Mathematical Aspects of Surface and Interface Dynamics 16
@The University of Tokyo, October 17-19, 2018

Crystal growth of two-dimensional materials and heterostructures

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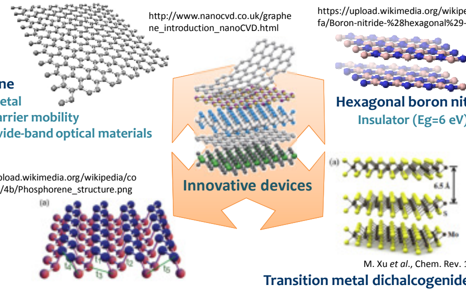
CONTENTS

2D materials and their heterostructures

Common properties of 2D materials: flexibility, transparency, large surface area, designability of heterostructures



http://www.nanocvd.co.uk/graphene_introduction_nanoCVD.html

https://upload.wikimedia.org/wikipedia/commons/f/fa/Boron-nitride-%28hexagonal%29-side-3D-balls.png

https://upload.wikimedia.org/wikipedia/commons/4/4b/Phosphorene_structure.png

M. Xu *et al.*, Chem. Rev. 113, 3766 (2013).

Graphene
Semimetal
High carrier mobility
Ultra-wide-band optical materials

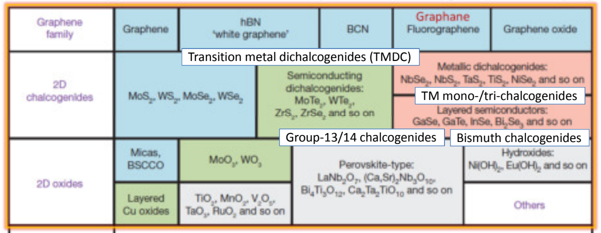
Hexagonal boron nitride (*h*BN)
Insulator (Eg=6 eV)

Phosphorene
Direct bandgap semiconductor
High carrier mobility
Thickness-dependent bandgap

Transition metal dichalcogenides (TMDCs)
Semiconductor
Thickness-dependent bandgap
Indirect-to-direct bandgap transition
Spin-valley coupling

Library of 2D Materials

A. K. Geim and I. V. Grigorieva, Nature 499, 419 (2013).



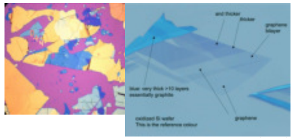
Graphene family	Graphene	hBN 'white graphene'	BCN	Graphane Fluorographene	Graphene oxide
2D chalcogenides	MoS_2, WS_2, $MoSe_2$, WSe_2	Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on		Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on	
2D oxides	Micas, BSCCO Layered Cu oxides	MoO_3, WO_3 TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on	Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on	Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on Others	

Transition metal dichalcogenides (TMDC)
TM mono-/tri-chalcogenides
Group-13/14 chalcogenides
Bismuth chalcogenides

Halides	ZrBr
Xenes	Phosphorene, Arsenene, Antimonene, Bismuthene Silicene, Germanene, Stanene Borophene, Gallenene
MXenes	Ti_2C, Ti_3C_2, Ti_4N_3, and so on (A is removed from $M_{n+1}AX_n$, transition metal carbides, nitrides, or carbonitrides).

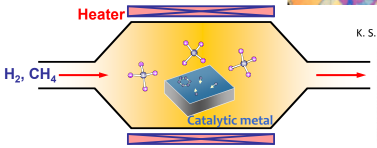
Graphene fabrication method

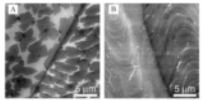
- ✓Exfoliation from graphite



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

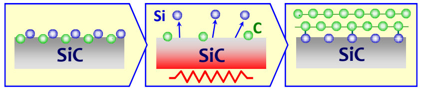
- ✓Chemical vapor deposition (CVD)
  - ☺ Scalability, low cost
  - ☹ Transfer required

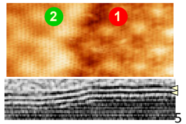




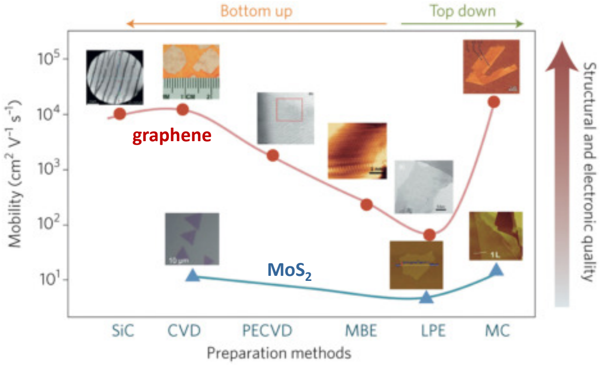
X. Li *et al.*, Science 324, 1312 (2009).

- ✓SiC thermal decompostion
  - ☺ Device fabrication of as-grown graphene
  - ☹ High cost



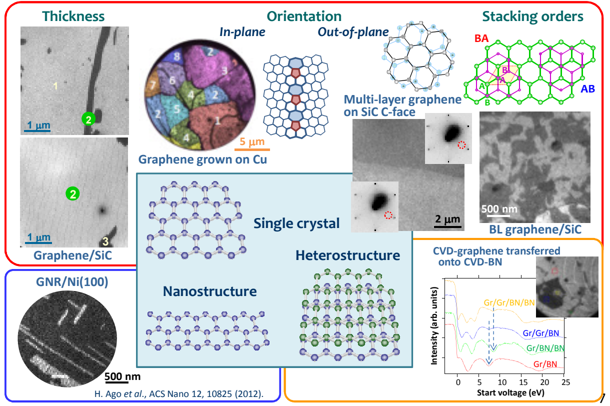


Fabrication methods of graphene



G. Fiori *et al.*,Nature Nanotechnol. 9, 768 (2014).

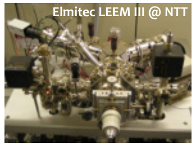
Growth control of 2D materials

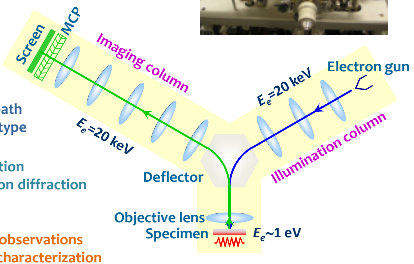


H. Ago *et al.*, ACS Nano 12, 10825 (2012).

Low-energy electron microscopy (LEEM)

**Low-energy electron microscopy (LEEM):
microscopy using elastically backscattered electrons with the typical energy of 1-100 eV**



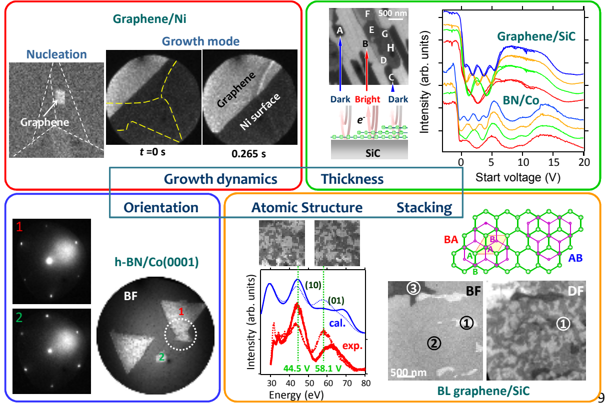


- ✓High reflectivity
- ✓Short inelastic mean free path
- ✓Projection (non-scanning) type

- ✓Fast image acquisition
- ✓Low-energy electron diffraction
- ✓Surface sensitivity

- ✓ Dynamical observations
- ✓ Structural characterization

Structure characterizations using LEEM



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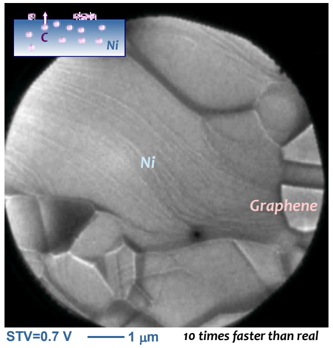
1. *2D materials: growth and characterization techniques*
2. *In-situ observations of graphene segregation on Ni*
3. *CVD growth of high-quality monolayer and bilayer graphene*
4. *Growth and structural characterization of hexagonal boron nitride and 2D heterostructures*

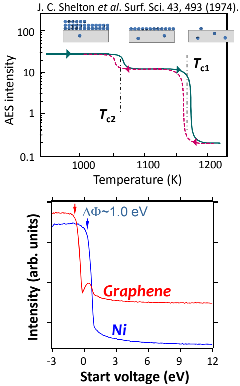
Graphene segregation on (111) grain in poly-Ni film

Graphene growth from Ni grain boundaries

During cooling from 893°C to 882°C

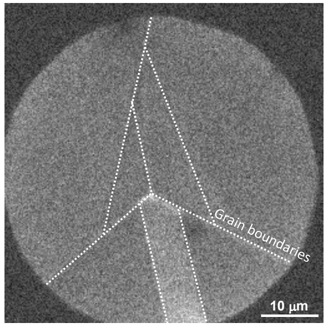


J. C. Shelton *et al.* Surf. Sci. 43, 493 (1974).



Graphene nucleation on poly-Ni foil

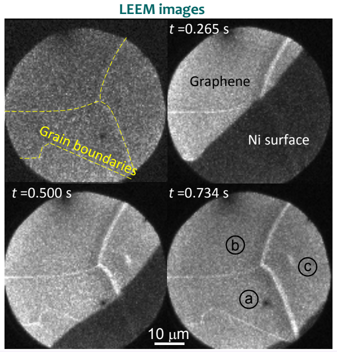
Real-time LEEM observations



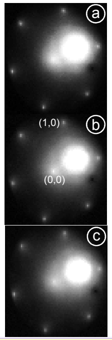
G. Odahara *et al.*, Appl. Phys. Exp. 5, 035501 (2012).

Carpet-like growth of graphene on poly-Ni foil

LEEM images



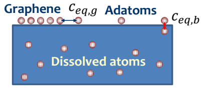
SA-LEED



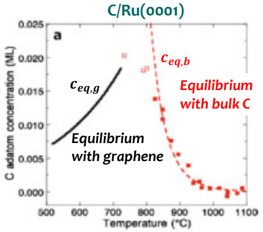
Graphene grows continuously across Ni grain boundaries.

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

Graphene segregation on poly-Ni foil

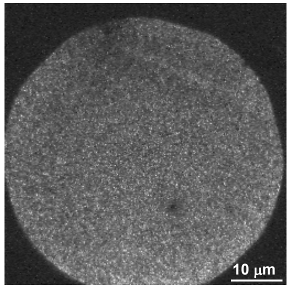


C/Ru(0001)



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

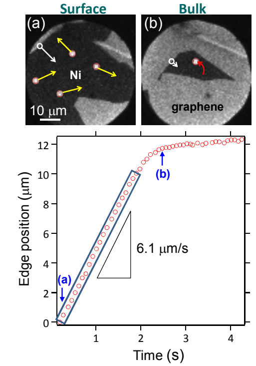
Real-time LEEM observations

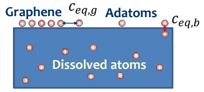


Hibino *et al.*, OYOBUTURI 82, 137 (2013).

Growth of monolayer graphene on Ni

Carbon supply from:





Linear dependence

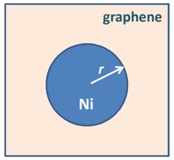
$v_{step} = Ka(c_{eq,b} - c_{eq,g})$

⇒ **Fast surface diffusion**

Slowing down

⇒ **Slow bulk-surface exchange and/or bulk diffusion**

Growth of monolayer graphene on Ni



Attachment/detachment limited

Flux from bulk:

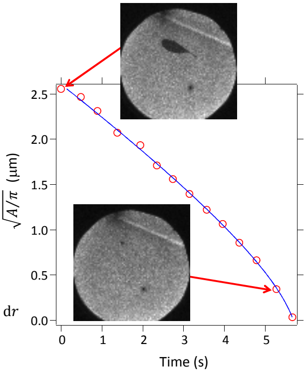
$F = K_1 \pi r^2 (c_{eq,b} - c)$

Flux to graphene:

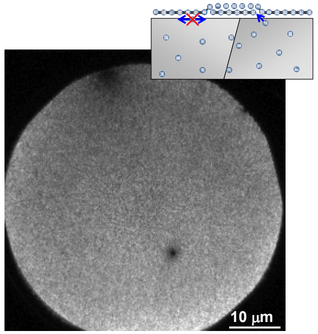
$F = K_2 2\pi r\ (c - c_{eq,g})$

$$\longrightarrow -\mathrm{d}t = \frac{1}{a\ (c_{eq,b} - c_{eq,g})}\left(\frac{1}{K_2} + \frac{2}{K_1 r}\right)\mathrm{d}r$$

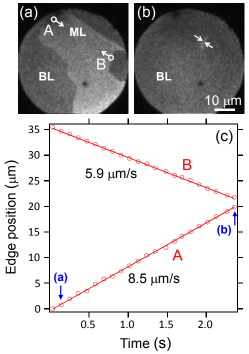
$$\longrightarrow -t + t_0 = \frac{1}{a\Delta c}\left(\frac{r}{K_2} + \frac{2}{K_1}\ln r\right)$$



Growth of bilayer graphene on Ni



Hibino *et al.*, OYOBUTURI 82, 137 (2013).



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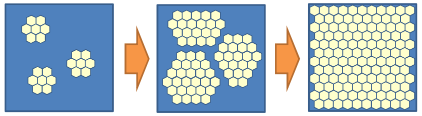
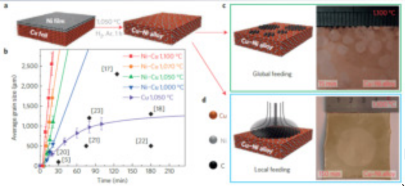
Approach towards single crystal growth

(1) Epitaxial growth;
coalescence of grains with the same orientation



(2) Isolated growth;
enlargement of a single grain as large as possible

Millimeter- to centimeter-sized graphene



Inch-sized graphene

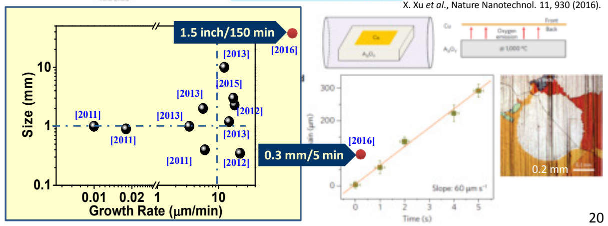
- ☐ Local supply of feedstock
- ☐ Cu-Ni alloy substrate

T. Wu *et al.*, Nature Mater. 15, 43 (2016).

Fast growth

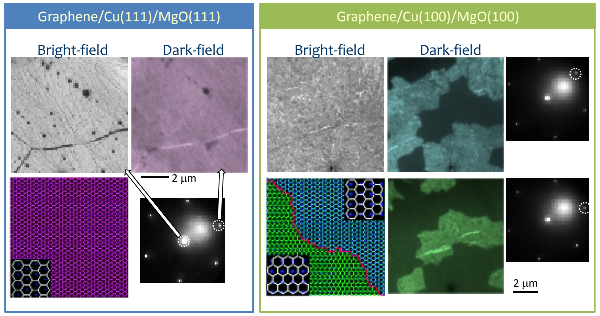
- ☐ Continuous Oxygen supply from oxide support

X. Xu *et al.*, Nature Nanotechnol. 11, 930 (2016).



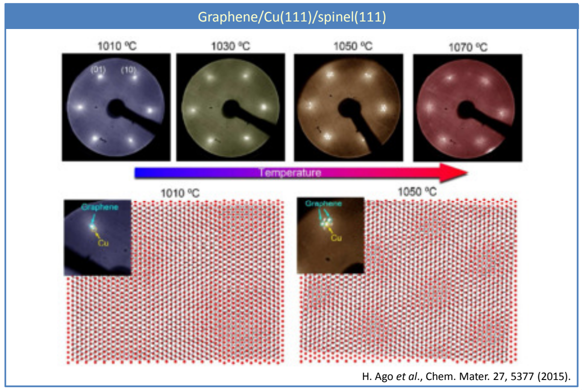
Single-orientation graphene grown by CVD

☐ CVD growth on heteroepitaxial metal films



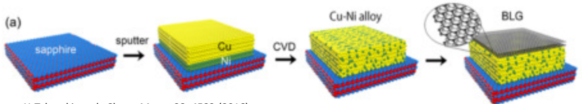
Y. Ogawa *et al.*, J. Phys. Chem. Lett. 3, 219 (2012).

Dependence of alignment on CVD temperature



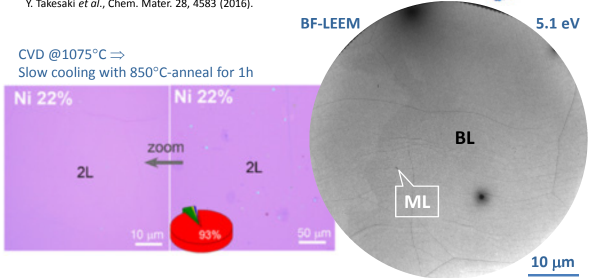
H. Ago *et al.*, Chem. Mater. 27, 5377 (2015).

Highly uniform bilayer graphene on Ni-Cu(111)

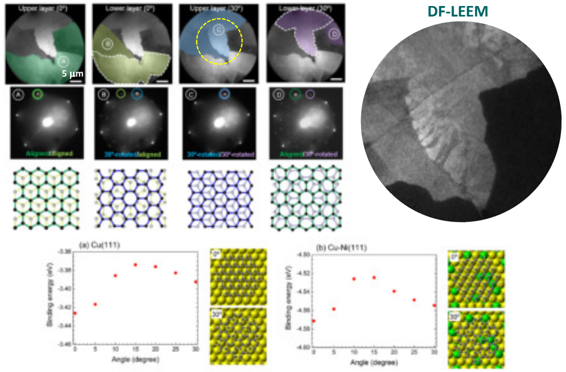


Y. Takesaki *et al.*, Chem. Mater. 28, 4583 (2016).

CVD @1075°C ⇒
Slow cooling with 850°C-anneal for 1h



Domain structure in bilayer graphene on NiCu



Y. Takesaki *et al.*, Chem. Mater. 28, 4583 (2016).

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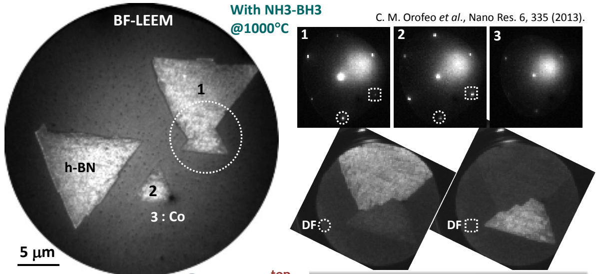
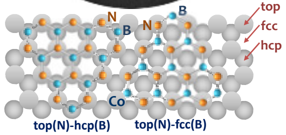
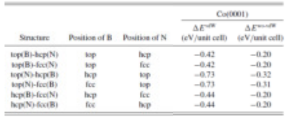
CVD growth of monolayer *h*-BN on Co(0001)



With NH3-BH3
@1000°C

C. M. Orofeo *et al.*, Nano Res. 6, 335 (2013).

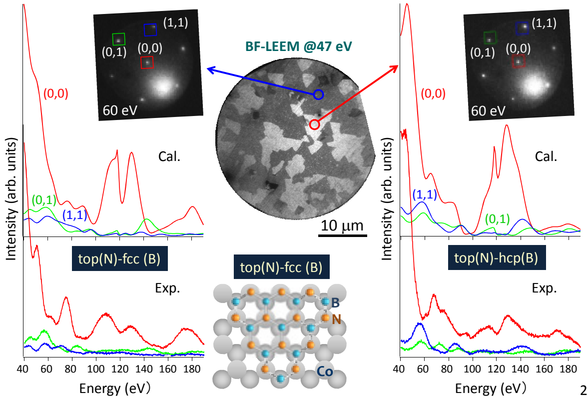




			Co(0001)	
Structure	Position of B	Position of N	ΔE [illegible] (eV/unit cell)	ΔE [illegible] (eV/unit cell)
top(B)-hcp(N)	top	hcp	−0.42	−0.20
top(B)-fcc(N)	top	fcc	−0.42	−0.20
top(N)-hcp(B)	hcp	top	−0.73	−0.32
top(N)-fcc(B)	fcc	top	−0.73	−0.31
hcp(B)-fcc(N)	hcp	fcc	−0.44	−0.20
hcp(N)-fcc(B)	fcc	hcp	−0.44	−0.20

N. Joshi and P. Ghosh, PRB 87, 235440 (2013).

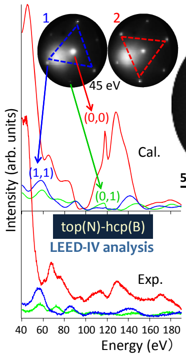
CVD growth of monolayer *h*-BN on Co(0001)

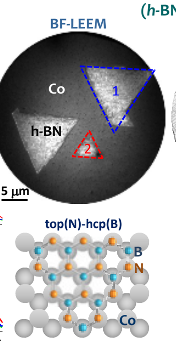


CVD-grown monolayer *h*-BN on Co(0001)

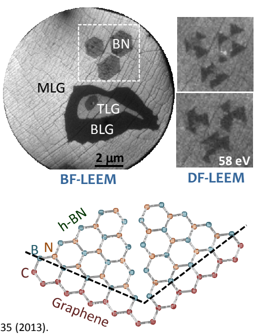
☐ **Monolayer *h*-BN on Co**

☐ ***h*-BN/graphene lateral heterostructure**
(*h*-BN growth after graphene growth)



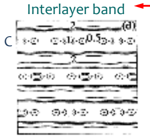


C. M. Orofeo *et al.*, Nano Res. 6, 335 (2013).

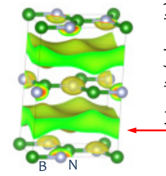


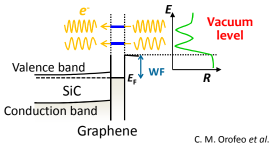
E. Maeda *et al.*, APEX 10, 055102 (2017).

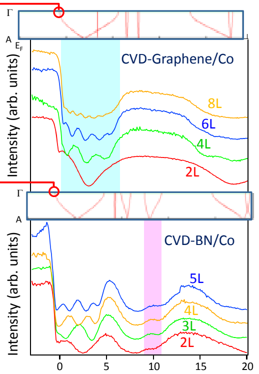
Low-energy electron reflectivity of graphene/*h*-BN



J. -C. Charlier et al., Phys. Rev. B 43, 4579 (1991).





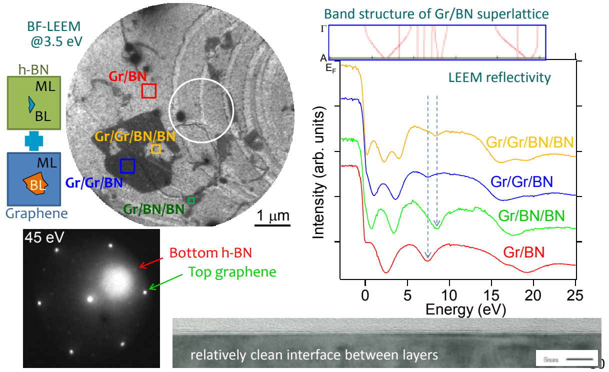


C. M. Orofeo *et al.*, Nano Res. 6, 335 (2013).

Artificial graphene/*h*-BN heterostructure

C. M. Orofeo *et al.*, RPGR 2013.

Graphene/*h*-BN/Co(0001): CVD-graphene grown on Cu foil was transferred onto h-BN.



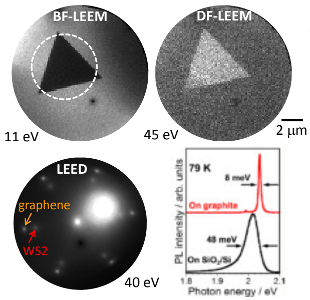
Direct growth of TMDCs on 2D materials

Merits of direct growth:
scalability, cost efficiency, clean interfaces

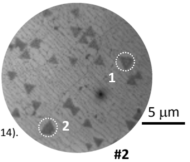
☐ **CVD-grown WS_2/ exfoliated graphite flake**

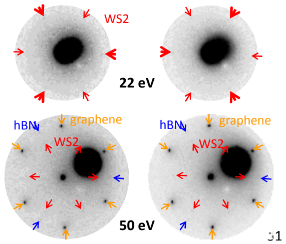
Y. Kobayashi *et al.*, ACS Nano 9, 4056 (2015).

☐ **CVD-grown WS_2/ exfoliated h-BN flake**



M. Okada *et al.*, ACS Nano 8, 8273 (2014).





SUMMARY

(1) 2D materials
- ✓ New physics and new applications from individual materials and their heterostructures

(2) Structural characterizations using LEEM
- ✓ Powerful tool for investigating growth dynamics and characterizing various structural features of 2D materials

(3) Growth processes of 2D materials
- ✓ Rapid progress in crystal quality and versatility
- ✓ Comparatively little knowledge about growth mechanism

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