UNIVERSITY OF TRIESTE

VINČA Institute of Nuclear Sciences

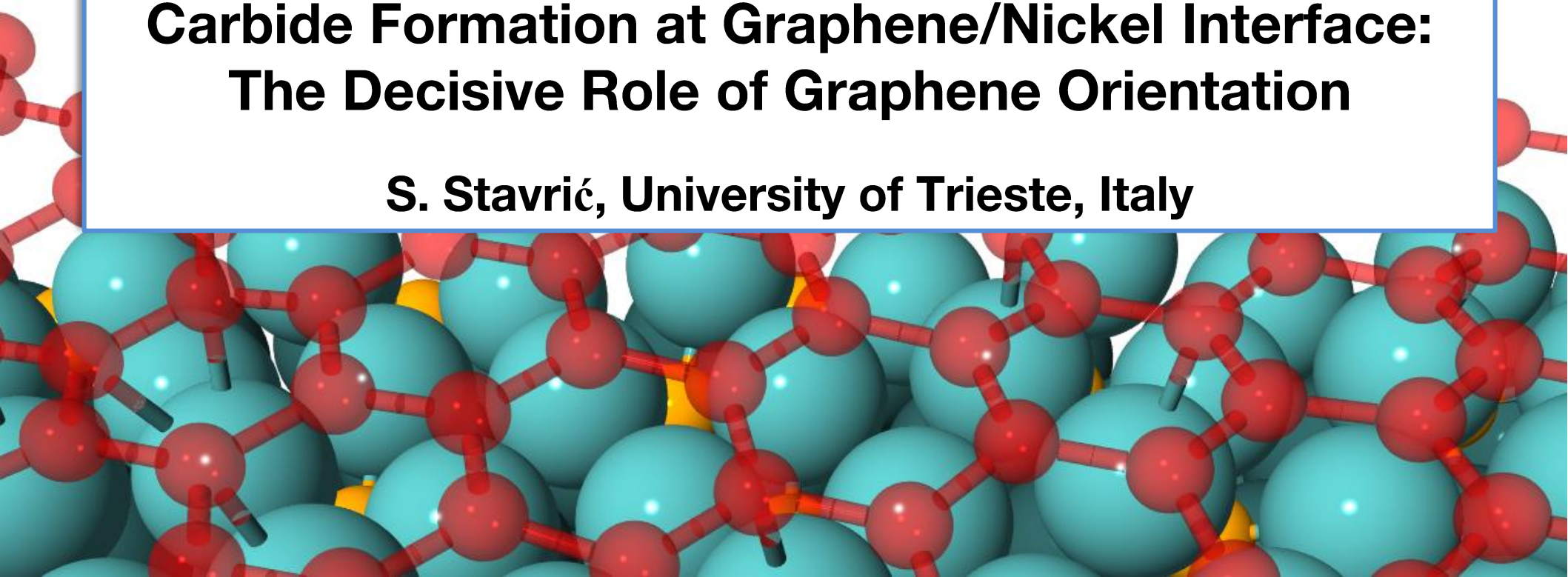
chem2Dmat

AUGUST 31 - SEPTEMBER 03, 2021 • ONLINE

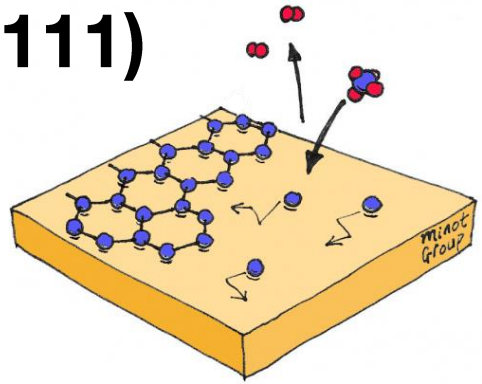
EUROPEAN CONFERENCE ON CHEMISTRY OF TWO-DIMENSIONAL MATERIALS

Carbide Formation at Graphene/Nickel Interface: The Decisive Role of Graphene Orientation

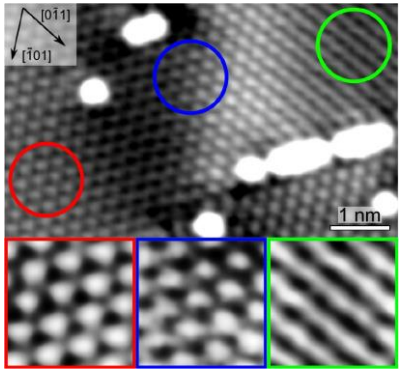
S. Stavrić, University of Trieste, Italy

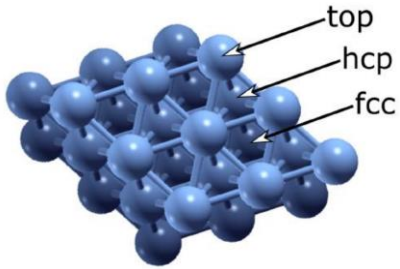


Epitaxial growth of graphene on Ni(111)



- Ni(111) is a suitable substrate for CVD growth of graphene due to their close lattice match
- the preference of 1x1 configurations – epitaxial graphene (EG)

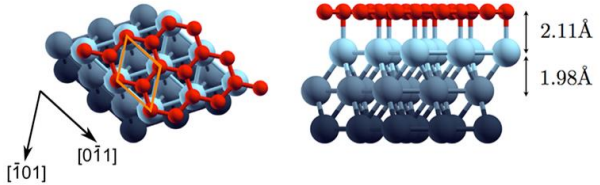


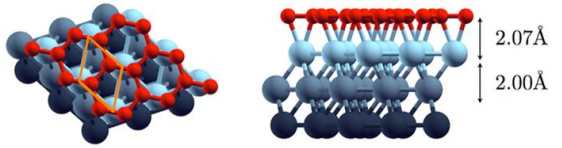


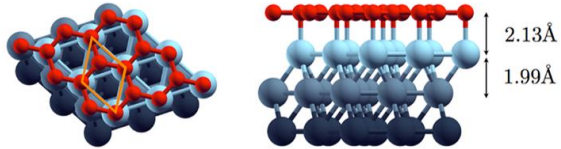
top-fcc
(-0.16 eV)

top-bridge
(-0.15eV)

top-hcp
(-0.14 eV)





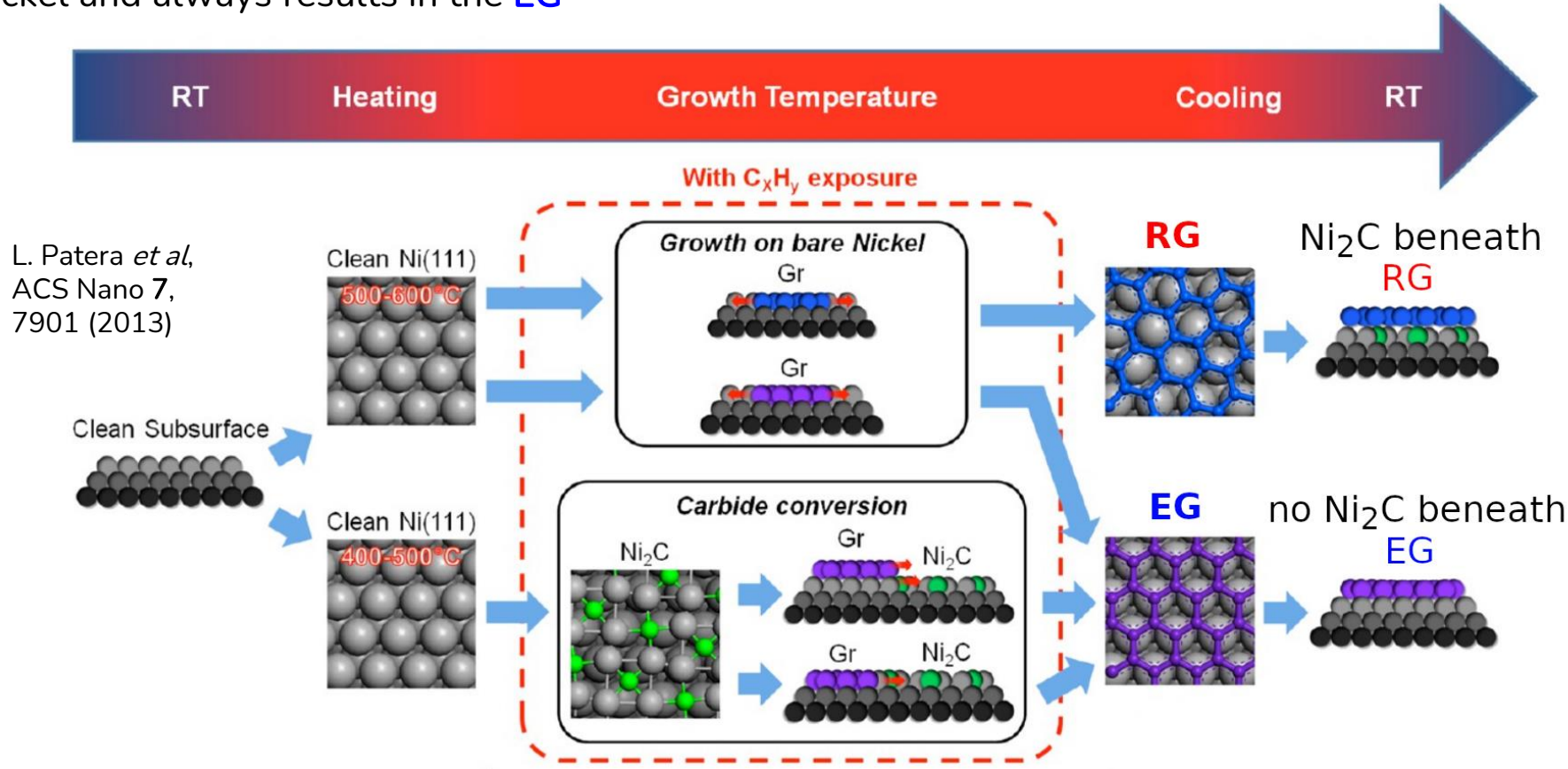


F. Bianchini *et al*, J. Phys. Chem. Lett. **5**, 467-473 (2014)

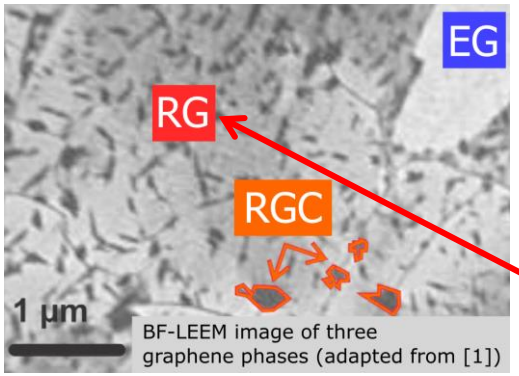
- top-fcc the most favorable of all configurations that appear in experiments, according to DFT calculations with GGA-PBE + vdW functional
- all experimentally observed epitaxial configurations display similar E_{ads}

Rotated G domains also appear

graphene growth via carbide conversion requires lower temperatures than the growth on bare nickel and always results in the EG



Characterization of different domains with XPS



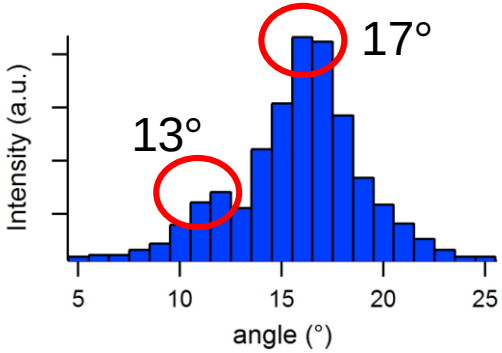
Ni_2C formation underneath G in RG domains = RGC domains

formed after the graphene is fully grown and the sample is cooled down to room temperature upon segregation of dissolved excess carbon.

EG – epitaxial graphene on Ni(111)
RG – rotated graphene on Ni(111)
~~**EGC** – epitaxial graphene on Ni(111) with Ni_2C underneath G~~
RGC – rotated graphene on Ni(111) with Ni_2C underneath G

C. Africh *et al*, Sci. Rep. **6**, 19734 (2016)

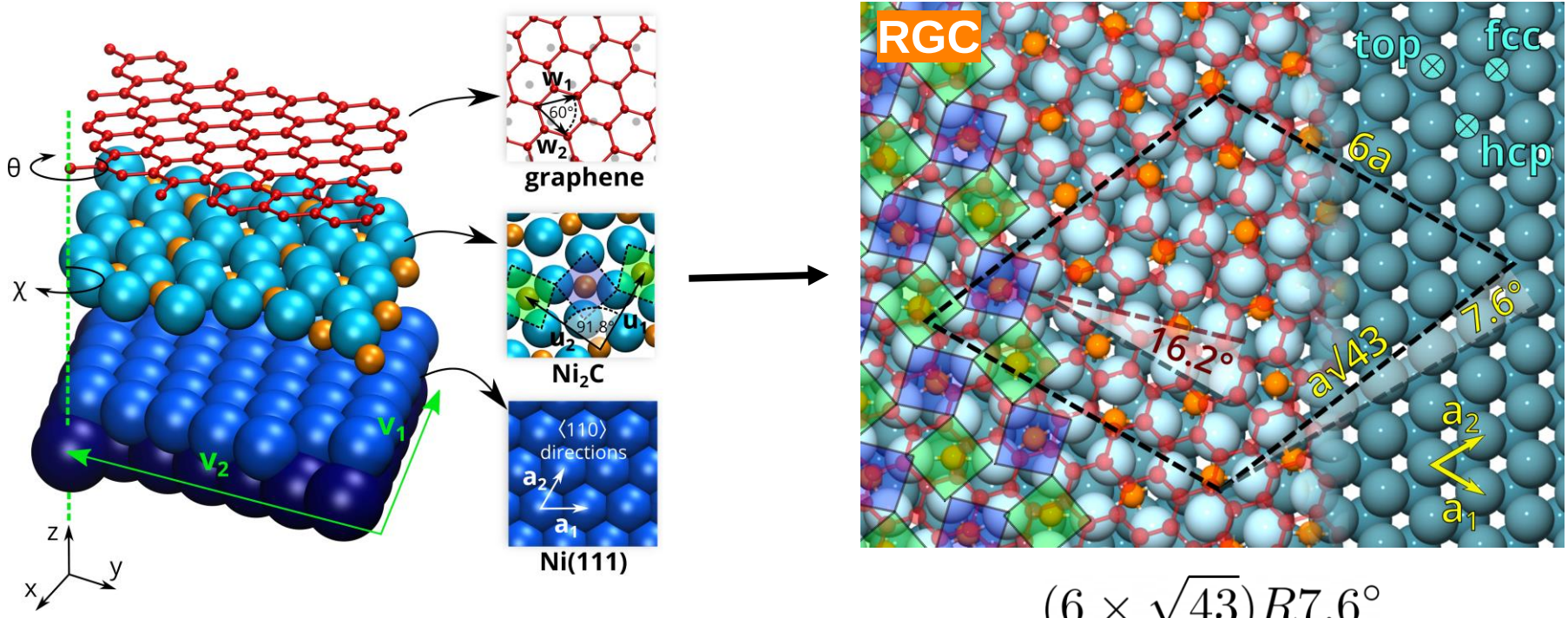
many angles of RG domains are observed, abundance of 13 and 17 domains



Why carbide forms only under RG and not under EG?

Modeling the RGC structure

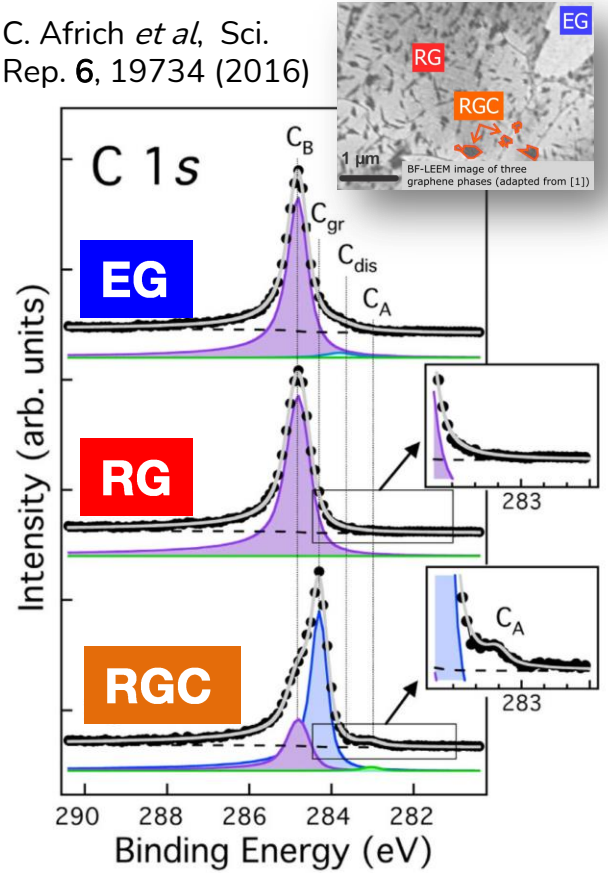
- **challenge of matching 3 different lattices** - construct the minimum periodically repeated cell able to accommodate hexagonal Ni(111), quasi squared Ni2C and G rotated by angle close to 13 or 17 degrees

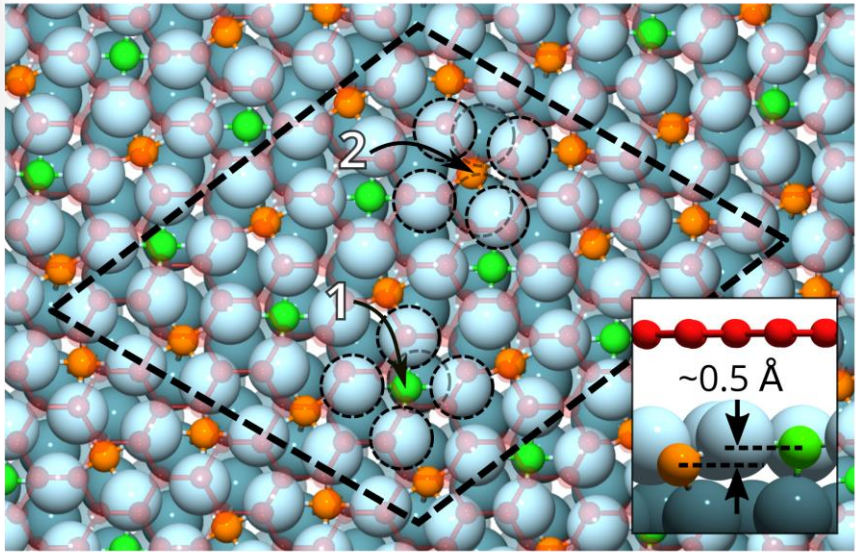


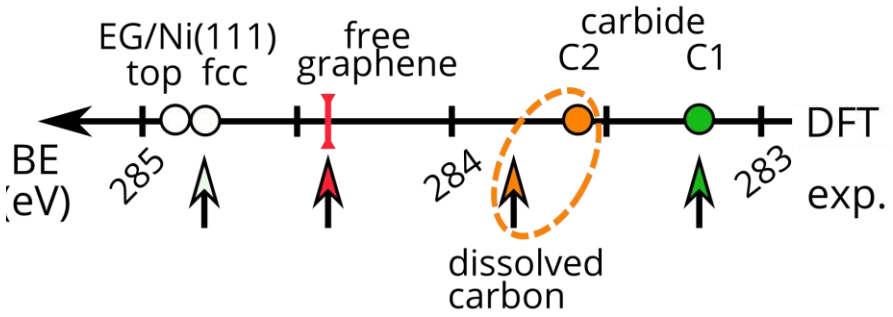
$$(6 \times \sqrt{43})R7.6°$$

Comparison of calculated and measured XPS spectra

C. Africh *et al*, Sci. Rep. **6**, 19734 (2016)





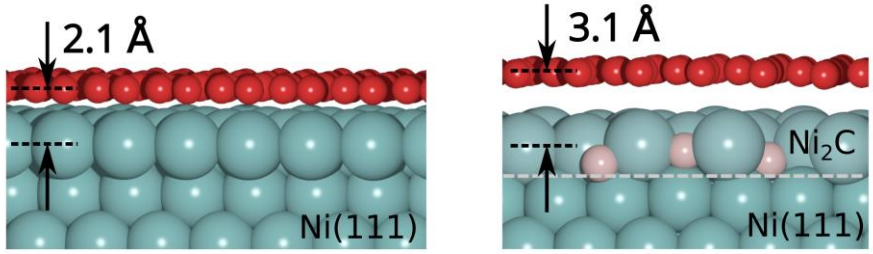


two types of C atoms of Ni_2C with different Ni-coordination

C 1*s* core-level shifts are calculated with DFT by constructing C pseudopotential with one missing core electron

The influence of carbide on the properties of G

EG (top-fcc) **EGC**



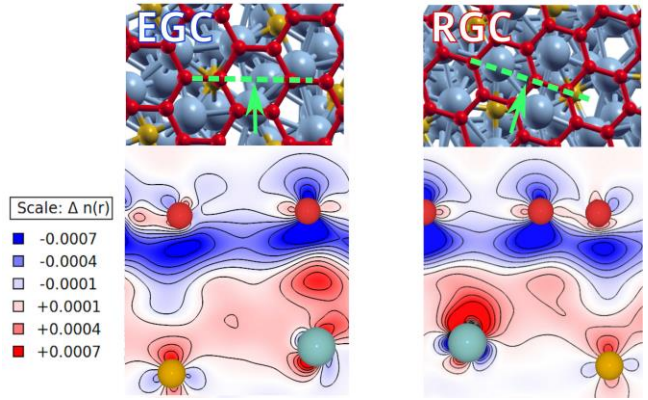
E_{ads} = -0.17 eV/C ⟶ E_{ads} = -0.10 eV/C

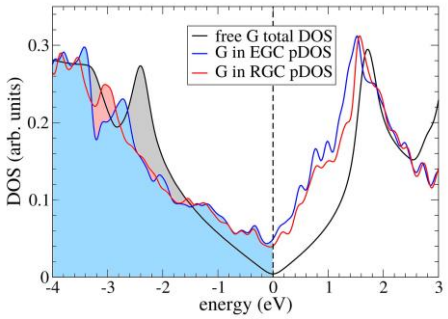
strong chemisorption **weak physisorption**

(calculated with GGA-PBE + vdW-DF2)

- carbide decouples G from the nickel surface
- carbide decouples G from the nickel surface - no difference in G electronic structure in EGC and RGC

very small electronic charge transfer from graphene to Ni atoms of Ni_2C

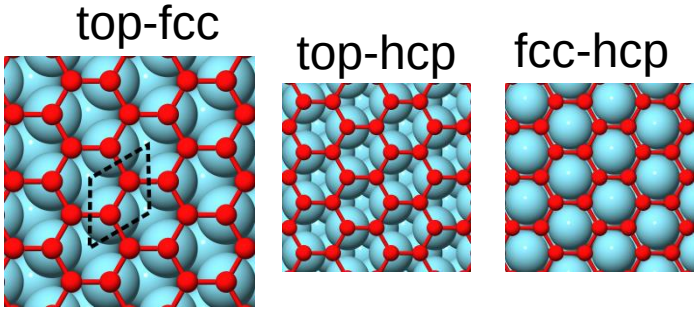




electronic structure of G does not depend on the rotation angle when Ni_2C is present underneath

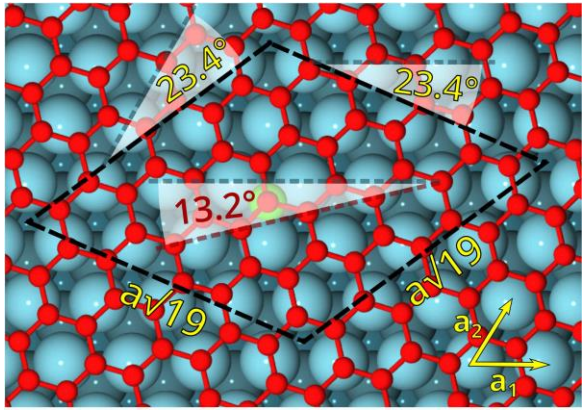
How the G rotation affects structural stability?

we construct smaller supercell that can accommodate G rotated by ~13° to compare the total energy of EG and RG structures
(38 C atoms and 19 Ni atoms per layer)



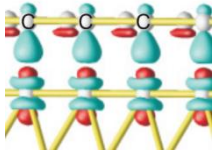
top	**-0.23 eV**
fcc	-0.11 eV
hcp	-0.08 eV

$(\sqrt{19} \times \sqrt{19})R\ 23.4°$

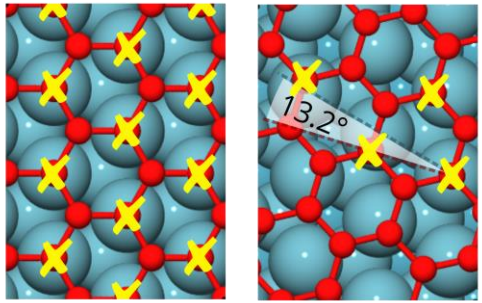


E(**RG**) – *E*(**EG**) = 1.48 eV
directly from DFT calc.

top sites the most important – overlap of Ni $3d_z^2$ orbitals and G π orbitals is essential for G stability



F. Mittendorfer *et al*, Phys. Rev. B **84**, 201401(R) (2011)

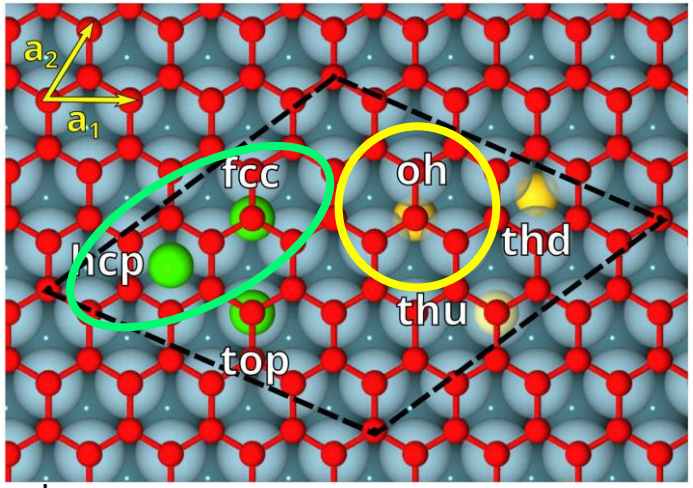


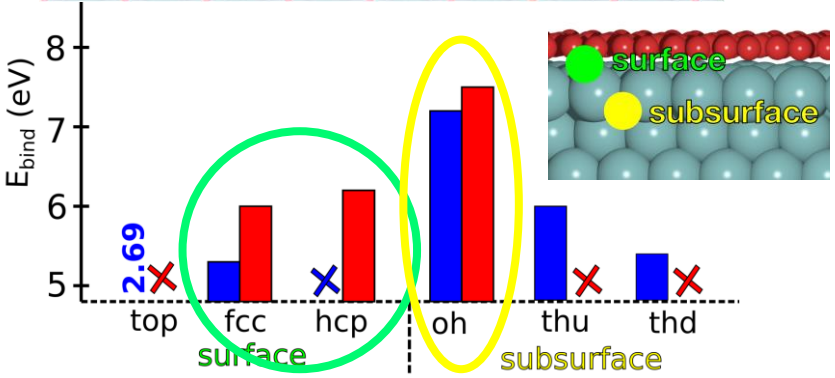
simple count of C atoms sitting in *top* sites can yield roughly the total energy difference between EG and RG

$$(19 - 8) \times (0.23 - (0.11 + 0.08)/2) = 1.49 \text{ eV}$$

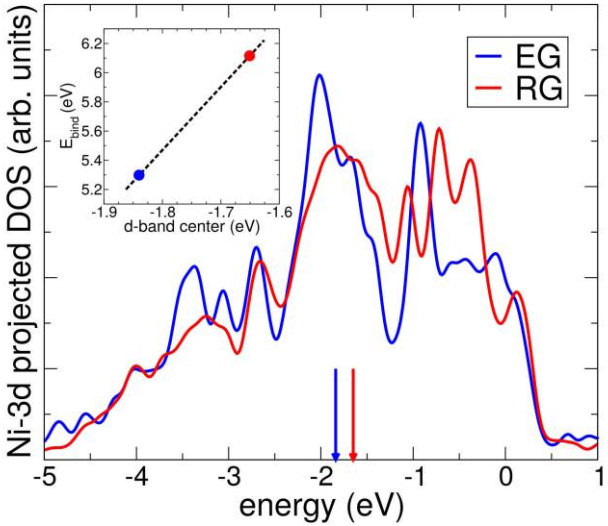
G rotation and the reactivity of the nickel surface

binding sites underneath G





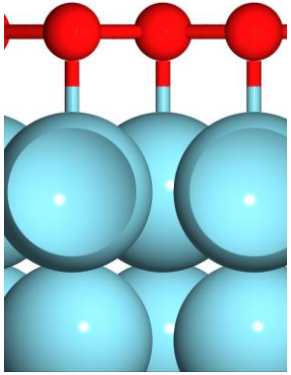
binding on the nickel surface

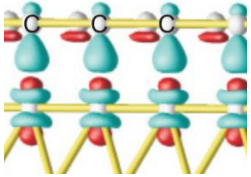


Ni 3d states centers under EG is 0.2 eV lower than under RG – the reactivity under EG is reduced, thus the destabilization of C atom in fcc and hcp sites under EG

binding in nickel subsurface
the most favorable site both in EG and RG structures is the subsurface octahedral site (*oh*)

Locking of the nickel surface under EG

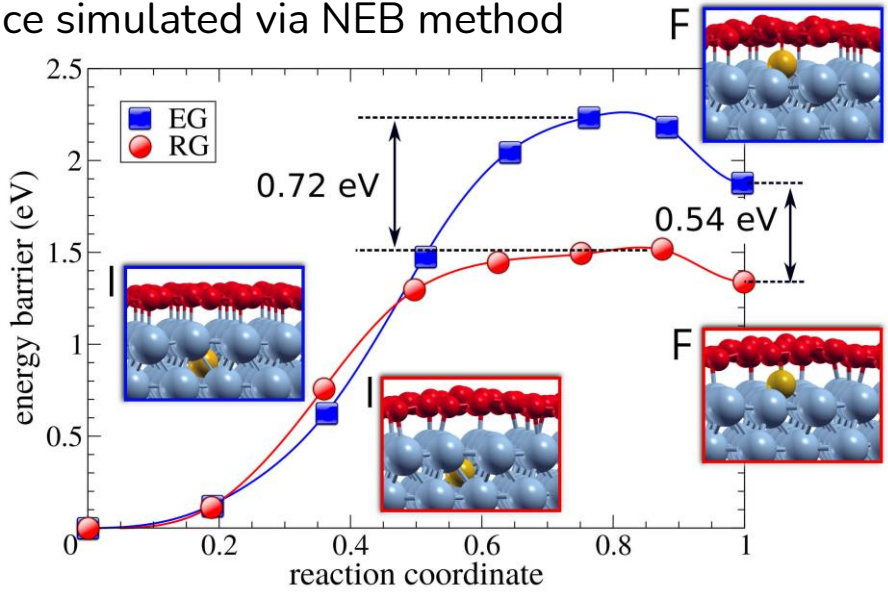




strong G-Ni bonds in EG structure are holding tight the nickel surface – any process that requires the movement of surface Ni atoms is more unlikely to happen under EG than under RG

barrier under EG is 0.72 eV higher than under RG due to **locking** of the nickel surface

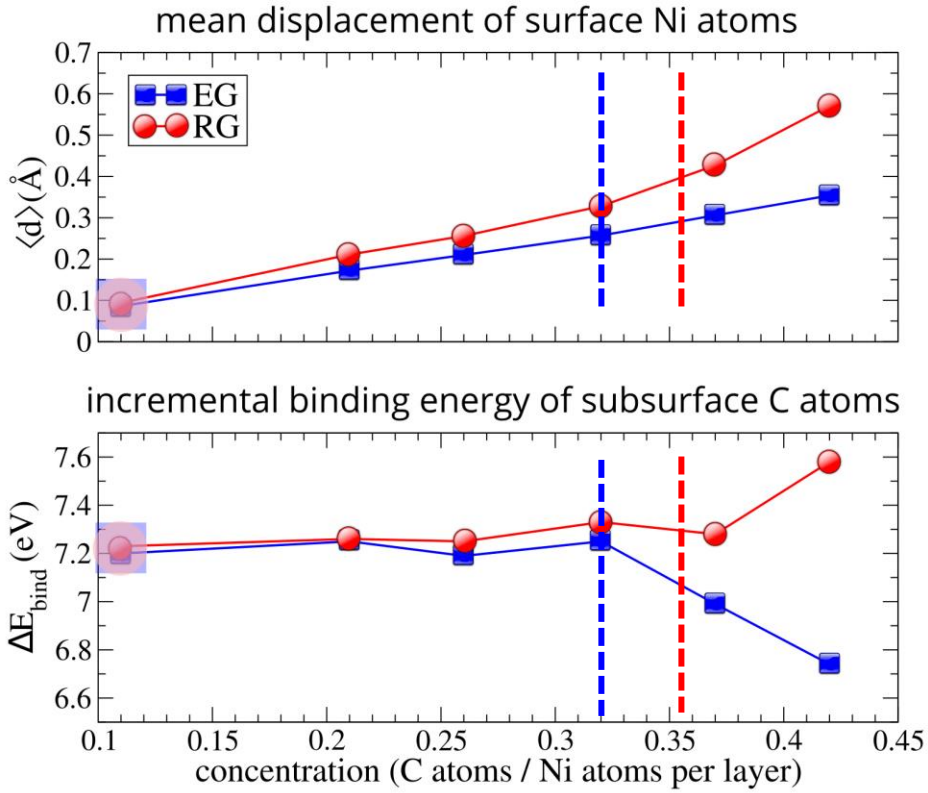
example : segregation of individual C atom from subsurface to the nickel surface simulated via NEB method

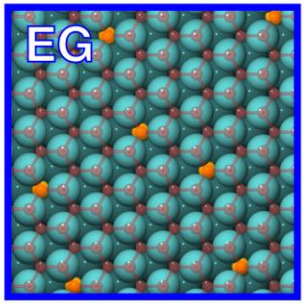


for the Ni_2C to form high concentration of $\Theta \sim 0.5$ ML of near surface C atoms is needed that must be supplied from the inner layers

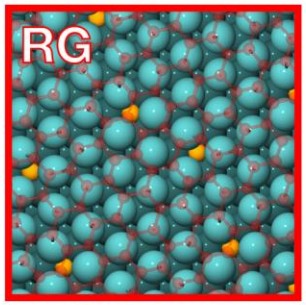
Increase the concentration of subsurface carbon

Upon cooling the sample dissolved carbon atoms segregate from bulk and occupy regions near the surface – in calculations add C atoms one-by-one to the *oh* sites to increase subsurface concentration





at concentrations higher than Θ ~ 0.32 ML it becomes progressively harder to add more C atoms – consequence of *locking* of Ni surface by EG



heavy restructuring of nickel surface under RG begins at carbon concentration of Θ ~ 0.35 ML

Summary

- nickel carbide completely decouples graphene from the surface, the rotation doesn't play any role anymore in G properties
- G rotation increases nickel reactivity as compared to EG
- EG locks the nickel surface and hinders the carbon segregation as surface Ni atoms resist to move and make space for C atoms
- in line with experiments carbide forms solely under RG as graphene rotation "unlocks" the nickel surface

Acknowledgements

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