Laser-Induced Photothermal Synthesis and Applications of Functional Nanomaterials

Seoung-Ki Lee

Materials Science and Engineering
Pusan National University

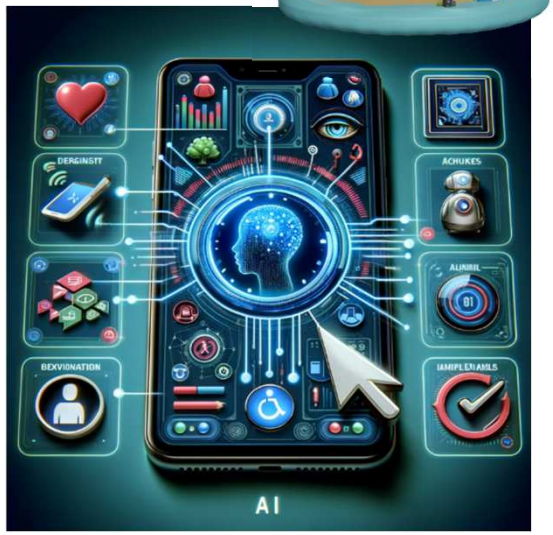
E-mail: ifriend@pusan.ac.kr

Contents

Contents

Introduction

History of electronic devices



Classic device	Portable device	On-device with AI
Performance	**Performance** + **Convenience**	**Performance** + **Convenience** + **Creativity**
Speed Capacity	Speed Capacity + Form factor + Design	+ Extreme performance + Intelligent + Low power
Limited area Passive type	Anywhere Passive type	Anywhere Intelligent type

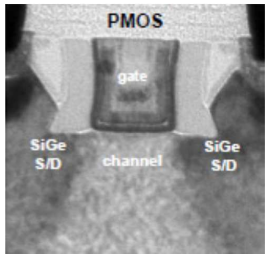
Introduction

History of electronic devices

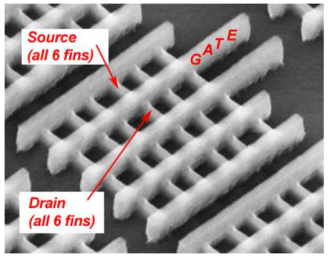
: To satisfy requirements

Moore's Law

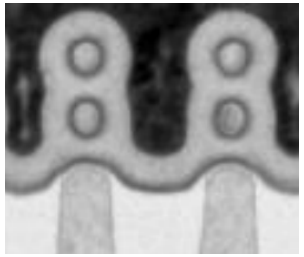
Transistor Level



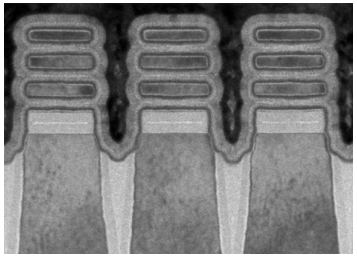
32 nm
Intel 2009



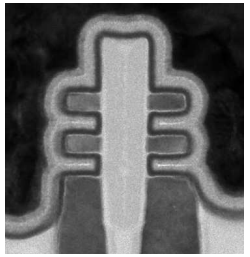
22 nm
IBM 2009



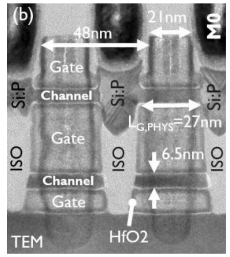
8 nm
IMEC 2016



2 nm
IBM 2021



2 nm
IMEC 2021

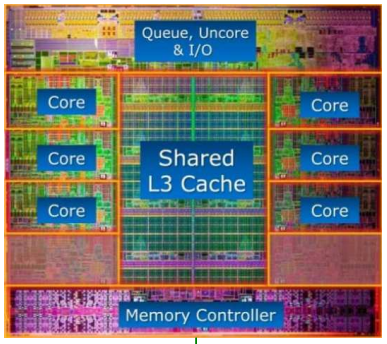


< 1 nm
IMEC 2023

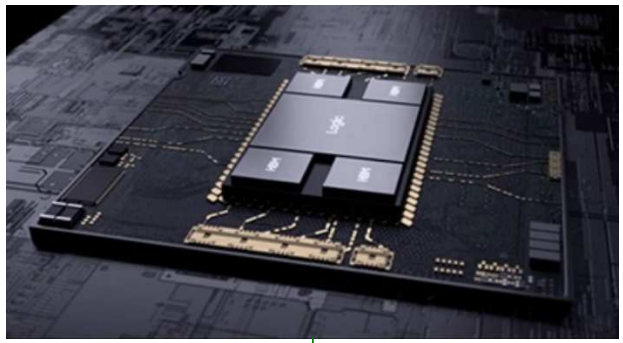
Planar → **FINFET** → **GAAFET** → **FSFET** → **CFET**

More Than Moore

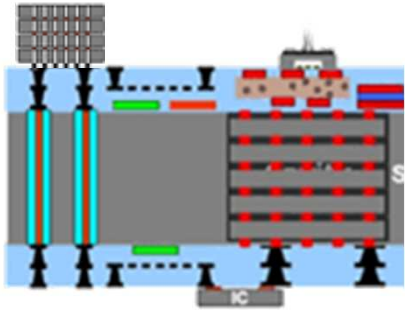
System Level



Source: Intel

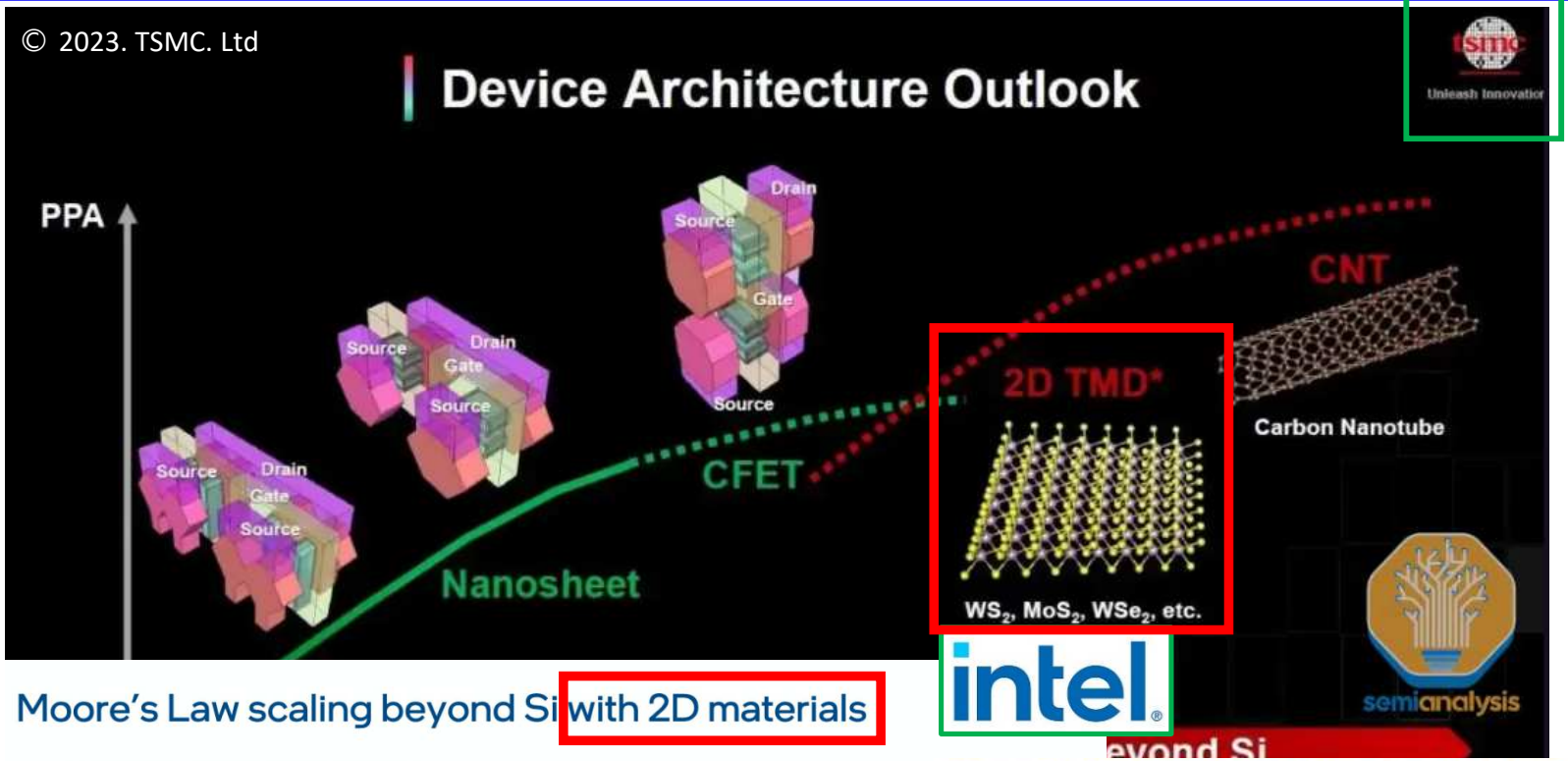


Source: Samsung

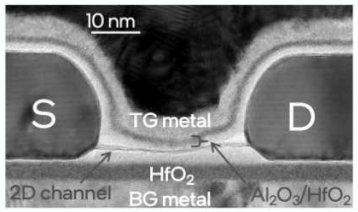


2D → 2.5D → 3D

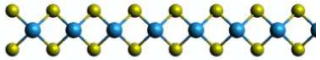
Introduction



Moore's Law scaling beyond Si with 2D materials

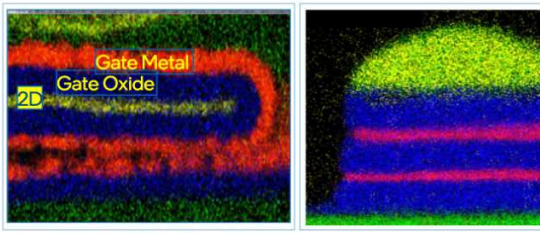


3 atoms thick



Super thin novel channel material to

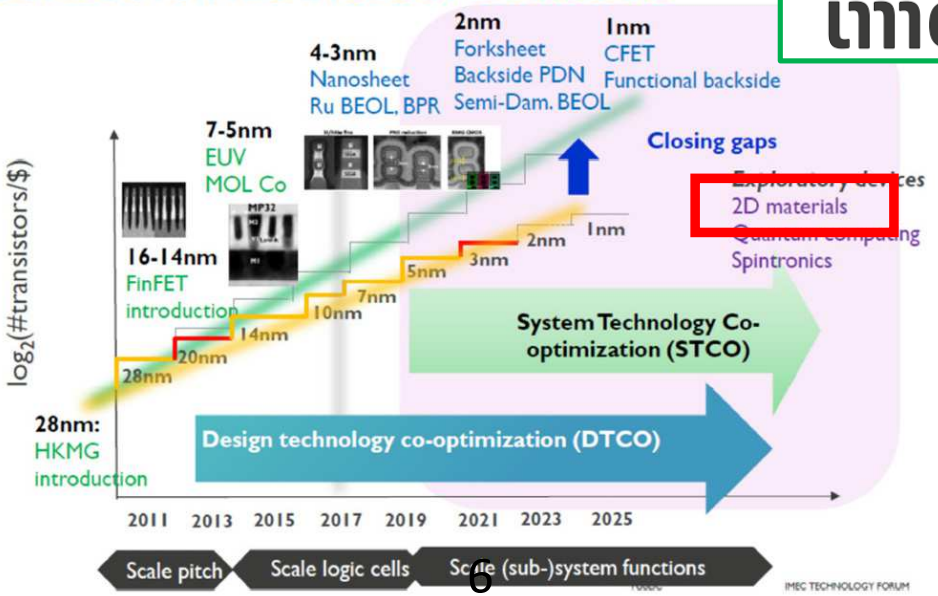
- Scaled 2D device fabrication – approaching Si state-of-the-art dimensions
- Specialized gate oxide growth for 2D surfaces achieves near ideal subthreshold slope (SS)



Paper #7.5: Gate length scaling beyond Si: Mono-layer 2D Channel FETs Robust to Short Channel Effects

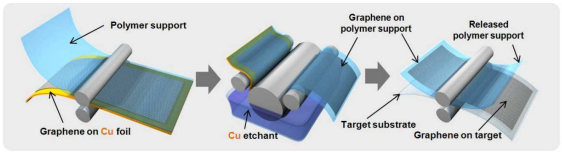
SEMICONDUCTOR TECHNOLOGY LANDSCAPE

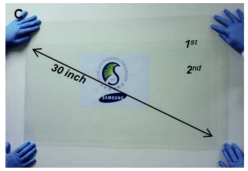
imec



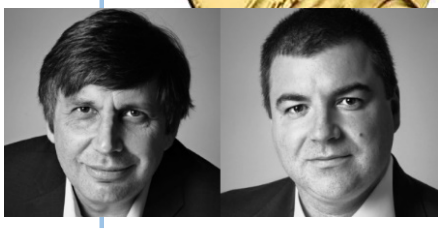
Introduction

Wide attention from academia to industry

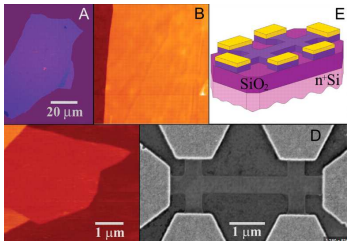


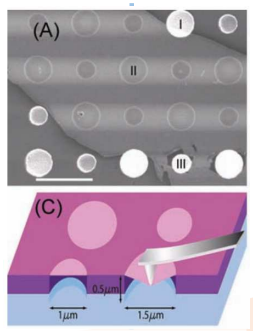


30" scale Graphene
[*Nat. Nanotech.*, SKKU]

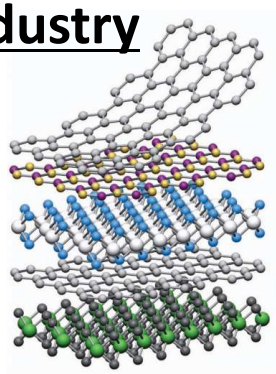


Graphene exfoliation
[*Science*, Manchester]

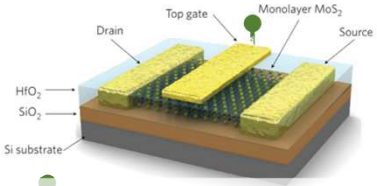




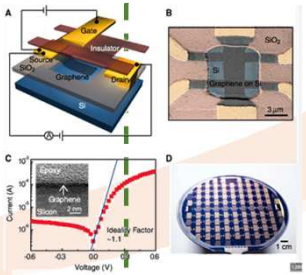
120 Gpa Graphene
[*Science.*, Columbia]



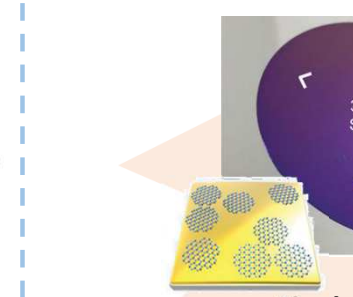
2D heterostructure
[*Nature*, Manchester]



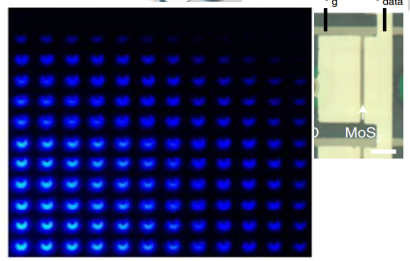
MoS_2 Transistor
[*Nat. Nanotech.*, EPFL]



Si/Gra. Barristor
[*Science.*, Samsung]

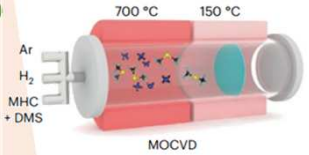


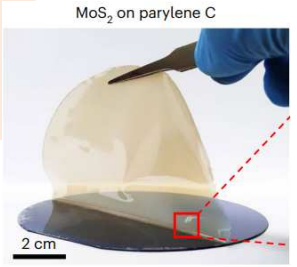
High qual. MoS_2 in wafer scale
[*Nature.*, Cornell]



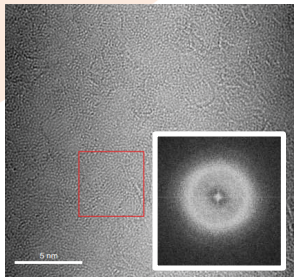
MoS_2 driving circuit
[*Nat. Mater.*, Nanjing]

Single crystal h-BN
[Science, SKKU]

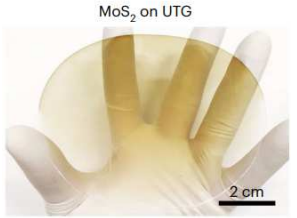




Large area MoS_2 synthesis
[*Adv. Mat.*, KRICT]



Ultra-low k BN
[*Nature*, UNIST]



150 °C synthesis of MoS_2
[*Nat. Nanotech.*, Yonsei]

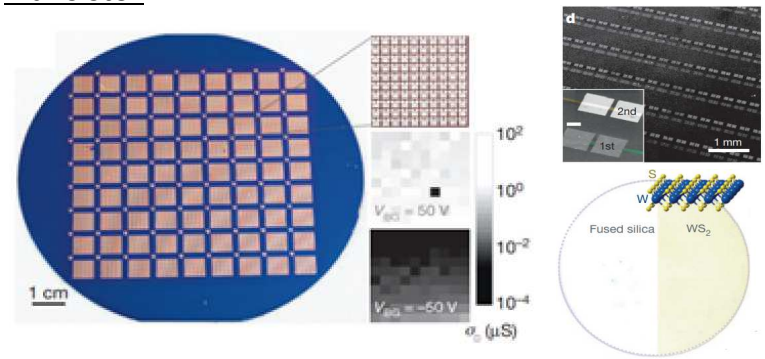
2004 2008 2009 2010 2011 2012 2013 2015 2017 2018 2020 2021 2023

Introduction

Applied research based on 2D mono-materials

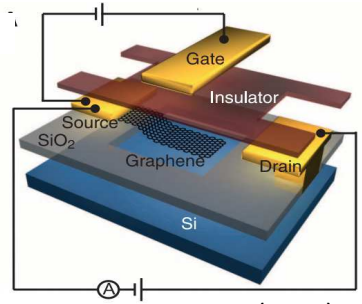
- Logic device

Transistor



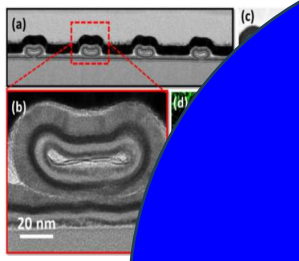
Nature (2015)

Barristor



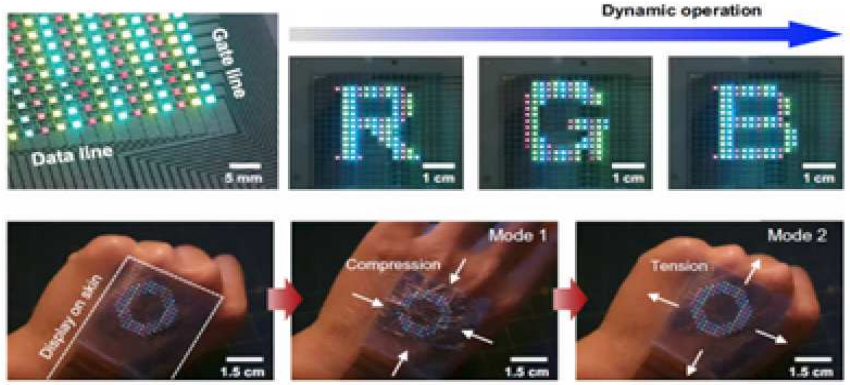
Science (2012)

3D architectured Tr.



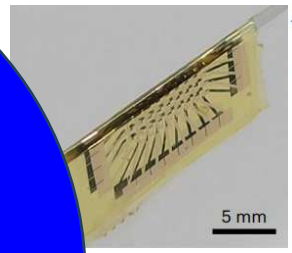
- Driving circuit

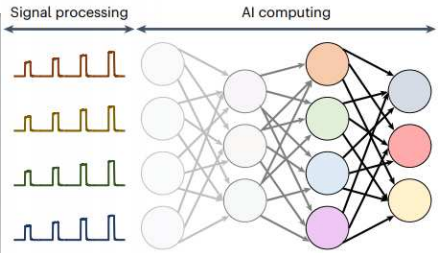
Flexible Transistor



Sci. Adv. (2020), *Nat. Nanotech.* (2022)

computing

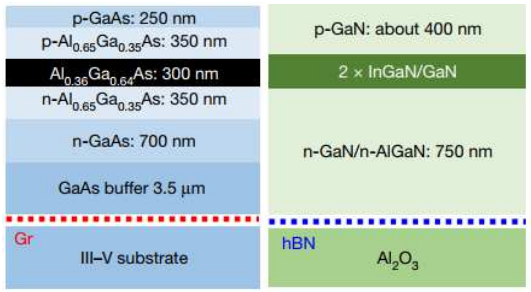


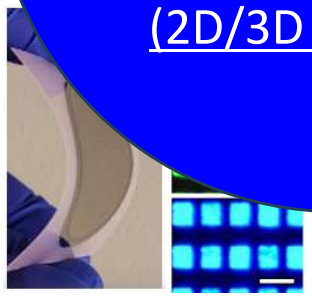


Nat. Mater. (2023)

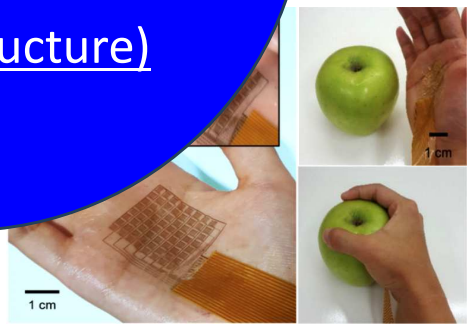
Synergistic integration of 2D Mat. with conventional Semi. Mat. &Tech. (2D/3D structure)

- 2D layer-assisted growth &

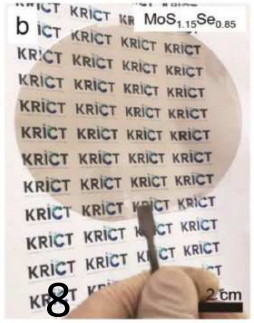


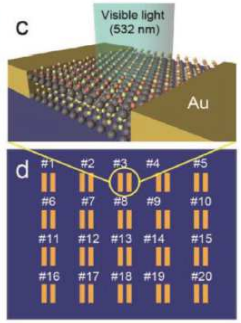


Nature (2023)



ACS Nano (2019)





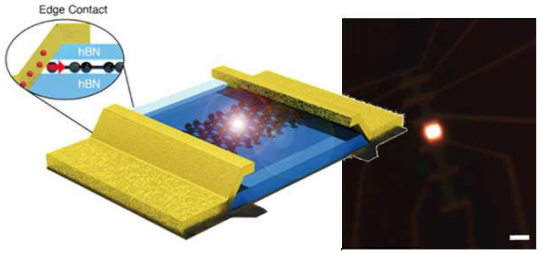
Adv. Mater. (2019)

Introduction

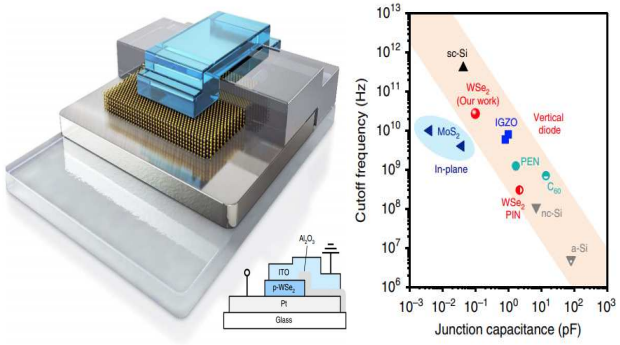
2D Heterojunction based Devices

: Opening the novel device system

- **Optoelectronics**

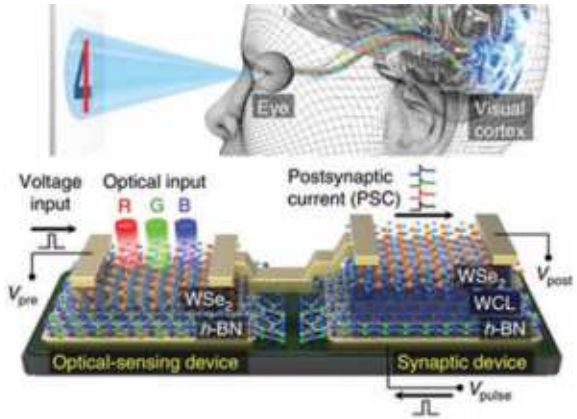


Nano Lett. (2018)

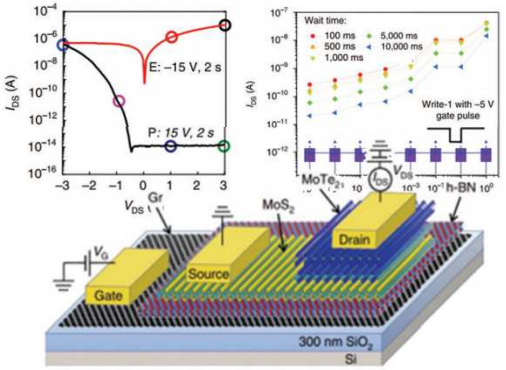


Nat. Commun. (2020)

- **Neuromorphic**



Nat. Commun. (2018)

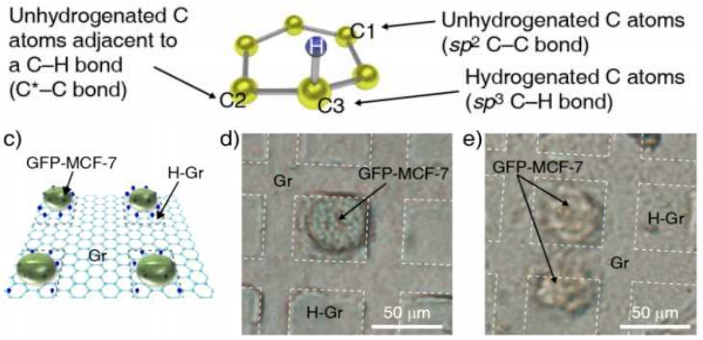


Nat. Electron. (2018)

Issue

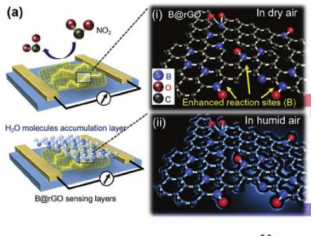
- **Promising** but limited in **"Unit Device"**
- **Uniformity** of 2D device **"ARRAY"**

- **Biology**

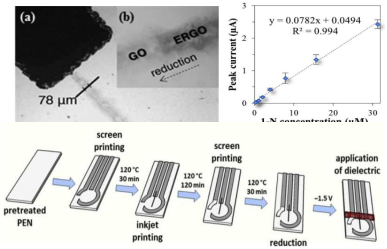


Nano Lett. (2020)

- **Sensor**

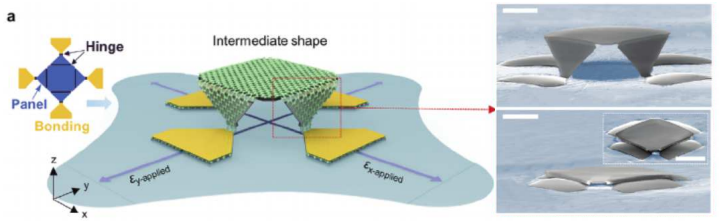


Adv. Sci. (2020)



Biosens. Bioelecton. (2020)

- **Mechanical engineering**

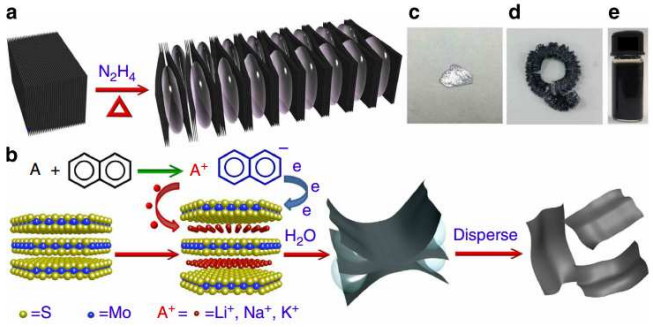


Adv. Mater. (2020)

Introduction

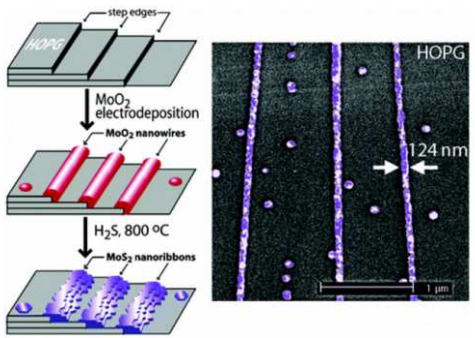
General method to synthesis TMDs

Intercalation assisted exfoliation



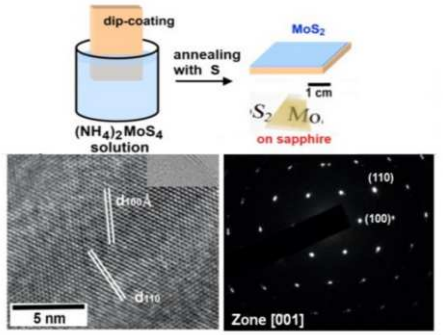
Nat. Comms., **2014**, 5, 2995

Electrochemical synthesis



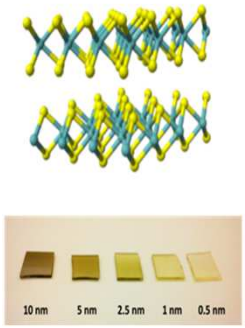
Nano Lett., **2004**, *4*, 277

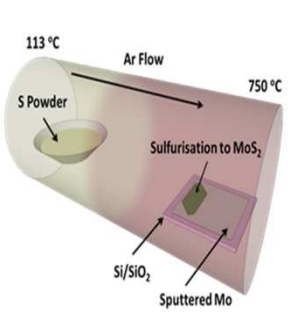
Thermolysis

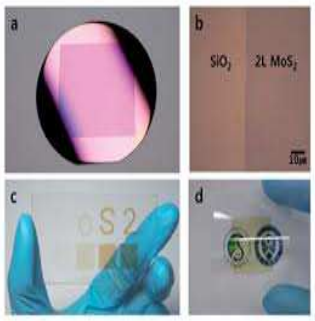


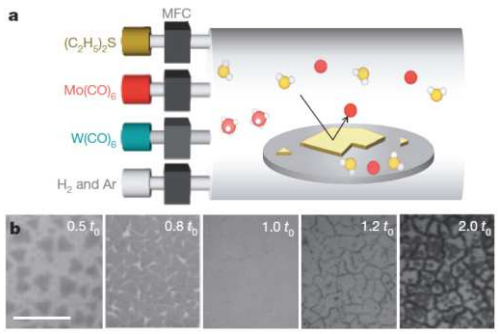
Nano Lett. **2012**, 12, 1538

Chemical valor deposition





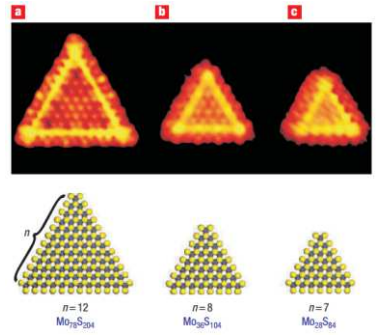




Molybdenum oxide
Molybdenum

Nano Lett., **2013**, *13* , 1852.
Nature **2015**, *520* , 656.
Nat. Maters., **2013**, *12*, 554.

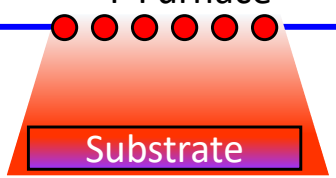
Physical vapor deposition

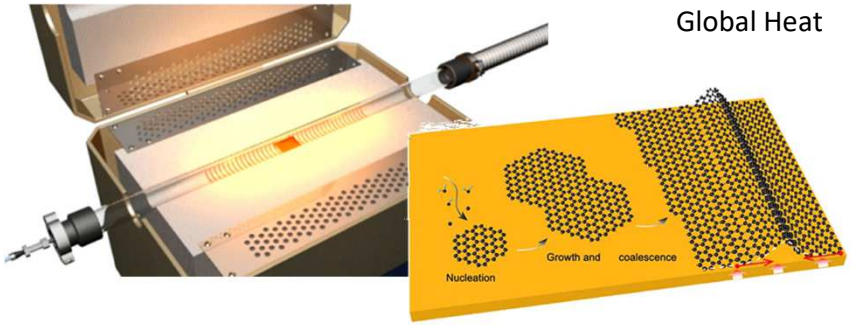


Nat. Nanotech., **2007**, 2, 53.

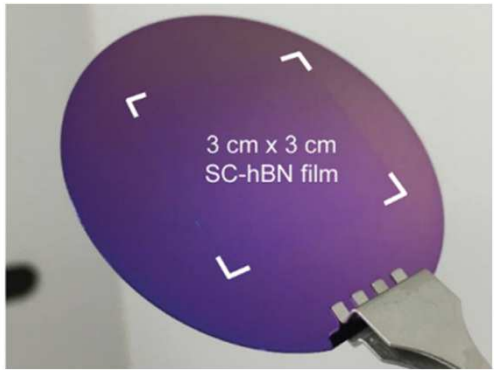
Introduction

CVD based method



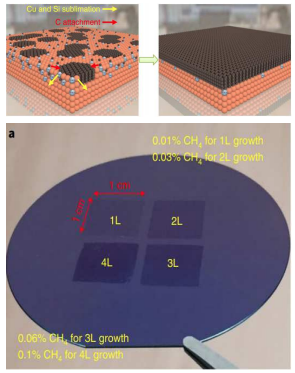


Single crystal



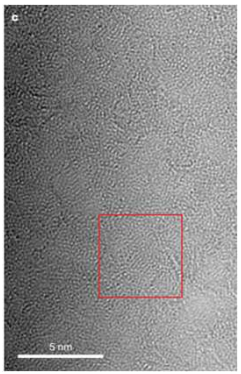
Science 362, **(2018)**

Layer control



Nat. Nanotech. **(2020)**

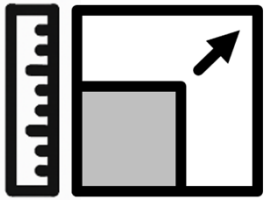
U. Low-k



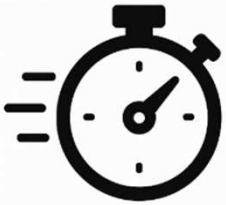
Nature **(2020)**

Better perform.

More Size

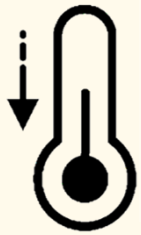


More Fast



(On the mother wafer)

More Low

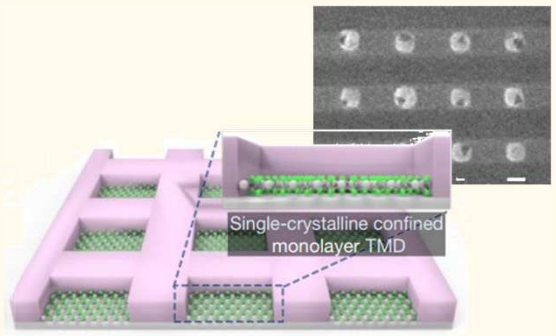


More Uniform

More Clean

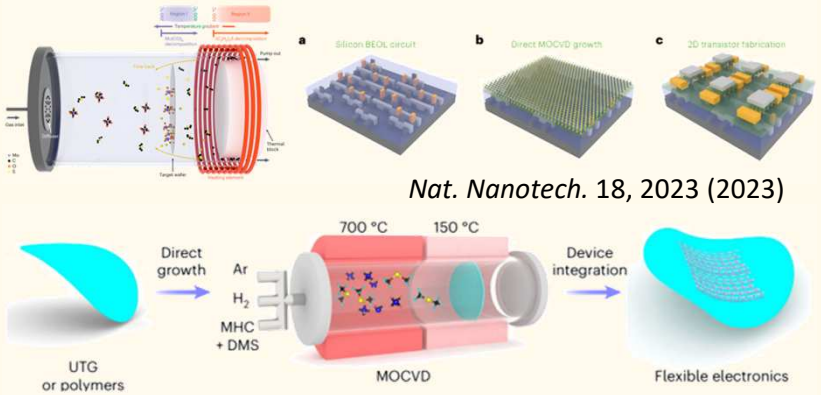
(On the Target wafer)

Confinement growth



Nature, 614, 88 (2023)

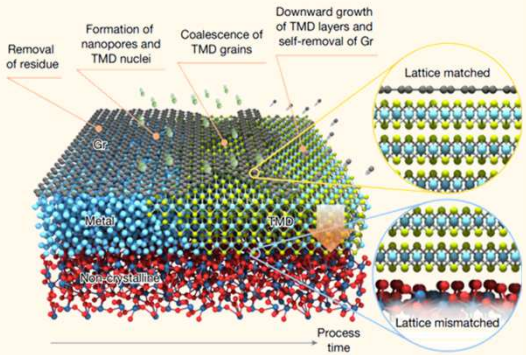
Low temperature growth



Nat. Nanotech. 18, 2023 (2023)

Nat. Nanotech. 18, 1439 (2023)

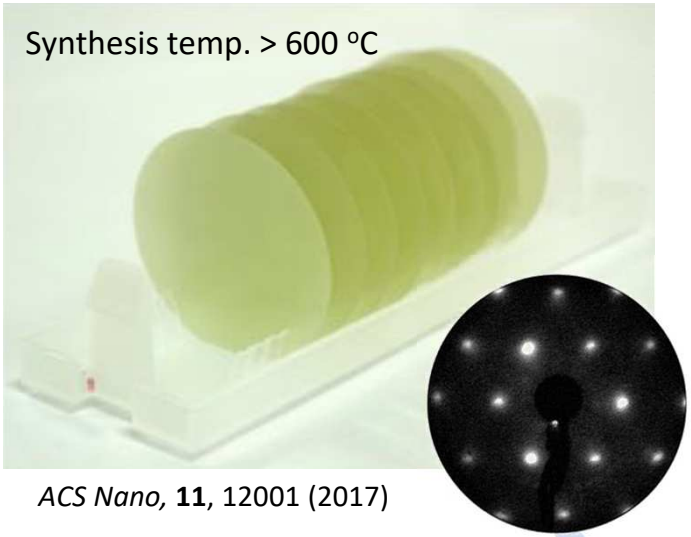
Hypotaxy methods



Nature 638, 957 (2025)

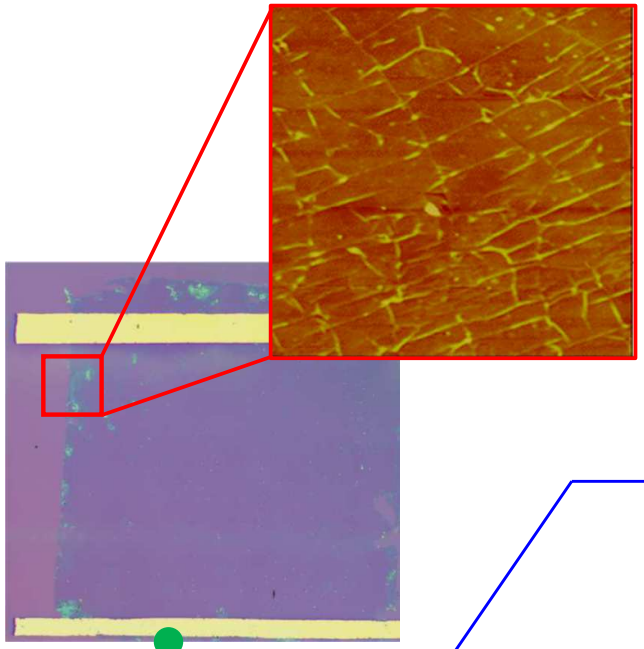
Introduction (issues in the process)

[Raw material - Uniform]

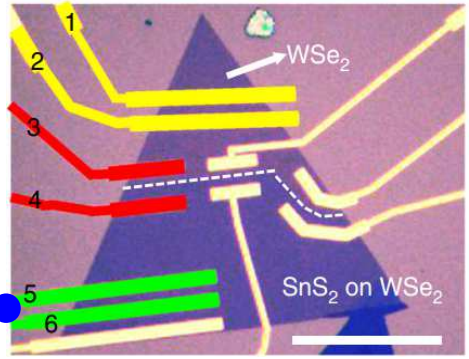


ACS Nano, **11**, 12001 (2017)

ii) Residue/contact problem



iii) Atomic-level etch



Adv. Mat,., **596**, 519 (2023)
ACS AMI., **13**, 1 (2021)

Supporting Mat.

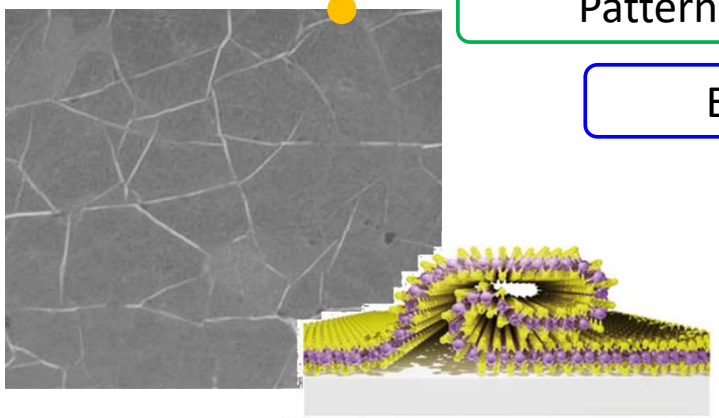
Transfer

Pattern

Etching

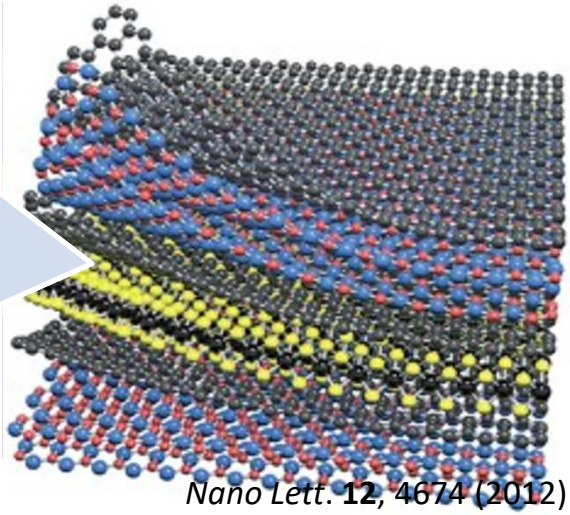
Cleaning

i) Wrinkle/bubble



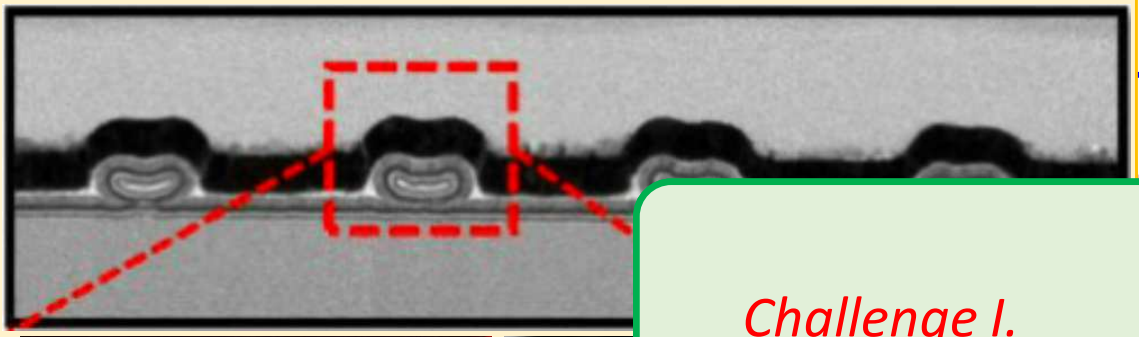
Nature, ***596***, 519 (2021)
Nat. Com., **13**, 1484 (2022)

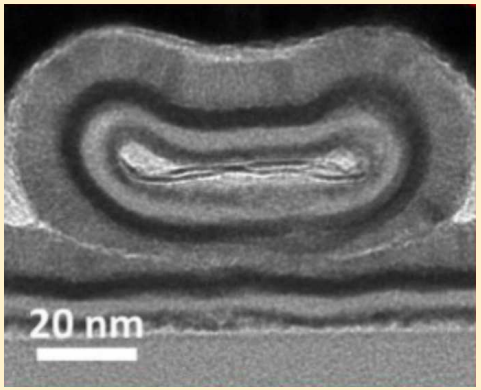
[Product – Non uniform]

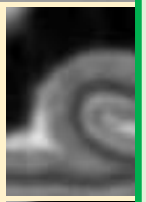


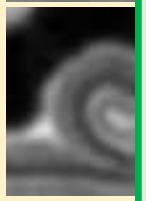
Nano Lett. **12**, 4674 (2012)

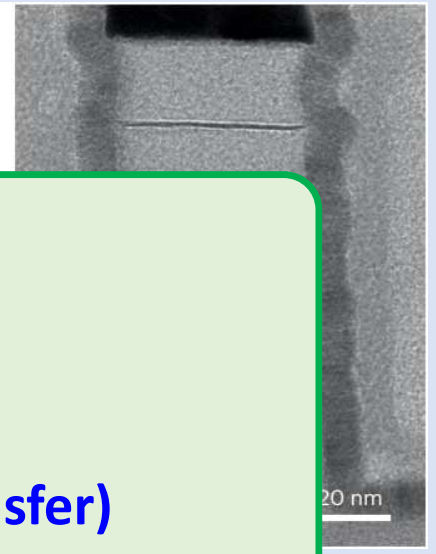
Fab. process → Contamination → Non-uniform-performance











2022)

Challenge I.

Improve uniformity of devices

A. Residue-free process (= Non-transfer)

→ Direct synthesis on target substrate

Challenge II.

Minimize thermal budget

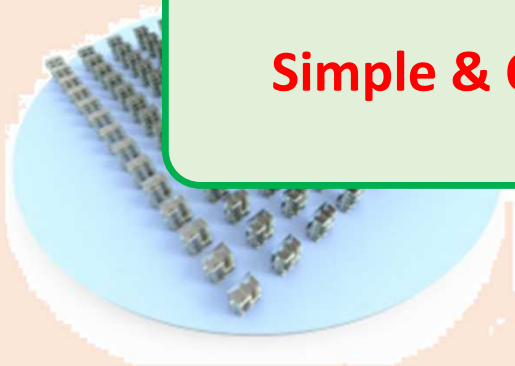
A. Confined heat treatment (vertic. & Horiz.)

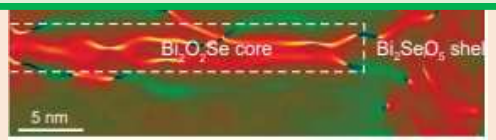
Challenge III.

Simple & Cost-effective method

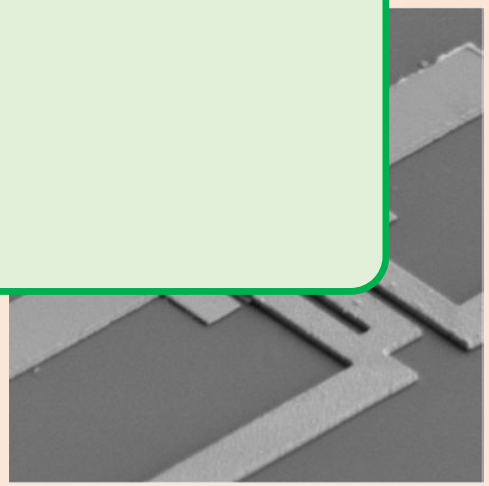
Transfer?
Fab. Process?
↓
Unintended contamination
↓
Nonuniform-performance

M3D integrat
at angstrom





Nat. Mat. **24**, 519 (2025)

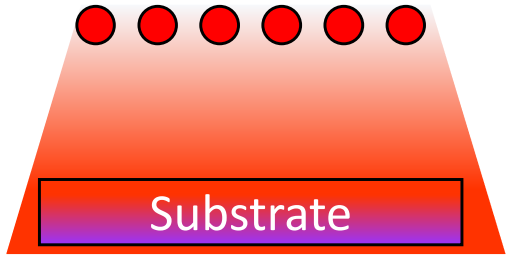


Motivation

Solution: Laser-based photothermal treatment

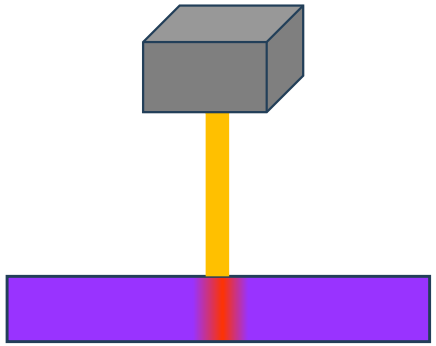
General CVD method

T-Furnace



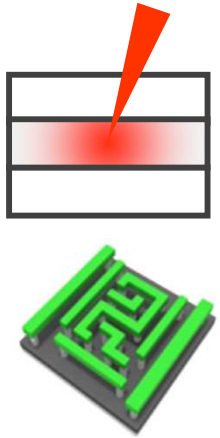
Global Heat

Laser

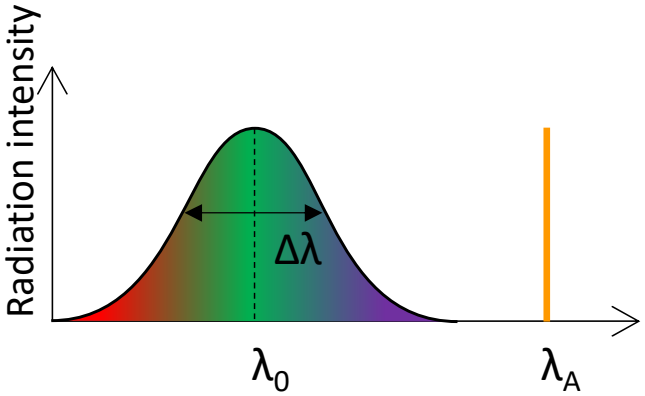


Confined Heat

- **Material selectivity (Target layer)**
- **Positioning (Pattern)**

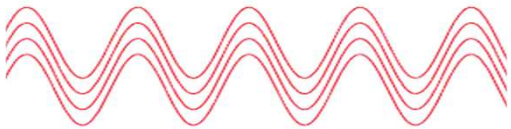


Monochromatic



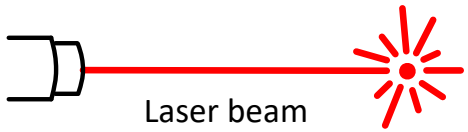
- Single wavelength

Coherent



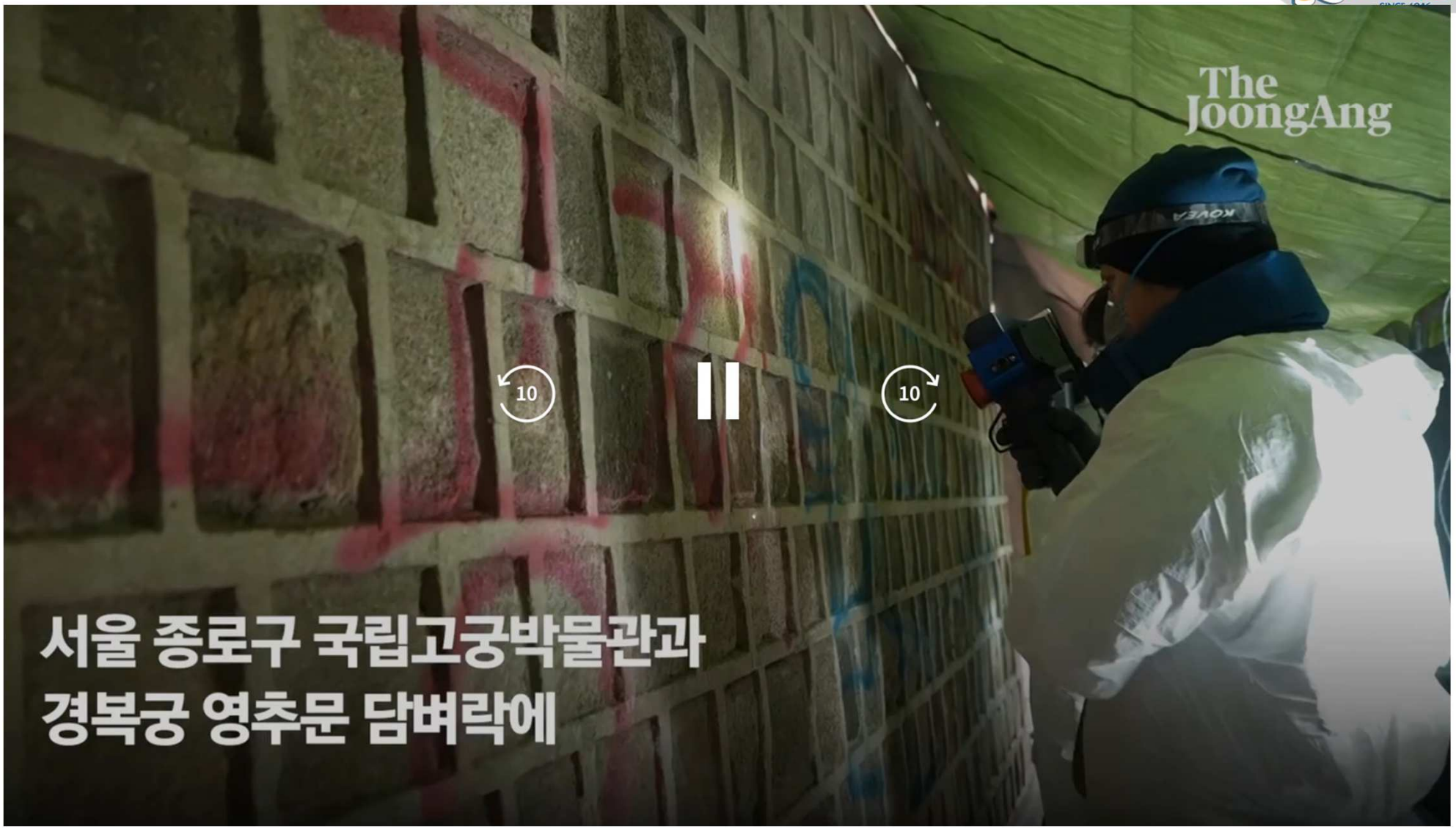
- Temporal coherence
- Spatial coherence
- Single frequency (Laser light)

Directional



- Collimated light
- Narrow beam in a specific direction
- High intensity

Motivation



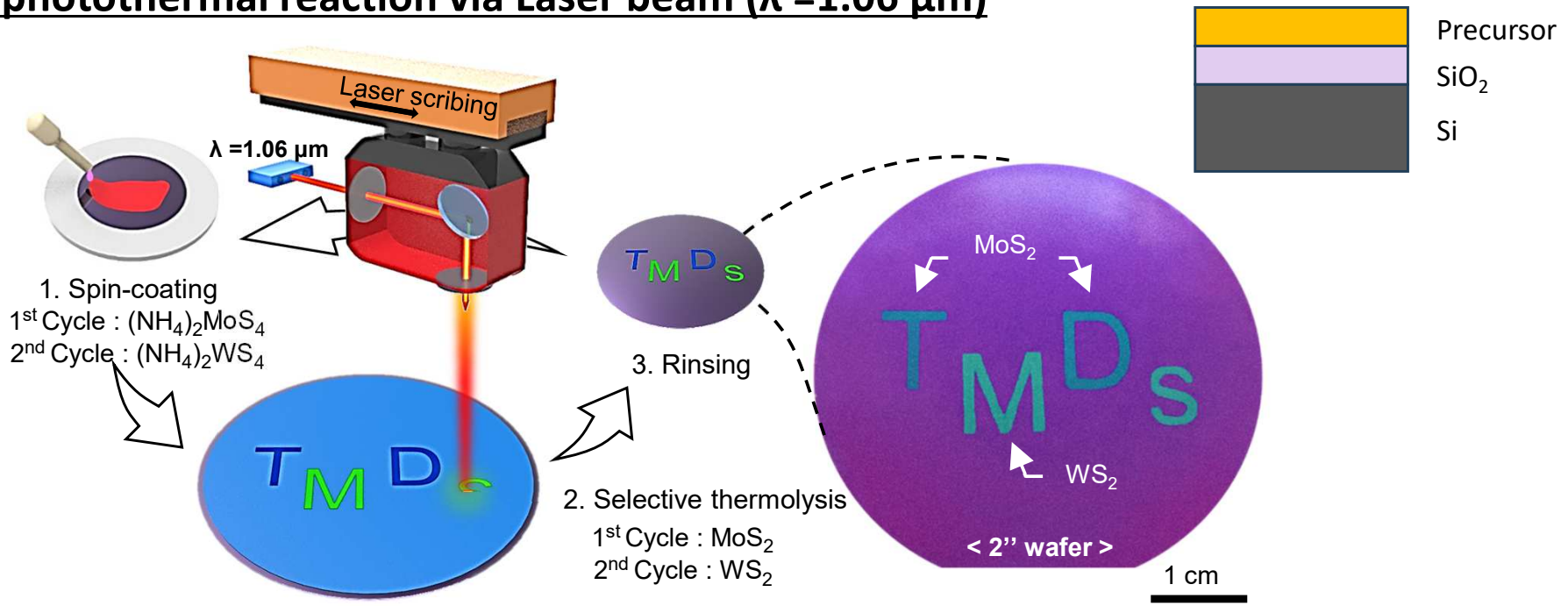
Erasing of Graffiti: Use a laser with a high absorption rate only on the target paint.

: Allows for a selective removal process.

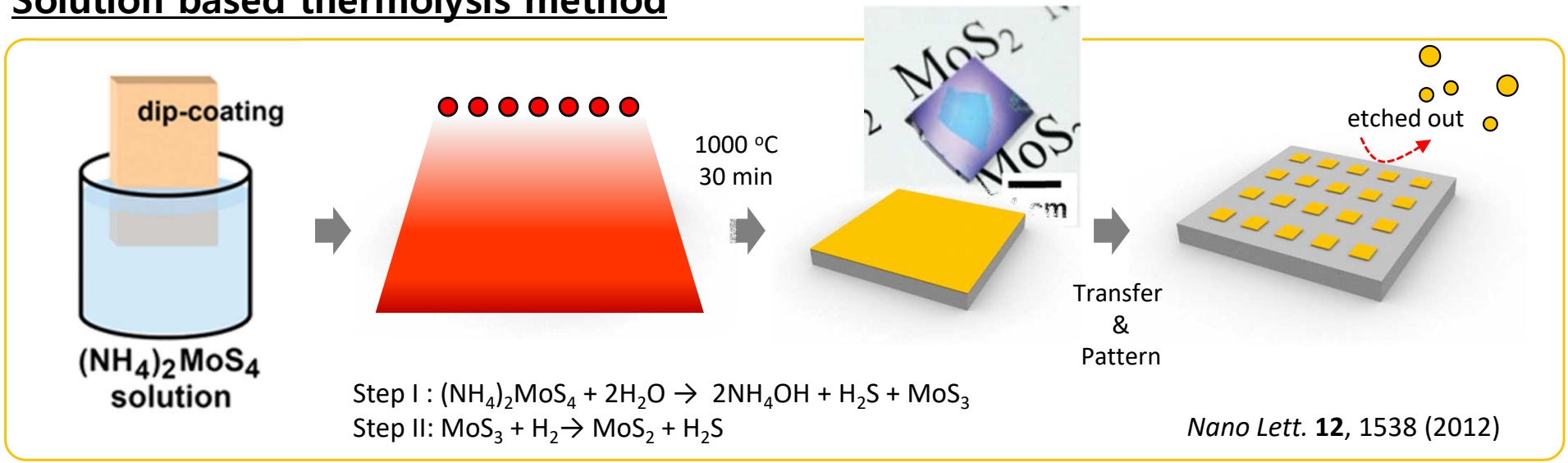
: Minimize the damage to the wall of the old palace.

Results and discussion

I. Partial photothermal reaction via Laser beam (λ =1.06 μm)



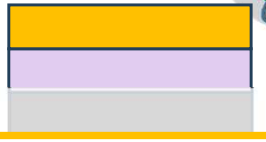
Solution based thermolysis method

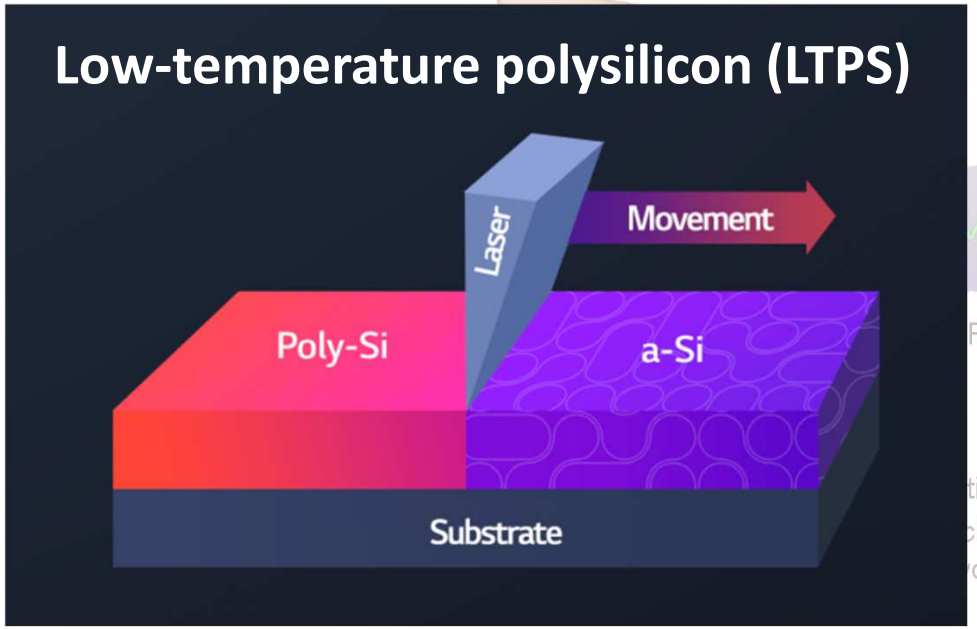


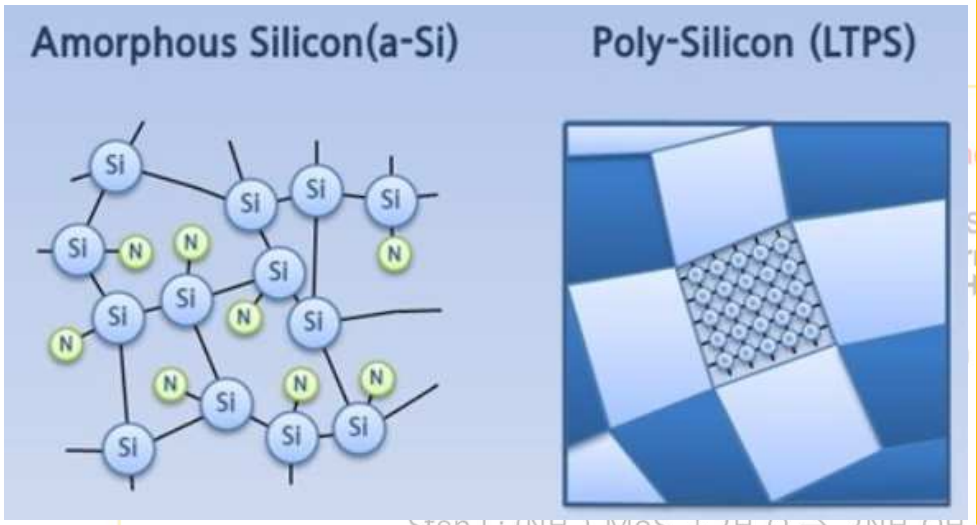
Nano Lett. **12**, 1538 (2012)

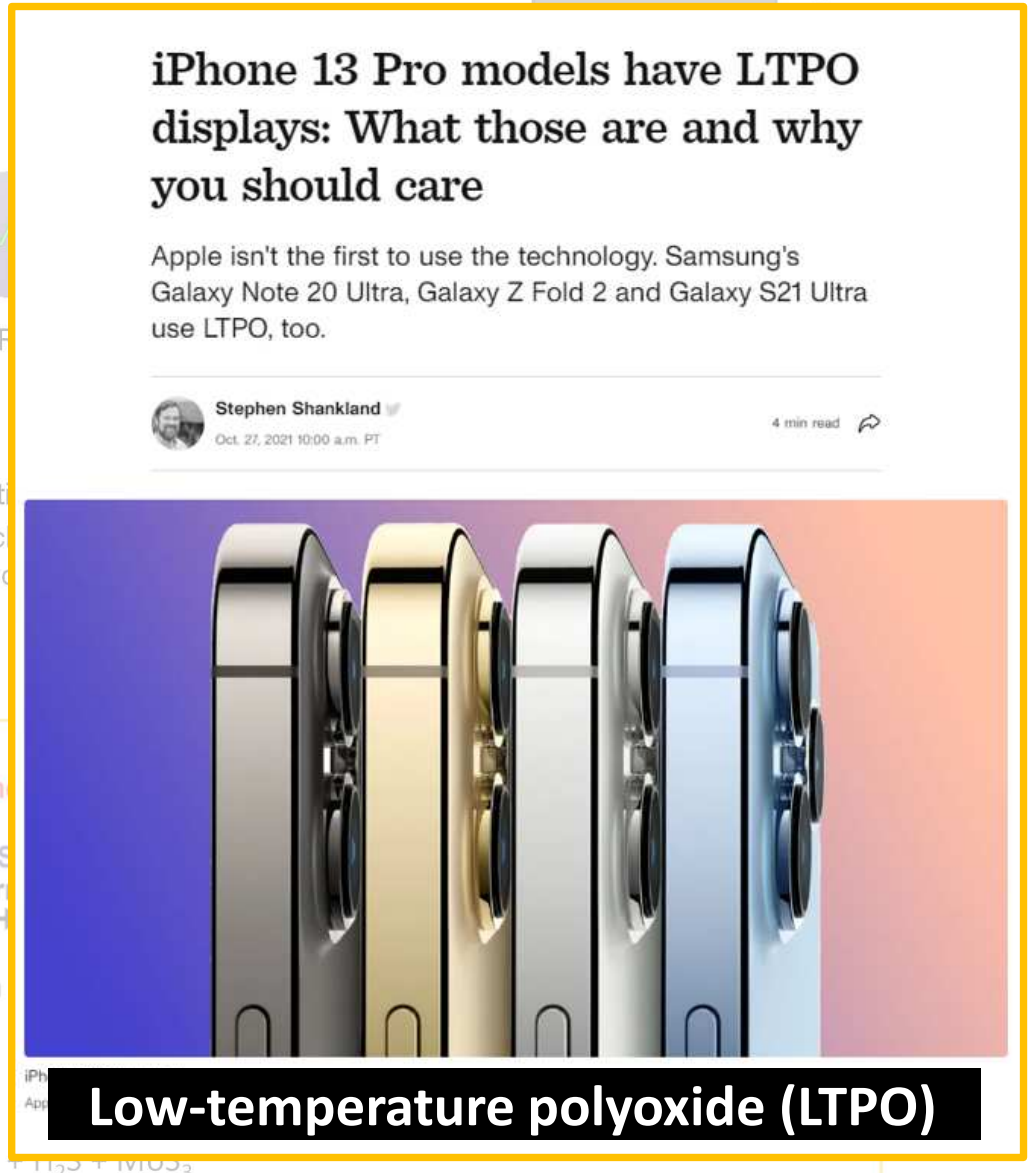
Results and discussion (LTPT)

I. Partial photothermal reaction via Laser beam (λ =1.06 μm)









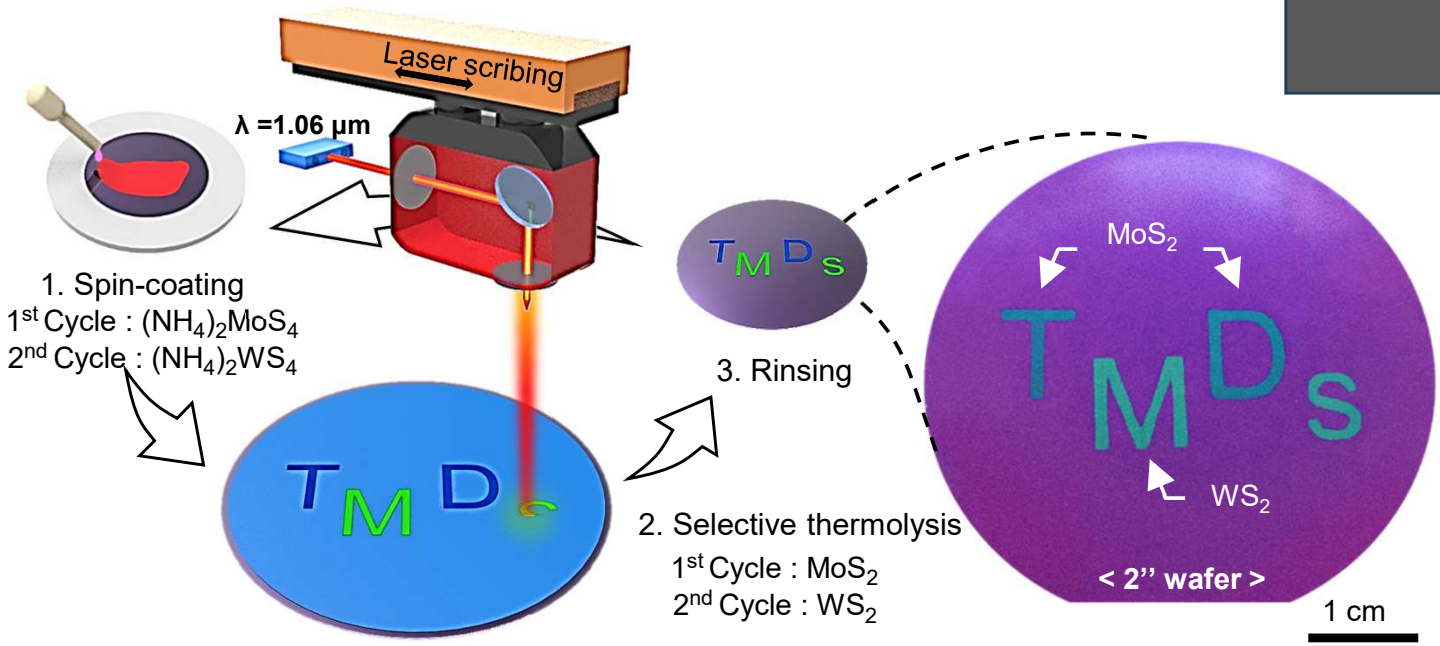
Step I : $(NH_4)_2MoS_4 + 2H_2O \rightarrow 2NH_4OH + H_2S + MoS_3$

Step II: $MoS_3 + H_2 \rightarrow MoS_2 + H_2S$

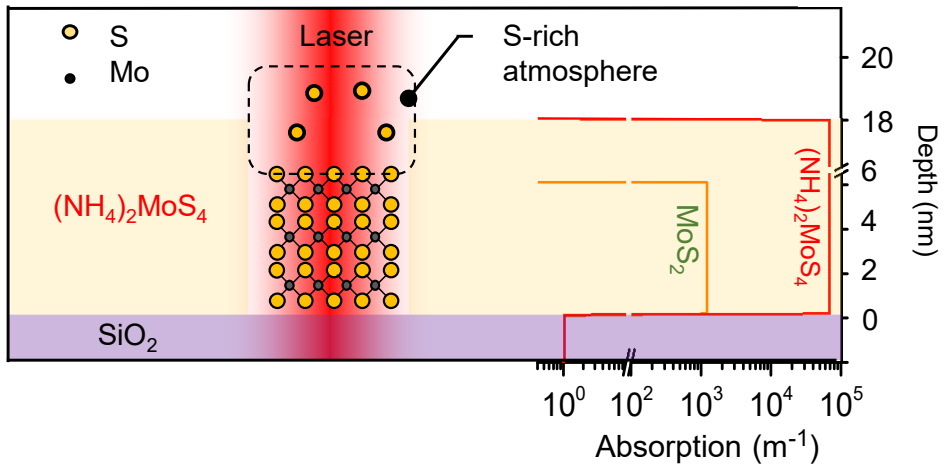
Nano lett. 12(3) 1538 (2012)

Results and discussion (LTPT)

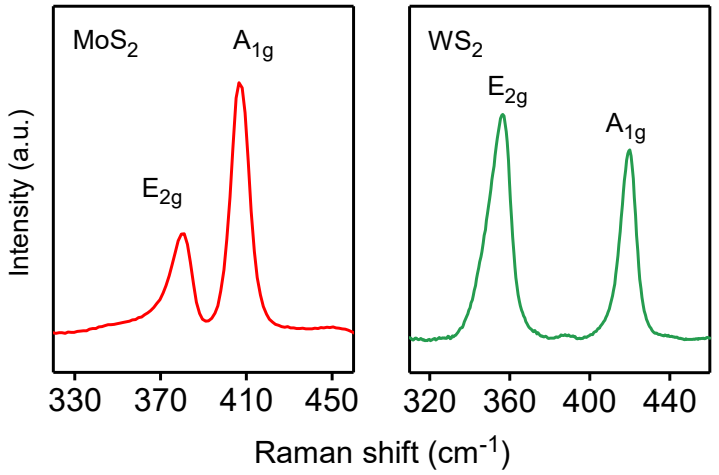
I. Partial photothermal reaction via Laser beam (λ =1.06 μm)



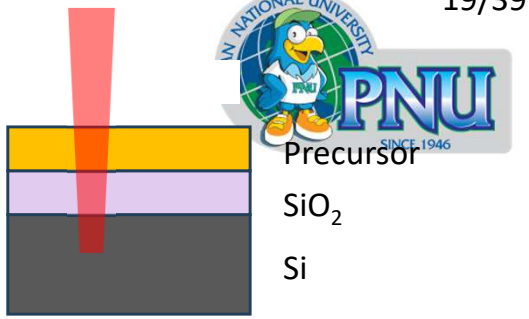
- Mechanism: Absorption rate



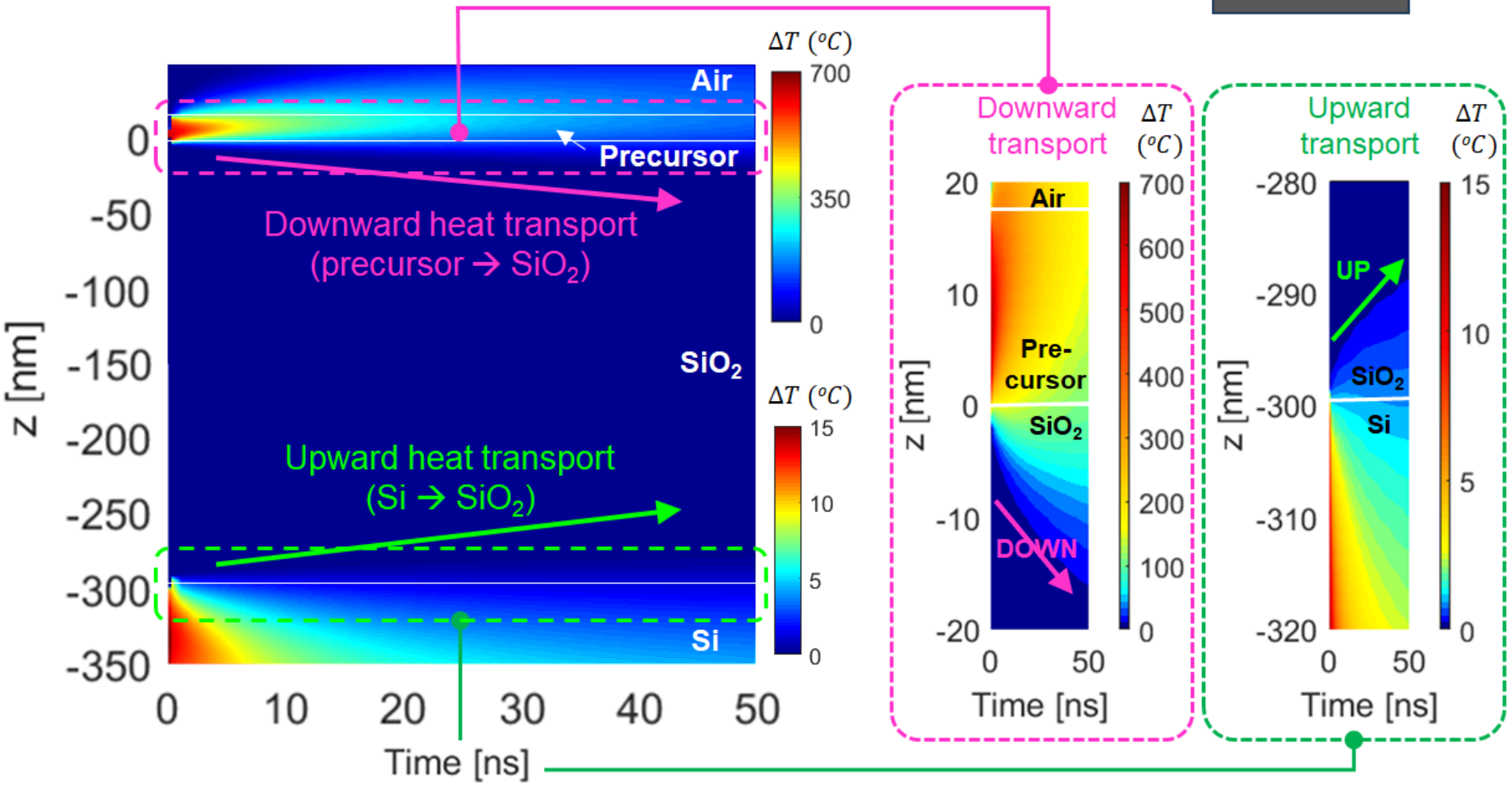
- Raman spectroscopy



Results and discussion (LTPT)



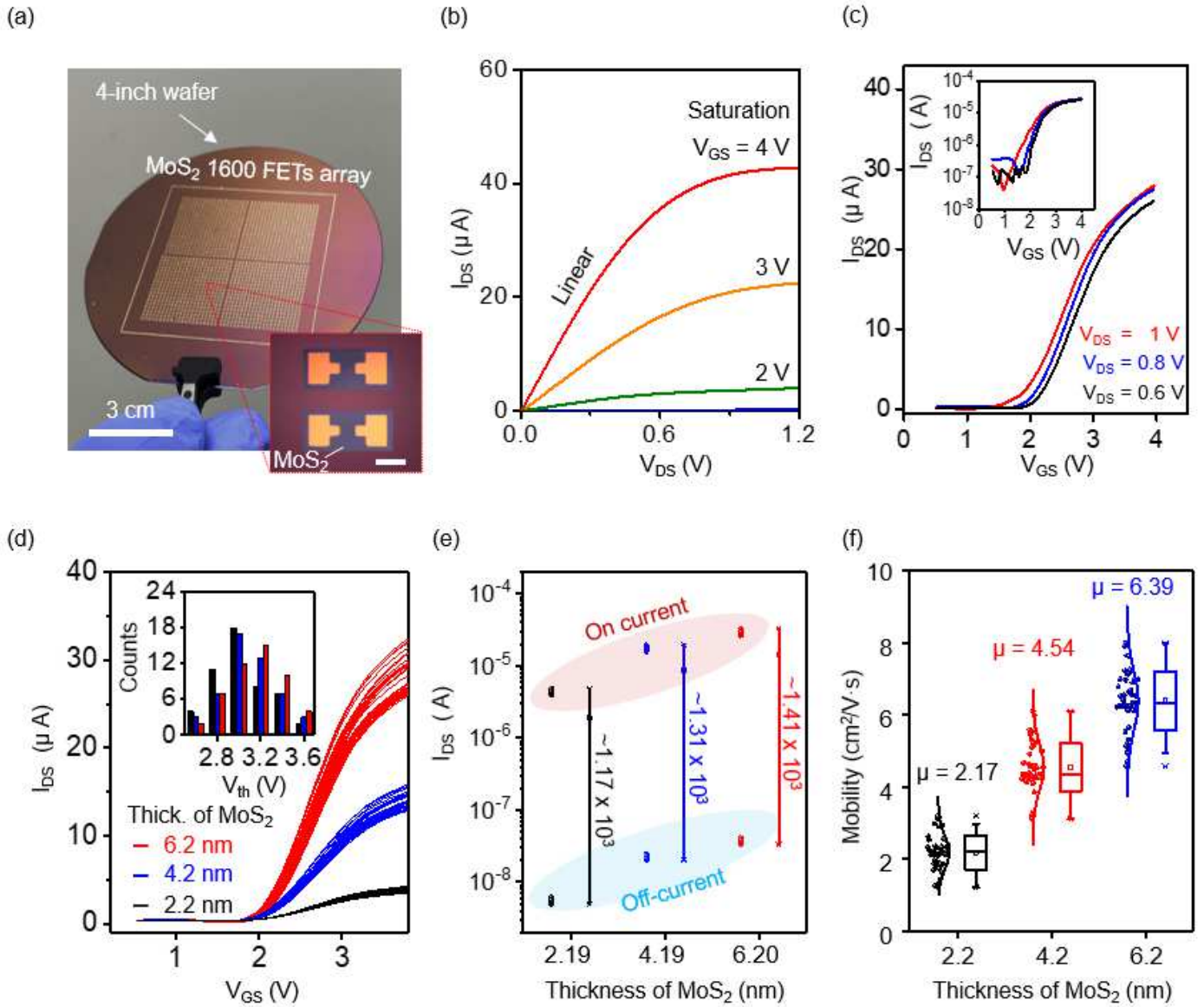
II. Time-domain thermal analysis



- 2 order of different temperature scales in each top and bottom regions
- The upward heat transport from Si to SiO_2 is suppressed due to the low thermal conductivity of SiO_2

Results and discussion (Advantage. I)

I. Ultra-fast & Uniform device performance



- Simple & fast process

: Processing time
for 1,600 array
: < 10 min
active area (150× 300 μm²)

- Uniform performance

: Transfer X
: Photolithography X
No wrinkle & PR residue

- Performance

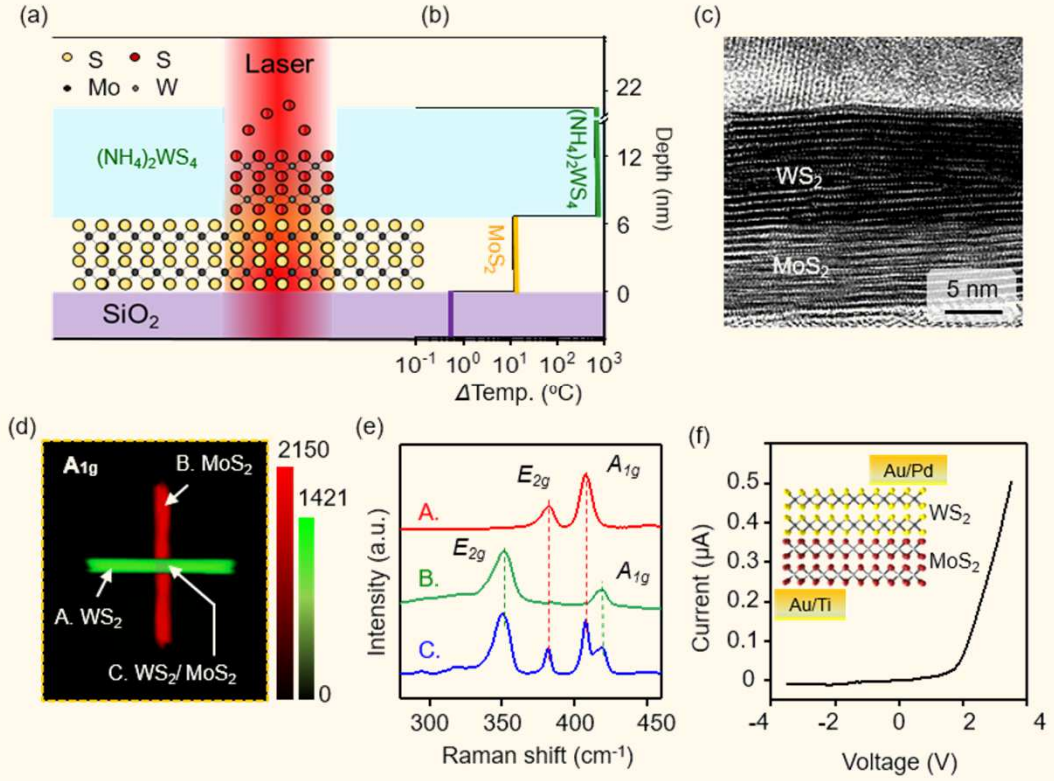
: Ion gel gated FET
: Mobility - ~5 cm²/Vs
: On/off ratio: ~ 10^3

Results and discussion (Advantage. II)

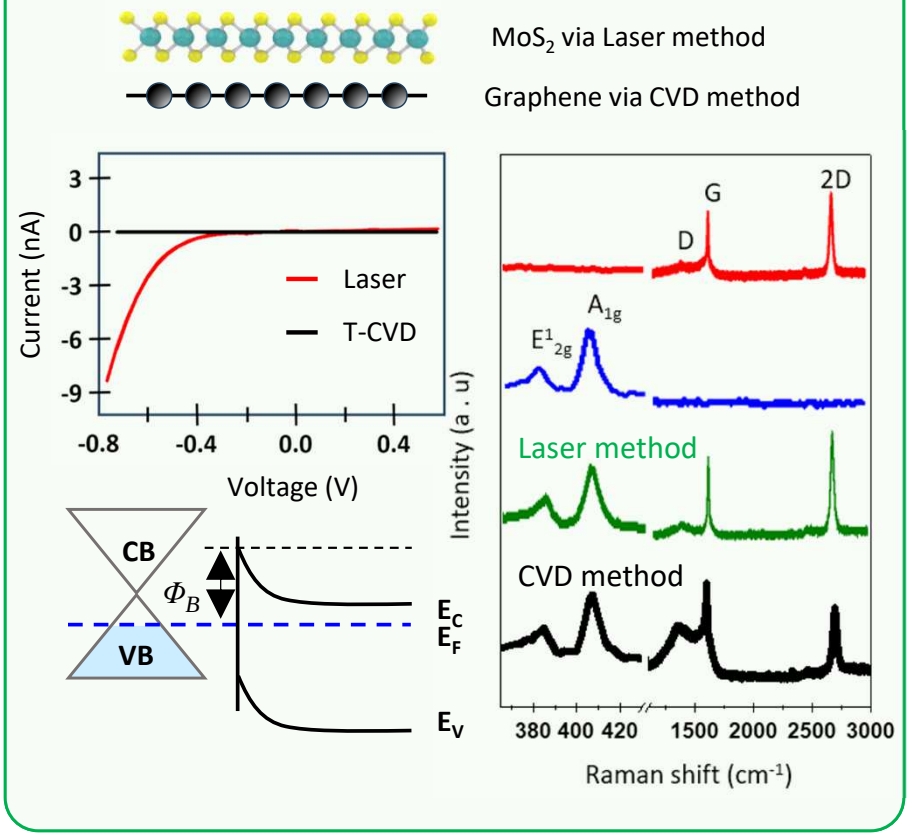
M.J. Jeon

II. Heterostructure

PN junction (WS_2/MoS_2)



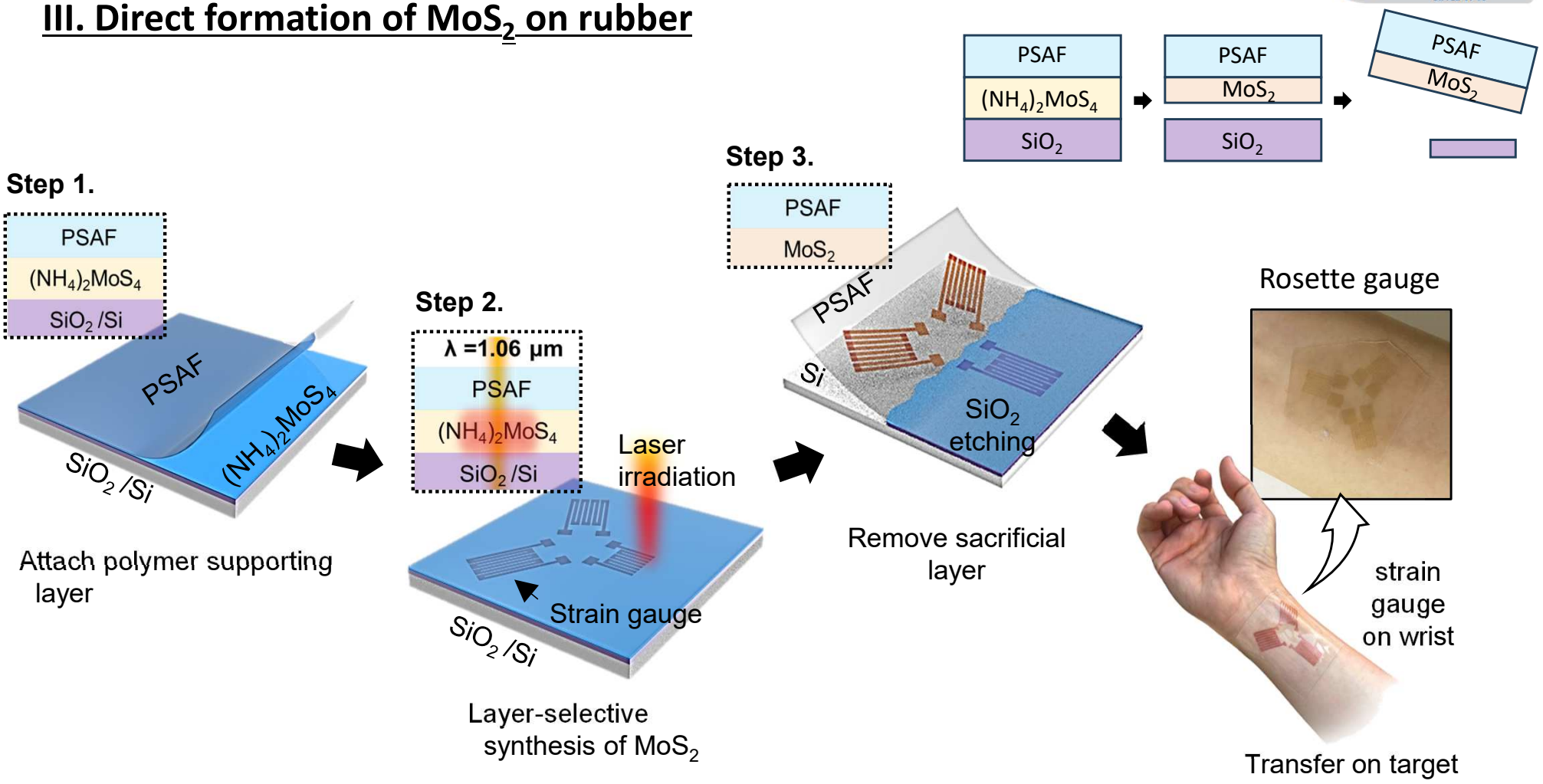
Schottky junction (MoS_2/Graphene)



- Demonstration of **Semiconductor/Semiconductor** and **Semiconductor/metal junctions**
- **Minimize thermal budget** → selective heat treatment
- Ensure rectifying behavior (current ratio ~ 10^3)

Results and discussion (Advantage. III)

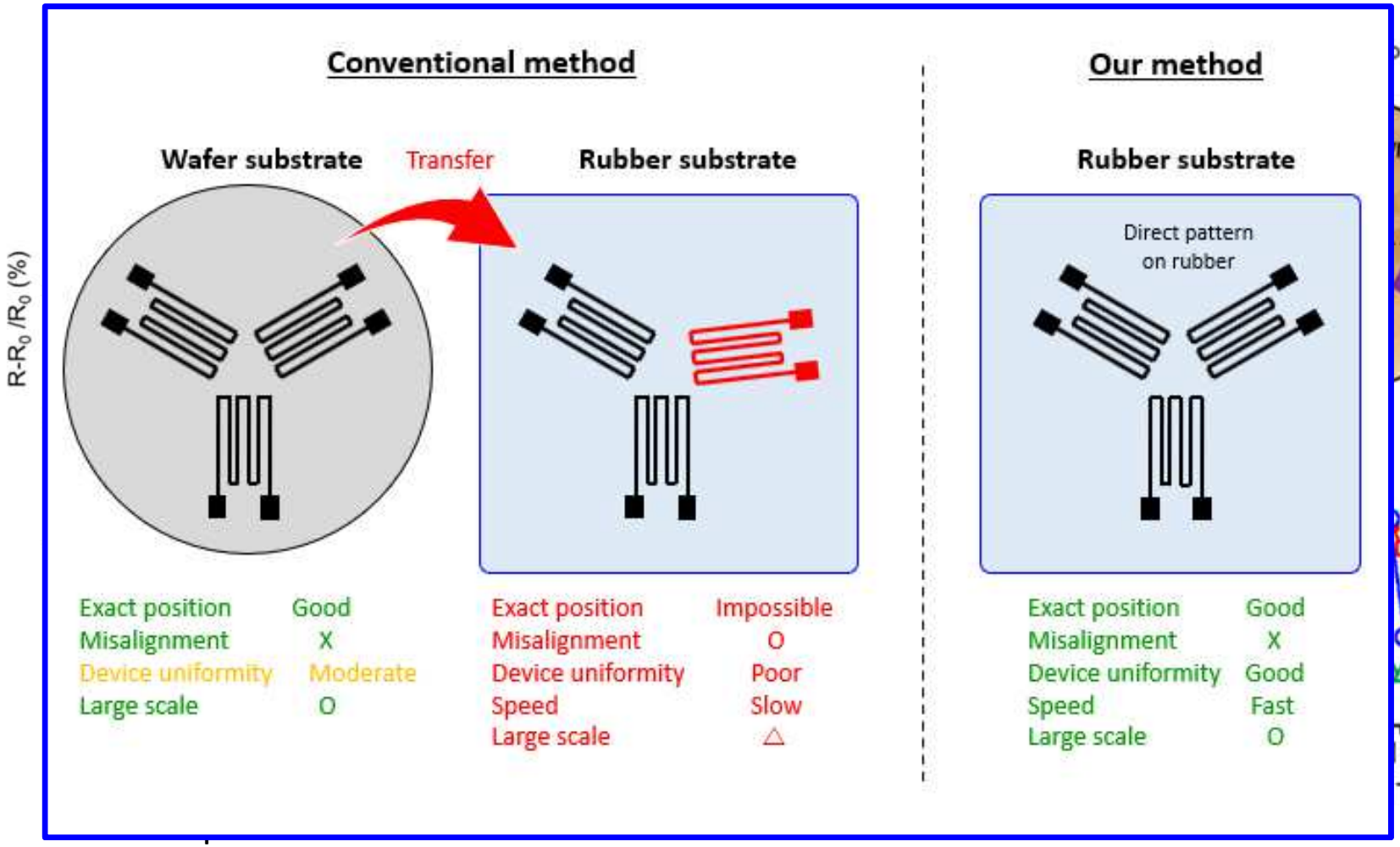
III. Direct formation of MoS_2 on rubber



- The fiber laser penetrates the rubber substrate(PAS) without damage.
- Selectively decompose only the inner ATM precursor.
- Direct formation of MoS_2 pattern on rubber substrate.

Results and discussion (Advantage. III)

III. Direct formation of MoS_2 on rubber



: piezo-resistance variation (G.F: ~ 50)

: Mathematical calculation of strain level and direction

Mini-summary

Direct synthesis of 2D based heterostructure

Challenge I.

Improve uniformity of devices

> Residue-free & Non transfer process

> Direct synthesis on target substrate

Challenge II.

Minimize thermal damage

> Confined heat treatment (vertic. & Horiz.)

Challenge III.

Simple & Cost-effective method

Solution

: Laser based
selective heat treatment

Key mechanism

: adsorption ratio against
exposed wavelength of laser

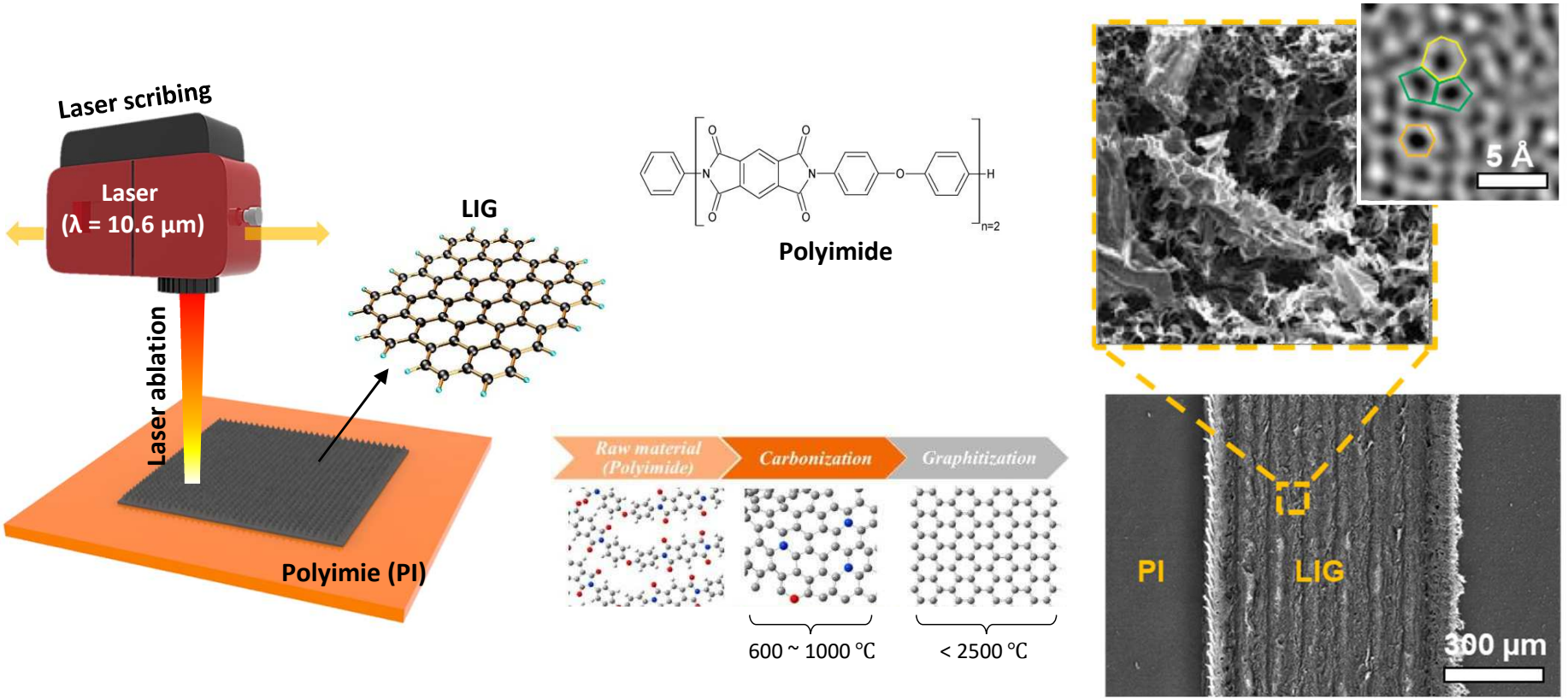
Advantages

: Fast and uniform performance
: Direct formation w/o damage
> realize heterostructure
> form on rubber
: Strain modulation

Contents

Results and discussion (LIG)

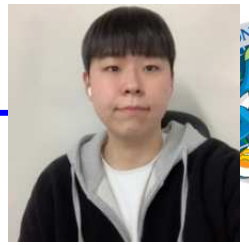
Synthesis of 3D porous carbon



- ✓ One-step graphene material synthesis strategy under ambient conditions
- ✓ Localized photo-thermal effect induces recombination of chemical bonds of a polymer substrate
- ✓ Rapid thermal decompose process → The degassing process forms porous structure

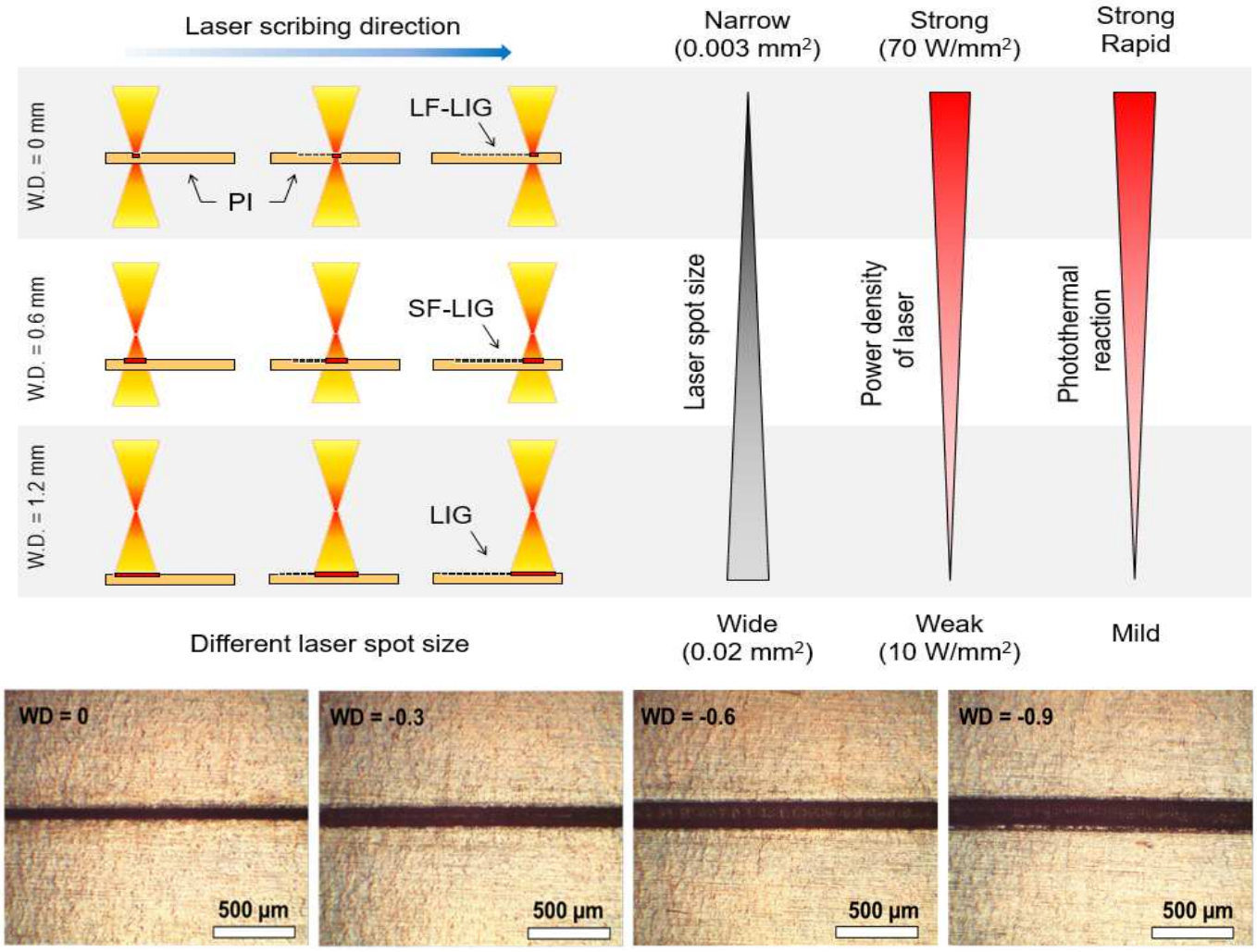
Nat. Comm. **2014**, 5, 5714 (2014)

Results and discussion (LIG)

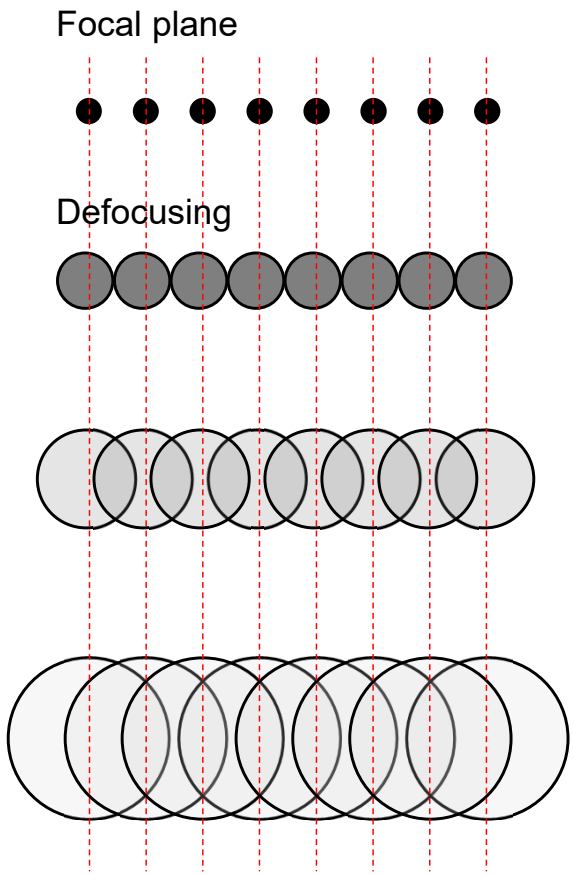


J.W. An

Synthesis of 3D porous carbon – Modulation of photothermal effect



Defocusing effect

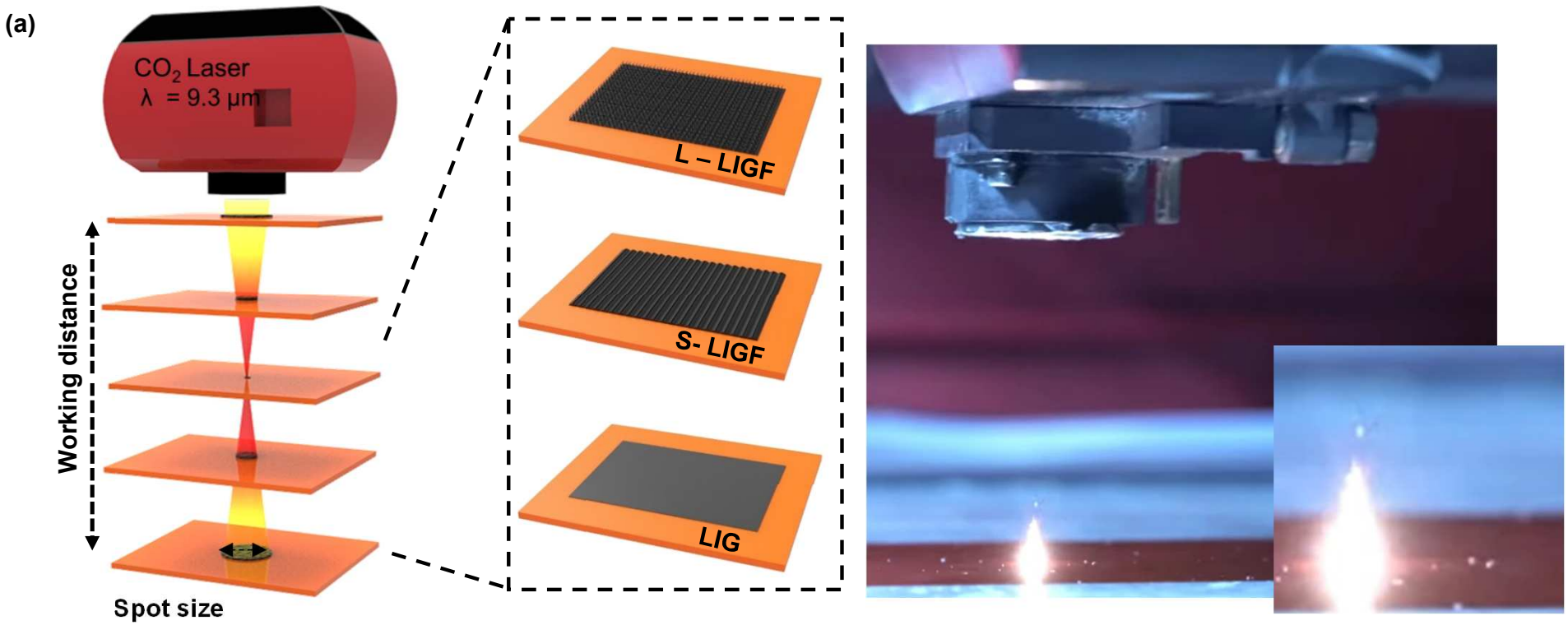


✓ Laser irradiation condition > **Photothermal effect** > Characteristics of LIG

✓ Laser spot size variation induce difference on laser power density (10 – 70 W/mm²) & spatial overlap

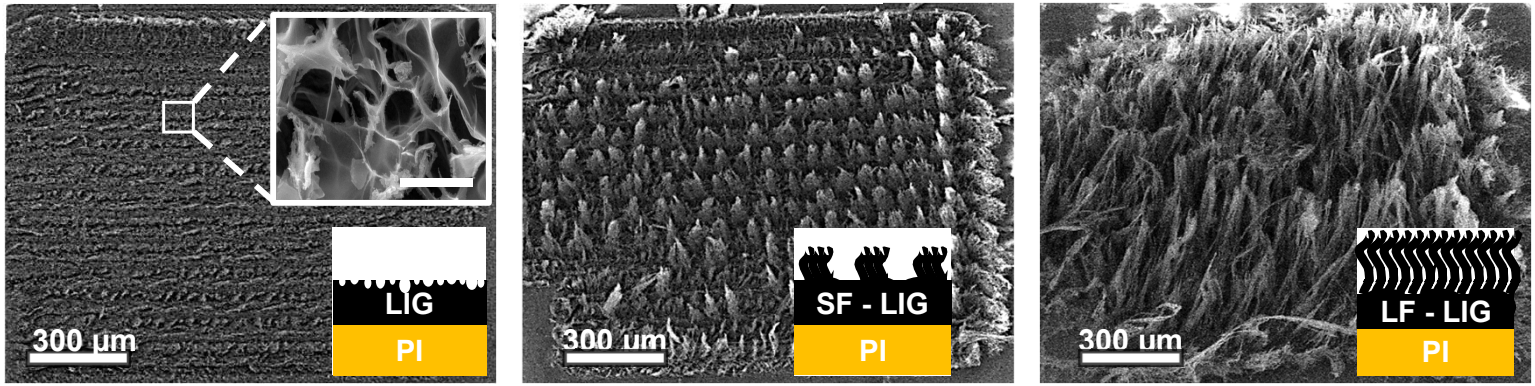
Results and discussion (LIG)

Synthesis of 3D porous carbon – (i) Macro structure control



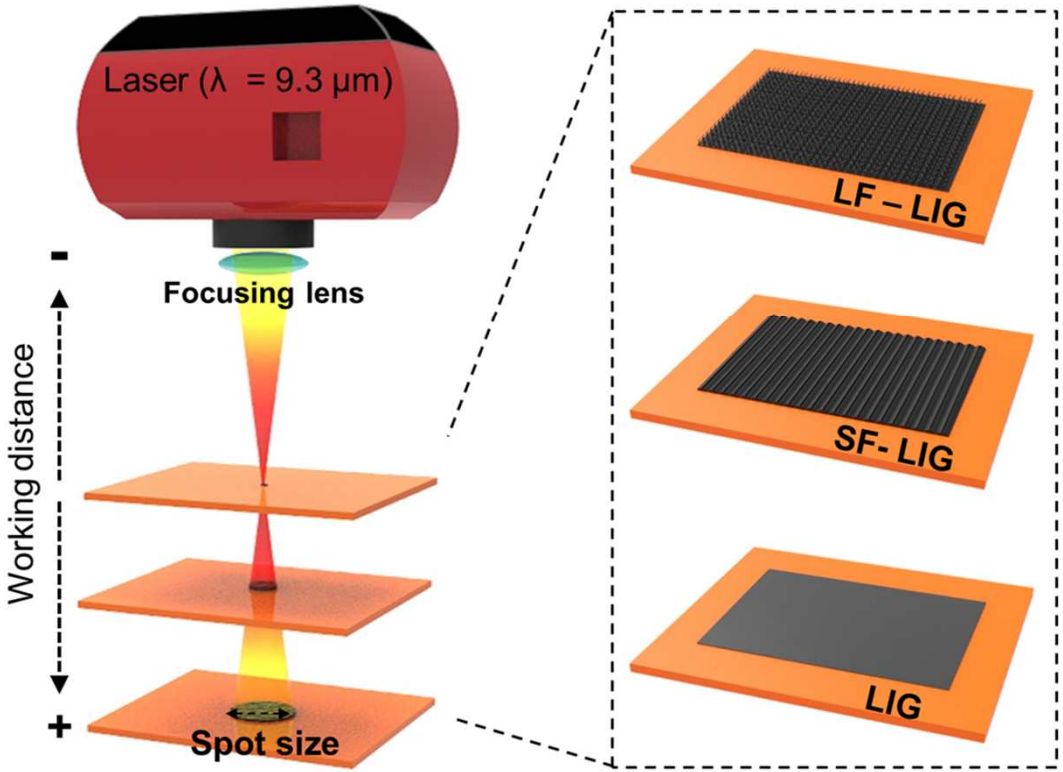
Variations

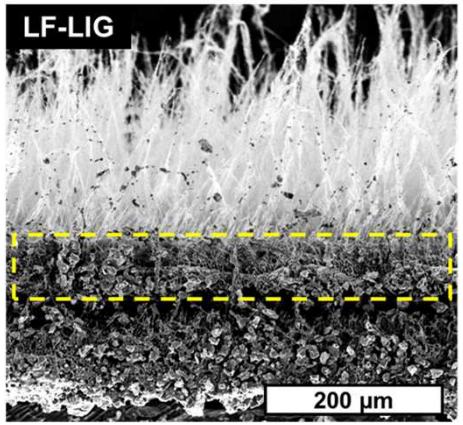
: Fluence
: Pulse
: Scribe speed
: Focal length

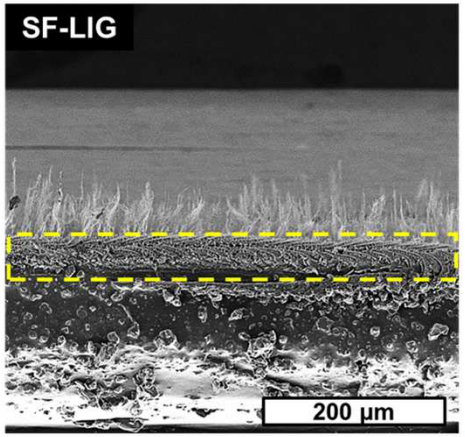


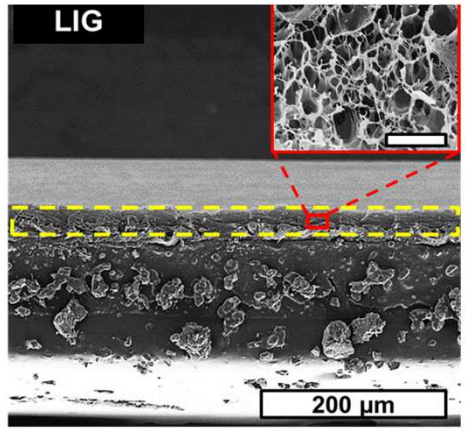
Results and discussion (LIG)

Synthesis of 3D porous carbon – (i) Macro structure control









✓ Laser irradiation condition > Photothermal effect > Characteristics of LIG

✓ Laser spot size variation induce difference on laser power density (10 – 70 W/mm^2)

✓ Surface structure of LIG tuned from **porous** to **fibrous** with the regulation of photothermal effect

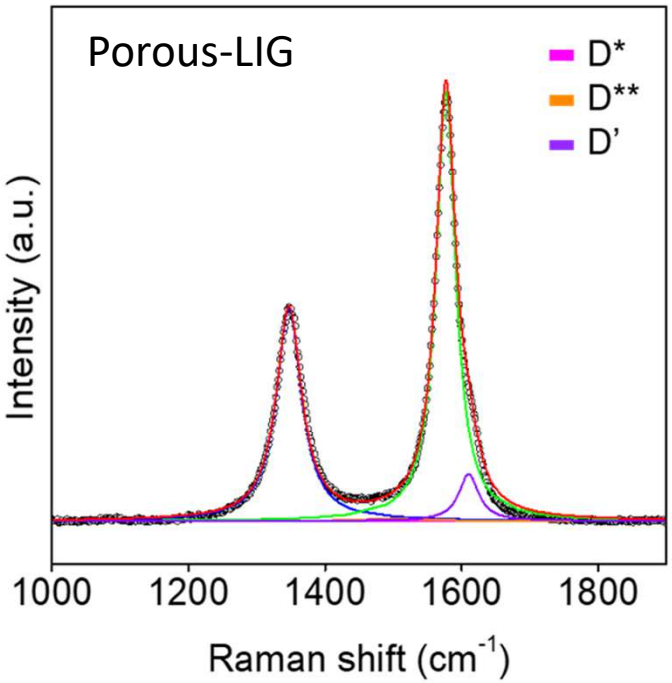
Results and discussion (LIG)

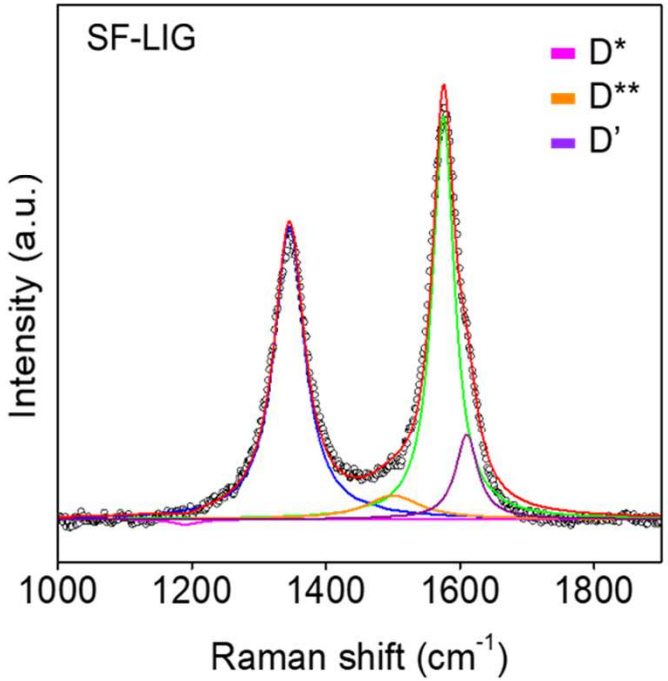
K.H. Choi

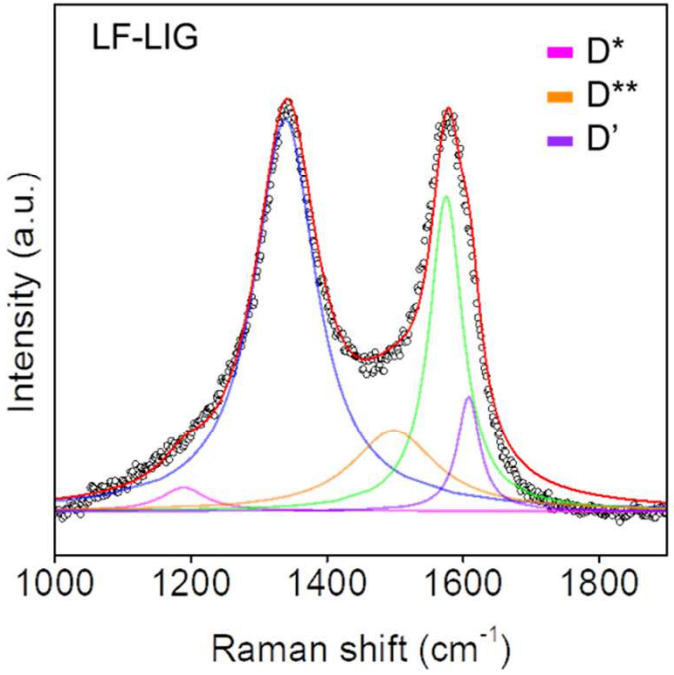
Raman spectroscopy

: crystal defect

D' : breaking of lattice symmetry
D* : heavily disordered carbon
D** : stacking faults







- Large surf. area
- Defect rich

✓ **Fibrous structure**

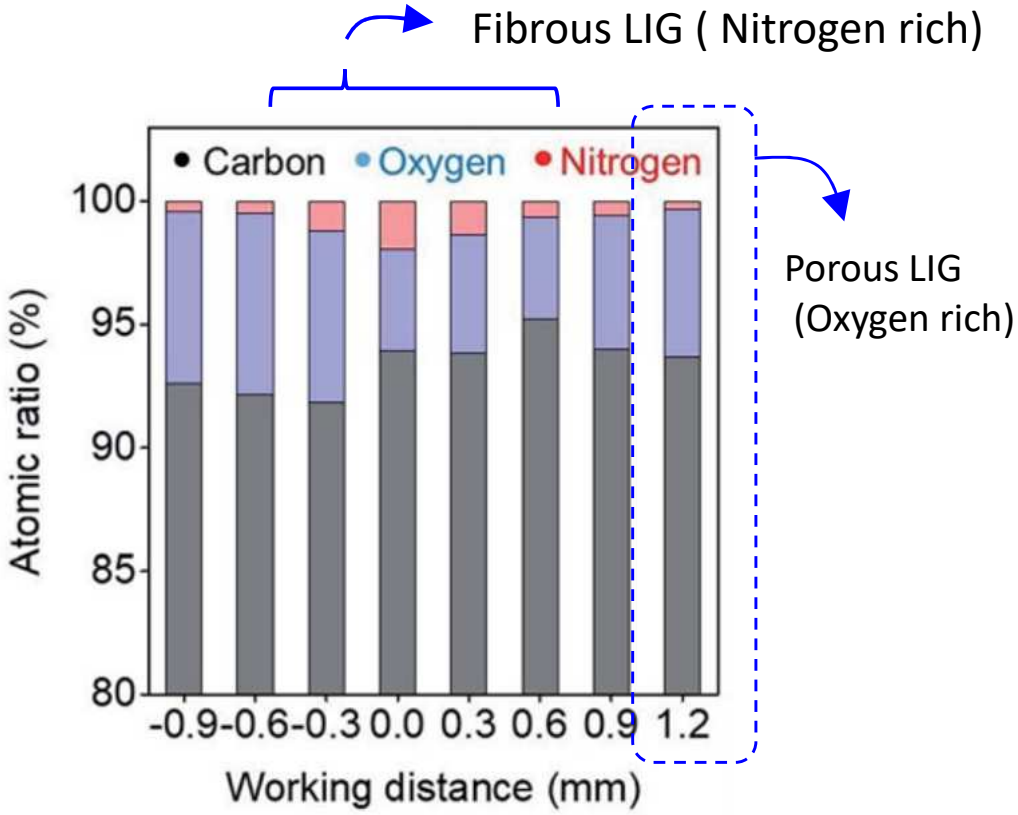
: broadening of peaks & decrease I_G/I_D ratio

→ observed D* & D** peak

→ crystal size : 32 nm → 16 nm

Results and discussion (LIG)

Chemical composition



Similar carbon content

But,

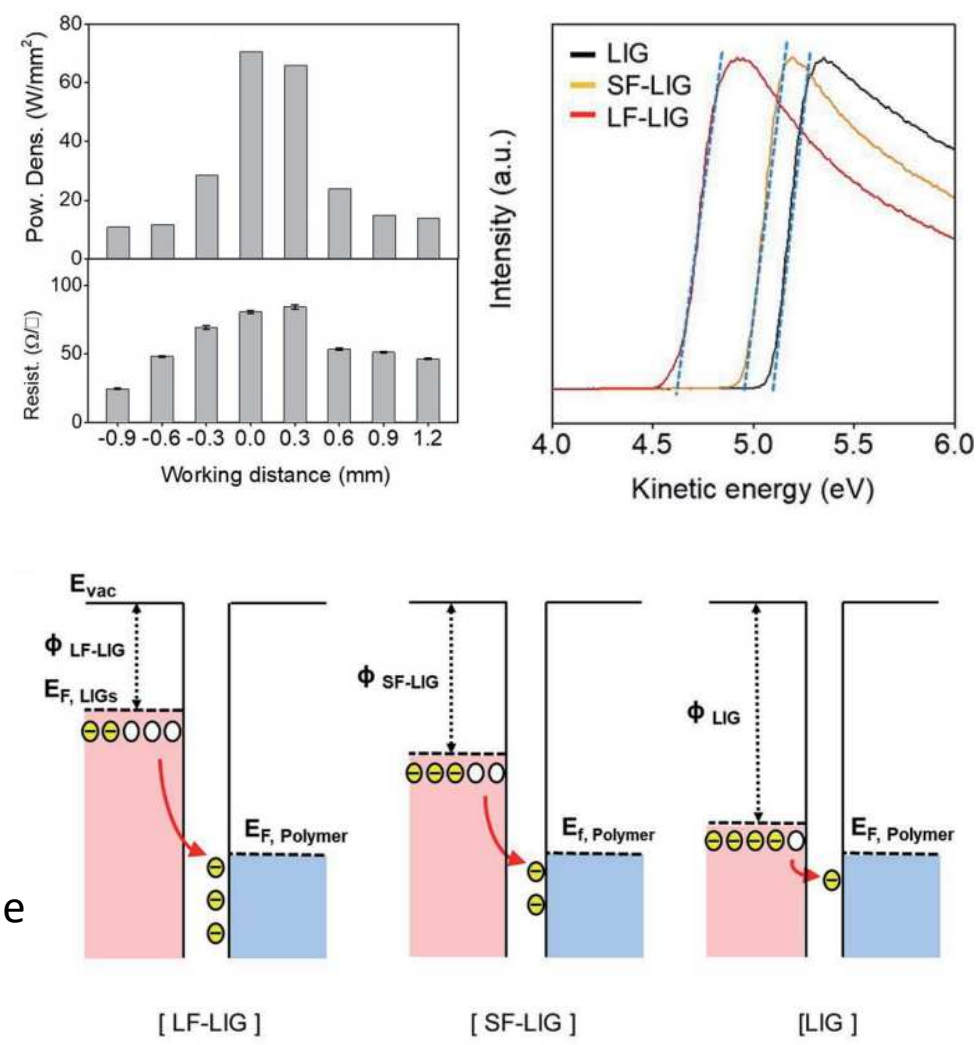
: Porous LIG – Oxygen rich

> withdraw electron from graphene

: Fibrous LIG – Graphitic N rich

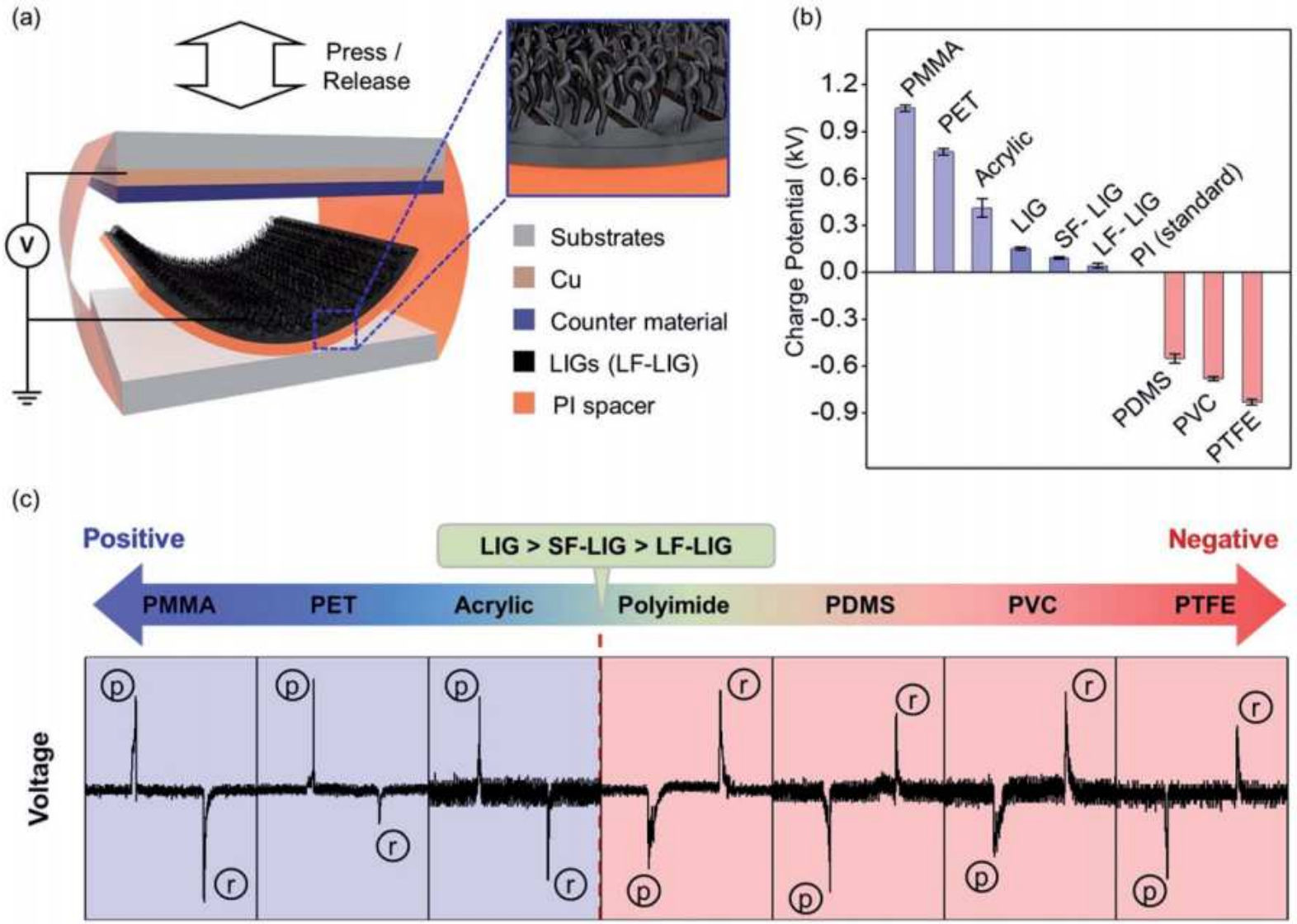
> donate electron to graphene

Electrical property



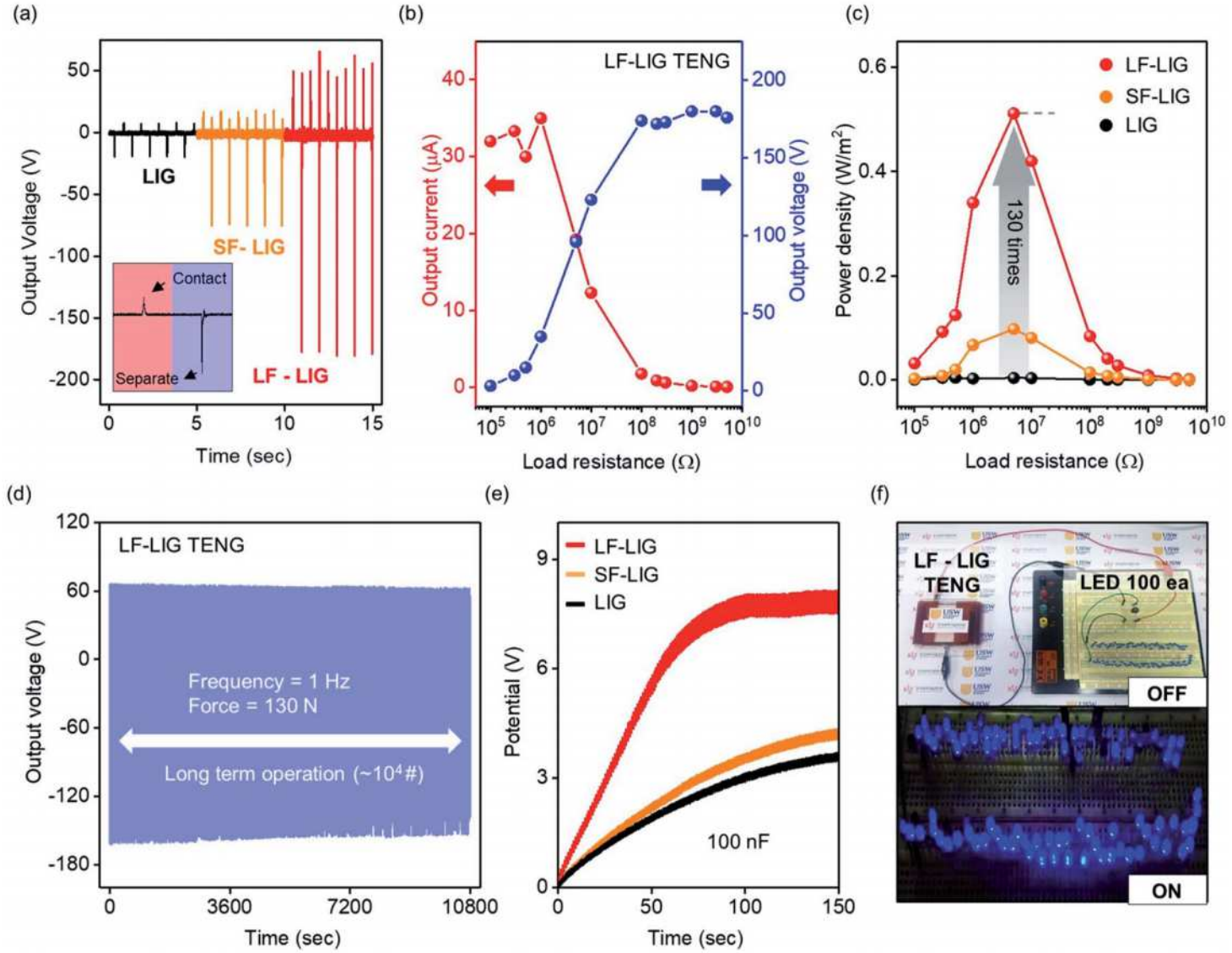
Results and discussion (LIG)

Triboelectric property of LIG



Results and discussion (LIG)

PMMA/LIG based TENG

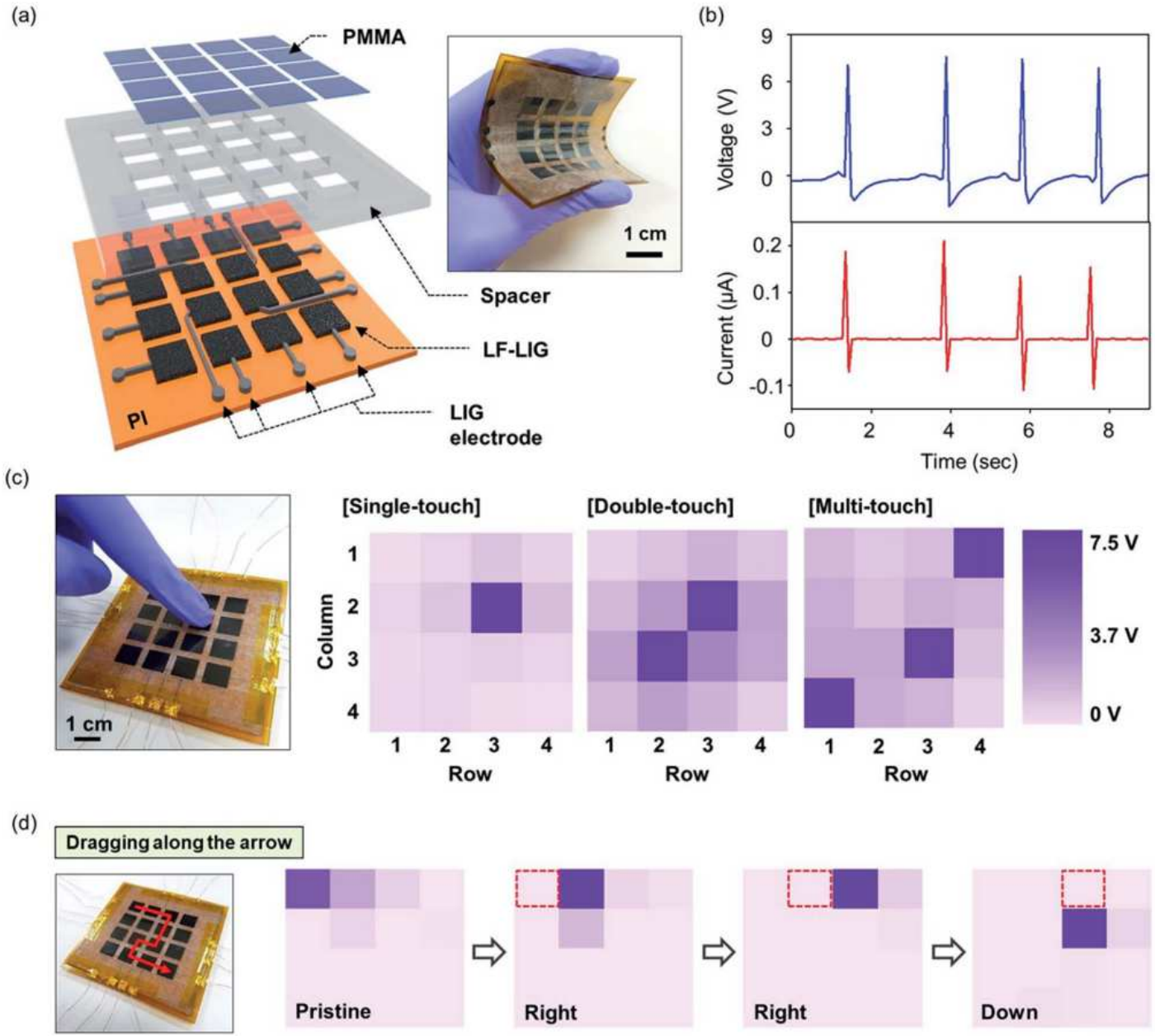


LF-LIG based TENG shows **130 times** higher power density

: Contact surface area / W.F. / surface charge potential

Results and discussion (LIG)

PMMA/LIG based TENG



< TENG based tough sensor

: Printing technique

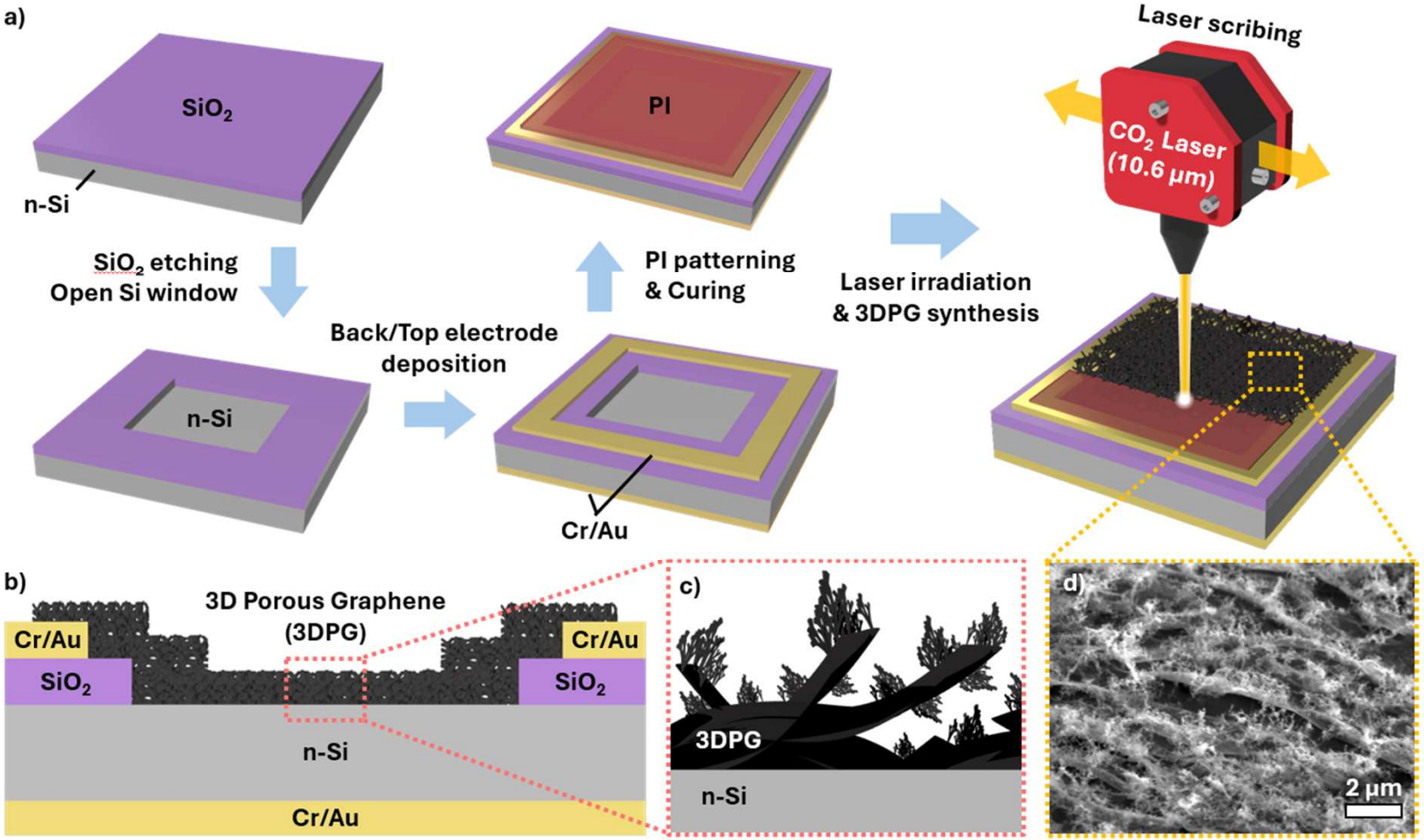
- Laser printing
- ink-jet printing

: array type

: flexible device

Results and discussion (LIG)

3D porous carbon on Si wafer



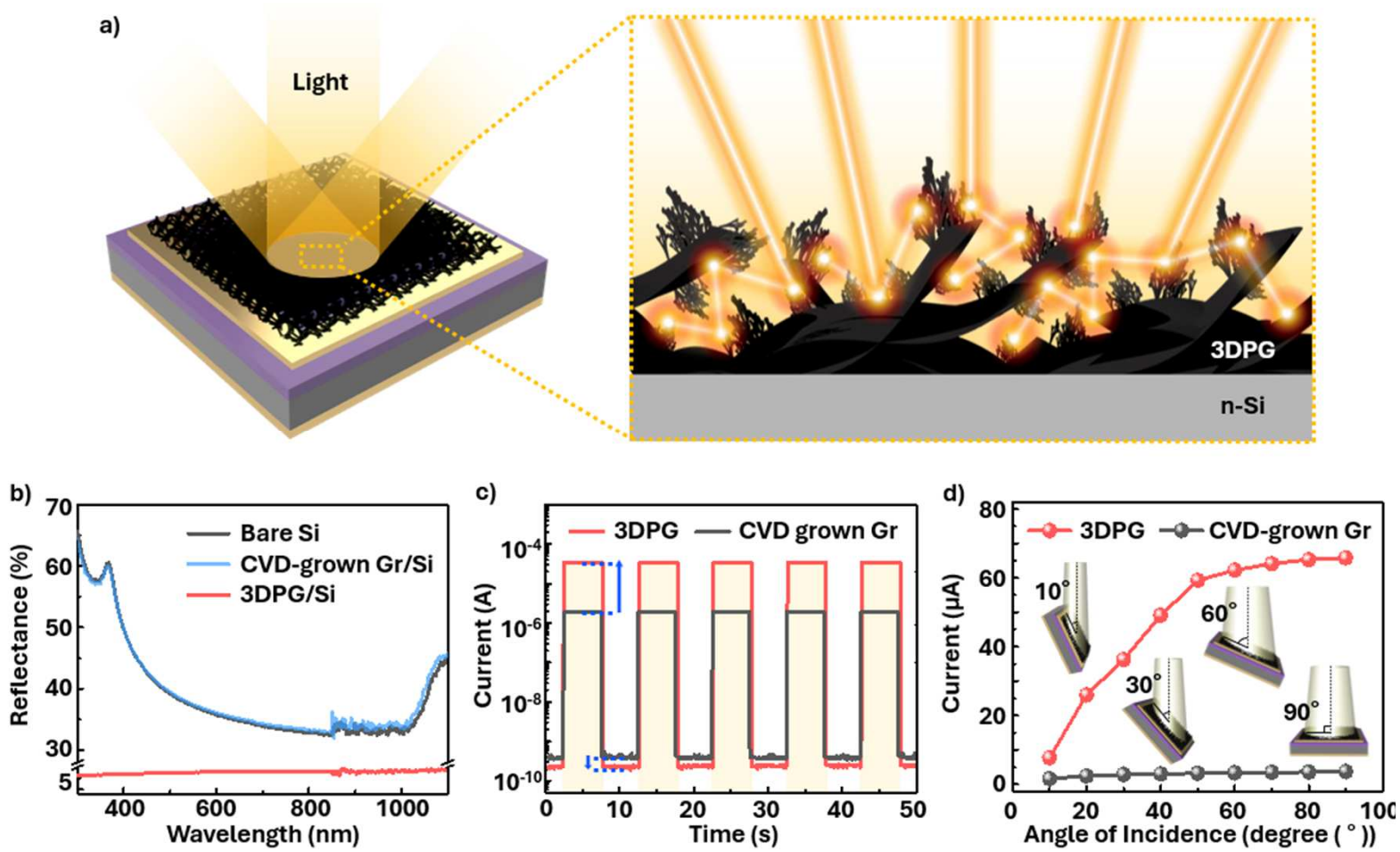
→ Low absorption of CO_2 laser energy

PI pattern on Si/SiO_2 wafer → 3D porous carbon synthesis

→ High absorption of CO_2 laser energy → photothermal heating

Results and discussion (LIG)

Photoresponse of a 3DPG/Si Schottky junction sensor (vs. conventional CVD graphene/Si)



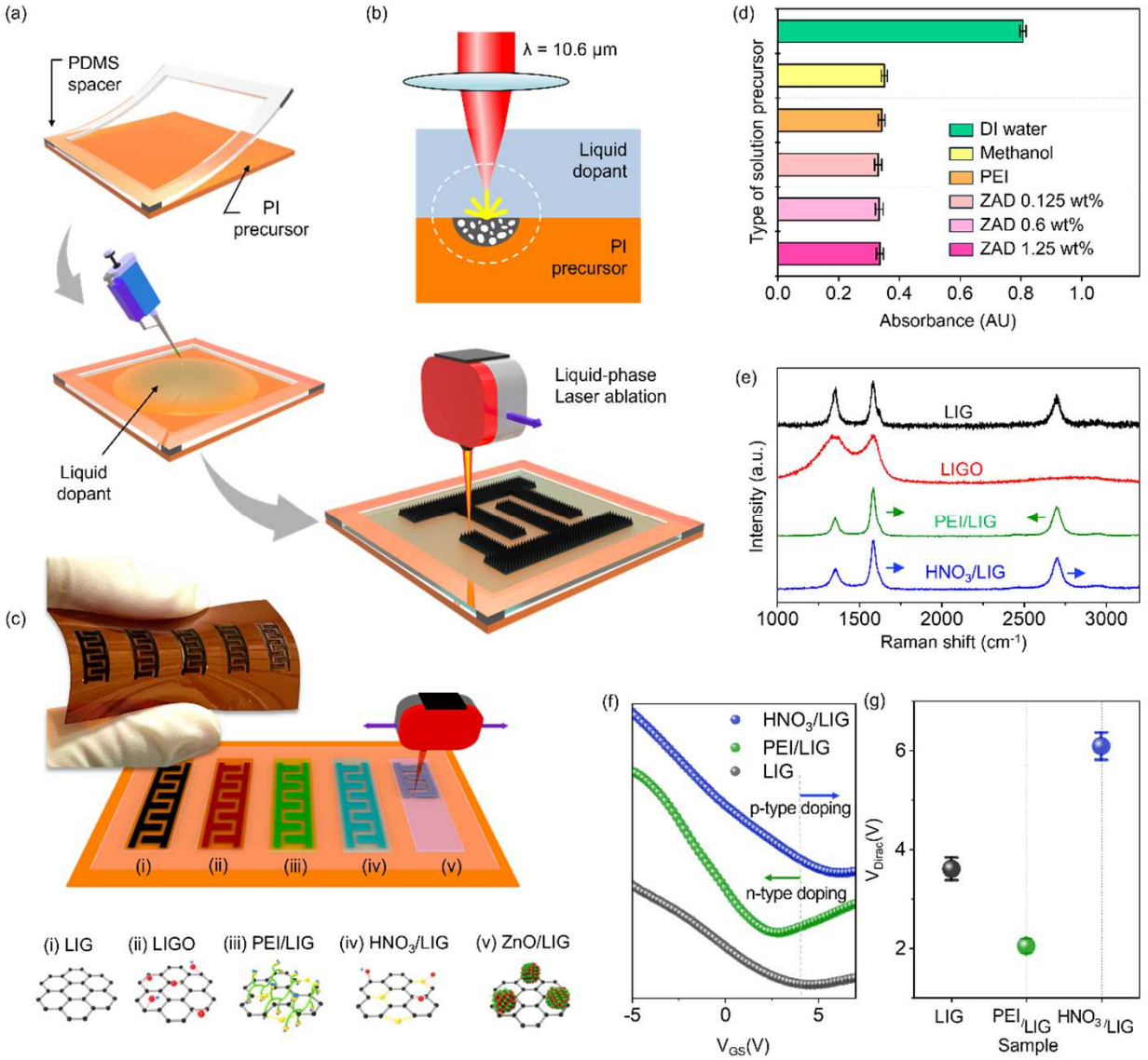
[Advantages of the Porous Structure]

: 3DPG exhibits very high absorption and low reflectance in the visible range

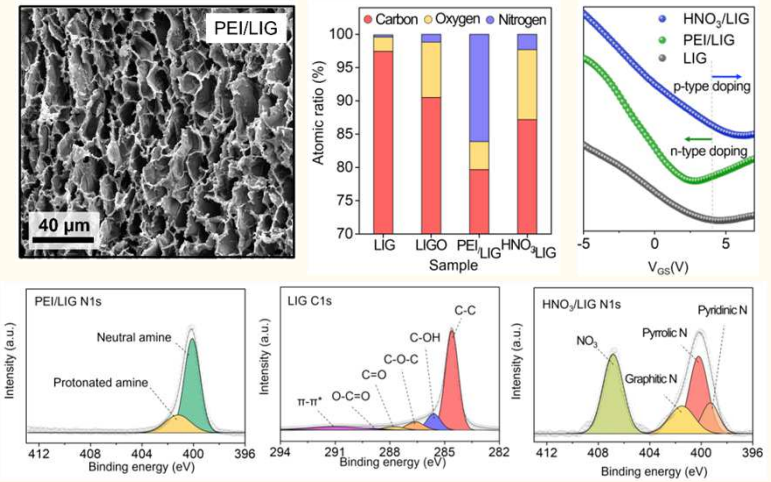
: Maintains high photoresponse over a wide range of incident angles due to surface scattering

Results and discussion (LIG)

Confined Liquid-phaser laser ablation

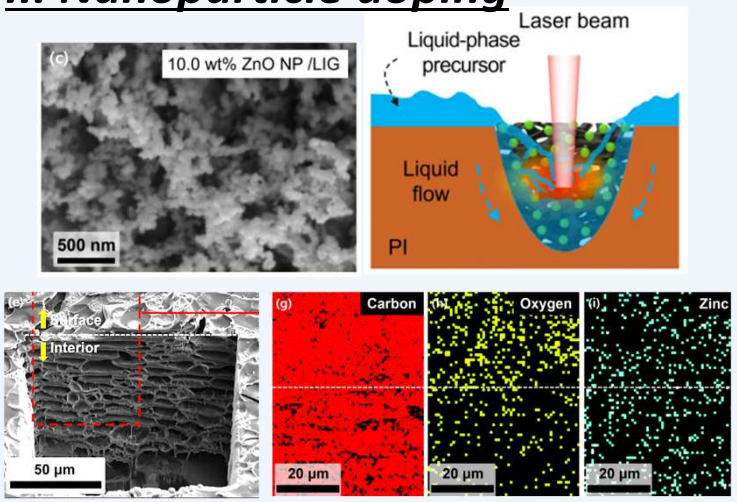


I. Chemical doping



n doping ⟷ p doping

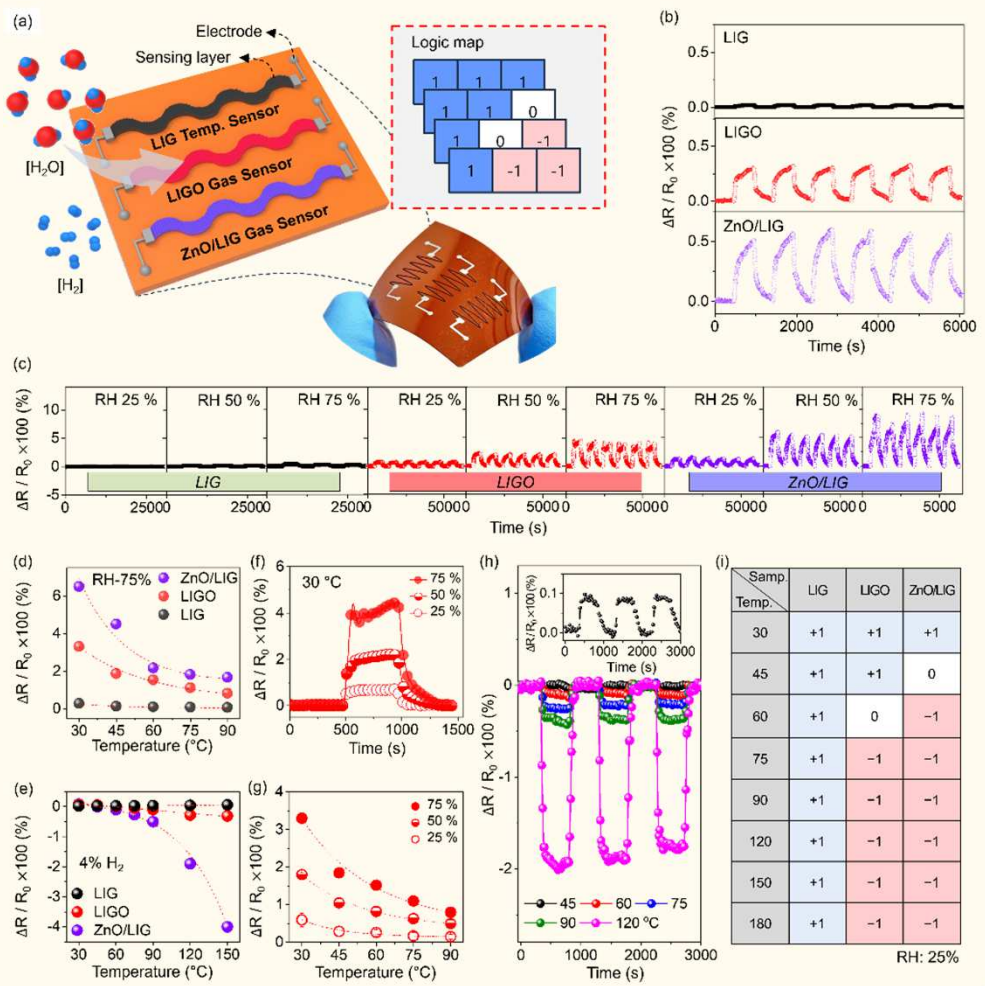
II. Nanoparticle doping



Results and discussion (LIG)

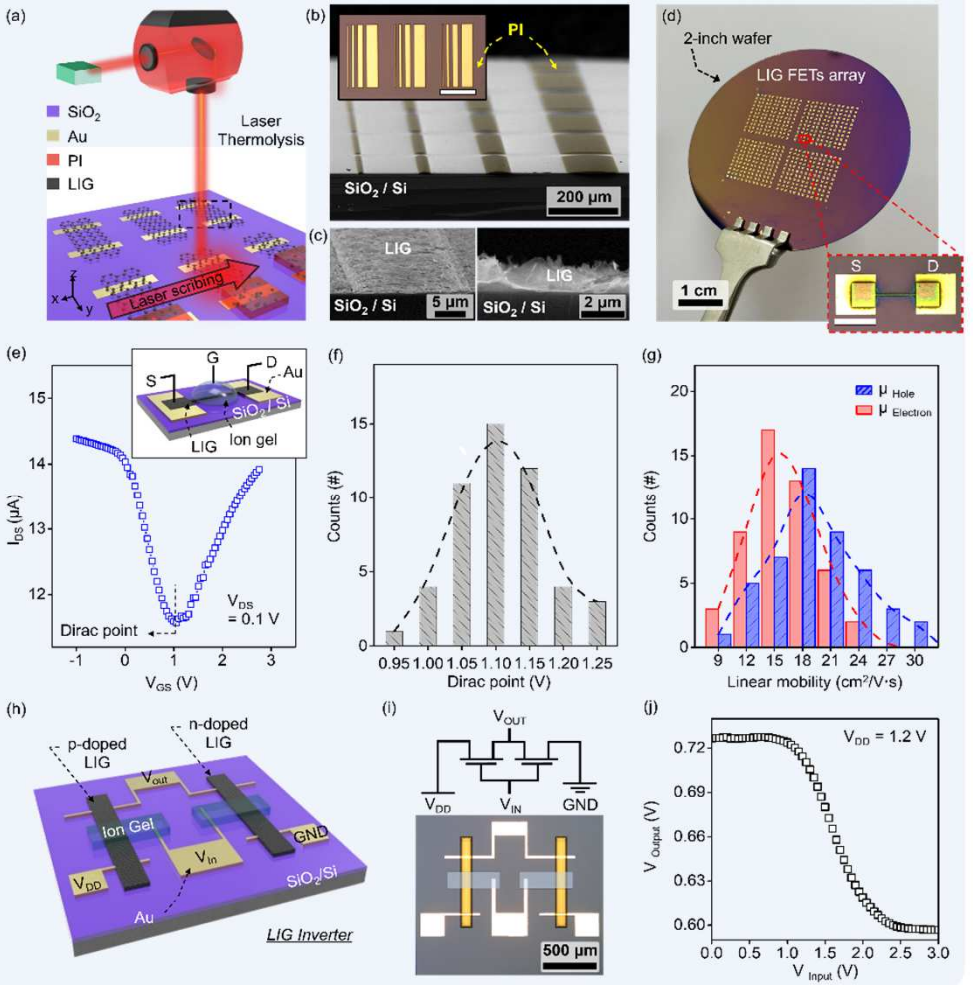
Selectively doped LIG-based active matrix device

Multi-gas sensing via integrated sensor array



Samp. / Temp.	LIG	LIGO	ZnO/LIG
30	+1	+1	+1
45	+1	+1	0
60	+1	0	−1
75	+1	−1	−1
90	+1	−1	−1
120	+1	−1	−1
150	+1	−1	−1
180	+1	−1	−1

CMOS circuit based on LIG NMOS & PMOS

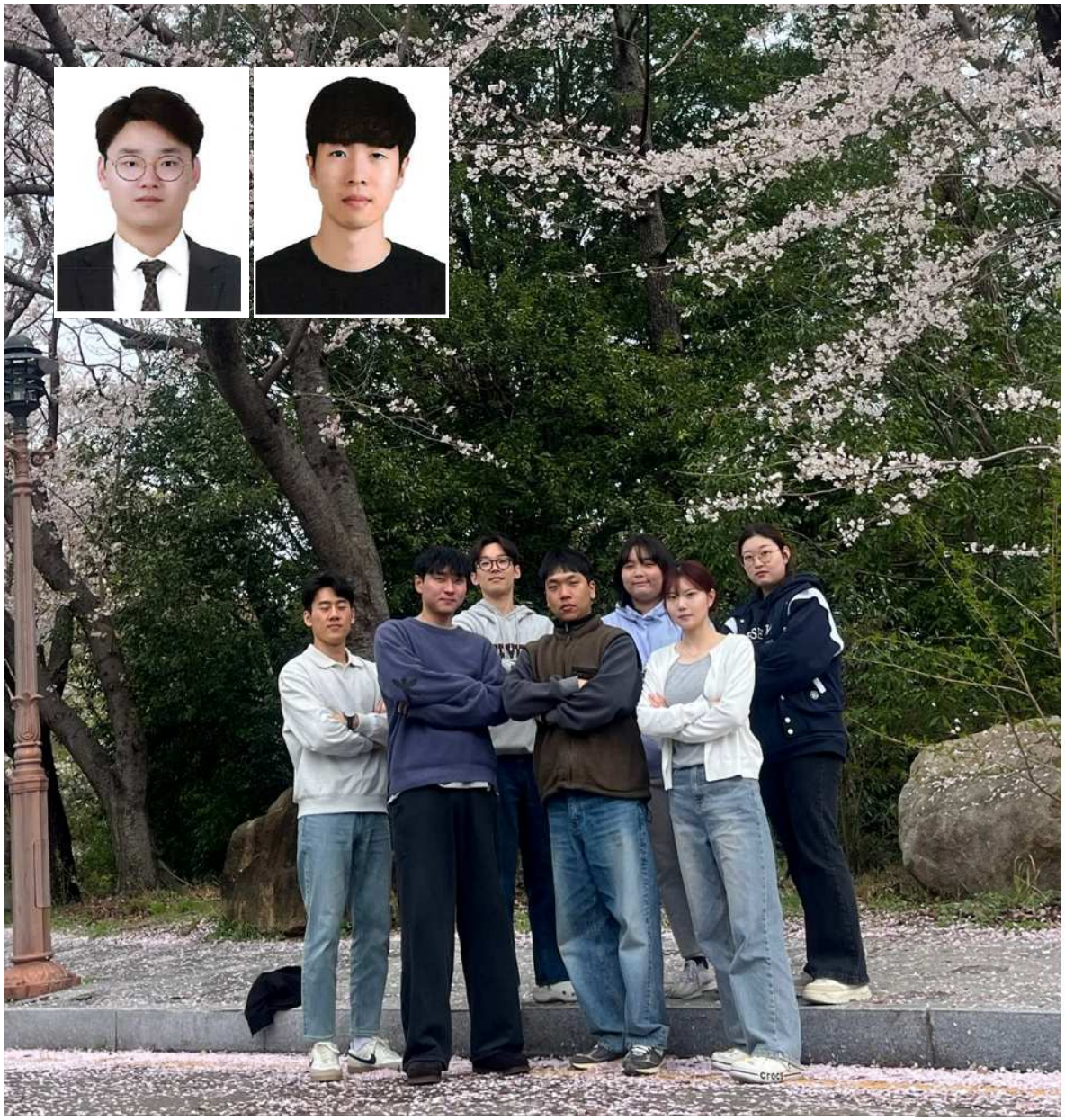


[Why LIG-based active device arrays have not been realized]

- **Challenging micropatterning of porous structures**
- **Limited selective doping of LIG on a single substrate**
- **Instability in metal–LIG contact characteristics**

Unpublished data

Acknowledgement



Special thanks to..

Prof. Jong-Hyun Ahn
Prof. Tae Wook Kim
Dr. Sukang Bae
Prof. Jae Hyun Lee
Prof. Sang Hoon Bae
Prof. Sang Hyun Lee
Dr. Houk Jang
Dr. Aram Lee
Dr. Sung woong Park
.
.

Homepage

Scan Me