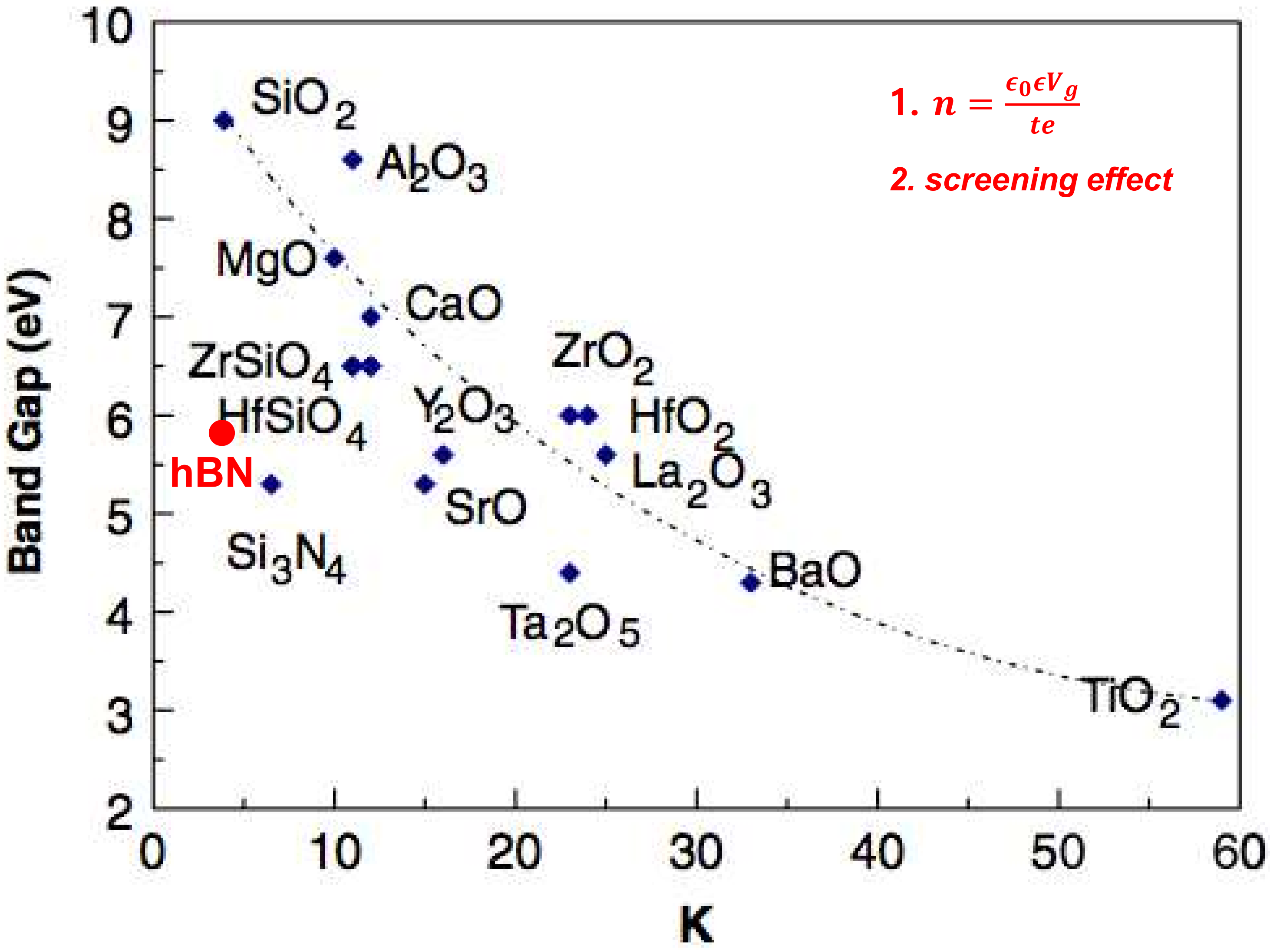
3. Properties of 2D Insulators

Search for High-k Dielectric Materials



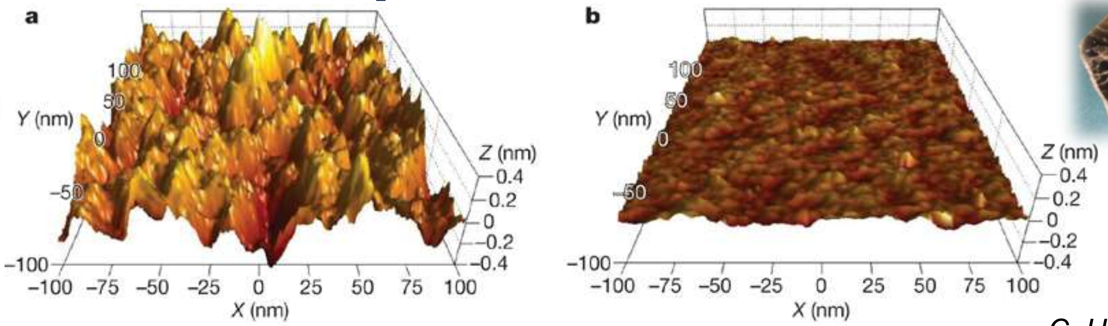
1. $n = \frac{\epsilon_0 \epsilon V_g}{te}$

2. screening effect

Perfect Substrate for Graphene Device

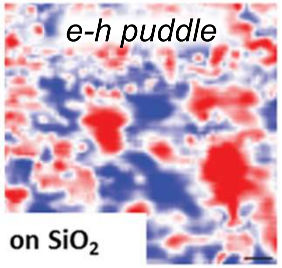
Problem #1. rough surface

Graphene on SIO_2 | **Graphene on mica**



C. H. Lui et al. Nature (2009)

Problem #2. charged impurities



J. Xue et al. Nat. Mater. (2011)

We need new substrate for graphene devices…

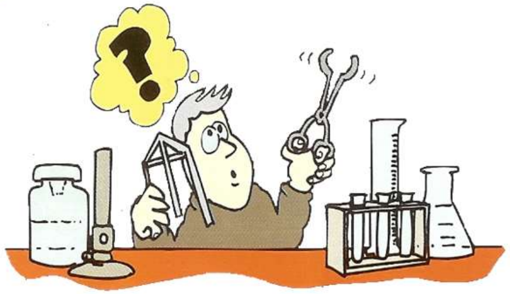
How about hBN? It has large bandgap, *i.e.* insulator, and smooth surface because it is a cousin of graphene.

I can place the graphene piece onto the hBN.

Philip

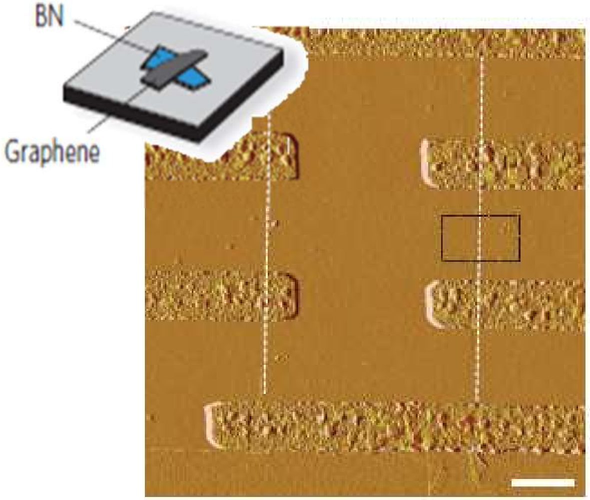
Jim

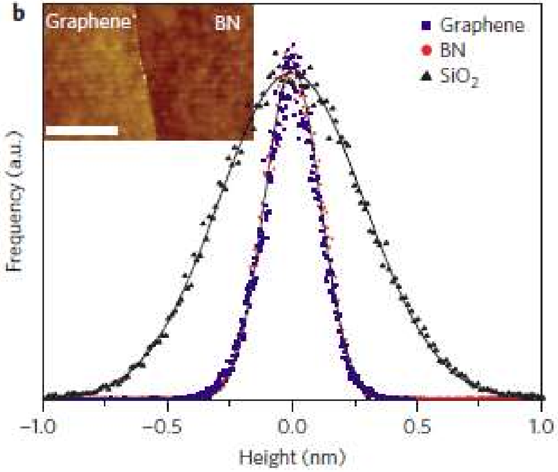
Ken



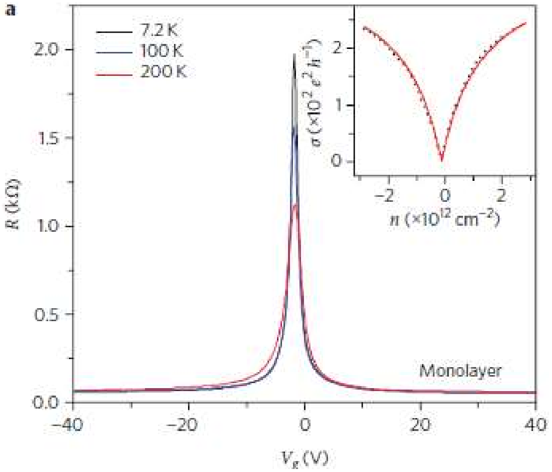
Emerging 2D Insulators

Graphene devices on hBN substrate



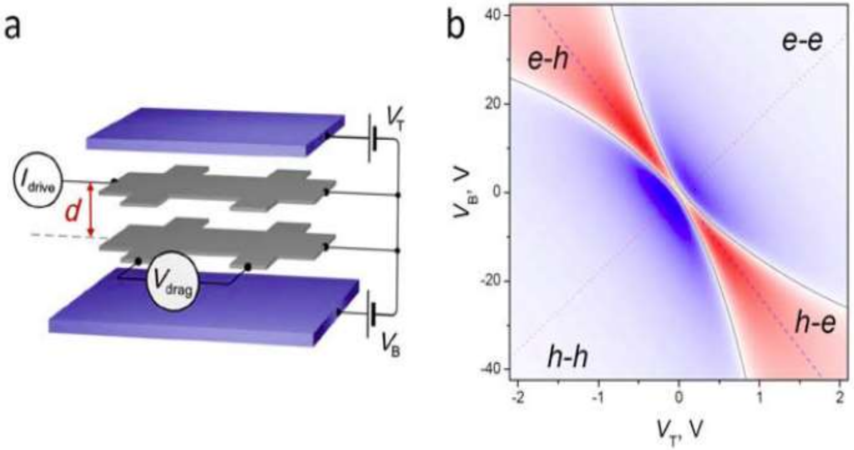


40,000 cm^2/V·s at 300K



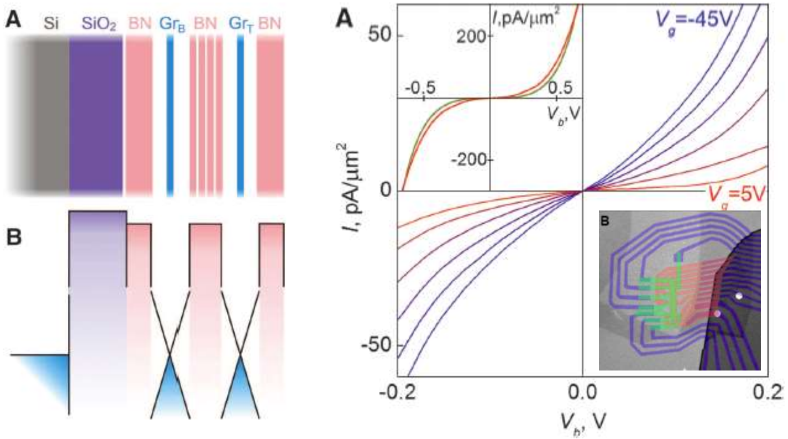
C. Dean, et al, Nature Nano. (2010)

Coulomb drag in graphene separated by hBN



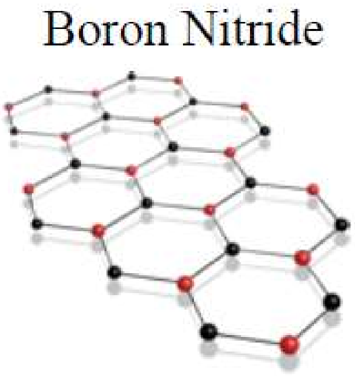
R. V. Gorvachev, et al, arXiv (2012)

Tunneling field effect transistors



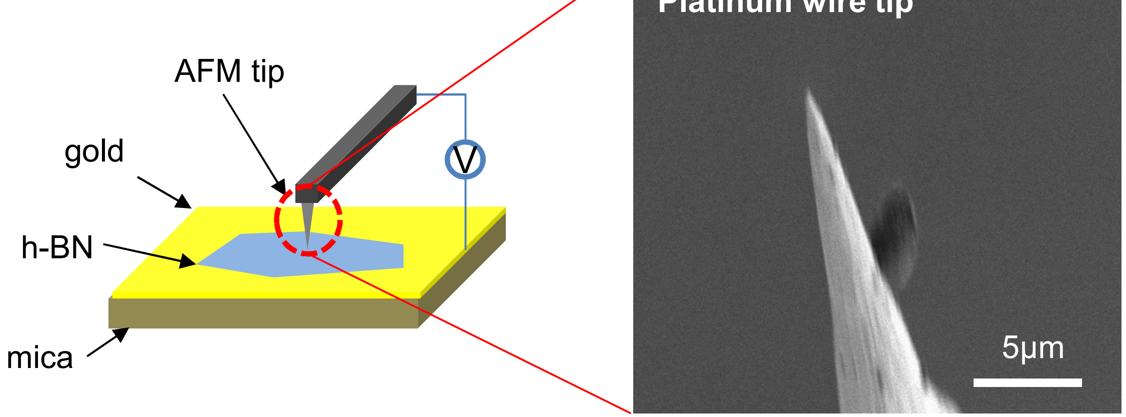
L. Britnell, et al, Science (2012)

Properties of hBN

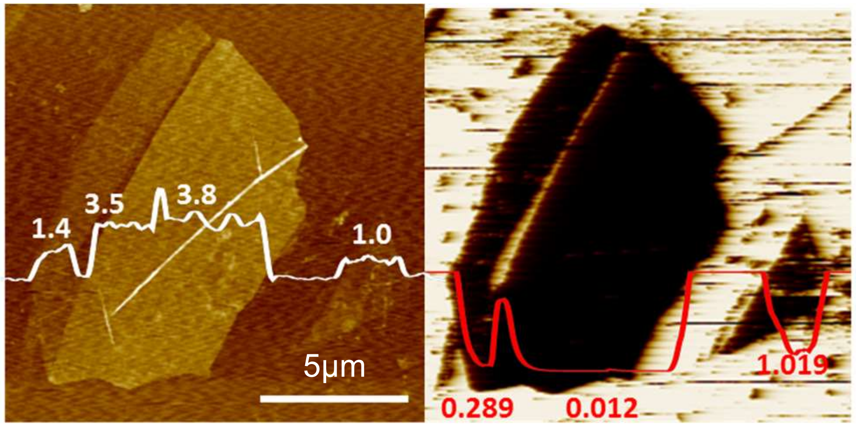


	Band Gap	Dielectric Constant	Optical Phonon Energy
BN	5.8 eV	~3.5	>100 meV
SiO2	8.9 eV	3.9	59 meV

Set-up of conductive AFM



AFM (Topology) **AFM (Conductance)**

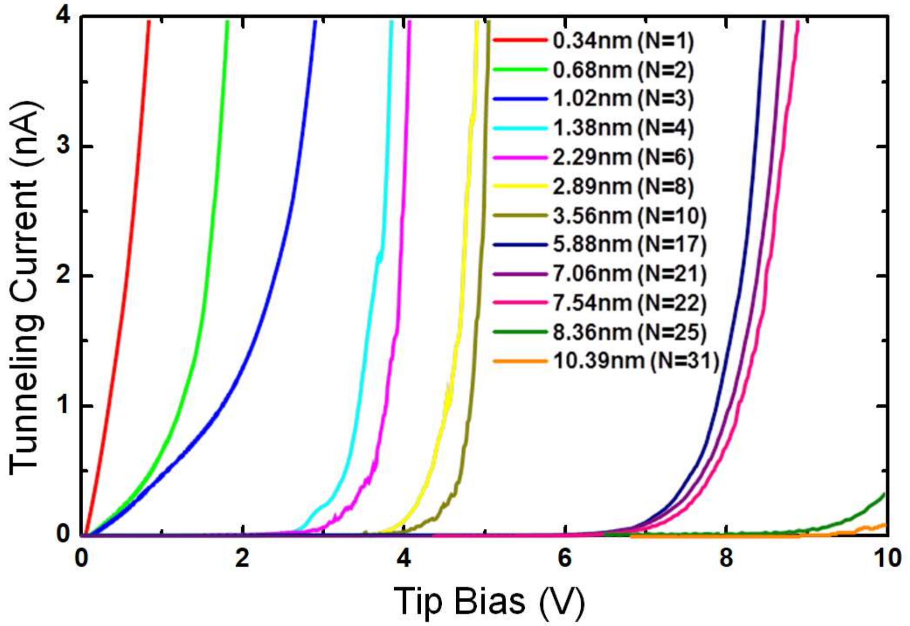


Unit: nm

Unit: nA, Tip bias=1V

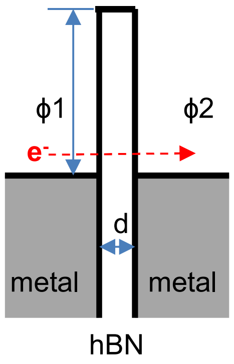
Uniform tunneling current within area of the same thickness without pinholes.

G. H. Lee et al. Appl. Phys. Lett. (2011)



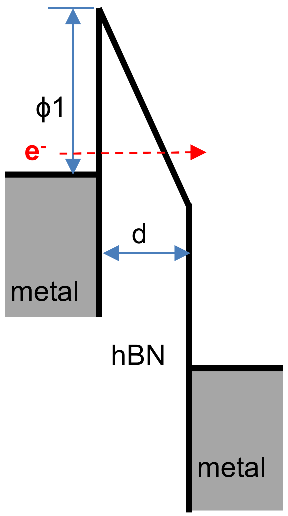
For low-bias regime

Direct tunneling

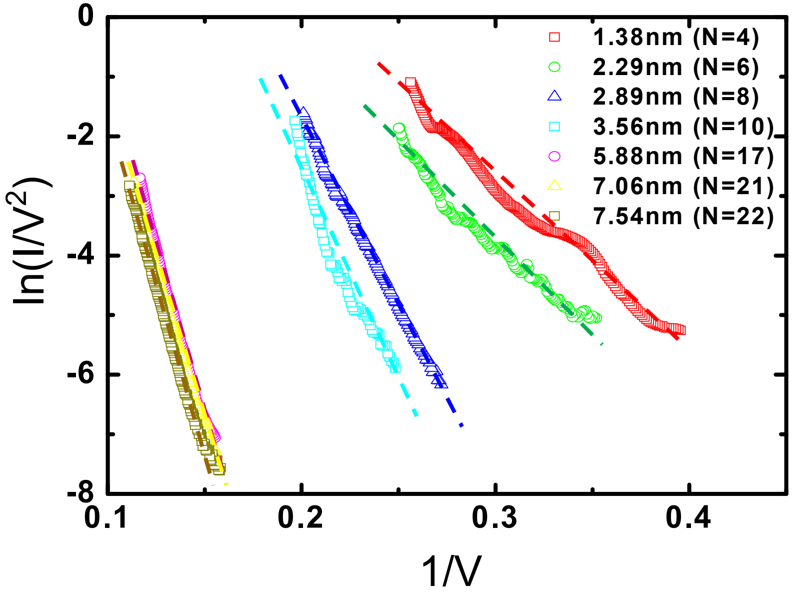


For high-bias regime

Fowler-Nordheim tunneling



G. H. Lee et al. Appl. Phys. Lett. (2011)

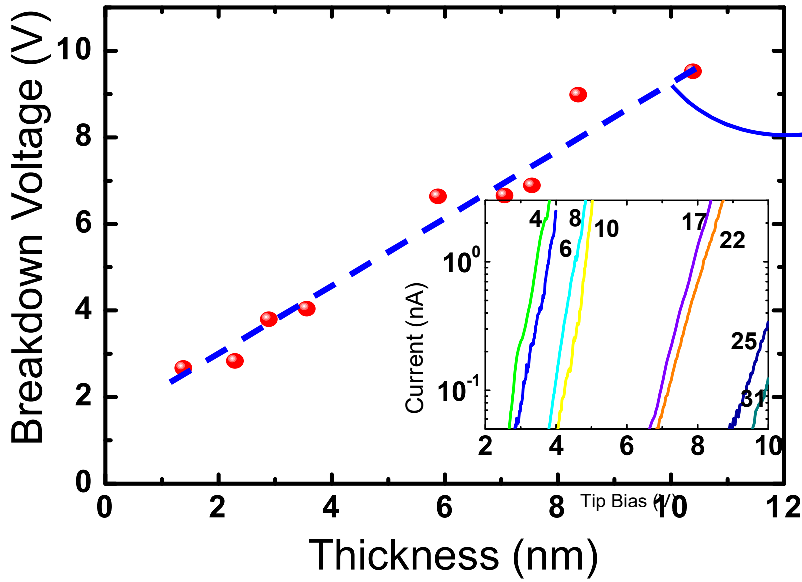


Fowler-Nordheim model for tunneling

$$I(V) = A\,V^2\,exp\left(-\frac{B}{V}\right) \quad ➡ \quad ln\frac{I}{V^2} = \ln A - \frac{B}{V}$$

$$A = \frac{A_{eff}q^3 m}{8\pi h\ \phi_B d^2 m^*}\quad , B = \frac{8\pi\sqrt{2m^*}\phi_B^{3/2} d}{3hq}$$

Barrier height (ϕ_B) = 3.07eV



Dielectric Strength = 7.94 MV/cm (0.794 V/nm)

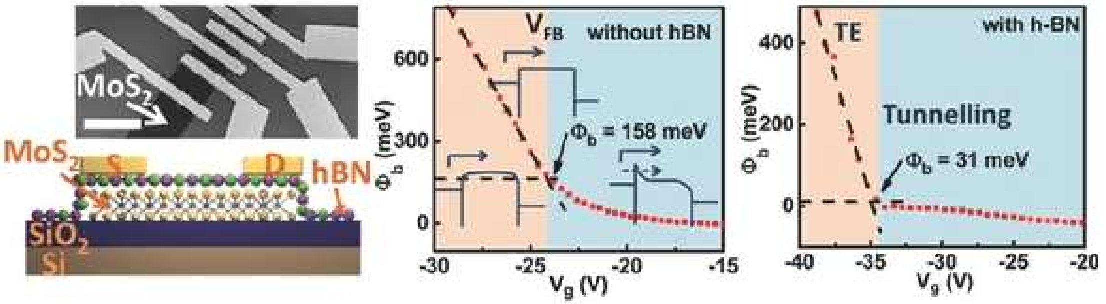
For SiO_2 , 1V/nm & 3.25eV
For HfO_2, 2V/nm & 3.6eV

hBN can be used as an atomically flat and ultrathin insulator or tunnel barrier instead of oxides.

G. H. Lee et al. Appl. Phys. Lett. (2011)

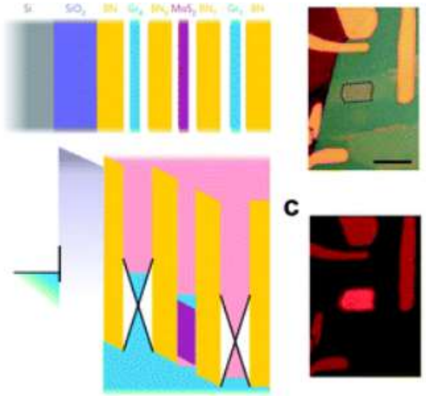
Devices using hBN as tunneling barrier

Fermi level depinning : schottky barrier reduction



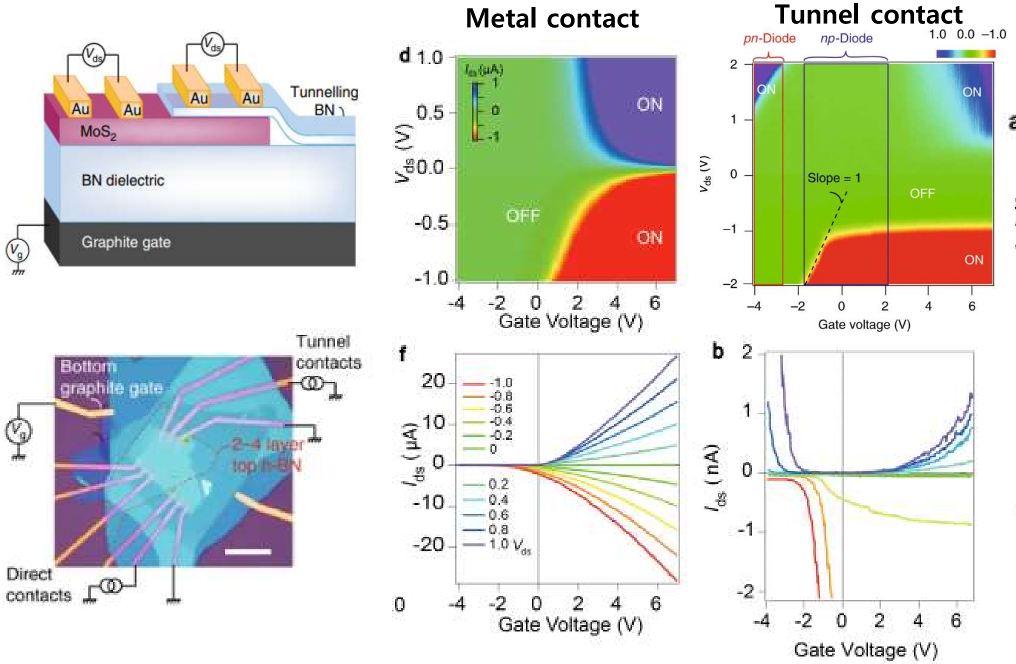
J. Wang. et al, Adv. Mater.(2016)

Light-emitting diodes

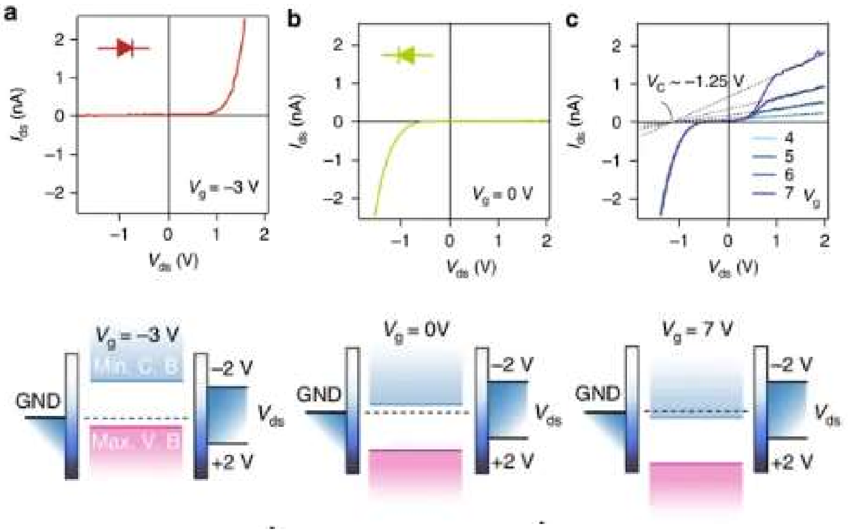


F. Withers. et al, Nat. Mater..(2015)

Gate-controlled rectifying behavior using hBN barrier



IV curves showing perfect rectifying behavior with reversible polarity characteristics of MoS2 FET

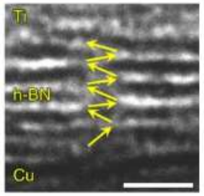


Xiao-Xi Li. et al, Nature Commun.(2017)

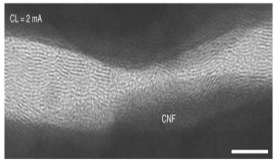
Neuromorphic devcie

Electronic synapse device

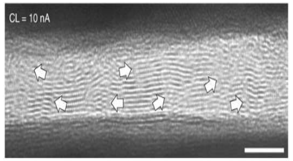
Defect path



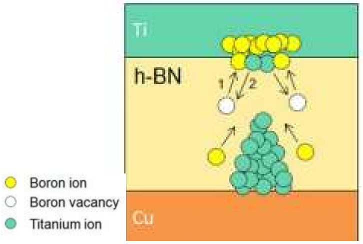
Current limit 0.2mA



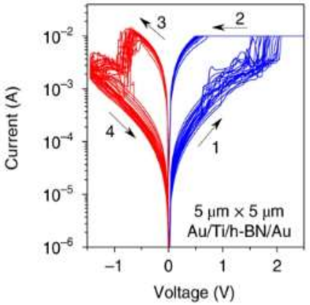
Current limit 10nA



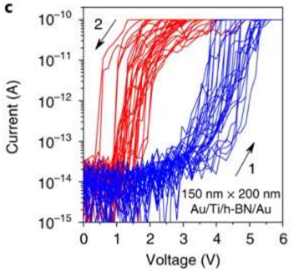
h-BN based RRAM:
(B out + Ti in)



Non volatile

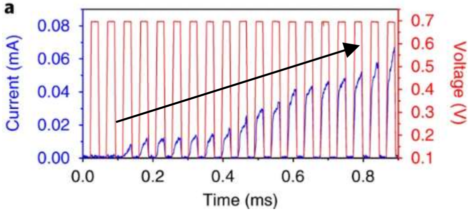


volatile

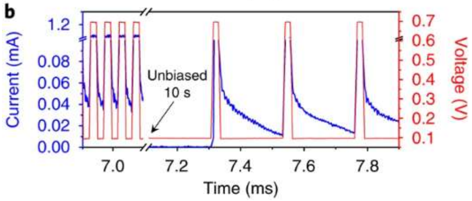


metal ions penetrates into boron vacancy

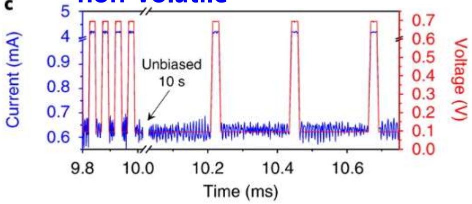
current across the synapse during increased progressively



volatile



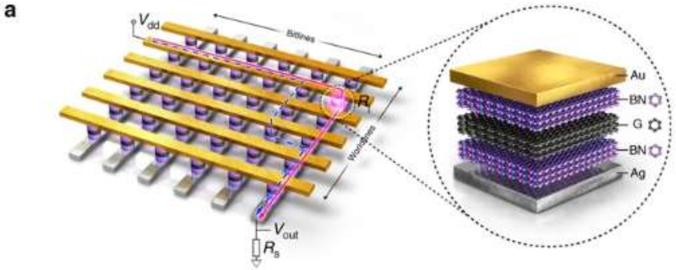
non-volatile

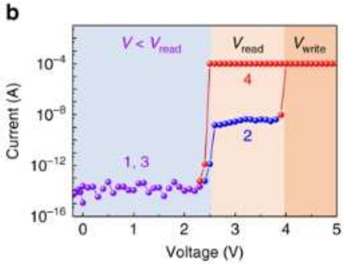


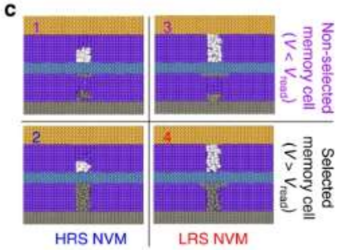
synapse completely relaxed and that no residual charge remained inside the h-BN stack

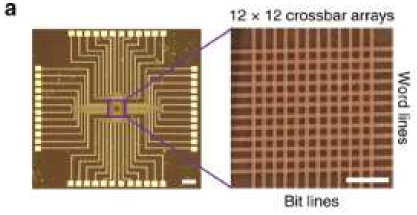
Yuanyuan Shi, et al, Nature Electronics (2018)

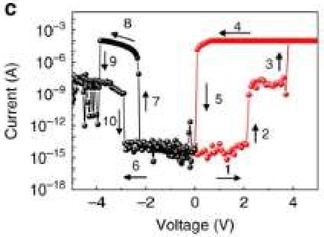
Large scale memory array

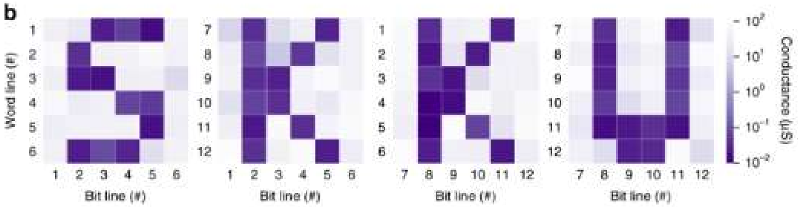








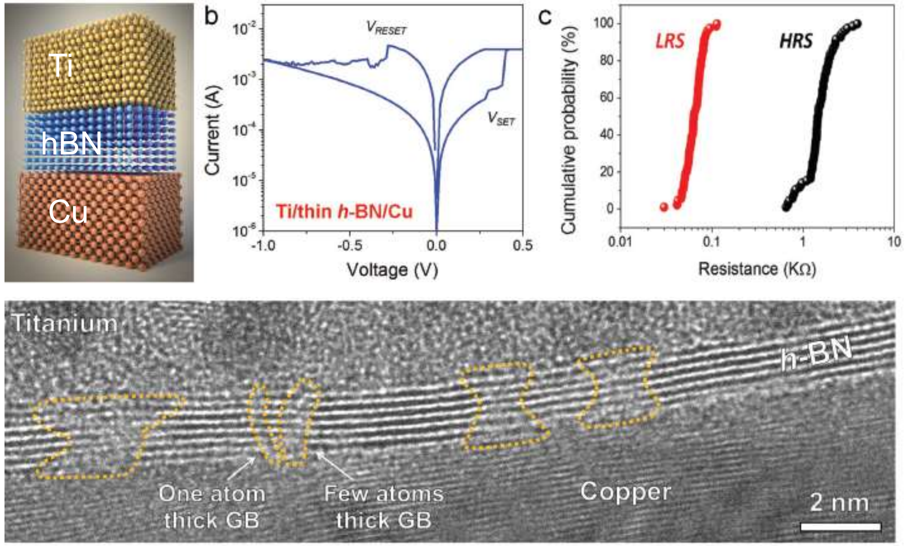




Linfeng Sun, et al, Nature Commun. (2019)

Neuromorphic devcie

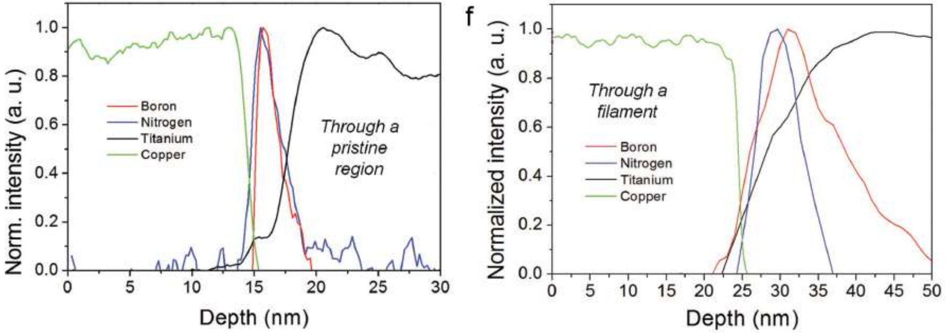
Resistive Switching behavior in CVD hBN



EELS cross-sectional analyses

Pristine region

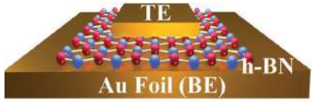
Grain boundary region



EELS profiles at the GB/CF locations show clear migration of B toward the Ti and, at the same time, penetration of Ti into the *h*-BN can be observed.

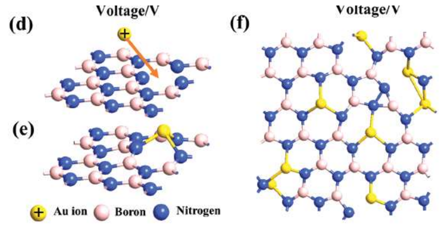
Mario Lanza. et al, Adv. Funct. Mater.(2016)

Non-Volatile memory

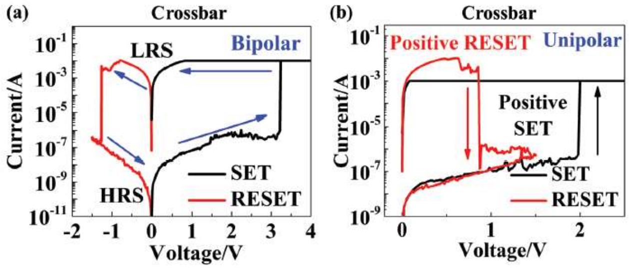


initial states

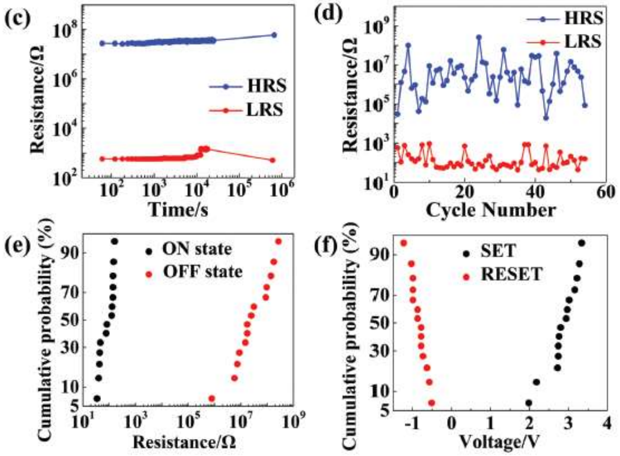
final state



optimization process for
gold ion and boron vacancies in hBN



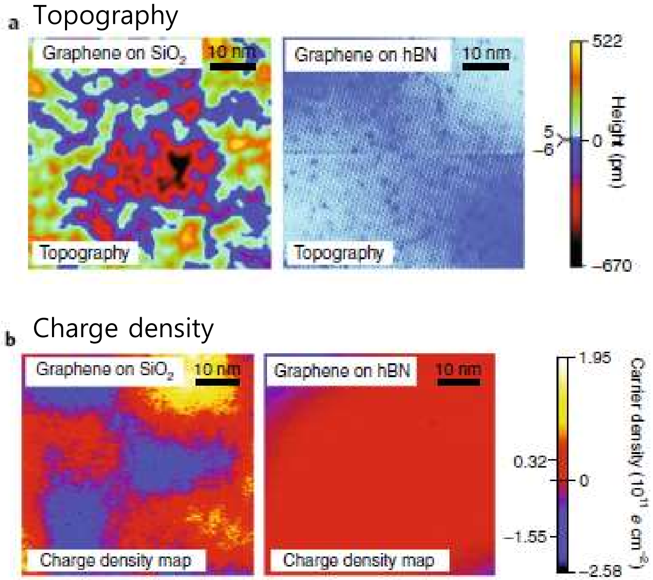
Reliability characterizations of nonvolatile resistance switches



Deji Akinwande. et al, Adv. Mater.(2018)

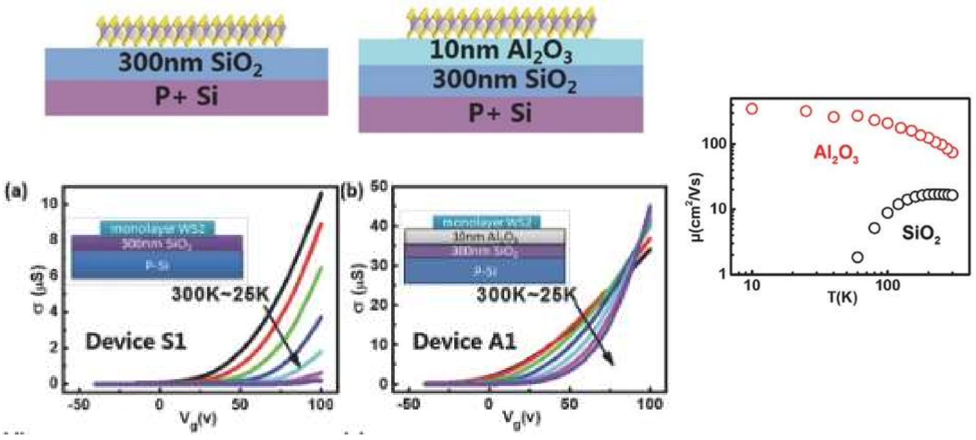
Passivation / Dielectrics

Comparison hBN vs SiO_2 substrate



Regis Decker., et al, Nano Letter (2011)

Effect of dielectric screening by Al_2O_3 for WS_2

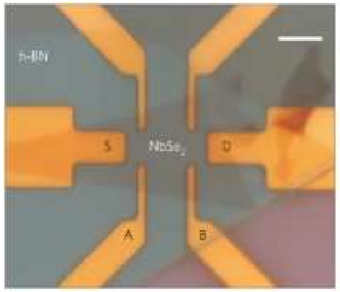


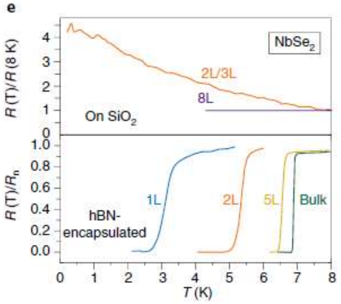
The combination of high-quality Al2O3 dielectric can effectively reduce the density of interface traps and Coulomb impurities, leading to a significant improvement of the mobility.

Yang Cui ., et al, Adv. Materials (2015)

Superconductivity behavior encapsulated by hBN

Superconductivity is only observed in encapsulated samples

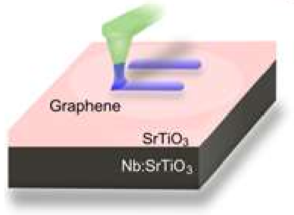


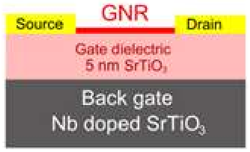


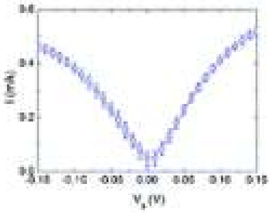
Xiaoxiang Xi,. et al, Nature Physics(2016)

Graphene nanoribbon FET behavior by STO

A GNR field-effect transistor (FET) shows bipolar FET behavior with a high mobility and low operation voltage at room temperature because of the atomically flat surface and the large dielectric constant of the insulating $SrTiO_3$ layer.

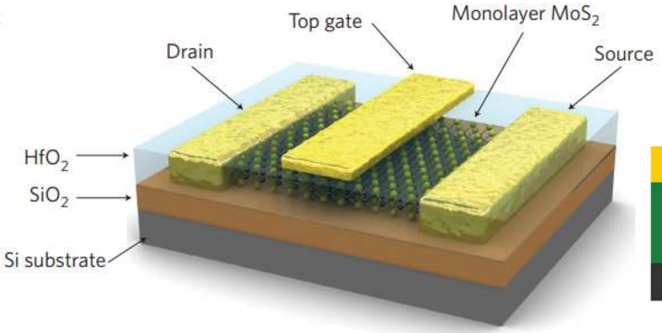




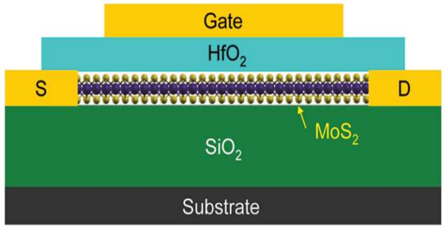


Yun-Sok Shin,. et al, JACS (2011)

Passivation / Dielectrics



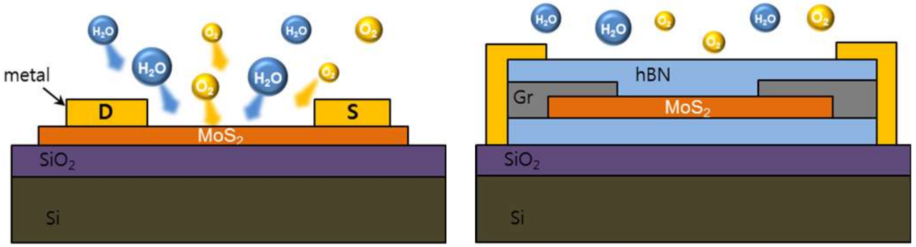
A. Kis et al. Nat. Nanotechnol. (2011)



Yoon et al. Nano letters (2011)

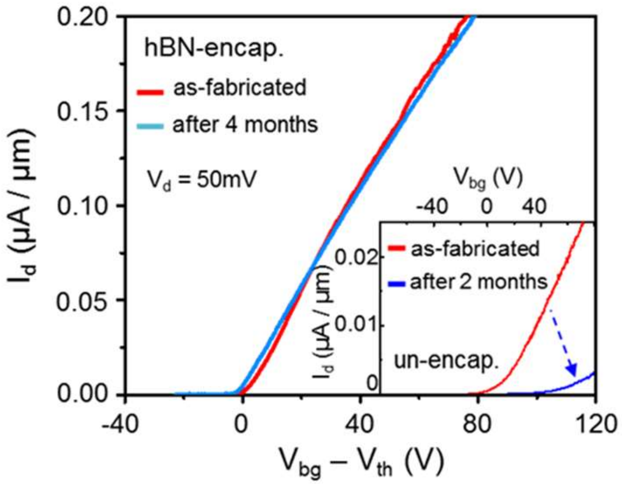
1. Instability of 2D materials: Need for passivation
2. Top-gate device structure: Individual operation of 2D devices (Back-gated FET is not compatible with integrated circuit as it cannot individually tune each device.)
3. Low operation voltage (further device scaling): Ultrathin dielectric with high k.

hBN-encapsulation of MoS_2



Open structure device

Encapsulated Device



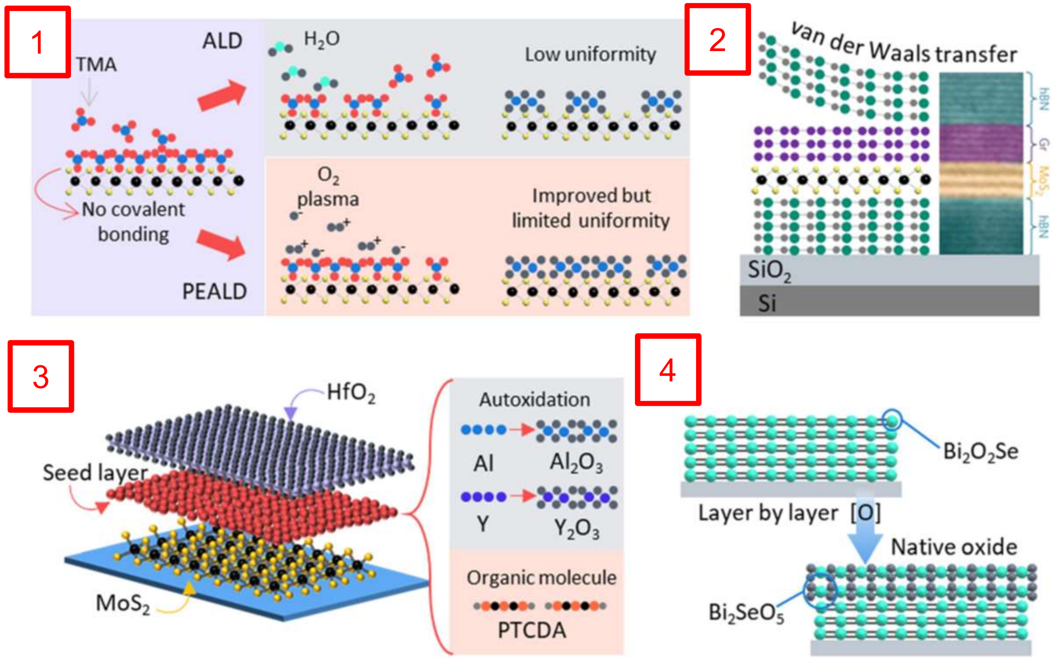
G. H. Lee et al. ACS Nano (2015)

Passivation / Dielectrics

Difficulties in deposition of dielectrics on 2D materials

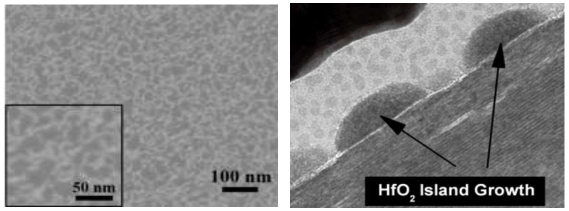
1. Not sufficient dangling bonds or nucleation sites on 2D materials
2. Island type growth of dielectrics due to lack of covalent bonding at dielectric/channel interface
3. Damage of 2D materials by surface functionalization of MoS_2 channel (oxygen plasma or UV ozone treatment for promotion of reactivity)

Ways to form dielectric film on 2D channels



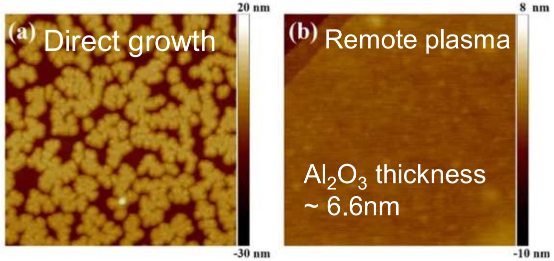
npj 2D Mater. Appl. 51 (2022)

ALD



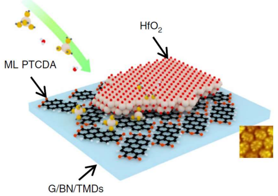
ACS Nano (2013); Chem. Phys. (2017)

PEALD

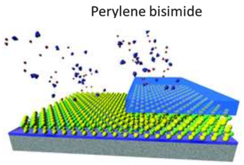


Wen Yang, et al. Sci. Rep(2015)

Seed-layer

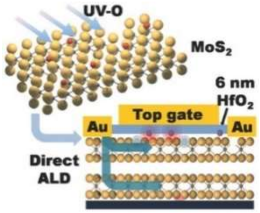


Nat. Elec. (2019)

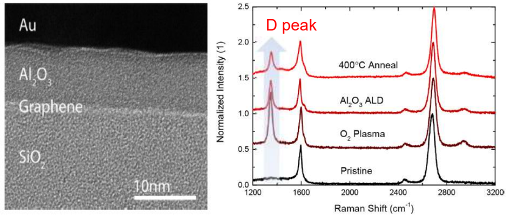


Chem, Commun. (2015)

Surface functionalization



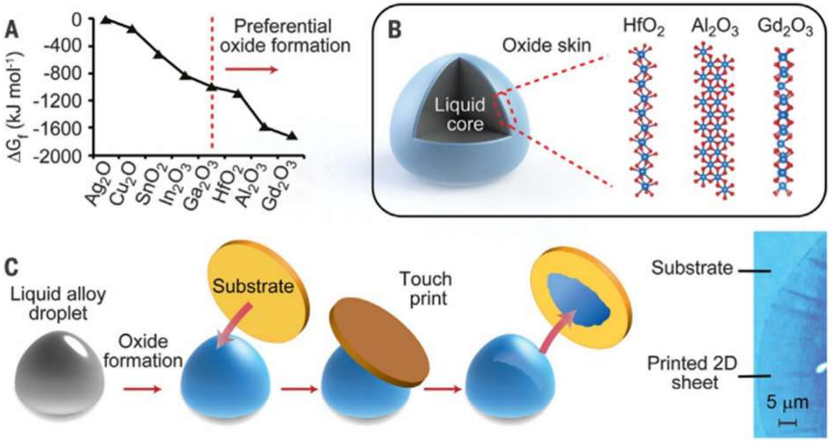
Small (2015)

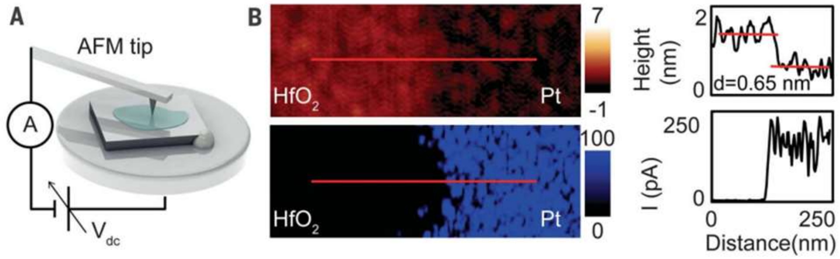


Chem. Mater. (2017)

2D Dielectric Materials

2D metal oxides by surface oxidation of liquid metal

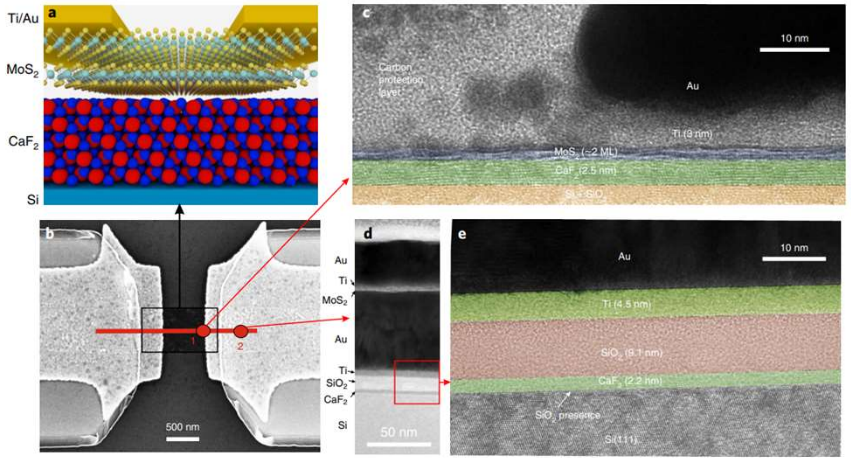


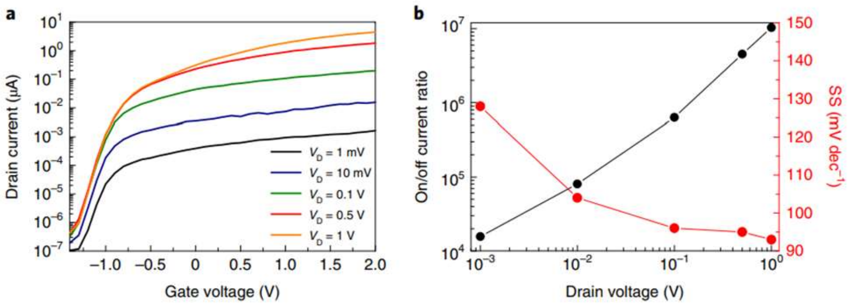


Science 358, 332–335 (2017)

- ❑ Liquid metal alloy in inert condition
- ❑ Surface oxidation in ambient condition
- ❑ Ultrathin 2D oxides transfer by touching liquid metal droplet

Quasi 2D CaF_2 dielectric



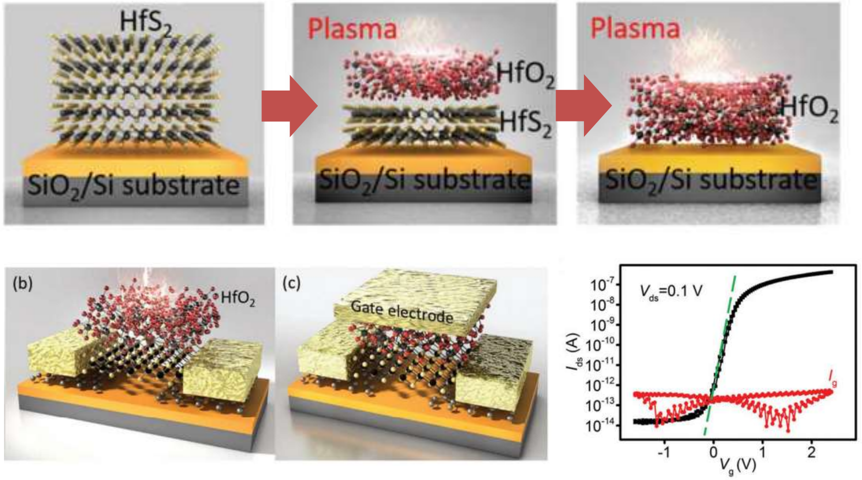


Nature Electronics, 2, 230–235 (2019)

- ❑ Quasi 2D CaF_2: Terminated by inert F atoms
- ❑ High dielectric constant: ε ~8.43
- ❑ Wide work function: E_g ~ 12.1 eV
- ❑ Improved device performance

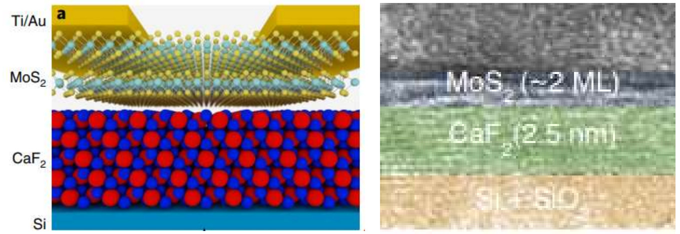
Advanced Dielectrics for 2D Materials

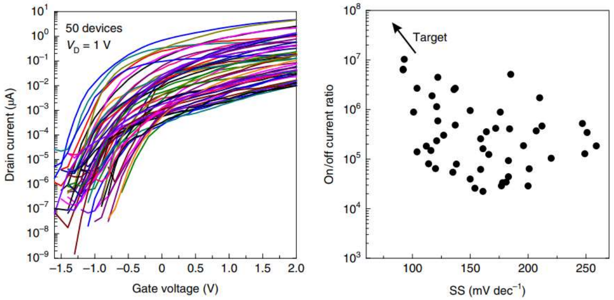
HfS_2 to HfO_2 monolithic conversion



Nanoscale, 2018, 10, 18758–18766

New quasi van der Waals dielectrics: CaF_2

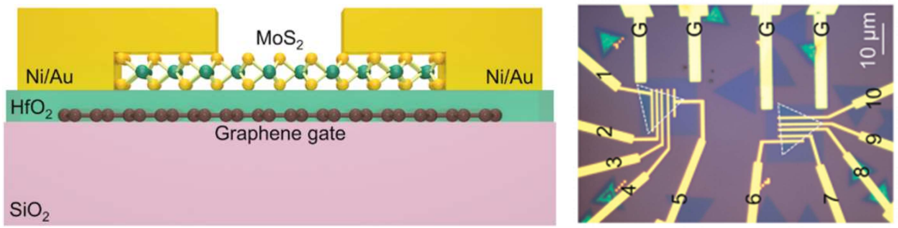


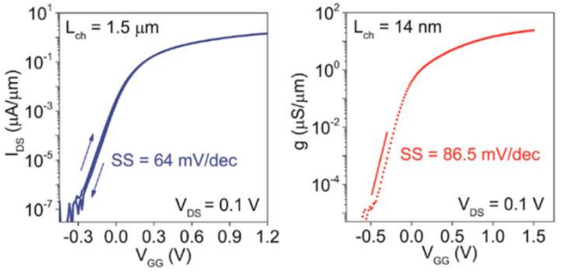


F terminated CaF_2 has high dielectric constant and inert interface, which induces hysteresis free dielectric properties to 2D materials.

Nature Electronics 2, 230–235(2019)

Single atom thick HfO_2 gate dielectric



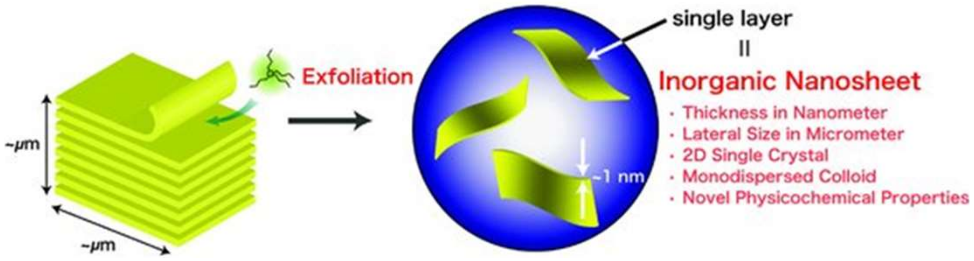


1.2 nm thick Ti layer on graphene works as seed layer for HfO_2 deposition (ALD), high quality ultrathin HfO_2 dielectric (8 nm) reduces short channel effects.

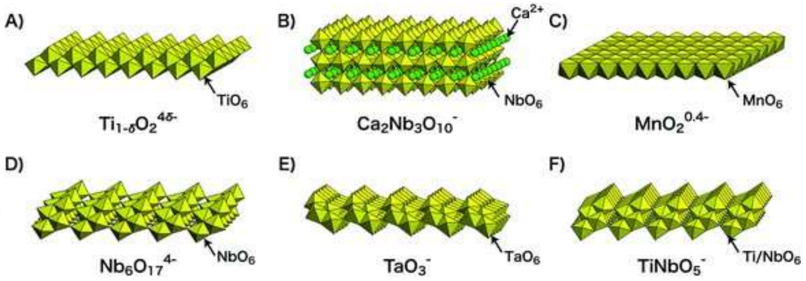
Nano Lett. 2018, 18, 3807−3813

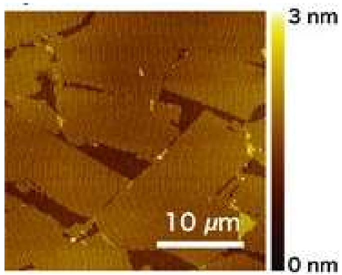
Properties of Other 2D Insulators

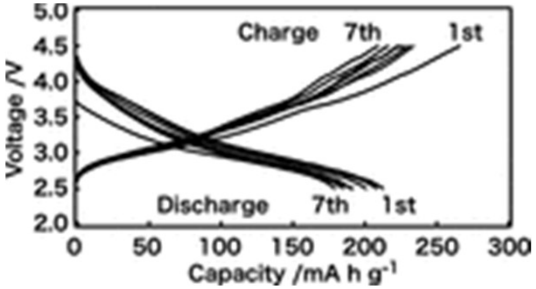
Oxide Nanosheets



- Thickness in Nanometer
- Lateral Size in Micrometer
- 2D Single Crystal
- Monodispersed Colloid
- Novel Physicochemical Properties

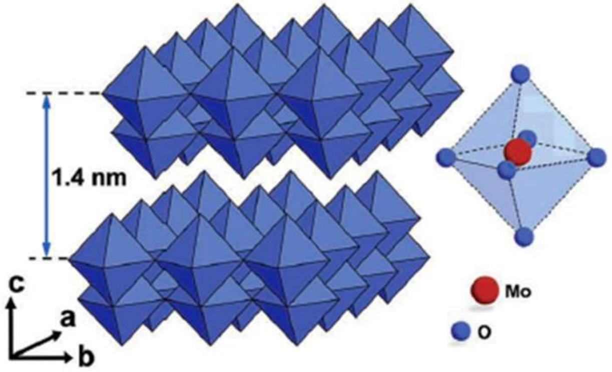


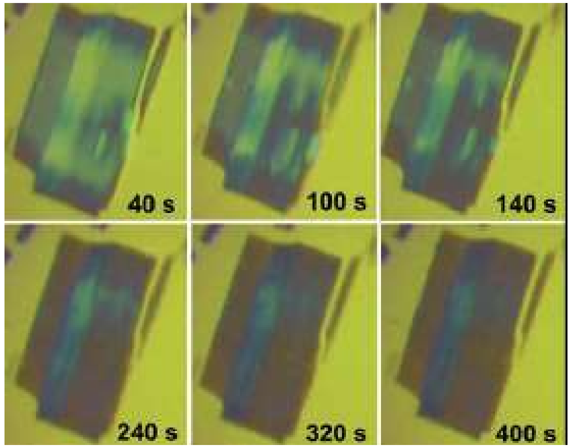


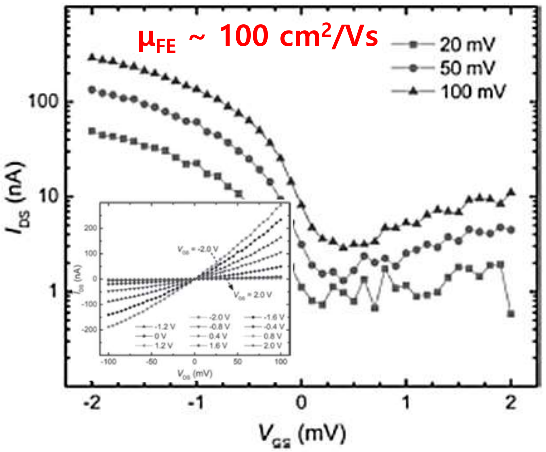


R. Ma et al. Adv. Mater. (2010)

Large bandgap Oxides

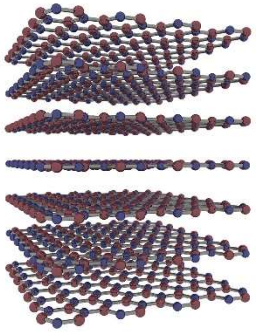






S. Balendhran et al. Adv. Mater. (2013)

Need for Wide Bandgap 2D Materials



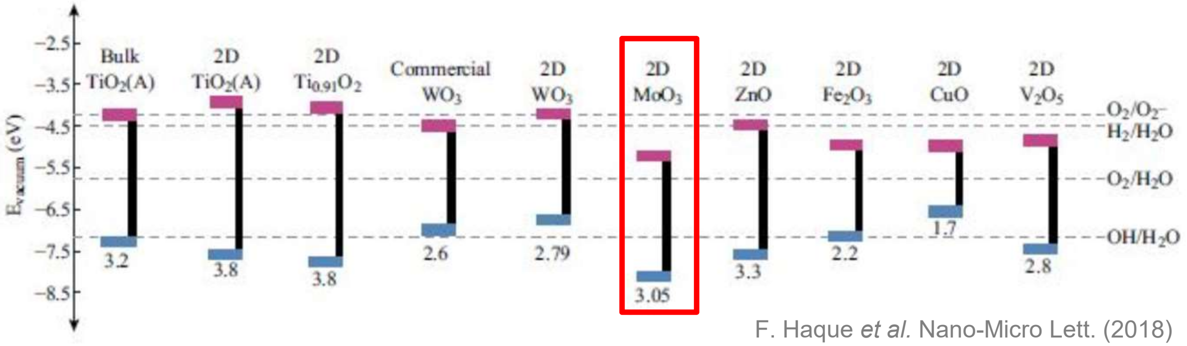
Large bandgap ~ 6 eV
Dielectric constant ~ 3.5
Low leakage current

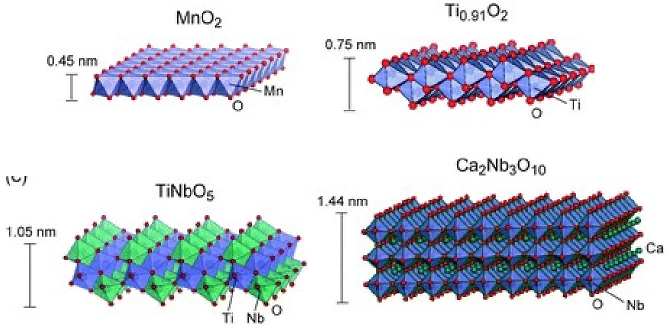
Hexagonal boron nitride (hBN)

Issues

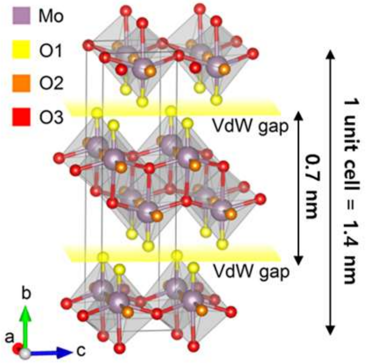
- ☐ High synthesis temperature (> 2000^{o}C) and high pressure
- ☐ No controllability of thickness
- ☐ Leakage current due to small grain size and grain boundary
- ☐ Difficulties in epitaxial growth of other 2D materials on hBN

Bandgap of 2D oxides





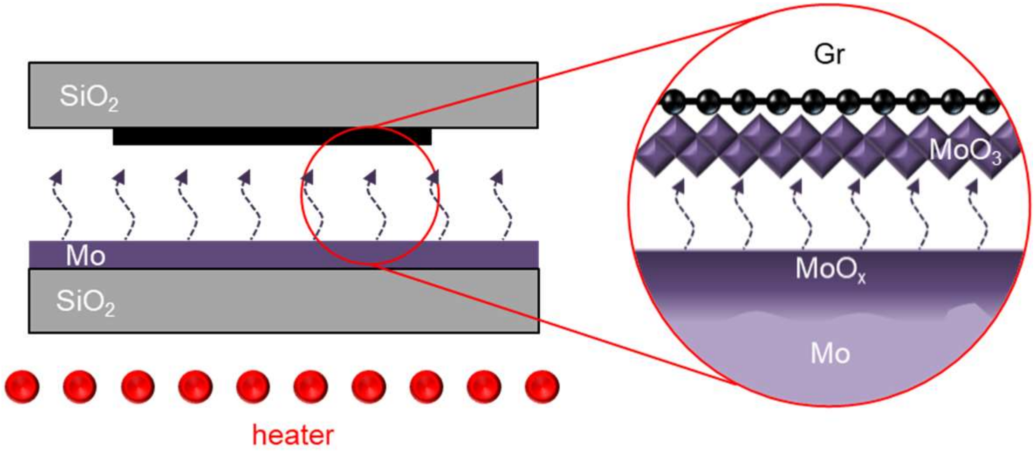
F. Haque *et al.* Nano-Micro Lett. (2018)

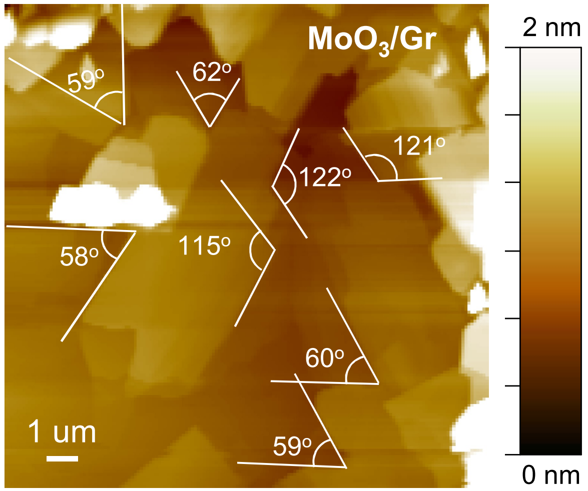


- Double-layer planar crystals of distorted MoO_6 octahedra
- Orthorhombic structure
- Wide band gap : ~ 3 eV.
- High dielectric constant (bulk) > 200
- Various applications: catalyst, HTL (solar cell, LED), anode (battery)

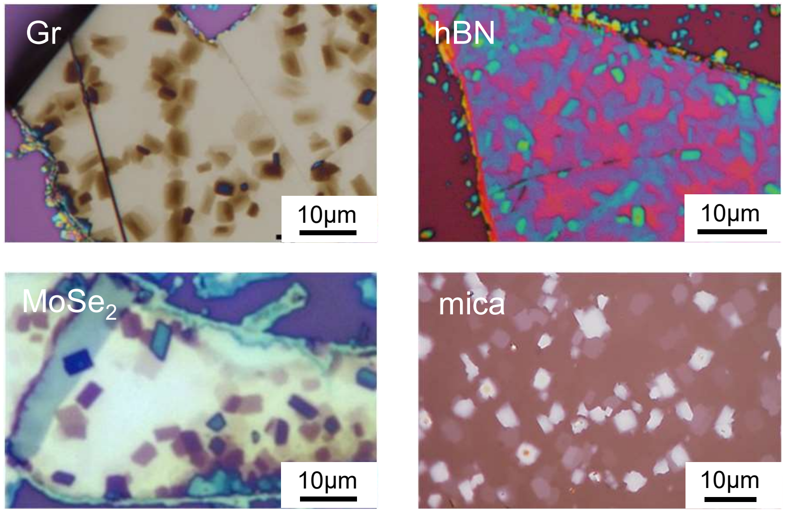
Epitaxial Growth of MoO_3 on 2D Templates

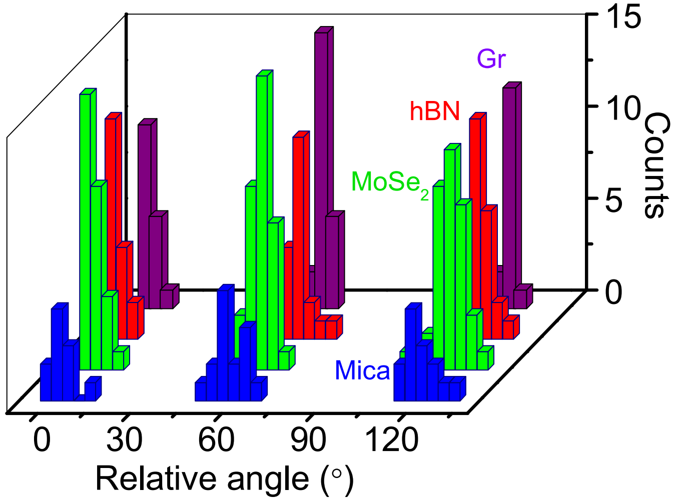
Growth of MoO_3 using 2D templates





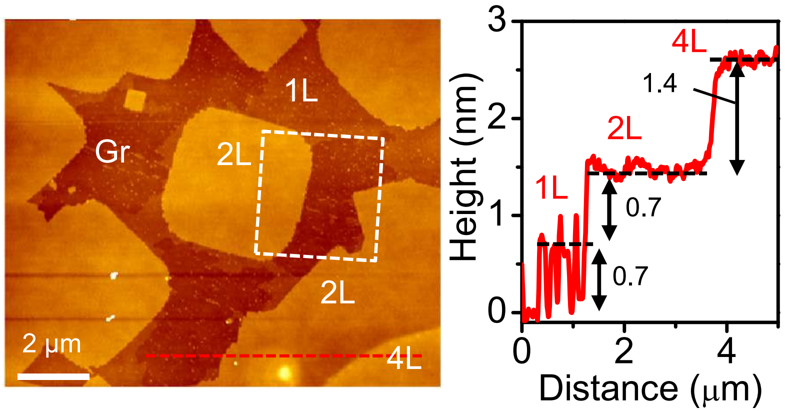
MoO_3 nanoplatelets on various 2D templates

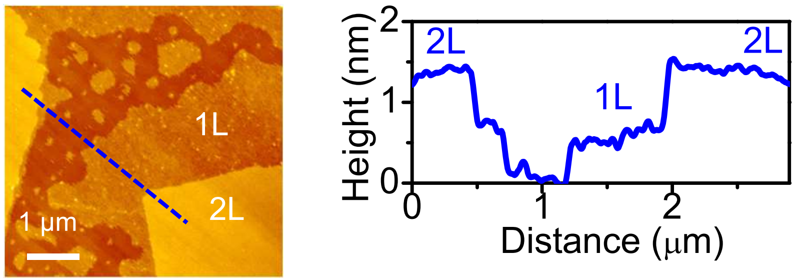


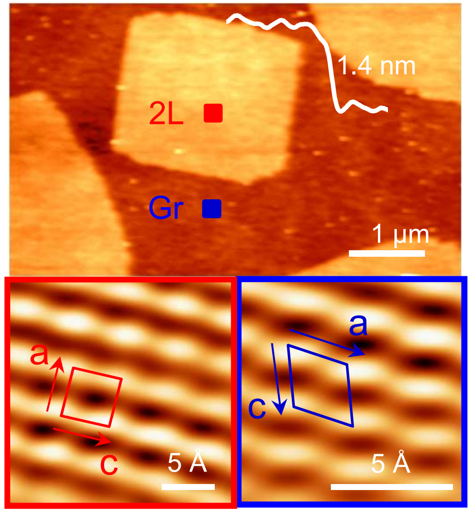


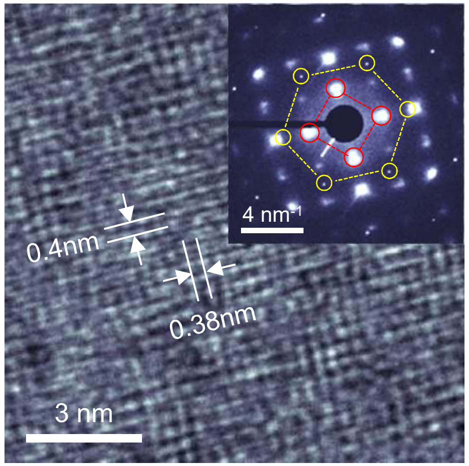
J.H. Kim, J. Dash, G.H. Lee **2D Materials** (2018)

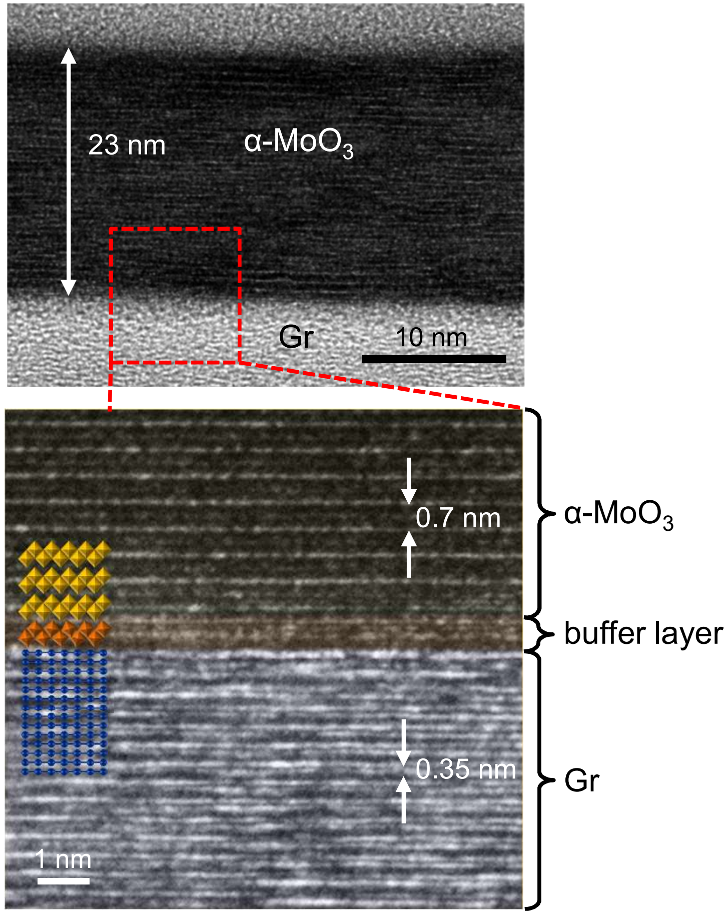
Epitaxial Growth of MoO_3 on 2D Templates

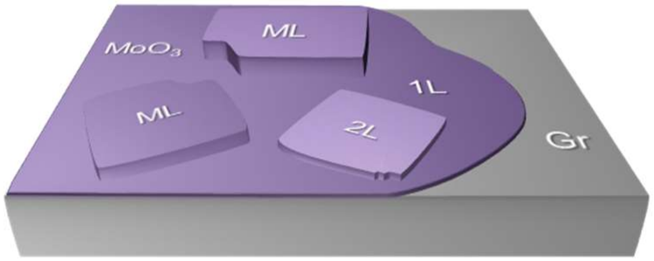












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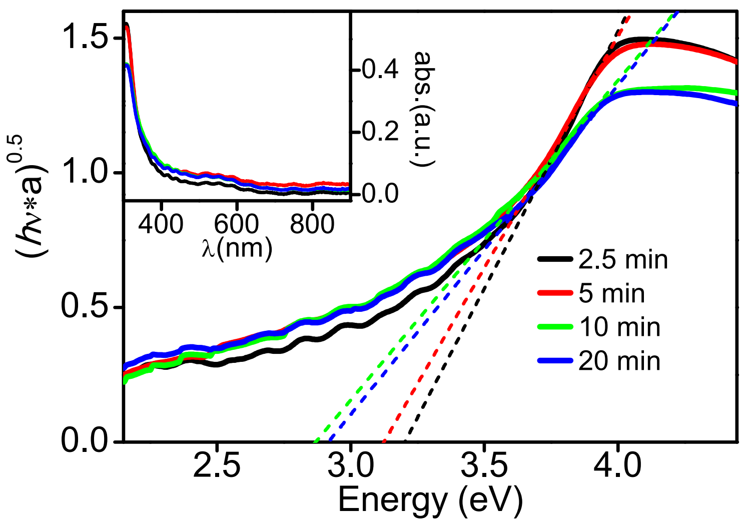
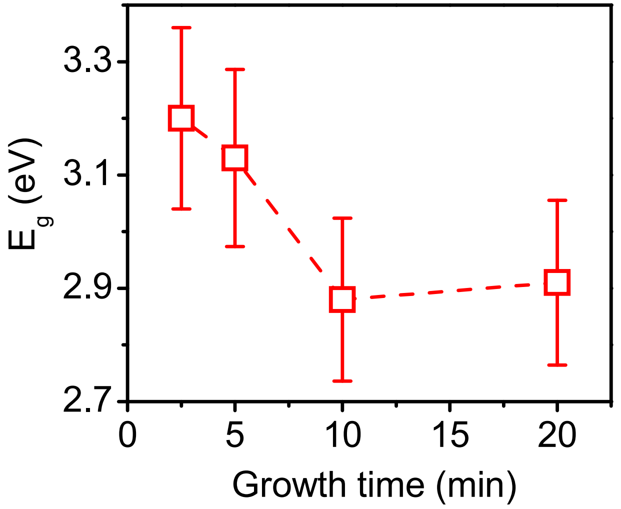
Band Structure of Epitaxially Grown MoO$_3$

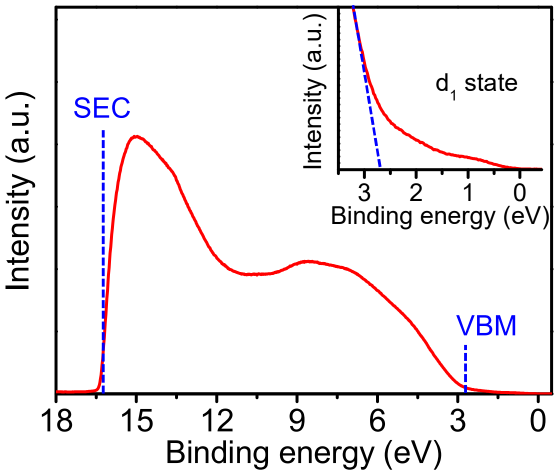
UV-Vis spectrometer



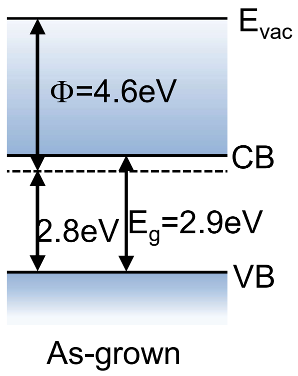
Thickness dependence of Band gap

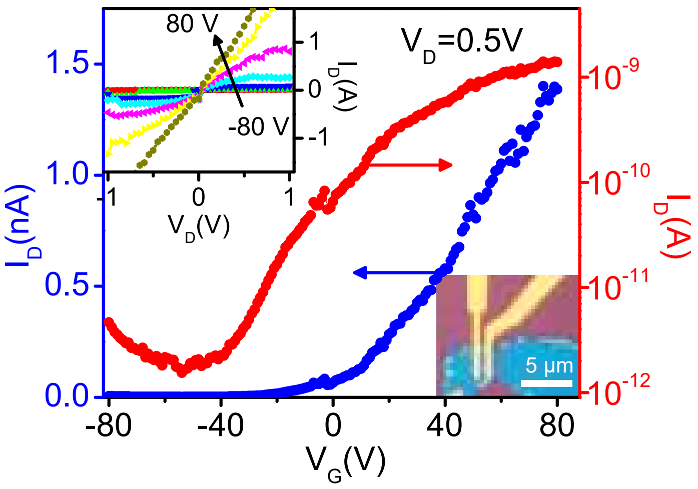


Ultraviolet photoelectron spectroscopy



Band structure

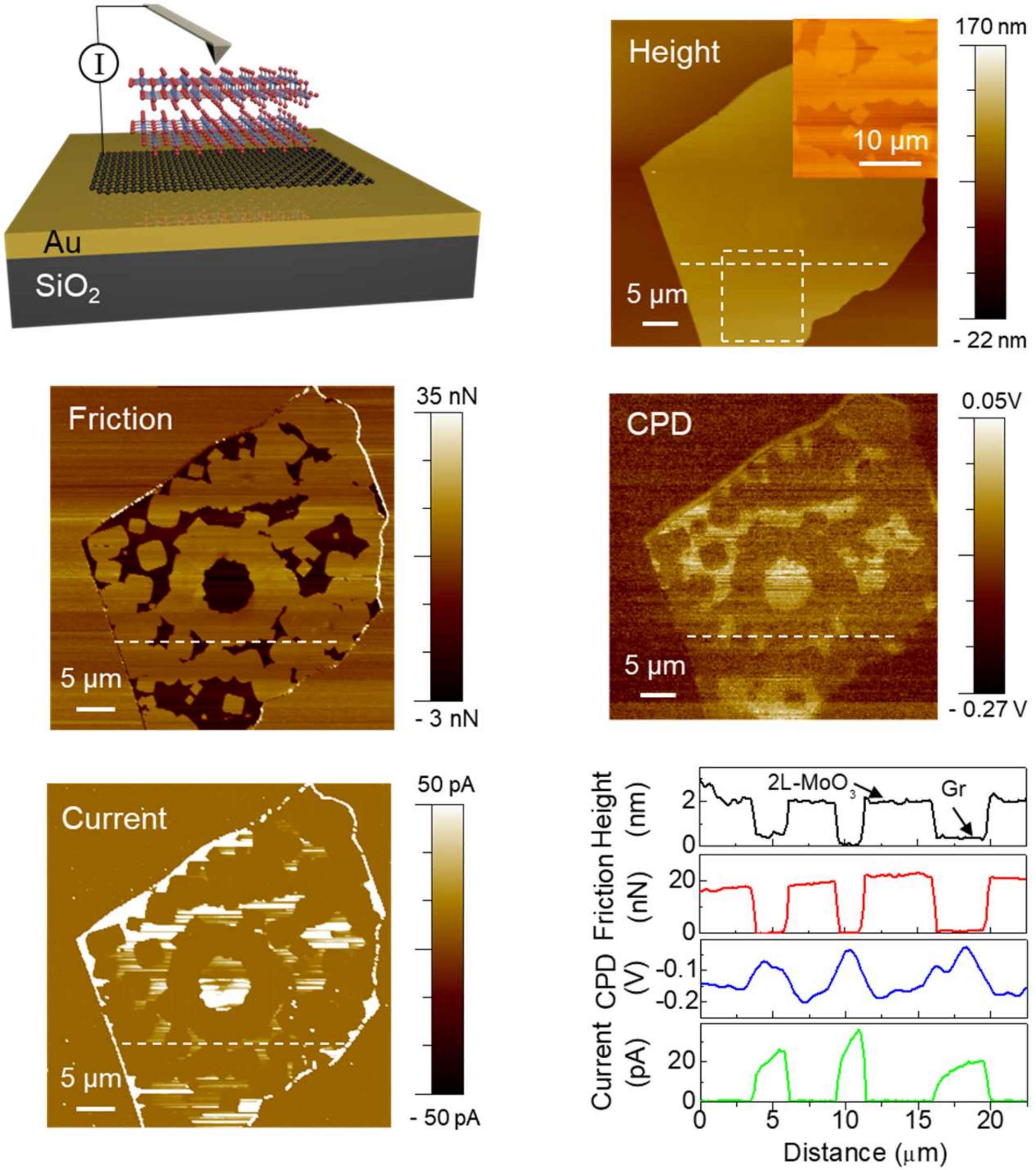




- ☐ n-type transport due to oxygen vacancies and surface contaminants
- ☐ μ_{FE} ~ 0.03 cm^2/Vs , On/off ratio ~ 10^3

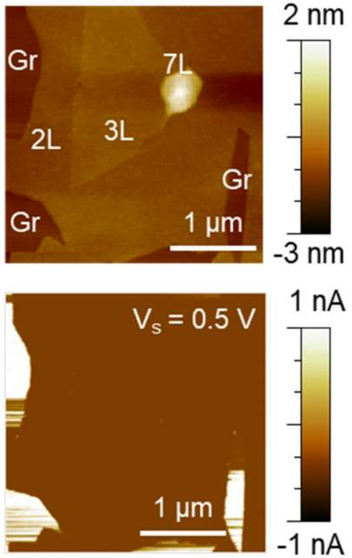
J.H. Kim, J. Dash, G.H. Lee **2D Materials** (2018)

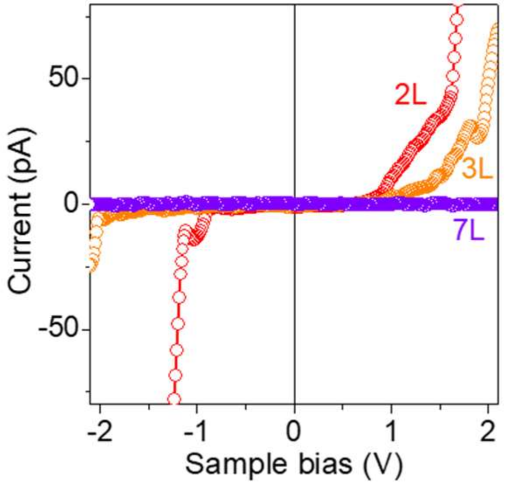
AFM Measurement of MoO_3

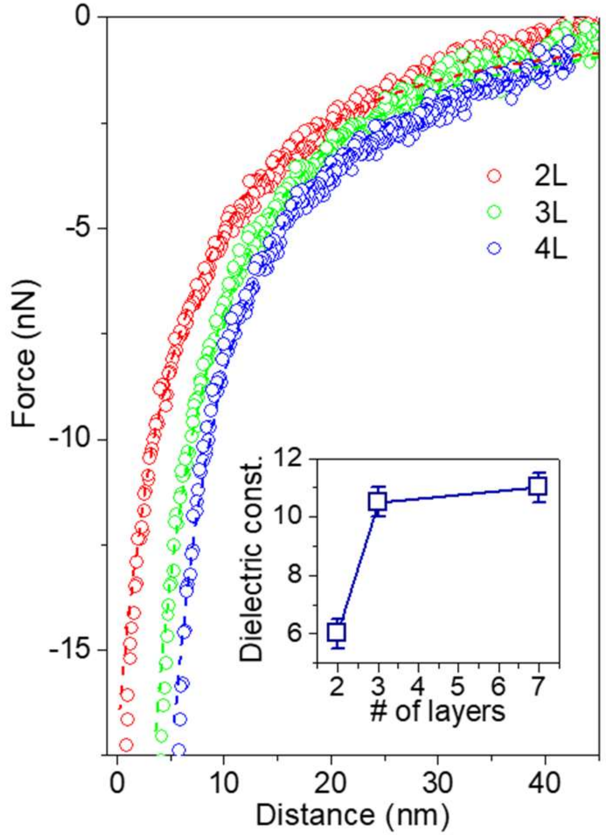


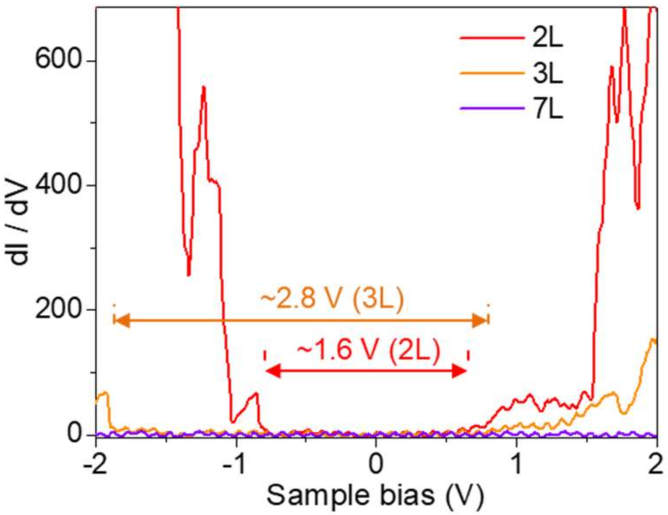
J.H. Kim, H.G Kim, G.H. Lee **Nano Lett.** (2019)

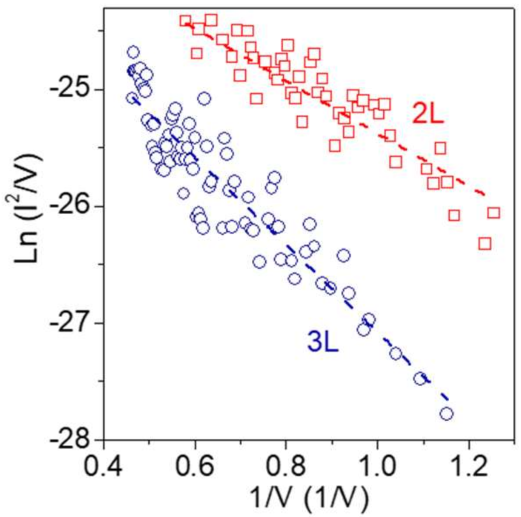
Electrical Properties of MoO_3











- ☐ Totally insulating (tunnel barrier)
- ☐ High dielectric constant
- ☐ Smaller layer-dependence in electrical properties

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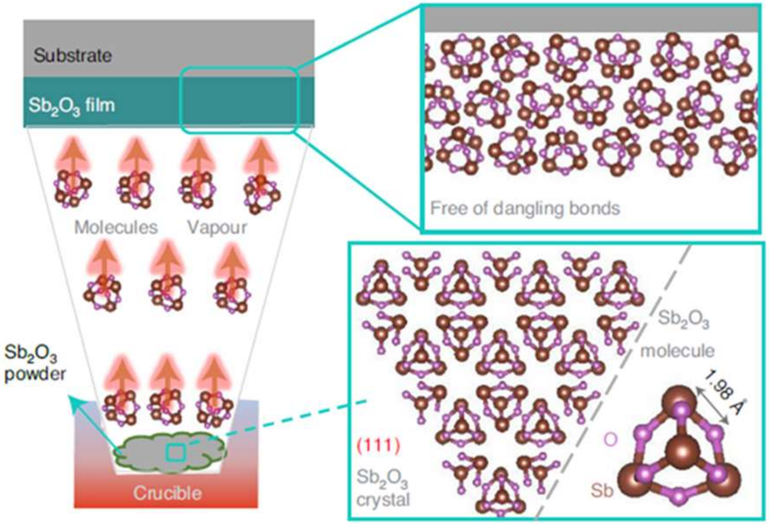
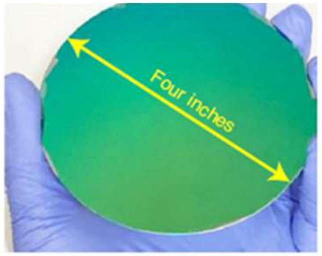
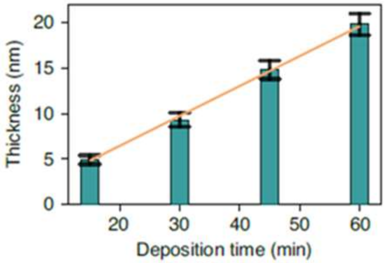
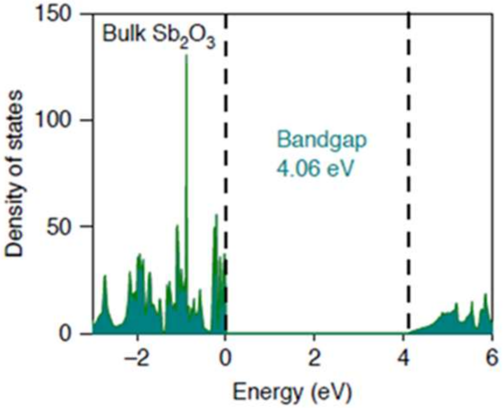
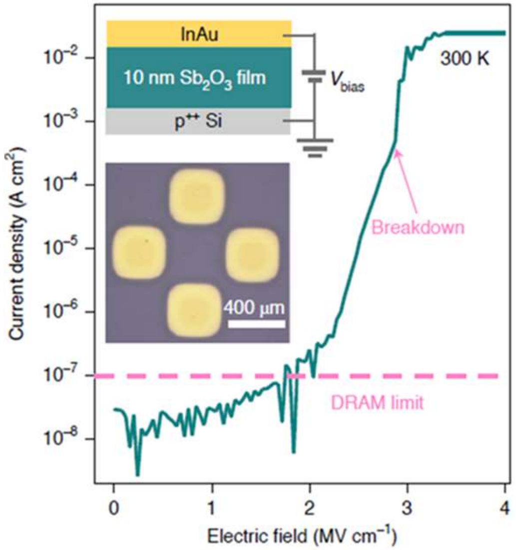
Molecular Crystal Dielectric

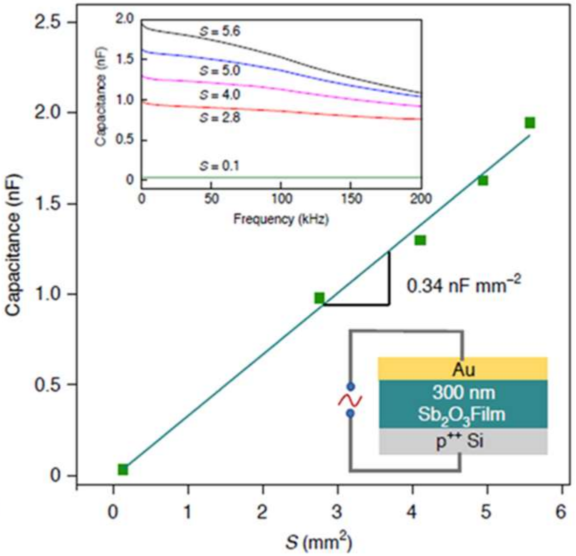


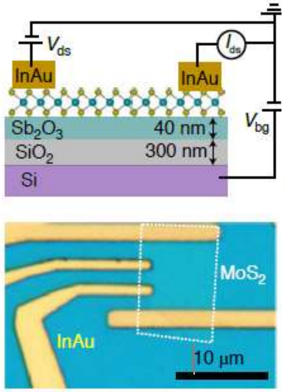


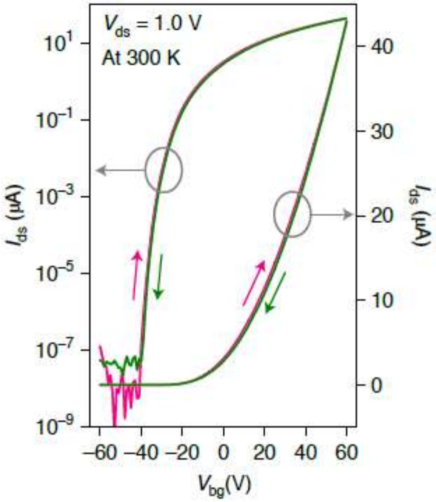












- Molecular crystal of Sb_2O_3 forms dielectric with high dielectric constant of 11.5, which is appropriate for 2D devices.

Nature Electronics 4, 906–913 (2021)