

# Graphene for Electronic Applications

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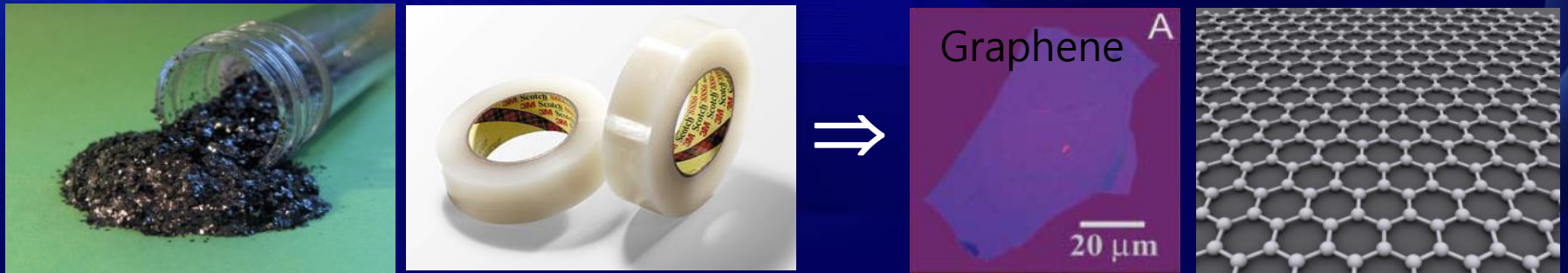
# Graphene

: Carbon allotrope with hexagonal arrangement in one-atomic-thick sheet.

- Andre Geim and Konstantin Novoselov (Manchester University) (2004)
  - Nobel Prize in Physics (2010)
- “Groundbreaking experiments regarding the two dimensional materials graphene”

## Isolation of Graphene

Isolated multi-layer Graphene from Graphite using scotch tape



KS Novoselov, *et al.*, *Science*, **306** 666 (2004)

# Properties of Graphene

Large Area

Mobility  
(cm<sup>2</sup>/V·s)



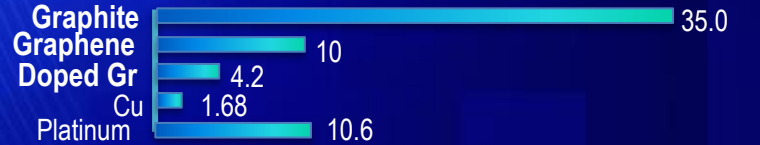
High Performance Tr

Transparency  
(%)



Transparent Electrode for Display & Solar Cell

Resistivity  
(μΩcm)



Interconnect

Current Density  
(A/cm<sup>2</sup>)

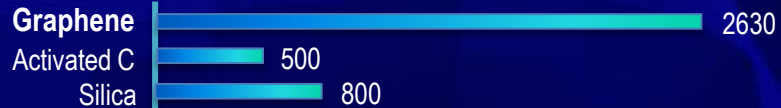


Barrier Flexible Device

Chemical Inertness & Flexibility

Flake base

Surface Area  
(m<sup>2</sup>/g)



Super capacitor

Thermal Conductivity  
(W/m·K)



Heat Sink

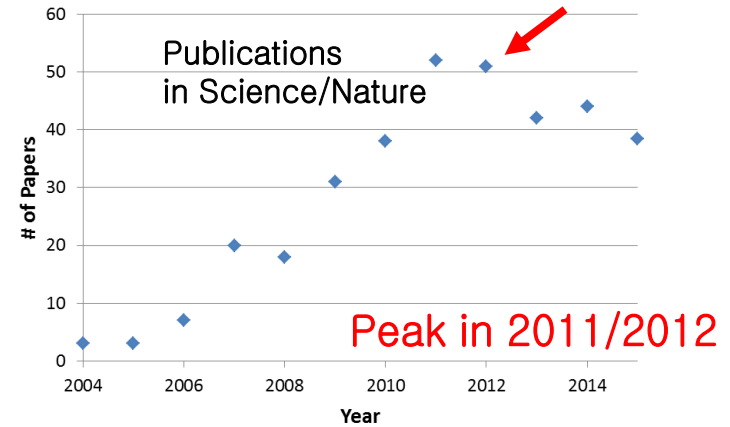
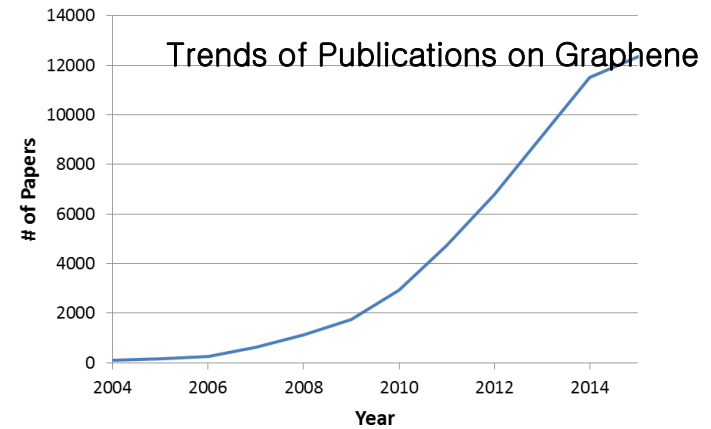
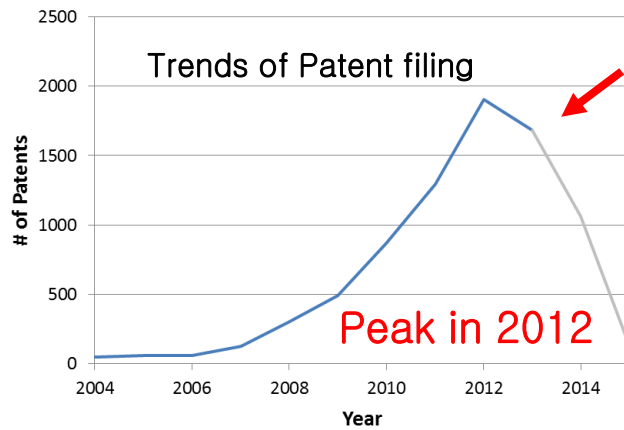
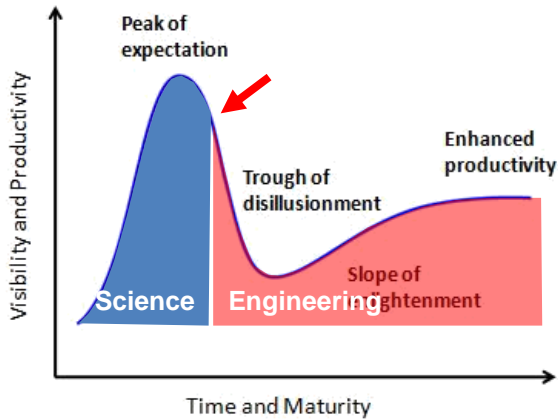
Ultimate Strength  
(GPa)



Composite

# Where are we?

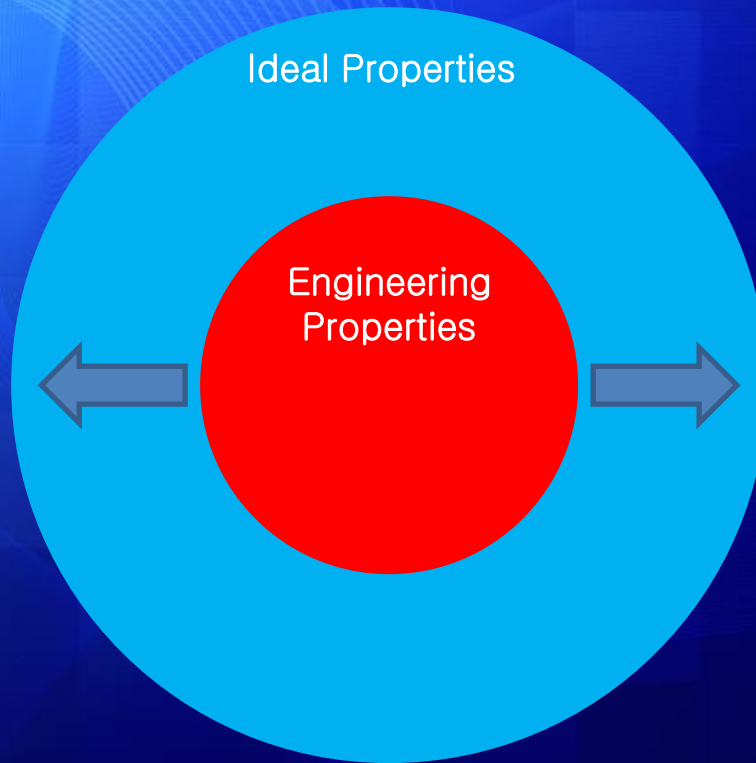
## : Gartner's Hype Cycle



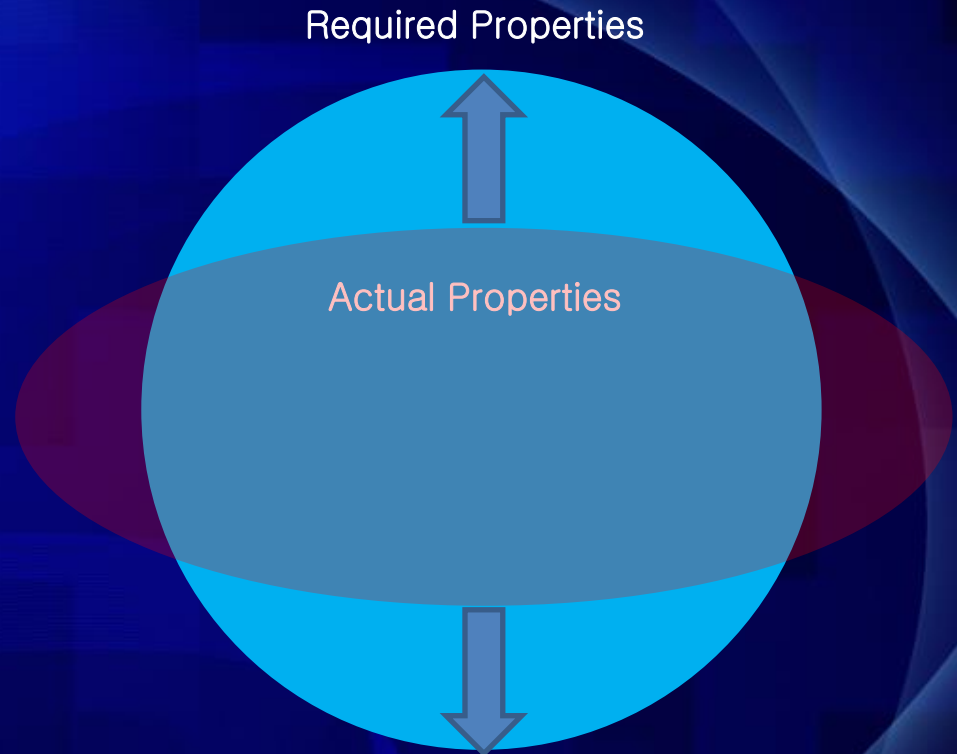


# Properties? Properties!

: Filling the gaps in properties



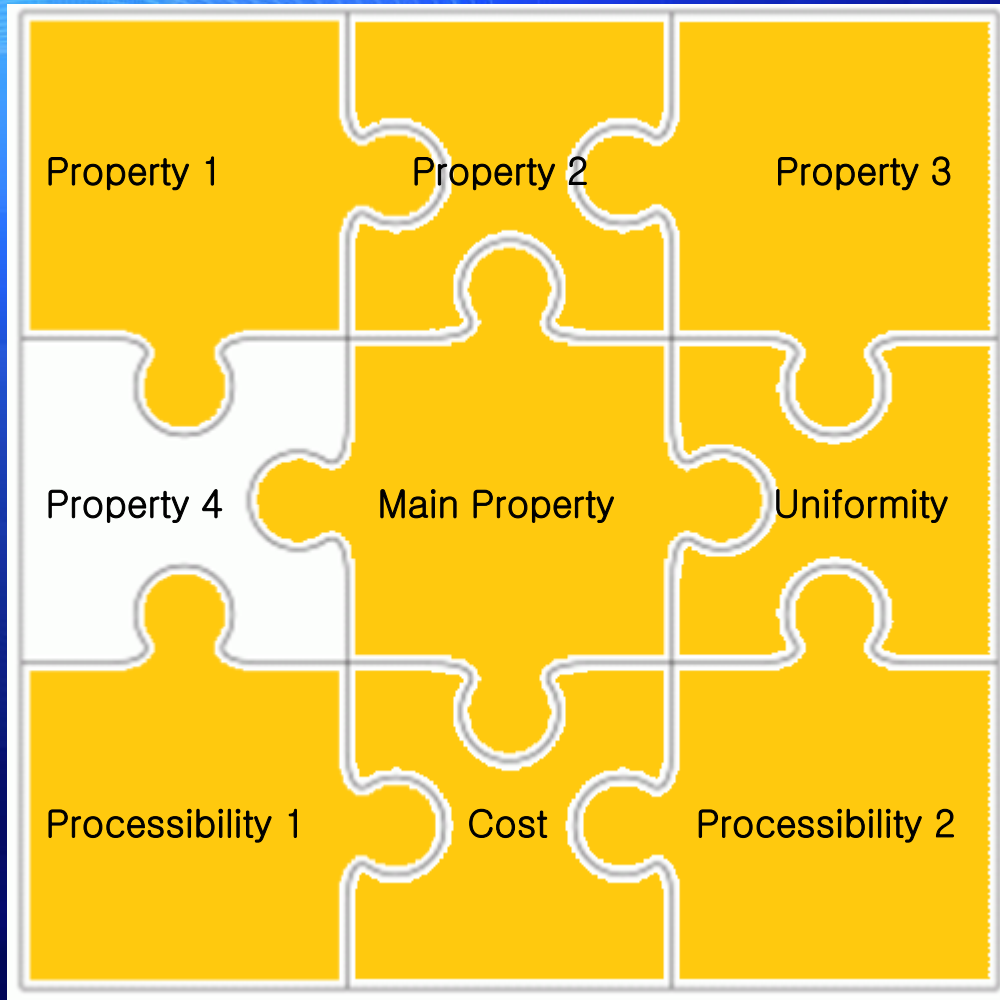
- **Mobility**  
200,000cm<sup>2</sup>/Vs → ~2000cm<sup>2</sup>/Vs
- **Thermal Conductivity**  
5300W/m·K → ~ 1000W/m·K



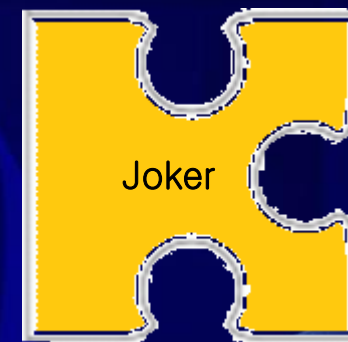
- **Mobility**  
200,000cm<sup>2</sup>/Vs > 1400cm<sup>2</sup>/Vs (Si)
- **On/Off**  
~ 10 ≪ 10<sup>4</sup> ~ 10<sup>11</sup> (Si)

# Filling the Puzzles

: All puzzles need to be filled to be commercialized.



- Properties → Processibility (Industry) → Cost (?) → Uniformity (Equipment)
- Everything needs to be satisfied all together
  - Actual/Engineering Properties
  - Processibility
  - Cost: \$281 for 5cm X 5cm (on Cu foil) → ~ \$700,000/m<sup>2</sup>
  - Uniformity



## Semiconductor

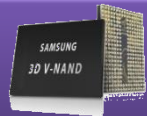
DRAM

(39%, 1<sup>st</sup> in 2014)



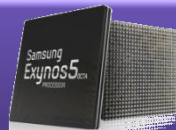
NAND

(30%, 1<sup>st</sup> in 2014)



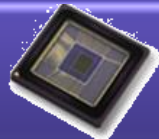
AP

(4%, 4<sup>th</sup> in 2014)



CIS

(29%, 2<sup>nd</sup> in 2014)



## Mobile

Smart Phone

(31%, 1<sup>st</sup> in 2014.Q1)



Smart Watch

(23%, 1<sup>st</sup> in 2014)



Tablet

(18%, 2<sup>nd</sup> in 2014)



## Appliances and other electronics

LCD TV

(22%, 1<sup>st</sup> in 2014)

French door refrigerator

(40%, 1<sup>st</sup> in 2010)

PC Monitor

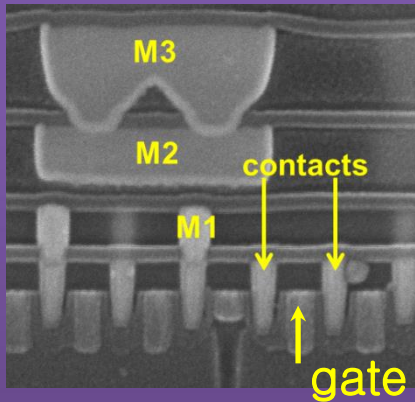
(13%, 2<sup>nd</sup> in 2014)

Digital Camera

(23%, 2<sup>nd</sup> in 2014.H2)

www.Statista.com; www.IDC.com; www.SmartWatchGroup.com Wikipedia, Gartner

## Semiconductor



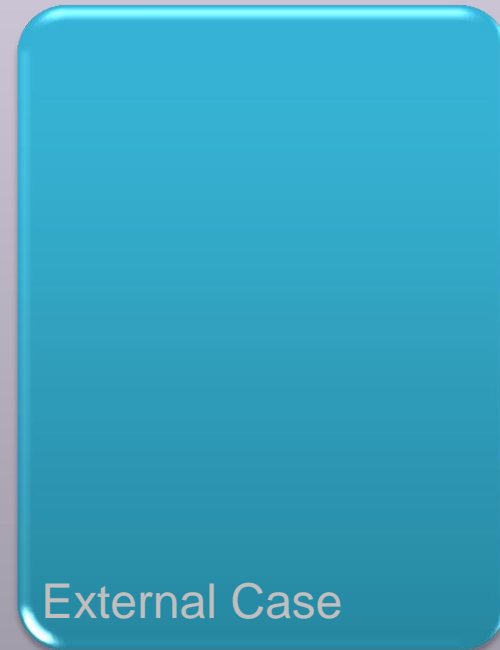
Active Materials  
Components

## Mobile



Touch Screen  
Battery

## Appliances and other electronics



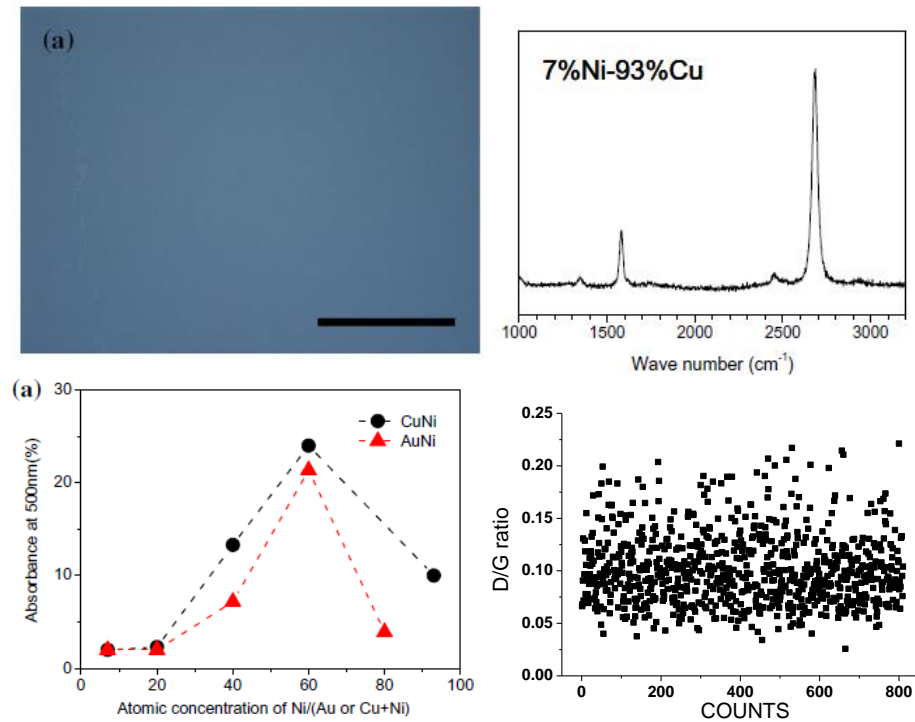
External Case



# Growth

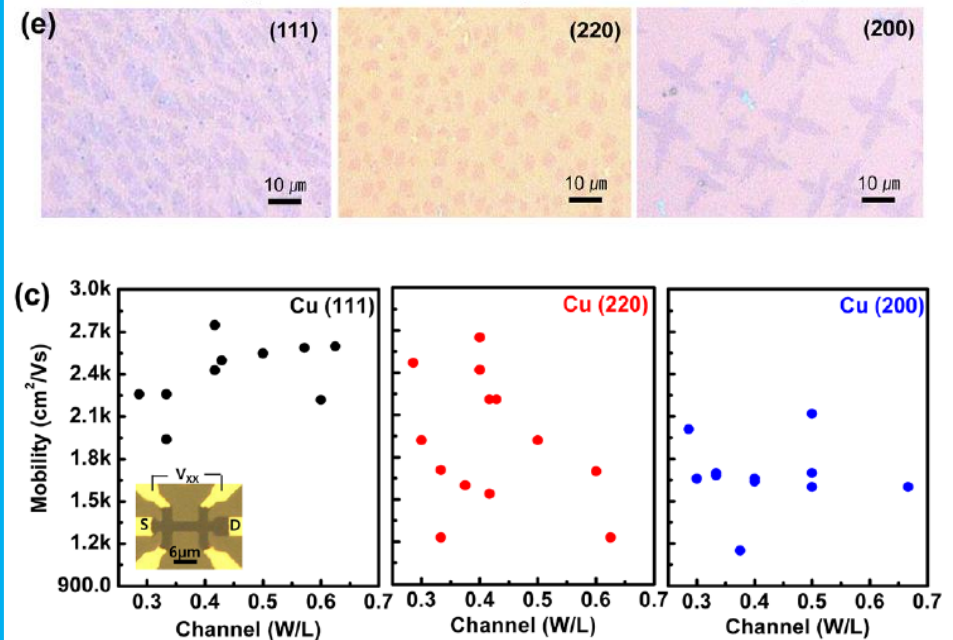
# Graphene Growth on Metal Catalyst

## Low temperature growth on Metal catalyst with ICP CVD



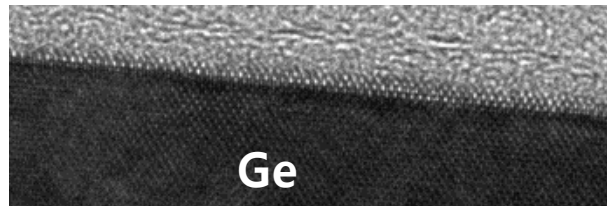
Y S Woo *et al.* *Carbon*, **64** 315 (2013)

## Graphene Growth on various Cu orientations



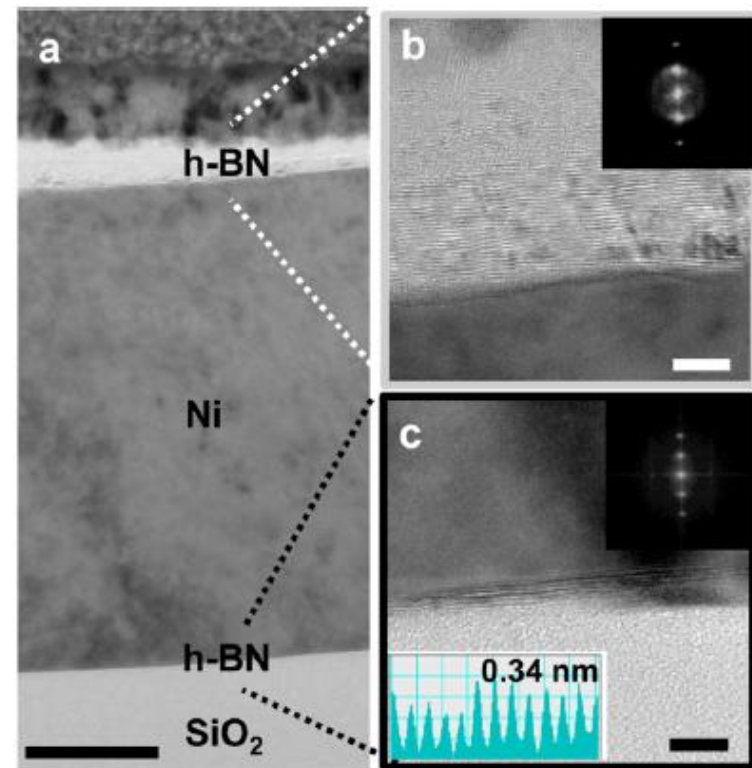
H-J Shin *et al.* *APL*, **102**, 163102 (2013)

## Graphene can be grown on Semiconductor



Y S Woo *et al.* *Carbon*, **64** 315 (2013)

## Growth of h-BN on and underneath of Ni



S Park *et al.* *ACS Nano*, **9**, 633 (2015)

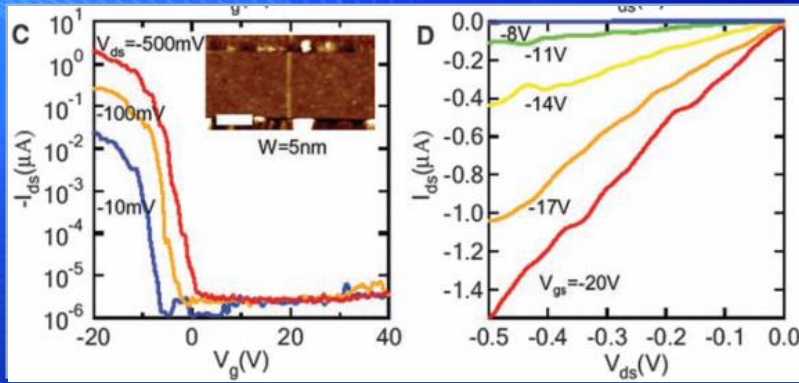
# Wafer-scale Integration of Graphene Tunneling Barristor



# How to Achieve Low Off Current

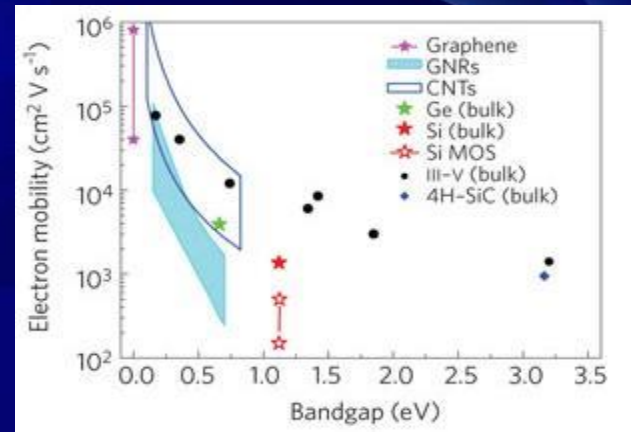
## Quantum Confinement: GNR

X. Li et al. Science (2008)



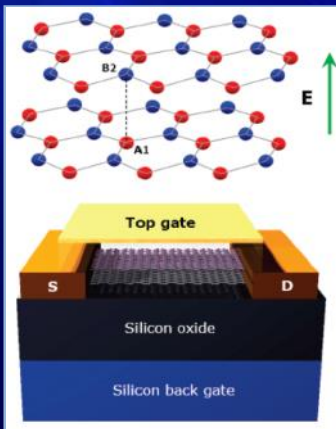
$w=5\text{nm}$ ,  $I_{on}/I_{off} \sim 10^6$ ,  $\mu=100\text{-}200\text{cm}^2/\text{Vs}$

F. Schwierz, Nature Nanotechnology(2012)

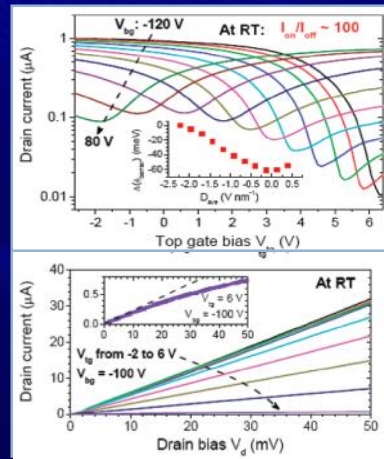


## Symmetry Breaking: Bilayer

F. Xia et al. Nano Lett.. (2010)

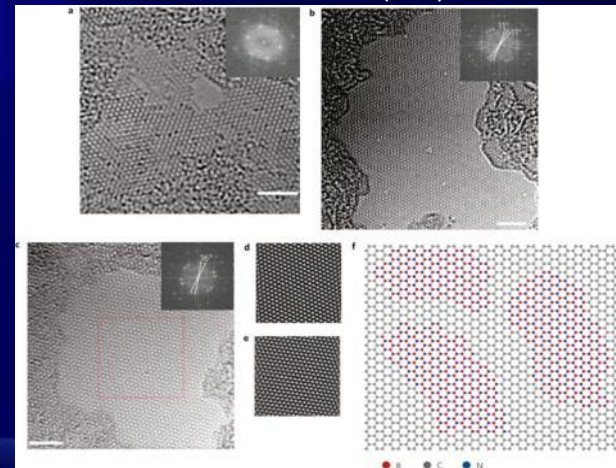


$I_{on}/I_{off} \sim 10^2$ ,  $D=2.2\text{V}/\text{nm}$



## h-BCN

L. Ci, Nature Materials(2012)

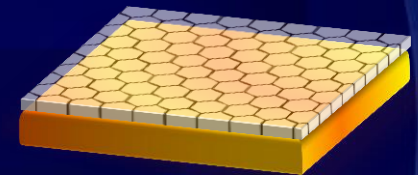


# Doping

## : DFT simulations on metal doped graphene Work functions

eV	Graphene	Ni	Co	Pd	Al	Ag	Cu	Au	Pt
WF Metal		5.47	5.44	5.67	4.22	4.92	5.22	5.54	6.13
WF Simulation	4.48	3.66	3.78	4.03	4.04	4.24	4.40	4.74	4.87
WF Exp	4.6	3.9		4.3					4.8

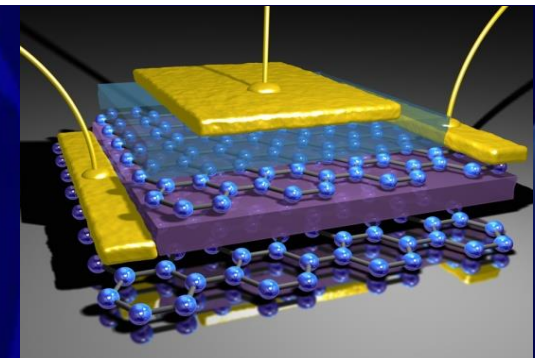
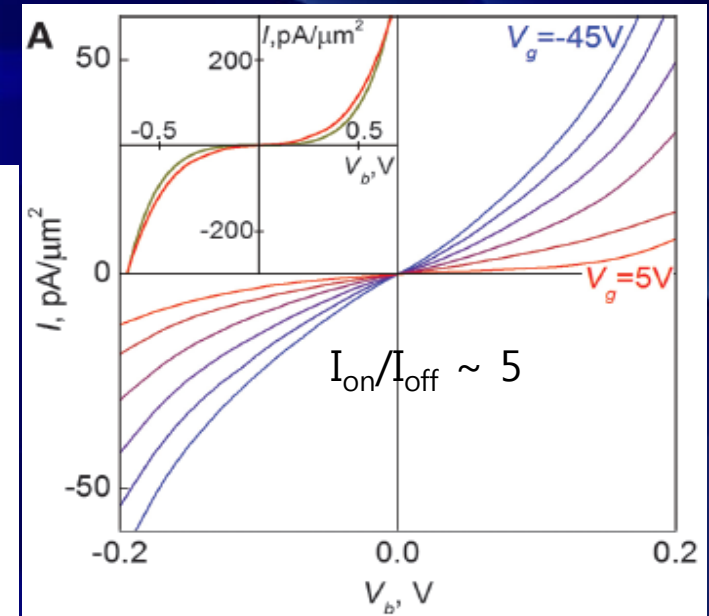
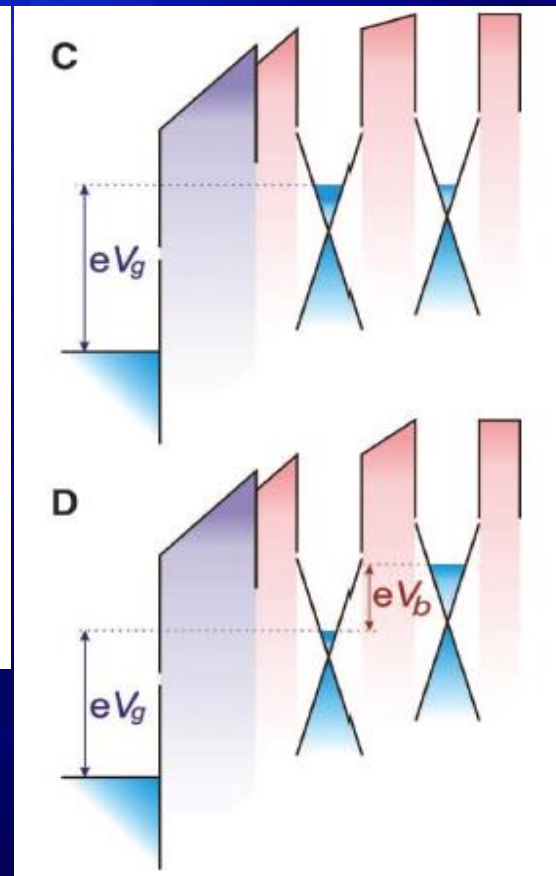
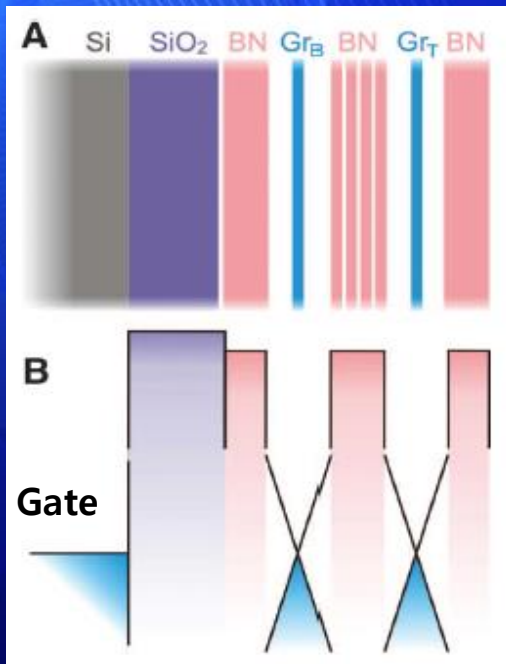
G Giovannetti *et al.*, *PRL*, 101 026803 (2008)



# Tunneling Transistor

: h-BN,  $I_{on} \sim 70 \text{ pA}/\mu\text{m}^2$ ,  $I_{off} \sim 12 \text{ pA}/\mu\text{m}^2$ ,  $I_{on}/I_{off} = 50$  @  $V_b = 0.2 \text{ V}$

With  $\text{MoS}_2$ ,  $I_{on}/I_{off} = 7000$

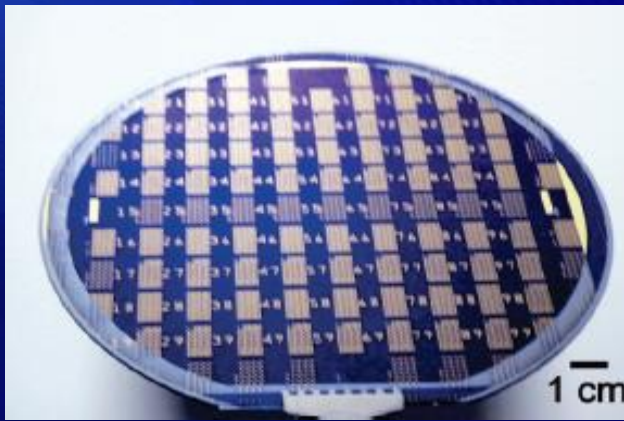
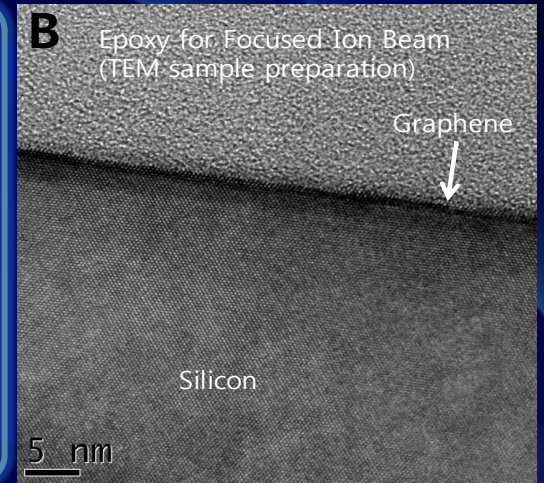
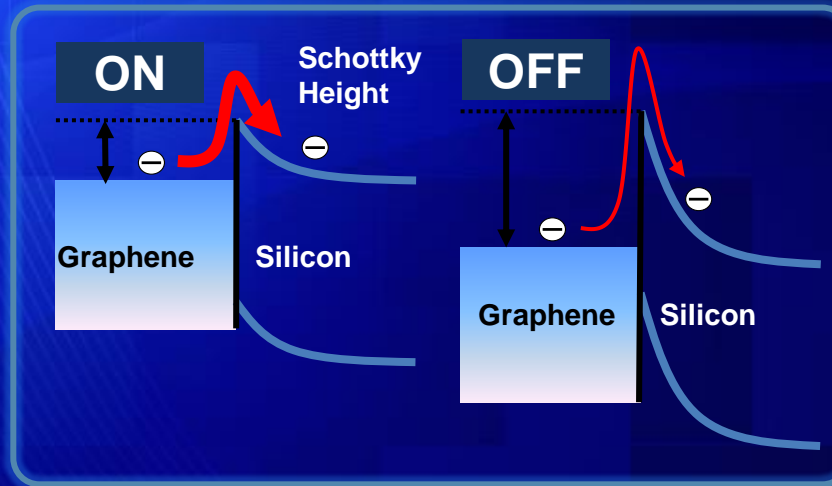
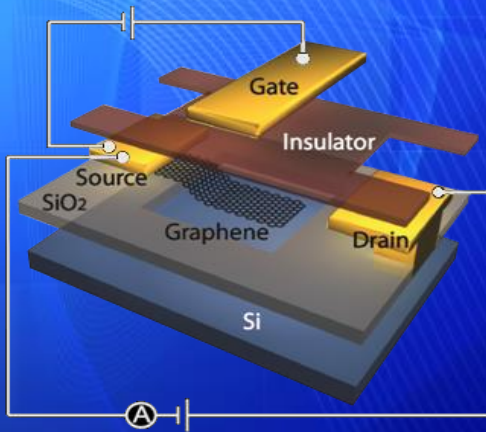


L Britnell et al., Science 335 947 (2012)

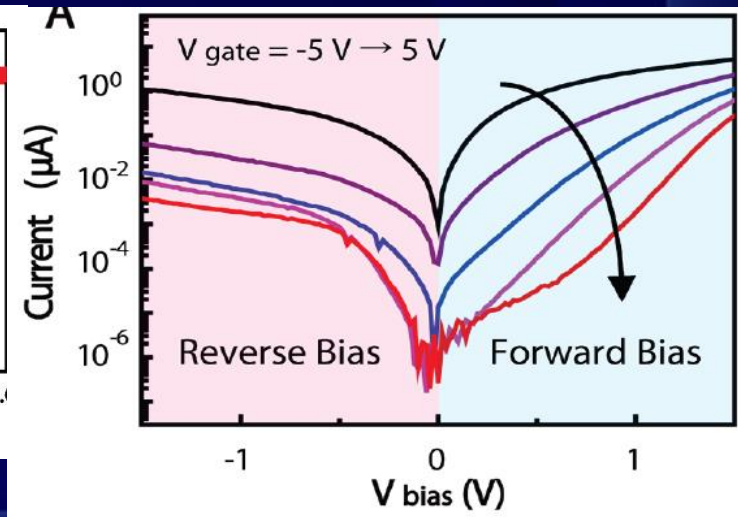
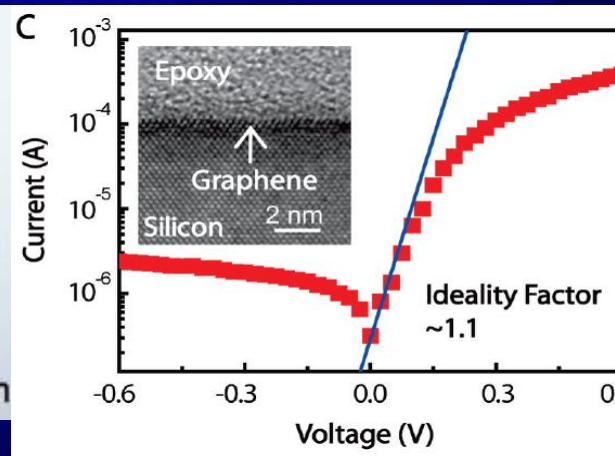


# Graphene Barristor

: Si,  $I_{on} \sim 10\mu A/\mu m^2$ ,  $I_{on}/I_{off} = 10^5$



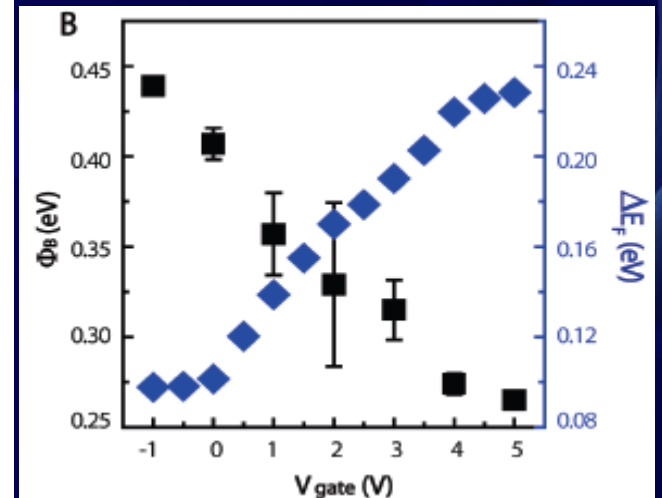
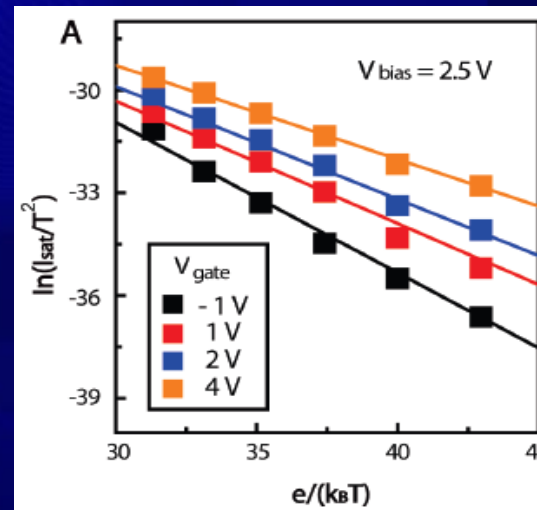
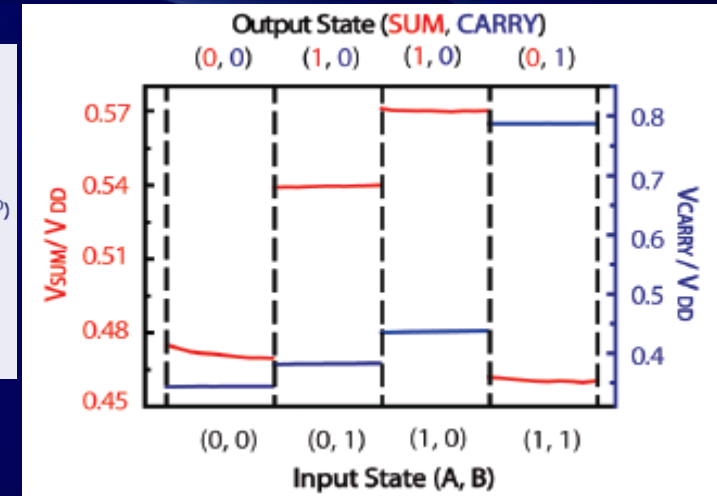
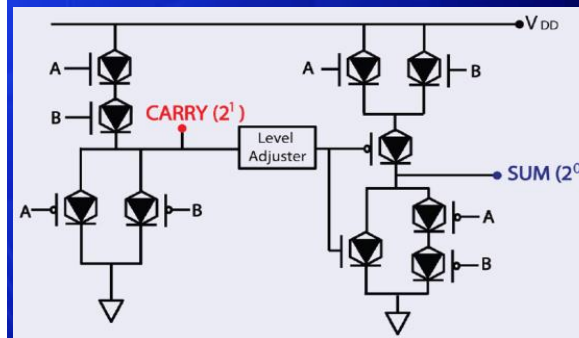
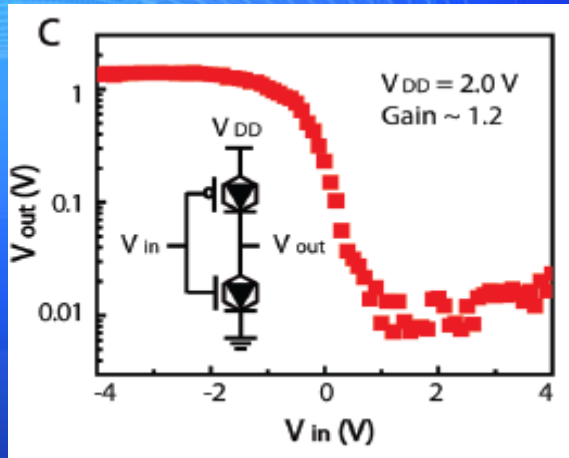
H Yang et al., Science 336 1140 (2012)





# Graphene Barristor

: Half adder & 1:1 Matching btw work function and Fermi level changes



H Yang *et al.*, *Science* **336** 1140 (2012)

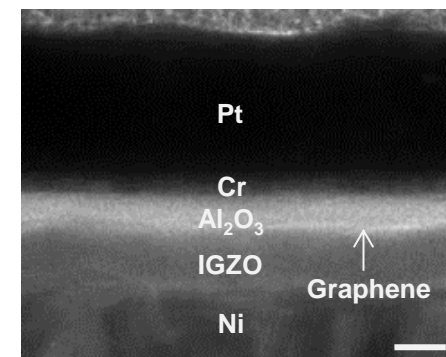
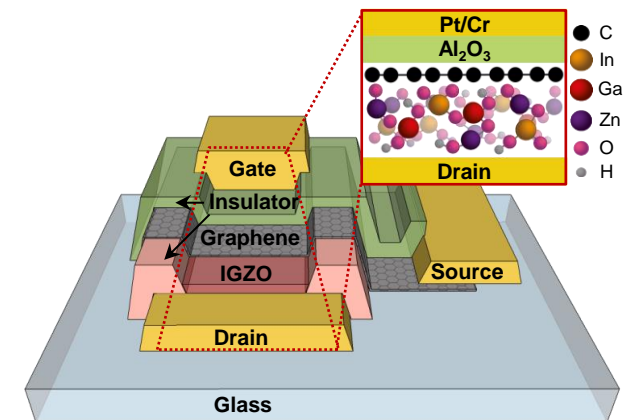
# Barrier Materials

## • Various Barrier Materials explored:

- 2D materials: MoS<sub>2</sub>, WS<sub>2</sub>
- Semiconductor: Si
- Graphene Family: Graphene Fluoride

	Barrier	On/Off ( $I_{on}$ )
U. Manchester Science (2012)	MoS <sub>2</sub>	10 <sup>4</sup> (0.1 $\mu\text{A}/\mu\text{m}^2$ )
SAIT Science (2012)	Si	10 <sup>5</sup> (0.1 $\mu\text{A}/\mu\text{m}^2$ )
U. Manchester Nature Nano (2013)	WS <sub>2</sub>	10 <sup>6</sup> (a few $\mu\text{A}/\mu\text{m}^2$ )
UCLA Nature Mat (2013)	MoS <sub>2</sub>	10 <sup>3</sup> (50 $\mu\text{A}/\mu\text{m}^2$ )
HRL EDL (2013)	Graphene Fluoride	10 <sup>5</sup> (5 $\mu\text{A}/\mu\text{m}^2$ )

## • Exploring Barrier Materials: IGZO

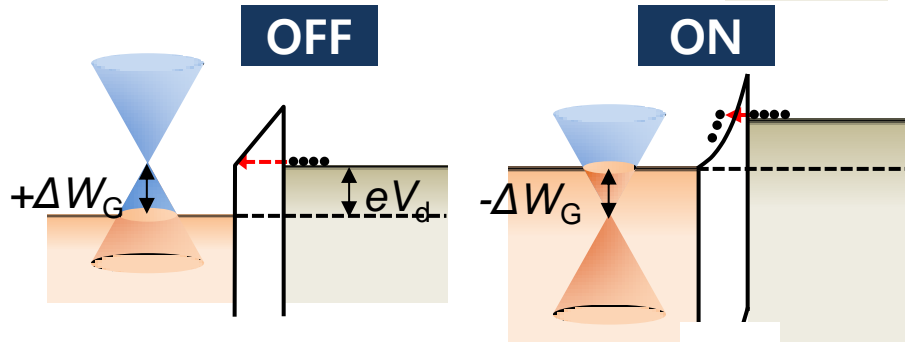
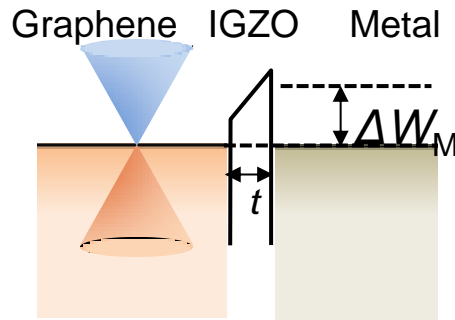


# Tunneling Barristor

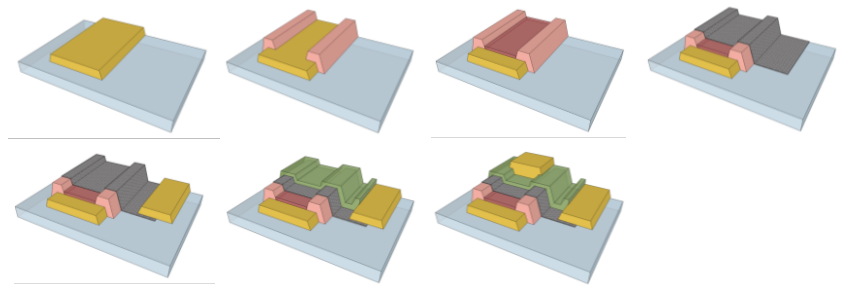
## : Working Principles: Barrier Thickness Modulations

- **Barrier Thickness Modulations**

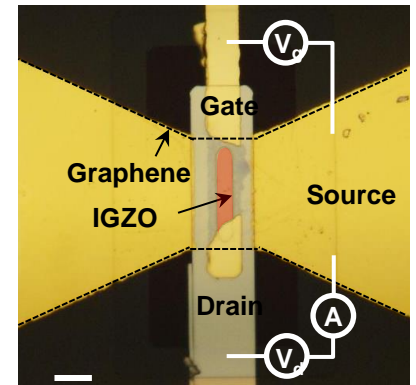
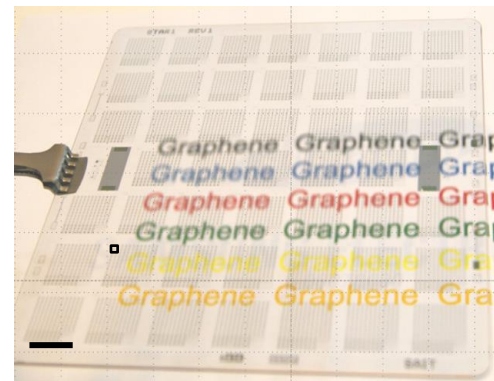
- Modulated thickness of tunneling Barrier



- **Conventional Fabrication Processes**



Fabricated on (15cm)<sup>2</sup> glass

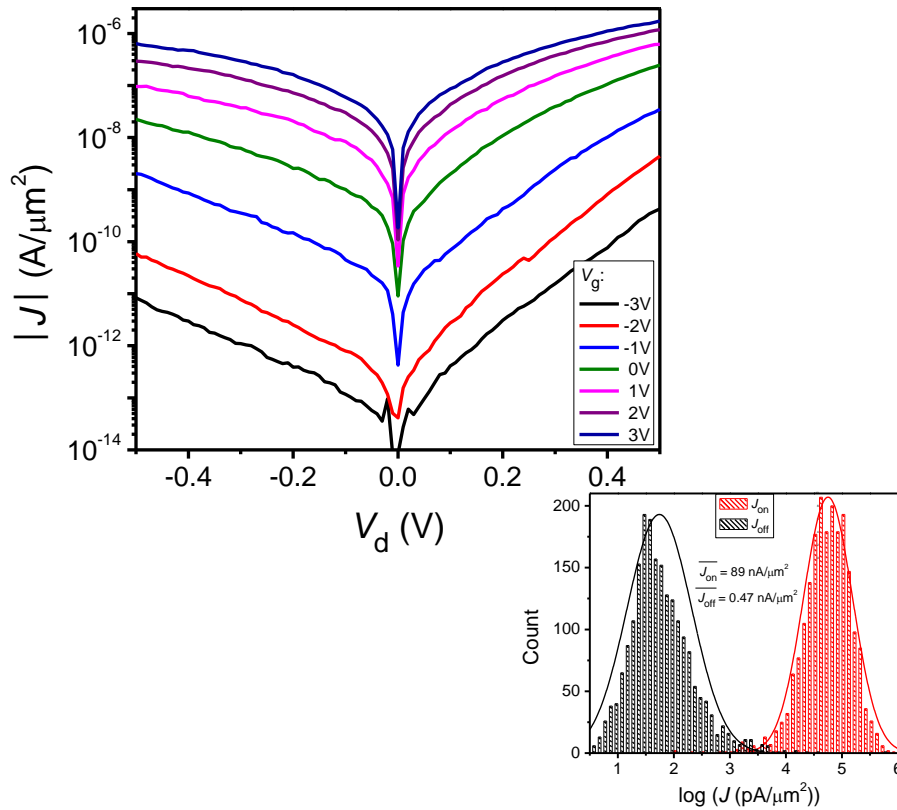


# IV Curves

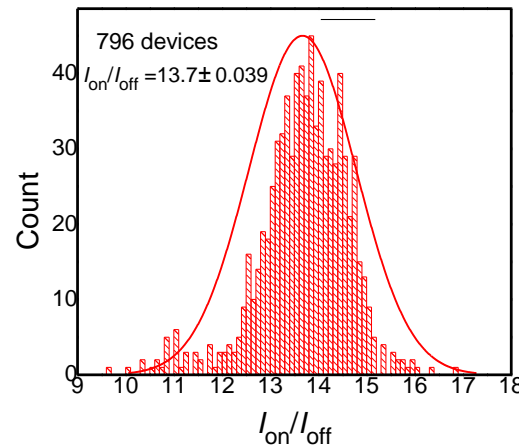
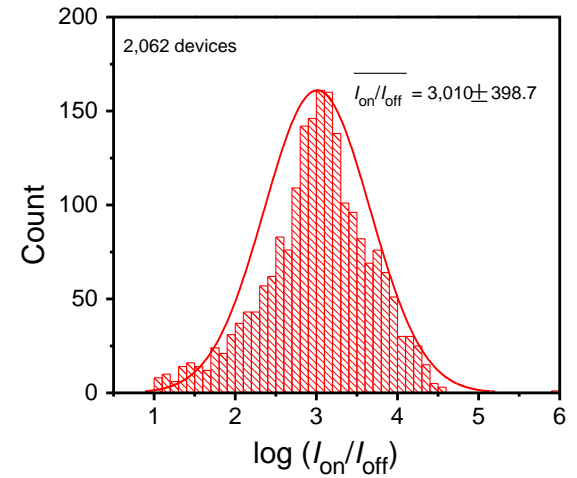
: High On/Off even at 0.1 VDS

## • Device Behavior

-  $I_{on}/I_{off} > 10^6$  @ 0.1 V



## • Statistics



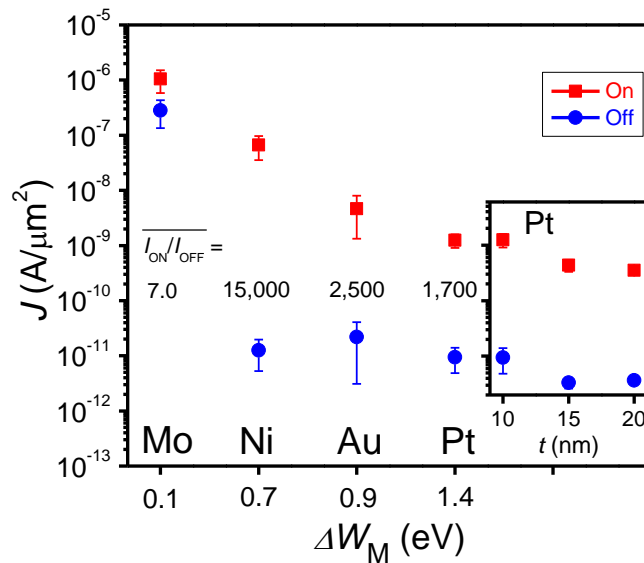
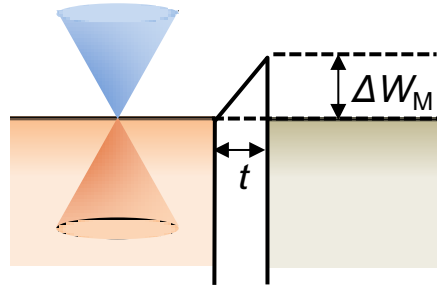


# Barrier Design

## : Barrier Modulation with metal work function

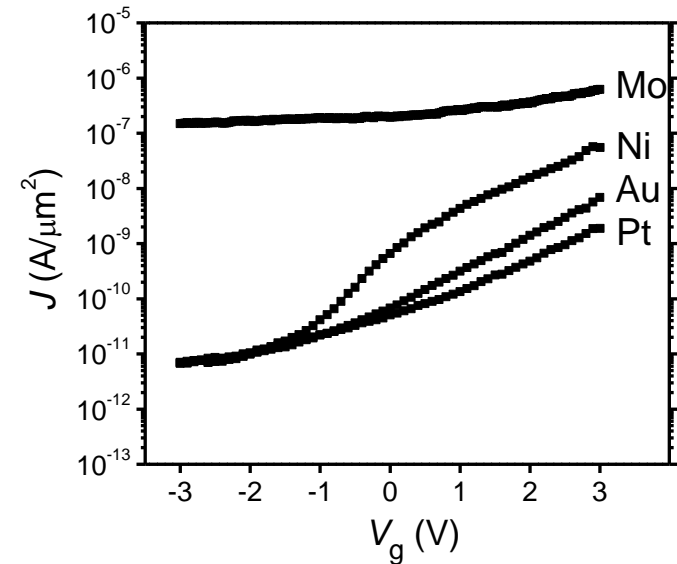
### • Barrier Modulation with Metal

- Large Barrier  
→ Low  $I_{\text{On}}$
- Small Barrier  
→ High  $I_{\text{Off}}$



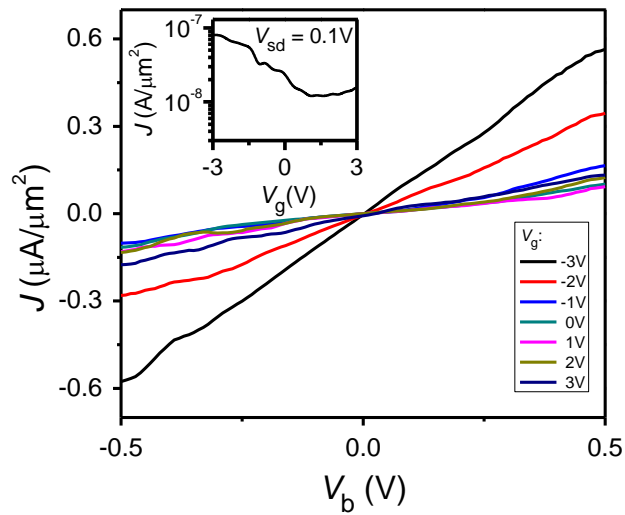
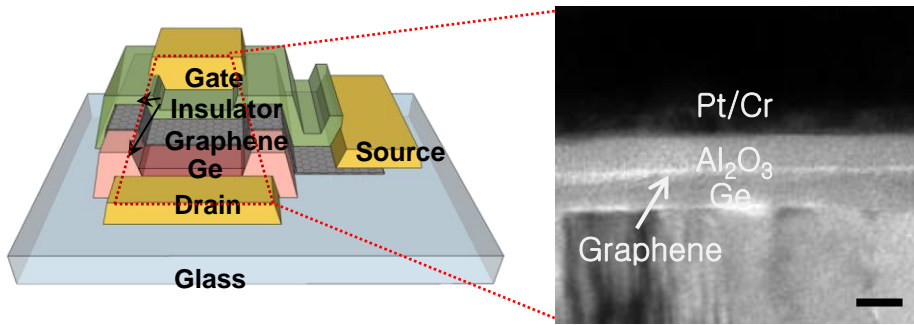
### • Exploring Barrier Materials

- Mo: Small response to gate and high off
- Pt: Small on current
- Ni: Small off current and high on current

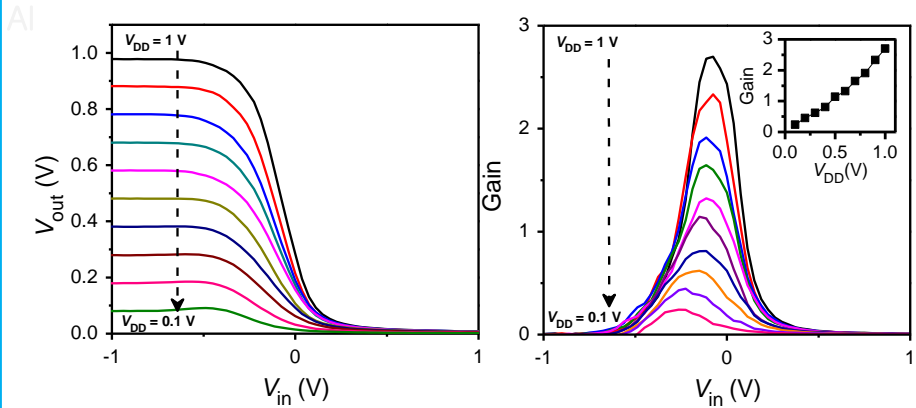
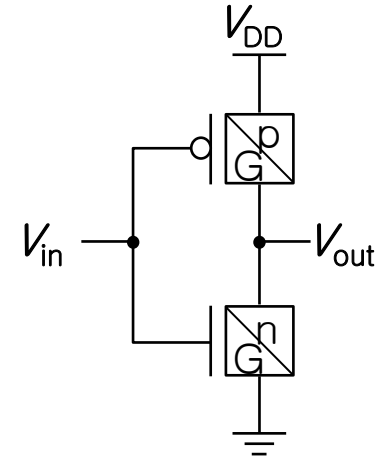


# Inverter

- p-type Barrier: Ge

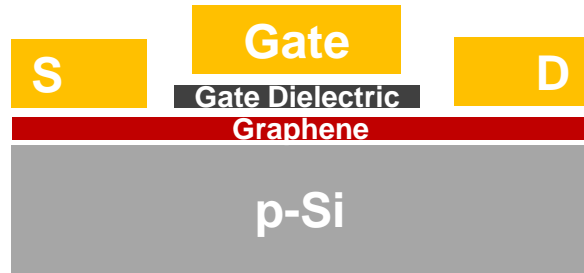


- Logic Inverter



# ALD on Graphene

# Graphene Incorporated Device Challenges



## Materials

- Direct Growth
- Analysis Tools

## Transfer

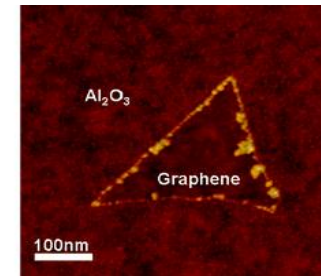
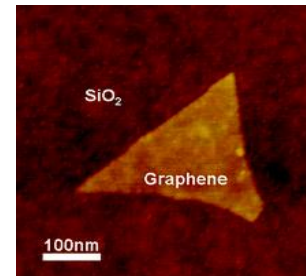
- Lamination
- Delamination
- Residue

## Interface

- ALD
- Metal contact

## ALD High-*k* Film on Graphene

:Non-conformal growth of high-*k* dielectric films

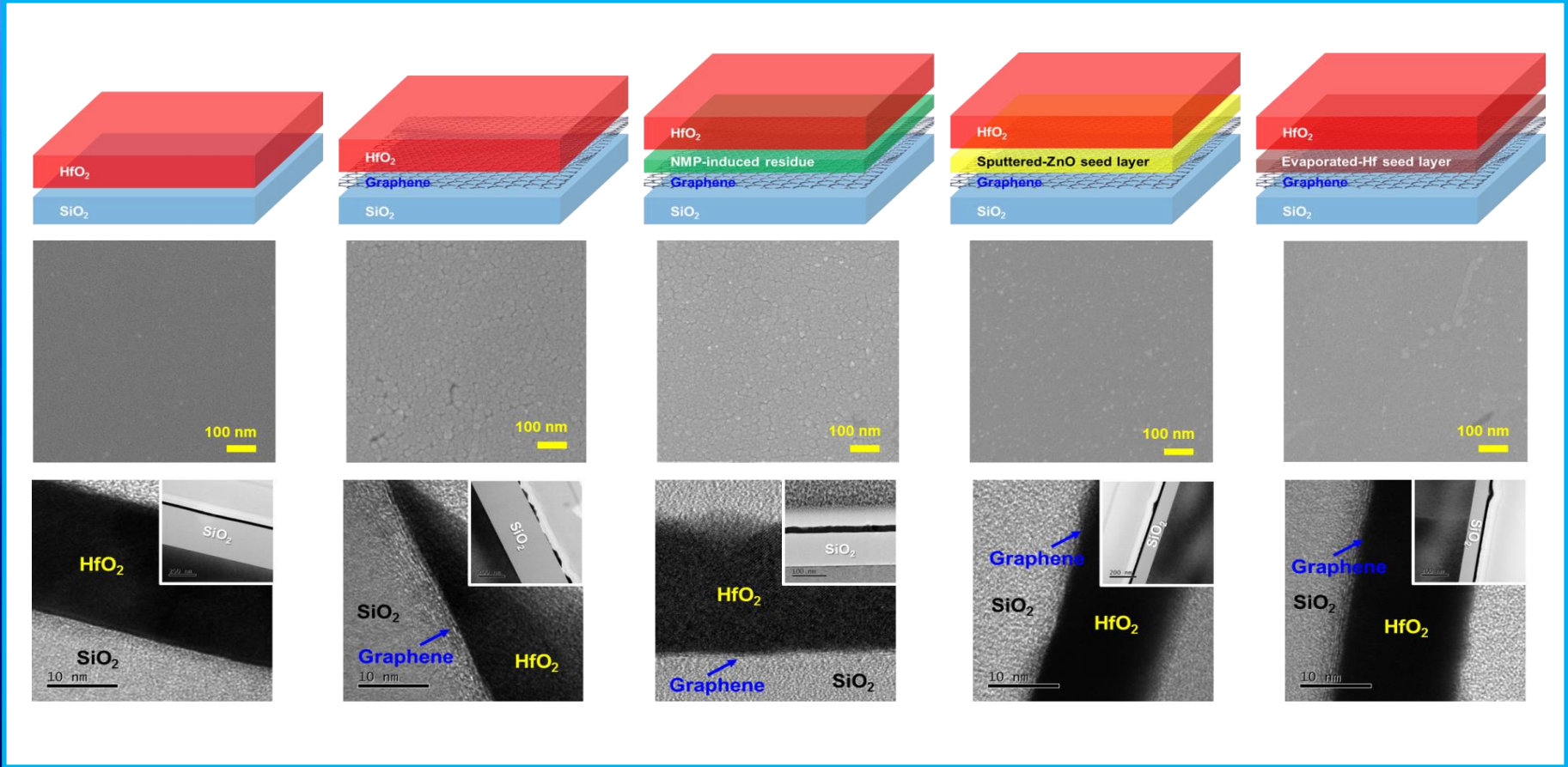


X. Wang *et al.* , *JACS*, 130(26), 8152 (2008)



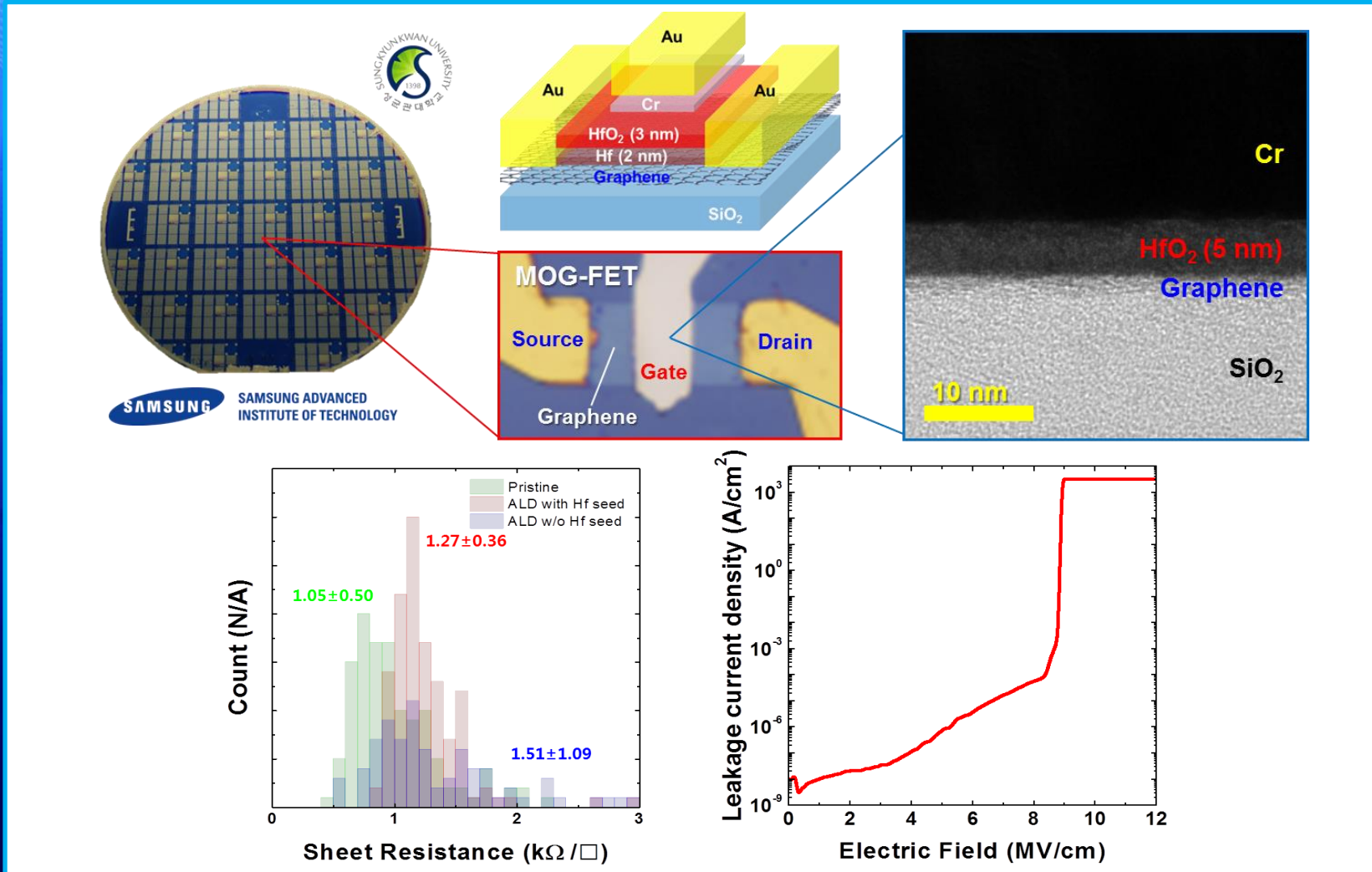
# ALD HfO<sub>2</sub> Films on Graphene

## : The effects of various surface modifications

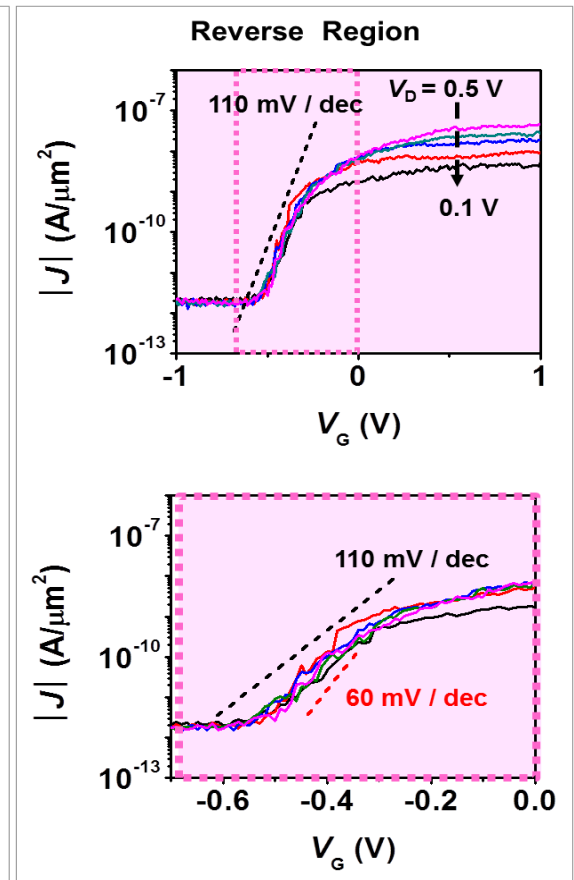
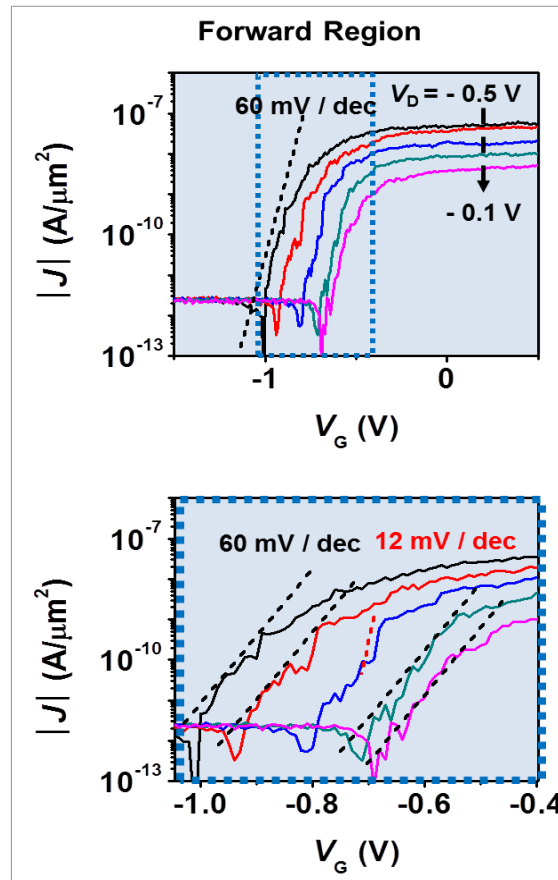
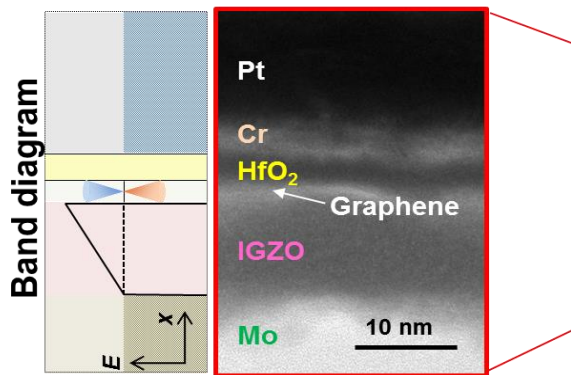
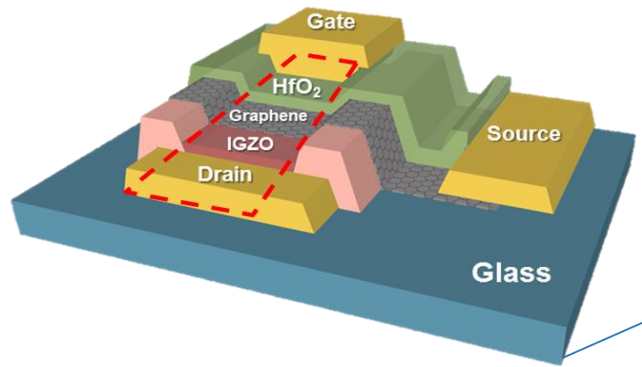


S-J Jeong, *et al.* (Submitted)

# Downscaling and Electrical Evaluation of ALD HfO<sub>2</sub> Films on Graphene



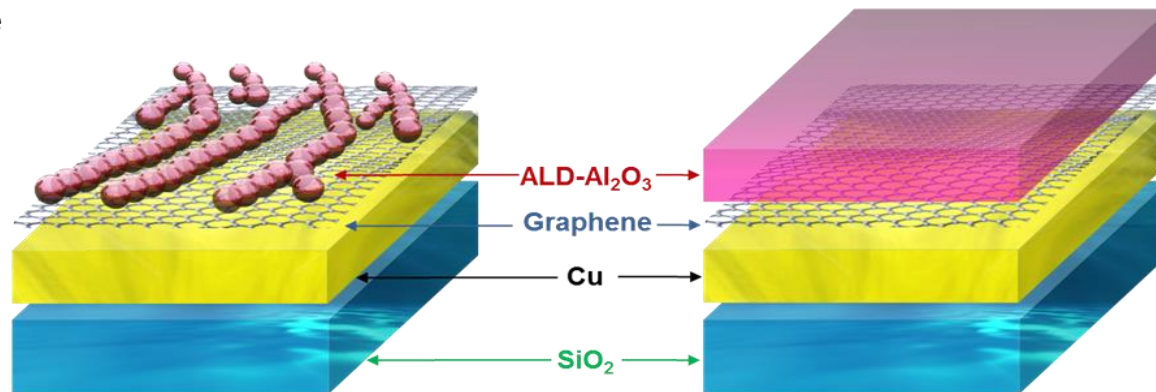
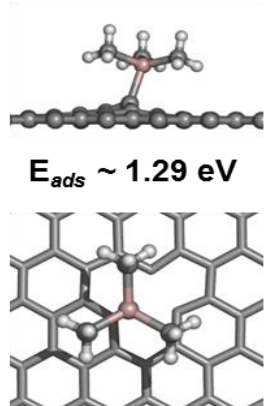
# Graphene Tunnelling Transistors



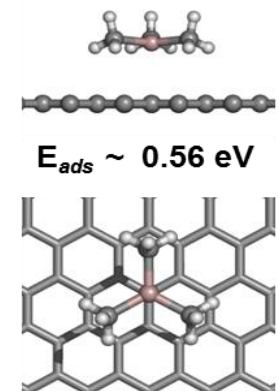


# Direct Growth of Metal Oxide Films on Graphene

Chemisorption of precursor molecule on defected-graphene



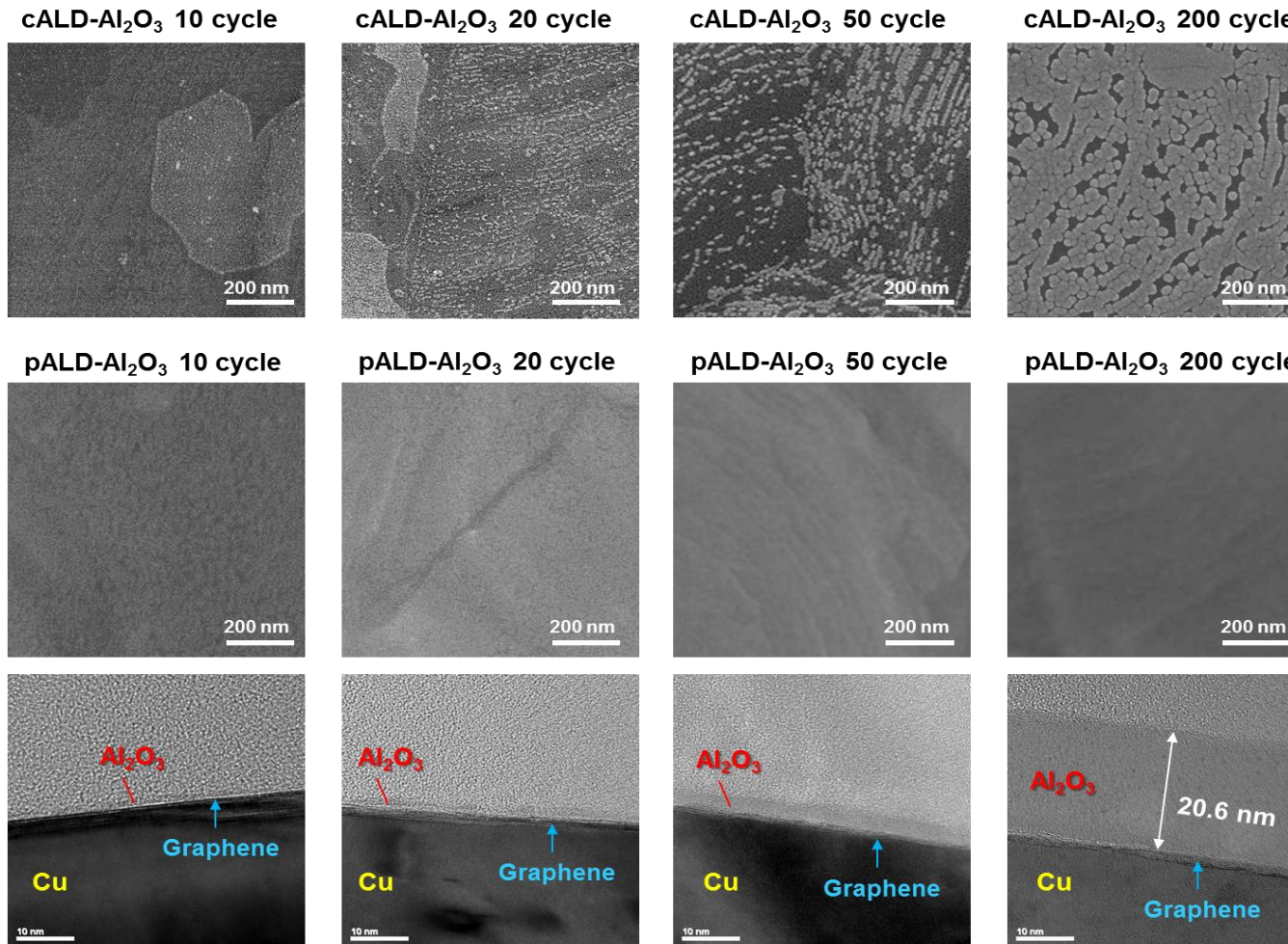
Physisorption of precursor molecule on pristine-graphene



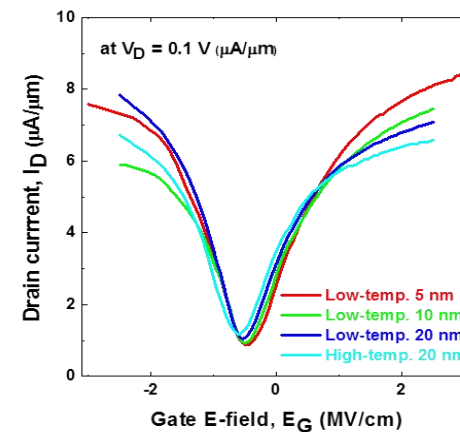
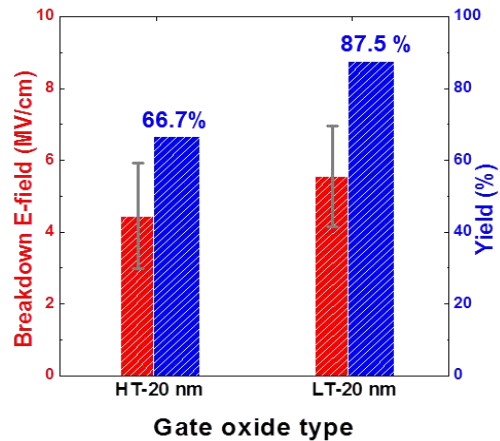
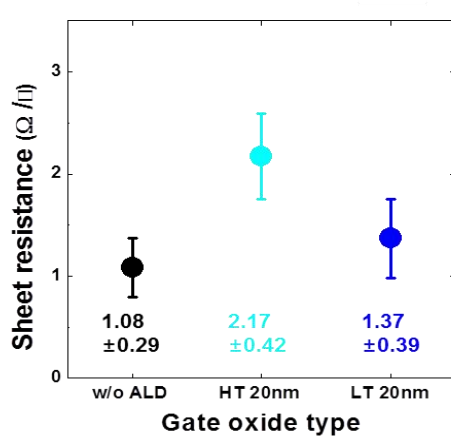
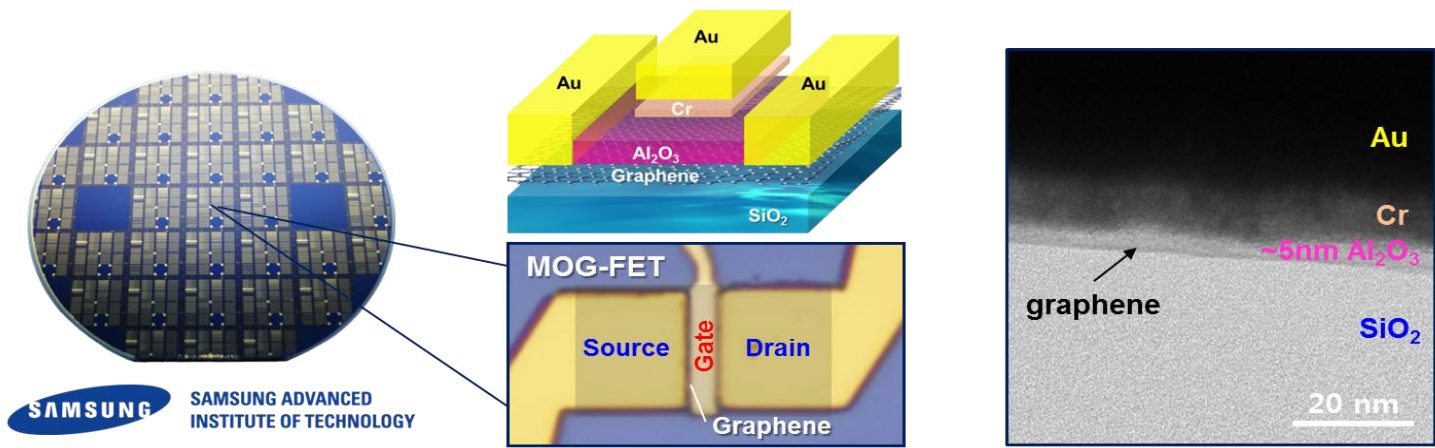
S-J Jeong, *et al.* (In preparation)



# Surface Morphology Evolution of pALD and cALD- $\text{Al}_2\text{O}_3$ thin films on Graphene



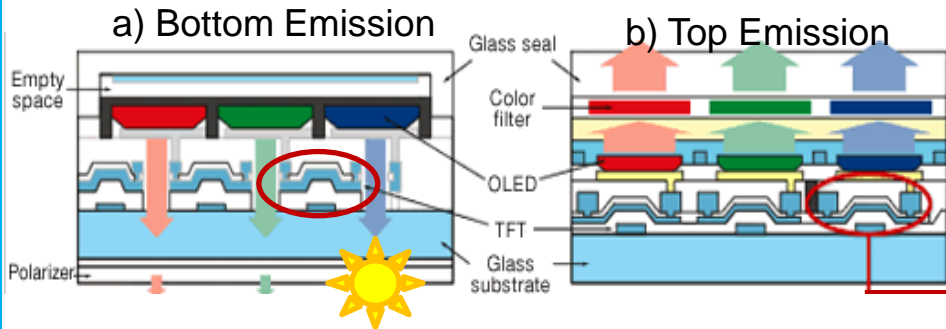
# Electrical Evaluation of pALD Al<sub>2</sub>O<sub>3</sub> Films on Graphene in a Wafer Scale



# Organic Light Emitting Transistor

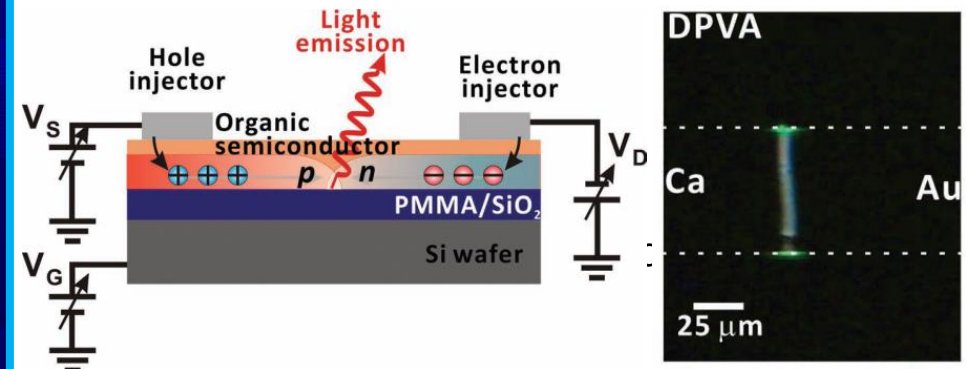


# Emission type of AMOLED



	Bottom emission	Top emission
Adv.	- Simple fabrication process	- Low power consumption - High colour purity - High resolution
Dis-Adv.	- Physical limitation - Low resolution (<1000dpi)	- Complexity of the fabrication process
Needs	Need to improvement light efficiency	Need to adapt large size device such as TV

- **Thin-film transistor based on an organic semiconductor**
  - The organic light-emitting field-effect transistor (OLET) emits light during transistor operation.

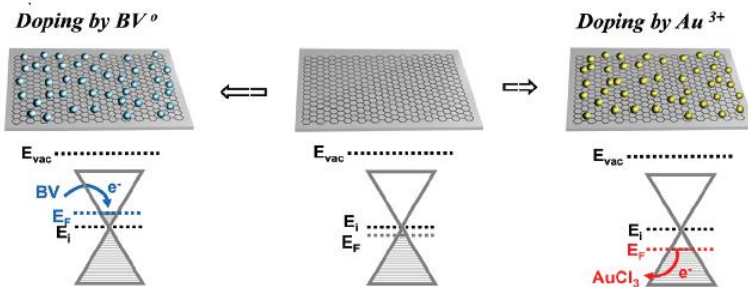




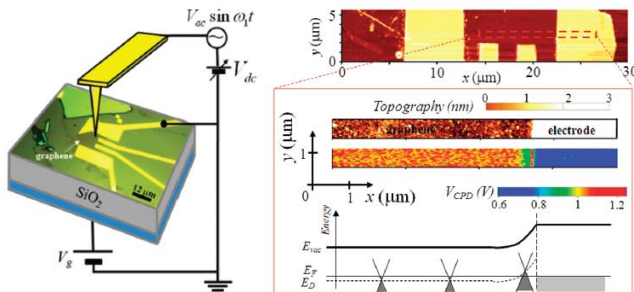
# Graphene Electrode

: 97.7% transparent and controllable work function with doping

- Transparency ~ 97.7%
- Work function can easily modulated by chemical and electric field

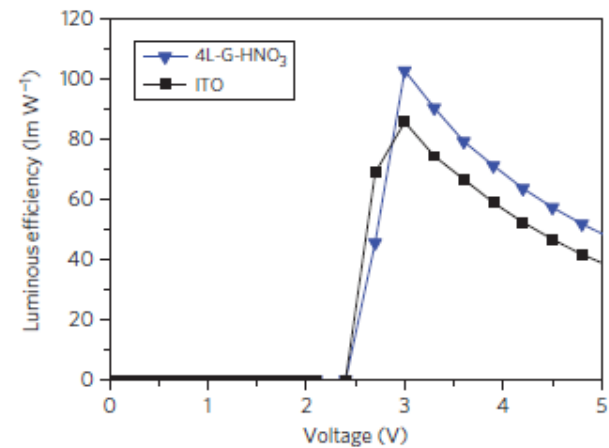
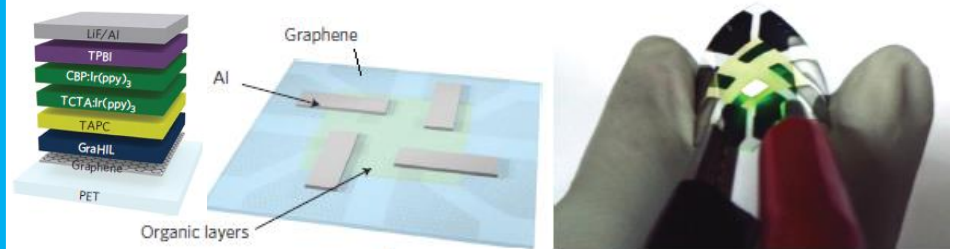


Shin *et al.*, *J. Am. Chem. Soc.*, **132**, 15603–15609, 2010



Yu *et al.*, *Nano Lett.*, **9**, 3430–3434, 2009

- Device performance with graphene electrode is similar to that with ITO



Ahn *et al.*, *Nature Photonics*, **6**, 105–110, 2012

# Vertically Stacked OLED and Graphene

: Graphene is used both electrode of OLED and channel in TFT

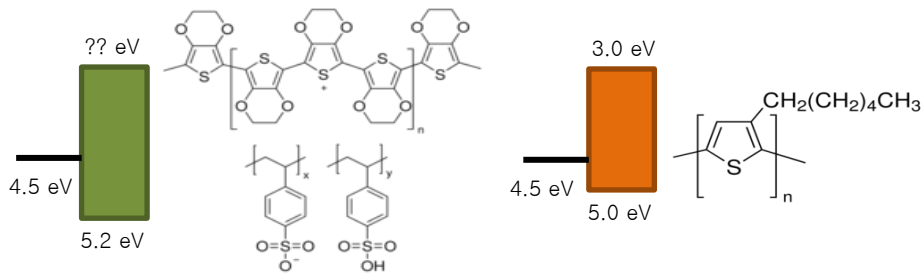
- Graphene together work as channel and electrode

Emitting part  
(EL with Graphene electrode)



Operating part  
(GB with Graphene channel)

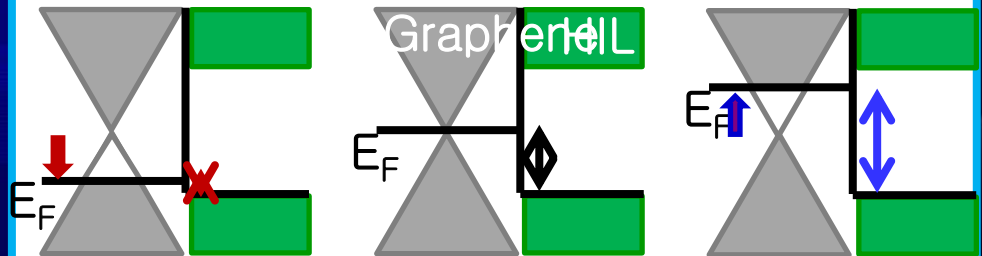
- Hole injection layer



- Controlling the number of injection hole by gate bias

- if Gate bias < 0, Graphene W/F increased speed of hole injection is faster
- if Gate bias > 0, Graphene W/F decreased speed of hole injection is slower

Gate bias < 0 ← Gate bias = 0 → Gate bias > 0

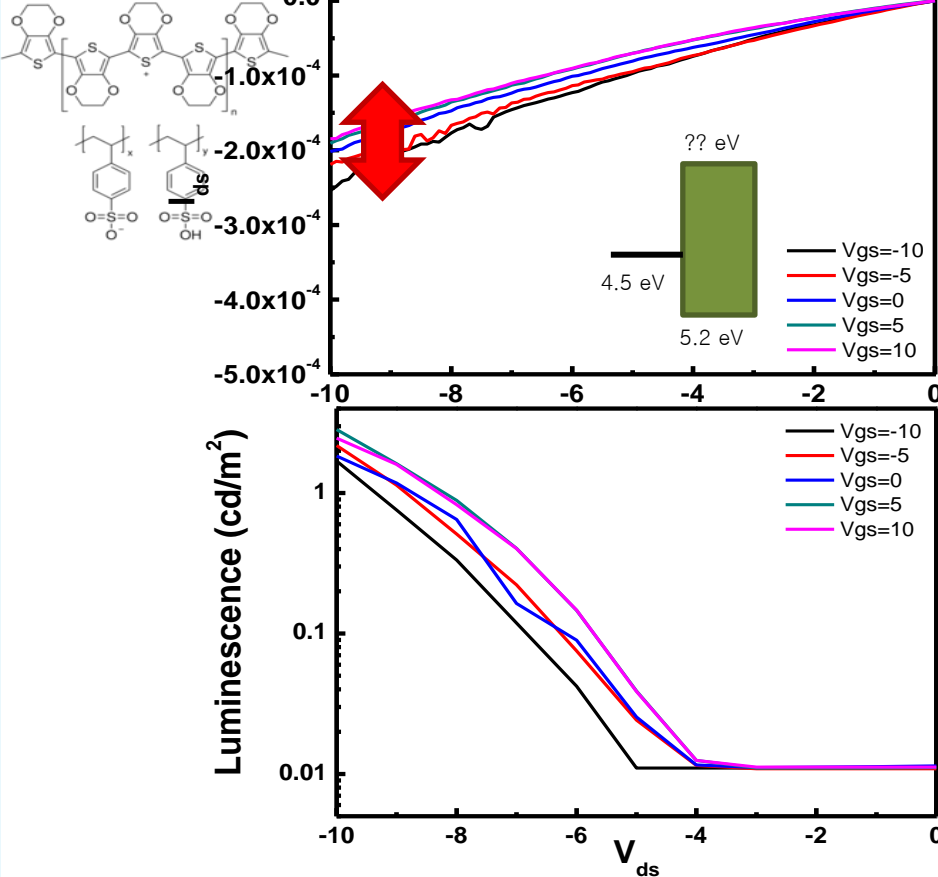


- Hole injection and recombination can be controlled by gate bias.

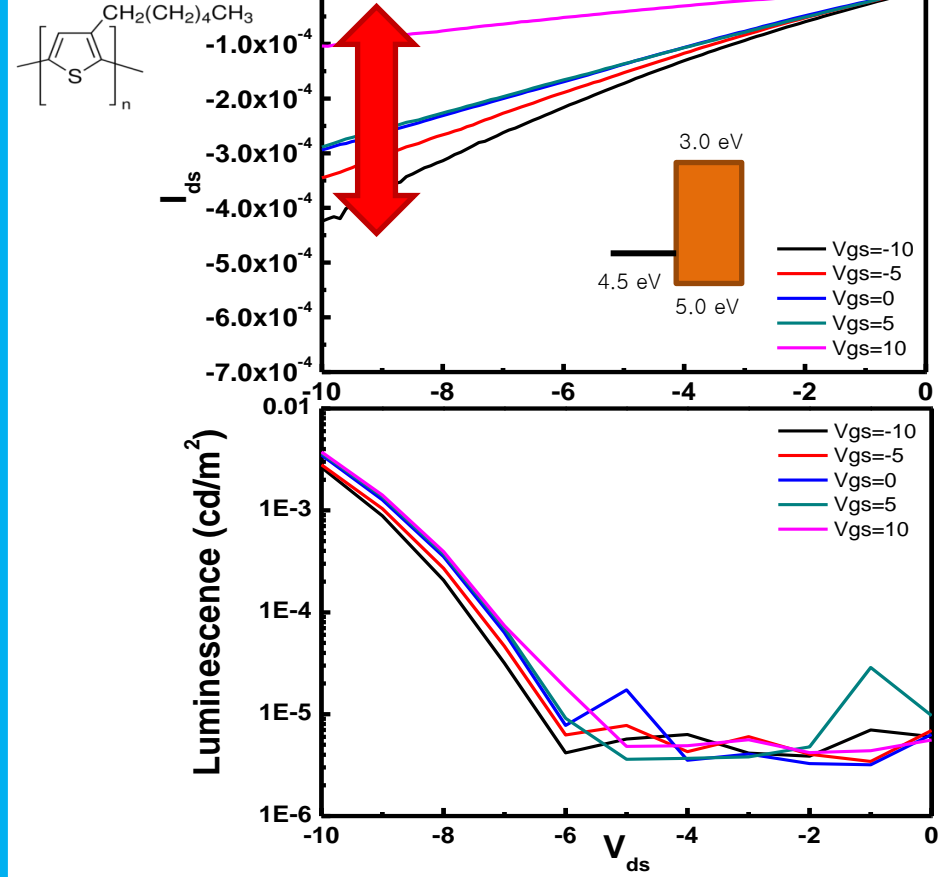
# Operation of OLEB (OLE Barristor)

: Drain current and luminescence efficiencies can be controlled by gating

## • PEDOT:PSS



## • P3HT



# Graphene for Si True Ohmic Contact



# Source/Drain Contact

: Contact Resistance became serious portion of total resistance of devices

## • Total Resistance of Device

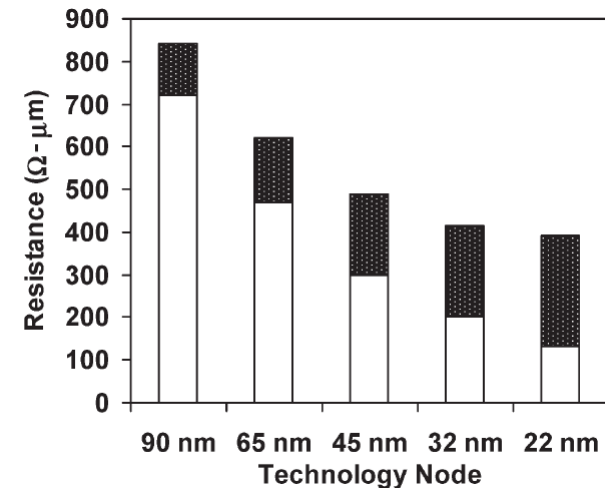
- Channel Resistance is getting smaller as the device getting smaller
- Specific contact resistance is constant and contact resistance is getting bigger as the contact area is getting smaller

$$R_{\text{Total}} = R_C(\text{S/n+}) + R(\text{p-Si}) + R_C(\text{n+/D})$$



## • Contact resistance of logic devices

- From 32 nm, contact resistance is higher than channel resistance.



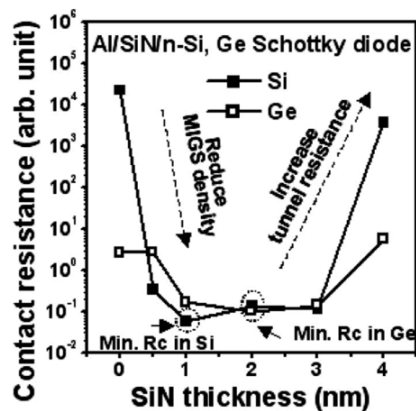
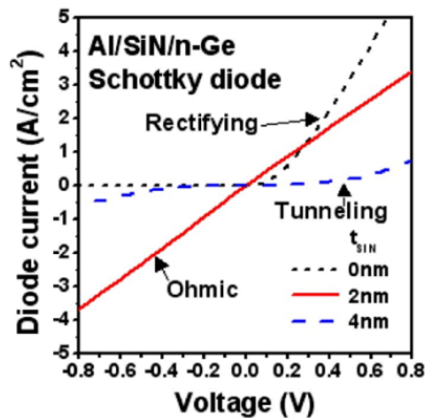
- 9.1% of PMOS's and 37.5% of NMOS's contact resistances are due to Schottky barrier between contact metal silicide and Si.

IEEE Trans Elec Dev **55**, 1259 (2008)

# De-pinning

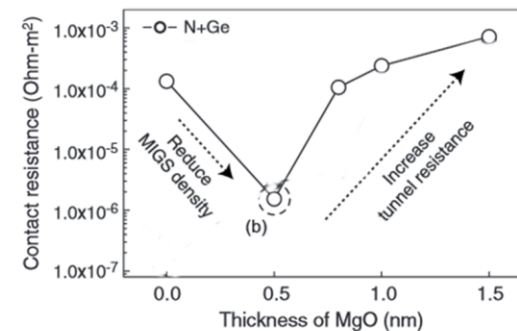
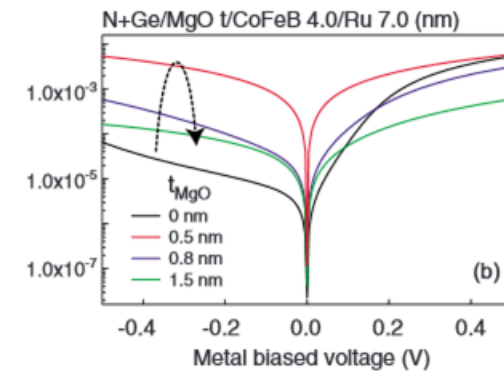
: Some may de-pin Si surfaces but hard to control its thickness (< 1 nm)

- De-pinning by inserting interfacial layer
  - 1nm SiN  $\Rightarrow$  Ohmic contact & contact resistance reduction by  $10^6$  times



*J. Appl. Phys.* **105**, 023702 (2009)

- 0.5nm MgO  $\Rightarrow$  Ohmic contact & contact resistance reduction by 100 times



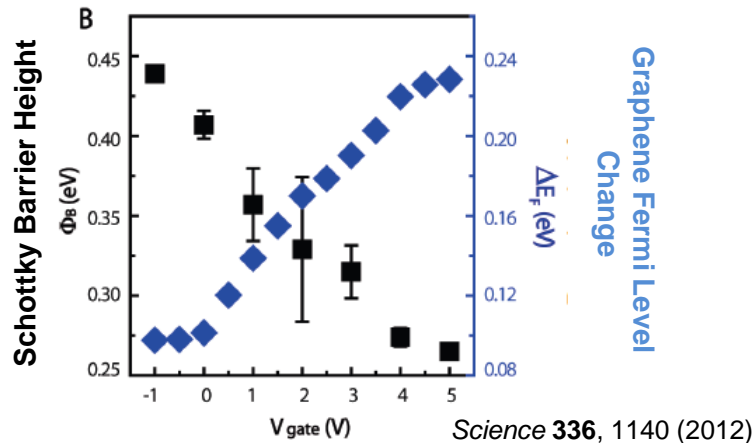
*Appl. Phys. Lett.* **96**, 052514 (2010)

# Graphene for De-pinning

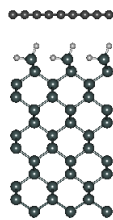
: AFM results show that Graphene improved contact resistances.

- De-pinning for Graphene on fully saturated Si

- 1:1 relationship btw work function & Schottky barrier height



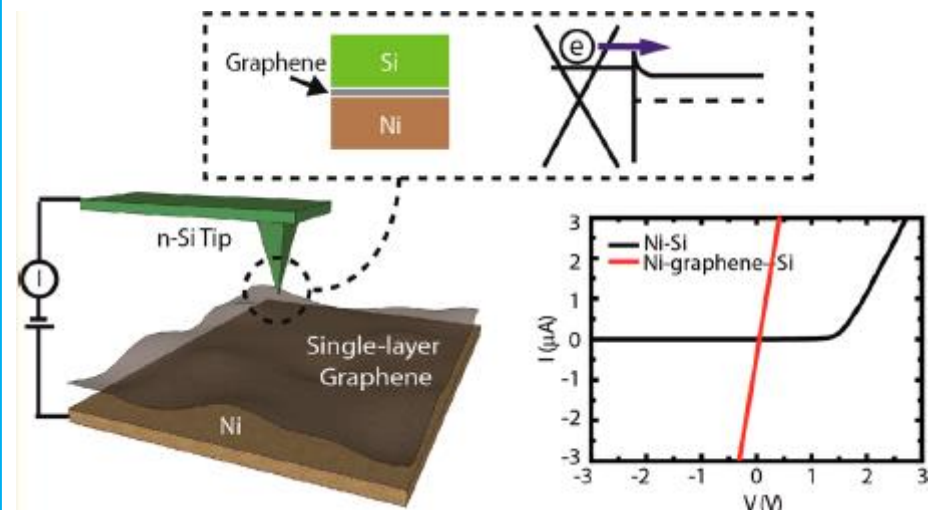
- Fully saturated Si Surface with 0.5 nm Separation with Graphene



*J. Appl. Phys.* **105**, 023702 (2009)

- Demonstrated that Schottky barrier height reduction

- Contact resistance was measured with AFM (Atomic Force Microscopy) and was  $10^{-8} \sim 10^{-9} \Omega\text{cm}^2$  (n-Si  $10^{17} \text{ cm}^{-3}$ ).



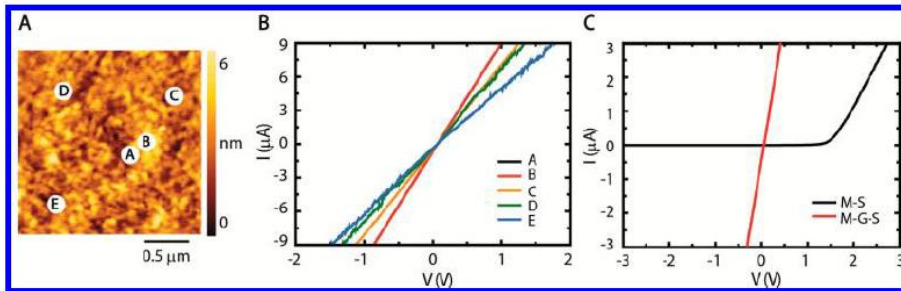
*Nano Letters* **13**, 4001 (2013)

# Graphene for Ohmic Contact

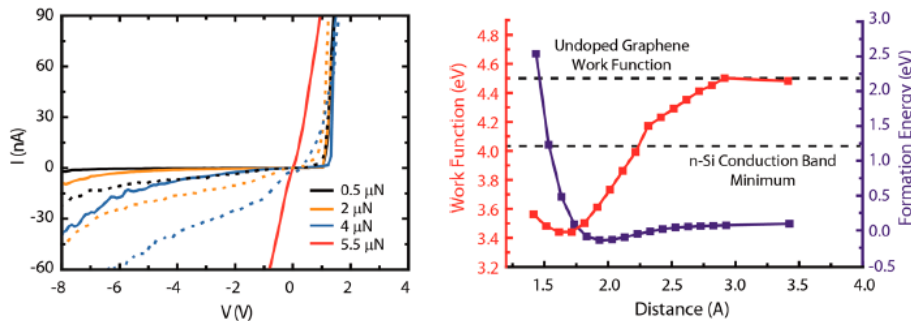
## : Ohmic Contact between Ni and Si with Graphene insertion

- Ohmic contact was demonstrated

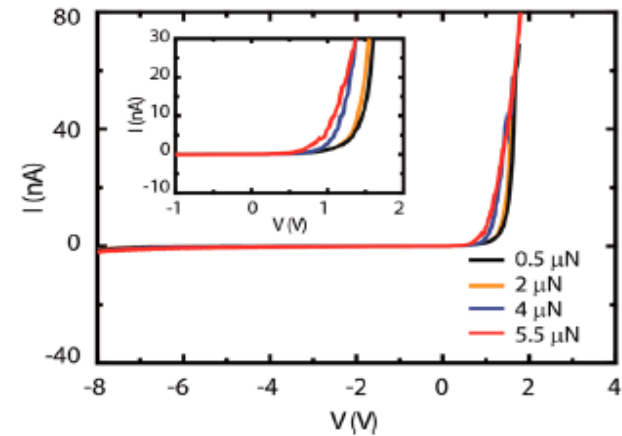
- 1:1 relationship btw work function & Schottky barrier height



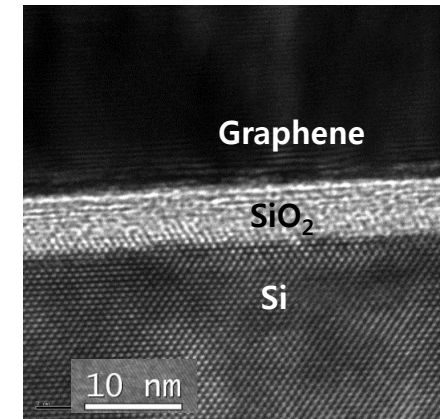
- Some cases shows Schottky but can be corrected



- Schottky Contact for Metal/Si



- Interface Issues





# Summary

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- **Graphene Properties**
  - High mobility, conductance, current density, transparency, chemical inertness
  - Surface area, thermal conductivity, ultimate strength
- **Applications**
  - New device concept: Gate-Tunable Schottky Diode / Barristor
  - High current on-off ratio ( $>10^5$ ) achieved
  - OLET
  - S/D Contacts
- **Too early to say what will happen: The Long Game**
  - Nature, Editorials, May 2011
  - It typically takes any technology some 20 years to emerge from the lab and be commercialized.

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