DFT and Quantum Transport Simulations of 2D Material-Based Resistive Memories

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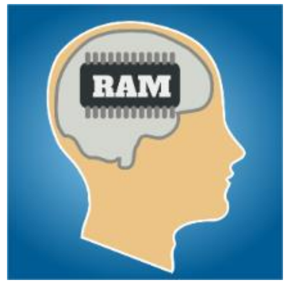
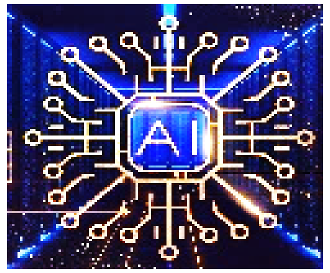
2D materials for future nanoelectronics and memories

Non volatile memories



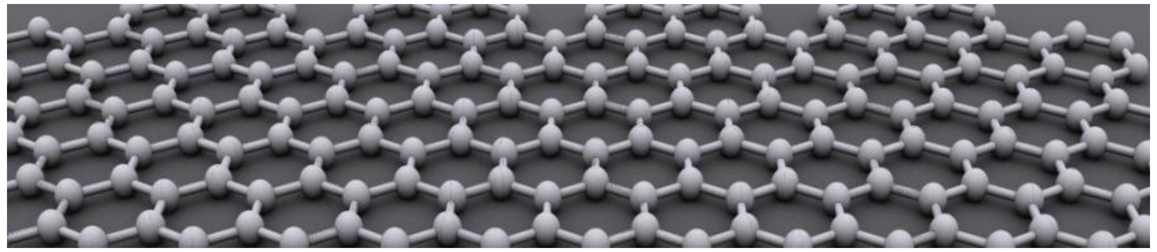
- Resistive RAM – **ReRAM**
- Magnetic RAM – **MRAM**
- Ferroelectric RAM – **FeRAM**

Applications of 2D based memories



- integration for **high density** memories
- **neuromorphic** computing: **artificial intelligence**
- radio frequency **switches**
- **in-memory computing**

2D material important properties



- atomic **thickness** < 1nm
- absence of **dangling bonds**
- mechanical **flexibility**
- different materials with different properties: **metallic** (TMDs in 1T phase…), **insulating** (hBN…), **semiconducting** (TMDs in 2H phase…), **semi-metallic** (graphene), **ferroelectric** (TMDs, In_2Se_3,…), **ferromagnetic** (CrI_3, Cr_2GeTe_2, Fe_2GeTe_2…), **multiferroic** ($CuCrP_2S_6$, $Cr_2Ge_2Se_6$…)

Advantages

- **stacking** in **van der Waals** heterostructures
- small amount of material is necessary: **sustainability**
- good electrostatic control: **low switching voltages**
- low power consumption: **green electronics**

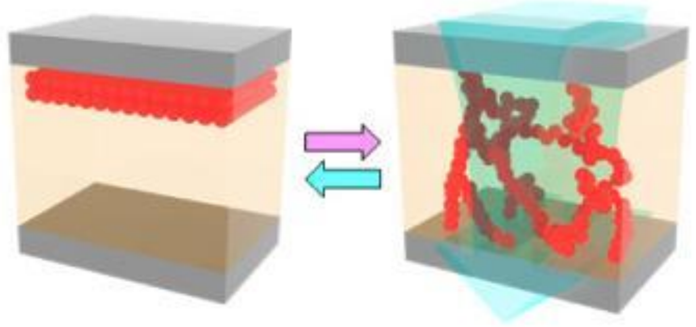
Challenges

- **large scale and size fabrication**
- **variability** due to defects, polycrystallinity, stability…
- limited **CMOS** compatibility

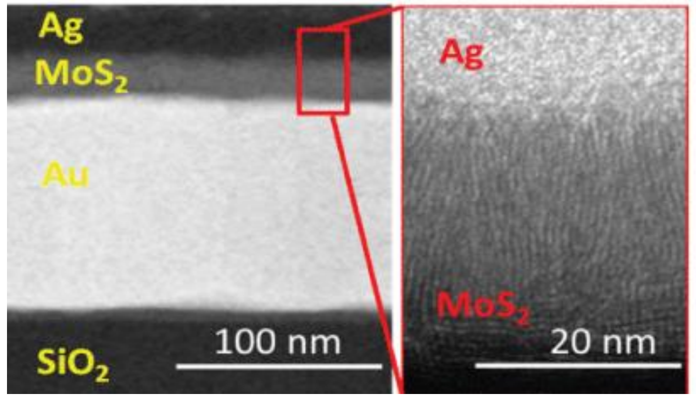
Resistive memories based on 2D materials

[K. C. Kwon *et al.*, Nano-Micro Lett. **14**, 58 (2022)]

Filament formation

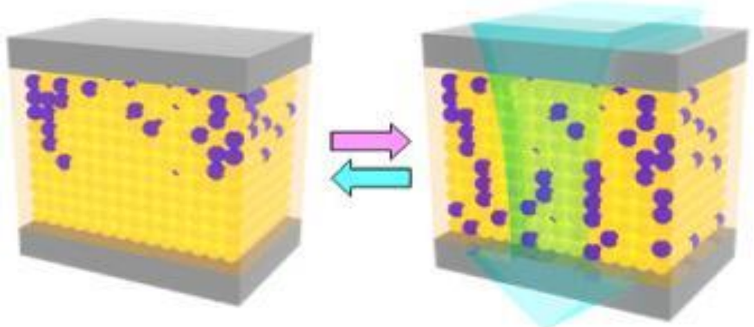


Ag/MoS_2/Ag	IEDL **41**, 936 (2020)
Cu/MoS_2/Au	Nano Lett. **19**, 2411 (2019)
Ni/Au/MoS_2/Gr	IScience **23**, 101676 (2010)
Ag/ZrO_2/WS_2/Pt	ACS Appl. Mater. Interfaces **11**, 48029 (2019)

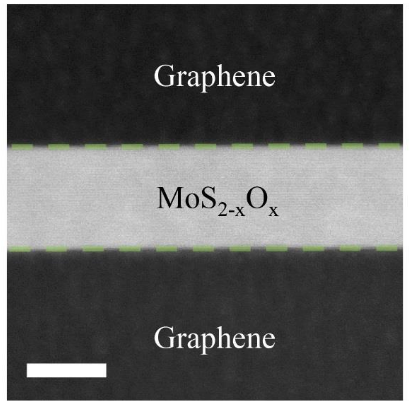


[D. Dev *et al.*, IEDL **41**, 936 (2020)]

Vacancy migration

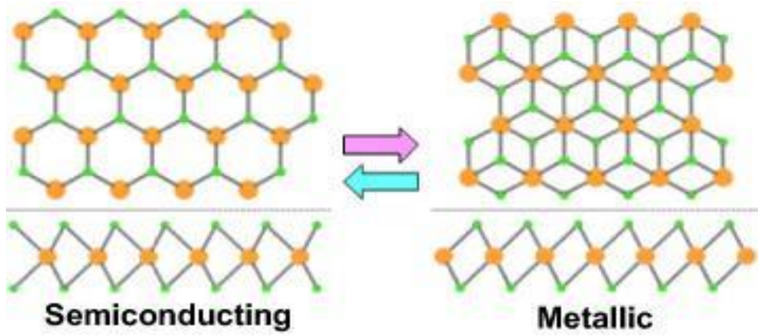


Pd/WS_2/Pt	Small **15**, 1901423 (2019)
Gr/$MoS_{2-x}O_x$/Gr	Nat. Electron. **1**, 130 (2018)
Ag/WO_{3-x}Au/WSe_2/Gr	Adv. Mater. **30**, 1801447 (2018)
Ag/MoO_x/MoS_2/Ag	Nat. Mater. **14**, 199 (2015)

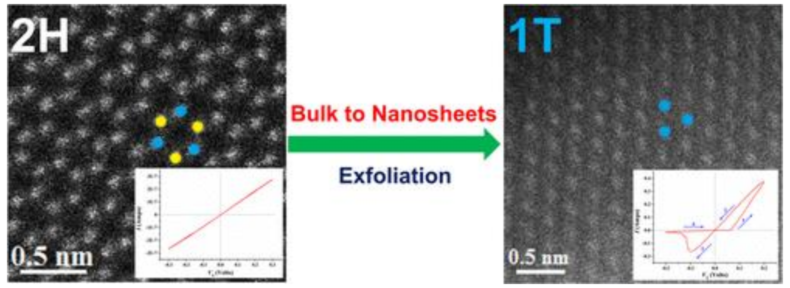


[M. Wang *et al.*, Nat. Elect. **1**, 130 (2018)]

Phase transition

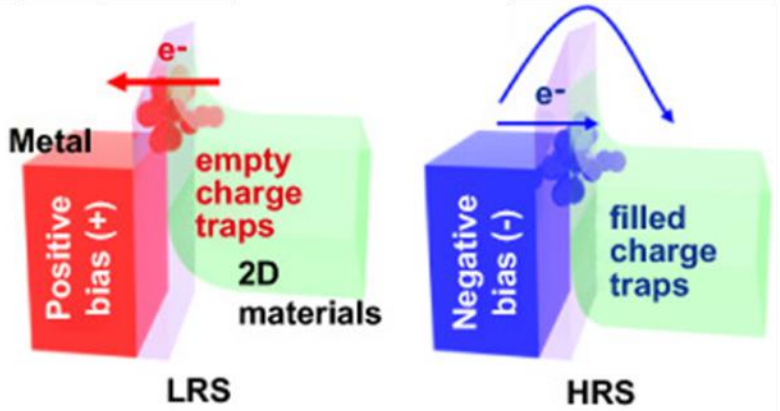


Au/MoS_2/Au	Nat. Mater. **18**, 141 (2019)
Ti/Ni/$MoTe_2$/Ti/Au	Nat. Mater. **18**, 55 (2019)
Ag/MoS_2/Gr	Nano Lett. **16**, 572 (2016)

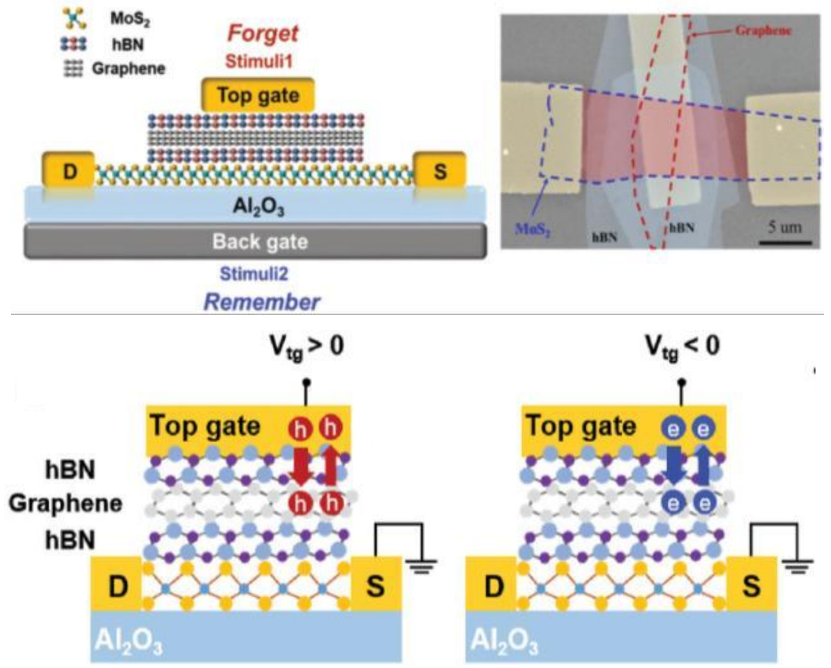


[P. Cheng *et al.*, Nano Lett. **16**, 572 (2016)]

Charge trapping



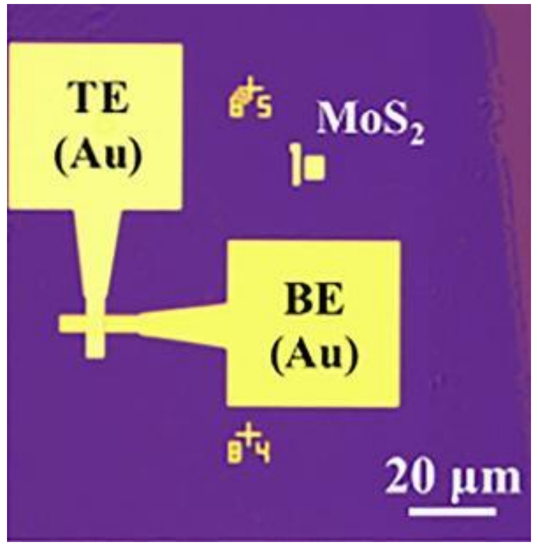
Cr/Au/hBN/Gr/hBN/MoS_2/Al_2O_3	Adv. Sci. **6**, 1901072 (2019)
Ti/Au/WSe_2/WCL/hBN/Pt/Au	Nat. Comm. **9**, 5106 (2018)
Cr/Au/MoS_2/hBN/Gr	Adv. Sci. **6**, 1901072 (2019)



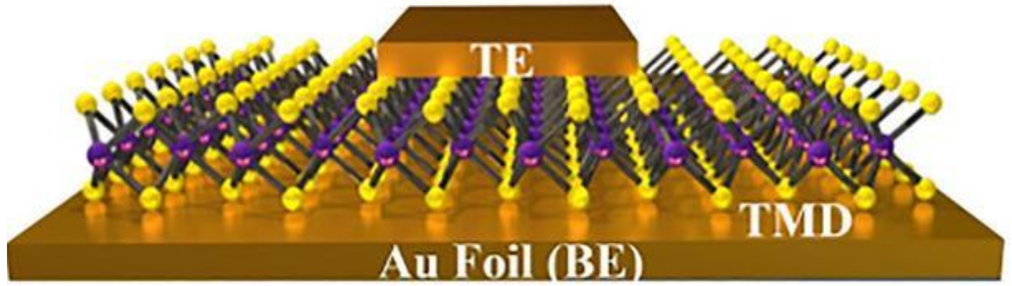
[H. Chen *et al.*, Adv. Sci. **6**, 1901072 (2019)]

Atomristors

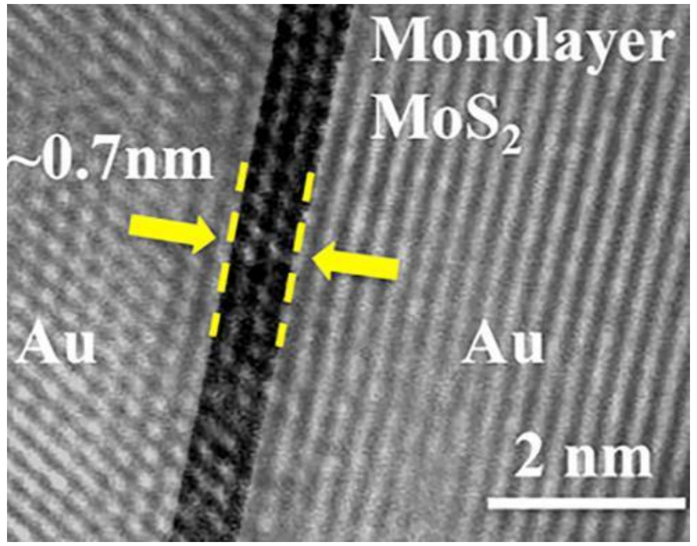
First realization of an atomistor: R. Ge, X. Wu, M. Kim, J. Shi, S. Sonde, L.Tao, Y. Zhang, J. C. Lee and D. Akinwande, Nano Lett. **18**, 434 (2018)



Optical image of metal–insulator–metal structures of TMD crossbar sandwich.

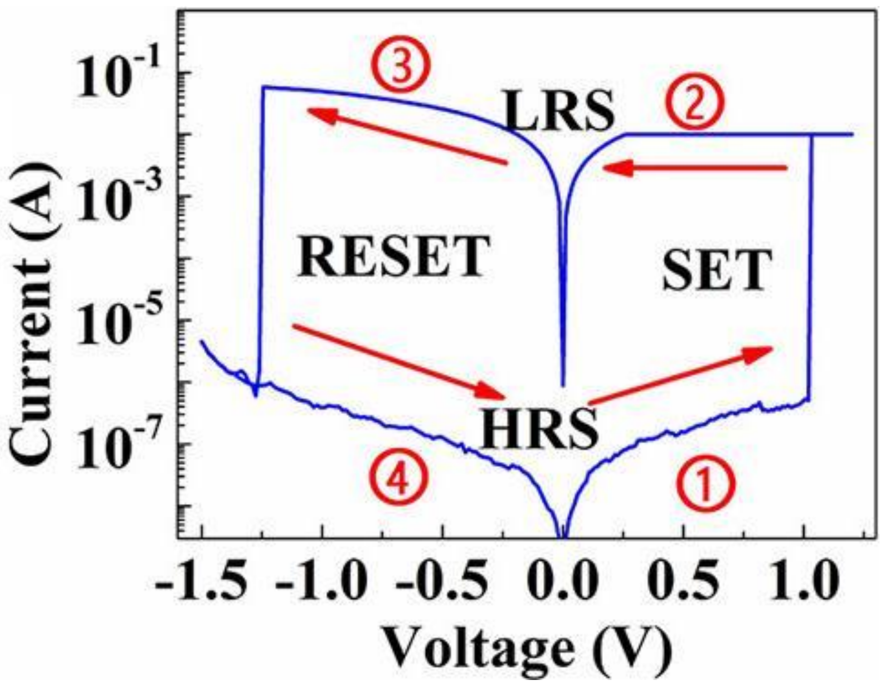


Schematic of TMD lithography-free and transfer-free sandwich.

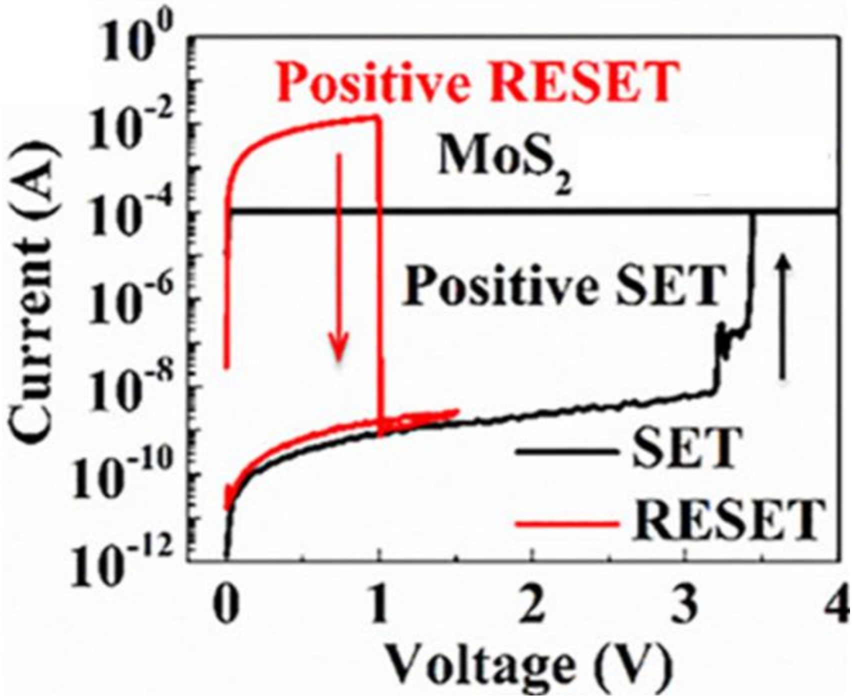


TEM cross-section image of Au/MoS_2/Au litho-free device revealing the atomically sharp and clean monolayer interface.

Bipolar switching

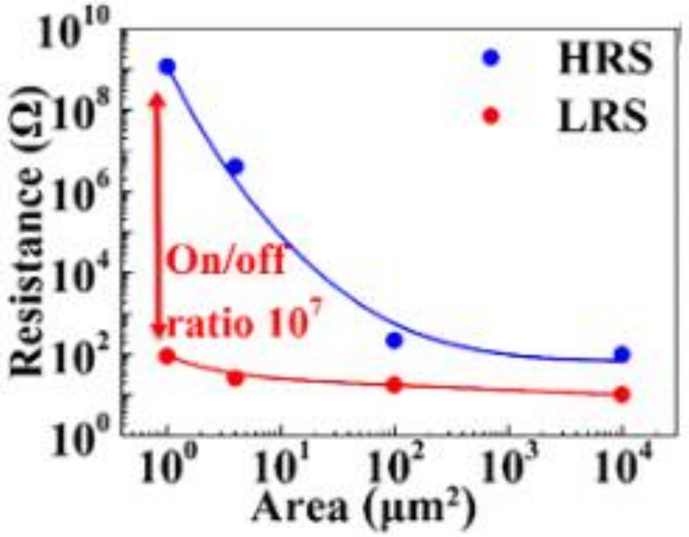


Unipolar switching



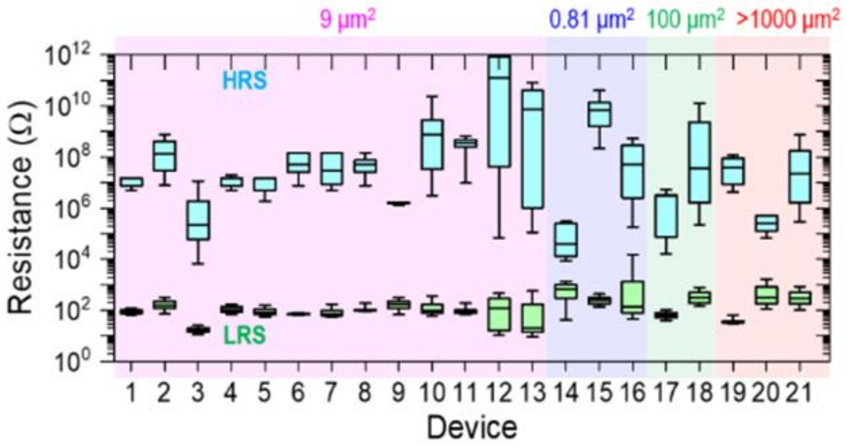
Properties of the high resistance state (HRS)

Generally, the **resistance decreases with device area**…



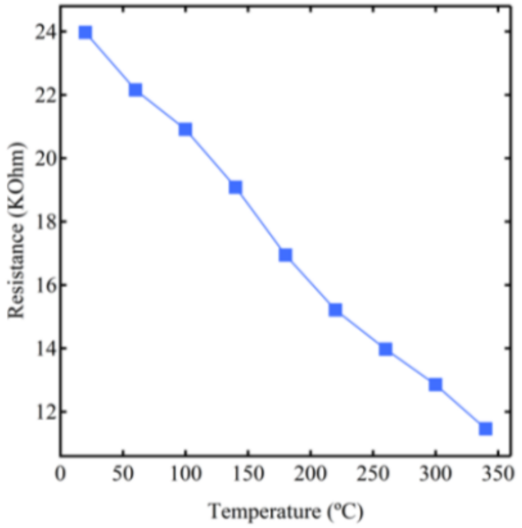
[Nano Lett. **18**, 434 (2018)]

Up to **8 orders** of magnitude of **device-to-device variability** and…



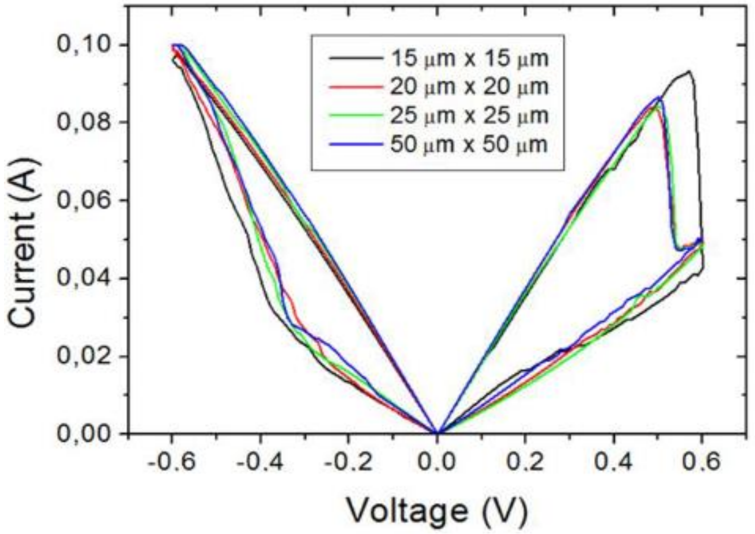
[Nat. Elect. **7**, 557 (2024)]

Generally, the **resistance decreases with temperature**…



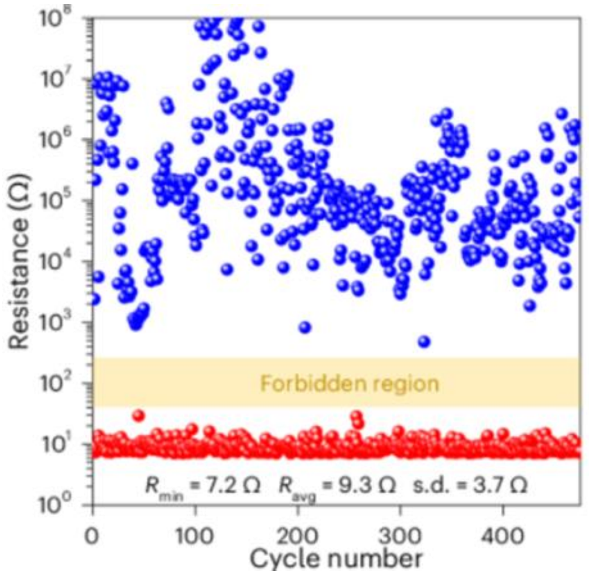
[Nat. Elect. **1**, 130 (2018)]

…but **not always**



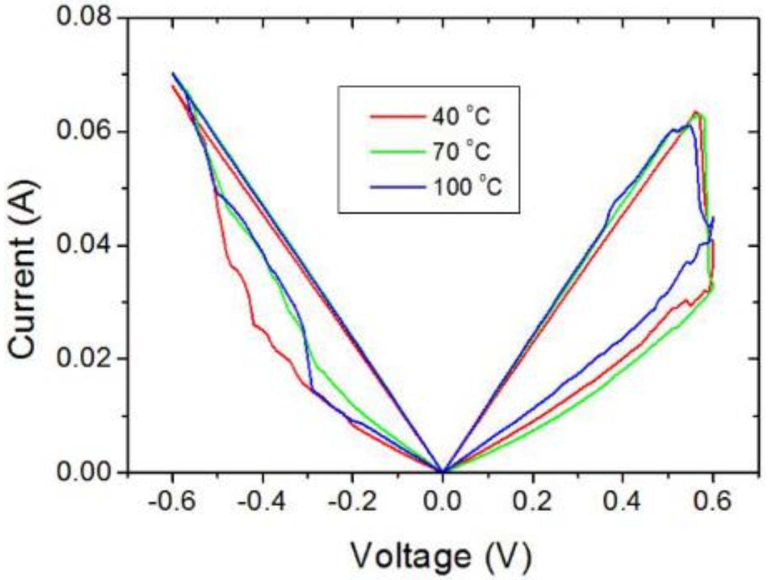
[Adv. Funct. Mater. **27**, 1604811 (2017)]

…**5 orders** of magnitude of **cycle-to-cycle variability**



[Nat. Elect. **7**, 557 (2024)]

…but **not always**

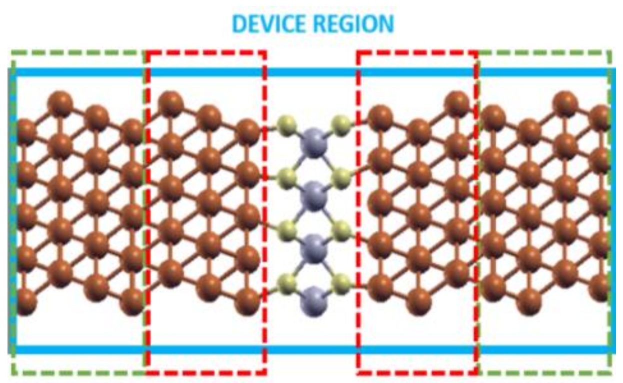


[Adv. Funct. Mater. **27**, 1604811 (2017)]

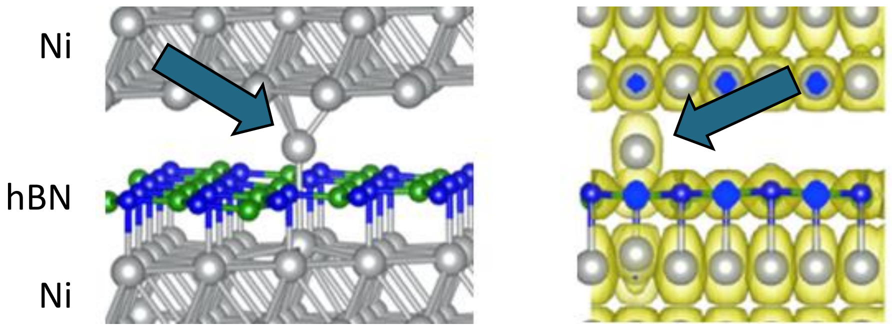
Plan

Large variety of behaviors... Origin of the switching mechanism? What does determine the LRS and the HRS?
How to optimize the performances?

- Few words about the simulation methodology

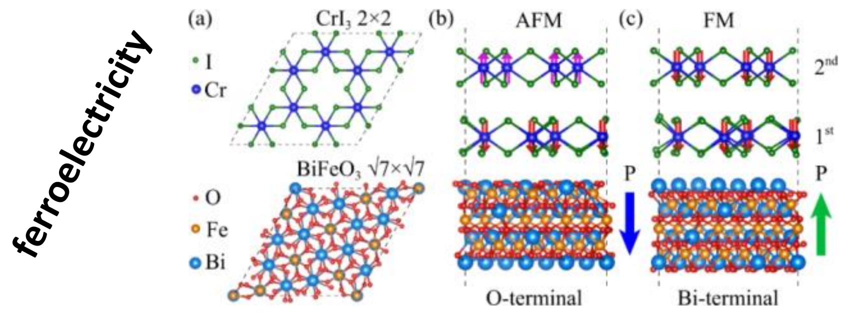


- HRS - Clean metal-2D heterojunctions with different materials and 2D layers

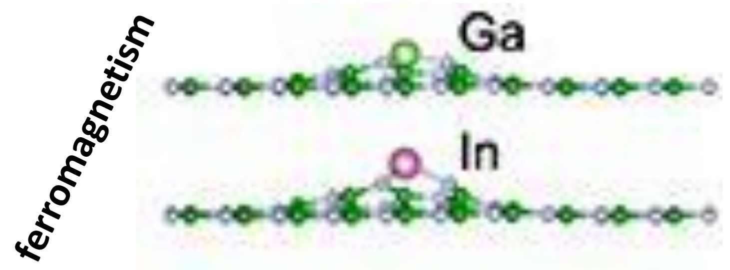


- LRS - Role of defects: the example of metal-ion substitution

- Perspectives we are interested in



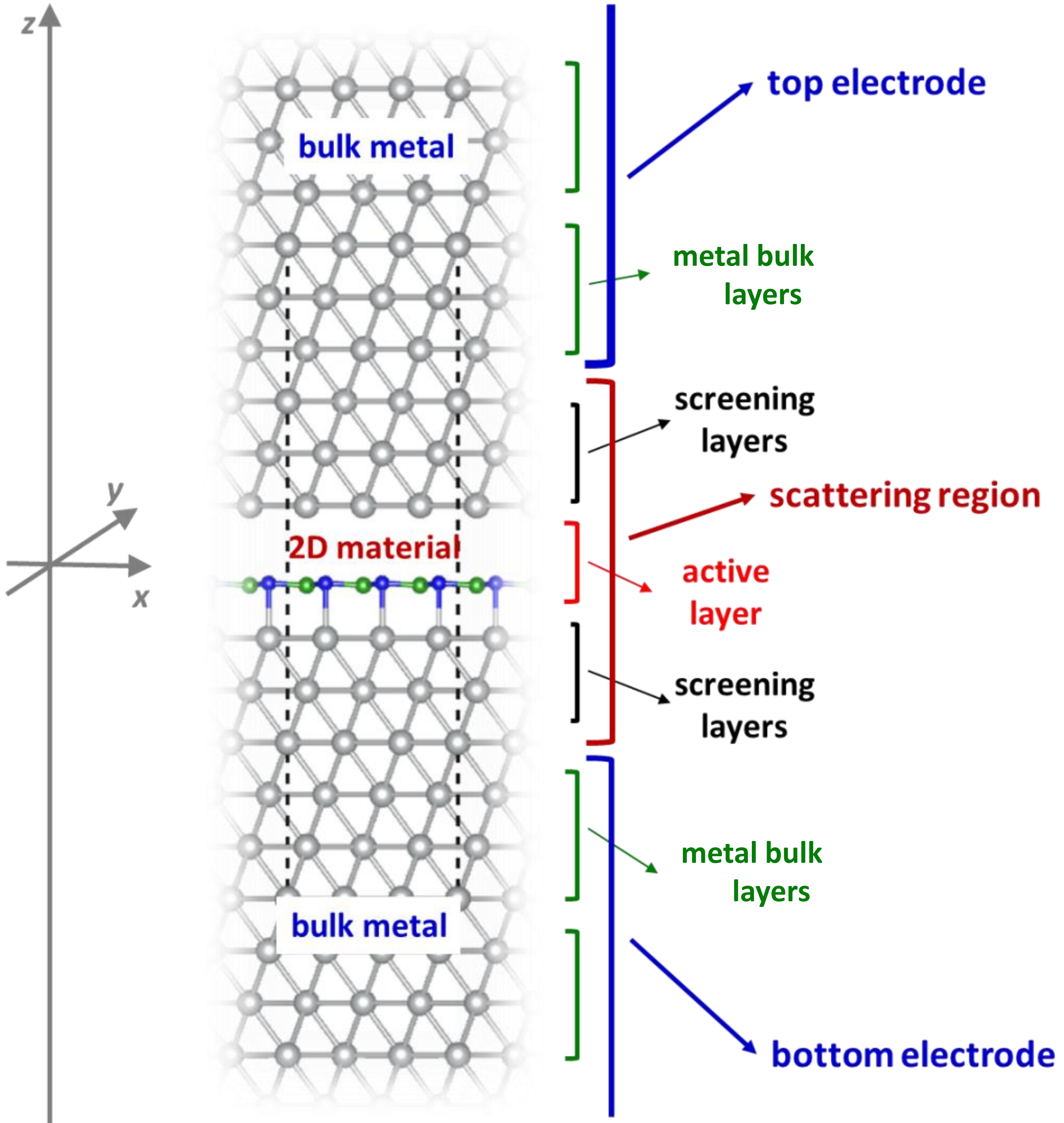
[npj Comput Mater **8**, 20 (2022)]



[2D Mater. **11**, 035019 (2024)]

Methodology

Vertical stacking



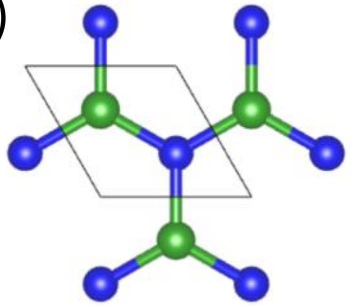
Structural relaxation and electronic properties

Density Functional Theory

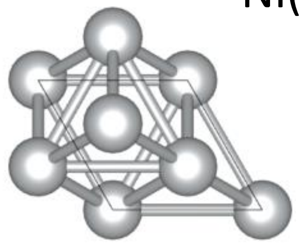
siesta™ Abinit

The "**problem**" of periodic primitive cell and **strain**

hBN (1x1)

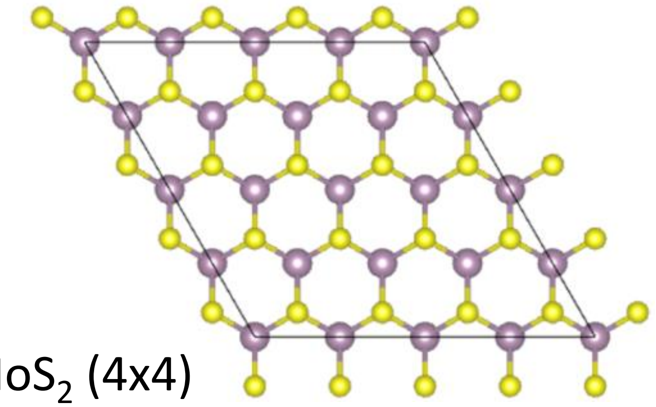


Ni(111) (1x1)

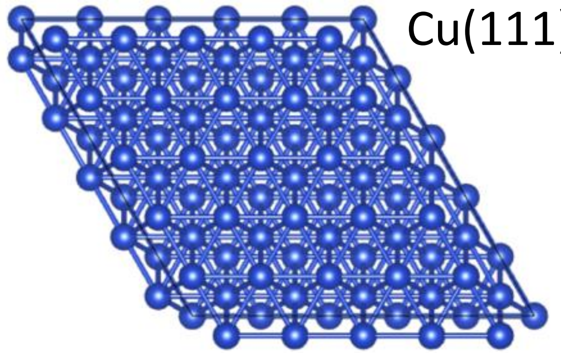


ε (hBN) = -0.56%

ε (Ni) = 1.44%



MoS_2 (4x4)



Cu(111) (5x5)

ε (MoS_2) = 0.11%

ε (Cu) = -0.79%

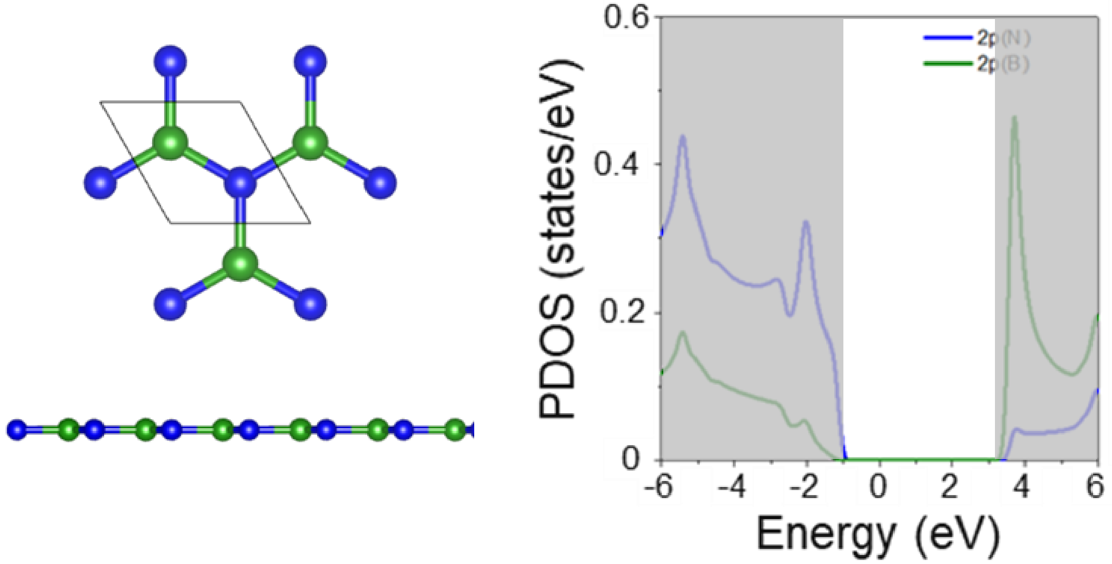
Electron transport

Non Equilibrium Green's Function

Transiesta

Stacking modes in small cells (1x1 – Ni and hBN)

Free-standing hBN



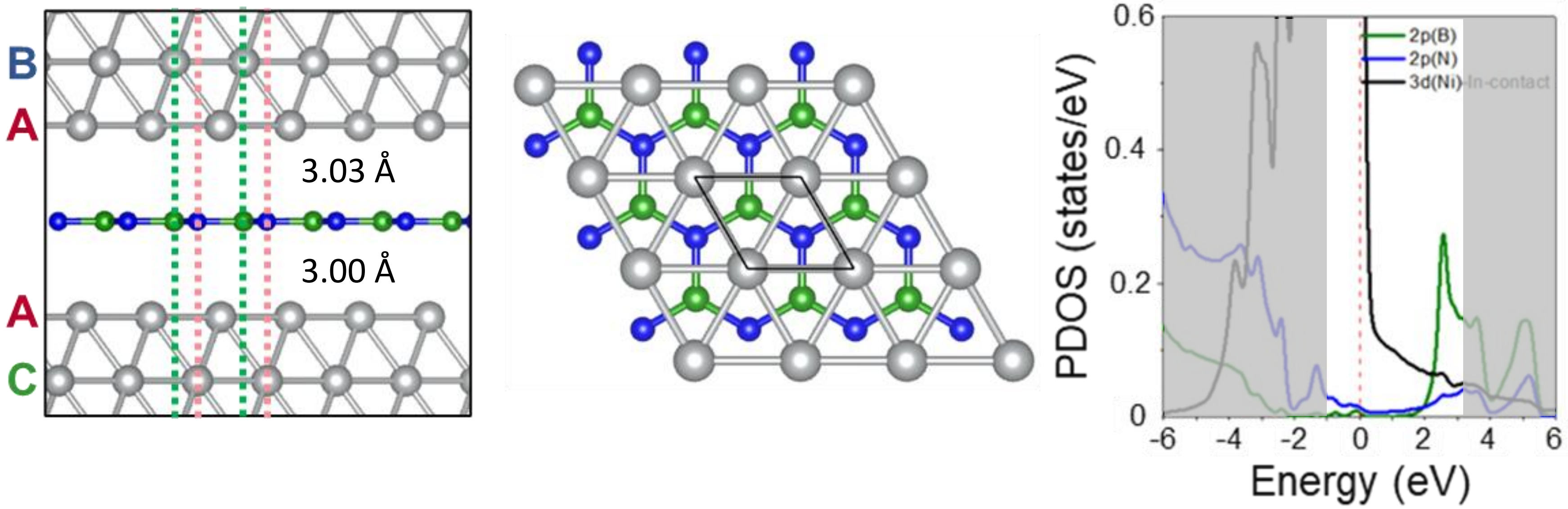
Free-standing hBN : gap ~4.5 eV

AA stacking: *h*BN at the same distance from the electrodes, mid-gap states

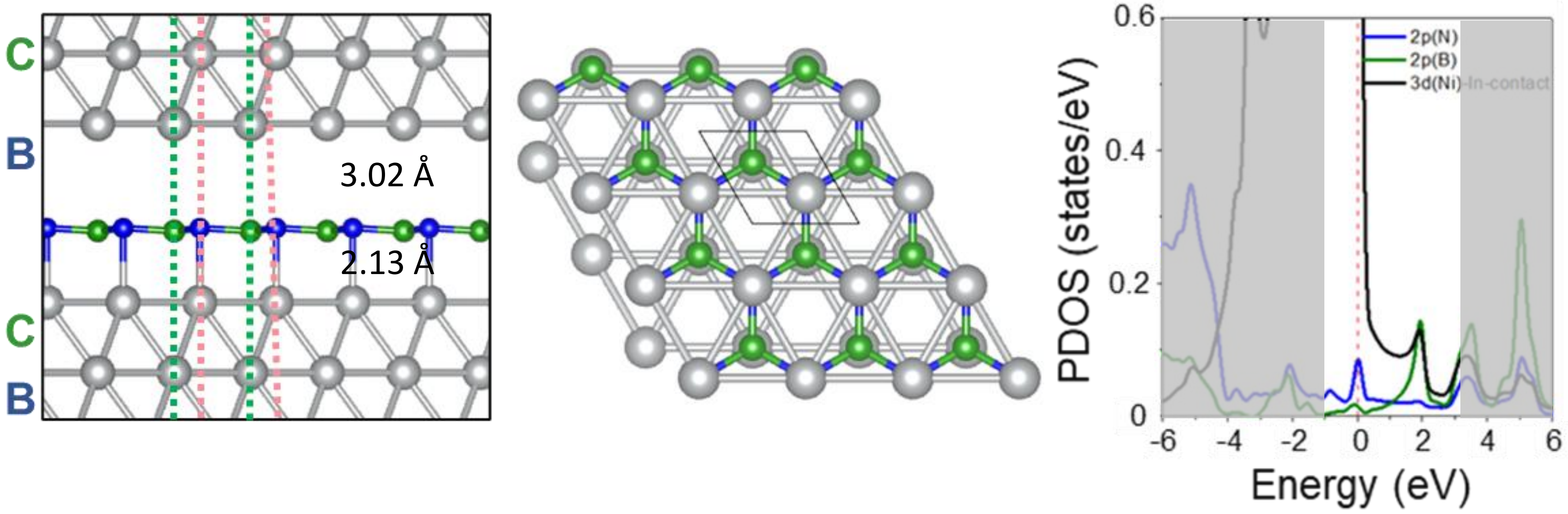
CB stacking: stronger Ni/N bond formation at one interface due to N affinity, different distances from the electrodes, stronger gap reduction

Strong influence of the stacking mode

AA stacking

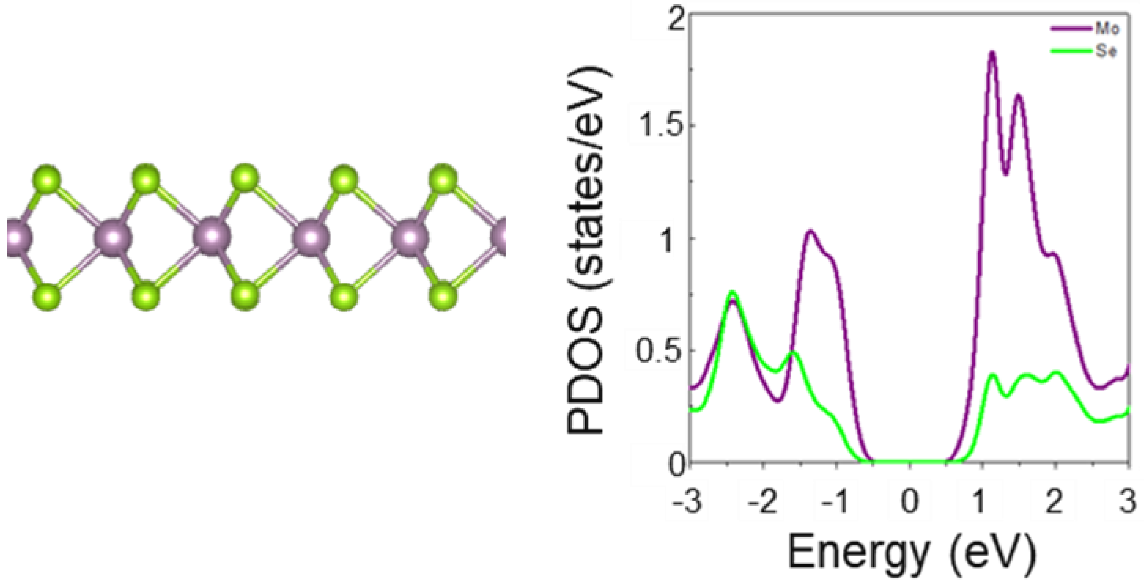


CB stacking



Stacking modes in large cells (5x5 and 4x4 – Cu and MoS_2)

Free standing MoS_2



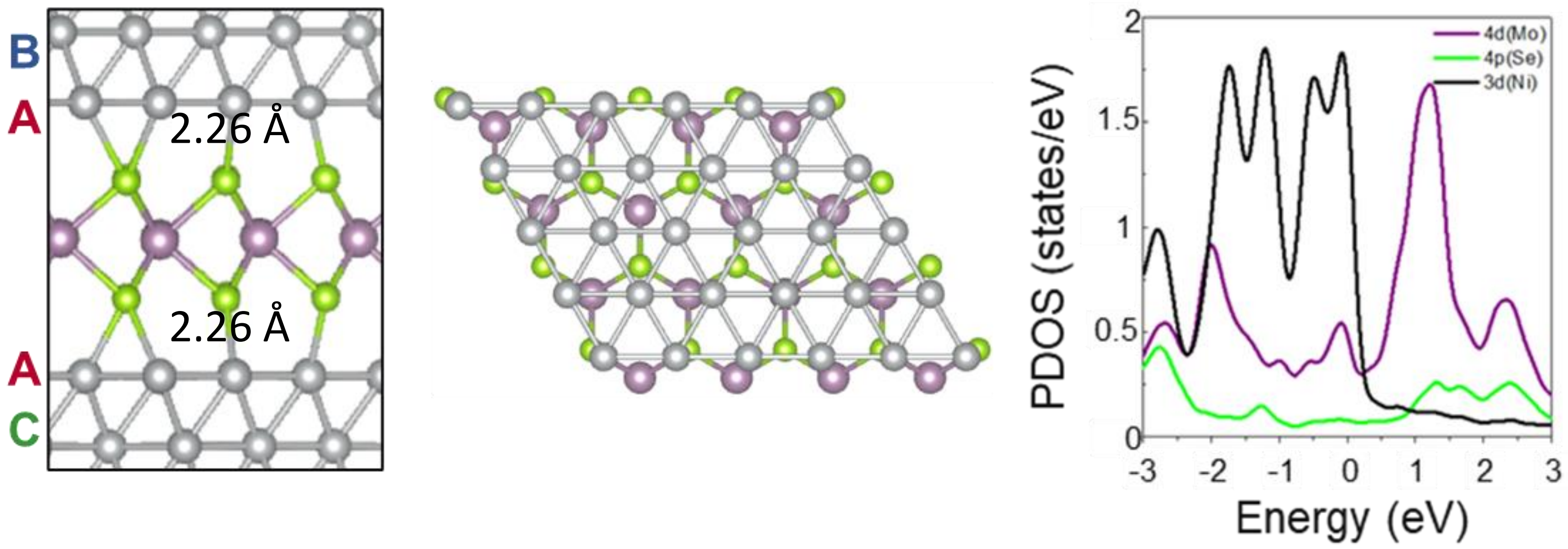
Free-standing MoS_2 : gap ~1.5 eV

Both AA an BA stacking: Ni/S bonds formation at the interface

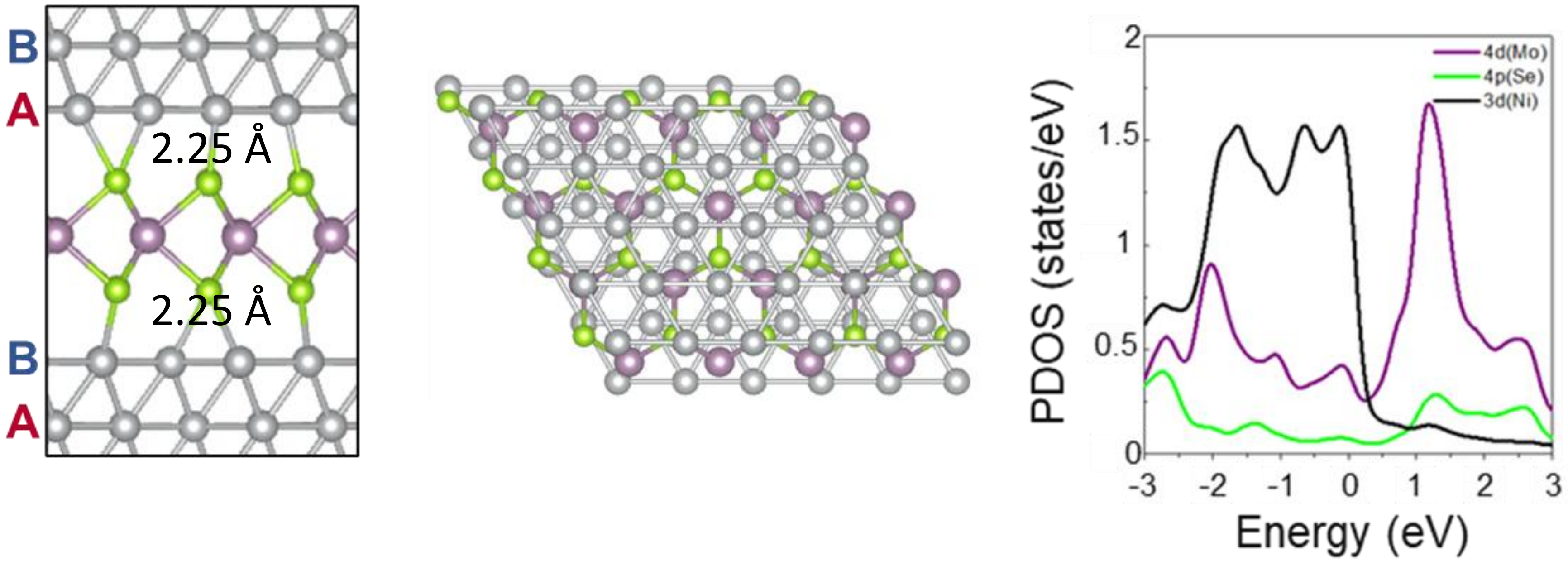
The gap is completely closed

Nearly same environment for S atoms at MoS_2/Cu interfaces

AA stacking



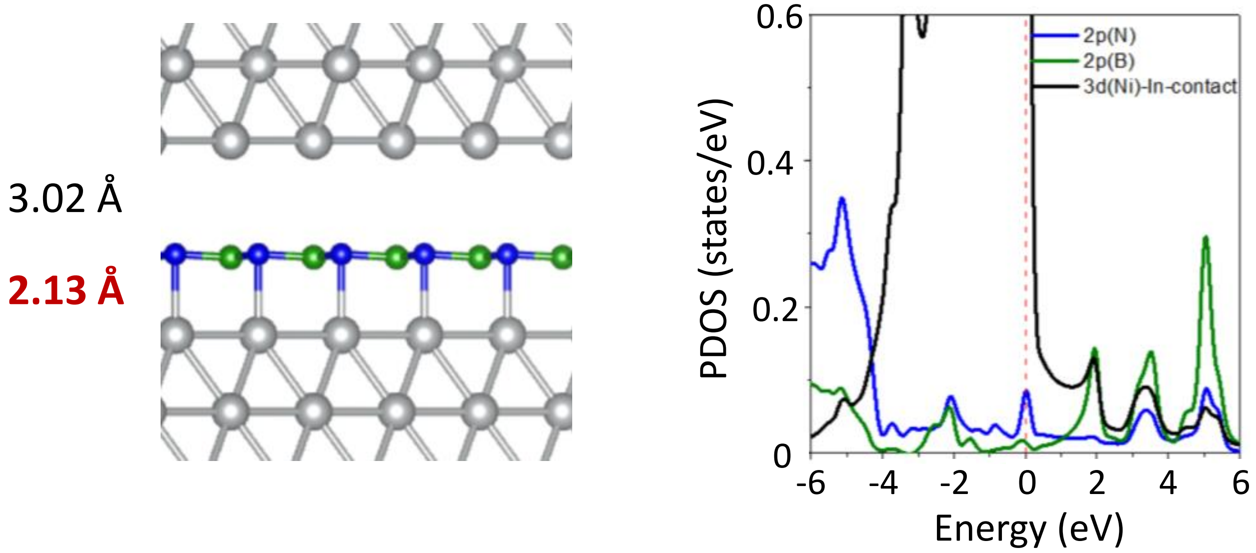
BA stacking



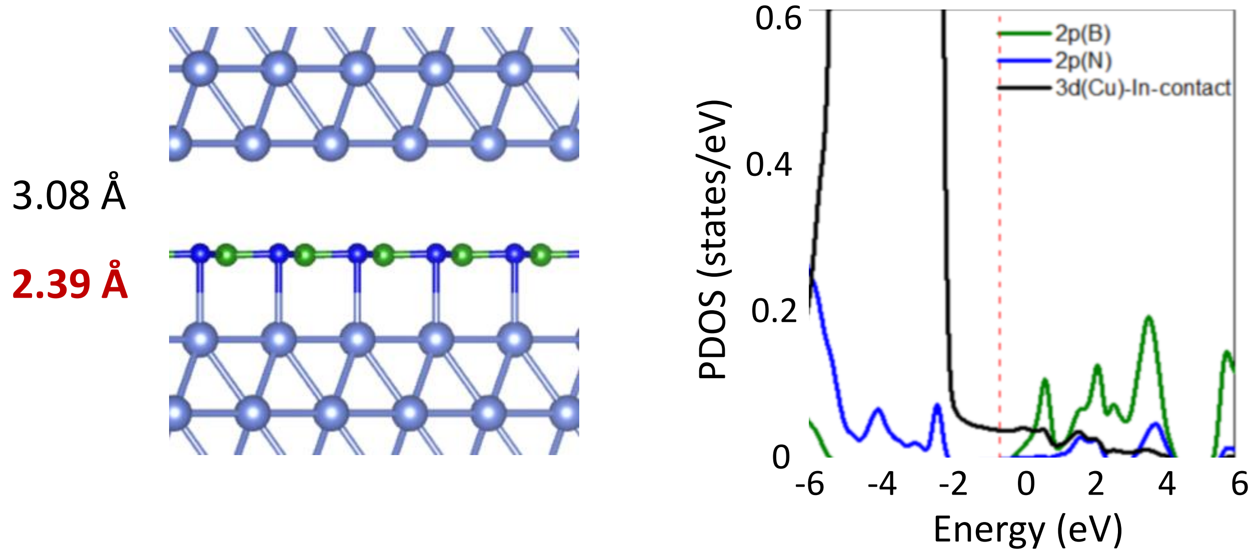
Different materials

Different electrode metal

Ni/*h*BN/Ni



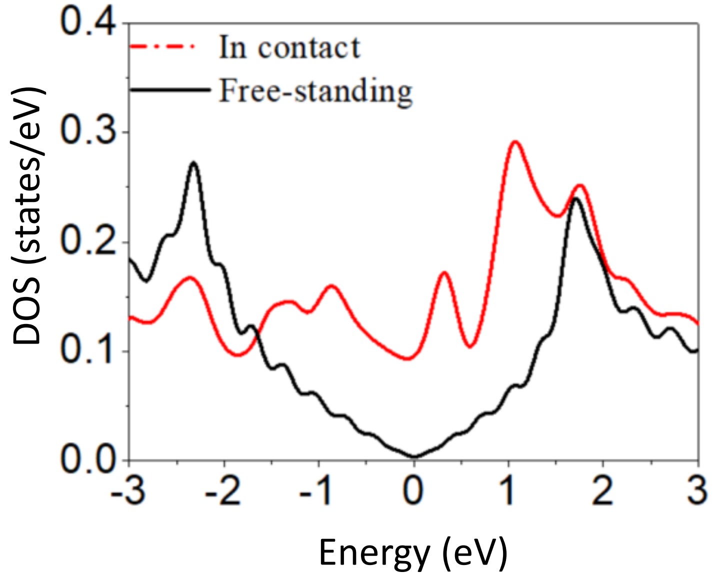
Cu/*h*BN/Cu



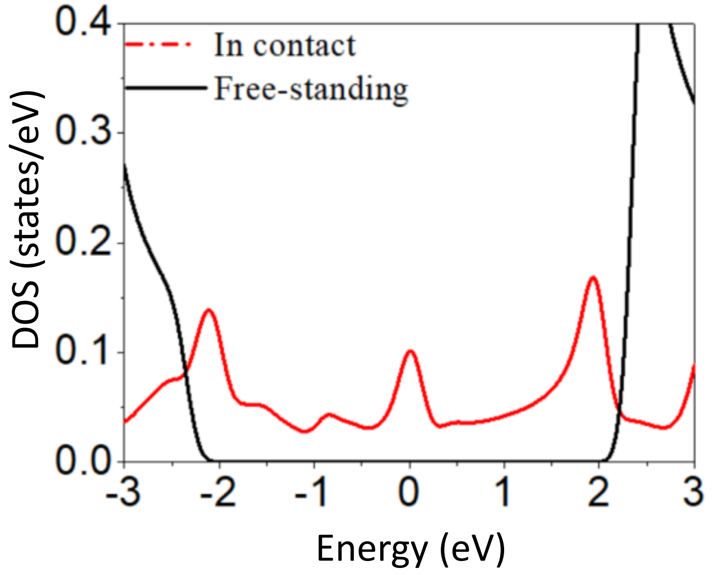
Larger charge transfer hBN/Ni than hBN/Cu

Different 2D material

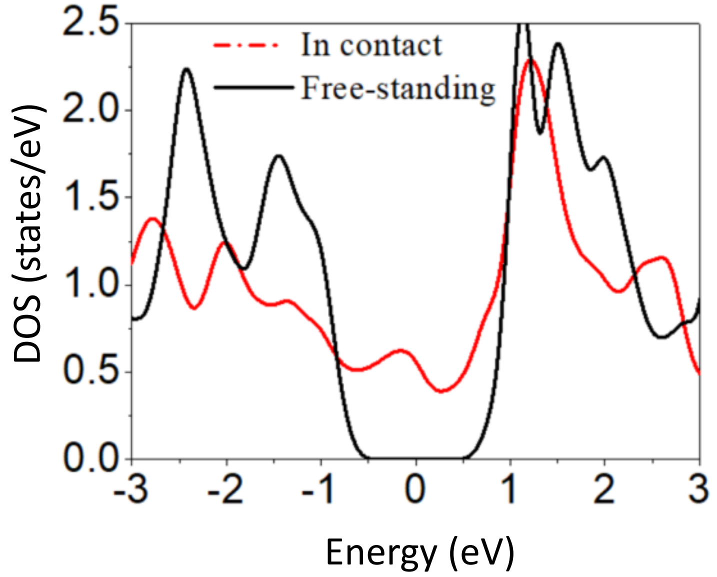
Ni/Graphene/Ni



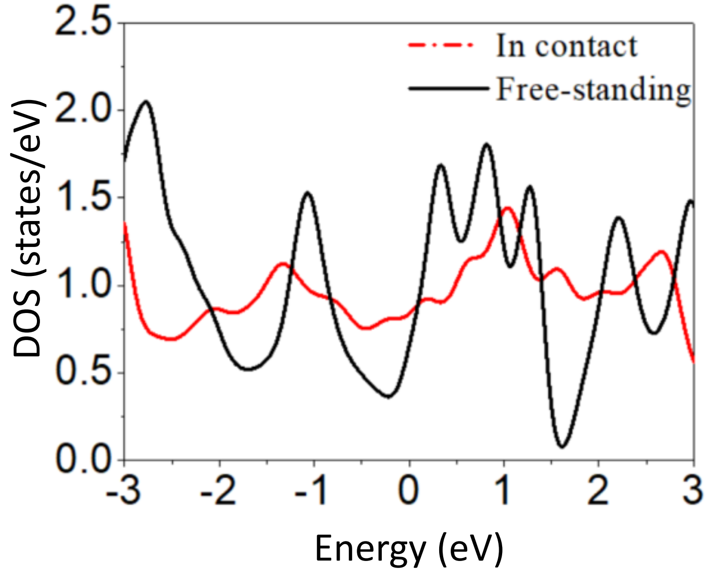
Ni/*h*BN/Ni



Ni/2H-$MoSe_2$/Ni

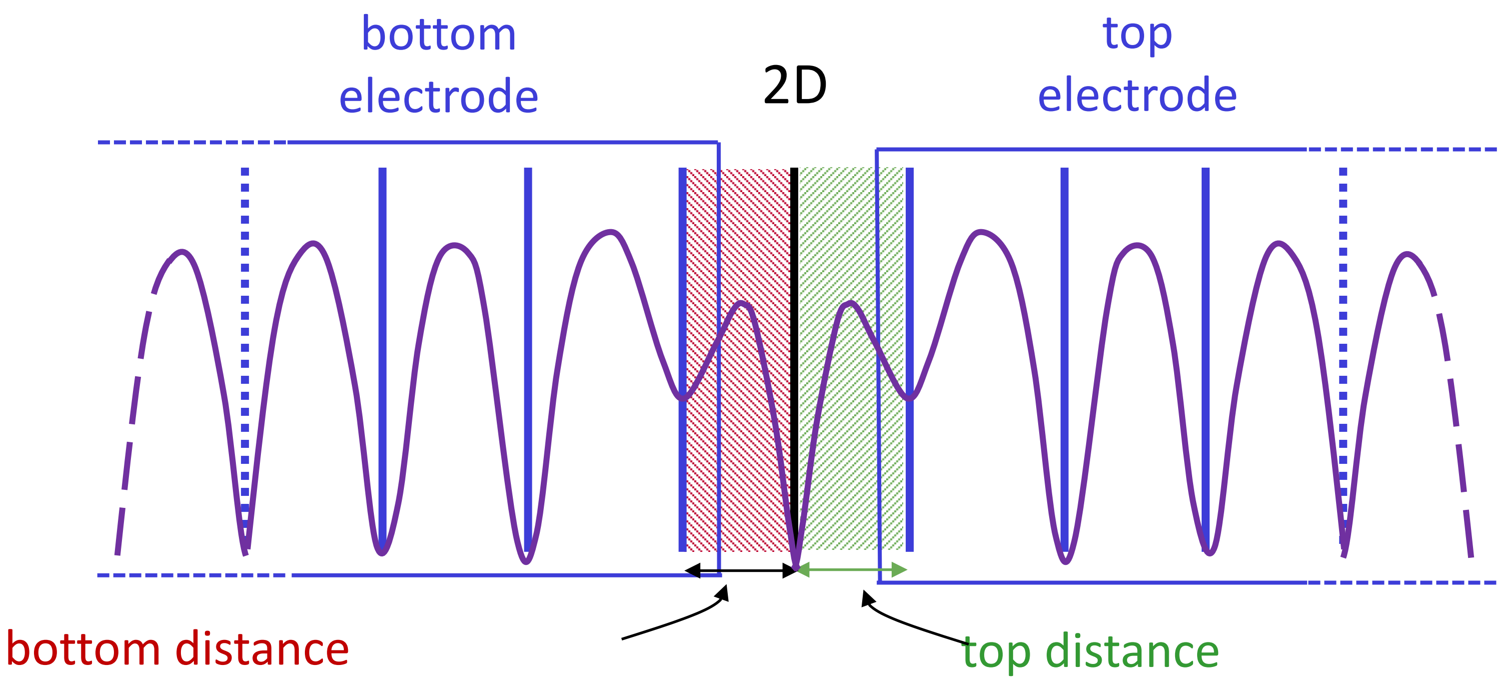


Ni/1T-$MoSe_2$/Ni

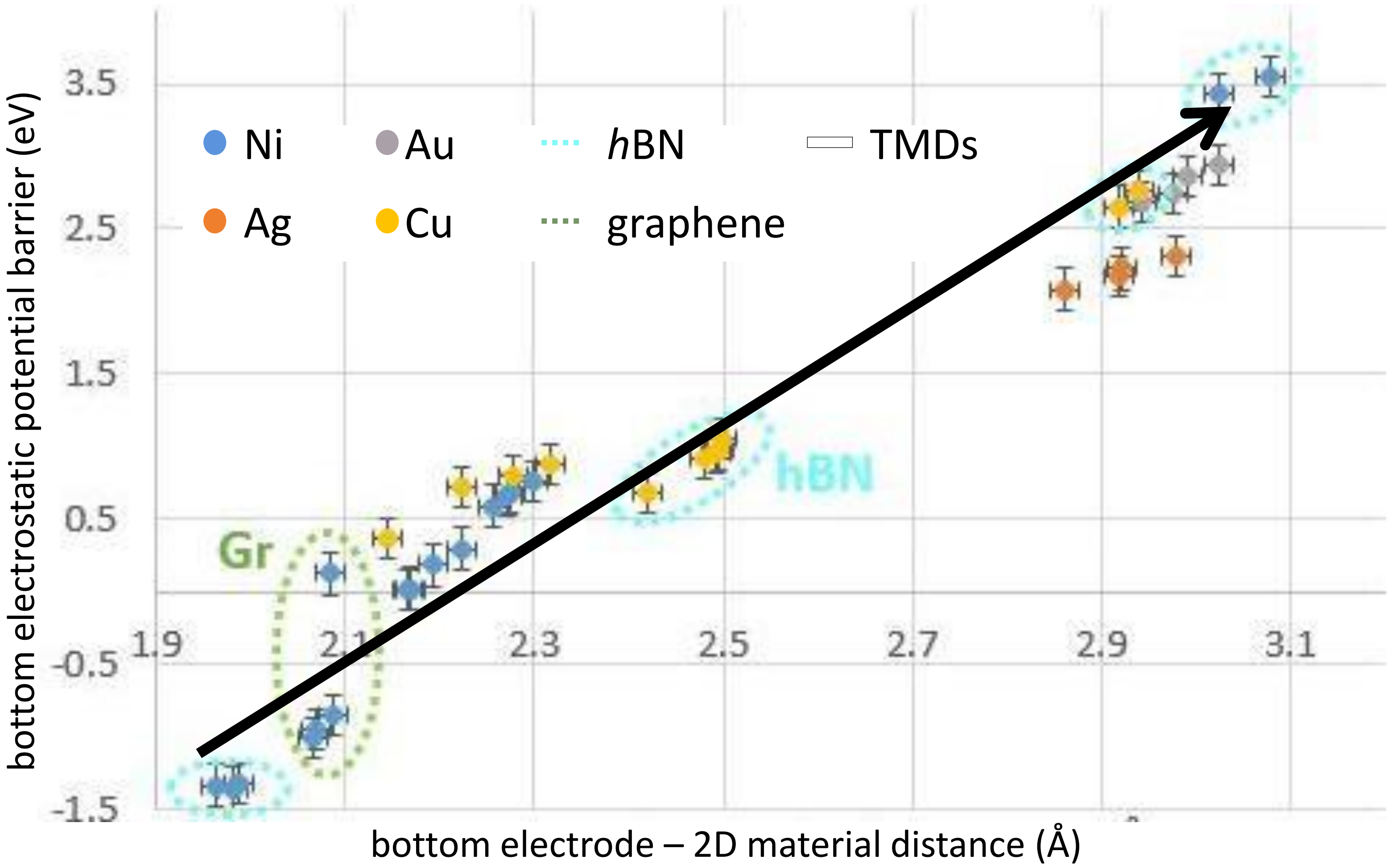


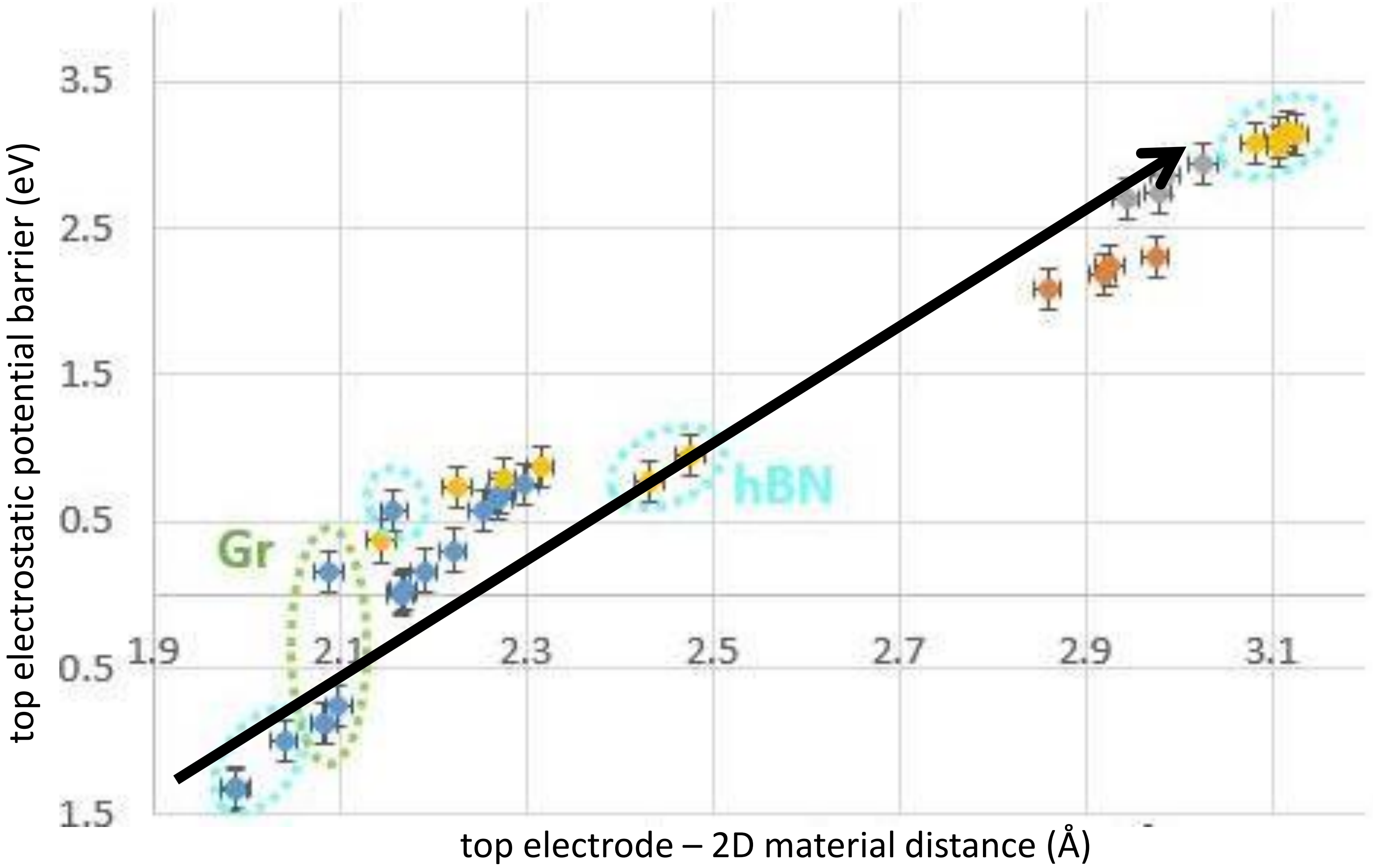
All 2D materials remain or become metallic

Tunneling barrier

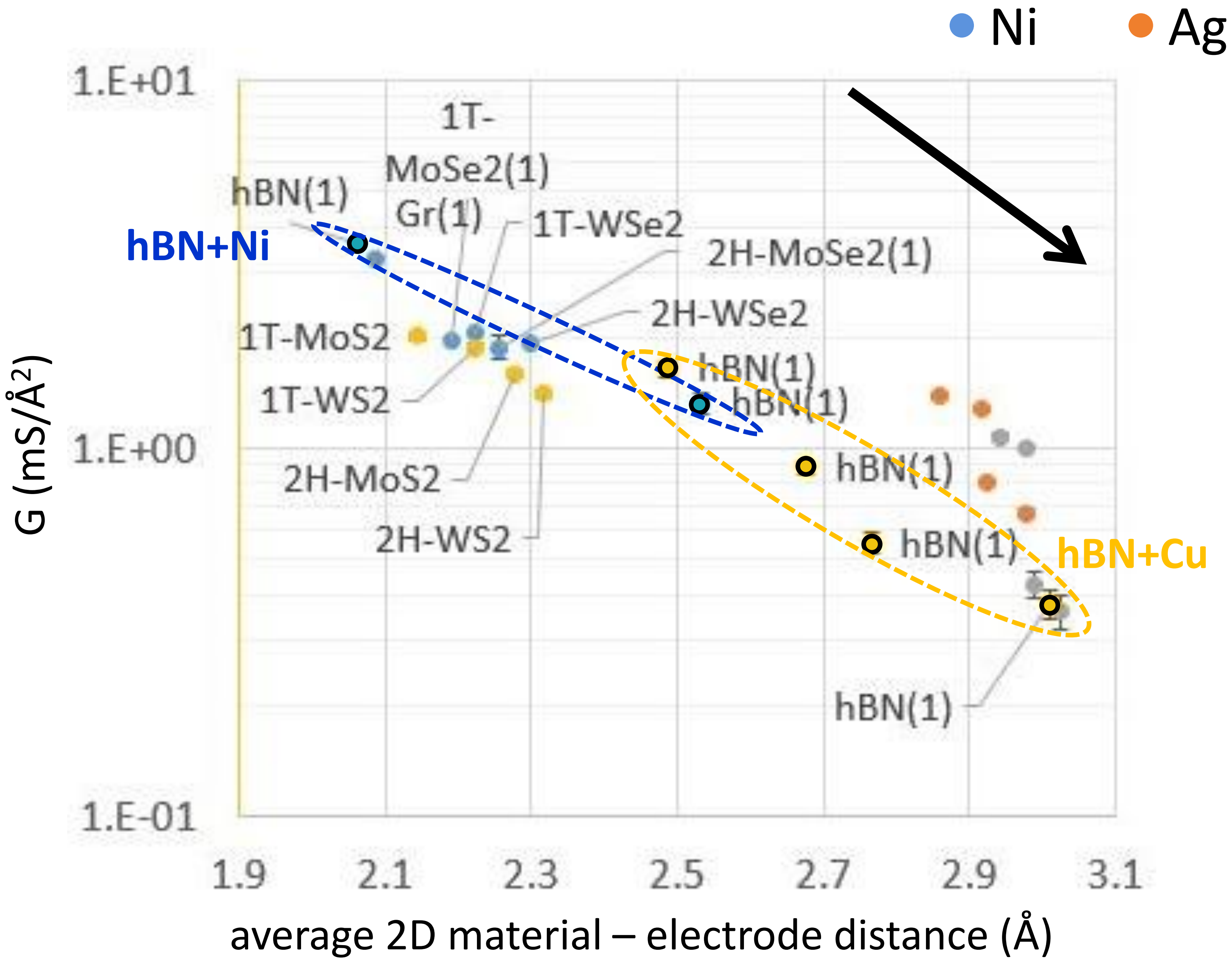


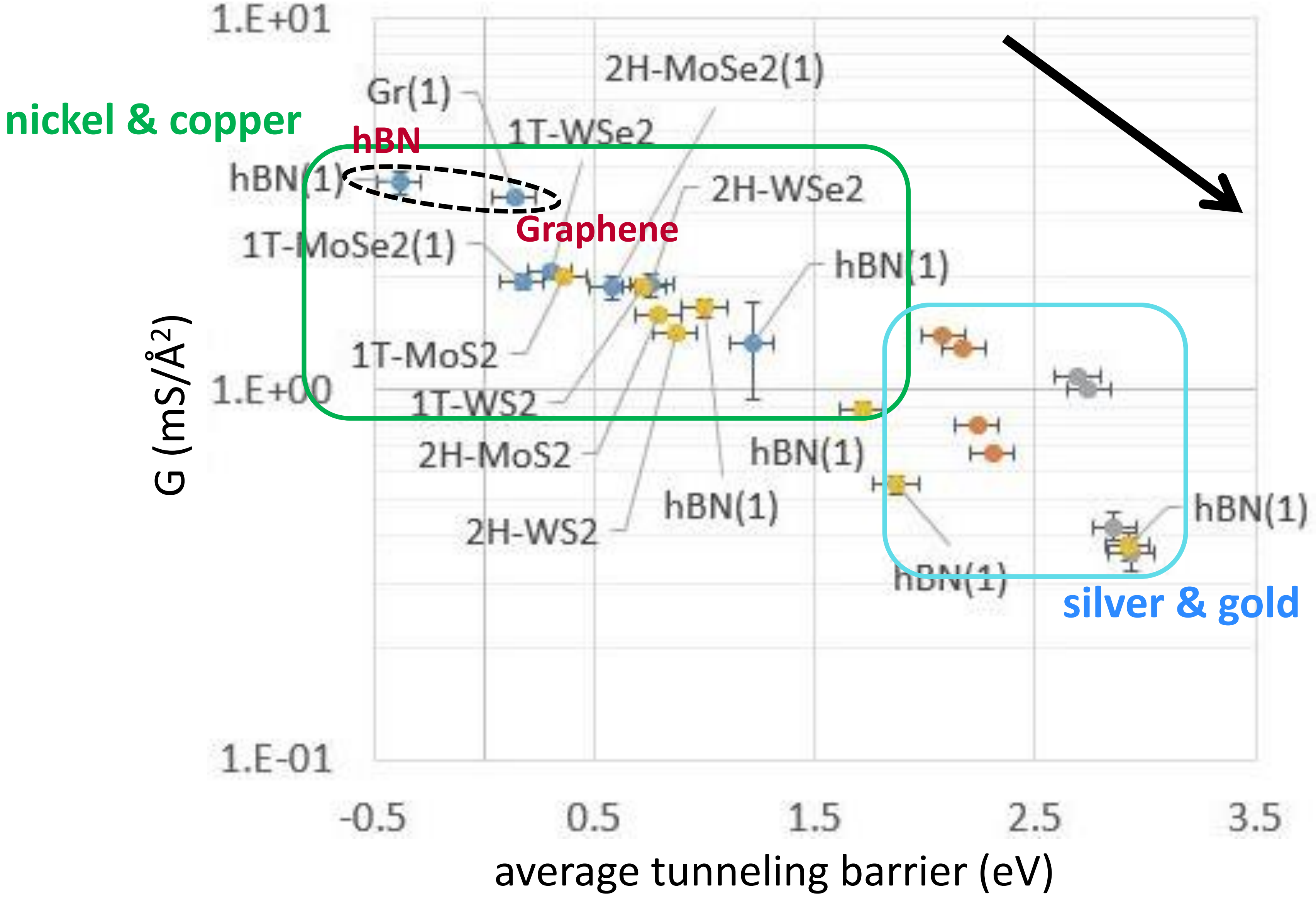
- Barrier height between -1.5 eV and 3 eV
- Higher for less-coupling bonds (hBN, Ag and Au)
- Increasing with distance between electrode and 2D material





Conductance of devices with monolayers





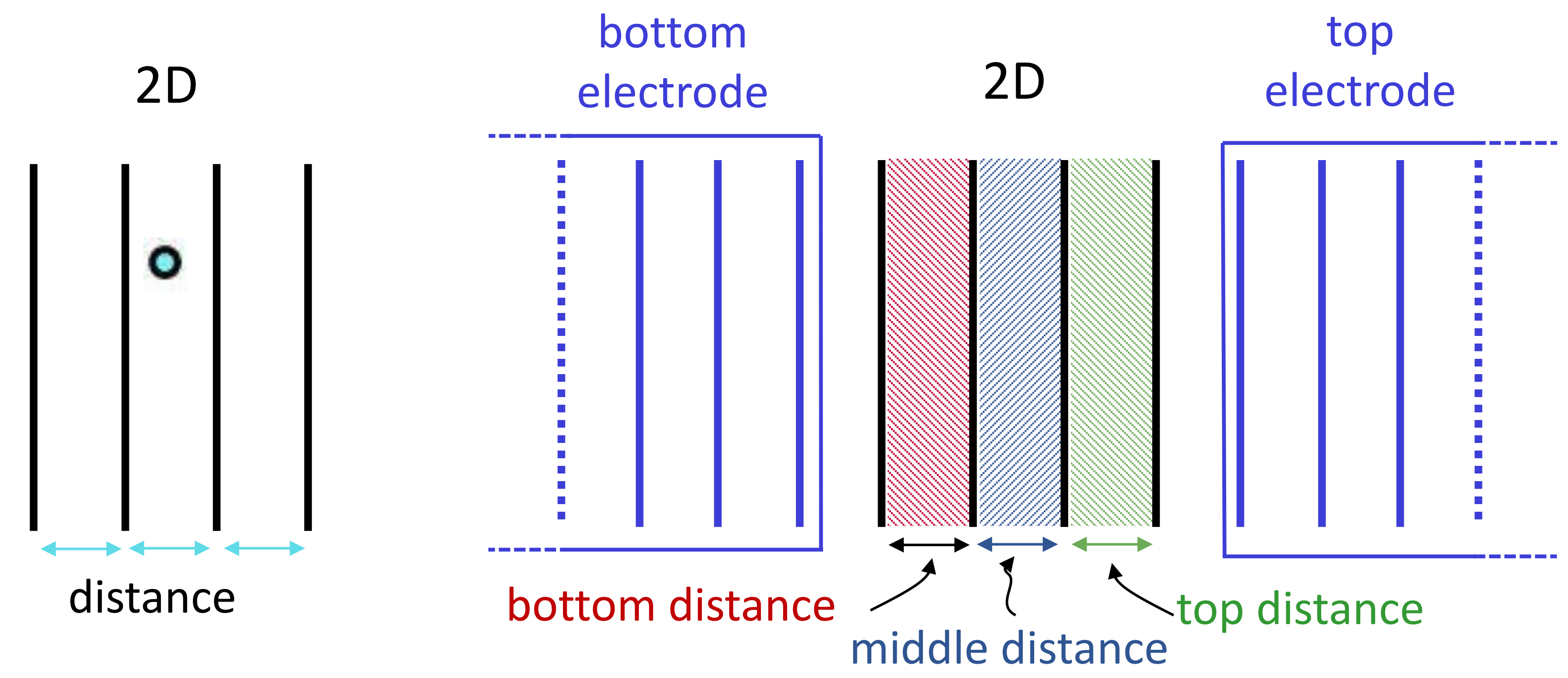
Conductance variations within one order of magnitude…

Stacking does not play an important role

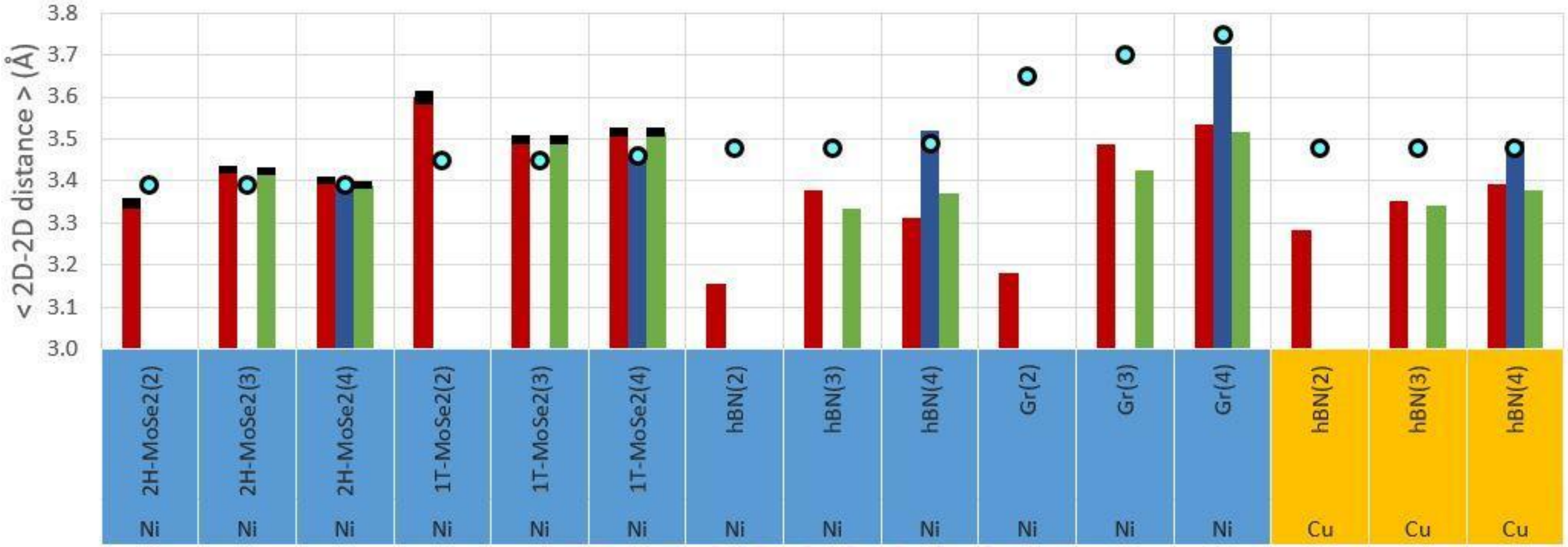
Different materials or **phases** do not play an important role (graphene *vs* hBN)

Only the **potential barrier** is important

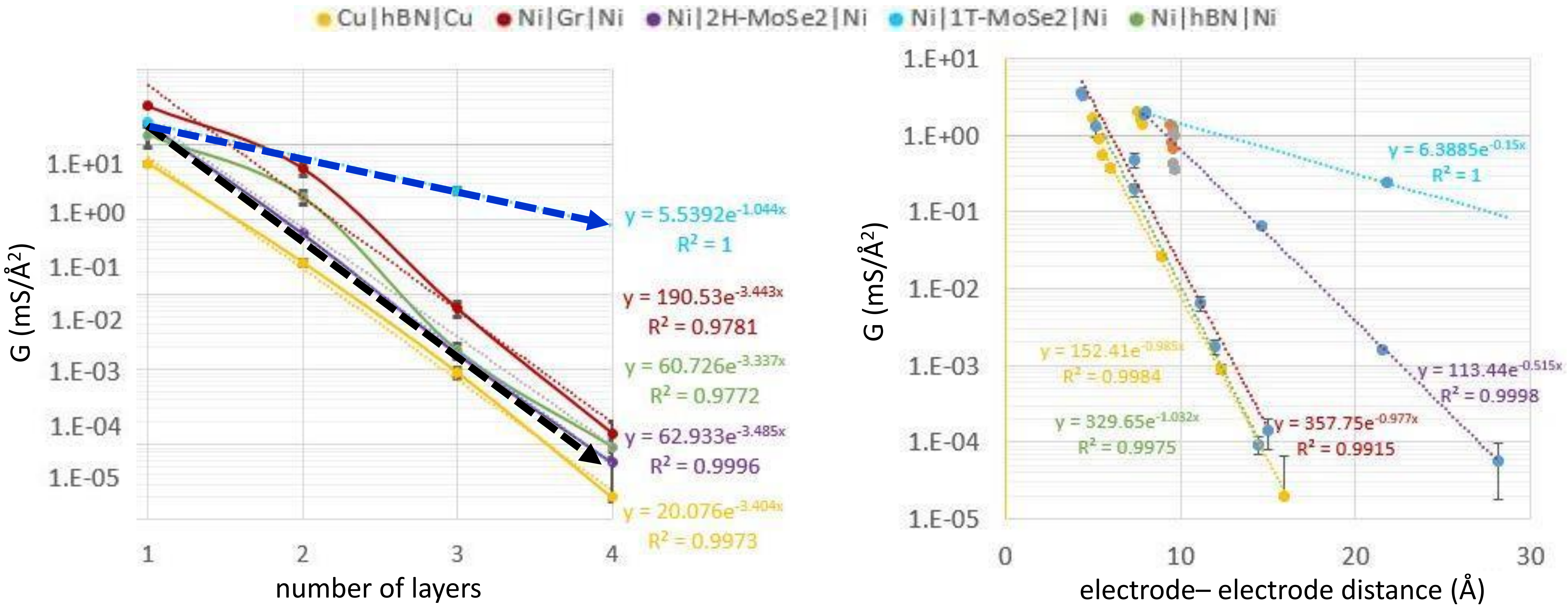
2D material - 2D material distance for multilayers



The **middle layers** behave as in the **isolated 2D materials**, while the **external layers** form **strong bonds** with the electrodes, thus decreasing the junction distance.



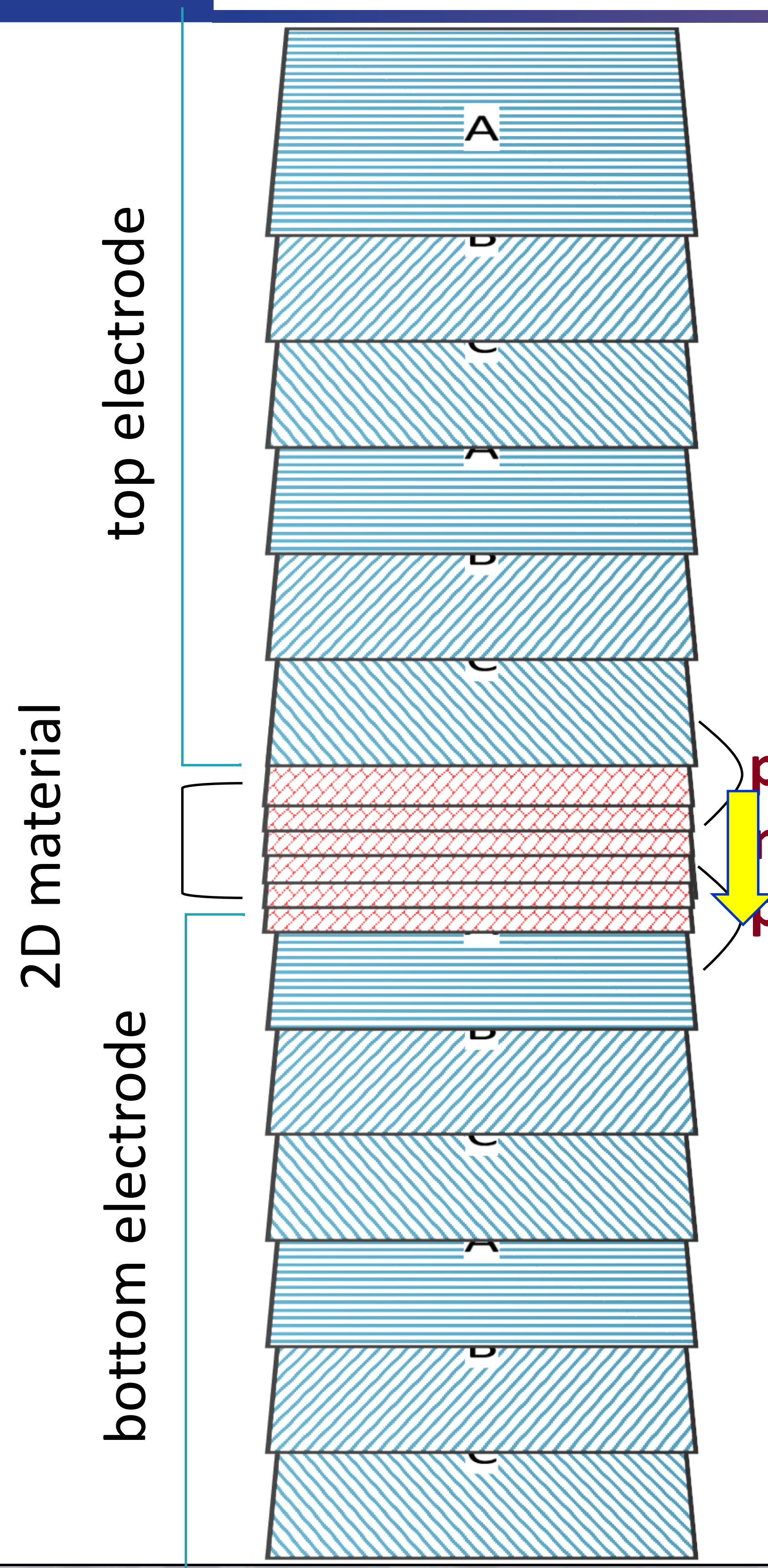
Conductance in multilayers



The **contact layers are strongly coupled with electrodes** and determine the initial conductance.

Then, the **conductance decreases exponentially**: **interlayer tunneling**

…in summary



Change the relative in-plane position of the electrodes to the 2D material

Change the electrode material

Change the 2D material phase (1T and 2H)

Change the 2D material

Conductance changes by less than an order of magnitude

The potential barrier generated by clean monolayers is not high enough to have a HRS, changing the phase of the 2D material does not have a strong impact

Change the number of 2D layers

Conductance changes much more and exponentially

Experimental conductance in the high resistance state

Experiments : **10^{-6} - 10^{-15} µS/Å² range** with **no clear dependence neither on the channel thickness nor 2D material**, but description compatible with **tunnelling for the high resistance state**, **large variability**.

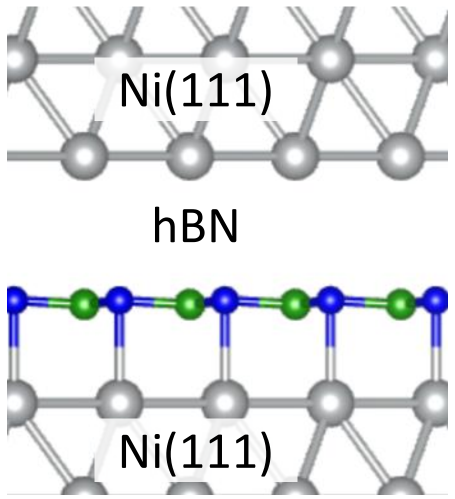
2D material	Electrodes	G (µS/Å²)	Reference
hBN (1L)	Ag || Ag	1.00E-15	Yang, ACS Nano 2024
hBN (1L)	Au | Cr || Cr | Au	1.00E-10	Wu, Adv. Mat. 2019
hBN (1L)	Ni || Au	1.90E-09	Li, APL 2022
hBN (3nm)	Au | Ti || Au	8.33E-14	Lin, APL 2019
hBN (6nm)	Au || Ti	4.00E-13	Zhuang, Adv. El. Mat. 2020
hBN (10nm)	Au || Au	1.11E-11	Pazos, Nat. Elect. 2024
hBN (9nm)	Au || Au	1.00E-06	Chen, Nanoscale 2023
hBN (5-7L)	Cu || Ti	5.00E-10	Pan, Adv. Funct. Mat. 2017
hBN (5-7L)	Au | Gr || Gr | Au	2.00E-12	Pan, Adv. Funct. Mat. 2017
MoS_2 (1L)	Au | Cr || Cr | Au	2.00E-07	Kim, Nat. Comm. 2018
MoS_2 (2.6nm)	Si | SiO_x || Al	2.00E-13	Li, ACS Appl. Elec. Mat. 2024
MoS_2 (2L)	Au | Cr || Cu	1.39E-05	Xu, Nano Lett. 2019
MoS_2 - PVA (200nm)	Pt || Ag	3.29E-10	Liu, J. Phys. D 2022

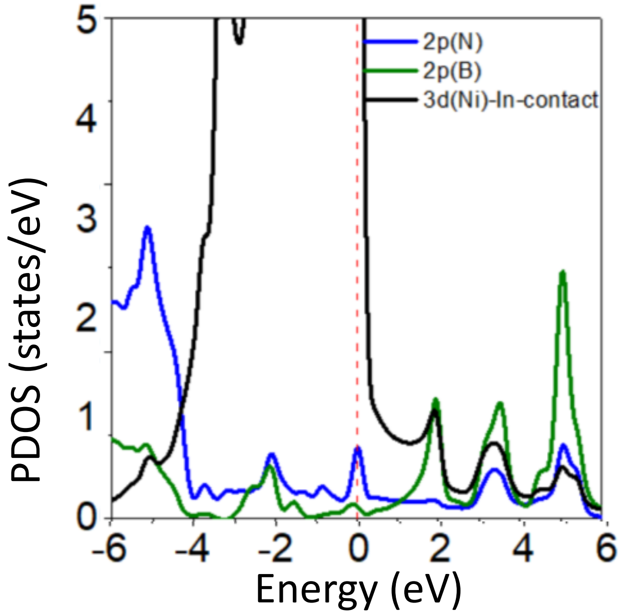
2D material	Electrodes	G (µS/Å²)	Reference
MoS_2 (1.92nm)	Au | Cr || Cr | Au	1.00E-10	Gu, Adv. Elec. Mat. 2022
$MoS_{2-x}O_x$ (30-40nm)	Gr || Gr	7.94E-06	Wang, Nat. Elect. 2018
MoS_2 (3-5L)	Au | Cr || Cr | Au	4.00E-08	Wu, RSC Adv. 2020
MoS_2 (1.4nm)	Au | Cr || Cr | Au	1.00E-06	Lee, ACS Nano 2024
MoS_2 (10nm)	Au || Ti | Au	4.00E-12	Krishnaprasad, ACS Nano 2022
MoS_2 (20nm)	Au || Au	5.56E-07	Yan, Adv. Elect. Mat. 2024
MoS_2 (300nm) MoO_x (3nm)	Ag || Ag	1.51E-13	Bessonov, Nat. Mat. 2015
MoS_2 (5nm)	Au || Au	1.33E-06	Zhuang, Mat. Today Nano 2023
MoS_2 (0.75nm)	Au || Au	2.50E-14	Bhattacharjee, ACS App. Mate. & Int.2020
MoS_2 (2185nm)	Ag || Ag	2.50E-14	Xia, Nat. Comm 2024
MoS_2 (7-20nm)	Au || Ni | Au	3.13E-08	Song, J. of All. and Comp. 2021
MoS_2 (1L)	Au || Cr | Au	1.00E-07	Ge, Nano Lett. 2018

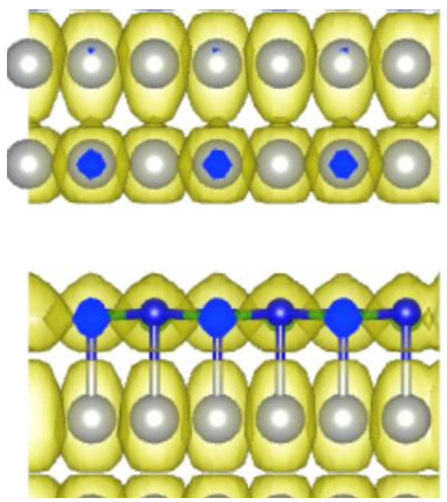
Simulations : **1 µS/Å² range** for monolayers and about **one order of magnitude lost per added 2D layer** and **exponential dependence on the potential barrier widths**.

Origin of the discrepancy: residues of polymers, oxides, multi-layered regions, roughness

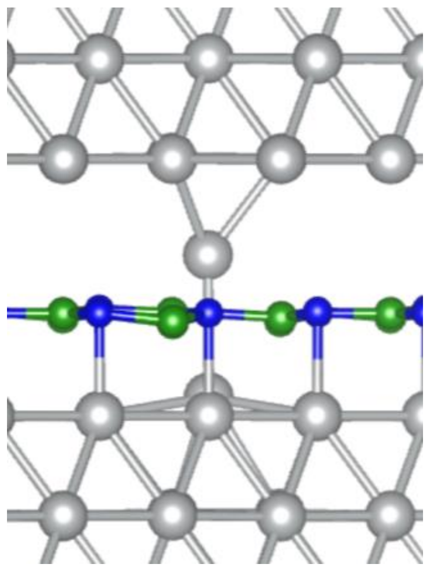
Ni(111)/hBN/Ni(111): Metal-ion substitution

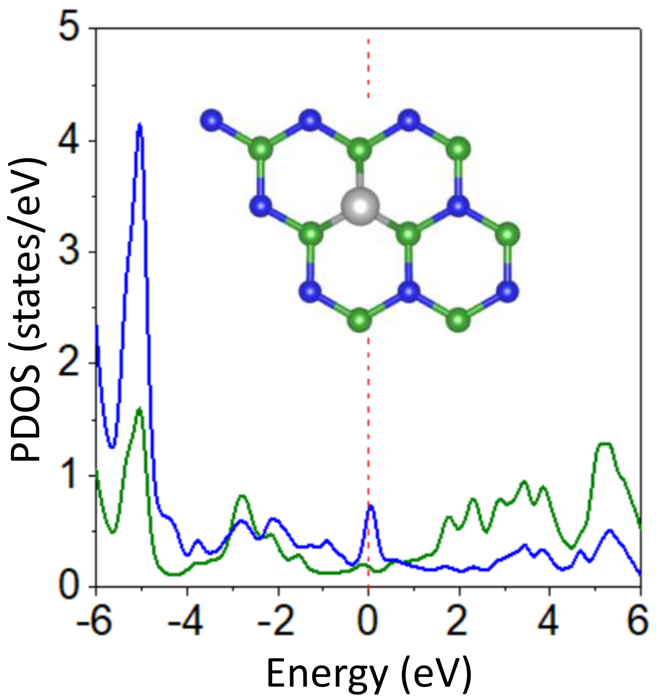


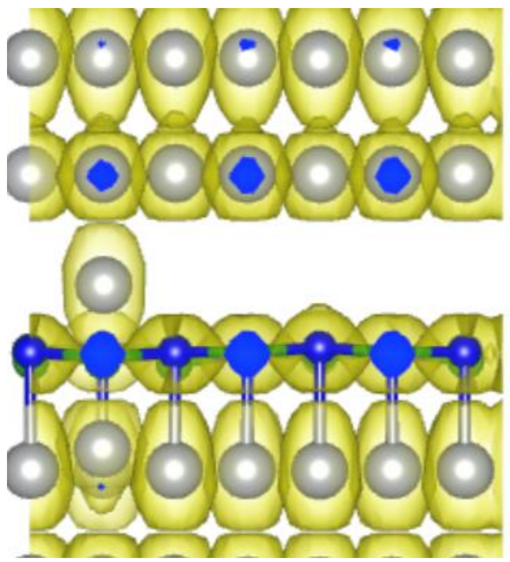




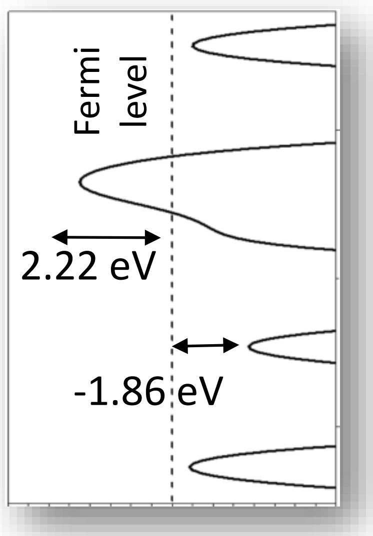
N substitution





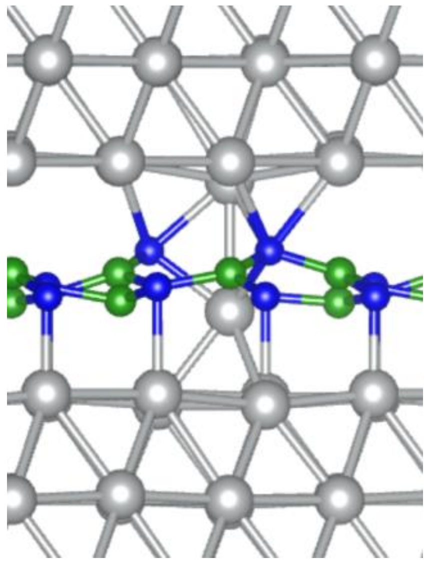


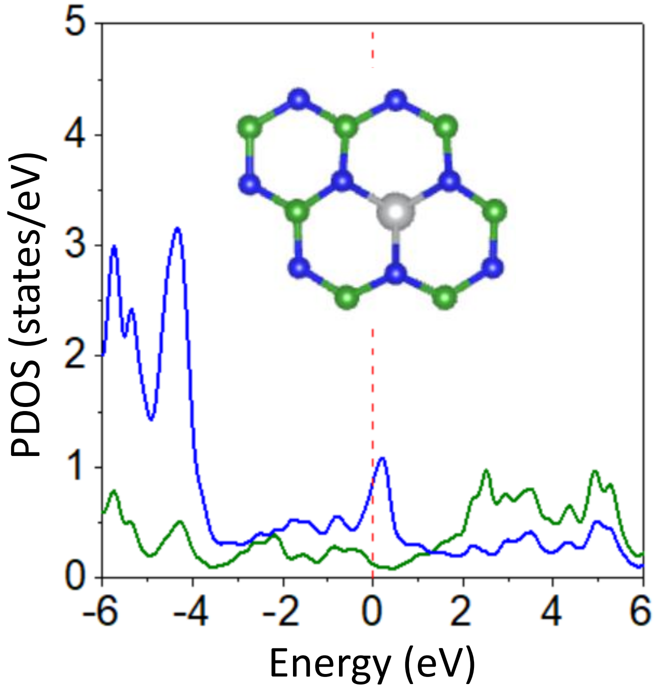
Charge distribution connecting electrodes via the Ni atom

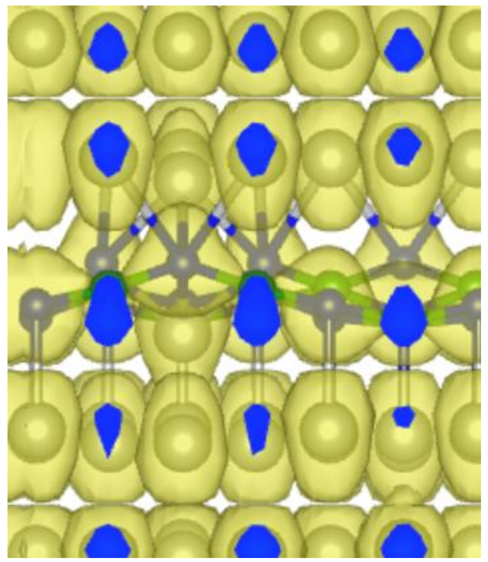


Average potential

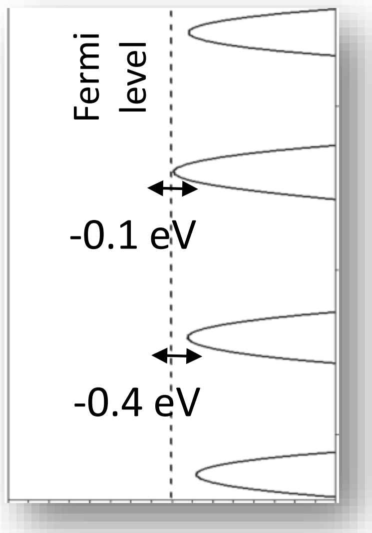
B substitution







Higher states density in hBN

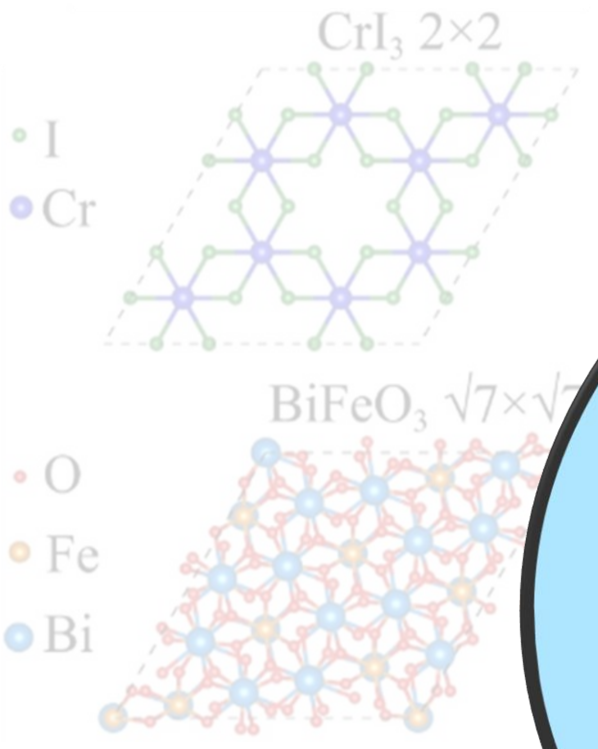


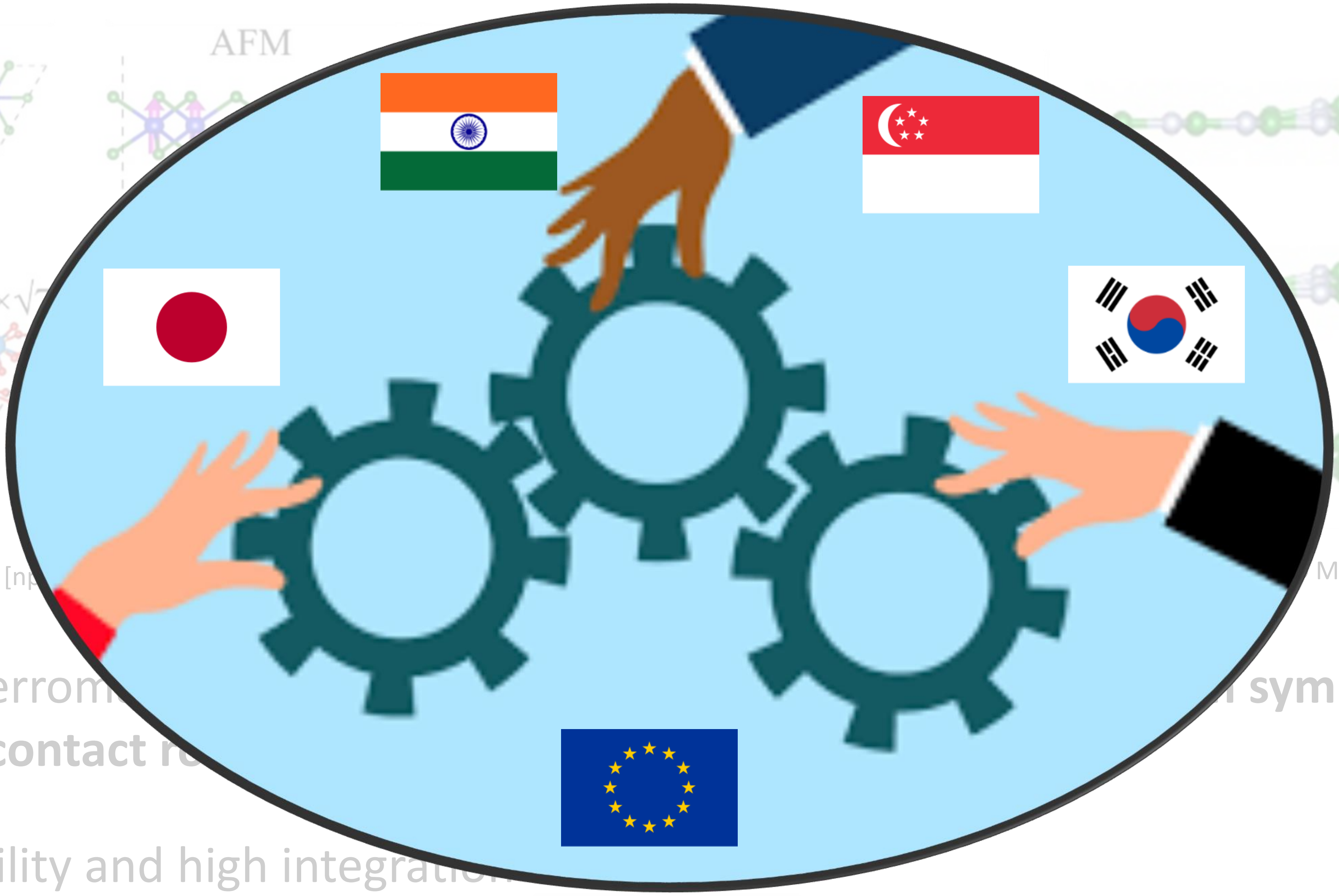
Average potential

Perspectives

Extension of our approach to **all-2D-material memories** based on **ferroelectricity**, **ferromagnetism** and their combination in **multiferroic** devices.

ferromagnetism





[np

Mater. **11**, 035019 (2024)]

Study of ferroelectric and ferrom … **symmetry** of 2D materials (Janus), **number of layers**, **contact re** …

Only 2D materials for flexibility and high integratio…

Multilevel memories for applications in neuromorphic computing

Acknowledgement and some references


G. Bigeard


Z. Kerrami
UM6P - Morocco


F. Triozon
Leti/CEA

G. Bigeard, Z. Kerrami, F. Triozon and A. Cresti, *Nanotechnology* **36**, 285201(2025)

Gaëlle Bigeard, “Quantum simulations of resistive switching in 2D material based stacks”, PhD manuscript (2025)

“Beyond-CMOS: State of the Art and Trends”, editor Alessandro Cresti, © ISTE Ltd 2023

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