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INSTITUTE FOR NANOTECHNOLOGY

UNIVERSITY OF TWENTE.

Interactions and charge transfer in heterostructures of 2D materials

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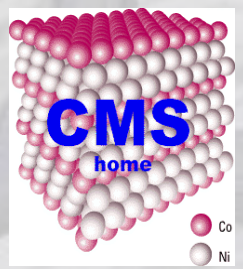
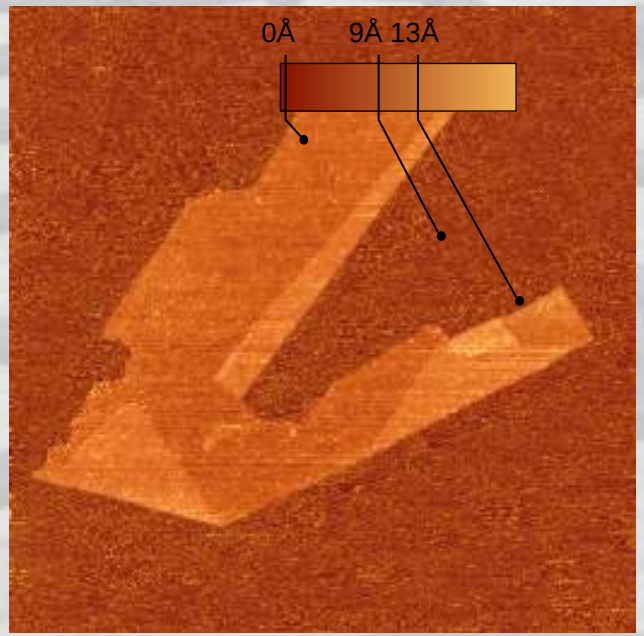


FOM

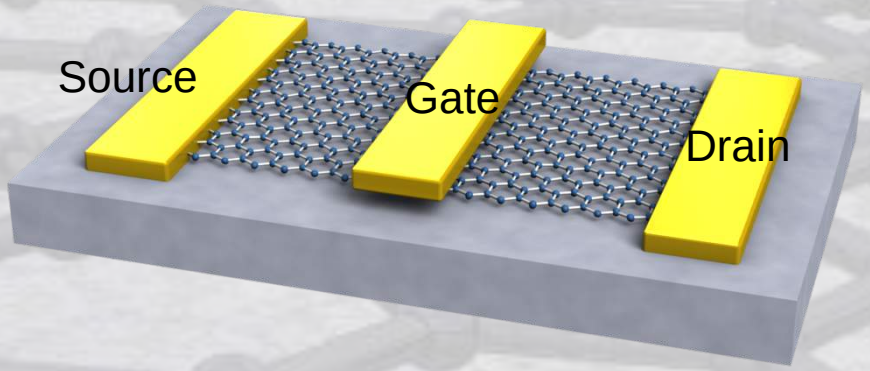
The rise of 2D materials

graphene



Novoselov, Geim, et al.,
Science **306**, 666 (2004)

Field Effect Transistor (FET)



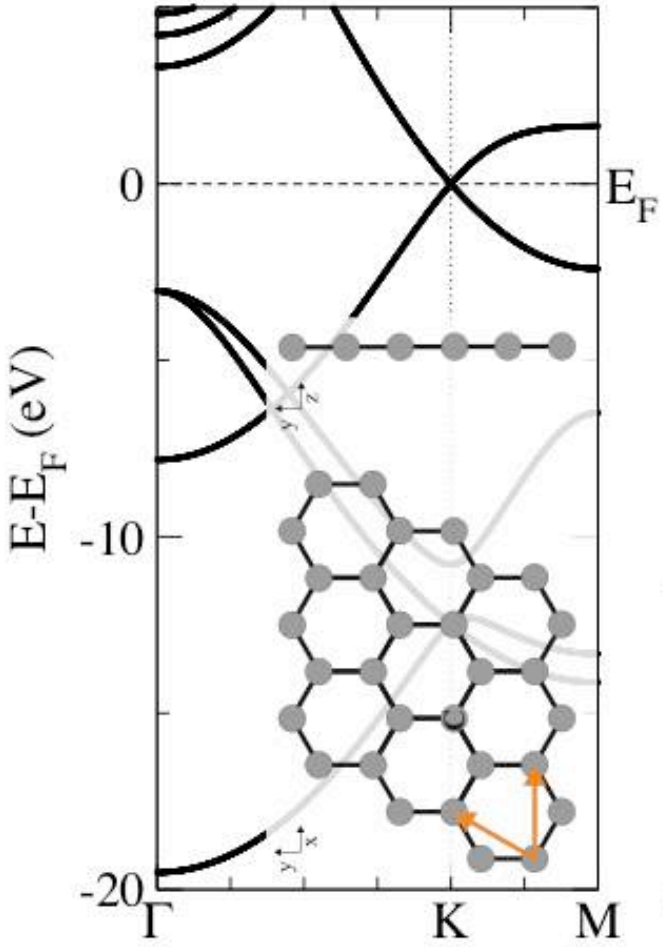
- very high carrier mobility $\mu \approx 10^5\ \mathrm{cm}^2/(\mathrm{Vs})$
- quantum Hall effect at room temperature
- "relativistic" effects (Klein tunneling)
- ... more and more ...

physics Nobel prize 2010: Andre Geim & Konstantin Novoselov

"for groundbreaking experiments regarding the two-dimensional material graphene"

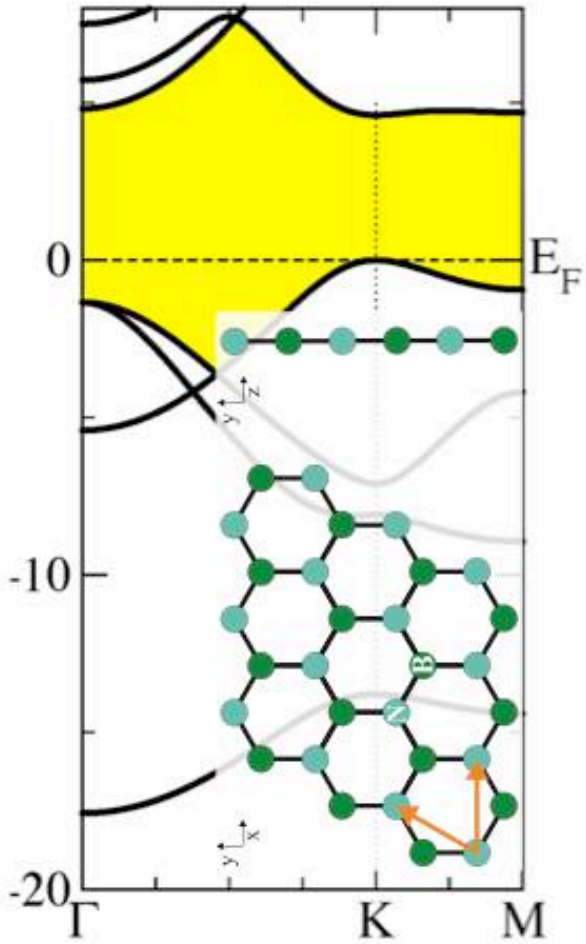
2D materials: expanding the family circle

graphene



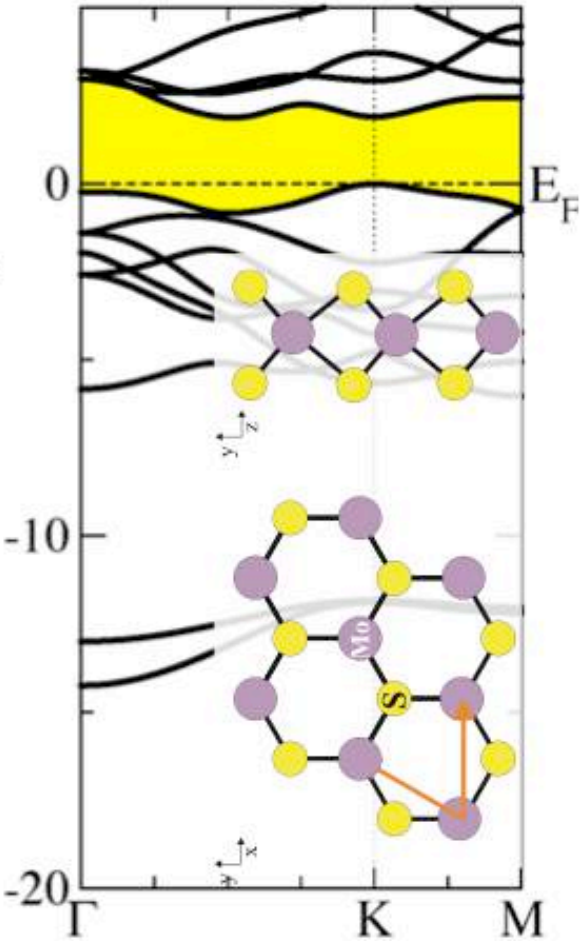
(semi)metal

boron nitride



insulator

MoS_2



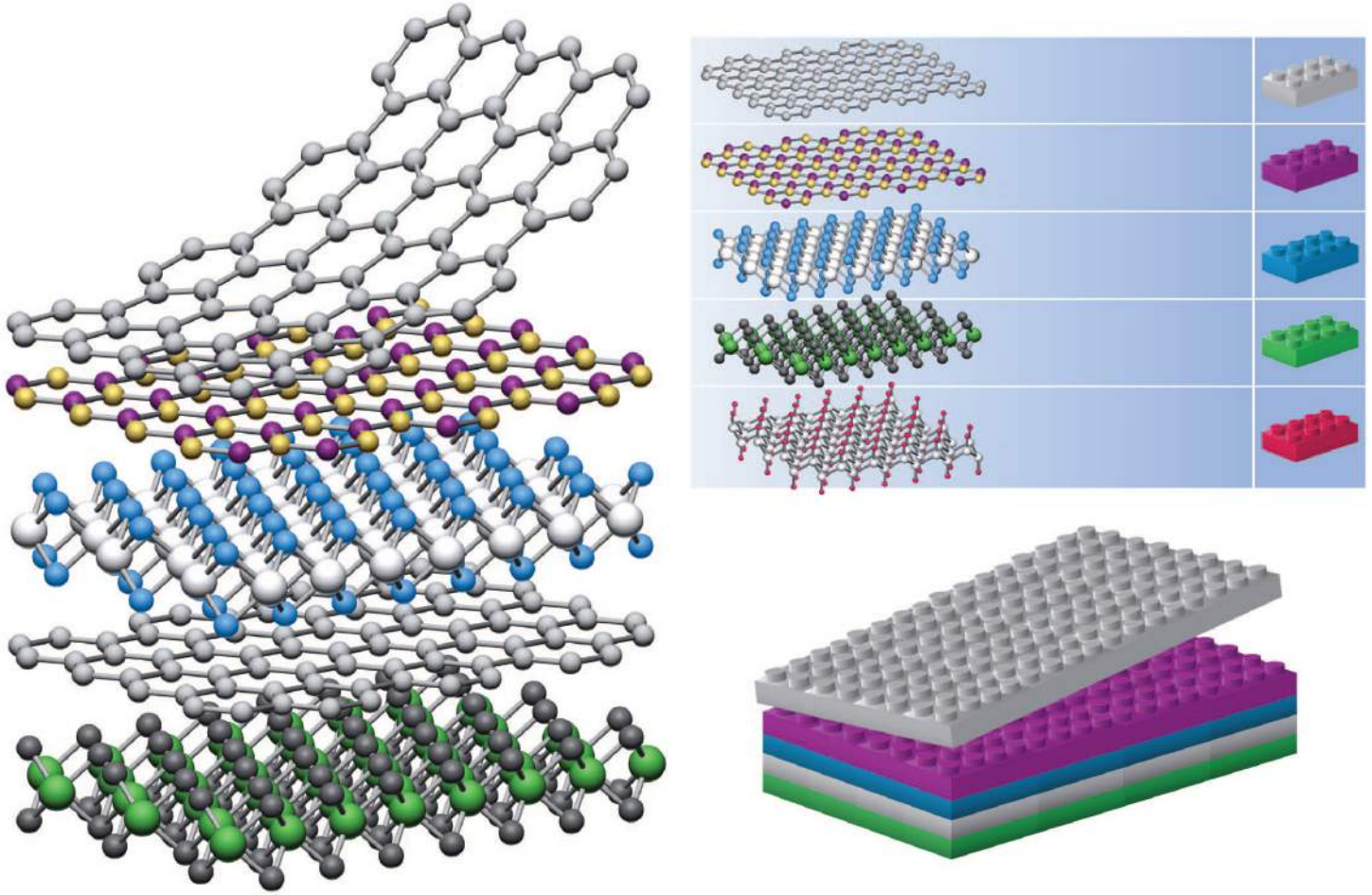
semiconductor

..... and many others .....

van der Waals heterostructures of 2D materials

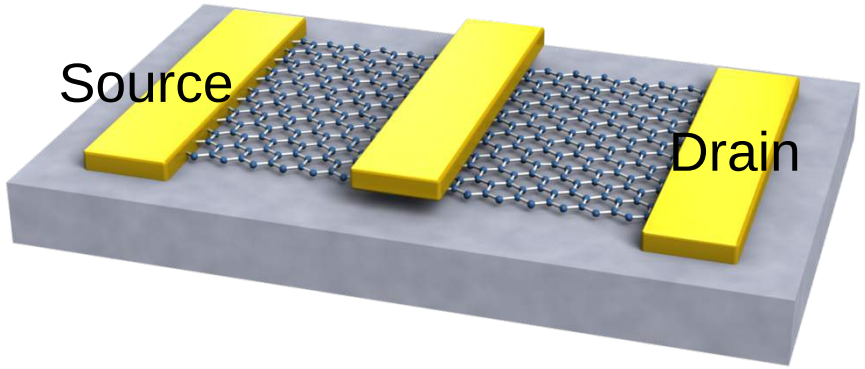
combine functionalities of different 2D materials

Geim & Grigorieva, Nature **499,** 419 (2013)



Doping of Graphene

Field Effect Transistor (FET)



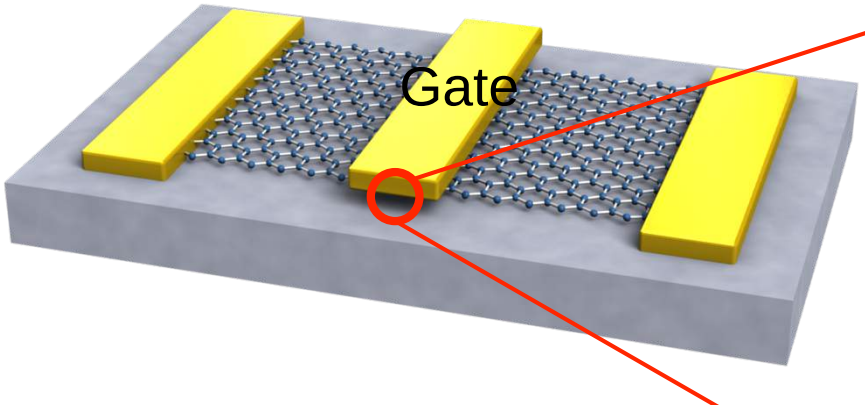
metal contact doping:

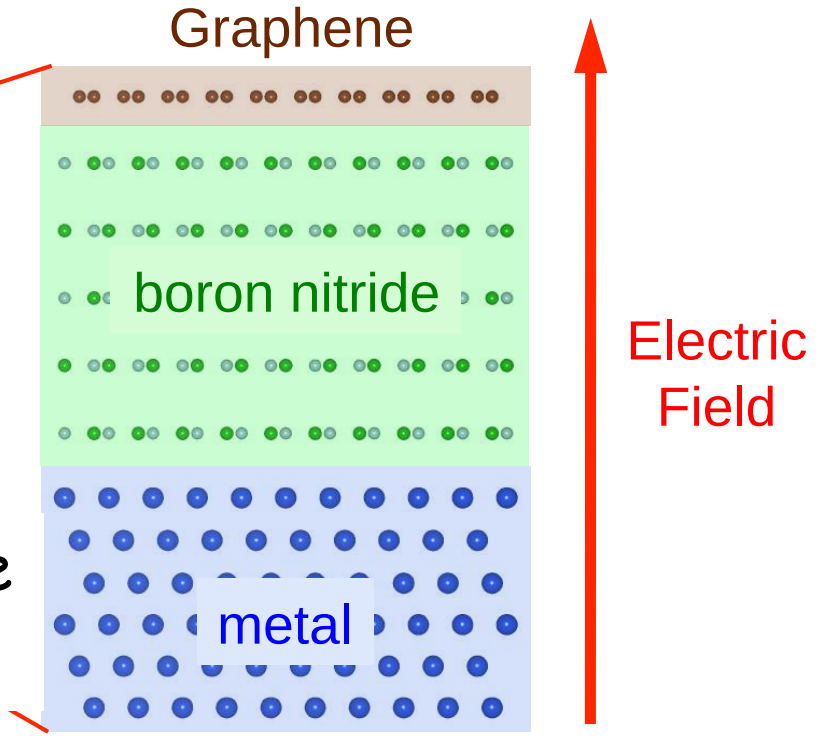
Giovannetti et al, PRL **101,** 026803 (2008)

Khomyakov et al, PRB **79,** 195425 (2009); PRB **82,** 115437 (2010)

Field effect doping of Graphene

Field Effect Transistor (FET)





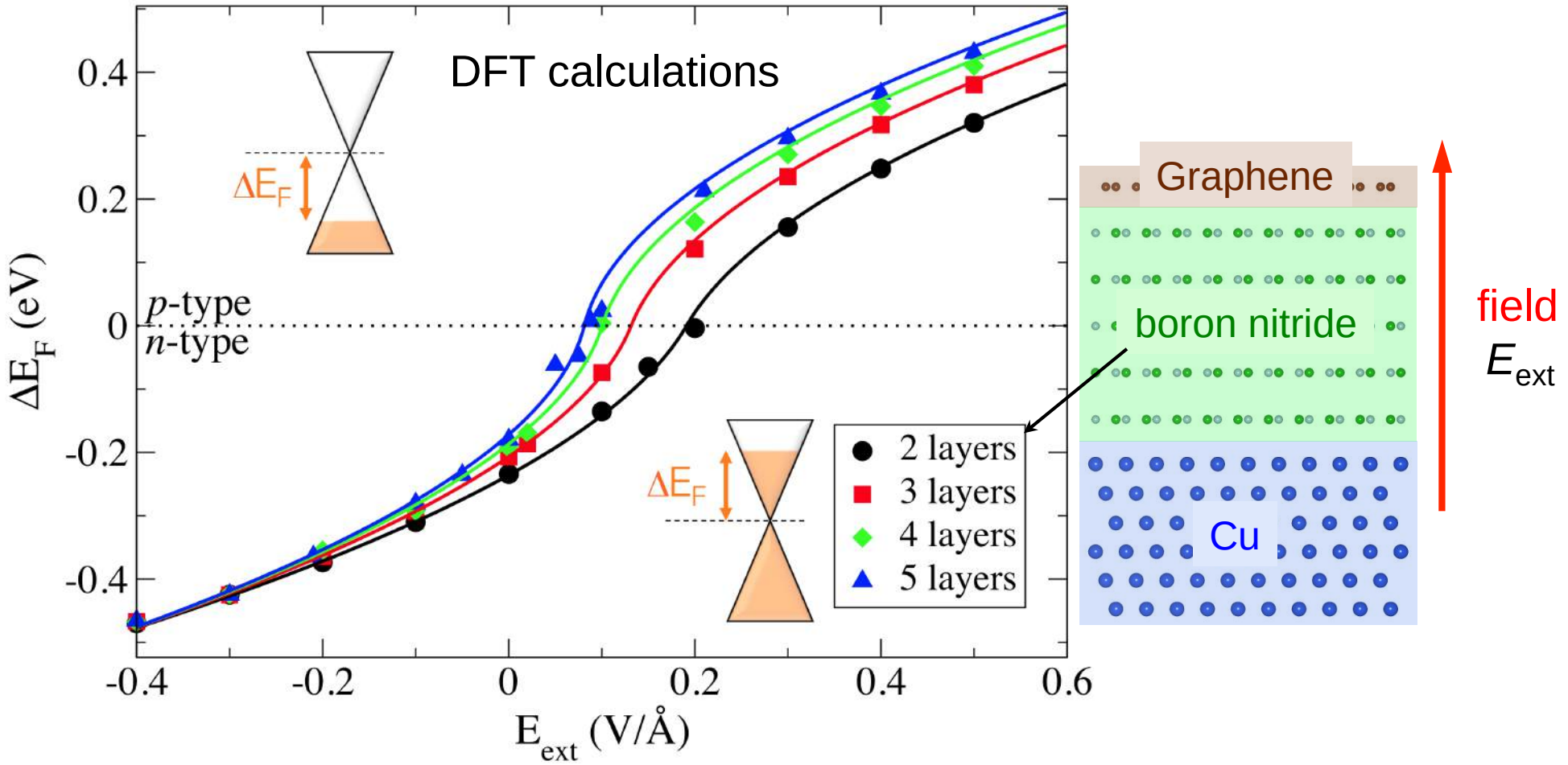
what is the doping level of graphene
as function of gate electric field ?

model field effect doping in DFT calculations
on metal | dielectric | Graphene slab in electric field

(dielectric = boron nitride)

Field effect doping in Cu(111) | h-BN | Graphene

doping level vs electric field for different BN thicknesses

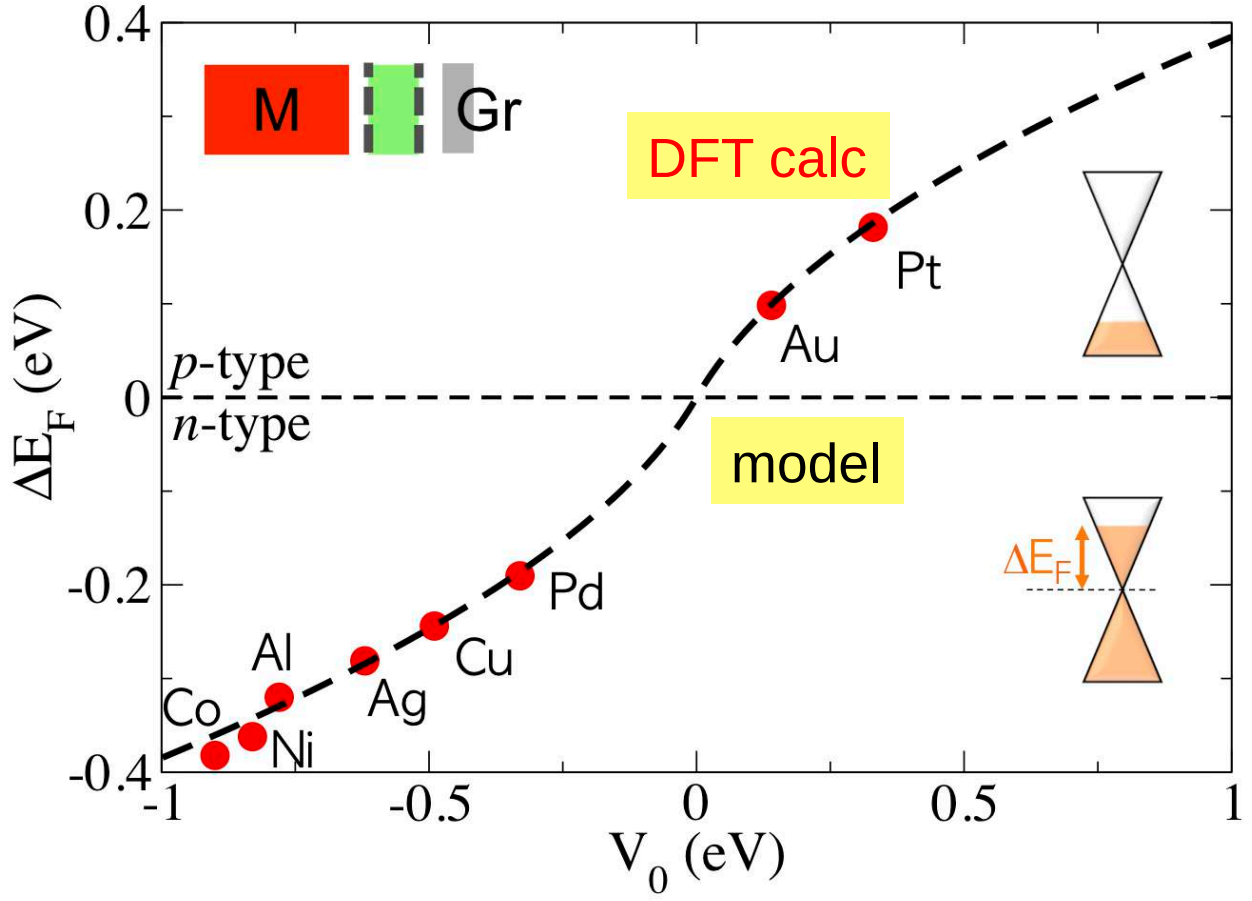


curves: electrostatic model

Bokdam et al, PRB **87**, 075414 (2013)

Zero field doping in metal | h-BN | Graphene

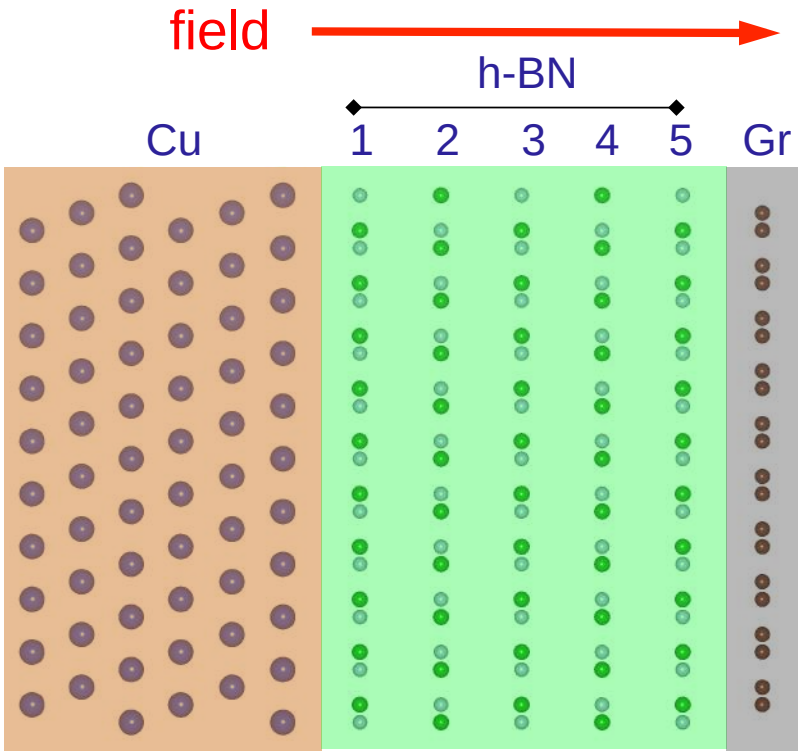
doping of graphene as function of metal substrate



work function $W_{Cu,Pd,Co,Ni} > W_{Gr} \approx 4.5$ eV

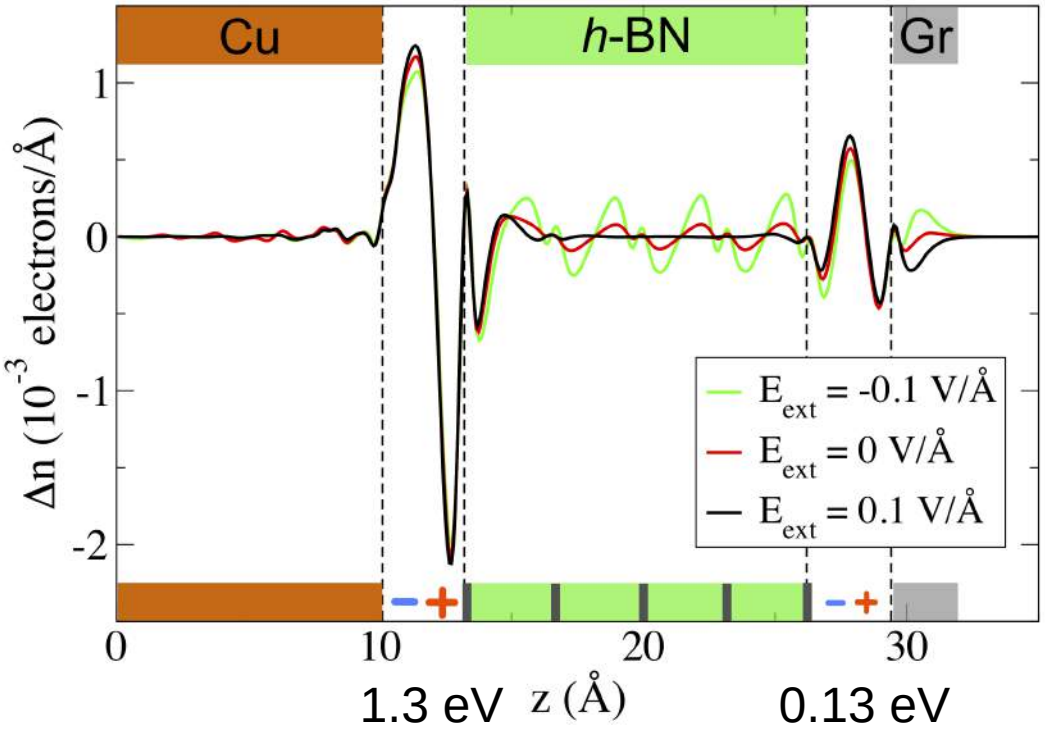
but n-type doped graphene !!

Charge distribution Cu | h-BN | Graphene



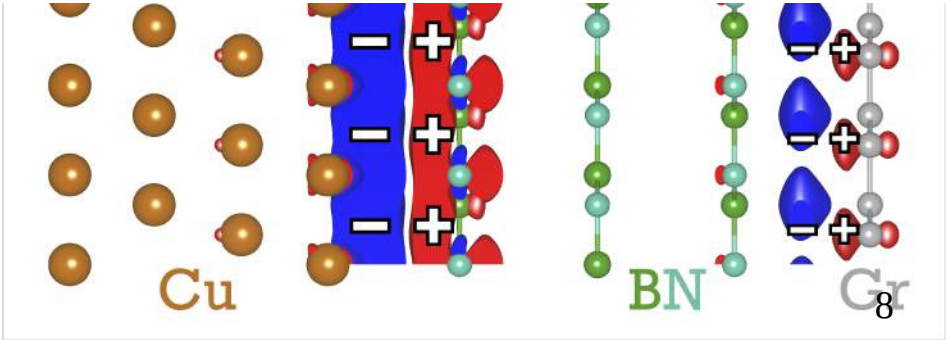
electron density displacement

$$\Delta n = n_{tot} - n_{BN} - n_{Gr} - n_{Cu}$$

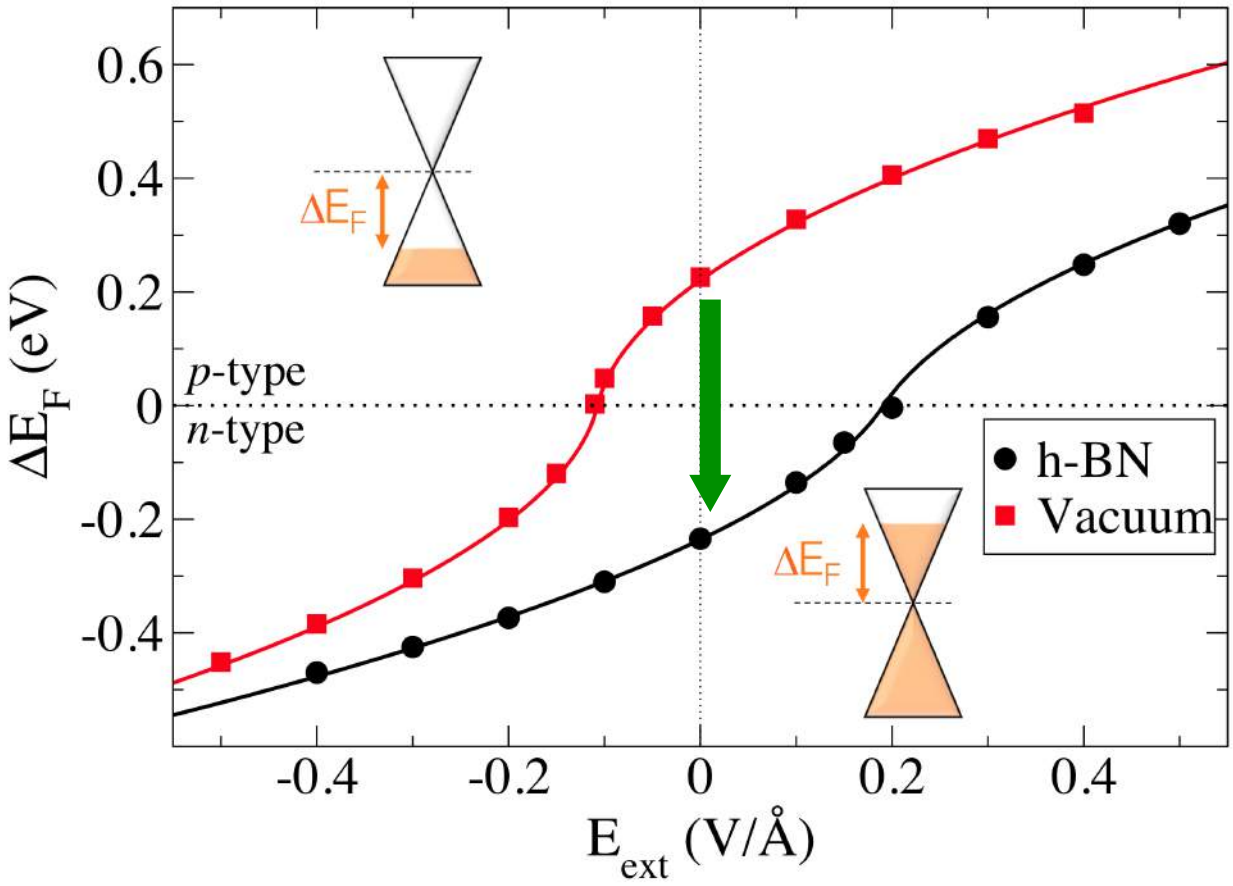


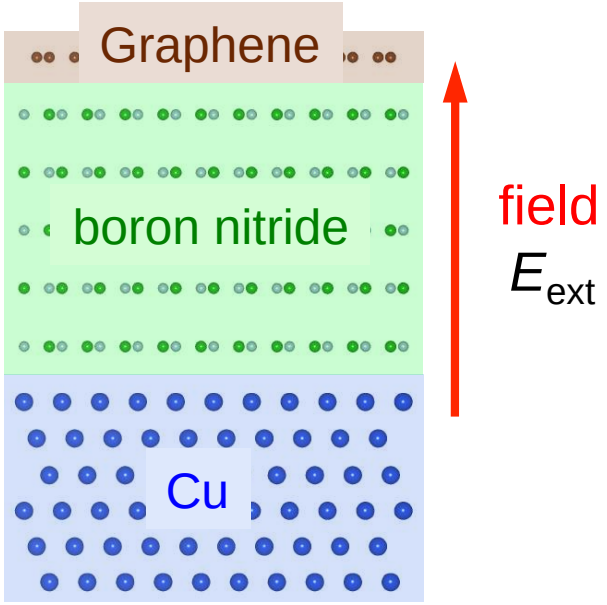
interface dipoles ->

potential steps



Effect of dielectric on doping level

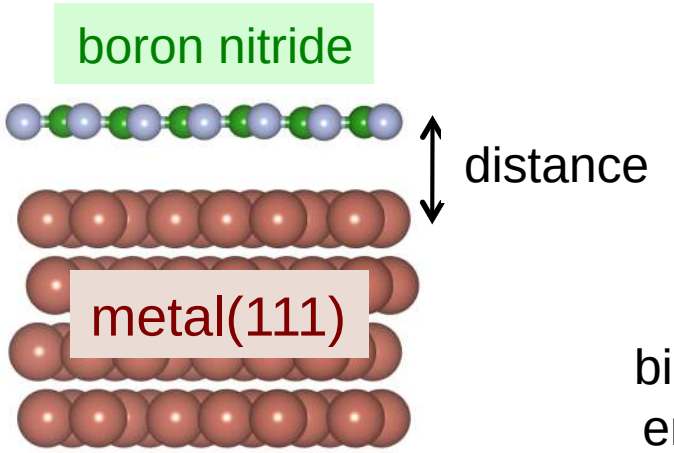


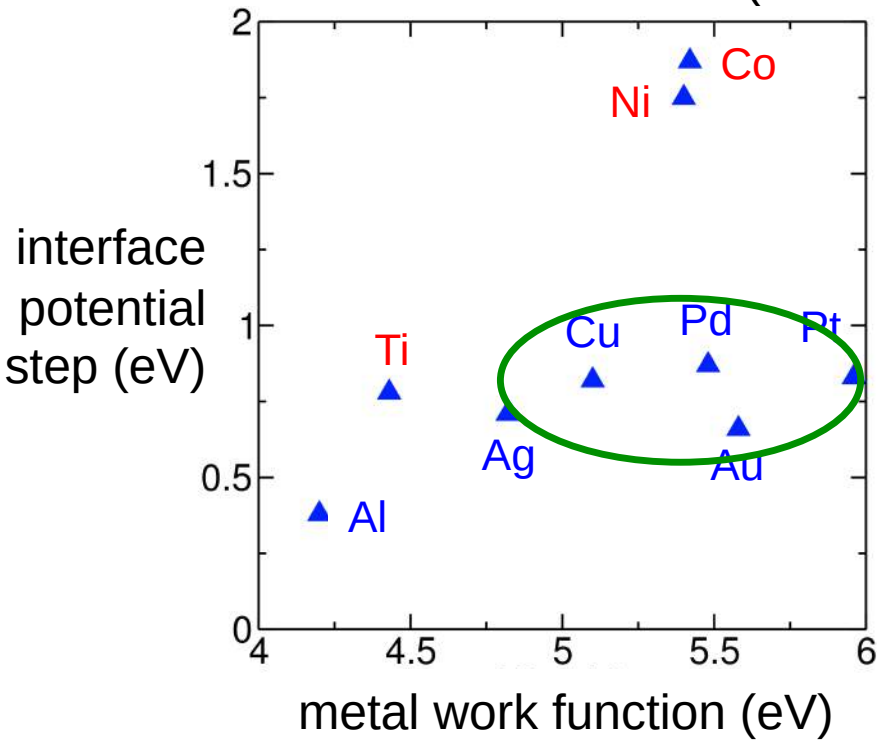


h-BN changes graphene doping from p-type to n-type

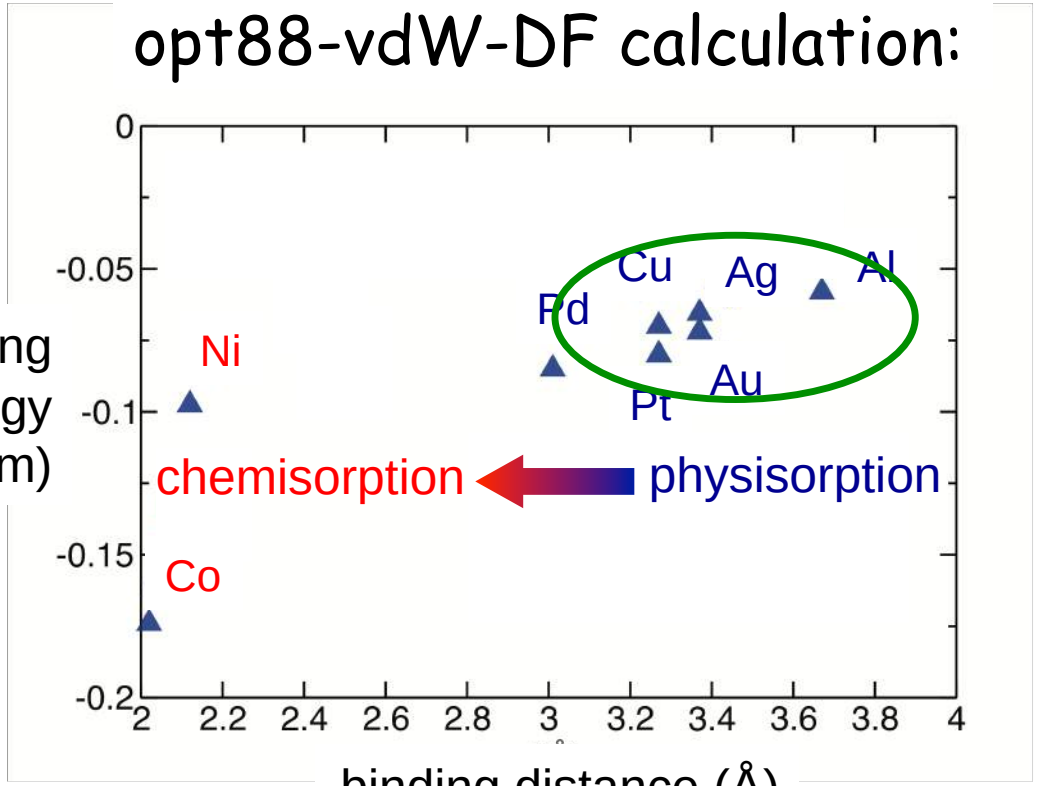
due to interface potential steps !!

monolayer h-BN adsorbed on metal (111) surface





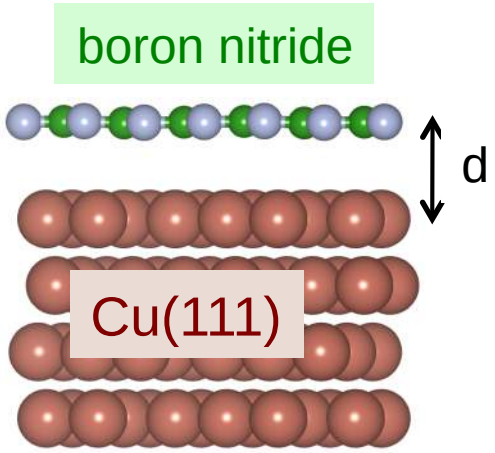
opt88-vdW-DF calculation:



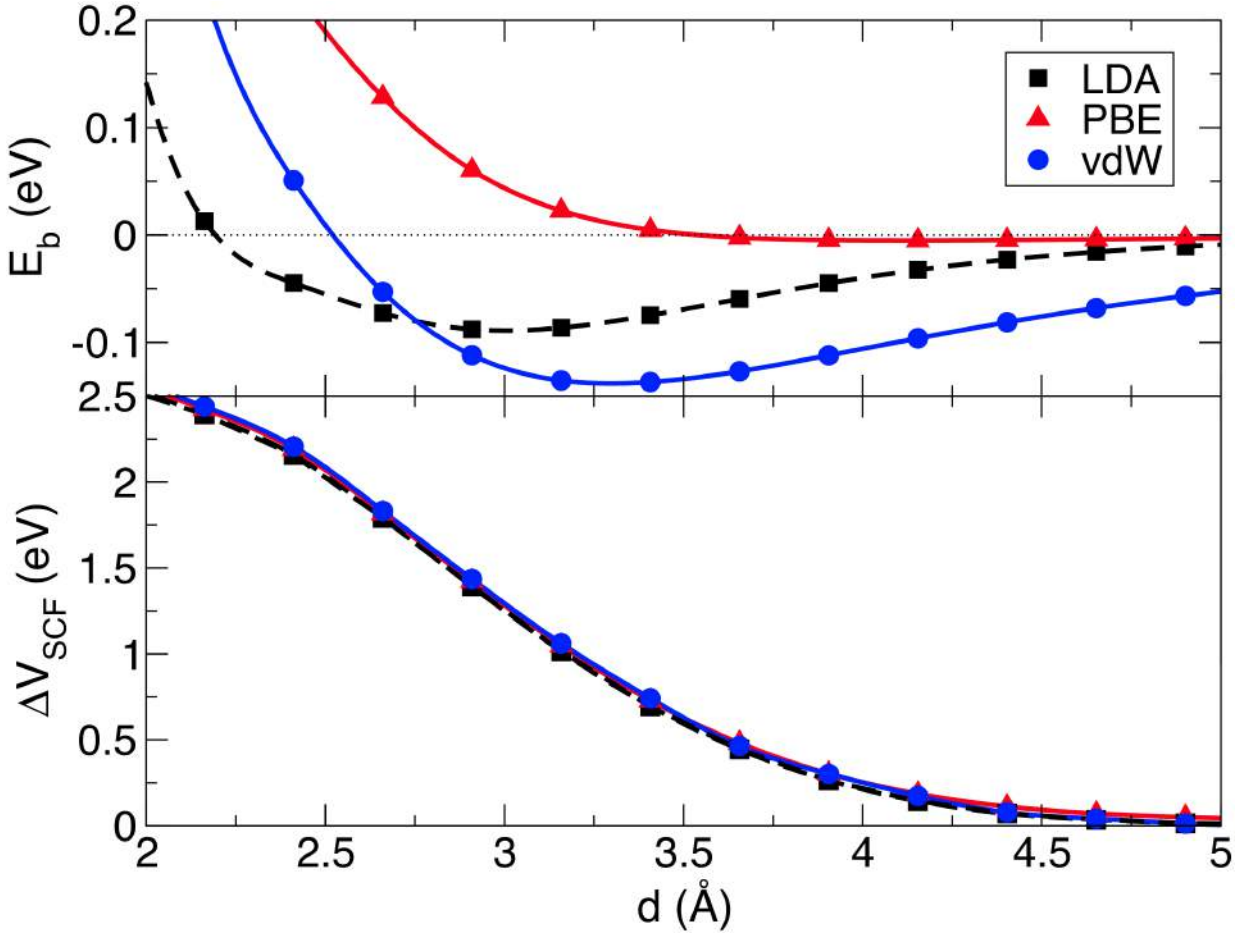
even weakly bonded h-BN gives large potential step

Bokdam et al, PRB **90**, 085415 (2014)

monolayer h-BN physisorbed on Cu(111) surface



bonding curve, potential step



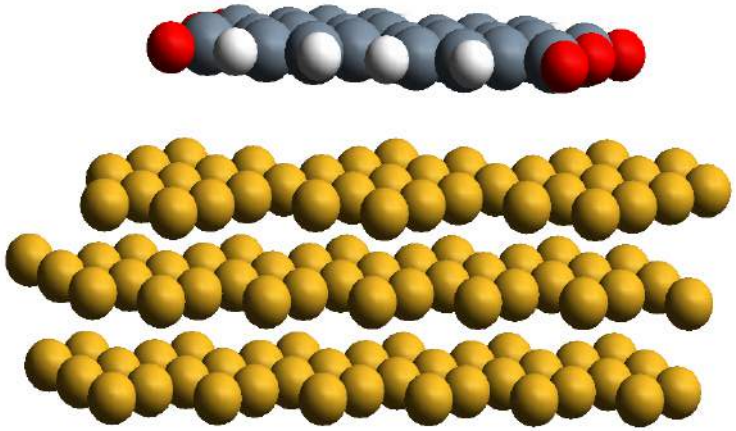
potential step

- is positive
- does not depend on functional

physical origin of the potential step?

Pillow effect for physisorbed molecules

ex: PTCDA on Au(111)



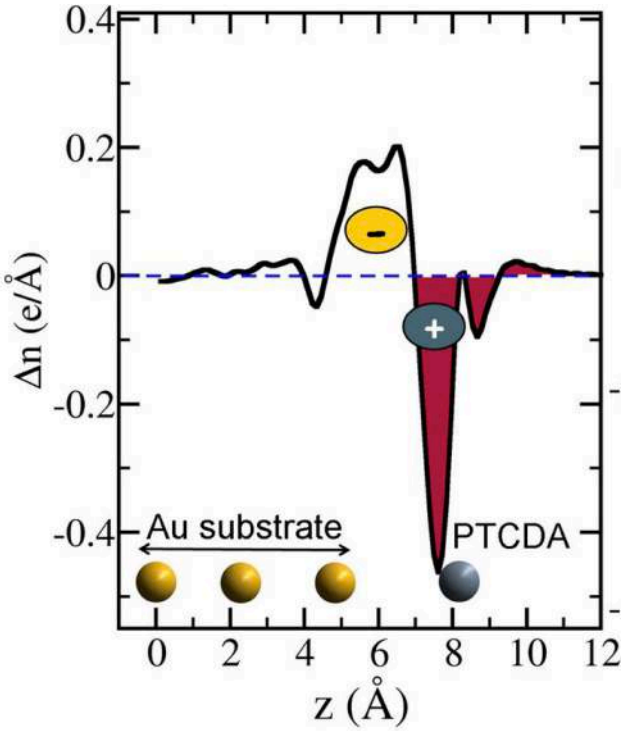
molecule pushes electrons
at interface into metal

dipole layer gives
positive potential step

"Pillow effect"

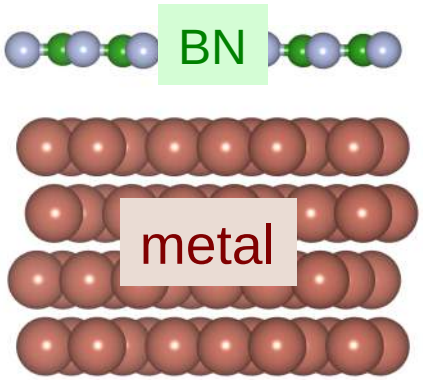
electron density displacement

$$\Delta n = n_{tot} - n_{mol} - n_{metal}$$



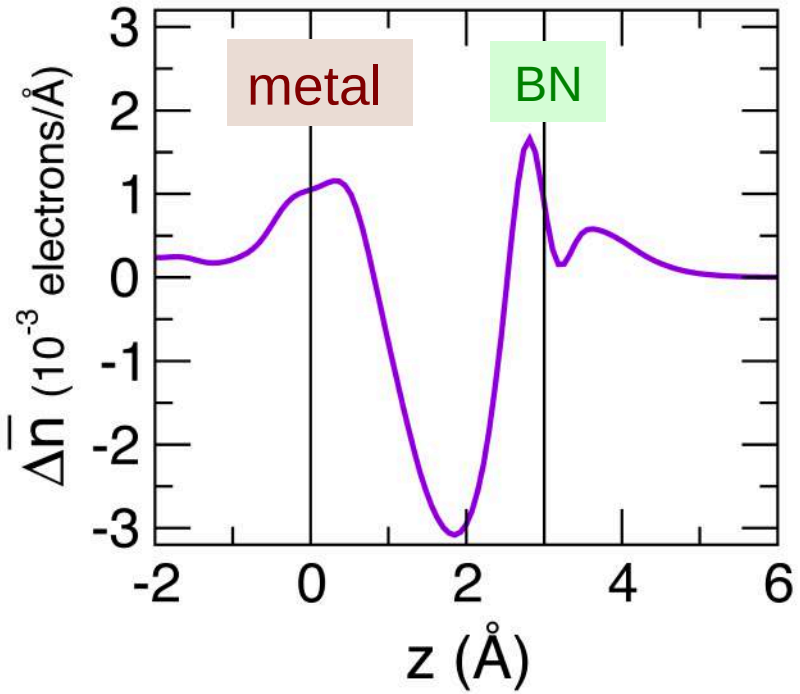
Rusu et al, JPCC **113**, 9974(L) (2009); PRB **81**, 125403 (2010)

Pillow effect = Pauli exchange repulsion



anti-symmetrized product wave function

$$\left|\Psi_{AS}\right\rangle = \hat{A}\left|\Psi_{BN}\right\rangle\left|\Psi_{metal}\right\rangle$$



difference charge density

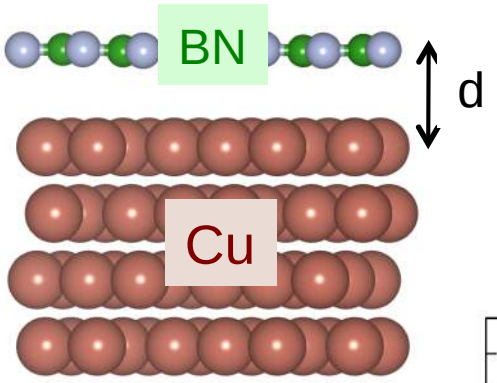
$$\Delta n_{AS} = n\left[\Psi_{AS}\right] - n_{BN} - n_{metal}$$

manageable form

$$\Delta n_{AS}(\mathbf{r}) = \sum_{\alpha,\beta}^{occ} \phi_{\alpha}^{*}(\mathbf{r})\,\phi_{\beta}(\mathbf{r})\left[S_{\beta\alpha}^{-1} - \delta_{\beta\alpha}\right]$$

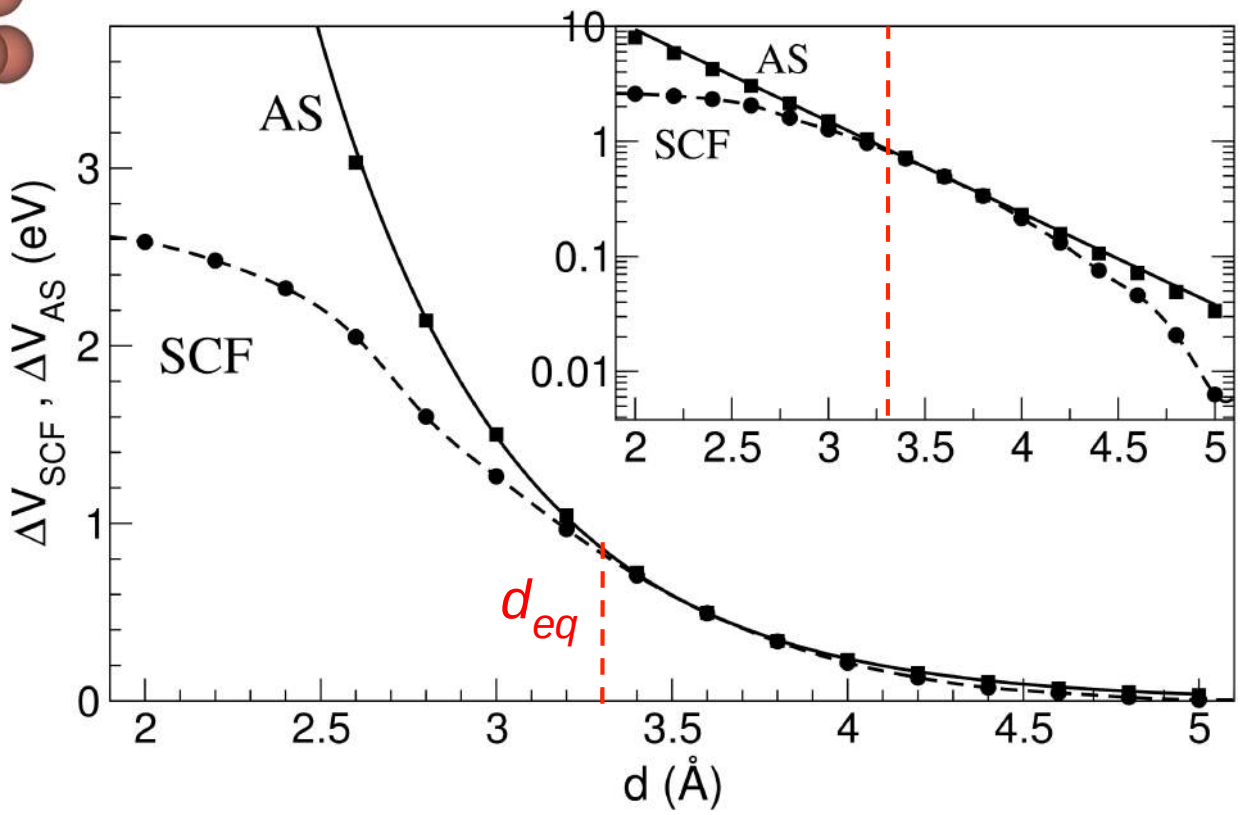
Bokdam et al, PRB **90**, 201411(R) (2014)

Pillow effect = Pauli exchange repulsion



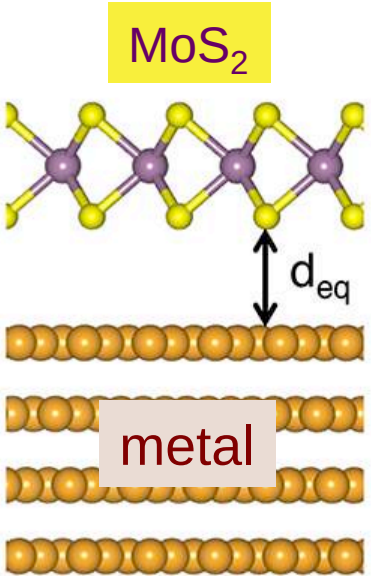
interface potential step

$$\Delta V_{AS} = \frac{e^2}{\varepsilon_0} \int_{-\infty}^{\infty} z\, \Delta\bar{n}_{AS}(z)\, dz$$



Pauli exchange repulsion gives interface potential step

Schottky barriers at metal | MX_2 interfaces

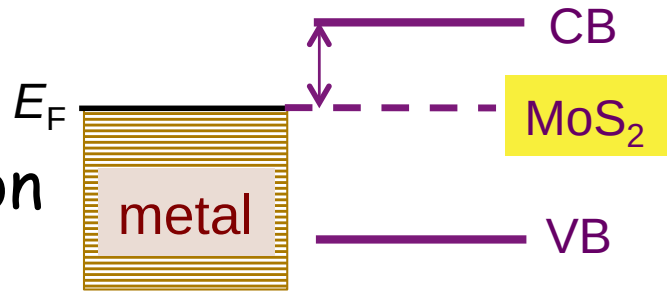


Schottky barrier

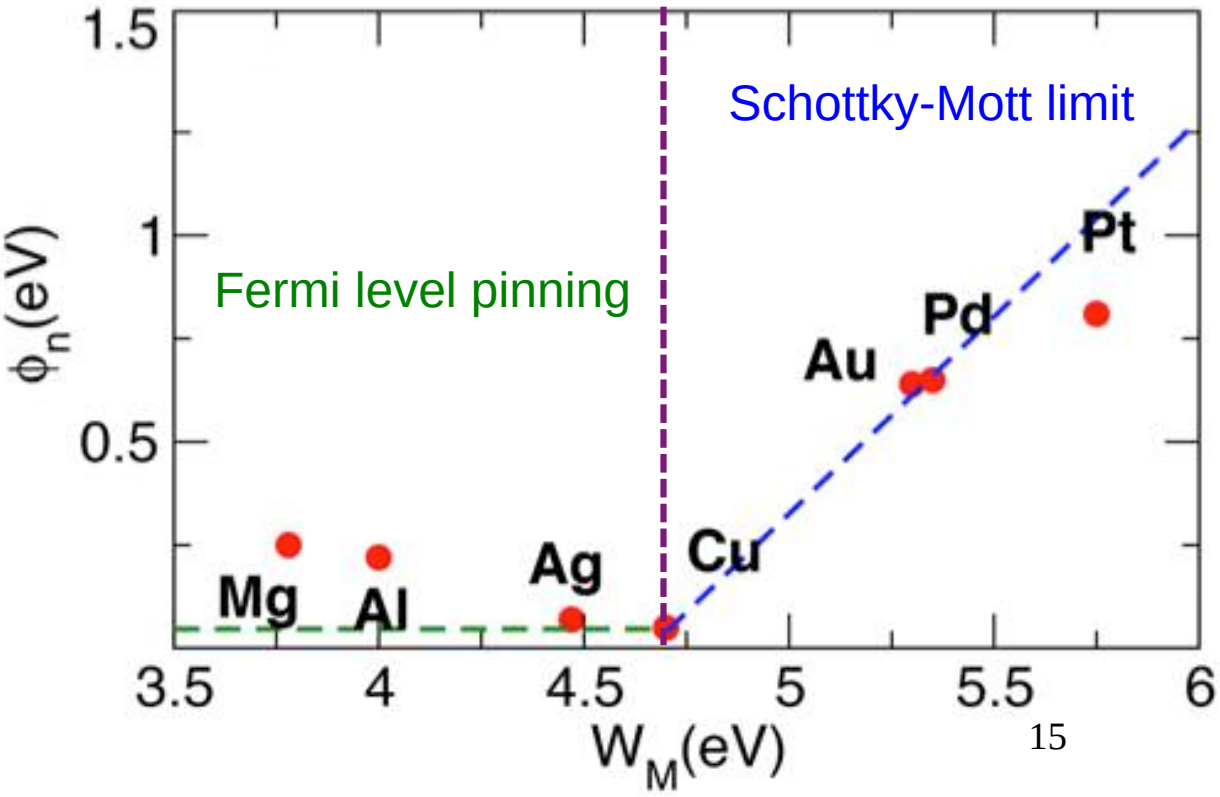
vs.

metal work function

$\Phi_n = E_{CB} - E_F$

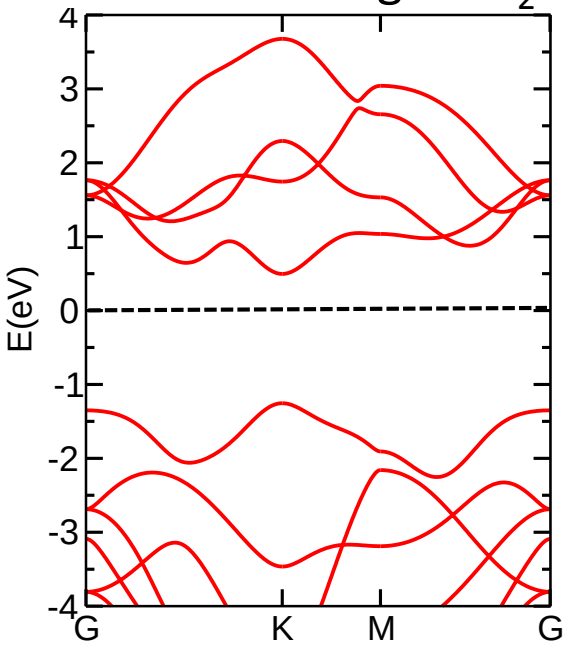


Why don't we get a zero Schottky barrier for low work function metals ?

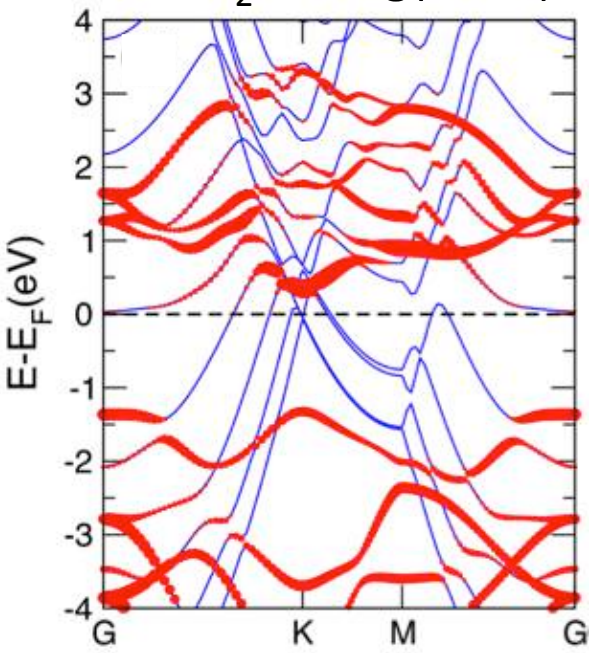


Interface states MoS_2 | Mg(0001)

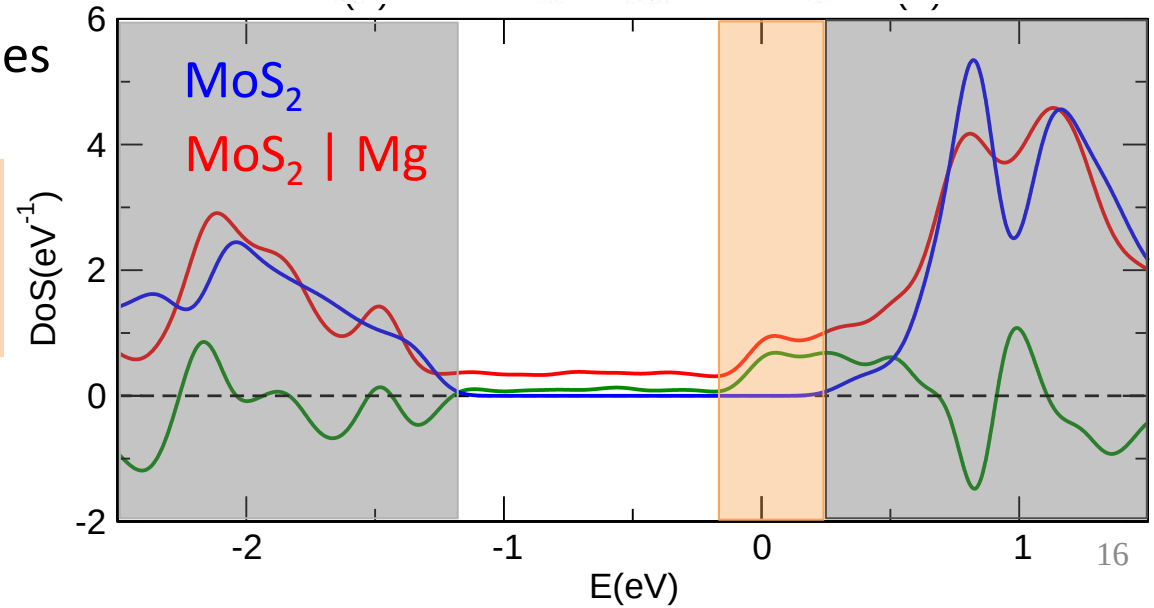
Free standing MoS_2



MoS_2 on Mg(0001)



Density of States

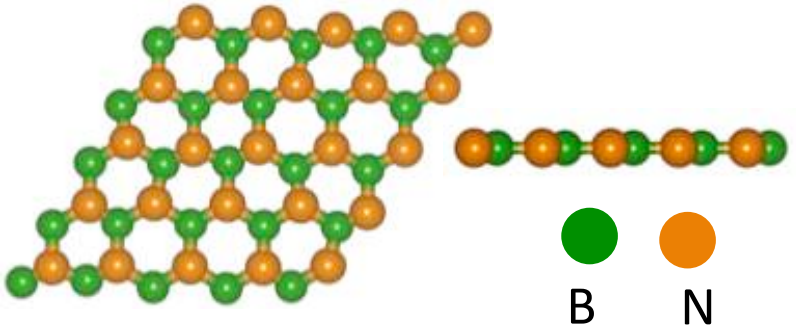


interface states pin the Fermi level

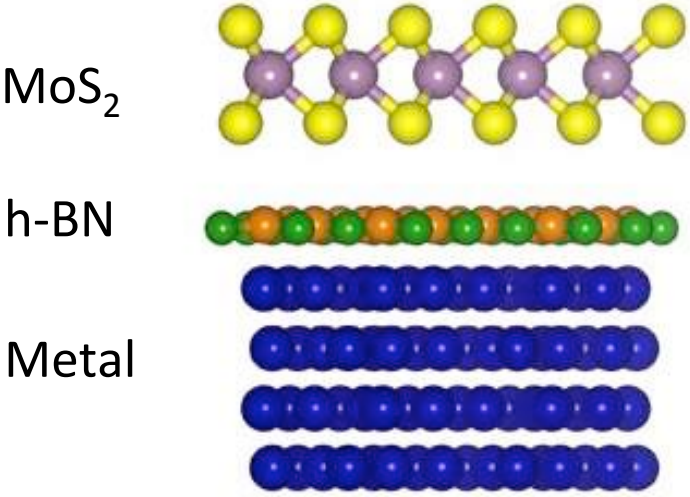
Unpinning the Fermi level

insert inert 2D layer between metal and MoS_2

e.g. h-BN



structure:

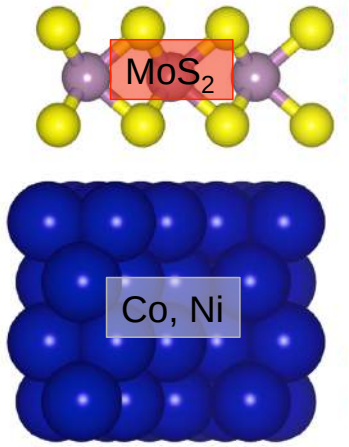


- breaks metal|MoS_2 interaction
- no states at BN|MoS_2 interface (vdW bonded)
- but potential step at metal|BN interface

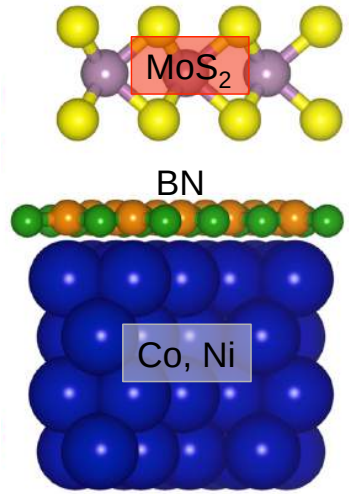
Farmanbar et al, PRB **91**, 161304(R) (2015)

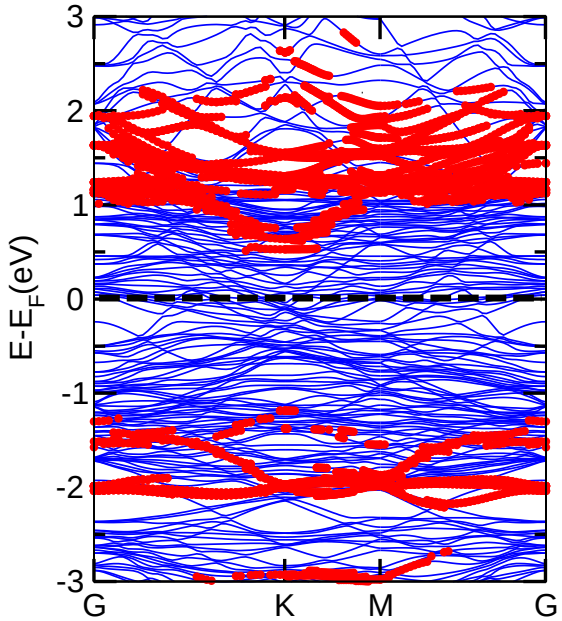
Unpinning the Fermi level

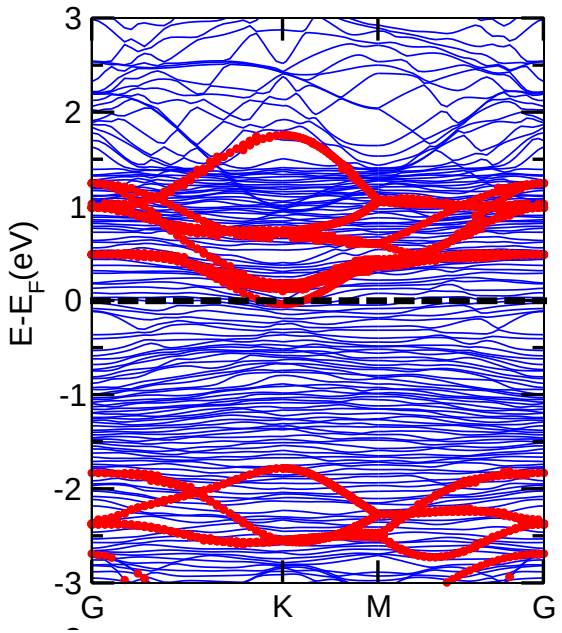
MoS_2 on Co



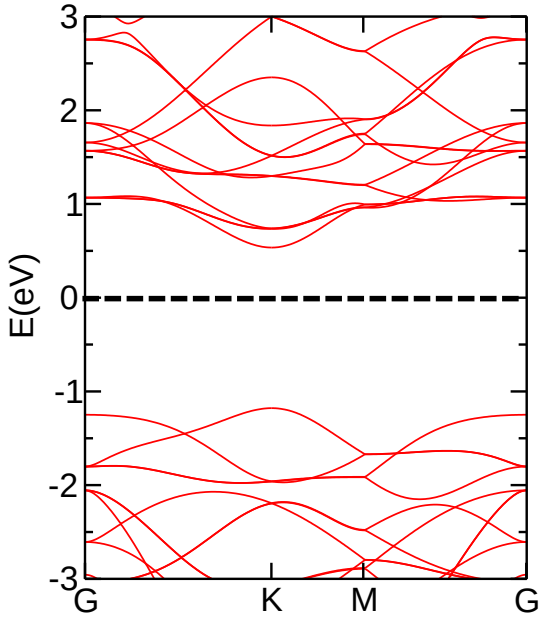
MoS_2 on Co|BN







Free standing MoS_2



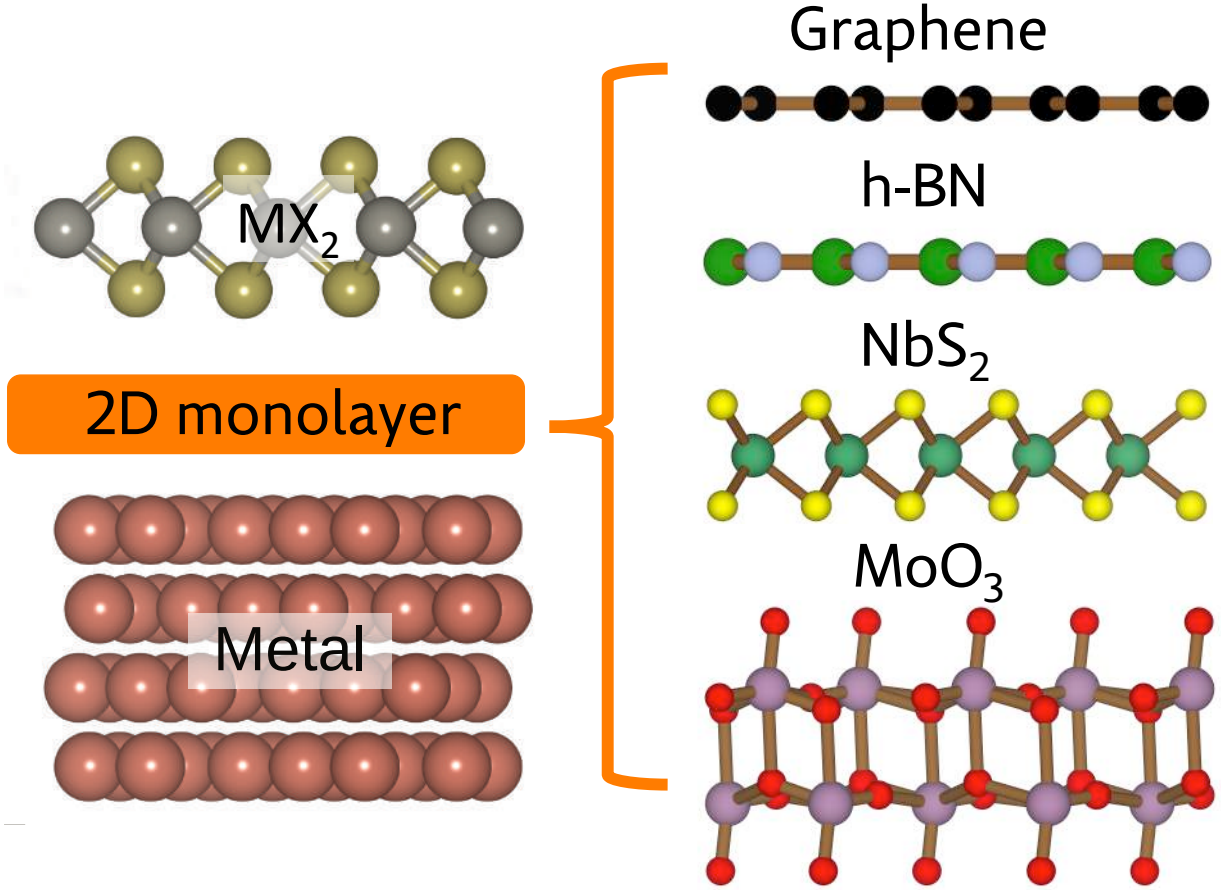
- zero Schottky barrier for electrons

n-type and p-type contacts

2D layer between metal and (2D) semiconductor

design n-type or p-type contacts

- vdW bonded layers give no interface states



n-type and p-type contacts

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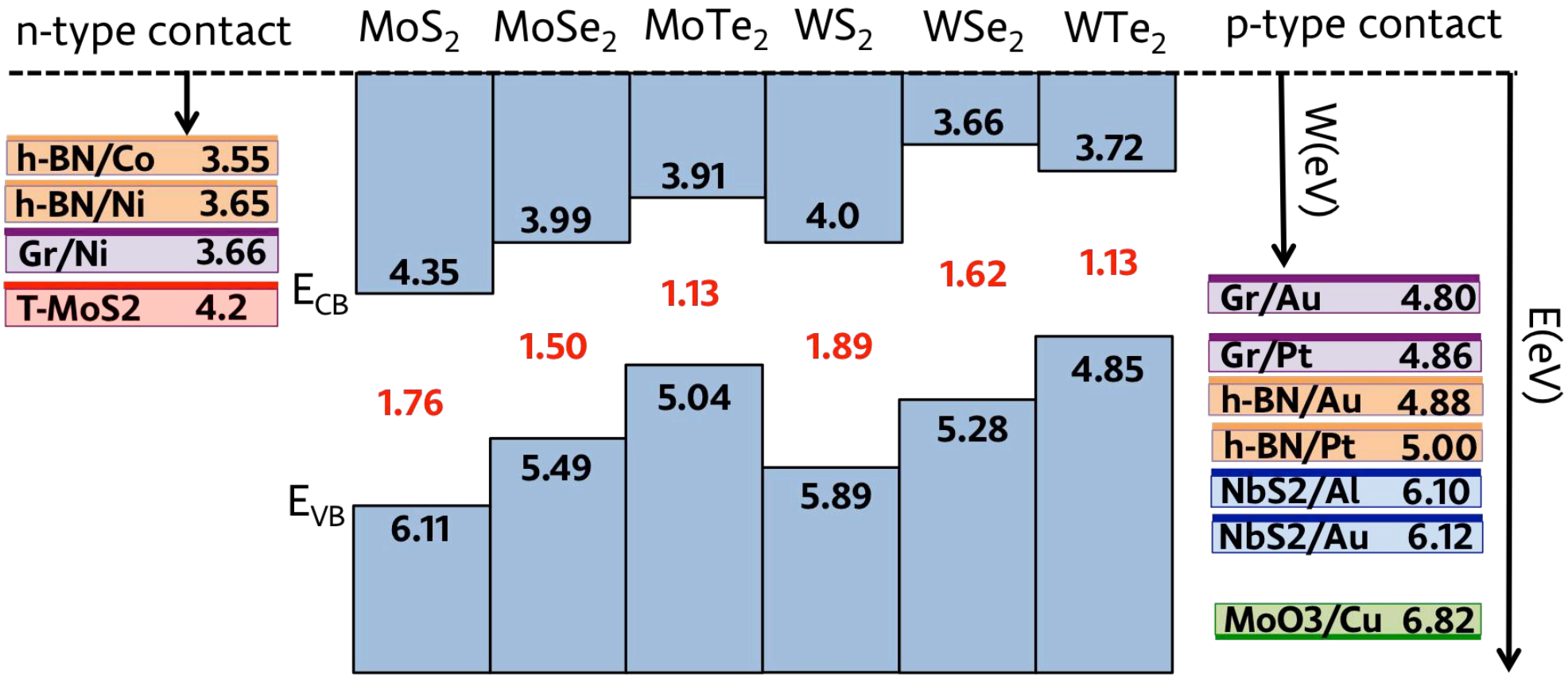

Farmanbar et al, Adv. Electron. Mater., *submitted*