Quantum Capacitance and Surface Charge of Germanene, Silicene, Blue Phosphorene, and Graphene Using First Principles Calculations

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Abstract: Supercapacitors have been the interest of many researchers because of their viability as storage devices and several materials are being examined to match their properties. This study aims to calculate the quantum capacitance and surface charge of graphene, germanene, silicene, and phosphorene as potential materials using computational methods such as spline interpolation and discrete numerical integration. The density of states (DOS) of the 2D materials were calculated using density functional theory (DFT) with a supercell size of 1x1. The DOS were fitted to a quadratic spline and integrated with respect to energy to solve for the quantum capacitance. Similarly, the quantum capacitance was fitted and numerically integrated with respect to the potential to solve for the surface charge for each material. The results show that germanene has the highest values for quantum capacitance and surface charge making it the most viable material for capacitors among the four materials. Silicene also showed higher values of quantum capacitance and surface charge as compared to graphene. On the other hand, phosphorene showed low values for quantum capacitance for lower potentials but exhibited an exponential increase around -0.8 V and 0.7 V. These results were further elucidated by taking the parabolic and exponential fit of the quantum capacitance and surface charge curves, respectively. The fitting confirmed that germanene and silicene have the highest quantum capacitance and surface charge values for the normal voltage range.

Key Words: density of states; germanene; graphene; silicene; phosphorene; quantum capacitance; numerical discrete integration

1. INTRODUCTION

Properties of materials such as conductivity, capacitance, ductility, and many others are all related to each other, and these relationships are quantified through equations. However, some of these equations are too complex to solve by hand. With that being said, computational methods could be employed to model the properties of a material using density functional theory (DFT). This study focuses on the field of renewable energy and energy storage, specifically supercapacitors.

Capacitors are energy storage devices that are made from two electrodes that are separated by a dielectric (Hussain, 2019). Supercapacitors are similar in structure, except for the presence of a separator in between the electrodes, and the

electrodes are soaked in electrolytes. This allows the supercapacitor to store energy through charge interactions and electrochemical reactions. Because of its properties, supercapacitors are now a staple in the field of energy storage.

Carbon-based electrodes, such as graphene, are commonly used for supercapacitors. Graphene is a 2D semiconducting material with a zero-bandgap energy(Hussain, 2019). Germanene, silicene, and phosphorene are also 2D materials that are arranged in hexes similar to graphene, and the density of states (DOS) of these systems were investigated by different studies for similar functionality (Zhan, 2015; Zhou, 2021).

Aside from DOS, quantum capacitance and surface charge are also essential determining factors for a material to be considered a viable material for a supercapacitor. The quantum capacitance of graphene (Zhan, 2015), and germanene (Zhou, 2021) were initially investigated and these results would serve as a reference to our findings.

The main objective of the study is to compare the quantum capacitance and surface charge values of graphene, phosphorene, silicene, and germanene with the aim of determining the best material as a capacitive storage device. This investigation is based on density functional theory and other computational methods in the field of material science. To achieve the said objectives, we focused on the following properties, namely, density of states, quantum capacitance and surface charge.

1.1 Density of States (DOS)

The density of states in material science refers to the "energy level of the electrons, phonons, photons in a solid crystal" (Marchiori, 2017). It quantifies "how packed the states of a particular particle are in energy levels" (Marchiori, 2017). In applying such mathematical functions one can determine the number of electrons for each energy level per unit volume which in turn is proportional to the electrical conductivity of solid material (Jr. & Rethwisch, 2013). These densities of allowed states are useful in determining the concentrations of electrons and holes which will, in turn, give an approximation for the electrical conductivity of the material.

1.2 Quantum Capacitance and Charge

Quantum capacitance is one of the components of the total capacitance which quantifies the efficiency of a capacitor, the other component is electric double-layer capacitance. Their relationship is quantified through this equation:

$$C_{total} = \frac{1}{C_Q} + \frac{1}{C_{EDL}} \quad \text{(Eq. 1)}$$

where

C_Q = Quantum capacitance

C_{EDL} = Electric double-layer capacitance

Metal capacitors draw their capacitance from electric double-layer capacitance. However, recent experiments show that materials that have lower occupied states in the Fermi level such as semiconductors are more reliant on quantum capacitance. This shows the quantum capacitance of a material is dependent on its DOS. (Zhang et.al, 2015). The formula for quantum capacitance is given in Eq. 2. Once quantum capacitance has been determined, the surface charge Q can then be calculated using Eq. 3 (Zhou et.al, 2021). The quantum capacitance and total surface charge were plotted as a function of the external potential. The material that exhibits higher quantum capacitance values would be the most viable material for supercapacitor electrodes.

$$C_Q = \frac{e^2}{4kT} \int_{-\infty}^{+\infty} D(E) sech^2(\frac{E - \varphi}{2kT}) dE \quad \text{(Eq. 2)}$$

where:

$D(E)$ = Density of states

e = charge of the electron

= Applied potential

T = 300 K, Room temperature

k = Boltzmann's constant

$$Q(\varphi) = \int_0^\varphi C_Q(\varphi) d\varphi \quad \text{(Eq. 3)}$$

where:

$C_Q(\varphi)$ = Quantum Capacitance

φ = Applied potential

2. METHODOLOGY

2.1 Density Functional Theory

Density functional theory (DFT) was employed to solve for the density of states using Quantum Espresso (Giannozzi et al., 2009, 2017). The exchange-correlation functional and the van der Waals correction were obtained using Perdew-Burke-Ernzerhof and the Grimme method, respectively. All materials were modelled using 1x1 supercell with a

vacuum size of 20Å as shown in Figure 1. The 1x1 supercell size is sufficient to calculate the quantum capacitance and surface charge based on the study of Paz et al. (2022). A 33x33x1 k-point gamma-centered sampling and cut-off energy was set to 550 eV.
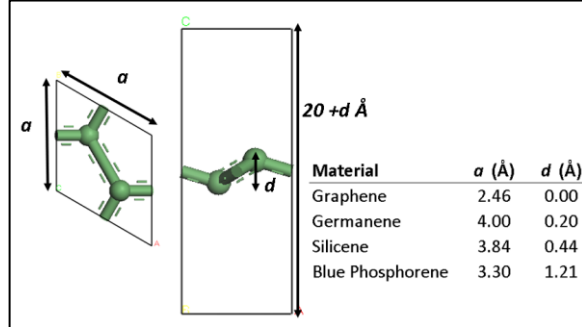

Figure 1. Unit Cell

2.2 Computational Method

The DOS, quantum capacitance. and surface charge functions were constructed out of the discrete data set with the use of spline interpolation. Splines, which were the separate lines bounded by two data points are expressed as quadratic polynomials. These quadratic polynomial functions will represent D(E), $C_q(\varphi)$, and $Q(\varphi)$ found in *Eq. 2* and *Eq. 3*. Numerical discrete integration was then employed to solve the equations.

2.3 Polynomial and Exponential Fitting

A parabolic function was fitted onto the quantum capacitance curves to accurately compare the quantum capacitance values of graphene, silicene, phosphorene and germanene. The parabolic function as

$$f(x) = a(x - h)^2 + k \qquad \text{(Eq. 4)}$$

where $\boldsymbol{a}$ represents the width of the parabola. The greater the value of $\boldsymbol{a}$, the narrower the width of the parabola. The $\boldsymbol{h}$ and $\boldsymbol{k}$ pertain to the vertices of the parabola.

The surface charge curves were plotted using an exponential fit. The exponential function used has two terms as shown below:

$$f(x) = ae^{bx} - ce^{-dx} \qquad \text{(Eq. 5)}$$

The two terms in Eq. 5 have a set of coefficients $\boldsymbol{a}$ and $\boldsymbol{b}$, and another with $\boldsymbol{c}$ and $\boldsymbol{d}$. The first term represents curves that are growing while the second term represents curves that are decaying as exhibited by the signs on the exponents. The rate at which a curve grows or decays is described by the $\boldsymbol{b}$ and $\boldsymbol{d}$ coefficients, respectively. A higher value of $\boldsymbol{b}$ ($\boldsymbol{d}$)

means a faster growth (decaying) rate. The other coefficients $\boldsymbol{a}$ and $\boldsymbol{c}$ represent the point in the x-axis to which the growth rate ($\boldsymbol{a}$) starts and the decay rate ($\boldsymbol{c}$) ends. A larger $\boldsymbol{a}$ ($\boldsymbol{c}$) coefficient means that the growth (decay) rate starts or ends at a point very near 0 while a lower value means they happen at a farther point.

3. RESULTS AND DISCUSSION

3.1 Fitting of the density of states to quadratic splines

The DOS functions D(E) were generated using spline interpolation. The original data points were then recovered to prove the function's precision. Figure 2 shows the DOS of graphene and silicene, and germanene and blue phosphorene, respectively. The x-axis represents the energy of the occupied states in eV, and the y-axis represents the number of occupied states per eV. Phosphorene and germanene have higher DOS values than graphene and silicene. Among the four materials, phosphorene has the highest band gap. This could lead to lower quantum capacitance values at lower voltage values.
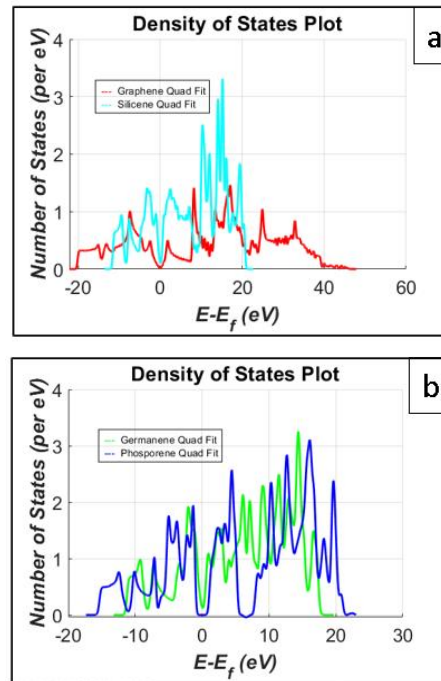

Fig. 2. DOS of (a) graphene and silicene (b) germanene and blue phosphorene

3.2 Solving for the quantum capacitance

With the D(E) solved, we proceeded with the calculations of quantum capacitance of germanene, silicene, blue phosphorene, and graphene. The

potential values inside the integral ran from -1 V to 1 V with 30 data points and then numerically integrated each one over the entire DOS function. The graph of quantum capacitance as a function of potential is shown in Fig. 3. The x-axis represents the potential in volts, while the y-axis represents the quantum capacitance in microfarads per square centimeter.
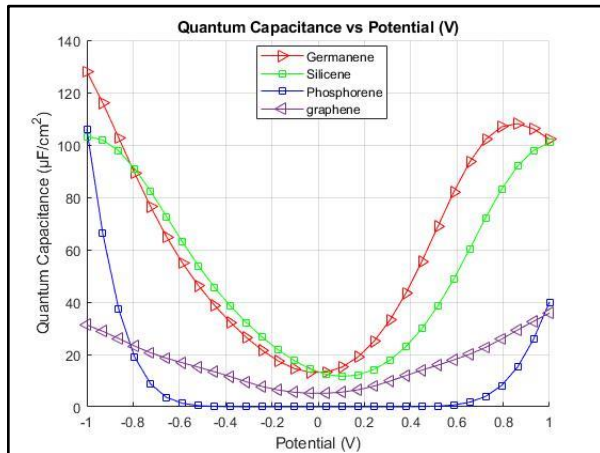

Fig. 3. The graph of quantum capacitance vs potential

The results show that silicene and germanene show superior quantum capacitance values, especially at lower values of applied potential. Graphene has a higher value of quantum capacitance at lower potentials but fails in comparison to germanene and silicene. Phosphorene has low values of quantum capacitance at low potential values, but experienced exponential increases around -0.7 V and 0.8 V surpassing the quantum capacitance of graphene. Germanene has the highest values among all the materials at -1 V and 1 V, making it the most viable material for a nanomaterial capacitor based on quantum capacitance. A study regarding the quantum capacitance of germanene exhibited higher values (Zhou, 2021). They reported that using a 5x5 unit cell, the highest values were about 81 $\mu F/cm^2$ and 100 $\mu F/cm^2$. Our results show that at -0.6 V and 0.6 eV, the quantum capacitance values are 60 $\mu F/cm^2$ and 81 $\mu F/cm^2$, respectively. Overall, the behavior of the graph is consistent. The difference in the calculated quantum capacitance could be attributed to the different parameters used in the study.

3.3 Solving for the surface charge

The resulting quantum capacitance from the previous calculation provided a discrete data set to be used in determining the surface charge. A quantum capacitance function $C_Q(\varphi)$ was constructed using spline interpolation. Eq. 3 was solved using numerical

discrete integration once again. The integration ran from 0 to all the potential values from -1 V to 1 V. The graph of the surface charge as a function of potential is shown in Fig. 4. The x-axis represents the potential in voltage, while the y-axis represents the surface charge in microcoulombs per square centimeter.
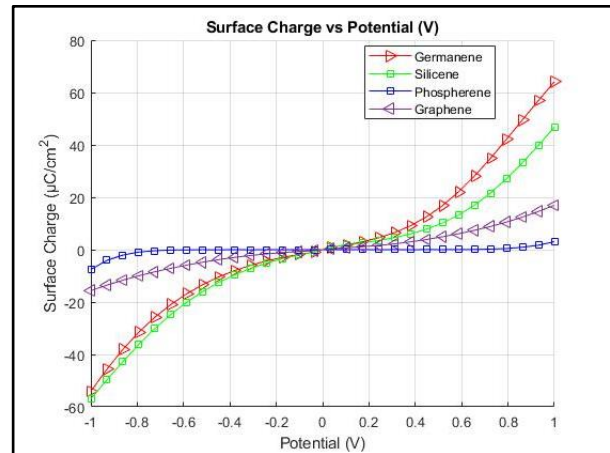

Fig. 4. Surface charge as a function of potential of all materials

As expected, the material that showed the highest values for quantum capacitance also had the highest values of surface charge. Germanene and silicene once again showed superior values for surface charge relative to the other two materials. Although phosphorene surpassed graphene in quantum capacitance values, its surface charge failed to surpass graphene at -1 V to 1 V. Germanene holds the highest surface charge value at 1 V (64.12 $\mu C/cm^2$ > 46.74 $\mu C/cm^2$) and silicene slightly edged out germanene at -1 V (56.89 $\mu C/cm^2$ > 54.07 $\mu C/cm^2$). With this result, germanene is the most viable material for capacitors based on its surface charge values.

3.4 Fitting quantum capacitance curves.

Table 1 lists the coefficients of the fitting quantum capacitance functions of the different materials. Due to the non-parabolic curves of germanene and silicene, the fit was run through from -0.8 V to 0.8 V only. Furthermore, phosphorene exhibited exponential behavior as seen in Fig. 3 and so an exponential fit was applied.

Looking at the parameters of the parabolic fit for negative potentials, germanene and silicene together dominate graphene with their high coefficients attesting to the greater slope of their curves in contrast to graphene's *a* value. Comparing germanene and silicene, silicene's *a* value is slightly larger than germanene. For negative potentials,

silicene has slightly higher quantum capacitance values than germanene.

Table. 1. Parameters of Polynomial and Exponential fitting of QC curves

Material	Negative Side	Positive Side
Graphene	a : 14.7330	a : 15.60483
Germanene	a : 35.02569	a : 50.4836
Silicene	a : 42.7656	a : 27.0598
Blue Phosphorene	c : 0.03246 d : -8.111	a : 0.01981 b : 7.633

Focusing on the exponential fit for phosphorene for negative potentials, a low a value was recorded meaning the growth rate happens at a point far from 0. With this in mind, even if the decay rate of phosphorene is very large, that "spike" in quantum capacitance values won't be seen until a high potential (at around ± 0.7 V) is applied as seen in Fig. 3. Hence, for negative low potentials, germanene has the highest quantum capacitance.

For positive potential, we see again germanene and silicene dominate graphene in terms of the coefficient. And this time germanene now has the higher a value representing its greater slope against silicene. Looking at the exponential fit of phosphorene, we see the same trend where the a value is very small attesting to phosphorene's "late" growth spike as it happens at a larger potential point. Despite its large growth rate of 7.63, it still falls behind germanene and silicene for potentials between -0.8 V to 0.8 V. So for positive potentials, germanene still has the highest quantum capacitance.

3.5 Fitting surface charge to an exponential equation.

For positive potentials, just looking at the exponent coefficient b in Table 2, it is easy to mistake phosphorene and graphene to have the highest surface charge values due to their b values being so high, corresponding to a very steep slope. But a look at their a values suggests that a steep slope occurs at a potential value far from zero. In fact, the a value of germanene and silicene are many times larger than that of blue phosphorene and graphene. This means that the growth point occurs at a potential value very near zero. With these observations, we can confirm that germanene and silicene have high surface charge values for small potential values confirming the data in Fig. 4.

For negative potentials, the same can be observed in the coefficients. The c values of graphene and phosphorene are very small suggesting that their decay points occur very far away from the center. In contrast, the c values of germanene and silicene are much larger than the other two suggesting that their decay points occur at a much smaller potential value. All these observations point to germanene and silicene having the highest negative surface charge value for small potential values. Again, these confirm the results shown in Fig.4.

Table. 2 Parameters of Exponential fitting of SC curve

Material	Positive Side	Negative Side
Graphene	a = 0.3678 b = 4.234	c = -0.00674 d = -8.701
Germanene	a = 4.417 b = 2.847	c = -5.934 d = -1.833
Blue Phosphorene	a = 0.01279 b = 5.349	c = -0.000501 d = -10.22
Silicene	a = 3.159 b = 1.831	c = -0.2864 d = -6.041

While phosphorene and graphene have lower surface charge values at low potential ranges, at some point they can overtake the surface charge values of germanene and silicene due to their very high b and d values, which might happen at larger potential points as their low a and c values suggest.

4. CONCLUSIONS

Germanium has the highest atomic number among the four materials, meaning it has more occupied states, this leads to a higher quantum capacitance value. Phosphorene has a higher atomic number than silicene, but it has a lower quantum capacitance value for lower voltages. This is due to its lack of occupied states around the Fermi level. If the chosen potential range for this study had been wider, it's highly likely that the values for the quantum capacitance of phosphorene will exceed that of silicene given the current trend.

In terms of surface charge, the material that has the highest values is the one that has consistently high values for quantum capacitance. Germanene showed the highest values for surface charge and quantum capacitance and therefore is the best material for a capacitor. The second best is silicene. In terms of application, germanene would do better as an anode material because of its higher quantum

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capacitance at +0.6 V (81 µF/cm²) as compared to -0.6 V (60 µF/cm²) which is a typical voltage range for capacitors. This implies that germanene and silicene could be better energy storage materials than graphene, assuming that the materials are structurally stable. Blue phosphorene exhibited low values for the same voltage range, so it is not a viable material for an electrode around the typical voltage range. Graphene and silicene have symmetry and relatively high quantum capacitance values for the typical voltage range, meaning that they can be used to fabricate electrodes and be deployed in AC systems. The parametric results from the fitting confirmed that germanene and silicene have the highest values of quantum capacitance and surface charge values for low values of potential.

This conclusion was reached based solely on quantum capacitance and surface charge of materials with one fundamental element. It is recommended that future investigations can include binding energies to determine the structural stability of the material, and the effects of different supercell sizes to minimize discrepancies in quantum capacitance. Adding impurities via doping or introducing vacancies could also enhance the properties of these materials for supercapacitors. As blue phosphorene eclipses graphene in terms of quantum capacitance at higher voltages, increasing the voltage range could also increase its quantum capacitance and may make blue phosphorene more viable as a supercapacitor material.

5. ACKNOWLEDGMENTS

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