Tuning Hydrogen Adsorption on Graphene with Charge Doping

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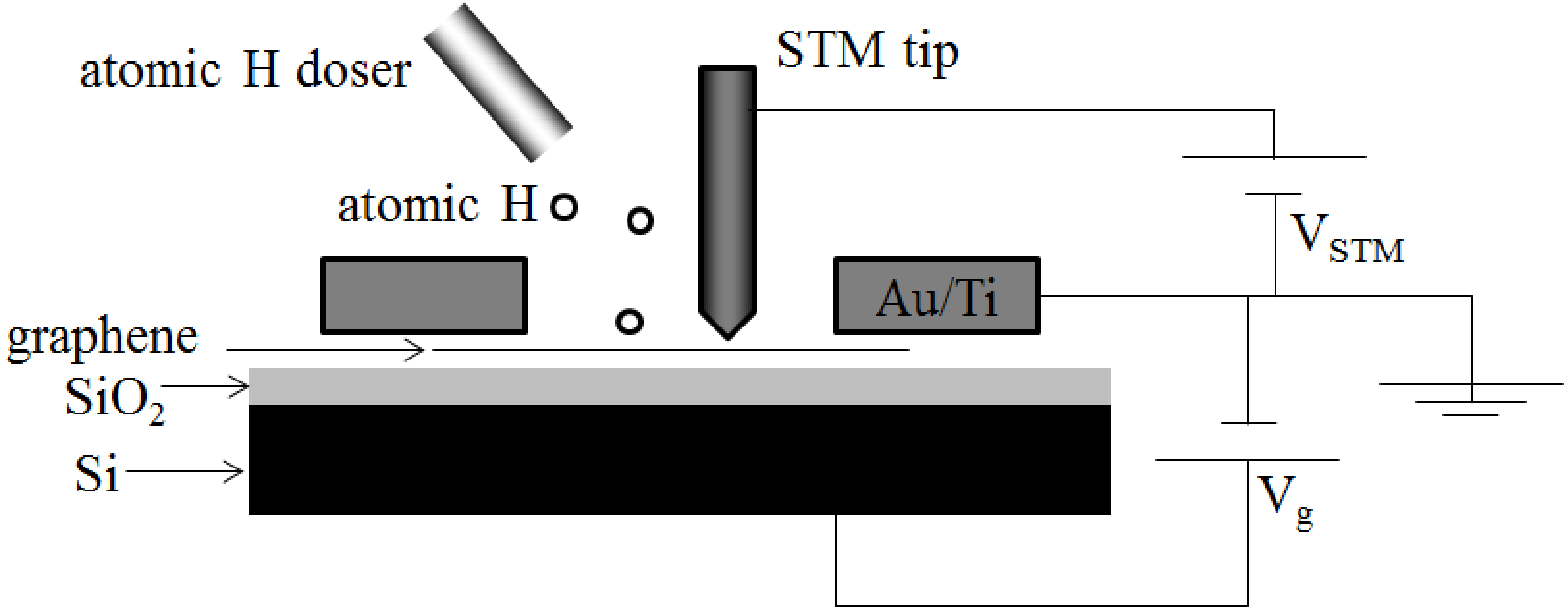
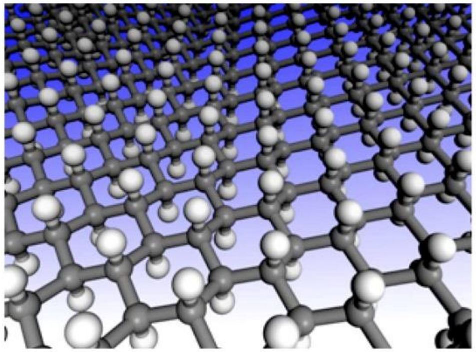


-> More hydrogen adsorb on graphene with hole doping.

H-chemisorbed graphene



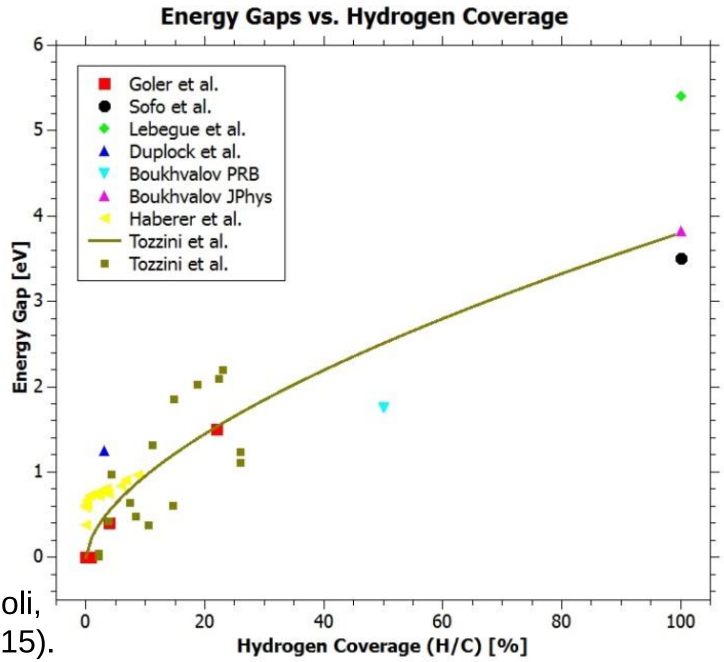
graphane
J. Sofo, A. Chaudhari, and G. Barber,
Phys. Rev. B 75, 153401 (2007).

1. H storage

high gravimetric density 8.3%

(compressed gas tank in FCV 5.7 %)

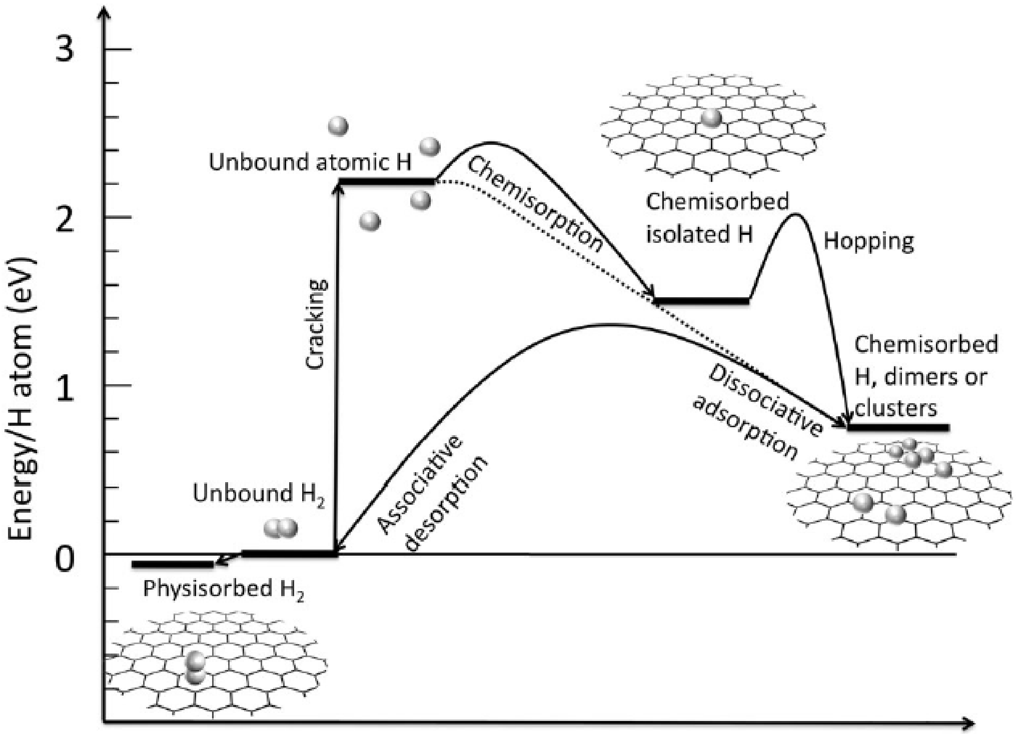
2. gap engineering



$$E_{gap} = 3.8(coverage/100)^{0.6}$$

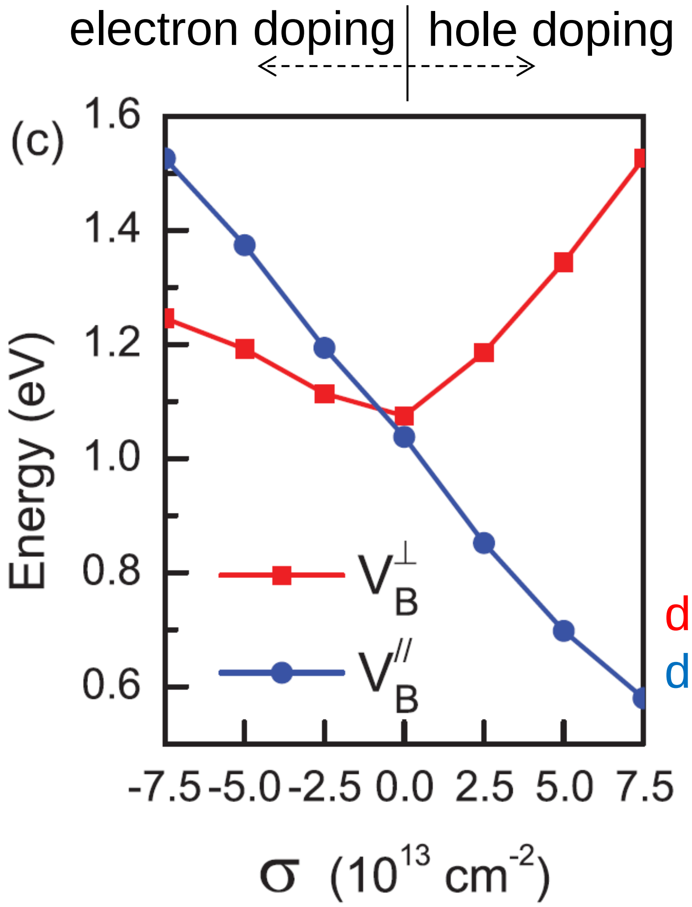
A. Rossi, S. Piccinin, V. Pellegrini, S. de Gironcoli,
and V. Tozzini, J. Phys. Chem. C 119, 7900 (2015).

energy level diagram of graphene – H system



Tozzini, et al., Phys. Chem. Chem. Phys. 15, 80 (2013).

DFT calculation of activation energy for H desorption - charge doping



desorption

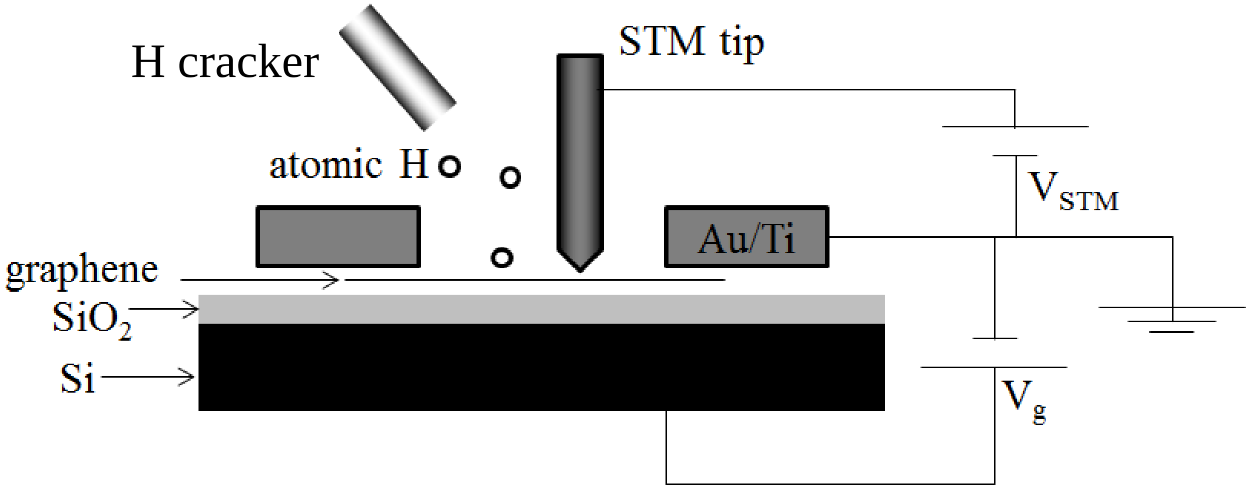
diffusion

- charge doping weakens C-C bonds
- more charges transfer from H to graphene with hole doping than electron doping and it makes C-H bonds stronger

L. F. Huang, M. Y. Ni, G. R. Zhang, W. H. Zhou, Y. G. Li, X. H. Zheng, and Z. Zeng, J. Chem. Phys. 135, 064705 (2011).

purpose of our work:
to experimentally investigate the influence of charge doping by a gate voltage V_g on the adsorption property of H on graphene

experiment



- atomic D exposure onto graphene with V_g at RT
  - partial pressure of $D_2 = 5 \times 10^{-9}$ mbar (base pressure $= 5 \times 10^{-10}$ mbar)
  - H cracker (Tectra); a tungsten capillary at 2000K
  - The vacuum chamber is evacuated immediately after D exposure.

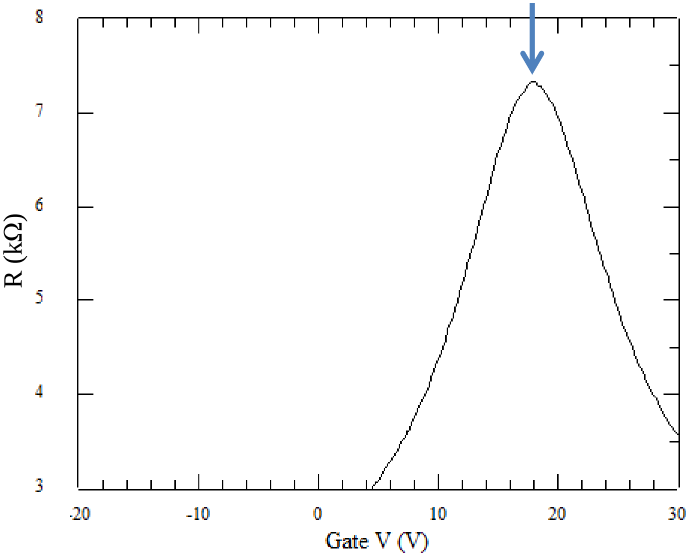
- characterization of electronic and morphological properties of graphene at RT
  - ☐ transport measurement
  - ☐ STM (RHK technology)

transport measurement

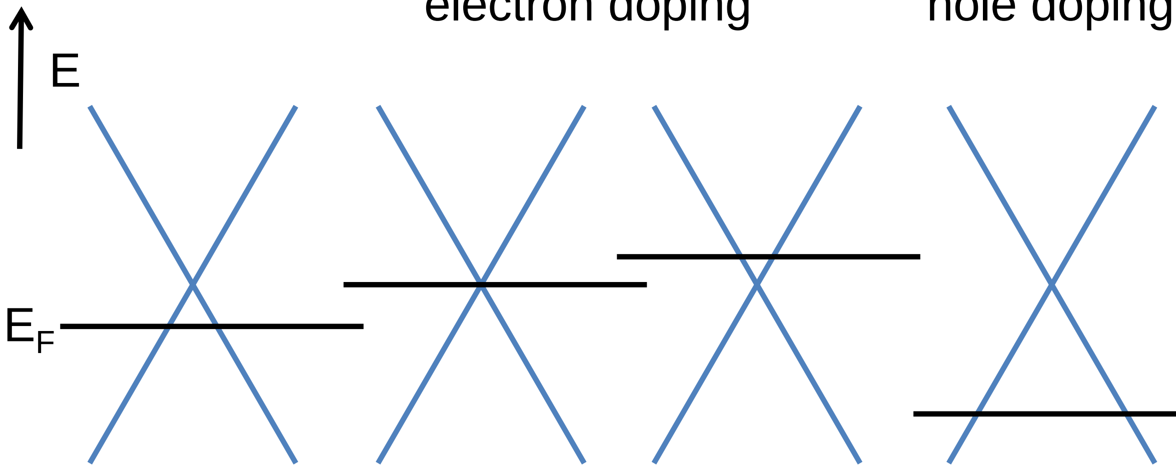
transport measurement

resistance of graphene as a function of V_g

CNP = +18V



graphene dispersion



V_g = 0 V

+18V

+30 V

electron doping

-30 V

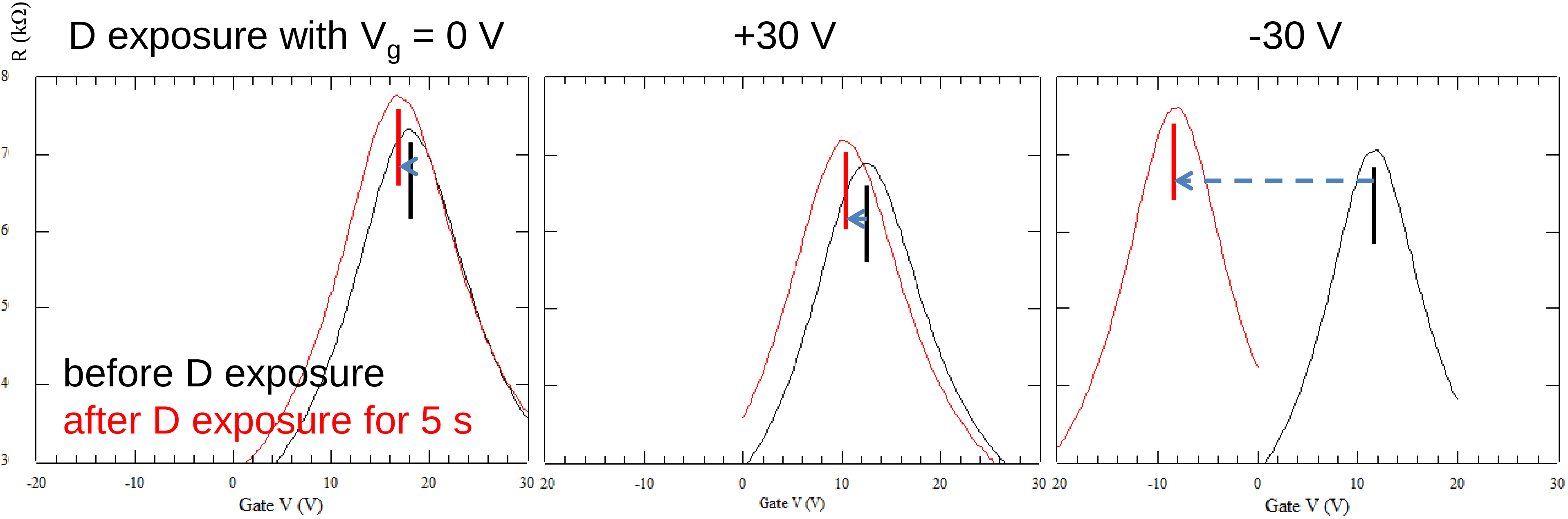
hole doping

- Graphene is doped by charge transfer from the substrate and/or impurity.

- When the initial charge doping is compensated by V_g, the resistance becomes maximum. This V_g is called charge neutrality point (CNP).

- net charge density = (capacitance per area / e) × (V_g – CNP)

transport measurement


D exposure with V_g = 0 V

+30 V

-30 V

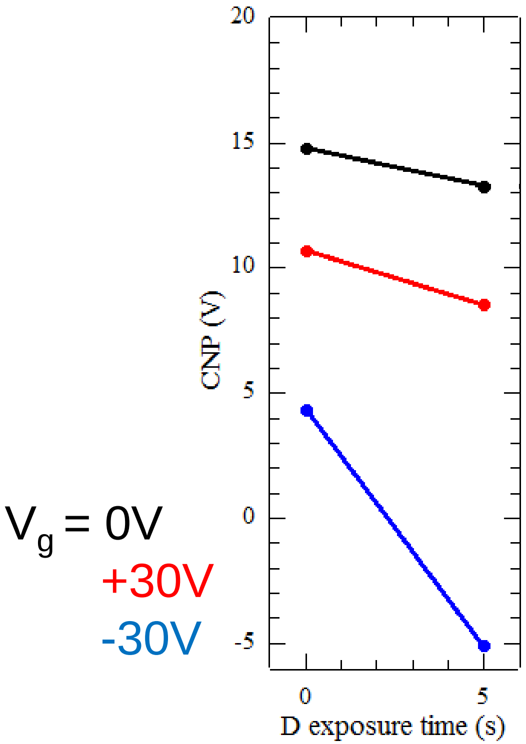
- After D exposure, the CNP shifted to negative value.
  -> electron doping
  H is donor for graphene. (J. Chem. Phys. 135, 064705 (2011).)

- The CNP shift is larger with V_g = -30V (hole doping), than 0V and +30V (electron).

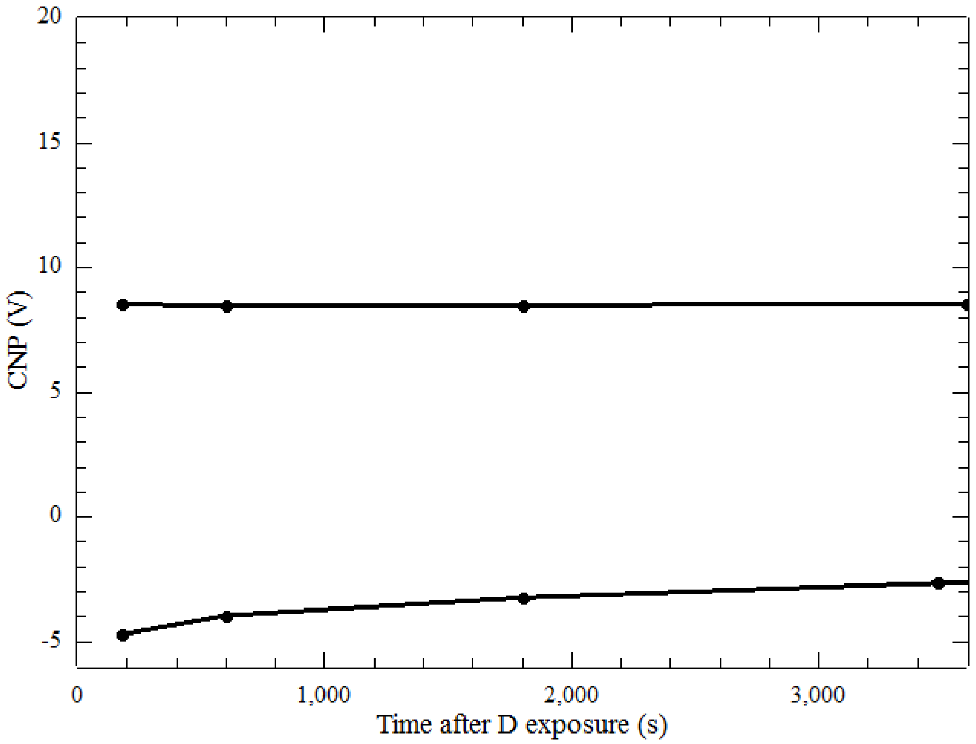
- After D exposure, the resistance increased. -> created carrier scattering centers

transport measurement

CNP shift by D exposure

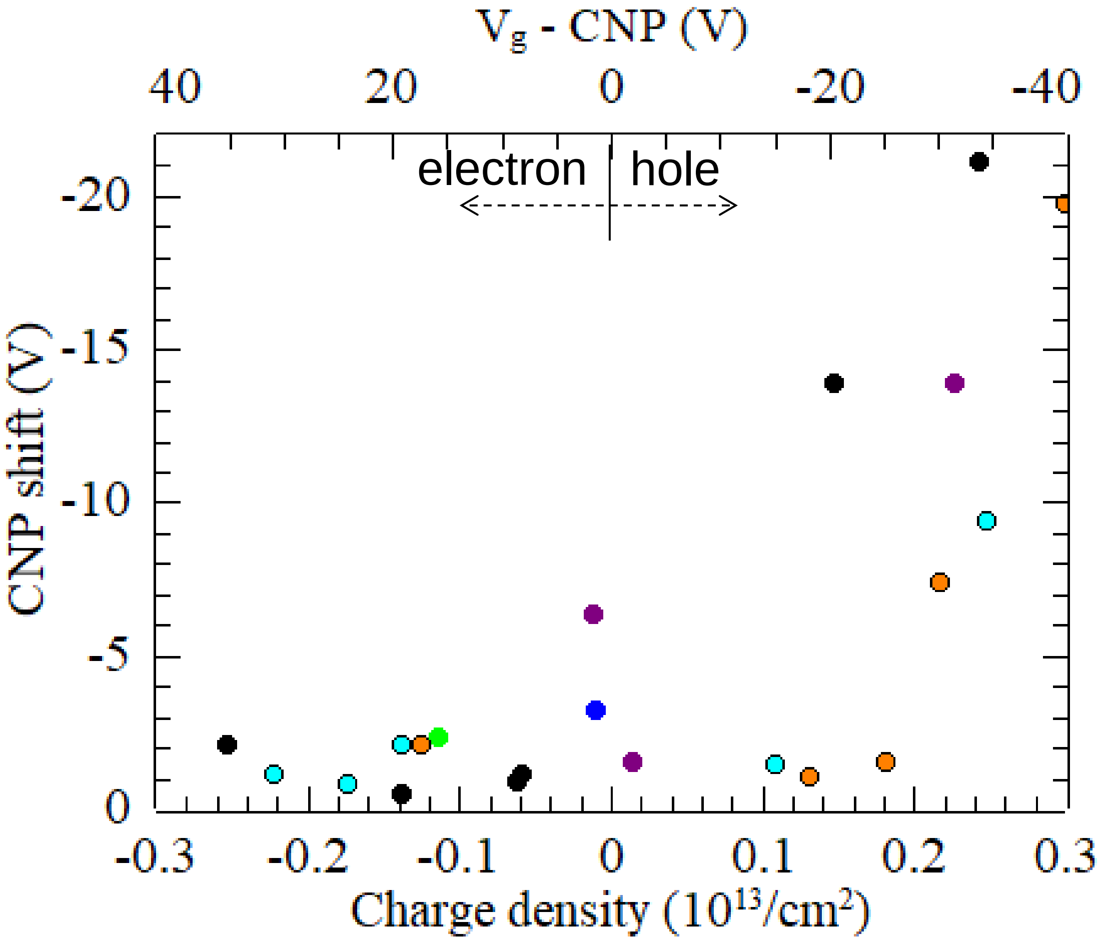


CNP shift after D exposure in vacuum $V_g = 0V$



- In vacuum, the CNP shifted back toward the initial value by 1-2 V 1 hour later.
  - The CNP shift during transport measurement (it takes 5 min) is negligibly small.
- The CNP and resistance recovered the initial values after vacuum annealing at 400ºC for 2 hours. -> The influence by D exposure is reversible, not damage to graphene.

CNP shift after D exposure as a function of charge density



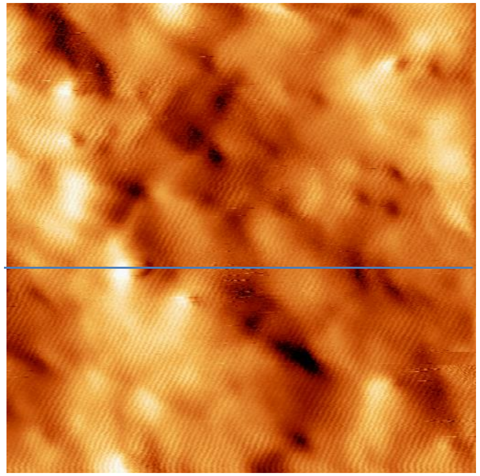
colors:
different samples

- The CNP shift is larger with hole doping, than no doping and electron doping.

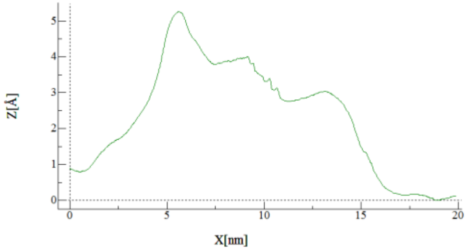
STM

STM

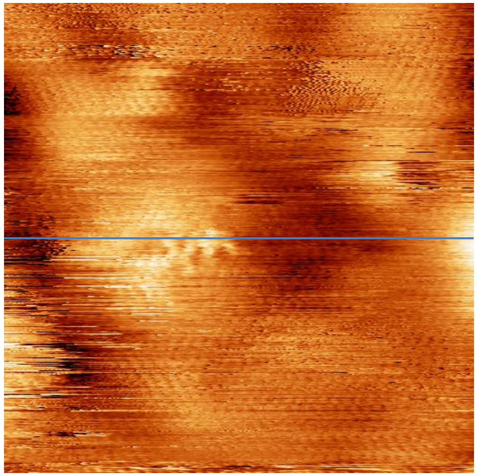
before D exposure



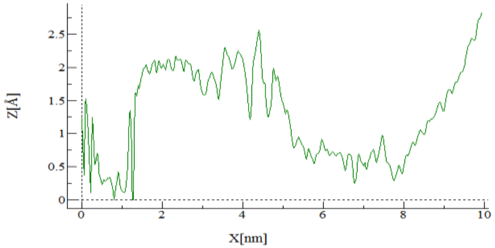
0.1V 0.16nA 20nm



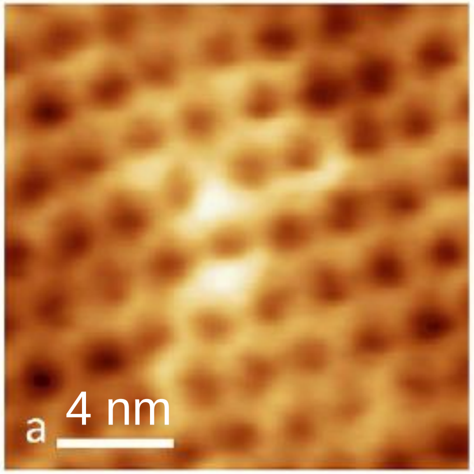
D exposure with V_g = -30V



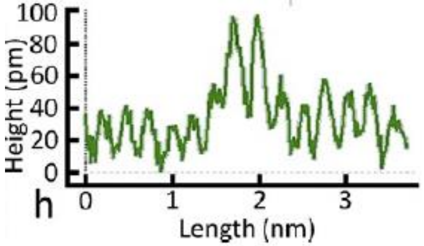
0.5V 0.03nA 10nm



H on graphene/SiC



0.05V 0.3nA



Goler et. al., J. Phys. Chem. C, 117, 11506 (2013)

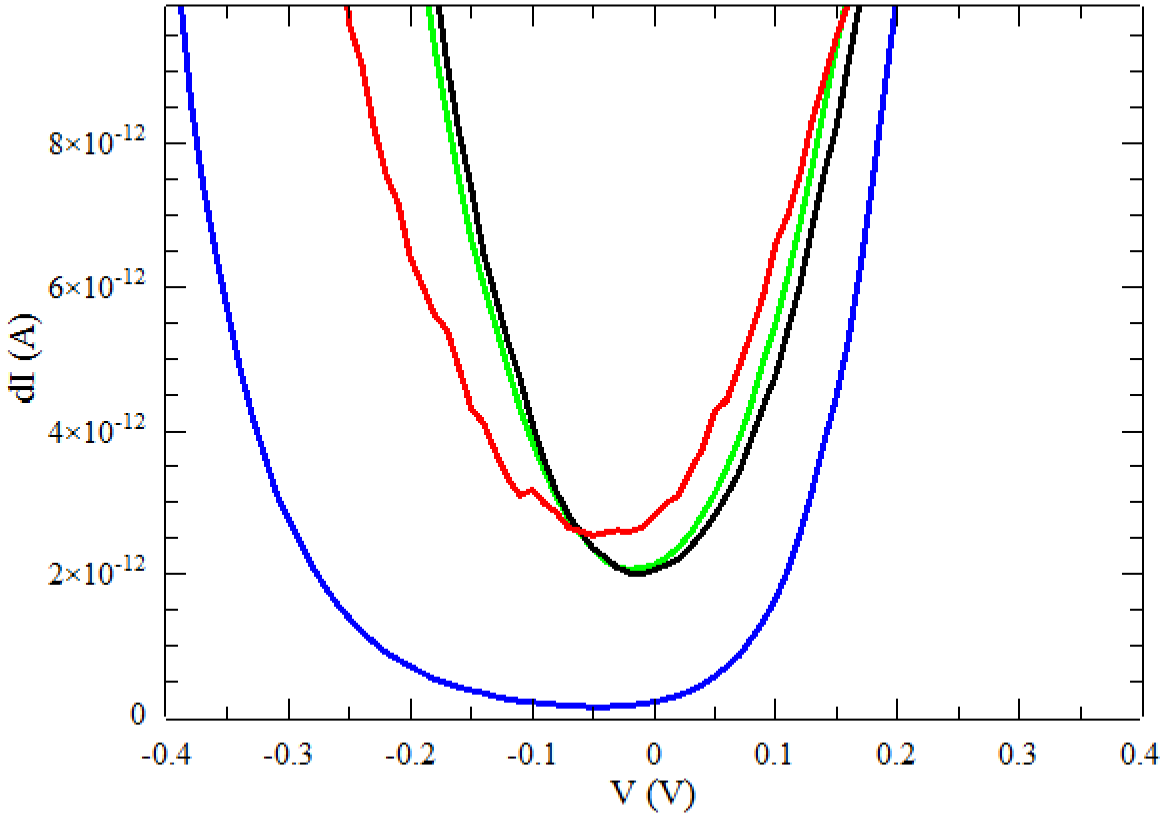
- graphene honeycomb lattice (amplitude ~0.02 nm, periodicity ~0.25 nm)
- corrugation of SiO_2 substrate (amplitude ~1 nm, periodicity ~15 nm)

- We could not identify D on graphene.
  - D density is too low?
  - The corrugation of SiO_2 substrate masks protrusions of D?

STM

STS

The differential tunneling current dI was measured by a lock-in amplifier as a function of bias V.



before D exposure

D exposure with

V_g = 0V

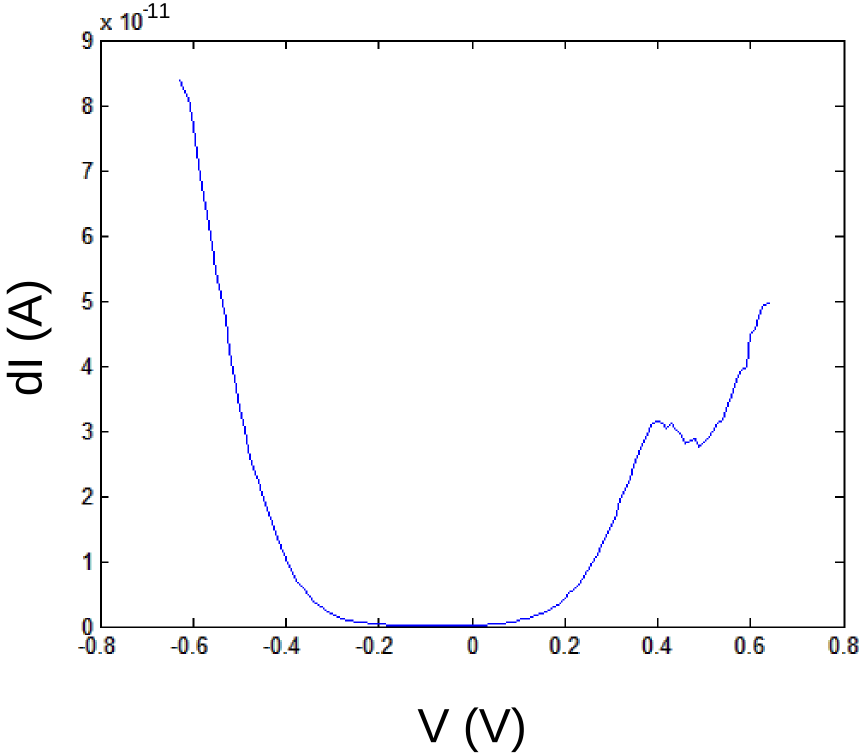
+30V (electron)

-30V (hole)

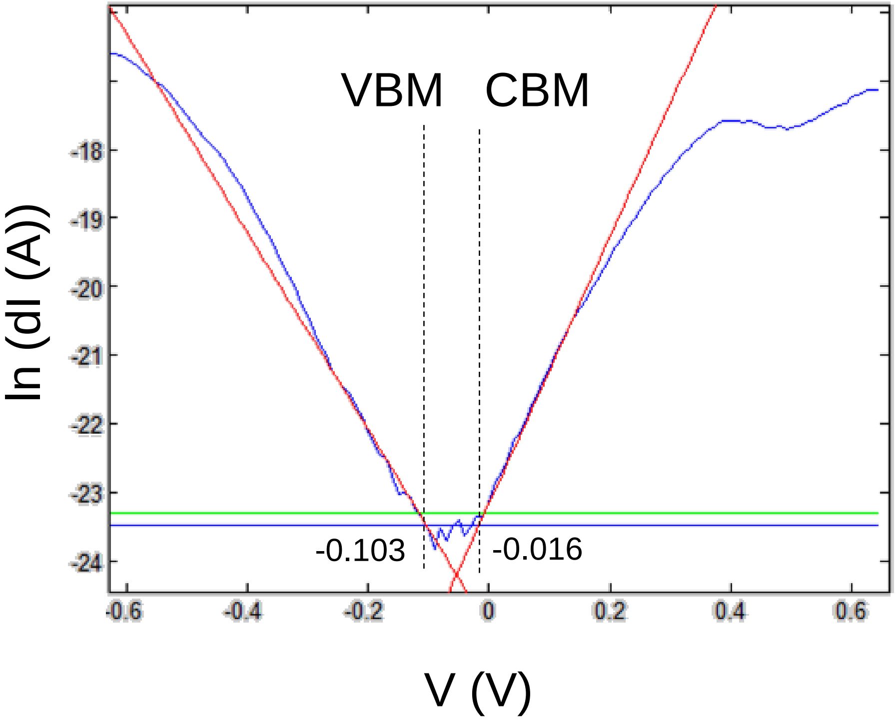
- after D exposure with -30V
  - dI became smaller -> band gap opening
  - slightly shifted to negative value of bias V -> electron doping

STM

typical STS in linear scale



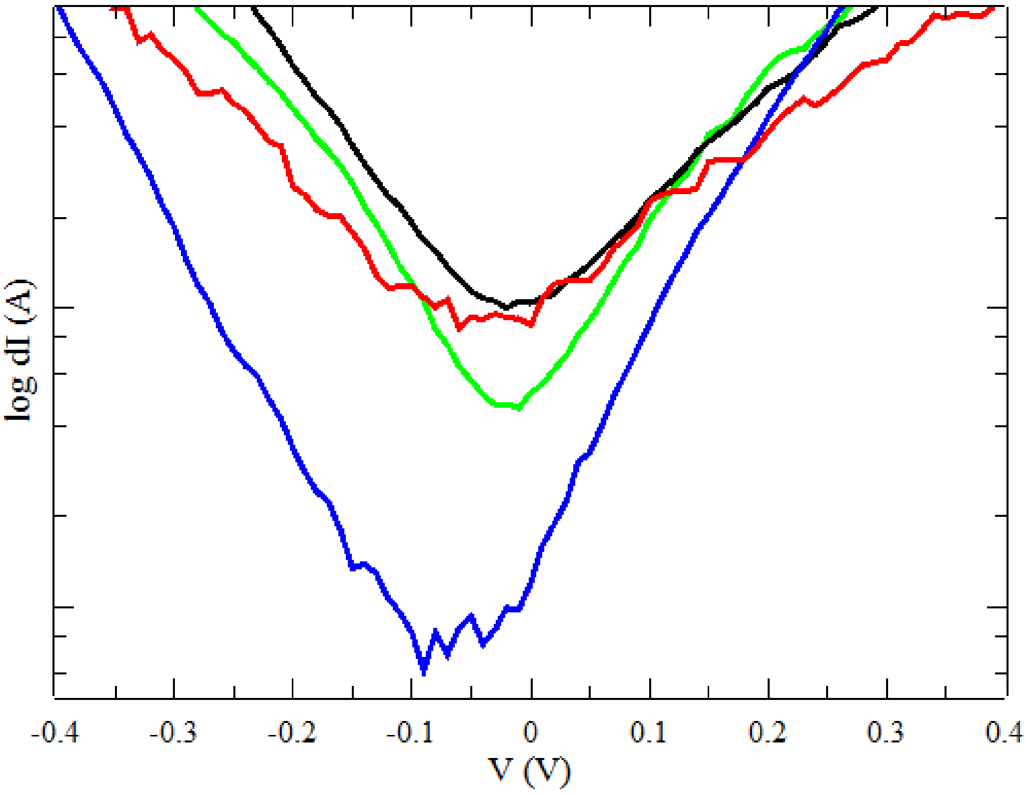
log scale



band gap determination following (Ugeda et. al., Nature mat. 13, 1091 (2014))

- take logarithm of dI
- find the noise floor (<0.1 pA), add the standard deviation of the noise floor
- draw lines between the point where the standard deviation crosses the spectra, and the point ±0.1V away
- define the band onsets (VBM and CBM) where the lines intersect the noise floor

typical STS in log scale



before D exposure
D exposure at:
$V_g = 0V$
+30V (elect)
-30V (hole)

no gap

average band gap = 0.14±0.05eV

charge transfer per D

assume that D adsorption opened the band gap, induced the charge transfer to graphene, and the charge transfer per D is constant,

relationship between a band gap and H coverage by DFT

$$E_{gap} = 3.8(coverage/100)^{0.6}$$

A. Rossi, S. Piccinin, V. Pellegrini, S. de Gironcoli, and V. Tozzini, J. Phys. Chem. C 119, 7900 (2015).

• band gap induced by D exposure	0.14±0.05 eV
• D coverage	0.4±0.2%
• CNP shift by D exposure	-14 V
• increase of carrier density	1.01×10^{12} /cm^2
• charge transfer per D	0.066 e (0.044-0.13e)

0.06 e per H by DFT

J. Katoch, D. Le, S. Singh, R. Rao, T. Rahman, and M. Ishigami, J. Phys. Cond. Matt. 28, 115301 (2016).

conclusion

- The influence of charge doping by a gate voltage V_g on the adsorption property of D on graphene was investigated by transport measurement and STM.

- The CNP shifted to negative value after D exposure. The shift was larger after D exposure on graphene with hole doping than without doping and with electron doping.

- The STS showed a band gap of 0.14 eV after D exposure on graphene with hole doping, while no gap without doping and with electron doping.

- Both the transport measurement and STS suggest that more D adsorb on graphene with hole doping than no doping and electron doping.

- This trend is consistent with theoretical report.

- This result demonstrated the possibility to control H adsorption/desorption on graphene via charge doping.