GRAPHENE-BASED ACTIVE PLASMONIC METAMATERIALS

A thesis submitted to The University of Manchester for the degree of

Doctor of Philosophy

in the Faculty of Science and Engineering

2018

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Abstract

This thesis presents novel results in the field of plasmonics and optoelectronics application. Plasmonics is the rapidly expanding branch of photonics. It opens up capabilities of electronic and photonic device implementation within the same integrated circuits as well as enhances the limit of detection for chemical and biological-based sensors. The first finding lies in solving the dilemma in search of ultimate plasmonics materials for plasmonics application. It is well known that Cu and Ag are metals that have incredible electric and optic properties. However, they are easily oxidized in contact with air. Both experimental and theoretical findings demonstrate that application of a mono or bilayer graphene protects Cu and Ag from oxidation and degradation of its plasmonic properties. The performance of each metal is evaluated based on the quality factor Q and the minima in amplitude of reflection intensity R_{min} of the Surface plasmon-polariton (SPP) curve.

The second novelty of this thesis comprises the fabrication of low loss, high efficient broadband, as well as narrowband, graphene-based electro-absorption modulators. The studied graphene-based modulators made use of Fabry-Perot resonator geometries. It has been shown that high-k dielectric hafnium dioxide (HfO₂) provides solid state "supercapacitor" effects and allows to observe light modulation from the near-infrared to shorter wavelengths close to the visible spectrum with remarkably low gate voltages (~4 V). The electro-absorption modulators based on Fabry-Perot resonator geometry reached the modulation depth in transmission mode of 28% at a wavelength of 1.1 μ m.

Declaration

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Acknowledgements

Studying and carrying out high level scientific research was a great honor for me and I am very grateful to all of people who have helped me a lot with their guidance, knowledge, assistance and patience. I am deeply thankful to my supervisor Alexander Grigorenko who is incredibly smart, good and very kind person. I am very thankful to Sasha for his guidance, support and all of the possibilities which were around to do high level research. I deeply grateful to Alexander Grigorenko for the opportunities not only to know how theoretically compute things but how to fabricate them so that the devices will work and show good properties. I am truly thankful to Francisco Rodriguez who was so kind and patient to me during my first steps in the devices fabrications. Thank you Fran for your time and sharing with me valuable knowledge and hints of graphene production, its complicated transfer process onto rough morphology of dielectric and all of the help which you provided during the optoelectronic device fabrication and its experimental testing. Without your support and help I would not have learned what I know right now. I would like to thank Vasyl Kravets for his kindness and support during the projects and I am very grateful to Owen Marshall and Dmytro Kundys for explanation in running the optical set up experiments. I would like to thank all of the guys at cleanroom that were around. Especially to those with whom we shared lovely moments during devices fabrication at the cleanroom during Friday and weekends late evenings. Finally, I would like to thank Konstantin Novoselov and Andre Geim for their incredibly fascinating work on graphene and other 2D materials.

Thesis Defending Statements

1) Graphene protective barrier for hybrid metal plasmonics.

The paradigm of plasmonics gives new possibilities for harvesting and confining the light with large free space wavelength down to nanoscale regime and utilizes this for the fabrication of a new branch of nanophotonic and electro-optical devices. The plasmonic devices are based on utilization of gold due to its high conductivity and chemical inertness. However, due to gold morphological roughness, the plasmonic devices made of gold exhibit large losses due to scattering. Hence, the search for ultimate active plasmonic materials continues to this day. The thesis presents another way to find a better material for plasmonic applications. It is well known that Cu and Ag are good metals with large electrical and optical conductivity, however, they oxidize easily. In this thesis, it has been shown experimentally as well as theoretically that an application of mono and bilayer of graphene makes possible to protect Cu and Ag from oxidation and degradation of their plasmonic properties. The performance of each metal is evaluated based on the quality factor Q and the minimum intensity R_{min} of the surface plasmon resonance (SPR) curve.

1.1. Graphene-based copper protective barrier for plasmonic application.

By using Turbadar-Kretschmann-Raether geometry, I studied the plasmonic properties of graphene - protected copper - based samples for surface plasmon polaritons excitation and propagation. The strongest resonance was observed at wavelength 588 nm and angle of light incidence of 49.5⁰ for graphene - protected copper samples. It has been observed that the minimum intensity of reflection of SPR curve equals to $R = 5 * 10^{-4}$ and the quality factor Q equals to 19. Having left graphene - protected copper-based samples for over 6 months in air environment, there was no degradation of plasmonic properties of the studied samples. Moreover, the conditions for SPP excitation even improved, which is confirmed by appearance of the deepest SPR curve with $R = 3 * 10^{-4}$ and quality factor Q of 20.

1.2. Graphene-based silver protective barrier for plasmonic application.

The new recipe to safeguard the plasmonic characteristics of silver plasmonics was developed, which focuses on a careful transfer protocol of CVD graphene onto freshly evaporated Ag films. By employing such a procedure, it was possible to protect silver from deterioration of its plasmonic properties which was confirmed in the observation of the minimum of SPR curve with $R = 5 * 10^{-4}$ at wavelength 435 nm and angle of light incidence of 53.5⁰.

It is worth mentioning that none of these characteristics have been achieved so far for Au films due to high surface roughness of deposited gold films. My personal contribution to this chapter of thesis was computational modeling of Cu and Ag-based plasmonic heterostructures as well as study of active plasmonic modulators.

2) Graphene-based electro-optical modulators.

Electro-optical modulators with nanoscale footprint, small leakage currents, room temperature operation, low power consumption are in great demand by industry. The task of creating such modulators can be solved by using optoelectronic properties of graphene in combination with HfO₂ solid nonstoichiometric electrolyte being incorporated into Fabry-Perot geometry. HfO₂ is promising candidate for dielectric spacers in graphene-based optical modulators due to its electrical, optical properties and compatibility with the fabrication of CMOS devices. It is well established that graphene has constant optical light absorption from the visible to near-infrared (NIR) wavelength region, which limits its application in electro-optical modulators domain. However, the problem is solved by implementing graphene into Fabry-Perot structure where, due to multiple interference effects, it is possible to enhance graphene optical absorption and overall field acting on graphene surface. The light modulation is achieved due to

graphene doping effect influenced by applying DC and AC bias to the modulator structure. To the best of our knowledge, we demonstrate for the first time experimentally the ability to achieve light modulation at wavelength $\lambda = 1.1 \,\mu\text{m}$ with modulation depth of 28% by the use of moderate gate of 4 V. This result presents a novelty for the scientific community being the first graphene light modulators with significant electro-optical modulation effect realized for solid state dielectric with small voltage gates have been applied. Overall, the innovation of the fabricated graphenebased electro-optical devices lie in a simple design of the modulator structure consisting of high quality graphene monolayer and high-k HfO₂ gate dielectric which plays role as ionic gate layer and gives the possibility to apply small gate biases and obtain significant electro-optical modulation effect.

My personal contribution to this work was theoretical modeling, fabrication of broadband and narrowband graphene-based electro-optical modulators with subsequent their characterization as well as electrical and electro-optical testing.

Introduction

Chapter 1

Literature review background

The modern trend of technology lies in miniaturization and, as a result, location more electrical or optical elements within the same electrical or electro-optical integrated circuits which, in turn, increase the efficiency and performance of devices [1, 2] Miniaturization entails the use of electro-optical phenomena in materials with the size less or in the order of several micrometers. The well-known chemical method [3, 4] with the help of which it is possible to observe relatively high value of electro-optical effects by specifically choosing the type of materials, its concentration and composition, at this stage reached its limitations. However, the optical properties of materials can be altered by not only changing the chemical composition of a material, but artificially tailoring its geometrical configuration. It should be noted that in this case the characteristic size of geometrical configuration could be less or equal the wavelength of the external irradiation. In the case where the geometrical sizes of nanostructured material are less than wavelength of incoming light, the optical response of such material can be treated as quasi-homogeneous and can be theoretically described with the help of effective medium theory [5, 6]. It should be mentioned as well that within the approach of effective medium theory an optical response of the material (either isotropic or anisotropic) is described by the tensor of its dielectric and magnetic permittivity which in turn profoundly depend on the wavelength of the incoming light [7-9].

These artificially created materials with engineered optical properties within a specific wavelength or frequency range are referred to as metamaterials [10]. As a result, by specifically engineering the type, structure, shape and size of elementary unit of

metamaterial, we can create resonant response of dielectric and magnetic permittivity within specific wavelength or frequency range of interest [10].

However, if sizes of elementary blocks of a metamaterial are of the order of light wavelength, the crucial role in the optical response of such metamaterial will play relative arrangements of elementary blocks with respect to each other (in addition to the elementary block shapes and sizes).

Recently, significant attention of scientific community attracted an investigation of periodically arranged materials, so-called photonic crystals [11-13]. A photonic crystal itself is a periodic nanostructured material which has the property to create an optical band gap for the specific wavelength of electromagnetic waves so that these waves, for example, will be absorbed by this photonic crystal and will not be allowed to pass thought it [14]. As a consequence, this gives an opportunity for researchers to create optical antireflection coatings, filters, polarizer, etc. in repeatable and controllable way. The other fascinating property of those crystals is that it is possible to significantly enhance optical resonances by several orders of magnitude by employing them in optical devices. The enhancement of the resonances of the photonic crystal is governed by the particular geometrical arrangement of the photonic crystal rather than its electronic structure. In this case, the excitation of electromagnetic modes of the material results in more effective light matter interaction between the incoming light and nanostructured photonic crystal which causes the occurrence of specific resonance conditions [14].

From another point of view, the nanocrystal consisting of alternating or specifically perforating layers of dielectrics and metals (a photonic crystal) can also support the appearance either surface (SPP) or localized surface plasmons (LSP) if the wave momentum conservation is preserved [15, 16]. The significance of SPP or LSP phenomena lies in high degree of electromagnetic field localization within some

specific area in the surface between dielectric and metal which in turn lead to the enhancement of electro-optical phenomena. The capability of localize high concentration of electromagnetic field opens the route to combine efficiently the optical elements with the electronic circuits.

In resemblance to the definition of photonic crystal, the nanocrystals, consisting of layers of dielectric and metal, are designed to be planar or have the periodic system of stripes, rings, triangles etc in which the wave momentum conservation will be preserved, could be called the nanoplasmonic crystals [17].

Furthermore, the periodic structuring of nanoplasmonic crystal gives researchers a controllable way to modify the optical properties and hence the optical response of the nanoplasmonic crystal. Moreover, SPP or LSP resonances excited on nanoplasmonic crystals provide possibility to highly confine and localize the concentration of the electromagnetic field at the nanoscale, thus enabling significant enhancement of electro-optical phenomena in the required range of wavelength. Therefore nanophotonic and nanoplasmonic crystals could pave the way for fabrication of highly efficient electro-optical devices with the required properties [18].

Still, these days there is an issue with effective light modulation with the help of either nanophotonic or nanoplasmonic materials not only in transmission or reflection mode in the far field but also modulation of own waveguide modes in the near field [19]. This is especially crucial for integrating optics in which the flow of information is transmitted with the help of waveguide impulse modes or surface plasmon polaritons waves. Consequently, the fabrication of newer, externally controllable, efficient, broadband nanoplasmonic electro-optical modulators is important and was the main purpose of this thesis. Carbon is a ubiquitous and fascinating element. Carbon has the ability to establish strong covalent bonding with other molecules forming new structures with unique properties. Moreover, the dimensionality of the formed molecule plays a significant part in establishing its physical and chemical properties. Three main allotrope forms of carbon have been distinguished - diamond, graphite and amorphous carbon. The most intriguing allotrope among them is graphite due to its electronic structure and similarity with ordinary metals. According to the Wallace [20] graphite is three dimensional crystal with sp² type hybridization between one *s* and two *p* orbits. It consists of hexagonal layers of carbon atoms coupled together by extremely strong covalent bonding in the in-plane direction and with an additional free $2p_z$ delocalized electronic states located normally to hexagonal carbon sheet. According to the Wallace [20] wave function of electrons in graphite can be written in the following way:

$$\frac{1}{\sqrt{3}} \left[\Psi_c \left(2s \right) + \sqrt{2} \Psi_c \left(\sigma_i 2p \right) \right] \qquad (i = 1, 2, 3), \tag{1.1}$$

where $\Psi_c(2s)$ attributes to the wave function describing 2s carbon's electrons and $\Psi_c(\sigma_i 2p)$ is the wave function of 2p carbon atoms whose axis lies in the σ_i direction which bonds together carbon atoms in the in-plane direction.

Additional free electron is supposed to belong to $2p_z$ states whose axis is normal to the in-plane hexagonal carbon rings. This delocalized free $2p_z$ states form a weak Wan der Waals forces between graphite layers and they are responsible for softness of graphite crystalline lattice.



Fig.1.1.Electronic structure of graphite. As stated by Wallace, the unit cell for hexagonal layer contains two carbon atoms A and B depicted in the unit cell of WXYZ (picture adapted from ref. [20])

Once graphite electronic structure and its potential was understood, some theoretical works [21, 22] began to point out that by extracting 2D hexagonal carbon layers from graphite lattice one may obtain a substance which would possess unique and unusual properties.

Unfortunately, as was predicted [23] such low two-dimensional systems could not exist in a free standing state due to the emergence of thermal fluctuations and atomic displacements, which would be trying to return the whole system to its original state and occupy the minimum of total energy.

Fortunately, this problem was solved when one atom thick layer of graphene was successfully extracted from graphite crystalline lattice by mechanical exfoliation technique in 2004 at the University of Manchester by the group of A. Geim [24]. Since then many fascinating phenomena of 2D carbon systems were found and newly appeared material opened new routes of investigations and applications.

1.1. Graphene

1.1.1. Graphene electronic structure

Graphene has two-dimensional electronic structure with tightly packed carbon atoms in hexagonal honeycomb lattice. According to the literature [25], graphene's atomic structure comprises with 2s, $2p_x$, $2p_y$ and $2p_z$ orbits where each carbon atom is strongly bounded to the three surrounding atoms via in-plane σ connections which give rise to the graphene mechanical properties. The fourth free $2p_z$ electron is delocalized and generates π - orbits lying in the perpendicular directions to the graphene's plane. These free delocalized electrons account for the high value of graphene conductivity and its fascinating transport properties.

Turning to the next point, graphene has two carbon atoms A and B per unit cell. By putting carbon atoms in a Bernal stacking arrangements [26] it is possible to obtain bilayer, multilayer or 3D graphite structures (Fig.1.1.1.1.) [27]. Moreover, by wrapping or rolling graphene sheet up it is possible to obtain different allotrope forms of carbon such as fullerene or single layer carbon nanotubes which depending on its geometry will possess different and remarkable physical properties. Consequently graphene can be considered as a 'building block' [24] of any sp² hybridized carbon molecules.



Fig.1.1.1.1.Graphene and its derivatives. (a) schematic view of graphene allotropes. (b) graphene unit cell. (c) carbon covalent bonding and orbitals in graphene. (d) graphene energy dispersion relation. (f) graphene energy band gap engineering by external means (picture adapted from ref. [27])

However, the most interesting graphene properties come from its electronic spectrum. Being two dimensional semimetal, graphene possess a wide range of unusual characteristics which is not observed in conventional semiconductors. First, its lowlevel electron excitations behave like massless particles which propagate though the graphene lattice with very small losses of energy due to the scattering on phonons, defects or impurities at the room temperature. They can be described by the Dirac equations for the relativistic particles. Second, due to high lattice symmetry, graphene's band structure gains a linear conical form E(k) which differs from the ordinary metals and semiconductors with their parabolic relation between energy and wave momentum. Third, the conduction and valence bands in graphene touch each other at the neutrality point (Dirac point) and form zero band gap semimetal (Fig. 1.1.1.2).



Fig.1.1.1.2.Graphene electronic structure. (a) graphene hexagonal honeycomb lattice for A-B Bernal staking. (b) graphene energy dispersion. c) valence and conduction band of graphene touching each other at the neutrality point (picture adapted from ref. [28])



Fig.1.1.1.3.The electronic spectrum E(k) of graphene. Zoom represents the valence and conduction bands near the Dirac point (the picture adapted from ref. [25])

The dispersion relation in the vicinity of the neutrality point can be represented as follows:

$$E(k) = \pm h v_f \sqrt{k_x^2 + k_y^2}, \qquad (1.1.1.1)$$

where *h* is Plank's constant, v_f is Fermi velocity, k_x and k_y are the projections of wave vector **k** on the *x* and *y* directions. The sign" + " is attributed to the conduction band whereas sign "-" due to the valence band.

Furthermore, it should be noted that in pristine graphene with zero Fermi energy (and zero occupancy of the conduction band at zero temperature), graphene optical

conductivity does not go to the zero value but takes minimum value equal to $\frac{e^2}{4\hbar}$ [29]. All these graphene's extravagant properties promise a wide range of graphene applications.

1.1.2. Transport properties of graphene

As a consequence of almost perfect crystalline structure of graphene flakes and properties of its electron spectrum, electrons in graphene can move ballistically over "submicron distances" [24, 30-32]. Unlike conventional semiconductors, where at low density of states the electrons do not contribute significantly to electrical conductivity, the electron mobility of graphene and electrical conductivity can still gain high values. In addition, graphene conductivity can be influenced and changed depending on the environment and a substrate on which graphene flake is deposited [33-35]. The substrate can induce fluctuations of electric potential and encourage charge creations in graphene layer which in turn can change electrical characteristics of the system. For instance, in the case when graphene layer was deposited on Si@SiO₂ substrate, the later ones induced charge carrier perturbations and additional electron-phonon scattering. This process can lead to decreasing the electron mobility of the whole system [36-40]. However, authors of the work [30] concluded that: "The electron-phonon scattering in graphene and its bilayer is so weak that, if the extrinsic disorder is eliminated, room temperature mobilities ~ 200 000 $\frac{cm^2}{V \cdot sec}$ are expected over a technologically relevant range of carrier concentration n". Apart from this, it was shown that, away from the Dirac point, the graphene resistivity is raising when placed on a substrate due to two factors – one is the long range electron-phonon scattering (substrate roughness) [41] which leads to following expression of graphene resistivity

$$\rho = \frac{1}{\mu en},\tag{1.1.2.1}$$

where e is electron charge, n is concentration of electrons and μ is mobility of electrons.

The second contribution to resistivity is due to the appearance of short-range scattering centers caused by atomic inhomogenety of the substrate [41, 42].

Both of them depend on the temperature and exhibit rise in different temperature range. By applying gate voltage to the system Graphene@SiO₂@Si (Fig. 1.1.2.1.) the electron concentration is induced and can be calculated using the following formula

$$n = \frac{\varepsilon \varepsilon_0 U}{de} = \alpha U, \qquad (1.1.2.2)$$

where *n* is concentration of charge carriers, ε_0 is free space permittivity with the value of $8.85 * 10^{-12} \frac{\text{F}}{\text{m}}$, ε is dielectric permittivity of SiO₂ with $\varepsilon \approx 3.9$, *d* is the thickness of SiO₂ layer, *e* is electron charge of $1.6 * 10^{-19}$ C and *U*(*V*) is the applied voltage



Fig.1.1.2.1.Conductivity of charge carriers in graphene as a function of applied gate voltage. The charge carrier's conductivity is measured at different temperatures from 20 K to 260 K (picture adapted from ref. [30])

By varying the gate voltage one can modify the number of electrons in graphene and, as a result, tune its Fermi level. Fermi level of pristine (undoped) graphene lies at the Dirac point where there is zero density of states, which means that there are no charge carriers contributing to the electro-conductivity (at zero temperature). Thus, for Fermi energy close to the neutrality point, graphene shows large resistivity of around 6 k Ω . Overall, by changing gate voltage it possible to change the position of the Fermi level and shift it to the valence band or to the conduction band.

A standard experimental graphene flake is doped either during the fabrication process or due to external environment. Hence, there is non-zero gate voltage U_{dic} which corresponds to the maximum value of graphene resistivity and should be taken into account while calculating the concentration of charge carriers being induced by external voltage for doped graphene. For undoped graphene $U_{dic} = 0 V$, however, once graphene is doped, U_{dic} shifts from zero voltage to some value, which is determined by the chemical doping level. Fermi level is shifted away from the neutrality point as well once dopants were introduced to the graphene system. As a result, the maximum of graphene resistivity should appear not at the $U_{dic} = 0 V$, but at some point, when gate voltage compensates the number of charges carries being introduced by dopants. Consequently, the formula (1.1.2.2) should be modified for doped graphene and described as voltage attributing to graphene with the presence of charge dopants

$$n = \alpha (U - U_{dic}), \qquad (1.1.2.3)$$

The presence of symmetrical energy spectrum E(k) between conduction and valence bands leads to the fact that electrons and holes in graphene have equal group velocity. Scattering of electrons or holes in graphene is isotropic and affects them equally with the same scattering strength, then, the drift velocity will be the same for electrons and holes and the mobility of charge carriers (electrons and holes) will be equivalent

$$v_{drift} = \mu E$$
, (1.1.2.4)

where μ is mobility of charge carriers, *E* is electric field.

Nevertheless, in ordinary samples, due to the presence of surface inhomogenety, roughness and defects the scattering mechanism for charge carriers will be determined by the surface conditions. Thus depending of the quality of a sample the mobility of charge carries will vary from sample to sample. As it was mentioned above, the homogeneity and purity of the wafer and underlying substrate directly influence the strength of charge carriers scattering and their mobility. For instance, the magnitude of charge carrier's mobility in graphene supported on SiO₂@Si substrate at room temperature varies significantly starting from 1000 to 70 000 $\frac{cm^2}{V \cdot sec}$ [43] while in the case of free standing graphene the mobility of electrons reaches remarkably high value of 200 000 $\frac{cm^2}{V \cdot sec}$ [44]. This magnitude is much higher compared to the conventional fastest semiconductors (InSb with 78 000 $\frac{cm^2}{V \cdot sec}$ [45]).

1.1.3. Graphene plasmonics and light matter interaction

Among other peculiar properties of graphene is its optical transparency. In pristine graphene, the optical transparency is determined by the fine structure constant which characterizes the light interaction with free conduction electrons of a metal

$$\alpha = \frac{e^2}{\hbar c} = \frac{1}{137},\tag{1.1.3.1.}$$

where α is fine structure constant, *e* is charge of electron, \hbar is Plank constant and *c* is speed of light in vacuum.

It was shown by authors [46], that one layer of graphene absorbs 2.3% of incident light with showing very small light reflectance less than 0.1 % (see Fig.1.1.3.1). Furthermore, it was found by the same authors that graphene absorption increases with increasing the number of layers. Consequently each additional graphene layer will add 2.3% to the overall light absorption of the bulk graphene.



Fig.1.1.3.1.Light transmission as a function of graphene layers. (a) light transmittance through the graphene layers being the function of aperture distance. (b) comparison of experimental data with theory for light transmission through graphene layers (pictures adapted from ref. [46])

The processes of optical absorption in graphene are governed by intraband and interband electron transitions as stated by authors [47, 48]. Their contributions to the optical absorption of graphene depend on the frequency range of interest. For instance, in the far-infrared spectral range the optical response of graphene is determined by the intraband electron transitions and can be described by the Drude model [49]. As for mid and near-infrared frequency ranges, the optical response of graphene is dominated by interband charge carrier's transition. Moreover, it was found that interband absorption is mainly frequency independent and can be solely determined by the fine structure constant with $\frac{e^2}{4\hbar}$ [46, 50-52]. In the ultraviolet range of the spectrum, the interband response increases and excitonic effects start taking place [53, 54].

Additionally, as shown in a number of papers, one may easily control the process of graphene absorption by either introducing chemical doping or applying gate voltage to the substrate on which graphene flake is deposited (Fig.1.1.3.2).



Fig.1.1.3.2.Schematic view of the bilayer graphene band structure in the case of undoped (left) and doped (right) bilayer graphene. Hence band gap of bilayer graphene can be easily changed via chemical or electrical doping (picture adapted from ref. [55])

Those processes give the possibility to shift Fermi level either to valence or conduction bands and prompt the appearance of Pauli blocking for the optical absorption (Fig. 1.1.3.3).



Fig.1.1.3.3.Schematic representation of saturable optical absorption process in single layer of graphene. The arrows denote interband transition in graphene due to light absorption. At higher intensities of incident light further optical absorption is blocked in graphene monolayer (picture adapted from ref. [55])

Thus, with the help of chemical doping as well as electrostatic gating, it is possible to change the density of conduction electrons in graphene (thus its electrical and optical conductivity) and take advantage of this in the terms of device fabrication. The evidence of such doping manipulation was presented in the works [56, 57] where charge carrier's concentration in graphene, placed on Si@SiO₂ substrate, was changed by different levels of gating voltage. The optical conductance $\sigma(\omega)$ spectra were fitted reasonably

well by the combination of Drude model with the Kubo formalism without taking into account the many-body interaction mechanism in graphene [58]. The interband absorption in graphene is governed by direct electron transition from valence to conduction band and can be described within the tight-binding model (Kubo formalism [52])

1.2. Nanophotonics and Plasmonics

1.2.1. Metal electromagnetics

Optical properties of a material can be described by frequency dependence of dielectric permittivity $\varepsilon(\omega)$ of a material [59]. Generally, dielectric permittivity $\varepsilon(\omega)$ is a complex value where its real part is responsible for light propagation in a medium whereas complex one is a result of absorption processes. The equation which describes dielectric permittivity response on the applied external frequency is called dispersion relation. Using free electron plasma model [60-62], one can easily obtain the expression for conductivity of a generic metal by solving the following equation

$$m_e \frac{d^2 x}{dt^2} = -eE_x , \qquad (1.2.1.1)$$

where m_e is mass of electron, x is electron displacement, e is charge of electron and E_x is electric field projection on X-axis

If we assume that intensity of electric field *E* changes harmonically with the time *t* as

$$E = E_o \exp(-i\omega t), \qquad (1.2.1.2)$$

where E_0 and ω is the amplitude of electric field intensity and frequency of electromagnetic field.

We obtain

$$-\omega^2 m_e x = -eE_x , \qquad (1.2.1.3)$$

The polarization P of free electrons in metals can be treated as volume density of dipoles:

$$P_x = -ex$$
, (1.2.1.4)

$$P = -N_e \frac{e^2}{m_e \omega^2} E , \qquad (1.2.1.5)$$

where N_e is the concentration of electrons in metal, ω is the frequency of external electromagnetic wave, *e* is electron charge, m_e is mass of electron and *E* is the intensity of applied electrical field.

We also need to take into account the material Maxwell equations:

$$\boldsymbol{D} = \varepsilon_0 \boldsymbol{E} + \boldsymbol{P} \,, \tag{1.2.1.6}$$

$$\boldsymbol{D} = \varepsilon \varepsilon_0 \boldsymbol{E} , \qquad (1.2.1.7)$$

where D is the electric displacement.

Using the equations above we derive the expression for dielectric permittivity in the case of free electron model as

$$\varepsilon(\omega) = 1 + \frac{P}{\varepsilon_0 E}, \qquad (1.2.1.8)$$

$$\varepsilon(\omega) = 1 + \frac{N_e e^2}{\varepsilon_0 m_e}, \qquad (1.2.1.9)$$

with $\omega_p^2 = \frac{N_e e^2}{\varepsilon_0 m_e}$ – plasma frequency of free electron gas in metal. Thus we obtain

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega^2},\tag{1.2.1.10}$$

Drude Model: In the optical frequency range, the electrical properties of metals can be understood with the help of the Drude model [60-62] in which electrons in metals are treated like free electron gas with density n moving through the immovable frame of positive ion cores. For alkali metals this frequency range can be extended up to ultraviolet whereas for noble metals interband electron transitions take place in the visible range of the spectrum, thus leading to the limitation of this approach. Moreover, in Drude model the details of lattice potential and electron-electron interactions are not

taken into account. It is assumed, however, that metal electronic structure and lattice potential are included into the effective mass of an electron. In the Drude model [60-62] it is supposed that, while electron moves due to the applied electromagnetic field, electron motion is influenced by dissipative force due to electrons collisions with characteristic frequency:

$$\gamma = \frac{1}{\tau},\tag{1.2.1.11}$$

where τ is known as relaxation time of electrons with the value around 10^{-14} sec at the room temperature.

Let us now solve the equation of electron motion in the applied electric field:

$$m_e \frac{d^2 x}{dt^2} + m_e \Gamma \frac{dx}{dt} = -eE , \qquad (1.2.1.12)$$

Assuming harmonic time dependence of electromagnetic field

$$E(t) = E_0 \exp(-i\omega t)$$
, (1.2.1.13)

where m_e is mass of electron, Γ is a phenomenological damping constant, component $eE_0 \exp(-i\omega t)$ is driving electromagnetic force in a metal, E_0 and ω is the amplitude and frequency of electromagnetic field, we get

$$x = \frac{1}{m_e(\omega^2 + i\Gamma\omega)} eE_0, \qquad (1.2.1.1.14)$$

$$\frac{dx}{dt} = -\frac{i\omega}{m_e(\omega^2 + i\Gamma\omega)}eE_0, \qquad (1.2.1.1.15)$$

$$\frac{d^2x}{dt^2} = -\frac{\omega^2}{m_e(\omega^2 + \mathrm{i}\Gamma\omega)}eE_0, \qquad (1.2.1.1.16)$$

This gives the expression for polarization *P* and the effective dielectric permittivity $\varepsilon(\omega)$ as

$$P = eNx$$
, (1.2.1.1.17)

$$\varepsilon(\omega) = 1 - \frac{Ne^2}{\varepsilon_0 m_e(\omega^2 + i\Gamma\omega)}, \qquad (1.2.1.1.18)$$

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{(\omega^2 + i\Gamma\omega)}, \qquad (1.2.1.1.19)$$

$$\varepsilon(\omega) = \frac{\omega_p^2 - \omega^2 + \Gamma^2}{\omega^2 + \Gamma^2} + i \frac{\omega_p^2 \Gamma}{\omega(\omega^2 + \Gamma^2)}, \qquad (1.2.1.1.20)$$

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega),$$
 (1.2.1.1.21)

Overall the response of the metal to the external electromagnetic field is characterized by the frequency dependence of dielectric permittivity. A lot of dielectrics such as glass, air and quartz have negligible absorption and thus have approximately zero value of imaginary part while real part of dielectric permittivity depends slightly on the external electromagnetic field. Metals poses real and imaginary components of $\varepsilon(\omega)$ which vary significantly at different range of the spectrum [63].

Lorentz model : Unlike the Drude model, the Lorentz model [60-62] characterizes medium consisting with number of classical driven harmonic oscillators in which electrons are connected to its nuclei. The incident electric field causes electron displacement, which has spring-like restoring force due to the presence of nuclei. Thus the equation of electron motion under external electromagnetic field can be expressed as

$$m_e \frac{d^2 x}{dt^2} + m_e \Gamma \frac{dx}{dt} + \omega_p^2 x = -eE, \qquad (1.2.1.1.22)$$

where Γ is the phenomenological damping constant, ω_p is resonant frequency, *e* is charge of electron, *E* is intensity of electric field.

The second term of equation is due to the process of energy loss in the medium, while the third term corresponds to the energy accumulation in the medium. By expressing Eand x through the time and frequency dependence as

$$E(t) = E_0 \exp(-i\omega t)$$
, (1.2.1.1.23)

$$x(t) = x_0 \exp(-i\omega t)$$
, (1.2.1.1.24)

After inserting these equations into (1.2.1.1.22) one may obtain the following expression

$$-\omega^2 x(\omega) + i\Gamma \omega x(\omega) + \omega_p^2 x(\omega) = -\frac{e}{m} E(\omega), \qquad (1.2.1.1.25)$$

$$x(\omega) = \frac{\frac{e}{m}E(\omega)}{\omega^2 - i\Gamma\omega - \omega_p},$$
(1.2.1.1.26)

As a result of charge displacement due to system illumination by electromagnetic field, the dipole moment is induced in the system. The macroscopic response of whole the medium takes into account the overall electron displacement which describes the contributions of the overall dipole moments induced in a specific volume

$$P = Nex$$
, (1.2.1.1.27)

$$P(\omega) = \frac{Ne^2}{m} \frac{E(\omega)}{\omega_p^2 + i\Gamma\omega + \omega^2},$$
(1.2.1.1.28)

Due to the fact that every atom has its own multiple resonant modes, the equation for $P(\omega)$ can be rewritten in the following way [62]

$$P(\omega) = \frac{Ne^2}{m} \sum_{i} \frac{\beta_i E(\omega)}{\omega_p^2 + i\Gamma\omega + \omega^2}, \qquad (1.2.1.1.29)$$

where β_i is the strength of oscillator with the quantum meaning of transition strength. The summation is going through all the modes of an atom with its characteristic parameters such as resonant frequency and damping value. By employing only single normal mode which reflects the processes of absorption and refraction in a material, we obtain

$$\boldsymbol{P}(\boldsymbol{\omega}) = \boldsymbol{\varepsilon}_0 \boldsymbol{\varkappa} \mathbf{E} , \qquad (1.2.1.1.30)$$

$$\varkappa = \varepsilon(\omega) - 1, \qquad (1.2.1.1.31)$$

$$\varepsilon(\omega) = n^2(\omega), \qquad (1.2.1.1.32)$$

$$\varepsilon(\omega) = 1 + \frac{Ne^2}{m} \frac{1}{\omega_p^2 + i\Gamma\omega + \omega^2}, \qquad (1.2.1.1.33)$$

where n and \varkappa is the optical density and dielectric susceptibility of the medium.

The formula (1.2.1.1.33) is Lorentz form of frequency dependent dielectric permittivity.
1.2.2. Metamaterials

Metamaterials are artificially fabricated, spatially and compositionally (periodically or non-periodically) constructed materials [10, 64]. Their optical properties are determined by not only physical properties of its composition elements, but also by its periodic and geometrical architecture. The artificially created periodic and geometric structure of metamaterials shapes and modifies effective dielectric and magnetic permeability of the metamaterials in ways that are not found in nature (Fig.1.2.2.1.).



Fig.1.2.2.1.Metamaterial crystal. (a) view at fishnet metamaterial consisting of seven layers of which four layers are metals and three layers are dielectrics. (b) SEM image of a fishnet metamaterial. (c), (d) fabricated metamaterial with higher resolution (picture adapted from ref. [65])

Unlike conventional materials, the building blocks of metamaterials are not atoms and molecules but periodically created inclusions which act as scatters or electromagnetic field resonators. The size, distance and relative arrangements of inclusions should be less or comparable with the wavelength of electromagnetic waves so that an array of such inclusions will be "treated" by the incoming electromagnetic waves as continuous environment with the specific values of effective dielectric permittivity and effective magnetic permeability. Modifying the shape, size and relative arrangements of metamaterial inclusions it is possible to dynamically change or modify the optical properties of metamaterials in a controllable and desirable way.

In recent years much attention has been devoted to the so-called left-handed metamaterials (LHM) [66], materials that simultaneously poses negative value of dielectric permittivity and magnetic permeability. The existence of such materials was first proposed theoretically by V.G.Veselago [67] who showed that physics of LHM can be very promising, fruitful and extremely unusual. For instance, for LHM attributable to have negative index of refraction, backward wave propagation, negative phase velocity, backward Cherenkov effect and reversed Doppler effect (the frequency shift of light being radiated by moving objects experience not red shift but blue shift) [68-70], etc. Despite promising such incredible effects, experimental LHM have their own drawbacks consisting in high losses of radiation and narrow working bandwidth. These drawbacks significantly limit the application of LHM in optical devices and make scientists to search for alternative metamaterials. Photonic crystals, the branch of composite metamaterials, emerged as a promising alternative.

Photonic crystals [71] are man-made materials in which, thanks to the specific spatial periodic change of refractive index, the properties of electromagnetic field propagation become similar to the propagation of electrons in the crystal lattice. Multiple interference of electromagnetic waves being diffracted by each unit cell of the photonic crystal leads to formation of optical bands for which it is not possible for light to propagate inside a photonic crystal, which is referred to as a photonic band gap. At those frequencies, the electromagnetic irradiation experience, for example, ideal reflection whereas at other frequencies light can easily pass thought the photonic crystal. Photonic crystal emphasizes an analogy between electron and photon. The presence of photonic band gaps in photonics crystals leads to the situation in which the density of states of photons equals to zero at specific frequency. The existence of

photonic band gap means that within specific frequency or wavelength range the electromagnetic waves cannot propagate in the photonic crystal in any direction. Similarly to the ordinary crystals, the photonic crystals can be produced from conductors, semiconductors, dielectrics and superconductors [72-78].

The photonic band gap phenomenon presents both practical and theoretical importance. It can be used for solving wide range of physical problems connected to the light localization and emission. Moreover, photonic crystals with the photonic band gaps allow scientists to create laser with microresonators, highly efficient waveguides and highly operated optical switches. Notwithstanding, photonic crystals which do not possess photonic band gap still have variety of interesting physical features connected with optical anisotropy, light dispersion and polarization effects attributable to the particular photonic crystals. Those physical effects of photonic crystal give the possibility to create optical polarizes and optical filters.

Overall, the photonic crystals can be classified into three groups: 1D, 2D and 3D photonic crystals. The one-dimensional photonic crystals can be represented as the periodic arrangement of either metal-dielectric or purely multilayered dielectric films with specially selected refractive indices. The one-dimensional photonic crystals are widely used as dielectric mirrors or antireflection coatings. Two-dimensional photonic crystals consist of parallel cylindrical rods being grown in a transparent substance medium. The application of such 2D photonic crystals can be found in fabrication of waveguides channels like planar waveguides or optical fibers. In this case, the optical waveguide being formed from longitudinal bars thereby creating periodicity in the cross section of fiber.

Three-dimensional photonic crystals have wide range of designs [71]. However, they usually can be fabricated in shape of combination of colloidal spheres creating the periodicity in all three dimensions. The key feature of 3D photonic crystals is the presence of full photonic band gaps which means no allowance of electromagnetic waves propagation in any directions within the photonic crystal for the specific range of frequencies. This, in turn makes it possible to create optical devices which will be able to reflect light with specific frequency at any arbitrary angle of incident light.



Fig.1.2.2.2.Representation of photonic crystals design. (a) 1-D photonic crystal in which the complex refractive index of material is periodically altered only in one direction, while in other two directions complex refractive index remains uniform and homogeneous. (b) 2-D photonic crystal represent the case when material's complex refractive index is changed along two directions simultaneously whereas in third direction it remains native. (c) in 3-D photonic crystal complex refractive index is varied in all three directions (picture adapted from ref. [71])

In addition, metamaterials can have more interesting characteristics even beyond the scope presented by Fig. 1.2.2.2. Depending on the needs, metamaterials can be designed and fabricated to be either weakly or highly anisotropic, to be highly reflective, transparent or absorptive in wide range of the wavelengths.

1.2.3. Surface plasmon-polaritons and localized surface plasmons

Plasmons are quantized collective electron oscillations in a metal [16]. Once coupled with external electromagnetic radiation it could create electromagnetic waves propagating along the interface between dielectric and metal which is called surface plasmon-polaritons (SPP). Surface plasmon polaritons at metal interfaces can be excited by incident light with careful choice of light polarization and geometry of the metal surface (for example holes, grooves, squares and etc.). Let us assume that an electromagnetic wave falls onto a metal plane aligned to the x-z plane (Fig.1.2.3.1.). Due to the boundary between a dielectric with z > 0 and metal with z<0 we have to distinguish two types of electromagnetic waves occurring at the interface of both mediums [62]. When vector of magnetic field H of the light wave is normal to the plane of light incidence, the electromagnetic wave is called TM wave (transverse magnetic waves). It has electromagnetic field's components as E_x , E_z , H_y . When vector of electric field E is oriented normally to the plane of light incidence we describe this situation as TE wave (transverse electric waves) with field component taking E_y , H_z , H_x components [62].



(b)



Fig.1.2.3.1.Schematic representation of the TE (a) and TM (b) polarized electromagnetic waves incident onto arbitrary planar surface substrate. H_z , E_y , H_x (a) and E_z , H_y , E_x (b) is electric and magnetic field vector projections onto the axis x, y, z (pictures adapted from ref.[62]

The interaction of an electromagnetic wave with both mediums can be described with

the help of Maxwell equations [62]

$$\nabla * \boldsymbol{D} = \boldsymbol{\rho} , \qquad (1.2.3.1)$$

$$\nabla * \boldsymbol{B} = 0 , \qquad (1.2.3.2)$$

$$\nabla \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t},\tag{1.2.3.3}$$

$$\nabla \times \boldsymbol{H} = \boldsymbol{J} + \frac{\partial \boldsymbol{D}}{\partial t}, \qquad (1.2.3.4)$$

If we consider linear, non-magnetic and isotropic media one can write additional material equations

$$\boldsymbol{D} = \varepsilon \varepsilon_0 \boldsymbol{E} , \qquad (1.2.3.5)$$

$$\boldsymbol{B} = \boldsymbol{\mu}_0 \boldsymbol{H} , \qquad (1.2.3.6)$$

We assume also that changes of electric and magnetic field with time can be presented as

$$\boldsymbol{E}(\boldsymbol{r},t) = E_0(\boldsymbol{r})\exp(\boldsymbol{k}\boldsymbol{r} - \omega t), \qquad (1.2.3.7)$$

$$\boldsymbol{H}(\boldsymbol{r},t) = H_0(\boldsymbol{r})\exp(\boldsymbol{k}\boldsymbol{r} - \omega t), \qquad (1.2.3.8)$$

Applying curl operator to the equation, we obtain the system of differential equations for TM polarized waves as

$$\frac{\partial H_y}{\partial z} = \mathrm{i}\omega\varepsilon\varepsilon_0 E_x\,,\tag{1.2.3.9}$$

$$\frac{\partial E_x}{\partial z} - \frac{\partial E_z}{\partial x} = i\omega\mu_0 H_y , \qquad (1.2.3.10)$$

$$\frac{\partial H_y}{\partial x} = -i\omega\varepsilon\varepsilon_0 E_z , \qquad (1.2.3.11)$$

It should be mentioned that wave vector k in the air and metal is different due to the fact that during its propagation through the medium it gains impulse proportional to the refractive index of the medium. Hence, for any medium, the wave vector can be written

$$k_d(\omega) = k_o n(\omega) , \qquad (1.2.3.12)$$

where *n* is refractive index and it can be expressed as $n(\omega) = \sqrt{\varepsilon(\omega)}$ [14, 59, 79].

Since the incident wave vector \boldsymbol{k} is lying in the *x*-*z* plane hence:

$$\boldsymbol{k}_{i}^{2} = k_{x}^{2} + k_{z}^{2} = \varepsilon_{d} k_{0}^{2} , \qquad (1.2.3.13)$$

$$k_i^2 = k_x^2 + k_z^2 = \varepsilon_d k_0^2 , \qquad (1.2.3.14)$$

Using the above mentioned equations one may obtain the solution for H_y component and thereafter with the help of it find other components E_x , E_z of electromagnetic field at both interfaces (Fig.1.2.3.2.). Hence we have

$$H_{y}^{d}(x,z) = H_{y0}^{d} \exp(i(k_{x}x + k_{z}z) - \omega t), \qquad (1.2.3.15)$$

$$E_x^d = \frac{k_z^d}{\omega \varepsilon \varepsilon_d} H_y^d(x, z) , \qquad (1.2.3.16)$$

$$E_z^d = -\frac{k_x^d}{\omega\varepsilon\varepsilon_d} H_y^d(x, z) , \qquad (1.2.3.17)$$

From the metal side of interface we obtain

$$E_x^m = \frac{k_z^m}{\omega \varepsilon \varepsilon_m} H_y^m(x, z) , \qquad (1.2.3.18)$$

$$E_z^m = -\frac{k_x^m}{\omega\varepsilon\varepsilon_m} H_y^m(x,z) , \qquad (1.2.3.19)$$



Fig.1.2.3.2.Surface plasmon-polariton waves at planar interface between metal and dielectric. (a) SPP waves propagation along metal and dielectric interface. (b) corresponding evanescent electromagnetic field in metal and dielectric (pictures adapted from ref. [80])

The boundary conditions at the interface with z = 0 can be written as [62]

$$E_x^d(x,0) = E_x^m(x,0), \qquad (1.2.3.20)$$

$$\varepsilon_d E_z^d(x,0) = \varepsilon_m E_z^m(x,0), \qquad (1.2.3.21)$$

$$\varepsilon_d E_z^d(x,0) = \varepsilon_m E_z^m(x,0), \qquad (1.2.3.22)$$

Hence we have

$$k_x^d = k_x^m = k_x \,, \tag{1.2.3.23}$$

$$\frac{k_z^d}{\varepsilon_d} = \frac{k_z^m}{\varepsilon_m},\tag{1.2.3.24}$$

This yields

$$\frac{(k_z^m)^2}{(k_z^d)^2} = \frac{\varepsilon_m k_0^2 - (k_z^m)^2}{\varepsilon_d k_0^2 - (k_x^d)^2},$$
(1.2.3.25)

And

$$k_x = k_0 \sqrt{\frac{\varepsilon_d \,\varepsilon_m}{\varepsilon_d + \varepsilon_m}},\tag{1.2.3.26}$$

$$k_x = \frac{\omega}{c} \sqrt{\frac{\varepsilon_d \,\varepsilon_m}{\varepsilon_d + \varepsilon_m}},\tag{1.2.3.27}$$

The derived expression (1.2.3.27) is called the dispersion relation for surface plasmon polaritons [16].



Fig.1.2.3.3.Dispersion relation of surface plasmon-polaritons with respect to the light photons in vacuum and dielectric. The dispersion relation of SPP attributes to the case of the plane interface between metal and dielectric (picture adapted from ref. [14])

For SPP excitation it is necessary to fulfill both energy and momentum conservation. As can be seen from Fig.1.2.3.3 the dispersion relation curves for free light photons and SPP do not cross each other except at the point where $\omega = 0$, k = 0. Thus it can be deduced that photon's momentum of light is not enough to satisfy the momentum conservation and as a consequence to excite surface plasmons. In order to overcome this obstacle the momentum and energy transfer should be fulfilled. This can be done by several techniques which will be described in the following section.

1.2.4. Methods of light coupling for generation of surface plasmonpolariton waves and localized surface plasmons

Excitations of surface plasmon polaritons by direct incident light at the interface between dielectric-metal are not possible as their wave momentums do not match (Fig.1.2.4.1.). Hence, some methods should be employed in order to overcome this problem. In this chapter several techniques will be described which were designed to achieve surface plasmons excitation.

Prism coupling: This method is based on the principle of total internal reflection and corresponds to the SPP coupling to evanescent electromagnetic waves formed as a result of total internal reflection of light in the optically dense substrate.

(a)

(b)



Fig.1.2.4.1.Configurations for surface plasmon-polariton waves excitation at planar interfaces. (a) Kretschmann prism configuration. (b) Otto prism configuration for excitation of SPP. Designation M corresponds to metal layer, designation L corresponds to Light source and designation D corresponds to Detector (picture adapted from ref. [14])

According to Trubadar-Kretschmann-Raether prism configuration, the metal is supposed to be evaporated onto the top of glass prism [16]. Once it is done, the metal 45

substrate is illuminated by polarized light through the optically dense prism at the angle of incidence being greater than total internal reflection of light in the prism. As a result of this process, the wave vector of light passing through the prism will gain some additional momentum. By varying angle of light incidence one may reach the condition when at the specific angle θ in plane component of photon wave vector in the prism will be equal to the wave vector of surface plasmons in the air. At those circumstances the resonant tunneling of electromagnetic waves through the metal substrate takes place leading to the light coupling with the electrons oscillation in the metal.

During the resonance conditions, the minimum of light reflectivity is observed as a function of wavelength or incident angle (with almost 100% of incident light energy being converted into the formation of surface plasmon-polariton waves). The observed resonant curve (as a function of either wavelength or incident angle) is referred to as surface plasmon resonance (SPR). Furthermore, the thickness of the deposited metal layer will be of the key criteria in SPP formation as it significantly influences on the tunneling process of the incoming light.

Thus, in order to excite SPP at the metal interface at different wavelengths or angles, an additional layer of dielectric with smaller refractive index compared to the optically dense prism could be used. This second dielectric layer should be deposited on top of the metal. Consequently, the tunneling of electromagnetic wave through the additional layer of dielectric will contribute to the resonance conditions of SPP. Hence SPP modes can be easily excited at any angles of light incidence.

In case of thick or bulk metals most preferable configuration for SPP excitation is Otto scheme. In Otto configuration, the prism is placed at some small distance from the metal interface and electromagnetic wave tunnels through the air gap between the prism and metal interface. By adjusting the air gap distance as well as angle of light illumination one may obtain the resonance condition for the SPP formation.

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Grating coupling: Another way for meeting the condition of momentum conservation between the incoming photons and surface plasmon-polariton waves is by employing diffraction grating patterned on the surface of metal (Fig. 1.2.4.3). As in the case of prism coupling, SPP excitation results in the minimum of light reflectivity in the SPR curve.



Fig.1.2.4.2.Grating mechanism for coupling wave vector of incident photons with SPP. The SPP excitations are performed by the use of metal grating embedded into dielectric substrate with the *a* being the period of metal grating, **k** is wave vector of inclined photons and $k_{||}$ is photon's wave vector component parallel to dielectric interface (picture adapted from ref. [16])

In case of one-dimensional grating with a given lattice constant, the matching condition

for SPP excitation can be expressed according to the [16] as

$$k_x = k_0 \sin\theta_0 + nG, \qquad (1.2.4.1.)$$

where $G = \frac{2\pi}{a}$ is the reciprocal vector of the grating with the n = 1,2,3...

1.3. Graphene active plasmonics and optoelectronics

1.3.1. Graphene-based optoelectronic modulators

Technology advancement in nanoscience has resulted in the possibility of developing structures with tunable optical and electro-optical properties, the dimensions of which is in nanometer scale. By using these structures it is possible to implement control over the optical radiation and electro-optical characteristics at dimensional scale smaller than free space wavelength of light. The control of efficiency is determined by material spatial arrangement, nanostructuring or chemical composition of materials. The interest in these material spatial arrangements and nanostructuring is stirred up by promising applications of nanostructured materials in optoelectronics which include signals processing, integrated optical devices as well as devices with high bioselectivity to chemical groups and biological organisms.

Plasmonics is the rapidly expanding branch of photonics which opens up new possibilities for electronic and photonic device implementation including optoelectronic circuits and biochemical sensing. The surface plasmon polaritons waves (SPP) are the key subject of plasmonics and they are the collective oscillation of electromagnetic wave with metal's or semiconductor's electron conductivity. To excite SPP waves by an optical radiation resource it is necessary to fulfill phase matching conditions. When SPP wave is excited electromagnetic energy is localized at dimensions smaller than the wavelength of incident radiation which leads to efficient interaction of photons and electrons. The most practical and important application of plasmonics is the ability to tune and control the optical characteristics of plasmonic structures, namely their coefficient of reflection and transmission. To control such characteristics the external electric, thermal and mechanical fields can be used. The dependence of optical properties of plasmonic structures upon the influence of external fields can be used as resource in different kind of sensors and electro-optical devices.

The major interest of plasmonic research lies in structures having some spatial periodicity or structuring medium which is composed of metals and dielectrics combinations. If specific conditions have been met at the interface of metal and dielectric, the appearance and propagation of SPP waves is possible. In the case where an electromagnetic wave propagates along a conductor surface there is its interaction with conduction electrons the properties of which are similar to plasma ones. Consequently, there is collective excitation of electromagnetic wave with electron plasma of a metal. The quantum of energy of this kind of interaction is called plasmonpolaritons waves. The excitation of plasmon-polariton waves in metal-dielectric heterostructures is normally revealed by heterostructure's optical response.

Modulation is a change in the parameters of optical signals in accordance with the changes of input (modulated) signal. There are various types of light modulation relevant to this work. In the case of direct modulation, e.g. mirrors, the modulation signal governs the direction of light propagation. Consequently, the light intensity can change in accordance with changes of modulation signal. More practical is external modulation, where modulation changes the optical properties of materials from which an optical device is made. For example, refractive index of some material could depend on electric, magnetic or acoustic fields. The modulation of light in this case is performed by changing the parameters of electric, magnetic or acoustic fields. If we consider the optical signal as electromagnetic oscillation, then the electric field intensity E(t) can be presented in the form of harmonic function as

$$E(t) = E_m \cos(\omega t + \varphi), \qquad (1.3.1.1)$$

where E_m is amplitude of the intensity of electric field, ω is angular frequency and φ is phase of electric field.

The modulation signal can change any of the above mentioned parameters of electromagnetic field. Thus one may perform amplitude, phase or frequency modulation of propagating electromagnetic wave. Moreover, the input signal can modify and control the intensity of optical oscillation as well as its polarization state. Despite having this entire plethora of optical modulation capabilities [81-85], the widely used technique is optical intensity modulation. External modulation of optical signals is usually performed with the help of electro-optical, magneto-optical and acousto-optical modulators [86]. Optical properties of any arbitrary media such as refractive index and

state of light polarization depends on the charges distribution in the medium. Under the influence of externally applied electrical fields it can be changed, which leads to the change of refractive index and hence state of light polarization. For a medium which does not possess center of symmetry, such variation of refractive index under the influence of external electric field appears in the form of linear electro-optical Pockel's effect [85]. For a medium which possess the central crystal symmetry the electro-optical effect is proportional to the square of applied external electric field intensity. This is socalled electro-optical Kerr effect [85] which is often used for amplitude modulation of optical signals. Kerr-based amplitude electro-optical modulation uses the appearance of optical anisotropy under the influence of external electric field in originally isotropic medium. In order to utilize Kerr effect, the transparent dielectric material should be mounted between plates of plane capacitor to which the electric voltage U should be applied which in turn should create strong electrical field E in the modulated medium. The Kerr unit is placed between the cross polarizer and analyzer so that the intensity of light equals to zero whereas, when U > 0 V, the modulated media acts as a birefringent crystal with optical path parallel to the direction of the external electric field E. If the light wave is passed thought the Kerr unit it is decomposed into two linear polarized components. One component is polarized so that the orientation of its electrical vector is perpendicular to the external field (so-called normal wave) while in other component the orientation of electric field is parallel to the external field, so-called extraordinary wave.

Due to the fact that ordinary and extraordinary waves have difference refractive indexes n_0 and n_e , the light will propagate with different speeds in such crystal. Having passed Kerr unit, light will be elliptically polarized and then would pass thought the analyzer.

$$\Delta n = n_e - n_0 = \alpha E^2 , \qquad (1.3.1.2)$$

The phase difference between ordinary and extraordinary waves after passing though optical path l in the modulated media can be expressed as follows

$$\varphi = \frac{2\pi\Delta nl}{\lambda} = \frac{2\pi\alpha E^2 l}{\lambda} = 2\pi E^2 lB , \qquad (1.3.1.3)$$

where $B = \frac{\alpha}{\lambda}$ is Kerr constant, *l* is optical path in the modulated media, λ is electromagnetic wavelength.

The quadratic Kerr effect comes from optical anisotropy of molecules placed in strong electric or magnetic fields. In the absence of an external electric field anisotropic molecules are oriented randomly and the substance is generally isotropic. If molecules have their own electric dipole moment then by the influence of external electric field induces those dipoles to orientate and the media itself become anisotropic macroscopically.

The Pockels based effects are usually employed for phase modulation of optical carrier. Pockels effect consists of linear refractive index change of non-symmetric crystals which are under the influence of external electric field. The refractive index dependence upon the external electric field is expressed as

$$n = n_0 + \frac{1}{2}n_0^3 rE , \qquad (1.3.1.4)$$

where n_0 is the value of refractive index of non-symmetric crystal in the absence of applied external electric field, r is electro-optical coefficient which depends on polarization state of light, E is intensity of electric field.

If the light is redirected and passed through such non-symmetric crystal which is exposed to the external electric field, then the phase shift of light beam takes place

$$\varphi = \frac{2\pi nl}{\lambda} = \varphi_0 + \frac{n_0^3 \pi r E l}{\lambda}, \qquad (1.3.1.5)$$

where λ is light wavelength in vacuum, φ_0 is initial light phase shift acquired due to the light passing thought the crystal in the absence of the external electric field applied to non-symmetric crystal.

The second part of the equation (1.3.1.5) corresponds to the phase shift due to the electrical field applied externally. This second part is responsible for light phase modulation of optical signal. It should be noted that Pockels linear effect has very small inertness which allows changing phase of optical signal. The electric field can be applied to the non-symmetric crystal either in the direction of light propagation, so-called longitudinal effect, or in the perpendicular direction, so-called transverse effect. There are well established non-symmetric crystals which are being used for light phase modulation. Among them are: LiNbO₃, LiTaO₃, NH₄H₂PO₄, KH₂PO₄ and KD₂PO₄.

To another branch of electro-optical modulators can be related to interferometric optical modulators such as Mach-Zehnder [87] and Fabry-Perot optical modulators [88]. Both of them are based on the multiple beam interference phenomena. As far as Mach-Zehnder optical modulator is concerned, the active material which is used in such electro-optical modulators is LiNbO₃. On the surface of LiNbO₃ crystal with the help of titanium diffusion method scientists create the required light guiding configuration, for instance optical fiber, and between those configurations the electrical electrodes are created. Having done so and by further applying the electrical voltage between those electrodes it is possible to dynamically change the speed with which the light will be propagating through those optical fibers.



Fig.1.3.1.1.Schematic view of electro-optical modulator based on Mach- Zehnder interferometer. Mach-Zehnder interferometer is constructed as two-arm interferometer embedded into LiNbO₃ substrate. The two-arms are connected by Y-shape junctions. The coherent light beam is directed into the input rib waveguide 1 which is splitted there into two coherent light beams by junction Y_1 . The coherent light rays then propagate through the arms 2 and 3 of Mach-Zehnder interferometer. By applying voltage between electrodes 4 and 5 or 5 and 6, situated in one of the two-arms of Mach-Zehnder interferometer based modulator, the refractive index of the material is changed resulting to phase shift between these coherent light waves. At junctions Y_2 these phase shifted coherent electromagnetic waves are combined again and interfere. The outcome light beam is collected by output rib waveguide 7. If the phase difference between coherent light beams is zero these waves interfere destructively, while if the phase difference equals to 180° coherent light waves interfere destructively. Hence, the amplitude of light modulation is achieved by varying the value of applied voltage between electrodes 4 and 5 or 5 and 6 (picture adapted from ref. [86])

The Y-shaped configuration acts as beam splitting elements and if the light waves came to the end of part of Mach–Zehnder interferometer in phase then they interfere constructively otherwise, if they came in antiphase, then those waves cannot propagate through optical fiber and it is radiated into the substrate.

As far as Fabry-Perot optical modulator is concerned, its work principle is as follows: the beam of light is directed to the structure consisting of at least two fixed flat mirrors, usually metals, between which the dielectric spacer is positioned. The light beams reflect multiple times from those mirrors and interfere with each other. As a result, there is appearance of whole spectrum range of discrete light frequencies being called standing waves or longitudinal modes of Fabry-Perot cavities. Only longitudinal modes sustain in the resonator cavity while all others are suppressed by interference conditions. Intensity of transmitted or reflected light can be modulated by applying the voltage between the two mirrors of Fabry-Perot interferometer.

1.4. Hafnium dioxide high-k gate dielectric

Among the family of high-k dielectrics, hafnium dioxide (HfO₂) has attracted significant attention compared to other dielectrics due to its high melting temperature, mechanical stability, wide transparency optical window, ease and control of fabrication as well as CMOS compatibility [89-91]. The value of the dielectric permittivity as well as the dielectric band gap are key criteria for dielectric application required by the electronic or optoelectronic industry. As an example, high value of dielectric permittivity is paramount for fabrication of capacitors whereas for transistors the value of the band gap is the key criterion as the lower band gap means the lower energy barrier for electron transition from valence to conduction band. However to find dielectric which can combine the above mentioned characteristics is quite challenging. Stoichiometric HfO₂ meets these benchmarks and represents good high-k dielectric with low leakage currents. Thanks to the availability of stoichiometric HfO₂ with wide band gap, high dielectric constant and small leakage current, HfO2 is considered as the main substitute for SiO₂ [92]. In addition, it poses lower thermal conductivity $(2.5 \frac{W}{m^2 K})$ [93] compared to others high-k dielectrics in combination with its high mechanical strength enables HfO₂ to be utilized for the manufacture of thermocouples and the protective shells of nuclear reactors. Due to wide transparency window spanning from visible to near-infrared wavelength range HfO_2 being used in optical coating layers and devices. As far as non-stoichiometric HfO₂ is concerned, it finds application in Random Access Memory Devices as viable reservoir of oxygen ions and vacancies. To summarize, HfO₂ is high temperature refractory material that poses distinctive physical and chemical properties and this ensures its application to a wide range of industrial applications. Nevertheless, depending on the growing condition of the dielectric it can end up as being non-stoichiometric, having amorphous structure or defects in crystal lattice the presence of which may lead to the appearance of additional energy levels between valence and conduction band of dielectric. As a consequence this leads to the increase of electric conductivity of dielectric.

It is known that perfect crystal, in which all atoms should be in positions with minimal energy, virtually does not exist. Deviations from the ideal crystal lattice are due to the defects presence which can be point defects (interstitial atoms, vacancies and impurities), linear defects (dislocation, chains of vacancies and interstitial atoms), surface defects (grain and crystal boundaries), volume defects or macroscopic disorders (pores, cracks or inclusions) and can be produced either due to fabrication process or during thermal fluctuations. The presence of defects in the crystalline lattice of HfO₂ impacts strongly on dielectric's conductivity which will be discussed in Chapter 4.

1.5. Resistance Random Access Memory

The novelty of dissertation is related to the possibility of applying resistance switching effects to the new generation of non-volatile memory devices. It is well established that Flash-memory is the prevailing mechanism of non-volatile memory which has good potential of integration but relatively low write speed and limited number of rewrite cycles. Therefore, these days there is active research in the direction of finding an alternative approach for the creation of elements for non-volatile memory, which has large number of rewrite cycles, high speed of recording and reading information, as well as the possibility of downscaling which can be less than 20 nm. Apart from that, the major issue for the device operation is the problem with energy consumption since without its reduction it is difficult to imagine progress in computational capabilities of modern electronic devices. One of the most promising areas for creation of next generation of non-volatile memory is considered to be resistive random access memory (RRAM).

Data storage in the resistance memory cells is implemented by changing the resistance state of metal-insulator-metal heterostructure (MIM) while applying the potential difference between the electrodes. For this reason we have the term 'memristor' [94], which is memory resistor whose resistance depends on the amount of charge passed through it. In this case, information is stored at the level of electro-physical properties of the material rather than electric charge, which undoubtedly contributes to stability of element, enhances recording density, data rate and decreases consumption power.

Furthermore, it is considered that memristors scaling as well as switching speed corresponds to current needs of modern non-volatile memory. Last but not least, low power consumption during the data writing cycles, the ability of memristors to be in multiple states suggests that memristors can be used in artificial computer systems with new technology of data storage, processing and its transmission. The first studies of resistance switching processes date back to 1960. However this technology gained worldwide interest only after research carried out by the Hewlett-Packard company led by R. Stanley Williams [95]. His group was the first to implement experimentally the solid based structure having memristor properties [95]. Since then a wide variety of thin film materials have been investigated. Moreover, the knowledge of the whole physical and chemical mechanism is still under debate. This motivates interest in the research of possible mechanisms responsible for switching and memory effects in the MIM heterostructures.

The aim of this chapter is to study the mechanism of memory and switching as well as electro-ionic transport in thin films of MIM heterostructures based on HfO_2 thin dielectric film fabricated by the electron-beam evaporation method. In the last decade, the high-k dielectric materials have been investigated extensively due to broad prospects of their practical application in microelectronics. Application of high- κ dielectrics in logic elements instead of SiO₂ allows solving number of problems associated with

further increase in data capacity and operation speed of silicon microelectronics elements. Apart from that many high-k dielectrics are used as active elements of non-volatile memory of the next generation devices.

The high-k dielectrics are used as gate dielectrics in metal-insulator-semiconductor (MIS) structures instead of traditional silicon dioxide dielectric. This solves the problem in the increase of tunneling leakage currents as topological dimensions of MIS transistors are further decreased. The high leakage currents lead to additional power dissipation (heating). Replacement SiO₂ by high-k dielectric can increase the thickness of the gate dielectric while maintaining electrical capacity of MIS structure. One of the prospective candidates for the role of gate dielectric is HfO₂ due to its incredible physical and chemical properties. Secondly, other application of high-k dielectrics associated with their use in electro-optical modulators and as a storage medium of resistive random access memory cell (RRAM) [96]. The RRAM element is composed of simple metal-insulator-metal (MIM) structure.

RRAM principle of operation is based on the reversible switching of dielectric properties from high to low resistance state by the influence of current pulse. This type of memory combines the advantages of a traditional flash-memory, namely volatility, high speed of reading/writing, possibility of large number of write cycles, radiation resistance and the possibility of three dimensional integration. The practical use of high- κ metal oxides in devices of microelectronics is faced with several difficulties. The main difficulty is an uncontrollable and unacceptable high electrical conductivity. The high conductivity of real dielectric layers is caused by high concentration of native defects such as Schottky and Frenkel defects, interstitial and substitution atoms [97].

The defects in high-k dielectrics namely in HfO₂, TiO₂ etc. play crucial role in device operation [98]. Defects can create localized states in dielectric's band gap, which can significantly influence its transport and optical properties. The trapping of charge

carriers on defects leads to MIS transistor's instability of threshold voltage, degradation and low device reliability. However, in the case of flash and resistive memory cell, the defects in insulators play a key role. For resistive memory cell, the state with low dielectric resistance corresponds either to a state with high defect concentrations or specific spatial arrangement of mutual defects. Presently, the most discussed model of the resistive memory effect is focused on the formation/dissociation of conductive filament in a dielectric. It is considered that the most probable defects in HfO₂, TiO₂ etc. are oxygen vacancies [99-101]. The oxygen vacancies can act as trap centers for charges and are responsible for the high dielectrics electrical conductivity. Most importantly, as far as RRAM devices are concerned, the oxygen vacancies play crucial part for the RRAM device operation. It is assumed that the conductive filament is formed by the influence of current pulse due to release and migration of oxygen atoms from the lattice sites in a region of the dielectric film.

We should expect that in real metal oxide high-k dielectrics such as HfO_2 , TiO_2 etc. especially in oxygen depleted non-stoichiometric layers alongside with oxygen vacancies there are complexes of several closely packed spaced oxygen vacancies. Available data suggest that these complexes play a key role in the mechanism of switching of resistive memory cells based on HfO_2 , TiO_2 [96, 102, 103].

The era of the memristor was launched thanks to Leon Chua who first postulated theoretically its existence in his famous work [94]. However, the global interest in research of memory resistors arose after experimental observation and Leon Chua's theory validation led by R. Stanley Williams research group at Hewlett-Packard company [95]. In their article they stated that the group was able to produce the memory cell based on thin layer of TiO₂ having the effect of resistance switch and showing current voltage characteristic that is attributed to the Memristor. The Fig. 1.5 depicts the typical current-voltage characteristics attributable for memristor.



Fig.1.5.Representation of memristor configuration and its current-voltage characteristics. (a) memristor is comprised of bottom and top electrodes between which the metal oxide insulator is sandwiched.(b) current-voltage curves representing the metal oxide resistance switching under applied gate voltages (picture adapted from ref. [104])

In order to explain the resistance switching effect, the group used the model based on oxygen vacancies movement as a result of which the oxygen depleted region of TiO₂ (consequently enriched region with oxygen vacancies) is formed nearby one of the contacts under the influence of applied bias to the structure presented in Fig. 1.5.

Therefore, between two Pt electrodes TiO₂ double layer is formed with one side having a region with oxygen vacancies concentration enrichment. Under the influence of applied electric field the boundary of TiO₂ double layer can be shifted resulting to change of device operation state. Applying bias with the amplitude of only 1V it was possible to change TiO₂ resistance from high to low state. In order to switch the resistance back to its original state (high resistance state) it was necessary to apply the reverse voltage polarity to Pt@TiO₂@Pt structure.

It has been assumed, for more than 40 years, that the effects of memory and switching at MIM heterostructures are the phenomenon of memristors. Those effects being observed in the variety of thin metal oxides films TiO₂, Ta₂O₃, Al₂O₃, HfO₂, ZnO, ZrO₂, SiO₂ etc in combination with different electrodes like Au, Pt, Ti, Ag, Cu etc [105-108]. Those facts motivate further research to understand the possible mechanism responsible for the memory and switching effects in MIM heterostructures.

1.6. Experimental equipment used for research

1.6.1. Spectroscopic ellipsometry

Spectroscopic ellipsometry [109] is a powerful non-destructive tool for extraction of optical constants (refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$) of thin films and heterostructures. In its origin, the ellipsometry is based on the analysis of changes of light polarization due to the reflection by thin films and can yield information about its thickness ranging from several angstroms, tenth or hundreds of nanometers or few micrometers with high accuracy. Most importantly, this technique is so sensitive to the condition of a surface that it can provide glimpse into its inhomogenety, roughness or flatness.

After interaction of linearly polarized light with substrate the parameters of electromagnetic wave undergo some changes due to the wave reflection from the substrate and linearly polarized light becomes generally elliptically polarized. This can be explained by the fact that electromagnetic oscillations in the plane of light incidence (*p*-polarization) and normally to it (*s*-polarization), presented in Fig. 1.6.1.1., change the amplitude *E* and phase Ω of the incident electric field differently upon the reflection from the sample. Parameters *E* and Ω are characterized by complex amplitude for *p* and *s* type of light polarization for the incident and reflected waves.



Fig.1.6.1.1.Scheme of spectroscopic ellipsometry for investigation of sample's optical constants and thickness. The incident linearly polarized light experiencing multiple reflections from the investigated sample becomes elliptically polarized (picture adapted from ref. [110, 111])

The complex reflection coefficients for s and p type of light polarization can be calculated as

$$\widetilde{E_{\iota p}} = E_p \mathrm{e}^{\mathrm{i}\,\Omega}\,,\tag{1.6.1.1}$$

$$\widetilde{E_{\iota s}} = E_s \mathrm{e}^{\mathrm{i}\,\Omega}\,,\qquad(1.6.1.2)$$

$$\widetilde{E_{rp}} = E_p' \mathrm{e}^{\mathrm{i}\,\Omega}\,,\tag{1.6.1.3}$$

$$\widetilde{E_{rs}'} = E_s' \mathrm{e}^{\mathrm{i}\,\Omega}\,,\tag{1.6.1.4}$$

$$\tilde{r} = \frac{\widetilde{E_{rs}'}}{\widetilde{E_{rs}'}}$$
(1.6.1.5)

$$\widetilde{E_{ls}} \,,$$
(1.6.1.6)

$$ilde{r}_p = rac{E'_{rp}}{\widehat{E_{\iota p}}}$$
 ,

$$\frac{\tilde{r}_p}{\tilde{r}_s} = \tan \Psi e^{i\Delta} , \qquad (1.6.1.7)$$

where $\tan \Psi$ is attributed to the complex reflection coefficients change while $e^{i\Delta}$ describes phase change of light due to the process of multiple reflection of light from the surface.

The equation (1.6.1.7) is known to be the main equation of ellipsometry since any ellipsometer software program is based on this equation for calculation of Ψ and

 Δ parameters at different wavelength range and angles of light incidence. The complex reflection and transmission coefficients can be found either by employing Fresnel's equations or characteristic matrix methods. The configuration of ordinary ellipsometer is presented on Fig. 1.6.1.2:



Fig.1.6.1.2.Schematic presentation of spectroscopic ellipsometer measurements. The light source generates electromagnetic radiation which is subsequently linearly polarized by Polarizer and incidents onto the Compensator and Sample under study. Having experienced multiple reflections inside the Sample, reflected electromagnetic wave falls onto Compensator, Analyzer and on the Detector where the change of polarization state of the reflected electromagnetic wave is processed

According to the ellipsometer configuration, an ellipsometer consists of a light source, polarizer, compensator, investigated sample, compensator, analyzer and detector. The light beam is generated by light source comes through the polarizer which converts it into linearly polarized light. The polarized light later is directed to the plane of the sample. Having reflected from the substrate surface the phase shift of the light takes place between p and s types of polarization. Then, the compensator makes phase shift between p and s polarizations equal to zero and again converts reflected light into linearly polarized light which can be later eliminated by analyzer. The elimination process is done by photodetector and the value of azimuths of polarizer and analyzer in the case of phase shift elimination are connected with Ψ and Δ values.

There are two main tasks of ellipsometry: direct and indirect. Direct ellipsometry studies the case of planar geometrical interface between two infinite mediums where

there exists an analytical relation between measured ellipsometric parameters and the optical properties of one medium (the second one is supposed to be known). Direct ellipsometry can also calculate Ψ and Δ values for complex planar system consisting of number of thin layers having specific thickness and optical parameters. Coincidence between theoretical calculation for Ψ and Δ parameters with Ψ and Δ values being received experimentally is based on correctly chosen method and accuracy in calculations. However, in most cases the indirect task of ellipsometry is used. According to this task, the optical parameters of an optical structure should be found based on measured Ψ and Δ values with the help of ellipsometer device at different conditions: variable angles of light incidence or wavelength range.

The reflection of linearly polarized light from an ideal (planar, homogenous, not rough) interface was solved a long time ago by taking into account the measured values of Ψ and Δ of a material in the case of different angles of light incidence by employing spectroscopic ellipsometer. Once it was done the optical constants (refractive indexes and extinction coefficients) of different materials were extracted. Nevertheless, even for a well-polished metallic interface, the model of an ideal planar and homogeneous surface cannot work properly every single time due to the presence and influence of surface's roughness. Thus by theoretically calculating ellipsometry parameters one should take into account the conditions of the layers, for example its inhomogenety, roughness, domain sizes, the formation of oxide layers onto the surface of a material. All of these parameters should be taken into account for accurate calculation while modeling.

In the case of bulk films, the measurement of angles of light incidence will be sufficient for determination both the refractive index and coefficient of extinction of a material. Most importantly in the case of substances whose optical constants are already known, the determination of the film's thickness can be easily performed. In practice, optical constants of thin film layers may differ from bulk samples due to the presence and influence of the substrate on which thin films layers were grown. The most complicated situation for ellipsometry is the case of multilayer system with processes of oxidation from one layer into another thus creating more complex structures. Consequently modern ellipsometer software device should have powerful software in order to come up with the solution of finding accurately either optical constants or thickness of bulk multilayer systems. Turning to the next point, interpretation of acquired experimental data begins with choosing the appropriate model from the ellipsometry database for describing film material. Having chosen the model, the programme starts to evaluate the reflectance and transmittance coefficients using Fresnel's equations for investigated multilayer structure, by attributing any material with its own thickness and optical constants. Later on, the evaluating optical constants should be compared with experimental data and a match between the experimental and computed curves should be found. To do so, one should vary the parameters of the material. Succeeding in finding the match between experimental and calculation curves can be done with the help of regression process. The mean squared error (MSE) is used as a criteria for better match between both curves. The best solution corresponds to the minimum of MSE.

1.6.2. Fourier transform infrared spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is a method of optical spectroscopy in which a sample's spectrum is received as a result of Fourier transformation of interferogram of the modulated reflected or transmitted infrared light (IR) beam [112]. The interferogram itself depends on optical path differences of two coherent monochromatic waves and presents itself as Fourier image of the spectrum. The optical scheme of typical Fourier spectrometer is often based on Michelson interferometer in which light generated by source of IR radiation is divided by semitransparent plane-parallel mirror beam-splitter onto two coherent beams. One beam is directed to the fixed flat mirror from which it is reflected back to the beam splitter. The second beam is directed to the movable flat mirror from which it is reflected back and again directed to the beam splitter where both of those two coherent beams are combined and interfere with each other. As a result, depending on the optical path difference of those two beams they interfere constructively or destructively. The mirror performs reciprocating movements and its displacement counts relative to the zero order position in which the optical path difference in the arm of Michelson interferometer equals zero. If the mirror is moved by quarter of IR light wavelength then the light strips in the interferogram are changed by dark ones. The detector registers interferogram of the intensity dependence of output beam flux from optical path difference between both beams. The interferogram itself contains all the information about spectral composition of radiation being produced by the IR source.



Fig.1.6.2.1.The Fourier transform infrared spectrometer scheme. Fourier transform infrared spectrometer consists of: the coherent Infrared Light source, Michelson interferometer, investigated Sample, Detector, Converter and Computer. A coherent electromagnetic beam is generated by the Infrared Light source that propagates thought the sample with the help of Michelson interferometer and then it is collected at the Detector where the coherent electromagnetic wave is amplified, analysed and processed (picture adapted from ref. [113])

By performing alternating movements of the second mirror, the light flux intensity which falls onto the light collector, changes by harmonic law. Let us assume that I(x) is intensity of the light which falls onto the light collector, x is the mirror displacement being measured in cm, $B(\mathbf{k})$ the intensity of light source as a function of wavenumber \mathbf{k} measured in cm^{-1} then one can calculate that the light intensity for coherent monochromatic source changes as

$$I(x) = B(k)\cos(2\pi kx)$$
(1.6.2.1)

As far as the real light sources are concerned, all of them are polychromatic light emitters and as a result of this, on the collector one have signal consisting of sum of cosine waves as

$$I(x) = \int_{-\infty}^{+\infty} B(k) \cos(2\pi kx) \, dk$$
(1.6.2.2)

To obtain the spectrum of source radiation it is necessary to perform Fourier transformation from the expression (1.6.2.2). The received spectrum can be presented in the following form

$$B(k) = \int_{-\infty}^{+\infty} I(x) \cos(2\pi kx) \, dx \tag{1.6.2.3}$$

In the case when in one of the Michelson interferometer's arm the absorptive sample is placed then from polychromatic source radiation there will be deducted some wavenumber range which corresponds to the absorption peaks of the sample.

To obtain the optical spectrum from the sample it is needed to register at the same condition the reference interferogram $B_{ref}(\mathbf{k})$ and interferogram with the investigated sample $B_{sample}(\mathbf{k})$ and by taking the relationship of its Fourier transformation one can obtain the transmission, reflection or absorption spectra from the sample as

$$T(\mathbf{k}) = \frac{B_{sample}(\mathbf{k})}{B_{ref}(\mathbf{k})}$$
(1.6.2.4)

66

 $(1 \land 0 \land 1)$

It should be noted that reference spectrum is the spectrum being measured without sample. Due to this fact, the comparisons spectra have the spectra from heat radiation sources, absorption of atmospheric water vapors, CO_2 and some other substances which can be present in the atmosphere. The kind of the absorption peaks are also registered in the samples spectra. By dividing $B_{sample}(\mathbf{k})$ on $B_{ref}(\mathbf{k})$ one is able to obtain the real absorptive spectrum from the sample itself.

Device Fabrication

Chapter 2

Fabrication of photonic and optoelectronic devices

Chapter 2 deals with required steps for device fabrication which have been done during the PhD programme. Using micromechanical exfoliation method we isolated graphene monolayer flakes and flakes of hexagonal boron nitride (hBN). Thereafter, Raman spectrometer was employed to analyze the excitation peaks of different samples on which graphene flakes were deposited. Thus by evaluating the position, width and intensity of Raman peaks it was possible to determine the quality of the samples in terms of amount of present defects in the investigated samples.

Employing Moorfield electron beam thin film deposition system, wet transfer technique, Laser Writer and Lift-off procedure, the Fabry-Perot interferometric cavity resonator, graphene–based broadband electro-optical modulator and graphene-based Fabry-Perot narrowband electro-optical modulators have been fabricated.

2.1. Methods of graphene and hexagonal boron nitride fabrication

2.1.1. Micromechanical exfoliation

Presently, there are several well developed methods for graphene and other 2D materials production. These are micromechanical exfoliation, chemical vapor deposition, liquid phase and thermal exfoliation as well as epitaxial growth on silicon carbide (SiC) substrate [114-118]. The micromechanical exfoliation method is commonly employed for the production of graphene and h-BN monocrystals especially for research purposes [114]. The main feature of this method lies in usage of graphite and h-BN crystals accompanied by the usage of adhesive tape. By peeling the graphite surface over and over with the adhesive tape it is possible to obtain either graphene multilayer or one single sheet of graphene. Having peeled a graphite surface, the adhesive tape should be further attached to the smooth and ideally cleaned Si@SiO₂ substrate surface, followed by tape detachment either mechanically or by the means of solvent (usually by applying methyl isobutyl ketone (MIBK) and isopropanol (IPA). The pictures of graphene monolayer crystal prepared by this method are presented on Fig. 2.1.1.1. - 2.1.1.3.



Fig.2.1.1.1.Graphene monolayer. (a) optical image of graphene monolayer obtained fabricated by micromechanical method and deposited onto $Si(1000 \text{ nm})@SiO_2(90\text{nm})$ substrate. (b) Raman spectrum of single layer of graphene



Fig.2.1.1.2.Graphene monolayers obtained with the help of micromechanical exfoliation technique and deposited onto $Si(1000nm)@SiO_2(90 nm)$ substrate



Fig.2.1.1.3.Graphene monolayers obtained with the help of micromechanical exfoliation technique and deposited onto $Si(1000nm)@SiO_2(90 nm)$ substrate



Fig.2.1.1.4.Optical images of hBN crystals obtained with the help of micromechanical exfoliation technique and deposited onto $Si(1000nm)@SiO_2(290nm)$ substrate
2.1.2. Chemical vapor deposition

Chemical vapor deposition (CVD) method [119, 120] is ubiquitous technique for graphene mass production since it does not require large scale, expensive equipment and can easily be utilized to grow, in a controllable way, the desirable number of graphene layers with large surface area. In its origin, CVD method is the process of polymer or hydrocarbons decomposition from the gas phase onto metal catalyst substrate by means of the heat.

Copper is the preferred metal for the catalyst substrate as solubility and diffusivity of carbon atoms in copper is lower compared to other substrates. This can be explained by another study where is has been shown that carbon atoms tend to interact weakly with the Cu surface states attributing to weak carbon diffusion through Cu surface. Graphene monolayer growth is triggered by nucleation of the inlet precursors onto Cu wafer mediated by heat and causing the island formation, which depending on precursors time exposure, conglomerates into a large uniform smooth area of mono or multilayered graphene. Typically, Cu wafer is inserted into a quartz furnace followed by adjusting the furnace to the low pressure. Having achieved this, the quartz tube is heated to 1000 °C and followed by methane and hydrogen injection into the tube with the aid of a system of valves and regulators which adjust the speed of chemical precursors into the tube. Once the graphene monolayer formation is achieved the rapid cooling of the Cu foil takes place. Once complete, the Cu foil with growing graphene layer is removed from the furnace and a protective layer of PMMA is deposited on top of it to guarantee its support and protection during subsequent graphene detachment and transfer onto the substrate of interest.

2.1.3. Electron-beam evaporation, Laser Writer and Lift-off techniques

During this project, electron beam evaporation method was heavily employed for deposition of metals and dielectrics. As mentioned previously, Fabry-Perot cavity resonators and graphene-based Fabry-Perot interferometric electro-optical-modulators were made with the help of this technique. To perform deposition we used Moorfield electron gun evaporation system shown in Fig. 2.1.3.1.

Material evaporation was performed by a highly energetic electron beam focused on the area of a material to be evaporated. As a result, high rates of material deposition can be accomplished due to significant heat accumulation within a small region by electron beam focusing. It should be mentioned that the process of material evaporation takes place in high vacuum (around $1 * 10^{-7}$ mbar) chamber with the electron gun being positioned far away from evaporation zone in order to eliminate contaminant accumulation in the main high vacuum evaporating chamber. Meanwhile, the substrate is set at a particular distance from target surface to achieve controllable deposition rate.



Fig.2.1.3.1.Representation of Moorfield electron-beam deposition equipment which has been utilized heavily for evaporation of thin films of metal and metal oxides. High-k dielectric HfO_2 has been deposited onto the substrate of interest by the use of Moorfield electron-beam system

High DC voltage is applied to the heat filament which in turns emits electrons from its surface. Using magnet focusing system those emitted electrons are accelerated and focused toward the surface of materials to be evaporated. Consequently, the material melts, vaporizes and then condenses onto a substrate. In order to make atomic heterostructures, we used graphene transfer procedures in addition to various depositions.

By applying graphene transfer procedure, single layers of graphene have been successfully transferred onto the Quartz@Cr@Cu@HfO₂ substrate and shown in Fig. 2.1.3.2.



Fig.2.1.3.2.Optical images of heterostructures comprised of (a) $HfO_2@Cu@Cr@Quartz$ and (b) Graphene@HfO_2@Cu@Cr@Quartz. The images were taken with 10X optical microscope magnification. Layers of Cr, Cu and HfO_2 have been deposited onto Quartz wafer using Moorfield electron-beam deposition system with the thickness of Cr 1.5 nm, Cu 30 nm and HfO_2 156 nm or 100 nm

After successfully accomplished graphene transfer process, the photolithography procedure has to be implemented to fabricate electrical contacts to the graphene surface.

Photolithography is a process widely used device fabrications of different types. This process is based on the photochemical effect that takes place at the photoresist sitting on substrate as a result of UV irradiation through the mask and subsequent formation of a pattern in a photoresist layer followed by its placement in developer solution. If a

photosensitive mask is used for the process of local etching then the quality of pattern depends upon pattern adhesion to the substrate and subsequent development as well as the etchers ability to penetrate though pattern boundaries. Photoresist adhesion increases as surface wettability of substrate increases, with the criteria of wettability being contact wettability angle of a solid surface by a liquid. For photolithography processes a suitable substrate surface is considered to be the surface that is well wetted by photoresist (so-called hydrophilic surface) and simultaneously to have poor wettability for water. Commonly, a change in substrate's surface properties occurs due to the impact of different impurities, which can be divided into physicochemical and mechanical. Physicochemical contaminations are adsorbed ionic impurities on the surface, which can be removed by chemical cleaning methods based on the impurities desorption in processing them in solutions, gaseous medium and in plasma. For mechanical impurity contamination removal requires physical methods of cleaning, namely hydro-mechanical cleaning. Having performed hydro-mechanical cleaning the wafer must be washed in solution of deionized water and dried on the hot plate at a temperature 120 °C for 15 minutes.

During plasmonic heterostructure and device fabrication in this thesis substrates were cleaned in Acetone and Isopropanol (IPA) in order to dissolve fatty and particulate contamination which prevents smooth photoresist coating as well as good photoresist adhesion to the substrate. The cleaning should be followed by the substrate rinse in Distilled Water (DI) to remove solvent traces. Having cleaned the wafer the next step is photoresist application. In this thesis the photoresist cover onto the wafers has been done using a spinner.

Photoresist is an organic polymeric complex containing forming layer that is sensitive to UV radiation. Chemical molecules excited by light are subject to a change that transforms their properties. The chemical binding energy in polymers lies in the energy range from 157,5-525 $\frac{kl}{mol}$ which is proportional to the energy of light radiation from visible to ultraviolet range of electromagnetic spectrum. Photochemical processes triggered in photoresist while it is exposed to UV radiation can be classified to have two phases; light and dark. First, in the light stage the weakly bonded chemical chain of photosensitive molecules are broken as a result of photon absorption and formation of free radicals. Within the dark phase, depending on the type of photoresist there are two possible scenarios of chemical reactions. The first one occurs when, during dark phase, the polymer chains undergoes destructive processes, whereas in the second scenario chemical polymer group reorganization is followed by molecule structuring into rigid networks. Consequently resilience of the irradiated type of photoresist to a developer is either increased or decreased after photochemical reactions. There are two types of photoresist: *Positive Tone Photoresist* and *Negative Tone Photoresist*.

Positive Tone Photoresist is the photoresist exposed region of which to UV radiation is easily dissolved and removed in developers while not exposed photoresist regions remain on substrate and form photoresistive contact mask. This occurs as illuminated areas of positive photoresist become hydrophilic, well wetted and easily removed by the developers.

Negative Tone Photoresist behaves in the opposite way and those parts which were subjected to UV radiation became cross-linked and resistant to developers, remaining on the substrate surface molding photoresist mask. In the process of plasmonic heterostructures, as well as electro-optical device fabrication, both types of photoresist have been used.

The wafer was placed on a rotating vacuum chunk and the photoresist was dropped in the center. Once the spinner lid was closed and angular speed of rotational chunk was chosen, liquid photoresist flows from the center to the edges and is spread evenly over the wafer by centrifugal force discarding the liquid excess into the hood. Thickness of deposited photoresist layer depends on the angular speed of chunk rotation as well as photoresist's viscosity, which can be expressed as

$$d \sim \sqrt{\frac{\gamma}{\omega}}$$
, (2.1.3.1)

where γ is photoresist viscosity, ω is angular speed of the spinner and *d* is thickness of deposited photoresist.

The average thickness of photoresist is decreased as the speed of angular rotation of the spinner is increased. The thickness of photoresist becomes constant when a certain number of cycles are achieved. This corresponds to the situation where there is equilibrium between centrifugal and cohesive forces during layer formation. However, it should be noted that the time of centrifugation has little impact on layer's parameters. While choosing the photoresist thickness one should take into account the facts that the resist should provide high resolution and should not be removed by the etcher. Aside from this, there should be no defects present at the spin coated photoresist layer. Consequently photoresist thickness should be kept to a minimum, but sufficient enough to guarantee its resilience to etchant and lift-off procedure.

The next step is to dry the photoresist on the hot plate. Depending on the type of photoresist and its consistency, a specific heating temperature should be used to completely remove the solvent from the photoresist. During the drying process the solvent is removed and the relaxation process of densely packed molecules in the photoresist takes place, leading to decrease of internal stress and increase in photoresist adhesion to the wafer. While drying, the solvent should be removed completely as it screens photosensitive chains of molecules during UV exposure. The solvent removal takes into two steps: first there is diffusion at the boundary layer-atmosphere while during the second step the solvent evaporation from surface takes place.

If evaporation prevails under the diffusion process, the surface layer of photoresist condenses earlier than the inner layer and prevents solvent removal from the inside. This causes the rise of internal stress in the layer which weakens it and leads to its rupture and crack formation. It is highly recommended to perform the drying process in an inert atmosphere since photoresist oxidation in contact with the air can occur. The drying process is characterized by two major parameters: temperature and time, which have significant impacts on photoresist qualities such as time of UV exposure as well as pattern precision after the development process. At low temperature range the photoresist adhesion to the substrate is very poor as the cohesion between polymer molecules within the photoresist dominates over substrate adhesion.

The critical drying temperature corresponds to photoresist hardening at which there is loss of photoresist photosensitivity. For most photoresist the critical value of temperatures lies at the range from 130-150 $^{\circ}$ C.

Before photolithography procedure it is necessary to design graphene-based Fabry-Perot interferometers using Inscape program followed by the application of the Laser Writer and Lift-off techniques.

(a)

(b)



Fig.2.1.3.3.Optical images of the fabricated graphene-based electro-optical modulator. (a) optical image of the modulator was taken in reflection mode with the red dashed line representing the area with graphene monolayer. (b) optical image of the device was reordered in transmission mode. The optical microscope magnification is 50X

To fabricate graphene-based Fabry-Perot electro-optical modulators the top layers of HfO₂ (thickness of 156 nm or 100 nm) and Cu (thickness of 30 nm) have been evaporated on top of heterostructures HfO₂@Cu@Cr@Quartz with the subsequent process of photolithography to make the top electrodes of the modulators. The optical images of graphene-based Fabry-Perot electro-optical modulators are presented in Fig. 2.1.3.4.



Fig.2.1.3.4.An optical image of fabricated graphene–based Fabry-Perot electro-optical modulators. The presented sample is comprised of two electro-optical modulators the areas of which are shown by the dashed red lines

Experimental and Theoretical Results

Chapter 3

Graphene plasmonic-based heterostructures and devices

3.1. Motivation for research

Many research groups have tried to find viable materials and alloys to satisfy the needs of optoelectronic or biosensors applications. With many different works and huge progress in the plasmonic research so far, gold is still considered to be the main candidate for plasmonic application due to its chemical inertness and ease of fabrication. Nevertheless, despite having high optical and electrical conductivity, chemical inertness and biocompatibility with living cells, gold suffers from optical scattering losses arising from its surface morphology. One could suggest that copper or especially silver are better candidates for plasmonic application, however, their employment is hindered by their quick oxidation in contact with air. The situation becomes even worse when these metals are subjected to liquids, promoting quick chemical reactions leading to metal corrosion. These bottlenecks, however, can be overcome using one of the incredible properties of graphene, namely its property of impermeability. It has been proven experimentally that a graphene layer is impermeable to most of the gases and liquids. In addition, graphene could be easily fabricated and transferred with high reproducible atomic precision on top of any substrate, and as graphene is chemically inert, it does not provoke any chemical reaction with the

underlying substrates as it binds with it by van deer Waals forces. Last but not the least, it is biocompatible and could be very sensitive to adsorbed molecules on its surface.

This thesis subchapter is focused on experimentally established methods of copper and silver plasmonic properties protection by the use of graphene impermeability properties. In addition, theoretical modeling of graphene-based plasmonic heterostructures has been implemented. Some part of the research was performed with the help of Woollam spectroscopy ellipsometer. Using Woollam spectroscopy ellipsometer, I found the dependence of optical parameters (the coefficients of refraction, reflection, transmission as well as reflective indexes and extinction coefficients) as the function of wavelength of external electromagnetic irradiation. Most importantly I succeeded in creating the model and found appropriate and accurate fitting parameters for determination either optical constants or thickness of different metals and dielectrics for our graphene - protected devices.

Described below is the method by which an application of specific transfer protocol of CVD graphene onto copper and silver substrates makes it possible to safeguard copper and silver from oxidation and plasmonic property degradation over a substantial period of time, in the investigated case, in the timescale of one year. By preserving metal properties from corrosion, it is possible to utilize them as sensors as well as active components of plasmonic and optoelectronic applications. To summarize, in this piece of work, I have performed the theoretical simulation of copper and silver based plasmonic heterostructures facing water and glycerol environment in the case when metallic properties have been and have not been safeguarded by a graphene layer.

3.2. Theoretical modeling of graphene - protected copper and silver plasmonics

My personal contribution to the theoretical modeling was to develop and write the mathematical model, by employing Mathcad 14.0, which simulates the response of the following processes:

- Based on theoretical work [121] I have simulated the intraband and interband graphene optical conductivity dependence as a function of frequency of incident light in the case of different charge doping level.
- The condition of surface plasmon excitation for multilayer structure (when taking into account the presence of oxide layers) faces air, water, water with glycerol for various angles of incident light and wavelength range.
- The electro-optical light modulation in graphene-based broadband and narrowband wavelength regime of operation.

First, let us assume plain electromagnetic wave moving in a flat stratified medium. In the case of linearly polarized light [79] two types of electromagnetic waves can be distinguished: one of them is TE polarized wave and another one is TM wave. Any polarized electromagnetic wave can be produced as a combination of TE and TM waves. As the boundary conditions on the interface for perpendicular and parallel components of electromagnetic waves are independent thus these two types of waves will also be self-independent. Furthermore, if someone interchanges vectors E and Hand simultaneously alter dielectric and magnetic permittivity ε and μ then the Maxwell equations will not change. Hence by deriving any solutions for TE wave, one can obtain immediately the solution for TM wave by the specific interchange of ε and μ . Let's find the propagation of TE wave through the multilayer medium by considering the plane of incidence with components y and z where z component lies normally to the medium. Hence Maxwell equations can be rewritten in the following way

$$\frac{\partial H_z}{\partial y} - \frac{\partial H_y}{\partial z} + \frac{i\varepsilon\omega}{c} E_x = 0, \qquad (3.2.1)$$

$$\frac{\partial H_x}{\partial z} - \frac{\partial H_z}{\partial x} = 0, \qquad (3.2.2)$$

$$\frac{\partial H_y}{\partial x} - \frac{\partial H_x}{\partial y} = 0, \qquad (3.2.3)$$

$$\frac{\mathrm{i}\omega\mu}{c}H_{\chi}=0\,,\qquad(3.2.4)$$

$$\frac{\partial E_x}{\partial z} - \frac{\mathrm{i}\omega\mu}{c} H_y = 0, \qquad (3.2.5)$$

$$\frac{\partial E_x}{\partial y} + \frac{\mathrm{i}\omega\mu}{c}H_z = 0, \qquad (3.2.6)$$

It can be seen from equations (3.2.1) - (3.2.6.) that components E_x , H_y , H_z depend only upon components y and z. By expressing every component in terms of E_x one can derive the following formula

$$\frac{d^2 E_x}{dy^2} + \frac{d^2 E_x}{dz^2} + n^2 k_0^2 E_x = \frac{d(\ln\mu)}{dz} \frac{dE_x}{dz},$$
(3.2.7)

where $n^2 = \varepsilon \mu$ and $k_0 = \frac{\omega}{c} = \frac{2\pi}{\lambda_0}$.

Let us seek the solution of equation (3.2.7) in the form of the product of two independent functions. One of these functions will be dependent only on *y* component whereas the other - from *x* component.

$$E_x(y,z) = Y(y) D(Z),$$
 (3.2.8)

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{1}{D}\frac{d^2D}{dz^2} - n^2k_0^2 + \frac{1}{D}\frac{d(\ln\mu)}{dz}\frac{dD}{dz},$$
(3.2.9)

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -H^2 , \qquad (3.2.10)$$

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$$\frac{1}{D}\frac{d^2D}{dz^2} - n^2k_0^2 + \frac{1}{D}\frac{d(\ln\mu)}{dz}\frac{dD}{dz} = H^2, \qquad (3.2.11)$$

If we assume that

$$H^2 = k_0^2 \alpha^2 , \qquad (3.2.12)$$

then the equation (3.2.12) will take a form

$$Y = \operatorname{const} \exp(i(k_0 \alpha y - \omega t)), \qquad (3.2.13)$$

$$E_x = D(z)\exp(i(k_0\alpha y - \omega t)), \qquad (3.2.14)$$

From these equations we obtain

$$H_y = V(z)\exp(i(k_0\alpha y - \omega t)), \qquad (3.2.15)$$

$$H_z = W(z)\exp(i(k_0\alpha y - \omega t)), \qquad (3.2.16)$$

Functions R(z), V(z), W(z) are coupled due to the expressions (3.2.1), (3.2.5) and (3.2.6) in the following way

$$\frac{dV}{dz} = ik_0(\alpha W + \varepsilon V), \qquad (3.2.17)$$

$$\frac{dD}{dz} = ik_0\mu V , \qquad (3.2.18)$$

$$\alpha D + \mu W = 0, \qquad (3.2.19)$$

From the equations (3.2.17) and (3.2.19.) we get

$$\frac{dD}{dz} = ik_0\mu V, \qquad (3.2.20)$$

$$\frac{dV}{dz} = ik_0 \left(\varepsilon - \frac{\alpha^2}{\mu}\right) D, \qquad (3.2.21)$$

where

$$\frac{d^2 D}{dz^2} - \frac{d(\ln\varepsilon)}{dz} \frac{dD}{dz} + k_0^2 (n^2 - \alpha^2) D = 0, \qquad (3.2.22)$$

$$\frac{d^2V}{dz^2} - \frac{d\left(\ln\left(\mu - \frac{\alpha^2}{\varepsilon}\right)\right)}{dz}\frac{dD}{dz} + k_0^2(n^2 - \alpha^2)D = 0, \qquad (3.2.23)$$

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$$|D(z)| = \text{const}, \qquad (3.2.24)$$

$$\varphi(z) + k_0 \alpha y = \text{const}, \qquad (3.2.25)$$

$$\varphi(z) = k_0 n z \cos \theta, \quad \alpha = n \sin \theta,$$
 (3.2.26)

Thus:
$$\alpha = \text{const}$$
 (3.2.27)

Taking into account equation (3.2.26) the equations (3.2.22) and (3.2.23) can be expressed as:

$$\frac{d^2 D}{dz^2} - (k_0^2 n^2 \cos^2 \theta) D = 0, \qquad (3.2.28)$$
$$\frac{d^2 V}{dz^2} + (k_0^2 n^2 \cos^2 \theta) V = 0, \qquad (3.2.29)$$

The solution of the equations (3.2.28 - 3.2.29) can be found with the help of Fourier transformation:

$$D(z) = A\cos(k_0 n z \cos\theta) + B\sin(k_0 n z \cos\theta), \qquad (3.2.30)$$

$$V(z) = \frac{1}{i} \sqrt{\frac{\varepsilon}{\mu}} \cos\theta [B\cos(k_0 n z \cos\theta) - A\sin(k_0 n z \cos\theta)], \qquad (3.2.31)$$

$$D_1 = \frac{i}{\cos\theta} \sqrt{\frac{\mu}{\varepsilon}} \sin(k_0 n z \cos\theta) , \qquad (3.2.32)$$

$$V_1 = \cos(k_0 n z \cos\theta), \qquad (3.2.33)$$

$$D_2 = \cos(k_0 n z \cos\theta), \qquad (3.2.34)$$

$$V_2 = i \sqrt{\frac{\varepsilon}{\mu}} \cos\theta \sin(k_0 n z \cos\theta) , \qquad (3.2.35)$$

Let us denote

$$p = \sqrt{\frac{\varepsilon}{\mu}} \cos\theta , \qquad (3.2.36)$$

Characteristic matrix for TE electromagnetic wave being solution of the equations (3.2.28) and (3.2.29) expressed as

$$M_{s}(z) = \begin{pmatrix} \cos(k_{0}nz\cos\theta) & -\frac{\mathrm{i}}{p}\sin(k_{0}nz\cos\theta) \\ -\mathrm{i}p\sin(k_{0}nz\cos\theta) & \cos(k_{0}nz\cos\theta) \end{pmatrix}, \qquad (3.2.37)$$

where k_0 is free space wave vector of photon, *n* is refractive index of a medium, *z* is thickness of a medium, θ is angle of refraction in the medium, ε_1 , μ_1 describes the medium in which the electromagnetic wave falls onto the multilayer structure, ε_l , μ_l is electric and magnetic permittivities of the last layer from which the light comes out, θ_1 is angle of incident electromagnetic wave and θ_l is the angle of transmitted electromagnetic wave through the multilayer system.

The obtained characteristic matrix has important meaning because with its help it is possible to describe the light propagation through the multilayer structure and calculate the phase change as well as reflection and transmission coefficient of light.

R and T is the amplitude of incident, reflected and transmitted electromagnetic wave

$$r_{s} = \frac{(m_{11} + m_{12}p_{l})p_{1} - (m_{21} + m_{22}p_{l})}{(m_{11} + m_{12}p_{l})p_{1} + (m_{21} + m_{22}p_{l})},$$
(3.2.38)

$$t_s = \frac{2p_1}{(m_{11} + m_{12}p_l)p_1 + (m_{21} + m_{22}p_l)},$$
(3.2.39)

where

$$m_{11} = m_{22} = \cos\beta , \qquad (3.2.40)$$

$$m_{12} = -\frac{i}{p} \sin\beta$$
, (3.2.41)

$$m_{12} = -\mathrm{i}p\mathrm{sin}\beta , \qquad (3.2.42)$$

$$\beta = \frac{2\pi}{\lambda} nz \cos\theta , \qquad (3.2.43)$$

where β attributes to the phase change acquired by electromagnetic wave while it propagates through each layer of multilayer structure, λ is wavelength of light, *n* is refractive index of the layer, *z* is thickness of the layer, θ is the angle of refraction, p_1 and p_l is expressed as

$$p_1 = \sqrt{\frac{\varepsilon_1}{\mu_1}} \cos\theta_1 , \qquad (3.2.44)$$

$$p_l = \sqrt{\frac{\varepsilon_l}{\mu_l}} \cos\theta_l , \qquad (3.2.45)$$

Hence the transmittance and reflectance amplitude of electromagnetic wave can be expressed as

$$R_s = |r_s|^2 , (3.2.46)$$

$$T_s = \frac{p_1}{p_l} |t_s|^2 , \qquad (3.2.47)$$

For calculation of changes in reflection and transmission amplitudes for TM electromagnetic wave propagation through the multilayer medium it is necessary to employ the system of the above mentioned formula, however instead of putting p_1 and p_l , q_1 and q_l must be used

$$q = \sqrt{\frac{\mu}{\varepsilon}} \cos\theta , \qquad (3.2.48)$$

$$q_1 = \sqrt{\frac{\mu_1}{\varepsilon_1} \cos\theta_1}, \qquad (3.2.49)$$

$$q_L = \sqrt{\frac{\mu_1}{\varepsilon_1}} \cos\theta_L , \qquad (3.2.50)$$

Characteristic matrix for TM electromagnetic wave is written as

$$M_p(z) = \begin{pmatrix} \cos(k_0 n z \cos\theta) & -\frac{i}{q} \sin(k_0 n z \cos\theta) \\ -iq \sin(k_0 n z \cos\theta) & \cos(k_0 n z \cos\theta) \end{pmatrix}, \quad (3.2.51)$$

$$r_p = \frac{(m_{11} + m_{12}q_l)q_1 - (m_{21} + m_{22}q_l)}{(m_{11} + m_{12}q_l)q_1 + (m_{21} + m_{22}q_l)},$$
(3.2.52)

$$t_p = \frac{2q_1}{(m_{11} + m_{12}q_l)q_1 + (m_{21} + m_{22}q_l)},$$
(3.2.53)

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Hence the transmittance and reflectance amplitudes can be expressed

$$R_p = \left| r_p \right|^2, \qquad (3.2.54)$$

$$T_p = \frac{q_1}{q_l} |t_p|^2, (3.2.55)$$

Final expression, which has been used for mathematical simulations in this PhD thesis and the result of which were compared to the experimental data presented in Chapters 3.4-3.7, is expressed as

$$\Psi = \operatorname{atan}\left(\frac{|r_p|}{|r_s|}\right),\tag{3.2.56}$$

The modeled multilayered system consisted of dielectric Glass substrate with Cr, Cu and Graphene layers placed on top of it. To model oxidation process, an additional layer of copper oxide was added to the fitting model. Schematics of the structure are presented in Fig. 3.2.1.



Fig.3.2.1.Schematic view on the heterostructures that were computationally simulated. (a) structure with unprotected copper film while (b) structure with copper layer being encapsulated with single layer of graphene

Using optical constants of layers either extracted by spectroscopic ellipsometry or provided in the literature such as Woollam software database or Palik database [122] I calculated all the important optical properties of layered structures – reflection, transmission, spectral ellipsometric parameters. Graphene optical conductivity and connected to it optical dielectric permittivity was computed theoretically with the help of the approach introduced by [121]. I then performed theoretical calculation of SPR

curve by tuning copper oxide thickness and angles of light incidence searching for which the minimum of Ψ (θ , λ) is reached. After finding and fitting the above mentioned parameters the minimum of Ψ (θ , λ) was obtained and was in a good agreement with experimental data. A typical spectrum simulation result for the structure Glass@Cr(1.5nm)@Cu(42.5m)@CuO(1nm)@Graphene(0.335nm) used for SPR measurements is presented in Fig. 3.2.2.



Fig.3.2.2.Computationally simulated optical spectra response of surface plasmon-polariton excitations for heterostructure Glass@Cr@Cu@CuO@Graphene at the angle of light incidence of 49°

3.3. Methodology of graphene plasmonic devices fabrication and optical scheme for devices characterization

Sample fabrication started with 25x25 mm glass substrate (thickness of 1 mm) being cleaned in sonicator with hot acetone and isopropanol followed by films deposition using Moorfield electron beam deposition chamber with base pressure of 10⁻⁷ mbar. To promote adhesion of metals the Cr layer with the thickness of 1.5 nm has been deposited before copper and silver deposition. The film growth rate has been monitored

by calibrated quarts microbalance situated inside evaporation chamber with the growth rate of 0.3 $\frac{nm}{s}$.

As far as CVD graphene transfers procedure is concerned, it has been done using wet transfer process. First, polymethyl polymethacrylate (PMMA) has been spin coated on top of CVD graphene to provide mechanical support as well as to preserve CVD graphene surface during transfer from crack formation. This has been followed by placing the sample into ammonium persulphate etchant to obtain PMMA@CVD graphene membrane. Once it was accomplished, the membrane was accurately fished up and placed into the DI water for a couple of hours to get rid of solvent. Using optical microscope PMMA@CVD graphene membrane was transferred with high precision on Quartz@Cr@Cu sample surface. To eliminate PMMA layer, the sample has been placed in acetone and graphene surface were further subject for cleaning employing hydrogen annealing of 200° C during 60 min. Once samples have been fabricated they were subject to experimental measurements using Woollam spectroscopic ellipsometer. Freshly evaporated samples of copper with the thickness of 43.5nm and 1 µm were studied with Woollam ellipsometer to obtain the copper's refractive index (Fig. 3.3.1.(a)). To study the plasmonic properties of graphene copper protected plasmonics the Turbadar-Kretchmann Raether ATR scheme has been used (Fig. 3.3.1.(d)).

Turbadar-Kretchmann Raether ellipsometric and polarized ATR spectra were recorded by focused and unfocused beams of M-2000F Woollam spectroscopic ellipsometer with light spot of 30x60 µm and 3.5x7.5 mm respectively. The wavelength range was from 250 to 1000 nm with step of 1 nm. As mentioned in Chapter 1 Section 1.6.2., the main measured parameters were ellipsometric reflection $\Psi(\theta, \lambda)$ and phase shift between *p* and *s* polarization light. To test the evolution of optical responses over the studied period of unprotected and graphene - protected samples, the exchange chamber was used to place water and water-glycerol solution in contact with the studied samples.



Fig.3.3.1.Graphene protection for copper plasmonics.(a) copper refractive index calculated from the data measured by Woollam spectroscopic ellipsometer. (b) schematic representation of planar structure of graphene - protected copper surface. (c) schematic view of ATR geometry for surface plasmon polaritons excitation. (d) SPR measurements using ATR geometry (pictures adapted from ref. [123])

3.4. Spectroscopic ellipsometry measurements and theoretical modeling of graphene - protected copper plasmonics

SRP characteristics of freshly prepared copper samples using ATR geometry has been examined. Samples had Cu thickness of 43.5 nm and unfocused ellipsometry beam spot of 3.5x7 mm was employed to acquire optical spectra. Strong deep SPR resonance was observed at angle of light incidence θ_R = 49.5° at the wavelength of λ = 558 nm. Ellipsometric parameter Ψ (49.5°, 558 nm) was 0.7° which attributes to minimum intensity of light reflection of *p* polarization R_p (49.5°, 558 nm) of 5x10⁻⁴ with the quality factor *Q* of 19. Having left samples in air for 30 days, we observed degradation of Cu properties due to its oxidation (Fig.3.4.1 (c), (d)). Those could be also observed in SPR curves, where the resonance minimum position redshifted to $\lambda = 637$ nm, the ellipsometric parameter Ψ increased to 11.5° and R_p (53°, 637 nm) equals to 4x10⁻² with quality factor Q of 7. This was a typical situation with copper plasmonic samples before we employed a graphene protection layer. The samples with copper encapsulation by graphene, however, showed no degradation of plasmonic characteristics over studied period of approximately one year.

It was found that the usage of graphene layer as a protector of copper samples even improved SRP characteristics. Those results are demonstrated in Fig. 3.4.1 (e), (f) where a SPR curve for graphene - protected sample is shown with the minimal ellipsometric parameter Ψ (49°, 603 nm) equals to 0.4°, reflection R_p (49°, 603 nm) equals to 3x10⁻⁴ and the resonance quality Q of 20. All these parameters are better than those of freshly deposited copper film alone without graphene protection. It is worth mentioning that none of such parameters were achieved so far for Au films due to strong scattering of SPP waves on gold grains.



Fig.3.4.1.Optical response of graphene-protected copper plasmonics over period of six month in contact with air. (a) dependence of ellipsometric amplitude reflection Ψ (θ , λ) on incident wavelength in the case of freshly prepared and unprotected copper plasmonic heterostructures. (b) dependence of reflection for *p*-polarized light on wavelength of incident light for freshly prepared unprotected copper plasmonic heterostructures. (c) dependence of ellipsometric amplitude reflection Ψ (θ , λ) on incident wavelength after 30 days of copper being exposed to air. The degradation effects from copper oxidation are easily observable here. (d) *p*-polarized light reflection dependence upon incoming light on unprotected copper plasmonic heterostructures. (e), (f) visible effect of graphene safeguarding copper plasmonic characteristics over 6 month period (pictures extracted from ref. [123])

Turning to results obtained by theoretical modeling, I calculated ellipsometry parameter Ψ (θ , λ) (as well as light reflection and transmission) for multilayer structures in the case of Kretschmann prism configuration facing air, water and water mixture with glycerol. The multilayer SPR samples consisted of Glass on which Cr, Cu or Cr, Cu and graphene layers.



Fig.3.4.2.Three-dimensional view of Kretschmann prism configuration presenting SPP waves excitation for structure Glass@Cr@Cu@CuO in contact with air

As deposited thin layer of copper on Glass substrate, had to be taken out from the chamber in order to perform subsequent CVD graphene transfer process, this could lead to copper oxide formation due to copper contact with the air. As results, a very thin layer of copper oxide could form on the surface of copper which was added to the simulation. Fig. 3.4.3-3.4.6 show results of the simulation modeling which were in good agreement with experimental data.

The structure of modeled sample is presented in Fig. 3.4.2. and consists from Glass substrate on top of which Cr layer with thickness 1.5 nm and Cu layer with thickness 43.5 nm being deposited using Moorfield electron-beam deposition equipment. As the sample was taken out from the Moorfield electron-beam deposition chamber a thin layer of CuO forms instantaneously in contact with air. This has been taken into account

while performing the mathematical modeling by putting the thickness of formed CuO thickness of 1 nm while Cu thickness was put as 42.5 nm.



Fig.3.4.3.P-polarized reflectance as a function of excitation wavelength at a fixed angle of light incidence of 49°

Fig.3.4.4.S-polarized reflectance as a function of excitation wavelength at a fixed angle of light incidence of 49°



Fig. 3.4.5.Ellipsometry parameter Ψ (θ , λ) as a function of incident wavelength for the case of angle of light incidence of 49° for heterostructure Glass@Cr@Cu@CuO

To show that copper oxidation can explain the deterioration of the SPR curve of unprotected sample (Fig 3.4.1. (c)), I have modeled the effect of copper film oxidation and compared it with experimental data. The results of modelling are presented in Fig. 3.4.6 (a). When Cu oxidizes, a thin layer of copper oxide is formed on top of Cu metal surface [124]. With time the thickness of CuO increases due to continuous exposure of Cu metal to ambient environment. Simultaneously, thickness of copper film decreases (by this value), so that the optimal conditions for surface plasmon resonance excitation are no longer preserved.

Consequently, oxidation of the copper film results in suppression of surface plasmon resonance as well as SPR broadening (caused by non-optimal condition of resonance excitation of SPP and possible roughness of oxide layer). This is confirmed by the computational simulations results presented in Fig. 3.4.6(a) which shows the change of the calculated SPR curves caused by the growth of copper oxide layer on top of Cu metal surface. One can notice the red shift and broadening of the SPR resonance curve induced by the increase of the thickness of the copper oxide layer. The calculated SPR curve for copper oxide thickness of around 14 nm agrees well with the measured SPR curve for 30-day old unprotected copper samples.



Fig.3.4.6.Influence of CuO thickness variation on the suppression of surface plasmon resonance and broadening of SPR curve. (a) calculated data for heterostructure of Glass@Cr@Cu@CuO facing air. (b) experimental data of copper oxidation after 30 days. Inset shows comparison of SPR curve for a fresh and 30 day old sample

To understand the reason for deterioration of SPR curves due to copper oxidation analytically, we should look into the conditions of SPR excitation. The surface plasmon polaritons waves are propagating along the plane boundary of metal-dielectric surface with the wave vector k_{SPP} whose value is determined by the following relation:

$$k_{SPP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_M \varepsilon_D}{\varepsilon_M + \varepsilon_D}},$$
(3.4.1)

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where k_{SPP} is wave vector of surface plasmon waves, ω is cyclic frequency of electromagnetic wave, *c* is the velocity of light in vacuum, ε_M is complex dielectric permittivity of metal and ε_D is dielectric permittivity of dielectric.

The phenomenon of surface plasmon resonance is the resonant excitation of surface plasmon polaritons by the photons on the conditions when the energy and momentum is conserved for the system photon-surface plasmon polariton

$$\hbar\omega = \hbar\omega_{SPP} , \qquad (3.4.2)$$

$$k_x = k_{SPP} , \qquad (3.4.3)$$

where \hbar is Plank constant, ω is cyclic frequency of electromagnetic wave, ω_{SPP} is cyclic frequency of surface plasmon-polariton waves, k_{SPP} is the wave vector of surface plasmon polaritons and k_x is the projection of wave vector of light on X-axis.

In Kretschmann prism configuration, dielectric and thin metal films are deposited onto glass substrate which comes into contact with glass prism with the help of immersion liquid having the same dielectric permittivity as the glass prism (Fig. 3.4.3 (a)). The glass prism should possess high dielectric permittivity $\varepsilon_{prism} > \varepsilon_{dielectric}$ to create optically dense media in order to satisfy the condition of total internal reflection for incident electromagnetic wave.

The polarized beam of light is directed into the glass prism in such a way that the angle of light incidence falling into glass prism facet, above which there is metal film, should exceed the angle of total internal reflection (TIR) $\theta_{incident} > \theta_{TIR}$. In this case the light undergoes complete total internal reflection and in the space above the prism the intensity of electromagnetic wave attenuates exponentially while propagating through the media. As the metal film is thin with its thickness of 43.5 nm, the evanescent electromagnetic field reaches the boundary of the metal-dielectric interface. The momentum of incident photon is enhanced while passing through the glass prism media under specific incident angle and becomes equal to

$$k_{SPP} = \frac{\omega}{c} \sqrt{\varepsilon_{prism}} \sin \theta_{SPPR} , \qquad (3.4.5)$$

In this case the condition presented in the formula (3.4.2) and (3.4.3) is satisfied and the resonance excitation of the surface plasmon polaritons waves is occurred. This is manifested as the prominent dip in the amplitude of reflected light or minima value of ellipsometric parameter at the specific angle of light incidence θ_{SPPR} that called angle of surface plasmon-polariton resonance.

The value of angle θ_{SPPR} at which it will be possible to obtain surface plasmonpolariton resonance for system metal-dielectric is easily calculated using the expression (3.4.1-3.4.3) and (3.4.5)

$$\sqrt{\varepsilon_{prism}}\sin\theta_{SPPR} = \sqrt{\frac{\varepsilon_M\varepsilon_D}{\varepsilon_M + \varepsilon_D}},$$
 (3.4.6)

Expression (3.4.6) is clearly states that the angle θ_{SPPR} depends upon dielectric permittivity of metal and dielectric around the metal. When copper oxidizes, the dielectric near metal changes from air to copper oxide and the conditions for resonance excitation of surface plasmon-polariton waves become non-optimal which leads to resonance red shift due to a decrease of k_{SPP} and SPR curve broadening due to an increase of imaginary part of k_{SPP} (this imaginary part comes from complex values of dielectric permittivity of copper).

Simulation results for surface plasmon-polaritons waves excitation for grapheneprotected copper sample for heterostructure Glass@Cr@Cu@CuO@Graphene facing air are presented in Fig. 3.4.7-3.4.11



Fig.3.4.7.Three-dimensional image of Kretschmann prism configuration depicting SPP excitation for heterostructure Glass@Cr@Cu@CuO@Graphene in contact with air



Fig.3.4.8.The dependence of real part of graphene's refractive index on the wavelength of the incident electromagnetic radiation for heterostructure Glass@Cr@Cu@CuO@Graphene



Fig.3.4.9.Calculated reflectance of *p*-polarized electromagnetic wave as a function of excitation wavelength at a fixed angle of light incident of 49°

Fig.3.4.10.Calculated reflectance of *s*-polarized electromagnetic wave as a function of excitation wavelength at a fixed angle of light incident of 49°



Fig.3.4.11.Dependence of ellipsometry parameter Ψ (θ , λ) on the excitation wavelength of incident light of 49° for heterostructure Glass@Cr@Cu@CuO@Graphene

Comparison between experimental and computational simulation results is presented in Fig. 3.4.12. The full mathematical model which has been used to simulate theoretical results that are presented in Fig. 3.4.12(a) has been described in Chapter 3.2 of this PhD thesis.

The simulation parameters were copper oxide thickness and angles of light incidence for which the minimum value of ellipsometric parameter $\Psi(\theta, \lambda)$ is reached.



Fig.3.4.12.Comparison between simulation (a) and experimental (b) results for ellipsometric parameter Ψ (θ , λ) which depends upon excitation wavelengths in cases of Cu, SLG, Cu@SLG samples at incident light angle of 49^o facing air

The following Chapters 3.5-3.7 address the work of our devices in a water environment, which is essential for bio-sensing applications. Indeed, fast, reliable and accurate biochemical sensors are important for biomedical and pharmaceutical researches. The detection methods for biosensors should provide sensitivity, selectivity, ability of monitoring in real time and in different biological solutions in combination with low cost and small size. In the field of optical biosensors, SPR detection technique plays an important role due to the fact that it is label-free. The operation principle of SPR-based biosensor is based on measurements of the refractive index changes at the conductor interface being functionalized with the probed molecules. The position of surface plasmon resonance angle shifts once the binding between investigated target analytes with the functionalized surface of the metal has been established, leading to a refractive

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index changes and the possibility of real time observation as well as detection of the binding species onto the functionalized metal surface. To detect the small concentrations of organic and non-organic molecules and investigate the interaction between them requires an increase in the biosensor sensitivity. Nowadays, the widely used approach to achieve this is to employ a binding layer that binds investigated biomolecules to the biosensor surface. Another way to improve the sensitivity of biosensors based on the phenomena of surface plasmon resonance is to utilize two dimensional materials, having very small thickness, as the binding layer. Graphene has already been highly recommended for the application in the field of plasmonics, electronics, photonics and optoelectronics due to its fascinating properties and ease of its fabrication as well as implementation onto arbitrary substrate with high precision. Most significantly, that graphene can be used for biosensor construction and boost its biomolecules sensitivity performance since graphene possess biocompatibility with different range of biomolecules, its atomically thin layer and has large surface area to volume ratio [125, 126]. Authors [127] have shown in their work that graphene has large values of surface area capable to adsorb molecules. Hence, graphene could be a good candidate for application in bio-detection and biosensors. Gold is commonly used these days for the construction of biosensors due to its chemical inertness. However, silver and even copper are more suitable metals for biosensor manufacturing due to their biological compatibility, low cost and low optical loss compared to gold. Although, copper and silver tends to oxidize very quickly in contact with the liquids and graphene with its excellent encapsulation capabilities can easily safeguard these metals from corrosion and construct low cost, state of the art high sensitivity biosensors.

The experimental validation as well as theoretical calculations of copper and silver plasmonic properties conservation by the use of single layer of is presented at the following Chapters 3.5- 3.7.

3.5. Graphene-protected plasmonics for biosensing applications

Plasmonics heterostructures and devices find a wide range of application in biosensing [128] with the main criteria being sensitivity to adsorbed chemical groups on a device surface. In order to achieve high phase sensitivity of SPR [129-131], we need to achieve the lowest value of the SPR reflectance minimum. To study whether graphene is capable of protecting copper thin films from corrosion in ambient and wet environments, in particular when samples are subjected to the coverage of liquids such as water or mixtures of water with glycerol, three types of samples have been fabricated. The first type of samples serves as the reference sample which consisted of freshly deposited unprotected copper thin film with the thickness of 43.5 nm sitting on 1.5 nm thin Cr layer both of which have been deposited on Quartz substrate and had the structure of Quartz@Cr(1.5nm)@Cu(43.5nm). In second type, copper thin layer has been covered by a single layer of graphene and had the configuration of Quartz@Cr(1.5nm)@Cu(43.5nm)@Graphene(0.335nm). In the third, the copper has been protected bilayer graphene with the placement of by a Quartz@Cr(1.5nm)@Cu(43.5nm)@Bilayer Graphene(0.67nm).

ATR geometry, as described in Section 1.2.4., was implemented to generate SPR response of samples. M-2000F Woollam spectroscopic ellipsometer was used to yield focused polarized light beam directed onto ATR geometry as well as to record the SPR response from investigated samples.

Fig. 3.5.1(a) represents the experimental SPR curves gauged in air for samples consisted of the freshly deposited unprotected thin copper film (black curve), thin copper film safeguarded by the single graphene layer (red curve) and thin copper film protected by the bilayer graphene (blue curve). Fig. 3.5.1(b) shows experimentally measured SPR curves of reference sample with the structure of Quartz@Cr(1.5nm)@Cu(43.5nm) covered by water.

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After 24 hours the reference sample with the configuration of Quartz@Cr(1.5nm) @Cu(43.5nm) covered by water had been measured again and the experimental results are presented in Fig. 3.5.1(c). Experimental results depicted in Fig. 3.5.1(c) exhibit a rapid process of copper oxidation which was accompanied by SPR characteristics degradation in just 24 hours.

As single layer of graphene is remarkable material that mostly impenetrable material [132, 133] thus it has been chosen to protect copper from oxidation. To test this idea, the sample with the configuration Quartz@Cr(1.5nm) @Cu(43.5nm)@Graphene(0.35nm) has been subjected to contact with the water. As can be seen from experimental results presented in Fig. 3.5.1(d) graphene fully encapsulates copper from contact with water, which demonstrated that there were no plasmonic property degradation over the studied period of time which proves that graphene is able to completely seal copper from any contact with wet environments and to prevent it from oxidation.



Fig.3.5.1.Graphene-protected copper plasmonics. (a) optical response of SPR measured at θ_R =49° in air for fabricated unprotected Cu films (black curve), Cu encapsulated with monolayer graphene (red curve), Cu being protected with graphene double layer (blue curve). The results of theoretical modeling are presented in the inset. (b) testing copper unprotected samples to corrosion in contact with water. (c) SPR response of samples being kept in water environment for 24 hours. (d) optical response of graphene-protected samples in water after 6 months. (e) dependence of ellipsometric amplitude reflection upon wavelength for unprotected silver samples in water. (f) dependence of ellipsometric amplitude reflection upon wavelength for the silver films covered by graphene (pictures adapted from ref.[123])


(a)

(b)



(b)

Fig.3.5.2.Computationally calculated Ψ (θ , λ) as a function of excitation wavelength for angles of light incidence from 58^o to 61^o in contact with water

Fig.3.5.3.Experimentally measured Ψ (θ , λ) as a function of excitation wavelength for angles of light incidence from 58^o to 61^o in contact with water



Glass@Cr@Cu@CuO@SLG@0.9Water+ 0.1Glycerol

Fig.3.5.4.Computationally calculated Ψ (θ , λ) as a function of excitation wavelength for angles of light incidence from 58^o to 61^o facing water with glycerol ambient

Fig.3.5.5.Experimentally measured Ψ (θ , λ) as a function of excitation wavelength for angles of light incidence from 58^o to 61^o facing water with glycerol ambient

3.6. Metrology of safeguarding silver plasmonic properties for biosensing applications

Highly accurate and quick biochemical and biophysical analysis is the paramount goal for pharmaceutical, healthcare and biomedical research communities. This objective can be achieved by biosensor utilizations. The preference of biosensor usage in analysis, detection and selectivity of biomolecular reactions is conditioned by the ease of its integration with microprocessors; electronics allowing the performance of fast signal processing and executing medical diagnostics. The methodology of a biosensor's detection is based on high sensitivity and selectivity to chemical groups. In addition to that, biosensors should enable monitoring in real time while being in contact with any solution; in addition, ideally they should have very small geometrical sizes. The methods of biosensor detections of change in aqueous environments are based on refractive index, e.g., SPR, optical absorption as well as Raman scattering measurements. The pivotal superiority of SPR usage relates to high sensitivity to the change of object's refractive index. Gauging refractive index change occurs at the interface between plasmonic material and chemical or biological groups. It is well known that silver is an ideal plasmonic material for medical and biosensor devices so that it is required to examine how graphene can protect silver from its oxidation as well. As far as graphene-based silver protective barrier for plasmonic application is concerned the new recipe to safeguard the plasmonic characteristics of graphene silver protective plasmonics is developed which lies in careful transfer process of CVD graphene onto freshly evaporated Ag films. By employing such as procedure we were able to protect silver from its plasmonic properties deterioration which was confirmed in the observation of minimum of SPR curve with $R = 5 * 10^{-4}$ at wavelength 435 nm and angle of light incidence of 53.5⁰. Experimental results are presented in Fig. 3.5.1 (e), (f).

3.7. Surface plasmon resonance sensitivity of graphene - protected plasmonics

Biomolecular detection with low molecular weight and slight change in local refractive index are vital characteristics of a biosensor. As it is stated in our common research work [123] that "established that graphene coatings efficiently protect plasmonic properties of copper and silver films, we have measured the sensitivity of our SPR devices to binding chemicals, which is one of the most important parameters for applications. To this end, we have chosen to use reversible graphene hydrogenation. Sensitivity to local environment (local refractive index) was also studied by utilizing glycerol-water mixtures. Fig. 3.7.1.(a) and 3.7.1.(b) show evolution of ellipsometric parameters when samples were exposed to atomic hydrogen, which led to partial hydrogenation of the graphene layer. The hydrogenation ratio was monitored by Raman spectroscopy through the ratio of the intensity of the G and D peaks [134]. The hydrogenation level after 30 min of the exposure was equal to 17% which corresponds to the areal mass density σ of adsorbed hydrogen of roughly 10 $\frac{pg}{mm^2}$ "Moreover, mass sensitivity of the graphene-protected sensor was as stated in the common work [123] " $\frac{\delta \lambda}{\sigma}$ of 0.15 nm and $\frac{\delta \Delta}{\sigma}$ approximately equals to 30 $\frac{pg}{cm^2}$ in terms of wavelength and phase measurements, respectively. Assuming a minimal detectable phase shift of 5×10^{-3} degrees we obtain the minimal detectable adsorbed mass of 0.2 $\frac{fg}{mm^2}$. This detection limit is similar to that of plasmonic metamaterials with topological darkness [134] and is 4 orders of magnitude better than the sensitivity achieved for gold based plasmonics [135]."



Fig.3.7.1.Sensitivity of copper-based surface plasmon-polaritons resonance. (a) position dependence of SPR curves on the varied level of graphene hydrogenation. (b) phase dependence of ellipsometric parameter in the case of varied hydrogenation levels. The Raman spectrum is depicted in the inset (pictures adapted from ref. [123])

3.8. Aspects of graphene copper protection for plasmonic waveguides application

As it has been shown in the common work [123] that "graphene-protected copper can also be used in complex plasmonic devices that require nanofabrication. To this end, Fig. 3.8.1(a) and 3.8.1(b) show representation and an optical micrograph of a plasmonpolariton waveguide that we have chosen as a test structure. The waveguide consists of a DLSPPW type made on top of graphene-protected copper and the coupling and decoupling gratings. We excited the waveguide by illuminating the coupling grating with a He-Ne laser (1 5632.8nm) and observed radiation coming out from the decoupling grating (Fig. 3.8.1(c)). The Fig. 3.8.1(d) shows the dependence of the transmitted light intensity as a function of the waveguide length. This yields the decay length for propagating waveguide modes of 10 mm, which suggests a strong contribution from photonic modes. While the detailed mode analysis of the fabricated DLSPPW and its wave guiding characteristics along with the excitation efficiency is still to be carried out, the fact of radiation transfer between the in and out-coupling gratings is well established (Fig. 3.8.1 (c)). It is important to mention that Cu films without graphene protection would not survive the nanofabrication procedures that take time and involve baking steps speeding up Cu corrosion."



Fig. 3.8.1.Fabricated dielectric-loaded surface plasmon-polatiron waveguide with grapheneprotected copper. (a) three dimensional representation of DLSPPW structure. (b) optical image of fabricated graphene-protected copper waveguide. (c) CCD picture of electromagnetic wave propagation along DLSPPW. (d) the intensity of transmitted light along the waveguide as function of waveguide's length (picture adapted from ref. [123])

Chapter 4

Graphene Optoelectronics

4.1. Motivation for research

Technological advancement in nanoscience makes possible the fabrication of structures with tunable optical and electro-optical properties and dimensions of hundreds or several nanometers. By using these structures it is possible to implement a control over optical and electro-optical characteristics of devices at the dimensional scale smaller than free-space wavelength of light. The efficiency of control is determined by material's spatial arrangement, nanostructuring or chemical material composition optimization. The interest in material's spatial arrangement and nanostructuring comes from their potential application in optoelectronics, integrated optical devices as well as devices with high bioselectivity to chemical groups and biological organisms.

This chapter deals with fabrication, study and modeling of graphene-based broadband and narrow band electro-optical modulators. The most important work was dedicated to fabrication of graphene-based modulator working in near-infrared range and even visible frequencies. Light modulation at around 1% was achieved at 900 nm in broadband modulator and 670 nm in narrow-band modulator. This breakthrough was made possible by novel solid state supercapacitance effect observed in HfO₂ fabricated with the use of Moorfield electron-beam evaporation system.

4.1.1. Free-space broadband graphene electro-optical modulator

Fast electro-optical modulators with small area footprints, low operating voltages, and low power consumption are in great demand by optoelectronic industry. Such modulators can be created using unique optoelectronic properties of graphene combined with high-k dielectrics. High-k metal oxides are promising materials for dielectric spacer in graphene-based optical modulators due to their electrical and optical properties, as well as their compatibility with the fabrication of CMOS devices. HfO₂ is the most promising dielectric to replace SiO₂ due to its high-k value, large band gap energy (5.68 eV) [136], thermal stability and ease of fabrication and integration. Furthermore, HfO₂ is an ionic crystal which has low potential of ionization [137]. Through strong ionic bonding and high Madelung energy, pure stoichiometric HfO₂ is stable and unlikely to engage in chemical reactions. On the other hand, graphene is increasingly being considered an extremely useful material, which can help in the creation of efficient electro-optical modulators [55, 138-145]. Graphene shows tunability of its optical conductivity by gating over a broad range of wavelengths, from mid-infrared to near-infrared [146].

Other significant advantages of graphene include its chemical inertness, mechanical stability, durability and ease of integration into optical devices. The simplicity of graphene monolayer fabrication, the possibility of direct assessment defect densities using Raman spectrometry, high transfer precision and integration with arbitrary structures, all pave the way toward graphene-based low loss electro-optical modulators. We fabricated and studied a planar electro-optical modulator where light modulation is achieved using a single layer of graphene.

The modulator itself is a simple heterostructure, consisting of a thin layer of metal (copper in our case), a HfO₂ and graphene. It possesses a small modulation volume ~ 5 μ m³ (potentially as small as $\frac{\lambda^3}{10}$), works at low gating voltages (~1-3 V), has low power

consumption (~ 1 nW), low insertion losses (<10%) and shows broadband light modulation down to a wavelength of $\lambda = 900$ nm. Our devices are CMOS compatible and could find a range of applications in the optoelectronic industry. Therefore, to the best of our knowledge, this is the first time where the operating parameters listed above have been achieved in a free space modulator with a solid dielectric [147-149].

The modulator is essentially a parallel plate capacitor where the light modulation is performed by electrical control of graphene optical conductivity via applied bias. The graphene modulator consists of a quartz substrate, a reflective copper mirror, a quarter wavelength thick high-k HfO₂ dielectric layer (the thickness *d* was chosen to be $\frac{\lambda}{4n}$, where λ is the desired working wavelength of the modulator and $n \approx 2$ is the refractive index of HfO₂ at telecommunication wavelengths) and a high quality, defect-free, mechanically exfoliated graphene monolayer.



Fig.4.1.1.1.Free space graphene-based electro-optical modulator. (a) schematic of the device. The modulator heterostructure consists of a quartz substrate, reflective copper mirror, sub-wavelength high-k HfO₂ dielectric layer and a graphene sheet. (b) microscope image of a graphene electro-optical modulator designed to operate at $\lambda = 1 \mu m$ (picture adapted from ref. [147])

As far as graphene-based electro-optical modulators fabrication is concerned, the quartz substrate was cleaned in acetone and isopropanol to ensure a clean surface and complete removal of dust particles, which could cause additional optical losses due to Rayleigh scattering. Prior to photolithography a chromium adhesion layer and the copper layer were deposited on the substrate using a Moorfield electron beam evaporator. The primary advantages of using copper as the bottom electrode are the good quality flat surface, high optical and electrical conductivity and low cost. As copper is a highly reactive material, the HfO₂ dielectric layer with quarter wavelength thickness was deposited on top of it immediately in order to protect it and increase electromagnetic fields at graphene location. The copper layer served two main functions in the operation of the electro-optical modulator , it forms a reflective metal mirror and also works as a back gate electrode for graphene electrostatic doping.

Graphene flakes were obtained from graphite by an exfoliation technique onto a SiO₂@Si substrate. Flake thickness and quality were assessed by optical microscopy and Raman spectroscopy. A polymethyl methacrylate (PMMA) layer was spin-coated onto the Si@SiO₂@Graphene structure in order to perform a wet transfer of the flake to the HfO₂ dielectric. The device was subsequently cleaned using acetone, IPA and water in order to fully remove the PMMA and any residue.

The electrical contacts to the graphene surface were made by laser-writer optical lithography, followed by chromium (2 nm thickness) and gold (30 nm) electron-beam deposition and Lift-off. During the electrical measurements it was found that the graphene flakes were p-doped, which could be explained by hydrocarbon contamination and water adsorption.

4.1.1.1. DC and AC electrical measurements

Transport properties of graphene as well as HfO₂ high-k dielectric have been tested by the use of two-probe technique. During electrical transport measurements the resistance switching processes in HfO₂ has been observed which will be discussed later in full detail. The schematic view of electrical circuit is presented in Fig. 4.1.1.1.1.(a). The DC source is connected in series to resistor R with resistance of 1 M Ω and graphene channel $R_{graphene}$ (Vg). The graphene resistance is changed by application of gate voltage across the device. The Lock-in Stanford SR830 amplifier was used to measure the voltage drop across graphene channel and Keithley 2400 SourceMeter was used as a DC source of gate voltage. The Fig. 4.1.1.1.(b) shows the dependence of graphene resistance as a function of gate DC voltage applied to the graphene-based modulator structure while Fig. 4.1.1.1.1.(c) represents HfO_2 dielectric leakage current as a function of gate DC voltage applied to the graphene-based modulator structure. In addition to this, LabVIEW program was used to acquire transport characteristics of graphene and HfO₂ electric resistance upon gate voltage sweeps from negative to positive values. While doing so, we manually changed the value of current compliance to 2µA with the help of Keithley 2400 SourceMeter. This has been done to safeguard device from breakdown and observe RRAM effects happing in HfO₂ dielectric layer. To know the capabilities of the fabricated modulators the high frequency measurements were also performed using two-probe technique. The graphene resistance with gate voltage and the gate current were measured in the usual way. Like all devices with hafnium dioxide, it showed pdoping.

(a)



Fig.4.1.1.1.Testing of transport properties of graphene-based electro-optical modulator. (a) scheme of the circuit. (b) graphene resistance as function of applied DC or AC gate voltage across the modulator structure. (c) gate current as function of applied gate voltage

4.1.1.2. DC and AC electro-optical measurements

Optical characterization of the graphene-based free-space modulators was performed using a Bruker Vertex 80 Fourier transform infrared (FTIR) spectrometer with a Hyperion 3000 microscope, operating in reflection mode. Modulators with small operational voltages have already been reported for supercapacitors, where the modulation effects were achieved with the help of an ionic liquid electrolyte. For conventional solid state dielectrics much higher voltages of around 50-150 V are usually necessary to observe modulation effects at near-infrared wavelengths. By taking advantage of the electrochemical "supercapacitor" effect observed in the HfO2 dielectric we were able to produce solid state modulators working at small operation voltages. The modulation mechanism can be explained in the following way. The change in reflectance of the devices is produced by the change in the graphene conductivity due to electrostatic doping. Interference between the incident electromagnetic wave and the wave reflected by the bottom copper mirror maximizes the optical field on the graphene layer and increases the contrast. The Fig. 4.1.1.2.1.(a) presents the results from a modulator in which the thickness of copper is 35 nm while the thickness of HfO_2 is d =156 nm. The relative reflectance $\frac{R(Vg)}{R(0)}$ is the ratio of reflectance of the modulator with an applied gate voltage V_q relative to the reflectance of the unbiased modulator. A modulation depth of 3% was obtained at the telecommunication wavelength of 1500 nm with an applied bias of 2 V. In fact, the device produces significant modulation across a large wavelength range (from $\lambda = 1200$ nm to >2000 nm). By reducing the thickness of HfO₂, the operational wavelength range of the modulator can be blue shifted. As an example, Fig. 4.1.1.2.1.(b) demonstrates light modulation in the wavelength range from 900 nm to >2000 nm for a second device, this time with a smaller thickness of HfO₂ (d = 100 nm). It should be noted that simple capacitance model for graphene gating suggests that much larger voltages are required in order to observe the measured

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modulation depths due to optical Pauli blocking (for the studied thicknesses of HfO₂). Indeed, the Fermi energy of the graphene ε_F that has central neutrality point at a gating voltage of $V_g = V_{CNP}$ can be estimated at zero temperature as

$$\varepsilon_F = \hbar v_F \operatorname{sign}(V) \sqrt{\frac{\varepsilon |V|}{4de}}$$
, (4.1.1.2.1)

where $V = V_g - V_{CNP}$, v_F is the graphene Fermi velocity, ε is the permittivity of dielectric and *e* is the electron charge.

Taking d = 100 nm and $\varepsilon = 18$ for HfO₂ at low frequencies, we obtain the gate voltage V required to achieve significant modulation at $\lambda = 1000$ nm due to optical Pauli blocking as $V = \left(\frac{\pi c}{\lambda v_F}\right)^2 \frac{4de}{\varepsilon} \approx 30$ V, which is an order of magnitude larger than observed experimentally. To elucidate the reason for the discrepancy between theory and experiment we measured the temperature dependence of the gating characteristics. The Fig. 4.1.1.2.2. shows the electrostatic gate effect on the graphene electrical resistance at low and high temperatures. These measurements were performed in a Linkam temperature controlled, liquid nitrogen cryostat at reduced pressure.

To investigate ionic conductivity in hafnium dioxide we carried out the temperature measurements. The graphene resistance measurements as function of gate voltage for different temperature regime has been investigated and the results are presented in Fig. 4.1.1.2.2.



Fig.4.1.1.2.1.Light modulation by the graphene-based heterostructures. (a) spectral dependence of the relative reflection with dielectric HfO₂ thickness d = 156 nm and gate voltages of -1 V (the blue curve) and -2 V (the red curve). (b) relative reflection spectra for d = 100 nm at gating voltages of -1 V (the blue curve), -2 V (the red curve), -3 V (the green curve). (c) and (d) results of numerical simulations based on Fresnel theory, corresponding to the spectra presented in (a) and (b) respectively (picture adapted from ref.[147])

Sweeps were made at a rate of 3 V/min, while limiting the voltage range to keep the gate current below 0.3 nA. The broadening of the $R(V_g)$ peak at low temperatures, presented in Fig.4.1.1.2.2.(a), indicates that the low values of modulation voltage are most probably connected with ionic conductivity of HfO₂. The width of the $R(V_g)$ peak increased by a factor of three when the temperature was lowered from 80°C to -80°C, which implies that the effective capacitance of the device decreased by the same order. The decrease of leakage current with the decrease in temperature, shown in Fig. 4.1.1.2.2.(b), also indicates that it is the ionic conductivity of HfO₂ that is responsible for the supercapacitance effect observed in our devices. At room (and higher) temperatures the ionic conductivity of HfO₂ is relatively large and the electrostatic doping of graphene is governed by a double layer near the graphene sheet. This results

in the "supercapacitance" effect and hence the low voltages required for optical signal modulation. However, at lower temperatures the ionic conductivity drops and gating is governed by the "normal" capacitance of the structure. Further modelling also supports the presence of a "supercapacitance" effect. The Fig.4.1.1.2.1.(c) and 4.1.1.2.1.(d) show the results of computational Fresnel modeling for our heterostructures. The optical conductivity of graphene was taken in the following form

$$\sigma = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{\hbar\omega - 2E_F}{2k_BT}\right) - \frac{i}{2\pi} \ln\left(\frac{(\hbar\omega + 2E_F)^2}{(\hbar\omega - 2E_F)^2 + 4k_B^2T^2}\right) + \frac{i}{\pi} \frac{8k_BT}{\hbar\omega + i\gamma} \ln(2\cosh\frac{E_F}{2k_BT}) \right],$$

$$(4.1.1.2.2)$$

where E_F is Fermi energy of graphene, *T* is temperature, k_B is Boltzmann constant and γ is the electron collision rate, ω is angular frequency of incident light, \hbar is Plank constant, *e* is charge of electron.

The last term in the expression (4.1.1.2.2) represents the Drude contribution to graphene's optical conductivity and it is negligible at near-infrared and visible frequencies. Using this expression, the actual experimental parameters and Fresnel theory, I have modeled the optical response of modulator. The results of fitting experimental data are shown in Fig. 4.1.1.2.1.(c) and 4.1.1.2.1.(d).



Fig. 4.1.1.2.2.Electric properties of a modulator at different temperatures. (a) Graphene sheet resistance *R* as a function of gate voltage at temperatures of - 80 °C, 0°C and 80 °C. (b) Leakage currents through HfO₂ dielectric during these resistance measurements (picture adapted from ref.[147])

From Fig. 4.1.1.2.1.(c) and 4.1.1.2.1.(d) we can conclude that in order to achieve the fit of the model to experiment, we have to assume that the chemical potential of graphene changes with gating much faster than it is predicted by a simple capacitance model. For example, in order to achieve a chemical potential of 0.5 eV in a heterostructure with d=100 nm (it is required to observed the measured level of modulation) one would need to apply a gate voltage of 18 V, whereas experimental data suggest that this value is reached at V_g = -2 V.

One of possible explanations to this phenomenon is electrochemical supercapacitance effect in HfO₂ dielectric. This is a novel effect which was not thoroughly studied in literature except a handful of works. For example, authors of paper [150] were also able to obtain significant light modulation and enhanced charge doping effect of graphene by utilizing free space-modulator with embedded high permittivity dielectric Ta₂O₅ [150]. The enhanced graphene charge doping effects and its optical absorption is due to the electrochemistry processes taking place inside high-k dielectrics which are triggered by applied DC and AC electric fields.

To explain the supercapacitance effect, let us consider a simple parallel plane capacitor structure of graphene-based modulators which can also be treated as typical configuration of random access memory cell, so-called memristor. It has already well established [95] that data storage in the resistance memory cells is implemented as the reversible switching effect of dielectric properties from high to low electric resistance state by the influence of electric current impulse. However, the practical use of high-k metal oxides in devices is faced with several difficulties the main of which is uncontrollable and unacceptable high electrical conductivity. The high electrical conductivity of real dielectric layers is caused by high concentration of insulator's native defects. The defects in high-k dielectrics namely in HfO₂, Ta₂O₅, ZnO, TiO₂ etc. play the crucial role during the device operation. Defects can create localized states in the dielectric's band gap which can significantly influence its transport properties [151]. For resistive memory cell, the state with low resistance corresponds either to state with high defect concentration or specific spatial arrangement of defects. These days, the most discussed model of the resistive memory effect is based on the formation/dissociation of conductive filament in high-k dielectrics. According to theoretical calculations presented by the authors [152, 153], oxygen vacancy (V_o) and oxygen interstitials (O_i) are the main defects present in HfO₂ as well as other high-k insulators like TiO₂, Ta₂O₅, CrO_x. The oxygen vacancies can act as trap centers for charges and are responsible for the high dielectrics electrical conductivity.

Usually, the point defects in a crystal are either Schottky or Frenkel defects. According to Frenkel point of view, under the influence of heat fluctuations ions might get sufficient energy to leave its place in the lattice and jump out into an interstitial site within the crystal. Subsequently such interstitial ions continue jumping from one interstitial site to another until it founds a vacancy site where it fixes at the lattice site again. Another way of this defect formation is interstitial atom migration when an atom does not jump from one interstitial site to another but pulls out adjusting atom, which sits in the lattice site, into interstitial position and jumps into its lattice site. This migration will lead to atoms positions interchange and hence lead to the diffusion processes. According to the mechanism of Schottky defects, ionic crystals have equal concentration of anion and cations vacancies but the absence of interstitials ion sites. Those defects usually formed at the crystal surface and at the region of grain boundaries, dislocations and pores. It should be mentioned that there are two types of Schottky defects: cation and anion vacancies as a results of which the dipole layer formation take place at the interface of defects. Namely, these layers are composed from

positively charged uncompensated cations on the crystal surface and at the same time uncompensated negatively charged cation vacancies at the surface interface of the crystal. The best way to deduce what kind of defects (Schottky or Frenkel) is most probable to be presented in the crystal, it is necessary to compare the values of Gibbs free energy of these defects formation [154, 155]. In usual the defect formation in the crystal leads to crystal structure disorder and therefore to its entropy increasing

$$S = k_B \ln W$$
, (4.1.1.2.3)

where *S* is entropy, k_B is Boltzmann constant and *W* is thermodynamic probability showing the number of possible ways that can be implemented to achieve the state of a system.

In the case of Schottky defects, vacancies concentrations are determined as

$$n_s = N \exp\left(\frac{-\Delta H_s}{2k_B T}\right),\tag{4.1.1.2.4}$$

where N is number of lattice sites, ΔH_s is enthalpy change of the system, k_B is Boltzmann constant and T is temperature.

As far as Frenkel defects are concerned, the vacancies concentration is defined as:

$$n_F = \sqrt{NN} \exp\left(\frac{-\Delta H_F}{2k_B T}\right), \qquad (4.1.1.2.5)$$

where N is number of lattice sites, N' is number of interstitials sites presented in the crystal, ΔH_s is enthalpy change of the system, k_B is Boltzmann constant and T is temperature.

As it has been pointed out by experimental results [156, 157] and theoretical calculations [158], in most metal based high-k dielectric metal oxides the oxygen anions and positively charged oxygen vacancies thought to be the mobile species. Furthermore, it has been stated by the colleagues from our research group of Manchester University in their article that the oxygen vacancies are responsible for conductive filament formation inside Cr_2O_3 dielectric [159].

According to the authors [160], the ion percolation pathways inside high-k dielectrics are defects such as grain boundaries [161-163] and dislocations [164] which possess low diffusion energy for ions migrations. Due to the applied gate bias across high-k dielectric, which has the thickness of hundreds of nanometers, the formed high electric field inside the dielectric is capable significantly accelerate ions and vacancies drift velocity due to their drift velocity exponential dependence as function of electric field

$$v = \mu E \exp\left(\frac{E}{E_0}\right),\tag{4.1.1.2.6}$$

where v is drift velocity of mobile species, μ is ionic mobility, E_0 is characteristic field of mobile charge, E is electric field inside high-k dielectric.

Once the gate voltage is applied across dielectric, the defects inside high-k insulator can be formed due to impact ionization process [165] and oxygen ions and vacancies generation can be described according to the following formula

$$0_o \to V_o^{2+} + \ 0_i^{2-}, \tag{4.1.1.2.7}$$

where O_o represents oxygen atom in the lattice, O_i^{2-} corresponds to interstitial position of oxygen ion in HfO₂ crystal and V_o^{2+} is oxygen vacancy site in the crystal lattice.

Therefore, due to an application of high electric field accompanied by Joule heating the positively charge oxygen vacancies migrate towards the cathode (graphene layer). Since graphene possess impermeability properties [132, 133], the positively charge oxygen vacancies accumulates nearby graphene interface forming positive space charge layer as stated at paper [166]. As graphene is grounded there is formation of double layer between HfO₂@Graphene interfaces.

Meanwhile, as stated by authors [160], the oxygen ions move to anode where happens oxidation reaction with the oxygen bubbles production according to the following reaction

$$O_i^{2-} \to 2e + \frac{1}{2}O_2 \uparrow,$$
 (4.1.1.2.8)

where O_i^{2-} is interstitial position of oxygen ion in HfO₂ crystal, *e* is electron charge and O_2 is gas oxygen production in the crystal.

As a result, the bubbles can be observed at the anode electrode. The authors of [102, 167] presented experimental results of verification of oxygen ions and vacancies migration and gas bubbles formation in high-k dielectric TiO₂. We also observed the formation of bubbles at large voltages applied across hafnium dioxide layer presented in Fig. 4.1.1.2.3.



Fig.4.1.1.2.3.Optical images of graphene-based Fabry-Perot electro-optical modulator with the structure $Cu@HfO_2@Graphene@HfO_2@Cu@Cr@Quartz.$ (a) and (b) displays the optical images of the device in reflection and transmission mode directly after fabrication in its initial state whereas (c)-(d) represents the appearance of the Fabry-Perot graphene modulator in reflection and transmission mode after the electro-optical measurements with the applied range of gate voltage from -3V to +3V, the value of dielectric leakage current was 1 mA. The emergences of bubbles at the anode surface are clearly seen at the optical images either in reflection or transmission mode

To elucidate the origin of the bubbles and whether its emergence due to the electrode presence rather than high-k dielectric HfO₂ the additional sample which presents the parallel plate capacitor with configuration Graphene@HfO₂@Graphene@Quartz has been fabricated. Graphene layers serves as electrodes to apply gate voltage across the high-k dielectric HfO₂. Fig.4.1.1.2.4. portrays the view of the parallel plate capacitor after electrical measurements.



Fig.4.1.1.2.4.Optical image of parallel plate capacitor with the structure Graphene@HfO₂@Graphene@Quartz where graphene layers represents electrodes to investigate the dynamics of HfO₂ dielectric. The value of applied gate voltage is 6 V. After electrical measurements the formation of bubbles on the graphene electrode is clearly observable

Thus, it has been experimentally shown that the bubbles appearance on the electrode surface originates due to physico-chemical process taking place inside high-k insulator HfO₂. The presence of bubbles provides an important argument in favor of ionic transport mechanism for explanation the supercapacitance effect observed in evaporated HfO₂. Another argument in favor of ionic transport mechanism comes from appearance of electrically conductive filaments in our devices at some large gating voltages (Fig.4.1.1.1.1.(c)) where one can observe large jumps in electrical resistance across gating dielectric at gating voltages of 3 or 4 Volts which can be recovered at smaller voltages and are connected with the appearance of electrically conductive filaments.

The Hall measurements is very useful technique to verify the polarity of charges by which graphene is doped. Apart from that, transmission electron microscopy (TEM) or scanning transmission synchrotron X-ray spectroscopy (STMX) is useful and powerful techniques to research in-situ and in-operando conditions the electrically conductive filament formation in metal oxide high-k dielectric HfO₂.

It is well known that dielectrics that possess mobile ions can produce electrically conductive filaments with low electric resistance. For example, Fig.4.1.1.2.5 shows the results of in-situ electrical measurements of electrically conductive filament formation in high-k dielectric of ZnO being encapsulated between two Pt electrodes. BE and TE attributes to the top and bottom electrodes in the work [168].



Fig.4.1.1.2.5.In-situ TEM measurements. (a) – (e) recording the dynamic growth of electrically conductive filaments inside high-k dielectric ZnO. (f) - (j) represents the evolution of dielectric leakage current through the insulator as function of voltage and time. BE and TE attributes to the bottom and top electrodes (picture adapted from ref. [168])

Direct observation of resistance switching effects due to oxygen movement in HfO_2 has been experimentally verified using scanning transmission synchrotron X-ray spectromicroscopy by the research group of R. Stanley Williams [169]. Here, using scanning transmission synchrotron X-ray spectromicroscopy (STMX) to study in-situ switching dynamics of HfO_2 memristors, the group directly recorded the formation of a localized oxygen-deficient and electrically conductive channel encircled by an area of low- conductivity ring of oxygen excess.



Fig.4.1.1.2.6.Ionic conductivity of HfO_2 . (a) current–voltage dependence representing the electric resistance switching phenomena in HfO_2 dielectric. (b)-(c) x-ray spectromicroscopy spectra of oxygen ions and vacancies agglomeration inside HfO_2 during the electrical measurements, TE is the top Pt electrode, BE is the bottom Pt electrode. (d) x-ray absorption spectra taking from the region of ring shape representing the concentration of oxygen ion on and insige the formed ring region. (e) representation of band gap level inside the ring and on the ring region (picture adapted from the ref. [169])

By employing transmission synchrotron X-ray spectromicroscopy [169] it has been possible to research the chemical as well as positional changes associated with oxygen atoms motion inside HfO₂ dielectric during its electrical switching operation from high to low electric resistance state. By utilizing STMX, the group has performed the chemical composition characterization using reference sample, which was freshly grown HfO₂ and the one which has been subject to electrical switching operation of HfO₂ based memristor. The Fig.4.1.1.2.6.(a) represents the current-voltage dependence of memristor cell after one cycle of electrical measurements. After this, the group applied STMX to image the cell after its electrical operation and two distinct features have been observed.

It has been shown that inside the dielectric there is formation of dark ring area encircled by bright area. Spectra have been taken from dark as well as bright regions to identify the chemical compositions of those areas. It has been shown and identified by authors [169] that STMX spectra received from dark ring area corresponds to higher concentration of oxygen while the spectra produced from bright center inhibited lower oxygen concentration and the both spectra were taken relative to the spectra of grown layer of HfO₂. As stated by R. Stanley Williams [169] the oxygen deficient region has been attributed to oxygen vacancies the presence of which leads to the formation inside dielectric band gap the sub-gap defect states which are responsible for dielectric electrical conductivity (Fig.4.1.1.2.6.(e)). Whereas it has been pointed out that dark ring area has been discerned as the oxygen abundant area with spectral signatures attributed to interstitial oxygen [169]. Hence after the HfO_2 electrical forming process there is formation of oxygen abundant and oxygen depleted regions which are due to the effects of applied electric field, charge and temperature concentration gradient, propagate inside dielectric. As graphene is impermeable to gases at the interface between graphene and HfO₂ there is formation of surface charge layer, the charge carriers of which are accumulated [166] during the applied electric field action across HfO₂. Therefore, the experimental results of the R. Stanley William's research group [169] support our hypothesis about the formation of double layer at the interface between HfO₂@graphene.

Alternative explanations of the experimental results and low voltage operation of our devices can be found in the rough surface of HfO_2 combined with the graphene transfer process, which includes the graphene interaction with water and organic compounds. Hence, during the graphene transfer protocols the water or organics may be trapped between the rough surface of HfO_2 (Fig.4.1.1.2.7) and graphene, which may form a double layer that enhances graphene doping during the electro-optical experiments with the water or other organic compounds providing supercapacitance effect.



Fig.4.1.1.2.7.Atomic Force Microscopy 3D image of the surface of fabricated dielectric HfO_2 produced by electron-beam deposition system. Thickness of dielectric HfO_2 is 85 nm with the grain sizes of about 10 nm in diameter

4.1.2. Fabry-Perot graphene-based narrowband electro-optical modulator

As stated in Chapter 1, graphene has a constant optical absorption of 2.3% from midinfrared to the visible wavelength range of the electromagnetic spectrum [46], which arises from its interband optical transitions and can be actively controlled by electrical field gating. Namely, graphene optical absorption can be switched on and off by the gate-tunable change of Fermi level position below which the Pauli blocking effect takes place, leading to graphene becoming transparent to the incident electromagnetic wave [170]. Even though the optical absorption of 2.3% is high enough for one single atomic layer, it is not sufficient for most optoelectronic devices applications as most of the incident light still will be transmitted. To overcome this bottleneck, the different modulator configurations have been proposed that allow enhancing graphene lightmatter interaction and achieve substantial graphene charge carrier doping via electrical gating. The proposed modulator's configuration was based on the use of structured graphene stacks [171], hybrid graphene plasmonic heterostructures [172] and coupling graphene to smart planar photonic cavities or waveguides [139, 144, 145, 173, 174]. Nonetheless, little progress has being made so far to realize graphene-based electrooptical modulators possessing large depth of light modulation under small gate voltages application at the near-infrared and visible spectrum regime by the use of solid state dielectrics. This realization is very challenging since it requires large electric field capable of changing graphene's optical absorption, which is at the range of insulating properties breakdown of the dielectric.

To achieve modulation of graphene's optical absorption in the near-infrared ($\lambda = 1.5 \mu m$) or even in the visible ($\lambda = 0.7 \mu m$) wavelength ranges necessitates the use of either high quality high-k dielectrics or ionic liquids [149, 175]. However, modulators based

on the use of ionic liquids usually have a slow speed of response, which is not suitable for high frequency electro-optical modulators for on-chip interconnect.

This chapter of dissertation presents the novel results for optoelectronic community where with the use of HfO₂, fabricated through electron-beam deposition technique, it was possible not only perform graphene gating with small gate voltages but also obtain high depth of light modulations in reflection and transmission modes at wavelengths $\lambda = 1.5 \,\mu\text{m}$, 1.1 μm and even 0.7 μm .

The proposed in dissertation novel benchmark for graphene-based electro-optical modulators is based on Fabry-Perot configuration. Due to multiple reflection of light inside the optical cavity the graphene light-matter interaction substantially increased giving rise to the possibility to amplify the modulation effect. Moreover, the utilization of high-k dielectric HfO₂ allows achieving high electrostatic doping of graphene. In my work, I employed thin metal films working both as reflector mirrors for Fabry-Perot resonator and the gate electrodes. This geometry has an advantage of the ability of simultaneously electrostatically gate graphene from top and bottom electrodes thus maximizing the modulation effect.

The schematic representation of graphene-based electro-optical modulator is depicted in Fig. 4.1.2.1. The modulator constructed with the metal electrodes, high-k HfO₂ dielectric with the thickness $\frac{\lambda}{4n}$ where λ is working wavelength of the modulator and *n* is refractive index. The graphene is positioned at the center of the optical cavity thus being fully encapsulated by HfO₂ layers. To provide electrical contacts to the graphene surface to perform subsequent electric and electro-optic measurements, graphene was contacted by the gold electrodes at its edges. By specifically optimizing the thickness of bottom metal electrode, the modulator can work both in reflection and transmission modes or if the thickness of bottom metal electrode designed to be thicker the device functions only in reflection mode.



Fig. 4.1.2.1.Schematic representation of graphene-based electro-optical modulator. (a) two dimensional image of the device which comprises from quartz substrate, metal electrodes, high-k HfO_2 dielectric layers which fully encapsulate the single layer of graphene. On the sides, graphene is contacted by gold electrodes in order to record graphene electric resistance change upon applied gate voltage to the modulator. (b) three dimensional display of the modulator with the representation of the applied gate voltage polarity to the metal electrodes and graphene layer

Fabry-Perot graphene-based modulator fabrication begins with quartz substrate cleaning with Acetone and IPA followed by electron-beam deposition of thin film layers of metals and dielectrics. Applying the shadow mask, I first deposited the adhesion layer of Cr with the thickness of 1.5 nm followed by Cu, Ag, or Au metal deposition. If the modulator was comprised from Cu or Ag gate electrodes, thin layer of HfO₂ with the thickness of 10 nm has been deposited on top of Cu or Ag before evacuating the samples out of evaporated chamber to prevent their oxidation and properties

(b)

degradation. Having performed this step, I covered the sample accurately by wide Teflon based shadow mask to deposit the required thickness of HfO₂.

The CVD graphene was originally grown onto the copper foil. To etch the copper, at first the layer of polymethyl methacrylate (PMMA) was spin-coated on top of graphene layer to guarantee its support for further wet transfer procedure. Then, copper base sheet was etched in a solution of ammonium persulfate and the obtained floating membrane of graphene-PMMA has been positioned into deionized water for couple of hours to clean it. Afterwards, graphene-PMMA membrane has been transferred onto the device followed by it baking at 170 °C for 10 min to promote graphene adhesion to dielectric HfO₂ surface. Once it has been accomplished, layer of PMMA was obviated in acetone accompanied by the device rinse into IPA.

Photolithography process with electron-beam deposition of Au and Cr has been performed to make contacts to the edges of graphene. The negative tone photoresist was exploited to define the geometry of the active device area with CVD graphene. The rest part of the CVD graphene was eliminated by the use of Ar:O₂ plasma etching.

Top HfO₂ layer was deposited directly afterwards on top of the area with CVD graphene while the area with gold contacts was covered by Teflon shadow mask. Top gate electrode was fabricated using photolithography procedure followed by Cu or Ag thin film deposition. Additional layer of HfO₂ with the thickness of 10 nm was deposited thereafter on top of Cu or Ag top electrode. Having performed these steps, the Lift-off procedure has been performed.

The optical spectra were measured with Bruker HYPERION Fourier transform infrared (FTIR) microscope. Results from the graphene-based electro-optical modulator that operates at telecommunication wavelength 1.55 μ m are depicted in Fig. 4.1.2.2. The modulator was optimized to work in reflection mode by choosing the bottom thickness of Cu electrode to be equal to 70 nm while the thickness of top Cu electrode was 30 nm. The electro-optical spectra show the modulation depth in reflection mode of 20 % with applied gate voltage from -1V till -3V.

(b)

(a)

1,1 1,1 1,0 1,0 0,9 0,9 Reflection 0,4 eV Reflection 0,8 0,8 0,7 0,7 0,6 0,6 ν -2 V 0,5 0,5 -2 V -3 V 0.7 e\ -3 V 0.4 0,4 1700 1400 1450 1550 1600 1500 1650 1400 1450 1500 1550 1600 1650 1700 Wavelength,nm Wavelength,nm (c) (d) Relative change in reflectance 1,10 1,10 Relative change in reflectance 1,05 1,05 1,00 1,00 0.4 e\ 0,95 0,95 0,90 0.5 eV 0,90 0,85 ν 1V 0,85 -2V 0,80 -2 V 0,7 eV -3 V -3V 0,80 0,75 1550 1600 1650 1700 1550 1600 1700 1400 1450 1500 1400 1450 1500 1650 Wavelength (nm) Wavelength,nm

Fig. 4.1.2.2.Effect of graphene electrostatic gating on the shift of cavity resonance wavelength position. (a) raw experimental data of amplitude of light reflection from gated graphene modulator. (b) computational simulation results in the case of absolute value of light reflection from the gated device and associated with this the value of Fermi energy change. (c) experimental data for relative change in the amplitude of light reflection from the gated device. (d) computational simulation results representing the relative change of amplitude of light reflection form the gated device.

As graphene is electrostatically gated, the Fabry-Perot cavity resonance is modified. This is due to graphene complex dielectric permittivity dependence on the applied gate voltage as [176]

$$\varepsilon(\omega) = 1 + \frac{i\sigma_{total}(\omega)}{\varepsilon_0 \,\omega \, d_{graphene}}, \qquad (4.1.2.1)$$

where ε_0 is free space dielectric permittivity, ω is angular frequency of light and $d_{graphene}$ is thickness of single layer graphene which is 0.335 nm.

$$\sigma_{total}(\omega) = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{\hbar\omega - 2E_F}{2k_BT}\right) - \frac{i}{2\pi} \ln\left(\frac{(\hbar\omega + 2E_F)^2}{(\hbar\omega - 2E_F)^2 + 4k_B^2T^2}\right) + \frac{i\,8k_BT}{\pi\hbar(\omega + i\gamma)} \ln\left(2\cosh\left(\frac{E_F}{2k_BT}\right)\right),$$
(4.1.2.2)

where E_F is Fermi energy of graphene, *T* is temperature, k_B is Boltzmann constant and γ is the electron collision rate, ω is angular frequency of incident light, \hbar is Plank constant, *e* is electron charge.

While graphene layer being electrostatically doped, its Fermi energy is changed due to the charges population as [176]

$$E_F = \hbar v_F \sqrt{\pi n}, \qquad (4.1.2.3)$$

where E_F is Fermi energy, \hbar is Plank constant, v_F is Fermi velocity which we take as $10^6 \frac{m}{s}$ and n is charge carrier density.

In a simple parallel capacitor model the charge carrier density can be calculated as [176]

$$n = \frac{k \varepsilon_0}{D \ e} V_{gate} , \qquad (4.1.2.4)$$

where k is relative dielectric permittivity of HfO₂, ε_0 is free space dielectric permittivity, D is the dielectric thickness of HfO₂, e is electron charge and V_{gate} is gate voltage.

As graphene Fermi energy changes its complex dielectric permittivity alters so as its optical conductivity. As graphene complex dielectric permittivity changes so as its

complex refractive index modifies which according to the mathematical model used and already discussed in Chapter 3.2 of this PhD thesis, leads to the optical response in reflection and transmission coefficients changes upon graphene gating. Consequently, the cavity resonance wavelength positions modifies and changes dramatically until graphene is sufficiently doped and Pauli blocking condition is reached as stated in [170, 176]. The character of this change is depicted in Fig. 4.1.2.2., where the simulation results are presented alongside with experimental data.

As presented in the research work [176], the results from another device operating around 1.1 µm wavelength both in transmission and in reflection regimes are shown in Fig. 4.1.2.3 (a), (b). In this case, the HfO₂ thickness was d = 100 nm, the top gate was gold (d = 30 nm) while the bottom gate was copper (d = 30 nm). In reflection mode, the modulation depth equals to 13% whereas in transmission mode the modulation depth grows to 28%. Finally, properties of the device operating around 830 nm are represented in Fig. 4.1.2.3 (c)-(e). The HfO₂ thickness was d = 70 nm and both gates were made from thin silver layer with d = 30 nm. In the devices operating in the transmission mode, the Fabry-Perot cavity acts as a band pass filter. When illuminated with white light, all the light waves in the transmission band are modulated. Thus, in this device, it was possible to observe the modulation in images taken with a silicon charge-coupled device (CCD) sensor using broadband illumination.



Fig.4.1.2.3.Characteristics of Fabry-Perot modulators. (a) relative change in reflectance of the device designed for reflection at 1.1 μ m for different gate voltages relative to 0 V (schematic view of the device operation is depicted at the inset). (b) relative change in transmittance of the device designed at 1.1 μ m for different gate voltages relative to 0 V (schematic view of the device is shown in the inset). (c) reflection and transmission of electromagnetic waves with the modulator working at the 830 nm wavelength. (d) CCD camera image taken in transmission regime. (e) maximum change in transmittance when the top and bottom gates voltage is modulated with a 2 Hz sinusoidal signal from -4 V to 4 V (picture adapted from ref. [176])

As it is stated in the common research work [176] "the frequency characteristics of fabricated graphene-based electro-optical modulators were studied by applying a sinusoidal signal to the gate (up to 1 MHz) and measuring the reflectance of a laser diode beam of 1571 nm wavelength (Fig. 4.1.2.4 (a)). The device reflectance followed the 1 MHz signal, although the voltages required to achieve strong modulation depth are higher than in the slow measurements. On the other hand, no damage in the device was observed after applied to it high gate voltages with high frequency. The modulated optical output changes from a 180° phase-shifted signal at 0 V offset to a double frequency signal at -0.6 V and to a signal with much bigger amplitude and the same phase as the excitation voltage at -1.2 V offset. The modulation depth reached 40% in this latter case. The fast rise and decay in the modulation obtained with a square signal of 14 V peak-to-peak and -0.9 V offset (Fig. 4.1.2.4 (b)) demonstrates that the speed of

response of the device can in fact be much higher and we were only limited by our measurement system. In Fig. 4.1.2.4 (c) presented the reflectance curve obtained with slow changes of the gate voltage." Furthermore in this common research work is explained that "superposed onto the experimental results, we also present the numerical simulation of the reflectance at the estimated Fermi energy. If we compare the traces in Fig. 4.1.2.4 (a) with the reflectance curve in Fig. 4.1.2.4 (c) it becomes evident why the gate voltage offset is a determining factor for the modulation. At 0 V offset, the modulation happens around 0.3 eV, with the negative slope of the reflectance curve giving the 180° phase shift. At - 0.6 V offset, the modulation happens around the peak in the reflectance curve at 0.4 eV, producing the double frequency response. Finally, at -1.2 V offset the modulation happens in the positive and steeper slope which yields the strongest modulation. To show that our devices can operate close to the visible region, the modulation of a white light source by the device is provided in Fig.4.1.2.4 (c). The electrical signal applied was a 2 Hz sinusoidal function with 8 V peak-to-peak and 0 V offset. The modulation in this case primarily arises from the slow mechanism, with the double frequency asymmetric response stemming [88] from the alternating movement of the Fermi energy to both sides of the charge neutrality point."



Fig.4.1.2.4.As stated in ref. [176] the high frequency modulation response of the fabricated modulator . (a) modulation of the reflectance at wavelength 1571 nm for the device designed to operate at telecommunication wavelength (Fig. 4.1.2.2). A 1 MHz sine function of 16 V peak-to-peak amplitude with different voltage offsets is applied to the gate. The reflectance curves are normalized to the reflectance for zero gate voltage and are shifted in the vertical axis for clarity. (b) modulation with a square signal. (c) black curve: normalized reflectance as a function of the gate voltage. gray curve: numerical simulation of the reflectance as a function of the estimated Femi energy. blue, green and red regions indicate the estimated regions of modulation of the similarly colored traces in (a) picture. Inset: numerical simulation of the change in reflectance as a function of the fabricate as a function of the Fermi energy and the wavelength. (d) modulation of the transmittance of white light (filtered by the 830 nm resonance) in the device from Fig. 4.1.2.3. A 2 Hz sine function of 8 V peak-to-peak amplitude is applied to top and bottom gates (picture adapted from ref. [176])

Thesis Summary

In the thesis, it was established that graphene-protected copper is a viable alternative to the conventional noble metals in plasmonics applications. It is relatively cheap, stable and reproducible and high-quality plasmonic material that is suitable for nanofabrication and which is CMOS compatible. The graphene-protected silver provides an exciting opportunity for applications which require low plasmonic losses. With the current rapid progress in CVD growth of hexagonal boron nitride and other 2D crystals, I envisaged that they can also be used as a quality protective coating for plasmonics.

I performed theoretical modeling, fabricated, characterized and tested simple, efficient and low-loss graphene-based electro-optical modulators working at near-infrared wavelengths. A modulation depth of 3 % was achieved at $\lambda = 1.5 \,\mu\text{m}$ (and 1.5 % at $\lambda = 1$ μm), with gate voltages of just a few volts applied to the graphene heterostructure. The unexpected supercapacitance effect observed in the high-k HfO₂ gate dielectric allowed me fabricate extremely simple free space, CMOS compatible, telecom modulators with significant electro-optical modulation effect, low power consumption and small modulation volume. This "supercapacitor" effect could be useful for other optoelectronic applications.

Finally, the Fabry-Perot geometry comprised of metallic mirrors and HfO₂ separators allowed to construct efficient graphene-based electro-absorption modulators with modulation depth of 30 %. By harnessing the "supercapacitor" effect found in HfO₂, electro-optical modulators working at small voltages and at wavelengths approaching the visible range of spectrum have created. Although the strong modulation response observed with small gate voltages is relatively slow, as it happens also with other electrolyte gated devices, it can be used to shift the Fermi level close to the desired energy range with DC voltage. The plane parallel capacitor structure permits to
accomplish modulation at higher frequencies. The device area can be reduced down to a diffraction limited laser spot, which would reduce the high frequency capacitance and allow extremely high operation speed. With additional optimization, our devices should also be able to modulate light at visible frequencies.

The obtained research results have been presented on the following scientific conferences:

- Ansell D., Thackray B., Aznakayeva D. E., Thomas P., Auton G. H., Marshall O. P., Rodriguez F. J., Radko I. P., Han Z., Bozhevolnyi S. I., Grigorenko A. N., Hybrid graphene plasmonic waveguide modulators, Proceedings of SPIE Conf., Synthesis and Photonics of Nanoscale Materials XIII, 97370B, San Francisco, California, United States, 2016.
- Aznakayeva D. E., Rodriguez F., Marshall O., Grigorenko A. N., Graphenebased electro-optical modulator operating at telecommunication wavelength range, Conf. Proceedings, 2nd International Conference on Smart Materials & Structures, Philadelphia, Pennsylvania, USA, 2016.
- 3) Aznakayeva D. E., Rodriguez F., Marshall O., Grigorenko A. N., Graphenebased electro-optical modulator operating at telecommunication wavelength range, Conf. Proceedings, 3rd Annual International Conference on Optoelectronics, Photonics & Applied Physics, Singapore,2016- I have been granted with "Best Student Research Paper".
- Kravets V.G., Grigorenko A.N.; Aznakayeva D.E.: Graphene-based active plasmonic metamaterilas: Poster presentation, Postgraduate Summer Research Showcase organized by Manchester Doctoral College, Manchester University, UK, 2014.

List of Publications:

- Aznakayeva D. E., Rodriguez F. J., Marshall O. P. and Grigorenko A. N., <u>Graphene light modulators working at near-infrared wavelengths</u>, Optics Express, 25 (9), 2017, pp. 10255-10260.
- Rodriguez Francisco J., Aznakayeva Diana E., Marshall Owen P., Kravets Vasyl
 G., Grigorenko Alexander N., <u>Solid-state electrolyte gated graphene in optical</u> <u>modulators</u>, Advanced Materials, **29** (19), 2017, pp. 1-6.
- Ansell D., Thackray B., Aznakayeva D. E., Thomas P., Auton G. H., Marshall O.
 P., Rodriguez F. J., Radko I. P., Han Z., Bozhevolnyi S. I., Grigorenko A. N., <u>Hybrid graphene plasmonic waveguide modulators</u>, Proceedings of SPIE Conf., Synthesis and Photonics of Nanoscale Materials XIII, 97370B, San Francisco, California, United States, 2016, pp. 97370B-1-97370B-13.
- Aznakayeva D. E., Rodriguez F., Marshall O., Grigorenko A. N., <u>Graphene</u> <u>based electro-optical modulator operating at telecommunication wavelength</u> <u>range</u>, Conf. Proceedings, 2nd International Conference on Smart Materials & Structures, Philadelphia, Pennsylvania, USA, 2016, p.53.
- Aznakayeva D. E., Rodriguez F., Marshall O., Grigorenko A. N., <u>Graphene</u> <u>based electro-optical modulator operating at telecommunication wavelength</u> <u>range</u>, Conf. Proceedings, 3rd Annual International Conference on Optoelectronics, Photonics & Applied Physics, Singapore, 2016, pp.20-23. I was honored with the title of Best Student Research Paper.
- Kravets V. G., Jalil R., Kim Y.-J., Ansell D., Aznakayeva D. E., Thackray B., Britnell L., Belle1 B. D., Withers F., Radko I. P., Han Z., Bozhevolnyi S. I., Novoselov K. S., Geim A. K. & Grigorenko A. N., <u>Graphene-protected copper</u> and silver plasmonics, Scientific Reports, 4, 2014, pp. 1-8.

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