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GATED QUANTUM CAPACITIVE DEVICES

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ABSTRACT

Graphene is a 2-dimensional allotrope of carbon which forms a honeycomb lattice. It is a material of great interest recently for the scientific community because of its unique electronic properties. Because the carbon atoms undergo sp^2 hybridization, graphene has delocalized p orbitals that form a semimetal. In our configuration, graphene is deposited on a silicon wafer with a conducting plate (top gate) located 1 cm above the surface. In this way, the configuration acts as a Field Effect Transistor (FET). The conductivity of graphene changes in a measurable way when NO and NO_2 gasses, are introduced into the region between the graphene and conducting plate. [2] We hypothesize that this change is due to the system's sensitivity to changes in the dielectric constant of the side exposed to changing gas composition. This is enhanced by the unique density of states of graphene. The system can be modeled as two capacitors in series that share a central interface. Region 1 is the gaseous region above the graphene and region 2 is the thin non-conducting oxide layer on the outside of the silicon wafer. This method for analyzing quantum capacitance was first explored by Luryi [1] where he studied the effect of replacing the central interface with an ideal 2-dimensional quantum well. We extend this method of analysis to our graphene system. The graphene system has a high dependence on the changes in the permittivity of region 1. The introduction of dipole gasses NO and NO_2 could be the cause of this due to the relative ease of polarization by reorientation of the dipoles.

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Chapter 1 Introduction

Experiment Overview

The project aims to understand why the conductivity of a layer of Graphene deposited on a silicon substrate changes when exposed to the polar gasses NO and NO_2. The voltages are controlled at all three interfaces and the charges are allowed to move freely and be distributed in an arrangement that requires the least amount of energy. A small potential difference is applied across the gold leads on the graphene to continuously measure changes in its conductivity. We hypothesize that the top plate is critical to allowing graphene to function as a field effect transistor. Previous experimentation has shown that the sensitivity of the sensor is highly dependent on the top gate voltage. [2] [3] We predict that partial screening of the electric field by the low DOS material at the interface is what allows these unique charge configurations. These small changes in the surface charge density of graphene are able to be measured due to the conductivity of graphene changing proportionally to the accumulated charge density. [2]

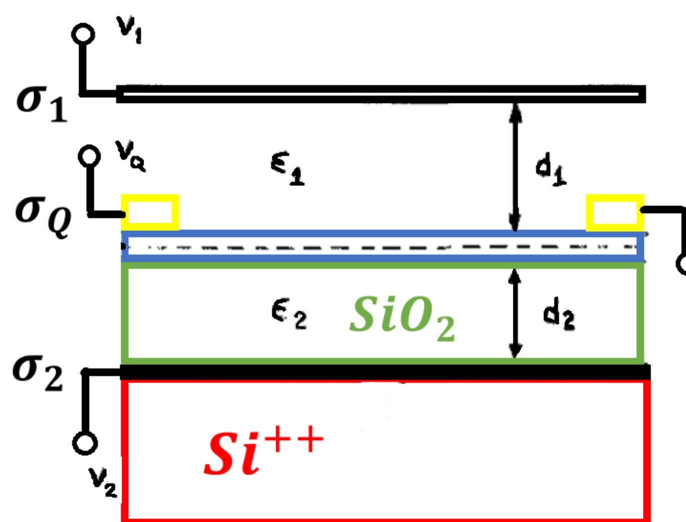

Figure 1: Experimental Setup

We will model this system as a pair of linked capacitors. We will also need to account for the energy required to add or remove charges from graphene. This requirement is due to graphene's density of states which dictates which energy states are available for electrons to occupy. It is important to determine the surface charge density on graphene because charge density is directly proportional to the conductivity of the graphene layer [2]. This change in conductivity is what is measured to detect changes in the gases in region 1.

Density of States

The density of states (DOS) of a system expresses the distribution of energy states that are permissible per unit energy. A DOS of zero means that there are no states at that energy that can be occupied. In our setup the density of states of the central interface is critical to the operation of the device. We will also obtain the density of states for several potential interface materials and compare their operation. Density of states is defined as the number of states per unit energy per unit volume. This can be found by integrating over a disc in k space. [4]

$$D(\varepsilon) = 2 * \ g * \left(\frac{1}{2\pi}\right)^2 \int_0^{2\pi} d\theta \int_0^{+\infty} \delta(\varepsilon - \varepsilon_k) k dk \tag{1.0}$$

The factor of 2 is for spin degeneracy, spin up and spin down. "g" is the valley degeneracy factor. Which is 1 for the 2D quantum well and is 2 for graphene. The 2π squared term is from periodic boundary conditions and the integral is modified to take advantage of rotational symmetry which is a disc in k-space for 2D materials such as the quantum well and Graphene. After a few minor simplifications we obtain a generalized formulation to find the density of states in axisymmetric 2D materials.

$$D(\varepsilon) = \frac{g}{\pi} \int_0^{+\infty} \delta(\varepsilon - \varepsilon_k) k dk \tag{1.1}$$

2D-Quantum well

The energy of individual electrons in a 2D Quantum well are equivalent to the free energy in an electron gas. We know how wavenumber relates to energy in free electrons and use this relation to perform a change of variables to utilize the properties of the Dirac delta function.

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \tag{1.2}$$

The derivative of equation (1.2) is useful for the change of variables for equation (1.1) to be in terms of energy rather than wavenumber.

$$d\varepsilon = \frac{\hbar^2}{m} k\, dk \tag{1.3}$$

To perform the change of variables, use the k dk term of equation (1.3) to substitute into equation (1.1) to change to an integral over occupied energies.

$$D(\varepsilon) = \frac{g}{\pi} \int_0^{+\infty} \delta(\varepsilon - \varepsilon_k) \frac{m}{\hbar^2}\, d\varepsilon$$

$$D(\varepsilon) = \frac{m}{\pi \hbar^2} \tag{1.4}$$

The 2D quantum well is found to have a constant density of states. This is confirmed by multiple sources [5] and relies on the assumption that the electrons do not interact with each other.

Graphene

Close to the fermi level we can approximate the energy states of individual electrons as $\varepsilon(k) = \hbar\, v_F \cdot |k|$ [5]; where k is the wavevector of the electron of interest. The same change of variable approach can be used to substituted for k dk.

$$\varepsilon = \hbar v_f |k| \tag{1.5}$$

To make the change of variables solve equation (1.5) for k and take the derivative.

$$k = \frac{|\varepsilon|}{\hbar v_f} \qquad\qquad dk = \frac{d\varepsilon}{\hbar v_f}$$

$$k * \ dk = \frac{|\varepsilon|}{\hbar^2 v_F^2} \ d\varepsilon \tag{1.6}$$

Once the relation for k dk has been obtained we can perform the same change of variables for equation (1.1). The integral can be evaluated directly due to the dirac delta.

$$D(\varepsilon) = \frac{g}{\pi} \int_0^{+\infty} \delta(\varepsilon - \varepsilon_k) \cdot \frac{1}{\hbar^2 v_f^2} \cdot |\varepsilon| \ d\varepsilon$$

$$D(\varepsilon) = \frac{g}{\pi \hbar^2 v_f^2} \cdot |\varepsilon| \tag{1.7}$$

Table 1: Density of States

Material	Density of States
2D quantum Well	$D(\varepsilon) = \frac{m}{\pi \hbar^2}$
Graphene	$D(\varepsilon) = \frac{g}{\pi \hbar^2 v_f^2} \cdot \lvert\varepsilon\rvert$

Field Effect Transistors

Modern electronics rely on a switching device known as a transistor. Transistors allow a small current source to control the current flow of an independent signal. Most field effect transistors use a semiconductor such a silicon that is doped with impurities to create regions with slight electron deficiencies (p) or excesses (n). An example of this is a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) which utilizes a N-P-N junction, a series of negative, positive and negatively doped regions. The conductivity change that is due to an external input mirrors what occurs with the

Graphene system. Because of this we describe our system as a Gated Quantum Capacitive Device because it functions similarly to a transistor as the conductivity changes as a function of an external input. The term Quantum Capacitance relates to a material dependent constant that is used to account for system energy which moves charges into the energy states determined by the material's DOS function.

Fermi Energy

The density of states of a material is the discrete set of states per energy interval that can be occupied. [4] The number of electrons in a given material is obtained by combining the density of possible states and the probability that each state is occupied. The probability is obtained via Fermi-Dirac Statistics which predicts the behavior of fermions, or particles that observe the Pauli exclusion principle, such as electrons.

$$f(\varepsilon) = \frac{1}{e^{\left(\frac{\varepsilon - \varepsilon_F}{k_B T}\right)} + 1} \tag{1.8}$$

This relation quantifies how electrons exist at energies above the fermi level due to thermal excitations. At absolute zero the fermi function evaluates to 1 for energies below the fermi level ε_F and 0 for energies above. For nonzero temperatures there becomes a small probability that electrons can exist above the fermi level.

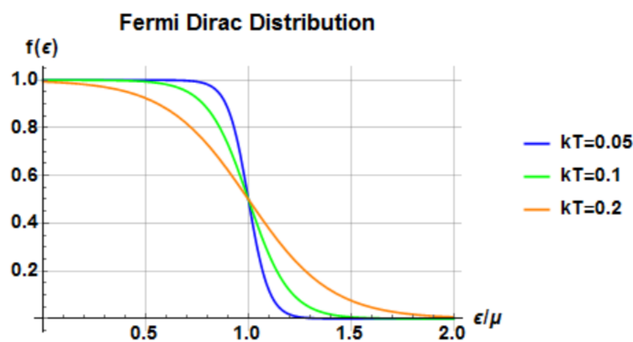

Figure 2: Fermi-Dirac Distribution

The fermi level is the maximum energy level that is occupied at absolute zero temperature. In the above plot we see that as temperature increases more fermions are able to move to energies above the fermi level. The integral over all energies is unity as is required for any probability density distribution. In our approximations for the system to simplify the math we will assume temperatures close to absolute zero so that we can approximate the fermi function as a step function. Future work on this topic should extend this analysis to systems with a temperature dependence. Another point of note is that the Fermi energy and the electrostatic potential energy of a material at a location are not explicitly the same. This divergence of these energies is critical to the function of this system and its sensitivity to changes in the dielectric constant of the gases in region 1.

Calculating Energies and Charge Density

The energy and charge density of the low DOS interface material can be calculated via integration when the chemical potential is known. [6] The voltage control for this experiment actually controls the chemical potential for the interfaces. For perfect metals the electrostatic and chemical potentials are equivalent because no additional energy is required to occupy a specific state. However, for the low DOS central interface there is a split due to energy requirements to add charges. This split in energy can be described in terms of a quantum capacitance. We can begin by creating formulations to describe chemical potential and surface charge density. Starting with the integral which integrates the product of the fermi function and the density of states of the material over all possible energies. [4]

$$\frac{N}{A} = \int_{-\infty}^{\infty} d\varepsilon \, f(\varepsilon) \, D(\varepsilon) \tag{1.9}$$

N is the total number of states. $f(\varepsilon)$ is the fermi function. $D(\varepsilon)$ is the Density of States. To simplify the calculations, we will take temperature to be close to absolute zero. In this case the fermi function acts as a step function with a cutoff at the fermi energy ε_F.

$$n = \int_{-\infty}^{\varepsilon_F} D(\varepsilon) d\varepsilon \tag{1.10}$$

We want to find the change from equilibrium so let ε_F^0 be the fermi energy at zero charge.

$$\Delta n = \int_{-\infty}^{V_Q} D(\varepsilon) d\varepsilon - \int_{-\infty}^{\varepsilon_F^0} D(\varepsilon) d\varepsilon = \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon) d\varepsilon \tag{1.11}$$

And we define the surface charge density as $\sigma = -e \cdot \Delta n$

$$\sigma_Q = -e \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon) d\varepsilon \tag{1.12}$$

This relation will be critical for implementation into the final charge conservation formulation.

Linked Capacitors and charge conservation

Linked capacitors describe a system where two capacitors in series share a common plate. If all three plates had a high DOS the same effects would not be seen due to full screening of the electric field. For example, let us observe the full screening that occurs with standard linked capacitors. For this hypothetical configuration we set the top gate to a potential V_1 and ground the interfaces $V_Q = 0$ and $V_2 = 0$. Start with the formulation of Maxwell's equation for electrostatic fields.

$$\nabla \cdot \vec{F_i} = \frac{\rho_i}{\epsilon_i} \tag{1.13}$$

Evaluating this equation over two gaussian pill boxes close to the surfaces of the top gate and the Si-SiO_2 interface gives equations for the surface charge density as a function of field strength which can be related directly to the potential difference between the plates.

$$F_1 = \frac{\sigma_1}{\epsilon_1} = -\frac{\phi_1 - \phi_Q}{d_1} \tag{1.14}$$

$$F_2 = \frac{\sigma_2}{\epsilon_2} = -\frac{\phi_2 - \phi_Q}{d_2} \tag{1.15}$$

Because the interfaces are perfect conductors the relationship for chemical potential energy is directly proportional to the electric potential and the fundamental charge constant.

$$V_1 = -e\,\phi_1 \qquad V_2 = -e\,\phi_2 \qquad V_Q = -e\,\phi_Q$$

Substituting these relations into equations (1.14) and (1.15) we obtain relations for the surface charge densities on surfaces 1 and 2.

$$\sigma_1 = \epsilon_1 \cdot \frac{V_1 - V_Q}{e\,d_1} \tag{1.16}$$

$$\sigma_2 = \epsilon_2 \cdot \frac{V_2 - V_Q}{e\,d_2} \tag{1.17}$$

Define $C_i = \frac{\epsilon_i}{d_i}$ where C_i is the capacitance per unit area.

Charge is conserved in the system and this can be rearranged to solve for the charge of the central interface.

$$\sigma_{interface} = -(\sigma_1 + \sigma_2)$$

$$\sigma_{interface} = -\left(\frac{C_1}{e}\left(V_1 - V_Q\right) + \frac{C_2}{e}\left(V_2 - V_Q\right)\right)$$

V_Q and V_2 are grounded to zero potential so the relation becomes

$$\sigma_{interface} = -\frac{1}{e}\left(C_1 V_1\right) \tag{1.18}$$

This is equivalent to

$$\sigma_1 = -\sigma_{interface}$$

We see that with no energy requirement to distribute the charges complete shielding of region 2 occurs as expected. Changes in the dielectric constant of region 1 would result in proportional changes in the surface charge density. We hypothesize that for our low DOS system the incomplete screening is the cause of higher order sensitivity to changes in the dielectric constant of the gases.

Quantum Capacitance

A voltmeter will read the difference in chemical potential between two points. In low DOS materials, a variable amount of energy is required to add electrons to the material. It is useful to describe this energy term as an additional capacitance added in series. A hypothetical situation in which we can show the implementation of this term would be in describing a two-plate capacitor where one plate is a perfect conductor and the other is a 2D Quantum well. To begin our analysis, we want to relate the potentials and the charge accumulation. We ground the metal plate $V_1 = 0$ and use our relation for surface charge density derived from earlier.

$$\sigma_1 = C_1 \frac{V_1 - \varepsilon_F^0}{e}$$

And that the charge on the low DOS plate is governed by equation

$$\sigma_Q = -e \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon) d\varepsilon \tag{1.12}$$

We apply the conservation of charge and substitute the density of states for a 2D quantum well that was obtained in equation (1.4).

$$\sigma_1 + \sigma_Q = 0$$

$$C_1(\varepsilon_F^0) = -\frac{e^2 m}{\pi \hbar^2} \left(V_Q - \varepsilon_F^0\right)$$

If we describe $C_Q = \frac{e^2 m}{\pi \hbar^2}$

$$-C_1 \varepsilon_F^0 = -C_Q V_Q + C_Q \varepsilon_F^0$$

$$\varepsilon_F^0 = V_Q \frac{C_Q}{C_1 + C_Q} \tag{1.17}$$

$$\sigma_Q = -e \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon) d\varepsilon$$

$$\sigma_Q = -\frac{C_Q}{e}\left(V_Q - V_Q \frac{C_Q}{C_1 + C_Q}\right)$$

$$\sigma_Q = -\frac{V_Q}{e}\left(\frac{C_1 C_Q}{C_1 + C_Q}\right)$$

$$\sigma_Q = \frac{-V_Q}{e}\left(\frac{1}{C_1} + \frac{1}{C_Q}\right)^{-1} \tag{1.18}$$

In equation (1.18) we show that the low DOS material's impact on the expected charge density is analogous to an additional quantum capacitance that acts in series, effectively lowering the overall capacitance of the system.

Chapter 2 System Analysis

General System Solution

The general system can be modeled as two capacitors in series that share a central interface which is has a specific density of states. We will compare the cases of a standard 2-D quantum well and Graphene which have different DOS functions. We will also observe the impact of a top Gate on the system. Analysis will start by looking at the governing electrostatic equations to determine how the charges will distribute themselves given the applied potentials. The derivation of the general case begins with one of Maxwell's equations

$$\nabla \cdot \vec{F_i} = \frac{\rho}{\epsilon_i} \tag{1.13}$$

From Maxwell's equation we derive equations (1.14) and (1.15) in the same manner as before. However, this time we will define the potential energies slightly differently.

$$V_1 = -e\,\phi_1 \qquad V_2 = -e\,\phi_2 \qquad \varepsilon_F^0 = -e\,\phi_Q$$

ε_F^0 is defined as the fermi energy of graphene with zero net charge. Substituting these values into equations (1.14) and (1.15) yields two new equations relating the potentials and the surface charge densities.

$$\sigma_1 = \epsilon_1 \cdot \frac{\varepsilon_Q^0 - V_1}{e\,d_1} \qquad \sigma_2 = \epsilon_2 \cdot \frac{\varepsilon_Q^0 - V_2}{e\,d_2}$$

Defining Capacitance per unit area as $C_i = \frac{\epsilon_i}{d_i}$ is a convenient substitution to make.

$$\sigma_1 = C_1 \frac{\varepsilon_F^0 - V_1}{e} \tag{2.1}$$

$$\sigma_2 = C_2 \frac{\varepsilon_F^0 - V_2}{e} \tag{2.2}$$

The charge on the interface is a function of the density of states and the Gate voltage that is applied via the gold contacts. This relation was derived earlier in chapter 1.

$$\sigma_Q = -e\int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon \tag{1.12}$$

The system must also satisfy the conservation of charge so we can combine equations (1.12) (2.1) and (2.2). The general solution for a three-plate system with a unique DOS central interface is defined as

$$(C_1 + C_2)\,\varepsilon_F^0 - C_1V_1 - C_2V_2 = e^2\int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon\,. \tag{2.3}$$

This general equation can be solved for ε_F^0 and then substituted into the original equation for the charge density on the low DOS interface.

Gated vs non-Gated Systems

We want to prove that the presence of the top gate is critical to the operation of the system as a FET. Analysis of the system without the top gate will also be included for comparison. To organize the analysis, we break down the system into four possible configurations to study the variation between effects due to the presence of a top gate, and effects due to variations in the density of states of the interface material.

Potential cases

-Gated system, Constant DOS material

-Gated system, Graphene at interface

-Non-Gated system, constant DOS material

-Non-Gated system, Graphene at interface

Gated system, Constant DOS material

We begin our analysis of the system with the relation derived in equation (2.3)

$$(C_1 + C_2)\,\varepsilon_F^0 - C_1V_1 - C_2V_2 = e^2 \int_{\varepsilon_F^0}^{V_Q} \left(\frac{m}{\pi\hbar^2}\right) d\varepsilon$$

$$(C_1 + C_2)\,\varepsilon_F^0 - C_1V_1 = \left(\frac{e^2m}{\pi\hbar^2}\right) \cdot \left(V_Q - \varepsilon_F^0\right)$$

Recall that $C_Q = \frac{e^2m}{\pi\,\hbar^2}$.

$$\varepsilon_F^0 = \frac{C_1V_1 + C_QV_Q}{C_1 + C_2 + C_Q} \qquad (2.4)$$

With the relation for ε_F^0 formulated we can substitute this into the relation for surface charge density in the central interface.

$$\sigma_Q = -e\int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\,d\varepsilon \qquad (1.12)$$

$$\sigma_Q = -\frac{em}{\pi\hbar^2}\left(V_Q - \varepsilon_F^0\right)$$

$$C_Q = \frac{e^2m}{\pi\hbar^2}$$

$$\sigma_Q = \frac{-C_Q}{e}\left(V_Q - \frac{C_1V_1 + C_QV_Q}{C_1 + C_2 + C_Q}\right) \qquad (2.5)$$

Gated system, Graphene at interface

Analysis of the system with graphene at the central interface will follow the same prosses. Equation (2.3) is modified with the density of states function equation (1.7).

$$(C_1 + C_2)\, \varepsilon_F^0 - C_1 V_1 = \; e^2 \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon = e^2 \int_{\varepsilon_F^0}^{V_Q} \frac{1}{\pi \hbar^2 v_F^2} \cdot \; |\varepsilon - \varepsilon_F^0|\, d\varepsilon$$

$$(C_1 + C_2)\, \varepsilon_F^0 - C_1 V_1 = \; \frac{e^2}{2\pi \hbar^2 v_F^2} \cdot \left(V_Q - \varepsilon_F^0\right) \cdot \left|V_Q - \varepsilon_F^0\right|$$

We will assume that $V_Q > \varepsilon_F^0$. This is a valid assumption for all V_Q because The chemical potential energy will always be greater than the fermi energy at zero net charge because the energy of the system will increase with both the addition and removal of charges as the system wants to return to its neutral state at the lowest energy. With this assumption we can remove the absolute value sign from the equation.

$$(C_1 + C_2)\varepsilon_F^0 - C_1 V_1 = \frac{e^2 D_1}{2} \left(V_Q - \varepsilon_F^0\right)^2$$

We want to solve this equation in terms of ε_F^0, with higher power terms of ε_F^0 the quadratic formula is a useful tool.

$$\left(\frac{e^2 D_1}{2}\right) (\varepsilon_F^0)^2 - \left(e^2 D_1 V_Q + (C_1 + C_2)\right) \varepsilon_F^0 + \frac{e^2 D_1}{2} V_Q^2 + C_1 V_1 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$V_0 = \frac{C_2}{e^2 D_1}$$

$$a = \left(\frac{e^2 D_1}{2}\right) = \left(\frac{C_2}{2\, V_0}\right)$$

$$b = -\left(e^2 D_1 V_Q + (C_1 + C_2)\right) = \; -\left(C_2 \frac{V_Q}{V_0} + (C_1 + C_2)\; \right)$$

$$c = \frac{e^2 D_1}{2} V_Q^2 + C_1 V_1 = \frac{C_2\, V_Q^2}{2\, V_0} + C_1 V_1$$

$$\varepsilon_F^0 = \frac{\left(C_2 \frac{V_Q}{V_0} + (C_1 + C_2)\right) \pm \sqrt{\left(C_2 \frac{V_Q}{V_0} + (C_1 + C_2)\right)^2 - 4\left(\frac{C_2}{2\,V_0}\right)\left(\frac{C_2\,V_Q^2}{2\,V_0} + C_1 V_1\right)}}{\left(\frac{C_2}{V_0}\right)}$$

$$\varepsilon_F^0 = V_Q + V_0\left(\frac{C_1 + C_2}{C_2}\right) \pm V_0\sqrt{\left(\frac{1}{C_2}\right)^2\left(C_2 \frac{V_Q}{V_0} + (C_1 + C_2)\right)^2 - \left(\frac{1}{C_2}\right)^2\left(\frac{C_2^2 V_Q^2}{V_0^2} + \frac{2C_1 C_2 V_1}{V_0}\right)}$$

$$\varepsilon_F^0 = V_Q + \left(\frac{C_1 + C_2}{C_2}\right)V_0 \pm\ V_0\sqrt{\left(\frac{V_Q}{V_0} + \left(\frac{C_1 + C_2}{C_2}\right)\right)^2 - \left(\frac{V_Q}{V_0}\right)^2 - \frac{2\,C_1 V_1}{C_2 V_0}}$$

$$\varepsilon_F^0 = V_Q + \left(\frac{C_1 + C_2}{C_2}\right)V_0 \pm\ V_0\sqrt{\left(\frac{C_1 + C_2}{C_2}\right)^2 + \left(\frac{C_1 + C_2}{C_2}\right)\frac{2\,V_Q}{V_0} - \frac{2\,C_1 V_1}{C_2 V_0}}$$

We need to determine which sign results in a real physical system. We use the limit where all potentials are zero. At the limit $V_1 = V_Q = 0$ we know that $\varepsilon_F^0 = 0$.

$$\varepsilon_F^0 = \left(\frac{C_1 + C_2}{C_2}\right)V_0 \pm \left(\frac{C_1 + C_2}{C_2}\right)V_0$$

Choose minus to satisfy limit.

$$\varepsilon_F^0 = V_Q + \left(\frac{C_1 + C_2}{C_2}\right)V_0 -\ V_0\sqrt{\left(\frac{C_1 + C_2}{C_2}\right)^2 + \left(\frac{C_1 + C_2}{C_2}\right)\frac{2\,V_Q}{V_0} - \frac{2\,C_1 V_1}{C_2 V_0}} \qquad (2.6)$$

Use the calculated Fermi Energy to find the surface charge density on graphene.

$$\sigma_Q = -e\int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\,d\varepsilon$$

$$\sigma_Q = -\frac{eD_1}{2}\left(V_Q - \varepsilon_F^0\right)^2$$

$$\sigma_Q = -\frac{eD_1}{2}\left(V_Q - V_Q - \left(\frac{C_1 + C_2}{C_2}\right)V_0 + V_0\sqrt{\left(\frac{C_1 + C_2}{C_2}\right)^2 + \left(\frac{C_1 + C_2}{C_2}\right)\left(\frac{2V_Q}{V_0}\right) - \frac{2C_1V_1}{C_2V_0}}\right)^2$$

$$\sigma_Q = -\left(\frac{C_2V_0}{2e}\right)\left(-\left(\frac{C_1 + C_2}{C_2}\right) + \sqrt{\left(\frac{C_1 + C_2}{C_2}\right)^2 + \left(\frac{C_1 + C_2}{C_2}\right)\left(\frac{2V_Q}{V_0}\right) - \frac{2C_1V_1}{C_2V_0}}\right)^2 \qquad (2.7)$$

Non-Gated system, constant DOS material

This arrangement would be a 2D quantum well on the surface of the silicon wafer. There is no conducting surface above this arrangement so there is no electric field in region 1 so we expect no sensitivity to changes in the dielectric constant of region 1. Modify the governing equation (2.3) and eliminate energy terms from capacitor 1.

$$C_2\, \varepsilon_F^0 = e^2 \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon = e^2 \int_{\varepsilon_F^0}^{V_Q} \left(\frac{m}{\pi\hbar^2}\right) d\varepsilon$$

$$C_2\, \varepsilon_F^0 = \left(\frac{e^2 m}{\pi\hbar^2}\right) \cdot \left(V_Q - \varepsilon_F^0\right) = C_Q \cdot \left(V_Q - \varepsilon_F^0\right)$$

$$\varepsilon_F^0 = \frac{C_Q \cdot V_Q}{C_2 + C_Q} \qquad (2.8)$$

$$\sigma_Q = -e \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon$$

$$\sigma_Q = -\frac{em}{\pi\hbar^2}\left(V_Q - V_Q * \left(\frac{C_Q}{C_Q + C_2}\right)\right)$$

Let: $C_Q = \frac{e^2 m}{\pi\hbar^2}$

$$\sigma_Q = \frac{-V_Q}{e}\left(\frac{C_Q C_2}{C_Q + C_2}\right)$$

$$\sigma_Q = \frac{-V_Q}{e}\left(\frac{1}{C_Q} + \frac{1}{C_2}\right)^{-1} \tag{2.9}$$

This arrangement is analogous to adding a capacitor in series, effectively lowering the overall capacitance and as a result also lowering the magnitude of charge that accumulates due to a potential difference. As expected the charge density on the exposed surface is not a function of C_1.

Non-Gated System, Graphene at interface

Using the same governing equations for a configuration without a gate we substitute the density of states for graphene.

$$C_2\,\varepsilon_F^0 = e^2\int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\,d\varepsilon = e^2\int_{\varepsilon_F^0}^{V_Q} \frac{1}{\pi\hbar^2 v_F^2}\cdot\,|\varepsilon - \varepsilon_F^0|\,d\varepsilon$$

$$C_2\,\varepsilon_F^0 = \frac{e^2}{2\pi\hbar^2 v_F^2}\cdot\left(V_Q - \varepsilon_F^0\right)\cdot\left|V_Q - \varepsilon_F^0\right|$$

To eliminate the absolute value term, we want to assume that ε_F^0 is greater than V_Q for all configurations. This is a valid assumption for all V_Q because the chemical potential energy will always be greater than the fermi energy at zero net charge because the energy of the system will increase with both the addition and removal of charges as the system wants to return to its neutral state at the lowest energy.

$$V_Q > \varepsilon_F^0 \quad and \quad D_1 = \frac{1}{\pi\hbar^2 v_F^2}$$

$$C_2\varepsilon_F^0 = \frac{e^2 D_1}{2}\left(V_Q - \varepsilon_F^0\right)^2$$

$$C_2\varepsilon_F^0 = \left(\frac{e^2 D_1}{2}V_Q^2 - e^2 D_1 V_Q \varepsilon_F^0 + \frac{e^2 D_1}{2}(\varepsilon_F^0)^2\right)$$

Use quadratic formula to solve for ε_F^0.

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$a = \frac{e^2 D_1}{2}$$

$$b = -(e^2 D_1 V_Q + C_2)$$

$$c = \frac{e^2 D_1 V_Q^2}{2}$$

$$\varepsilon_F^0 = \frac{e^2 D_1 V_Q + C_2 \pm \sqrt{\left(e^2 D_1 V_Q + C_2\right)^2 - 4\left(\frac{e^2 D_1}{2}\right)\left(\frac{e^2 D_1 V_Q^2}{2}\right)}}{e^2 D_1}$$

$$V_0 = \frac{C_2}{e^2 D_1}$$

$$\varepsilon_F^0 = V_Q + V_0 \pm \sqrt{\left(V_Q + V_0\right)^2 - V_Q^2}$$

At the limit where all potentials are set to zero we can make the assumption that $\varepsilon_F^0 = 0$ also. This allows us to determine the sign in the formulation.

$$\varepsilon_F^0 = 0 + V_0 \pm \sqrt{(V_0)^2 - 0}$$

We chose minus to satisfy this limit.

$$\varepsilon_F^0 = V_Q + V_0 - \sqrt{\left(V_Q + V_0\right)^2 - V_Q^2} \tag{2.10}$$

Once the formulation for ε_F^0 has been obtained we can use the original equation for surface charge density.

$$\sigma_Q = -e \int_{\varepsilon_F^0}^{V_Q} D(\varepsilon)\, d\varepsilon \tag{1.12}$$

$$\sigma_Q = -\frac{e D_1}{2}\left(V_Q - \varepsilon_F^0\right)^2$$

$$\sigma_Q = -\frac{eD_1}{2}\left(-\frac{C_2}{e^2D_1} + \sqrt{\left(V_Q + \frac{C_2}{e^2D_1}\right)^2 - V_Q^2}\right)^2$$

$$\sigma_Q = -\frac{C_2V_0}{2e}\left(-1 + \sqrt{\left(\frac{V_Q}{V_0} + 1\right)^2 - \left(\frac{V_Q}{V_0}\right)^2}\right)^2 \qquad (2.11)$$

As expected, non-gated systems do not depend on changes in the dielectric constant of region 1.

Calculation of constants

To obtain numerical solutions we need to define some of the constants of the system. The capacitance of region 1 is defined as $C_1 = \kappa\frac{\epsilon_0}{d_1}$. ϵ_0 is the permittivity of free space and is defined as

$\epsilon_0 = 8.851419 * 10^{-12}\frac{C^2}{J*m}$ [4]. The top gate is located 1cm above the interface so we can define the capacitance of region 1 as $\frac{C_1}{\kappa} = \frac{\epsilon_0}{d_1} = \frac{8.851419*10^{-12}}{0.01} = 8.851419 * 10^{-10}\frac{F}{m^2}$. Region 2 is the layer of silicon dioxide on the surface of the wafer with typical thickness $d_2 = 300\ nm$ and dielectric constant $\kappa = 3.9$.[7] Using this we can calculate the capacitance of region 2 as $C_2 = \kappa_2\frac{\epsilon_0}{d_2} = 3.9 * \frac{8.851419*10^{-12}}{300*10^{-9}} = 0.000115\frac{F}{m^2}$. The quantum capacitance for a 2D quantum well is defined as $C_Q = \frac{e^2m}{\pi\hbar^2}$, where e is the fundamental charge and m is the rest mass of an electron. We can evaluate the expression as for the quantum capacitance of a 2D quantum well. $C_Q = \frac{e^2m}{\pi\,\hbar^2} = \frac{(1.60218*10^{-19})^2*(9.10939*10^{-31})}{\pi\,(1.05457*10^{-34})^2} = 0.6693\frac{F}{m^2}$

We defined a variable V_0 to in the energy relations for graphene to simplify calculations. We noted that the fermi velocity was on the order of $v_F = 10^6 m/s$. Using values obtained earlier we can evaluate this term numerically.

$$V_0 = \frac{e^2 D_1}{C_2} = \frac{e^2}{C_2} * \frac{1}{\pi \hbar^2 v_F^2} = \frac{\left(1.60218 * 10^{-19}\right)^2}{(0.000115) * \pi * \left(1.05457 * 10^{-34}\right)^2 * \left(10^6\right)^2} = 0.001\, eV$$

These values are collected for use in the Mathematica notebook for plot creation and can be found in Table 2: System Constants.

Table 2: System Constants

Constant	Value
$\frac{C_1}{\kappa}$	$8.851419 * 10^{-10} \frac{F}{m^2}$
C_2	$0.000115 \frac{F}{m^2}$
C_Q	$0.6693 \frac{F}{m^2}$
V_0	$0.001\, eV$

Surface charge density relations

Collecting all of the expressions obtained earlier we can see similarities in their forms

Table 3: Surface charge density relations

Configuration	**Relation for σ_Q**
No top gate, 2D Quantum well	$\sigma_Q = \frac{-V_Q}{e}\left(\frac{1}{C_Q}+\frac{1}{C_2}\right)^{-1}$
No top gate, Graphene	$\sigma_Q = -\frac{C_2 V_0}{2e}\left(-1+\sqrt{\left(\frac{V_Q}{V_0}+1\right)^2-\left(\frac{V_Q}{V_0}\right)^2}\right)^2$
Top gated 2D Quantum well	$\sigma_Q = \frac{-C_Q V_Q}{e}\left(\frac{C_2+C_1\left(1-\frac{V_1}{V_Q}\right)}{C_1+C_2+C_Q}\right)$
Top gated Graphene	$\sigma_Q = -\left(\frac{C_2 V_0}{2e}\right)\left(-\left(\frac{C_1+C_2}{C_2}\right)+\sqrt{\left(\frac{C_1+C_2}{C_2}\right)^2+\left(\frac{C_1+C_2}{C_2}\right)\left(\frac{2V_Q}{V_0}\right)-\frac{2C_1V_1}{C_2V_0}}\right)^2$

Chapter 3 Results and Discussion

Charge density plots

The Charge density relations obtained in the previous chapter can be used to investigate the properties of this system. Using Mathematica we are able to visualize the variation of parameters to see which configurations yield the greatest sensitivity in the area of interest. See appendix A for Mathematica commands. Tests on air have shown a change of about 2% in dielectric constant due only to changes in relative humidity. [6] We expect that the introduction of polar gasses will increase the dielectric constant of the air gas mixture as a function of concentration. We also expect the Dielectric constant to be greater than 1, or vacuum, and remain less than one order of magnitude larger than standard air. Using Mathematica we can incrementally change the dielectric constant to observe changes in surface charge density.

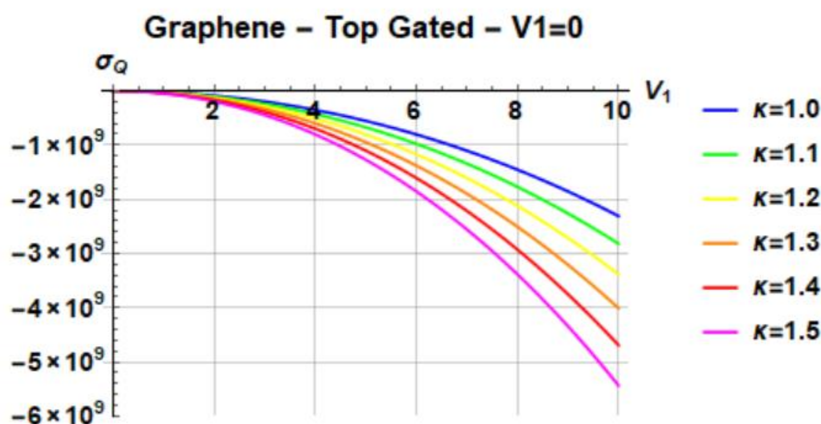

Figure 3: Top Gated Graphene - Full Range

Our first plot shows our system, the top gated graphene configuration over the full range of top gate potentials. The variation in surface charge density as a function of dielectric constant increases as the top gate potential increases. In each of the experiments the potentials at the graphene interface and the

potential of the silicon wafer are held at zero. The top gate is held at predetermined potentials between 0eV and 10 eV.

The next three plots, Figures 4-6, show the charge density when the central interface is close to ground. The top gate is held at a different potential in each plot. We notice that splitting does occur when the system is operated in a configuration that grounds the V_Q and V_2. The graphene interface partially screens the electric field due to its low density of states so more unique charge configurations are possible than with high DOS materials. Looking farther into this configuration, we see that the system is more sensitive to changes in dielectric constant with increasing top gate potential. This result matches experimental findings. [2]

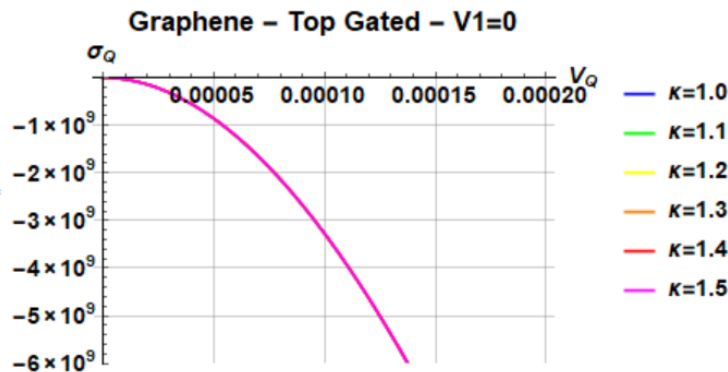

Figure 4: Top gated Graphene V1=0eV

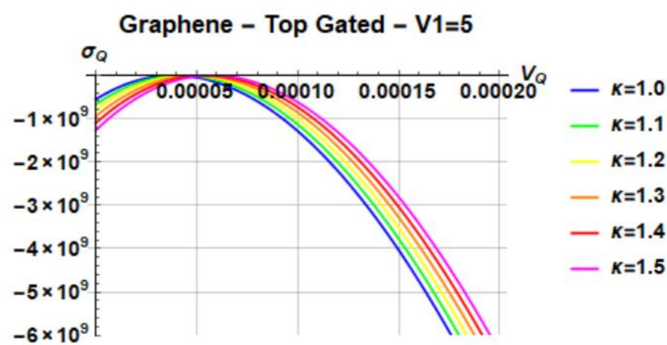

Figure 5: Top gated graphene V1=5eV

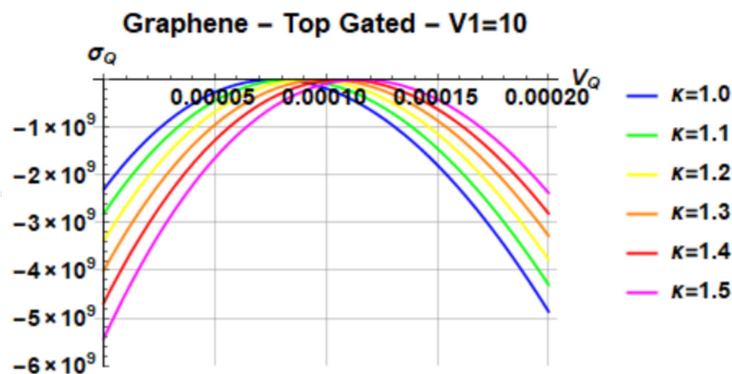

Figure 6: Top gated Graphene V1=10eV

We ground the central interface and the silicon wafer for follow up calculations. We generate plots that quantify the magnitude changes in surface charge density with changes in dielectric constant for various top gate voltages. The magnitude of changes in surface charge density increase with increasing top gate voltage as shown in Figure 7.

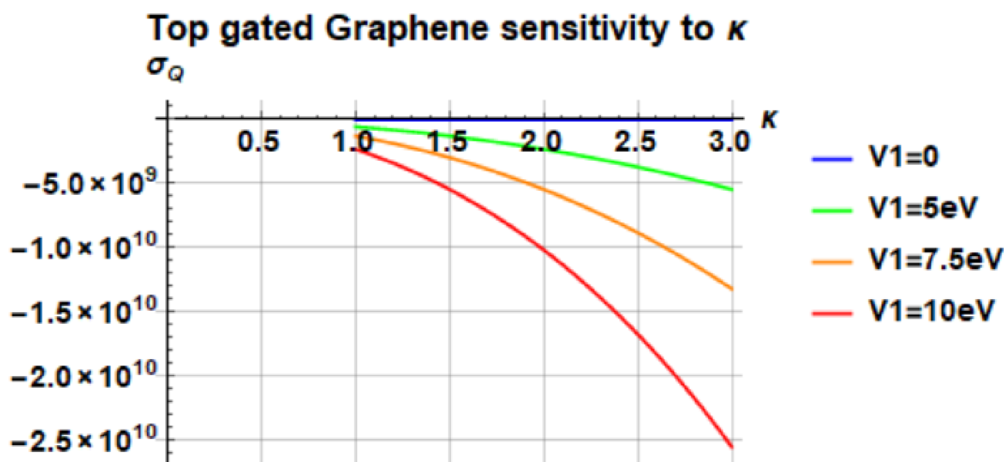

Figure 7: Sensitivity to changes in gas composition

Over a broader range of top gate potentials and dielectric constants we look to see the limits of this relation. Using the formulation obtained for a perfect metal system, equation (1.18), we see that the relations terminate once they reach the charge that would accumulate on a metallic interface under the same top gate conditions, this is shown in figure 8 below.

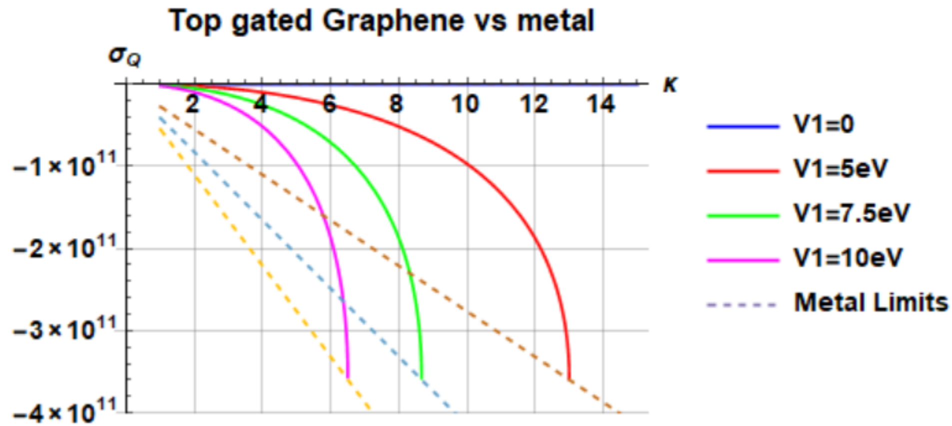

Figure 8: System Limits

With knowledge about the expected system behavior. Altering the gate voltage would allow the system to be tuned to have the greatest sensitivity across the band of expected dielectric constant change to yield the greatest sensitivity.

Expected system limits and operating ranges

According to Figure 8 charge densities do not exceed $-3.5 * 10^{11}\ C$ in the regions of expected operation. This means that the approximation used for equation (1.5) will still hold. Also, the relations all terminate once the charge density reaches the limit that matches the configuration where the central interface is a perfect conductor. It is expected that at dielectric constants above this point that the system behaves with the same properties as a perfect metallic surface.

2D-Quantum Well

The 2D quantum well does not share the same properties due to its constant density of states. This allows electrons to accumulate in a less restricted manner because there are no energy bands that are unavailable. In figure 9 below we can see that in this way the 2D quantum well exhibits other unique behavior.

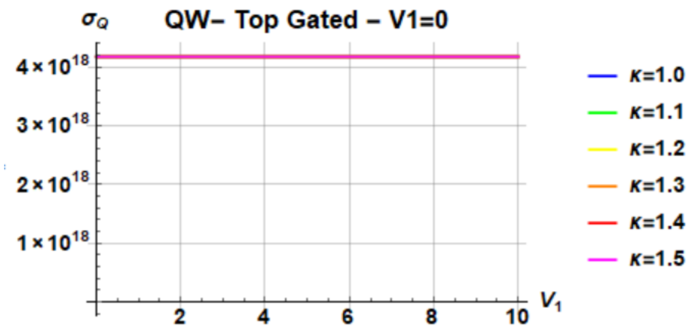

Figure 9: 2D Quantum Well

This difference shows that the properties of the system are unique to graphene due to its density of states. We can expect that carbon nanotubes [2] and other materials that have a low DOS near the fermi level would exhibit similar characteristics to the graphene system. Future work should introduce temperature effects and extend analysis to other materials such as bilayer graphene or single-walled carbon nanotubes.

Appendix A

Mathematica Commands

```
(* ====== System Constants ====== *)
C2= 0.000115104 ;(* F/m^2 *)
\[Epsilon]0=8.854187*10^-12;(* F/m *)
d0=0.01;(* m *)
m0=9.109*10^-31; (* kg *)
vf=8*10^5; (* m/s *)
ele=1.602176*10^-19; (* C *)
dsio=300*10^-9 ;(* m *)
ksio=3.9;
V0=0.001;(* eV *)
CQ=0.669251;(* F/m^2 *)
(* ====== Controlled variables ====== *)
C0=\[Epsilon]0/d0;(* F/m^2 *)
\[Kappa]1=1;
\[Kappa]2=1.1;
\[Kappa]3=1.2;
\[Kappa]4=1.3;
\[Kappa]5=1.4;
\[Kappa]6=1.5;
\[Kappa]range=15;
V10=0; (* eV *)
V11=5; (* eV *)
V12=7.5;(* eV *)
V13=10;(* eV *)
V14=20;(* eV *)
range=0.0002; (* eV *)
range1=10;(* eV *)

(* ====== Formulations ====== *)
\[Sigma]QGTG[\[Kappa]_,VQ_,V1_]:=((-C2*V0)/(2*ele))*(-
(((\[Kappa]*C0)+C2)/C2)+Sqrt[(((\[Kappa]*C0)+C2)/C2)^2+(((\[Kappa]*C0)+C2)/C2*(2*VQ)/
V0)-((2*(\[Kappa]*C0)*V1)/(C2*V0))])^2;
\[Sigma]QWTG[\[Kappa]_,VQ_,V1_]:=(-CQ/ele)*(VQ-
(((\[Kappa]*C0)*V1)+(CQ+VQ))/((\[Kappa]*C0)+C2+CQ));
\[Sigma]QGNG[\[Kappa]_,VQ_,V1_]:=(-((C2*V0)/(2*ele)))*(-1+Sqrt[(VQ/V0+1)^2-
(VQ/V0)^2]) ^2;
\[Sigma]QWNG[\[Kappa]_,VQ_,V1_]:=-VQ/ele*(1/CQ+1/C2)^-1;
\[Sigma]QMETAL[\[Kappa]_,VQ_,V1_]:=-((((\[Kappa]*C0)*V1)-
((C2+(\[Kappa]*C0))*VQ))/ele);

(* ===== Graphene Top Gated  ===== *)
```

```
Plot[{\[Sigma]QGTG[\[Kappa]1,0,V1],\[Sigma]QGTG[\[Kappa]2,0,V1],\[Sigma]QGTG[\[Kappa]3,0,V1],\[Sigma]QGTG[\[Kappa]4,0,V1],\[Sigma]QGTG[\[Kappa]5,0,V1],\[Sigma]QGTG[\[Kappa]6,0,V1]},{V1,0,10},GridLines ->Automatic,AxesLabel->{"Subscript[V, 1]","Subscript[\[Sigma], Q]"} ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Green,Yellow,Orange,Red,Magenta},PlotLabel->"Graphene - Top Gated - V1=0",PlotLegends->{"\[Kappa]=1.0","\[Kappa]=1.1","\[Kappa]=1.2","\[Kappa]=1.3","\[Kappa]=1.4","\[Kappa]=1.5"},PlotRange->{-6*10^9,0}]

Plot[{\[Sigma]QWTG[\[Kappa]1,0,V1],\[Sigma]QWTG[\[Kappa]2,0,V1],\[Sigma]QWTG[\[Kappa]3,0,V1],\[Sigma]QWTG[\[Kappa]4,0,V1],\[Sigma]QWTG[\[Kappa]5,0,V1],\[Sigma]QWTG[\[Kappa]6,0,V1]},{V1,0,10},GridLines ->Automatic,AxesLabel->{"Subscript[V, 1]","Subscript[\[Sigma], Q]"} ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Green,Yellow,Orange,Red,Magenta},PlotLabel->"QW- Top Gated - V1=0",PlotLegends->{"\[Kappa]=1.0","\[Kappa]=1.1","\[Kappa]=1.2","\[Kappa]=1.3","\[Kappa]=1.4","\[Kappa]=1.5"}]

(* ===== Graphene Top Gated V1=5eV ===== *)
Plot[{\[Sigma]QGTG[\[Kappa]1,VQ,V11],\[Sigma]QGTG[\[Kappa]2,VQ,V11],\[Sigma]QGTG[\[Kappa]3,VQ,V11],\[Sigma]QGTG[\[Kappa]4,VQ,V11],\[Sigma]QGTG[\[Kappa]5,VQ,V11],\[Sigma]QGTG[\[Kappa]6,VQ,V11]},{VQ,0,range},GridLines ->Automatic,AxesLabel->{"Subscript[V, Q]","Subscript[\[Sigma], Q]"} ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Green,Yellow,Orange,Red,Magenta},PlotLabel->"Graphene - Top Gated - V1=5",PlotLegends->{"\[Kappa]=1.0","\[Kappa]=1.1","\[Kappa]=1.2","\[Kappa]=1.3","\[Kappa]=1.4","\[Kappa]=1.5"},PlotRange->{-6*10^9,0}]
(* ===== Graphene Top Gated V1=10eV ===== *)
Plot[{\[Sigma]QGTG[\[Kappa]1,VQ,V13],\[Sigma]QGTG[\[Kappa]2,VQ,V13],\[Sigma]QGTG[\[Kappa]3,VQ,V13],\[Sigma]QGTG[\[Kappa]4,VQ,V13],\[Sigma]QGTG[\[Kappa]5,VQ,V13],\[Sigma]QGTG[\[Kappa]6,VQ,V13]},{VQ,0,range},GridLines ->Automatic,AxesLabel->{"Subscript[V, Q]","Subscript[\[Sigma], Q]"} ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Green,Yellow,Orange,Red,Magenta},PlotLabel->"Graphene - Top Gated - V1=10",PlotLegends->{"\[Kappa]=1.0","\[Kappa]=1.1","\[Kappa]=1.2","\[Kappa]=1.3","\[Kappa]=1.4","\[Kappa]=1.5"},PlotRange->{-6*10^9,0}]


(* ===\[Equal] Sensitivity as a function of Gate voltage ===\[Equal] *)
Plot[{\[Sigma]QGTG[\[Kappa],0,V10],\[Sigma]QGTG[\[Kappa],0,V11],\[Sigma]QGTG[\[Kappa],0,V12],\[Sigma]QGTG[\[Kappa],0,V13]},{\[Kappa],1,3},GridLines ->Automatic,AxesLabel->{"\[Kappa]","Subscript[\[Sigma], Q]"} ,AxesOrigin-
```

```
>{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Green,Orange,Red,Magenta},PlotLabel->"Top gated Graphene sensitivity to \[Kappa]",PlotLegends->{"V1=0","V1=5eV","V1=7.5eV","V1=10eV"}]
```

```
(* ===\[Equal] graphene vs metal surface *)
Plot[{\[Sigma]QGTG[\[Kappa],0,V10],\[Sigma]QGTG[\[Kappa],0,V11],\[Sigma]QGTG[\[Kappa],0,V12],\[Sigma]QGTG[\[Kappa],0,V13],\[Sigma]QMETAL[\[Kappa],0,V10],\[Sigma]QMETAL[\[Kappa],0,V11],\[Sigma]QMETAL[\[Kappa],0,V12],\[Sigma]QMETAL[\[Kappa],0,V13]},{\[Kappa],1,15},GridLines ->Automatic ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Red,Green,Magenta,Dashed,Dashed,Dashed,Dashed},PlotLabel->"Top gated Graphene vs metal",PlotLegends->{"V1=0","V1=5eV","V1=7.5eV","V1=10eV","Metal Limits"},FrameTicks->All,AxesLabel->{"\[Kappa]","Subscript[\[Sigma], Q]"},PlotRange->{-4*10^11,0}]
```

```
(* ===\[Equal] Quantum Well vs metal surface *)
Plot[{\[Sigma]QWTG[\[Kappa],0,V10],\[Sigma]QWTG[\[Kappa],0,V11],\[Sigma]QWTG[\[Kappa],0,V12],\[Sigma]QWTG[\[Kappa],0,V13]},{\[Kappa],1,10},GridLines ->Automatic ,AxesOrigin->{0.,0},AxesStyle->Directive[Black,Bold],LabelStyle->Directive[Larger,Black,Bold],PlotStyle->{Blue,Red,Green,Magenta,Dashed,Dashed,Dashed,Dashed,Dashed},PlotLabel->"Top gated QW vs metal",PlotLegends->{"V1=0","V1=5eV","V1=7.5eV","V1=10eV","Metal Limits"},FrameTicks->All,AxesLabel->{"\[Kappa]","Subscript[\[Sigma], Q]"}]
```

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Education: **The Pennsylvania State University, University Park – Class of 2017**

Bachelor of Science in Mechanical Engineering, December 2017
Minor in Physics
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Dean's List: Fall 2013, Spring 2014, Spring 2015, Fall 2015, Spring 2016, Spring 2017

Experience: **Volvo Group Trucks – Combustion Hardware Co-op** **Fall 2016**

- Tested existing and prototype Exhaust After Treatment Systems (EATS) for diesel trucks
- Implemented improvements in data collection processes that reduced manual effort by about 75% and introduced automated data quality checks
- Created a MATLAB simulation of exhaust systems operating in extreme low temperatures. Thaw patterns of diesel exhaust fluid were assessed to determine theoretical times to meet operational standards. Resulted in significant cost savings by avoiding additional physical testing in remote locations.

Schreyer Honors Thesis – Graphene NOx Detector: **Fall 2015 – Fall 2017**

- Attempting to determine the quantum mechanism that causes a change of surface charge density on a graphene capacitor exposed to automotive emissions

Penn State Formula SAE Racing Team – Cooling Group: **Fall 2014 - Spring 2015**

- Designed and tested cooling systems with the PSU Formula SAE Racing Team.
- Used heat transfer calculations and experimental data to resize and redesign the radiator.

Physics Research with Prof Jorge Sofo – Thin Slab Polarization: **Fall 2013 - Fall 2014**

- Worked with a Condensed Matter group in the Penn State Physics Department modeling the surface charge response of thin dielectric slabs to external charges.
- Created models of polarization in thin dielectric slabs and modeled the self-interaction of networks of discrete dipole systems.

Skills:

- Proficiency in MATLAB, Mathematica, ANSYS, SolidWorks, CREO and Autodesk inventor
- Machining and power tool certification for PSU Learning Factory

Leadership: **Treasurer & Climbing/Mountaineering Chair of Penn State Outing Club** **Fall 2015 – Spring 2017**

- Managing club finances and reimbursing trip expenses
- Planning and leading backpacking, climbing, and mountaineering trips
- Ice climbing on Gothics Peak ADK, backpacking long distance trails across the east coast, whitewater kayaking on local rivers, rock climbing and bouldering at local crags.

Eagle Scout Rank **Earned Spring 2011**

- Planned and led a community service project of over 150 man-hours of work