

A Review of Graphene Technology and its Applications for Electronic Devices

Ashok K. Sood, Isaac Lund and Yash R. Puri

Magnolia Optical Technologies, Inc. 52-B Cummings Park, Suite 314, Woburn, MA

Nibir K. Dhar

*Night Vision & Electronics Sensors Directorate, 10221 Burbeck RoadFort
Belvoir, Virginia 22060*

Jay Lewis

DARPA/MTO, 675 North Randolph Street, Arlington, VA 22203

Madan Dubey, Priyalal Wijewarnasuriya and Eugene Zakar

Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783

Harry Efstathiadis and Pradeep Haldar

College of Nanoscale Science and Engineering (CNSE), Albany, NY 12222

Michael Fritze

*Senior Fellow, Potomac Institute for Policy Studies, 901 N. Stuart Street,
Arlington, VA 22203*

Abstract:

Graphene has amazing abilities due to its unique band structure characteristics defining its enhanced electrical capabilities for a material with the highest characteristic mobility known to exist at room temperature. The high mobility of graphene occurs due to electron delocalization and weak electron phonon interaction making graphene an ideal material for electrical applications requiring high mobility and fast response times. In this review we are going to focus on the benefits along with some of the limitations with using graphene

in infrared (IR) devices, electro-optic (EO) devices, and field effect transistors (FET) for radio frequency (RF) applications.

Keywords: Graphene, Infrared detectors, radio frequency (RF), graphene field effect transistors (GFET), electro-optics (EO)

1. INTRODUCTION

Graphene is a two dimensional analogue of graphite (carbon) material that has exceptional characteristics derived from the bonding characteristics of the C bonding sheets. C has 4 valence electrons with 3 of these electrons participating in σ -bonding with its closest neighbors creating a honeycomb structure.¹The 4th of these valence electrons occupy an orbital perpendicular to the one dimensional sheet creating *delocalized* π -bonding as shown in Figure 1 that allows for the creation of a 2 dimensional electron gas (2DEG) with high mobility within the sheets.^{1,2}

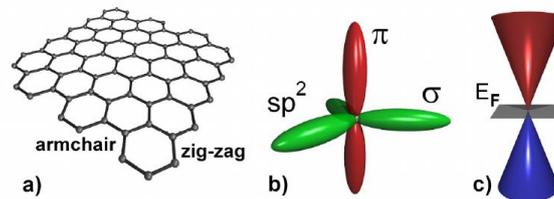


Fig 1. Graphene geometry as well as bonding and related band diagram [1].

For electronic applications the structure of graphene creates a semi-metal with a direct Fermi-Dirac band structure as shown in Figure 1c having charge carriers interacting as Dirac Fermions (with zero-effective mass) that allows for high mobility up to 15000-200000 cm^2/Vs and ballistic transport up to a micron at room temperature.³The Fermi-Dirac cone as shown in Figure 1c however is modified either by the addition of multiple layers as shown in Figure 2iii), the addition of two layers and doping from contaminant particles (metal or polymer particles lying on the surface shown in 2iv) or contaminants doping a single layer as shown in Figure 2ii).⁴ The doping mechanisms operate by breaking graphene's periodicity moving the Fermi level either up or down the Dirac cone causing a rounding of the k states resulting in a decrease in the mobility of the current carriers (electron or holes).⁴

Graphene's provides an interesting solution for certain electronic applications such as the channel in a field effect transistor, since it can be doped electrostatically and has extremely high mobility allowing for quick response (operating frequency).⁵ The replacement of Si by graphene for logic gates might be considered due to the high potential switching speed, however the absence of a band gap means that a relatively large bandgap would have to be induced through a variety of doping or other symmetry breaking mechanisms.⁵ The absence of a bandgap in graphene limits

voltage and power gains that is achieved through operation of a device in the saturation regime, along with having a low Ion/Ioff ratio.⁵To overcome this several doping strategies as shown in Figure 3 have been proposed and tested including: electrostatic doping, chemical doping, and stress or geometry restricted doping by breaking the graphene periodicity (and band properties).⁵We are only going to touch on some issues encompassed within doping graphene for device fabrication since a thorough review of graphene doping techniques can be found in reference 5.

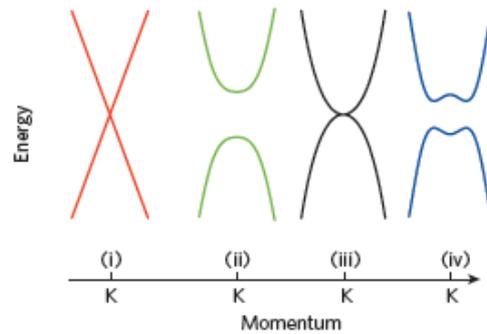


Fig. 2. Diagram showing the Dirac Fermi cone in i), the modification of the k states by chemical or geometry restrictive doping in ii), the modification of the k states by bilayer graphene shown in iii), and finally the modification of the k states in doped bilayer graphene as shown in iv) [4].

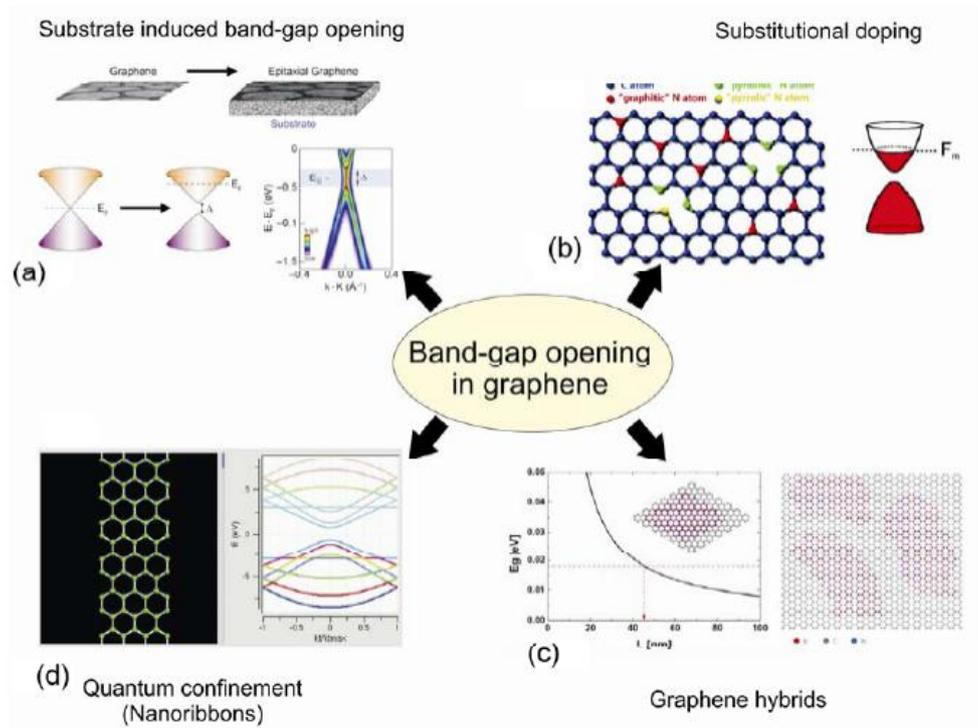


Fig. 3. Diagram showing multiple mechanisms for inducing a band gap in graphene [5]

The induction of a band gap has been attempted by multiple groups creating transistors with low on/off ratio and high mobility with a tradeoff between on/off ratio and mobility possible through graphene functionalization techniques.¹ This makes graphene more desirable for applications that require fast response times but not necessarily big on/off ratios such as radio-frequency (RF) electronics and infra-red (IR) detectors.

2. DEVICE FABRICATION CHALLENGES WHILE UTILIZING GRAPHENE

Graphene is an inherently thin, self-contained sheet with no real interface layer. Graphene relies upon its symmetrical properties for its amazing electrical characteristics thus there are several issues with device integration that should be quickly reviewed.

2.1 Oxide trapped states

Since graphene is a self-contained sheet it should be noted that process integration with oxide dielectrics as shown in Figure 4 can be difficult due to trapped impurities at the interface in terms of creating floating gates for voltage controlled variable gate transistors.⁶ It should also be noted that the introduction of trap centers and doping sites through contamination will degrade the continuity of the 2DEG at the trap or dopant site causing electron and hole pooling to occur.^{4,7}

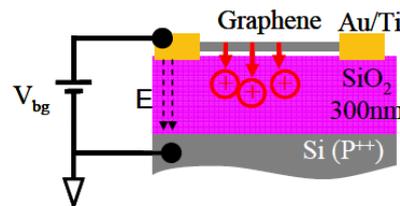


Fig.4. Image showing trapped charges at graphene oxide interfaces [6]

Multiple groups have been experimenting with different types of oxides with either an aluminum deposition and oxidation or a nitrogen dioxide surface pretreatment prior to a hafnium oxide, silicon dioxide, or aluminum oxide deposition.⁷ The dielectric which seems to work the best (but has not yet been implemented in a complementary metal-oxide semiconductor (CMOS) fabrication process due to lack of reliable deposition and patterning techniques) is another 2D self-contained dielectric BN with which graphene has shown mobilities of $140,000\text{cm}^2/\text{Vs}$ which is very close to completely suspended graphene grown from a SiC step edge, demonstrating low interaction and good isolation between the two substrates.⁷

2.2 Graphene metal contacts

Graphene is a self-contained electronic sheets showing no classical band bending interactions when coupled to a metallic contact as shown in Figure 5. This creates an

abrupt transition in the vacuum level creating a large potential buildup, charge buildup at the band edges, and large contact resistances.⁸

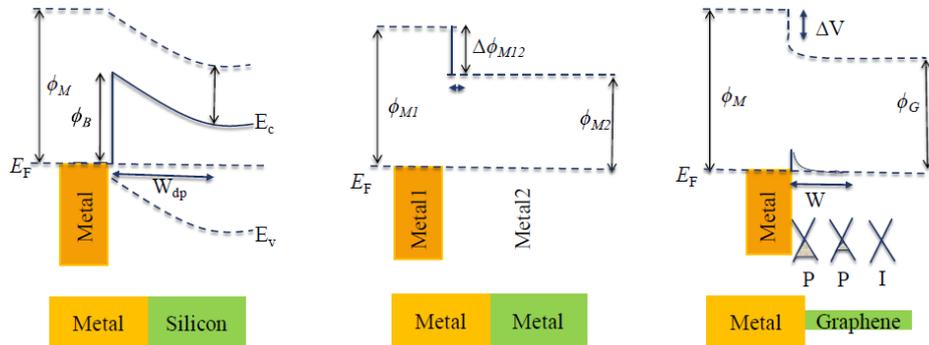


Fig. 5. Classical band diagrams for a metal-silicon interface, a metal-metal interface, and a metal graphene interface.

In conjunction to this challenge is the relative inertness of a graphene sheet making good electrical contacts only occur at defect sites and grain edges.⁸ This creates a situation at the graphene/metal contact interface where the bulk of the contact sits over the graphene electrostatically doping it with only a small amount of direct bonding between the metal contact and the graphene interface.⁸ The lack of adhesive qualities between the graphene metal interface along with finding a metal with the correct Fermi level for minimizing Schottky formation and contact resistant creates a search for the correct metal stack for the contact.⁸ To achieve this goal a double or triple metal stack is commonly used with an oxygen scavenger interfacial the graphene (normally Ti), followed by one or a couple of Fermi level contacts (Au, Pd, Ni).⁸ The metallic doping effect however can be utilized for some interesting devices such as one using asymmetric contacts to create an internal electric field making an IR detector through the photothermoelectric effect, or using large gap superconducting contacts to confine electrons and holes in a graphene sheet to enhance bolometric response.^{9,10}

2.3 Twist angle and layer isolation

For the formation of a bandgap in graphene electrostatic gating can be accomplished by utilizing layered materials with different opposing bandgaps with the higher bandgap being the acceptor and the lower being the donor as shown in Figure 6.⁵ The layered electrostatic doping is accomplished through utilizing bilayer graphene and creating an electric potential through the graphene sheet by sandwiching it between two layered materials with different bandgaps.¹¹

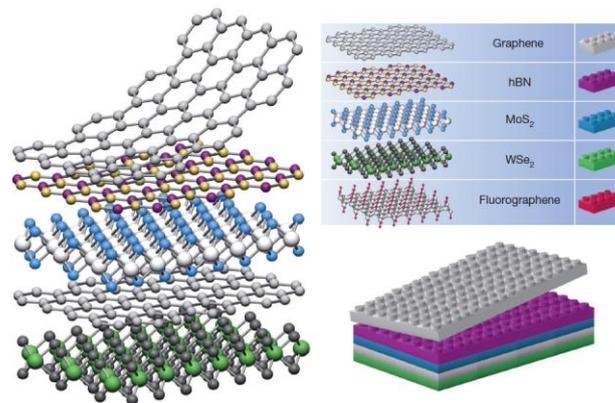


Fig.6. Diagram showing the stacking of multiple Van der Waals materials in order to create unique and tunable electrical properties [12]

The use of 2D stacked devices is interesting but it should be remembered that many of these layers have not been shown to be readily deposited on top of the other requiring transfer techniques that can induce defects, transfer contaminants, and have alignment issues between the lattices creating different properties across the lattice due to misalignment as shown in Figure 7.^{12, 13}

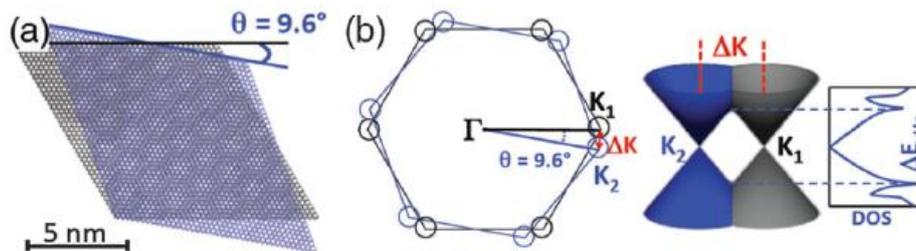


Fig.7. Image showing that the misalignment of 2D materials can electrically isolate the two sheets by separating the Dirac cones [14]

It has been shown that a twist angle between 2 graphene sheets above 2° electrically isolates the 2 graphene sheets from one another except at certain twist angles as shown in Figure 7.¹³ Most 2D materials have also been shown to have intrinsic doping due to vacancies and edge defects that create more problems for device integration.¹³

2.3 Chemical doping and environmental sensitivity

The chemical doping mechanism of graphene works by having the dopant bond either ionically through the breaking of a C-C bond or covalently to the delocalized p_z orbital.¹⁵ The covalent bonding of a dopant with graphene occurs through modification of the delocalized p_z orbitals to electrostatically hold an ad atom onto the surface with stoichiometry of the resulting *alloy* and strength of the bond being reliant upon the electronegativity of the dopant particle.¹⁵ Thus it has been shown that only fluorine

creates a stable covalent bond with graphene, where all other dopant elements have to bond ionically to graphene.¹

2.4 Geometry restriction

Geometry restricted doping of graphene works through reducing one dimension of the graphene sheet below the Bohr radius creating quantum confinement within the sheet and opening the band gap.^{3, 16} This has been shown to be accomplished through the patterning of graphene into ribbons with one dimension restricted to under 10nm thus opening a gap of 2.5-3.0eV in theory and .5eV experimentally.^{5, 16} Graphene nanoribbons has a large resistance created by scattering from line edge roughness.^{5, 16} The end terminations in graphene nanoribbons as shown in Figure 8, either “zig-zag” or “arm-chair” provide different conductivity values.^{5, 16, 17} The difference between end terminations coupled with the resistivity provided from scattering points in the line edge roughness provide a challenge towards integrating graphene nanoribbons into devices.^{5, 16, 17}

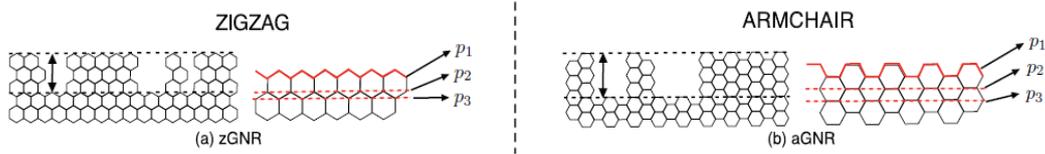


Fig. 8. A picture showing the difference between zig-zag and armchair graphene end terminations [17]

The induced line edge roughness produces many scattering defect reducing the lattice periodicity, obliterating the induced bandgap, and decreasing the mobility ultimately limiting the usefulness of graphene nanoribbon formation.^{4, 5}

2.5 Current saturation and voltage gain

Saturation current is normally attained through saturation of charge carrier velocity which for graphene the high mobility layer the velocity saturation is unattainable without going to extremely high source drain voltage.⁴ Current saturation in graphene devices gated devices is obtained through current pinch off effects under the gate as shown in Figure 9 which can be created in graphene through band gap formation.⁴

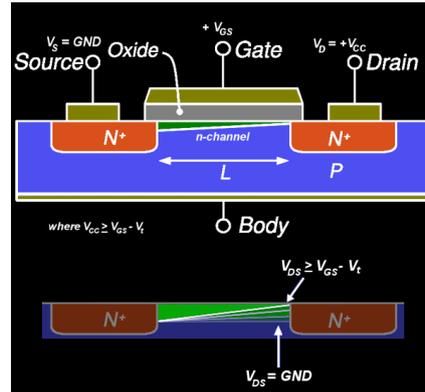


Fig. 9. Diagram showing current pinchoff in a Si MOSFET

2.6 Short Channel effects

Graphene normally has a grain size of several to tens of microns with the desire to use a single grain as the channel material to avoid scattering at grain edges.⁴This reduces that channel size normally used and creates many of the short channel effects commonly seen in MOSFETS such as drain induced barrier lowering, surface scattering, velocity saturation, impact ionization, and hot-electron effects.⁴Specifically for graphene the drain induced barrier lowering, surface scattering, and hot electron effects are all in play. The surface scattering is due to the intrinsic susceptibility of graphene to surface contamination and scattering sites, while the hot electron and barrier lowering effects affect graphene due to the pinch off formation needed to have the large I_{on}/I_{off} ratio required for typical electronics applications and to create large enough voltage and power gains for RF applications.

2.7 FET design and gate coupling

To overcome some of the short channel issues and problems with graphene integration into common process flows, a wafer bonding type of integration has been suggested as shown in Figure 10.¹⁸This allows for the separation of the drain and gate contacts, which reduces coupling and alleviates some of the issues with drain induced barrier lowering.¹⁹

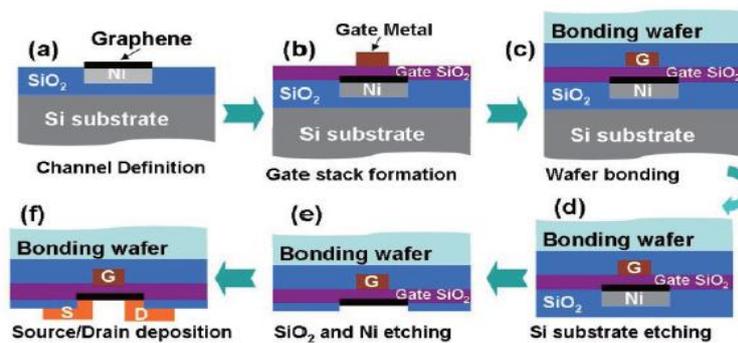


Fig. 10. Wafer bonding with subsequent source drain contact deposition [18]

The gate coupling is a significant issue with graphene FETs due to the large gate voltages needed to create sufficient barriers for high I_{on}/I_{off} ratios.¹⁹ The use of a high k thin gate oxide and opposing gate and source drain contact geometry allows for less gate coupling, and better gate control.¹⁹

Graphene devices have a very thin cross section where the active electric field can effect one another. It has been shown that by using tapered contacts as shown in Figure 11 the amount of source drain coupling is reduced due to electric field reduction.¹⁹ This is especially effective if utilizing a back gate design as shown later in Figure 10, or a large gate that could overlap the source and drain contacts on the opposing side of the devices channel.^{19, 20}

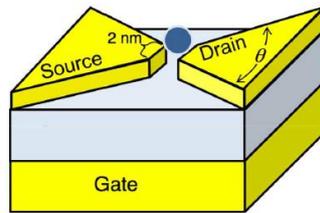


Fig. 11. Tapered contacts used on opposing sides of the gate to reduce [19]

3GRAPHENE FET AND RF ELECTRONIC PERFORMANCE

In order to create a device that allows for the opening of a bandgap required for current saturation and appropriate voltage and current gains several device geometries have been proposed.^{4, 20} The main mechanisms for increasing graphene performance in FETs is to increase the gate coupling with the graphene layer and to optimize the graphene dielectric interface to reduce scattering to make the conduction and valence states continuous.⁴

One possible device geometry shown in Figure 12 utilizes a bilayer graphene channel with a large backgate voltage to induce an electric field of 1.7V/nm that opens a bandgap in bilayer graphene of 80meV with the Mexican hat shape shown in Figure 2iv).^{4, 20} The bandgap creates a saturation current due to pinchoff at the drain contact resulting in a voltage gain of 35 which is relevant for RF electronics.

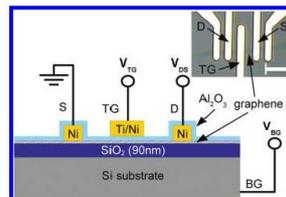


Fig. 12. Diagram of a bilayer graphene FET with back contact to create a pinchoff region and voltage gain [20]

This mechanism works much better for bilayer graphene than monolayer graphene as bilayer graphene more easily forms a pinchoff region. To demonstrate this, the amount of voltage gain in such a graphene FET is graphed as contour plots with voltage gain axis on the right hand side of the graph as shown in Figure 13.²⁰

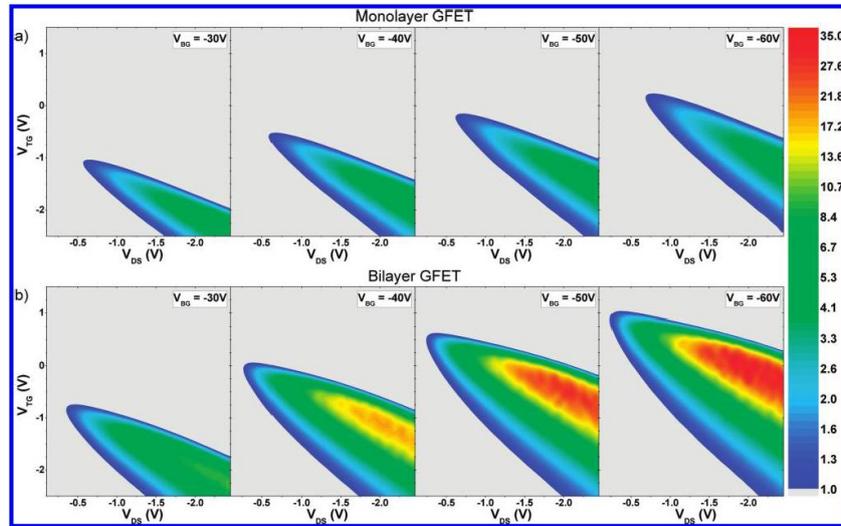


Fig. 13. Contour maps of voltage gain in a single layer and bilayer graphene channel with modification of back gate voltage [20]

Current designs for graphene FET's are shown in Figure 14, with the back gated design commonly used to overcome any doping in the graphene channel due to substrate, atmospheric, or dielectric effects.⁴ The back gate and top gate design are the most common since these allow for the shifting of the Dirac point to zero through an induced electric field and proper gate modulation.⁴

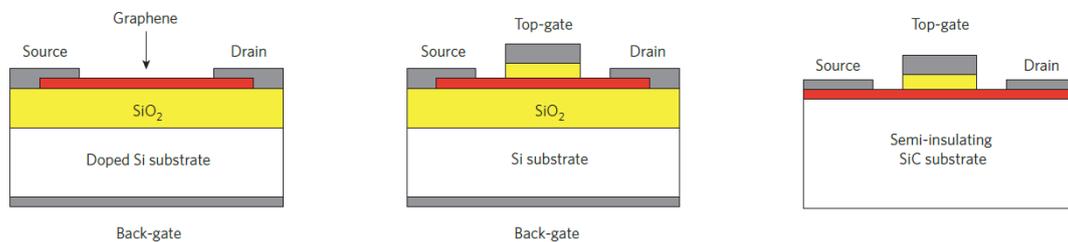


Fig. 14. Image showing the most common designs for GFETs [4]

Utilizing a the three terminal top gate design of CVD graphene grown on a SiC substrate one group was able to achieve a 350GHz cutoff frequency utilizing a channel length of 40nm as shown in Figure 15.²¹

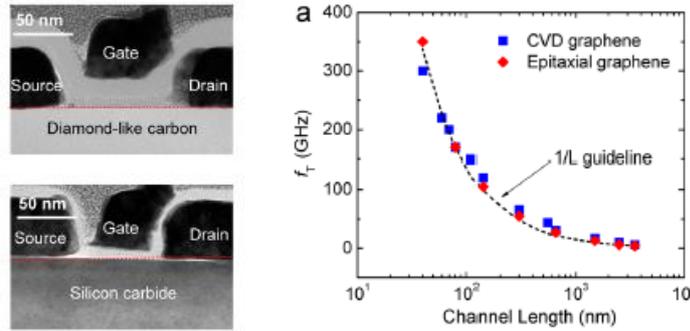


Fig. 15. Image showing the threshold frequency versus gate length for the device architectures shown on the left, the epitaxial graphene is on the SiC substrate, and the frequency shows a 1/L dependence [21].

This group showed that the threshold frequency has a 1/L dependence where L is the channel length of the graphene FET. This has been modeled and pushed to the limit with an understanding that graphene might be able to break the 1THz limit that In GaAs and SiGe HEMTs can't break.²² One group theoretically tuned all of the parasitic capacitances that would limit the graphene channel mobility, this includes removing Schottky interactions at the source and drain contacts, removal of any trapped states in the oxide, ignoring any electron/hole pooling effects, and having the gate voltage perfectly coupled to channel potential, would allow for a GFET that operates at 1.5THz.²² This GFET is optimized to have zero gain due to current saturation in the 50nm channel.²² By allowing for current saturation in the GFET a voltage gain can be engineered in the graphene channel however this would deteriorate the operating frequency of the GFET as shown in Figure 16.²²

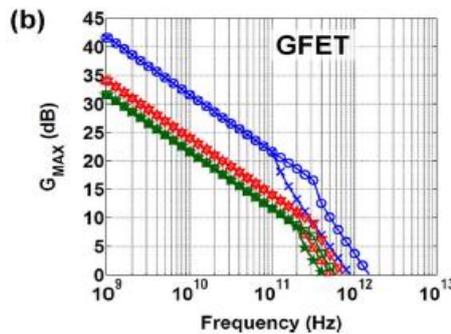


Fig. 16. An image showing the threshold frequency for each possible gain in a GFET for systems with different amount of tuning of parasitic resistance, the blue line has no parasitic resistance [22].

4. GRAPHENE USE IN ELECTRO-OPTICAL (EO) DEVICES

One of the interesting applications for graphene is its use in electro-optical devices and lasers. Graphene can absorb wavelengths from the visible to the mid IR with

wavelength modulation enabled through electrostatic gating.^{23, 24} The electrostatic gating interacts with light either by modulating the bandgap width up to a certain wavelength working as an absorption modulating element, or it modifies the graphene surface plasmon modes that interact with light.^{23, 24} The last example is how graphene was utilized for mode locking a laser.^{23, 24} The problem with utilizing graphene for pure optical devices is due to its inherent thinness only absorbing 2.3% of the incident light per monolayer.^{23, 24} This makes it more desirable to integrate graphene with other electro-optical components such as photonic cavities or plasmonic waveguides with an example shown in Figure 17.^{23, 24}

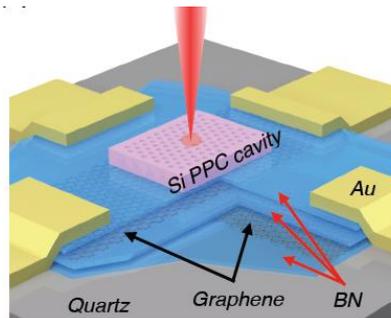


Fig. 17. Integration of a tunable graphene capacitor with an EO modulator [23]

The EO modulator pictured in Figure 17 was created through the coupling of Si plasmonic nanocavities to a tunable graphene capacitor made from stacked layers of graphene and BN dielectric film.²³ The top and bottom graphene layers are electrostatically doped differently from one another with varying voltages for optical modulation of absorbed light.²³ The modulator worked up to 1.2GHz frequency which was limited by the RC time constant of the capacitor.²³

Although on its own graphene is not practical for use as a waveguide or modulator it can be combined with already active materials to increase the performance of such devices.

5 GRAPHENE IR DETECTORS

Infrared (IR) detectors can be separated into two separate categories: either thermal-based IR detection or photon-based detection.²⁵ In thermal-based detectors, the incident IR radiation is absorbed raising the temperature of the material.²⁵ The raised temperature affects some temperature dependent property of the material; for pyrometers this is a change in electrical polarization, while for bolometers this is a change in materials resistance.²⁵ Another more recent study utilized the photothermoelectric effect in graphene to create a net electric field due to electron diffusion into dissimilar metal contacts.⁹ Photon-based detectors utilize band gap-based detection with the arriving photon being absorbed and utilized to promote electron hole pairs to create a photocurrent.²⁵ The photon-based detectors can be tuned to certain wavelengths by creating a quantum well structure.²⁵ Photon based IR absorbers are characterized by having fast absorption response but usually require

cooling due to thermal effects while thermal-based IR detectors have high responsivity over a large wavelength and can be utilized at room temperature but normally have slow absorption response.²⁵ This is where utilizing a graphene based sensing element is attractive due to the high mobility with little temperature sensitivity making it ideal for IR detectors.²

Several groups have attempted to integrate graphene into IR detectors. The groups have tried both photon and the thermal-based absorption methods.^{9, 26-28} For photon-based absorption methods the main focus has been the opening of a band gap through geometric modification.^{9, 26} One group utilized bilayer graphene to open a small band gap which is sensitive to thermalization requiring cooling to 5K for operation.²⁶

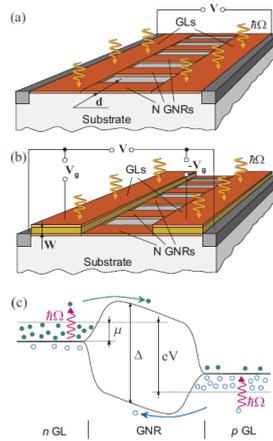


Fig.18. The utilization of graphene nanoribbons to open a small bandgap which is enhanced through the use of p and n type graphene contacts [26]

Another group utilized an array of aligned graphene nanoribbons as shown in Figure 18 to open up a small band gap which has significant difficulties in fabrication and noise properties from the nanoribbon edges.²⁶ Groups that have tried thermal-based IR detectors seem to have created more novelty, with one group utilizing multiple vertically aligned graphene flakes, while another group utilized a resonant structure of 2 graphene sheets separated by a dielectric to tune the photon wavelength of absorption as shown in Figure 19.²⁷ Finally another group utilized the photothermoelectric effect as shown in Figure 20 to induce an electric current in graphene due to electric gating or dissimilar metal contacts.^{9, 27, 28} The bolometer utilizing vertically aligned graphene sheets used distance based tunneling between sheets for the bolometric effect, which is sensitive to contamination between sheets and alignment of the graphene flakes making reproduction difficult.²⁸

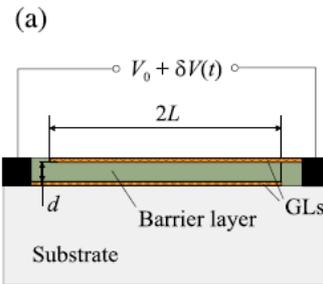


Fig.19. Phonon resonance based IR detector [27]

The resonance based IR detector shown in Figure 19 utilizes the phonon resonance of two separate graphene sheets separated by a dielectric allowing for the tuning of wavelength detection based upon separation distance, but the fabrication is difficult requiring pristine graphene and no trapped states in the oxide which would both modify the resonant frequency and could possibly contaminate the detector out of detection range.²⁷

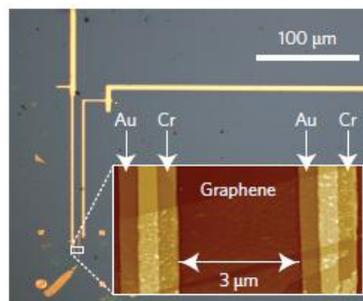


Fig.20. Image of a detector based upon the photothermoelectric effect [9]

The photothermoelectric effect detector shown in Figure 20 is relatively straight forward with contamination only affecting the speed of the detector and the noise only susceptible to trap states of the insulating oxide that the graphene is transferred onto.⁹

7. CONCLUSION

We have shown graphene to have many amazing properties due to its unique bonding and subsequently bandgap characteristics having electronic carriers act as “massless” Dirac-Fermions. The material characteristics of graphene are anisotropic having phenomenal characteristic within a single sheet and diminished material characteristics between sheet with increasing sheet number and grain boundaries. This restricts the applications of graphene to technology that is consistent with miniaturization such as microelectronics. Therefore the integration of graphene into several electronic device applications was reviewed.

Graphene has the highest mobilities values measured in a material at room temperature making integration into fast response time devices such as a HEMT for

RF applications. It has been shown that although the integration of graphene is challenging due to mobility degradation due to surface contamination in the graphene and trapped states in the oxide dielectric that a graphene RF detector with an overall response frequency of 300GHz was achieved utilizing a three terminal design on a SiC substrate with a channel length of 40nm.

Graphene use in optical devices is limited due to the absorption of 2.3% of incident light per layer making graphene's use for optical devices a tradeoff between getting enough layer for good optical absorption and modulation versus restricting number of layers for fast carrier propagation. On its own graphene is not practical for use as a waveguide or modulator but when it is combined with already active materials it increases the performance of such devices thus an EO modulator utilizing a stacked graphene-BN capacitor along with a Si microcavity array displays the ability to modulate light at a rate of 1.2 GHz.

Graphene for IR detectors has shown some promising results utilizing graphene in thermal-based detection regimes since the photon-based absorption regimes all require inducing a bandgap adding complexity and reliability issues. The unique thermal-based properties of graphene either in a traditional bolometric type of device or one based upon current produced from the photoelectric effect allowed for the creation of a graphene IR detector with sensitivity to a 2.5THz (119 μ m) laser.

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