March 14, 2018

Large area quantum capacitance limited graphene field effect transistors for high precision sensing

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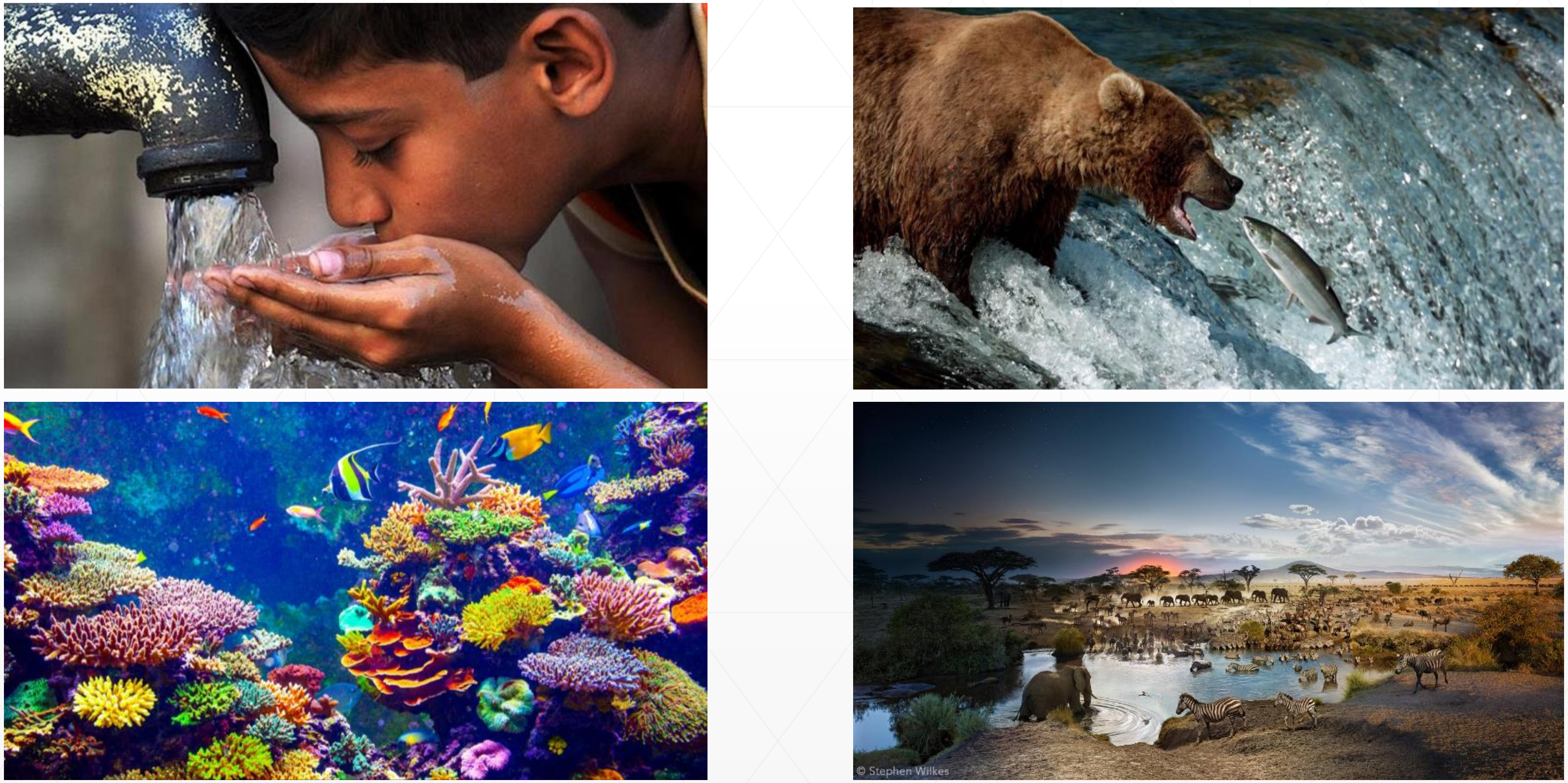
Outline

- Growing need for high precision potentiometric sensors
- Graphene Ion Sensing Field Effect Transistors (ISFETs)
- Graphene ISFET model and the key parameters for optimizing SNR
- Improving pH detection limit by 20 times over the state-of-the-art
- I. Fakih, F. Mahvash, M. Siaj, T. Szkopek, Phys. Rev. Appl. 8 (2017) 044022

Importance of Water Quality

- Water is fundamental for existence of all living species on the planet



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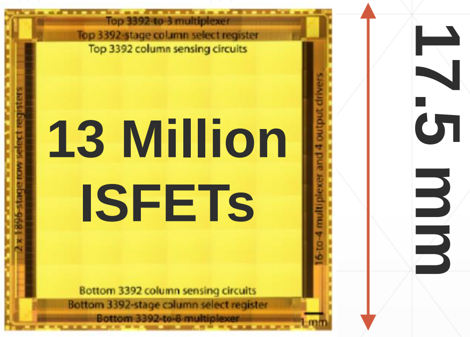
Limitations of current pH sensors

- Spectrophotometers are large and expensive
- Potentiometric sensors detection limit: 2 mpH
- Thermodynamically limited response to pH
- Noise (charge fluctuation, Johnson etc.)

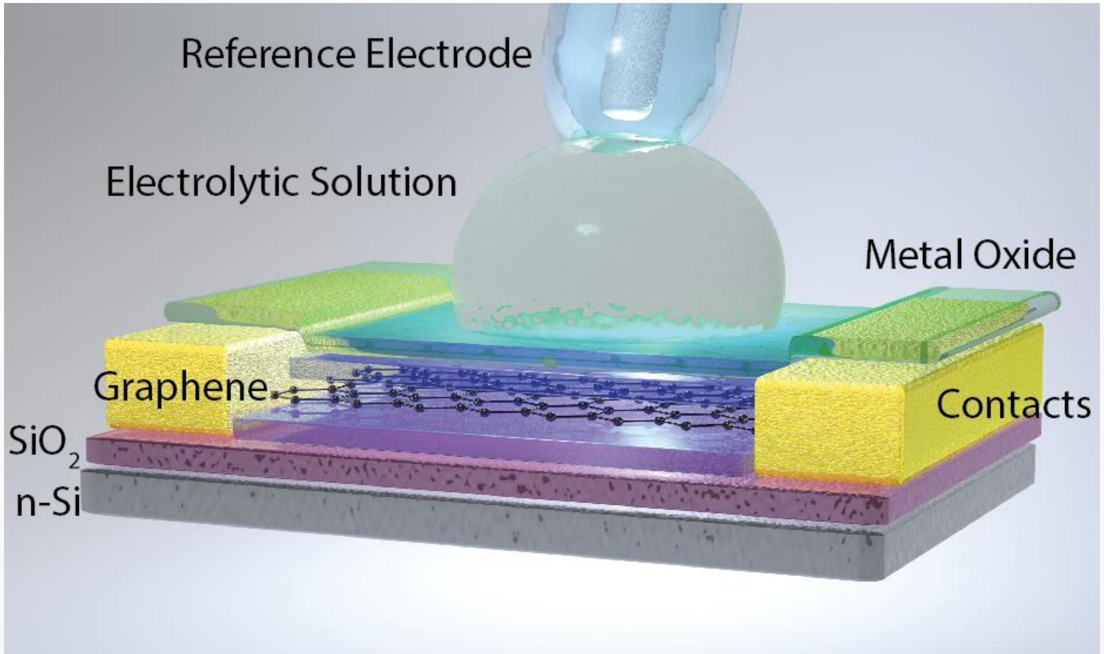


	Detection Limit	Price	Active Area
Spectrophotometry	0.1 mpH	> $10,000	
Silicon ISFET	2 mpH	$150 - $200	~ µm
Glass Electrode	5 mpH	$300 - $500	~ mm

J. Rothberg et al. “An integrated semiconductor device enabling non-optical genome sequencing,” Nature 475, 348–352 (2011).
http://www.coleparmer.ca/Product/Hach_9316900_Replacement_Sensor_for_95941_02_04_06/RK-95941-52
https://www.thermofisher.com/ca/en/home/life-science/lab-equipment/ph-ion-conductivity-oxygen-measurement/ph-measurement/ph-electrodes.html

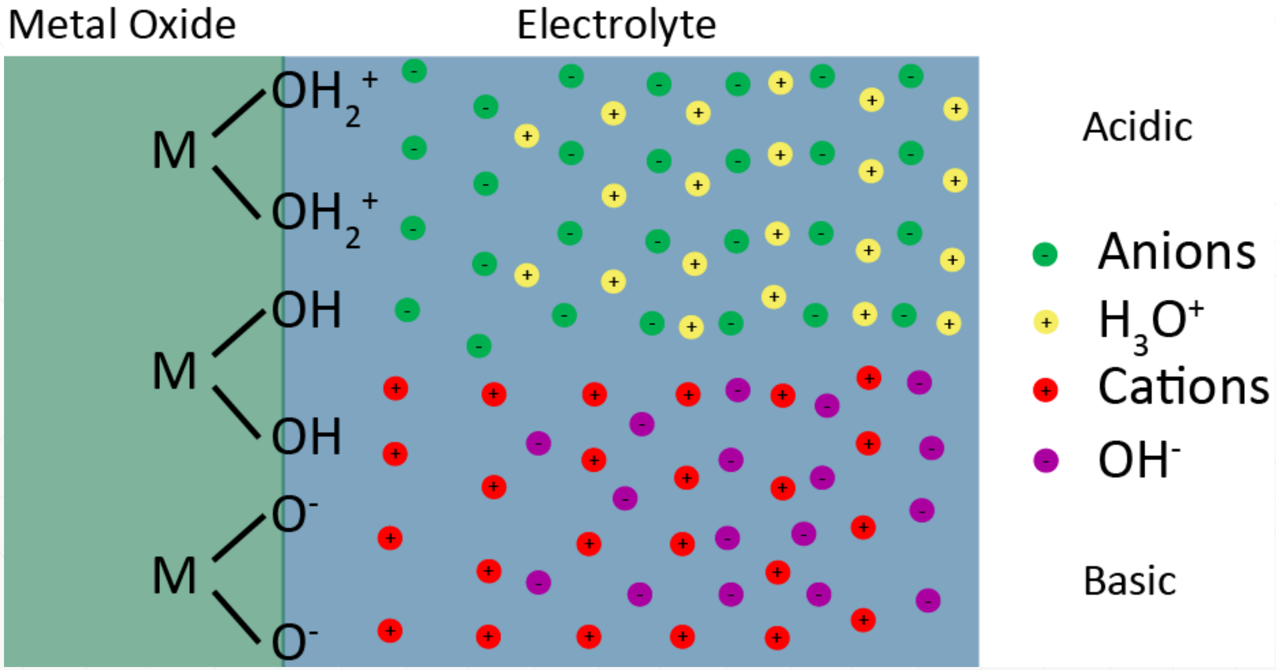
Why Graphene FETs for sensing?

- Coupling between the charge carriers and surface potential
- Low Johnson noise
- Relatively inexpensive fabrication process
- High field effect mobility



Why metal oxides?

- Surface hydroxyl groups will protonate or deprotonate.
- In the 1970s, Bergveld discovered that metal oxides have an intrinsic buffering capacity



The Nernst limit

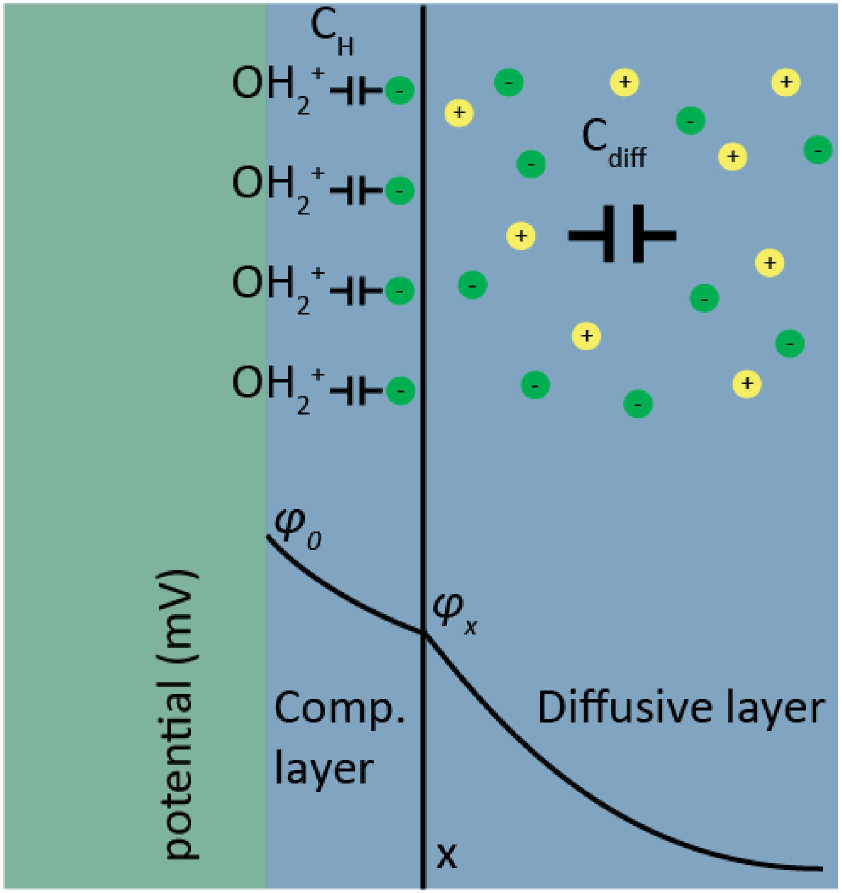
- Difference in proton density between surface and bulk solution
- Surface charges modulate surface potential φ_0:

$$[H^+]_{\text{surface}} = [H^+]_{\text{bulk}}\, e^{-\frac{q\varphi_0}{k_B T}}$$

- Change in φ_0 with pH:

$$\frac{\partial\varphi_0}{\delta \text{pH}_{\text{bulk}}} = \ln 10\, \frac{k_B T}{q}$$

- At room temperature ~ 59 mV/pH



P. Bergveld, "Thirty years of ISFETOLOGY," Sens. Actuators B-Chem. **88**,1 -20 (2003).

ISFET signal to noise ratio

- Signal to noise ratio:

$$SNR = \frac{< i_s^2 >}{< i_n^2 > + < i_x^2 >} = \frac{\delta\varphi_o^2}{\frac{e^2 N_0}{C^2 A} \cdot \frac{\Delta f}{f} + {< i_x^2 >}\big/{g_m^2}}$$

- For large g_m,

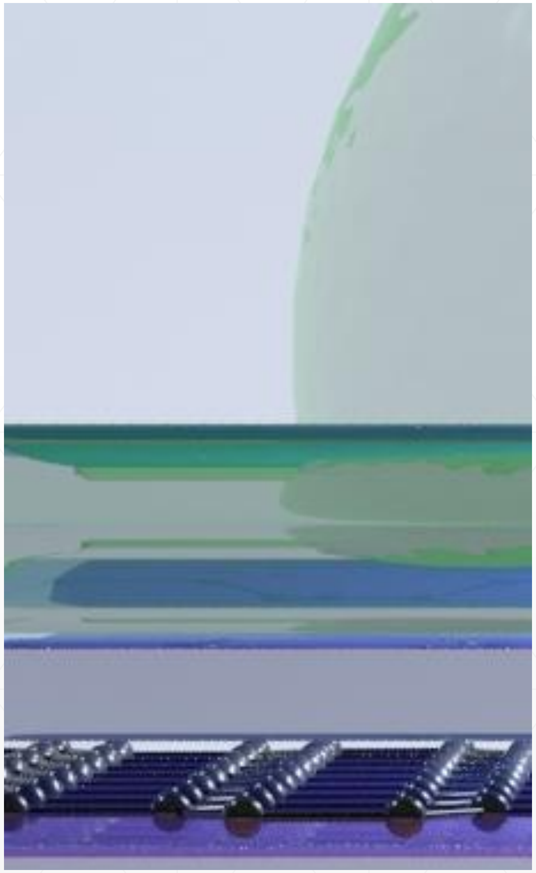
$$SNR \approx \frac{C^2 A}{e^2 N_0} \cdot \frac{f}{\Delta f} \cdot \delta\varphi_o^2$$

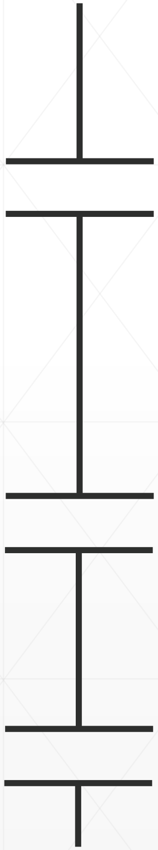
- Maximize SNR:

$$\mu_{FET} \uparrow \qquad C \uparrow \qquad A \uparrow$$

Capacitance of ISFET

- Capacitance C is a series combination of:

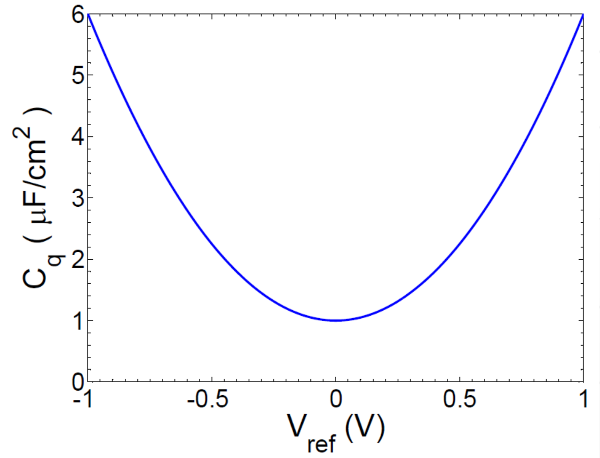




C_d ~ 17 μF/cm^2

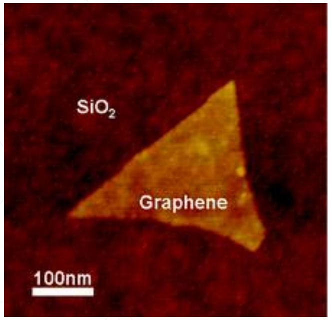
$$C_{ox} = \epsilon / t$$

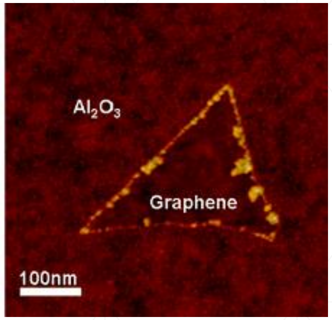
$$C_q = \frac{e^2 \delta n}{\delta E_F} = e^2 2E_F / \pi(\hbar v_F)^2$$

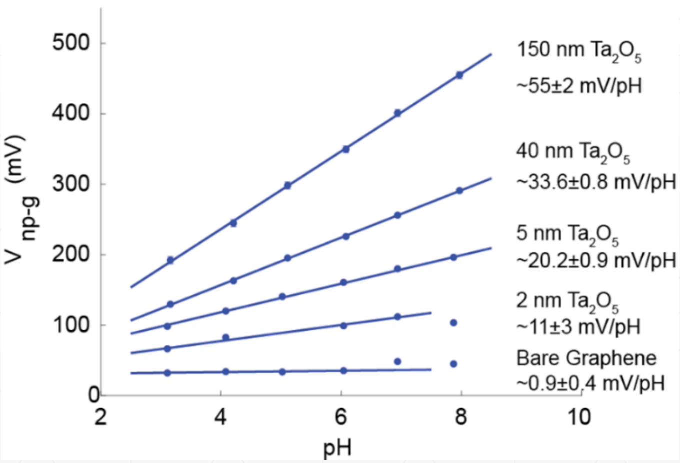


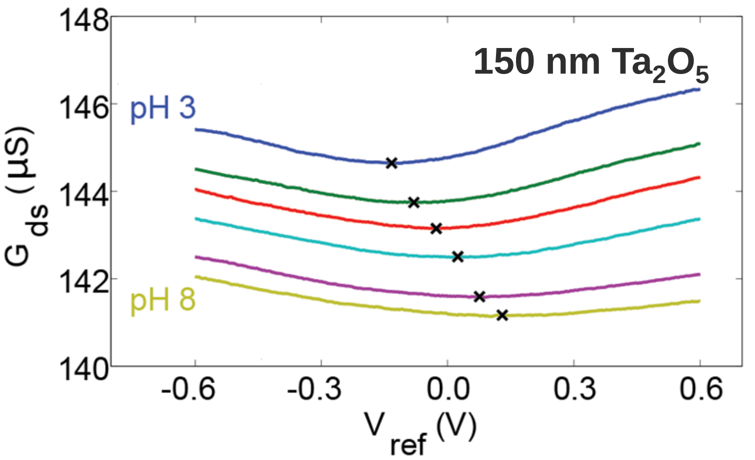
Challenges with Graphene FETs

- Difficult to grow stoichiometric oxides on graphene with ALD
- Mobility ~ 250 cm^2/Vs
- Capacitance < 0.1 µF/cm^2









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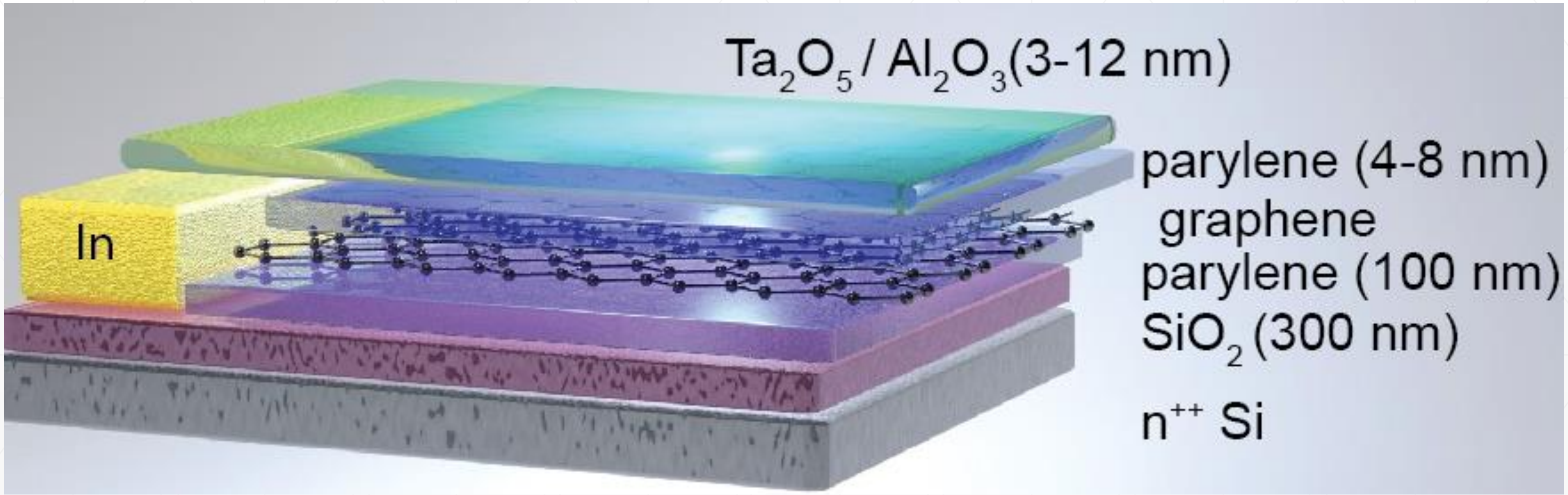
I. Fakih, S. Sabri, F. Mahvash, M. Nannini, M. Siaj, T. Szkopek, Applied Physics Letters, **105** (2014) 083101.

Encapsulating graphene with parylene

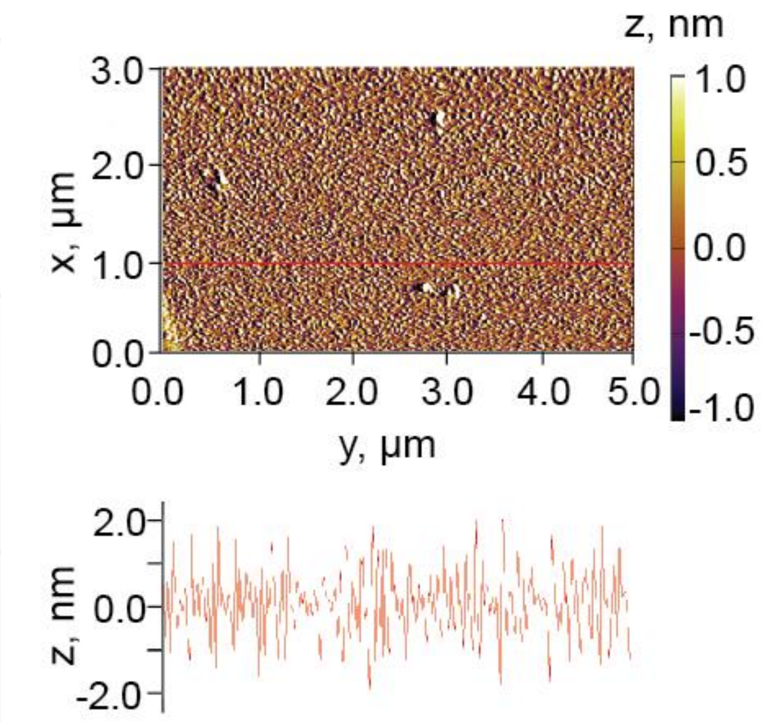
- 4 – 8 nm of parylene is grown on the graphene using CVD
- Protects the graphene during ALD
- Acts as a seeding layer for oxide pre-cursor
- High quality 3nm oxide with uniform coverage



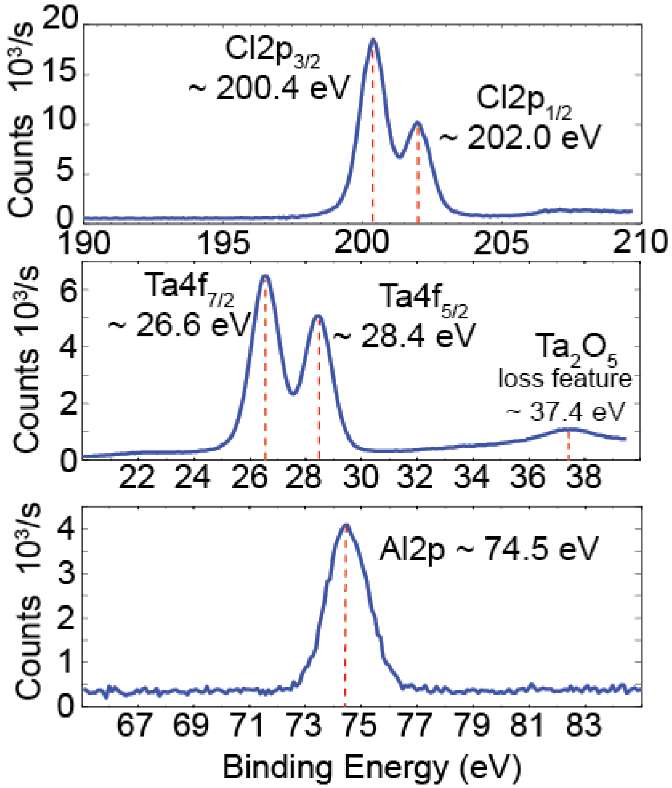
I. Fakih, F. Mahvash, M. Siaj, T. Szkopek, Phys. Rev. Appl. 8 (2017) 044022

Quality of parylene and metal oxides

- AFM of 4 nm of parylene



- XPS of parylene and metal oxides



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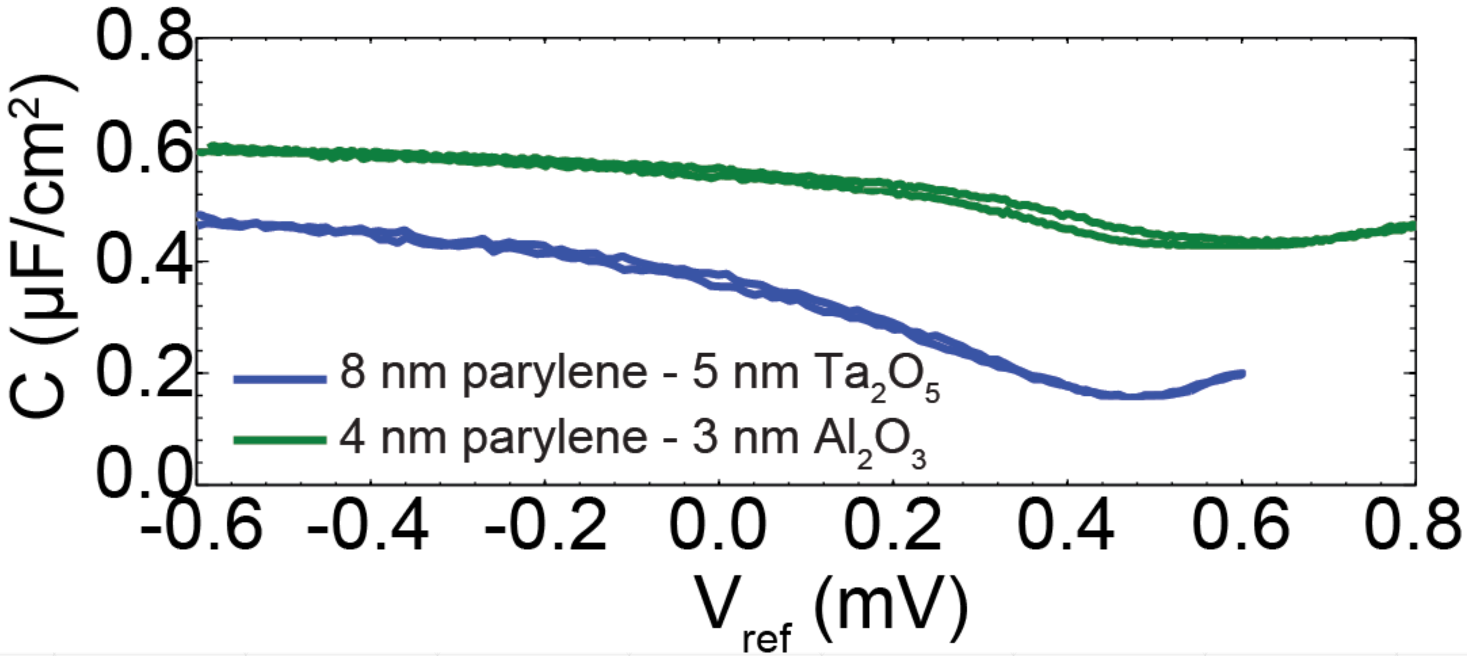
Approaching the quantum capacitance limit



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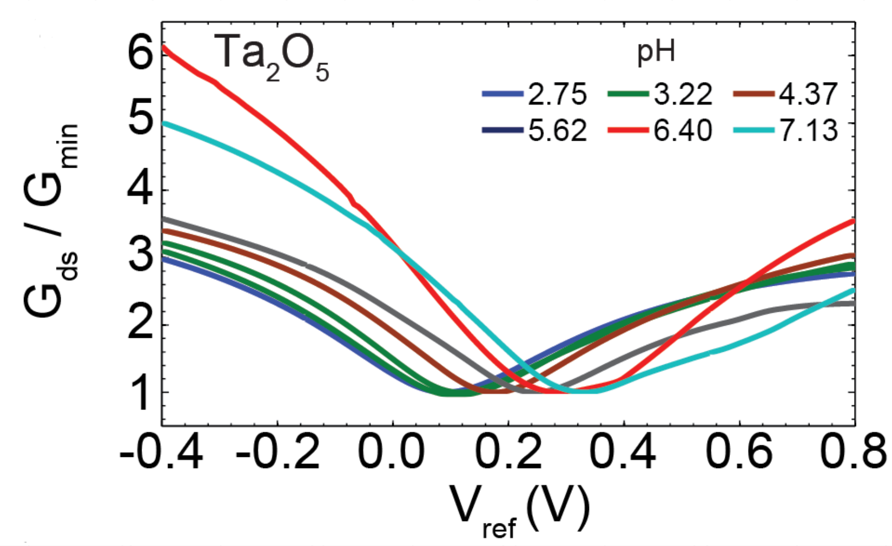
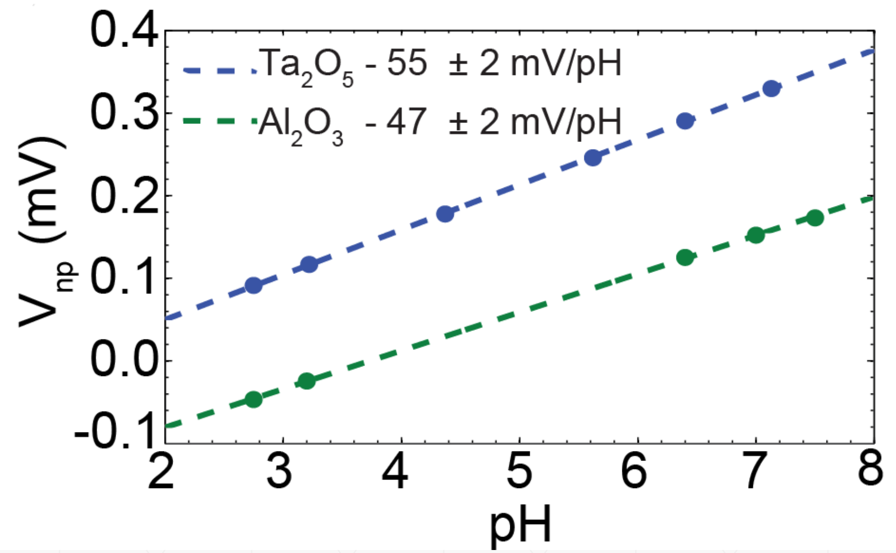
Significant improvements in transconductance and mobilities

- Sensitivities of ~ 55 mV/pH with Ta_2O_5 and ~ 47 mV/pH with Al_2O_3
- Mobilities of ~ 7,000 cm^2/Vs





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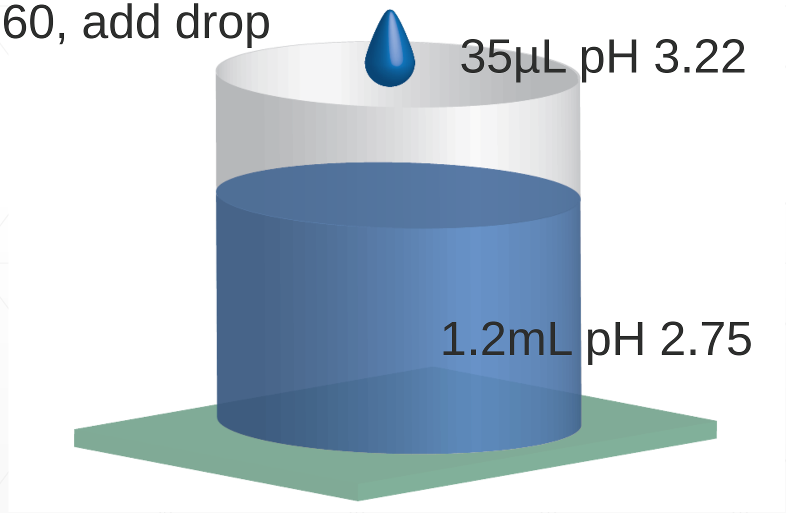
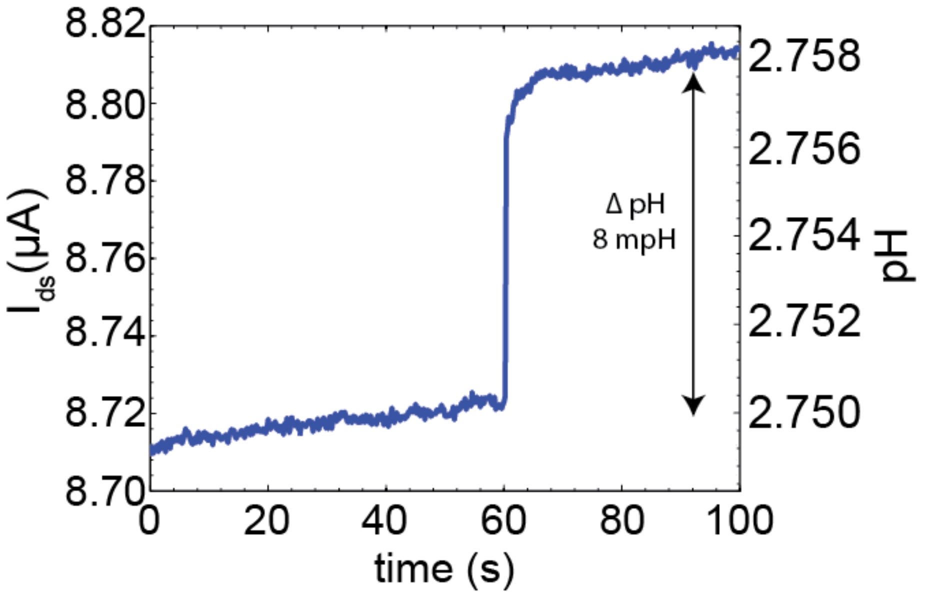
sub mpH Detection Limit

- Δ85 nA corresponds to Δ8 mpH
- Background RMS noise of ~ 1 nA → Detection limit is 0.1 mpH

t = 60, add drop



$$\Delta\mathrm{pH} = -\Delta\log([\mathrm{H_3O^+}])$$
$$\Delta\mathrm{pH} = 8\ \mathrm{mpH}$$



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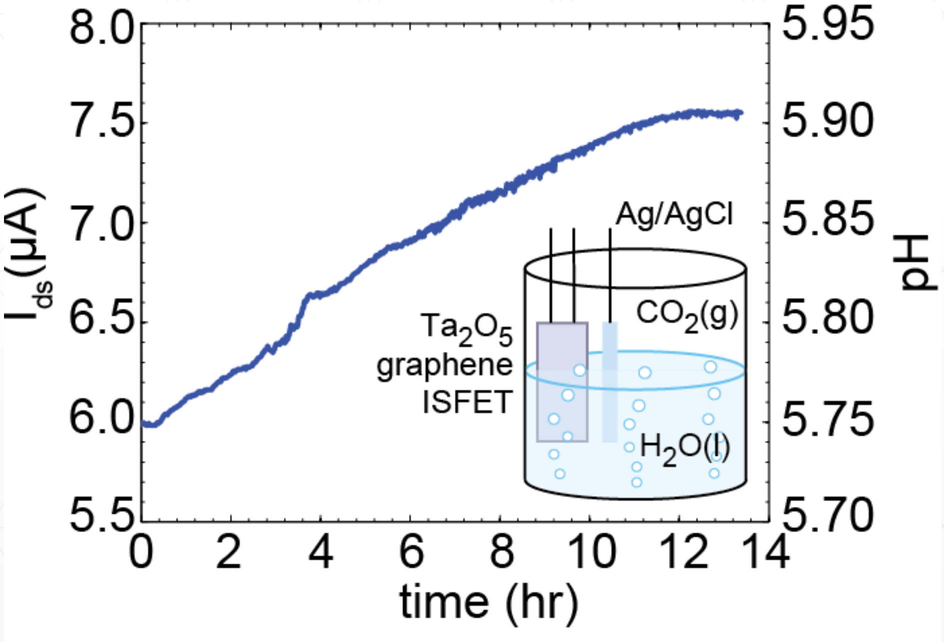
Monitoring acidity of carbonated water in real time

- 1.2 mL of potable carbonated water with pH = 5.75 over 14 hours



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Conclusion and Future Work

- Parylene encapsulation protects graphene from degradation
- Parylene acts as a seeding layer for high quality metal oxide films
- Improved minimum detection limit by 20 times over current sensors
- Other ion and molecules can be measured by replacing the sensing layer

	Detection Limit	Price	Size
Silicon ISFET	2 mpH	\$150 - \$200	~ µm
Glass Electrode	5 mpH	\$300 - \$500	~ mm
Graphene ISFET	0.1 mpH	< \$25 ?	~ mm

Acknowledgments

- *McGill University*
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    - **Farzaneh Mahvash**
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- *FRQNT*
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McGill

NSERC
CRSNG

RQMP

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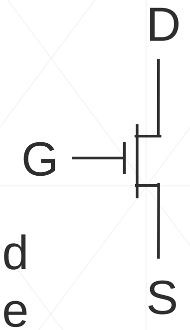
ISFET Operation

The drain current I_{DS} for an ISFET in non-saturation mode is identical to that of a MOSFET :

$$I_{DS} = \frac{\mu C_{ox} W}{L}\left[(V_{GS} - V_t)V_{DS} - \frac{1}{2}V_{DS}^2\right]$$



where C_{ox} is the oxide capacitance per unit area, W and L the width and the length of the channel, respectively, and μ is the electron mobility of the channel.

V_t for a MOSFET:

$$V_t = \frac{\Phi_{\mathrm{M}} - \Phi_{\mathrm{Si}}}{\mathrm{q}} - \frac{\mathrm{Q_{ox}} + \mathrm{Q_{SS}} + \mathrm{Q_B}}{\mathrm{C_{ox}}} + 2\phi_f$$

V_t for a ISFET:

$$V_t = E_{ref} - \Psi_0 + \chi^{sol} - \frac{\Phi_{\mathrm{Si}}}{\mathrm{q}} - \frac{\mathrm{Q_{ox}} + \mathrm{Q_{SS}} + \mathrm{Q_B}}{\mathrm{C_{ox}}} + 2\phi_f$$

The Differential Double Layer

Surface charges modulate surface potential φ_0:

$$[H^+]_{surface} = [H^+]_{bulk}\, e^{-\frac{q\psi_0}{k_B T}}$$

Small changes in $[H^+]_{surface}$ on the surface charge density σ_0

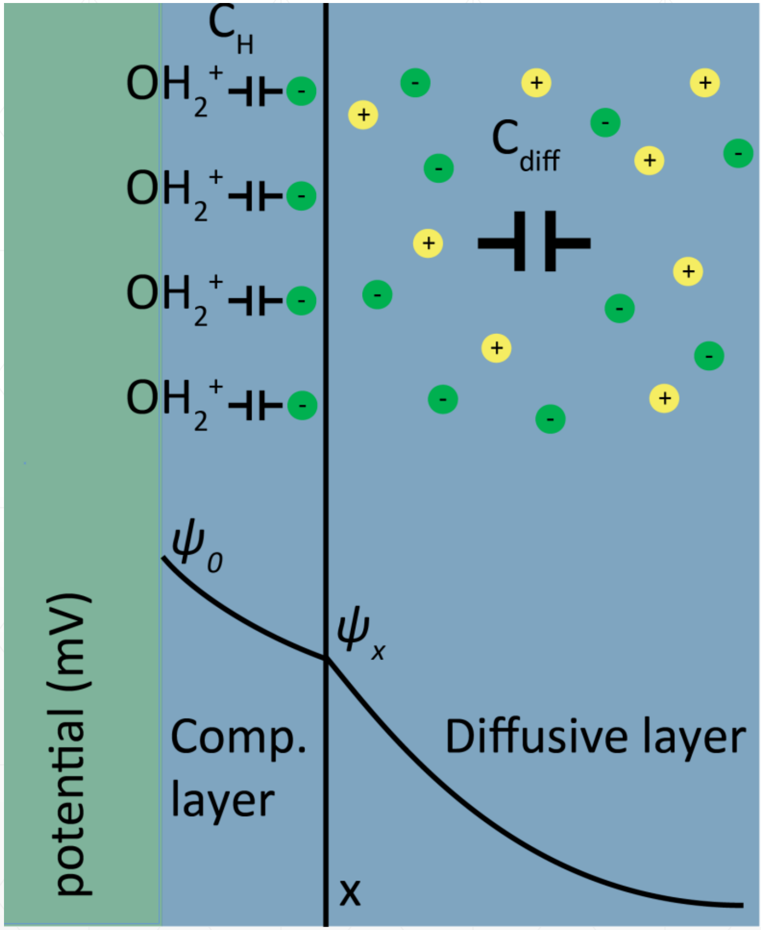
$$\frac{\partial\sigma_0}{\partial \mathrm{pH}_S} = -q\beta_{int}$$

σ_0 is balanced out by charges σ_d in electrolyte

$$\sigma_0 = -\sigma_d = C_d\,\psi_0 \text{ where } C_d = \frac{C_H C_{diff}}{C_H + C_{diff}}$$

So,

$$\frac{\partial\psi_0}{\partial \mathrm{pH}_S} = \frac{\partial\psi_0}{\partial\sigma_0}\frac{\partial\sigma_0}{\partial \mathrm{pH}_S} = -\frac{q\beta_{int}}{C_\mathrm{d}}$$



Sensitivity factor α

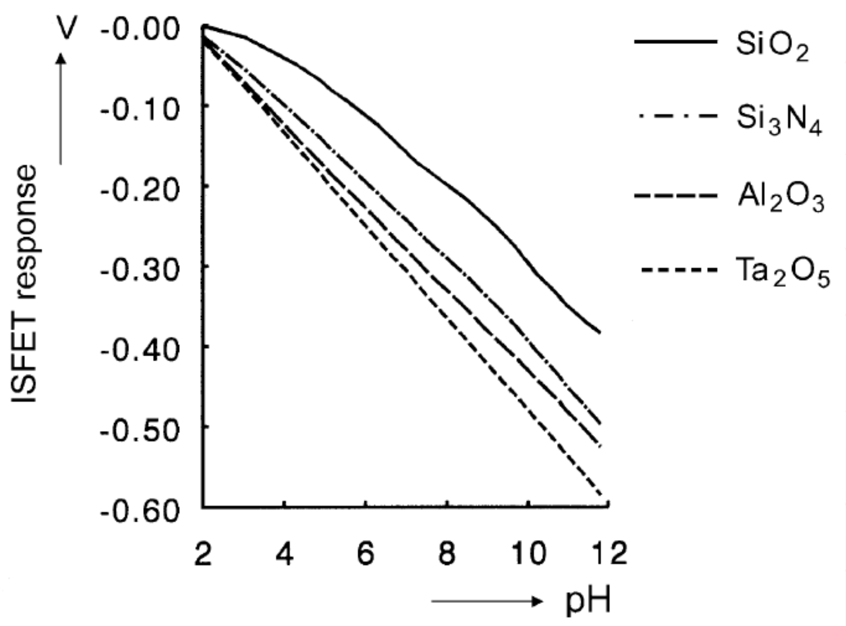
- The sensitivity of ISFETs are a fraction of the Nernstian limit:

$$\frac{\partial \varphi_0}{\delta pH_{bulk}} = \alpha \ln 10 \; k_B T/q$$

- ISFET sensitivity factor α:

$$\alpha = 1/(1 + \ln 10 . \frac{kT}{q} . \frac{C_d}{q \, \beta_{int}})$$

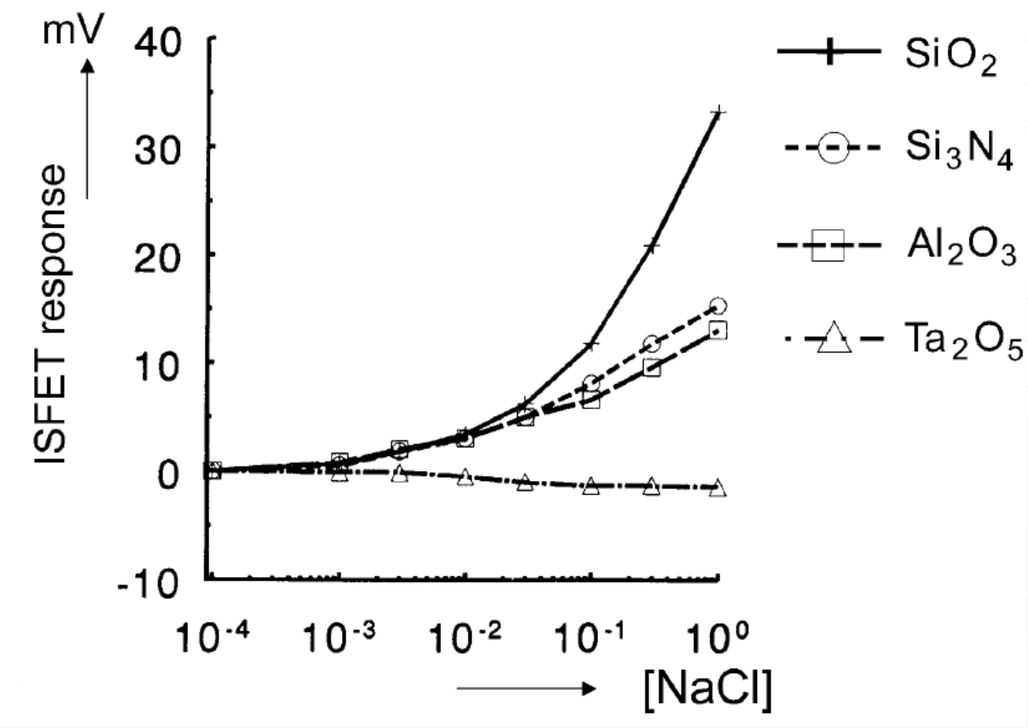
- Ta_2O_5 α ~0.98 Al_2O_3 α ~0.84



P. Bergveld, "Thirty years of ISFETOLOGY," Sens. Actuators B-Chem. **88**,1 -20 (2003).

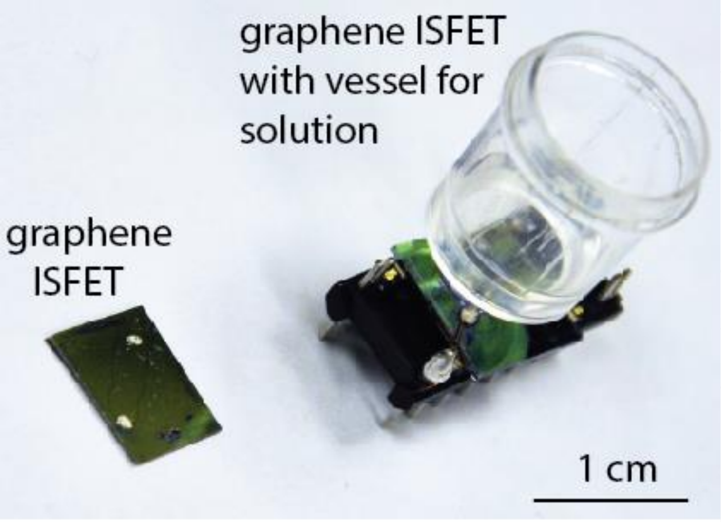
Ta_2O_5 insensitive to other ions

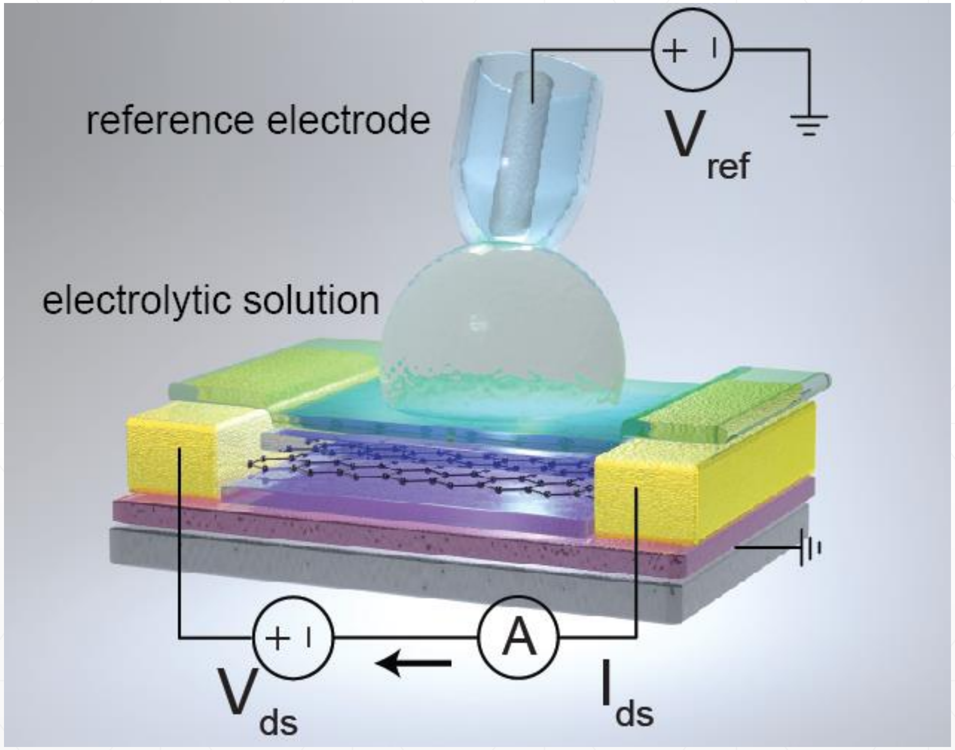
- At a constant pH, Ta_2O_5 exhibits no response to changes in concentrations to other ions.



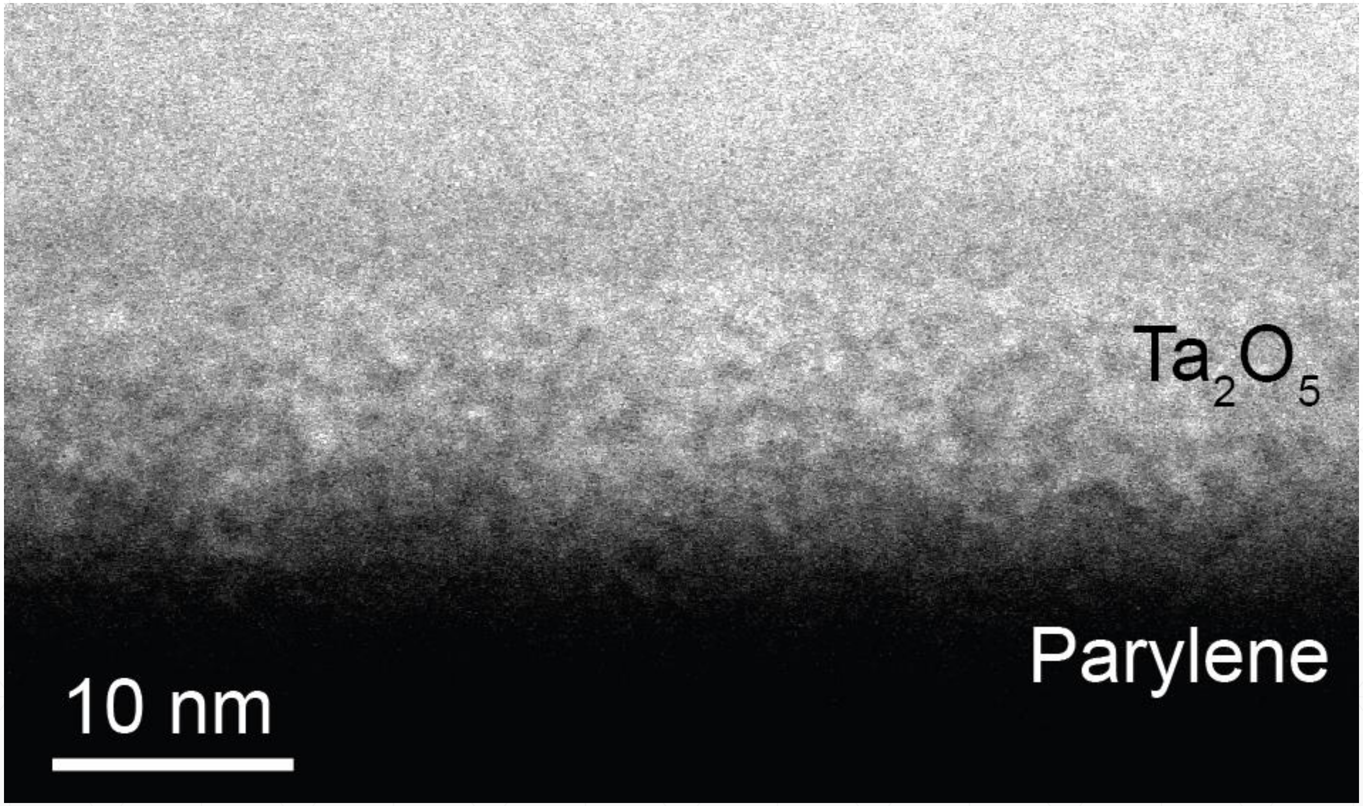
P. Bergveld, "Thirty years of ISFETOLOGY," Sens. Actuators B-Chem. **88**,1 -20 (2003).

Device Setup





TEM



ISFET signal and noise

- ISFET signal current is $i_s = g_m \times \delta\varphi_o$
- Power noise current arises from ISFET $< i_n^2 >$ and read-out electronics $< i_x^2 >$
- ISFET noise is dominated by charge fluctuation in the sensing layer

$$< i_n^2 > = g_m^2 \frac{e^2 N_0}{C\ A} \cdot \frac{\Delta \mathrm{f}}{\mathrm{f}}$$

Sources of Noise

- Brownian motion of the ions

$$N_{BN} = 4k_BTRe(Z)$$

- Fluctuation of dipoles in the oxide

$$N_{DP} = \frac{2k_BTtan(\delta)}{\pi C} \cdot \frac{1}{f}$$

- Trapping of carriers in defects at the insulator/electrolyte interface

$$N_{CT} = \frac{e^2N_{trap}}{C^2WL} \cdot \frac{1}{f}$$

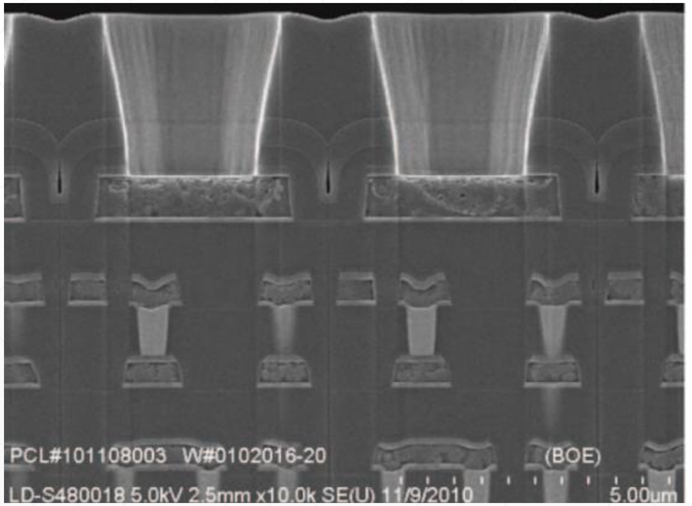
- Thermal fluctuation of electrons in the channel

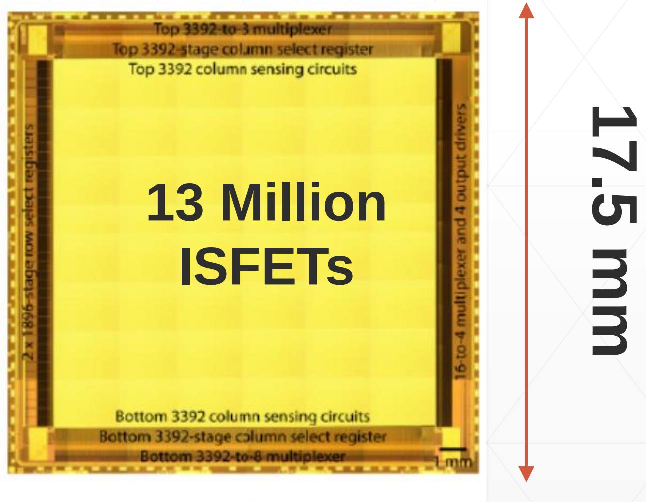
$$N_{JN} = 4k_BT\gamma/g_m$$

Silicon ISFETs and glass electrode

- Fabricated using standard CMOS process
- Detection limit of ~ 20 mpH

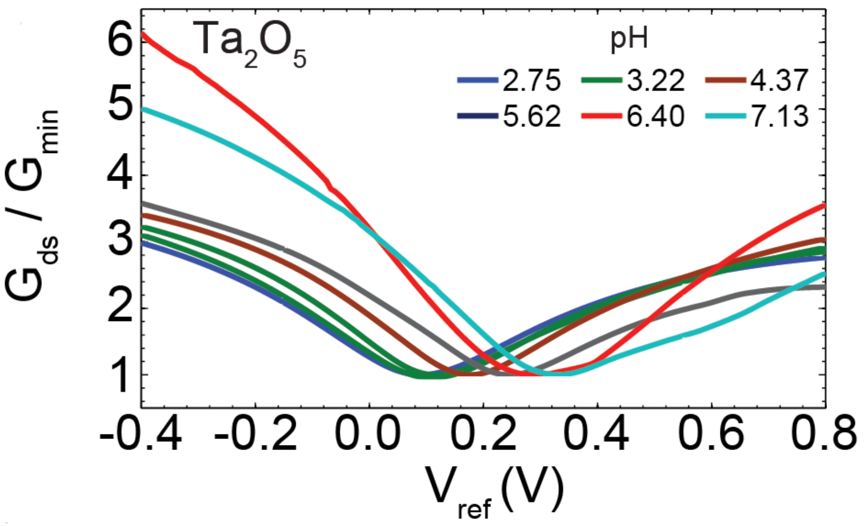
- Ta_2O_5 is grown back end of line (BEOL)
- Charge trapping in oxide layers

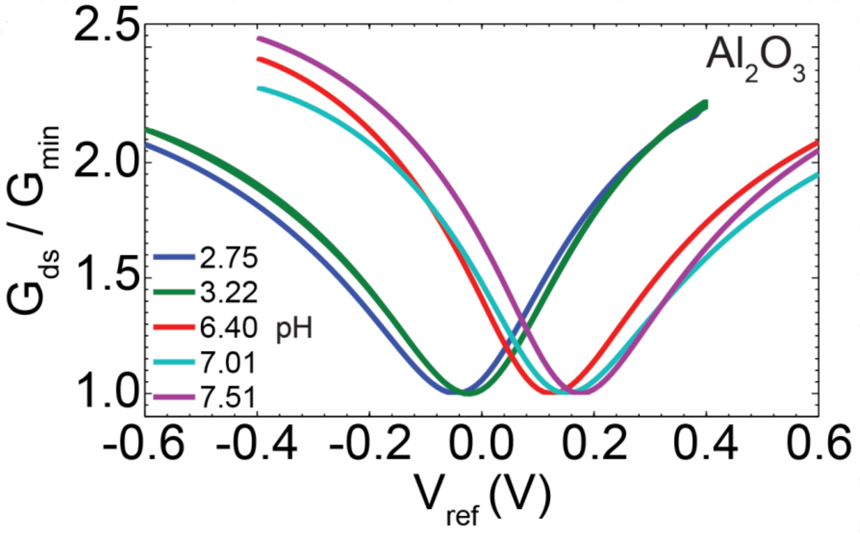


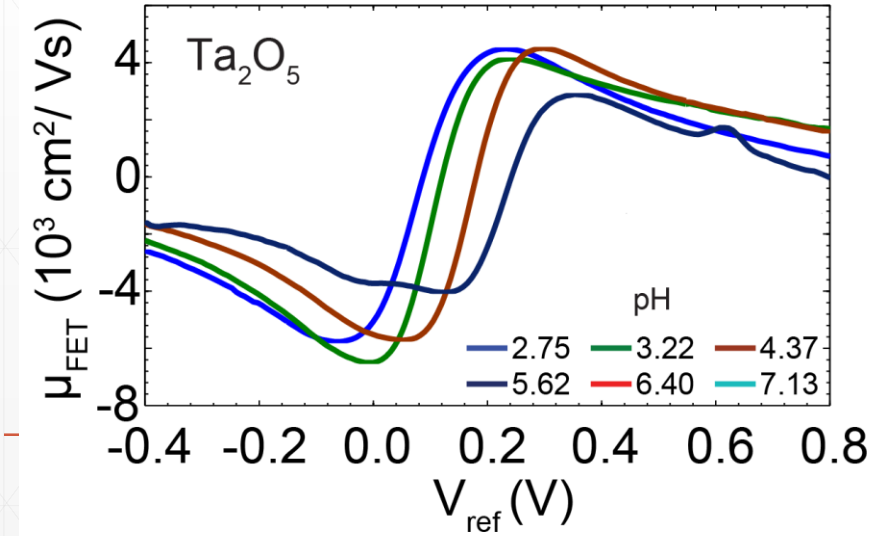


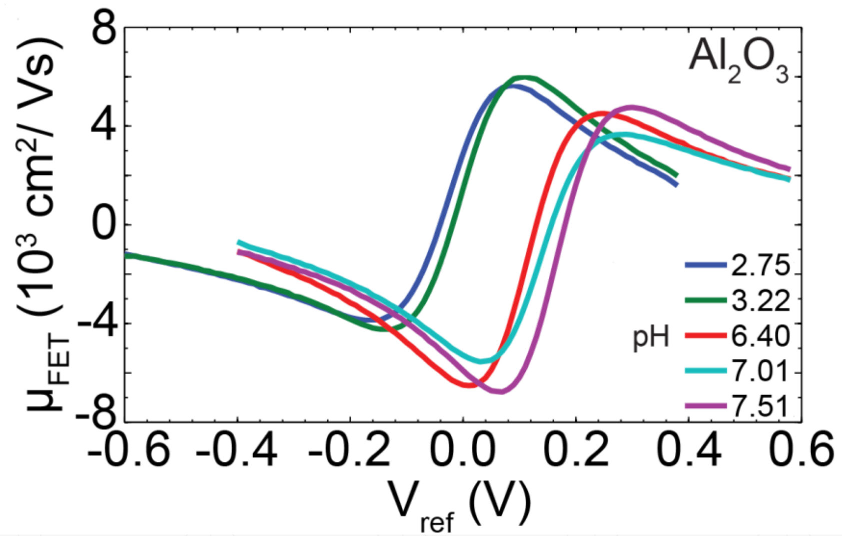
Nature 475, 348–352 (21 July 2011)

pH response and mobility









Time sensitivity and stability