First-principles study of nickel reactivity under 2D cover: Ni$_2$C formation at the graphene/Ni(111) interface

S. Stavrić[1,2], S. del Puppo[1], Ž. Šljivančanin[2], M. Peressi[1]

[1]Physics Department, University of Trieste, Italy [2]Vinča Institute of Nuclear Sciences, University of Belgrade, Serbia

UNIVERSITY OF TRIESTE

VINČA INSTITUTE

INTRODUCTION

In recent experiments of graphene (G) growth on Ni(111) surface, besides epitaxial G perfectly aligned with the substrate (**EG**), rotated G domains without (**RG**) and with nickel carbide monolayer (Ni$_2$C) underneath G (**RGC**) were observed [1]. Intriguingly, carbide is detected exclusively within RG domains. In this study we modeled G/Ni(111) and G/Ni$_2$C/Ni(111) heterostructures and performed first-principles calculations to reveal the microscopic mechanisms governing the formation of Ni$_2$C under G cover. We explain the necessity of G rotation for enabling the increase of subsurface carbon concentration needed to trigger the structural phase transition, in line with strong experimental evidence.


EG
RG
RGC

1 μm

BF-LEEM image of three graphene phases (adapted from [1])
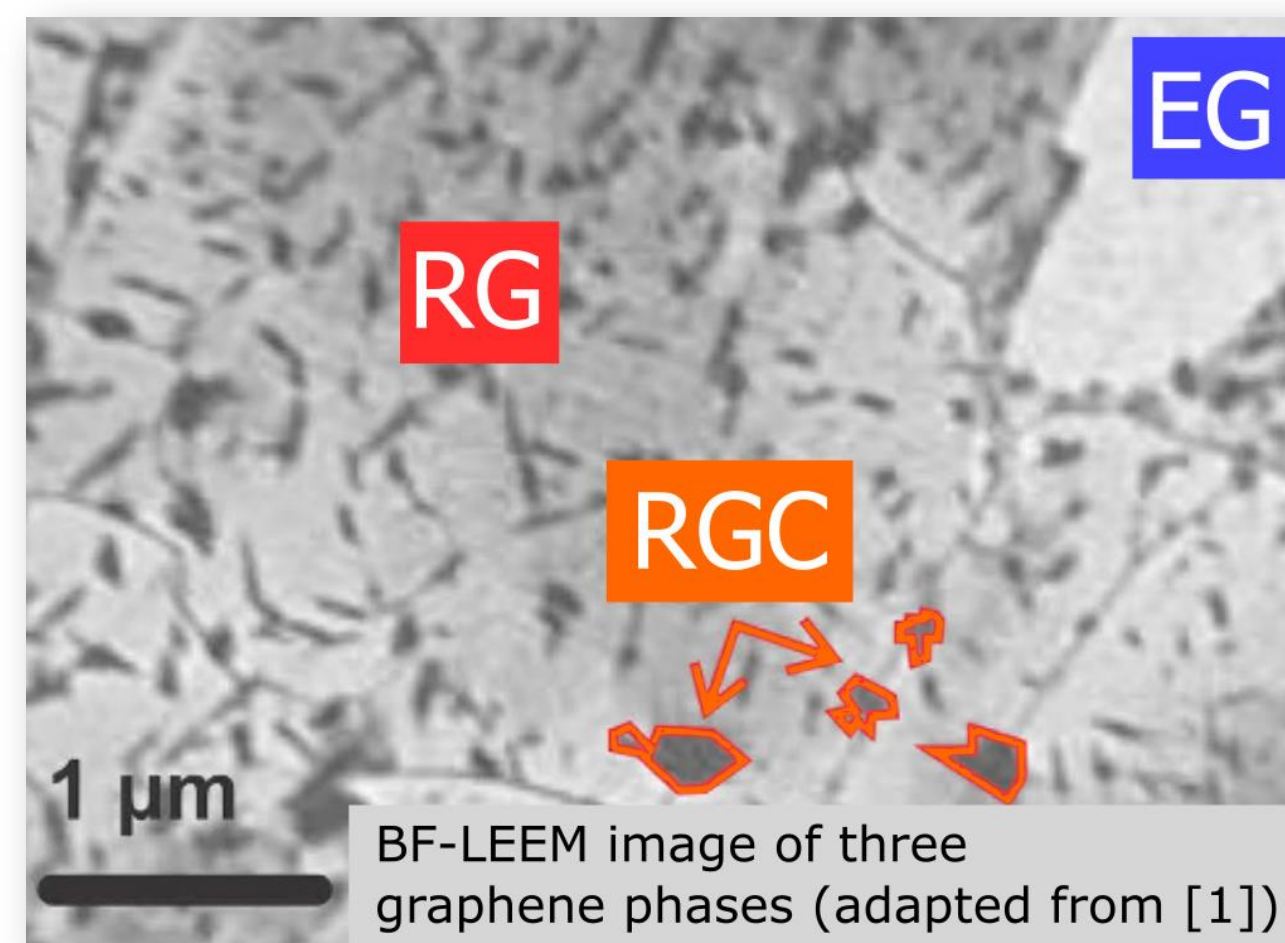
- **EG** – epitaxial graphene on Ni(111)
- **RG** – rotated graphene on Ni(111)
- ~~**EGC** – epitaxial graphene on Ni(111) with Ni$_2$C underneath G~~
- **RGC** – rotated graphene on Ni(111) with Ni$_2$C underneath G

WHY NICKEL CARBIDE FORMS ONLY UNDER THE ROTATED GRAPHENE?

A COMPUTATIONAL CHALLENGE

θ
χ
w$_1$ 60° w$_2$
graphene
Ni$_2$C
(110) directions a$_2$ a$_1$
Ni(111)
z y x
v$_2$ v$_1$
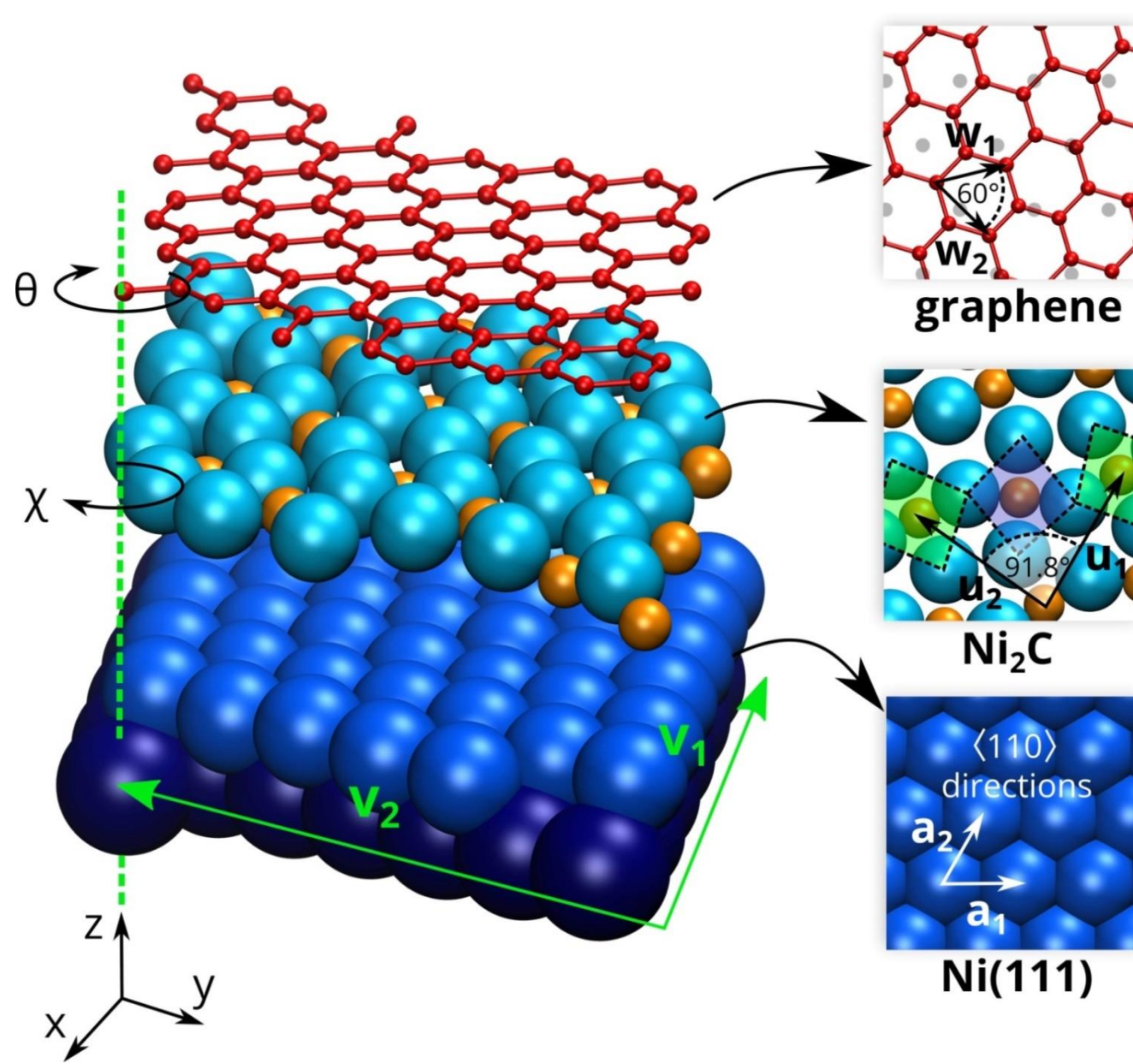
EXPERIMENTS - most abundant RG domains are 17° and 13°

GOAL – construct the minimum periodically repeated cell that can accommodate 3 lattices:
- hexagonal Ni(111)
- quasi-squared Ni$_2$C
- G rotated by 17° or 13° (try both and use the smaller one)
In this way we constructed RGC.

When G is aligned with Ni(111) the EGC structure is obtained. It is already reported [3], but RGC is not!

Computational details
- Quantum ESPRESSO - density functional theory (DFT) code based on plane waves and pseudopotentials
- GGA-PBE exhange-correlation functional with van der Waals corrections employed (vdw-DF2)

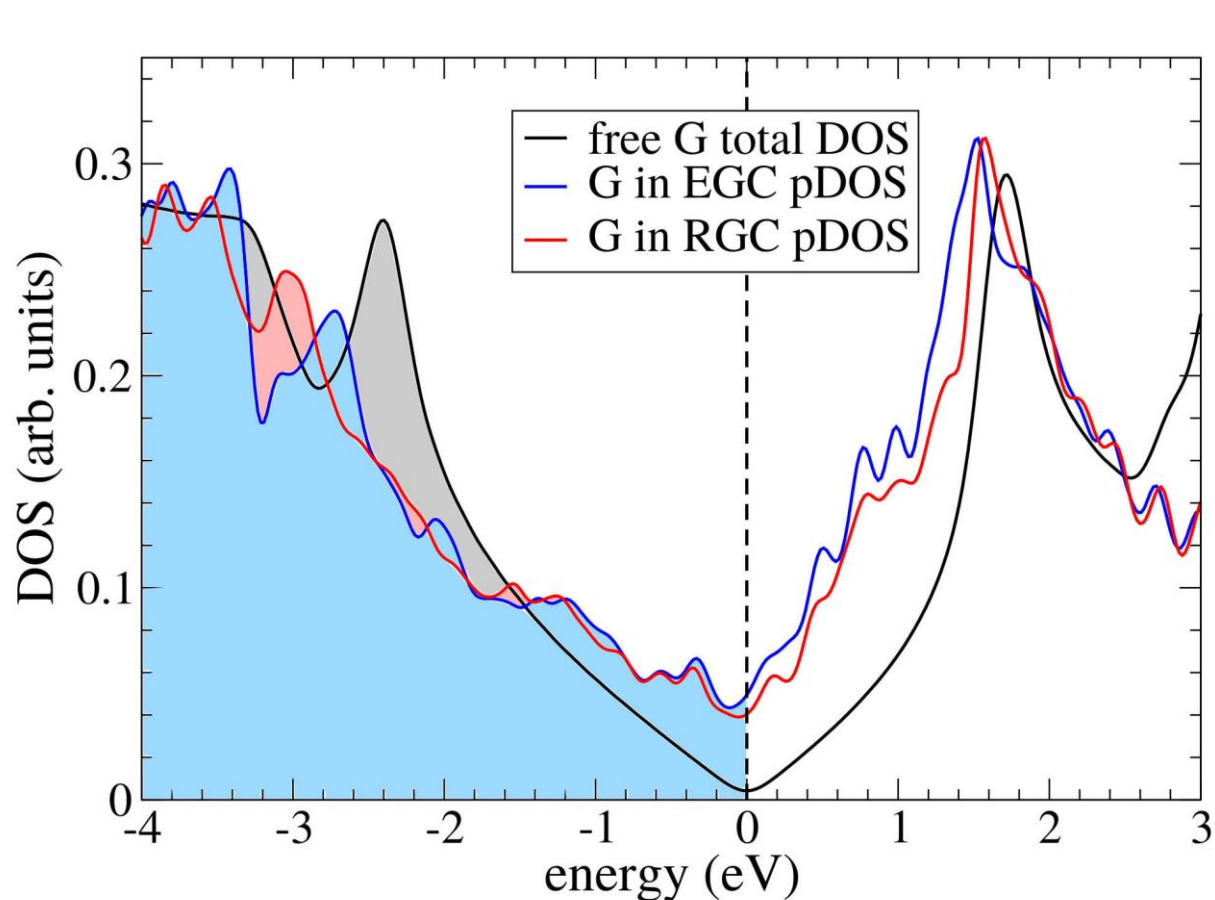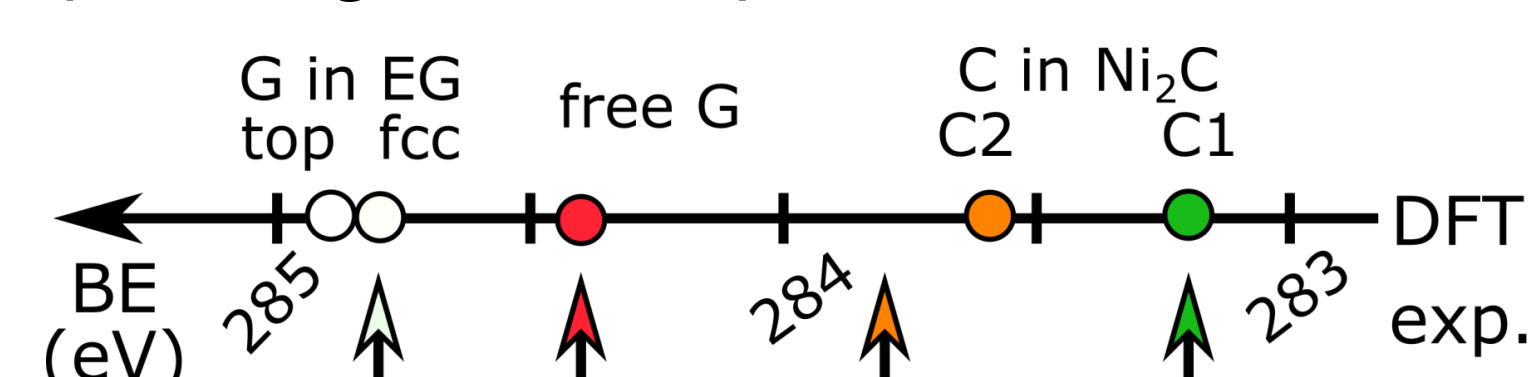QUANTUM ESPRESSO

CARBIDE STRUCTURES CHARACTERIZATION

In RGC structure G is rotated by ~ 16°. Carbide increases graphene-nickel distance by 1 Å both in **EGC** and **RGC** !

RGC
top fcc
6a
hcp
15.5°
16.1°
7.6°
a√43
a$_2$ a$_1$
$(6 \times \sqrt{43})R7.6°$
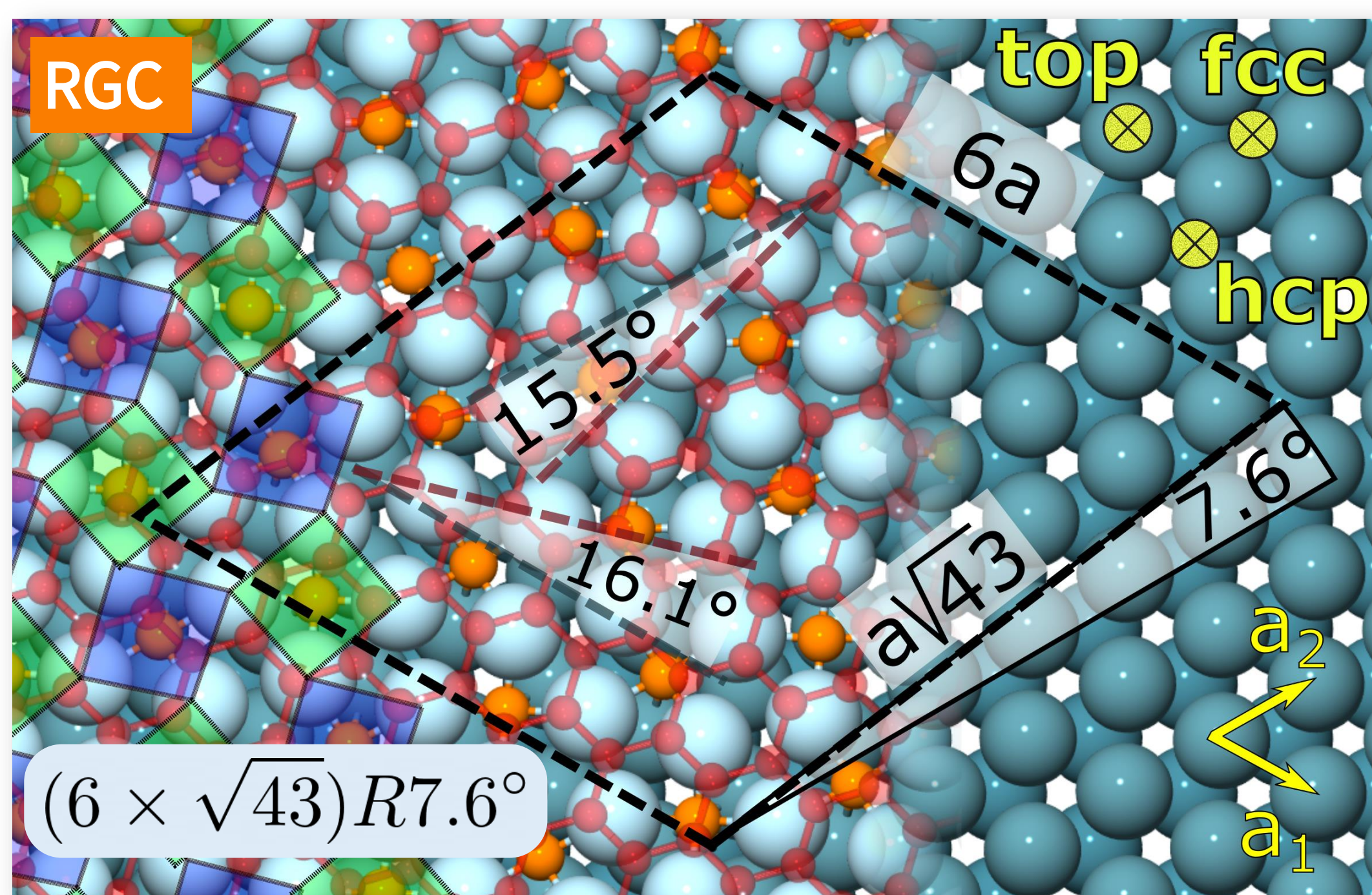
Very small G adsorption energy (E_{ads}) both in **EGC** and **RGC** of only -0.10 eV/C$_G$ as compared to -0.16 eV/C$_G$ found in EG/Ni(111) reveal **weak physisorption** with modest charge transfer from G to carbide


0.4 Å 3.1 Å
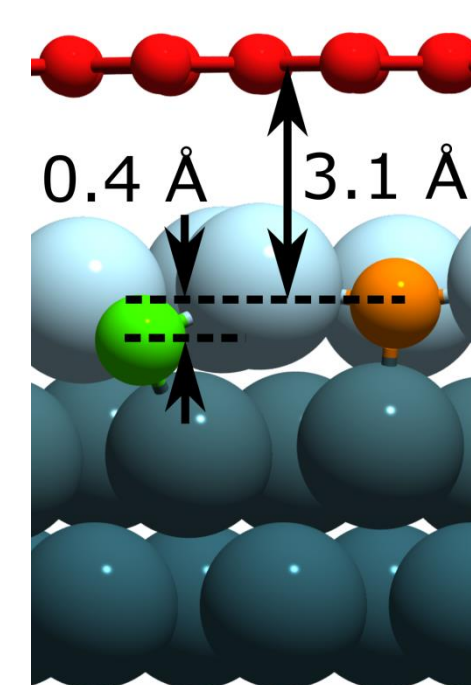
DFT-calculated C1s core-level shifts of carbon species agree with experimental measurements

G in EG top fcc | free G | C in Ni$_2$C C2 C1
BE (eV) 285 | 284 | 283
DFT exp.

free G total DOS
G in EGC pDOS
G in RGC pDOS

DOS (arb. units)
energy (eV)

Atomic projected density of states very similar to that of free G. Dirac cone is restored. Carbide totally decouples G from Ni in both **EGC** and **RGC** . Both structures equally stable – we need to take a step back to find out why carbide forms only under **RG**.

CARBIDE STRUCTURES FORMATION: bulk-to-surface carbon segregation

Step back – construct G/Ni(111) interfaces with no carbide in between (**EG** and **RG**) and put additional C atoms in surface and subsurface. Study the effects that G cover has on C atoms. Progressively increase the C concentration and inspect the structural stability
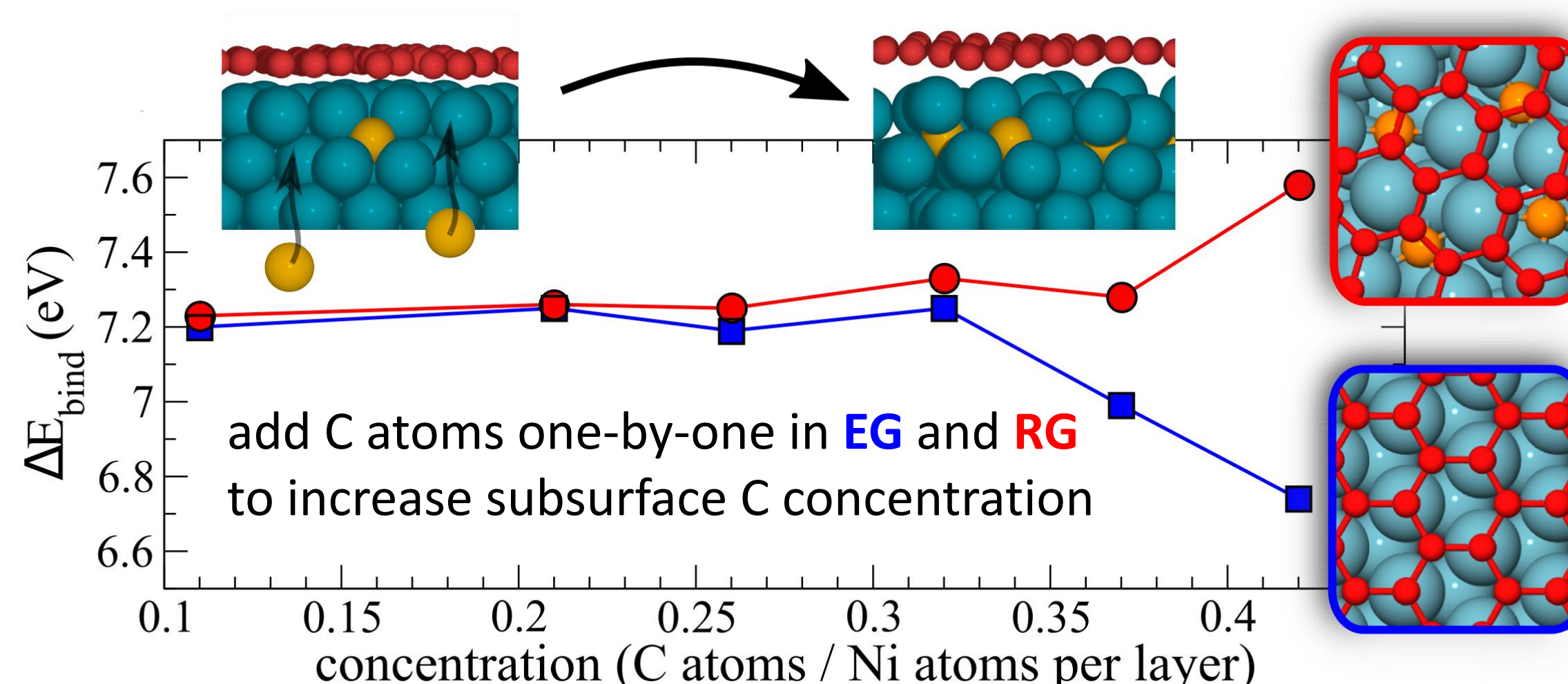

EG
RG
13.2°

F
I
I
F
0.72 eV
0.54 eV
energy barrier (eV)
reaction coordinate
EG
RG
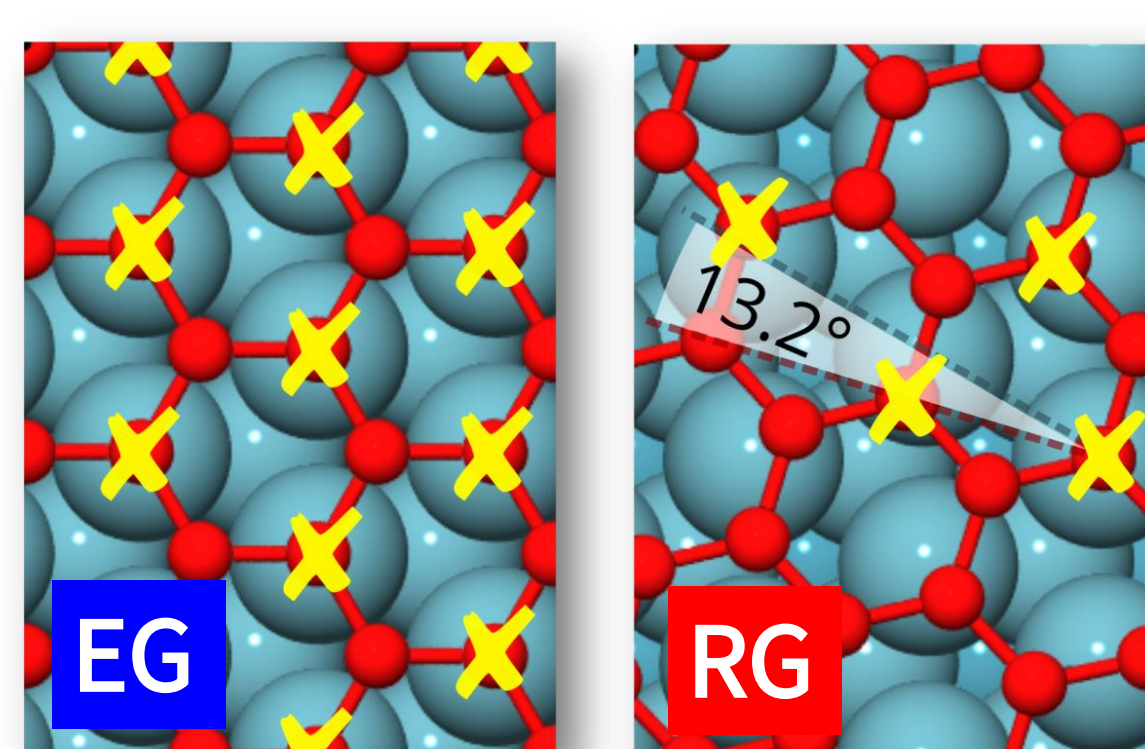
C atoms of graphene (C$_G$) can sit in *top* (X), *fcc,* and *hcp* site (image on the left). Each site contribute to E_{ads} by -0.23, -0.11, and -0.08 eV, respectively. Number of C$_G$ atoms in *top* sites determines the G/Ni(111) stability and explains why **EG** is more stable than **RG**
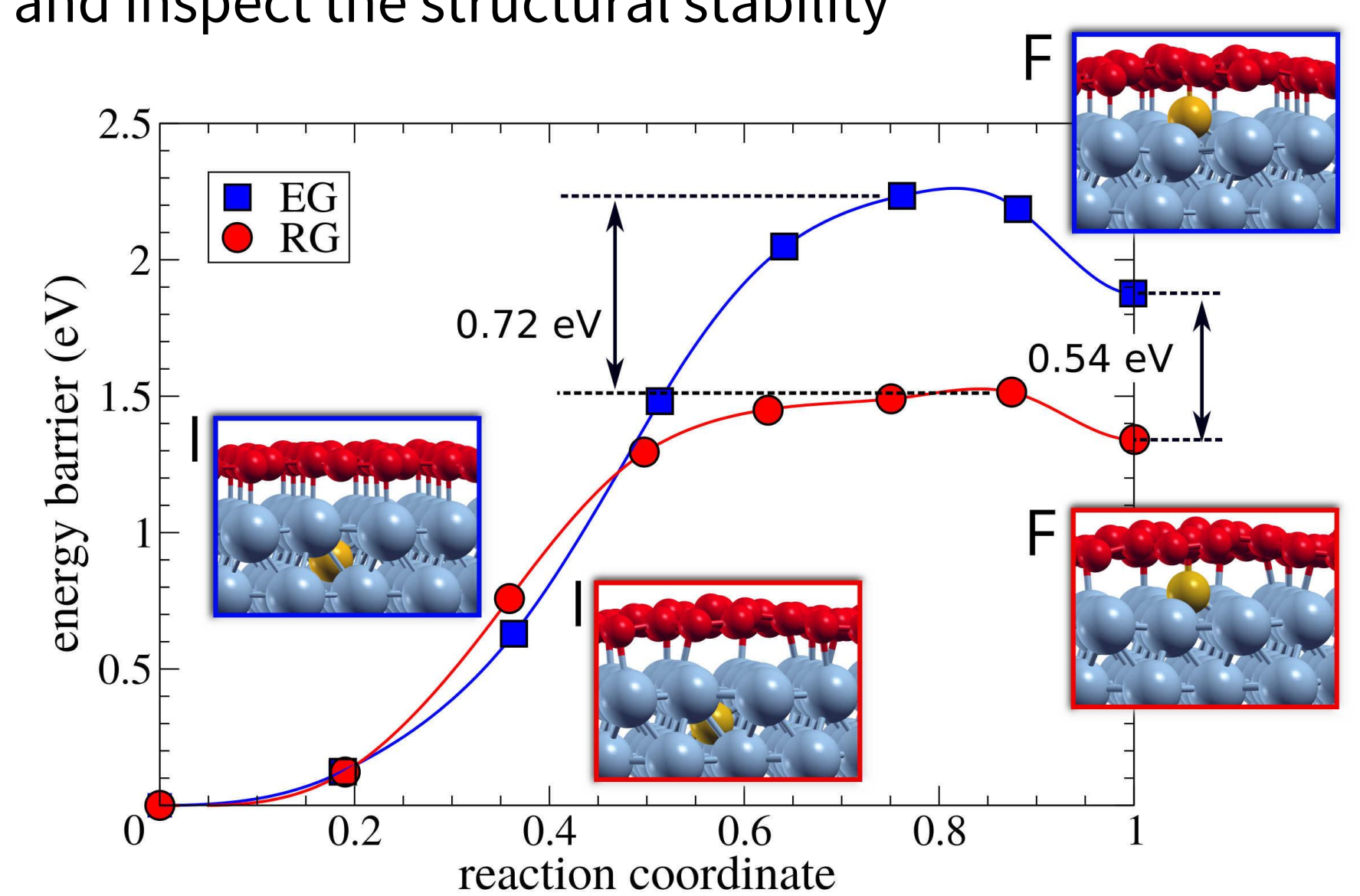
Diffusion of single C atom from subsurface to surface under G cover reveals **the locking** mechanism – surface Ni atoms must move to allow C atom to pass. **EG** hinders their displacement. This does not happen under **RG** and therefore smaller diffusion barrier

Individual C atom bound in Ni(111) – binding energy of C atom (E_{bind}) on Ni(111) surface of 7.0 eV is reduced to 5.3 eV and 6.0 eV when it is covered with **EG** and **RG**

Increase of subsurface C concentration is easier under **RG**, as the incremental binding energy (ΔE_{bind}) increases with C concentration increase. Under **EG** it is completely opposite.

ΔE_{bind} (eV)
concentration (C atoms / Ni atoms per layer)

add C atoms one-by-one in **EG** and **RG** to increase subsurface C concentration

CONCLUSIONS
- ✓ G cover reduces Ni surface reactivity
- ✓ EG locks Ni surface and hinders C segregation
- ✓ carbide forms only under the rotated G
- ✓ carbide totally decouples G from Ni and restores its semi-metallicity

REFERENCES

1. C. Africh, et al., *Sci. Rep.* **6**, 19734 (2016)
2. S. Stavrić, et al., First-principles study of nickel reactivity under 2D cover: Ni$_2$C formation at rotated graphene/Ni(111) interface, *submited* (2020)
3. P. Jacobson, et al., *ACS Nano* **6**, 3564 (2012)

Graphene online 2020