Electronic, Thermal, and Unconventional (?) Applications of 2D Materials

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http://poplab.stanford.edu

Acknowledgements

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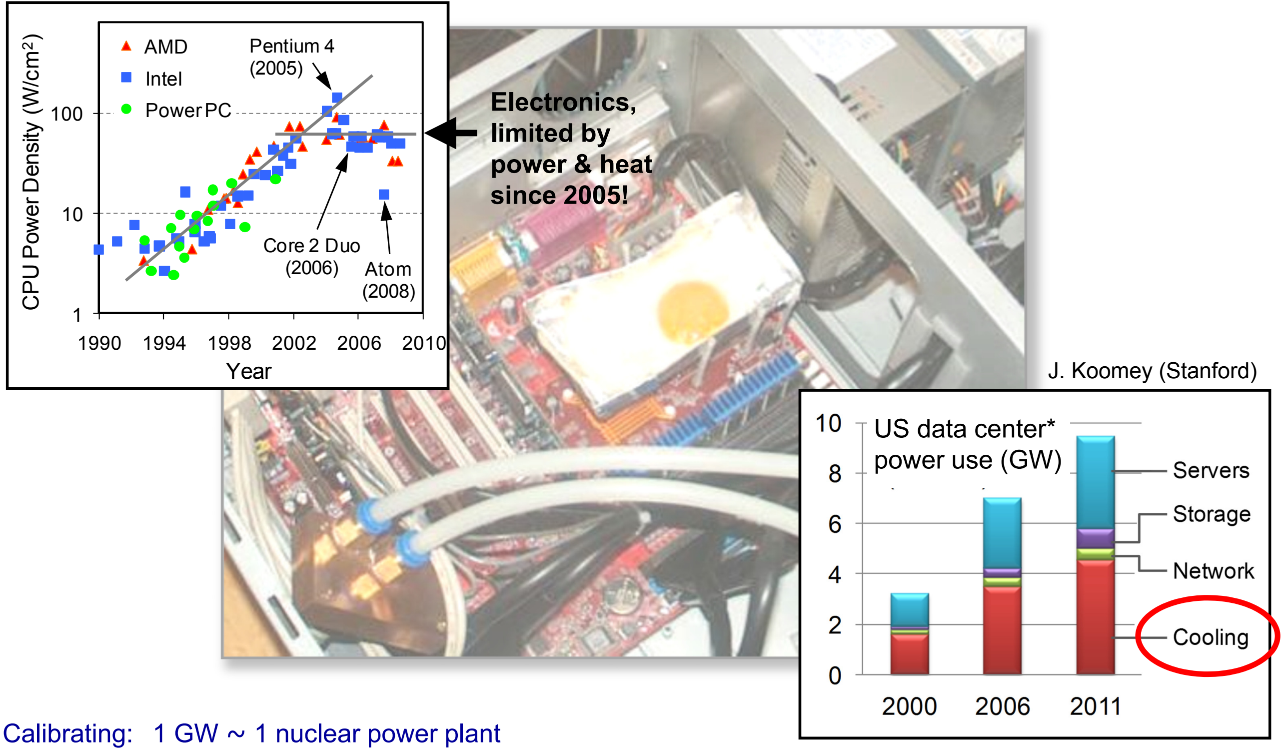
Electronics Use (and Waste) Much Power

E. Pop, *Nano Research* 3, 147 (2010)
new course: Energy in Electronics, EE 323



Electronics, limited by power & heat since 2005!

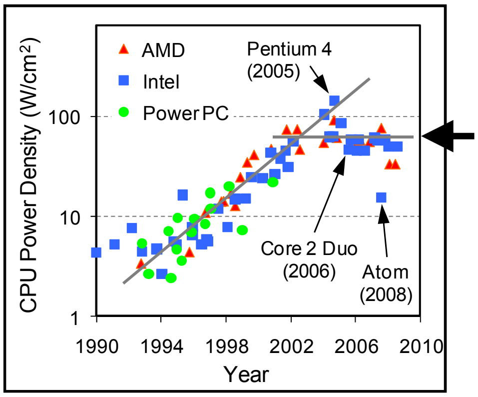
J. Koomey (Stanford)

Calibrating: 1 GW ~ 1 nuclear power plant
12 GW ~ all electricity used by Argentina

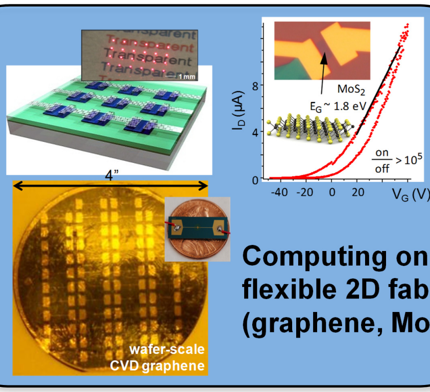
*World-Wide about 30 GW

Pop Lab: Energy and Electronics

Review: E. Pop, *Nano Research* 3, 147 (2010); new course: EE 323 “Energy in Electronics” at Stanford



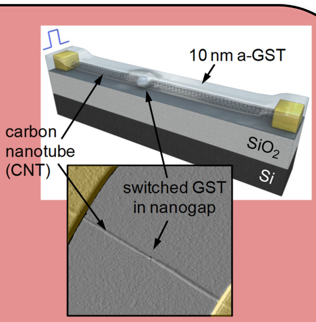
Electronics, limited by power & heat since 2005!



Computing on flexible 2D fabrics (graphene, MoS_2)

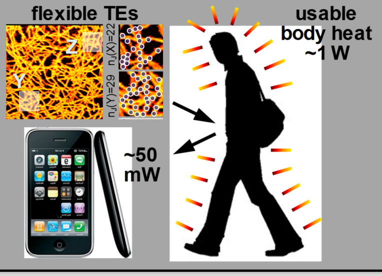
Energy-efficient data storage:

100x lower power in phase-change memory (PCM)



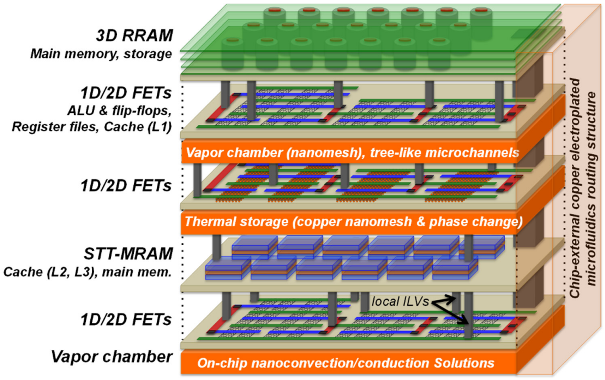
Xiong et al, *Science* (2011)

Energy harvesting: up to ~1 W from body heat using flexible thermoelectrics (TE)



What's Driving the 2D Work at Stanford?

- Heterogeneous Integration (HI) in SystemX Alliance
- Integration of "beyond-Si" platforms for "beyond Moore" applications
  - **3D integration** of logic, memory, sensors, thermal management, flexible substrates…
  - **Energy-efficient** design and energy-harvesting opportunities



M. Aly et al. *IEEE Computer* 48, 24 (2015)

Going 3D…

- Collaborators: Y. Cui, D. Goldhaber-Gordon, K. Goodson, T. Heinz, A. Lindenberg, Y. Nishi, E. Pop, E. Reed, A. Salleo, K. Saraswat, H.-S.P. Wong, X. Zheng

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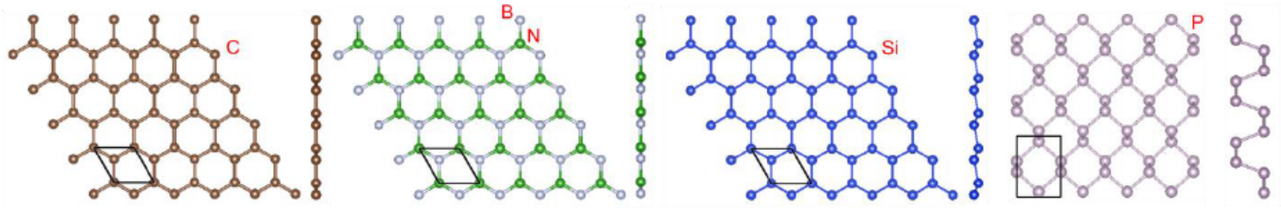
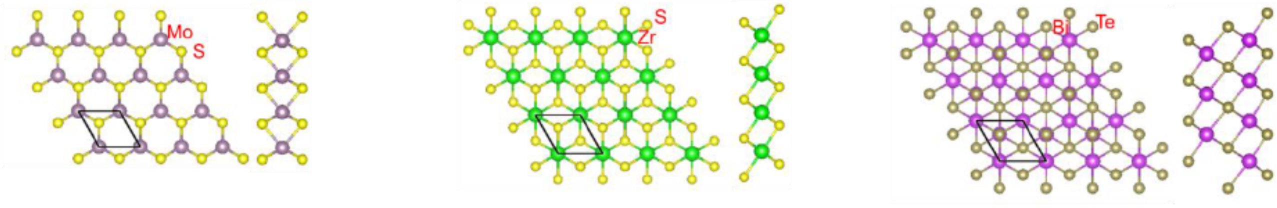
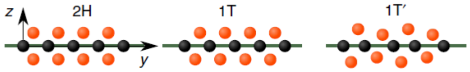
Atomic Structure of Some 2D Materials


(a) graphene (b) Boron nitride (c) silicene (d) Black phosphorus


(e) 2H transition metal dichalcogenides: MoS_2 (f) 1T transition metal dichalcogenides: ZrS_2 (g) Bismuth telluride

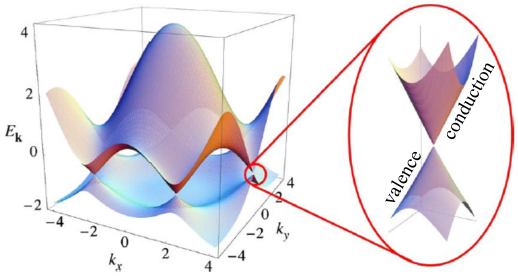
- 2D lattices can be planar (graphene, BN), buckled (Xenes), 1T, 2H, 3R
- Transition metal dichalchogenides (TMDs) are 2H or 1T$^{(')}$
- Phase change 2H (semic.) to 1T or 1T' (metallic) by ΔT, strain or Li interc.

M. Chhowalla et al., *Nat. Chem.* **5**, 263 (2013)
Duerloo et al., *Nat. Comm.* **5**, 4214 (2014)

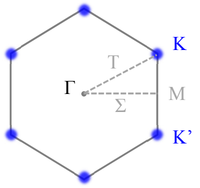


Electronic Band Structure of 2D Materials

graphene: semimetal



Castro-Neto, Rev. Mod. Phys. (2009)

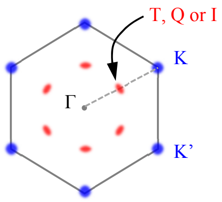


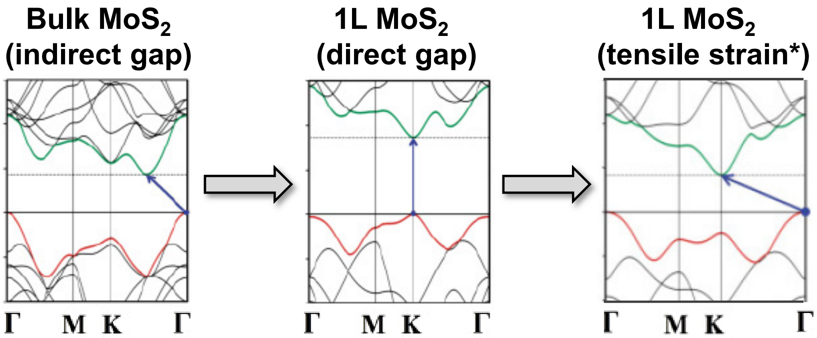
$E = \hbar v_F k$

$v_F \approx 10^8$ cm/s

K = K' degeneracy

MX$_2$ TMDs




Bulk MoS$_2$ (indirect gap)

1L MoS$_2$ (direct gap)

1L MoS$_2$ (tensile strain*)

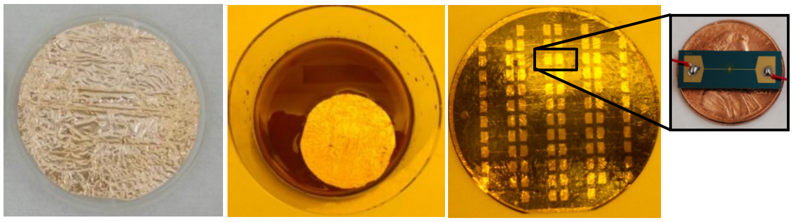
K = 2x degenerate

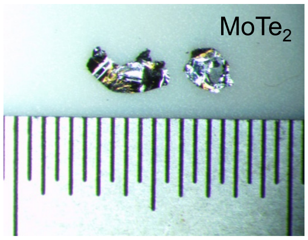
Q = 6x degenerate (along <u>T line</u>, sometimes mislabeled Σ or Λ)

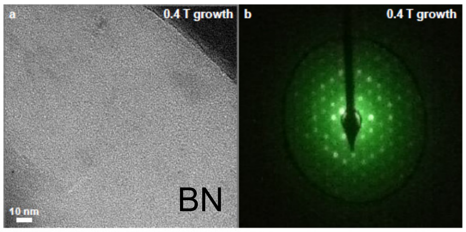
(*less is known about strain)

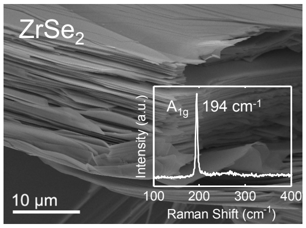
2D Materials at Stanford

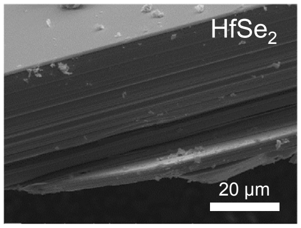
CVD growth of <u>monolayer</u> graphene, BN and MoS$_2$

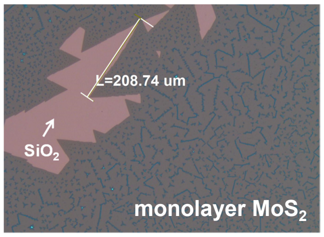


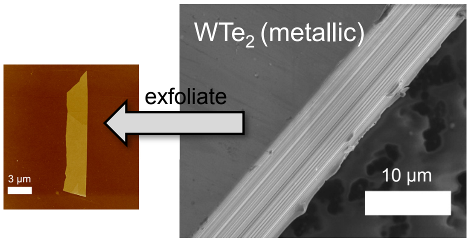


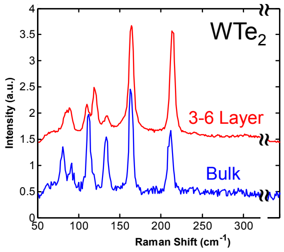






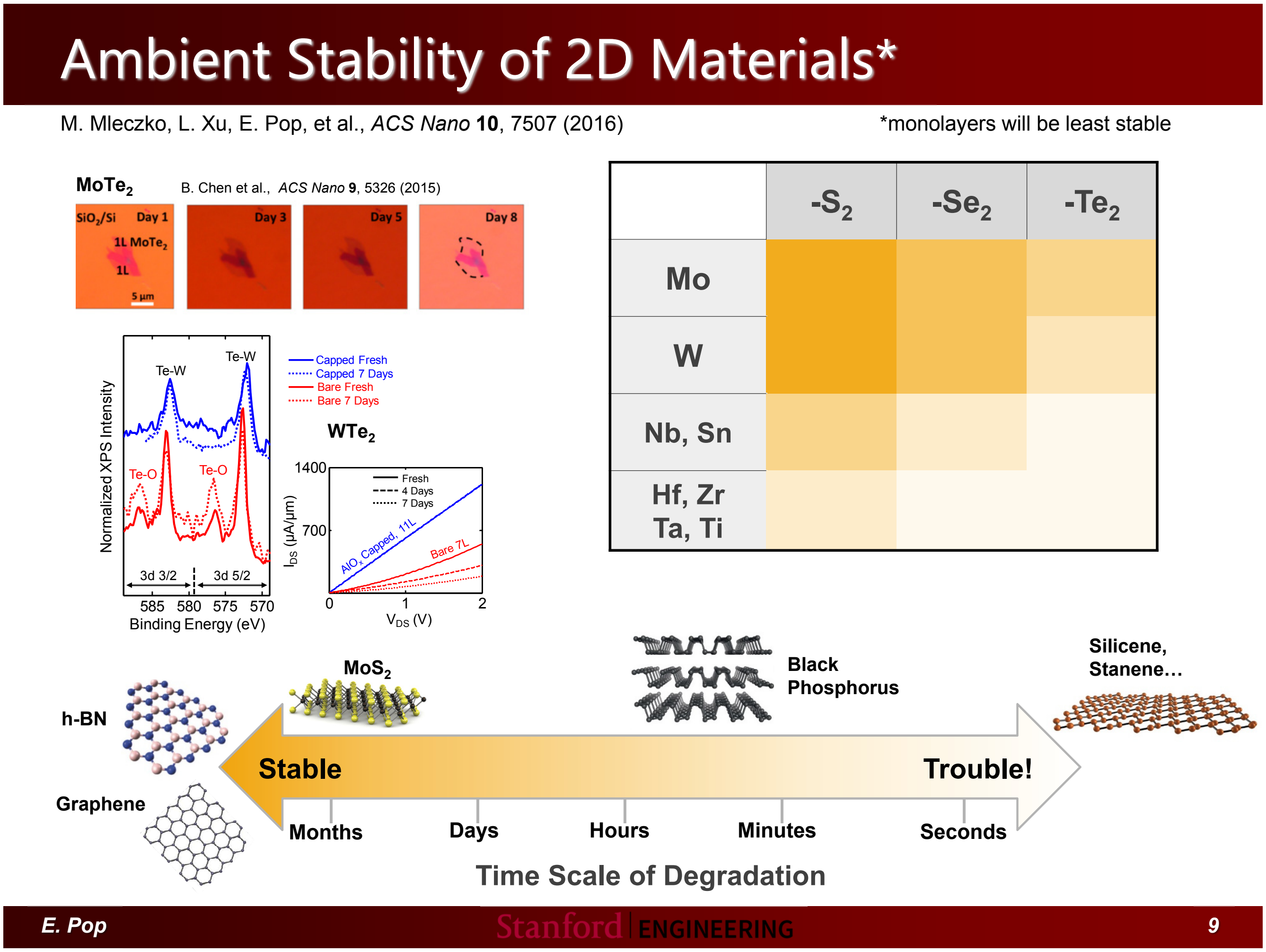






E. Pop, H.-S.P. Wong, Y. Nishi, I. Fisher

CVT growth of MoTe$_2$, WTe$_2$, ZrSe$_2$, HfSe$_2$



Ambient Stability of 2D Materials*

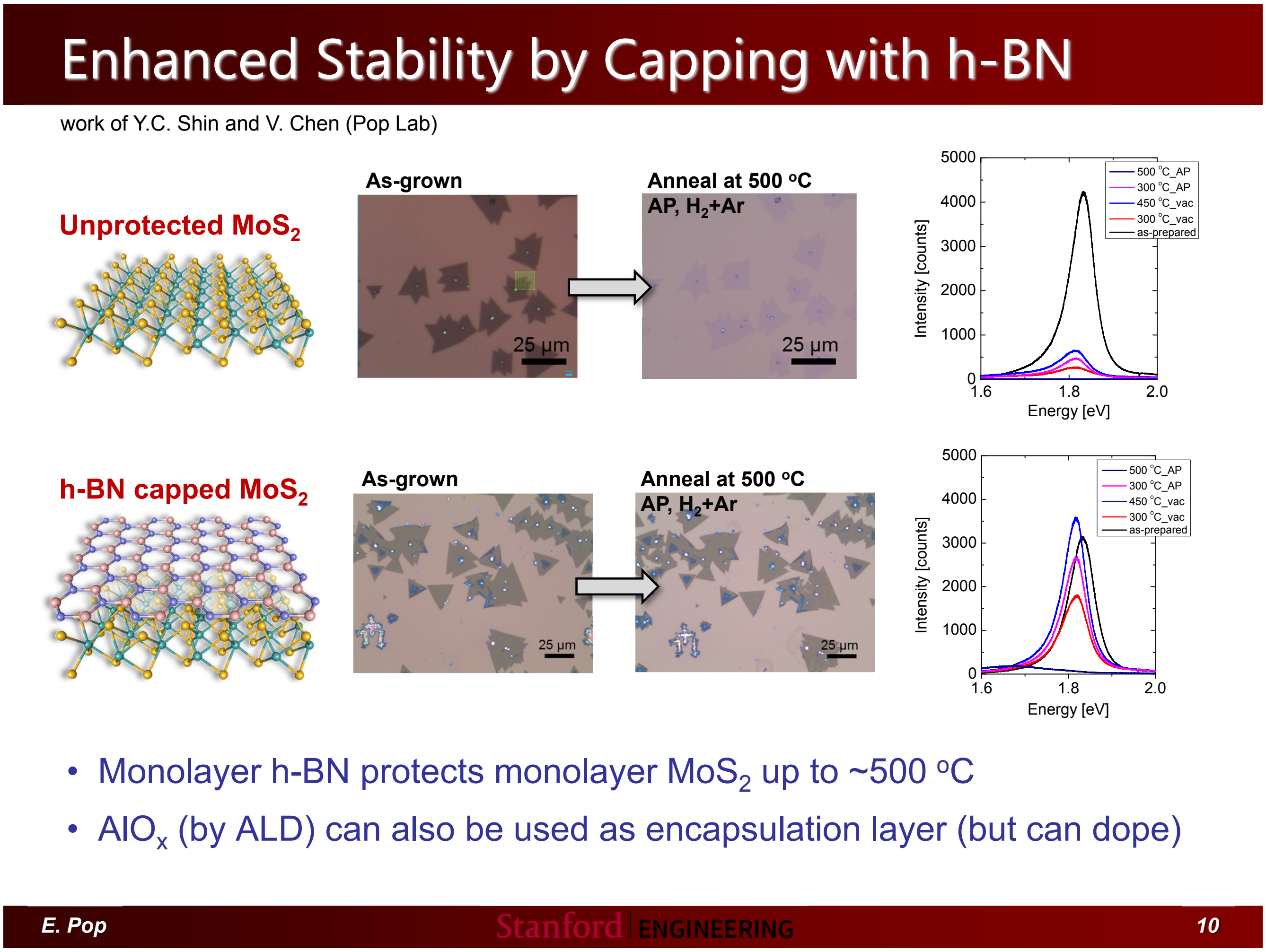
M. Mleczko, L. Xu, E. Pop, et al., *ACS Nano* **10**, 7507 (2016)

*monolayers will be least stable

$MoTe_2$ B. Chen et al., *ACS Nano* **9**, 5326 (2015)

	$-S_2$	$-Se_2$	$-Te_2$
Mo	█	█	▓
W	█	█	▒
Nb, Sn	▓	▒	░
Hf, Zr Ta, Ti	▒	░	░

Time Scale of Degradation



Enhanced Stability by Capping with h-BN

work of Y.C. Shin and V. Chen (Pop Lab)

Unprotected MoS_2

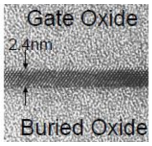
h-BN capped MoS_2

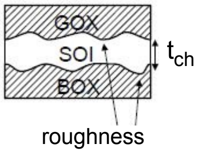
- Monolayer h-BN protects monolayer MoS_2 up to ~500 °C
- AlO_x (by ALD) can also be used as encapsulation layer (but can dope)

Transistors Beyond Silicon?

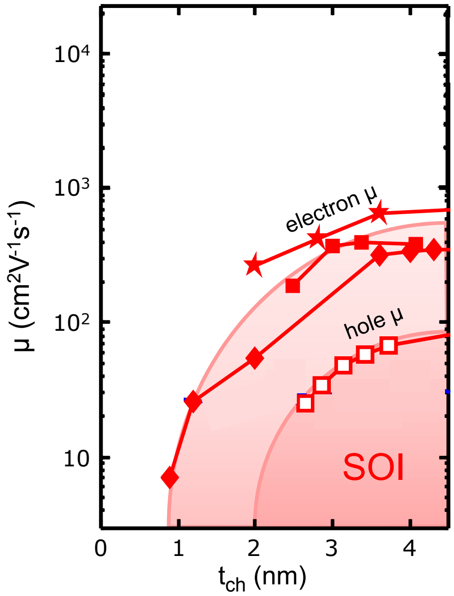
- **Problem:** 20th century transistors “carved” out of bulk materials (Si) → surface roughness restricts mobility, band gap, variability

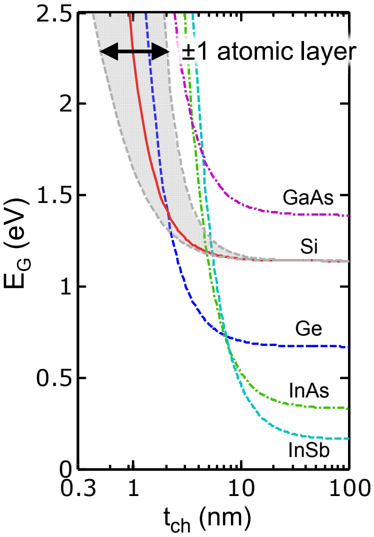
3D





Uchida & Takagi, *APL* 2003





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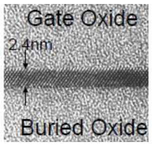
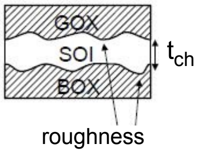
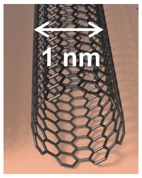
3D



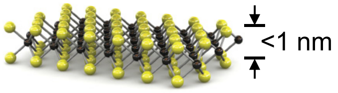


- **Solution?** 21st century atomically thin materials

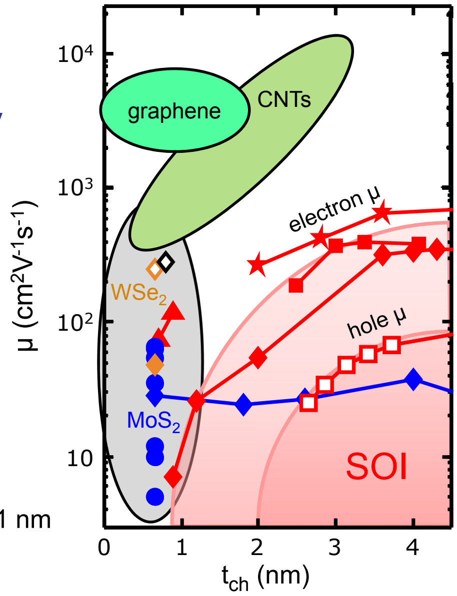
1D carbon nanotube (CNT)

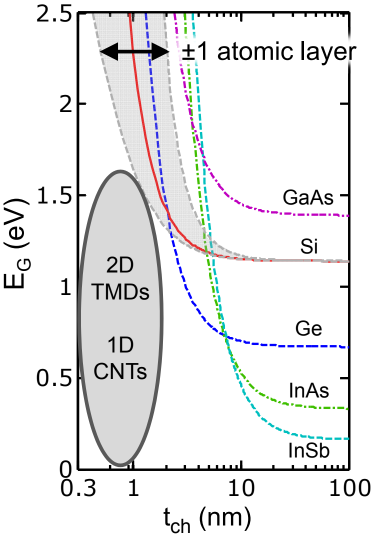


2D TMD (MoS_2, WTe_2, $ZrSe_2$)

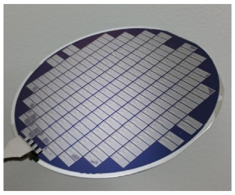


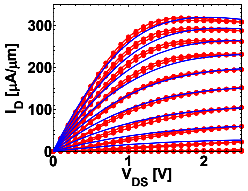
C. English, E. Pop, et al., *Nano Lett.* **16**, 3824 (2016)

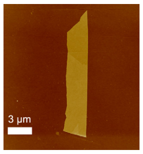


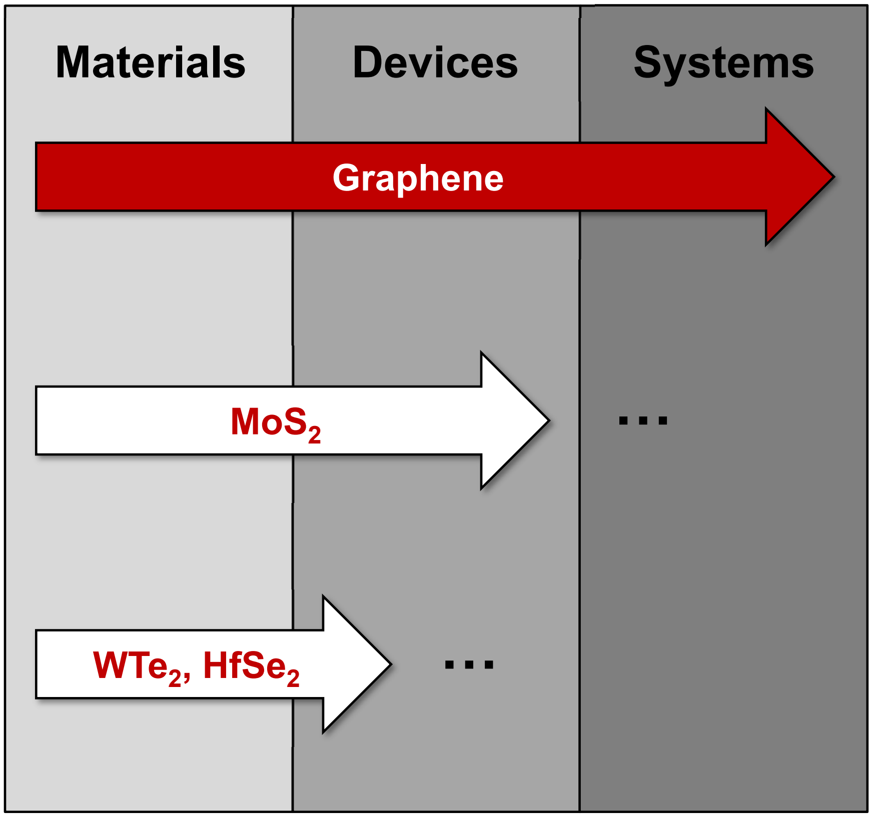


2D Materials to Systems (Today)









Materials

Devices

Systems

Graphene

MoS_2

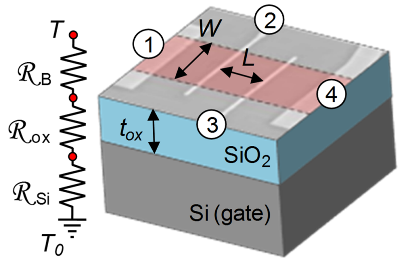
…

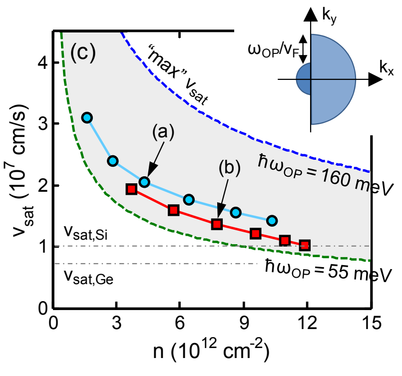
WTe_2, $HfSe_2$

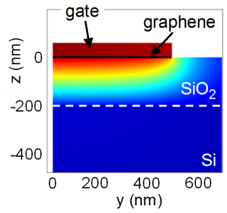
…

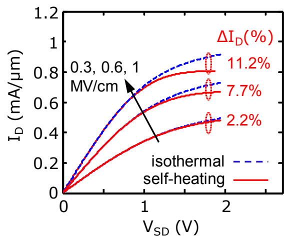
Early Work: Graphene Device Transport

V. Dorgan, M.-H. Bae, E. Pop, *Appl. Phys. Lett.* **97**, 082112 (2010)
S. Islam, Z. Li, V.E. Dorgan, M.-H. Bae, E. Pop, *IEEE EDL* **34**, 166 (2013)









$$\Delta T = T - T_0 \approx P\left(\mathcal{R}_B + \mathcal{R}_{ox} + \mathcal{R}_{Si}\right)$$

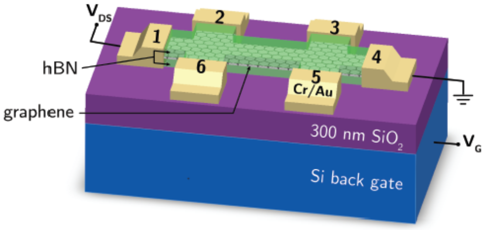
$$v_{sat}(n,T) = \frac{2}{\pi}\frac{\omega_{OP}}{\sqrt{\pi n}}\sqrt{1-\frac{\omega_{OP}^2}{4\pi n v_F^2}}\frac{1}{N_{OP}+1}$$

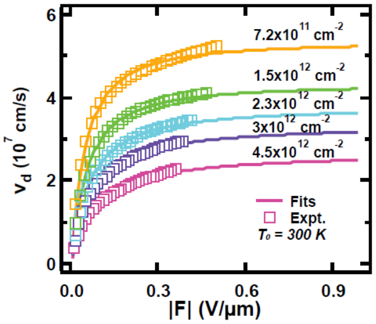
- Lack of transport studies* at T > 300 K and high-field v_{sat} (>1 V/µm)
- High-field **saturation velocity** (measurement needs constant field)
- Extracted practical electrical and thermal **compact models**

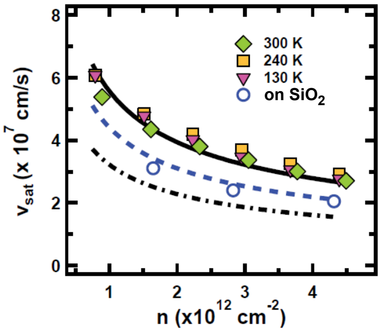
*at the time

Today: Record Drift Velocity in Graphene-hBN

M. Yamoah, W. Yang, E. Pop, D. Goldhaber-Gordon, *ACS Nano*, DOI:10.1021/acsnano.7b03878 (2017)





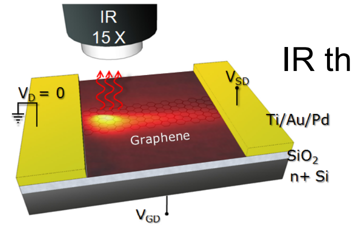


$$\Delta T = T - T_0 \approx P\left(\mathcal{R}_{BN} + \mathcal{R}_B + \mathcal{R}_{ox} + \mathcal{R}_{Si}\right) \qquad v_{sat}(n,T) = \frac{2}{\pi}\frac{\omega_{OP}}{\sqrt{\pi n}}\sqrt{1 - \frac{\omega_{OP}^2}{4\pi n v_F^2}}\frac{1}{N_{OP}+1}$$

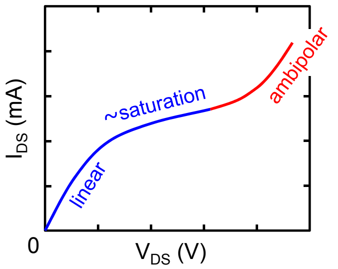
- Ultra-high quality hBN-graphene-hBN → μ ~ 50 to 100 x 10^3 $cm^2/V/s$
- Velocity saturation achieved at (relatively) low fields ≥ 0.2 V/μm
- hBN surface phonons ~100 meV → **record v_{sat} = 3 to 6 x 10^7 cm/s**

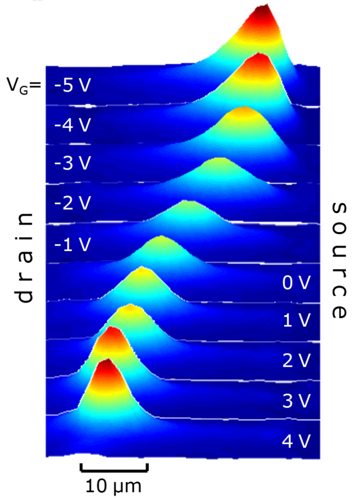
Early Work: Thermal Imaging Graphene FETs

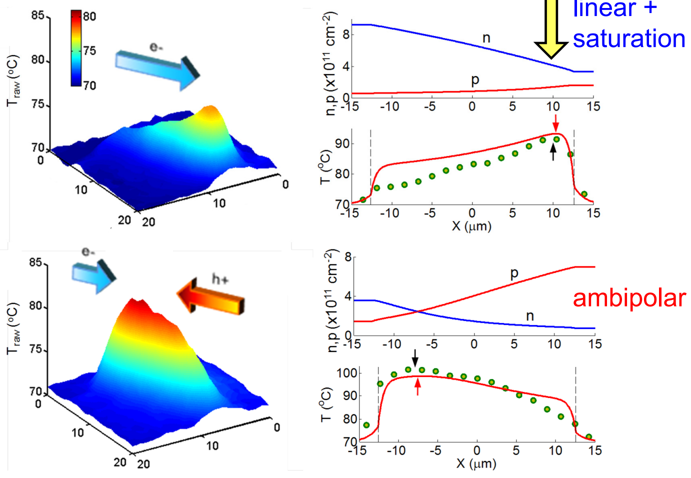
M.-H. Bae, Z.-Y. Ong, D. Estrada, E. Pop, *Nano Letters* **10**, 4787 (2010)
M.-H. Bae, S. Islam, V.E. Dorgan, E. Pop, *ACS Nano* **5**, 7936 (2011)



IR thermal imaging

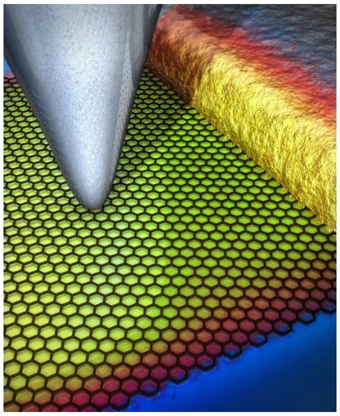




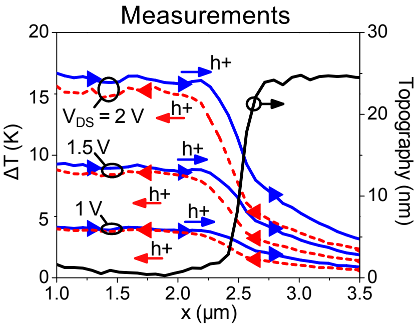


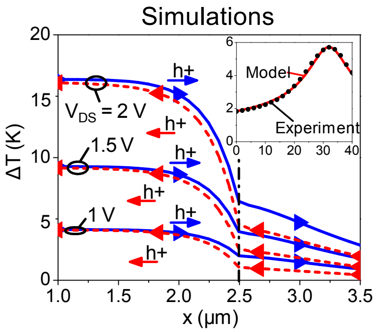
Thermoelectric Effects at Graphene Contacts

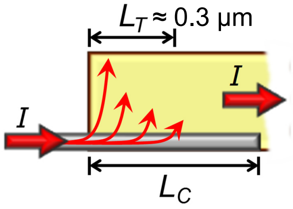
K. Grosse, M.-H. Bae, F. Lian, E. Pop, W. King, *Nature Nanotechnology* 6, 287 (2011)



scanning Joule expansion microscopy (SJEM)







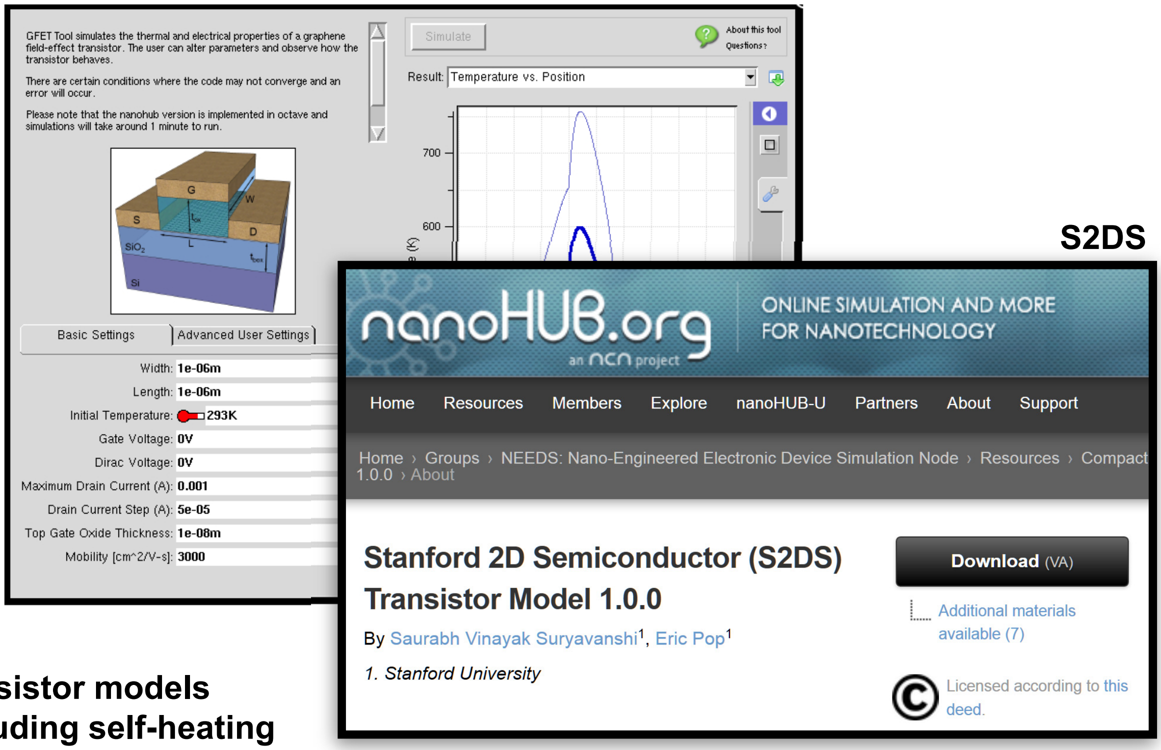
- AFM-based thermometry (SJEM)
- Contact temperature due to:
  - Current crowding (CC) } 2/3
  - **Thermoelectric effect (TE)** } **1/3**
- Some 2D materials have large thermopower S
  - Engineer cooling at device contacts?
  - Design built-in TE coolers?

Simulation Tools Available Online

available on http://nanoHUB.org

GFET Tool

S2DS



GFET Tool simulates the thermal and electrical properties of a graphene field-effect transistor. The user can alter parameters and observe how the transistor behaves.

There are certain conditions where the code may not converge and an error will occur.

Please note that the nanohub version is implemented in octave and simulations will take around 1 minute to run.

Result: Temperature vs. Position

Width: 1e-06m
Length: 1e-06m
Initial Temperature: 293K
Gate Voltage: 0V
Dirac Voltage: 0V
Maximum Drain Current (A): 0.001
Drain Current Step (A): 5e-05
Top Gate Oxide Thickness: 1e-08m
Mobility [cm^2/V-s]: 3000

Stanford 2D Semiconductor (S2DS) Transistor Model 1.0.0

By Saurabh Vinayak Suryavanshi[1], Eric Pop[1]

1. Stanford University

Licensed according to this deed.

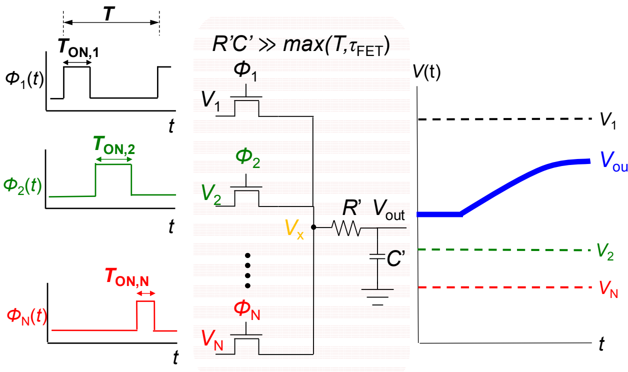
transistor models including self-heating

Today: Graphene-Based *Systems*

N. Wang, S. Gonugondla, I. Nahlus, N. Shanbhag, E. Pop, *VLSI Symp.* (2016)

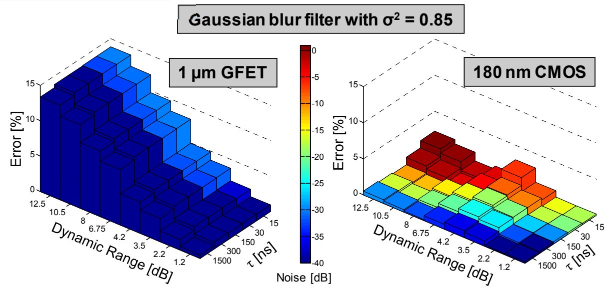
- **Dot product** nanofunction used for image processing, neural networks…
- Takes advantage of native graphene properties (**high μ**, flexible…)
- Tolerates graphene drawbacks (low I_{ON}/I_{OFF} ratio)

Idea:



switched analog circuit (SAC)
weights encoded by pulse widths $p_i T$

Simulation:



1 µm GFET	180 nm CMOS
+ Fast	+ High accuracy
+ Smaller area	+ Wide input range
+ Low noise	- Slow and noisy
- Narrow input range (due to low I_{ON}/I_{OFF})	- Larger area

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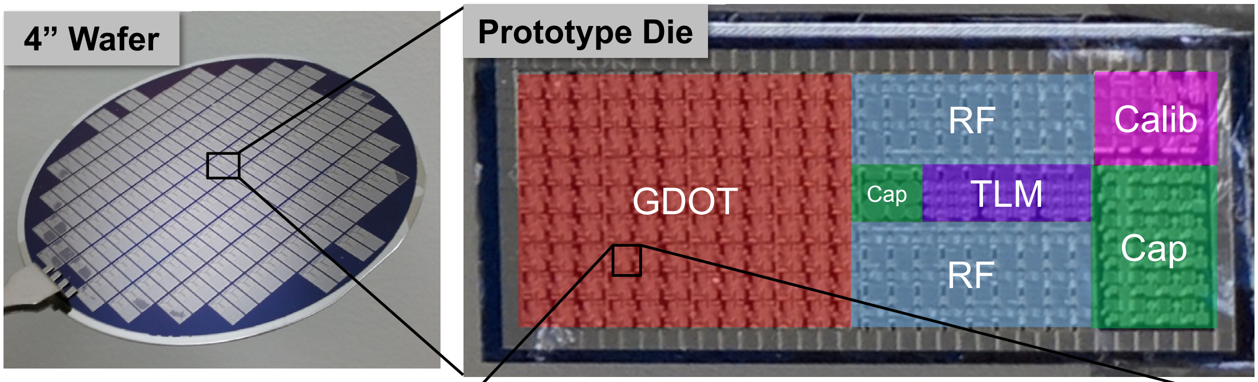
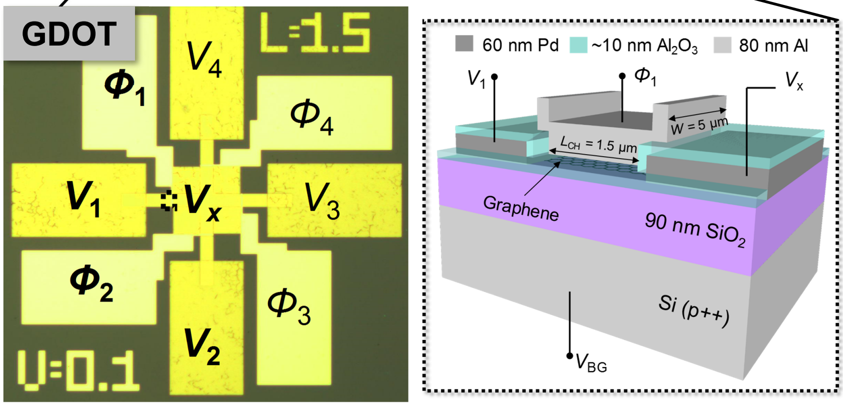
… and Implementation

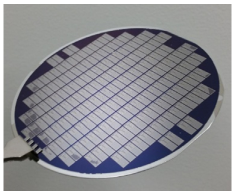
N. Wang, S. Gonugondla, I. Nahlus, N. Shanbhag, E. Pop, *VLSI Symp.* (2016)

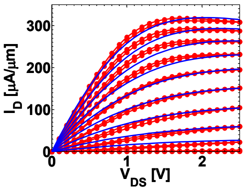


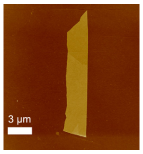


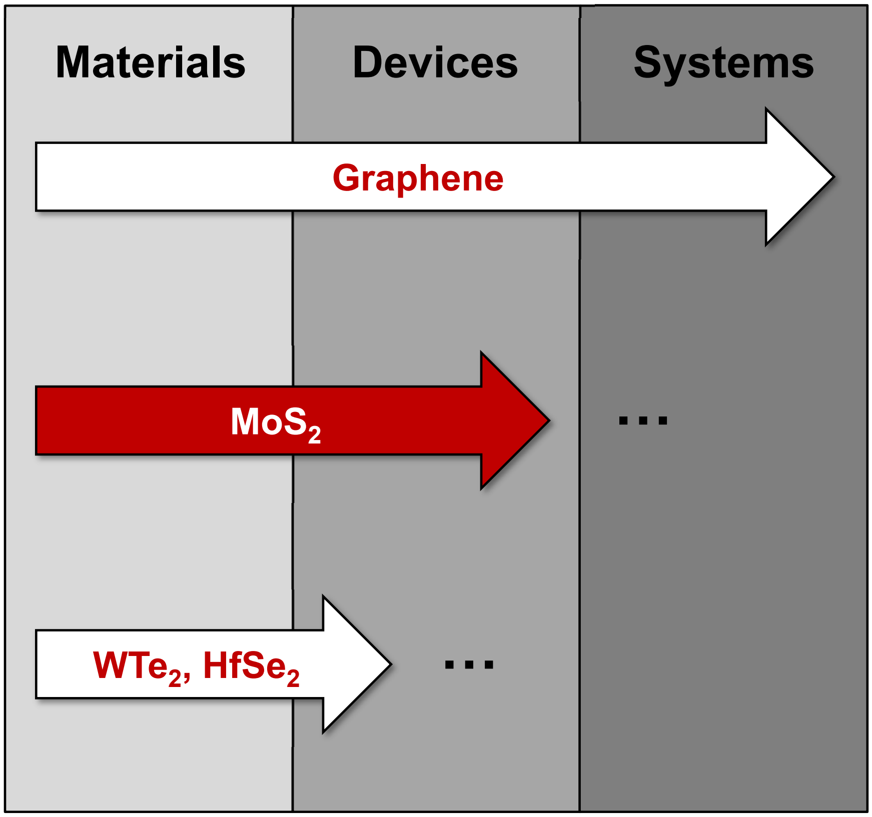
- Wafer-scale graphene growth
- Advances in heterogeneous integration
- "Average" devices but unique function

2D Materials to Systems (Today)



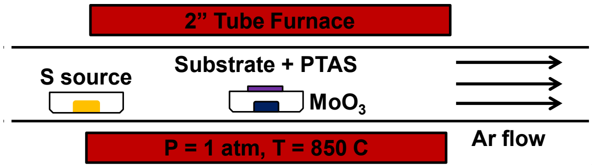




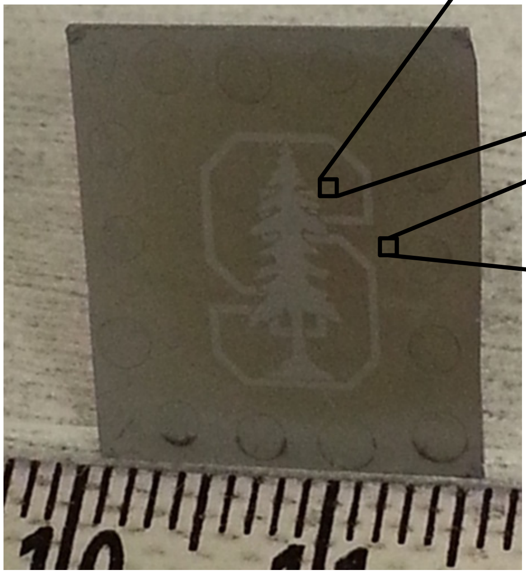


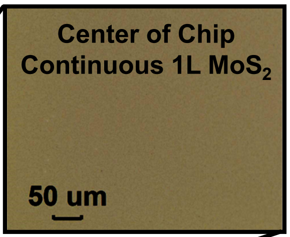
CVD Growth of MoS_2 Monolayers

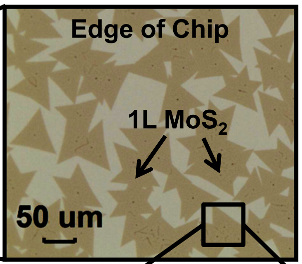
K. Smithe, C. English, S. Suryavanshi, E. Pop, *2D Materials* **4**, 011009 (2017)

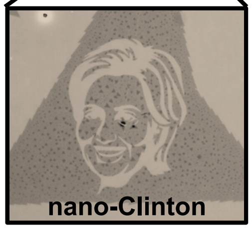


Similar to J. Kong (MIT) work



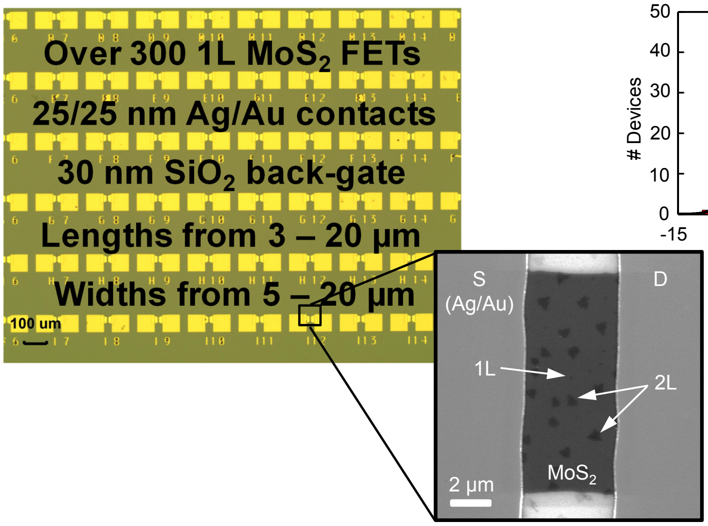




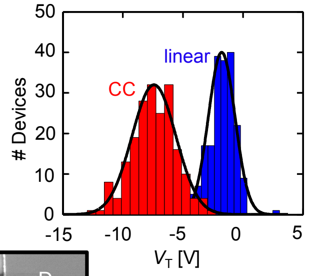


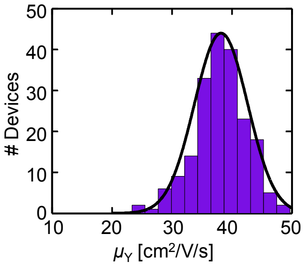
Electrical Properties of 1L MoS_2 Transistors

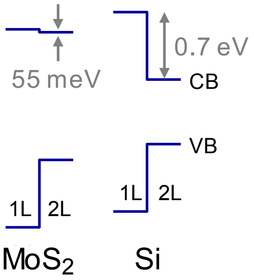
K. Smithe, S. Suryavanshi, M. Munoz Rojo, A. Tedjarati, E. Pop, *ACS Nano* **11**, 8456 (2017)



Over 300 1L MoS_2 FETs
25/25 nm Ag/Au contacts
30 nm SiO_2 back-gate
Lengths from 3 – 20 µm
Widths from 5 – 20 µm



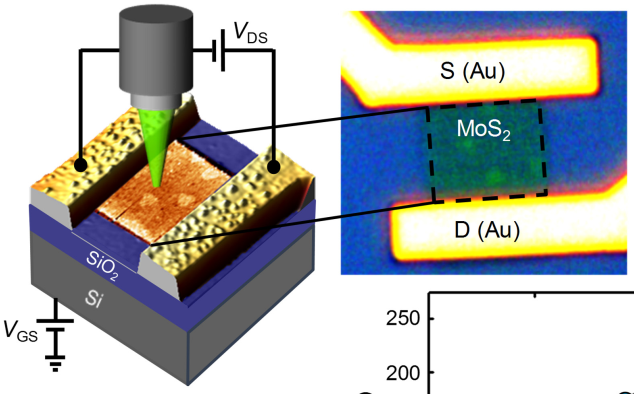




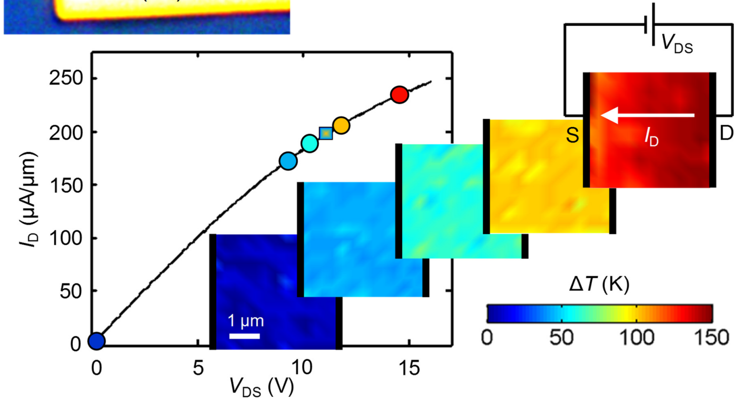
- Large area monolayer (1L) MoS_2 devices
- Mobility μ = 30 to 50 cm²/V/s and R_C ~ 1 kΩ-µm
- Surprise: **<u>less</u>** variability due to "patches" of 2L than ultra-thin silicon!
- Why? Because 1L-2L conduction band offset is small (~55 meV)

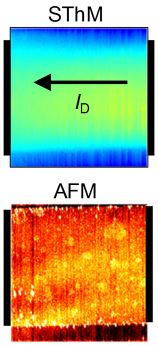
Energy Dissipation in MoS_2 Transistors

E. Yalon, C. McClellan, K. Smithe, R.L. Xu, M. Munoz-Rojo, S. Suryavanshi […] E. Pop, *Nano Letters* **17**, 3429 (2017)



- Raman thermal imaging of functioning MoS_2 transistors
- Bilayer (2L) regions do not heat or cool differently





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Energy Dissipation in MoS_2 Transistors

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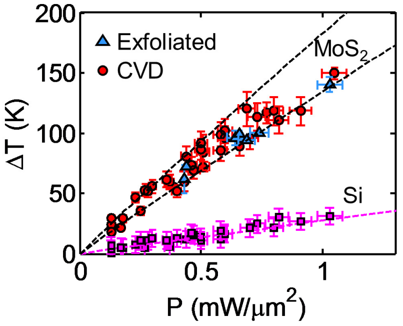
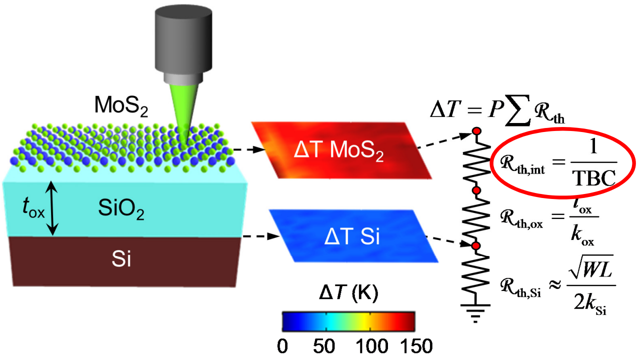
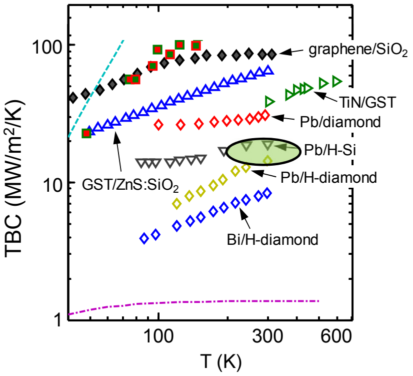




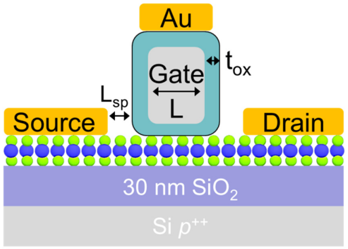
Simultaneously get ΔT of MoS_2 and substrate

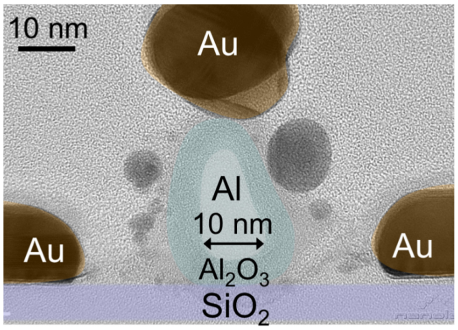
- Accurate thermal boundary conductance (TBC) of MoS_2-SiO_2 = 14 ± 4 $MW/m^2/K$
- Kapitza length is ~90 nm of SiO_2 (!)
- Very low TBC, comparable to Pb-diamond

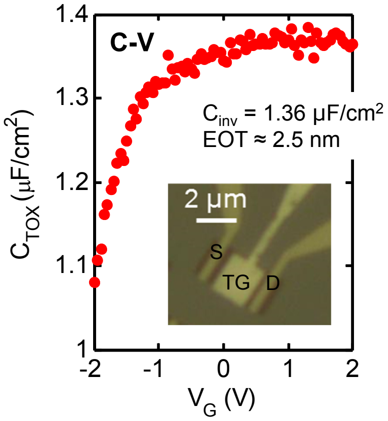


Nanoscale MoS_2 Channel (~10 nm)

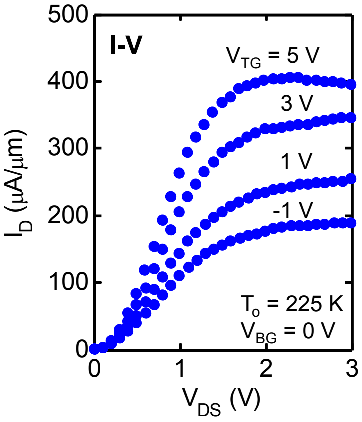
C. English, K. Smithe, R.L. Xu, E. Pop, *IEDM* (2016)







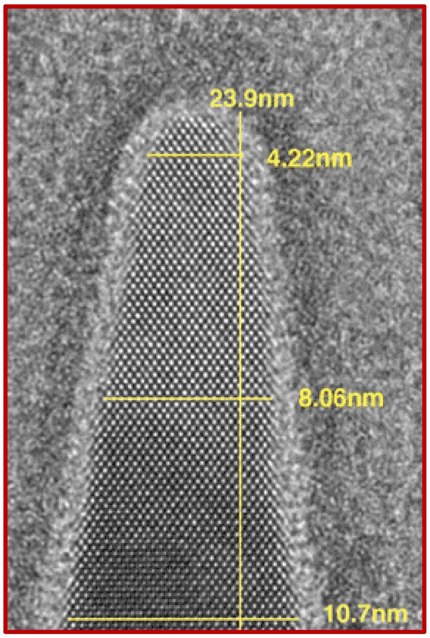
- Self-aligned top-gated monolayer CVD MoS_2
- Similar to SOI, but with 6.15 Å "thick" channel
- **Record I_{Dsat} > 400 μA/μm for monolayer MoS_2**
- Simulations suggest devices are ~20% ballistic
- Must improve contacts, long-channel μ, EOT…



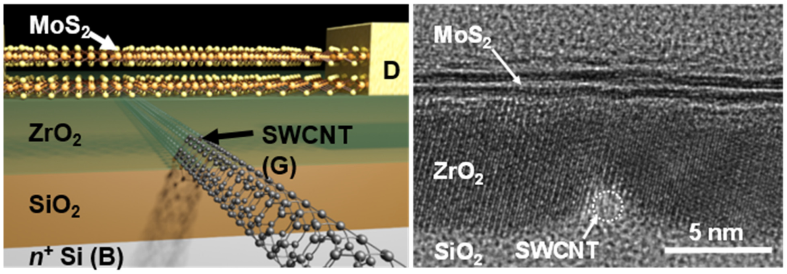
Modern FinFET vs. Atomically Thin MoS_2 FETs

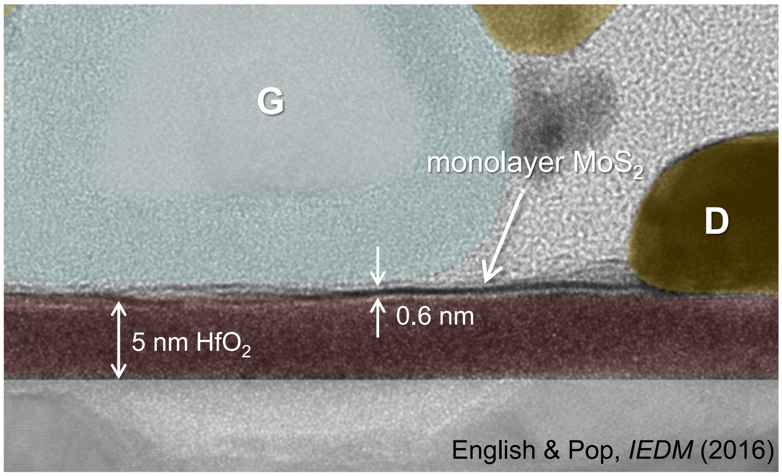
(note same scale)

Desai, Wong & Javey, *Science* (2016)



Intel “14 nm” FinFET

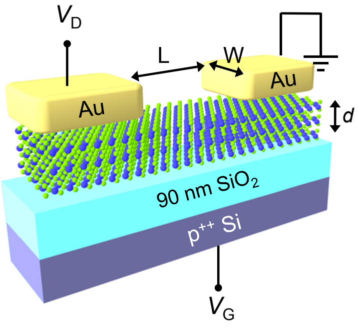


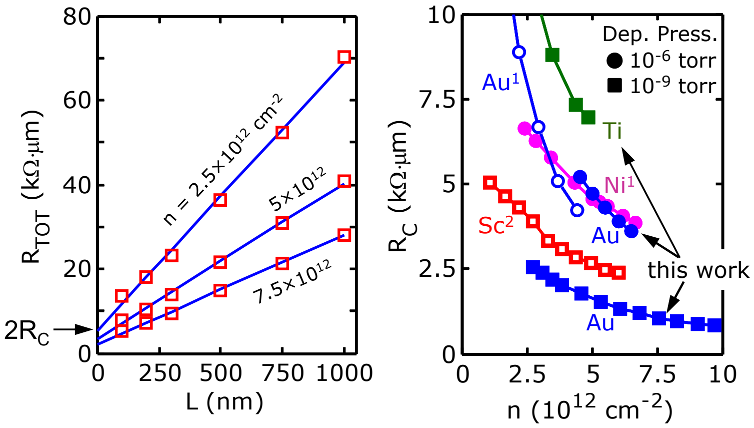


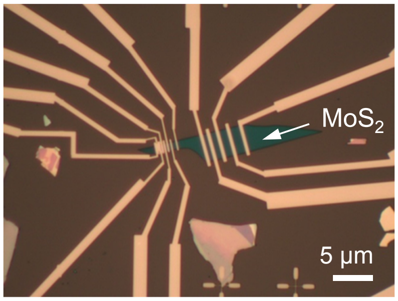
English & Pop, *IEDM* (2016)

Metal Contacts to MoS_2 (Clean but Undoped)

C. English, G. Shine, V. Dorgan, K. Saraswat, E. Pop, *Nano Lett.* **16**, 3824 (2016)







Transfer Length Method (TLM)

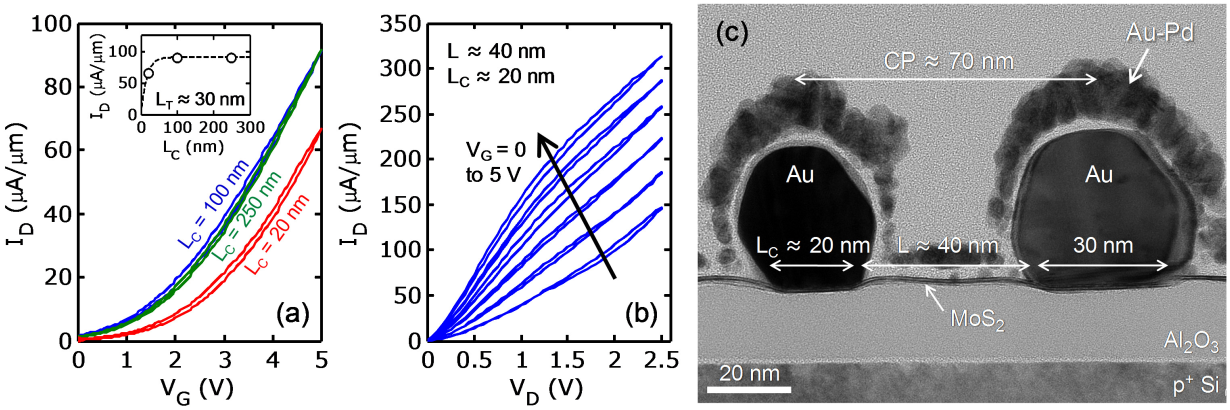
- Contacting 2D materials is **difficult**
- Careful TLMs are important
- **Cleaner Au deposition ($\sim 10^{-9}$ torr)** leads to improved contacts
  - $R_C \sim 740\ \Omega\cdot\mu m$ and $\rho_C \approx 4 \times 10^{-7}\ \Omega\cdot cm^2$

[1] H.Liu & P. Ye (2013), [2] S. Das & J. Appenzeller (2013)

Nanoscale MoS_2 Contacts

C. English, G. Shine, V. Dorgan, K. Saraswat, E. Pop, *Nano Lett.* **16**, 3824 (2016)

Goal: scale both channel length <u>and</u> contacts of MoS_2 FETs → what happens?



- **Smallest MoS_2 contacts to date**
  - L = 40 nm and variable contacts (L_C = 20 to 100 nm)
  - Smallest contact pitch CP ~ 70 nm, **equivalent to "14 nm" tech. node**
- **Contacts are limiting** the performance of small MoS_2 transistors

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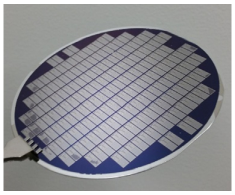
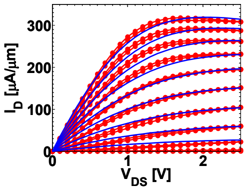
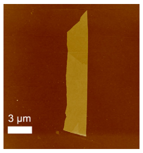
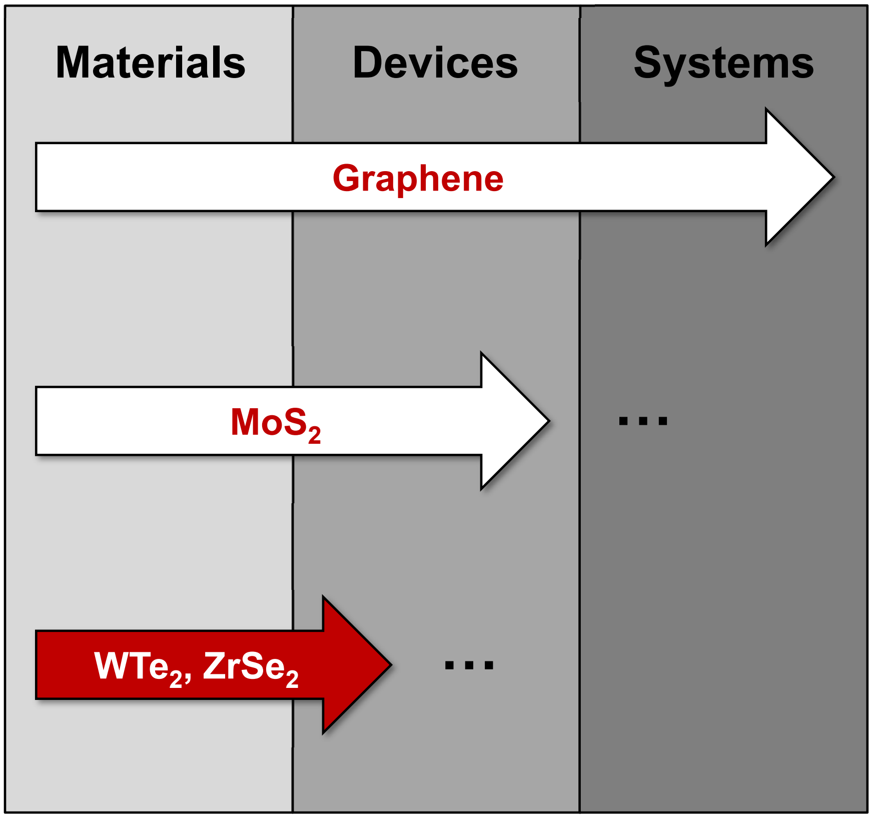
2D Materials to Systems (Today)









Materials | **Devices** | **Systems**

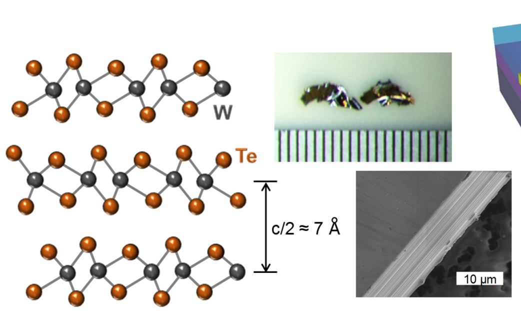
Graphene

MoS_2 …

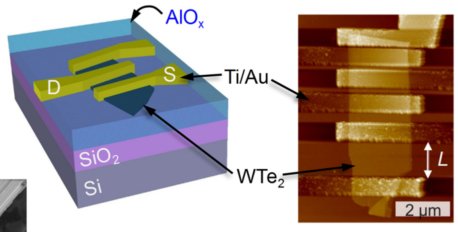
WTe_2, $ZrSe_2$ …

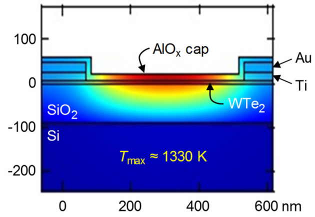
2D Semi-Metal: WTe_2

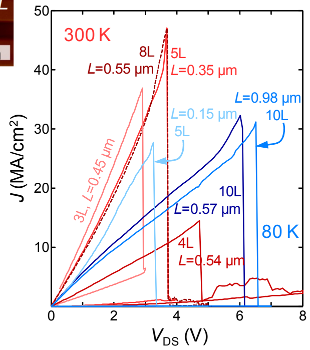
M. Mleczko, R. Xu, K. Okabe, H.-H. Kuo, I.R. Fisher, H.-S.P. Wong, Y. Nishi, E. Pop, *ACS Nano* **10**, 7507 (2016)



WTe_2 grown by CVT







- Thin (<6 layer) WTe_2 unstable in air, but **stable after capping** with AlO_x
- **High-current density** (40-50 MA/cm²) and low thermal conductivity (3-5 W/m/K)
- Potential applications as electrode in low-power phase-change memory

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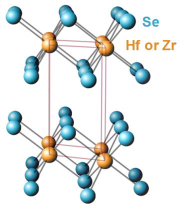
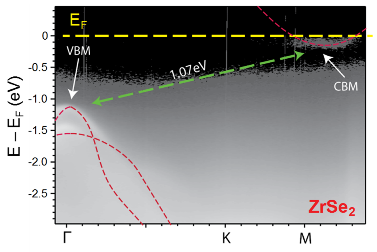
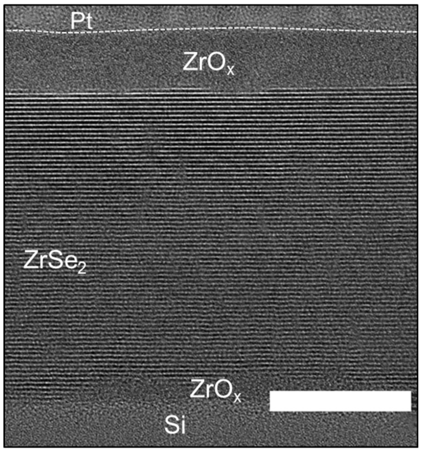
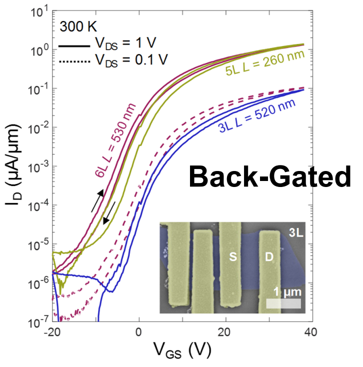
2D Semiconductors with Native High-K Oxides

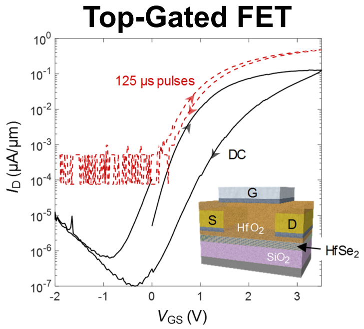
M. Mleczko, C. Zhang, […], I. Fisher, Y. Nishi, E. Pop, *Science Advances* **3**, e1700481 (2017)











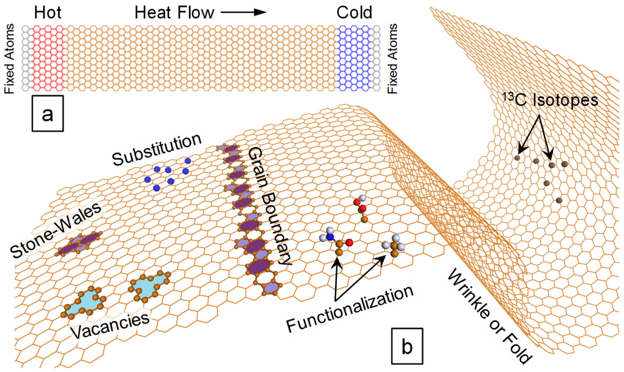
- **$HfSe_2$ and $ZrSe_2$** have band gaps around 1 eV
- … and native **HfO_2 and ZrO_2**

similar to silicon
but in 2D form!

2D Material Thermal Properties

- **Large in-plane** thermal conductivity of graphene, BN (>500 W/m/K)
- **Ultra-low cross-plane** thermal conductivity of layered WSe_2 (<0.1 W/m/K)
  - Lower than plastics and ***comparable to air***
- Huge thermal anisotropy in all layered 2D materials (>10-100x)
- MRS Bulletin review with AFRL:

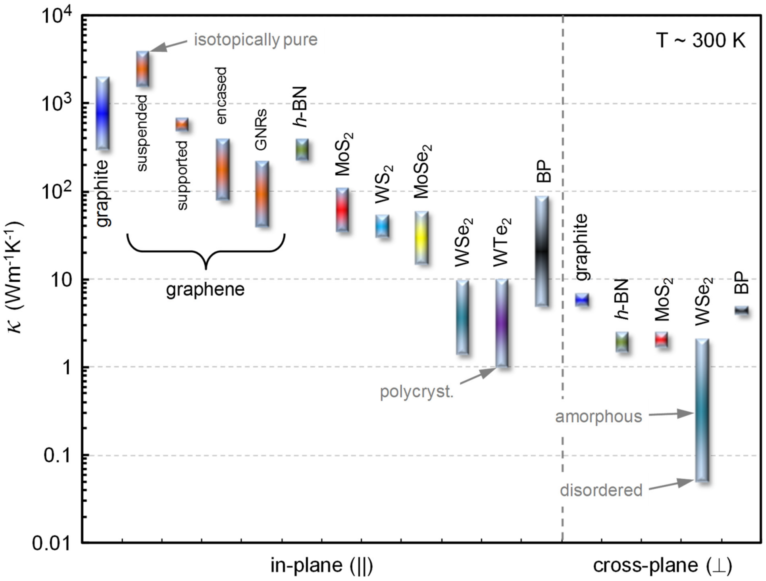
E. Pop, V. Varshney, A.K. Roy, "Thermal Properties of Graphene: Fundamentals and Applications," *MRS Bulletin* **37**, 1273 (2012)



- **Large thermopower** in TMDs (*S* ~ 0.5 mV/K) → Thermoelectrics?

$$ZT = \frac{S^2 \sigma T}{k}$$

Thermal Conductivity of 2D Materials



$$Q'' = -\kappa \nabla T$$

heat flux

thermal conductivity

T gradient

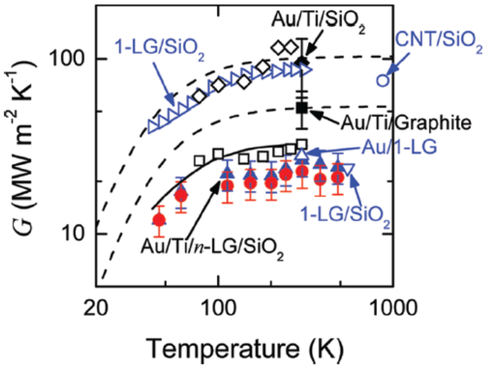
- **Huge thermal anisotropy** of 2D materials: in-plane $\boldsymbol{\kappa}_{||}$ >> cross-plane $\boldsymbol{\kappa}_{\perp}$
- Note: must use "**correct thickness**" of monolayers from XRD or TEM, e.g. 3.35 Å for graphene and 6.15 Å for MoS_2 (**not** thickness from AFM)

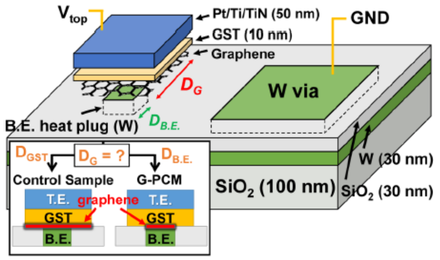
E. Pop, V. Varshney, A. Roy, *MRS Bull.* 37, 1273 (2012); Table courtesy of Z. Li (Pop Lab)

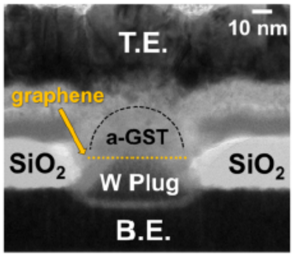
Unusual: Graphene as Thermal Barrier for PCM

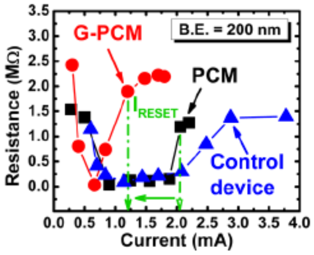
Y.K. Koh, M.-H. Bae, D.G. Cahill, E. Pop, *Nano Lett.* **10**, 4363 (2010)
C. Ahn, S.W. Fong, Y. Kim, S. Lee, A. Sood, C. Neumann, K. Goodson, E. Pop, H.-S.P. Wong, *Nano Lett.* **15**, 6809 (2015)

- Phase-change memory (PCM) needs good thermal insulation









- Exploiting graphene thermal boundary resistance (TBR) ~ 30 nm SiO$_2$
- Ultra-thin **thermal barrier** limits PCM heat loss → 40% lower current

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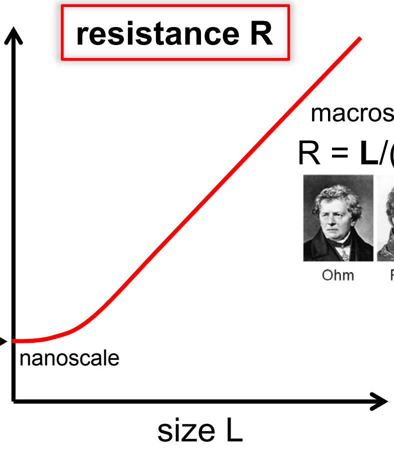
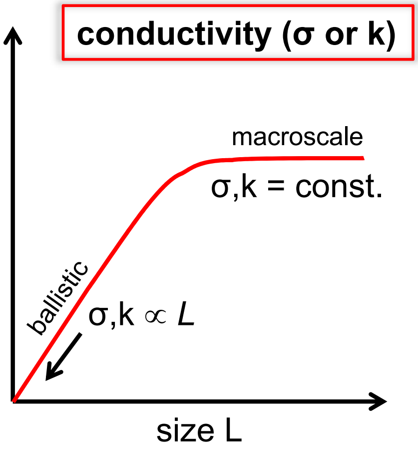
Heat (and Current) Flow in Nanoscale Samples

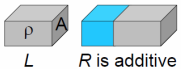
quantized,
ballistic

$$R_b = \frac{M}{25.8\,\mathrm{k\Omega}} \propto \frac{h}{q^2}$$





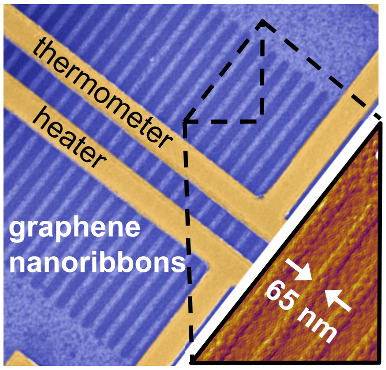
- Macroscale, R is additive: 1 + 1 = 2

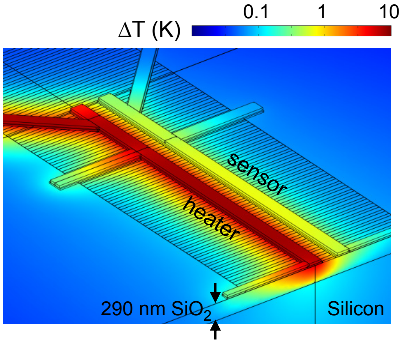


- ***Nanoscale***, R is quantized: 1 + 1 = 1
  - Occurs when system size is comparable to electron or phonon (heat) wavelengths and mean free path (10-100 nm)
  - Both electrical and thermal resistance can be **quasi-ballistic**

Thermal Conductivity of Nanoscale Graphene

M.-H. Bae, Z. Li, Z. Aksamija, P. Martin, F. Xiong, Z.-Y. Ong, I. Knezevic, E. Pop, *Nature Comm.* **4**, 1734 (2013)

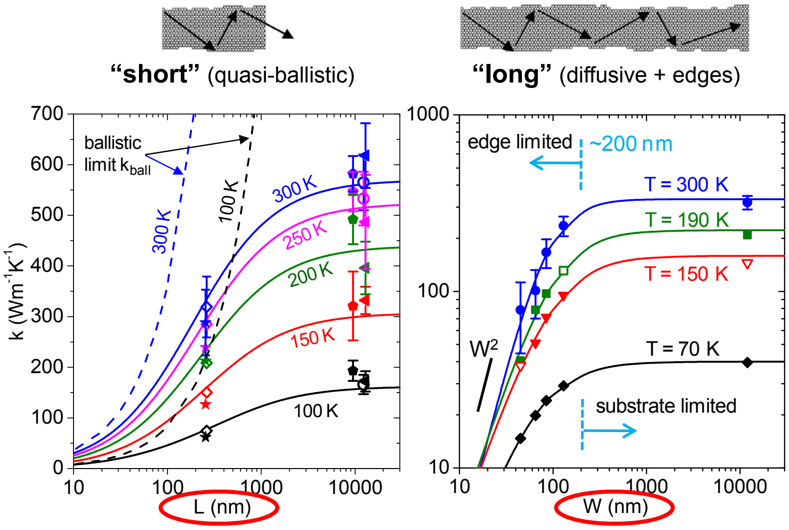




Bulk thermal properties do not apply at <1 µm!

Thermal conductivity **k(T) = f(W,L)** even at room T

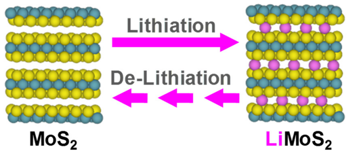
- 35% (quasi-)ballistic heat flow in short devices (λ ~ 100 nm)
- Strong edge scattering in narrow devices



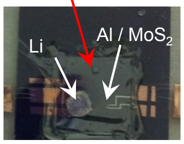
Unusual Application: Thermal Transistors

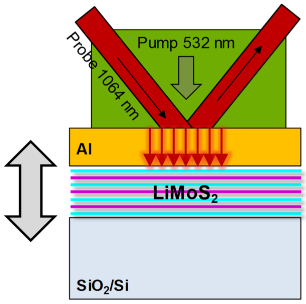
A. Sood, F. Xiong, […], Y. Cui, E. Pop, K Goodson, *submitted* (2017)

- Could we… manipulate & **switch heat flow?** (e.g. thermal circuits)
- Ex: using reversible Li intercalation in MoS_2

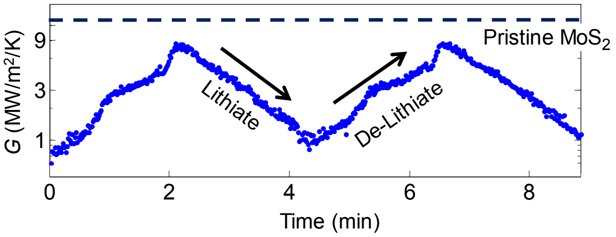


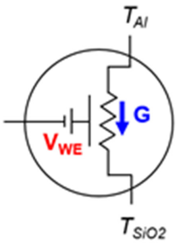
electrolyte $LiPF_6$

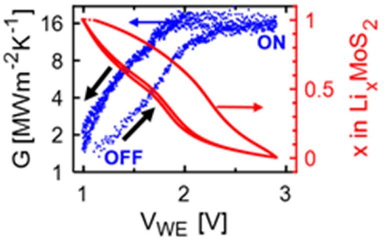




Thermal Switching

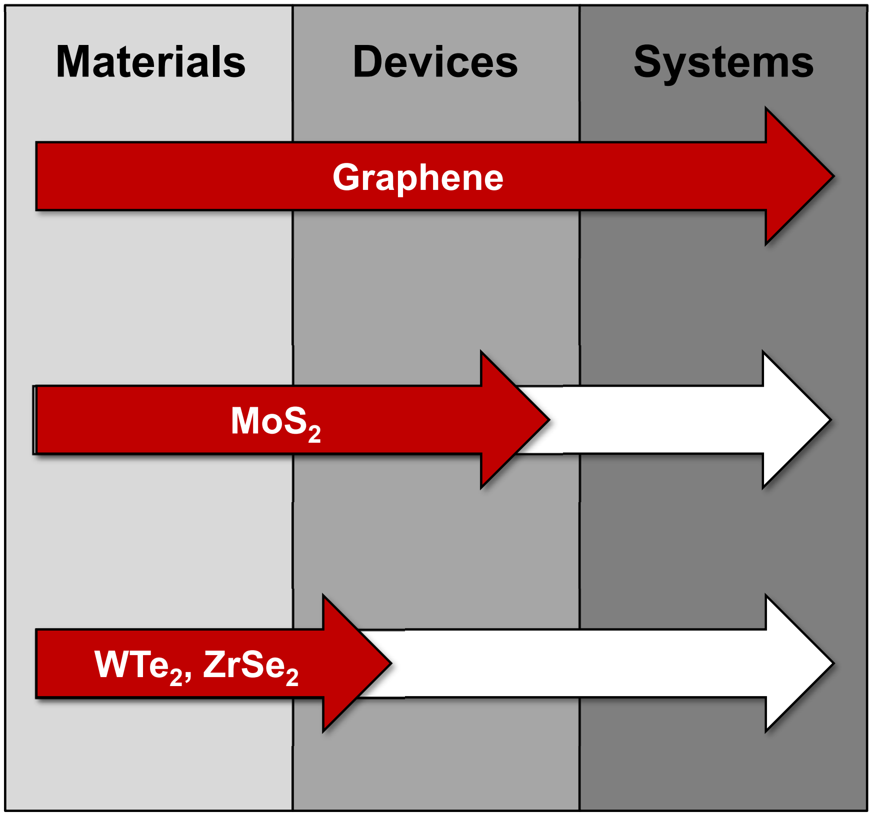


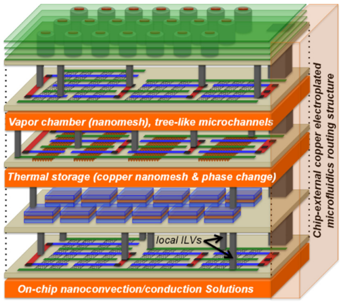




Thermal Transistor (On/Off ~10)

2D Materials to Systems – Future (?)

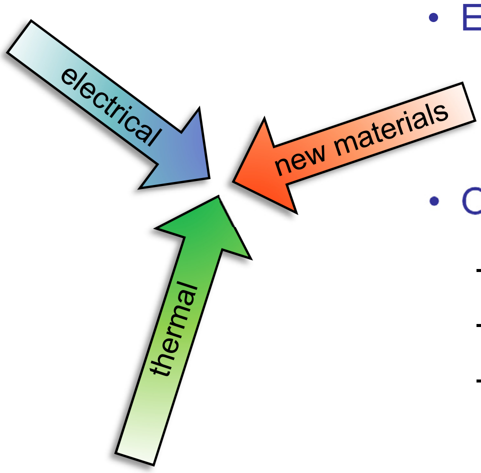




M. Aly et al., "Energy-Efficient Abundant-Data Computing: The N3XT 1,000X," *IEEE Computer* 48, 24 (2015)

Summary

- Moore's Law ~10x → slowing down
- Energy scaling & harvesting ~10^4x → exciting



- Opportunity for convergence of:
  - Novel 2D nanomaterials
  - Anisotropic electrical & thermal properties
  - Heterogeneous integration
- From fundamentals to systems
- Collaborations with industry & academia

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