

# 低次元物質の結晶成長: グラフェンを中心に

NTT物性科学基礎研究所

日比野浩樹

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# 内容

1. グラフェンとは
2. グラフェン評価法
3. グラフェン成長法
  - 3-1 化学気相成長法
  - 3-2 析出法
  - 3-3 SiC熱分解法

# 炭素の同素体

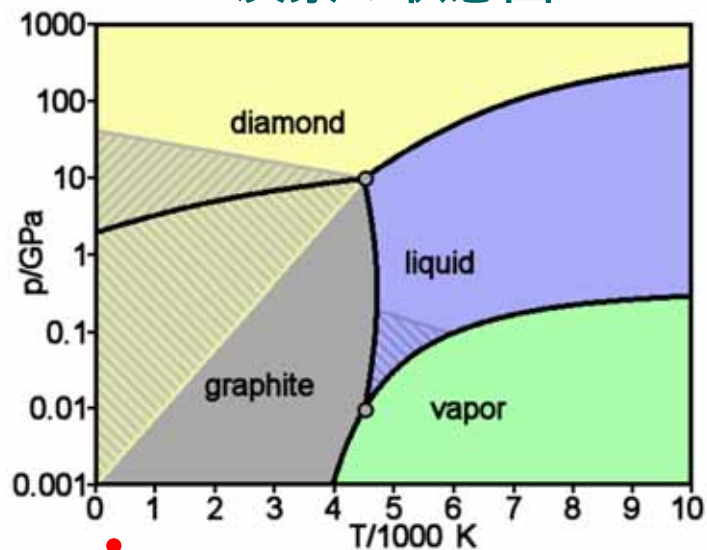
炭素：単体・化合物において極めて多様な形状、生物の構成材料（重量比~18%）

Graphene (2D)

(2004~)

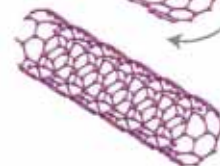
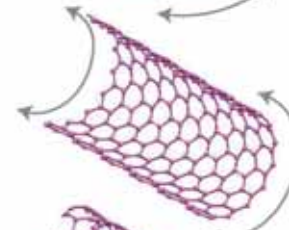
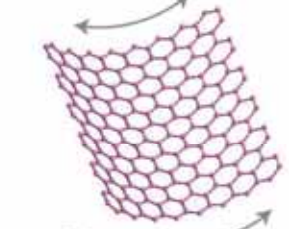
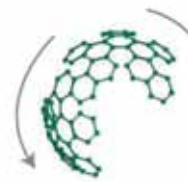
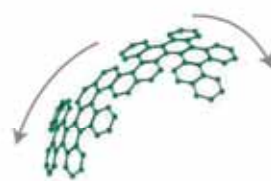
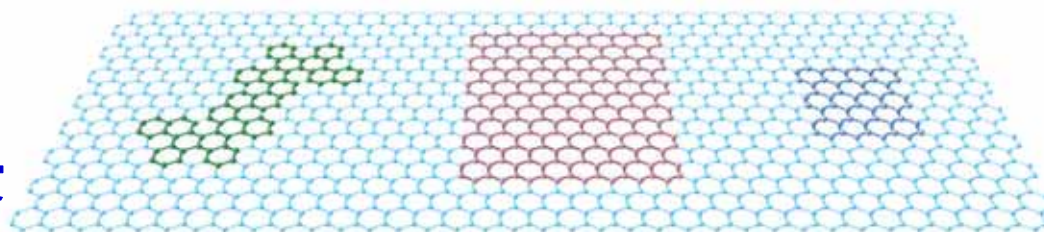
2010年 ノーベル物理賞

炭素の状態図



~100 kPa, 300 K

<http://ja.wikipedia.org/wiki/>



Buckyball (0D)

(1985~)

1996年 ノーベル化学賞

Nanotube (1D)

(1991~)

Graphite (3D)

(1564~)

# グラフェンの実験的な発見

22 OCTOBER 2004 VOL 306 SCIENCE

## Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,<sup>1</sup> A. K. Geim,<sup>1\*</sup> S. V. Morozov,<sup>2</sup> D. Jiang,<sup>1</sup>  
Y. Zhang,<sup>1</sup> S. V. Dubonos,<sup>2</sup> I. V. Grigorieva,<sup>1</sup> A. A. Firsov<sup>2</sup>

We describe **monocrystalline graphitic films, which are a few atoms thick** but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to  $10^{13}$  per square centimeter and with **room-temperature mobilities of  $\sim 10,000$**  square centimeters per volt-second can be induced by applying gate voltage.

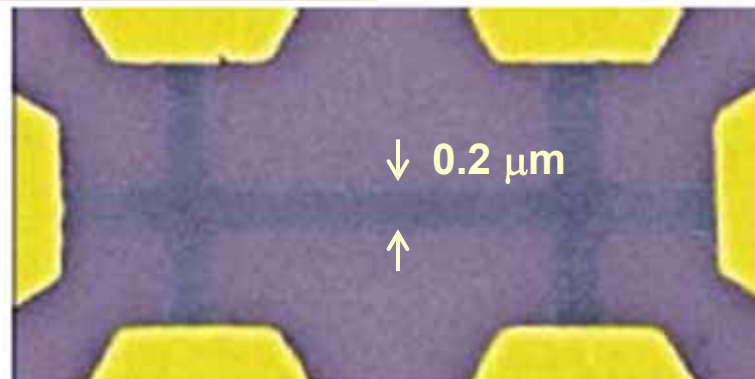
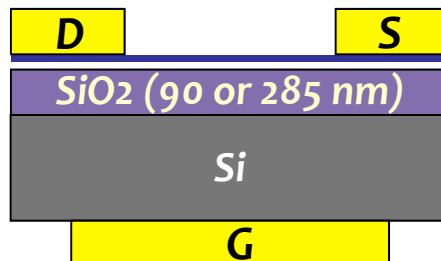
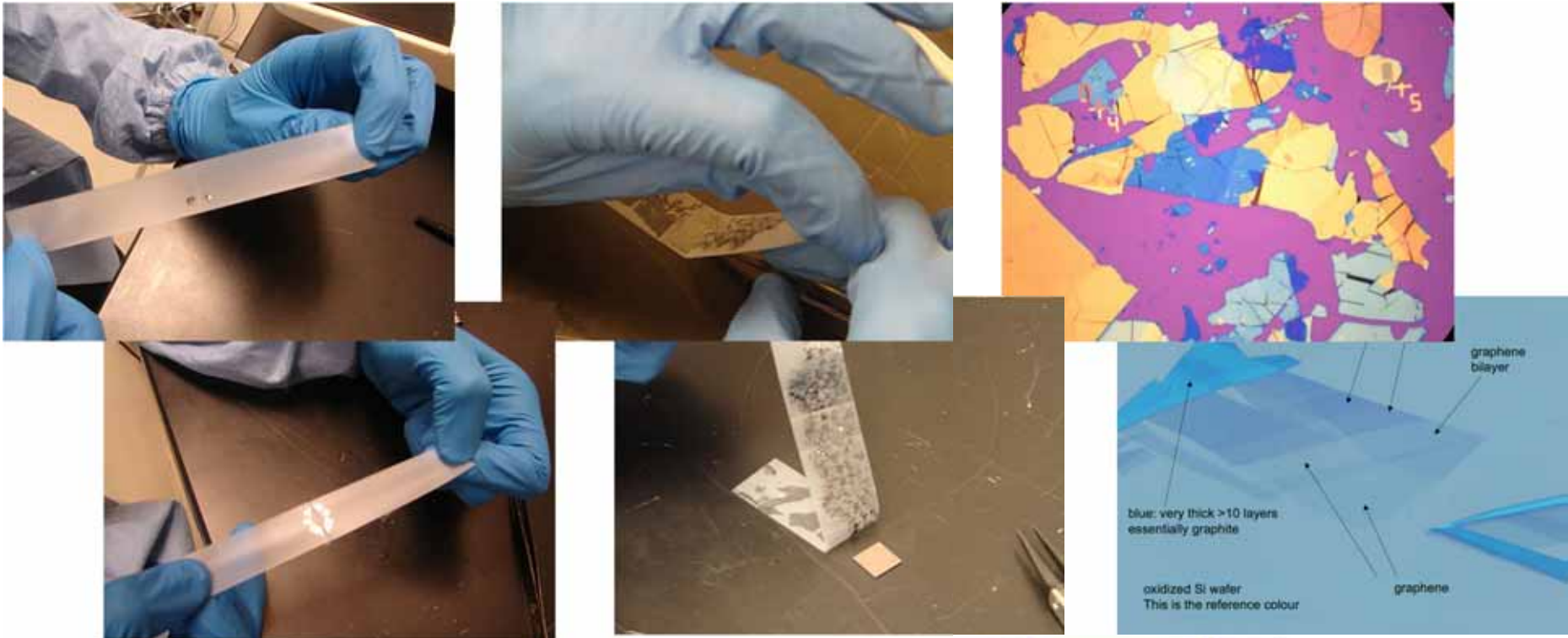
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<sup>1</sup>Department of Physics, University of Manchester, Manchester M13 9PL, UK. <sup>2</sup>Institute for Microelectronics Technology, 142432 Chernogolovka, Russia.

# D.I.Y. グラフェン

## How to Make One-Atom-Thick Carbon Layers With Sticky Tape

<http://www.sciam.com/article.cfm?id=diy-graphene-how-to-make-carbon-layers-with-sticky-tape>



K. S. Novoselov et al., *Nature* 438, 197 (2005).

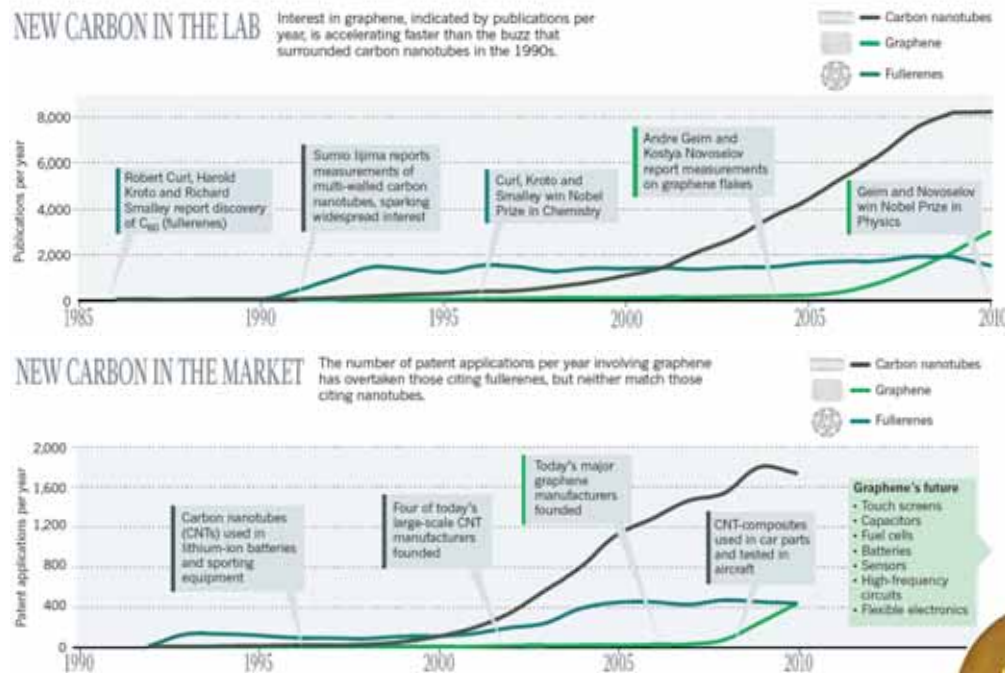
# グラフェン研究の爆発的進展

- ✓ 簡単な作製方法
- ✓ 特異な物性(理論的蓄積1947~)
- ✓ 幅広い応用分野

基礎から応用まで  
爆発的に研究が進展

産業応用?

## 2010 ノーベル物理学賞



Richard Van Noorden, *Nature* 469, 14-16 (2011).



Andre Geim



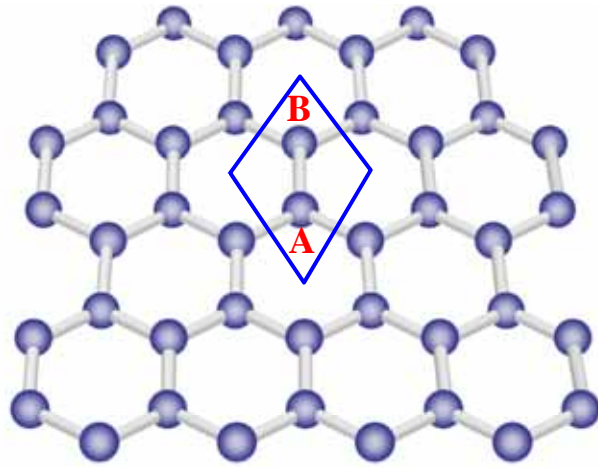
Konstantin Novoselov



For groundbreaking experiments regarding the two-dimensional material graphene

... Playfulness is one of their hallmarks.

# グラフェンの電子構造



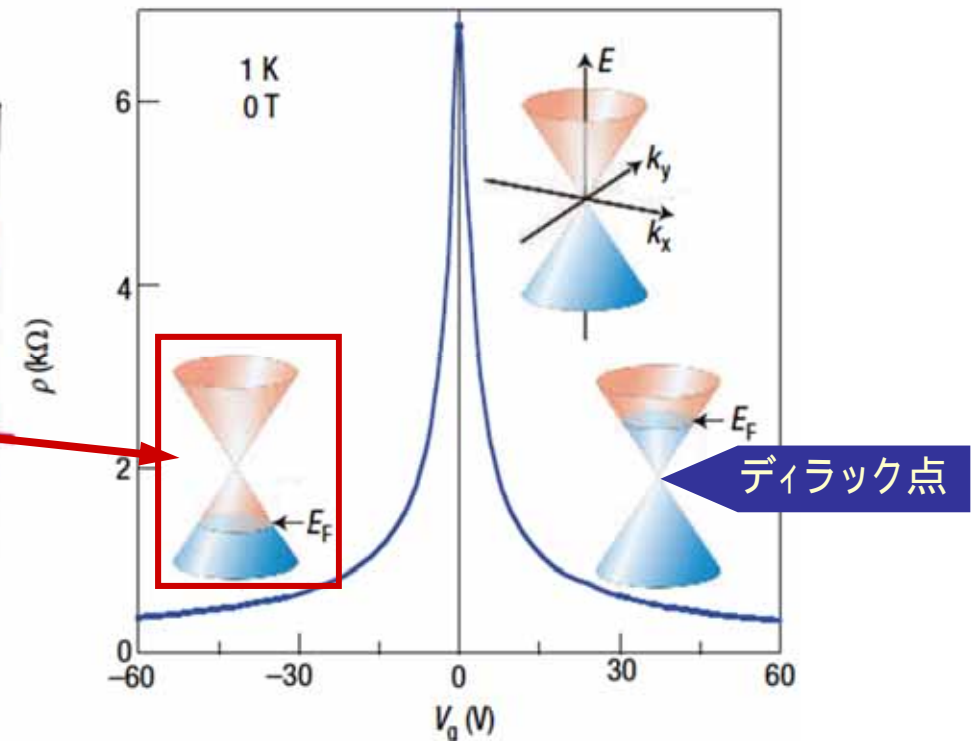
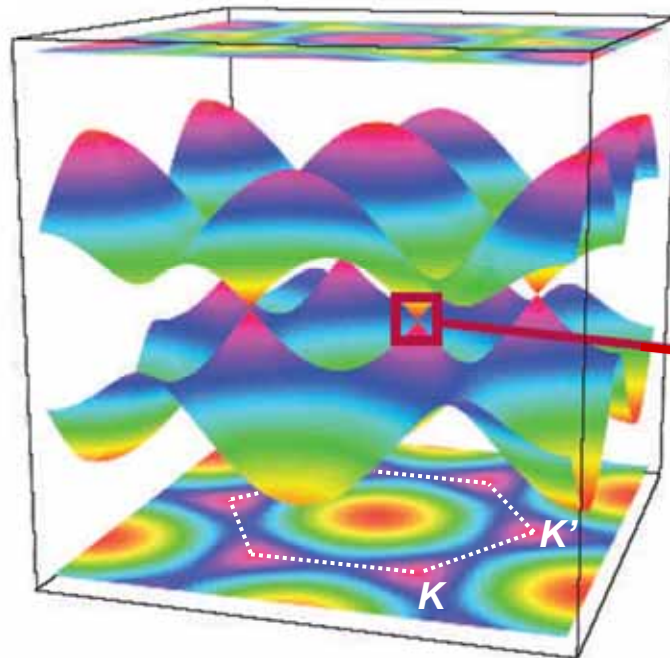
質量の無いディラック型のフェルミ粒子

- ✓線型なエネルギー分散  $\approx$  光子
- ✓相対論的量子力学に従う電子

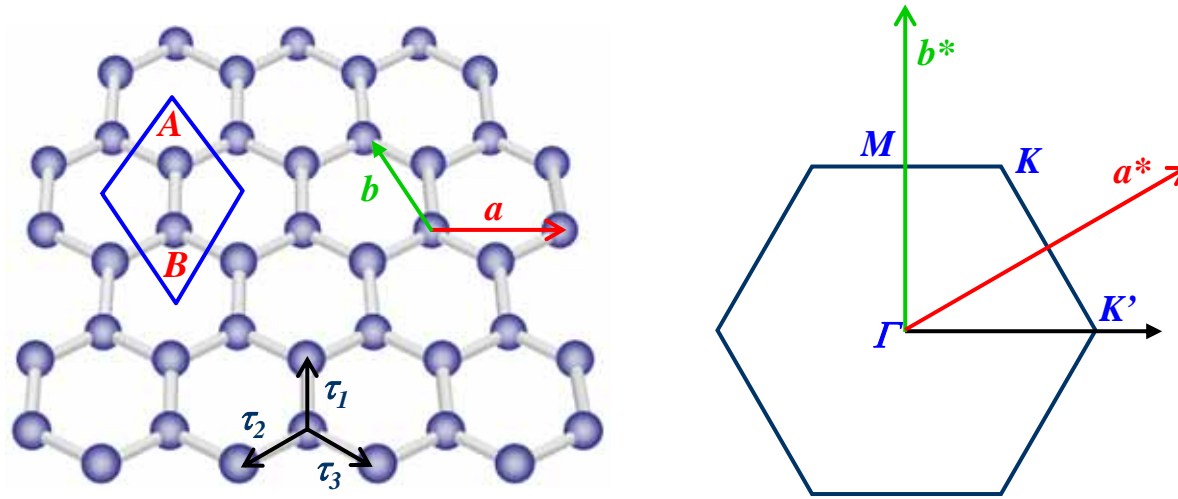
$$\varepsilon_s(k) = s\gamma|k|, \quad s = \pm 1$$

$$v = \frac{\gamma}{\hbar} \approx \frac{c}{300}$$

$\pi$ -バンド構造



# グラフェンの電子構造



$$\gamma \begin{pmatrix} 0 & k_x - ik_y \\ k_x + ik_y & 0 \end{pmatrix} \begin{pmatrix} \tilde{f}_A(\vec{k}) \\ \tilde{f}_B(\vec{k}) \end{pmatrix} = \varepsilon \begin{pmatrix} \tilde{f}_A(\vec{k}) \\ \tilde{f}_B(\vec{k}) \end{pmatrix} \longrightarrow \varepsilon_{\pm}(\vec{k}) = \pm \gamma |\vec{k}|$$

$$\gamma = \frac{\sqrt{3}}{2} a \gamma_0 = -\frac{\sqrt{3}}{2} a \langle \varphi(x-R) | H | \varphi(x-R-\tau) \rangle, \text{ ホッピング積分 } -\gamma_0 \ (\gamma_0 \sim 3 \text{ eV})$$

$$f(\vec{k}) = \begin{pmatrix} \tilde{f}_A(\vec{k}) \\ \tilde{f}_B(\vec{k}) \end{pmatrix} \longrightarrow \begin{cases} @K & \gamma(\sigma \cdot \vec{k}) f(\vec{k}) = \varepsilon f(\vec{k}) \\ @K' & \gamma(\sigma^* \cdot \vec{k}) f(\vec{k}) = \varepsilon f(\vec{k}) \end{cases}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

ニュートリノのWeyl方程式と形式的に同じ

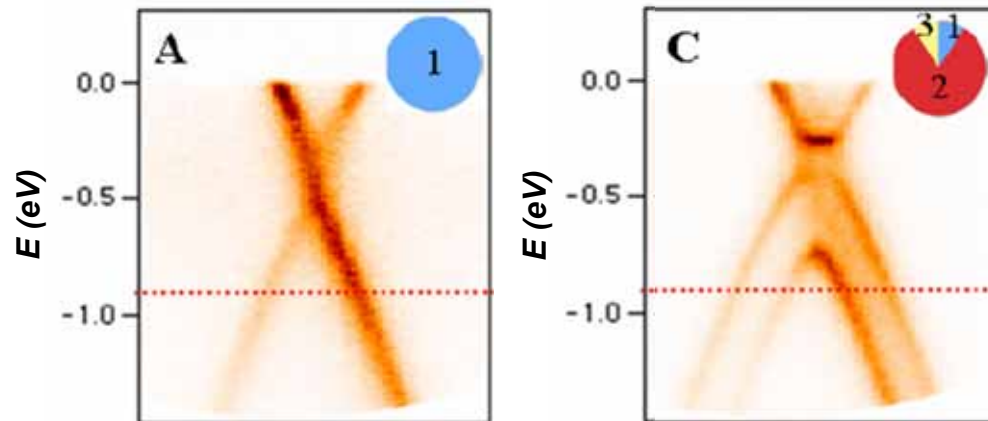
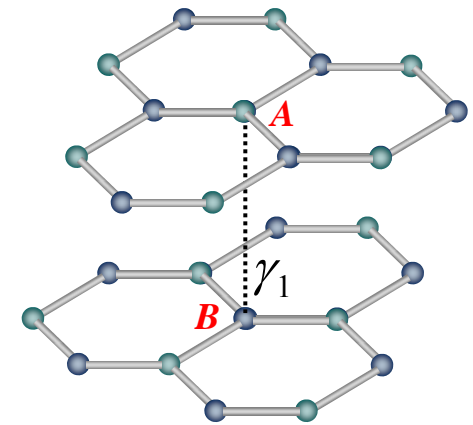


# 2層グラフェンのバンド構造

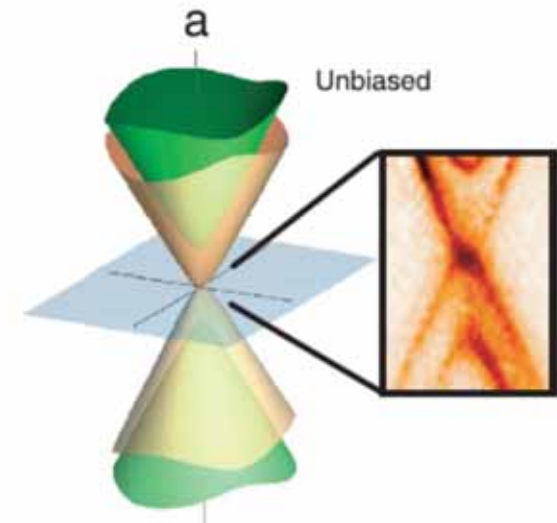
$$H^K = \begin{pmatrix} 0 & v(p_x - ip_y) & 0 & 0 \\ v(p_x + ip_y) & 0 & \gamma_1 & 0 \\ 0 & \gamma_1 & 0 & v(p_x - ip_y) \\ 0 & 0 & v(p_x + ip_y) & 0 \end{pmatrix}$$

$$\varepsilon_{\mu,s}(p) = s \left( \frac{\mu\gamma_1}{2} + \sqrt{\frac{\gamma_1^2}{4} + (vp)^2} \right) \quad \mu = \pm 1, s = \pm 1$$

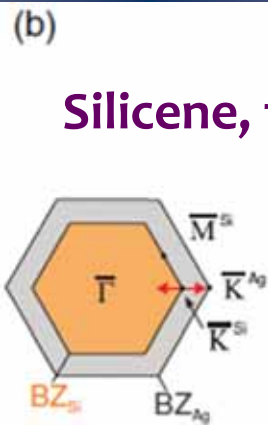
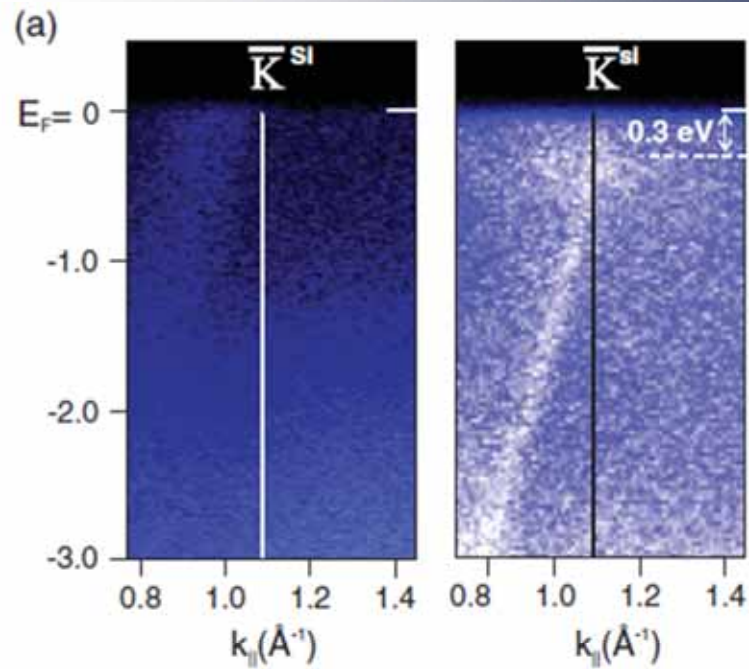
$$\longrightarrow \varepsilon_{-,s}(k) = s \frac{p^2}{2m^*} \quad m^* = \frac{\gamma_1}{2v^2}$$



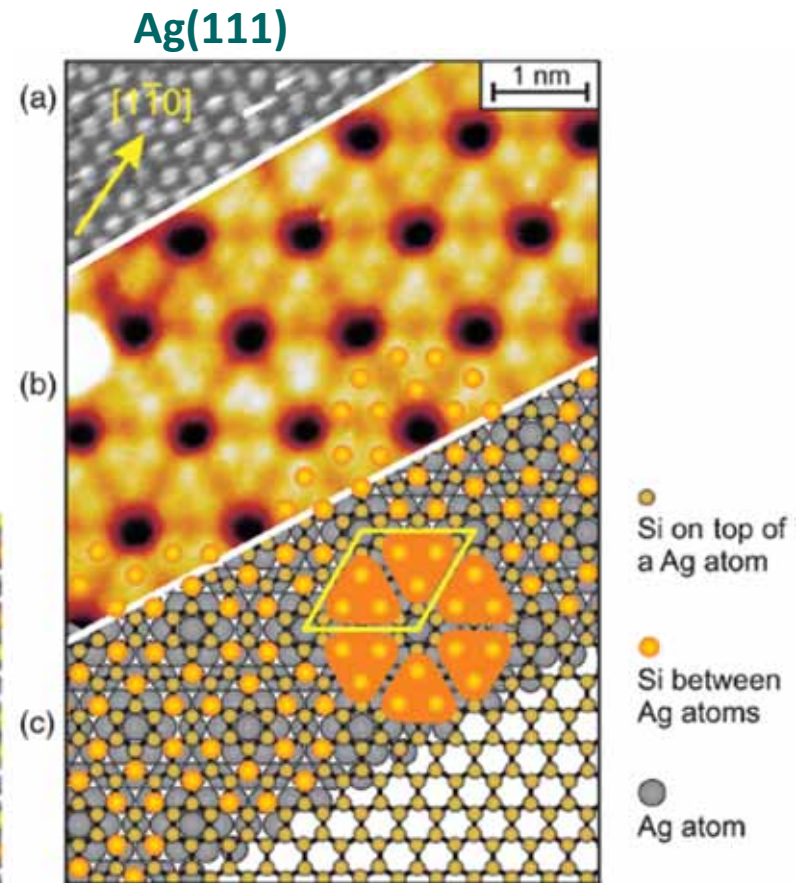
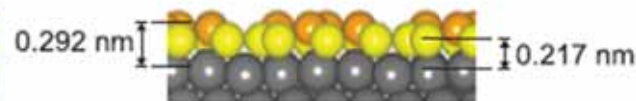
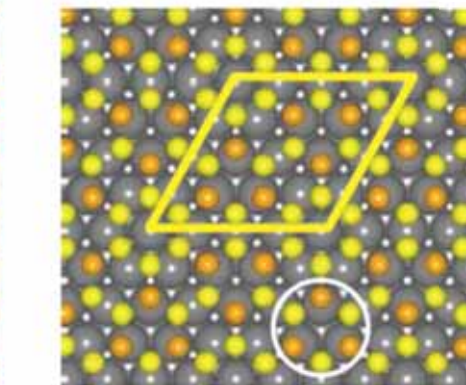
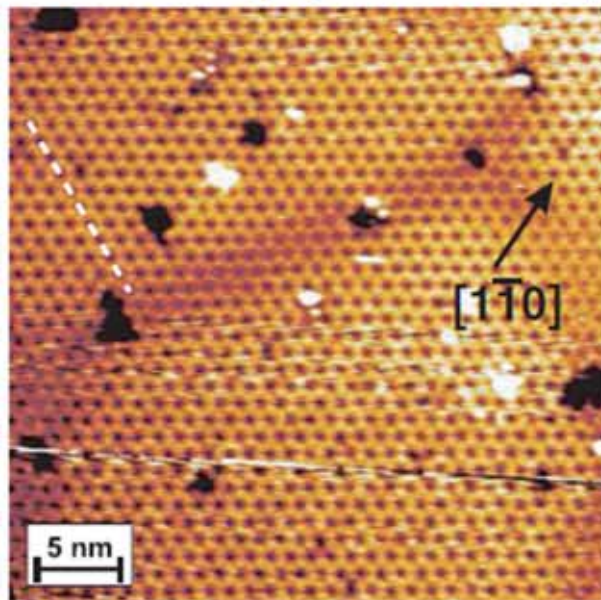
T. Ohta et al., Science 313, 951 (2006).



# シリセン

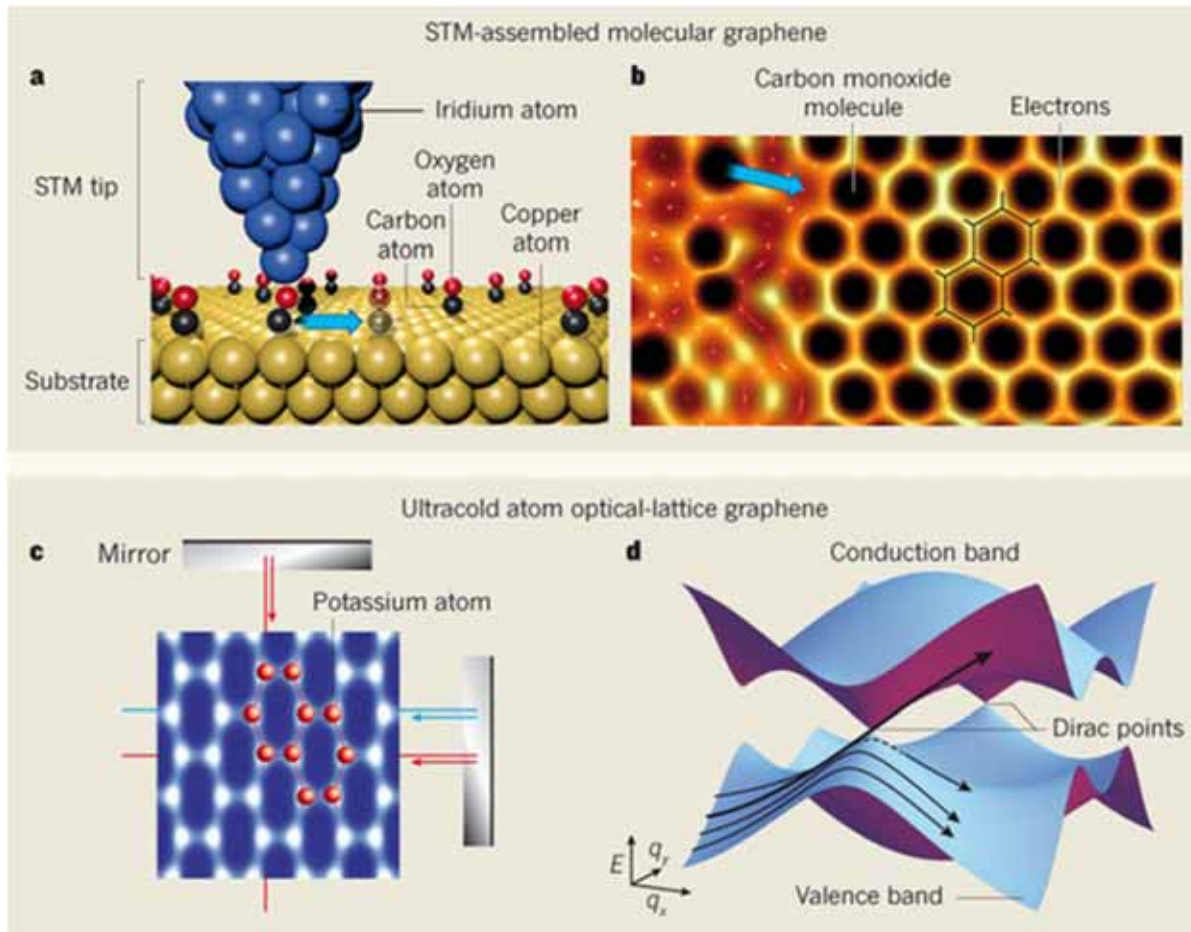


Silicene, the graphene equivalent for silicon

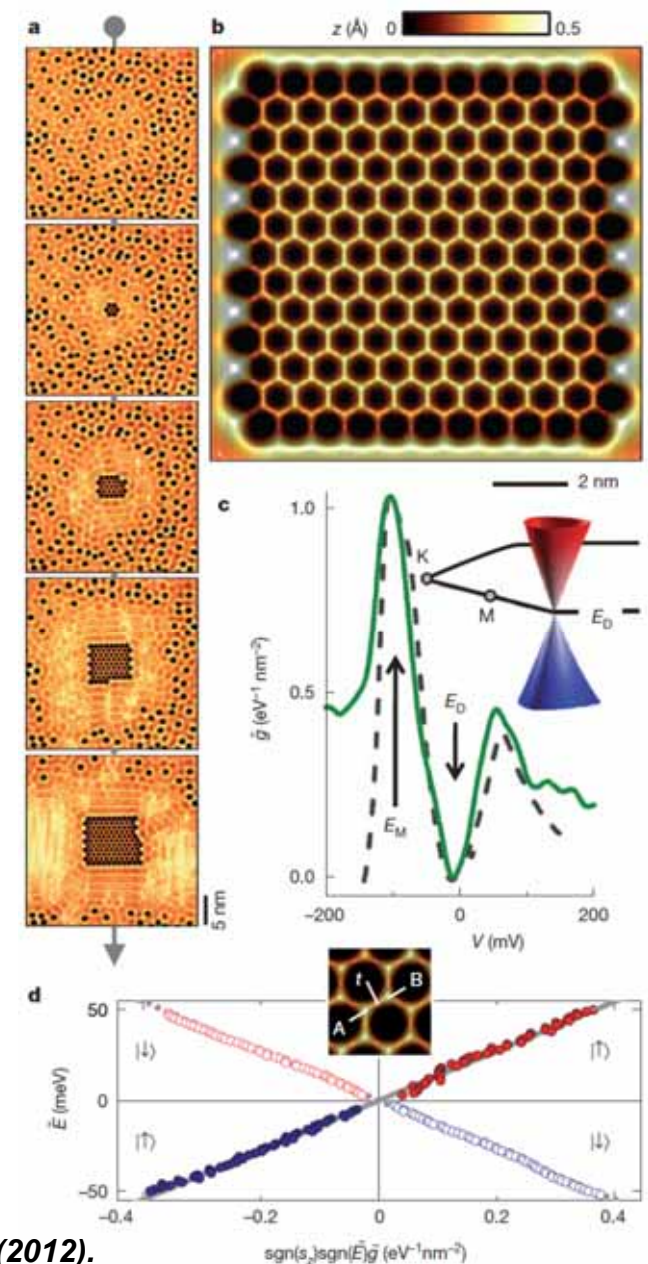


*P. Vogt et al., PRL 108, 155501 (2012).*

# グラフェン模倣構造



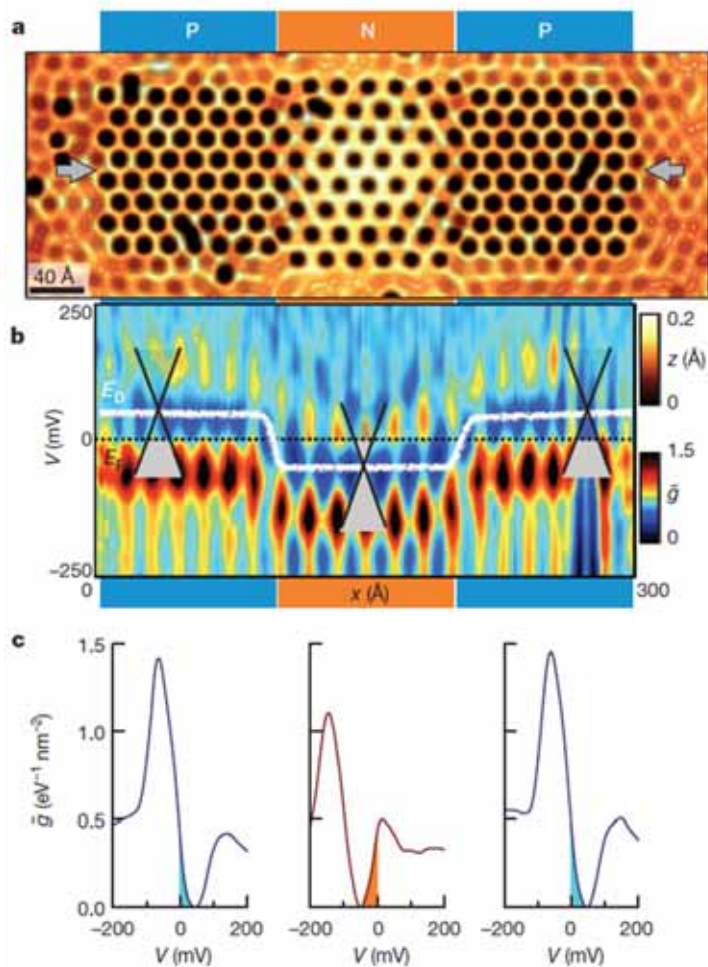
*J. Simon et al., Nature 483, 282 (2012).*



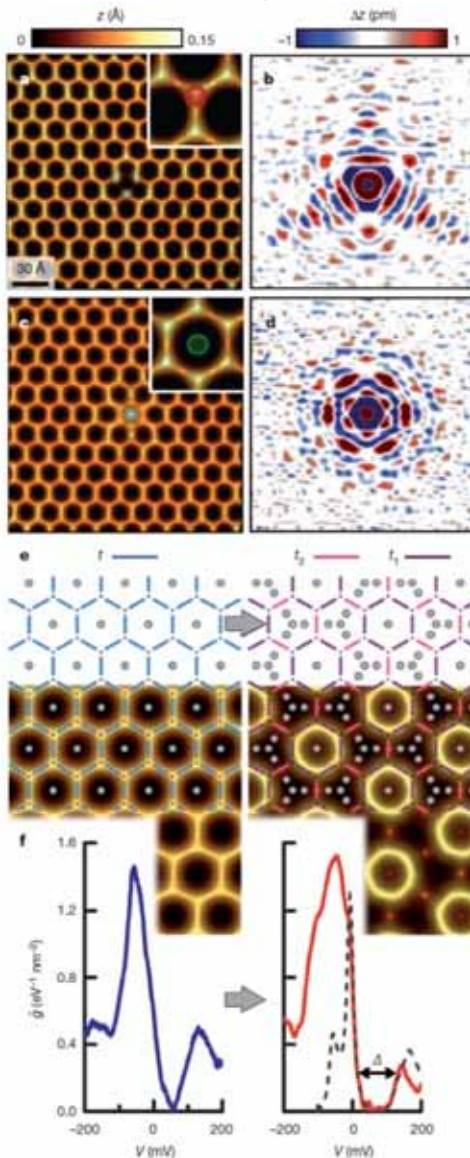
*K. K. Gomes et al., Nature 483, 306 (2012).*

# グラフェン模倣構造

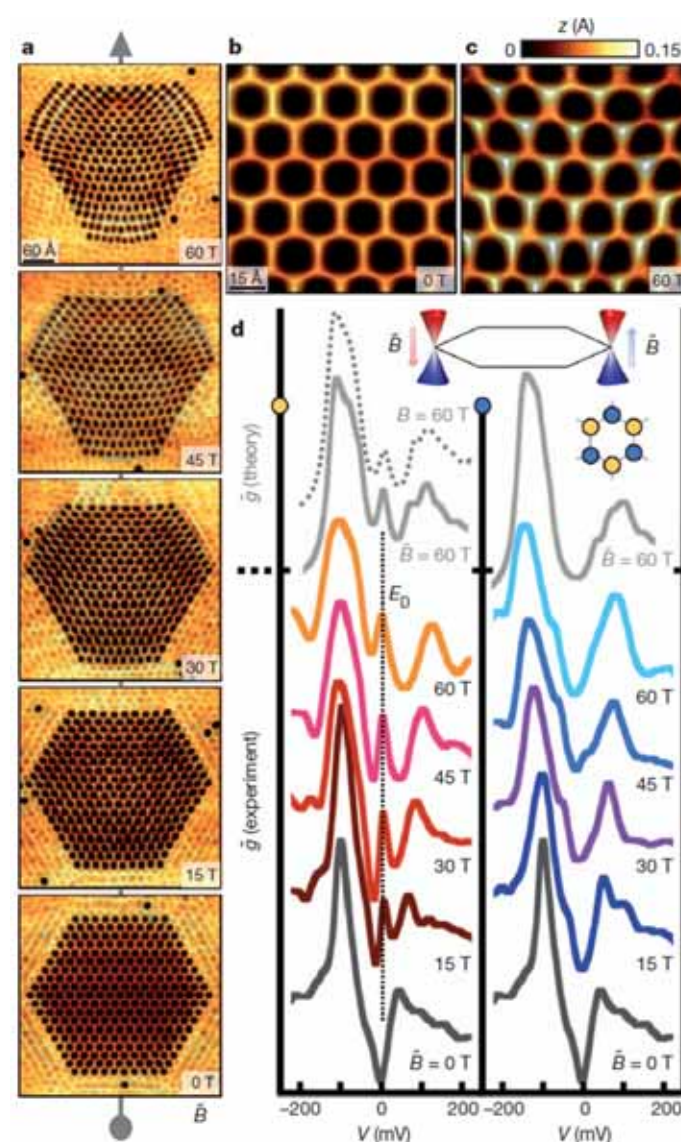
✓pn接合



✓対称性



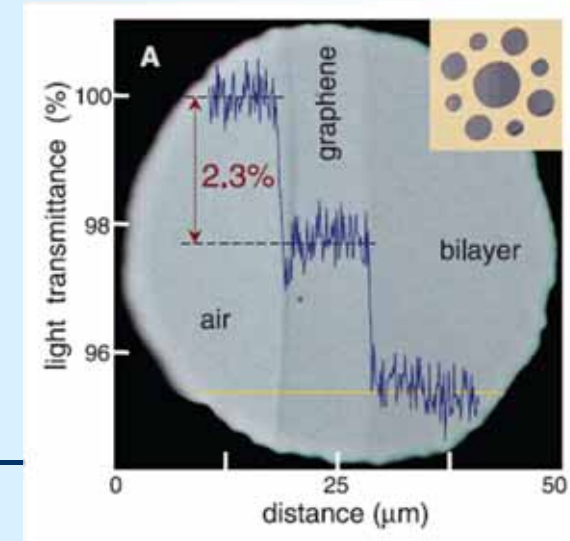
✓歪



K. K. Gomes et al., Nature 483, 306 (2012).

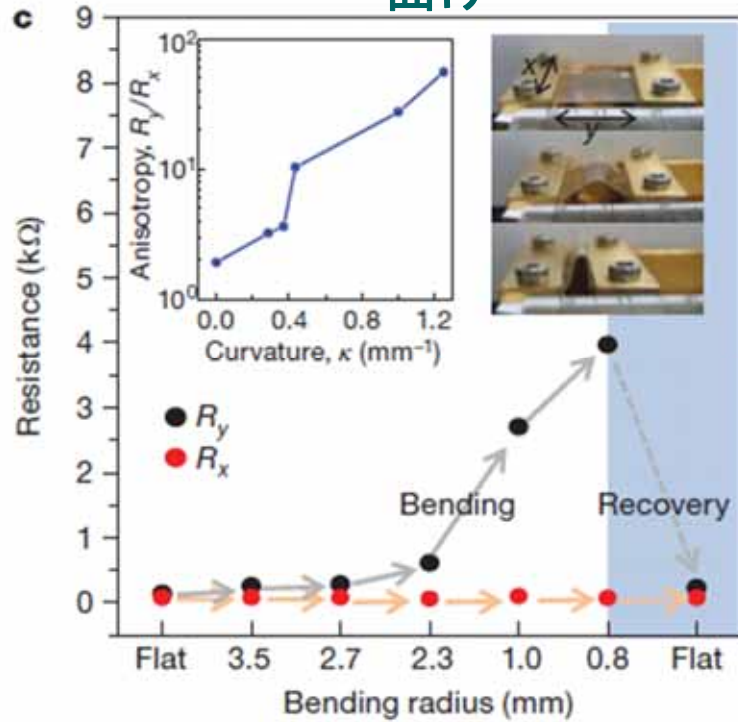
# グラフェンの特異な性質

厚さ	1原子層	
重量	0.77 mg/m <sup>2</sup>	
ヤング率	~1.1 TPa	
弾性限界	~20%	
透明度	光透過率 97.7%	
室温でのキャリア移動度	200,000 cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> (予測)	77,000 cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> (InSb)
電気伝導度	シート抵抗 31 Ω/ @ n=10 <sup>12</sup> cm <sup>-1</sup>	
最大電流密度	>10 <sup>8</sup> A/cm <sup>2</sup>	>10 <sup>7</sup> A/cm <sup>2</sup> (Cu)
熱伝導率	~5000 W/mK	900-2300 W/mK (ダイヤモンド)

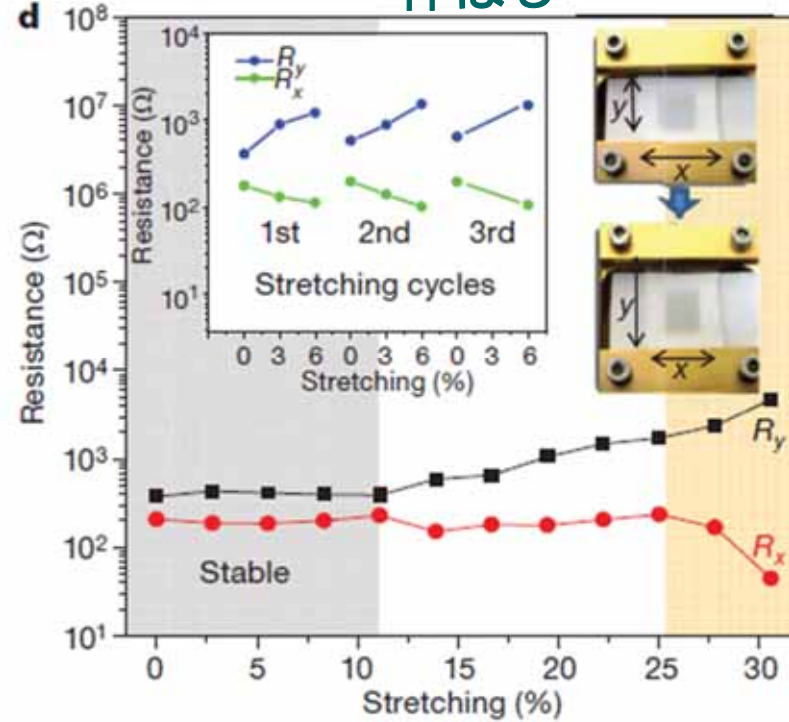


# グラフェンの特異な性質

✓曲げ



✓伸ばし

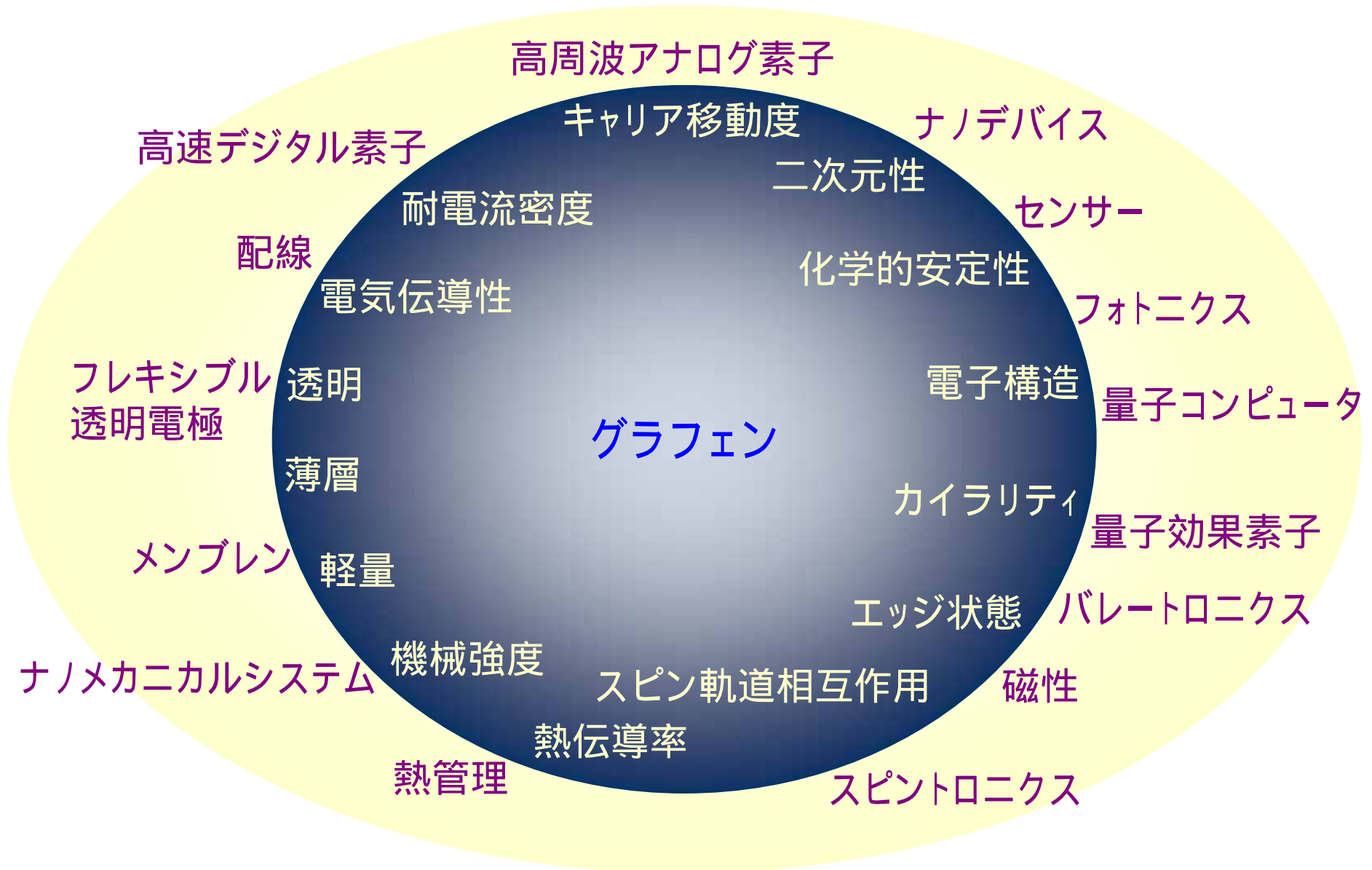


K. S. Kim et al., Nature 457, 706 (2009).

✓グラフェンハンモック

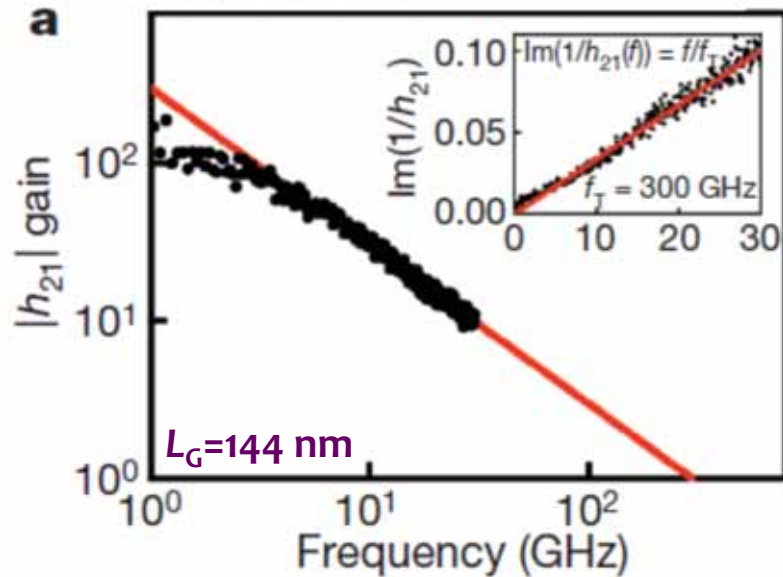
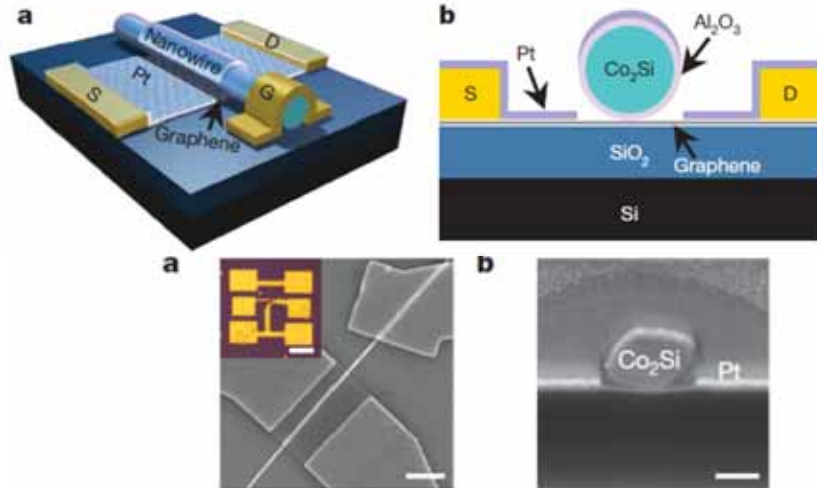


# グラフェンの潜在的応用



# グラフェンエレクトロニクス

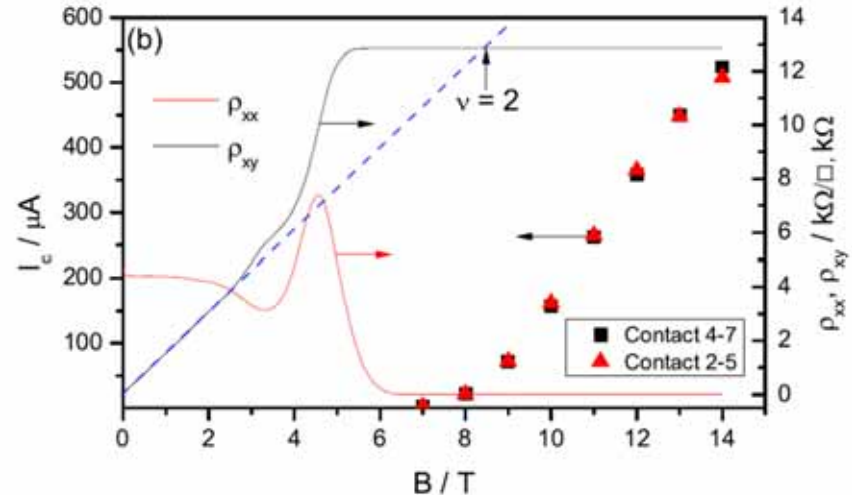
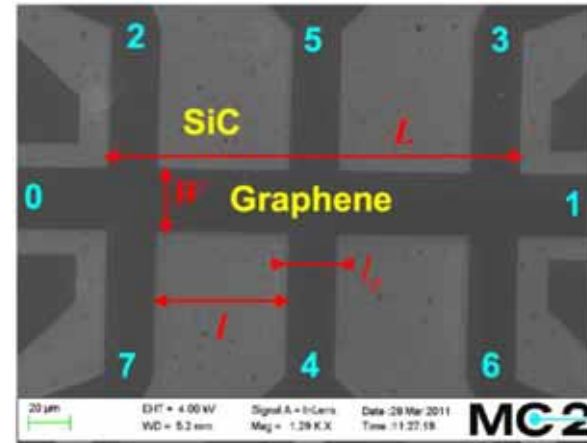
✓ 超高周波素子



同じゲート長のSi-MOSFETより高い遮断周波数

L. Liao et al., Nature 467, 305 (2010).

✓ 電気抵抗標準



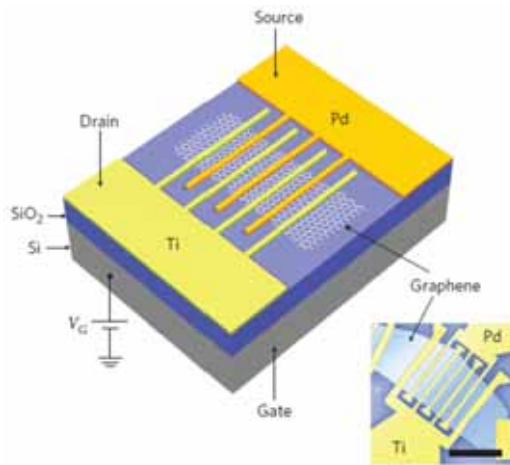
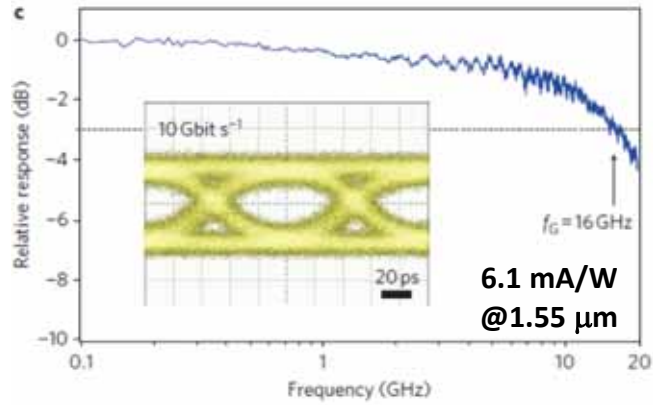
グラフェンとGaAs/AlGaAsを比較  
 相対標準不確かさ =  $8.7 \times 10^{-11}$

A. Tzalenchuk et al., Nat. Nanotech. 5, 186 (2010);  
 T.J.B.M. Janssen et al., Metrologia 49 (2012) 294.



# グラフェンフォトニクス

## ✓グラフェン受光素子

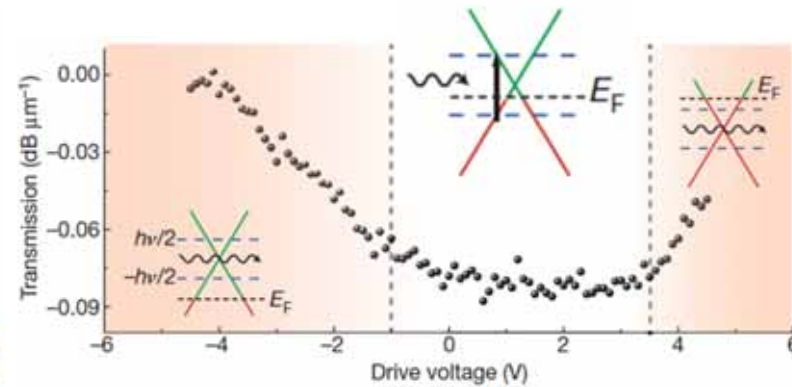
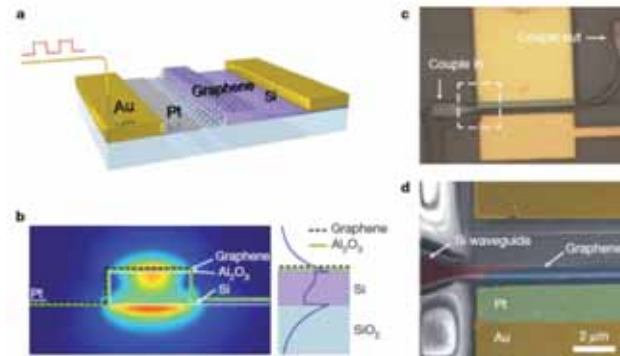


*T. Mueller et al., Nature Photon. 4, 297 (2010).*

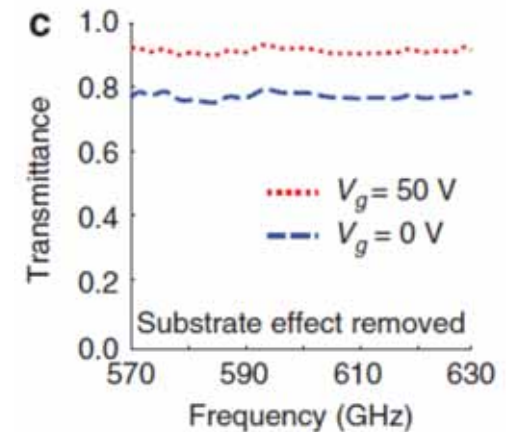
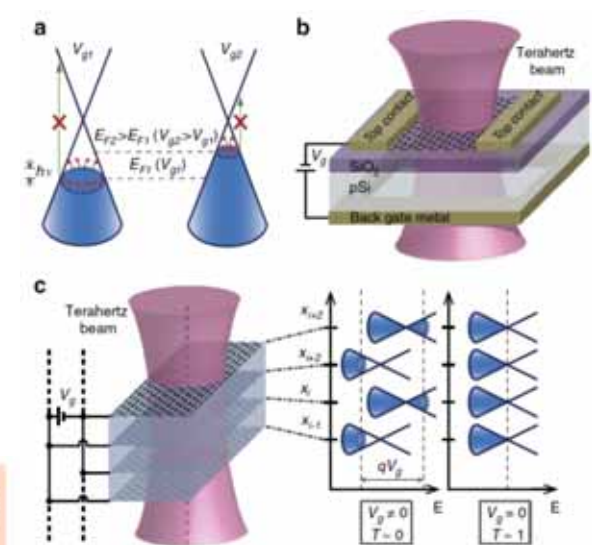
## ✓グラフェン光変調器

光通信波長帯

テラヘルツ帯



*M. Liu et al., Nature 474, 64 (2011).*

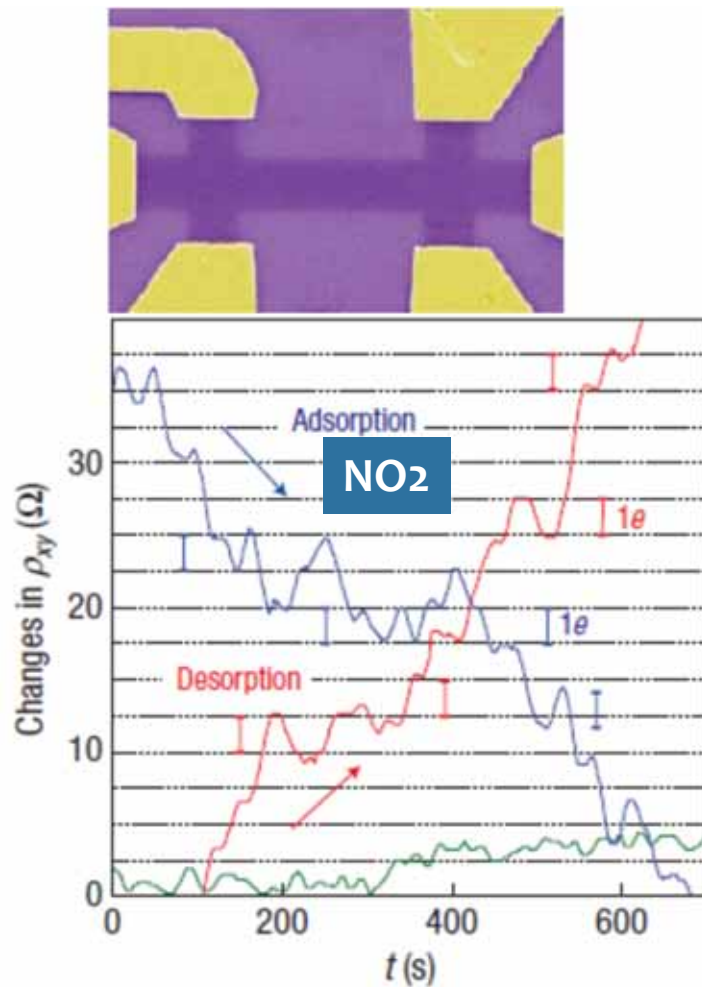


*B. Sensale-Rodriguez et al., Nat. Commun. 3:780 (2012).* 17

# グラフェンデバイスの例

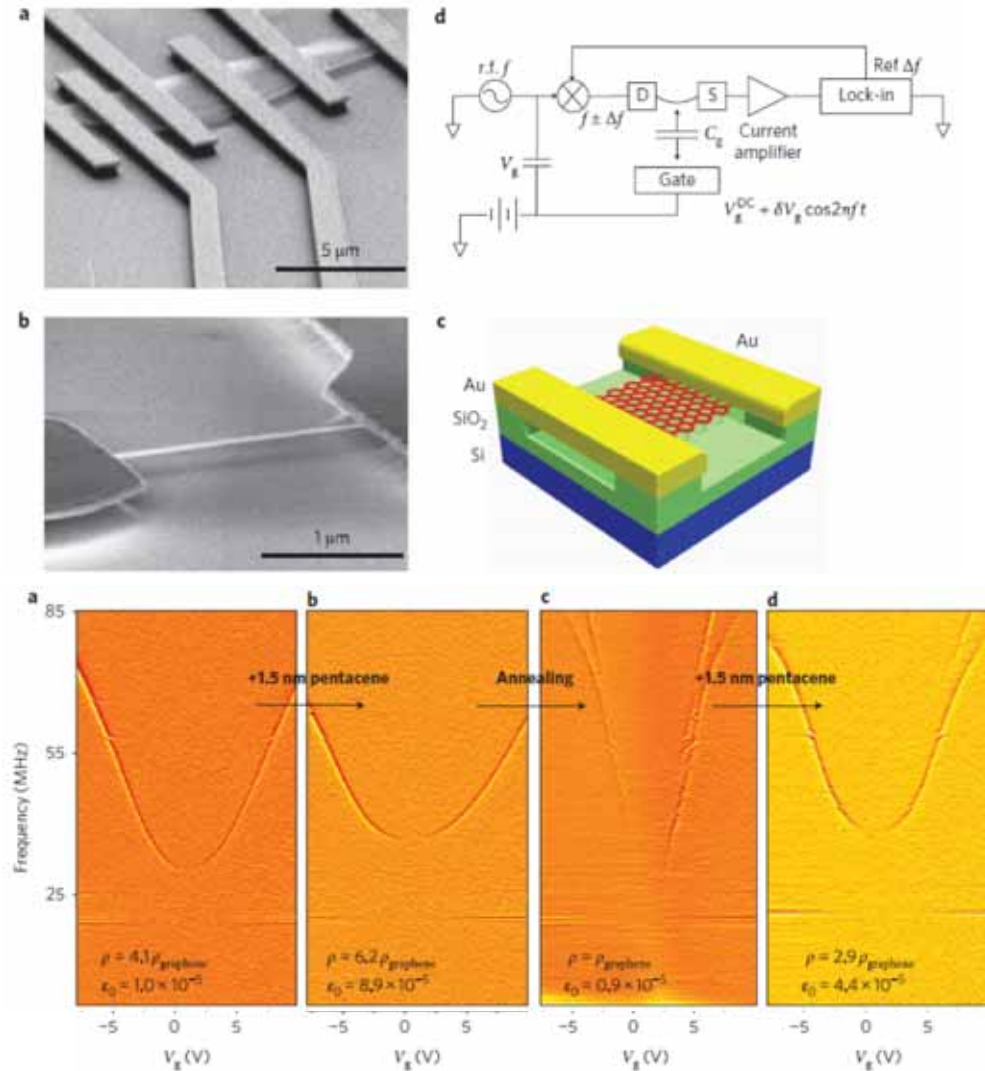
✓高感度センサ

分子1個の感度



F. Schedin et al., Nature Mater. 6, 652 (2007).

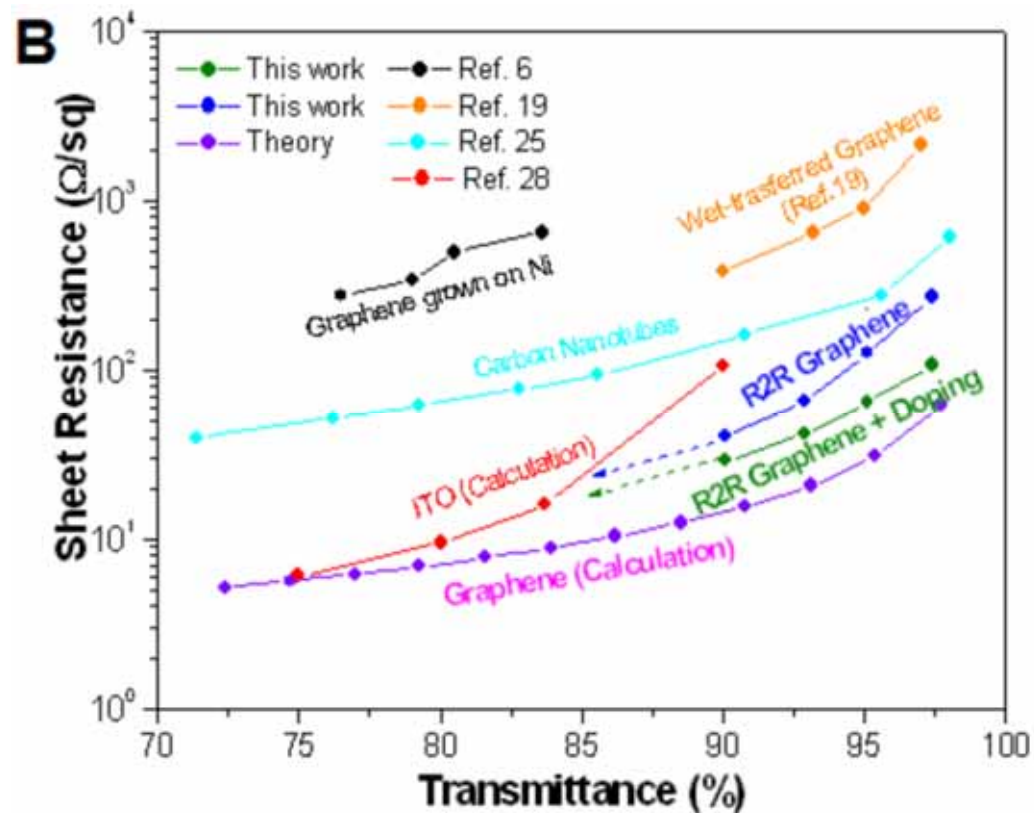
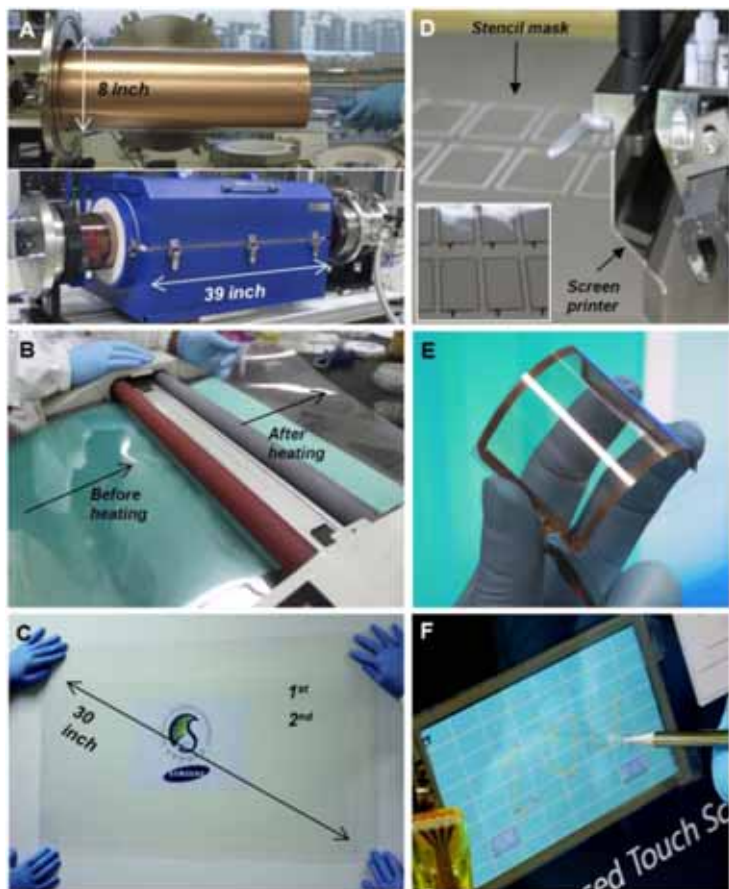
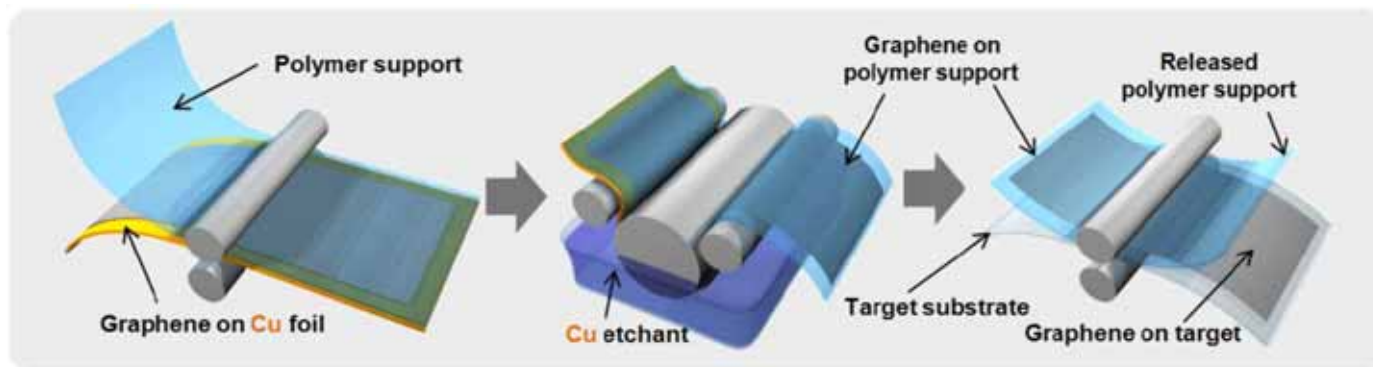
✓機械共振器



C. Chen et al., Nature Nanotechnol. 4, 861 (2009). 18

# フレキシブル透明電極

大面積CVD成長  
ロールtoロール転写  
タッチスクリーンデモ

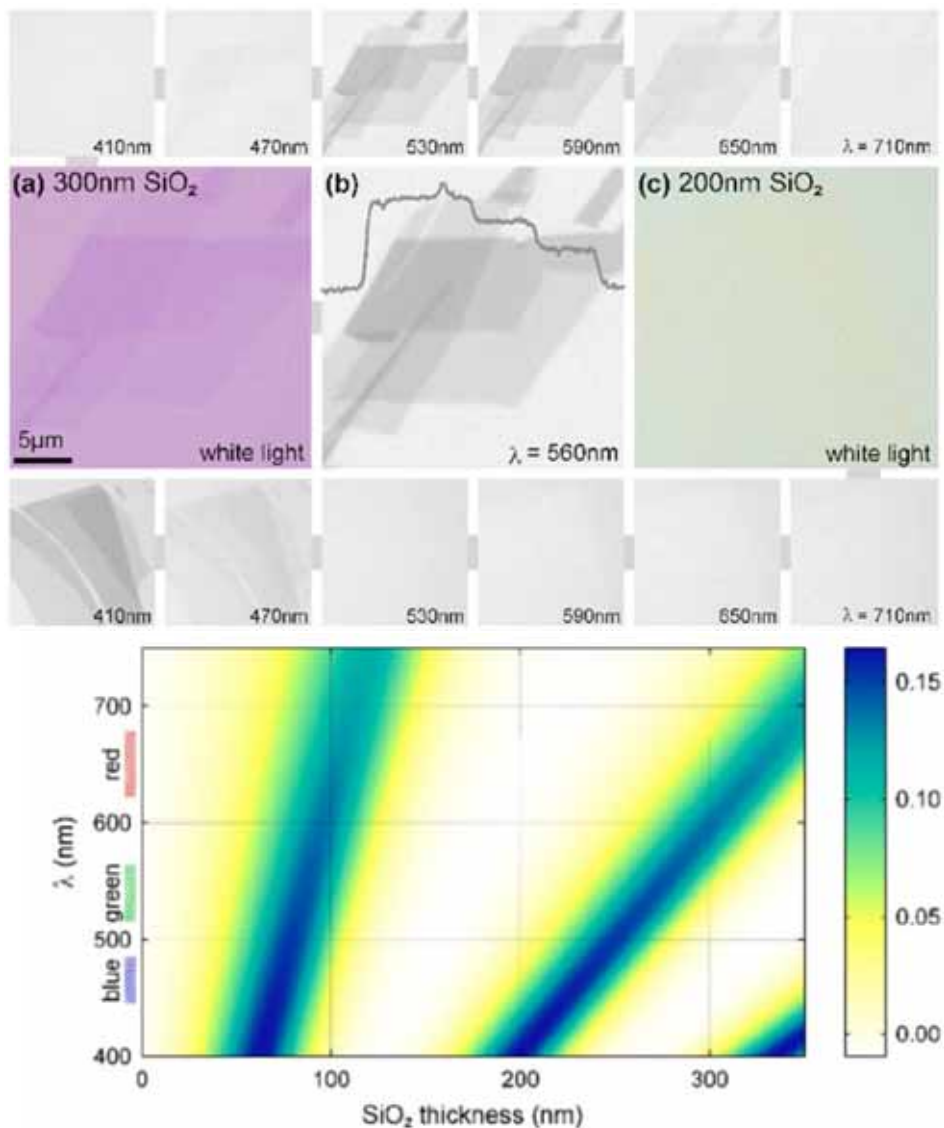


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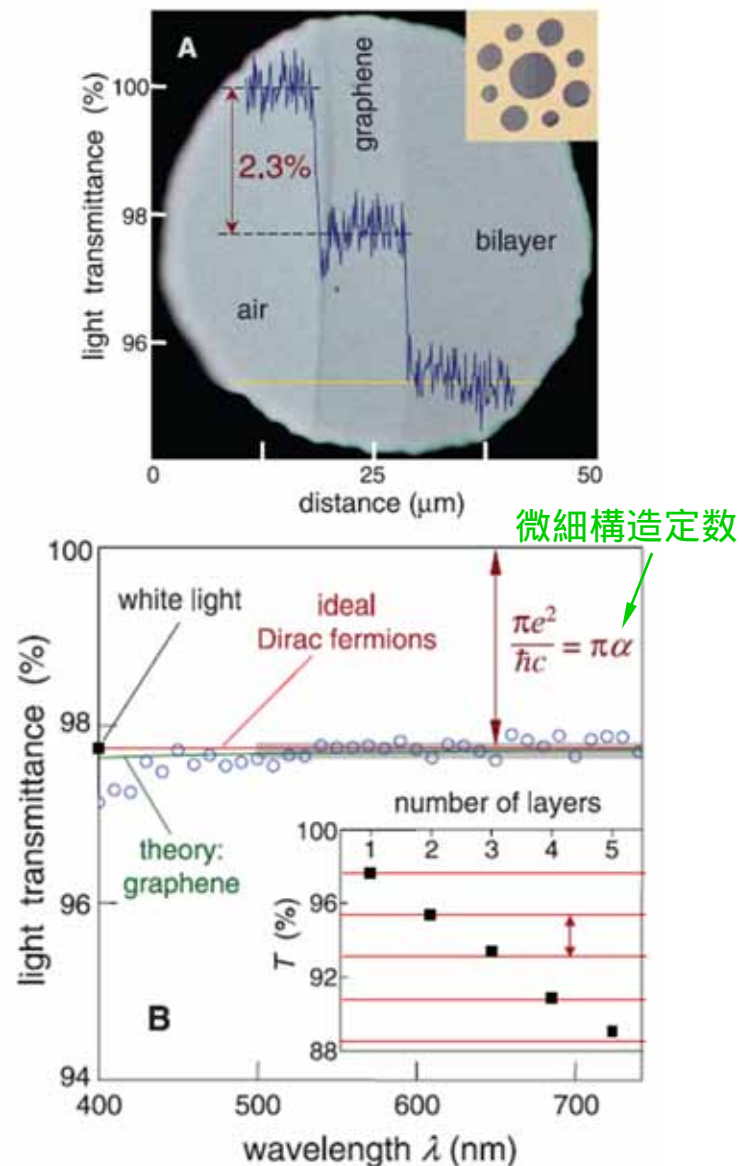
# 光学顕微鏡

## Graphene flakes on SiO<sub>2</sub>/Si



P. Blake et al., *Appl. Phys. Lett.* 91, 063124 (2007).

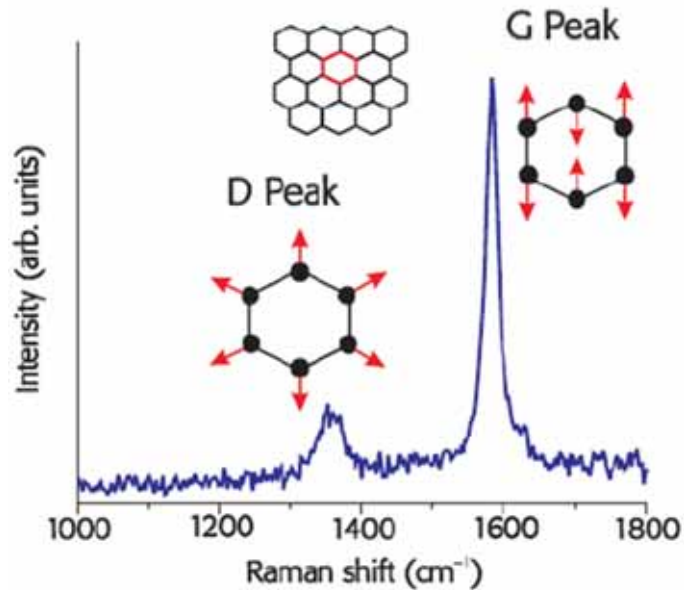
## Suspended graphene flakes



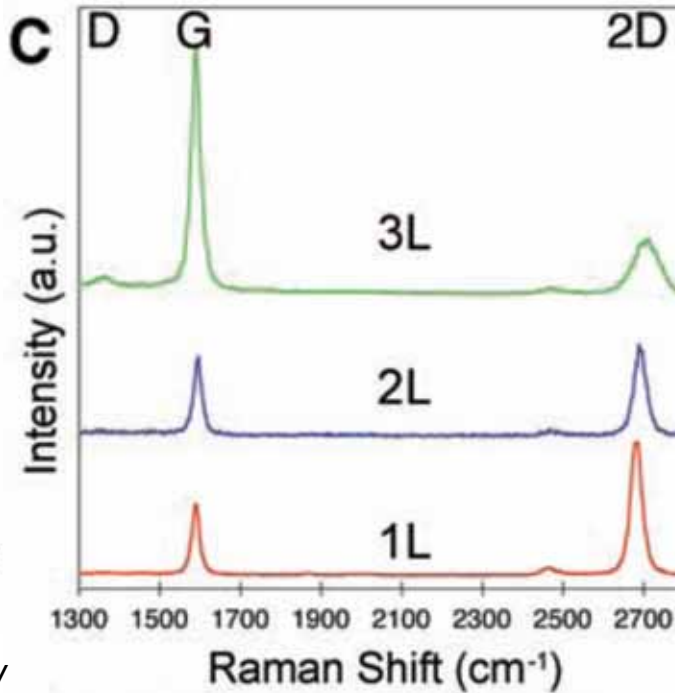
Nair RR, et al., *SCIENCE* 320, 1308 (2008).21

# ラマン分光

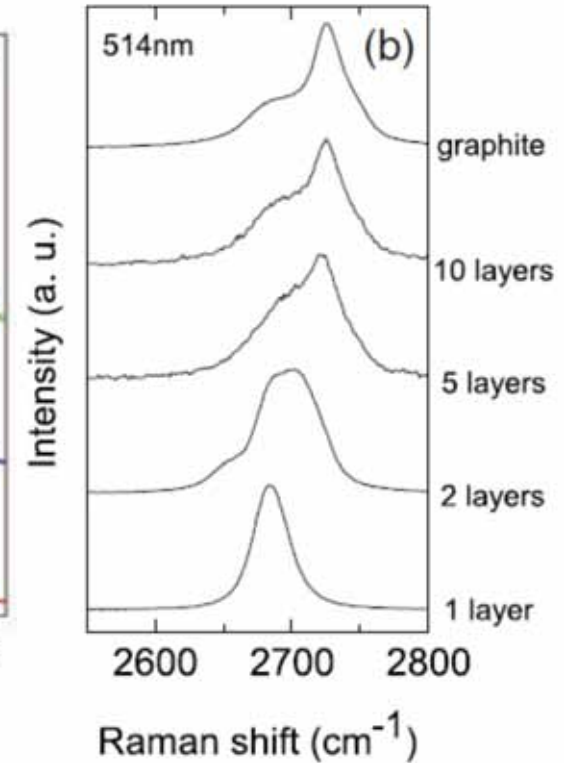
グラファイト



CVDグラフェン



剥離グラフェン



<http://www.soest.hawaii.edu/HIGP/Faculty/zinin/images/lectures/GG711/GG711Spectroscopy06RamanDiamond.pdf>

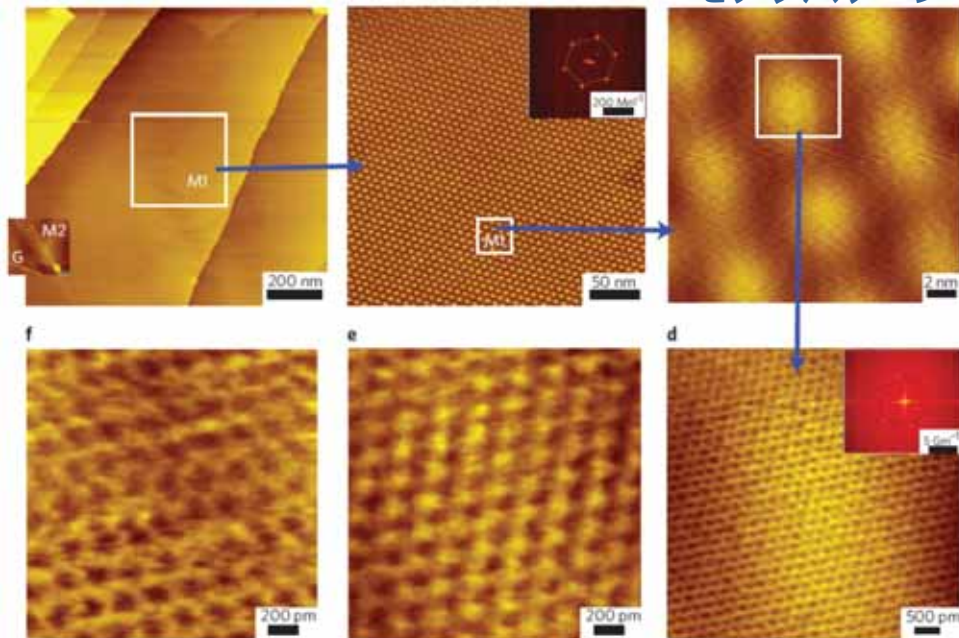
X. Li et al., *Science* 324, 1312 (2009).

A. C. Ferrari et al., *PRL* 97, 187401 (2006).

層数: G/2D比、2D半値幅、Gバンド強度  
 欠陥: Dバンドの存在  
 ドメインサイズ: G/D比  
 キャリア濃度: G,2Dバンド位置  
 歪: G,2Dバンド位置  
 エッジ構造: 偏光依存性

# 走査プローブ顕微鏡

## HOPGの走査トンネル顕微鏡像

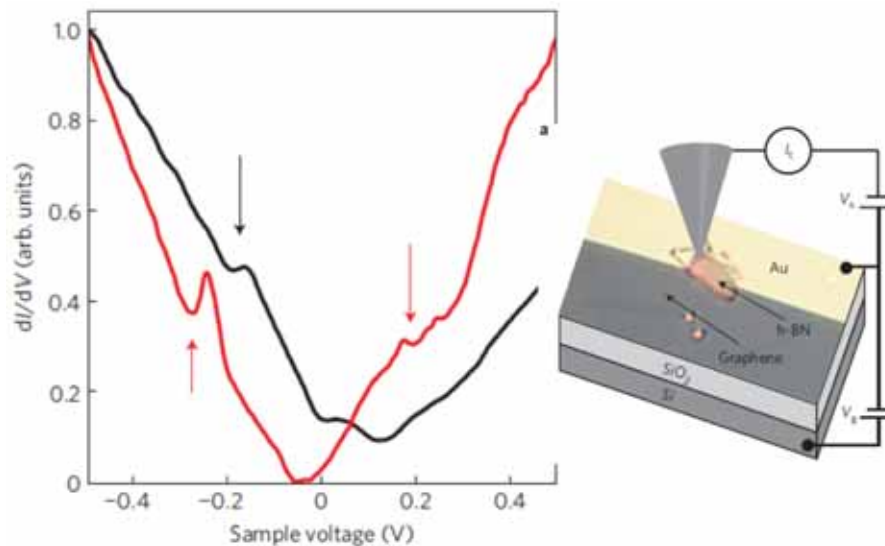


G. Li et al., *Nature Phys.* 6, 109 (2010).

## モアレパターン

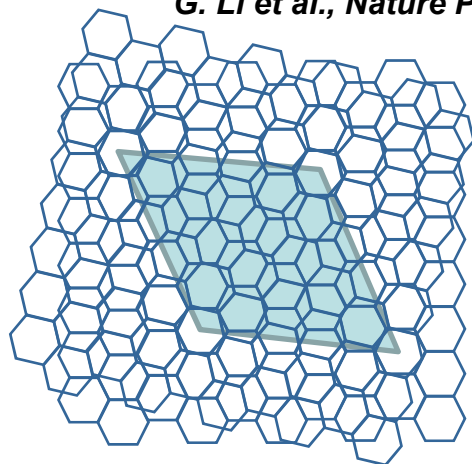
## BN上グラフェンのトンネル分光スペクトル

M. Yankowitz et al., *Nature Phys.* 8, 382 (2012).

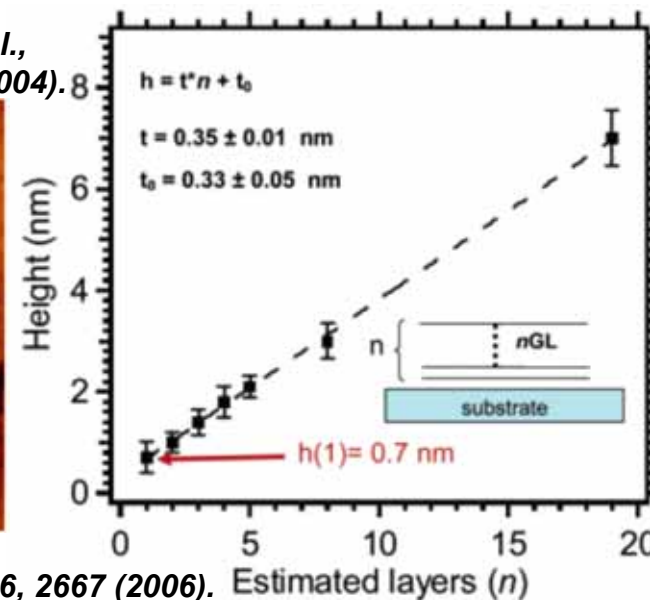
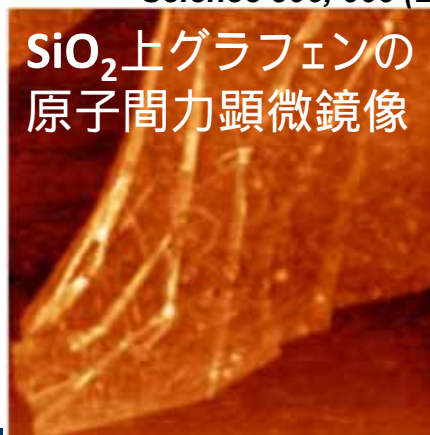


## 原子像

K.S. Novoselov et al., *Science* 306, 666 (2004).



## SiO<sub>2</sub>上グラフェンの原子間力顕微鏡像

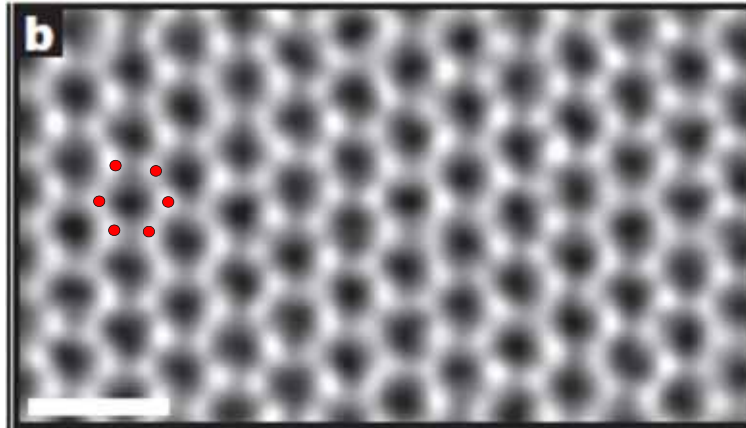


A. Gupta et al., *Nano Lett.* 6, 2667 (2006).

原子構造、層数、電子構造、

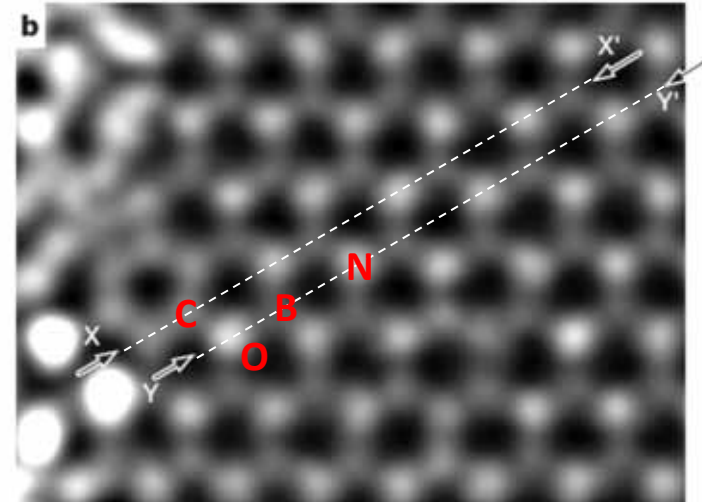
# 電子顕微鏡

グラフェンの透過電子顕微鏡像

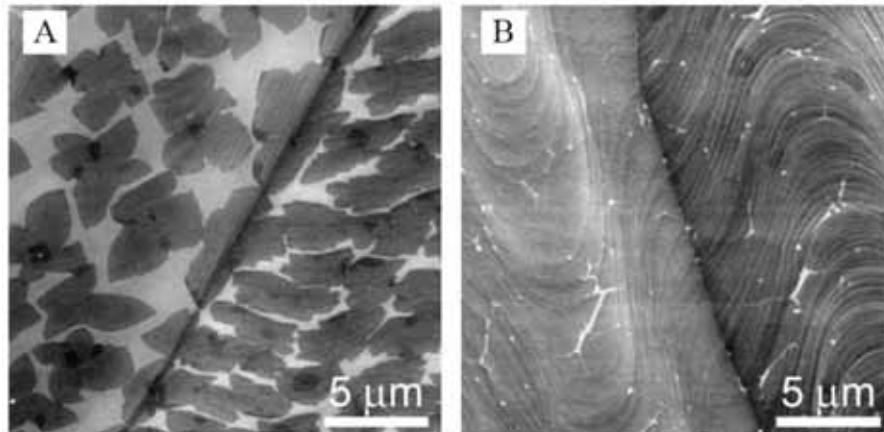


*P. Y. Huang et al., Nature 469, 389 (2011).*

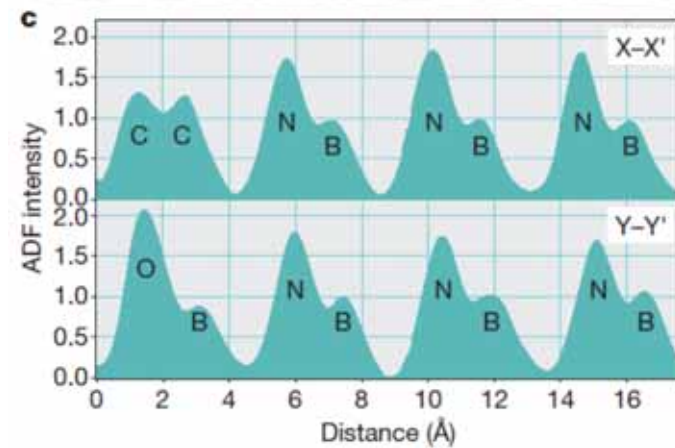
BNの走査型透過電子顕微鏡像



Cu上グラフェンの走査電子顕微鏡



*X. Li et al., Science 324, 1312 (2009).*



*O. L. Krivanek et al., Nature 464, 571 (2010).*

原子構造、原子種、層数、ドメイン構造、化学結合、、、

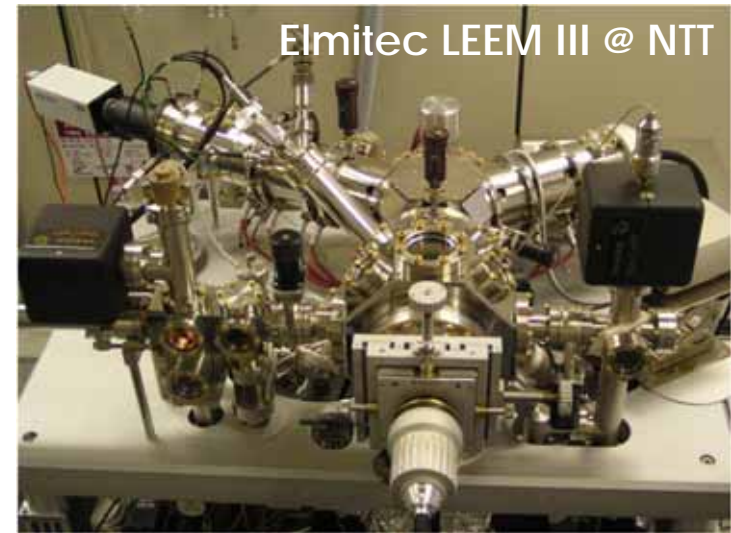


# 低エネルギー電子顕微鏡(LEEM)

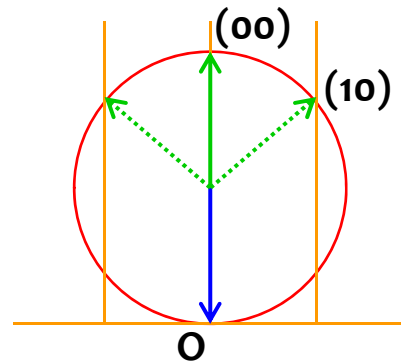
Low-energy electron microscopy (LEEM)

Photoelectron emission microscopy (PEEM)

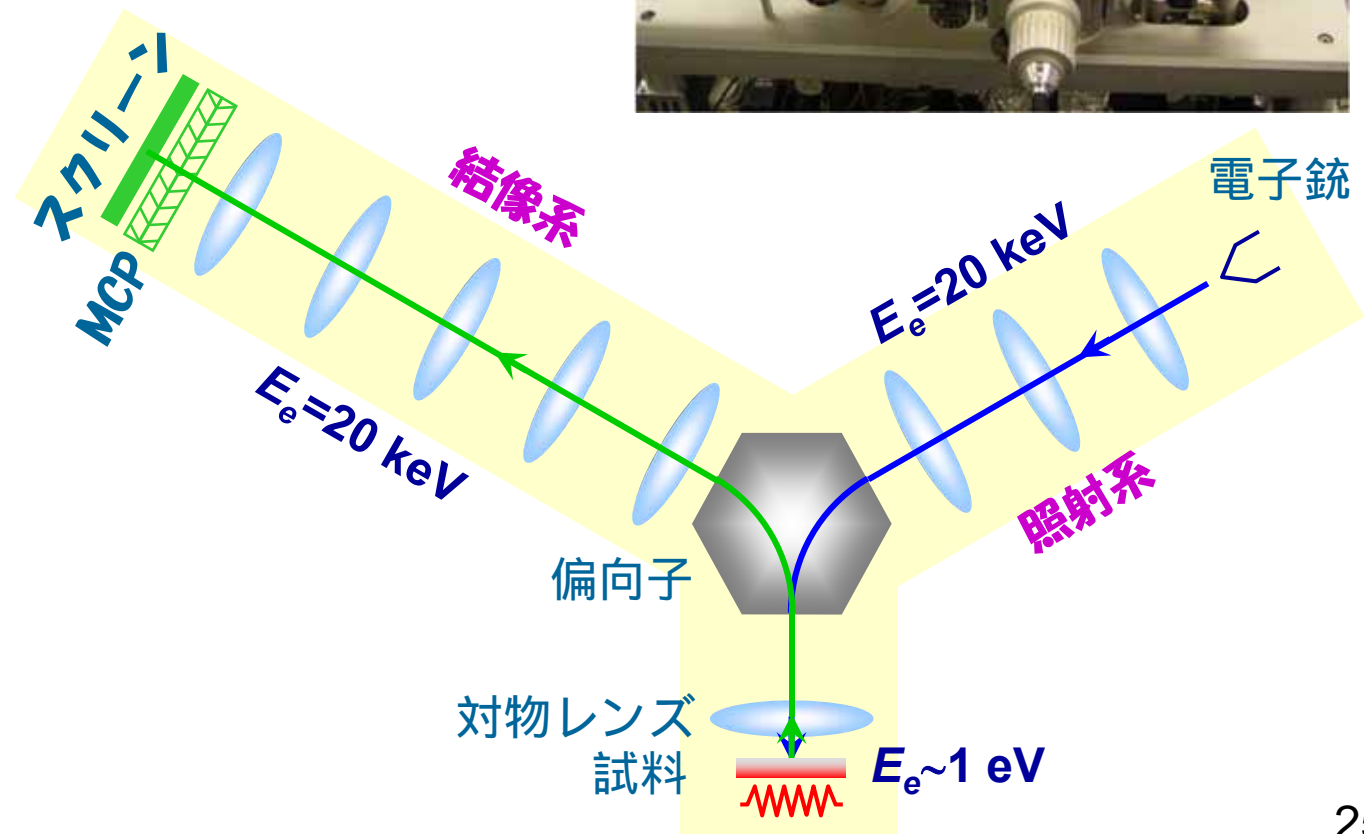
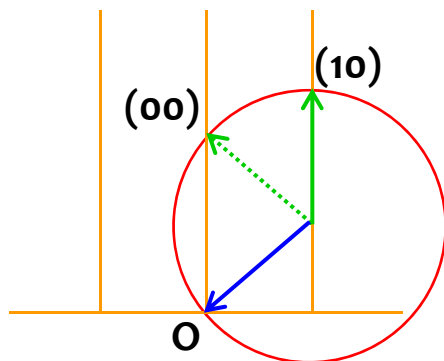
Thermionic electron emission microscopy (TEEM)



明視野LEEM

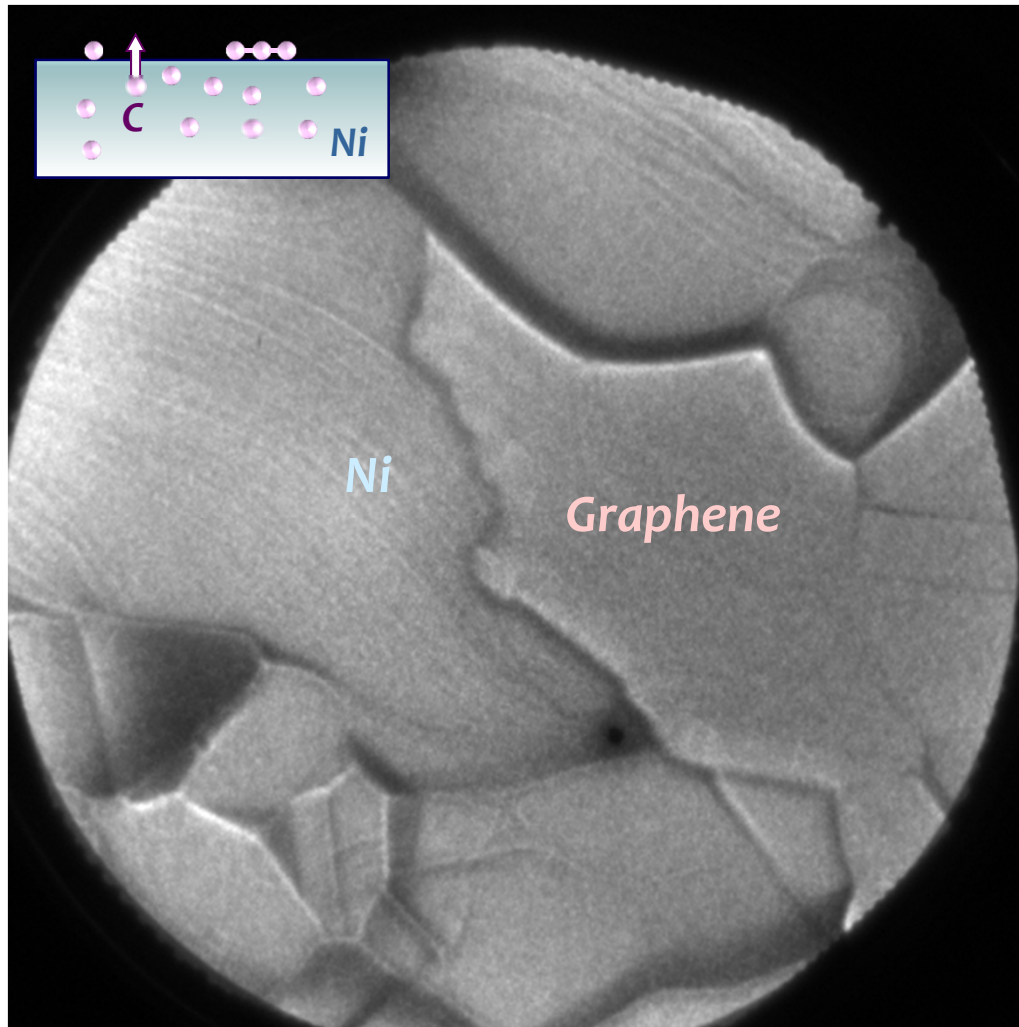


暗視野LEEM

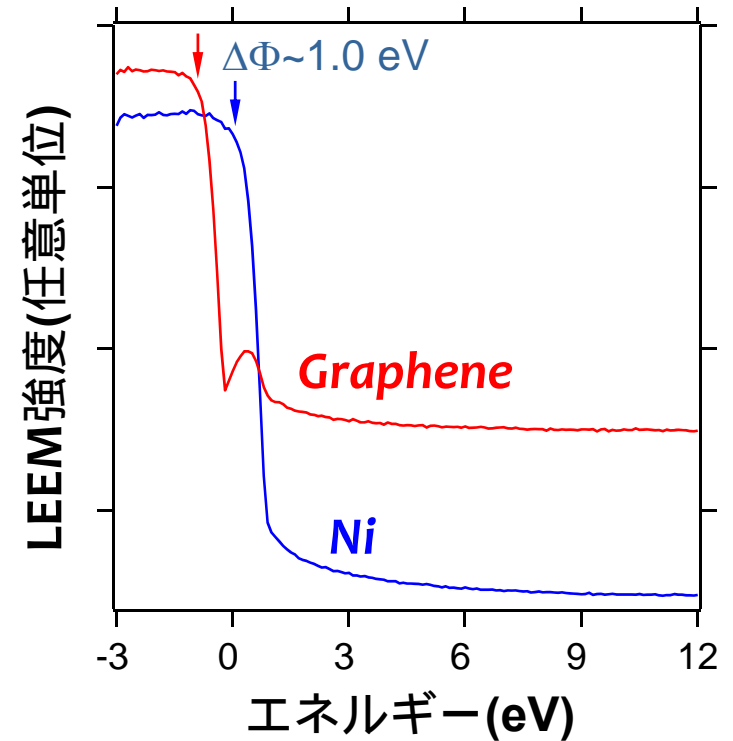


# グラフェン成長の動的観察

多結晶Ni薄膜上へのグラフェンの析出  
893°Cから882°Cへの冷却時



10 times faster than real



Reported  $\Delta\Phi=1.4$  eV  
C. Oshima and A. Nagashima,  
*J. Phys.: Condens. Matter* 9, 1 (1997).

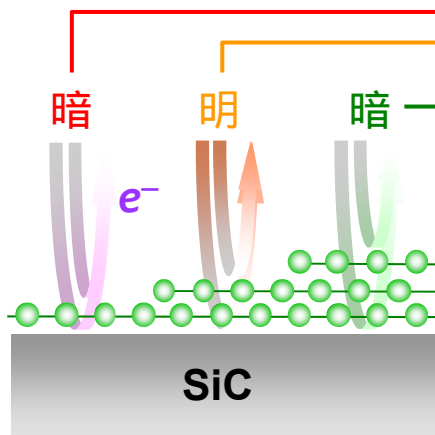
STV=0.7 V

1  $\mu$ m

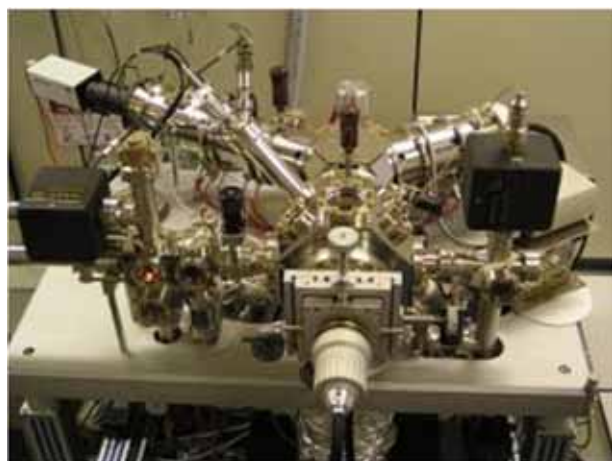
# LEEMを用いたグラフェン層数評価

電子線の干渉を使い、LEEMによって、グラフェン層数を~10 nmの空間分解能でデジタルに決定できる。

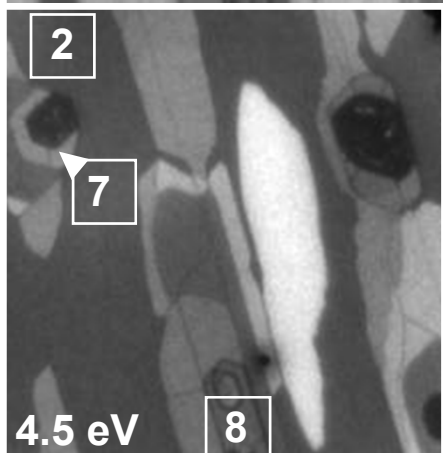
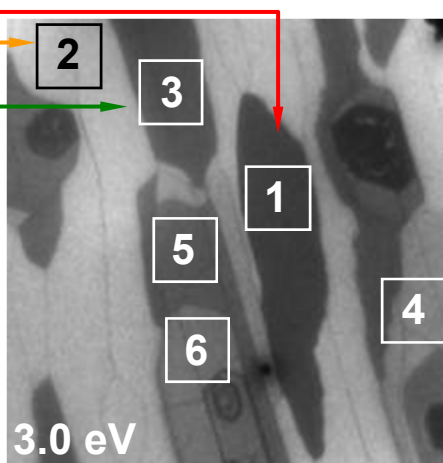
H. Hibino *et al.*, Phys. Rev. B 77, 075413 (2008); e-J. Surf. Sci. Nanotechnol. 6, 107 (2008).



電子線の干渉

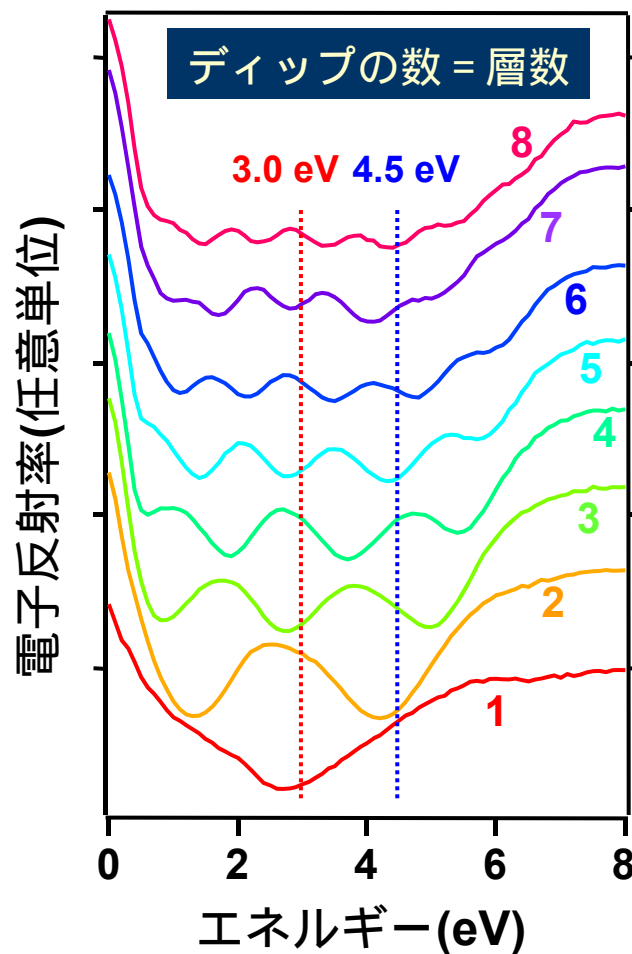


LEEM装置



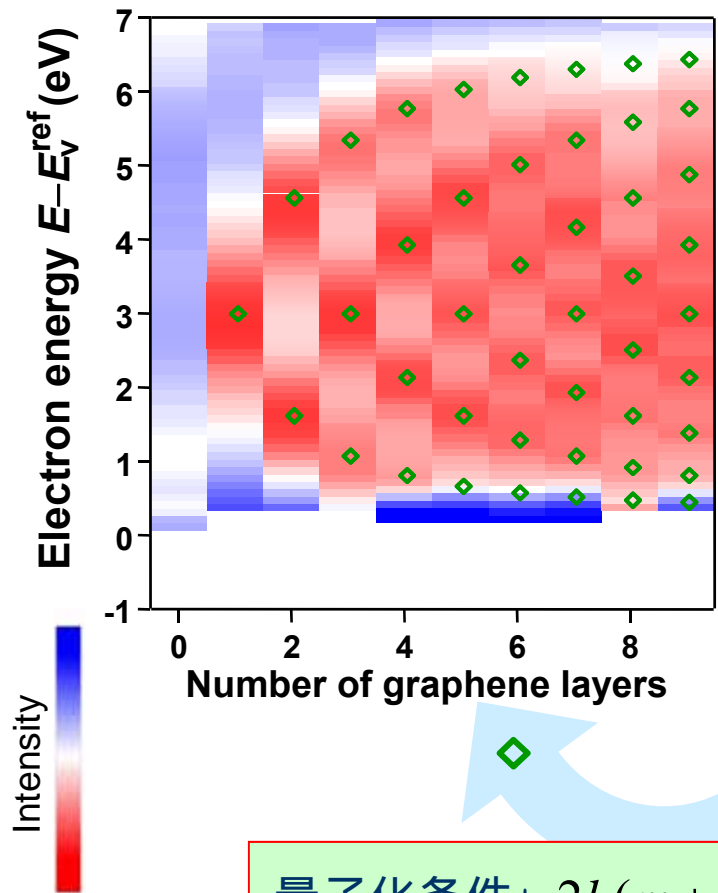
LEEM像

## 反射率のエネルギー依存性

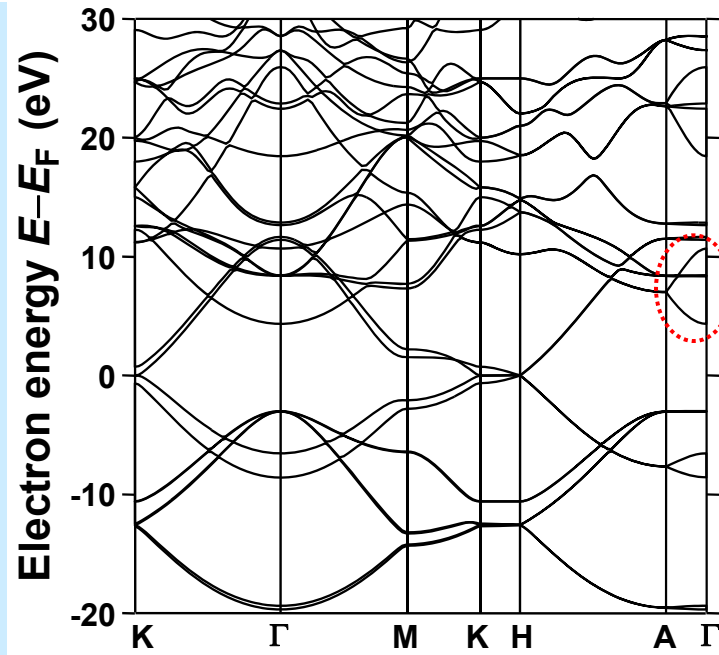
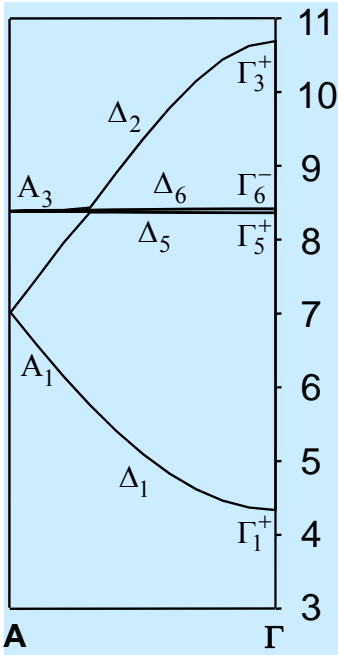


# 電子反射率の量子的振動

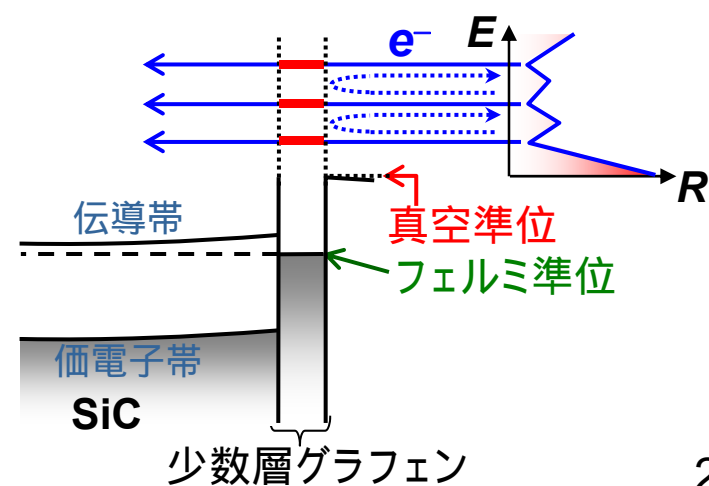
反射率マップ (実験結果)



グラフェンのバンド構造 (計算結果)



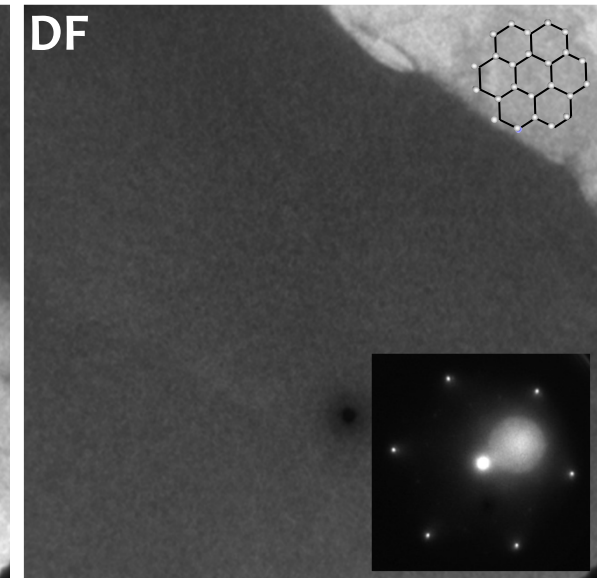
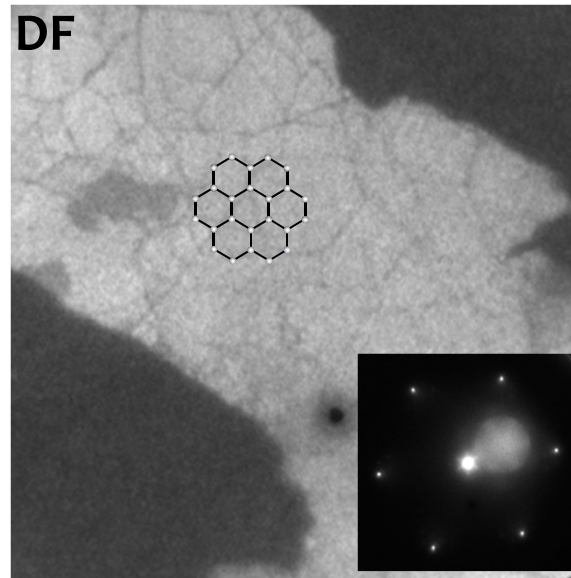
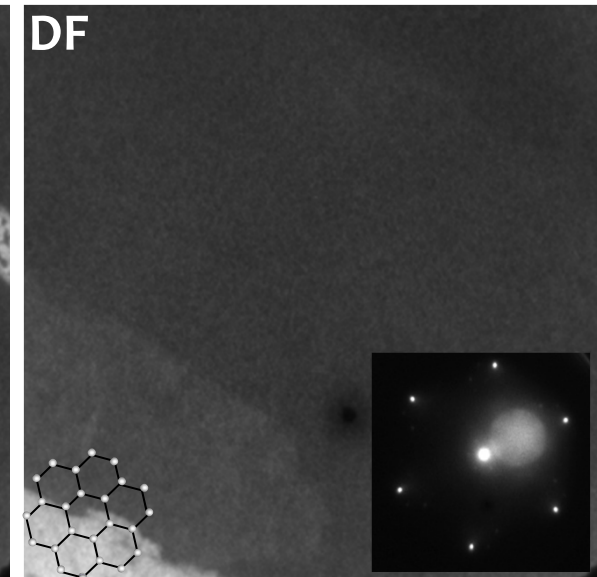
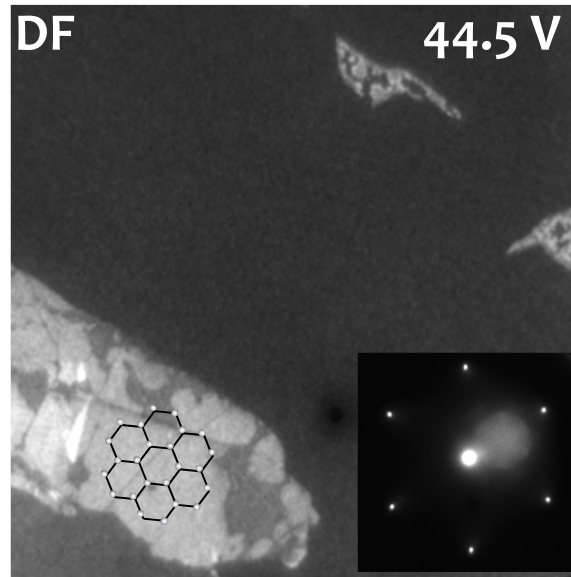
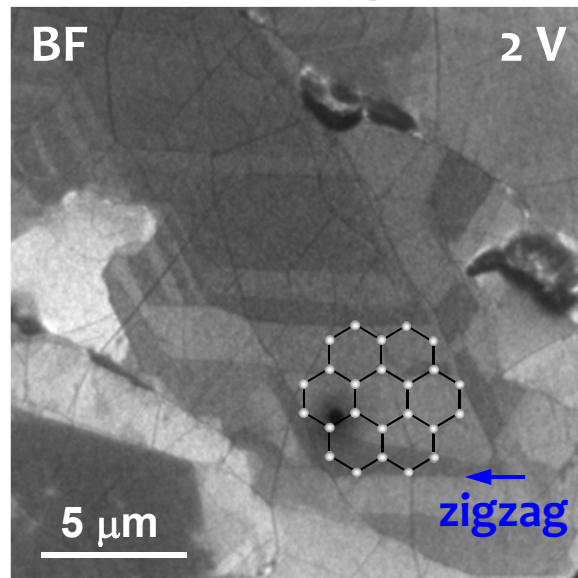
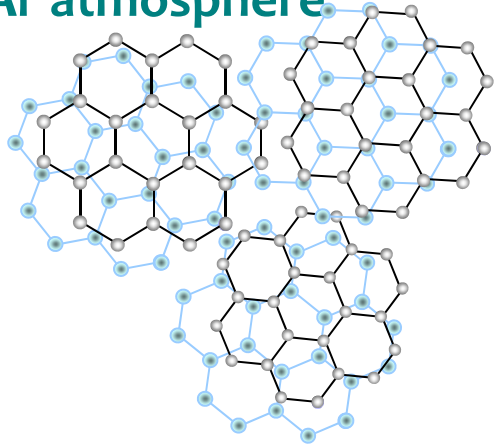
量子化条件:  $2k(m+1)a = 2\pi n$



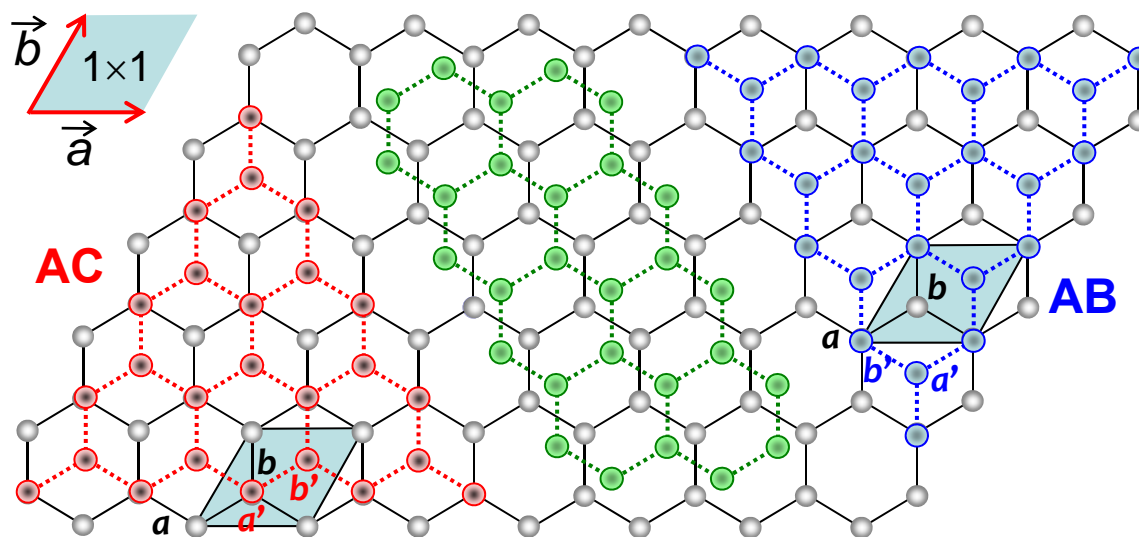
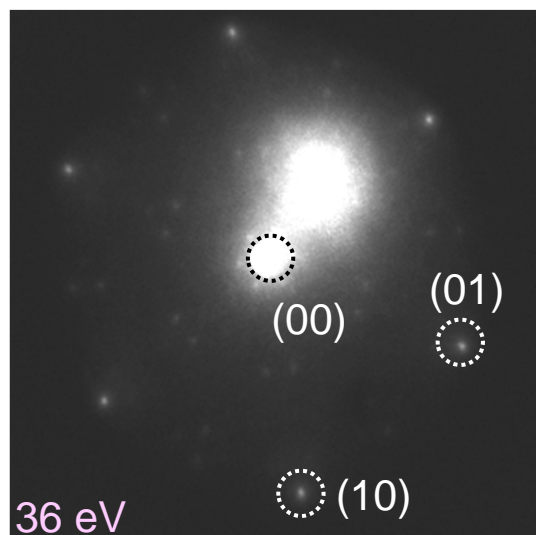
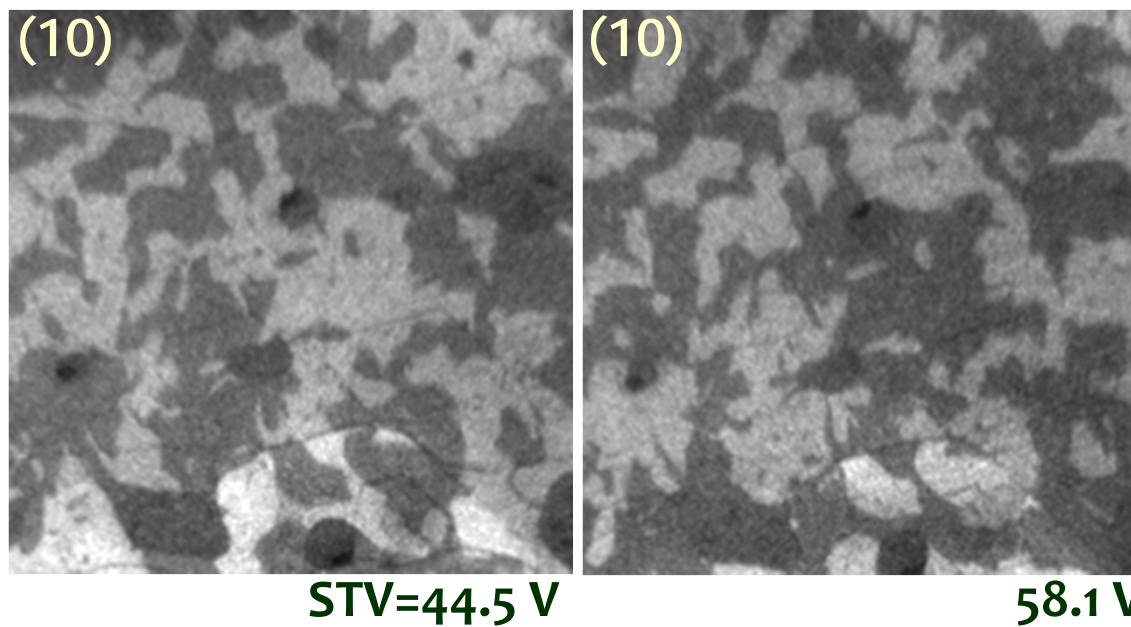
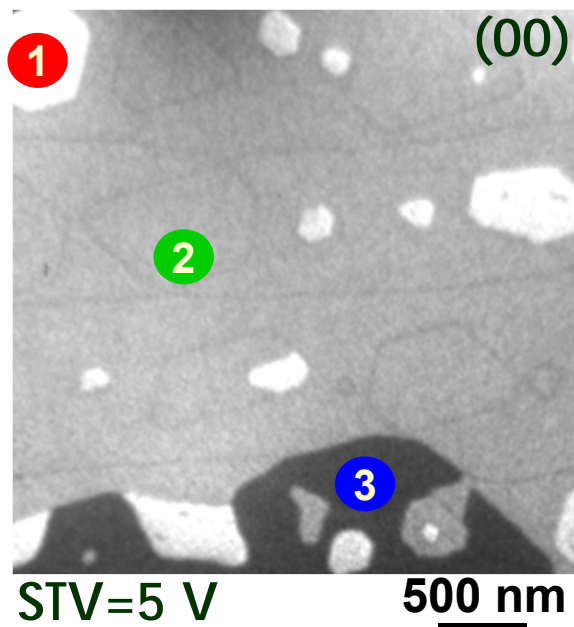
H. Hibino *et al.*, Phys. Rev. B 77, 075413 (2008).

# C面上グラフェン

Multilayer graphene grown  
✓ on C-face SiC  
✓ in Ar atmosphere

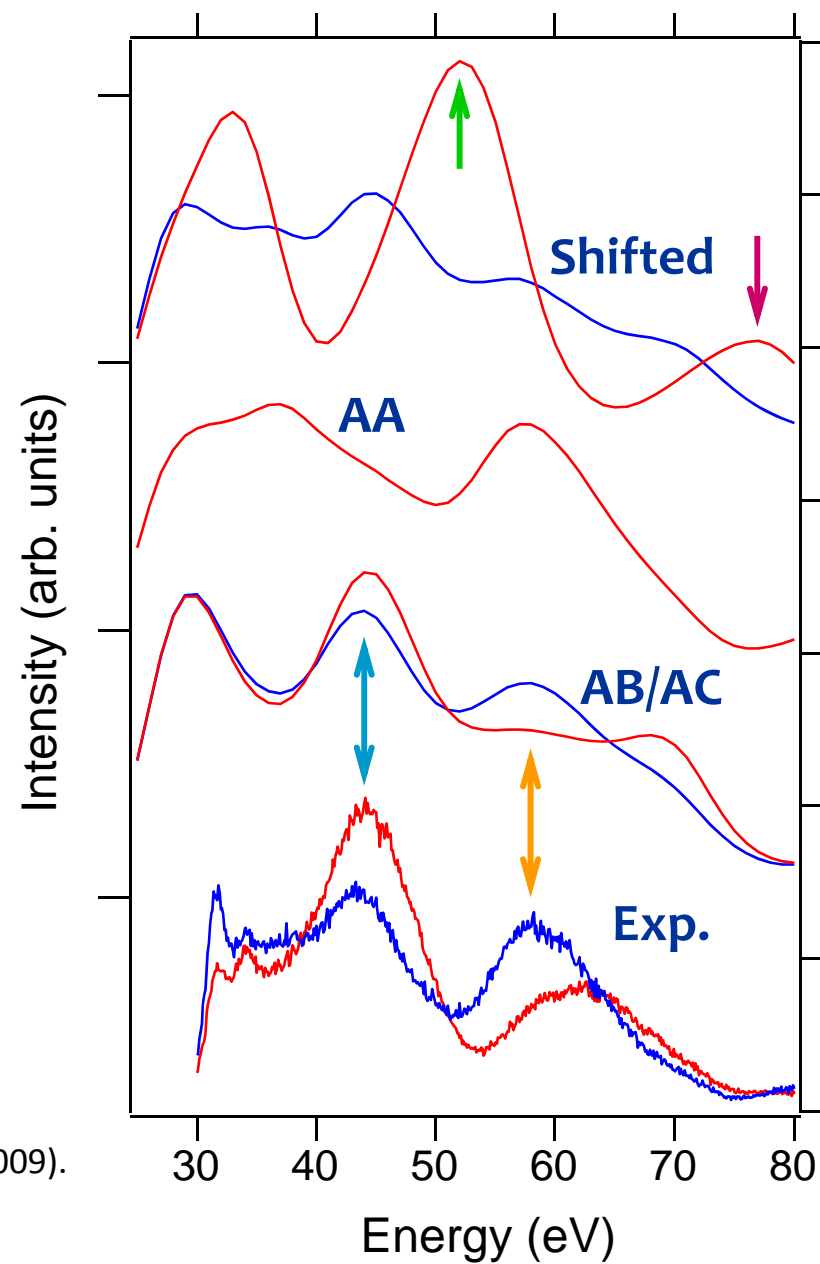
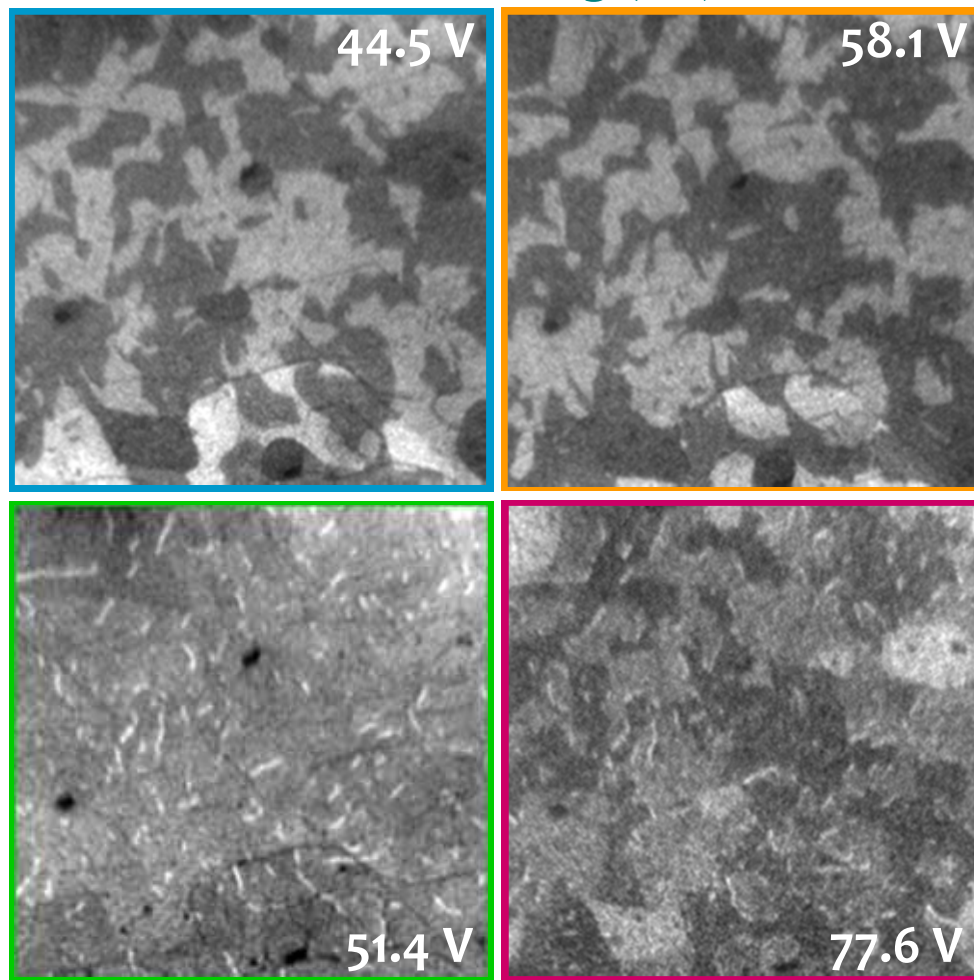


# SiC上2層グラフェンの積層ドメイン



# 2層グラフェンの積層ドメイン

DF LEEM using (1,0)



H. Hibino *et al.*, Phys. Rev. B 80, 085406 (2009).

# 内容

1. グラフェンとは
2. グラフェン評価法
3. グラフェン成長法
  - 3-1 化学気相成長法
  - 3-2 析出法
  - 3-3 SiC熱分解法



# グラフェン製造法

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## 剥離法

- ✓ 機械的剥離
  - ✓ 化学的剥離(含む、酸化グラフェン)
- 

## 合成法

- ✓ 化学気相成長(CVD)
  - ✓ 直接成長(MBE, CVDなど)
  - ✓ 析出(金属、金属カーバイドなど)
  - ✓ SiC熱分解
  - ✓ 分子カップリング
- 

## 加工法

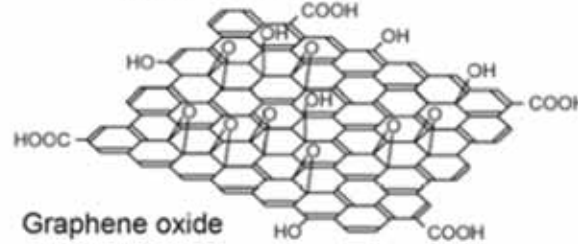
- ✓ CNTの展開
- 
-

# 酸化グラフェン

## Modified Hummers法

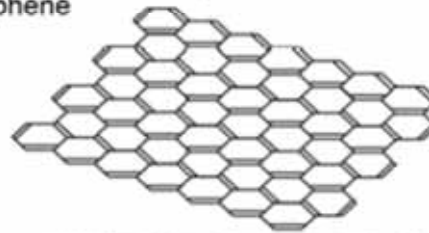
- ・グラファイト単結晶粉末 (1 g), 硝酸ナトリウム (0.75 g) を濃硫酸 (34.5 mL) に加える。
- ・氷浴, 攪拌しながら過マンガン酸カリウム (2.0 g) を加える。

Graphite



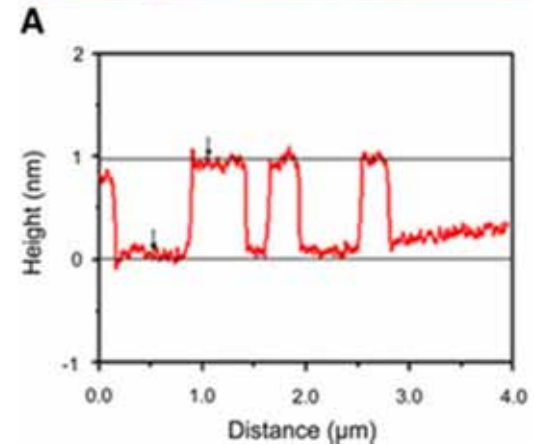
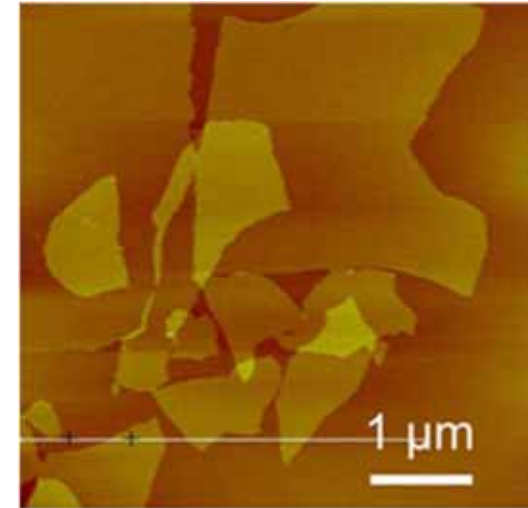
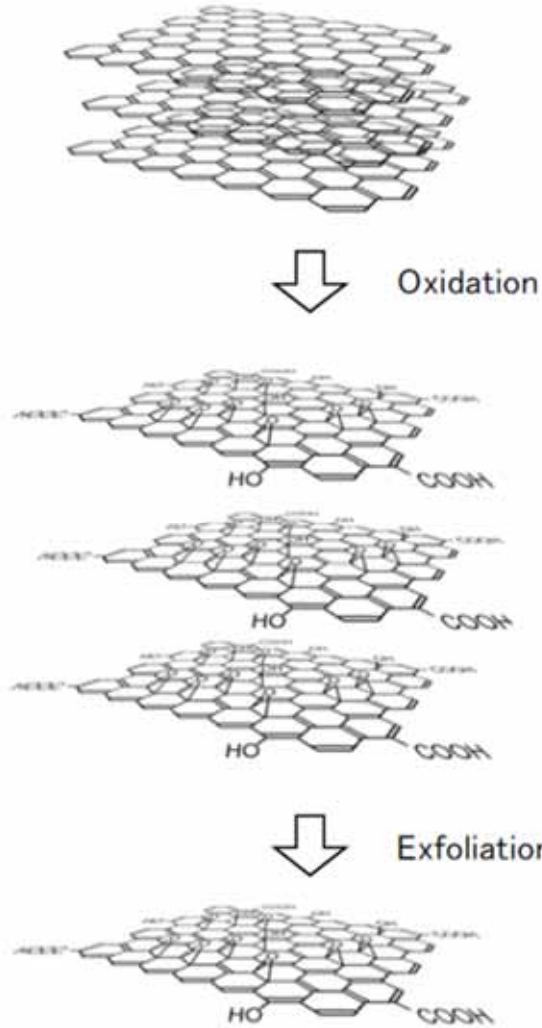
Reduction

Graphene



分散/遠心分離操作を20回繰り返す。

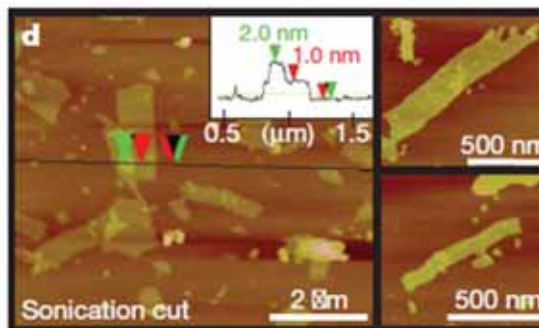
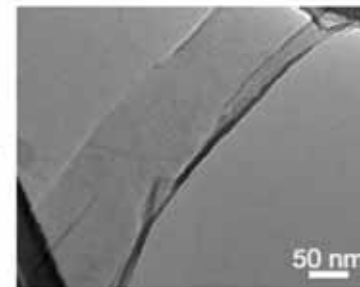
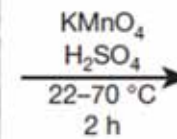
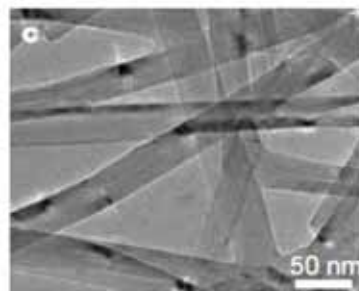
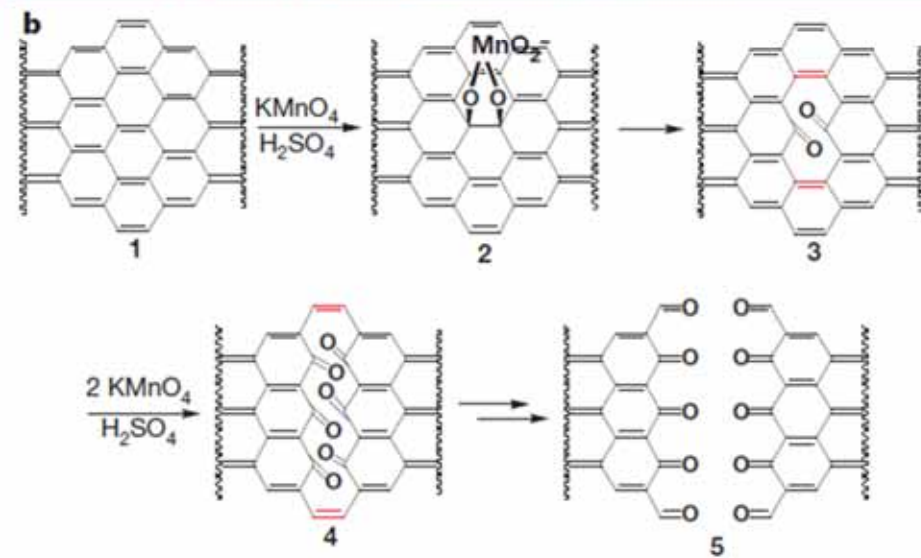
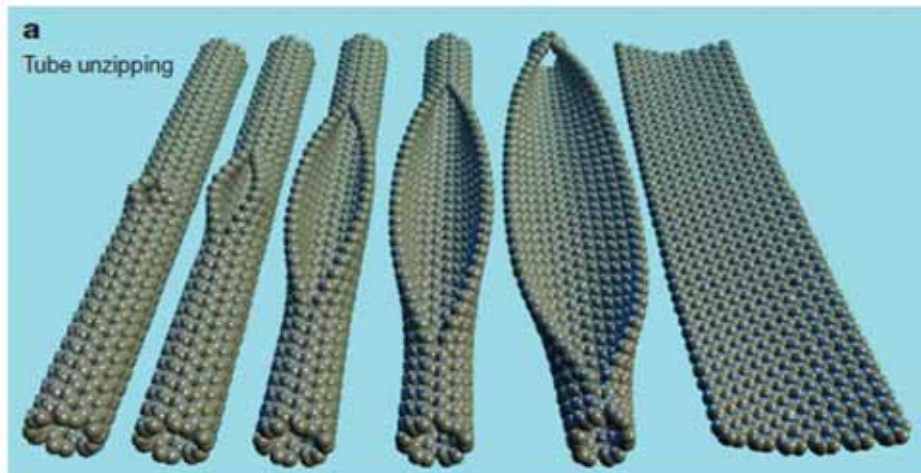
- ・純水を加えて攪拌し, 酸化グラフェン分散水溶液を得る。



上野啓司、「グラフェン/酸化グラフェンの応用研究」  
from <http://surface-www.chem.saitama-u.ac.jp/wiki/>

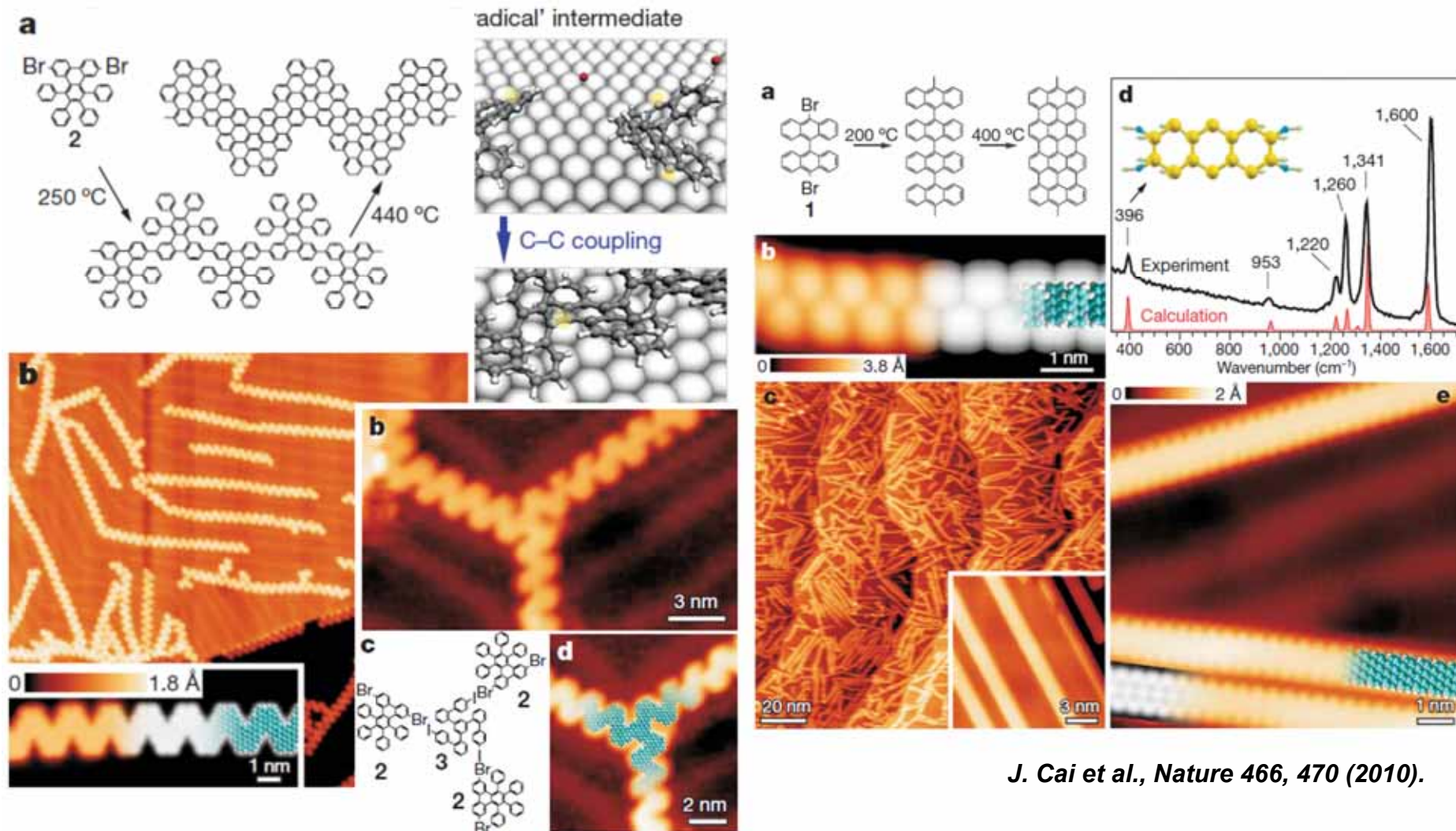
[http://www.springerimages.com/Images/RSS/1-10.1007\\_s11671-010-9751-6-1](http://www.springerimages.com/Images/RSS/1-10.1007_s11671-010-9751-6-1)

# CNT展開



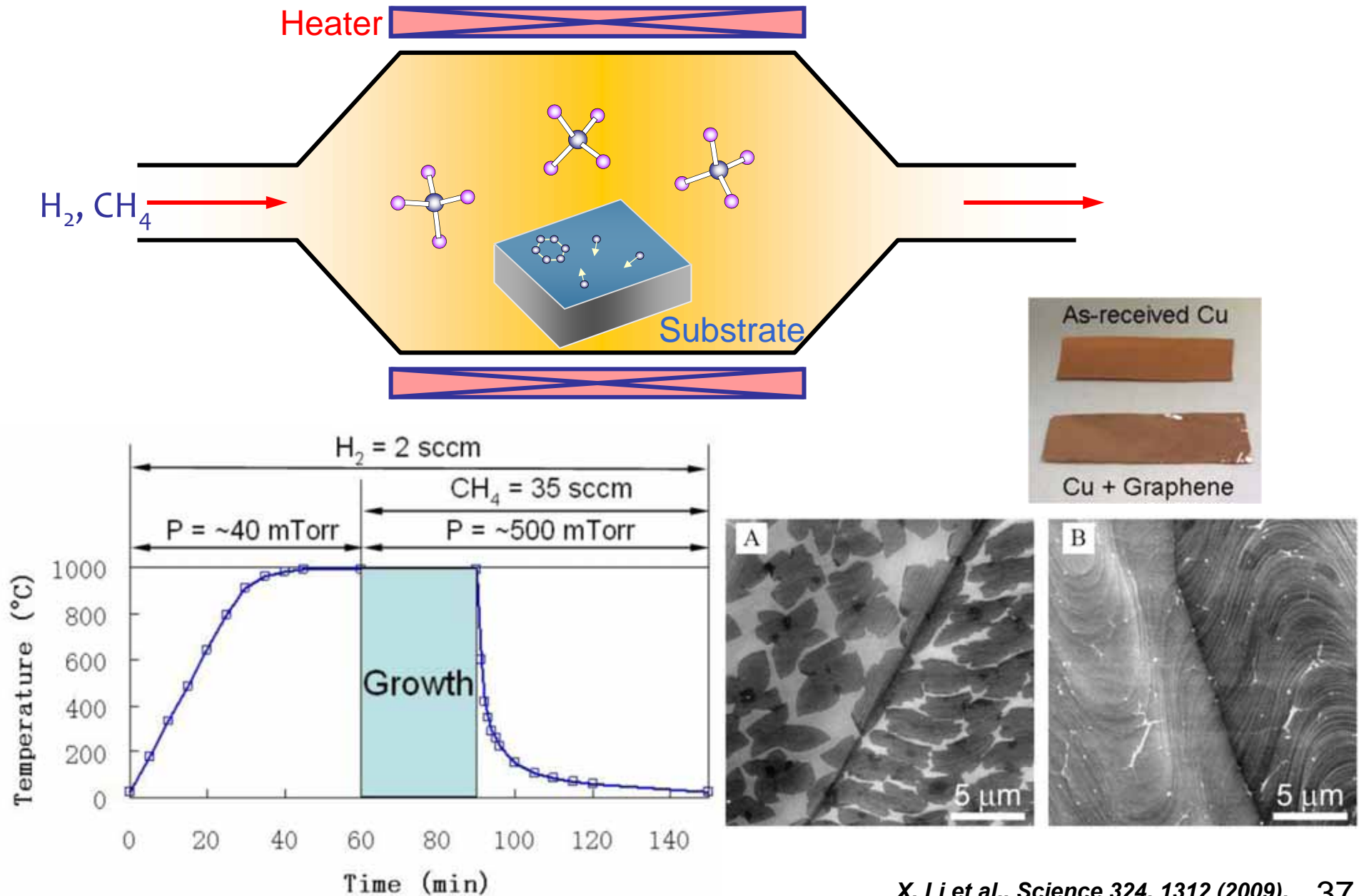
*D. V. Kosynkin et al., Nature 458, 872 (2009).*

# 表面アシスト分子カップリング

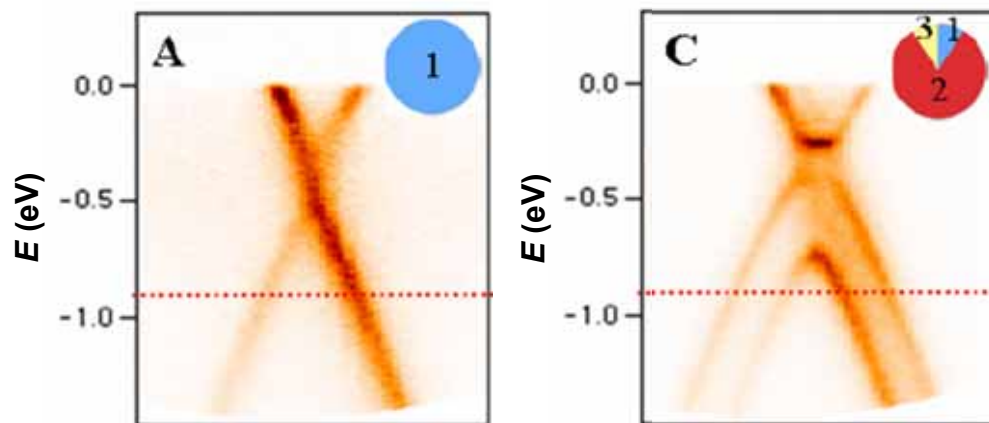
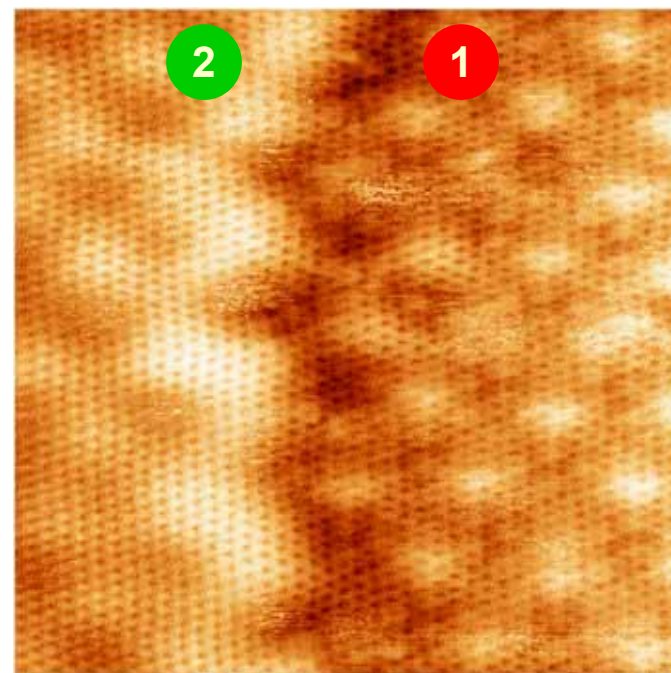
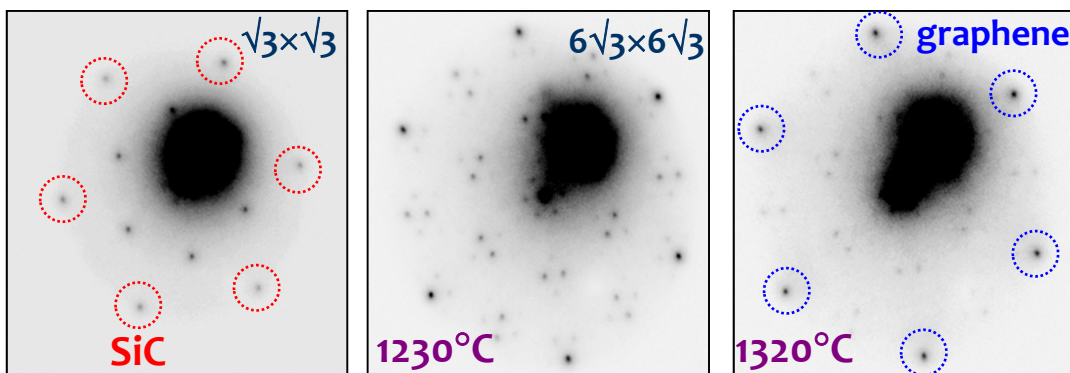
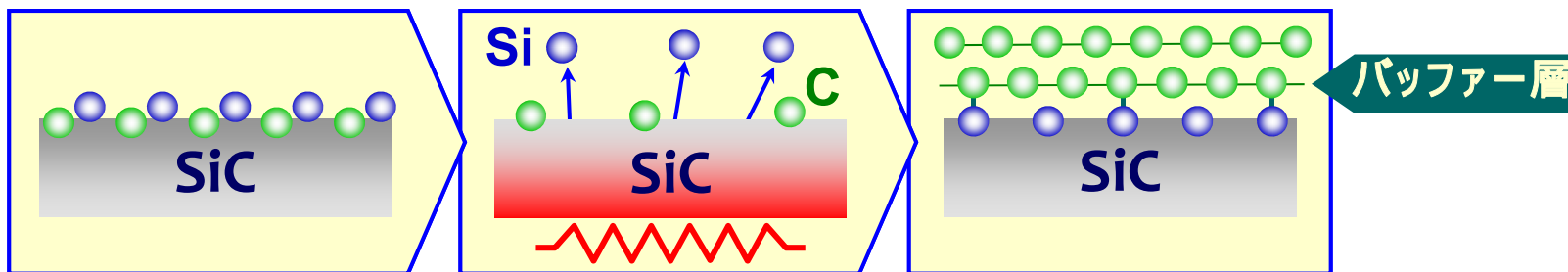


*J. Cai et al., Nature 466, 470 (2010).*

# グラフェンCVD成長



# SiC熱分解法



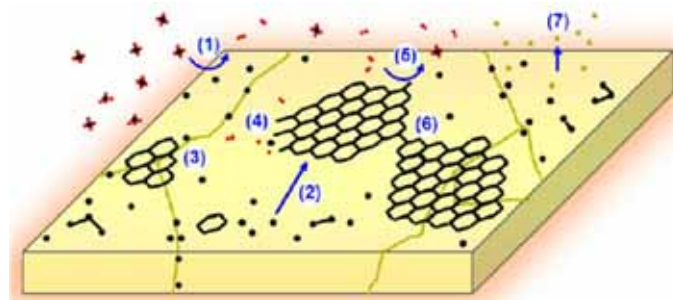
T. Ohta et al., *Science* 313, 951 (2006).

M. Nagase et al., *Nanotechnology* 20, 445704 (2009). 38

# グラフェン成長の特殊性

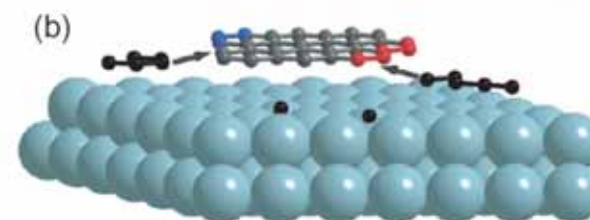
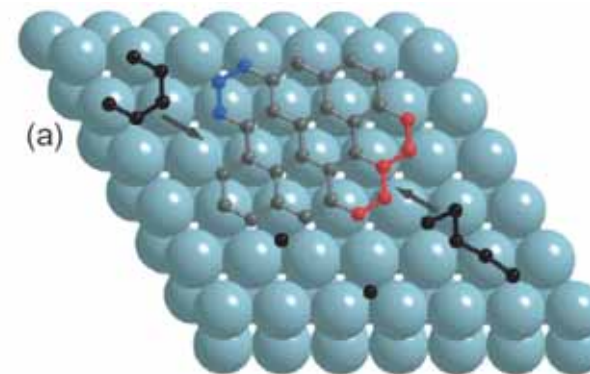
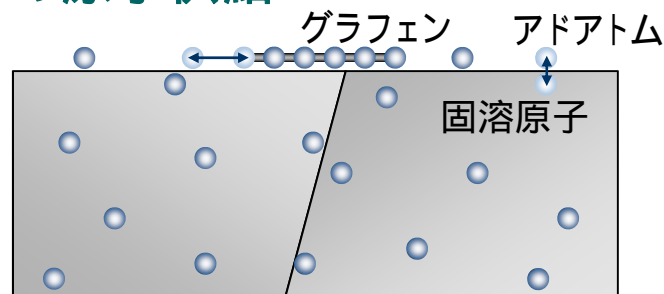
結晶構造の非類似性(二次元物質、蜂の巣状、van der Waals力)

CVD法：触媒反応



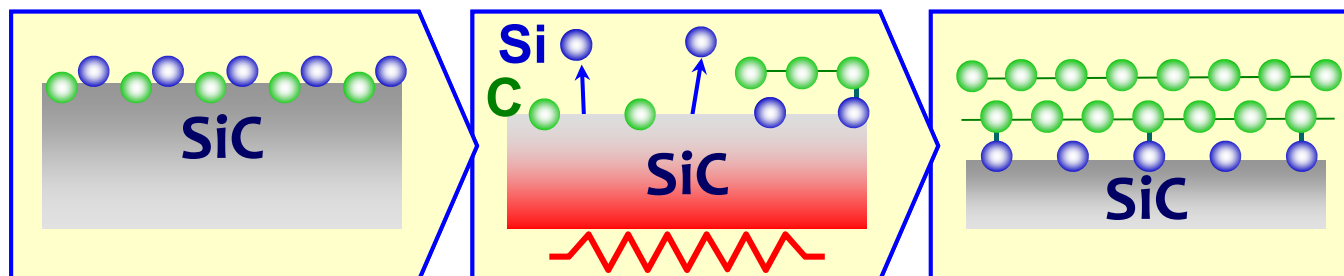
H. Ago et al., J. Phys. Chem. Lett. 3, 2228 (2012).

析出法：基板からの原子供給



E. Longinova et al., New J. Phys. 10, 093026 (2008).

SiC熱分解法：基板からの原子供給、基板のエッチング



# グラフェン製造法

	機械的剥離	SiC熱分解	金属上CVD成長
品質(移動度)	◎ 120,000 cm <sup>2</sup> /Vs (240 K)	○ ~4,000 cm <sup>2</sup> /Vs ~15,000 cm <sup>2</sup> /Vs (室温)	○ ~10,000 cm <sup>2</sup> /Vs (室温)
サイズ/コスト	△ 小(≤100 μm) 低生産性	○ 大(数インチ) SiC基板(高価)	◎ 巨大(数十インチ) 箔/薄膜(安価)
層数制御	△ 困難	○ 1 ~ 数層	○ 1 ~ 数層
結晶品質	◎ 単一ドメイン	○ エピタキシャル 積層ドメイン	△ 方位/積層が乱雑
基板	◎ 任意基板 (視認にはSiO <sub>2</sub> /Si)	○ 半導体	△ 金属 (基板除去)
転写	○ 粘着テープ	△ 金属接着層	○ 金属基板除去

応用分野

基礎科学  
単体デバイス動作デモ

エレクトロニクス

材料~デバイス



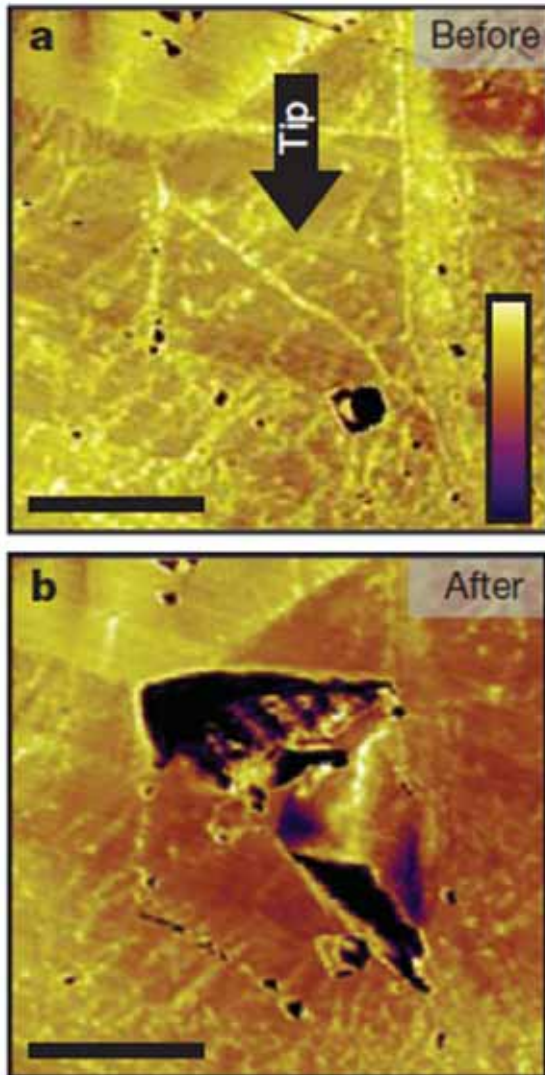
# グラフェン成長における課題

---

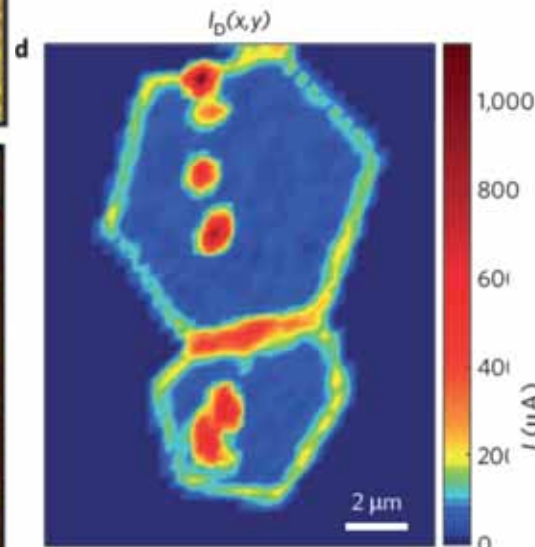
1. 結晶性 (グレイン、層数、段差、シワ)
2. 面積
3. コスト
4. 基板
5. 物性制御 (バンドギャップ、ドーピング)

# グレイン境界の影響

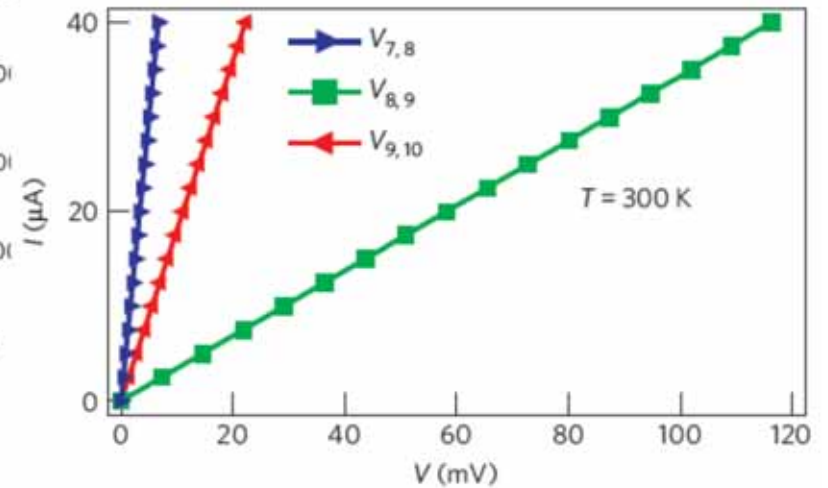
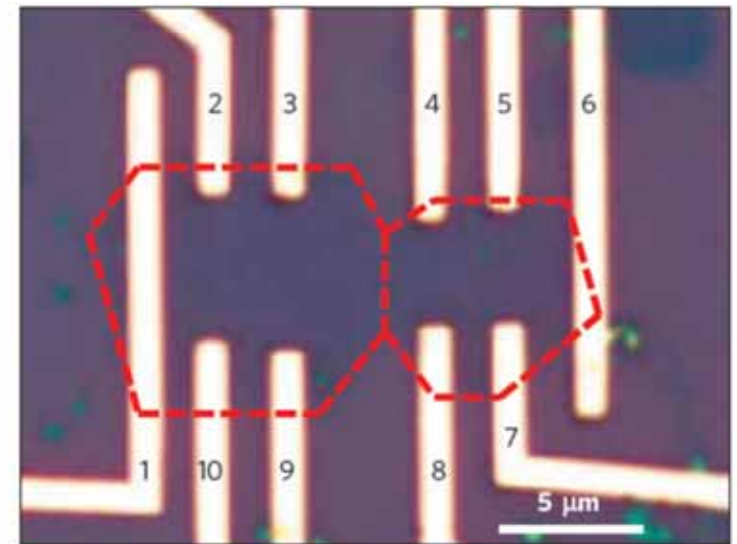
## AFM indentation



- ✓ 多結晶基板
  - ✓ 回転ドメイン
- 多結晶グラフェン



## Electrical measurement

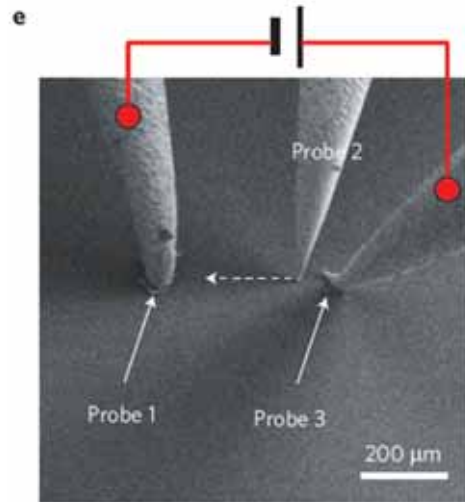


P. Y. Huang et al., Nature 469, 389 (2011).

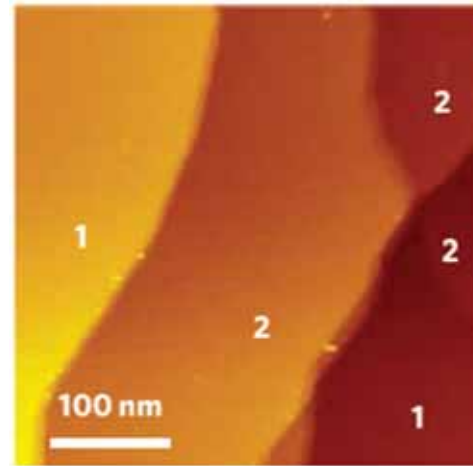
Q. Yu et al., Nature Mater. 10, 443 (2011).

# 段差の影響

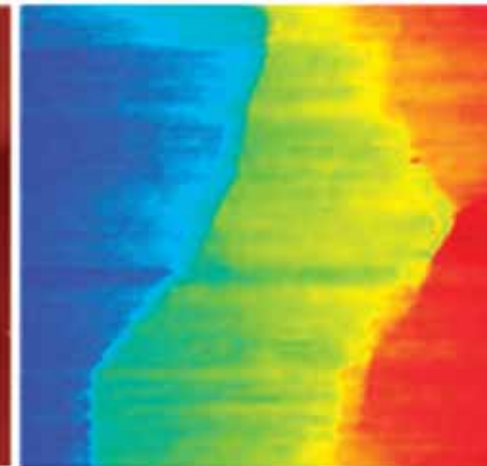
## Multiprobe electrical measurement



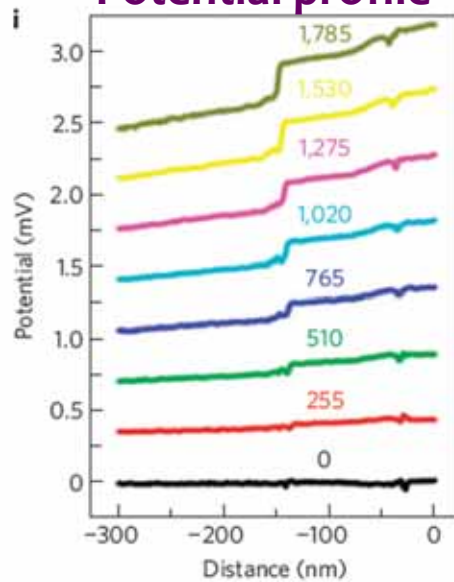
## STM



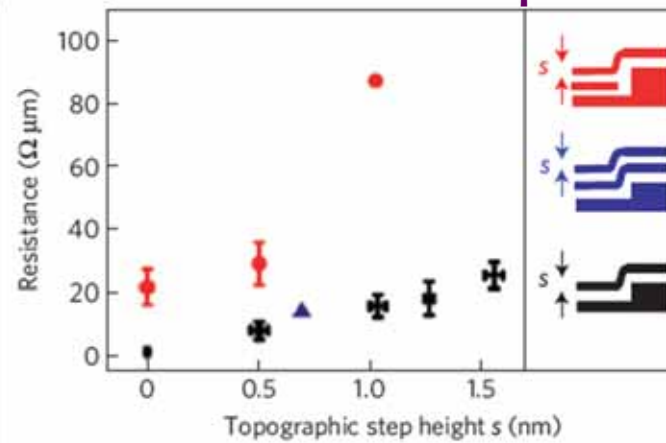
## Potential map



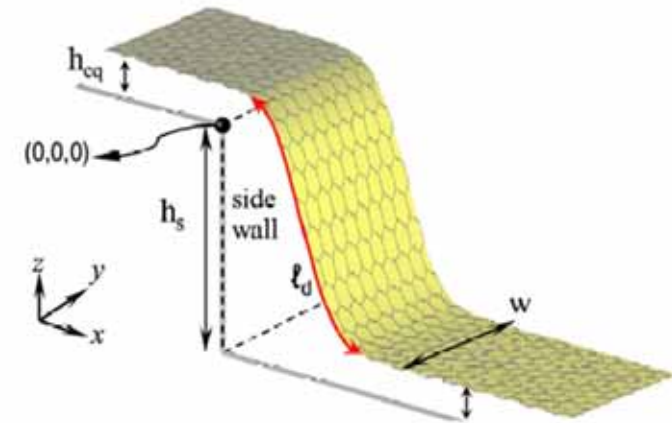
## Potential profile



## Resistance at steps



*S.-H. Ji et al., Nature Mater. 11, 114 (2012).*

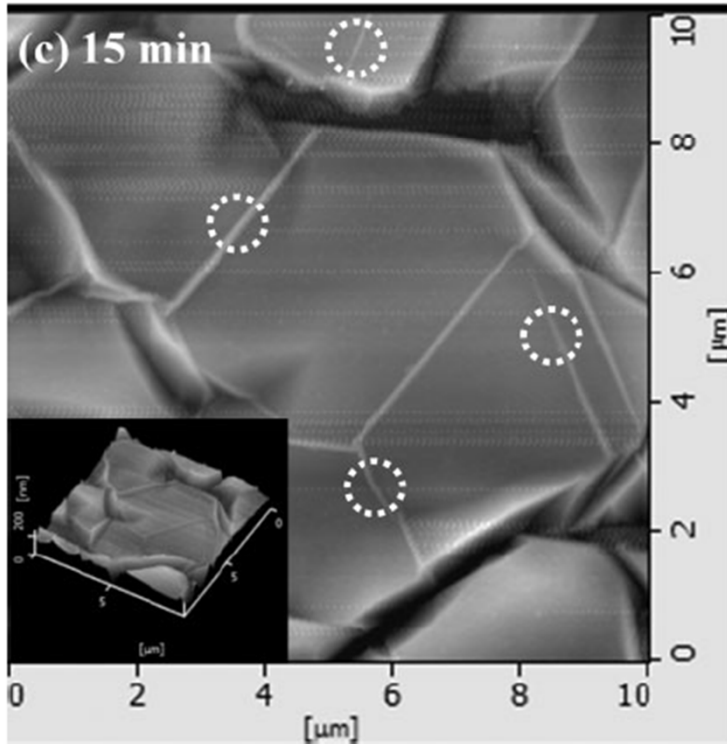
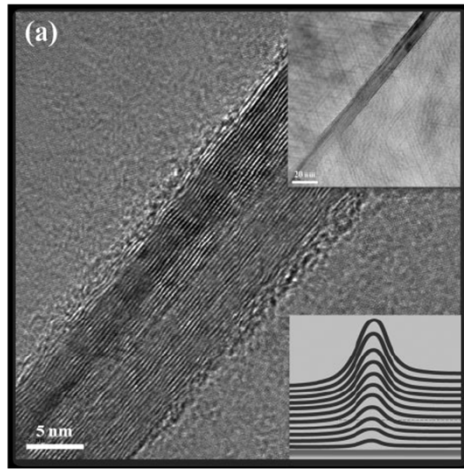


*T. Low et al., PRL 108, 096601 (2012).*

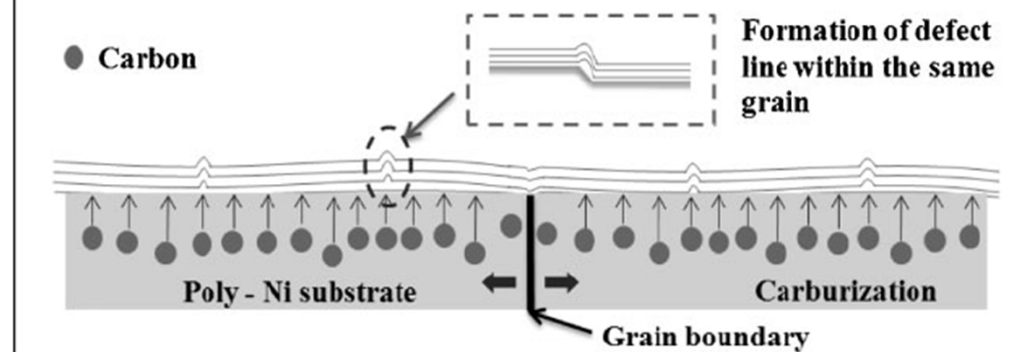
# シワ形成

- ✓ 異なるグレインの合体
- ✓ 熱膨張係数の違い

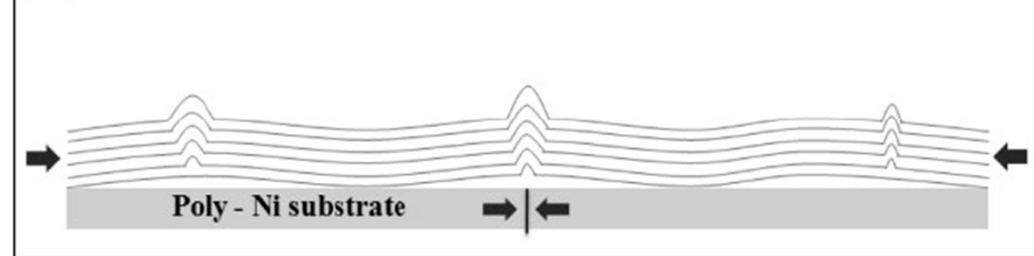
シワ



(a) Nucleation of defect lines on step edges between Ni terraces

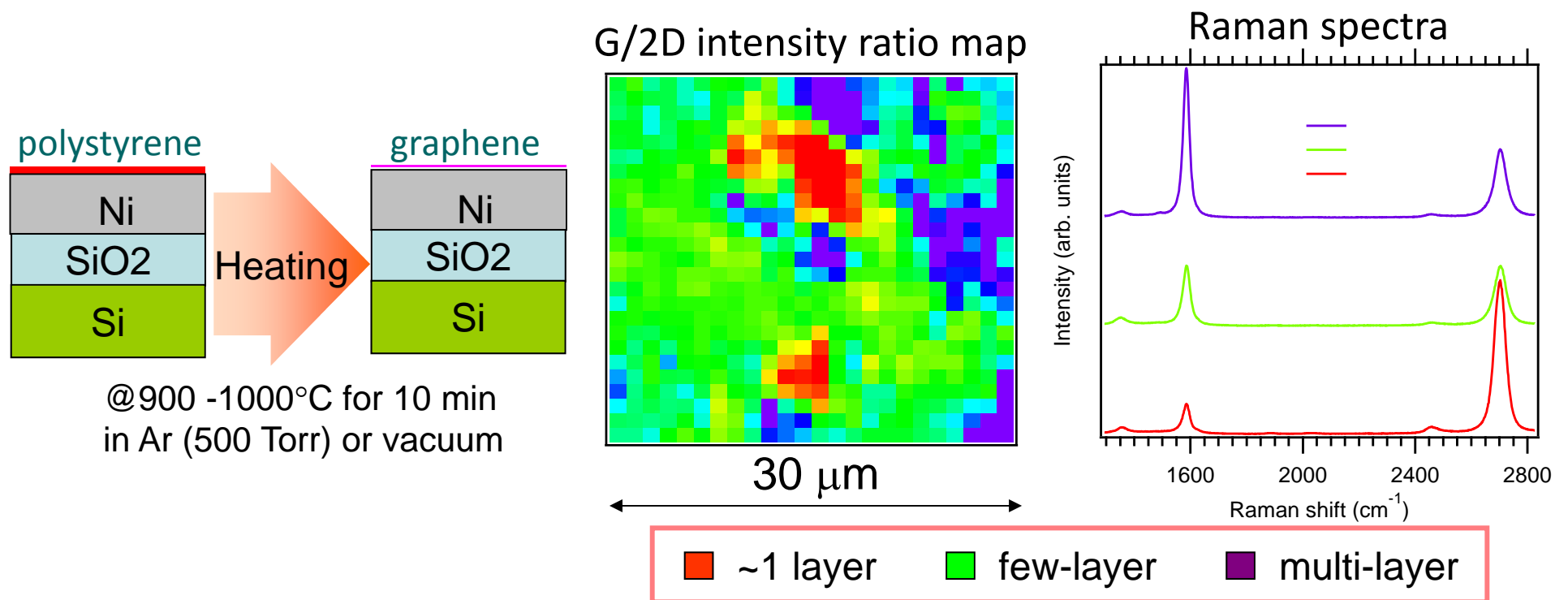
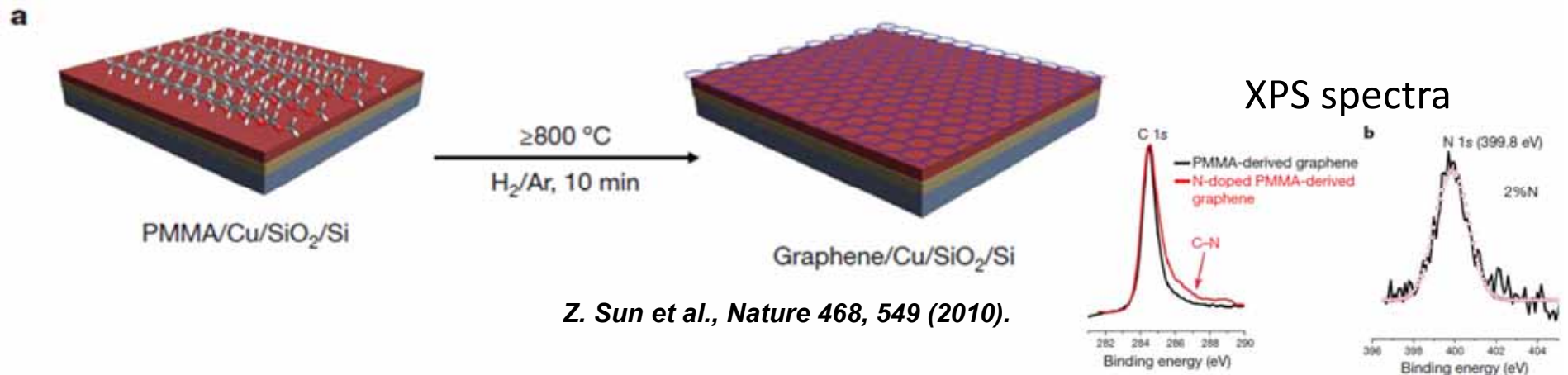


(b) Thermal stress-induced formation of wrinkles



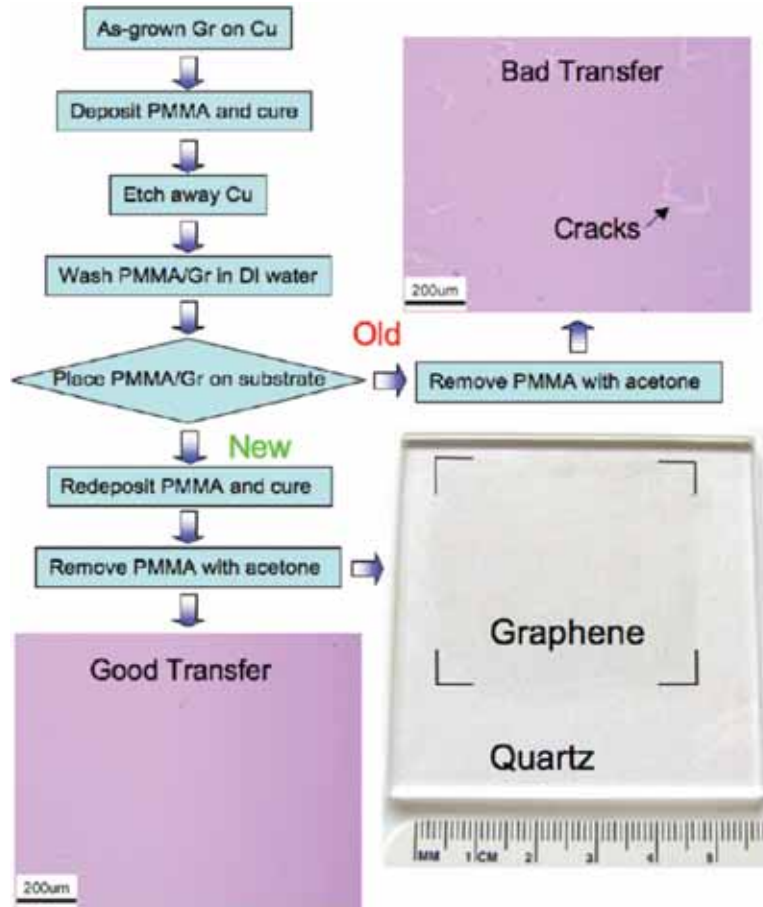
S. J. Chae et al., *Adv. Mater.* 21, 2328 (2009).

# スピコートしたポリマーからのグラフェン成長

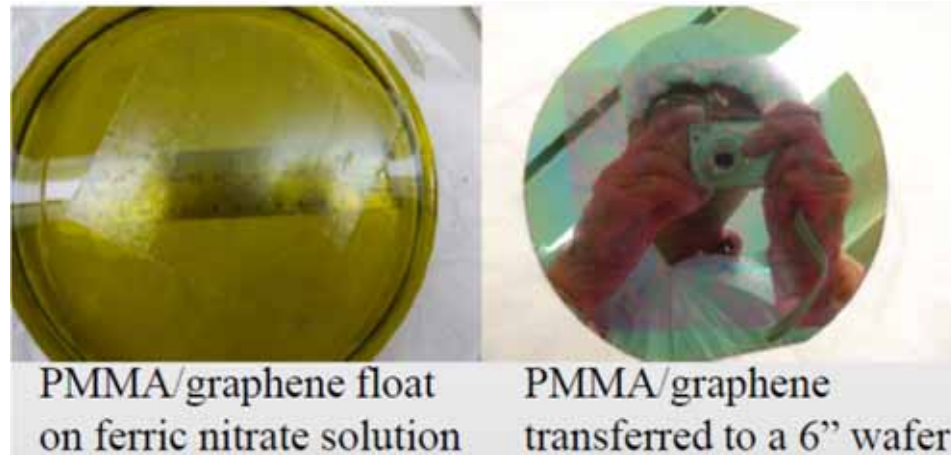


# グラフェン転写法

## ✓Cu上グラフェン転写

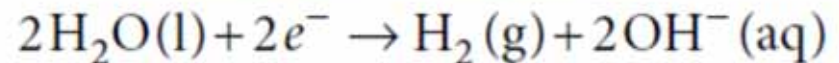
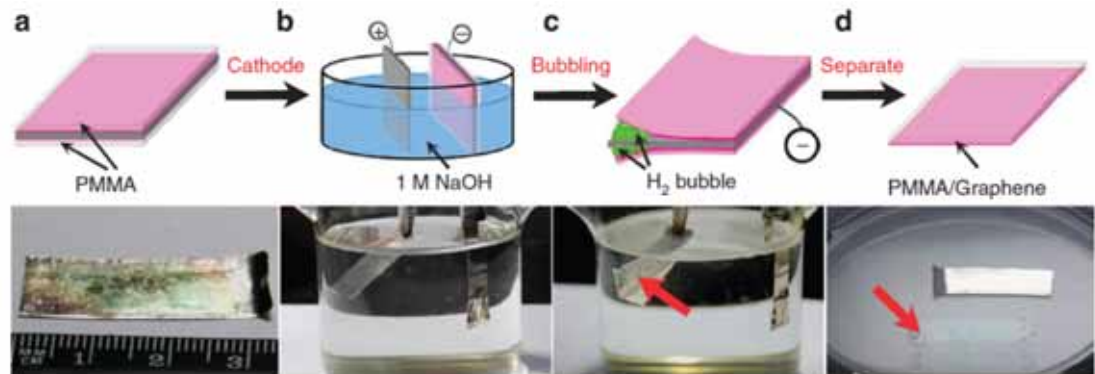


X. Li et al., *Nano Lett.* 9, 4359 (2009).



[http://www.nanoadvancement.org/nanotechnology-presentations/ANI\\_short\\_version.pdf](http://www.nanoadvancement.org/nanotechnology-presentations/ANI_short_version.pdf)

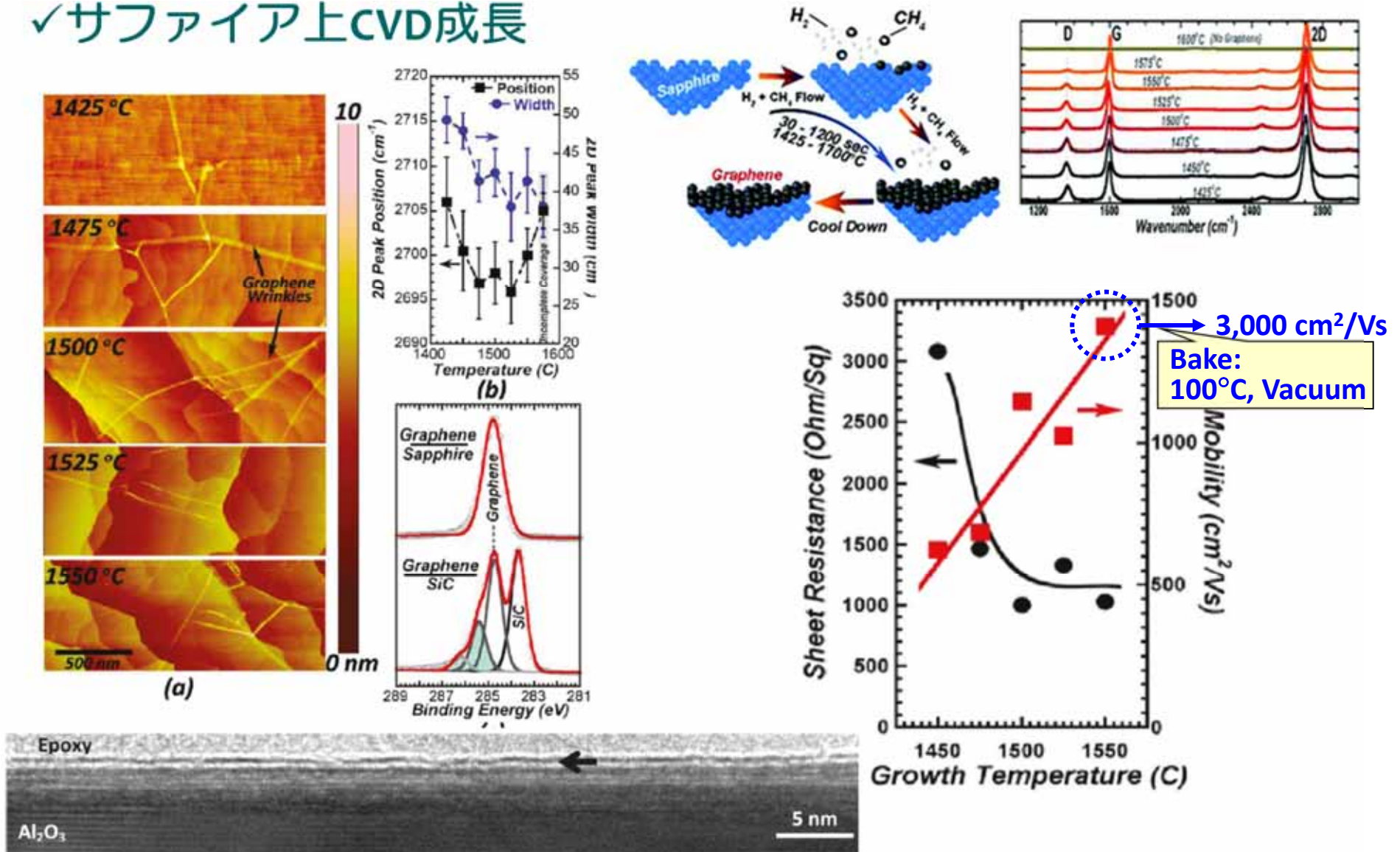
## ✓Pt上グラフェンのバブリング転写



L. Gao et al., *Nature Commun.* 3:699 (2012). 46

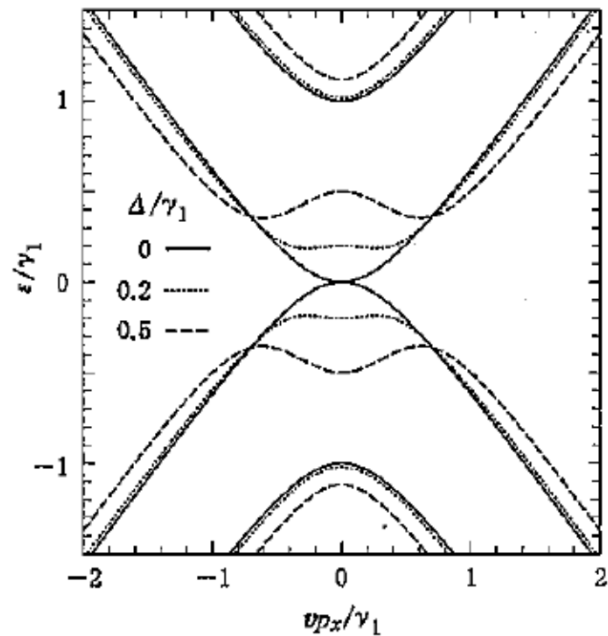
# サファイア上でのグラフェン直接成長

## ✓サファイア上CVD成長



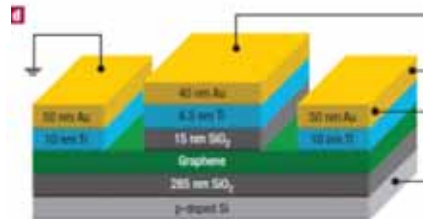
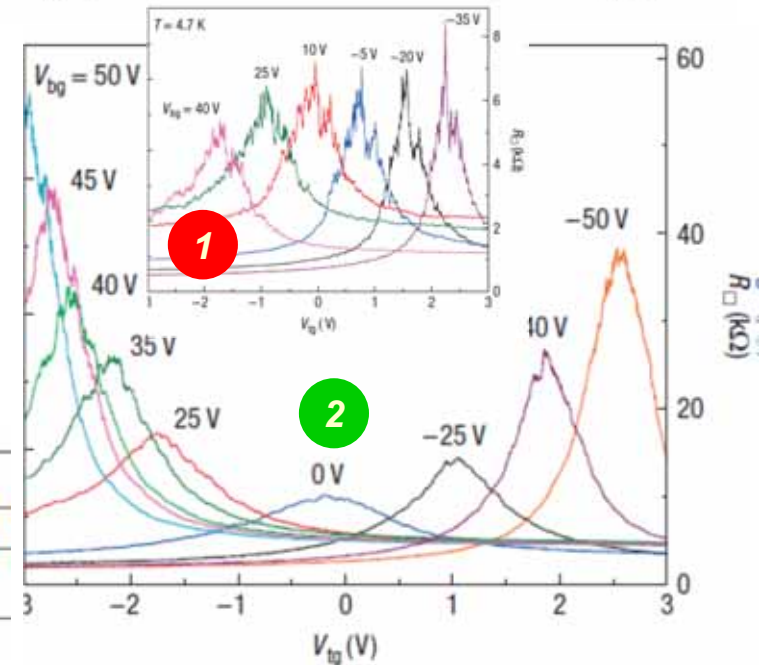
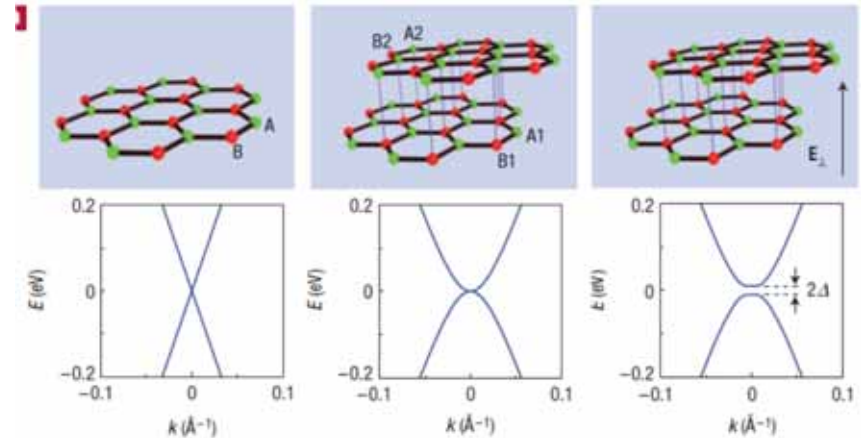
# バンドギャップ形成:2層グラフェンへの電界印加

$$H^K = \begin{pmatrix} \Delta & vp_- & 0 & 0 \\ vp_+ & \Delta & \gamma_1 & 0 \\ 0 & \gamma_1 & -\Delta & vp_- \\ 0 & 0 & vp_+ & -\Delta \end{pmatrix}$$



越野幹人 固体物理 45, 47 (2010).

✓ External electric field



J. B. Oostinga et al., *Nature Mater.* 7, 151 (2008). 48

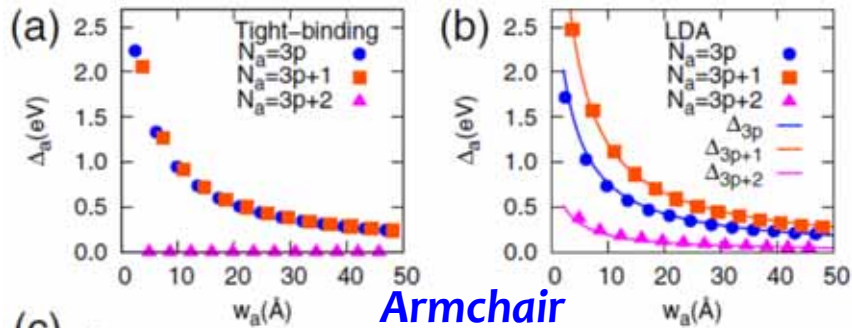


# バンドギャップ形成:ナノリボン

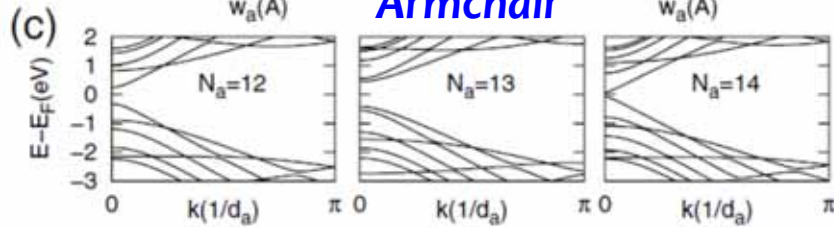
✓ Nanoribbon

$$E_g \sim \hbar v_F \Delta k \sim \hbar v_F / W$$

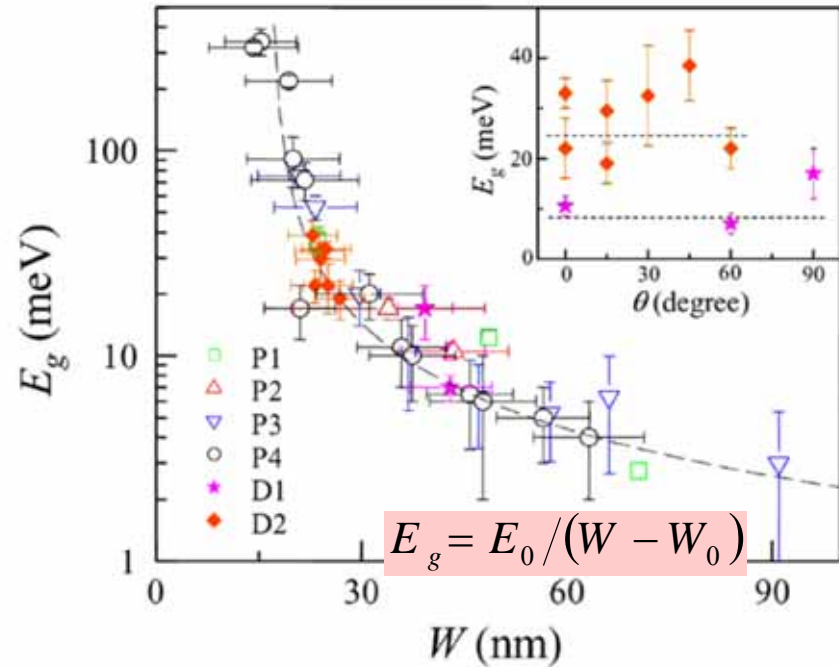
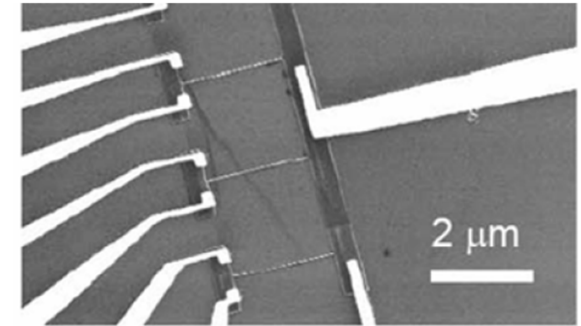
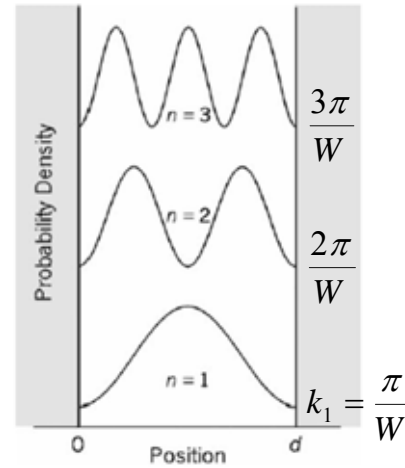
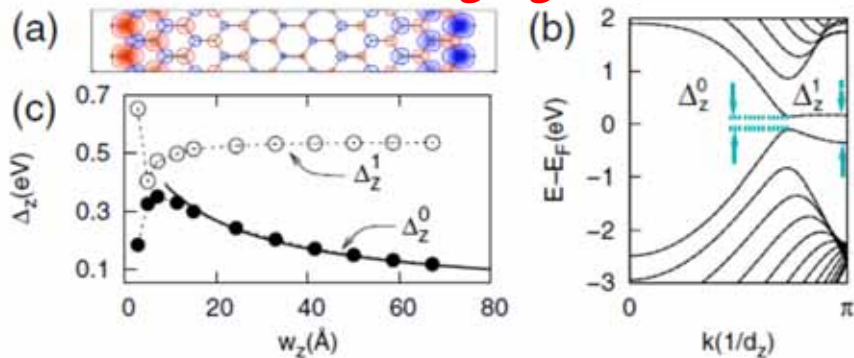
$$\alpha = 0.2-1.5 \text{ eV/nm,}$$



Armchair



Zigzag



Y.-W. Son et al., Phys. Rev. Lett. 97, 226803 (2006).

M. Y. Han et al., Phys. Rev. Lett. 98, 206805 (2007).

# 内容

1. グラフェンとは
2. グラフェン評価法
3. グラフェン成長法
  - 3-1 化学気相成長法
  - 3-2 析出法
  - 3-3 SiC熱分解法

# 金属基板上グラフェン成長

Surface	Method of preparation	Main experimental technique
Co(0001)	Segregation	AES
Ni(111)	Segregation	AES
	Decomposition	ELS
	Decomposition	UPS
	Decomposition	HREELS
	Decomposition	ARUPS
	Decomposition	STM
	Decomposition	LEED
	Decomposition	ICISS
Ni(100)	Segregation	LEED
	Decomposition	ARUPS
Ru(0001)	Segregation	LEED
	Segregation	STM
	Segregation	LEEM
	Decomposition	ARUPS
	Decomposition	XPS
	Decomposition	STM
Rh(111)	Segregation	LEED
	Decomposition	LEED
Rh(100)	Decomposition	LEED
Pd(111)	Segregation	AES
Pd(100)	Segregation	AES
Ir(111)	Decomposition	LEED
	Decomposition	STM
	Decomposition	ARUPS
Pt(111)	Segregation	LEED
	Decomposition	LEED
	Decomposition	HREELS
Pt(100)	Decomposition	STM
	Segregation	LEED
Pt(110)	Decomposition	LEED
	Segregation	LEED

Substrates	Conditions		References
	Gases	temperatures, etc.	
TiC(111)	C <sub>2</sub> H <sub>4</sub>	1400 K, 200 L	[24]
TaC(100)	C <sub>2</sub> H <sub>4</sub>	1400 K, 2000 L	[25]
TaC(111)	C <sub>2</sub> H <sub>4</sub>	1100–1500 K, 200 L	[26, 27]
HfC(100)	C <sub>2</sub> H <sub>4</sub>	1100–1800 K, 100 L	[28, 29]
HfC(111)	C <sub>2</sub> H <sub>4</sub>	1400 K, 500 L	[30]
WC(0001)	Hydrocarbon	1800–2000 K, 100 L	[31]
LaB <sub>6</sub> (100)	Segregation		[32]
Ni(100)	CO, C <sub>2</sub> H <sub>4</sub>		
	CO	600 K, 90 000 L	[33]
Ni(111)	C <sub>2</sub> H <sub>4</sub>		LEED, AES [25]
	Segregation		1975年 [26, 27]
Pt(111)	C <sub>3</sub> H <sub>6</sub>	1150 K, 13 L	LEED, AES [28, 29]
	C <sub>6</sub> H <sub>6</sub>	1100 K, 25 L	
Ir(100)	Segregation		
	C <sub>6</sub> H <sub>6</sub>	1600 K, 150 L	AES, TDS [30]
Ir(111)	Segregation		
	C <sub>6</sub> H <sub>6</sub>	1600 K, 150 L	AES, TDS [30]
Pd(100)	Segregation		LEED, AES [28]
	Segregation		LEED, AES [28]
Re(1010)	C <sub>6</sub> H <sub>6</sub>	1500–1800 K	AES, TDS [31]
	Segregation		UPS [32]

## Lattice constant:

✓ Graphite=0.246 nm

✓ Ni(111)=0.249 nm

✓ Rh(111)=0.269 nm

✓ Ru(0001)=0.271 nm

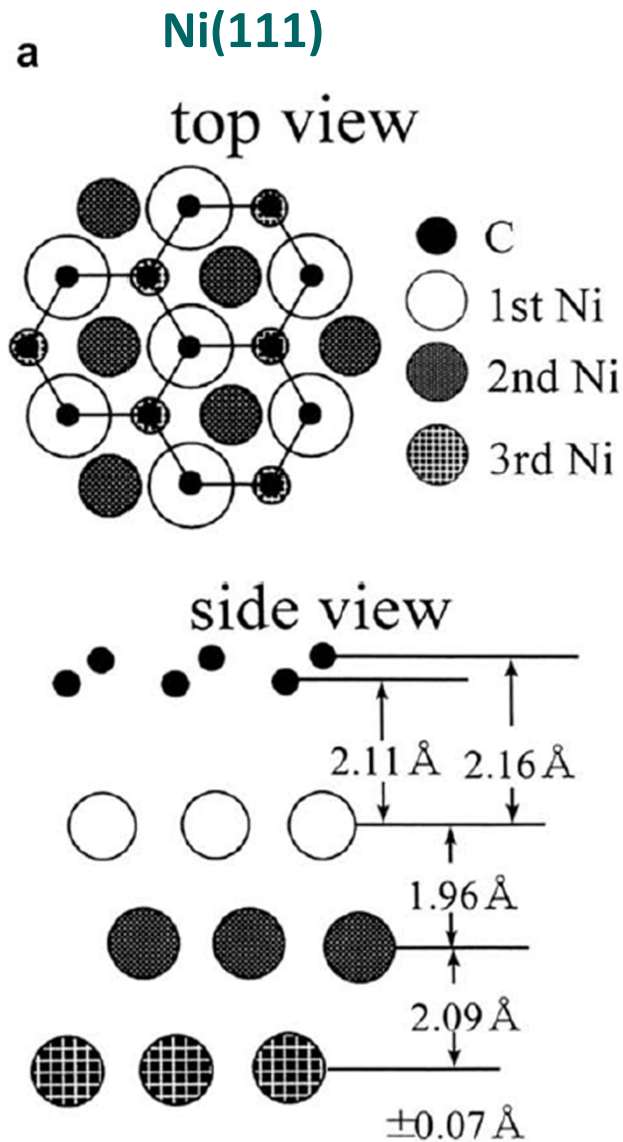
✓ Ir(111)=0.272 nm

✓ Pt(111)=0.277 nm

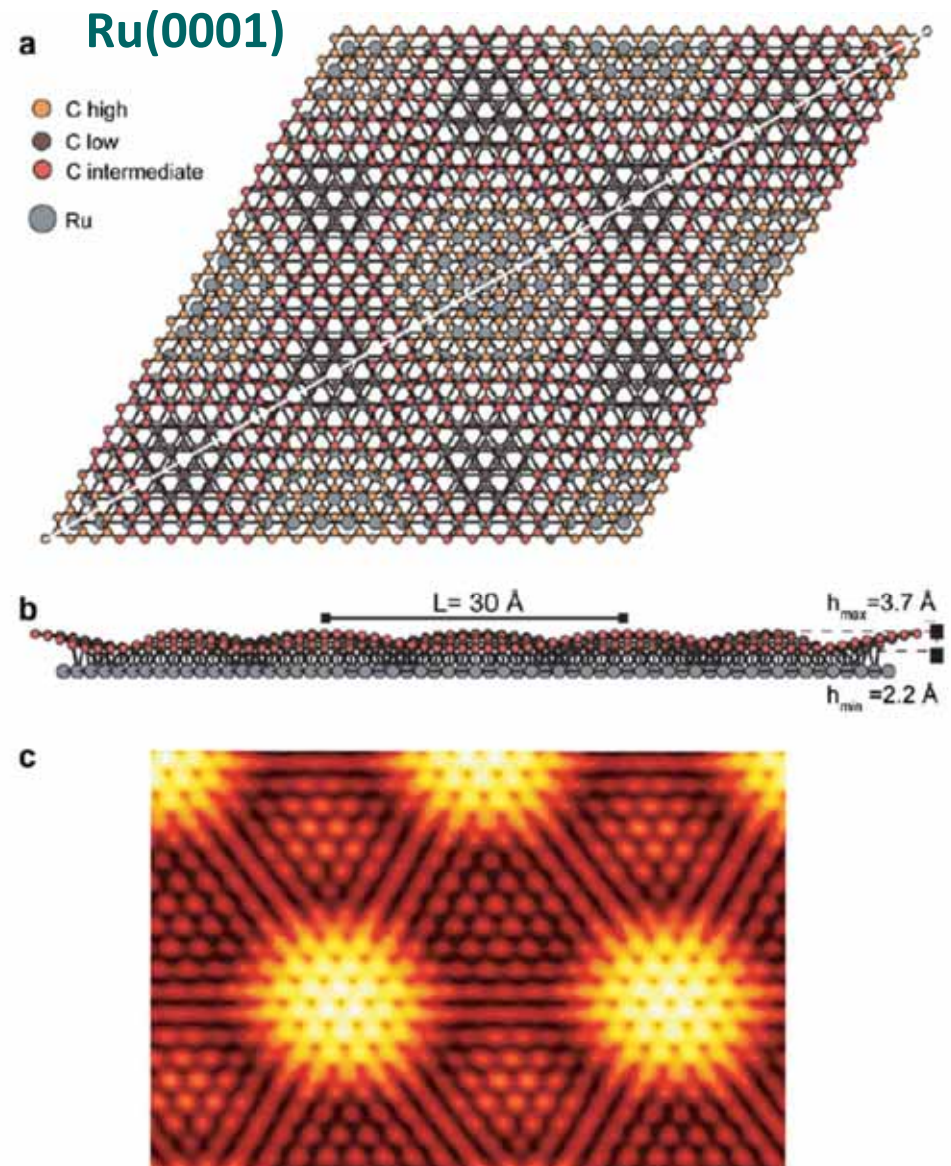
C. Oshima and A. Nagashima: *J. Phys.: Condens. Matter* 9 (1997) 1.

J. Winterlin, M.-L. Bocquet/*Surface Science* 603 (2009) 1841–1852

# 金属基板上のグラフェン



Y. Gamo et al., *Surf. Sci.* 374, 61 (1997).

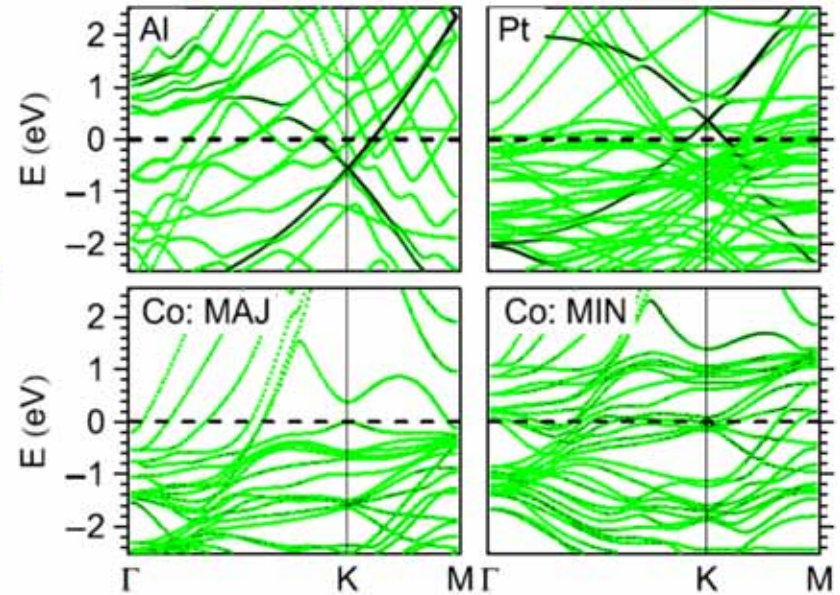
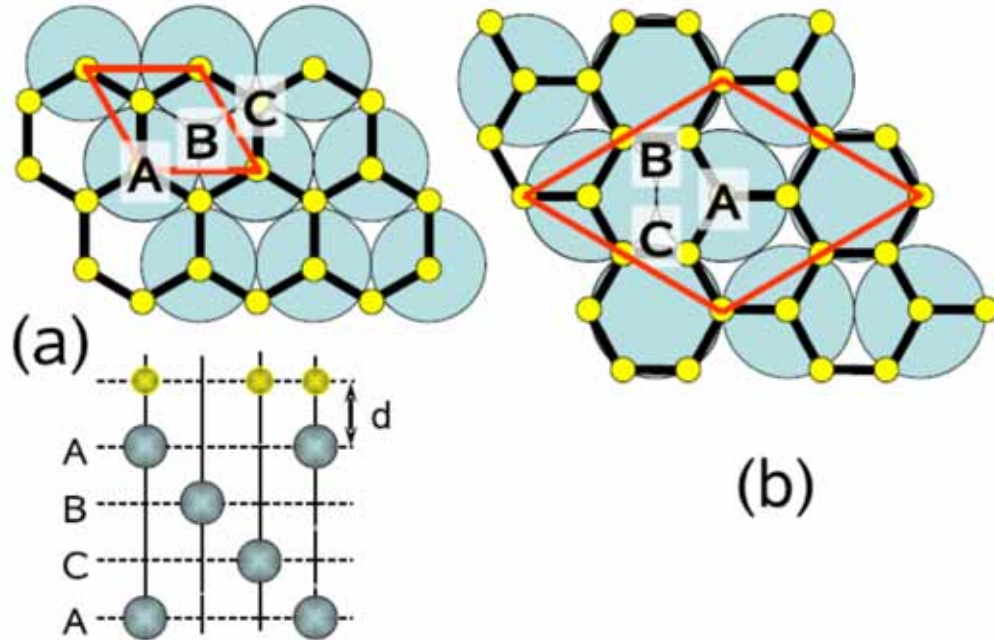


J. Winterlin, M.-L. Bocquet / *Surface Science* 603 (2009) 1841–1852 52

# 金属基板上のグラフェン

Cu, Ni, and Co(111)

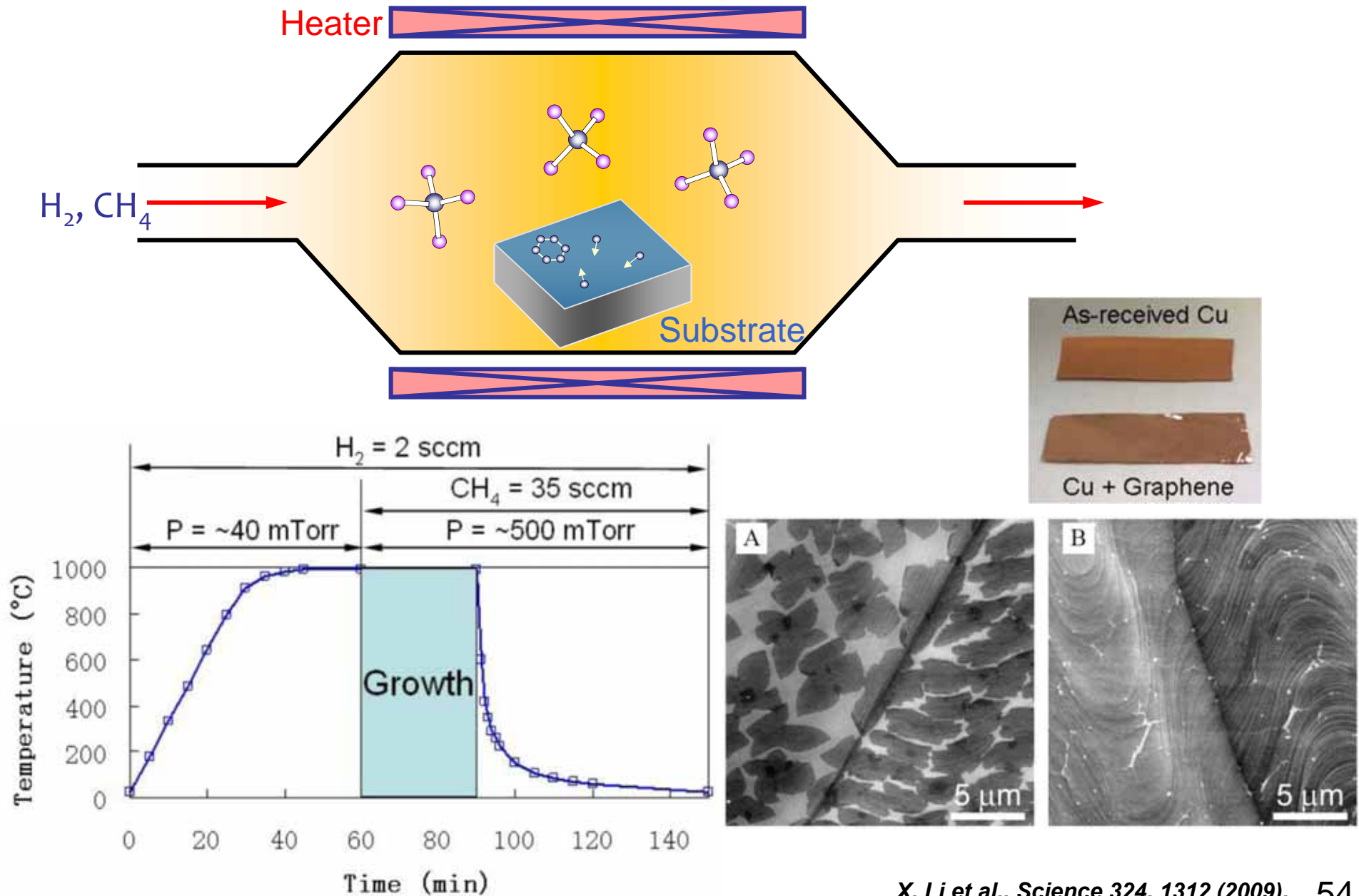
Al, Au, Pd, and Pt(111)



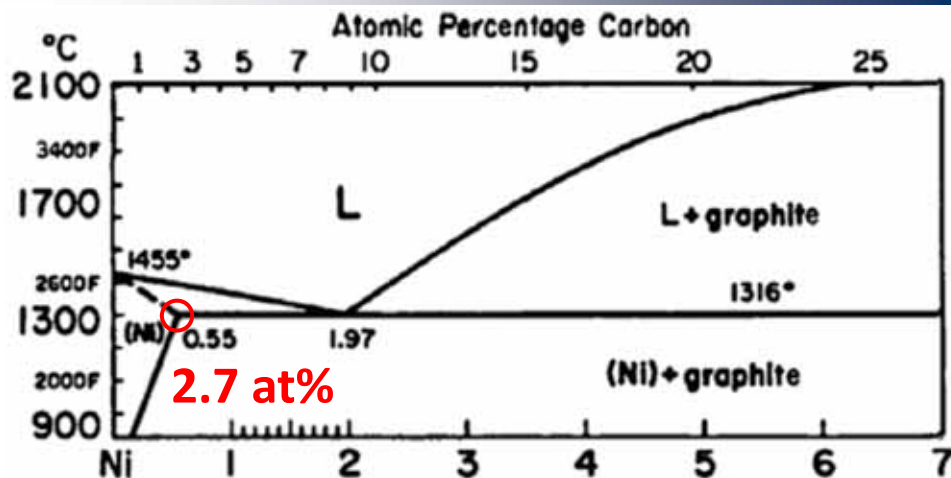
	Gr	Ni	Co	Pd	Al	Ag	Cu	Au	Pt
$d_{\text{eq}}$ (Å)		2.05	2.05	2.30	3.41	3.33	3.26	3.31	3.30
$\Delta E$ (eV)		0.125	0.160	0.084	0.027	0.043	0.033	0.030	0.038
$W_M$ (eV)		5.47	5.44	5.67	4.22	4.92	5.22	5.54	6.13
$W$ (eV)	4.48	3.66	3.78	4.03	4.04	4.24	4.40	4.74	4.87
$W_{\text{expt}}$ (eV)	4.6 <sup>a</sup>	3.9 <sup>a</sup>		4.3 <sup>a</sup>					4.8 <sup>a</sup>

G. Giovannetti et al., PRL 101, 026803 (2008).

# グラフェンCVD成長

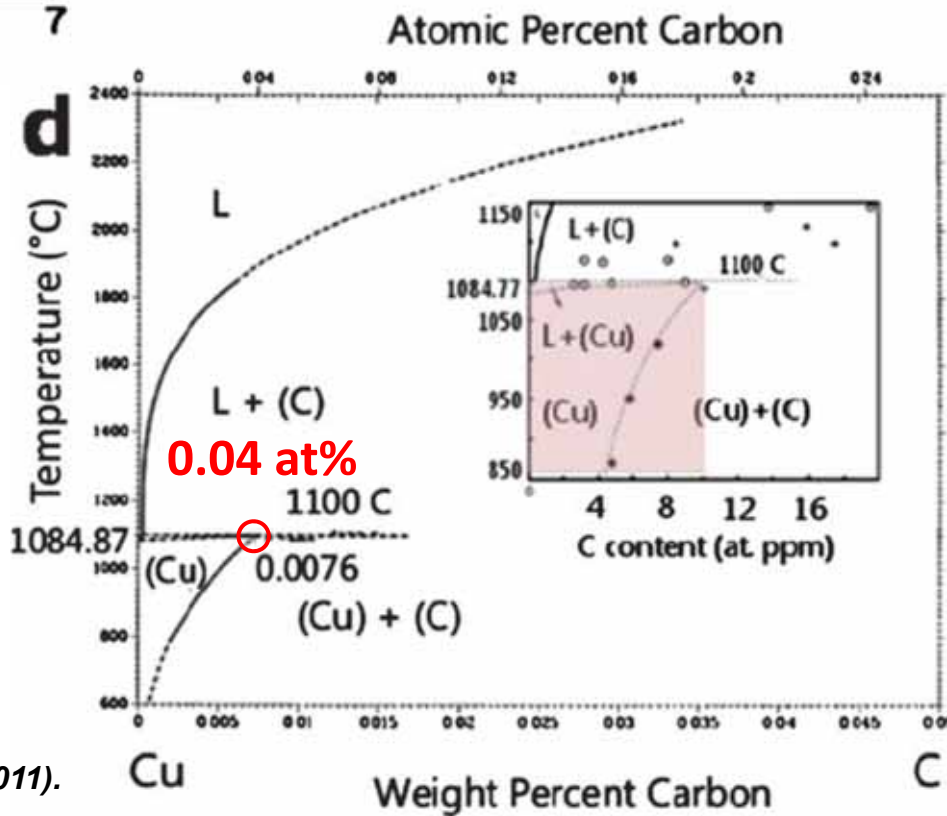
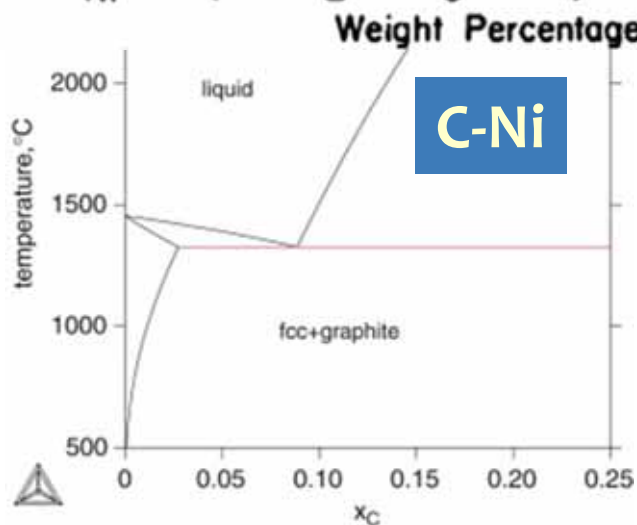


# CVD成長の基板依存性



[http://www.nanoadvancement.org/nanotechnology-presentations/ANI\\_short\\_version.pdf](http://www.nanoadvancement.org/nanotechnology-presentations/ANI_short_version.pdf)

C-Cu



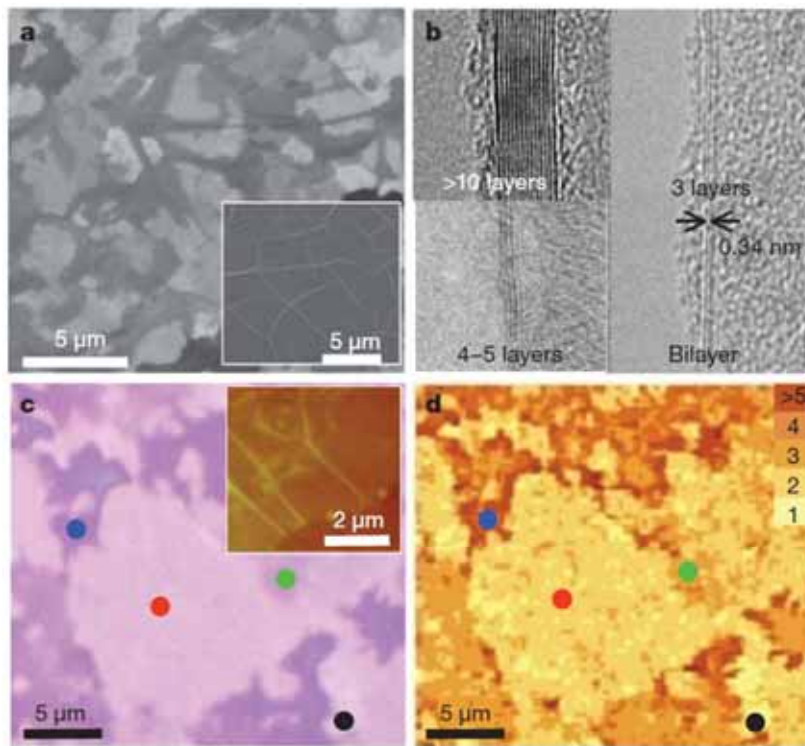
L. Kjellqvist and M. Selleby, *Calphad* 33, 393 (2009).

C. Mattevi et al., *J. Mater. Chem.* 21, 3324 (2011).

# CVD成長の基板依存性

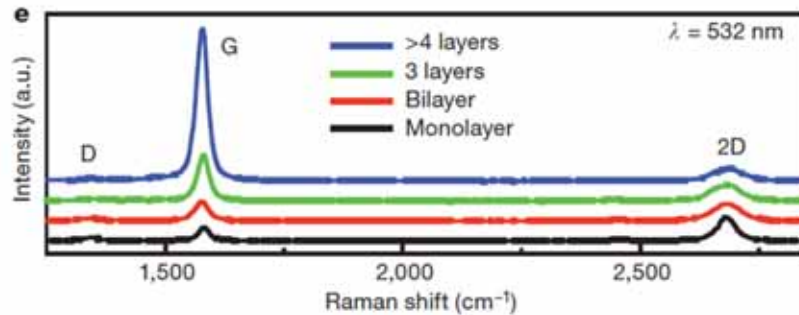
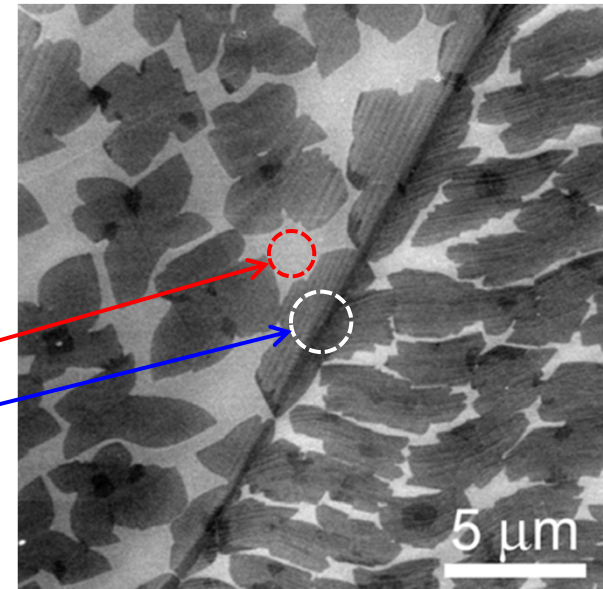
✓Ni上の偏析/析出

✓Cu上の二次元核形成/成長

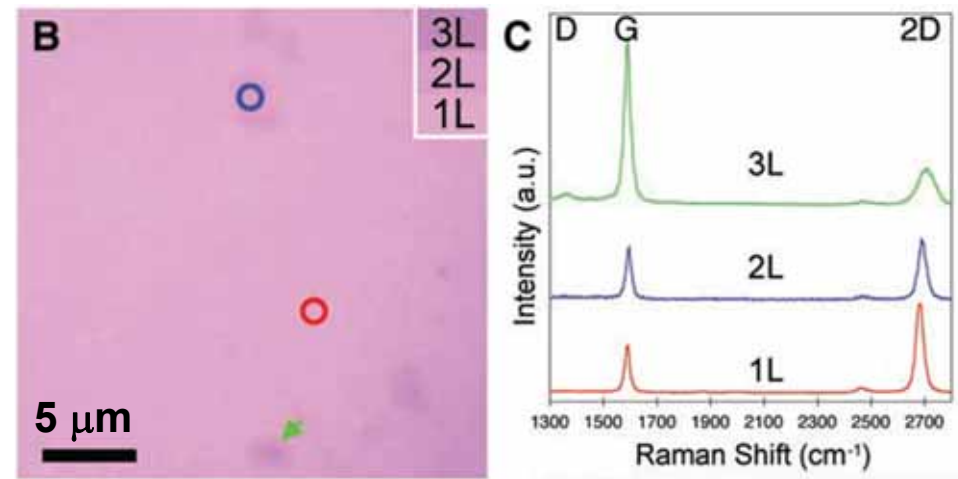


Cu catalyst

Graphene  
w/o catalytic  
activities



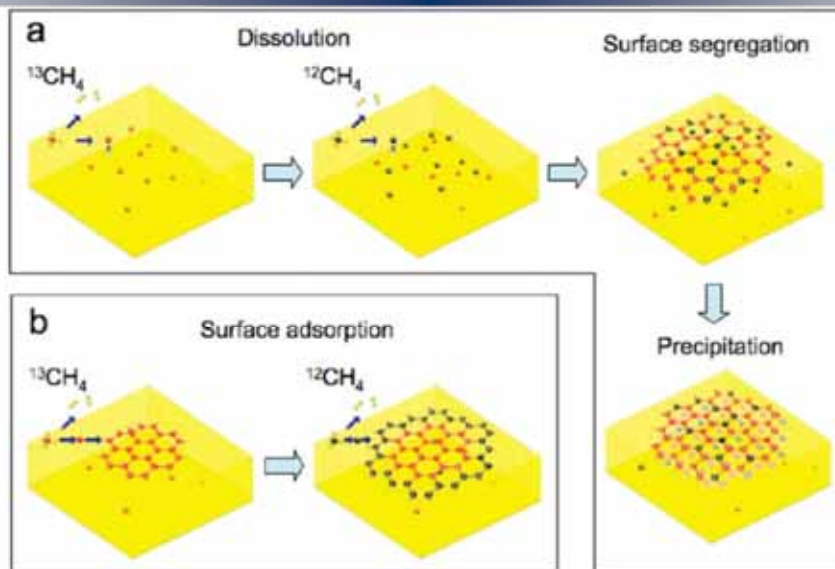
K. S. Kim et al., Nature 457, 706 (2009).



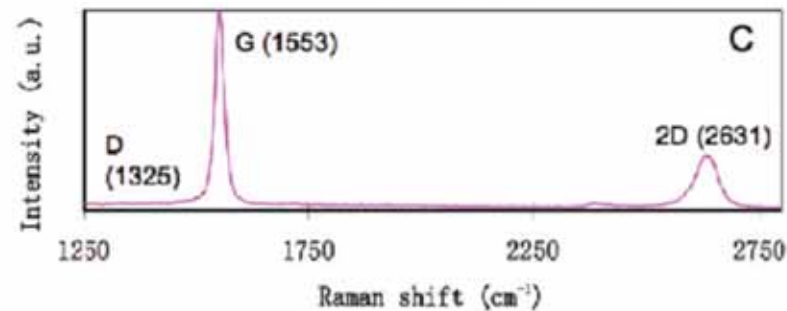
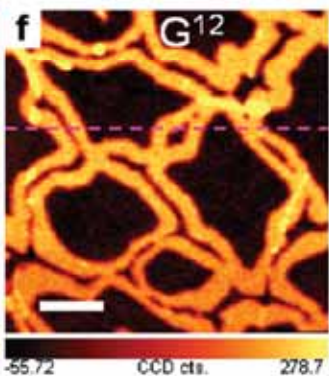
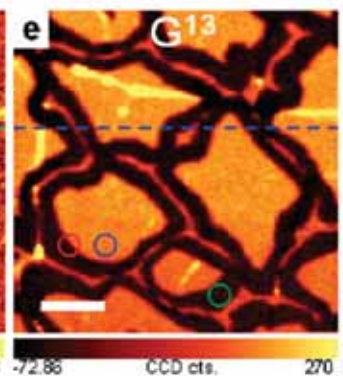
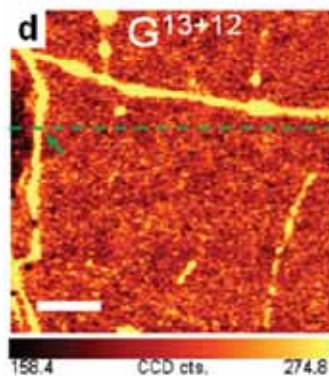
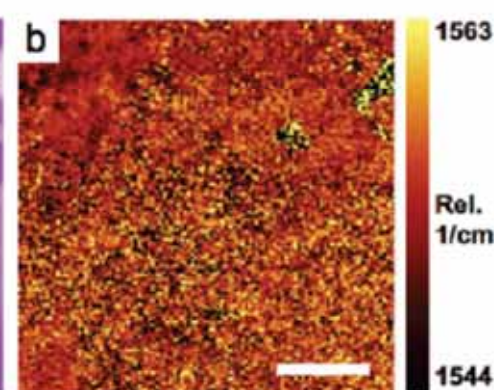
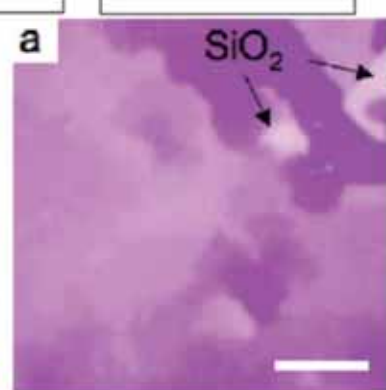
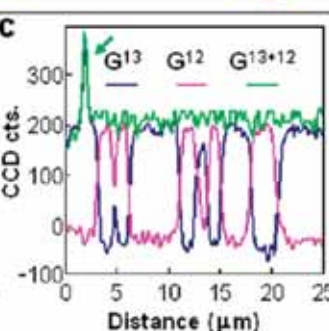
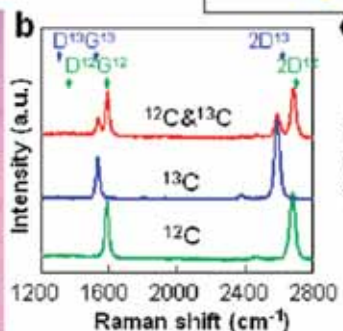
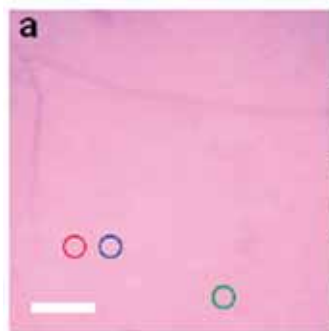
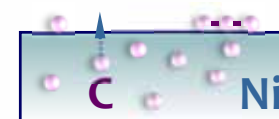
X. Li et al., Science 324, 1312 (2009). 56



# グラフェン成長様式

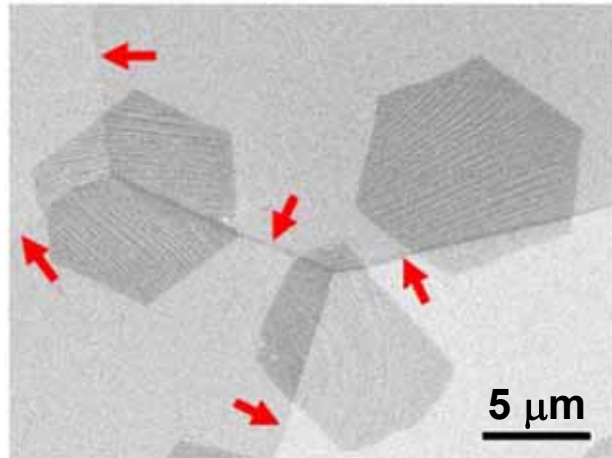


X. Li et al., *Nano Lett.*  
9, 4268 (2009).

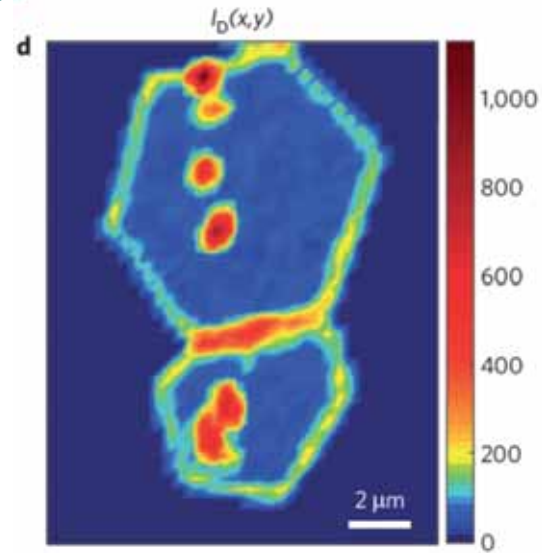


# 多結晶グラフェン

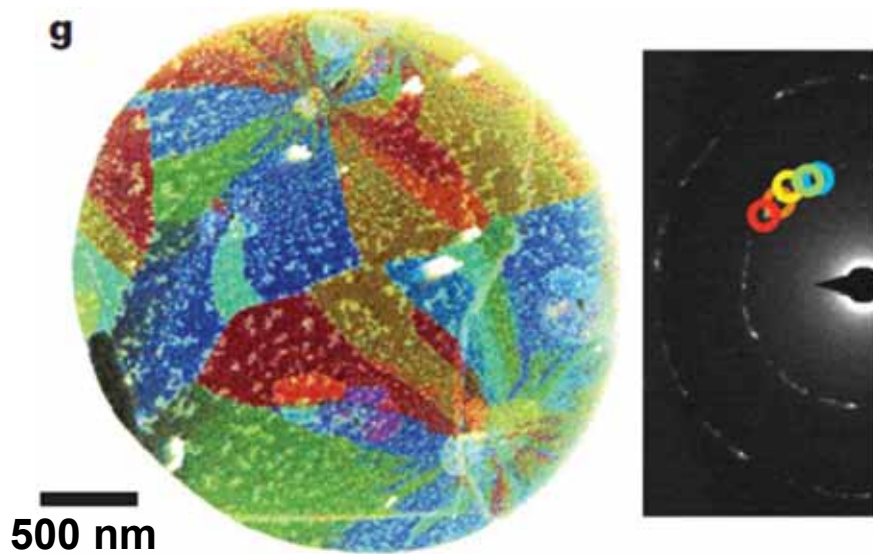
## ✓多結晶Cu箔上の多結晶グラフェン



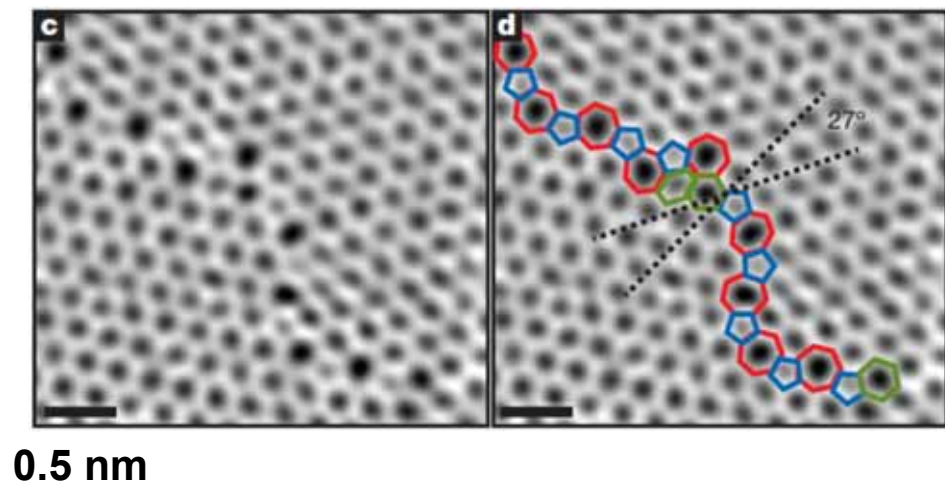
Q. Yu et al., *Nature Mater.* 10, 443 (2011).



Q. Yu et al., *Nature Mater.* 10, 443 (2011).

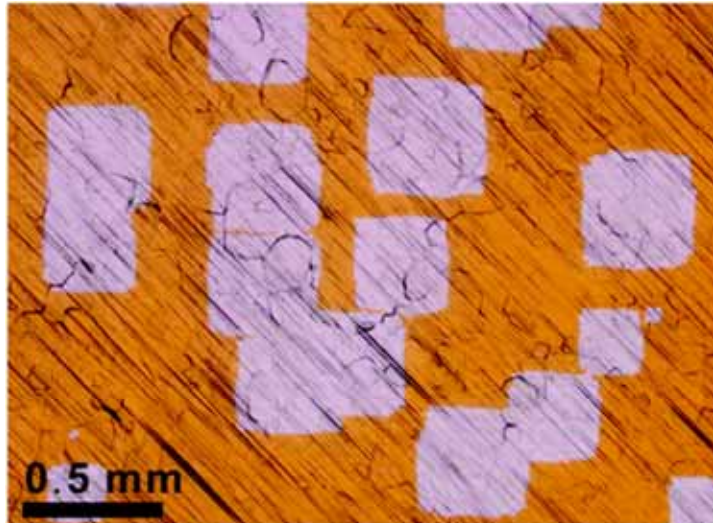


P. Y. Huang et al., *Nature* 469, 389 (2011).



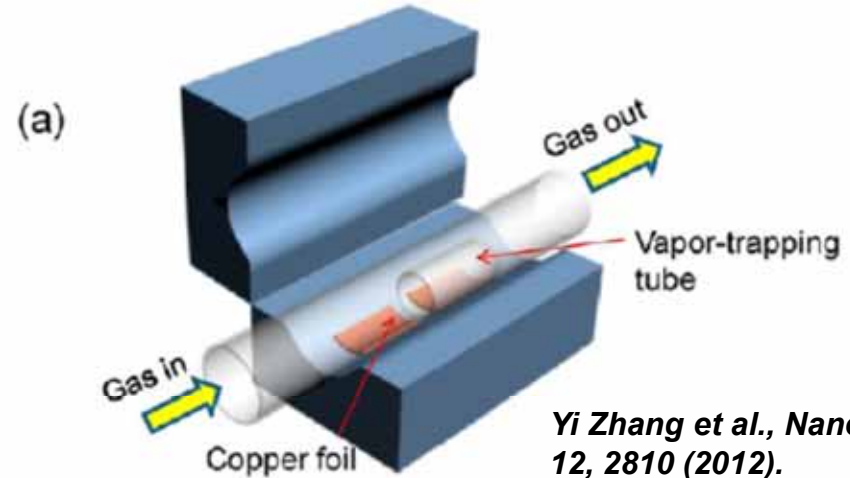
# グラフェン成長形

APCVD: 0.5 sccm CH<sub>4</sub> and 500 sccm H<sub>2</sub>



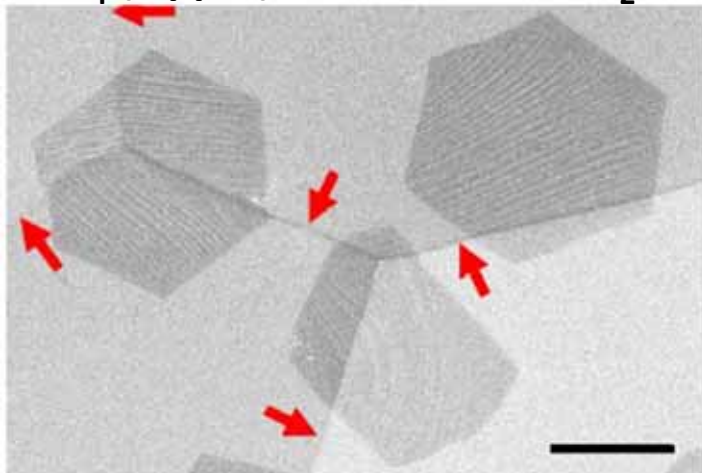
H. Wang et al., *J. Am. Chem. Soc.* 134, 3627 (2012)

Vapor Trapping Growth

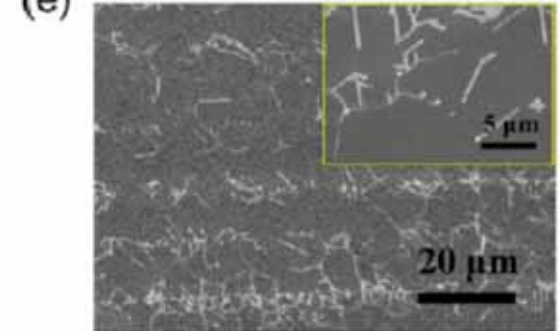
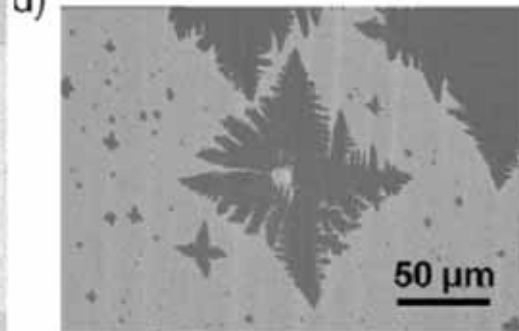
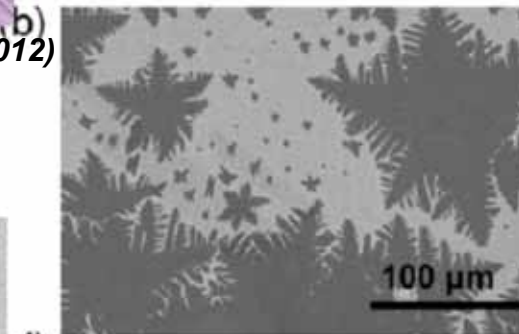


Yi Zhang et al., *Nano Lett.* 12, 2810 (2012).

APCVD: 300 sccm diluted (in Ar)  
CH<sub>4</sub> (8 ppm) and 10 sccm of H<sub>2</sub>

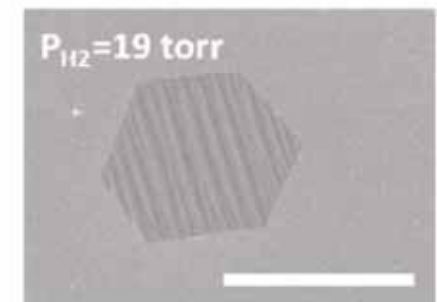
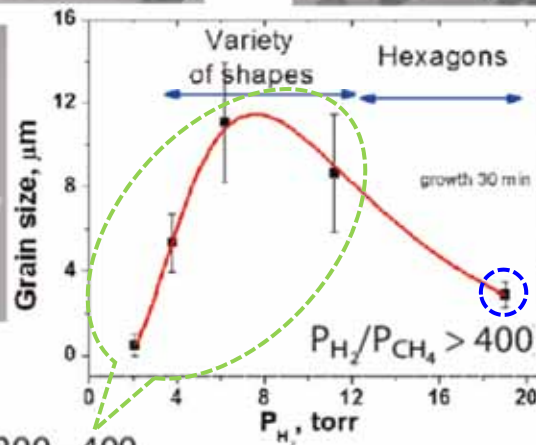
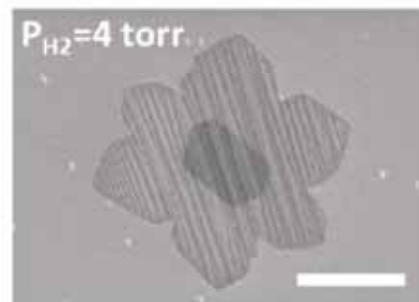
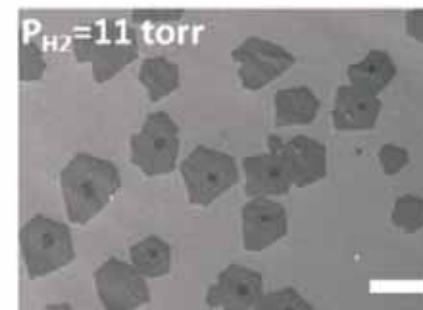
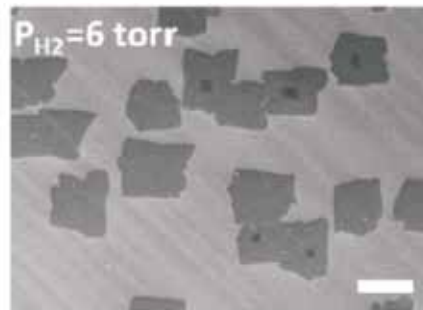
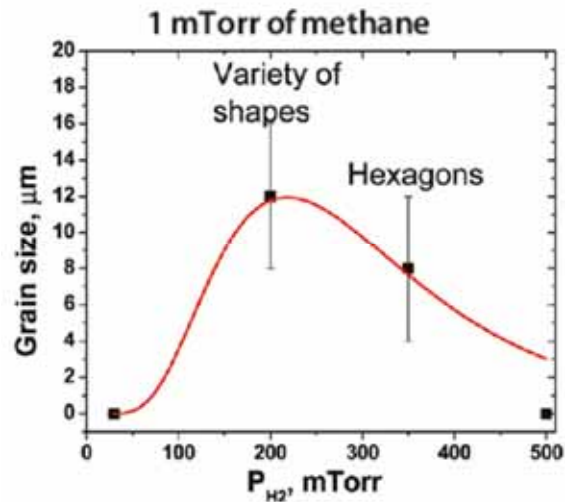


Q. Yu et al., *Nature Mater.* 10, 443 (2011).



# グラフェン成長形:水素の影響

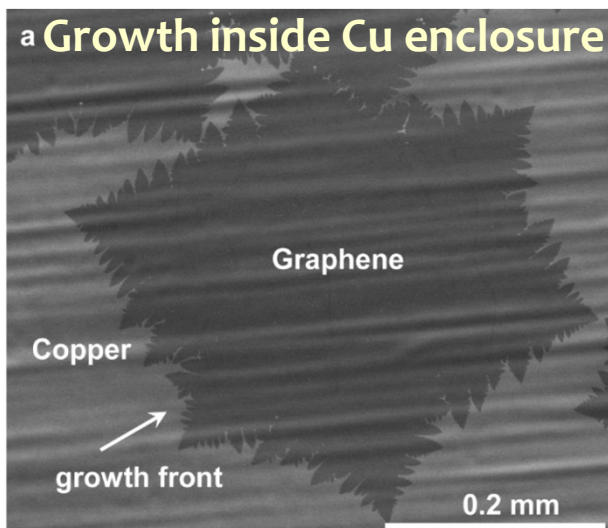
Thus we have shown that hydrogen plays a dual role in the process of graphene growth by CVD on copper foil with methane as a carbon source. It acts as a cocatalyst in formation of active surface bound carbon species ( $C_yH_x$ )<sub>s</sub> required for graphene growth and controls the grains shape and dimension by etching away the "weak" carbon-carbon bonds. Graphene



$P_{H_2}/P_{CH_4} = 200-400$

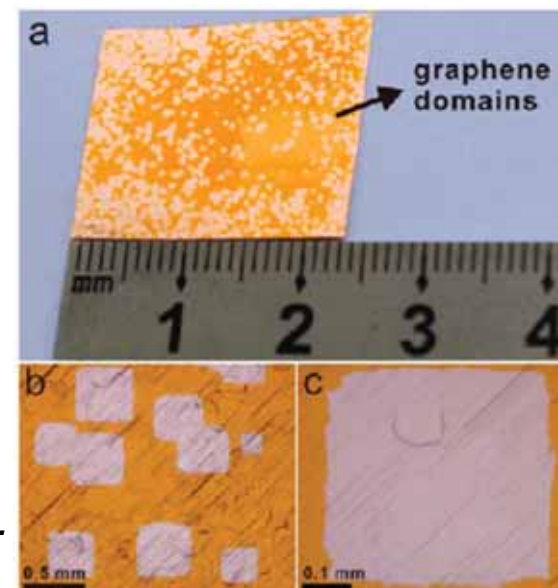
# 単結晶グラフェンCVD成長

## ✓多結晶Cu箔上の核形成制御

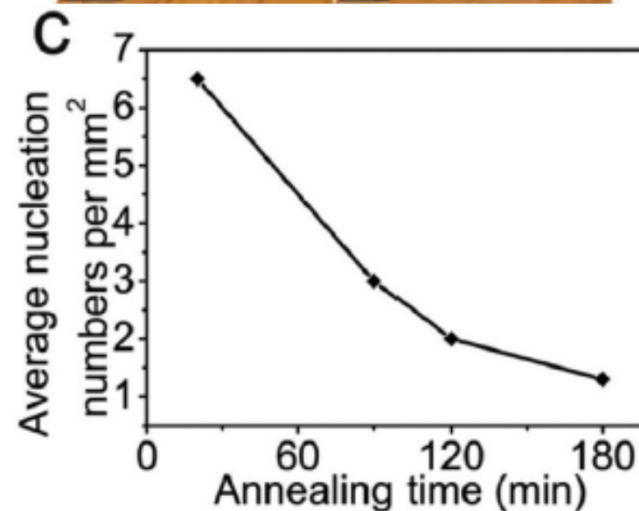
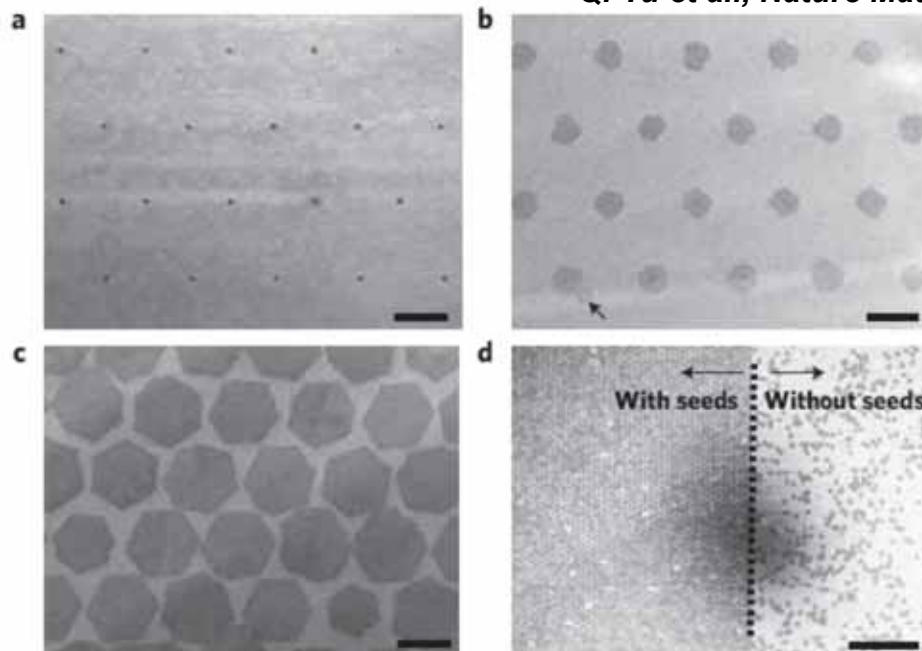


X. Li et al., *J. Am. Chem. Soc.* 131, 2816 (2011).

## 基板クリーニング + 低CH<sub>4</sub>圧成長



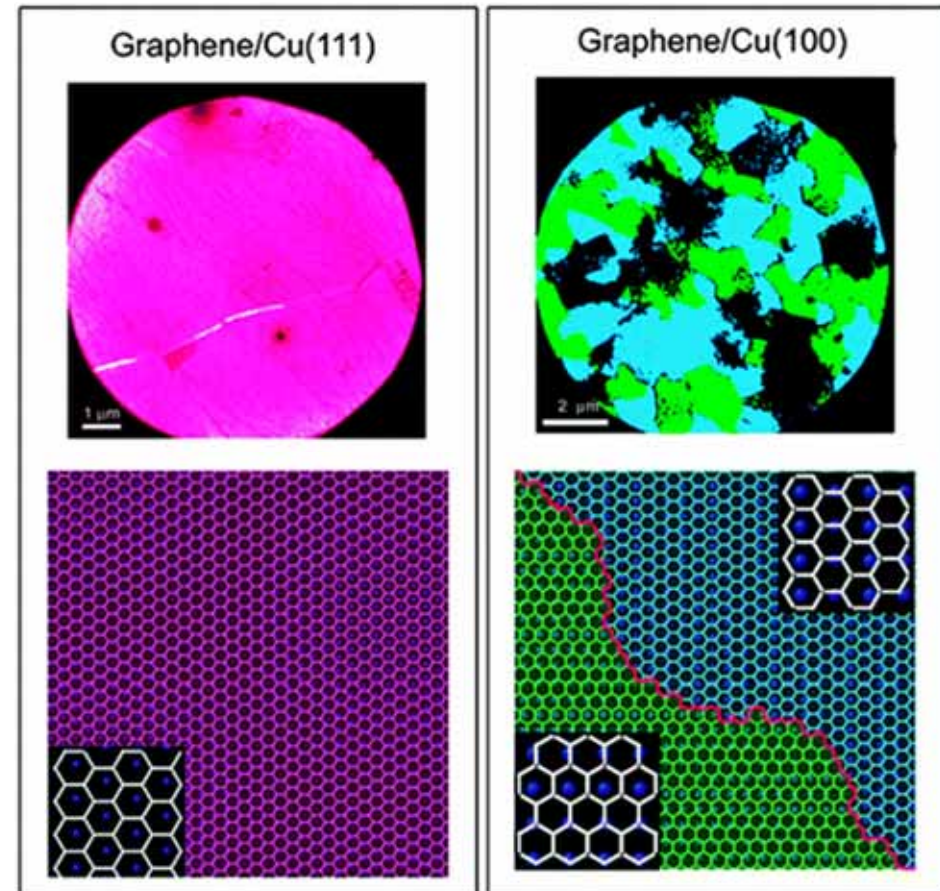
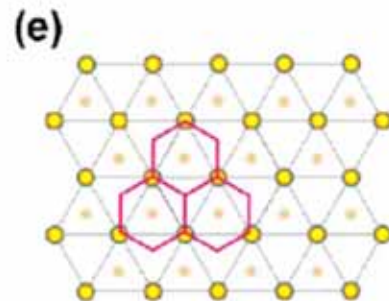
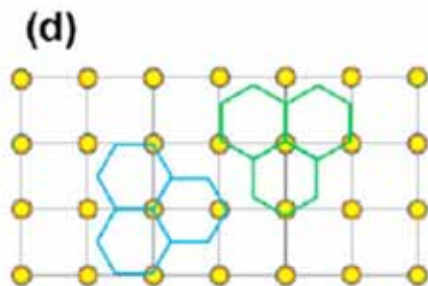
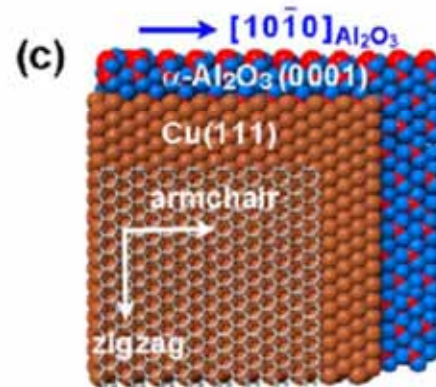
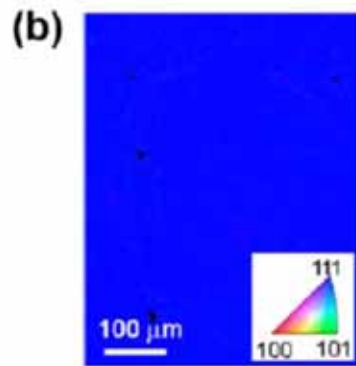
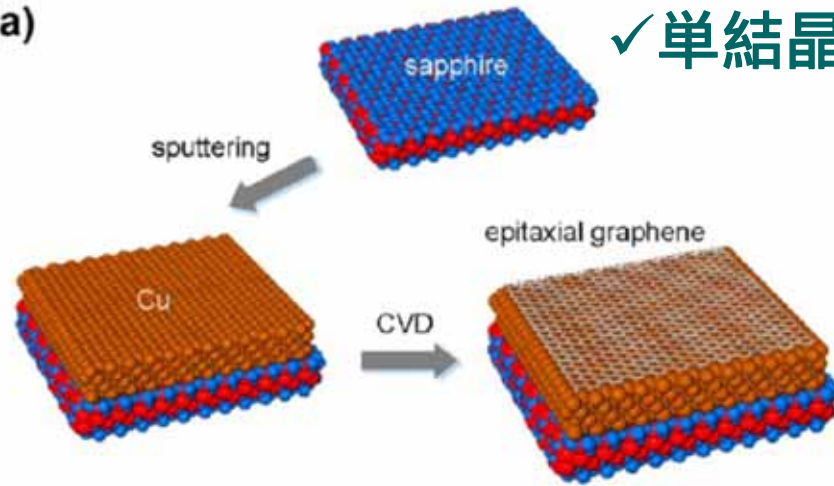
Q. Yu et al., *Nature Mater.* 10, 443 (2011).



H. Wang et al., *J. Am. Chem. Soc.* 134, 3627 (2012).

# 単結晶グラフェンCVD成長

(a) ✓ 単結晶薄膜上成長



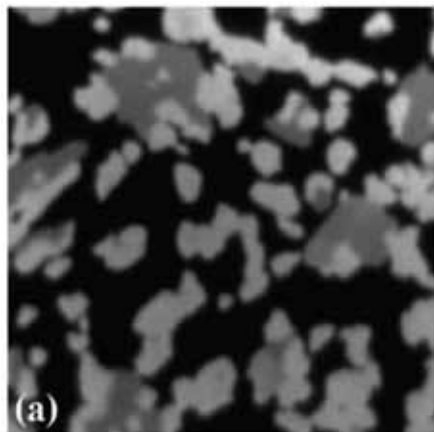
Y. Ogawa *et al.*, J. Phys. Chem. Lett. 3, 219 (2012).

# 単結晶グラフェンCVD成長

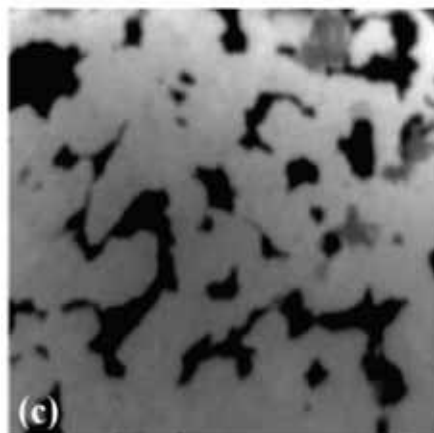
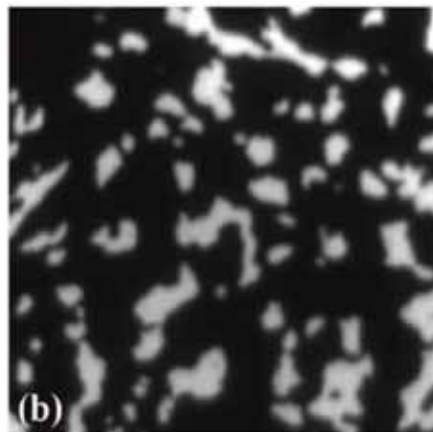
✓成長中断による単結晶化

Ir(111)

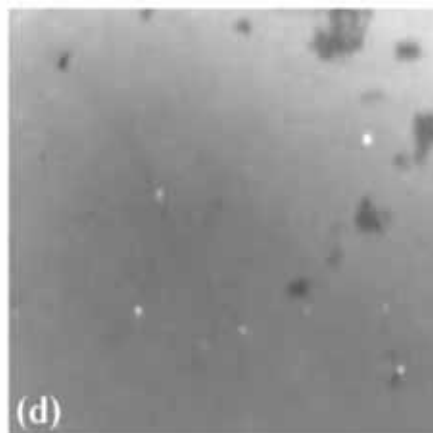
$t=344$  s



$t=1374$  s

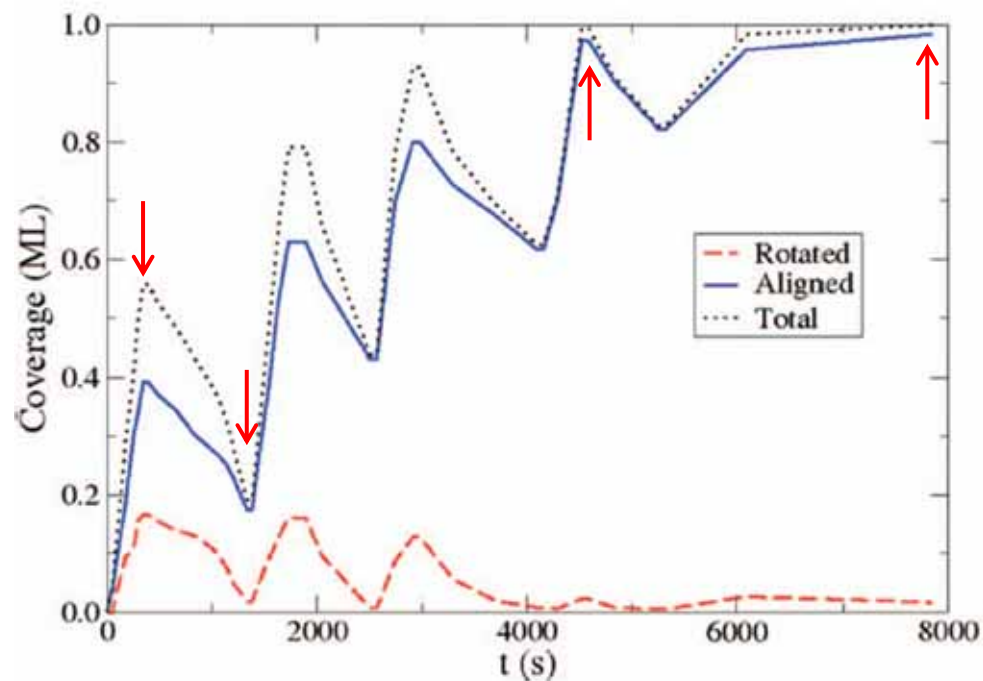


$t=4564$  s



$t=7865$  s

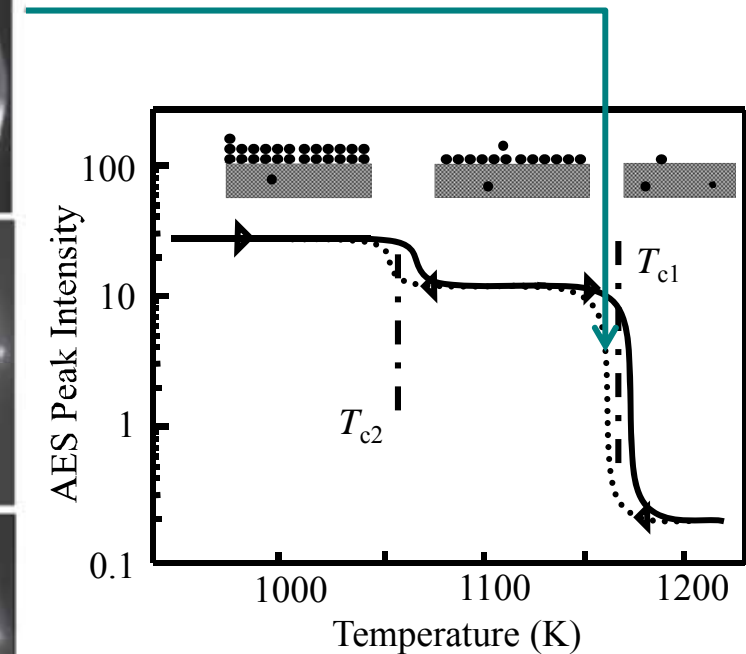
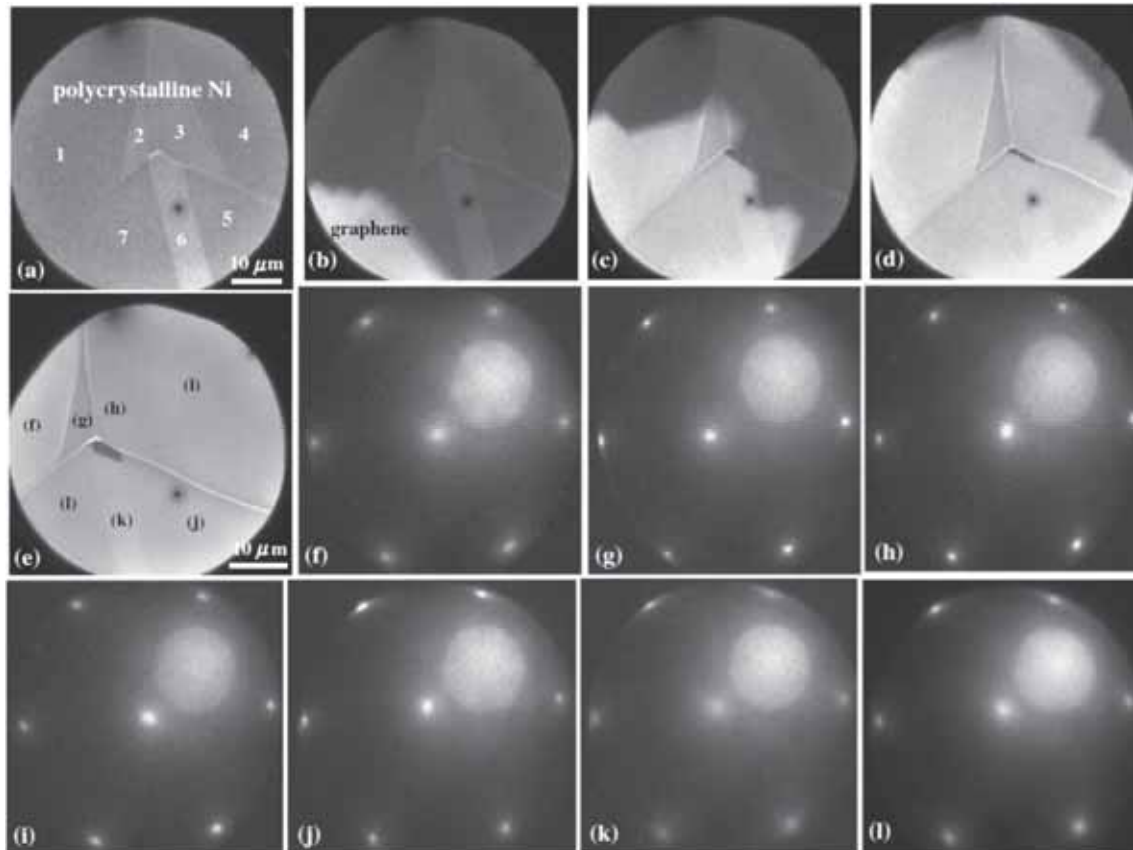
C<sub>2</sub>H<sub>4</sub> @ 1126 K



*R. van Gastel et al., APL 95, 121901 (2009).*

# 多結晶Ni箔上の単結晶グラフェンのカーペット状成長

## LEEDを用いたグラフェンの結晶方位評価



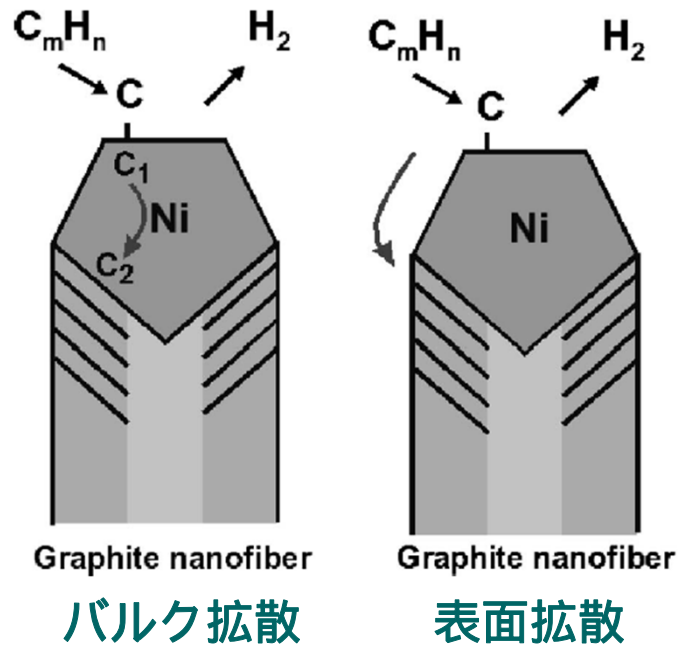
J. C. Shelton et al. Surf. Sci. 43, 493-520 (1974).

Single-domain graphene grows continuously in a carpet like manner, not only over steps on the substrate, but also over its grain boundaries.

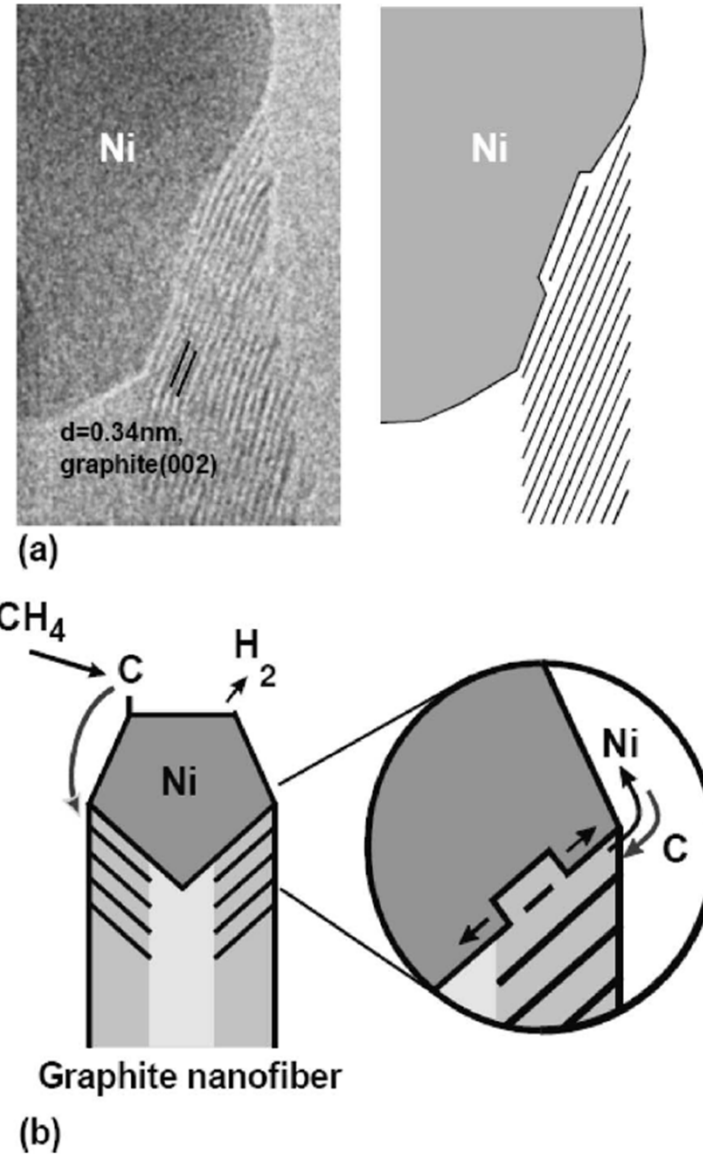
G. Odahara et al., Appl. Phys. Exp. 5, 035501 (2012).



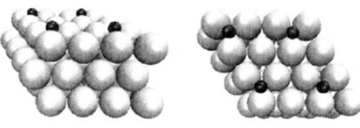
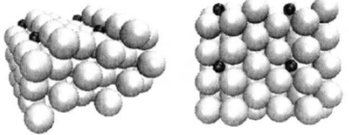
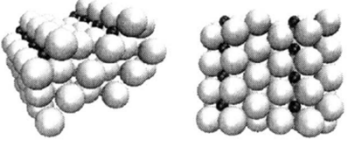
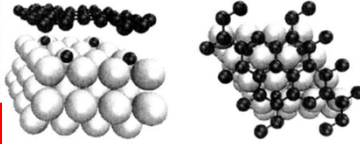
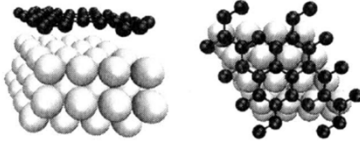
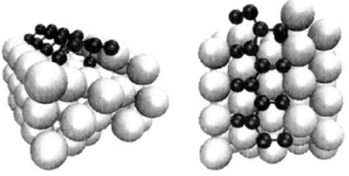

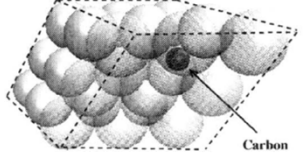
# Ni上カーボンナノファイバ成長



## TEM観察



# Ni上カーボンナノファイバ成長:第一原理計算

Structure	$E_{ads}$ (eV)	Structure	$E_{ads}$ (eV)
<p><b>Surface</b> 1</p>  <p>Ni(111) hcp site with <math>\theta_C = \frac{1}{4}</math> ML.</p>	0.55	<p><b>Step</b> 2</p>  <p>Ni(211) step-edge with <math>\theta_C^{st} = \frac{1}{2}</math>.</p>	-0.45
<p><b>Step</b> 3</p>  <p>Ni(211) step-edge site with <math>\theta_C^{st} = 1</math>.</p>	0.00	<p><b>Interface</b> 4</p>  <p>Interface hcp site on Ni(111) with <math>\theta_C = \frac{1}{4}</math> ML.</p>	0.92
<p><b>Graphene</b> 5</p>  <p>Infinite graphene layer.</p>	-0.75	<p><b>Interface</b> 6</p>  <p>Interface site at step-edge with <math>\theta_C^{st} = \frac{1}{2}</math>.</p>	0.20
<p><b>Subsurface</b> 7</p>  <p>Subsurface (octahedral site) with <math>\theta_C^{stab} = \frac{1}{27}</math>.</p>	0.21	<p><b>Bulk</b> 8</p>  <p>Bulk (octahedral site) with <math>\theta_C^{bnik} = \frac{1}{27}</math>.</p>	0.53

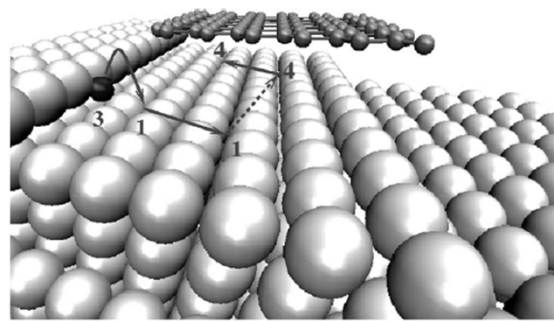
形成エネルギー

拡散障壁

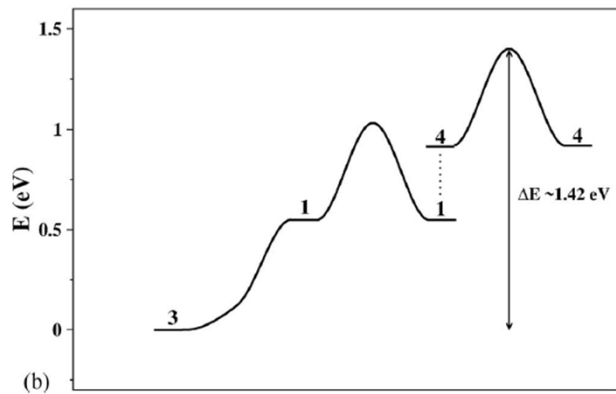
Diffusion Step	$E_{diff}$ (eV)
Clean surface (1) → clean surface (1)	0.50
Interface (4) → interface (4)	0.50
Step edge (3) → clean surface (1)	0.55
Clean surface (1) → subsurface (7)	1.00
Hcp step edge (1) → step edge (3)	0.75
Step edge (3) → subsurface (7)	0.75
Subsurface (7) → subsurface (7)	0.80
Subsurface (7) → interface (4)	1.34
Bulk (8) → bulk (8)	1.80

# Ni上カーボンナノファイバ成長:第一原理計算

Surface diffusion

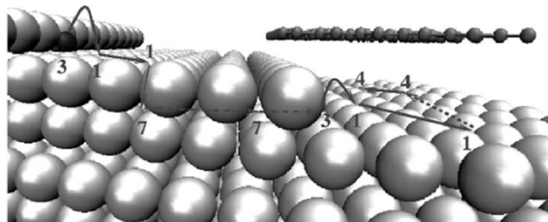


(a)

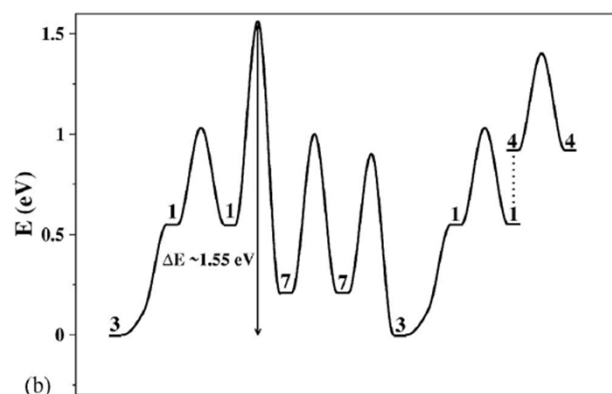


(b)

Subsurface diffusion

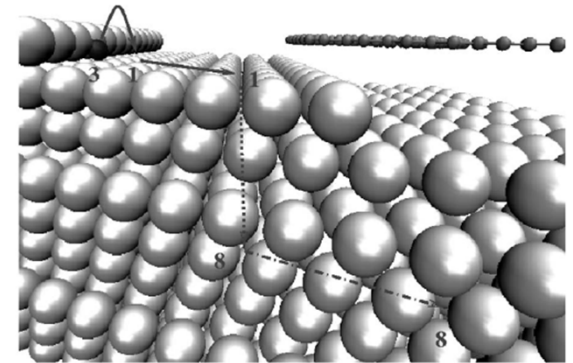


(a)

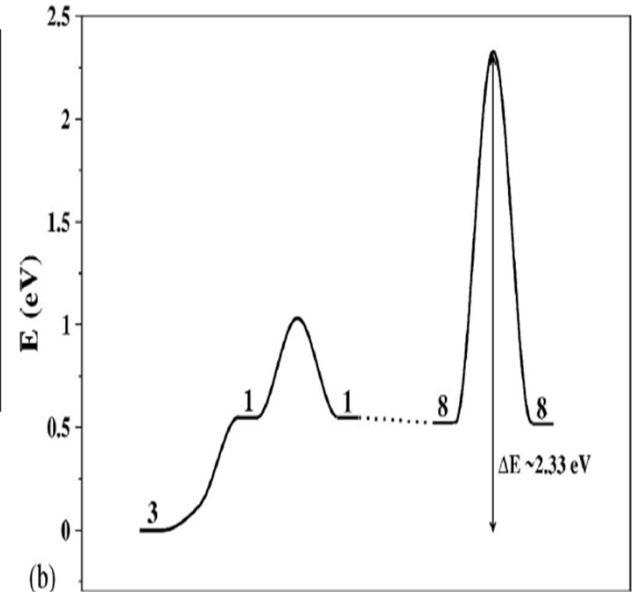


(b)

Bulk diffusion



(a)

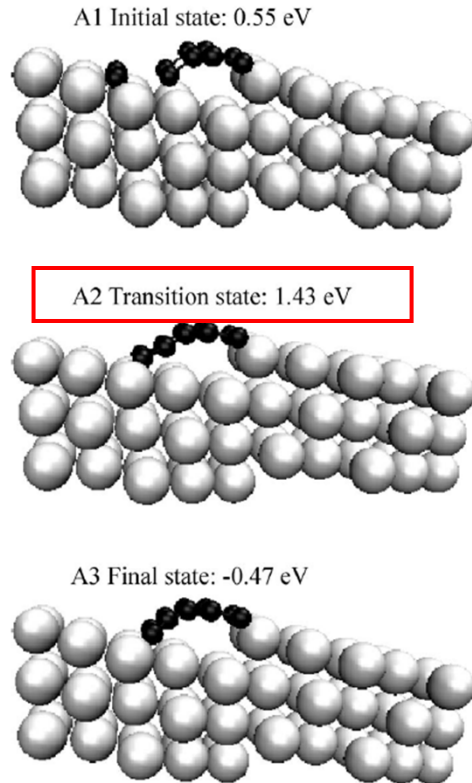


(b)

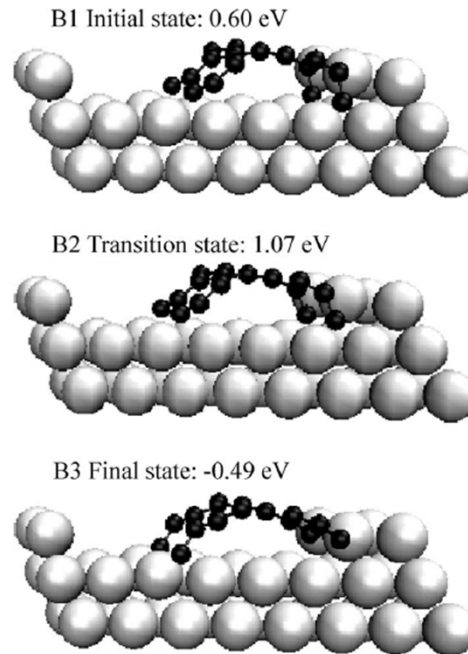
F. Abild-Pedersen et al., PRB 73, 115419(2006).

# Ni上カーボンナノファイバ成長:第一原理計算

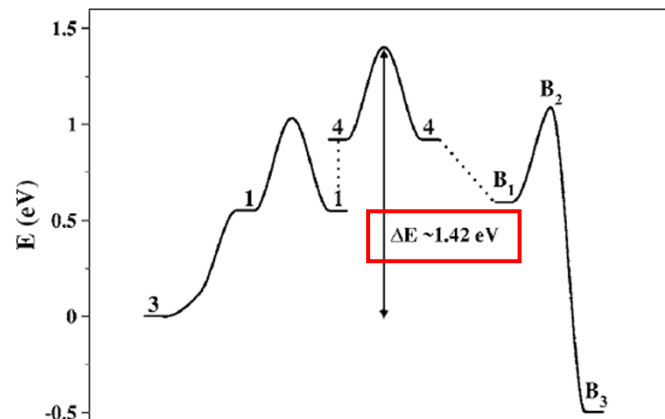
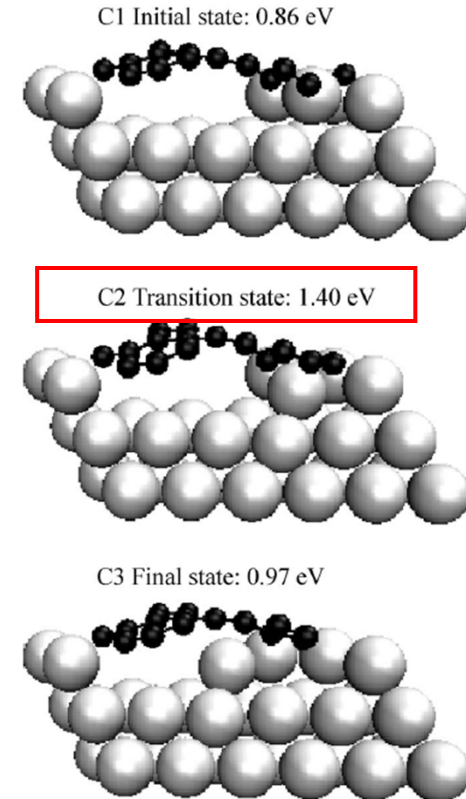
## Front growth



## Base growth

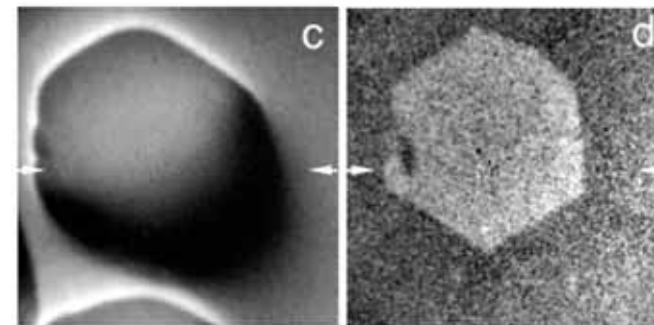
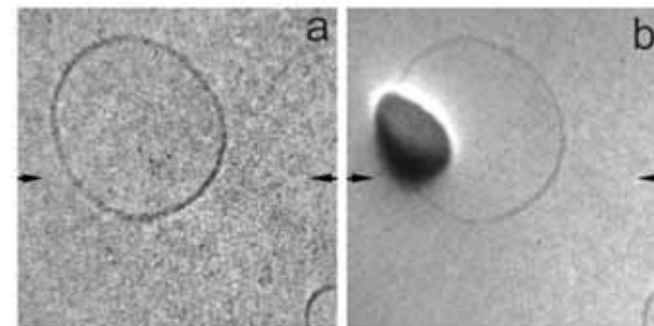
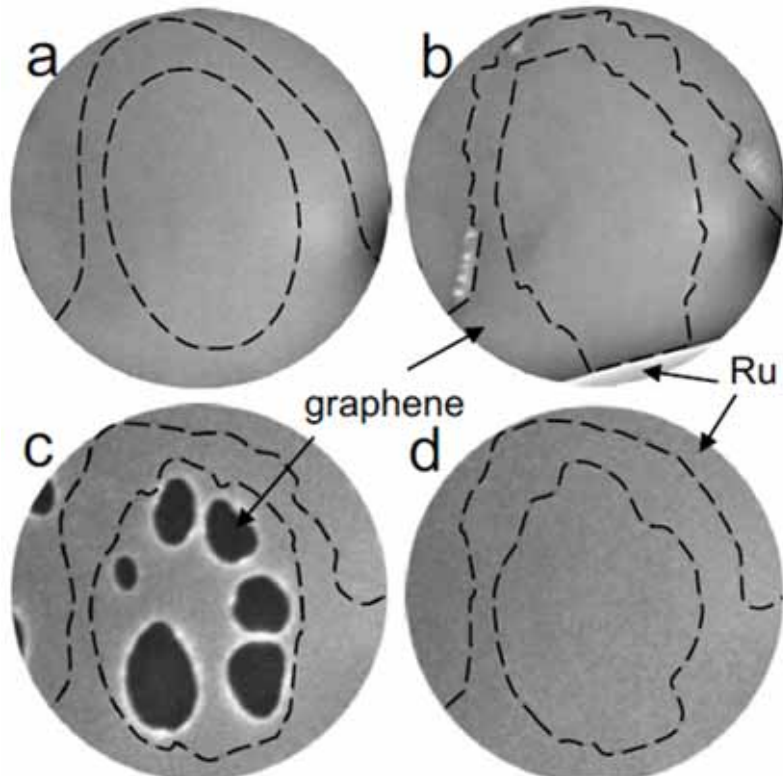
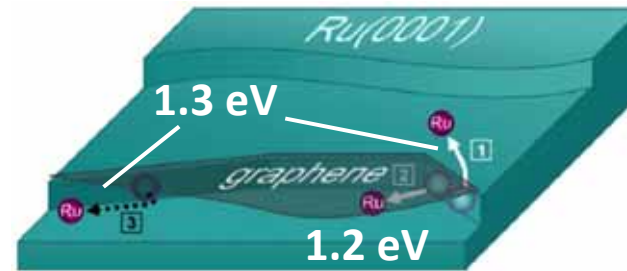
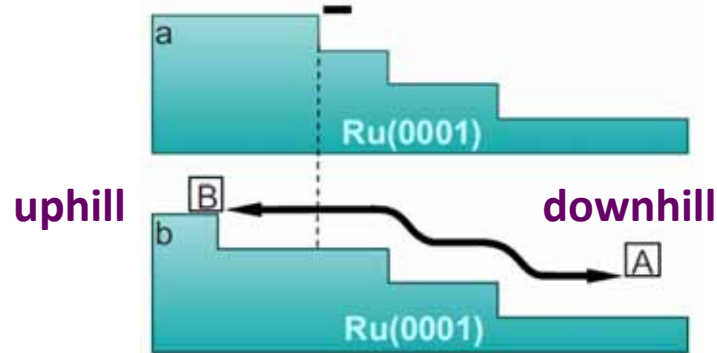


## Base growth by atom exchange



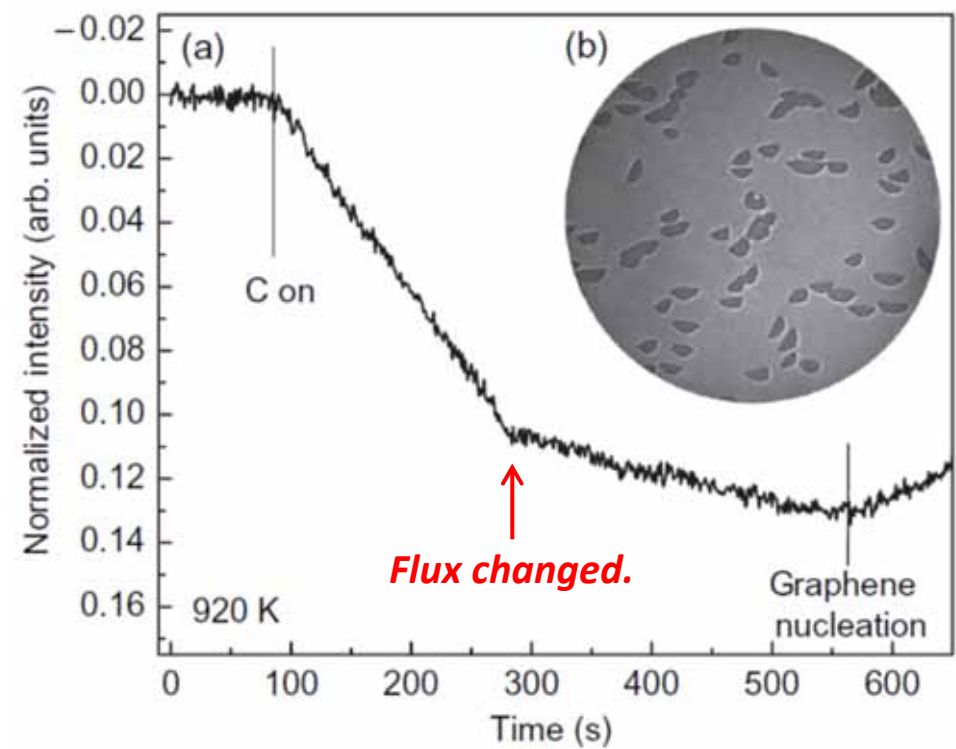
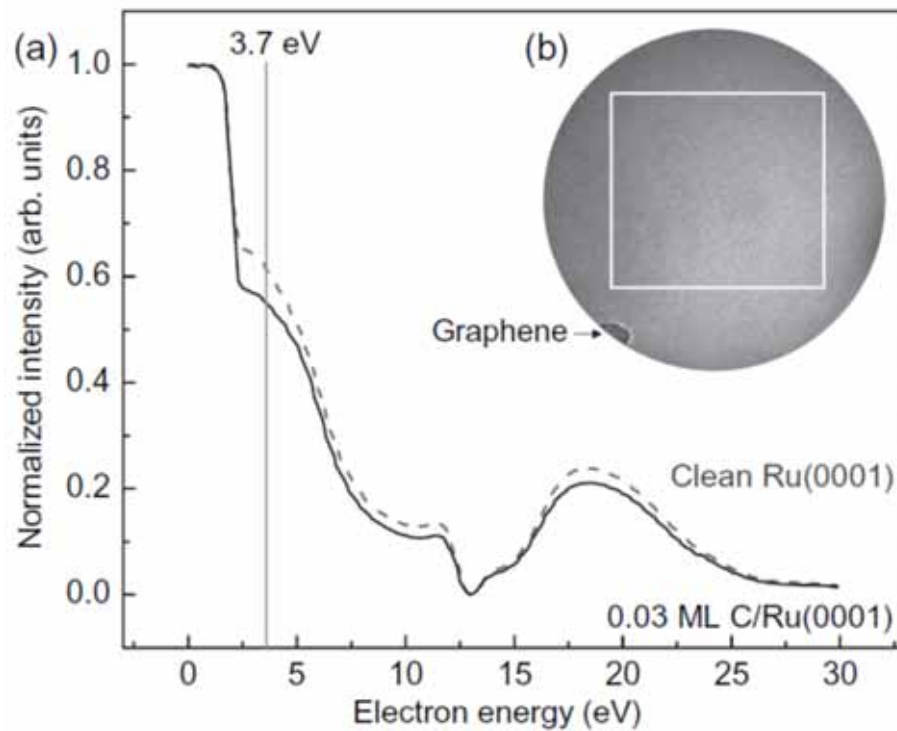
# グラフェン成長中のRu基板エッチング

Ru(111),  $\sim 1000$  K,  $C_2H_4 \sim 1 \times 10^{-8}$  Torr

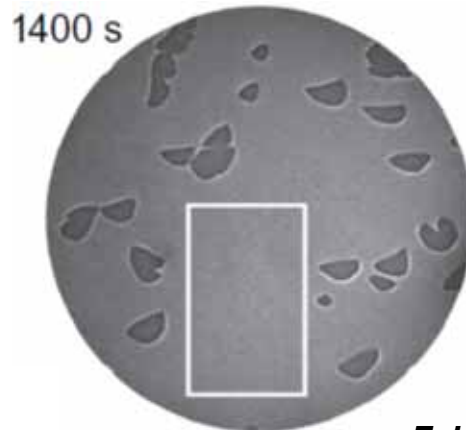
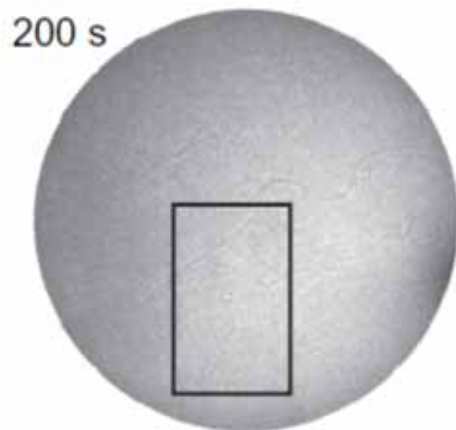
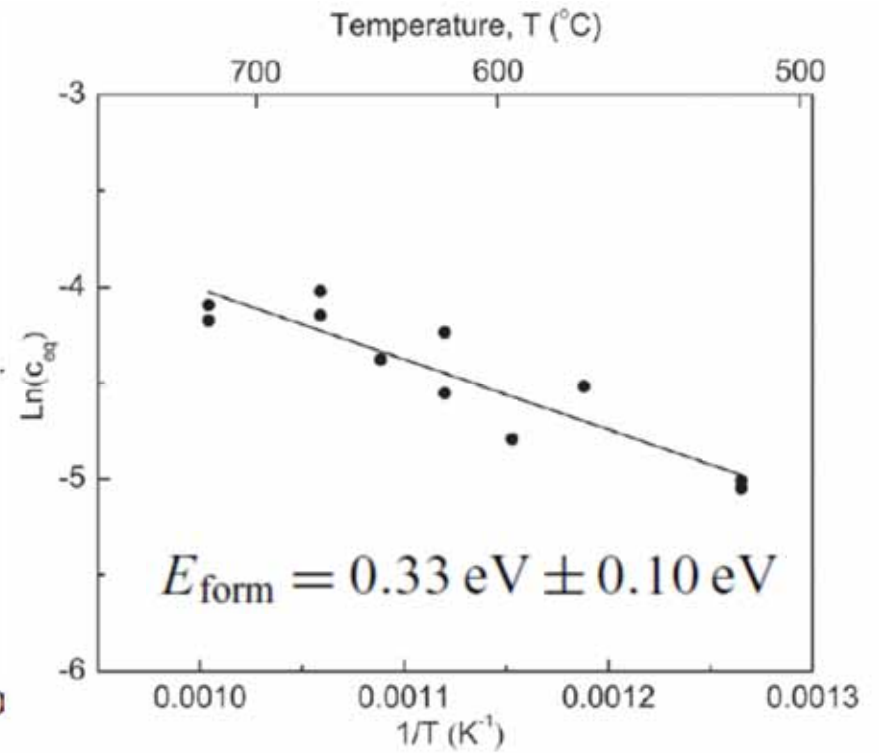
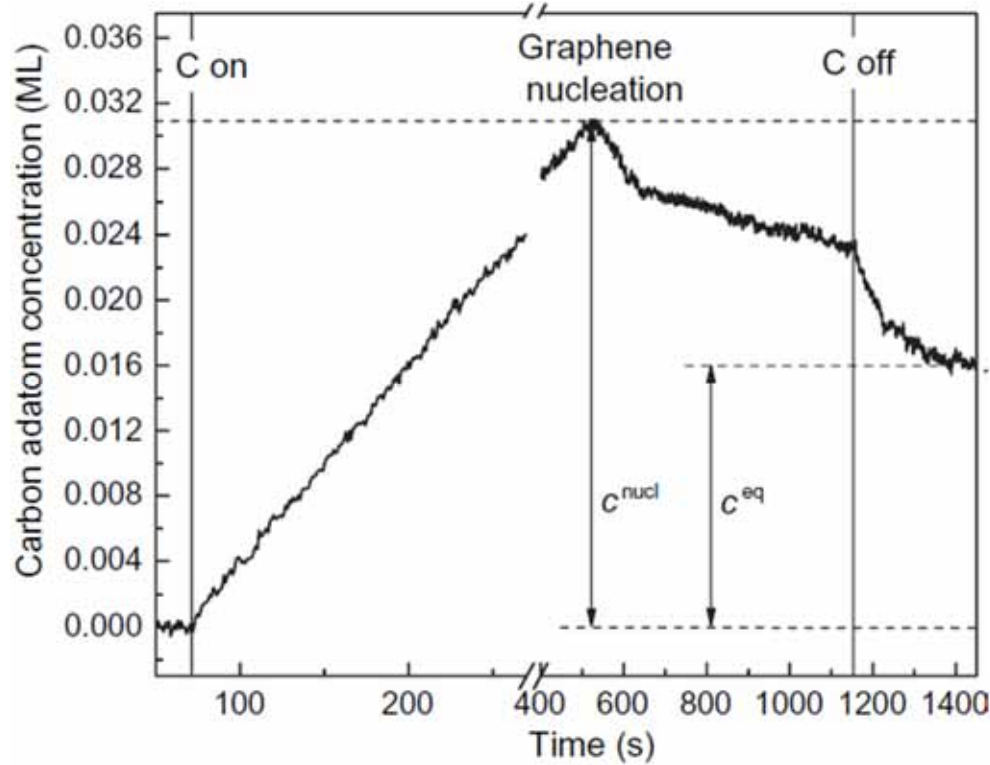


E. Starodub et al., PRB 80, 235422 (2009).

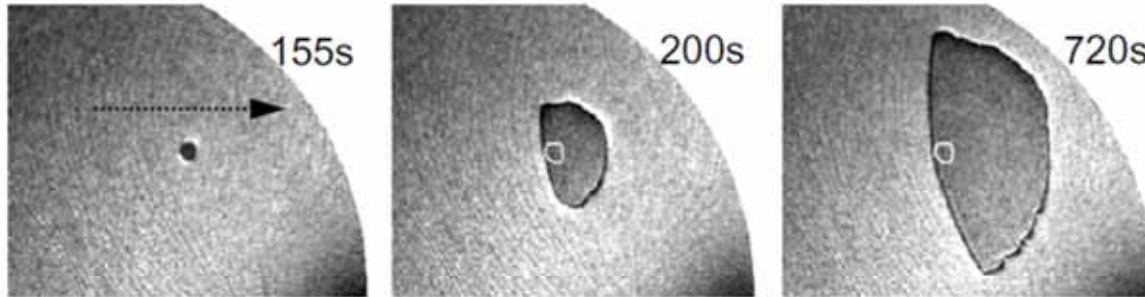
# グラフェンCVD成長



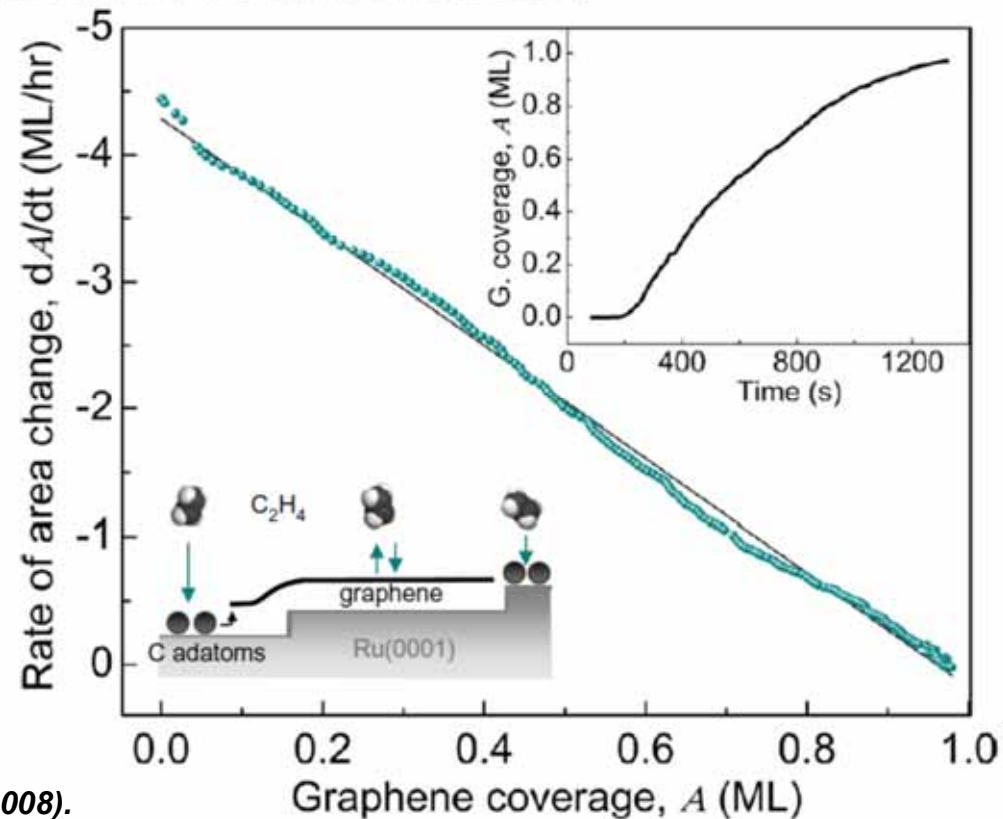
# グラフェンCVD成長



# グラフェンCVD成長

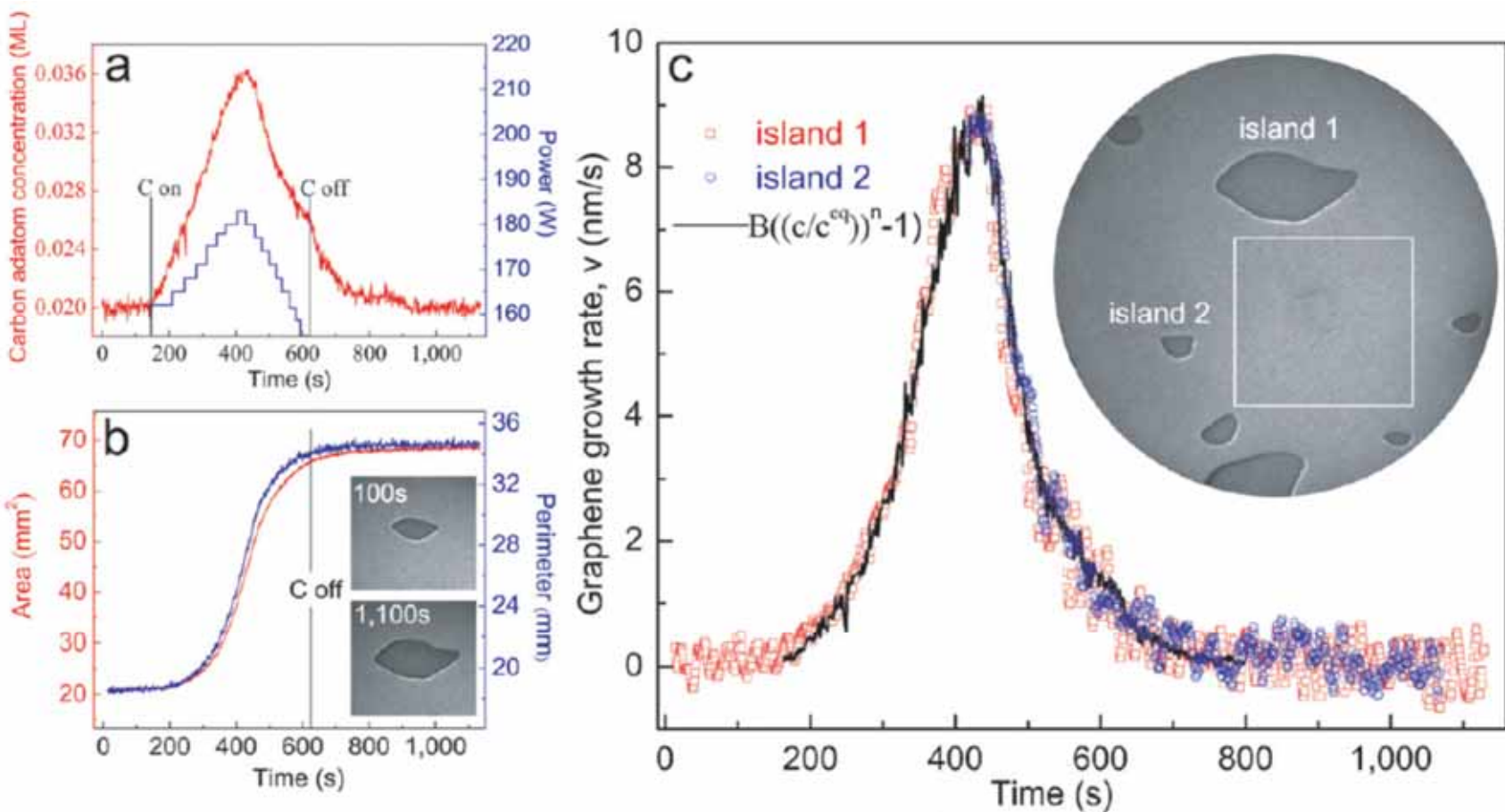


$$dA/dt \propto (1 - A)$$





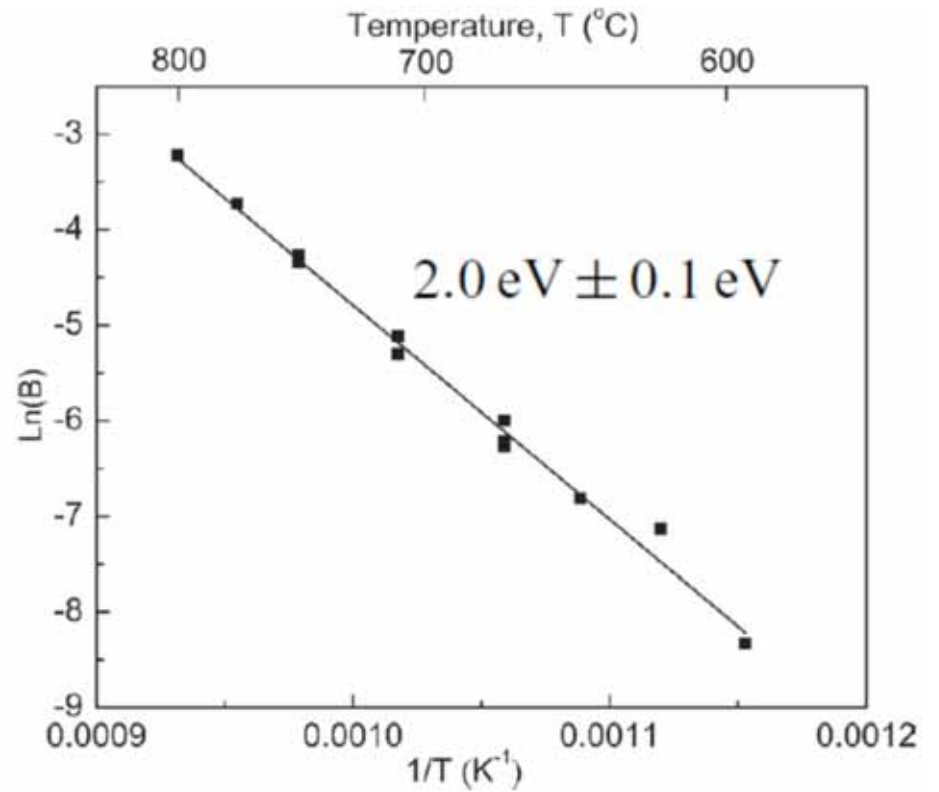
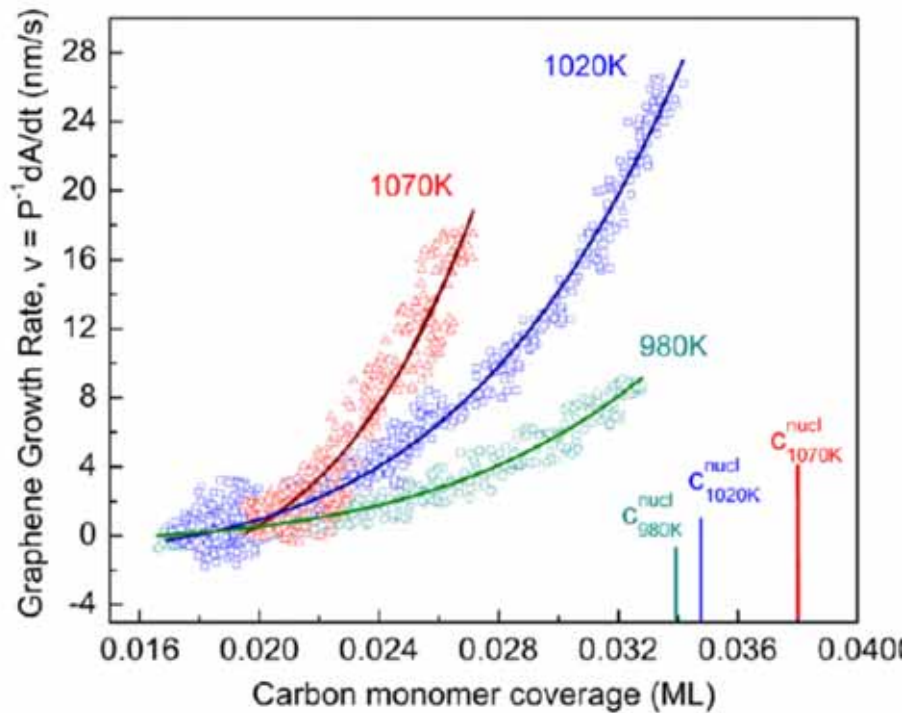
# グラフェンCVD成長



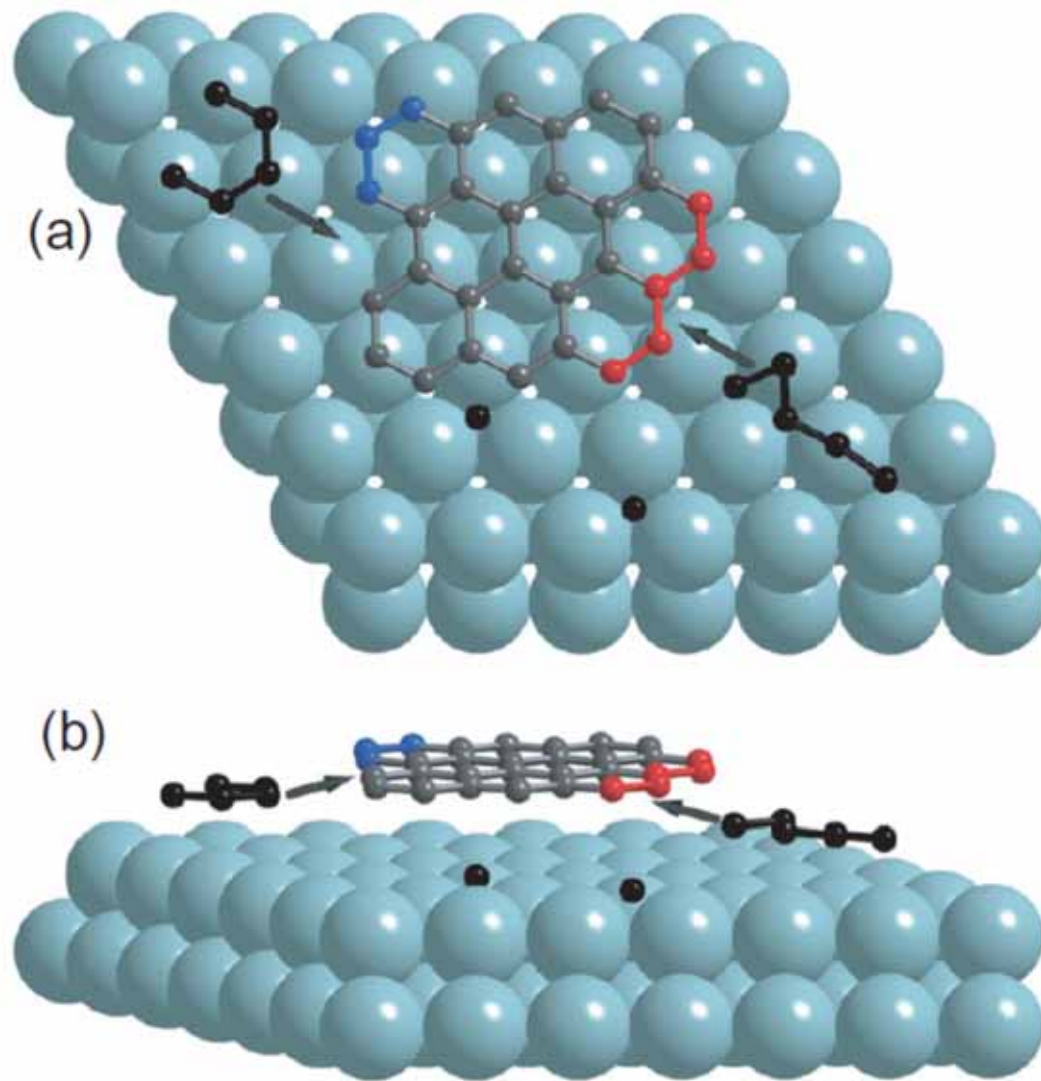
$$C_n = e^{n\mu/kT - E_n/kT} = \left(\frac{C}{C^{eq}}\right)^n e^{-E_n/kT}$$

$$v = m_n(C_n - C_n^{eq}) = m_n e^{-E_n/kT} \left[ \left(\frac{C}{C^{eq}}\right)^n - 1 \right] = B \left[ \left(\frac{C}{C^{eq}}\right)^n - 1 \right]$$

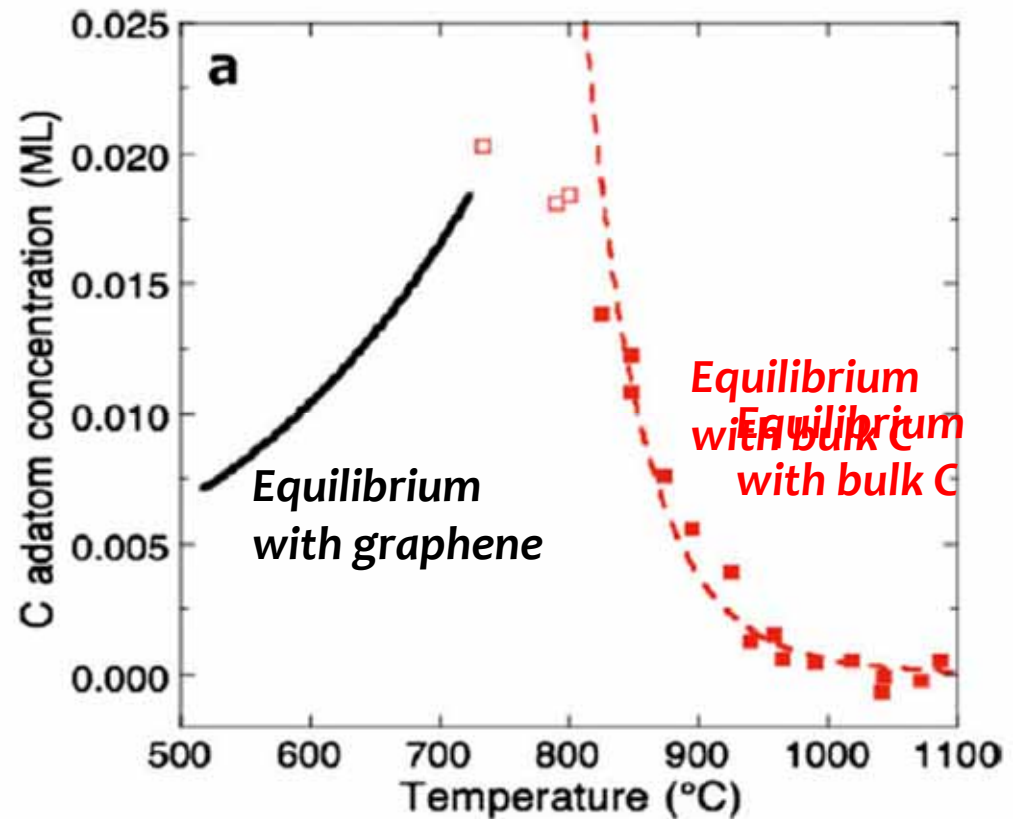
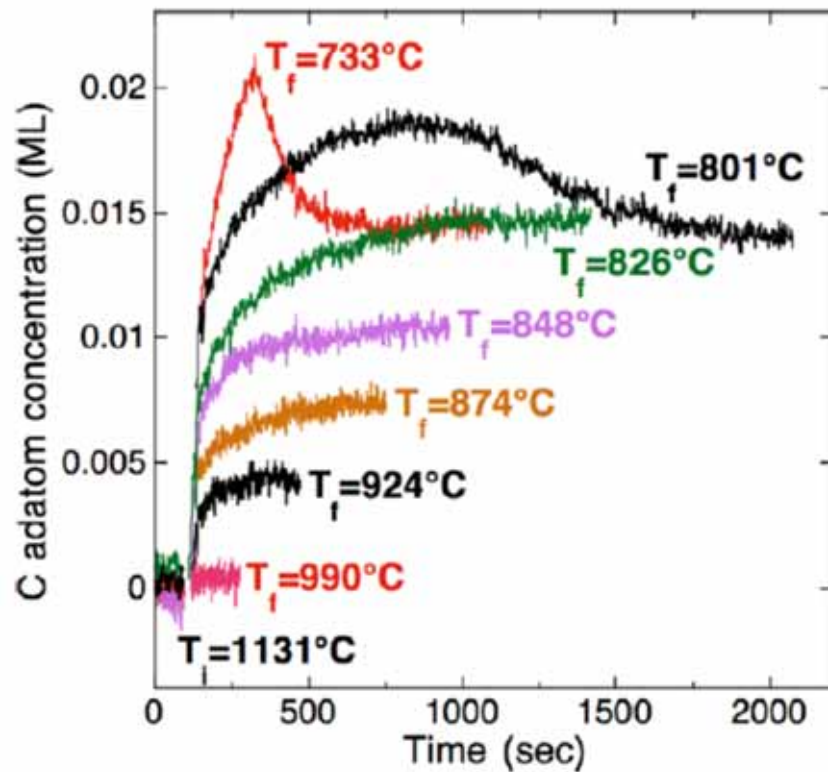
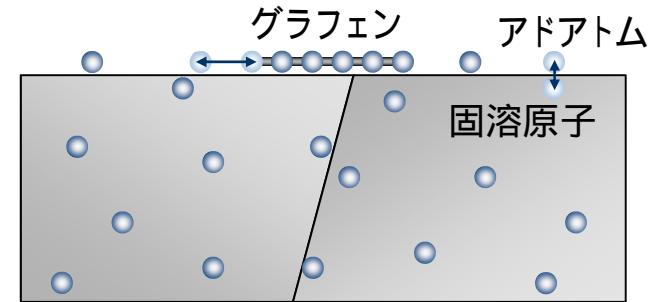
# グラフェンCVD成長



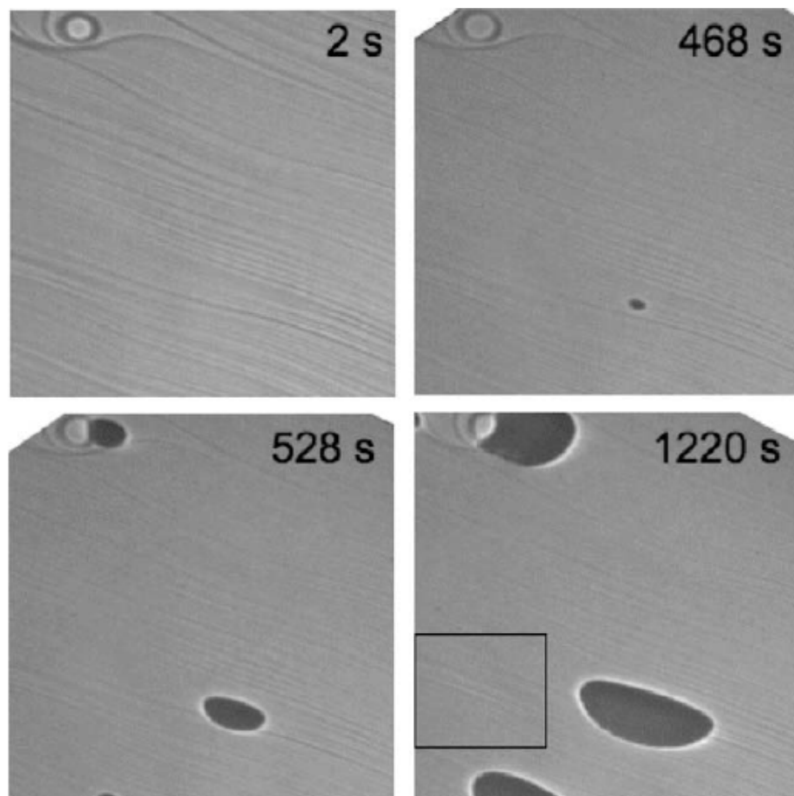
# グラフェンCVD成長



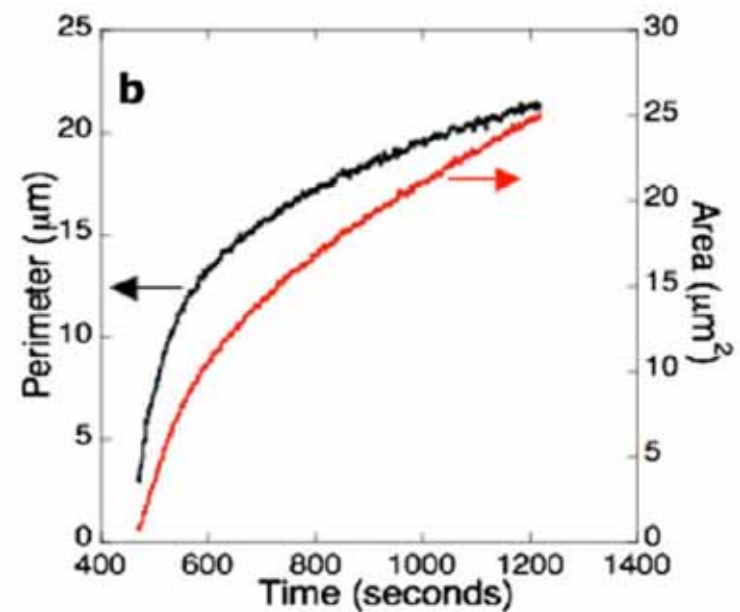
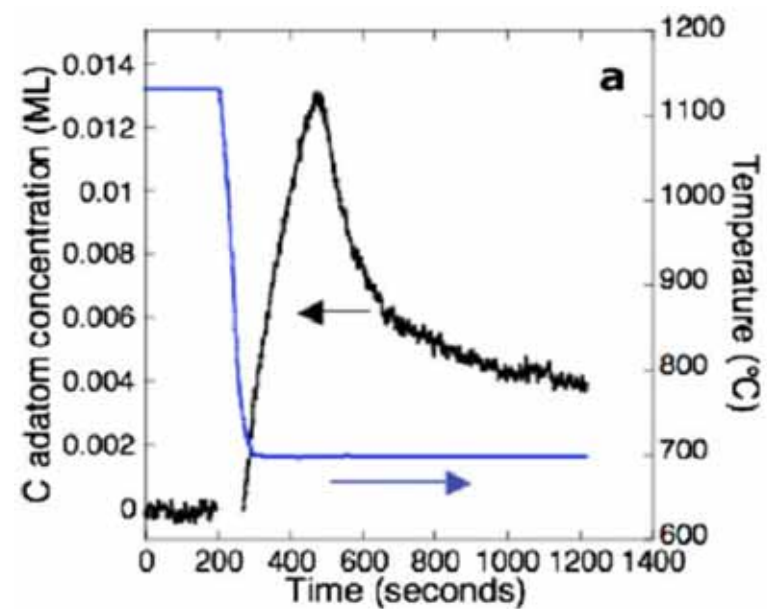
# グラフェン析出



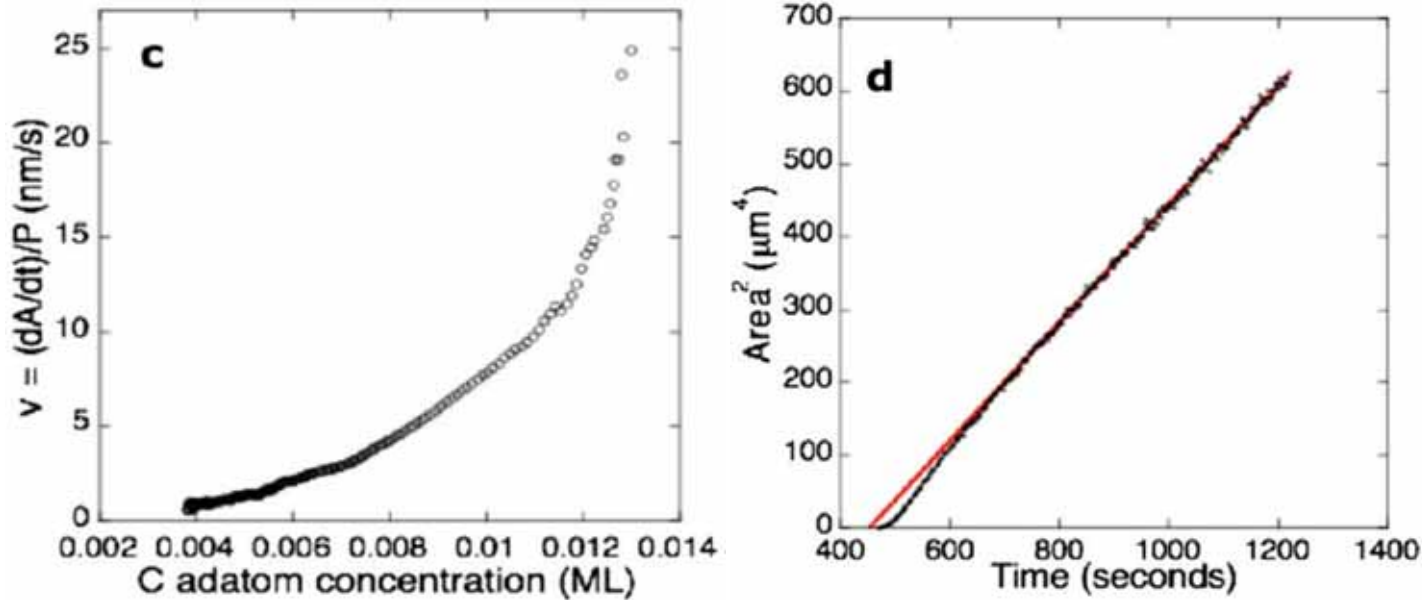
# 単結晶グラフェン析出



*K. F. McCarty et al., Carbon 47, 1806 (2009).*



# グラフフェン析出



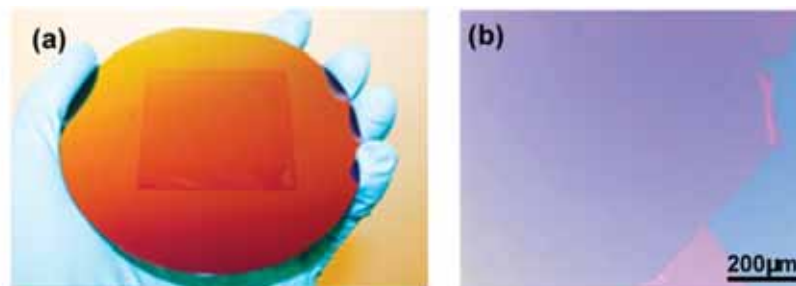
$$\frac{\partial c_b}{\partial t} = D_b \nabla^2 c_b \quad \begin{array}{c} c_b(z=0, t) = c_0 \\ c_b(z > 0, t=0) = c_1 \end{array} \rightarrow \frac{c_b(z, t) - c_0}{c_1 - c_0} = \operatorname{erf}\left(\frac{z}{2\sqrt{D_b t}}\right)$$

$$\begin{aligned} A(t) &= A_0 \int_0^t D_b \nabla c_b|_{z=0} dt = \frac{A_0 D_b (c_1 - c_0)}{\sqrt{\pi D_b}} \int_0^t \frac{dt}{\sqrt{t}} \\ &= \frac{2A_0 (c_1 - c_0) \sqrt{D_b t}}{\sqrt{\pi}} \end{aligned}$$

# 金属上2層グラフェン成長

## ✓ Growth control

*S. Lee et al., Nano Lett. 10, 4702 (2010).*

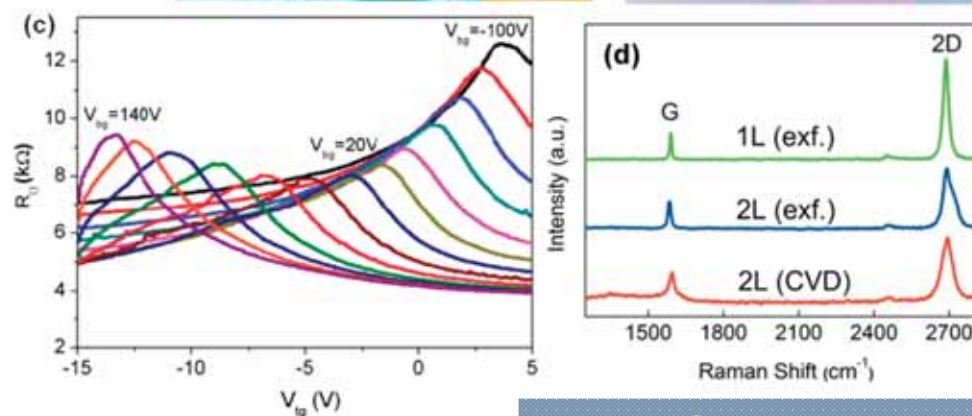
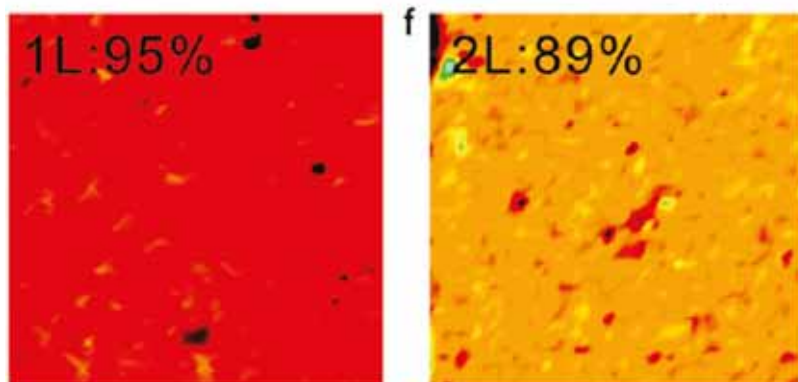
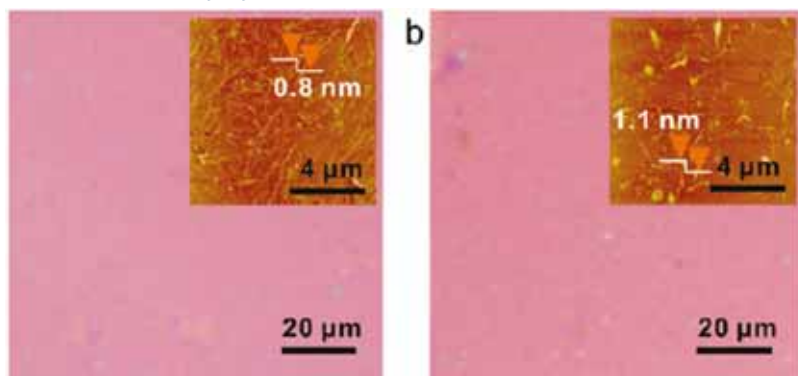


## ✓ Segregation control

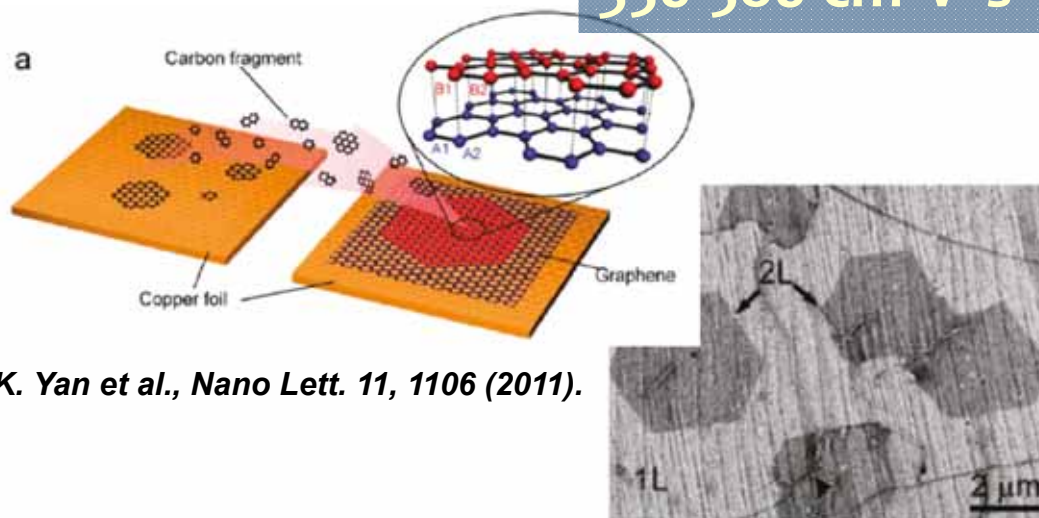
### Growth on CuNi alloy

Ni at. 5.5%

Ni at. 10.4%



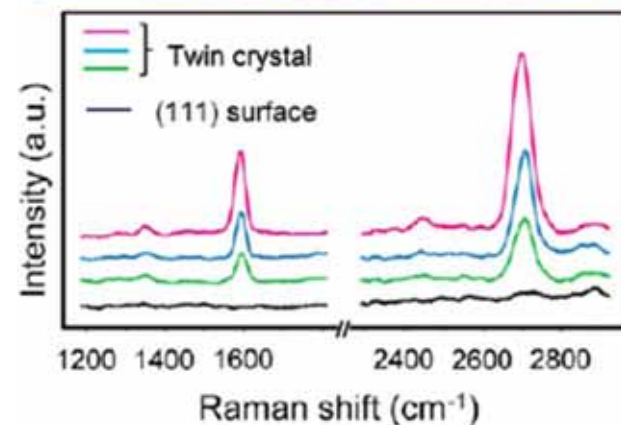
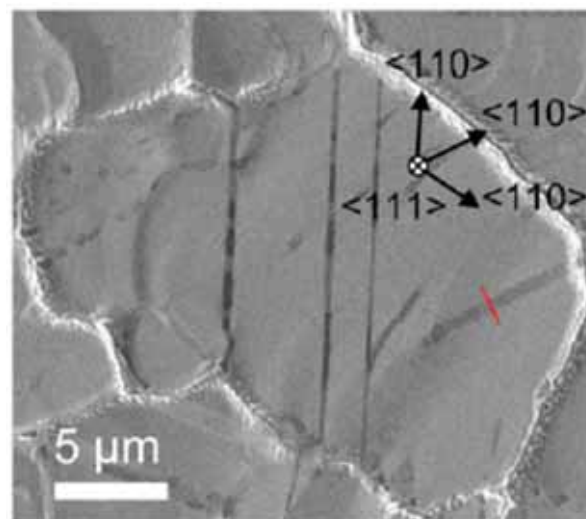
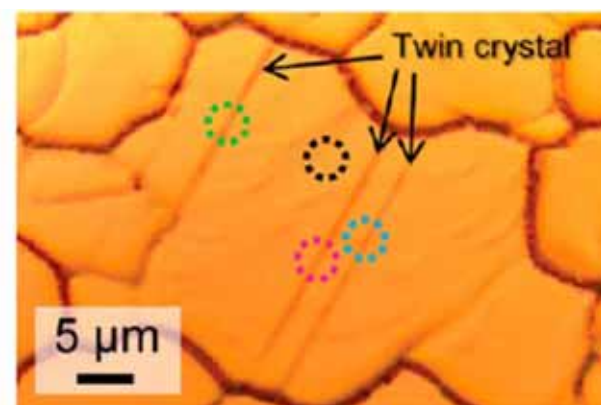
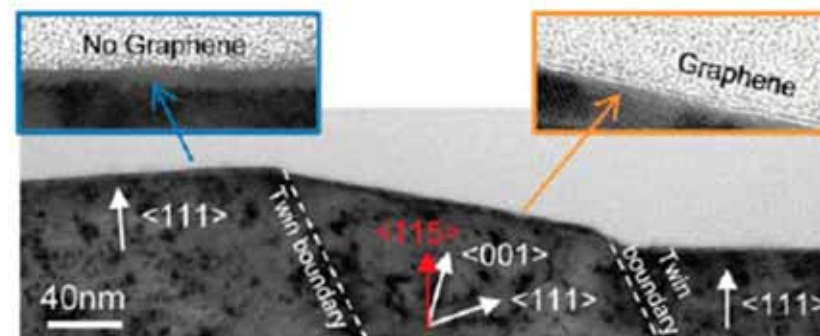
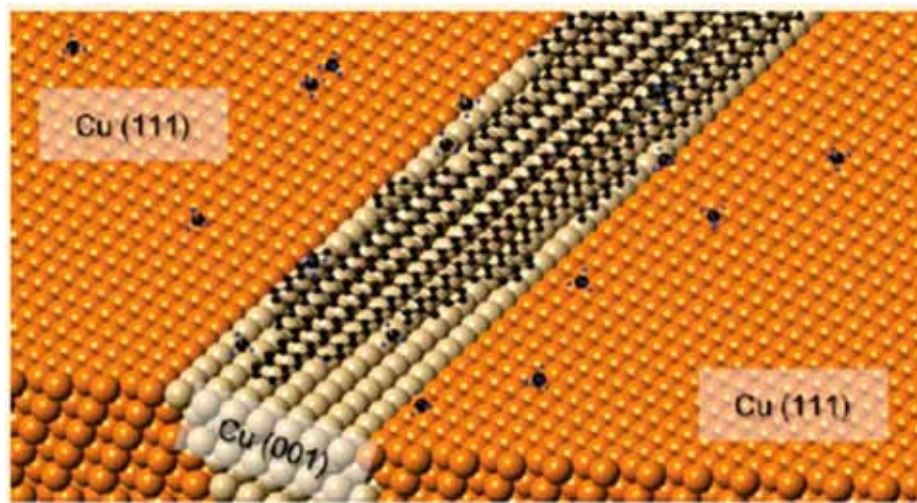
$350-580 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$



*K. Yan et al., Nano Lett. 11, 1106 (2011).*

*X. Liu et al., J. Phys. Chem. C 115, 11976 (2011).*

# 多結晶Cu薄膜上のグラフェンナノリボン成長



K. Hayashi et al., *J. Am. Chem. Soc.* 134, 12492 (2012).



# 多結晶Cu薄膜上のグラフェンナノリボン成長

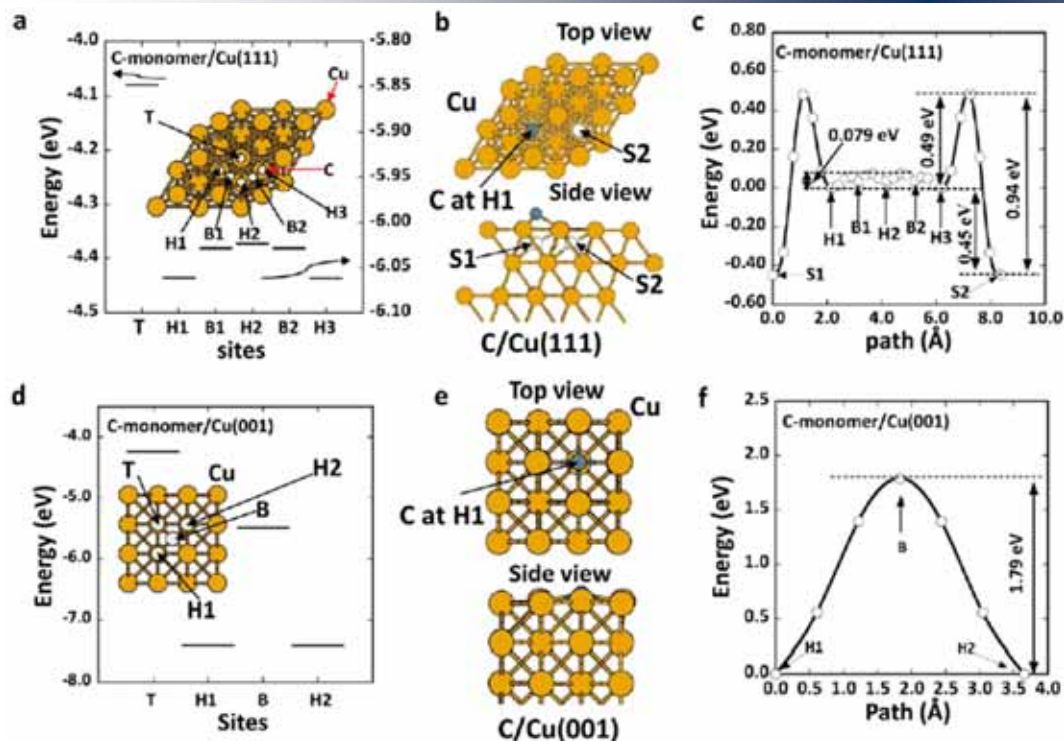
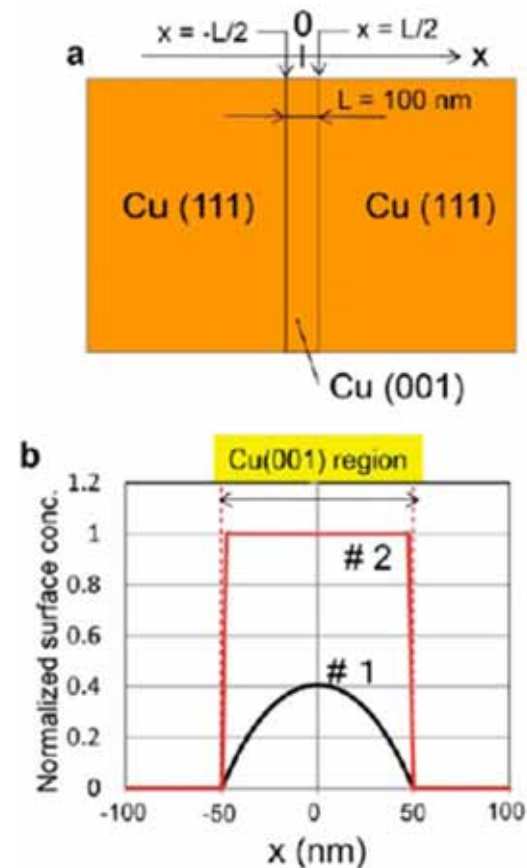


Table 1. Adsorption Energy (eV)

	carbon monomer	carbon dimer	C <sub>2</sub> H <sub>2</sub>
Cu (111)	-6.67	-5.84	-1.39
Cu (001)	-7.42	-5.93	-1.53

Table 2. Diffusion Barrier (eV)

	carbon monomer	carbon dimer	C <sub>2</sub> H <sub>2</sub>
Cu (111)	0.94	0.48	0.37
Cu (001)	1.79	0.86	0.76



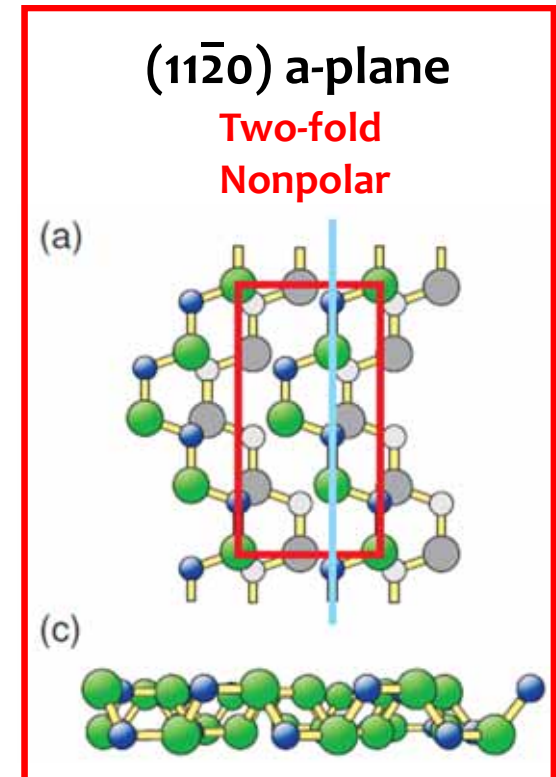
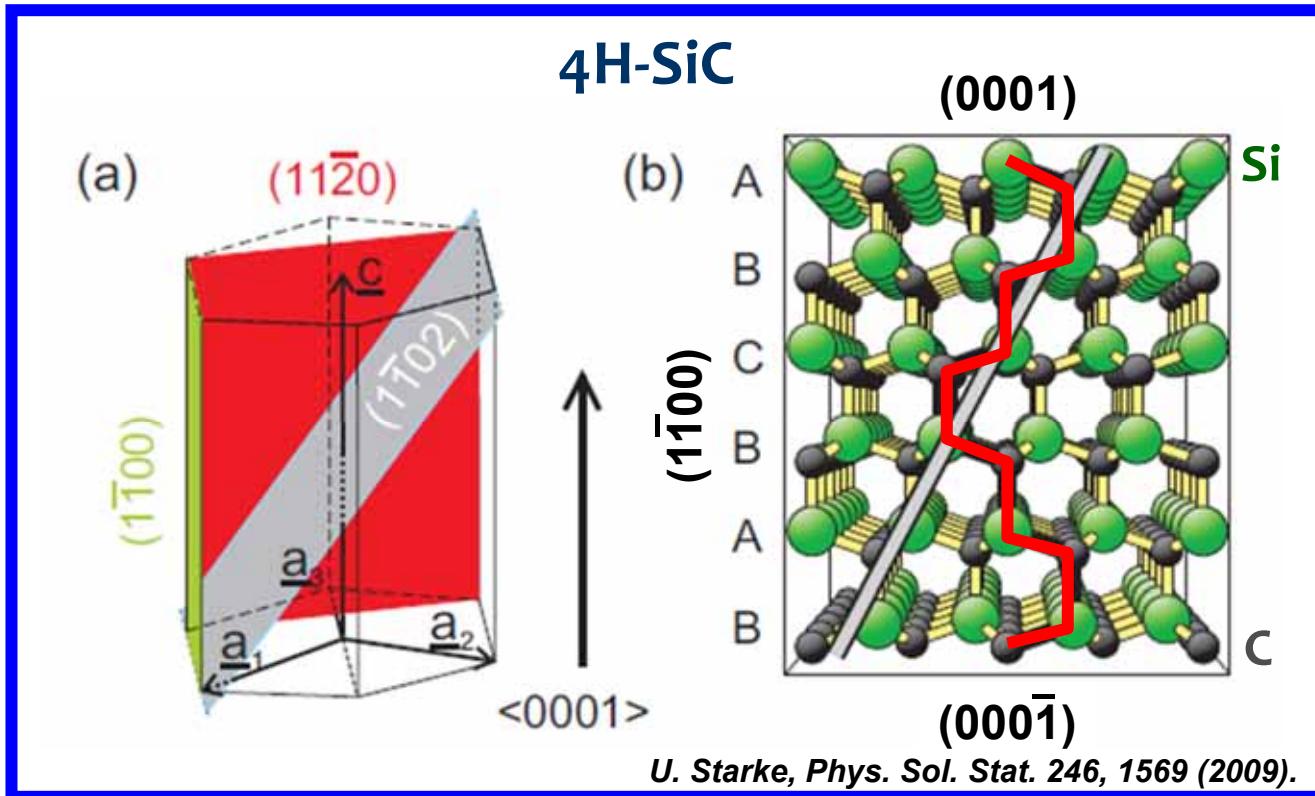
molecules on the surface normalized by  $c_{001}$ : #1:  $E_{diff, 001} = 0.86$ ,  $E_{diff, 111} = 0.48$  eV ( $E_{diff}$  values for carbon dimers were used),  $E_{ads, 001} = -1.8$ , and  $E_{ads, 111} = -1.0$  eV; #2:  $E_{diff, 001} = 1.79$ ,  $E_{diff, 111} = 0.94$  eV ( $E_{diff}$  values for carbon monomers were used),  $E_{ads, 001} = -1.8$ , and  $E_{ads, 111} =$

K. Hayashi et al., *J. Am. Chem. Soc.* 134, 12492 (2012).

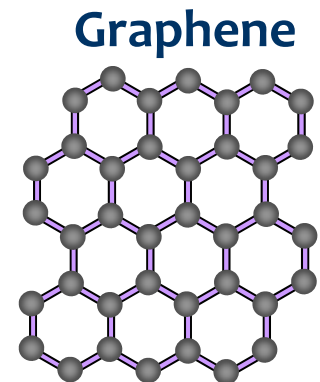
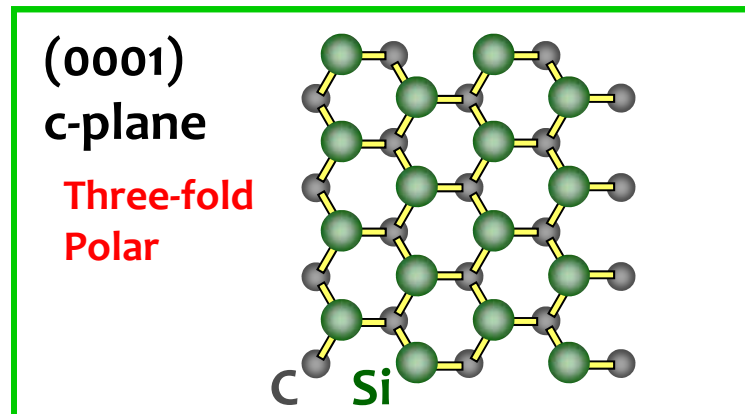
# 内容

1. グラフェンとは
2. グラフェン評価法
3. グラフェン成長法
  - 3-1 化学気相成長法
  - 3-2 析出法
  - 3-3 SiC熱分解法

# SiC結晶



1. Symmetry
2. Polarity

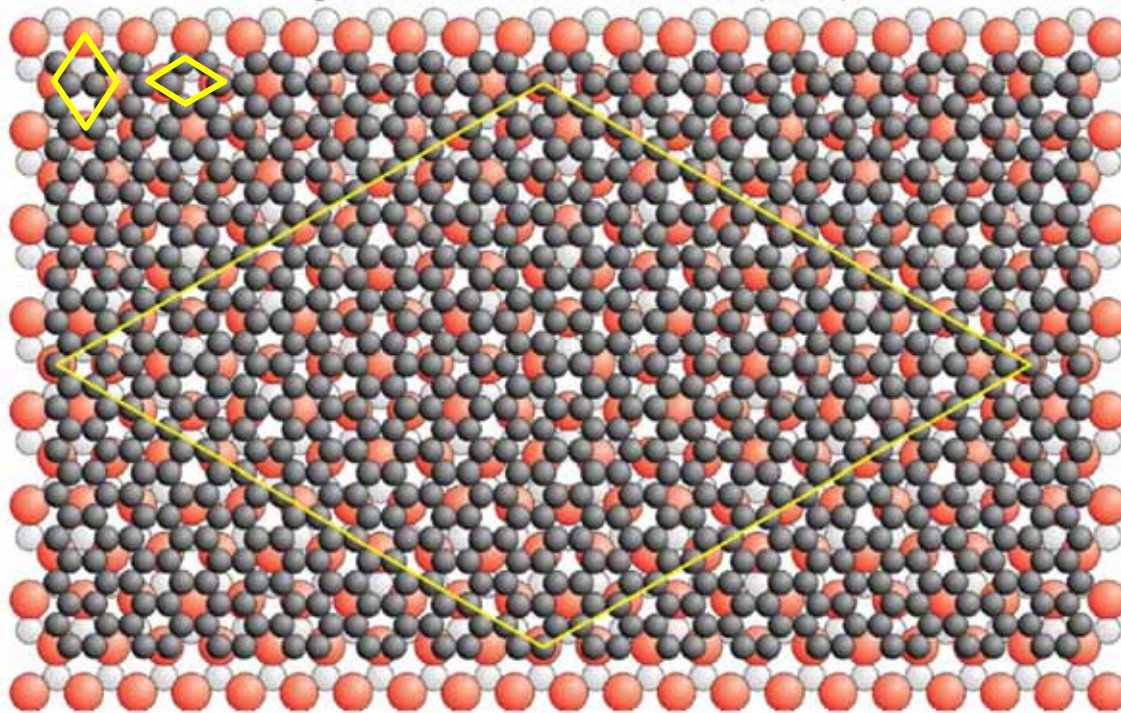


# Si面上グラフェン

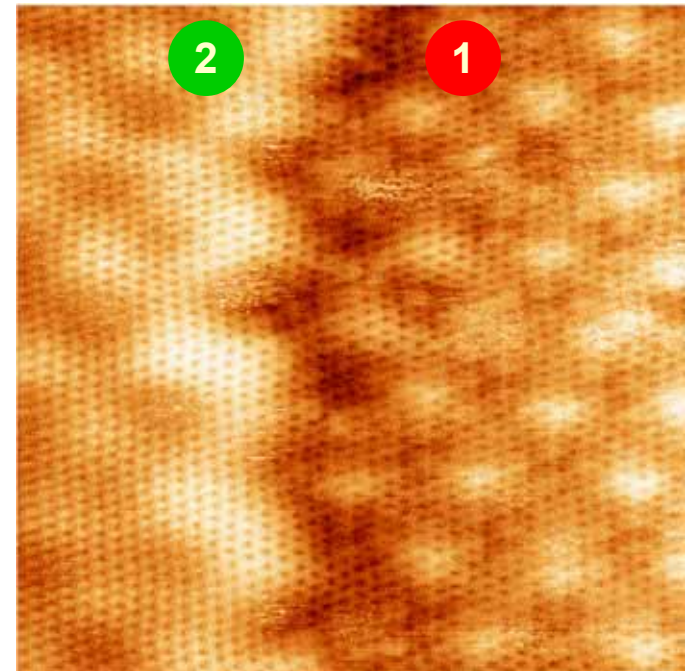
$\text{SiC}-6\sqrt{3}\times 6\sqrt{3} = 3.1936 \text{ nm}$

$\text{Graphene}-13\times 13 = 3.1993 \text{ nm}$

Graphene on bulk-truncated SiC(0001)



*K. V. Emtsev et al., Phys. Rev. B 77, 155303 (2008).*

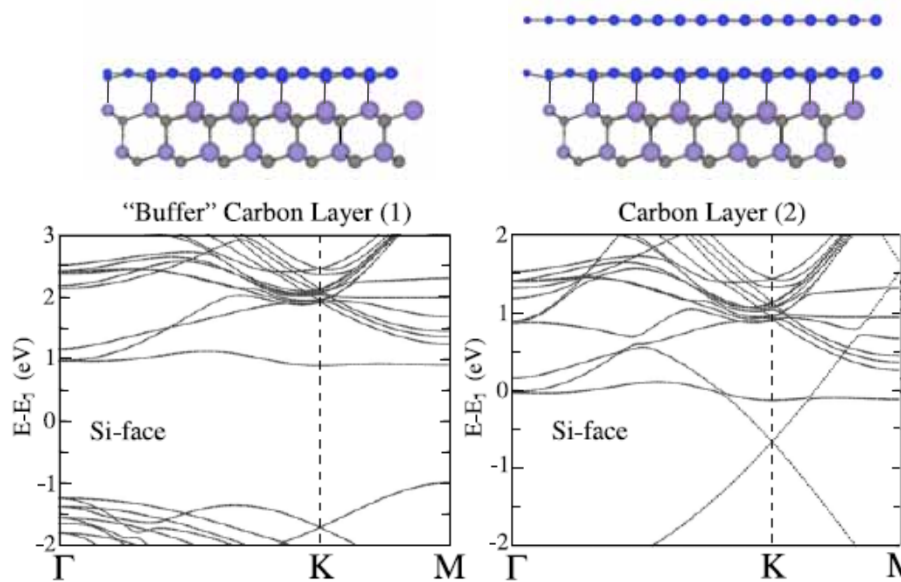


*M. Nagase et al., Nanotechnology 20, 445704 (2009).*

# Si面、C面上グラフェン成長

## Si-face SiC(0001)

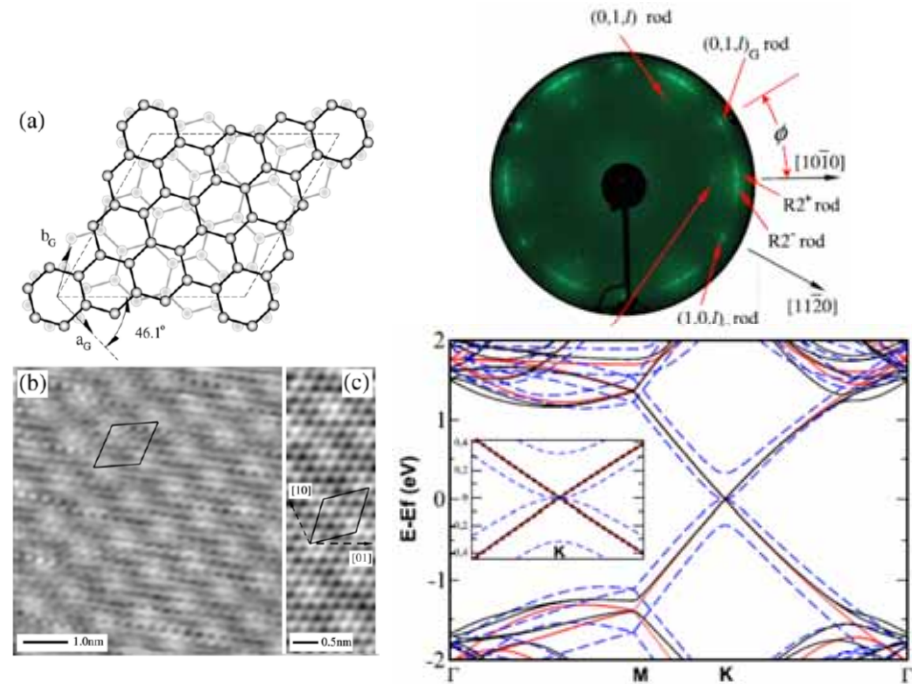
- ✓ One to a few layers
- ✓ Epitaxial growth
- ➡ Graphene ~ few-layer graphite
- ✓ Interfacial layer ( $6\sqrt{3}$  structure)



$$\mu \approx 4,000 \text{ cm}^2/\text{V}\cdot\text{s}$$

## C-face SiC(000 $\bar{1}$ )

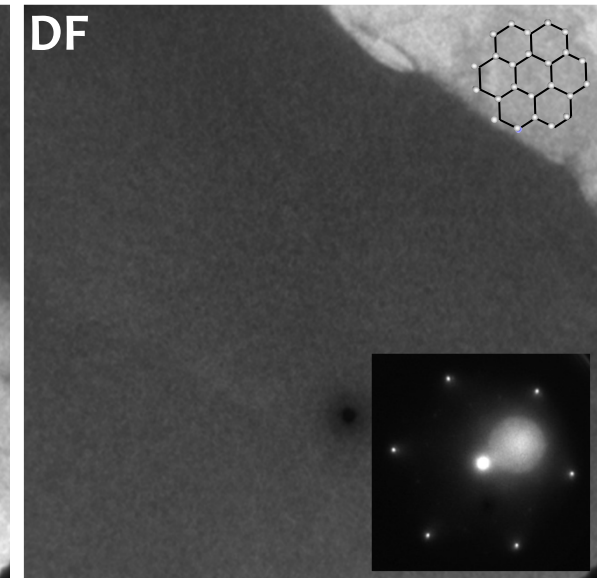
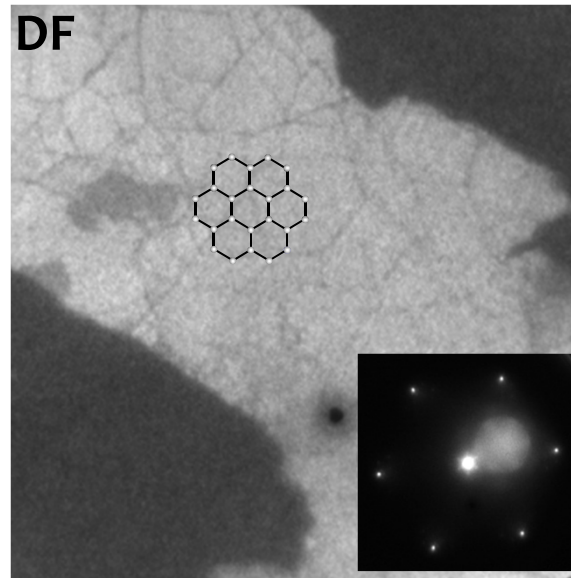
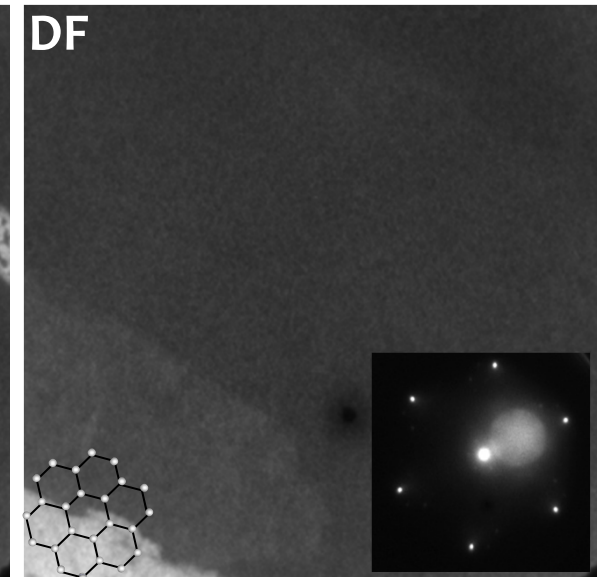
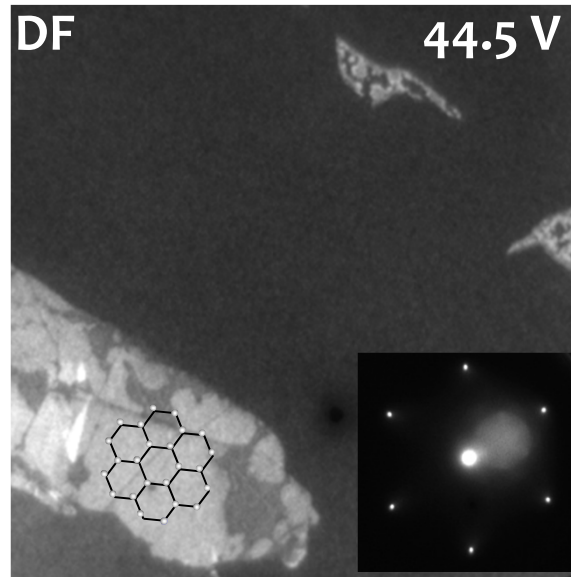
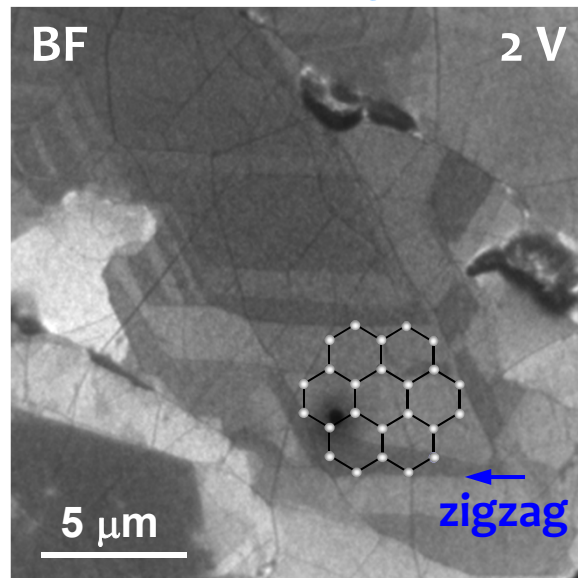
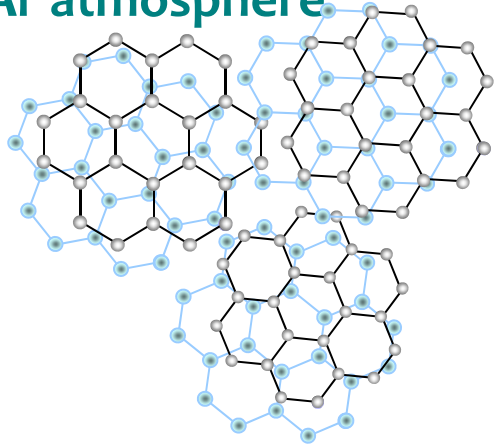
- ✓ Multilayer
- ✓ Rotational disorder
- ➡ Multilayer graphene
- ✓ No interfacial layer



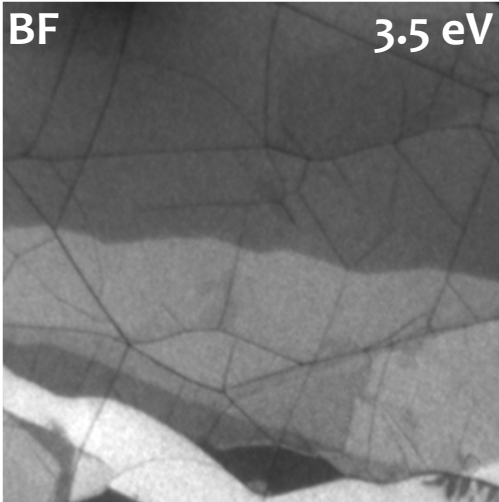
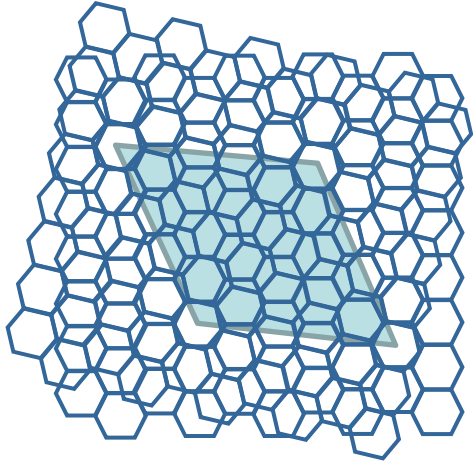
$$\mu = 250,000 \text{ cm}^2/\text{V}\cdot\text{s}$$

# C面上グラフェン:層内の回転

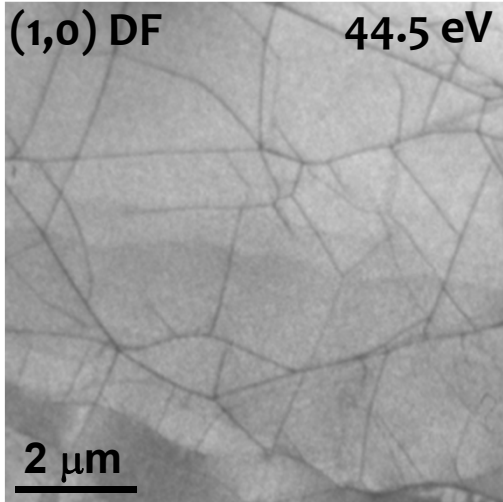
Multilayer graphene grown  
✓ on C-face SiC  
✓ in Ar atmosphere



# C面上グラフェン:層間の回転



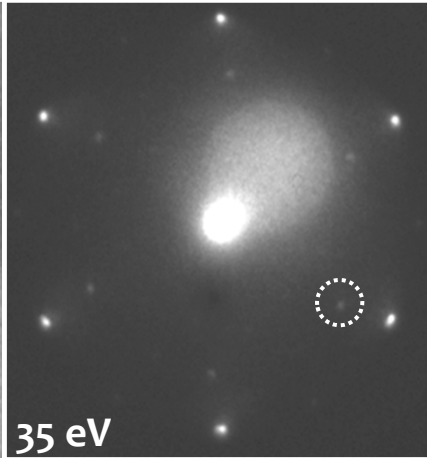
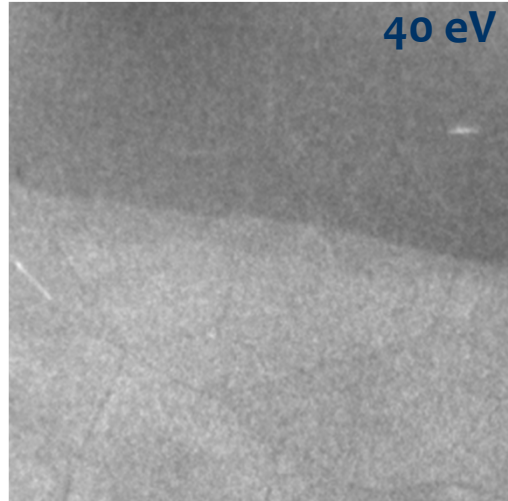
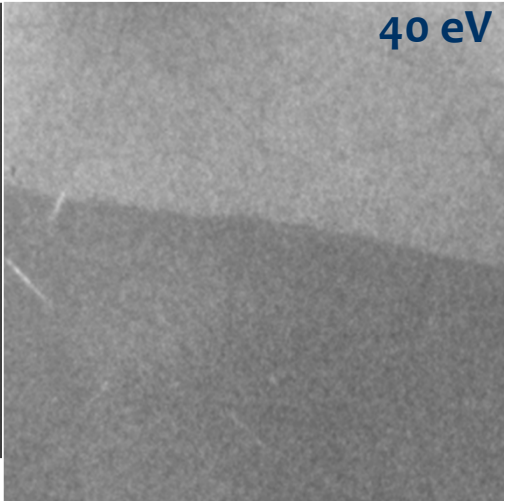
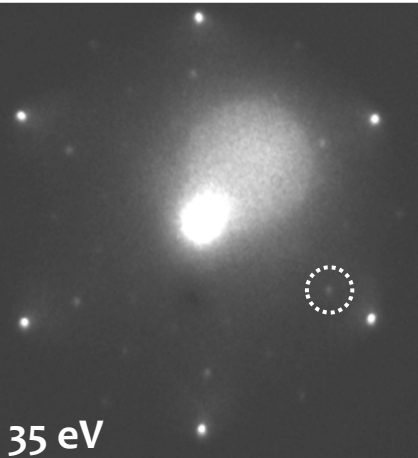
層数コントラスト



最上層の方位分布

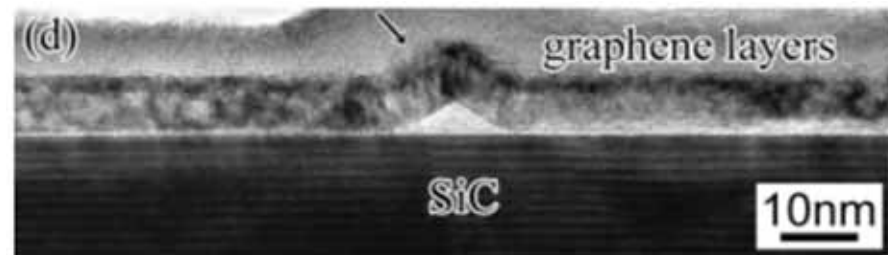
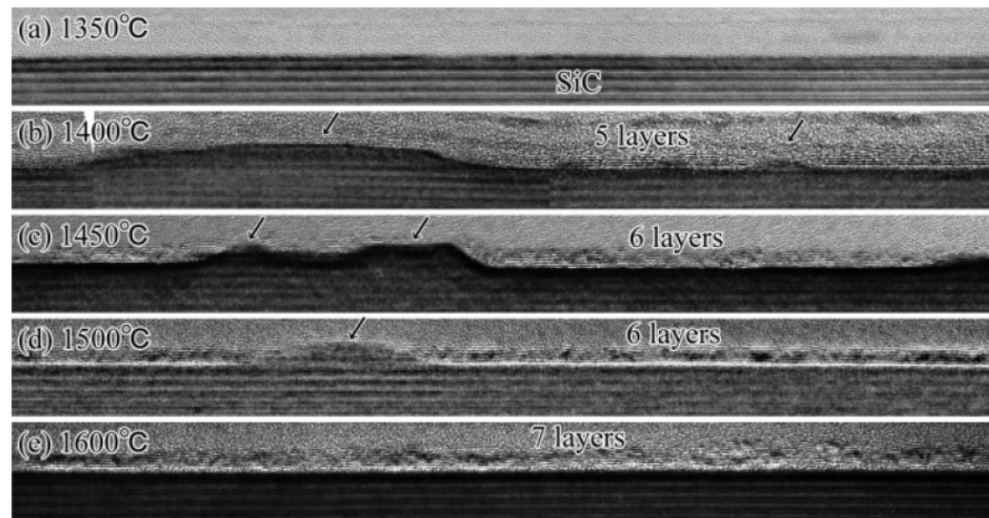
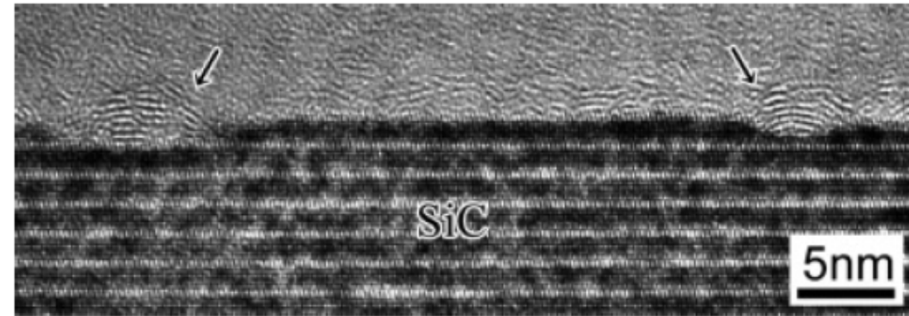
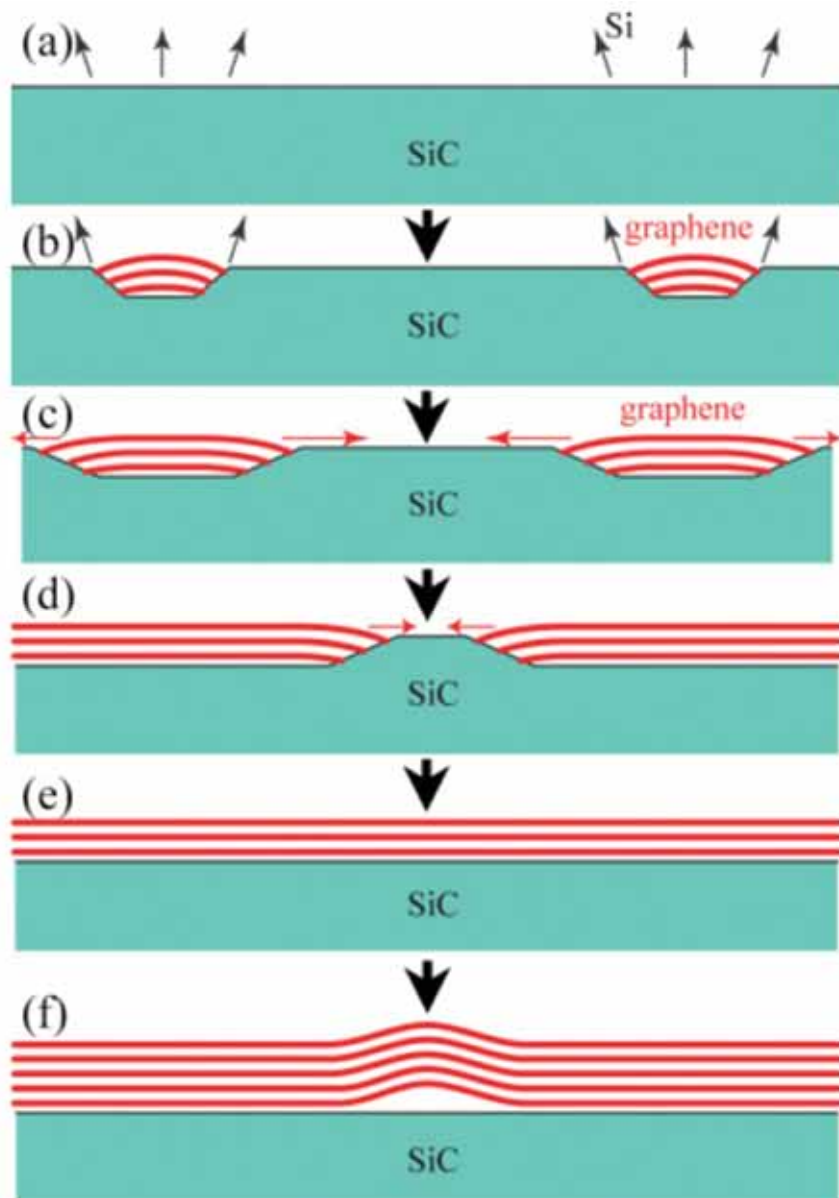
moiré DF

H. Hibino *et al.*, J. Phys. D: Appl. Phys. 45, 154008 (2012).



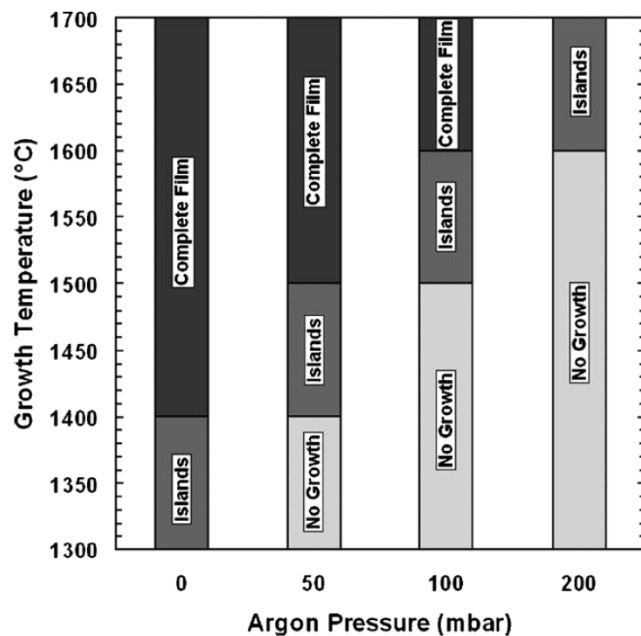
第二層の方位分布

# C面上グラフェン成長過程

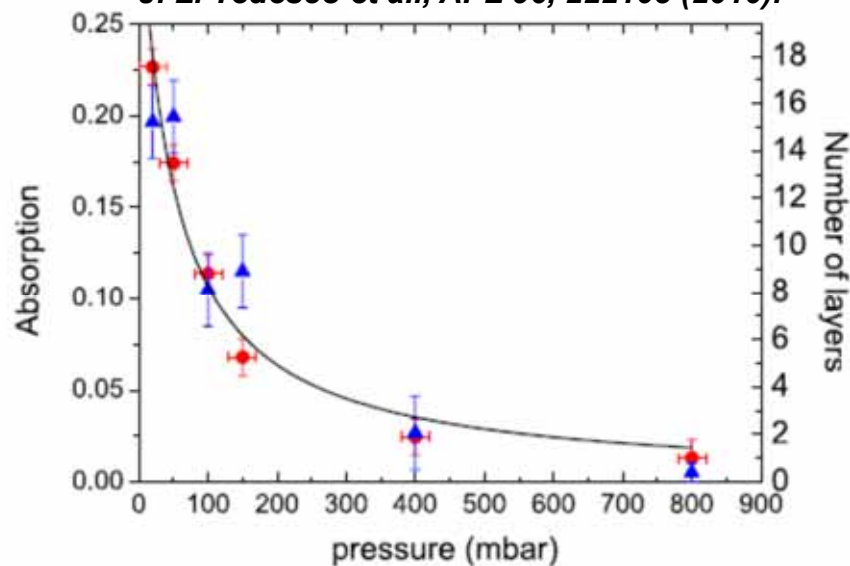




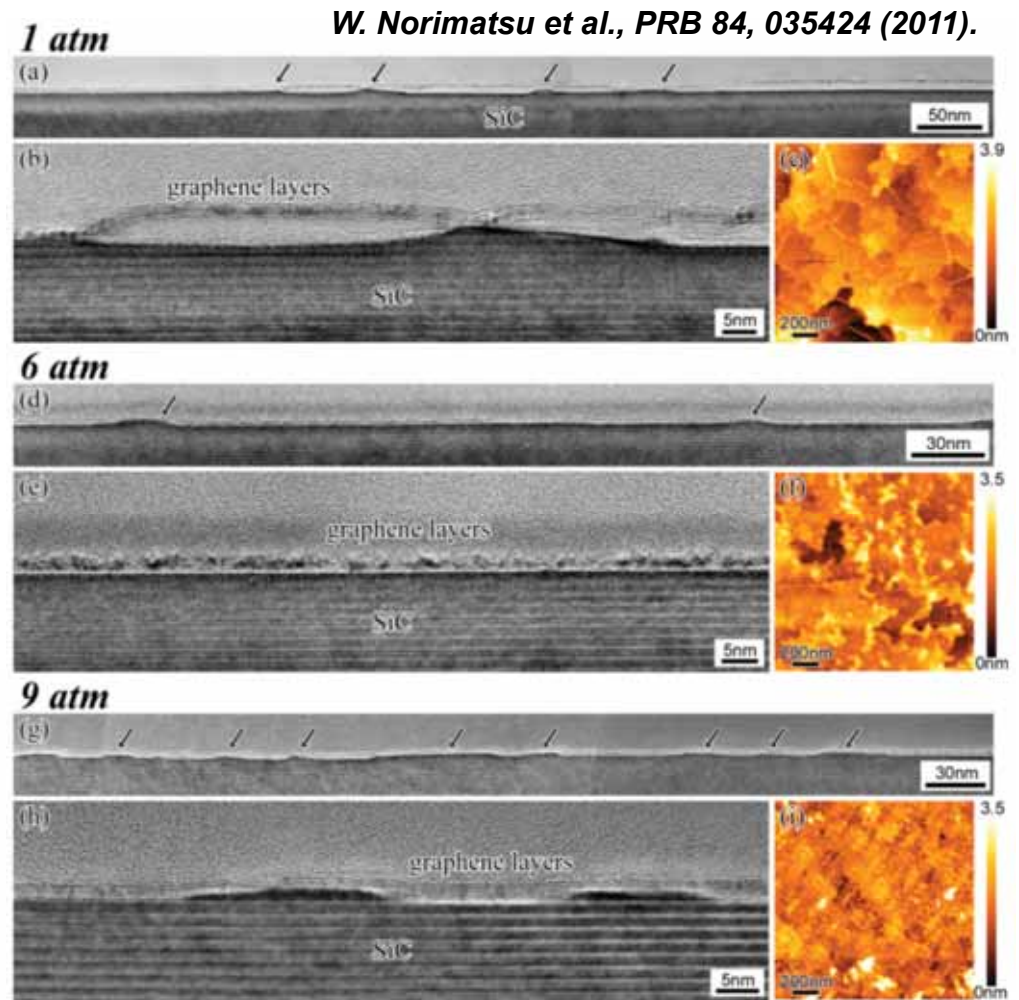
# グラフェン成長過程:圧力効果



*J. L. Tedesco et al., APL 96, 222103 (2010).*



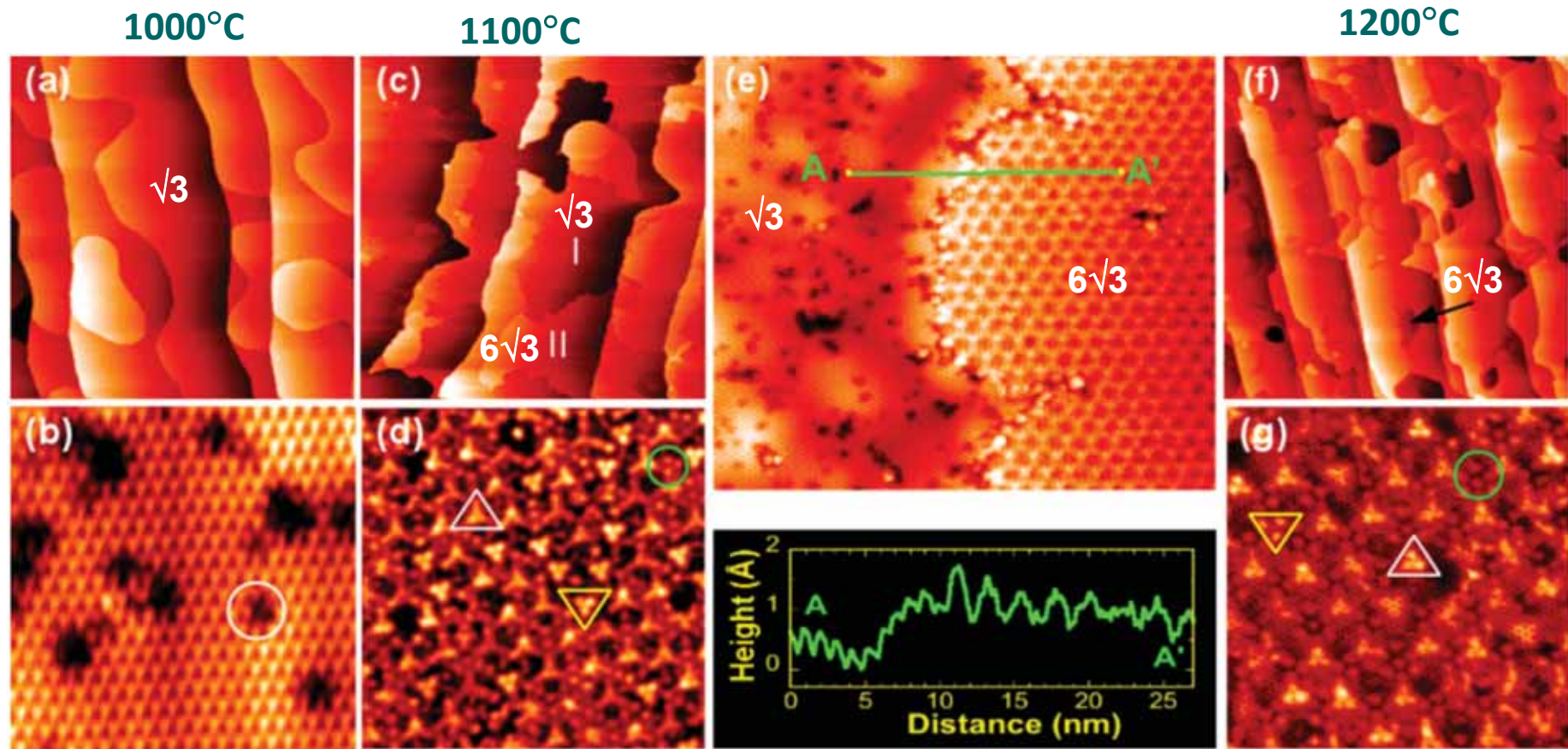
*A. Drabińska et al., PRB 81, 245410 (2010).*



$$N = \frac{C}{p + p_0} \neq \frac{C}{p} \quad (3)$$

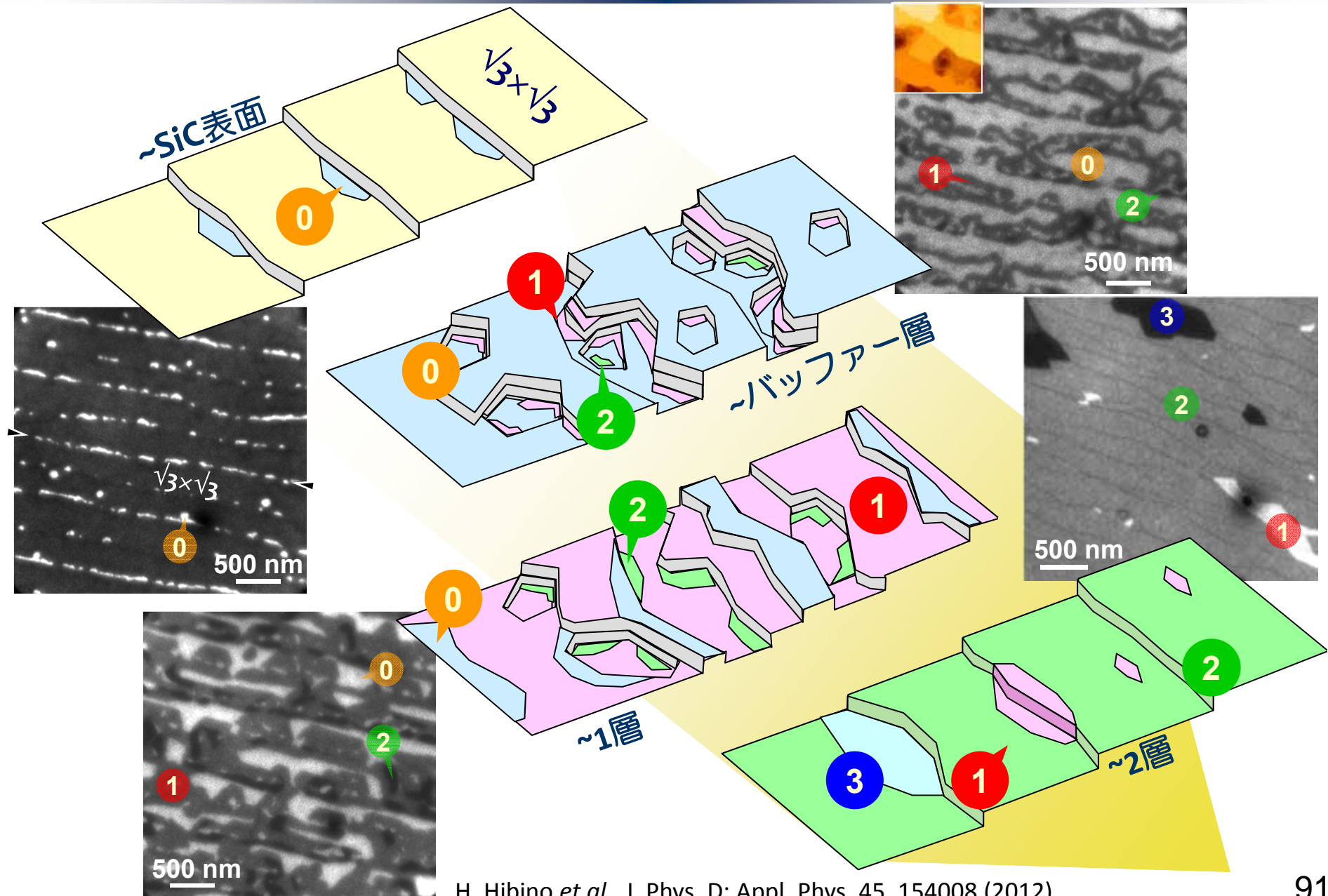
with  $p_0 = 48 \pm 9$  mbar. We assign this value to “effective pressure” of Si vapor interacting with graphene layers and/or graphene-SiC interface. It could be understood that Si atoms

# グラフェン成長中の表面形状



G. F. Sun et al., *Phys. Rev. B* 84, 195455 (2011).

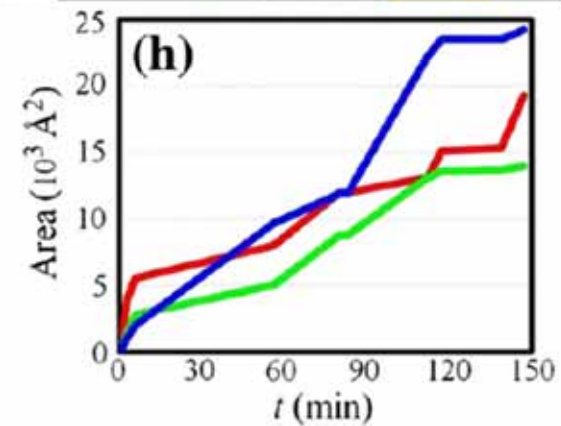
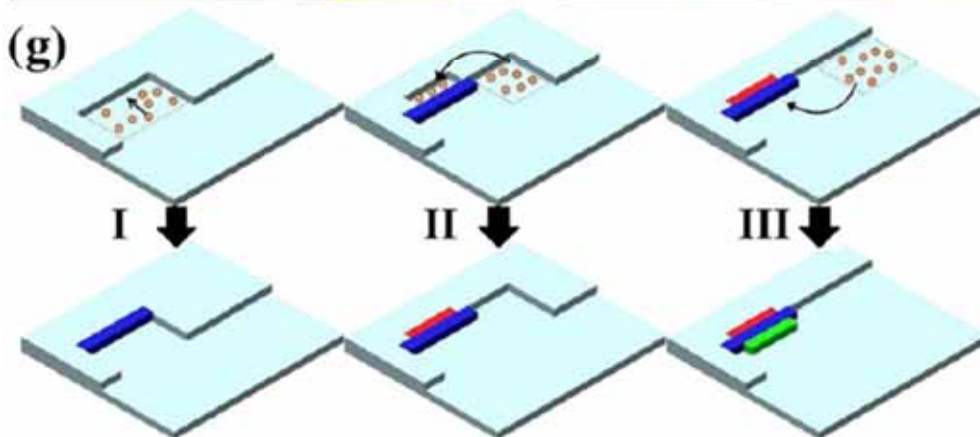
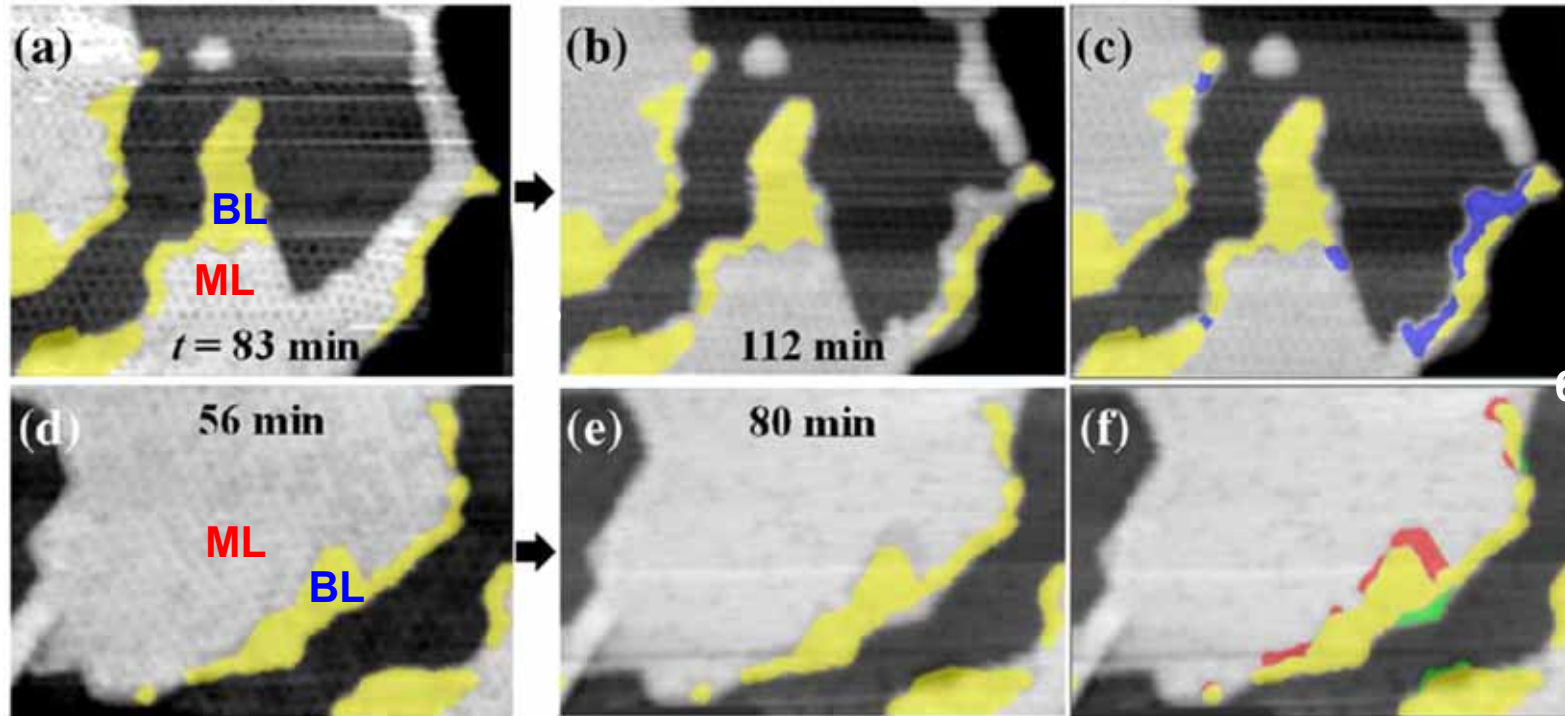
# 超高真空中でのグラフェン成長過程の模式図



H. Hibino *et al.*, J. Phys. D: Appl. Phys. 45, 154008 (2012).

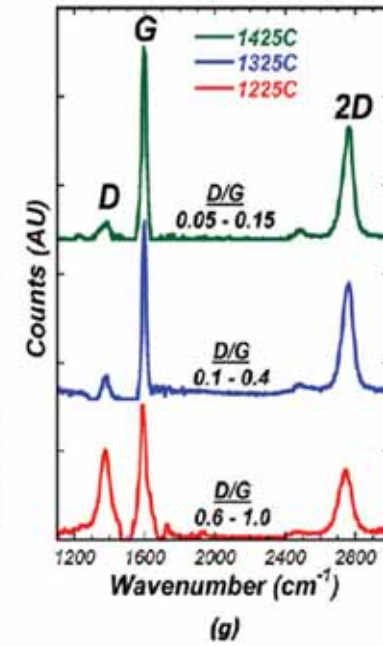
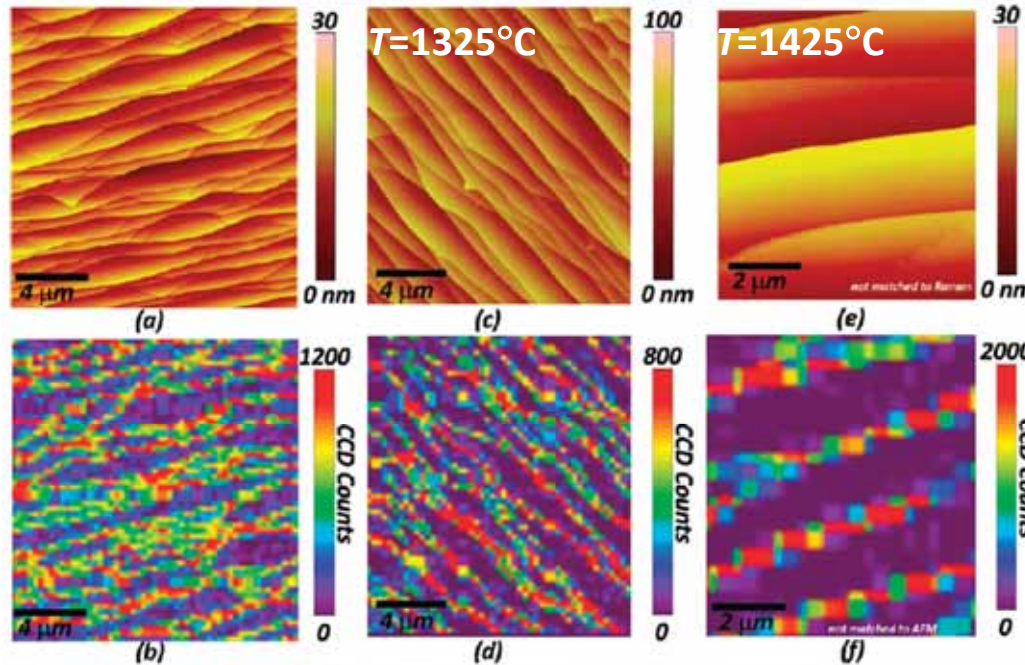
# グラフェン成長中のC原子輸送

1395 K

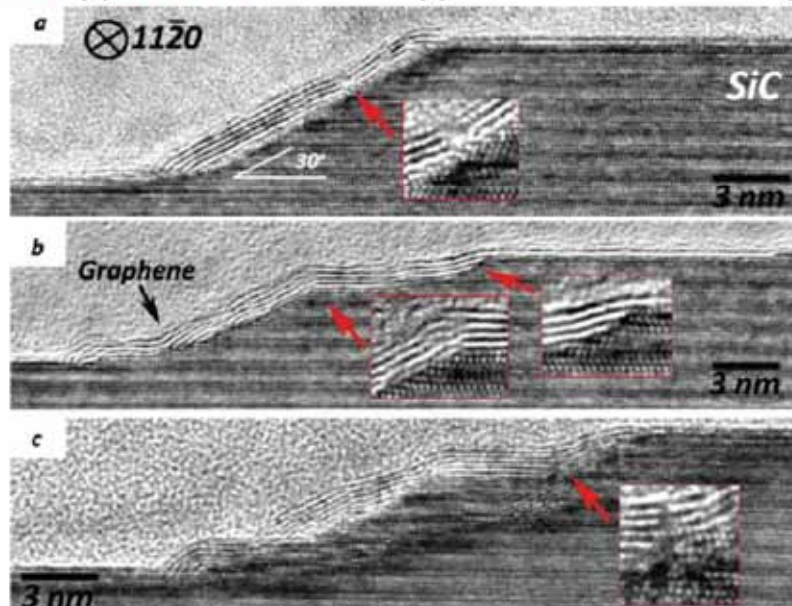


# グラフェン成長過程:ステップの役割

$T=1225^{\circ}\text{C}$   
 $p=1\times 10^{-6}$  Torr

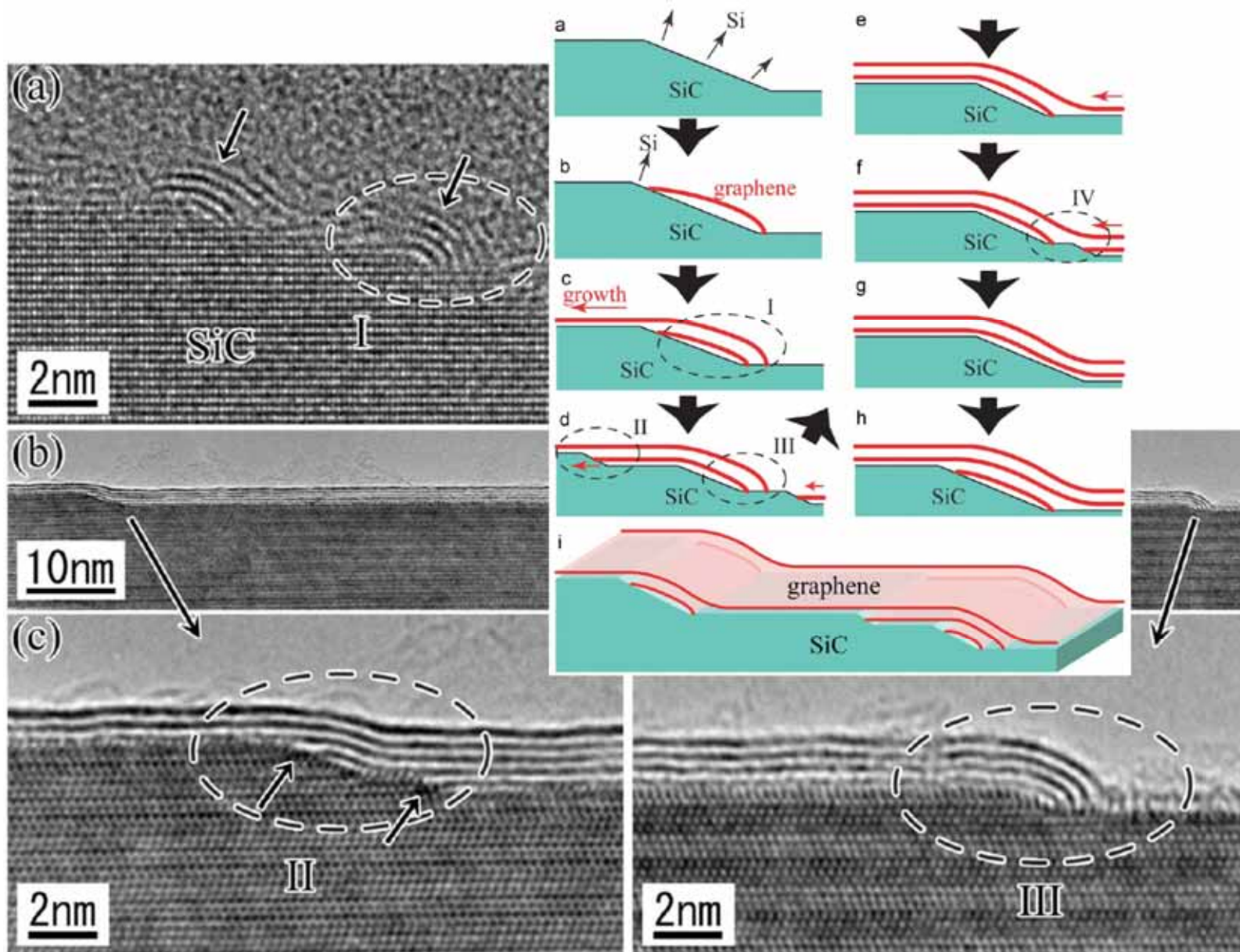


$T=1325^{\circ}\text{C}$



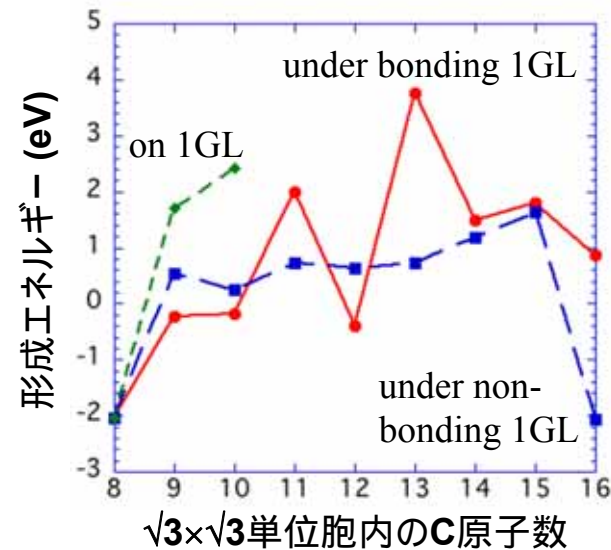
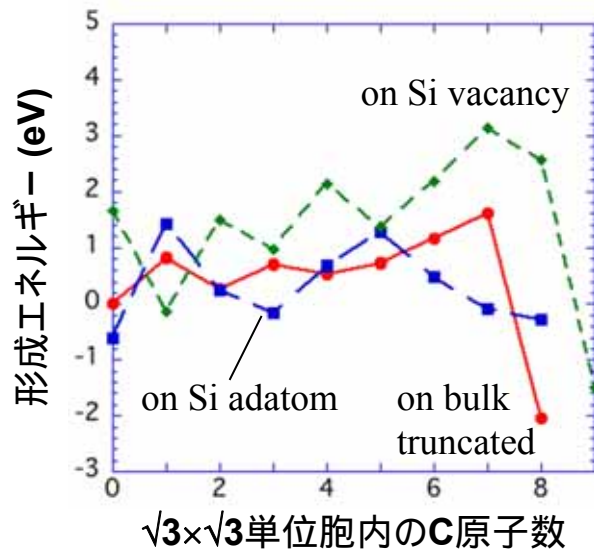
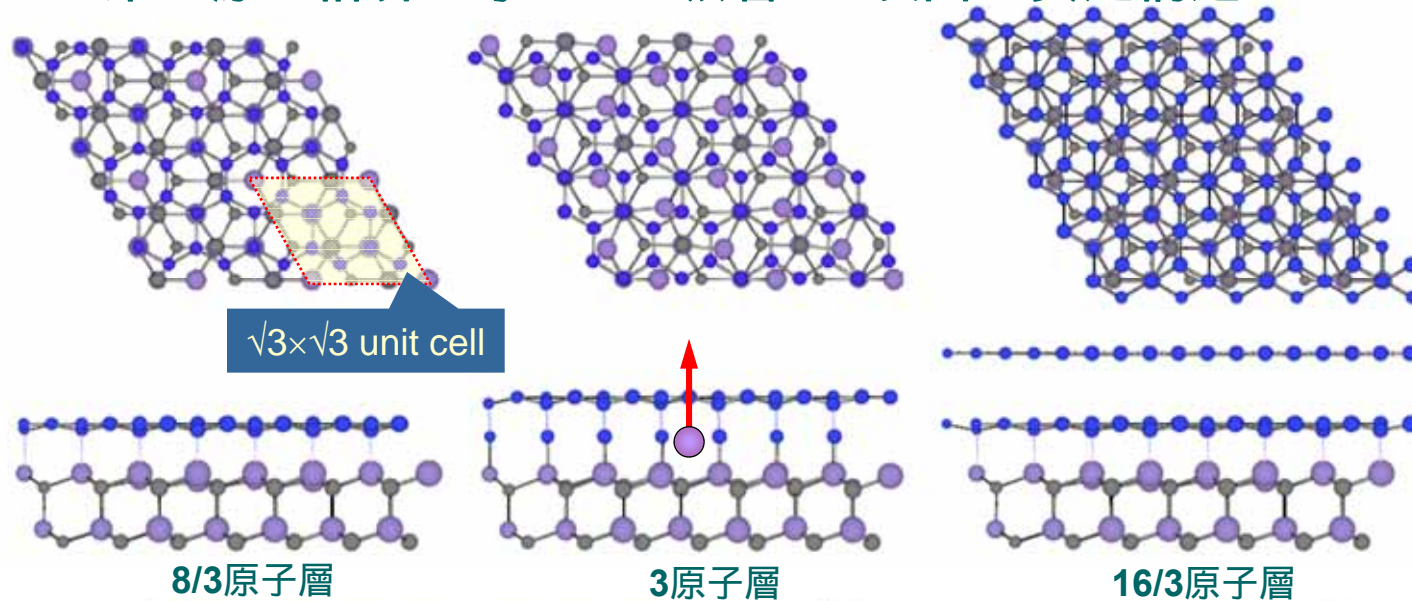
*J. Robinson et al., ACS Nano 4, 153 (2010).*

# グラフェン成長過程:ステップの役割

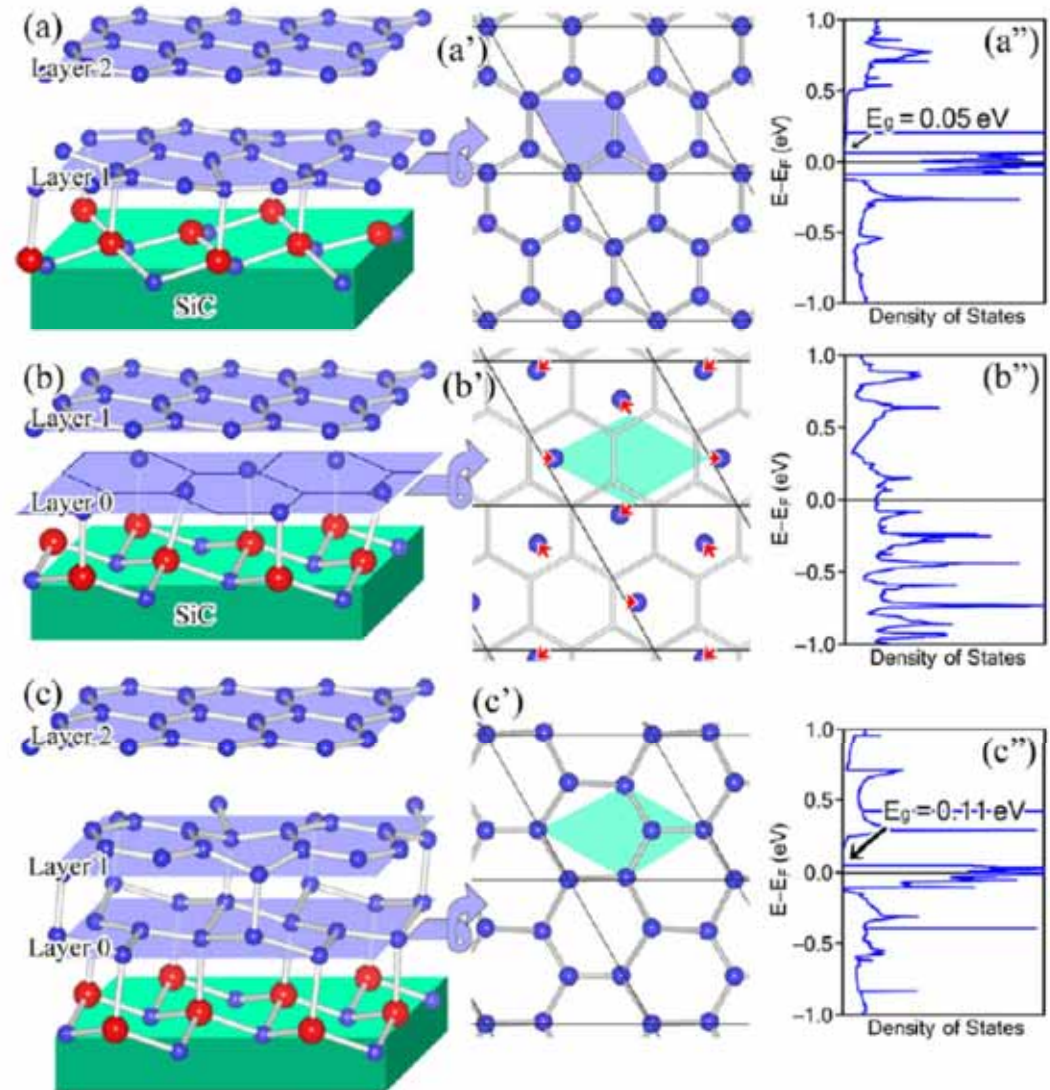
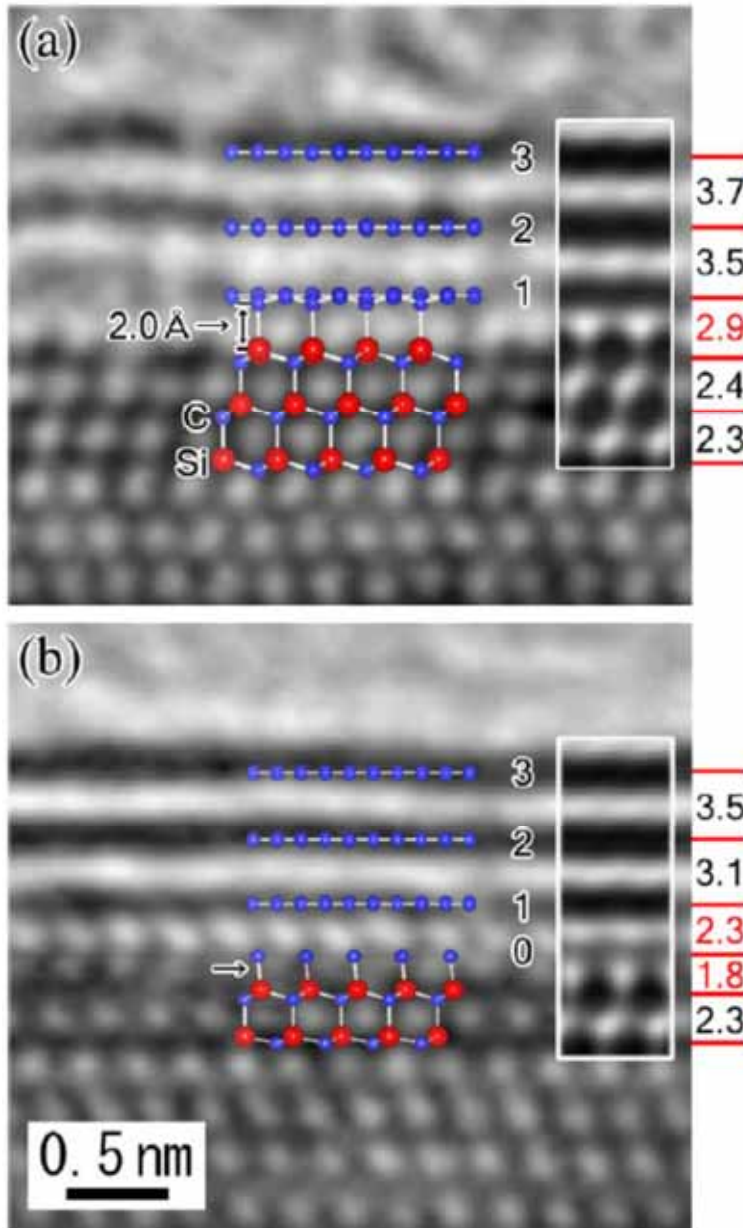


# グラフェン成長過程の理論的考察

## 第一原理計算で求めたC吸着SiC表面の安定構造



# グラフェン成長過程



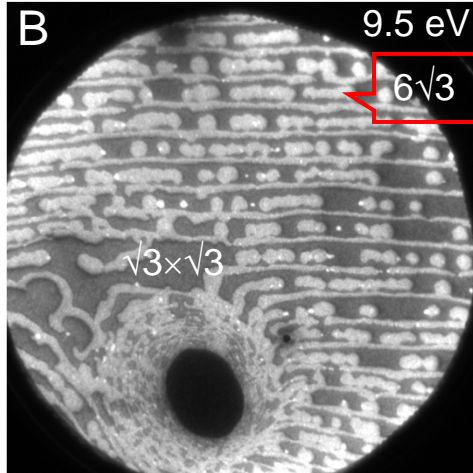
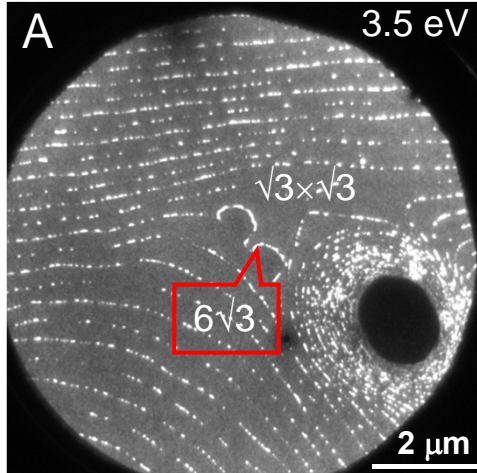


# バッファー層形成過程

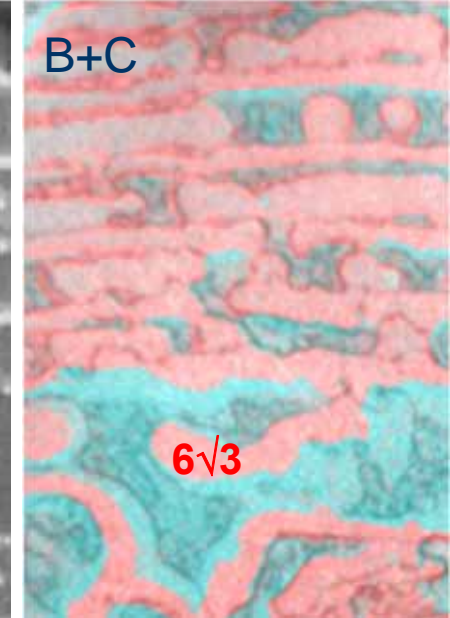
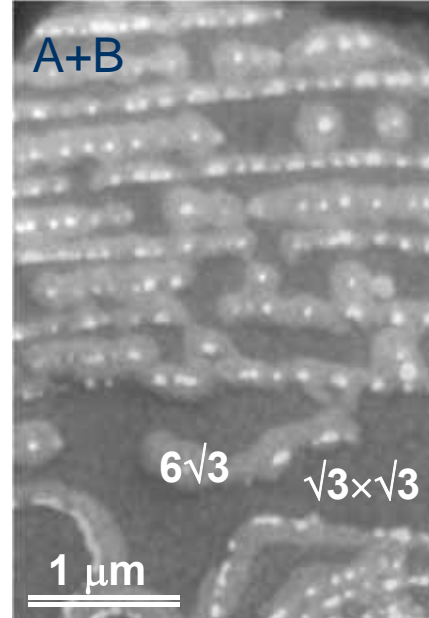
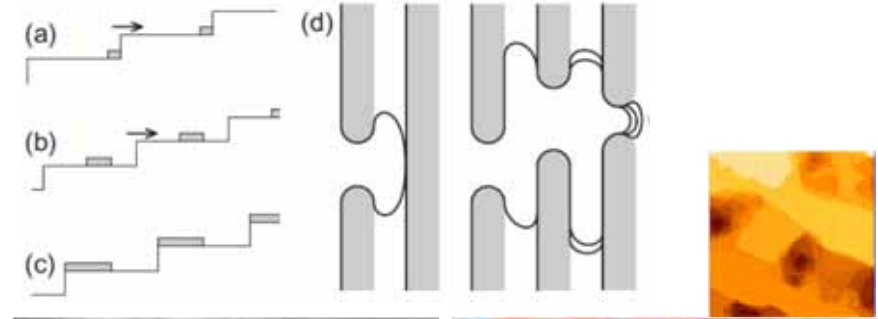
$\sqrt{3}\times\sqrt{3}+6\sqrt{3}\times6\sqrt{3}$

$\sqrt{3}\times\sqrt{3}+6\sqrt{3}\times6\sqrt{3}$

J. B. Hannon and R. M. Tromp, Phys. Rev. B 77, 241404(R) (2008).

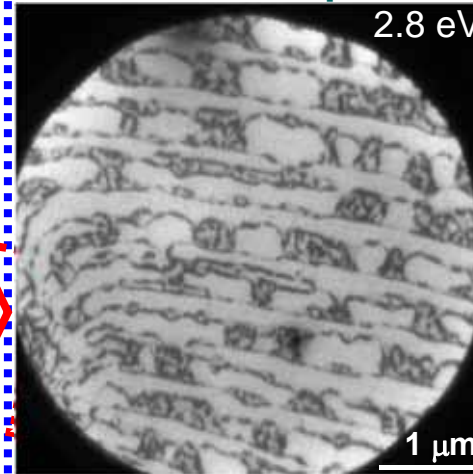
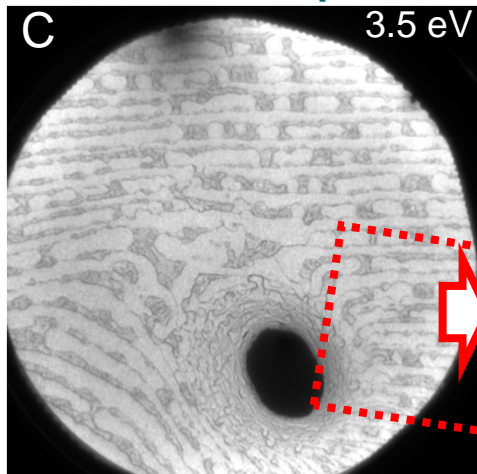


During anneal at 950°C After anneal at 990°C

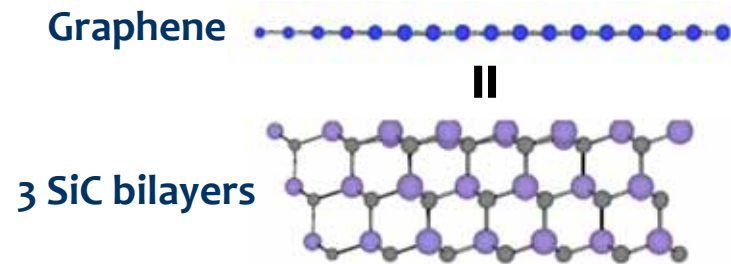


$6\sqrt{3}\times6\sqrt{3}+\text{Graphene}$

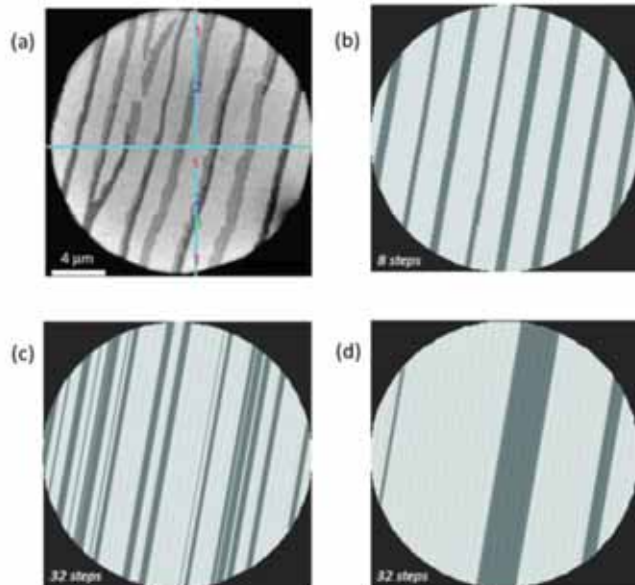
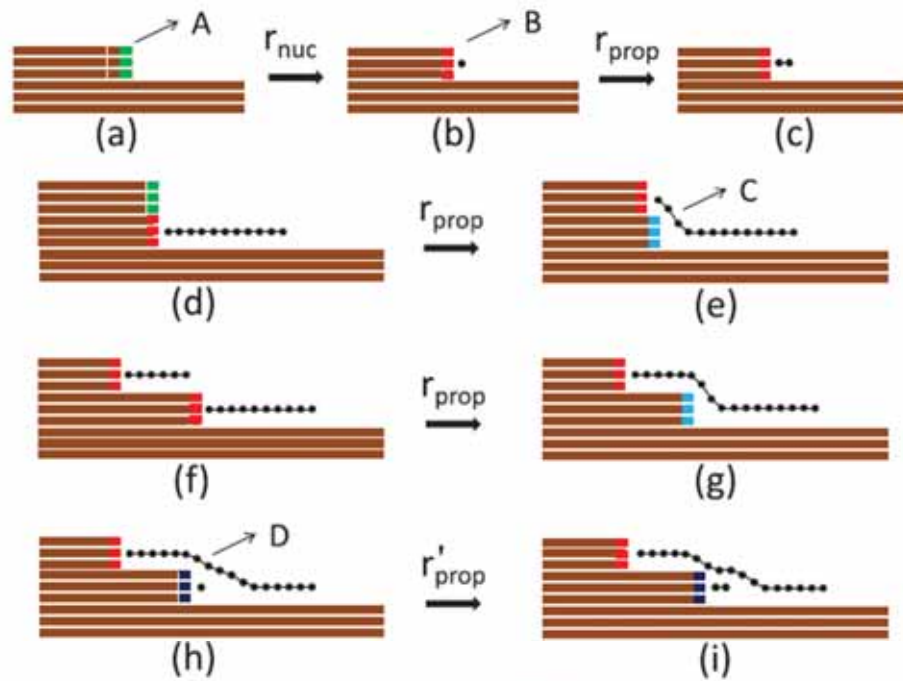
$6\sqrt{3}\times6\sqrt{3}+\text{Graphene}$



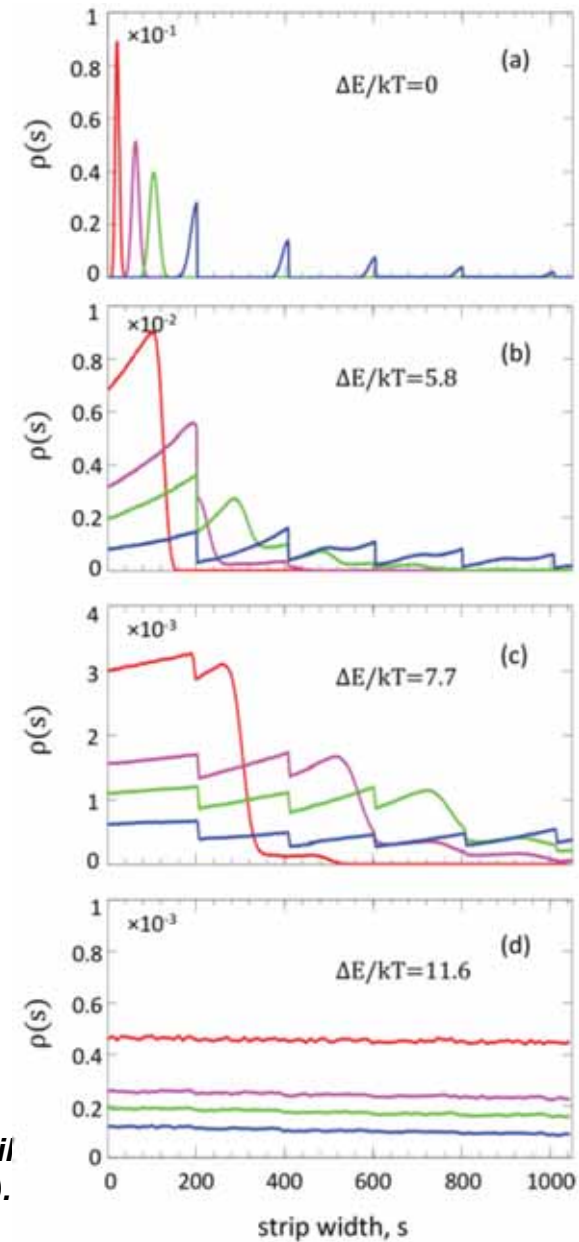
After anneal at 1050°C After anneal at 1090°C



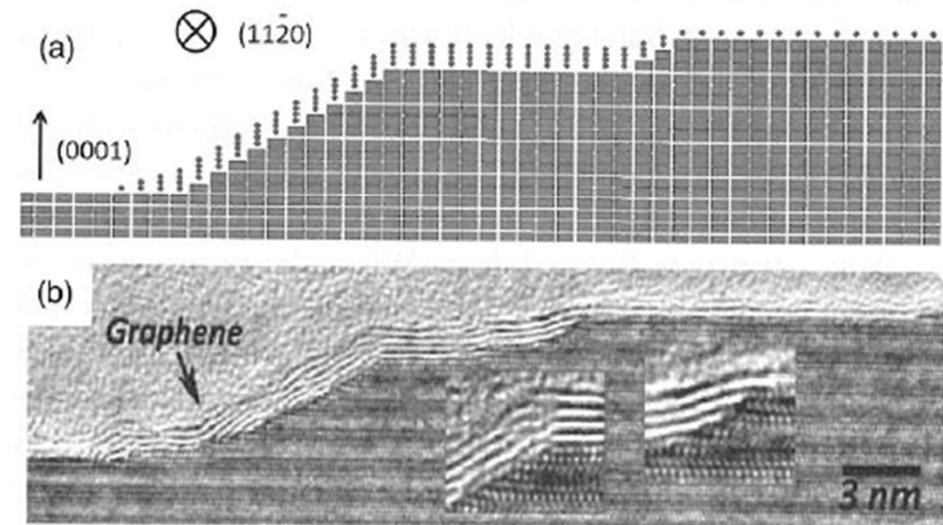
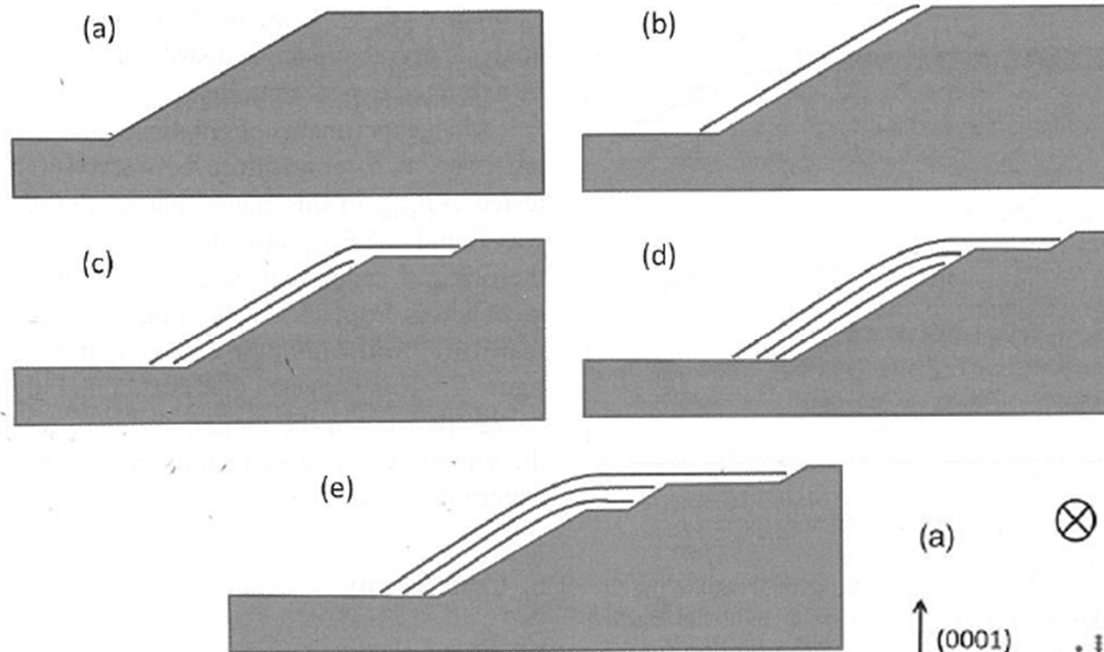
# Si面上グラフェン成長モデル



F. Ming and A. Zangwil  
PRB 84, 115459 (2011).

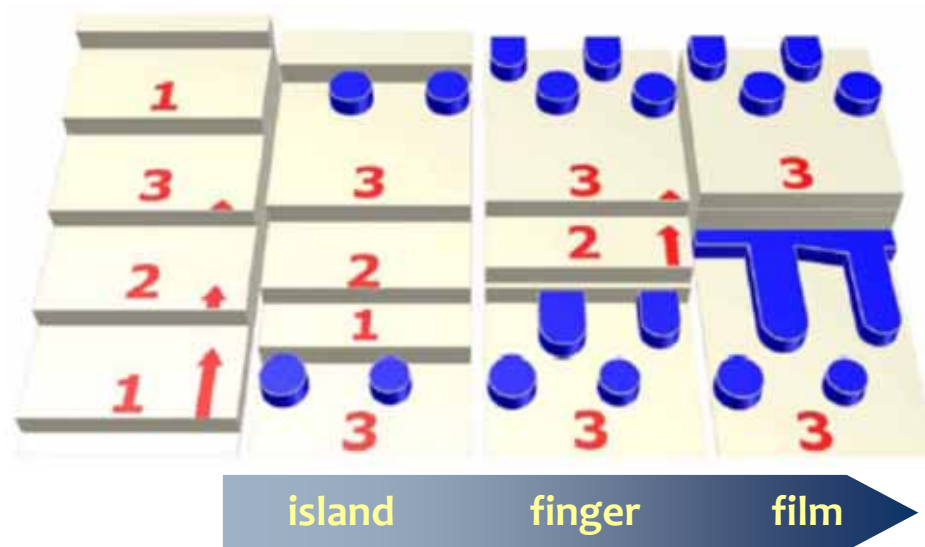
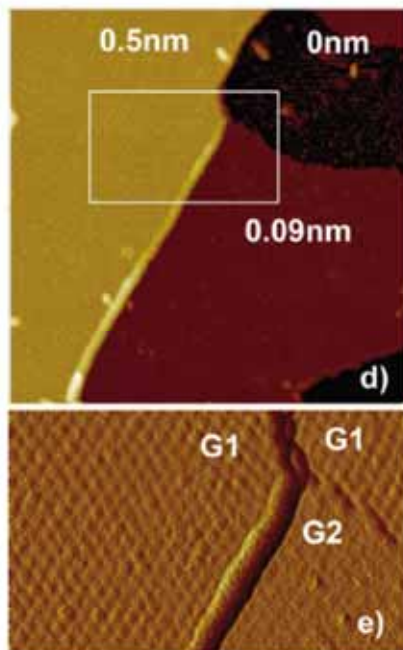
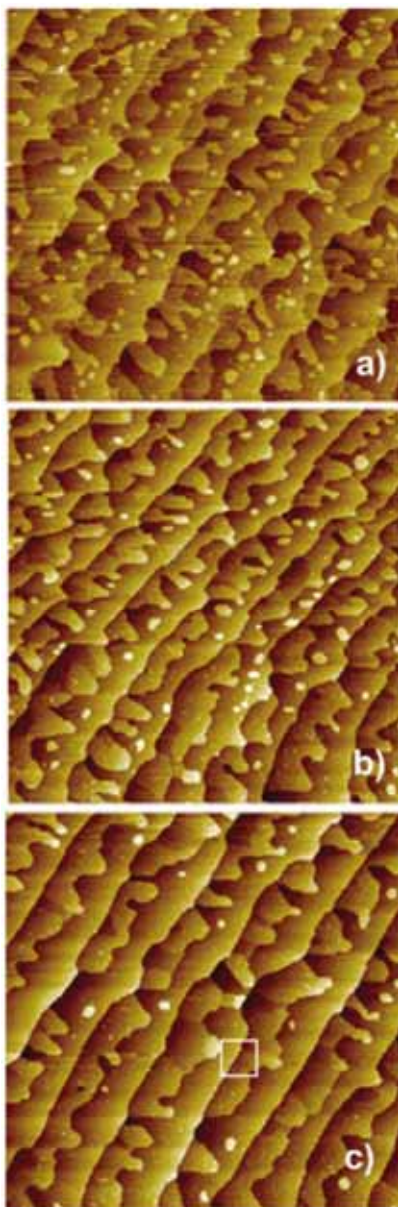


# Si面上グラフェン成長モデル

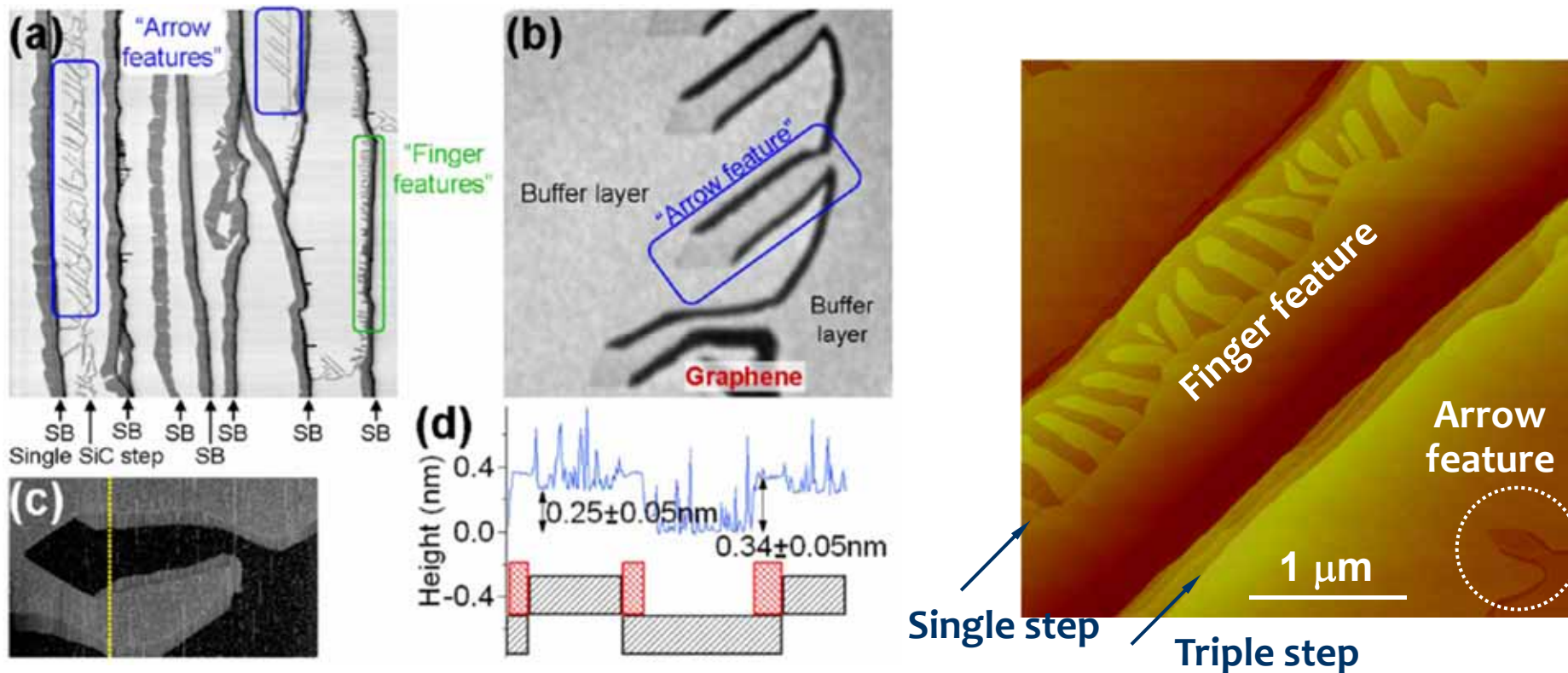


F. Ming and A. Zangwill,  
*J. Phys. D: Appl. Phys.* 45, 154007 (2012).

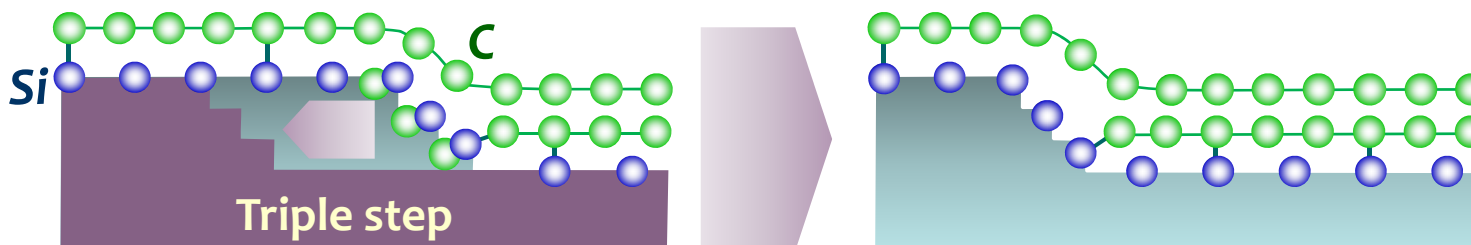
# 1層→2層成長



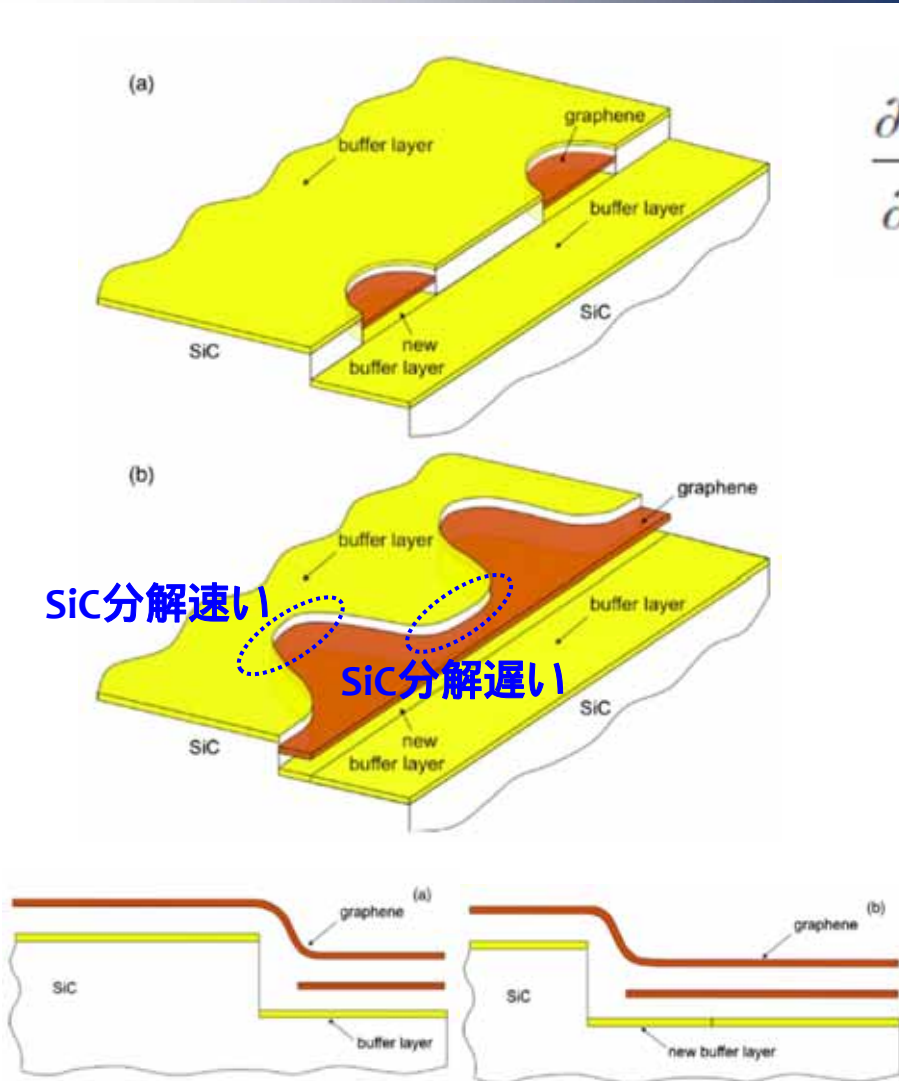
# グラフェン成長中のステップ不安定化



T. Ohta et al., *Phys. Rev. B* 81, 121411(R) (2010).



# 指状構造の形成機構



SiC分解速い

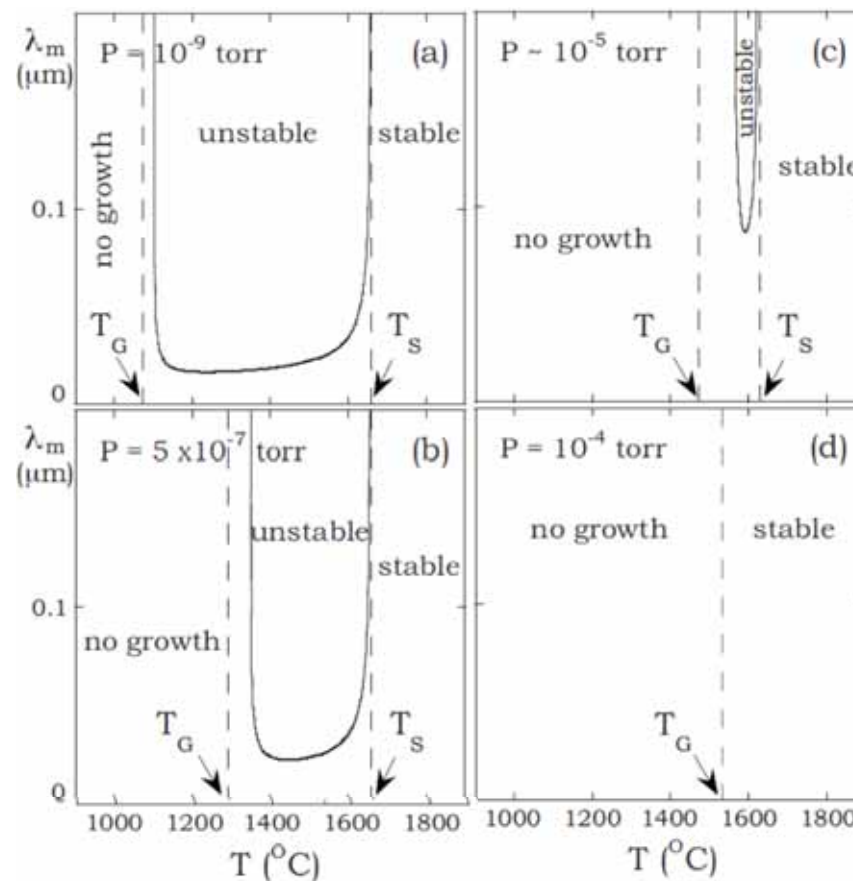
SiC分解遅い

蒸発/凝集

$$\frac{\partial h}{\partial t} = -V - aV \frac{\partial^2 h}{\partial x^2} + \sigma \Gamma \frac{\partial^2 h}{\partial x^2} - \sigma D \frac{\partial^4 h}{\partial x^4}$$

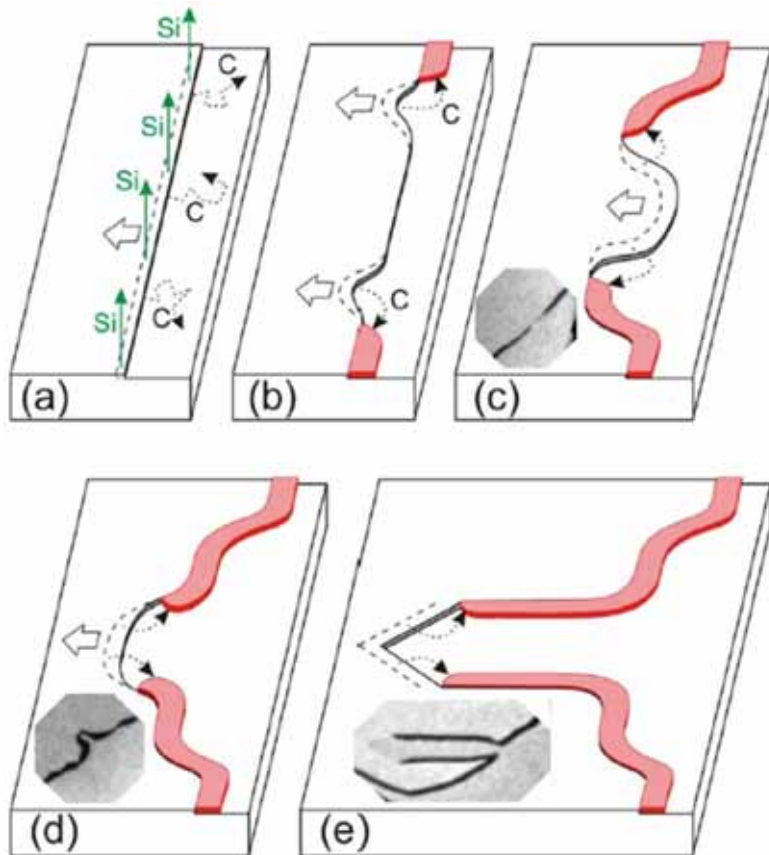
ステップ曲率に依存した  
SiCの分解

エッジ拡散



V. Borovikov et al., PRB 80, 121406(R) (2009).

# グラフェン成長中のステップ不安定化

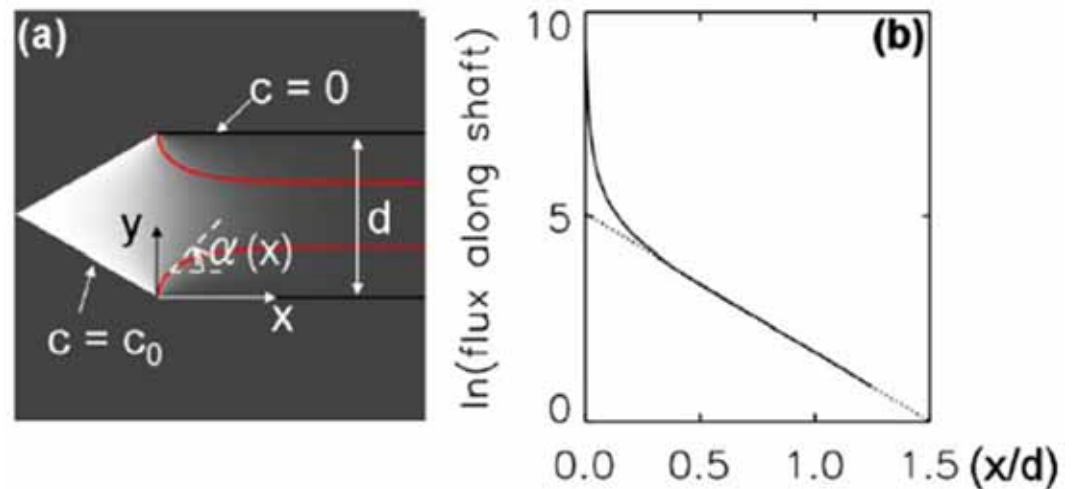


$$\frac{\partial y}{\partial t} = \frac{f(x)}{\cos(\alpha)} = f(x) \left[ 1 + \left( \frac{\partial y}{\partial x} \right)^2 \right]$$

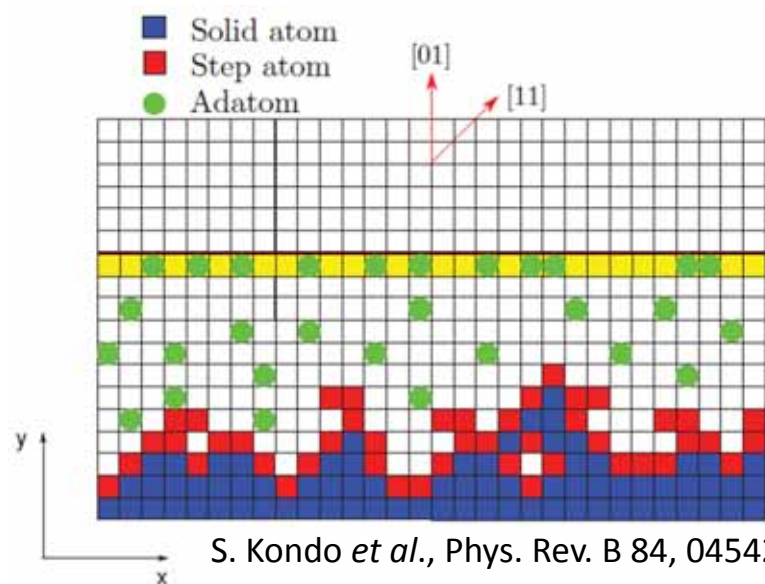
Looking for steady-state translating solutions of the form  $y(x,t) = z(x+vt)$

If  $f(x) = \exp(-x/a)$

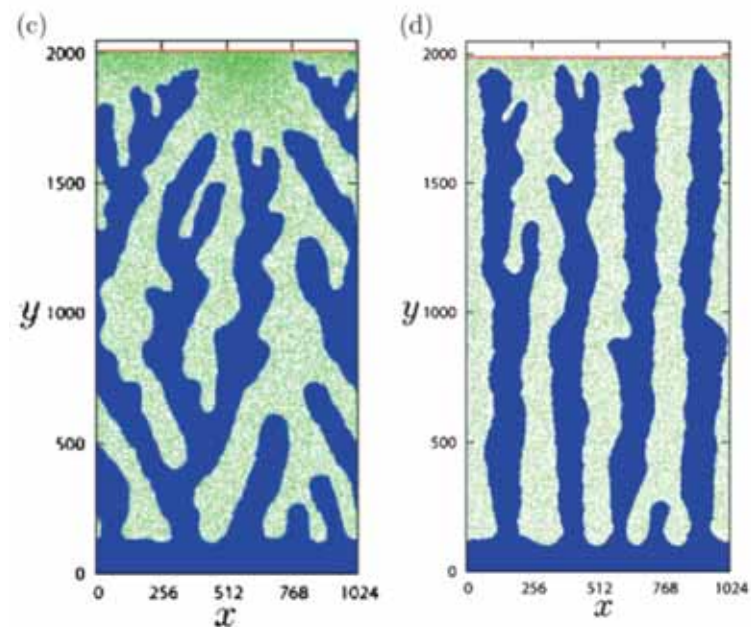
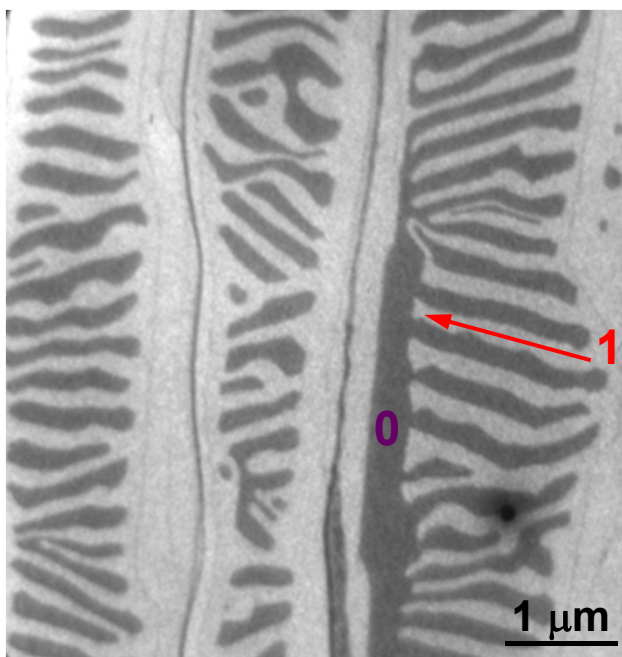
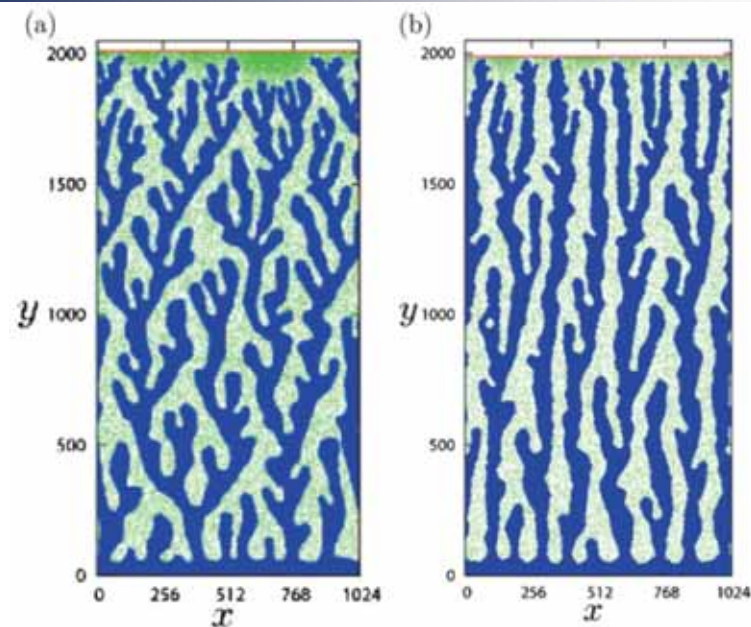
Then the solution  $z(x) = 2a \ln \cos(x/2a)$



# グラフェン成長中のステップ不安定化

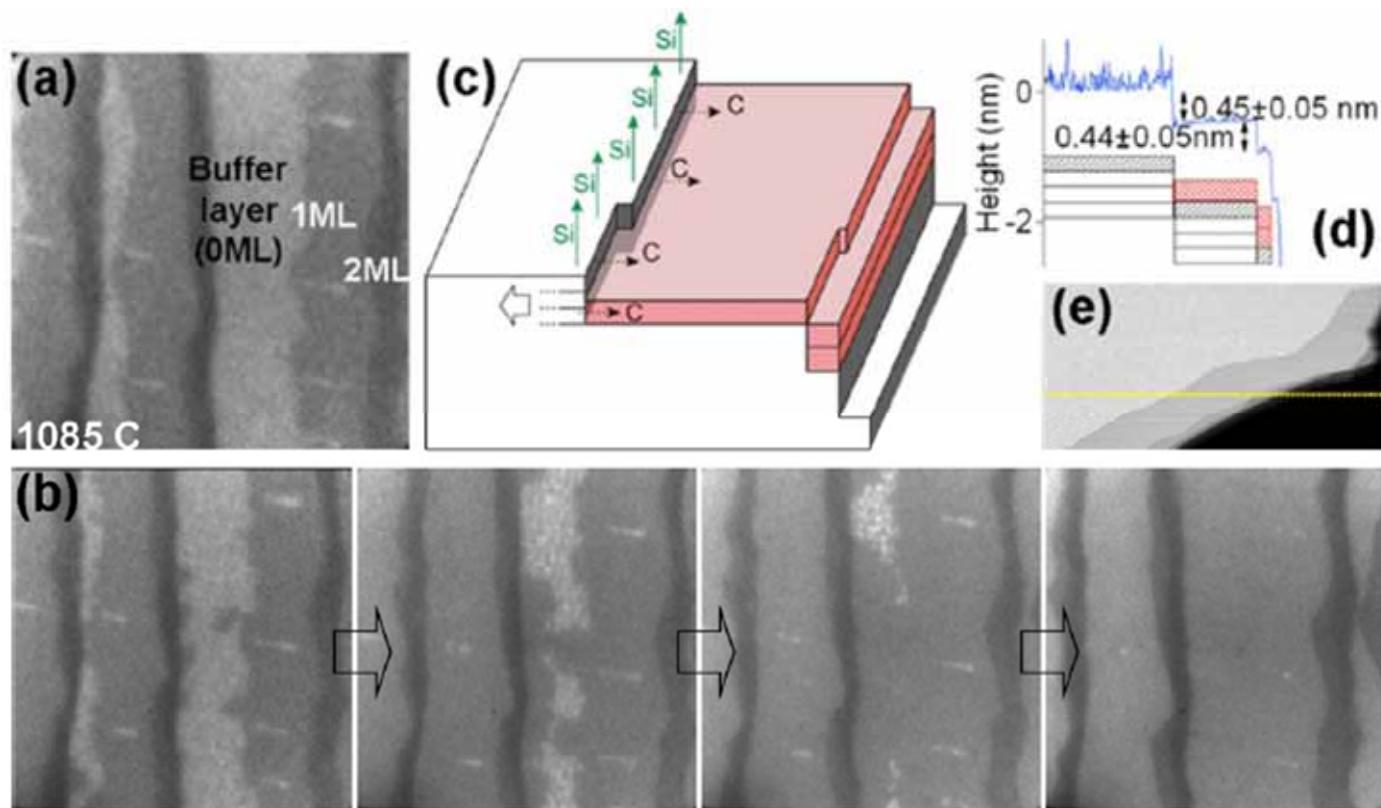


S. Kondo *et al.*, Phys. Rev. B 84, 045420 (2011).

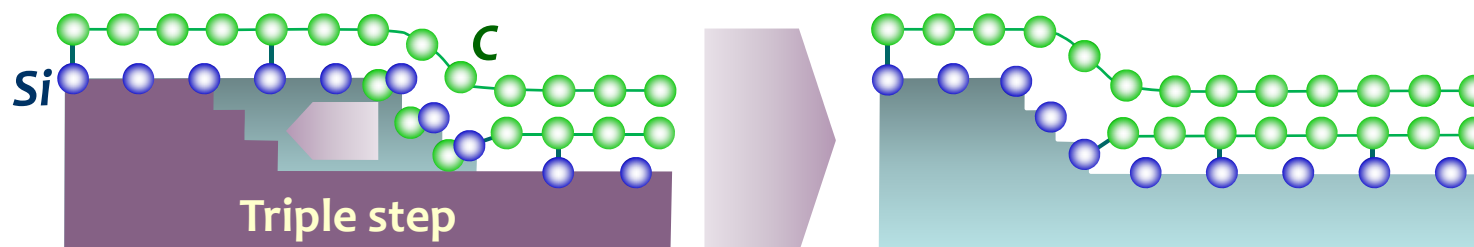




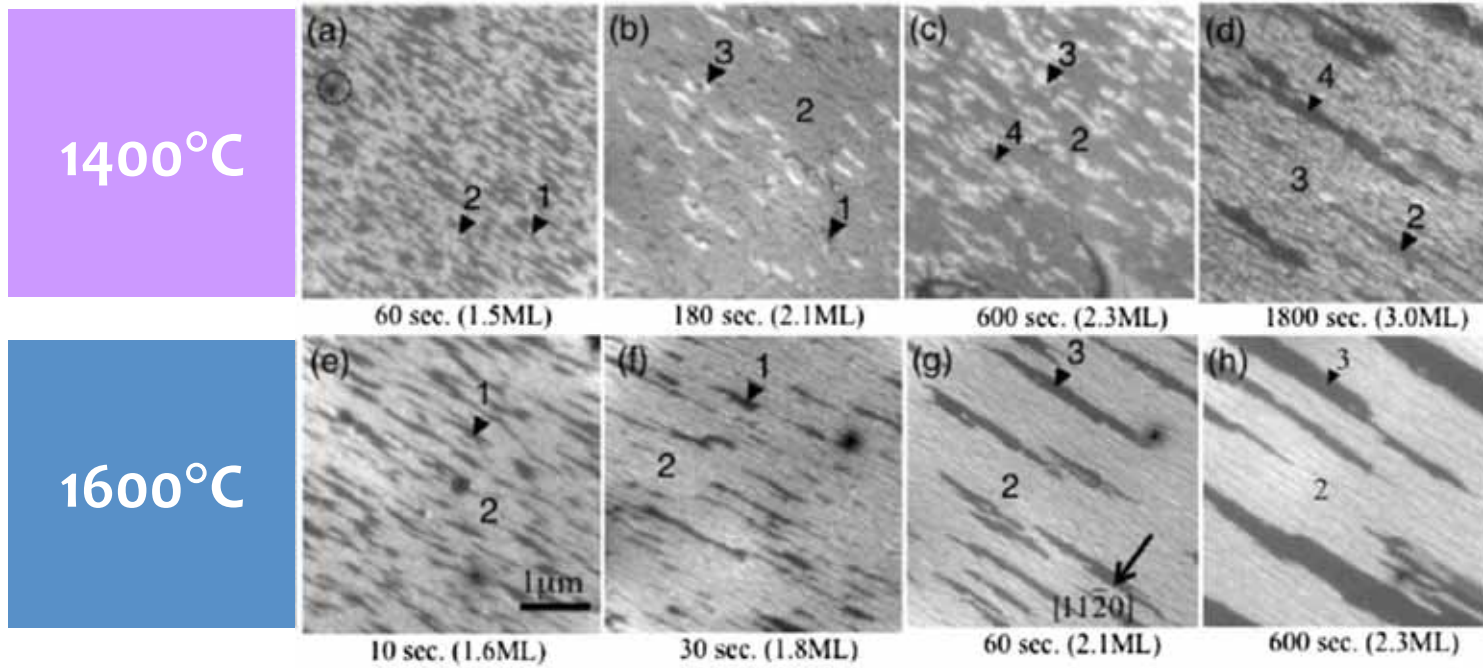
# グラフェン安定成長



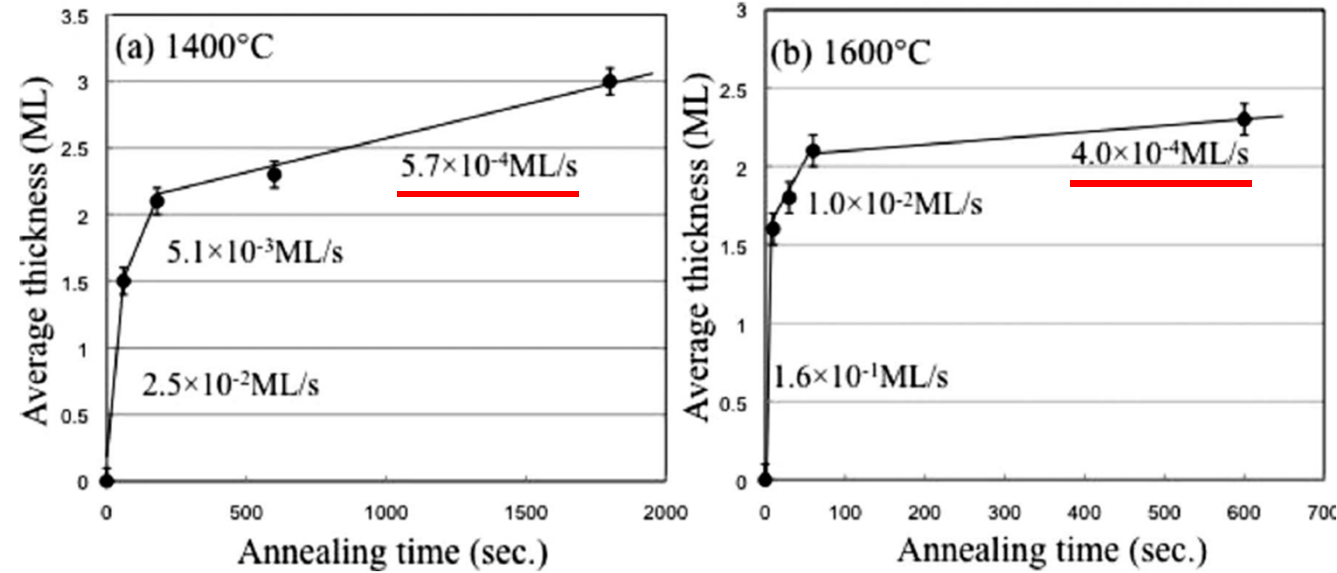
T. Ohta et al., *Phys. Rev. B* 81, 121411(R) (2010).



# グラフェンのSiに対する非透過性

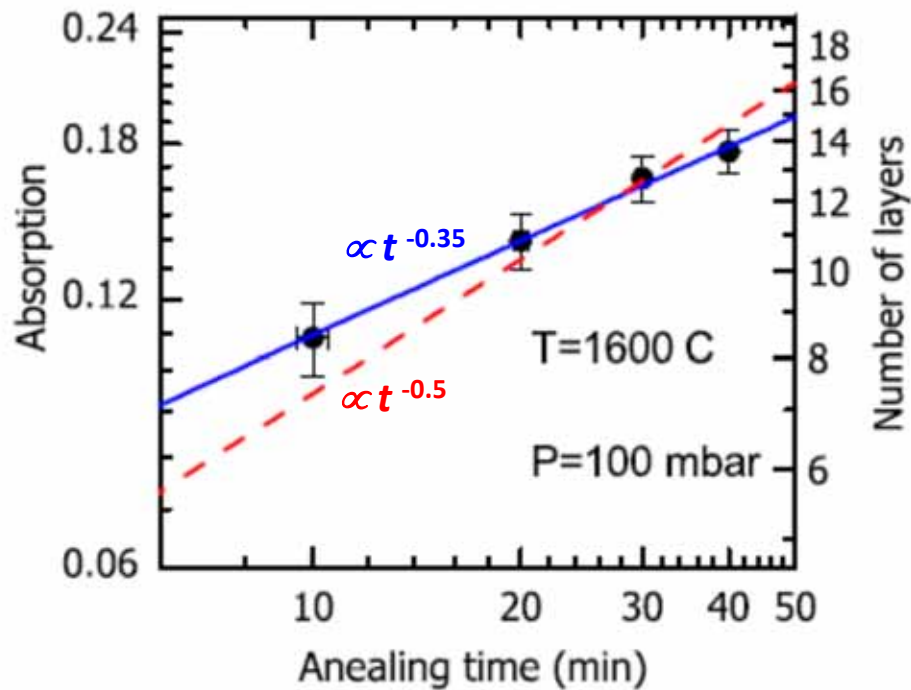


S. Tanaka *et al.*, Phys. Rev. B 81, 041406(R) (2010).

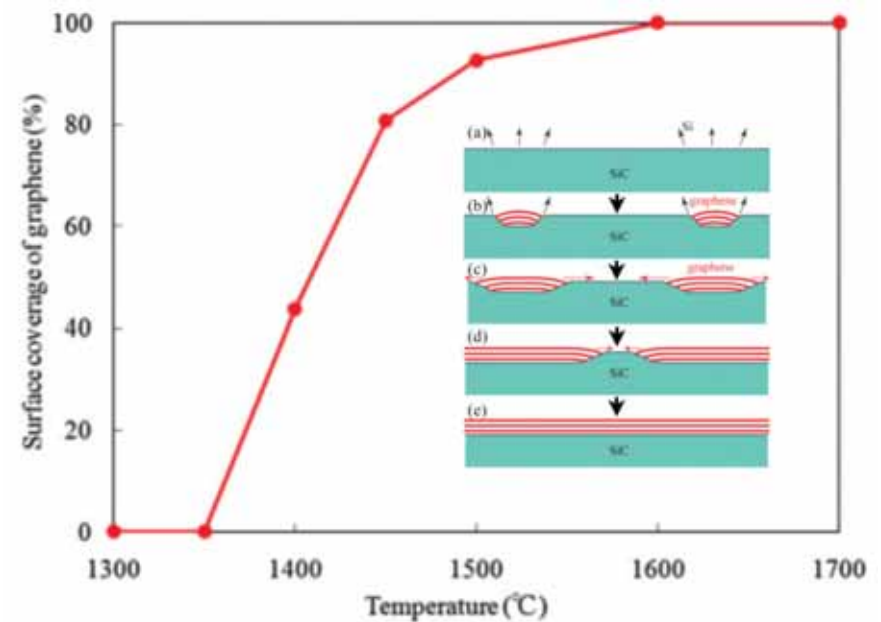


# グラフェン成長過程:成長速度

## c面上グラフェン



A. Drabińska et al., PRB 81, 245410 (2010).



W. Norimatsu et al., PRB 84, 035424 (2011).

# グラフェンのSiに対する非透過性

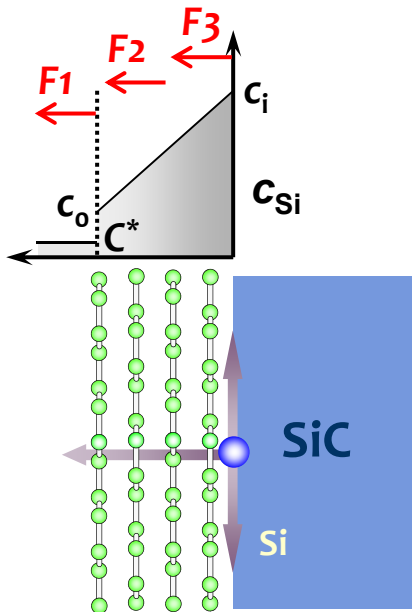
**Deal-Grove model** B. E. Deal and A. S. Grove, J. Appl. Phys. 36, 3770 (1965).

$$F_1 = h(c^* - c_0) \quad F_2 = \frac{D(c_0 - c_i)}{x_0} \quad F_3 = k_s c_i$$

$$F_1 = F_2 = F_3 = F$$

$$\frac{dx_0}{dt} = \frac{F}{N_1} = \frac{k_s c^*}{N_1(1 + k_s/h + k_s x_0/D)}$$

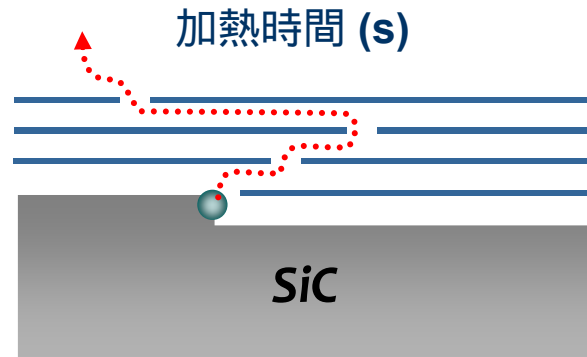
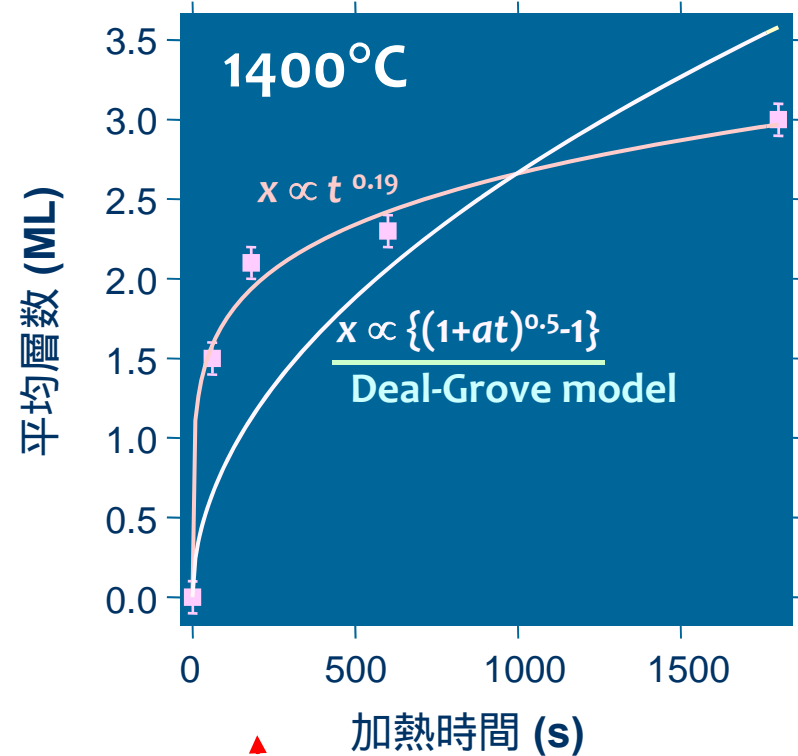
$$\longrightarrow x_0^2 + Ax_0 = B(t + \tau)$$



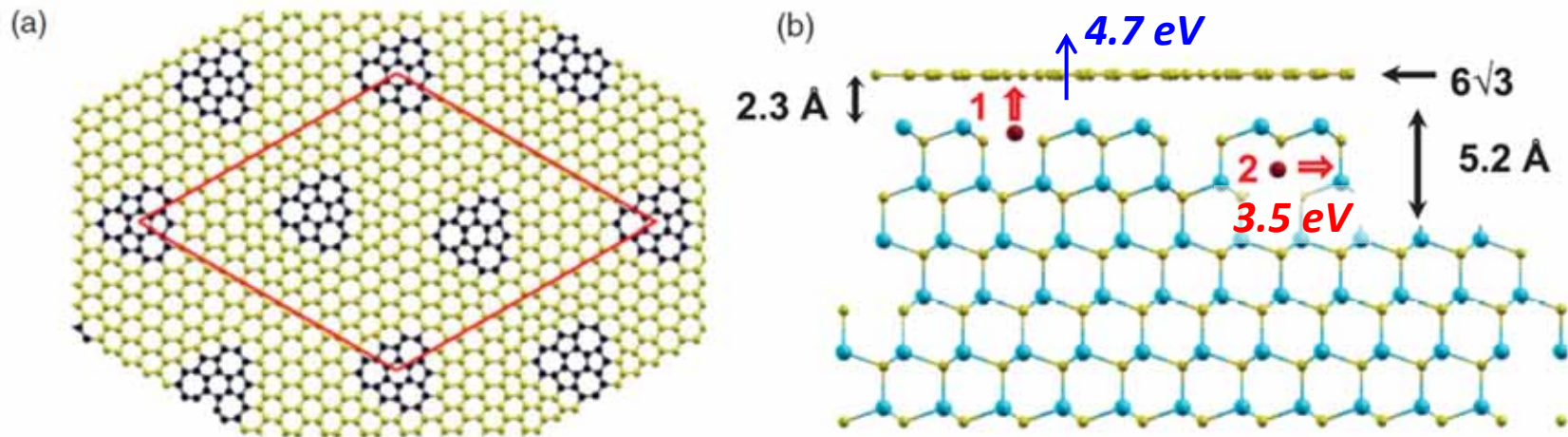
$$\left\{ \begin{aligned} A &= 2D \left( \frac{1}{h} + \frac{1}{k_s} \right) \\ B &= \frac{2Dc^*}{N_1} \\ \tau &= \frac{x_i^2 + Ax_i}{B} \end{aligned} \right.$$

$$\longrightarrow \frac{x_0}{A/2} = \left( 1 + \frac{t + \tau}{A^2/4B} \right)^{1/2} - 1$$

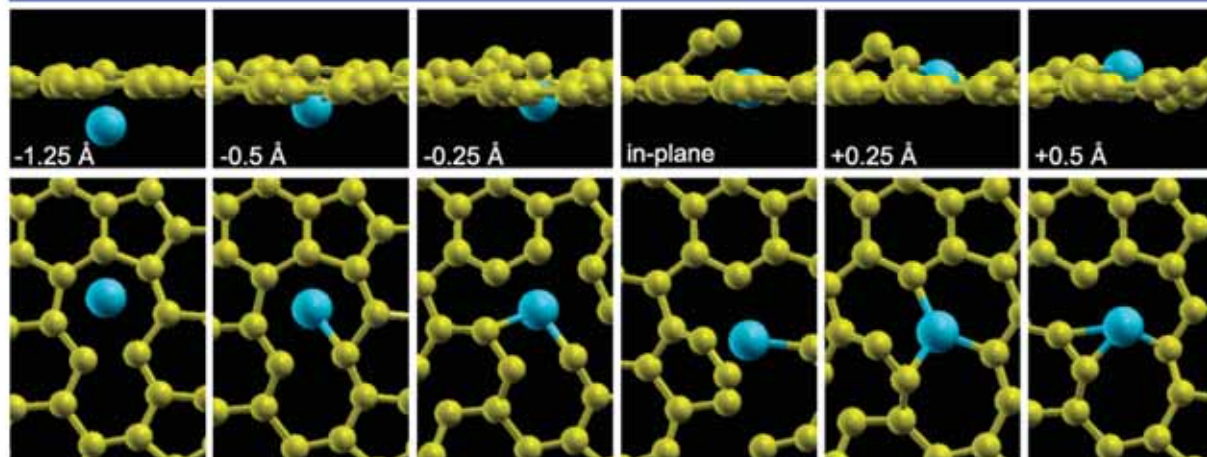
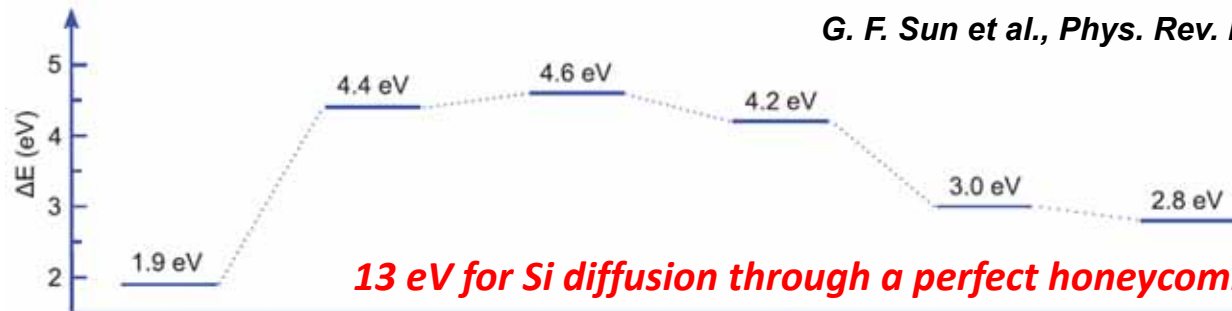
S. Tanaka et al., Phys. Rev. B 81, 041406(R) (2010).



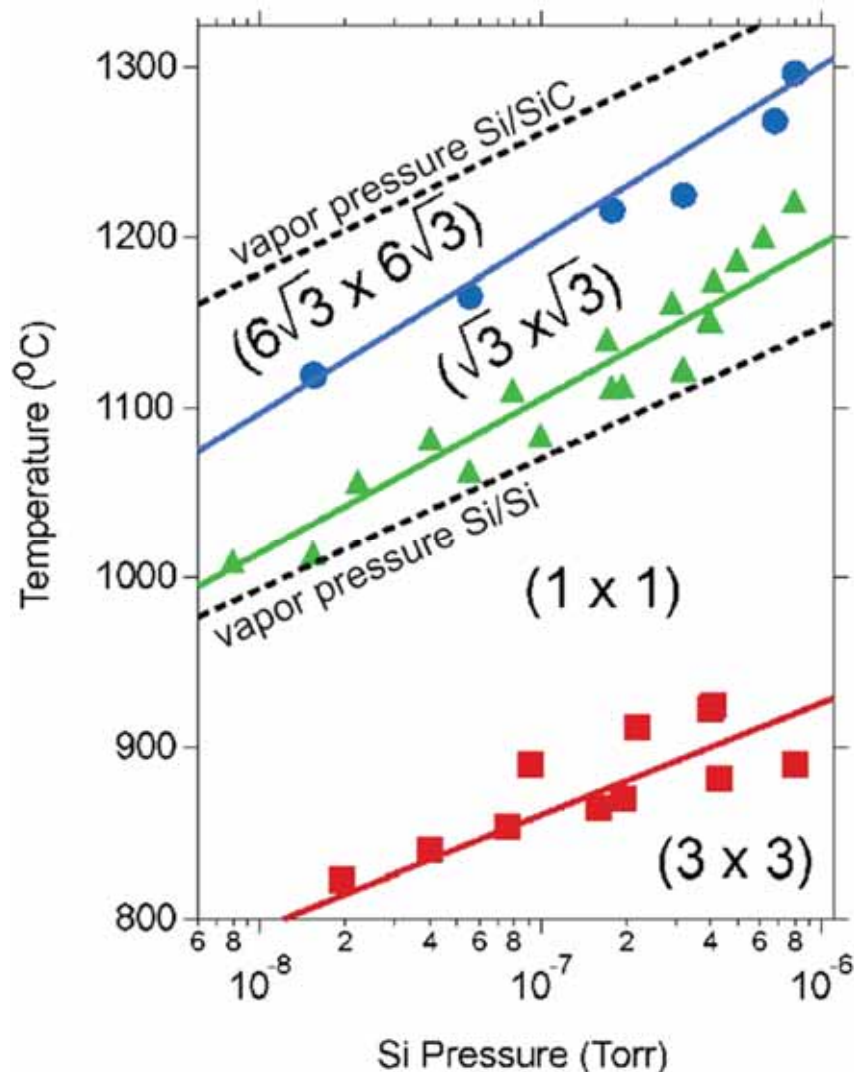
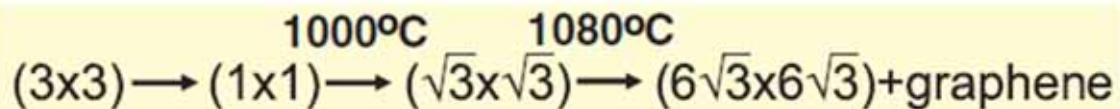
# Si外部拡散



G. F. Sun et al., Phys. Rev. B 84, 195455 (2011).

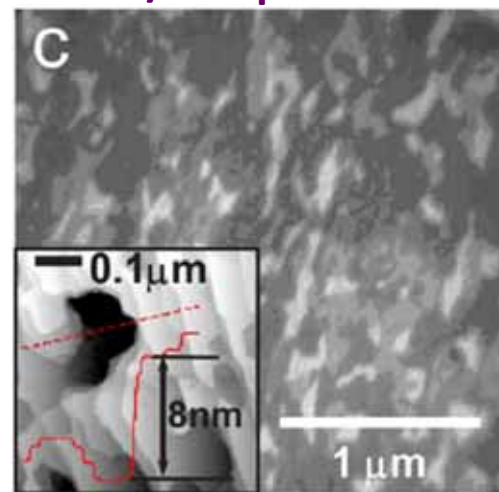


# グラフェン成長の熱力学



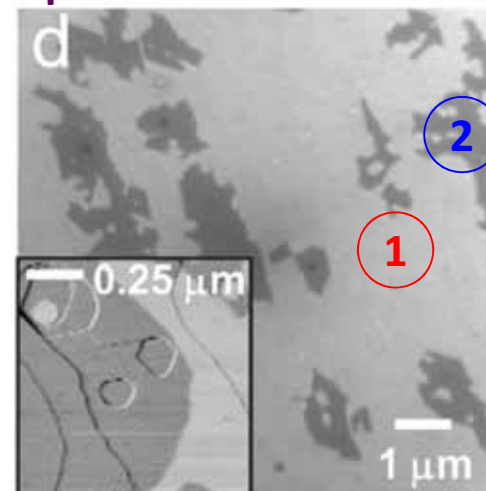
R. M. Tromp and J. B. Hannon, PRL 102, 106104 (2009).

W/O Si pressure



1300°C  
1-4 layers

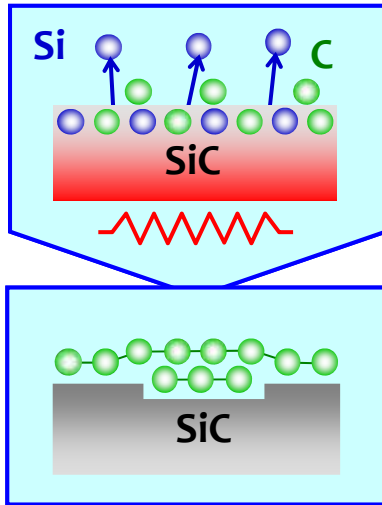
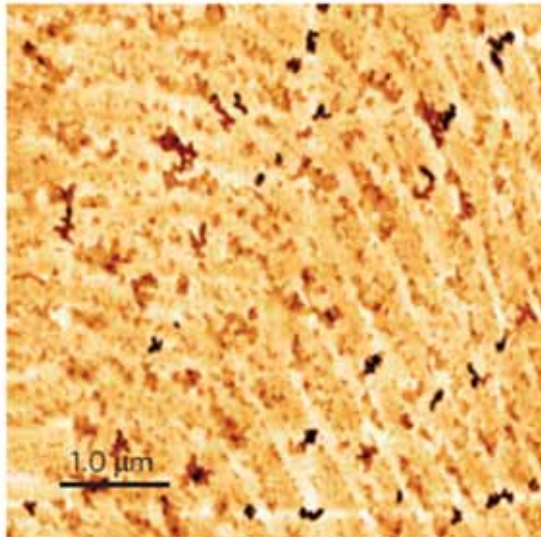
Si pressure of  $2 \times 10^{-5}$  Torr



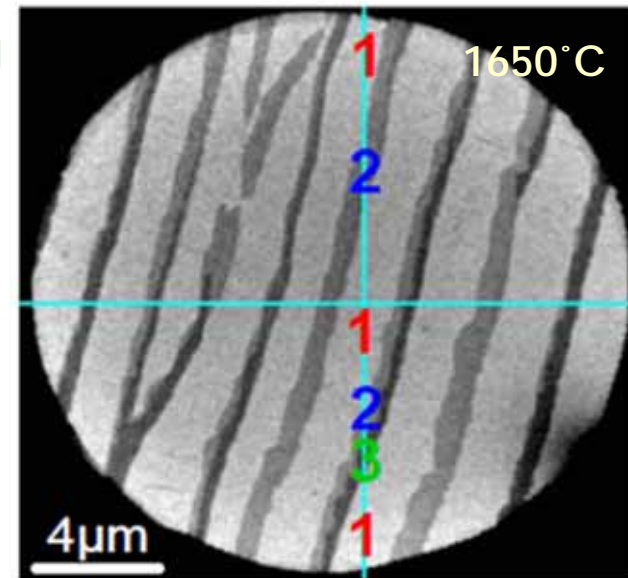
1300°C  
1-2 layers

# Ar中でのグラフェン成長

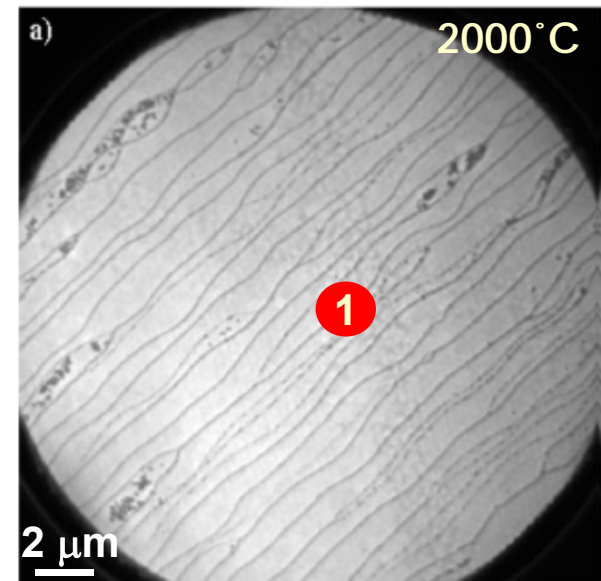
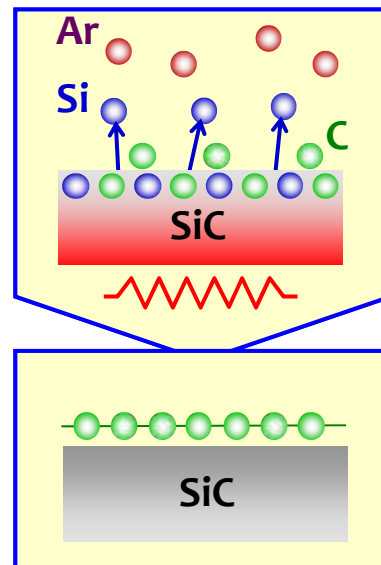
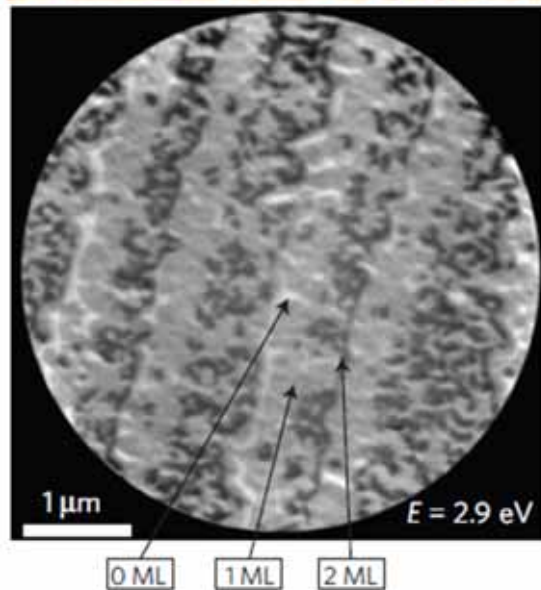
真空中



Ar中



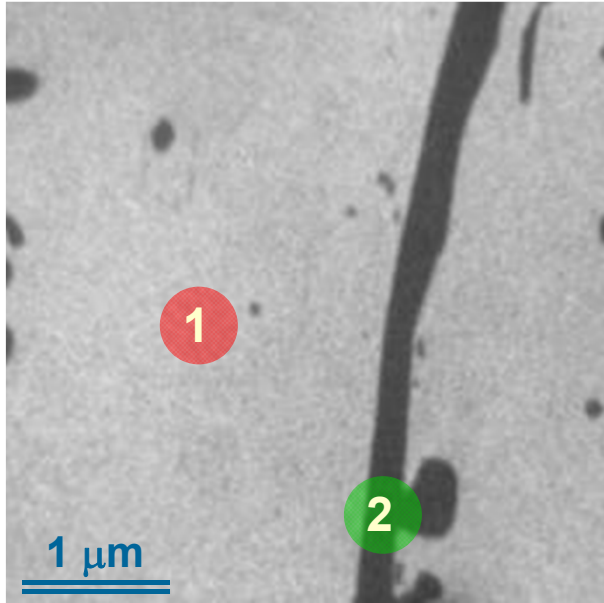
K. V. Emtsev et al., *Nature Mater.* 8, 203 (2009).



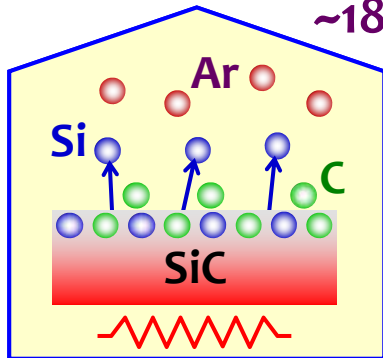
C. Virojanadara et al., *Phys. Rev. B* 78, 245403 (2008). 111

# 高均一グラフェン成長

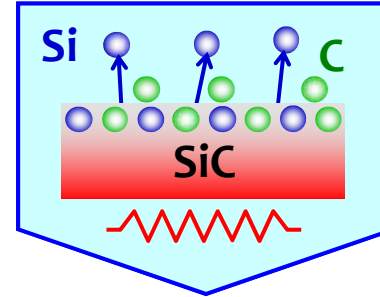
Ar ~25 Torr中



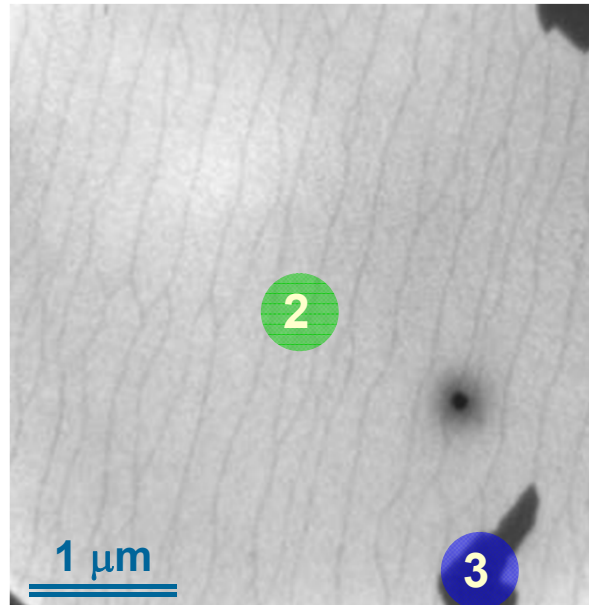
~1800°C



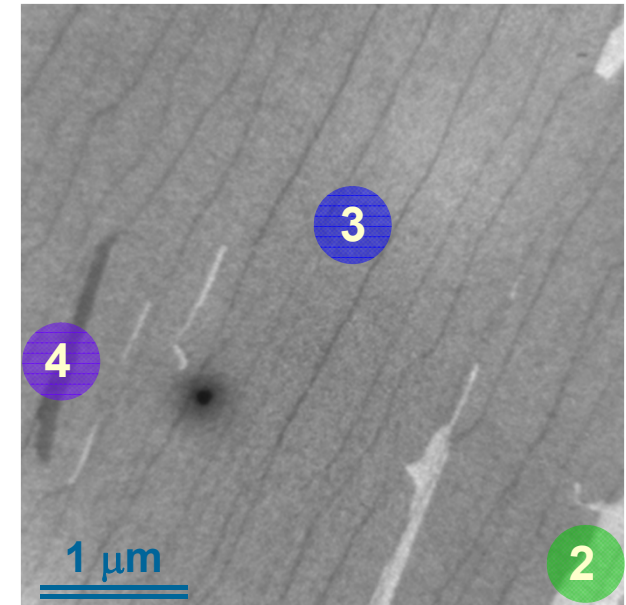
ArによるSi昇華抑制  
成長温度の上昇



~1250°C



~1150°C



超高真空中

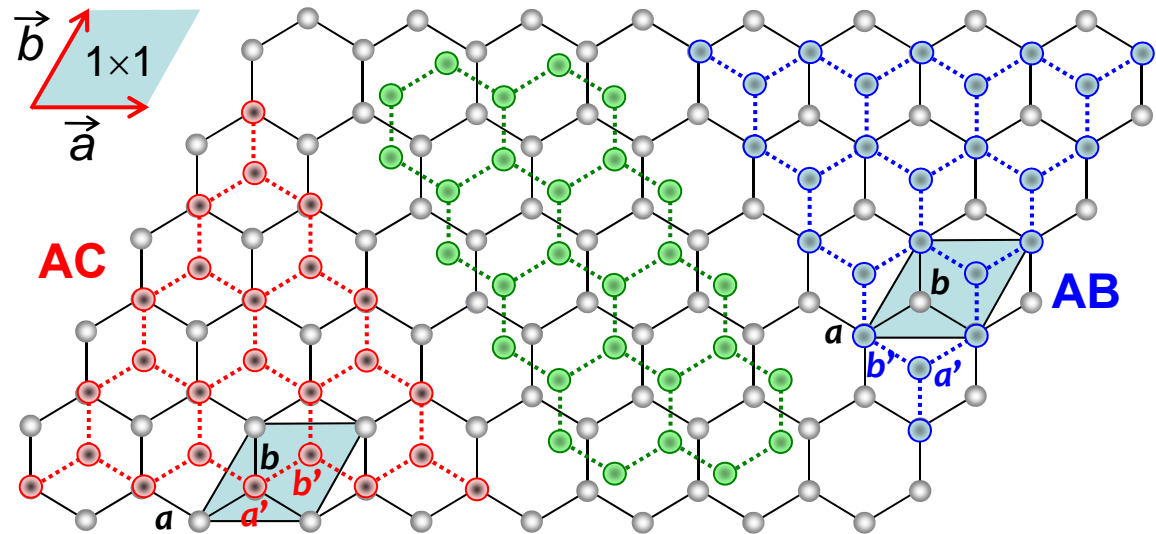
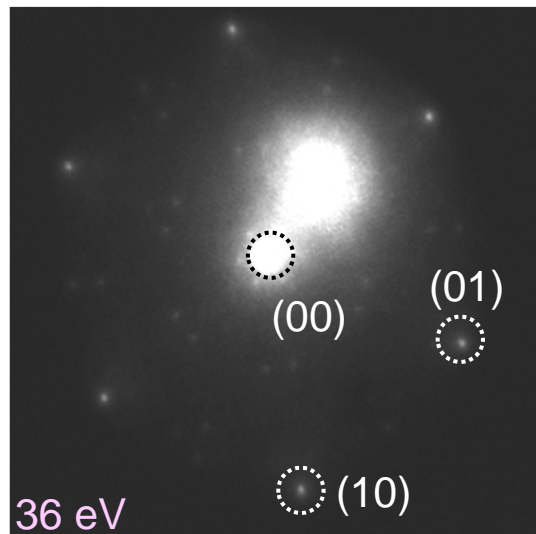
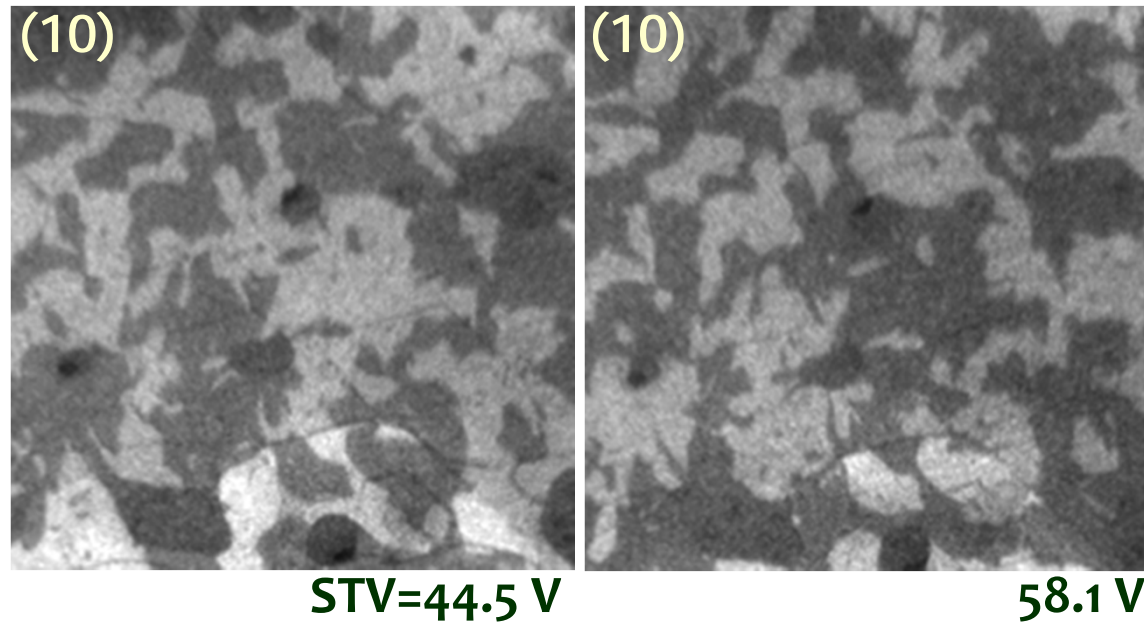
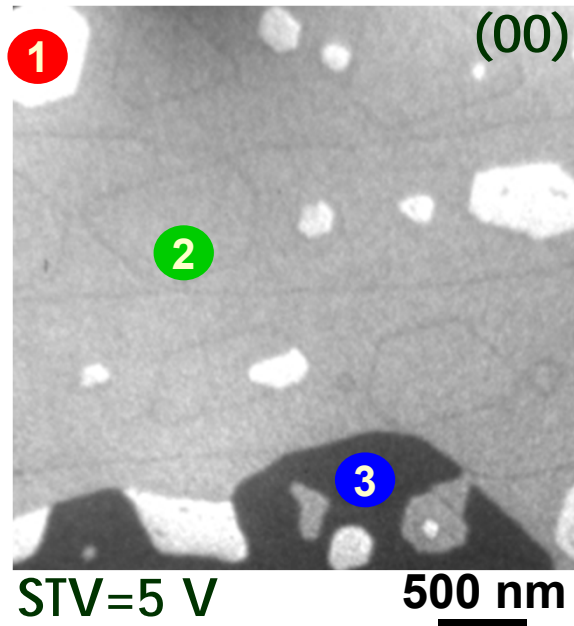
H. Hibino *et al.*, *J. Phys. D: Appl. Phys.* 43, 374005 (2010);  
ibid 45, 154008 (2012).

C. Virojanadara *et al.*, *Phys. Rev. B* 78, 245403 (2008).

K. V. Emtsev *et al.*, *Nature Mater.* 8, 203 (2009).

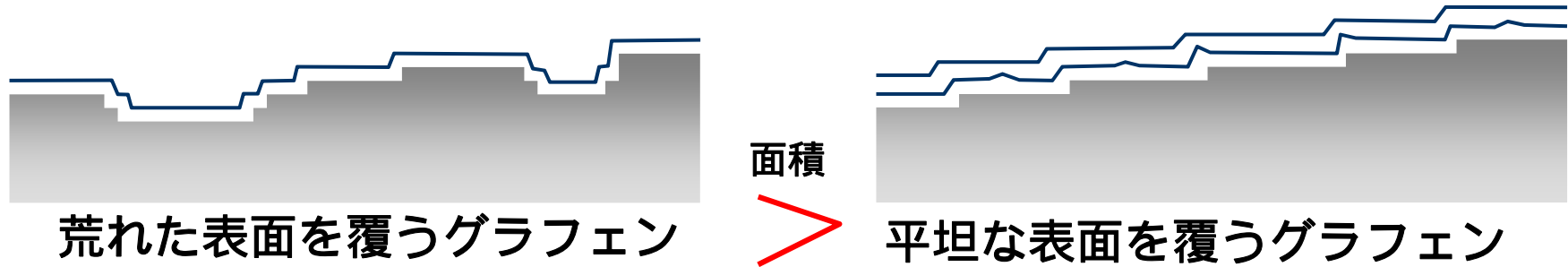


# SiC上2層グラフェンの積層ドメイン



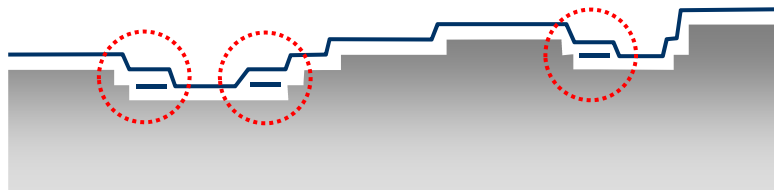
# 積層ドメインの起源

## (A) グラフェン間の面積差

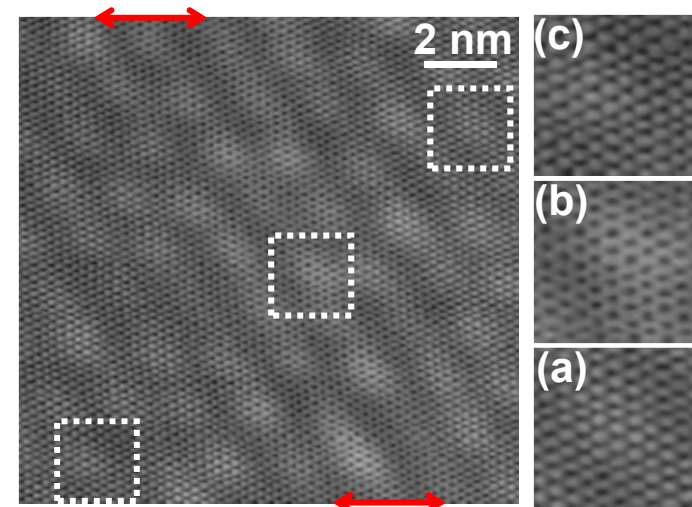


→ 面積差を境界で補償

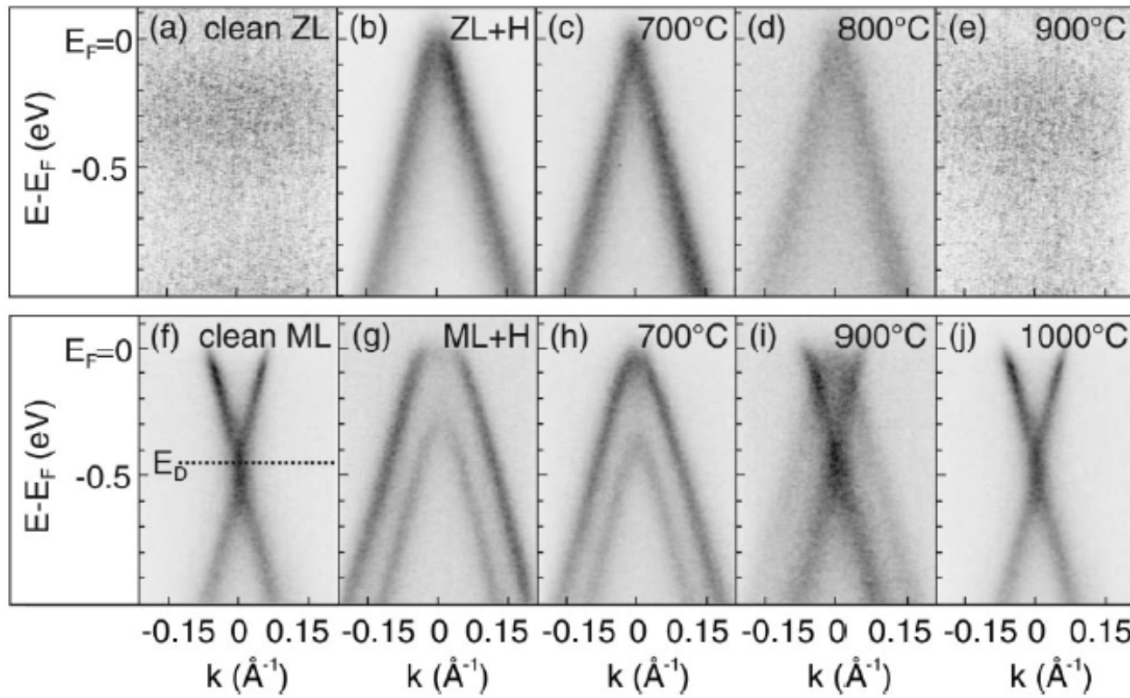
## (B) グラフェン核形成



AB or AC積層がランダムに選択され、固定される



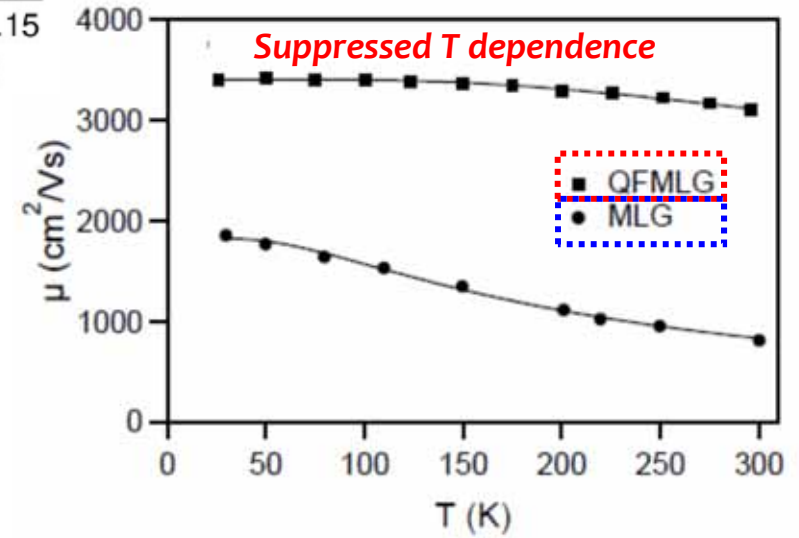
# 擬似フリースタンディンググラフェン



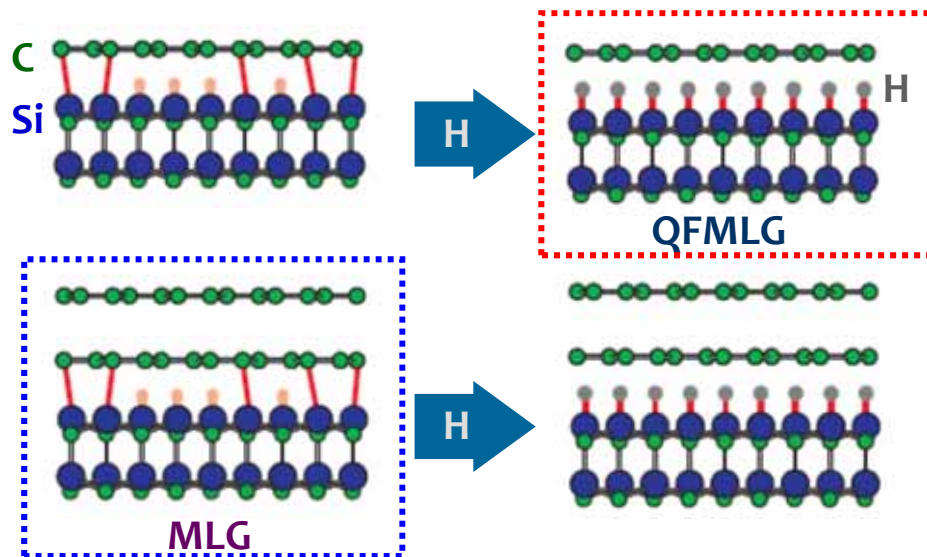
## 水素処理によるバンド構造変化

C. Riedl et al., *Phys. Rev. Lett.*  
103, 246804 (2009).

## 1層グラフェンの移動度



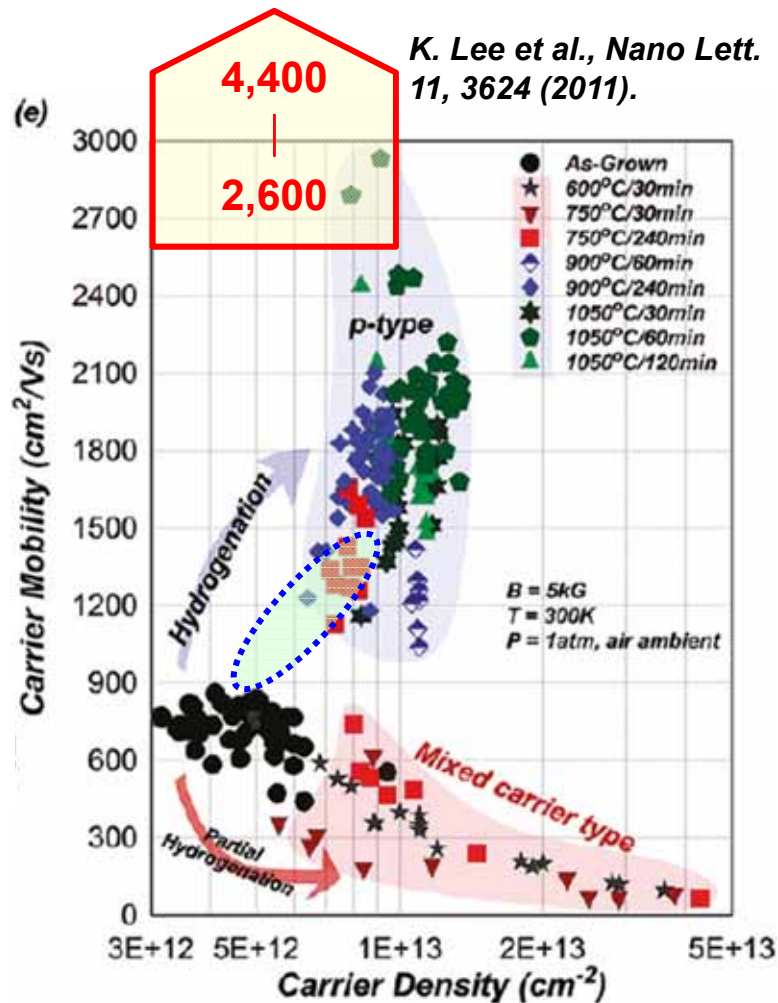
F. Speck et al., *Appl. Phys. Lett.* 99 122106 (2011).



# エピタキシャルグラフェンの高移動度化

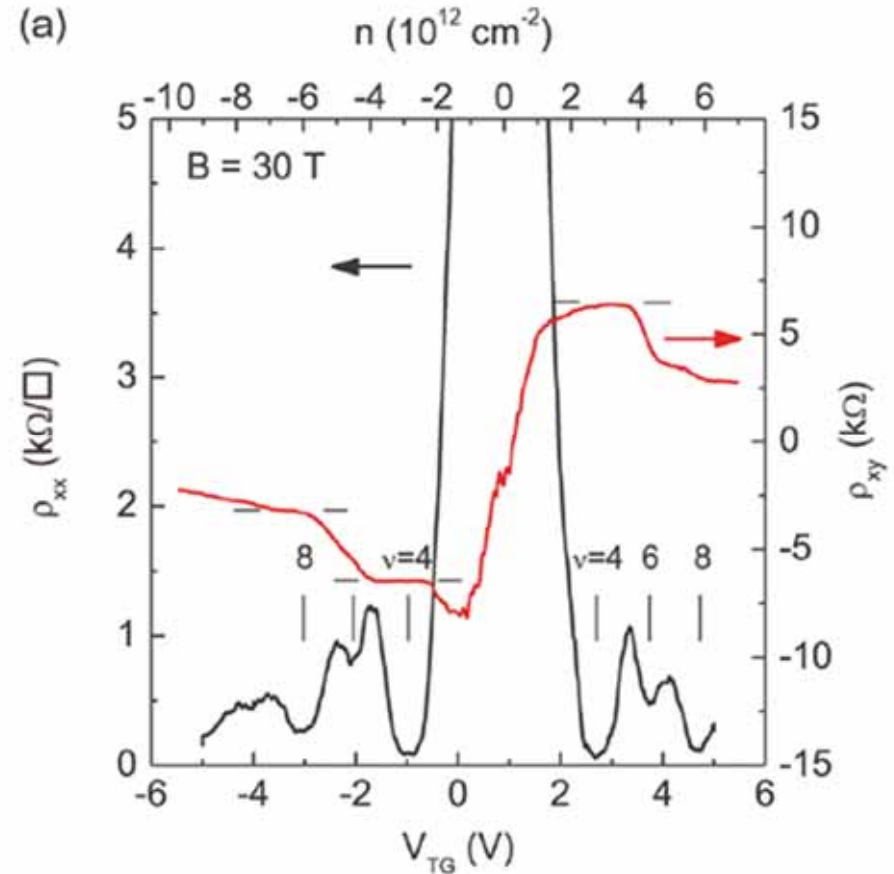
## ✓ 擬似フリースタンディング2層グラフェン

移動度向上



J. A. Robinson et al., *Nano Lett.* 11, 3875 (2011).

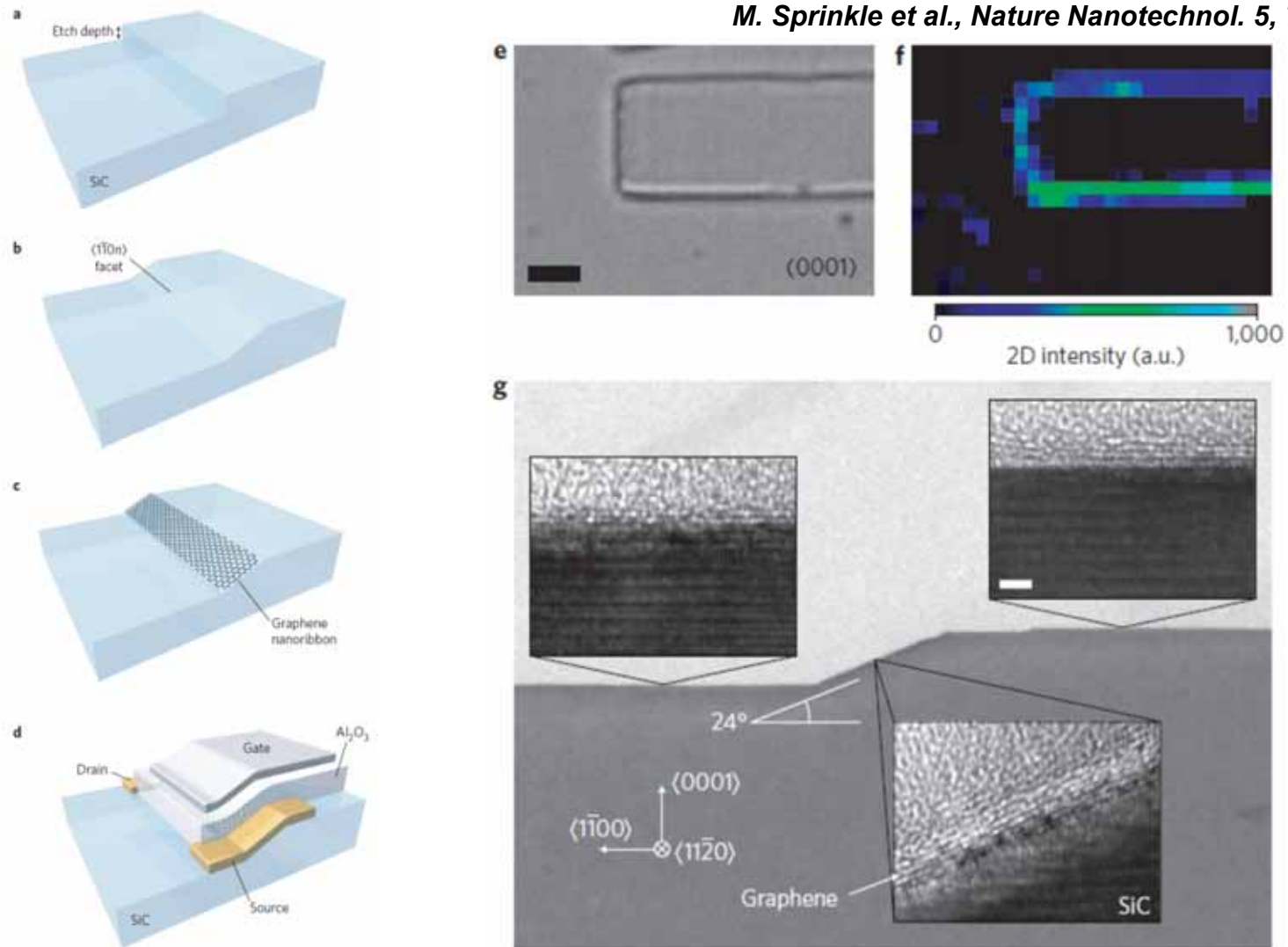
量子ホール効果



K. Lee et al., *Nano Lett.* 11, 3624 (2011).

# Structured エピタキシャルグラフェン

M. Sprinkle et al., Nature Nanotechnol. 5, 727 (2010).



グラフェン成長速度の面方位依存性を利用して、パターン  
SiC基板上にグラフェンナノリボンを位置選択成長

# まとめ

1. 金属上グラフェンCVD成長:  
大面積、低コスト、転写可      転写プロセス、多層化  
炭素固溶度により異なる成長機構  
単結晶グラフェンを目指した成長制御
2. 金属上グラフェン析出:  
大面積、低コスト、転写可      転写プロセス、単層化  
炭素アドアトムを介した成長  
基板平坦処理による単一ドメイン化
3. SiC上グラフェン成長機構:  
大面積、層数制御、転写レス      高コスト、転写難  
面方位に依存した成長  
加熱環境による層数制御  
グラフェンのSi原子に対する非透過性