

PERFORMANCE ENHANCEMENT OF GRAPHENE BASED OPTOELECTRONIC DEVICES

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By
Onur Özdemir
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OPTOELECTRONIC DEVICES

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

Ekmel Özbay(Advisor)

Hümeysra Çağlayan (Co-advisor)

Coşkun Kocabaş

Hamza Kurt

Approved for the Graduate School of Engineering and Science:

Levent Onural
Director of the Graduate School

ABSTRACT

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Onur Özdemir

M.S. in Electrical and Electronics Engineering

Advisor: Ekmel Özbay

Co-advisor: Hümeysra Çağlayan

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Graphene is a strong candidate for active optoelectronic devices because of its electrostatically tunable optical response. Current substrate back-gating methods are unable to sustain high fields through graphene unless a high gate voltage is applied. In order to solve this problem, ionic liquid gating is used which allows substrate front side gating, thus eliminating major loss factors such as a dielectric layer and a thick substrate layer. On the other hand, due to its two dimensional nature, graphene interacts weakly with light and this interaction limits its efficiency in optoelectronic devices. However, V-shaped plasmonic antennas can be used to enhance the incident electric field intensity and confine the electric field near graphene thus allowing further interaction with graphene. Combining V-shaped nanoantennas with the tunable response of graphene, the operation wavelength of the devices that employ V-shaped antennas can be tuned in situ. We demonstrate a reflection enhancement by utilising different V-shaped nanoantenna geometries on a Si-SiO₂ substrate. After studying the response of these nanoantennas, we demonstrate a graphene-based device with ionic liquid gating and V-shaped plasmonic antennas to both enhance and more effectively tune the total optical response. We are able to tune the transmission response of the device for up to 389 nm by changing the gate voltage by 3.8 Volts in the mid-infrared regime.

Keywords: graphene, plasmonics, nanoantennas, ionic liquid, photomodulation.

ÖZET

GRAFEN TABANLI OPTOELEKTRONİK AYGITLARDA PERFORMANS ARTIRILMASI

Onur Özdemir

Elektrik ve Elektronik Mühendisliği, Yüksek Lisans

Tez Danışmanı: Ekmel Özbay

Tez Eş Danışmanı: Hümeysra Çağlayan

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İki boyutlu bir malzeme olan grafen, elektrostatik olarak ayarlanabilir optik yanıtı sayesinde ayarlanabilir optoelektronik cihazlar için güçlü bir adaydır. Bugüne kadar kullanılan ve alttaşın arka yüzeyinden uygulanan kapı voltajı –çok yüksek voltajlar uygulanmadığı halde- grafen üzerinde güçlü elektromanyetik alanlar oluşturma açısından zayıf bir yöntemdir. Bu soruna bir çözüm olarak, iyonlu sıvı yöntemi alttaşın ön yüzeyinden uygulanan kapı voltajı sayesinde alttaş kayıpları olmadan grafen üzerinde güçlü elektromanyetik alanlar oluşturmaktadır. Öte yandan, iki boyutlu doğası gereği grafen, ışık ile sınırlı bir etkileşime sahiptir. Bu sınırlı etkileşim grafenin optoelektronik uygulamaları konusundaki verimini sınırlamaktadır. V-şeklindeki plazmonik nanoantenler, yakınlarındaki elektrik alanı hapsedtikleri ve görece şiddetini artırdıkları için grafen-ışık etkileşimini artırmakta kullanılabilirler. Bu nanoantenler ve grafenin ayarlanabilir yapısı birleştirilip, dalgaboyu yanıtı aktif olarak değiştirilebilir cihazlar yapmak mümkündür. Bu tezde ilk olarak, Si- SiO₂ alttaş üzerine yerleştirilen V-şeklindeki plazmonik antenlerin yansıma özelliklerini inceledik. Bu sayede nanoantenlerin rezonans dalgaboylarının yakınında yansıma artışı gözlemledik. Daha sonra nanoantenler ile grafeni birleştirip, geçirgenlik ölçümü yapılabilecek geometride bir cihaz tasarladık. Bu cihazı oluşturduk ve iyonlu sıvı yöntemi ile kapı voltajı uyguladık. Bu cihaza 3.8 Volt kapı voltajı uygulayarak cihazın orta-kızılötesi optik geçirgenlik rezonans dalgaboyunda 389 nm’lik bir kayma oluşturduk.

Anahtar sözcükler: grafen, plazmonik, nanoantenler, iyonlu sıvı, ışık modülasyonu.

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Chapter 1

Introduction

Silicon industry is slowly reaching its limits. In order to maintain a performance increase in current silicon-based electronic devices, the device dimensions are getting smaller and smaller. Some fundamental limits on operating frequency and leakage currents make it impossible to produce faster devices. Light, on the other hand, is much faster than the electrical currents inside current silicon-based devices. It can be used to increase device performance and can replace the electronic circuitry. One major obstacle is the wavelength of light, which is very large compared to current devices. In order to confine light in nanodimensions, plasmonics, the collective oscillations of electrons, can be a solution. The term "plasmonics" is coined by the research group in California Institute of Technology by Atwater et al. in 2000s [1] and since then, it has been a growing field of research.

By confining light at nanodimensions, plasmonics enable the formation of high electric fields. Plasmonic nanoantennas, which operate as a medium to excite plasmonic modes, are able to induce high electric fields near their vicinity. These fields are useful in increasing the light-matter interaction and have been proven useful in optoelectronic devices like photodetectors [2], photomodulators [3] and in solar cells [4] by utilizing the optical response of plasmonic nanoantennas near their resonance frequencies.

Unless their dimensions are changed, plasmonic nanoantennas have a fixed spectral response. This limits their versatility and hinders their use in actively tunable devices. In order to solve this problem, graphene has been proposed as an actively tunable medium on which plasmonic structures can be placed. [5] By changing the surface conductivity of graphene through electrostatic gating, the optical response of the plasmonic antennas can be shifted.

Having an atomic thickness and large tunable optical characteristics, graphene is a very suitable candidate for utilizing light in nanodimensions. Its extraordinary properties such as high carrier mobility, conical band diagram, Dirac-like carrier dynamics and tunable interband and intraband transitions make graphene an interesting candidate in nanophotonics.

In this thesis, we propose V-shaped plasmonic nanoantennas to enhance the reflection response of a Si-SiO₂ substrate and having investigated the resonance response of these antennas, we utilize them in a graphene based tunable photomodulator with ionic liquid gating for effective tuning. Proposed methods increase the performance of the graphene based device and allow plasmonic nanoantennas to be tunable in their optical response.

1.1 Outline of the Thesis

In Chapter 2, a background on graphene is provided. Following a general introduction on the material itself, we move to its optical response. Mechanisms of light-graphene interaction are described. Tunability of graphene and various tuning mechanisms are investigated.

In Chapter 3, V-shaped plasmonic nanoantenna geometry is discussed after an introduction of the plasmonic nanoantennas. The design process and the fabrication is explained. Spectral reflection measurements conducted on nanoantenna-SiO₂-Si geometry is presented with a discussion of the resonances.

In Chapter 4, nanoantenna geometry in Chapter 3 is further utilized in a graphene based tunable optoelectronic device. The efficiency of ionic liquid gating in comparison with traditional electrostatic gating methods are discussed. Device geometry and fabrication is explained in detail. Spectral transmission measurements and their detailed analysis is presented.

In Chapter 5, conclusive remarks and a glimpse into possible future work ideas are given.



Chapter 2

Graphene

Graphene is a flat monolayer honeycomb lattice of carbon atoms. It is one of the building blocks of many "graphitic" forms that may come in all dimensionalities, such as the zero dimensional fullerenes (buckyballs), one dimensional carbon nanotubes or the three dimensional graphite that is widely abundant. These different forms can be seen in Figure 2.1. Although, graphene is often called as being two dimensional, it still has a thickness ranging from 0.06 nm to 0.09 nm. [6] Despite that, it is still safe to call graphene a 2D material as it is the thinnest material that we can have and use in our electronic devices.

Graphene is one of the first members of the recently emerging category of 2D crystalline materials. For many years, it remained unclear whether free-standing atomic layers could exist; thin films become thermodynamically unstable (decompose or segregate) below a certain thickness, typically, of many dozens layers; however, graphene proved that this category of materials are not only stable, but they exhibit a high crystal quality. [8] First graphene samples are produced and analyzed by Novoselov et. al. which involves mechanical exfoliation (repeated peeling) of small mesas of highly oriented pyrolytic graphite by using Scotch tape.[9] Some examples of the first samples that are transferred on top of a Si-SiO₂ substrate can be seen in Figure 2.2.

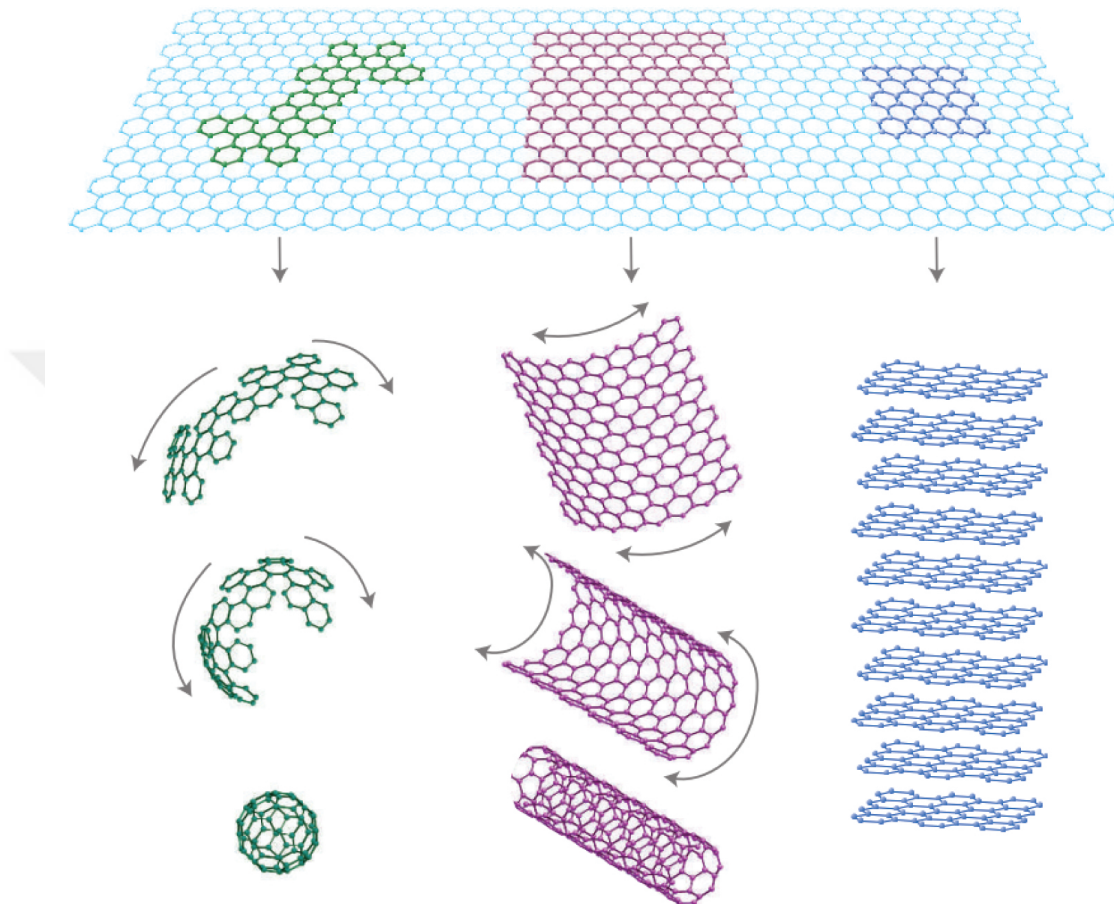


Figure 2.1: Mother of all graphitic forms. Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite. [7]

As this recent category of materials started being explored, graphene attracted notable attention due to its interesting mechanical and electrical properties. Some of its exotic properties, such as ballistic transport of charge carriers [10], quantum Hall effect [11], Klein paradox [12] and tunable interband transitions [13, 14] allowed this material to maintain its popularity since the Nobel Prize in 2010.

Measurements performed on single layer graphene sheets revealed breaking strengths of 42 Nm^{-1} . That corresponds to a Young's modulus of about 1.0 terapascals. These experiments establish graphene as the strongest material ever

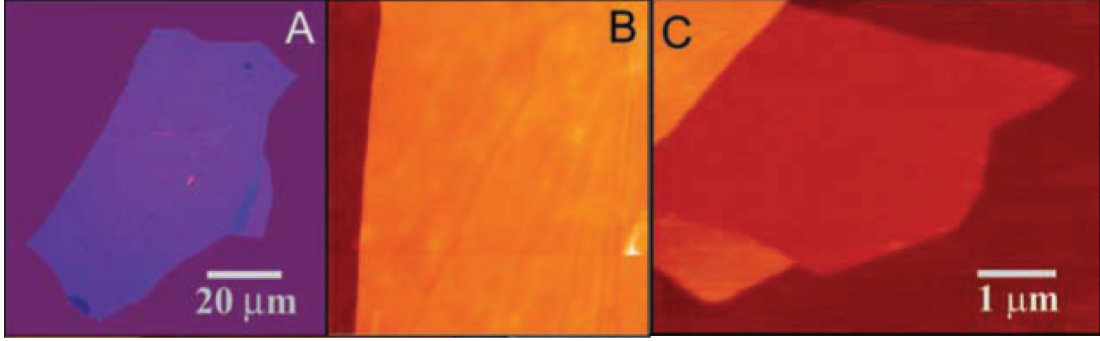


Figure 2.2: Graphene films. (a) Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness ≈ 3 nm on top of an oxidized Si wafer. (b) Atomic force microscope (AFM) image of $2 \mu\text{m}$ by $2 \mu\text{m}$ area of this flake near its edge. Colors: dark brown, SiO_2 surface; orange, 3 nm height above the SiO_2 surface. (c) AFM image of single-layer graphene. Colors: dark brown, SiO_2 surface; brown-red (central area), 0.8 nm height; yellow-brown (bottom left), 1.2 nm; orange (top left), 2.5 nm.[9]

measured, and show that atomically perfect nanoscale materials can be mechanically tested to deformations well beyond the linear regime. [15] The famous "cat carrying graphene hammock" example illustrated in the Scientific Background of Nobel Prize in Physics 2010, depicts a 4 kg cat that is supported by 1 m^2 graphene sheet. This invisible hammock weighs only as much as one of the cat's whiskers; however, it is able to support the cat. [16]

The interesting electrical properties of graphene arises from its two-dimensional nature. Compared to bulk graphite, graphene has a unique band structure and an electrical behavior. The charge carriers in graphene behave as a two-dimensional gas of massless Dirac fermions and mimic relativistic particles with zero rest mass and have an effective 'speed of light' $c_* \approx 10^6 \text{ m s}^{-1}$. [17] This means that an electron inside a monolayer graphene has zero effective mass and it can travel for micrometers without scattering, even at room temperature. [18] Due to ballistic transport of charge carriers, these carriers have mobilities up to $200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in suspended graphene samples at low temperatures. At room temperature, this value is still as high as $15000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [10]. This makes graphene an attractive candidate for electronic applications that require low losses and rapid response time; while still occupying a small area.

2.1 Band Diagram

The electronic structure of graphene is very different from its three dimensional counterparts. In graphene, each carbon atom in the honeycomb lattice has three neighbouring carbon atoms. The bonds between them are sp^2 hybridized with an average length of 0.142 nm. [8] These are known as the σ bonds oriented towards these neighboring atoms and formed from three of the valence electrons. These covalent carbon-carbon bonds are nearly equivalent to the bonds holding diamond together, giving graphene similar mechanical and thermal properties as diamond. The fourth valence electron does not participate in covalent bonding. It is in the $2p_z$ state oriented perpendicular to the sheet of graphite and forms a conducting π band. [19] The π electrons happen to be those responsible for the electronic properties at low energies, whereas the σ electrons form energy bands far away from the Fermi energy. [20]

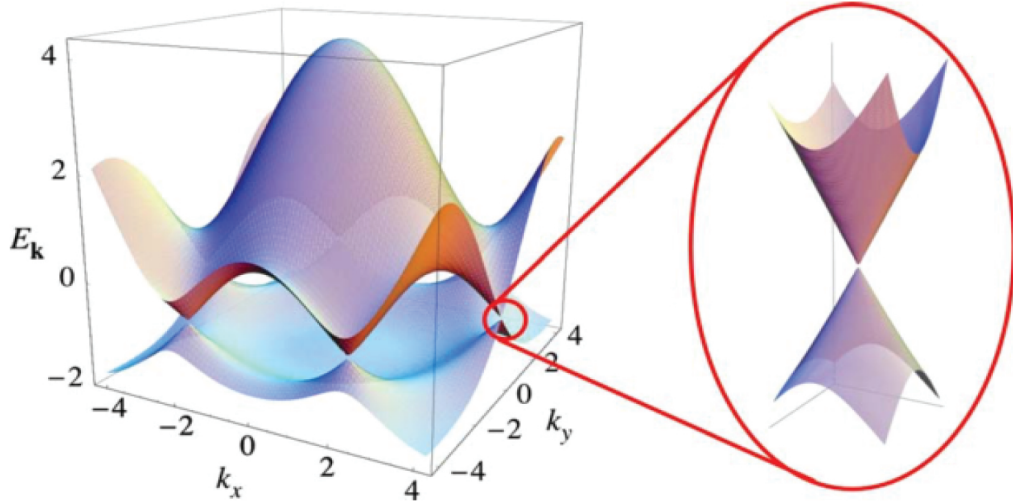


Figure 2.3: Electronic dispersion in the honeycomb lattice. Left: Energy spectrum of graphene. Six conical bands, distributed over the first Brillouin zone can be seen. Right: zoom in of the energy bands close to one of the Dirac points. [21]

The described arrangement of carbon atoms produce a Fermi surface of six double cones, as seen in Figure 2.3. The points where the conduction and valance

band meet are called Dirac points, and are depicted in the close-up inset in Figure 2.3. In the vicinity of these points, energy bands become almost conical and the dispersion relation becomes linear. Electrons near these conical valleys behave as massless Dirac electrons. [17]

In an ideal intrinsic (undoped) graphene, Fermi level (E_f) is located at the connection points of these cones. [16]. Fermi level of graphene scales with the charge density and is described as:

$$E_f = \hbar v_f \sqrt{\pi n} \quad (2.1)$$

where $\hbar$ is the reduced Planck's constant, v_f is the Fermi velocity (1.1×10^8 cm s⁻¹) and n is the charge density. [22] By influencing the charge density, one can influence the Fermi level and vice versa.

2.2 Optical Response

In describing the optical response of graphene, the conical band diagram is the key element used for defining the dynamics of light-graphene interaction. Two types of band transitions are possible when a photon hits the graphene surface. Depending on the Fermi level of graphene and energy of the incident photons, light absorption in graphene is either dominated by intraband or interband transitions of charge carriers. For a fixed Fermi level, this threshold is defined by the Pauli exclusion principle. When the incident photon energy is lower than $2E_f$, intraband transitions become dominant due to the lack of available states for this particular energy level at that momentum. At photon energies higher than $2E_f$, interband transitions dominate. [23, 24] The interplay between these transitions define the total optical response of graphene.

A schematical description of the interband and intraband transitions in the conical band diagram, as well as a graphical representation for the calculated

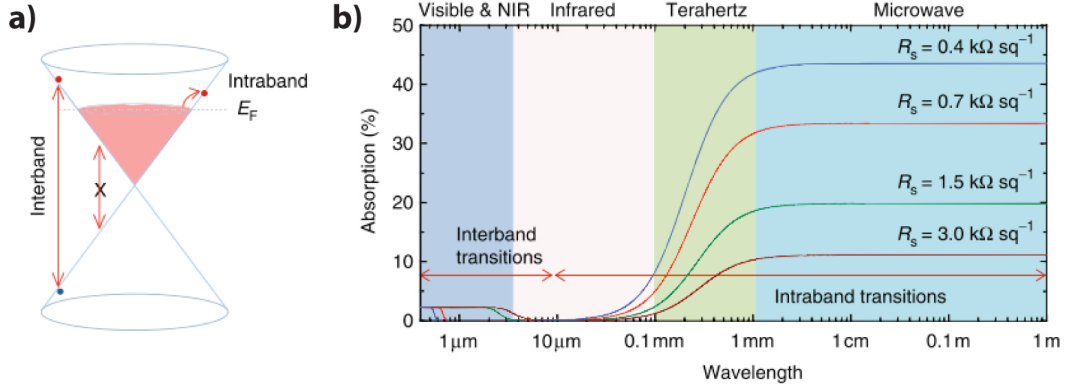


Figure 2.4: (a) A graphical representation of the intraband and interband transitions in the conical band structure of graphene that define the optical response. Graphene is assumed to be doped with a Fermi energy of E_f . (b) Calculated broadband absorption spectra versus wavelength of single-layer graphene at different sheet resistance values, ranging from visible to microwave wavelengths. [25]

absorption spectra can be seen in Figure 2.4. We can see a widely varying optical response ranging from visible to microwave frequencies. By studying the band transitions, we can have an understanding of graphene-light interactions.

A widely used model for graphene's complex surface conductivity is proposed by Falkovsky et al. that incorporates both intraband and interband transitions:

$$\sigma(\omega) = \frac{e^2\omega}{i\pi\hbar} \left[\int_{-\infty}^{\infty} \frac{|\varepsilon| df_0(\varepsilon)}{\omega^2 d\varepsilon} d\varepsilon - \int_0^{\infty} \frac{f_0(-\varepsilon) - f_0(\varepsilon)}{(\omega + i\delta)^2 - 4\varepsilon^2} d\varepsilon \right] \quad (2.2)$$

where ω is the angular frequency ε is the characteristic electron energy and $f_0(\varepsilon)$ is the Fermi function expressed as:

$$f_0(\varepsilon) = \{ \exp[(\varepsilon - \mu)/T] + 1 \}^{-1} \quad (2.3)$$

where μ is the chemical potential and T is the temperature. The first term in equation 2.2 corresponds to intraband electron-photon scattering process and the second term owes its origin to interband transitions. [26]

2.2.1 Intraband Transitions

When a photon with relatively low energy hits the graphene surface, its energy is not sufficient for electrons to make a transition from the valance band to conduction band while conserving its momentum. In most samples, due to unintentional doping of graphene, Fermi level is not at the center of the conical bands. Available states near the Dirac point are occupied. As a result, band to band transitions require higher energies. Photons such as far-infrared and microwave photons do not have enough energy to stimulate such transitions. [24] Therefore, for these wavelengths, the dominant absorption mechanism becomes intraband transitions.

During intraband transitions, since the speed of light c is much higher than the Fermi velocity v_F of graphene ($c/v_F \approx 300$) [11], direct absorption of a photon by an intraband optical transition does not satisfy momentum conservation. To conserve momentum, extra scattering with phonons or defects, is required. [27]

In equation 2.2, after carrying the integration, the intraband term reduces to:

$$\sigma^{intra}(\omega) = \frac{2ie^2T}{\pi\hbar(\omega + i\tau^{-1})} \ln[2\cosh(\mu/2T)] \quad (2.4)$$

The explicit dependence of surface conductivity to the Fermi level, and as an extension to the surface charge concentration (2.1) implies that optical response in the intraband-dominated region is susceptible to change by changing Fermi level. This is one of the major mechanisms in graphene's widely tunable nature. By controlling the low-frequency conductivity of graphene, it is possible to obtain a significant change in absorption, as Balci et al. have demonstrated in Figure 2.4b [25].

2.2.2 Interband Transitions

When a photon with relatively high energy (such as visible photons) hits the graphene surface, its energy is sufficient to trigger an interband transition, depending on the position of Fermi level. In Figure 2.4, we can see that as we move to shorter wavelengths, we reach a constant interband-dominated absorption of 2.3%. This value arises from one of the fundamental constants in physics, the fine structure constant:

$$\alpha = e^2/\hbar c \approx 1/137 \quad (2.5)$$

where e is the elementary charge, $\hbar$ is the reduced Planck's constant and c is the speed of light. Note that all the elements that make up this parameter are fundamental constants and do not depend on material parameters. The fine structure constant, α , defines the coupling between light and relativistic electrons that is traditionally associated with the quantum electrodynamics rather than materials science. The absorption of monolayer graphene in interband dominated region of the electromagnetic spectrum turns out to be a constant value of $\pi\alpha \approx 2.3\%$ [28] Figure 2.5 shows the optical transmission measurements performed by Nair et al. on suspended graphene. We can clearly see the 2.3% reduction in transmitted light for a single-layer graphene, and with each additional graphene layer this value follows a linear trend. As a two-dimensional material, this relatively strong interaction between graphene and light makes graphene an attractive candidate for optics applications.

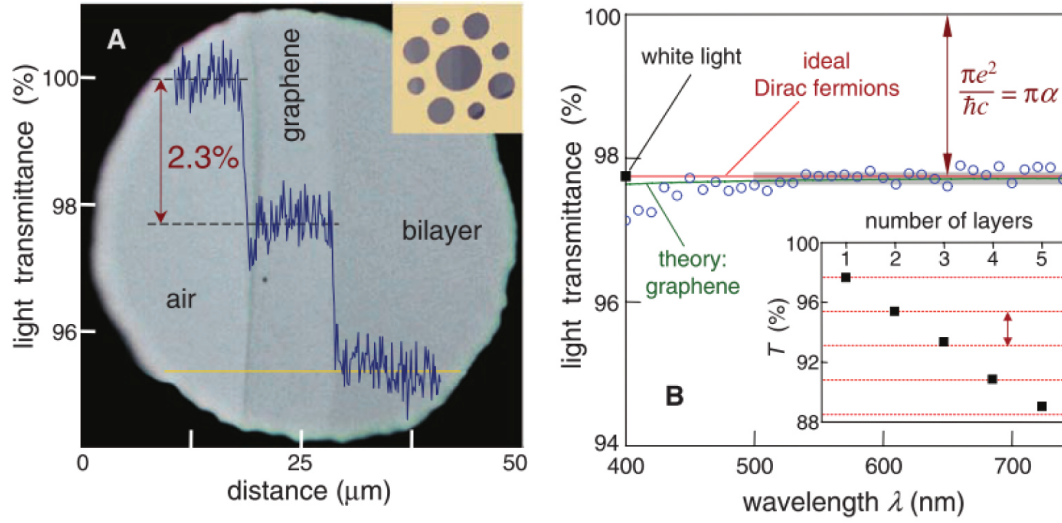


Figure 2.5: (a) Photograph of a 50 μm aperture partially covered by single layer and bilayer graphene. The intensity line scan of these layers are superposed on the image. Intensity measurements show a decrease of 2.3% with each layer of graphene. (inset: measurement setup) (b) Transmittance spectrum of single-layer graphene (open circles), theoretical calculations (green line) and transmission expected from ideal Dirac fermions (red line). Inset shows the decrease in transmission with each additional graphene layer. [28]

2.3 Tunability

Widely tunable nature of graphene makes it an attractive candidate in the optoelectronics field. By tuning the optical response of this two dimensional material, interesting devices can be constructed. In fact, many groups have demonstrated devices that employ graphene's tunability. Bludov et al. demonstrated tunable graphene-based polarizers [29], Yao et al. demonstrated tunable infrared optical modulators [30], Wang et al. demonstrated tunable waveguide photodetectors [31] and Copuroglu et al. demonstrated gate-tunable photoemission from graphene transistors [32].

Tunability in graphene can be achieved by several methods. It can be controlled via hetero-atom, chemical and electrostatic doping [33], as well as unconventional methods such as plasmon-induced doping [34] and optical doping [35]. Electrostatic doping is widely preferred in optoelectronic applications for active

tuning of optical response, with a relatively simple and versatile setup. In most applications that utilise electrostatic tuning of graphene, substrate back-gating method is used. [9, 14, 13, 30] In this geometry, electrostatic gating is performed through the substrate; one electrode is chosen as the back surface of the substrate and the other electrode is chosen as the graphene layer. When a gate voltage is applied between these electrodes, an electric field forms that penetrates the substrate. Usually the substrate is chosen as a 285-300 nm thick SiO_2 on Si. This choice of substrate has two benefits: The interference effects of this substrate enables the researchers to identify graphene under an optical microscope. This approach is used in the early days of graphene research by Novoselov et al. in order to observe the quality and number of layers of exfoliated graphene. [8] Another benefit is the reduction of the effective substrate thickness during gating. The silicon layer under SiO_2 has a p-doping and therefore conductive. When a back-gate voltage is applied, the voltage drop occurs mainly on the dielectric SiO_2 layer which is much thinner than the Si layer. Therefore, maximum gate voltage depends on the breakdown voltage of SiO_2 .

As mentioned before, one of the major tunability mechanisms in graphene arises from the direct dependence of the surface conductivity to varying Fermi level especially when the intraband transitions dominate. By controlling the Fermi level, surface carrier concentration can be changed and the optical response of graphene can be modified. Balci et al., demonstrated this in microwave frequencies by large adaptive radar-absorbing surfaces with tunable reflection suppression ratio up to 50 dB. [25]

Another major mechanism is by changing the onset point of interband transitions by changing the Fermi level. As discussed before, at photon energies lower than $2E_f$, interband transitions cannot take place due to Pauli blocking. However, changing the Fermi level changes this threshold. This allows active devices that operate at visible - near infrared frequencies to have a tunable response. Li et al. demonstrated this tunable interband response between the wavelengths of 1.25 - 10 μm at temperatures of 45 K on a Si/ SiO_2 substrate with back gating. Their results are presented in Figure 2.6.

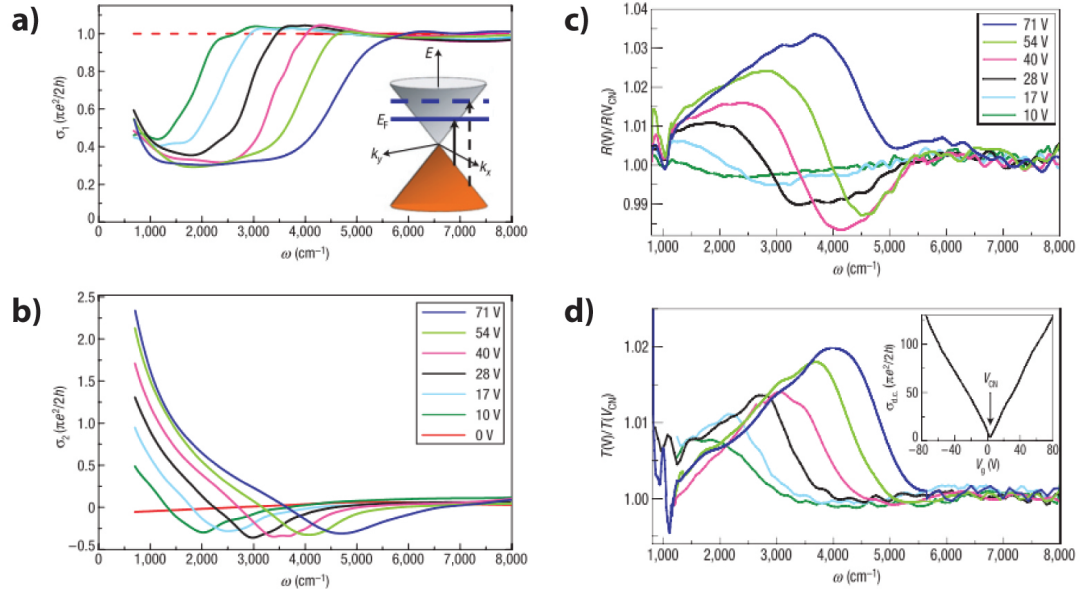


Figure 2.6: (a) Real part of surface conductivity at several gate voltages with respect to the response at charge neutrality point, corresponding to E_f on the electron side. Inset: Band structure of graphene near the Dirac point and the interband transition at $2E_f$. (b) Imaginary part of the surface conductivity in (a). (c) Reflection and (d) Transmission spectra of graphene at several gate voltages with respect to the response at charge neutrality point, corresponding to E_f on the electron side where $V = V_g - V_{\text{CNP}}$. Inset of (d) shows the d.c. conductivity data of the sample as a function of gate voltage. [14]

When the gate voltage moves away from the charge neutrality point (CNP), complex surface conductivity changes as plotted in Figure Figure 2.6a-b. This affects the infrared transmission and reflection response as shown in Figure 2.6c-d. A substantial shift in comparison with the case in CNP occurs in both the transmission and reflection spectra as a result of the shift in the threshold point, $2E_f$.

Chapter 3

Reflection Enhancement by Using V-shaped Plasmonic Nanoantennas

3.1 Introduction

Plasmonics play a major role in controlling light at nanodimensions. In both confining the incident light to subwavelength dimensions and increasing the interaction between light and matter, they have proven much more useful than traditional diffraction-limited dielectric lenses and resonators. Along with the rapid development in nanofabrication technologies, such as electron beam lithography, focused ion beam milling, and self-assembly, many routes became available to engineer complex arrays of metal nanostructures in which plasmons can be excited, directed, and manipulated. [36] Studies illustrating the coupling of plasmons to optical emitters [37], plasmon focusing [38], nanoscale waveguiding [39], plasmonic lasers [40] and materials with negative refractive index [41] demonstrate the potency of the field.

When light interacts with a metal structure, its conduction electrons can be driven by the incident field in collective oscillations known as localized surface plasmon resonances (LSPR). These give rise to a drastic alteration of the incident

radiation pattern. Since LSPRs enable an efficient transfer of electromagnetic energy from the near to the far-field of metal nanoparticles and vice versa, we can consider plasmonic nanostructures as nanoantennas, because they operate in a similar way to radio antennas but at higher frequencies. Typically, plasmonic nanoantennas at optical and infrared wavelengths are made of gold and silver due to their good metallic properties and low absorption. [42] At these wavelengths, conduction electrons can move as almost free electrons and their response can be described by the Drude model as following:

$$\varepsilon_{Drude}(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\gamma)} \quad (3.1)$$

where ω_p is the metal plasma frequency, γ is the collision frequency representing the damping of electron oscillations within the material and ε_{∞} accounts for the residual polarization due to the positive background of ion cores. [43] This allows metals like gold and silver to be used as low-loss metals in plasmonic nanoantennas at infrared frequencies. [44]

Among many designs of plasmonic nanoantennas, V-shaped nanoantennas have significant additional benefits. They are used in applications such as energy localization in nanosystems [45] and quantum generation of coherent surface plasmons [46]. Unidirectional side-scattering is demonstrated by Vercruysse et al. [47] They have demonstrated a directivity as large as 15 dB in the wavelengths between 750 nm to 800 nm. Yu et al. demonstrated complete beam shaping by using different arrays of V-shaped nanoantennas in various combinations by introducing abrupt phase changes to the incident light. [48] By utilizing this particular geometry of varying α values (the angle between the arms of the V-shaped antennas) they are able to construct devices that operate at mid-infrared frequencies. In a recent publication, by decreasing the dimensions of the antennas, they achieved to blueshift the operating frequency to near-infrared frequencies. [49]

In this work, we have designed, fabricated and measured the reflection response of V-shaped nanoantennas. We have investigated the resonance wavelengths of antennas in context to their changing geometrical parameters. Near the resonance

wavelength of these antennas, we have demonstrated a 4 fold enhancement in the reflection response on a Si-SiO₂ substrate. The physical mechanism is investigated in detail with FDTD simulations. The antenna designs are then used in other works, described in Chapter 4.

3.2 Design and Simulations

A schematic of a single V-shaped nanoantenna can be seen in Figure 3.1. A single nanoantenna repeats itself in order to form a plasmonic nanoantenna array. In order to observe the effect of both the length (L) and angle (α) variation on the resonance wavelength, several nanoantenna arrays are designed. Length of the arms of a single nanoantenna (L) is chosen as 250 nm and 500 nm. α values are chosen as 60°, 90° and 120°.

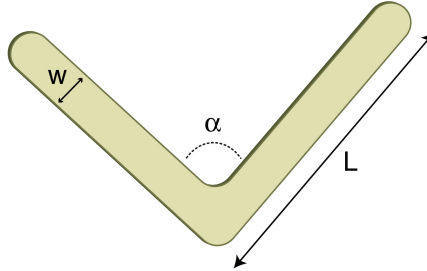


Figure 3.1: Schematic of a single plasmonic antenna with varying dimensions of length (L) and angle (α) that repeats itself to form the nanoantenna array. Width, w, of the structures are fixed as 50 nm and height of the structures are fixed as 50 nm.

Finite-difference time domain (FDTD) simulations are carried out using the commercially available software package, Lumerical FDTD Solutions. The FDTD technique is used in computational electromagnetics, where a wide bandwidth is required. [50] By using the differential form of Maxwell's equations and consequently calculating the electric field and magnetic field vectors in finite sized voxels, the spatial distribution and evolution of the electromagnetic fields can be traced. A schematic from the simulation environment can be seen in Figure 3.2.

On a silicon substrate that is extending to infinity, 285 nm of SiO_2 is placed as a dielectric layer with varying permittivity. Gold V-shaped nanoantennas of 50 nm thickness are placed on top of the substrate with varying L and α values. Gold nanoantennas are modelled as 3D rectangular prisms with rounded ends in order to realistically represent the fabrication results. The radius of curvature at the ends of the antennas is obtained from the SEM images of these structures (approximately 25 nm). Au (Palik) material model is used for gold nanoantennas. Boundary conditions in the x and y directions are defined as periodic boundaries and boundaries in the k -direction are defined as perfectly matched layer, which prevents reflections from this boundary and absorbs the remaining electromagnetic energy.

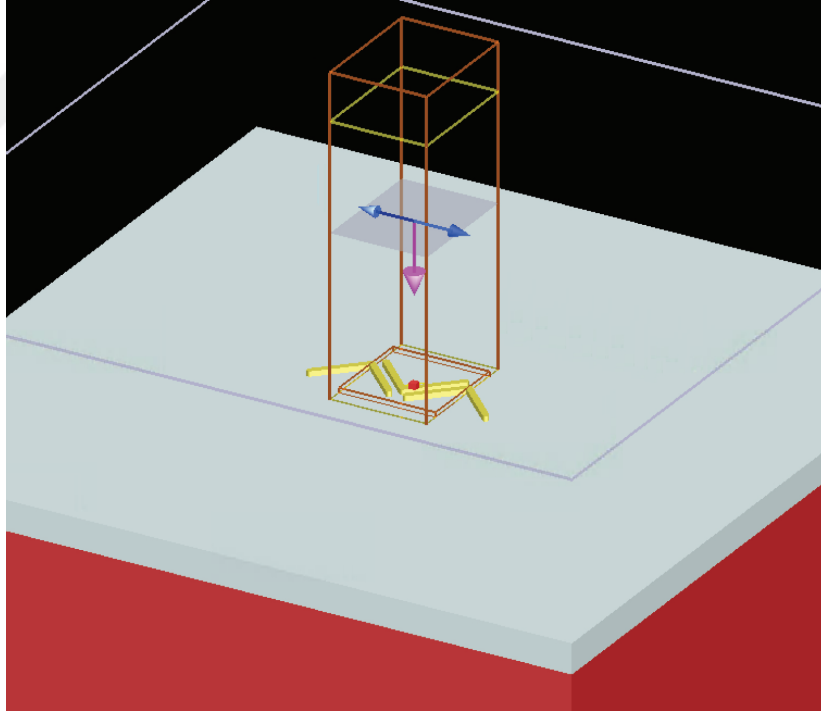


Figure 3.2: A schematic from the FDTD simulation environment. V-shaped nanoantennas of $L=500$ nm and $\alpha = 90^\circ$ is being simulated on a Si- SiO_2 substrate with SiO_2 (white) thickness of 285 nm and Si layer (red) extending to infinity. Polarization of the plane wave source is indicated with the blue arrows.

Electric field distributions on the boundary between SiO_2 substrate and gold nanoantennas are obtained from the simulations. These distributions are shown and explained in the Measurements section.

3.3 Fabrication

Fabrication process for the V-shaped antennas begun with a cleaning of the substrate. 1 cm x 1 cm SiO₂ on Si samples were cleaned by using acetone and ultrasonic cleaner for 20 seconds. The sample was cleaned with isopropanol and blow-dried using nitrogen.

Once the sample was cleaned, electron beam lithography resist was coated. By using a spincoater, Poly(methyl methacrylate) PMMA 950 A4 was spincoated on the substrate at 4000 rpm for 40 seconds. The sample was baked on the hot plate for 90 seconds at 180°C in order for the solvent in the resist to evaporate. A conductive liquid, AquaSAVE, was coated via the spin coater at 4000 rpm for 40 seconds on the sample to reduce the charging effects during e-beam lithography.

Using Raith e-line lithography system several V-shaped plasmonic antennas were defined under 15 kV electron acceleration voltage, by using 10 μm electron gun aperture and 100 μm write field. An approximate electron dose in the range of 1700 to 2000 pC/cm was applied in order to define different patterns. After e-beam lithography, the substrate was developed using the developer MIBK/IPA (1:3) solution for 40 seconds. Substrate was cleaned with isopropanol and blow dried with nitrogen.

Metallization was done with the electron beam evaporator system, Leybold Univex 350 E-beam Evaporator Coating System. 5 nm of Ti and 45 nm of Au was coated on the sample. Sample was left in acetone overnight for lift-off and the following day, cleaned with isopropanol and blow-dried using nitrogen. After this process, V-shaped patterns were revealed.

After the fabrication, scattering electron microscope (SEM) images were obtained using Raith e-line system. The images for the case when $L=250$ nm are shown in Figure 3.3 and images for the case when $L=500$ nm are shown in Figure 3.4.

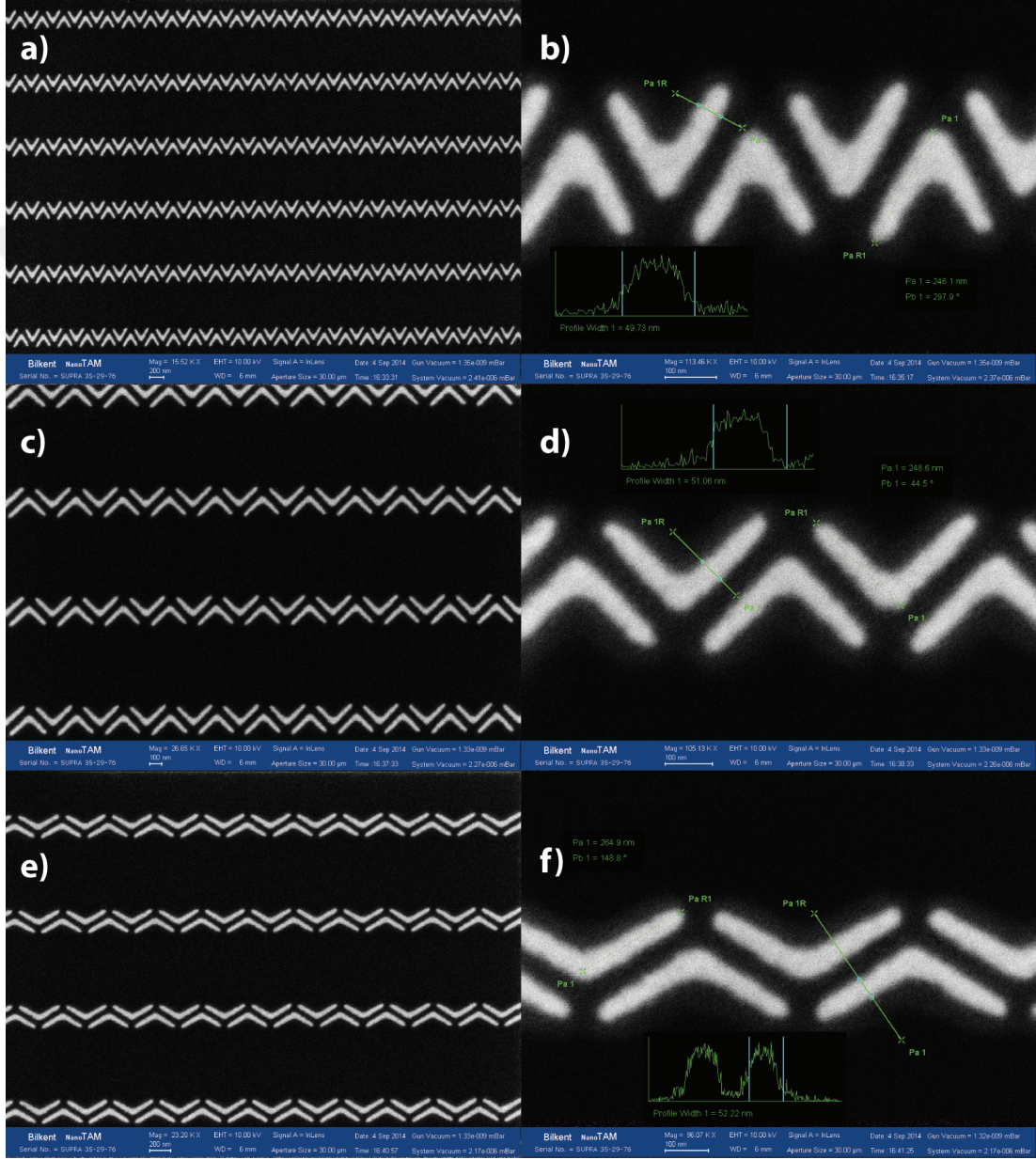


Figure 3.3: SEM images of the V-shaped nanoantenna arrays after fabrication with $L=250$ nm. (a) A larger area and (b) a close-up image for the case when $\alpha = 60^\circ$. (c) and (d) represents the case for $\alpha = 90^\circ$ and (e),(f) represents the case for $\alpha = 120^\circ$

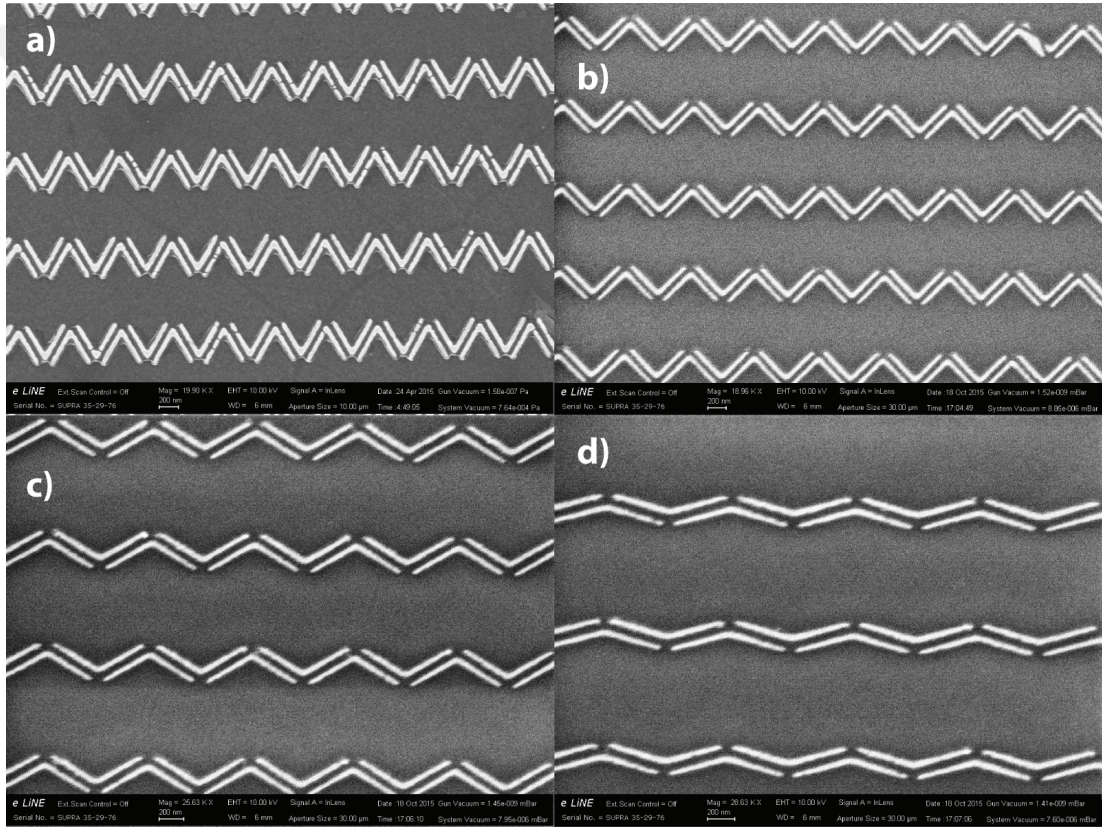


Figure 3.4: SEM images of the V-shaped nanoantenna arrays after fabrication with $L=500$ nm. Different variations for the angle: (a) $\alpha = 60^\circ$, (b) $\alpha = 90^\circ$, (c) $\alpha = 120^\circ$ and (d) $\alpha = 150^\circ$.

3.4 Measurement and Discussion

Spectral transmission measurements are carried out using a Fourier transform infrared spectroscopy setup, Vertex 70V FTIR, with a Hyperion 2000 IR microscope in order to focus on individual units on the sample. The sample is illuminated with normal incidence by a near infrared source with a CaF_2 beam splitter and a polarizer that is polarized in the x-direction. A liquid nitrogen cooled InGaAs detector inside a Hyperion 2000 Microscope detector compartment was used to take measurements between the 2500 and 15000 nm wavelength range. Both mid-infrared and near-infrared measurements are taken. Near infrared measurements are performed between the wavelengths of 1000 nm and 2500 nm. The infrared beam is focused on the plasmonic structure arrays by using the microscope. For each case, 32 measurements are taken and averaged in order to reduce the noise in the measurements.

FTIR measurement results for the case when $L=250$ nm are shown in Figure 3.5 as well as FDTD simulation results for the same nanoantenna configuration. Reflection resonance wavelength vary between 1.6 to 2.1 μm . As the value of angle, α increases, both the reflection intensity and resonance wavelength increases. The simulation result for the reflection from a bare Si-SiO₂ substrate is indicated with the black dashed line. Near the resonance wavelengths of the nanoantennas, a reflection enhancement of approximately 2.5 fold can be seen.

For the case when $L=250$ nm and $\alpha = 60^\circ$, FTIR measurement result is significantly lower than the simulated case. Also, this dataset does not follow the slowly decreasing intensity trend, which is valid for other cases. A possible explanation for this mismatch can be explained by investigating Figure 3.3b. This SEM image shows that due to small dimensions and limitations of the e-beam lithography system, the intended V-shaped design is distorted in the fabrication process. The apex has an unintended thick profile. This enlarged profile, combined with the relatively low L/w ratio disrupted the intended device geometry and its optical response. Therefore, for this case, the reflection intensity and quality factor for the resonance is lower than it should have been according to the simulation data.

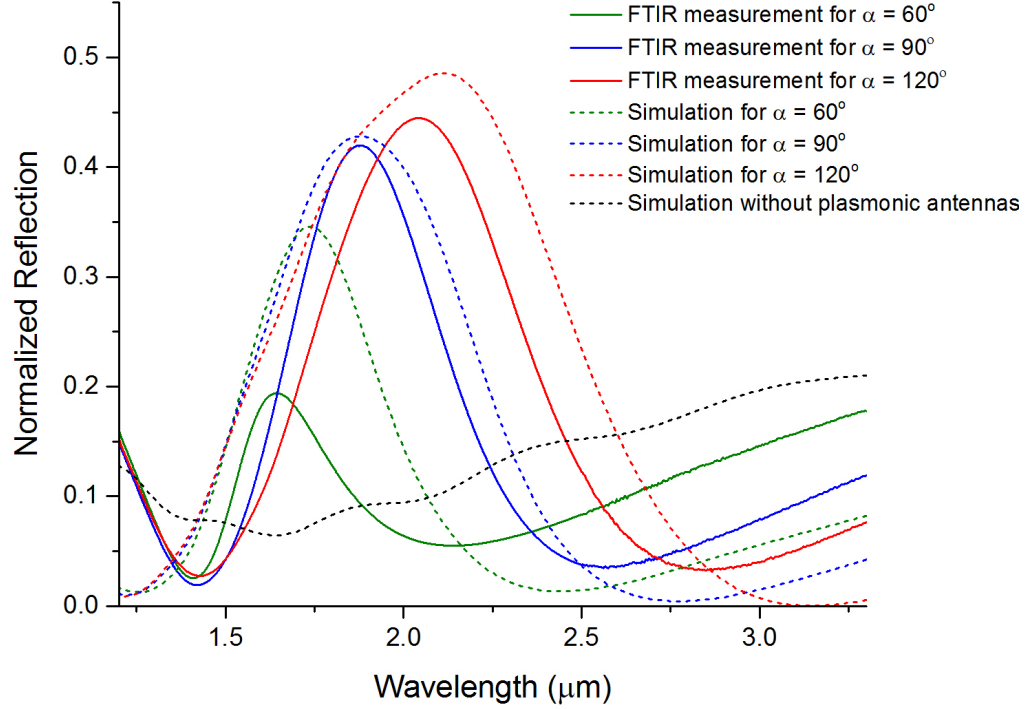


Figure 3.5: Spectral reflection measurements of V-shaped nanoantennas with $L=250$ nm, obtained using FTIR spectroscopy. Reflection measurements for the cases when $\alpha = 60^\circ$ (green), $\alpha = 90^\circ$ (blue) and $\alpha = 120^\circ$ (red) are indicated with solid lines and FDTD simulation results for the same configurations are indicated with dashed lines. Simulated background reflection curve is indicated with black dashed line.

Spectral reflection measurements for the case when $L=500$ nm can be seen in Figure 3.6, accompanied with the simulation results. A similar trend as in the case of $L=250$ nm can be observed. As the α values increase, both the intensity and wavelength of the resonance curve increases. As compared to the bare substrate, near the resonance wavelengths, a reflection enhancement of about 4 fold can be seen.

Electric field distributions on the nanoantenna-substrate boundary can be seen in Figure 3.7. Major field localizations are near the ends of the nanoantennas and in the gap region between adjacent nanoantennas. The coupling between

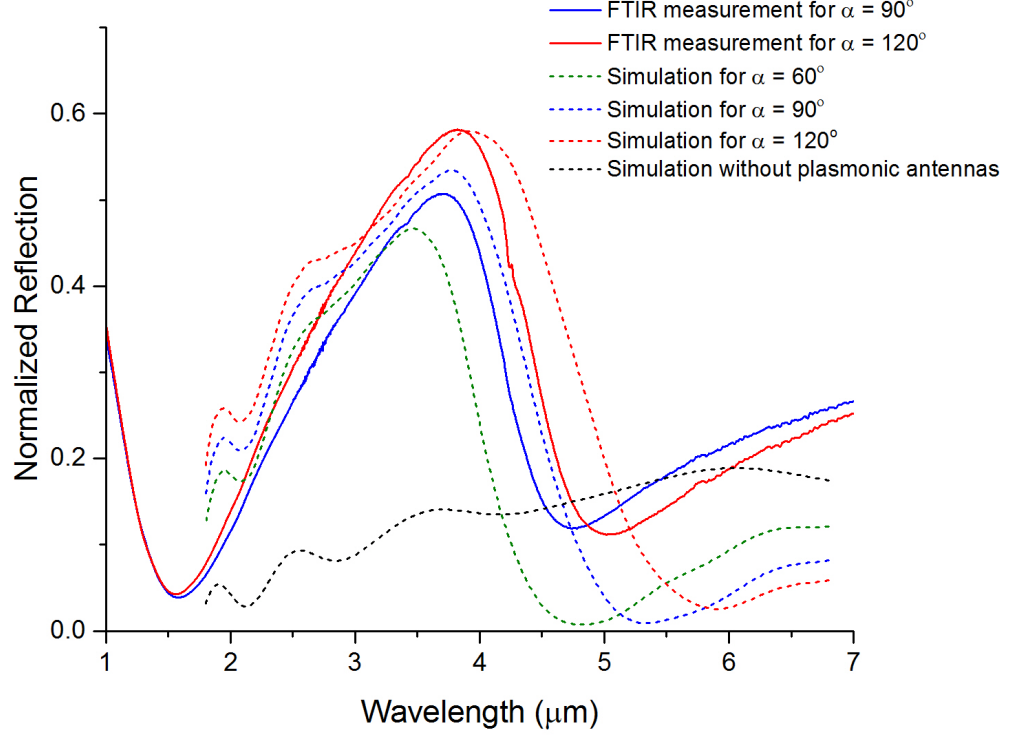


Figure 3.6: Spectral reflection measurements of V-shaped nanoantennas with $L=500$ nm, obtained using FTIR spectroscopy. Reflection measurements for the cases when $\alpha = 90^\circ$ (blue) and $\alpha = 120^\circ$ (red) are indicated with solid lines and FDTD simulation results for the same configurations are indicated with dashed lines. Simulated background reflection curve is indicated with black dashed line.

nanoantenna and incident field depends on the angle, α . As α angle is increased, the incident field that is polarized in the x-direction couples to these antennas with different coupling intensities such that; if the length of the nanoantenna is longer in the x-direction, then the incident field will influence more charge carriers in the metallic structure and these carriers will contribute to the plasmon resonance magnitude. Therefore, when α increases, the effective length of the antennas in the x-direction increases and the interaction between the nanoantenna and incident field increases. An increased interaction with the incident field translates to higher electric field magnitudes in the areas where plasmonic modes are formed, which are the gap regions of the plasmonic antennas. These higher fields are able

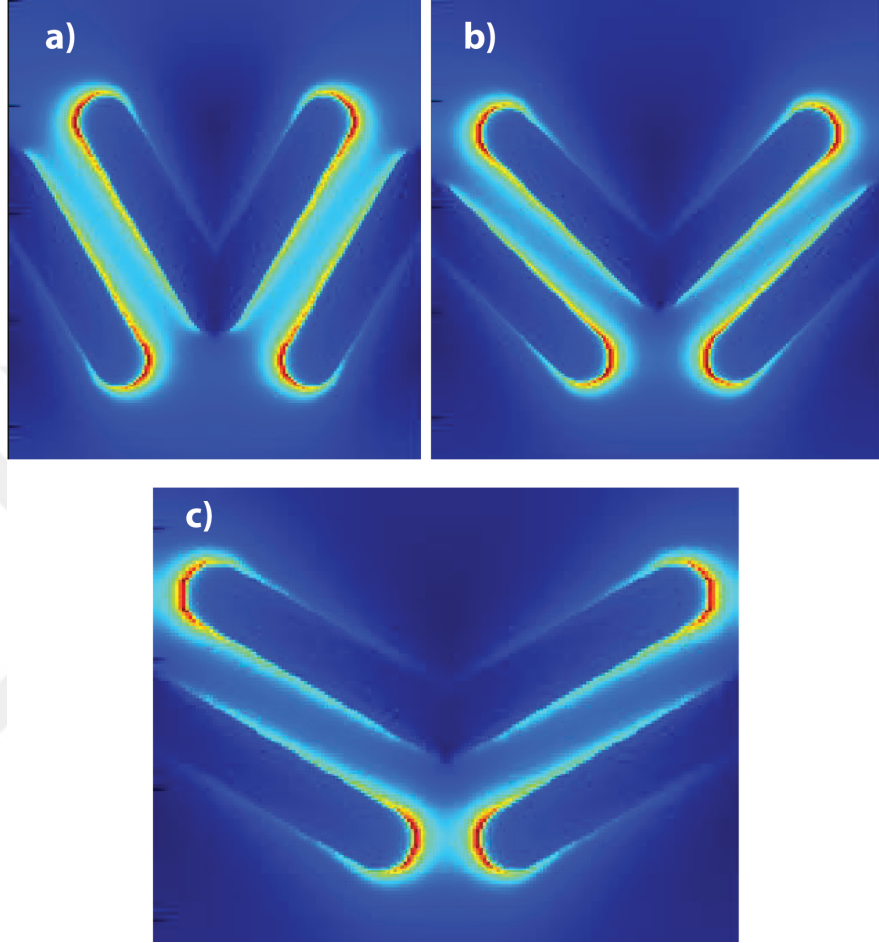


Figure 3.7: Electric field distributions on the SiO_2 - nanoantenna interfaces for $L=250$ nm with various angles obtained via FDTD simulations (a) $\alpha = 60^\circ$, (b) $\alpha = 90^\circ$ and (c) $\alpha = 120^\circ$. Blue indicates low electric field intensities and red indicated high field intensities.

to influence the reflection intensity of the total device. As a result, we see an increase the reflection intensity with increasing α .

3.5 Conclusion

In this work, we designed and fabricated V-shaped nanoantenna arrays. V-shaped antennas of varying lengths and α values are studied. On a Si-SiO₂ substrate, the reflection spectra of thesea antennas are measured. We observed a 4 fold

enhancement in the reflection response near the resonance wavelengths of the V-shaped antennas. We observed the effect of L and α on the resonance wavelength. This nanoantenna design is further used in other works in this thesis.



Chapter 4

Enhanced Tunability of V-shaped Plasmonic Structures Using Ionic Liquid Gating and Graphene

4.1 Introduction

Graphene is a strong candidate for active optoelectronic devices because of its electrostatically tunable optical response as previously discussed in Chapter 2. By electrostatically gating a graphene based device, its interband and intraband transitions can be utilised in order to have a desirable tunable response. While tuning the Fermi level of graphene, current substrate back-gating methods have major disadvantages. They are unable to sustain high fields through graphene unless a high gate voltage is applied. In order to solve this problem, ionic liquid gating is proposed as an alternative gating approach. [51] Ionic liquid gating allows substrate front side gating by using ions to create an electric field near graphene. It enables higher magnitudes of electric field to be formed near graphene with relatively low voltages when compared to back-gating methods. [52] Due to the absence of factors such as a thick dielectric layer and a much thicker substrate (although in most applications conductive doped silicon is used,

there is still a voltage drop on this layer), electric field formed by the application of a gate voltage can reach to the graphene layer without such major losses. The applied voltage falls across the double layer formed at the graphene-ionic liquid interface. The double layer thickness is determined by the size of the ions (≈ 1 nm) [51], which is several orders of magnitude thinner than that of the oxide (varies between 285 - 300 nm) used in a back gate configuration. [14, 13, 9, 30] This technique enables Fermi level tuning with less voltage applied through the gating electrode.

In graphene based devices that are tuned by using an ionic liquid gating scheme, interband transitions become effective at photon energies higher than near infrared and visible photons. [53, 54] As the ionic liquid is applied directly on top of the graphene layer, a chemical doping is induced on graphene. When a gate voltage is applied, ions in the ionic liquid move toward and penetrate the graphene layer, which results in a shift in Fermi level away from the Dirac point. As a result, interband transitions at mid-infrared frequencies are blocked due to Pauli blocking. The response of our device in the mid-infrared is therefore mainly due to intraband transitions.

One of the fundamental challenges in using graphene in optoelectronic applications is its relatively weak interaction with the incident field due to its atomically thin nature. [28] Echtermeyer et al. showed that plasmonic structures can be used in order to increase the interaction of graphene with the incident light by demonstrating an increase in the photocurrent of a graphene based photodetector. [55] In this device, we have decided to use V-shaped plasmonic antennas. Among many candidates of plasmonic structures, V-shaped plasmonic nanoantennas have also proven useful in many applications including energy localization in nanosystems [45], quantum generation of coherent surface plasmons [46], unidirectional side scattering [47] and even sub-wavelength scale devices that can create abrupt phase changes and allows complete beam shaping [48]. The resonance frequency of the antennas used in these previous works depends on the geometry of the antennas and the substrate, therefore in situ control of the optical response was not possible. In order to achieve active control of resonance in V-shaped antennas, surface conductivity of the underlying substrate may be modified which shifts

the refractive index and the permittivity of the medium. Graphene is a suitable candidate for this application in order to be used as a tunable substrate. This will allow devices which utilize V-shaped plasmonic structures to be versatile in their operating wavelength range.

In this work, for the first time, we have experimentally demonstrated that it is possible to increase and tune the optical transmission response of a graphene based device substantially by applying less gate voltage compared to the back-gating methods via ionic liquid gating and nanoplasmonic antennas in the same device. Designing and utilizing V-shaped plasmonic structures enabled us to increase the interaction between the graphene layer and the incident field in the mid-infrared wavelengths. Moreover, by using an ionic gating scheme, we are able to induce high electric fields near graphene to efficiently tune graphene's Fermi level and control its carrier concentration, therefore shifting the transmission response of nanoantennas and the response of the device. Previous attempts that utilize substrate back-gating methods to tune graphene's Fermi level use much higher gate voltages in order to tune the optical response. Yao et al. demonstrated 650 nm of wavelength shift by varying the gate voltage by 26.4 Volts. [56] In a recent publication they have increased the wavelength shift up to 1100 nm by using 28 Volts by utilizing a different antenna design. [57] Cakmakyapan et al. demonstrated 95 nm of wavelength resonance shift in split-ring resonators by varying the gate voltage by 170 Volts. [58] These maximum gate voltages depend mainly on the substrate thickness and type; however, they are much higher than the gate voltage range that is used in this work, which reaches a maximum of 3.8 Volts. The techniques presented in this thesis will have a promising effect in designing future devices that employ graphene's tunability, as well as devices utilizing V-shaped nanoantennas. This highly effective tuning scheme may be used in future applications of actively tunable graphene based optical devices.

4.1.1 Device Description

The graphene based optoelectronic device incorporates both V-shaped plasmonic nanoantennas and ionic liquid gating. The device is designed such that optical transmission measurements will be performed in an FTIR setup under a microscope. A schematic of the device can be seen in Figure 4.1.

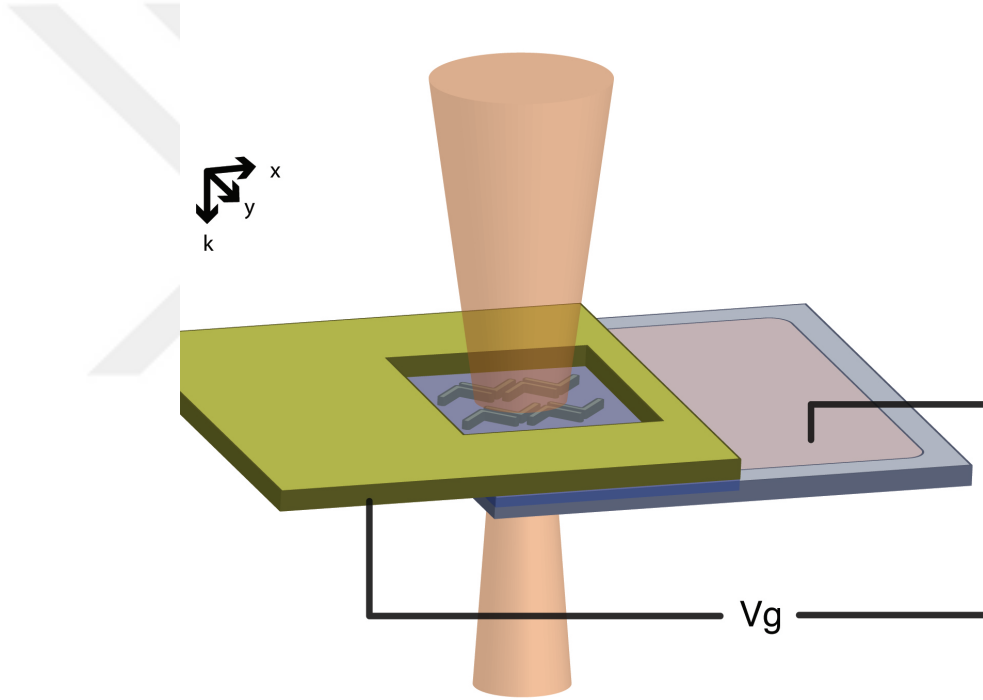


Figure 4.1: Schematic of the tunable device. Metallic V-shaped plasmonic structures are fabricated on top of a mid-infrared transparent BaF_2 substrate and graphene (purple) is transferred on top. Another BaF_2 substrate is coated with Ti/Au (yellow) to form a gating window. Two substrates are aligned as shown and ionic liquid (blue) is injected between them. Infrared radiation is sent through the gating window in the k -direction during FTIR transmission measurements. Gate voltage (V_g) is applied between the graphene layer and top gating window.

The device design process started with the choice of an infrared transparent substrate with minimal losses in the mid-infrared range. The final device consists of two substrates that are aligned on top of each other. Transmission measurements would have been inaccurate if the relative losses in these substrates were high. Double-side polished BaF_2 came out as a suitable material for this case.

After purchasing 1 cm x 1 cm double side polished substrates of about 500 μm thickness, transmission measurements of the bare substrate are made in an FTIR setup in order to determine the losses in the mid-infrared spectra. The measurement results are shown in Figure 4.2. Between the wavelengths of 2 to 11 μm , BaF_2 has a constant transmission response of about 0.93. As the resonance wavelengths of the V-shaped nanoantennas are also in this range, this choice of substrate was accurate.

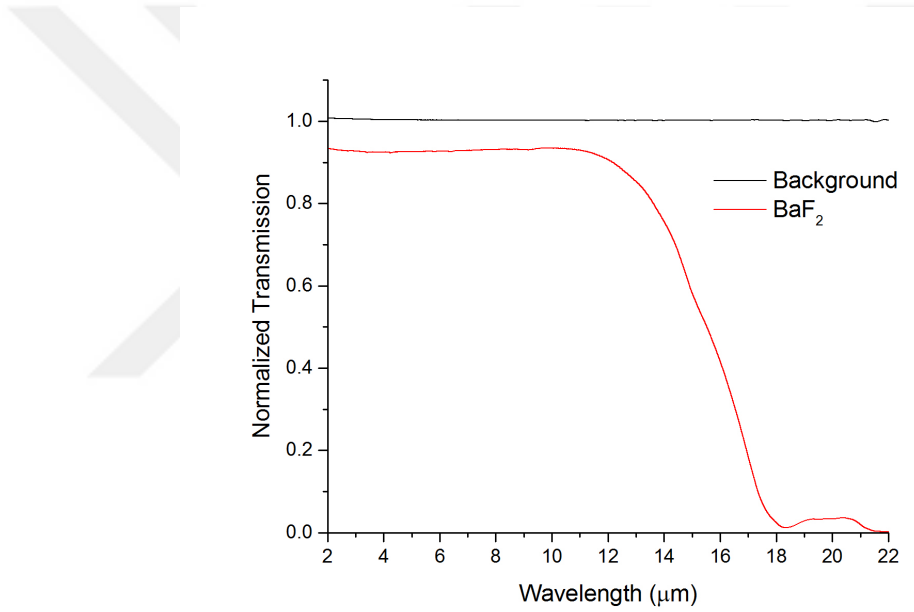


Figure 4.2: FTIR transmission measurements on a bare BaF_2 substrate, which is double-side polished and has a thickness of 500 μm . Both the background and the sample measurements can be seen.

The V-shaped plasmonic nanoantennas are designed to be on top of the BaF_2 substrate with varying angles between their arms. These angles are denoted as α through the text and are selected as 90° , 120° and 150° in order to observe the effect of different light-antenna coupling efficiencies.

4.2 Fabrication

The fabrication steps of the device can be listed as following:

1. Alignment mask photolithography
2. E-beam lithography of V-shaped structures
3. Photolithography for gating window
4. Graphene transfer
5. Alignment of the two substrates and device formation

4.2.1 Design and Fabrication of the Alignment Photolithography Mask

The fabrication process of this device consists of many fabrication steps, including both photolithography and e-beam lithography. As different V-shaped nanoantennas require different electron acceleration voltages during e-beam lithography, multiple e-beam lithographies were needed for this case. All these layers should be aligned perfectly with respect to each other in order to obtain a working device. Also, relatively large markers (large enough to be visible under an optical microscope) were required for the measurement steps in order to visually align the measurement area on the substrate. Keeping these in mind, a quartz photolithography mask was designed for alignment purposes. The mask contains several alignment elements that are commonly used in multi-step photolithography processes, such as fingered structures and metallic crosses. The design of the alignment photolithography mask is shown in Figure 4.3.

In order to fabricate the alignment photolithography mask, a double side polished 5 cm x 5 cm quartz substrate was used. To get rid of a possible contamination, substrate was cleaned by using acetone and isopropanol. The quartz substrate was then spincoated with the e-beam photoresist, Poly(methyl methacrylate) PMMA 950 A6, at 2000 rpm for 40 seconds and then baked on a hot plate at 180°C for 90 seconds. The substrate was then spincoated with the conductive AquaSAVE at 4000 rpm for 40 seconds, in order to avoid charging effects during e-beam lithography. In the Raith E-Line e-beam lithography system, an

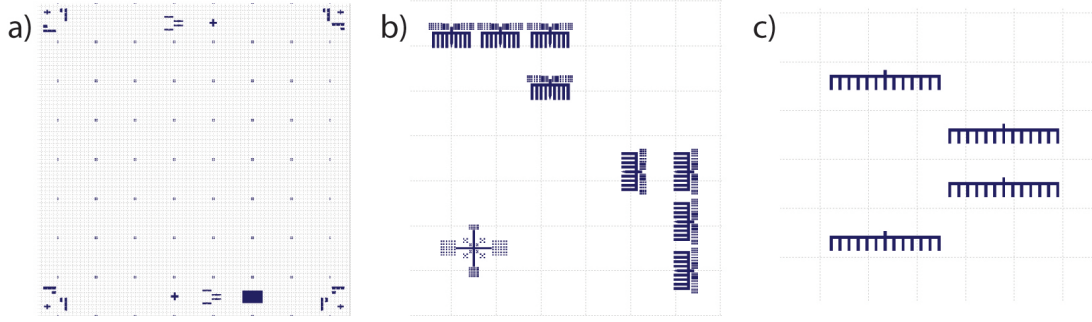


Figure 4.3: Design of the photolithography mask used for alignment procedures, displayed in a .gds environment. a) Overview of the complete mask that covers an area of 8mm x 8mm b,c) Some elements on the mask that are used for visual alignment during electron beam lithography and measurement steps

acceleration voltage of 10 kV with a 20 μm electron gun aperture and 1 mm write field is used while patterning the e-beam lithography resist. After patterning the substrate, topmost conductive AquaSAVE layer is cleaned with deionized water. Substrate is then developed in a MIBK:IPA (1:1) developer solution for 40 seconds. After development, substrate is cleaned with isopropanol and blow-dried with nitrogen. Chrome coating is carried out by using Leybold Univex 350 E-beam Evaporator Coating System. The desired chrome thickness is set as 120 μm . After metal coating, the substrate is immersed in acetone overnight for the lift-off process. Excess chrome layers are removed by flushing the sample with acetone by using a glass syringe. Sample is cleaned with isopropanol and a nitrogen blow-dry. This photomask is then used for subsequent fabrication steps.

4.2.2 Fabrication of the Alignment Markers on BaF_2

Fabrication of the device begins with a 1 cm x 1 cm double-side polished BaF_2 substrate. The substrate was cleaned with acetone and isopropanol to get rid of any possible contamination on the substrate. A photoresist, AZ 5214, was spincoated at 6000 rpm for 40 seconds. As the photoresist thickness is higher near the edges than the center of the substrate (edge bead effect) an edge bead removal process is needed. This process was simply performed by using a slab dipped in acetone. This step is required in order to keep both the substrate and

mask clean. Sample was then baked at 110°C for 60 seconds. Suss Microtech MA-6 mask aligner was used to align the substrate and the mask. Mask and substrate were aligned optically and hard exposure was performed for 1.6 seconds at 10 mW of UV lamp power. To reverse the polarization of the photoresist and to create a desirable resist side-wall geometry, image reversal process was performed. For the image reversal process, the substrate was baked at 120°C for another 120 seconds. By using the mask aligner, flood exposure was done for 6 seconds at 10 mW of UV lamp power. The substrate was then developed in AZ400K/DI (1:4) solution for 30 seconds. Substrate is then cleaned with deionized water, isopropanol and blow-dried with nitrogen. For the metal coating step, Leybold Univex 350 E-beam Evaporator Coating System was used to coat 10 nm of Ti as an adhesion layer and 90 nm of Au afterwards. Alignment patterns were revealed by acetone lift-off.

4.2.3 E-beam lithography of V-shaped nanoantennas

For the electron-beam lithography step, fabrication was continued on the BaF₂ substrate with alignment markers. Poly(methyl methacrylate) PMMA 950 A4 was spincoated on the substrate at 4000 rpm for 40 seconds. The sample was baked on the hot plate for 90 seconds at 180°C. AquaSAVE was coated via the spin coater at 4000 rpm for 40 seconds on the sample to reduce the charging effects during e-beam lithography. Using Raith e-line lithography system several V-shaped plasmonic antennas were defined under 15 kV electron acceleration voltage, by using 10 μ m electron gun aperture and 100 μ m write field. An approximate electron dose of 1800 pC/cm was applied in order to define the patterns. After e-beam lithography, the substrate was developed using the developer MIBK/IPA (1:3) solution for 40 seconds. Substrate was cleaned with isopropanol and blow dried with nitrogen. Metallization was done again with the electron-beam evaporator system. 5 nm of Ti and 45 nm of Au was coated on the sample. Samples were left in acetone overnight for lift-off. After this process, V-shaped patterns were revealed.

4.2.4 Graphene growth and transfer

For the graphene electrode, single layer graphene was synthesized by a chemical vapor deposition (CVD) system on a 2 cm x 2 cm ultra-smooth copper foil (Mitsui Mining and Smelting Company, Ltd., B1-SBS). The copper foil was heated to 1035°C under 100 sccm H₂ flow to remove the native oxide. 10 sccm of CH₄ was sent at 1035°C to initiate the growth of graphene on the copper foil for 1 minute. After terminating the growth, system was cooled down to room temperature under 100 sccm H₂ flow. At the end of this process, single-layer graphene on a copper foil was obtained.

To transfer graphene on the BaF₂ that contains the V-shaped nanoantennas, Shipley 1813 photoresist was dripped on graphene grown copper. The copper-graphene-photoresist compound was baked at 80°C overnight. Annealed photoresist becomes hard and behaves as a mechanical support for graphene during the transfer process. The copper layer was etched by using 5 mM FeCl₃ aqueous solution for 5 minutes. Photoresist-graphene compound was then cleaned with deionized water and blow dried by nitrogen. After that, the hard photoresist-graphene compound was carefully placed on the BaF₂ substrate. BaF₂-graphene-photoresist compound was first baked at 80°C for 60 seconds and then immediately at 110°C for another 15 seconds to ensure proper sticking of graphene onto BaF₂ substrate. Photoresist was removed by acetone. Substrate was cleaned with isopropanol and blow-dried with nitrogen.

4.2.5 Fabrication of the Gating Window

To produce the gating window that was placed on top of the BaF₂ substrate, a single photolithography process was performed. In this step, a different photolithography mask was used that only contains a 2.5 mm x 2.5 mm square. A second 1 cm x 1 cm double side polished BaF₂ was cleaned with acetone and isopropanol. The photoresist, AZ 5214, was spincoated at 6000 rpm for 40 seconds. Edge bead removal process was performed by using a slab dipped in acetone. The

sample was baked at 110°C for 60 seconds. Suss Microtech MA-6 mask aligner was used to align the substrate and the mask. After the alignment, hard exposure was performed for 1.6 seconds at 10 mW of UV lamp power. The substrate was then developed in AZ400K/DI (1:4) solution for 30 seconds. After that, substrate was cleaned with deionized water, isopropanol and blow-dried with nitrogen. After photolithography, 10/90 nm of Ti/Au was coated via electron-beam evaporator system. With acetone lift-off, gating window was ready.

4.2.6 Formation of the device

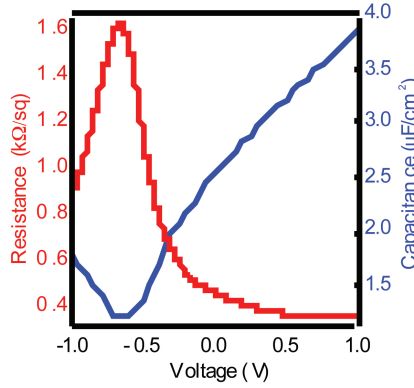


Figure 4.4: Applied gate voltage versus resistance (red curve) and capacitance (blue curve) of the final device. Graphene is assumed to be at its charge neutrality point (CNP) when gate voltage is -0.6 Volts.

Two BaF₂ substrates, one with metallic plasmonic structures and graphene on top and one with a Ti/Au coating and an opening for a square gating window were aligned visually. Insulating adhesive spacer bands of about 50 μm thickness are placed on the sides of the lower substrate for mechanical support and rigidity. The two BaF₂ substrates are then stucked together via the spacer bands. In order to form the gating contacts, carbon bands are used. One carbon band is placed on the graphene layer on BaF₂ and the other on the metal coated gating window. The gap between two substrates was then filled with ionic liquid, (Diethylmethyl(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide, [deme][Tf₂N]).

After the device is fabricated, resistance and capacitance measurements on the graphene layer are performed in order to determine the charge neutrality point (CNP) of graphene. As graphene was transferred and the transfer process may shift graphene's Fermi level by chemical doping [59], a determination of the CNP is required for further analysis. Figure 4.4 shows the measurement results of resistance and capacitance change with respect to gate voltage. Resistance reaches its maximum value and capacitance drops to its minimum value at -0.6 V, which is adopted to be the CNP of graphene layer for further measurements.

4.3 Simulations

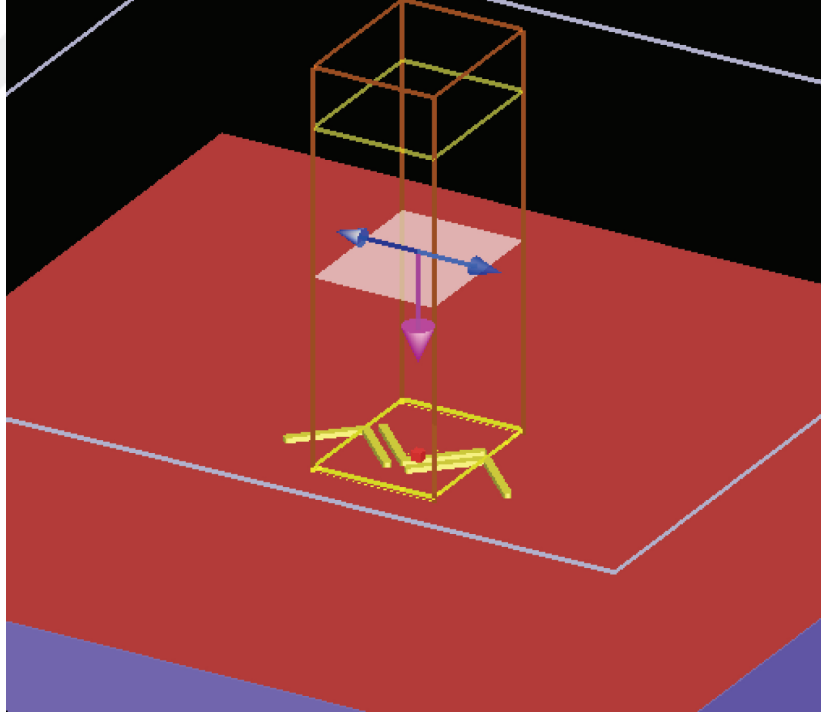


Figure 4.5: A perspective view from the FDTD simulation environment. 3D simulation region is shown by the orange box, which extends through the substrate. Graphene layer (red) and BaF₂ layer (blue) stands below the V-shaped gold nanoantennas (yellow). Plane-wave source polarization is indicated by the blue arrows and source injection direction is indicated by the purple arrow.

Finite-difference time domain (FDTD) simulations were performed by the commercially available software package developed by Lumerical Inc. A perspective view from a particular simulation in which $\alpha = 90^\circ$ can be seen in Figure 4.5. BaF_2 is modelled as a lightly absorbing medium with a constant refractive index of 1.45. Graphene was modelled as a 2-dimensional rectangle with a scattering rate of 0.514 meV and varying chemical potentials between 500 and 1000 meV in order to simulate the gating effect. Gold nanoantennas were modelled as 3D rectangular prisms with rounded ends in order to realistically represent the fabrication results. The thickness of these antennas were taken as 50 nm and the radius of curvature at the ends of the antennas was obtained from the SEM images of these structures (approximately 25 nm). Au (Palik) material model is used for gold nanoantennas. Ionic liquid is modelled as a non-absorbing medium and incorporated in the simulations as a background refractive index of 1.419. An x-polarized (as depicted in Figure 4.1) plane wave source was sent in the k-direction with a wavelength bandwidth between 2.5 μm and 6.5 μm . Simulation mesh were non-uniformly distributed with mesh sizes getting smaller near the graphene layer (down to 0.5 nm) by introducing a mesh-override region near graphene. Boundary conditions in the x and y directions were defined as periodic boundaries and boundaries in the k-direction were defined as perfectly matched layer, which prevents reflections from this boundary and absorbs the remaining electromagnetic energy.

4.4 Measurements

Spectral transmission measurements were carried out using a Fourier transform infrared spectroscopy setup, Vertex 70V FTIR, with a Hyperion 2000 IR microscope in order to focus on individual units on the sample. The sample was illuminated with normal incidence by a near infrared source with a CaF_2 beam splitter and a polarizer that is polarized in the x-direction. A liquid nitrogen cooled InGaAs detector inside a Hyperion 2000 Microscope detector compartment was used to take measurements between the 2500 and 15000 nm wavelength range. An infrared beam was focused on the plasmonic structure arrays by using the

microscope one by one while changing the gate voltage through a voltage source in steps of 0.2 V. Background transmission measurements were taken at the gate voltage of -0.6 V, the charge neutrality point of graphene, at a region inside the device with no plasmonic structures. For each case, 32 measurements were taken and averaged in order to reduce the noise in the measurements.

4.5 Results and Discussion

The transmission spectra of the three different V-shaped plasmonic structures each having different α values between their arms (SEM images depicted on the insets) on graphene, biased by using the ionic gating method is presented in Figure 4.6a. The transmission measurements are obtained at different gate voltages to observe the effect of changing the carrier sheet concentration of graphene and its effects to the plasmonic antenna resonance wavelength. An x-polarized field is sent through the device and transmission measurements are obtained. Background measurements are taken at the gate voltage level where graphene reaches its CNP, -0.6 V in an adjacent area on the device with no plasmonic structures. Gate voltage is increased in steps of 0.2 V, up to 3.2 V for each case separately. When the gate voltage is increased, the Fermi level of graphene moves away from its charge neutrality point. As the sheet charge density of graphene changes, the resonance wavelength of the plasmonic modes that are supported on the graphene layer shifts. As a result, the dips in the transmission spectra are blueshifted.

Figure 4.6b shows the maximum shifts of the transmission spectra for each plasmonic structure with different α values. Maximum spectral transmission shifts have occurred as the Fermi level of graphene moves away from the CNP; in our case, between the gate voltages of -0.6 V and 3.2 V. Transmission peaks have shifted 293.25 nm for $\alpha = 90^\circ$, 370.49 nm for $\alpha = 120^\circ$, and up to 389.79 nm for $\alpha = 150^\circ$ with a total of 3.8 V gate voltage tuning, in agreement with the simulations.

When the gate voltage is decreased from 3.2 V back to -0.6 V, a hysteresis

is observed in the dip locations of the transmission curves. This hysteresis is common to ionic-liquid based devices and is well described in both graphene-ionic liquid[60] and gold-ionic liquid[61] interfaces. One of the major mechanisms for this phenomenon is the formation of electrical double layers and slow response of the electrolyte due to low mobility of the ions in the electrolyte, which is common in supercapacitors. The other mechanism is the electrochemical doping of graphene electrodes. When a voltage is applied close to the electrochemical window of the ionic liquid, a small leakage current induces chemical doping on graphene, which shifts the CNP.[25] This mechanism may have a similar effect in our measurements. However, the tunability due to the graphene is more profound in our devices.

As the gate voltage increases, the shift in the spectral transmission curves diminishes. When the gate voltage is close to 3.2 Volts, we see that the spectral transmission curves are almost identical. In order to further analyze the blueshift in the transmission curves and the limits of this shift, we have investigated the locations of the dips in the FTIR measurements. Figure 4.7 shows the gate-voltage dependent shift of the transmission dips for 3 cases of α . For each curve, the wavelength shifts are calculated with respect to the dip when gate voltage at the CNP. The shift values follow an almost linear trend with the increasing gate voltage up to about 2.2 Volts. After that, regardless of the α of the plasmonic structure, all curves reach a saturation in their shifts.

A proposed explanation for the diminish in the spectral transmission shifts with the increasing gate voltage focuses on the behavior of ions in the ionic liquid. When the gate voltage increases, ions move towards the gating window and the graphene layer and accumulate in these interfaces. This accumulation of ions distorts the electric field and diminishes its magnitude near the graphene layer. This “screening” of the electric field causes the Fermi level of graphene to become less affected by the changing gate voltage. This limits the sheet carrier density change of graphene and the resonance frequency of the plasmonic modes remain unchanged.

Further investigation of the localizations near plasmonic structures can be

investigated in Figures 4.8 and 4.9. Figure 4.8 shows electric field magnitude distributions on graphene layer at the resonance wavelength of the plasmonic antennas. Major localizations of the electric field are in the gaps between the long arms and in the gaps between the end points of the plasmonic structures. These field localizations originate from the metallic plasmonic antennas and radiate to the nearby layers, such as graphene and BaF_2 layer. The penetration of these fields into the nearby structures can be seen in Figure 4.8. In each case, there is a localization of electric field on the graphene layer above the gap regions of the plasmonic antennas and that allowed further light interaction with the graphene.

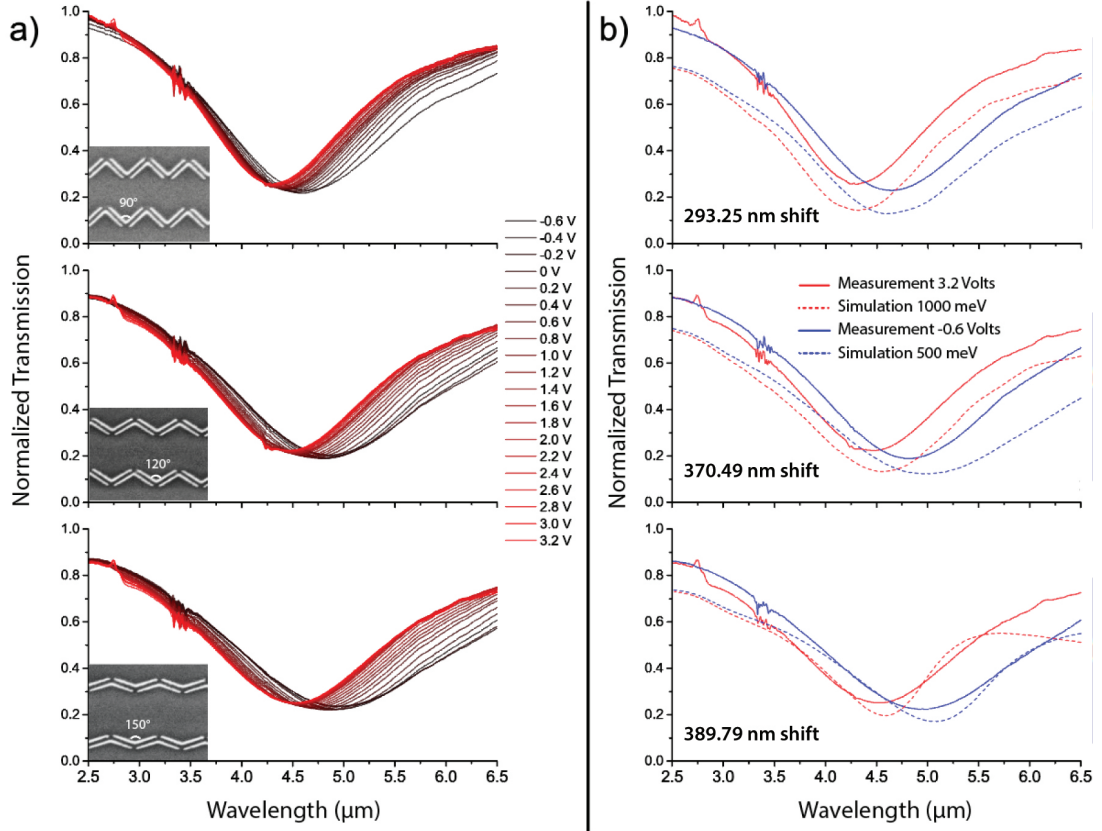


Figure 4.6: Measured and simulated infrared transmission spectra of the device under different gate voltages. (a) FTIR transmission measurements under different gate voltages from -0.6 V to 3.2 V in steps of 0.2 V. Line colors shift from black to red as gate voltage increases. Background measurements are obtained at -0.6 V (CNP) without the plasmonic structures. Three different plasmonic structures (Scanning Electron Microscope images for each case is shown on the inset) are measured. (b) Maximum shifts in transmission curves (solid lines). FDTD simulation results of the transmission curves with graphene having different Fermi levels (dashed lines).

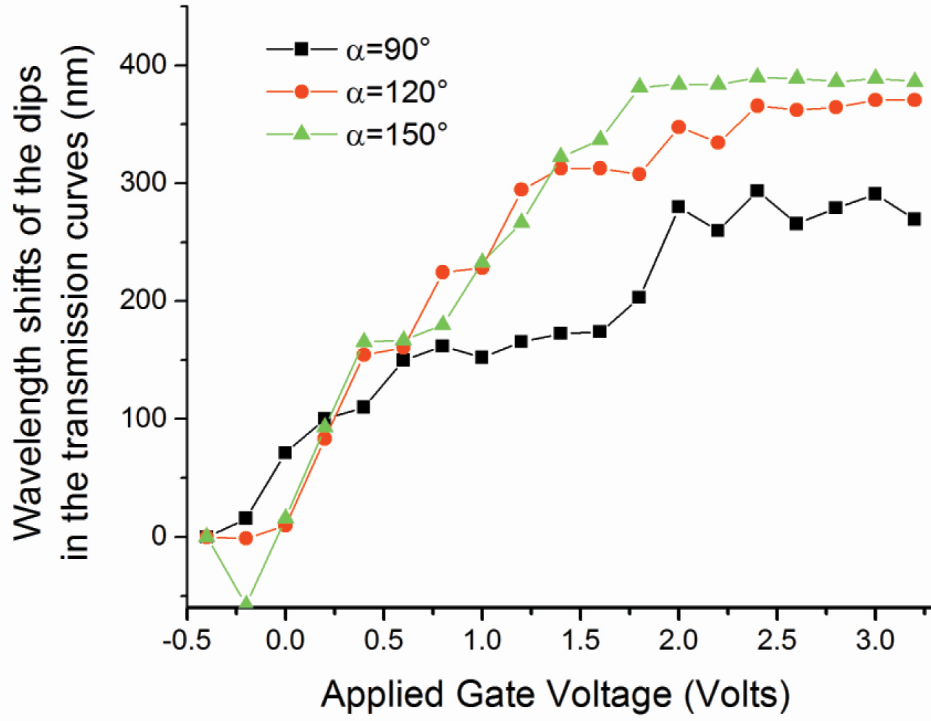


Figure 4.7: Wavelength shifts of the dips in the transmission curves in Figure 4.6a with respect to applied gate voltage for plasmonic structures with different values of α . Shifts are calculated with respect to the dip in the frequency of -0.6 Volts (assumed CNP) for each case.

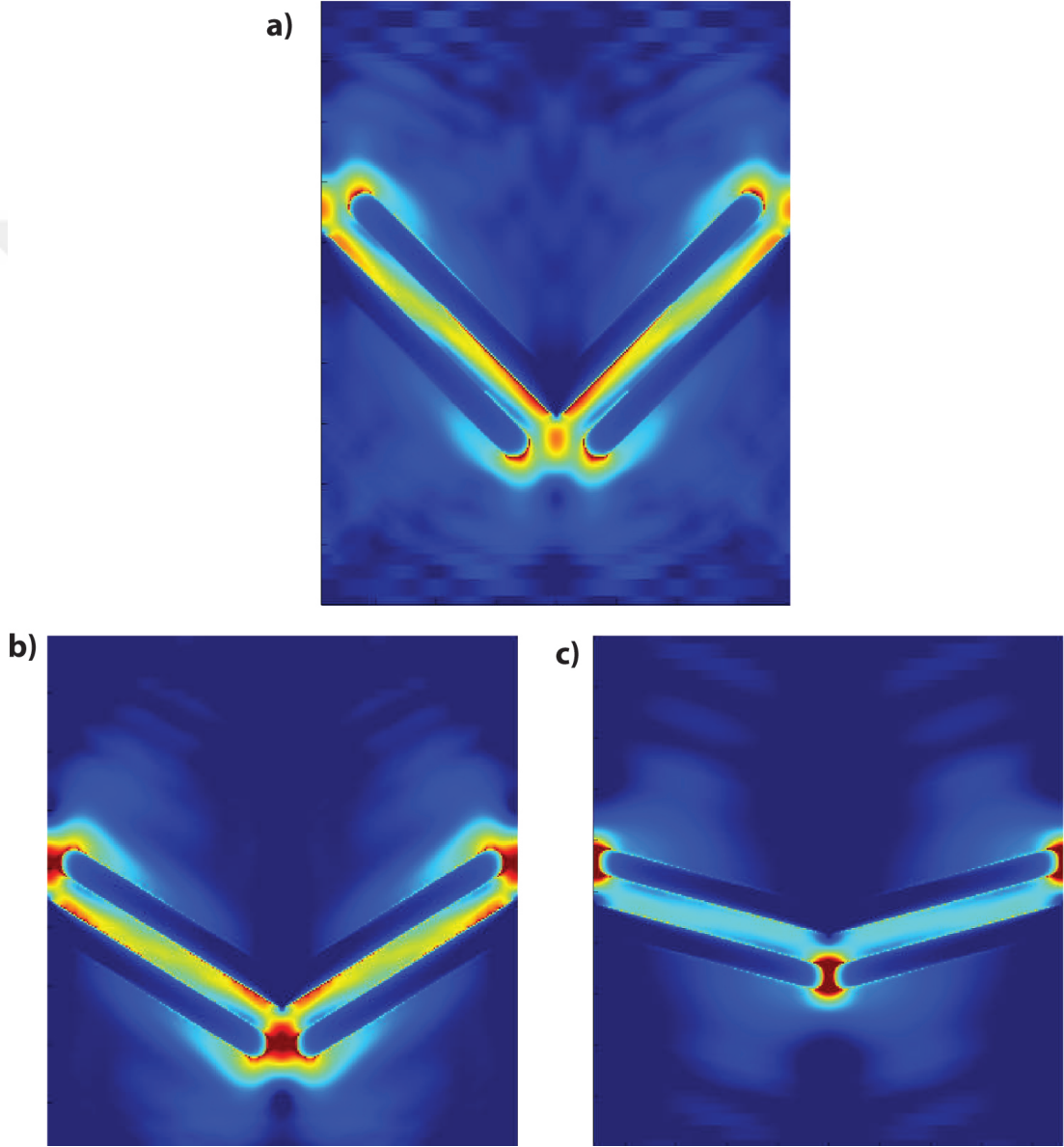


Figure 4.8: Electric field magnitude distributions on graphene at the resonance wavelength of the plasmonic structures for the cases (a) $\alpha = 90^\circ$, (b) $\alpha = 120^\circ$ and (c) $\alpha = 150^\circ$ obtained via FDTD simulation results. Blue represents low and red represents high electric field magnitudes. Results are obtained in all polarization directions for $E_f=500$ meV case.

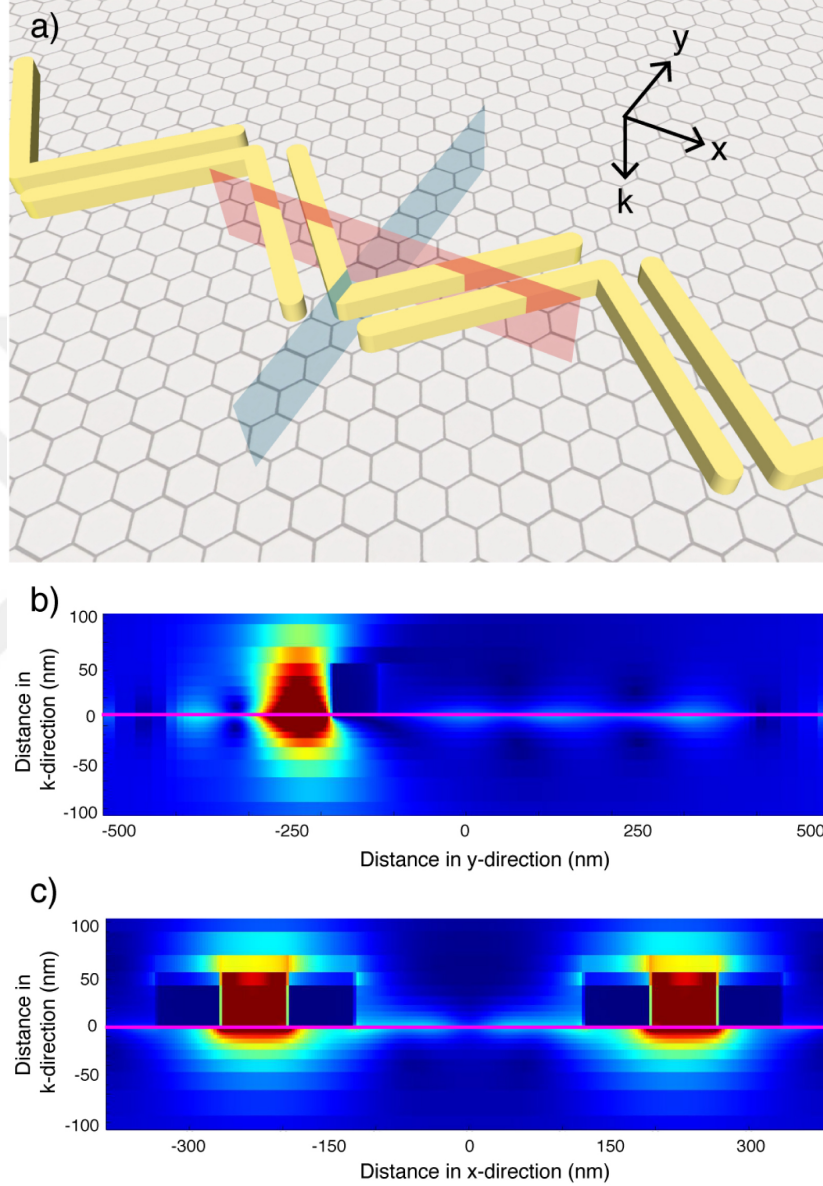


Figure 4.9: Cross-sectional electric field magnitude distributions for the $\alpha = 90^\circ$ and $E_f = 500$ meV case. (a) Schematic of the plasmonic structures on top of graphene layer and the location of the x (red) and y (blue) cross section cuts. Electric field magnitude distribution of a (b) y-cross section and (c) x-cross section of the device. Blue represents low and red represents high electric field magnitudes. Graphene layer is indicated with a pink line. Field localization in the plasmonic structures and their extensions to the underlying graphene and BaF_2 layers can be seen.

4.6 Conclusion

In this work, we demonstrated a large tuning range in the transmission response of V-shaped plasmonic antennas using graphene as the tuning medium. In addition to that, we are able to efficiently tune the spectral response of the device by applying a gate voltage in the range of 3-4 Volts through graphene via ionic liquid gating. By using this method, we are able to generate a 389 nm shift in the transmission spectra by applying only 3.8 V gate voltage. It is possible to use such devices in optoelectronic applications utilizing plasmonic antennas that require low gate voltages.

Chapter 5

Conclusions and Future Work

We have designed and fabricated different V-shaped gold nanoantenna arrays on top of a 285 nm SiO₂ on Si substrate. We have measured their spectral reflection responses in the mid to near infrared wavelengths. By performing FDTD simulations, we demonstrated the confinement and enhancement of electric field near the vicinity of V-shaped structures. With changing geometry, the resonance response of the antennas also change. By fabricating structures with different dimensions of arm length (L) and apex angle (α) we observed the spectral reflection resonance wavelength shift. Near the resonance wavelength of these nanoantennas, we demonstrated a 4 fold enhancement of reflection response. This study of the V-shaped nanoantennas allowed us to utilize them in advanced optoelectronic devices.

Taking advantage of graphene's highly tunable optical characteristics, we used it in a transmission geometry along with V-shaped nanoantennas. We fabricated the nanoantennas we have studied previously on an infrared-transparent substrate. We transferred graphene on top of these structures and constructed an ionic liquid gating scheme. By measuring the spectral transmission response and changing the gate potential, we observed 389 nm of resonance wavelength shift by applying only 3.8 Volts in the infrared regime.

A demonstration of graphene's tunable optical characteristics and its influence on plasmonic nanoantennas has been made in this thesis. Furthermore, ionic liquid gating method is demonstrated to be a much more efficient method than substrate back-gating. These demonstrations show that graphene can be used as a highly tunable medium in active optoelectronic devices, in combination with plasmonic structures. They can be used in producing efficient optoelectronic devices such as photomodulators and photodetectors that may be used in future generations of processors of optical communication systems. By varying the geometrical parameters of nanoantennas, a wide range of operation wavelengths can be selected. Incorporating graphene in the design further allows wide active span of operation frequency during operation.

Apart from using graphene as a tunable medium, graphene has a lot to offer. Its extraordinary electrical properties, such as the Dirac fermion characteristics of charge carriers which allows near light speed velocities, can be manipulated in the metamaterials field. Metamaterials have attracted attention, since they can be used to design structures with desired permeability and permittivity values, which makes it possible to construct negative refractive index materials. A subclass of metamaterials are the split-ring resonators (SRR). They have been proposed by Pendry et al. [62] in 1999. After that, several demonstrations of negative index metamaterials using SRRs have been made experimentally. [63, 64, 65] The geometrical parameters of an SRR determine their resonance wavelength and optical response. When the SRRs dimensions get smaller, their resonance wavelength shifts to smaller wavelengths. [65] However, this decrease is limited with the losses in the metal. At smaller wavelengths, most of the electromagnetic energy is lost in the metal and resonance responses are diminished.

Electrons in graphene have very high mobilities, as discussed in Chapter 2. They travel across the material with very low damping. These electrical characteristics makes graphene an attractive candidate to be used in graphene patterning applications. [66] By etching graphene into desired SRR shapes, it is possible to create metamaterial responses with high quality factors and low damping. Our early simulations show that for a highly-doped graphene SRR, this resonance is noticeably high. Further investigation and fabrication may prove our hypothesis.

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