Black Phosphorus n-type doping by Cu: a microscopic surface investigation

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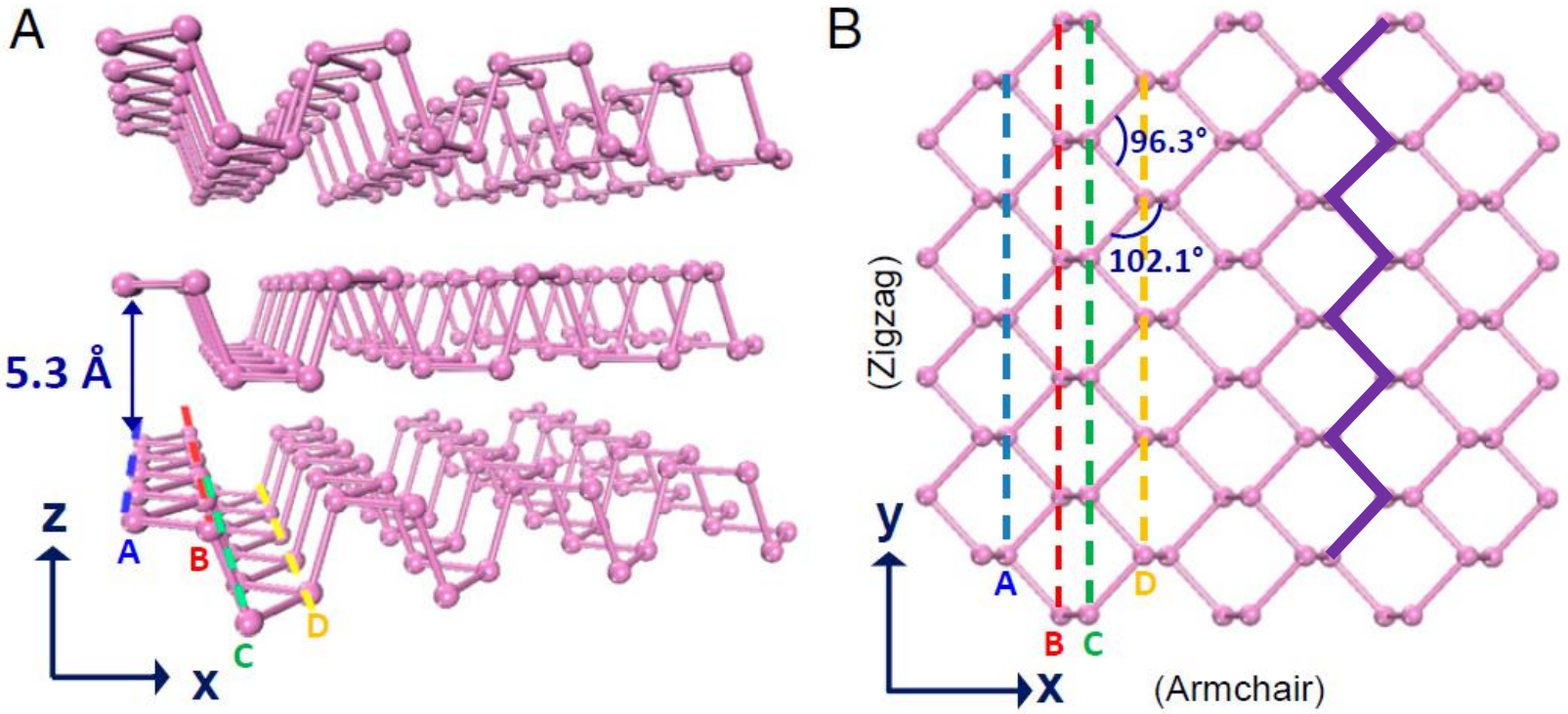
National Enterprise for nanoScience and nanoTechnology

NEST

Black phosphorus (bP)

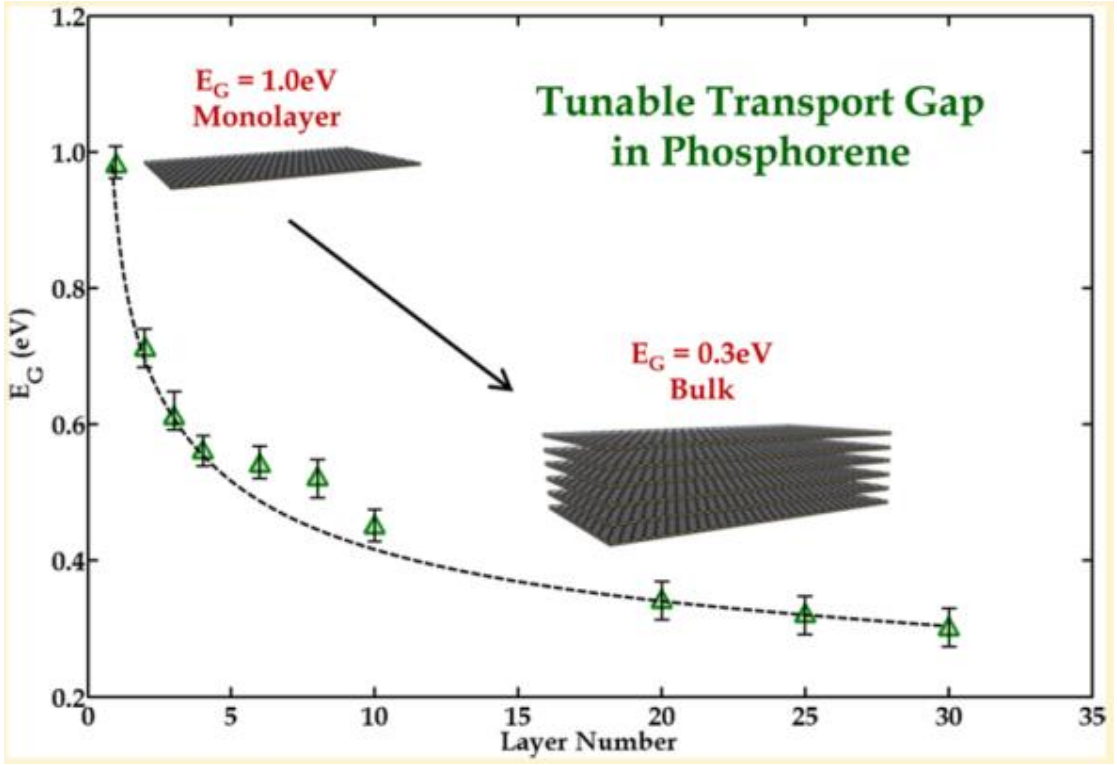
- Black Phosphorus is a layered van der Waals crystal with a puckered structure



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

Black phosphorus (bP)

- Black Phosphorus is a layered van der Waals crystal with a puckered structure
- Direct band gap which ranges from 0.3 eV (bulk) to ~2.0 eV (monolayer)



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

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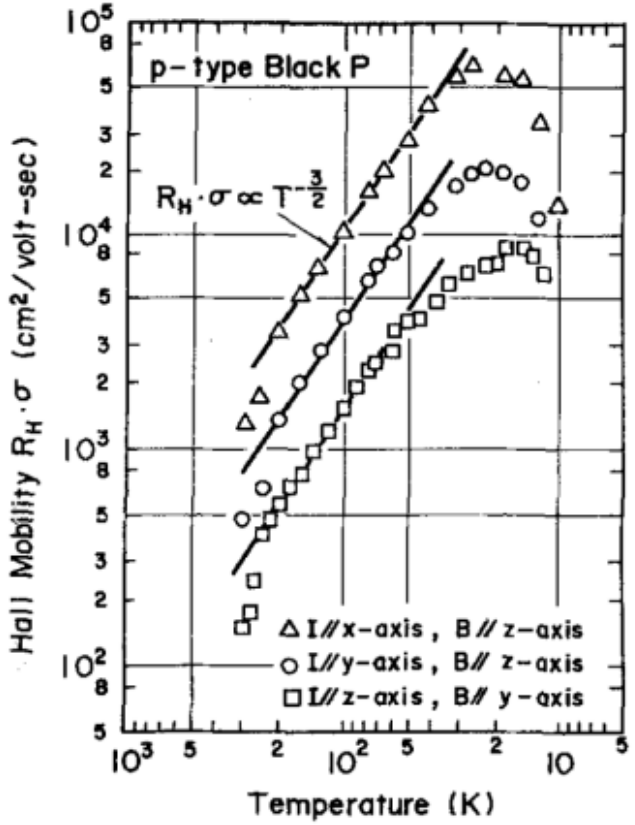

A. Morita, Appl. Phys. A 39 (1986) 227.

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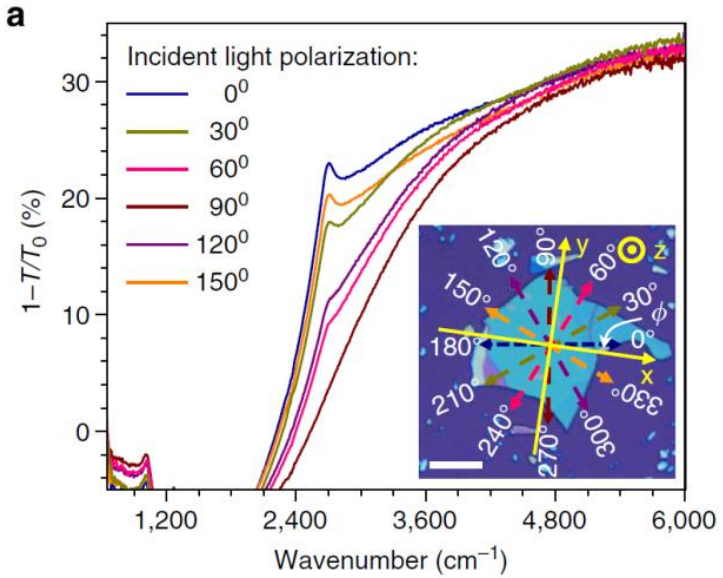
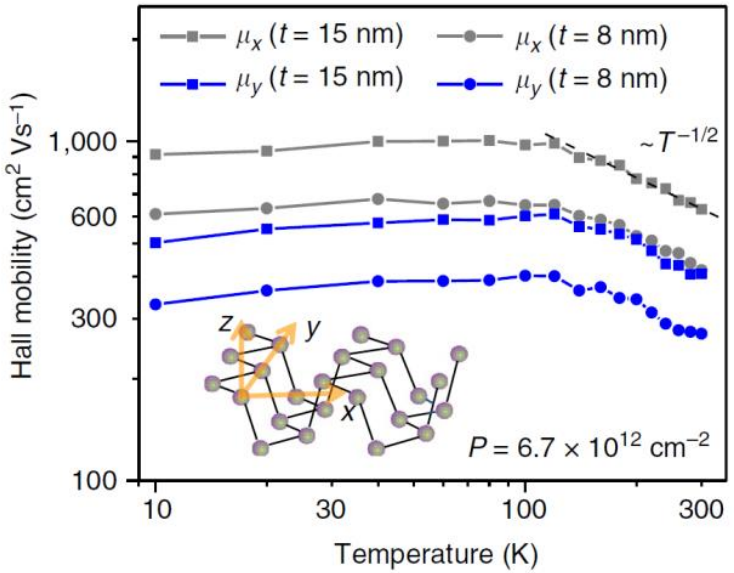
- In-plane anisotropy of its optical and transport properties





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

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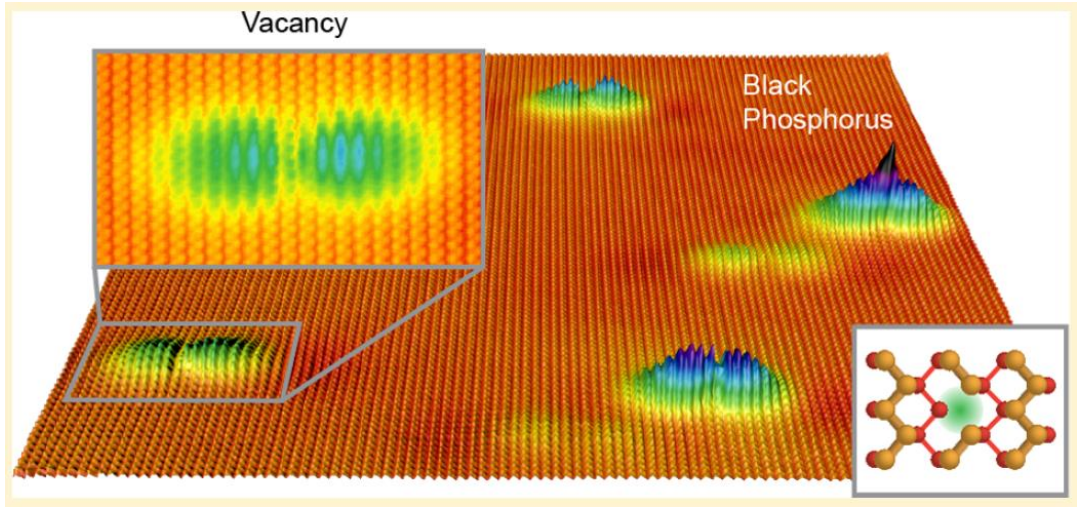
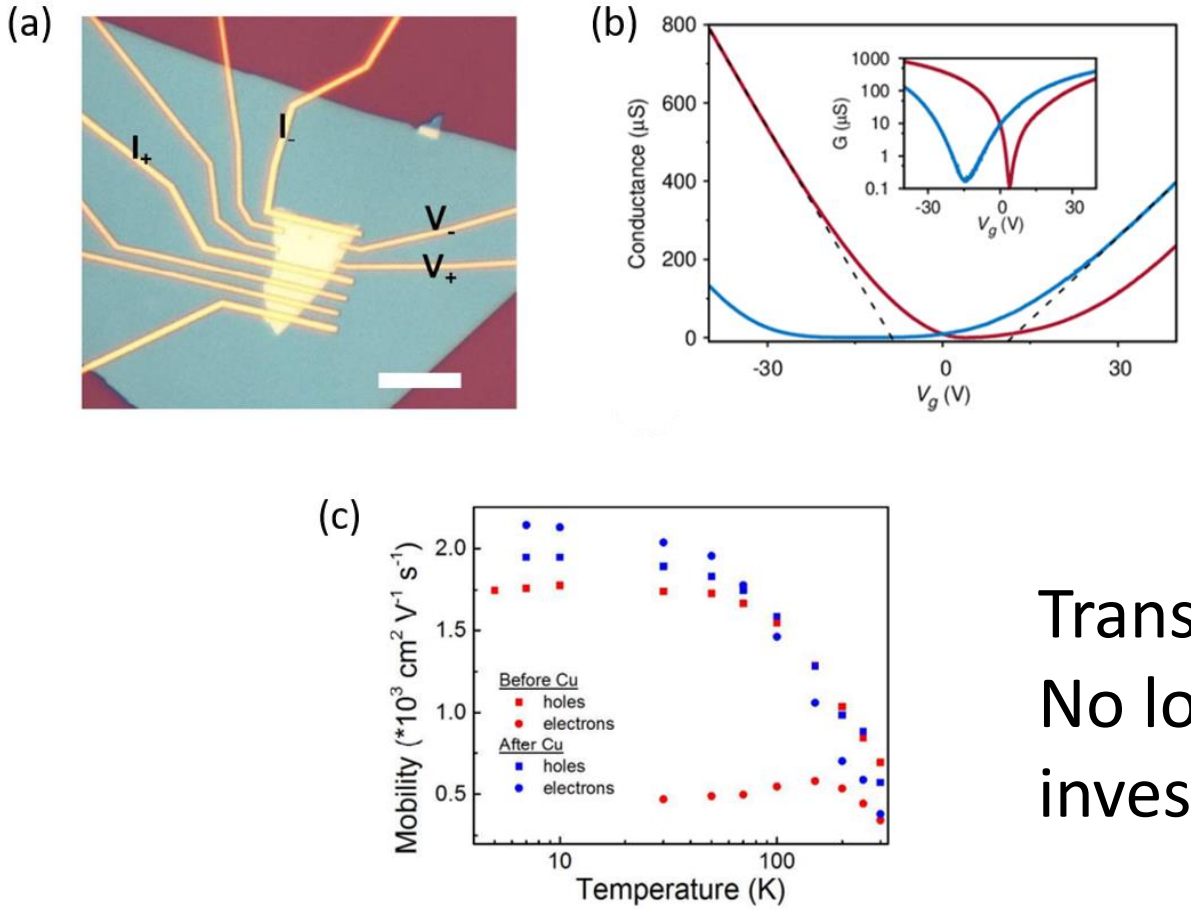
- Direct band gap which ranges from 0.3 eV (bulk) to ~2.0 eV (monolayer)
- High carrier mobility
- In-plane anisotropy of its optical and transport properties
- Intrinsic p-type semiconductor due to P vacancies



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

n-type doping of bP by Cu



Transport Study;
No local spectroscopic investigation so far

S. P. Koenig et al., Nano Letters, 2016, 16, 2145.

IOP Publishing 2D Mater. 6 (2019) 015005 https://doi.org/10.1088/2053-1583/aadd20

2D Materials

OPEN ACCESS

PAPER

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]

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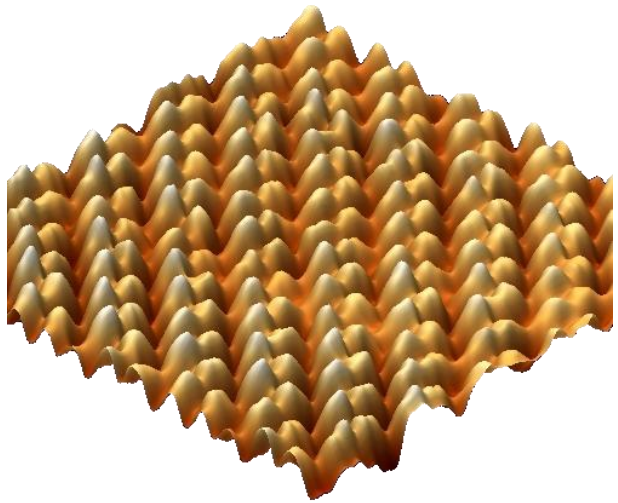
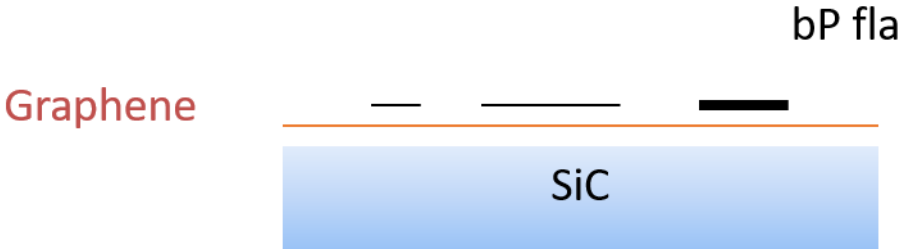


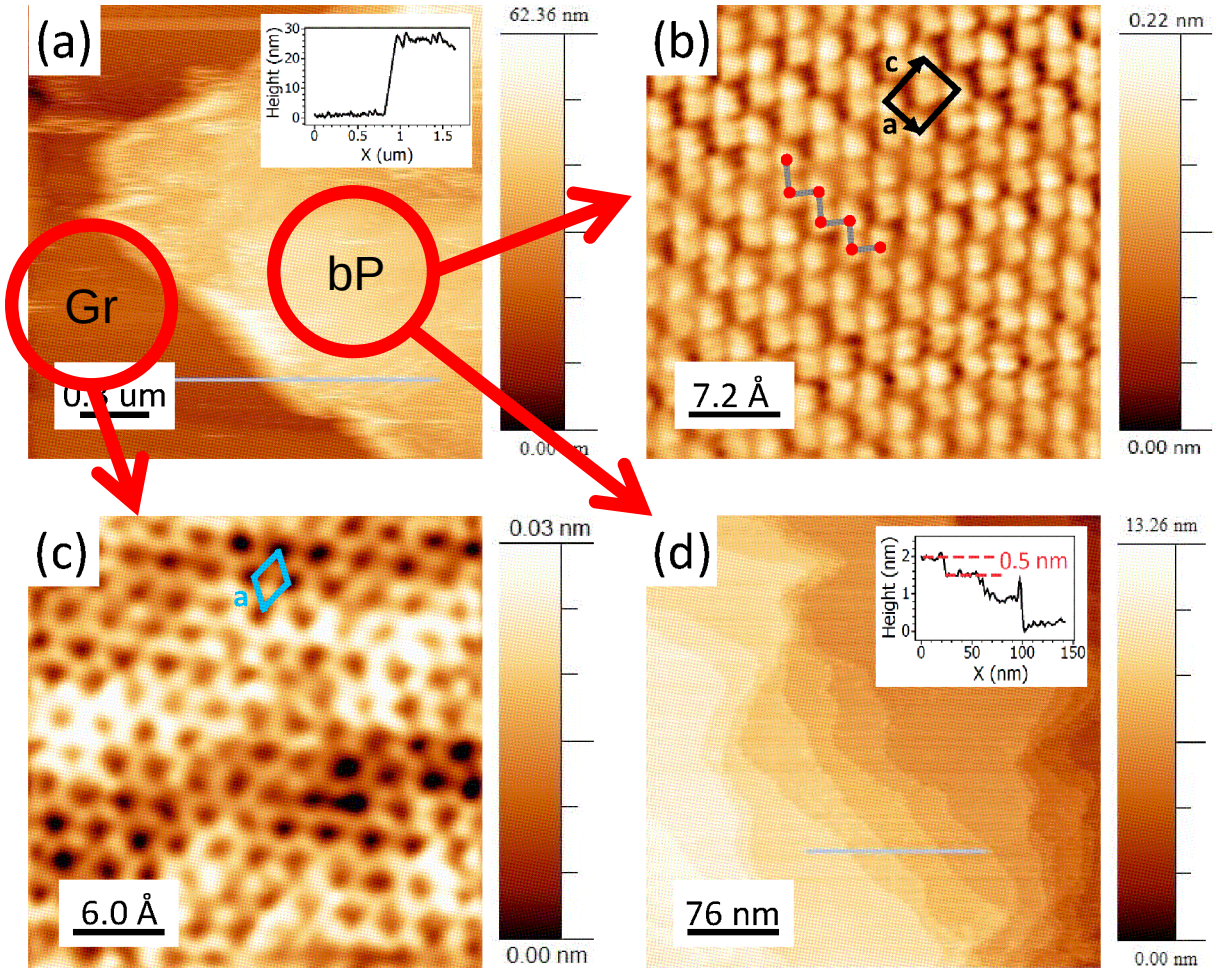
Glove Bag Exfoliation

- MLG on SiC – conducting substrate for STM
- Inert atmosphere exfoliation
- 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



STM of pristine bP exfoliated on graphene

h ~ 25 nm

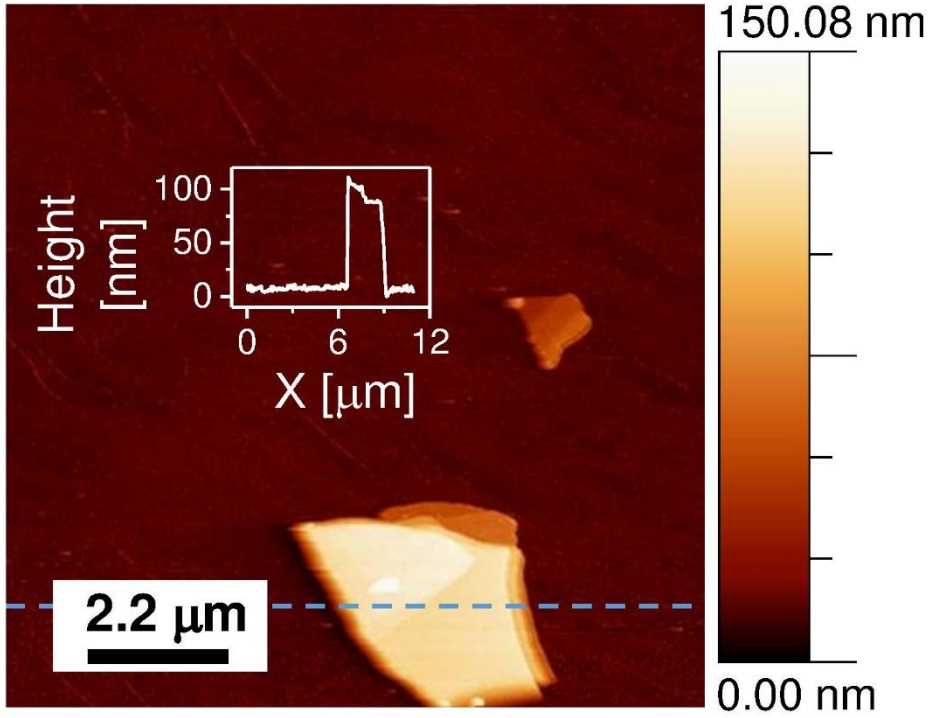


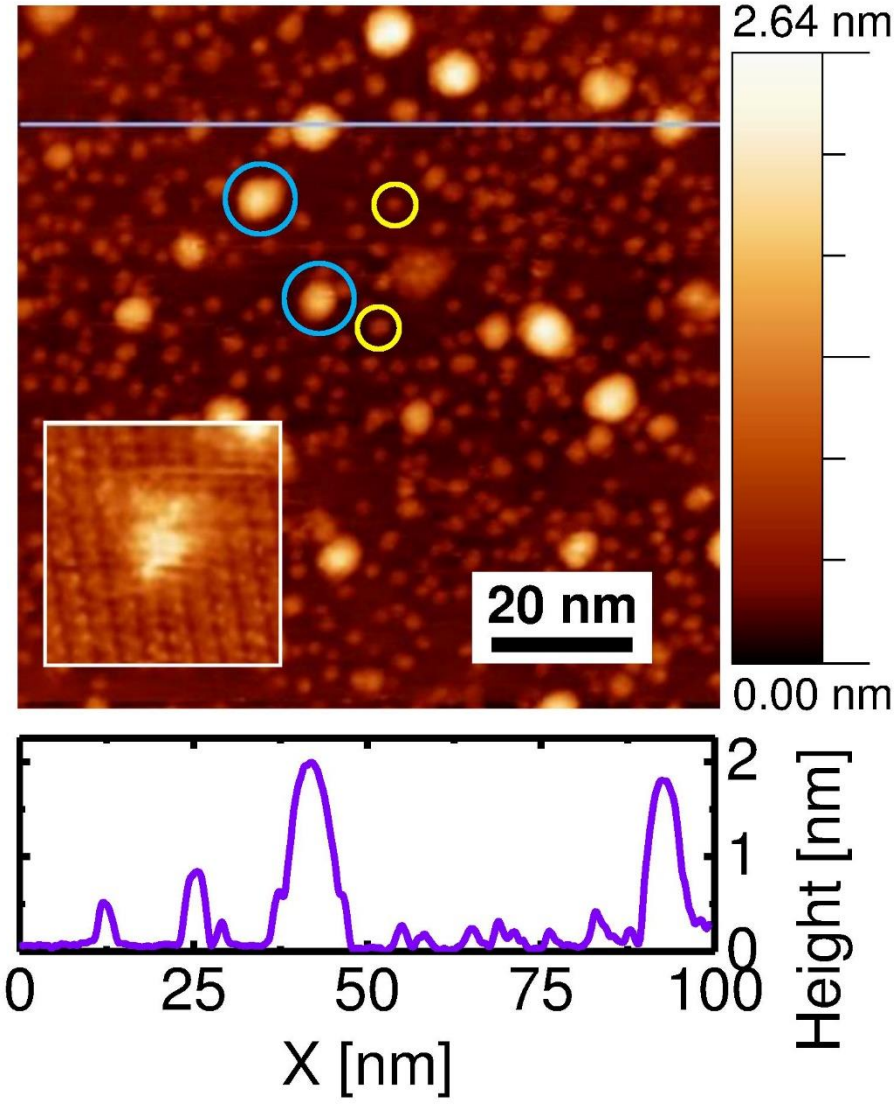
a = 3.45 Å
c = 4.40 Å

Abhishek Kumar *et al.*, 2D Mater. 6 (2019) 015005

STM: 0.8 ML Cu on bP

Cu grows in Volmer-Weber mode





Atomic resolution of bP after copper deposition demonstrates the high quality of copper-deposited bP sample

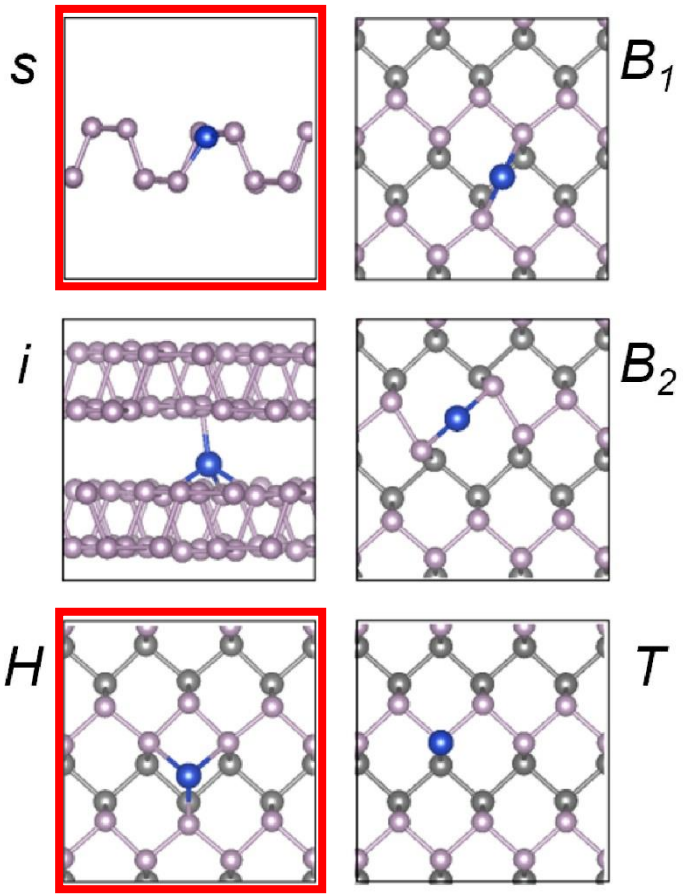
A. Kumar et al., J. Phys. Chem. C, in press.

DFT: Cu on bP

s: substitutional

i: interstitial

H: hollow



B1: bridge

B2: bridge

T: top

site	ΔE (eV)
s	-4.47
i	-3.46
H	-2.68
B_1	-2.55
B_2	-1.61
T	-1.51

A. Kumar et al., J. Phys. Chem. C, in press.

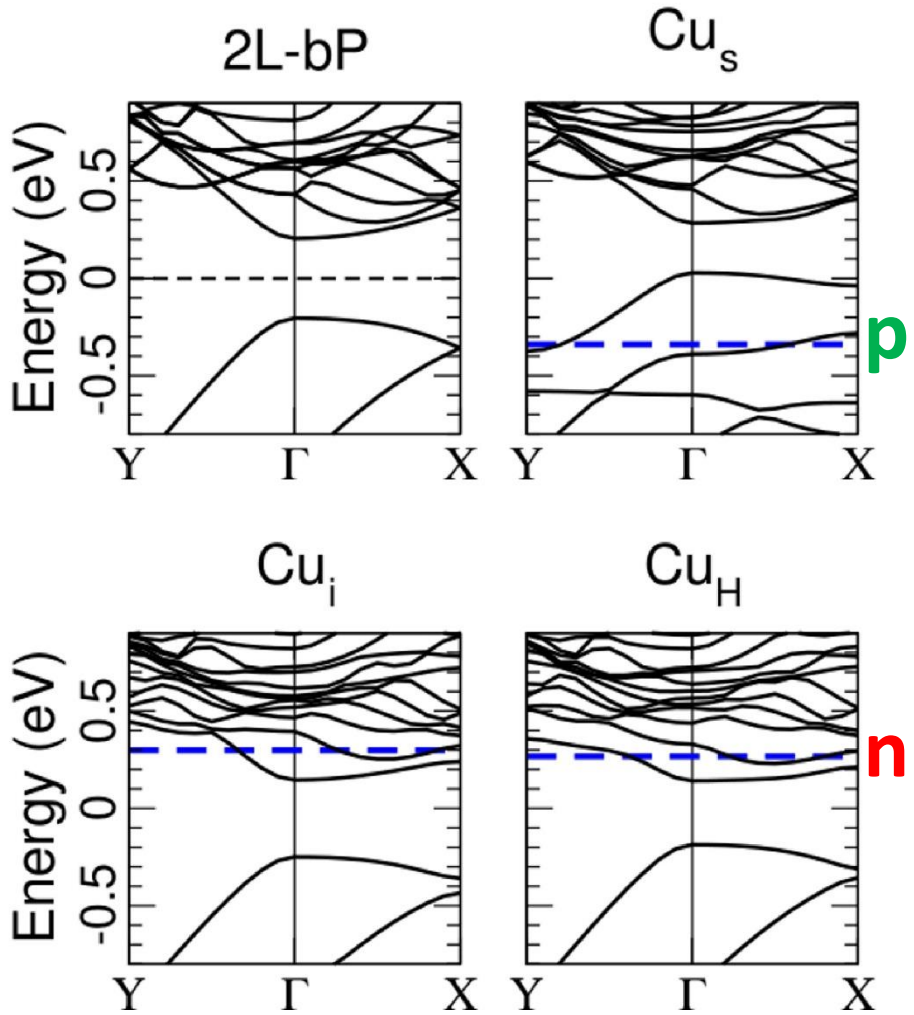
DFT: Cu on bP

site	ΔE (eV)	cluster	$\Delta E/N_{Cu}$ (eV)	$\delta E/N_{Cu_{ads}}$ (eV)
s	-4.47	Cu_{1+s}	-4.01	-0.87
i	-3.46	Cu_{3+s}	-3.56	-0.58
H	-2.68	Cu_{7+s}	-3.36	-0.51
B_1	-2.55	Cu_{9+s}	-3.42	-0.62
B_2	-1.61	Cu_3	-2.85	-0.08
T	-1.51	Cu_7	-3.03	-0.35

- Cluster formation is always favored, in overall agreement with experimental observations.
- Cluster nucleation around Cu_s sites is the (thermodynamically) most favorable process.

A. Kumar et al., J. Phys. Chem. C, in press.

DFT: Cu on bP



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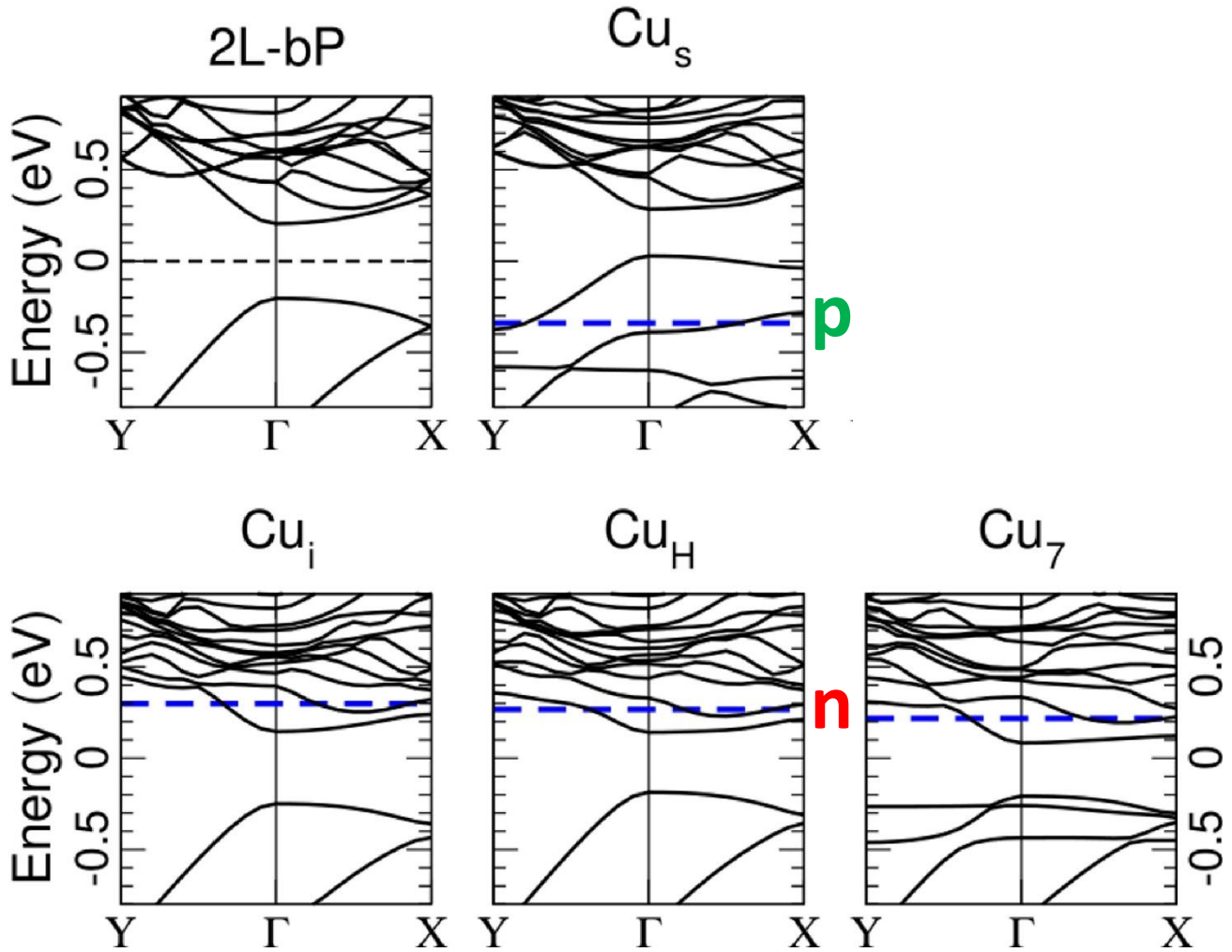

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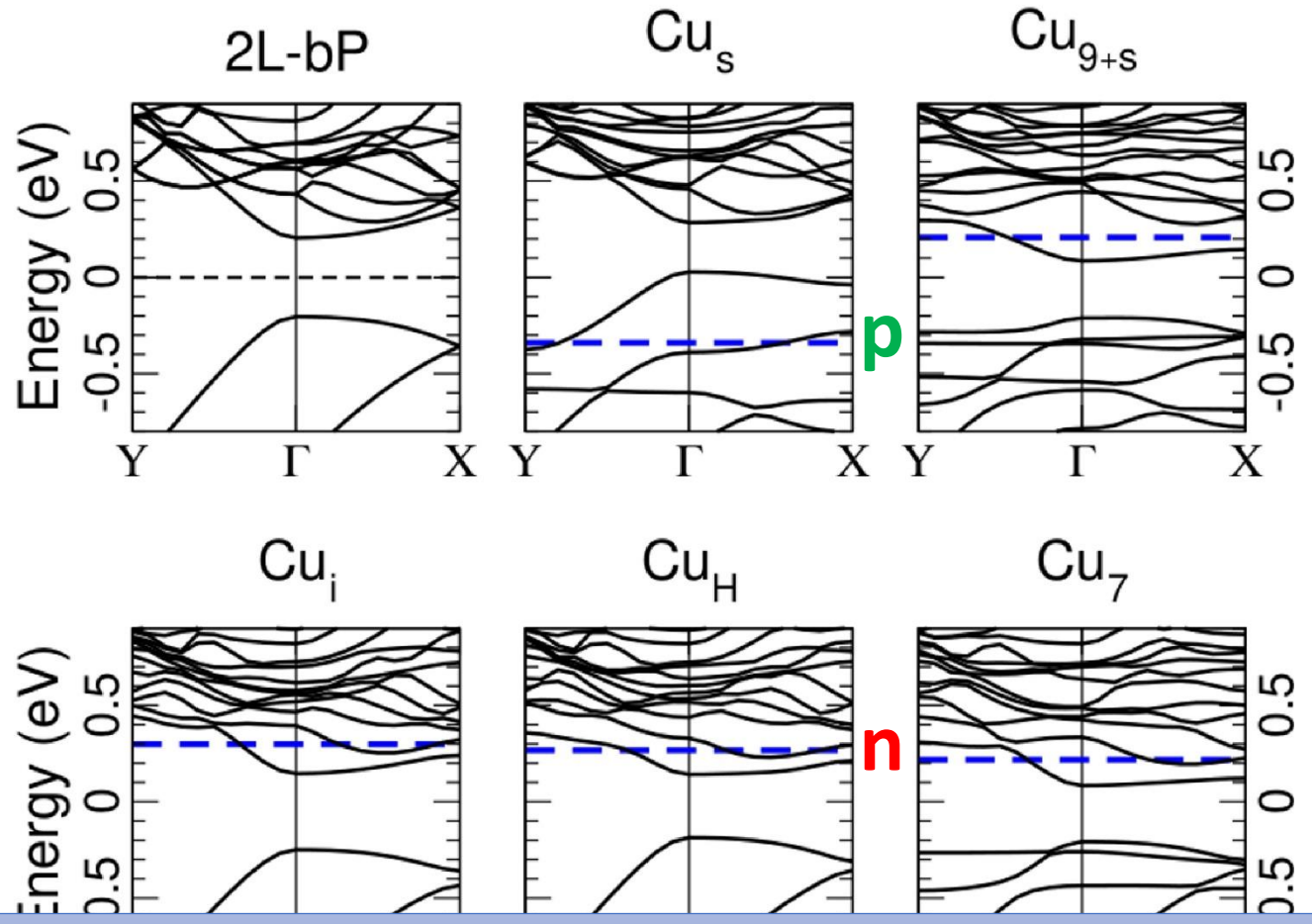
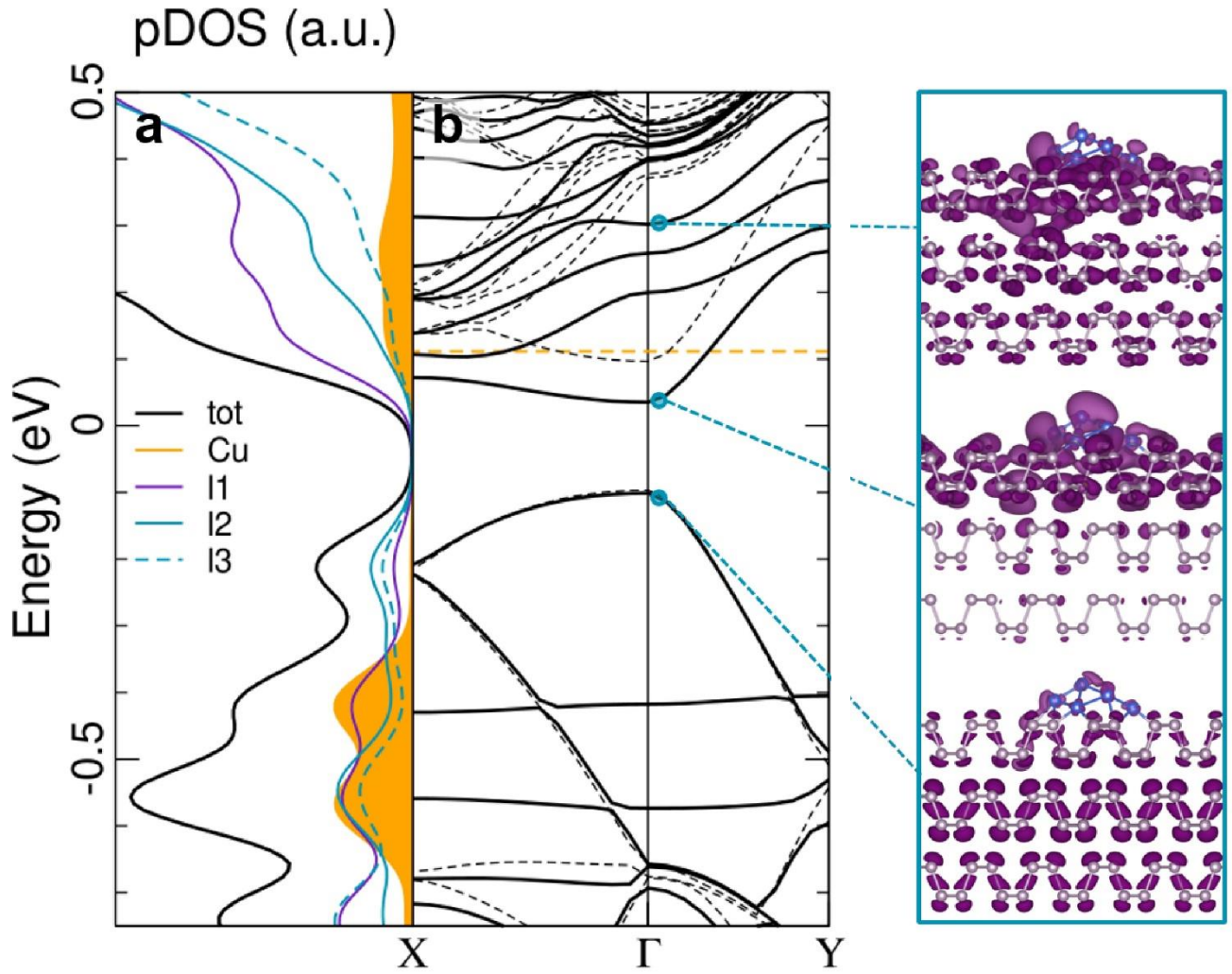
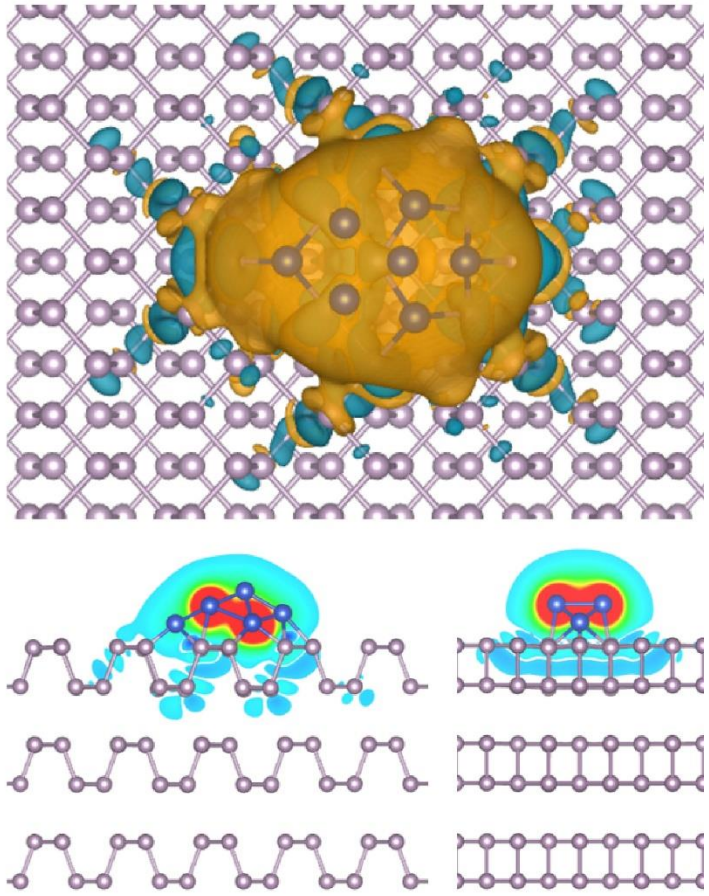


Band gap reduction in presence of Cu atoms

A. Kumar et al., J. Phys. Chem. C, in press.

DFT: Cu_7 on bP

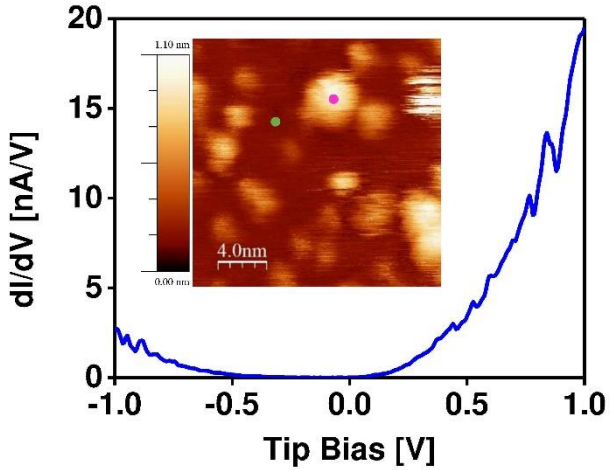




A. Kumar et al., J. Phys. Chem. C, in press.

STS: bP and Cu

pristine bP



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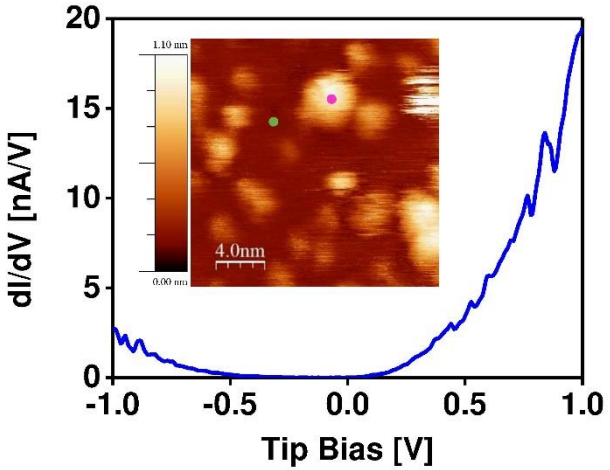
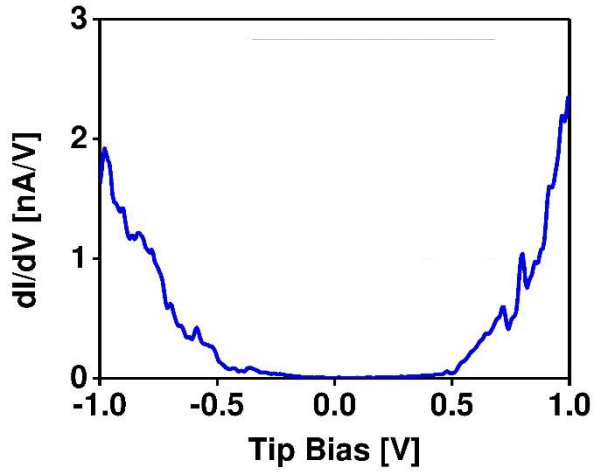


Cu on bP



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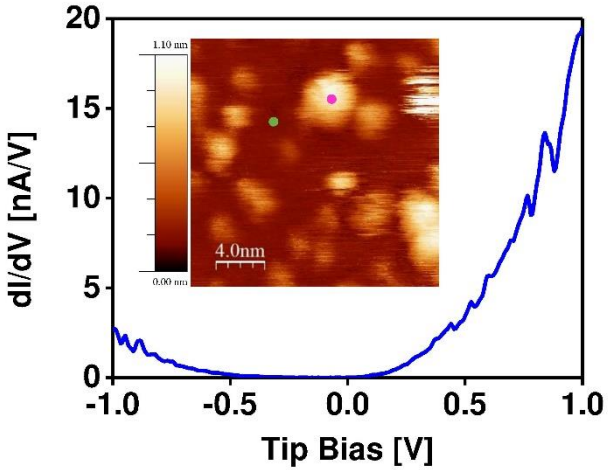

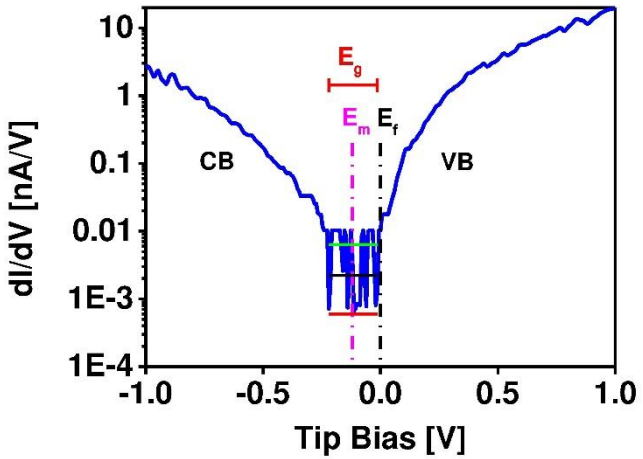

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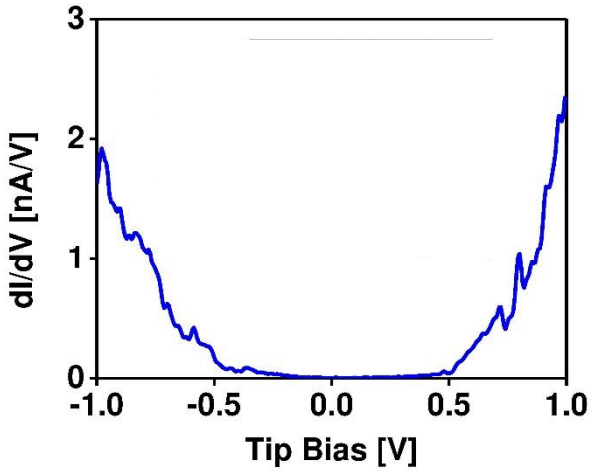
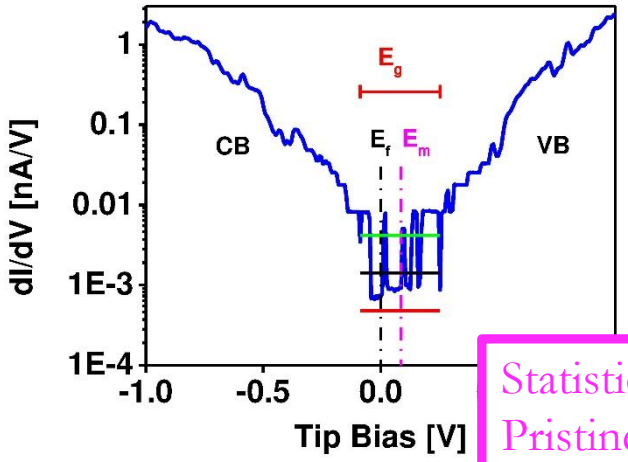


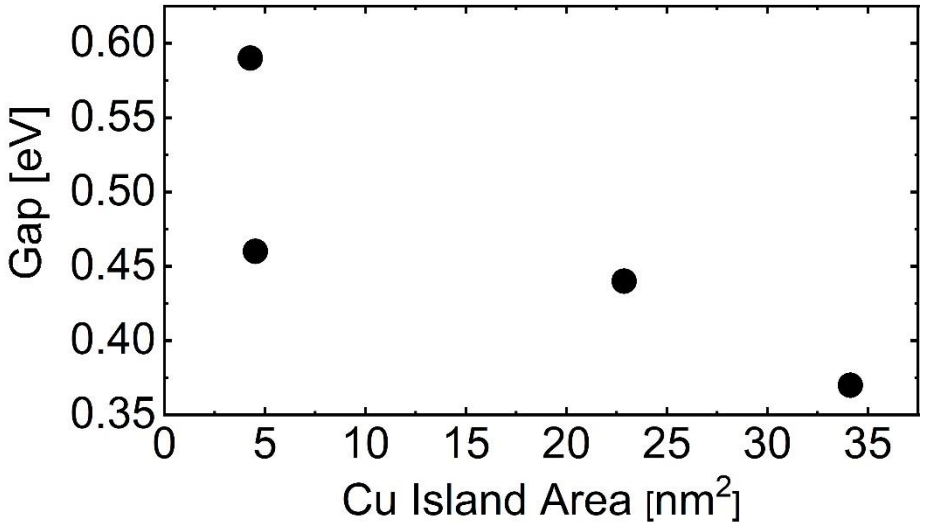


Statistical analysis of 42 spectra
Pristine bP → (0.25 ± 0.10) eV
Cu-Doped bP → (0.46 ± 0.20) eV

A. Kumar et al., J. Phys. Chem. C, in press.

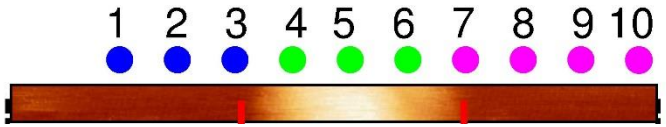
Coulomb blockade

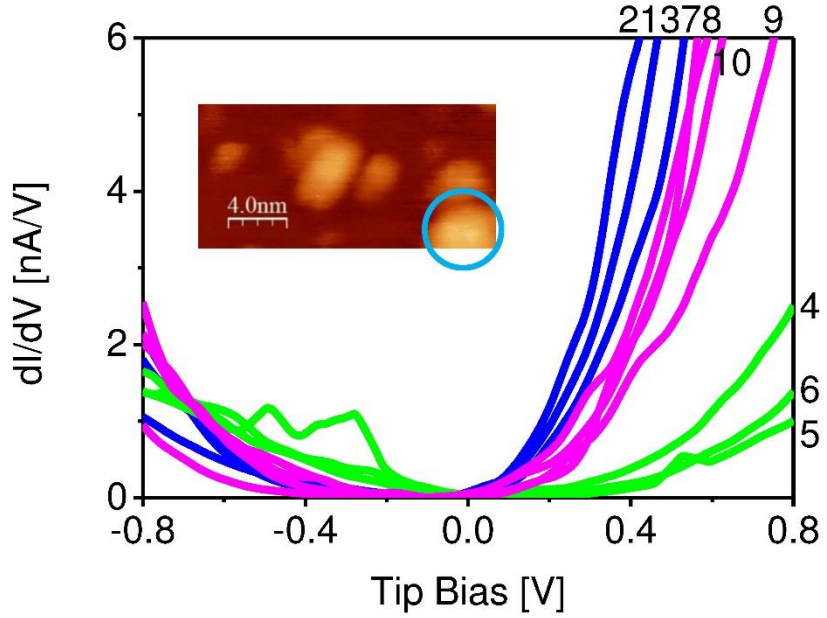
- Gap increase is in apparent contradiction with DFT
- Can be understood invoking Coulomb blockade of the Cu islands
- Parallel plate capacitor model: $C \approx 10^{-18}$ F → charging energy 100 meV
- Experimentally observed gap = Coulomb gap



A. Kumar et al., J. Phys. Chem. C, in press.

STS across a copper island





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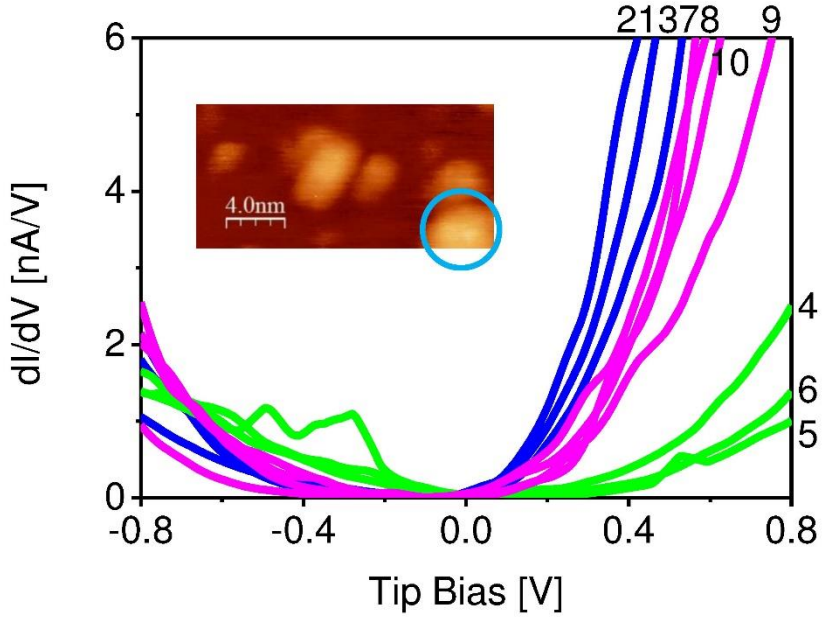

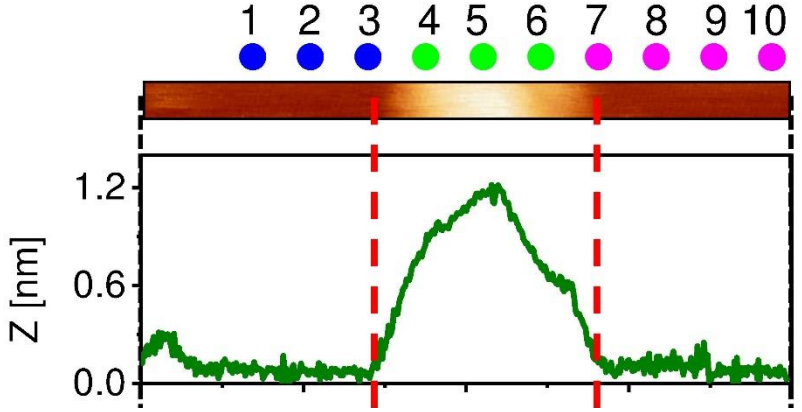

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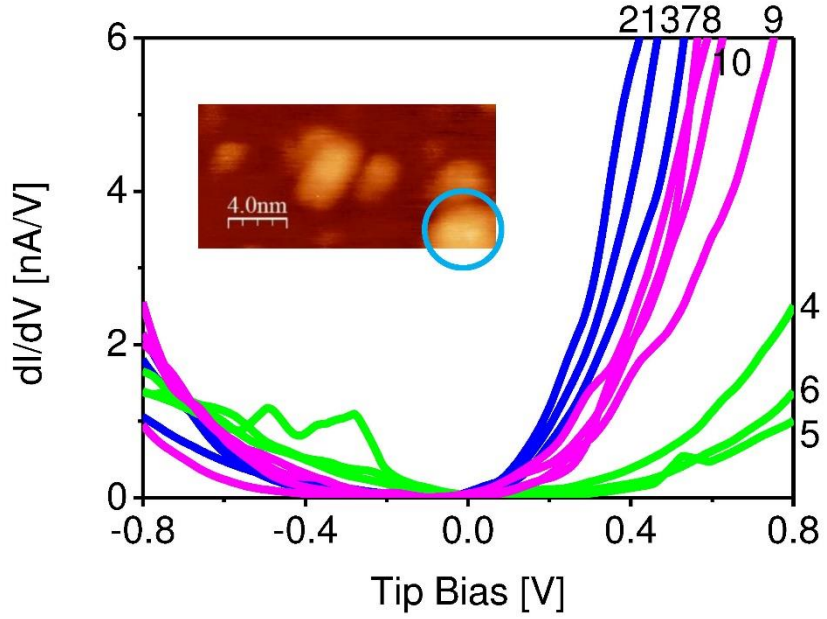
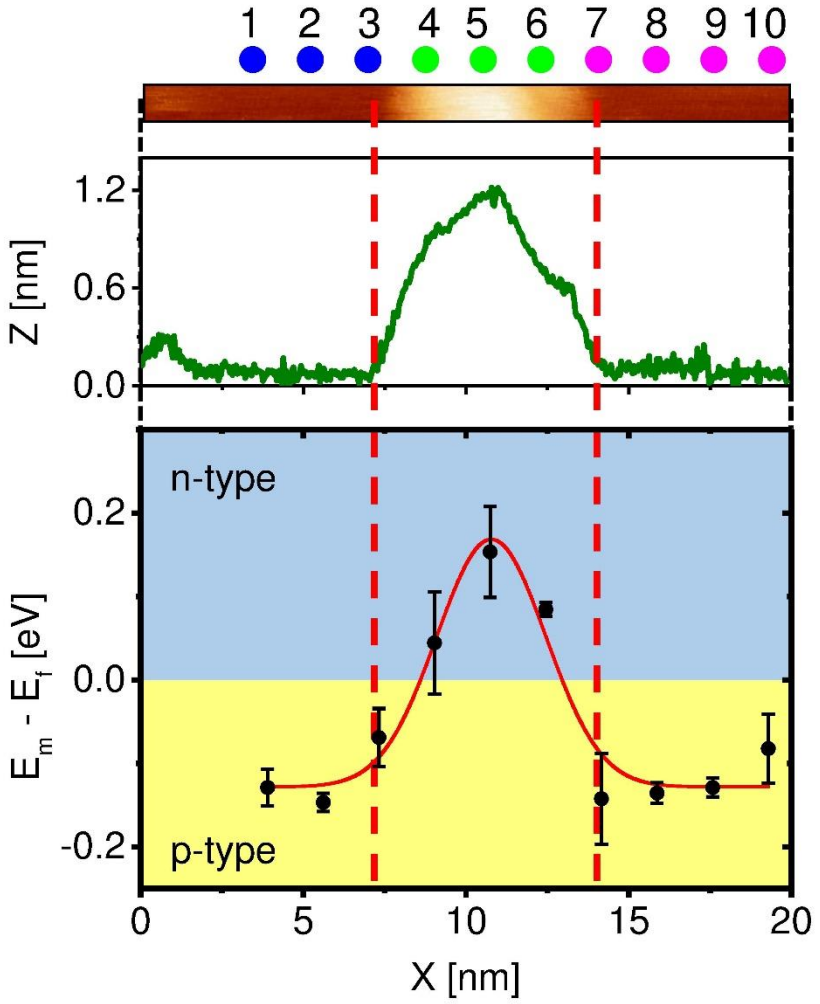


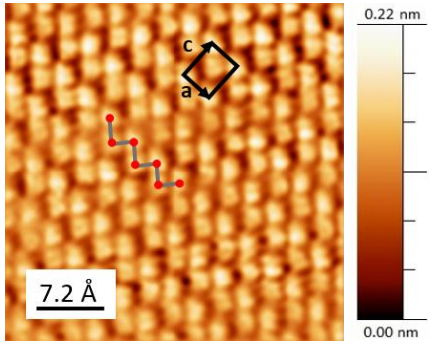


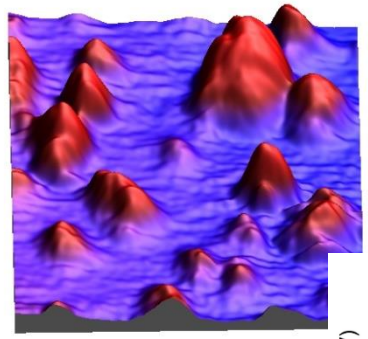
Lateral doping influence comparable to width of copper island

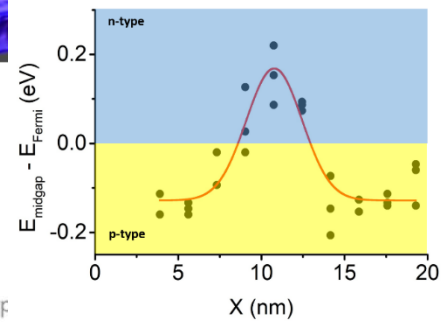
A. Kumar et al., J. Phys. Chem. C, in press.

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 and doping effects of copper on bP
- Can be used to make high performance p-n junctions







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Camilla Coletti

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Manuel Serrano-Ruiz

Maurizio Peruzzini

National Enterprise for nanoScience and nanoTechnology

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