

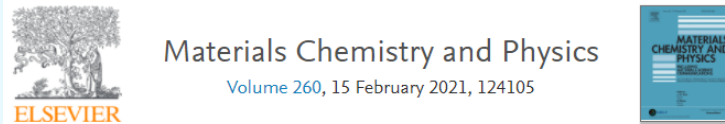
# Rb-functionalized epitaxial graphene on SiC(0001)

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NEST, Istituto Nanoscienze-CNR and Scuola Normale Superiore, Pisa, Italy

# Rb on Graphene - Motivation

## Gas Sensing

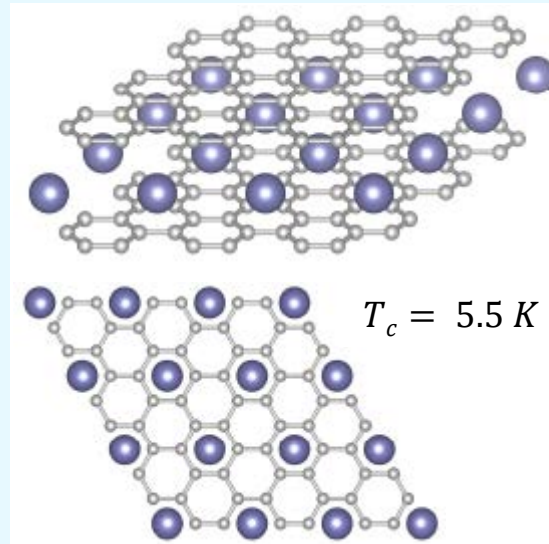


Enhanced hydrogen gas sensing characteristics of graphene modified with rubidium (Rb)

Shivani A. Singh <sup>a</sup>, Pravin S. More (Associate Professor (Physics)) <sup>a</sup> ✉, Yogesh B. Khollam <sup>b</sup>, Subhash B. Kondawar <sup>c</sup>

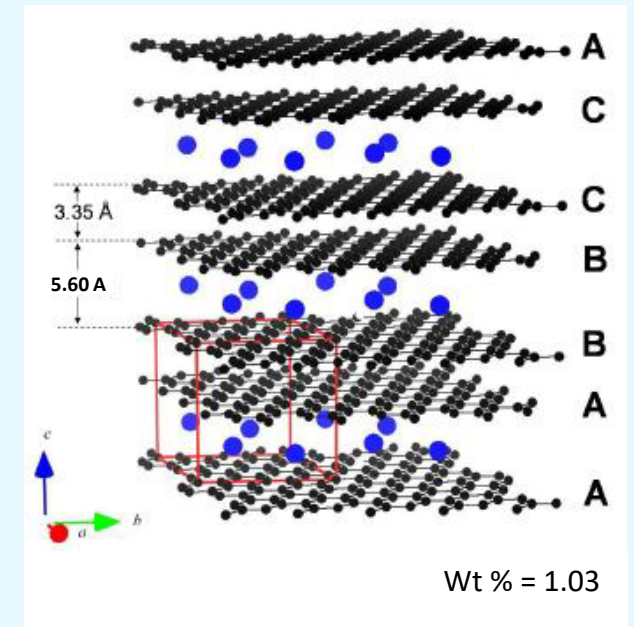
*Singh et al.*,  
Mat. Chem. Phys. 260 (2021) 124105

## Superconductivity



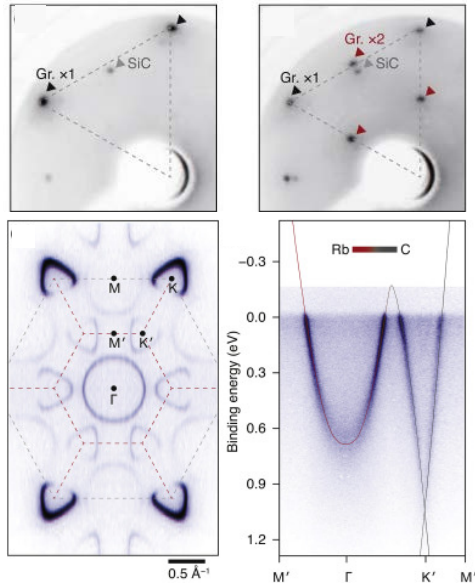
*Durajski et al.*,  
Phys. Chem. Chem. Phys. 21 (2019)  
5925-5931

## Hydrogen Storage



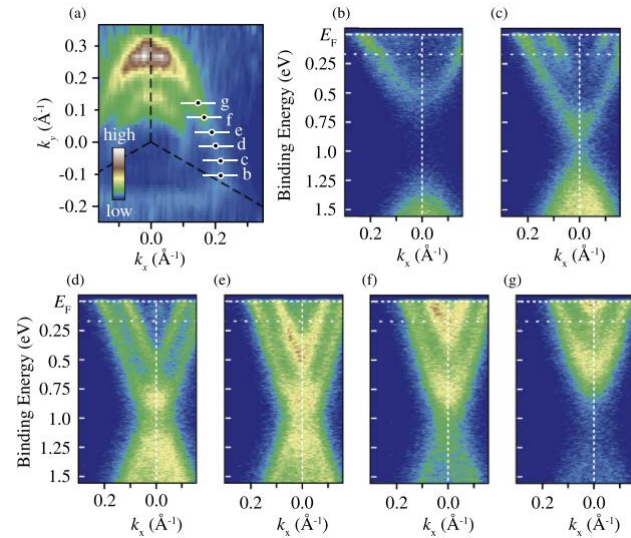
*Ahn and Purewal*,  
Int. J. Hydrog. Energy 39 (2014)

# Rb-intercalation



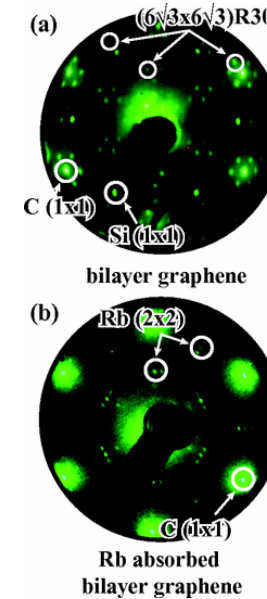
*Shin et al.,*

*Curr. Appl. Phys.* 20 (2020) 484-488

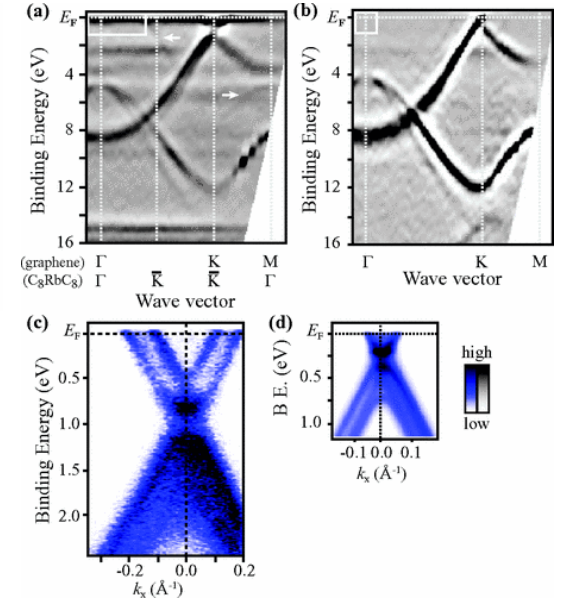


*Kleeman et al.,*

*J. Phys. Soc. Jpn.* 83 (2014) 124715

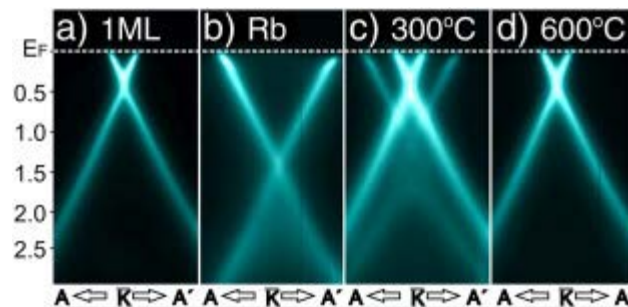


**Rb absorbed bilayer graphene**



*Kleeman et al.,*

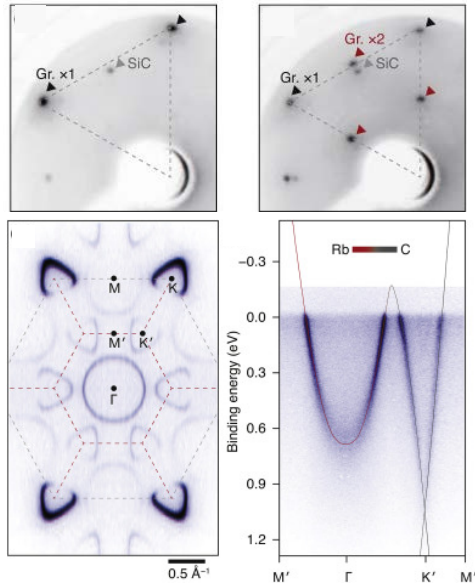
*Phys. Rev. B* 87 (2013) 195401



*Watcharinyanon et al.,*  
*Surf. Sci.* 605 (2011) 1918-1922

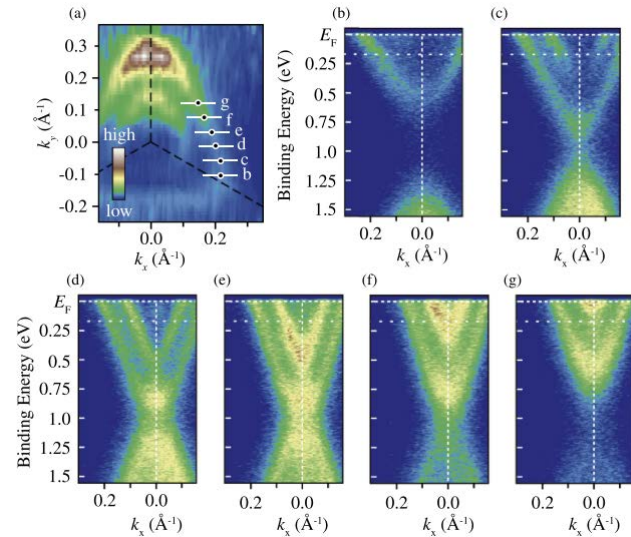


# Rb-intercalation



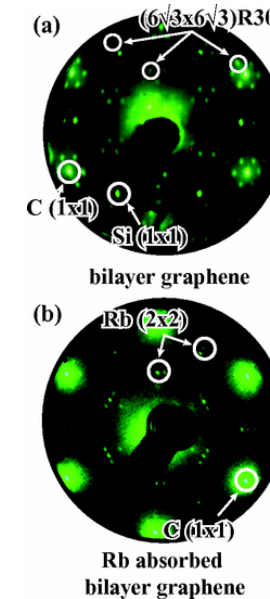
*Shin et al.,*

*Curr. Appl. Phys.* 20 (2020) 484-488

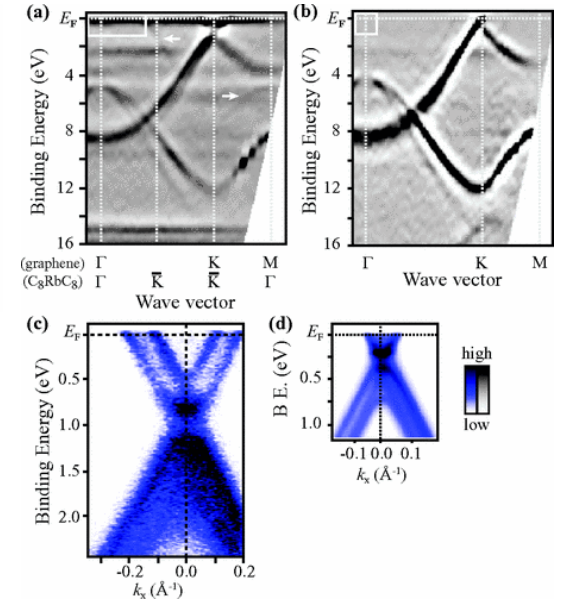


*Kleeman et al.,*

*J. Phys. Soc. Jpn.* 83 (2014) 124715

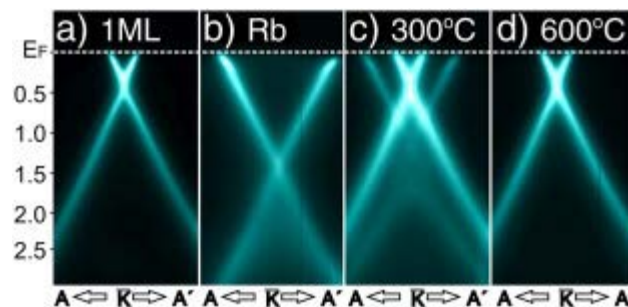


**Rb absorbed bilayer graphene**



*Kleeman et al.,*

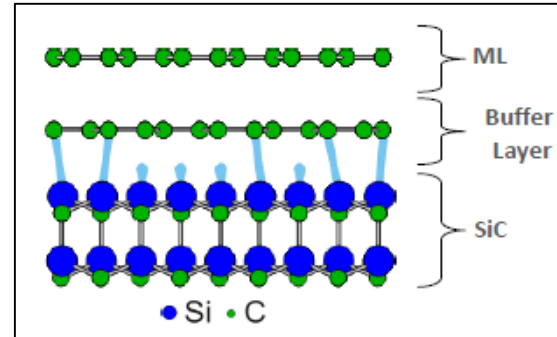
*Phys. Rev. B* 87 (2013) 195401



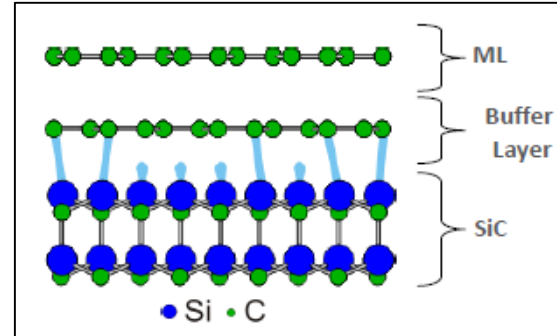
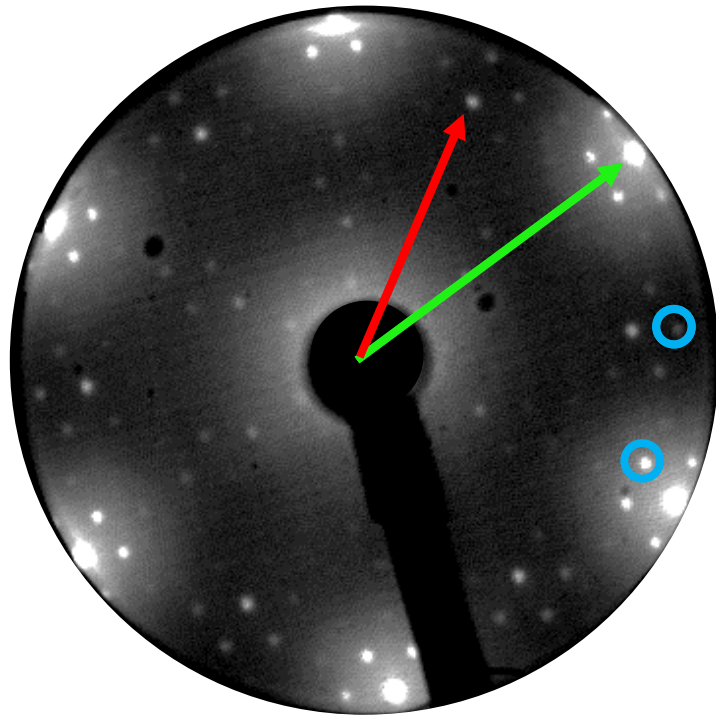
*Watcharinyanon et al.,*  
*Surf. Sci.* 605 (2011) 1918-1922

Only LEED, PES  
No microscopy studies

# Epitaxial Graphene on SiC(0001)

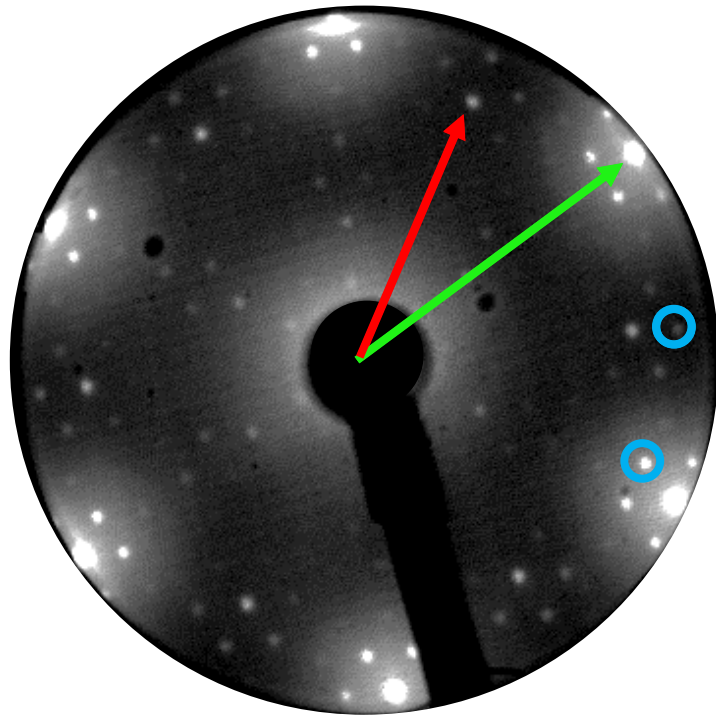


# Epitaxial Graphene on SiC(0001)

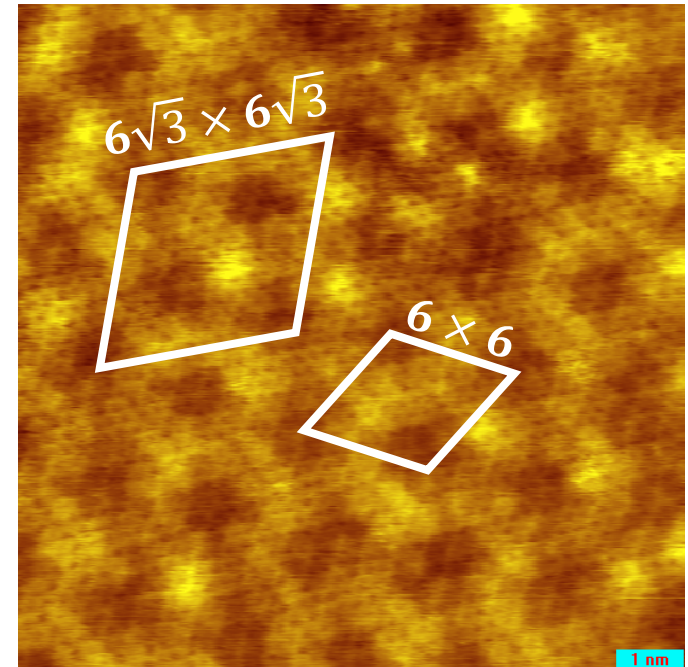
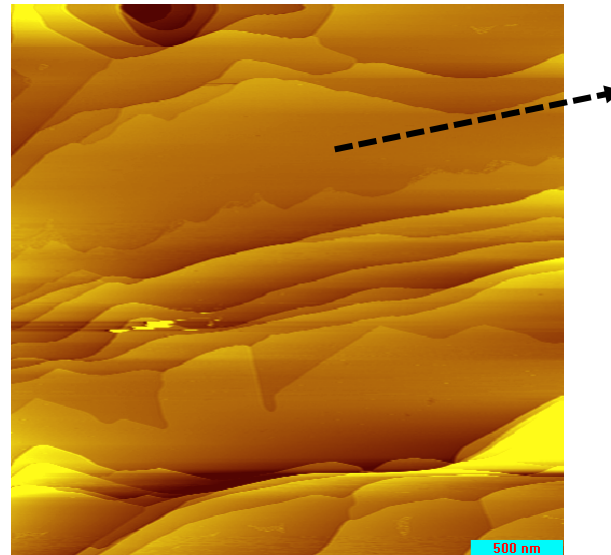
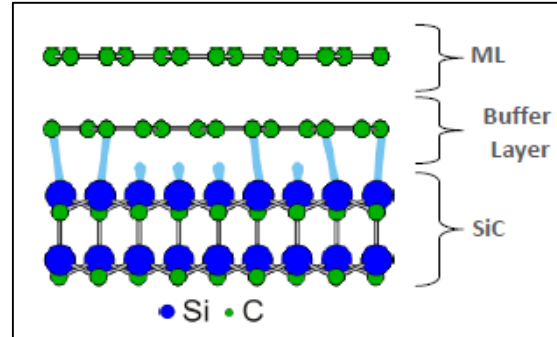


— Graphene  
— SiC — Moirè ( $6\sqrt{3}$ )  
LEED

# Epitaxial Graphene on SiC(0001)



— Graphene  
— SiC    — Moiré ( $6\sqrt{3}$ )  
 LEED



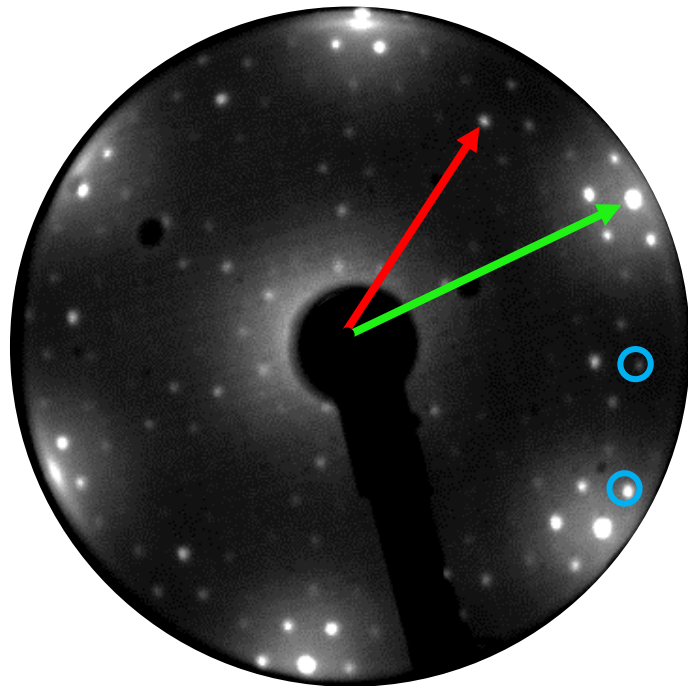
STM



# Rubidium on EG/SiC(0001)

LEED

— Graphene — SiC — Moirè ( $6\sqrt{3}$ )



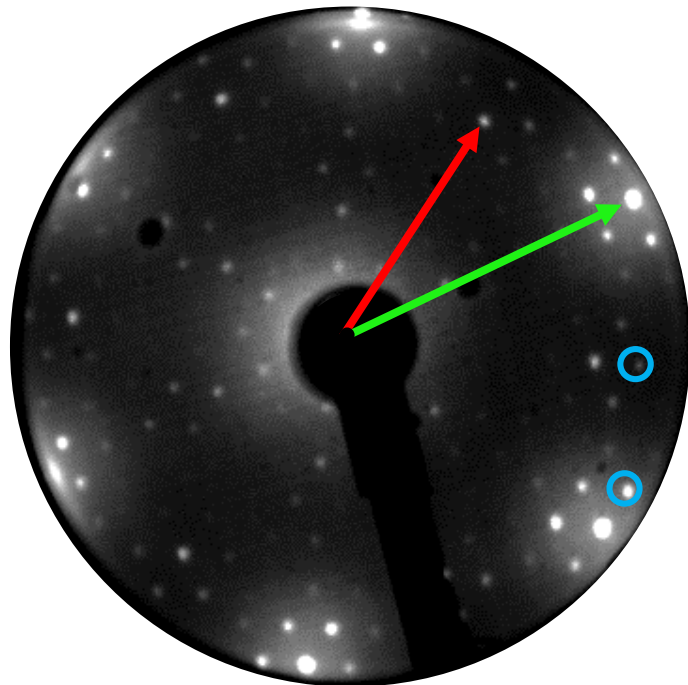
0 min Rb  
 $6\sqrt{3} \times 6\sqrt{3} R30^\circ$



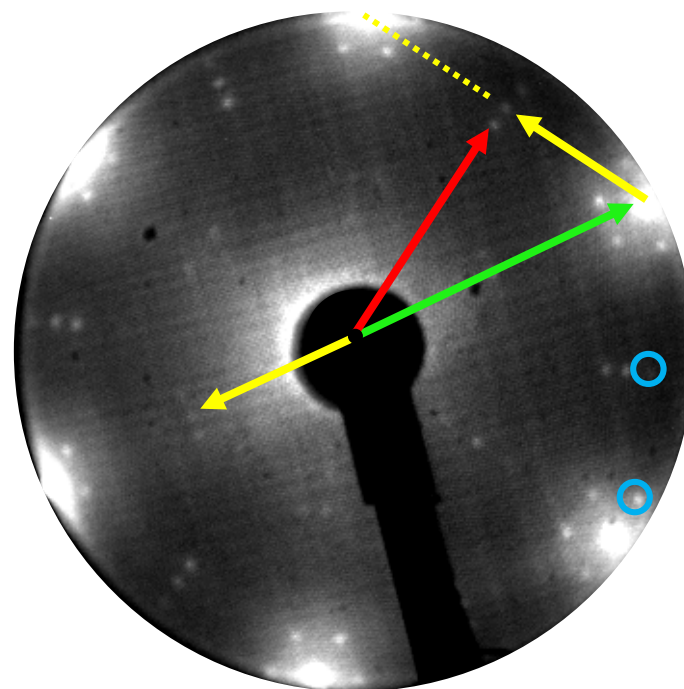
# Rubidium on EG/SiC(0001)

LEED

— Graphene — SiC — Moirè ( $6\sqrt{3}$ ) — Rb( $2 \times 2$ )



0 min Rb  
 $6\sqrt{3} \times 6\sqrt{3} R30^\circ$

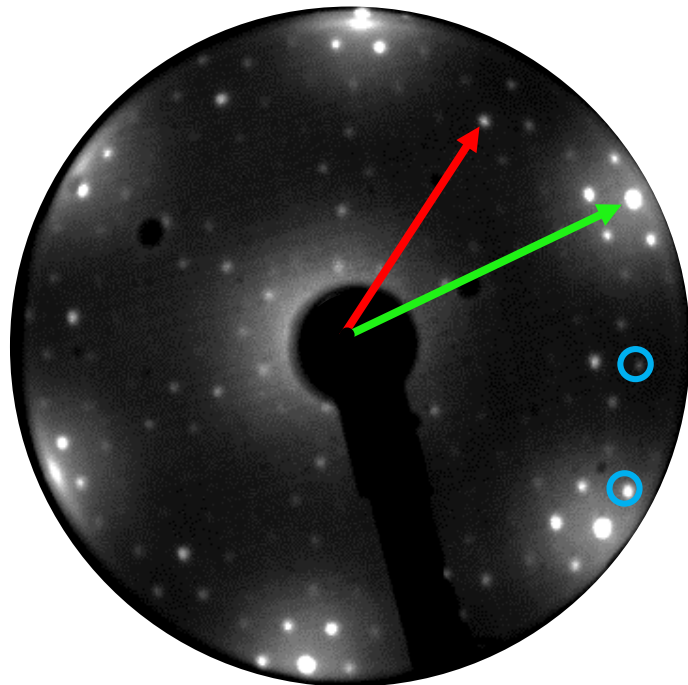


1 min Rb  
 Rb( $2 \times 2$ )

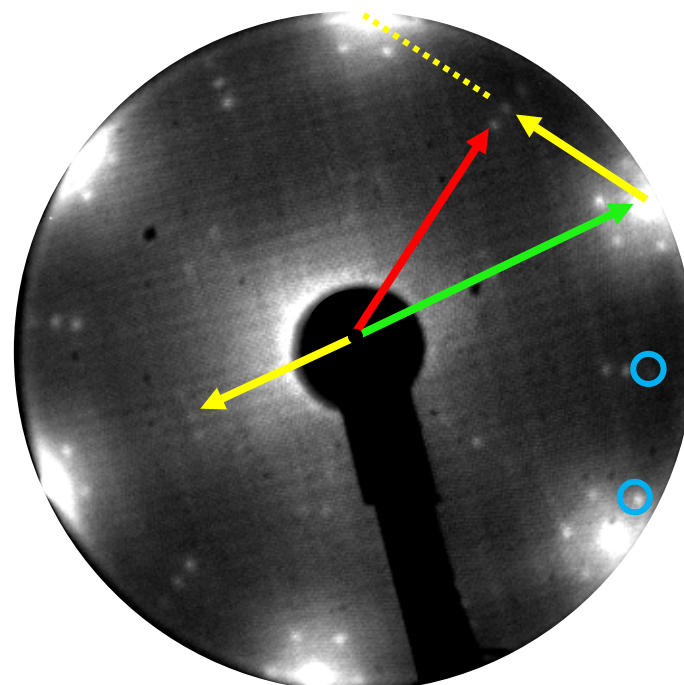
# Rubidium on EG/SiC(0001)

LEED

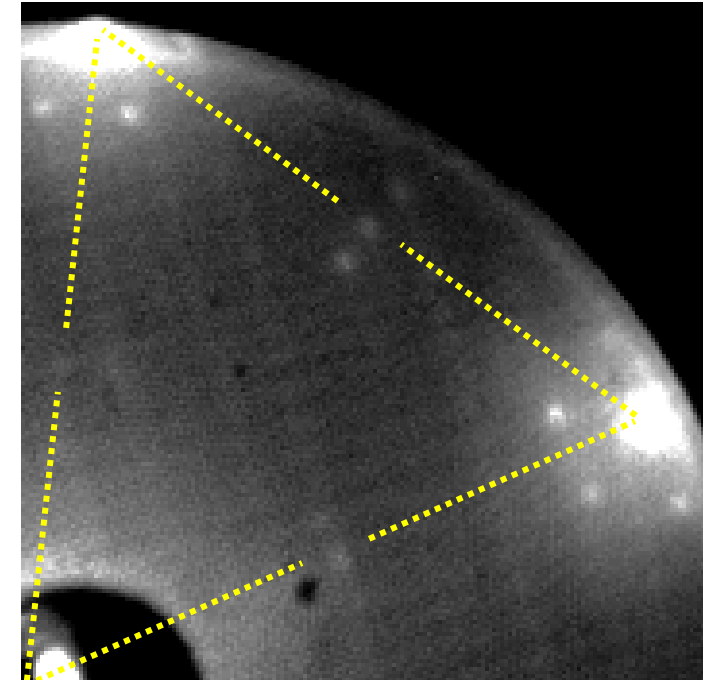
— Graphene — SiC — Moirè ( $6\sqrt{3}$ ) — Rb( $2 \times 2$ )



0 min Rb  
 $6\sqrt{3} \times 6\sqrt{3} R30^\circ$



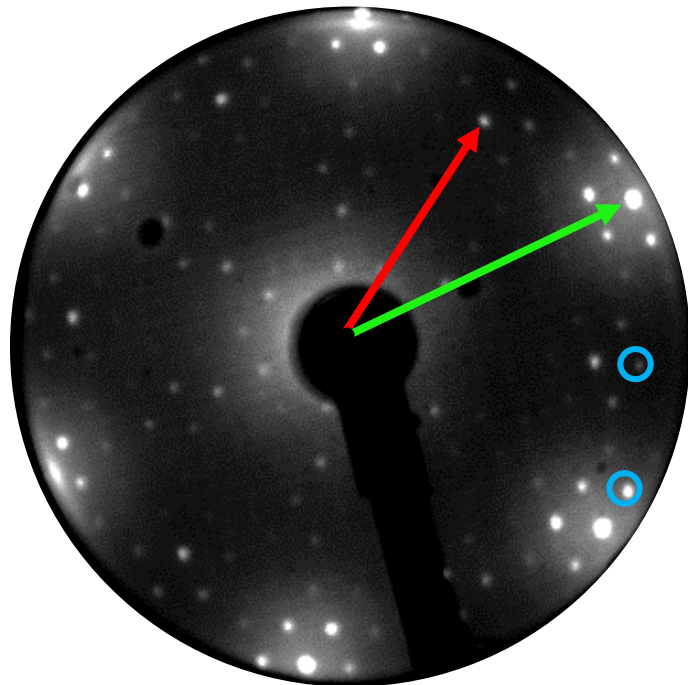
1 min Rb  
 Rb( $2 \times 2$ )



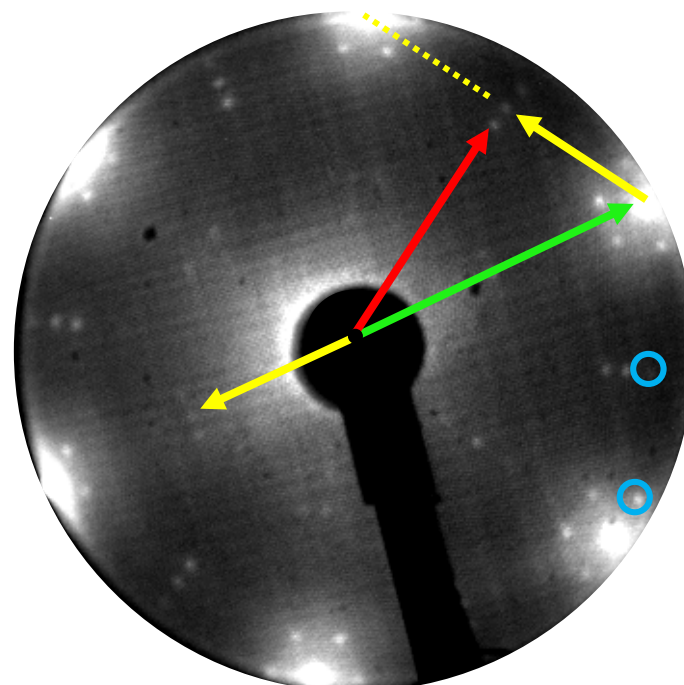
# Rubidium on EG/SiC(0001)

LEED

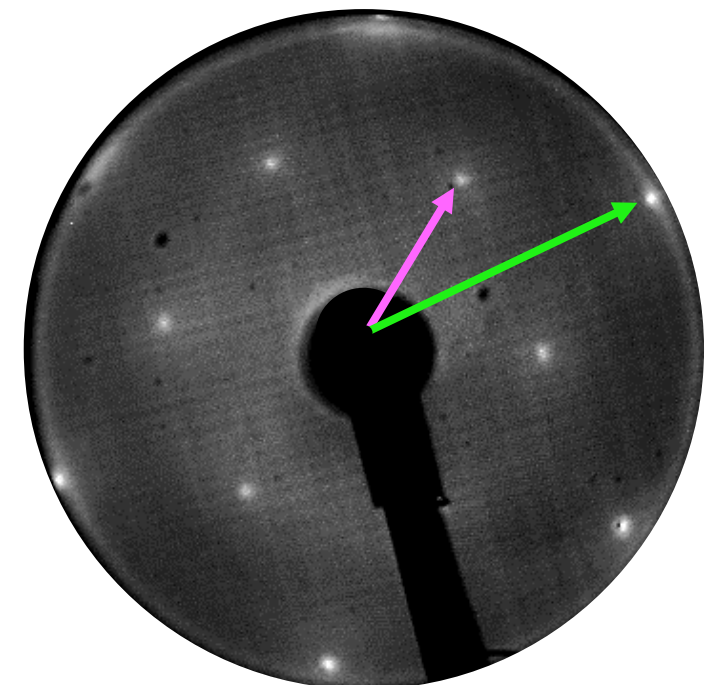
— Graphene   
 — SiC   
 — Moirè ( $6\sqrt{3}$ )   
 — Rb( $2 \times 2$ )   
 — Rb( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$



0 min Rb  
 $6\sqrt{3} \times 6\sqrt{3} R30^\circ$



1 min Rb  
 Rb( $2 \times 2$ )

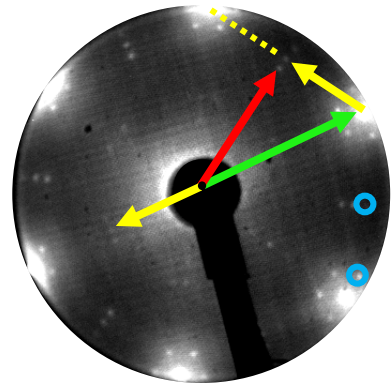


3 min Rb  
 Rb( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$

# Rubidium on EG/SiC(0001)

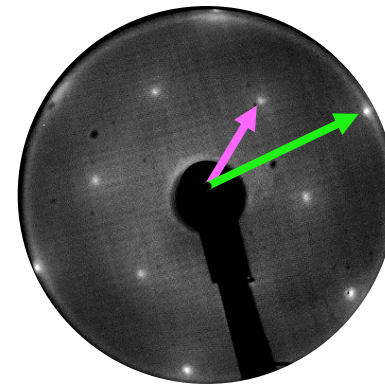
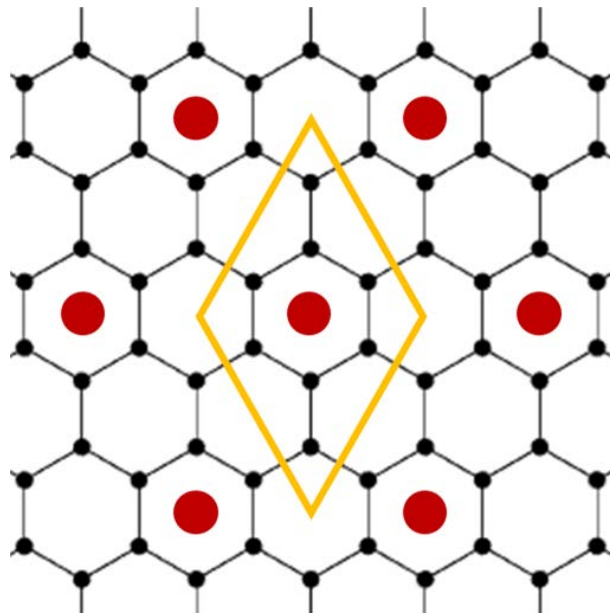
LEED

— Graphene   
 — SiC   
 — Moirè ( $6\sqrt{3}$ )   
 — Rb( $2 \times 2$ )   
 — Rb( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$



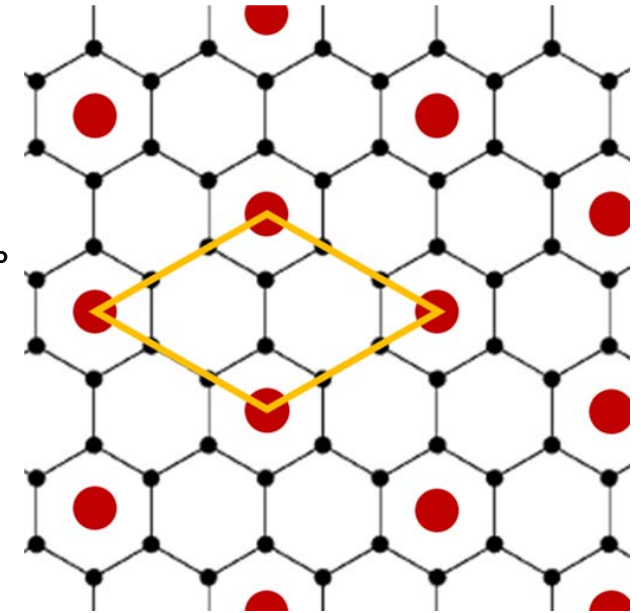
1 min Rb  
Rb( $2 \times 2$ )

Rb coverage 1/4 ML  
(0.25 ML)



3 min Rb  
Rb( $\sqrt{3} \times \sqrt{3}$ ) $R30^\circ$

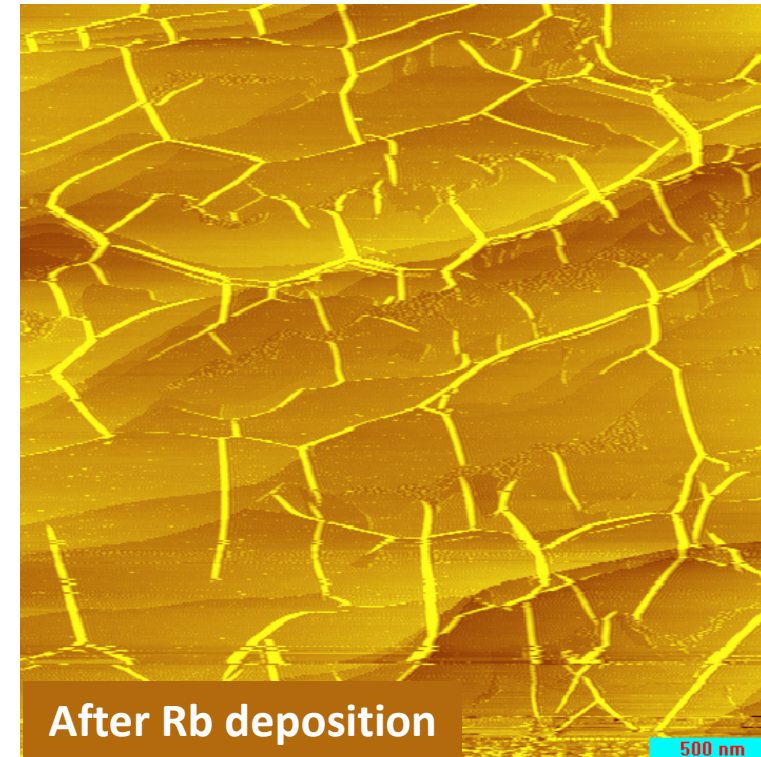
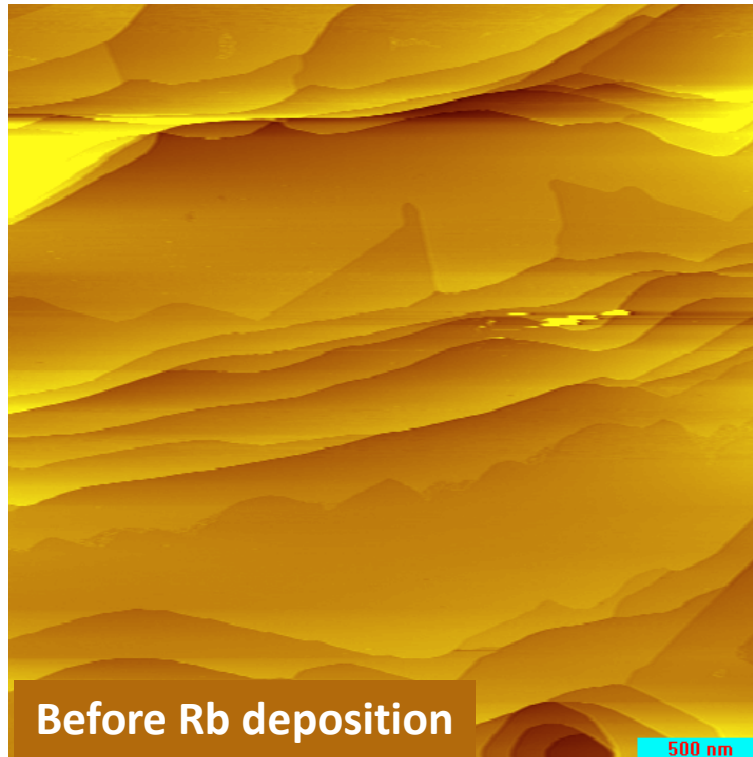
Rb coverage 1/3 ML  
(0.33 ML)





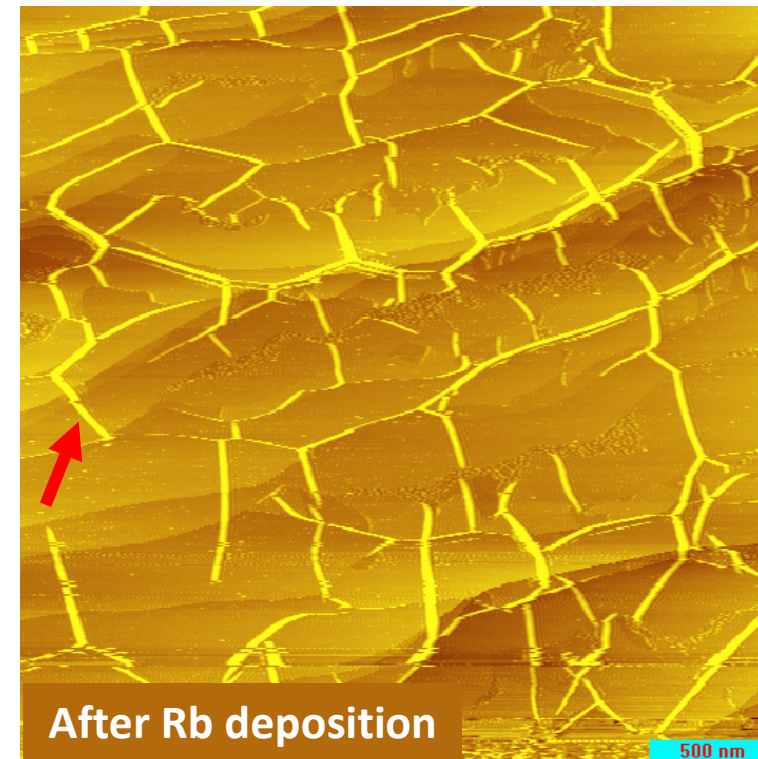
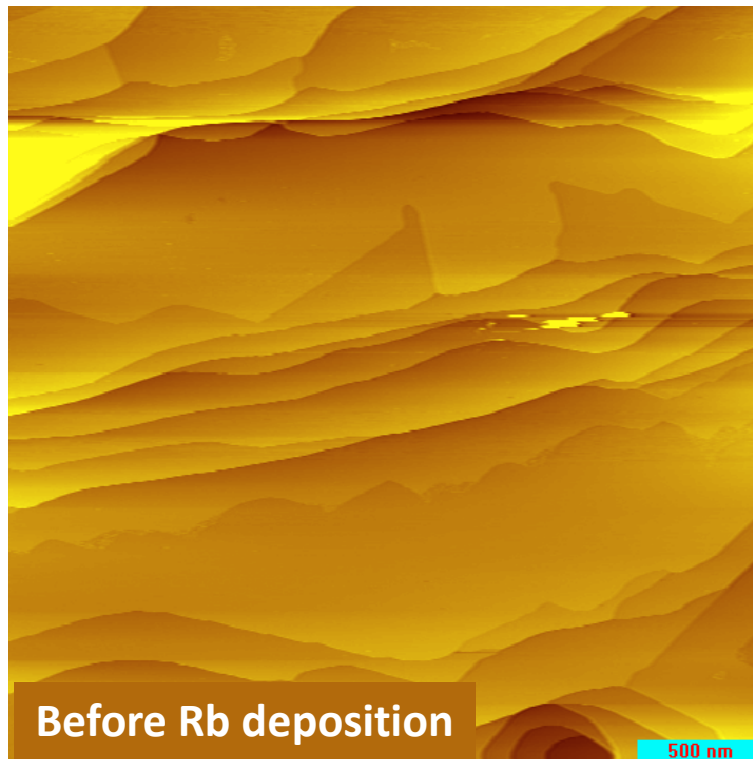
# Rubidium on EG/SiC(0001)

Step-terrace morphology still well recognizable



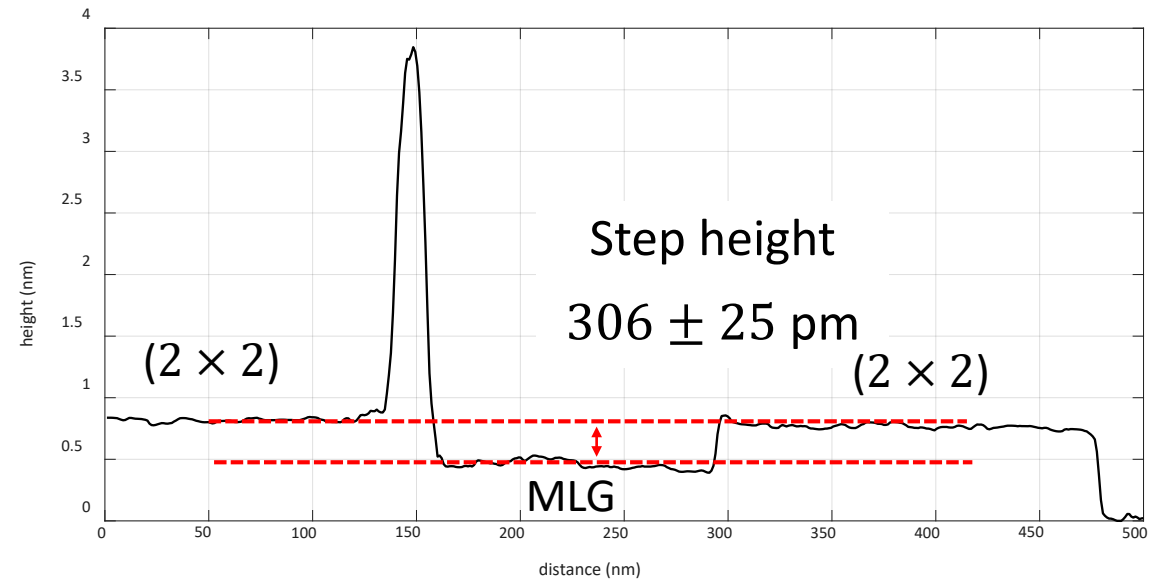
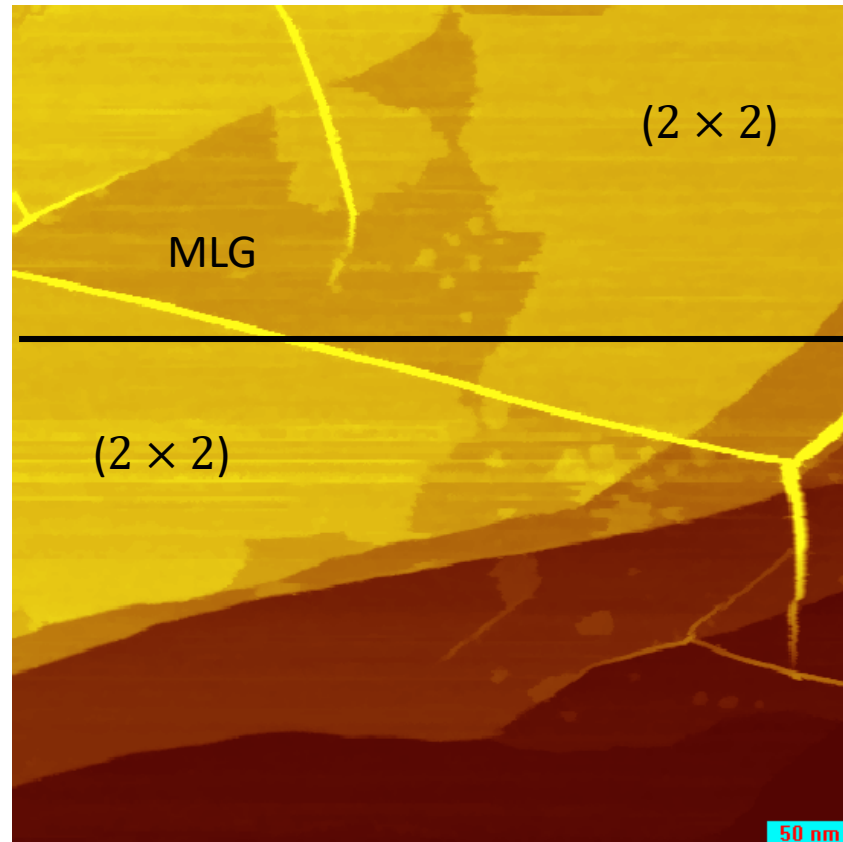
# Rubidium on EG/SiC(0001)

One-dimensional lines a few nm high form (red arrow)



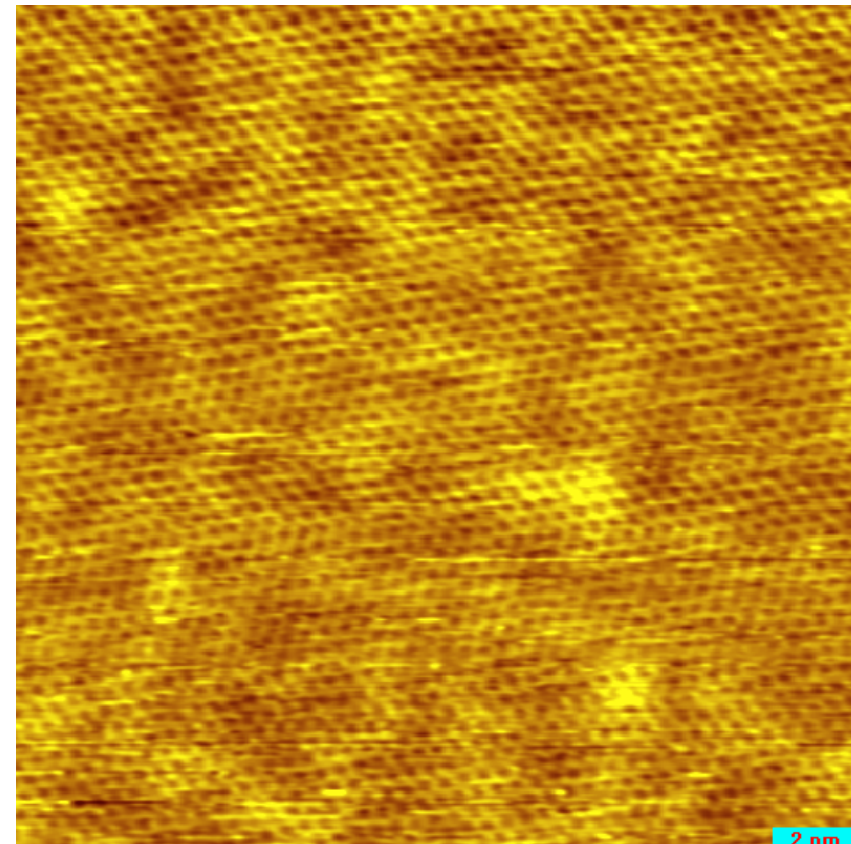
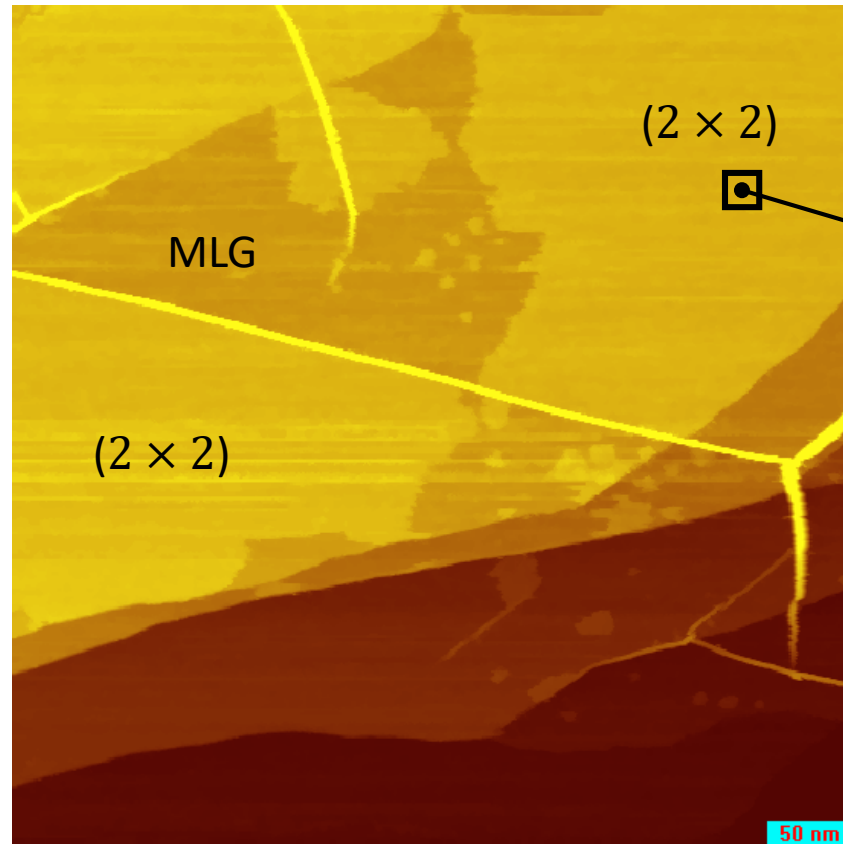
# Rubidium on EG/SiC(0001)

1 min Rb deposition ( $2 \times 2$ )



# Rubidium on EG/SiC(0001)

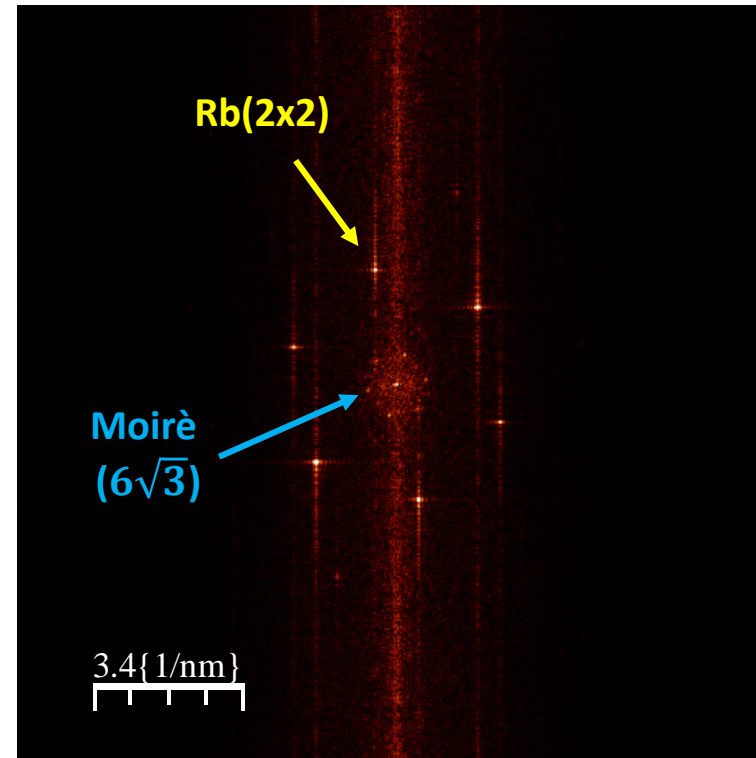
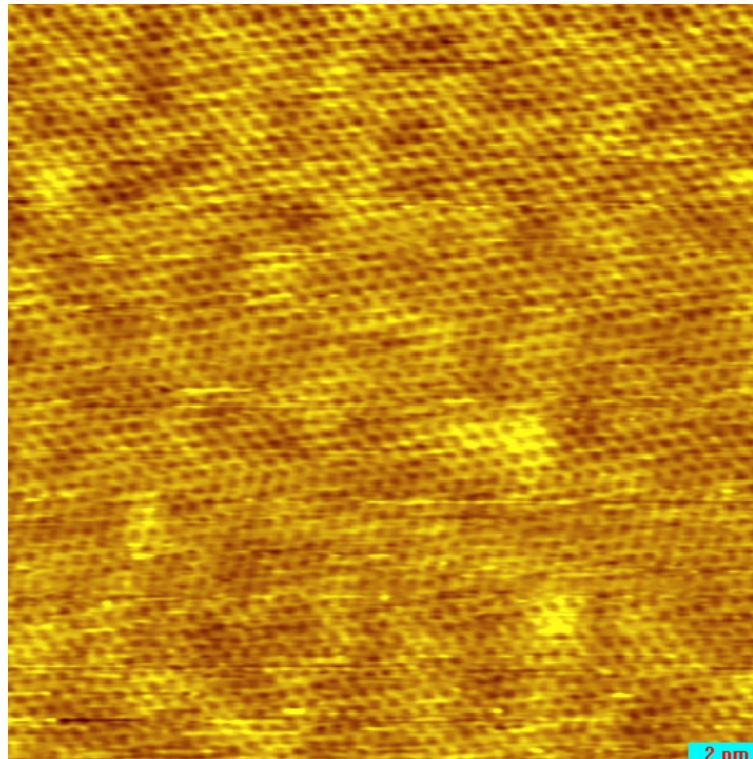
1 min Rb deposition ( $2 \times 2$ )





# Rubidium on EG/SiC(0001)

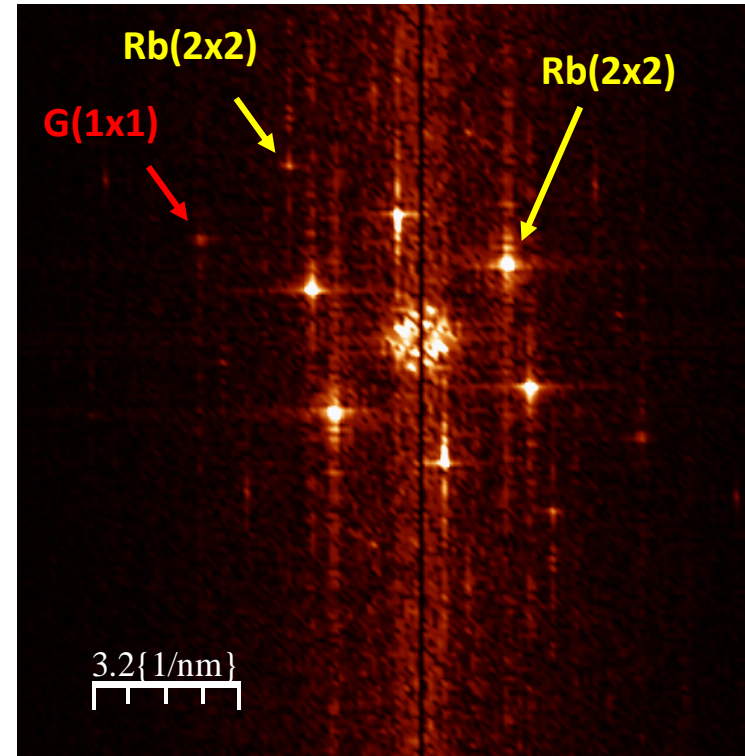
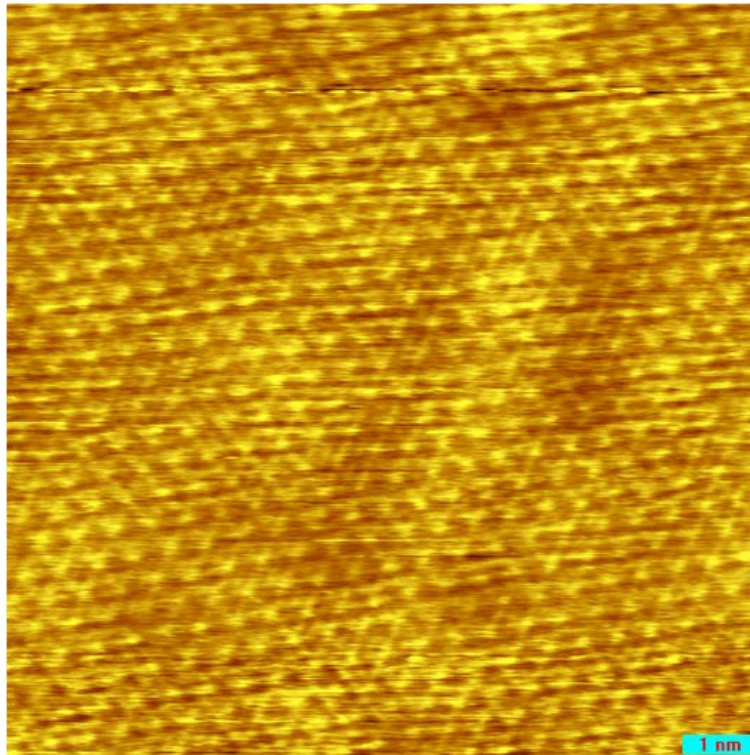
1 min Rb deposition ( $2 \times 2$ )



Moiré ( $6\sqrt{3}$ ) is faintly visible and only in larger size STM images while the ( $2 \times 2$ ) superstructure is clearly distinguishable.

# Rubidium on EG/SiC(0001)

1 min Rb deposition ( $2 \times 2$ )

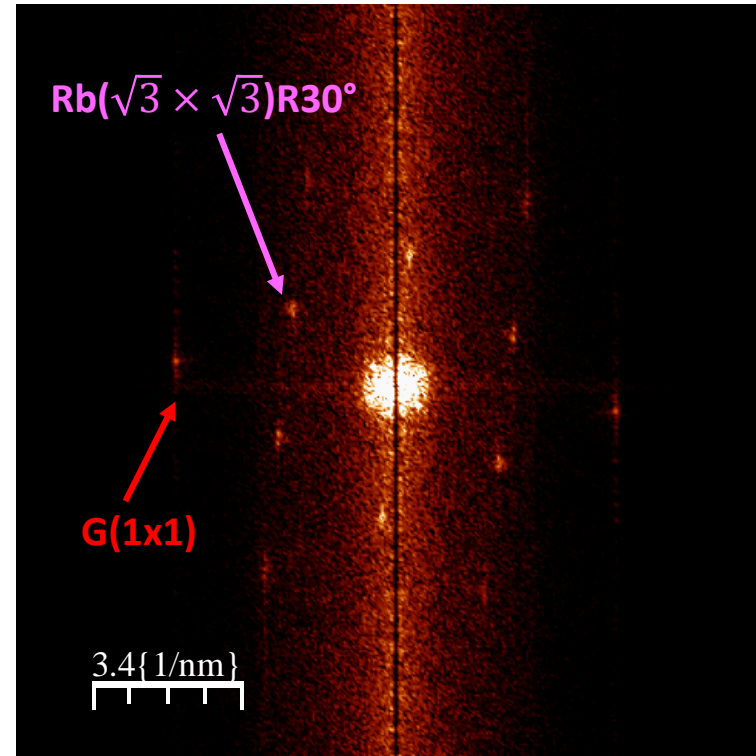
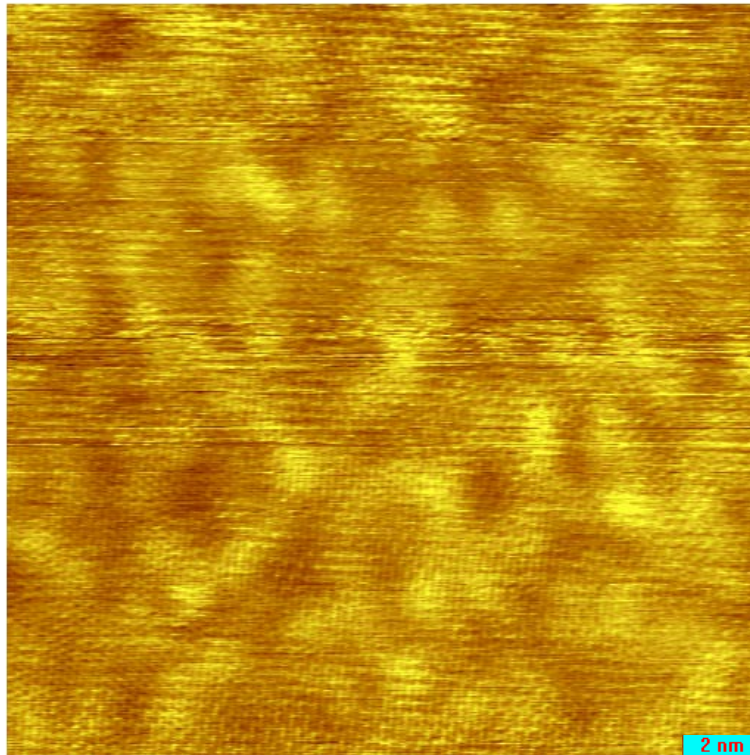


The  $(2 \times 2)$  superstructure and at the same time the graphene lattice can be resolved.



# Rubidium on EG/SiC(0001)

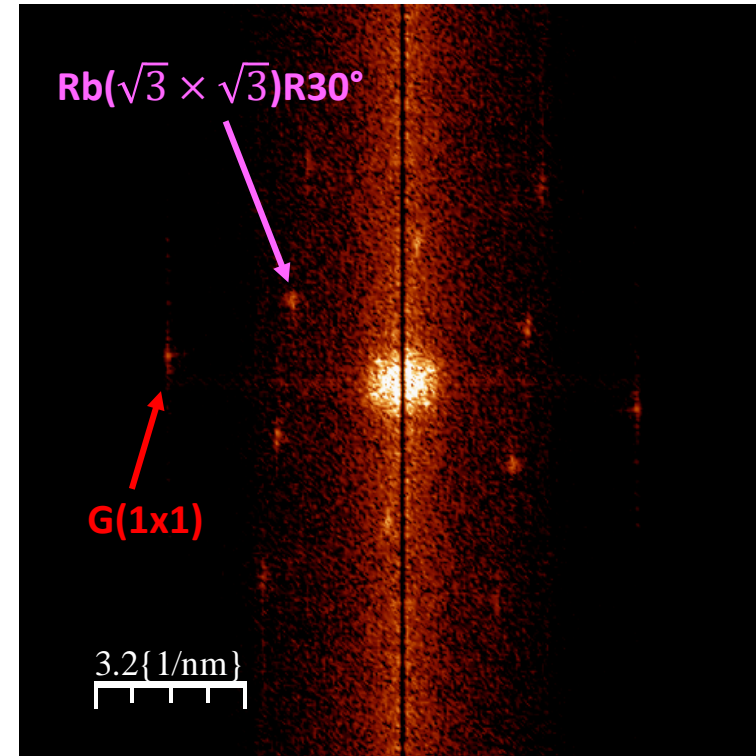
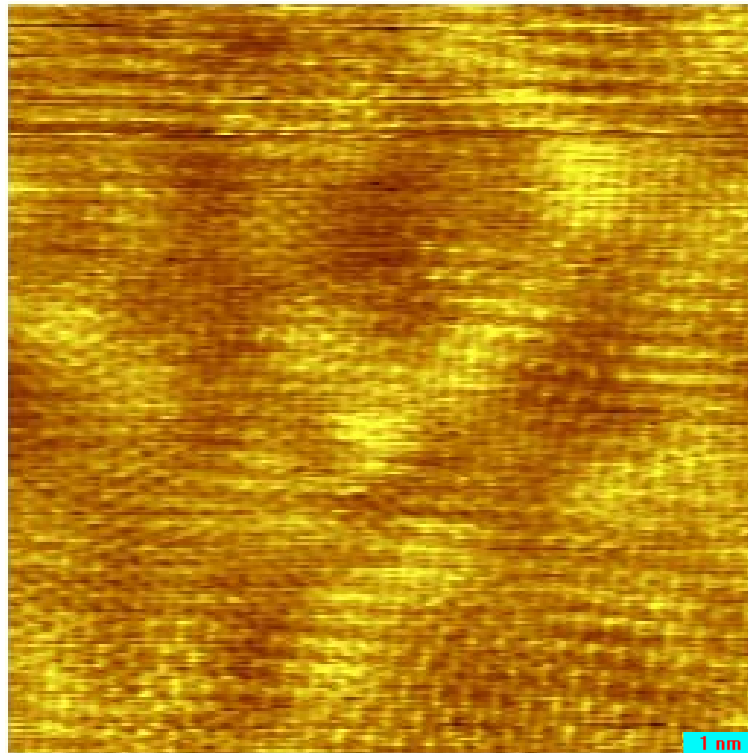
3 min Rb deposition ( $\sqrt{3} \times \sqrt{3}$ )R30°



Moirè ( $6\sqrt{3}$ ) is not present, not even faintly visible in larger size STM images.  
 A ( $\sqrt{3} \times \sqrt{3}$ )R30° superstructure is present.

# Rubidium on EG/SiC(0001)

3 min Rb deposition  $(\sqrt{3} \times \sqrt{3})R30^\circ$

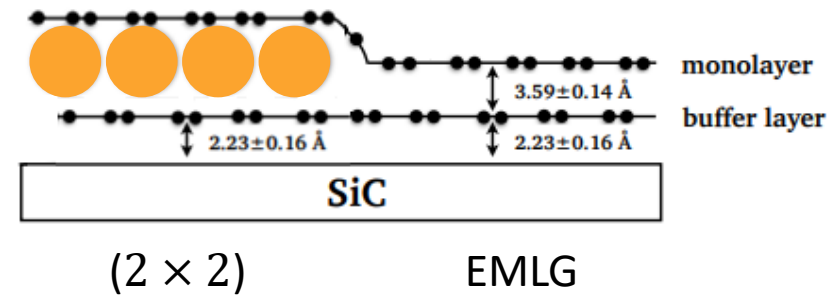
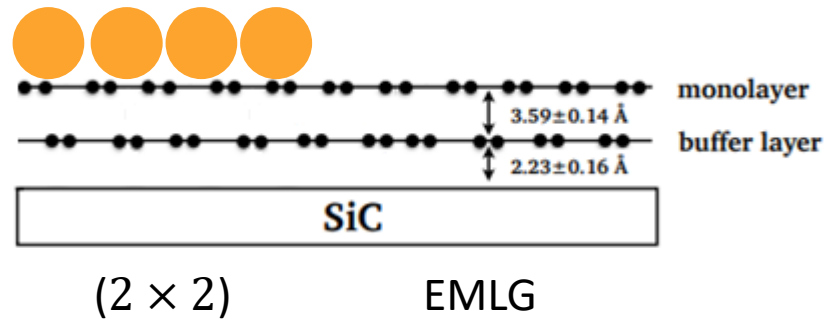


The  $(\sqrt{3} \times \sqrt{3})R30^\circ$  superstructure and at the same time the graphene lattice can be resolved.



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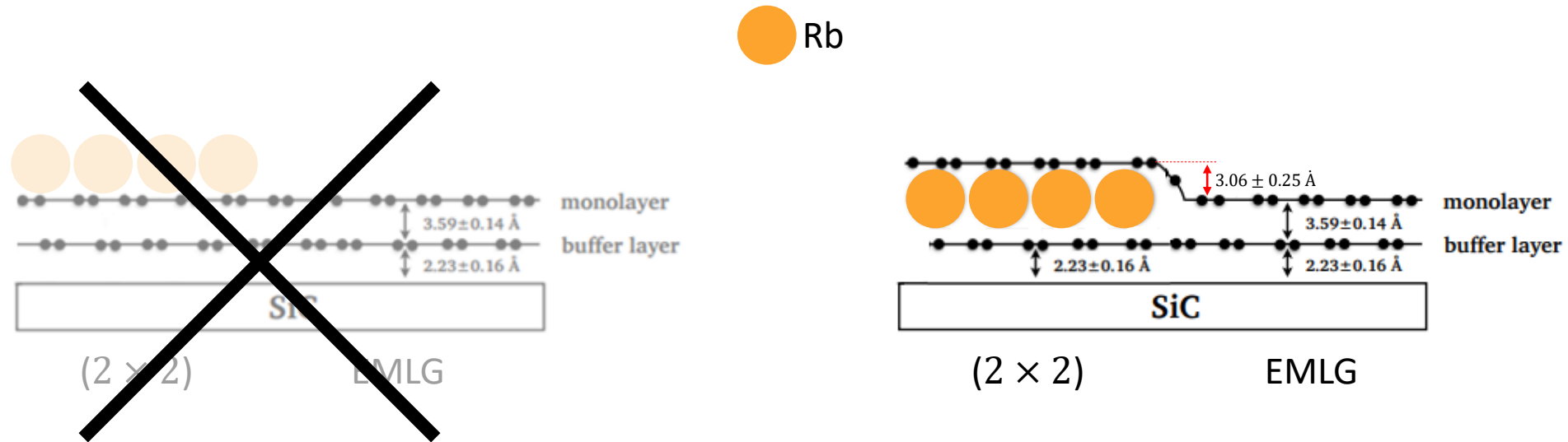
Model Rb(2 × 2)



The (2 × 2) has been associated in literature to Rb either on top or intercalated between the two graphene layers. Phase with Rb coverage 1/4 ML.

# Rubidium on EG/SiC(0001)

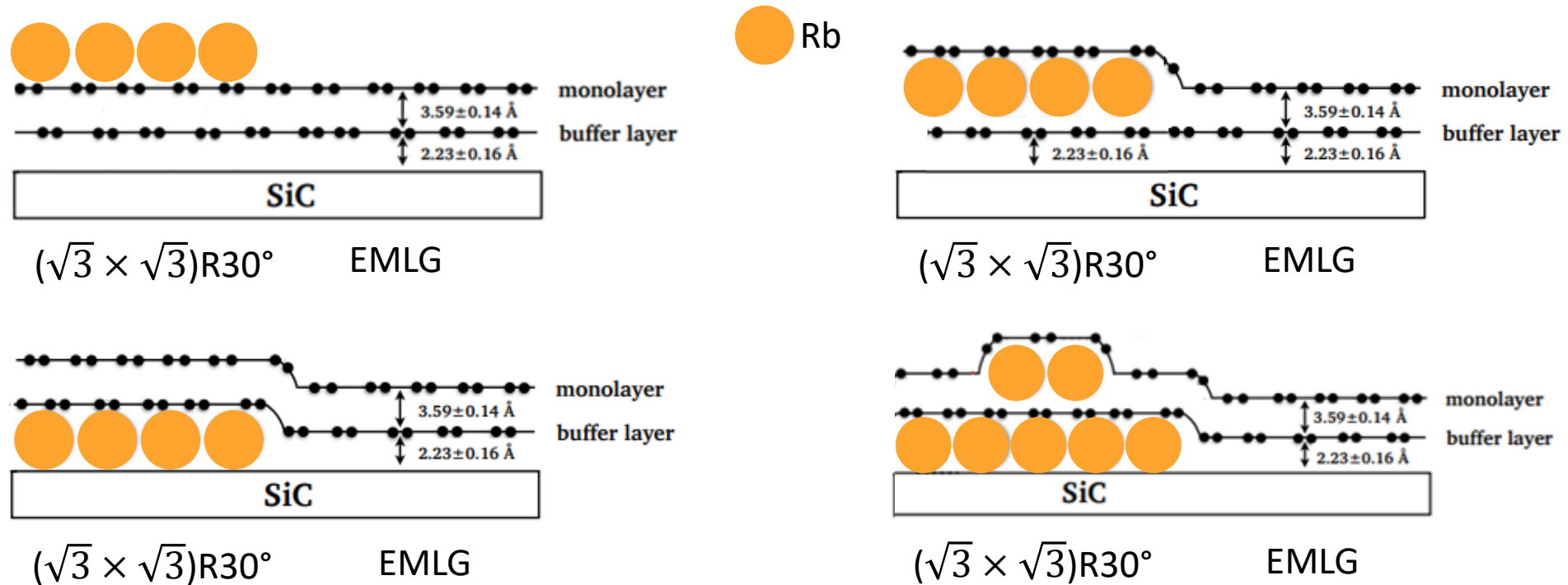
Model Rb(2 × 2)



The graphene lattice can be resolved by STM. Both LEED and STM show the presence of the Moiré ( $6\sqrt{3}$ ) superstructure thus suggesting that Rb is not intercalated below the buffer layer but rather between buffer layer and monolayer graphene.

# Rubidium on EG/SiC(0001)

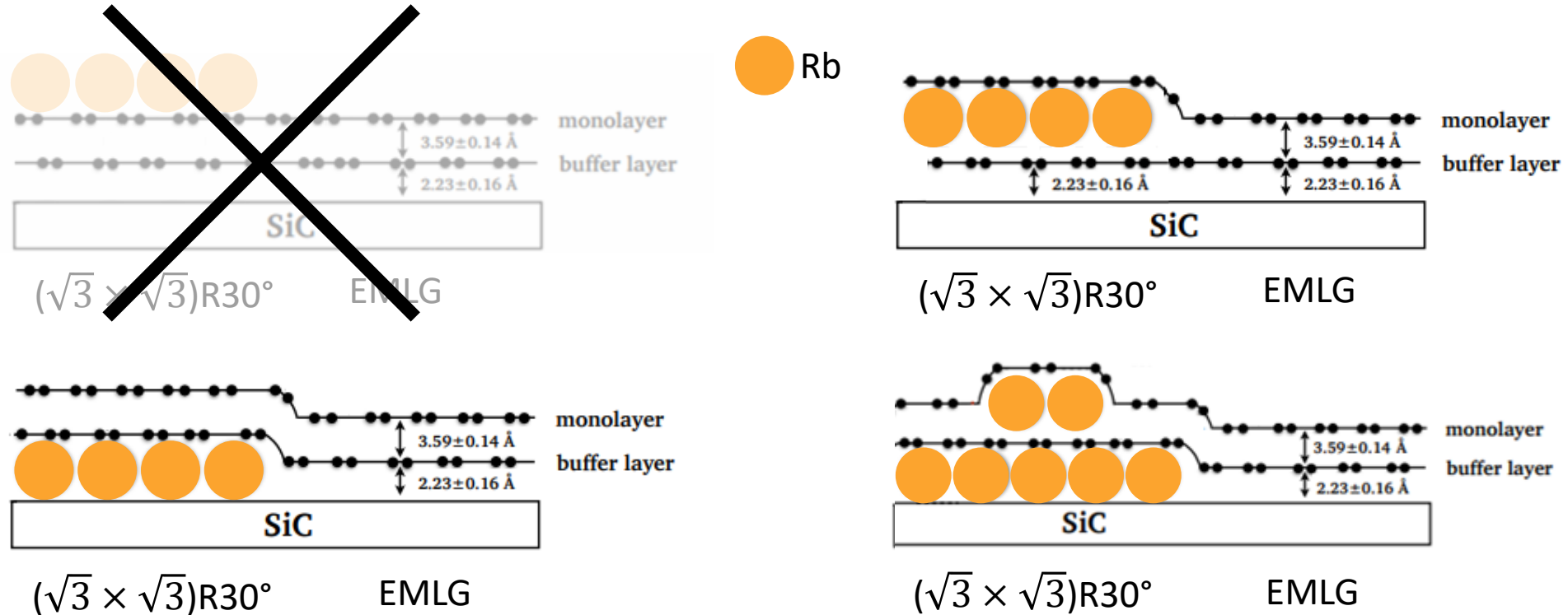
Model  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$



The  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  has been associated in literature to AM either on top or intercalated between the two graphene layers. Phase with AM coverage  $1/3$  ML.

# Rubidium on EG/SiC(0001)

Model  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$

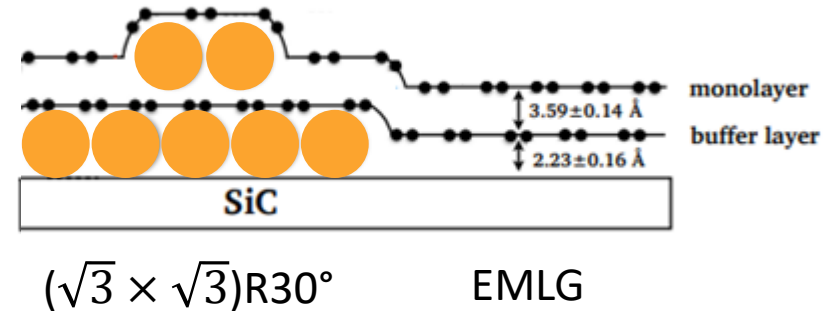
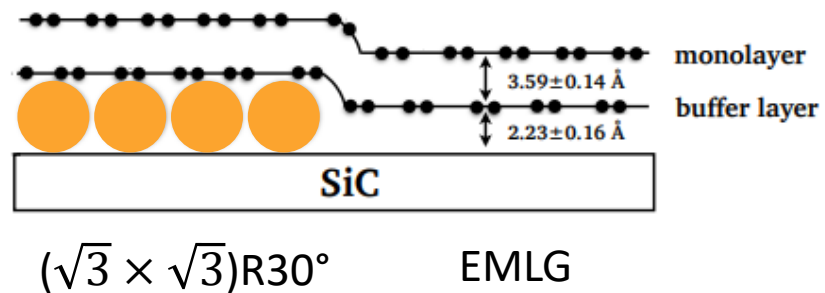
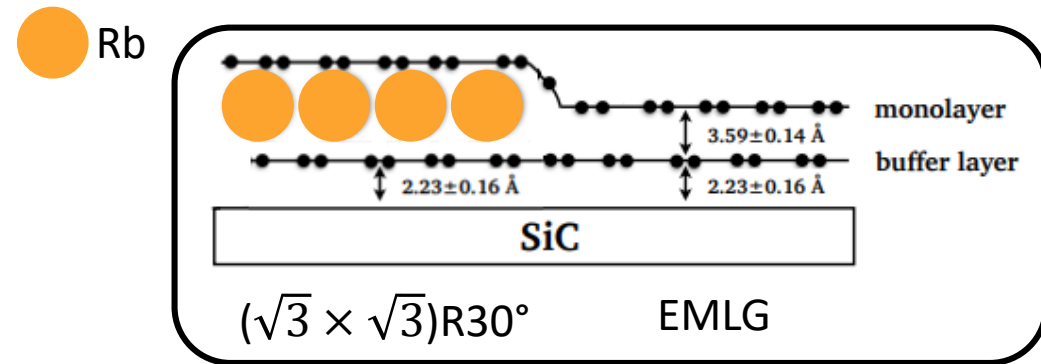
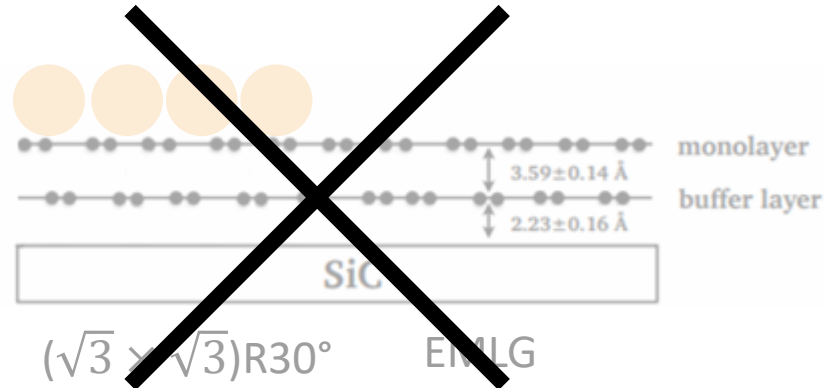


The graphene lattice can be resolved together with the  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  by STM. Thus Rb cannot be on top.



# Rubidium on EG/SiC(0001)

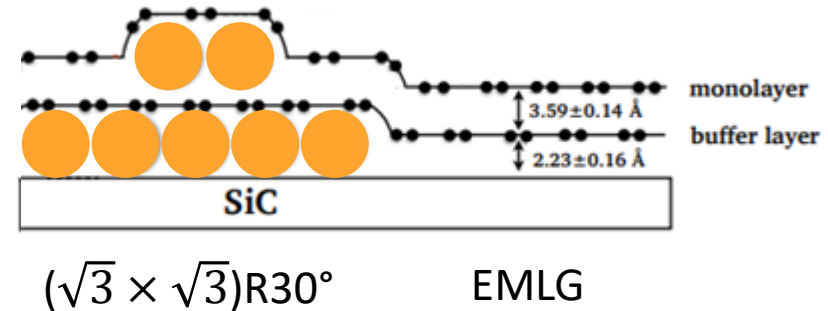
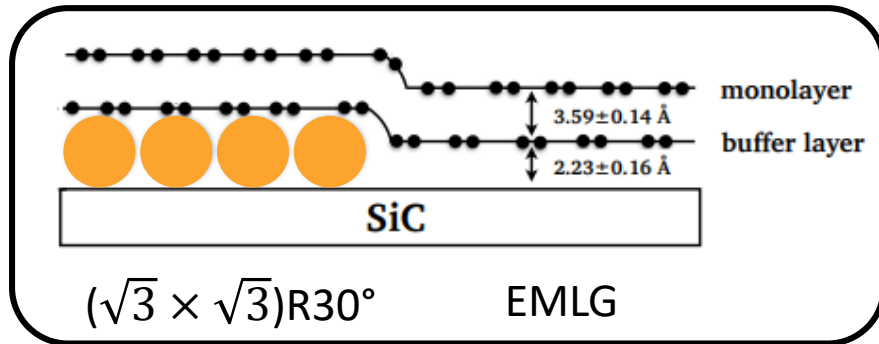
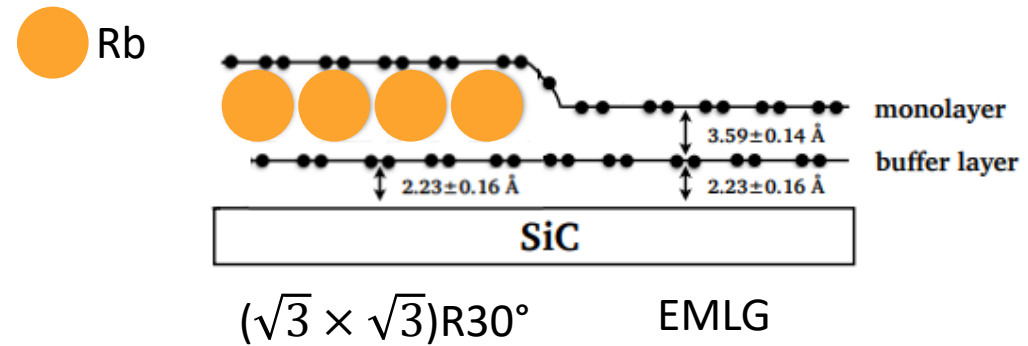
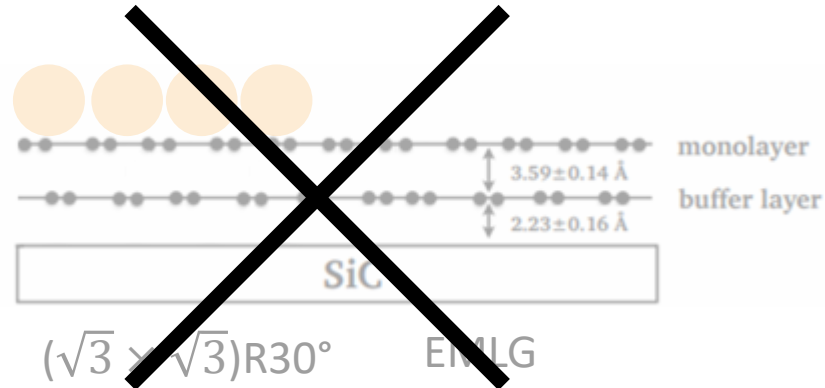
Model  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$



To obtain a  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  it is necessary more than double the amount we need to obtain a  $\text{Rb}(2 \times 2)$  and no Moirè ( $6\sqrt{3}$ ) superstructure can be observed neither at LEED nor at STM.

# Rubidium on EG/SiC(0001)

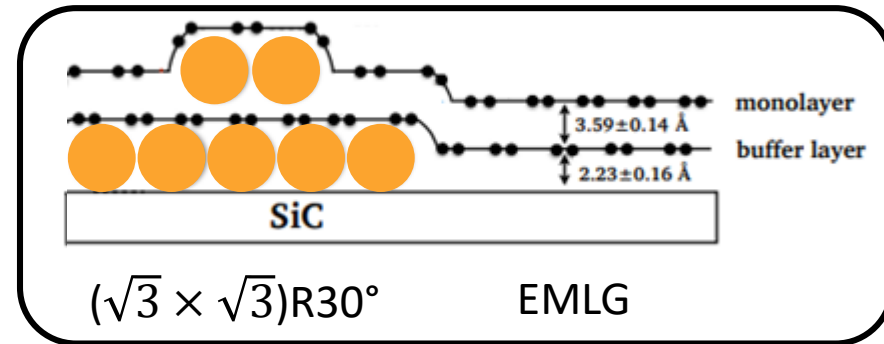
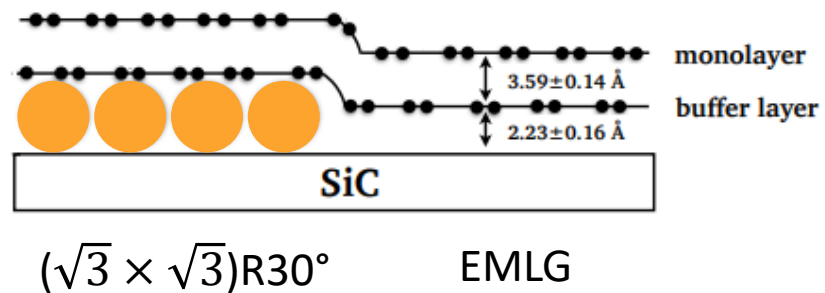
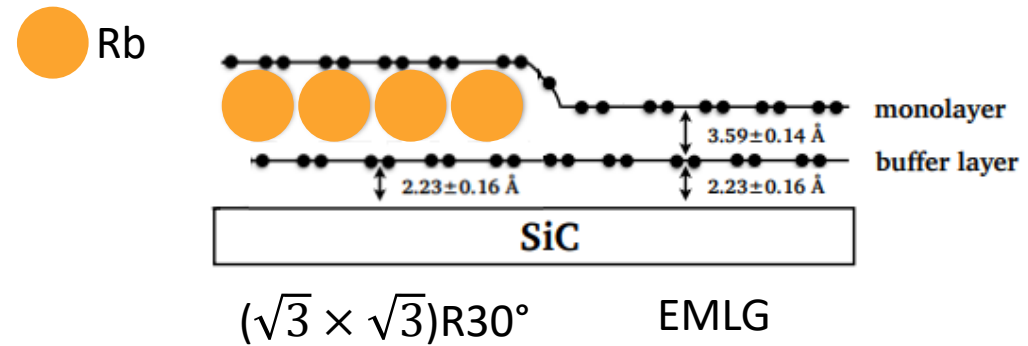
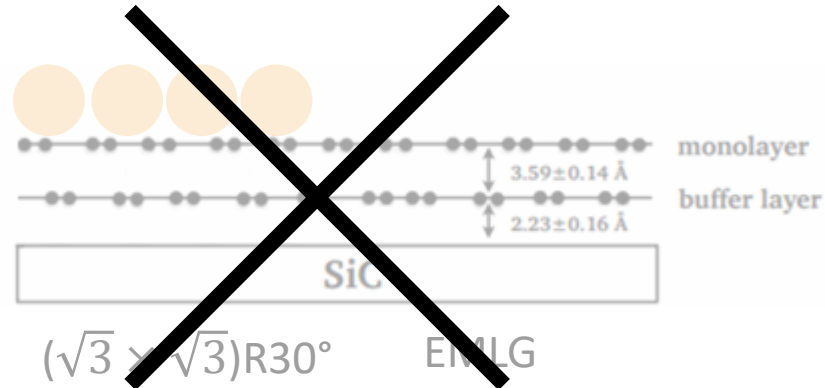
Model  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$



It has been reported for some metal that intercalation below the buffer layer can create a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ . However, to obtain a  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  it is necessary more than double the amount we need to obtain a  $\text{Rb}(2 \times 2)$ .

# Rubidium on EG/SiC(0001)

Model  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$



This option is the most plausible. Both by LEED and STM no Moirè ( $6\sqrt{3}$ ) superstructure can be observed. In STM the graphene lattice is resolved together with the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ . Moreover to obtain a  $\text{Rb}(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  it is necessary more than double the amount we need to obtain a  $\text{Rb}(2 \times 2)$ .



# Conclusions



- LEED and STM allows for the first evidence of Rb intercalated monolayer graphene.





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  - Two Rb ordering have been observed, i.e.  $(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3})R30^\circ$ .

# Conclusions

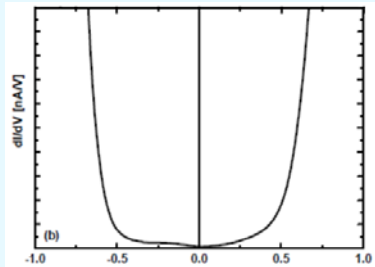
- LEED and STM allows for the first evidence of Rb intercalated monolayer graphene.
  - Two Rb ordering have been observed, i.e.  $(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3})R30^\circ$ .
    - At RT, Rb immediately intercalates monolayer graphene.

# Conclusions

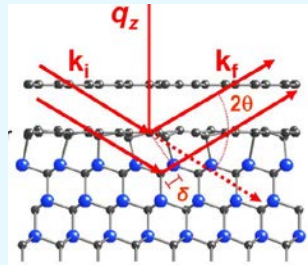
- LEED and STM allows for the first evidence of Rb intercalated monolayer graphene.
  - Two Rb ordering have been observed, i.e.  $(2 \times 2)$  and  $(\sqrt{3} \times \sqrt{3})R30^\circ$ .
    - At RT, Rb immediately intercalates monolayer graphene.
- Intercalation occurs through SiC step sites or near phase boundaries .

# Further studies

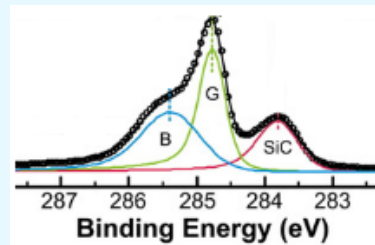
## Structural and Electronic properties



STS



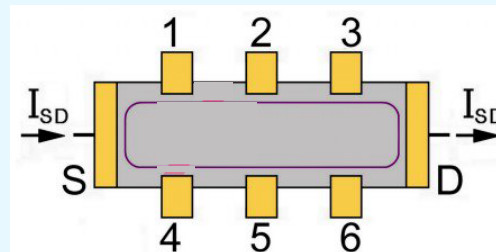
XSW



PES

## Superconductivity

Fabrication of electrical contacts

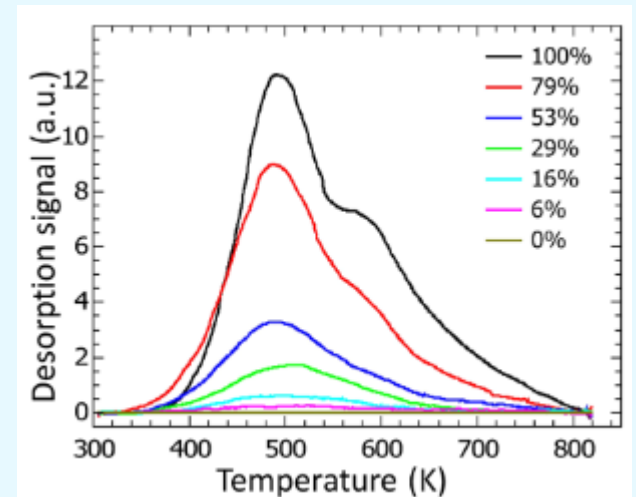


*Iagallo et al.,  
Semicond. Sci. Technol. 30 (2015) 055007*

Transport measurements at low temperature (300 mK)

## Hydrogen Storage

Thermal Desorption Spectroscopy



*Mashoff et al.,  
Appl. Phys. Lett. 103 (2013) 013903*





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**Thank you for your  
attention!**

