van der Waals layered magnetic semiconductors

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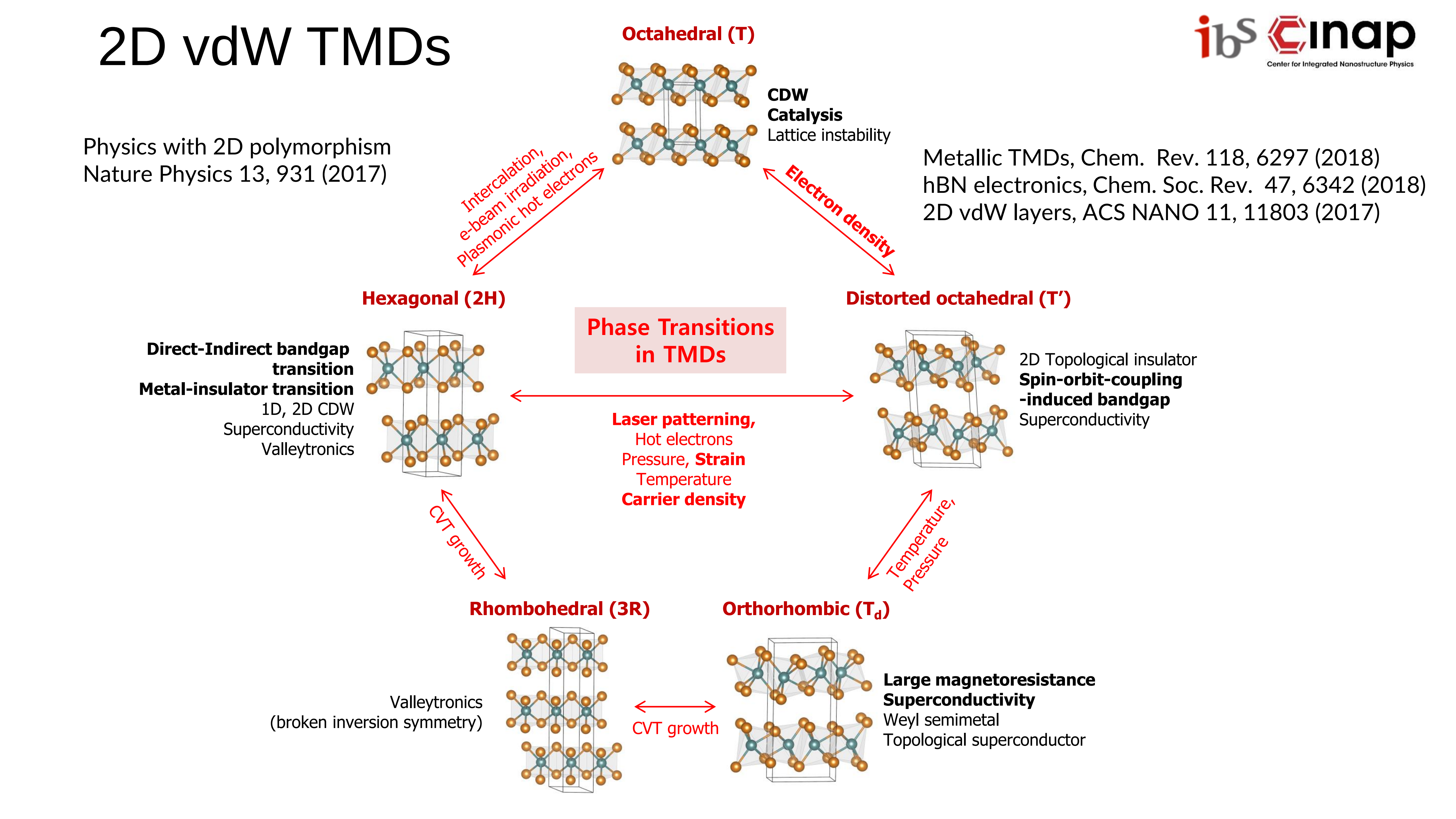
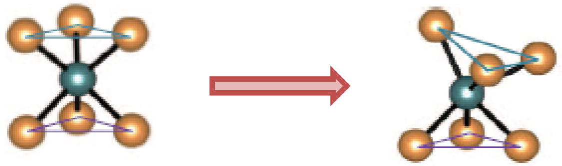

2D vdW TMDs
Physics with 2D polymorphism
Nature Physics 13, 931 (2017)
Metallic TMDs, Chem. Rev. 118, 6297 (2018)
hBN electronics, Chem. Soc. Rev. 47, 6342 (2018)
2D vdW layers, ACS NANO 11, 11803 (2017)
Center for Integrated Nanostructure Physics
Octahedral (T)
CDW
Catalysis
Lattice instability
Intercalation,
e-beam irradiation,
Plasmonic hot electrons
Electron density
Hexagonal (2H)
Direct-Indirect bandgap transition
Metal-insulator transition
1D, 2D CDW
Superconductivity
Valleytronics
Phase Transitions in TMDs
Laser patterning,
Hot electrons
Pressure, Strain
Temperature
Carrier density
Distorted octahedral (T')
2D Topological insulator
Spin-orbit-coupling -induced bandgap
Superconductivity
CVT growth
Temperature,
Pressure
Rhombohedral (3R)
Valleytronics
(broken inversion symmetry)
CVT growth
Orthorhombic (T_d)
Large magnetoresistance
Superconductivity
Weyl semimetal
Topological superconductor

Phase transformation in $MoTe_2$

ibs Cinap
Center for Integrated Nanostructure Physics

2H phase → 1T′ phase

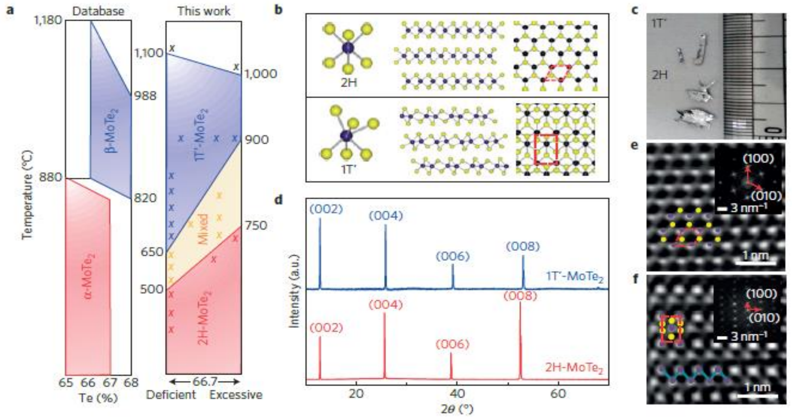
Park *et al.*, ACS Nano (2015)



2H 1T′

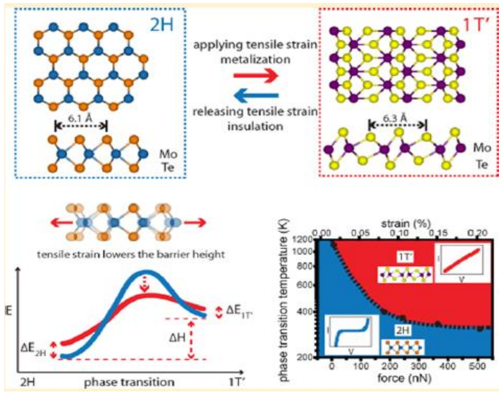
CVD approach

Temperature



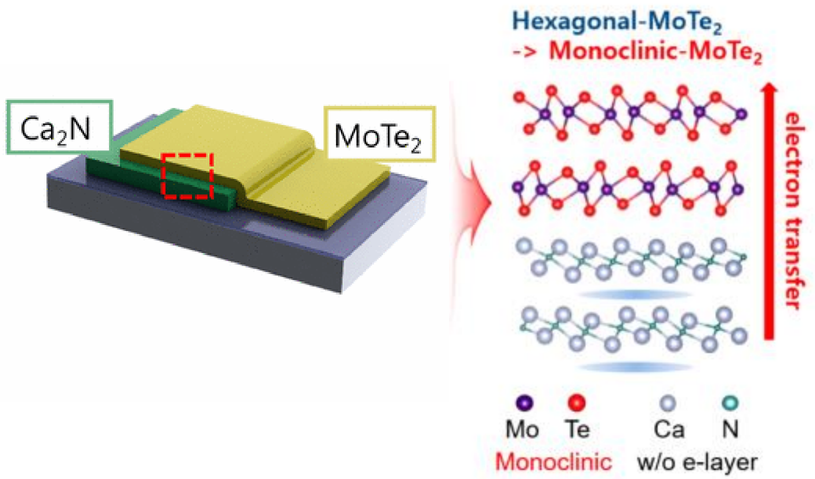
Keum *et al.*, Nat.Phys (2015)

Strain



Song *et al.*, Nano lett.(2016)

External electron doping

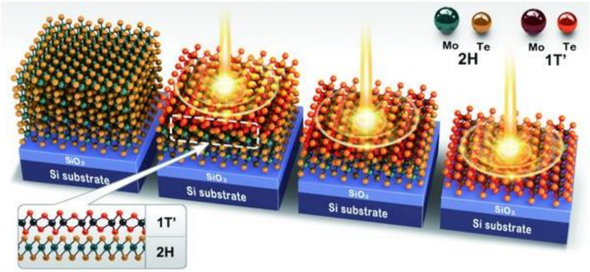


~100 nm lattice symmetry breaking by the transferred charge density >10^{14} cm^{-2}

Kim *et al.*, Nano Lett. (2017)

Laser irradiation

Homojunction contact

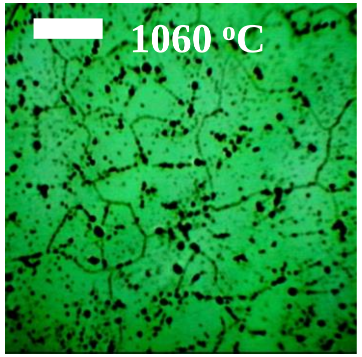


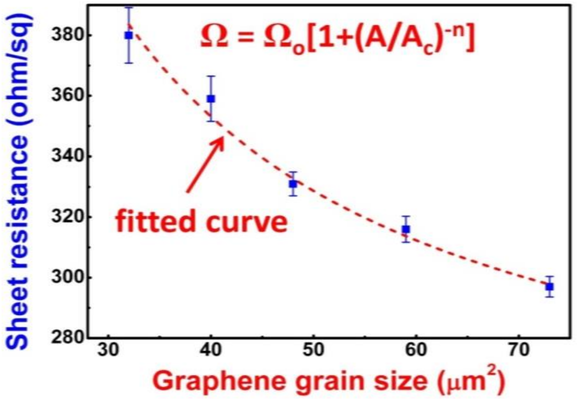
Cho *et al.*, Science (2015)

Single-crystal growth of 2D materials: wafer-scale

monolayer poly-Gr

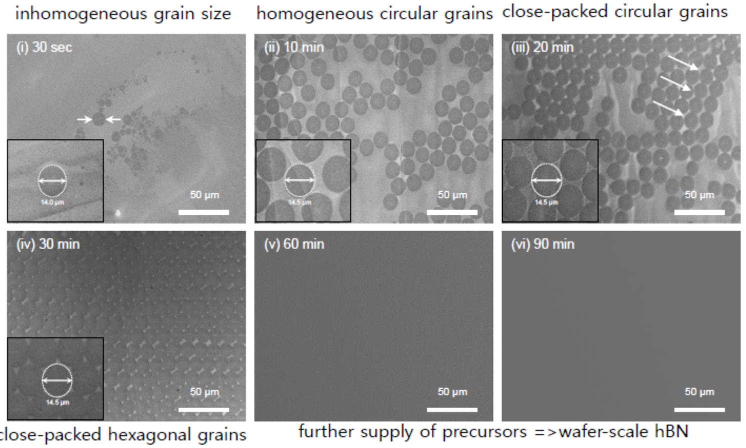
Nature 490, 235 (2012)



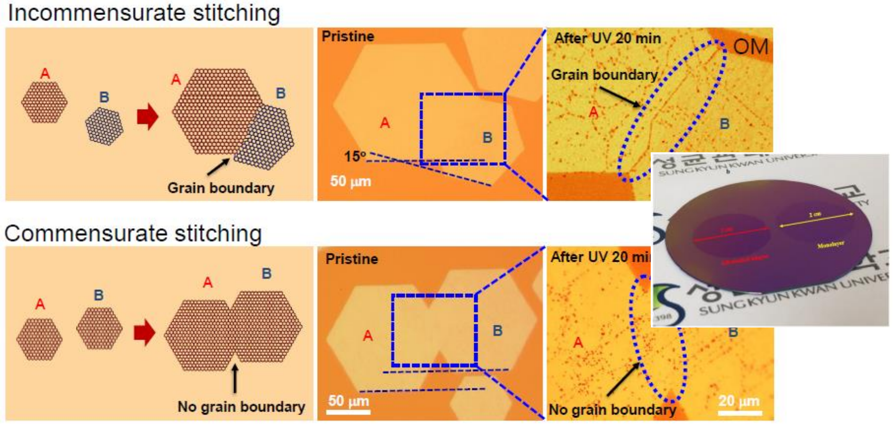


Single-crystal Gr/hBN heterostructure

Key: liquid Au on W foil



monolayer single-crystal Gr

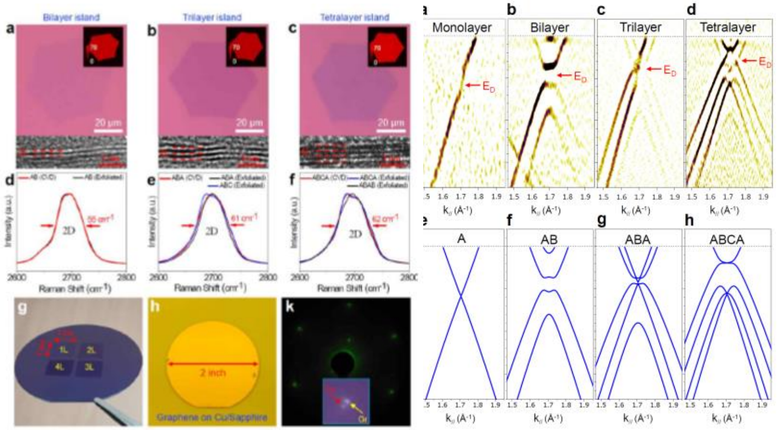


Adv. Mat. 27, 1376 (2015)

Adv. Mat. 28, 8177 (2016)

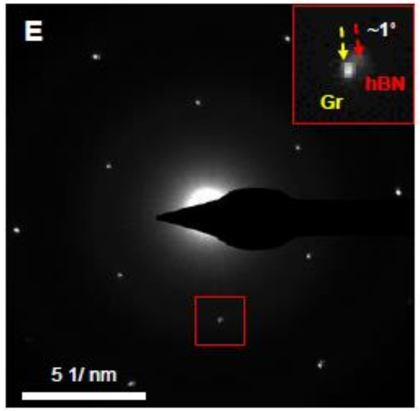
Key: single-crystalline Cu(111) film

multilayer single-crystal Gr



Nature Nanotech. 2020, doi.org/10.1038/

Key: Si-diluted Cu(111) film



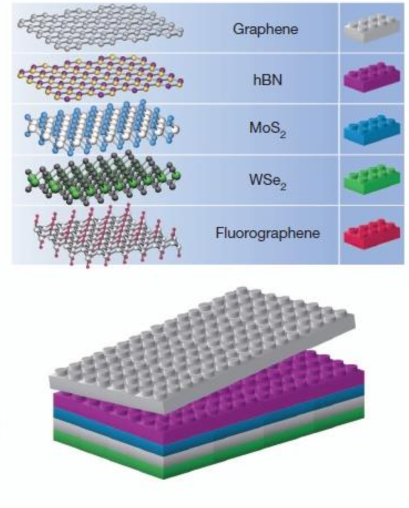
Science, 362, 817 (2018)

Coherent Gr/hBN single-crystal

Challenges for heterostructures via direct CVD

Keyword : Waferscale + singlecrystal

- Monolayer, multilayer graphene up to 4 layers
- Monolayer hBN film
- Monolayer WS_2, MS_2
- Heterostructure: Gr/hBN



Q: growth platform for wafer-scale SC TMDs from CVD?

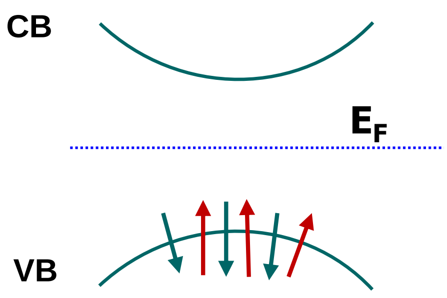
Q: Is there an opportunity in unique science phenomena for van der Waals 2D materials?

- 2D ferromagnetism

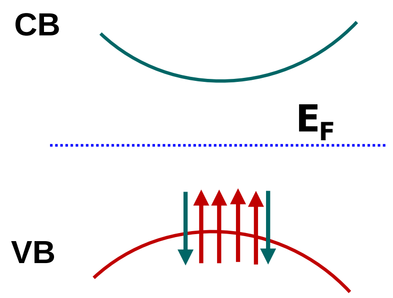
- vdW 2D ultimate solar cell

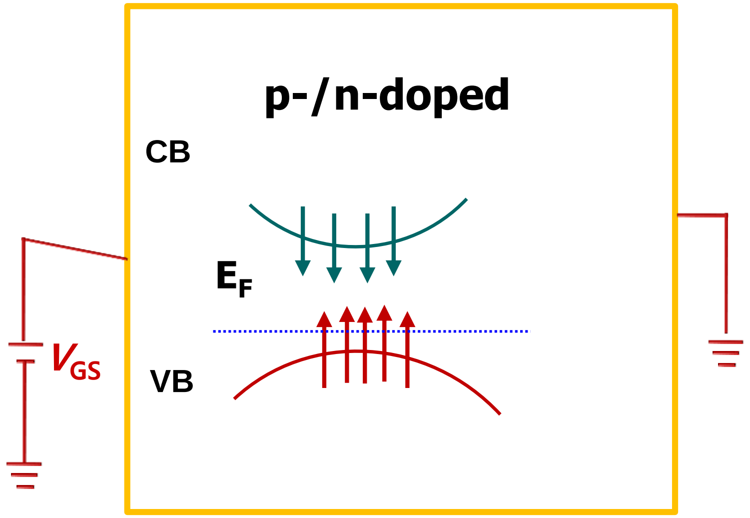
Challenge: diluted magnetic semiconductors

Semiconductors



Magnetic Semiconductors

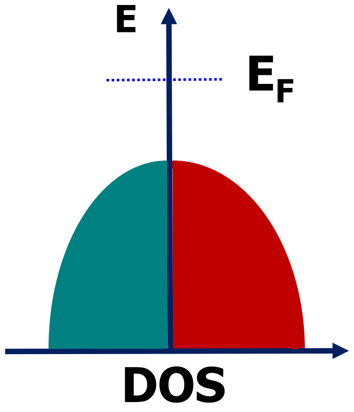




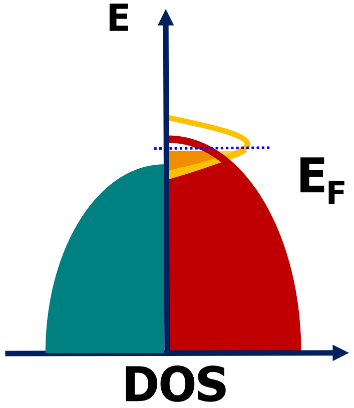
gate-tunable magnetic properties

Diluted Magnetic Semiconductors (DMSs)

undoped

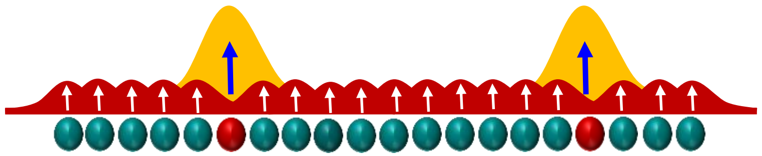


doped



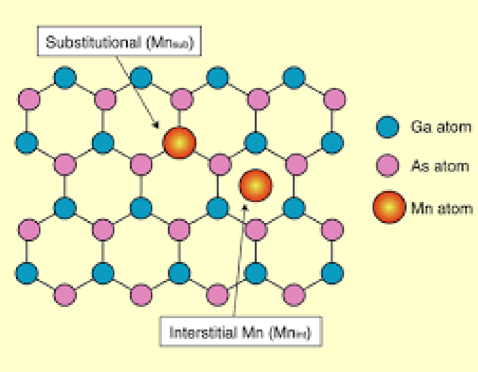
low impurity concentration

long-range magnetic order



carrier-mediated magnetic properties

Milestone



III-V semi.
(Mn doped in GaAs)

first report: Ohno H. et al.
(Phys. Rev. Lett. 68, 2664 (1992))

T_c: 170 K

gate tunable: Yes
Ohno H. et al. Nature 408, 944 (2000)

1970s

2000s

II-VI semi.
(Mn doped CdTe, HgTe, ZnTe)

first report: Zh. Eksp. Teor. Fiz. 73, 608618 (1977)
Solid State Commun. 25, 193 (1978)
(Review:J.K. Furdyna. J. Appl. Phys. 53, 7637(1982))

T_c: < 10 K
gate tunable: No

1990s

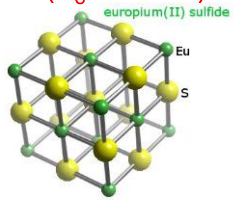
large band-gap semi.
(Nitrides, Oxides)
first report: Undefined
(T. Dietl et al. Science 287, 1019 (2000))

T_c: > 300 K

gate tunable: No

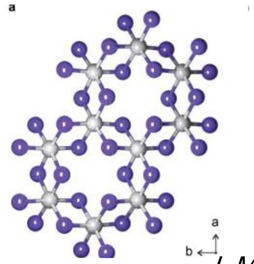
2010

EuS (T_c : ~ 16K)



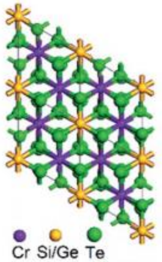
Phys. Lett. A, **24**, 242, 1967

CrI_3 (T_c : ~ 60K)



Nature **546**, 270–273, 2017

$CrGeTe_3$ (T_c : ~70K)



J. Mater. Chem. C, **2**, 7071, 2014

PbSnMnTe
(Story, T. *et al.* Phys. Rev. Lett. 56, 777–780 (1986))

125 Unsolved Questions in 2005

Diluted magnetic semiconductor (DMS)

Is it possible to create magnetic semiconductors that work at room temperature?
Such devices have been demonstrated at low temperatures but not yet in a range warm enough for spintronics applications.

2D vdW DMSs: What dopant?

Center for Integrated Nanostructure Physics

TMDs?: MoS_2, $MoSe_2$, WS_2, WSe_2, $MoTe_2$, …

+5, +4, +3 **V** [Ar] $3d^34s^2$	+6, +3, +2 **Cr** [Ar] $3d^54s^1$	+7, +4, +2 **Mn** [Ar] $3d^54s^2$	+3, +2 **Fe** [Ar] $3d^64s^2$	+3, +2 **Co** [Ar] $3d^74s^2$	+2 **Ni** [Ar] $3d^84s^2$
	+6, +4 **Mo** [Kr] $4d^5\ 5s^1$				
	+6, +4 **W** [Xe] $4f^{14}5d^46s^2$				

+6,+4, -2, -4	**S** [Ne] $3s^23p^4$
+6,+4, -2, -4	**Se** [Ar] $3d^{10}4s^24p^4$
+6,+4, -2, -4	**Te** [Kr] $4d^{10}5s^25p^4$

pd hybridization

Different from Mn-GaAs => s-p hybridization??

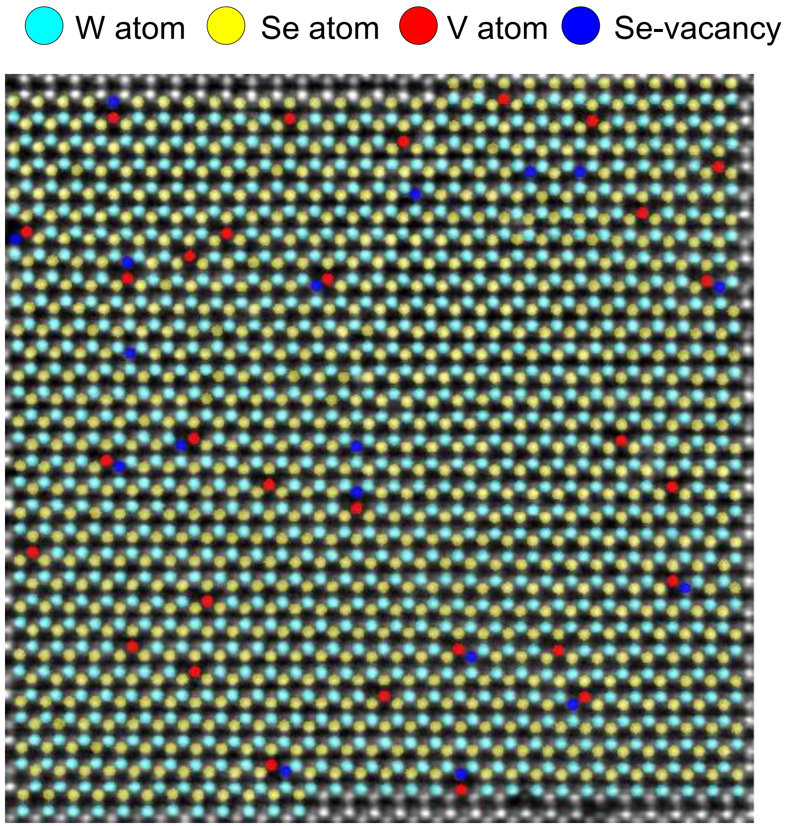
- VS_2, VSe_2 and VTe_2 exist as 1T phase
- VS and VSe are antiferromagnetic

Choice of materials: semiconductor (WSe_2), homogeneity (V)

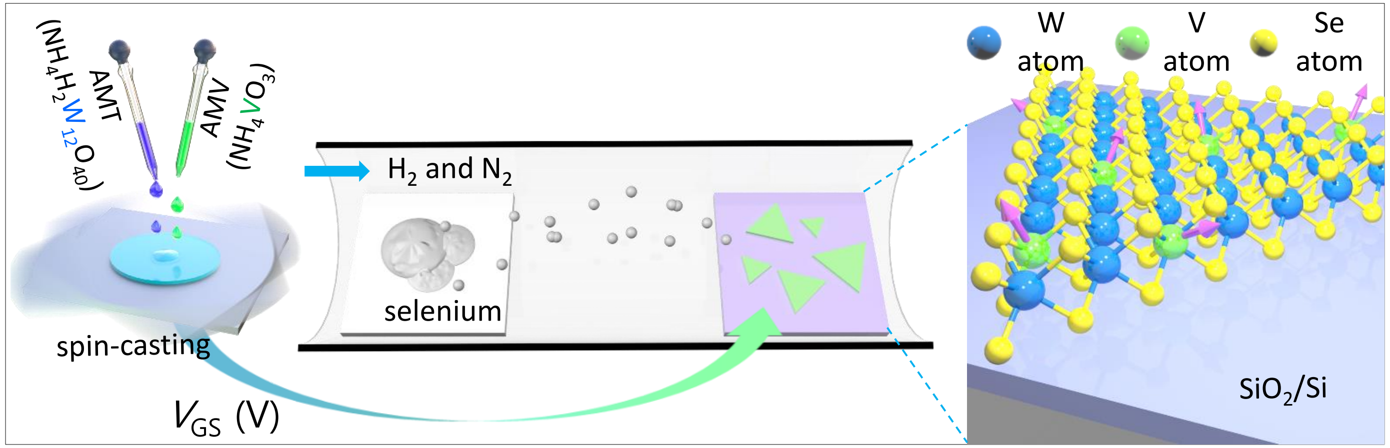
What are the challenges in DMS?

Challenge: i) T_c over RT
ii) Gate modulation
iii) Long-range magnetic order (no phase segregation)

Approach: Room-temperature ferromagnetism in WSe_2 semiconductor via vanadium dopant



Does CVD work for monolayer V-doped WSe_2 ?



Yun & Loc et al., Adv. Sci. 7, 1903076 (2020)

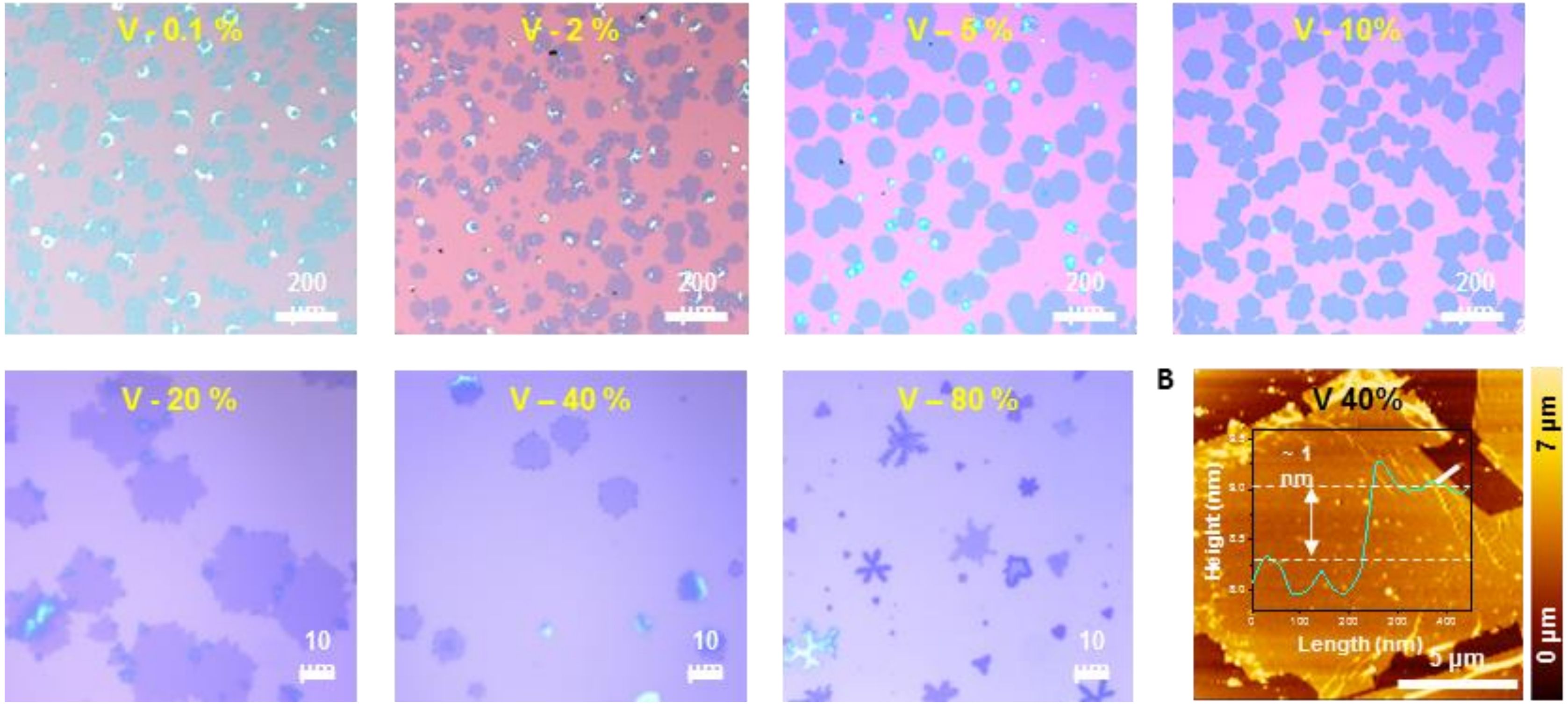
Precursor solution

W precursor : AMT in DI water
V precursor : AMV in DI water
Promoter : NaOH in DI water

--> Control V-dopant content

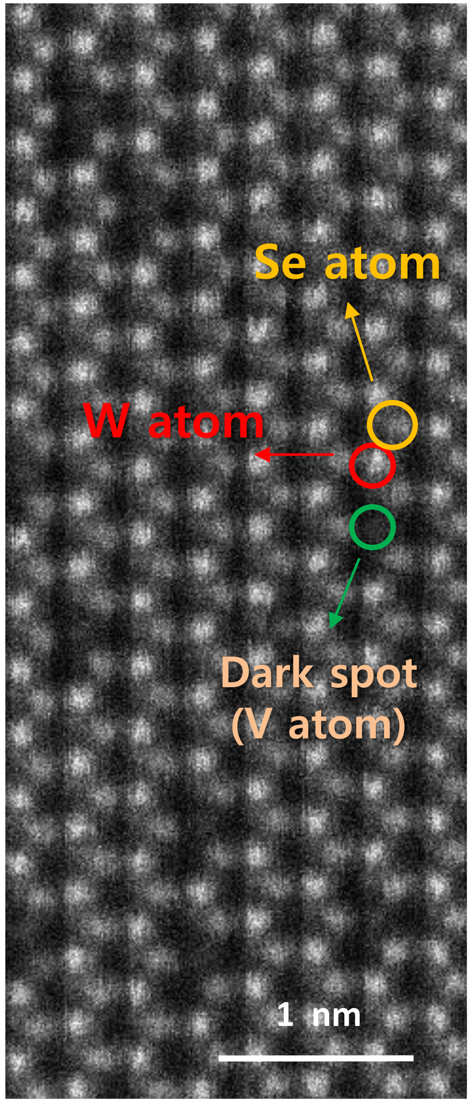
Monolayer until V-10%

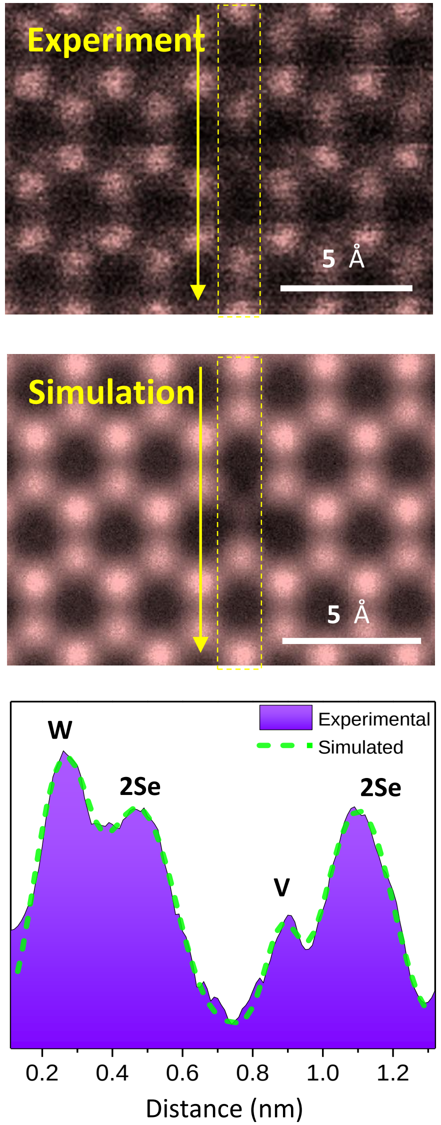
Dendritic and multilayer flakes over 20%

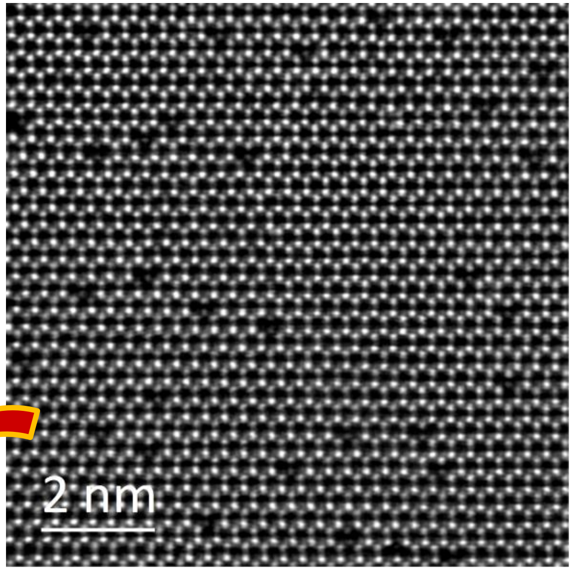


Where is the V site in WSe_2?

ADF-STEM image of 2% V-doped WSe_2

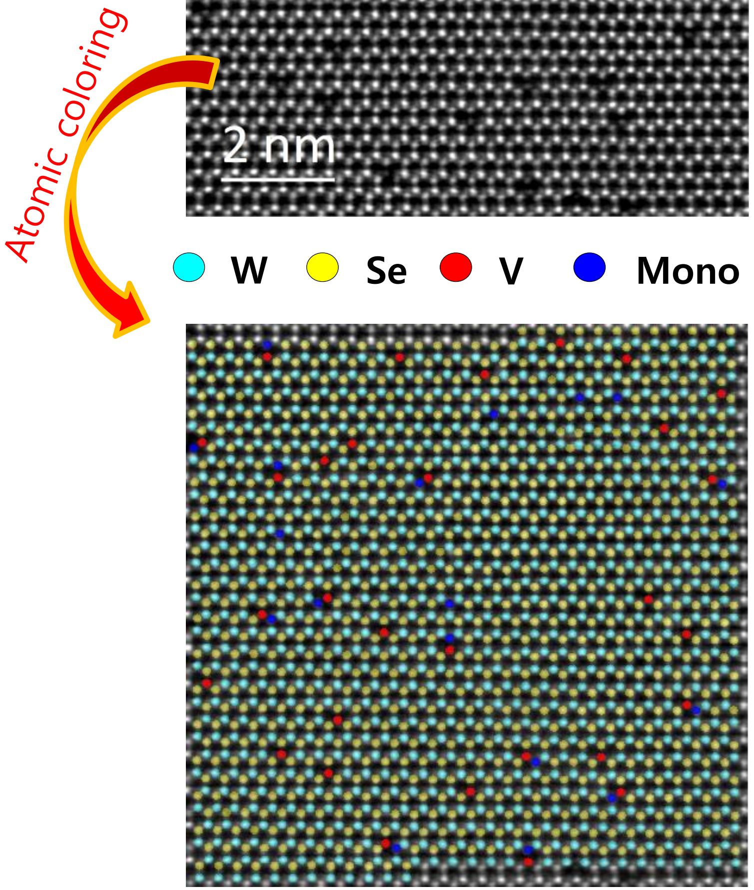






Filtered STEM image

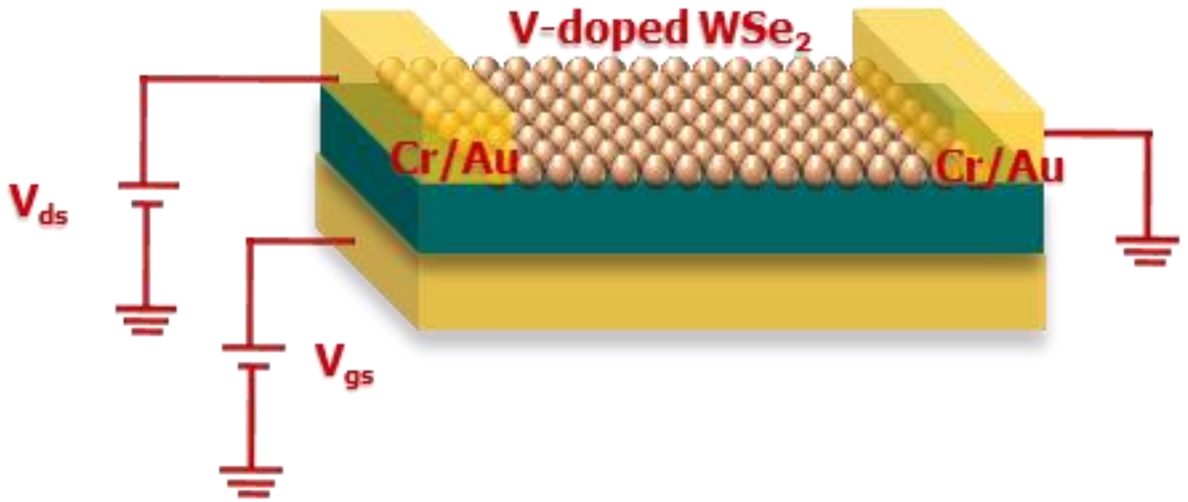
W Se V Mono Se-vacancy

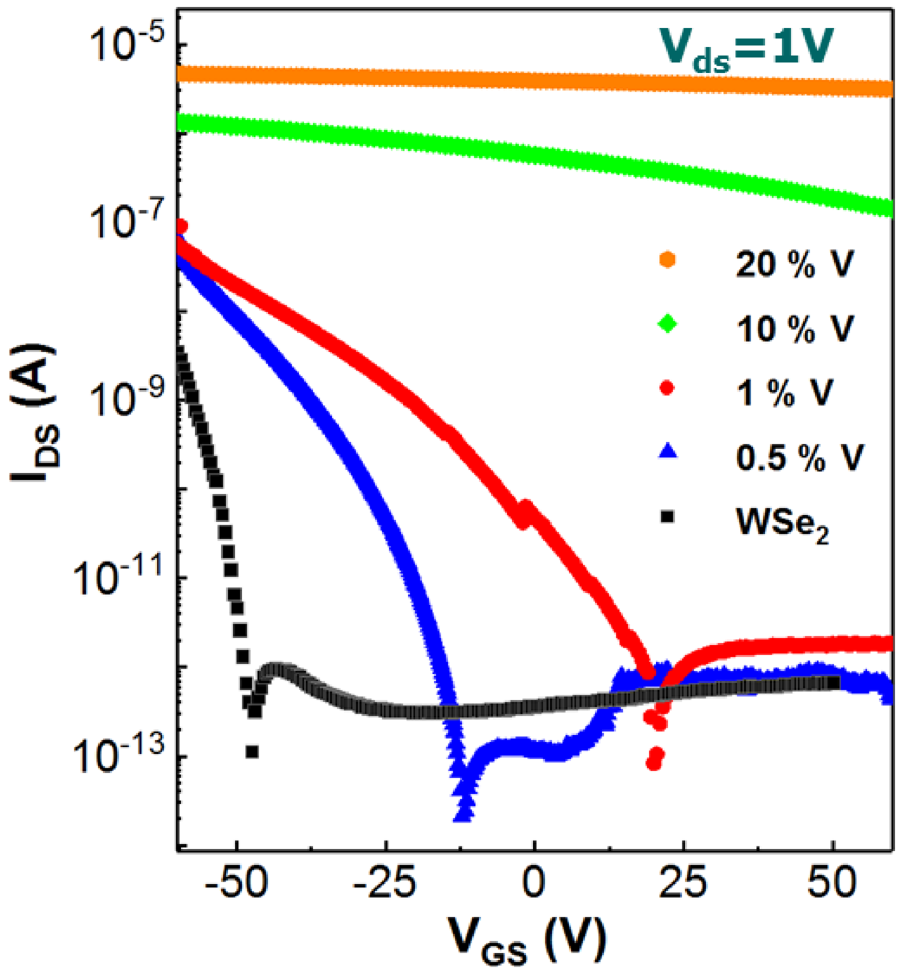


Substitutional V atoms are uniformly distributed

Is V-doped WSe_2 really semiconductor?

vanadium: strong p-type dopant for WSe_2

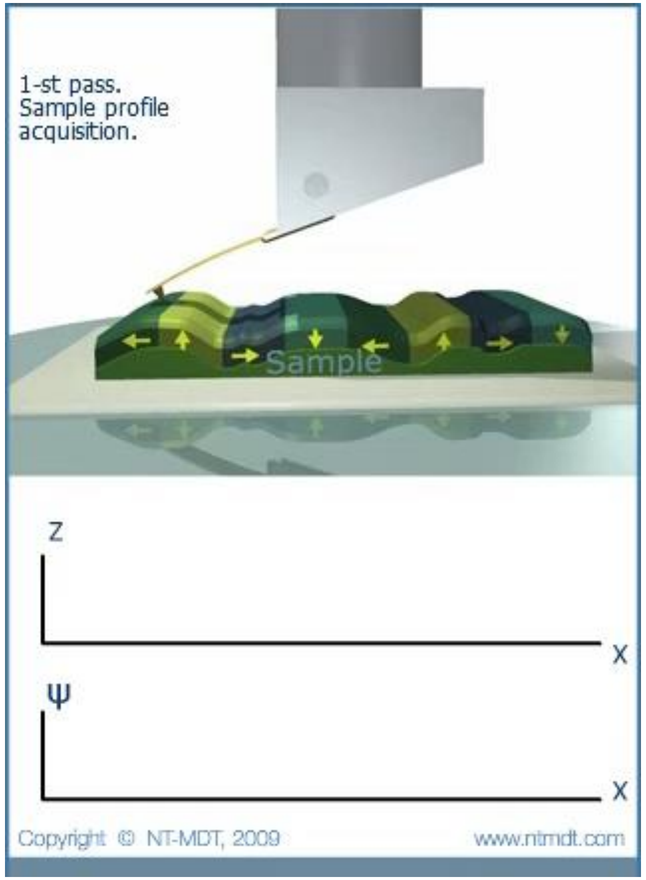




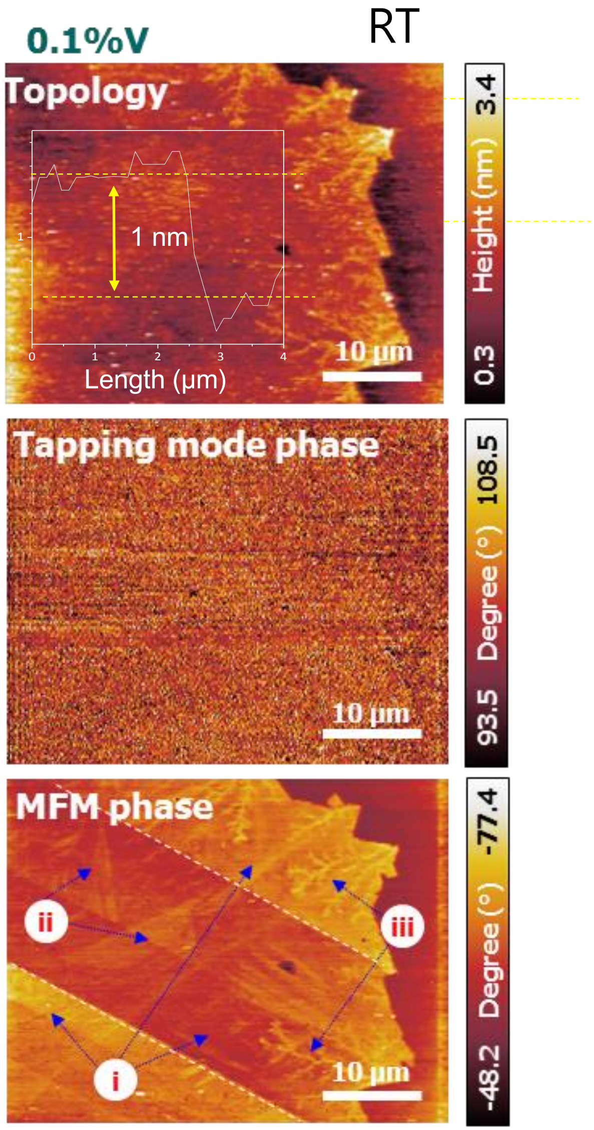
large gate-modulation with doping concentration below 1%

Can we observe magnetic domain from MFM?

magnetic force microscopy (MFM)

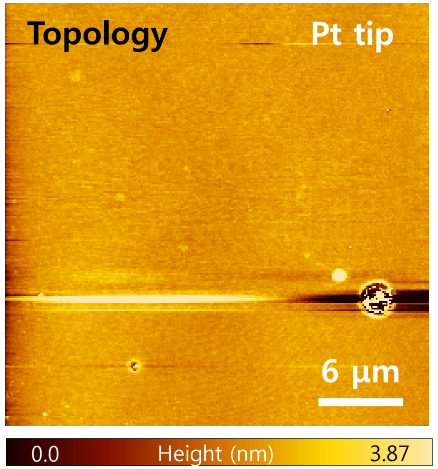


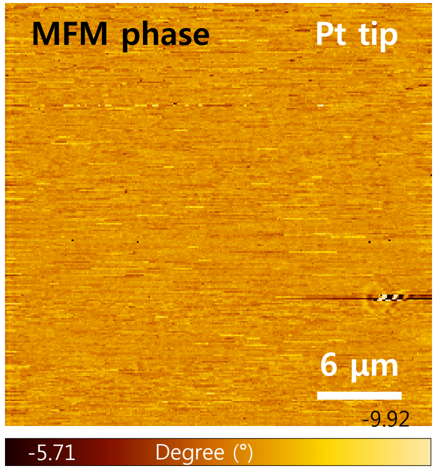
https://www.ntmdt-si.com/resources/spm-principles/atomic-force-microscopy/mfm/dc-mfm



What is the best choice of the tip?

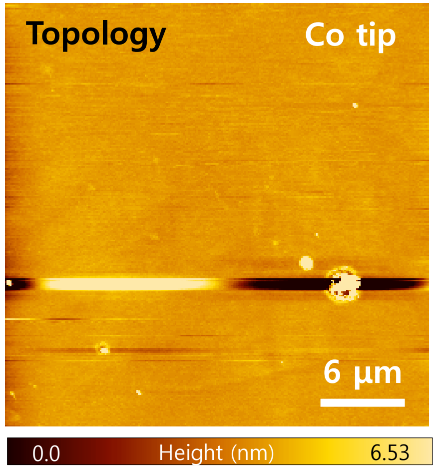
: Pt vs Co tip

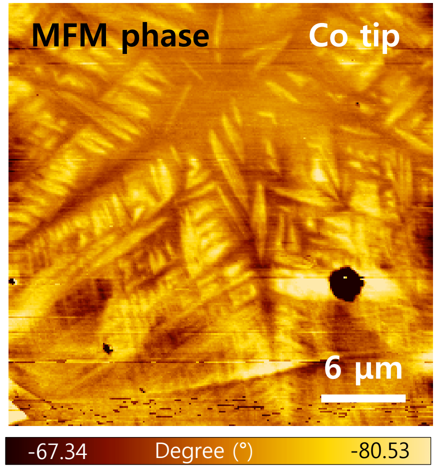




Neither morphology nor magnetic phase domains with Pt tip!

No morphology but magnetic phase domains with Co tip!

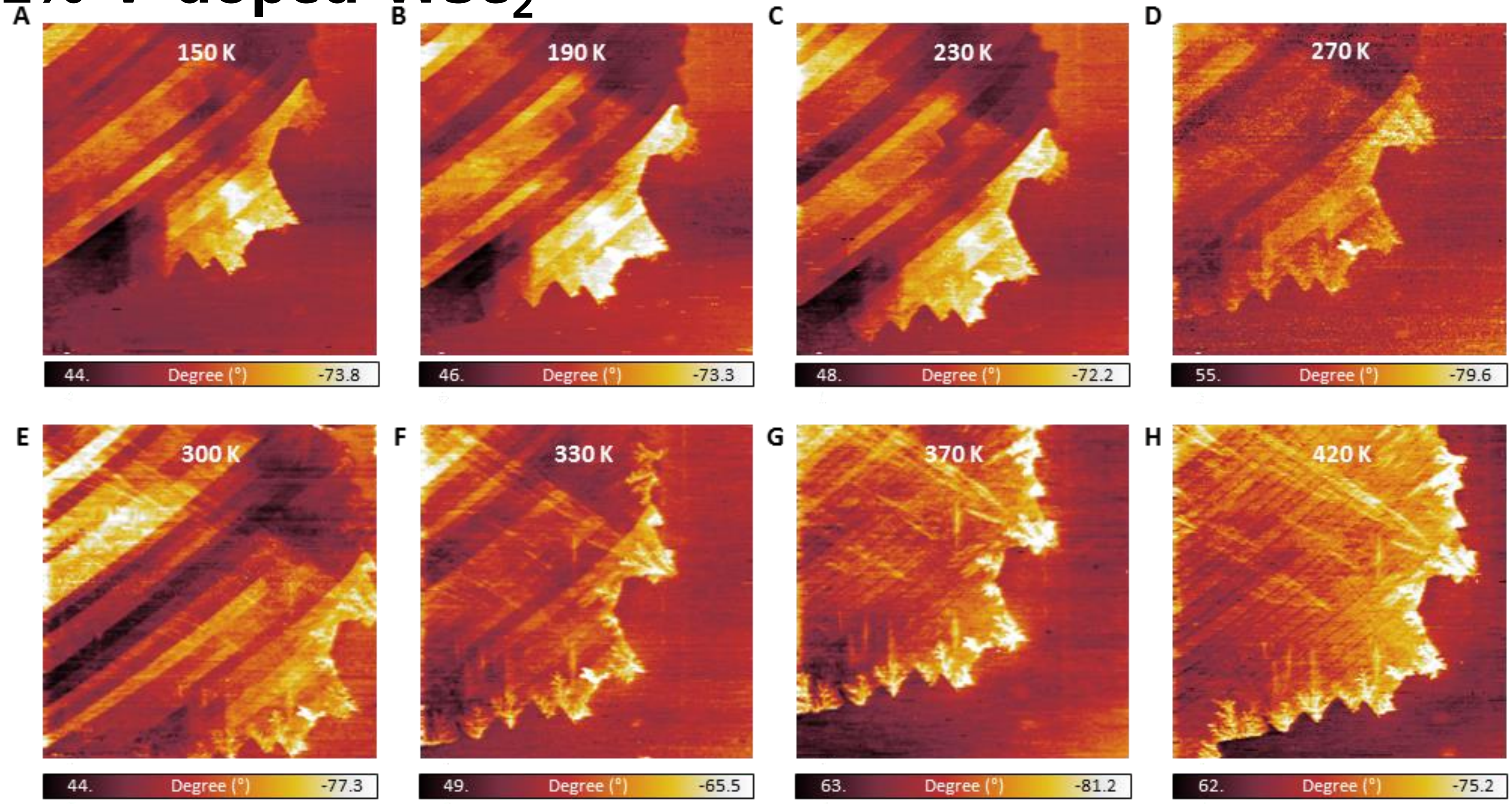




Evidence of magnetic force interaction!

Evolution of MFM phase contrast with temperature

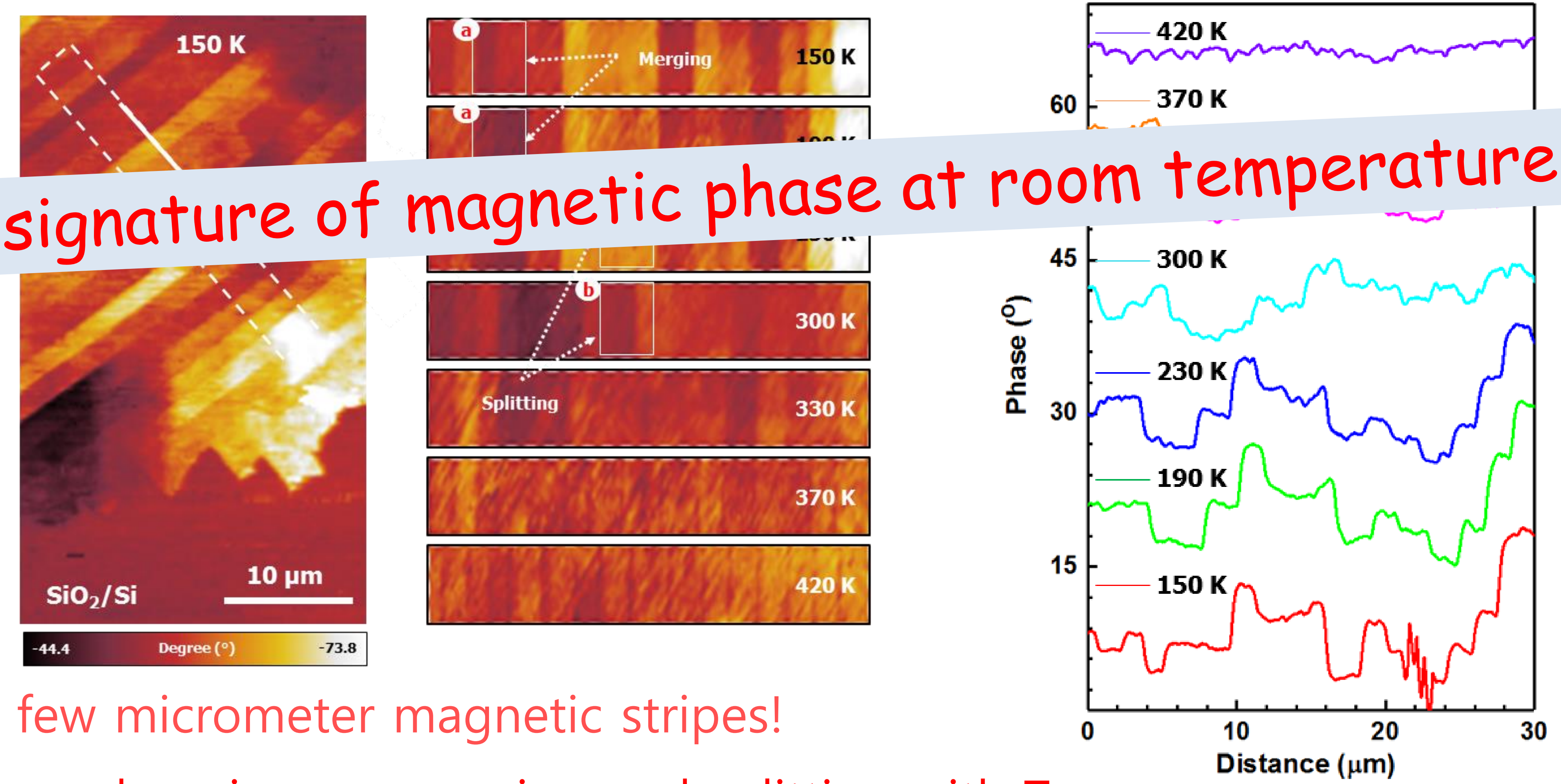
0.1% V-doped WSe_2



Temperature-dependent MFM domains?

Yun & Loc et al., Adv. Sci. 7, 1903076 (2020)

0.1% V-doped WSe_2



A signature of magnetic phase at room temperature!

a few micrometer magnetic stripes!

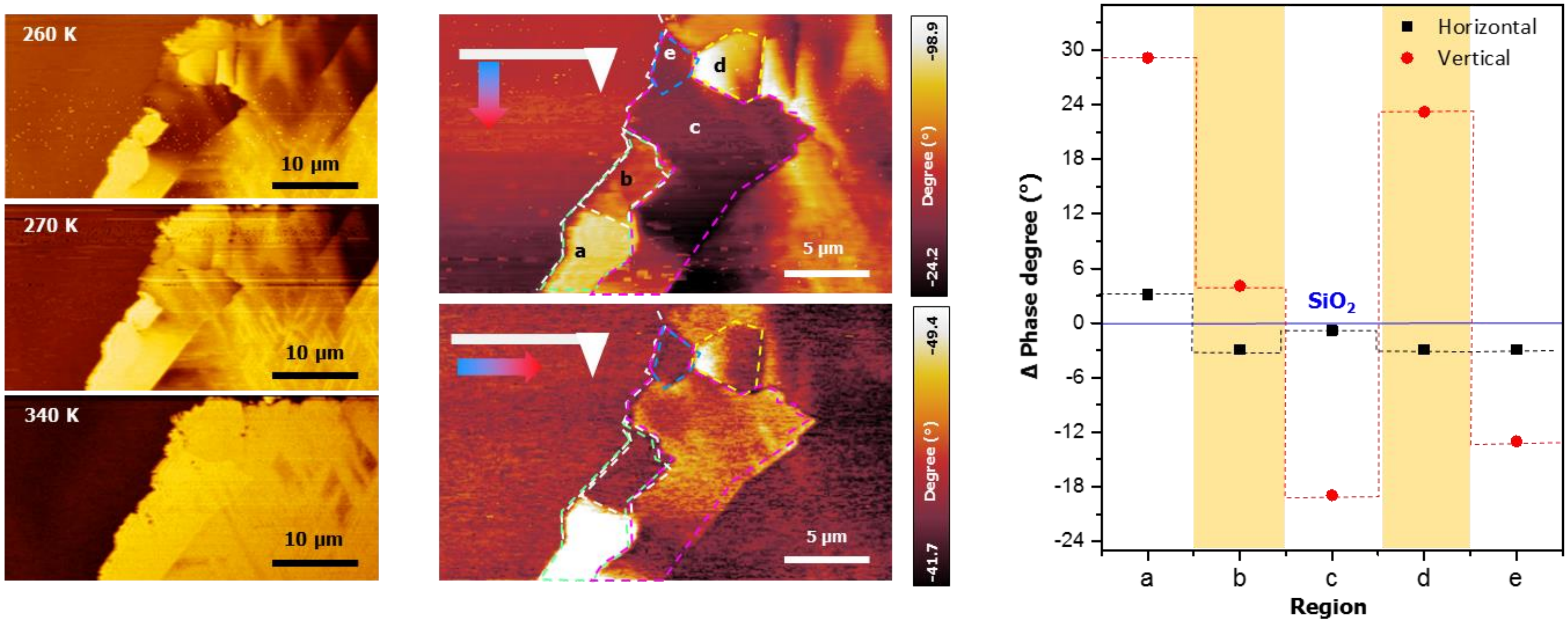
domains are merging and splitting with T

→ Evidence of magnetic signal but not electrostatic response

Is magnetic domain modulated with magnetized sample?

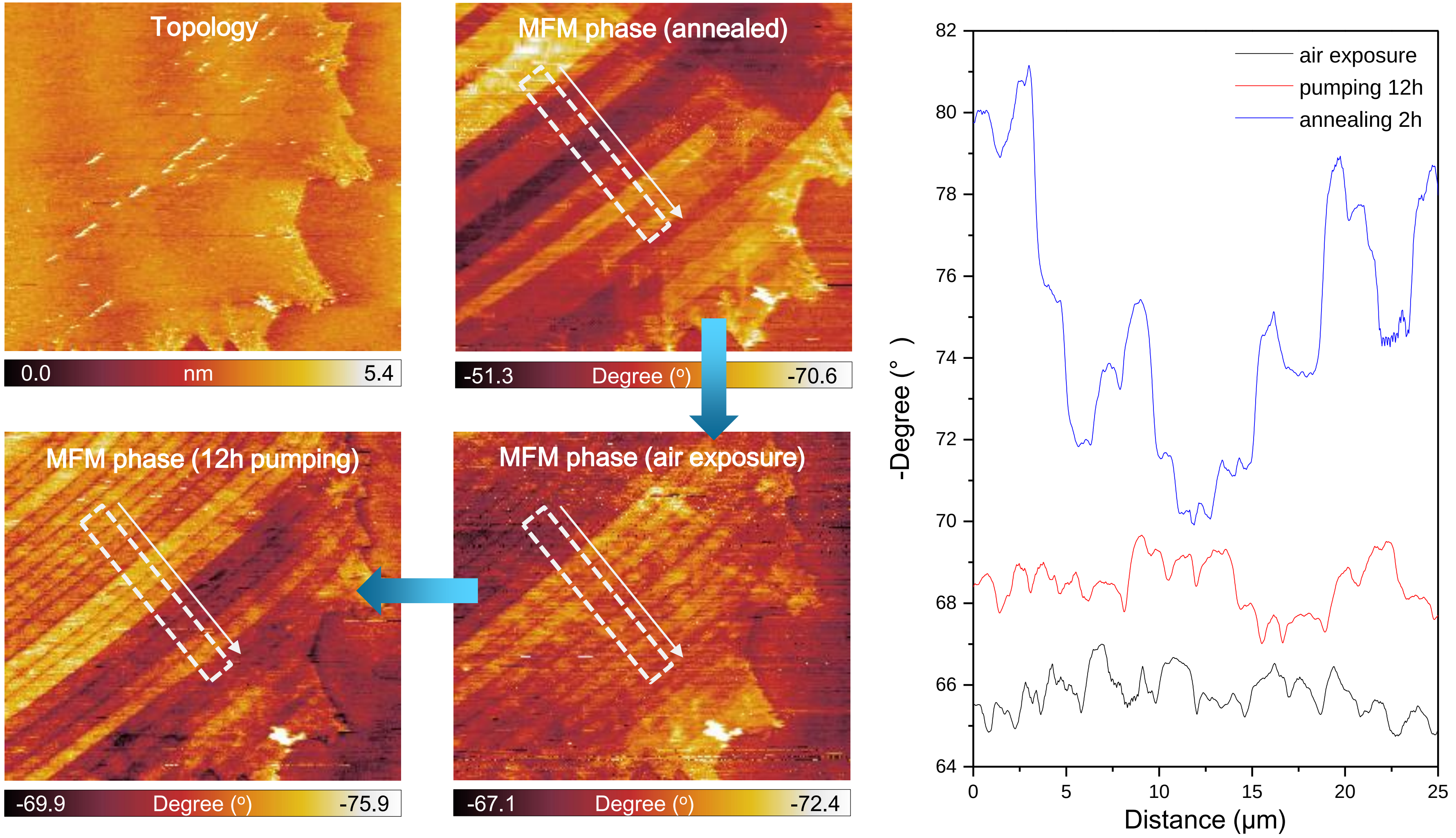
observation of magnetic domains

dependence of the tip-polarized direction



evidence of the magnetic force interaction!

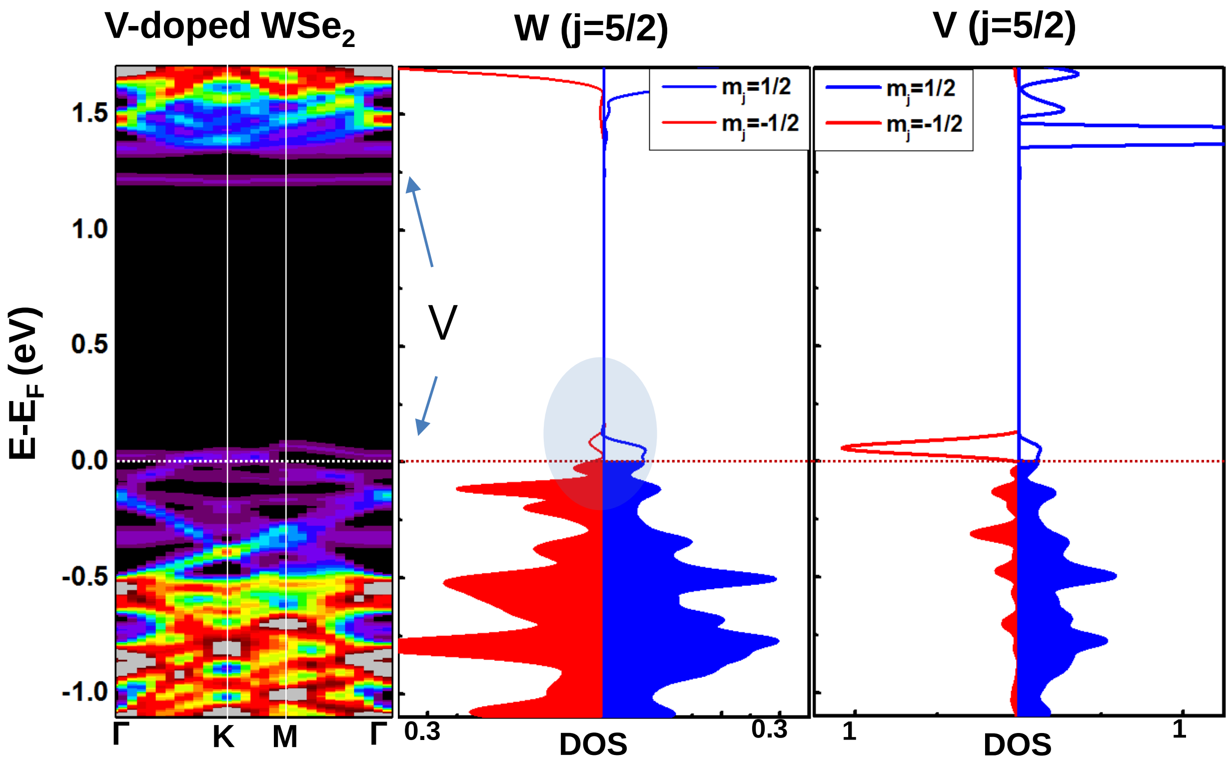
Is the sample inert under ambient conditions?

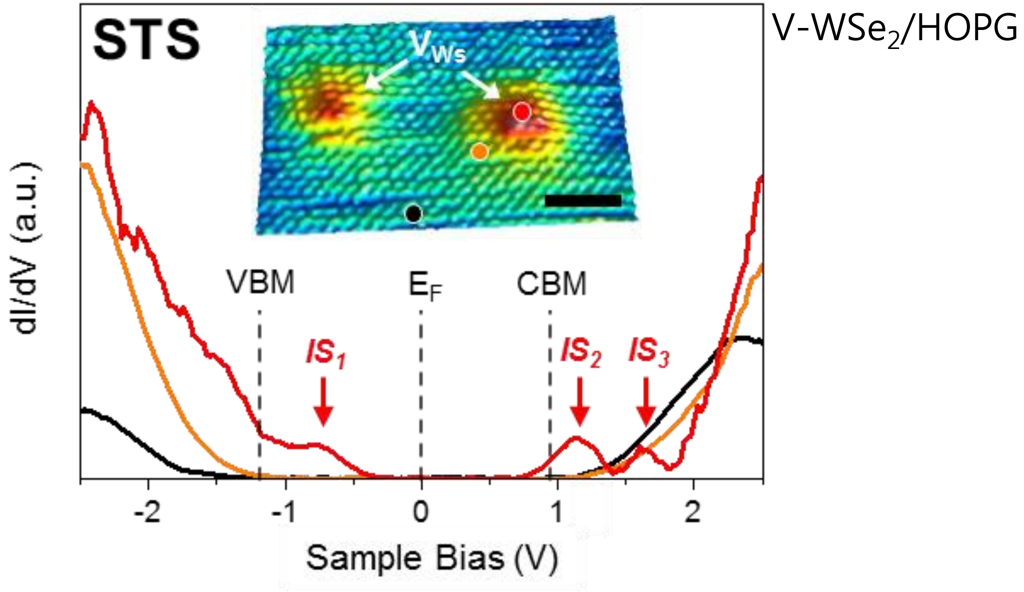


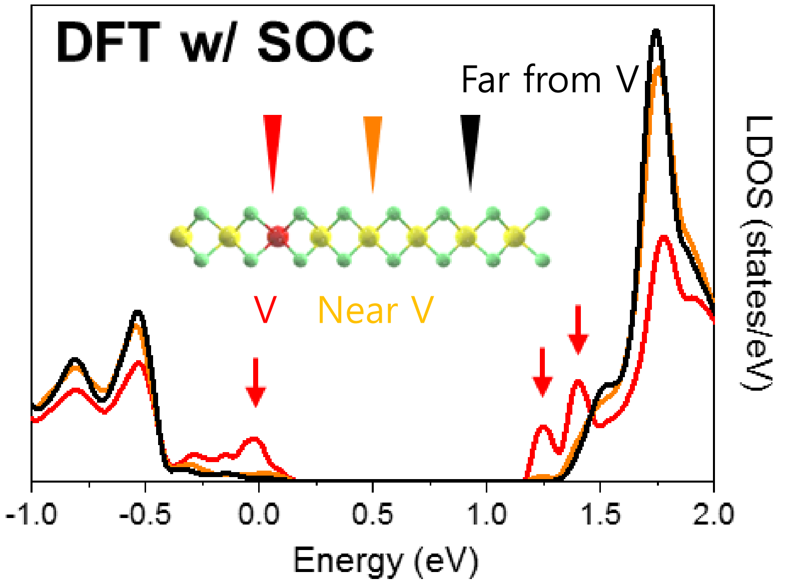
MFM phase contrast is partially disrupted in air but recovered by annealing!

V-doping level??: dI/dV STS for density of states

Song and Loc et al., arXiv preprint arXiv:2002.07333





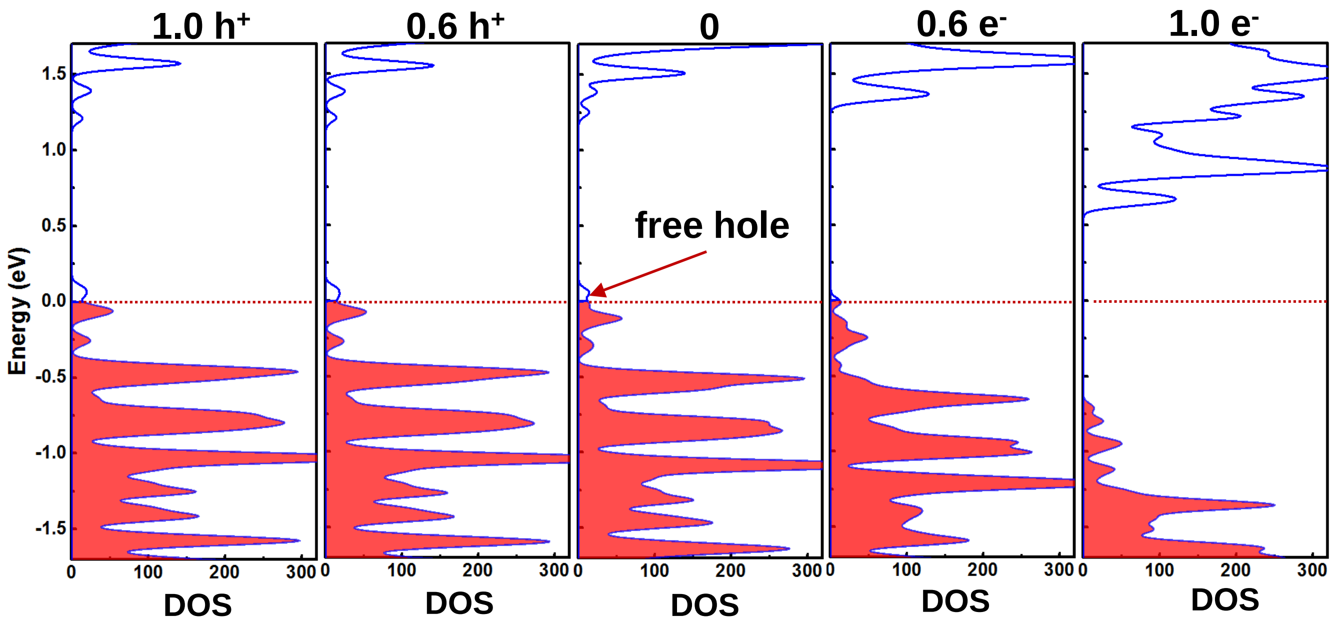


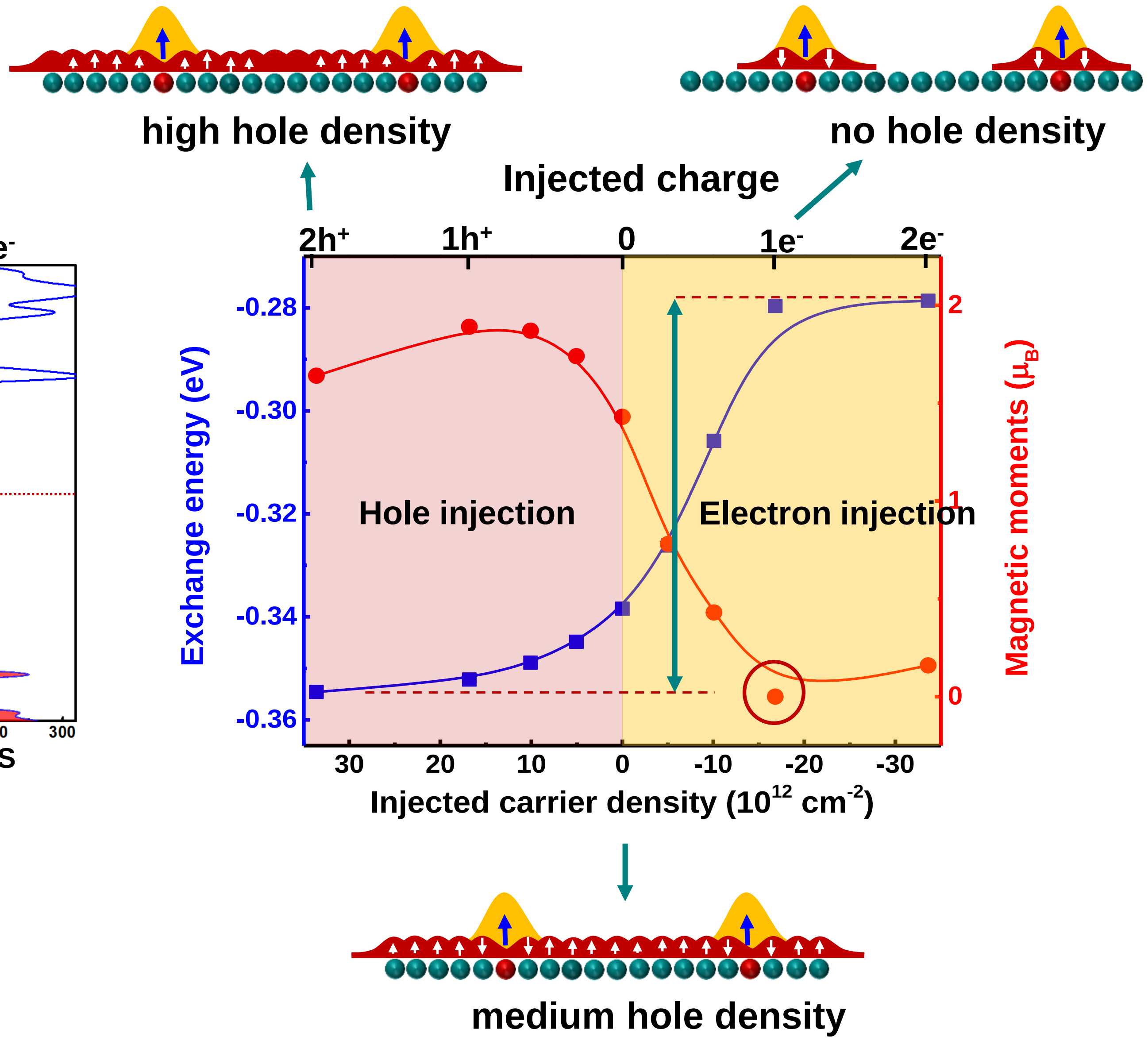
Magnetic ordering can be modulated by gate-bias?

AIP Adv. 10, 065220 (2020)

DFT calculations

carrier injection

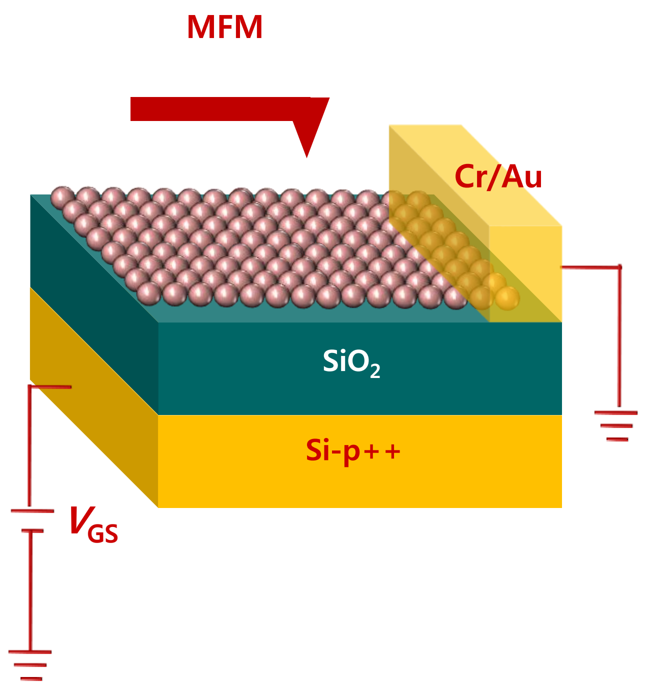




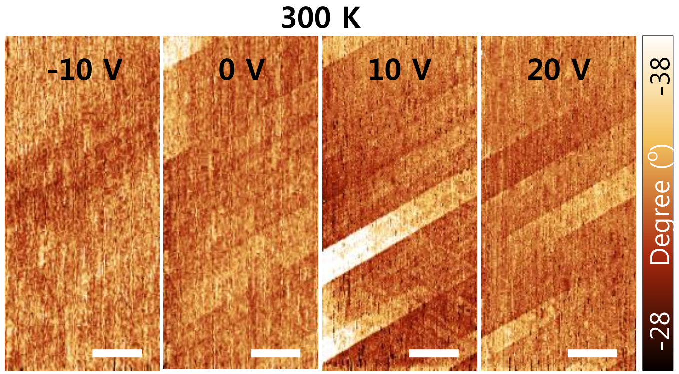
Spin modulation by gate-bias with MFM ?

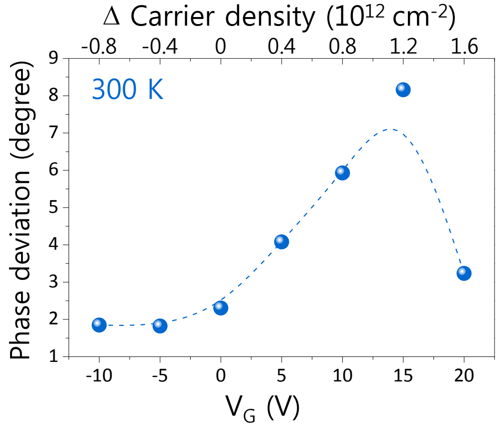
Yun & Loc et al., Adv. Sci. 7, 1903076 (2020)

Backgate via MFM tip

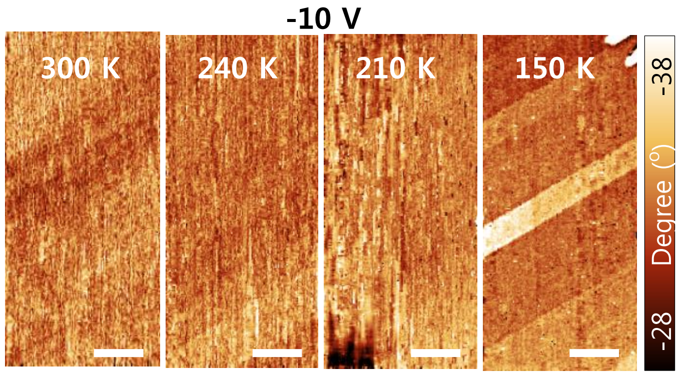


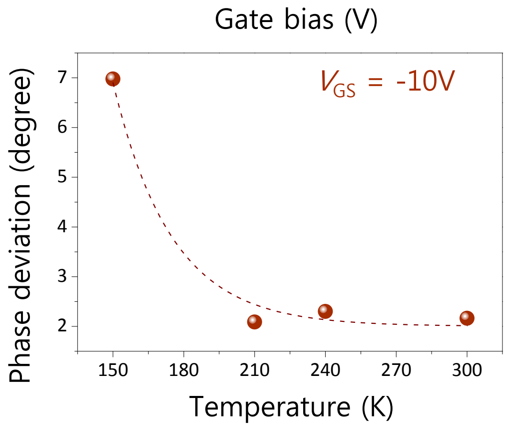
Control magnetic domains by gating





Control T_c by gating

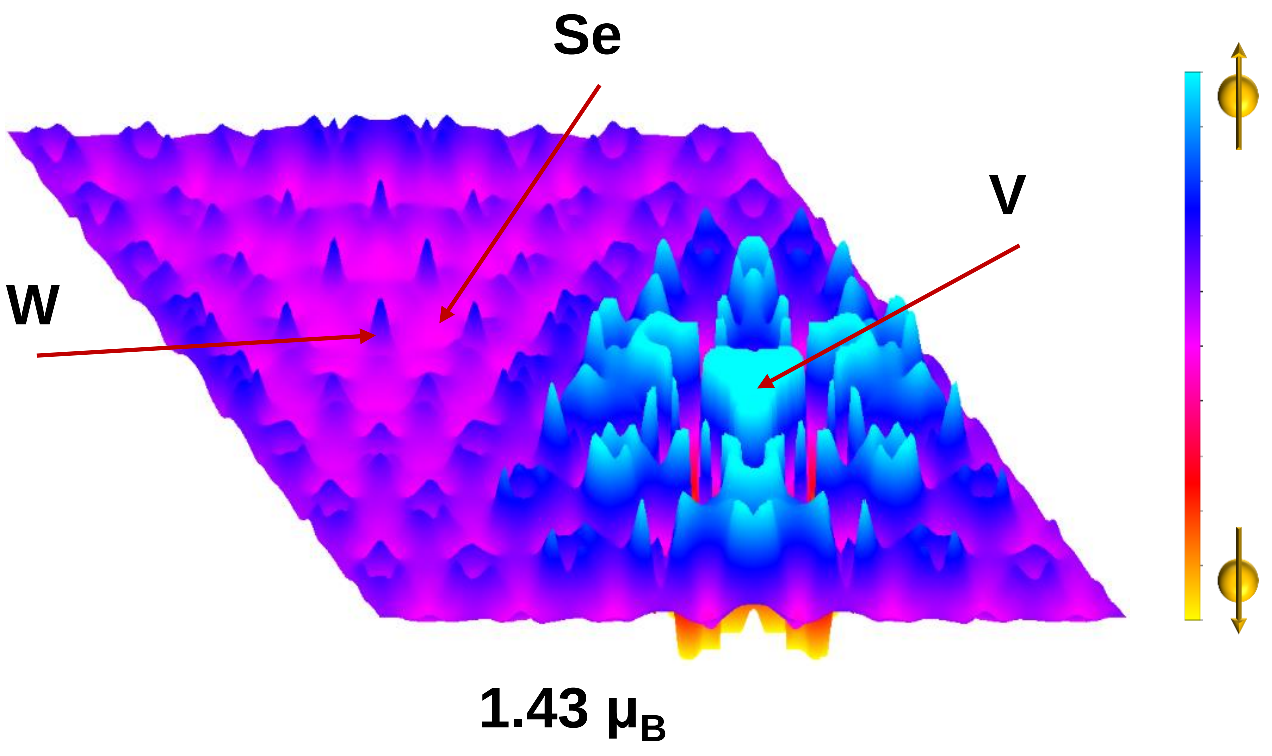


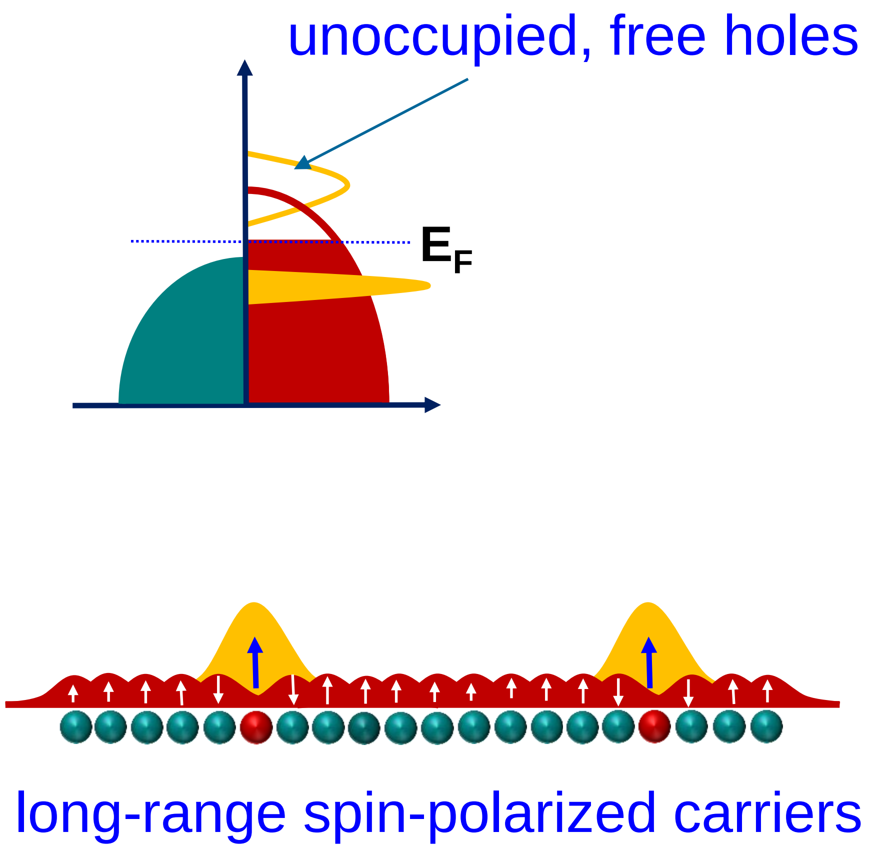


Does V-doped WSe_2 reveal long-range magnetic order?

Loc et al., Appl. Phys. Lett. 115, 242406 (2019)
AIP Adv. 10, 065220 (2020)

Carrier-mediated magnetic order is persistent very far from V!





1970s

II-VI Semi.
(Mn doped CdTe, HgTe, ZnTe)

First report: Undefined

Zh. Eksp. Teor. Fiz. 73, 608618 (1977)

Solid State Commun. 25, 193 (1978)

(Review:J.K. Furdyna. J. Appl. Phys. 53, 7637(1982))

T_c: < 10 K

Gate tunable: No

PbSnMnTe

(Story, T. *et. al.* Phys. Rev. Lett. 56, 777–780 (1986))

1990s

III-V Semi.
(Mn doped in GaAs)

First report: Ohno H. et. al.

(Phys. Rev. Lett. 68, 2664 (1992))

T_c: 170 K

Gate tunable: Yes

Ohno H. et al. Nature 408, 944 (2000)

2000s

Large band-gap Semi.
(Nitrides, Oxides)

First report: Undefined

(T. Dietl et al. Science 287, 1019 (2000))

T_c: > 300 K

Gate tunable: No

2018

2D vdW semiconductors
(V doped WSe_2)

First report: Yun, Duong, Lee et al.

(arXiv:1806.06479)

T_c: 350 K

Gate tunable: Yes

(Yun, Duong, Lee et. al. arXiv:1806.06479)

Take-home lesson:

Room-temperature ferromagnetism in monolayer TMDs and bulk!

Plenty of room for spintronics!