4pE1-5

Correlation between morphology and transport properties of quasi-free-standing monolayer graphene (QFMLG)

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3 NTT Basic Research Laboratories, NTT Corporation, Japan

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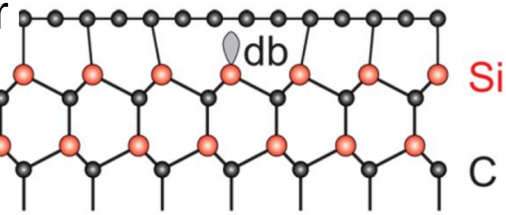
Introduction

Graphene on silicon carbide (SiC) (0001)

buffer layer

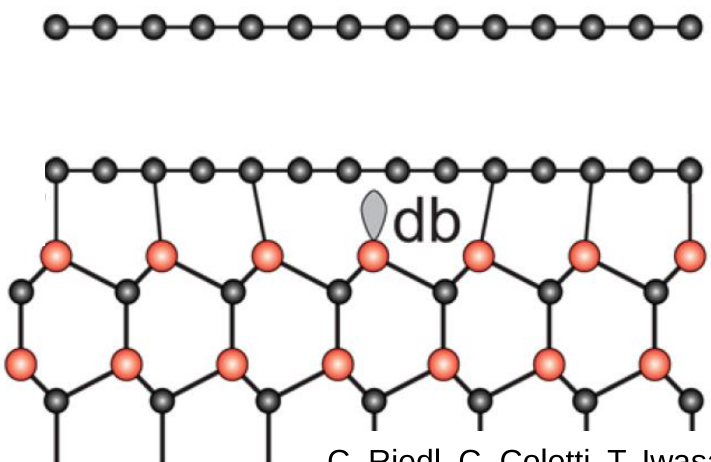


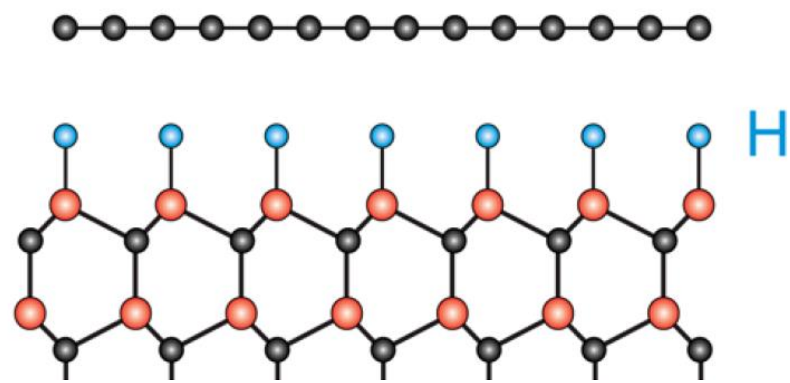
annealing

H intercalation

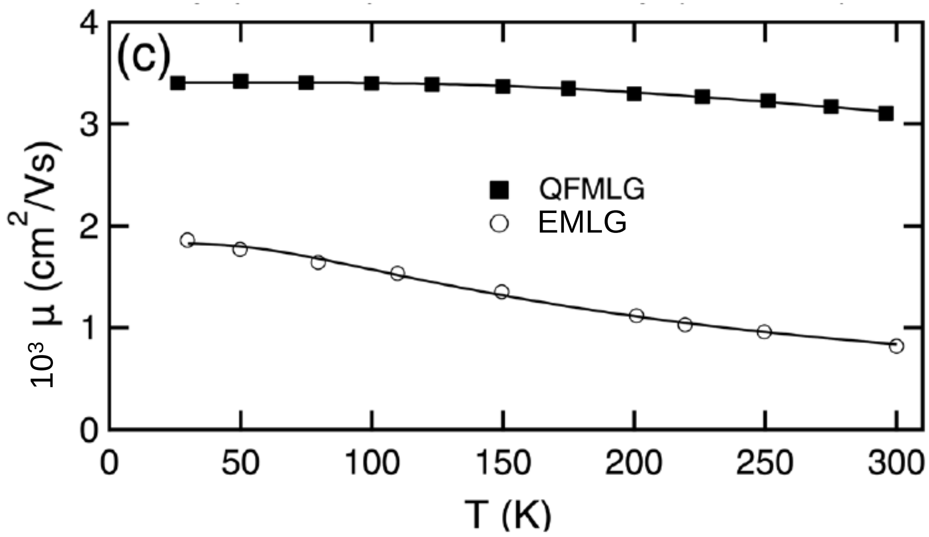
epitaxial monolayer graphene (EMLG)

quasi-free-standing monolayer graphene (QFMLG)





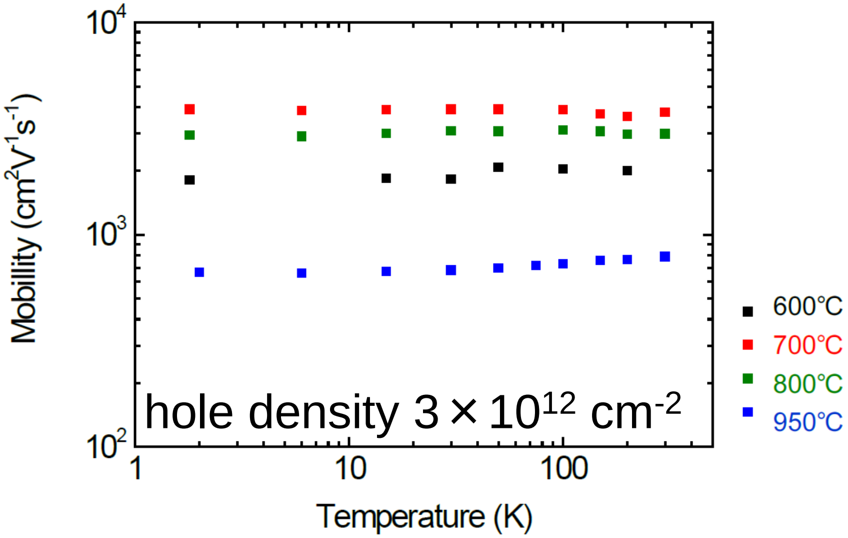
C. Riedl, C. Coletti, T. Iwasaki, A. A. Zakharov, and U. Starke, Phys. Rev. Lett. **103**, 246804 (2009)

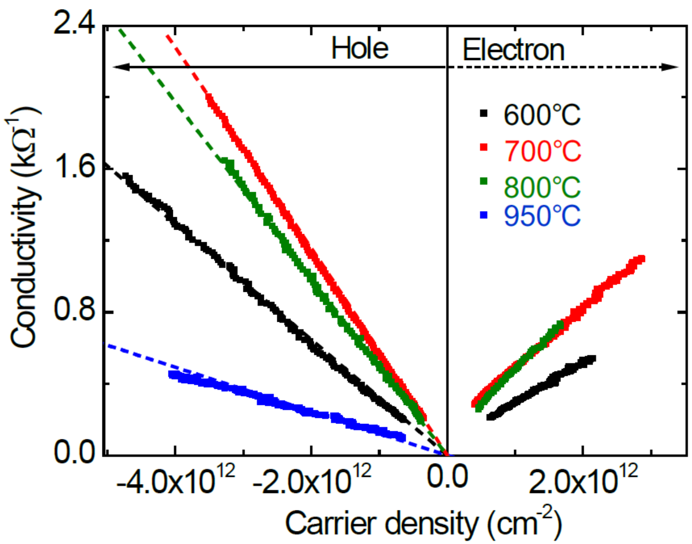


The carrier mobility of QFMLG shows less temperature dependence than EMLG, indicating less interaction between QFMLG and the SiC substrate.

However, the mobility of QFMLG (-3000 $cm^2V^{-1}s^{-1}$) is still lower than exfoliated graphene on SiO_2 or free standing graphene.

F. Speck, J.Jobst, F. Fromm, M. Ostler, D. Waldmann, M. Hundhausen, H. B. Weber, and Th. Seyller, Appl. Phys. Lett. **99**, 122106 (2011)





S. Tanabe, M. Takamura, Y. Harada, H. Kageshima, and H. Hibino, Jpn. J. Appl. Phys. **53**, 04EN01 (2014).

The QFMLG mobility depends on T_H,
the substrate temperature during H intercalation

highest mobility by $T_H = 700^oC$

conductivity – carrier density

- linear for $T_H = 600$-800^oC
  - charged impurity

- sublinear for $T_H = 950^oC$
  - additional scattering by defect

Purpose :
to observe the morphology of QFMLG formed at different T_H and investigate the relationship with transport property

Experiment

sample: 4H or 6H-SiC(0001)

cleaning anneal at 1500ºC for 5 min in H_2 of 33 mbar

buffer layer growth

anneal at 1650ºC for 5 min in Ar of 800 mbar

H intercalation

anneal at **600 - 1200ºC** for 1 hour in H_2 of 1 atm

characterization

- STM in ultra-high vacuum (1×10^{-10} mbar)
- AFM in air
- TEM

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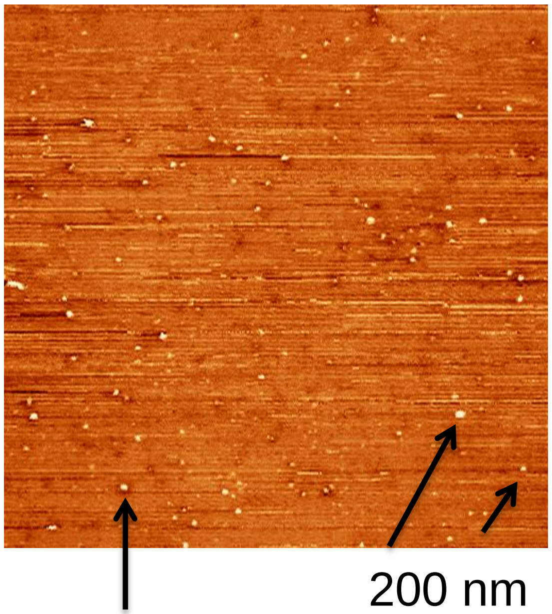
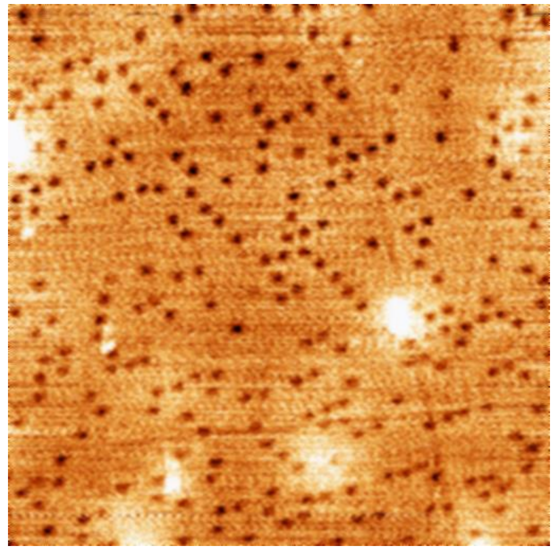
STM $T_H = 600^{\circ}C$



200 nm

- bright spots

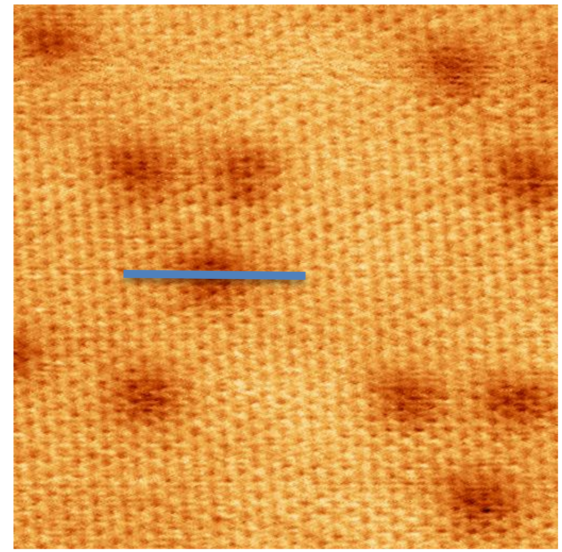
width: 2-3 nm
height: 50 pm



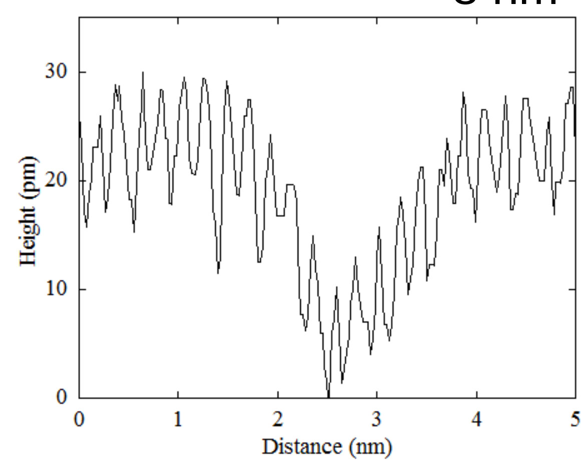
50 nm

- small dark spots

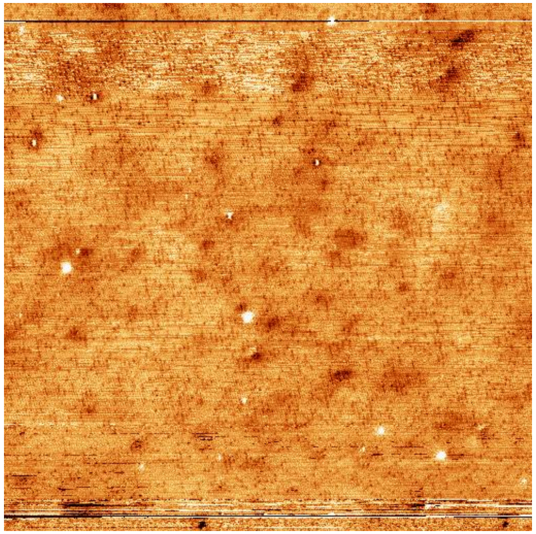
width: 1.5 nm
depth: 15-25 pm



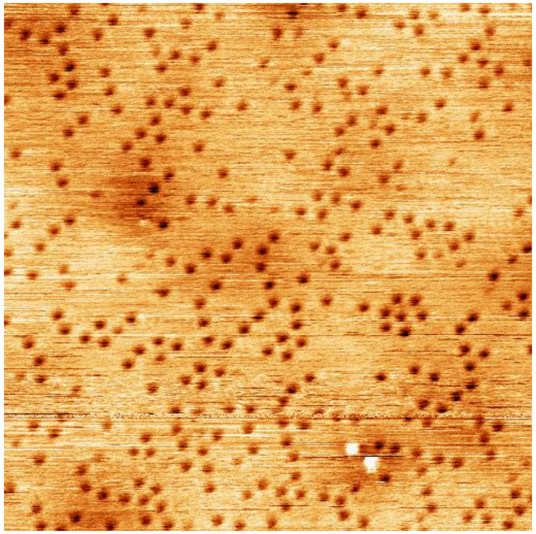
8 nm



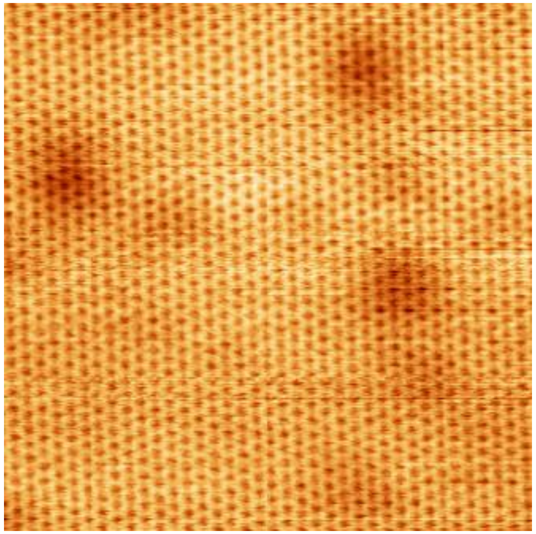
STM $T_H = 800ºC$



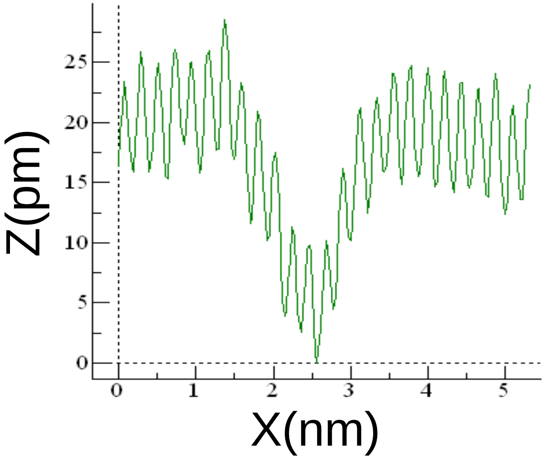
200 nm



50 nm



8 nm



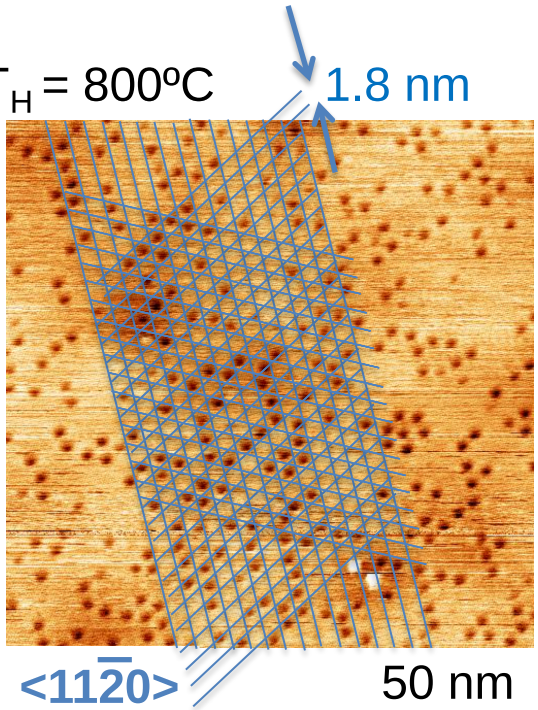
- small dark spots

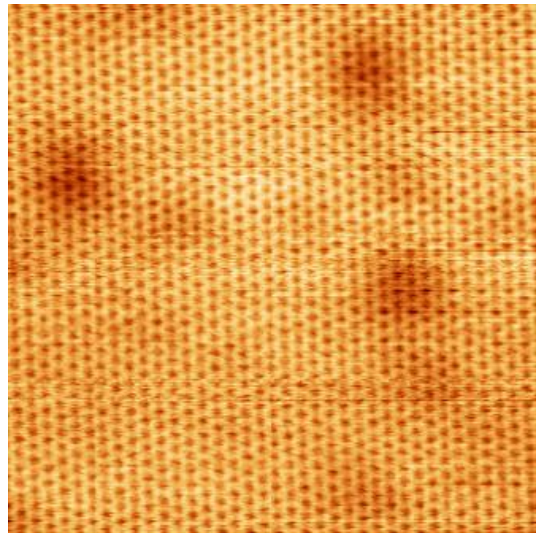
- bright spots

almost same morphology as $T_H = 600ºC$

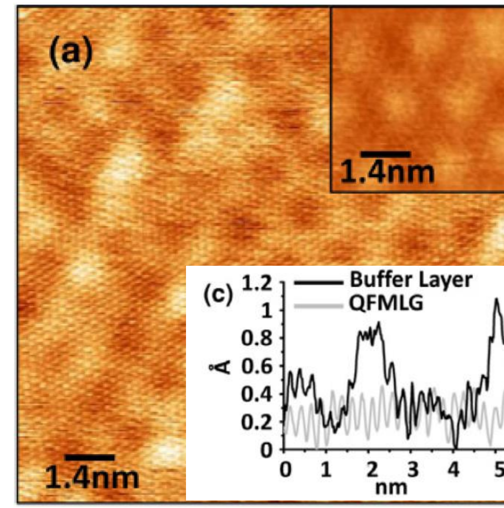
Small dark spots

T_H = 800ºC





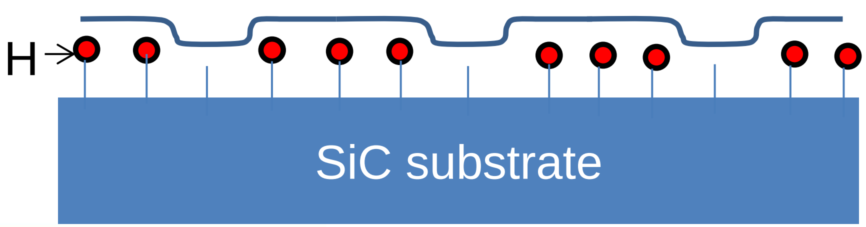
STM of a buffer layer corrugation – 60 pm



Goler, Carbon **51**, 249 (2013)

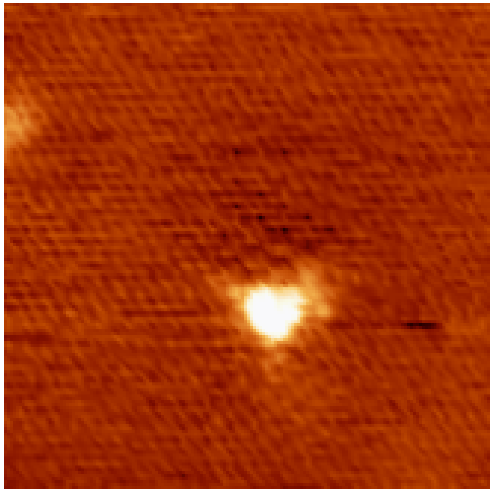
- width: 1.5 nm
- depth: 15-25 pm
- honeycomb inside, no defect
- align along SiC<11$\bar{2}$0>
- periodicity: 1.8 nm = SiC-6 × 6

incomplete H intercalation
– Si dangling bond at interface

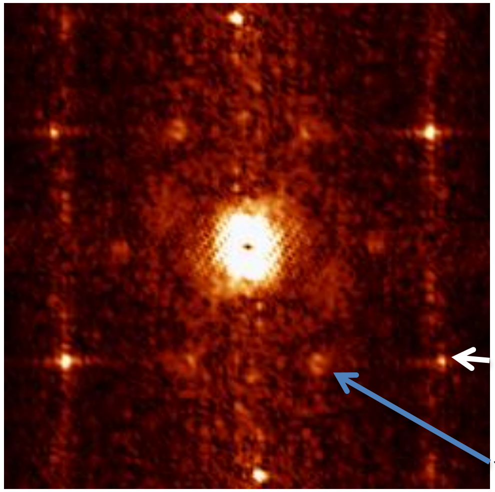


Bright spots

8 nm



2D Fourier transform

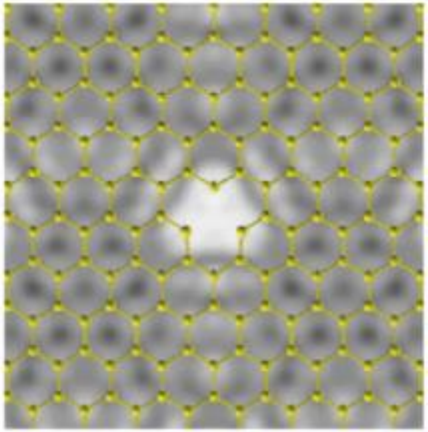


graphene-1 × 1

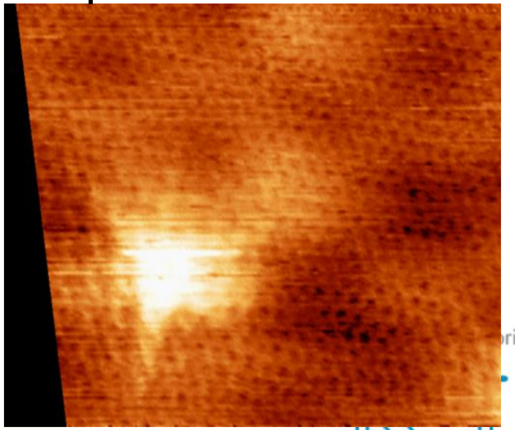
$\sqrt{3} \times \sqrt{3}$

electron scattering at defect

defect of EMLG



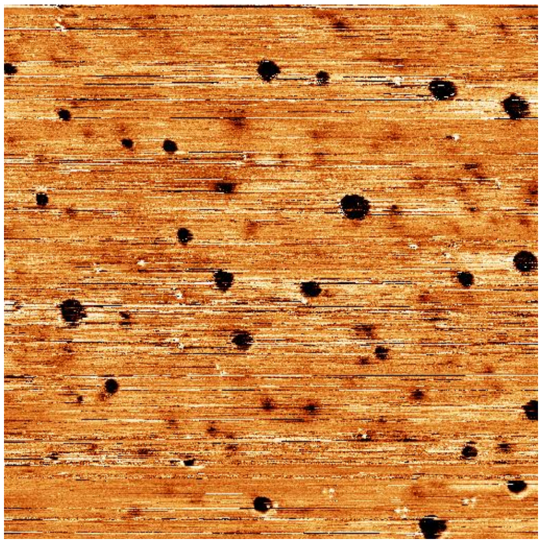
N-sputtered EMLG



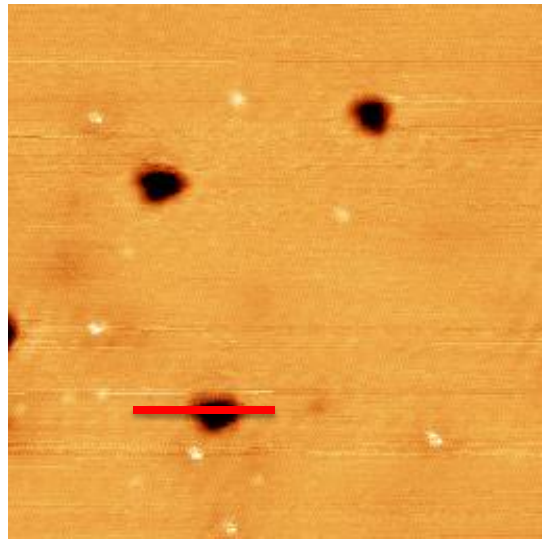
Mashoff, et.al., arXiv:1410.2741

Rhim, Appl. Phys. Lett. **100**, 233119 (2012)

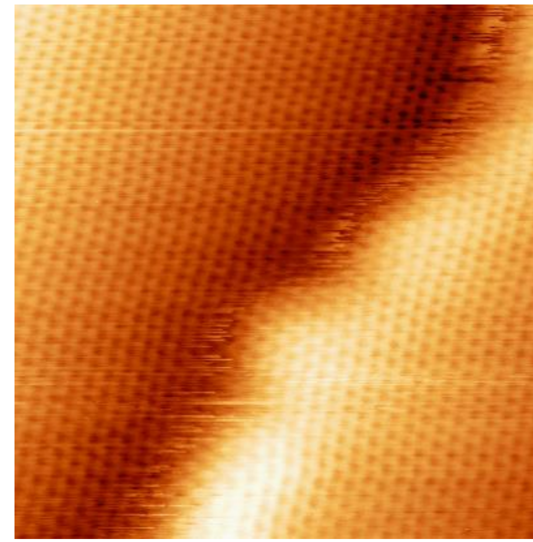
STM $T_H = 1000^{o}C$



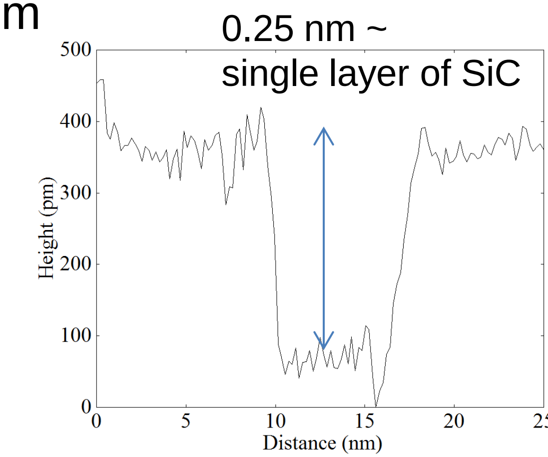
200 nm



50 nm

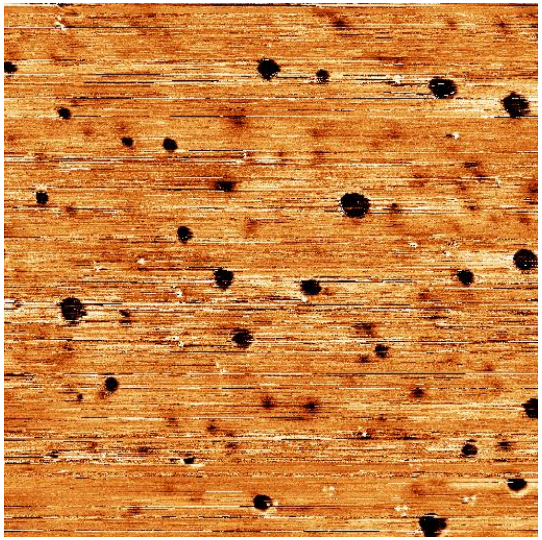


8 nm

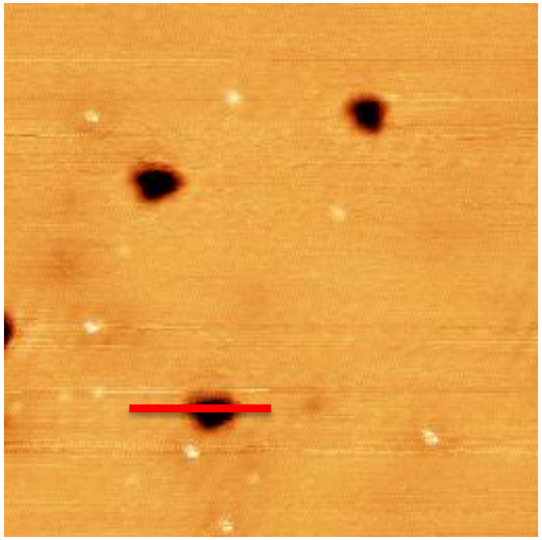


- large dark spots (width: 4-10 nm, depth: 0.25-0.3 nm)
- small dark spots (width: 1.5 nm, depth: 15-25 pm)
- bright spots

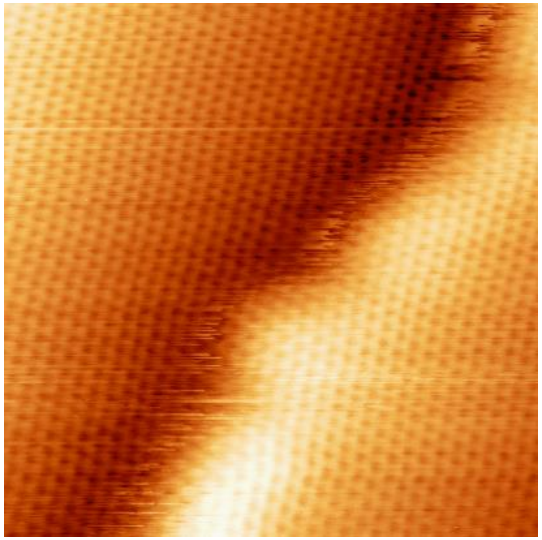
Large dark spots



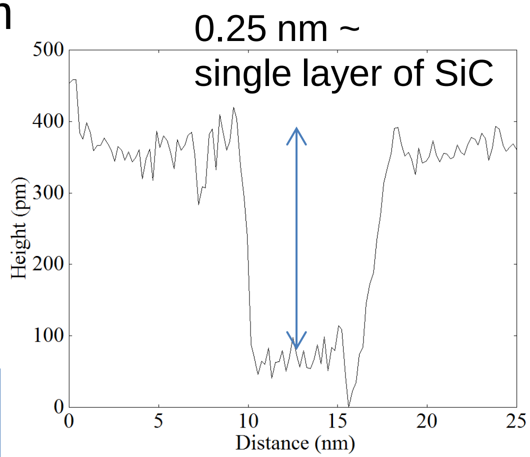
200 nm



50 nm



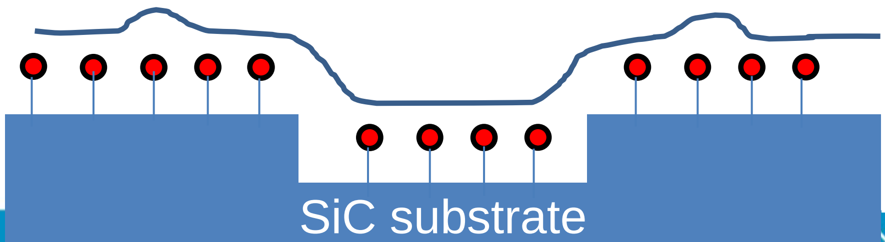
8 nm



- width: 4-10 nm, depth: 0.25-0.3 nm

- distribute randomly
- honeycomb inside

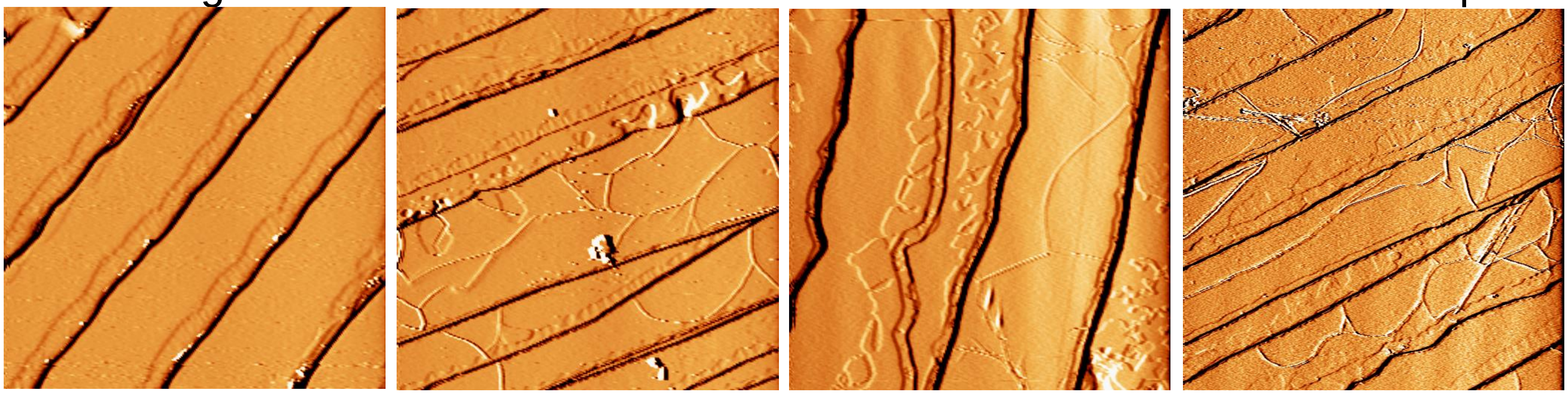
hole in the SiC substrate



etched at high T_H

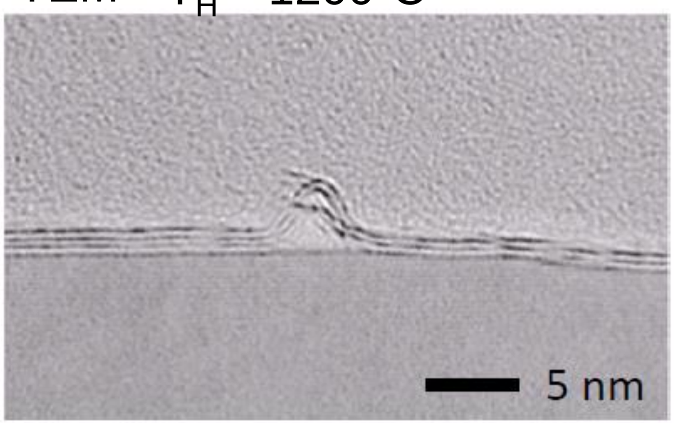
Wrinkles of graphene

AFM images differentiated in horizontal axis 14 µm



T_H = 650ºC 800ºC 950ºC 1100ºC

TEM T_H = 1200ºC



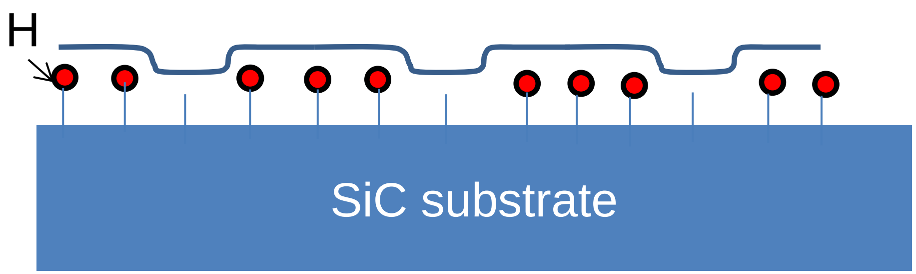
wrinkles appear at T_H > 800ºC

more pronounce at T_H > 1100ºC

the difference in thermal expansion coefficients between graphene and SiC

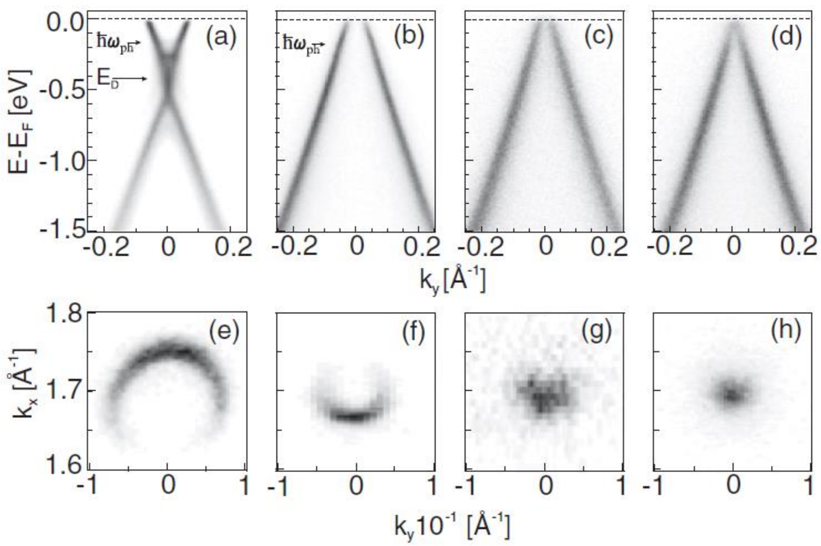
Morphology and transport

T_H = 600-800ºC



- small dark spots

  incomplete H intercalation
  - Si dangling bonds



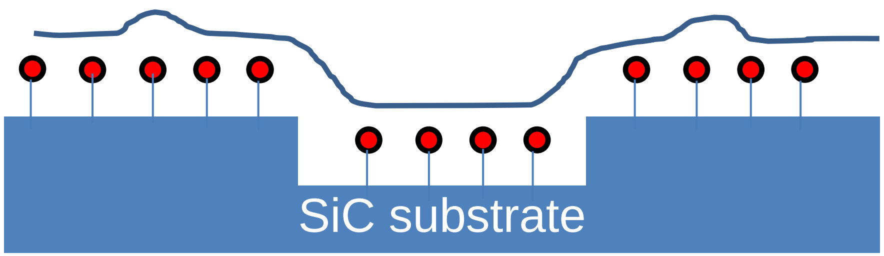
ARPES Forti, et.al., Phys. Rev. B 84, 125449 (2011).

annealing QFMLG in vacuum

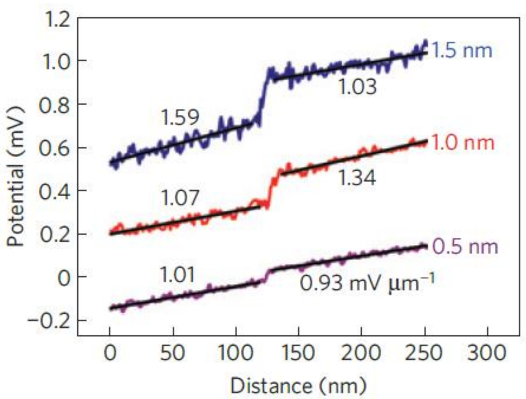
-H atoms desorb
-Si dangling bonds donate charge to graphene and act as charged scattering centers.

Morphology and transport

$T_H = 1000^oC$



- dark spot – hole in SiC substrate
- wrinkle of graphene



Scanning tunneling potentiometry

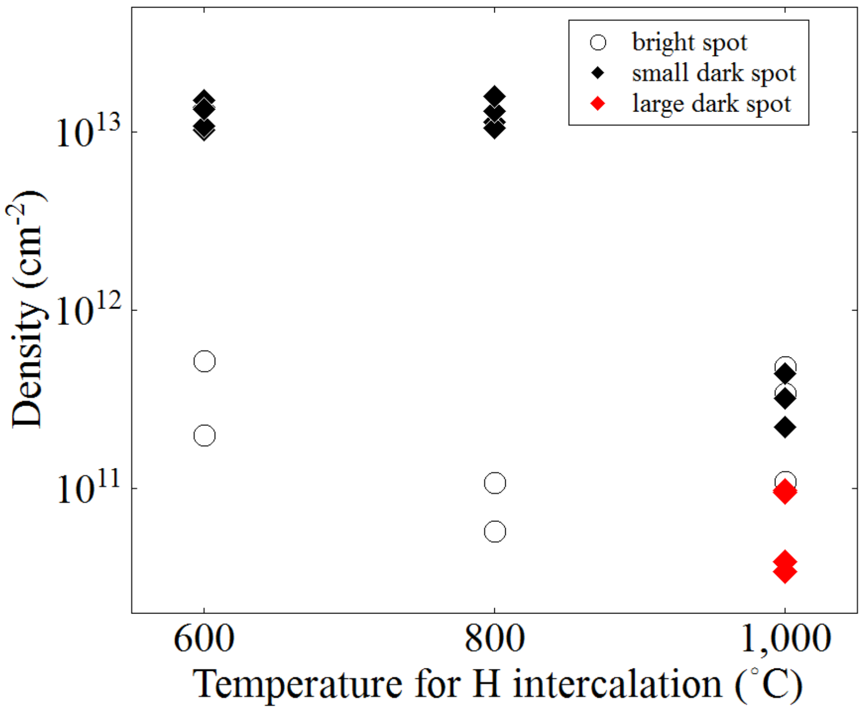
Ji, et.al., Nature Materials 11, 114 (2012)

resistance of EMLG increases over SiC substrate steps

- π-σ hybridization by curvature of graphene
- strain of graphene
- reduced doping due to a larger distance at the interface

T. Low, V. Perebeinos, J. Tersoff, and Ph. Avouris, Phys. Rev. Lett. 108, 096601 (2012)

Morphology and transport



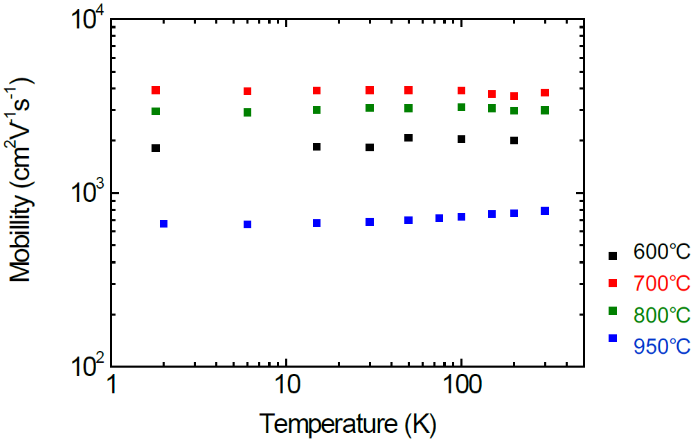
- bright spot – constant at any T_H

As T_H increases from 600-800 to 1000ºC,

- small dark spot decreases.
  -more H intercalation

- hole in SiC substrate and wrinkles of graphene appear

The formation of holes and wrinkles has a larger influence on the QFMLG mobility than increased H intercalation.



S. Tanabe, Jpn. J. Appl. Phys. **53**, 04EN01 (2014).

Conclusion

- We investigated the morphology of QFMLG formed at several temperatures by H intercalation with STM, AFM, and TEM.

- We found that Si dangling bonds due to incomplete H intercalation at the graphene-substrate interface cause carrier scattering as charged impurities in QFMLG at T_H = 600 and 800ºC.

- At T_H = 1000ºC, holes in the SiC substrate and wrinkles of graphene appear and decrease the mobility of QFMLG, despite a better H intercalation.

- In order to obtain a higher mobility of QFMLG, we need to optimize the H intercalation condition to intercalate more H, below the temperature at which holes and wrinkles appear.

arXiv:1409.0457

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Thank you for your attention!

Funding:

Consiglio Nazionale delle Ricerche

Japan Society for the Promotion of Science
日本学術振興会

Repubblica Italiana
Ministero degli Affari Esteri

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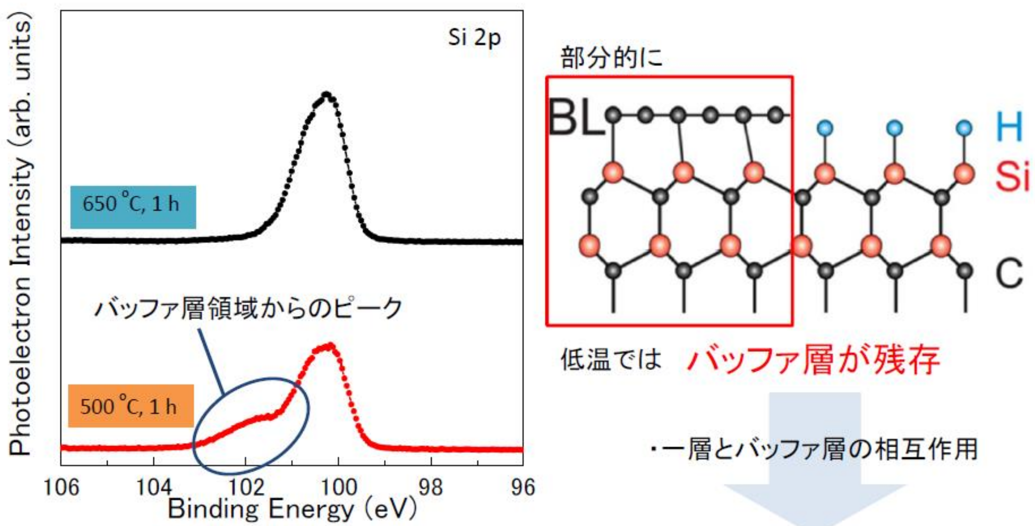
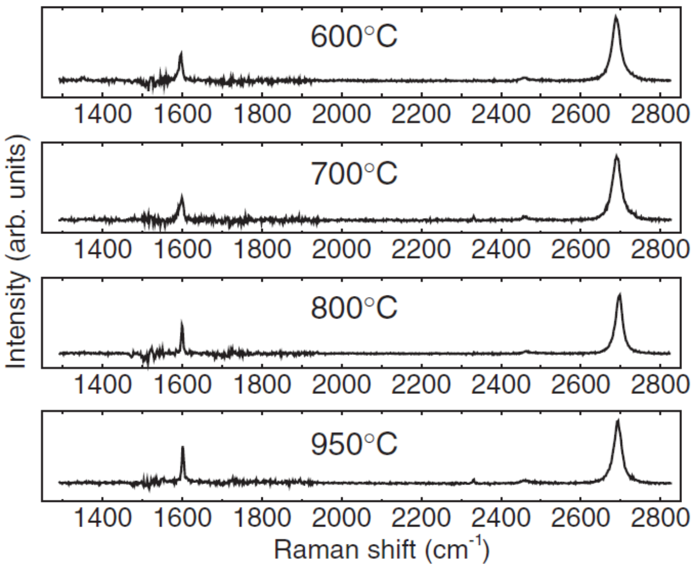
XPS

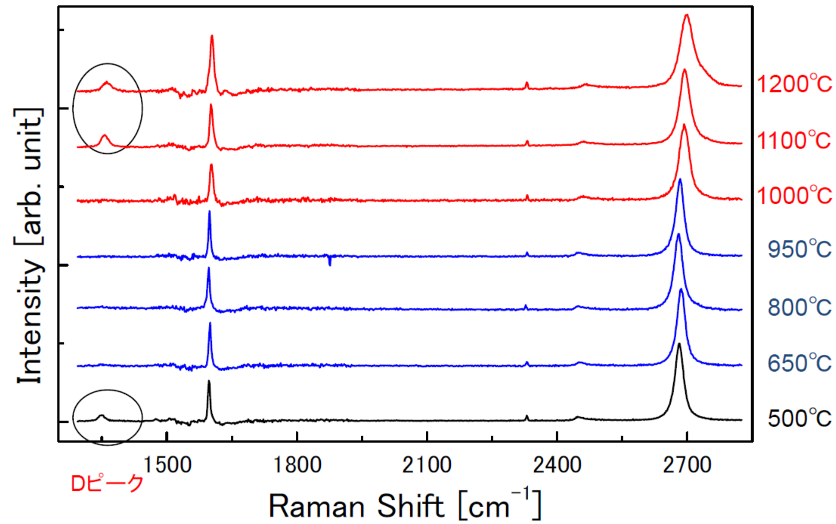


各サンプルのXPS分析結果 (Siの2p軌道)

The signal from buffer layer was obtained at T = 500C, but not at 650C.

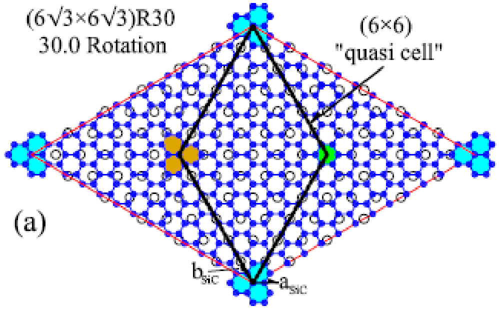
Raman





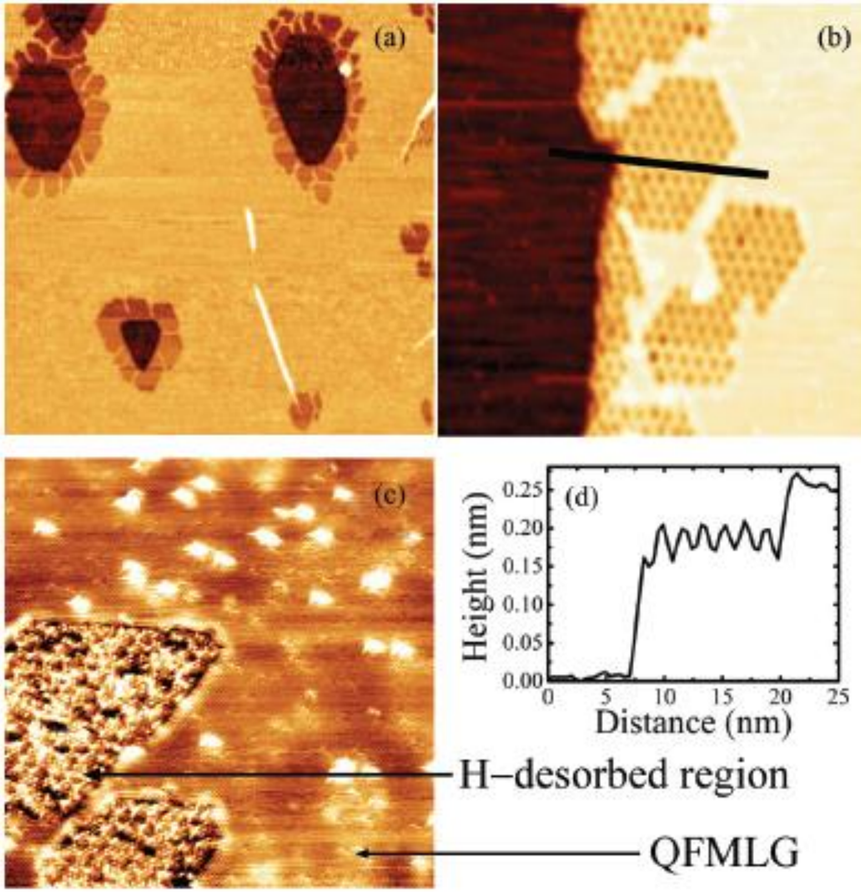
低温域および高温域ではDピークが見られた。
グラフェン中に欠陥が導入されることで低い移動度を示すと思われる。

D peak at 600C, 500C and > 1100C



A buffer layer (SiC(0001)1x1) has 1.22 x 10^{15} Si atoms cm^{-2}.

The density of small dark spots is <1.4 x 10^{13} cm^{-2} (~ 1% of Si atoms).



(a)
(b)
(c)
(d)
Height (nm)
0.25
0.20
0.15
0.10
0.05
0.00
0
5
10
15
20
25
Distance (nm)
H−desorbed region
QFMLG

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PHYSICAL REVIEW B 86, 045453 (2012)

binding energy of chemisorbed H on graphene = 1.18 eV
binding energy of H2 on graphene ~ 0.1 eV

formation energy of QFMLG = -2.9 eV
H intercalation is energeticaly favorable

energy barrier for diffusion of an H atom through a graphene layer = 3.73 eV

energy barrier for diffusion of an H atom through a buffer layer = 4.7 eV

energy barrier for diffusion of an H atom and H2 molecules through a buffer layer with defects

	Pristine	SW	V_2	V_4
H	2.55	1.52	0.13	0.23
H_2	. . .	6.89	3.64	0.69

barrier for migration of an H atom at the interface between a buffer layer and SiC = 0.6 eV
barrier for migration of a H2 molecule at the interface between QFMLG and SiC = 0.3 eV