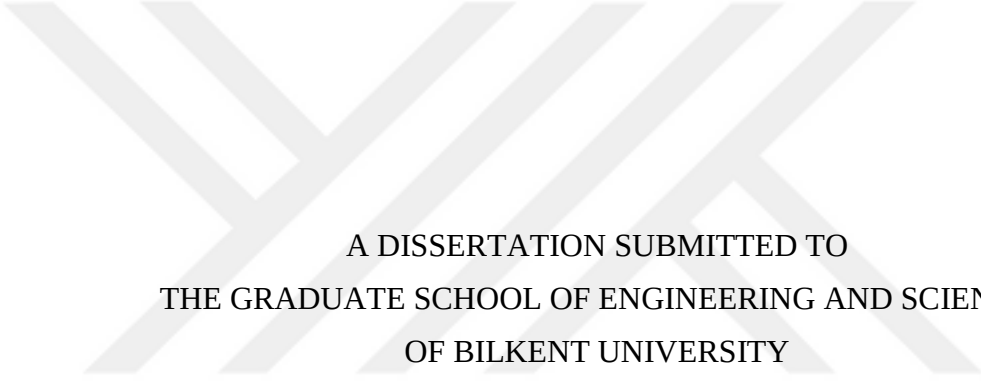


GRAPHENE-BASED ELECTRICALLY TUNABLE TERAHERTZ OPTOELECTRONICS



A DISSERTATION SUBMITTED TO
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IN
PHYSICS

By
Nurbek Kakenov
September 2016

GRAPHENE-BASED ELECTRICALLY TUNABLE
TERAHERTZ OPTOELECTRONICS

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September 2016

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a dissertation for the degree of Doctor of Philosophy.

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ABSTRACT

GRAPHENE-BASED ELECTRICALLY TUNABLE TERAHERTZ OPTOELECTRONICS

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September 2016

Advances in terahertz (THz) research and technology, has bridged the gap between radio-frequency electronics and optics. More efficient control of THz waves would highly benefit noninvasive, high-resolution imaging and ultra-fast wireless communications. However, lack of active materials in THz, hinders the realization of these technologies. Graphene, 2d-crystal of carbon atoms, is a promising candidate for reconfigurable THz optoelectronics due to its unique electronic band structure which yields gate-tunable optical response. Here, we studied gate-tunable optical properties of graphene in THz frequencies. Using time-domain and continuous wave THz spectroscopy techniques, tunable Drude response of graphene is investigated at very high doping levels with Fermi energies up to 1 eV. Our results show that, transport scattering time decreases significantly with doping. Unlike conventional semiconductors, we observed nearly perfect electron-hole symmetry even at very high doping levels. In the second part, we implemented using these unique tunable properties for novel THz optoelectronic devices such as THz intensity modulators and THz spatial light modulators. These devices are based on various designs of mutually gated capacitive structures consisting of ionic liquid electrolyte sandwiched between graphene and metallic electrodes. Low insertion losses (<2 dB), high modulation depth (>50 %) over a broad spectrum (0.1-2 THz), and the simplicity of the device structure are the key attributes of graphene

based THz devices. Furthermore, with the optimized device architectures, gate tunable coherent perfect absorption is observed in THz which yields modulation depth of nearly 100 %. The approaches developed in this work surpass the challenges of generating high carrier densities on graphene, and introduce low-loss devices with practical fabrication methods which we believe can lead to more responsive and sophisticated optoelectronic devices.



Keywords: graphene, Drude conductivity, modulator, THz-Spatial light modulators, terahertz optoelectronics, electrolyte gating, coherent perfect absorption

ÖZET

GRAFEN-TABANLI ELEKTRİK AYARLI TERAHERTZ OPTOELEKTRONİĞİ

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Radyo-frekans elektroniği ile optiğin arasında boşluk olan terahertz (THz) bandı son yıllardaki gelişmelerle birlikte dolmaya başladı. Daha verimli terahertz dalga kontrolü optoelektronik uygulamaları olumlu yönde etkileyecek en önemli parametrelerden biri. Var olan yöntemlerin daha aktif, uygulanabilir, az masraflı, ve verimli hale gelmesi için detaylı çalışmaların sürdürülmesi gerekli. Grafen bu alandaki gelişmeler için en önemli materyal adayı konumunda. Eşsiz elektronik ve optik özelliklere sahip olan grafen terahertz alanında aktif olarak kullanabilme potansiyelini taşımaktadır. Bu çalışmada grafen tabanlı modülatör, rezonans kavite, ve THz mekansal ışık modülatörleri geliştirildi. Geliştirilen yeni yöntemler daha verimli yük yoğunluğu yaratmakta, sistemdeki kayıplar (<2 dB) azaltmakta ve aygıt yapılarını kolaylaştırmakta. Grafen elektrodlarının ortak iyoniksel kapılamalarını kullanarak 0.1 ve 2 THz frekans aralığında %50 modülasyon değişikliğini elde etmiş olduk. Yansınma bazlı kavite geliştirerek terahertz dalga absorpsiyonunu 2.8 THz frekansında yaklaşık %100 oranında arttırabildik. Son olarak geniş bantta çalışabilen THz mekansal ışık modülatör aygıtlarını grafen süperkapasitörlerini kullanarak elde ettik. Grafenin aktif olarak terahertz bandında kullanılması, daha verimli ve sofistike THz optoelektronik aygıtların gelişmesini sağlayabilir.

Anahtar sözcükler: grafen, Drüid iletkenliği, modulator, THz mekansal ışık modülatörler, terahertz optoelektroniği, elektrolit kapılama, koherent absorpsiyon

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In dedication to my family

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Chapter 1

Introduction

Since its discovery, graphene research has taken considerable amount of progress in synthesis and device implementations. Both theoretical and experimental studies have manifested extraordinary electrical, mechanical, and optical properties of graphene. Its distinct nature lie in hexagonal lattice structure where carbon atoms undergo sp^2 hybridizations to create in-plane sigma and out of plane π bondings. In-plane covalent bondings make graphene mechanically strong, while weak out of plane orbitals account for the unique electronic and optical properties. The linear relationship between energy and momentum give rise to massless Dirac fermions within Dirac approximation. Unlike semiconductor carriers with parabolic dispersion relation, electrons and holes in graphene mimic zero mass particles which exhibit very large carrier mobilities. High carrier mobility ($200,000 \text{ cm}^2/\text{Vs}$) [1], together with electrically tunable optical response of graphene, offers new opportunities in optoelectronic devices especially at terahertz frequencies. Although graphene is only one-atom-thick, it can be seen by the naked eye. This phenomenon arises from nearly frequency independent 2.3 % absorbance at optical wavelengths [2-4]. These interesting optical properties can be tuned by controlling charge density on graphene which could yield new optical devices operating in a very broad spectrum.

Especially graphene could be a unique active material for terahertz frequencies. Electromagnetic waves with terahertz frequencies can be used for very high-speed communication [5] or nonionizing, high resolution imaging systems [6, 7]. These systems require active optoelectronic components such as emitters, detectors, modulators, switches, and other devices. With recent developments in THz research, THz sources and detectors have become more advanced however, active THz modulators and switches still need further improvements. Due to the lack of active THz materials it has been a challenge to control terahertz waves [8]. The submillimeter spatial resolution, and nonionizing nature are the essential properties of terahertz waves that can enable improvements in medicine, pharmaceuticals, security, communications, etc. These emerging technologies would greatly benefit from more efficient control of THz waves [9, 10]. Due to its unique electronic band structure which yields gate-tunable optical response, graphene is a promising material for reconfigurable THz optoelectronics.

In Chapter 2, we explain the electronic and optical properties of graphene followed by synthesis and transferring methods. Many studies [11-13] demonstrated the electronic band structure of graphene approximating by tight-binding model. The optical conductivity can be derived from Kubo formalism [4, 14]. Under Dirac cone approximation, graphene exhibits linear dispersion relation. Optical responses of graphene arise from its unique band structure. Graphene has nearly frequency independent absorption at visible and near-infrared region of the spectrum. This absorption arises from universal conductance of $e^2/4h$, Figure 1.1. For longer wavelength, THz and microwave region, intraband absorption is successfully explained with frequency dependent Drude model. By combining interband and intraband transitions, graphene provides a unique platform to control light-matter interaction in a very broad spectrum ranging from visible to microwave. This broad band activity enables us to design new electrically tunable optoelectronic devices.

After an enormous amount of research, methods to synthesize graphene have been improved. In this thesis, chemical vapor deposition (CVD) method is utilized to grow large graphene samples that enable us to realize active THz devices. By using CVD method, it is possible to produce large area graphene sheets limited only by the chamber size. This technique is more practical compared with mechanical exfoliation and epitaxial growth, also it is industrially promising. CVD grown graphene can be transferred on both solid and flexible substrates. We have optimized our technique to transfer graphene on terahertz transparent substrates such as quartz, polyethylene, PVC, and others. At the end of Chapter 2, the details of these methods were summarized.

In Chapter 3, we briefly discuss terahertz optoelectronics and graphene based THz devices reported in the literature. Advances in science and technology have greatly contributed in closing the THz gap by developing more efficient emitters, detectors modulators, and other devices. More efficient control of THz waves would highly benefit noninvasive, high-resolution imaging and ultra-fast wireless communications. There are two main methods for THz characterization, the time-domain and continuous wave. Conventional time-domain spectroscopic systems use photoconductive (PC) antennas and nonlinear crystals for both emitting and detecting terahertz signals. Terahertz time-domain spectroscopy (THz-TDS) offers broadband spectral range measurements and extra freedom in measuring parameters such as phase information. However, THz-TDS systems utilize femtosecond lasers which brings complexity to these measuring systems. Unlike THz-TDS, continuous wave systems are more practical and compact. It can use YIG oscillators, quantum cascade lasers, Photomixing devices, etc.. To detect CW terahertz radiation thermal detectors can be used such as bolometers, Golay cell, and pyroelectric devices. Still lack of active materials hinders the realization of more efficient THz optoelectronic devices. Graphene with its unique electrical and optical properties is a promising candidate to facilitate more efficient THz devices. Graphene has gate-tunable Drude like response

in the THz band. Graphene based field effect transistors have already been demonstrated to function as detectors with fast image acquisition and high spacial resolutions.

In Chapter 4, we study gate-tunable optical properties of graphene in THz frequencies. In the literature, THz response of graphene has been investigated using transistor type devices based on dielectric capacitors. These devices are limited to 300 meV Fermi energies due to dielectric breakdown of the gate dielectric. In this work, we developed an electrolyte gating method to achieve very large Fermi energies. Using time-domain and continuous wave THz spectroscopy techniques, we investigated tunable Drude response of graphene at very high doping levels with Fermi energies up to 1 eV. Time-domain and CW spectroscopy measurements were performed in collaboration with Professor Hakan Altan's group, from Middle East Technical University. Infrared spectroscopic measurements elucidated the Drude-like response of charge carriers shedding light on its transport and optical properties. The tunable charge density yield significant changes in the Drude weight and transport scattering time of graphene. Our results show that, transport scattering time decreases significantly from 150 fs to 50 fs as Fermi energy varies between 0.2 – 0.9 eV. Changing polarity of the gate voltage, enables us to change the carrier type on the graphene. In contrast to conventional semiconductors, we observed nearly perfect electron-hole symmetry even at very high doping levels.

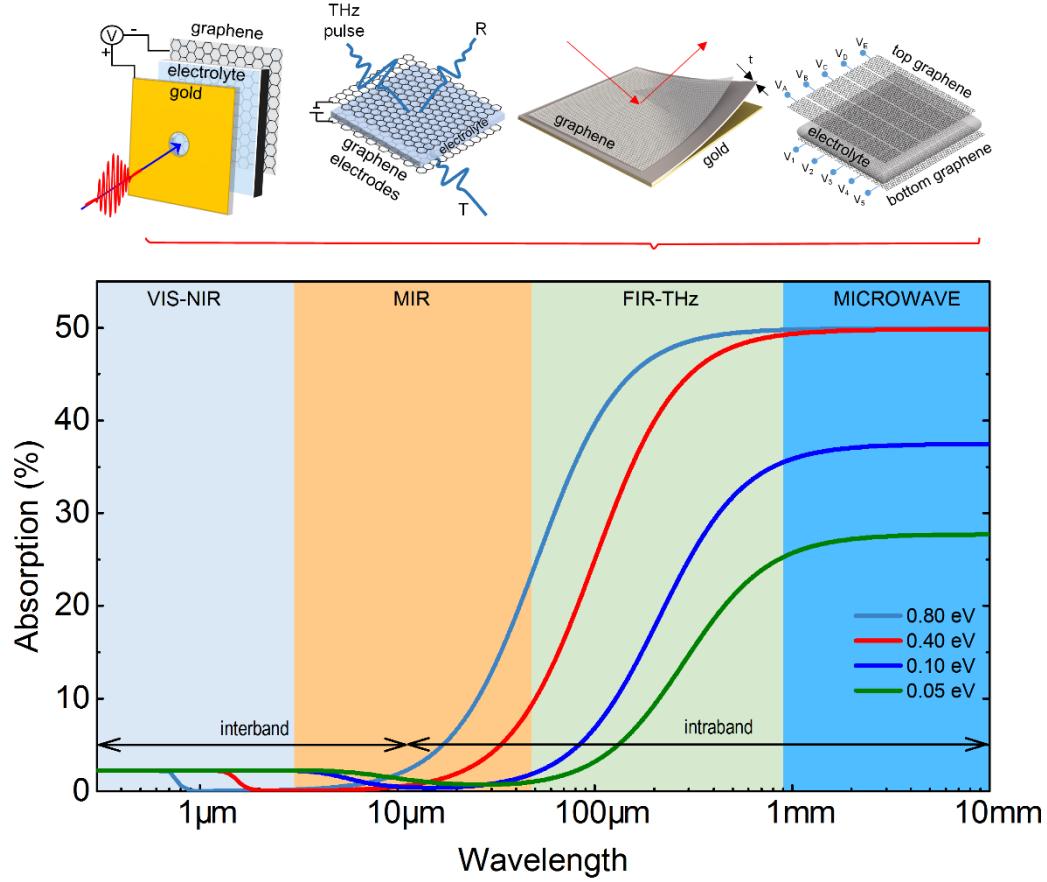


Figure 1.1 Absorption spectrum of single layer graphene from visible to microwave wavelengths. The images shows the active THz devices studied in this thesis.

In Chapter 5, we used tunable THz response of graphene to control THz waves. Many studies aiming to manipulate THz waves are based on high mobility of carriers on semiconductors such as in Schottky diodes, or metamaterials. Nevertheless, high insertion loss, inefficient modulation depth, and the requirement of complex fabrication methods are challenges that still need attention. With graphene based supercapacitor structure we addressed these issues at the expense of switching speed which is limited with the ionic motion. Figure 1.1 summarizes graphene-based THz devices that we have developed in this thesis. Two mechanisms, interband and intraband electronic transitions, govern the electronic and optical properties of

graphene. Absorption of a single layer graphene from visible to microwave frequencies is demonstrated in Figure 1.1. At optical frequencies, strong interband transitions take place, while at lower frequencies even more pronounced free-carrier absorptions arise. The former transitions are highly dependent on the presence of free-carriers on graphene. Hence, by tuning the concentration of carriers one is able to attenuate the THz transmittance. Here, we used a capacitor structure device consisting of two large area graphene electrodes. The mutual electrolyte gating of graphene electrodes efficiently tunes the Fermi energy from 0.2 to 1.0 eV. Using terahertz time-domain spectroscopy we achieved a modulation of THz waves by more than 50% on average from 0.1 – 1.5 THz frequencies.

In Chapter 6, results on observation of coherent perfect absorption (CPA) of THz radiation in graphene enabled by optimizing the device architecture is discussed. Although, the intraband absorptions are limited to a maximum of 50 %, it is possible to enhance the terahertz absorption at the expense of broad spectral modulation. The enhancement of absorption can be done by exciting plasmons on patterned graphene, by coupling graphene with metamaterials, and by introducing resonant devices where attenuation occurs by multi-pass of photons. In phase illumination of coherent light on an absorbing media result in total attenuation of the beam. This phenomena is known as coherent perfect absorption. Recent studies focused on the realization of tunable optoelectronic devices with enhanced absorptions in 2d-conductors. 20 % of absorption was observed at far-infrared region when graphene was placed on a photonic crystal. The device we developed possesses resonant nature. It is composed of hybrid structure of metal electrode and graphene layer placed at a quarter wavelength distance. Electrolyte medium is sandwiched between the two electrodes which is one of the key parameters to fulfil the requirement of resonant absorption. With the optimized device architectures, we were able to observe gate tunable coherent perfect absorption in THz with modulation depth nearly 100%.

Implementation of such devices are crucial in the development of more efficient terahertz components.

In the final part of this thesis, we demonstrated more complex integration of the active devices to fabricate spatial light modulators (SLMs) which are the key components of terahertz imaging systems. These functional devices enable spatial control of either transmission or reflection of terahertz waves. Direct processing of terahertz beams by manipulating the wave front information are essential in many optoelectronic applications. SLMs would highly effect the terahertz beam steering, compressive imaging systems, communication systems [15-20]. A main component in THz SLMs is specific addressing of pixel which modulates the transmission or reflection of the wave. Different methods can be applied to overcome this challenge. One study suggested interconnecting metamaterial to form matrix configuration, and addressing each array component would modify terahertz beam. Another way of approaching is to design back-gated individual pixel and apply compressing sensing technique. Complicated device fabrications, low modulation depth, and narrow band functionality are the challenges requiring attention. These issues can be coped by introducing graphene based arrays of supercapacitors. High carrier mobility and tunability makes graphene an active material with strong terahertz response. Advances in synthesis and transferring processes allow more practical device designs. Using graphene on suitable substrate as electrodes with electrolyte gating induces high carrier densities and introduces no source for loss.

The approaches developed in this work surpass the challenges of inducing high charge carrier densities on graphene, and introduces low loss, new type of device structures with practical fabrication methods which we believe can lead to more responsive and highly sophisticated optoelectronic devices.

Chapter 2

Terahertz Optoelectronics

In this chapter, terahertz optoelectronic systems are discussed, mainly the time-domain and continuous wave sources and detectors, also graphene-enabled terahertz devices are reviewed. Conventional time-domain spectroscopic systems use photoconductive (PC) antennas and nonlinear crystals for both emitting and detecting terahertz signals. Terahertz time-domain spectroscopy (THz-TDS) offers broadband spectral range measurements and extra freedom in measuring parameters such as phase information [21]. However, THz-TDS systems utilized femtosecond lasers which brings complexity to these measuring systems. Unlike THz-TDS, continuous wave systems are more practical, cost-effective and compact. The commonly used sources are YIG oscillators, free-electron lasers (FELs), quantum cascade lasers (QCLs), Photomixers, etc.. To detect CW terahertz radiation thermal detectors can be used such as bolometers [22], Golay cells [23], and pyroelectric devices [24, 25]. Still lack of active materials hinders the realization of more efficient THz optoelectronic devices. Graphene with its unique electrical and optical properties is a promising candidate to facilitate more efficient THz devices. Its pronounced THz response has already been demonstrated in graphene based field effect transistors [26], modulators [27] and so on.

2.1 Introduction

Terahertz (THz) region is located between infrared and microwave wavelengths in the electromagnetic spectrum. Specifically, it spans the wavelengths from 1 mm (300 GHz) to 10 μm (10 THz), Figure 2.1. High spatial resolution, low ionizing energy, and high bandwidth of terahertz waves offers advances in security, medicine, and in communication systems. Due to the lack of sources and detector devices with terahertz functionality, for many years terahertz band remained least explored. Already established electronic devices could not respond to THz frequencies because their working range is limited to few gigahertz frequencies. On the other part of the spectrum, terahertz photons, with energies of ~ 4 meV, cannot excite electron hole pairs since the band gap of the typical semiconductors are on the order of 1 eV. Hence, the band was known as the terahertz gap. Nowadays, advances in research and technologies gave rise to terahertz emitters, detectors, switches, modulators, and other functional components; however, absence of active material in THz band hinders the realization of these technologies [28-30]. More efficient control of THz waves would highly benefit noninvasive, high-resolution imaging and ultra-fast wireless communications.

In this chapter, we briefly review the terahertz optoelectronic devices, explain the time domain and continuous wave sources, detectors and measurement systems.

2.2 Terahertz optoelectronic devices

The rotational and vibrational energies of molecules, intraband electronic transitions in semiconductor, water absorption take place at terahertz frequencies [31, 32]. Most of the packaging materials such as plastics, polyethylene, teflon, and others are transparent while metals are highly reflective at this band [33]. Hence, the most important application that THz field can offer is THz imaging and sensing. High spatial resolution and noninvasive property are the key features of the terahertz waves. THz imaging constitutes devices such as emitters, detectors, modulators, and

so on both for time-domain and continuous-wave systems [20, 34-36]. Another field where THz band carries value is communications systems. The internet traffic expected to reach 130 exabytes by 2018 [5]. Implementing terahertz band in wireless communication systems is expected to meet the increased demand for higher bandwidth data transmissions. Due to strong atmospheric absorption in THz band, long distance data transmission remains a great challenge. On short distances THz wireless communications have been tested. Still, high signal-to-noise (S/N) ratio must be developed to enable THz communication. The studies on developing new and more effective approaches are an active research area. A lack of active material, is the main challenge of the THz band. More and more materials are tested at terahertz band as they are developed. Graphene, a hexagonal lattice of carbon atoms, is a promising candidate to be implemented in THz devices. Graphene has gate-tunable, pronounced response at THz frequencies due to its unique electrical and optical properties. Using graphene as an active material in terahertz devices has already shown promising results [37, 38]. Graphene-based field effect transistor have also been developed to detect THz radiations [26], other components such as plasmonic antennas [39], oscillators , THz metamaterials [40], and so on have been demonstrated [41-43].

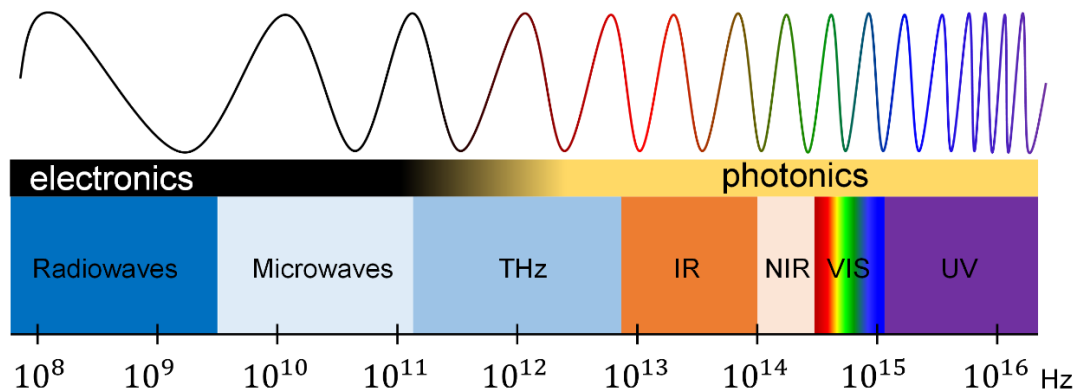


Figure 2.1 Electromagnetic spectrum. THz region is located between microwaves and infrared frequencies.

2.3 Continuous wave terahertz components

Although, continuous-wave terahertz systems lack broad spectral range, they are more compact, simple, and cost-effective compared to time-domain counterparts. CW systems result in a faster and more practical processing than THz pulsed configurations. The most commonly used generation of CW terahertz include Photomixing, Gunn effect, free electron and quantum cascade lasers, frequency multiplication of microwaves, difference frequency generations and so on [29, 30, 44, 45]. Some of these techniques will be discussed in this section.

Photomixing, known also as optical heterodyne downconversion, in principle is the frequency conversion from high to low. It uses photoconductive (PC) switch to induce CW THz radiations. Two laser with different frequencies are used to form optical beats which generate THz waves. Due to its high carrier mobility and short carrier lifetime LT-GaAs crystal is commonly used photoconductive material. An essential component of photomixing is the high-quality, tunable, dual-frequency laser systems. Continuous beats formed from dual laser, oscillates the photocarriers in the medium at the difference frequency of two lasers. The terahertz radiation is emitted when the beat frequency is tuned to terahertz range. Since the beats are continuously incident on active area, the substrates must be good thermal conductors. The main disadvantages of photomixing are low output power and low optical to terahertz conversion efficiency.

A free electron laser (FEL) is one of the highest output power terahertz source. It can generate tunable terahertz radiation with output powers from several hundred watts to kilowatts [46, 47]. Basically, FEL is a device which converts the energy of accelerated free electrons into electromagnetic radiations. The main components of FEL are injector, accelerator, and undulator [46]. The free electron pulses are generated in the injector and then accelerated to relativistic speeds. Following the acceleration the bunches of electrons interact with static magnetic field in the undulator and undergo wiggling motions. Due to interaction of electron bunch and

static magnetic field electrons emit terahertz wave by synchrotron radiations. Free electron lasers offer high power, tunable, coherent sources of terahertz radiation. The disadvantages of FEL are high cost and complex structures.

Another known source for terahertz radiations are quantum cascade lasers. In such systems, emission relies on intersubband electronic transitions in quantum wells. These quantum wells can be engineered to match the energy levels in question. The levels required for terahertz radiations are around meVs. To overcome thermal excitations quantum cascades lasers are operated at cryogenic temperatures. The main challenges include narrow separations between sub-bands, thermal agitations, and carrier scatterings. Another limitation of QCLs are low output power, which is the result of weak coupling of the gain medium to optical fields. On average output power is nearly at μ Ws.

The generating terahertz radiation is not the only challenge. Detection of THz waves is another major issue. Since most of the terahertz sources have limited output power, detecting them can be challenging. Thermal detectors are commonly used components to detect terahertz radiations. For example, bolometers, pyroelectric devices, and Golay cells are classified as thermal detectors which can sense CW terahertz radiations [29, 30]. The basic principle behind thermal detectors is to convert electromagnetic radiation into heat and track the temperature changes. An absorber with a low heat capacity is suitable in this type of sensor to efficiently convert absorbed energy into detectable temperature changes. First of all, bolometers are widely used thermal detectors that sense terahertz waves. Mainly, bolometers constitute an absorbing media and a temperature sensor. The absorbing media collects the incident radiation while thermometer converts the changes in temperature into readout data. Since thermal conversions are nearly wavelength independent, bolometers have very broad detection range. Although, bolometers are the most sensitive terahertz detectors ($10^{-12} \text{ W}/(\text{Hz})^{1/2}$) they require to be cooled to cryogenic temperatures for operation, they are also not portable and expensive. A pyroelectric

devices are another type of thermal detectors based on pyroelectric effect. In certain materials the change in temperature causes release of electrons, known also as the pyroelectric effect. Advantages of pyroelectric devices include room temperature operation, relatively compact design, and cost-effective price. However, compared to other thermal detectors, pyroelectric devices have rather limited sensitivity.

Lastly, another commonly used thermal detector is Golay cell. Since its invention Golay cell proved to be a sensitive detector for broadband radiations from infrared to millimeter waves. The typical sensitivity of Golay cells are at $10^{-10} \text{ W}/(\text{Hz})^{1/2}$. It can sense terahertz radiations at room temperature. Basic schematics of Golay cell structure is represented in Figure 2.2.

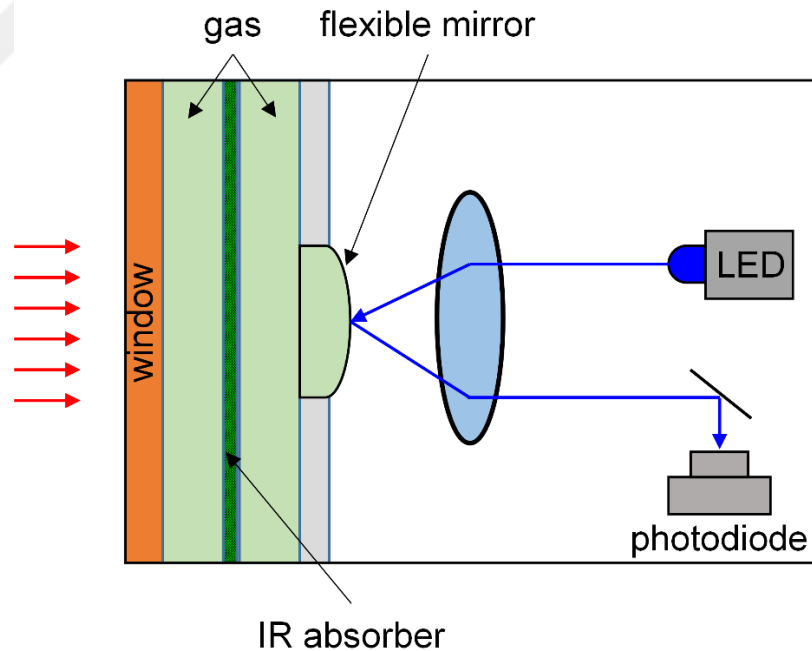


Figure 2.2 Schematic drawing of Golay Cell thermal detector.

The main components of the Golay cell is pneumatic chamber, absorbing area, and flexible mirror. When terahertz wave is incident through Golay cell window, it is absorbed by the absorbing film. Small portion of the volume heats up on absorption, thus expanding the gas in the chamber. This expansion induces deformations in the

flexible mirror. The LED light which is focused on the flexible mirror changes path once the mirror is deformed. The changes in the reflected beam are picked up by the photodiode. The Golay cell is the most sensitive sensor of the thermal detectors with sensitivities at noise equivalent levels. These sensitivities rely on the resistive heat chamber filled with Xenon inert gas. Thus, most of the radiation heat is traced by the photodiodes.

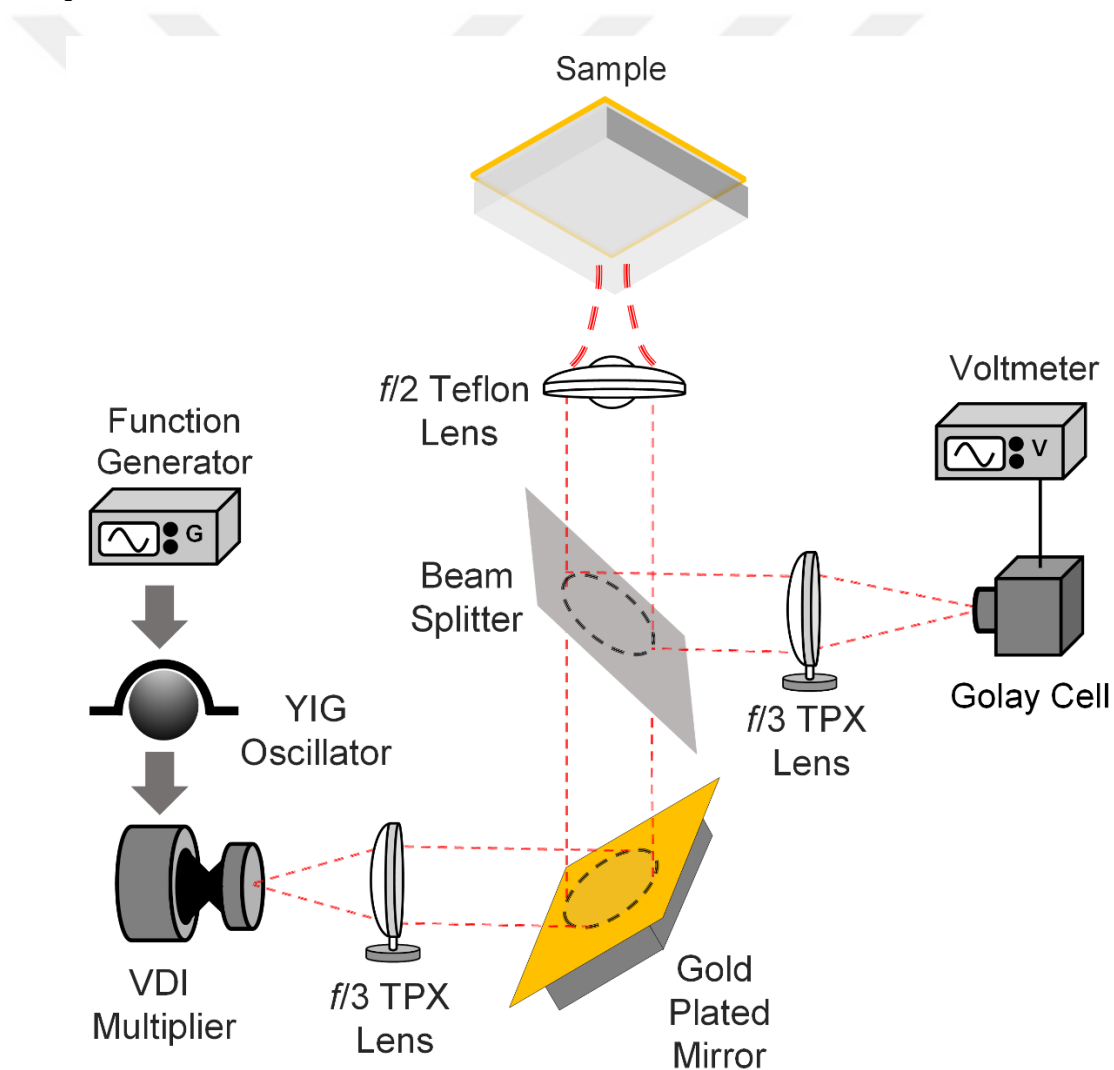


Figure 2.3 CW terahertz reflectance measurement system. To generate CW (0.24 to 0.38 THz) a YIG oscillator integrated with VDI multiplier is used.

Figure 2.3 illustrate CW terahertz measurement system that we used in our experiments. The system consists of YIG oscillator as the CW source. YIG stands for yttrium iron garnet, a magnetic crystal with very high quality factor. THz wave generation arises from YIG crystal's resonant oscillations. When DC magnetic field is applied to YIG crystal, it resonates at microwave frequencies. This response is linear with the applied magnetic field. The YIG oscillator used here can be tuned between 8-13.2 GHz. By employing VDI (Virginia diode) multiplier we were able to generate THz waves with frequency range from 0.24 – 0.38 THz. All components of CW system are movable enabling both transmission and reflection modes of measurements. TPX and teflon lenses are used to collimate and focus the THz wave respectively. The detection is done by employing a Golay cell detector which possess high dynamic range at room temperature.

2.4 Time domain terahertz spectroscopy

Terahertz time-domain spectroscopy (THz – TDS) is a powerful technique to study physical and chemical processes [30]. In principle, THz – TDS is system where THz pulses are generated and detected at high rate. The detected signal is a time-varying electric field whose Fourier transform produces both amplitude and phase spectra over broad spectral range. Optical parameters of materials are extracted by comparing signals from the sample to a reference signal with known properties. Usually the reference signal is taken in air medium with reduced water vapor molecules. The Figure 2.4 illustrates the scheme of terahertz spectroscopy system. There are various ways to generate and detect terahertz radiations [30]. Most often photoconductive antenna and nonlinear optical crystals are used as emitting and detecting components [29]. According to the schematics, high power, femtosecond duration pulses are engaged to excite and detect THz waves. The echelon of ultra-short pulses are split into two beams by a beam splitter. First beam is sent to terahertz emitter; while the second one is used as probe beam. When the pump pulse hit the THz emitter, the terahertz pulses are excited. These pulses pass through the sample and focus on the

THz detector. To readout any signal, the probe pulse and terahertz pulse must both be incident on the THz detector. By sweeping the time delay of the probe pulse the profile of THz beam is extracted (Figure 2.4). To extract the transmitted, reflected, or absorbed spectrum of a sample, the Fourier transform of the terahertz pulses is performed. The refractive index, extinction coefficient, and phase changes of a sample can also be extracted from Fourier transform of the THz pulse. In that sense, time-domain terahertz spectroscopy is an indispensable method to measure optical parameters of materials.

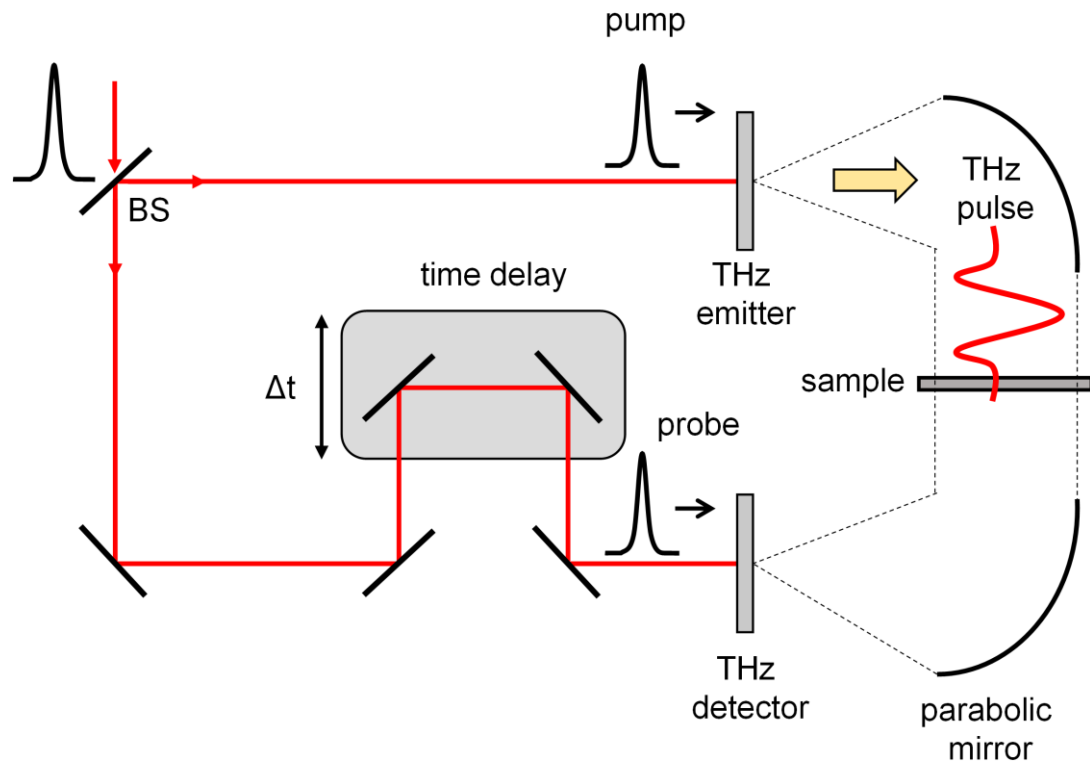


Figure 2.4 Terahertz time-domain spectroscopy (THz-TDS) schematics. Optical beam is split into two pulses. First pulse (pump) impinges on THz emitter (nonlinear crystal, or PC diode) to generate subpicosecond THz pulse. The second pulse (probe) undergoes time delay and impinges on THz detector. The probe pulse is used to gate the THz detector (Schottky diode, PC antenna).

The terahertz radiation is generated and detected by PC antennas or nonlinear crystals. The photoconductive antennas can both be utilized as emitters and receivers. The design of the antennas effect the strength and the bandwidth of the resultant terahertz beams. Most common configuration is dipole structure. The figure demonstrates the side view of PC emitter. The two metallic stripes separated by gap sit on substrate. The stripes are illustrated as black protrusions, and are kept at certain bias level. The substrates are semiconductors with fast carrier relaxation time. When the femtosecond pulse impinges on dipole medium, it excites extra charge carriers. The charges are then accelerated by the bias voltage. As result of transient photocurrents, the THz pulse is emitted. The strength and the bandwidth of the emitted THz pulse depends on various parameters.

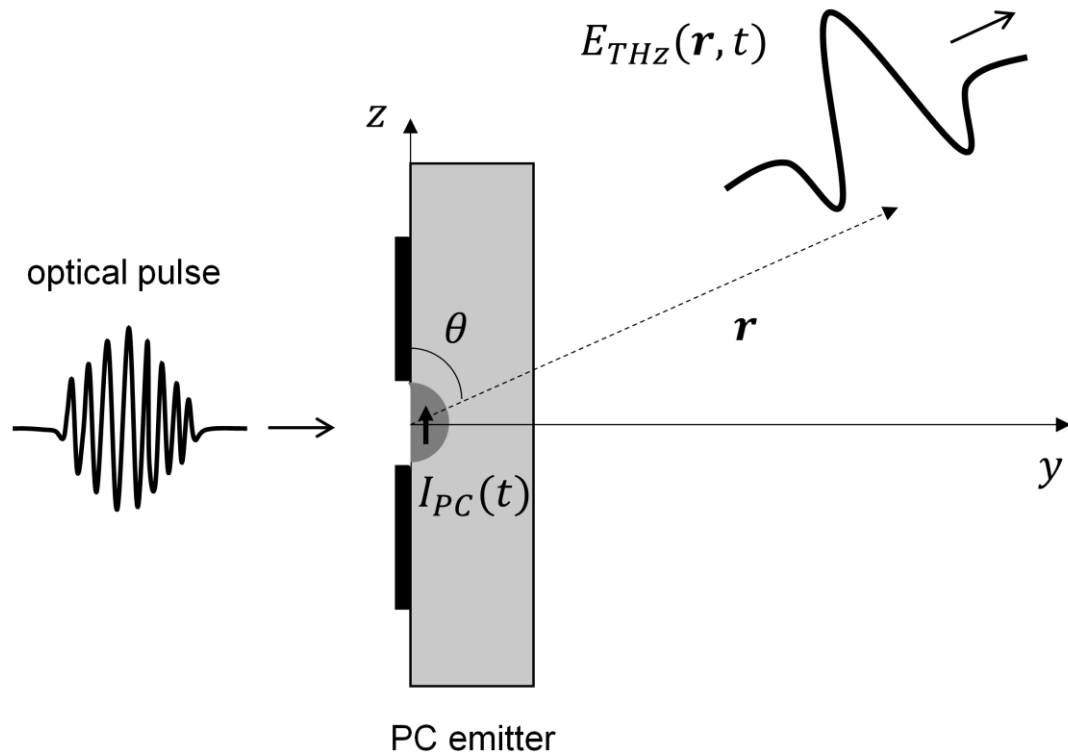


Figure 2.5 THz pulse emitter based on photoconductive antenna.

The terahertz emitter is shown in Figure 2.5. It consists of photoconductive antenna and metal contacts. DC bias is applied to coplanar metal-strips to induce accelerating electric field. Semiconductor with high carrier mobilities and rapid relaxation times are suitable for PC antennas. Most commonly, gallium arsenide (GaAs) or low temperature gallium arsenide (LT-GaAs) are preferred. High mobilities of charge carriers is favorable for the rapid response to electric fields which is crucial for THz pulse excitations. Ultra-short optical pulse excite electron hole pair up on incidence. These pairs are then separated by the DC field resulting in transient current. It is this transient current that induces picosecond terahertz pulses. The bandwidth of the THz pulse dependence on the time duration of pump pulse. Subfemtosecond pulses can excite terahertz pulses with 3 THz bandwidth.

The detection of terahertz pulses with photoconductive antennas are similar in mechanism to emission of the pulses. In this case, both optical pulse and terahertz pulse must be incident on the PC antenna. Figure illustrates the schematic view of PC antenna. Similar design structure is used as with PC emitter. Coplanar metallic stripes are fabricated on semiconductor substrate, Figure 2.6. A probe pulse and terahertz pulse are directed as shown in the figure. The optical pulse upon incidence keeps the semiconductor gated exciting electron hole pairs. In other words, optical pulses changes the state of semiconductor from insulating to conducting by creating charge carriers. Once the terahertz pulse reaches the gated medium, it act as a switch on state inducing current flow between metallic stripes which are picked-up by the detector. Hence, the optimal semiconductor material must have high carrier mobility and short carrier lifetime.

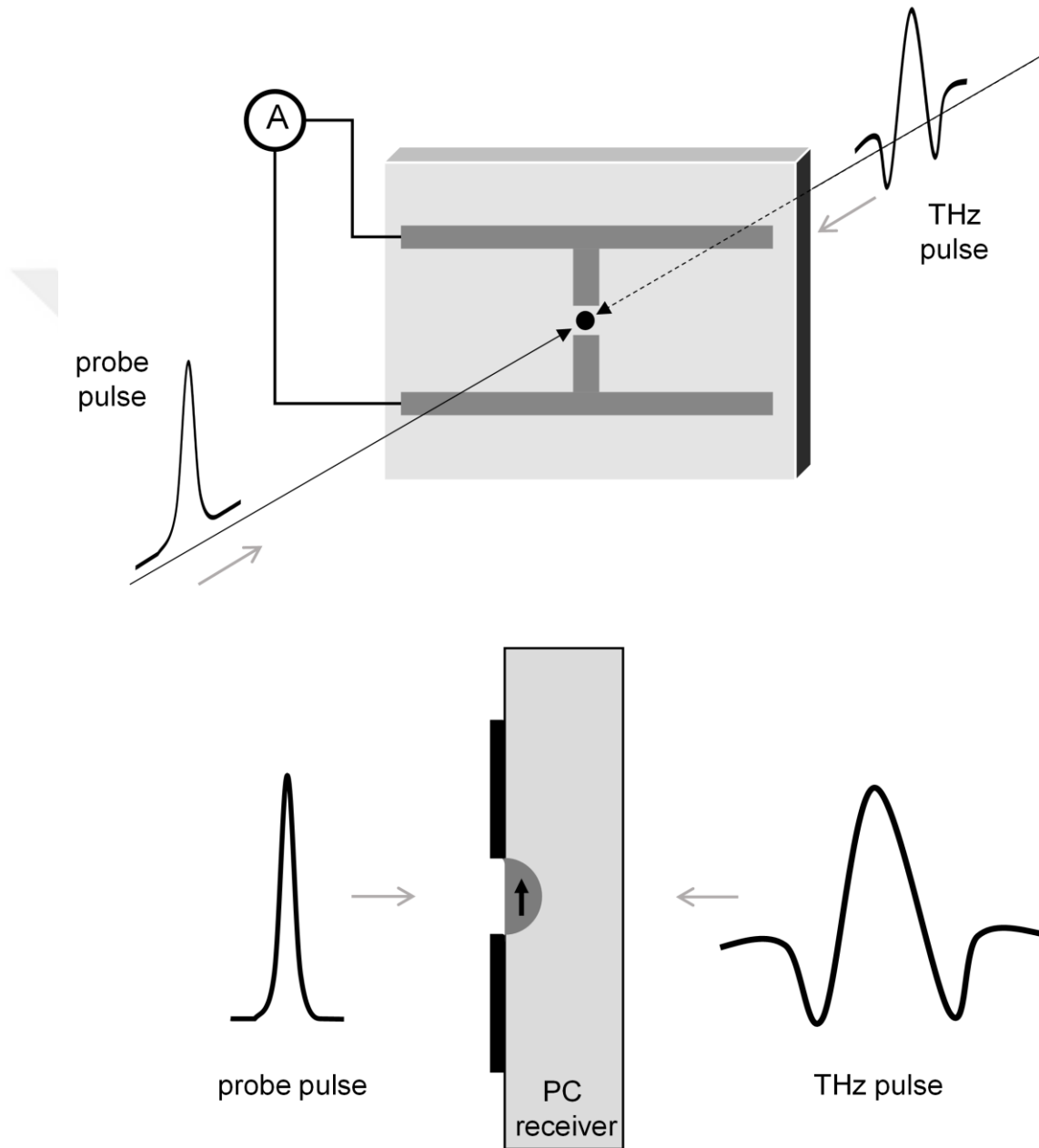


Figure 2.6 THz receiver. (a) Probe pulse is impinges on dipole structure of THz receiver causing extra free carriers. When THz pulse hit on dipole structure, it causes detectable photocurrent flow. (b) Side view of THz detector antenna. By changing the time delay, whole electric field profile of THz pulse is mapped out.

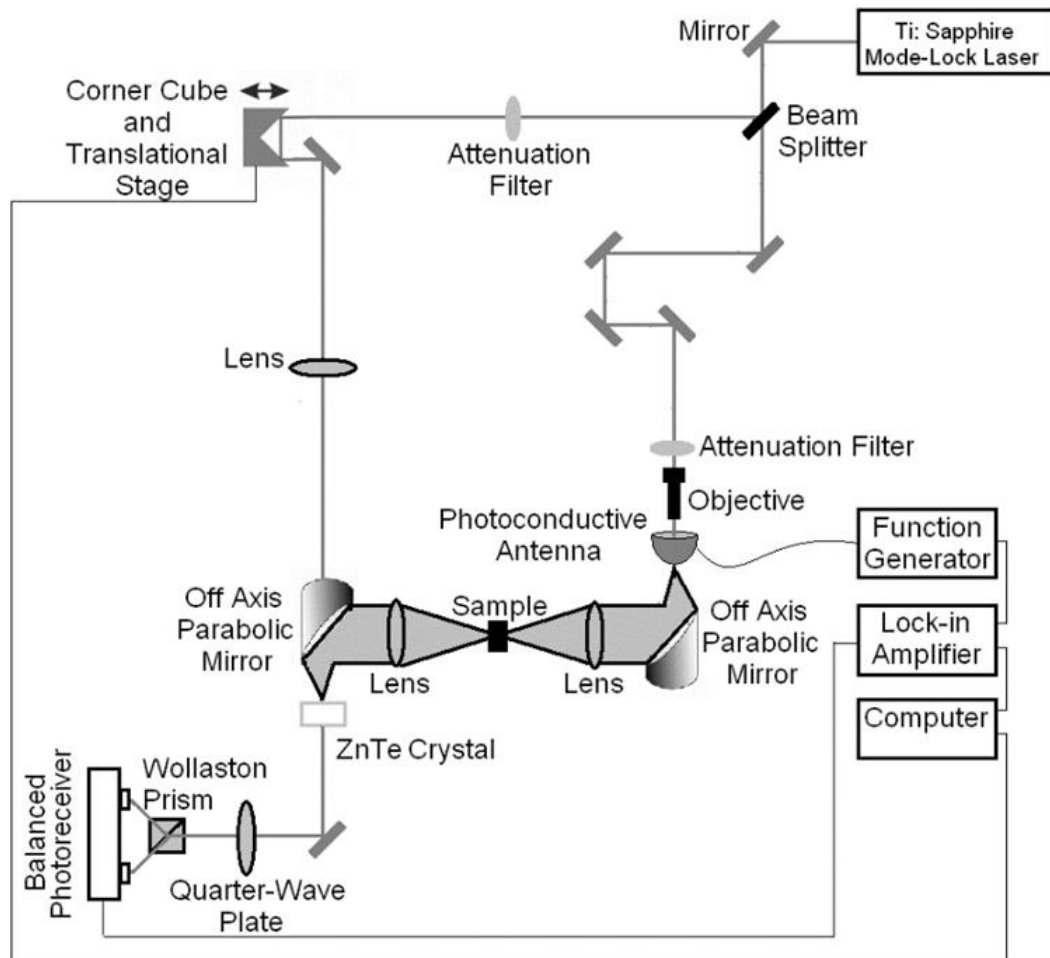


Figure 2.7 Schematic view of terahertz time domain spectroscopy measuring system.

Figure 2.7 show the schematic representations of time-domain terahertz spectroscopy. The mode-lock laser of femtosecond duration pulses is used as the emitter pump and detector probe pulses. The laser beam is split into two. The first beam impinges on photoconductive antenna, figure. The antenna consists of semiconductor medium. When the femtosecond pulses hit the PC antenna, it generates the photocarriers, which are then accelerated by the bias voltage. The terahertz pulses are generated by these transient carriers. The subpicosecond THz pulses are focused on the sample, and falls on THz detector. To detect terahertz pulses another PC antenna can be used. The detection is carried out via nonlinear crystal.

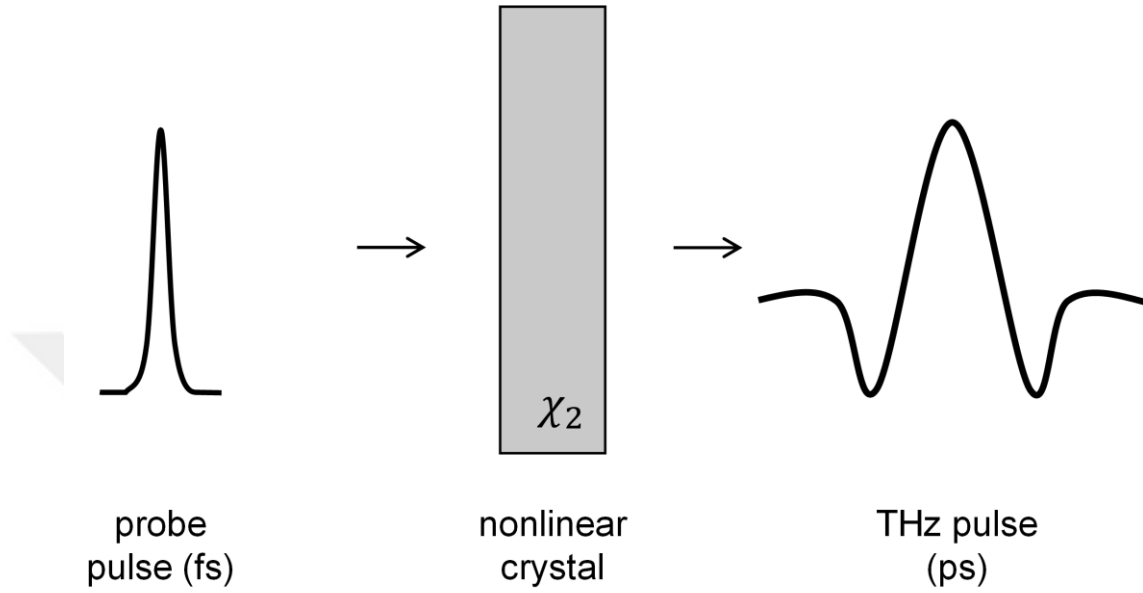


Figure 2.8 THz pulse emission in a nonlinear crystal.

Figure 2.8 illustrates the basic scheme for terahertz generation where ultrashort pulses induce THz pulses in nonlinear medium due to optical rectification. In linear systems polarization state is proportional to electric field by the equation 2.1. At nonlinear regime higher order contributions of the susceptibility starts to be significant. When we expand equation 2.1 we end up with higher order terms of electric susceptibility.

$$\vec{P} = \chi(E)\vec{E} \quad 2.1$$

The expansion of χ , susceptibility, is represented in the equation 2.2.

$$P = \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \dots \quad 2.2$$

The optical rectification and the Pockel's Effects are the second order nonlinear effects describe by the second term in the equation 2.2. For a field with $E = E_0 \cos(\omega t)$, the second order effect is,

$$P_2 = \chi_2 E^2 = \frac{1}{2} \chi_2 E_0^2 (1 + \cos(2\omega t)) \quad 2.3$$

where second order term of polarization has two components. The first component corresponds to DC, or low frequency, polarization state. The second component is result of second harmonic generations of the crystal. The later has no contribution to optical rectification. Hence, the nonlinear optical rectifications is caused by the DC component of the polarization state.

For fields at different frequencies, $E_1 = E_0 \cos(\omega_1 t)$ and $E_2 = E_0 \cos(\omega_2 t)$, the second order polarization is,

$$P_2 = \chi_2 E_1 E_2 = \frac{1}{2} \chi_2 E_0^2 (\cos(\omega_1 - \omega_2)t + \cos(\omega_1 + \omega_2)t) \quad 2.4$$

Here, we have $\cos(\omega_1 - \omega_2)$ and $\cos(\omega_1 + \omega_2)$ terms. The higher frequency term has no contribution to emission or detection. The lower frequency term is a result of the optical rectification effect.

Detection of THz pulses can be done using crystal with second order nonlinear property. The figure demonstrates the basic principles of detecting terahertz pulses. Both probe pulse (with femtosecond pulse duration) and THz pulse must be collinearly incident on nonlinear crystal. When the probe and terahertz pulses coincide in the nonlinear optical medium, the latter pulse changes the refractive index of the medium, which is proportional to the terahertz field amplitude, causes the phase modulation of the probe pulse. Then it passes through quarter waveplate and Wollaston prism to be detected by photodiodes. In other words, variations of the optical medium causes the probe pulse to undergo birefringence. The phase retardation between ordinary and extraordinary pulses are then picked up by the photodiodes, (Figure 2.9). The complete profile of the terahertz pulse is extracted by sweeping the time delay.

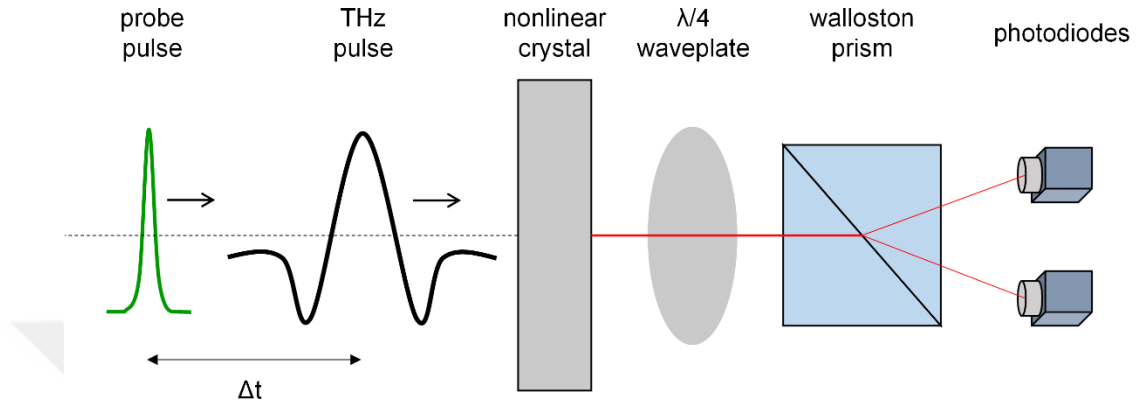


Figure 2.9 Electro-optic system to detect terahertz pulses based on nonlinear crystals.

2.5 Graphene-enabled terahertz optoelectronic devices

Graphene is a promising material to be used in terahertz optoelectronics. Many studies already showed the promises of graphene usages in terahertz devices. Graphene mainly was demonstrated as a material to control THz waves. For instance, using graphene enabled field effect transistor Ren et al demonstrated both interband and intraband response of back-gated graphene [37]. Figure 2.10(a) illustrates the devices structure used to study terahertz response of graphene. Their device structure consisted of graphene transferred on $\text{SiO}_2/\text{p-Si}$ substrate. The p-Si was used as the back-gate, and SiO_2 dielectric separating graphene layer. By applying gate voltage they were able to tune the Fermi energy of graphene from 0.2 to 0.5 eV, and track the changes in mid-infrared and terahertz region. Both THz time-domain spectroscopy and Fourier transform spectroscopy were utilized to measure the transmittance from the graphene device. Ren et al confirmed the Drude-like conductance at terahertz frequencies and also observed the interband transition at mid-infrared region demonstrating strong terahertz activity of graphene. Similar device structure was applied as a THz intensity modulator, Figure 2.10(b). A 20 % modulation was achieved from 570 GHz to 630 GHz frequencies on a single layer graphene device [27]. The modulation is a result of free carrier absorption in graphene. By the same group a reflection type terahertz modulator were developed [48]. In Figure 2.10(c),

the graphene enabled resonant device structure is shown. They used back-gating scheme to generate charges on graphene. The device consisted of CVD grown graphene on top of a dielectric, and a evaporated metal on the back of highly doped silicon. By applying bias voltage to gating electrode and graphene they were able to attenuated the terahertz reflectance by 64 % at 620 GHz frequency. These studies demonstrated the feasibility of graphene as an efficient material to manipulate terahertz radiations.

Apart from controlling THz waves, graphene was utilized in terahertz wave detection [26]. Figure 2.10(d) demonstrates the developed terahertz detector based on graphene field effect transistor. By coupling graphene field effect transistor with antenna they were able to achieve responsivity of 100 mV/W. Their device facilitates more efficient and fast terahertz detection at room temperatures. As an application coffee capsules and leaf were imagined in a transmission mode. To produce the images by raster scanning it took 200x550 points, consuming 20 ms for each point. Hence, one image was reproduced at nearly few hundreds seconds which is fast for THz imaging with reasonably good resolution.

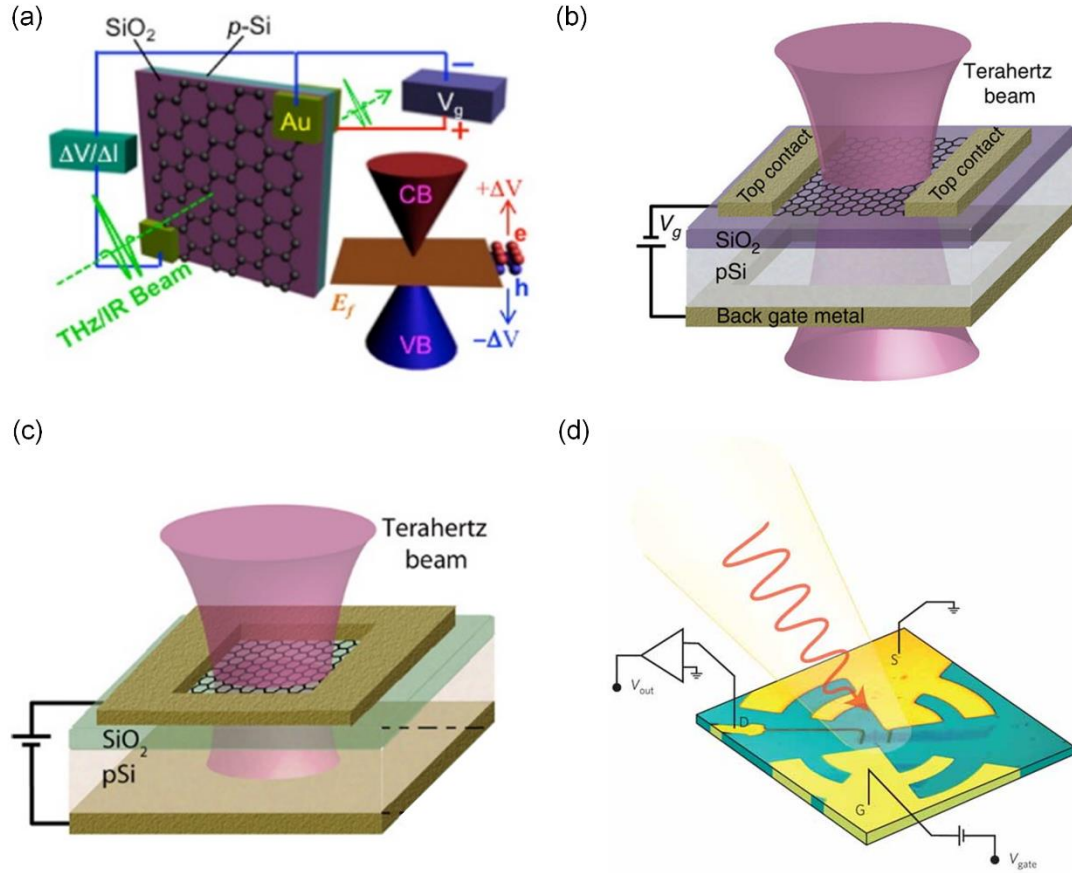


Figure 2.10 (a) Transistor type graphene device [©2012 ACS](#) [37]. (b) Graphene based THz intensity modulator [©2012 NPG](#) [27]. (c) Reflection type THz intensity modulator [©2012 ACS](#) [48]. (d) Graphene-based field effect THz detector [©2012 NPG](#) [26]. All figures were reprinted with permission from corresponding publication groups.

2.6 Conclusion

The unique properties such as noninvasive nature, low ionizing energy, high spatial resolution, and wide bandwidth of terahertz waves offer novel opportunities for imaging, communication systems, and other industrial applications. However, low output power of sources, complexity of the terahertz detection systems, and high insertion loss of modulators, switches, and other components limits the wide

exploitations in everyday life applications. Graphene has been demonstrated as an efficient material to control and sense terahertz radiations, due to its unique optical and electronic properties. Using graphene as an active material in THz band have a great promise in the realizations of more efficient, compact, cost-effective, and lossless terahertz components.



Chapter 3

Optical Properties of Graphene

Graphene is a two-dimensional crystal of carbon atoms with honeycomb lattice structure [2, 49, 50]. Due to its strong interlayer bonding, graphene exhibits high tensile strength and stability at standard conditions. The carbon atoms in the lattice create sigma bonding along the plane and π bonding perpendicular to the plane of crystal. These bondings arise from the hybridization of outer shell electrons. Carbon has four electrons in its outer orbitals. Valence electrons are distributed filling 2s and 2p orbitals, hence resulting in sp^2 hybridizations. S orbital interacts with only p_x and p_y orbitals leaving free perpendicular p_z orbital. The three hybridization states of sp^2 orbitals results in a hexagonal structure of graphene. So carbon atoms are bonded by in plane sigma bonding exhibiting hexagonal structure. Neighboring p_z orbitals interact with each other creating perpendicular to lattice plane π -bonding and π^* -antibonding. Moreover, the half-filled p_z orbitals are responsible for the conductance of graphene sheet.

3.1 Electronic band structure of graphene

Extraordinary electronic property of graphene is a result of linear band dispersion at Dirac cone approximation [51-53]. The band theory of graphene were studied long before the first successful isolation of graphene [11, 12]. At that time it was believed that single layer of 2d-crystal of carbon atom would be unstable due to thermal excitations. Figure 3.1 demonstrates the lattice structure of graphene. The dashed area constitutes the unit cell with vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. The unit cell contains the two symmetric atoms A (red) and B (blue). Figure 3.1a shows the first Brillouin zone with vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. Each corner at the Brillouin zone represents Dirac point where conduction and valence bands meet. The Γ point is the zone center and the M is saddle point.

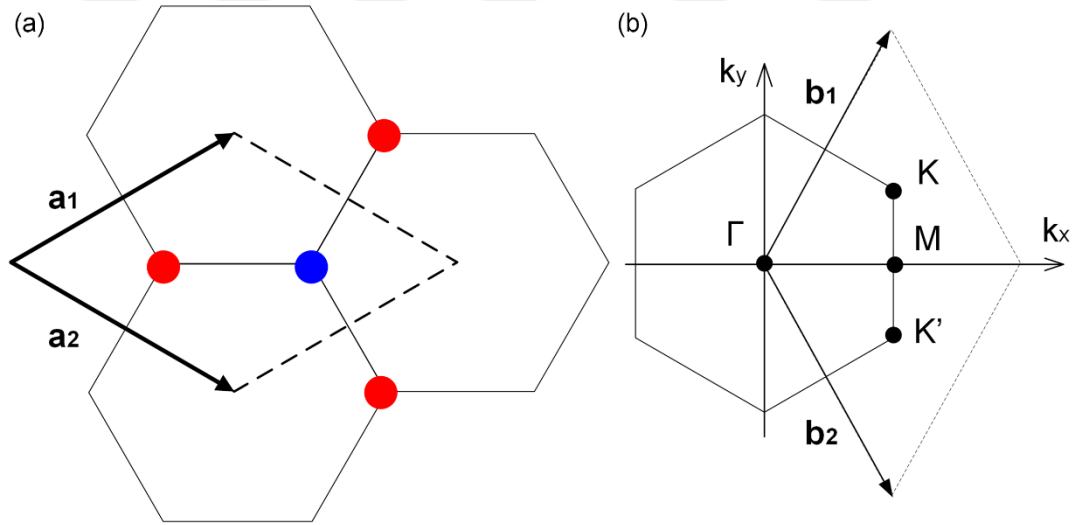


Figure 3.1 Crystal structure of graphene (a) Hexagonal crystal structure of graphene (left). Units cell indicated as dashed area with corresponding unit vectors ($\mathbf{a}_1$, $\mathbf{a}_2$). There two atoms in unit cell. (b) reciprocal lattice and vectors. First Brillouin zone of hexagonal structure with unit vectors ($\mathbf{b}_1$, $\mathbf{b}_2$). Dirac points are each hexagon corners. First Brillouin zone, Figure 3.1(b), contains six corner points also known as the Dirac points. These Dirac points fall into two groups of symmetry, hence it suffices to expand at K and K' points to determine the dispersion relation of the whole crystal.

$$\mathbf{K} = \frac{2\pi}{3a} \left(1, \frac{1}{\sqrt{3}}\right), \quad \mathbf{K}' = \frac{2\pi}{3a} \left(1, -\frac{1}{\sqrt{3}}\right) \quad 3.1$$

The band energy dispersion of graphene can be approximated using s-band tight-binding formalism. Equation 3.2 represents the energy band dispersion relation of graphene.

$$E_{\pm}(k_x, k_y) = \pm\gamma_0 \sqrt{1 + 4 \cos \frac{\sqrt{3}k_x a}{2} \cos \frac{k_y a}{2} + 4 \cos^2 \frac{k_y a}{2}} \quad 3.2$$

where $a = 1.42\sqrt{3} \text{ \AA}$ is the lattice constant, γ_0 is the nearest neighboring hopping energy and the k_x and k_y are the x and y components of $\mathbf{k}$ momentum respectively. By expanding the equation 3.2 at Dirac points for momentum of $\mathbf{K} + \mathbf{\kappa}$, with ($\mathbf{K} \gg |\mathbf{\kappa}|$), and applying small angle approximation we end up with linear dispersion relation.

$$E_k = \pm \hbar v_f |\mathbf{k}| \quad 3.3$$

where v_f is the Fermi velocity of Dirac fermion, $\mathbf{k}$ is a vector in momentum space. This linear relationship of momentum and energy is valid only near the Dirac points.

3.2 Electrical gating of graphene

Different electrostatic gating methods have been developed to control charge carrier concentrations on graphene. Figure 3.2 illustrates the schematic representations of the electrostatic gating techniques. One of the most commonly used methodology is to exploit a doped silicon as the back-gate electrode and a thin oxide layer as the gate dielectric. Graphene is transferred on top of oxide layer. Hence, dielectric medium isolates graphene from back-gate electrode and is used the gating medium. Using this method carrier densities of 10^{12} cm^{-2} with corresponding Fermi energy of 0.3 eV can be induced on graphene at high applied voltages ($>50 \text{ V}$). The limiting factor of back-

gate configuration is the dielectric breakdown which prevents to excite higher charge densities on graphene.

Another method to induce carriers on graphene is top-gating configuration (Figure 3.2(b)). This method was developed to address individual cells on the device chip, and requires more photolithographic steps than the back-gating approach. Graphene on a solid substrate is deposited with thin dielectric layer to isolate graphene from the top-gate electrode. After several steps in photolithography, by metallization process gating electrodes are designed. Applying bias voltage to the graphene and top-gate electrodes induces similar order of carrier densities with back-gating scheme. Although, top-gating method has advantages of individually addressing each device on a multipixel chip, it is also limited by the dielectric breakdown. Moreover, poor plasma exposure endurance and hydrophobic nature of graphene cause the dielectric layer to be bad in quality.

Final method of exciting charge carriers on graphene is by electrolyte gating. Figure 2.2c illustrates the schematic view of the electrolyte gating technique. Electrolyte liquid consists of mobile ions of both positive and negative polarity. When the bias voltage is applied electrical double layers (EDL) are created at the interfaces of graphene and gating electrodes. The thickness of the EDL is around few nanometers. Polarized ions at the interface create strong electric fields which excites carrier densities of 10^{14} cm^{-2} , with corresponding $\sim 1 \text{ eV}$ Fermi energies on graphene. Figure 2.2d demonstrates the voltage drop across the gating terminal for both dielectric and electrolyte based gating. For solid dielectric gating the voltage linearly drops across two electrodes. However, for electrolyte gating the voltage is fairly constant across the terminals and rapidly drops at the interfaces. The limiting factor of this gating approach is the electrochemical window of the electrolyte to achieve high densities of charge carriers on graphene. Electrolyte with large electrochemical window is ionic liquid which can be used to shift Fermi energy of graphene to more than 1 eV.

Alternatively, liquid crystal proton gels have been recently demonstrated to achieve Fermi energies of around 1.5 eV on graphene [54].

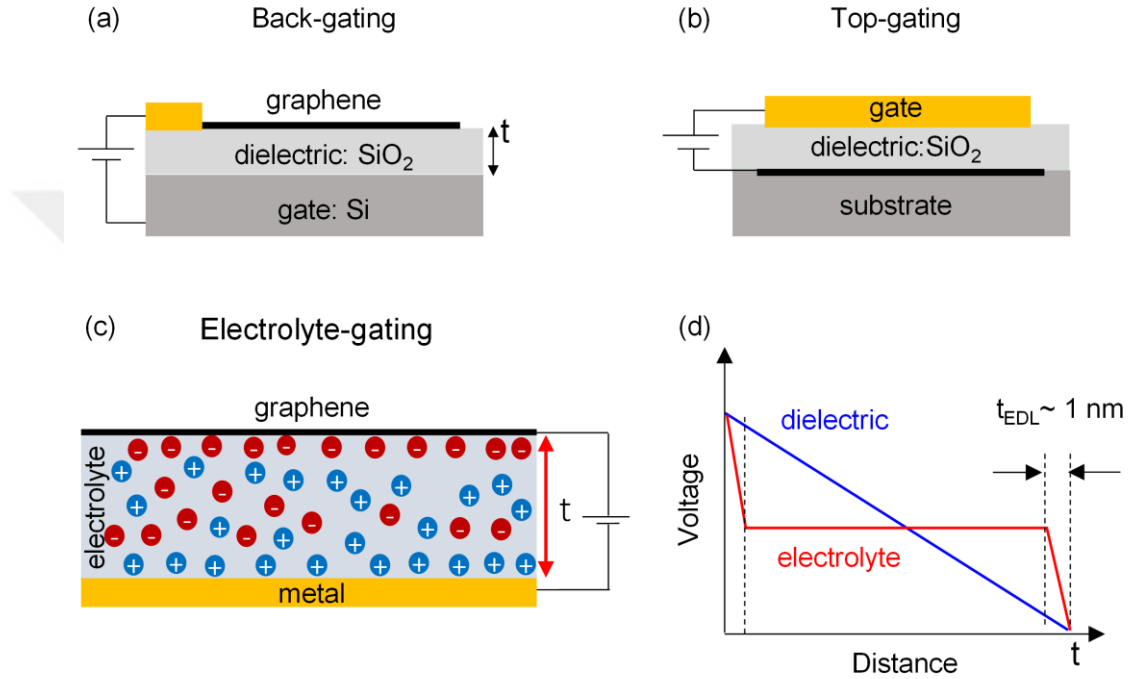


Figure 3.2 Gating methods of graphene (a-c) General gating methods used to control the electronic properties of graphene. (d) Schematic representation of the voltage drop across the gate terminals of dielectric and electrolyte devices. Voltage linearly drops between the graphene and gating electrodes for solid dielectric based devices, blue line. However, voltage is constant across the electrodes and drops rapidly at the interfaces of the electrodes, red line. Electrical double layers created induce high electric fields at the interfaces.

3.3 Optical properties of graphene

Due to its unique electronic and optical properties, graphene has wide electromagnetic response from UV to microwave frequencies [37, 51, 55, 56]. The mechanism of graphene's response can be summarized by two electronic transitions, interband and intraband. Interband electronic transitions dominate at higher photon

energies, namely, at visible and near-infrared range of electromagnetic spectrum. These transitions are nearly frequency independent, and amounts to universal constant $\pi\alpha = e^2/4\hbar$. The latter mechanism is free-carrier absorption of electromagnetic waves within the band. The photons with low energies are scattered by phonons or impurities to give off its energy. Figure 3.3 demonstrates the estimated absorption of single layer graphene over a broad range of electromagnetic spectrum. Both of the absorption mechanisms are highly dependent on Fermi energy of graphene. Relying on the Fermi level of graphene the cut-off frequency of interband transitions shifts to higher energies preserving constant value while more charge carriers enhance the intraband transitions at greater levels of doping.

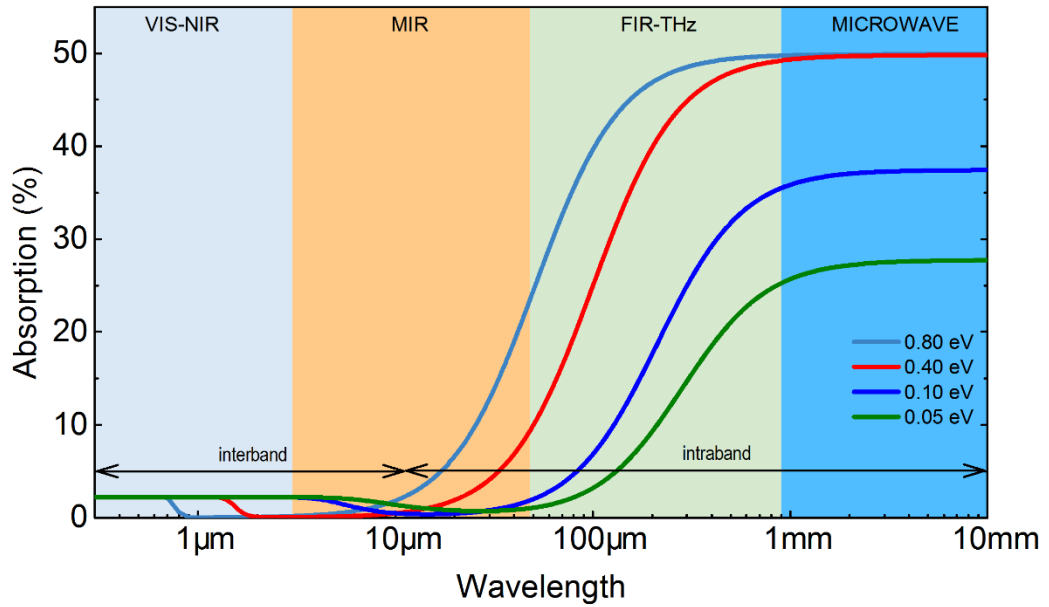


Figure 3.3 Optical response of graphene from visible to microwave region of electromagnetic spectrum. At visible-near infrared, interband transitions dominate absorbing 2.3 % of incident energy. At low energies, THz-microwave, intraband transitions dominate. The maximum of 50 % energy can be absorbed by single layer graphene.

The extraordinary electromagnetic response of graphene is quantified by its frequency dependent conductivity. The derivation of the conductivity is determined from Kubo formalism [57] or alternatively by introducing perturbation on density matrix. Equation 3.4 shows the integrations for both interband and intraband terms respectively. Using Dirac cone approximation

$$\sigma(\omega) = \frac{e^2 \omega}{i\pi \hbar^2} \left(\int_0^\infty d\epsilon \frac{f(-\epsilon) - f(\epsilon)}{(\omega + i\delta)^2 - 4\epsilon^2} - \int_{-\infty}^\infty d\epsilon \frac{|\epsilon|}{\omega^2} \frac{df(\epsilon)}{d\epsilon} \right) \quad 3.4$$

where e is the electronic charge, $\hbar$ is the reduced Plank's constant, and i being complex number. The Fermi-Dirac distribution function is expressed as,

$$f(\epsilon) = \left(\exp \left(\frac{\epsilon - \mu}{k_B T} \right) + 1 \right)^{-1} \quad 3.5$$

where μ is the chemical potential, k_B is the Boltzmann constant, and T is the temperature.

Using Dirac cone approximations and Fermi-Dirac distribution for the carrier densities equation 3.4 will result in interband and intraband conductivities.

3.3.1 Interband electronic transitions

Interband carrier transition arises when photon gives off its energy exciting an electron from valence to conduction band. When a photon with right amount of energy impinges on graphene, it excites an electron from the valence band to the conduction band creating electron-hole pair. This is known to be interband absorption. The condition for this absorption to take place is that the photon energy must be greater than the twice Fermi energy of graphene ($2E_F \leq \hbar\nu$). The photons with satisfying energies are absorbed, and all other photons pass through graphene sheet. Due to Pauli blocking, Figure 3.4b, the onset of interband transitions are varied

for various values of Fermi energy. By simply shifting the Fermi level of graphene, the interband transitions can be blocked.

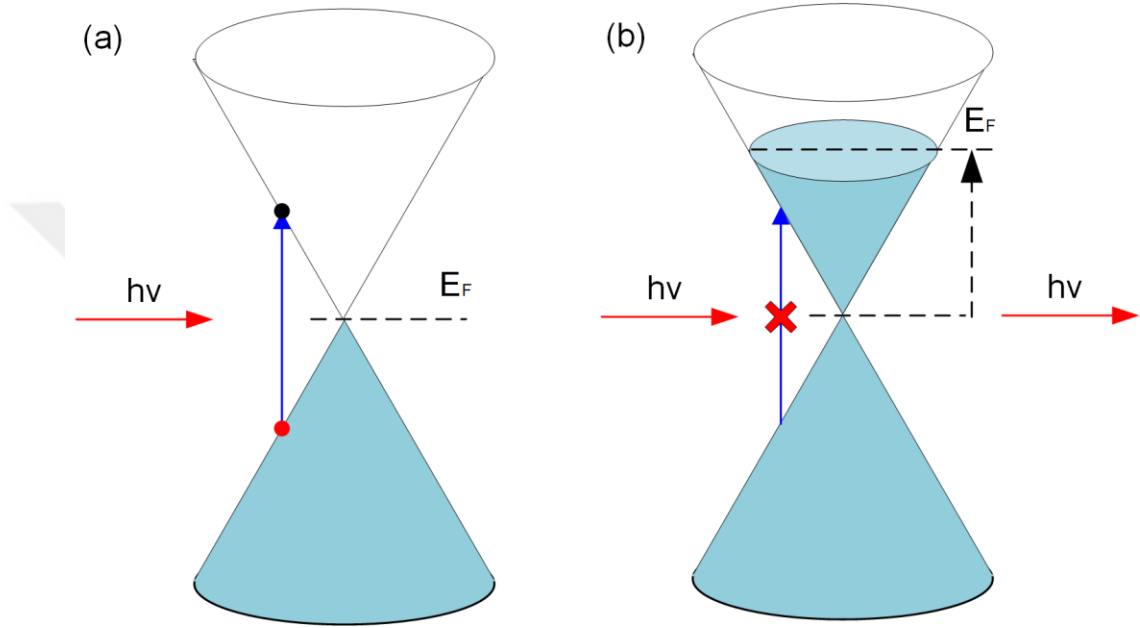


Figure 3.4 Pauli blocking. (a) Interband electronic transition occurs when the electron in valence band is excited to conduction band by photon absorption. The photon is absorbed when its energy exceed $2E_F$. (b) This absorption cannot take place if the Fermi energy of graphene is higher than photon's energy.

Figure 3.4 illustrates the band to band carrier transitions. When photons hit graphene with energies equal or greater than the twice Fermi energy, they excite electron from valence to conduction band creating electron-hole pair, Figure 3.4(a). The created pair, then undergoes non-radiative recombination. If the photon energy is less than $2E_F$ then the band to band carrier transition is blocked, and photon passes through graphene without losing its energy, Figure 3.4(b). Hence, the interband absorption mechanism can be monitored by simply shifting the Fermi energy of graphene. The Fermi level can be changed by electrostatic gating, or electrolyte gating. The optical conductivity of graphene is a complex function depending on Fermi energy of graphene,

$$\sigma_{\text{inter}}(\omega, E_F, T) = \sigma'(\omega, E_F, T) + i\sigma''(\omega, E_F, T) \quad 3.6$$

Solving the first integral in equation 2.3 yields real and imaginary part of the optical conductivity as,

$$\sigma'(\omega, E_F, T) = \frac{\sigma_0}{2} \left(\tanh\left(\frac{\hbar\omega + 2E_F}{4k_B T}\right) + \tanh\left(\frac{\hbar\omega - 2E_F}{4k_B T}\right) \right) \quad 3.7$$

where k_B is the Boltzmann constant, $\sigma_0 = 60 \mu\text{S}$ is the universal conductance, E_F is the Fermi energy, $\hbar$ is the reduced Plank's constant, and ω is the angular frequency of photons.

$$\sigma''(\omega, E_F, T) = \frac{\sigma_0}{2\pi} \ln\left(\frac{(\hbar\omega + 2E_F)^2}{(\hbar\omega - 2E_F)^2 + (2k_B T)^2}\right) \quad 3.8$$

where universal conductance σ_0 is defined as,

$$\sigma_0 = \frac{e^2}{4\hbar} \quad 3.9$$

The real and imaginary terms of optical conductivity $\sigma_{\text{inter}}(\omega)$ is plotted as a function of frequency in [Figure 3.5]. The real part of the conductivity exhibits step like behavior and accounts for the interband absorption, and the imaginary part of the conductivity diverges at low temperatures [14].

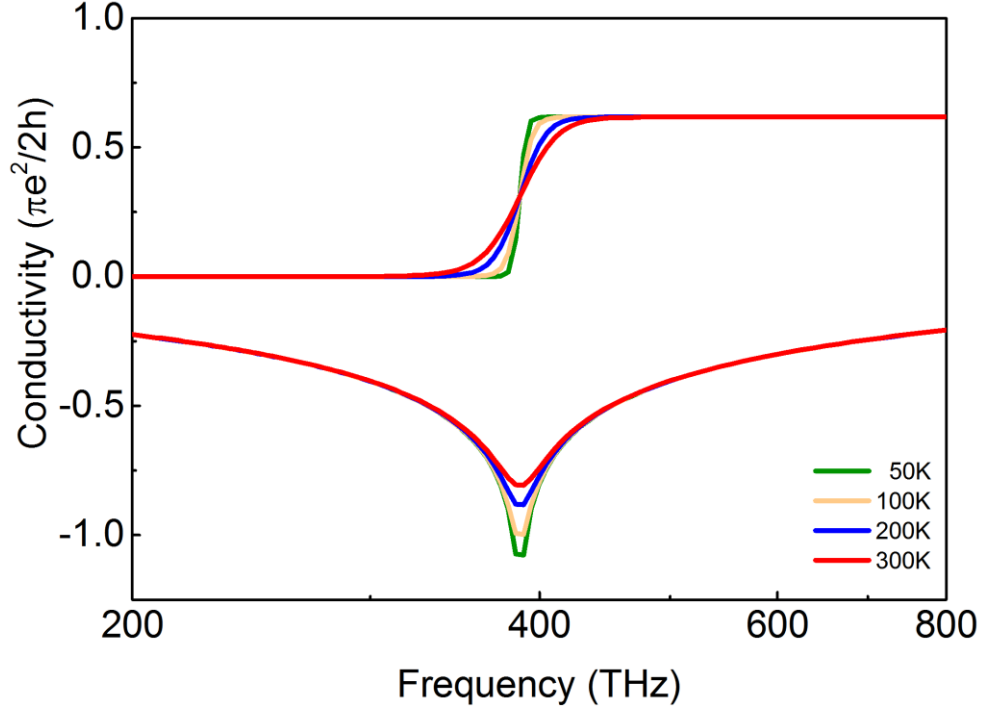


Figure 3.5 The dependence of real and imaginary values of complex conductivity of graphene on temperature.

Figure 3.6(a) shows the calculated spectrum of absorption from 0.6 to 1.2 eV Fermi level of graphene. The step-like behavior comes from the real part of the complex conductivity, Equation 4. The absorption is proportional to universal optical conductance $\sigma_0 = e^2/4\hbar$ as $A(\omega) = (4\pi/c)\sigma(\omega) = \pi\alpha$ (Figure 3.6(a)). The transmittance of a monolayer graphene is determined by Fresnel equations [4]

$$T = \left(1 + \frac{\pi\alpha}{2}\right)^{-2} \approx 1 - \pi\alpha = 97.7\% \quad 3.10$$

where $\alpha = e^2/(4\pi\epsilon_0\hbar c) \approx 1/137$ is the fine structure constant. The Figure 3.6(b) shows the transmission spectrum for different values of Fermi level. Since the reflection from single layer graphene is negligible, the absorbance $A \approx 1 - T = 2.3\%$.

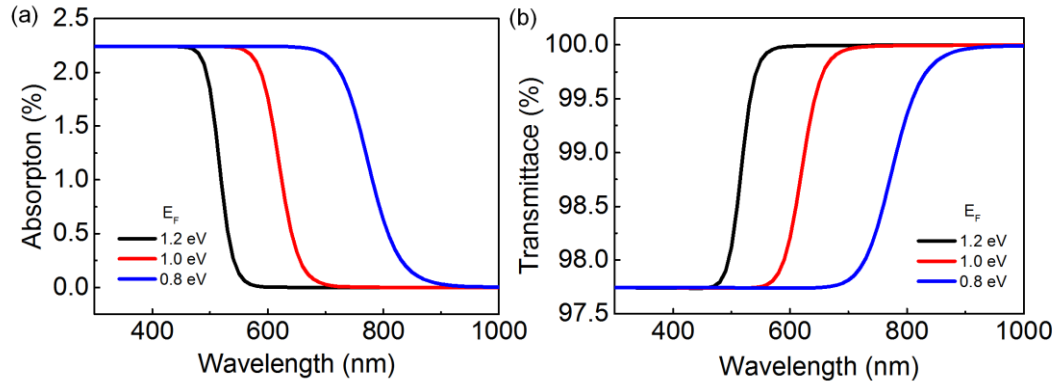


Figure 3.6 (a) Absorption of a single layer graphene as a function of Fermi energy. 2.3 % of incident wave is absorbed when the photon energy is the twice the Fermi energy. As the Fermi energy shifts to higher levels, the more energetic photons are blocked. (b) Transmittance spectrum of monolayer graphene at various values of Fermi level.

3.3.2 Intraband electronic transitions

At low frequencies the electromagnetic absorption in graphene is more pronounced. The presence of free carriers in conduction band highly effects the intensity of absorption. Intraband carrier transitions are the generation of hot electrons in the conduction band or hot holes in the valence band up on electromagnetic wave absorption. These free carriers then are thermally dissipated in the lattice. The absorption is enhanced with the carrier concentration, (Figure 3.7). Due to energy and momentum selection rules, direct absorption of photons cannot take place in the same band. Hence, photon absorptions are mediated by imperfections, or phonons. To understand the free carrier absorption we have to look at the frequency dependent conductivity.

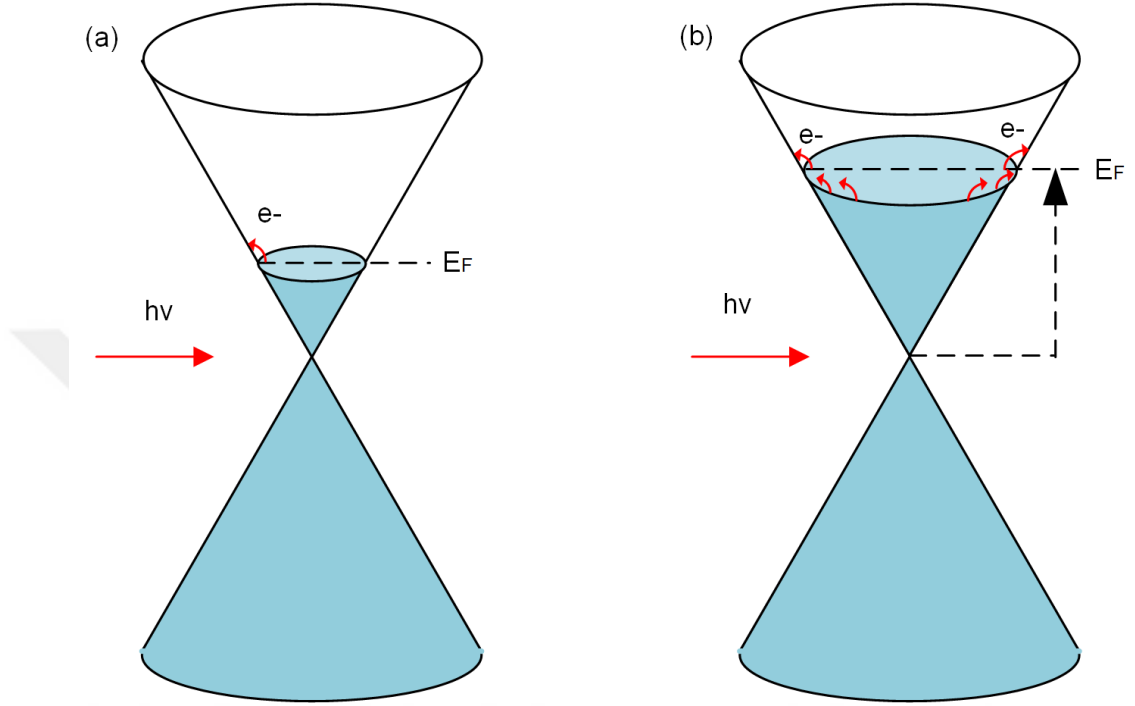


Figure 3.7 Intraband electronic transitions. (a) Photons with low energies are absorbed by the charge carrier in the conduction band. (b) The absorption is enhanced as more carriers are introduced into the conduction band.

At low frequencies the electromagnetic response of graphene can be represented by Drude model. Solving the second integral in the equation 3.4, we end up with,

$$\sigma_{\text{intra}}(\omega) = \frac{i2e^2T}{\pi\hbar(\omega + i\tau^{-1})} \log\left(2 \cosh\left(\frac{E_F}{2k_B T}\right)\right) \quad 3.11$$

In the limit $E_F \gg k_B T$ the conductivity takes the form,

$$\sigma(\omega) = \frac{\sigma_{\text{DC}}}{1 + i\omega\tau} \quad 3.12$$

$$\sigma_{\text{DC}} = \frac{e^2}{\pi\hbar^2} E_F \tau \quad 3.13$$

$$R_S E_F \tau = \frac{\pi \hbar^2}{e^2} = 8.495 (\text{k}\Omega \text{eVfs}) \quad 3.14$$

where e is electron charge, $\hbar$ is reduced Plank's constant, τ is transport scattering time, R_S sheet resistance of graphene. Equation 3.14 demonstrates the relation among the sheet resistance, Fermi energy and scattering time of graphene.

$$\text{Re}(\sigma(\omega)) = \frac{\sigma_{\text{DC}}}{1 + \omega^2 \tau^2} \quad 3.15$$

$$\text{Im}(\sigma(\omega)) = \frac{\sigma_{\text{DC}} \omega \tau}{1 + \omega^2 \tau^2} \quad 3.16$$

Equations 4.12 and 4.13 are plotted in the figure (b) and (c) for various values of Fermi level respectively. The half values of real term of the conductivity determine the scattering time frequency. The shift to higher frequencies is an indication of scattering time frequency. Carrier scattering time is highly dependent on doping level, dropping exponentially at higher values of Fermi level and saturating at certain value for undoped graphene.

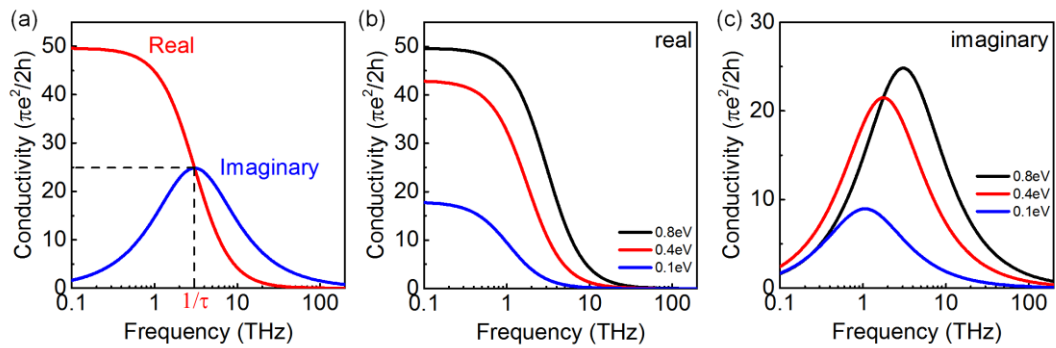


Figure 3.8 Drude conductivity of monolayer graphene. (a) Real and imaginary parts of Drude conductivity. The frequency value at the intersection of two curves corresponds to carrier scattering rate. (b) Real conductivity at different Fermi energy values. (c) Imaginary conductivity at different Fermi energy values.

3.4 Synthesis of graphene

The first graphene film was isolated by exfoliation method. It produced high quality, single atom thick graphene. However, this method is not practical for large scale graphene, since produces few micron sized sheets. Other ways to produce graphene are chemical vapor method (CVD), epitaxial growth on SiC substrates, reducing graphene oxide, etc. Above all, industrially promising method is chemical vapor deposition in terms of scalability, cost, etc. Using CVD both single- and multi-layer graphene sheet can be produced depending on metal catalyst.

We use copper foils to synthesize single layer graphene in a quartz chamber, Figure 3.9. Due to copper's limited solubility of carbon atoms, synthesis of graphene is self-terminating process. That's, when the synthesis process starts by breaking out of carbon atoms from either methane (CH_4) or other hydrocarbon source, the carbon atom combine to produce hexagonal crystal structure and this process is terminated once the copper surface is fully covered with carbon atoms. Thus, copper is not suitable to produce multilayer graphene. Instead nickel substrate is utilized in chemical vapor method. Since nickel has high solubility of carbon atoms, several layers of graphene sheet can be grown. Graphene samples produced by CVD method is polycrystalline with grain boundaries. Compared to micromechanical cleavage graphene [1], CVD graphene has relatively low mobilities (around few thousand [58]). However, the former method is limited to micrometer sized graphene flakes and is not practical for large are applications. In addition, mobilities of CVD graphene can be improved by optimizations [59]. Transferring of graphene to various substrates is another essential issue for implementing graphene in applications. In this section synthesis of graphene by chemical vapor deposition method and transferring techniques are described.

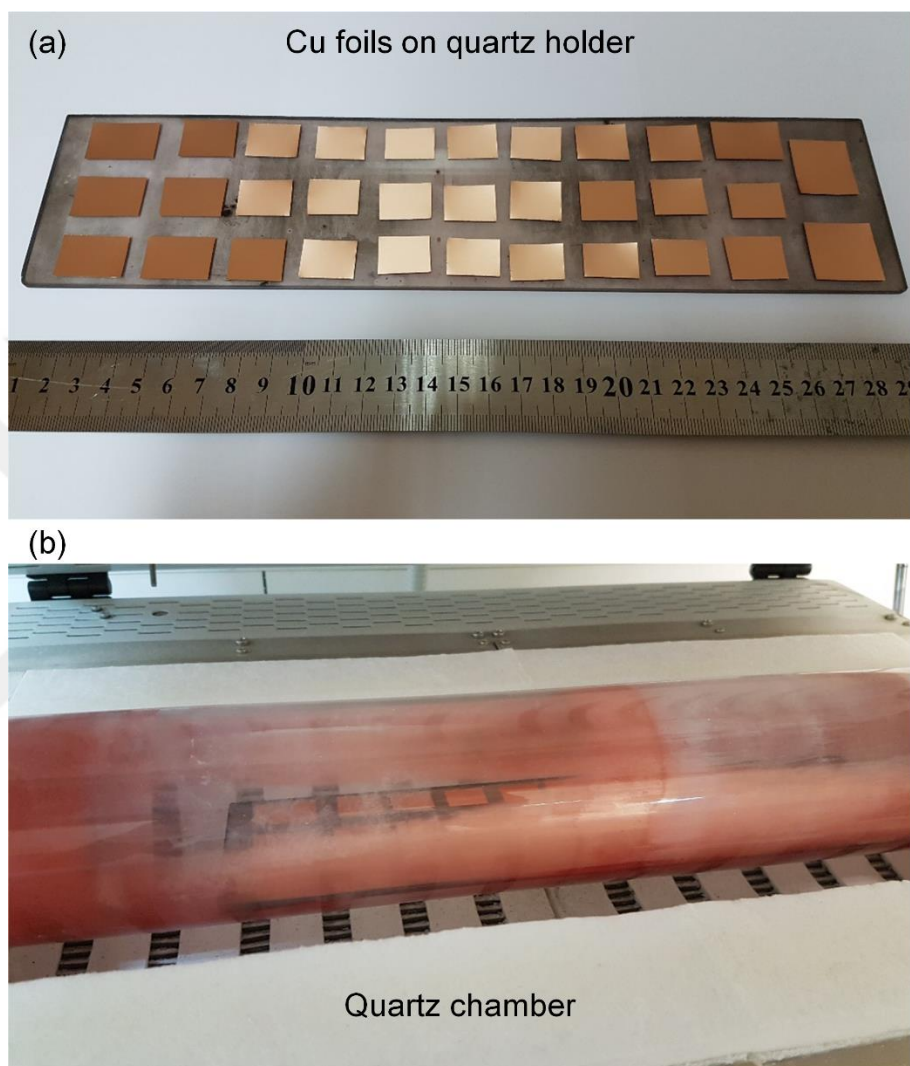


Figure 3.9 (a) Copper foils are cut and placed on quartz holder. The size is limited by the holder $7 \times 30 \text{ cm}^2$. (b) Quartz chamber embedded in furnace, where the synthesis occurs.

Conventional chemical vapor deposition (CVD) systems constitute of gas sources, a furnace, a chamber, and flow controlling units. The commonly used gases are hydrogen (H_2) and methane (CH_4). The hydrogen gas is utilized as the hat can go above 1000 degrees of Celsius, and an electronic flow control unit. Alternatively, methane, ethylene, and other hydrocarbon gases are usually used as a source for

carbon atoms. Hydrogen gas is used to anneal the surface of copper foils by removing chemical residues during the growth process. Specific to our system, we have chiller unit to reduce the temperatures on the edges of the chamber, and prevent damaging the O ring materials.



Figure 3.10 CVD system. (a) Furnace with quartz chamber, which can go up to 1070 degrees. The pump is used to vacuum the chamber. (b) Before the growth the chamber is vacuumed down to 3-6 mTorr.

Our CVD system is shown in Figure 3.10(a). The synthesis process starts with taking the chamber into vacuum down to 3-6 mTorr, Figure 3.10(b). To grow single layer graphene we use ultra-smooth copper foils (20 μm thick). Under hydrogen gas flow (100 sccm) we heat the furnace up to 1035 $^{\circ}\text{C}$. When the favorable temperature is reached, the methane (CH_4) is sent (10 sccm) for 1 minute under 100 sccm hydrogen, Figure 3.11(b). After 1 minute we terminate the growth process by shutting the methane (CH_4) flow and opening the gate of the furnace. When the chamber temperature reaches the ambient values, we stop the hydrogen flow and take out the samples from the chamber.



Figure 3.11 (a) The gases used during the growth are methane (CH_4) as carbon source and hydrogen (H_2) to anneal the copper surfaces.

3.5 Transfer process of graphene

Since the discovery of graphene, several methods have been developed to grow graphene. However, not all methods have the advantage of transferring graphene on different surfaces. For example, graphene cannot be transferred from SiC substrate. Since the graphene cannot be grown on any surface, the ability to transfer grown graphene is essential. Using CVD method has advantage on transferring graphene to almost all kinds of surfaces, whether it's solid or flexible.

Once graphene is grown on copper foil, it is possible to transfer it to various surfaces with the help of polymers. First we drop photoresist (Shipley 1813) on copper foil with graphene, Figure 3.12(a). It is baked overnight in oven at 65 °C. Once photoresist is baked the copper is removed by wet etching, Figure 3.12(b). The iron chloride (FeCl_3) or nitric acid or any other suitable solution can be used to remove the copper. The difference in the usage of iron chloride and nitric acid are reflected on the resultant graphene quality. If the iron chloride solution is used to etch the copper foils, it leaves chemical residues on the surface of graphene. These residues are hard to remove and stays with graphene samples. Unlike iron chloride, nitric acid removes copper neatly leaving graphene sample less contaminated. However, nitric acid solution dopes graphene samples. It may take days for graphene to return to its undoped state.

At final stage we end up with photoresist holding graphene layer. To transfer graphene on to polyethylene or any other substrate, we place graphene on photoresist on polyethylene graphene facing the surface, Figure 3.12(c). Then we heat the sample up to 90 °C and remove the photoresist using acetone and IPA, Figure 3.12(c,d). Finally, we have graphene on polyethylene membrane, Figure 3.12(e). Similarly, graphene can be transferred to solid (glass, quartz, SiO_2/Si , etc.) or flexible substrates. This technique can be applied to any substrates which can be heated up to certain temperatures.

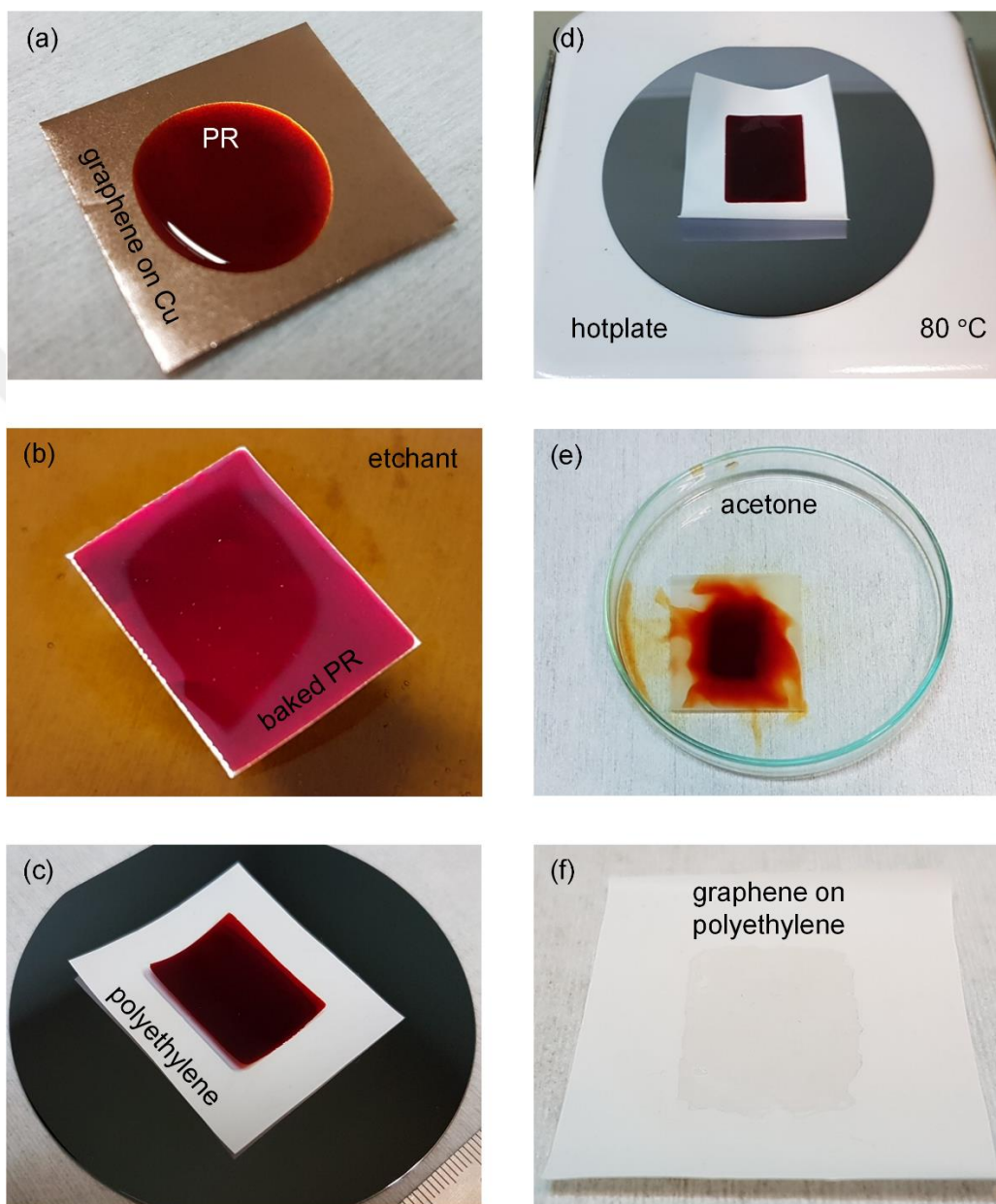


Figure 3.12 Transfer printing process. (a) Shipley 1813 PR is dropped on CVD grown graphene, and baked overnight at 65 degrees. (b) Copper is etched in iron chloride solution. The baked PR is used as a holder of graphene. (c) When all copper is etched, PR holding graphene is placed on a substrate (Polyethylene). (d) To transfer graphene on to substrate the sample is heated. (e) Then PR is washed with acetone/IPA. (f) The transferred single layer graphene on polyethylene membrane.

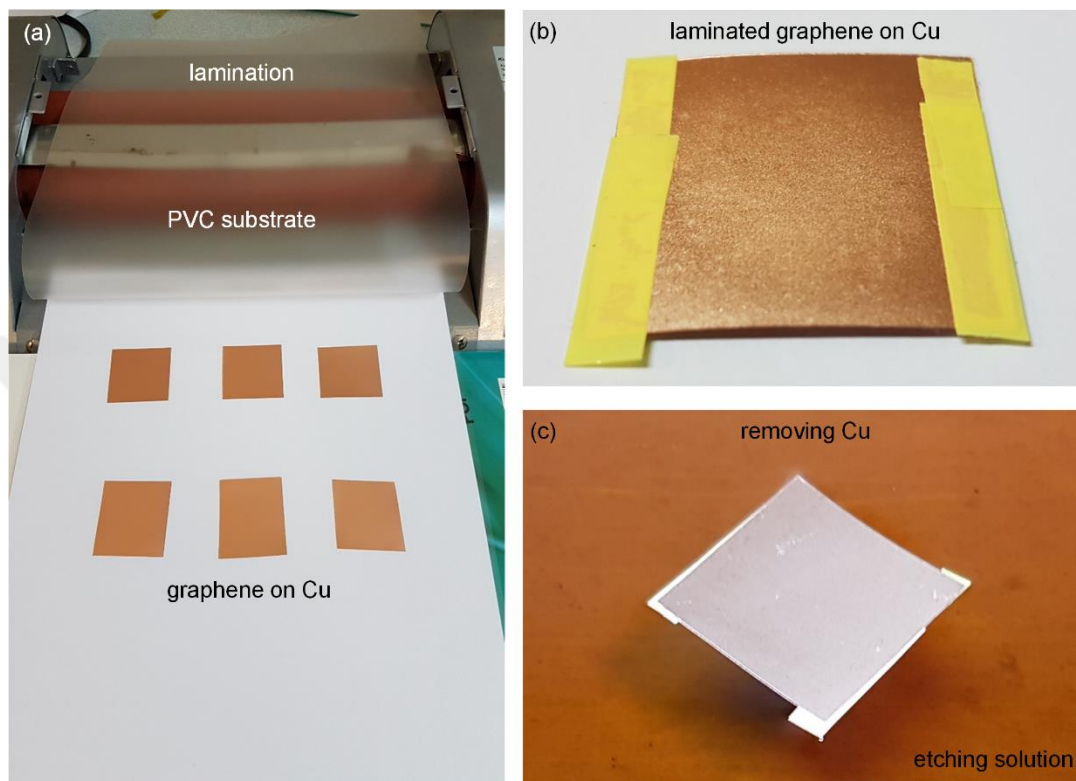


Figure 3.13 Transferring graphene via lamination. (a) Laminating machine. CVD grown graphene samples are arranged on paper covered by PVC from both sides. (b) Laminated graphene. Graphene is sandwiched between Cu film (top) and PVC polymer (bottom). The tapes are used to cover the contacts. (c) Copper is removed via wet etching.

Another technique that we apply to transfer graphene is lamination. The area of synthesized graphene depends on the diameter of the chamber and the size of the holder. Our holder size is limited to $7 \times 30 \text{ cm}^2$; hence our samples are at most that size. However, larger size graphene growth can be optimized by using cylinder shaped holders. With that graphene samples of $30 \times 30 \text{ cm}^2$ can be grown. Large area graphene can be transferred to PVC, or polyethylene substrate by lamination. Figure 3.13 illustrates the transferring steps. To transfer graphene we use PVC (polyvinyl chloride) flexible polymer. PVC has an adhesive layer which has a melting point at around 90-100

°C. We place graphene on copper foils as shown in Figure 3.13(a) between two PVC sheets. The paper is used to separate the back copper from adhering to PVC. Then we laminate samples by rolling through laminating machine. Once the samples are laminated, we remove copper by wet etching, Figure 3.13(b,c). We intentionally leave copper stripes to make contact, Figure 3.14. The easiest way to check if graphene was grown is by looking at the resistance of graphene on PVC, Figure 3.14(c).

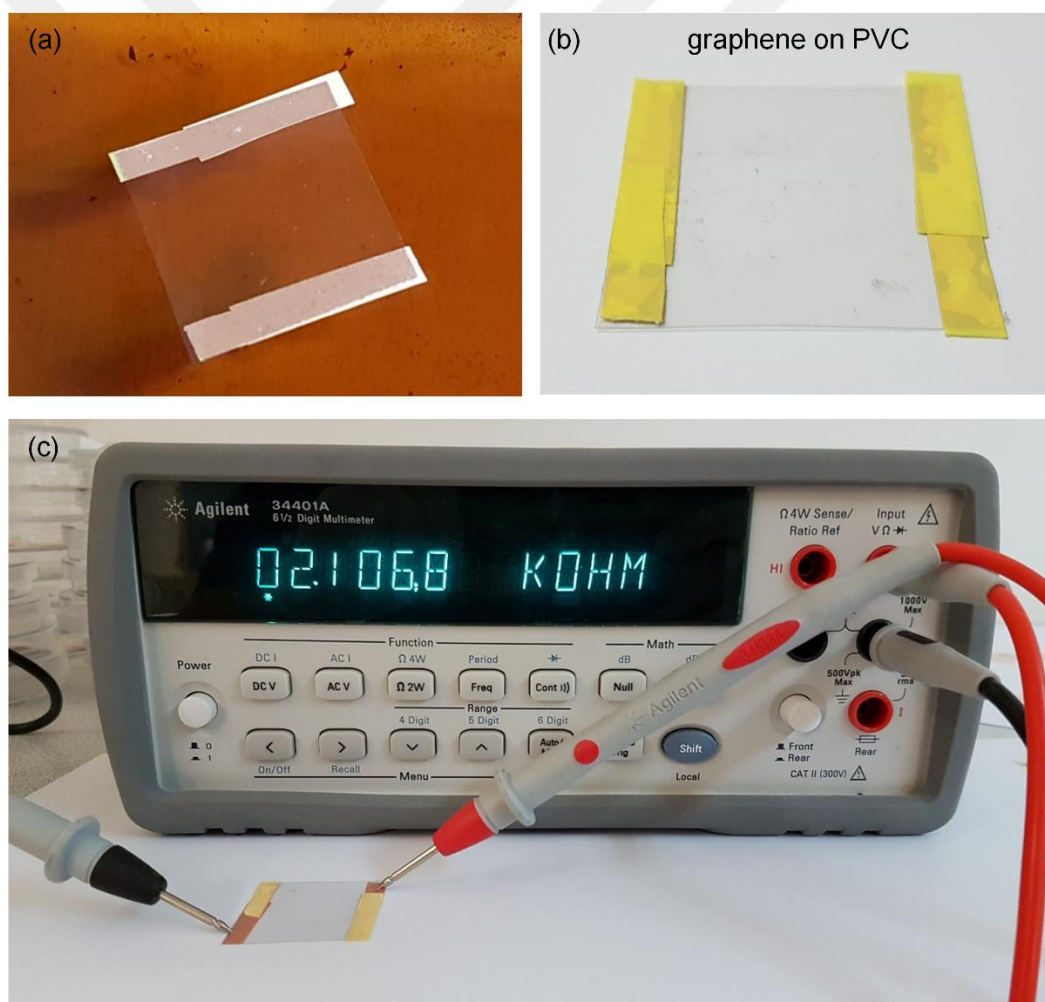


Figure 3.14 Laminated graphene. (a) Graphene sample after copper has been removed. (b) The laminated graphene sample with contacts. (c) The conductance of transferred graphene.

Chapter 4

Drude Response of Highly Doped Graphene

In this chapter, Drude response of highly doped graphene is studied. Graphene grown on copper foil is transferred on 20 μ m thick polyethylene membrane. Doping of graphene is changed via electrolyte gating. Gold on a substrate with circular opening was used as the gating electrode. The transmittance through the sample were measured with FTIR system for each Fermi energy from visible to terahertz range. We observed an increase in the transmittance due to Pauli blocking of interband electronic transitions. The Fermi energy of graphene were extracted from visible-NIR transmittance spectrum. The change in Fermi energy of graphene with gating voltage is linear up to 1 eV and similar for both electrons and holes. The terahertz transmittance decreased down to 55 % for highly doped graphene. Transport scattering time changed from 150 fs to 50 fs with Fermi level of graphene. Graphene's response satisfies Drude conductivity, and electrons and holes exhibit symmetric conductivities.

4.1 Introduction

Graphene, honeycomb lattice of carbon atoms, display amazing electronic and optical properties. Charge carriers in graphene behave like massless quasiparticles, also known as Dirac fermions. High crystallinity of graphene allows carriers to travel micrometer distances without scattering. Indeed, electrons in graphene possess one of the highest room temperature mobilities. Moreover, electronic band structure of graphene shows linear relation between energy and momentum suggesting high symmetry of charge carriers. Optical conductance of pristine graphene is nearly frequency independent and amounts to $\sigma_0 = e^2/4\hbar$ [2]. As a consequence of this conductance the transmittance of free standing graphene is also frequency independent and expressed by fine structure constant $\alpha = e^2/\hbar c$, [2, 50, 52, 56].

$$T_{\text{optical}} = \left(1 + \frac{\pi\alpha}{2}\right)^{-2} \approx 1 - \pi\alpha = 0.977 \quad 4.1$$

However, at low photon energies frequency dependent free-carrier absorptions dominate in graphene samples. These carrier transitions are highly dependent on carrier concentrations, or Fermi level, causing strong attenuations in wave amplitudes at higher values. High carrier mobilities and unique optical properties make graphene suitable to be used in optoelectronic device especially for terahertz applications. In fact, many studies suggested that graphene can be actively used in THz field which lacks the abundance of suitable materials. Graphene's extraordinary far-infrared activity is successfully explained by frequency dependent Drude conductivity. At THz frequencies graphene's conductivity satisfies Drude model. Infrared spectroscopic measurement confirmed the Drude-like response of charge carriers shedding light on its transport and transition mechanism. In their study, Horng et al experimentally probed the Drude weight and the scattering rate in a transistor type device [51]. They showed that both holes and electrons exhibit Drude like behavior.

In that configuration, anomalous Drude weight reduction was observed and was smaller than theoretically predicted results.

Two independent studies showed the semiconductor – to – metal transitions of a gated graphene by a pump-probe experiments [60, 61]. According to their studies, graphene on SiC and CVD grown graphene have different behaviors due to different induced charges. Anomalous reduction of Drude weight were observed for CVD graphene. As reported the terahertz photoconductance, in CVD graphene, had positive value near Dirac point and changed sign for higher values of Fermi level. This difference is a result of graphene's transition from semiconducting state to metallic state. Both photoinduced changes in Drude weight and scattering rate contributed to the terahertz conductivity. In charge neutral graphene, any extra pair of carriers would contribute to conductivity. Nevertheless, as the density of carriers increase scattering effect starts to be more effective. Hence, like in metals, conductivity suffered reduction with extra induced hot carriers. Interplay of two main parameters Drude weight and scattering time of carriers, accounted for the transitions in graphene.

4.2 Fourier transform spectroscopy measurement of graphene

In our study, we probed graphene far-infrared response at extremely high doping levels, using FTIR spectroscopy. We measured the transmittance single layer CVD graphene from 5000 cm^{-1} down to 100 cm^{-1} , or 3 THz. Transistor type of gating the graphene is rather limited and fails to shift the Fermi energy to more 4 meV due to dielectric breakdown. Different approaches must be addressed to accurately measure graphene response. Here, we applied electrolyte gating to generate high carrier concentrations on graphene. This method prevails transistor type devices by the ability of efficient Fermi energy shift up to 1 eV at moderate bias voltages. Another challenging factor is to employ suitable substrate in order to isolate graphene from substrate effects. Undoped silicon is commonly used for infrared applications because of moderate transparency in that range. However, it requires to be passivated to reduce the substrate effects. For our device structure porous polyethylene (PE) was

suitable substrate since it has high transparency at terahertz frequencies, graphene can be easily transferred on it, and it also show electrolyte-philic.

Within the Boltzmann transport theory, the frequency dependent sheet conductivity of graphene can be approximated as,

$$\sigma(\omega) = \frac{D}{\pi(\Gamma - i\omega)} \quad 4.2$$

where D corresponds to Drude weight, Γ is scattering rate. In metals or semiconductors with parabolic dispersion relation the Drude weight is $D = \pi n e^2 / m$. In graphene, it takes different form, $D = (v_F e^2 / \hbar) (\pi n)^{\frac{1}{2}}$ [61]. Here, n is charge concentration, $v_F = 10^6$ m/s. Hence, both scattering rate Γ and Drude weight D , are the key parameters governing the behavior of Dirac fermion in graphene at far-infrared region. Determining these parameters is crucial for optoelectronic applications. Studies revealed that Drude weight is found to be less than theoretically predicted values. Such results is accounted for approximations in determining Drude weight that electron-electron interactions could cause the anomalous reduction. Here we investigated Drude conductivity at highly doped graphene. Our results show that charge carriers in graphene exhibit symmetric behavior in Drude conductivities with varying bias voltages.

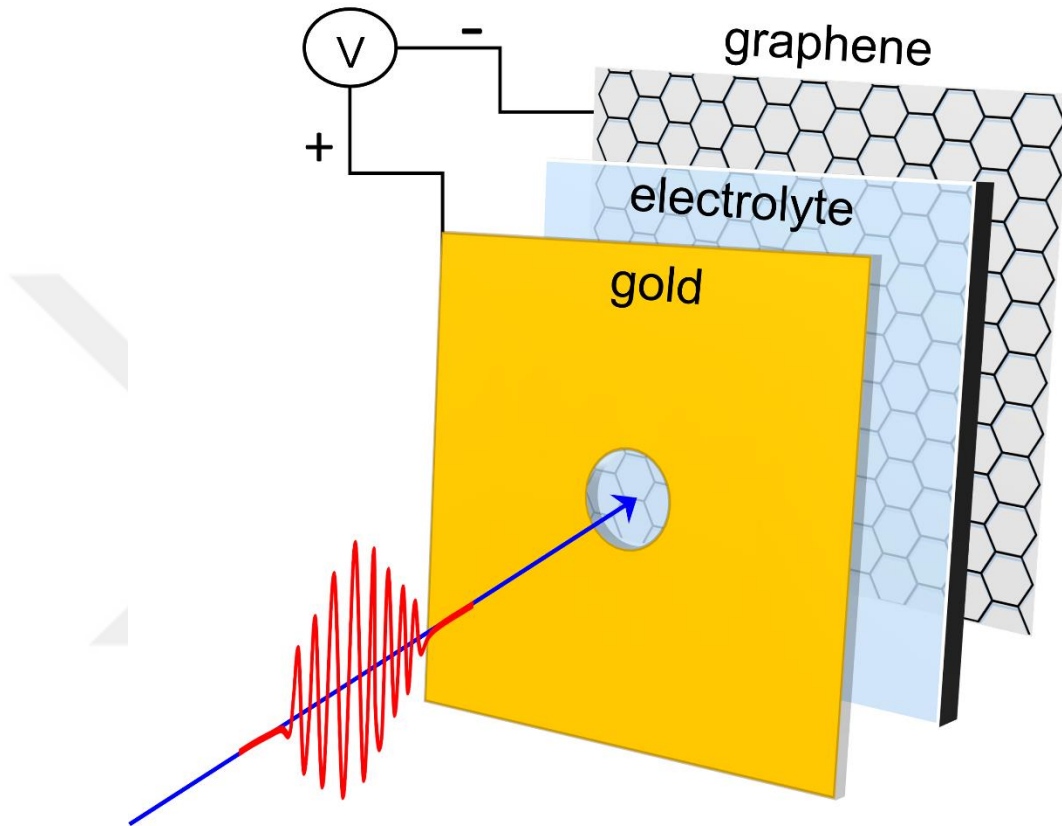


Figure 4.1 Schematic representation of device design. The device consists of gold layer, electrolyte medium and graphene on membrane. The gold on substrate with circular opening allows beam to pass through graphene without any interaction. As an electrolyte we used ionic liquid to efficiently gate graphene. The graphene is CVD grown and transferred on THz transparent polyethylene membrane.

The device structure, to measure the Drude response, is represented on Figure 4.1. It is formed of gold layer, electrolyte medium, and graphene. The gold layer is used as a gating contact. The 60 nm gold is evaporated on PVC substrate then the 6 mm circular opening is made. The incident beam passes through the opening unaffected. The graphene was synthesized in CVD system and transfer-printed on 20 μm polyethylene membrane. This membrane has 42 % porosity and transparency at

terahertz frequencies. Thus, the polyethylene functions as a separation between graphene sheet and gold electrode, and container for electrolyte. To shift the Fermi energy of graphene the bias voltage is applied as shown in the Figure 4.1. At zero bias the ionic liquid is neutral. However, at nonzero bias voltage, ionic liquid becomes polarized creating electrical double layers in the proximity of graphene layer. Thus, polarized ions result in high electric field in the medium inducing charge carrier up to 10^{14} cm^{-2} at relatively low voltages.

FT-Infrared Spectroscopy

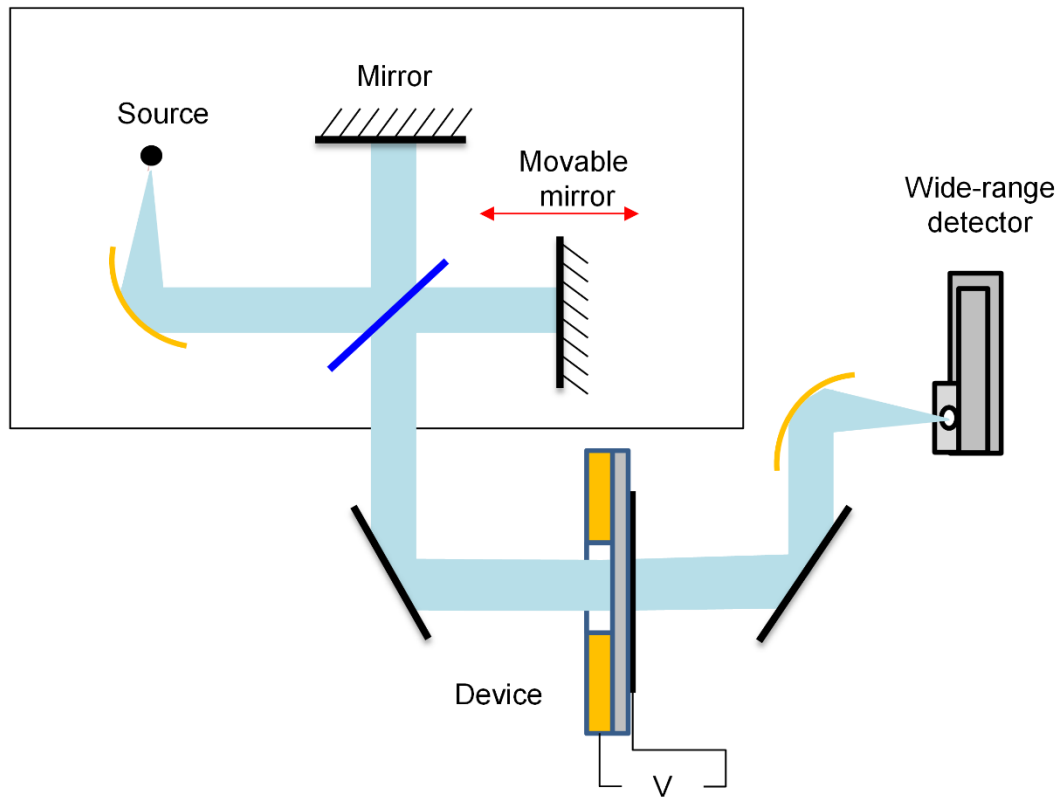


Figure 4.2 FTIR measurement setup. FTIR has both wide range source (VIS, NIR, FIR) and detectors.

To observe Drude response of graphene at extremely high doping levels, we used Bruker's V70x Fourier-Transform Infrared spectroscopy system. The FTIR system

consists of two sources a lamp for optical, and heated tungsten filament for low frequencies, corresponding detectors. we placed graphene device in a collimating beam as shown in the Figure 4.2. As a reference we took the whole device structure at the charge neutrality point of the graphene. Then, by changing the gating voltage we took the differential transmittance from the device.

The charge neutrality point of graphene is dynamic and relies on the gating structure. Figure 4.3 shows the measured capacitance and resistance of the graphene device from -2 V to 2 V. The Dirac point of the graphene determined as the extremum values of the capacitance (minimum) and the resistance (maximum). According to the Figure 4.3, the charge neutrality point is at 1.1 V. For capacitive structure of gold and graphene electrodes the Dirac point shifts toward positive (negative) bias voltage values from the neutral 0 V bias. This is related to the difference at work functions of gold and graphene. When the positive voltage is applied to gold layer keeping the graphene at ground, the electrons are induced at the graphene interface, and vice versa. Hence, for particular device structure where the positive terminal of the source meter is connected to gold electrode, and the ground terminal is connected to graphene layer, going from Dirac point to negative voltage would induce holes at graphene. Similarly, applying positive voltage to gold from reference point would induce electrons in graphene. In that sense, the capacitance plot reveals that to induce same amount of electron carriers the bias voltage must be at higher value due to the shift of Dirac point from zero bias. Thus, in this work hole regime is defined as going from charge neutrality point to negative values, and electron regime is defined as going from CNP to positive voltage values valid for connecting configuration shown in Figure 4.1.

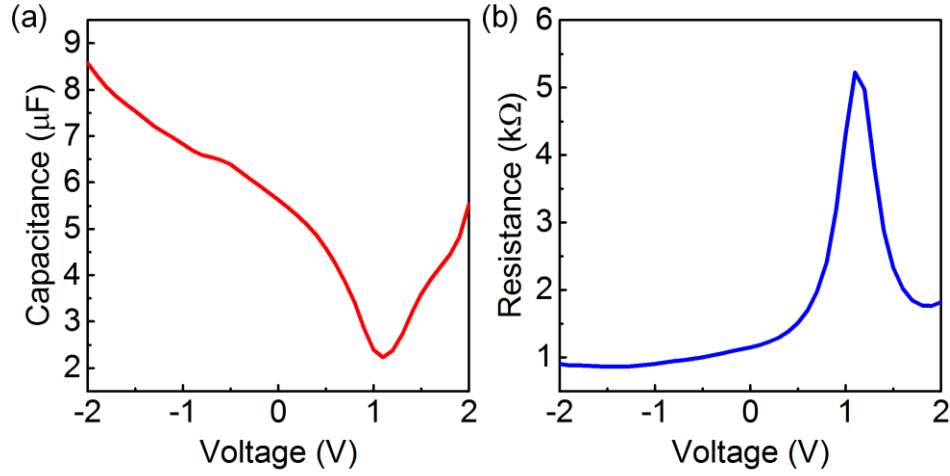


Figure 4.3 (a) Capacitance, (b) resistance of the graphene device as a function of bias voltage. The charge neutrality point occurred at 1.1 V.

In order to determine the Fermi level of graphene for corresponding bias voltages we measured the graphene device at visible and near-infrared wavelengths. Figure 4.3 demonstrates the resultant spectra for both hole and electron doping regimes. The absorption of suspended graphene is $A = \alpha\pi = 2.3\%$, where $\alpha = 1/137$ is the fine structure constant [2]. However, for graphene on dielectric substrate absorption is no longer 2.3 % due to substrate effects. The correction term must be included in the absorption equation [62, 63].

$$A = \pi\alpha \left(\frac{2}{n+1} \right)^2 \quad 4.3$$

where n is a refractive index of a medium. Hence, for graphene on microscope slide with $n=1.5$, the absorption is 1.5 %. Figure 4.4 demonstrates the measured transmittance at visible and near-infrared range of the spectrum for different bias voltages. The reference signal was recorded at the Dirac point of graphene. By varying the applied voltage we observed 1.5 % increase in the transmittance due to Pauli blocking. Since graphene has negligible reflectance at optical frequencies, we

can amount the change in the transmittance to absorption which is around 1.5 %. A glass slide is opaque after 5 μm , hence, we used 20 μm polyethylene membrane as a substrate. This membrane with ionic liquid is transparent from visible to terahertz frequencies, and has refractive index of ~ 1.6 . The change in the spectrum is similar for both holes and electrons.

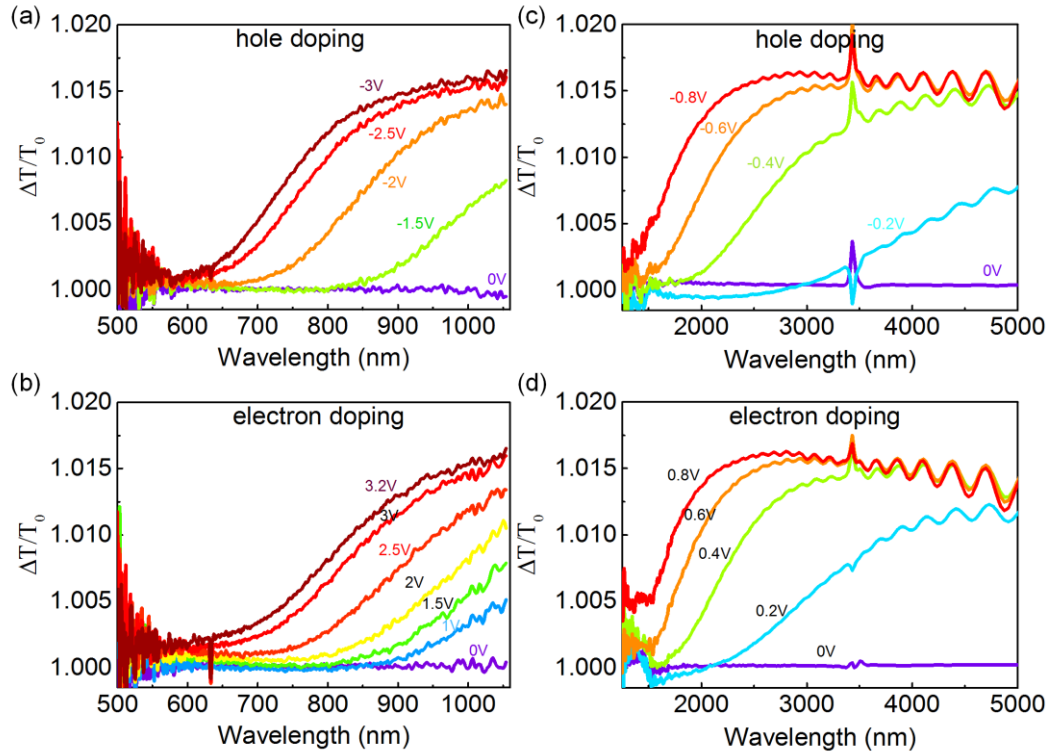


Figure 4.4 Visible and NIR spectrum of graphene device. Differential transmittance of for (a) hole (b) electron doping at different Fermi energies. (c) and (d) represents the mid infrared differential transmittance for hole and electron doping of graphene device at various Fermi energies.

4.3 Extracting Fermi energy of graphene

The Fermi energy of graphene can be determined utilizing Pauli blocking principle at each bias voltage. Single sheet of freely standing graphene can absorb 2.3 % of incident beam. At optical frequencies, the photons have enough energies to overcome

the $2E_F$ energy barrier and excite electron-hole pair. Each Fermi energy shift to higher levels, more energetic photons are blocked. The Figure 4.4(a), (b) show the differential transmittance for hole and electron doping respectively. The cutoff wavelength determines the $2E_F$ level. To determine The low values of Fermi level we extended the measurement to mid-infrared region. The Figure 4.4(c,d) demonstrates the Fermi energy shift.

Using ionic liquid gating method we were able to shift the Fermi energy of graphene to more 0.9 eV. Figure 4.5 shows the plot of extracted Fermi energy values from -4 V to 4 V. Both hole and electron doping exhibits symmetric behavior. The discrepancy stems from the gating structure where it's harder to induce electrons due to charge neutrality point shift. Thus, by electrolyte gating we were able to tune the Fermi level from nearly 0.1 to 0.9 eV.

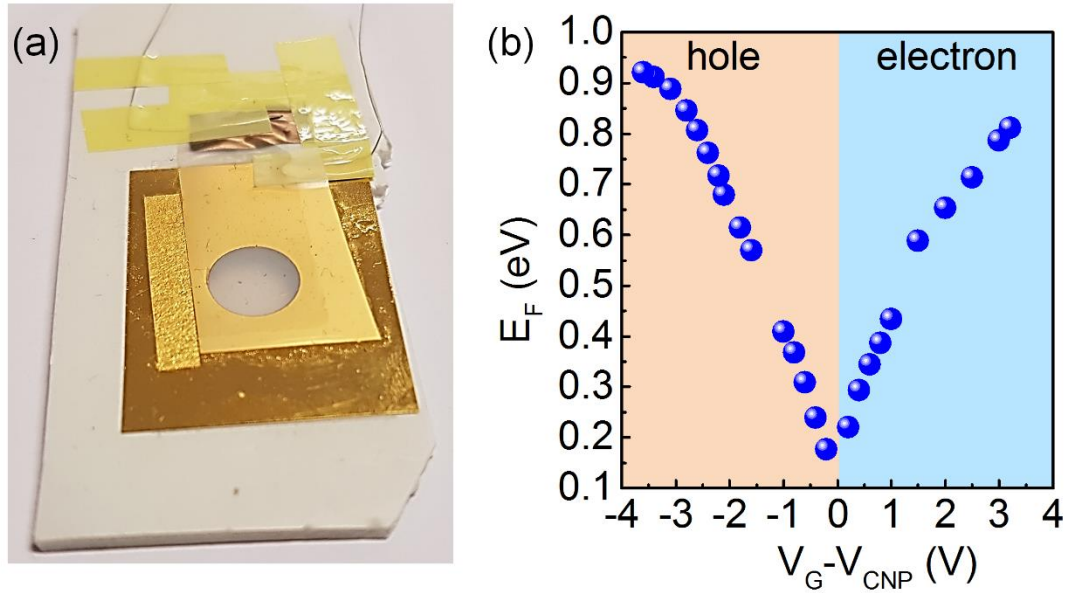


Figure 4.5 (a) Photograph of fabricated device. Graphene on polyethylene membrane on top of 60 nm gold on PVC substrate with 8 mm opening. (b) The Fermi level shift of graphene from -4 V to 4 V.

4.4 Measuring Drude-like response of graphene

Once, the Fermi energy of graphene for each gating voltage is known, we can measure the low frequency response of graphene. For that, we changed to far-infrared source and detector of the FTIR system. At this configuration, the measurable range can go down to 100 cm^{-1} wavenumbers, or 3 THz. Graphene's response at low frequencies can be summarized by Drude model. Of two absorption mechanisms, interband and free carrier, the intraband carriers transitions govern the terahertz wave manipulations. Basically, low energetic photons are dissipated by inducing hot carriers in the band. Thus, the intraband mechanism highly relies on free carrier concentrations. By electrolyte gating we were able to shift the Fermi energy of graphene to higher levels, and observe the suppression of transmittance at terahertz frequencies. Figure 4.6 demonstrates the transmittance and conductivity of graphene for both hole and electron doping regimes.

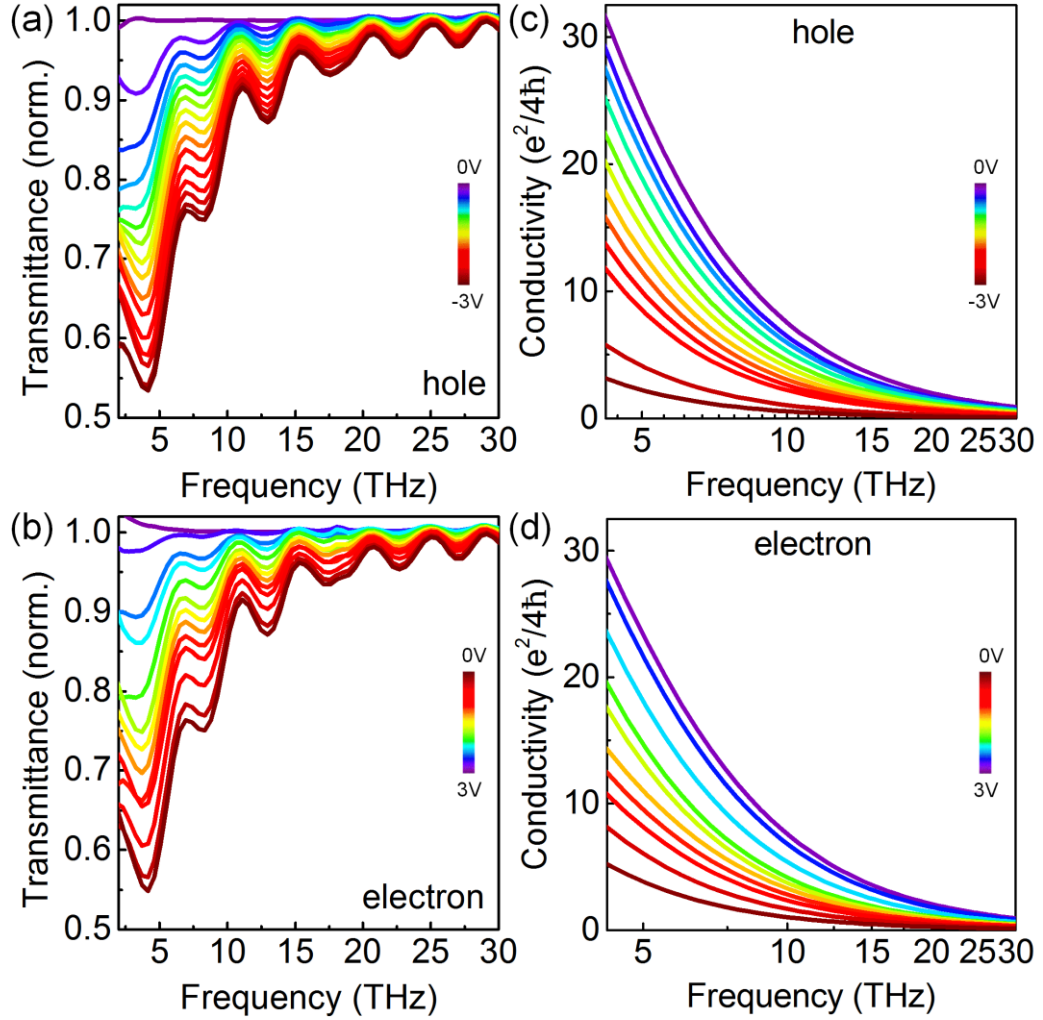


Figure 4.6 Graphene's response at THz frequencies. Transmittance of single layer graphene as a function of frequency at various gating voltages (a) hole (b) electron regime. The extracted ac conductivity of single layer graphene from transmittance for (c) and (d) hole and electron doping. The color bar represents the gating voltage levels.

The reference measurement was taken at the charge neutrality of graphene since the carrier concentration is lowest. Thus, the terahertz wave transmittance is at its extremum values. For gold and graphene combination structure the Dirac point is shifted to 1 V, in this particular case. So the reference measurement was taken at 1 V

bias voltage. The color bar in Figure 4.6 represents the gate voltage values, Dirac point to positive for electron and negative for hole regimes. Figure 4.6(a, b) shows the normalized transmittance spectra for hole and electron doping respectively. At high doping levels the transmittance modulation depth is 45 %. Theoretically graphene can absorb 50 % of the electromagnetic radiation via free carrier absorption. The transmittance of graphene is related to its frequency dependent conductivity by,

$$T = \frac{T_{\text{gate}}}{T_{\text{CNP}}} = \frac{4n}{|1 + n + Z_0\sigma|} \quad 4.4$$

where n is the refractive index of the medium and $Z_0 = 377 \Omega$ is the free space impedance. To track the changes in transmittance through single layer graphene at different gating voltages, the transmitted beam is normalized to reference signal at charge neutrality point of graphene. Each shift in Fermi energy corresponds to extra free carriers in the band which increases the absorption. The free carrier absorption can be explained by the conductivity. We extracted frequency dependent conductivity of graphene for each Fermi energy shift from the transmittance spectrum. To do so we used equation 4.4.

$$\sigma' = \left(\left(\frac{4n}{T} \right)^{\frac{1}{2}} - (n + 1) \right) / Z_0 \quad 4.5$$

where T is transmittance, n is the refractive index of the medium, σ' is the real part of the complex conductivity. Figure 4.6(c, d) depicts the conductivities both for hole and electron dopings at various voltage values. As can be seen from the plots, at extreme doping levels the conductivity curve shifts to higher frequency. This is the clear indication of carrier to carrier scattering time change. By fitting the conductivity curve, we were able to extract the transport scattering time for high doping levels of graphene. Figure 4.7 depict the transport scattering time against Fermi energy shift for both holes and electrons.

In Drude materials, the Drude weight and the scattering rate are the two main parameters that govern the optical response. For graphene, we are able to determine the Fermi level via FT spectroscopy. For low doping concentrations, THz response of graphene can be modeled with Drude model with constant scattering time, since scattering rate does not undergo significant changes. However, this is not the case at high doping levels, since the changes in scattering rate becomes more effective with increased Fermi energy. The long-range charge impurity scattering (τ_c) and the short-range disorder scattering (τ_s) as ($\tau^{-1} = \tau_c^{-1} + \tau_s^{-1}$) are the main mechanisms of the transport scattering rate [64, 65]. Their effects differ with changing Fermi energy. While at short-range, scattering time is proportional to Fermi level, at long range the scattering inversely changes with Fermi level. According to conductivity plots, Figure 4.6(c, d), as the Fermi level shifts towards higher values, the conductivity curve decays slower, indicating faster scattering rate. The frequency dependent Drude conductivity of graphene is a function of Fermi energy, sheet resistance or Drude weight (1/sheet resistance), and scattering rate. All of these parameters govern the response of graphene at terahertz frequencies. In situ measurement of Fermi energy, Drude weight, and scattering parameter is a challenge. We extracted the Fermi level values of graphene from transmittance change in the visible-NIR spectrum. The sheet resistance of graphene is determined from the maximum value of the real part of the AC conductivity of graphene. Figure 4.7(a) illustrates the extracted results. The sheet resistance of undoped graphene is around 4 k Ω /sq, while in highly doped graphene it's 500 Ω /sq. The Drude weight is DC conductivity of graphene which is the inverse of the sheet resistance. Figure 4.7(b) shows the values of Drude weight. It linearly changes with the gate voltage and shows symmetric behavior for holes and electrons. The scattering time of carriers can be determined from the frequency value that corresponds to the half maximum of the real part of the ac conductivity. Similarly, it can also be determined by fitting the real part function of the Drude conductivity to extracted conductivity.

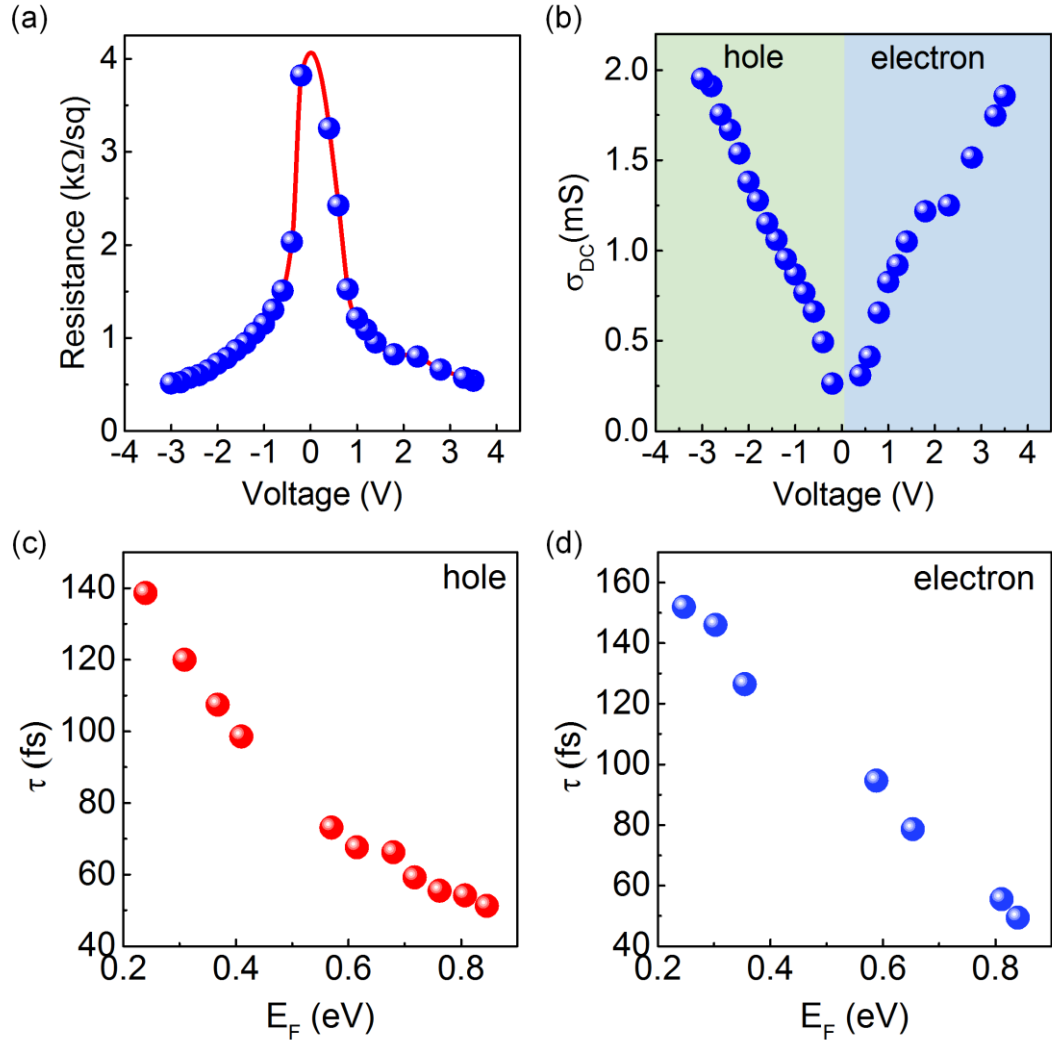


Figure 4.7 Drude parameters of highly doped graphene. (a) Sheet resistance of graphene changes from doped (500 Ω/sq) to undoped (4 $k\Omega/sq$). (b) DC conductivity or (Drude weight) changes linearly for both electrons and holes. The transport scattering time as a function of Fermi energy of graphene at (c) hole (d) electron regimes. The hole and electron carries exhibit symmetric behavior. The mean free path of carriers are highly dependent on Fermi energy.

We fitted real conductivity function (Equation 4.5) to our extracted conductivities for each Fermi energy value of graphene. Equation 4.6 represents the real part of the frequency dependent conductivity of graphene.

$$\text{Re}(\sigma(\omega)) = \frac{\sigma_{\text{DC}}}{1 + \omega^2\tau^2} \quad 4.6$$

where σ_{DC} is the DC conductivity or Drude weight, τ is the transport scattering time of charge carriers. In Figure 4.7 (c,d), the scattering time for hole and electron dopings are plotted as a function of Fermi energy. Both regimes exhibit similar behavior varying from at around 150 fs down to 50 fs for Fermi energies from 0.2 eV to 0.9 eV.

4.5 Conclusion

In conclusion, we investigated Drude conductivity of graphene at far-infrared region for both electron and hole regimes. We determined the Fermi energies of graphene using Pauli blocking principle at visible and near-infrared range. The charge carriers in graphene possess symmetric behavior. The symmetry of carriers can change for different gating methods. At terahertz frequencies graphene demonstrates Drude like behavior. The transmittance spectra revealed that at high doping levels the modulation depth exceeds 40-45 %. The transport scattering time for both electrons and holes showed symmetry and changes from 150 fs to 50 fs against Fermi energy. An accurate determinations of Drude weight and scattering rate is crucial in the development of terahertz optoelectronic devices.

Chapter 5

Controlling Terahertz Waves with Graphene Supercapacitors

In this chapter, we demonstrate a terahertz intensity modulator using a graphene supercapacitor which consists of two large-area graphene electrodes and an electrolyte medium. The mutual electrolyte gating between the graphene electrodes provides very efficient electrostatic doping with Fermi energies of 1 eV and a charge density of $8 \times 10^{13} \text{ cm}^{-2}$. We show that the graphene supercapacitor yields more than 50 % modulation between 0.1 and 1.4 THz with operation voltages less than 3 V. The low insertion losses, high modulation depth over a broad spectrum, and the simplicity of the device structure are the key attributes of graphene supercapacitors for THz applications.

5.1 Introduction

Optical modulators play a key role in optoelectronics and communication systems. Electro-optic, acousto-optic, and thermo-optic effects are well-established mechanisms to control intensity, phase, or polarization of light in the visible and near-infrared frequencies. Efficient control of terahertz (THz) waves, however, has been a

challenge because of the lack of a THz active material [8]. Because of the high spatial resolution and nonionizing nature of THz waves, many emerging technologies require the ability to control and manipulate the intensity and phase of THz waves [9, 10]. These technologies would benefit greatly from a THz modulator that has a simple device structure with efficient modulation. Tuning the bulk materials properties, such as dielectric constant and electrical conductivity, does not generate efficient reconfigurable THz components. Recent THz research is focused on controlling THz waves using high-mobility, two-dimensional electron gas or high-mobility carriers on semiconductor surfaces[9]. Reverse bias voltage applied on Schottky contacts extends the depletion area under the metal-semiconductor interface that decreases the free carrier absorption. However, the metallic gate electrodes attenuate the THz waves and screen the surface charges that result in large insertion losses and limited modulation depth. Patterning the metallic gate electrodes as interconnected metamaterials eliminates some of these drawbacks. Chen et al. used interconnected split ring resonators as a gate electrode on GaAs substrates to control the depth of the depletion area under the gap of the resonator [32]. Various forms of metamaterial THz modulators have been demonstrated [15]. Requirements of the high-resolution photolithography process for large active device area and narrow spectral window hinder the realization of efficient THz modulators.

Graphene and other two-dimensional (2D) crystals provide new opportunities for THz technologies [31, 66-69]. Atomic thickness and very large carrier mobility, together with the tunable optical properties, create a unique combination for active THz components. Since the thickness of 2D crystals (~ 0.3 nm) is much thinner than the wavelengths of the THz waves, there is no bulk material that can effectively introduce large insertion losses. The THz response of the 2D crystals solely originates from high-mobility carriers which can be tuned by electrostatic doping. Particularly, graphene-based active THz devices have raised great interest in the last few years. The charge density in graphene can be tuned between 10^{12} and 10^{14} cm⁻², which

could yield efficient THz modulators with a wide dynamic range. Sensale-Rodriguez et. al. reported a graphene-based THz modulator using a back-gated transistor structure. In their device, THz-transparent Si substrate operates as a back-gate electrode [27]. Using a graphene-dielectric-Si capacitor structure, the conductivity of graphene was modified by applying voltage between the Si back-gate and graphene. They further demonstrated individual and arrays of reflection and transmission-type THz modulators using back-gated device geometry [38, 41, 48]. The dynamic range of the back-gated device structure is limited by the electrical breakdown of the gate dielectric. Another approach is based on tuning the plasmon oscillations on structured graphene [70-72]. The frequency of plasmon oscillations on graphene ribbons can be tuned by the ribbon width and the charge density. Integrating graphene with metamaterials can yield another design parameter to improve the modulation depth; however, it narrows the spectral window. It has been predicted that graphene-based modulators can create a modulation depth of >90 % [69]. However, because of the limited charge modulation with dielectric capacitors ($<10^{13} \text{ cm}^{-2}$), the full potential of graphene for THz technologies has yet to be achieved.

Recently, we have discovered that the supercapacitor geometry provides a very efficient device structure to control and manipulate optical properties of single-layer and multilayer graphene electrodes [73]. Using graphene supercapacitors, we fabricated optical modulators [73], electrochromic devices [74], tunable saturable absorbers [75], and radar absorbing surfaces [76] operating in visible, near-infrared, and microwave frequencies. Now, we would like to study the THz response of these graphene supercapacitors. In this paper, we demonstrate a simple, yet very efficient, broadband THz modulator using graphene supercapacitors.

The device consists of two large-area graphene electrodes transferred onto THz transparent substrates with ionic liquid electrolytes between them. Figure 5.1(a) shows the schematic drawing of the device layout. In this device geometry, there is no need for a metallic gate electrode which could introduce large insertion losses.

Two graphene electrodes provide mutual gating. The bias voltage applied between graphene electrodes polarizes the electrolytes and yields efficient electrostatic doping on the graphene electrodes. The optical properties of graphene change with the doping [77-79].

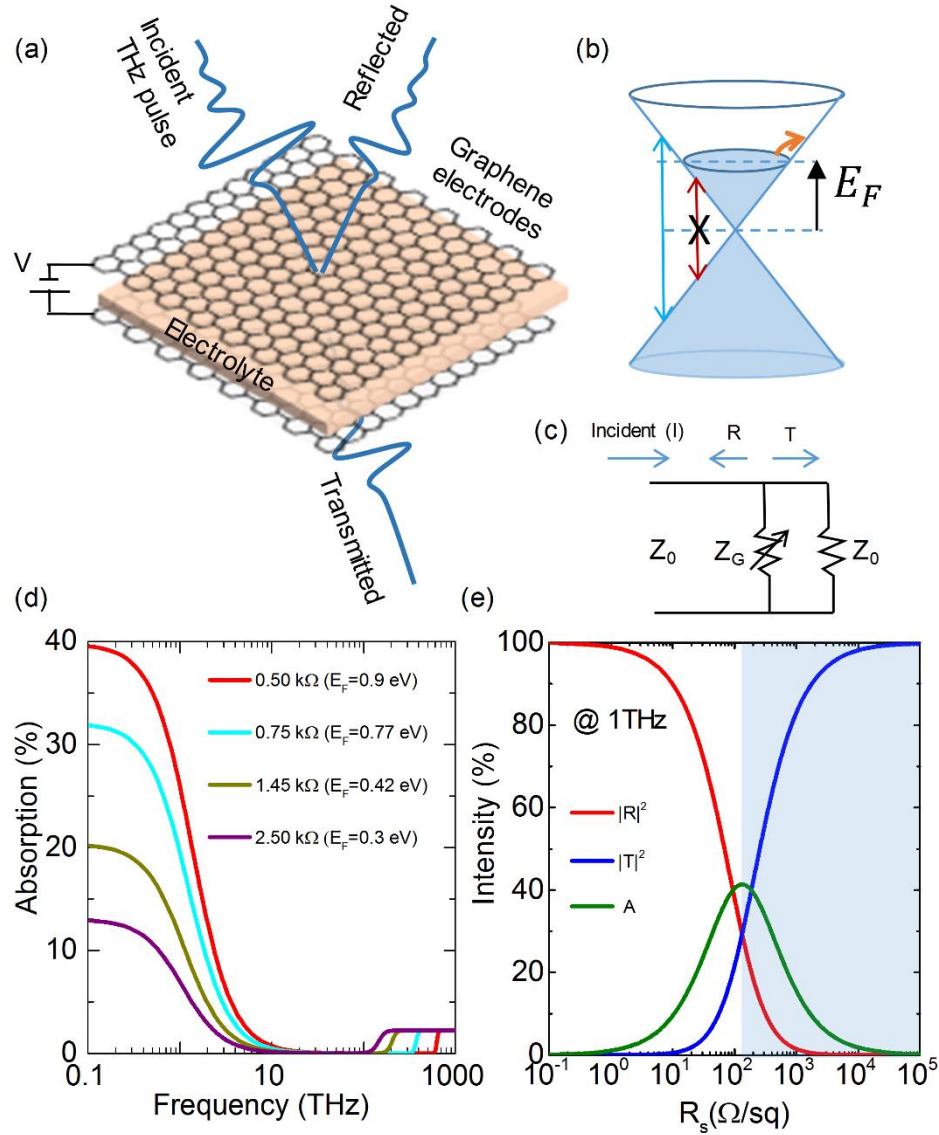


Figure 5.1 (a) Schematic representation of the graphene supercapacitor used as a broadband THz modulator. The supercapacitor consists of ionic liquid electrolyte sandwiched between two large-area graphene electrodes. The charge density on

graphene electrodes is modulated efficiently by an external voltage applied between the graphene electrodes. (b) Schematic band structure of electrostatically doped graphene electrodes. The arrows represent the interband and intraband electronic transitions. (c) Equivalent transmission line model of the graphene layer. (d) Calculated optical absorption of single-layer graphene plotted against the frequency for different doping levels. (e) Change of reflection, transmission, and absorption of graphene as a function of sheet resistance. The shaded area indicates the experimentally accessible sheet resistance for CVD graphene. ©2015 OSA

Figure 5.1(b) shows the schematic band structure of doped graphene. There are two main electronic transitions that characterize the tunable optical response. The vertical interband electronic transition can be blocked via Pauli blocking when the Fermi energy is larger than the half of the photon energy. In supercapacitor configuration, the efficient gating of ionic liquid electrolyte and low electronic density of the states of graphene enable us to shift the Fermi energy in the order of one electron volt which modulates optical transmittance in the visible spectrum. In addition to the interband transitions, shifting the Fermi energy modifies the rate of intraband electronic transition because of the change in the electronic density of states [69]. These interband and intraband electronic transitions yield broadband absorption. We calculated the optical absorption of graphene using the transmission line model which provides an intuitive picture to understand the spectral response of our device [80]. The inset in Figure 5.1(c) shows the equivalent transmission line model for single-layer graphene.

Graphene layer can be modeled as a thin film with thickness of L (~ 0.3 nm) with a dynamic optical conductivity of

$$\sigma(\omega) = \sigma_{\text{intra}} + \sigma_{\text{inter}} \quad 5.1$$

where σ_{intra} and σ_{inter} represent the optical conductivity due to intraband and interband transitions, respectively. The reflection (R) and transmission (T) coefficients can be written as [80]

$$R = \frac{Z_R - 1}{Z_R + 1} \quad 5.2$$

$$T = (1 + R) \cos(kL) - j \frac{Z}{Z_0} (1 - R) \sin(kL) \quad 5.3$$

$$Z_R = \frac{1 + j \left(\frac{Z_G}{Z_0} \right) \tan(kL)}{1 + j \left(\frac{Z_0}{Z_G} \right) \tan(kL)} \quad 5.4$$

j is the imaginary number, and Z_0 represents characteristic impedance of the free space

$$Z_0 = \left(\frac{\mu_0}{\epsilon_0} \right)^{\frac{1}{2}} = 377 \Omega \quad 5.5$$

Z_G is the characteristic impedance of graphene layer

$$Z_G = \left(\frac{\mu_0}{\epsilon' - \frac{\sigma}{j\omega}} \right)^{\frac{1}{2}} \quad 5.6$$

Here k is the complex wavevector of the THz wave. Figure 5.1(c) shows the calculated absorption of single layer graphene

$$A = 1 - |R|^2 - |T|^2 \quad 5.7$$

from THz to visible spectra. In the THz regime, the absorption is due to intraband transition where graphene behaves as a tunable Drude metal with a frequency-dependent optical conductivity of

$$\sigma(\omega)_{\text{intra}} = \frac{\sigma_{\text{DC}}}{1 + j\omega\tau} \quad 5.8$$

where σ_{DC} is the conductivity of graphene, ω is the frequency, and τ is the mean scattering time of graphene electrodes. For the calculation, we used a scattering time of 200 fs which yields a cutoff frequency of 5 THz. In the optical frequencies, the intraband contribution diminishes because of a large momentum mismatch, resulting in a constant optical conductivity of $e^2/4h$ because of the interband transitions. Figure 5.1(e) shows the variation of reflection, transmission, and absorption of graphene at 1 THz with sheet resistance from 0.1 Ω/sq to 100 $\text{k}\Omega/\text{sq}$. By tuning the sheet resistance of the graphene layer, the absorption can be altered from 40 down to 5% [Figure 5.1(e)]. The maximum THz absorption can be achieved when the characteristic impedance of graphene is matched to the free space impedance. The shaded area in Figure 6.1(e) shows the experimentally accessible sheet resistance of CVD-grown graphene [49].

We fabricated the THz modulators using CVD-grown, large-area graphene layers. We used a chemical vapor deposition system to synthesize the large-area (2×2 cm) graphene samples on ultra-smooth copper foil substrates (Mitsui Mining and Smelting Company, Ltd., B1-SBS, 100 nm surface roughness). The oxide layer on the foils was removed by a hydrogen flow during the annealing step. The graphene was synthesized at 1035°C using 40 sccm CH_4 and 80 sccm H_2 gases. After 20 min of growth time, the samples were cooled to the room temperature with the natural cooling rate of the furnace (20°C/min). After the growth, we coated the samples by drop casting thick Shipley 1813 photoresist which functions as a mechanical support for the transfer process. After etching the copper foils in an FeCl_3 solution, the photoresist layer with graphene was transferred onto a quartz wafer. Reflowing the photoresist layer at 110°C on a quartz wafer results in conformal coating of graphene on the fused quartz surface. We attached two graphene-coated quartz wafers with a 25 μm thick spacer, and filled the gap with ionic liquid electrolyte (Diethylmethyl(2-

methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide, [deme][Tf2N]). The inset in Figure 5.2(a) shows the fabricated THz modulator.

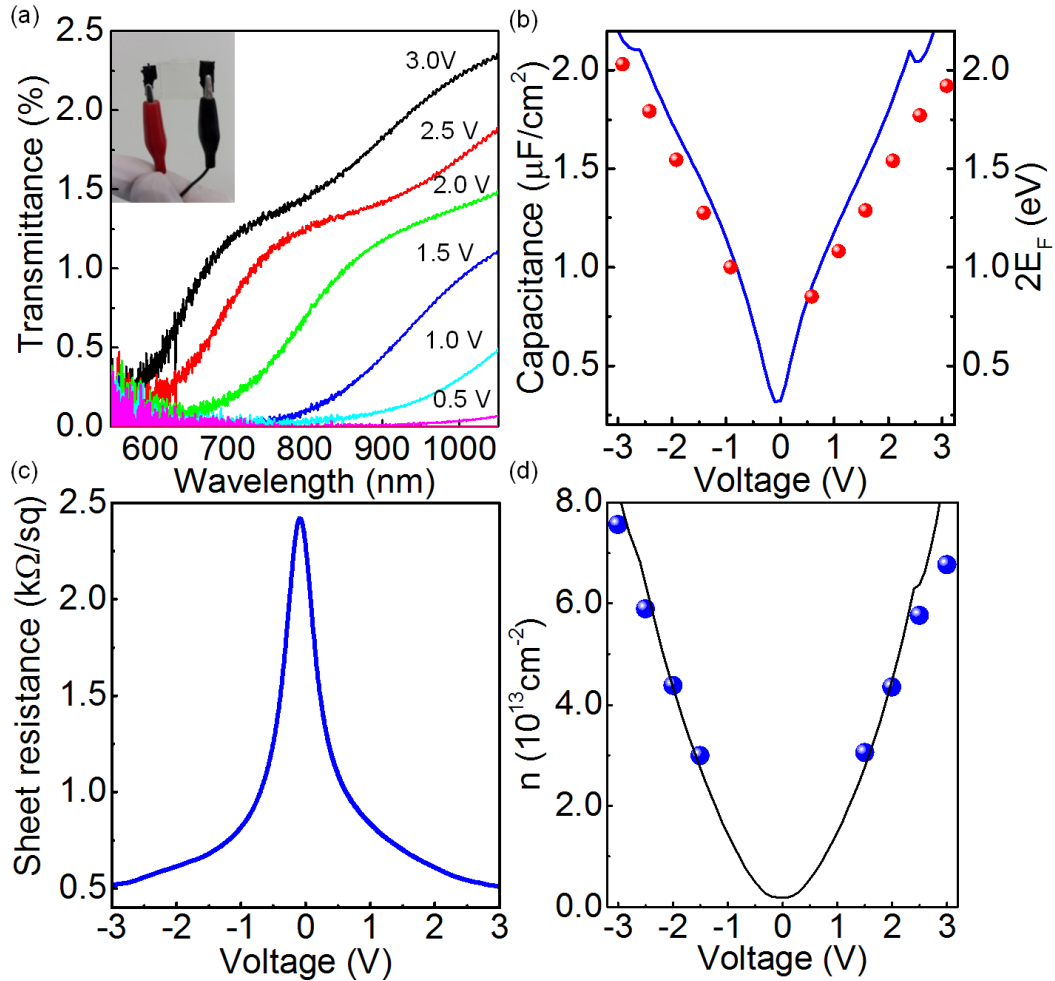


Figure 5.2 (a) Modulation of the optical transmittance of the graphene supercapacitor in the visible spectra. (b) Variation of the capacitance of the devices and extracted Fermi energy of the graphene electrodes as a function bias voltage. (c) Variation of the resistance of the graphene electrodes with the bias voltage. (d) Calculated charge density is plotted against the bias voltage. The solid line is calculated from the capacitance, whereas the scattered points are calculated from the measured Fermi energy. ©2015 OSA

5.2 Optical and electrical characterizations of graphene devices

Fermi energy (E_F) of graphene is the primary parameter to describe the doping level. To extract the Fermi energy, we measured optical transmittance in the visible and near-infrared wavelength. The electrolyte gating yields Fermi energies on the order of 1 eV, which results in the blocking of interband transition in the near-infrared regime. The variation of the optical transmittance of the device with the bias voltage is shown in Figure 5.2(a). The modulation of the transmittance shows a step-like function with a cutoff wavelength of $2E_F$. As the bias voltage increases, the cutoff wavelength shifts to the higher energies. Since there are two graphene electrodes with slightly different charge neutral points (Dirac point), we observe two steps in the transmittance spectra associated with each graphene layer.

Figure 5.2(b) shows the extracted Fermi energy of one graphene electrode as a function of bias voltage. The Fermi energy varies between 0.3 and 1.0 eV, as the bias voltage increases from 0.5 to 3 V. The minimum Fermi energy associated with unintentional doping can be estimated to be 0.2 eV. The capacitance of the device provides more insight about the density of states of graphene electrodes. Figure 5.2(b) shows the variation of the capacitance as a function of bias voltage. To measure the voltage dependent capacitance, we superimposed 0.1 V alternating voltage and variable DC bias voltage. The variation of the capacitance between 0.3 and 2.2 μF with the bias voltage is because of a change in the density of states as the Fermi energy shifts. The total capacitance of the device is limited by the low quantum capacitance (CQ) of the graphene electrodes which is directly related with the density of states of graphene electrodes. At the same time, the resistance of the graphene electrodes varies from 2.4 k Ω (at the Dirac point) down to 0.5 k Ω (at a bias voltage of 3 V) [Figure 5.2(c)]. Unlike a dielectric capacitor, in supercapacitors, both resistance of the electrodes and capacitance of the device change with the bias voltage. The calculated charge density on graphene is plotted against the bias voltage.

At a bias voltage of -3 V, the charge density increases up to $8 \times 10^{13} \text{ cm}^{-2}$ with Fermi energy of 1 eV. In Figure 5.2(d), we plotted the total charge density as

$$n = (n_0^2 + n_g^2)^{1/2} \quad 5.9$$

where $n_0 = 1.9 \times 10^{12} \text{ cm}^{-2}$ is the estimated unintentional doping, and n_g is the gate induced charges. To ensure the correct charge densities, we used measured Fermi energy and capacitance of the device. The solid line in Figure 5.2(d) is calculated using the measured capacitance of the device, whereas the scattered point is calculated from the measured Fermi energy

$$E_F = \hbar v_F \sqrt{n\pi} \quad 5.10$$

where v_F is the Fermi velocity and n is the charge density.

5.3 Broadband THz beam modulation using graphene supercapacitors

Then we measured the THz response of the fabricated modulator. We used conventional time domain THz spectroscopy to measure the modulation of the intensity of transmitted THz signal. A Ti:Al₂O₃ mode-locked laser output with an average power of 200 mW, a repetition rate of 75 MHz, and a pulse width of 15 fs is used to drive the THz-TDS system. An AC-biased (30 V_{pp}, 1 KHz) photoconductive antenna is used for the generation of the THz pulses. The THz beam is collected and collimated by an off-axis parabolic mirror and then focused to a ~ 8 mm spot size at the sample with the aid of a TPX lens (D=50 mm, F#2). After passing through the sample, the beam is collected by an identical lens and then focused by another off-axis parabolic mirror onto the detector crystal ($\langle 110 \rangle$ ZnTe) which allows it to be sampled using the electro-optic detection method. The entire THz beam path is enclosed in a box allowing it to be purged with dry nitrogen during the measurements. Figure 5.3(a) shows the time-varying electric field of the THz pulse recorded with the THz-TDS system. To remove the substrate effects, we fabricated an identical test

device without the graphene electrodes. The reference signal is recorded using this test device. We measured the transmitted THz-pulse through the graphene supercapacitor at different bias voltages. Figure 5.3(b) shows the modulation of the maximum electric field which is normalized by the reference signal. The normalized transmitted electric field decreases with the bias voltage from 0.87 down to 0.61 at a bias voltage of -2.5 V. The asymmetry in the modulation is because of the hysteresis caused by the shift in the Dirac point. Small leakage current induces unintentional doping on graphene which shifts the Dirac point. By performing Fourier analysis, we obtained the spectral amplitude and phase of the transmitted signal [Figure 5.3(c)]. We observed clear Fabry–Perot resonances with a period of ~ 0.12 THz. These Fabry–Perot resonances originate from the parallel quartz surfaces. The amplitude of the transmitted signal is modulated by around 55 % in broad spectra from 0.1 to 1.4 THz which is limited by the transparency of the quartz substrate. The modulation of the transmittance at 0.6 THz is shown in Figure 5.3(d).

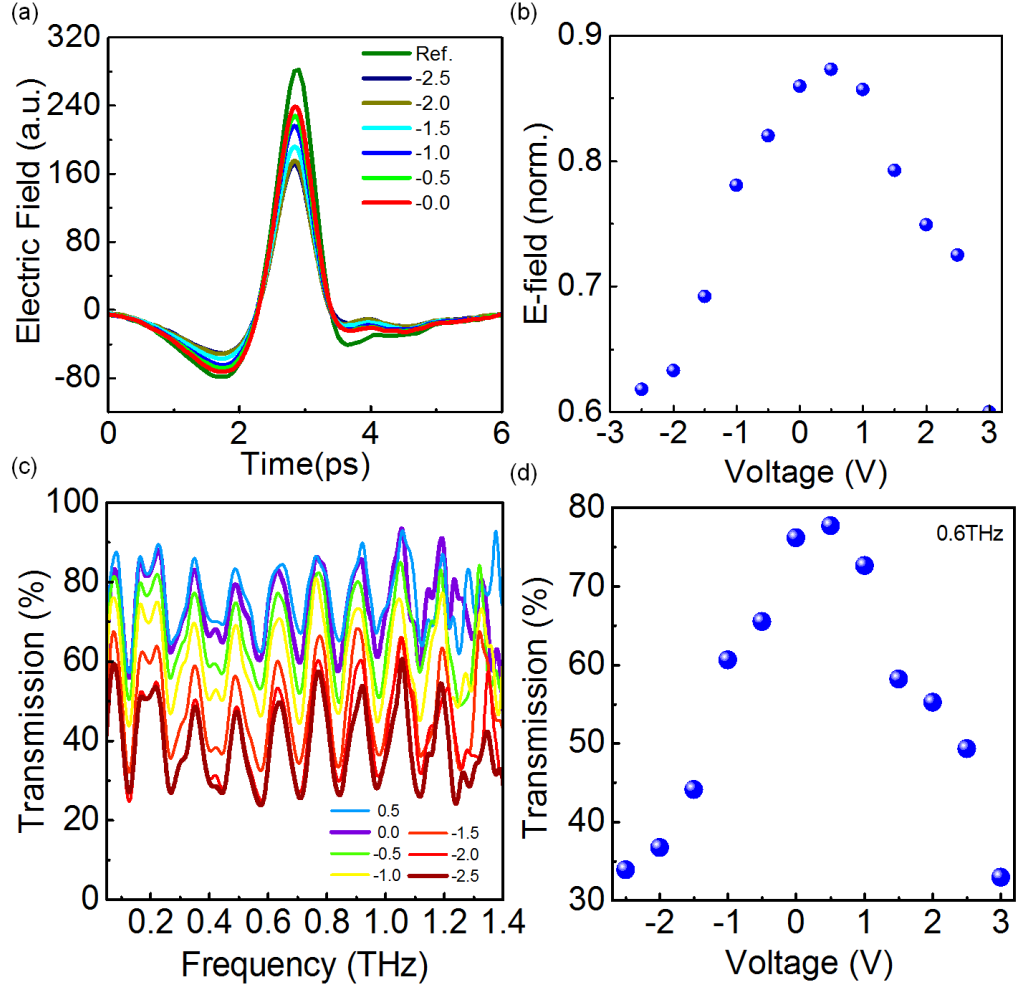


Figure 5.3 (a) Time-varying electric field of the THz pulse at various voltage bias between 0 and -2.5 V. The reference THz signal is measured without the graphene supercapacitor. (b) Modulation of the maximum electric field as a function of bias voltage. (c) Spectrum of the transmitted THz pulse obtained after Fourier transform of the transmitted signal and normalization with the reference signal. (d) Modulation of signal at 0.6 THz. ©2015 OSA

5.4 Graphene based large-area terahertz modulator

Because of the material cost and requirement of high-resolution lithography, fabrication of large-area THz modulators has been a challenge. The simplicity of our

device structure allows us to fabricate a very large-area broadband THz modulator. To demonstrate the promise of our approach, we synthesized large-area $7 \times 7 \text{ cm}^2$ graphene, and then we laminated flexible 125 μm thick PVC (polyvinyl chloride) substrate on a graphene-coated surface of the foil at 120 $^\circ\text{C}$. Etching the copper foil yields large-area crack-free graphene on a THz-transparent and flexible PVC substrate. The PVC substrate is THz transparent between 0.1 and 1.7 THz. Figure 4(a) shows the fabricated large-area THz modulator. During the etching process, we covered the edges of the sample and left thin copper strips which function as metal electrodes. First, we measured the variation of the capacitance of the device with the bias voltage [Figure 5.4(b)]. The total capacitance varies between 70 μF at -3 V down to 10 μF at 0 V. This corresponds to capacitance per unit area of 3 $\mu\text{F}/\text{cm}^2$. As the area of the device increases, the total capacitance of the modulator increases which limits the cutoff frequency. To quantify the cutoff frequency, we fabricated various THz modulators and measured their frequency-dependent capacitance [Fig. 4(c)]. Figure 5.4(d) shows the variation of the extracted cutoff frequency with the device area. We observed that the cutoff frequency is inversely proportional with the device area. Figure 5.4(e) shows the modulation of the THz signal. The performance of the device is similar to the one based on a quartz substrate with lower insertion loss. Unlike the quartz, the two flexible PVC substrates are not flat enough to support Fabry–Perot resonances Figure 5.4(f).

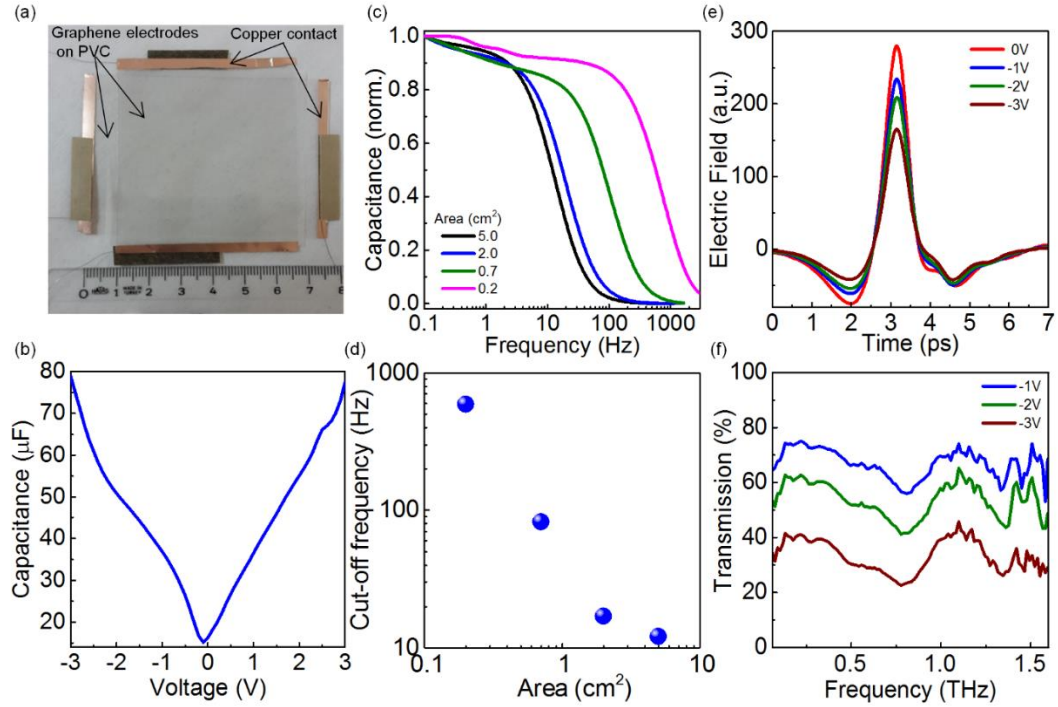


Figure 5.4 (a) Picture of the large-area (7×7 cm) THz modulator. (b) Variation of the capacitance of the modulator as a function of bias voltage. (c) Capacitance of the modulator at different sizes. (d) Extracted cutoff frequency as a function of device size. (e) Time-varying electric field of the THz pulse at various voltage bias between 0 and -3 V. (f) Spectrum of the transmitted THz signal obtained after Fourier transformation of the recorded signal and normalization with the signal at a bias voltage of 0 V. ©2015 OSA

Insertion loss and modulation depth are the two important parameters for THz modulators. In Figure 5.5(a) we show the intrinsic insertion loss resulting from the two graphene electrodes and the total insertion loss of the graphene supercapacitor, including a quartz substrate for a frequency range from 0.1 to 1.4 THz. The intrinsic insertion loss is around 0.7 dB. In Figure 5.5(b), we compare our device performance with the THz modulators reported in the literature [6,28–31]. Our device shows a maximum modulation of 62 % and an intrinsic loss of 0.7 dB. This combination

provides a clear advantage over the previous modulators. In addition, our device provides the largest reported spectral window.

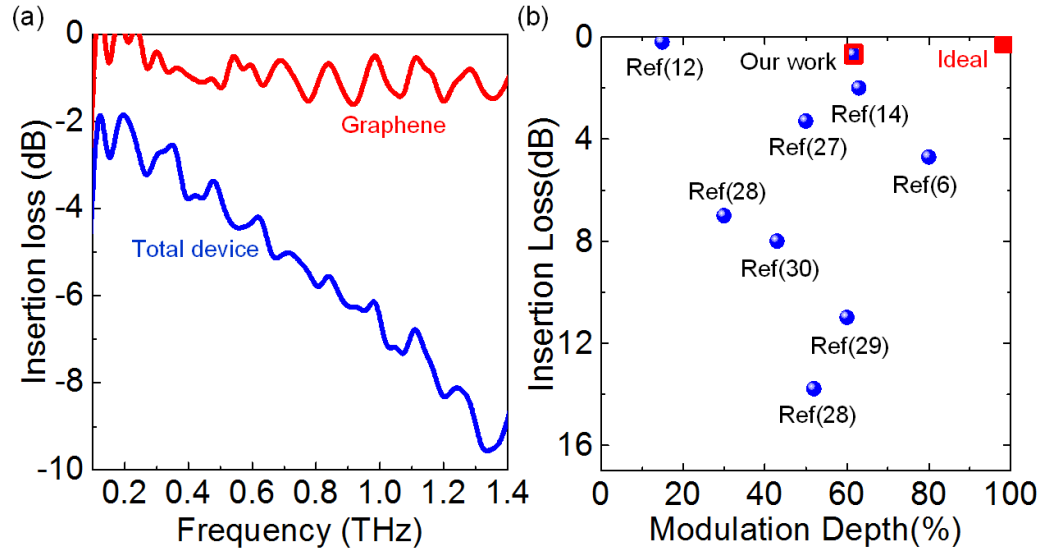


Figure 5.5 (a) Insertion loss of the total device and the graphene electrodes plotted against the frequency. (b) Comparative graph showing the modulation depth and intrinsic insertion loss of graphene modulators. ©2015 OSA

5.5 Conclusions

In conclusion, we demonstrated a THz intensity modulator using large-area graphene supercapacitors. We fabricated the graphene supercapacitors using CVD-grown graphene layers and ionic liquid electrolyte. The supercapacitor structure provides efficient mutual gating between two graphene electrodes. With this simple device structure, we were able to modulate the intensity of THz waves with a modulation depth of 50% between 0.1 and 1.4 THz with operation voltages less than 3 V. This device can operate as a reflection type modulator as well. Furthermore, we demonstrated a very large area 7×7 cm² THz modulator on a flexible substrate. The low insertion loss, the simplicity of the device structure, and polarization independent device performance are the key attributes of graphene supercapacitors for THz

applications. Another interesting aspect of this device is that the graphene supercapacitor is active in a very broad spectrum, ranging from visible to THz frequencies. The slow response time and the requirement of liquid electrolyte are the drawbacks of our approach.



Chapter 6

Coherent Perfect Absorption of THz Radiation in Graphene

In this chapter, we report experimental observation of electrically tunable coherent perfect absorption (CPA) of terahertz (THz) radiation in graphene. We developed a reflection-type tunable THz cavity formed by a large-area graphene layer, a metallic reflective electrode, and an electrolytic medium in between. Ionic gating in the THz cavity allows us to tune the Fermi energy of graphene up to 1 eV and to achieve a critical coupling condition at 2.8 THz with absorption of 99 %. With the enhanced THz absorption, we were able to measure the Fermi energy dependence of the transport scattering time of highly doped graphene. Furthermore, we demonstrate flexible active THz surfaces that yield large modulation in the THz reflectivity with low insertion losses. We anticipate that the gate-tunable CPA will lead to efficient active THz optoelectronics applications.

6.1 Introduction

The phenomena of coherent perfect absorption (CPA) is the time-reversed analog of stimulated emission [81-83]. The optical absorption of a conducting thin film, which

is limited to maximum of 50 % in free standing form, can be enhanced under illumination of two coherent light beams when they are in-phase on the film. The concept of CPA have been implemented to various materials systems such as, metamaterials [84], two-level atomic systems [85], phase change materials[86], plasmonic systems [87] and radar absorbing surfaces [76]. Very recently the enhancement of optical absorption in 2-dimensional conductors has attracted great attention for realization of gate-tunable optoelectronic devices. Enhancement of optical absorption in graphene, in particular, plays an important role for broadband tunable optoelectronic devices. The ability to control rates of interband [78, 88, 89] and intraband [48] electronic transitions via electrostatic gating, enables novel active optoelectronic devices. At optical wavelengths, the optical absorption in graphene is limited to 2.3 % [73, 78, 89], however for longer wavelengths (THz [27, 90, 91] and microwave [76]) absorption can be increased up to 50 %. The conditions to achieve maximum absorption in graphene for free standing graphene and graphene in quarter wavelength distance away from metallic surface can be explained by transmission line model, Figure 6.1. When the surface impedance of graphene (Z_G) matches the half of the free space impedance [80], $Z_G = 1/\sigma(\omega) = Z_0/2$ where Z_0 is the free space impedance and $\sigma(\omega)$ is the optical conductivity. For graphene at quarter wavelength distance away from the reflecting surface the conductance of the graphene must match the free space impedance, $Z_G = Z_0$.

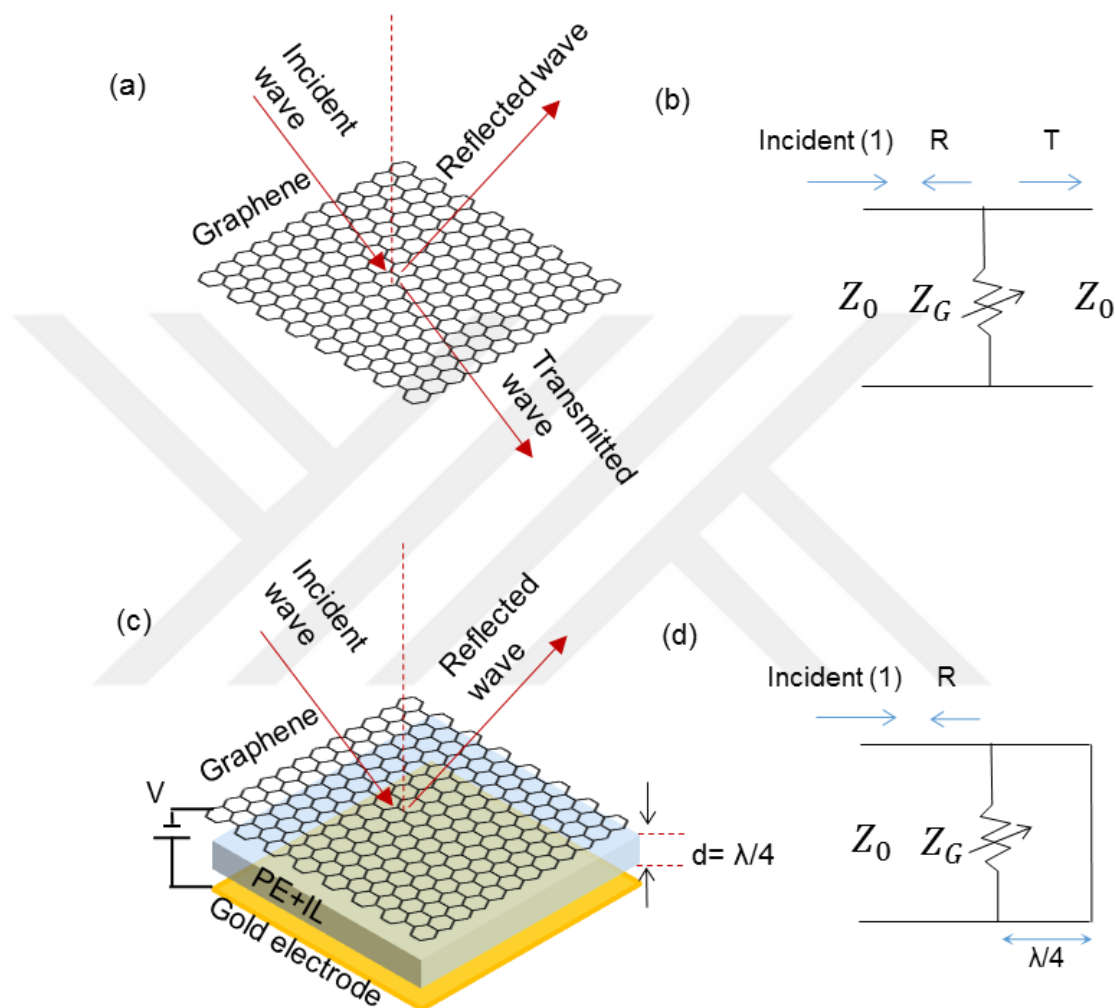


Figure 6.1 Schematic drawing of free standing graphene and active THz surface and their transmission line models. In the case of free standing graphene, the maximum absorbance is achieved when the surface impedance of graphene (Z_G) matches the half of the free space impedance (Z_0). For the device, metallic reflecting surface is modeled as a short circuit at a quarter wave distance from the graphene. The quarter wave transmission line converts the short circuit in to an open circuit. In this case, the maximum absorbance is achieved when the surface impedance of graphene is Z_0 . Here the surface impedance of graphene refers impedance due to optical conductivity. ©2016 ACS

To enhance the optical absorption further, various device structures have been explored. Patterning graphene into ribbons leads to enhanced absorption due to the localized plasmon oscillations. Fang *et al* demonstrated absorption of 20 % in far-IR frequencies [92]. Placing graphene on a photonic crystal cavity [93] or inside a microcavity [94, 95] enhances the absorption due to multiple passes. Very recently, Thareja *et al* placed graphene at a quarter-wave-distance from a metallic surface and showed enhancement up to 5.5 % in IR wavelengths [42, 96, 97]. With the help of local plasma frequency, complete optical absorption at IR frequencies has been proposed using periodically patterned doped graphene [98, 99].

6.2 Graphene-based terahertz cavity

Gate-tunable coherent absorption in graphene at terahertz frequencies has more technological importance because of being a low cost alternative material for active THz devices. The recent theoretical studies show that gating graphene near a reflective surface, would yield gate-tunable CPA for terahertz radiation [64, 100]. They predicted that, under coherent illumination, 100 % of THz radiation can be absorbed by a highly doped monolayer graphene, when the Fermi energy is close to 1eV. Varying the doping level, THz absorption can be controlled efficiently by electrical means. This is a challenging requirement. Although, the static CPA in graphene for microwave [76] and visible [101, 102] spectra has been reported, due to the limitation of conventional gating schemes, the gate-tunable CPA of THz radiation in graphene has not been observed yet.[27, 31] In our previous works, we used ionic gating to control optical properties of graphene in a very broad spectrum extending from visible to microwave wavelengths.[73, 76, 90, 103] In this chapter, we demonstrate a new type of tunable THz cavity which enables us to observe gate-tunable CPA. Figure 6.3(a) shows the schematic drawing of our device structure. The large-area monolayer graphene is synthesized by chemical vapor deposition on copper foils and then transferred on 20- μ m-thick porous polyethylene membrane (42% porosity) which is placed on a reflective gold electrode. The thickness of the

membrane defines the cavity length and the resonance wavelength. The gold electrode operates both as the back reflecting mirror and the gate electrode. We soaked the membrane with room temperature ionic liquid ((Diethylmethyl(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide, [deme][Tf2N])) which has large electrochemical window that yields tunable Fermi energy on graphene up to 1 eV. Both electrolyte and PE membrane are transparent between 0.1-15 THz, Figure 6.2. The transmittance spectrum of porous polyethylene and PE with ionic liquid was extracted by Fourier transforming the time-domain THz measurements. The transmittance of PE was taken as the reference measurement.

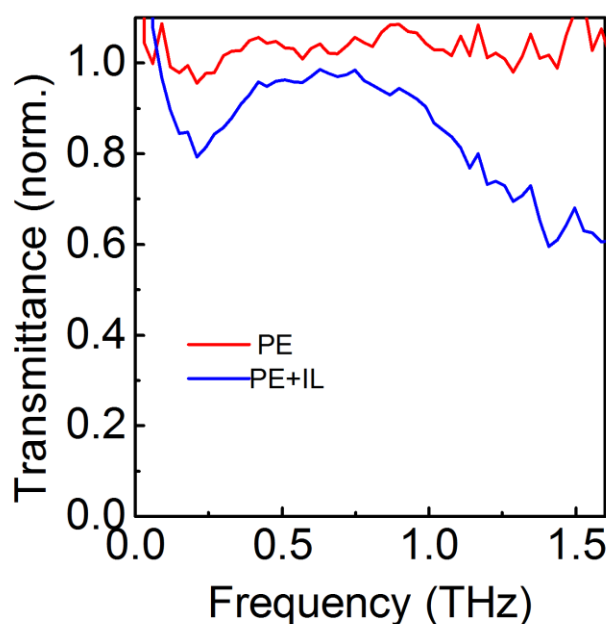


Figure 6.2 Terahertz transmittance spectrum of porous polyethylene (PE) and PE with ionic liquid. ©2016 ACS

Figure 6.3(b) shows a schematic cross-sectional view of the device under a bias voltage that polarizes the ionic liquid in the membrane and forms electrical double layers (EDL) near the graphene and gold interface. The EDL electrostatically dopes the graphene layer and alters its conductivity. Since the thickness of EDL is very thin

for ionic liquids, this configuration yields very large electric field and induced charges on the surface. The advantage of this device is that it provides a very efficient gating scheme with charge density up to 10^{14} cm^{-2} and Fermi energy of 1 eV of open graphene surface. These doping levels are enough to satisfy the CPA condition at THz frequencies. Our device yields a single channel CPA, when the incident and reflected THz beams are in phase at the graphene interface. For our device structure, the resonance condition can be written as $t \cos(\theta) = (2m + 1)\lambda/4n$ where θ is the incidence angle, t is the thickness of the membrane, m is an integer and n is the index of refraction of the cavity. Spectroscopic measurements provide the resonances and anti-resonances which yield perfect and no absorption conditions, respectively.

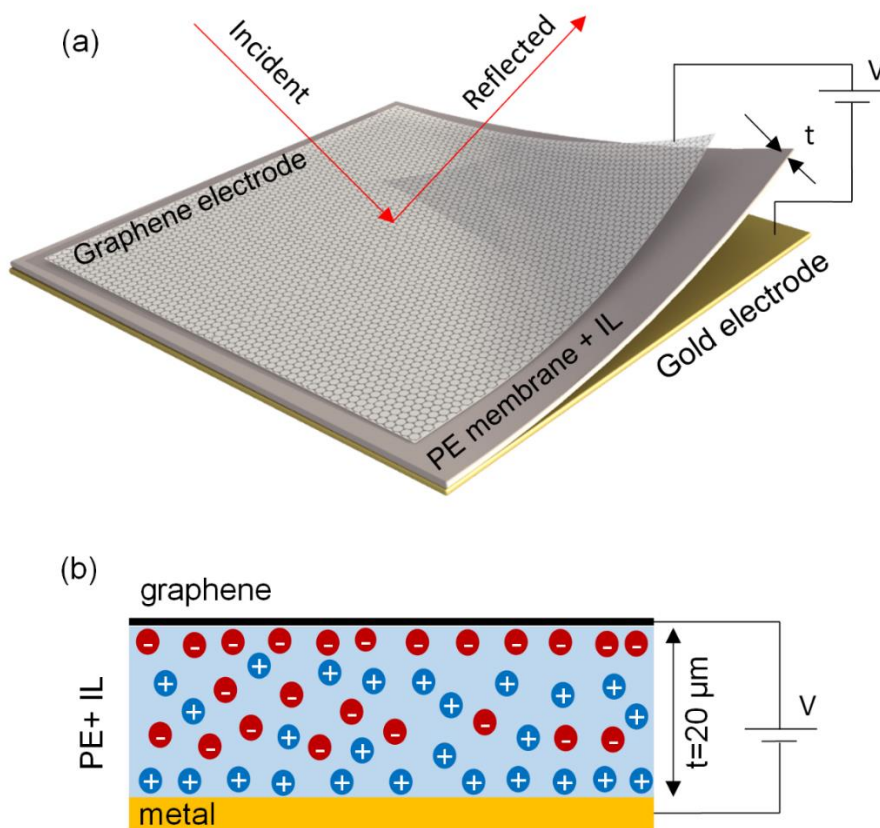


Figure 6.3 Active THz surfaces (a) Schematic representation of electrically tunable THz cavity used for the coherent perfect absorption in graphene. The THz cavity is formed by a porous membrane sandwiched between graphene and gold electrodes. The thickness of the membrane is 20 μm . The ionic liquid electrolyte is soaked into the membrane. (b) Cross-sectional view of the cavity showing the formation of electrical double layers on the graphene and gold electrodes. ©2016 ACS

6.3 Observation of coherent perfect absorption in graphene

Figure 6.4(a) shows the fabricated device. We measured THz reflection from the biased device using a Fourier transform infrared spectrometer (FTIR) equipped with Far-IR detector and a Far-IR source (Figure 6.4(b)). Since ionic liquids have very low

vapor pressure, we recorded the reflection spectrum under the vacuum (10 mTorr) to remove the absorption of water. Figure 6.4(c) shows the measured reflectivity spectrum from the device under different bias voltages. For the membrane thickness of 20 μm and incidence angle of 30° , we observed multiple resonance absorptions at 2.83, 8.24, and 13.23 THz frequencies. For the first resonance, we obtained absorption of 99 % at 2.0 V bias voltage. Unlike the condition of the freestanding film, CPA occurs when the real part of the optical conductivity of doped graphene reaches the values $\sigma(\omega) = 1/Z_0$ where Z_0 is the free space impedance. The optical conductivity of graphene in THz frequencies can be described with Drude response as,

$$\sigma(\omega) = \frac{e^2}{\pi\hbar} \frac{iE_F}{\omega + i\tau^{-1}} \quad 6.1$$

where, E_F is the Fermi energy, τ is the transport scattering time. For high doping levels, τ varies with the Fermi energy. We observed the perfect absorption at low THz frequencies (< 5 THz). For higher frequencies however, the required doping levels exceed the accessible levels with the present device. The variation of the resonance reflectivity of the first three resonances are plotted in Figure 6.4(d) against the bias voltage. The reflectivity is normalized by the reflection at the charge neutrality point (CNP, around -1 V). The large shift in the CNP is associated with the work function difference between the graphene and gold electrodes. We obtained 99, 76, and 42 % absorption for 2.83, 8.24, and 13.23 THz frequencies respectively. To observe perfect absorption for higher order modes, we need larger voltages which exceed the electrochemical window of the electrolyte and introduce irreversible damage on graphene electrode.

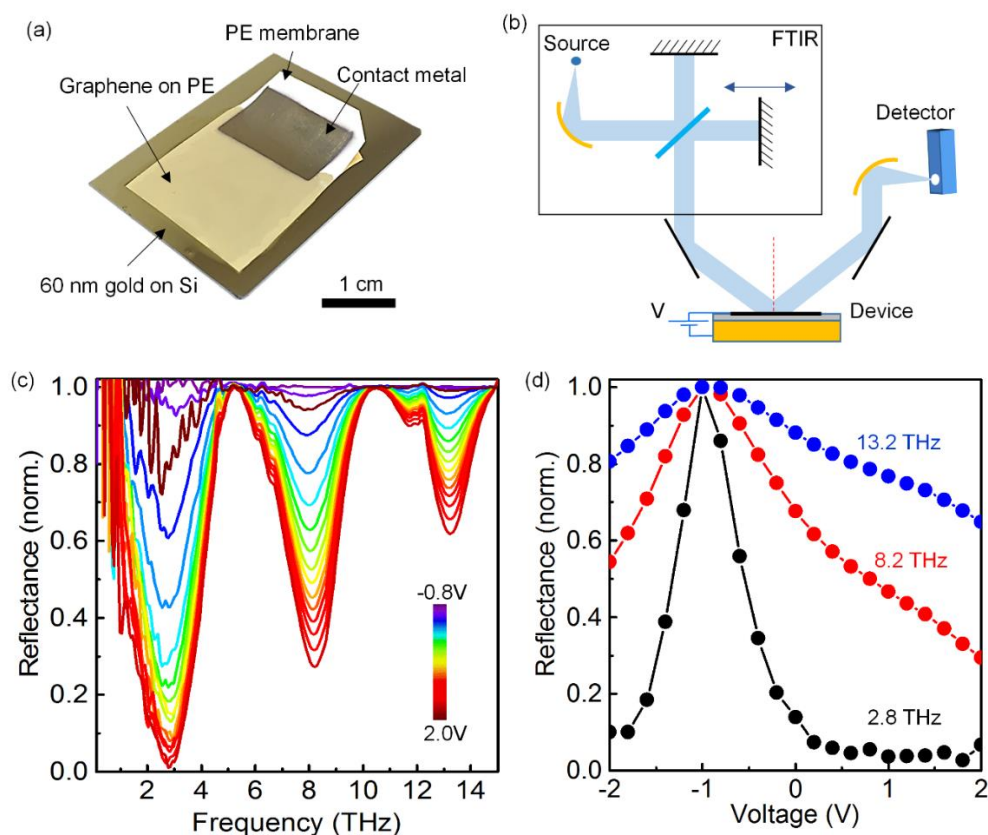


Figure 6.4 Coherent perfect absorption of THz radiation (a) Photograph of the fabricated THz cavity. The monolayer graphene is transferred on PE membrane and placed on a gold coated substrate. The 20- μm -thick membrane defines the cavity length, holds the electrolyte and forms the mechanical support graphene. (b) Experimental setup used for the THz measurements. (c) The Reflectivity spectrum from the device at different bias voltages. (d) The variation of the resonance reflectance with gate voltage. The charge neutrality point is at -1 V. ©2016 ACS

The Fermi energy provides wealth of information about the electrical and optical properties of the device. Liu et al, predicted that, to achieve CPA in THz, the Fermi energy of graphene should be close to 1eV that yields the required optical conductance for the critical coupling. Near-IR and IR (Figure 6.5) reflection spectra from the device provide direct measurement of the Fermi energy of the doped

graphene. Figure 6.5(a) shows the electronic band structure of doped graphene. Due to the Pauli blocking, doped graphene has a gap in the optical absorption for photon energies $E < 2E_F$. Gating graphene results an increase in the absorption gap and a step-like change in the reflectivity spectrum. Figure 6.5(b) shows the measured reflectivity spectra which show a step-like change in the reflectivity with a cutoff wavelength at $2E_F$. Although, a monolayer graphene absorbs around 1.8 % on a dielectric substrate, in our cavity structure, the reflectivity shows about 3 % modulation due to multiple passes. Figure 6.5(c) shows the extracted Fermi energy as a function of bias voltage. At charge neutrality point ($V_{CNP} = -1$ V) the unintentional doping level is 0.2 eV and increases linearly with the gate voltage up to 1 eV. At $V_G=0$ V, graphene is significantly doped with Fermi energy of 0.55 eV due to work function difference between the gold and graphene electrodes.

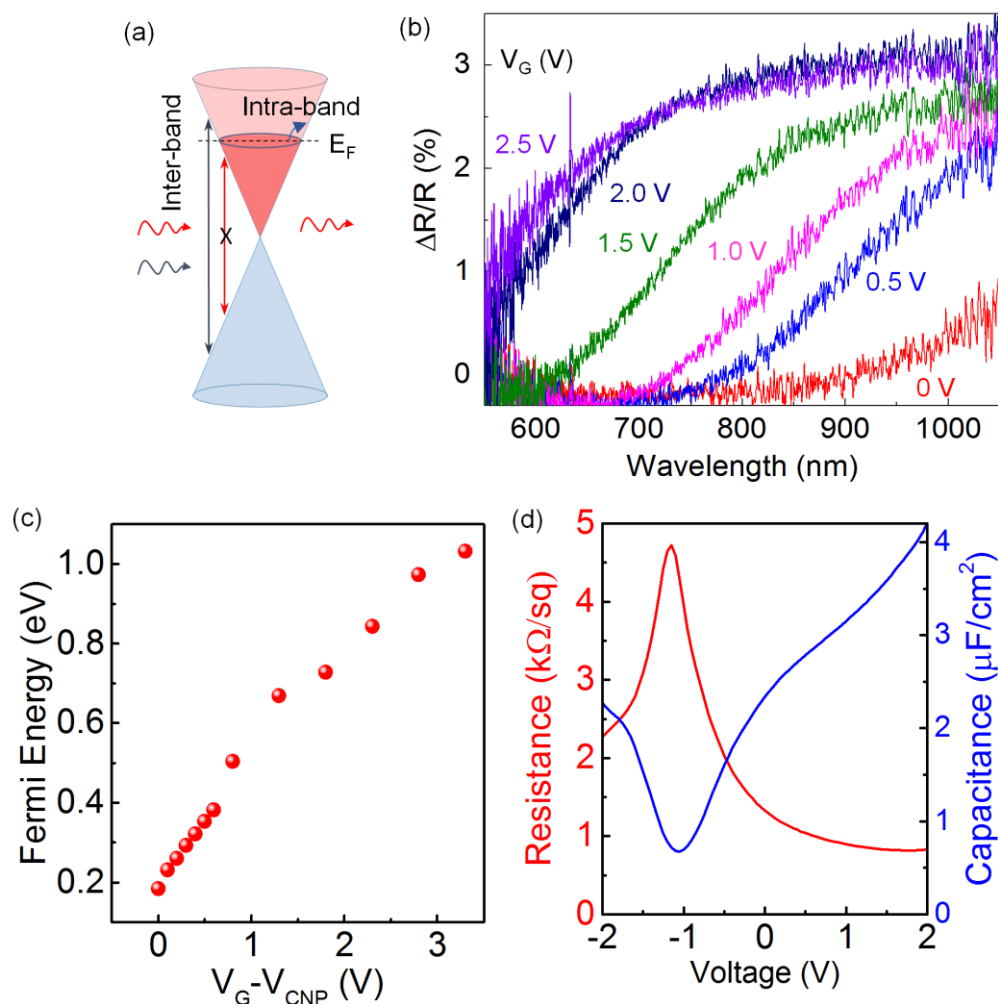


Figure 6.5 Electrical and optical characterization of the device (a) Schematic representation of the band structure of graphene and possible electronic transitions. (b) Gate-tunable near-IR optical reflection from the graphene surface at different bias voltages. The number on the curves shows the bias voltage. (c) Fermi energy extracted from the reflection spectrum. (d) Variation of the resistance and capacitance of the devices with the bias voltage. At charge neutrality point, resistance reaches a maxima of 4.5 $k\Omega$ and the capacitance goes to a minima of 0.8 $\mu F/cm^2$. ©2016 ACS

To get more insight, we performed electrical characterization of the device using an LRC meter. Figure 6.5(d) shows the variation of the resistance and capacitance of the

devices with the bias voltage. At charge neutrality point, the sheet resistance reaches up to 4.5 k Ω and decreases down to 0.8 k Ω which also includes the contact resistance of the electrodes. The capacitance of the device shows a minima (0.8 $\mu\text{F}/\text{cm}^2$) at the charge neutrality point due to the minimum quantum capacitance of the graphene layer. The electrical characterization show a good agreement with the spectroscopic measurements. Our results suggest that the critical coupling condition is achieved when the Fermi energy is around 1 eV.

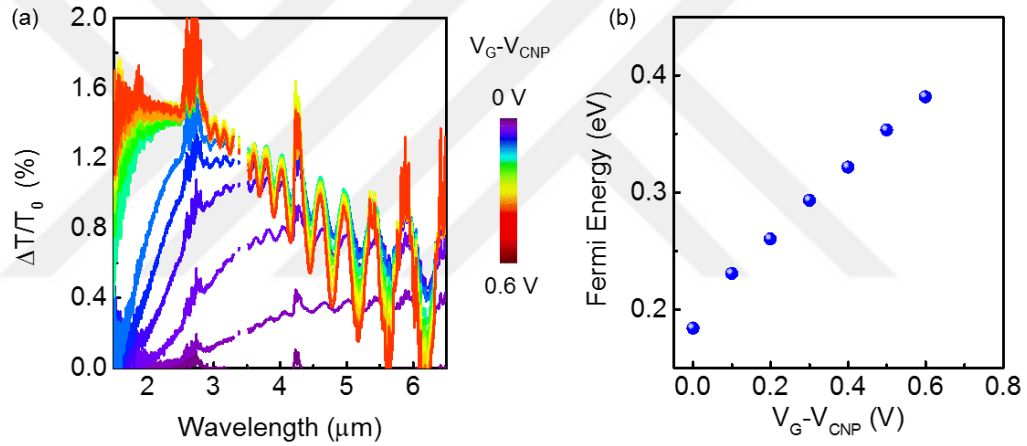


Figure 6.6 (a) Voltage-controlled IR reflectivity of the active THz surface and (b) the extracted Fermi energies at low bias voltages. ©2016 ACS

To quantify the Fermi energy degrees at low doping levels we measure the reflectance at mid-infrared range via FT-spectroscopy. We used the same device structure consisting of gold and graphene electrodes. Figure 6.6 shows the voltage-controlled infrared reflectance of the terahertz surface and the extracted values of the Fermi energy of graphene. The oscillations in the reflectance curves are due to Fabry-Perot oscillations, Figure 6.6(b). In the mid-infrared region we observed lower interband absorption (2.3 %) as compared to the measurements at visible spectrum. At charge neutral state graphene is already doped by ~ 0.2 eV, and changes up to 0.4 eV under low gating voltages.

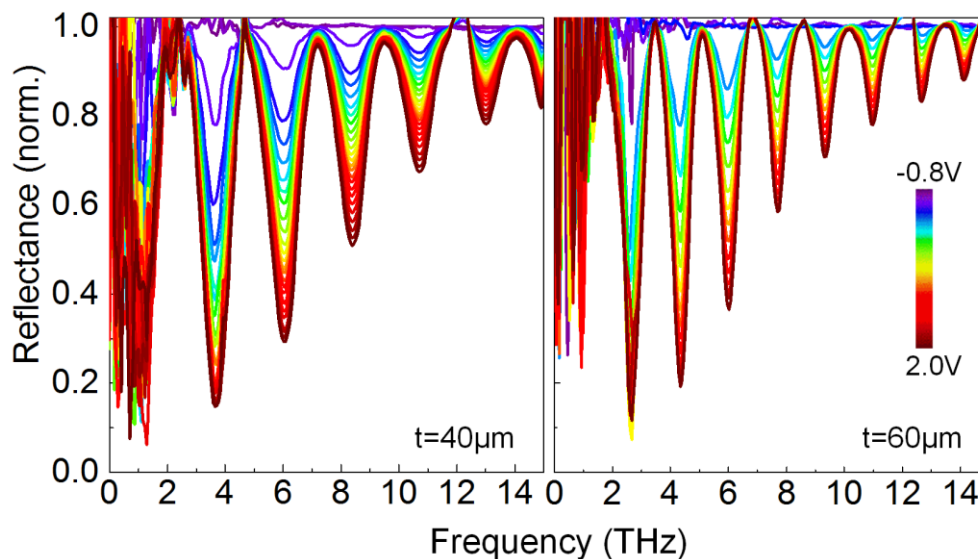


Figure 6.7 Tunable reflectivity from various THz cavities: Reflectance spectrum of THz cavities with 40 and 60 μm membrane thickness. ©2016 ACS

The thickness of the porous substrates and the incidence angle define the frequency of the resonance absorption. We repeat our measurements with different membrane thicknesses. Figure 6.7 shows the gate tunable reflectivity spectrum from two different device with 40 and 60 μm cavity length. The observed resonance wavelengths satisfy the critical coupling condition as $\lambda_m = 4nt\cos(\theta)/(2m + 1)$. We don't observe a significant change in the frequency however, the width of the resonance varies slightly with the bias voltage. Figure 6.8, illustrates the closer characterizations of resonance dips. Figure 6.8 (a, b) show the zoomed resonance dips of 3.6 and 8.5 THz frequencies at various voltages for 40 μm cavity length. The resonance frequency is constant, Figure 6.8(c), and the full width at half maximum (FWHM) increases with gating voltages, Figure 6.8(d).

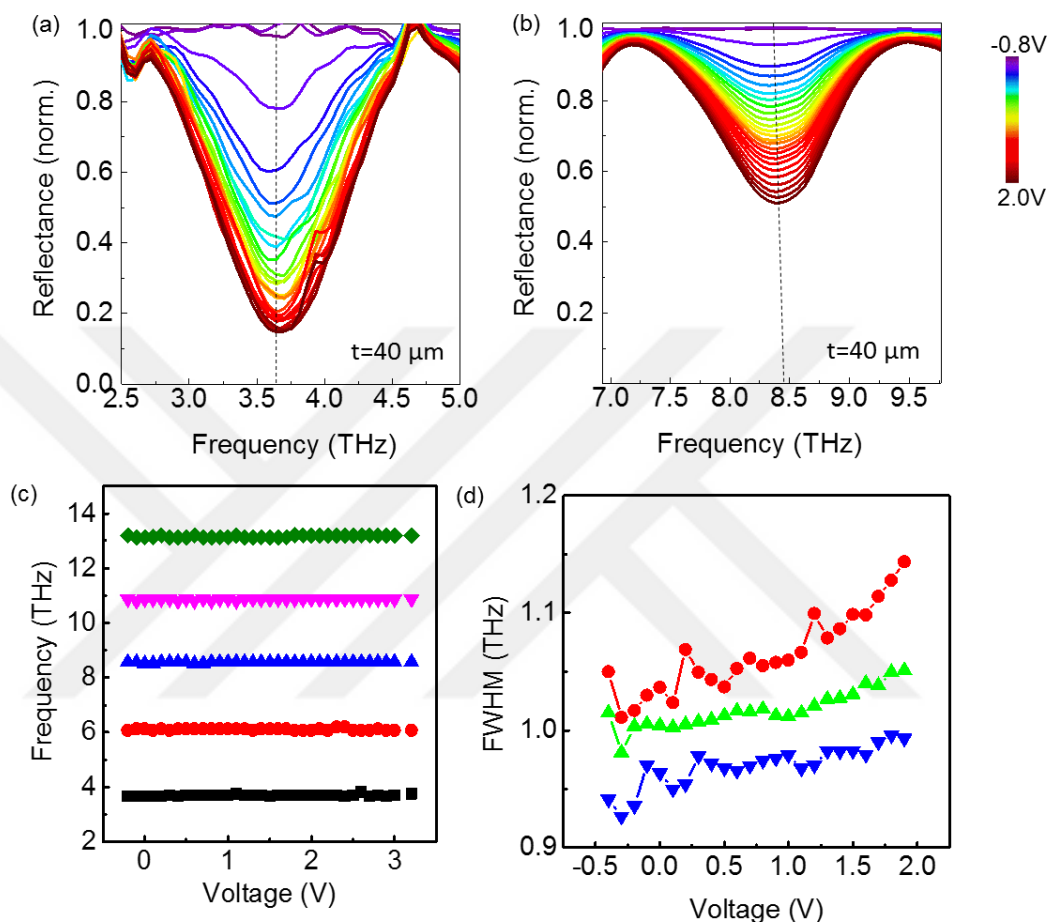


Figure 6.8 (a, b) The reflectivity spectra of individual resonances at 3.6 and 8.5 THz at different gate voltages. (c) Variation of the resonance frequency and the FWHM of the resonances. We do not observe a significant shift in the resonance frequency however, the FWHM increases slightly with the bias voltage. ©2016 ACS

6.4 Sub-terahertz continuous wave reflectance

The fundamental resonance of the large cavities are buried under the noise level, due to the sensitivity of the FTIR system at low frequencies (< 2 THz). We performed additional experiments using continuous wave tunable frequency. Figure 6.9 illustrates the measuring system and the reflectance of the graphene device. We used a tunable frequency signal source (WR9.0AMC+WR2.8X3) by Virginia Diode, Inc.

Schottky diode (VDI), driven by a voltage-controlled frequency-tunable YIG oscillator as a THz CW source, Figure 6.9(a). This system can provide a minimum average output power of about 1 mW. The output of the source is amplitude modulated via function generator in order to detect the radiation with a Golay Cell (Tydex TC-1T). Figure 6.9(b) shows the resultant reflections at various bias voltages. Similarly, we obtained 98 % modulation at 0.368 THz.

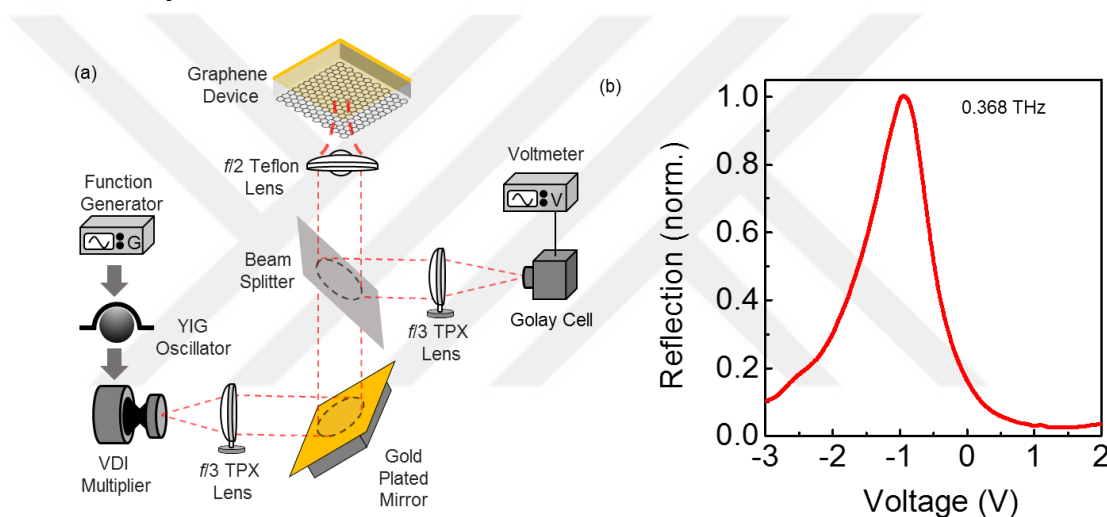


Figure 6.9 (a) Schematic drawing of the experimental setup used for reflectivity measurements at 0.368 THz. A Virginia Diode, Inc. Schottky diode (VDI), based, multiplied mm-wave/THz emitter is used as a tunable frequency signal source (WR9.0AMC+WR2.8X3). Driven by a voltage-controlled frequency-tunable YIG oscillator, the system can provide a minimum average output power of about 1 mW. The output of the source is amplitude modulated via function generator in order to detect the radiation with a Golay Cell (Tydex TC-1T). (b) The normalized reflectivity plotted as a function of bias voltage. We obtained a modulation of 98 % at 0.368 THz. ©2016 ACS

6.5 Transport scattering time at highly doped graphene

Recently, several THz pump-probe studies reveal semiconducting-to-metallic photoconductivity crossover in doped graphene.[60, 61, 104] These observations are accounted for the changes of Drude weight and transport scattering time by the doping level. The enhanced optical absorption of graphene in the tunable THz cavity could provide a new platform to elucidate non-ideal Drude response of graphene at high doping levels. Due to the frequency dependence of the optical conductivity, the maximum absorbance decreases with frequency. By combining this frequency dependence with the direct measurement of Fermi energy, we can extract the transport scattering time and its dependence on Fermi energy.

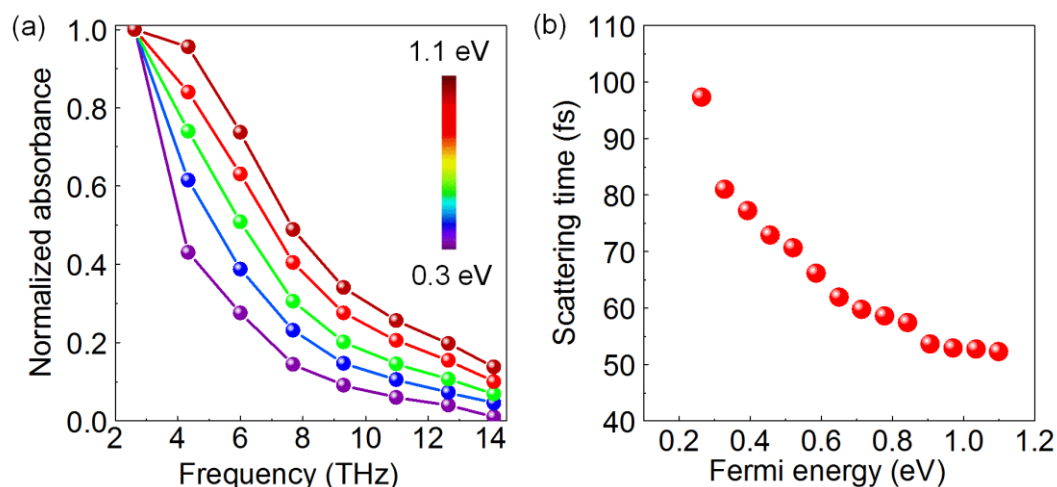


Figure 6.10 Drude response of graphene at high doping level (a) Frequency dependence of the resonance absorbance at different Fermi energies. The absorbance is normalized by maximum absorbance at 2.8 THz. (b) The variation of the transport scattering time with the Fermi energy. ©2016 ACS

In Figure 6.10(a), we plot the normalized resonance absorbance, which is proportional to the real part of the normalized optical conductivity, $\sigma(\omega)/\sigma_{DC} = i/(\omega + i\tau^{-1})$, against the frequency for varying Fermi energy between 0.3 to 1.1 eV.

Although at low doping concentration, THz response of graphene can be modeled with Drude model with constant scattering time, at high doping levels, however the scattering rate changes with Fermi energy. The transport scattering time has two contributions associated with the long-range charge impurity scattering (τ_c) and short-range disorder scattering (τ_s) as $(\tau^{-1} = \tau_c^{-1} + \tau_s^{-1})$. [64, 65] These scattering mechanisms scale differently with the Fermi energy. For short-range scattering, the scattering rate is proportional to E_F , however, for long-range scattering, the scattering rate is inversely proportional to E_F . Our results show that, as the Fermi energy increases, the absorbance decays slower with the increasing frequency indicating a smaller scattering time. Using the Drude model, we extracted the Fermi energy dependence of the total scattering time (Figure 6.10(b)). Around charge neutrality point, the scattering time is close to 100 fs and decreases down to 50 fs at Fermi energies of 1.1 eV.

6.6 Flexible active terahertz surface

Simplicity in device structure allowed us to fabricate device based on both solid and flexible substrates. To show the promises of our approach, we demonstrate flexible active THz surfaces as the application part of our work. The tunable coherent absorption of THz radiation can lead new types of active THz devices. Conventional THz devices are rigid which prevents realization of flexible THz components. The atomic thickness of graphene together with the simple device geometry allows us to fabricate a tunable THz cavity on a flexible polymer substrate.

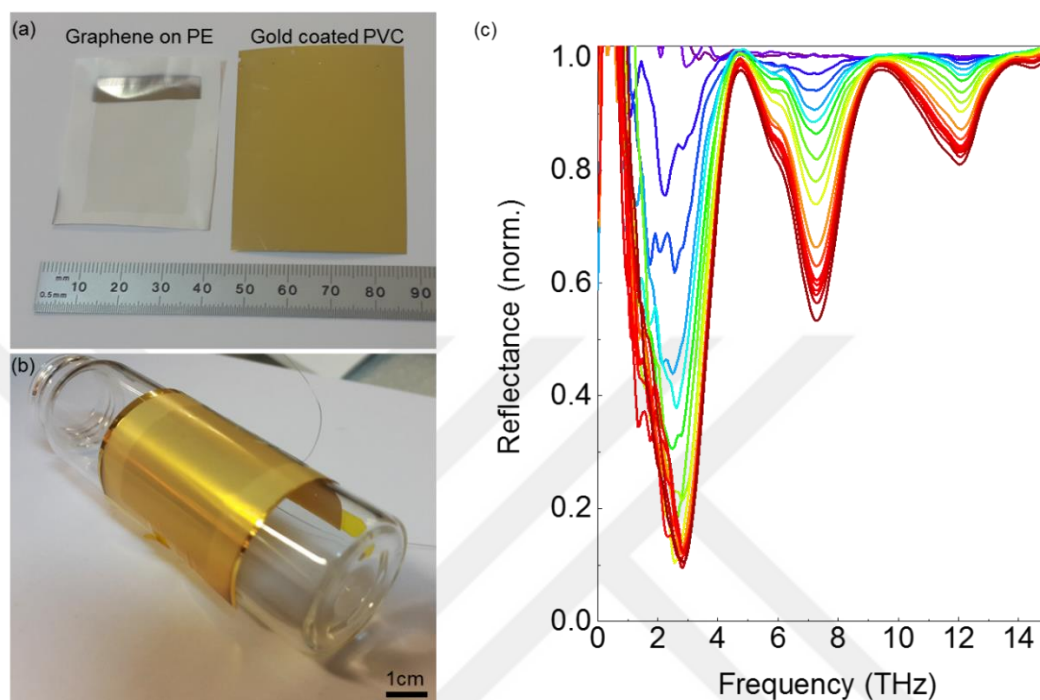


Figure 6.11 Flexible active THz surfaces (a) Photograph of the large area graphene on PE membrane and gold coated PVC substrate. (b) The fabricated device rolled around a glass cylindrical with diameter of 2.7 cm. (c) THz reflectivity spectrum from the curved surface at different bias voltages. ©2016 ACS

Figure 6.11(a) shows the photograph of large area graphene ($2.5 \times 3.0 \text{ cm}^2$) on porous PE membrane and gold coated PVC substrate. After injecting ionic liquid into the PE membrane ($20 \text{ }\mu\text{m}$ thick), we placed it on the gold coated PVC substrate and rolled the device around a glass cylindrical with diameter of 2.7 cm (Figure 6.11(b)). We measured the variation of the THz reflectivity from the curved surface. During the measurement the beam size is set to 6 mm in diameter. Similar to the rigid devices, we observed three resonances at 3, 7.2 and 12.2 THz (Figure 6.11(c)). The first resonance yields gate tunable absorption up to 95 % at 2V bias voltage.

6.7 Conclusion

In conclusion, we report experimental observation of gate-tunable coherent perfect absorption of terahertz radiation in highly doped graphene. Our work has four novel parts. First, we developed an electrically tunable THz cavity using a THz transparent porous membrane soaked with ionic liquid electrolyte sandwiched between graphene and gold electrodes. In this device geometry gold electrode operates both as reflecting mirror and the gate electrode. Second, we observed the coherent perfect absorption of THz radiation in graphene. Ability to gate graphene up to 1 eV Fermi levels in the THz cavity, allows us to observe critical coupling condition which yields absorption of 99 %. Third, this novel device configuration allows direct measurement of Fermi energy and to elucidate the doping dependence of the transport scattering time which varies from 100 fs down to 50 fs as the Fermi energy changes between 0.2 to 1.1 eV. Finally, using these structures we demonstrated flexible active THz surfaces with voltage controlled THz reflectance. We anticipate that the our work provide a developed device structure provides a new platform to study gate-tunable CPA would lead to efficient active THz components such as tunable THz mirrors and modulators.

Chapter 7

Terahertz Spatial Light Modulators

In this chapter, we demonstrate a broadband terahertz (THz) spatial light modulator using 5×5 arrays of large area graphene supercapacitors. Our approach relies on controlling spatial charge distribution on a passive matrix array of patterned graphene electrodes. By changing the voltage bias applied to the rows and columns, we were able to pattern the THz transmittance through the device with high modulation depth and low operation voltage. We anticipate that the simplicity of the device architecture with high contrast THz modulation over a broad spectral range could provide new tools for THz imaging and communication systems.

7.1 Introduction

Due to the nonionizing nature and submillimeter resolution of terahertz (THz) radiation, it promises to enable new technologies ranging from homeland security to biomedical applications [8-10]. Although THz sources and detectors have significantly advanced, the active THz components are still underdeveloped due to the lack of an active material that works in THz frequencies [8]. The quest for active THz devices has led researchers to use high mobility free carriers to manipulate light-matter interactions in the THz regime [8, 105]. Active devices such as modulators

[106] and phase shifters [106, 107] have been demonstrated by tuning the charge density on semiconductor surfaces. Spatial light modulators (SLMs) are the key components for beam steering and imaging systems, which involve sophisticated integration of many active components [15-17, 19, 20, 108]. A THz SLM requires individually addressable pixels that independently control the transmittance and reflectance of THz signals at different locations. Chan et al. used an interconnected THz metamaterial on a semiconductor surface to form Schottky contacts [106]. By wiring the group of split-ring resonators, the local transmittance of the THz waves was controlled by electrically tuning the depletion area under the Schottky contacts [15, 34]. More recently, Watts et al. applied the same principle for compressive THz imaging [36]. Other approaches such as microelectromechanical systems and photo-generated carriers on semiconductors have also been investigated [17, 35, 109].

7.2 Fabrication of graphene-enable multipixel THz device

The ability to synthesize large scale graphene, two-dimensional (2D) crystal of carbon [56], provides a new foundation for the development of active THz devices [39, 55, 66, 69]. The linear band structure, together with the atomic thickness of graphene, yield a high mobility 2D electron gas with gate-tunable charge density. Unlike other buried 2D electronic systems based on semiconductor heterostructures [110], graphene can be transfer-printed on an open dielectric surface that can be electrostatically doped with a back-gate electrode. In pioneering work by Sensale-Rodriguez et al. [27], a back-gated transistor was used to control transmission of THz waves. Shifting the Fermi energy of graphene changes the rate of intraband electronic transitions that alters the absorption and reflection of THz waves in broad spectra. The researchers extended their technique by fabricating arrays of transistors that operate as a THz SLM [38, 40, 43, 48, 67, 70, 111]. However, the dielectric breakdown of a back-gated transistor limits the dynamic range of these devices due to the limited charge density on the order of 10^{12} cm^{-2} . To solve this problem, we developed a high contrast THz modulator using graphene supercapacitors [73, 76].

In our device, we used two large area graphene electrodes separated by an ionic liquid electrolyte ([deme][Tf2N]) sandwiched between two graphene electrodes. This simple device architecture results in a very efficient electrolyte gating that generates charge densities on the order of 10^{14} cm^{-2} , which corresponds to Fermi energies of $\sim 1 \text{ eV}$. The efficient electrolyte gating is achieved by very thin (a few nanometers) electrical double layers on the graphene surface. In this Letter, we demonstrate an electrically controlled, high contrast, broadband THz SLM using arrays of graphene supercapacitors. We were able to pattern the THz transmittance through a 5×5 passive matrix array of a graphene capacitor by switching the voltages applied to the rows and columns of the array. Figure 1 shows the schematic drawing of the passive matrix array of a graphene supercapacitor that operates as a THz SLM. The voltage difference between the top and the bottom electrodes polarizes the electrolyte and accumulates high mobility charges at each pixel. By changing the bias voltages applied on rows and columns of the passive matrix array, we were able to reconfigure the THz transmittance. We fabricated the SLM using large area graphene ($5 \times 5 \text{ cm}^2$) synthesized by chemical vapor deposition on copper foils and transferred on to a THz transparent polymer substrate. After the transfer process, we patterned the graphene electrodes into ribbons with a width of 8 mm. We attached the patterned graphene electrodes on a printed circuit board [Figure 7.1(b)] and made electrical contacts with the aid of a conductive epoxy. The intersections of rows and columns define individually addressable pixels. To address a pixel (reduce the transmittance), we apply a voltage difference between the corresponding row and column. We used a switch box and a two-channel source-measure unit (Keithley, 2600) to apply voltages to the rows and columns.

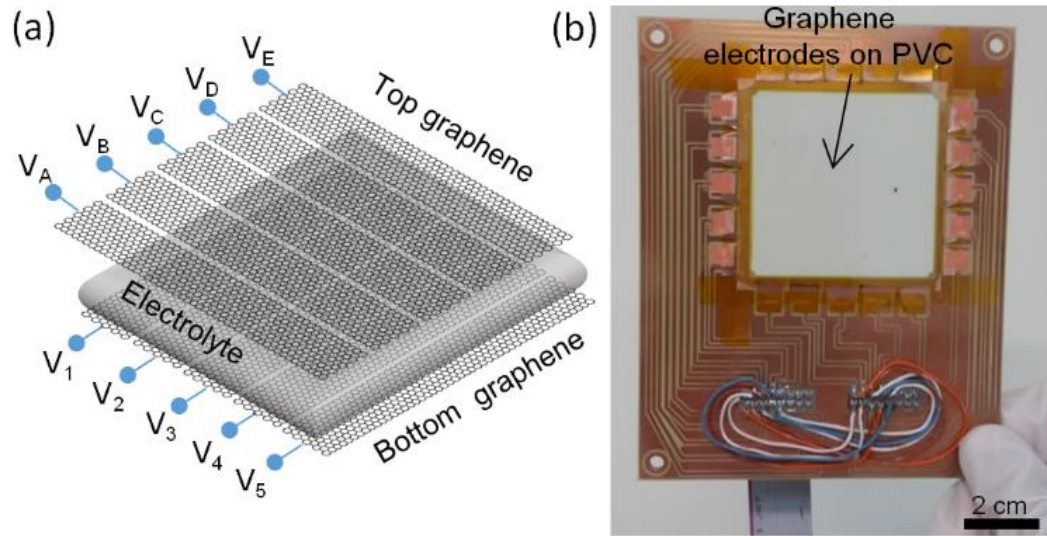


Figure 7.1 (a) Schematic drawing of the THz spatial light modulator consisting of a 5×5 array of graphene supercapacitors. (b) Photograph of the fabricated device mounted on a printed circuit board. The size of an individual pixel is $8 \text{ mm} \times 8 \text{ mm}$.
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7.3 Controlling THz transmittance with graphene-enabled THz-SLM

To measure a transmittance, Virginia Diode, Inc.'s Schottky-diode-based, multiplied millimeter (mm)-wave/THz emitter is used as a tunable frequency signal source (WR9.0AMC+WR2.8X3). Driven by a voltage-controlled frequency-tunable YIG oscillator, the system can provide a minimum average output power of about 1 mW. The source can operate in two frequency regions: 80–125 GHz and 240–380 GHz. The output of the source is amplitude-modulated via a function generator in order to detect the radiation with a Golay cell (Tydex, TC-1T). The output beam was collimated with an F#3, $D=50 \text{ mm}$ TPX lens and then focused onto the device with an F#2, $D=50 \text{ mm}$ Teflon lens. The mm-wave and THz spot diameters were measured to be $\sim 9 \text{ mm}$ and 3 mm , respectively, at the device position. The radiation was then collected by a duplicate set of optics and focused onto the receiver. The modulator was positioned in a computer-controlled xy -scanner (Marzhauser Wetzlar

GmbH), which allowed the device to be raster-scanned around the focused THz beam.

Figure 7.2(a–d) show the recorded transmission images of the THz SLM with various voltage configuration at a frequency of 0.37 THz. First we measured the transmittance image when all electrodes were grounded [Figure 7.2(a)]. For this configuration, the average transmittance is around 62 ± 5 %. The variation (± 5 % of the incidence power) of the transmittance over the device area is due to inhomogeneous charge density caused by unintentional doping on graphene. When we applied +1 and –1 V to the rows and columns, respectively, we observed a minimum transmittance of 30 ± 5 % [Figure 7.2(b)]. To address a single pixel in a passive matrix array, one needs three distinct states. For our device, we chose 0, 1, and 2 V voltage differences, which yielded 65 %, 45 %, and 32 % of transmittance, respectively. By switching the voltages on the rows and columns, we were able to modulate the transmittance pattern. At the intersection of the grounded row and column, the voltage difference is 0 V, which yields a high level of transmittance. However, the maximum transmittance through a single pixel depends on voltage applied to the adjacent pixel due to the cross talk. We obtained a transmittance image [the checkerboard image seen in Figure 7.2(d)] with maximum and minimum transmittance of 52 % and 30 %, respectively.

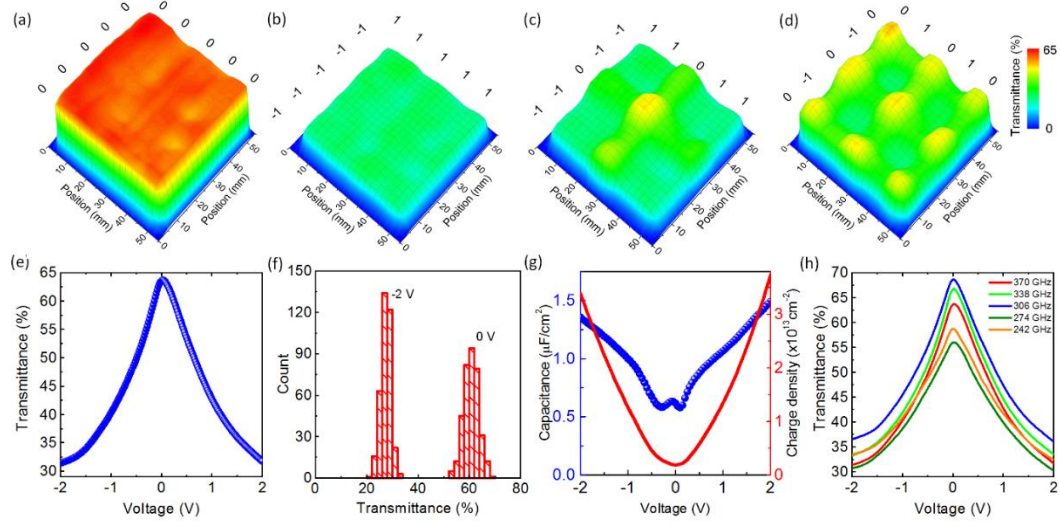


Figure 7.2 (a)–(d) THz transmission images of the SLM with various voltage configurations recorded at a frequency of 0.37 THz. (e) Transmittance of the device at 0.37 THz as a function of bias voltage. (f) Histogram of the transmittance at bias voltage of 0 and 2 V. (g) Variation of the capacitance (left axis) of the device and estimated charge density (right axis) as a function of bias voltage. Two distinct minima are associated with the Dirac points of the top and bottom graphene electrodes. (h) Voltage-dependent transmittance at different frequencies. ©2015 OSA

By varying the voltage from 0 to 2 V, we can tune the transmittance from 65 % down to 30 % [Figure 7.2(e)]. Due to the unintentional doping of graphene and hysteresis effects, there is around 5 % variation in the transmittance over the device area of 25 cm×25 cm. The histogram of the transmittance at 0 V and 2 V is given in Figure 7.2(f). To quantify the amount of charge accumulated on the graphene electrodes, we measured the variation of capacitance of the device by applying a small AC voltage (0.1 V) with a variable DC bias voltage (–2 to 2 V). The capacitance of the device varies from 17 to 45 μF . The capacitance of the device can be reconfigured by the switch box. We observed two distinct minima at –0.3 V and 0.2 V associated with the difference of the Dirac points of the top and bottom graphene electrodes. From

the measured capacitance, we estimated that the charge density varies from 0.2×10^{13} to $3.7 \times 10^{13} \text{ cm}^{-2}$. The response time of our device is slower than the dielectric based modulators due to the large capacitance and device area. The dynamic range of our modulator is limited by the minimum charge density on graphene and the electrochemical window of the electrolyte. Unintentional doping and charge puddle formation limit the minimum charge density to around 10^{12} cm^{-2} . The electrochemical window of the electrolyte determines the maximum voltage of 4 V, which yields a charge density of 10^{14} cm^{-2} [74].

An important aspect of our device is that it can operate over a very broad spectrum. We recorded the voltage dependent THz for a frequency range between 0.24 and 0.37 THz [Figure 7.2(h)]. This frequency range is limited by our experimental setup. The recorded transmittance varies between 67 % down to 30 % for this frequency range. The variation of transmittance between various frequencies over different applied potentials is most likely due to the variation of the spot size on the sample.

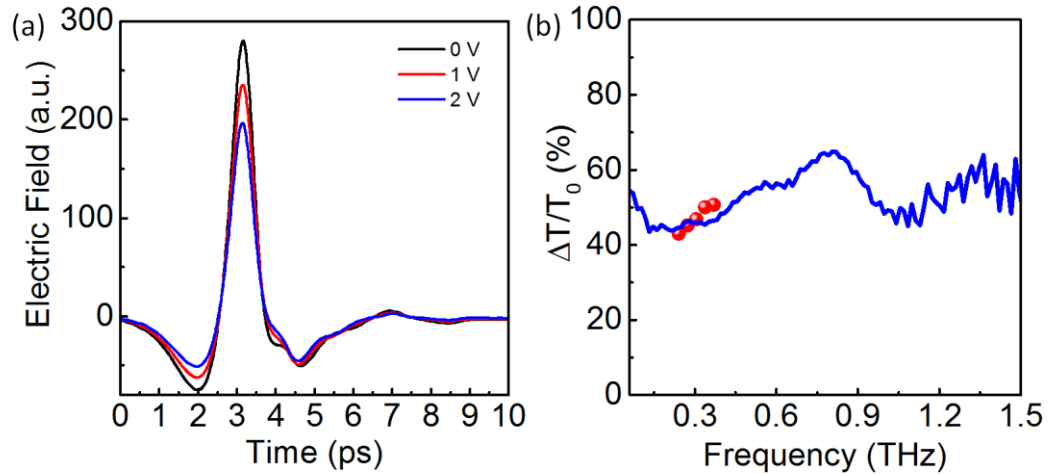


Figure 7.3 (a) THz pulse recorded at bias voltages of 0, 1, and 2 V. (b) Modulation plotted against frequency. The scattered points show the data recorded with our mm-wave/THz system. ©2015 OSA

Since the modulation of THz waves is due to a changing Drude-like metallic behavior, graphene can inherently respond in a very broad spectrum. To test the broadband spectral response, we measured the spectral response using conventional time-domain THz spectroscopy of a single-pixel graphene device. We measured the transmitted THz pulse through the device at different bias voltages [Figure 7.4(a)]. We took the fast Fourier transform of the time-varying electric field, calculated the transmission spectrum from 0.1 to 1.5 THz, and plotted the modulation ($M=(T_{0V}-T_{2V})/T_{0V}$) in Figure 7.4(b). The modulation varies between 40 % and 60 % in a frequency range of 0.1 to 1.5 THz. The scattered plot in Figure 7.4(b) shows the modulation obtained from the mm-wave/THz emitter system [Figure 7.2(h)]. We observed a good agreement between the two measurement systems.

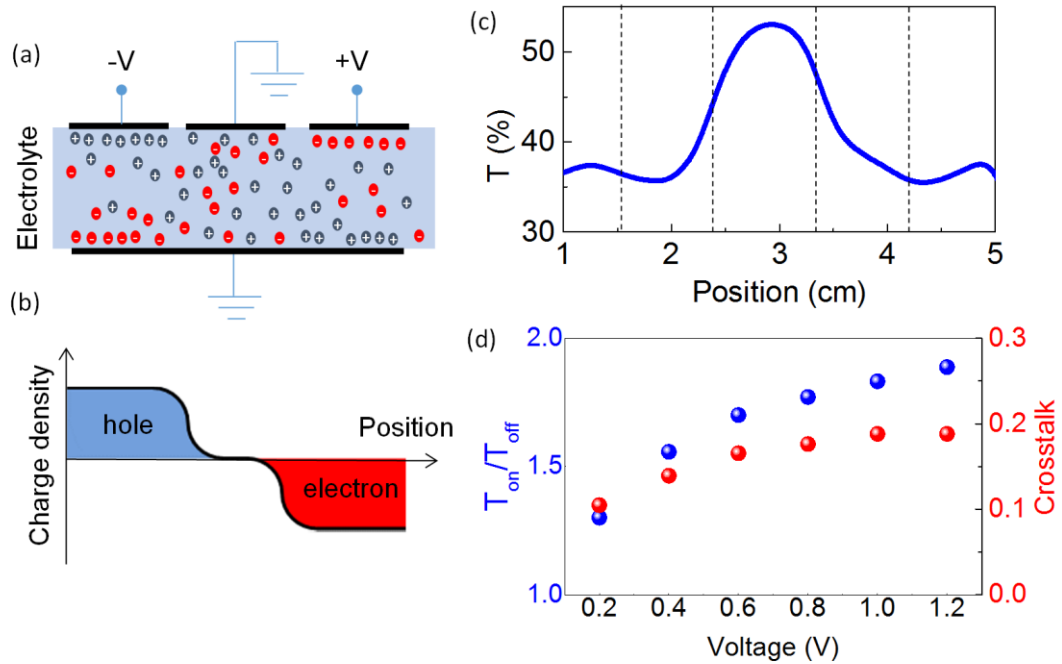


Figure 7.4 (a) Schematic illustration of cross section of the device and (b) charge distribution on the graphene electrodes biased at different voltages. (c) Line profile of the THz transmission along the grounded row. (d) Variation of the modulation and cross talk of single pixel with bias voltage. ©2015 OSA

The ions of the electrolyte distribute themselves to screen the voltage of the graphene electrodes. Furthermore, the accumulated ions change the conductivity on the graphene electrodes via electrostatic doping. The charge accumulated on a pixel depends on not only the voltage difference between the top and bottom electrodes, but also the applied voltage on adjacent pixels. Figure 7.3(a) illustrates this process. The voltage difference between the adjacent pixels causes a cross talk. Due to the cross talk, the charge distribution (also the THz transmission) is not an ideal step-like function. Instead, the charge distribution changes gradually between the pixels. Figure 7.3(b) illustrates this complex charge distribution of a grounded bottom graphene electrode when the top graphene electrodes are biased at different voltages. Graphene shows ambipolar charge transport; therefore, the grounded electrode could be *n*-doped, *p*-doped, or neutral depending on the polarity of the voltage bias of the top electrode. Figure 7.3(c) shows measured THz transmittance along the center row of the image shown in Figure 7.2(d). To quantify the cross talk, we defined a figure of merit as ($C=1-R_{av}/R_{max}$) where R_{av}/R_{max} is the ratio of averaged and maximum transmittance between two adjacent pixels. In the absence of cross talk, for example, the average and center values are the same, which yield $C=0$. In Figure 7.4(d), we plotted the contrast (T_{max}/T_{min}) and cross talk ($C=1-R_{av}/R_{max}$). We observe that there is a tradeoff between the contrast and the cross talk. The contrast increases with the bias voltage and saturates after a bias voltage of 2 V [Figure 7.3(d)]. At the same time, cross talk increases with the bias voltage.

7.4 Modelling THz transmittance of the device

Finally, to understand the device performance in the high THz frequency range, a quantitative model based on a transfer matrix method for calculating the transmission coefficient of single-layer graphene was applied to our device [99, 112]. We model the graphene electrodes as 0.3-nm-thick layers with Drude-like optical conductivity $\sigma(\omega)=\sigma_{DC}/(1+i\omega\tau)$, where σ_{DC} is the low frequency conductivity of graphene, ω is the frequency, and τ is the mean scattering time of graphene electrodes, estimated to

be about 200 fs. Figure 7.5(a) shows the calculated transmission of single-layer graphene with three different sheet resistances ($R_s=1/\sigma$). The modulation diminishes at 10 THz. These simulations suggest that our device can operate even in a broader frequency range. Using the measured values for the refractive index of the polymer substrate ($n_s=1.66$, 75 μm thick) and ionic liquid ($n_{\text{IL}}=2.31$, 80 μm thick), the overall modulator structure is simulated. Figure 7.5(b) shows the calculated THz transmittance spectrum of the device including the geometry of the device and the optical constant of the materials. The calculated modulation amplitude in the low THz frequency range agrees with the experiments.

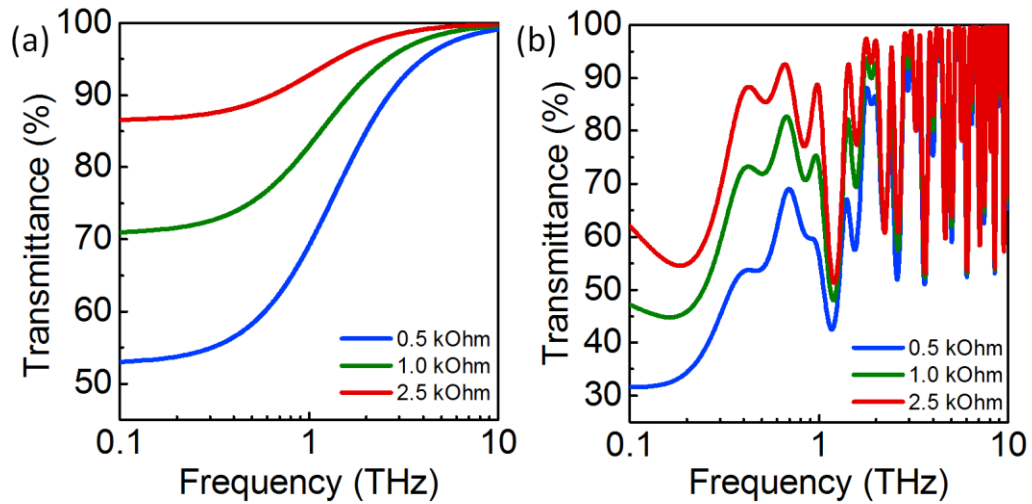


Figure 7.5 (a) Calculated THz transmittance of single-layer graphene. (b) Simulated THz transmittance of graphene device. ©2015 OSA

7.5 Conclusions

In conclusion, we have demonstrated a broadband THz spatial light modulator using arrays of large area graphene supercapacitors. The THz transmittance of a single pixel is controlled using a passive matrix addressing. We anticipate that controlling THz waves by tuning high mobility carriers on large area CVD-grown graphene via efficient electrostatic gating would provide new opportunities to bridge the THz gap.

Chapter 8

Summary

We studied the gate-tunable optical properties of highly doped graphene at terahertz frequency band, and demonstrated graphene-enabled terahertz optoelectronic devices. Using efficient electrolyte gating scheme, we were able to control the charge density on graphene from 10^{12} up to 10^{14} cm^{-2} which yields at maximum value the Fermi energies of 1 eV. Drude conductivity of graphene at high doping levels were investigated with time-domain and continuous wave THz spectroscopy techniques. Our results confirmed non-ideal Drude response of graphene at low photon energies, and revealed nearly perfect electron-hole symmetry from low to high doping levels. Moreover, we extracted the transport scattering time values for different Fermi energies. The scattering time of carriers change from 50 fs to 150 fs for undoped and highly doped cases of graphene. Highly doped graphene has carrier concentrations on the orders of 10^{14} cm^{-2} which was accomplished by ionic liquid electrolyte gating. The Fermi energies of the gated graphene were determined by Fourier-transform infrared spectroscopy. Using charge carrier tunability of graphene we developed graphene-based THz intensity modulator. The capacitive structure of modulator consisted of two large area graphene electrodes sandwiching ionic liquid medium. By

mutual gating of graphene electrodes we achieved 60 % modulation from 0.1 to 1.5 THz. Furthermore we enhanced free carrier absorption in graphene by introducing resonant device structure comprising of gold and graphene electrodes. Exploiting similar gating method we observed gate-tunable coherent perfect absorption of terahertz radiation. Terahertz radiation at 2.8 THz were attenuated by nearly 100 %. From the proportionality of absorption to conductivity we were able to extract scattering rates of carriers which confirms the results from Drude measurements. Finally, we developed broadband THz spatial light modulator from arrays of graphene supercapacitors. By changing the voltage bias applied to the rows and columns, we were able to reconfigure the THz transmittance.

The devices we developed offer low insertion losses (< 2 dB), high modulation depth (> 50 %) over broad spectrum (0.1 – 2.0 THz), and the simplicity of the device design are the key attributes of graphene enabled terahertz devices. Moreover, with the optimized device structures, we observed gate-tunable coherent perfect absorption of THz radiation with modulation depths of 100 %. The approaches developed in this work can lead to more efficient and sophisticated terahertz optoelectronic devices by surpassing the challenges of generating high carrier concentrations on graphene, and introducing low loss devices with practical fabrication methods.

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