

# Nanoscale probing the electronic transport in transition metal dichalcogenides by conductive atomic force microscopy

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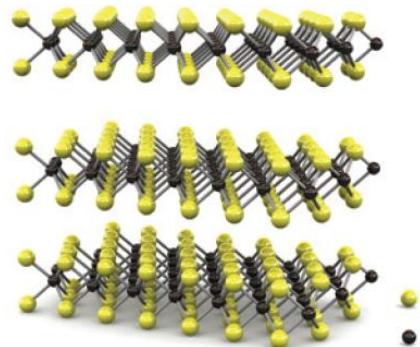
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Catania, Italy

# The 2D materials family

Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS <sub>2</sub> , WS <sub>2</sub> , MoSe <sub>2</sub> , WSe <sub>2</sub>	Semiconducting dichalcogenides: MoTe <sub>2</sub> , WTe <sub>2</sub> , ZrS <sub>2</sub> , ZrSe <sub>2</sub> and so on	Metallic dichalcogenides: NbSe <sub>2</sub> , NbS <sub>2</sub> , TaS <sub>2</sub> , TiS <sub>2</sub> , NiSe <sub>2</sub> and so on	Layered semiconductors: GaSe, GaTe, InSe, Bi <sub>2</sub> Se <sub>3</sub> and so on	
2D oxides	Micas, BSCCO	MoO <sub>3</sub> , WO <sub>3</sub>	Petrovskite-type: LaNb <sub>2</sub> O <sub>7</sub> , Ca <sub>2</sub> Nb <sub>3</sub> O <sub>10</sub> , Bi <sub>4</sub> Ti <sub>3</sub> O <sub>12</sub> , Ca <sub>2</sub> Ta <sub>2</sub> TiO <sub>10</sub> and so on	Hydroxides: Ni(OH) <sub>2</sub> , Eu(OH) <sub>2</sub> and so on	Others

	MoS <sub>2</sub>	WS <sub>2</sub>	MoSe <sub>2</sub>	WSe <sub>2</sub>
E <sub>g</sub> (bulk), indirect	1.2 eV	1.4 eV	1.1 eV	1.2 eV
E <sub>g</sub> (1L), direct	1.8 eV	1.9 eV	1.5 eV	1.7 eV

A. Geim, I. Grigorieva, *Nature* **499**, 419–425 (2013)

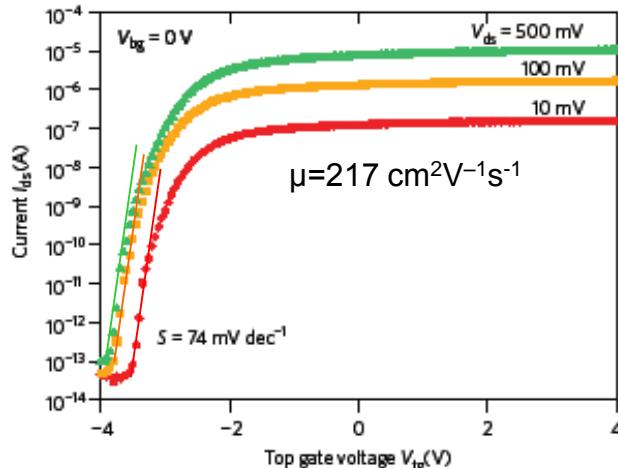
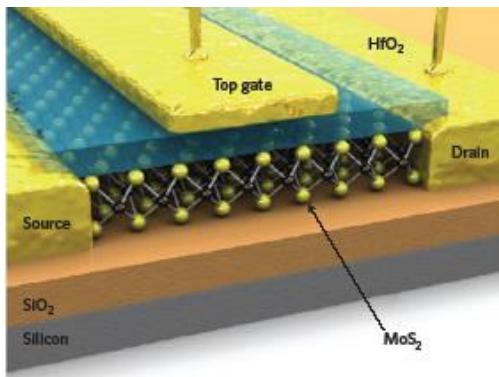


Layered materials with the formula MX<sub>2</sub>  
M transition metal: Mo, W,..  
X chalcogen: S, Se,...

● X  
● M

Q.H.Wang, K.Kalantar-Zadeh, A.Kis, J.N.Coleman and M.S.Strano, *Nature Nanotechnology* **7**, 699–712 (2012).

# Field effect transistors based on TMDs

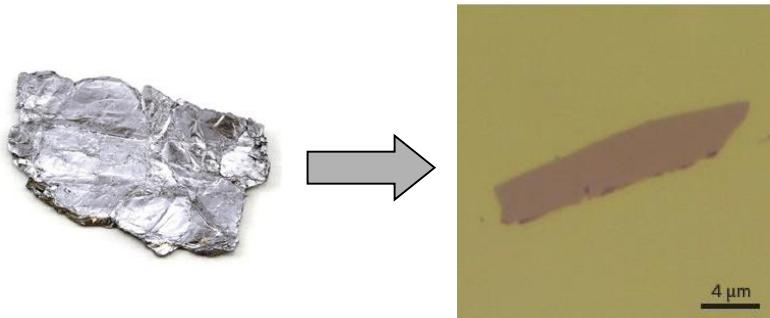


- ultrathin, uniform channel thickness for excellent gate control
- On/Off current ratio  $>10^7$
- nearly ideal subthreshold swing ( $S \approx kT \log(10)$ )

B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, A. Kis, Nature Nanotechnology **6**, 147 (2011)

## Production methods for electronic quality TMDs

### Exfoliation from bulk crystals



- Micrometer size flakes

### Chemical vapour deposition



Y.-H. Lee, et al., Advanced Materials **24**, 2320-2325 (2012)

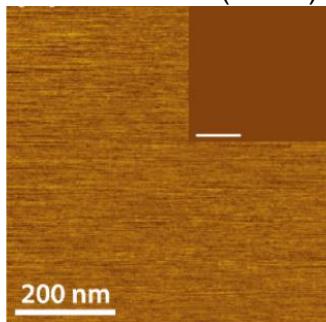
- Direct deposition on insulating or semiconductor substrates ( $\text{SiO}_2$ , sapphire, GaN)
- Growth temperature range:  $700 - 900^\circ\text{C}$

**Electronic properties of state of the art TMDs strongly affected by electrically active point and extended defects**

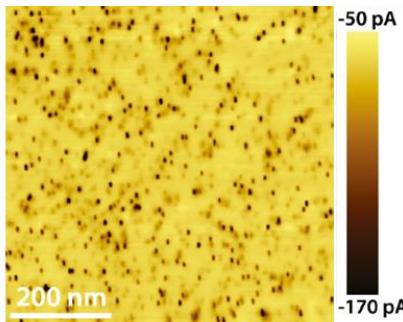
# Nanoscale defects in exfoliated MoS<sub>2</sub>

MoS<sub>2</sub> surface after exfoliation

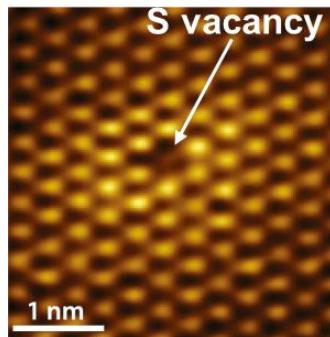
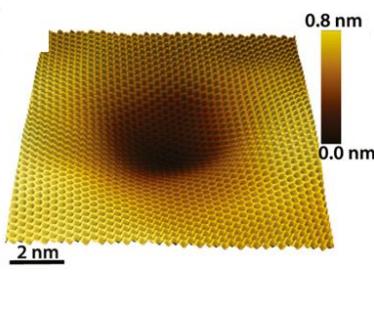
LFM and AFM (insert)



C-AFM

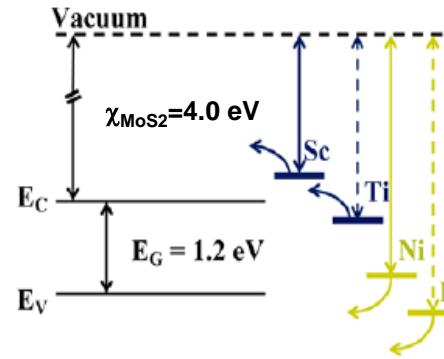


STM of a nanometer defect and a S vacancy

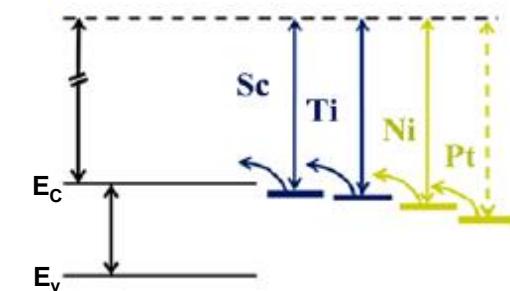


Origin of the contact resistance typically observed at the interface between metals and MoS<sub>2</sub>

Ideal band alignment of common elementary metals to MoS<sub>2</sub>



Fermi level pinning below E<sub>c</sub>



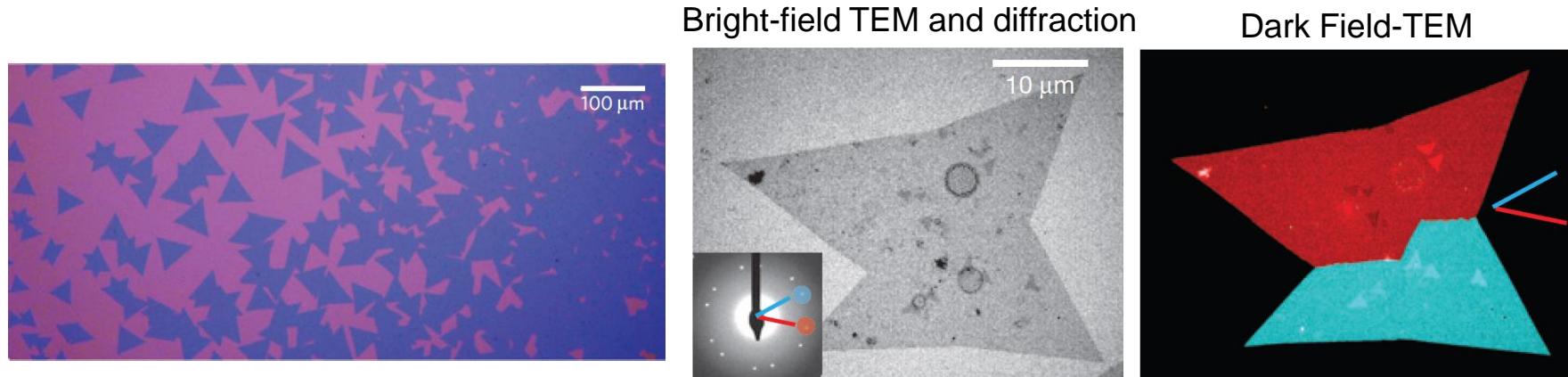
F. Giannazzo, E. Schilirò, G. Greco, F. Roccaforte, Conductive Atomic Force Microscopy of Semiconducting Transition Metal Dichalcogenides and Heterostructures, *Nanomaterials* **10**, 803 (2020)

P. Bampoulis, et al. Defect Dominated Charge Transport and Fermi Level Pinning in MoS<sub>2</sub>/Metal Contacts. *ACS Appl. Mater. Interfaces* **9**, 19278–19286 (2017).

S. Das, et al., High Performance Multi-layer MoS<sub>2</sub> Transistors with Scandium Contacts, *Nano Lett.* **13**, 100 (2013).

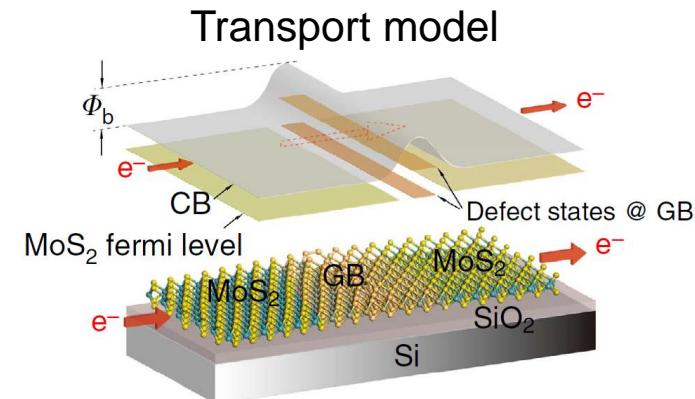
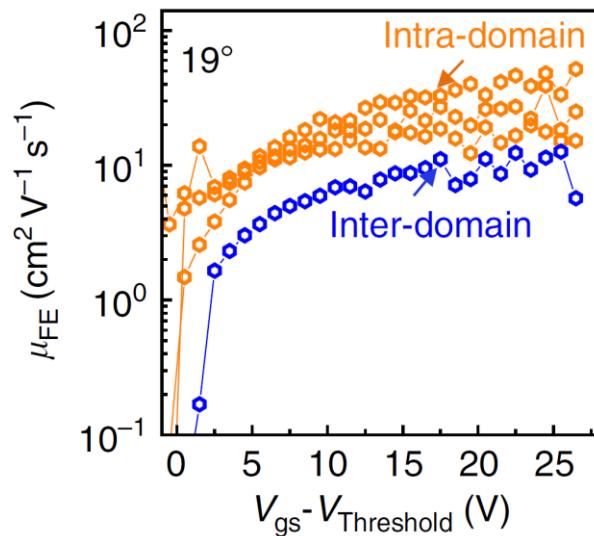
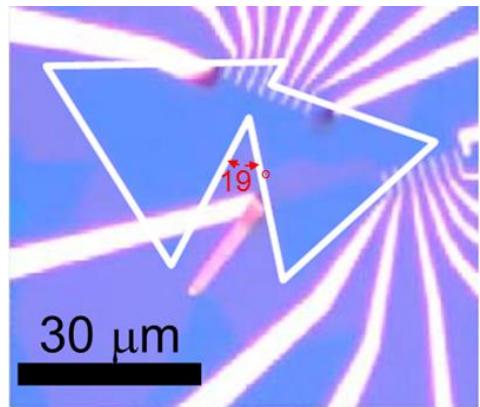
# Extended defects in CVD grown MoS<sub>2</sub>

2D polycrystalline material: grain boundaries (GBs)



A. M. van der Zande, et al., Grains and grain boundaries in highly crystalline monolayer molybdenum disulphide, *Nature Materials* 12, 554–561 (2013).

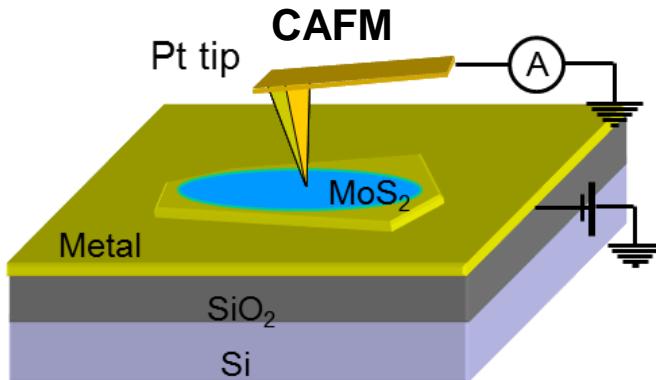
## Impact of GBs on the electronic transport in MoS<sub>2</sub> transistors



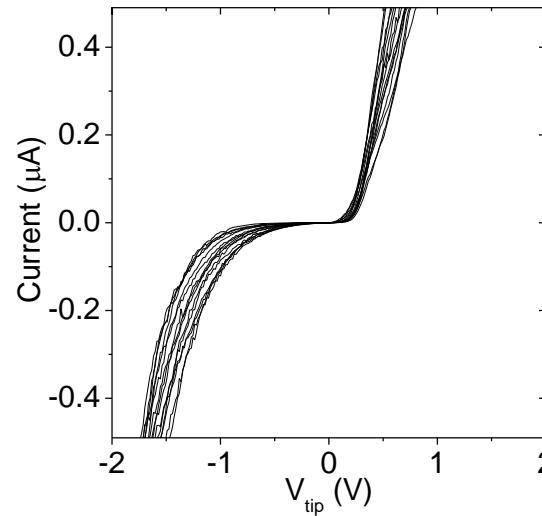
T. H. Ly, et al., Misorientation-angle-dependent electrical transport across molybdenum disulfide grain boundaries, *Nature Communications* 7, 10426 (2016).

# Nanoscale resolution electrical investigation of exfoliated and CVD MoS<sub>2</sub> by conductive atomic force microscopy (C-AFM)

# Nanoscale Schottky barrier distribution on exfoliated MoS<sub>2</sub> surface

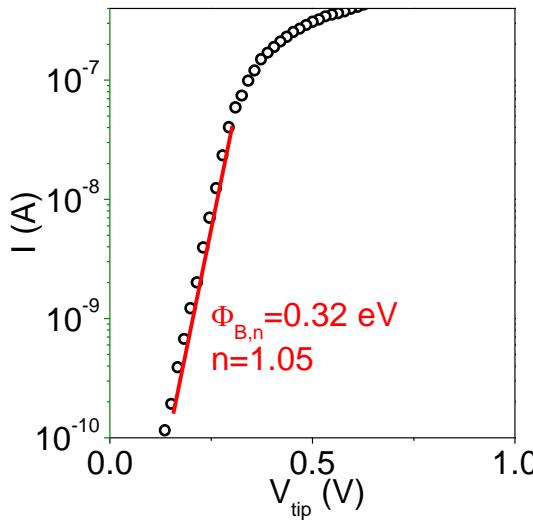


Array of 5x5 local I-V curves, 50 nm spacing

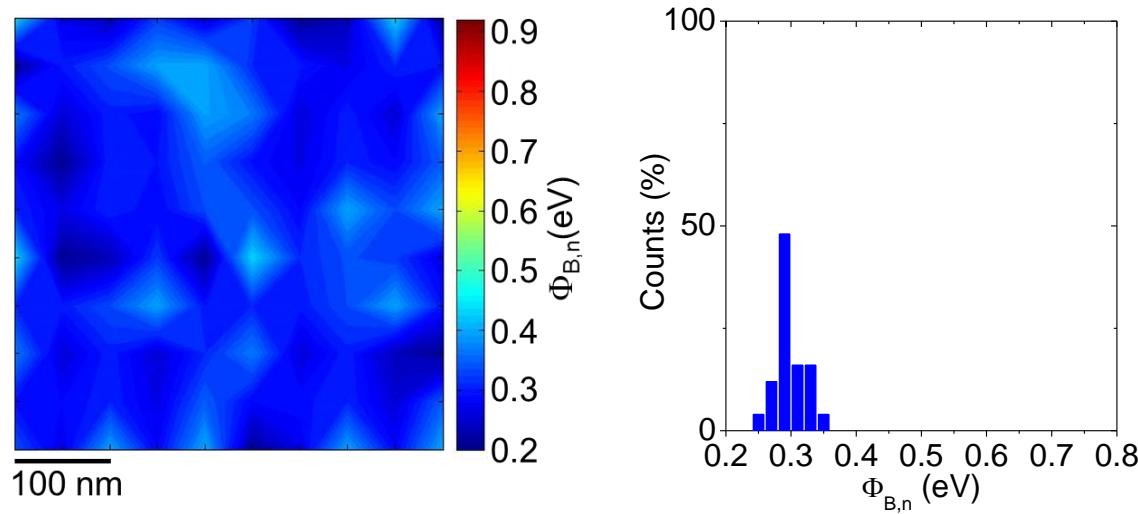


Evaluation of the local Schottky barrier height by thermionic emission model

$$I = A_{\text{tip}} A^* T^2 \exp\left(-\frac{\Phi_{B,n}}{kT}\right) \exp\left(\frac{qV_{\text{tip}}}{nkT}\right)$$

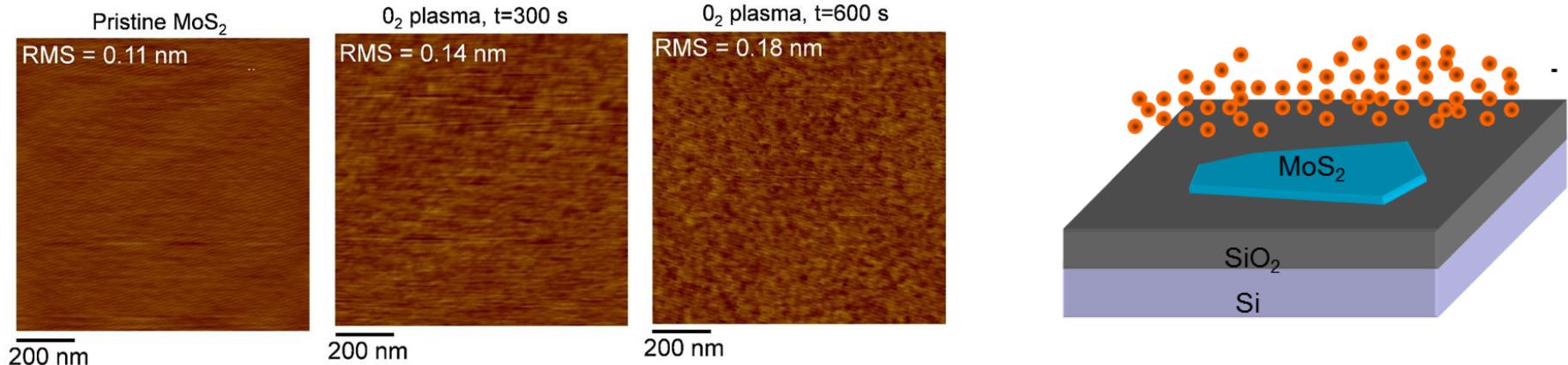


MoS<sub>2</sub> Schottky barrier map and histogram

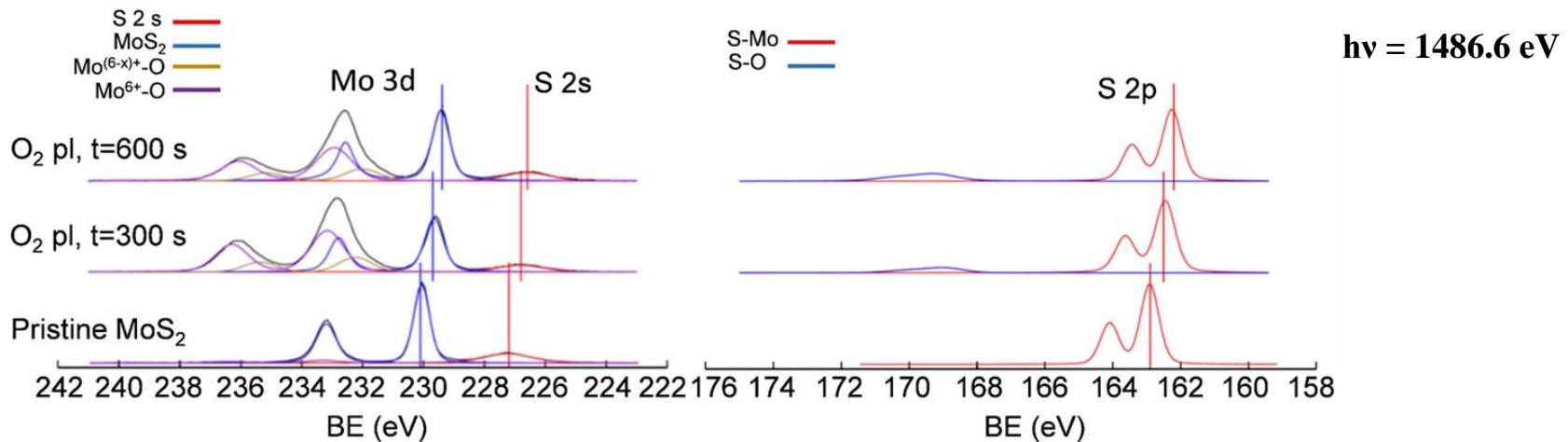


# Soft O<sub>2</sub> plasma functionalization of MoS<sub>2</sub> surface

Remote O<sub>2</sub> plasma source and no accelerating bias, to avoid physical etching of MoS<sub>2</sub>



XPS of pristine and O<sub>2</sub> functionalized MoS<sub>2</sub> surface

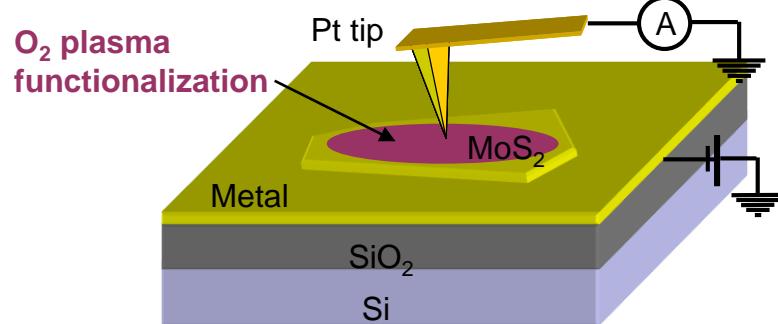


-Partial oxidation of the MoS<sub>2</sub> surface: Mo<sup>6+</sup> and substoichiometric Mo<sup>(6-x)+</sup> states

-Negative shift of S 2p, Mo 3d and S 2s peaks: Fermi level shift towards the valence band (MoS<sub>2</sub> p-type doping)

# Nanoscale investigation of Schottky barrier distribution: O<sub>2</sub> plasma functionalized MoS<sub>2</sub>

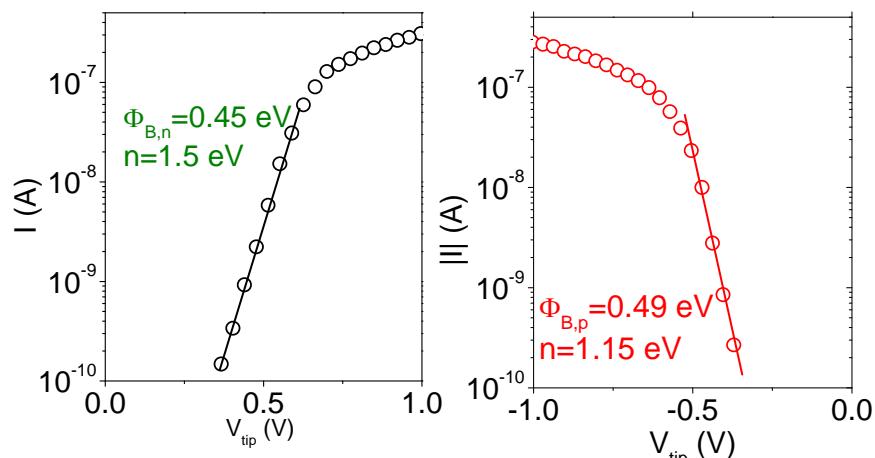
O<sub>2</sub> plasma, t=600 s



Thermionic emission model

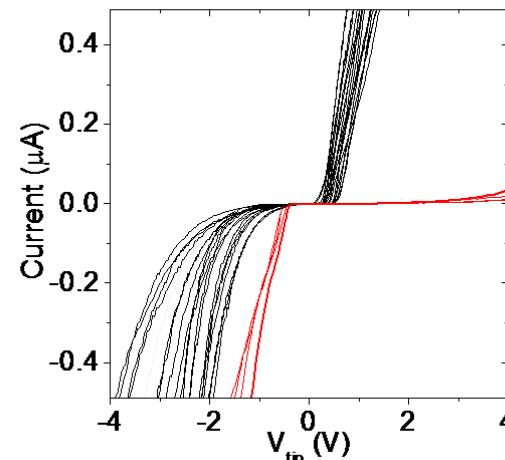
$$I = A_{tip} A^* T^2 \exp\left(-\frac{\Phi_{B,n}}{kT}\right) \exp\left(\frac{qV_{tip}}{nkT}\right)$$

$$I = A_{tip} A^* T^2 \exp\left(-\frac{\Phi_{B,p}}{kT}\right) \exp\left(-\frac{qV_{tip}}{nkT}\right)$$

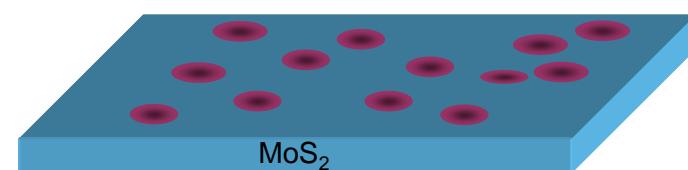
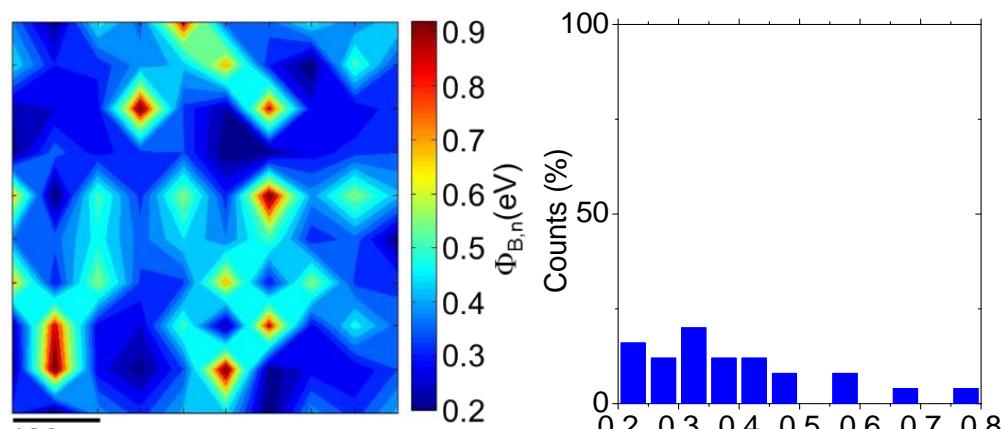
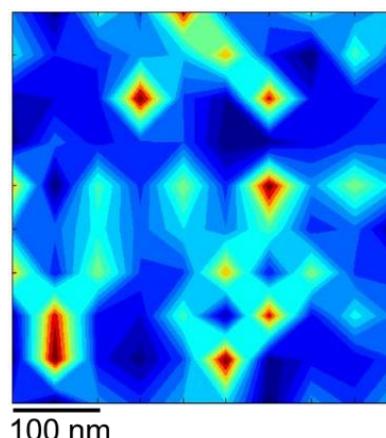
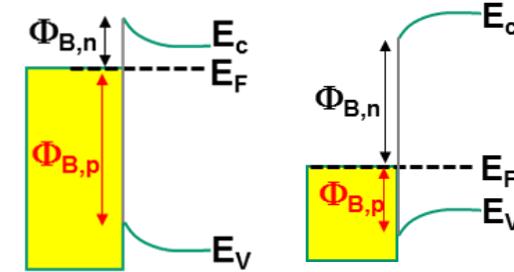


Inhomogeneous distribution of patches with low Schottky barrier height for holes (high for electrons)

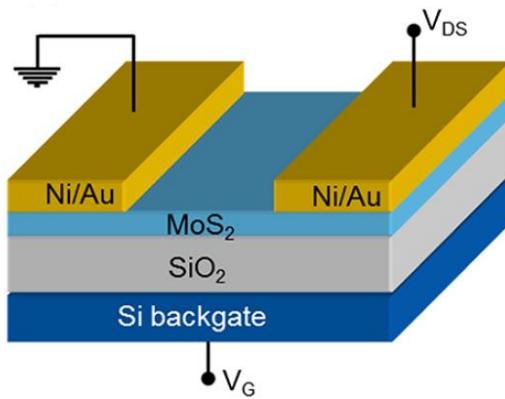
Array of 5x5 local I-V curves,  
50 nm spacing



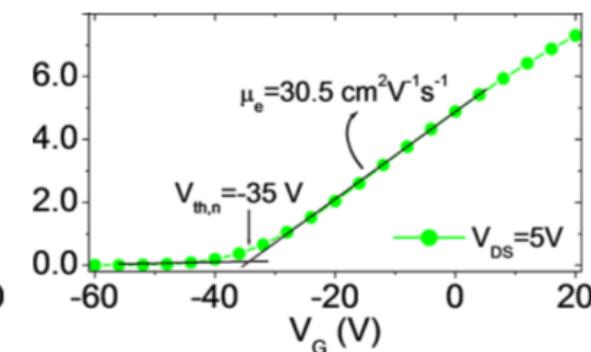
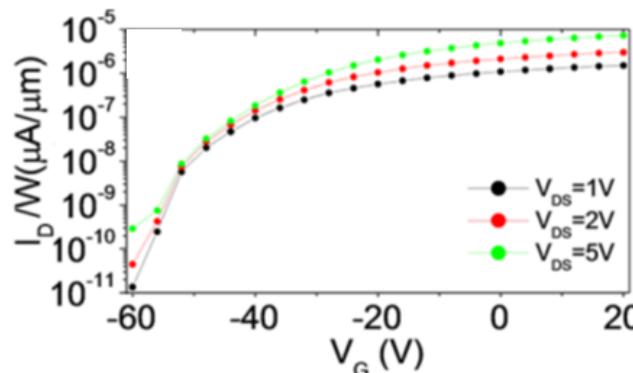
Both I-V curve shapes of Schottky contacts on n-type and p-type semiconductors



# Pristine MoS<sub>2</sub> field effect transistor

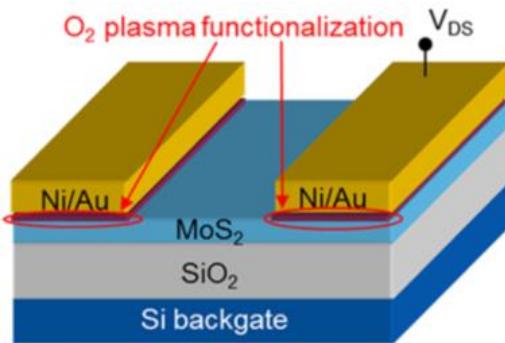


*Transfer characteristics n-type behavior*

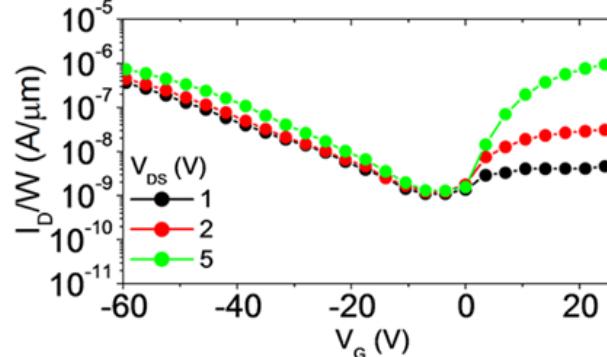


F. Giannazzo, et al., Phys. Status Solidi –RRL 10, 797 (2016)

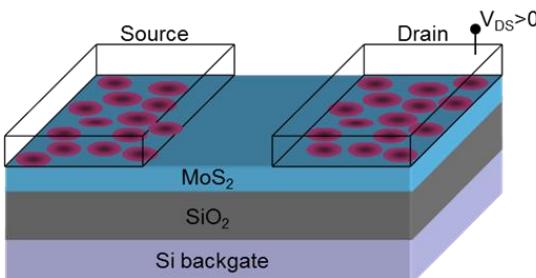
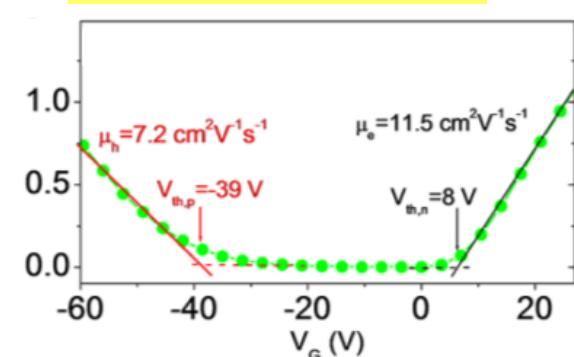
## MoS<sub>2</sub> FET with selective O<sub>2</sub> plasma functionalization under the contacts



*Transfer characteristics*



*Ambipolar behavior*

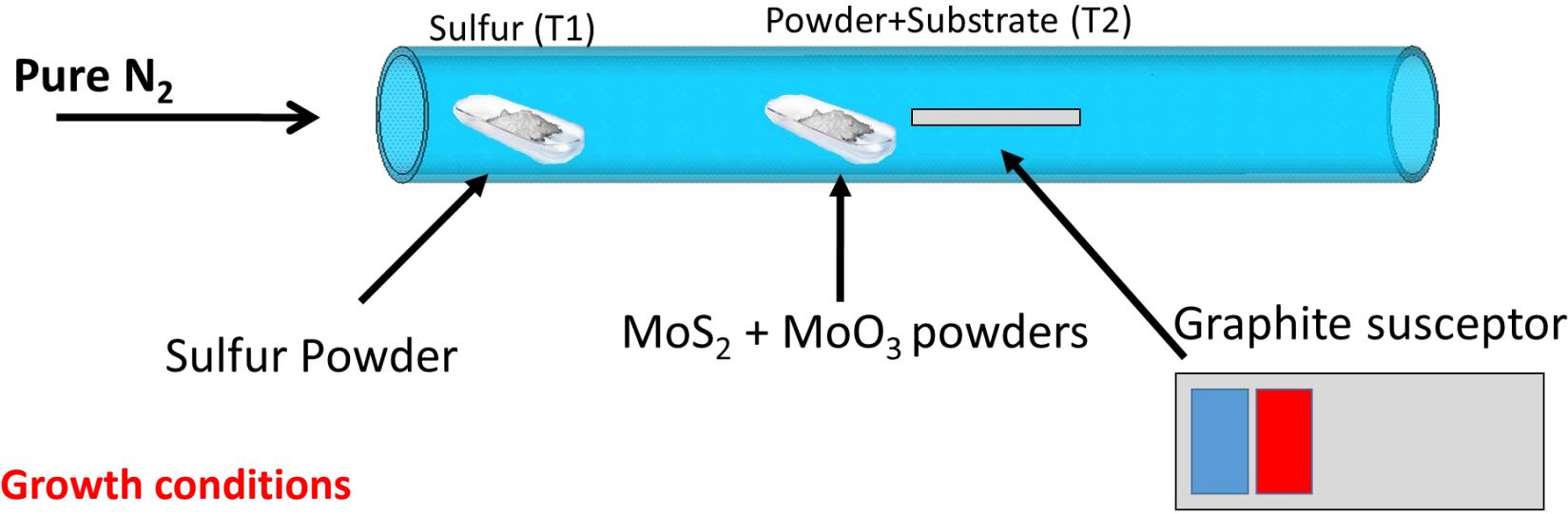


$V_G < 0$ : holes injection through p-type MoS<sub>2</sub> regions

$V_G > 0$ : electron injection through n-type MoS<sub>2</sub> regions

F. Giannazzo, et al., ACS Appl. Mater. Interfaces 9, 23164–23174 (2017).

# CVD growth of MoS<sub>2</sub> onto a SiO<sub>2</sub>/Si substrate



## Growth conditions

Sulfur T1=170°C

T2 = 785°C

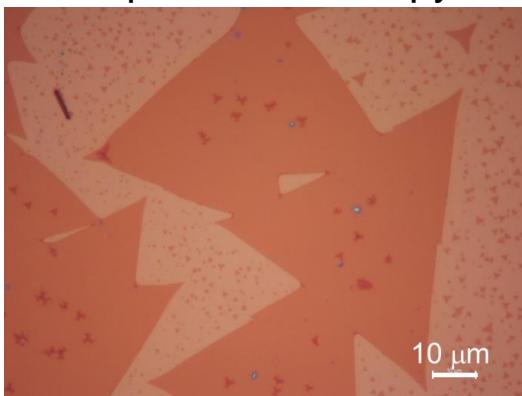
Flows= 3 sccm N<sub>2</sub>

Powders: 50 mg MoS<sub>2</sub> + 75 mg MoO<sub>3</sub> powders were placed in the quartz boat

Y. Okuno, O. Lancry, A. Tempez, C. Cairone, M. Bosi, F. Fabbri, M. Chaigneau, *Nanoscale* **10**, 14055-14059 (2018).

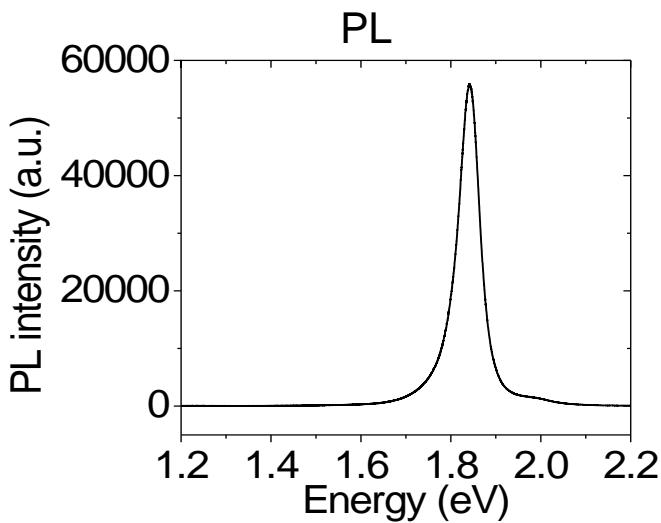
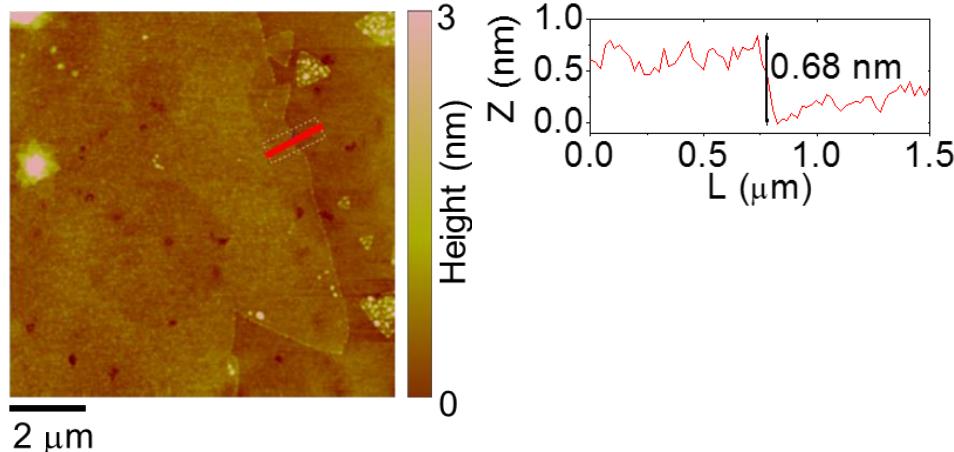
# Morphological and spectroscopic characterization

## Optical Microscopy

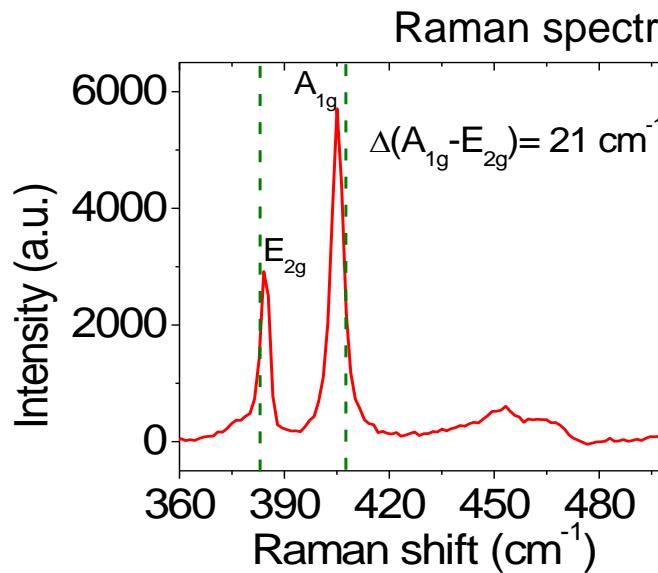


- Large triangular MoS<sub>2</sub> domains (up to 50 μm).
- Domains coalescence: presence of GBs

## Tapping mode AFM



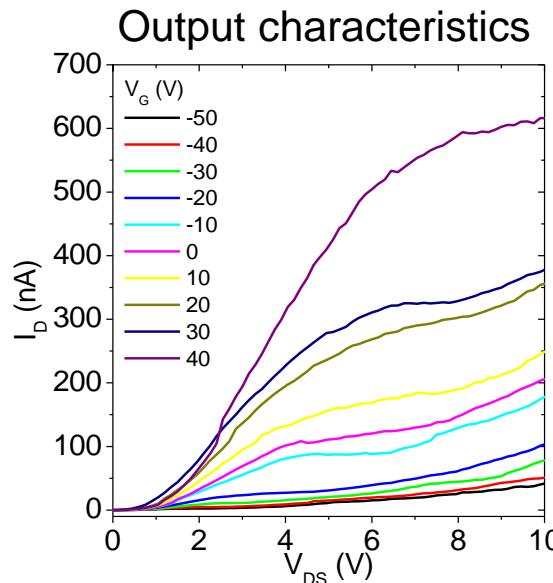
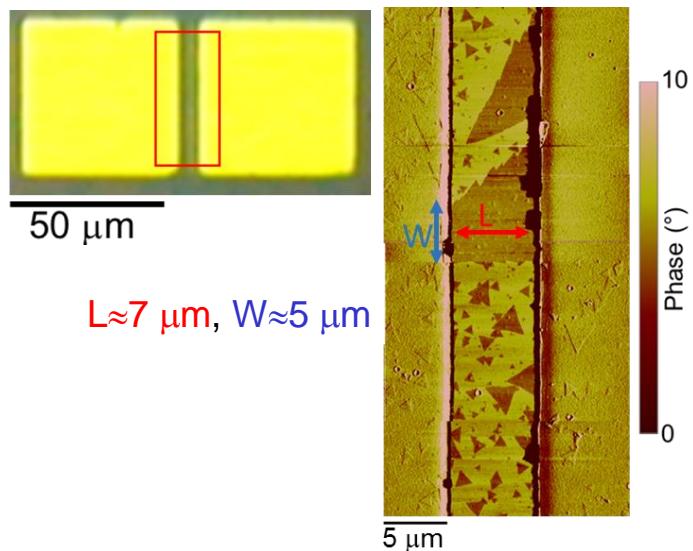
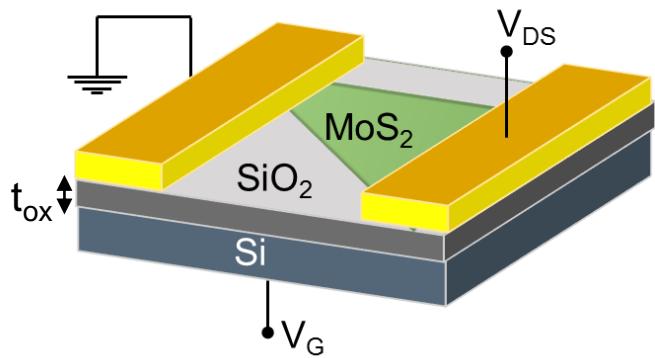
Strong emission at 1.85 eV: excitonic direct bandgap of MoS<sub>2</sub> monolayer



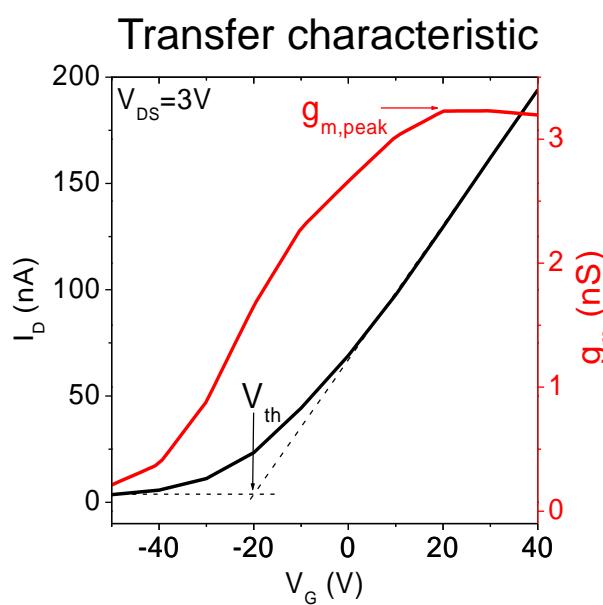
- E<sub>2g</sub> in-plane and A<sub>1g</sub> out-of-plane phonon modes of MoS<sub>2</sub>.
- Vertical dashed lines: nominal E<sub>2g</sub> and A<sub>1g</sub> positions for bulk MoS<sub>2</sub>.
- Wavenumber difference between the peaks' positions  $\Delta=21\text{ cm}^{-1}$ : mono- or bilayer MoS<sub>2</sub> domains



# Monolayer MoS<sub>2</sub> field effect transistor



- Linear behavior at intermediate  $V_{DS}$  values, followed by saturation at higher  $V_{DS}$ .
- Non-linear current onset at low bias ( $V_{DS} < 1$ ): high contact resistances to MoS<sub>2</sub>, due to the Schottky barrier at metal/MoS<sub>2</sub> interface



### Field effect mobility

$$\mu = \frac{L}{W} \frac{g_{m,peak}}{C_{ox} V_{DS}} = 0.12 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$$

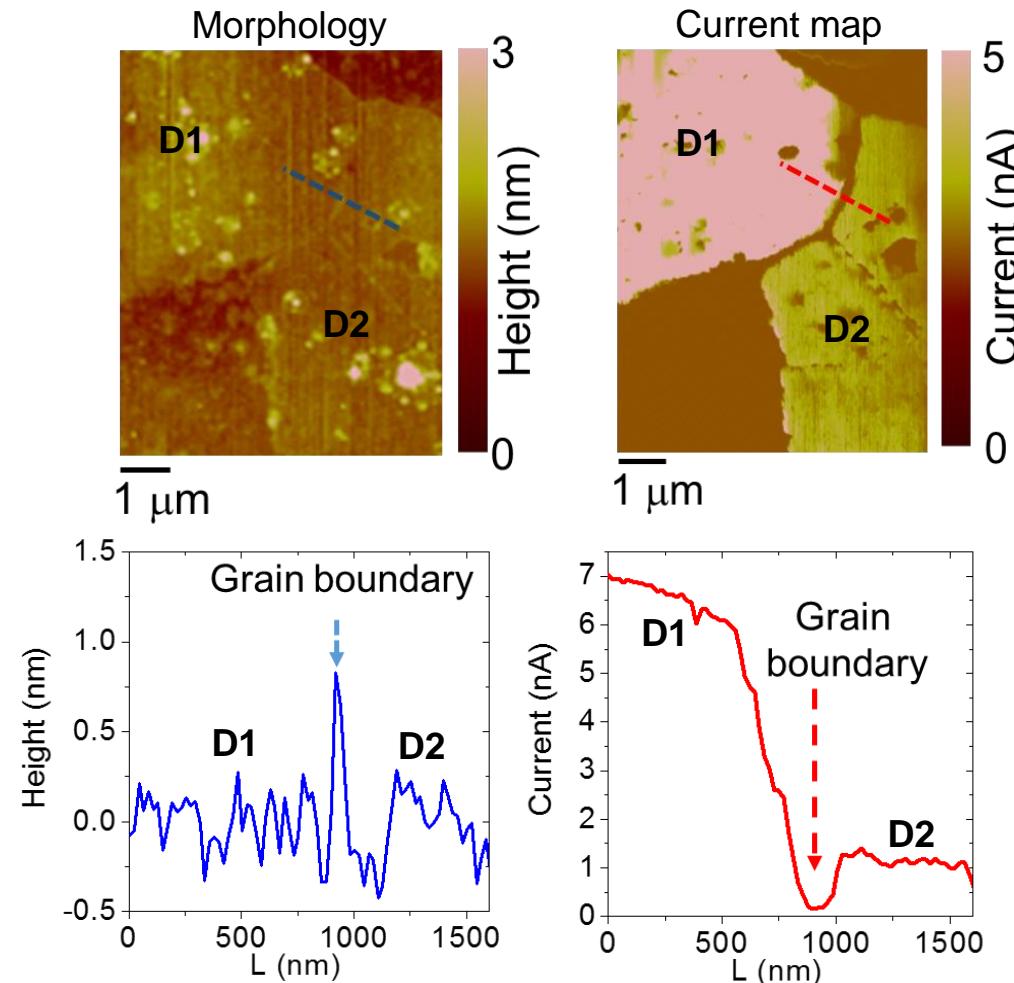
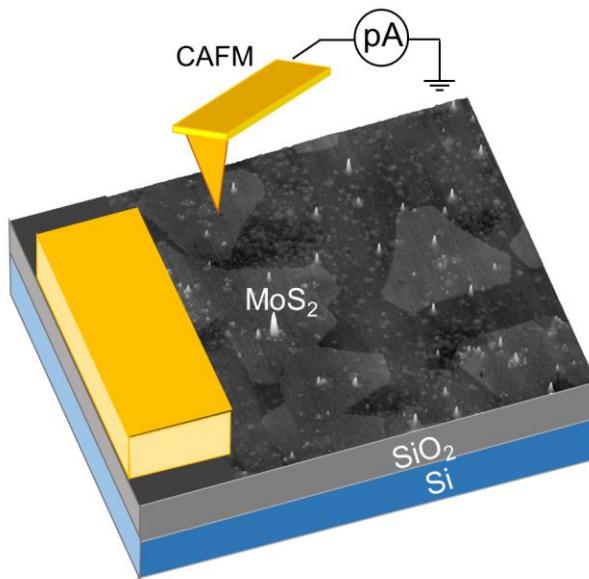
consistent with typical values  $\mu = 0.1 - 2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$  for 1L MoS<sub>2</sub> onto a SiO<sub>2</sub> substrate, without high-k dielectric capping.

B. Radisavljevic, et al. Nature Nanotechnol. 6, 147–150 (2011).

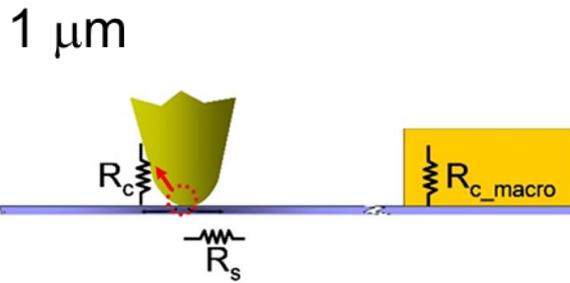
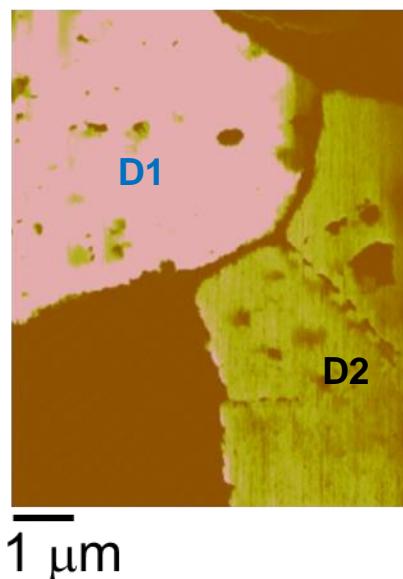
# Nanoscale current mapping by conductive atomic force microscopy (CAFM)

CAFM powerful tool to probe local current injection in 2D materials

F. Giannazzo, G. Greco, F. Roccaforte, C. Mahata, M. Lanza, *Conductive AFM of 2D Materials and Heterostructures for Nanoelectronics*, Chapter 10 of “Electrical Atomic Force Microscopy for Nanoelectronics”. Editor U. Celano. Springer Nature, 2019.

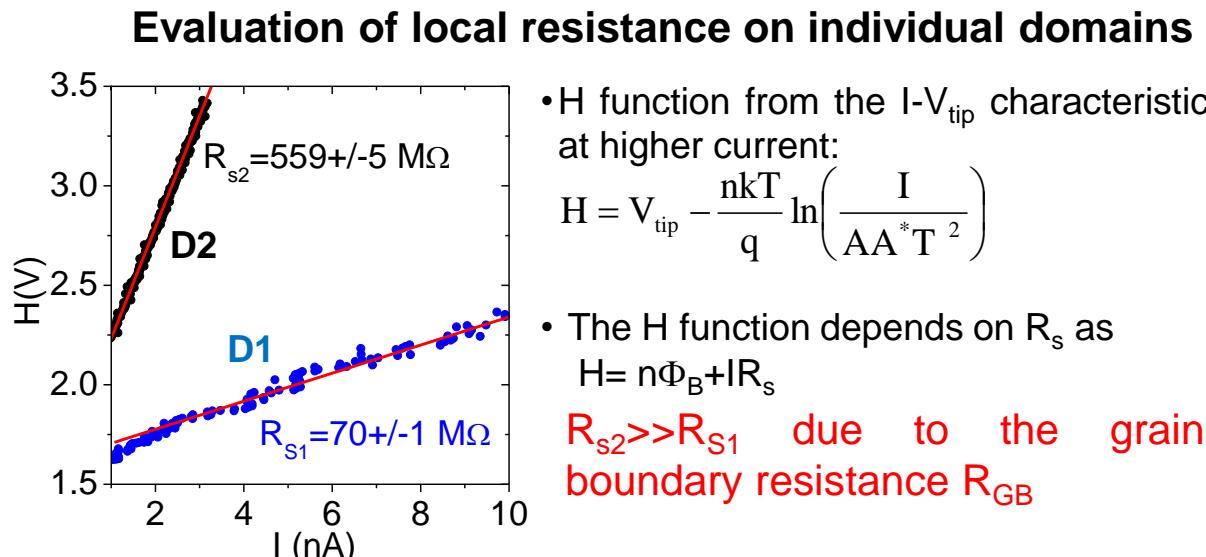
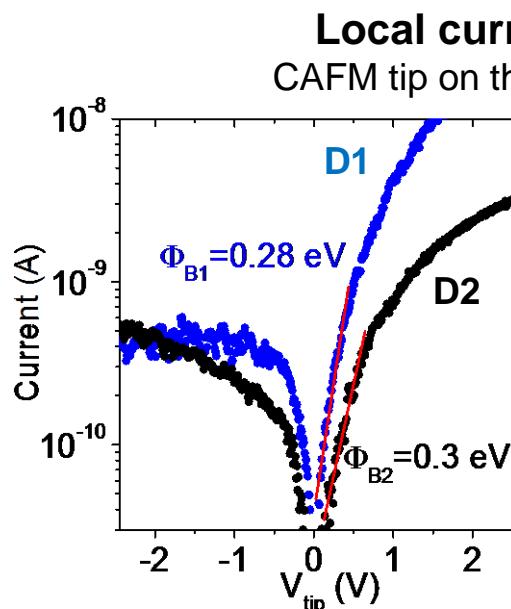


# Local Schottky barrier height and resistance within individual MoS<sub>2</sub> domains



F. Giannazzo, M. Bosi, F. Fabbri, E. Schilirò, G. Greco, F. Roccaforte,  
*Phys. Status Solidi RRL* **14**, 1900393  
(2019)

5  
Current (nA)  
0



# Summary

- Electronic properties of TMDs strongly affected by electrically active point and extended defect
- Conductive Atomic Force Microscopy powerful technique to investigate current injection mechanism in TMDs and lateral conductivity:
  - *Local Schottky barrier height mapping*
  - *Resistance contribution of grain boundaries in monolayer CVD MoS<sub>2</sub>*

## Acknowledgments



E. Schilirò, S. E. Panasci, G. Greco, I. Deretzis, G. Nicotra, A. La Magna, R. Lo Nigro, P. Fiorenza, F. Roccaforte, C. Spinella



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