2024 KOR-EU Joint Workshop

Large-Scale Synthesis of 2-Dimensional Transition Metal Dichalcogenide (TMDCs) by Low-Temperature Plasma and their Applications

Taesung Kim

School of Mechanical Engineering and SAINT
Department of Semiconductor Convergence Engineering
Sungkyunkwan University (SKKU)

성균관대학교 SUNGKYUNKWAN UNIVERSITY(SKKU)
SAINT 성균나노과학기술원
NPTL Nano Particle Technology Lab.

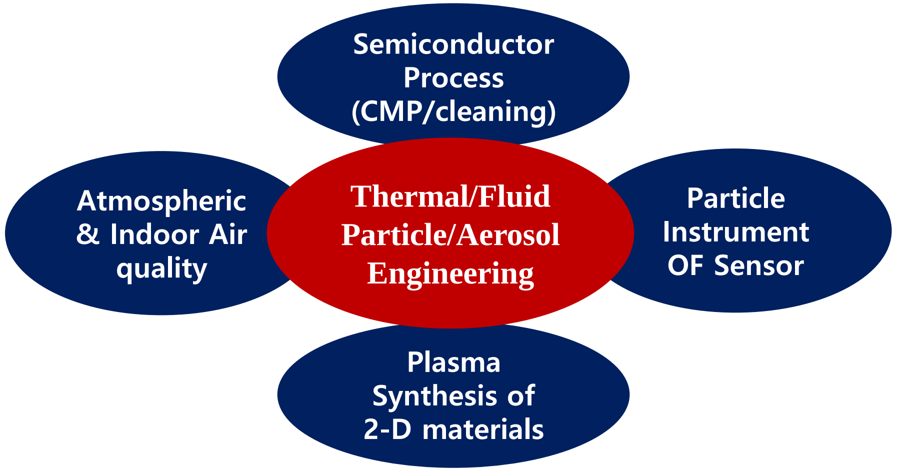
Prof. Taesung Kim

Education

Year	Degree	Institute	Major
2002	Ph. D.	U. of Minnesota, Twin Cities	Mechanical Engineering
1998	M. S.	U. of Minnesota, Twin Cities	Mechanical Engineering
1994	B. S.	Seoul National University	Mechanical Engineering

Work experience

Period	Institute/Company	Rank
2005. 3 - present	SKKU School of Mechanical Engineering	Professor
2023. 1 - present	SKKU College of Engineering	Dean
2019. 1 – 2020.12	SKKU Admissions Office	Vice President
2014. 3 – 2018. 12	SKKU Business Foundation	Vice President
2011. 10 – 2015. 4	Samsung Display	Technical Advisor
2002. 3 – 2005. 2	Seagate Technology, USA	Senior/Staff Engineer
1994. 3 – 1996. 6	ROK Army	2nd/1st Lieutenant



Semiconductor Process (CMP/cleaning)

Atmospheric & Indoor Air quality

Thermal/Fluid Particle/Aerosol Engineering

Particle Instrument OF Sensor

Plasma Synthesis of 2-D materials

Graduate Student

Semiconductor Process

2D Materials and application

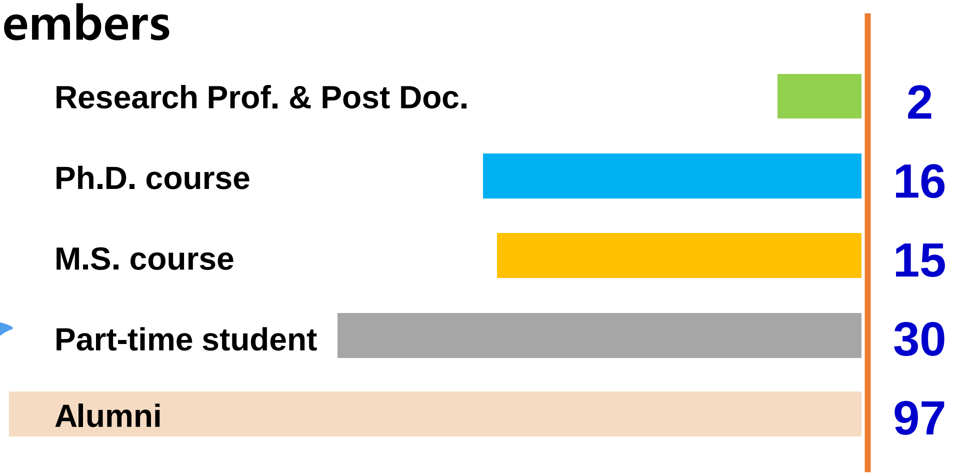
Aerosol Technology & Machine Learning

Research Professor
Dr. Keunseok H. Kim

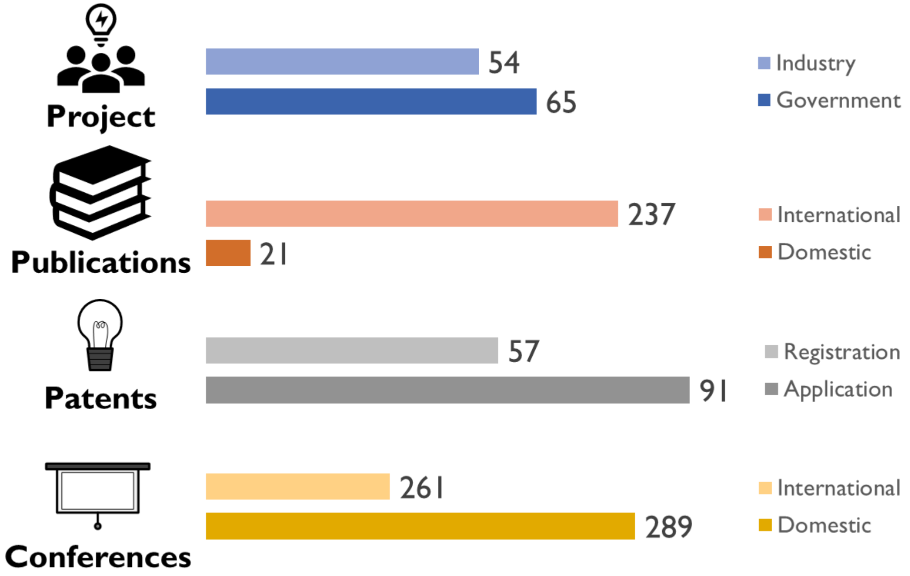
Post Doc.
Dr. Vinit Kanade

Research Group

Members



Achievements

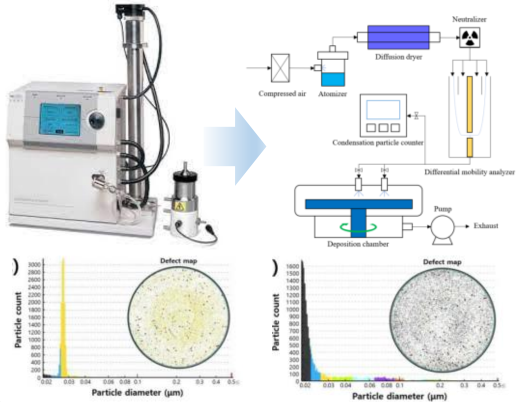


Nano Particle Technology Lab.

Research Area

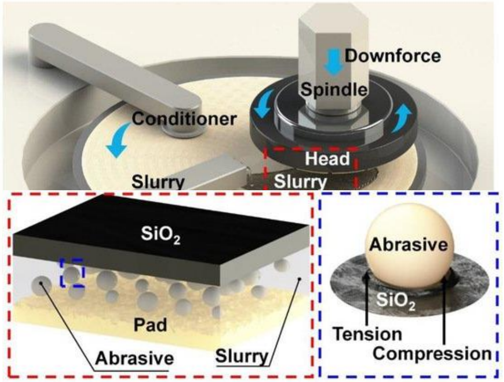
Particle / Aerosol Technology

Aerosol particle measurement
Aerosol deposition



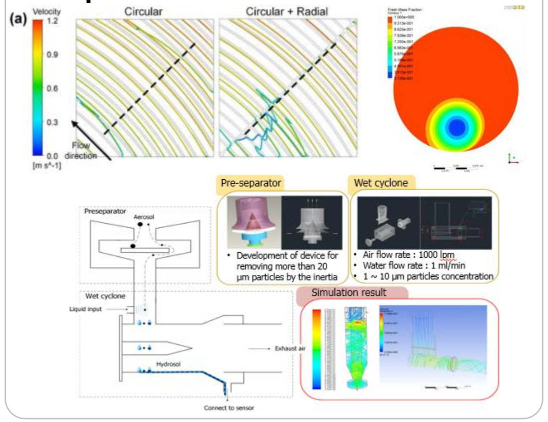
Semiconductor Process

Chemical Mechanical Polishing
CO_2 gas cluster/wet cleaning



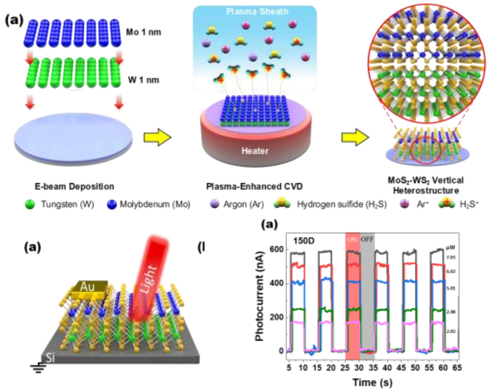
Fluid / Thermal Engineering

CFD simulation to study CMP process and aerosol behavior



Plasma Process

Synthesis of 2D-Materials using PE-CVD and applications



Collaboration Partners

Univ.

서울대학교
포항공과대학교
중앙대학교
가천대학교
Universita Campus Bio Medico (Italy)
상하이 대학교 (China)
심바이오시스 국제 대학교 (India)

Research Institute

한국기계연구원
한국표준과학연구원
한국생산기술연구원
한국철도기술연구원
한국화학연구원

Industry

삼성전자
삼성 디스플레이
삼성SDI
SK 하이닉스
SKC
SK siltron
현대자동차
Wonik IPS
3M
Merck
KPX Chemical
SEMES

Contents

Part 1. TMDC Research in NPTL

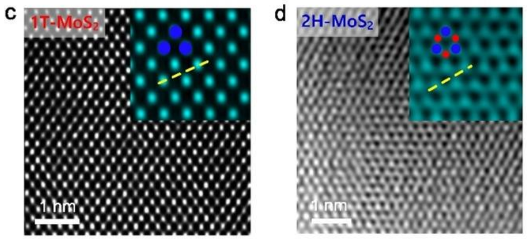
1-1. Advantage of PECVD-based 2D Material Synthesis

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a widely used technique in various industries, including semiconductors, optics, and nanotechnology.

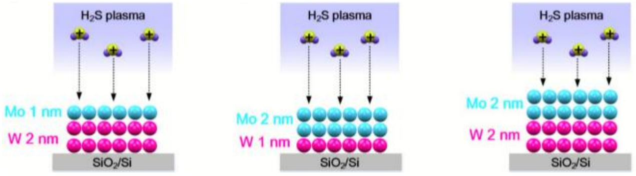
- Lower Temperature Processing (< 300ºC)
- Controlled Film Properties
- Compatibility with various Substrates
- Uniform and Large-scale Films

- Enhanced Chemical Reactions
- Industrial Compatibility
- Customization

Phase Controlled Synthesis

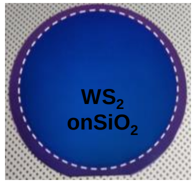


One-step heterostructure Synthesis



Heterostructure Synthesis

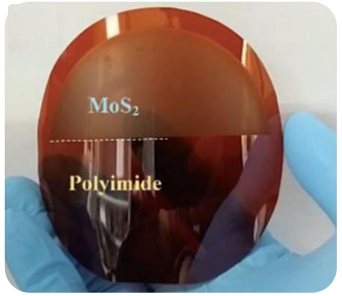
Wafer Scale and Uniform thin film on Different Substrate



4-inch Substrate

Part 1. TMDC Research in NPTL

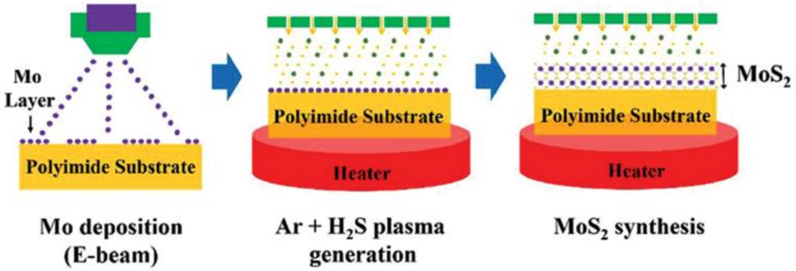
1-1. History of 2D Material Research



2015

The First Plasma-Based TMDC Synthesis

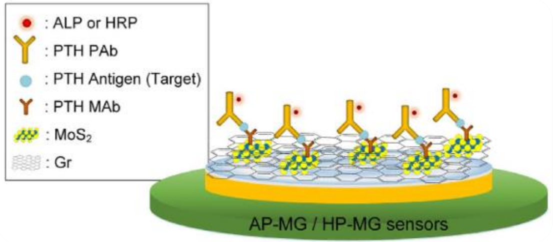
Dr. Chisung Ahn
KITECH (Korea Institute of Industrial Technology)



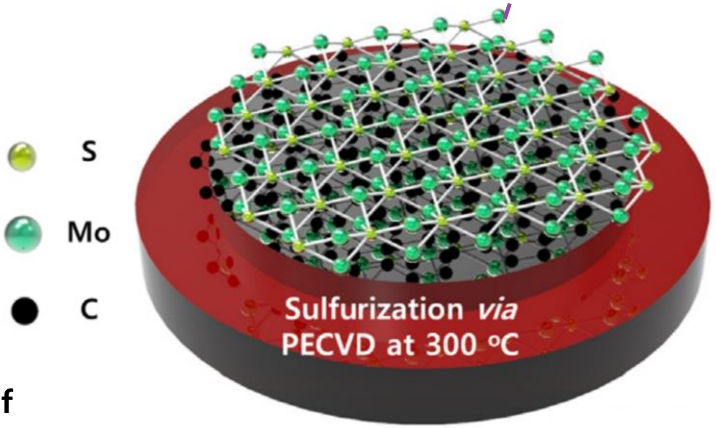
Low-Temperature Synthesis of Large-Scale MoS_2 on Polyimide
(2015) *Advanced Materials*

2016 — 2017 — 2018 — 2019 — 2020

MoS_2-Graphene Hormone Sensor On PCB (2016) *Scientific Reports*

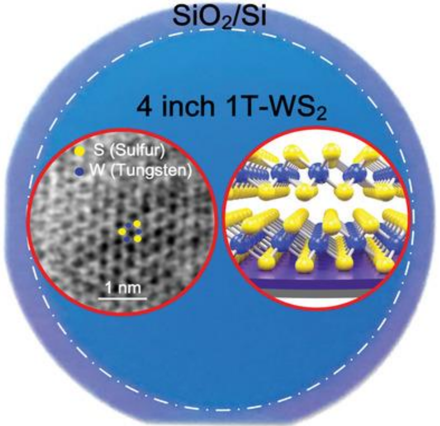


Dr. Hyeong-U Kim
KIMM (Korea Institute of Machinery & Materials)



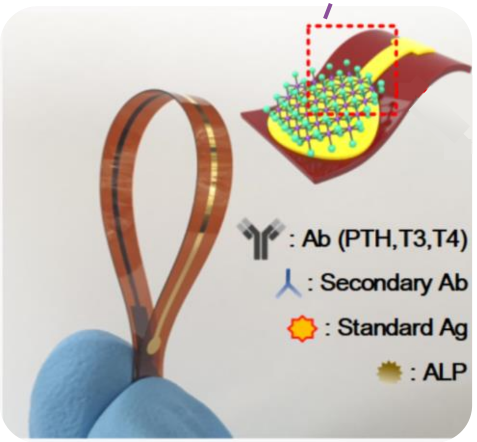
Wafer-Scale MoS_2 / Graphene
(2018) *Applied Surface Science*

Dr. Vinit Kanade
NPTL, Sungkyunkwan University



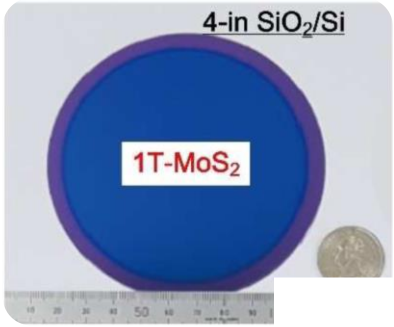
Wafer-Scale 1T-WS_2
(2020) *Small*

Flexible Endocrine Sensor
(2020) *Analytical Chemistry*

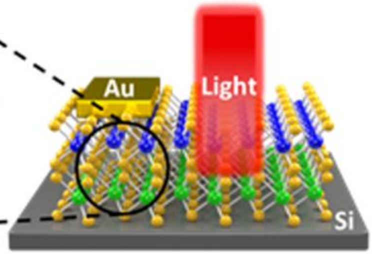


Part 1. TMDC Research in NPTL

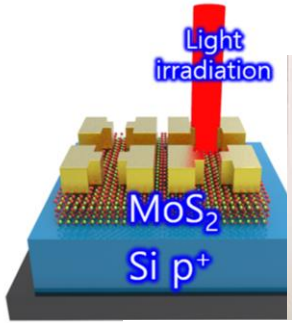
Wafer-scale 1T MoS_2 for HER reaction
(2021) *ChemSusChem*



Photodetector Device by Plasma synthesized TMD
(2021) *ChemSusChem,* (2021), *ACS Applied Materials & Interfaces*

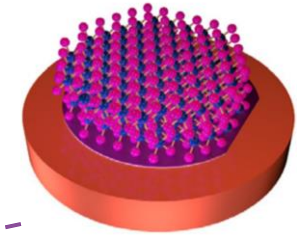


Dr. Chaitanya Kanade
Centre for Materials for Electronic
Technology, Pune (C-MET, Pune)



Gunhoo Woo (Ph.D. student)
NPTL, SKKU

Multiphase MoS_2 Heterostructure for
Photodetector (2023) *Nanoscale*

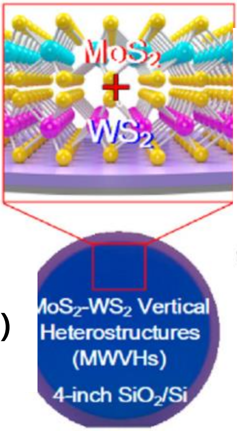


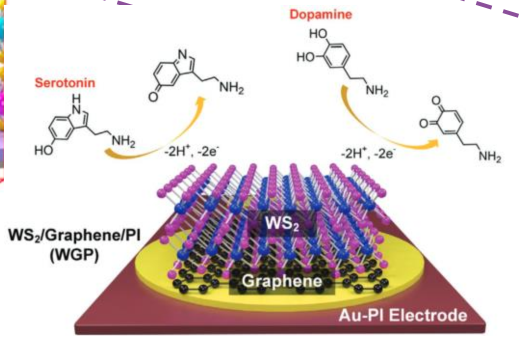
1T/2H-MoS_2
heterostructure

Kubra Aidin (Ph.D. student)
NPTL, SKKU

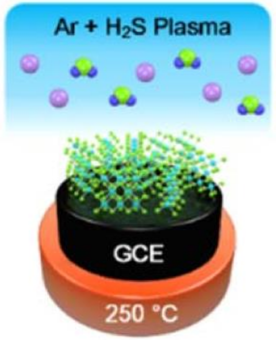
2021 — 2022 — 2023 — 2024 ~ →

Hyunho Seok
(Ph.D. student)
NPTL, SKKU



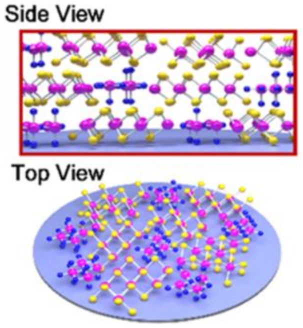


WS_2/Graphene Hormone Sensor
(2021) *Small*



Vertically Aligned TaS_2 for HER
(2022) *Nanotechnology*

Patchwork-Structured 1T-WS_2/a-WO_3
(2022) *ACS Applied Materials & Interfaces*



Nanograin
1T-WS_2 / a-WO_3

Jinil Cho (Ph.D. student)
NPTL, SKKU

Wafer-scale Vertical Heterostructure of MoS_2/WS_2

Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-1. Trends in Two-Dimensional Materials Research

2-2. Types and Characteristics of Two-Dimensional Materials

2-3. Synthesis Methods and Limitations of Two-Dimensional Materials

2-4. Potential to Overcome Limitations of 2-D material synthesis via Plasma-assisted Processes

2-5. Advantages of Synthesizing 2D Materials using Low-Temperature Plasma Technology

2-6. 2D Material Synthesis Technology via Low-Temperature Plasma

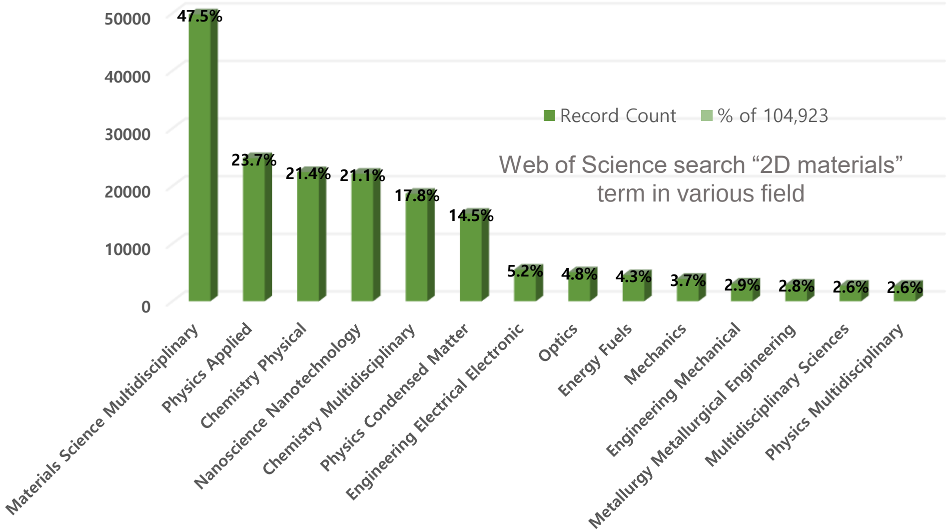
Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-1. Trends in Two-Dimensional Materials Research

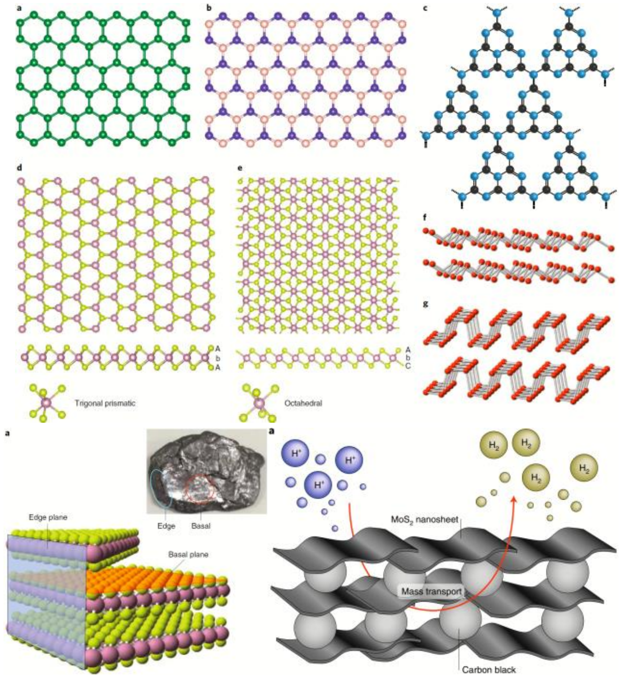
2D materials, often exhibit different physical behaviors compared to their 3D counterparts due to quantum confinement.

- High Surface Area
- Electrical Properties
- Thermal Conductivity
- Quantum Effects

- Optical Properties
- Chemical Reactivity
- Bandgap Tunability
- Mechanical Strength



Catalytic Application

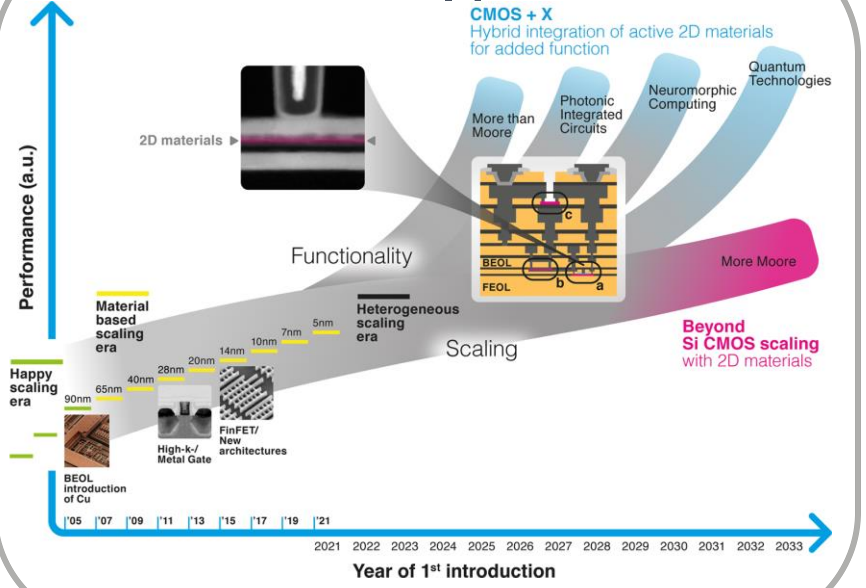


Chia, X., et al. *Nat. Catal.* 1, 909–921 (2018).

Challenges

- Large-scale production
- Integration into existing technologies
- Technology Readiness Level (TRL)

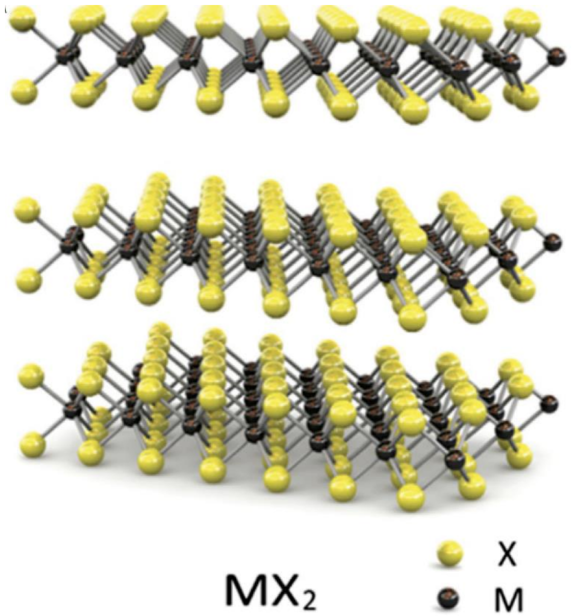
Electrical Application



Lemme, M.C., et al. *Nat. Commun.* 13, 1392 (2022).

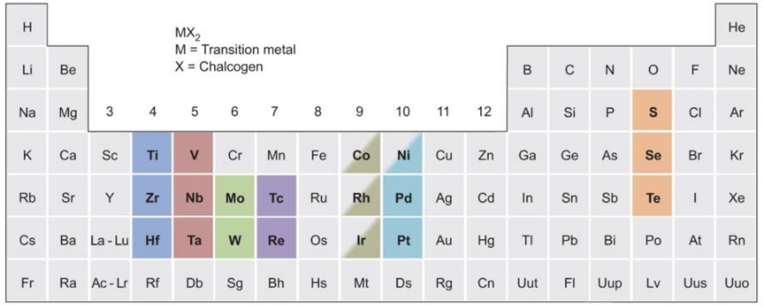
Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-2. Types and Characteristics of TMDC Materials



- Due to strong in-plane covalent bonds, it exhibits high physical and chemical stability along with excellent mechanical flexibility
- The presence of the 'quantum confinement effect' results in properties such as band gap being different from those in three-dimensional structures due to discrete energy states.
- A two-dimensional structure composed of one transition metal (M) and two chalcogen elements (X: S, Se, Te) bonded together

(MX_2 : MoS_2, WS_2, $PdSe_2$, WTe_2 …)



MX_2
M = Transition metal
X = Chalcogen

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	**S**	Cl	Ar
K	Ca	Sc	**Ti**	**V**	Cr	Mn	Fe	**Co**	**Ni**	Cu	Zn	Ga	Ge	As	**Se**	Br	Kr
Rb	Sr	Y	**Zr**	**Nb**	**Mo**	**Tc**	Ru	**Rh**	**Pd**	Ag	Cd	In	Sn	Sb	**Te**	I	Xe
Cs	Ba	La - Lu	**Hf**	**Ta**	**W**	**Re**	Os	**Ir**	**Pt**	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

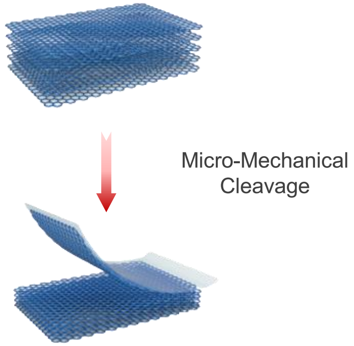
Nature chemistry, 2013, 5.4: 263-275.

- Due to its excellent mechanical properties, it can be applied to flexible substrates, and its atomic-scale structure plays a crucial role in enhancing circuit integration
- Promising as a building block for next-generation electronic devices, thanks to its structural stability, high electron mobility, and direct bandgap characteristics

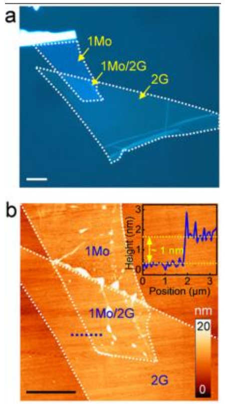
Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-3. Synthesis Methods and Limitations of Two-Dimensional Materials

Mechanical delamination method



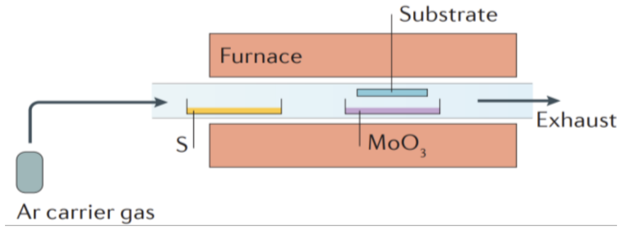
Wang, X. Y., et al. Nature reviews chemistry, 2018



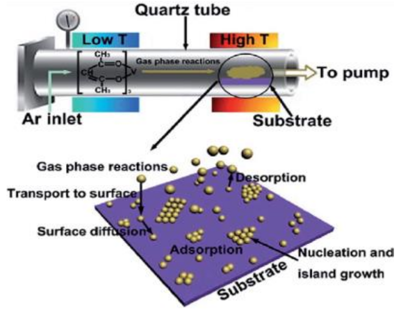
Li, D., et al. ACS Nano, 2016

Low productivity and difficulty in size control

Synthesis of 2D Materials through CVD

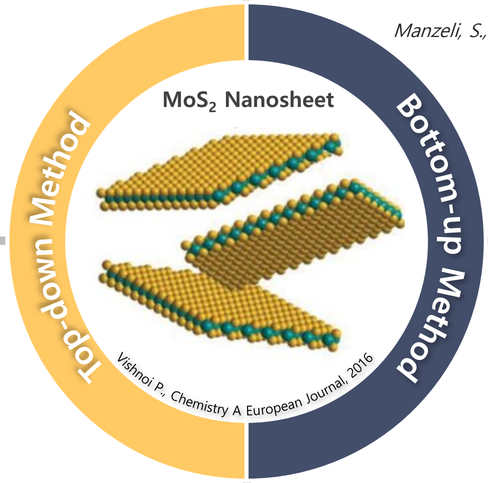


Manzeli, S., et al. Nature Reviews Materials 2.8 (2017): 17033



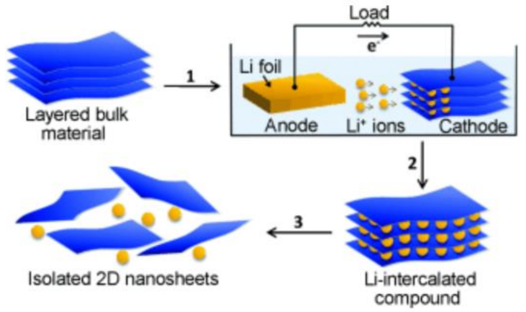
Tummala P., et al. Materials 2020, 13, 2786

High Process Temperatures and Non-Uniform Thin Film Formation



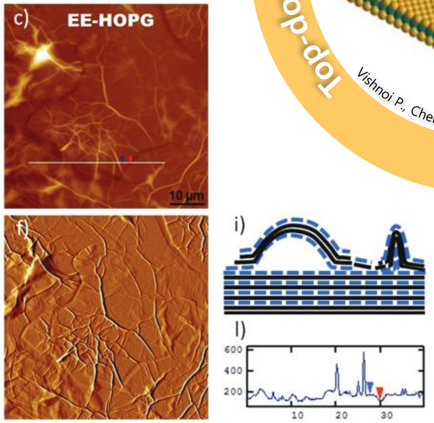
Vishnoi P., Chemistry A European Journal, 2016

Chemical delamination method



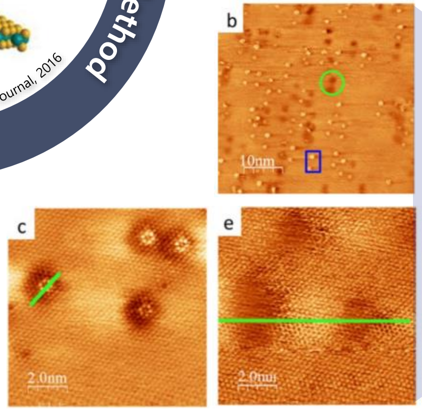
Zhang, W., et al. Nanoscale, 2015,7, 18364-18378

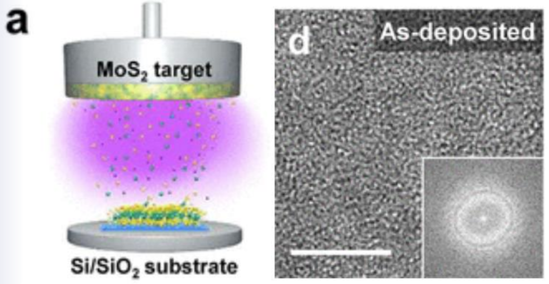
Difficulty in achieving consistent reproducibility due to uneven manufacturing



Xia, Z.Y., et al. Adv. Funct.Mater.2013, 23, 4684–4693

Synthesis of 2D Materials through PVD





Defect Formation Due to High Energy

Lu W., et al. Appl. Surf. Sci., 2020, 532, 147461

Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

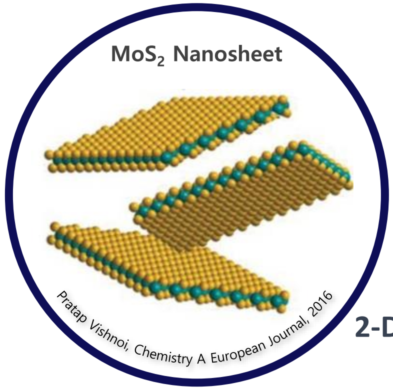
2-4. Potential to Overcome Limitations of 2-D material synthesis *via* Plasma-assisted Processes

Limitations of 2-D Material Synthesis Processes

Alternative Processes and Outstanding Challenges

MOCVD	ALD	Laser-CVD
Organic Metal Gases	Atomic Layer Deposition	Nucleation via Patterning
Above 350 ℃	Below 350 ℃	Above 600 ℃
Anticipated Low Yield as a Nucleation-Driven Growth Process	Slow Synthesis Speed Due to Stepwise Processing	Multi-Process and Limited Partial Synthesis

Sebastian, A., et al. Nat. Commun. (2021) 12, 693
Lau, C. S., et al. Adv. Mater. (2021) 2103907
Li, J., et al. Nature (2020) 579, 368

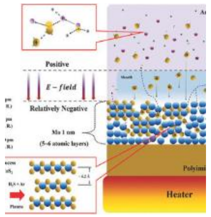

MoS$_2$ Nanosheet

Pratap Vishnoi, Chemistry A European Journal, 2016

Addressing Challenges Through Plasma Processing Tech

Characteristics and Benefits of Low-Temperature Plasma Processing

Schematic of Low-Temperature



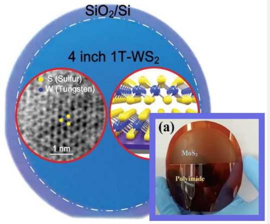
Adv. Mater. (2015) 27, 5223-5229.

Bottom-Up Approach for Crystalline Formation Induced by **Ion Activation Species**

Low-temp：150-300 ℃

Large-Area Deposition and Synthesis Possible Through Plasma Processing

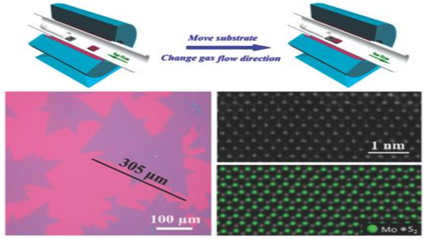
Large-Area Synthesis



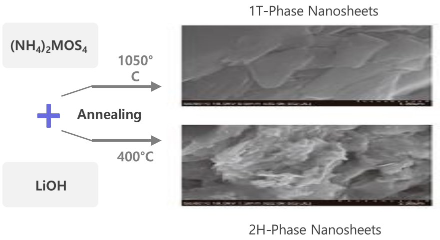
Small (2020), 16, 1905000.

Absence of 2-D Material Property Control Techniques

01 Nanocrystal Control Technology Needed for High Ion Mobility



02 The Challenge of Large-Area and formation of Heterointerfaces



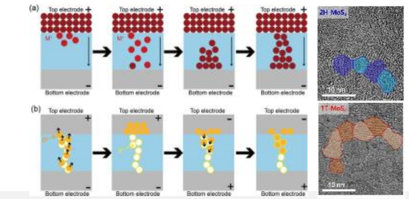
Chen, J., et al. Adv. Sci., (2016). 3. 1600033. Li, Y., et al. ACS Appl. Energy Mater. 2020, 3, 1, 998–1009

- Traditional high-temperature processes only allow for the synthesis of high-crystalline/single-crystalline materials
- Additional Processes Required for Material Process Property Control

Feasibility of 2-D Material Property Control

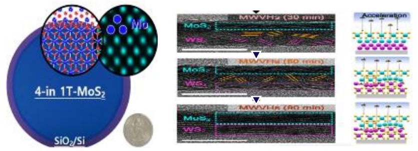
2-D Material Property Control Technology Through Plasma Characterization

01 Nano Control Technology for 2-D Materials



ChemSusChem (2021), 14, 1344.

02 One-Step Heterointerface Synthesis

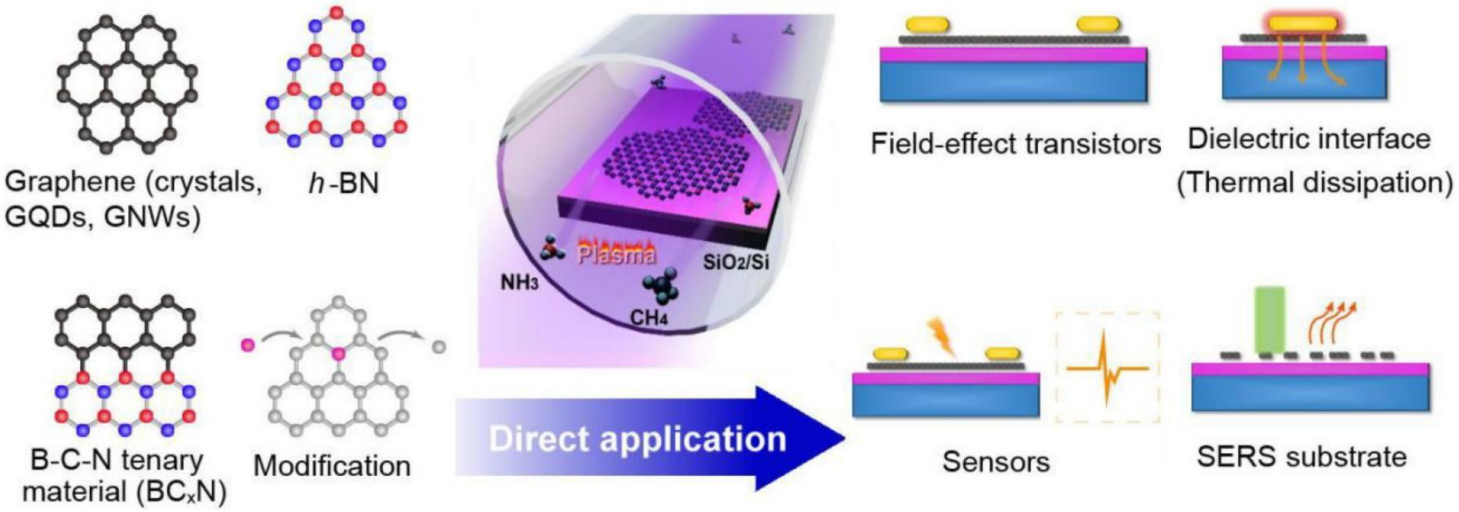


ACS Nano 2021, 15, 1, 707–718

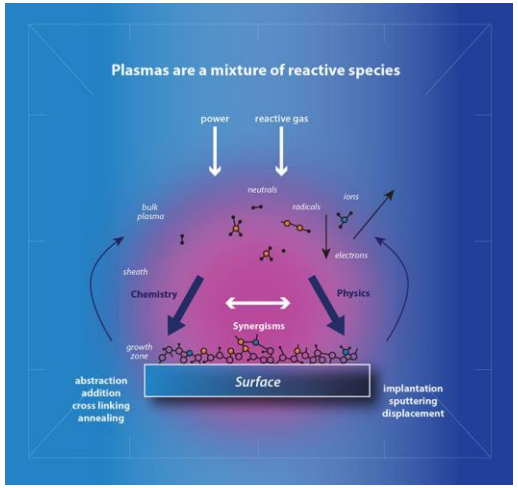
- Enhanced Ion Mobility Based on Crystal Structure and Interfaces
- Simplified Process with Single Synthesis Technology

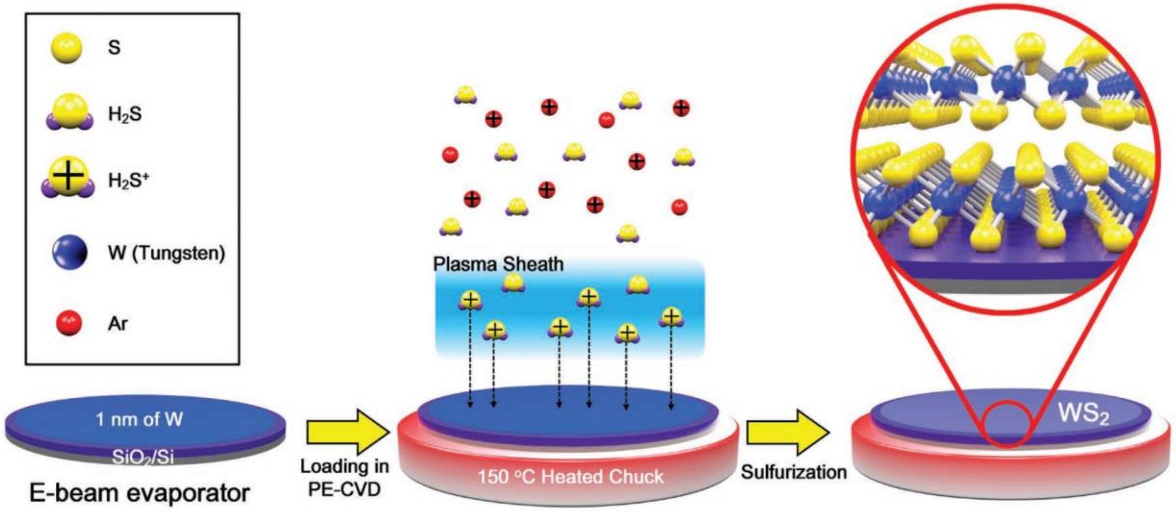
Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-5. Advantages of Synthesizing 2D Materials using Low-Temperature Plasma Technology



Yi, K., et al. Accounts of Chemical Research (2021) 4, 1011-1022



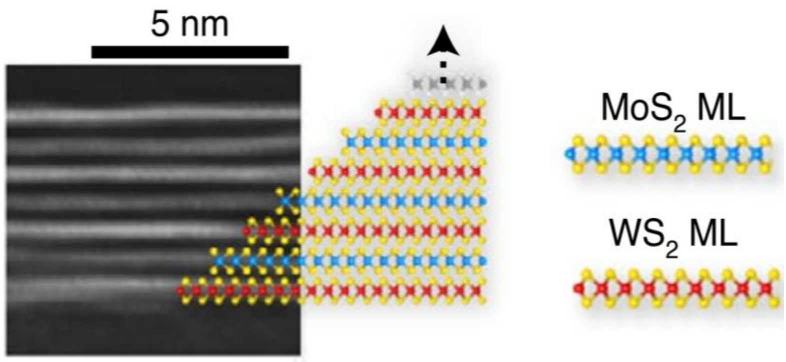


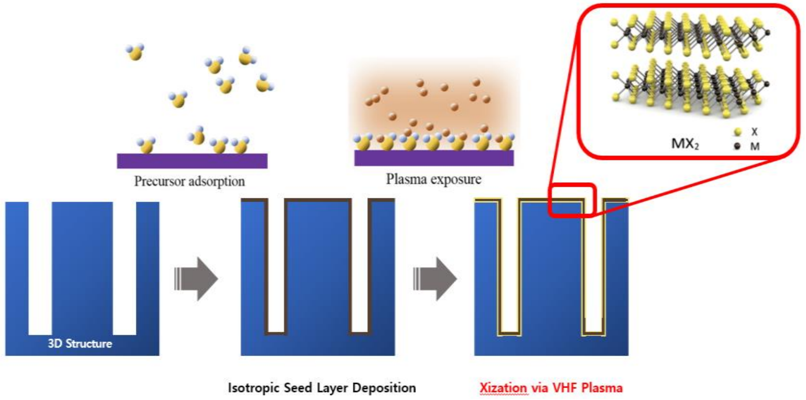
Small 2020, 16, 1905000

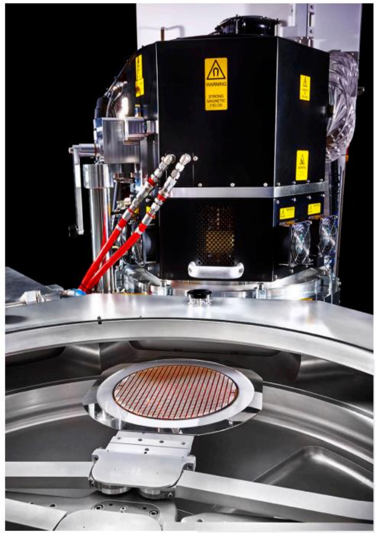
- By controlling various process variables, it is possible to synthesize 2D materials with desired characteristics
- The synthesis of large-area 2D materials enables the smooth fabrication of devices
- Synthesized by harnessing kinetic energy within the plasma field, it supplements the energy required for forming crystalline structures, enabling the synthesis of 2D materials even at low process temperatures (< 150 ℃)

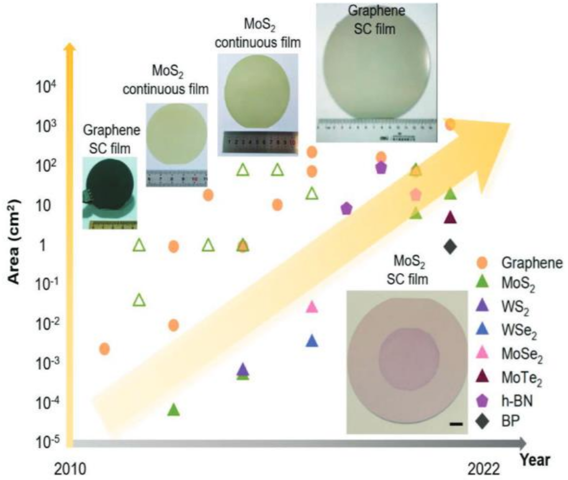
Part 2. Two-dimensional Transition Metal Dichalcogenide Materials

2-6. 2D Material Synthesis Technology *via* Low-Temperature Plasma

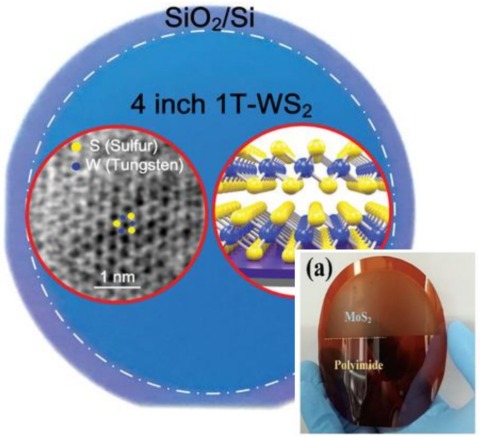








Large-scale synthesis on flexible substrates



- For the synthesis of 2D materials, it is possible to utilize a plasma containing chalcogen elements. The transition metal(M) seed layer can be directly chalcogenized through the Xization process
- Efficient heterostructure synthesis technology can be achieved, surpassing conventional processes
- Even in three-dimensional curved areas, which were limitations of conventional synthesis methods, it is possible to deposit 2D materials
- Enhanced production capacity with large-area uniformity and reduced processing time
- The absence of a separate transfer process reduces process steps and increases production yield

Part 3. Electronic Applications – Tunneling Device

3-1. Need for Next Generation Devices

3-2. Next-Generation Device Application Based on 2D Materials

3-3. One-Step MoS_2-WS_2 Vertical HT Using Penetrative H_2S Plasma

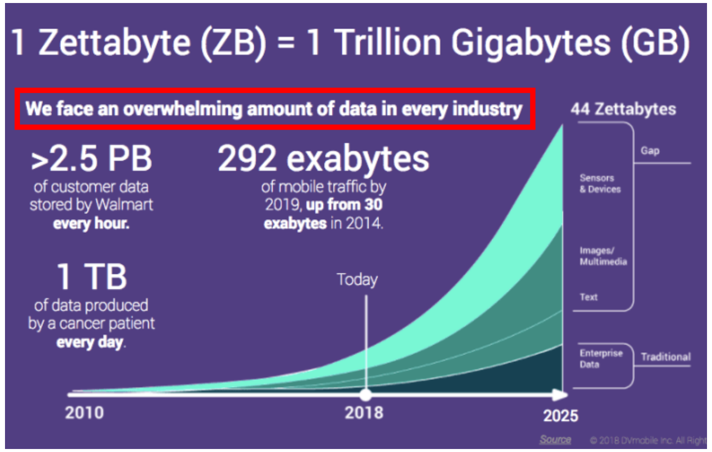
3-4. Negative differential resistance (NDR) photodetector using MoS_2/*p*-Si HT

3-6. TMDC Layer Phase Transition via Process Temperature Control

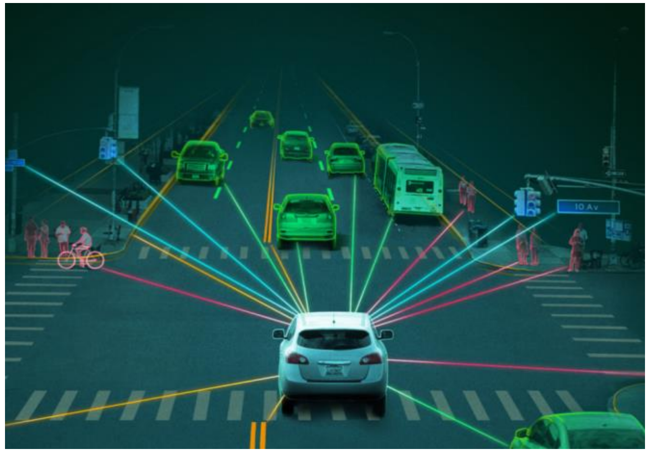
3-7. Enhancement of the NDR Performance via Phase Transition

Part 3. Electronic Applications

3-1. Need for Next Generation Devices

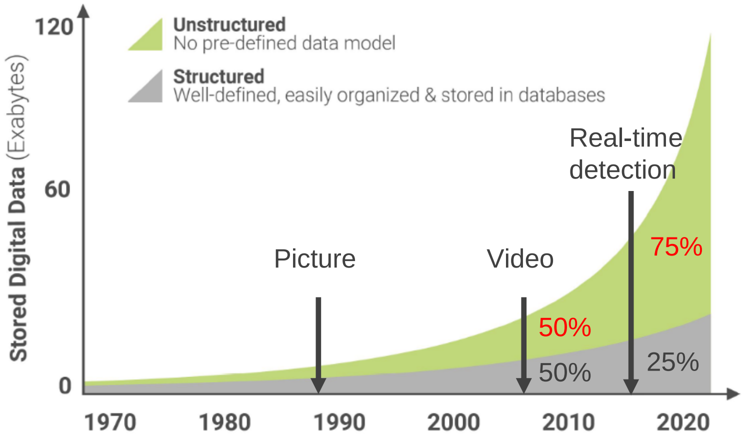


Source : https://www.gregverdino.com/everything-is-exponential/

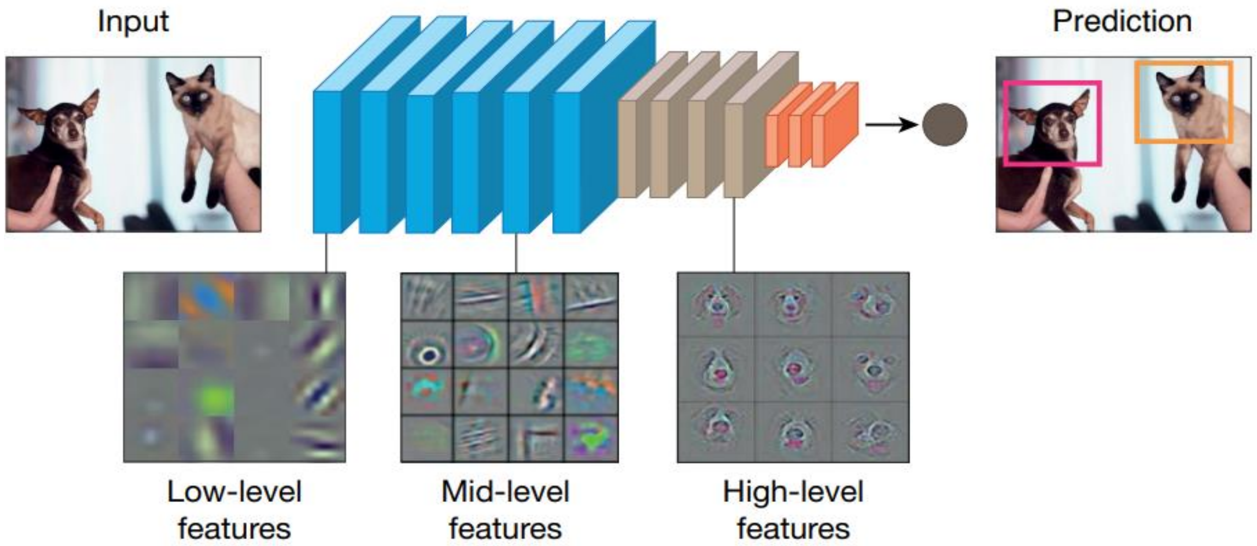


Source : http://www.newstof.com/news/articleView.html?idxno=1134

- With the development of AI, IoT, and industries, **the need for strong data processing means is emerging**.
- Two-dimensional materials are in the spotlight as core materials for next-generation devices due to **their excellent electrical properties and usability based on various band characteristics**.
- Research on **high-performance devices and high-density data storage devices** using two-dimensional materials is attracting a lot of attention



Source : Harvard Business Review. By way of Zorroa

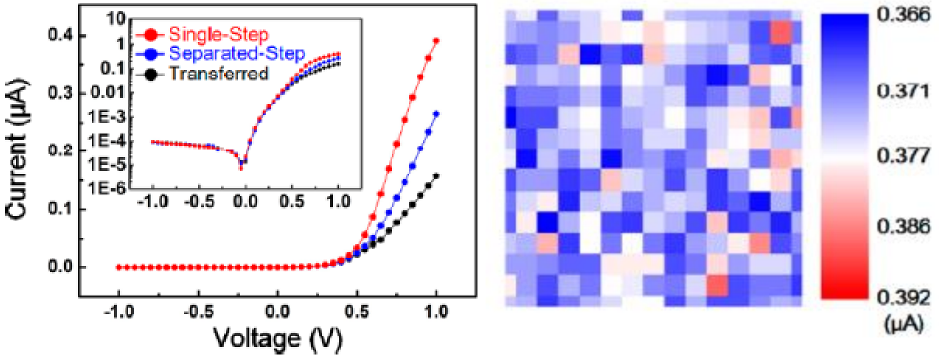


Source : Towards spike-based machine intelligence with neuromorphic computing

Part 3. Electronic Applications

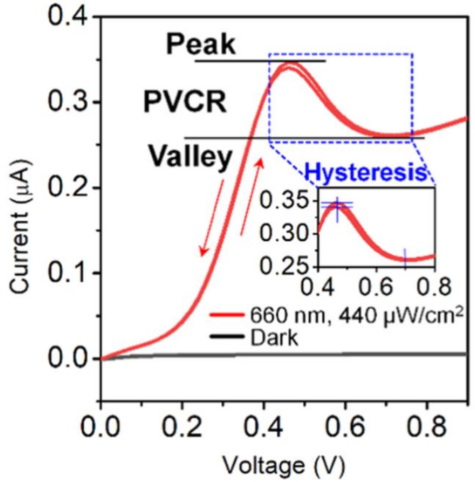
3-2. Next-Generation Device Application Based on 2D Materials

High Functional Optical Sensor



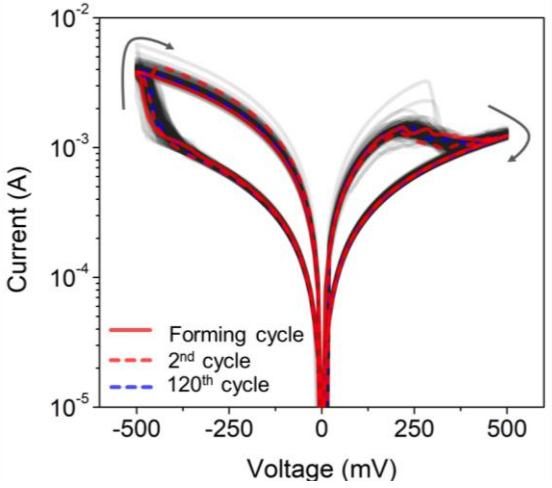
- **Principle of operation:** By inducing electron-hole separation through Type-II heterojunction using two-dimensional semiconductor materials, excited photoelectrons are induced according to light irradiation, thereby inducing photoreactivity
- **advantage:** Photoreactive Device with High Performance and Uniformity Based on Large Area Two-Dimensional Material Synthesis Technology Using PECVD

Negative Differential Resistance device (NDR device)



- **Principle of operation:** A phenomenon in which negative differential range appears in a specific voltage region due to tunneling in type-Ⅲ heterojunction
- **advantage:** High functional devices can be manufactured through selective NDR phenomenon control depending on light irradiation.

Memristor

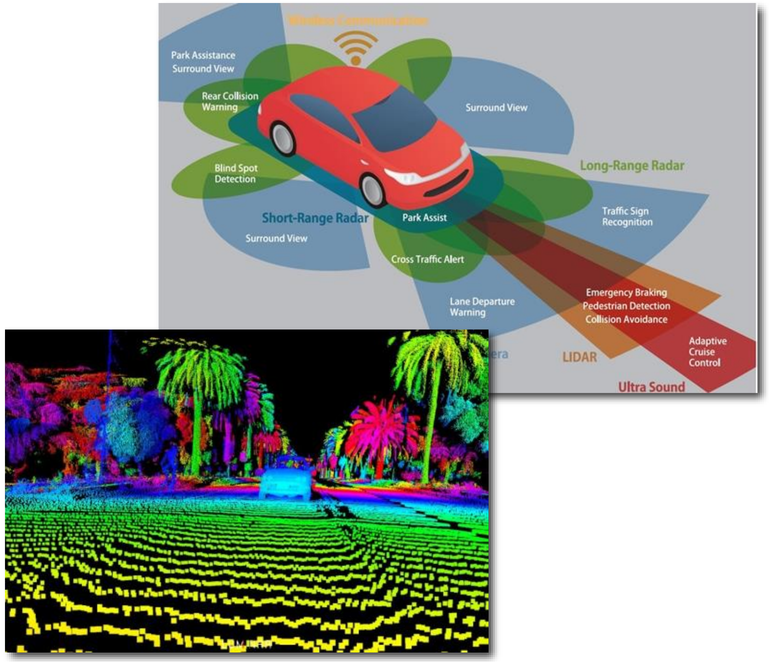


- **Principle of operation:** By utilizing a highly scalable electrode material, conductive filaments are formed inside the channel according to the applied voltage. Memory state changes depending on whether filaments are formed.
- **advantage:** Two-terminal device-based memory simplifies circuits and enables high integration of devices.

Part 3. Electronic Applications

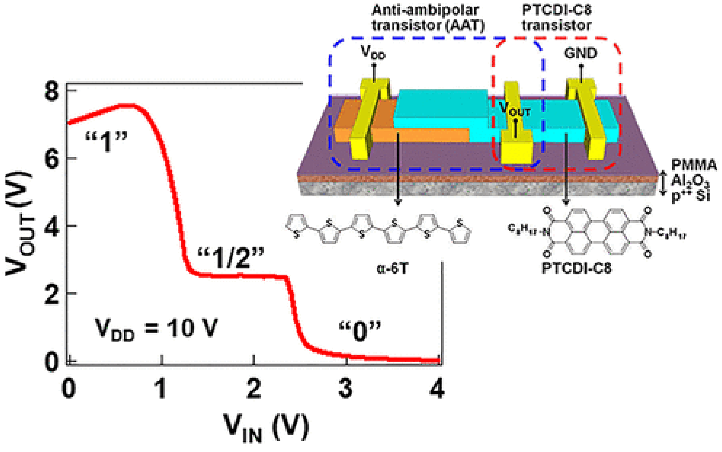
3-2. Next-Generation Device Application Based on 2D Materials

High Functional Optical Sensor



- **<u>application:</u>** Based on heterojunction property control, controls the detectable light area, Adjust the sensing point to be applied to LiDAR and infrared sensors

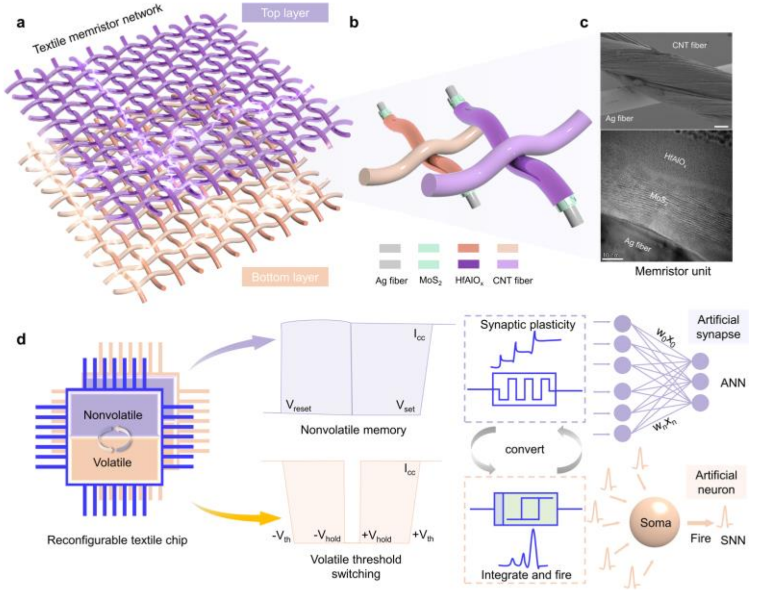
Negative Differential Resistance device (NDR device)



Nano Lett. 2018, 18, 7, 4355–4359

- **<u>application:</u>** Implementation of a multi-value logical system based on multi-threshold voltage characteristics. Deploy high-density data processing devices in simple circuits

Memristor



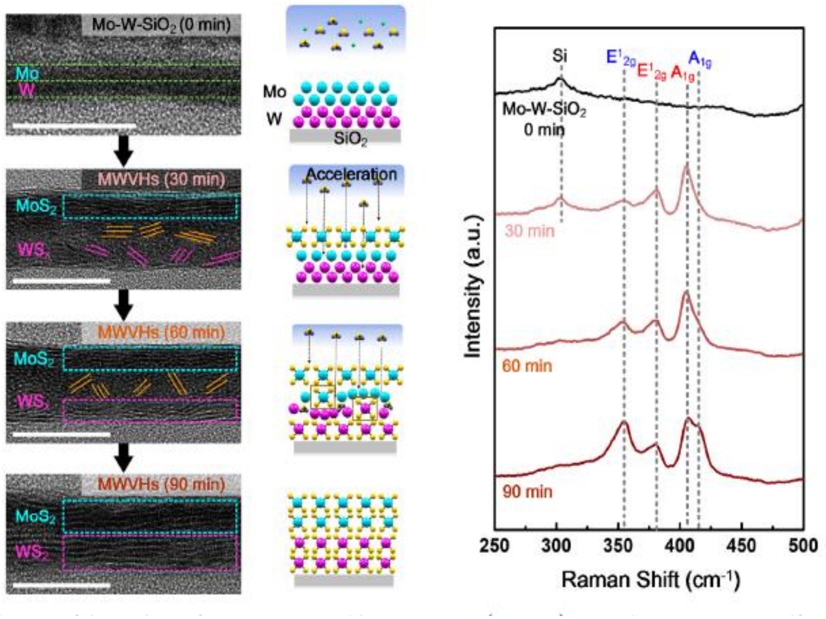
Nature Communications **volume 13**, Article number: 7432 (2022)

- **<u>application:</u>** Application in the study of neural simulation systems that simulate information transmission processes in the brain based on continuous data state changes.

Part 3. Electronic Applications

3-3. One-Step MoS_2-WS_2 Vertical HT Using Penetrative H_2S Plasma

Single step heterojunction synthesis



ACS Nano 2021, 15, 707−718

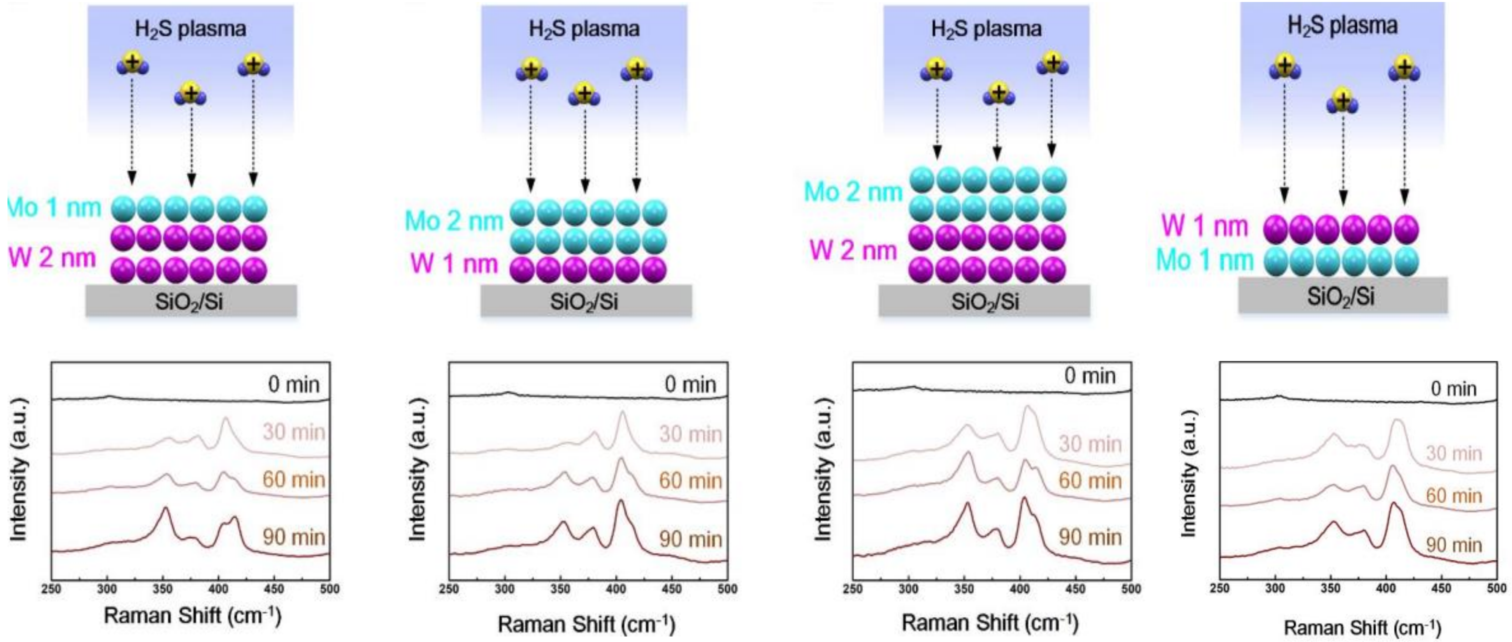


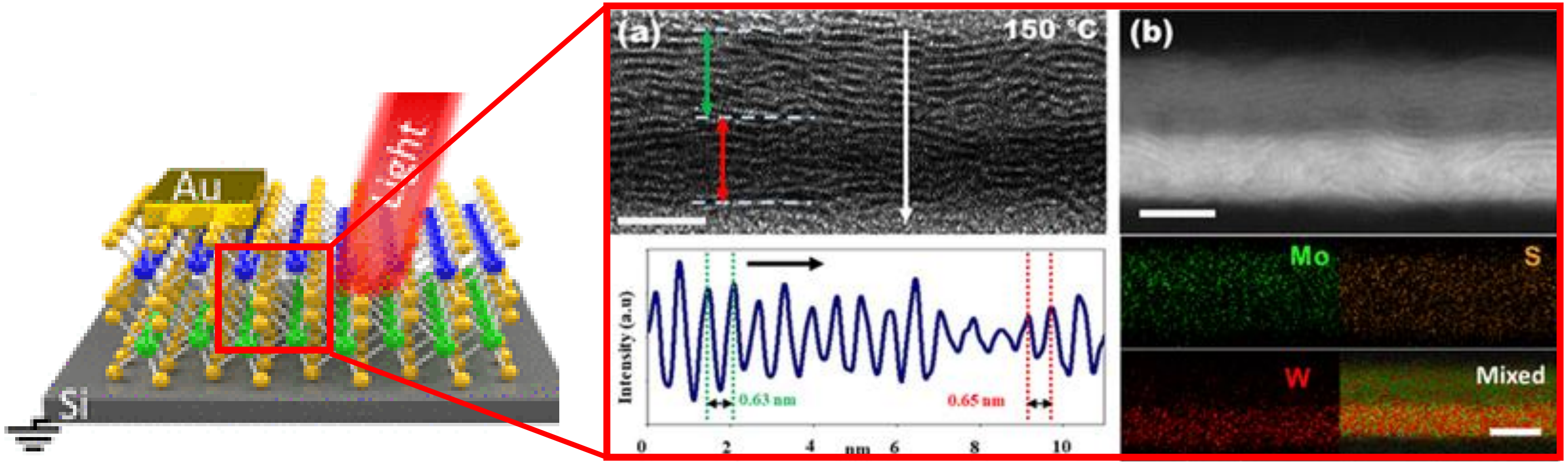
Figure. Time-dependent HR-TEM images, their schematic, Raman spectra.

Figure. Time-dependent Raman spectra along to different thickness and order of metal layer

- H_2S^+ ions travel to the **Mo-W** metal layer by an electric field, penetrating from top to bottom.(ion penetration)
- The Top **Mo** layer is converted to **MoS_2**, and the Bottom **W** layer is converted to **WS_2**.
- Raman results reflect the position and thickness of the synthesized MoS_2 and WS_2 layers.

Part 3. Electronic Applications

3-3. One-Step MoS_2-WS_2 Vertical HT Using Penetrative H_2S Plasma



ACS Appl. Mater. Interfaces 2021, 13, 7, 8710–8717

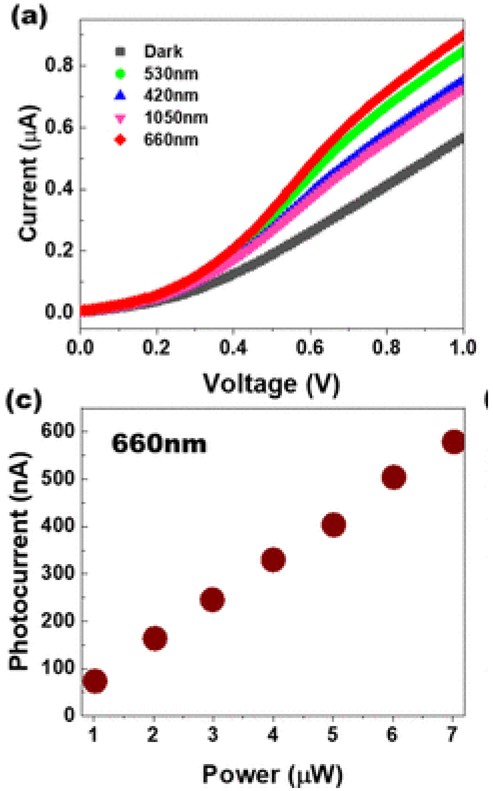


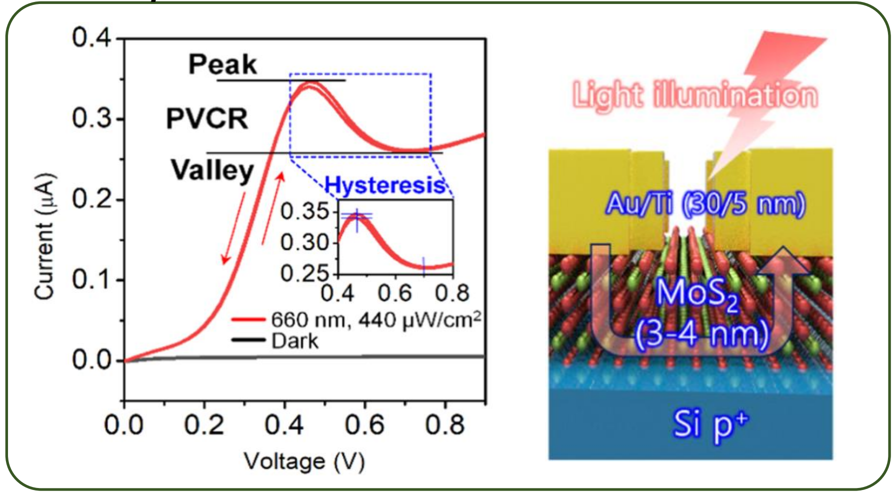
Figure. Cross-sectional and in-plane HR-TEM images with EDS mapping of MWVHs and wafer-scale diode fabrication

- **MoS_2 (Top) and WS_2 (Bottom)** were synthesized with a uniform thickness of 5 layers each, and the spacing of the film was uniform at 0.63/0.65 nm
- The manufactured optical sensor showed photo reactivity of 83.75 mA/W and power consumption of 6μW.

Part 3. Electronic Applications – Tunneling Device

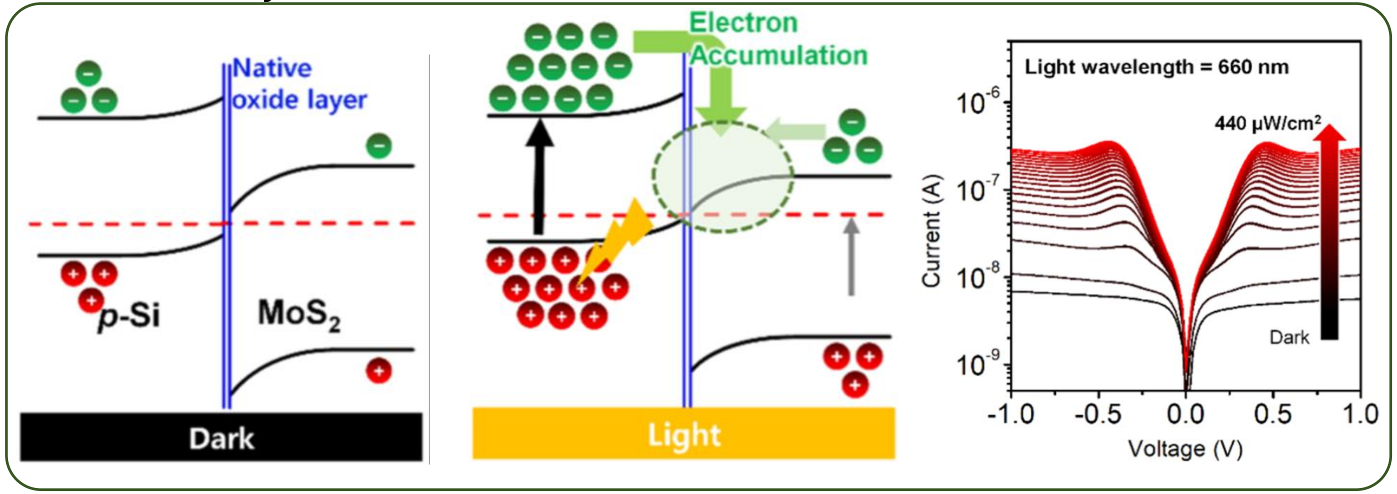
3-4. Negative differential resistance (NDR) photodetector using MoS_2/*p*-Si HT

NDR implementation



- **Fabrication:** Deposition of **$2H\text{-}MoS_2$** layer using PECVD process on p-Si substrate through **water transfer process**
- **Mechanism :** **Under light irradiation,** photo-excited electrons from the Si wafer are accumulated in the conduction band to bend the band structure. **The photogating effect** enhances tunneling between each band from MoS_2 to a p-Si substrate.
- **Operation :** During the main **charge transportation change** from Tunneling to Thermionic current, **NDR characteristics** appear.

Photoreactivity



Performance reliability

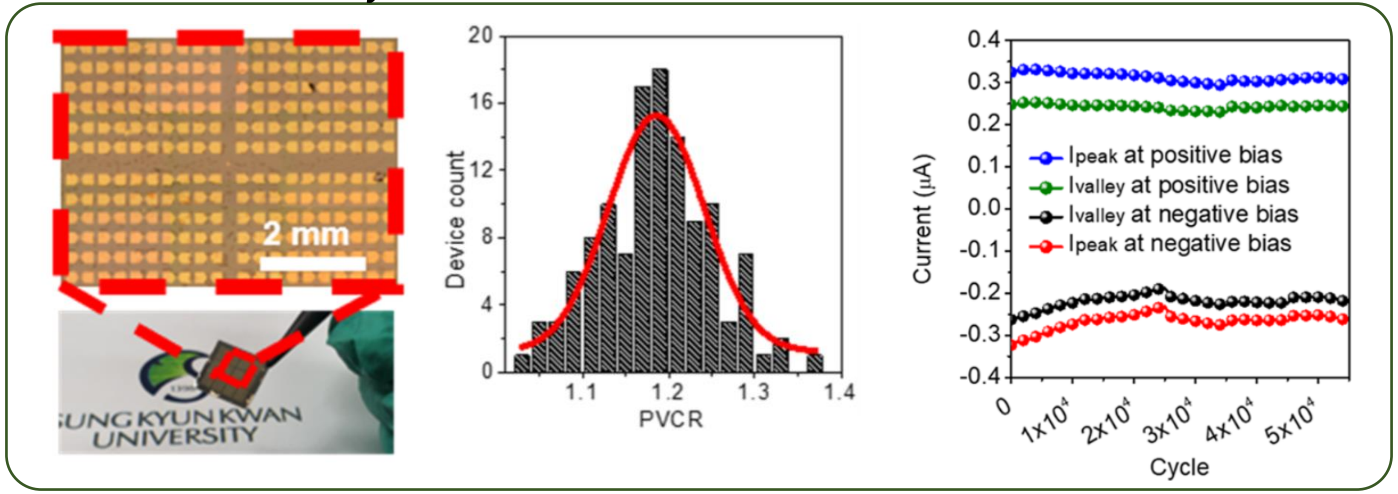


Figure. Mechanism and electrical characteristic of MoS_2/*p*-Si heterostructure

ACS Appl. Mater. Interfaces2021, 13, 25072−2508125075

Part 3. Electronic Applications – Tunneling Device

3-5. TMDC Layer Phase Transition via Process Temperature Control

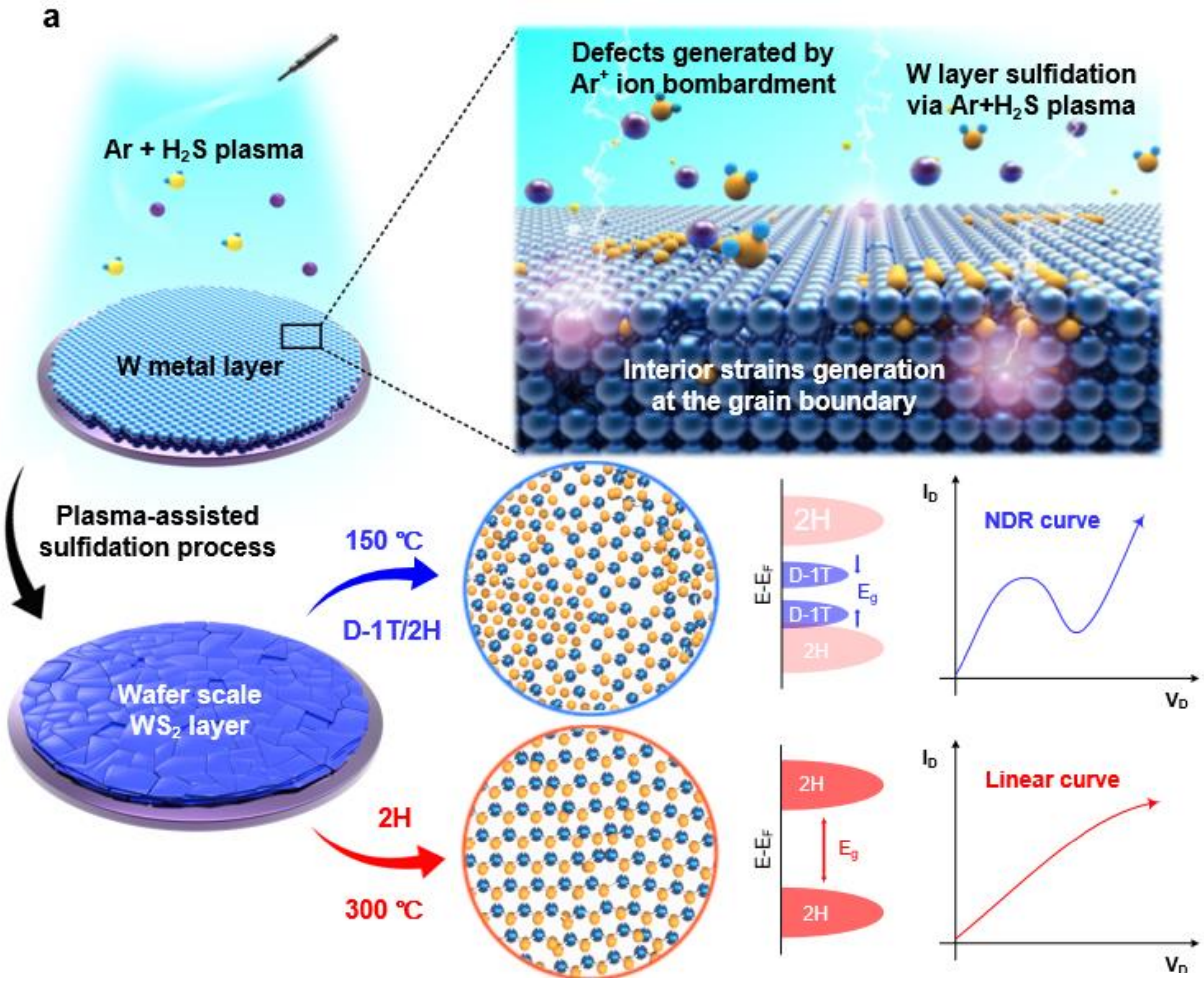


Figure. Temperature-dependent phase modulation process

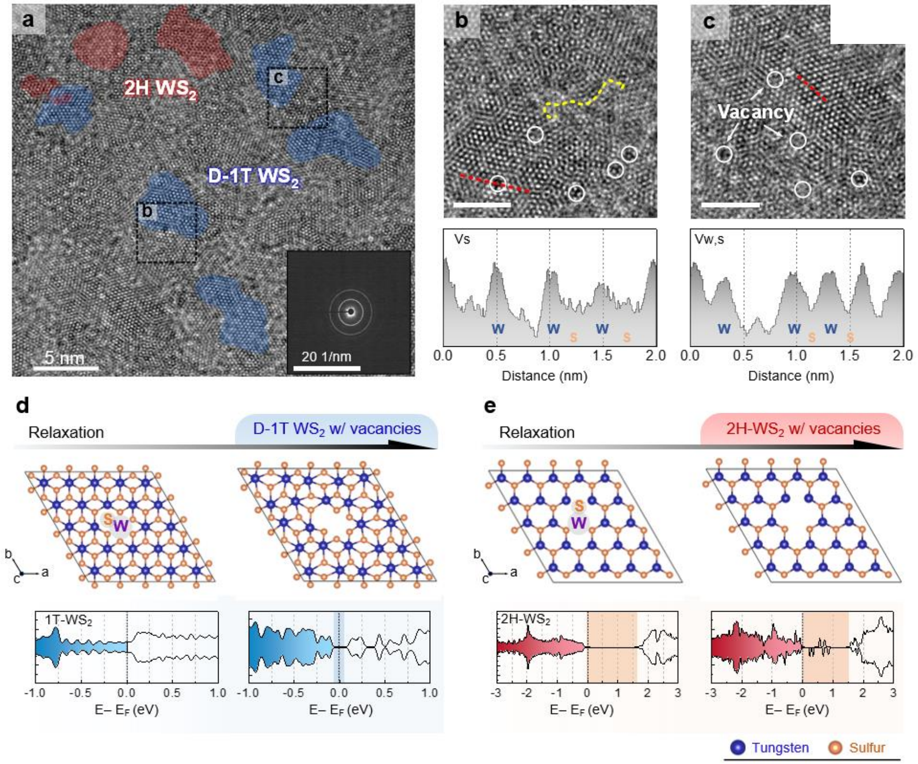


Figure. Calculation of the material characteristics of the defect accompanied D-1T/2H WS_2

- **low-temperature sulfidation process** → WS_2 layer **2H phase** → **Distorted 1T phase** change.
  (Cause → Internal stress and defects)
- By controlling the TMDC phase, it is possible to control electrical properties between semiconductors and semi-metals.

Small Sci., 2023

Part 3. Electronic Applications – Tunneling Device

3-6. Enhancement of the NDR Performance via Phase Transition

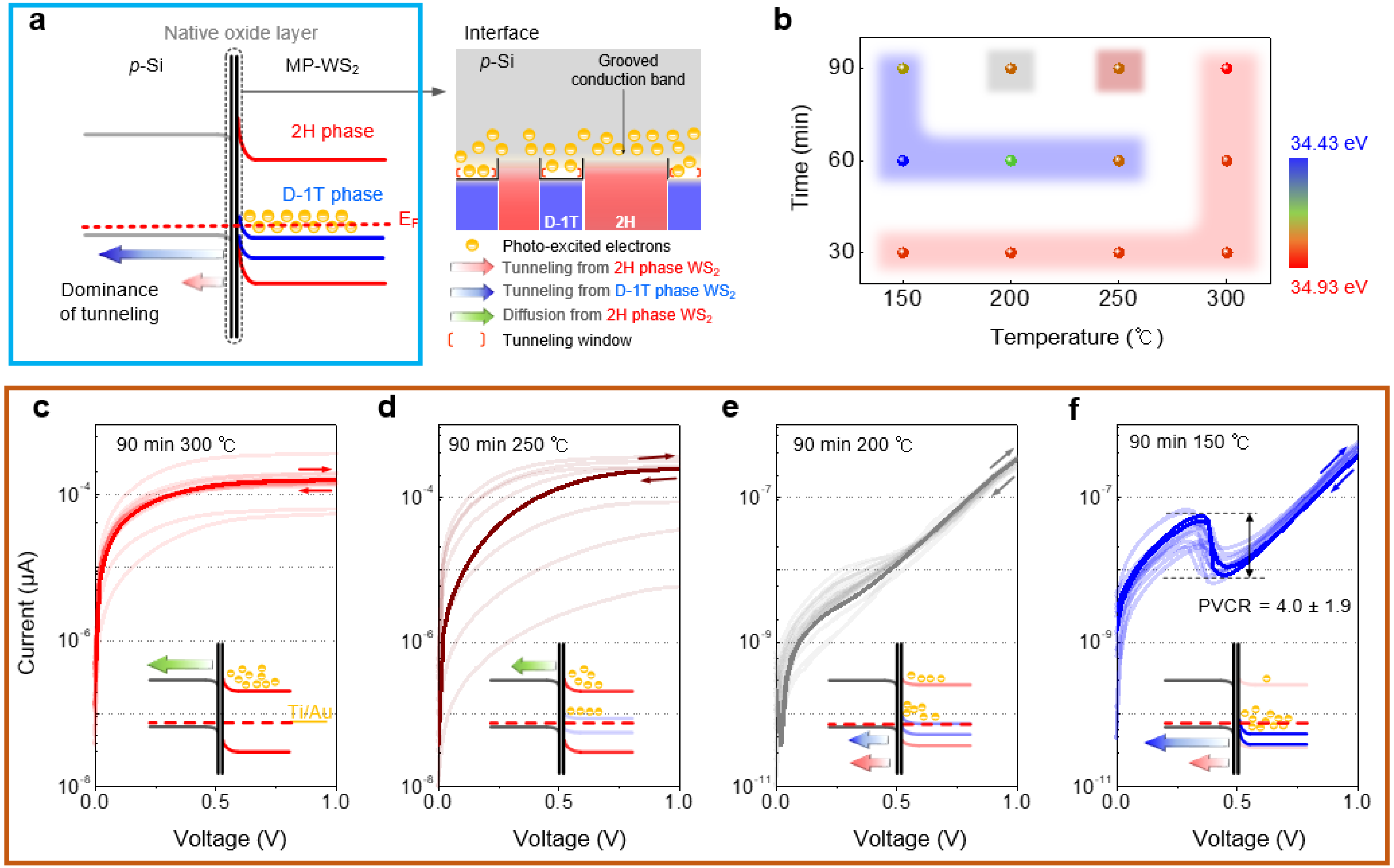


Figure. Mechanism analysis and optimization of the MP-WS_2/p-Si heterostructure.

- According to process temperature decrease, distorted 1T phase WS_2, **which shows semi-metallic characteristics**, is increased.
- Distorted 1T phase WS_2 expands the tunneling window between and WS_2 and Si substrates.
- **Photon-Electron Accumulation at Interface layer by Illumination**

  ➔ Promote **electron tunneling** throughout the window.
- The proposed NDR device is applied to the photoreactive-RAM application based on the resistive bi-stability.

Small Sci., 2023

Part 4. Electronic Applications – Neuromorphic Device

4-1. Mechanism of Neuromorphic Device

4-2. 2D Materials for Neuromorphic Applications

4-3. Grain Confinement via Low-temperature Synthesis

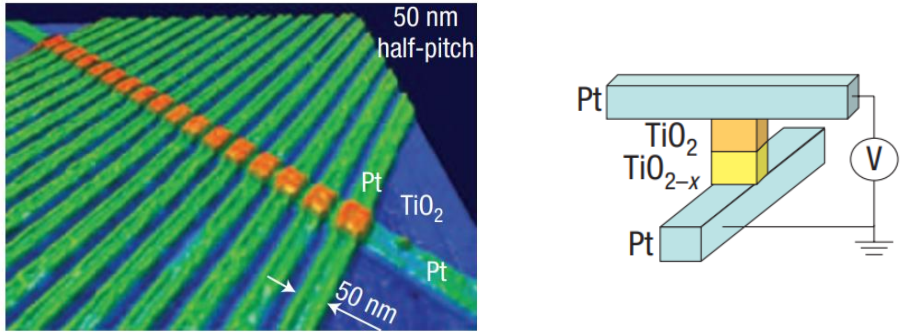
4-4. Nanograin Memristor

4-5. Grain Boundary Effect in Neuromorphic Performance Reliability

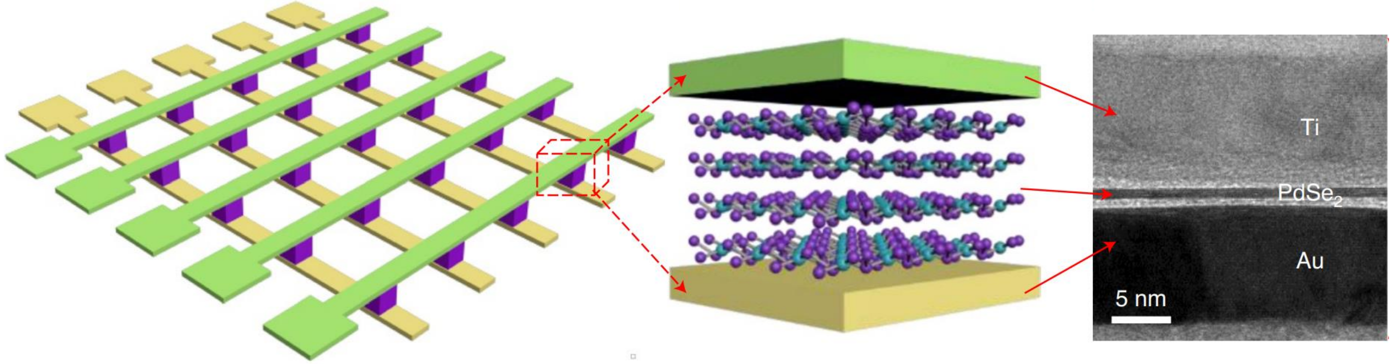
4-6. Patents

Part 4. Electronic Applications – Neuromorphic Device

4-1. Mechanism of Neuromorphic Device



Yang, J., et al. Nat. Nanotech., 2008, 3: 429–433.

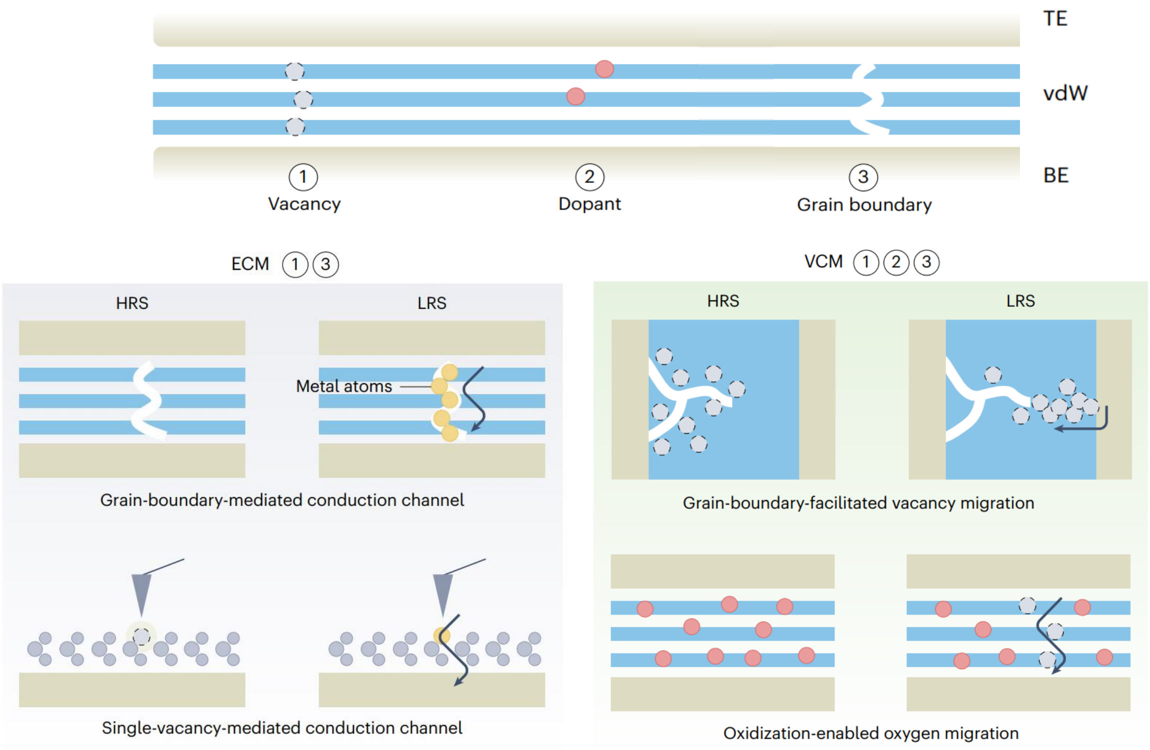


Li, Y., et al. Nature electronics, 2021, 4: 348–356.

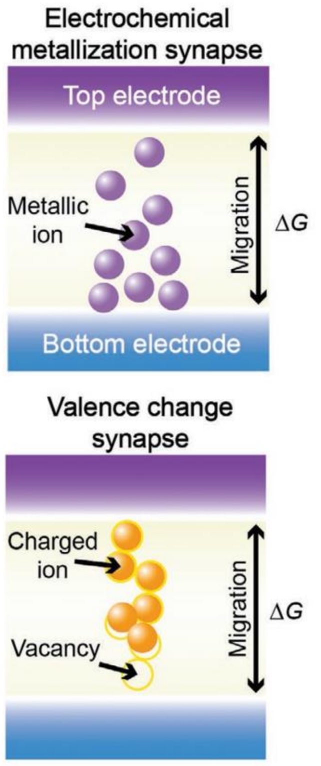
- Early memristors were made of metal-oxide-based oxide materials, but as the size of the device scaled down, it became a problem to stabilize the uniform resistive switching of the device.
- In addition, as the area and thickness of the metal-oxide-based oxide material decreases, excessive filament formation occurs, which worsens the reliability of resistive switching.
- As an alternative, the use of van der Waals structured materials to provide atomic-level uniformity while simultaneously having a low electron density of states is gaining attention for low-power resistive switching at the nanoampere level or below.
- An additional hot topic of research is to utilize the feature that all surfaces are geometrically uniform, so that various defects can be given to form filaments wherever desired.

Part 4. Electronic Applications – Neuromorphic Device

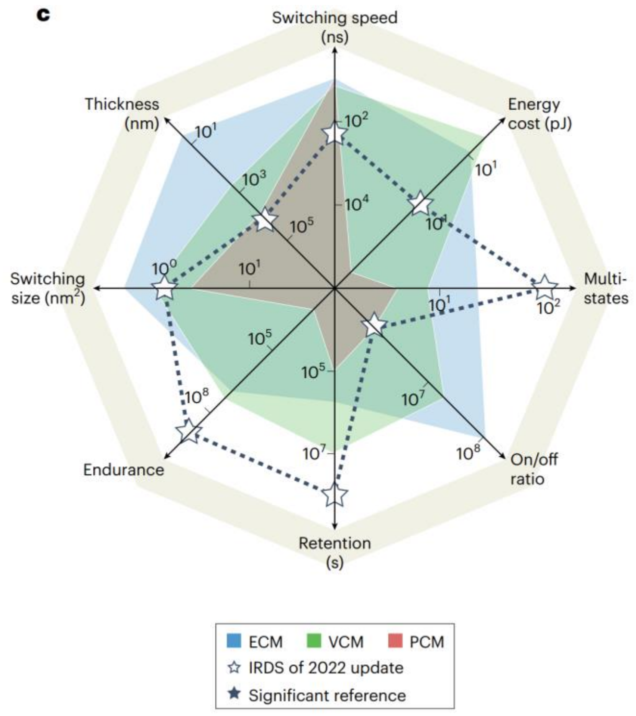
4-2. Mechanism of Neuromorphic Device



Kang, J.H., et al. Nature electronics, 2023, 6: 491–505.



Choi, S., et al. Adv. Mater. (2020) 32, 2204659.



Huh, W., et al. Advanced Materials (2020) 32, 2002092

- Filament-based resistive switching devices can be broadly categorized into VCM and ECM according to their operating principles.
  - VCMs: resistive switching occurs only with internal conduction channel materials without the intervention of external materials when a voltage is applied to the electrode
  - ECMs: conduction channel materials from the outside enter and cause resistive switching depending on the voltage applied to the electrode.

- VCM-based devices have the advantage of high stability and reliability because the operation is performed only internally, unlike ECMs, which are artificially pierced by external materials.

- On the other hand, ECM-based devices have the advantage of having a lower threshold voltage than VCM, which requires overall movement inside the device because filaments are formed by migration of external metal atoms.

Part 4. Electronic Applications – Neuromorphic Device

4-3. Generation of Nanograin Based on Low Process Temperature

Formation of nanograin TMDC materials via PECVD sulfidation

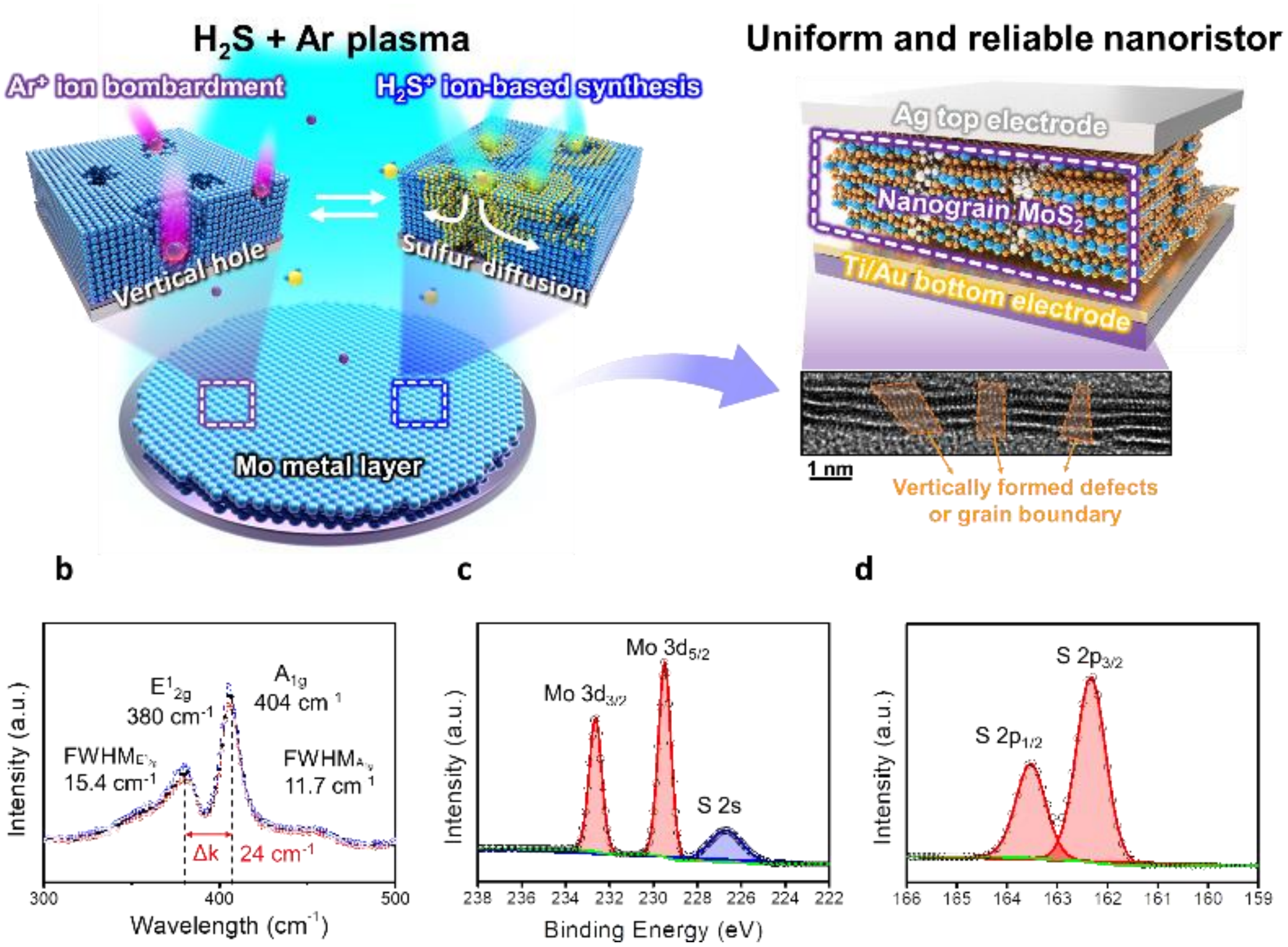


Figure. Schematic of nanograin MoS2 synthesis process

- During plasma treatment, **H_2S ion penetrate the Mo layer, diffused into the layer**.
- **Numerous nuclei** make the grain hard to grow with large size over 10 nm.
- Because of the uniform metal layer thickness, the MoS_2 can be prepared with **uniform thickness of 5 nm**

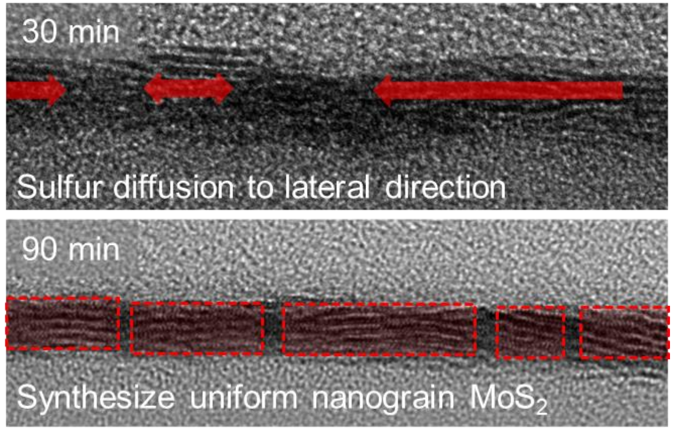


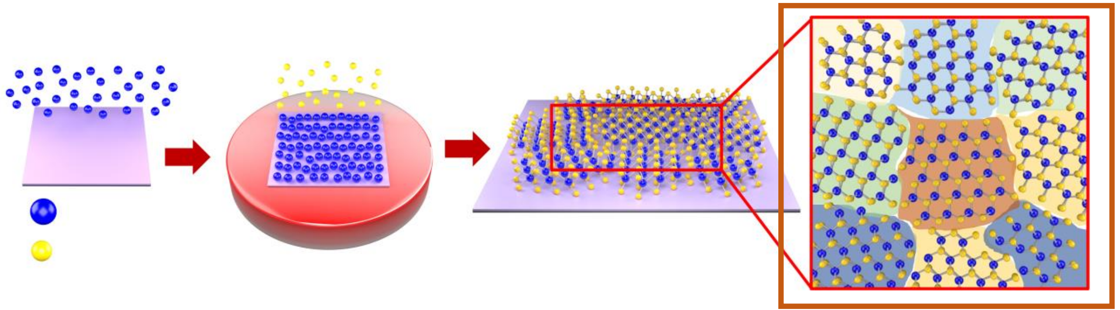
Figure. Synthesized MoS_2 depending on process time

J. Mater. Chem. C (2024) Accepted

Part 4. Electronic Applications – Neuromorphic Device

4-3. Generation of Nanograin Based on Low Process Temperature

Formation of nanograin TMDC materials via PECVD sulfidation



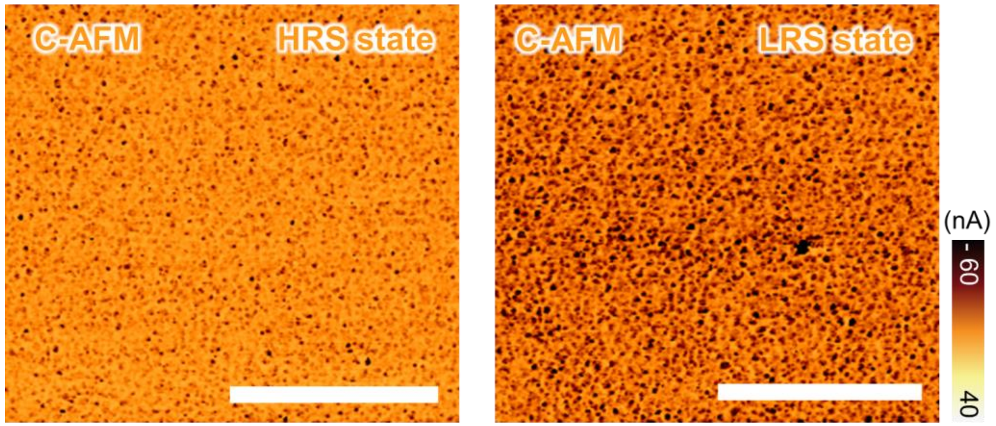


Figure. C-AFM current map of the MoS_2 nanograins layer

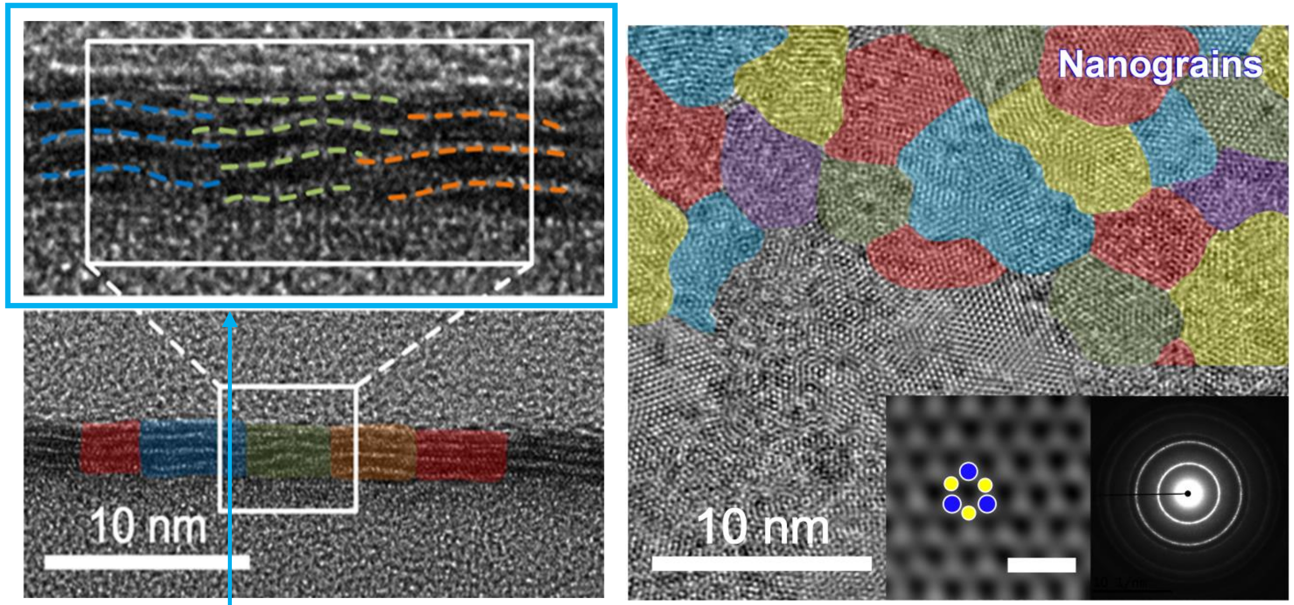


Figure. In-plane HRTEM image with color marked nanosize of grain

- The grain size is formed **within a size of 10 nm** by a low synthesis temperature.
- The generated **grain boundary** may serve as **a guideline** for diffusible metal electrode ions.
- TEM images and C-AFM results represent the effect of guidelines on the presence of small grain sizes and ion migration.

J. Mater. Chem. C (2024) Accepted

Part 4. Electronic Applications – Neuromorphic Device

4-4. Memristor Application Using Nanograin TMDC Materials

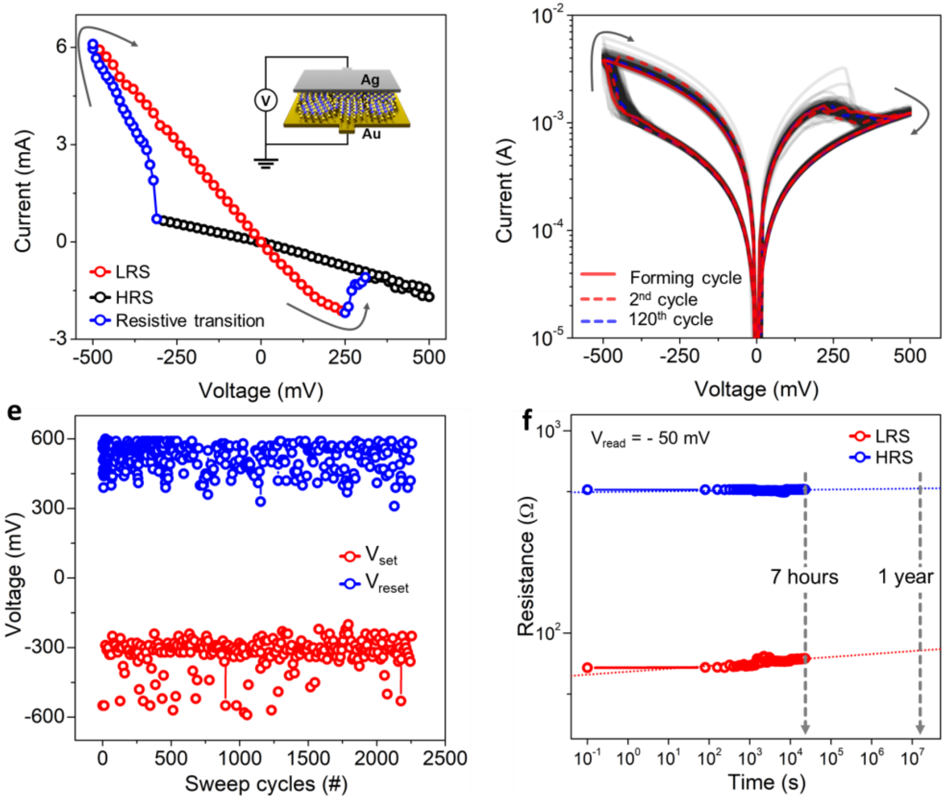


Figure. Performance of nanograin MoS_2 memristor

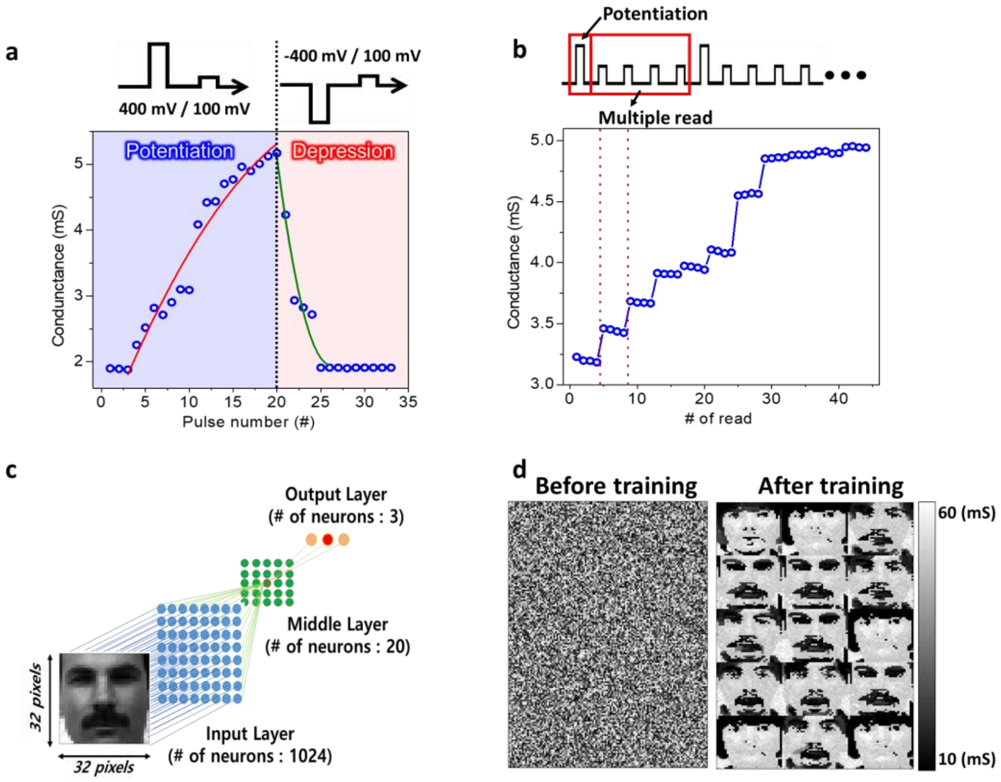


Figure. Potentiation-depression characteristics of the MoS_2 nanoristor.

- Grain boundary makes it easier for metal electrode ions to move along the applied electric field.
- This creates a **forming-free memristor device** so that memory performance does not change during durability tests.
- The manufactured memristor device is applied to **electronic synapse device applications** and shows great viability as SNN.

J. Mater. Chem. C (2024) Accepted

Summary

- ✓ Plasma assisted metal layer sulfurization method is one of the most promising method to achieve highly uniform/reliable/reproducible production process for wafer-scale TMDCs materials.
- ✓ We have successfully implemented homostructured/heterostructured TMDCs layer and observed temperature-dependence phase tunability from 2H to 1T phase or vice versa.
- ✓ The intrinsic semiconductive/semi-metallic characteristic of the PECVD grown TMDCs layers are feasible to fabricate functional electronic device with superior photo-reactivity and unique NDR characteristics
- ✓ A nanograined TMDCs layer serves as a resilient pathway for metal-ion transport, bolstering the reliability and uniformity of memristor and synaptic applications

- **Project**: 차세대 이차원 소재 상용화를 위한 플라즈마 공정 최적화 (리더연구)
- **Period**: 2022.06.01 ~ 2031.02.28
- **Support**: National Research Foundation of Korea

- **Project**: 수전해 전극 공정을 위한 저온 플라즈마 기초연구실 (BRL)
- **Period:** 2022.06.01 ~ 2025.02.28
- **Support**: National Research Foundation of Korea

- **Project**: 플라즈마 공정 최적화 프로세스를 활용한 이차원 소재 합성 및 뉴로모픽 소자개발 연구
- **Period**: 2020.09.16 ~ 2025.09.15
- **Support**: Samsung electronics

- **Project**: In-situ 결함분석을 통한 고품위 MX2 소재 및 공정기술 개발 (반도체고급인력양성사업)
- **Period**: 2023.04.01 ~ 2027.12.31
- **Support**: Korea Evaluation Institute of Industrial Technology

2024 KOR-EU Joint Workshop

Q&A

Taesung Kim

School of Mechanical Engineering and SAINT
Department of Semiconductor Convergence Engineering
Sungkyunkwan University (SKKU)