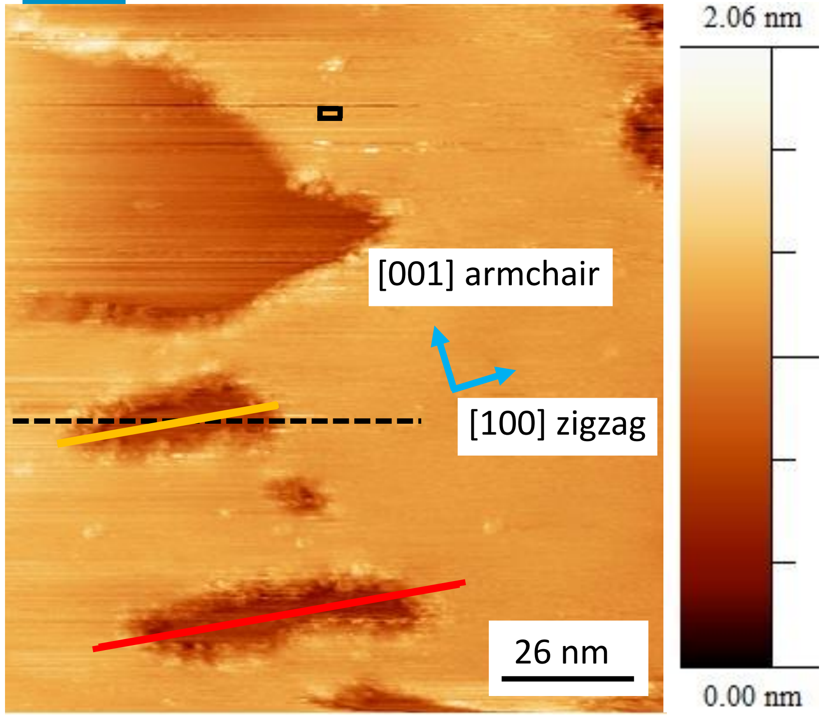


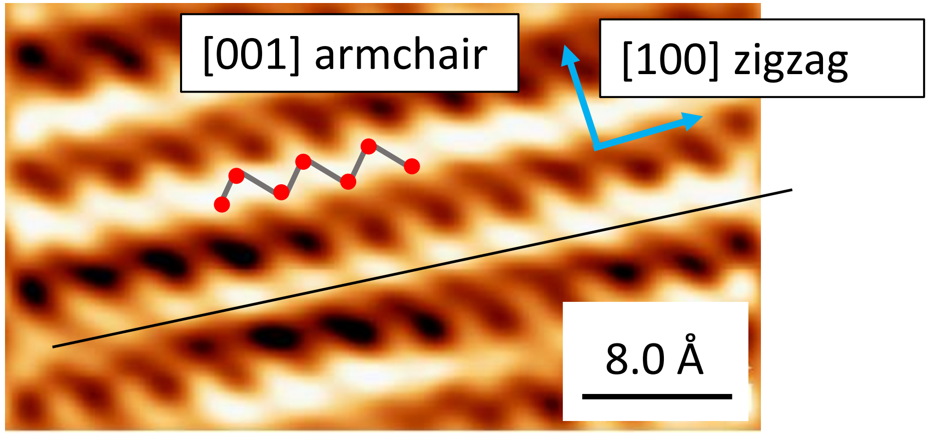
National Enterprise for nanoScience and nanoTechnology

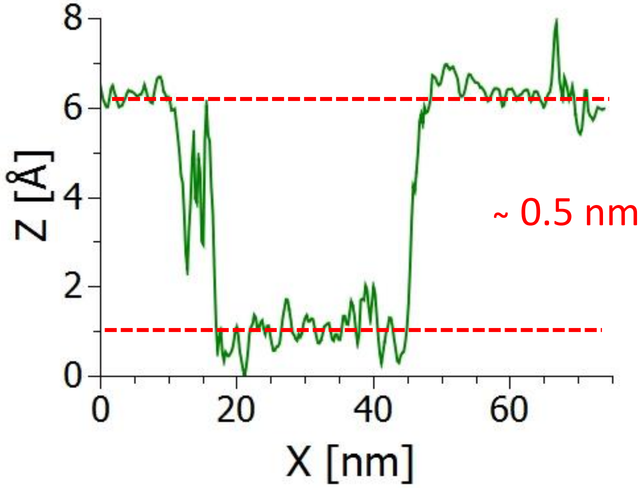
Craters alignment statistics

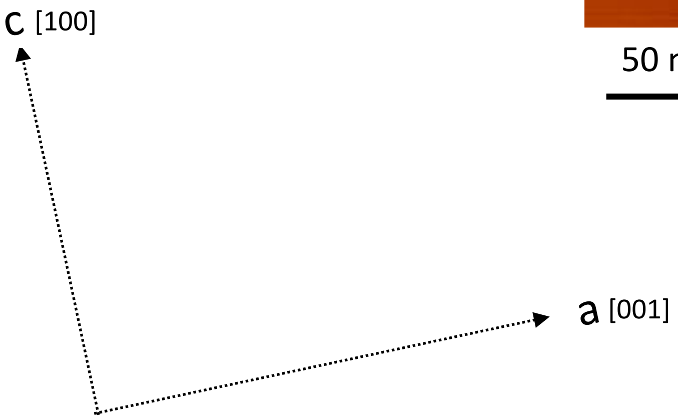


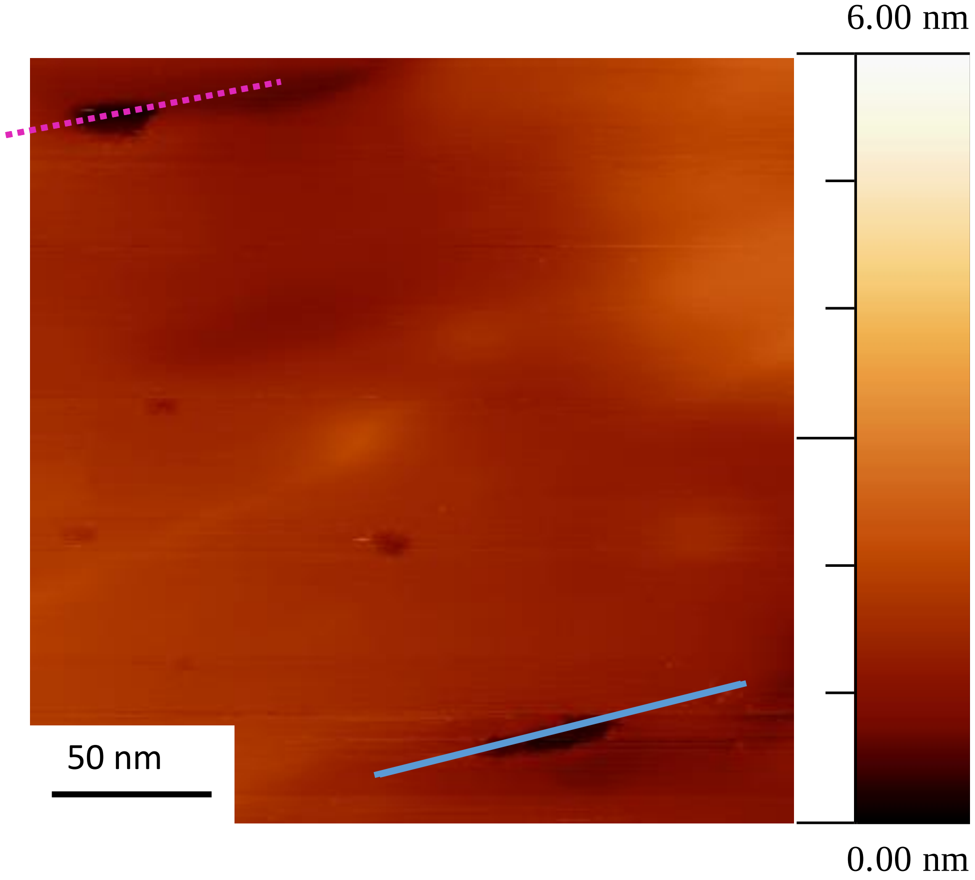
bP craters alignment











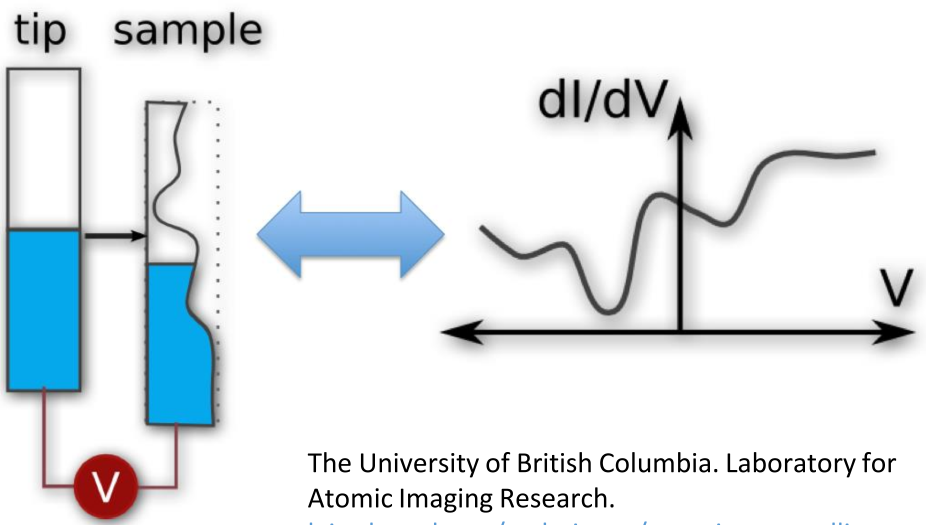
Scanning Tunneling Spectroscopy

- Feedback is switched off
- dI/dV $\propto$ LDOS
- Energy resolution,

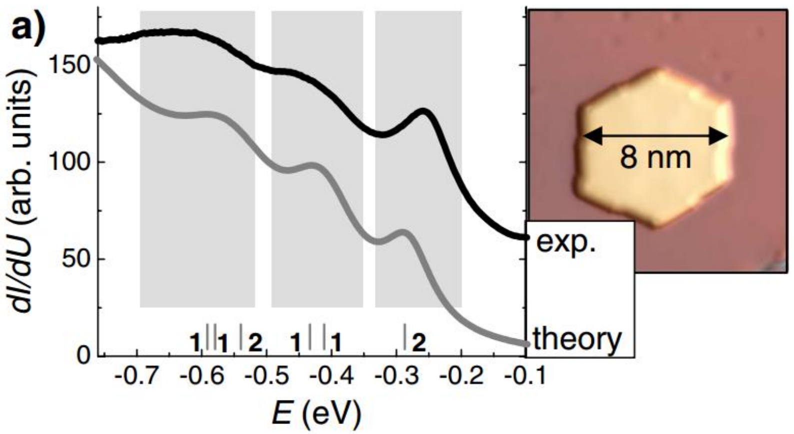
$$\delta E \approx \sqrt{(3.3K_BT)^2 + (1.8eUmod)^2}$$

with U_{mod} = modulation voltage (~ 20 mV)

- $\delta E \sim 83meV(300K)$, 42meV(80K), 36meV(5K)
- dI/dV image is reconstructed from recorded dI/dV curve

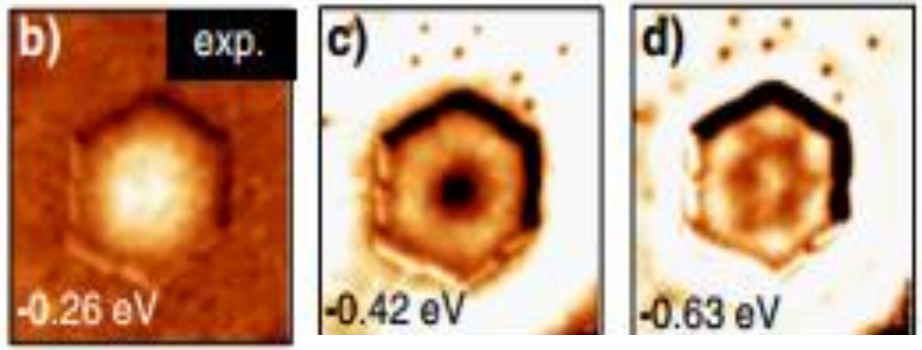


The University of British Columbia. Laboratory for Atomic Imaging Research. lair.phas.ubc.ca/techniques/scanning-tunnelling-microscopy Accessed 21 Oct. 2016.



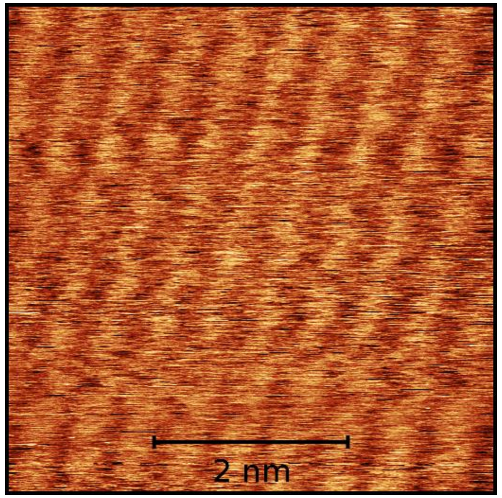
C. J. Chen. *Introduction to Scanning Tunneling Microscopy*. New York, Oxford University Press, 2008. Print

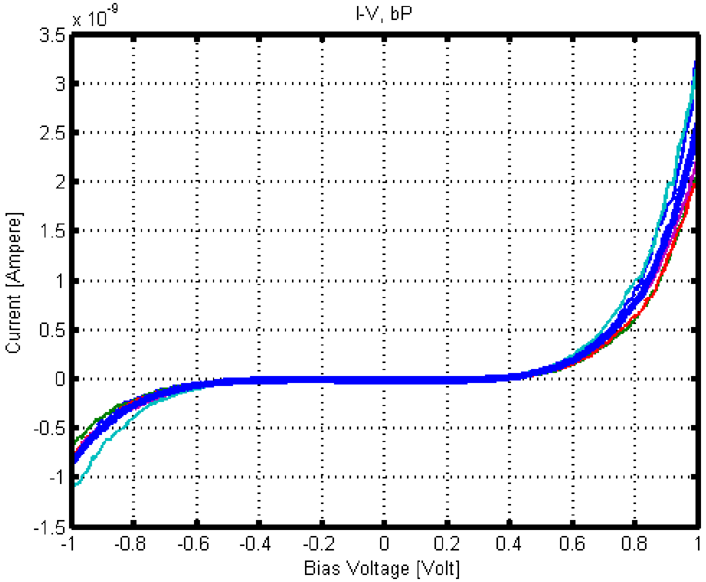
U_{mod} = 10mV, 5K, $\delta E = 18meV$

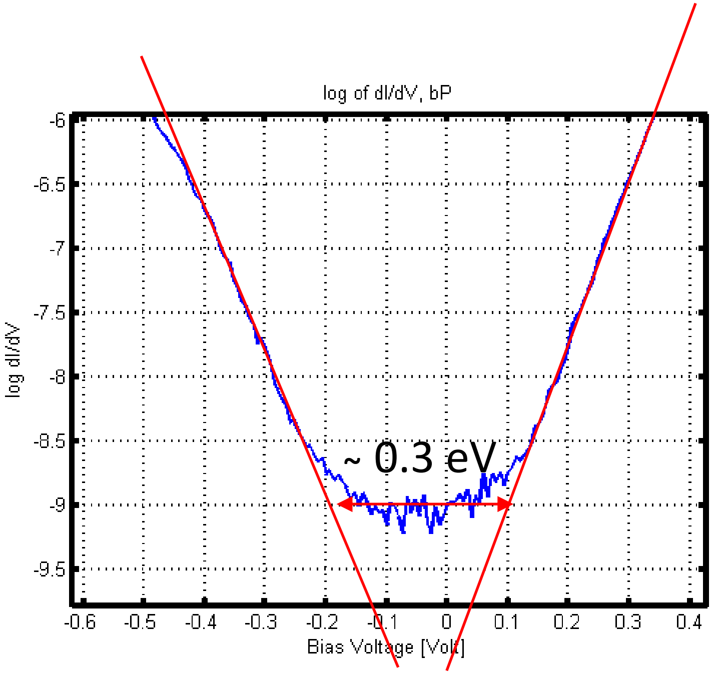


D. Subramanian et. al. PRL **108, 4**, 046801 (2012)

STS on bP

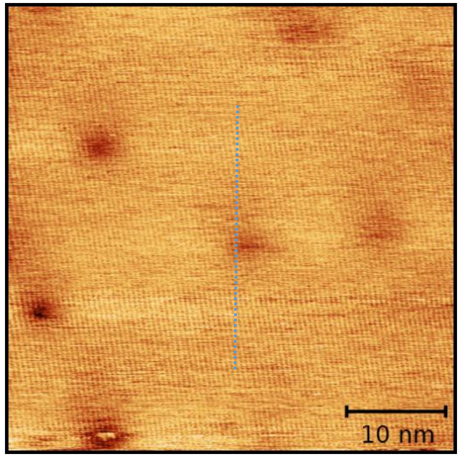


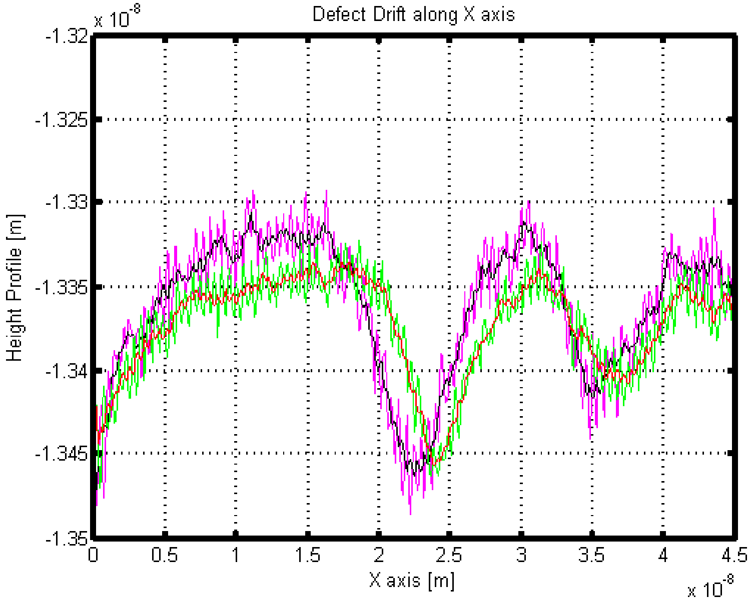


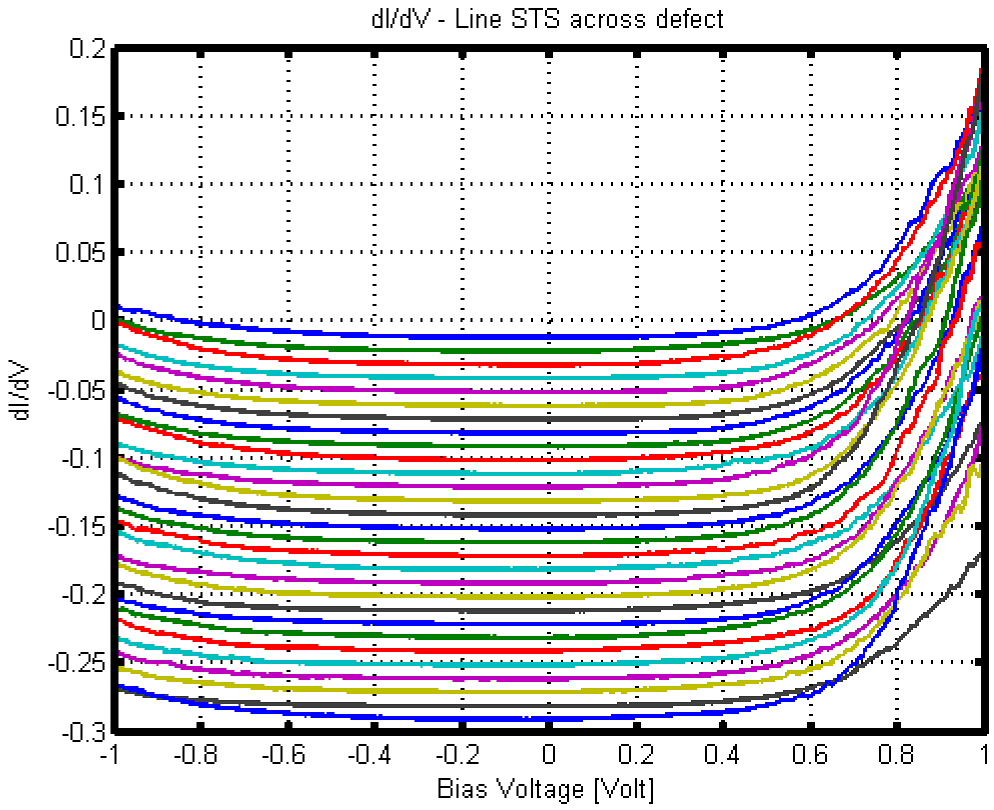


National Enterprise for nanoScience and nanoTechnology

STS across a bP defect



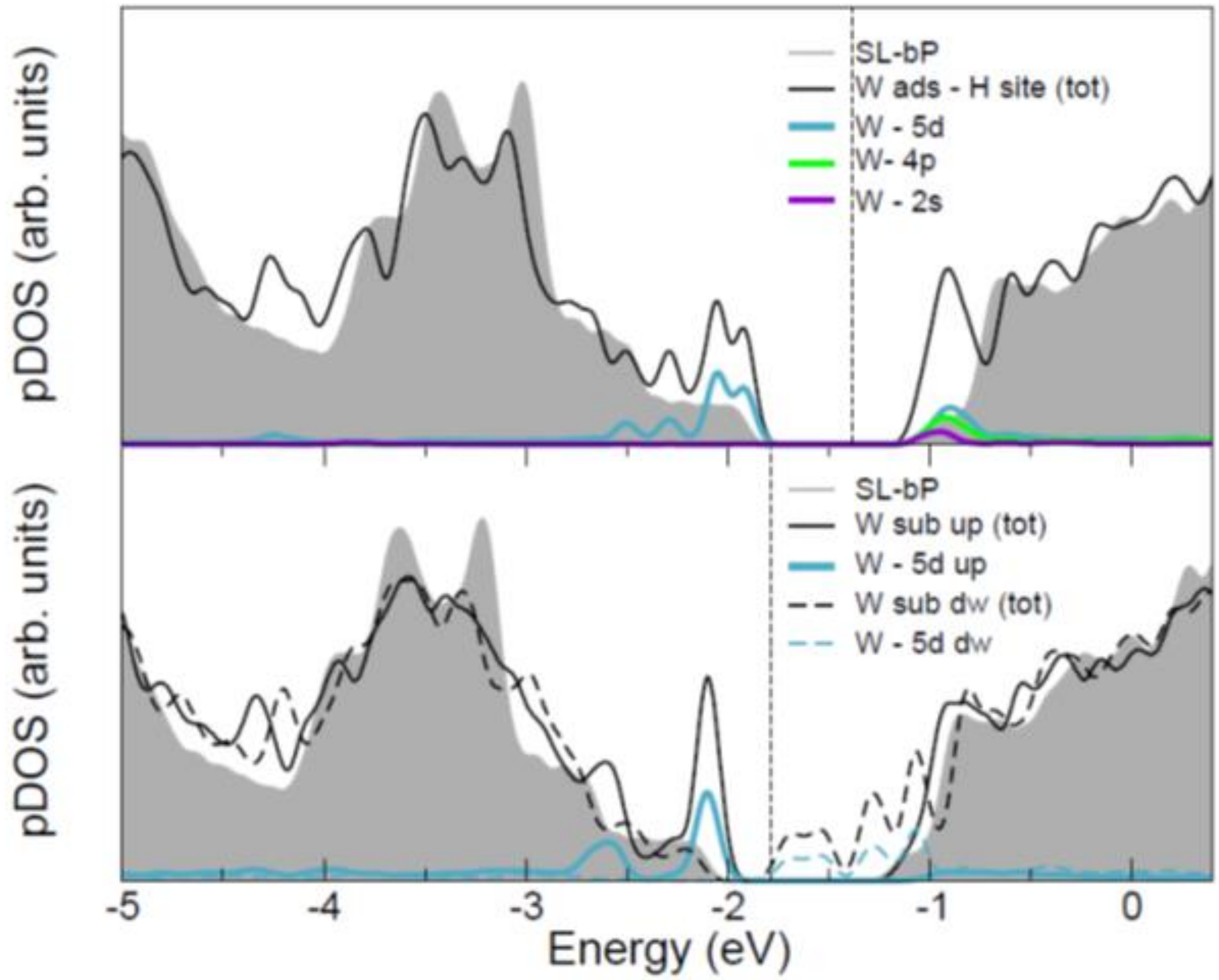




We don't observe any defect signature at room temperature

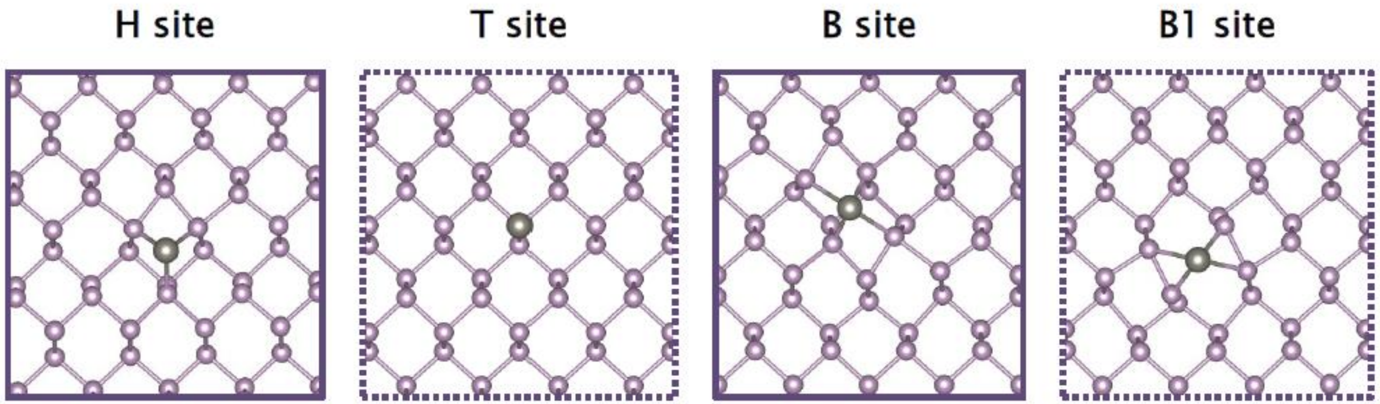
National Enterprise for nanoScience and nanoTechnology

Adsorbed and substitutional W



National Enterprise for nanoScience and nanoTechnology

Doping:1st trial W doping



E_F=–4.036 eV, NM | unstable (reverts to H) | E_F=–3.908 eV, NM | E_F=–2.762 eV, μ = 1.97 μ_B/cell

Supercell approach: **4x3 - to be converged wrt formation energy**
Ecut–wfc = 52 Ry (ecut–rho = 624 Ry); kpts mesh (non–shifted): 5x5x1
Pseudopot: P.pbe–n–rrkjus_psl.0.1.UPF & W.pbe–spn–rrkjus_psl.0.2.3.UPF (from pslibrary)
Formation energy calculated as: $E_F = E_{tot,d} - n_P \cdot \mu_P - n_W \cdot \mu_W$
with μ_P chemical pot of P in SLbP; μ_W chemical pot of atomic W.
Note that there is a significant distortion of the lattice (also visible in the figures), whose energy contribution is ~ 0.65 eV/cell for the H site.