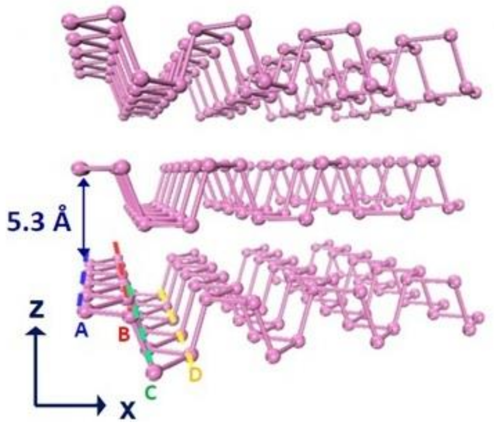
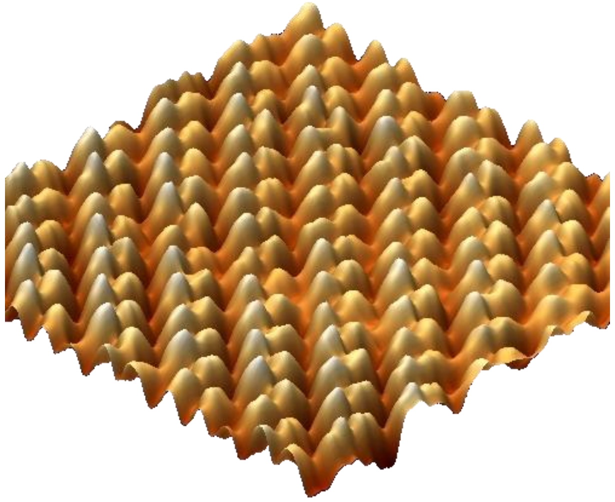


Black Phosphorus: Pristine and doped surface investigations using Scanning Tunneling Microscopy

PhD. Thesis in Condensed Matter Physics



Candidate:

Abhishek Kumar

Supervisors:

Prof. Stefan Heun

Prof. Vittorio Giovannetti

NEST

SCUOLA NORMALE SUPERIORE

OUTLINE

- Introduction
- Experimental Methods
- bP surface study
- bP doping study

VAN DER WAALS MATERIALS (LAYERED MATERIALS)

Giuseppe Franco Bassani

Director of Scuola Normale Superiore (1995-1999)

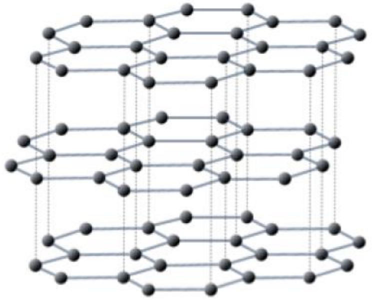
IL NUOVO CIMENTO   VOL. L B, N. 1   11 Luglio 1967

Band Structure and Optical Properties of Graphite and of the Layer Compounds GaS and GaSe (*).

F. BASSANI (**) and G. PASTORI PARRAVICINI (**)

Istituto di Fisica dell'Università - Messina
Gruppo Nazionale di Struttura della Materia del CNR

(ricevuto il 12 Dicembre 1966)

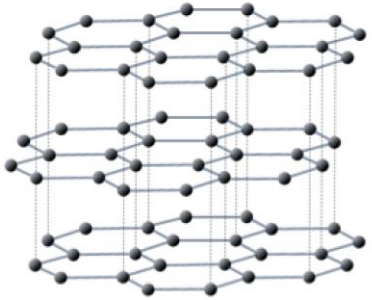


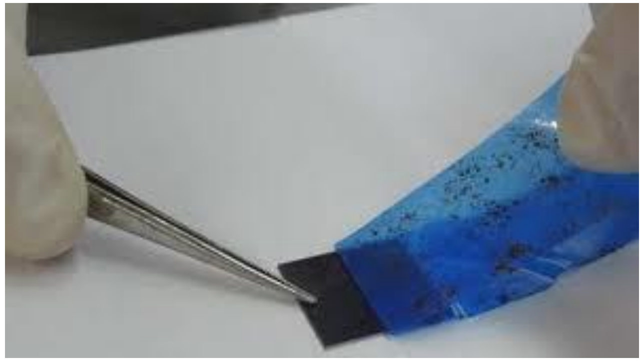
- Transition metal layer compounds
- Graphite films on metals and metal carbides
- Hexagonal Boron Nitride thin films
- Black Phosphorus

F. Bassani et. al. Il Nuovo Cimento B, 1967, 50(1), 95.
C. Oshima et. al. Japanese Journal of Applied Physics, 1977, 16(6), 965.
A. D. Yoffe et. al. Annual Review of Materials Science, 1973, 3(1), 147.
A. Nagashima et. al. Phys. Rev. Lett., 1995, 75, 3918.
P. W. Bridgman et. al. Journal of the American Chemical Society, 1914, 36(7), 1344.

GRAPHENE

- Single atomic layer of carbon
- First 2D material to be realized
- Andre Geim & Kontantin Novoselov – Nobel Prize (2010)
- Scotch tape exfoliation method





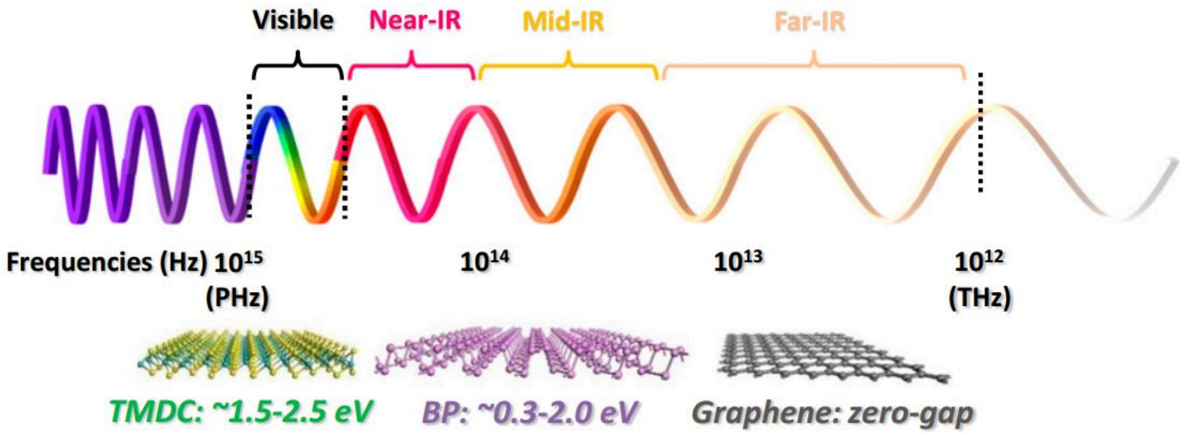
Two Dimensional Materials

Graphene – Zero band gap, high mobility, high electrical and thermal conductivity and high tensile strength.

TMDCs – Semiconducting: MoS_2 (1.8 eV), WS_2 (2 eV)

h-BN – Insulating, free of dangling bonds

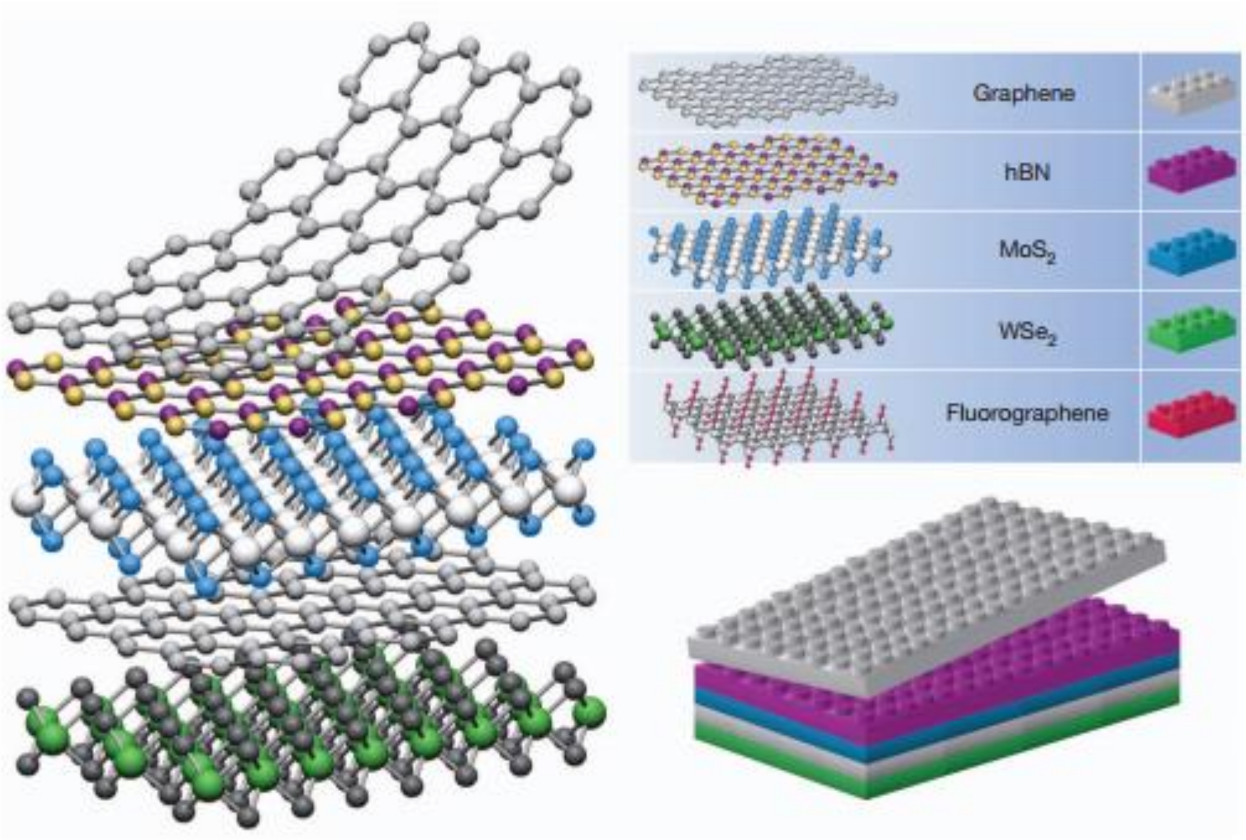
Xenes – Silicene, Germanene, Stanene, Plumbene



V. Tran et. al. Phys Rev B 89,235319(2014)

K. I. Bolotin et. al. Solid State Communications 146 (2008) 351–355

ENGINEERED VAN DER WAALS MATERIALS



Atomic Scale Lego

No need to worry about lattice matching

A. K. Geim et. al. Nature 499 (2013) 419.

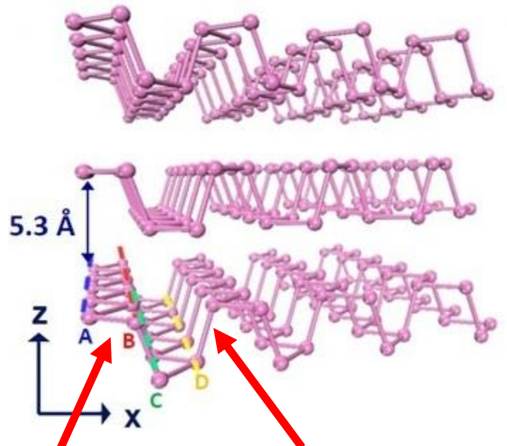
BLACK PHOSPHORUS (BP) AND PHOSPHORENE

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 Brigdman in 1914



A-B = 2.224 Å

B-C = 2.244 Å

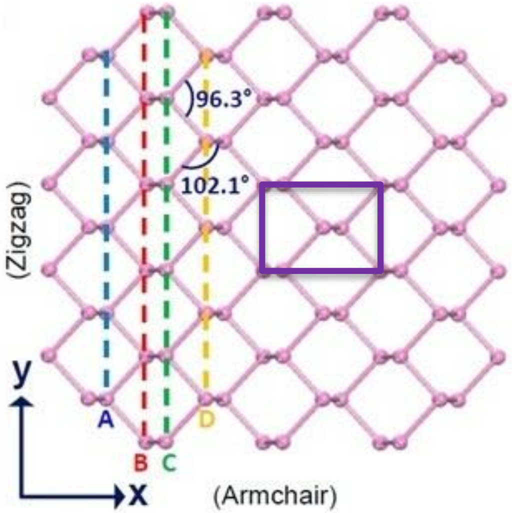
Phosphorene

→ Single Layer of Black P

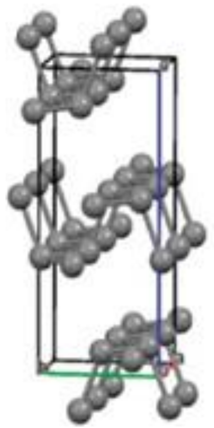
→ Honeycomb network similar to Graphene.

→ Exfoliated in 2014

→ Armchair along X and Zig-Zag along Y



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



Orthorhombic Structure

a =3.31 Å

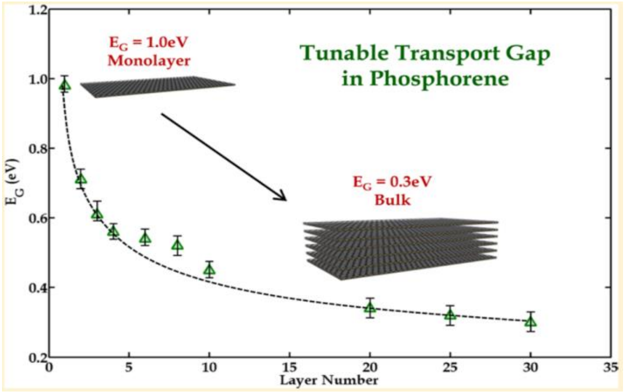
b = 4.38 Å

c = 10.50 Å

$\alpha = \beta = \gamma = 90$ °

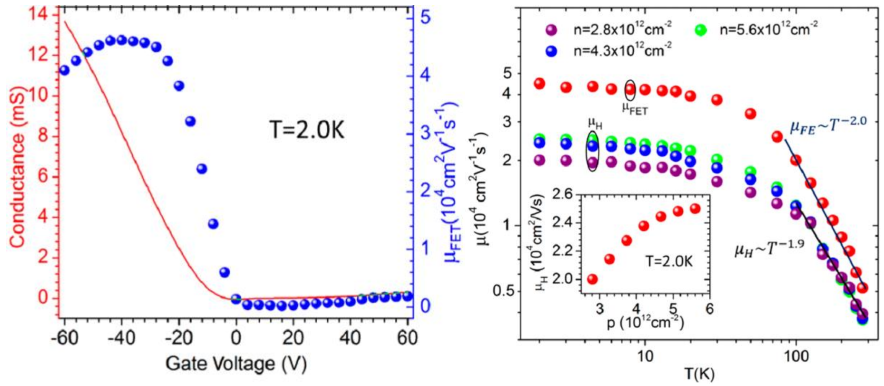
PROPERTIES OF BP

- Direct and Tunable Band Gap
- Intrinsically p-type doped
- High hole mobility
- Anisotropy

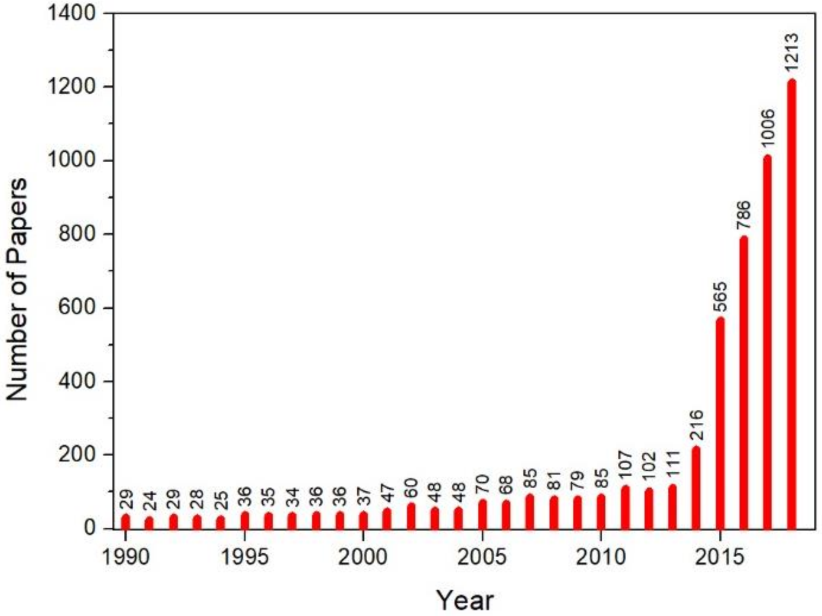


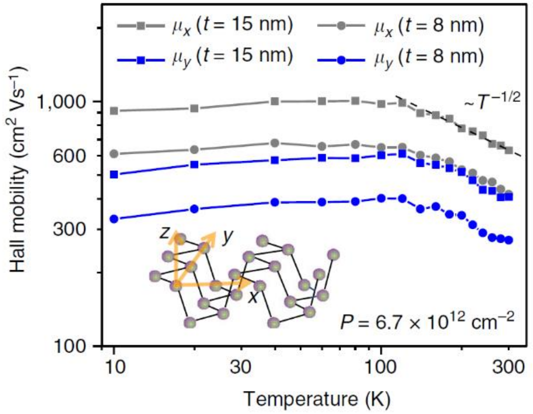
S. Das et al., Nano Lett. 14 (2014) 5733

5,200 cm^2/(V·s) at RT
45,000 cm^2/(V·s) at 2 K

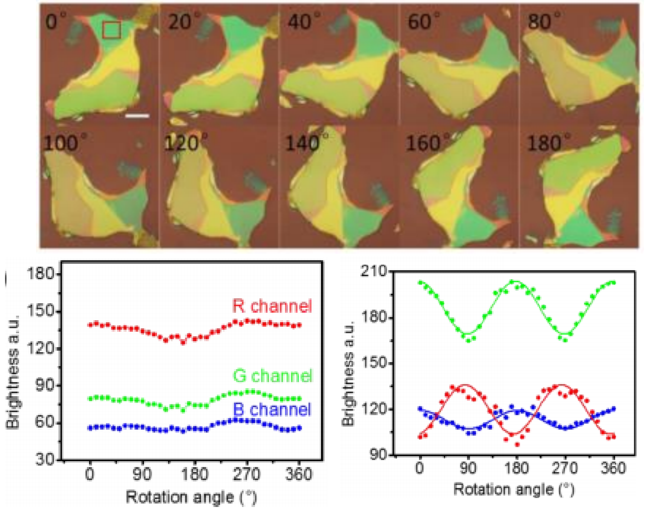


G. Long et al., Nano Lett. 16 (2016) 7768



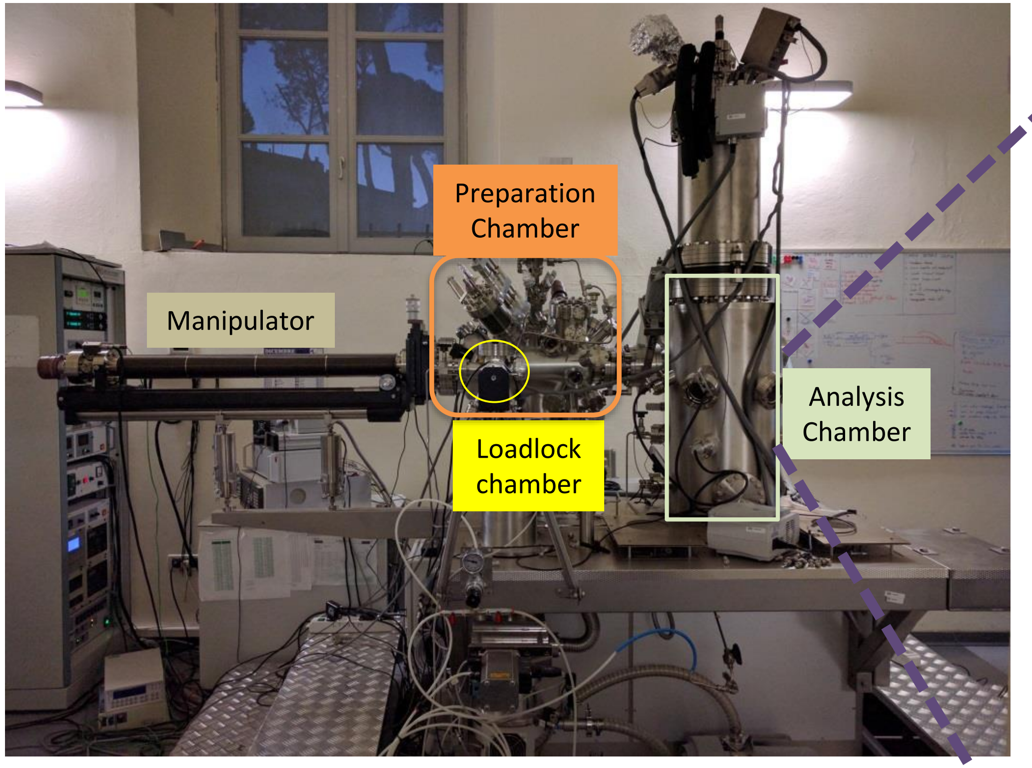


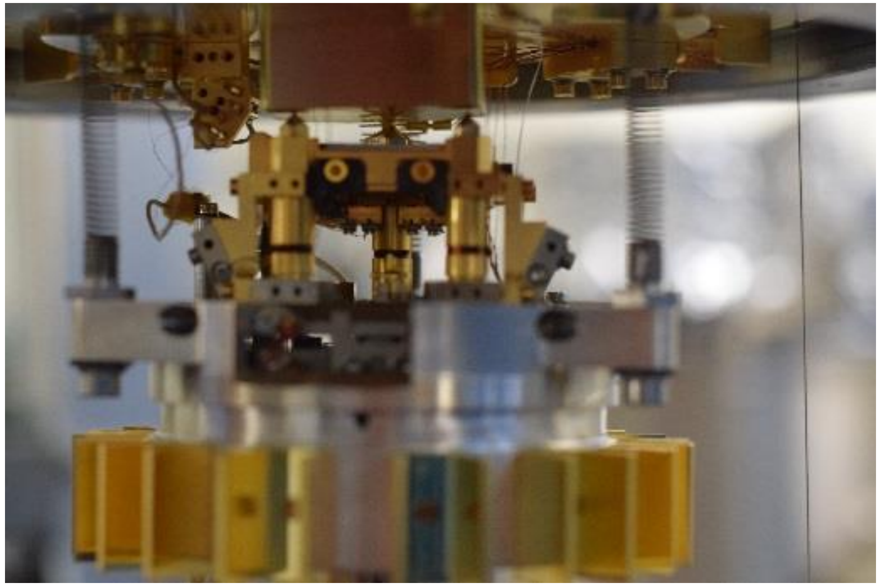
F. Xia et al., Nat. Comm. 5 (2014) 4458.

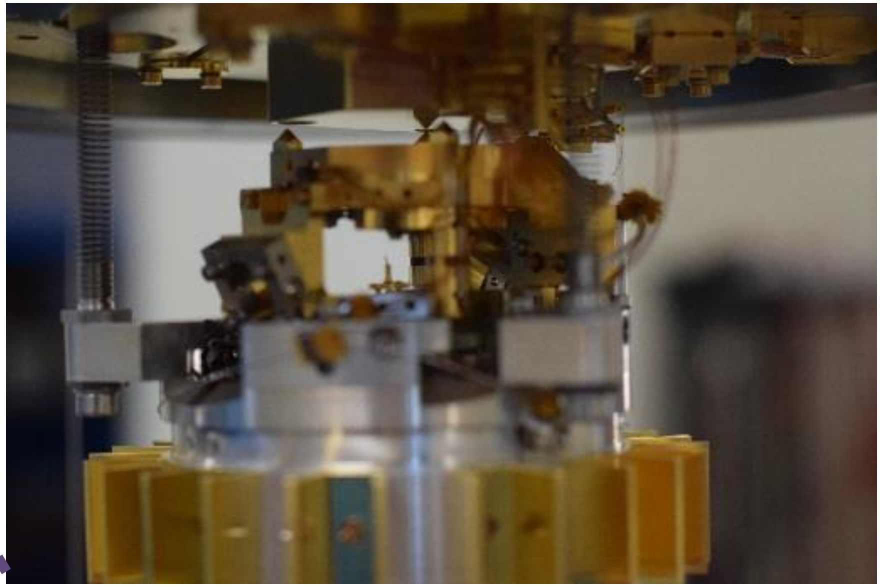


N. Mao et. al. J. Am. Chem. Soc. 2016, 138, 1, 300-305.

SCANNING TUNNELING MICROSCOPY (STM)



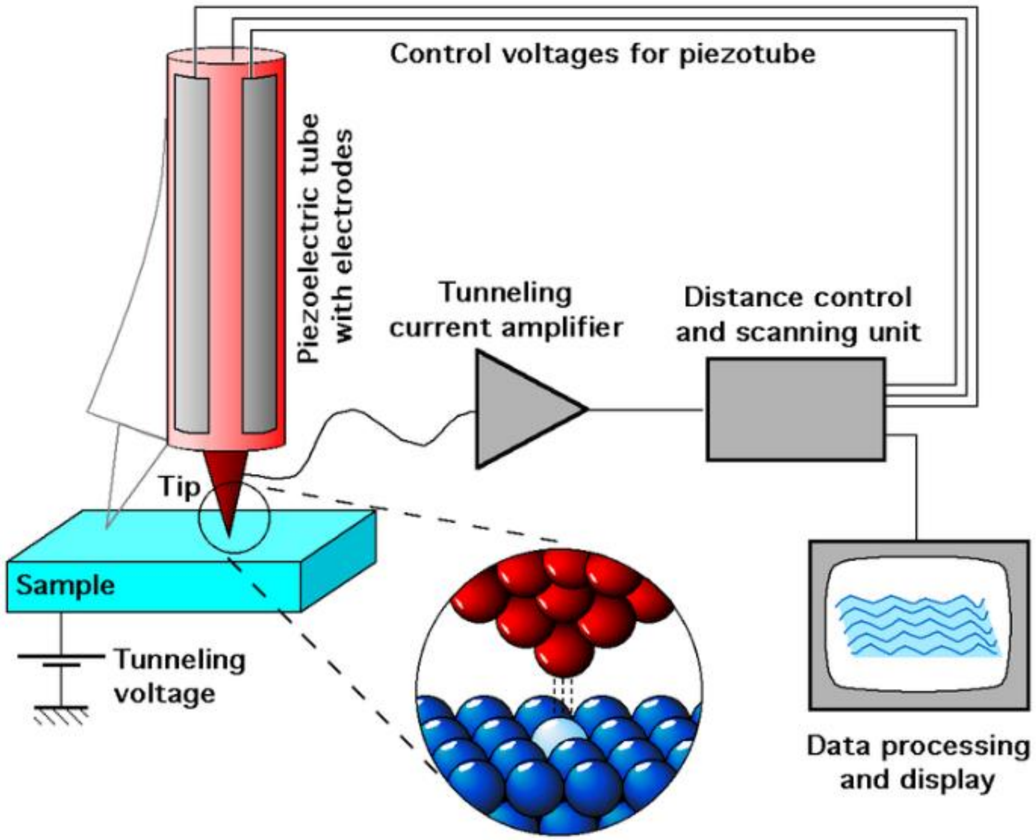




<u>Omicron UHV LT-STM</u>

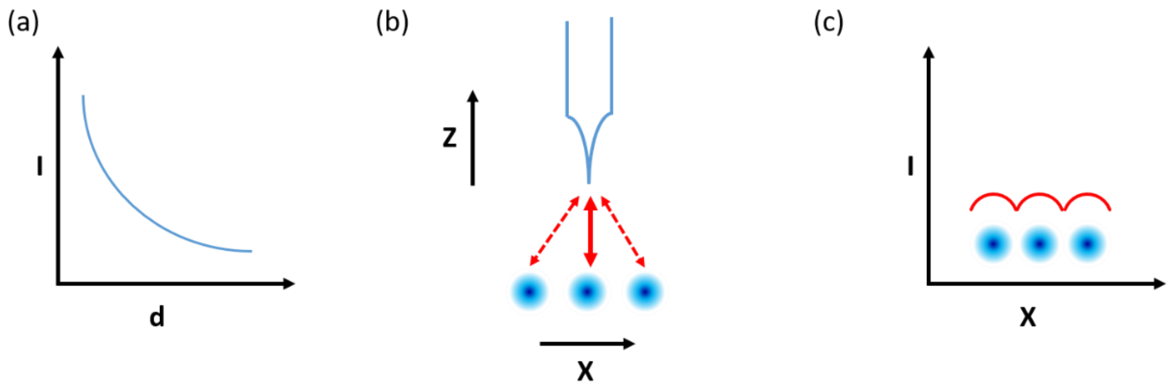
- Base Pressure – 1.0e-11 mbar
- In-situ sample preparation facilities:
  Annealing, Sputtering, Metal Evaporation

SCANNING TUNNELING MICROSCOPY (STM)

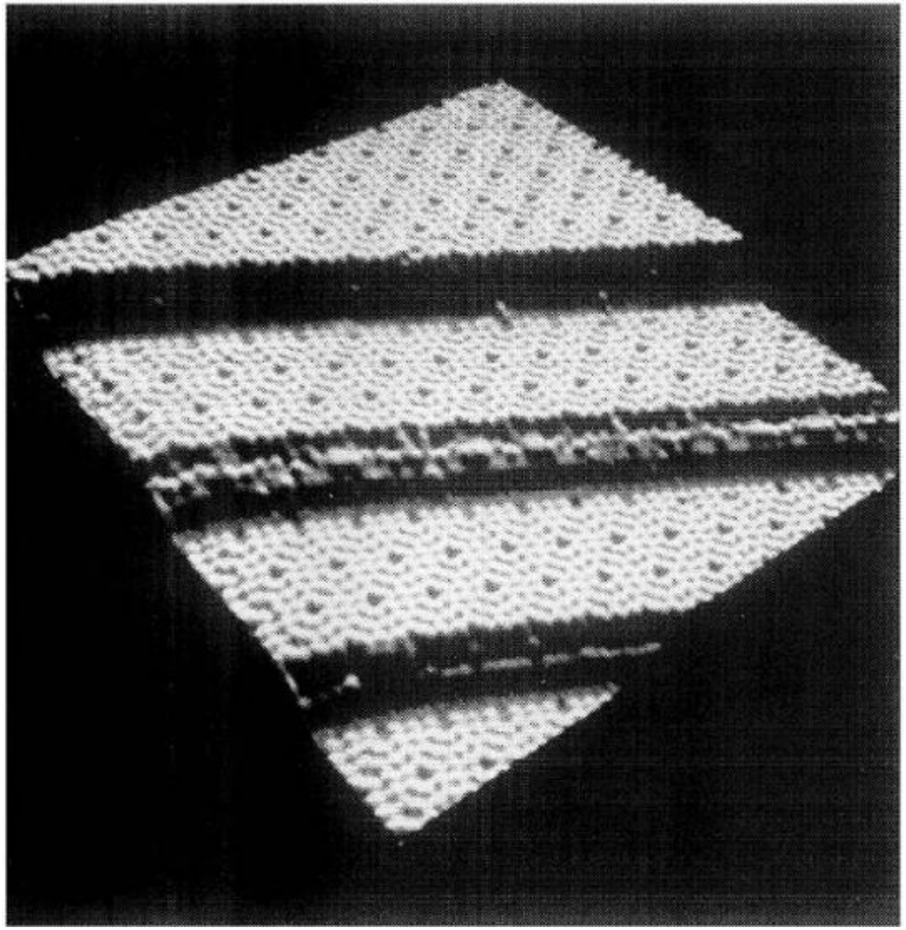


- Requires conducting substrate
- Tunneling current, I ∝ exp (-2kd),

$$k = \frac{\sqrt{2m\Phi}}{\hbar},\ \Phi = \text{potential barrier.}$$



SCANNING TUNNELING MICROSCOPY (STM)



<u>"Stairway to Heaven"</u>
To touch atoms and molecules

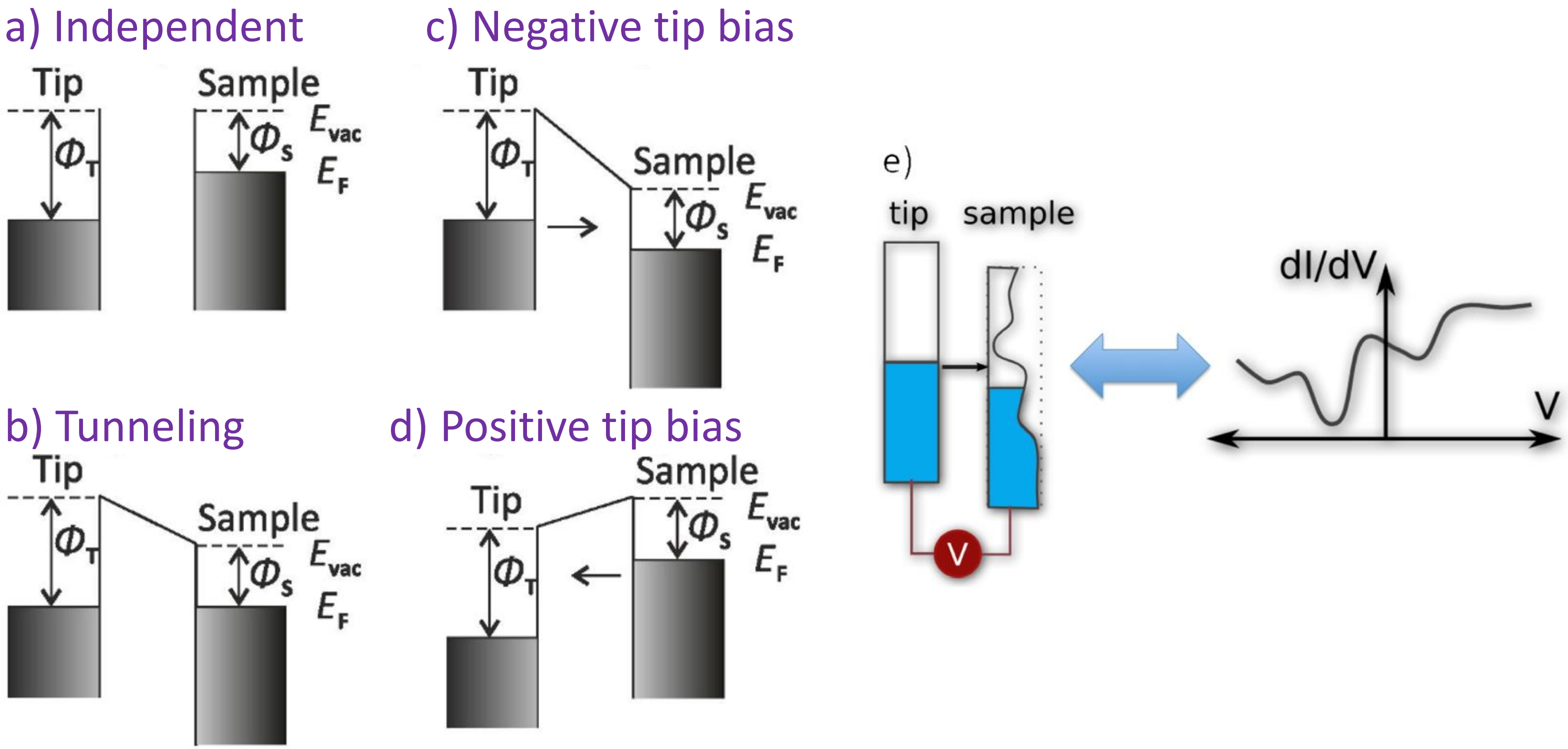
Gerd Binnig Heinrich Rohrer

Nobel Prize in Physics, 1986

For the design of the scanning tunneling microscope.

SCANNING TUNNELING SPECTROSCOPY (STS)

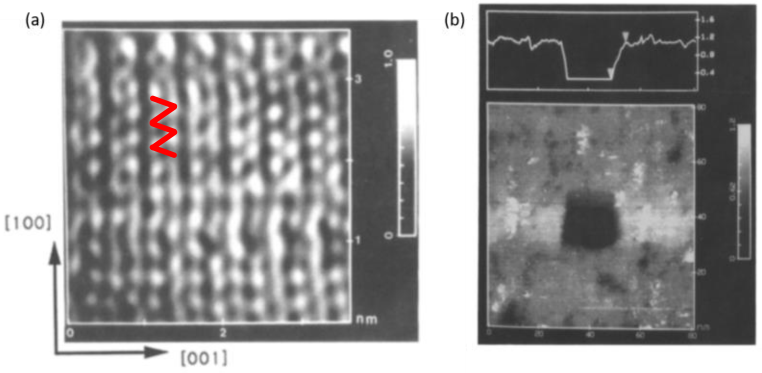
- Feedback is switched off
- Bias voltage is swept
- dI/dV ∝ LDOS



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

STM INVESTIGATION OF BP

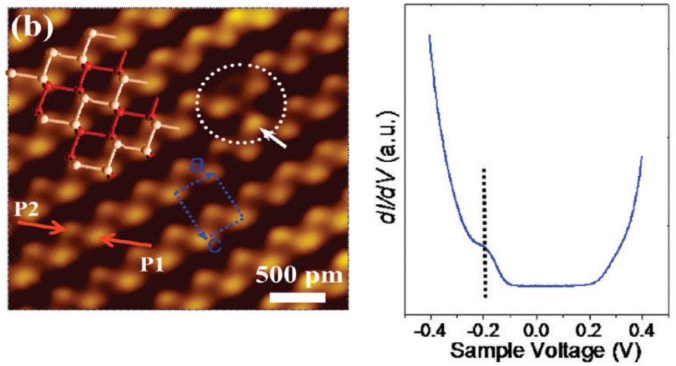
➢ Cleaved bP in air - (010) surface



S. L. Yau et. al. Chem, Phys, Lett, 1992, 198, 383.

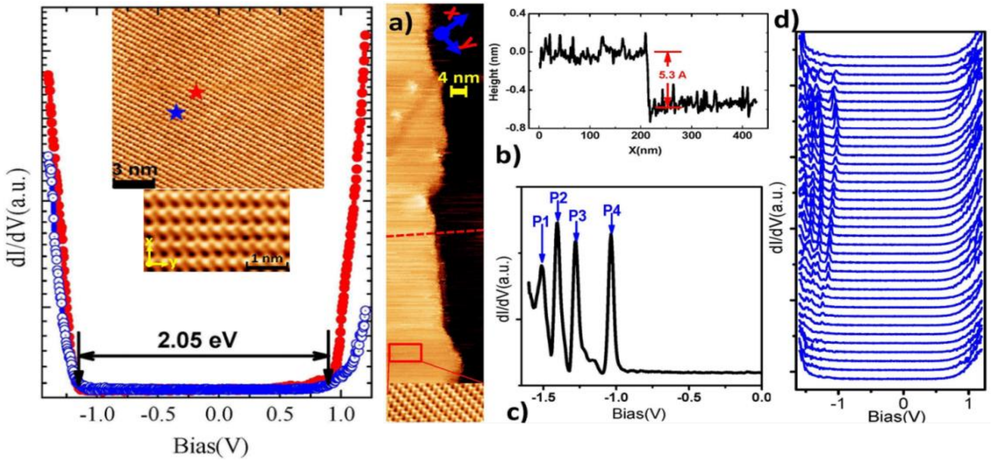
All These Studies Have Been Performed On Cleaved Black Phosphorus

➢ Cleaved bP in dry N_2 – measured at 77K and 4.3K
Band gap of 0.4 eV, surface state at -0.17 V



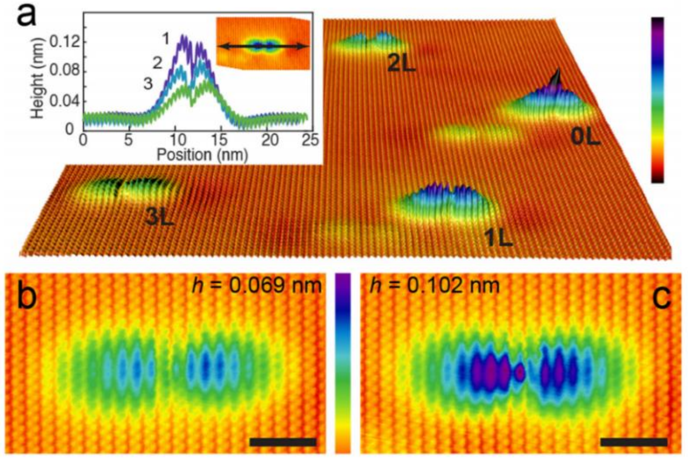
C. D. Zhang et. al. J. Phys. Chem. C 2009, 113, 18823

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



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

➢ Single Vacancies in BP – measured at 4.6K

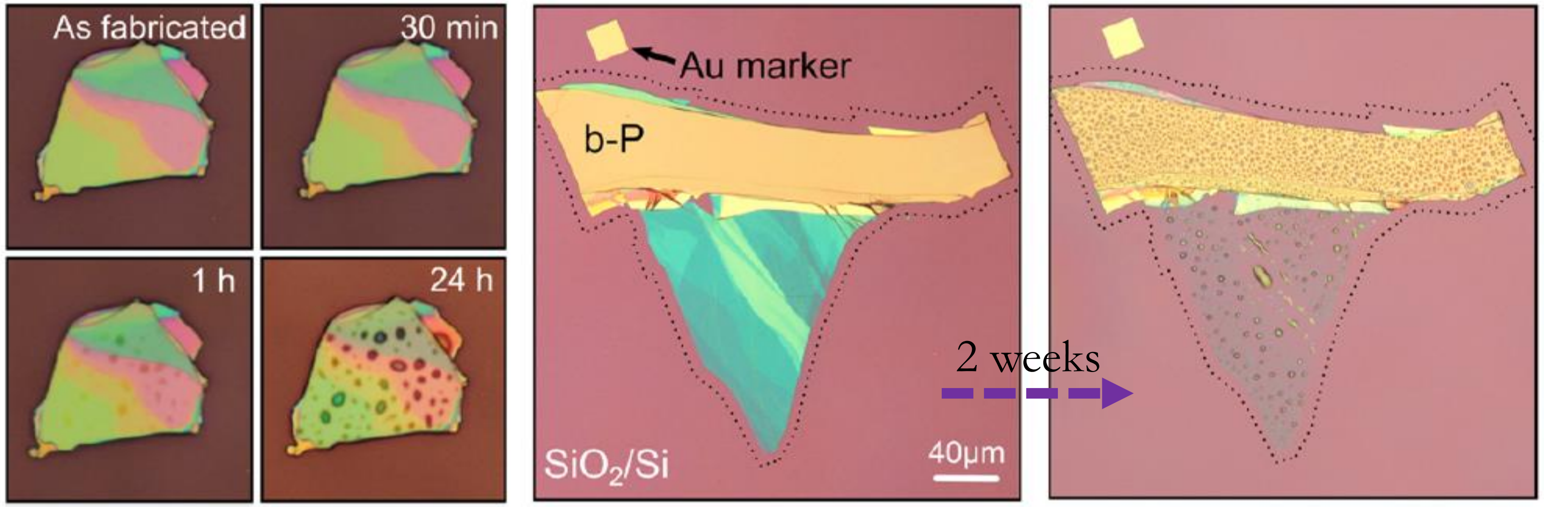


B. Kiraly et. al. Nano. Lett. 2017, 17(6), 3607.

BP SURFACE REACTIVITY

- Exposure to ambient air

A. Castellanos-Gomez et. al. 2D Materials, 2014, 1 (2), 025001.



- Also seen in the first STM study in 1992 performed on bP in air
- Very challenging to prepare thin samples
- Most experiments performed on encapsulated bP for electrical and optical characterizations
- Study of surfaces of thin bP flakes is necessary – with annealing and functionalization

AIM

- Prepare clean thin bP flakes
- Study surface morphology of bP
- Probe bP by heating – temperature dependence
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP

BP AND STM

bP

- Highly reactive in air
- Surface morphology
- Temperature
- Doping

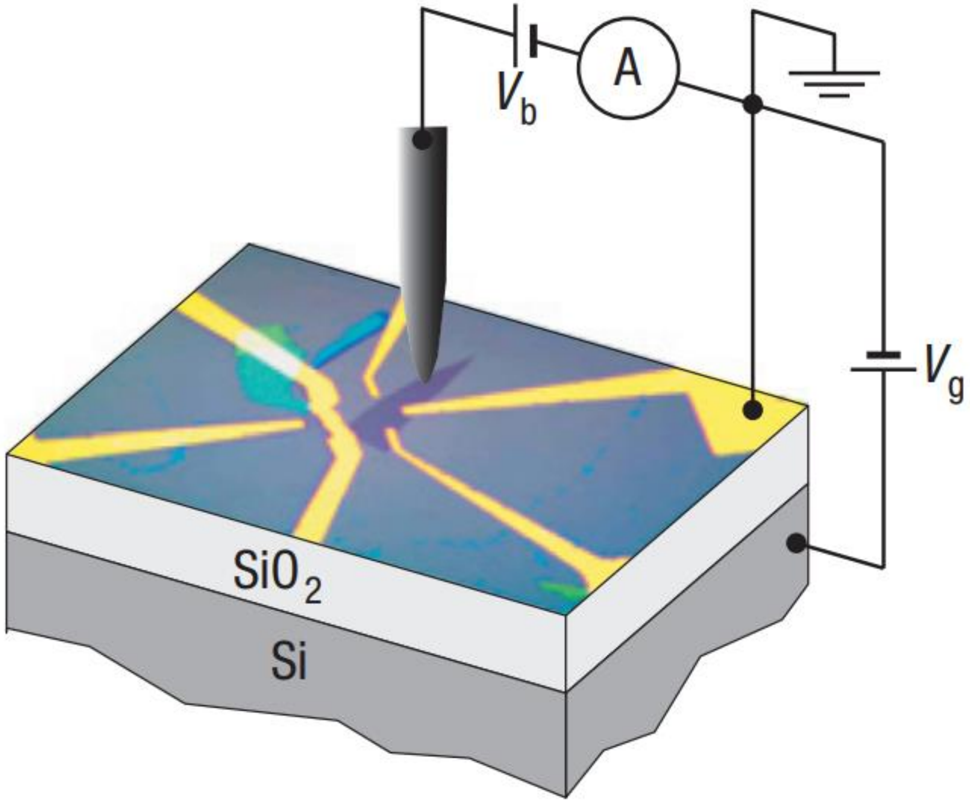
STM

- UHV
- Atomic resolution
- Preparation chamber
- Tunneling spectroscopy

- STM technique is apt for bP surface investigation

AIM

- Prepare clean thin bP flakes
- Study surface morphology of bP
- Probe bP by heating – temperature dependence
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP



LETTERS

Giant phonon-induced conductance in scanning tunnelling spectroscopy of gate-tunable graphene

YUANBO ZHANG[1]*, VICTOR W. BRAR[1,2], FENG WANG[1], CAGLAR GIRIT[1,2], YOSSI YAYON[1], MELISSA PANLASIGUI[1], ALEX ZETTL[1,2] AND MICHAEL F. CROMMIE[1,2]*

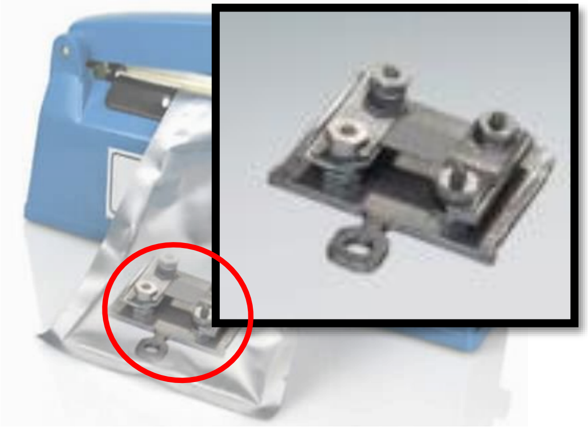
[1]Department of Physics, University of California at Berkeley, Berkeley, California 94720, USA
[2]Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720, USA
*e-mail: zhyb@berkeley.edu; crommie@berkeley.edu

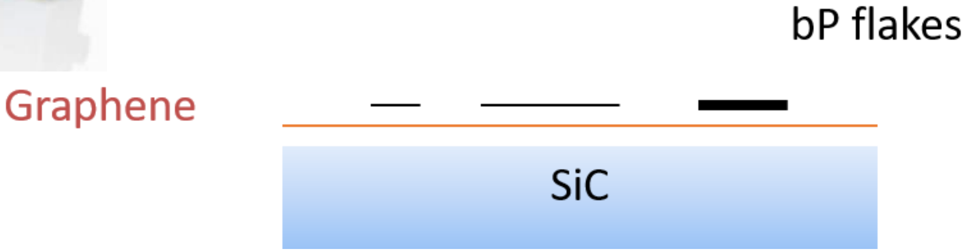
Drawbacks

- SiO_2 is an insulator – no STM possible on SiO_2
- Needs fabrication of electrical contacts
- Processing will make the flake dirty
- Need to follow the gold line – time consuming
- Processing will also expose the flakes to ambient air

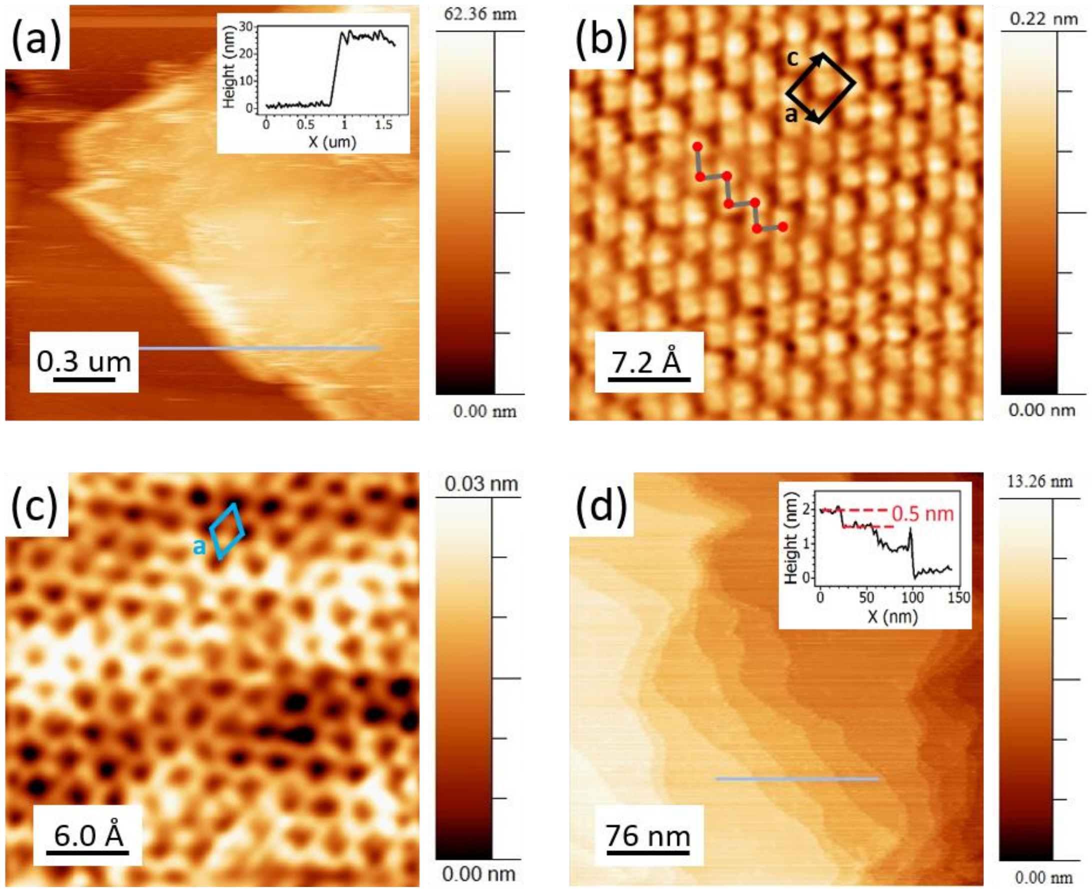
Glove Bag Exfoliation

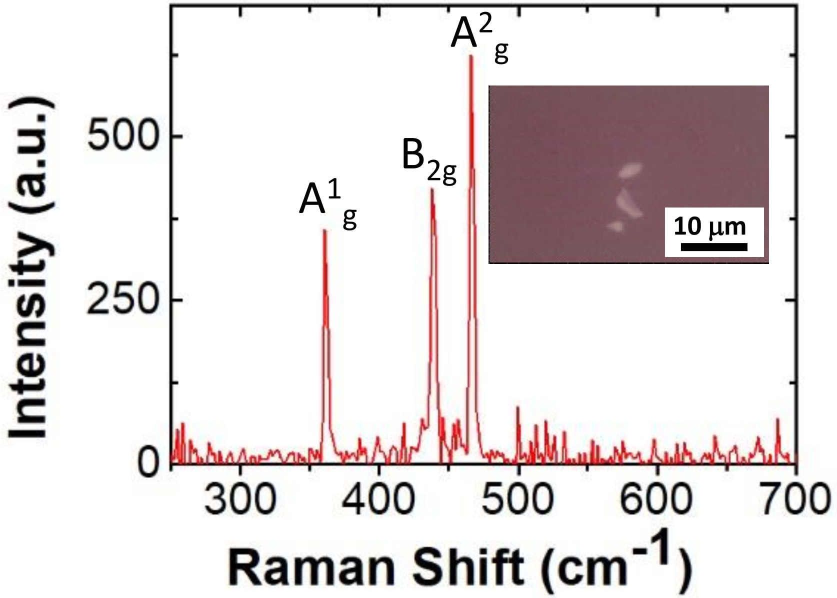
- Inert atmosphere exfoliation
- MLG on SiC – conducting substrate for STM
- Exfoliation, transfer, mounting and transportation to STM chamber – all inside N_2 atmosphere
- Loadlock (STM) also flushed with N_2
- Exposed to air for few seconds only





BP Flake Identification

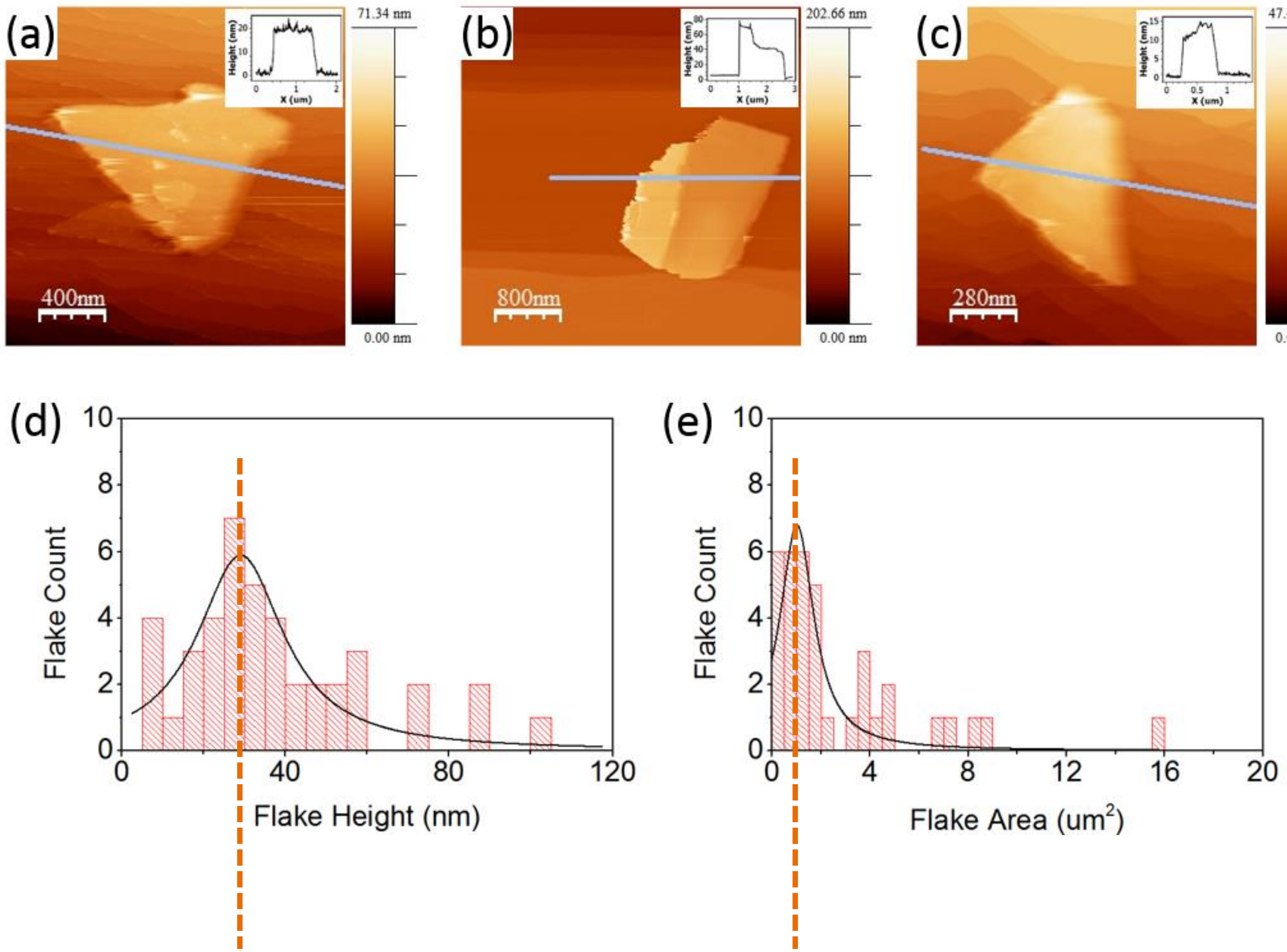




Overcame the challange of preparation of degradation-free exfoliated bP surface

BP Flake Sizes

Height of 42 flakes
Area of 36 flakes



(29.1 ± 1.6) nm

(1.0 ± 0.1) μm^2

AIM

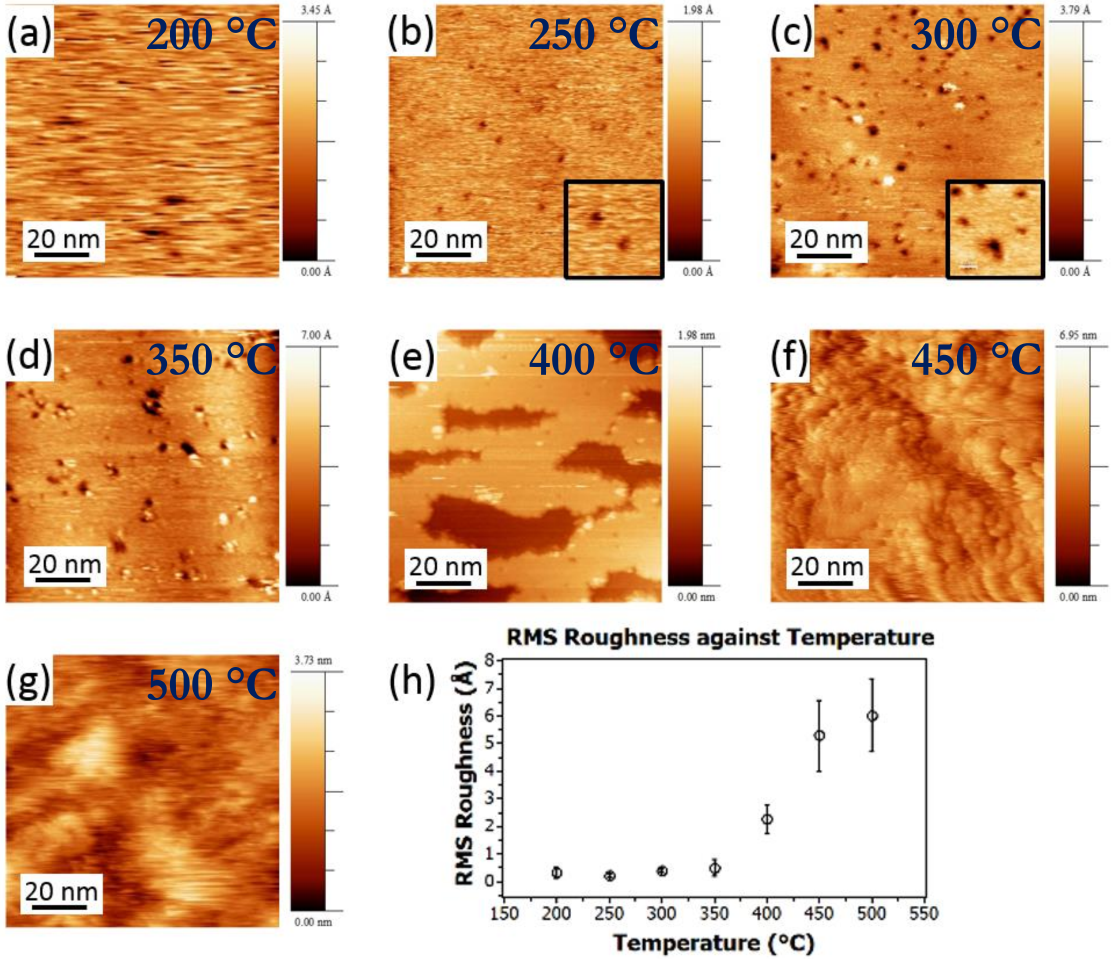
- Prepare clean thin bP flakes
- Study surface morphology of bP
- Probe bP by heating – temperature dependence
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP

BP Surface With Temperature

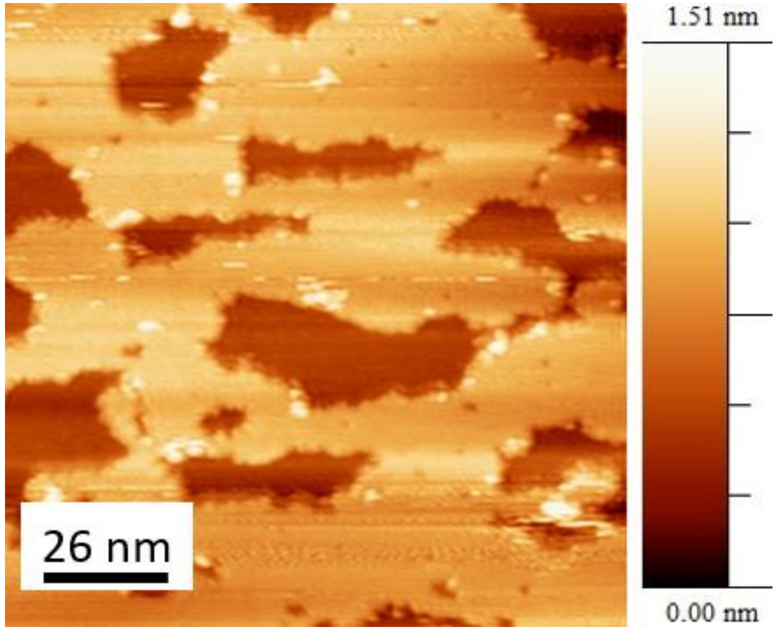
Samples were annealed in-situ (on annealing stage in UHV)

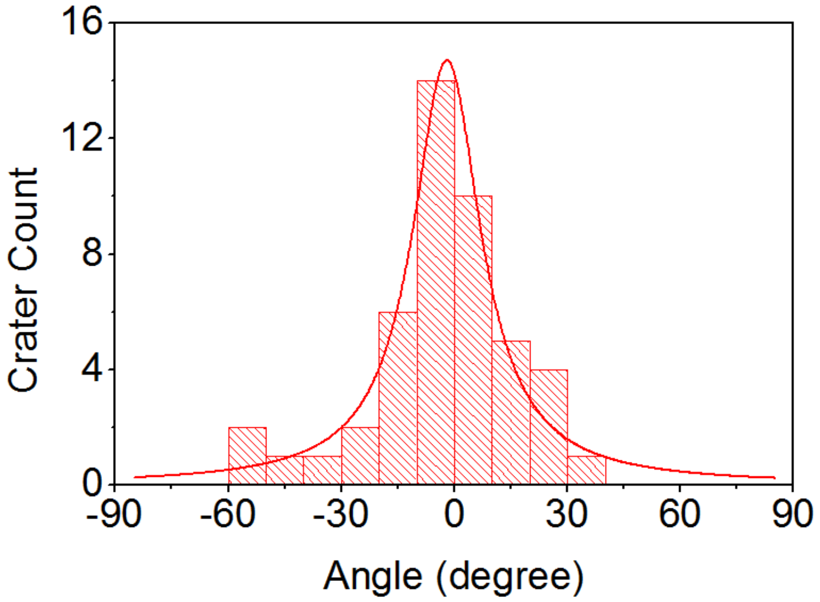
Annealing was performed for two hours at each temperature

STM measurements were performed after each annealing step



ALIGNED CRATERS ON BP SURFACE

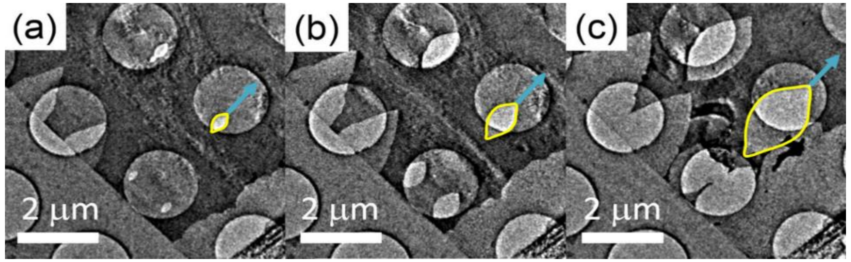




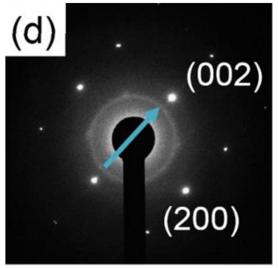
All craters are aligned along one direction, with no crater oriented perpendicularly.

Aligned Craters On BP Surface (Literature)

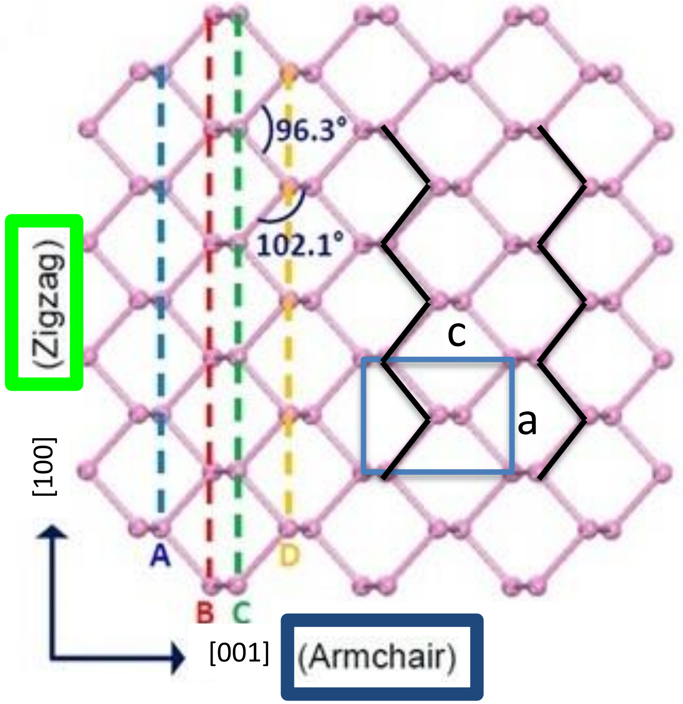
Xiaolong Liu et. al., J. Phys. Chem. Lett. 2015, 6, 773.



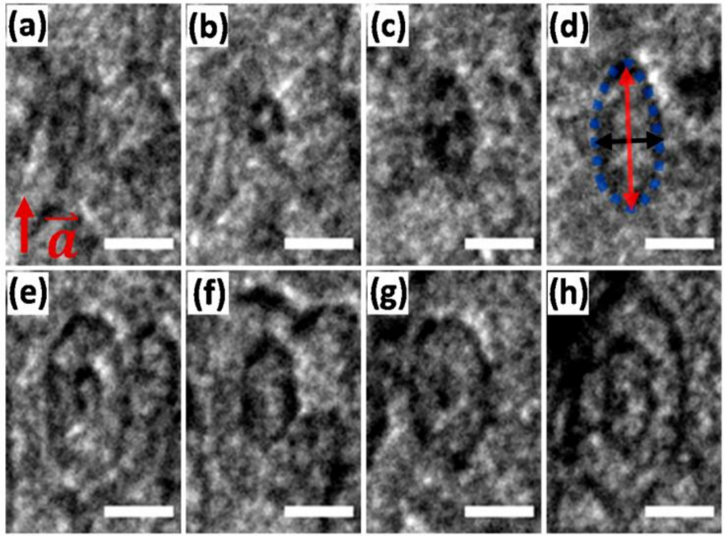
TEM image of eye shaped crack opening on heating bP flake at 400°C for 5, 8 and 12 min.



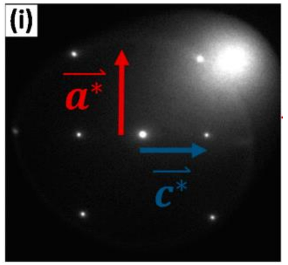
- This decomposition initiates via eye-shaped cracks along the [001] direction



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

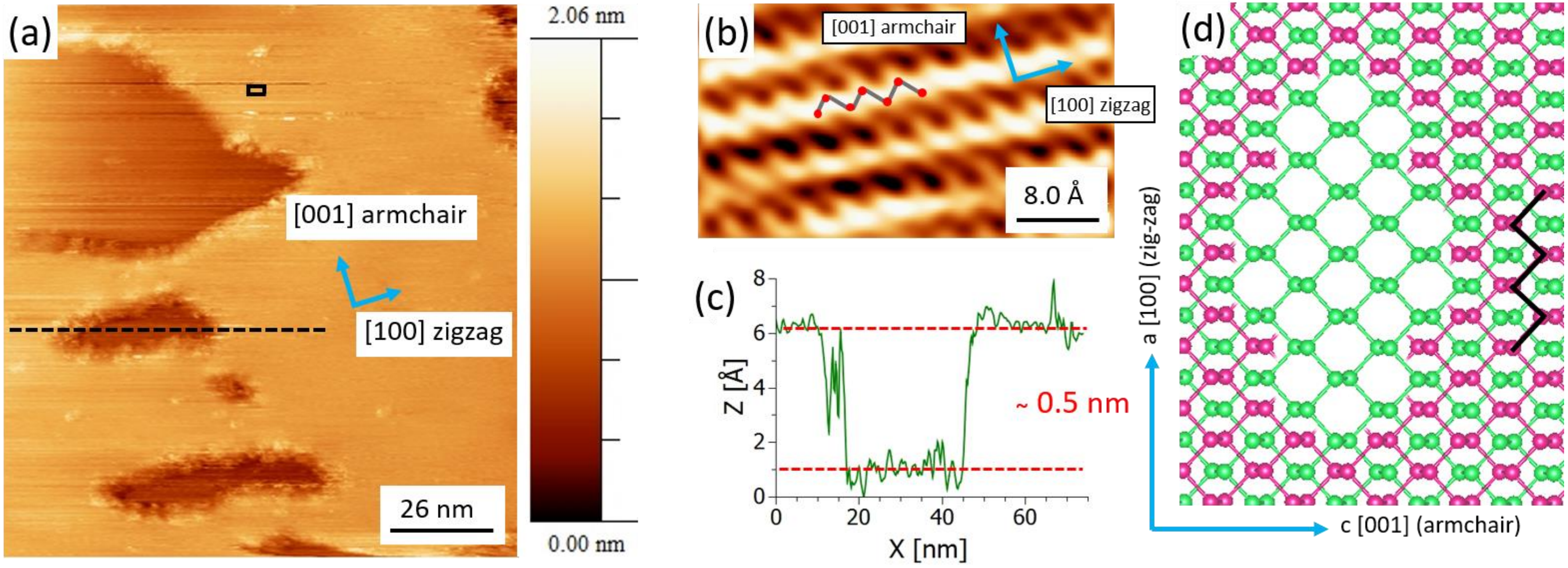


Bright-field LEEM snapshots of hole expansion during sublimation of exfoliated bP.



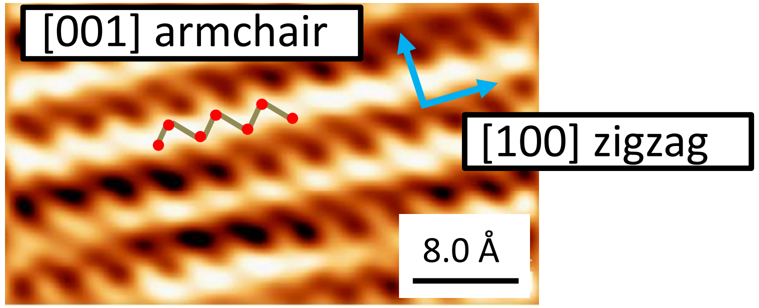
- Faceted holes with the long axis aligned along the [100] direction

CRYSTALLOGRAPHIC DIRECTION OF ALIGNED CRATERS



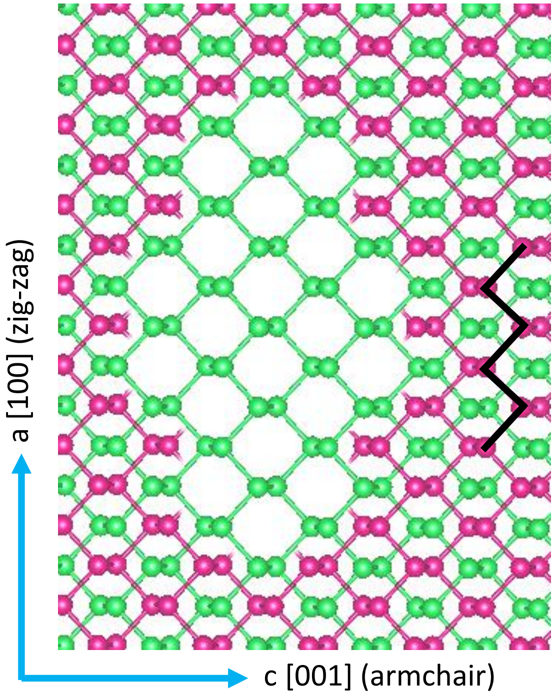
Craters align along the zigzag direction

STUDY COMPLETED



We showed the behaviour of surface morphology with temperature of exfoliated thin bP flakes for the first time

We studied orientation of crater and found it consistent with the result of Deschenes et. al. paper
Gives a very clear evidence to settle the debate



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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

➢**Can be used to perform controlled thinning of bP flakes by annealing**

AIM

- Prepare clean thin bP flakes
- Study surface morphology of bP
- Probe bP by heating – temperature dependence
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP

N-TYPE DOPING OF BP (LITERATURE)

Electrical Properties of Black Phosphorus Single Crystals

Yuichi AKAHAMA,† Shoichi ENDO†
and Shin-ichiro NARITA†*

†*High Pressure Research Laboratory and*
**Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560*

(Received January 10, 1983)

Large single crystals of black phosphorus have been grown under high pressure, and by using the crystals, the Hall measurements have been done in a range from 4.2 K to 550 K. All the undoped samples have exhibited *p*-type conduction, while we have succeeded in obtaining *n*-type crystals by doping Te impurity. The effective acceptor concentrations N_A-N_D of the *p*-type samples and those of donor in *n*-type samples N_D-N_A have been in the range of $2\sim5\times10^{15}$ cm^{-3} and $2\sim3\times10^{16}$ cm^{-3}, respectively. From the intrinsic range of the conductivity, the energy gap has been estimated to be 0.335 eV. The acceptor and donor activation energies have been determined to be ~18 meV and ~39 meV, respectively. The Hall mobility of the hole reaches its maximum of 6.5×10^4 cm^2/V·sec around 20 K. The anisotropies of the conductivity and the mobility along the three crystal axes have been investigated.

Y. Akahama et. al. Journal of Phys. Soc. of Japan, 1983, 52 (6), 2148.
N. Suvansinpan et. al. Nanotechnology, 2016, 27 (6), 065708.
P. Rastogi et. al. IETE Journal of Reserch, 2017, 63 (2), 205.
A. Sanna et. al. 2D Materials, 2016, 3(2), 025031.

DFT Calculation for Doping

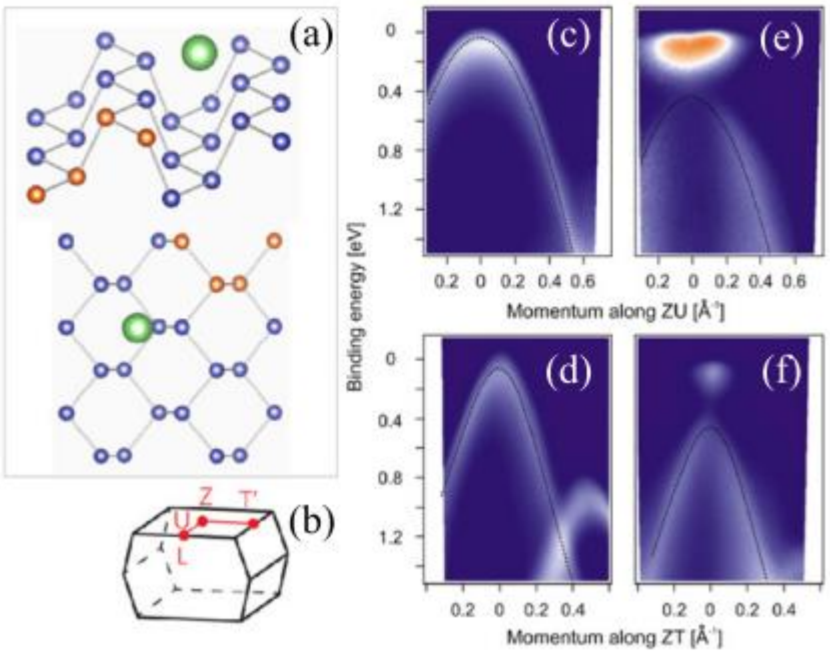
Substitutional doping

Dopant	Δq (e)
Li	0.99
Na	0.99
Ag	0.23
Au	−0.07
Pd	0.03
Pt	−0.23
Fe	0.68
Co	0.35
Ni	0.29
Pb	1.91
Al	3.00
C	−4.11
O	−2.17
S	−0.52
Bi	2.59
F	−1.10
I	−0.10

Transfer doping

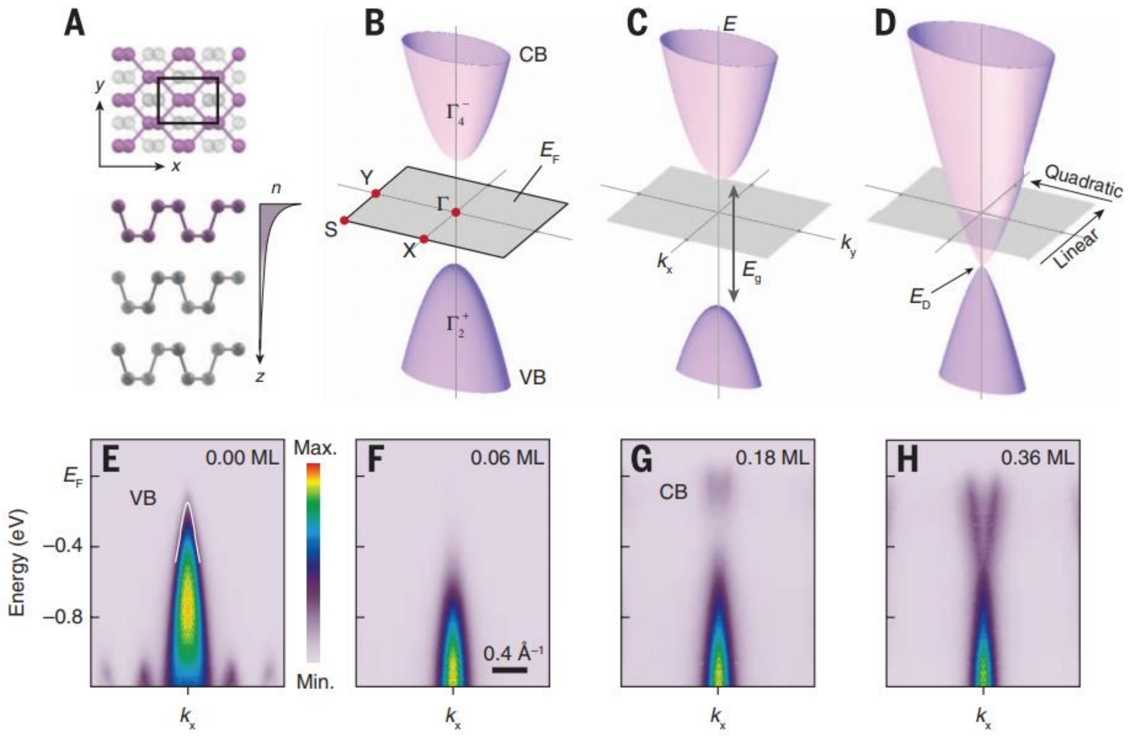
Group	Adatom	Charge transfer (e)
I	Li	−0.024
	Na	−0.176
	K	−0.348
II	Ca	−0.056
	Mg	−0.170
III	Al	0.380
	Ga	0.448
	In	0.36
IV	C	−0.01
	Si	0.274
	Ge	0.14
V	N	−0.028
	As	0.036
VI	O	0.136
	S	0.104
VII	F	0.206
	Cl	0.124
	Br	0.149
Nobel metals	Cu	0.214
	Ag	0.046
	Au	0.064
Transition	Ti	−0.056
	Fe	−0.006
metals	Ni	−0.042
	Pd	0.522
	Pt	0.208
	Sn	0.092

Lithium doping



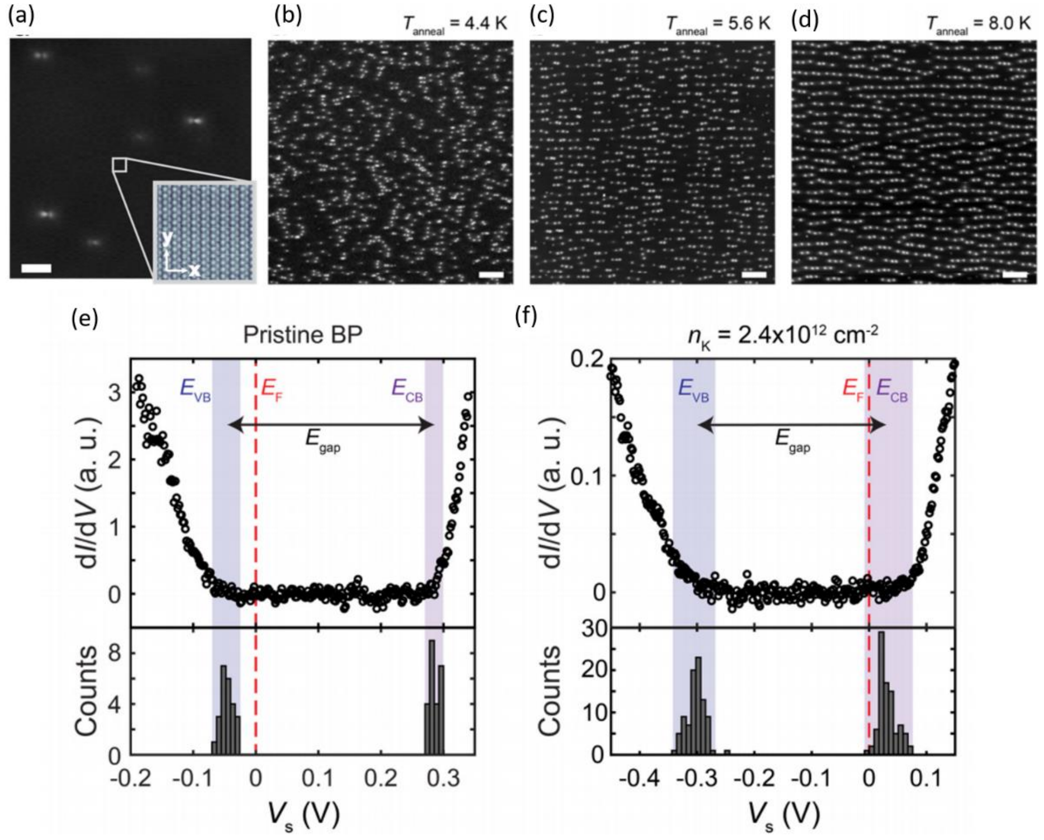
K-DOPING OF BP (LITERATURE)

ARPES Study



J. Kim et. al. Science, 2015, 349 (6249), 723,

STM Study



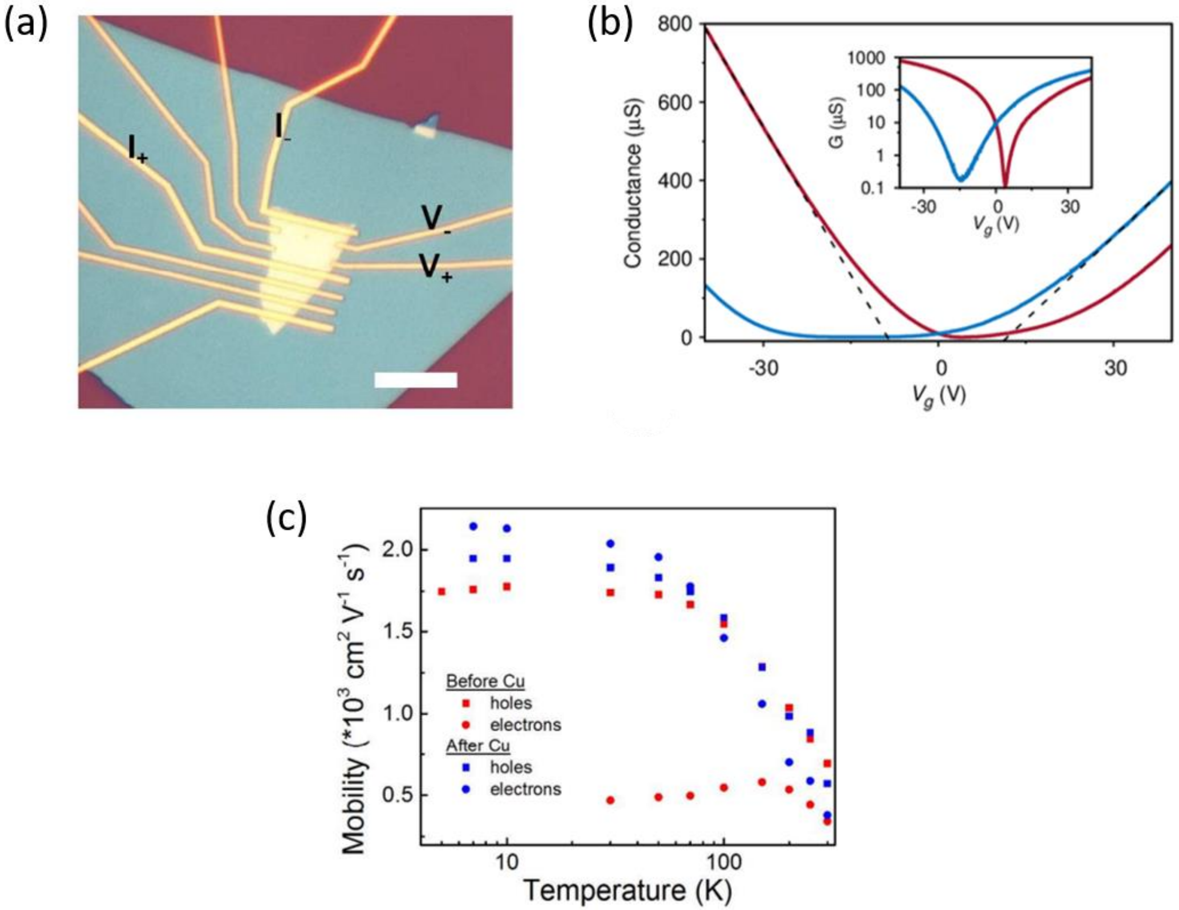
B. Kiraly et. al. arXiv, 2019, 1906.02627

Complementary studies provide a complete picture

CU-DOPING OF BP (LITERATURE)

Transport Study

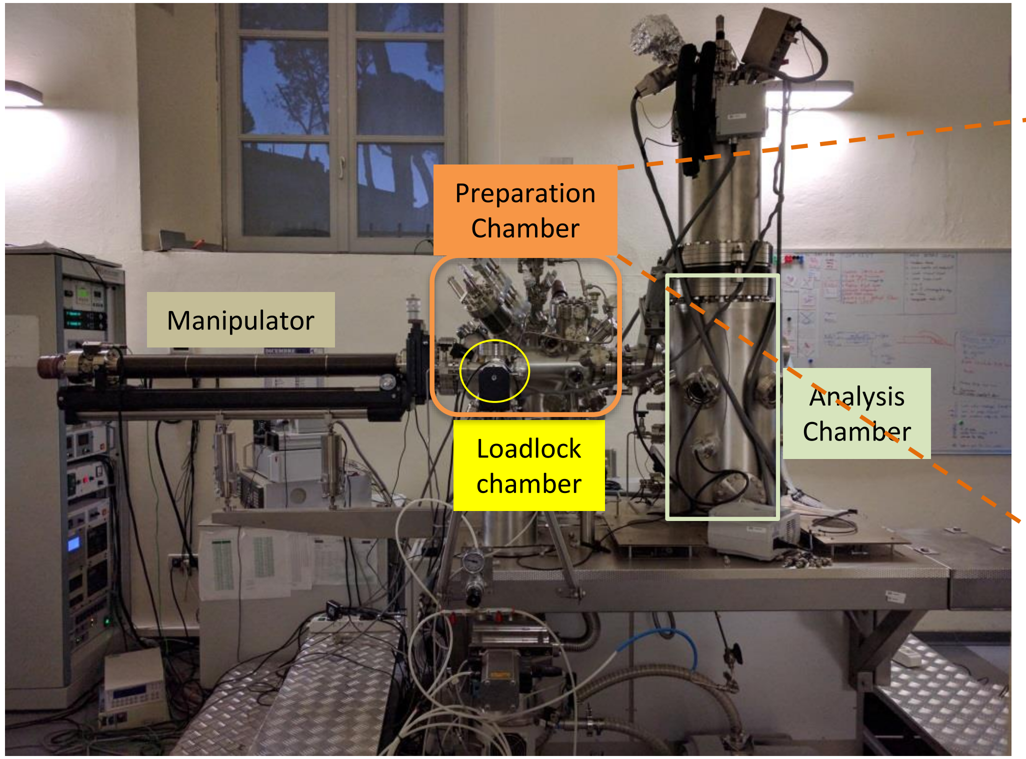
STM Study

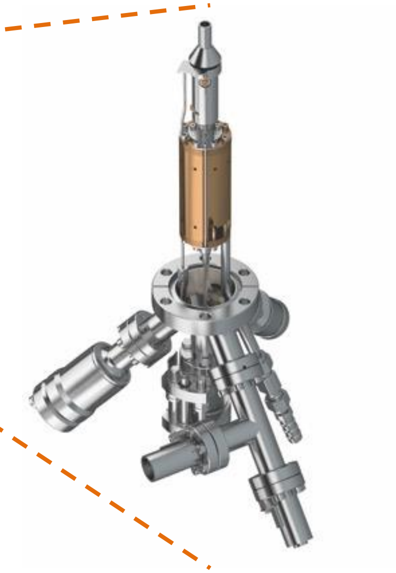


NOT AVAILABLE SO FAR

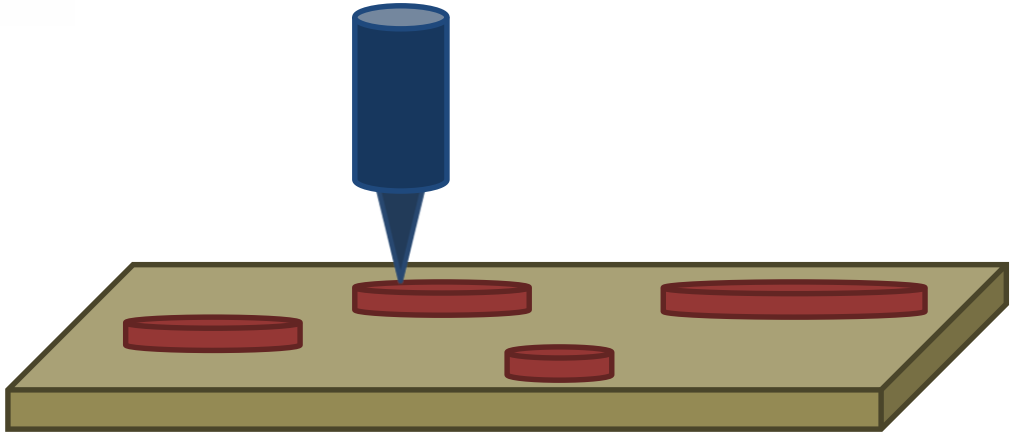
S. P- Koenig et. al. Nano Letters, 2016, 16 (4), 2145.

Copper Deposition on BP

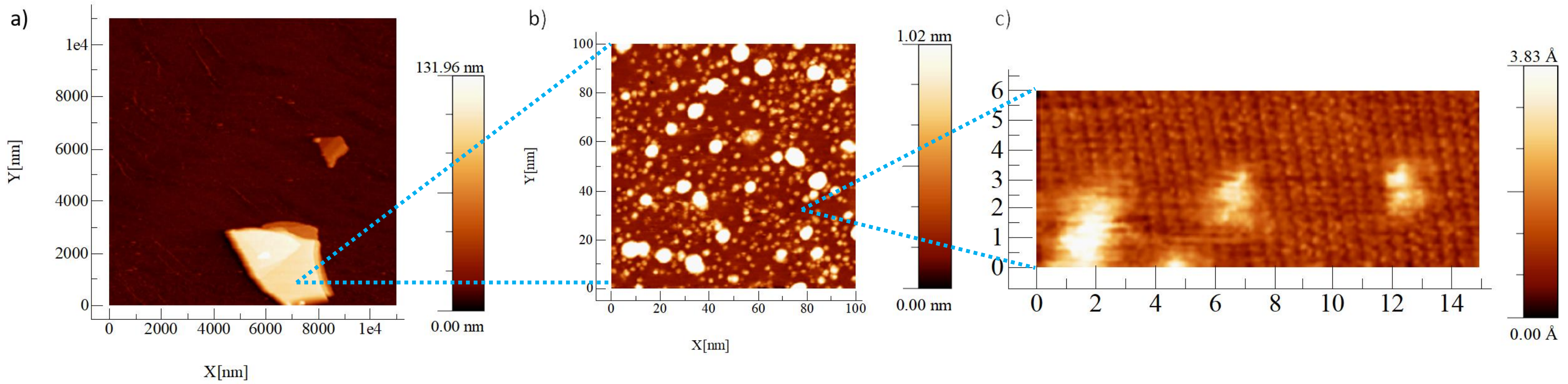




Omicron EFM-3s UHV metal evaporator



- Atomic resolution of bP after copper deposition

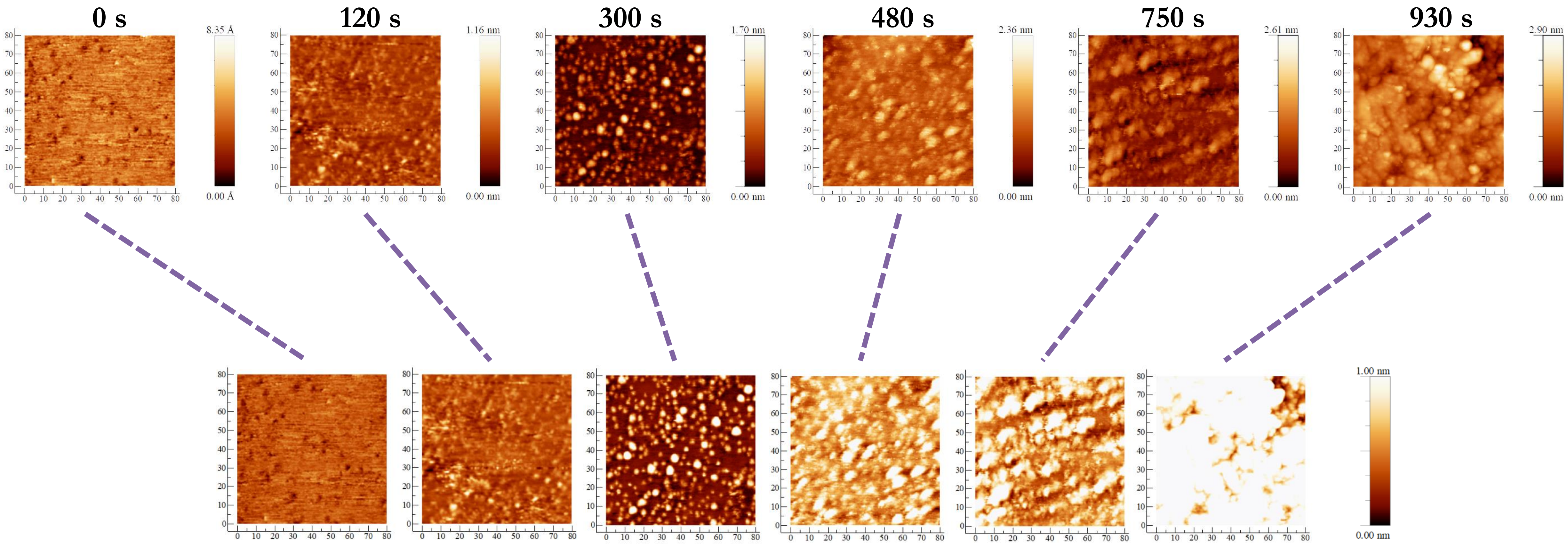


Demonstrates the high quality of copper deposited bP sample

AIM

- Prepare clean thin bP flakes
- Study surface morphology of bP
- Probe bP by heating – temperature dependence
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP

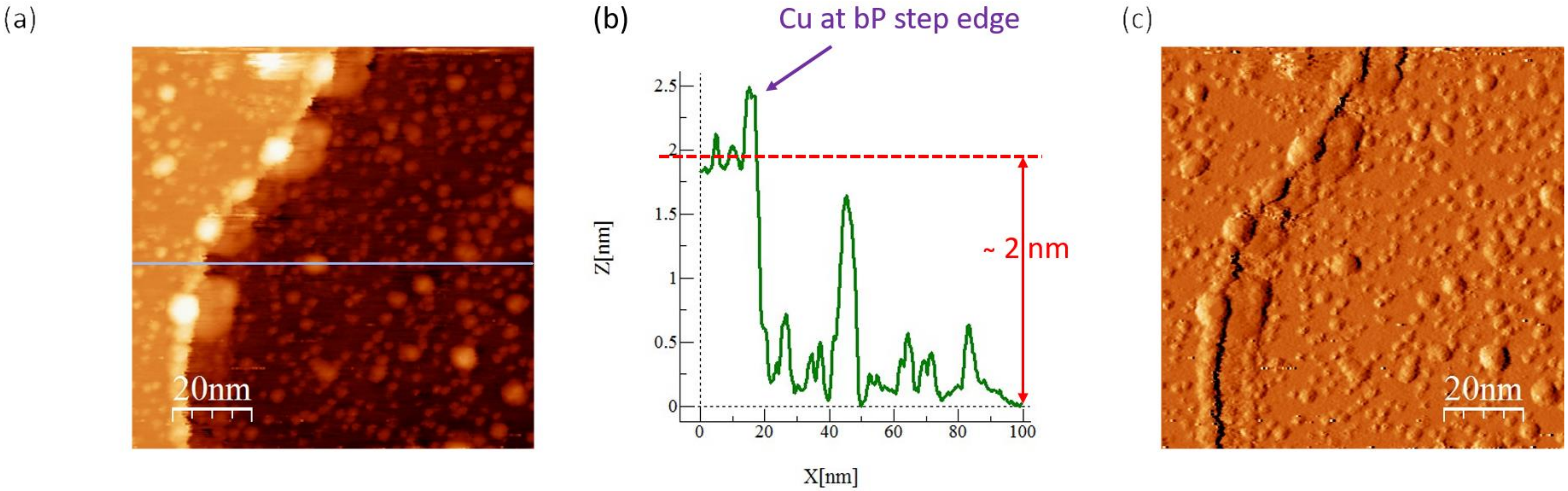
MORPHOLOGY OF COPPER ON BP



80 nm × 80 nm

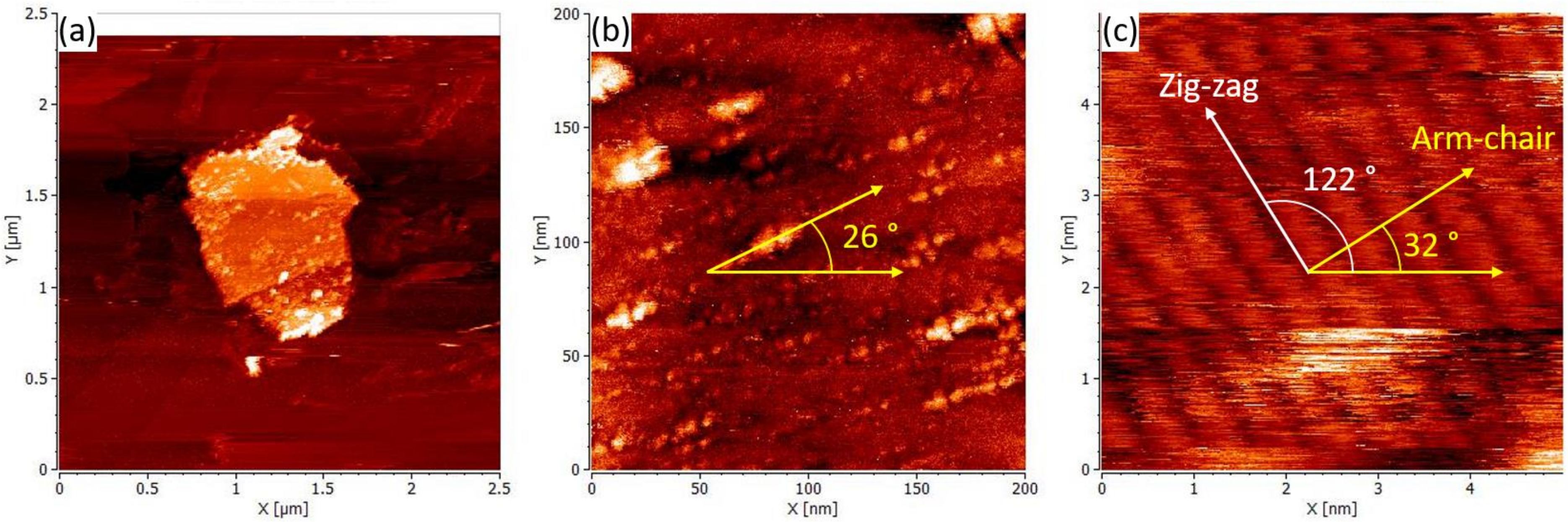
Increasing amount of copper on bP

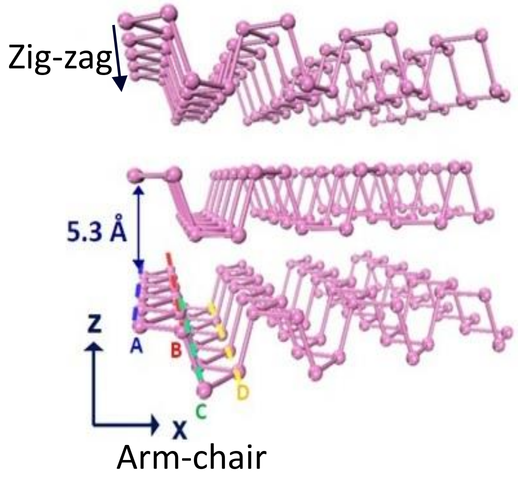
STEP DECORATION



- ➢ Ornamentation of copper islands along the bP step edge
- ➢ Evidence that copper atoms are mobile on bP at room temperature

Copper Island Alignment





Copper islands align along the arm-chair direction

AIM

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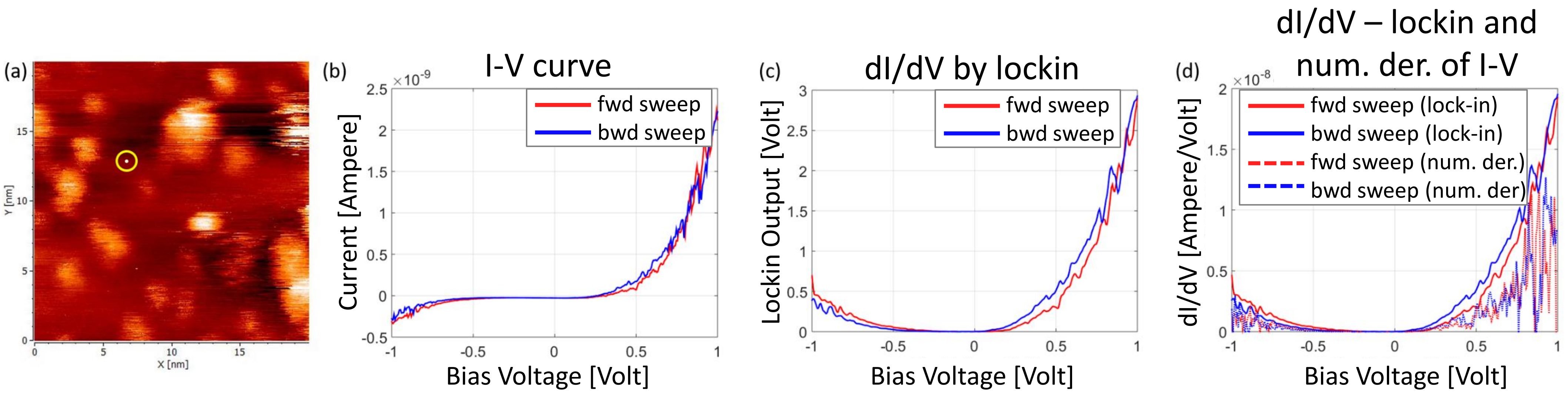
STS – BP

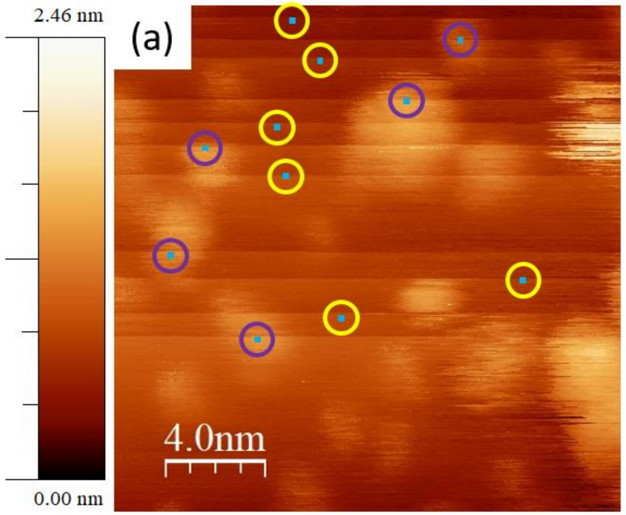
- Scanning tunneling spectroscopy

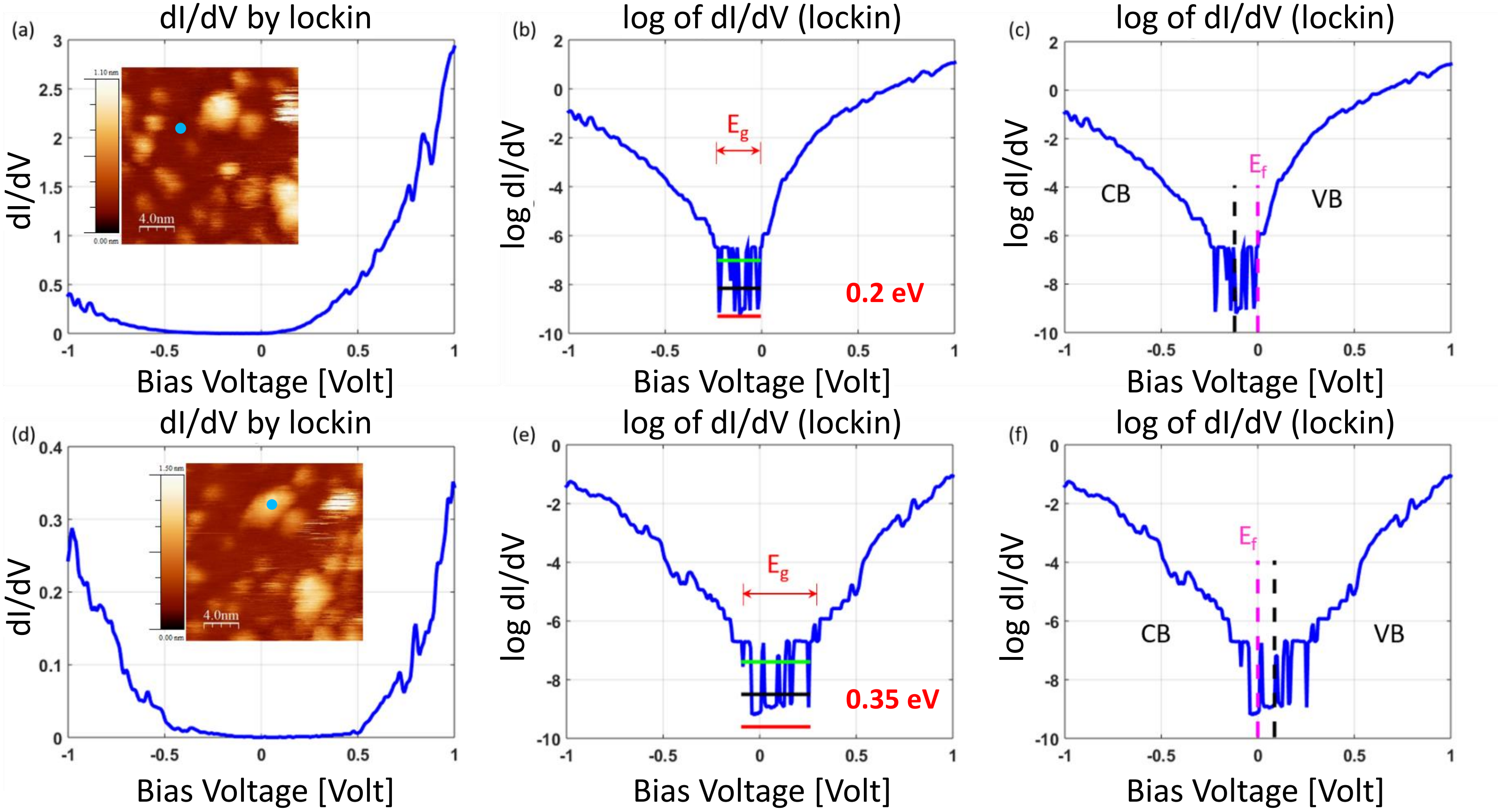


Consistent measurement of tunneling spectra

STS – BP AND COPPER

➢ Spectra measured on flat bP region (yellow circles) and on copper islands (purple circles)





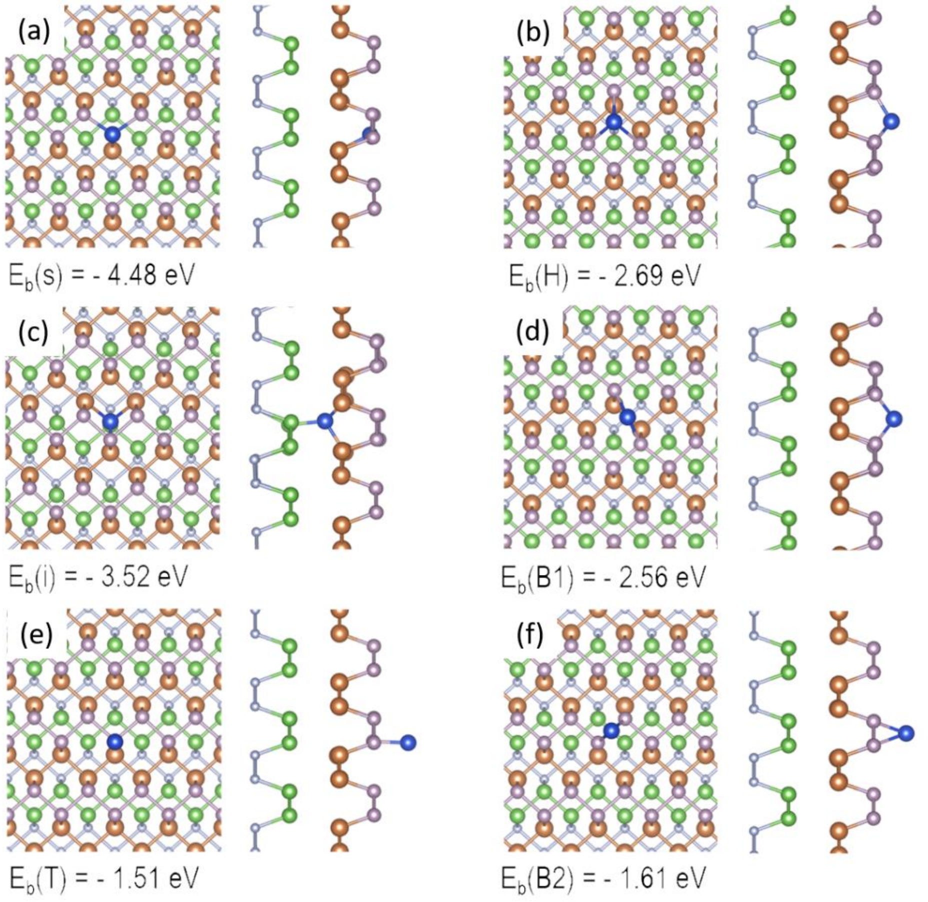
Statistical analysis of 42 spectra

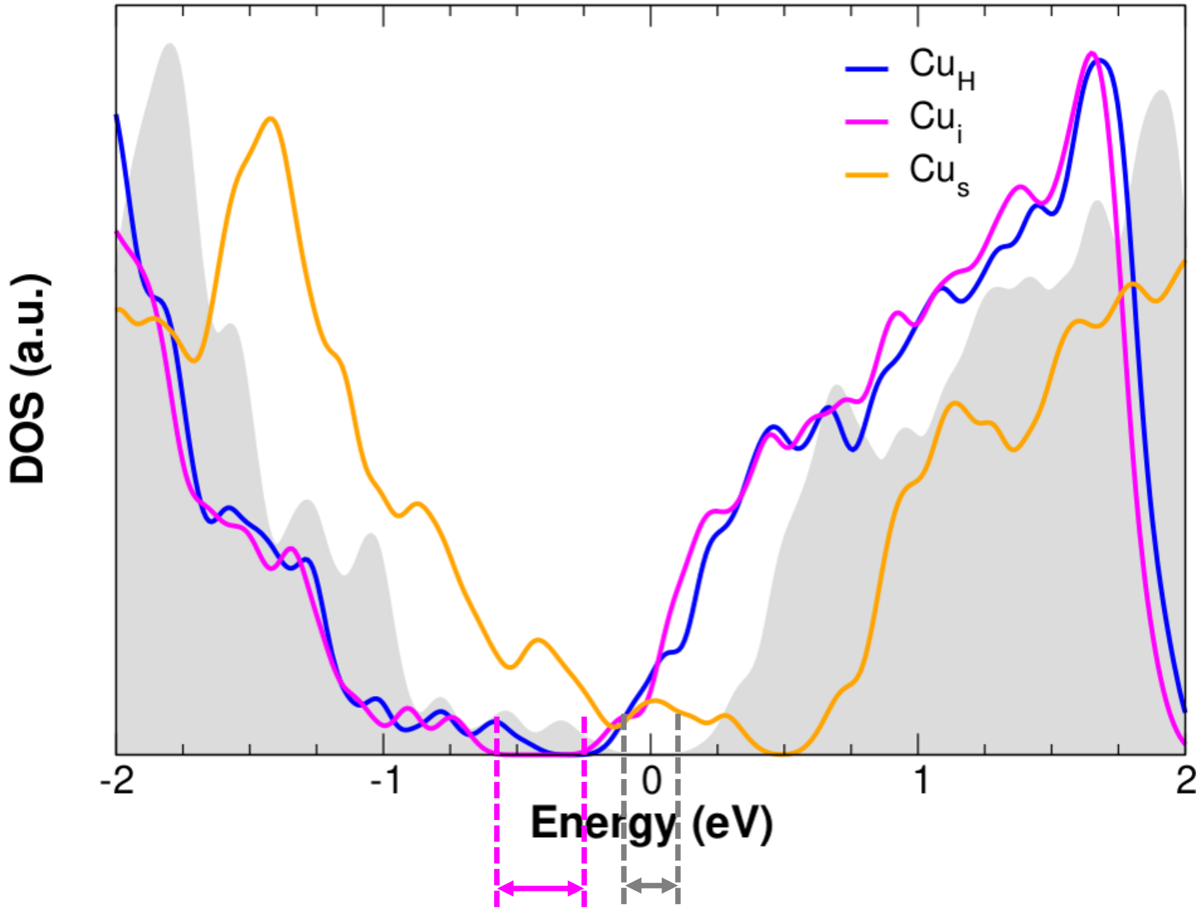
Pristine bP → (0.25 ± 0.10) eV

Cu-Doped bP → (0.46 ± 0.20) eV

n-type doping and apparent band gap broadening due to copper

- Doping type and band gap calculation using DFT for different configurations of copper on bP



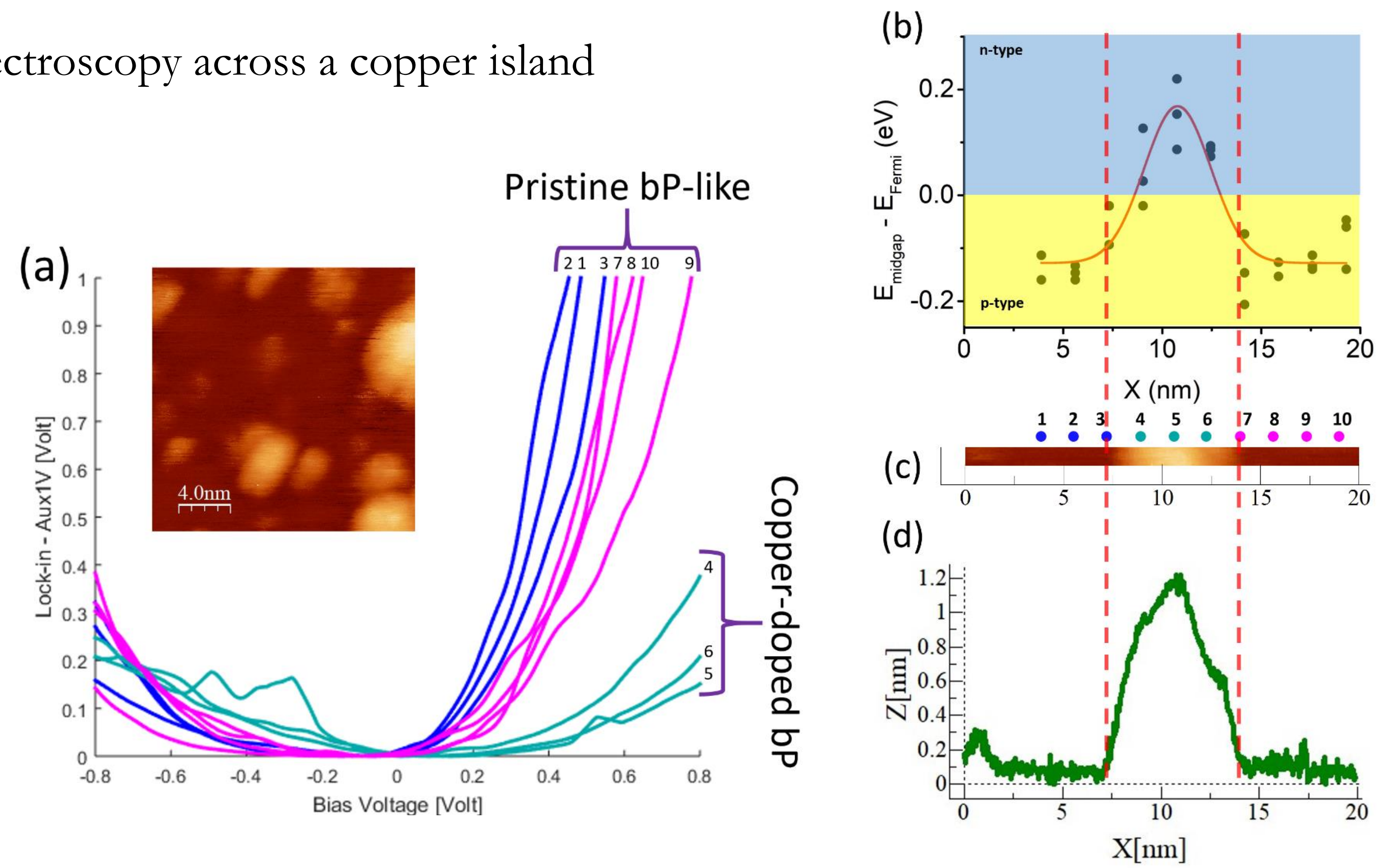


- n-type doping for Cu_H and Cu_i
- Increase in bandgap for Cu_i

Collaboration with Dr. Deborah Prezzi from CNR-Nano Modena, Italy

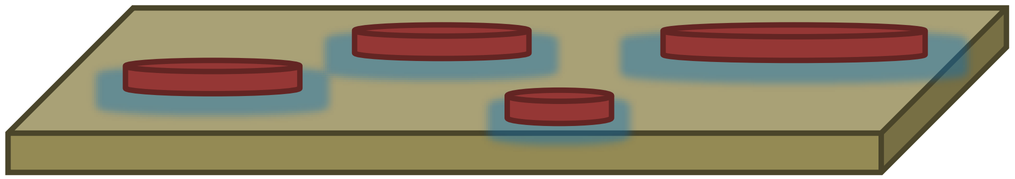
STS Across a Copper Island

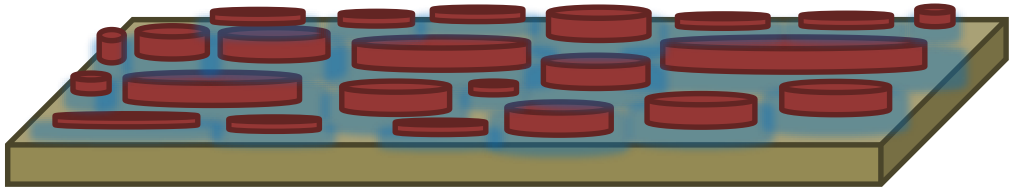
- Spectroscopy across a copper island



Lateral doping influence comparable to the width of the copper island

DISCUSSION – COPPER DOPING





Necessity of thin and uniformly spread copper islands for best result

➢ **Can be used to make a high performance p-n junction on bP**

AIM

- Prepare clean thin bP flakes
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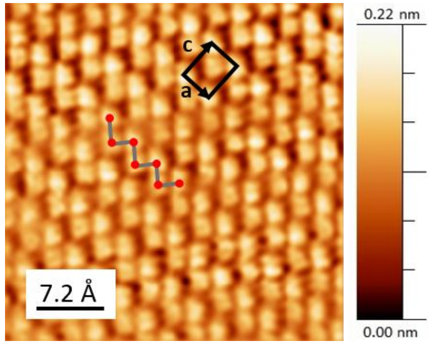
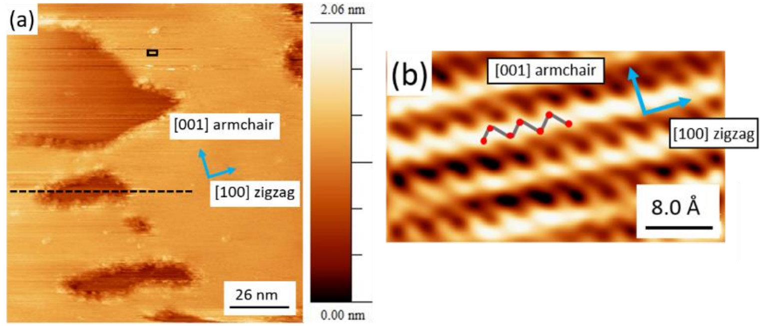
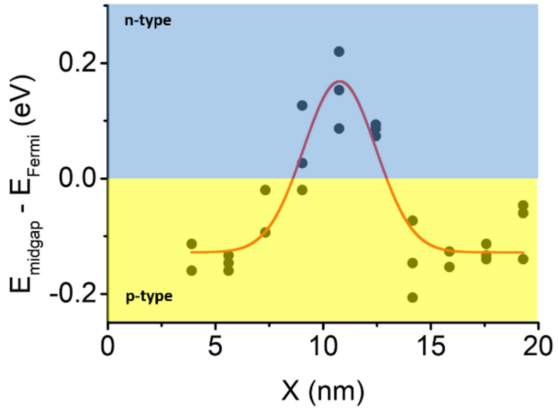
- Functionalize bP with metals, like copper
- Study surface morpholgy of copper on bP
- Doping effect of copper on bP

SUMMARY

- Developed an innovative method that allows to perform STM on exfoliated clean nanometer thin bP surfaces
- Can be applied to other air sensitive 2D materials also
- Studied surface morphology of bP with temperature and crater alignment
- Can be used to perform controlled thickness of bP flakes by annealing
- Studied surface morpholgy and doping effects of copper on bP
- Can be used to make a high performance p-n junction







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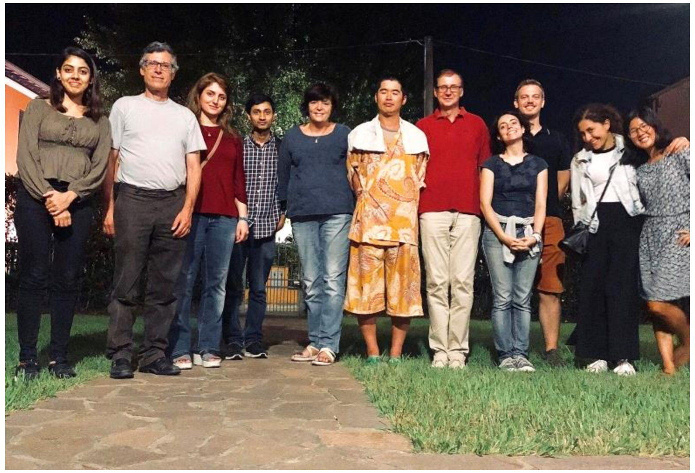
Prof. Camilla Coletti


Prof. Maurizio Peruzzini

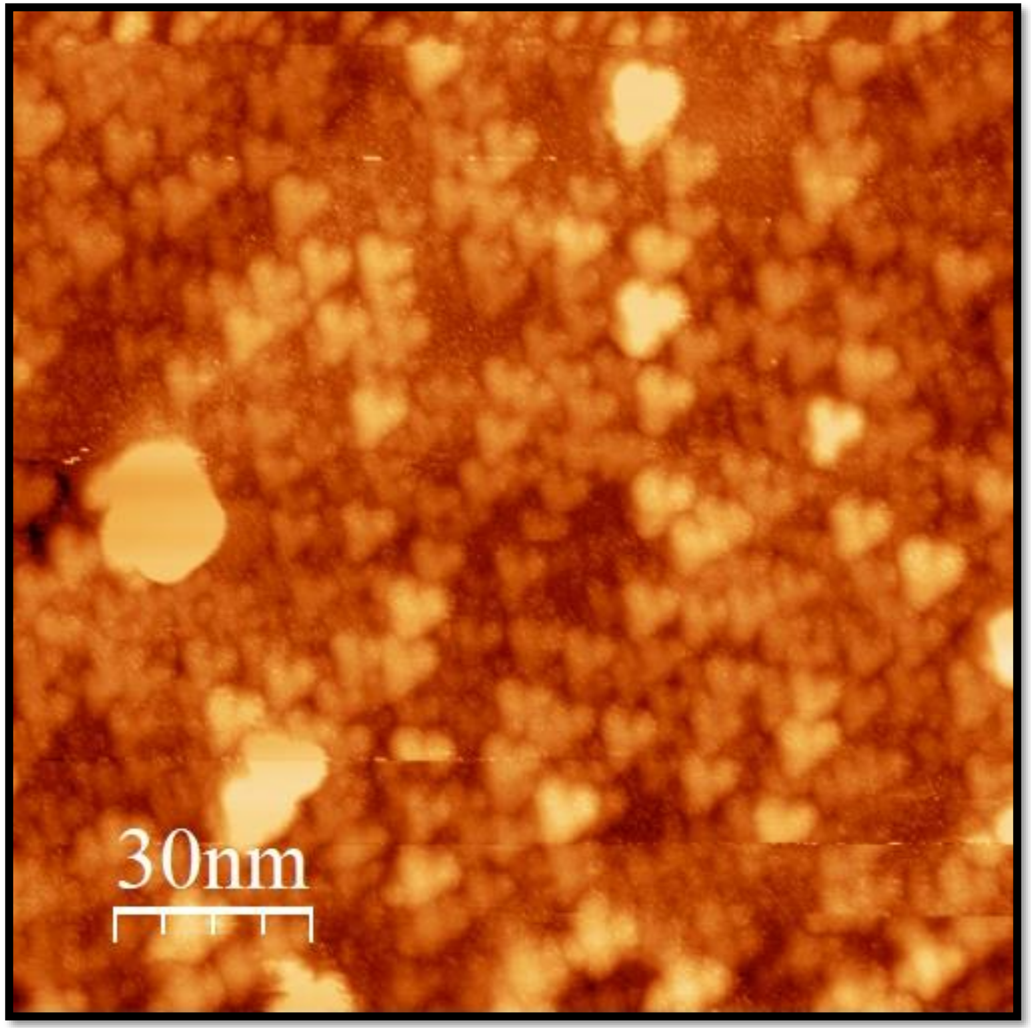


NEST

SCUOLA NORMALE SUPERIORE


Dr. Deborah Prezzi

THANK YOU!



Nano Hearts