CVD graphene/Ni interface evolution in acidic media

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Summary

INTRODUCTION

- ✓ The graphene/Ni interface
- ✓ The basic role of the environment
- ✓ CVD graphene /Ni interface as a prototypical system

THE EXPERIMENTAL APPROACH

- ✓ HOPG graphite = graphene multilayer
- ✓ HOPG blistering in acidic media
- ✓ The experimental set-up

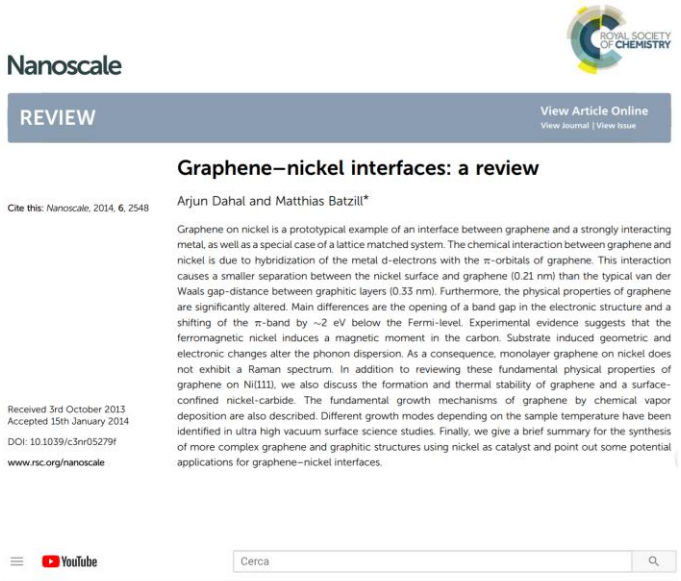
EXPERIMENTAL RESULTS

- ✓ The bare Ni substrate
- ✓ 50 nm CVD graphene/Ni
- ✓ 100 nm CVD graphene/Ni

DISCUSSION

- ✓ The interpretative model
- ✓ The Pourbaix diagrams

CONCLUSIONS



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REVIEW

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Graphene–nickel interfaces: a review

Arjun Dahal and Matthias Batzill*

Cite this: *Nanoscale*, 2014, **6**, 2548

Graphene on nickel is a prototypical example of an interface between graphene and a strongly interacting metal, as well as a special case of a lattice matched system. The chemical interaction between graphene and nickel is due to hybridization of the metal d-electrons with the π-orbitals of graphene. This interaction causes a smaller separation between the nickel surface and graphene (0.21 nm) than the typical van der Waals gap-distance between graphitic layers (0.33 nm). Furthermore, the physical properties of graphene are significantly altered. Main differences are the opening of a band gap in the electronic structure and a shifting of the π-band by ~2 eV below the Fermi-level. Experimental evidence suggests that the ferromagnetic nickel induces a magnetic moment in the carbon. Substrate induced geometric and electronic changes alter the phonon dispersion. As a consequence, monolayer graphene on nickel does not exhibit a Raman spectrum. In addition to reviewing these fundamental physical properties of graphene on Ni(111), we also discuss the formation and thermal stability of graphene and a surface-confined nickel-carbide. The fundamental growth mechanisms of graphene by chemical vapor deposition are also described. Different growth modes depending on the sample temperature have been identified in ultra high vacuum surface science studies. Finally, we give a brief summary for the synthesis of more complex graphene and graphitic structures using nickel as catalyst and point out some potential applications for graphene–nickel interfaces.

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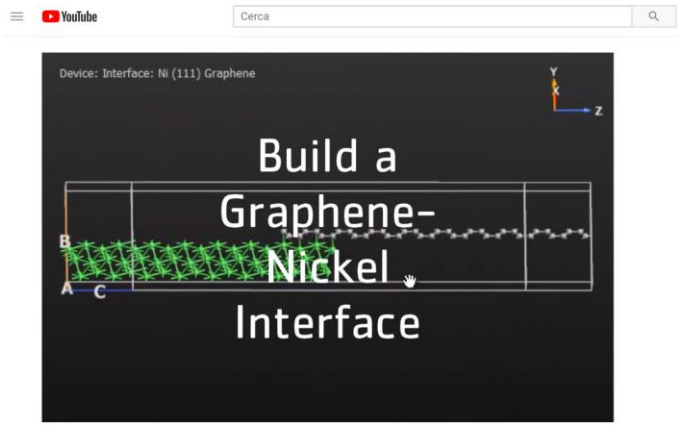
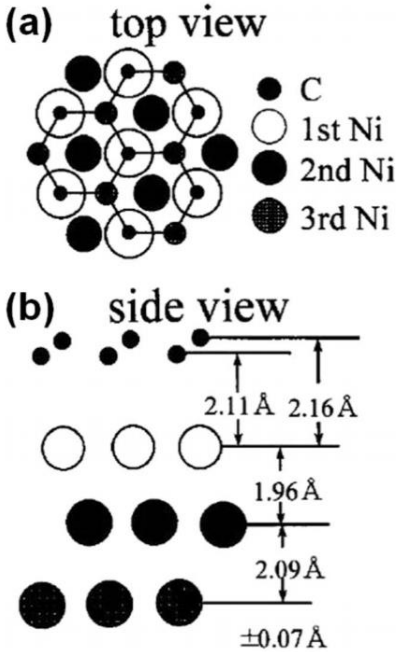
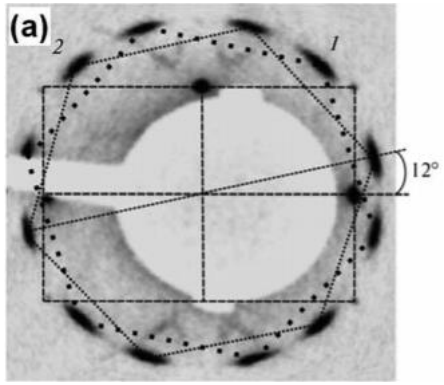
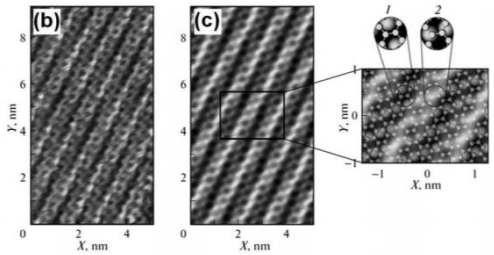


Graphene/Ni interface represents a prototypical interface between a strongly interacting metal (Ni) and an ultra-thin protective layer (Gr). In addition, it is a special case of a lattice matched system.



UHV



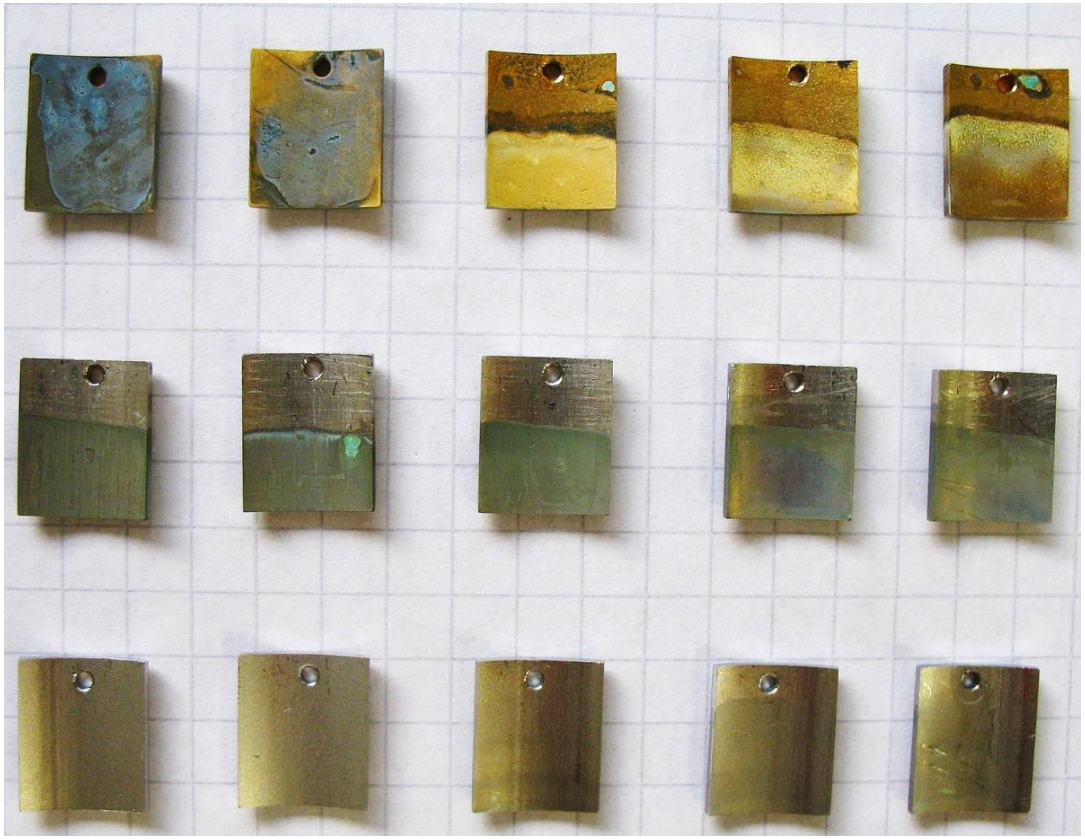


The basic role of the environment: e.g., sea-water effect

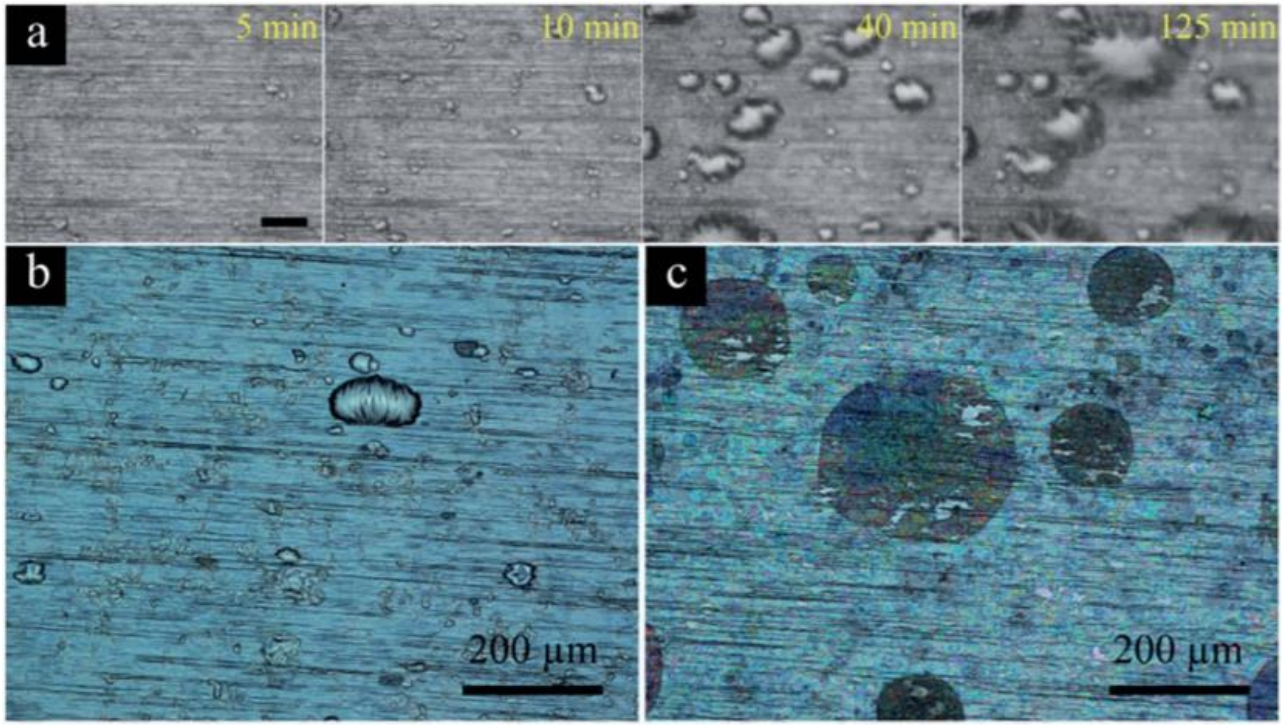
Aluminium-bronze alloys

Nickel alloys

Stainless steel specimens



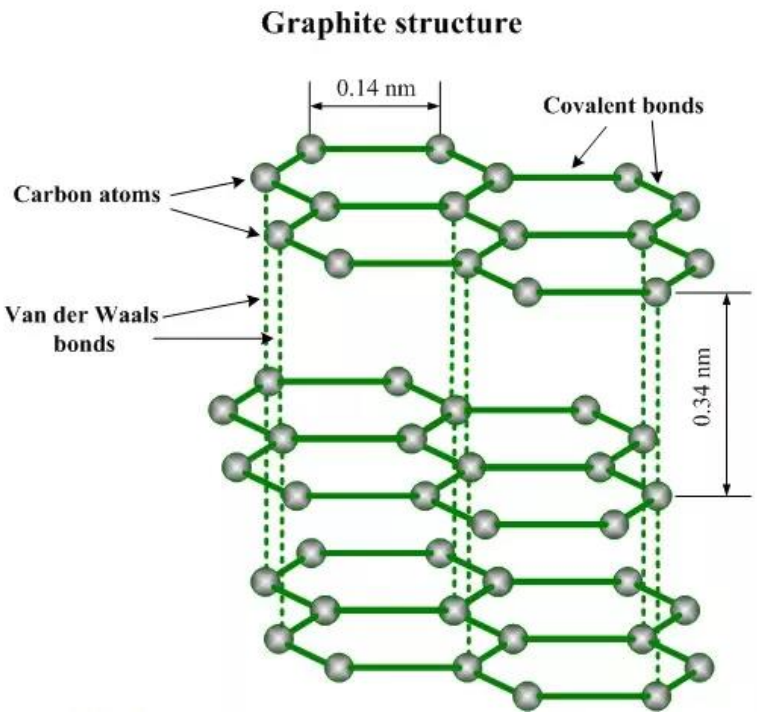
Evolution of blisters as a function of time in the CVD/Ni system immersed in acidic media.



WHY?

F. Yu *et al. RSC Adv.* (2016)

The experimental approach: HOPG as a multilayered graphene sheets system

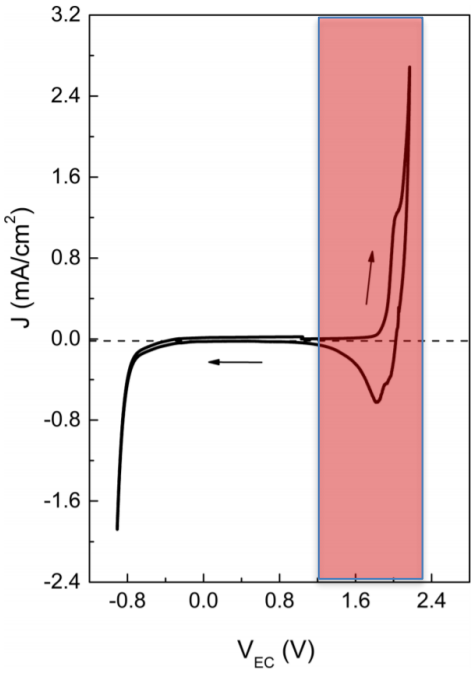


graphene sheet

multilayer

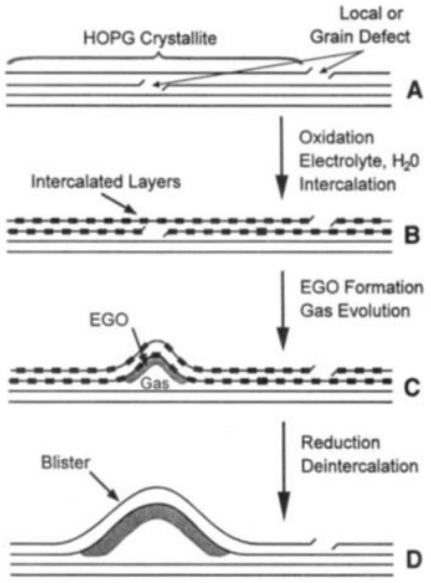
The experimental approach: HOPG blistering model in acidic media

$$C_x^+ y(H_2O)HSO_4^- + H_2O \rightarrow "C_xOH" + CO + CO_2 + O_2$$



R. Yivlialin *et al.,*

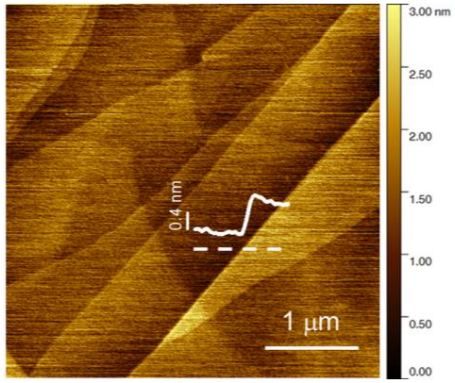
Langmuir (2018)



K. W. Hathcock *et al.,*

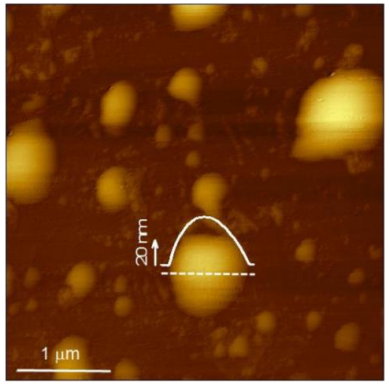
Anal. Chem. (1995)

pristine HOPG



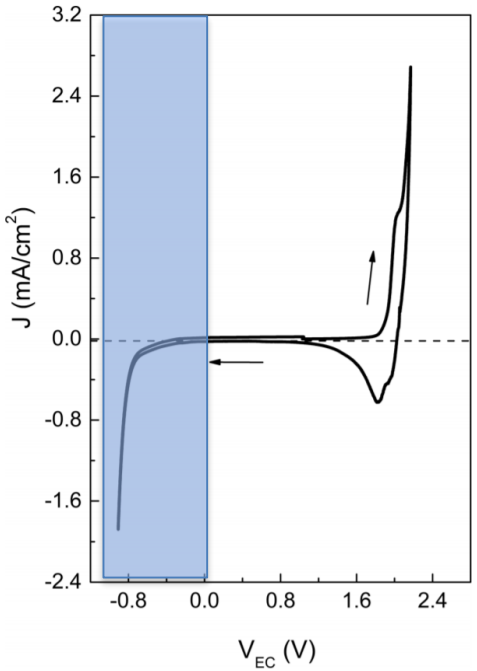
R. Yivlialin *et al., Langmuir* (2018)

post CV treatment



R. Yivlialin *et al., Appl. Mater.* (2017)

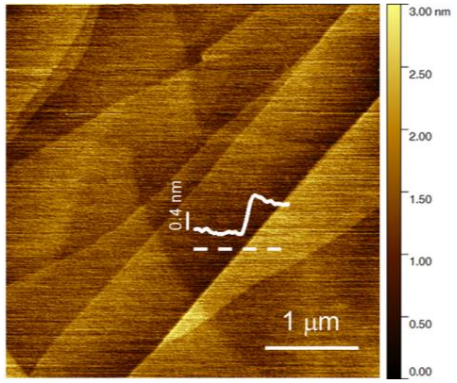
The experimental approach: HOPG blistering model in acidic media



R. Yivlialin *et al.,*

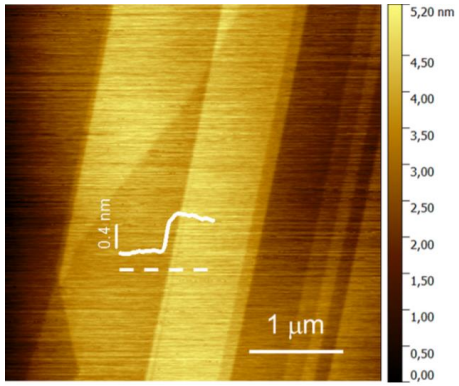
Langmuir (2018)

pristine HOPG



R. Yivlialin *et al., Langmuir* (2018)

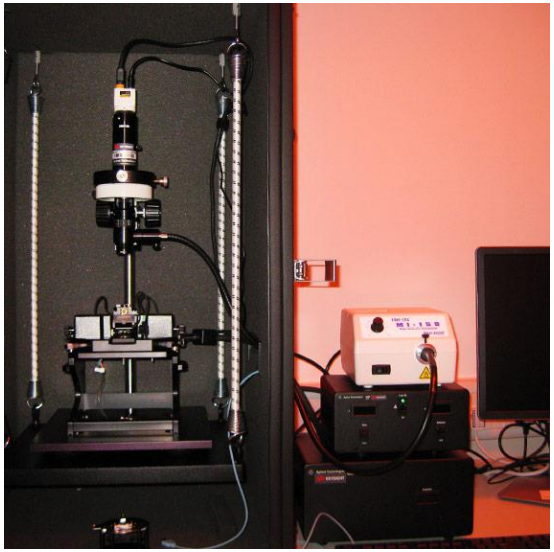
post CV treatment



R. Yivlialin *et al., Langmuir* (2018)

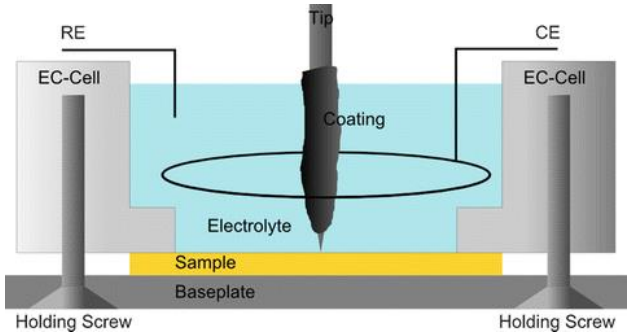
The experimental approach: set-up

Keysight 5500 EC-SPM



Both STM and AFM scanners can be used with the sample placed inside a protective atmosphere (Ar) at a defined temperature

EC-SPM system



Electrolyte purification

purification by Ar bubbling

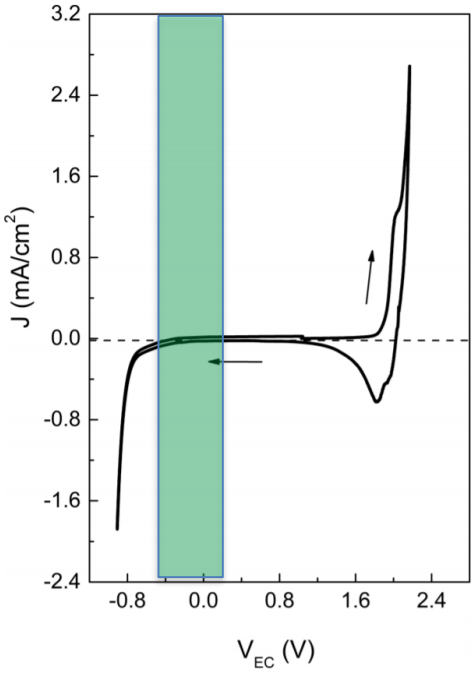
Sulfuric acid diluted in type 1 water (Merck-Millipore).

pH = 0.3

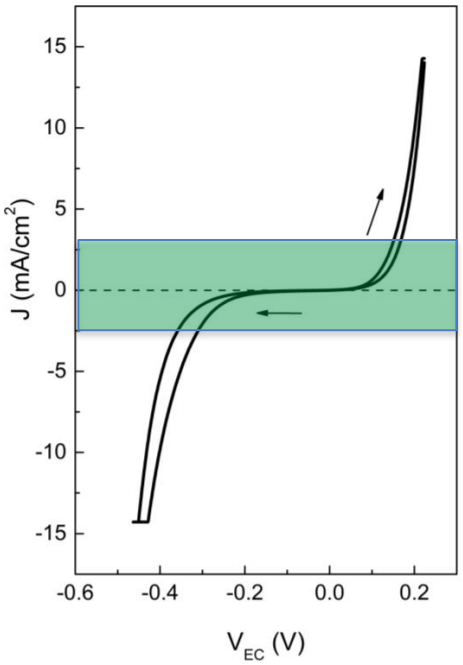
CVD graphene/Ni interface: results – bare nickel

Electrochemical characterization

HOPG



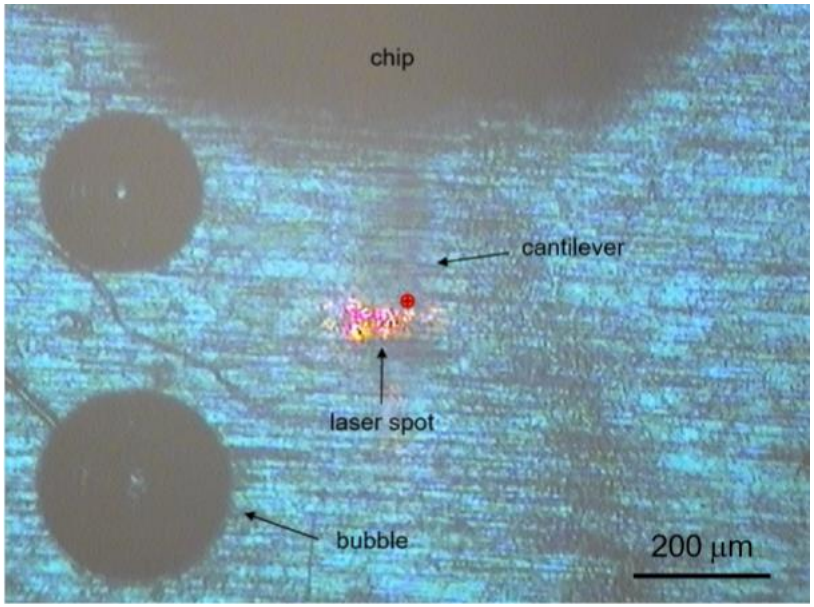
bare nickel



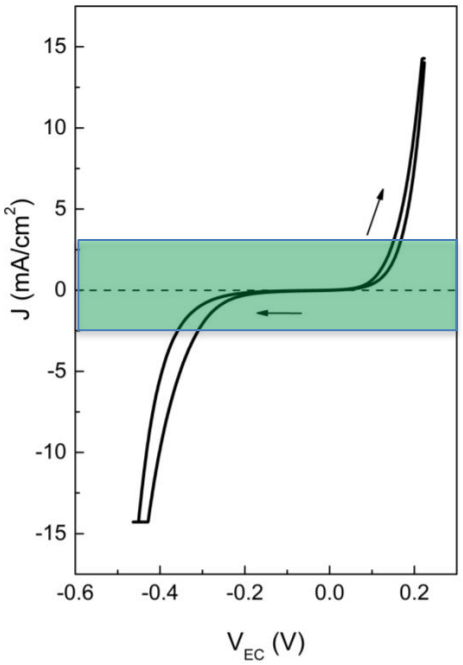
R. Yivlialin *et al., Langmuir* (2018)

CVD graphene/Ni interface: results – bare nickel

Electrochemical characterization



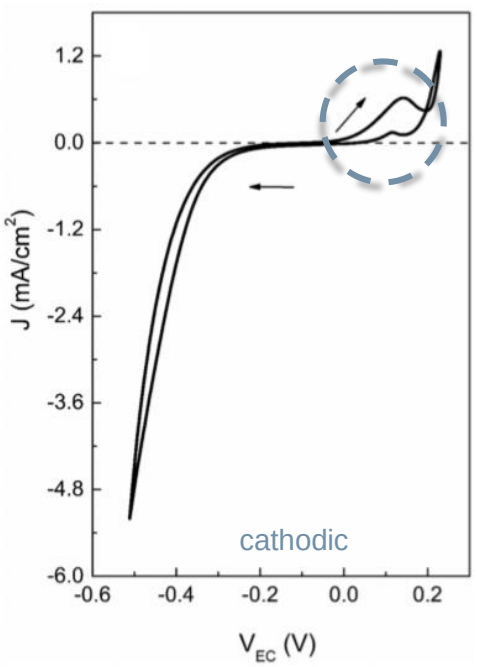
bare nickel



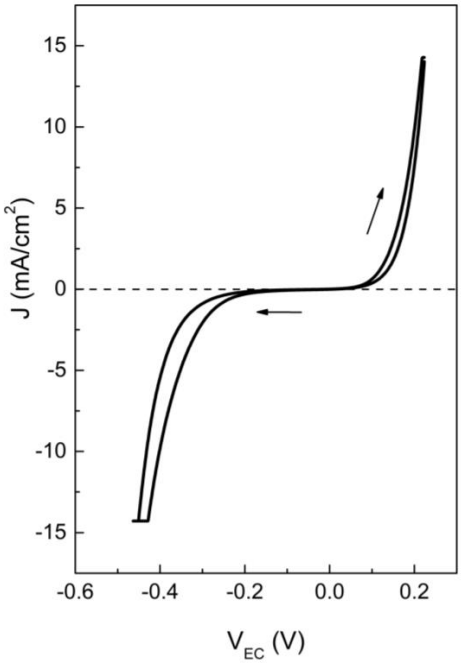
R. Yivlialin *et al., Langmuir* (2018)

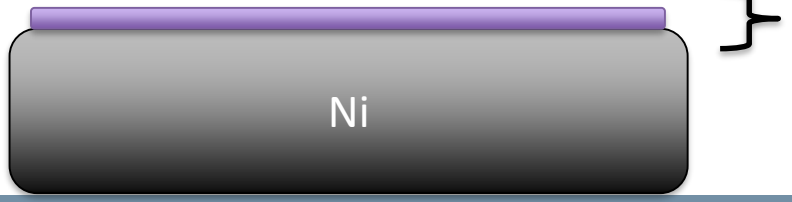
CVD graphene/Ni interface: results – 50 nm CVD graphene/nickel

50 nm CVD Gr



bare nickel



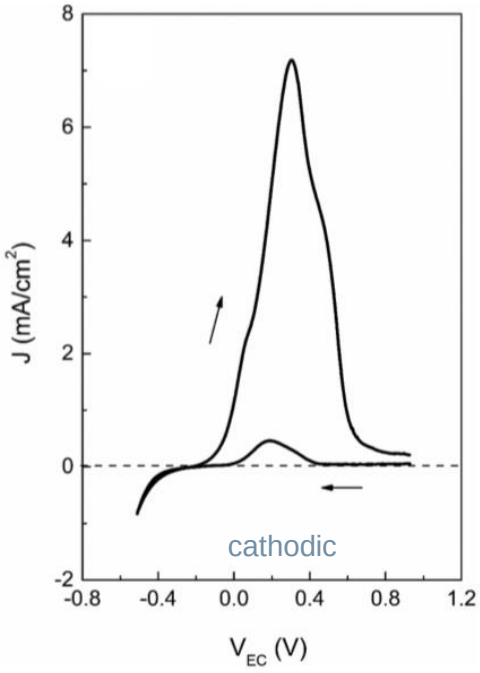


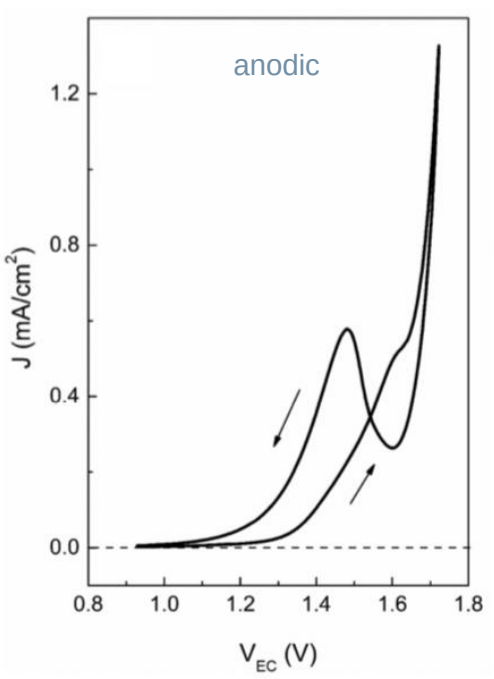
CVD Gr film thickness = 50 nm

R. Yivlialin *et al., Langmuir* (2018)

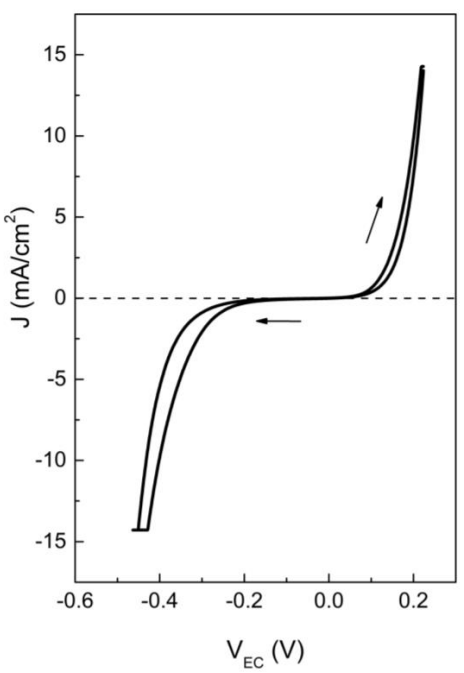
CVD graphene/Ni interface: results – 100 nm CVD graphene/nickel

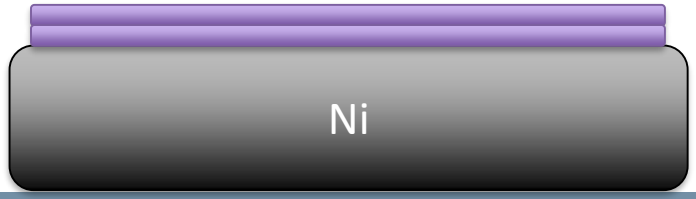
100 nm CVD Gr





bare nickel



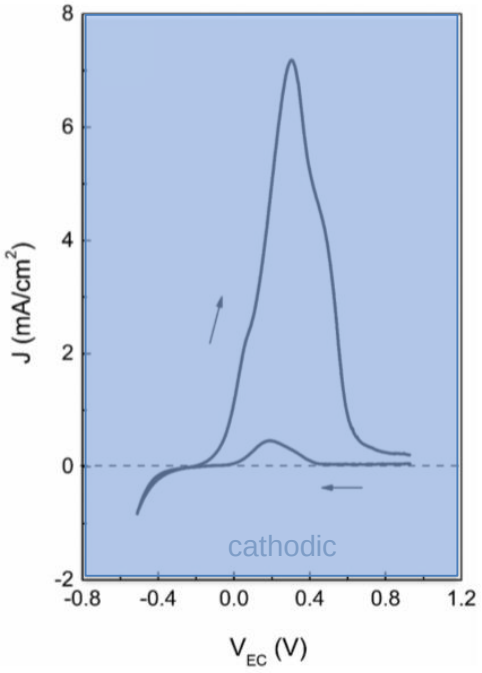


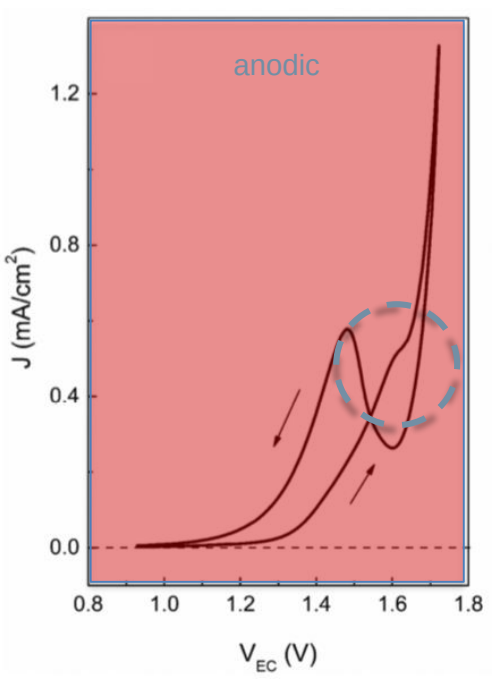
CVD Gr film thickness = 100 nm

R. Yivlialin *et al.*, *Langmuir* (2018)

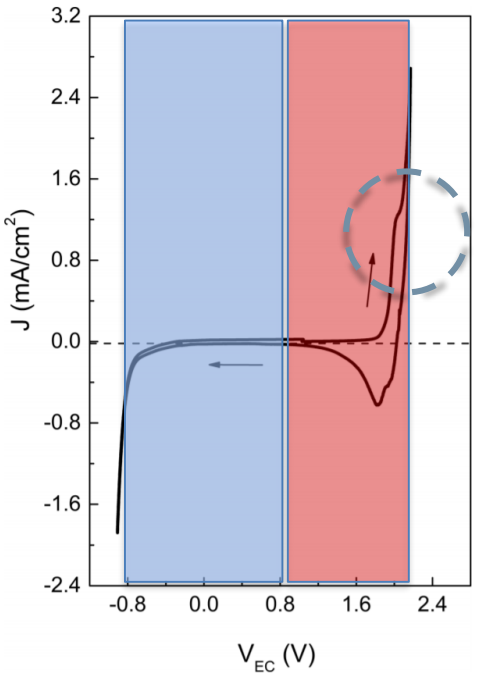
CVD graphene/Ni interface: results – 100 nm CVD graphene/nickel

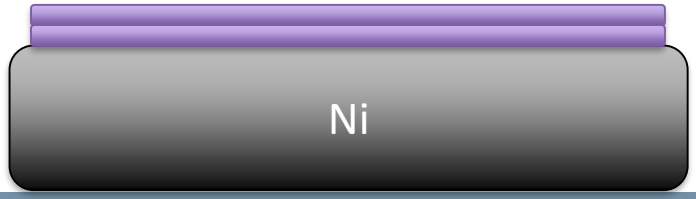
100 nm CVD Gr





HOPG





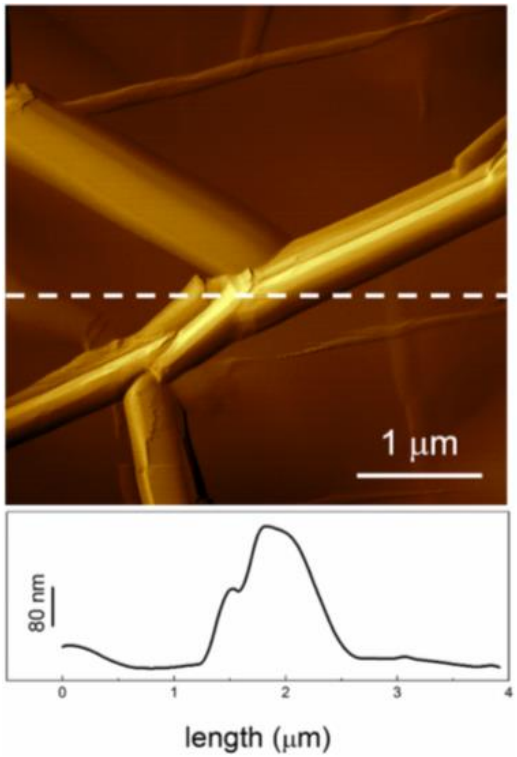
CVD Gr film thickness = 100 nm

R. Yivlialin *et al., Langmuir* (2018)

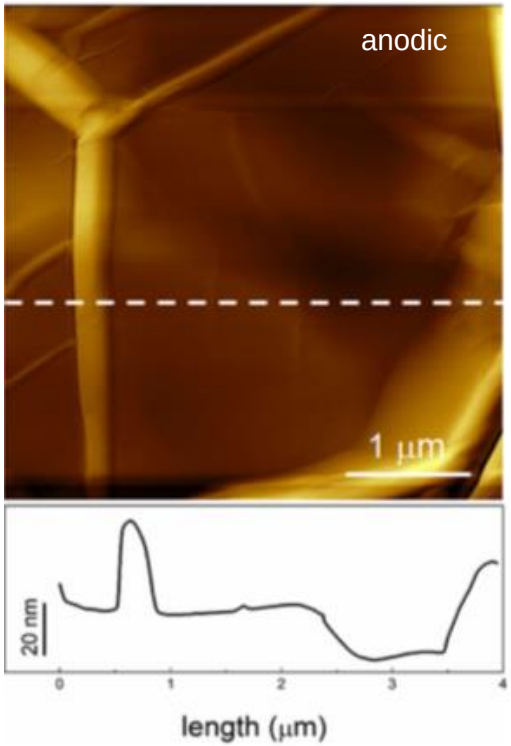
CVD graphene/Ni interface: results – 100 nm CVD graphene/nickel

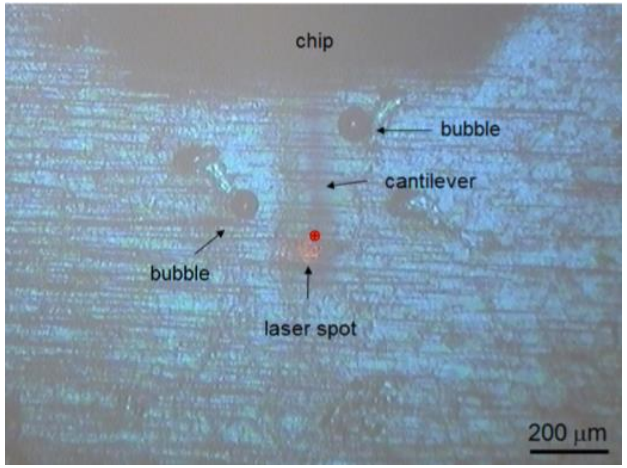
Morphological characterization

100 nm CVD Gr – IN AIR



100 nm CVD Gr – *IN-SITU*

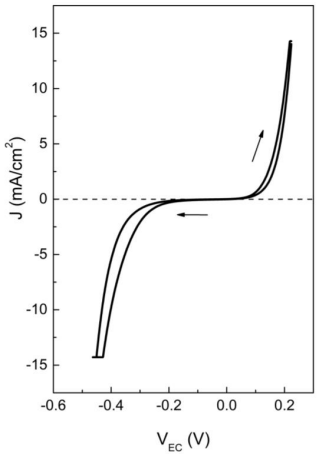


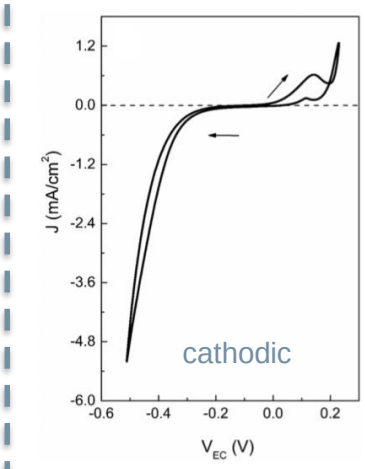


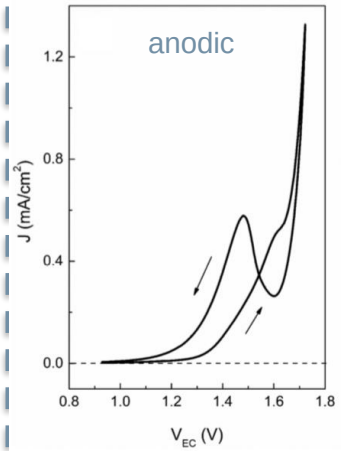
No blisters but bubbles!!!

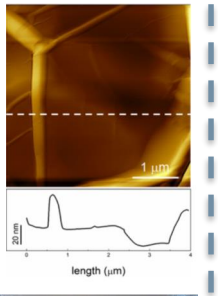
R. Yivlialin *et al., Langmuir* (2018)

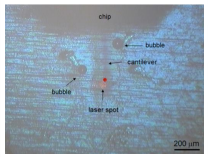
CVD graphene/Ni interface: discussion – the interpretative model

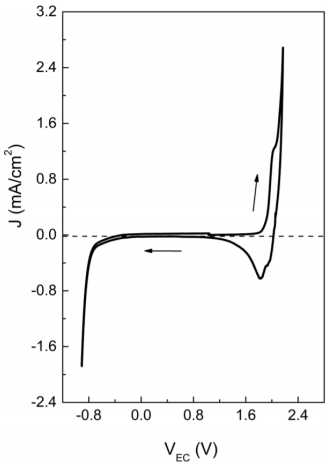


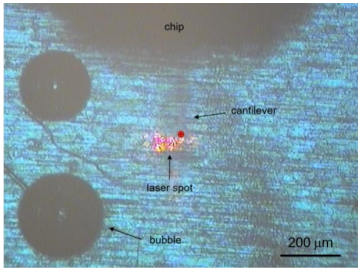


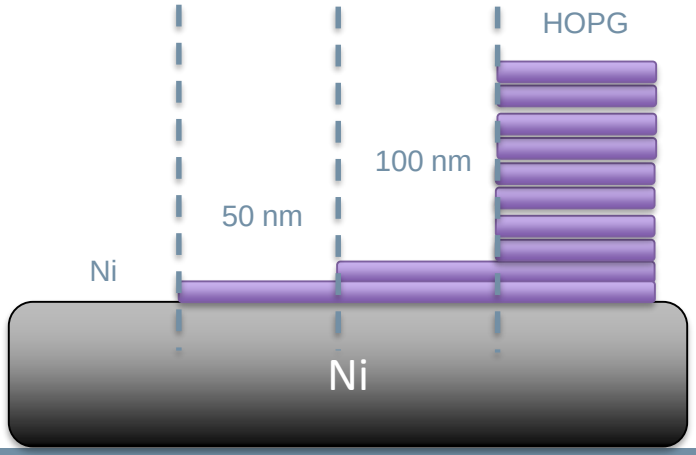


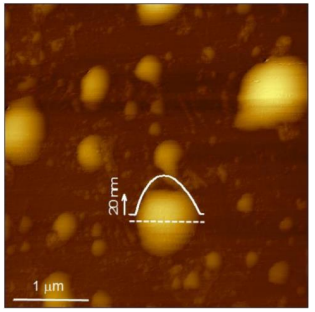








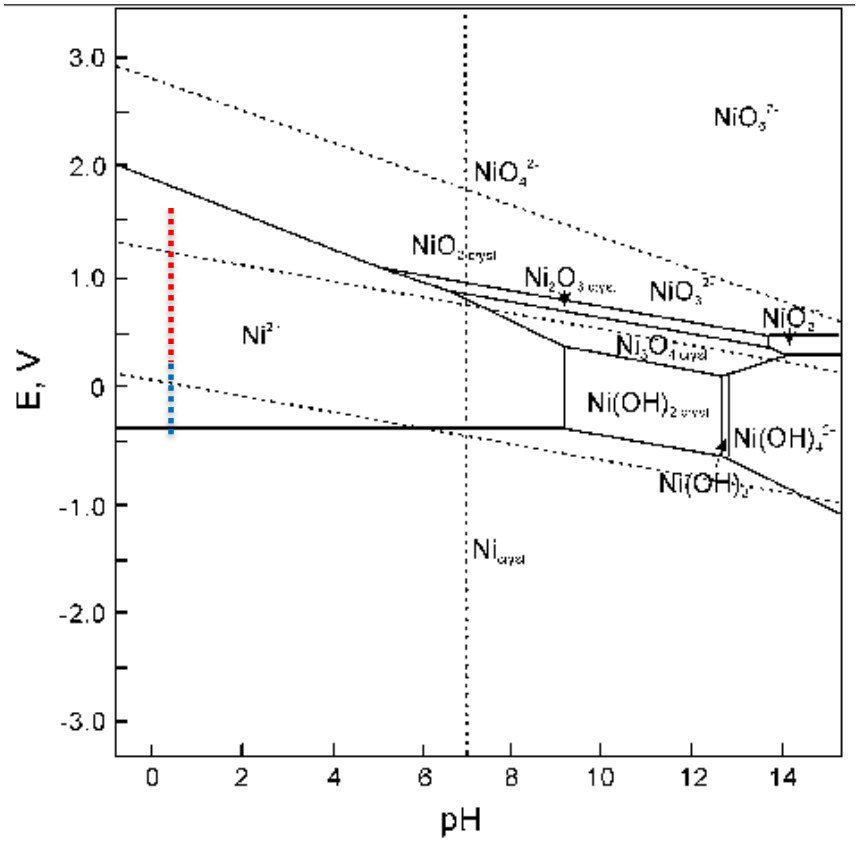


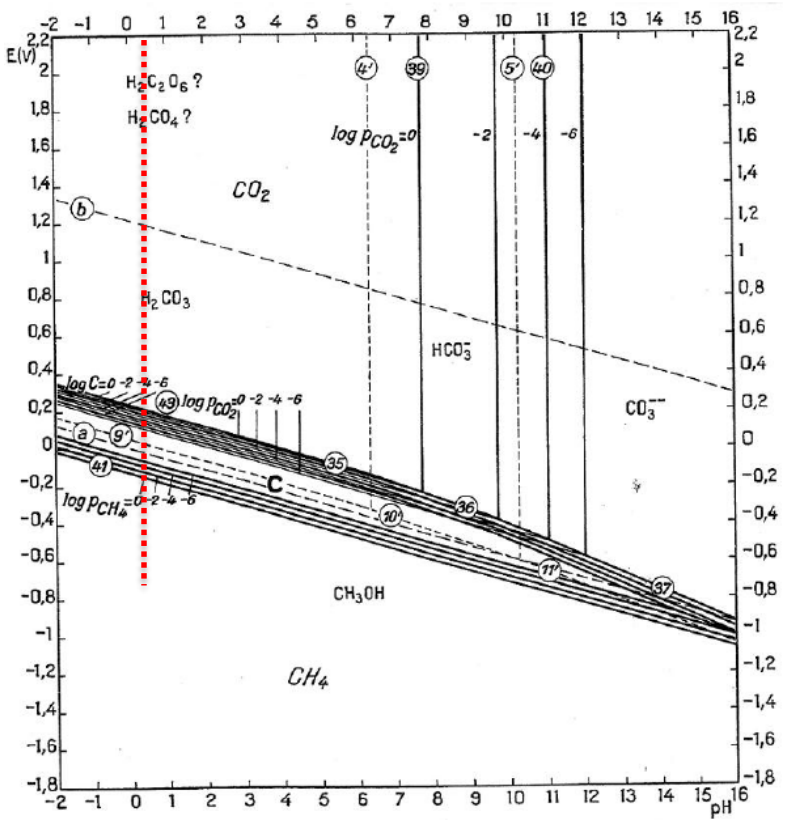


R. Yivlialin *et al., Langmuir* (2018)

CVD Gr can be thought as a defect HOPG

CVD graphene/Ni interface: discussion – the Pourbaix diagrams





Conclusions

HOPG can be used as a model system and considered as a low-defect graphene multilayer

The bare Ni substrate is not perfectly protected and the electrolyte can reach the Ni surface

If the CVD graphene film thickness is increased, the sample recalls the graphite specimen

Acknowledgments

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