ECE 538: 2D Material Electronics and Photonics

Chapter 4: 2D Ferroelectrics

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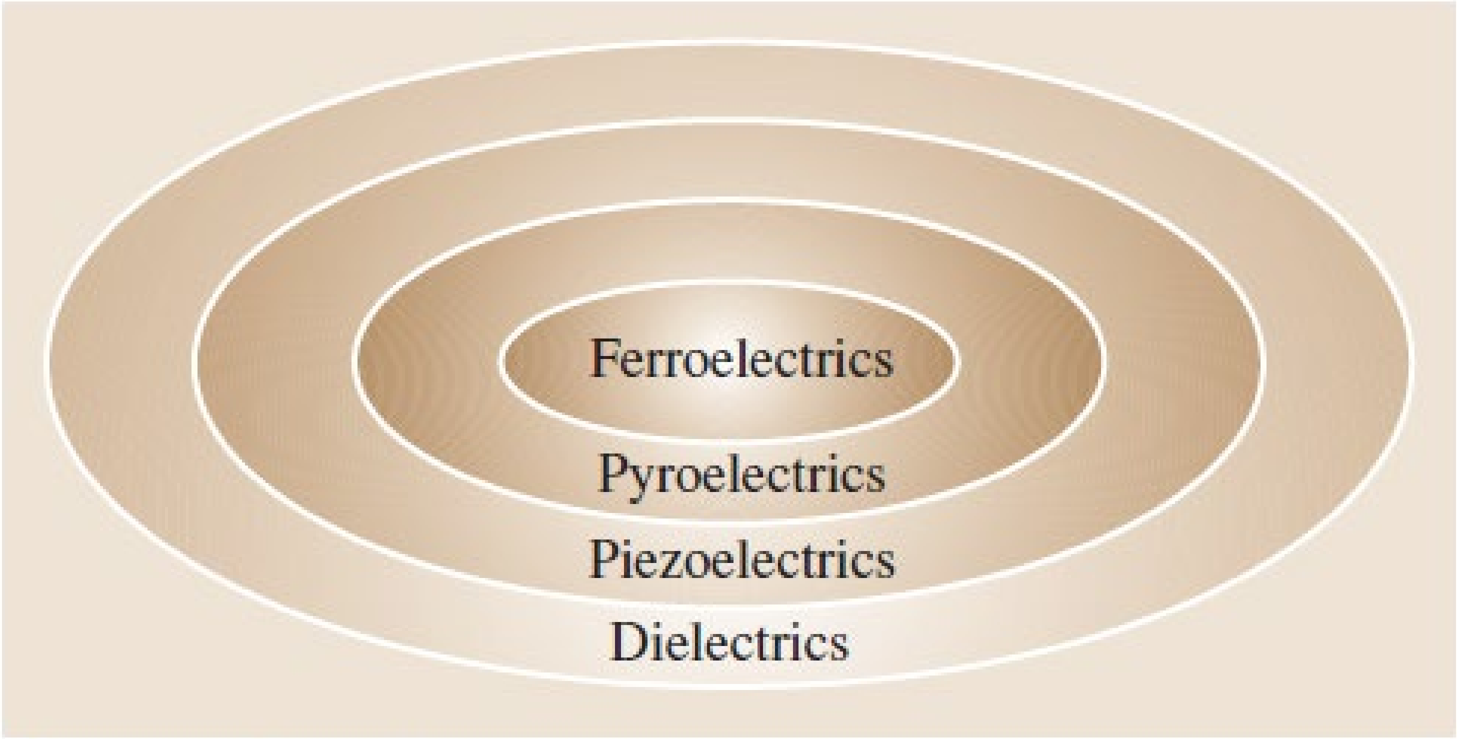
Outline

- Introduction of ferroelectricity
- 2D ferroelectric materials
- 2D and ferroelectric material stacks

Piezeoeletric, Pyroelectric and Ferroelectric Crystals

- **Piezeoelectric: generation of electricity or of electric polarity in dielectric crystals subjected to mechanical stress, or the generation of stress in such crystals subjected to an applied voltage.**
- **Pyroelectric crystal: has spontaneous dielectric polarization and the polarization can be changed by temperature.**
- **Ferroelectric crystal is a subset of pyroelectric crystal. In ferroelectric crystal, the spontaneous dipole moment can be reversed by the application of an electric field.**



R. Whatmore, Ferroelectric Materials. Springer Handbook of Electronic and Photonic Materials, (2006).

Polarizability

- **The total polarizability may usually be separated into three parts: electronic, ionic and dipolar.**

- **The electronic contribution arises from the displacement of the electron shell relative to a nucleus.**
- **The ionic contribution comes from the displacement of a charged ion with respect to other ions.**
- **The dipolar polarization arise from molecular with a permanent electric dipole moment that can change orientations in an applied electric field.**

Paraelectric and Curie temperature

- **Ferroelectric usually disappears above a certain temperature called the transition temperature or Curie temperature T_c.**

- **Above the transition the crystal is said to be in a *paraelectric* state.**

- **Antiferroelectricity: is one type of deformation where the neighboring lines of ions displaced in opposite senses. These deformations, even if they do not give a spontaneous polarization, may be accompanied by changes in the dielectric constant.**

Fundamental types of phase transition from a centrosymmetric prototype

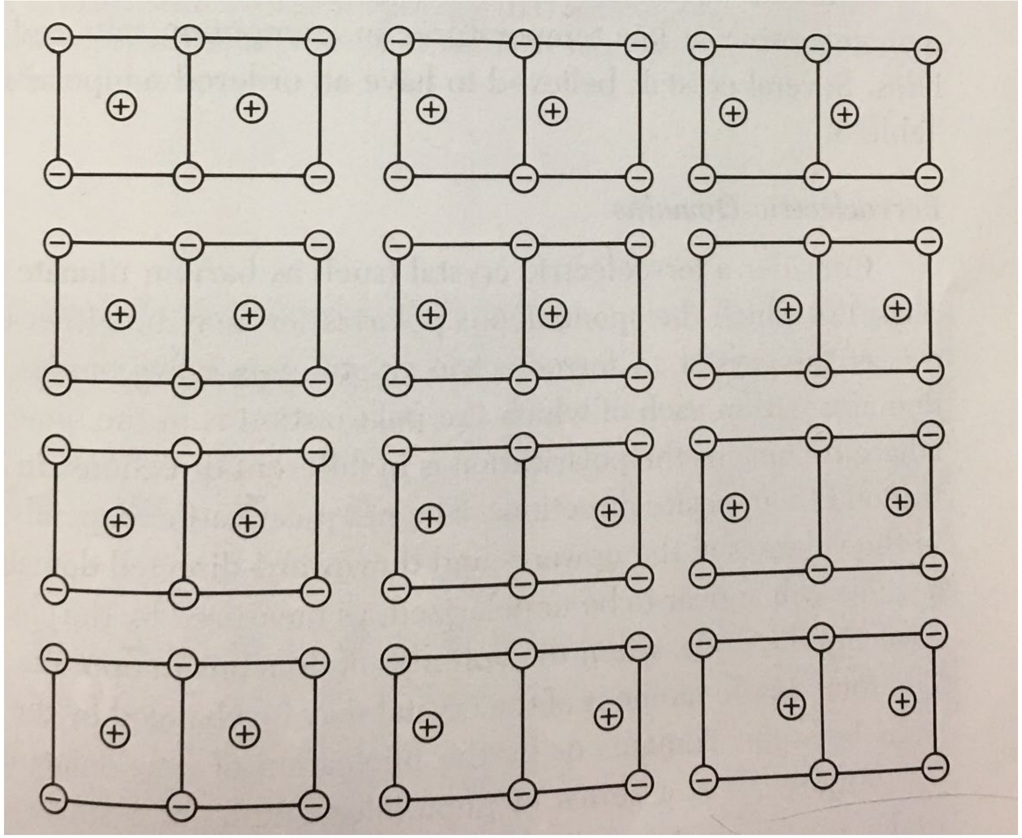
$T > T_c$ $T < T_c$ $T < T_c$ Applied field

Pyroelectric (non-ferroelectric)

Ferroelectric

Antipolar

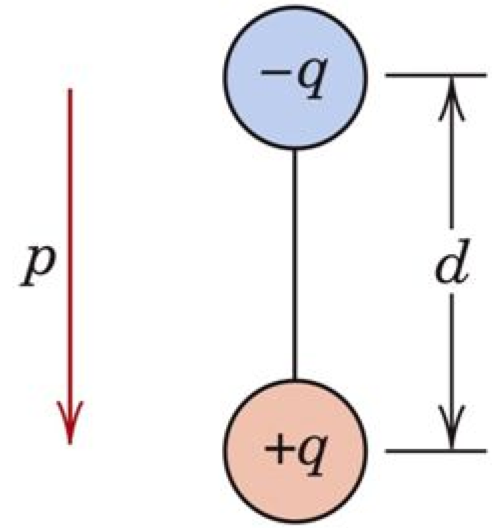
Antiferroelectric



Definition of polarization

- The electric dipole moment is a measure of the separation of positive and negative electrical charges within a system, that is, a measure of the system's overall polarity.

- Two point charges, one with charge +q and the other one with charge −q separated by a distance d, constitute an electric dipole. For this case, the electric dipole moment has a magnitude of qd.

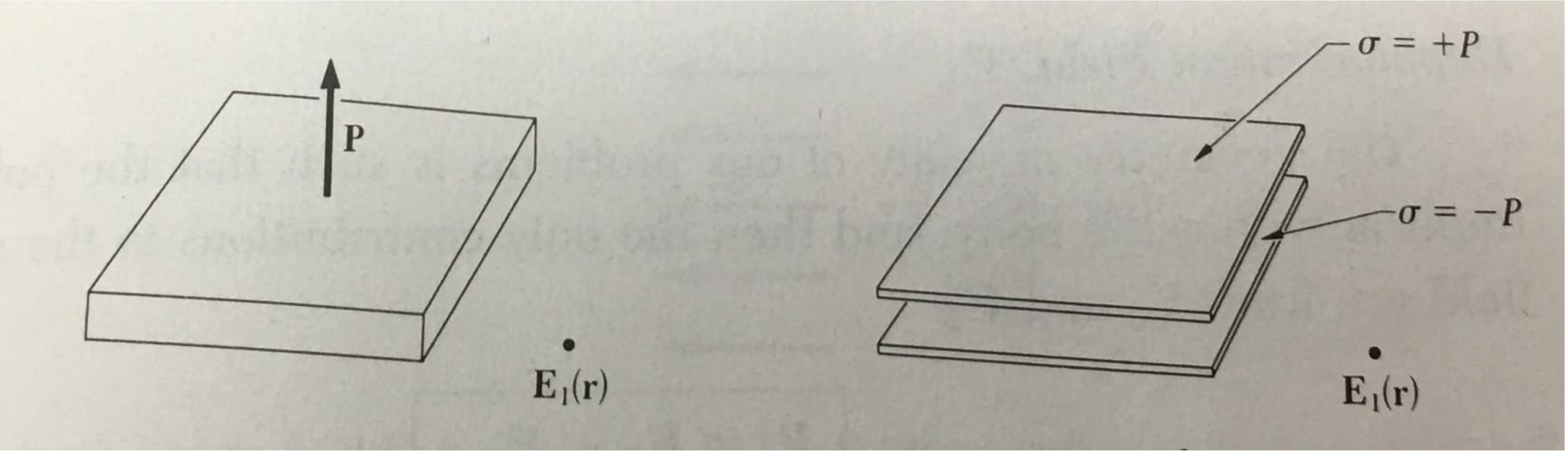


$$p = q\,d$$

- The polarization P is defined as the dipole moment per unit volume, average over the volume of a cell.

$$\boldsymbol{P} = \sum \boldsymbol{q_n d_n}$$

Polarization induced electric field



The macroscopic electric field caused by a uniform polarization is equal to the electric field in vacuum of a fictitious surface charge density

$$\sigma = \hat{\boldsymbol{n}} \cdot \boldsymbol{P}$$

Here $\hat{\boldsymbol{n}}$ is the unit normal to the surface, draw outward from the polarization matter

The electric field due to these charges is

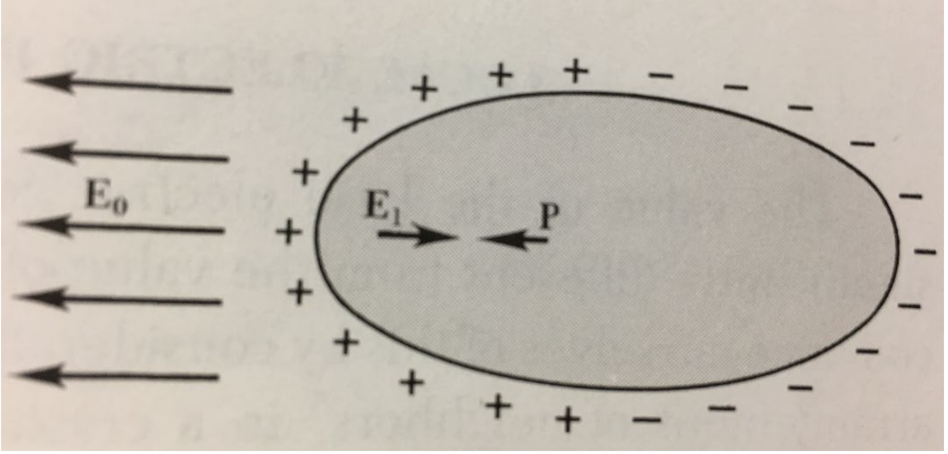
$$E_1 = -\frac{|\sigma|}{\epsilon_0} = -\frac{P}{\epsilon_0}$$

Depolarization field

If the external applied electric field is E_0, then the total macroscopic electric field is

$$\boldsymbol{E} = \boldsymbol{E}_0 + \boldsymbol{E}_1$$

The electric field E_1 is also called the depolarization field, since within the dielectric body it tends to oppose the applied field E_0.



Definition of dielectric constant

A uniform applied field E_0 will induce uniform polarization

$$P = \epsilon_0 \chi E$$

Where χ is called dielectric susceptibility $\chi = \frac{P}{\epsilon_0 E}$

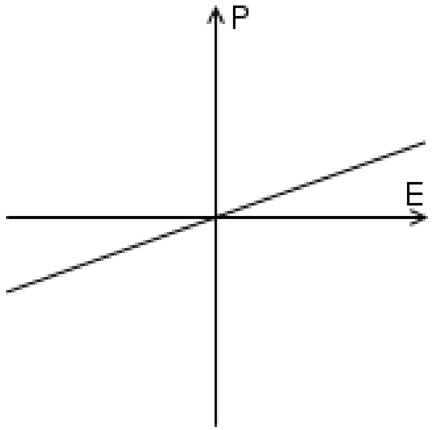
The dielectric constant is defined as

$$\epsilon = \frac{E_0}{E} = \chi + 1$$

Hysteresis in ferroelectric materials

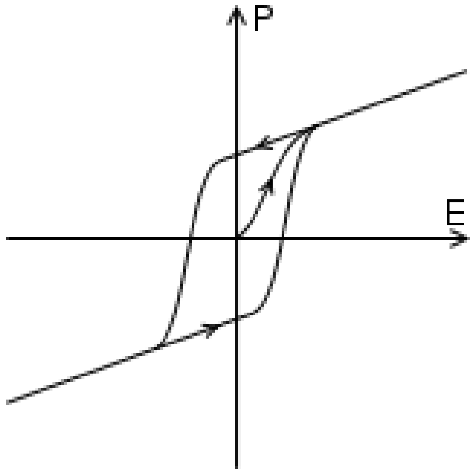
- **A crystal in a normal dielectric state usually does not show significant hysteresis when the electric field is increased and reversed.**
- **The plot of polarization versus electric field for the ferroelectric state shows a hysteresis loop.**

Normal dielectrics



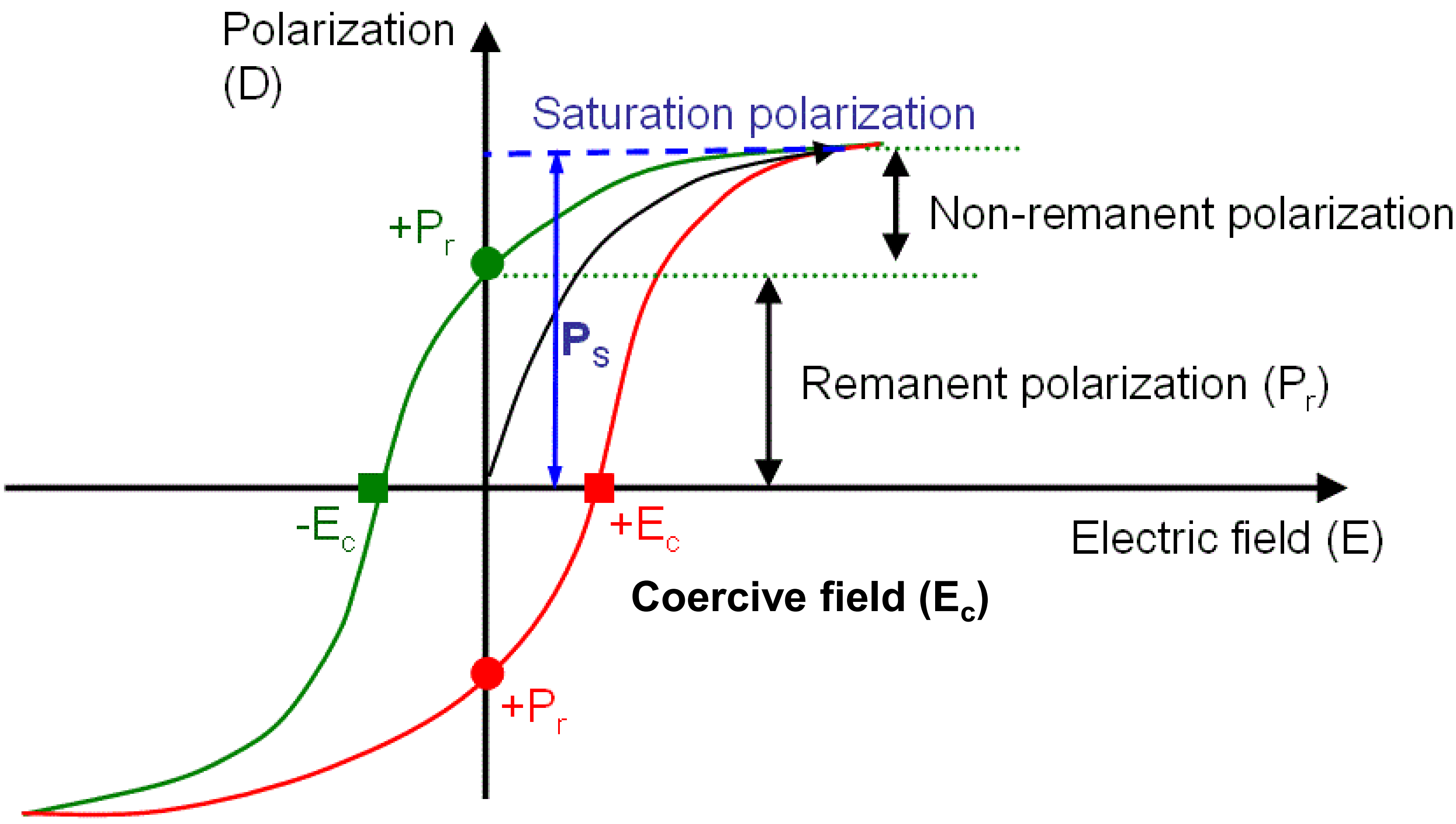
Linear dielectric polarization

Ferroelectric materials

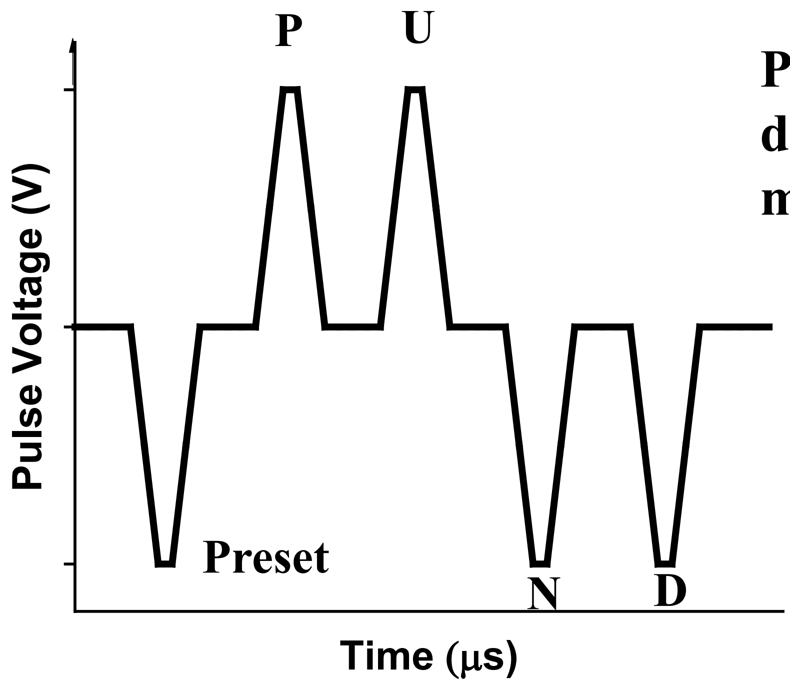


Non-linear dielectric polarization
Non-zero spontaneous polarization

Basic parameters of ferroelectric materials



Measurement of ferroelectricity



Positive-up–negative-down (PUND) measurement

The preset pulse set the ferroelectrics in negative polarization $-P_s$ state.
The first positive pulse applied (P) will switch the polarization vector into the $+P_s$ state and the displacement current for this "switching" pulse is

$$i_s(t) = \frac{\partial D}{\partial t} = \frac{\partial(\epsilon E + P)}{\partial t}$$

where P is the polarization due to the ferroelectric dipoles, E is the electric field, and ϵ is the dielectric constant of the dielectric.

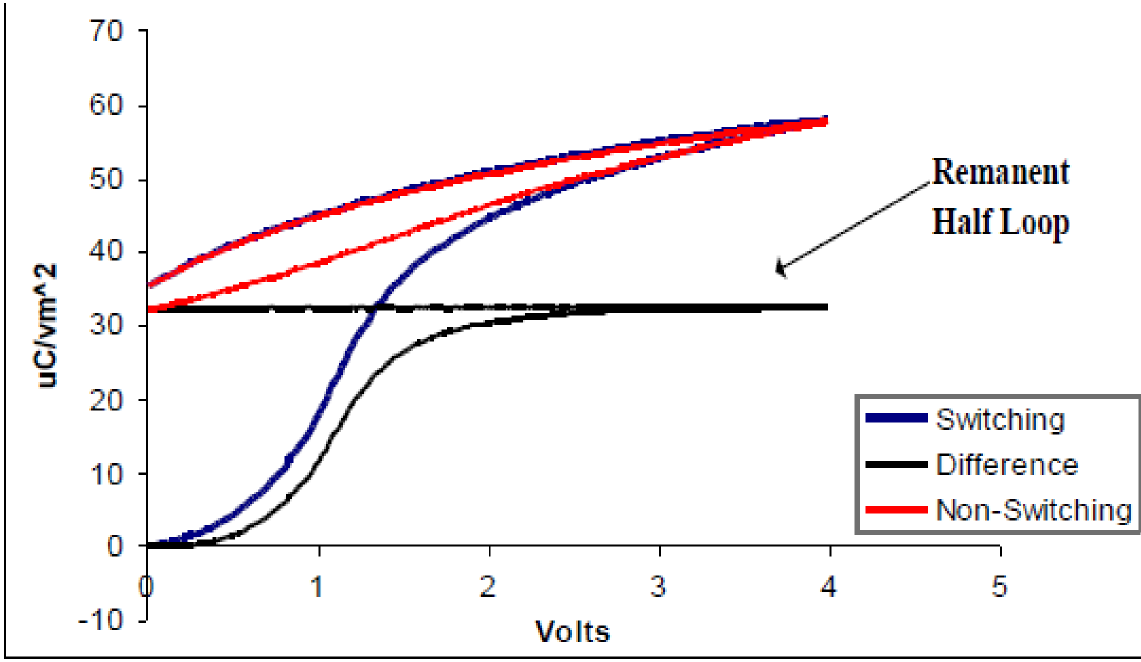
Since the film has already been polarized positively $+P_s$, applying the second positive pulse (U) will not switch the polarization, and displacement current for this "non-switching" pulse is:

$$i_{ns}(t) = \frac{\partial(\epsilon E)}{\partial t}$$

The difference between the two currents is therefore given by:

$$\Delta i(t) = i_s(t) - i_{ns}(t) = \frac{\partial P(t)}{\partial t}$$

The polarization can then be extracted from $P(t) = \int_0^t \Delta i(t) dt$.

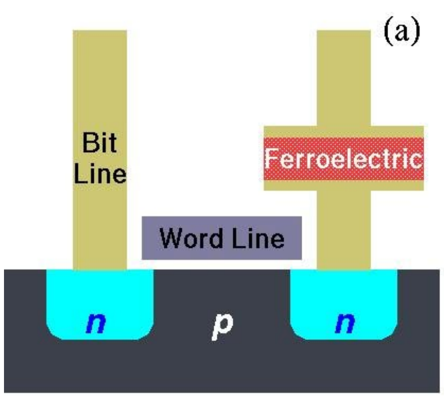


Ferroelectric Radom Access Memory

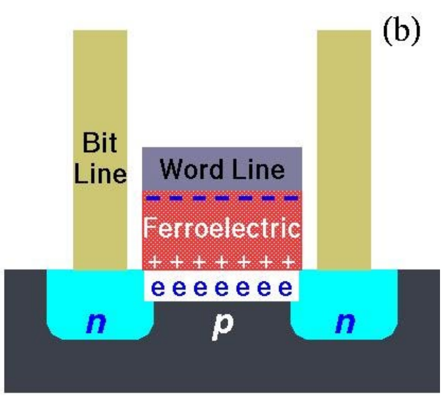
- Ferroelectric RAM (FeRAM, F-RAM or FRAM) is a random-access memory using a ferroelectric layer to achieve non-volatility.

- FRAM has two types:
  - 1T1C: Each storage element, a cell, consists of one capacitor and one transistor
  - 1T: Each storage element consists of one transistor only.

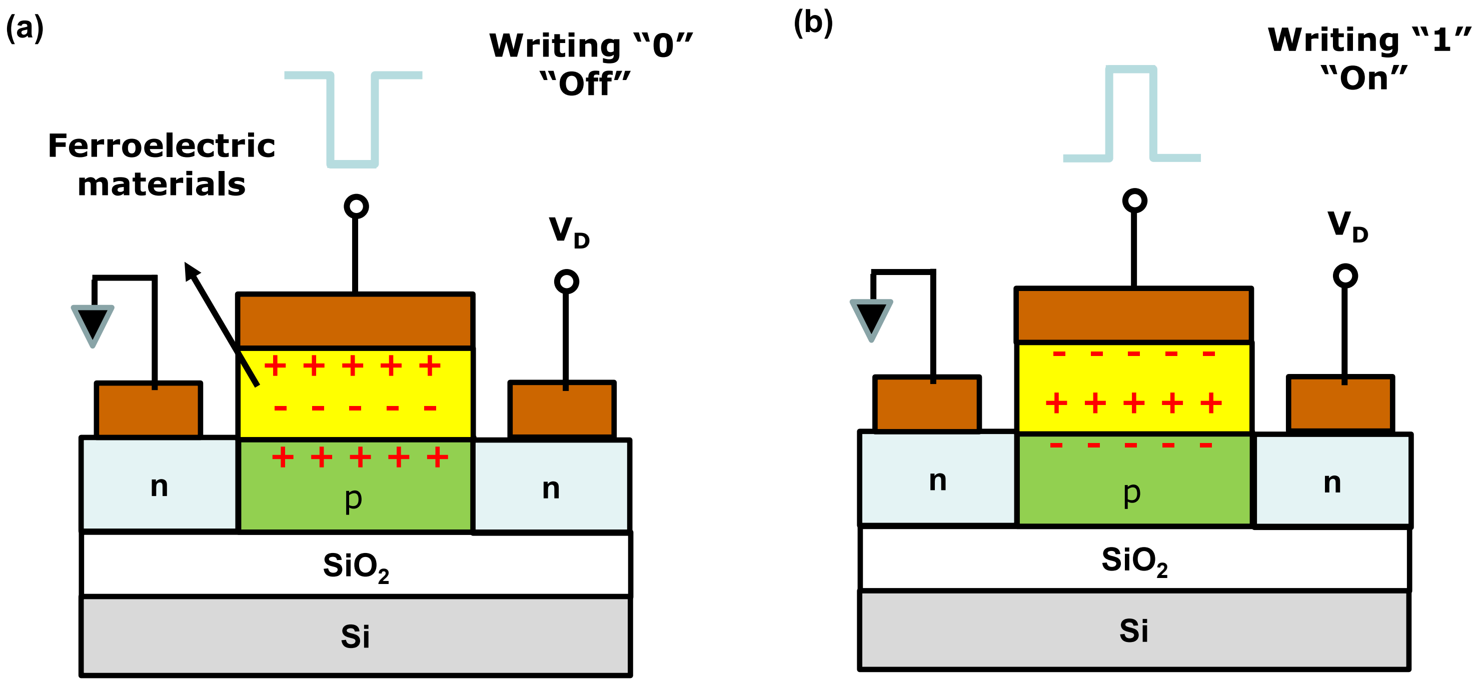
1T1C FRAM



1T FRAM



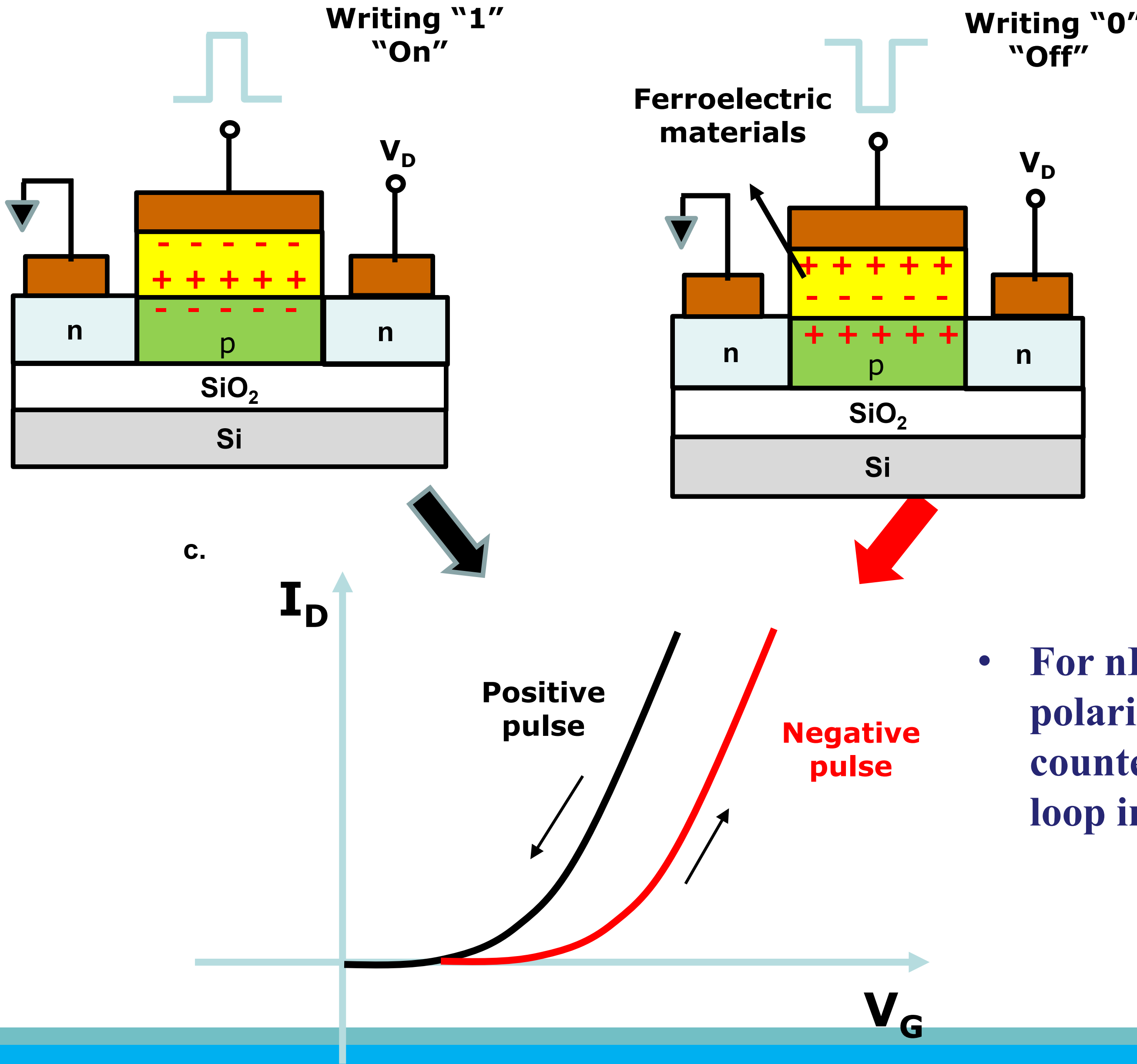
1T FRAM Operation



Operating principle of the 1T FRAM.

- **The application of a negative gate pulse induces a ferroelectric polarization that causes the transistor to be "off" with a zero gate voltage.**
- **The application of a positive gate pulse induces a ferroelectric polarization that causes the transistor to be "on" with a zero gate voltage.**
- **The read operation in 1T FRAM is non-destructive, so write-back is not needed.**

Effect of ferroelectricity on the hysteresis



- For nFET, ferroelectric polarization will result in counterclockwise hysteresis loop in the $I_d V_g$ characteristics.

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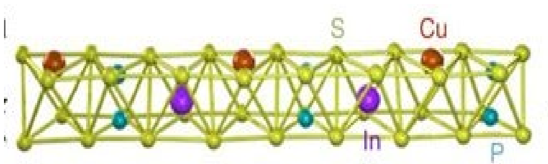
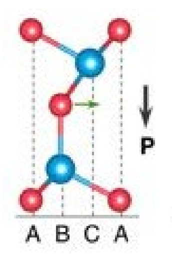
Van der Waals Ferroelectric Materials

Material	$CuInP_2S_6$	In_2Se_3	SnS	SnTe	WTe_2
Bandgap (bulk)	2.9 eV	1.36 eV	1.0–1.2 eV	0.18 eV	NA (Semimetal)
Polarization Direction	Out-of-plane	In-plane Out-of-plane	In-plane	In-plane	Out-of-plane
T_C (bulk)	315 K	>473 K	800 K	98 K	≥300K
Thickness Scaling	4 nm	Monolayer	Monolayer	Monolayer	Bilayer

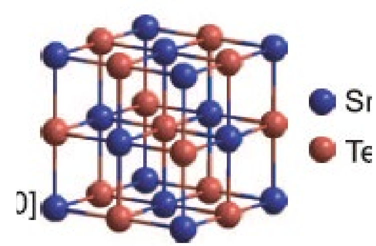
- **VdW materials have excellent scalability (down to 1 unit-cell thickness).**
- **VdW ferroelectrics can be grown or transferred on any substrate, offering high fabrication flexibility**



$CuInP_2S_6$

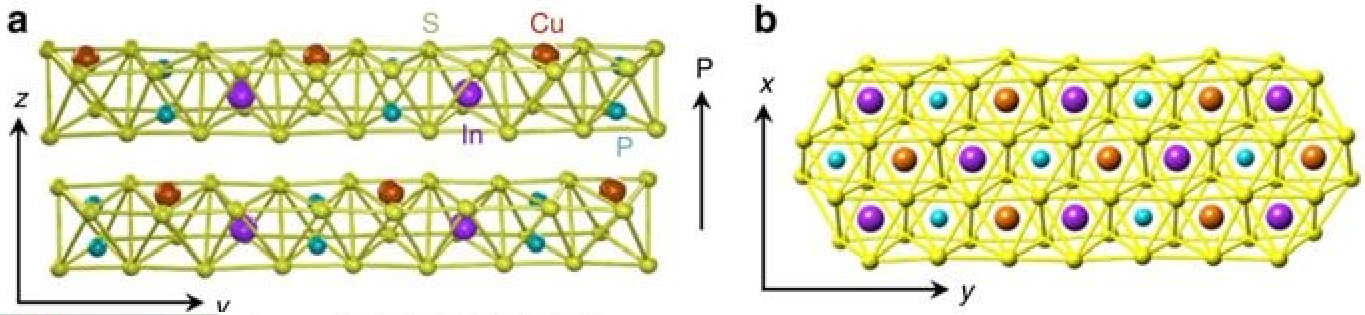


In_2Se_3



SnTe

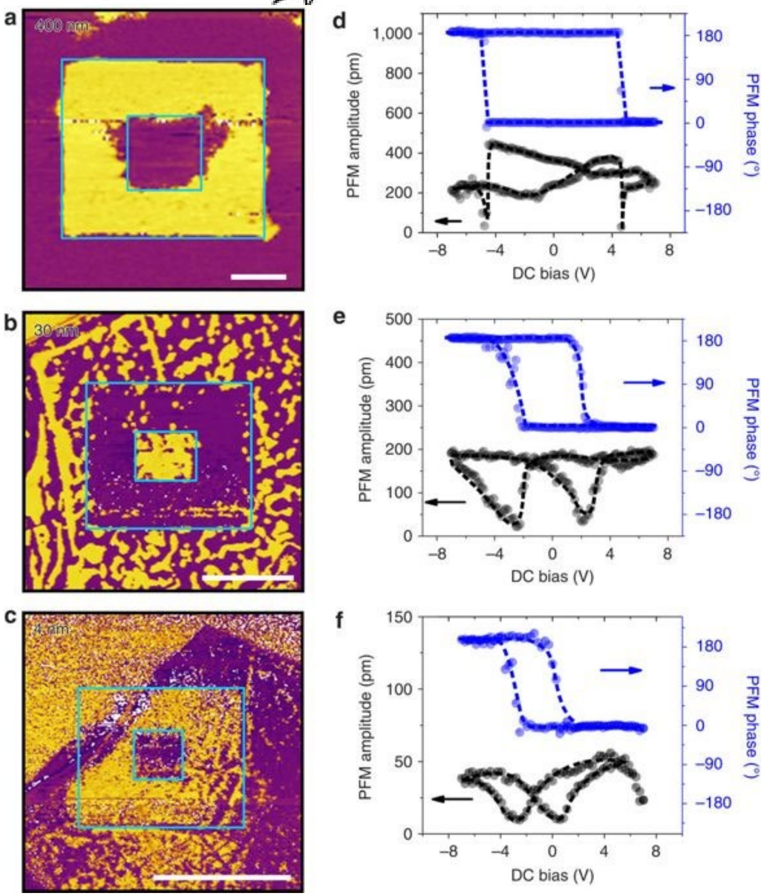
Polarization switching in $CuInP_2S_6$



400nm

30nm

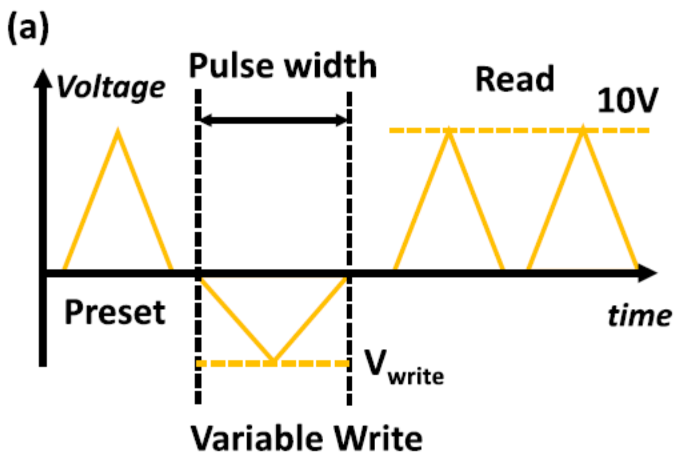
4nm

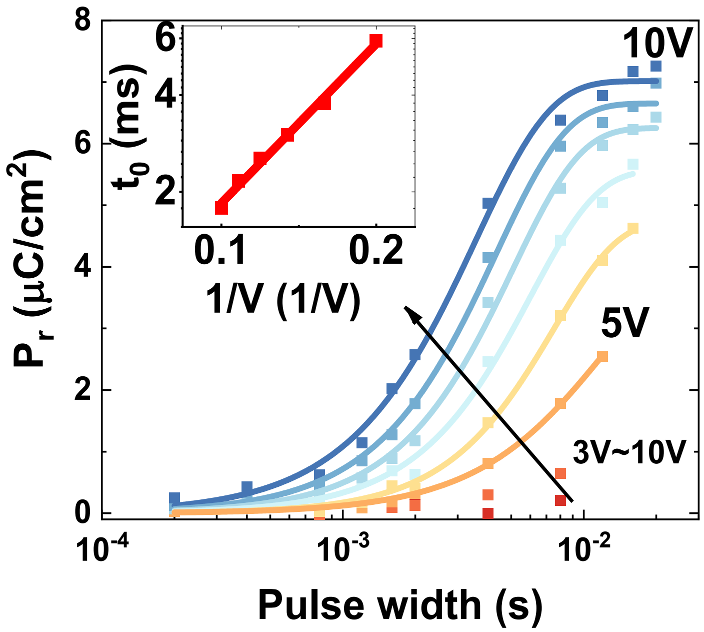


- **The atomic structure of copper indium thiophosphate $CuInP_2S_6$ (CIPS) contains of a sulfur framework with the octahedral voids filled by the Cu, In and P–P triangular patterns.**
- **Switchable polarization is observed in thin CIPS of ~4 nm.**

F. Liu, et.al., Nature Communications, 7, 12357, 2016

CIPS Switching Speed





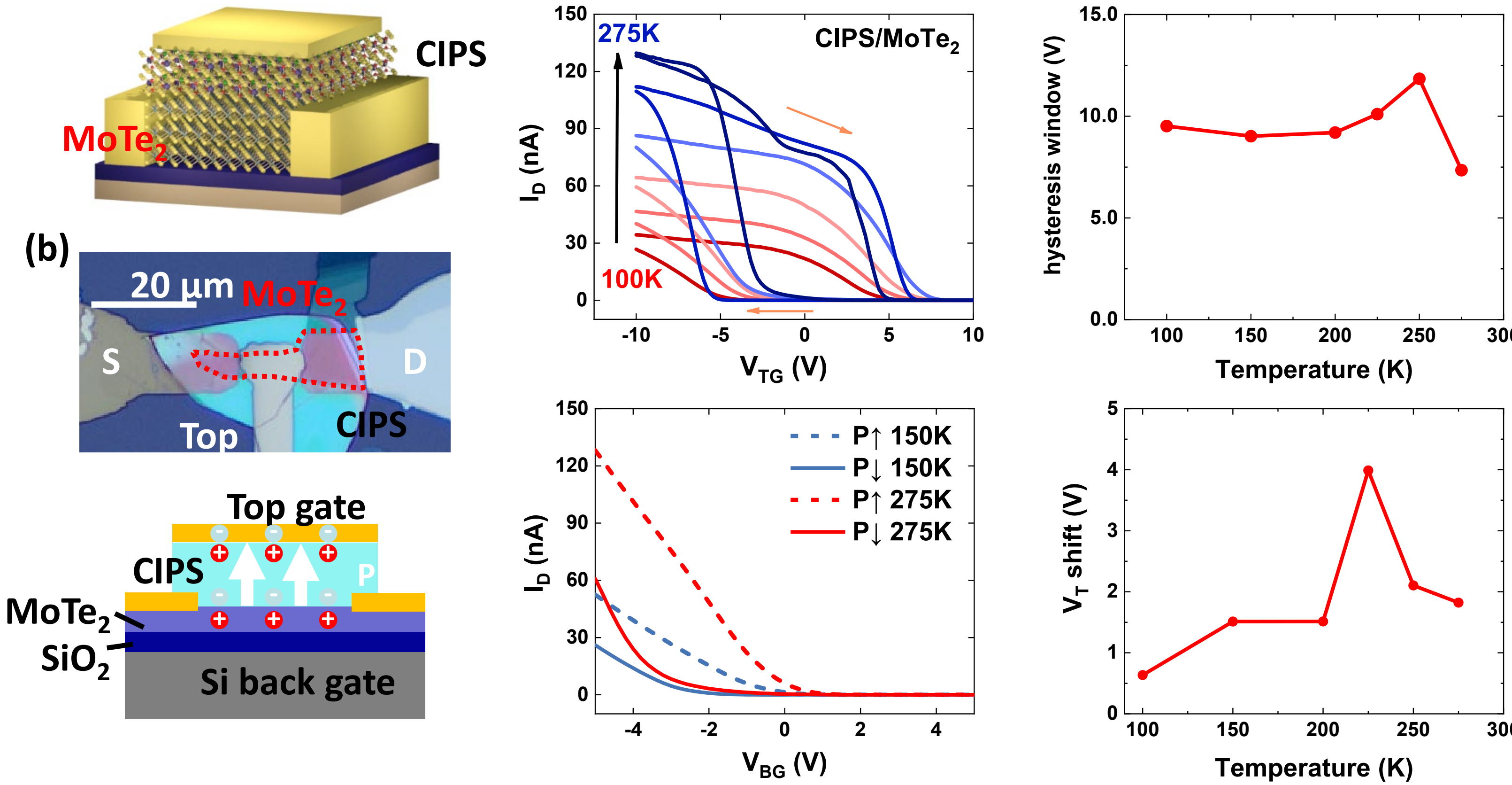
Nucleation-limited-switching (NLS) model: $p(t) = 1 - e^{-(t/t_0)^n}$

Merz's Law: $\tau = \tau_0 e^{(V_0/V)^n}$, $\tau_0 = 0.59\ ms$

The switching time in CIPS is several orders of magnitude longer than that in traditional ferroelectric such as doped HfO_2, indicating that the polarization switching in CIPS is very slow.

Z. Zhao, W. Zhu, ACS Appl. Mater. Interfaces, (2020)

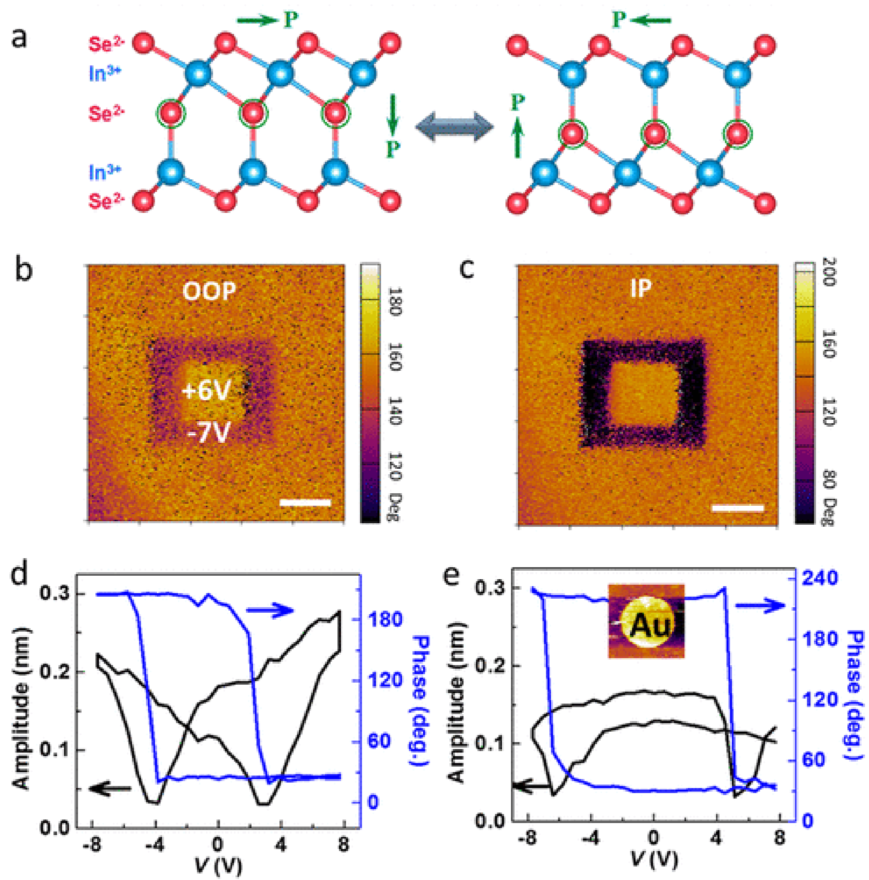
CIPS/$MoTe_2$ Memory



- **For CIPS/$MoTe_2$ dual-gate transistor, temperature-dependent non-volatile memory window is observed, which can be attributed to the interplay between ferroelectric polarization and interface traps**

Z. Zhao, W. Zhu, ACS Appl. Mater. Interfaces, (2020)

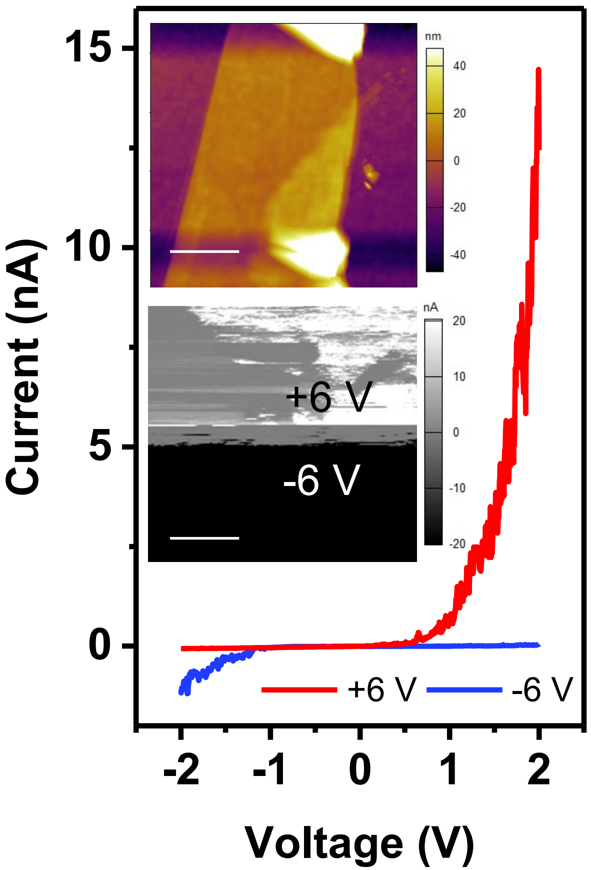
Out-of-plane and in-plane polarization in In_2Se_3

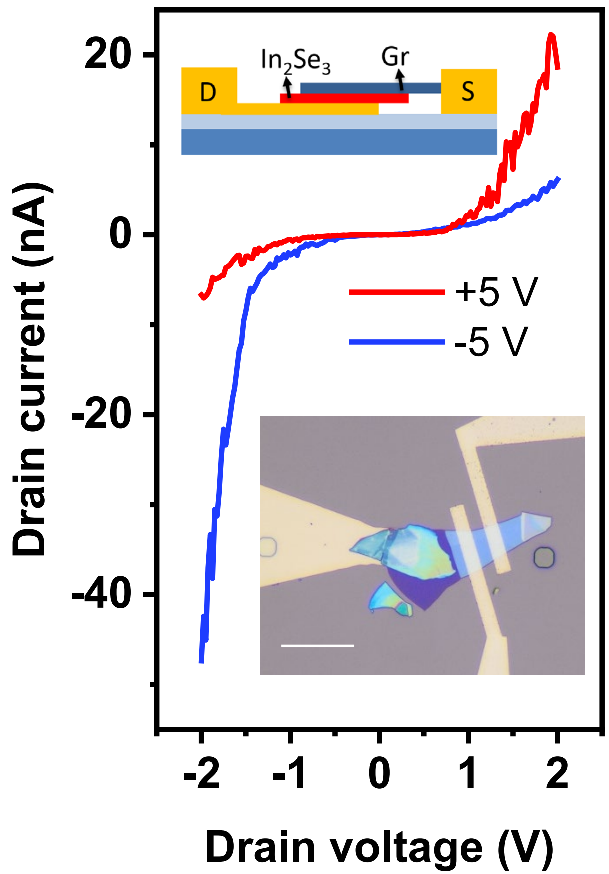


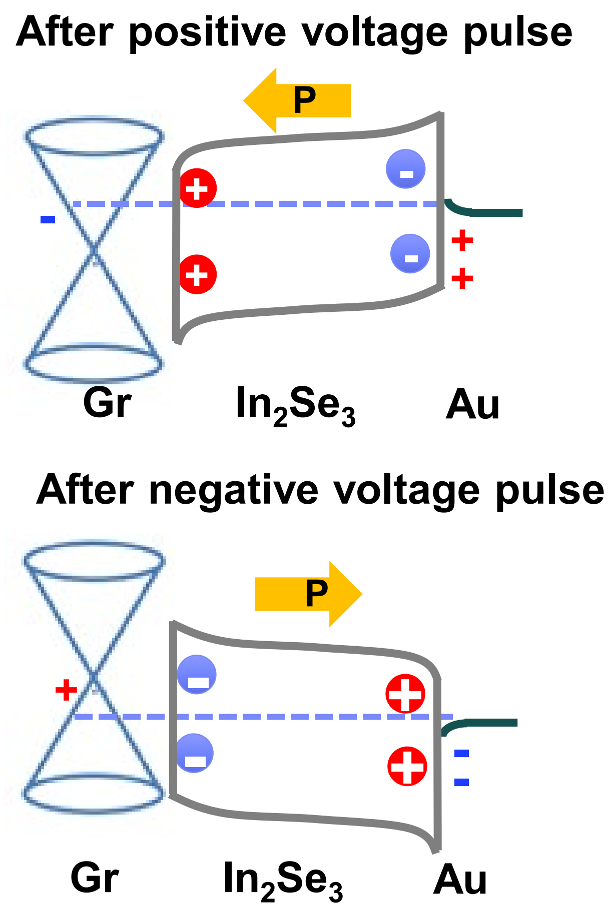
- **The reversal of the out-of-plane polarization by a vertical electric field also induces the rotation of the in-plane polarization.**

Chaojie Cui, Lain-Jong Li, Nano Letter, 18, pp 1253, 2018

Reversible Schottky diodes



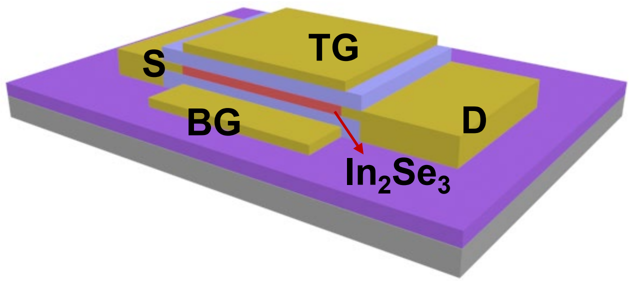


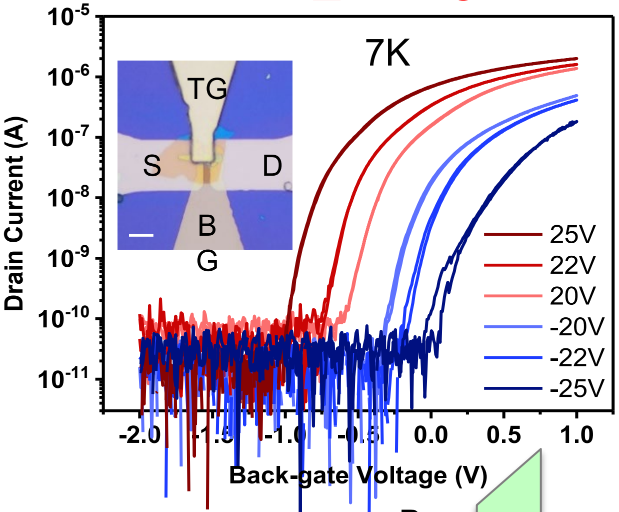


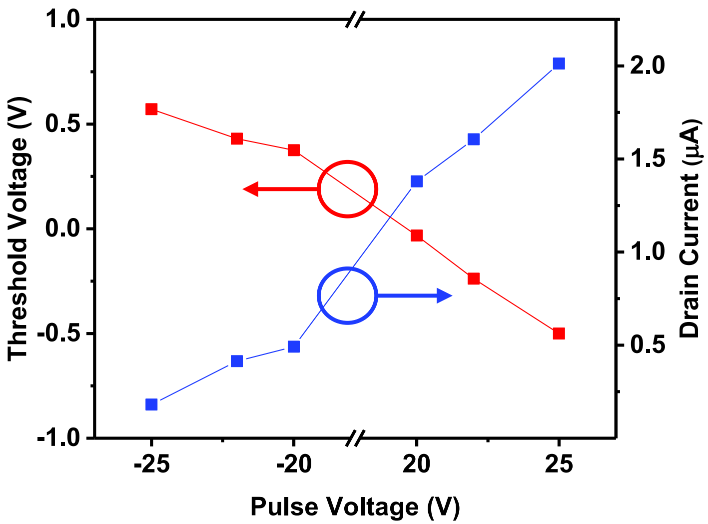
- **In_2Se_3 has a bandgap of 1.36 eV, i.e. is semiconductor.**
- **In_2Se_3 can be used to built reversible Schottky diodes. The out-of-plane polarization in In_2Se_3 can affect the Schottky barrier height and switch the diode polarity.**

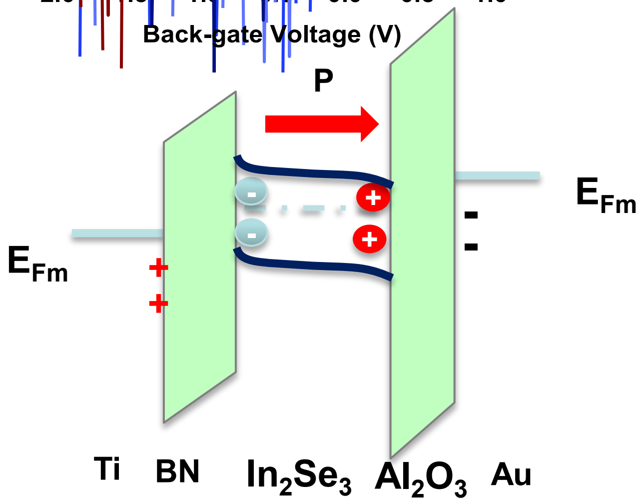
X. Kai and W. Zhu et.al., Nanoscale, 12, 23488, (2020)

Memory based on In_2Se_3





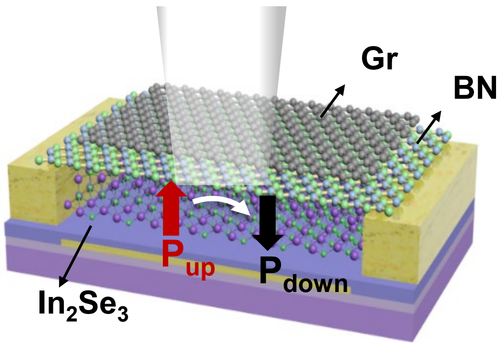


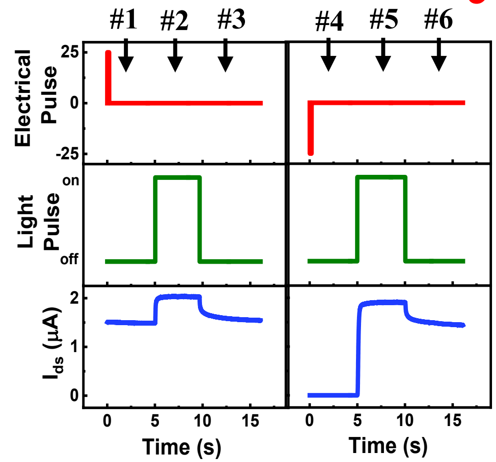


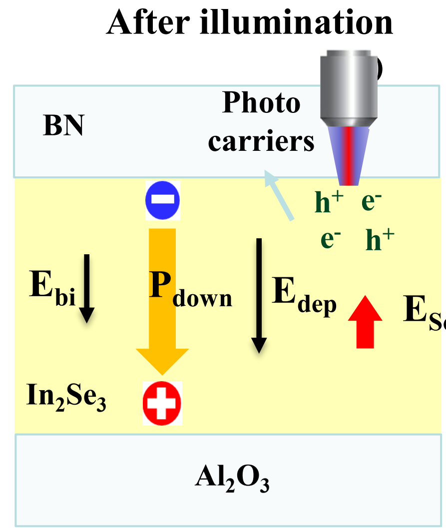
- The polarization in In_2Se_3 can be effectively switched by vertical electric field in double-gate structure.
- The threshold voltage of the transistor can by tuned by the polarization in In_2Se_3 channel. This can be explained by the polarization dependence of electron affinity in In_2Se_3.

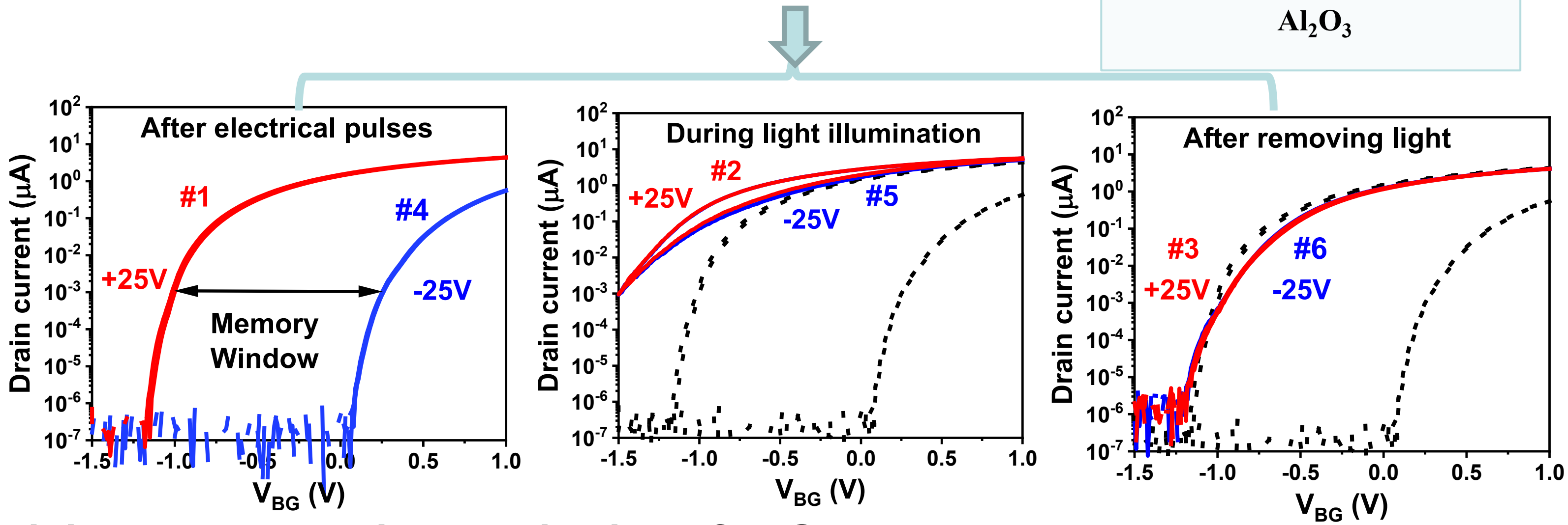
K. Xu, W. Zhu, Nanoscale 2020

Optical erasable memory based on In_2Se_3





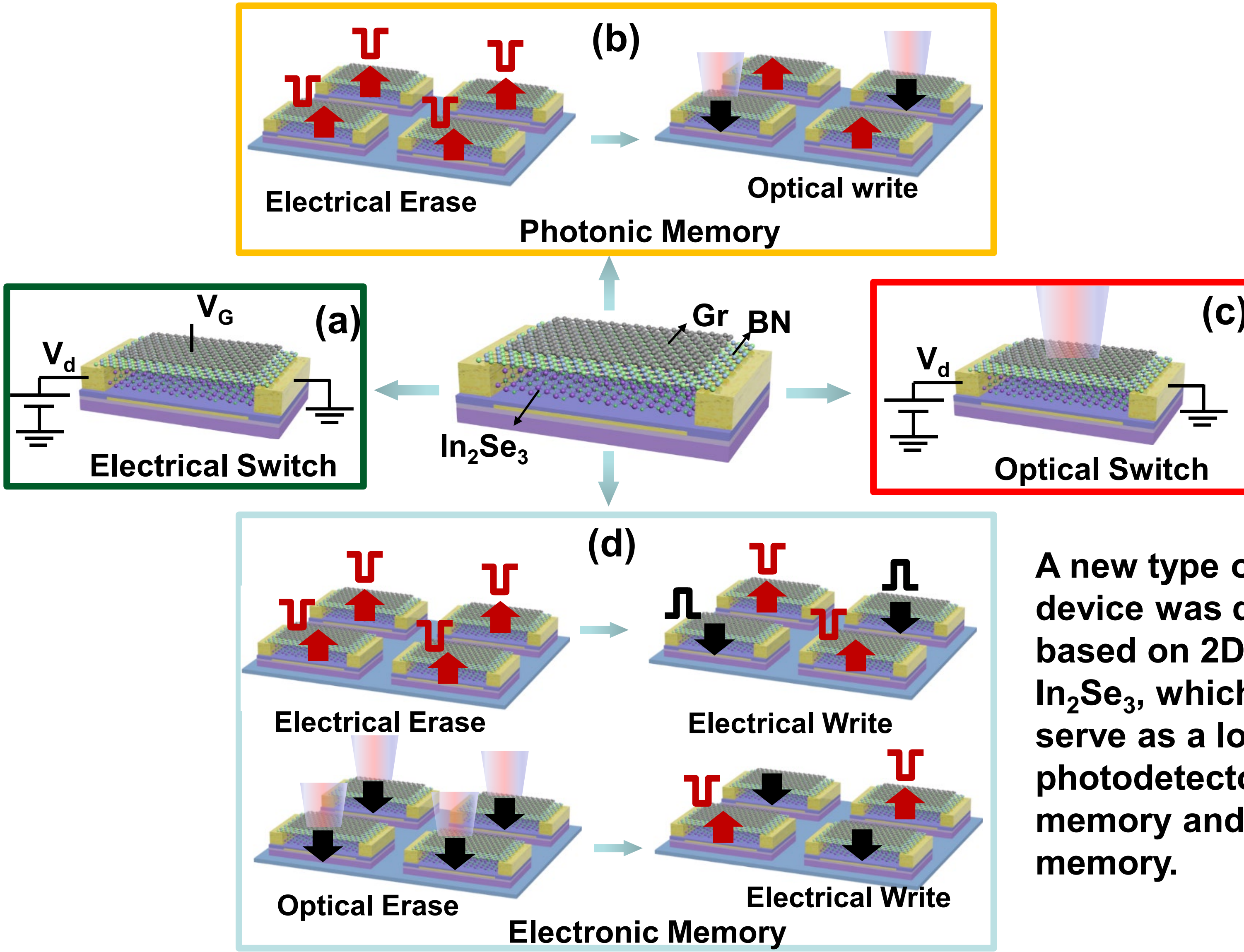




- Light can reverse the polarization of In_2Se_3
- Multifunctional devices based on In_2Se_3 can detect light, storage the information non-volatilly, and process these optical signals concurrently.

K. Xu, W. Zhu, Nanoscale 2020

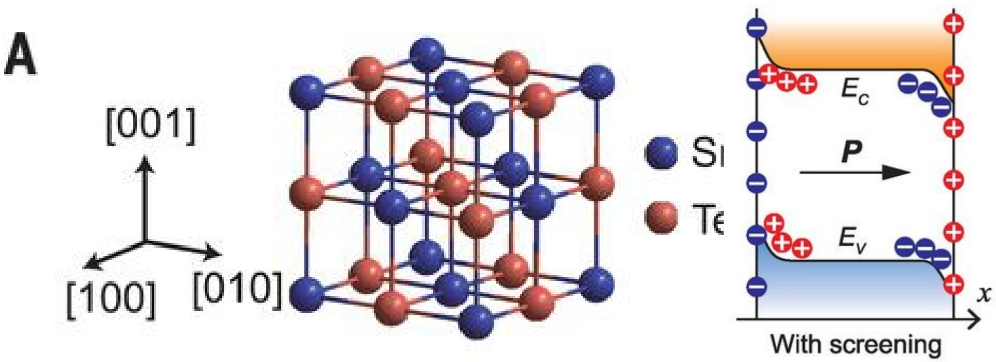
Multifunctional device based on 2D ferroelectric In_2Se_3

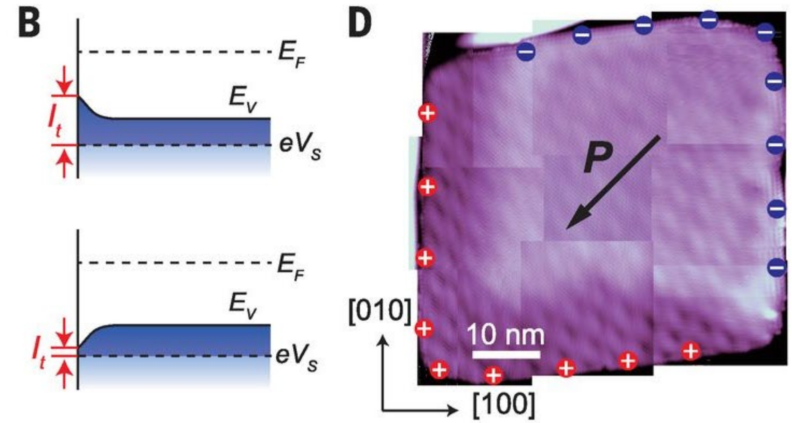


A new type of multifunctional device was demonstrated based on 2D ferroelectric In_2Se_3, which can concurrently serve as a logic gate, photodetector, electronic memory and photonic memory.

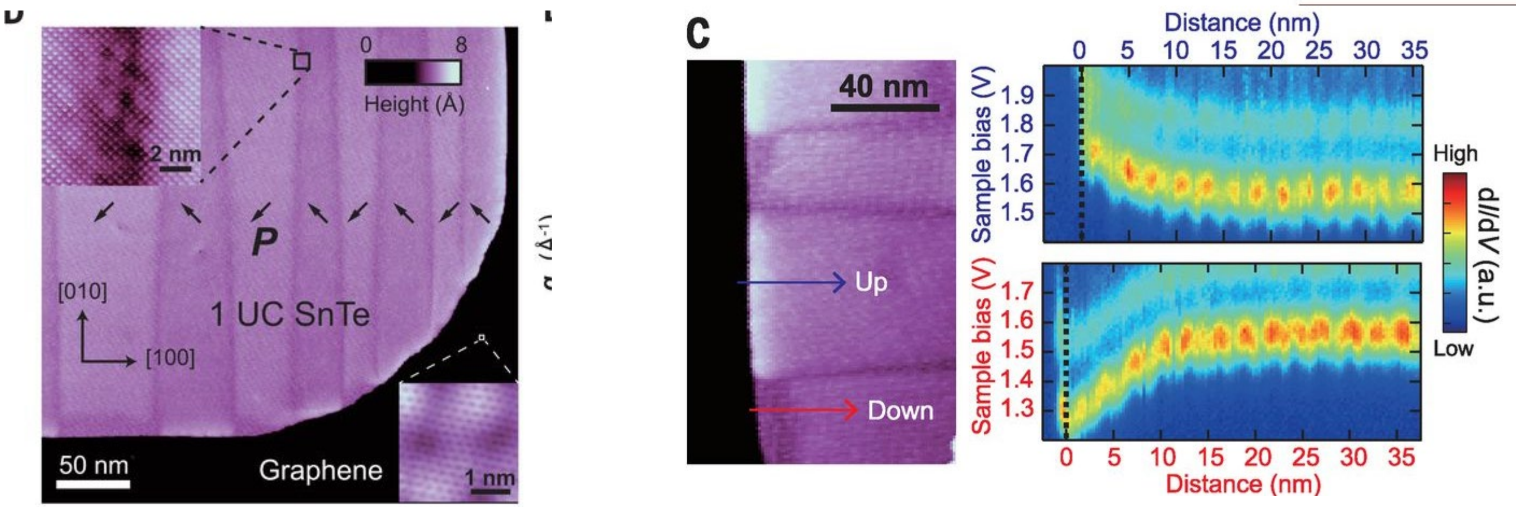
K. Xu, W. Zhu, Nanoscale 2020

In-plane ferroelectricity in SnTe





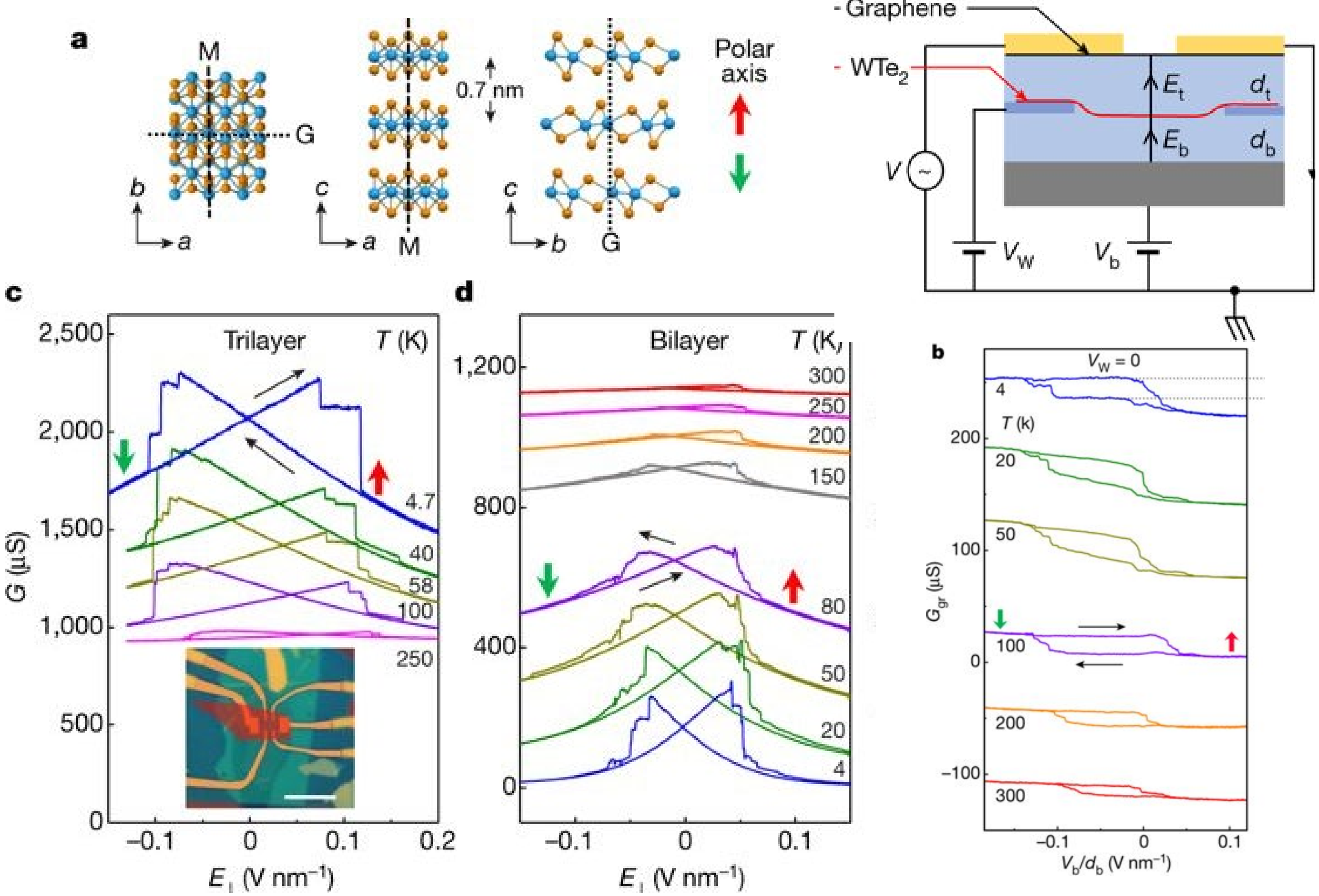
K. Chang, Science, Vol 353, 274, 2016



Bandgap 0.18 eV (bulk)

- **Stable in-plane spontaneous polarization was observed in telluride (SnTe), down to 1–unit cell limit.**
- **In-plane polarization and carrier screening results in band-bending at edge of a domain. The band bending in SnTe was observed in the STM measurement.**

Polar metal WTe_2



Two- or three-layer WTe_2 exhibits spontaneous out-of-plane electric polarization that can be switched using gate electrodes. Directly detection and quantification of the polarization were achieved using graphene as an electric-field sensor.

Zaiyao Fei, David H. Cobden, Nature, Vol. 560, p.336 (2018)

Outline

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- 2D ferroelectric materials
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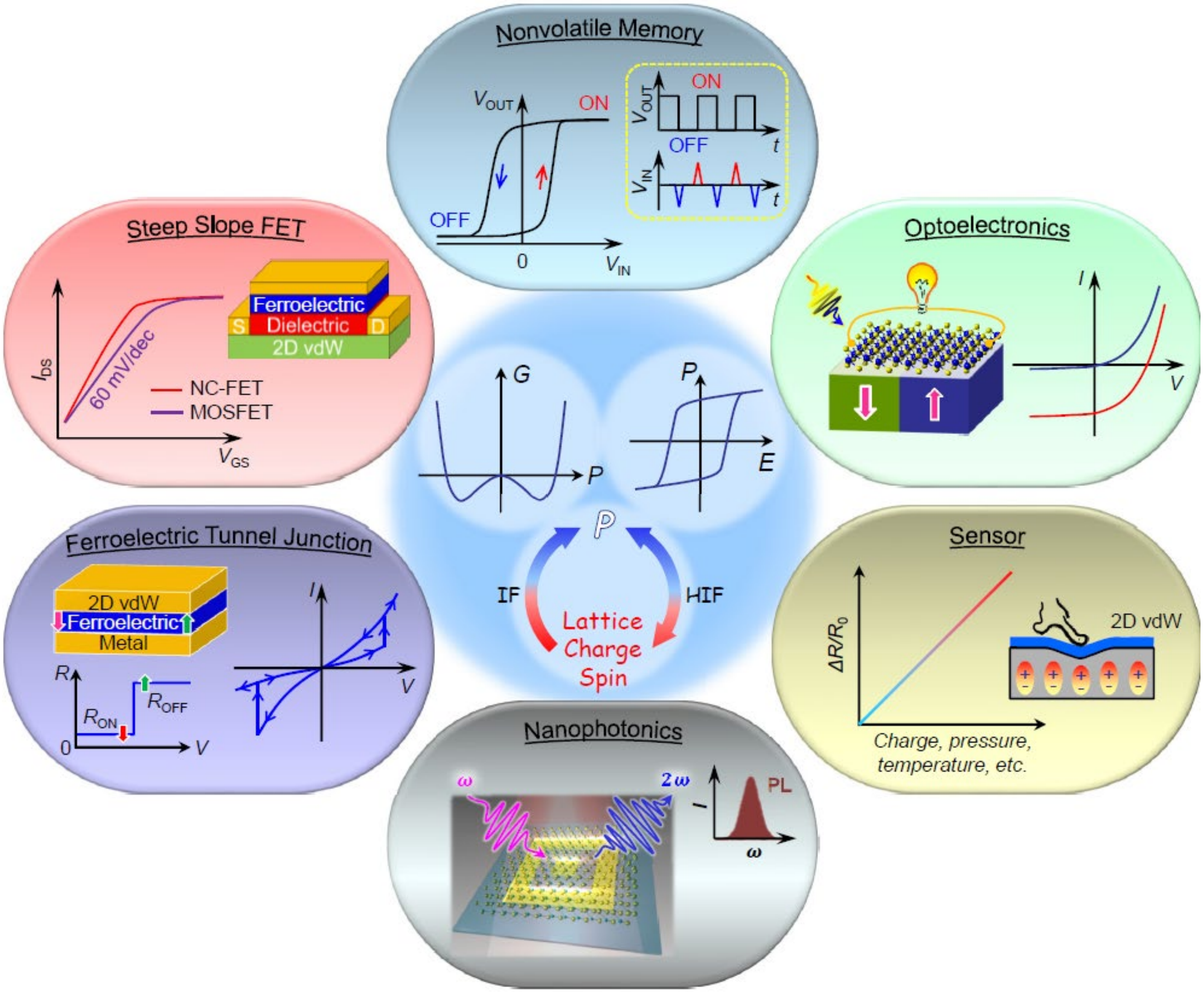
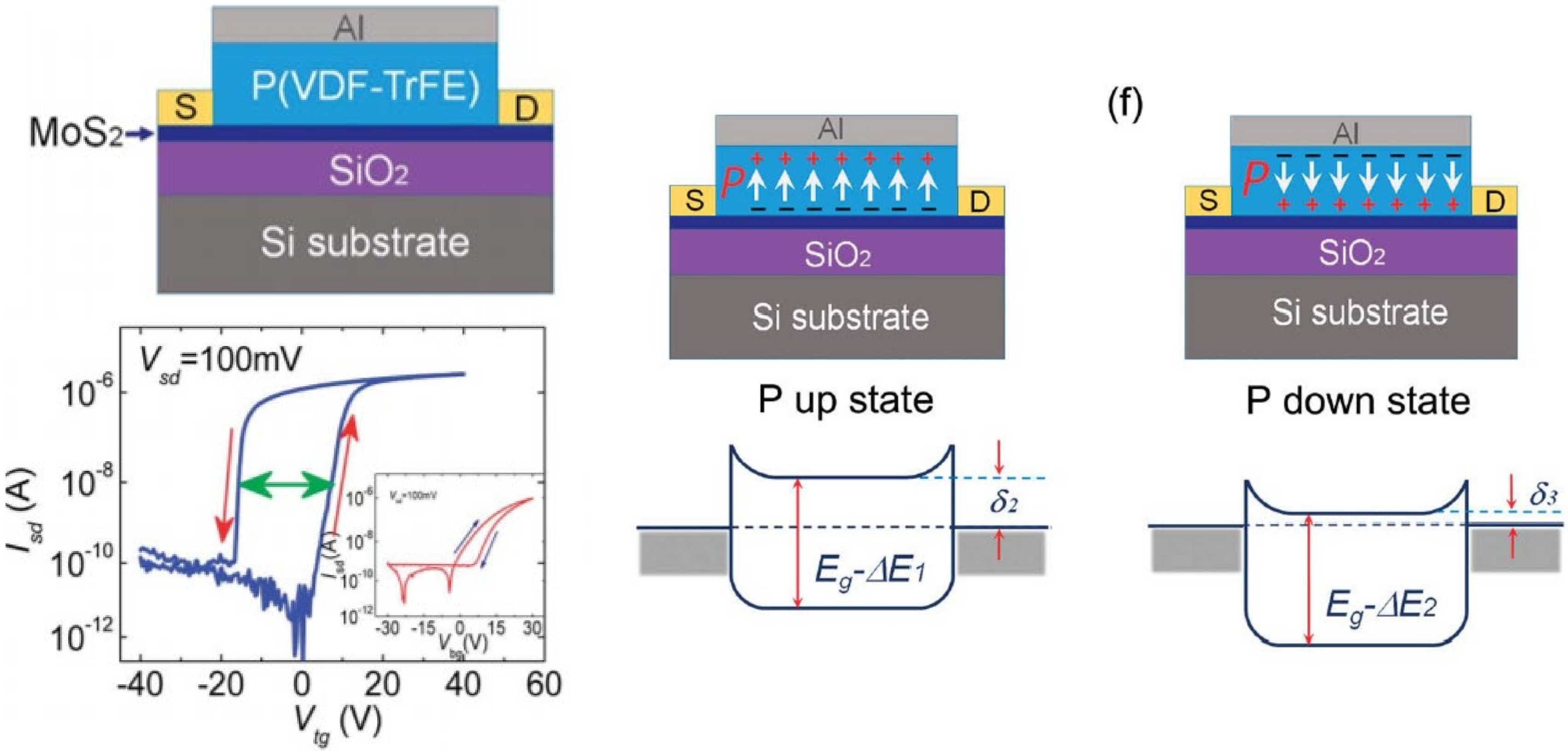
Devices based on 2D/Ferroelectric Stacks



H. Ryu, H. Xia, W. Zhu, Topical Review, Appl. Phys. Lett. 117, 080503 (2020)

2D/Ferroelectric Memory (1)

-- Electrical writing and electrical reading

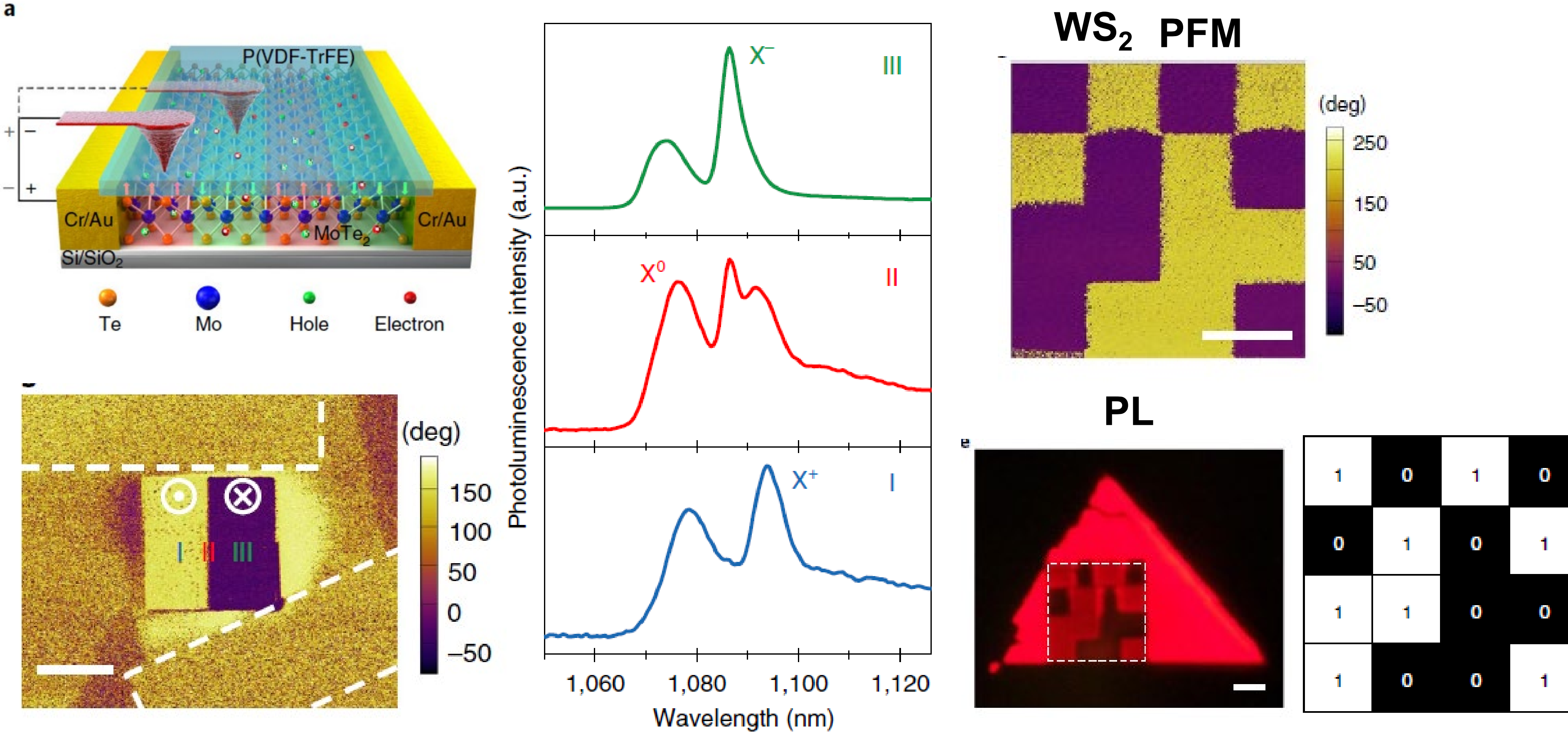


- **In 2D ferroelectric transistor, switching the polarization direction in ferroelectric materials can lead to bi-stable conduction states in the 2D channel, which serves as a nonvolatile memory.**

X. Wang, Advanced Materials 27, 6575 (2015),

2D/Ferroelectric Memory (2)

-- Electrical writing and optical reading

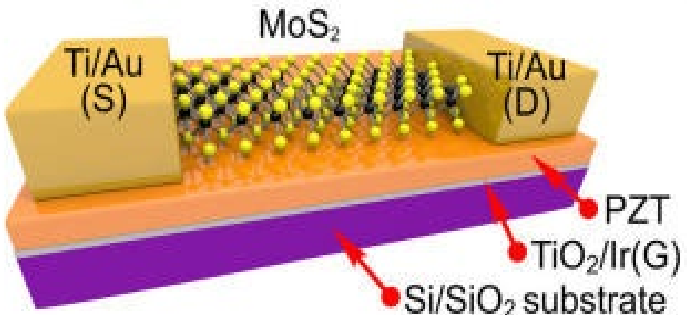


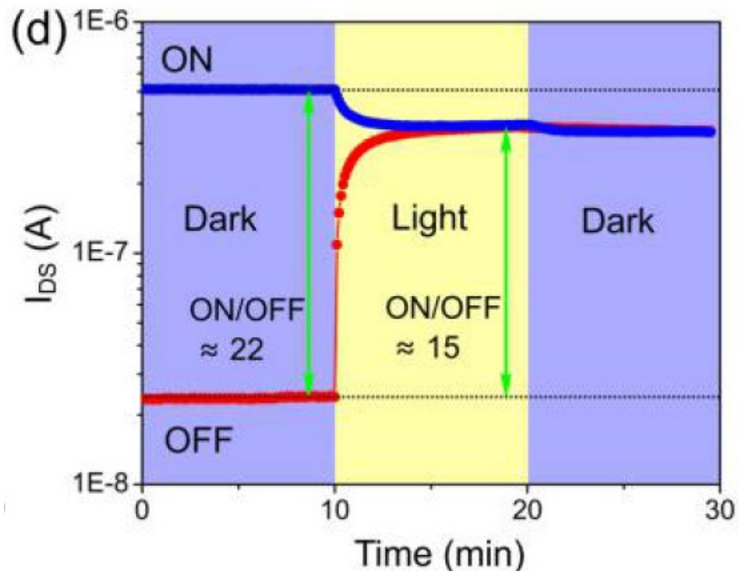
- **Polarization in ferroelectric induces positive and negative charged trions in 2D which has different binding energies, i.e. PL peak positions. Local patterning of the ferroelectric domain leads to high density optical memory.**

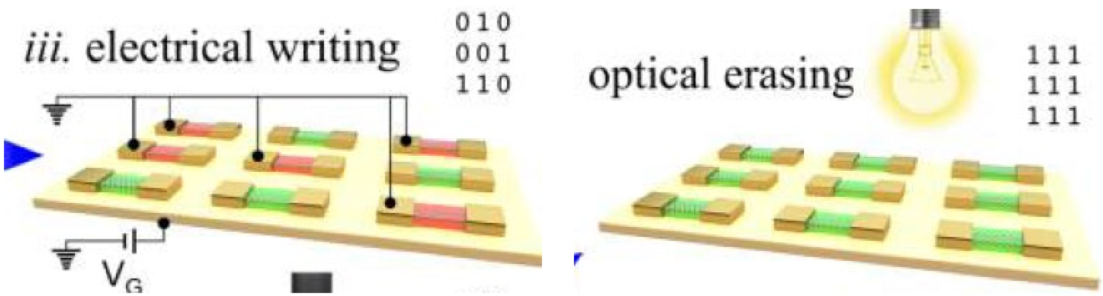
G. Wu, et al. Nature Electronics, 3, 43, 2020

2D/Ferroelectric Memory (3)

-- Electrical writing and optical erasing memory



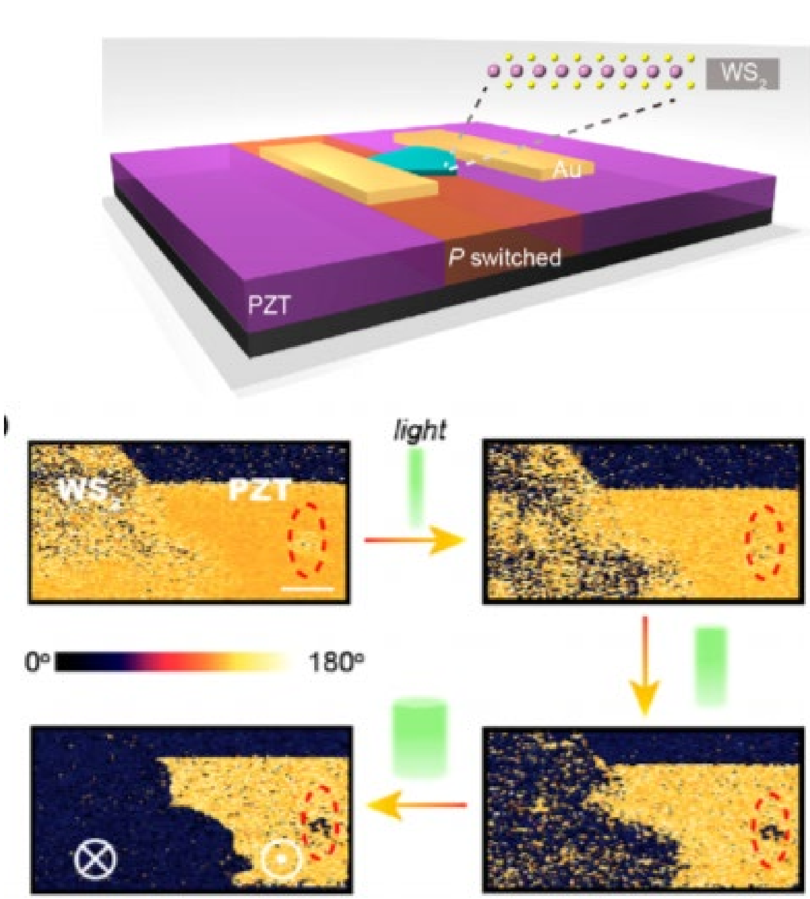


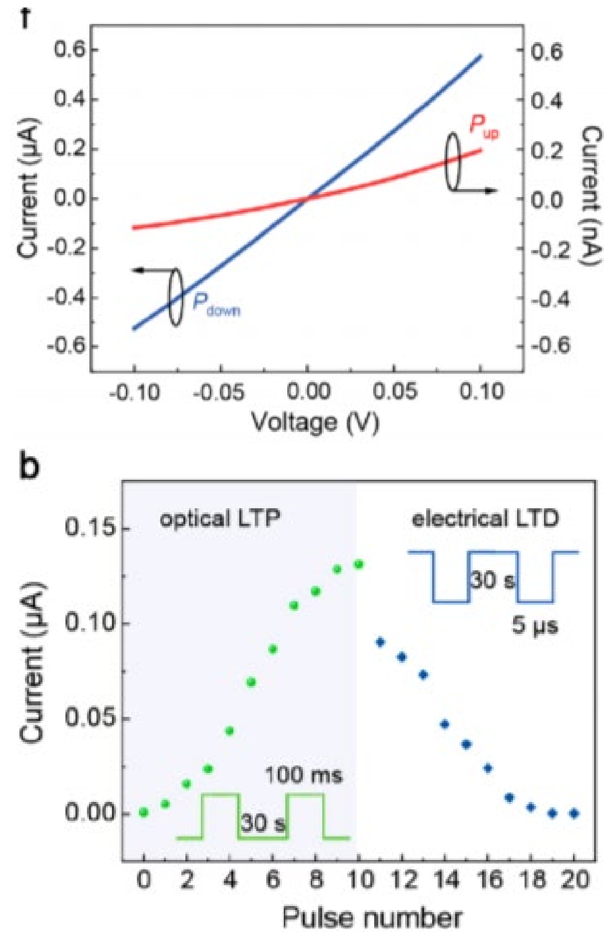


- **MoS_2/PZT ferroelectric memory can be written and erased both electrically and optically.**

Alexey Lipatov, Alexander Sinitskii, et.al., ACS Nano, 9, 8089, 2015

Memristive transistor for neuromorphic computing

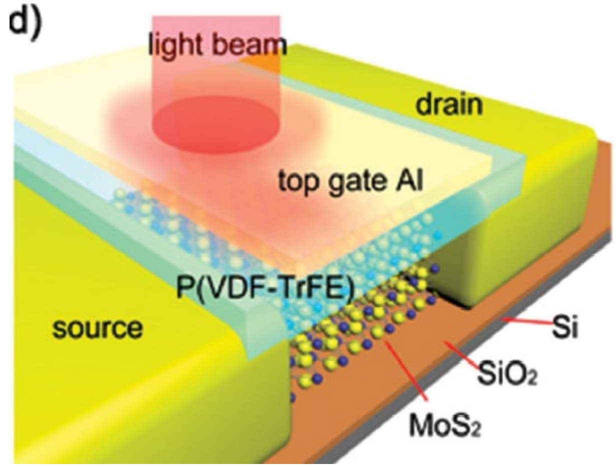


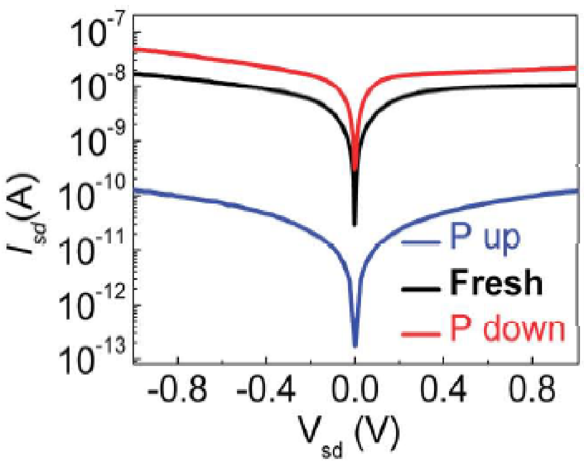


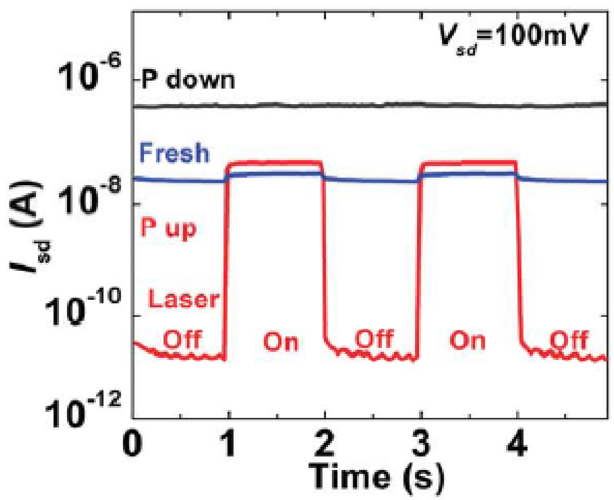
WS_2 channel exhibits voltage- and light-controllable memristive switching, dependent on the optically and electrically tunable ferroelectric domain patterns in the underlying PZT layer. These devices emulate the synaptic functionalities.

Z. Luo, et al. ACS Nano **14**, 746 (2020)

Optoelectronic devices based on 2D/ferroelectrics



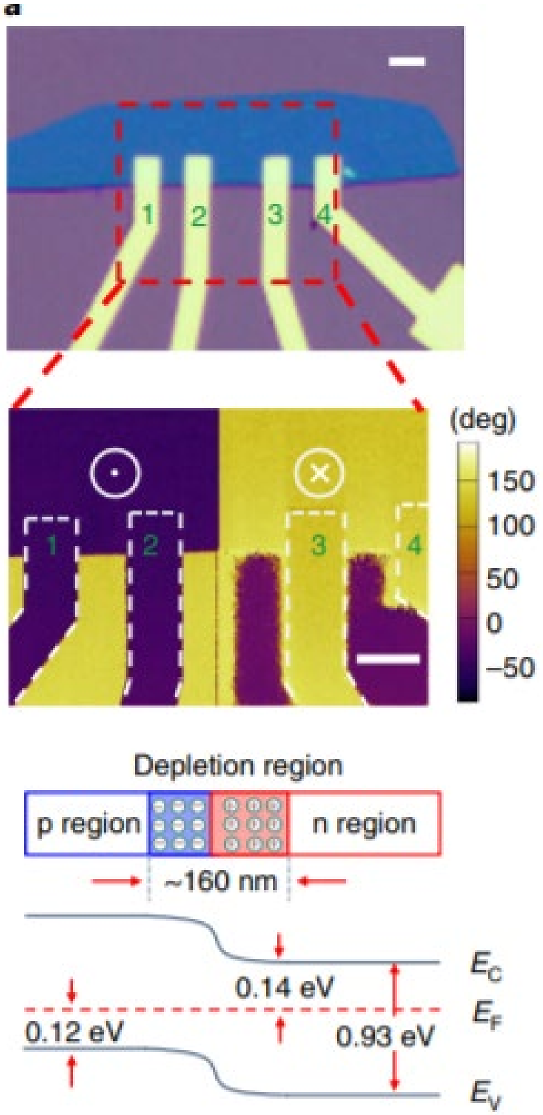




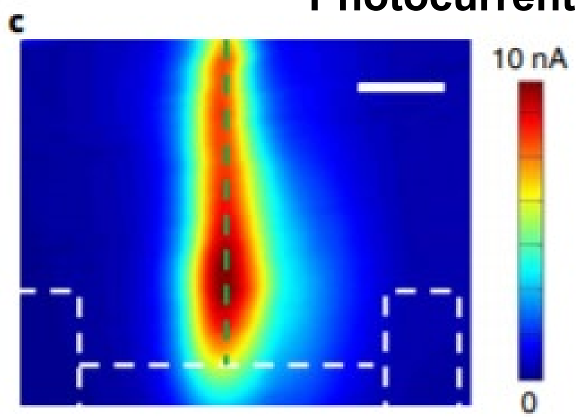
- **The remnant polarization of P(VDF-TrFE) is employed to depress the dark current of the MoS_2 semiconducting channel**

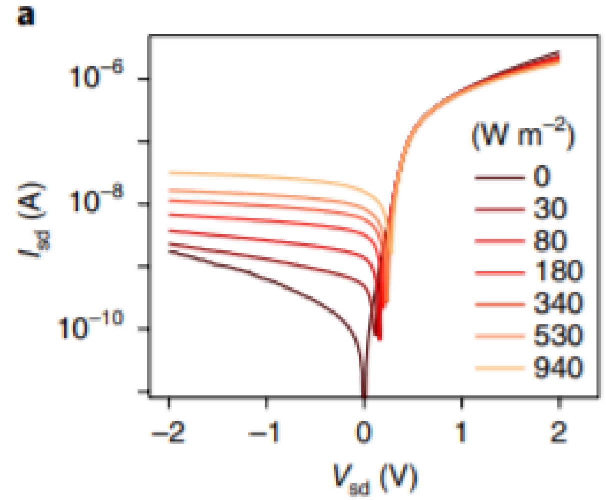
X. Wang, Advanced Materials 27, 6575 (2015)

Optoelectronic devices based on 2D/ferroelectrics



Photocurrent

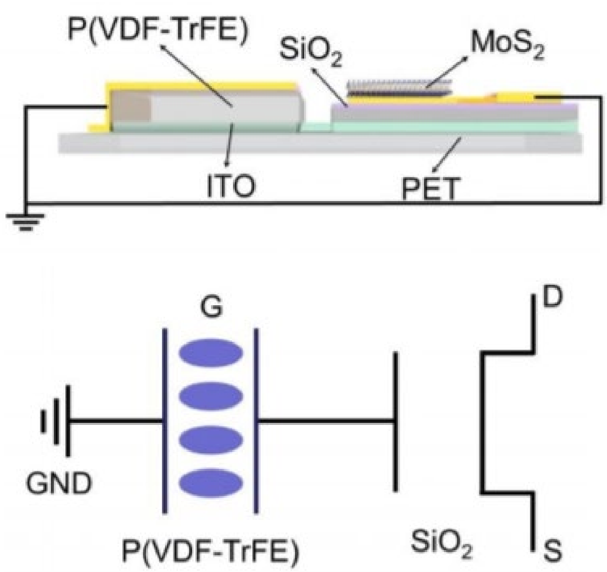


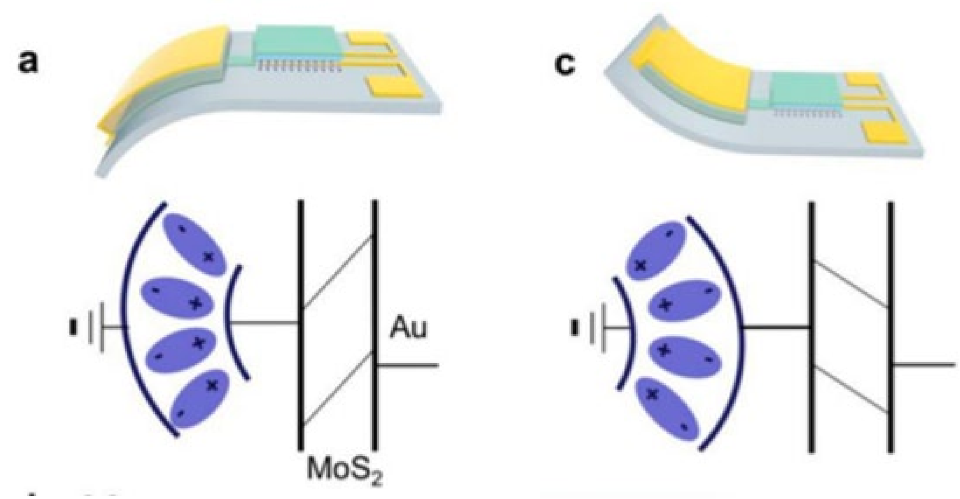


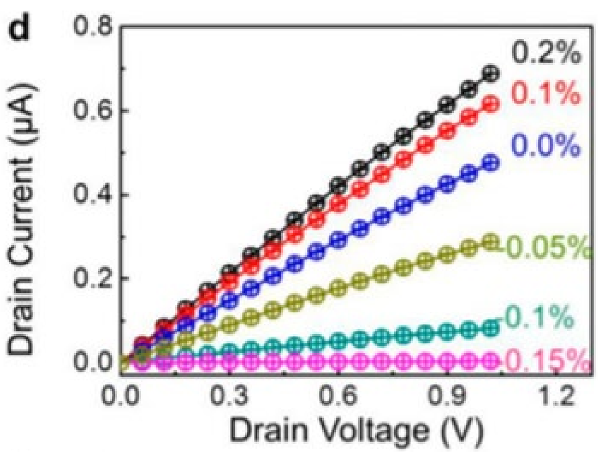
- **The local polarization of ferroelectric polymers induces lateral p–n homojunctions in $MoTe_2$, which exhibit high current rectification ratios of 10^3 and high responsivity of 1.5 A W^{-1}.**

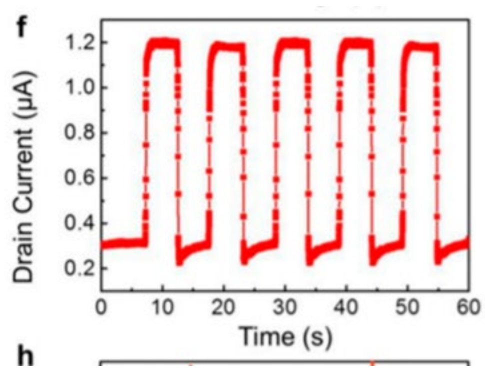
G. Wu, et al. Nature Electronics, 3, 43, 2020

Sensors based on 2D/Ferroelectrics







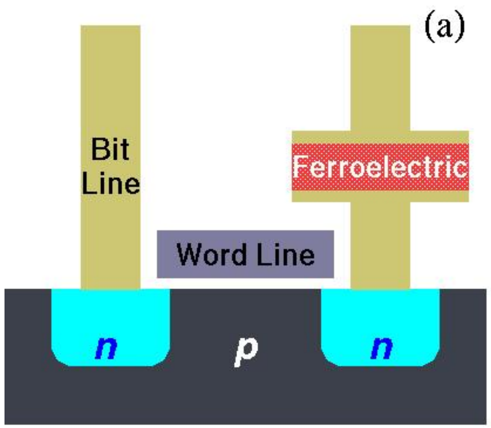


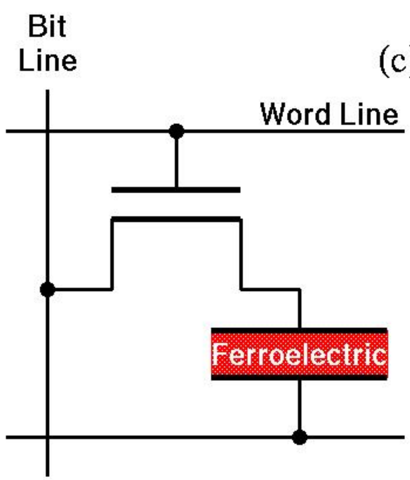
The external strain can induce piezo-potentials and affect the energy band bending of MoS_2 channel, which enables strain sensors.

J. Zhao, et al. ACS Nano,13, 1, 582, 2019

FRAM types

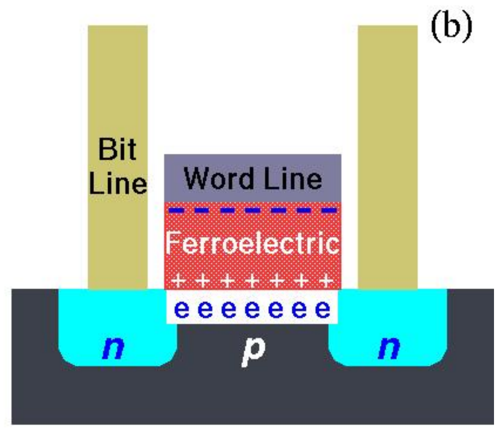
1T1C FRAM

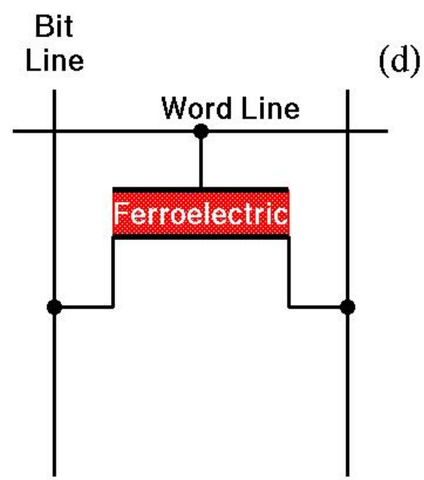




1T1C type

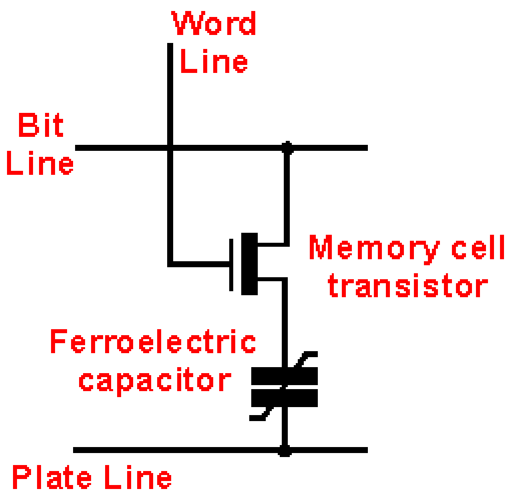
1T FRAM





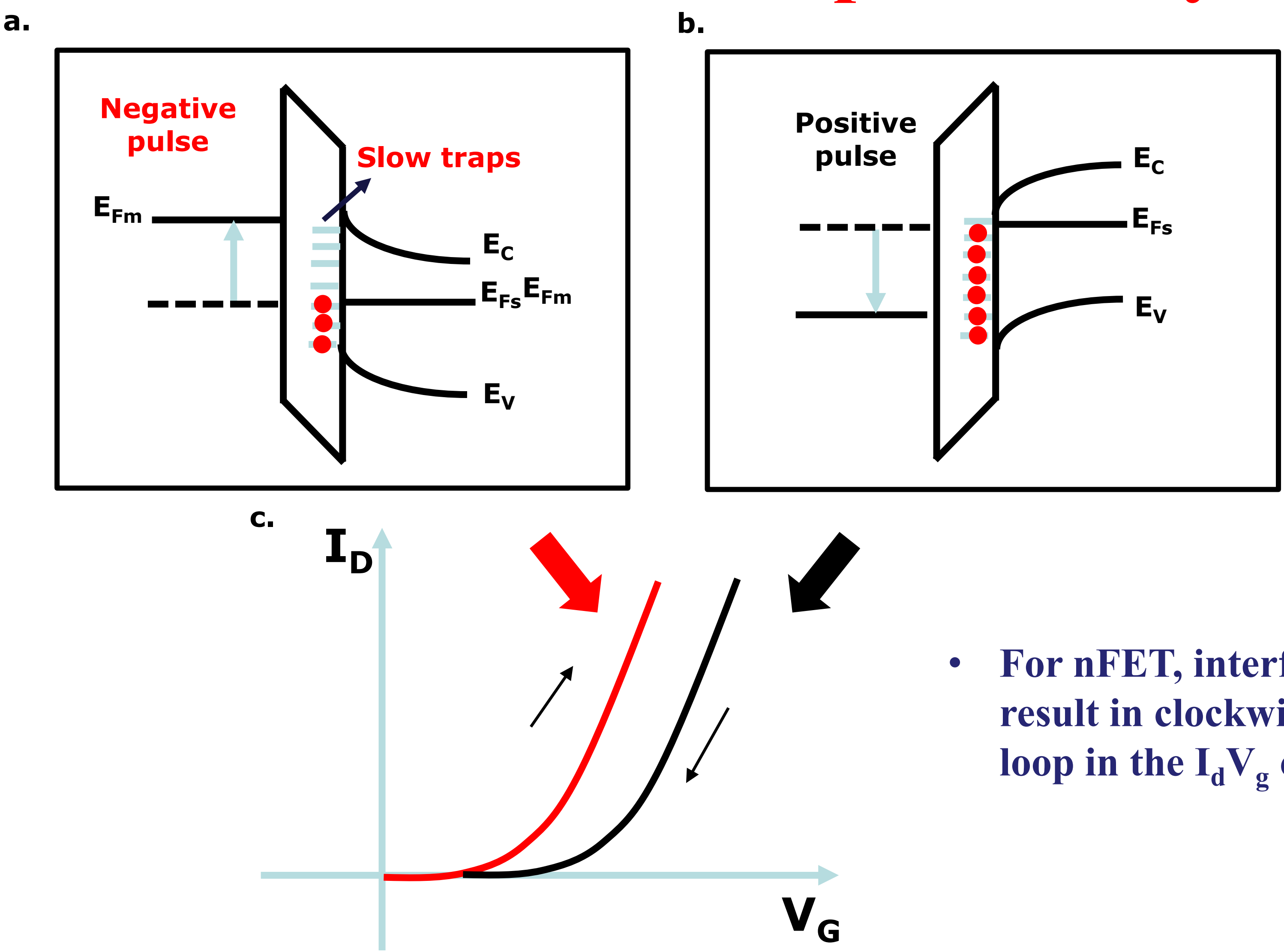
1T type

1T1C FRAM Operation



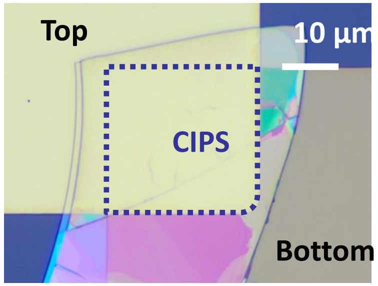
- Writing is accomplished by applying a field across the ferroelectric layer by charging the plates on either side of it, forcing the atoms inside into the "up" or "down" orientation thereby storing a "1" or "0".
- Reading: The transistor forces the cell into a particular state, say "0". If the cell already held a "0", nothing will happen in the output lines. If the cell held a "1", the re-orientation of the atoms in the film will cause a brief pulse of current in the output. The presence of this pulse means the cell held a "1".
- Since this read process overwrites the cell, reading FeRAM is a destructive process, and requires the cell to be re-written if it was changed.

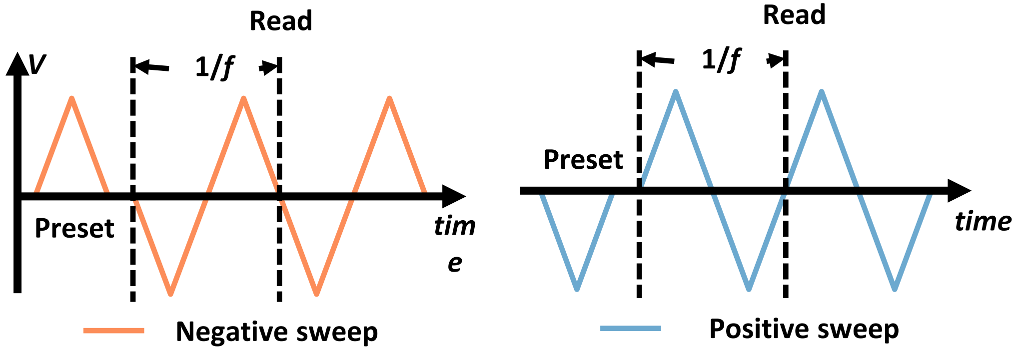
Effect of interface trap on the hysteresis

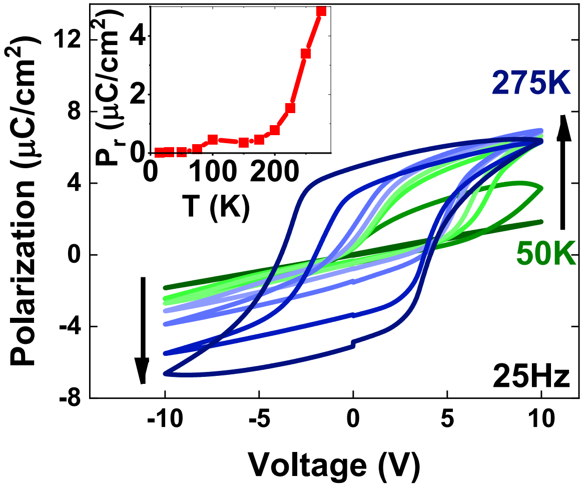


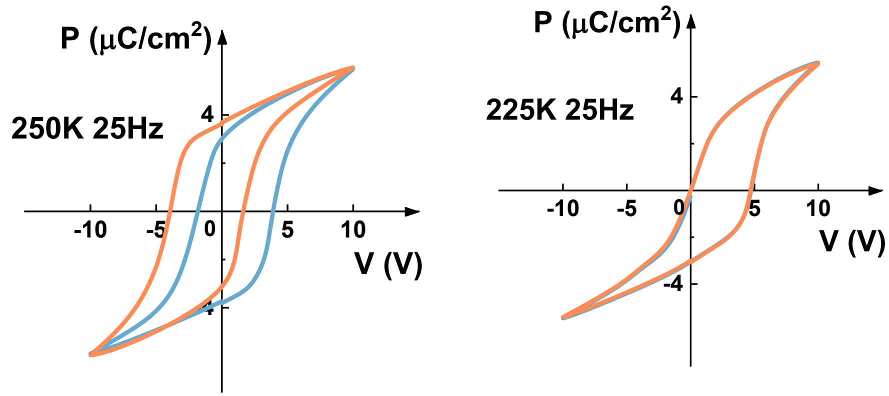
- **For nFET, interface trap will result in clockwise hysteresis loop in the I_dV_g characteristics.**

Strong Temperature Dependence of Ferroelectricity in $CuInP_2S_6$









- There is a large imprint in the CIPS capacitor, which can be attributed to the fixed dipoles induced by defects.
- At high temperatures, the amplitude and direction of the imprint become tunable by the preset pulse, as the copper ions are more mobile and these dipoles become switchable.

Z. Zhao, W. Zhu, ACS Appl. Mater. Interfaces, (2020)