RESEARCH LABORATORY OF ELECTRONICS AT MIT

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- The views expressed herein do not necessarily represent the views of the U.S.Department of Energy or the United States Government.

Graphene nanopattern for single-crystal film growth, defect reduction, and layer transfer

2022 MRS Fall Meeting

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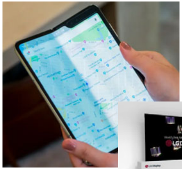
Massachusetts Institute of Technology

Outline

- ***Introduction***
  - Motivation for freestanding membranes
  - Remote epitaxy
- ***Producing epitaxial membranes*** by epitaxy on 2D materials
  - Limitations of remote epitaxy
  - Selective-area epitaxy on nanopatterned 2D materials
- ***Conclusion***

Future directions of Electronics

Bendable Electronics

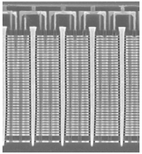


Samsung foldable phone

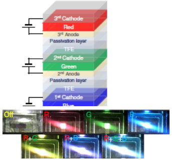
LG Rollable TV
CES 2019/2020

3D Electronics

Samsung 3D NAND flash

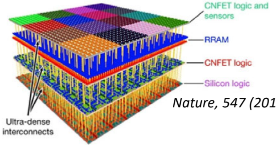


Vertically stacked organic LED



Nature Comm (2020) 11:2732

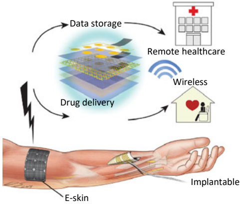
Edge computing 3D chip: Logic + memory + sensors



Nature, 547 (2017) 74-78

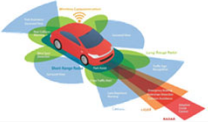
Sensor platforms and IoT

Wearable/Bioelectronics



Smart sensor network
Monitoring / Surveillance

Autonomous vehicles



AR/VR devices

Integration of Flexible layers

Integration of Functional layers

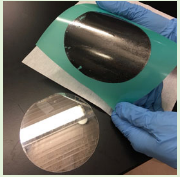
Integration with Target platforms

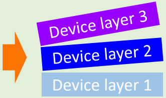
Heterogeneous Integration **is the key for next-generation electronics**

How can we integrate device layers?

Performance | **Compatibility** | **Flexibility** | **Cost**

	Method	Electronic / Photonic Performance	Process Compatibility	Flexibility	Cost
	Coating	Not as good a			
(					



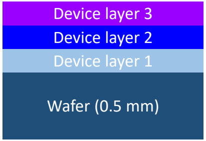


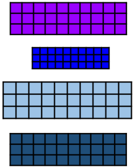
UNIVERSAL approach:

"Detachment from wafers" and "Layer transfer" for stacking flexible epitaxial layers

Integration of single-crystalline electronics

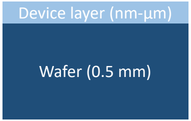
Restricted due to lattice mismatch

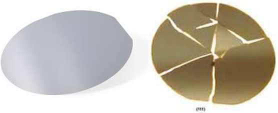




Flexibility of single-crystalline electronics

Too thick to be flexible





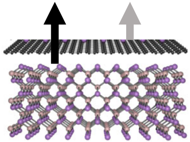
Remote epitaxy for single-crystal membrane production

Graphene transparency enables epitaxy through graphene

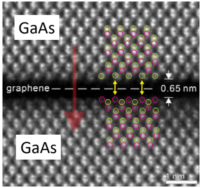
Penetrated interaction >> Van der Waals interaction

Graphene

Wafer



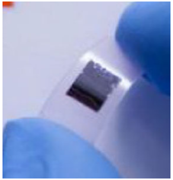
x-TEM



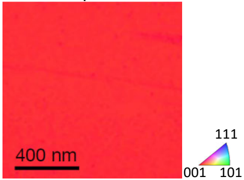
H. Kim, *et al.*, ***J. Appl. Phys.***, 130, 174901 (2021)

Weak vdW interface enables membrane exfoliation

Exfoliated GaAs

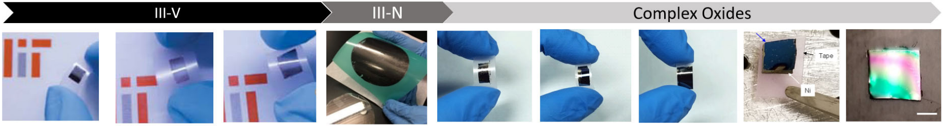


EBSD map



Nature, 544, 340 (2017)

Various materials work for remote epitaxy



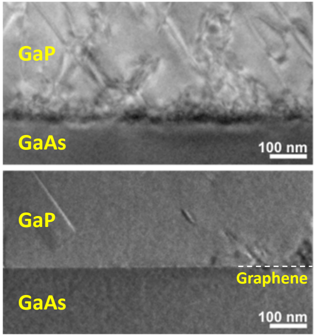
GaAs | InP | GaP | GaN | $SrTiO_3$ | $CoFe_2O_4$ | $Y_3Fe_5O_{12}$ | $BaTiO_3$ | PMN-PT

Remote "heteroepitaxy" reduces dislocation density

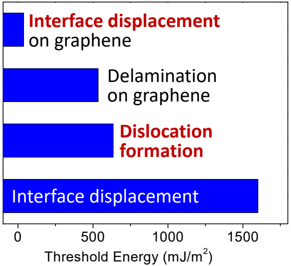
Epitaxy of GaP on GaAs
(4% lattice mismatch)

Conventional
Heteroepitaxy

"REMOTE"
Heteroepitaxy



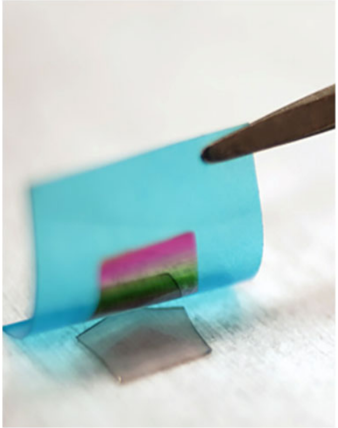
Energy barrier for relaxation



Reduced dislocation by "spontaneous relaxation" on graphene

S. Bae, et al., ***Nature Nanotechnology*** 15,272 (2020)

Prospects of Remote Epitaxy



Thin films that are…
1. **Freestanding**
2. **Flexible**
3. **Single-crystalline**
4. **Ultrathin**

Materials library is expanding!

But still mostly on materials development

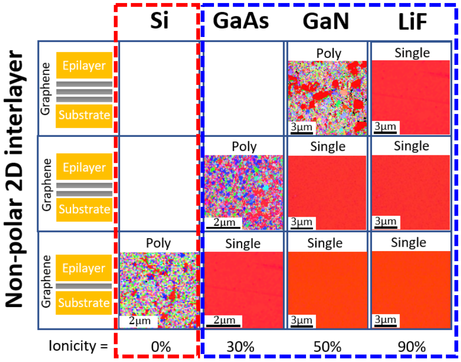
Reported materials and processes for remote epitaxy [redacted]

Grown layer	Substrate material	2D interlayer material	Interlayer formation	Growth method	Note
GaAs	GaAs	Monolayer graphene	Dry transfer	MOCVD	Transfer method significantly affects the quality of remote epitaxy
InP	InP	Monolayer graphene	Dry transfer	MOCVD	N_2 carrier is used for growth
GaP	GaP	Monolayer graphene	Dry transfer	MOCVD	N_2 carrier is used for growth
(In)GaP	GaAs	Monolayer graphene	Dry transfer	MOCVD	Graphene allows for spontaneous relaxation of epilayer
GaN	GaN, Al_2O_3	One or two-layer graphene	Dry transfer, wet transfer	MOCVD, MBE	Single-crystal growth up to two graphene layers
GaN	SiC	Monolayer graphene	Grown	MBE, MOCVD	Both epitaxial graphene and graphene buffer layer can be used
AlN	AlN, Al_2O_3	Monolayer graphene	Grown, wet transfer	MBE, MOCVD	Nucleation density is generally higher for AlN than GaN
ZnO	SiC	Monolayer graphene	Grown	Radio-frequency sputtering	Graphene buffer layer is used
STO	STO	Two-layer graphene	Dry transfer	PLD	High-temperature growth results in the worst yield out of all complex-oxide materials
CFO	MAO	One or two-layer graphene	Dry transfer	PLD	Owing to the low-temperature growth condition, monolayer graphene also works
YIG	GGG	Two-layer graphene	Dry transfer	PLD	Post annealing helps improve crystallinity
BTO	STO	Monolayer graphene	Dry transfer, wet transfer	MBE	Using ozone as an oxygen source will instantly etch graphene
$CsPbBr_3$	NaCl	Monolayer graphene	Wet transfer	CVD	Modified wet transfer process is used
VO_2	Al_2O_3	Monolayer graphene	Wet transfer	PLD	Post annealing of the epitaxial film is needed
$LiNbO_3$	Al_2O_3	Monolayer graphene	Wet transfer	PLD	Post annealing of the epitaxial film is needed
Copper	Al_2O_3	Monolayer graphene	Wet transfer	Thermal evaporation	Before the growth, the vacuum chamber was coated with copper film to block any contaminations
GdPtSb	Al_2O_3	Monolayer graphene	Wet transfer	MBE	Successfully exfoliated without the need for a metal stressor layer
HfS_2	Al_2O_3	One or two-layer h-BN	Wet transfer	CVD	Modified wet transfer process; photodetectors are demonstrated; h-BN is used as an interlayer
ZnO (nanorod)	Polycrystal ZnO	Monolayer graphene	Wet transfer	Hydrothermal method	Lattice transparency of graphene is reduced by increased graphene thickness
ZnO (micro-rod)	ZnO on r-Al_2O_3 and c-GaN	One to three-layer graphene	Wet transfer	Hydrothermal method	High-temperature annealing is required to heteroepitaxially crystallize the spin-coated ZnO layer on r-Al_2O_3 and c-GaN substrates
ZnO (nanorod)	ZnO nanorod	Monolayer MoS_2	Wet transfer	Hydrothermal method	Remote epitaxy is conducted on nanorods; MoS_2 is used as an interlayer
ZnO (rod, disc, needle)	GaN	One to three-layer graphene	Wet transfer	Hydrothermal method	Morphology is controlled by chemicals and additives, and position can be controlled by mask patterns
GaN (rod, polyhedron)	Al_2O_3	One or two-layer graphene	Wet transfer	MOCVD	High III/V molar flow ratio is needed to form rod-shaped structures
GaN (polyhedron)	AlN	Monolayer graphene	Wet transfer	MOCVD	Nuclei emerge from triangular to hexagonal shape
GaN (tetrahedron)	SiC	Monolayer graphene	Grown	MOCVD	Pre-annealing treatment in H_2/NH_3 mixture environment is required to grow remote epitaxial structures before the nucleation step

H. Kim, et al., ***Nature Reviews Methods Primers*** 2, 40 (2022)

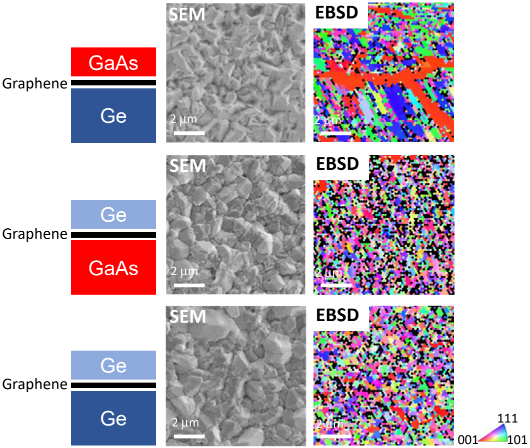
Limitations of Remote epitaxy

Ionicity of material governs surface electronic potential



Nature Materials, 17, 999 (2018)

Polycrystal growth from non-ionic material

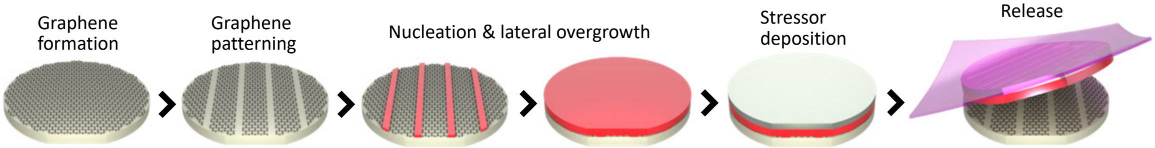


Ionicity (polarity) governs field penetration through graphene.

Elemental materials cannot be utilized as substrates or epilayer.

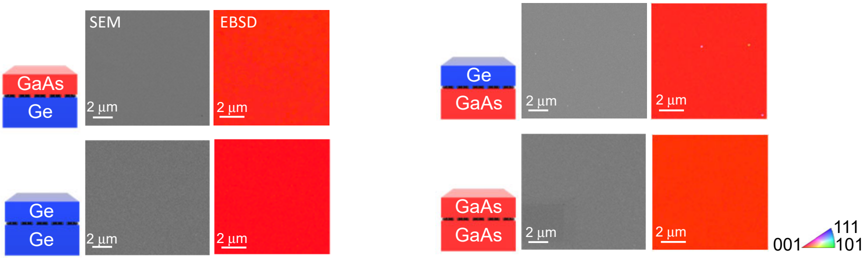
*H. Kim, et al., **ACS Nano**, 15, 10587 (2021)*

"Nanopatterned graphene" for universal layer transfer



Chemical inertness of graphene enables **selective nucleation**

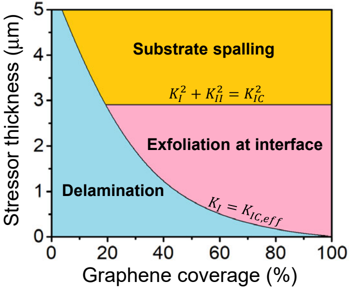
→ Single-crystal film growth



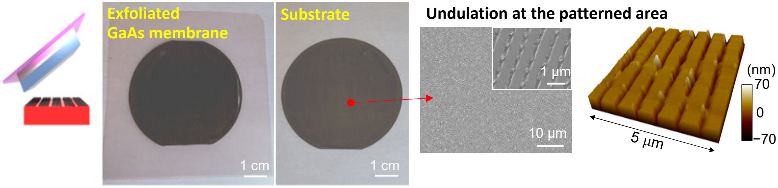
H. Kim, et al., ***Nature Nanotechnology***, 17, 1054 (2022)

“Nanopatterned graphene” for universal layer transfer

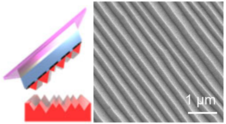
Three modes of peeling



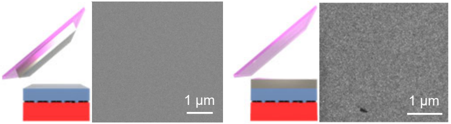
“Wafer-scale exfoliation” at the interface



“Spalling” of wafer



“Delamination” of stressor/tape

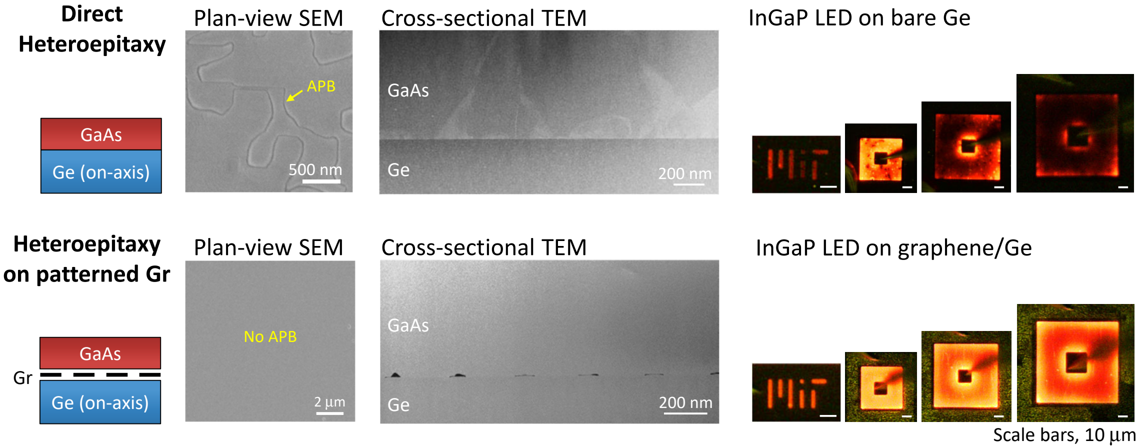


Exfoliation at the 2D interface can be achieved.

H. Kim, et al., ***Nature Nanotechnology***, 17, 1054 (2022)

Antiphase boundary elimination on nanopatterns

TEM in collaboration with Prof. Hwang (OSU)



- APBs are eliminated by epitaxy through nanopatterned Gr.
- Improved optoelectronic performance by nanopatterned Gr.

H. Kim, et al., ***Nature Nanotechnology***, 17, 1054 (2022)

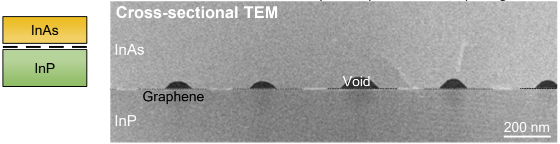
Dislocation reduction by graphene nanopatterns

TEM in collaboration with Prof. Hwang (OSU)

InAs on InP (3.3% lattice mismatch)

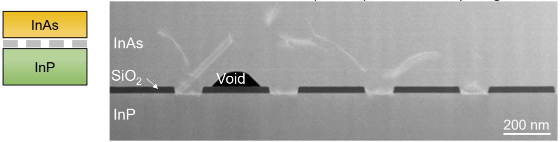
(1) Graphene nanopattern

Nanopattern pitch=400nm, opening=100nm

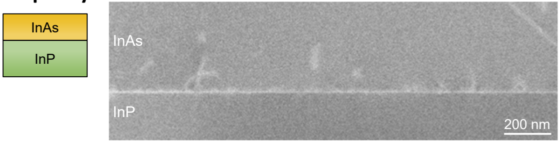


(2) SiO_2 mask (30nm thick)

Nanopattern pitch=400nm, opening=100nm



(3) Direct heteroepitaxy



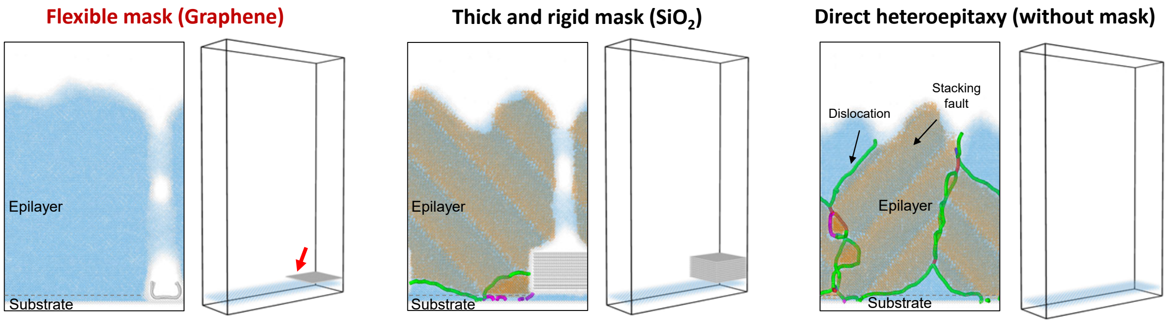
Lattice-mismatched heteroepitaxy

→ Graphene nanopattern reduces dislocation density.

H. Kim, et al., ***Nature Nanotechnology***, 17, 1054 (2022)

Revealing dislocation reduction mechanism

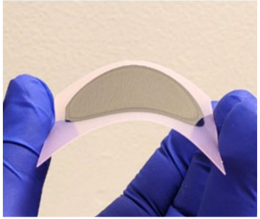
MD in collaboration with Prof. Shi (RPI)



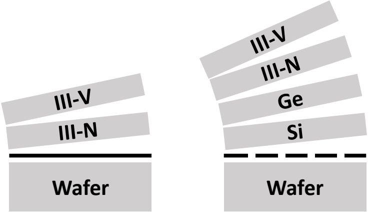
***'Flexibility'** of graphene suppresses defect formation*

H. Kim, et al., ***Nature Nanotechnology***, 17, 1054 (2022)

Advanced Epitaxy-on-2D technology



Scalability
by wafer-scale process



Universality
by grown 2D & nanopattern

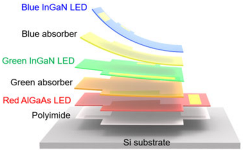
Epitaxy-on-2D enabled "Flexible" "Stackable" epitaxial membranes as building blocks for heterogeneous integration

Summary

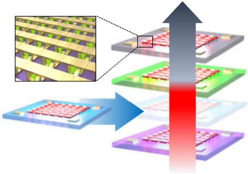
- **Epitaxy on 2D materials** enables producing freestanding membranes.
- Freestanding membranes offer new opportunities.

Applications

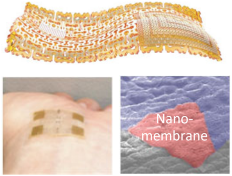
Vertically stacked Micro-LEDs



Reconfigurable AI processor



Chip-less & battery-less E-skin



Please find out more on these Applications at:

NM07.02.02. Vertically Stacked Full Color Micro-LEDs via Two-Dimensional Material-Based Layer Transfer

NM07.10.02. Reconfigurable Heterointegration of Artificial Intelligence Chips Using GaAs/InGaP-Based Optoelectronic Devices

NM07.10.09. Chip-less Battery-less Wireless Electronic Skin by Single Crystalline Freestanding Membranes

Acknowledgement

Collaborators

Materials / Devices

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- Prof. Sang-Hoon Bae (WashU)
- Prof. Kyusang Lee (UVA)
- Prof. Wei Kong (Westlake Univ.)

Theory / MD / DFT

- Prof. Yunfeng Shi (RPI)
- Prof. Suklyun Hong (Sejong Univ.)

Characterization / TEM

- Prof. Jinwoo Hwang (OSU)
- Prof. Sungkyu Kim (Sejong Univ.)
- Prof. Geun Young Yeom (SKKU)

Acknowledgement (Jeehwan Kim group)

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- The views expressed herein do not necessarily represent the views of the U.S.Department of Energy or the United States Government.