Graphene Varactors as a Sensing Platform for Biotechnology Applications

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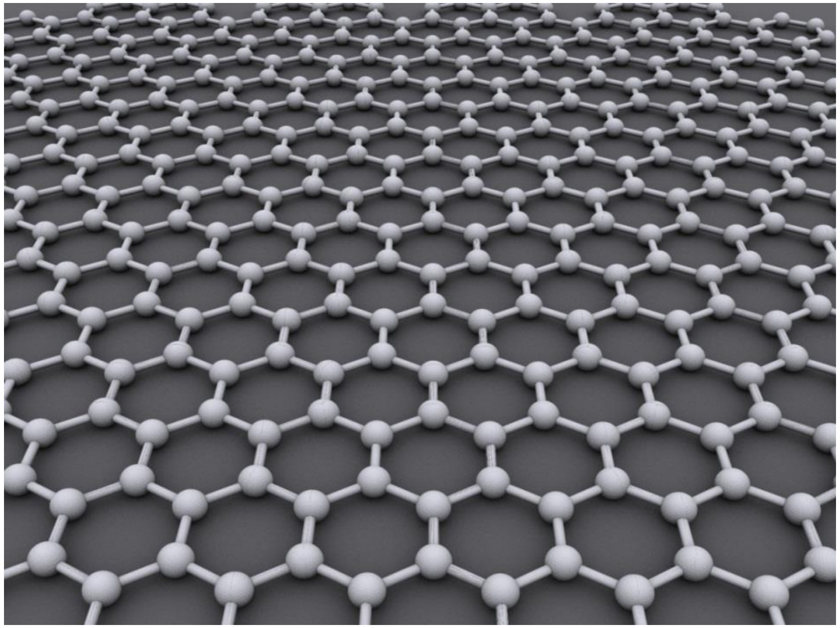
Graphene

- Graphene is single atomic sheet of sp^2 bonded carbon that has many unique and remarkable properties:



Source: AlexanderAlUS, Wikimedia Commons.

High mobility (> 100,000 cm^2/Vs)

Zero band gap – symmetric band structure

Transparent (97.7% transmitting for single layer)

High mechanical strength (> 10x stronger than steel)

High surface sensitivity

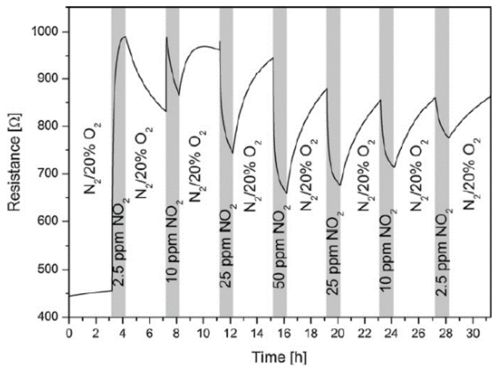
- **One of the most interesting applications for graphene is for use in sensors → nearly all of these properties can be useful.**

Graphene Sensors

- Different transduction mechanisms for graphene sensors:

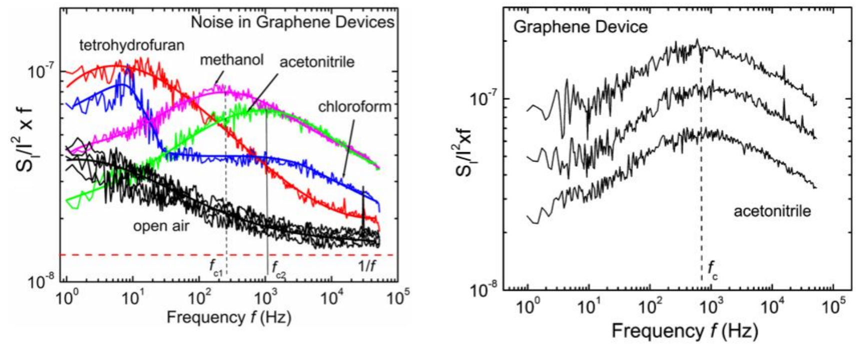
Resistance change

R. Pierce, et al., Sens. & Act. B (2011).



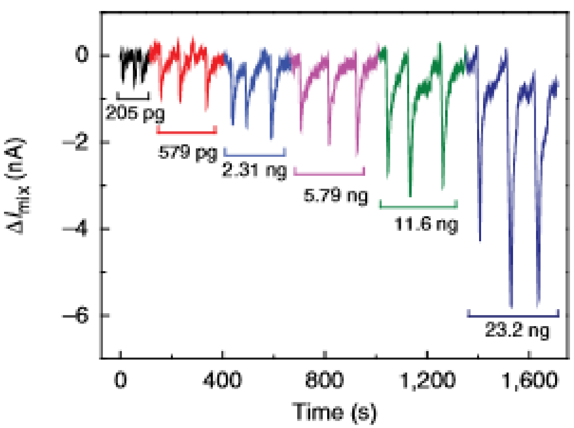
Noise spectrum change

S. Rumyantsev, et al., Nano Lett. 12, 2294 (2012).



Heterodyne mixing

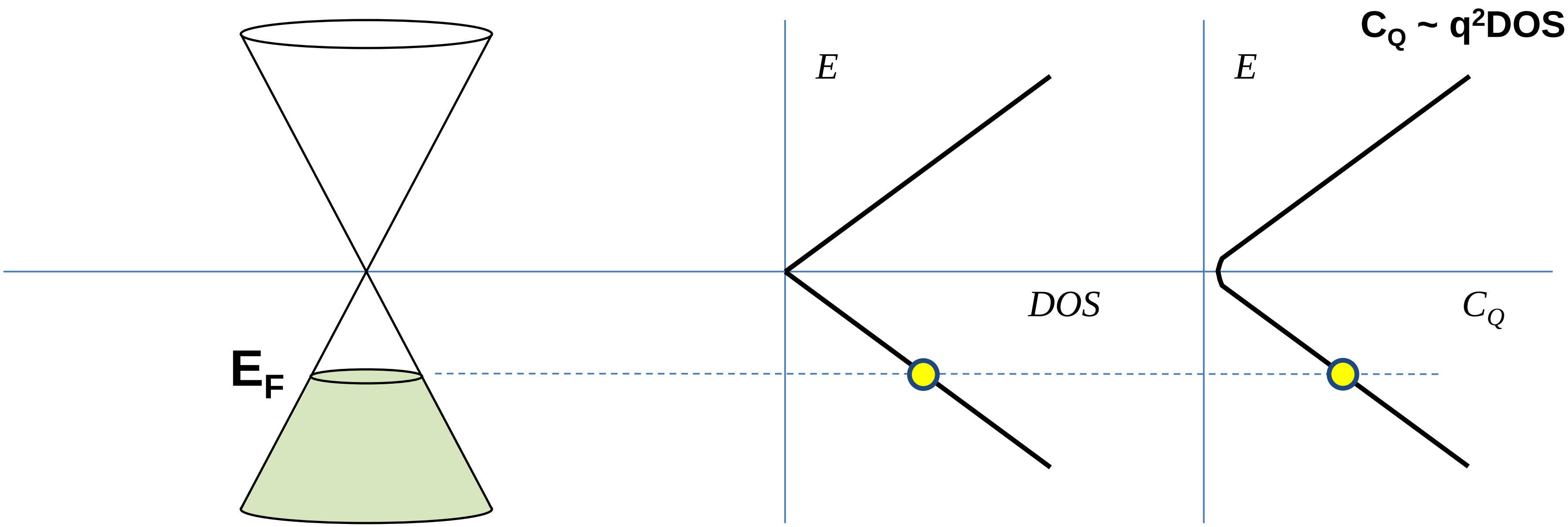
G. S. Kulkarni, et al., Nature Commun. 5, 4376 (2014).



- **Despite the variety of sensor concepts, nearly all previous sensor demonstrations have required wired connections to the graphene.**
- **Is there a way to realize a truly wireless sensor using graphene?**

Quantum Capacitance in Graphene

- <u>Quantum capacitance</u> changes when electron or hole concentration in graphene is changes:



- **When the Fermi-level is near the Dirac point, the <u>quantum capacitance</u> is low.**

Quantum Capacitance in Graphene

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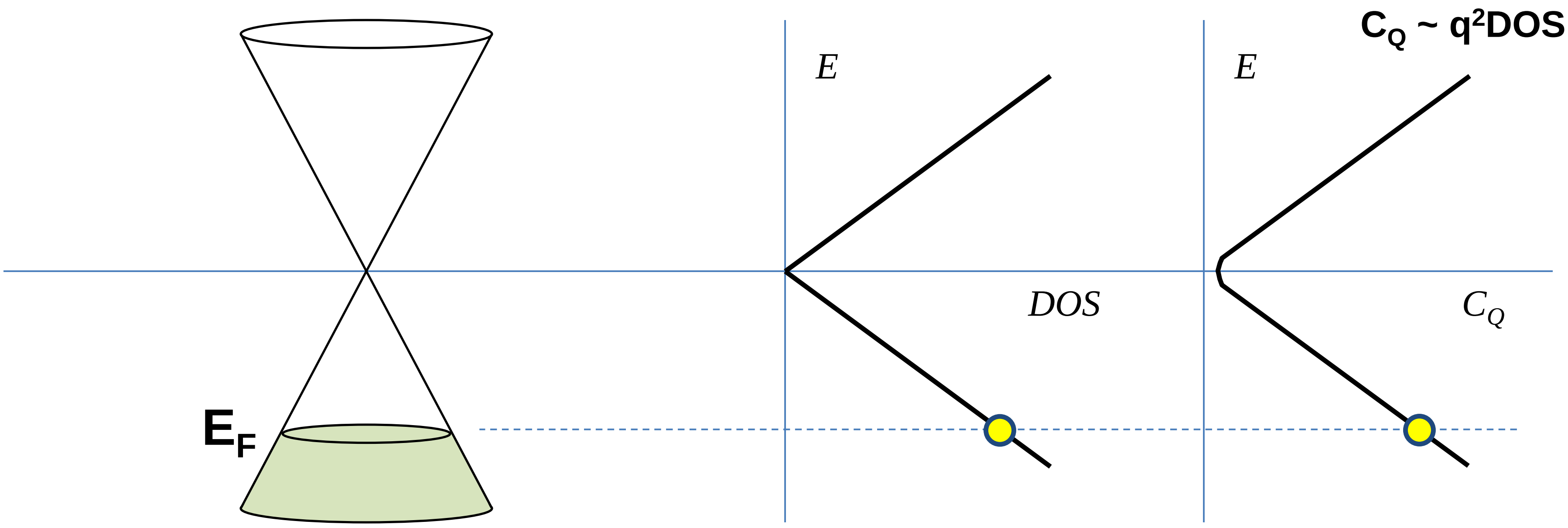
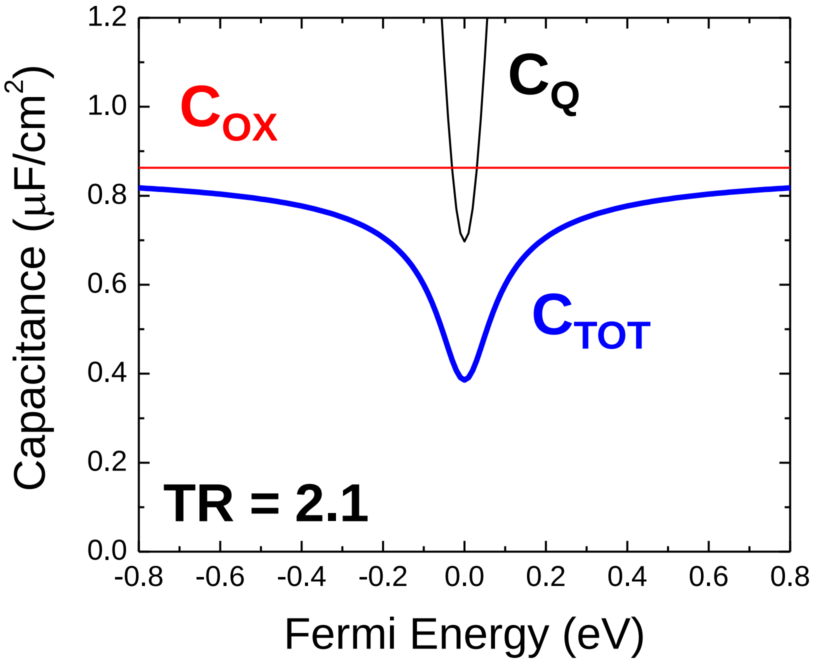


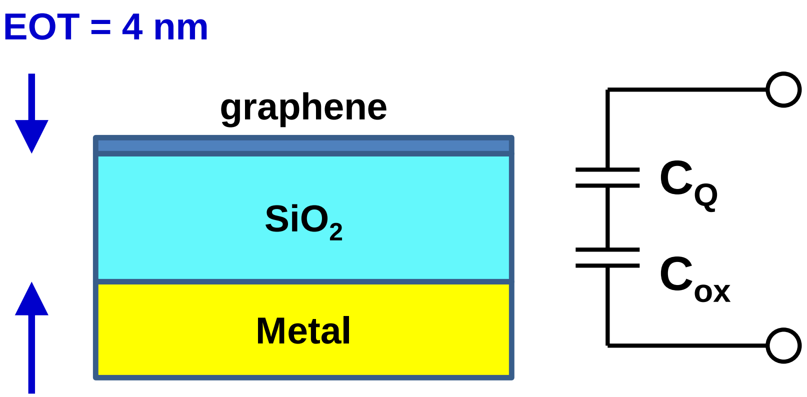
- **When Fermi-level moves away from the Dirac point, quantum capacitance increases.**

Quantum Capacitance in Graphene

- Capacitance in a metal-oxide-graphene capacitor is the series combination of oxide and quantum capacitances:

S. J. Koester, Appl. Phys. Lett. 99, 165105 (2011).





$$C_{tot}^{-1} = C_Q^{-1} + C_{ox}^{-1}$$

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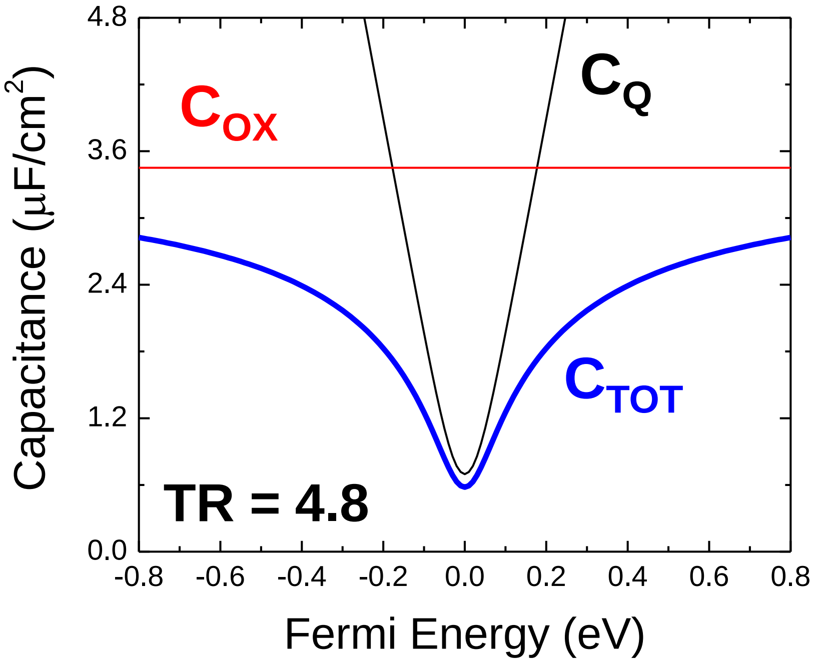

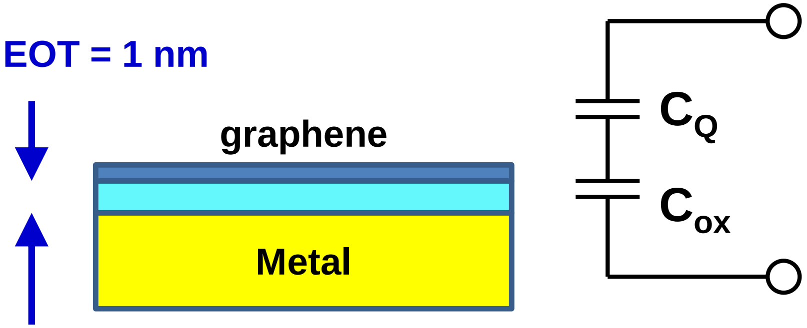

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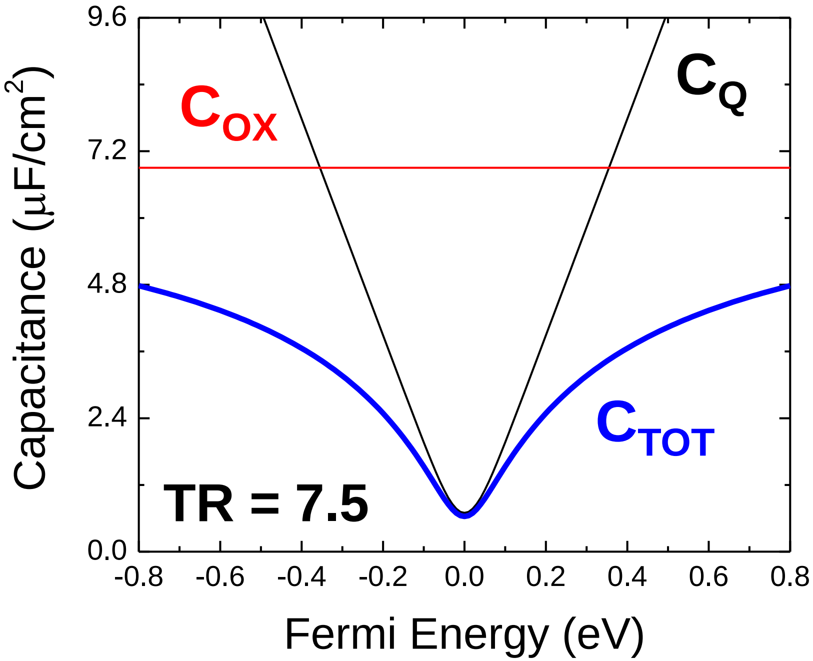
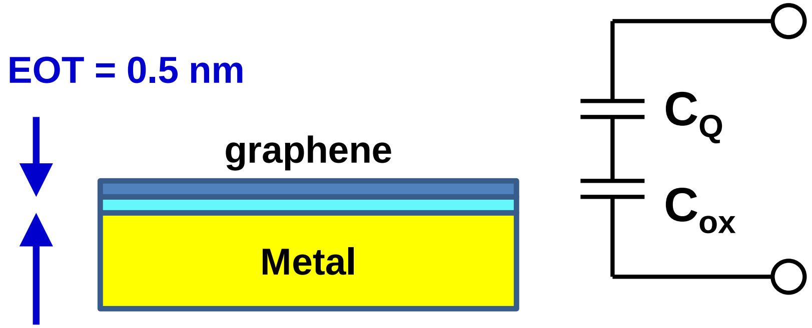




$$C_{tot}^{-1} = C_Q^{-1} + C_{ox}^{-1}$$

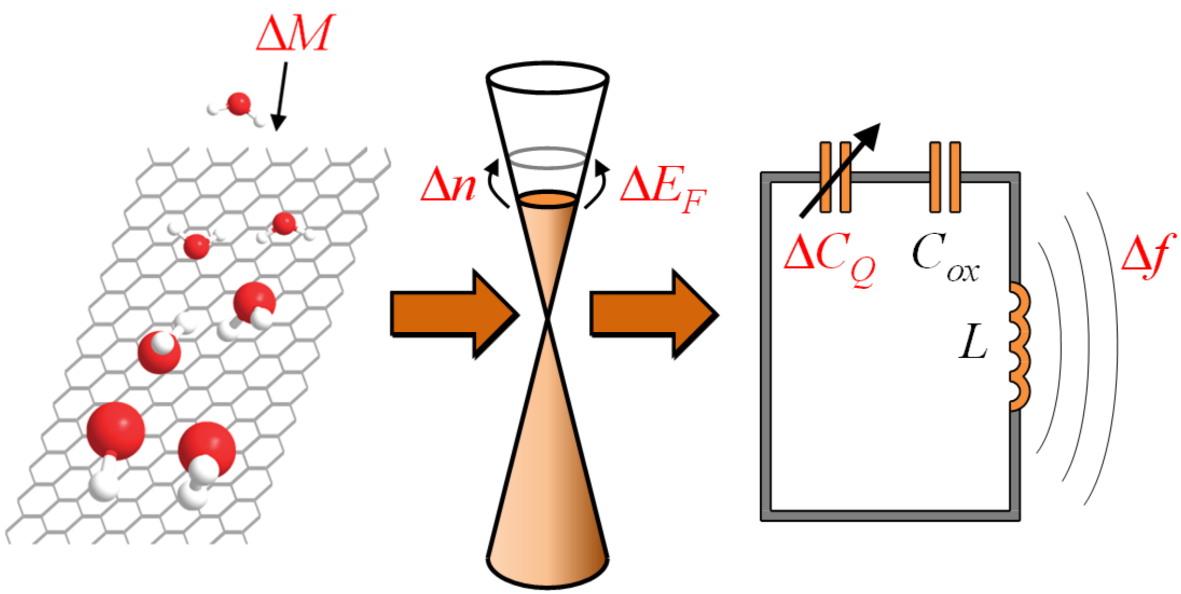
- **Metal-oxide-graphene capacitors should act as variable capacitors (varactors). Can this be observed experimentally?**

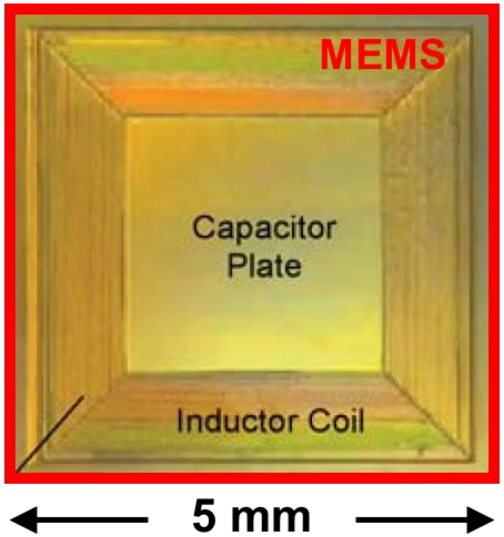
Graphene Varactor Wireless Sensors

- Adsorbed molecules can modulate the carrier concentration and thus the quantum capacitance in graphene varactors:

S. J. Koester, Appl. Phys. Lett. 99, 165105 (2011).

M. Lei, et al., Diabetes Tech. & Therapeutics (2006).





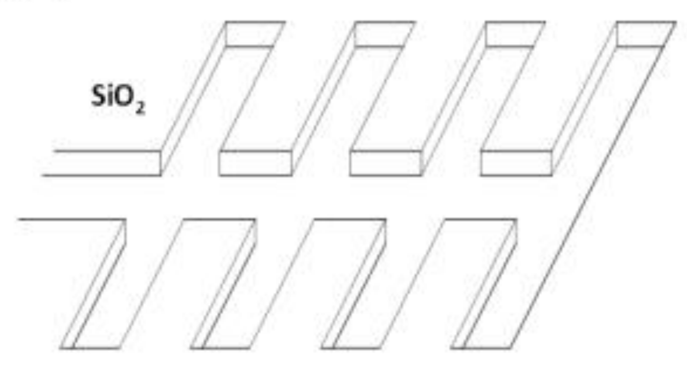
Graphene varactor

- **Advantages:**
  - **Passive, wireless operation.**
  - **Small size due to high capacitance density.**
  - **Adaptability → can be functionalized to sense different targets.**

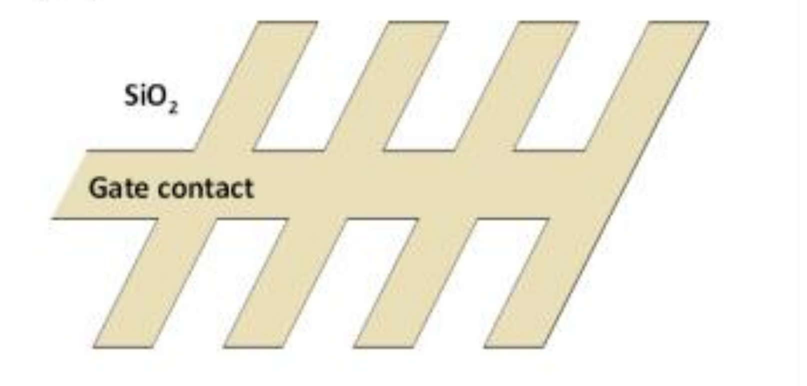
Graphene Varactors

- Fabrication process for graphene varactors:

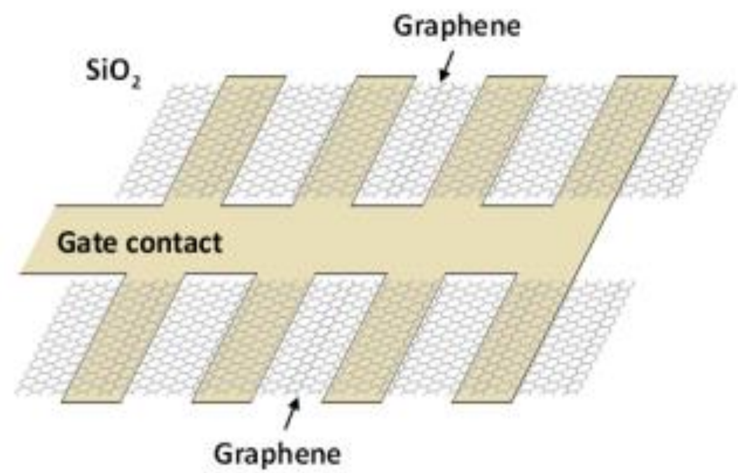
(1) Gate recess etch



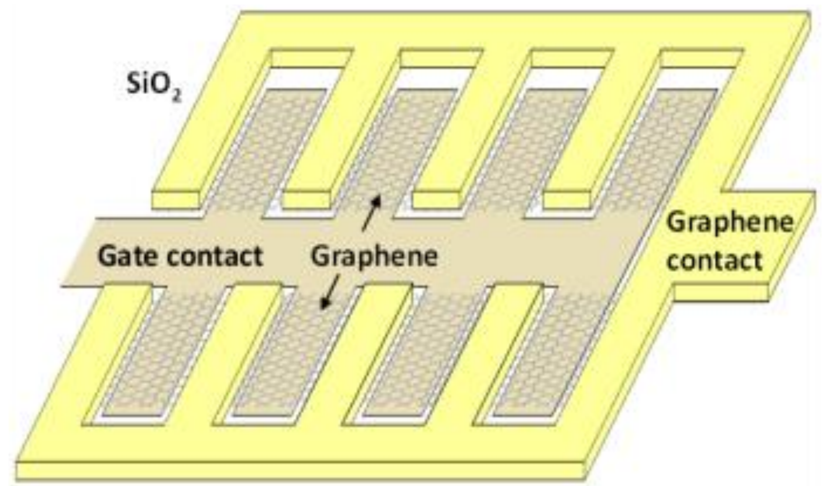
(2) Gate metal deposition + HFO_2 ALD



(3) Graphene transfer and etch

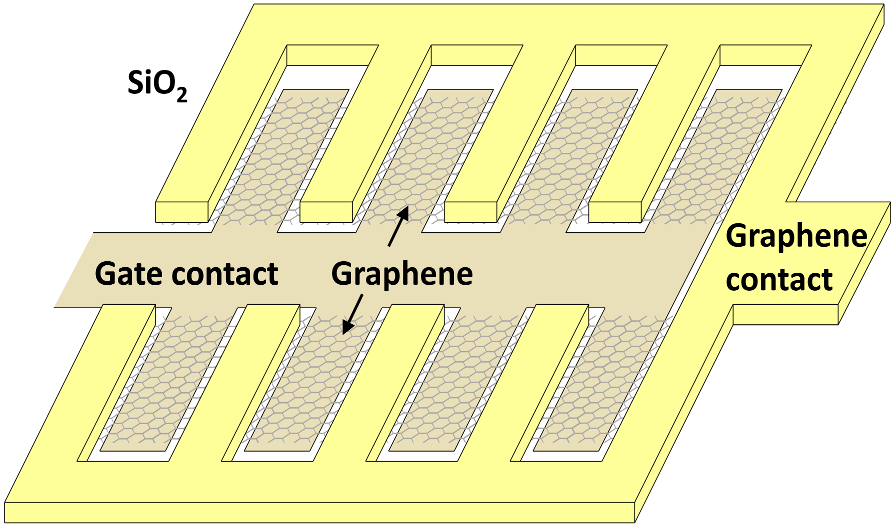


(4) Graphene contact metallization

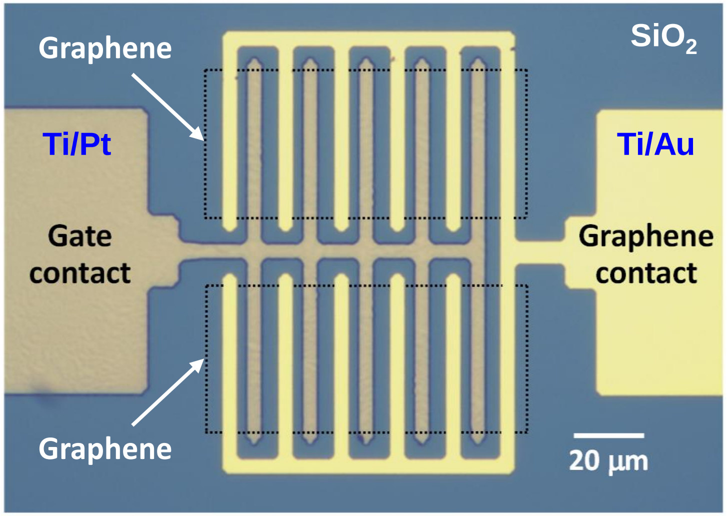


Graphene Varactors

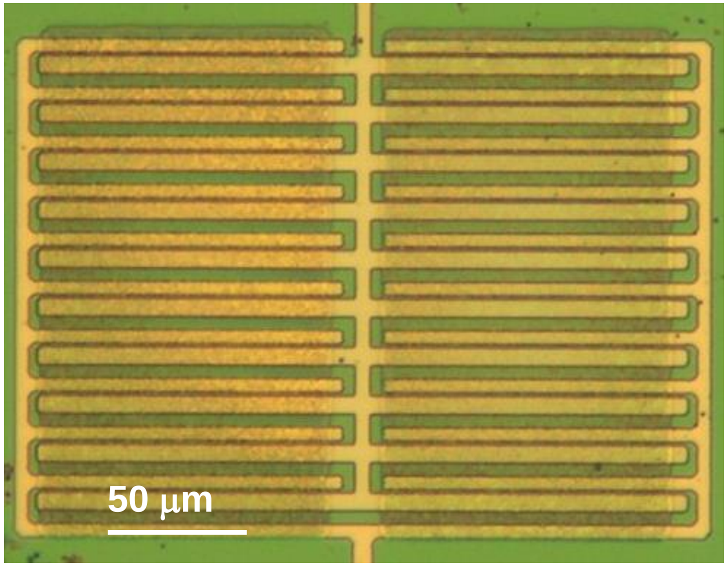
- Fabricated devices using optical lithography and transfer of CVD graphene:



M. A. Ebrish, et al., Appl. Phys. Lett. 100, 143102 (2012).



M. A. Ebrish, et al., EMC, 2013.

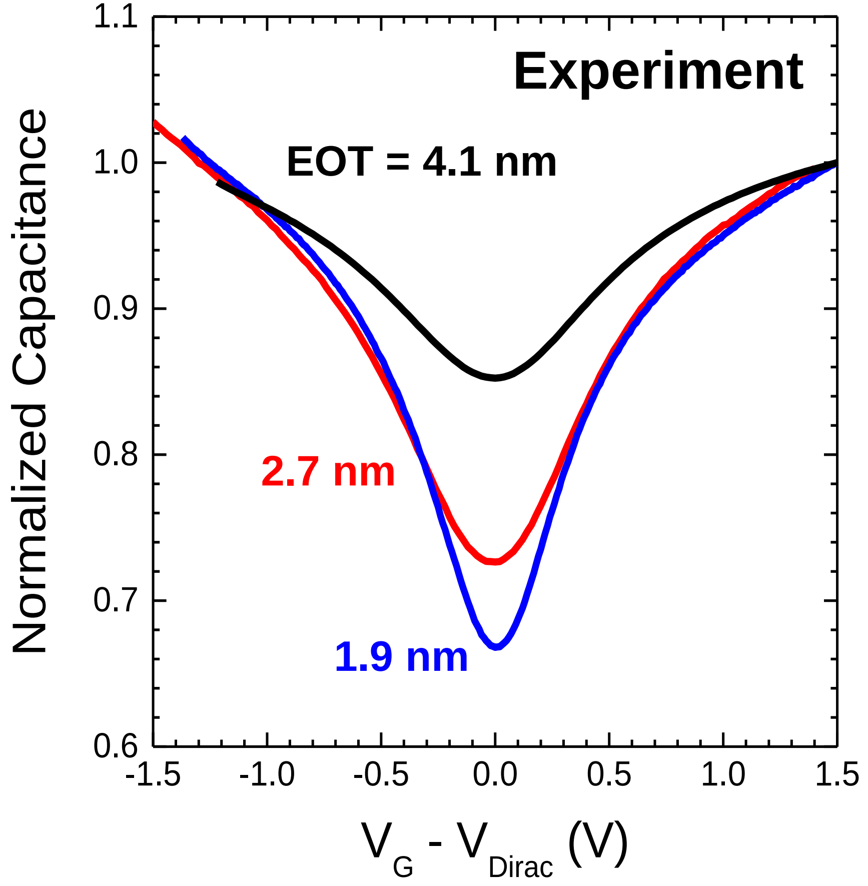


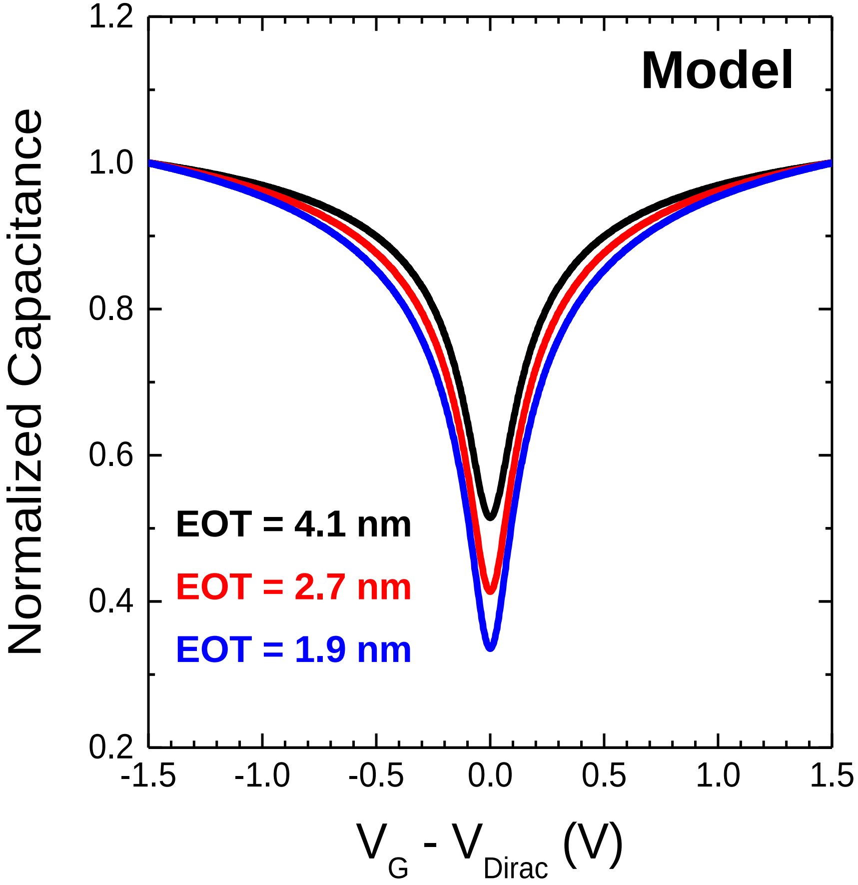
- **Typical devices typically, have L_g = 2-5 μm, R_C = 1-2 Ω-μm, t_{HfO2} = 7-20 nm, Area = 500-10,000 μm^2.**

Graphene Varactor C-V Characteristics

- Performed oxide-thickness scaling experiments:

M. A. Ebrish, et al., DRC, 2012.



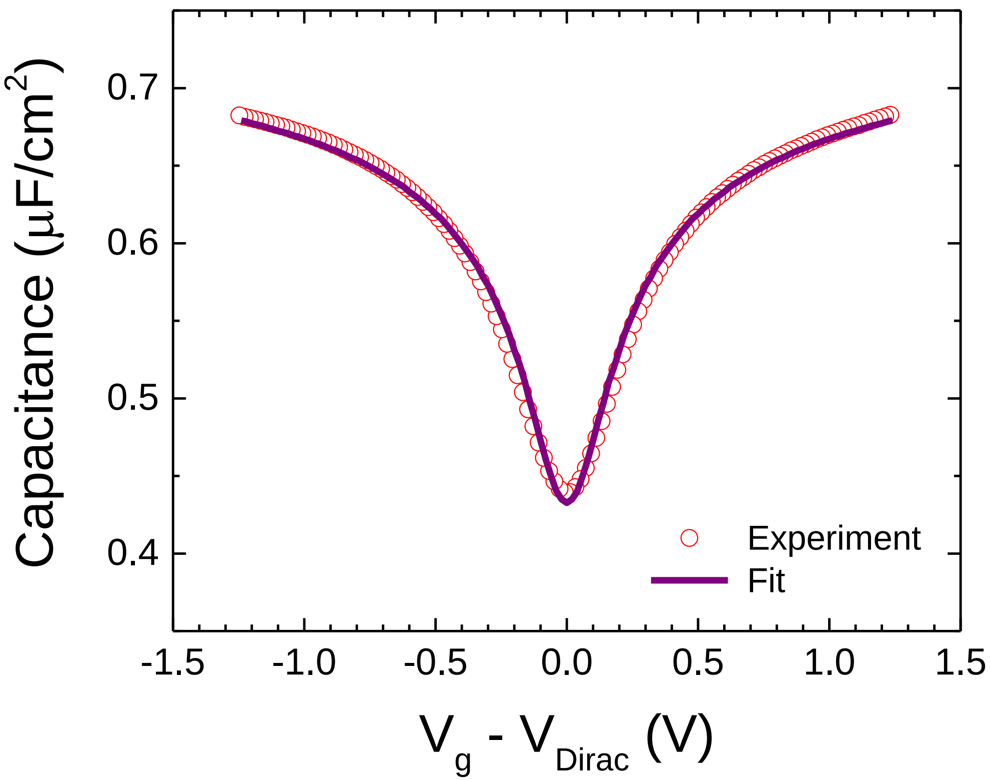


- **Tuning range (TR) improves with decreasing oxide thickness. TR values as high as ~ 1.6-to-1 achieved. Limited by <u>disorder</u>.**

Model Fitting

- Results of fitting to effective temperature model for disorder:

M. A. Ebrish, et al., ACS Appl. M & I, 6, 10296 (2014).



$$T_0 = 283\text{K}$$

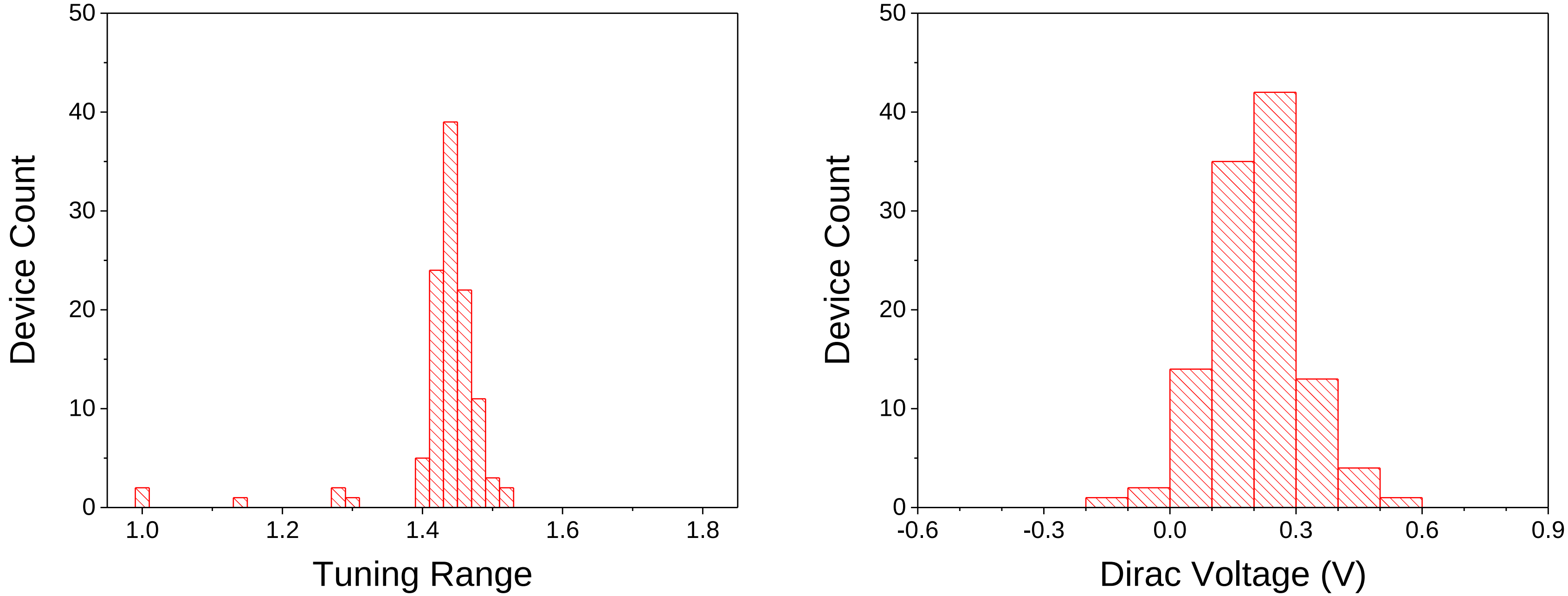
$$\downarrow$$

$$\sigma = 42\ \text{mV}$$

- **Effective temperature model provides excellent agreement with experimental data. T_0 values as low as 283 K obtained, corresponding to potential fluctuations as low as 42 mV.**

Graphene Varactor Uniformity

- Fabricated and tested > 100 graphene varactors in a single device run. Measured capacitance vs. voltage and determined capacitance tuning range and Dirac voltage:

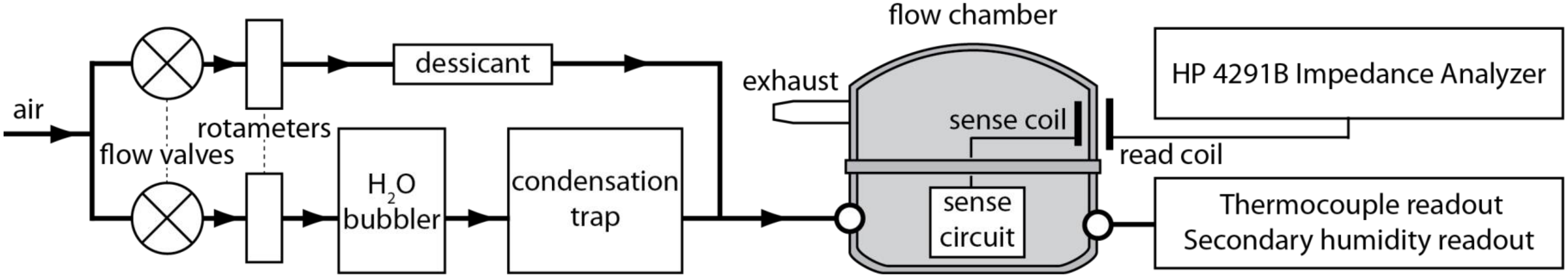


- **Over 97% yield observed. Tight distribution observed for tuning range and Dirac voltage values. Results show graphene varactors can be made with high yield and uniformity.**

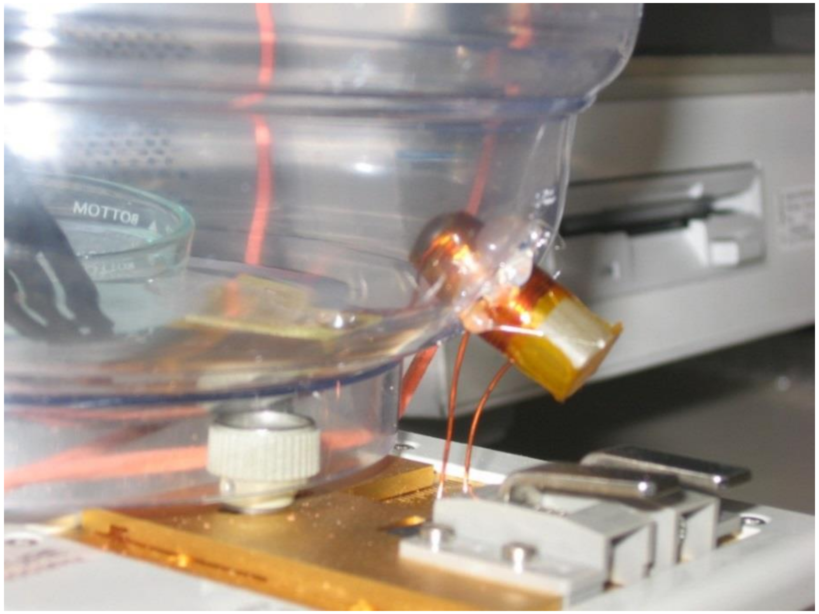
Wireless H_2O Sensing

- Variable capacitance can readily be observed, but can we really make a wireless sensor?

D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).



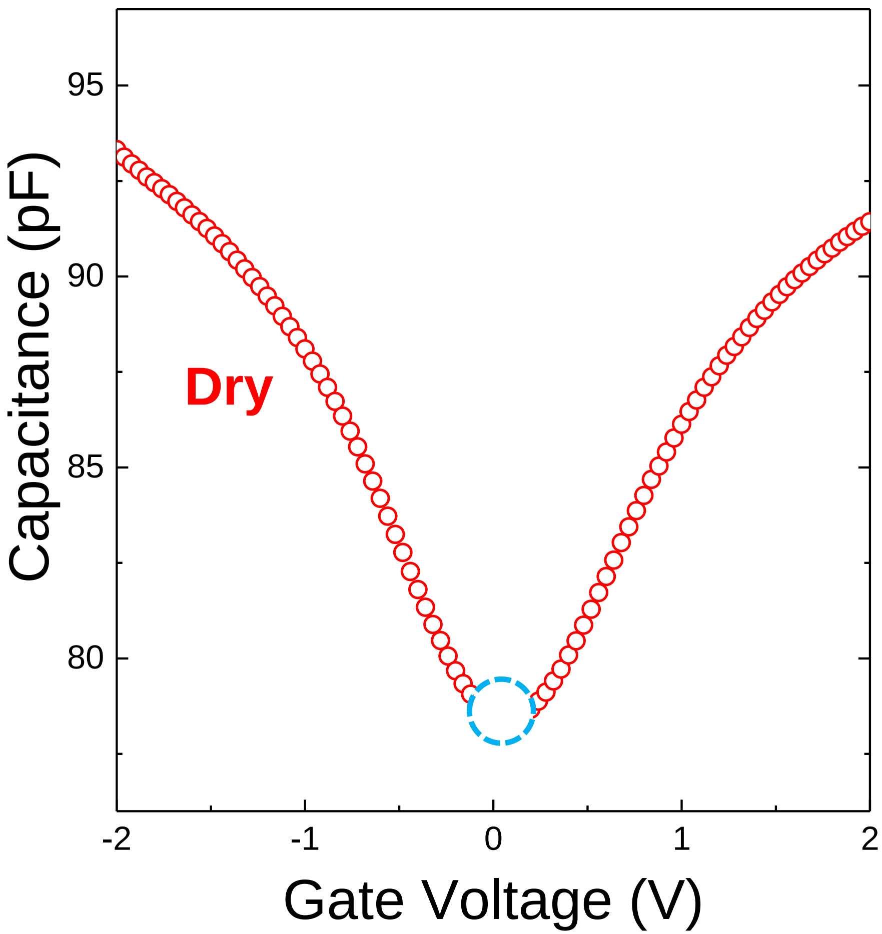
- **Constructed a simple H_2O vapor sensing system → known to cause positive Dirac-point shift in graphene.**
- **Wire-bonded graphene varactors and connected in series with a an inductor to form an LC resonator.**

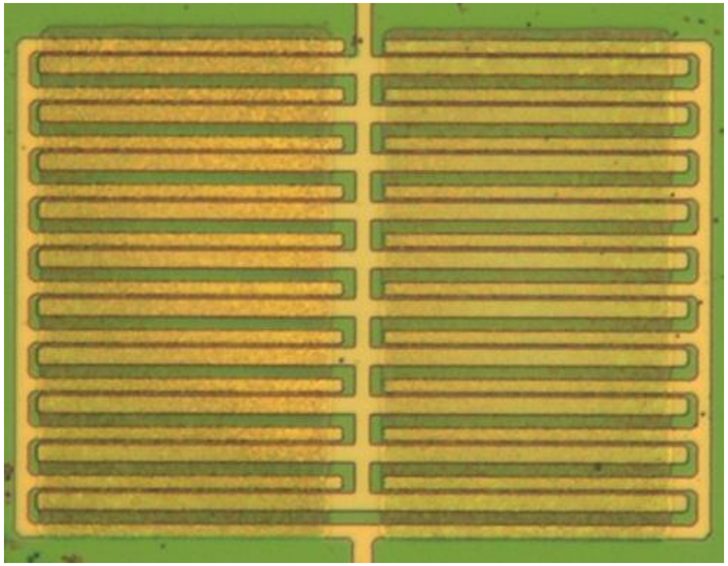


Wireless H_2O Sensing

- Measured varactors before inductor integration to determine capacitance characteristics:

D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).



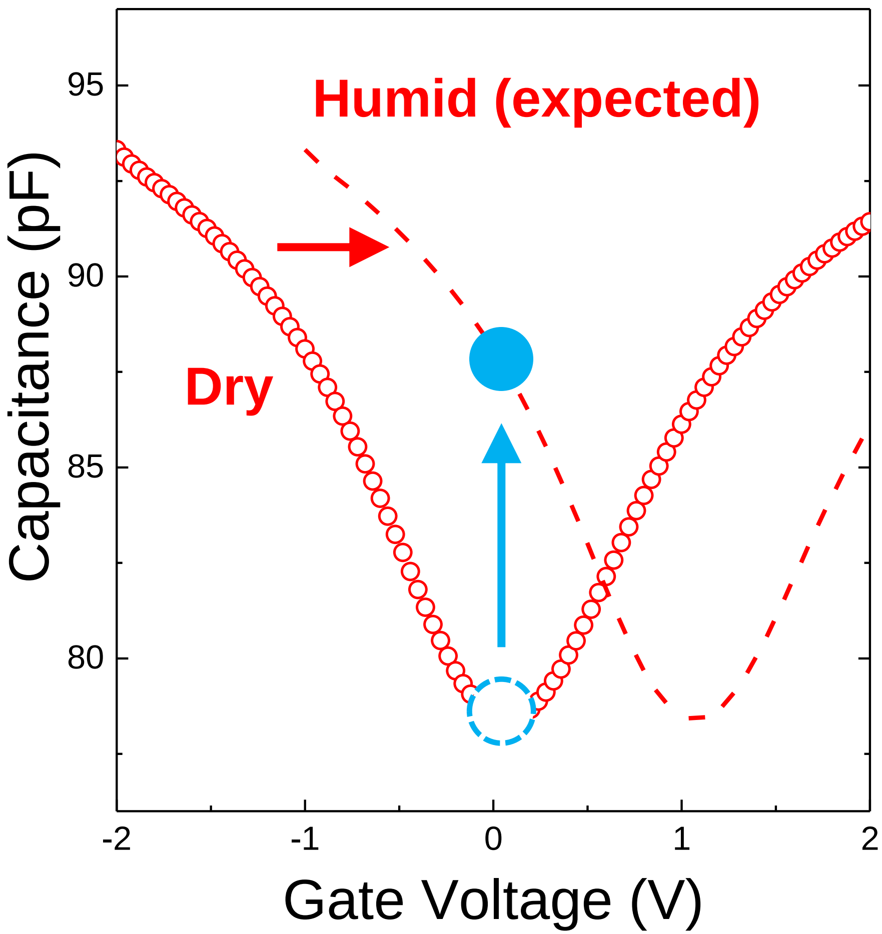


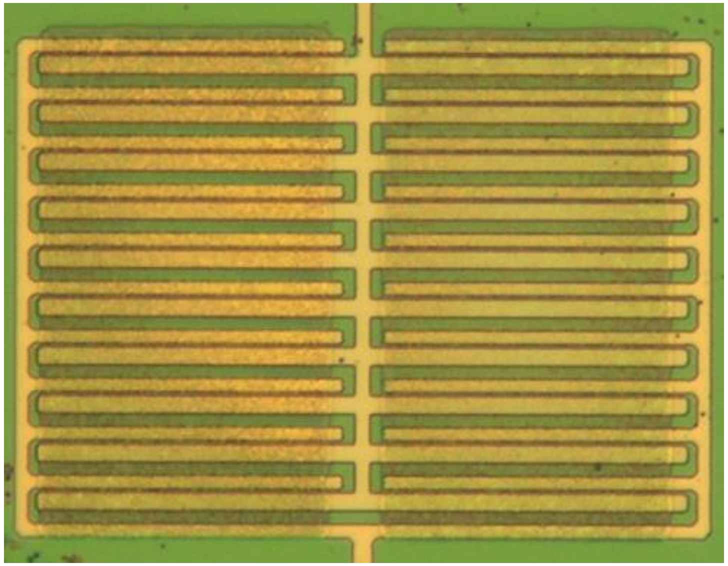
- **Tuning range 1.18-to-1.**
- **Large amount of variability due to very large size of device.**

Wireless H_2O Sensing

- Measured varactors before inductor integration to determine capacitance characteristics:

D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).



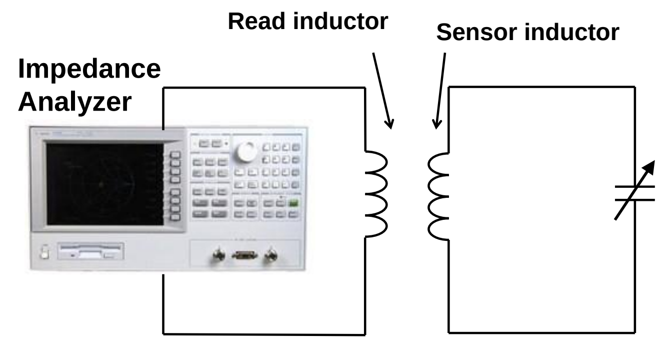


- **Expectation is to see p-type shift with H_2O.**
- **C ↑, frequency ↓.**

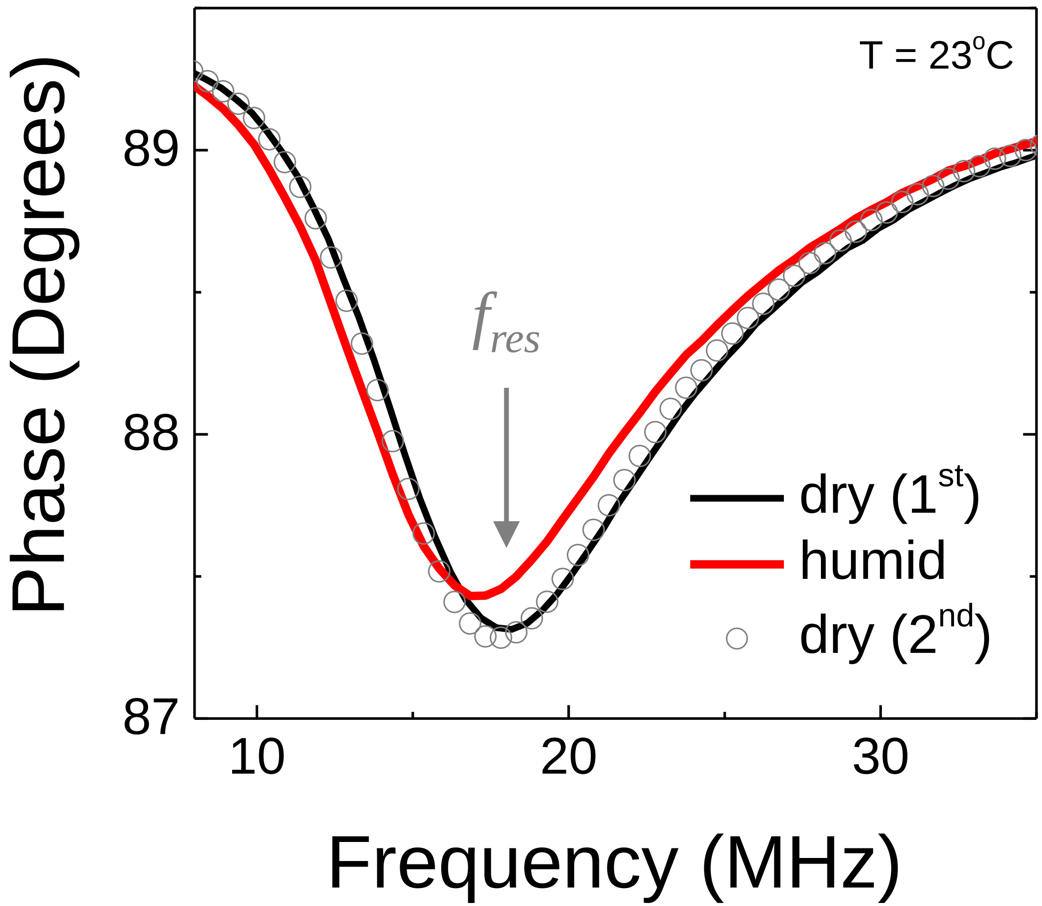
$$f = 1/2\pi\sqrt{LC}$$

Wireless H_2O Sensing

- Utilized "phase dip" technique to determine resonant frequency of sensor circuit:



D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).

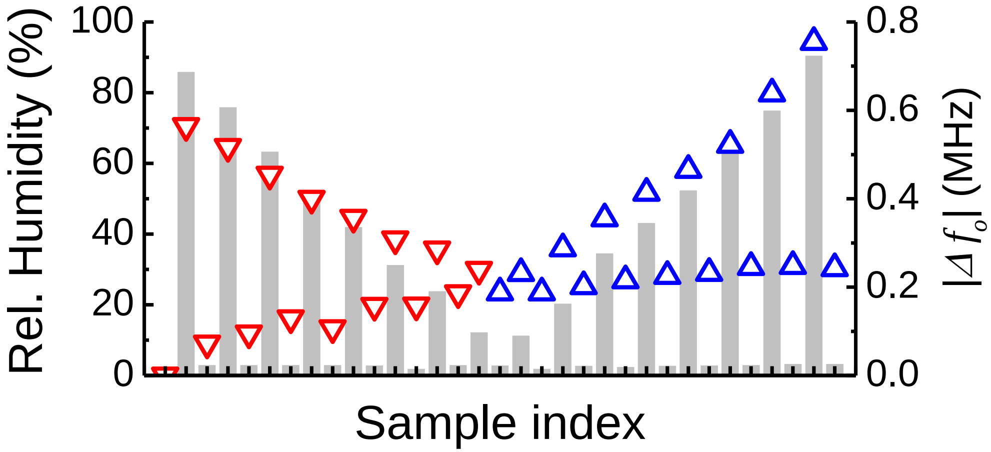


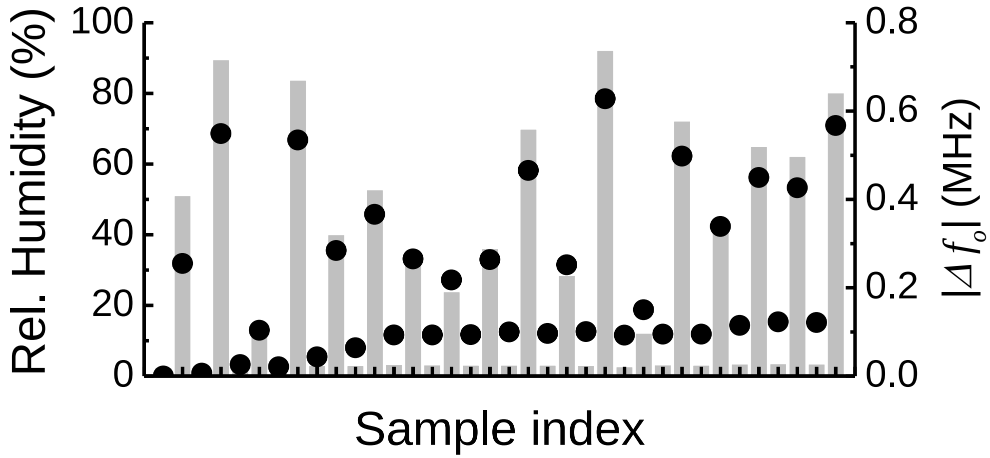
- **Resonant frequency initially about 18 MHz in dry air.**
- **In humid air (~ 95% RH), resonant frequency shifts lower by ~ 1 MHz.**
- **Resonant frequency recovers upon re-exposure to dry air.**

Wireless H_2O Sensing

- Measured frequency shift for different humidity sequences:

D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).



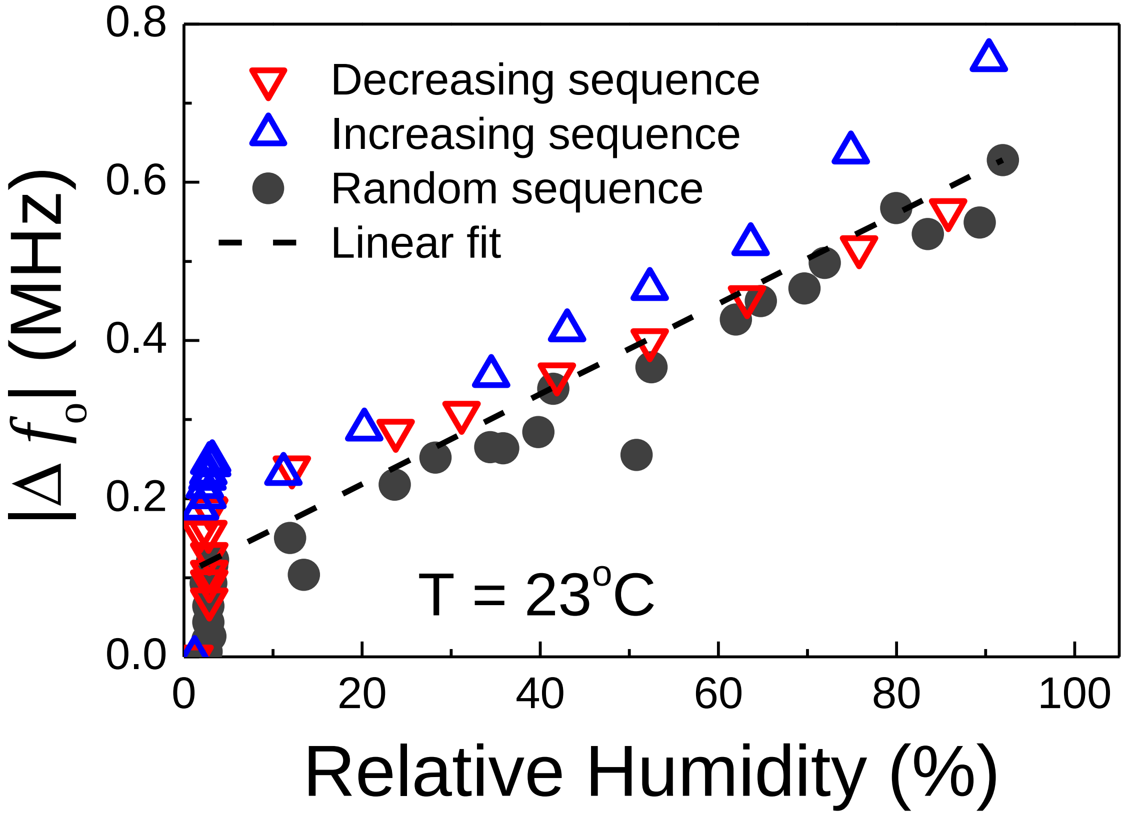


- **Similar dependence found for up / down humidity sequences. Small baseline drift observed.**
- **Random humidity sequence also performed. Baseline drift observed to saturate.**

Wireless H_2O Sensing

- Summary of concentration dependence of frequency shift:

D. A. Deen, et al., IEEE Sensors J. 14, 1459 (2014).

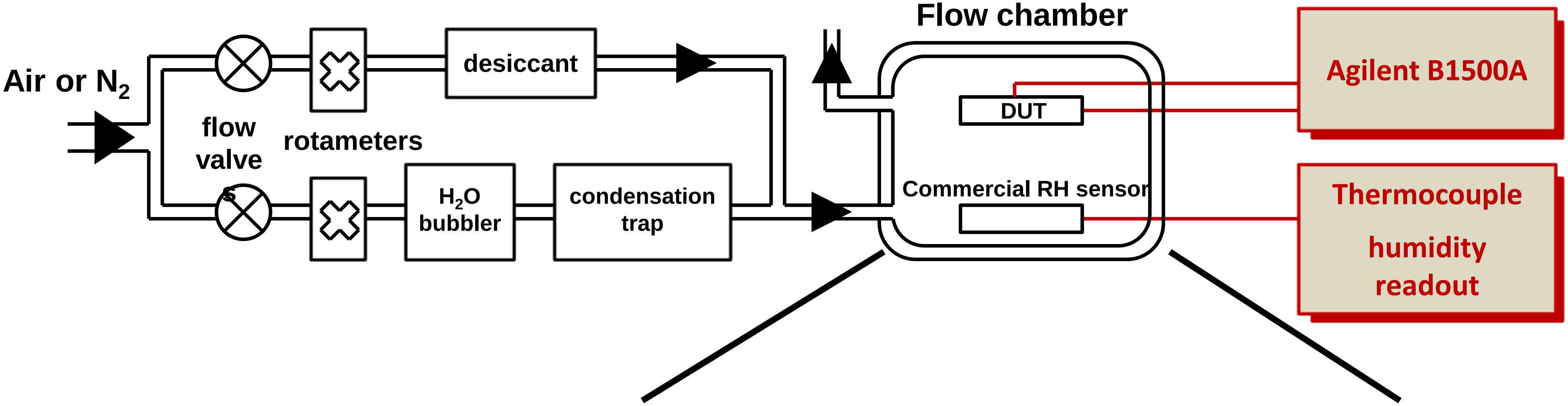


- **Results indicate that reliable <u>wireless</u> humidity sensing can be achieved.**

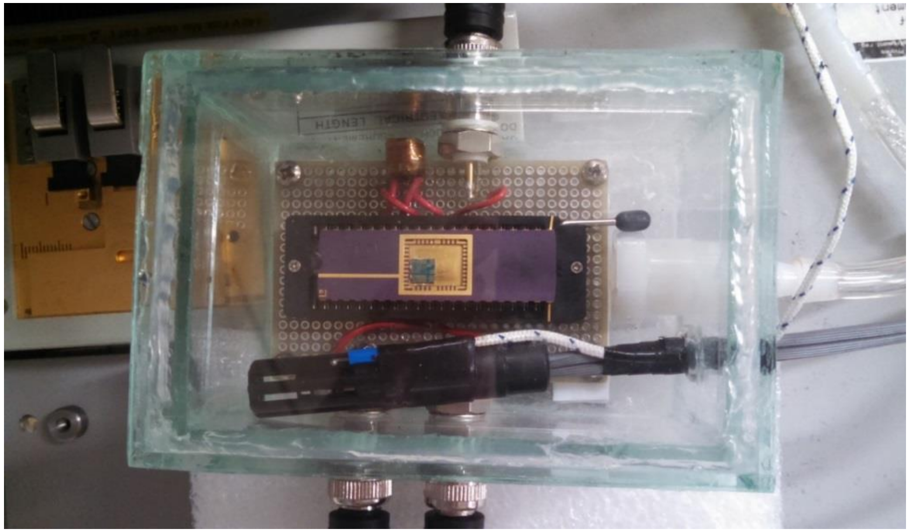
Direct H_2O Capacitive Sensing

- Used wired C-V measurements as a function of relative humidity (RH) of carrier gas:

E. J. Olson, et al., ACS Appl. M & I 7, 25804 (2015).



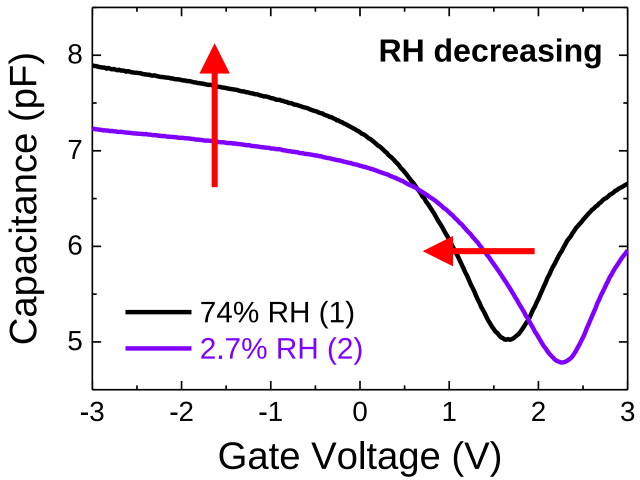
- **Wired sensing measurements provide more information about sensing mechanism that wireless measurements.**

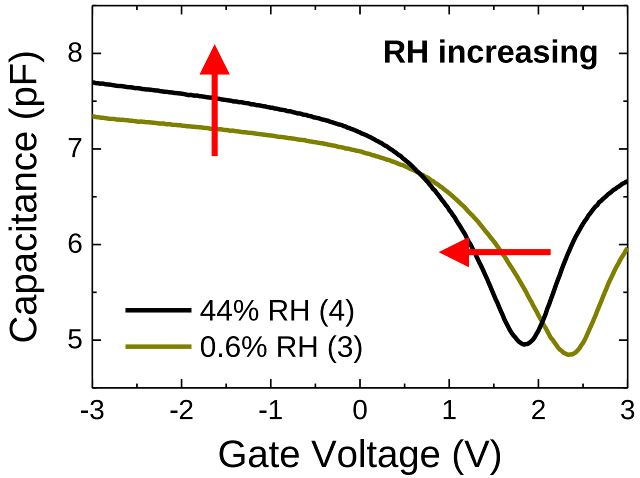


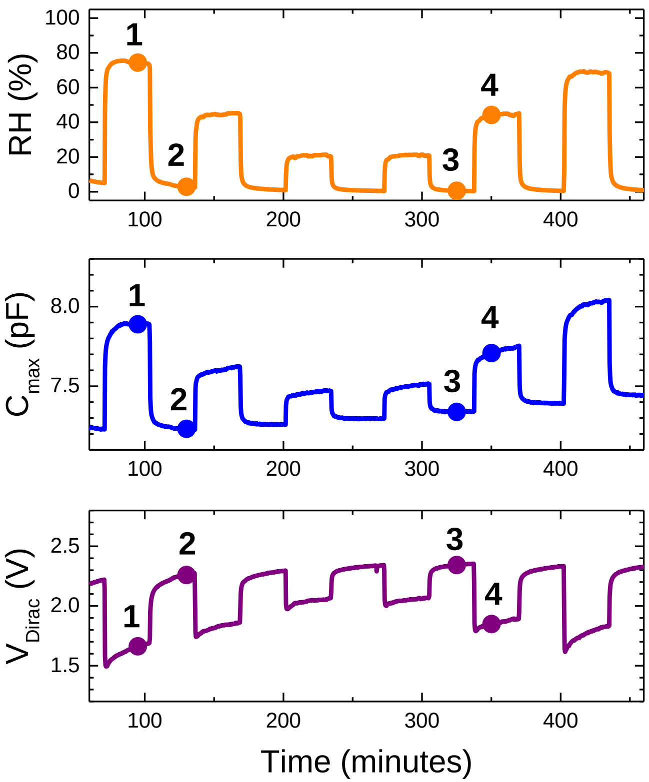
Direct H_2O Capacitive Sensing

- Summary of C-V measurements for varying RH in air:

E. J. Olson, et al., ACS Appl. M & I 7, 25804 (2015).





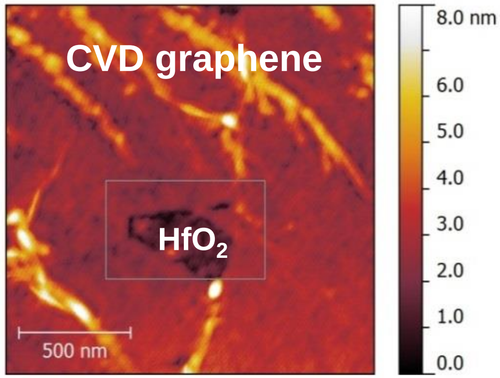


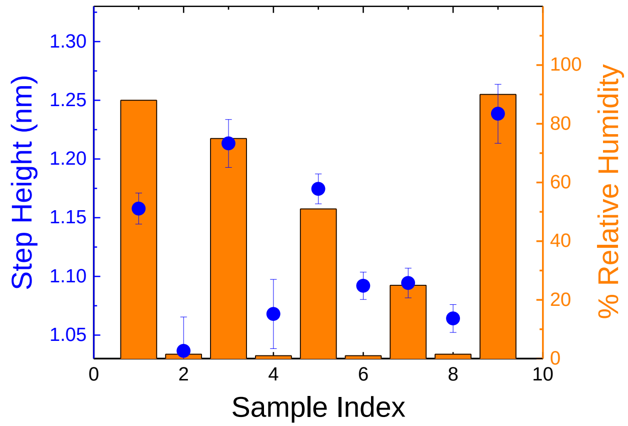
- **Capacitance change not only due to “horizontal” shift, but also “vertical” shift.**

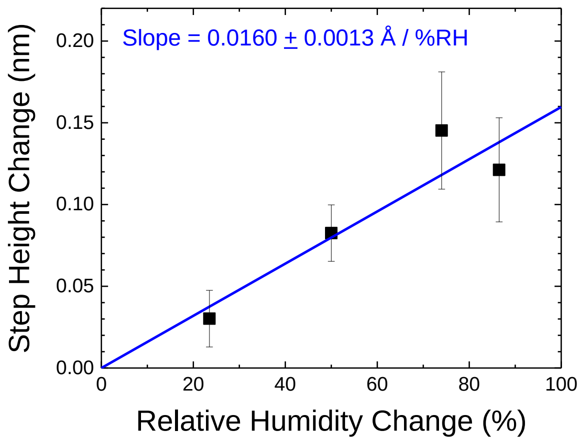
AFM Characterization

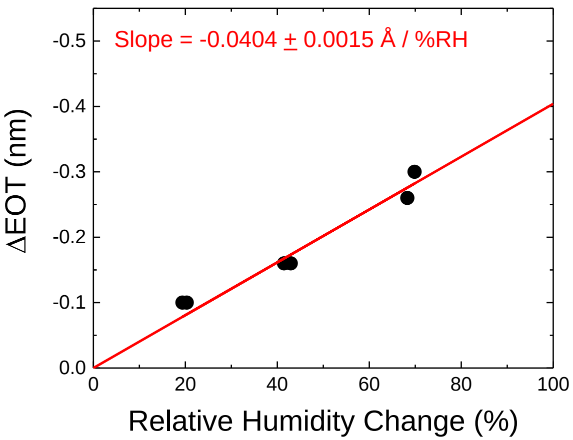
- Humidity-dependent atomic force microscopy (AFM):

E. J. Olson, et al., ACS Appl. M & I 7, 25804 (2015).







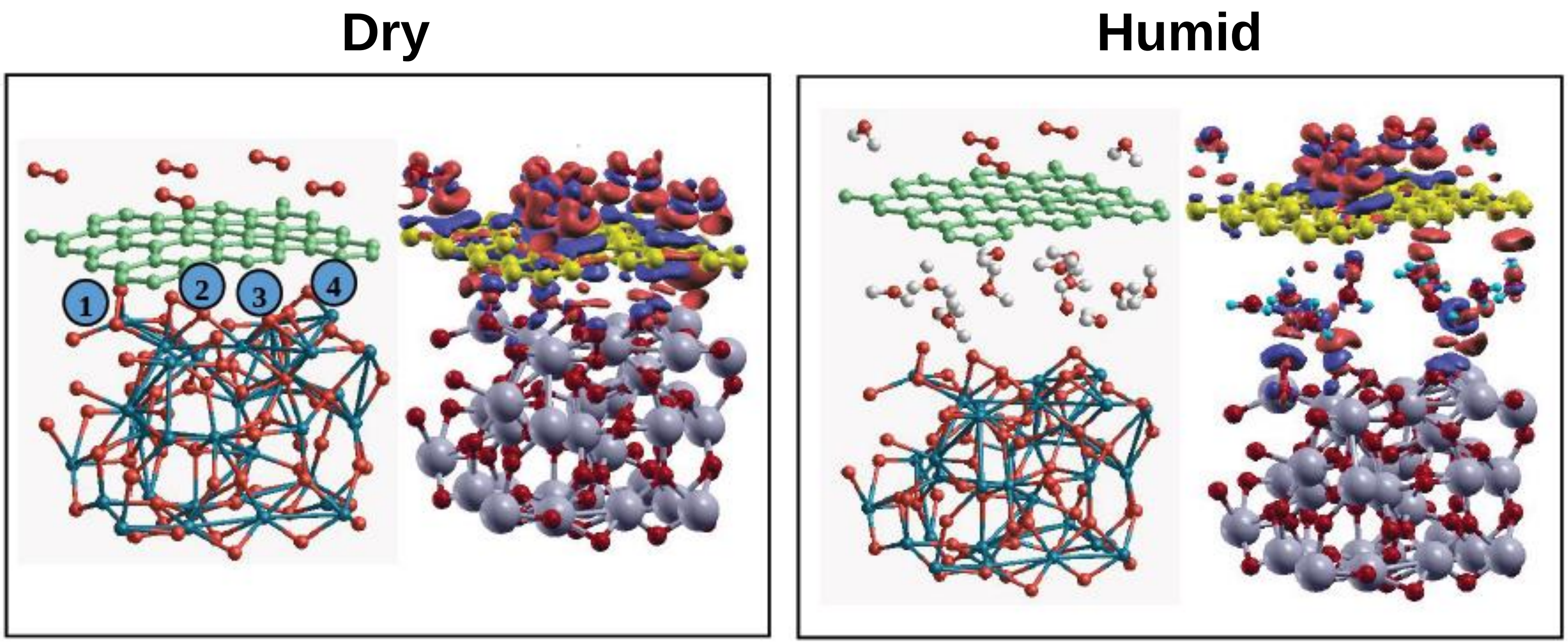


- **Humidity increases separation between graphene and HfO_2, by about ~ 0.1 nm for 60% RH.**

Understanding H_2O Effects

- Explanation of mechanism provided by DFT calculations:

E. J. Olson, et al., ACS Appl. M & I 7, 25804 (2015).

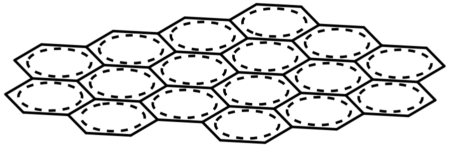


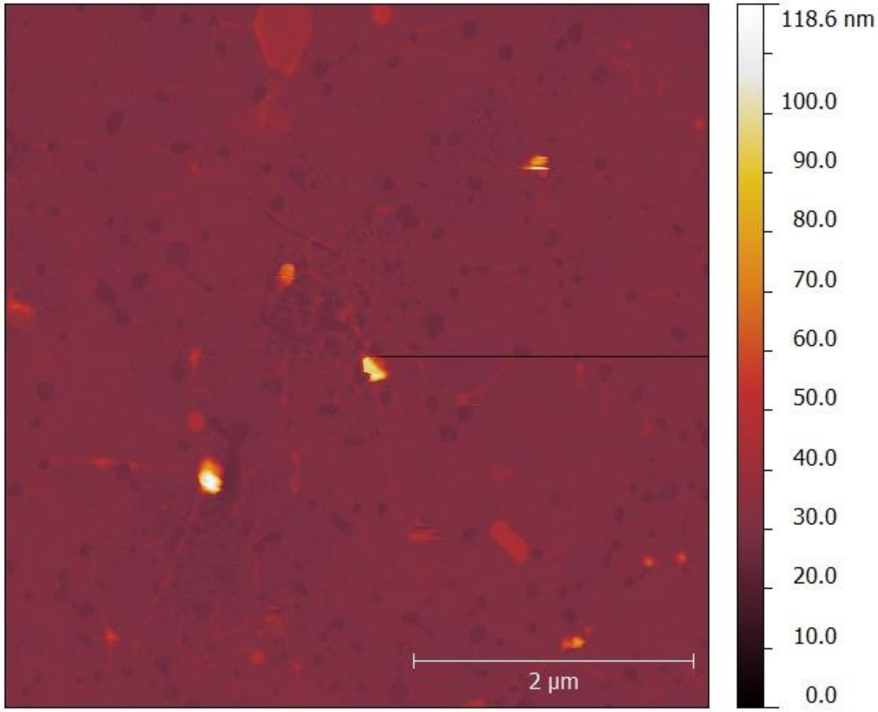
- **Higher dielectric constant of H_2O compared to vacuum <u>reduces EOT</u>, despite larger separation, leading to higher capacitance.**

GOx Functionalization

- AFM on graphene surface <u>before</u> functionalization:

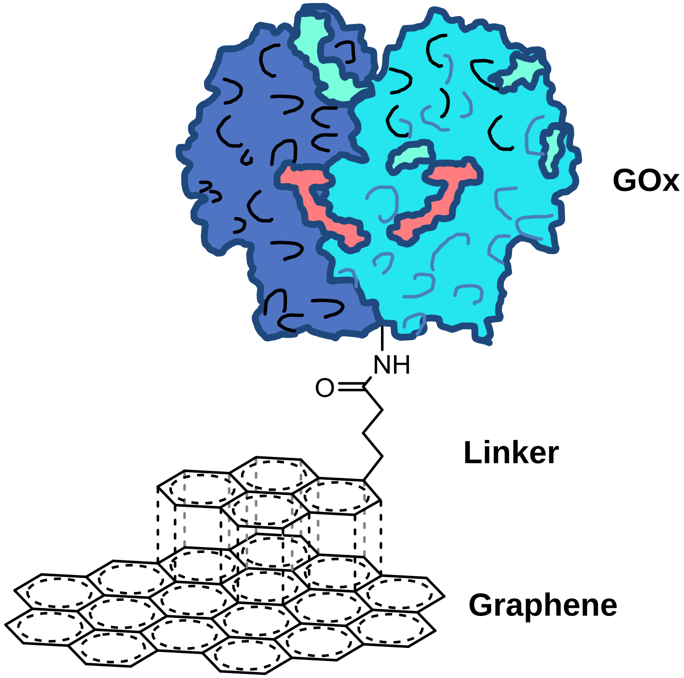
M. A. Ebrish, et al., ACS Appl. M & I, 6, 10296 (2014).



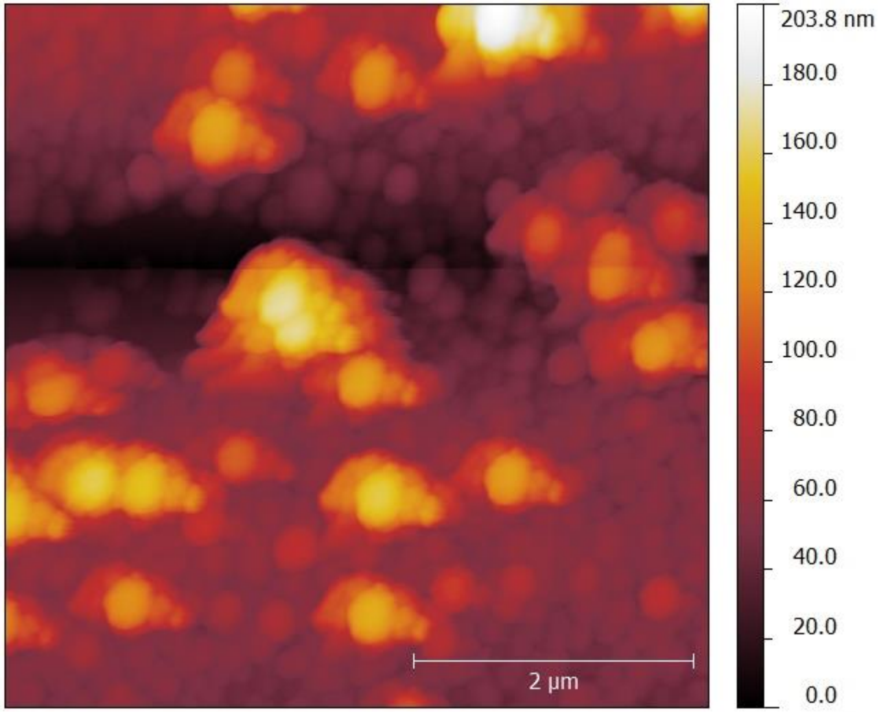


GOx Functionalization

- AFM on graphene surface after functionalization:



M. A. Ebrish, et al., ACS Appl. M & I, 6, 10296 (2014).

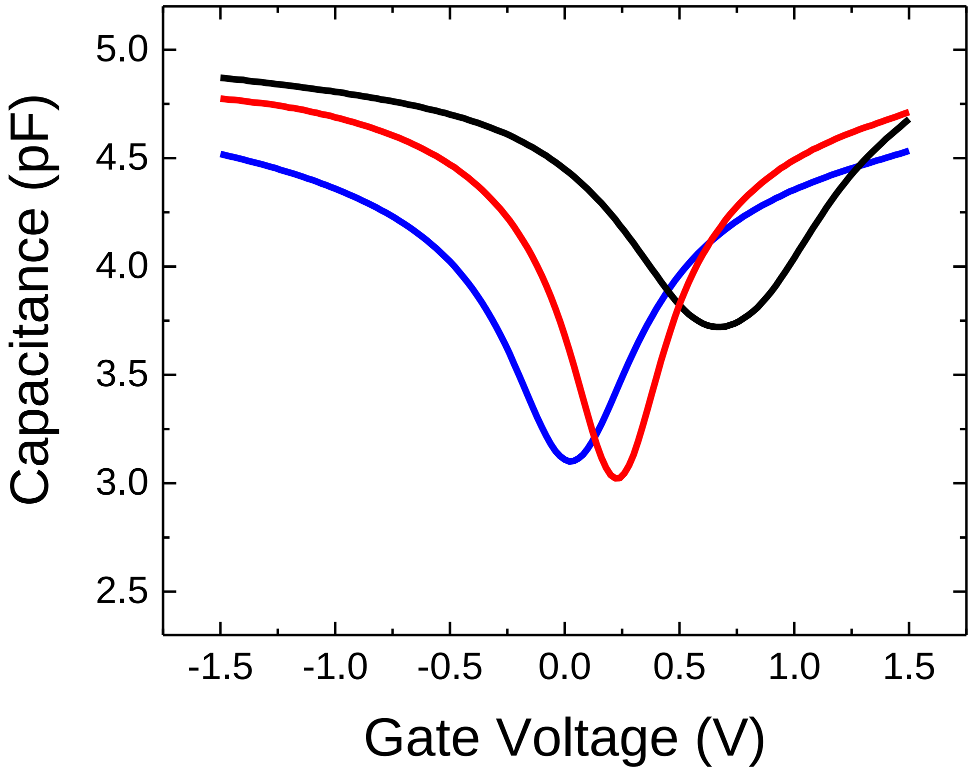


- **Topography consistent with published size of glucose oxidase.**
- **Do the graphene varactors still work after functionalization?**

Effect of Surface Functionalization

- Studied effect of surface functionalization on graphene varactor properties:

M. A. Ebrish, et al., ACS Appl. M & I, 6, 10296 (2014).



Vacuum – Before Functionalization

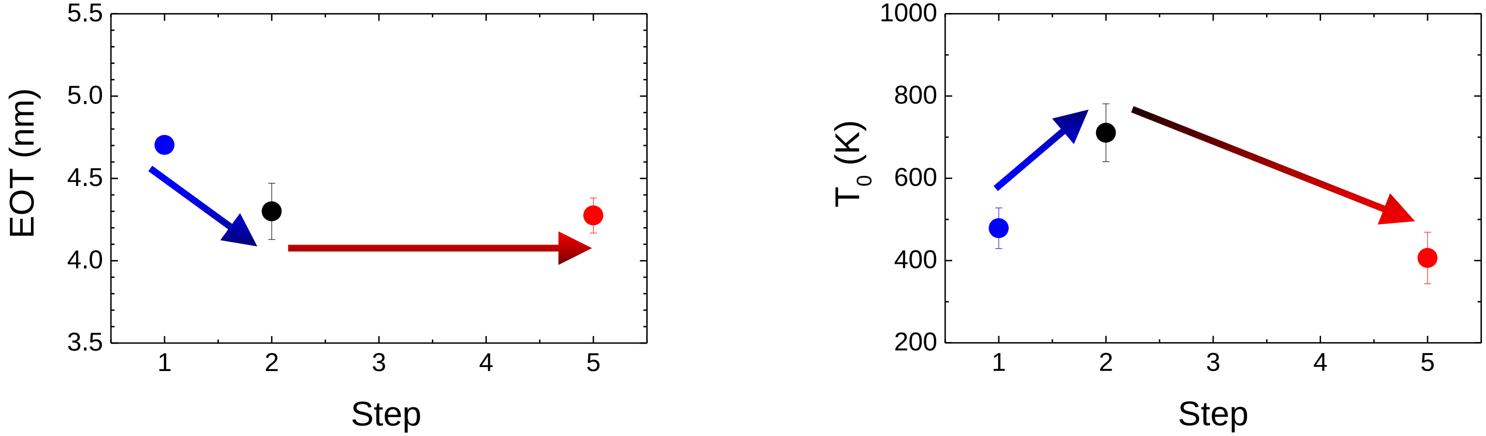
In Air - Before Functionalization

In Air – Fully Functionalized

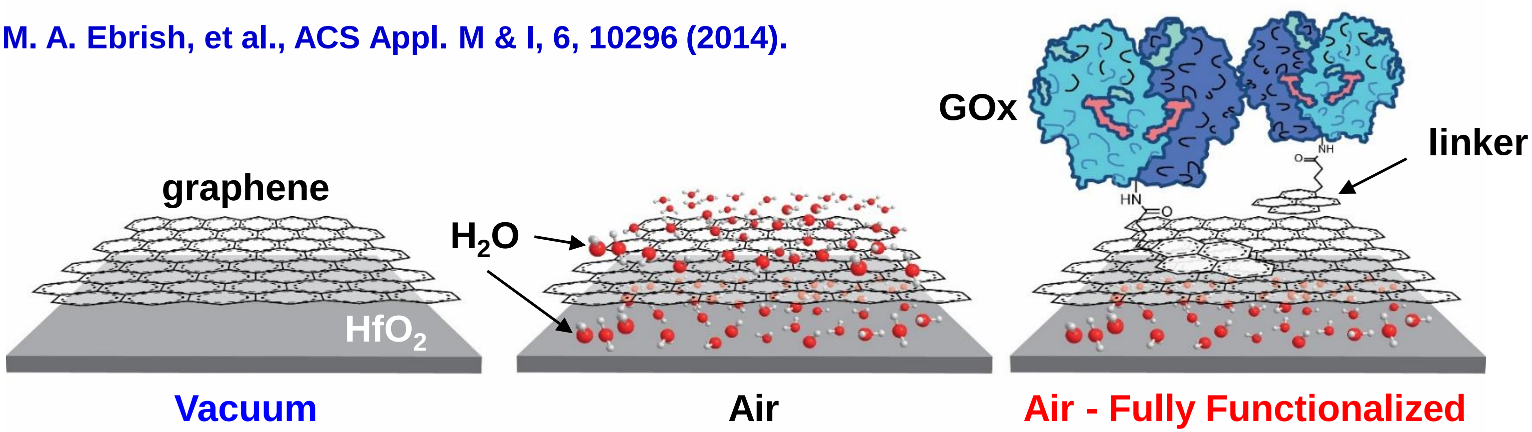
- **Functionalization increases maximum capacitance and also increases the tuning range.**

Effect of Surface Functionalization

- Modeling used to extract EOT and disorder parameter, T_0:



M. A. Ebrish, et al., ACS Appl. M & I, 6, 10296 (2014).



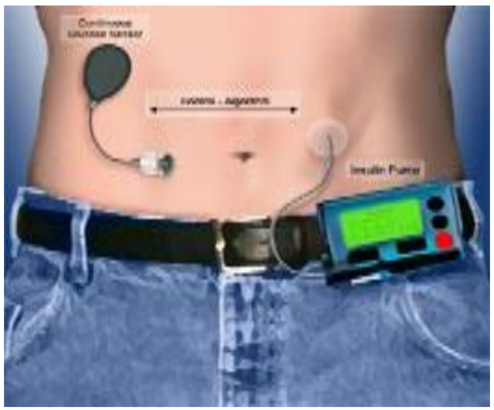
- **After functionalization, intercalated H_2O remains → EOT unchanged.**
- **After functionalization, linker displaces surface H_2O → reduced disorder.**

Wireless Sensor Applications

- Wide range of applications in healthcare and beyond where ultra-small size and wireless readout needed:

Source: E. L. Tan, IEEE Sens. Conf., (2007).

Artificial Pancreas



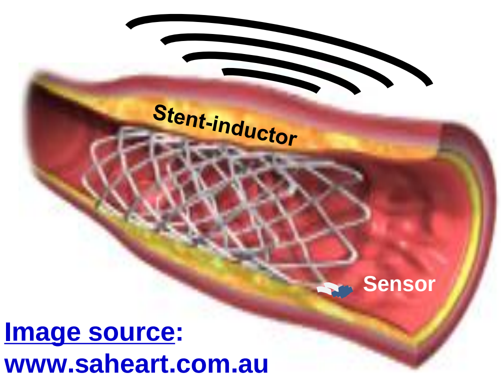
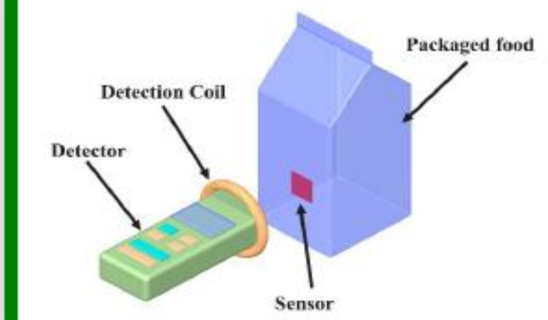
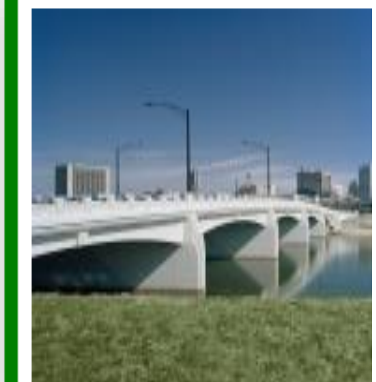


Image source: www.saheart.com.au



Food safety



Structural monitoring

Implantable biosensors:

- Glucose
- Bacteria
- Dopamine
- Cancer biomarkers
- Oxidative stress biomarkers

Personal chemical / radiation monitoring

Conclusions

- Graphene-based variable capacitors (varactors) using the quantum capacitance effect can readily be achieved experimentally with high yield and uniformity.
- Demonstrated wireless vapor sensors using water as a test analyte. Also studied effect of water intercalation on varactor properties.
- Characterized functionalization of graphene for glucose sensing and demonstrated improved varactor operation compared to devices in air or vacuum.

- **Graphene wireless sensors are a powerful platform for a wide range of sensing applications in healthcare and beyond.**

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