

Graphene based plasmonic photodetection

Viktoryia I. Shautsova

Supervisors: Prof. Stefan A. Maier, Prof. Lesley F. Cohen, Dr. Rupert F. Oulton

A thesis submitted to Imperial College London for the degree of
Doctor of Philosophy

Experimental Solid State Group (EXSS)
Department of Physics
Imperial College London
London SW7 2AZ

September, 2017

"There is no easy way from the earth to the stars"

— *Seneca*

Declaration of Originality

I hereby declare that to the best of my knowledge, the content presented in this thesis is my own. I certify that I appropriately acknowledged and referenced the work of others. In particular, the nanoparticles used in Chapter 5 were fabricated by Adam Gilbertson and Tyler Roschuk; the differential reflection (DR) measurements of graphene/plasmonic nanoparticle complexes reported in Chapter 5 were performed in collaboration with Adam Gilbertson; the theoretical calculations of the DR signal presented in Chapter 5 were done in collaboration with Yan Francescato and Dr. Rupert Oulton; the FTIR spectra reported in Chapter 5 were partially measured by Nicola Black; the idea of the device with asymmetric plasmonic contacts discussed in Chapter 6 was suggested by Adam Gilbertson; the optical set up for the time resolved experiments was built by Themistoklis Sidiropoulos and Adam Gilbertson.

Viktoryia Shautsova

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-Commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Abstract

Graphene is a promising material for novel photonic devices due to its broadband optical absorption, ultrafast carrier dynamics and electrical tunability. However, the quantum efficiency of graphene devices is intrinsically limited by low absorption of graphene (2.3% of normal incident light). To enhance light-matter interaction, optical focusing elements such as plasmonic metal nanoparticles (NPs) can be utilized. This thesis examines the interaction between graphene and plasmonic NPs with special emphasis on mechanisms of enhanced photocarrier generation, which is further applied to improve photodetection efficiency of graphene plasmonic hybrid devices.

In order to study graphene based devices, CVD graphene must first be transferred from the Cu growth substrate to a target substrate. To this end, various parameters of a transfer technique were studied focusing on the source of extrinsic doping. Next, a novel transfer process based on an hBN spacer layer between graphene and a polymethyl-methacrylate film was developed to facilitate large scale CVD graphene transfer and encapsulation. The demonstrated devices showed improved electrical and aging properties.

Following successful demonstration of the transfer technique, graphene was combined with gold NPs to study structural and optical properties of these complexes. Using ultrafast measurements, carrier dynamics of the hybrid structures were analysed focusing on hot carrier generation under plasmon excitation. Based on the observed results, hot carrier generation in the graphene was attributed to direct photoexcitation through the intense plasmonic electromagnetic fields with a minimal contribution from charge transfer over the graphene/NP interface. Furthermore, highly localised carrier heating in graphene is anticipated to result in strong electronic temperature gradients. Asymmetric plasmon-nanobar electrical contacts were designed with a view to exploit plasmon-induced electronic temperature gradients via the thermoelectric effect.

The findings of this work lead to improved knowledge of the internal graphene photodetection mechanisms as well as contributing to the understanding of graphene/plasmonic hybrids and their interactions.

Acknowledgements

First and foremost, I would like to thank my supervisors Prof. Lesley Cohen, Prof Stefan Maier and Dr. Rupert Oulton, who have given me this great opportunity to carry out my PhD and fulfil my passion to study nanoworld. Their supervision with constant support and valuable feedback has helped me to develop professionally and to become a more complete scientist. I am very grateful for their patience reviewing my thesis and endless versions of the papers. Additionally, I would like to thank them for giving me great opportunities to learn new things with all the fabulous equipment available and to visit conferences and workshops.

Next, I would like to give a special thank you to Dr. Adam Gilbertson, who has helped and supported me a lot at the beginning of my PhD, which has ensured my quick progress in the topic. His input has been invaluable and had a very important effect on the direction of my research. I am very grateful for his support and scientific discussions after leaving, which greatly helped me during some dark times of my PhD path.

I am very thankful to Nicola Black for everything. It has been great pleasure working with her in the labs and discussing our results and progress over coffee and worshipping the Graphene God :)

Of course, great thanks to Michael Nielsen and Themis Sidiropoulos for all their help and advice on both experimental and personal matters. My ultrafast experiments would not have been so fun without their input.

I consider myself a very lucky person since I have had an opportunity to be part of truly great scientific groups, EXSS and plasmonics groups. To thank everyone individually would probably result in a book as long as this thesis. Without their help, training, valuable discussions and endless tips my research would have been a real struggle. Additional thanks to Material department group of Prof. Norbert Klein and, in particular, to Mohammad Adabi and Stefan Goniszewski for our fruitful discussions about graphene transfers and how to make this “naughty” material work.

I would like to thank all the people from my office for all the fun times, great discussion, moral support and encouragement on my PhD path.

I am grateful to Carolyn Dale and Juraci Didone for their great help and support.

Special thanks to Nicola Black and Ed Lovell who have helped me fixing English grammar in this thesis and have hunted my constant “the” down.

I am very grateful to my ex-supervisor Prof. Peter Gaiduk, with whom we worked for three years, for noticing and nurturing my interest in science. I think it worked out so far :)

Most of all, I want to thank my husband and my family for their great support and encouragement. And of course my husband for his extreme patience, when I had to stay late at work or work over weekends or holidays or take work with me to our holiday trips... This thesis would have not been possible without their help.

Contents

1	Introduction.....	15
1.1	Motivation.....	15
1.2	Thesis overview.....	18
2	Literature review.....	21
2.1	Localised surface plasmon resonance.....	21
2.2	Optoelectronic properties of graphene.....	25
2.2.1	Electronic properties of graphene.....	25
2.2.2	Graphene phonon dispersion.....	27
2.2.3	Optical properties of graphene.....	28
2.2.4	Carrier relaxation process in graphene.....	30
2.3	Graphene photodetection mechanisms.....	35
2.3.1	Photovoltaic effect.....	36
2.3.2	Photo-thermoelectric effect.....	37
2.3.3	Sensitivity enhancement by plasmonics.....	39
2.4	Graphene formation techniques.....	41
2.5	Graphene transfer technique overview.....	43
2.6	Raman spectroscopy of graphene.....	49
2.7	Kelvin force probe microscopy (KFM) of graphene.....	62
3	Experimental and computational methods.....	64
3.1	Assessment of graphene quality.....	64
3.1.1	Optical microscopy.....	64
3.1.2	Scanning electron microscopy (SEM).....	65
3.1.3	Atomic force microscopy (AFM).....	65
3.1.4	Kelvin force probe microscopy (KFM).....	66

3.1.5	Raman spectroscopy	67
3.1.6	Electrical transport measurements	69
3.2	Device fabrication techniques	70
3.2.1	Photolithography	70
3.2.2	Electron beam lithography	72
3.2.3	Metal deposition.....	73
3.3	Scanning photocurrent microscopy	73
3.4	Time resolved measurements	74
3.4.1	Differential reflection spectroscopy	75
3.4.2	Transient photocurrent spectroscopy	75
3.5	Dark-field (DF) microscopy and spectroscopy	76
3.6	Fourier-transform infrared (FTIR) spectroscopy	77
3.7	Finite-difference time-domain (FDTD) calculations	78
4	The effect of transfer process on graphene properties	80
4.1	Sample fabrication.....	80
4.1.1	Wet and dry transfer techniques	80
4.1.2	Effect of contact fabrication technique on graphene properties	82
4.2	Graphene and hBN CVD material quality	85
4.3	PMMA influence on the graphene quality	88
4.4	Graphene and hBN cleaning with annealing	92
4.5	Substrate influence	95
4.6	hBN-assisted graphene transfer technique	100
4.7	Electrical and aging properties of graphene samples	103
4.8	Conclusions	106
5	Graphene-plasmonic nanoparticle hybrids	108

5.1	Sample fabrication.....	108
5.1.1	Sample design and structural properties	108
5.1.2	Plasmonic response of hybrid graphene/NP system	110
5.2	Doping variations in the hybrid system.....	111
5.2.1	Raman spectroscopy study.....	111
5.2.2	Kelvin Force Probe Microscopy (KFM) study	117
5.3	Pump probe spectroscopy characterization	119
5.3.1	Impact of substrate and doping on the differential reflection (DR).....	120
5.3.2	Plasmonic induced carrier heating in the hybrid system	125
5.3.3	DR mapping as a characterisation tool	130
5.4	Conclusions	131
6	Graphene based plasmonic photodetector	132
6.1	Sample fabrication.....	132
6.2	Photoresponse in metal-graphene-metal devices	132
6.3	Photodetector based on asymmetric plasmonic contacts	133
6.3.1	Concept of asymmetric contacts	133
6.3.2	Device design optimization.....	134
6.3.3	Sample structure and graphene quality	136
6.3.4	Polarization dependent photoresponse.....	138
6.3.5	Wavelength dependent photoresponse.....	139
6.3.6	Gate dependent photoresponse	141
6.3.7	Graphene transport measurements and Seebeck coefficient.....	144
6.3.8	Gate dependent thermoelectric response	146
6.3.9	Analytical model of the device response	148
6.3.10	Time resolved photovoltage spectroscopy	151

6.3.11	Hot carrier temperature estimate.....	153
6.3.12	Graphene destruction in presence of electromagnetic field.....	155
6.4	Conclusions.....	156
7	Conclusions and future work.....	157
7.1	Summary.....	157
7.2	Outlook.....	160
7.2.1	Imaging ultrafast hot carrier transport.....	160
7.2.2	Hot carrier injection.....	161
7.3	Publications or papers in progress related to work conducted during the Ph.D. project.....	163
8	Appendix.....	164
8.1	Reflection derivation for single layer substrate.....	164
8.2	Reflection derivation for multilayer substrate.....	166
	References.....	167
	List of figures.....	187
	List of tables.....	197
	Permissions.....	197

1 Introduction

In this chapter, the motivation behind the thesis work is discussed with a short overview of recent advances in photodetection based on graphene two-dimensional materials. Next, a short summary of each chapter is provided.

1.1 Motivation

Photodetection, whereby light is converted to an electrical signal, lies at heart of various technologies widely used in modern society including imaging, optical communication, healthcare and security. With the growing scale and diversity of applications, it is desirable to develop photodetectors that fulfil the requirements of compatibility with complementary metal–oxide–semiconductor (CMOS) technology, demonstrate high speed, high quantum efficiency and broadband detection. Furthermore, for novel applications flexibility and transparency are additionally required.

Due to their remarkable mechanical, electronic and optical properties, two-dimensional (2D) materials have rapidly become appealing for development of novel optoelectronic devices with special emphasis on various photodetection platforms [1–7]. 2D materials exhibit diverse optical properties, ranging from wide bandgap (~ 6 eV) insulating hexagonal boron nitride (hBN) via intermediate bandgap ($\sim 1.0 - 2.5$ eV) semiconducting transition metal dichalcogenides such as molybdenum disulphide, down to narrow bandgap ($\sim 0.3 - 2$ eV) semiconducting black phosphorous and gapless semimetallic graphene [5]. Compared to traditional 3D photonic materials, vertically stacked heterostructures can be easily realized using 2D materials without the need for lattice matching, since the surfaces of 2D materials are naturally passivated and inter-layer interactions through van der Waals forces are only weak. This provides additional benefits for the realization of various optoelectronic devices.

Graphene, a single layer of carbon atoms arranged in a hexagonal honeycomb lattice, has attracted significant attention from the scientific community due to its potential for various light detection and modulation applications [4,6,8–10]. While the absence of a bandgap hinders graphene’s development for transistor logic devices, this property becomes beneficial for photonics and optoelectronics, enabling broadband photodetection that includes the commercially important telecommunication wavelengths as well as the mid-infrared and THz spectral regimes [1,10]. This is in a stark contrast with conventional photonic materials, such

as Si and GaAs, which typically suffer from the long-wavelength limit, where they become transparent when the excitation energy is smaller than the bandgap [11].

Due to their linear dispersion relationship, carriers in graphene behave as massless Dirac fermions exhibiting extremely high mobility up to $10^5 \text{ cm}^2/\text{Vs}$ at ambient temperature and up to $10^6 \text{ cm}^2/\text{Vs}$ at low temperatures [12,13]. This excellent electronic property means that graphene can facilitate high-speed optoelectronics, since the maximum possible operating bandwidth of photodetectors is typically limited by the carrier transit time [11]. For the conventional photonic materials used in optical communication and interconnects, the maximum bandwidths are limited to 150 GHz [14] and 80 GHz [15] for InGaAs and Ge photodetectors, respectively. The transit-time-limited bandwidth of graphene photodetectors could be over 1,500 GHz [16] at the reported saturation velocity [17], which is well beyond state-of-the-art photodetectors. In practice, the operating bandwidth is limited by a photodetector's time constant (RC), which is defined by the device resistance and capacitance. Xia et al. demonstrated a graphene photodetector operating at a modulation frequency of 40 GHz, while estimated an RC-limited bandwidth of about 640 GHz [16]. Moreover, graphene photodetectors were used in an optical data link with error-free recovery of a $10 \text{ Gbit}\cdot\text{s}^{-1}$ data stream [18].

Compared to conventional semiconductor materials with a bandgap, the photogeneration and transport processes are fundamentally different in graphene. Due to the gapless nature of graphene, initial relaxation of carriers through electron-electron scattering and optical phonon emission quickly thermalizes photoexcited electrons and holes in the conduction and valence bands creating a hot carrier distribution with a well-defined electronic temperature T_e [19–22]. At the same time, electron-lattice relaxation pathways are quenched due to the large optical phonon energy and the velocity mismatch between electron and acoustic phonons [23,24]. As a result, a novel transport regime is reached when the carrier population remains hot while the lattice stays cool [21,22]. In contrast, for 3D semiconductors, the photogenerated electrons and holes are typically characterized by a carrier temperature that does not significantly differ from the lattice [11]. In graphene, hot carriers play an important role in its optoelectronic response leading to photocurrent generation through the photothermoelectric effect that can dominate over the traditional photovoltaic effect [25]. A strong thermoelectric effect was reported for graphene devices at the interface of monolayer and bilayer graphene [26], or at the interface between regions of graphene with different

Fermi energies, such as at a supported/suspended graphene interface [27], graphene p-n junctions with buried split-gates [28] or top-gate control [29,30].

While the photodetection mechanism is still debatable, the performance of graphene-based photodetectors is significantly limited by the small effective photodetection area. The photocurrent generation is observed in the submicrometer-wide region of the created p-n junction [31]. The small area of internal electric field results in recombination of most photogenerated carriers that cannot be separated. Owing to graphene's semimetallic nature, applying an external electric field by biasing the device is problematic due to high dark current [32,33]. The metal/graphene interface is a most common geometry where a p-n junction is created close to the contacts because of the local modification of graphene's Fermi energy when in contact with metal [31,32,34,35]. For detectors with symmetric contacts made of the same metal, the photoresponse produced at each contact is of opposite polarity to the other, under uniform illumination, producing zero net signal [34]. To increase the effective photodetection area, an interdigitated finger structure with asymmetric metallization was proposed [18]. However, this geometry complicates device fabrication processes.

Although for a single atomic layer absorption of 2.3% is extremely high, it is desirable to increase this value to facilitate highly efficient graphene based photodetectors. Possible ways to overcome this limitation is by integration with optical focusing components such as cavities [36], waveguides [37] and plasmonic nanostructures [38]. The latter approach has received particular attention due to the versatile nature of plasmonic nanostructures that present an ease of spectral selectivity by just tailoring the size and shape of a plasmonic antenna. Under resonance conditions, incident light generates plasmonic oscillations in the nanostructures leading to a dramatic enhancement of the local electric field and the generation of hot electrons inside of the metal via nonradiative decay [39]. There have been several reports of the photoresponse enhancement in graphene devices upon integration with plasmonic nanoantennas [38,40–42]. It should be noted that the enhancement was observed in the areas close to the metal contacts where the in-built internal electric field resides. Therefore, the symmetry problem mentioned earlier remains evident in these proposed device geometries [40].

The plasmon induced enhancement mechanism also remains debateable. While the primary studies attributed enhanced absorption to the improved light harvesting in graphene due to the presence of intense electromagnetic fields surrounding the nanoparticle [38,40], hot carrier

transfer into the graphene film from the plasmonic particles has also been proposed [41,42]. Furthermore, once the photocarriers are generated in the graphene layer, they can be effectively separated by the internal field present at graphene/metal nanoparticle interface and thus contribute to the photovoltaic effect. However, local generation of hot carriers can also result in electronic temperature gradients thus leading to an enhanced thermoelectric effect. A complete understanding of how the plasmon induced photocarriers contribute to the photocurrent in graphene devices remains topical.

To facilitate the design and engineering of high speed graphene based optoelectronic devices, a deep understanding of their optical properties and ultrafast carrier relaxation dynamics is required. The goal of this thesis is to explore the interaction between graphene and plasmonic nanostructures with a particular emphasis on the optical properties of the hybrid devices, photocarrier generation processes and physical mechanisms enabling photocurrent. A few other challenges facing graphene based devices are explored along the way including graphene transfer and device fabrication, each with the end goal of maximising electronic and structural properties of the graphene material. First, a transfer process and device fabrication techniques are developed in order to preserve the high quality of the graphene layer. Then plasmonic nanostructures are combined with graphene layers with and without an insulator barrier (hBN) to facilitate the study of hot carrier dynamics in the hybrid system. Finally, asymmetric plasmon-nanobar electrical contacts are designed to investigate the role of plasmon-induced carrier heating on the photocurrent generation in a graphene photodetector.

1.2 Thesis overview

Chapter 2 gives a general survey of literature related to the work presented in the thesis. We review optical properties of plasmonic nanoparticles with a special emphasis on hot carrier generation. Then the optoelectronic properties of graphene are discussed with a particular focus on carrier dynamics and photocurrent generation mechanisms. This is followed by review of the literature concerning the techniques used for the formation of graphene, its transfer and quality assessment. Particular attention is given to Raman spectroscopy that is utilized in this thesis as a major technique for graphene quality assessment.

The experimental methods used throughout this thesis for the sample fabrication and characterization are discussed in **Chapter 3**. Here, the techniques used for graphene quality assessment are introduced in detail. Then, time-resolved measurement methods are examined

in the context of the carrier dynamics study. Finally, the use of numerical calculations for plasmonic applications is presented.

In order to achieve high quality devices based on CVD graphene, a transfer method that preserves or even enhances the material quality is required. As such, **Chapter 4** examines various parameters of the transfer technique and their influence on the graphene quality focusing on concentration of induced defects and extrinsic dopants during this process. In particular, the source of charge impurities in graphene is discussed by analysing the effect of polymer residues and surface states of the substrate. Finally, by utilizing a hBN layer as a spacer between graphene and PMMA, a novel transfer method is developed and demonstrated to facilitate large area graphene transfer and encapsulation resulting in devices with enhanced electrical properties and environmental stability.

As graphene based optoelectronic devices suffer from low intrinsic absorption, the combination of graphene with light focusing plasmonic nanostructures is considered as a promising way to strongly enhance graphene's photoresponse. In **Chapter 5** the properties of graphene/plasmon-nanoparticle (NP) hybrids are studied with special emphasis on the absorption enhancement mechanism. The structural properties and doping variation in these complexes are analysed using SEM, AFM, KFM and Raman spectroscopy techniques. Time resolved differential reflection (DR) spectroscopy is employed to characterize the ultrafast carrier dynamics first of bare graphene and then of the graphene/NP structures. By analysing samples with graphene/hBN/gold and graphene/gold interfaces, it is established that enhanced absorption in graphene originates from direct photoexcitation by the strong electromagnetic fields surrounding plasmonic NPs, while a contribution from charge transfer from the gold, debated in the literature [41,42], is found to be minimal. Furthermore, an observed nonlinear anisotropy of the graphene/NP system is explained by a highly localised hot carrier population in graphene that suggests the presence of strong electronic temperature gradients over nanoscale dimensions.

With the demonstration of plasmon-induced electronic temperature gradients in graphene, **Chapter 6** is an experimental study of the effective application of this phenomenon in a photodetector device. Formed of two electrical contacts, one bare and one decorated with plasmon-nanobars, this asymmetric device generates a significant electronic temperature gradient under plasmon excitation across the graphene channel. Numerical modelling is used to design and optimize the device structure. Scanning photovoltage microscopy is employed

to analyse the photoresponse of plasmonic and nonplasmonic contacts with a particular focus on the mechanism of photoresponse generation. Pump-probe measurements are utilized to study the response time of the device and thereby estimate the hot carrier temperature generated in the structure.

Finally, **Chapter 7** summarizes the findings of the thesis and discusses impact of the results on the field of graphene photodetection. Furthermore, based on the results of this work, future potential studies of hybrid structures based on combination of 2D materials and plasmonic elements are proposed.

2 Literature review

This chapter provides an overview of the literature related to the work reported in Chapters 4 to 6. Firstly, the optical properties of plasmonic nanoparticles are presented. This is followed by a discussion of the optoelectronic properties of graphene including carrier relaxation dynamics and photocurrent generation mechanisms. The second part of this chapter (Sections 2.4-2.7) has a slightly different focus and concerns literature review on experimental techniques used for graphene formation, transfer and quality assessment. Since Raman spectroscopy is a major technique for graphene characterization and greatly used throughout this thesis, the literature review is covered here in depth with special emphasis on spectral data interpretation.

2.1 Localised surface plasmon resonance

Optical properties of plasmonic nanoparticles.

Under optical excitation, metal nanoparticles (NPs) can exhibit collective oscillations of conduction electrons known as localised surface plasmon resonances (LSPRs) [43]. The resonant behavior leads to strong light matter interaction with the formation of subwavelength high intensity electromagnetic hot spots at the NP surface. This results in enhanced absorption and scattering of light. Typically, plasmonic NPs are made of gold and silver that exhibit strong LSPRs in the visible range of light. The optical properties of NP ensembles can be analysed using conventional far-field extinction spectroscopy. For sufficient spacing, the interaction between NPs is weak resulting in the optical response of the ensembles to be similar to the LSPR of an individual particle [44,45]. Therefore, for the purpose of this thesis, it is possible to limit our discussion to optical properties of a single NP.

To simplify the discussion, we consider a spherical NP with a size much smaller than the wavelength of light ($R \ll \lambda$). In this case, the electromagnetic normal mode of the sphere can be obtained using electrostatic equations rather than a full set of Maxwell's equations [46]. In other words, in the small particle limit, the electrostatic approximation is valid and only the lowest dipolar order of the modal expansion of the scattered fields has to be considered. Therefore, for spherical metal NPs surrounded by the non-absorbing medium of dielectric constant ϵ_m , the NP polarisability α can be expressed as following:

$$\alpha = 4\pi R^3 \frac{\varepsilon - \varepsilon_m}{\varepsilon + 2\varepsilon_m}, \quad (2.1)$$

where $\varepsilon(\omega)$ is the dielectric response of the metal. From this equation, it is clear that the magnitude of polarisability can be resonantly enhanced at a specific frequency, when the denominator approaches zero. This corresponds to the resonance condition given by $\varepsilon(\omega) = -2\varepsilon_m$, that becomes $Re(\varepsilon) = -2\varepsilon_m$ for small values of $Im(\varepsilon)$. This relationship is known as the Fröhlich condition and can only be fulfilled when $Re(\varepsilon)$ is negative, which is the case for metals. As an example, dielectric properties of gold are presented in Figure 2.1 (a,b). At long wavelengths ($\lambda > 600 \text{ nm}$), the large negative real part of permittivity determines the optical response of gold material. The conduction electrons screen the external electromagnetic excitation result in high reflection. At shorter wavelengths ($\lambda < 600 \text{ nm}$), interband transitions in gold can occur resulting in an increase of the imaginary part of permittivity.

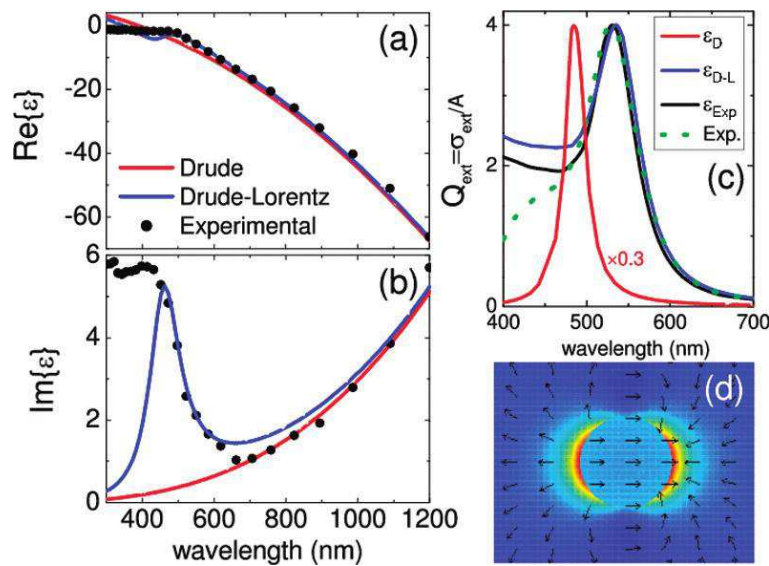


Figure 2.1. (a) Permittivity of gold with real ($Re(\varepsilon)$) and imaginary ($Im(\varepsilon)$) parts. Experimental data is compared to Drude (red line) and Drude-Lorentz (blue) models. (c) Experimental extinction cross section of 50 nm gold NPs in water (green) compared to theoretical calculations performed with the Drude (red) and Drude-Lorentz (blue) models. (d) Electromagnetic field distribution for the 50nm gold NP at resonance wavelength of 535nm. Reprinted with permission from [47]. Copyright 2011 American Chemical Society.

The resonant electromagnetic behavior of metal NPs is due to high electron confinement that under optical excitation produces a dipolar field outside the particle (Figure 2.1 d). This leads to a strongly enhanced near field in the immediate vicinity of the particle surface, as well as to enhanced absorption and scattering cross sections for electromagnetic waves that can be clearly observed in an extinction spectrum (Figure 2.1 c). For larger particles, the spectral response is modified due to the excitation of higher-order modes and retardation effects. In

fact, the LSPR broadens and shifts to longer wavelengths providing an effective way to tune the resonance position.

In general, the spectral position and strength of the LSPR of single metal NPs strongly depend on the NP characteristics (material, size, geometry), as well as on the dielectric function of the surrounding host. The medium dependence can be easily seen from the resonance condition (Equation (2.1)). Since the absolute value of $\varepsilon(\omega)$ for metals decreases as ω increases, the resonance frequency also decreases, as ε_m increases. This results in the LSPR shift to longer wavelengths. The shift can be explained in terms of the buildup of polarization charges on the dielectric side of the interface that causes the total restoring force to weaken. The shift to the near-infrared part of the spectrum for higher refractive indices of the surrounding material can be used to effectively tune the LSPR position.

Hot carrier generation

In nanostructures, plasmon decay can occur radiatively through emission of a photon or non-radiatively through electron-hole excitation during Landau damping [48]. The branching ratio of these two effects determines the amount of energy captured by the carrier system in the NPs. The ratio is related to the radiance of the plasmon mode that can be significantly altered and even suppressed for the structures supporting dark plasmon modes such as Fano resonances [49]. Landau damping is expected to occur on a timescale of 1-100 fs [48] and results in excitation of strongly out-of-equilibrium carriers, as illustrated in Figure 2.2 (b). The carrier distribution is determined by properties of the plasmonic nanostructure including the NP size, the density of states and electronic properties of the material and the supported plasmon energy [50].

Typically, the generated hot electrons have energies ranging from the Fermi level E_F up to $E_F + \hbar\omega_{LSPR}$, where $\hbar\omega_{LSPR}$ is the LSPR energy that is lower than material's work function [39]. Therefore, under these conditions the hot electrons cannot be emitted into the vacuum and are bound to the NP. After photoexcitation, the hot carriers rapidly decay through carrier-carrier interactions such as Auger transitions [50] to form the hot carrier distribution that can be described by the Fermi–Dirac function with a large effective electron temperature T_e (Figure 2.2 c). The thermalization process can occur on a timescale of 100 fs to 1 ps [51,52]. Next, the equilibration with the lattice takes place through electron-phonon interactions that is characterized by a longer timescale of several picoseconds [53]. Finally,

the heat can be further transferred from the nanostructure to the surrounding media (Figure 2.2 d).

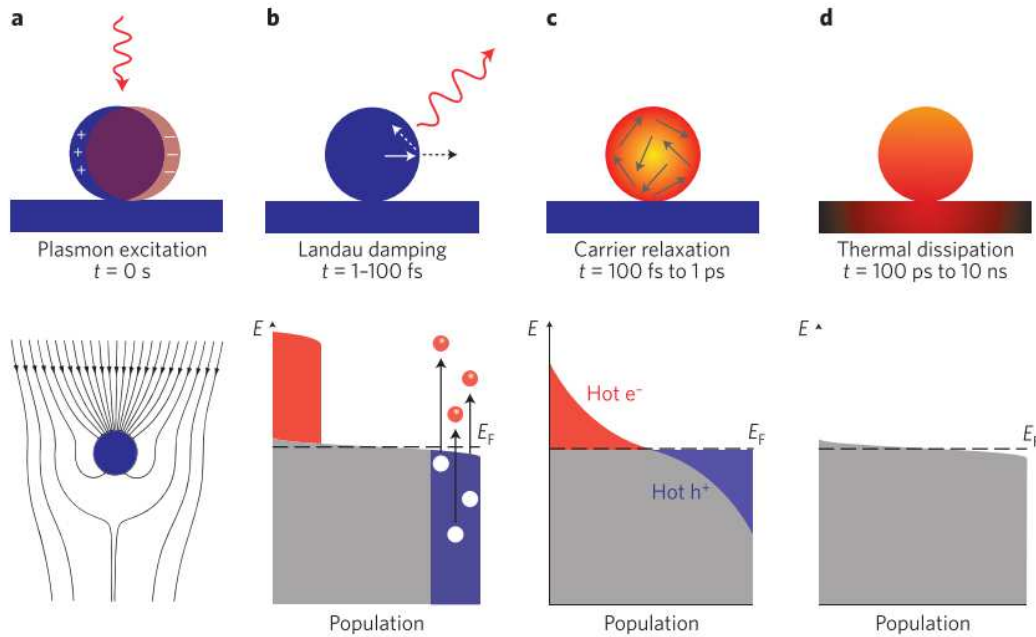


Figure 2.2. Localised surface plasmon excitation and relaxation. (a) Optical illumination results in plasmon excitation that modified the flow of light (Poynting vector) towards the NP. (b) After Landau damping, the out-of-equilibrium carriers decay radiatively through emission of photons or nonradiatively through carrier multiplication due to carrier-carrier interaction. (c) The hot carrier distribution is formed. Subsequent decay occurs through carrier-phonon interactions to equilibrate the carrier and lattice temperatures. (d) Heat conduction results in heat transfer to the NP surroundings. Reprinted by permission from Macmillan Publishers Ltd: [39], copyright 2015.

Hot carriers can be extracted from the NPs utilizing the Schottky barrier formed between metal and semiconductor material. However, the timescales determine significantly the efficiency of the extraction process, since the hot carrier decay results in a decrease of transferring probability. There are successful device geometries that have been explored for the hot carrier harvesting [54–57], suggesting that the timescales for the charge transfer processes are faster than timescales for carrier cooling. Efficient hot carrier capture has been reported for the graphene/plasmonic nanostructure complexes [41,42]. This is perhaps surprising, since graphene material does not form a Schottky barrier with the metal making the backward carrier flow to be of same efficiency. The interaction of graphene with plasmonic nanostructures is discussed in more detail in Section 2.3.

2.2 Optoelectronic properties of graphene

2.2.1 Electronic properties of graphene

Graphene is a one atom thick allotrope of carbon with the atoms arranged in a two-dimensional (2D) honeycomb structure [58,59]. Graphitic materials of all other dimensions can be obtained from graphene (Figure 2.3 a): 0D fullerenes C_{60} can be described as wrapped-up graphene, 1D carbon nanotubes as graphene rolled along a given direction and 3D graphite as stacked graphene. The various types of carbon allotropes are produced through the different interaction between carbon valence electrons. The four valence electrons occupy the 2s and 2p orbitals in elemental form (Figure 2.3 b). In crystal form, one of the 2s electrons is excited to the 2p_z orbital and new hybrid orbitals are formed due to the interaction between the 2s and 2p orbitals of neighboring carbon atoms. Multiple types of hybridization define the capability of carbon to form various allotropes.

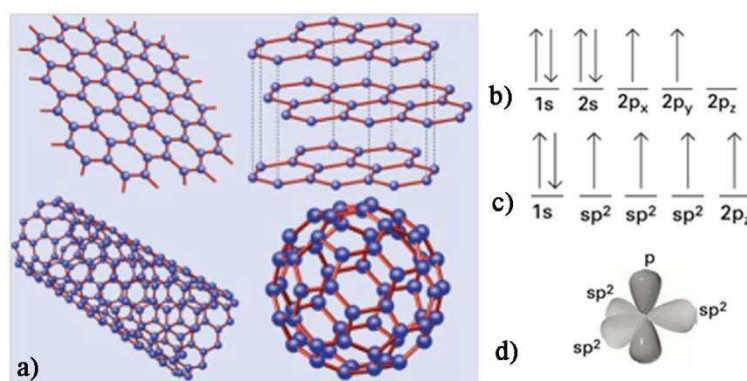


Figure 2.3. (a) Carbon allotropes: graphene (top left), graphite (top right), carbon nanotubes (bottom left) and fullerenes C_{60} (bottom right). Adapted with permission from Ref. [60]. Copyrighted by the American Physical Society. The electron arrangement in (b) elemental carbon and (c) graphene. (d) Illustration of the orbitals in graphene [61].

In graphene, three sp^2 hybrid orbitals are formed due to interaction between the 2s orbital and the 2p_x and 2p_y orbitals (Figure 2.3 c). The sp^2 hybridization leads to a formation of three σ -bonds, which are responsible for the robustness of the lattice structure in all allotropes. The σ -bonds connect carbon atoms into a trigonal planar structure with a separation of 1.42 Å. While the electrons in the σ -bonds are localised along the plane of the lattice, the remaining 2p_z electrons form covalent π -bonds with the electron cloud distributed normally to the plane (Fig. 1d). The σ -bonds form a deep valence band as they have a filled shell due to the Pauli principle. In contrast, the π -bonds are half filled due to one extra electron and these electrons are relatively delocalised due to a weak binding with the nuclei. The electronic properties of graphene are generally determined by these delocalised electrons.

The graphene has a honeycomb lattice that can be seen as a hexagonal lattice with a basis of two atoms per unit cell [61]. The primitive unit cell can be considered as an equilateral parallelogram with a side of $2.46 \text{ \AA}$. The lattice vectors as defined in Figure 2.4 (a) can be written as $a_1 = \frac{a}{2}(3, \sqrt{3})$, $a_2 = \frac{a}{2}(3, -\sqrt{3})$, where $a=1.42 \text{ \AA}$ is the carbon-carbon distance [60]. Fig. 2a (right) shows the graphene reciprocal lattice, that is a hexagonal lattice rotated 90° with respect to the direct lattice. The reciprocal lattice vectors are $b_1 = \frac{2\pi}{3a}(1, \sqrt{3})$, $b_2 = \frac{2\pi}{3a}(1, -\sqrt{3})$.

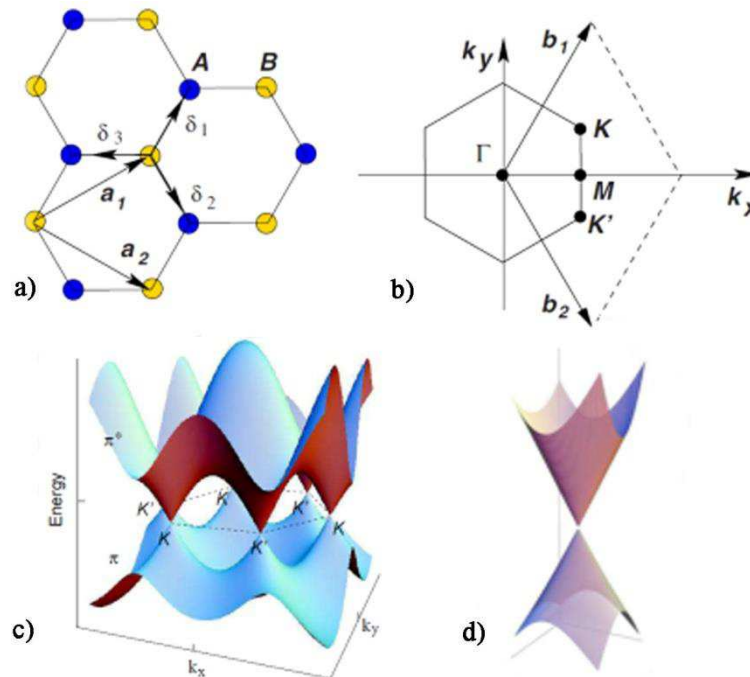


Figure 2.4. The honeycomb lattice of graphene (a) and corresponding Brillouin zone (b). Electronic dispersion in the honeycomb lattice: energy dispersion as a function of the wave-vector components k_x and k_y (c) and zoom in of the energy bands close to one of the Dirac points (d). Adapted with permission from Ref. [60]. Copyrighted by the American Physical Society.

As we have discussed, in each carbon atom three electrons form σ -bonds, while the remaining electron forms a π -bond. It has been demonstrated [62] that π -electrons are responsible for graphene electronic properties at low energies and energy bands for σ -electrons are located far away from the Fermi energy. Figure 2.4 (b) shows the energy dispersion for the π -electrons obtained using the tight-binding approximation [63]. Here, two bands can be clearly observed. The lower band, the π or valence band, is completely filled, while the upper band, the π^* or conduction band, is completely empty. Therefore, the Fermi energy is located at the K-points, called Dirac points, where the π band touches the π^* band.

At these points the band structure has a linear dispersion (Figure 2.4 d) and the density of states approaches zero indicating that the carriers behave as massless Dirac fermions.

2.2.2 Graphene phonon dispersion

Next, the phonon dispersion of graphene is discussed. In general, the phonon dispersion of a crystal can be determined theoretically using ab-initio density functional theory (DFT) or experimentally using inelastic X-ray scattering (IXS) or Raman spectroscopy measurements. Figure 2.5 shows calculated graphene phonon dispersion from DFT (lines) and experimental IXS measurements on graphite demonstrating excellent agreement [64]. The phonon dispersion of graphene consists of six branches: three acoustic (A) and three optical (O) branches [64,65]. Two phonon branches are perpendicular to the graphene plane, i.e. out-of-plane (o), and four phonon branches are parallel to the graphene plane, i.e. in-plane (i) [65]. Longitudinal (L) or transverse (T) phonon branches are determined as the parallel or perpendicular vibrations with respect to the direction of the A-B carbon-carbon atoms (Figure 2.4 a) [65]. The active Raman modes in graphene are the iLO and iTO phonon branches, as discussed in detail in Section 2.6.

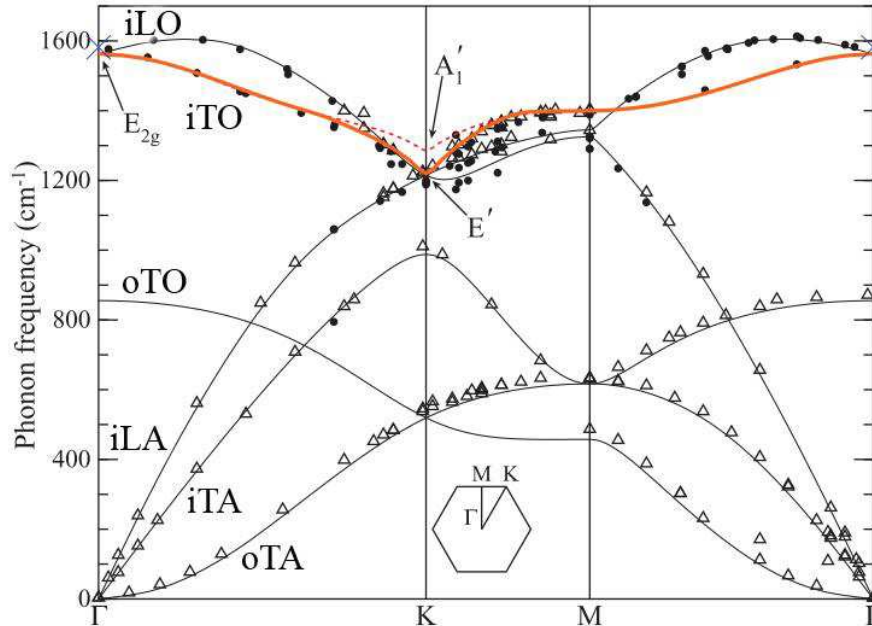


Figure 2.5. Theoretical and experimental phonon dispersion of graphene showing the iLO, iTO, oTO, iLA, iTA and oTA phonon modes. adapted with permission from Ref. [64].

Copyrighted by the American Physical Society.

2.2.3 Optical properties of graphene

The exceptional optical properties of graphene originate from its two-dimensional nature and unique electronic structure. Figure 2.6 illustrates the main mechanisms involved in the optical transition processes and a resultant absorption spectrum characteristic to graphene layer with doping level of E_F [10]. It is possible to identify three main regimes of absorption processes in graphene (Figure 2.6 a). (1) For photon energies $E_{ph} = \hbar\omega \ll 2E_F$, graphene absorption is due to intraband carrier transitions that can be well described by the Drude response. This absorption regime is mainly observed at THz frequencies [66]. (2) At the mid-infrared regime, the optical conductivity is minimal due to Pauli-blocking, since $E_{ph} < 2E_F$. However, the nonzero absorption can be observed when the necessary momentum is provided by disorder in the graphene [67]. This effect is a characteristic of low quality graphene and significantly reduces for high quality encapsulated samples. (3) Finally, for photon energies $E_{ph} > 2E_F$, direct interband transitions are allowed resulting in electron-hole pair generation. In this regime, universal 2.3% absorption is observed for a wide range of frequencies [68], as discussed in details below.

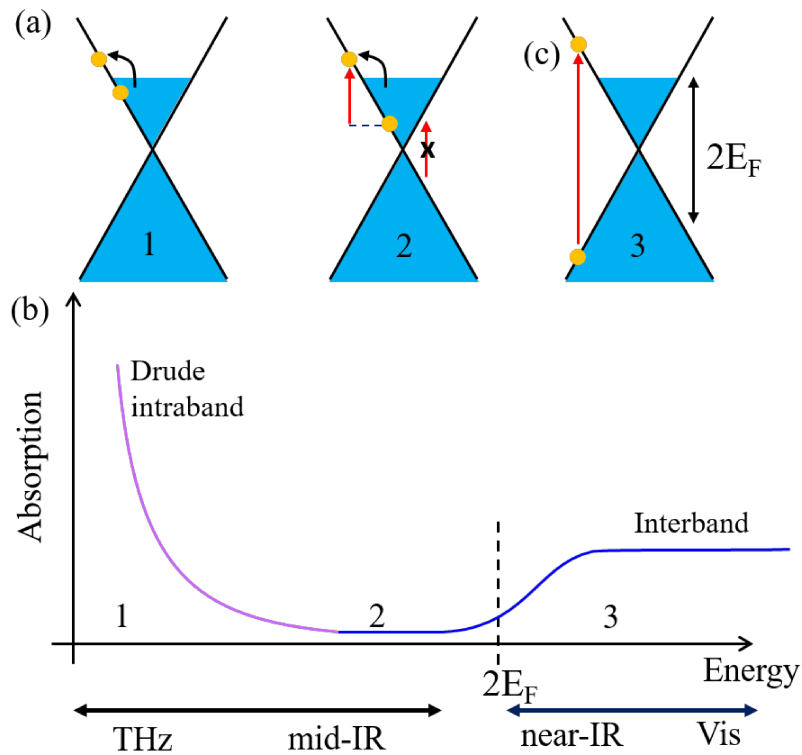


Figure 2.6. Graphene's optical absorption. (a) Absorption mechanism: (1) intraband, (2) defect mediated and (3) interband. The red arrow indicates excitation photons. The yellow spheres represent carriers. (b) Typical absorption spectrum of doped graphene.

A single layer of graphene can absorb a significant fraction (2.3%) of incident light across the infrared and visible range, while reflectance remains remarkably low in the visible region ($<0.1\%$) [68]. Transmittance of white light decreases with number of graphene layers, as each layer absorbs additional 2.3% (Figure 2.7 a). Using Fresnel equations in the thin-film limit, one can derive the transmittance of a freestanding graphene, $T = (1 + 0.5\pi\alpha)^{-2} \approx 1 - \pi\alpha \approx 97.7\%$, where $\alpha = e^2/(4\pi\epsilon_0\hbar c) = G_0/(\pi\epsilon_0 c) \approx 1/137$ is the fine-structure constant [68]. Here, $G_0 = e^2/4\hbar \approx 6.08 \times 10^{-5} \Omega^{-1}$ is a fixed universal optical conductance [69]. A single graphene layer has almost constant absorption over quite a broad range of wavelengths from 300 to 2,500 nm (Figure 2.7 b) [70]. The only peak is observed in the ultraviolet region (270 nm), where there is a van Hove singularity present in the density of states. However, multilayer graphene can exhibit other absorption properties due to interband transitions [71].

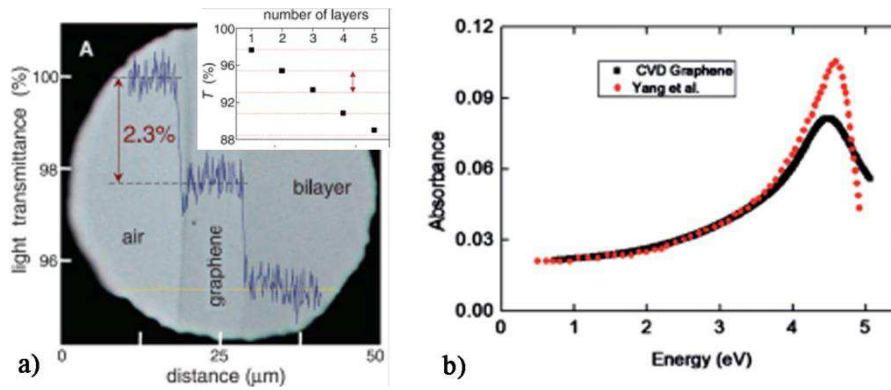


Figure 2.7. (a) Photograph of a 50-mm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (Inset) Transmittance of white light as a function of the number of graphene layers. Adapted from [68]. Reprinted with permission from AAAS. (b) Optical absorbance of a monolayer graphene calculated from dispersion model values of n and k . Reprinted from [70], with the permission of AIP Publishing.

Due to high graphene absorption, even a single layer with a thickness of only 0.34 nm can be observed on a SiO_2/Si substrate using optical microscopy. This is the result of interference with SiO_2 acting as a spacer. In general, the adjustment of the SiO_2 spacer thickness can maximize the optical image contrast [72,73]. For the naked eye observation, a SiO_2 thickness of ~ 90 nm and ~ 290 nm is commonly used. These conditions provide a contrast peak of around 560 nm (green) where the spectral sensitivity of the human eye is also maximal.

2.2.4 Carrier relaxation process in graphene

In the following, we discuss the ultrafast dynamics of the photocarrier generated in graphene after the interband transition. The generated photocarriers undergo a very complex process of relaxation, as presented in Figure 2.8. The photocarriers in graphene exhibit two distinct properties significantly different from conventional semiconductors: strong carrier-carrier interaction and slow electron-phonon cooling [74]. The first effect arises from enhanced Coulomb interaction due to reduced screening and quantum confinement of the low dimensional materials [74]. Strong electron-electron interaction can lead to an Auger process of carrier multiplication giving technological promise of graphene based energy harvesting [75]. The second effect, slow electron-lattice relaxation, stems from the high optical phonon energy and large velocity mismatch between the electrons and the acoustic phonons [23]. In fact, the strong carbon-carbon bonds result in an unusually high optical phonon energy of $\hbar\omega_{op} \approx 200 \text{ meV}$ [65,76]. Therefore, optical phonons can mediate cooling only for very hot electrons and this channel becomes quickly suppressed [24]. For electrons with energy below $\hbar\omega_{op}$, the cooling occurs through emission of acoustic phonons. However, this cooling pathway is inefficient due to a large mismatch in Fermi velocity of carriers and sound velocity of acoustic phonons ($v_F/s \approx 100$). Furthermore, additional requirements due to momentum conservation restrict the energy of emitted acoustic phonons to several meV resulting in an extremely inefficient cooling process with cooling times exceeding 300 ps [77]. However, the momentum restriction can be lifted by disorder mediated acoustic phonon emission, so-called supercollision, with relaxation times of 1–10 ps comparable to experimental results [78]. Strong carrier-carrier and slow carrier-phonon interactions result in thermal energy being primarily distributed among electronic charge carriers leading to the thermal decoupling of the carrier and lattice systems. There are numerous reports indicating that hot carriers dominate graphene's intrinsic optoelectronic response [25,26,28–30]. Therefore, it is crucial to understand hot carrier dynamics in graphene to facilitate development of optoelectronic devices.

After photoexcitation with photon energies $E_{ph} > 2E_F$, high-energy electron hole pairs form an outlying distribution of carriers in the conduction and valence bands high above and below the Fermi energy, respectively (Figure 2.8 a) [23]. The high-energy carriers relax through scattering with ambient carriers within tens of femtoseconds [19,20], during which optical phonon emission can also occur (Figure 2.8 b,c). The amount of energy captured by the

electronic system in the fast thermalization process depends on the competition between the rates for carrier-carrier scattering and optical phonon emission. Due to the high carrier density typically present in doped graphene and the large phase space available for carrier-carrier scattering, this process is expected to dominate over optical phonon emission [23]. Indeed, recent experimental results confirm this concept demonstrating that more than 50% of the photon energy remains in the electronic system [79]. The hot carrier distribution subsequently cools down by the emission of acoustic phonons to the lattice through both the normal momentum-conserving process and the disorder-assisted supercollision process (Figure 2.8 d, e).

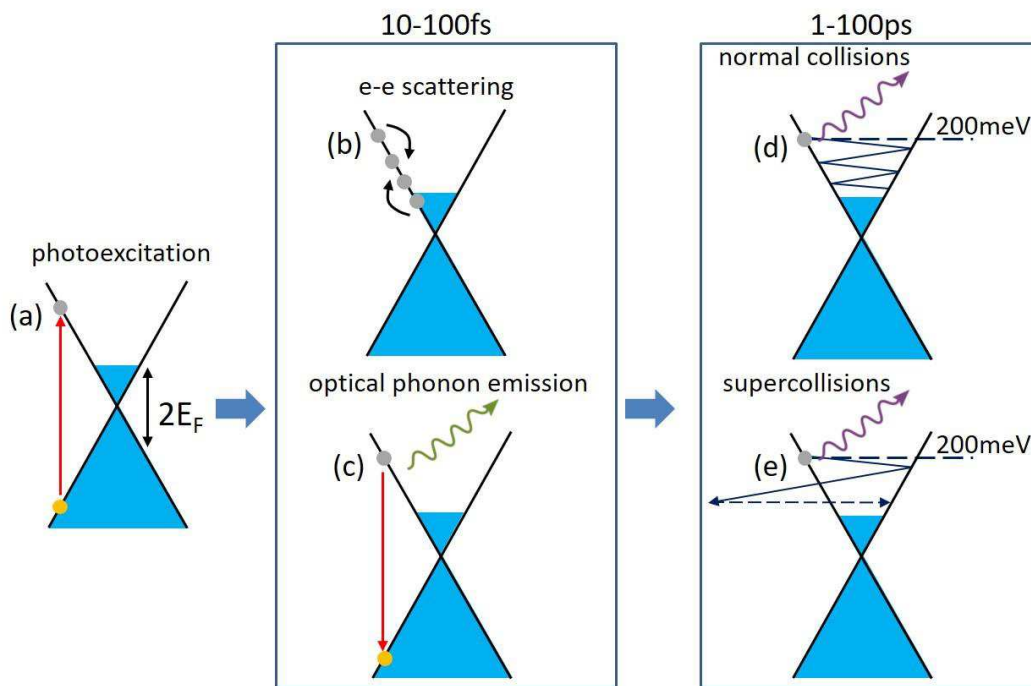


Figure 2.8. Schematic illustration of carrier dynamics in graphene. (a) Photoexcitation results in highly energetic electron-hole pair generation. (b) Part of the carrier energy is transferred to a carrier system via scattering processes. (c) Emission of strongly coupled optical phonons (~ 200 meV) results in the energy transfer to the lattice. (d) The hot carriers cool down through normal momentum-conserving process of low energy ($\approx$ several meV) acoustic phonon emission. (e) The hot carrier cooling is facilitated by a disorder-assisted supercollision process that relaxes momentum restrictions enabling faster cooling through emission of high-energy ($\sim k_B T$) acoustic phonons.

Several authors remark the importance of the hot phonon (HP) bottleneck effect on the cooling dynamics of the hot carriers in graphene [22,80,81]. In the HP model, thermalized carriers relax primarily by emission of optical phonons. The generated phonons can transfer energy back to the carrier system resulting in a slower cooling process. The carrier and optical phonon systems reach a quasi-equilibrium ($T_e \approx T_{ph}$) and their dynamics become

closely coupled. In this case the decay of the hot carriers is controlled by the relaxation of the optical phonons through emission of low energy acoustic phonons. This forms a cooling bottleneck when the carrier cooling time is determined by the relaxation of the optical phonons. However, Song et al. theoretically demonstrated that the disorder-assisted supercollision (SC) processes dominate the carrier relaxation in graphene [82]. Recent experimental results by Graham et al. confirmed limitations of the HP model and demonstrated the ability of the SC model to predict graphene's optical and photocurrent response under a wide range of the system parameters [78,83].

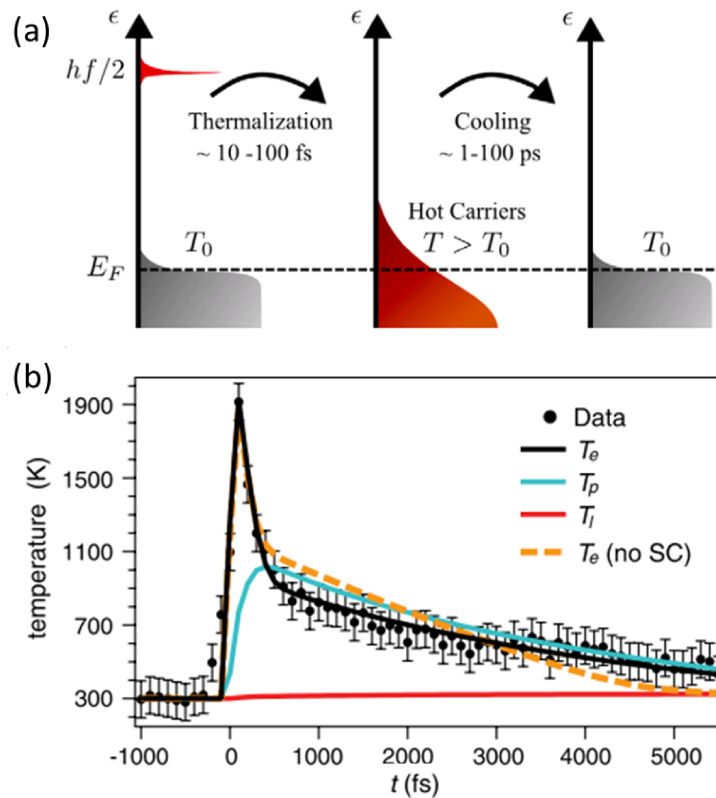


Figure 2.9. (a) Carrier distribution during relaxation process. The first schematic describes strongly out-of-equilibrium carrier distribution due to photoexcitation. The photocarriers thermalize through carrier-carrier scattering and optical phonon emission to create a relatively long-lived hot carrier distribution (the second schematic). The hot carrier distribution relaxes back to equilibrium (the third schematic). Adapted from [23].

(b) Electronic temperature evolution. The experimental data is fitted using a three temperature model with (solid black line) and without (dashed amber line) the supercollision (SC) term. Additionally, the temperatures of the optical phonons (solid blue line) and the acoustic phonons (solid red line) are included. Reprinted with permission from [20].

Copyright 2013 by the American Physical Society.

Following the photoexcitation, the thermalization process results in the formation of a hot carrier distribution with an elevated electronic temperature T_e well described by the Fermi-Dirac function $f_{FD}(E) = 1/[e^{(E-\mu)/k_B T_e} + 1]$, where μ is the Fermi energy and k_B is

Boltzmann's constant (Figure 2.9). Importantly, for intraband transitions ($E_{ph} < 2E_F$), where the carrier density must remain conserved, the increase in electron temperature is accompanied by a lowering of the Fermi energy [84]. This effect comes from graphene's electronic density of states being linearly dependent on energy $D(E) = \frac{2}{\pi\hbar^2 v_F^2} |E|$. Therefore, an increase in electron temperature would result in an increase of carrier density in case of constant Fermi energy. However, for interband transitions, generation and recombination of carriers influences the overall carrier dynamics. While some authors still suggest using temperature dependent Fermi energy [20,85], the carrier density is no longer constant due to recombination processes that occur on the time scales ranging from less than a picosecond to more than hundreds of picoseconds [86,87]. Furthermore, recent ARPES work has demonstrated that following initial carrier inversion, single carrier distribution is established characterised by constant Fermi energy [19].

Figure 2.9 (b) shows the evolution of electronic temperature in graphene after photoexcitation with a pump laser energy of 0.95 eV [20]. The electronic temperature is extracted from the time- and angle-resolved photoemission spectroscopy (TR-ARPES) measurements performed on hydrogen-intercalated so-called quasi-free-standing monolayer graphene (QFMLG) on SiC [20]. The temperature relaxation clearly demonstrated two distinct time constants $\tau_1 \sim 150$ fs and $\tau_2 \sim 3050$ fs, that can be assigned to processes involving optical phonons and acoustic phonons, respectively. As discussed above, the rapid thermalization of hot carriers is accompanied by optical phonon emission which raises the temperature of the optical phonon subsystem (T_{ph}) (Figure 2.9 b solid blue line). During the second part of the relaxation process the carrier and phonon temperatures are in quasi equilibrium $T_e \approx T_{ph}$. This is in good agreement with previous results by Graham et al. demonstrating that the graphene's transient optical response at room temperature is well described by both the SC and HP models [83]. The carrier relaxation and thus the temperature decay are well described by a biexponential model $T(\Delta t) \sim A_1 e^{-(\Delta t)/\tau_1} + A_2 e^{-(\Delta t)/\tau_2}$. The amplitudes correspond to the initial (A_1) and secondary (A_2) decay components which are directly related to the peak hot carrier and hot phonon temperatures, respectively. Therefore, the amplitude ratio A_1/A_2 being proportional to T_e/T_{ph} can be considered as a useful qualitative parameter related to the fraction of energy lost to the phonon bath during the cooling process.

Differential transmission (reflection) spectroscopy of graphene

Differential transmission (reflection) spectroscopy is a widely used technique to analyse relaxation dynamics of optically excited carriers. Graphene has been extensively studied using a degenerate [88] and a dual colour optical pump probe experiment [21,80,89], an optical-pump infrared-probe experiment [90–92], an optical-pump THz-probe experiment [86,93] and a THz-pump optical-probe experiment [94].

In a pump-probe experiment, the sample is typically excited with a strong pump pulse introducing changes in the carrier population, while a time-delayed weaker probe pulse is used to monitor temporal change in the carrier population (Figure 2.10 a,b). Typically, both beams are focused on the same spot on the sample. However, experiments with one fixed beam have been recently suggested to study hot carrier diffusion processes [95,96]. As previously discussed, optical pumping results in a nonequilibrium distribution of carriers that rapidly thermalizes into a hot carrier distribution. When the excited carriers are present at the relevant energies, the probe pulse demonstrates increased transmission due to Pauli blocking. Therefore, in the pump-probe experiments, a typical measured value is the differential transmission (DT): $\Delta T/T_0 = (T - T_0)/T_0$, where T and T_0 are transmission with and without optical excitation, respectively. A positive change of transmission is equivalent to a negative change of absorption. In the case of opaque substrate, the reflection geometry can be used. In this case, the measured value is the differential reflection (DR), $\Delta R/R_0$. It should be noted that interference of the underlying substrate can affect the measured values, as will be discussed in detail in Section 5.3.

Figure 2.10 (c) shows a typical DT signal of a graphene layer at various probe energies from 88 to 138 meV close to the Fermi energy. The DT traces exhibit characteristic biexponential decay with an initial fast component followed by a slower secondary component consistent with the earlier discussion of carrier temperature evolution due to optical and acoustic phonon emission. Interestingly, the sign of DT signal changes for the probe pulses with lower energy. This effect can be explained by relative changes in carrier distribution during the heating process (Figure 2.10 d): after optical excitation, the transient occupation probability becomes larger (smaller) for the areas above (below) the Fermi energy. Therefore, at photon energies below $2E_F$, the DT signal switches from positive to negative sign. Since this transition is abrupt, by varying the probe energy the Fermi energy of the graphene can be identified.

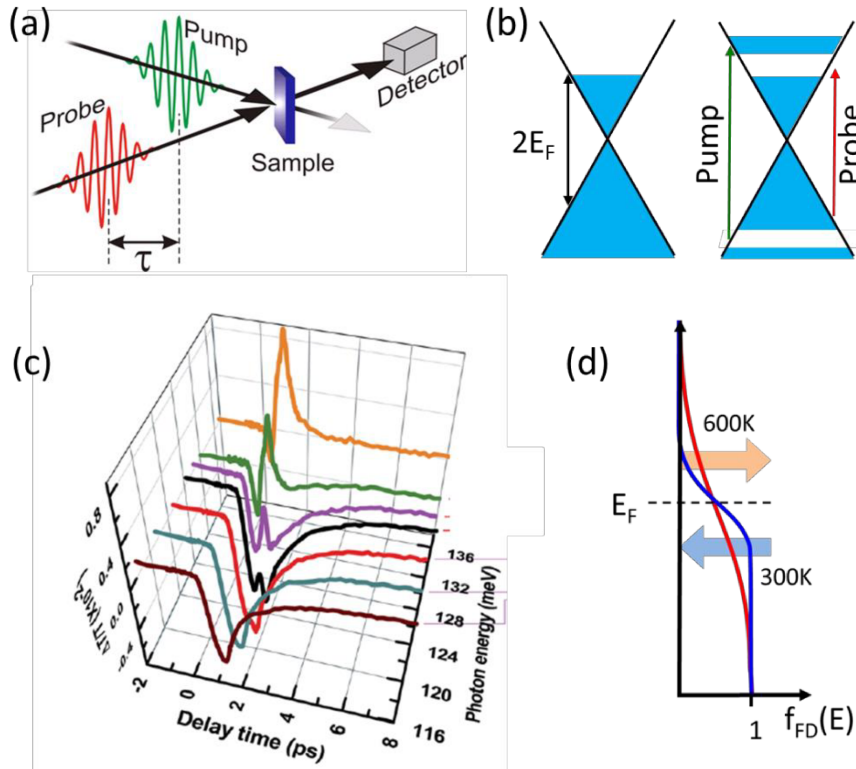


Figure 2.10. (a) Schematic of a pump-probe experiment. The sample is excited with a strong pump pulse while being monitored with a weak probe pulse. The time delay between pulses (τ) is varied. (b) The pump pulse creates carrier inversion in graphene. The relaxation of photocarriers is monitored by the probe pulse. (c) Differential transmission (DT) signal of monolayer graphene at various photon energies from 88 to 138 meV demonstrating the sign change close to the Fermi energy [97]. (b) The Fermi-Dirac distribution $f_{FD}(E)$ at different carrier temperatures representing equilibrium distribution (blue line) and distribution after carrier thermalization (red line). Blue and orange arrows indicate regions with negative and positive DT signal, respectively.

2.3 Graphene photodetection mechanisms

Photodetection and optoelectronic devices rely on efficient light to electric signal conversion. For graphene, several mechanisms of photoconversion have been reported including a photovoltaic effect [18,32,34], a photothermoelectric effect [25,26,30], a bolometric effect [98], a photogating effect [99,100] and a plasma-wave-assisted mechanism [101]. In this work, we focus on metal-graphene-metal photodetectors characterised by photocurrent generation at the graphene/metal interface due to the photovoltaic and photothermoelectric effects [1]. Under contact with the metal, charge transfer occurs due to the difference in work function of the materials leading to a change in the local doping of graphene in the region above or below the metal pads [102]. The doping gradually equilibrates to that of the contact-

free graphene leading to the formation of a band-bending area that is typically $\sim 100\text{--}200\text{ nm}$ from the end of the metal pad to the metal-free graphene channel [31]. Such band-bending effects can be controlled by changing the doping level of the contact-free region of the graphene using a back gate [34]. In contrast, the doping of graphene over the metal pads remains unaffected due to Fermi level pinning [102]. The presence of a band-bending region enables the photovoltaic process in graphene-metal devices, since it results in an internal electric field. Meanwhile, the thermoelectric contribution is enhanced by the strong spatial dependence of the Seebeck coefficient near the graphene/metal interface. Here, we discuss these two major contributing effects in more details.

2.3.1 Photovoltaic effect

Photogenerated electron–hole (e–h) pairs in graphene can be separated by a built-in electric field at the junction between differently doped areas leading to photovoltaic (PV) photocurrent generation (Figure 2.11) [18,32,34]. To produce an external electric field, a source–drain bias voltage can be additionally applied, but this leads to a large dark current due to the semimetal nature of graphene and, thus, this technique is undesirable. An alternative approach is based on the creation of local chemical [103] or electrostatic doping [29,104] or on the work-function difference between graphene and a metal contact [18,32,34].

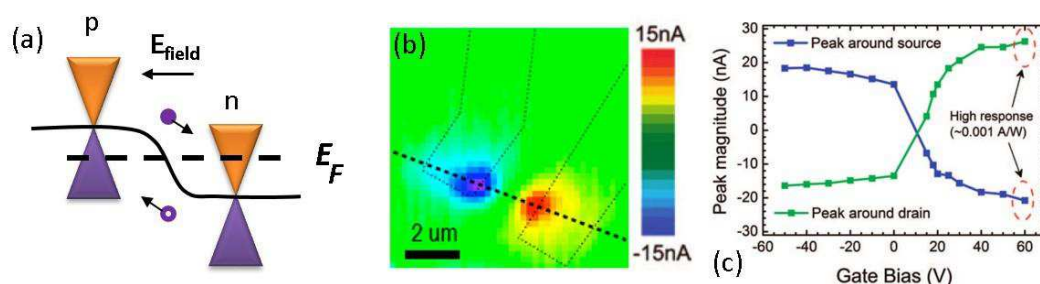


Figure 2.11. (a) Schematic representation of the photovoltaic mechanism where electron–hole (solid and open circle) pairs are separated by an internal electric field. (b, c) Photocurrent response of a graphene transistor: scanning photocurrent image (b) and peak photocurrent magnitude around source and drain contacts as a function of the gate bias (c). The incident excitation laser power is about $30\text{ }\mu\text{W}$, and the wavelength is 632.8 nm . Adapted with permission from [34]. Copyright 2009 American Chemical Society.

At the graphene-metal interface, the generated photocarriers can be separated by the band-bending region close to the metal contact creating an electric field that drives currents outside the excitation region towards the contacts [25]. The direction of the built in electric field determines the direction of the photocurrent in graphene leading to an opposite sign when

going from p–n to n–p or from p–p⁺ to p⁺–p and similar for other doping regimes (Figure 2.11 b). The PV contribution is directly proportional to the electric field and can be estimated by $I_{PV} \sim qn\mu\xi$, where ξ is the electric field, n is the steady state photo-induced carrier density and μ is the carrier mobility [25]. At steady state, the photo-induced carrier density n depends on its non-equilibrium carrier temperature T_e and the chemical potential [33]. Since the carrier concentration of graphene over the metal is pinned, the band-bending conditions can be tuned by a monotonic sweep of gate voltage which changes the doping of the graphene channel. In fact, the photovoltaic current will be initially cancelled due to band flattening and then will reverse sign due to the change of electric field direction (Figure 2.11 c). Note that the point of vanishing photovoltage is usually quite different from the Dirac point for the graphene channel material. It is primarily controlled by the metal induced doping and thus changes for electrodes made from different metals [32]. This has been previously utilized to break the mirror symmetry of the built-in potential profile [18]. It should be noted that the photovoltaic response is characterized by a single sign reversal that is in contrast to the photothermoelectric effect [25].

2.3.2 Photo-thermoelectric effect

Recent studies have demonstrated that hot carriers in graphene play a key role in its optoelectronic response [25,30]. In graphene, as discussed in Section 2.2.4, photoexcited carriers can remain “hot” compared to the lattice for many picoseconds due to the quenching of electron-lattice energy relaxation known as the hot phonon bottleneck effect [77]. This results in a thermal decoupling of the carriers from the crystal lattice and, thus, the energy transport in the system is mainly governed by hot carriers [25]. See detailed discussion of the carrier relaxation in Section 2.2.4.

The hot carrier contribution to the photocurrent is captured by the photothermoelectric (PTE) effect that results from local heating of graphene junctions with materials of different Fermi energies [30]. The Seebeck coefficient is a measure of the induced thermoelectric voltage due to a temperature gradient and strongly depends on the Fermi-level according to Mott’s formula [105]:

$$S = - \frac{\pi^2 k_B^2 T}{3q} \frac{1}{\sigma} \frac{d\sigma}{dE_F}, \quad (2.2)$$

where k_B is the Boltzmann constant, σ is the conductivity, q is the carrier charge and μ is the chemical potential. This formula can be evaluated by substituting $\frac{d\sigma}{dE_F}$ with $\frac{d\sigma}{dV_g} \frac{dV_g}{dE_F}$, where $\frac{d\sigma}{dV_g}$ can be determined by numerical differentiation of the measured conductivity σ with respect to applied gate bias V_g . For single layer graphene the dependence of E_F on the charge density n is described by $E_F = \hbar v_F (\pi n)^{\frac{1}{2}}$ with $n = \frac{\epsilon_0 \epsilon_{SiO_2} (V_g - V_D)}{et}$, where t is the oxide thickness, e is elementary charge and V_D is the Dirac point, or the charge neutrality point. Therefore, the $\frac{dV_g}{dE_F}$ term can be described by $\frac{dV_g}{dE_F} = \frac{2}{\hbar v_F} \sqrt{\frac{et|V_g - V_D|}{\pi \epsilon_0 \epsilon_{SiO_2}}}$.

A difference in Seebeck coefficients results in a net electron flow thus producing a photothermoelectric voltage generated at the junction (PTE-j), $V_{PTE-j} = (S_1 - S_2) \Delta T_e$, where $S_{1,2}$ is the Seebeck coefficients of the two regions of the junction and ΔT_e is the electronic temperature increase within the junction. The dependence of photothermoelectric current on $S(\mu_1) - S(\mu_2)$ results in multiple sign reversals due to the nonmonotonic character of the function $S(\mu)$, as shown in Figure 2.12 (b). Utilizing top gate control a six-fold pattern has been demonstrated for the photocurrent generation at a graphene pn junction, for example [29,30]. This is in stark contrast with the photovoltaic effect where a two-fold pattern is typically observed (Figure 2.12 c).

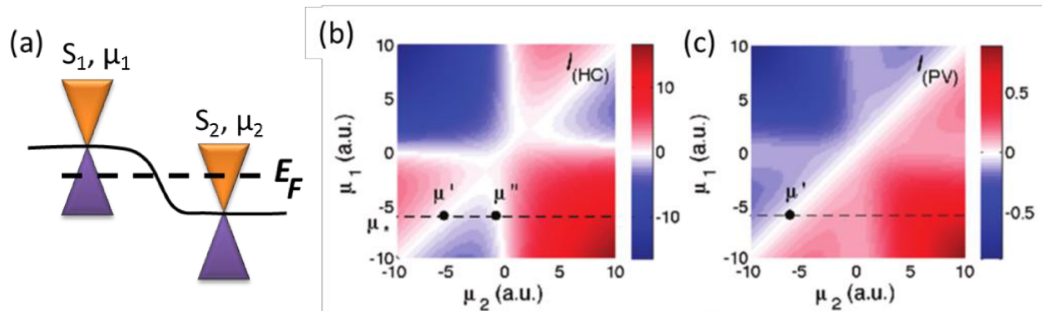


Figure 2.12. (a) Schematic representation of the photothermoelectric (PTE) mechanism where $S_{1,2}$ and $\mu_{1,2}$ Seebeck coefficients and chemical potential in graphene areas. (b,c) Calculation of the photocurrent from PTE and PV effects. The PV contribution changes sign only once due to the change of the electrical field direction, while the PTE contribution changes sign twice. Adapted with permission from [25]. Copyright 2011 American Chemical Society.

In the metal-graphene-metal photodetector, there is also the possibility for an additional thermoelectric contribution. In this geometry with contact induced junctions, the heating of one side can result in a global temperature difference across the device: when light is absorbed around the source electrode, a high temperature imbalance of the carrier system can be created, as the graphene close to the drain electrode is not heated. This will result in a

photothermoelectric voltage generated in the channel (PTE-ch) of $V_{PTE-ch} = S_1 \Delta T_e$, where S_1 is the Seebeck coefficient of the graphene channel and ΔT_e is the electron temperature difference between the contacts. It is clear, that this photovoltage will have only one vanishing point, namely at the Dirac point, when the Seebeck coefficient switches sign. This behaviour is reminiscent of the typical thermoelectric effect, where experiments confirm polarity reversal at the Dirac point for both optical [30,35] and electrical heating [105,106]. Table 2.1 presents a summary of the points where different effects are cancelled.

Effect	Flat band	Dirac point
PV	✗	✓
PTE-j	✗	✓
PTE-ch	✓	✗

Table 2.1. Summary of contributing effects: ✓ – the effect is active and ✗ – the effect is cancelled.

Both PTE effects can be described simultaneously by using a more accurate calculation of the current I_{PTE} [25,29,33]:

$$I_{PTE} = - \frac{1}{RW} \iint \frac{\partial T(x, y)}{\partial x} S(x, y) dx dy, \quad (2.3)$$

where R and W are the device resistance and channel width, respectively; x is the direction along which the current flows; T is the excitation induced electronic temperature increase and S is the spatially varying Seebeck coefficient in the graphene device. It should be noted that the spatial temperature profile is required to perform these calculations.

2.3.3 Sensitivity enhancement by plasmonics

A single layer of graphene can absorb a significant (2.3%) fraction of incident light across the infrared and visible range [68]. While this is remarkable for an atomically thin material and beneficial for some devices in flexible and transparent optoelectronics, it is still highly desirable to increase graphene's absorption efficiency, especially for photodetection applications. To enhance light-matter interactions, plasmonic nanostructures can be used. The first use of plasmonic nanoparticles in combination with graphene was demonstrated for surface-enhanced Raman scattering [107] and to investigate strong field enhancements within subnanometre gaps [108]. To improve graphene based photodetectors, plasmonic nanostructures near the contacts were utilized resulting in a significant improvement of performance [38,40]. In Ref. [38] a 20-fold increase in the efficiency has been mainly

attributed to the significant electromagnetic field concentration in the area of a p–n junction (Figure 2.13 a,b).

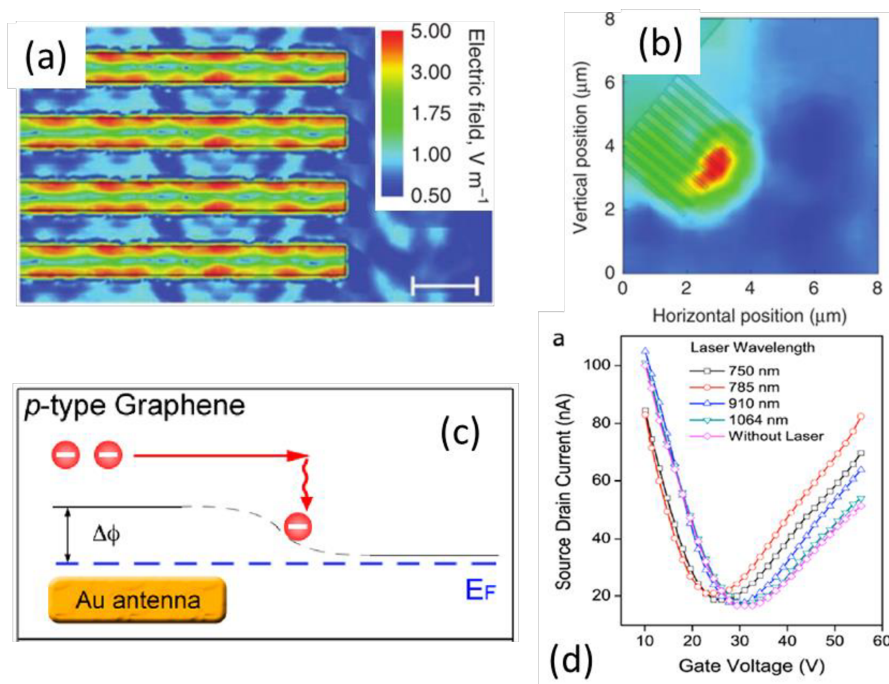


Figure 2.13. (a, b) Numerical finite element simulations of local electric field in the presence of gold finger structure (finger width 110 nm, pitch 300 nm) and the corresponding photogenerated signal (normalized to laser power) as a function of the position of the illumination spot (514 nm, transverse polarization, spot size $\sim 1.5 \mu\text{m}$; Gate voltage 90 V. Colour scale from 0 μV (blue) to 20 μV (red)). Adapted by permission from Macmillan Publishers Ltd: [38], copyright 2011. (c, d) Schematics of hot carrier injection from plasmonic nanoparticle in graphene and the Dirac point shift for antenna/graphene transistor under different excitation lasers with a 1 mV source-drain bias. Adapted with permission from [42]. Copyright 2011 American Chemical Society.

An alternative mechanism of plasmon harvesting for graphene photocurrent improvement has been suggested by Halas' group [41,42]. The demonstrated graphene based plasmonic photodetector achieved up to 20% internal quantum efficiency in the visible and near-infrared regions of the spectrum. The contribution from plasmonic nanoparticles was described not only in terms of direct near-field-enhanced excitation of intrinsic graphene carriers, but also in terms of hot electron transfer (Figure 2.13 c,d). Furthermore, plasmon induced doping has been observed electrically as a shift of the Dirac point. While the gapless nature of graphene makes it an ideal hot electron collector, a significant back carrier transfer from graphene to nanoparticles should be expected due to the absence of an energy barrier (in particular a Schottky barrier) at the graphene-metal interface. Our recent results on the graphene-metal nanoparticle systems suggest that that plasmon-induced hot carrier generation in graphene is

dominated by direct photoexcitation through the intense electromagnetic fields [109] (See Section 5.3).

While the mechanism of plasmon induced carrier generation is still debatable, it is also unclear how the generated photocarriers contribute to the photocurrent. Since the photocarriers generated at the graphene-nanoparticle interface are in the region of a potential gradient characteristic for a pn junction, they can be effectively separated by the internal field contributing to the photovoltaic effect. However, the presence of plasmonic nanostructures also results in a strong electronic temperature gradient [109], thus, enhancement of the thermoelectric effect can also be anticipated. We return to this question in Chapter 6 utilising regimes set out in Table 2.1 to isolate the various contributions to the photovoltage generation.

2.4 Graphene formation techniques

Recent progress in graphene synthesis has proven the possibility to synthesize graphene in various ways and on different substrates [110–115]. Nevertheless, graphene synthesis in large quantities and of high quality remains challenging. At the moment there is no reliable method for a controllable synthesis of graphene with well-defined size, shape, and edge structure that are crucial for investigation of graphene fundamental physical properties and for development of graphene based devices.

The production of graphene with required properties is essential for the market of graphene applications. Currently, there are numerous methods developed to prepare graphene material of various dimensions and quality that define the range of potential applications, see Figure 2.14 and Table 2.2. It is possible to distinguish two main strategies for graphene synthesis: exfoliating graphite towards graphene (top-down) and building up graphene from molecular building blocks (bottom-up) [111].

The mechanical exfoliation of graphite developed by the Manchester group [58,59] was the first successful technique resulting in single layer graphene. This is a quite simple and low-budget technique that can produce high quality graphene flakes of a several-micron size. However, this technique lacks controllable size and shape of graphene flakes as well as precise positioning of the flakes. Therefore, this method is mainly used in research of the fundamental graphene properties and is considered to have a limited relevance to commercial high-end electronic applications.

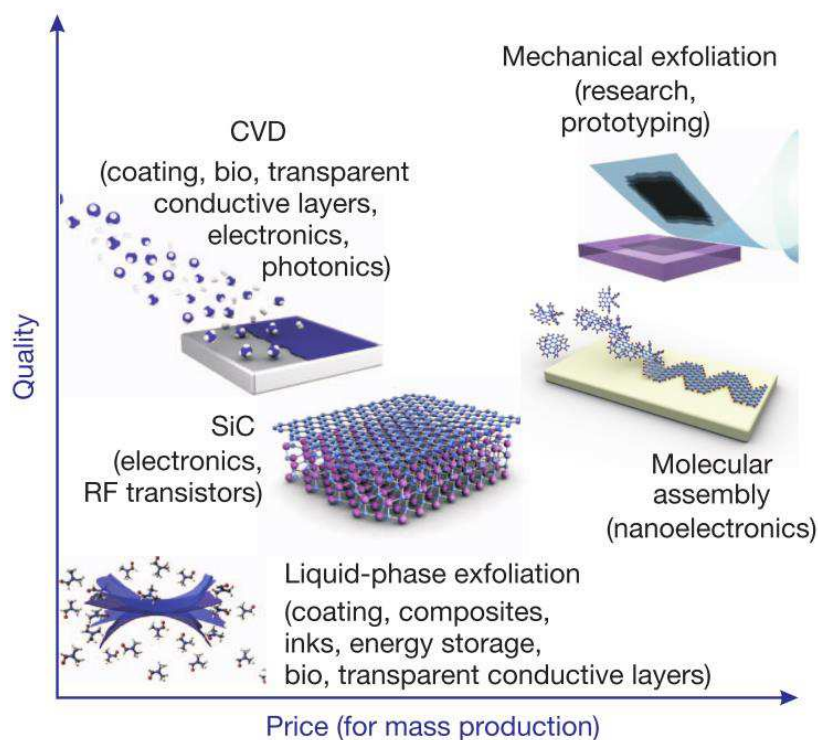


Figure 2.14. Summary of methods for graphene production with estimated quality and price indicated for possible applications. Reprinted by permission from Macmillan Publishers Ltd: [116], copyright 2012.

The graphitization of hexagonal SiC crystals is a representative of bottom-up techniques for graphene synthesis. Annealing of hexagonal 4H- and 6H-SiC crystals has been demonstrated to result in single layer and few layer graphene [112,113]. During the annealing process the top layer of SiC crystal decomposes, Si atoms desorb from the substrate and the remaining carbon atoms rearrange to form epitaxial graphene layers. In this method the reactor pressure and the type of gas atmosphere are crucial parameters, which define the quality and structure of the resulting graphene. The growing process is generally slow due to the fact that three bilayers of Si and C atoms correspond to only a single graphene layer. The resulting graphene layers are usually electron doped ($\sim 10^{12} \text{ cm}^{-2}$) and have areas of different thickness, which is undesirable in device applications. However, graphene grown on semi-insulating SiC can be used without transfer to another insulating substrate [117].

One of the most popular bottom-up techniques for graphene synthesis is chemical vapour deposition (CVD) from C-containing gases on catalytic metal surfaces. At the moment Cu is generally used for this process [114]. Due to low solubility of C in Cu the graphene growth occurs by a surface adsorption process rather than a precipitation process observed for Ni [115]. It has been demonstrated that graphene growth on Cu is self-limiting and practically stopping after a single layer is formed [114]. The quality of the copper foil is one of the most

crucial factors affecting the number of layers and the quality of the resulting graphene. It is well known that copper grain boundaries serve as graphene nucleation sites favouring multilayer growth. In this case the resulting graphene is of a multidomain structure due to the rotational disorder between domains and the many grain boundaries. The effect of the grain boundaries strongly limits the electrical transport properties of CVD graphene comparing to those of exfoliated graphene flakes. Therefore, it is desirable to use single crystal Cu with an atomically smooth surface and an absence of grain boundaries.

Method	Crystalline size (μm)	Sample size (mm)	Charge carrier mobility (300K) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Applications
Mechanical exfoliation	>1,000	>1	$>2 \times 10^5$ and $>10^6$ (at low temperatures)	Research
CVD	1,000	1,000	10,000	Photonics, nanoelectronics, transparent conductive layers, sensors, bioapplications
SiC	50	100	10,000	High-frequency transistors and other electronic devices

Table 2.2. Properties of graphene material obtained by different fabrication methods. Adapted by permission from Macmillan Publishers Ltd: [116], copyright 2012.

In this work, we utilize CVD graphene material on copper due to its large area, uniformity and commercial availability. However, the fact that the underlying substrate is copper means that transfer to a dielectric surface is required to facilitate photodetector development. At the moment, the transfer process is quite complicated and minimizing damage to the graphene film remains challenging. Since this process is crucial for the control of graphene's film quality, we perform a detailed study of the various transfer techniques affecting graphene's properties with the aim to develop an improved transfer method that will retain material quality (Chapter 4).

2.5 Graphene transfer technique overview

Due to recent progress in chemical vapour deposition (CVD) technique, graphene sheets of 30 inch have become available bringing graphene research one step closer to industrial application [118]. To facilitate most of practical applications CVD-grown graphene should be transferred from the growth metal-foil substrate onto various desired substrates and this step

remains challenging. Structural defects and chemical contamination are usually introduced during the transfer step significantly limiting the electrical properties of graphene.

Since CVD-grown graphene is located on the metal-foil substrate, most of the transfer methods include the chemical etching of the underlying growth substrate. However, this step can introduce defects as well as chemical doping into the graphene layer [119]. It has been demonstrated [120–122] that the use of exfoliation/peeling transfer methods allows the avoidance of the etching process entirely. In this method special carrier film with “glue” qualities (polystyrene substrate with linker molecules or an epoxy layer) [120,121] is attached to the graphene followed by the peeling of graphene from the growth metal (Figure 2.15). In [122] the process was improved using hot deionized (DI) water that penetrates graphene/copper interfaces and separates them. The major advantage of these methods is that graphene is not exposed to any chemicals preventing the degradation of the electrical properties. Additionally, the growth metal substrate can be reused without significant quality degradation resulting in almost identical graphene layers. However, there is still a challenge in removing the “glue substance” [120,121] and improving the uniformity of the transferred graphene layer [122].

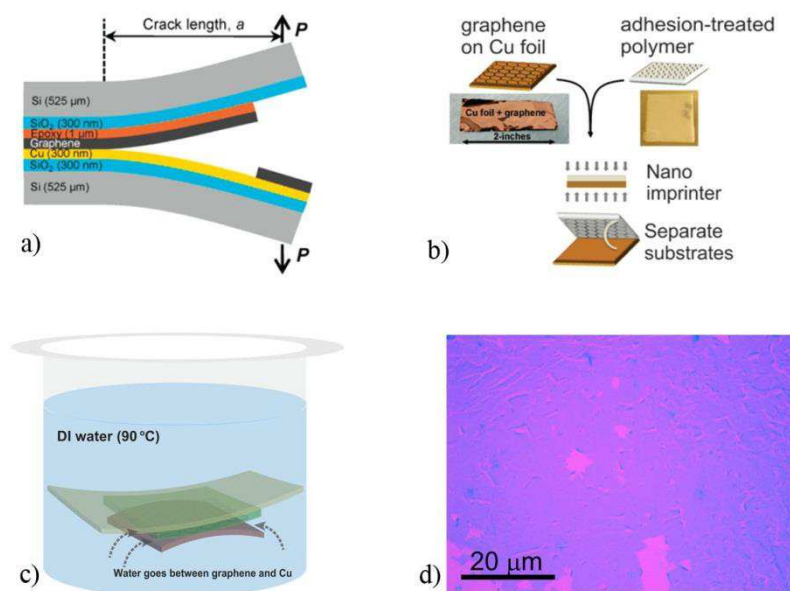


Figure 2.15. (a-c) Schematic illustration of the transfer procedures used in [120–122], respectively. (d) Optical image of the transferred CVD graphene grown on Cu [122].
 (a) Adapted with permission from [120]. Copyright 2012 American Chemical Society.
 (b) Adapted with permission from [121]. Copyright 2012 American Chemical Society.

The most common approach is a polymer-assisted transfer, utilising a polymer layer (typically PMMA) deposited directly on top of the graphene/copper foil to provide

mechanical support after removal of the copper. The PMMA/graphene stack is generally released from the growth substrate using a wet chemical etchant (such as ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$) followed by thorough rinsing in deionized (DI) water [123,124]. In the wet transfer process, the PMMA/graphene film is scooped out of the DI water using the target substrate (so-called **wet transfer**). Notably, this technique is inappropriate for water-sensitive substrates [125] and substrates with cavities [123] where freestanding graphene is easily broken by surface tension during the drying process. Furthermore, trapped DI water between the graphene and substrate is unavoidable, leading to wrinkles, cracks [126] and doping from residual water molecules [127]. **Dry transfer** techniques that avoid direct contact of the target substrate with water have been reported by several groups [123,124,128]. In this case, additional layers (such as polydimethylsiloxane (PDMS) stamps, polyimide tape or thermal release tape) are placed on top of the PMMA/graphene stack to provide sufficient mechanical support enabling sample pick up and placement. Micro-patterned PDMS stamps have been demonstrated as a means of lithography-free pattern transfer [129], however, mechanical defects (tears, cracks etc.) can be introduced during stamp-substrate separation. This drawback is largely eliminated by using a frame-like support structure as discussed below [123,128].

To facilitate the dry transfer technique, a special holder is generally placed on top of the graphene or polymer/graphene stack. Substantially thick PDMS can be used as a stamp providing “pick-and-place capability” [52]. PDMS has quite low surface energy providing a considerable advantage during graphene transfer. When the PDMS/graphene stack is brought into contact with the target substrate, graphene prefers to adhere to the substrate with relatively higher surface energy. Furthermore, to improve this method graphene can be covered with an appropriate thin polymer that usually has a work of adhesion with the PDMS stamp smaller than that between the graphene and the target substrate acting as a “self-release layer” [124]. The presence of the self-release layer significantly improves the quality of transferred CVD graphene (Figure 2.16 a). PDMS can be also used in frame shape to support PMMA/graphene stack [123]. In this work CVD graphene was dry transferred on perforated substrates (Figure 2.16 b), where freestanding graphene can be broken by surface tension during drying of the liquid trapped in the wells. The use of a frame support was also demonstrated by Petrone et al. [128]. In this study the PMMA/graphene/Cu stack was adhered from the Cu side to a small window cut in polyimide tape (Figure 2.16 c) providing mechanical support for PMMA/graphene film suspended across the window. Using this

method CVD graphene crystals were successfully transferred both on SiO₂ and on hexagonal boron nitride (h-BN), which is known to minimize substrate-induced scattering [12]. The graphene grain transferred on h-BN showed carrier mobility ranging between 27 000 and 45 000 cm² V⁻¹ s⁻¹, comparable to that of exfoliated graphene. The dry transfer techniques allow reduction of the trapping of impurities present in DI water and facilitates precise placement of graphene on the target substrate. However, in these methods the graphene layer is still covered with a protective polymer that may leave residues on the graphene surface increasing the doping level of the material.

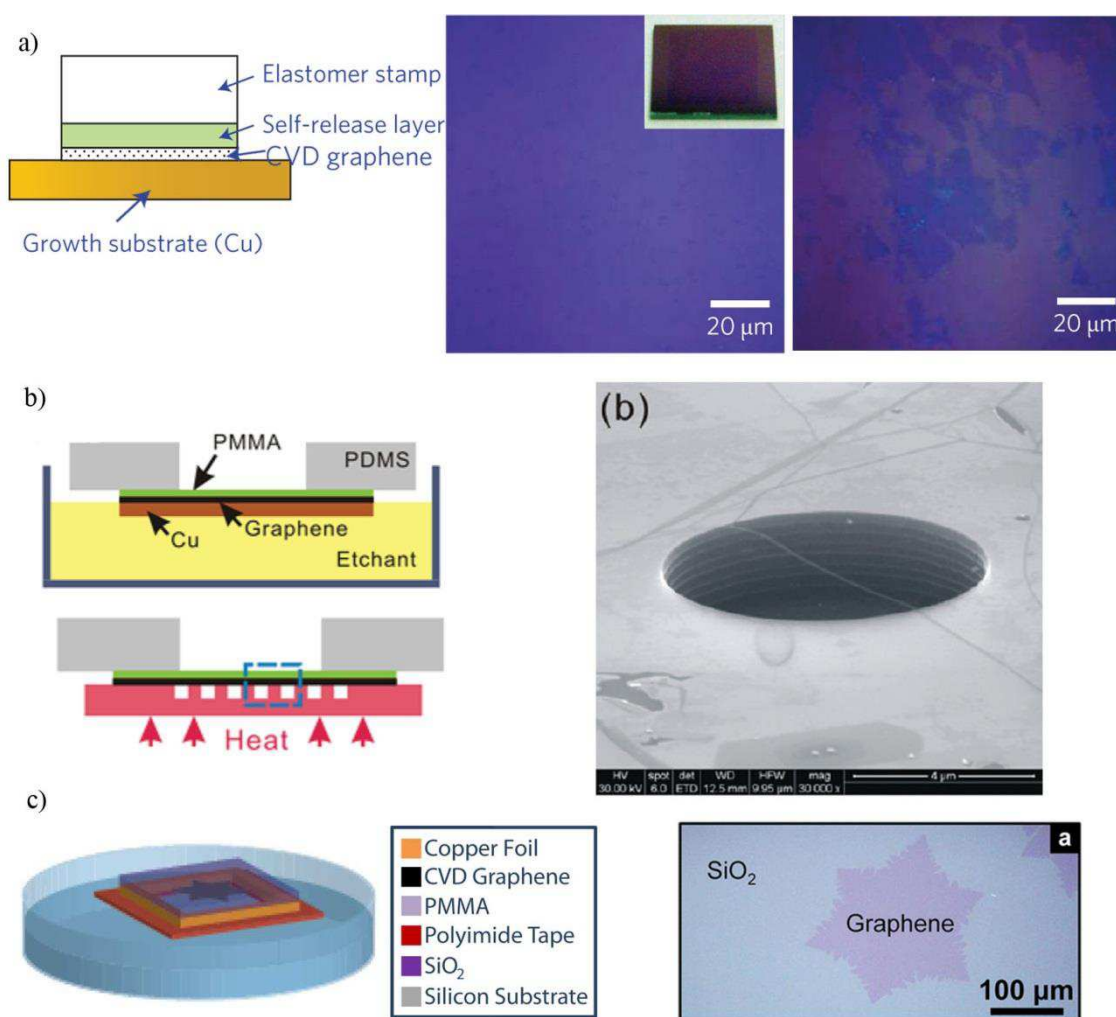


Figure 2.16. (a) Schematic illustration of the PDMS stamp method in combination with the self-release layer. Optical images of successful and failed transfers with and without the self-release layer, respectively. Reprinted by permission from Macmillan Publishers Ltd: [124], copyright 2013. (b) Schematic illustration of PDMS frame method. SEM image of single layer graphene suspended over 2 μm deep well with 5.1 μm diameter. Adapted with permission from [123]. Copyright 2011 American Chemical Society. (c) Schematic illustration of the polyimide tape frame method used by Petrone et. al. Optical image of large-grain CVD graphene transferred on SiO₂. Adapted with permission from [128]. Copyright 2012 American Chemical Society.

In both wet and dry transfer techniques, a post-transfer heating step is required to promote uniform adhesion of the graphene film to the substrate via polymer relaxation [130] (see Figure 2.17). This step is essential since the PMMA/graphene film conforms to the relatively rough surface morphology of the copper foil growth substrate [123,130]. Finally, the PMMA layer has to be removed. This is currently the most significant obstacle towards achieving clean high quality CVD graphene: incomplete dissolution in solvents such as acetone and toluene leave polymer residues $\sim 1\text{--}2$ nm thick on the graphene surface [131,132]. High-temperature annealing ($350\text{--}500^\circ\text{C}$) in an Ar/H₂ atmosphere [133,134] or in high-vacuum [135] can be used to remove such residues, but leads to heavy p-doping and mobility degradation of graphene on SiO₂ substrates [127,133] and is further incompatible with heat sensitive substrates (e.g. pre-patterned, plastic or organic substrates).

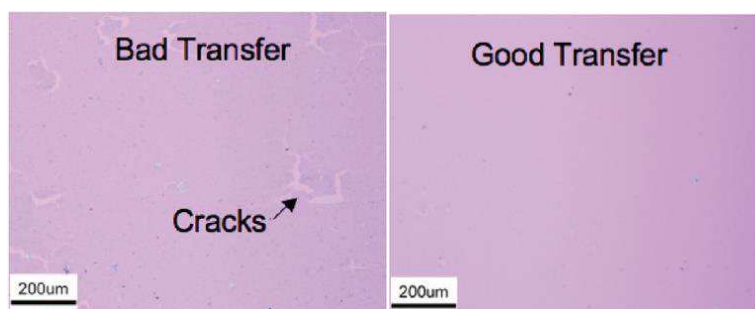


Figure 2.17. The optical microscopy images of graphene films wet transferred on SiO₂/Si using PMMA as supportive polymer with and without double coating [130]. adapted with permission from [130]. Copyright 2009 American Chemical Society.

The entirely polymer-free methods have been recently demonstrated by Regan et al. [136] and Lin et al. [137]. In [136] CVD graphene was transferred using holey amorphous carbon transmission electron microscopy (TEM) grids (Figure 2.18 a). The contact between graphene and the target grid was achieved using IPA that during evaporation brings graphene and the grid together into intimate contact. However, this process results in the transfer of relatively small graphene areas of a few tens of micrometres (Figure 2.18 a). Lin et al. has presented the polymer free method for CVD graphene transfer using a special graphite holder and a mixed solution with reduced surface tension (Figure 2.18 b). The transferred graphene was free of organic residues that are typically found on polymer supported graphene. The carrier mobility of graphene transferred on h-BN was as large as $63\,000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$. However, the optical microscopy and atomic force microscopy results have not been discussed in the study leaving the large scale quality of the transferred graphene film questionable.

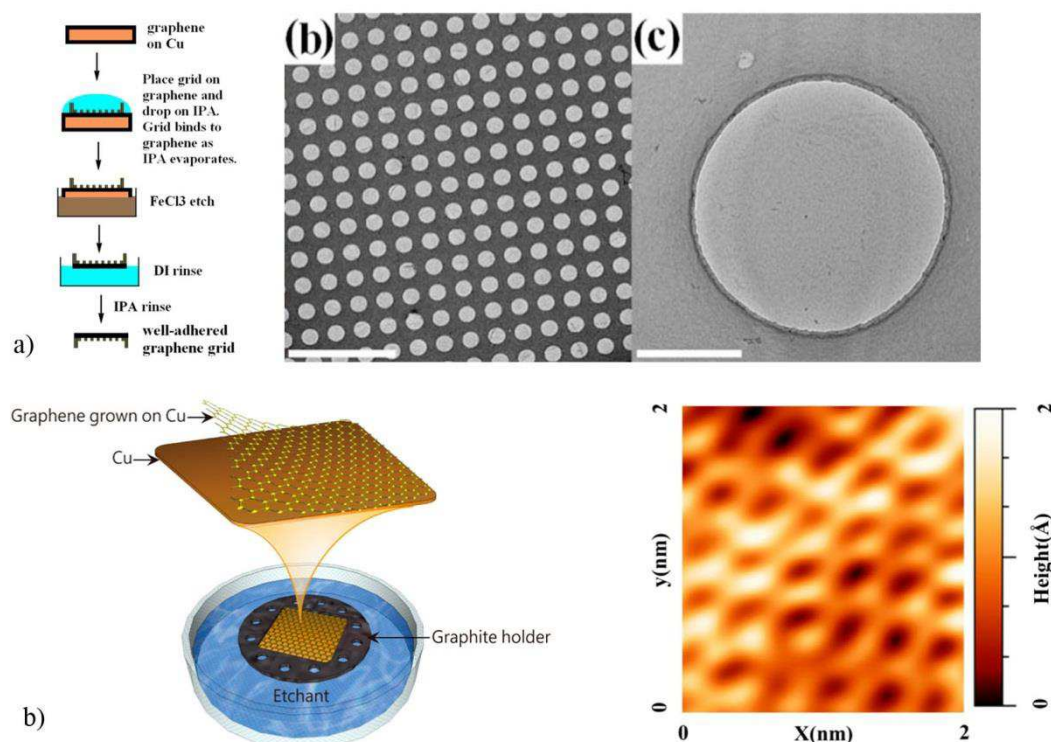


Figure 2.18. (a) Schematic illustration of the polymer-free transfer process used in Ref. [136]. Optical images of the transferred CVD graphene. Scales are 10 μm and 0.5 μm . Adapted from [136], with the permission of AIP Publishing. (b) Schematic illustration of the polymer-free transfer process used in Ref. [137]. STM image of the transferred graphene on the Si (1 1 1) substrate. Adapted with permission from [137]. Copyright 2014 American Chemical Society.

The electrical properties of graphene devices are strongly influenced by the substrate characteristics. While SiO_2/Si substrates provide a straightforward layer structure for electrostatic gating and a necessary optical contrast for graphene visualization, the carrier mobility in graphene/ SiO_2 structures is generally limited by charged surface states and impurity scattering [138–140], surface optical phonons [140,141] and substrate roughness [131,142,143]. SiO_2 surface passivation techniques such as SAMs or hBN buffer layers have been demonstrated to improve the electrical properties of CVD graphene [12,144–146]. In particular, CVD graphene on an hBN layer has been recently reported with electrical properties comparable to those of exfoliated graphene demonstrating low temperature mobilities up to 50 000 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [128,147]. It is important to emphasise that exfoliated hBN was utilized in Ref [128,147]. In contrast, CVD hBN buffer layers have been reported to provide much lower mobilities of only 3100 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [148] and 2560 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ [146], which is mainly related to transfer-induced polymer residues between graphene and hBN layers.

While surface engineering can be used to improve the electrical properties of graphene, control of the graphene/dielectric interface is crucial to provide large-area continuous graphene films. In general, exfoliated graphene has poor adhesion to the SiO₂ substrate leading to small sizes of transferred flakes, which can be easily detached from the substrate during the subsequent device fabrication processes [149]. The size of exfoliated graphene flakes is significantly improved by O₂-plasma treatment demonstrating the stronger interaction between graphene and the O₂-plasma-treated SiO₂ surface [150]. During the wet transfer process of CVD graphene, adhesion is provided by the evaporation of trapped liquid between the graphene and underlying substrate, which draws the graphene film into intimate contact with the substrate [151]. However for the dry transfer processes, this adhesion mechanism is no longer present, resulting in poor robustness of the graphene film to subsequent processing steps such as solvent treatment. In this case, additional surface engineering, such as the use of O₂-plasma treatment, SAM modification and hBN deposition, is needed in order to provide good graphene adhesion.

2.6 Raman spectroscopy of graphene

Raman spectroscopy is a fast and non-destructive method, which is widely used for the characterization of structural and physical properties of materials [152]. This technique is especially appealing for graphene analyses, since almost all the incident wavelengths are resonant due to the absence of a band gap in graphene. Raman spectroscopy allows identifying the presence of graphene and a number of layers in the structure. Furthermore, Raman spectrum contains information about graphene atomic structure and electronic properties. Using this technique it is possible to analyse doping, defects, strain, disorder and chemical modifications in graphene [153].

Single layer graphene has three acoustic and three optical branches in the phonon dispersion (Section 2.2.2). Since the unit cell of graphene contains two atoms, there are six normal modes present at the Brillouin zone centre Γ [154]: A_{2u}, B_{2g}, E_{1u} and E_{2g} (Figure 2.19 a), where E_{2g} and B_{2g} are doubly degenerate. Unlike Raman and infrared inactive optical B_{2g} phonons, the optical E_{2g} phonons are Raman active and define main bands in the graphene Raman spectrum.

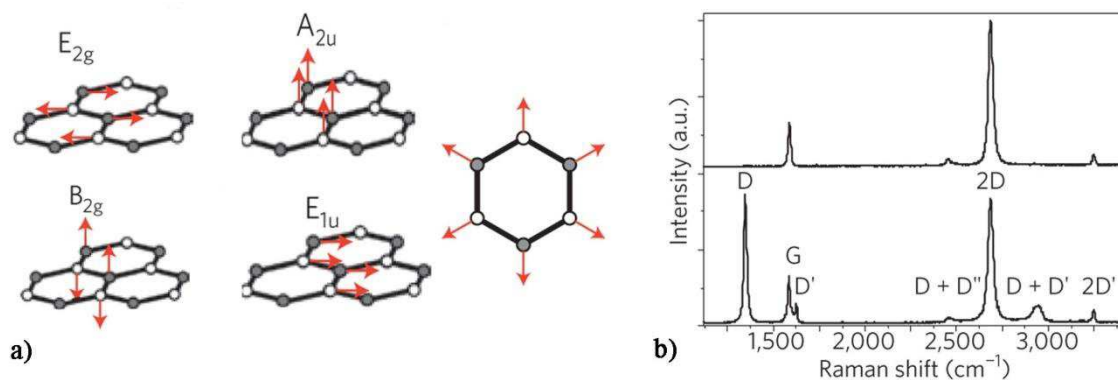


Figure 2.19. (a) Γ -point phonon-displacement pattern for graphene. Empty and filled circles represent inequivalent carbon atoms. Red arrows show atom displacements. Atom displacements (red arrows) for the A_{1g} mode at K. (b) Raman spectra of pristine (top) and defected (bottom) graphene. Adapted by permission from Macmillan Publishers Ltd: [153], copyright 2013.

The typical Raman spectrum of single layer graphene consists of distinct bands (Figure 2.19 b). The band in the $1500\text{--}1700\text{ cm}^{-1}$ region, the G band, is the first order Raman band that corresponds to high-frequency E_{2g} phonons at Γ -point. The G band is characteristic of sp^2 -hybridised carbon-carbon bonds and is common for graphitic materials, where the detailed material structure defines the band position. All the other bands in graphene Raman spectrum are the result of double resonance processes that might be described in the following way (Figure 2.20): after excitation of an electron-hole pair two electron-phonon scattering events occur followed by electron-hole recombination [155,156]. The D band around 1350 cm^{-1} is defined by the breathing modes of six-atom rings (Figure 2.19 a) and represents an intervalley process, when one of the electron-phonon scattering events occurs elastically due to the presence of defects (Figure 2.20). This electron-phonon scattering process can also happen as an intravalley event resulting in the D' peak appearance. The 2D and 2D' peaks are the overtones of the D and D' peaks, respectively. The 2D and 2D' peaks are always present due to the momentum conservation satisfied by two phonons with opposite wave vectors (Figure 2.20) [155]. The band around 2450 cm^{-1} , frequently called the D'' peak [157] (indicated as D+D'' in Figure 2.19 b), is detected in defected samples and might be assigned to a combination of a D phonon and a phonon from the LA branch [153].

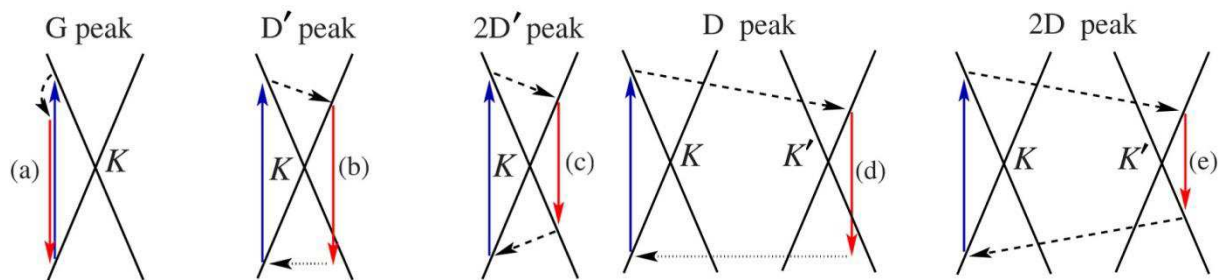


Figure 2.20. Electron and phonon interactions responsible for the common peaks in graphene Raman spectrum: (a) intravalley one-phonon G peak, (b) defect-assisted intravalley one-phonon D' peak, (c) intravalley two-phonon 2D' peak, (d) defect-assisted intervalley one-phonon D peak, and (e) intervalley two-phonon 2D peak. Vertical solid arrows represent interband transitions accompanied by photon absorption (upward arrows) or emission (downward arrows) (the photon wave vector is neglected). Dashed arrows represent phonon emission. Horizontal dotted arrows represent defect scattering. Reprinted with permission from [155]. Copyright 2009 by the American Physical Society.

Determination of the number of graphene layers

As we have discussed, the graphene Raman spectrum contains information about the electronic structure and electron-phonon interactions. Therefore, any variation of electronic properties significantly affects positions, widths and intensities of the Raman peaks enabling easy detection of single, bilayer and few-layer graphene.

The 2D peak has been reported [158,159] to significantly change its shape and intensity depending on the number of graphene layers (N). The sharp 2D peak with the full-width at half maximum of $\sim 30 \text{ cm}^{-1}$ is typically observed for undoped single layer graphene, while bilayer graphene has been demonstrated to have a much broader 2D peak of $\sim 60 \text{ cm}^{-1}$ (Figure 2.21). With an increasing number of layers ($N > 5$) the spectrum becomes barely distinguishable from bulk graphite. It should be noted that the 2D peak for bilayer graphene is quite different comparing with both single layer graphene and bulk graphite. The 2D peak in bulk graphite can be approximated with 2 Lorentzian components, whereas for bilayer graphene 4 components are present. The 2D peak evolution can be explained by the splitting of the electronic bands (Figure 2.21 d) due to the interaction of the graphene planes.

The effect of the number of layers on the G peak has also been described [158,159]. In contrast to the behaviour of the 2D peak, the full width at half maximum of the G peak remains almost unaltered, while the integrated intensity of the G peak monotonically increases with the number of layers. Since the integrated intensity of the 2D peak changes only slightly, the ratio between two peaks can be used as an indicator of the number of

graphene layers (Figure 2.21 b). For undoped single layer graphene the ratio is typically ~ 0.3 and increases almost linearly from one to four layers and saturates for $N > 5$. However, caution should be taken when identifying the number of graphene layers through the peak ratio only as the G peak intensity is highly affected by the doping level of graphene. Therefore, one should always analyse the full width at half maximum of the 2D peak along with the ratio of the integrated intensities for G and 2D peaks.

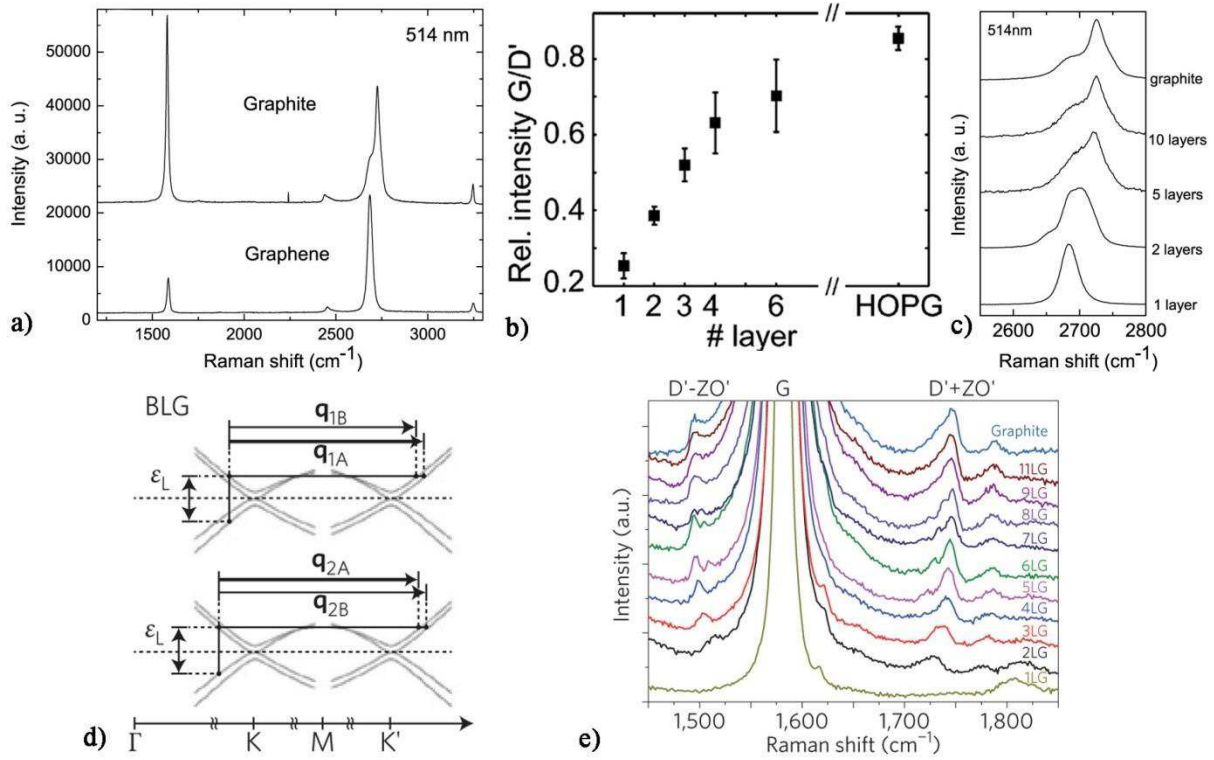


Figure 2.21. (a) Comparison of Raman spectra at 514 nm for bulk graphite and graphene (scaled to have similar height of the 2D peak) [158]. (b) Evolution of the ratio of the integrated intensities for the G and 2D peaks at 532 nm with the number of layers [159]. (c) Evolution of the 2D peak at 514 nm with the number of layers [158]. (d) Phonon wave vectors corresponding to the 2D peak in BLG [158]. (e) Combination modes close to the G peak as a function of the number of layers [160,161]. (a,c,d) Adapted with permission from [158]. Copyright 2006 by the American Physical Society. (b) Adapted with permission from [159]. Copyright 2007 American Chemical Society. (e) Adapted by permission from Macmillan Publishers Ltd: [153], copyright 2013.

An alternative approach to probe the number of graphene layers is based on the analyses of out-of-plane vibrations [160,161]. The activation of out-of-plane modes A_{2u} and B_{2g} (Figure 2.19 a) has been reported for few-layer graphene, where additional peaks located around 1500 and 1700 cm^{-1} were detected. These peaks can be assigned to the combination of the E_{2g} phonon and the B_{2g} phonon of the layer-breathing modes. The peak positions strongly depend on N enabling determination of the number of graphene layers up to $N=8$. Since the

activation of out-of-plane vibrations is not restricted to graphene, this approach might be applicable to other layered materials.

Defects and disorder analysis

Analysis of defects and disorder in graphene is crucial to the understanding of the graphene properties. It is an important step in any device fabrication and these parameters can be used to compare different samples as well as different parts of the same sample. Raman spectroscopy provides an easy approach for the defect probing in graphene using defect-activated peaks. As we have discussed, the D and D' bands appear in the spectrum in presence of defects. These bands originate from intervalley and intravalley scattering processes, where defects provide the missing momentum satisfying the momentum conservation rule in the Raman scattering process [155,156].

A three stage classification of disorder has been proposed recently [162] for carbons to describe the Raman spectrum evolution from graphite to amorphous carbon: (1) graphite to nanocrystalline graphite; (2) nanocrystalline graphite to low sp^3 amorphous carbon; (3) low sp^3 amorphous carbon to high sp^3 amorphous carbon. Since stages 1 and 2 are the most relevant in the study of graphene, they are summarized here.

The evolution of the Raman spectrum during the transition process from single layer graphene to nanocrystalline graphene (stage 1) can be described as a following set of steps [162,163]: (a) a D peak appears and $I(D)/I(G)$ increases; (b) a D' peak appears; (c) all peaks broaden; (d) the D + D' peak appears; (e) at the end of stage 1, the G and D' peaks widen resulting in a single, upshifted, wide band at $\sim 1,600\text{ cm}^{-1}$ (Figure 2.22 a samples with $L_D = 24, 14, 13, 7, 5\text{ nm}$). In stage 2 the spectrum evolves in the following way [162,163]: (a) the G peak position shifts from $\sim 1,600\text{ cm}^{-1}$ towards $\sim 1,510\text{ cm}^{-1}$; (b) the $I(D)/I(G)$ ratio decreases towards 0; (c) the G peak position becomes strongly dispersive with the excitation laser energy getting stronger with higher disorder; (d) second order peaks lose their sharp feature becoming a broad modulated bump between ~ 2300 and $\sim 3200\text{ cm}^{-1}$ (Figure 2.22 a the onset of stage 2 is the sample with $L_D = 2\text{ nm}$).

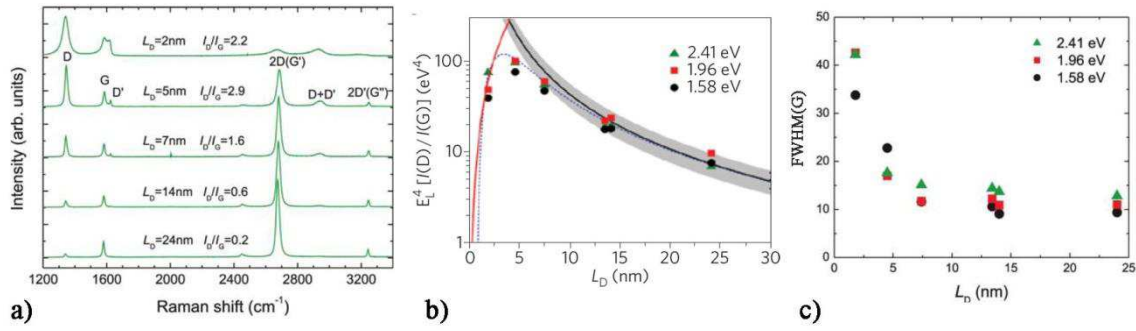


Figure 2.22. (a) Raman spectra of five ion bombarded single layer graphene measured at 514.5 nm. The respective I_D/I_G and L_D values are indicated for each spectrum.

(b) Amorphisation trajectory $E_L^4 [I(D)/I(G)]$ as a function of L_D for different excitation energies E_L . The dashed blue line is obtained from the empirical model [164]. The solid black and red lines are L_D^{-2} and L_D^2 dependences, respectively. The shaded area accounts for the upper and lower limits given by the 30% experimental error. (c) Full width at half maximum of G peak as a function of L_D . (a-c) Adapted with permission from [163].

Copyright 2011 American Chemical Society.

It has been demonstrated [162,163] that the intensity ratio of D and G peaks $I(D)/I(G)$ increases with a decreasing average interdefect distance L_D reaching a maximum at $L_D \sim 3$ nm followed by a decrease toward zero for $L_D < 3$ nm (Figure 2.22 b). In stage 1 $I(D)$ is proportional to the defects probed by the laser spot and increases due to the contribution from each defect that sums independently. In this regime $I(D)/I(G)$ is proportional to $1/L_D^2$. However, the defect contributions stop adding up independently when the distance between two defects becomes smaller than the average distance an electron-hole pair travels before scattering with a phonon, which can be estimated as $v_F / \omega_D \sim 3.5$ nm, where $v_F \sim 10^6$ m/s is the Fermi velocity at the Γ -point. In this regime (stage 2) $I(D)$ is proportional to the number of 6-fold rings in the laser spot and decreases with higher disorder. For the stage 2 a new relation has been established $I(D)/I(G) \sim L_D^2$. Using the fitting functions to the experimental data it is possible to estimate the defect density n_D :

- $n_D^2 (\text{cm}^{-2}) = 7.3 \times 10^{-9} E_L^4 (\text{eV}^4) \frac{I(D)}{I(G)}$ for the low defect density regime (stage 1 with $L_D > 10$ nm) and
- $n_D^2 (\text{cm}^{-2}) = \frac{5.9 \times 10^{14}}{E_L^4 (\text{eV}^4)} \left[\frac{I(D)}{I(G)} \right]^{-1}$ for the high defect density regime (stage 2, with $L_D < 3$ nm), where $E_L = \hbar \omega_L$ is the laser excitation energy in eV.

Since samples in stage 1 and stage 2 could have the same ratio $I(D)/I(G)$, it is important to analyse other parameters of the spectrum that depend on the defect density. It has been reported [34] that the full width at half maximum of G peak FWHM(G) remains almost constant at ~ 14 cm⁻¹ during stage 1 and doubles for the onset of stage 2 when $L_D < 3$ nm.

Therefore, combining $I(D)/I(G)$ and $FWHM(G)$ allows easy identification of the stage of disorder in the sample.

It should be noted that this analysis is limited to the Raman active defects contributing to the D peak. There are number of “silent” defects that do not activate the D peak in the Raman scattering process, for example, perfect zigzag edges, charged impurities, intercalants, uniaxial and biaxial strain. For analyses of these defects other Raman signatures might be used.

Doping level analysis

The control of the doping level and the identification of different doping domains are crucial for the development of graphene devices. Raman spectroscopy has proven to be a powerful tool for probing the doping level in graphene [165–168].

The evolution of the Raman spectrum with carrier concentration has been investigated for intentionally doped graphene, where the Fermi energy was modulated in back gate and top gate configurations [165–168]. Here, we discuss only low doping levels below $\sim 3 \times 10^{13} \text{ cm}^{-2}$. The position of the G peak is highly sensitive to the doping and increases by up to 30 cm^{-1} for hole doping and up to 25 cm^{-1} for electron doping (Figure 2.23 a). The full width at half maximum of the G peak $FWHM(G)$ significantly decreases for both hole and electron doping (Figure 2.23 b). The 2D peak shows a very different dependence on the gate voltage. The $FWHM(2D)$ stays quite constant, while the position of the 2D peak decreases for electron doping and increases for hole doping (Figure 2.23 c). Therefore, the position of the 2D peak can be used to discriminate between electron and hole doping. The intensity ratio of the G and 2D peaks ($I(2D)/I(G)$) significantly decreases with higher doping (Figure 2.23 d), which is mostly connected with the vanishing of the 2D peak.

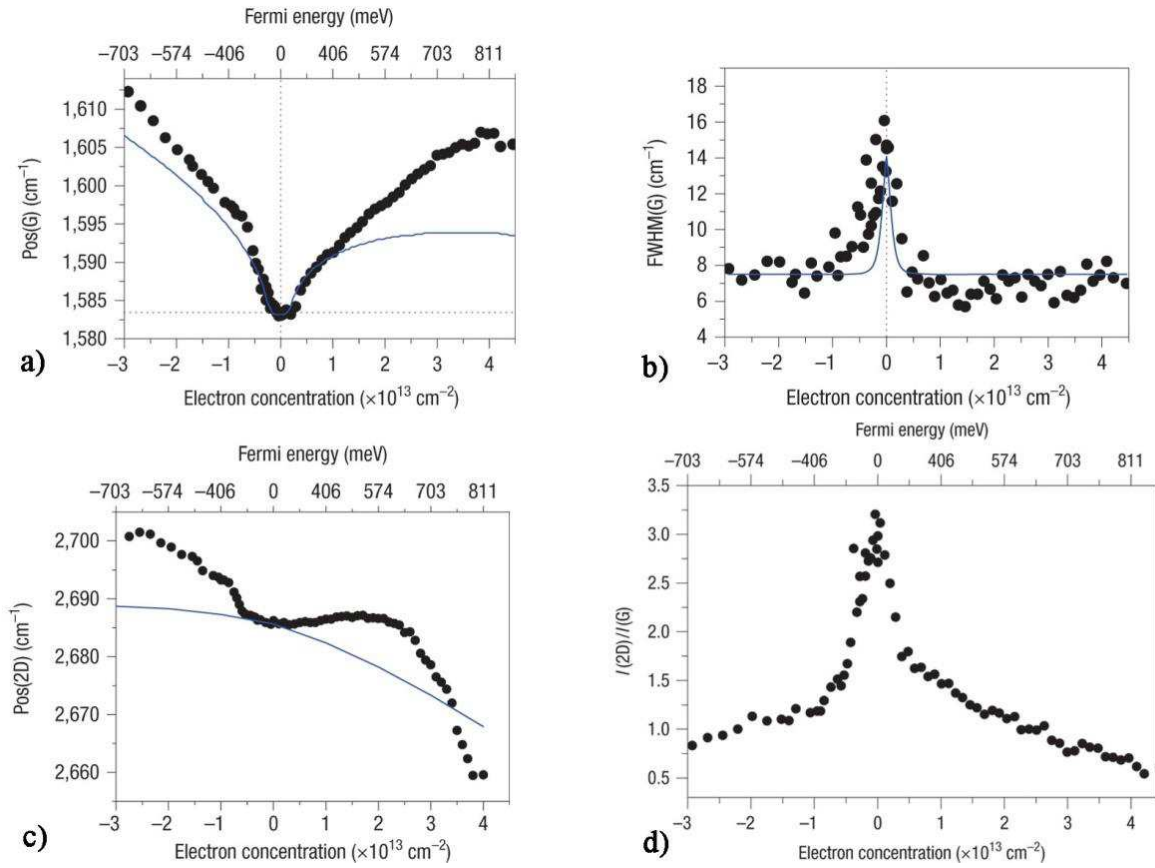


Figure 2.23. (a) Pos(G), (b) FWHM(G), (c) Pos(2D) and (d) $I(2D)/I(G)$ as a function of electron and hole doping. Adapted by permission from Macmillan Publishers Ltd: [166], copyright 2008.

The shift of the Fermi energy has two major effects in graphene [168]: (1) a change of the equilibrium lattice parameter leading to a phonon stiffening/softening, and (2) the nonadiabatic removal of the Kohn anomaly from the Γ -point that changes the phonon dispersion. The Pos(2D) upshift for p doping and downshift for n doping originate from the first effect. The second effect results in Pos(G) sensitivity to the doping level. The decrease in FWHM(G) can be ascribed to the Pauli exclusion principle leading to a blockage of the decay channel of phonons into electron-hole pairs when the electron-hole gap becomes higher than the phonon energy (Figure 2.24 a) [165]. The suppression of the 2D peak with doping occurs when the conduction band becomes filled at the energy probed by the laser (Figure 2.24 b) [168]. By varying the excitation energy, it is possible to determine the energy when the 2D peak is observable (Figure 2.24 c) and, thus, assess the Fermi energy (E_F) using the relation $\frac{2E_F}{\hbar} < \omega_L - \text{Pos}(2D)$, where ω_L is the laser frequency.

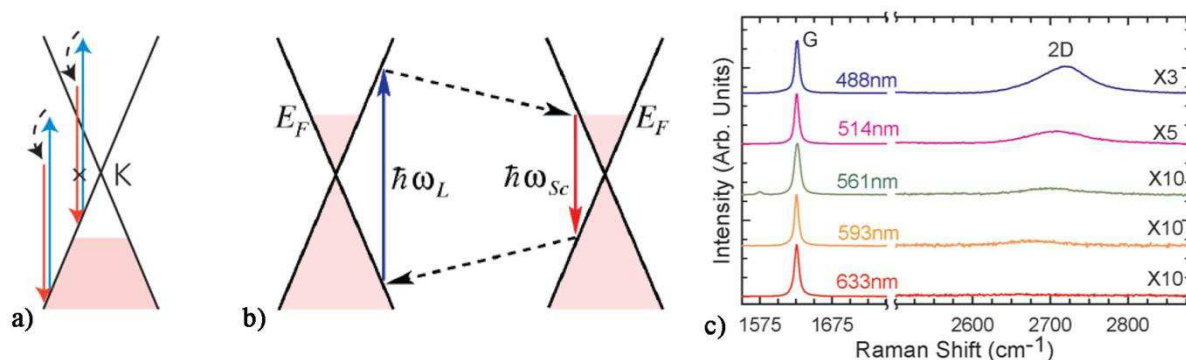


Figure 2.24. (a) One-phonon processes responsible for the G peak can be eliminated by doping, such as the one that is crossed out. (b) Schematic diagram of 2D Raman processes in doped graphene. (c) Raman spectra of highly doped graphene monolayer measured at 488, 514 532, 561, 593 and 633 nm, normalized to have the same $I(G)$ [168]. (a) Adapted by permission from Macmillan Publishers Ltd: [153], copyright 2013. (b) Adapted with permission from [168]. Copyright 2011 American Chemical Society.

Strain analysis

Due to graphene's 2D nature, it exhibits a high level of flexibility. While this property is of high importance for a range of applications, in particular for flexible electronics, this also means that uncontrollable strain can be induced during various processes involved in the preparation of graphene films and devices. For example, CVD graphene is typically grown at high temperatures (in excess of 1000°C) leading to thermal expansion of the underlying metallic substrate such as copper. However, the difference in thermal expansion coefficients means that during the cooling process compressive strain is introduced to graphene [169,170]. Furthermore, the strain can be induced during the transfer technique and post-transfer treatment. In fact, it has been demonstrated that during annealing at 300 °C graphene on SiO₂ substrate exhibits structural deformation forming sub-nm ripples with a lateral quasi-period of several nm [127] indicating the presence of corrugation-induced strain [131].

Raman spectroscopy has proven to be a useful tool in strain characterization for crystalline and semi-crystalline materials, since changes in lattice constants typically affect the phonon frequencies [171]. Numerous studies have been performed to analyse strain-sensitivity of the Raman properties for graphene material [172–177]. Under mechanical strain, graphene's Raman spectrum demonstrates several key changes: tensile strain causes phonon softening (red shift of the signature graphene Raman peaks), while compressive strain leads to phonon hardening (blue shift). Furthermore, the peak splitting is observed for both G and 2D bands.

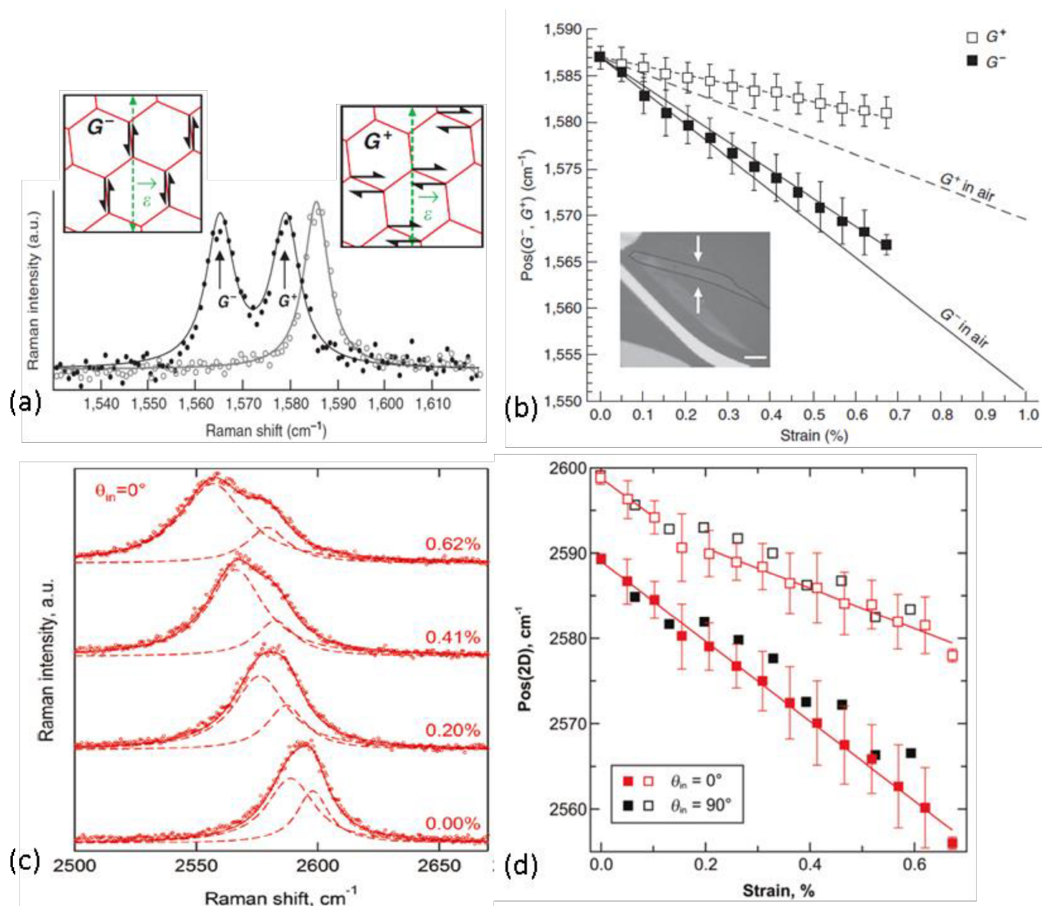


Figure 2.25. Graphene's Raman spectrum under strain. (a) G peak of graphene at 0% (grey) and 1% (black) strain. Inset shows the origin of the G⁺ and G⁻ peaks due to the angle between strain axis and lattice. (b) Dependence of G⁺ (empty squares) and G⁻ (filled squares) frequency on increasing uniaxial tensile strain. Inset shows an optical image of the measured flake with 10nm scale bar, arrows indicate the strain direction. Adapted from [178]. (c) 2D peak modification with increasing tensile strain applied in parallel to the polarisation of incident laser excitation. The 2D peak has been fitted with two Lorentzian peaks in each spectrum. (d) Dependence of 2D frequency on increasing strain with filled and empty squares representing the two individual Lorentzian components for the 2D peak. Red and black colours correspond to different laser polarization being parallel and perpendicular to the applied stress. The perpendicular data points are offset by -4cm⁻¹ for clarity. Adapted with permission from [179]. Copyright 2011 American Chemical Society.

Due to strain-induced symmetry breaking, the G peak splits into two distinct sub-peaks G⁺ and G⁻ (Figure 2.25). The degree of peak separation depends strongly on the relative angle between the graphene lattice and the strain axis. The shift of the G peak with increasing strain demonstrates linear dependence for both sub-peaks. The slope of this relationship is known as the Gruneisen parameter and is $\frac{\partial \omega_G}{\partial \epsilon}$, where ω_G is the frequency of the G peak and ϵ is the applied strain. The Gruneisen parameters have been reported by several groups and differ depending on the method of calculation or the experimental set up [173,180,181]. The typical values for uniaxial strain of the G⁻ and G⁺ are 33 cm⁻¹/‰ and 15 cm⁻¹/‰ [181].

As shown in Figure 2.25, the 2D peak also undergoes splitting under strain conditions [175,179]. The 2D peak generally contains two Lorentzian components that demonstrate different strain sensitivity [182,183]. This can be explained by the double resonance nature involving two photons that is the origin of the 2D peak [184]. Under strain the distorted lattice can allow new resonant conditions leading to a shift of the 2D band [179]. The dependence of the 2D peak position with increasing strain is presented in Figure 2.25 (b), where a clear linear trend is observed. The strain sensitivity of the 2D peak ($\frac{\partial\omega_{2D}}{\partial\varepsilon}$) is approximately double that of the G peak, with typical values of 63.1 cm⁻¹/‰ and 44.1 cm⁻¹/‰ for the 2D⁻ and 2D⁺ sub-peaks respectively observed for uniaxial strain [175].

Typically strain-sensitivity experiments have been performed utilizing mechanically exfoliated graphene samples that are single crystal material with well-defined lattice orientation. However, in our study we employ CVD graphene where numerous domains with differing orientation are present. The domain nature of CVD graphene strongly influences its mechanical properties [185,186]. In fact, the presence of domain boundaries affects graphene smoothness causing deviations from an ideal flat surface due to inherent strain on the surrounding lattice [186]. Moreover, mechanical strain applied to polycrystalline graphene does not disperse homogeneously across the lattice, but defects that are present in the areas such as domain boundaries undergo significant strain [186]. Furthermore, as discussed above, the relative orientation of the strain and lattice is an important factor. However, in CVD graphene this cannot be controlled and the orientation of the domains and their boundaries can be considered random.

The strong sensitivity of the G and 2D peaks to both strain and induced charges complicates independent determination of either effect that is crucial for graphene quality analysis. Recently, it has been demonstrated that strain and charge doping in graphene can be separated using correlation coefficients between the doping and strain-induced Raman shifts $\Delta\omega(2D)$ and $\Delta\omega(G)$ [187]. The correlation between the G and 2D peak positions can be described as $\Delta\omega(2D) \approx \gamma \Delta\omega(G)$, where γ is a correlation coefficient for the specific process.

For the biaxially strained graphene, either compressive or tensile, a number of correlation coefficients have been reported in the range of $\gamma^{\text{biaxial}} \sim 2.25\text{-}2.8$ both experimentally and theoretically [173,176,180,188]. For uniaxial stress, as discussed above, the direction of the strain with respect to the crystallographic axes of graphene is important due to the strain-induced symmetry breaking that results in G peak splitting. In fact, for graphene strained

along the zigzag (arm-chair) directions, the correlation coefficients of 2.05 (1.89) and 2.00 (3.00) have been observed for G^- , $2D^-$ and G^+ , $2D^+$ peaks, respectively [175]. In experiments where insufficient peak splitting is observed, the correlation coefficient can be approximated as an average of coefficients for G^- , $2D^-$ and G^+ , $2D^+$ peaks leading to 2.02 and 2.44 for stress applied along zigzag and arm-chair directions, respectively. Due to lack of control over native stress and the stress induced during exfoliation and subsequent contact with target substrate, the strain can be aligned along any direction between the zigzag and arm-chair axes of exfoliated graphene, but is still expected to lie in the range of 2.02–2.44. In the case of CVD graphene where domain orientation is randomly distributed, the correlation coefficient can be approximated as an average of coefficients for different strain/lattice orientations leading to $\gamma^{\text{uniaxial}} \approx 2.2$. As discussed in the previous section, the effect of induced charges is more pronounced for the position of the G peak than the 2D peak. In fact, the correlation coefficient of 0.7 ± 0.05 has been reported for hole doping [187]. Interestingly, the relative shift of $\omega(G)$ and $\omega(2D)$ with electron doping becomes quite nonlinear for high charge density which complicates correlation coefficient calculations. However, the CVD graphene used in the current study is known to exhibit predominantly hole-doping. Thus, we can concentrate only on hole-doping effects.

With known correlation coefficients it is possible to extract the doping and strain contributions using a vector model, as depicted in Figure 2.26. The origin (O point) corresponds to intrinsic undoped and unstrained graphene and can be determined by analysing freestanding exfoliated graphene. The values for $\omega(G) \approx 1581 \text{ cm}^{-1}$ and $\omega(2D) \approx 2677 \text{ cm}^{-1}$ have been reported for graphene suspended over a circular well with 7 μm in diameter and 5 μm in depth [187]. Freestanding graphene has been previously reported to have a residual charge density less than $2 \cdot 10^{11} \text{ cm}^{-2}$ and thus can be considered charge-neutral [189]. While there is a probability of pretension in the suspended graphene, there are a number of evidences to consider it as strain free material [187]. It should be noted that the origin values are crucial for the vector model since they define absolute values of the strain and doping. Therefore, care should be taken while selecting the origin values. This is particularly important for dispersive second-order Raman peaks, such as the 2D peak. In this thesis, Raman spectroscopy measurements are performed with 532 nm laser excitation that is very close to the 514.5 nm laser excitation used in Ref. [187]. Therefore, the above-mentioned values measured for the freestanding graphene can be directly used for the origin.

Using the unit vectors corresponding to strain ($\vec{e}_T$, $\gamma^{\text{uniaxial}} = 2.2$) and hole doping ($\vec{e}_H$, $\gamma = 0.7$), each point in the $\omega(\text{G}) - \omega(2\text{D})$ space can be represented by $\vec{OP} = a \cdot \vec{e}_T + b \cdot \vec{e}_H$, where a and b are constants describing independent components of strain and hole-doping, respectively. The unit vectors divide the $\omega(\text{G}) - \omega(2\text{D})$ space into four quadrants (Q1-Q4). With increasing charge doping the values will move from the O point along the $\vec{e}_H$ vector. Similar behaviour is expected in the case of strain increase, where the points will move up or down along the $\vec{e}_T$ vector corresponding to compressive or tensile strain, respectively. Interestingly, the quadrants Q2 and Q3 are not allowed since the induced doping always increases the Pos (G).

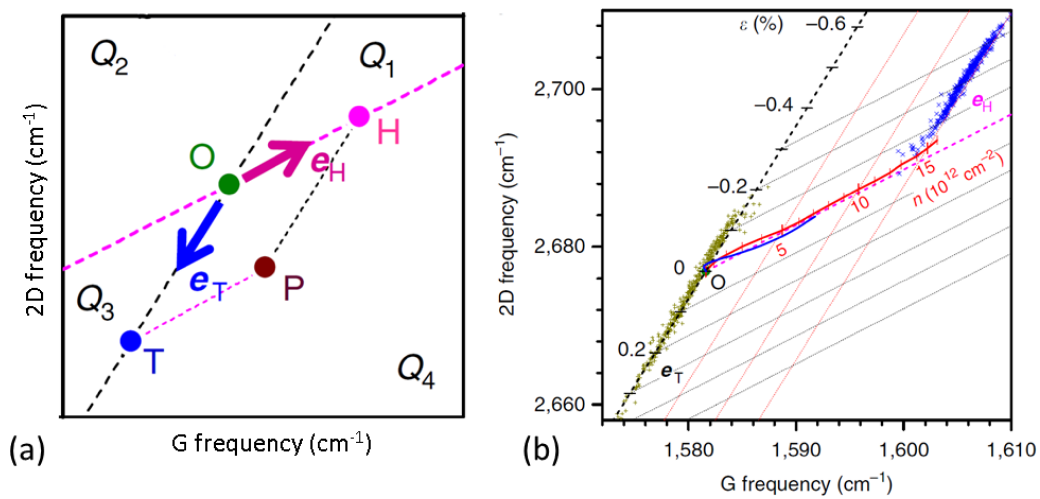


Figure 2.26. Correlation between the G and 2D peak positions. (a) A vector model decomposition of the effects of hole-doping and strain. The green dot (denoted O) is the peak position for a freestanding graphene sample that is not affected by strain or charge doping. The dashed magenta and black lines represent the summary of observed peak shifts for increasing hole doping and randomly oriented uniaxial stress, respectively. The vectors $\vec{e}_H$ and $\vec{e}_T$ corresponds to strain-free and charge-neutral unit vectors, respectively. (b) The scatter plot represents data obtained from Raman mapping of three graphene samples before (+) and after (x) thermal annealing at 400 °C. The theoretical and experimental trajectories of G and 2D peak positions affected by strain and doping are presented by black and magenta lines, respectively. Adapted by permission from Macmillan Publishers Ltd: [187], copyright 2012.

The described model can be used to perform quantitative analysis of strain and charge density in the samples, as presented in Figure 2.26 (b). Here, the properties of an exfoliated graphene flake are analysed before and after thermal annealing in vacuum at 400°C for 2 hours [187]. It is clear that the annealed graphene demonstrates an increased hole-doping with a charge density of about $1.4 \times 10^{13} \text{ cm}^{-2}$. Interestingly, the native tensile strain has been relieved by annealing, while compressive strain of -0.3% - 0 has been induced. It should be noted that the strain values presented in Figure 2.26 (b) have been calculated under assumption of uniaxial

strain and in particular the strain sensitivity of $\Delta\omega(G)/\Delta\epsilon \approx -23.5 \text{ cm}^{-1}/\%$ [175]. In the case of biaxial strain, the exact values are quite different due to higher average sensitivity factor of G peak shift of $-69.1 \text{ cm}^{-1}/\%$ [173,176,180].

2.7 Kelvin force probe microscopy (KFM) of graphene

Analysis of the local electronic properties of graphene can provide crucial information for understanding device functionality. Scanning measurement techniques, and in particular Kelvin probe force microscopy (KFM), are widely used for mapping of graphene's surface potential. For example, KFM has successfully been used to distinguish between areas of single and multilayer graphene [190] and to study the effects of charge transfer from substrate to graphene [191].

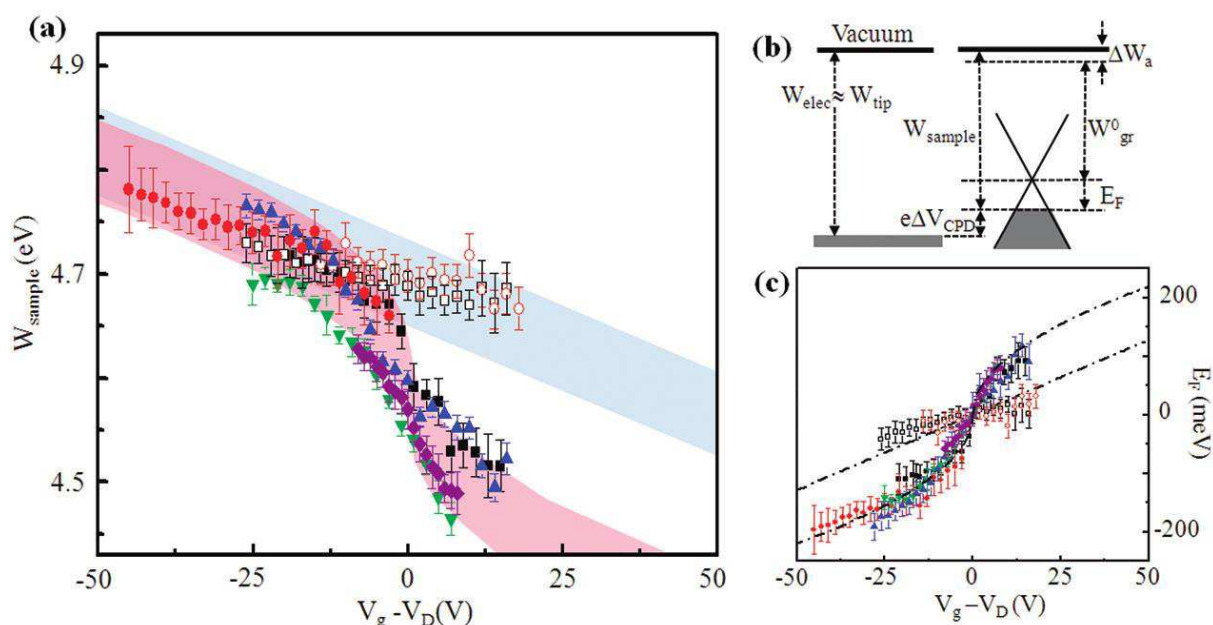


Figure 2.27. Back gate modulation of work function (a) and Fermi energy (c) for single layer (filled symbols) and bilayer (open symbols) graphene. (b) The energy levels for KFM tip and graphene samples. Adapted with permission from [192]. Copyright 2009 American Chemical Society.

As discussed in details in Section 3.1.4, the KFM technique provides measurements of the surface contact potential difference, $e\Delta V_{\text{CPD}} = W_{\text{tip}} - W_{\text{sample}}$, where W_{tip} and W_{sample} are work functions of the tip and sample, respectively. With a known work function of the tip it is possible to extract the work function of the material. In the case of the scanning technique, information on local variations of work function can be obtained. Figure 2.27 demonstrates the application of KFM to characterise the electronic structure of graphene under back gate conditions [192]. A successful modulation of graphene's work function is

observed. The variation of work function can be explained by the change of E_F in graphene devices, since $W_{sample} \approx \Delta W_a + W_{gr0} - E_F$, where W_{gr0} is the intrinsic work function of undoped graphene and ΔW_a is the offset of the work function due to the adsorbate dipole layer formation present under ambient conditions. As the adsorbate layer is similar over the whole of the graphene film, the local fluctuations of work function can also be related to the local changes in E_F due to charge fluctuations [193].

3 Experimental and computational methods

In this chapter, the experimental methods for the sample fabrication and characterization used throughout this thesis are discussed. Particular attention is devoted to the techniques used for graphene quality assessment. The principles of time resolved experiments are presented in details. Additionally, the technique of numerical calculations, in particular finite difference time domain (FDTD) method, is discussed with particular focus on plasmonic applications. Further specific details are typically provided where relevant in the corresponding chapters.

3.1 Assessment of graphene quality

3.1.1 Optical microscopy

As discussed in Chapter 2.2, a single layer of graphene can absorb a significant fraction (2.3%) of incident light across the infrared and visible range [68]. Furthermore, transmittance of white light decreases with number of graphene layers, as each layer absorbs additional 2.3% [68]. As a consequence, even single layer with a thickness of only 0.34 nm can be observed on a SiO₂/Si substrate using optical microscopy. This is the result of interference with SiO₂ acting as a spacer. In general, the adjustment of the SiO₂ spacer thickness can maximize the optical image contrast [72,73]. For the naked eye observation a SiO₂ thickness of ~90 and ~290 nm is commonly used. These conditions provide a contrast peak around 560 nm (green) where the spectral sensitivity of the human eye is also maximal.

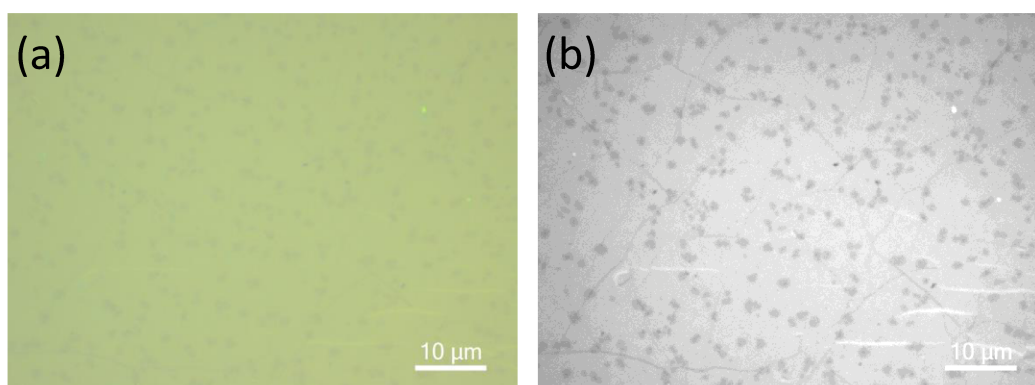


Figure 3.1. Optical microscopy image of graphene on SiO₂/Si before (a) and after contrast enhancement (b).

In this study, we use the SiO₂/Si substrates with both ~90 and ~300 nm. Both substrates result in an excellent image contrast. The multilayer areas and wrinkles as well as tears are clearly observed using optical microscopy Figure 3.1. It should be noted that software for image

enhancement (FastStone Image Viewer) is used to provide even better contrast conditions (Figure 3.1 b).

3.1.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a common technique used to study the sample's surface topography and composition. The method is based on scanning the surface with a focused electron beam that interacts with the material producing secondary electrons, back-scattered electrons, characteristic X-rays and light (cathodoluminescence) [194]. The secondary electrons being emitted very close to the sample surface typically carry information about the surface topography. Detection of the secondary electrons is performed using an Everhart-Thornley detector consisting of a scintillator and a photomultiplier. A scintillator converts the electrons into photons that are detected by the photomultiplier tube and converted back into electrical signal. The output voltage from the photomultiplier tube is brightness intensity that forms an image of the sample surface. Resolution of the SEM technique is not diffraction limited and typically depends on an electron beam spot that is determined by the electron wavelength and the electron-optical system. Furthermore, the resolution is limited by the interaction between the sample and the beam, since the secondary effects can significantly increase the sampling volume. The typical resolution of SEM systems is between 1 and 20nm.

SEM images presented in this thesis are taken using Raith E-line system with 10keV acceleration voltage and a 30 μm aperture. It should be noted that graphene is sensitive to electron beam exposure [195,196]. Therefore, low accumulation time is used whenever possible.

3.1.3 Atomic force microscopy (AFM)

Atomic force microscopy (AFM) is a powerful surface analyses technique providing information on micro- and nanoscales. AFM facilitates surface imaging in real-space and can be used to analyse surface topography and additional surface properties such as adhesion, stiffness, magnetic properties, conductivity and many more [197].

The operating principles of an AFM are described in Figure 3.2. An AFM probe, that typically consists of a cantilever (100 to 200 μm long) and a sharp tip (less than 10nm across), is scanned over a sample, while tip/surface interactions are used as feedback mechanisms to

trace the surface topography [197,198]. When tip is brought into contact with the surface, the interaction between the tip and the surface bends cantilever that is detected using a focused laser beam deflection system. The bending of the AFM cantilever is typically caused by several forces and in particular the interatomic van der Waals forces [197]. When the tip approaches the surface, attractive forces act between the tip and sample before repulsive forces start to dominate.

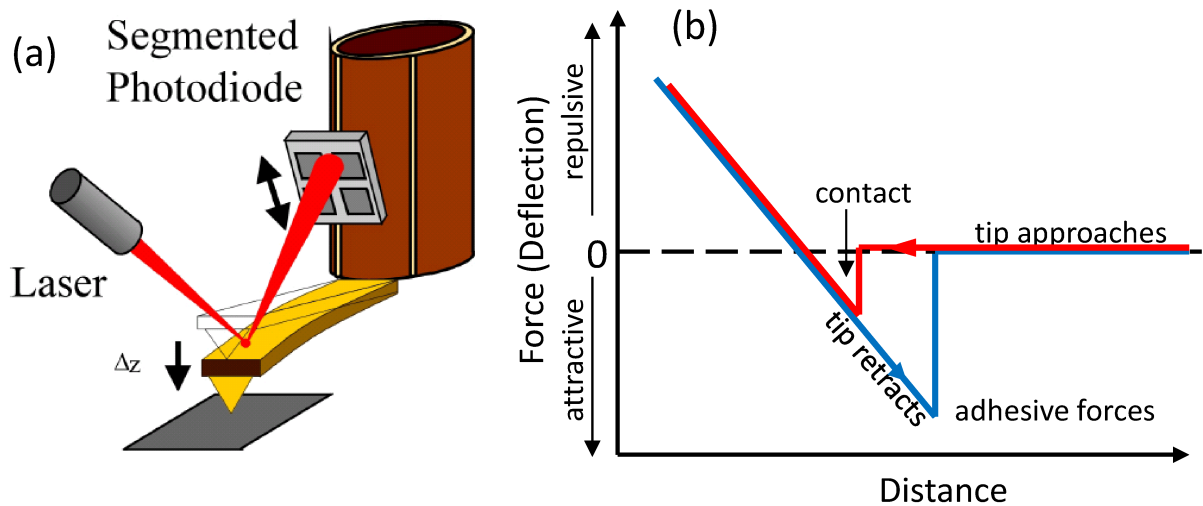


Figure 3.2. (a) Schematic of AFM operation. Adapted from [199]. (b) The dominating forces during AFM measurements.

During the contact mode AFM, the bending of the cantilever is used as the feedback parameter to ensure a constant force between tip and surface. The up and down movement of the scan stage is recorded as surface topography. However, the contact mode of operation can be invasive in case of sensitive samples and the nanostructure samples with low adhesion to the substrate, where the particles can be moved by the AFM tip. To avoid this drawback, tapping or AC mode of operation can be used. In this mode, the cantilever is oscillated at its resonance frequency with free space amplitude A_0 . When the cantilever approaches the surface, the oscillating amplitude is decreased due to tip/surface interaction (A). By keeping the ratio between free space and contact amplitudes (A/A_0) constant, the surface topography can be imaged.

3.1.4 Kelvin force probe microscopy (KFM)

Kelvin probe force microscopy can be considered as an extension of AFM technique. In this method, a conducting AFM tip is used to spatially resolve the local contact potential difference (CPD) that is defined as $eV_{CPD} = W_{tip} - W_{sample}$, where W_{tip} and W_{sample} are the

work functions of the tip and the sample, respectively, and e is the electronic charge [200]. The difference of material work functions lead to a charge reassembling upon an electrical contact as depicted in Figure 3.3. The external bias equal to V_{CPD} can be applied to cancel the tip-surface electrical force and thus the measurement of CPD is performed. It should be noted, that the KFM technique is a relative measurement method due to its physical origin. Therefore, initial calibration of the tip work function is required to extract absolute values from these measurements.

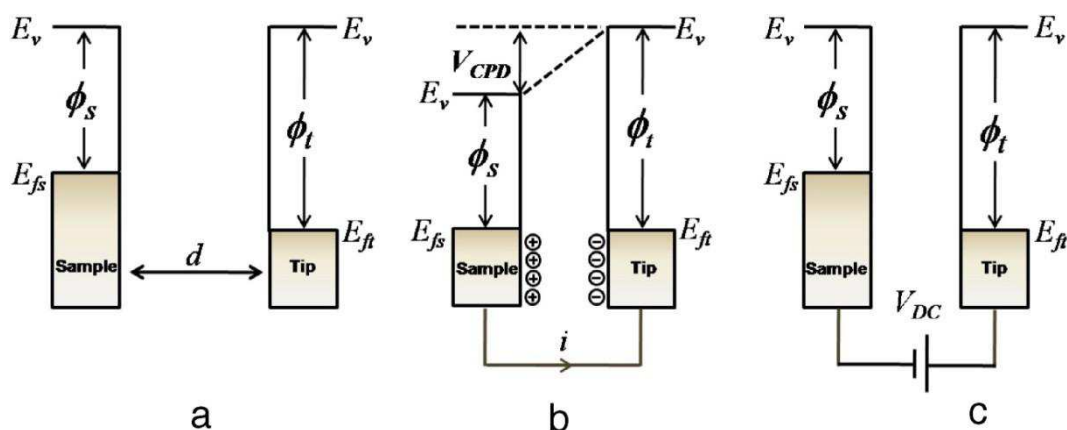


Figure 3.3. Schematic of electronic energy levels for the sample and AFM tip for three different cases: (a) tip and sample are not interacting due to distance d and no electrical contact, (b) tip and sample are brought in electrical contact, and (c) external bias (V_{DC}) is applied between tip and sample to cancel the contact potential difference and thus the tip-sample electrical force. Adapted from [200].

KFM measurements are performed in lift mode. In this regime, two-pass technique is used with AFM and KFM measurements performed alternative Firstly, tapping mode AFM is applied to determine the surface topography. Then, the tip retraces the topography at a set lift height from the surface (10nm is used in our measurements) while detecting V_{CPD} . During KFM scan mechanical oscillations are switched off and instead an electrical driving signal (an AC voltage V_{AC} plus a DC voltage V_{DC}) is applied to the tip. V_{AC} creates oscillating electrical forces between the AFM tip and surface, while V_{DC} is used to cancel these forces in a similar way as described above [200].

3.1.5 Raman spectroscopy

Raman spectroscopy is a widely used technique to study structural properties of materials [201]. The technique is based on analysis of inelastically scattered light from the medium that contains information on vibrational and rotational states of the system. The shift in energy between the excitation photons and the scattered photons reflects interaction of light with the

vibrational modes. Therefore, the energy shift, typically presented in cm^{-1} , is the main quantity measured in a Raman spectroscopy experiment.

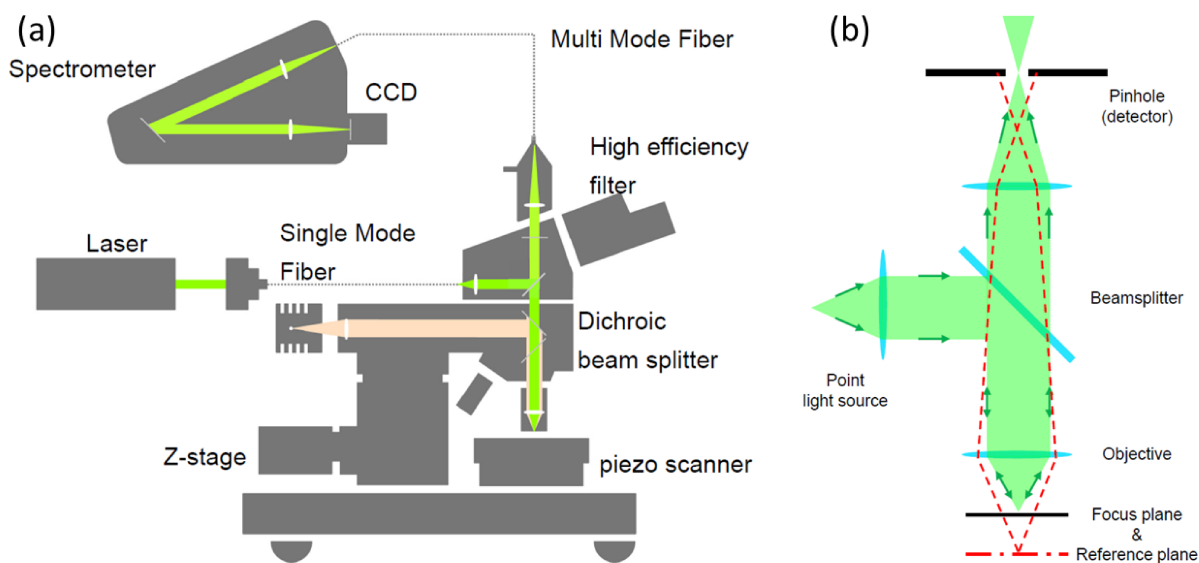


Figure 3.4. (a) Schematic illustration of the beam path in Witec Alpha300 system.
 (b) Schematic of a confocal microscope. Adapted from [199].

All the Raman spectra presented in this thesis have been measured using a confocal scanning Raman microscope (WiTec Alpha300 system) in backscattering geometry with 532 nm excitation and a $100\times$ objective (0.9 NA). Figure 3.4 (a) illustrates schematically the beam path in WiTec Alpha300 system. A typical Raman spectroscopy system consists of three major parts: a laser, an optical microscope and a spectrometer. The laser light is delivered through a single mode optical fibre that enables focusing into a diffraction-limited spot. The microscope objective is used to focus the excitation beam as well as to collect the back-scattered light for analysis. The reflected light is filtered from the Rayleigh emission and collected by a multi-mode fibre that directs beam to a spectrometer where the light is passed through a diffraction grating and recorded by a CCD camera to analyse spectral components. The spectral resolution depends on the grating's diffraction capability and can be improved with higher groove density. The grating used for the measurements in this thesis has 1800 grooves/mm that provides the spectral resolution of 3 cm^{-1} .

To increase image contrast and enable in-depth scanning, confocal microscopy is utilized in the WiTec Alpha300 system. The confocal microscopy is based on selective collection of the reflected beam where only light from the image focal plane is collected (Figure 3.4 b). For this purpose, a pinhole is typically introduced at the confocal plane of the lens to eliminate

out-of-focus light. In the WiTec Alpha300 system, the core of the multi-mode fibre (100 μm) acts as a pinhole for the confocal microscopy.

Spatial Raman measurements are performed by scanning the sample in x and y direction that is facilitated by a piezo-electric scan table with 3nm positioning accuracy in the lateral direction. The spatial resolution of the technique is determined by a diffraction limited laser spot. Therefore, the maximum resolution is given by the Rayleigh criterion $\Delta x = 0.61\lambda/NA$, where Δx is the smallest distance between two resolved points, λ is the wavelength and NA is the objective's numerical aperture. For our measurement conditions, the spatial resolution of 360 nm is expected.

In this thesis, Raman spectroscopy measurements on graphene are performed using 532 nm with 1 mW laser power to avoid laser induced heating of graphene samples [201]. All the measurements are carried out at room temperature under ambient conditions. Typical integration time of 0.5s is used. To provide sufficient statistical description of the overall graphene quality, areas of $15 \times 15 \mu\text{m}$ (unless stated otherwise) are mapped out and analysed.

3.1.6 Electrical transport measurements

Electrical characterization is a crucial technique for graphene quality assessment, since it provides information on carrier mobility and extrinsic doping concentration. Two terminal transport measurements are performed using the 2636B SourceMeter instrument. Two-channel source-measurement unit (SMU) instrument allows to simultaneously source and measure both voltage and current. To perform field effect transistor (FET) characterization, two probe graphene devices are connected in the way displayed in Figure 3.5 (a). The SMU instrument is used to apply Source/Drain and Source/Gate bias, while detecting Source/Drain and Source/Gate currents. The latter is recorded to observe the leakage current through SiO_2 dielectric. The applied Source/Gate voltage mostly drops over the substrate dielectric (here SiO_2) due to low resistance of heavily doped Si substrate. Since the backgate Si and the graphene form a plate capacitor, charge carriers can accumulate in the graphene as a function of the applied bias. Thus, electrical properties of graphene can be effectively tuned demonstrating ambipolar behaviour (Figure 3.5 b).

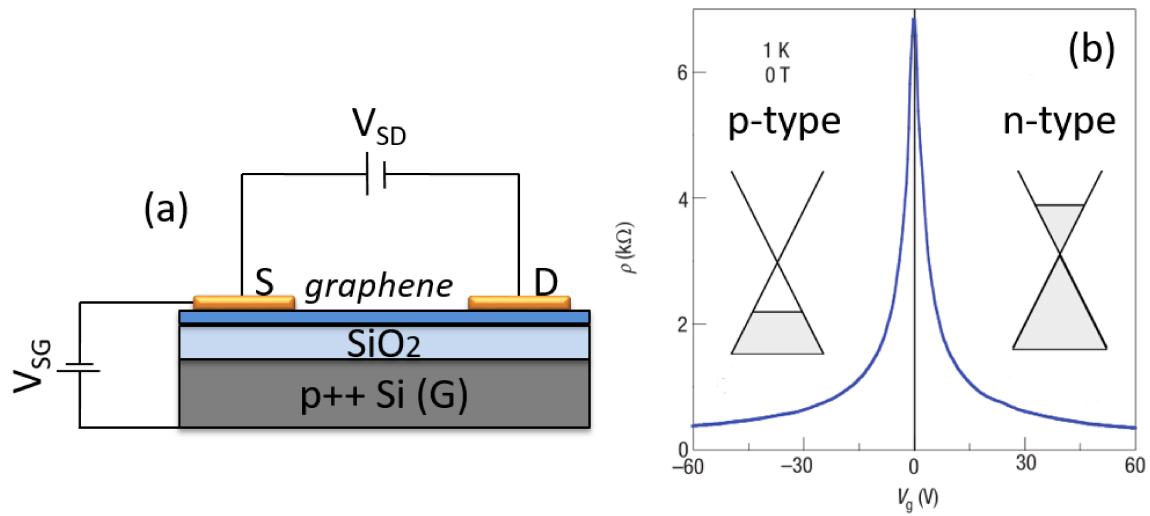


Figure 3.5. (a) Schematic of measurement set up for FET characterization. (b) Typical resistance dependence for graphene devices demonstrating ambipolar behaviour with n-type and p-type carriers dominating for $V_G > 0$ and $V_G < 0$, respectively [59]. The inset shows the Fermi energy position.

FET measurements allow extraction of the extrinsic carrier mobilities of the graphene films using the following equation:

$$\mu = \frac{\partial \sigma}{\partial V_g} \times \frac{1}{C_g} = \frac{\partial I_{ds}}{\partial V_g} \times \frac{L}{WC_g V_{ds}}, \quad (3.1)$$

where L and W are the channel length and width, respectively, and V_{ds} is the drain-source voltage. The capacitance $C_g = 3.93 \times 10^{-8} \text{ F cm}^{-2}$ is calculated using $C_g = \epsilon \epsilon_0 / d_g$, where ϵ is the dielectric constant of SiO₂ (~ 4), ϵ_0 is the permittivity of free space and d_g is the thickness of SiO₂ (90 nm). This method is employed in the current work, since it provides results comparable to those reported previously from two-point measurements of graphene FET devices [144,202–204].

3.2 Device fabrication techniques

3.2.1 Photolithography

Photolithography is a commonly used technique to pattern thin films or to perform selective metallization of a target substrate. The technique utilizes light sensitive chemical photoresist that under light exposure changes chemical properties and becomes dissolvable by a special solution, called developer. The patterning is performed by photolithography mask that is typically brought in direct contact with the target substrate. Selective metallization of the

mask allows partial light exposure of the photoresist thus transferring the geometrical pattern on photoresist layer. In general, the resolution of the contact printing technique is given by $L \approx 3/2\sqrt{\lambda(s + d/2)}$, where λ is the wavelength of the exposure light, s is the distance from the mask to the photoresist layer and d is the thickness of the photoresist layer [50]. According to the manual of the photolithography system (SUSS MJB 3) employed in our study, under optimum conditions the resolution of $\sim 1.5 \mu\text{m}$ can be obtained in vacuum contact mode with alignment accuracy of $\sim 0.2 \mu\text{m}$. However, with decreasing size of the structures, the metal lift off becomes more problematic. To facilitate higher efficiency of residual metal removal, two-layer photolithography process can be utilized. In this case, a sacrificial layer is deposited before photoresist to enable undercut formation (Figure 3.6).

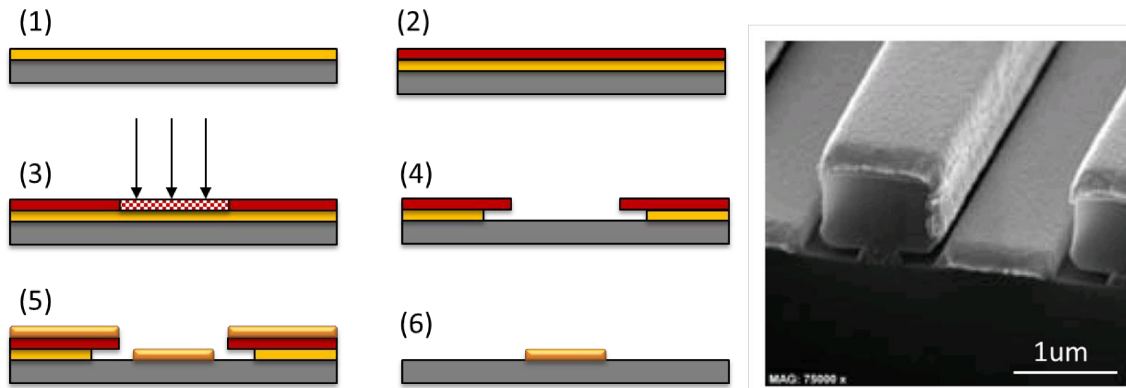


Figure 3.6. (Left) Photolithography process: (1) Coat and soft-bake first layer SF6. (2) Coat and soft-bake imaging resist S1805. (3) Expose imaging resist through photolithography mask. (4) Develop S1805/SF6. (5) Deposit metal film. (6) Lift-off bi-layer stack and residual deposition. (Right) SEM image of bi-layer lift-off in gold metallization. The presence of undercut allows complete lift-off removal of resist and residual deposition. Adapted from [205].

In our work, we utilize the following photolithography procedure. Firstly, the substrates are cleaned by submersion and sonication in acetone for 5 mins followed by an isopropyl alcohol (IPA) rinse and nitrogen drying. Next, the substrates are annealed at 180°C for 15 mins. This procedure reduces the presence of contaminants and water molecules on the substrate surface that improves fabrication consistency and material adhesion. This is the standard cleaning procedure used for all the substrates throughout this work. After the substrate cleaning, a sacrificial layer of SF6 is spin coated for 10s at 3500rpm followed by soft-baking at 95°C for 10mins. Then, a photosensitive layer of S1805 is spin coated for 10s at 3500rpm followed by soft-baking at 80°C for 5mins. The desired pattern is exposed during 4s. The development is performed during 10s in MF26A followed by deionized (DI) water rinsing and drying with nitrogen flow. The sample is ready for the metal deposition. However, typically small amount of

photoresist can be left in the developed regions. Therefore, O₂-plasma treatment (30s 100W with 20sccm) is required to facilitate additional cleaning and improve adhesion between the metal layer and the substrate. Next, the metal lift off is performed. To facilitate high efficiency of residual metallization removal and protection of underlying film, two step lift off is used. During the first step, acetone dissolves S1805 layer for 2h and thus provides lift-off for residual metal. During the second step, 1165 removes all residual polymers from the surface.

3.2.2 Electron beam lithography

Electron beam lithography (EBL) is a widely used technique for high resolution patterning. This method utilizes a focused electron beam to selectively expose an electron-sensitive resist film. EBL can be used to fabricate patterns at the sub-5nm scale [206]. Unlike diffraction limited techniques, EBL resolution is determined not by the beam size but by the electron beam interaction with the resist [207]. During EBL process, the electron beam can excite secondary electrons, phonons, photons and plasmons that can further transfer energy in the resist resulting in an increase of the feature size [207]. Although, EBL technique facilitates controlled fabrication of the nanostructures, the method is characterised by low throughput due to low writing speed.

The nanostructures discussed in this thesis are fabricated using Raith e-Line system using the following recipe. After substrate cleaning (Section 3.2.1), a layer of positive tone polymethylmethacrylate (PMMA A4 950K) resist is deposited using spin coating at 3500 rpm for 60s followed by annealing at 180°C for 5 mins. The desired patterns are exposed using dosage of 200 $\mu\text{C}/\text{cm}^2$ with 2 nm step size. The exposed PMMA is developed in solution of Methyl Isobutyl Ketone (MIBK) and IPA (IPA:MIBK~3:1) for 60s accompanied with gentle stirring. Next, the sample is placed in IPA for 30s and then dried with compressed nitrogen. Similar to photolithography process, residual PMMA can be left in the exposed regions. Therefore, additional cleaning is performed with O₂-plasma treatment before the metal deposition. At this step, the O₂-plasma treatment can be used to remove exposed graphene layer. The lift off step is done by emerging the sample in Acetone overnight followed by IPA wash and drying with compressed nitrogen. It should be noted that in presence of graphene layer the sample is left to dry naturally to avoid the graphene damage.

3.2.3 Metal deposition

Resistive thermal evaporation is a popular technique for vapour deposition mainly due to its simplicity. As presented in Figure 3.7, a material of interest is heated to reach its evaporation point by passing electrical current. The created vapour then travels towards the substrate where it forms a thin film. The vacuum quality inside the chamber determines the quality of the deposited film. For instance, presence of oxygen molecules in the chamber can result in film oxidation. Furthermore, collisions with gas molecules can lead to modification of deposition direction that significantly deteriorates the film coverage.

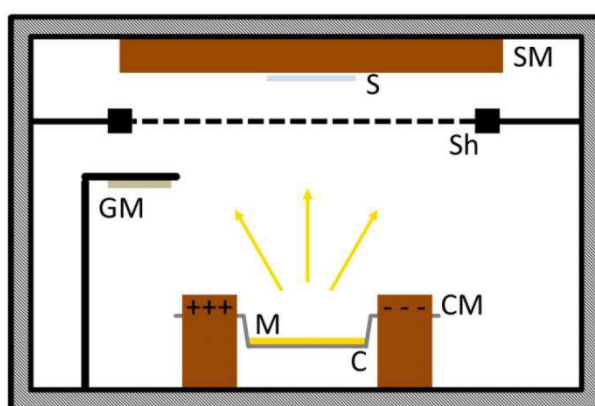


Figure 3.7. Schematic diagram of a resistive thermal evaporation system. SM – Sample Mount, S – Sample, Sh – Deposition Shutter, GM – Growth Monitor, CM – Crucible Mount, C – Crucible, M – Material. Adapted from [208].

The Au and Cr film deposition is performed using Angstrom A-mod at vacuum pressure of $\sim 1 \times 10^{-7}$ Torr. The deposition rates of 0.2 and 2 Å/s are used for Cr and Au deposition, respectively.

3.3 Scanning photocurrent microscopy

The spatial optoelectronic properties of the devices are characterized using a scanning photocurrent (photovoltage) microscopy set up (Figure 3.8). The sample is fixed to a piezo-stage that provides scanning capabilities with 20 μm travel range. Laser light is focused onto the sample using a microscope objective (typically Nikon 40x, 0.6NA, CFI S Plan Fluor ELWD). The laser spot is scanned across the device and the resulting photoresponse (photocurrent or photovoltage) is recorded to form a 2D spatial map. Reflected light from the sample is collected by Si photodiode (ThorLabs DET10M) to provide a simultaneous reflectivity image of the device. Therefore, the location of photo-induced signal is determined through correlation of reflection and photocurrent (photovoltage) maps. The laser power is

recorded before the objective using a Newport optical meter (Model 1835C) and a calibrated photodiode (Newport 818-UV).

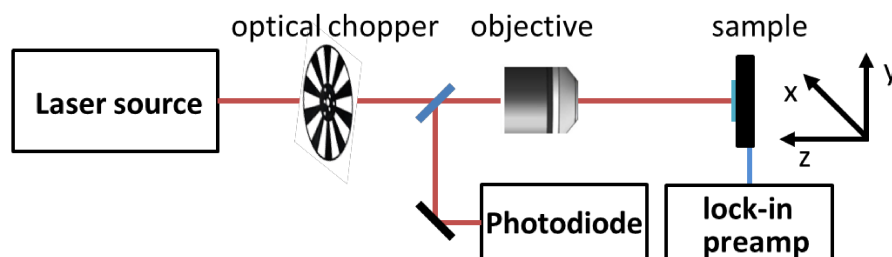


Figure 3.8. Schematic diagram of the scanning photocurrent microscopy. Electronic devices are mounted on piezo-stage and modulated optical illumination from various laser sources is focused on the device.

The photocurrent (photovoltage) is detected using the lock-in technique to improve the signal to noise ratio. To facilitate this technique, the excitation source is externally modulated using optical chopper with a typical frequency of 416 Hz. This frequency has been determined as optimal by a range of tests with varying frequency from 150Hz to 3000Hz. Additionally, current (SR570) or voltage preamplifiers (SR560) were used whenever necessary to increase the signal before the lock-in readout performed by a DSP lock-in amplifier SR830. It should be noted that both current and voltage preamplifiers were used with a band-pass filter of 300-1000 Hz. All the measurements are performed at room temperature and in ambient atmosphere. The photovoltage amplitudes reported in this work are peak-to-peak values throughout.

3.4 Time resolved measurements

Ultrafast pump probe measurements are typically used to characterize internal carrier dynamics of the material. A pump-probe set up is presented in Figure 3.9. Ultrafast pulses (~ 150 fs) are provided by a tunable (640-1040 nm) Coherent Chameleon Ultra II mode locked Ti:Sapphire laser operating at 80 MHz. The initial pulse is split and part of it is coupled to a Coherent Chameleon Compact OPO to produce a signal beam in the range of 1100-1600nm. Furthermore, the signal beam can be frequency doubled with second harmonic generation (SHG) crystal (Harmonixx-APE), if necessary. The initial pulse is delayed using a retro-reflector mounted onto a motorised translation stage (Thorlabs PT1-Z8), with a spatial resolution of about 200 nm that corresponds to a minimum delay of ~ 1.3 fs. The maximum travel of the translation stage is 25cm providing a maximum delay of ~ 167 ps. Next the two

pulses are combined using a beam splitter and focused on the sample to form overlapping beams. The beams are aligned to insure near normal incidence.

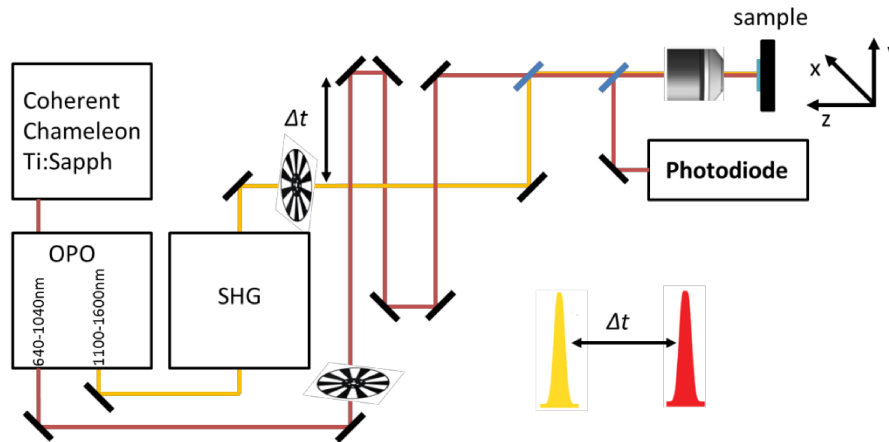


Figure 3.9. Schematic diagram of the time resolved measurements.

3.4.1 Differential reflection spectroscopy

As discussed in Section 2.2.4, a strong pump pulse is typically used to introduce changes in the carrier population, while a weak pulse is used to monitor relaxation dynamics in time due to present time-delay between pulses. To facilitate these measurements, the pump pulse is modulated with an optical chopper at 416Hz, while the reflected probe beam is detected with photodiode (Si or InGaAs) connected to a lock-in preamplifier (SR 830). In this way, the difference in the reflected light with/without the pump pulse is recorded. It should be noted, that a high quality band filter is required in front of the photodetector to avoid residual illumination by the pump beam.

3.4.2 Transient photocurrent spectroscopy

Transient photocurrent spectroscopy can be considered as an extension of scanning photocurrent microscopy, discussed in Section 3.3. Similarly, an optical chopper is used to introduce modulation of one of the beams, while a lock-in amplifier (SR830) is used to detect the resulting photocurrent. Thus, the measured signal can be considered as photocurrent (photovoltage) induced by the modulated beam in the presence of the second excitation pulse. If the two excitation pulses arrive within the device's response time, then absorption saturation reduces the average photocurrent. A temporal scan thus reveals a device's response time. Previously performed time-resolved photocurrent studies of graphene devices typically utilize a single wavelength cross-polarized beam configuration to minimize interference near

zero time delay point [78,209,210]. However, as will be discussed in Chapter 6, to characterize plasmon based photodetectors, the cross polarization cannot be used, since plasmonic nanostructures are sensitive to incident polarization. To overcome this issue, a two-colour experiment configuration with wavelengths of 650 and 750 nm is employed using SHG crystal to double the output of OPO.

3.5 Dark-field (DF) microscopy and spectroscopy

Dark-field (DF) microscopy and spectroscopy are widely used techniques to study the scattering properties of plasmonic nanostructures. This method facilitates collection of the extinction spectrum of a single scattering object rather than the averaged optical response of arrays that is typically measured with FTIR spectroscopy (Section 3.6). In DF microscopy, the sample is illuminated at an angle, while only scattered light is collected resulting in a “dark” background and illuminated scattering objects. In the DF microscope used in our study (Figure 3.10 a), the measurements are performed in backscattering geometry. The illumination beam is partially blocked using a special ring that permits light travelling on the outer edges, while the collection of scattered light is performed through the central column. The reflected light is coupled into a multimode optical fibre. Similar to Raman spectroscopy set up discussed in Section 3.1.5, the optical fibre is used as a pinhole to facilitate confocal microscopy.

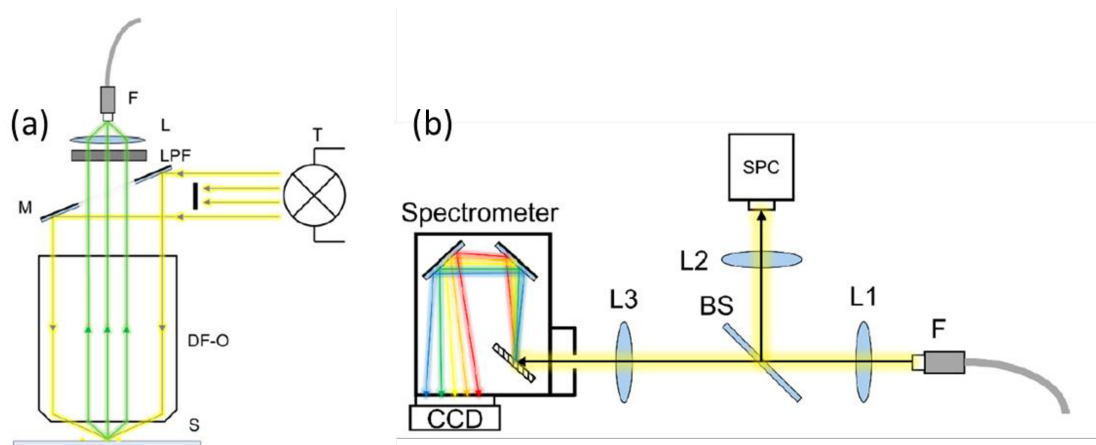


Figure 3.10. Schematic of dark field microscopy and spectroscopy. (a) Principles of dark field microscopy. (b) Reflection beam path towards the detectors: spectrometer and single photon counter (SPC). T – tungsten filament lamp, F – optical fibre, DF-O – dark-field objective, S – sample, Lx – lenses, LPF – linear polarising filters. Adapted from [208].

Next, the scattered light is recorded using a single photon counter (SPC) with model SR400 (Figure 3.10 b). The set up provides a mapping facility, since the sample position can be

changed by a piezoelectric stage, while the scattered light is simultaneously recorded. The resulted map shows the spatial variation of the intensity of the scattered light. In this way, the structures of interest can be easily identified. By positioning the microscope's collection point over the structure of interest, the scattering light of a single nanostructure can be recorded. Furthermore, the light can be directed into a spectrometer (Princeton Instruments Acton SP2500) with a CCD camera (Princeton Instruments Pixis 100) to analyse extinction spectra of the scattering object. Since the collected spectra are affected by the spectrum of the illumination light, the normalisation is required by $I_{norm} = I_{sample}/I_{ref}$, where I_{sample} and I_{ref} are the spectra of the sample and the reflective standard surface (Labsphere WS-1), respectively.

3.6 Fourier-transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy is a widely used technique to study matter interaction with near-, mid and far- infrared illumination resulting in absorption or reflection spectra. The technique is based on two main components: a Michelson interferometer and Fast Fourier Transform (FFT) calculations. Figure 3.1 shows a schematic of the Michelson interferometer that typically consists of a beam splitter with a pair of mirrors, where one mirror is fixed and the other is mobile. The displacement of the mobile mirror induces a path difference $2x$ leading to interference of the two beams. Therefore, the resulting beam registered by a detector is modulated with its intensity expressed as $I(x) = S(\nu)\cos(2\pi\nu x)$, where ν is the wavenumber of the excitation light and $S(\nu)$ is the source spectrum. The maximum is reached when $2x = n\lambda = n/\nu$ with n being an integer value. For a broadband source, the resulted signal intensity is an integral of the previous expression over available frequency range at different values of the mirror displacement. The measured data is called an interferogram and contains information across the entire frequency range. A reverse Fourier transform is used to yield a spectrum, hence the term Fourier Transform Infrared spectroscopy. Since the measured spectrum is affected by the spectrum of the light source, normalisation on a reference spectrum is required. In case of reflectance, the reference spectrum is typically measured for a metal (gold) mirror that corresponds to 100% reflection baseline. Compared to traditional dispersive instruments, FTIR spectroscopy simultaneously collects data over a wide spectral range that results in much faster data acquisition.

FTIR measurements reported in this thesis were performed using FTIR microscope (Bruker Hyperion 2000) coupled to a FTIR bench (Bruker Vertex 70). The nanoparticle arrays were selected using an aperture inserted in the back focal plane. Spectra in the visible range were taken with a Si diode, while a Peltier-cooled InGaAs detector permitted measurements in the near-infrared region. In both cases, a quartz beam splitter and a tungsten lamp were used.

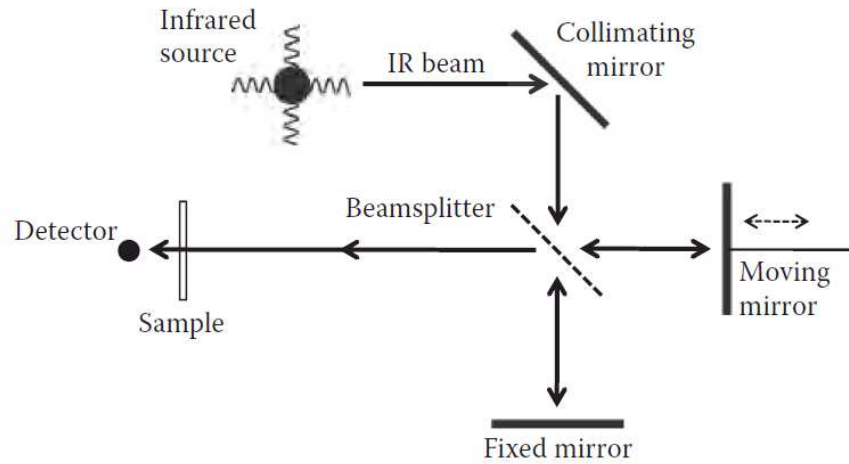


Figure 3.11. Schematic of a Michelson interferometer. Adapted from [50].

3.7 Finite-difference time-domain (FDTD) calculations

Modelling the optical properties and electromagnetic field distribution for nanostructures is a crucial step for the system optimization. The Finite-Difference Time-Domain (FDTD) method is a widely used technique in the field of plasmonics owing to the fact that results for a wide range of frequencies may be obtained with a single run of the simulation [211,212]. The method is based on discretization of time and space, when all spatial and temporal derivatives in the Maxwell equations are replaced by finite difference variables. The space discretisation is typically performed following a Yee cell arrangement [212] with a Cartesian volume element of sides Δx , Δy and Δz , while Δt time step is used for the time discretisation [211]. The calculation starts with injection of the illumination such as plane wave at initial time. The new field components are computed using the central difference approximation based on the field components from the previous time interval. In fact, the electric field components are calculated at a given time, then the magnetic components are calculated at the next time point and the process repeats until the steady-state solution is reached. The simulation volume is typically limited leading to field reflection from the simulation boundaries. To avoid this effect, perfectly matched layers (PML) are implemented to absorb fields at the boundaries. Since the calculations are performed in the time domain, the dispersive properties of the

materials have to be specified over a wide range of frequencies using approximation with permittivity models as opposed to using experimental values. As a result, strong dispersion can lead to the method instability. The optical response in the frequency domain is restored using a Fourier transformation of the time domain signal. Although the FDTD method is extremely versatile with geometries and system complexity, the method suffers from high computational cost due to calculations being performed in every point of the simulation volume.

The calculation results presented in this thesis are performed using Lumerical FDTD Solutions software. The periodic boundary conditions are used in x- and y- directions, while PMLs are set for z-direction. The mesh size of 3 nm is used to take into account rapidly changing electromagnetic fields close to the plasmonic structures. The structure is illuminated with a plane-wave source, while reflection is recorded by the monitor above the structure. The near-field distributions for plasmonic nanostructures are registered by the horizontal monitor located at the half height of the structure. The wavelength dependency of electromagnetic field is usually captured by a single-point monitor in close proximity (3 nm) to the nanostructure.

4 The effect of transfer process on graphene properties

In this chapter, the quality of graphene material is carefully analysed for different transfer techniques, post-transfer treatment and device fabrication. Firstly, the quality of commercially acquired 2D materials is discussed. Next, the influence of extrinsic dopants on graphene is analysed by considering PMMA and substrate induced charge impurities. Finally, an improved transfer method is proposed. The novel technique is based on hBN-assisted transfer method that is utilized to prevent direct contact between the graphene and polymer support permitting the fabrication of encapsulated graphene structures (hBN/graphene or hBN/graphene/hBN). The encapsulation effect is studied by analyzing stability of graphene based FET devices.

4.1 Sample fabrication

4.1.1 Wet and dry transfer techniques

In this thesis, we utilize CVD grown two-dimensional materials (graphene and hBN) on Cu foils. The materials are purchased from commercial sources: Graphenea and Graphene Supermarket for graphene and hBN layers, respectively. Since the 2D materials are on Cu substrates, a transfer process is required to deposit them on target substrates. As discussed in Section 2.5, the transfer technique is crucial for the optimization of graphene based device performance. In this chapter, most of the samples are fabricated following a conventional transfer technique whereupon the graphene is protected by a layer of polymethylmethacrylate (PMMA). The alterations of this technique are discussed in each section separately.

Figure 4.1 presents a schematic of the conventional wet/dry transfer technique. The process starts by spin coating of PMMA (A4 495K) layer at 3500rpm for 60s on the hBN/Cu or graphene/Cu foils. At this stage, care should be taken to avoid PMMA leakage on the bottom side of the Cu foil. Furthermore, high porosity spin coater chucks are required to avoid mechanical deformations of the thin 25 μ m Cu foils. After the spin coating, the sample is left to dry at room temperature overnight. Next, the 2D material from the bottom side of the Cu foil is removed using O₂-plasma treatment at 100W for 2 mins. Then the Cu foil is etched using ammonium persulfate solution (15 g/L) followed by a thorough rinse in deionized (DI)

water to remove residual reaction products. After this step, the sample is ready for transfer to the target substrate. In case of the wet transfer (WT), the substrate is immersed into liquid and used to directly “fish” out the PMMA protected 2D layer floating on the surface. In contrast, during the dry transfer (DT), the polymer protected 2D film is first removed from the solution and dried prior to application on the target substrate. However, without additional support the PMMA/Gr or PMMA/hBN layers would undergo significant mechanical damage during handling. Therefore, to facilitate dry transfer technique a kapton tape frame is applied before the etching step. Additionally, a relatively thick PMMA layer (2000 rpm) is required to avoid film collapse during handling. The drying of the stack is typically performed at 60 °C on a hot plate for 1h. After the film is dried, it is transferred to the substrate and annealed at 180 °C for 30 mins to relax PMMA layer and thus facilitate full contact with the target substrate. Finally, the PMMA is removed in acetone followed by isopropyl alcohol (IPA) rinse. It should be noted that drying the sample with compressed nitrogen should be avoided since this typically results in partial removal of the 2D film.

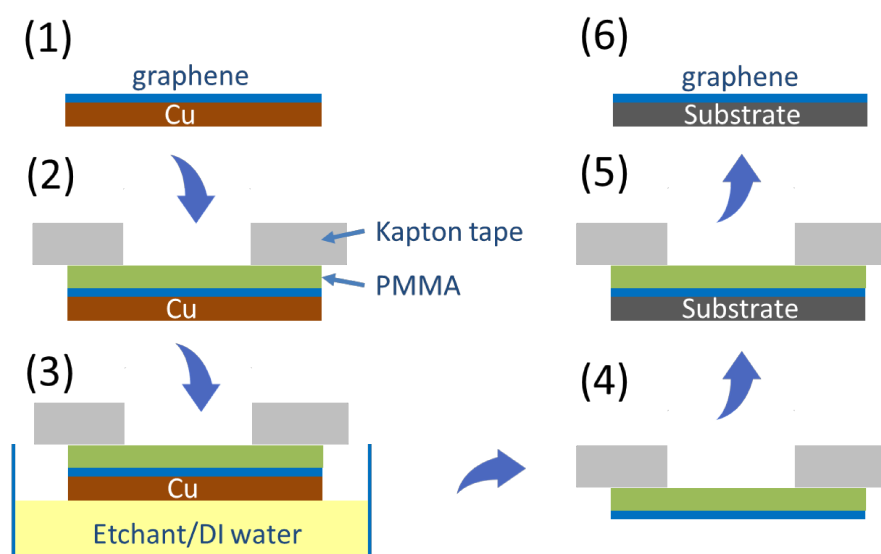


Figure 4.1. Schematic of the wet/dry transfer process.

4.1.2 Effect of contact fabrication technique on graphene properties

To analyse the graphene's quality, transport measurements can be performed. Using this technique, carrier mobility and charge neutrality point are typically analysed providing the information on extrinsic dopant concentration as well as an estimate of the defect density. These are crucial parameters for electrical device performance. However, contact fabrication is required to facilitate transport measurements.

Due to graphene's low density of states, small charge fluctuations significantly change the material properties. Polymer residues are a major source of charged impurities in graphene films that introduce local doping variations as well as scattering centres [213]. Typically, photolithography is used to facilitate fabrication of graphene field effect transistor devices that are necessary to characterize graphene's electrical properties. However, photoresists introduce additional polymer impurities that as discussed below can significantly limit device performance. Moreover, while comparing different transfer method, these additional doping can fully mask the results. Therefore, careful consideration is required while choosing a contact fabrication method.

Shadow masking

Shadow masking is a common technique of metal contact deposition that utilizes a metal mask, as described in Figure 4.2 (a). During the deposition process, the target substrate is mechanically pressed towards the mask to provide the contact. However, typically the gaps between the substrate and the mask are unavoidable leading to shading region formation that increases with higher gap size (Figure 4.2). Despite this disadvantage, a shadow masking technique prevents exposing the graphene to additional polymer residues, for example during a photoresist or e-beam resist step, thus facilitating isolation of extrinsic doping induced by the transfer method alone. Additionally, shadow masking improves graphene quality by avoiding removal and delamination that occurs during photolithography lift off process [214]. However, the shading effect limits the size of the devices to large scales (of the order of 100 x 1000 microns in our case). At these length scales the highest mobility, defect free value, cannot be reached due to the typical defects present in CVD graphene (such as multilayers, grain boundaries, wrinkles and occasional tears), but the mobility value can still provide a useful measure of the defect density. Submicron devices would be necessary to reach the intrinsic mobility.

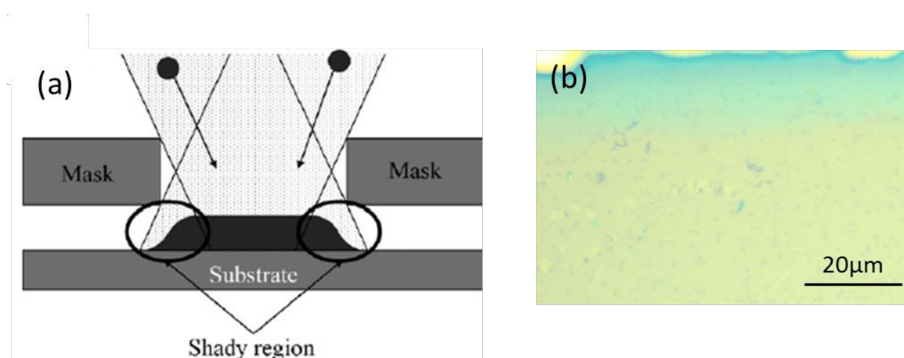


Figure 4.2. (a) Schematic of “shadow effect” caused by poor contact between the substrate and the mask pattern. Adopted from [215]. (b) Optical microscopy image of the Cr/Au contact fabricated on graphene layer; Shadow region ($\sim 20\mu\text{m}$) can be clearly seen in the top part of the image by the change in colour.

Photolithography

To fabricate microelectronic devices with CVD grown graphene, photolithography is commonly used followed by deposition of metal contacts on top of the transferred graphene layer. However, this technique is invasive for graphene material leading to large variations in device parameters. Figure 4.3 demonstrates invasive nature of the conventional photolithography process (the fabrication details are provided in Section 3.2.1). While the graphene layer uniformly covers the untreated SiO_2 substrate before photolithography, after lift-off step parts of the graphene layer are removed (Figure 4.3 (a)). This is attributed to the weak adhesion of graphene to the untreated SiO_2 substrate [214]. As demonstrate in Figure 4.3 (b,c), the film quality can be significantly improved by surface engineering such as oxygen (O_2) plasma treatment or coverage with hBN layer. In the latter case, substrate still needs to be O_2 -plasma-treated to provide good adhesion for hBN layer.

As mentioned above, the exposure to photoresist polymers is another limiting factor for applicability of the conventional processing technique to graphene device fabrication. Here, Raman spectroscopy has been used to control the graphene quality before and after photolithography (Figure 4.3). A detailed description of the photolithography method employed in this study can be found in the Section 3.2.1. An increase in the G-peak position together with decrease of intensity ratio for the G and 2D peak clearly demonstrates the introduction of charged impurities during the contact of graphene with SF_6 polymer. The G-peak shift can be used to estimate the carrier concentration. The upshift from 1587cm^{-1} to 1591cm^{-1} corresponds to an introduction of additional $\sim 2.4 \times 10^{12} \text{ cm}^{-2}$ carriers. Moreover, an increase of the D peak intensity signifies introduced disorder. Similar results have been observed for the AZ6624 photo-sensitive resist [216]. Furthermore, it has been demonstrated

that the contamination caused by the photo-sensitive resists is more difficult to eliminate with post-process cleaning techniques, such as thermal annealing [216].

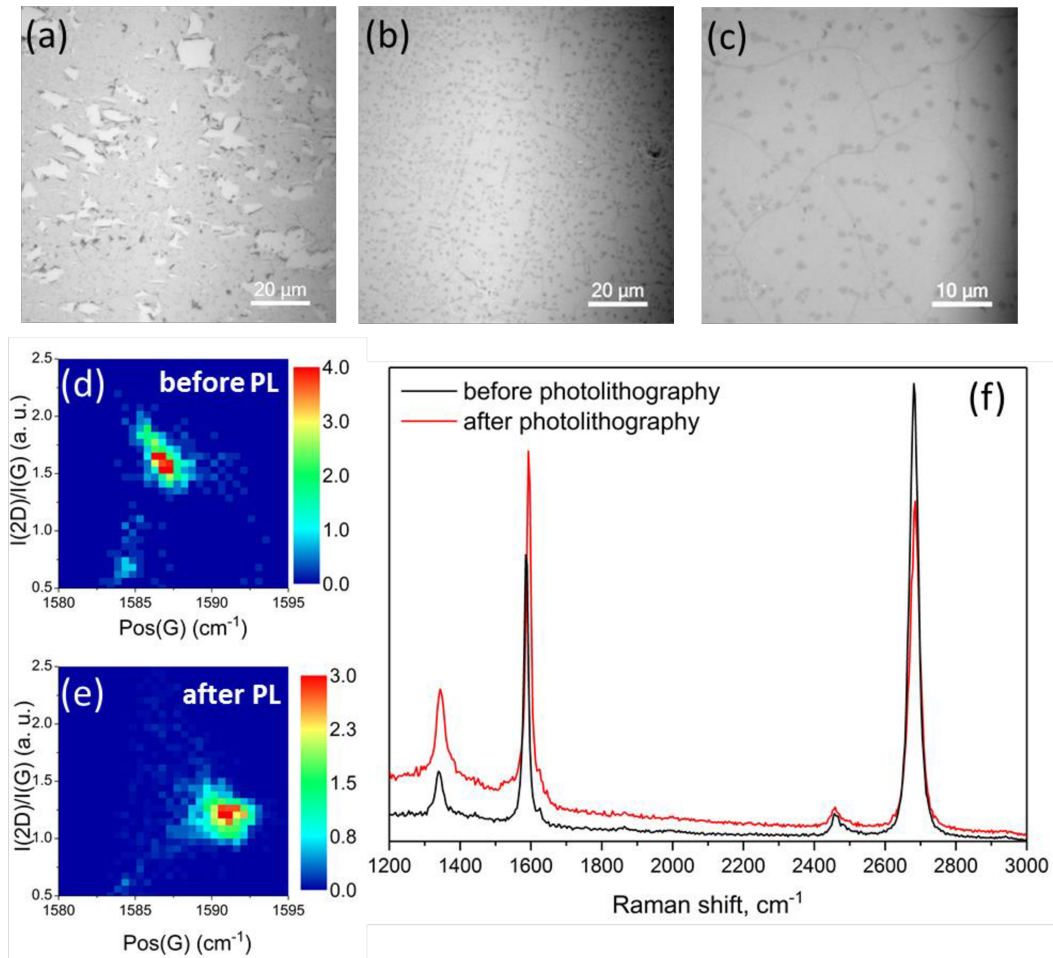


Figure 4.3. Optical microscopy images of graphene films after photolithography lift-off step for untreated (a), O₂-plasma-treated (b) and hBN-covered (c) SiO₂ substrates. Raman spectroscopy results for graphene before and after photolithography (PL) processing: 2D histograms describing correlation between the I(2D)/I(G) ratio and the G-peak position (d,e) and representative Raman spectra (f).

To avoid the necessity of photolithography step, shadow masking can be used for metal deposition, as discussed earlier. However, for micro and nano device fabrication, the size limitation of shadow masking technique makes it unsuitable. In this case, an alternative process technology can be utilized. Firstly, the target substrate with all required electrodes and interconnects is fabricated using e-beam or photolithography techniques. Then CVD graphene is transferred on top adopting the topography of the prepatterned substrate. In this case, processing related structural damage to the CVD graphene layer is minimized. As will be discussed in Chapters 5 and 6, the graphene transfer on a prepatterned substrate does not lead to a significant increase in extrinsic defects like cracks or film discontinuities. This is in a good agreement with previous studies that demonstrated conformal transfer of graphene on

photolithography patterned substrate leading to Ohmic contact with low contact resistance [214].

4.2 Graphene and hBN CVD material quality

Two dimensional materials used in this study were acquired from commercial sources: Single layer graphene on Cu substrate and single layer hBN on Cu substrate were purchased from Graphenea and Graphene supermarket, respectively. Before using 2D layers, it is necessary to check the material quality. As discussed previously, Raman spectroscopy can be considered as a non-invasive characterization technique providing rich information on the graphene quality. However, the presence of the underlying Cu substrate complicates the measurements due to developed surface morphology leading to constant defocusing. Additionally, a strong fluorescent background is typically observed for Cu substrates and to limit this effect application of blue lasers as excitation sources is required. Furthermore, the areas typically analysed using Raman spectroscopy are no larger than tens of microns that complicated analysis of large scale material properties. In the case of single layer hBN material, only weak Raman scattering is observed thus completely excluding the possibility of using this technique for initial characterization.

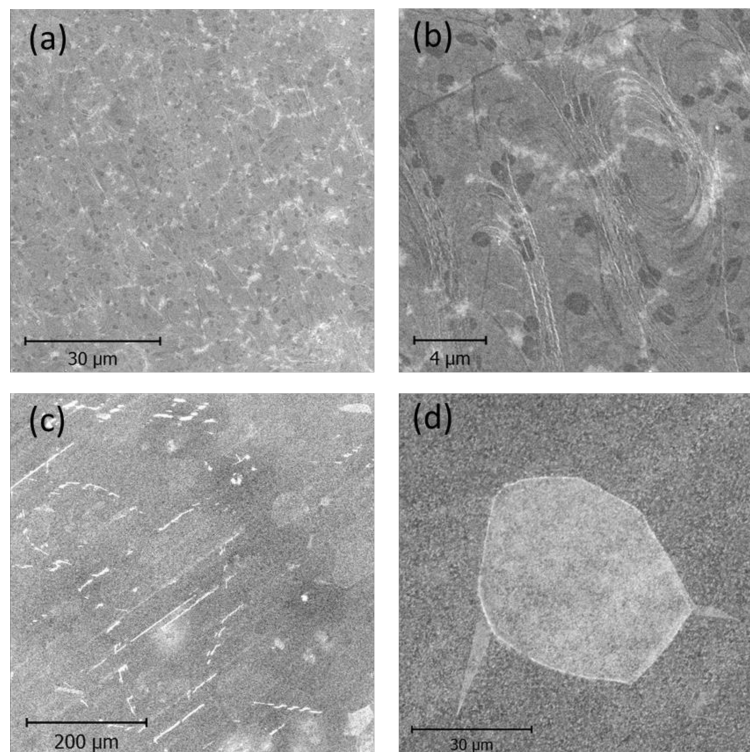


Figure 4.4. SEM images of graphene/Cu and hBN/Cu. Bright areas are tears, while darker areas in graphene are multilayers.

Due to high conductivity of the underlying Cu substrate, SEM measurement technique can be considered for initial material characterization for both highly conductive graphene and insulating hBN layers. It should be noted that graphene is highly sensitive to electron beam exposure since high energy radiation can significantly damage the crystal lattice [196]. Initial characterization of the film quality demonstrates the presence of multiple large scale tears (bright areas in Figure 4.4) for both graphene and hBN layers. This is most likely the result of roll-to-roll technique typically used by large scale manufacturers. High-resolution SEM images show a developed Cu surface with wave like pattern (Figure 4.4 (b)). Interestingly, this pattern is preserved after graphene transfer on SiO₂/Si substrates and observed on numerous occasions during Raman, AFM and KFM characterization. In addition to a continuous graphene monolayer, numerous multilayer areas are present, as can be seen from SEM images where these areas are darker. The typical size of multilayer area is about 2 μ m.

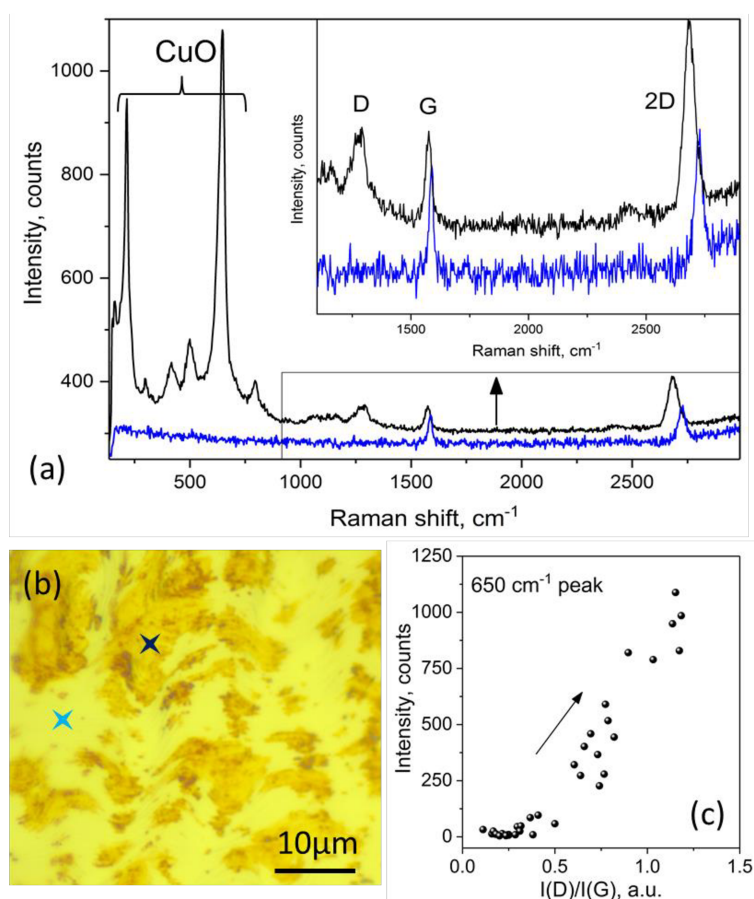


Figure 4.5. (b) Optical microscopy image of graphene/Cu, the oxidised areas are clearly visible (black cross). (a, c) Raman spectroscopy results for areas with (black) and without (blue) oxidation. Raman spectroscopy measurements have been performed using 473nm laser excitation at 200 μ W power.

It is important to analyse the graphene/Cu material to identify the presence of oxidation. Although graphene is impermeable for most molecules and can be used to protect the metallic

surface from air oxidation [217], the tears induced during graphene fabrication can lead to oxide growth. Therefore, graphene/Cu foils stored in ambient conditions demonstrate the presence of significant oxide layers after 2 months of storage, as can be seen from Figure 4.5. The oxidation process leads to the copper surface deformation and thus can introduce disorder in graphene lattice. Raman spectroscopy confirms increased defect density in the areas of oxidation, as clearly demonstrated by the correlation between the intensity of copper oxide peak and the ration between D and G graphene peaks that corresponds to the defect density. To avoid oxidation process, the graphene/Cu foils are typically stored under vacuum conditions. It should be noted that while commercially available material is typically in vacuum seal packages, copper oxidation has been observed for newly delivered material on a number of occasions. Thus the inspection on the presence of oxidation is crucial before the material use.

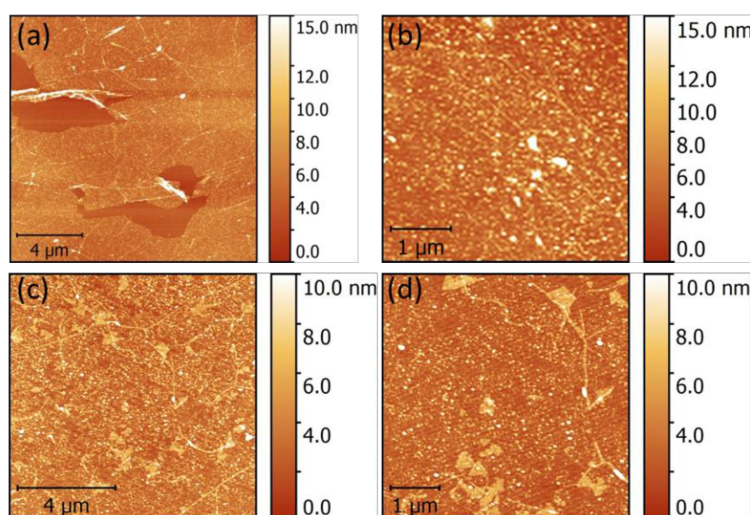


Figure 4.6. AFM images of graphene (a,b) and hBN (c,d) transferred on SiO₂/Si substrates. To analyse surface morphology of the 2D materials, the layers have been transferred on flat target substrate such as SiO₂/Si using wet transfer technique as discussed in Section 4.1. This analysis is complicated on the native growth substrate due to highly developed surface morphology of Cu foils. The transfer process introduces wrinkles that are present for both graphene and hBN layers. Occasional tears are also present (Figure 4.6 (a)). Interestingly, while multilayer areas can be clearly resolved for hBN material, there is no evidence of their presence in AFM measurements for graphene. This can be explained by the graphene multilayer growth mechanism during CVD process, where the second layer nucleation takes place underneath the first graphene layer [218]. Therefore, the first graphene layer acts as a veil masking the underlying multilayer areas. Higher resolution images show the presence of

wave like wrinkles in graphene layer that are reminiscent of the Cu foil morphology previously observed (Figure 4.6 (b)). Both layers show high density of polymer impurity that significantly increase the surface roughness and can be seen in the AFM images as small islands of about 100 nm with height reaching 10nm. The discussion of post-transfer polymer cleaning will be presented in Section 4.4.

4.3 PMMA influence on the graphene quality

Due to its two dimensional nature, graphene is highly sensitive to the presence of extrinsic doping. The source of doping can be charged impurities incorporated during polymer supported transfer or the charged surface states of the target substrate. To understand the influence of both types of impurities, we first consider techniques to reduce polymer residues and then discuss the influence of the substrate engineering.

In general, polymer-assisted transfer methods provide an advantage in the form of 2D material protection from mechanical damage and facilitates easy handling and processing. However, the residual surface contamination is a significant problem limiting the device performance. To facilitate CVD graphene without organic residues, polymer-free transfer methods can be utilised [136,137]. Here, we perform PMMA free transfer of graphene to provide a quality benchmark in terms of polymer residues. In contrast to the conventional wet transfer method, the graphene film was not protected with PMMA layer during the transfer process. To decrease the probability of mechanical damage a kapton tape frame was applied to the graphene/Cu foil. Furthermore, the liquids in the beaker were gently replaced using syringes that provide higher control over the liquid movement. The polymer free transfer is compared to PMMA supported wet transfer after different time of Acetone treatment and to commercially available transferred graphene (Graphenea). All the films are transferred on SiO₂/Si substrate.

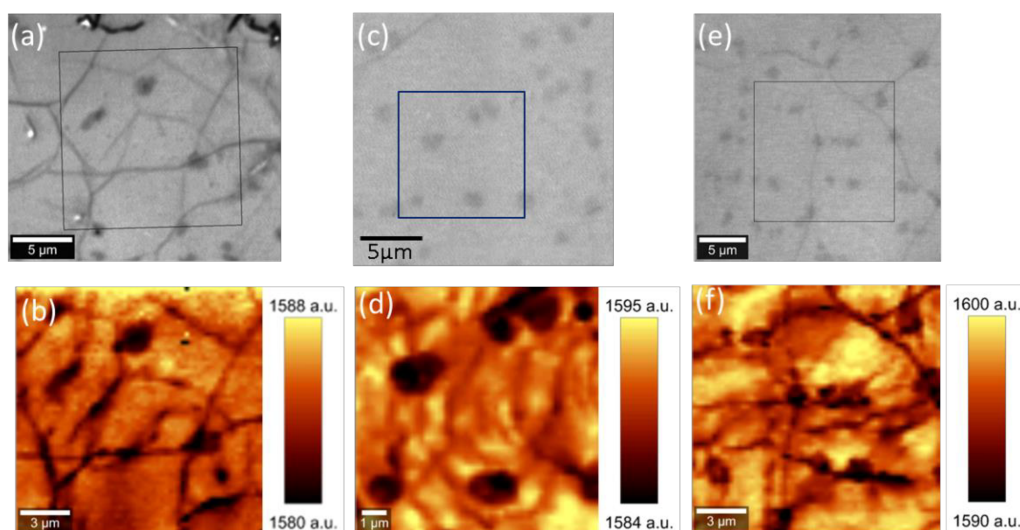


Figure 4.7. Optical microscopy (a, c, e) and Raman spectroscopy (b, d, f) for PMMA free (a, b), PMMA supported (c, d) and pretransferred graphene (e, f).

Optical microscopy and Raman spectroscopy confirm the presence of continuous graphene film for all type of transfers (Figure 4.7). Interestingly, the graphene resulted from PMMA free transfer has a much higher density of wrinkles compared to PMMA supported and commercially available graphene. This can be explained by the absence of rigid support provided by PMMA film, leading to wrinkle formation during the transfer process and subsequent drying on the substrate. Low defect concentration has been confirmed for all the transferred graphene films by Raman spectroscopy (Figure 4.8), where the $I(D)/I(G)$ ratio is typically less than 0.2 [163]. Since defects induced through wrinkle formation are localised, their presence does not significantly contribute to the large scale material analysis. Therefore, the PMMA-free transfer is characterised by low average defect density that is comparable to PMMA supported methods. By analysing the intensity ratio for the 2D and G peak combined with G peak position (Figure 4.8 (i-l)), it is possible to analyse the extrinsic doping concentration. Raman spectroscopy confirms that PMMA-free transfer results in the material with lower density of charge impurities even when compared to the graphene sample after extensive acetone cleaning (24h).

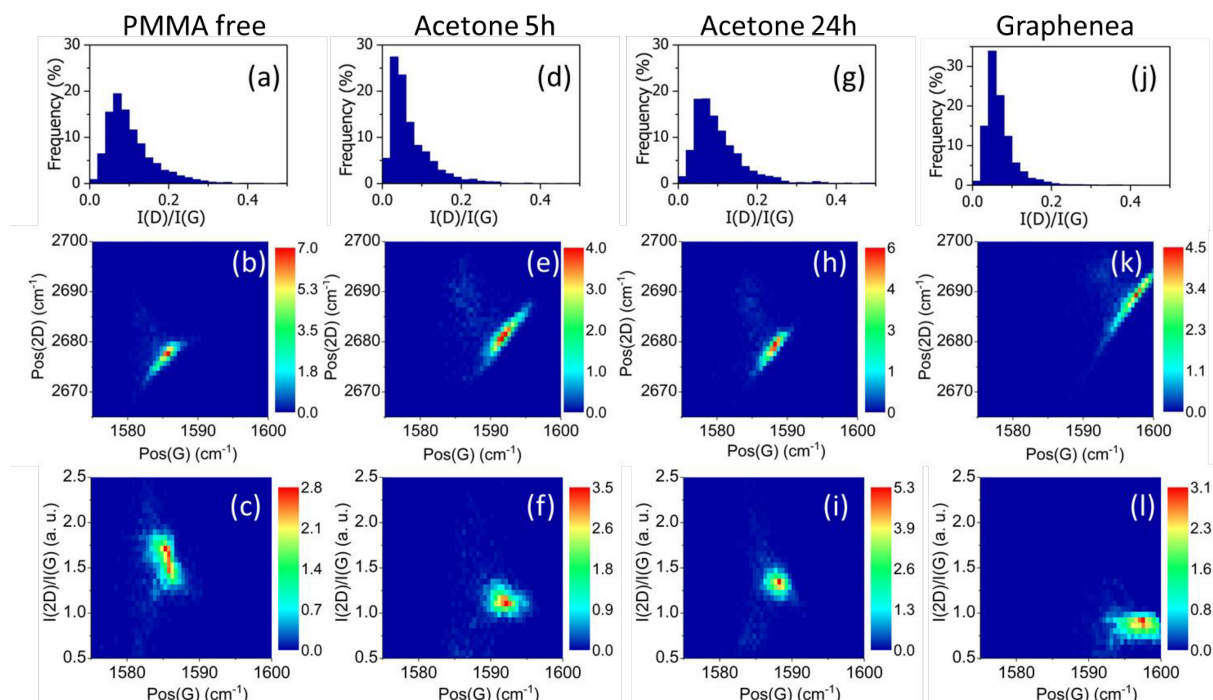


Figure 4.8. Raman spectroscopy results for PMMA free (a-c), PMMA supported after 5h Acetone treatment (d-f) and 24h Acetone treatment (g-i) and pretransferred graphene (j-l). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the $I(2D)/I(G)$ ratio and the G-peak position, respectively.

To have a direct comparison between the samples, the distributions are combined and presented in Figure 4.9 with strain and doping lines included. It should be noted, that to facilitate this comparison, the data is limited to statistically significant points. The data filtering is performed based on initial two-dimensional distribution presented in Figure 4.8. Only the data points corresponding to the areas with point frequency higher than 0.5% are included in Figure 4.9. From the trends observed in Figure 4.8, it is clear that the variations in $Pos(G)$ and $Pos(2D)$ are largely due to strain present in all samples. This observation is consistent with previous results for exfoliated graphene samples [187]. Interestingly, PMMA free and PMMA supported transfer result in the graphene material with similar tensile strain characteristics. It is reasonable to assume that transferred CVD graphene exhibits predominantly biaxial strain due to the transfer process employed where liquid evaporation and PMMA relaxation processes would typically result in biaxial mechanical stress. Therefore, the values of 0 – 0.06% are expected for biaxial strain. The similarities of strain properties for both PMMA free and PMMA supported transfers indicate the possible strain origin. It is likely that the mismatch between Cu surface morphology and flat SiO_2 surface causes the internal strain in graphene films. Interestingly, the commercially transferred

material demonstrates a mixture of tensile and compressive strain (-0.05% – 0.05% for biaxial). This can be an indicator of possible surface engineering of the substrate, but the exact technique used during commercial transfer is unknown.

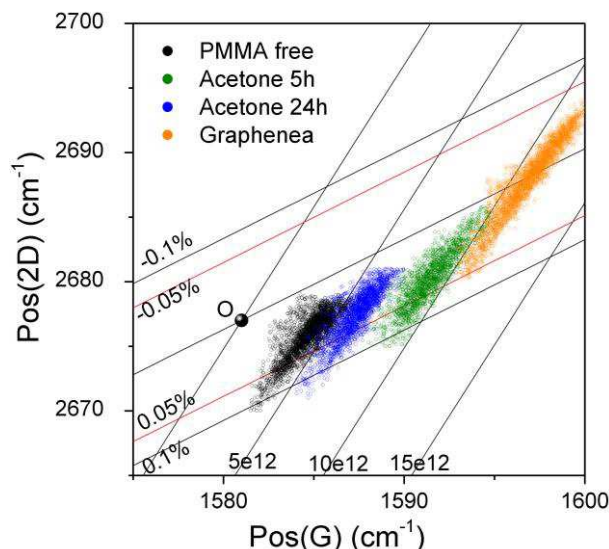


Figure 4.9. Correlation between the G and 2D peak positions for PMMA free (black), PMMA supported after 5h Acetone treatment (green) and 24h Acetone treatment (blue) and pretransferred graphene (orange). The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.

As the next step we compare the dopant concentration in the films. Consistently with previously observed trends of 2D and G peak intensity ratio (Figure 4.8), the position of G peak clearly indicates that PMMA free transfer resulted in the graphene with low charge impurity density. However, compared to freestanding exfoliated material, this graphene film still exhibits extrinsic carrier concentration of about $2.5\text{--}5 \times 10^{12} \text{ cm}^{-2}$. The possible source of these charge impurities can be the surface states of SiO_2 substrate [150] and the trapped liquid molecules [128] due to wet transfer technique used. PMMA supported transfer introduces additional charge impurities from polymer residues with the density of about $8.5 \times 10^{12} \text{ cm}^{-2}$ for 5h acetone treatment. Extensive Acetone treatment significantly reduces dopant concentration to about $6 \times 10^{12} \text{ cm}^{-2}$. Interestingly, the commercially available transferred graphene exhibits very high charge concentration on the order of $11 \times 10^{12} \text{ cm}^{-2}$. This again indicates the possible surface engineering that can potentially increase the amount of charge states on SiO_2 surface.

4.4 Graphene and hBN cleaning with annealing

To eliminate contamination and restore clean surface of 2D materials, thermal annealing has been suggested [127,133–135,219]. Nevertheless, a wide range of annealing conditions and conflicting results have been reported due to different environment during characterization measurements. Here, we apply thermal annealing in vacuum as a straightforward method to remove polymer contaminants. The graphene quality is controlled using KFM and Raman spectroscopy measurements, while the hBN layer is analysed using AFM. Both the graphene and hBN layers were transferred to SiO₂/Si substrates using a typical PMMA supported wet transfer.

Figure 4.10 shows AFM results of surface characterization for the hBN monolayer before and after thermal annealing in vacuum for 5h. The root-mean-square (rms) surface roughness of the film after the transfer was measured to be 1.46 nm whereas the SiO₂ substrate had a much smoother surface with rms of 0.2 nm. This indicates that acetone treatment does not completely remove PMMA. The film roughness significantly decreased after thermal annealing in vacuum with rms of 0.658 nm being detected.

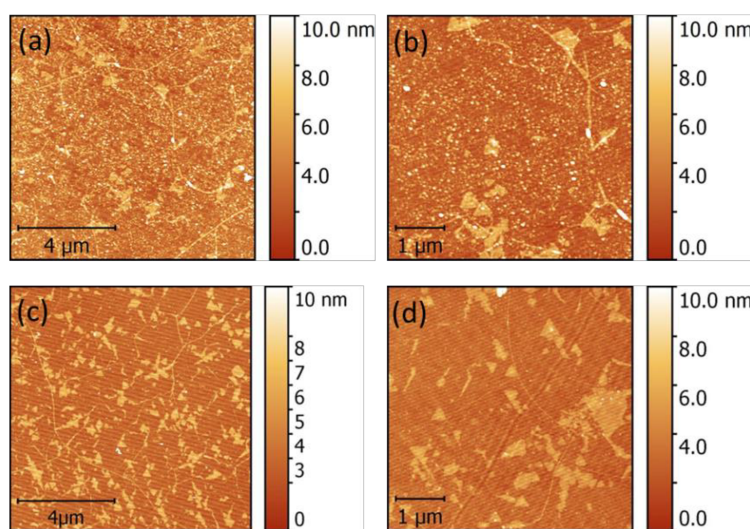


Figure 4.10. AFM images of hBN/SiO₂ before (a, b) and after thermal annealing for 5 hours at 350°C in vacuum (c, d).

A similar trend has been observed for graphene layer with the rms roughness value changing from 1.55 nm to 0.35 nm before and after thermal treatment, respectively (Figure 4.11 (a, d)). Interestingly, multilayer areas became clearly resolved for the graphene film after thermal annealing. As mentioned before, the multilayer growth process takes place underneath of the first layer [218]. Therefore, the fact that the multilayers appeared after annealing is an

evidence of an increased contact between the monolayer graphene and the underlying substrate. This is in a good agreement with previous observations of exfoliated graphene flakes deposited on SiO₂/Si substrate, where the height of freshly cleaved flake decreased from 0.6-0.8 nm to 0.4 nm after annealing in vacuum at 300°C for 3h [133].

The effects of thermal treatment on electronic properties of graphene are further studied using KFM technique. As discussed in the Section 2.7, the contact potential difference is typically extracted during these measurements. The relative changes inside of the graphene film with same amount of layers typically correspond to the local changes of the work function due to the shift of Fermi energy position with regard to Dirac point.

The results of the KFM characterization of the graphene film before and after annealing are presented in Figure 4.11 and Figure 4.12. Surface potential maps (Figure 4.11 (b,e)) reveal predominantly single-layer graphene with occasional multilayer areas which is in good agreement with optical microscopy and Raman spectroscopy studies of this graphene material. After thermal annealing, the graphene film demonstrates much higher density of small wrinkles (~1nm height) forming cellular like structure in the KFM map. In contrast, in the original material the occasional large wrinkles are present with height in the range of 5-15nm, while the rest of the film stays unperturbed. This can be explained by mechanical deformations of graphene films during thermal annealing. It has been previously reported that annealing at 300°C results in drastic structural deformation of exfoliated graphene flakes [127]. In fact, sub-nm high ripples with lateral separation of several nm have been observed. As previously discussed, in CVD material the induced strain is accumulated over the grain boundaries [186], therefore, it is possible to suggest that in our case the wrinkle formation might predominantly happen over the grain boundaries.

Since an identical AFM tip has been used to characterise both samples, the surface potential values can be directly compared. The difference in V_{CPD} can be explained by the shift of the Fermi energy in graphene material after annealing. In fact, surface potential changes from -23.3 ± 1 meV to -53.3 ± 3 meV after annealing, that corresponds to E_F shift of $V_{CPD}(\text{before}) - V_{CPD}(\text{after}) = E_F(\text{before}) - E_F(\text{after}) \approx 28.7 \pm 3$ meV. The positive shift is due to a decrease of the Fermi energy level with respect to the Dirac point that is an evidence of increased p-doping. This finding is in a good agreement with the annealing activated concept of hole doping, where increased graphene coupling to SiO₂ facilitates diatomic oxygen sites to accept charge carriers [127].

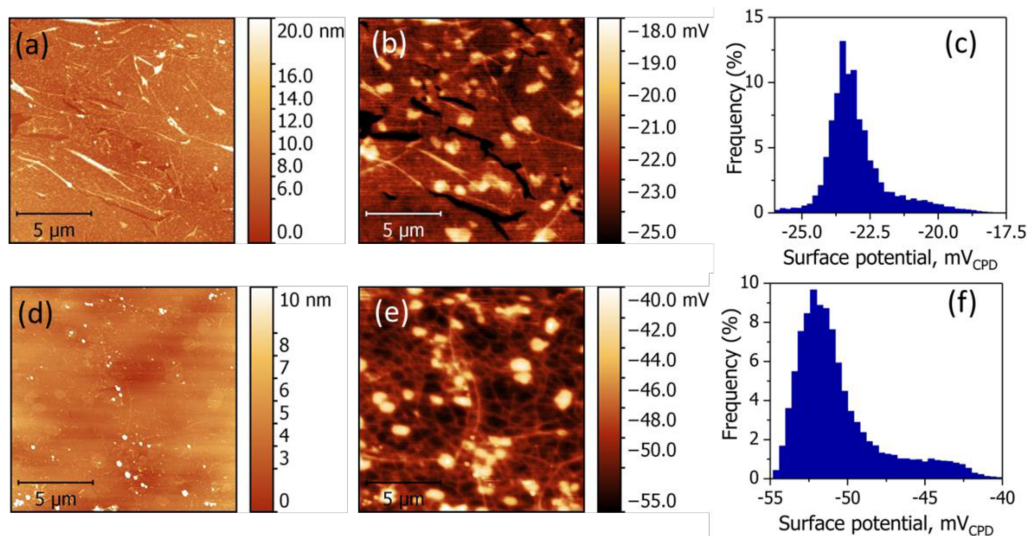


Figure 4.11. AFM (a, d) and KFM (b-f) results of graphene/SiO₂ before (a-c) and after thermal annealing for 5 hours at 350°C in vacuum (d-f).

The multilayer areas can be further used to confirm the increased p-doping. The relative surface potential difference between single and multilayer areas has increased almost twice after thermal annealing (Figure 4.12). This observation can be explained by an interlayer screening effect when multilayer areas are less susceptible to the induced charge [192,220]. Therefore, by comparing single layer material to multilayer areas it is possible to analyse the amount of charge injected in the material.

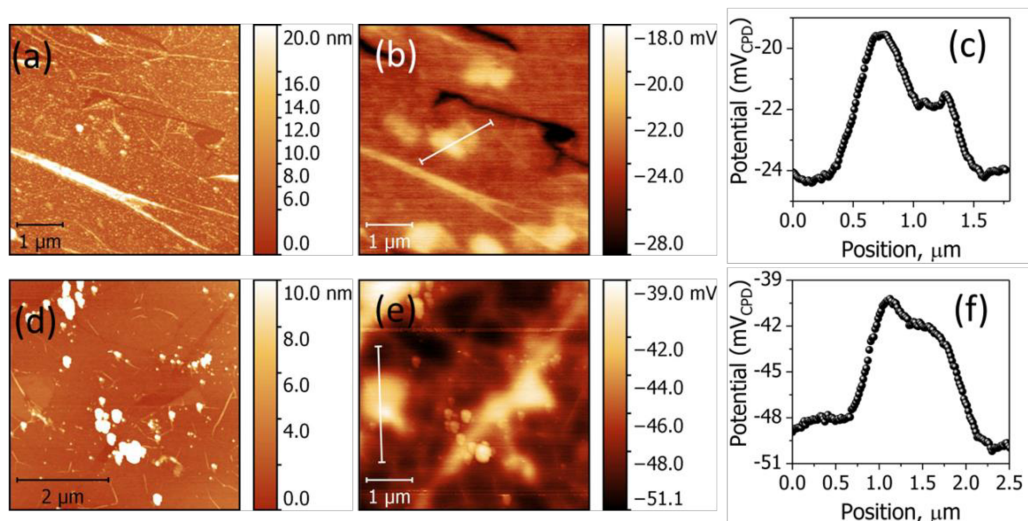


Figure 4.12. AFM (a, d) and KFM (b-f) results of graphene/SiO₂ before (a-c) and after thermal annealing for 5 hours at 350°C in vacuum (d-f). The cross-section over a multilayer is presented.

To understand the annealing induced changes in strain and doping of graphene films, Raman spectroscopy has been utilised. In a similar way as used in Section 4.3, the statistically significant points (>1%) are presented in Figure 4.13. It is clear that the thermal annealing

slightly decreases tensile strain and introduces compressive strain resulting in the material with higher strain variations in the range of about $-0.025 - 0.05\%$ for biaxial strain. While similar trends have been observed for exfoliated graphene, thermal annealing at 300°C and 400°C typically results in a complete removal of tensile strain and introduction of compressive strain [187]. Different behaviour of thermally induced strain in CVD graphene can be explained by higher adhesion to the SiO_2 substrate after wet transfer compared to graphene after mechanical exfoliation. This adhesion might reduce the level of strain relief that is typically associated with graphene slippage effect caused by the differences in thermal expansion coefficients of graphene and underlying SiO_2 [221,222]. Next, we compare the dopant concentration in the films. The shift of G peak position clearly indicates thermally induced p-doping. In fact, the thermally annealed film exhibits extrinsic carrier concentration of about $9.5 \times 10^{12} \text{ cm}^{-2}$ compared to its initial $7.5 \times 10^{12} \text{ cm}^{-2}$. This result can be interpreted as the Fermi energy shift of 40 meV that is consistent with the results of KFM measurements.

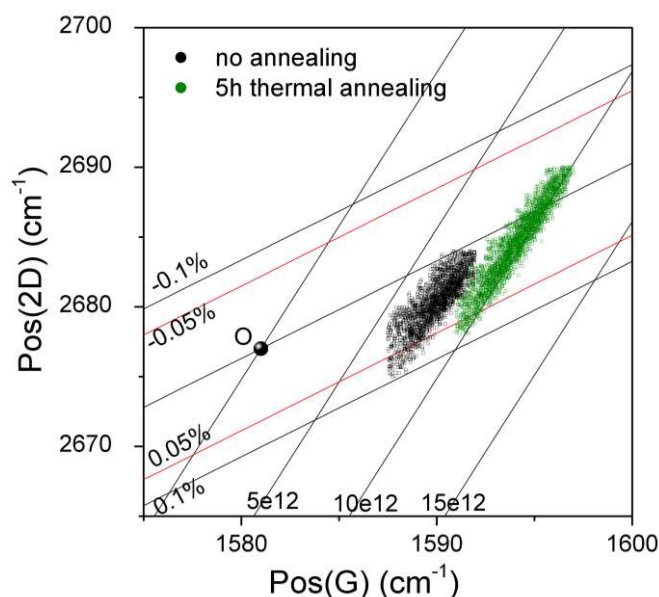


Figure 4.13. Correlation between the G and 2D peak positions for graphene before (black) and after thermal annealing in vacuum for 5h at 350°C . The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.

4.5 Substrate influence

As discussed in Section 2.5, the substrate plays a crucial role for graphene based devices. The substrate surface charge states can introduce extrinsic graphene doping and act as scattering centres thus significantly limiting carrier mobility. On the contrary, surface engineering can

be utilised to improve adhesion between graphene layer and the substrate. In this section we compare properties of graphene films transferred on untreated substrate and substrates after surface modifications such as O_2 -plasma treatment and passivation with SAM and hBN layers.

O_2 -plasma is a widely used technique to perform surface cleaning by removing hydrocarbon contaminants. This technique is known to increase the density of silanol groups (Si-OH) [223,224]. The target substrate was exposed to O_2 -plasma treatment for 2mins at 100 W. This sample is called “Gr/SiO₂ (O_2 -plasma)” further in this chapter. For SAM treatment, a hydrophobic octadecyltrichlorosilane (ODTS) layer was used due to its high efficiency of screening the charge impurities present on SiO₂ layer [144]. The ODTS layer was deposited on SiO₂ substrate after O_2 -plasma activation (1min 100W) by spin casting from toluene solution [225]. This sample is called “Gr/SAM/SiO₂”. In the case of passivation with hBN layer, the CVD hBN film was transferred first on untreated SiO₂ substrate using the same wet transfer technique as discussed in Section 4.1. Furthermore, thermal annealing for 5h at 350C in vacuum was performed on one of the samples with hBN film to facilitate polymer free surface, as discussed in a previous section. These samples are called “Gr/hBN/SiO₂” and “Gr/hBN(TA)/SiO₂” in this chapter.

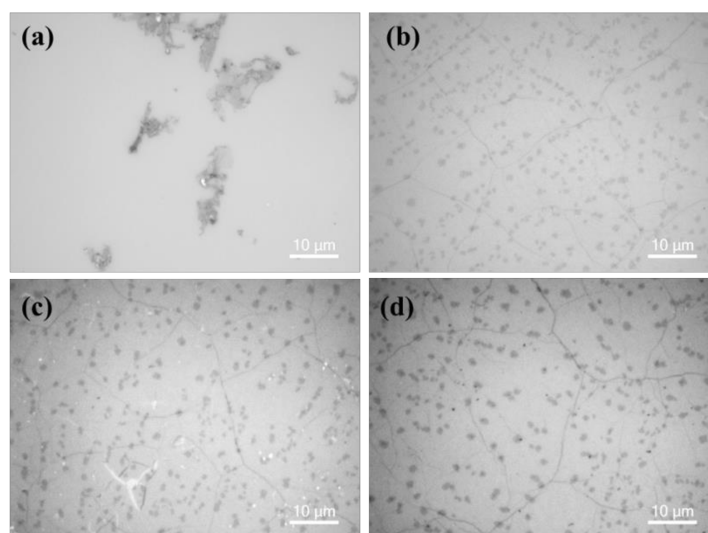


Figure 4.14. Graphene transferred with dry transfer technique on untreated (a), O_2 -plasma treated (b), SAM-modified (c) and hBN covered (d) SiO₂ substrate. Only small-size graphene flakes are transferred in the case of the untreated SiO₂ substrate

Firstly, the graphene/substrate interaction is considered from the viewpoint of the quality of the transferred graphene. Here, the adhesion strength is analysed by transferring graphene using a dry transfer technique as described in Section 4.1. The dry transfer technique is selected for this test, since there is no additional adhesion provided by liquid evaporation, as

typically observed for wet transfer technique [151]. Figure 4.14 shows optical microscopy images of graphene films transferred on untreated and modified SiO₂ substrate. Continuous films are observed only for substrates after surface modifications. This is consistent with results presented in Section 4.1.2, where surface engineering significantly improved quality of graphene films after photolithography lift off process.

Next, Raman spectroscopy technique is used to further analyse the quality of graphene films on SiO₂ substrates with different surface modifications. Here, we use wet transfer technique to facilitate adhesion to untreated SiO₂ substrate. As demonstrated in Figure 4.15, the transferred graphene films demonstrate low defect concentration with the I(D)/I(G) ratio is typically less than 0.2 [163]. Notably, the Gr/hBN/SiO₂ sample has a slightly higher defect concentration, as observed by higher I(D)/I(G) ratio. This can be attributed to the presence of polymer residues left on the hBN surface after the wet transfer. Furthermore, the graphene sample transferred on the hBN film after thermal annealing (Gr/hBN(TA)/SiO₂) has lower defect concentration and thus supports the suggested hypothesis.

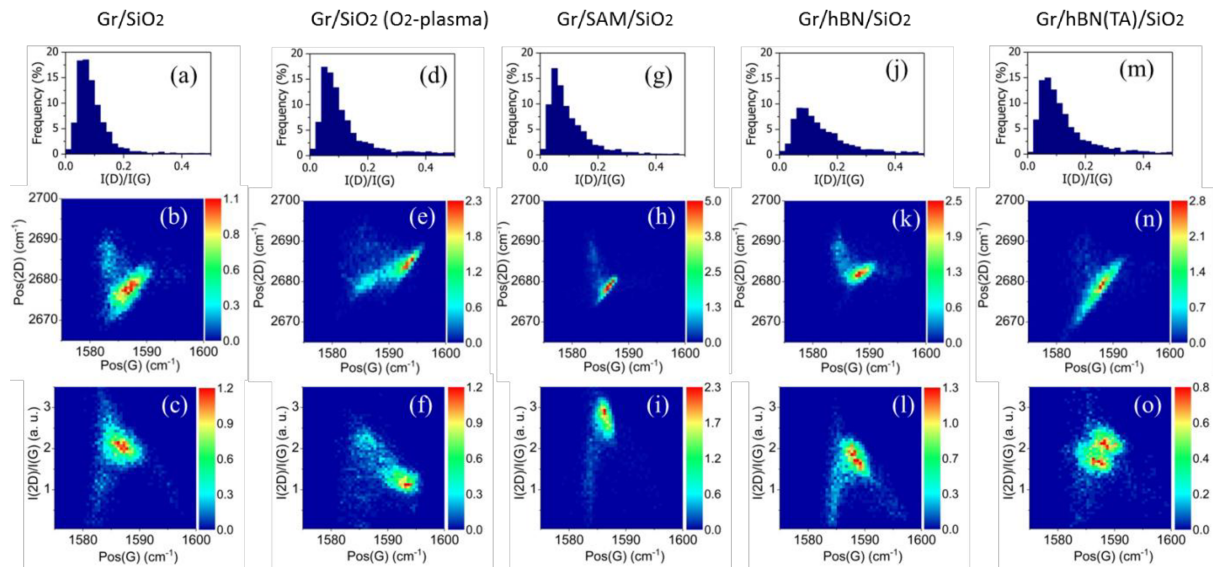


Figure 4.15. Raman spectroscopy results for graphene transferred using a wet transfer technique on untreated SiO₂ (a-c), SiO₂ after O₂-plasma treatment (d-f), SAM modified SiO₂ (g-i) and hBN covered SiO₂ with (m-o) and without thermal annealing (j-l). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio (I(D)/I(G)). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the I(2D)/I(G) ratio and the G-peak position, respectively.

To understand the doping level present in the samples, I(2D)/I(G) ratio can be used, as discussed in Section 2.6. It is clear that the Gr/SAM/SiO₂ sample demonstrates the largest average ratio indicating low doping. This is consistent with the screening effect provided by

SAM layer and is in good agreement with previous results for graphene transferred on SAM-modified substrates [144]. In contrast, Gr/hBN/SiO₂ sample shows lower I(2D)/I(G) ratio compared to the sample on untreated substrate Gr/hBN. This observation confirms that polymer residues left on the hBN surface after the transfer introduce additional extrinsic doping that can be even higher than doping introduced by substrate surface states. Interestingly, thermal annealing partially improves the I(2D)/I(G) ratio as shown for Gr/hBN(TA)/SiO₂ sample. However, bimodal distribution additionally appears for this sample. This effect will be discussed in more details below. The lowest average I(2D)/I(G) ratio is observed for Gr/SiO₂ (O₂-plasma) sample suggesting increased external doping from the substrate to graphene. This result can be considered consistent with an increase in density of silanol groups, since the silanol group is bipolar with positive side oriented towards graphene and therefore can introduce additional positive charge in the material [150].

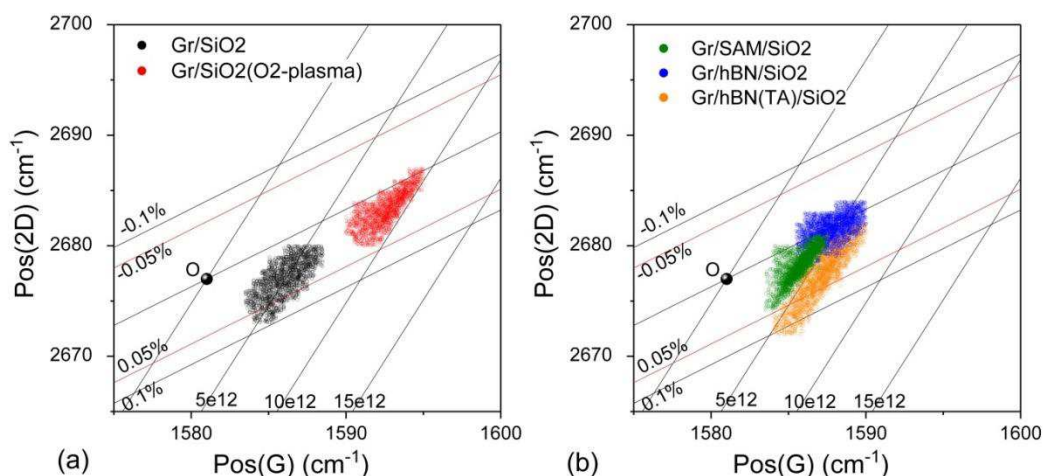


Figure 4.16. Correlation between the G and 2D peak positions for graphene transferred using a wet transfer technique on untreated SiO₂ (black), SiO₂ after O₂-plasma treatment (red), SAM modified SiO₂(green) and hBN covered SiO₂ with (orange) and without thermal annealing (blue). The data is separated in two graphs to avoid overlaps. The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm⁻². The O point represents suspended exfoliated graphene.

Sample	Doping, cm ⁻²	Biaxial strain, %
Gr/SiO ₂	5x10 ¹²	0.01 – 0.06
Gr/SiO ₂ (O ₂ -plasma)	8x10 ¹²	0.00 – 0.05
Gr/SAM/SiO ₂	4x10 ¹²	0.00 – 0.04
Gr/hBN/SiO ₂	5x10 ¹²	-0.01 – 0.01
Gr/hBN(TA)/SiO ₂	6x10 ¹²	0.01 – 0.06

Table 4.1. Graphene film properties based on Raman spectroscopy data presented in Figure 4.16.

To have a direct comparison between the samples, the distributions are combined and presented in Figure 4.16 with strain and doping lines included. Using a similar analytical technique as in previous sections, only statistically significant points ($>1\%$) are presented. The extracted average doping density and strain are summarized in Table 4.1. Notably, the doping levels obtained from correlation of Pos(G) and Pos(2D) are consistent with earlier observations based on $I(2D)/I(G)$ ratio. The lowest doping level is observed for Gr/SAM/SiO₂ sample, while O₂-plasma treatment results in the highest doping density. The surface treatment significantly affects the strain present in the graphene films. In fact, graphene transferred on SAM and hBN covered substrates have lower level of biaxial strain compared to untreated or O₂-plasma treated substrates. Surprisingly, the thermal annealing of the hBN layer prior to graphene transfer (Gr/hBN(TA)/SiO₂) results in much higher strain compared to Gr/hBN/SiO₂ sample. In fact, large strain variations are present in the graphene film on hBN after thermal annealing. This can be explained by surface inhomogeneity of CVD hBN layer where wrinkles and multilayer areas are present.

The present multilayers in hBN film not only introduce strain in the transferred graphene, they can locally modify graphene's doping density due to more efficient screening from SiO₂ substrate. This is confirmed through analyses of spatial distribution of $I(2D)/I(G)$ ratio (Figure 4.17 a), where the multiple areas of higher ratio values are observed. The area size (200nm-1 μ m) and distribution are in good agreement with multilayer areas observed in hBN films. The hBN multilayer areas underneath of graphene film can be clearly recognized in AFM image of the sample (Figure 4.17 b). Therefore, the bimodal distribution mentioned previously can be assigned to the multilayer distribution of the CVD hBN film.

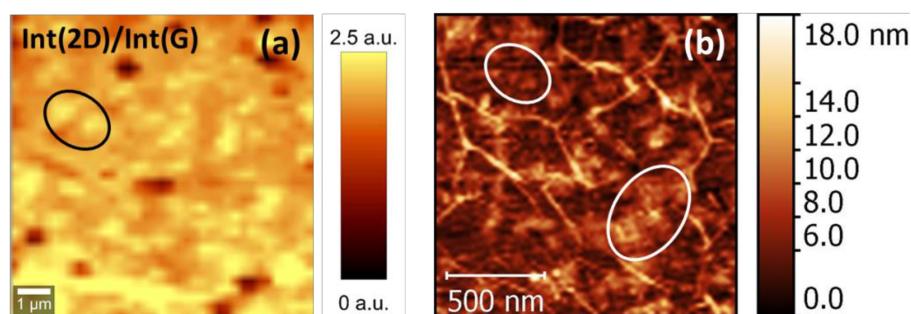


Figure 4.17. Effect of hBN multilayer areas in graphene transferred on hBN-covered SiO₂ after thermal annealing. (a) Raman spectroscopy map demonstrating spatial variations of 2D and G peak ratio. The multilayer area effect is highlighted by the circle. (b) AFM image of the surface topography confirming presence of hBN multilayer areas underneath of continuous graphene layer.

4.6 hBN-assisted graphene transfer technique

To avoid direct contact with a polymer film during transfer process, an intermediate layer can be used. In this section, we present a novel hBN-assisted transfer (AT) transfer technique that facilitates polymer free graphene transfer and encapsulation with hBN layer. Moreover, since CVD layers are utilized, the suggested technique results in large scale material production. This technique is based on a conventional transfer method with a difference in the target substrate, where the polymer supported 2D layer is applied directly to the next layer of interest. By these means, a polymer free interface between 2D layers can be created, while a conventional transfer technique leads to the accumulation of polymer residues with every next layer and thus significantly limits the final properties of the structure [226].

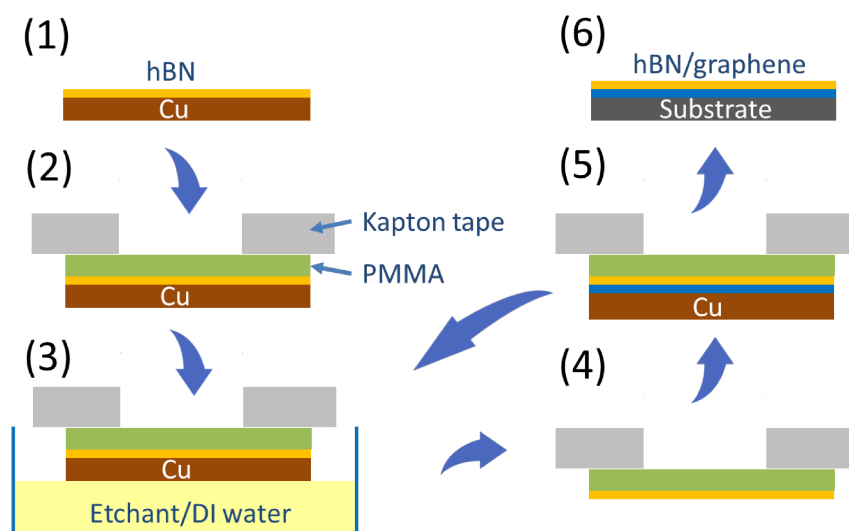


Figure 4.18. Schematic of the hBN-assisted transfer process.

A schematic of the hBN-assisted transfer (AT) technique is presented in Figure 4.18. Firstly, PMMA layer is spin coated over hBN/Cu foil. After drying overnight, a kapton tape (or PDMS) frame is applied to the PMMA/hBN/Cu stack. Then the sample is exposed to ammonium persulfate solution (15 g/L) followed by a thorough rinse in DI water. Since the frame can facilitate the dry transfer process, the stack is removed from DI water and dried at 60°C for 1 hour. After this step, the sample is directly applied to the next layer that is the graphene/Cu foil. Then the sample is heated for 30 mins above the glass transition temperature at 180°C. This step is used to increase the contact with the target substrate when PMMA/hBN layer becomes flexible and thus adapts to the new copper surface morphology. Then the sample is ready for a new cycle of Cu etching and DI water rinsing. It should be noted that the graphene or hBN located on the back side of the copper foil are removed prior

to transfer using an O₂-plasma treatment at 100 W during 2 mins. In principle, any number of 2D layers can be stacked in any order using this technique provided that the 2D material is grown on an etchable metal substrate. In this section, we limit ourselves to hBN/Gr and hBN/Gr/hBN stacks that are applied to the SiO₂ layer through wet transfer procedure to avoid the necessity of surface treatment, as discussed in the previous section. The samples produced by the novel transfer method (AT-hBN/Gr and AT-hBN/Gr/hBN) are compared to Gr/hBN stack made using the conventional wet transfer (WT) technique (sample WT-Gr/hBN).

Optical microscopy images confirm that continuous films with low density of defective structures such as tears and cracks are obtained for both transfer methods (Figure 4.19). It should be noted, that in the AT transfer process a topological mismatch of PMMA/hBN and Gr/Cu interfaces is expected, since the PMMA film replicates the morphology of underlying Cu foil [130]. Therefore, an increased density of wrinkles and tears might be expected. However, the results suggest that AT method leads to the same quality of graphene as films resulted from WT technique.

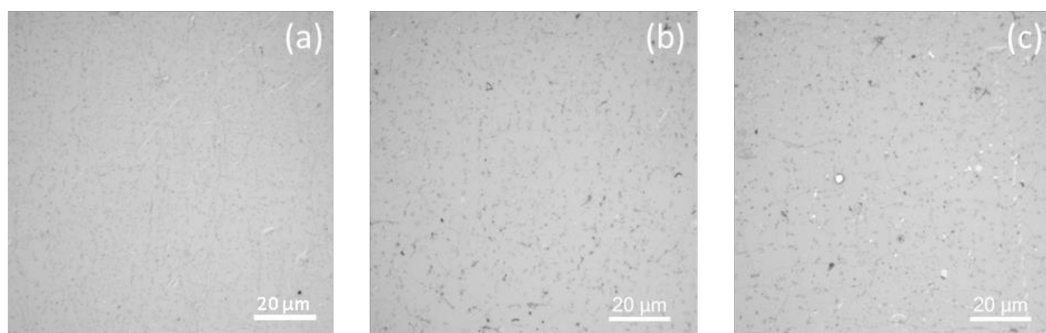


Figure 4.19. Optical microscopy images of the graphene transferred using a WT technique on hBN covered SiO₂ (a) and using AT method resulting in hBN/Gr (b) and hBN/Gr/hBN stacks (c).

Next, Raman spectroscopy is employed to analyse the crystalline quality of the graphene films, as shown in Figure 4.20. Using the I(D)/I(G) ratio, it is possible to conclude that the defect density is low for all of the samples, since the ratio is mostly below 0.2 [163]. Interestingly, the At-hBN/Gr/hBN sample demonstrates has a slightly higher defect concentration that can be explained by increased topology mismatch of the films due to presence of one more layer, as discussed earlier.

From the correlation of Pos(2D) and Pos(G) peaks, it is possible to conclude that there is no significant variation in the doping concentration present in the films. All the films show doping density of approximately $\sim 5 \times 10^{12} \text{ cm}^{-2}$. It should be noted, that AT-hBN/Gr/hBN layer demonstrates wider range of doping density of $3\text{-}6 \times 10^{12} \text{ cm}^{-2}$ including regions with

lower doping concentration compared to WT-Gr/hBN. To provide more information on doping density the $I(2D)/I(G)$ ratio can be used. Interestingly, the AT-hBN/Gr sample shows a slightly lower ratio compared to WT-Gr/hBN, while AT-hBN/Gr/hBN sample demonstrates increased ratio to the same level as the WT sample. The change in the ratio observed for AT-samples can be attributed to the additional extrinsic doping provided by the substrate, where in the case of AT-hBN/Gr sample the film is in direct contact with the substrate, while for At-hBN/Gr/hBN sample the bottom hBN layer provides screening of the charges.

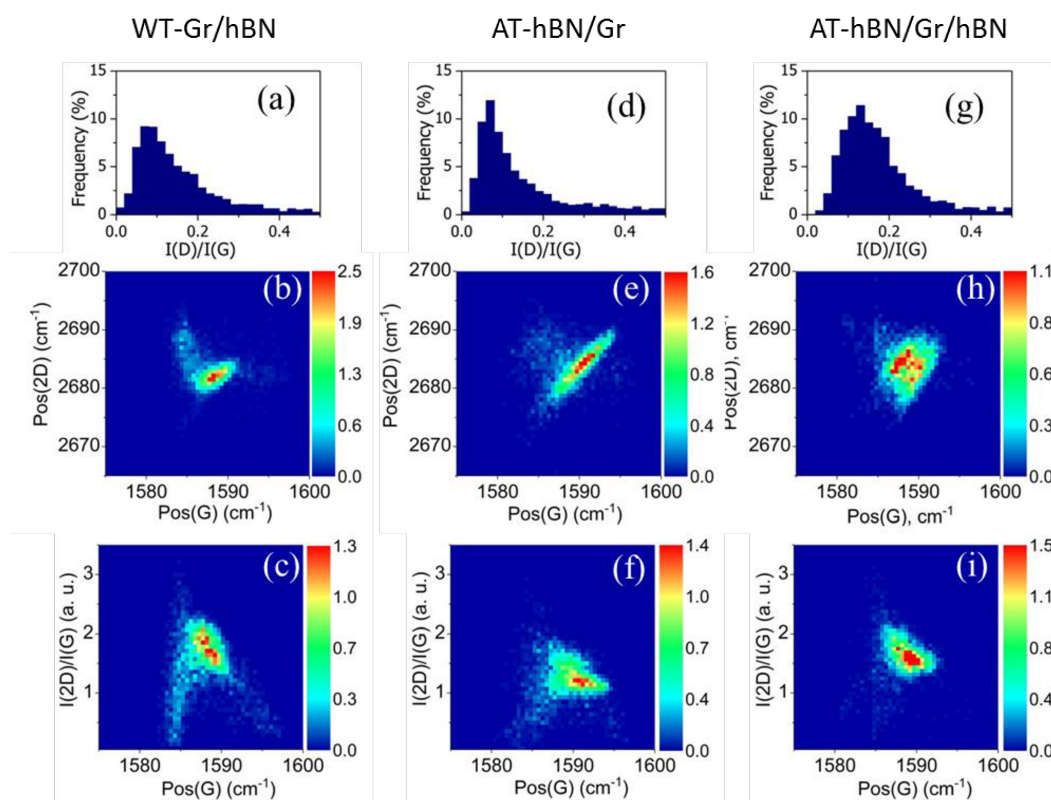


Figure 4.20. Raman spectroscopy results for graphene transferred using a wet transfer technique on hBN covered SiO₂ (a-c) and using hBN-assisted transfer method resulting in hBN/Gr (d-f) and hBN/Gr/hBN stacks (g-i). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the $I(2D)/I(G)$ ratio and the G-peak position, respectively.

Next, the strain present in the films is discussed. Interestingly, the AT-samples demonstrate higher biaxial strain variations of -0.03 – 0.025% and -0.05 – 0.025% for AT-hBN/Gr and AT-hBN/Gr/hBN, respectively. In contrast, WT-Gr/hBN sample shows strain in the range of -0.02 – 0.02% of biaxial strain. These wider variations can be explained by the topological mismatch of the PMMA film and target Cu substrate, as mentioned earlier. It should be noted that high strain variations can hinder the doping analysis. Therefore, additional

characterization, such as electrical measurements, is required for a thorough analysis of the films.

4.7 Electrical and aging properties of graphene samples

In this section, electrical and aging properties of graphene films are analysed. The AT-hBN/Gr sample resulted from the novel AT-transfer method is compared to the graphene films transferred using wet transfer technique on the substrates with/without surface treatments: WT-Gr/SiO₂, WT-Gr/SiO₂ (O₂ plasma), WT-Gr/SAM and WT-Gr/hBN. The discussion of Raman spectroscopy results for the selected samples can be found in Sections 4.5 and 4.6 for WT and AT samples, respectively.

As discussed in details in Section 3.1, a field-effect transistor (FET) geometry can be utilized to analyse the electrical properties of the transferred graphene films. To avoid contact with polymers, a shadow mask technique is used to create top-contact Cr (5nm)/Au (40nm) electrodes directly on graphene films. However, for hBN encapsulated sample (AT-hBN/Gr), a two-step photolithography process is required to access the graphene layer by creating edge-contact [227]. The shadow mask technique typically results in large area devices (of the order of 100 x 1000 microns in our case). At these length scales, CVD graphene films contain multiple defects such as multilayers, grain boundaries, wrinkles and occasional tears. Therefore, the extracted carrier mobility does not reflect defect free intrinsic values that typically require submicron devices. Nevertheless, the obtained mobility in these large area devices can still be considered as a useful parameter, since it provides direct comparison of additional extrinsic defects introduced by the transfer techniques.

The dependence of the two-terminal conductivity on the gate voltage is presented in Figure 4.21 (a). The different samples show significant variation in the charge neutrality point, or the Dirac point (VD), that is generally defined as position of the conductivity minimum (Table 4.2). It should be noted that in two terminal measurements the contact resistance influences the absolute value of the conductivity minimum making it less informative. The sample WT-Gr/SAM demonstrates VD at lower gate voltages compared to WT-Gr/SiO₂ suggesting reduced p-doping that is in agreement with the passivation effect of SAM layer on the SiO₂ surface. Interestingly, modification of SiO₂ surface with the hBN buffer layer results in a negative effect with a VD upshift compared to WT-Gr/SiO₂ sample indicating an increased p-type doping that is consistent with extrinsic doping introduced by the polymer residues

present on the hBN surface after the transfer. Importantly, the hBN-assisted transfer (AT-hBN/Gr/SiO₂) results in the lowest doping with a VD $\sim$ 7V that is significantly downshifted compared to WT-Gr/SiO₂. Taking into account graphene's direct contact with the SiO₂ substrate, this result can be explained by the absence of polymer residues on the graphene surface. A further decrease in doping can be anticipated by performing additional surface engineering using SAMs or by creating an hBN-Gr-hBN stack.

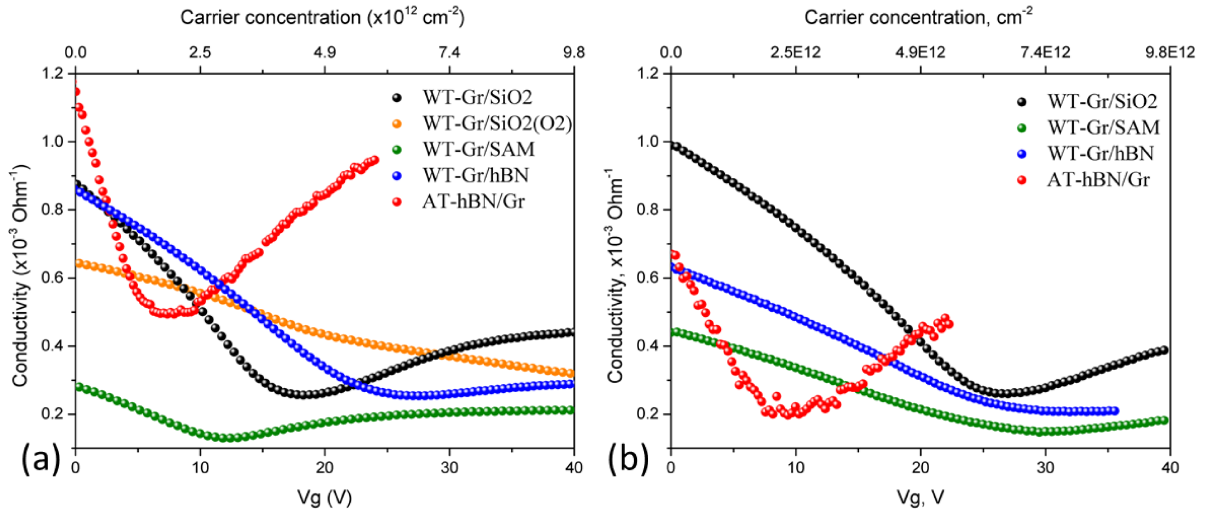


Figure 4.21. Conductivity of the graphene FETs obtained after wet transfer on untreated SiO₂, SiO₂ after O₂-plasma treatment, SAM- and hBN- covered SiO₂ and from hBN-assisted transfer after preparation (a) and after 1 month storage in ambient conditions (b).

Next, using the method described in Section 3.1, the electron and hole mobilities are extracted and summarized in Table 4.2. It should be noted that doping fluctuations inside the material can result in lower gradient of conductivity affecting the extracted mobility values. This effect is for example observed in the graphene samples with induced p and n doping regions by various SAM layers underneath [103]. Therefore, Raman spectroscopy measurements are performed at different positions to confirm the material consistency over large areas. The Gr-SiO₂ sample demonstrates a carrier mobility of approximately $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ that is consistent with the literature values reported for CVD material [202,228]. Moreover, a significant asymmetry in the hole and electron mobilities ($\mu_h/\mu_e \sim 3.2$) is observed, which can be explained by the presence of charge trap states on the SiO₂ substrate [229] or drift in the charged impurities from the substrate [230]. Surprisingly, the sample WT-Gr/SAM shows a reduced mobility of $400 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ compared to WT-Gr/SiO₂. This is perhaps an unexpected result, since the scattering sites present on SiO₂ surface should be passivated by the SAM layer [144]. However, there is a significant variation in the carrier mobilities of Gr/SAM samples presented in the literature. For example, a three-time increase

of the carrier mobility reaching $3000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been demonstrated for graphene on an ODTS layer by Lee et al. [144], while Cernetic et. al observed only a slight improvement in the mobility ($2500 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [202]. Furthermore, there are reports of significant improvements that can be obtained after additional thermal annealing due to removal of the trapped DI water between graphene and the underlying SAM covered substrate [145,231]. We stress that due to a hydrophobic nature of used SAM layer, delamination can be observed for graphene films transferred using WT method caused by high contact angle between DI water and the substrate. This can result in formation of macro-cracks limiting the overall device mobility. Interestingly, the WT-Gr/SAM sample exhibits a lower hole to electron mobility ratio of $\mu_h/\mu_e \sim 2.2$ that is consistent with the screening effect of ODTS layer on charge states present in the SiO_2 . For the WT-Gr/hBN sample, although quite high hole mobility is observed at approximately ($\sim 700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), the hole/electron mobility imbalance is much stronger with $\mu_h/\mu_e \sim 9$ that clearly confirms the presence of polymer dopants on the hBN surface. Finally, a three-fold increase in both electron and hole mobilities is revealed for the AT-hBN/Gr/ SiO_2 sample compared to the standard WT-Gr/ SiO_2 sample. However, the hole/electron mobility ratio remains high ($\mu_h/\mu_e \sim 3.7$) that is likely due to direct contact of the graphene film with the SiO_2 substrate.

sample	Dirac point as prepared (V)	mobility as prepared ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)		Dirac point after 1 month (V)	mobility after 1 month ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	
		hole	electron		Hole	electron
WT-Gr/ SiO_2	18	1069	331	26.5	872	301
WT-Gr/hBN	26	718	79	32.5	415	--
WT-Gr/SAM	12	380	170	30	288	95
AT-hBN/Gr	7	3105	836	9.6	1529	639

Table 4.2. The position of the Dirac point and hole/electron mobility for graphene transistors measured after preparation and after 1 month of storage in ambient conditions.

To examine the long term stability of the samples, the electrical properties were analysed again after one month of storage in ambient conditions (Figure 4.21 b). As mentioned earlier, the absolute conductivity values are considered to be less informative, since they additionally capture changes in contact resistance. Therefore, we concentrate our attention on changes of VD and mobility. The unprotected samples WT-Gr/ SiO_2 , WT-Gr/SAM and WT-Gr/hBN demonstrate significant degradation of the electrical properties as confirmed by an upshift of VD position and decrease of carrier mobility (see Table 4.2). Interestingly, WT-Gr/SAM sample exhibits the most significant VD increase. This is perhaps surprising, as the

hydrophobic SAM layers are generally expected to be less susceptible to water or oxygen adsorbents and, thus, anticipated to provide higher stability. However, to the best of our knowledge there are no reports on aging characteristics of graphene/SAM complexes. As expected, a high stability with a slight increase of the VD (only 2.6V) is observed the encapsulated AT-hBN/Gr/SiO₂ sample. These findings are consistent with previously reported negligible environmental sensitivity of fully encapsulated exfoliated graphene samples [232]. However, although the change in doping is negligible, the degradation of the carrier mobility is still observed. This can be explained by direct contact of the graphene film with the underlying SiO₂ that is known to attract dipolar adsorbates and, thus, facilitates sample aging [127]. Therefore, a complete encapsulation using AT method is anticipated to result in further improvements in mobility and aging characteristics.

4.8 Conclusions

In this chapter, the influence of transfer methods and post processing treatments on graphene quality has been discussed. Firstly, the impact of PMMA layer on graphene quality has been studied in terms of extrinsic doping. It has been demonstrated, that using PMMA layer introduces additional extrinsic doping on the order of $\sim 3 \times 10^{12} \text{ cm}^{-2}$. Although thermal annealing in vacuum results in PMMA removal, the extrinsic doping generally increases by $\sim 2 \times 10^{12} \text{ cm}^{-2}$ due to higher graphene/SiO₂ interaction. Therefore, this method is considered to be unsuitable for the sample cleaning when graphene is in direct contact with SiO₂ surface. Next, the substrate engineering, namely O₂-plasma treatment, SAM and hBN layer coating, has been confirmed to provide improved adhesion of the graphene layer, while modifying its carrier density. The lowest extrinsic doping has been observed for SAM layer (ODTS) consistent with the screening effect of the charged states present on SiO₂ surface. Interestingly, hBN layer has been shown to result in higher extrinsic doping likely due to polymer residues left on the surface after material transfer. Thermal annealing of the hBN layer prior to graphene transfer decreased the injected dopant concentration in graphene layer that supports previous suggestion about the doping source. The highest extrinsic doping has been observed for O₂-plasma treatment technique that can be explained by increased density of silanol groups on SiO₂ surface. Finally, a novel hBN-assisted transfer method has been presented. The improved technique enables a polymer free transfer and subsequent encapsulation of CVD-grown large-area graphene. We have demonstrated that this transfer method results in much lower doping concentration and improved carrier mobilities

compared with the results of the conventional wet transfer method for untreated SiO₂, SAM-modified and hBN covered SiO₂. Moreover, the encapsulation effect of the top hBN layer resulted in greater stability to ambient exposure. It is stressed that the novel transfer technique can be applied to other CVD-grown 2D materials enabling the preparation of van der Waals structures with polymer-free interfaces.

5 Graphene-plasmonic nanoparticle hybrids

This chapter considers the properties of graphene/plasmon-nanoparticle (NP) hybrids. Firstly, we discuss the structural properties and doping variation in these complexes analysed using SEM, AFM, KFM and Raman spectroscopy. Then we introduce time resolved differential reflection (DR) spectroscopy, which has been employed to characterize the ultrafast carrier dynamics of bare graphene. We show that the amplitude and sign of the DR signal is influenced by both the doping and the structure of the supporting substrate. After this the chapter moves on to discuss the measurements performed on the hybrid graphene/NP structures including the absorption enhancement and hot carrier generation processes. Finally, preliminary results are presented demonstrating that DR spectroscopy can be used as a mapping characterisation tool providing complementary information to Raman spectroscopy and KFM techniques.

5.1 Sample fabrication

5.1.1 Sample design and structural properties

The main samples explored in this chapter are graphene/plasmonic nanoparticle (NP) hybrids. Figure 5.1 shows the three main layered structures considered in this chapter. This first is simply graphene deposited on NP arrays on a Si/SiO₂ substrate with 300 nm of SiO₂ after O₂-plasma treatment (Gr/NP/SiO₂). The other two are hybrid structures combining plasmonic NPs with both hBN and graphene layers; in one sample the NPs are sandwiched by the hBN and graphene layers (Gr/NP/hBN/SiO₂), and in the other, both 2D layers are on top of the NPs (Gr/hBN/NP/SiO₂). The samples are made in the following way. Firstly, plasmonic NPs are fabricated on either a bare or hBN-covered Si/SiO₂ substrate using electron beam lithography followed by thermal deposition of 40 nm thick Au. No adhesion layer is used to avoid plasmon resonance damping (see Section 6.3.2 for detailed discussion). Before metal deposition the substrate is cleaned by O₂-plasma treatment at 50W for 20s. NP arrays with lattice periods (P) ranging between 400 and 1000 nm are patterned typically to extend over an

area of $40\ \mu\text{m} \times 40\ \mu\text{m}$. The 2D layers are transferred using a dry transfer method¹, as discussed in Section 4.1.1. Since a dry transfer technique is used, additional surface treatment is required to improve the layer adhesion, as discussed in Section 4.5. Therefore, O_2 -plasma is used to treat the Si/SiO_2 substrate for 2 mins at 100W before the first 2D layer deposition. For the subsequent 2D layers, the adhesion is provided by the first layer.

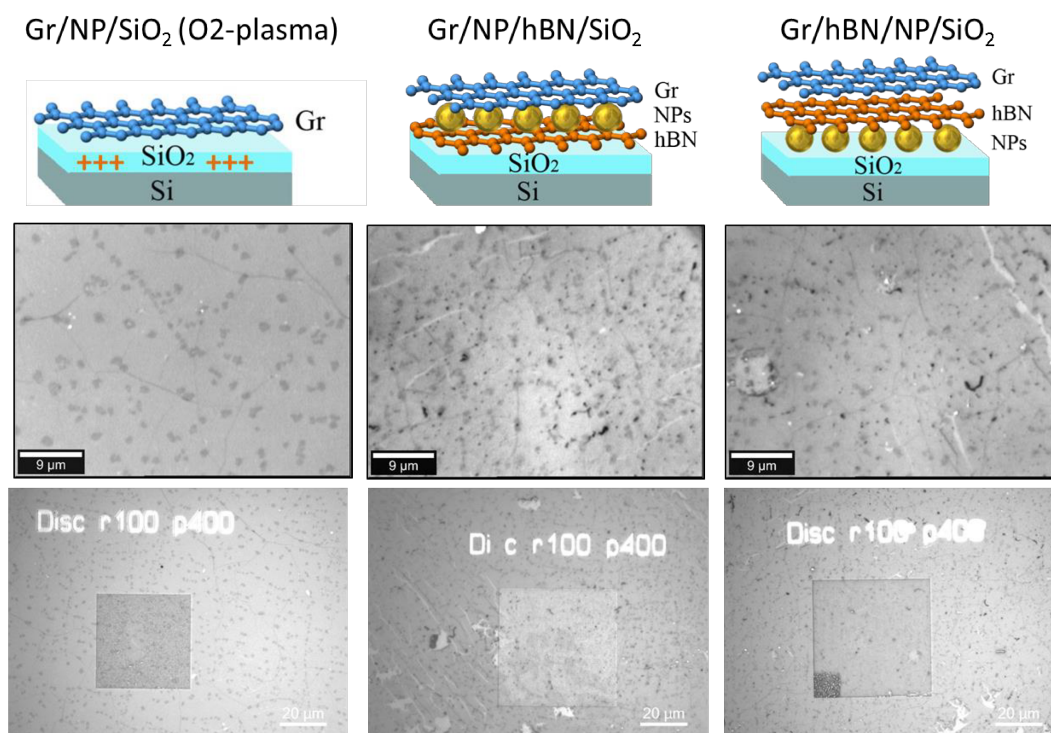


Figure 5.1. Sample schematic (first row) and optical microscopy images of bare graphene films (second row) and graphene/NP arrays ($R=100\text{nm}$ $P=400\text{nm}$).

Optical microscopy images confirm the presence of continuous graphene layers for all the samples (Figure 5.1). Interestingly, additional residues are present in graphene films on substrates with the hBN layer. This can be explained by additional polymer residues left on the hBN surface. SEM images of graphene/NP and graphene/hBN/NP complexes confirm the presence of the graphene and graphene/hBN layers (Figure 5.2). Due to the material's flexibility, the 2D layers appear to drape conformally over the plasmonic NPs relaxing

¹ Graphene/Cu or hBN/Cu layers are covered with PMMA A7 950 by spin coating at 3500 rpm for 60 s and left to dry at room temperature overnight. O_2 -plasma treatment (100 W, 2 mins) is used to remove residual graphene/hBN layers present on the bottom side of the foils. Kapton tape frames are applied to the PMMA-covered hBN or graphene Cu foils from the top side to facilitate dry transfer process. The exposed Cu foil is etched in an ammonium persulfate solution (15 g/L) followed by a thorough rinse in DI water. The floating PMMA/graphene stack is then removed from the liquid using the kapton tape as a holder. The films are dried at 60°C for 1h before application to the Si/SiO_2 substrates. Samples with PMMA/Gr or hBN film are annealed at 180°C for 30 mins to facilitate good contact between 2D material and the substrate. PMMA layer is removed using acetone followed by IPA rinse. After polymer removal, for multilayer samples the graphene layer is transferred on top following the similar procedure.

around them to make contact with the substrate in between NPs. This “veil” effect is further confirmed by AFM measurements, where the direct contact of 2D layers with the substrate is observed even for the smallest 200nm interparticle spacing considered in this work (within the spatial limitations of the AFM method).

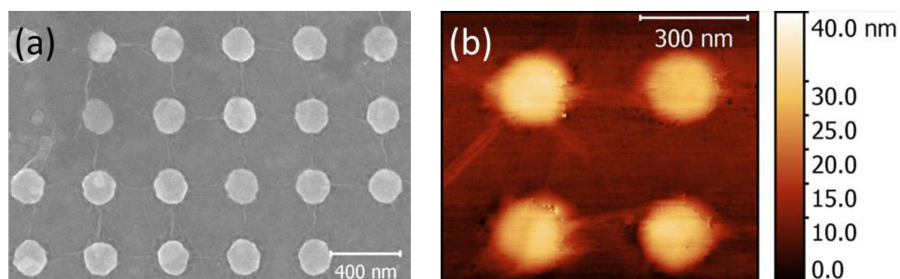


Figure 5.2. Representative SEM and AFM images of Gr/NP/hBN/SiO₂ sample.

5.1.2 Plasmonic response of hybrid graphene/NP system

Gold nanodisks with a radius of 100 nm are expected to support localized plasmon resonance in the near-IR region, far from gold’s interband transitions. To confirm the presence of a plasmon resonance, reflectance measurements are performed using Fourier Transform Infrared (FTIR) spectroscopy, as discussed in Section 3.6. The results demonstrate significantly enhanced reflection from the plasmonic NP arrays (Figure 5.3). However, the underlying multilayer Si/SiO₂ substrate causes additional Fabry-Perot oscillations that complicate the analysis of plasmon resonance position, as seen in the reflectance spectrum of the bare substrate (red line). Therefore, numerical calculations are employed to determine the plasmon resonance position. FDTD simulations are performed with the commercial package Lumerical FDTD solution following the method described in Chapter 3. The simulated spectra show good agreement with experimental data (Figure 5.3). The simulated near field enhancement spectrum, I/I_0 , where I_0 is the incident field intensity, extracted from a point 3 nm outside the NP, indicates that the localized plasmon resonance position is at around ~780nm for the gold NP array with $R=100\text{nm}$ and $P=400\text{nm}$. It should be noted that both graphene and hBN layers, being a single atom thick, have little effect on the plasmon resonance position in the visible range of spectrum.

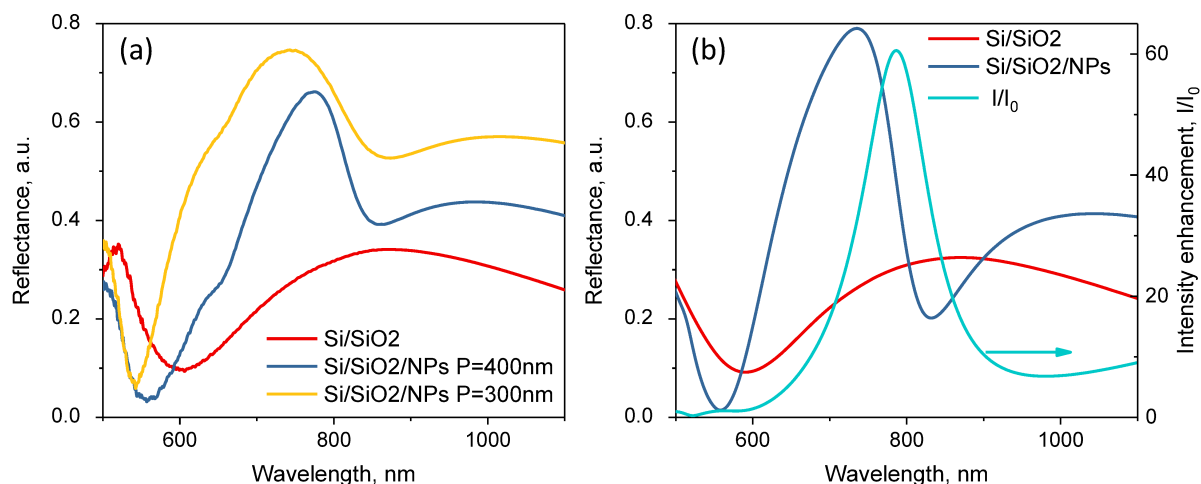


Figure 5.3. Plasmonic response of graphene/NP hybrids. (a) Experimental reflectance spectra of the graphene/NP/substrate system with periods of 400 and 300nm. The graphene/substrate response is included for comparison. (b) The simulated reflectance spectra for substrate with/without NPs. Calculated near-field intensity enhancement indicating plasmon resonance at ~ 780 nm.

5.2 Doping variations in the hybrid system

5.2.1 Raman spectroscopy study

As discussed in Chapter 4, graphene is highly sensitive to the surrounding environment and, in particular, to the underlying substrate surface. Therefore, it is expected that the gold NPs will significantly affect graphene's properties such as doping, strain and defect density. Here, we utilize Raman spectroscopy to analyse graphene's structure when draped over gold NPs. Firstly, we discuss the effect of NP density on graphene's properties by comparing areas of with and without NP arrays for the Gr/NP/SiO₂ sample. Then, we examine the influence of the hBN spacer layer on graphene/NP interaction by analysing the Gr/NP/hBN/SiO₂ and Gr/hBN/NP/SiO₂ samples.

NP period influence on graphene properties

Figure 5.4 shows the optical microscopy image and corresponding micro-Raman map depicting G-peak position variations of the sample Gr/NP/SiO₂ at the interface of regions with and without NPs. In the presence of high density gold NPs, optical microscopy can no longer be used for primary analysis of the graphene film continuity. In contrast, Raman spectroscopy offers a robust technique to identify graphene coverage. Representative Raman spectra (Figure 5.4 c) of the bare graphene as well as graphene/NP structures demonstrate prominent graphene features with clearly resolved G and 2D peaks superimposed on broad

background fluorescence from the gold. Notably, this fluorescence signal increases with increasing NP density. Since the 532 nm laser illumination employed for the Raman study is far from the plasmon resonance expected at 780 nm (Section 5.1), the SERS effect is negligible, as confirmed by almost identical peak intensity detected for graphene with and without NPs. The observed graphene Raman peaks from the array region suggest that the integrity of the graphene film is well preserved in the presence of NPs. This is in good agreement with the results of graphene structural characterization performed using SEM and AFM techniques (Section 5.1). Furthermore, the continuous micro-Raman map of G-peak position provides additional evidence of the uniform coverage of the graphene film. Interestingly, significant down-shift of the G-peak position is observed for the graphene/NP structure when compared to the bare graphene. This effect can arise from a decreased doping level or modified strain in the presence of NPs.

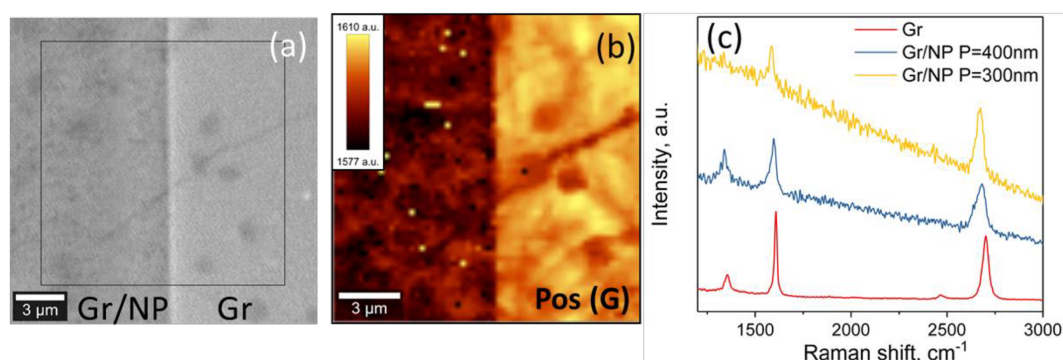


Figure 5.4. (a,b) Optical microscopy image of sample Gr/NP/SiO₂ with NP-array/graphene interface and corresponding spatial map of G-peak position. The NP array period is P=300nm. (c) Representative Raman spectra of the bare graphene and graphene/NP structure with NP period of 300 and 400nm.

Next, the quality of the bare graphene film is compared to those over the NP arrays with varying density by compiling statistics from the Raman spectroscopy data (Figure 5.5). The graphene defect concentration is significantly increased in the presence of NPs as confirmed by the enhanced I(D)/I(G) ratio. Notably, higher ratios are evident for arrays with smaller periods, which is consistent with correlation between NPs and defect densities. The observed increase in the defect density could be attributed to mechanical deformation of the graphene layer by NPs or to gold induced defects of the graphene layer particularly during sample annealing. To distinguish between these possible effects, the sample with an hBN spacer layer between the graphene and the NPs was also studied, as discussed below.

The extrinsic doping density present in the samples can be analysed by examining the I(2D)/I(G) ratio, as discussed in Section 2.6. Interestingly, the I(2D)/I(G) ratio is quite similar for all studied

samples. However, it is well known that the $I(2D)/I(G)$ ratio is highly sensitive to the interference effects of the underlying substrate [233]. Therefore, the gold NPs can minimize enhancement provided by the Si/SiO₂ substrate suggesting that the $I(2D)/I(G)$ ratio is not a reliable parameter for analysing the extrinsic carrier density in presence of NPs.

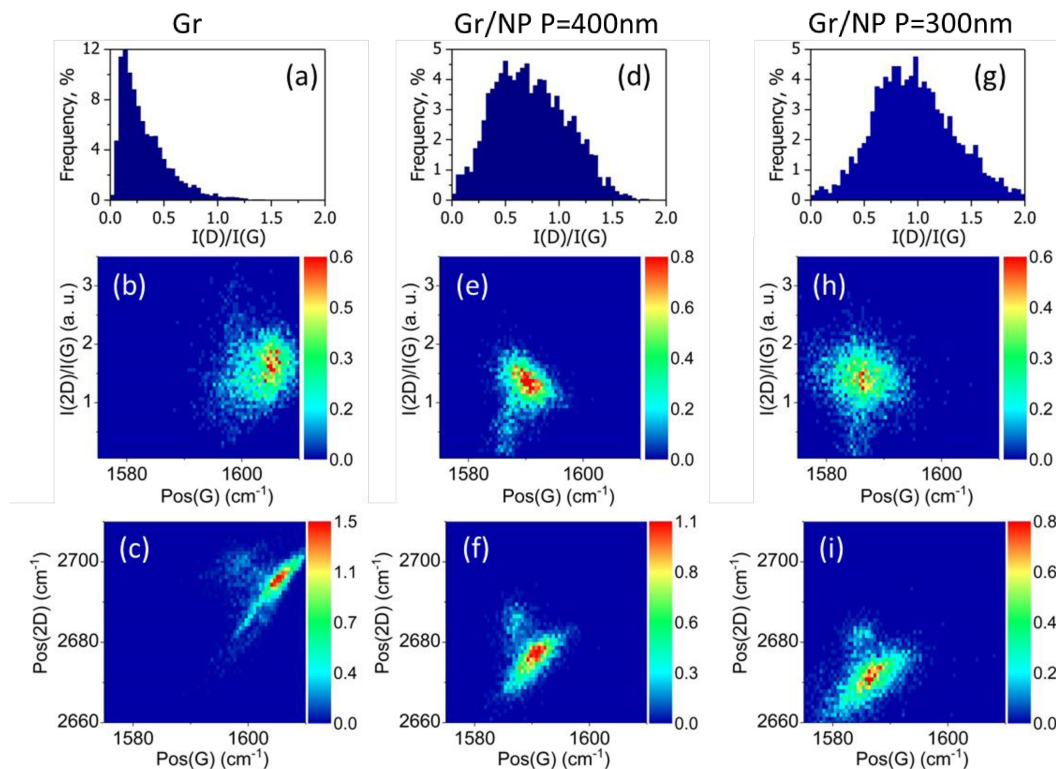


Figure 5.5. Raman spectroscopy results for sample Gr/NP/SiO₂ with bare graphene (a-c) and graphene/NP complexes with P=400nm (d-f) and P=300nm (g-i). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the $I(2D)/I(G)$ ratio and the G-peak position and the G and 2D peak positions, respectively.

To facilitate a direct comparison between the samples, the statistically significant points (>0.5%) describing correlation between the G and 2D peak positions are combined and presented in Figure 5.6 following the method used in Chapter 4. The trends of the data distribution suggest that the variations in Pos(G) and Pos(2D) are largely due to strain fluctuations present in all samples, which is consistent with previous results for CVD graphene discussed in Chapter 4. Strikingly, there are significant differences in both doping and strain present in the graphene/NP structures compared to bare graphene. The extrinsic doping density of $\sim 1.6 \times 10^{13} \text{ cm}^{-2}$ is detected for bare graphene in direct contact with SiO₂ substrate after O₂-plasma treatment. This finding is consistent with increased p-doping due to higher density of silanol groups activated by the treatment on the SiO₂ substrate, as discussed in details in Section 4.7. Surprisingly, graphene/NP structures exhibit a much lower doping

density of $\sim 8 \times 10^{12} \text{ cm}^{-2}$ and $\sim 1 \times 10^{13} \text{ cm}^{-2}$ for NP periods of 300 nm and 400 nm, respectively, where the doping density decreases with higher NP density. There are two major effects that can potentially contribute to the observed doping reduction. Firstly, as confirmed by AFM and SEM results (Section 5.1), the graphene is partially decoupled from the substrate by being draped over the NPs, which would decrease substrate induced doping. This effect is typically observed for samples with suspended graphene film [123]. Secondly, under interaction with gold, charge transfer is expected between graphene and metal resulting in a modification of the doping level. There is a significant variation in the Au-induced doping of graphene reported in the literature. For instance, theoretical calculations suggest that interaction with gold can result in p-doping of the graphene layer [102], while there are also numerous reports of experimentally observed n-doping of graphene after gold deposition [234–236]. Special attention is paid to the work reported by Liu et. al where NPs deposited on graphene FET devices using a PMMA film resulted in n-doping of the underlying graphene film [40]. This device fabrication technique results in weak graphene/NP interaction that is similar to our work, since the graphene layer is transferred on top of the NPs. Furthermore, similar to Ref. [40] the samples reported in the current work are not exposed to high temperature treatments that are known to result in strong graphene-metal binding [237]. Therefore, it is reasonable to conclude that n-type doping is expected in the case of direct contact of graphene with Au NPs. This question is discussed in more details below where the influence of the hBN spacer layer is analysed.

The discussion now moves to the strain properties of graphene films are discussed. Analysing Figure 5.6, it is clear that NPs significantly modify the graphene film's strain due to expected mechanical deformation. The bare graphene film exhibits biaxial strain variations in the range of $-0.037 - 0.075\%$. This is consistent with our previous results for the graphene on SiO_2 surface after O_2 -plasma treatment, where decreased tensile strain and increased compressive strain are observed (Section 3.7). In contrast, graphene/NP structures demonstrate significantly increased tensile biaxial strain in the range of $0.1 - 0.22\%$ and $0.07 - 0.19\%$ for 300 nm and 400 nm period, respectively. Notably, the tensile strain increases with higher NP density. This result is consistent with increased mechanical deformation of the graphene and a higher probability of areas with suspended graphene.

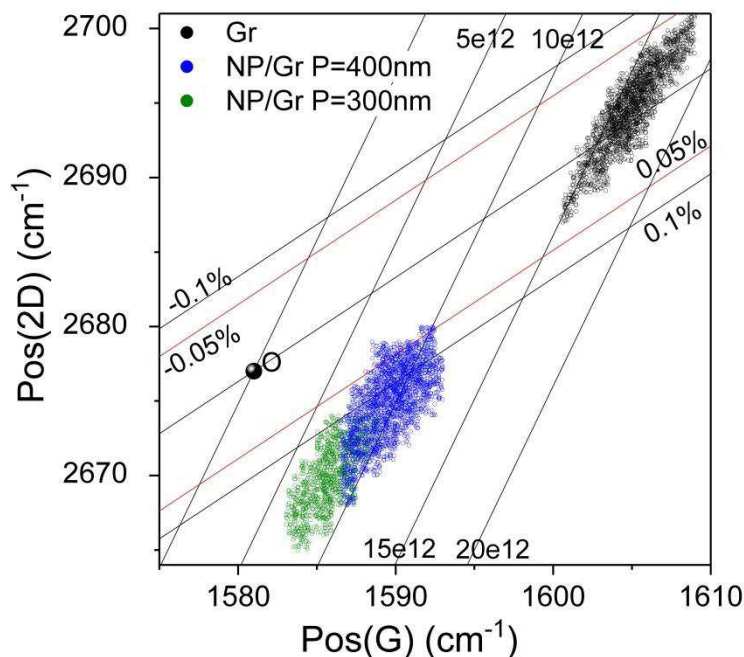


Figure 5.6. Correlation between the G and 2D peak positions for bare graphene (black) and graphene/NP complexes with P=400nm (blue) and P=300nm (green). The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping. The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.

Graphene/NP interaction with/without hBN spacer layer

Next, the influence of hBN spacer layer on graphene/NP interaction is studied. Figure 5.7 presents Raman spectroscopy results for the Gr/NP/SiO₂, Gr/NP/hBN/SiO₂ and Gr/hBN/NP/SiO₂ samples. The spatial variation of the G peak position and the 2D and G peak intensity ratio $I(2D)/I(G)$ confirm the presence of continuous graphene films for both the substrate and NP array regions. Interestingly, compared to the Gr/NP/SiO₂ sample, both samples with the hBN layer demonstrate low variations in the G peak position and $I(2D)/I(G)$ ratio when on and off the arrays suggesting minimal change in the doping level of graphene over NPs.

By analysing the statistical results of Raman spectroscopy data, the quality of the graphene film with/without NPs for various sample can be compared (Figure 5.8). The defect density, which is related to the $I(D)/I(G)$ ratio, is significantly higher for graphene/NP structures compared to bare graphene for all samples. Notably, the presence of hBN layer only slightly reduces the defect density indicating that the graphene/metal interaction has negligible contribution to defect formation. This reinforces the assertion that defects are mainly induced due to mechanical modifications of the graphene layer in the presence of the NPs.

Interestingly, for bare graphene regions, both samples with a hBN layer exhibit significantly higher $I(2D)/I(G)$ ratio of ~ 2 compared to the Gr/NP/SiO₂ sample where the ratio of ~ 0.9 is detected. Moreover, for the samples with hBN layer, the intensity ratio remains almost constant for graphene/NP area. In contrast, the Gr/NP/SiO₂ sample shows higher ratio for the graphene/NP structures that could be evidence of decreased doping level. However, as previously discussed, the $I(2D)/I(G)$ ratio is sensitive to substrate interference and should be used with caution while analysing the doping variations in the presence of Au NPs.

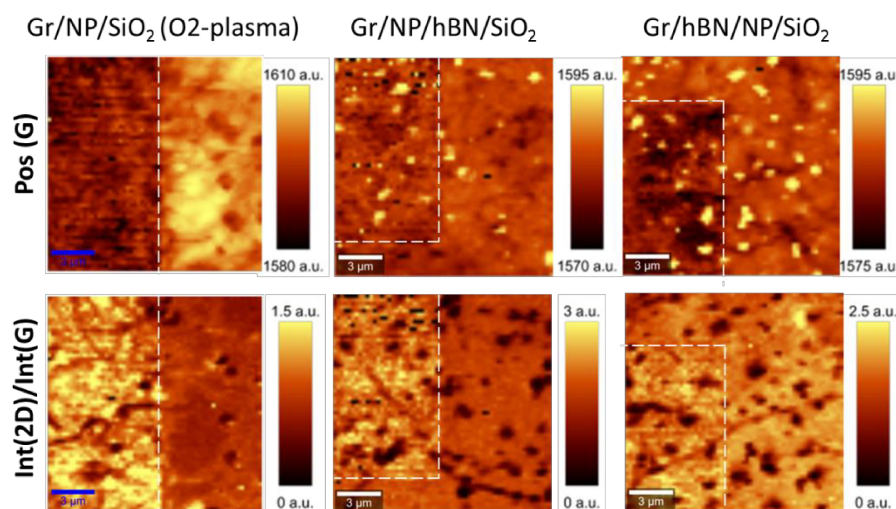


Figure 5.7. Raman spectroscopy results for the Gr/NP/SiO₂, Gr/NP/hBN/SiO₂ and Gr/hBN/NP/SiO₂ samples. Spatial variation of the G-peak position and the 2D and G peak intensity ratio $I(2D)/I(G)$ are presented in the first and the second row, respectively.

Similar to the previous section, the statistically significant points are extracted for bare graphene ($>1\%$) and for graphene/NP structures ($>0.5\%$) to directly compare the correlation between the G and 2D peak positions (Figure 5.8 c,f,i). Note that a lower threshold was applied to the data selection for graphene/NP structures due to a broader distribution of Raman features. Compared to the Gr/NP/SiO₂ sample, the samples with hBN layers demonstrate much lower variation in the doping level for bare graphene and graphene/NP structures. Interestingly, the presence of the hBN spacer layer between graphene and Au NPs does not significantly modify the doping concentration providing evidence that direct doping from graphene/metal interaction is negligible. Furthermore, bare graphene for Gr/NP/SiO₂ exhibits much higher doping compared to the samples with hBN layers. This is in agreement with our previous results for graphene interaction with substrates after the surface engineering discussed in Section 4.5. These findings support the idea of partial detachment of the graphene layer. All samples demonstrate increased tensile strain in the presence of NPs. Interestingly, the strain variation is higher for the Gr/hBN/NP/SiO₂ sample compared to other

samples. This can be possibly due to additional wrinkles introduced by the hBN layer around the NPs leading to higher mechanical stress present in the graphene.

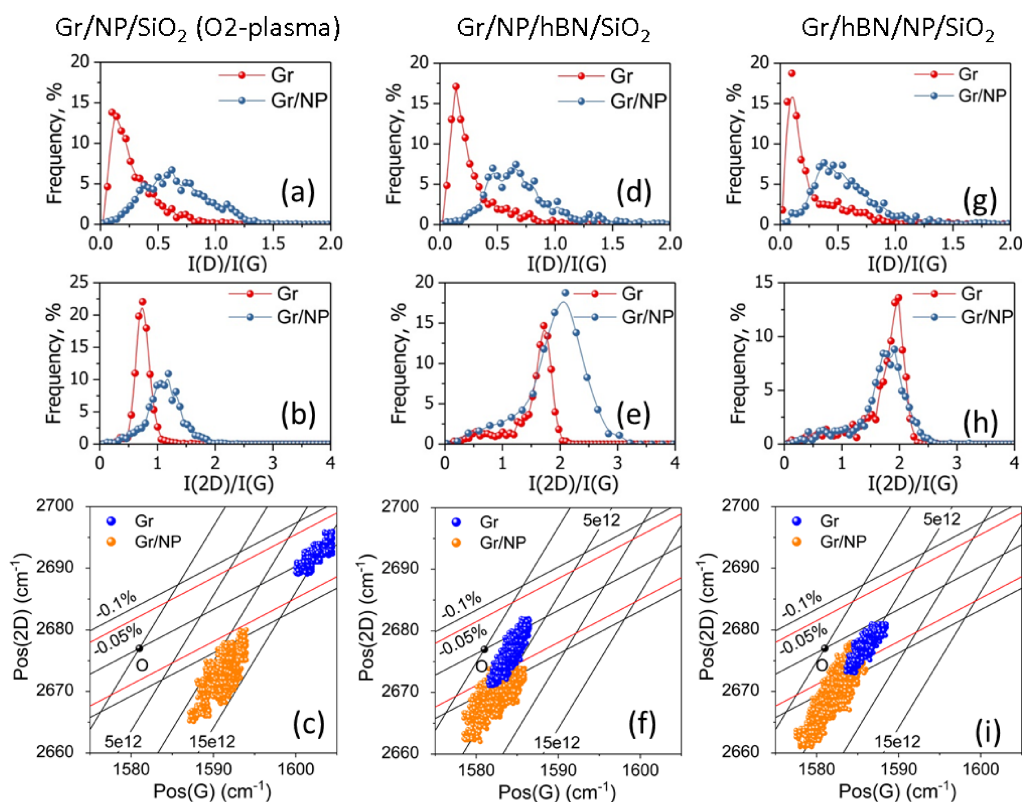


Figure 5.8. Raman spectroscopy results for Gr/NP/SiO₂ (a-c), Gr/NP/hBN/SiO₂ (d-f) and Gr/hBN/NP/SiO₂ (g-i) samples with bare graphene (Gr) and graphene/NP complexes with P=400nm (Gr/NP). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio I(D)/I(G). The second row shows the I(2D)/I(G) ratio. The third row presents 2D histograms describing correlation between the G and 2D peak positions.

5.2.2 Kelvin Force Probe Microscopy (KFM) study

Raman spectroscopy provides diffraction limited resolution of ~ 286 nm for our measurement conditions (532 nm and 0.95 NA objective) that is significantly larger than a single NP of 200 nm diameter. To analyse graphene properties with higher resolution, the KFM technique can be employed, as discussed in Section 4.4. Here, we study the local variations in Fermi energy of graphene near NPs. The samples under investigation are Gr/NP/SiO₂ and Gr/NP/hBN/SiO₂ where the graphene layer is in direct contact with the gold nanostructures.

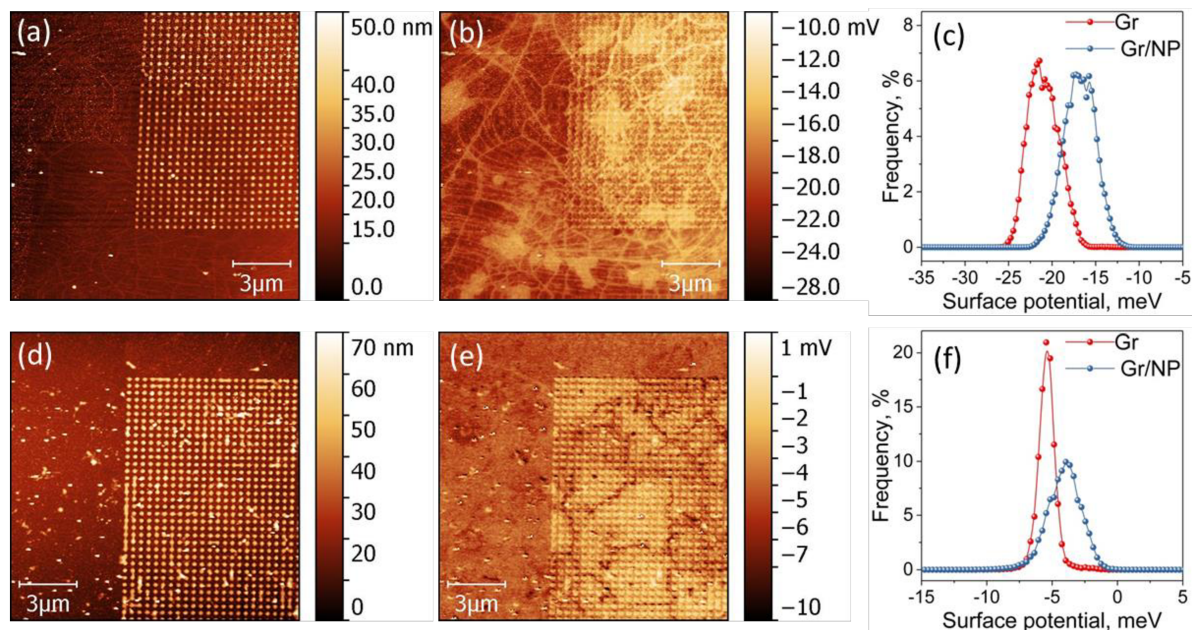


Figure 5.9. AFM and KFM images of Gr/NP/SiO₂ (a,b) and Gr/NP/hBN/SiO₂ (d,e) samples. The distributions represent contact potential difference measured for bare graphene and graphene/NP areas for Gr/NP/SiO₂ (c) and Gr/NP/hBN/SiO₂ (f) samples.

Figure 5.9 shows the measurement results of the graphene/array interface for the Gr/NP/SiO₂ and the Gr/NP/hBN/SiO₂ samples. In the case of the Gr/NP/SiO₂ sample, the graphene layer demonstrates high variations of surface potential (V_{CPD}) with clearly resolved wrinkles and multilayer areas (Figure 5.9 b). As discussed in Section 4.4, multilayer areas are known to screen the doping induced by the underlying substrate. Therefore, strong KFM contrast where the multilayers exist is typically an indication of the higher doping present in single layer graphene directly in contact with the SiO₂ substrate. This is consistent with Raman spectroscopy results confirming high doping induced by direct contact of graphene layer with SiO₂ substrate after O₂-plasma treatment, as discussed in the previous section. In contrast, negligible variations in the surface potential of the graphene layer are observed for the Gr/NP/hBN/SiO₂ sample. See Section 4.5 for detailed discussion of the surface engineering effect on graphene properties.

Next, the influence of NPs on the graphene surface potential is discussed. For both samples, graphene in presence of NPs exhibits lower surface potential corresponding to lower doping present in the layer (Figure 5.9 c,f). In fact, the Fermi energy shift between bare graphene and graphene/NP areas of ~ 4.5 and 1.5 meV is observed for the Gr/NP/SiO₂ and Gr/NP/hBN/SiO₂ samples, respectively. The Gr/NP/SiO₂ sample exhibits three times higher shift in the Fermi energy compared to the Gr/NP/hBN/SiO₂ sample. These findings are in good agreement with Raman spectroscopy results presented in the previous section.

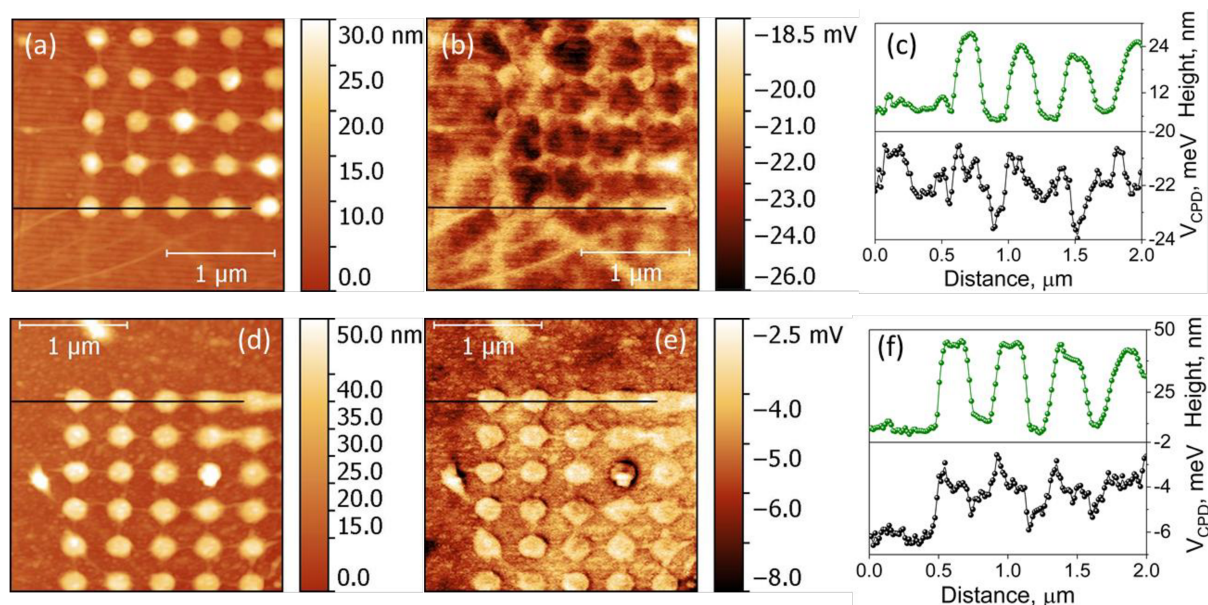


Figure 5.10. High resolution AFM and KFM images with corresponding cross sections of Gr/NP/SiO₂ (a, b, c) and Gr/NP/hBN/SiO₂ (d, e, f) samples.

High resolution AFM and KFM images provide additional information on local properties of the graphene/NP complexes (Figure 5.10). For the Gr/NP/SiO₂ sample, the graphene layer abruptly changes surface potential around the NPs. Interestingly, there is clear decrease of surface potential between the particles suggesting that the graphene layer mechanically relaxes and creates a good contact with the substrate. This is confirmed by AFM measurements where the graphene layer between the NPs takes approximately the same height as the bare graphene away from the NPs. Interestingly, for the Gr/NP/hBN/SiO₂ sample, the surface potential of the graphene between the NPs appears to remain slightly higher compared to the bare graphene. Although this might be an artefact of the measurement of additional residues left between the NPs in this particular instance, the colour contrast across the whole scan is rather convincing.

5.3 Pump probe spectroscopy characterization

To study the carrier dynamics in the graphene/NP system, we utilize the time resolved differential reflection (DR) spectroscopy technique, which is a direct probe of electron and phonon temperatures on ultrafast time scales (Section 2.2.4). Hot carrier excitation in the graphene/NP structures is of particular interest. As discussed in Section 2.3.3, the graphene's absorption can be drastically enhanced in by plasmonic NPs due to locally enhanced electromagnetic fields and due to potential hot carrier injection from the metal in the graphene. The major focus of this section is to identify the dominant process of hot carrier

generation in the graphene/NP system. Initial DR measurements are performed on bare graphene to understand the influence of material doping and underlying substrate on the DR response. As discussed in Section 2.2.4, the time resolved DR response of graphene is highly sensitive to the Fermi level as the sign of the DR signal changes when the probe photon energy is close to twice the Fermi level. The origin of the sign change in the DR signal is primarily discussed in Section 5.3.1. The properties of the graphene/NP system are studied in Section 5.3.2. The results presented in this section are partially published in Ref. [109].

5.3.1 Impact of substrate and doping on the differential reflection (DR)

Experimental results.

Optical pump-probe measurements are used to provide insight into the effects of substrate interactions and doping on the graphene carrier dynamics in the vicinity of the Fermi level. We study the ultrafast carrier dynamics of graphene using a pump pulse at a fixed wavelength of 830 nm at 2 mW with $\sim 6 \mu\text{m}$ spot size ($\sim 45 \mu\text{J}/\text{cm}^2$) and a probe pulse with tunable wavelength in the range of 1200 – 1600 nm at 100 μW with $\sim 2 \mu\text{m}$ spot size ($\sim 4.5 \mu\text{J}/\text{cm}^2$). Four additional samples were fabricated to compare with the results for the graphene/NP samples discussed earlier in this chapter. Details of the additional samples are summarized in the Table 5.1.

Sample	Substrate	Substrate treatment	Fermi energy*
<i>Gr/SiO₂</i>	quartz	no	$0.25 \pm 0.05 \text{ eV}$
<i>Gr/SiO₂ (O₂-plasma)</i>	quartz	O ₂ plasma	$0.4 \pm 0.05 \text{ eV}$
<i>Gr/SiO₂/Si</i>	Si/SiO ₂ (300nm)	no	$0.25 \pm 0.05 \text{ eV}$
<i>Gr/SiO₂/Si (O₂-plasma)</i>	Si/SiO ₂ (300nm)	O ₂ plasma	$0.4 \pm 0.05 \text{ eV}$

Table 5.1 Details of the samples discussed in this section including the substrate structure and treatment. The Fermi energy is extracted from Raman spectroscopy data (not shown). See Section 4.5 for detailed discussion of the doping induced by engineering of the substrate surface.

The first two additional samples consist of CVD graphene deposited using a wet transfer technique on a quartz substrate with and without O₂-plasma treatment, which are labelled as “Gr/SiO₂ (O₂-plasma)” and “Gr/SiO₂”, respectively. The next set of additional samples (labelled “Gr/SiO₂/Si” and “Gr/SiO₂/Si (O₂-plasma)”) is fabricated on typical back-gated substrates that consist of doped silicon, covered by a 300 nm thick layer of SiO₂. Similar to

the first set of additional samples, half of the second batch was exposed to an O₂-plasma treatment. In this way, the second set of additional samples is similar to the graphene/NP samples discussed earlier in this chapter.

Figure 5.11 shows the DR spectra for all samples under investigation. First, we discuss the samples without O₂-plasma treatment with a Fermi level of 0.25eV, which is estimated from Raman spectroscopy measurements (Section 4.5). Interestingly, the two samples, Gr/SiO₂ and Gr/SiO₂/Si, exhibit DR signals of opposite sign for all of the probe energies in the study. Since the graphene properties are similar for both samples, as confirmed by Raman spectroscopy, the sign change must arise from the differing substrates. This will be verified in calculations to be shown later in this section.

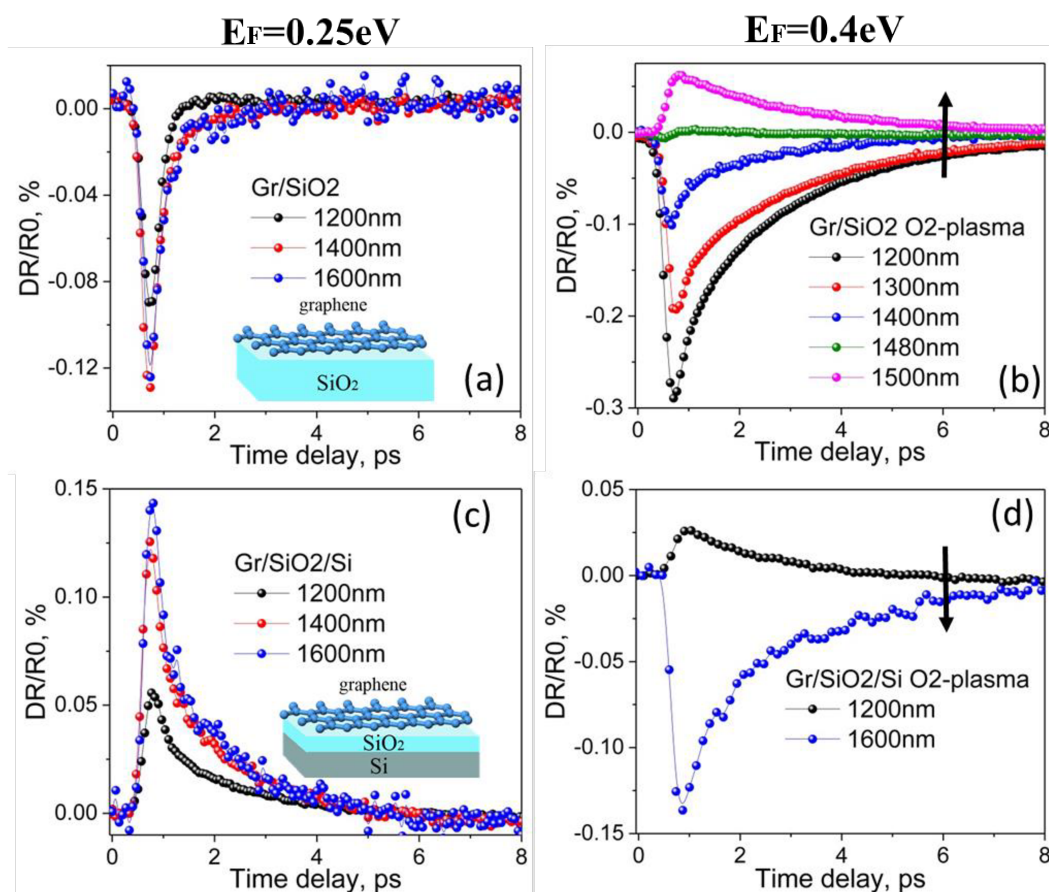


Figure 5.11. Time-resolved DR response for Gr/SiO₂ (a, b) and Gr/SiO₂/Si (c, d) samples with/without O₂-plasma treatment of the substrate.

Next, the samples with and without O₂-plasma treatment are compared. For both substrates, at high probe energy the DR signal has a similar sign to untreated samples. As the probe energy decreases, the DR amplitude gradually diminishes and reverses sign at around 1500nm, which is close to twice the Fermi level of the graphene. Under the selected pump

conditions, the interband contribution dominates the transient optical response of the graphene resulting in saturable absorption at the probe wavelength due to Pauli blocking of the optical transitions, as discussed in details in Section 2.2 and in Ref. [238]. After an optical pump pulse, the carrier relaxation results in the smearing effect when the transient occupation probability above (below) the Fermi energy becomes larger (smaller) compared to an unperturbed state (Figure 5.12 and Section 2.2). Therefore, a pump-induced change in probe transmission (differential transmission) is positive (negative) for probe transitions above (below) the Fermi energy. While the reflection from the graphene is a more complicated process, the sign change that would be observed in transmission is still preserved. These results are consistent with previous studies reported for graphene with tunable Fermi level and fixed probe energy [90,93] and graphene with fixed Fermi level and tunable probe energy [97,83].

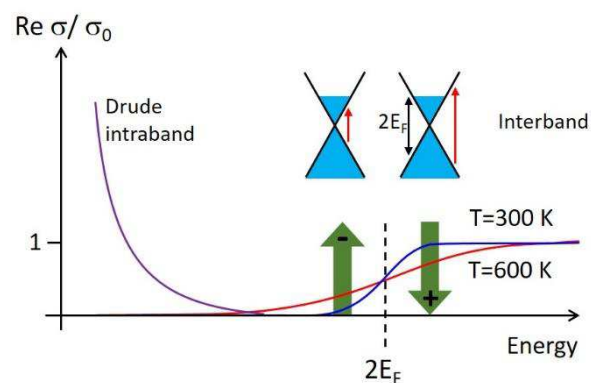


Figure 5.12. Graphene conductivity following the pump pulse ($T=600\text{K}$) is compared to the equilibrium case. The optical probe position is indicated by vertical green arrows; the “-” and “+” indicators mark the sign of the resulting DT signal. Inset: the graphene band structure for a doped layer; probe excitation is indicated by the vertical red arrow.

Theoretical results.

In the following, we present a simple theoretical model to study the substrate interference effect on the transient optical response of graphene. Following photoexcitation, the excited photocarriers in graphene rapidly thermalize forming a hot carrier distribution that can be described by a quasi-equilibrium electronic temperature (T_e), greatly exceeding that of the lattice (Chapter 2.2.4 and Ref. [20]). The occupation of states in the extended tail of the hot carrier distribution results in a DR signal with the form, $\Delta R_{max}/R_0 = [R(T_e) - R(T_{e0})]/R(T_{e0})$, where T_{e0} and T_e are the equilibrium ($T_{e0} = 300\text{K}$) and the pump-induced electron temperatures in graphene, respectively. For finite temperature the conductivity of

graphene can be described according to the local random phase approximation of the Kubo formula [239,240] with the interband and intraband contributions $\sigma = \sigma_{intra} + \sigma_{inter}$ where

$$\sigma_{intra} = \frac{2ie^2T}{\hbar^2\pi(\omega + i\Gamma)} \ln[2\cosh(\frac{\mu}{2T})] \quad (5.1)$$

and

$$\sigma_{inter} = \frac{e^2}{4\hbar} \left[\frac{1}{2} + \frac{1}{\pi} \arctan\left(\frac{\hbar\omega - 2\mu}{2T}\right) - \frac{i}{2\pi} \ln \frac{(\hbar\omega + 2\mu)^2}{(\hbar\omega - 2\mu)^2 + (2T)^2} \right], \quad (5.2)$$

where T is the thermal energy, Γ is the charge carriers scattering rate, μ is the chemical potential (Fermi level) and $\hbar\omega$ is the photon energy.

Next, we write down the reflection coefficient of a multilayer structure (Figure 5.13 a) by solving Maxwell equations with the graphene layer as a conductive boundary condition, as derived in Appendix 1. The obtained reflectivity is $R = |r|^2$ with

$$r = \frac{(n_1 - \sigma\sqrt{\mu_0/\epsilon_0}) \cdot (1 + r_{23}e^{2ikt}) - n_2(1 - r_{23}e^{2ikt})}{(n_1 + \sigma\sqrt{\mu_0/\epsilon_0}) \cdot (1 + r_{23}e^{2ikt}) + n_2(1 - r_{23}e^{2ikt})}, \quad (5.3)$$

where $r_{23} = (n_2 - n_3)/(n_2 + n_3)$ with n_1, n_2, n_3 being refractive indices of air, SiO₂ and Si, respectively; $k = 2\pi n_2/\lambda$ is the wave vector inside the SiO₂ layer; t is thickness of the SiO₂ layer; μ_0 and ϵ_0 are vacuum magnetic permeability and electric permittivity, respectively; and σ is graphene's temperature dependent conductivity calculated using the formulae ((2.1)(5.2)). The optical properties of Si and SiO₂ were taken from experimental data in the literature [241].

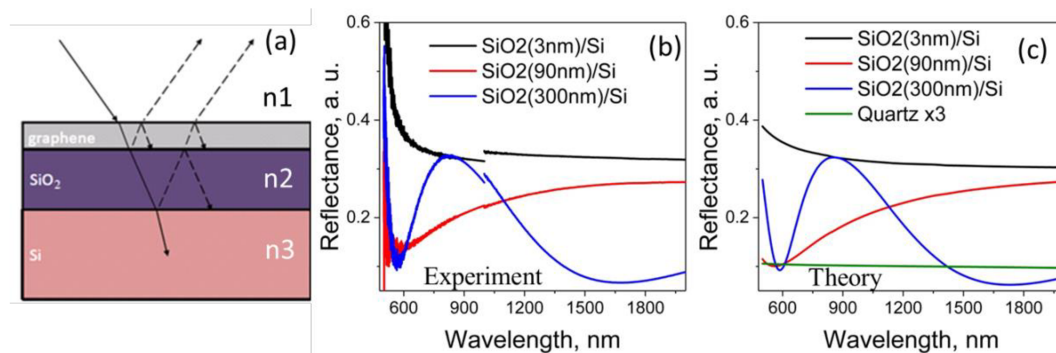


Figure 5.13. (a) Schematic of graphene on a multilayer substrate. (b, c) FTIR reflection spectra of different multilayer substrates and corresponding calculation results. The break in the experimental data at ~950nm is due to a change in the detector used.

Figure 5.13 presents a comparison of calculations with experimentally measured reflection of the various multilayer substrates. Excellent agreement with experimental results is observed confirming applicability of the formula. Next, the amplitudes of the DR signals are calculated

and shown in Figure 5.14. To reproduce the experimental results, the Fermi levels of the graphene layers are fixed at 0.25 eV and 0.4 eV corresponding to p-doping present in the samples without and with O₂-plasma treatment, respectively. Calculation results are in good qualitative agreement with experimental data. Importantly, a relative sign change is observed for the Gr/SiO₂ and Gr/SiO₂/Si substrates providing proof of the role of optical interference on the DR response. Furthermore, in the case of doped graphene, there is a clear sign change observed close to twice the Fermi energy. Interestingly, due to optical interference in multilayer substrates, the sign transition of the DR response does not necessarily occur at near twice the Fermi energy and can be observed even at higher probe energies for increasing carrier temperature in the system.

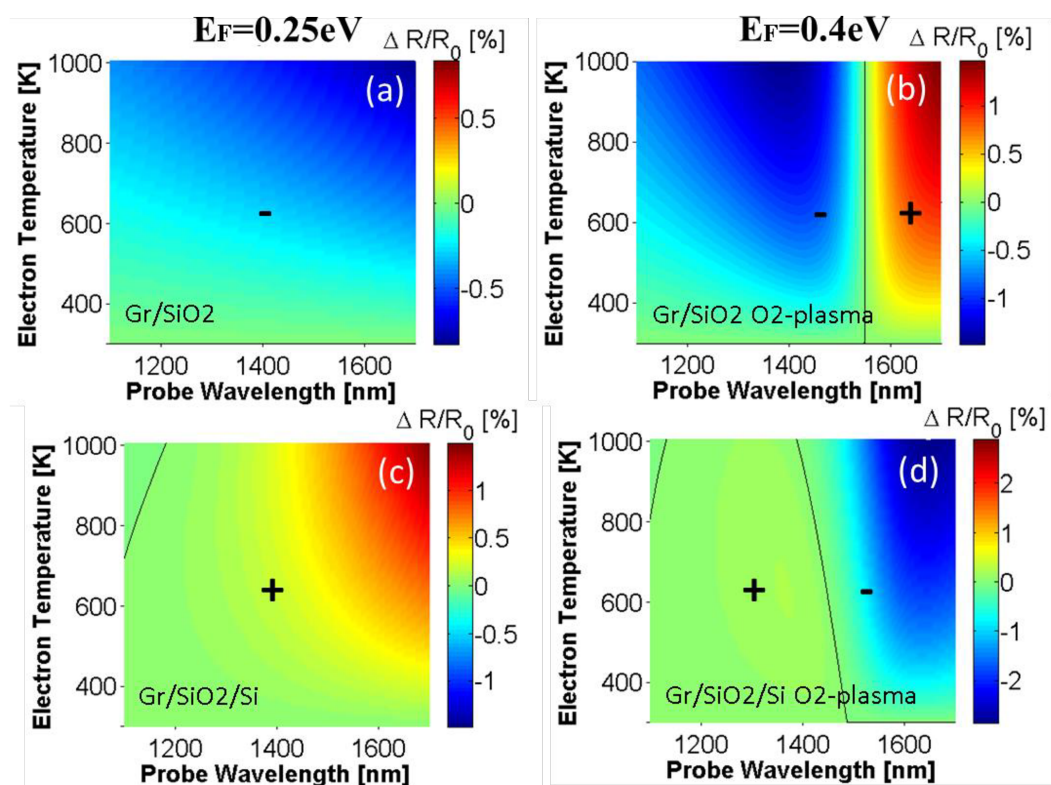


Figure 5.14. Amplitude of DR signal calculated for Gr/SiO₂ (a, b) and Gr/SiO₂/Si (c, d) samples with different carrier temperature and fixed Fermi energy at 0.2 eV (a, c) and 0.4 eV (b, d) corresponding to effect of O₂-plasma treatment.

Next, we compare experimental data with the results of calculations. The Gr/SiO₂ sample with the heavily doped graphene is selected due to the clear transition from negative to positive DR response (Figure 5.11 b). In our experiment with temporal resolution >150 fs, the photocarriers can be considered as fully thermalized (Section 2.2.4), so that the carrier population is well-described by the Fermi-Dirac distribution with an elevated carrier temperature T_e (Section 2.2.4). As the pump-probe delay time increases, the carrier

temperature must steadily decay due to the equilibration process with the lattice, so it is expected that a given delay time corresponds to a carrier distribution at a specific electronic temperature. This can be compared with the theoretically predicted DR response versus temperature curve. Providing the optical excitation conditions are preserved for each sample, it is also possible to study the occupation probability of the hot carrier distribution at specific electronic temperature T_e , as function of probe energy [75]. Therefore, we extract DR points at a number of delay times ($\tau = 1, 2, 4$ ps) to compare to the calculated DR signal for varying carrier temperature in graphene (Figure 5.15). Surprisingly, there is a strong deviation from the theoretically predicted trend. This can be attributed to experimental uncertainties and, in particular, to the probe fluence control due to laser spot variation with different wavelength. Until the discrepancies between the experimental and theoretical results are fully understood, we will not be able to use DR spectroscopy as a characterization technique of the carrier temperature in graphene.

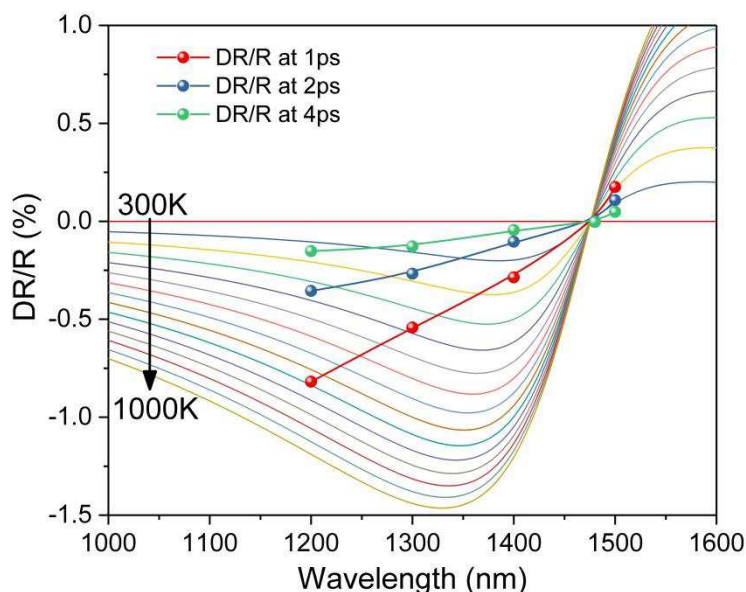


Figure 5.15. Comparison of calculated and experimental results for Gr/SiO₂ sample with O₂-plasma treatment. Continuous lines present calculation results for different carrier temperature in the system after pump excitation. Experimental data points are extracted at varying delay time (1 ps – red, 2 ps – blue and 3 ps – green) from DR traces in Figure 5.11 (b).

5.3.2 Plasmonic induced carrier heating in the hybrid system

Next, the influence of the plasmonic NPs on graphene's carrier dynamics is studied. We investigate the relaxation dynamics of photocarriers in the graphene by distinguishing

graphene's response from that of the NPs. To facilitate selective probing, two-colour pump-probe spectroscopy is employed with widely separated wavelengths. The sample is optically excited with a near-IR pump pulse of 840 nm ($\sim 45 \mu\text{J}/\text{cm}^2$), close to plasmon resonance wavelength of the NP array, and is probed with a 1300 nm probe pulse ($\sim 4.5 \mu\text{J}/\text{cm}^2$). While the pump pulse resonantly excites the plasmonic NPs, the probe pulse selectively monitors the hot carrier dynamics in the graphene layer.

Initially, DR measurements are performed on the NP array prior to graphene deposition. As discussed earlier, it is expected that the probe beam of 1300 nm does not interact with the NP array. Indeed, a negligible DR response is detected for the bare NP array, as shown by the green symbols in Figure 5.16 (b). Therefore, it is reasonable to suggest that any variations in the graphene's response are a direct indication of the interaction between the plasmon mode and the graphene carrier system. The impact of the plasmonic NPs is analysed by direct comparison of graphene's DR signal with and without resonant structures. The $\Delta R/R_0$ traces obtained with parallel pump/probe beams are presented in Figure 5.16 for the bare graphene and Gr/NP system with a period of 400nm for three samples Gr/NP/SiO₂, Gr/NP/hBN/SiO₂ and Gr/hBN/NP/SiO₂. The bare graphene and graphene/NP complexes exhibit a $\Delta R/R_0$ signal decaying on a similar time scale as discussed in the Section 5.3.2. Two characteristic time scales are observed with an initial fast decay of $\tau_1 \approx 180 \text{ fs}$ due to carrier-carrier scattering and optical phonon emission followed by a slower secondary decay of $\tau_2 \approx 1.7 \text{ ps}$ due to acoustic phonon emission (see Section 2.2.4 for more details on carrier relaxation in graphene).

Interestingly, the Gr/NP/SiO₂ sample shows a DR sign change for graphene regions with and without NPs, which is in contrast to Gr/NP/hBN/SiO₂ and Gr/hBN/NP/SiO₂ samples where both areas show positive DR response. In the Gr/NP/SiO₂ sample, the negative signal is observed when the graphene is in direct contact with the Si/SiO₂ substrate. This is most likely due to p-type doping following O₂-plasma treatment, which is confirmed by Raman spectroscopy and KFM studies presented earlier (Section 5.2). Furthermore, the previous results indicate that in this sample the doping is significantly reduced in regions with NPs due to partial detachment of graphene from the underlying substrate. Therefore, the DR sign change can be attributed to doping variation in the graphene, which is consistent with the findings presented in Section 5.3.2.

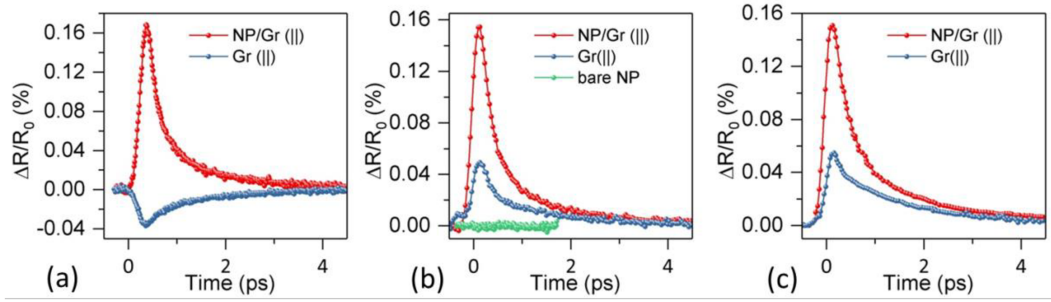


Figure 5.16. Time-resolved DR response for Gr/NP/SiO₂ (a), Gr/NP/hBN/SiO₂ (b) and Gr/hBN/NP/SiO₂ (c). The $\Delta R/R_0$ signal for bare graphene (Gr) is compared to Gr/NP structure with NP period of 400nm. All the measurements are performed with parallel (||) pump and probe beams. Solid lines are guide for the eye.

The absolute amplitude of the DR signal for the bare graphene for all three samples is almost identical. Furthermore, all three samples show an increased DR response in the presence of plasmonic NPs. In fact, the DR amplitude is directly proportional to the geometrical NP fill factor, $(\pi R^2)/P^2$, where R and P are radius and period of the NP array, respectively (Figure 5.17). The NP influence becomes negligible at about 1000 nm period as it shows an indistinguishable DR response to bare graphene.

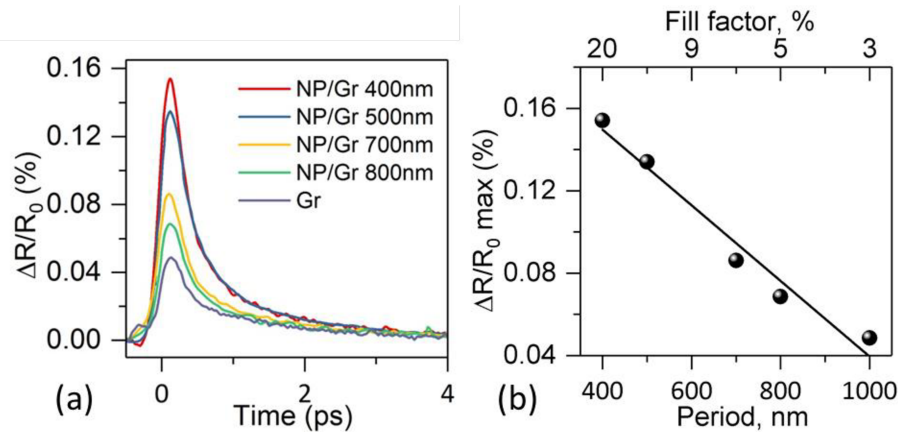


Figure 5.17. (a) Time resolved DR response for Gr/NP structures with varying NP lattice periods (P) obtained with parallel pump–probe polarizations. (b) DR amplitude dependence on the NP period (metal fill factor), solid line is guide for the eye. The measurements are performed on Gr/NP/hBN/SiO₂ sample.

To explore the plasmonic nature of the enhancement further, polarization dependent DR measurements are performed. In contrast to bare graphene, the graphene/NP structures show a pronounced dependence on the relative pump-probe polarization angle (θ), as presented in Figure 5.18 (a,b). It is well known that in semiconductors an intrinsic anisotropy can arise after optical excitation with a linearly polarized light pulse [242–244]. This effect has been explained by the initially anisotropic distribution of photocarriers in k -space that is immediately formed after excitation with the pump pulse. Mittendorff et al. [245] has

reported a similar anisotropic behaviour in graphene observed using a pump-probe experiment with sub 50fs resolution. However, in their experiments the anisotropic DR response became isotropic again within the first 100-150 fs, due to carrier-carrier and carrier/optical phonon interactions [245], which were in good agreement with theoretical calculations [246]. However, since the temporal resolution of our experiment (~ 150 fs) is longer than the time required for the carrier momentum homogenisation, it is reasonable to exclude this effect. Furthermore, the polarization-independent response of the bare graphene confirms the absence of any intrinsic pump-induced anisotropy (Figure 5.18 b). Another possibility are the acoustic vibrations of NPs, so-called breathing modes, that following plasmon excitation with ultrafast pulses; however these typically occur on time scales longer than 10ps and, therefore, should not influence the carrier dynamics discussed in our experiment [247].

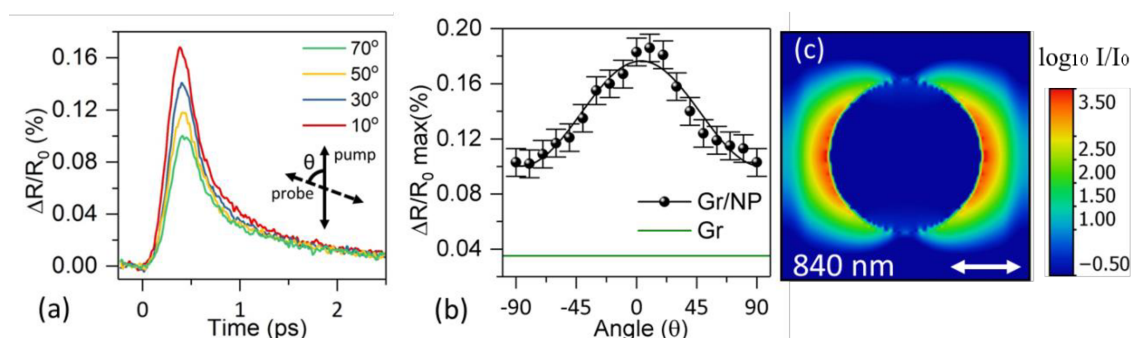


Figure 5.18. (a) Time resolved DR signal dependent on the probe polarization angle θ for Gr/NP structure with period of 400nm. (b) Dependence of the DR amplitude. Polarization-independent response of bare graphene is included for comparison. The measurements are performed on Gr/NP/SiO₂ sample. (c) Spatial distribution of near-field intensity enhancement for a gold NP in the array with period of 400nm. The NP is excited with x-polarized light at 840 nm demonstrating the dipole mode of the plasmon resonance.

Since the intrinsic carrier anisotropy in graphene cannot be resolved under our experimental conditions, it must originate from either the NPs or a graphene/NP interaction. However, the probe wavelength of these measurements is at 1300nm, which is where the NPs show an undetectable DR response. Some graphene/NP interaction is therefore the origin of the observed extrinsic anisotropy. There are two major mechanisms that can possibly contribute to carrier generation in graphene/NP structures: direct hot carrier excitation in the graphene layer enhanced via the intense electromagnetic fields surrounding the NP and hot carrier injection from the plasmonic NPs into the graphene, as presented in Section 2.3.3.

We start by exploring the possibility of carrier injection from the metal NPs into the graphene. The samples with (Gr/hBN/NP/SiO₂) and without the hBN (Gr/NP/hBN/SiO₂)

spacer layer between graphene and NPs are considered. The graphene/hBN interface is characterized by a low electron tunneling probability $\approx 20\%$ thus providing an effective barrier to carrier transfer [248]. Meanwhile, the thin hBN layer does not affect the NP's field enhancement that influences light absorption in the graphene. Table 5.2 provides a summary of the peak DR signal ($\Delta R_{max}/R_0$), that is directly related to the peak carrier temperature. By comparing the average DR response $(\Delta R(\parallel)/R_0 + \Delta R(\perp)/R_0)/2$ from the structures with and without a hBN barrier, almost identical signals are observed. This confirms that the hBN layer does not significantly reduce the NP's field enhancement of graphene absorption and it is unlikely that any significant hot electron transfer occurs between the NPs and the graphene on the time scales considered here.

Sample	Area	$\Delta R_{max}/R_0$ (%)	A_2 (%)	A_1/A_2^*
Gr/NP/hBN/SiO₂	Gr/NP ($\parallel$)	0.154	0.043	1.52
	Gr/NP ($\perp$)	0.099	0.032	1.31
	Gr	0.049	0.021	1
Gr/hBN/NP/SiO₂	Gr/NP ($\parallel$)	0.151	0.062	1.52
	Gr/NP ($\perp$)	0.118	0.054	1.36
	Gr	0.047	0.029	1

Table 5.2 Parameters for the DR response observed for the Gr/NP/hBN/SiO₂ and Gr/NP/hBN/SiO₂ samples obtained with parallel ($\parallel$) and perpendicular ($\perp$) pump-probe polarizations. A_2 is the amplitude of the secondary decay component. The ratio A_1/A_2^* is normalised to the bare graphene value extracted for each sample.

Next, we use the amplitudes of the bi-exponential decay model to further characterize the heating process observed in the samples. As discussed in Section 2.2.4, carrier dynamics in graphene are well described by a biexponential model $\Delta R(\Delta t) \sim A_1 e^{-(\Delta t)/\tau_1} + A_2 e^{-(\Delta t)/\tau_2}$, where the amplitudes corresponding to the initial (A_1) and secondary (A_2) decay components are related to the peak hot carrier and hot phonon temperatures, respectively. Therefore, the amplitude ratio A_1/A_2 being proportional to T_e/T_{ph} gives a qualitative parameter that describes the fraction of energy lost to the phonon bath during the cooling process. As evident from Table 5.2, the extracted ratio is increased for the Gr/NP structures, which indicates enhanced carrier heating efficiency in the presence of plasmonic NPs. Interestingly, the relative increase of the amplitude ratio is quite similar for both samples with and without the hBN layer. These observations indicate that hot carrier injection has only a minor contribution to plasmon induced carrier generation in graphene. Thus, it is possible to

conclude that direct photoexcitation in the graphene layer is the major mechanism of hot carrier generation for hybrid graphene/NP structures.

The drastic near-field enhancement around the NPs (Figure 5.18 c) leads to a highly nonuniform spatial distribution of hot carriers in graphene, since local photoabsorption in graphene is directly proportional to electromagnetic field intensity. Therefore, the initially inhomogeneous spatial distribution of the hot carriers in the graphene can produce the observed anisotropic DR response. More precisely, the DR signal can be represented as $\Delta R_{max}/R_0 = [R(T_e(x,y)) - R(T_{e0})]/R(T_{e0})$, where $R(T_{e0})$ and $R(T_e(x,y))$ are the reflectance of the structure under equilibrium electron temperature ($T_{e0} = 300K$) and the inhomogeneous pump-induced electron temperature in graphene, respectively. When the pump and probe are co-linearly polarized, the probe experiences the modified absorption of the hot electrons in the graphene. However, when cross polarized, the probe beam now experiences a much cooler hot electron distribution. As presented in Ref [109], the carrier temperature in close proximity to the plasmonic NPs can reach up to 1500K, while being close to equilibrium temperature only 400nm away from a NP's surface. These strong electron temperature gradients can be exploited to drive an electrical current via the Seebeck effect, and this idea is explored in details in Chapter 6.

5.3.3 DR mapping as a characterisation tool

As discussed in Section 5.3.1, the DR spectroscopy technique is highly sensitive to Fermi level position in the graphene layer. Therefore, this technique can be used as a spatial mapping tool to characterize local variations of the carrier dynamics. Figure 5.19 shows the DR amplitude variation for bare graphene and a graphene/NP-array interface for Gr/NP/SiO₂ sample and Gr/NP/hBN/SiO₂ sample, respectively. Clearly, the enhanced DR response of graphene in the presence of NPs is straightforward to resolve. Moreover, variations in DR signal for bare graphene are also quite apparent and can be attributed to the local differences in the doping level due to the graphene/substrate coupling and due to the screening effect of multilayer areas consistent with previous reports [80,90,249]. In fact, the average size of regions with increased DR signal ($\sim 2\text{-}3\ \mu\text{m}$) is similar to multilayer areas present in CVD graphene film (Section 5.1 and 5.2). However, to generate a direct correlation, additional characterization measurements such as Raman spectroscopy of the same sample area are required. Furthermore, the DR mapping can be performed at various delay times to give insight into the carrier relaxation time in different regions of the sample

[80]. To reach the optimal resolution of this technique, objectives with higher NA can be employed to provide diffraction limited laser spot.

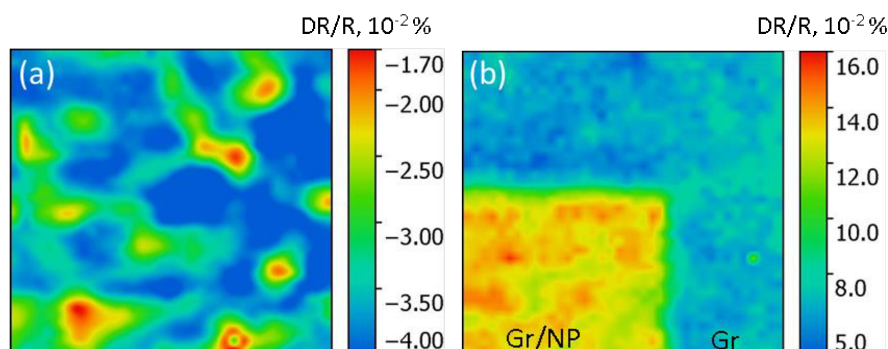


Figure 5.19. Spatial variation of DR amplitude for bare graphene of the Gr/NP/SiO₂ sample (a) and for graphene/NP-array interface of the Gr/NP/hBN/SiO₂ sample (b). The scanned area is 20x20 μm .

5.4 Conclusions

In this chapter, properties of graphene/plasmonic-nanoparticle (NP) structures have been discussed. SEM and AFM measurements confirm that the graphene layer demonstrates conformal contact with the underlying plasmonic nanostructures. Further analysis performed with Raman spectroscopy suggests increased defect concentration and tensile strain in the presence of plasmonic nanostructures consistent with mechanical modification of the graphene layer. Additionally, graphene/NP complexes show reduced doping concentration that is attributed to partial graphene decoupling from the substrate. Next, it has been demonstrated that both graphene doping variation and substrate interference can result in a sign change of the differential reflection (DR) signal of the graphene/substrate complexes. Furthermore, spatial variation of the DR signal can be used to study the local modifications in graphene doping level. Finally, by selectively probing the plasmon-induced hot carrier dynamics in samples with tailored graphene-gold interfaces, we show that plasmon-induced hot carrier generation in the graphene is dominated by direct photo-excitation, with minimal contribution from charge transfer from the gold. Furthermore, an observed nonlinear anisotropy of the graphene/NP system confirms generation of a highly localised hot carrier population in graphene due to the intense inhomogeneous electromagnetic fields surrounding plasmonic NPs. The generated electronic temperature gradients have the potential to enable photo-thermoelectric devices, as explored in details in Chapter 6.

6 Graphene based plasmonic photodetector

In this chapter, the optoelectronic response of CVD graphene is studied. Asymmetric plasmon-nanobar electrical contacts are employed to analyse the impact of plasmon-induced hot carriers on the device photoresponse. The devices are characterized using a scanning photovoltage microscopy technique. Time-resolved photovoltage measurements are further employed to analyse the timescale of photovoltage generation.

6.1 Sample fabrication

The devices explored in this chapter are fabricated in the following way. First, microscopic contacts are designed on SiO₂(90nm)/Si substrates using photolithography technique as described in Section 3.2.2. Chromium-gold electrodes (5 nm Cr, 25 nm Au) are deposited by resistive thermal evaporation (Section 3.2.3). Next, electron beam deposition is used to define nanocontacts followed by evaporation of 40nm Au material. It should be noted that prior metal deposition the substrate was cleaned with O₂-plasma treatment at 50 W for 20 s. Graphene is then transferred using the typical wet transfer method² as discussed in Chapter 4. Since after the transfer process, graphene covers the vast majority of the substrate effectively shorting out all the devices, an additional photolithography step is utilized to pattern graphene with O₂-plasma treatment at 100 W during 1min. The graphene nanostructuring is performed with electron beam lithography followed by similar O₂-plasma treatment. As the final step, the substrate is cleaved and placed in chip carriers followed by wire bonding.

6.2 Photoresponse in metal-graphene-metal devices

To analyse the graphene photoresponse, a simple graphene transistor geometry is first considered (Figure 6.1). The device is analysed using scanning photocurrent microscopy, where reflection and photovoltage images are simultaneously recorded (Section 3.3). The obtained reflection image of the device shows distinct source and drain metal contacts in

² Graphene/Cu layers are covered with PMMA A4 495 by spin coating at 3500 rpm for 60 s and curing at room temperature overnight. Graphene layer present on the bottom side of the foils is removed using an O₂-plasma treatment at 100 W during 2 mins. The exposed Cu foil is then etched in an ammonium persulfate solution (15 g/L) followed by a thorough rinse in DI water. The floating PMMA/graphene stack is then scooped out using the target substrate. After drying, the sample is annealed at 180 °C for 30 mins. Finally, the PMMA is removed in acetone followed by IPA rinse.

good agreement with the optical microscopy image. A photovoltage image demonstrates that in addition to the photoresponse near the contact areas, there is a photoresponse from the graphene channel. This confirms the existence of local electric fields in the continuous graphene layer that can be attributed to grain boundaries arising from polycrystalline nature of the material [250] or to charged impurities in the substrate and residues of e-beam resist leading to spatial variations of the local potential [31]. It has been previously observed [31] that in the low carrier density regime, a small variation in the carrier concentration can cause quite a strong variation in the local potential. In the high carrier density regime, this contribution vanishes. The overall trends of photoresponse are in good agreement with previously reported results for exfoliated graphene [31,34,251].

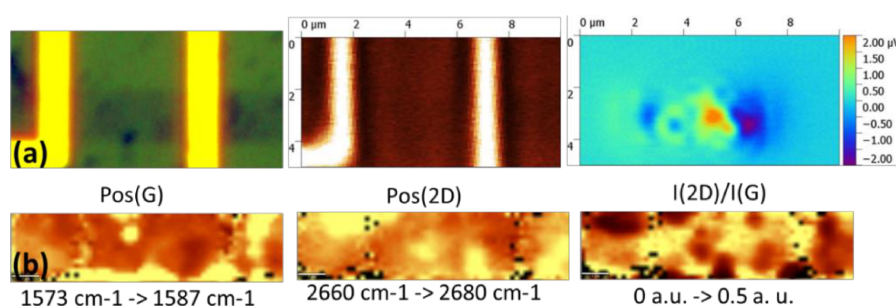


Figure 6.1. (a) Photovoltage scanning microscopy results. Left to right: optical microscopy, optical reflection and photovoltage images of the graphene nanoribbon device. (b) Micro-Raman maps of the device (10x2.5 μm). Left to right: spatial distribution of position of the G- and 2D- peaks and of intensity ratio of 2D- and G- peaks.

Raman spectroscopy has also been employed to analyse spatial variations in carrier concentration (Figure 6.1 b). The obtained micro-Raman maps confirm structural uniformity of the graphene ribbon. To analyse the doping profile, the position of the G-peak and the intensity ratio between the 2D- and G- peaks can be used (Figure 6.1 b). It is also clear that local fluctuations in the doping are present. This provides a confirmation of the origins of localized photovoltage response.

6.3 Photodetector based on asymmetric plasmonic contacts

6.3.1 Concept of asymmetric contacts

To improve the graphene photoresponse, a new plasmonics based photodetector geometry is proposed (Figure 6.2). As mentioned previously, the metal-graphene-metal photodetector has a disadvantage of negligible photoresponse under complete illumination. To solve this issue, an asymmetric metallization scheme has been utilized [18]. In the proposed geometry, an

asymmetric plasmonic structure is adopted to break the mirror symmetry of the internal electric-field profile. The idea is based on our previous observations of effective carrier heating near plasmonic nanostructures where the carrier temperature of 1400K has been reached [252]. Therefore, we expect a strong temperature gradient in the proposed contact geometry that will facilitate an improved thermoelectric effect. Notably, a similar contact geometry has been previously utilized for hot carrier injection into MoS₂ [253]. However, in our graphene-based system no significant hot carrier injection is expected under zero bias conditions [252].

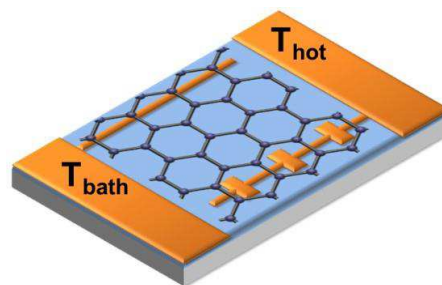


Figure 6.2. Schematic of the graphene device with plasmonic (T_{hot}) and nonplasmonic (T_{bath}) contacts.

6.3.2 Device design optimization

To provide plasmonic enhancement, bar nanoparticles are integrated directly into the contact. However, due to the resolution of e-beam lithography, these particles are actually elliptical. This type of plasmonic nanostructures has been chosen due to the ease of fabrication and wavelength tunability. The resonant antennas support longitudinal (L) and transverse (TR) resonances typical for elliptical nanoparticles excited under different polarization of the illumination source [54,254]. In the suggested contact geometry, we utilize the longitudinal resonance, since it is not highly disturbed by the presence of the contact bar (Figure 6.3 a). To perform device design optimisation, the Lumerical finite-difference time-domain (FDTD) simulation software is utilized. Since carrier heating is strongly improved in the presence of high electromagnetic fields [252], the field enhancement, or intensity enhancement ($|E|^2/|E_0|^2$), near plasmonic nanoparticle (NP) is considered as a figure of merit for the structure design optimisation (Figure 6.3 b).

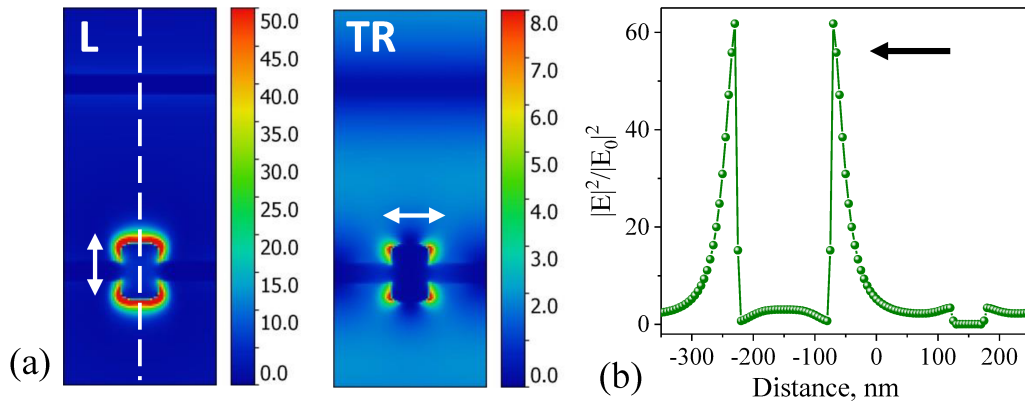


Figure 6.3. (a) Electromagnetic field distributions for the longitudinal and transverse resonance and (b) corresponding cross-section for the longitudinal resonance at 740 nm excitation. The structure parameters are: NP of 150x100 nm, NP period 500 nm and contact spacing 300 nm.

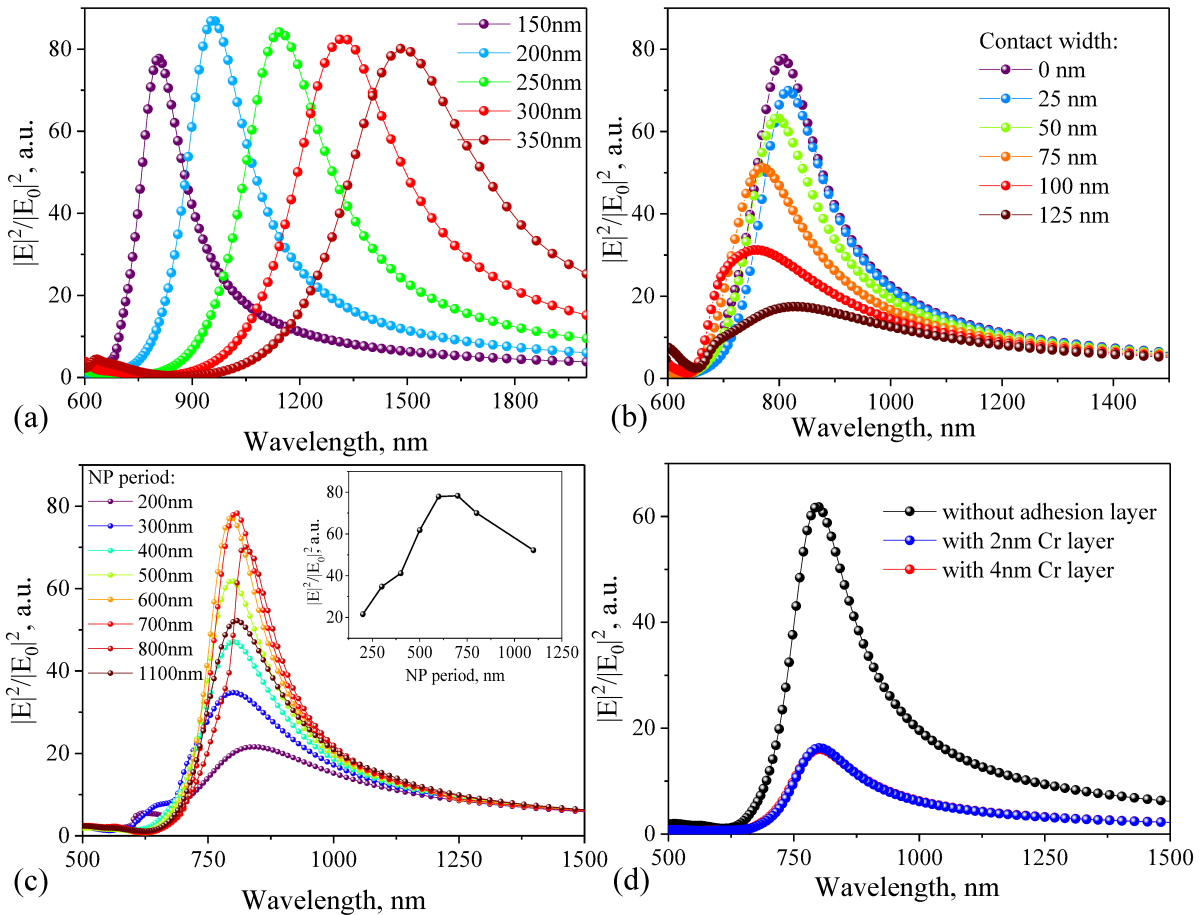


Figure 6.4. Results of numerical calculation. (a) Shift of longitudinal resonance with NP length, NP width is 100 nm. (b-d) Influence of contact width (b), NP period (c) and Cr adhesion layer (d) on NP field enhancement.

As expected, the longitudinal plasmon resonance is highly sensitive to the NP length, resulting in the resonance shift towards longer wavelength with increasing NP length (Figure 6.4 a). Notably, resonance at telecom wavelengths can be effectively achieved with a length

of ~ 350 nm. To provide a good overlap with available experimental facilities, the resonance at ~ 800 nm, corresponding to NP length of 150 nm, has been chosen. The integration of NPs with metallic contacts results in a plasmon resonance that is significantly weakened compared to an individual isolated NP (Figure 6.4 b). To keep this effect low, the contact is fabricated with a width of only 40 nm. The next important parameter under consideration is NP period. Whilst a higher number of focusing elements is desirable, under small separation destructive plasmon interference is observed decreasing the field enhancement, as can be seen in Figure 6.4 (c). Therefore, we have determined 500 nm to be an optimal NP period to provide high NP density, while keeping field enhancement only weakly affected. As the last optimization parameter, we consider the material of the contacts and, in particular, the influence of an adhesion layer. It is clear from Figure 6.4 (d), that even the presence of 2 nm of a Cr layer results in a significant damping of the plasmon resonance. This effect has been previously observed for Ti adhesion layer as well [255,256]. The contacts thus are fabricated from gold (40 nm in thickness) without an adhesion layer.

6.3.3 Sample structure and graphene quality

The fabricated devices are first analysed with scanning electron (SEM) and atomic force microscopy (AFM) to confirm the presence of graphene and nanocontacts (Figure 6.5). The SEM image demonstrates that the graphene layer covers the device uniformly. The resulting NPs have sizes of 140×90 nm that is slightly smaller than was intended. The contact width is ~ 40 nm confirmed by AFM image. The graphene layer is also clearly distinguished in the AFM image by its characteristic wrinkles and polymer residues.

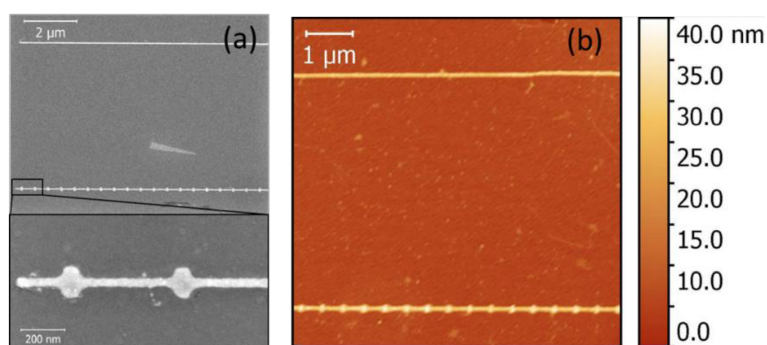


Figure 6.5. Structural characterization of the fabricated devices with SEM (a) and AFM (b) techniques.

Optical microscopy images of the devices tested in this Chapter are presented in Figure 6.6. Due to the high electrostatic sensitivity of graphene devices, operation failure has been quite common whilst performing electrical measurements. Furthermore, connections to a chip

carrier has been made using a wedge bonding technique that utilizes ultrasonic power and force applied to the target substrate contacts. This technique can lead to damage of the thin SiO₂ layer (90 nm) limiting the range of devices available for back gating experiments. Devices 1-3 are typical photodetectors based on asymmetrical plasmonic contacts, as can be seen from optical microscopy images where the plasmonic contact appears to be much darker. Device 4 is a representative two contact device. Device 1 has been used to perform polarization and wavelength dependent measurements discussed in Sections 6.3.2 and 6.3.5, while gate dependent measurements have been performed on device 2 (see Section 6.3.6). Ultrafast measurements have been carried out on device 3 (see Section 6.3.9). Device 4 has been used for transport and thermoelectric measurements discussed in Section 6.3.7.

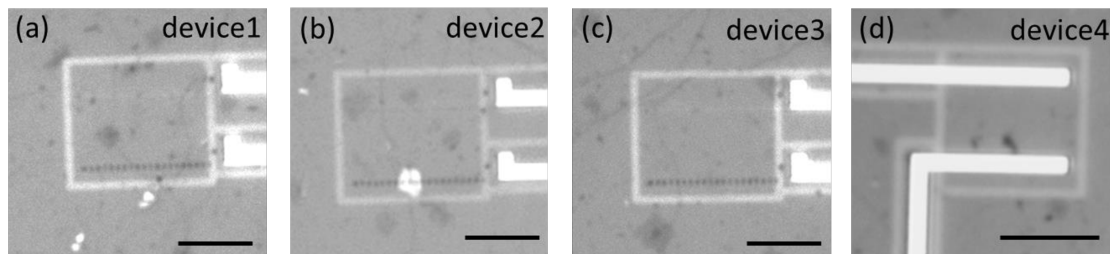


Figure 6.6. Optical microscopy images of the devices tested in Section 6.3.
The scale bar is 5 μ m.

The presence of a high quality graphene layer is confirmed by Raman spectroscopy (Figure 6.7). The measurements are performed with 532 nm excitation laser at 1 mW power. The integration time for graphene/SiO₂ and Graphene/Au regions are 10 s and 120 s, respectively. Representative spectra demonstrate that the material has low defect density which is confirmed by the low intensity of the D-peak. The spectra of graphene over the gold contact contain a strong fluorescence background that complicates analysis of the peak intensities. Therefore, we use the peak positions as the main characteristic to discuss the doping level in the graphene. It is clear that the graphene over the gold contact exhibits lower doping compared to the graphene on top of the SiO₂, with doping concentration of 2.5×10^{12} and 5×10^{12} , corresponding to 203 and 287 meV for the two regions, respectively. Notably, from the Raman spectra we can determine that the graphene over the gold contacts exhibits compressive biaxial strain of -0.05 – 0%, while the graphene over the substrate SiO₂ is characterized by tensile biaxial strain of 0 – 0.06%.

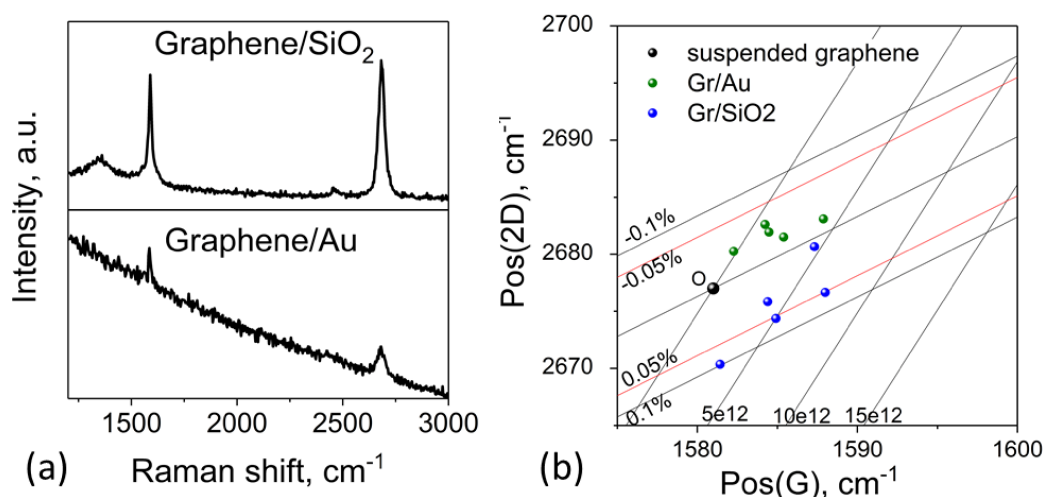


Figure 6.7. Raman spectroscopy characterization of graphene over the substrate (SiO₂) and the gold contacts. (a) Representative spectra. (b) Correlation between the G and 2D peak positions. The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm⁻². The O point represents suspended exfoliated graphene.

6.3.4 Polarization dependent photoresponse

To analyse the photoresponse of plasmonic and nonplasmonic contacts, we utilize scanning photovoltage microscopy as discussed in Section 3.4. Device 1 is scanned with an elliptical laser beam (1x20 μm), while the induced open-circuit photovoltage is recorded as a function of laser spot position. It should be noted that the positive open-circuit voltage in these measurements arises due to lower voltage of the contact under illumination (B) and higher voltage of the other contact (A), while the measurements are performed in differential regime (A-B).

We first examine the polarization dependence of the photoresponse under 740nm excitation provided by Coherent Chameleon Ultra II mode locked Ti:Sapphire laser operating at 80 MHz with ~150 fs. As shown in Figure 6.8, a long device channel of 5.5 μm allows us to clearly separate the photovoltage response from individual electrodes, where different polarities are observed. The presence of plasmonic NPs clearly results in a significant increase of the photoresponse under longitudinal polarization that is expected to couple resonantly with the plasmonic mode at this wavelength based on numerical calculation results presented in Section 5.6.2. A detailed study of resonant wavelength will be discussed in the next section. Strong polarization dependence is observed for the plasmonic contact resulting from the nanoparticle geometry. The angular dependence can be fitted with $\cos^2\theta$ that is

characteristic of a dipole antenna (solid line Figure 6.8 c). In contrast, the nonplasmonic contact shows a photoresponse that is almost insensitive to excitation polarization.

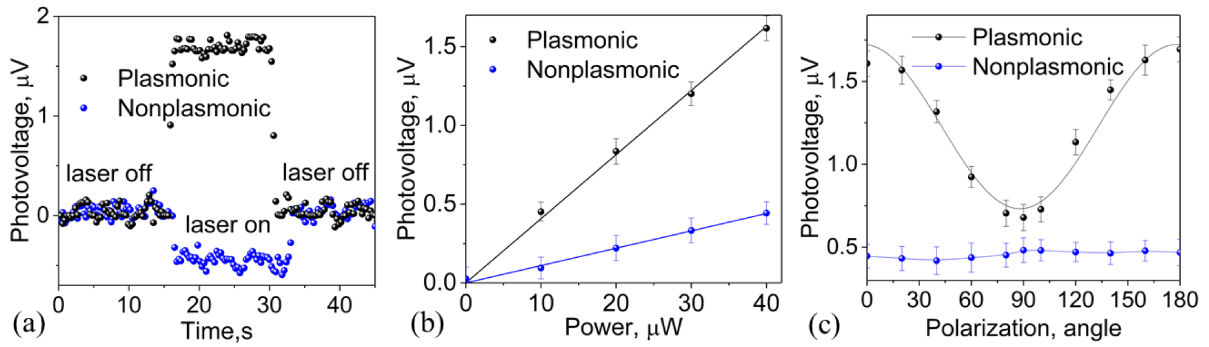


Figure 6.8. Photovoltage response of plasmonic and nonplasmonic contacts at $\lambda = 740$ nm as a function of time (a), laser power (b) and polarization (c).

The observed experimental results are in a good agreement with FDTD calculations (Figure 6.3). For longitudinal polarization the electromagnetic field is strongly enhanced around the plasmonic NP at 740 nm wavelength, which is close to the NP longitudinal resonance. Interestingly, for transverse polarization the field enhancement around nanoparticle is still present. This explains the photoresponse that remains enhanced for the plasmonic contact compared to nonplasmonic one under transverse polarization.

6.3.5 Wavelength dependent photoresponse

In the following, the wavelength dependence of the device photoresponse is discussed. The presented results are collected for device 1. Firstly, dark field spectroscopy is used to characterize the NP plasmonic resonance (Figure 6.9 a,b). It is clear from the dark field microscopy image (Figure 6.9 a) that plasmonic NPs significantly enhance scattering. Furthermore, the representative spectra confirm the presence of the plasmonic resonance at ~ 700 nm corresponding to the longitudinal dipole mode. This observation is in good agreement with the calculated results discussed in Section 6.3.2. While the resonance at 800 nm was expected, there is a shift towards lower wavelengths in experimentally observed resonance position. This can be explained by the final size of plasmonic NPs. In fact, the experimentally fabricated NPs have sizes of 140×90 nm that is slightly smaller than the intended 150×100 nm, therefore, the plasmonic longitudinal resonance exhibits an associated blueshift.

To characterize the photovoltage response, the device was illuminated with an elliptical beam (1×20 μm) using different wavelengths ranging from 500 to 900 nm (Figure 6.9 c,d). A photovoltage spectrum is generated by plotting absolute values of the photovoltage maxima

and minima for plasmonic and nonplasmonic contacts, respectively. It is clear that the photovoltage spectral response of the plasmonic contact closely follows the observed resonance measured by dark field spectroscopy. The photovoltage generated at the plasmonic contact is strongly enhanced compared to nonplasmonic contact. In fact, the maximum enhancement factor of ~ 5 times is reached at the plasmon resonance wavelength. Notably, the enhancement is facilitated by the presence of just 19 NPs that are integrated into the plasmonic contact. Considering the active area of the contact and the device resistance of 1 kOhm, at the resonance wavelength a responsivity of 0.125 mA/W was reached that is only one order of magnitude lower than the best reported result for a metal-graphene-metal photodetector of 6.1 mA/W [1,18]. It should be noted that the best responsivity has been previously observed for exfoliated graphene that is known to be a single crystalline material with low defect density. Our device however utilizes large area CVD graphene that is suitable for mass production. The drawback of CVD material is its polycrystalline nature and the presence of defects due to the roll-to-roll production technique [118]. The mobility of our devices is measured to be in the range of $700\text{-}1000\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ using an FET measurement method, as discussed in Section 3.1.6. Additional limiting factors for the device performance are surface states in SiO_2 and the PMMA residues introduced during the transfer. These charge impurities act as scattering centres further decreasing the carrier mobility. We note that significant improvement can be achieved by covering the substrate with exfoliated hBN [12,227] and using the hBN assisted transfer method to limit the PMMA residues, as discussed in Chapter 4.

Next, we analyse the electromagnetic field distribution in the structure with parameters similar to the experimentally produced one (Figure 6.9 e,f). To replicate the illumination conditions, the electromagnetic field is integrated over an area of $1\text{ }\mu\text{m}$ corresponding to the laser spot width. Furthermore, the Gaussian intensity profile is incorporated through simple multiplication with $e^{-(x-x_L)^2/R_L^2}$, where x_L is the position of the laser spot and R_L is the laser spot size. The calculation results demonstrate a good agreement with experimental photovoltage scanning measurements as well as with photovoltage spectrum. Therefore, the observed photoresponse improvement can be attributed to electromagnetic field enhancement around the plasmonic NPs.

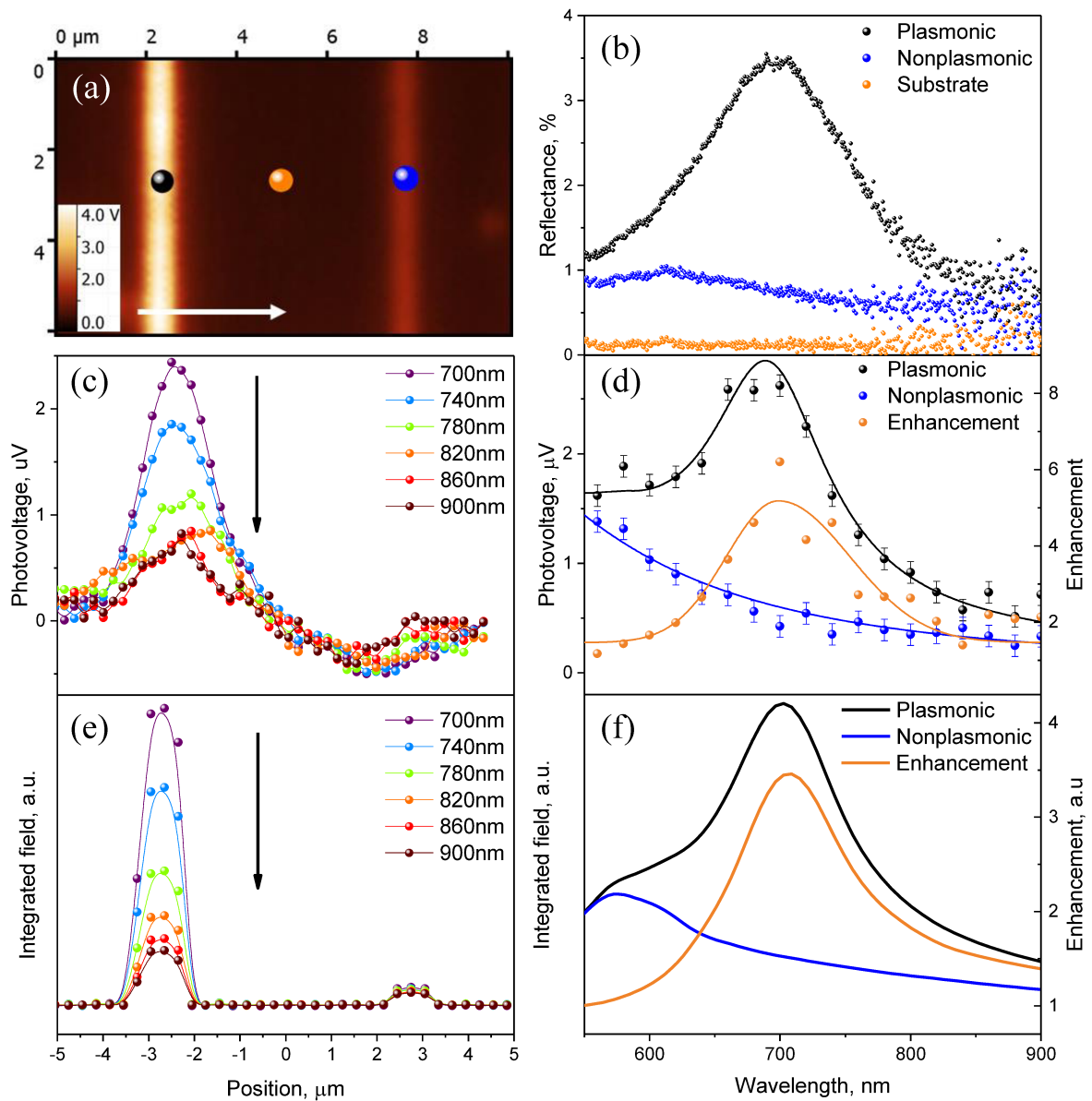


Figure 6.9. (a, b) Scanning dark field microscopy image and corresponding reflection spectra for plasmonic and nonplasmonic contacts and substrate. (c, d) Wavelength dependent photovoltage response measured with elliptical laser spot of $40 \mu\text{W}$ power under longitudinal polarization. (e, f) FDTD calculation results.

6.3.6 Gate dependent photoresponse

To gain insight into the mechanisms of photovoltage generation in the device, we tune the carrier density in the graphene channel using the back gate. All the measurements are performed on device 2. Keithley 2636B was used to apply the back gate voltage. It should be noted that the connection of an additional power supply resulted in a higher noise level that was particularly strong during bias switching. Therefore, the gate bias was applied in a step-

like manner with 5 V resolution with a dwell time of 30 s for each step, as shown in Figure 6.10.

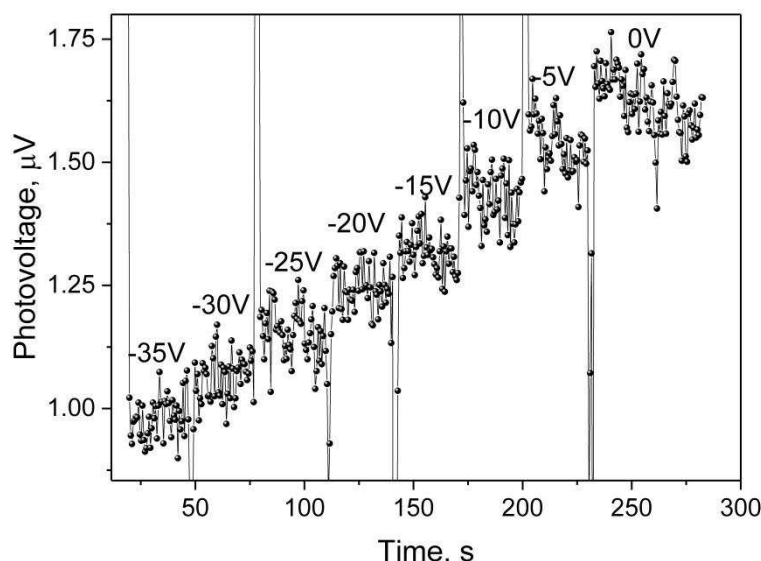


Figure 6.10. Typical gate dependent photovoltage measurements with gate bias ranging from -35 V to 0 V and step size of 5 V. Each bias value is applied for 30 s to let the measurement to settle down.

Since all the measurements are performed in air and the graphene is in direct contact with SiO₂, we observe typical hysteresis effects when cycling graphene back gating [257,258]. While this is detrimental to the performance of some devices, here we use this effect to effectively precharge the graphene and, thus, shift the Dirac point (see discussion of transport measurements in Section 6.3.7). From this point of view the hysteresis effect allows us to effectively increase the range of the back gate biasing. We start by performing the measurements from positive towards negative gate bias that is known to shift the Dirac point towards higher positive back gate values (Figure 6.11 a). We first compare the gate dependent photovoltage response for the plasmonic contact under longitudinal and transverse polarization. While the overall shape of the photoresponse is preserved, there is a significant enhancement due to the longitudinal mode of the plasmonic resonance, which is in a good agreement with our previous measurements.

We next compare the gate dependent photovoltage response for the nonplasmonic contact to the plasmonic contact under longitudinal polarization. As expected, a significant enhancement is observed for the plasmonic contact under longitudinal polarization; however, the photoresponse of the nonplasmonic contact is higher than that of the plasmonic contact under transverse polarization, which is in contrast with previous polarization dependent measurements (Figure 6.8). This can be explained by structural differences of the contacts of

device 2 compared to the contacts of device 1. As confirmed by optical microscopy (Figure 6.6), the plasmonic contact has a defect, which would decrease its overall photoresponse. Furthermore, nonplasmonic contact contains a multilayer region that can additionally contribute to the amplitude of the signal. Therefore, a direct comparison in terms of absolute values of these data is complicated. Given the defect in the plasmonic contact, we anticipate that the optimal photovoltage enhancement can be larger than is observed here. However, the overall trend of the photoresponse is still preserved and is in a good agreement with gate dependent measurements of the representative nonplasmonic contact (Figure 6.12).

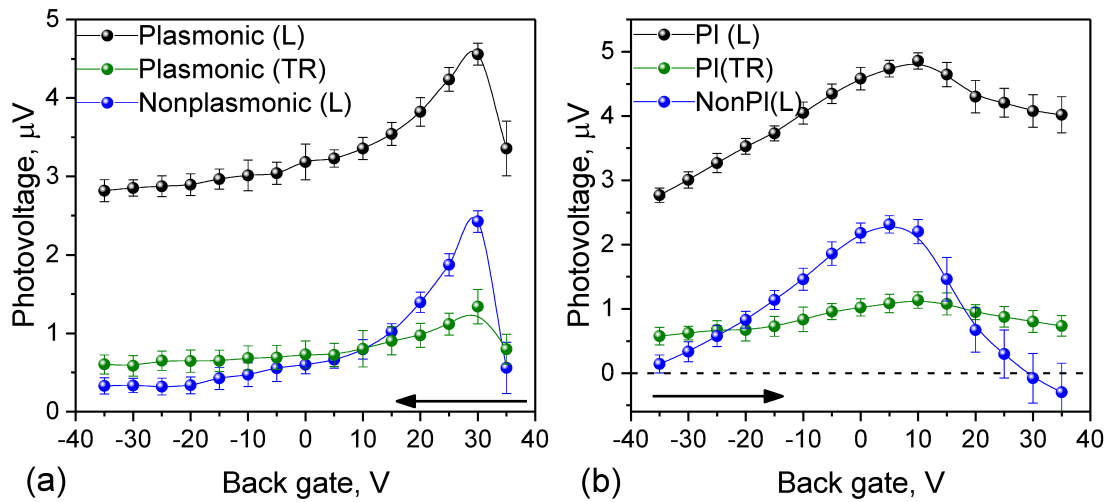


Figure 6.11. Gate dependent photovoltage response of plasmonic (PI) contact under longitudinal and transverse polarization and nonplasmonic (NonPI) contact under longitudinal polarization. The gate bias is tuned from positive voltage towards negative (a,b) and reverse (c,d) as indicated by arrows. The photovoltage measurements are performed with elliptical laser spot at 700 nm with 40 μ W power.

To shift the Dirac point into an accessible region for our measurements, we utilize the hysteresis effect by sweeping the back gate bias from negative towards positive voltages. The results are summarised in Figure 6.11 (b). Similar to previous results, strong enhancement is observed for the plasmonic contact under longitudinal polarization. However, the most interesting result is the photovoltage sign change observed for nonplasmonic contact at around 25 V. A similar trend has been observed for the representative device 4 under reverse back gate conditions (Figure 6.12). In contrast, the plasmonic contact while demonstrating a steady signal decrease is still quite far away from the sign change for both longitudinal and transverse polarizations. To understand the mechanism behind this gate dependent photovoltage generation, we perform the transport and thermoelectric measurements discussed in Section 6.3.7 and explore an analytical model of the device's operation discussed in Section 6.3.8.

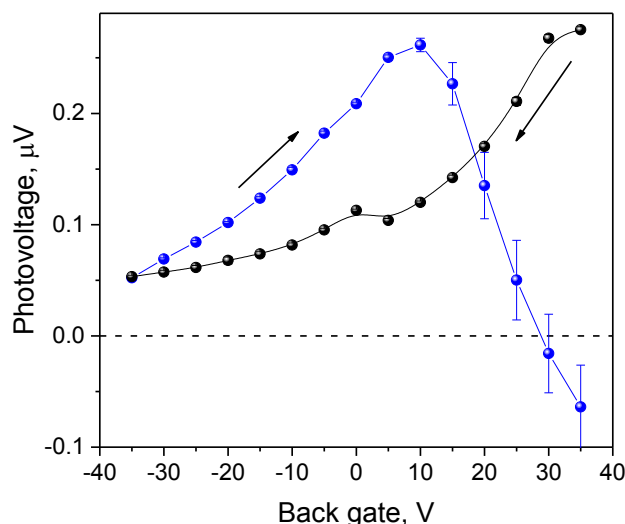


Figure 6.12. Gate dependent photovoltage response of representative device 4 with nonplasmonic contacts under longitudinal polarization. The gate bias is tuned from positive voltage towards negative (black) and reverse (blue) as indicated by arrows. The photovoltage measurements are performed with elliptical laser spot at 700nm with 40uW power.

6.3.7 Graphene transport measurements and Seebeck coefficient

The electrical properties of a representative two terminal graphene device (dev4) are first characterized by recording the source-drain current under 1 mV bias by sweeping the gate voltage from -40 to 40 V with 1 V steps and 10 ms stabilization time (Figure 6.13 a). From this measurement the Dirac point is observed at ~ 28 V. Furthermore, under these measurement conditions, the hysteresis effect does not lead to a significant shift of the Dirac point. Next, the source-drain current is recorded for the gate voltage sweeping from -35 to 35 V with 5 V step and 30 s stabilization time (Figure 6.13 b,c). These settings correspond to the photovoltage measurement conditions, as discussed in Section 6.3.6. Interestingly, when the gate voltage is swept from positive to negative, the Dirac point is no longer reached. Furthermore, under reverse sweeping conditions, the Dirac point is only partially reached and is expected at ~ 40 V, which is a significant positive shift compared to the ~ 28 V obtained with 10ms stabilization time. This result is in agreement with previous reports on the hysteresis behaviour of FET devices based on graphene/SiO₂ [257,258]. In fact, it has been demonstrated that the magnitude of the Dirac point shift significantly increases with low sweeping rate of the gate voltage (dV_{BG}/dt) [257]. The hysteresis behaviour originates from charge trapping at the interface of the graphene and SiO₂. Interface traps are populated continuously as the gate voltage is tuned. Typically, oxide traps are charged in the presence of gate fields above $0.03 \text{ V} \cdot \text{nm}^{-1}$ [259], that corresponds to 2.7 V for 90 nm thick SiO₂ used in our experiments. This additional charge introduces doping in graphene and thus shifts its

Dirac point. Therefore, when the gate voltage is swept from negative to positive values this typically shifts the Dirac point down due to additional charge screening from injected holes into trap states. Similarly, reverse gate voltage sweeping facilitates electron injection into the trap states resulting in the Dirac point being shifted up [257].

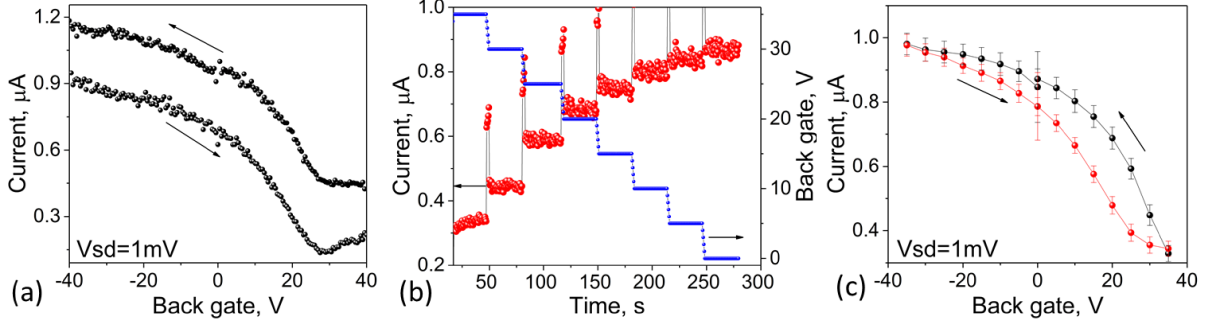


Figure 6.13. Transport measurements of representative two contact graphene device 4. (a) Gate dependent source-drain current measured with 10 ms stabilization time per 1V step. (b) Temporal dynamics of source-drain current at gate bias ranging from 35 to 0V with 5V step and 30s stabilization time. (c) Gate dependent source-drain current extracted from (b). All measurements are performed with 1mV source-drain bias.

To estimate the Dirac point position, we model the graphene conductivity using a rounded V-shape, as previously described for single layer graphene [260,261]:

$$\sigma = \sigma_{\min} \left(1 + \frac{E_F^4}{\Delta^4} \right)^{\frac{1}{2}} \quad (6.1)$$

where $\sigma_{\min}$ is the minimum conductivity and Δ is the width of charge neutrality region, that is related to the disorder strength [25]. This function is expected to correctly describe the graphene conductivity for the highly doped region where $\sigma \sim E_F^2$ as well as the charge neutrality region where $\sigma \sim \text{constant}$. Figure 6.14 (a) shows a comparison of the conductivity model with experimental results. The experimental conductivity is calculated following $\sigma = 1/R_s = I_{sd}L/U_{sd}W$, where R_s is sheet resistance, I_{sd} and U_{sd} are source-drain current and bias, respectively, L and W are length and width of the graphene channel, respectively. Clearly, the conductivity model with Dirac point at 40 V demonstrates much better agreement with experimental data. Additional model parameters are as following $\sigma_{\min} = 0.171$ mS and $\Delta = 0.236$ eV. Thus, we conclude that the Dirac point for our device is ~ 40 V.

As discussed in Section 2.3, the Seebeck coefficient can be directly calculated from graphene's conductivity using Mott's equation. Figure 6.14 (b) shows a comparison between the Seebeck coefficients extracted from the experimental data and the conductivity model.

The Seebeck coefficient exhibits typical features previously observed for graphene devices demonstrating a nonmonotonic behaviour with peaks close to the Dirac point [105]. All investigated graphene samples showed a positive Seebeck coefficient in the range of 10-50 $\mu\text{V/K}$ that is in a good agreement with previously published experimental results obtained with an external resistive heater [105,262].

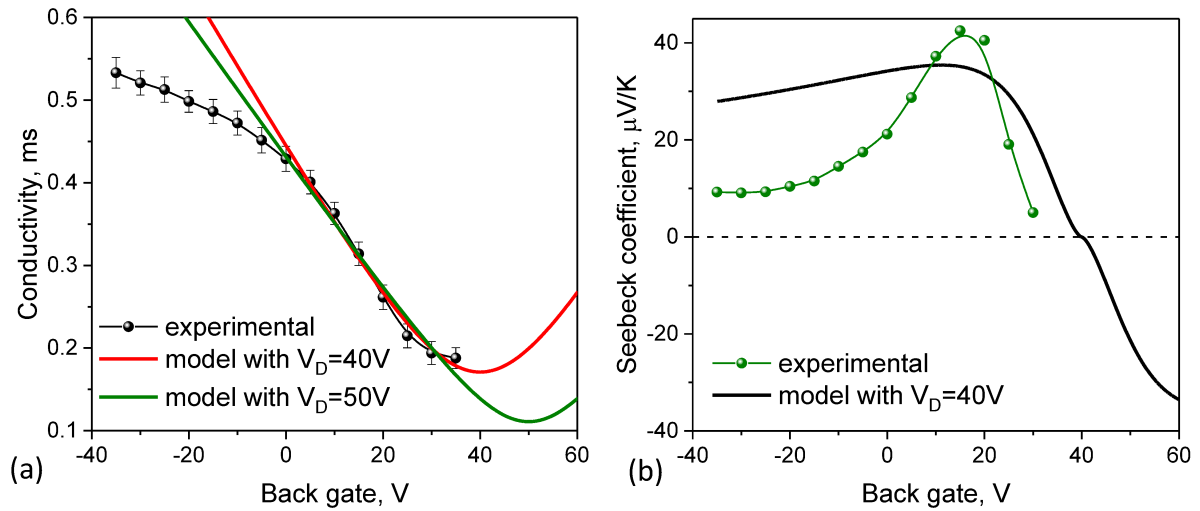


Figure 6.14. Experimental and theoretical conductivity (a) and corresponding Seebeck coefficients (b).

The sign of the Seebeck coefficient that indicates the sign of the majority charge carrier is expected to change from positive to negative as gate voltage crosses the Dirac point and the majority carriers change from holes to electrons. Since the Dirac point is not reached during the measurements, the sign change of experimental Seebeck coefficient is not observed. Due to a significant discrepancy between experimental and model Seebeck coefficient, we use experimental data for the analytical model discussion presented in Section 6.3.9.

6.3.8 Gate dependent thermoelectric response

To deepen our understanding of the mechanism behind the photovoltage generation, we analyse the gate dependent thermoelectric response. Thermoelectric measurements have been performed using a representative graphene two terminal device (dev4) with $5 \times 8 \mu\text{m}$ channel. Heating was introduced by positioning a focused laser spot with $1 \mu\text{m}$ width over one of the contacts far away ($15 \mu\text{m}$) from the photoactive area of graphene junction. By heating the contact, a controlled fixed temperature difference between the source and drain electrodes could be established. The thermovoltage measured across the device has a gate voltage dependence originating from Seebeck coefficients and thus gives a characteristic footprint of the thermoelectric effect. It should be noted, that the thermovoltage will have a dominant gate

dependent contribution from the Seebeck coefficient in the graphene channel material and a small contribution from the graphene/metal interface. It has been previously demonstrated that the later contribution is negligible [30].

As can be seen from Figure 6.15, the thermovoltage measured as a function of back gate bias demonstrates typical features previously observed for graphene devices [105]. The thermovoltage is characterized by nonmonotonic behaviour with peaks close to the Dirac point. Since the thermovoltage is directly related to the Seebeck coefficient of the channel graphene, the sign of the thermovoltage indicates the sign of the majority charge carrier. For both types of gate sweeping settings, the observed thermovoltage remains positive. This provides additional confirmation that the Dirac point is not reached under these measurement conditions.

It is instructive to compare the thermoelectric voltage responsivity to induced photovoltage responsivity. For the peak position at 30 V gate bias the thermoelectric responsivity is about 80 $\mu\text{V/W}$ (Figure 6.15 a), while the photoresponsivity of our device is 112mV/W, which is three orders of magnitude higher. This result confirms that direct heating of the contact metal has a negligible contribution to the detected photoresponse. Additionally, it is possible to estimate the induced temperature difference between the contacts using the calculated Seebeck coefficients for sweeping conditions from negative to positive voltage. For these sweeping conditions, the peak thermoelectric voltage of $V_{TE} \approx 625 \text{ nV}$ is observed at $V_g = 15\text{V}$ (Figure 6.15 c). Taking into account Seebeck coefficient of $S = 42.5 \mu\text{V/K}$, the temperature difference between the contacts induced by direct laser heating is estimated to be of $\Delta T \sim 14.7 \text{ mK}$.

To analyse the overall trends, the photoresponse is normalised to the maximum value and compared to the normalised thermovoltage (Figure 6.15 b,d). It is evident that the gate voltage dependence of the photoresponse for the plasmonic contact demonstrates quite similar behaviour to the thermovoltage and, in particular, no sign change is observed for both gate sweeping conditions. In contrast, the photoresponse of the nonplasmonic contact indicates a clear polarity reversal at $\sim 25 \text{ V}$, which is a much lower gate bias than the Dirac point position $\sim 40 \text{ V}$. While these observations already suggest that the photothermoelectric effect due to a contact temperature difference is dominant for the plasmon enhanced photoresponse, we proceed with the analytical model in Section 6.3.9.

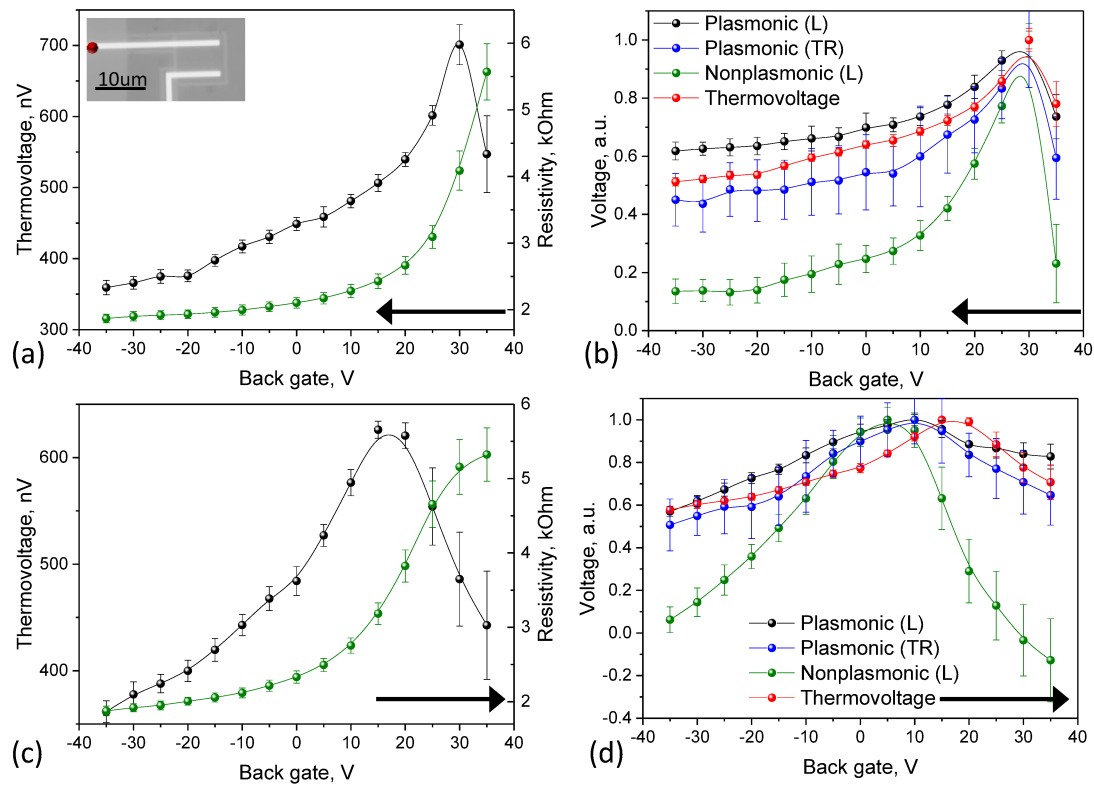


Figure 6.15. (a, c) Gate dependent thermoelectric voltage (black) and square resistance (green). Inset in (a): optical microscopy image of the device with the laser position marked by red dot. The measurements performed with 750nm at 3mW power. (b, d) Photovoltage response of plasmonic (longitudinal and transverse polarizations) and nonplasmonic contacts normalised to the maximum value. For comparison purposes normalised thermoelectric voltage is included. The gate bias is tuned from positive voltage towards negative (a,b) and reverse (c,d) as indicated by arrows.

6.3.9 Analytical model of the device response

To understand the mechanisms behind the photovoltage generation in our device we develop an analytical model as presented in Figure 6.16. Since the Fermi level in graphene in the region on top or below the metal pads is fixed [102], back gating affects the Fermi level of the channel graphene changing its thermoelectric properties and the band-bending conditions near the graphene/metal contact regions. This provides an opportunity to distinguish between the various effects involved in the photodetection process, as discussed in Section 2.3. (1) The band-bending region results in an internal electric field giving rise to **photovoltaic effect (PV)**. For the PV mechanism the generated current is expected to follow Fermi energy difference across the p-n junction $V_{PV} \sim \Delta E_F = (E_F(Gr/Au) - E_F(Gr/SiO_2))$. (2) Strong spatial variation of Seebeck coefficients enhances the **junction photothermoelectric effect (PTE-j)** which is proportional to $V_{PTE,j} = (S(Gr/SiO_2) - S(Gr/Au))\Delta T_e$, where S is the Seebeck

coefficients of the two regions of the junction and ΔT_e is the electron temperature increase within the junction. (3) When light is absorbed around the source electrode, a high temperature imbalance of the carrier system can be created, as the graphene close to the drain electrode is not heated. This will result in **channel photothermoelectric effect (PTE-ch)** with of $V_{PTE,ch} = S(Gr/SiO_2)\Delta T_e$, where S is the Seebeck coefficient of the graphene channel and ΔT_e is the electron temperature difference between the contacts.

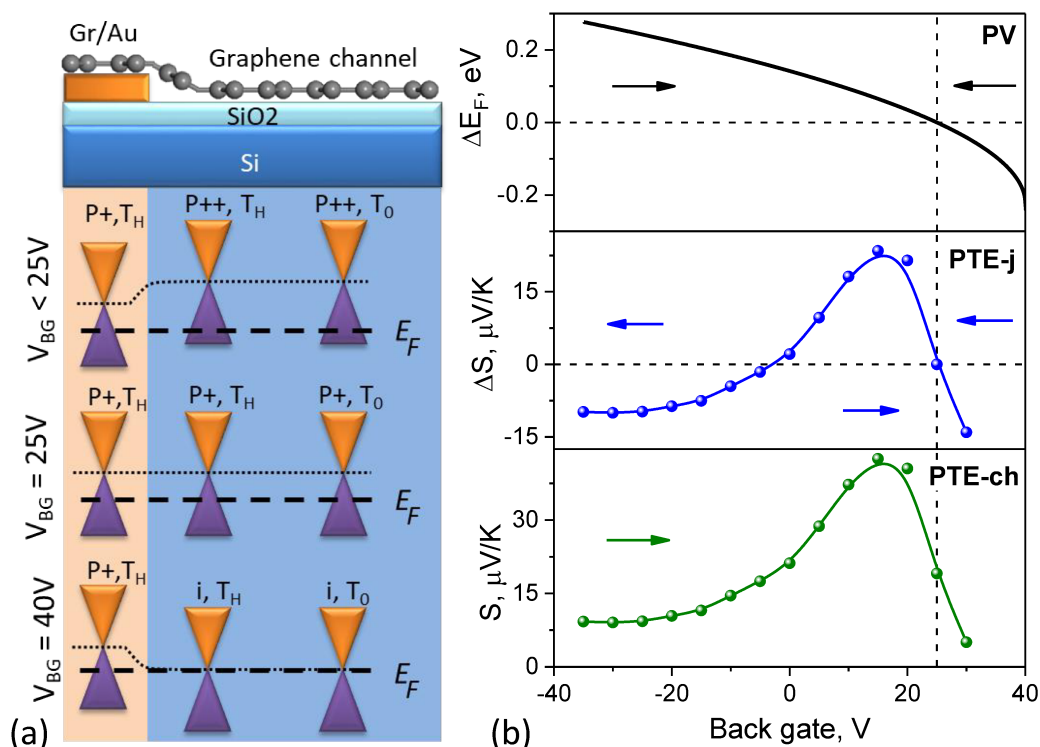


Figure 6.16. (a) Band diagram of the device with graphene/Au interface and graphene channel. Black dash line represents the Fermi level; black fine dash line represents the Dirac point of the graphene. The illumination is located at graphene/Au interface resulting in higher carrier temperature (T_H). (b) Calculated gate dependent Fermi level difference (top) and Seebeck coefficient difference (middle) between the Gr/Au and Gr/SiO₂ areas and gate dependent Seebeck coefficient (bottom) for graphene channel. The contributing currents are indicated by arrows. Vertical dash line corresponds to band flattening point observed at 25 V. As previously discussed in Section 2.3, at the band-flattening point both PV and PTE-j effects are cancelled which typically results in a near zero photoresponse in the case where these two effects are dominant. In contrast, the PTE-ch effect remains significant especially when the band flattening occurs under different back gate bias compared to the Dirac point. Nonplasmonic contacts of our device demonstrate a sign change of the photoresponse at 25 V back gate bias, which is 15 V lower than the Dirac point position (~ 40 V). This is in a good agreement with previously observed photocurrent response of graphene/metal junction, where the sign reversal was frequently detected before the Dirac point [32,34,35,263]. Therefore,

the point of vanishing photovoltage corresponds to the band flattening condition where the graphene doping levels above the metal contact and in the channel are equal. From the carrier density $n = \frac{\epsilon_0 \epsilon_{SiO_2} (V_g - V_D)}{et}$, where t is the oxide thickness, the Fermi level $E_F = \hbar v_F (\pi n)^{1/2}$ can be derived to be 0.25 eV and 0.4 eV for graphene over the contact and SiO₂, respectively. Higher p-doping in the graphene channel can be explained by SiO₂ induced charges [150]. The doping values are in a good agreement with the estimates from the Raman measurements as discussed in the Section 6.3.4. Furthermore, at the band flattening point the Seebeck coefficients of two regions S_1 and S_2 should be equal meaning that $S(Gr/Au) \approx 19 \mu V/K$.

To confirm that the PV and PTE-j effects only dominate for nonplasmonic contact, we additionally estimate the contribution of PTE-ch effect due to local heating by laser excitation. Previously, the temperature increase of 1 K has been estimated for room temperature measurements with 600 nm excitation at 40 μW and with 0.5 μm laser spot [29]. For our illumination conditions, the temperature increase of 5 mK is expected. Taking into account the peak Seebeck coefficient of 42.5 $\mu V/K$ observed at 15 V back gate bias, the PTE-ch effect results in maximum voltage of $\sim 0.2 \mu V$, which is 8 times lower than the nonplasmonic contact photoresponse of 1.5 μV at this back gate bias. It should be noted that the PTE-ch current will typically result in a shift of the band flattening point. However, as indicated above, this effect is expected to be low.

Effect	As prepared $V_{BG} = 0$	Flat band $V_{BG} = 25V$	Dirac point $V_{BG} = 40V$
PV	✓	✗	✓
PTE-j	✓	✗	✓
PTE-ch	✓	✓	✗

Table 6.1. Summary of contributing effects under different gate bias: ✓ – the effect is active and ✗ – the effect is cancelled.

The extracted Fermi energies and Seebeck coefficients for the graphene/metal junction and the channel graphene allow us to separate the contributions to the photovoltage described in Figure 6.16 and summarised in Table 6.1. The modelled PV and PTE-j effects confirm the sign reversal at the band flattening point. Interestingly, the PTE-j changes the current direction again at ~ 0 V resulting in opposite direction compared to the PV current. Since only these two effects contribute to photoresponse of the nonplasmonic contact, these competing

currents can explain the experimentally observed significant decrease of photoresponse under negative bias. Meanwhile, the PTE-ch effect demonstrates a positive current over the whole range of tested back gate bias values, which is consistent with the photoresponse of the plasmonic contact seen experimentally. Therefore, it is possible to conclude that PTE-ch plays a dominant role in the photovoltage generation process of the plasmonic contact.

6.3.10 Time resolved photovoltage spectroscopy

We finally use ultrafast pump probe measurements to characterize the photodetector's ultimate speed limitations which are determined by the internal carrier dynamics. Following the method described in Section 3.4, two pulsed beams were overlapped at the same position on one of the device's contacts. An optical chopper is used to introduce modulation of the probe beam and a lock-in amplifier to detect the resulting photocurrent. The measured signal thus can be considered as the probe-induced photovoltage that is sensitive to the presence of the pump. Previously performed time-resolved photocurrent studies of graphene devices typically utilize cross-polarized beam configuration to minimize interference near zero time delay point [78,209,210]. However, in our plasmon based photodetector cross polarization method is inapplicable due to polarization sensitivity of the plasmonic contact. To overcome this issue, we select a two-colour experiment configuration with wavelengths of 650 and 750 nm to be on resonance with plasmonic nanostructures.

We study the photovoltage response as a function of the time delay Δt between pump of 650 nm and probe of 750 nm laser pulses for a fixed probe power of 100 μ W and a range of incident pump powers. Figure 6.17 (a,b) shows the corresponding photovoltage traces with a subtracted baseline that is given by the signal far away from zero time delay point, where the two pump saturation effects are reduced. The pump pulse affects the probe-induced photovoltage response only near zero time delay point and results in a sharp photovoltage dip. The presence of the dip is due to saturation of the photocurrent generation with coincidence of the two pulses, within the time response of the device. In graphene the saturation regime is determined by Pauli blocking effect and is observed when the photogeneration rate is comparable to the rates of energy relaxation and recombination [264,265] (Section 2.2). Thus, increasing the pump excitation power is expected to result in higher saturation that is clearly observed in the experimental results (Figure 6.17 c). Furthermore, a higher saturation amplitude is reached for the plasmonic contact, which is in agreement with the higher responsivity observed for this contact.

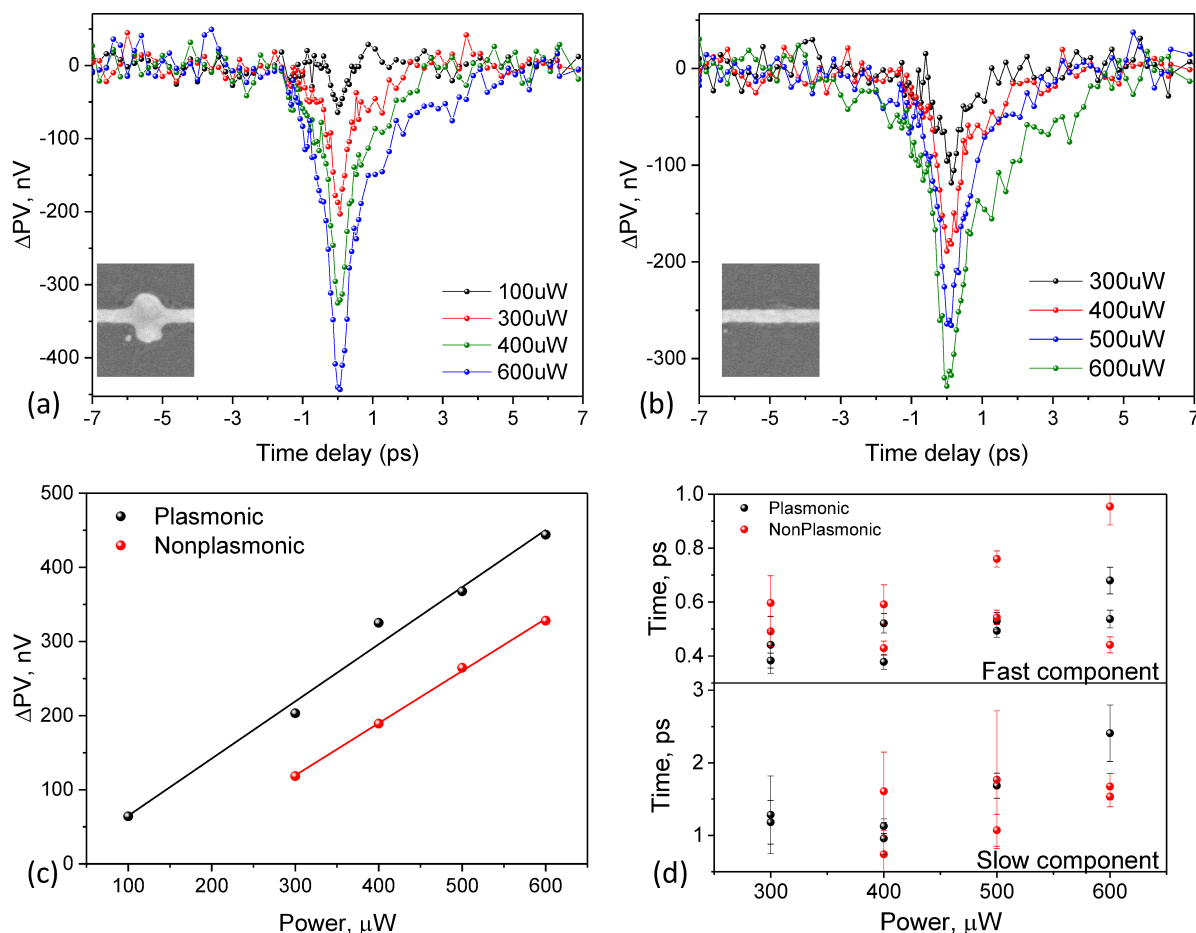


Figure 6.17. (a, b) Probe-induced photovoltage at plasmonic and nonplasmonic contacts as a function of pump–probe pulse delay time. Probe at 750 nm and 100 μW power, pump at 650 nm and power as indicated; both beam spots have elliptical shape. Insets are SEM images of the contacts. (c,d) Probe-induced photovoltage at zero time delay point and response time, extracted from bi-exponential decay of the dip in (a) as a function of pump power.

The width of a dip/peak observed for laser pulses overlap corresponds to the carrier relaxation time that is needed for the graphene detector to return to equilibrium. A bi-exponential decay is used to describe the temporal response of the system. The photovoltage signal exhibits a short subpicosecond component immediately after the temporal overlap of both laser pulses and a longer picosecond component (Figure 6.17 d). After optical interband excitations with ultrashort pulses a nonequilibrium carrier distribution is established for electrons in the conduction band and holes in the valence band. The excitation is followed by an equilibration process through carrier–carrier scattering and emission of optical phonons, that takes place on a sub-ps timescale, and through subsequent electron cooling by thermal equilibration with the lattice, that typically occurs on a picosecond timescale [209,266]. A detailed discussion of carrier relaxation process in graphene is presented in Section 2.2. The

response time of the photodetector increases slightly with increasing laser fluence, which is in agreement with previous observations [209,261] and can be explained by the higher saturation with increasing laser fluence indicating that more carriers accumulate in the high field region.

6.3.11 Hot carrier temperature estimate

As discussed previously, the PTE-ch effect dominates the photoresponse of the plasmonic contact. Furthermore, due to PV and PTE-j effects cancelled at gate bias of $V = 25\text{V}$, the signal generated due to PTE-ch can be separately analysed. As discussed in Section 2.3, the PTE-ch effect arises due to the carrier temperature difference between two contacts and thus provides an opportunity to analyse the plasmon induced carrier temperature in graphene.

The peak photovoltage generated by a single pulse can be restored taking into account laser duty cycle $V_{peak} = V_{exp}/v_0\tau$, where v_0 is laser repetition rate of 80 MHz and τ is the device response time (Figure 6.18 a). The time resolved photovoltage measurements demonstrate that the average response time of our devices is approximately ~ 4 ps (Section 6.3.10).

The hot carrier population established in graphene after photoexcitation can be described by a thermal distribution with a well-defined hot carrier temperature T_C [25,79]. Therefore, the voltage generated due to PTE-ch effect for plasmonic contact can be expressed as

$$V_{PTE-ch} = - \int_{T_0}^{T_C} S(T_C) dT_C, \quad (6.2)$$

where T_C and T_0 are the carrier temperatures at plasmonic and nonplasmonic contact, respectively. Taken into account the hot carrier diffusion coefficient of $5500 \text{ cm}^2\text{s}^{-1}$ recently extracted for CVD graphene [96] and the device response time of 4 ps, the estimated diffusion length is ~ 740 nm that is significantly lower than the distance between the contacts ($5.5 \text{ }\mu\text{m}$). Therefore, the carrier temperature at nonplasmonic contact can be estimated as $T_0 \sim T_{bath} \sim 300\text{K}$.

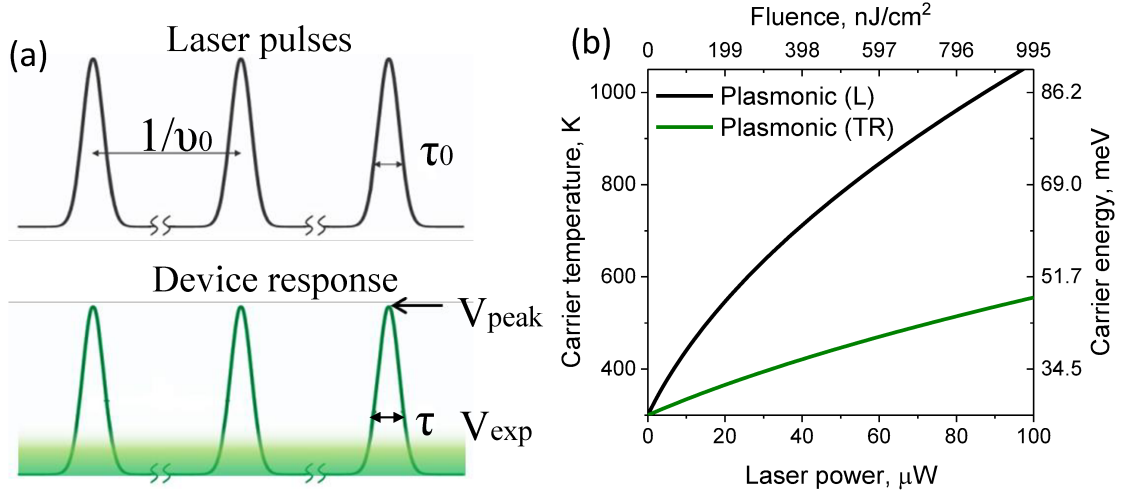


Figure 6.18. (a) Schematic diagram of an excitation laser pulse train with $\nu_0 = 80$ MHz and $\tau_0 = 150$ fs and corresponding photovoltage (PV) response with $\tau = 4$ ps including photovoltage peaks (V_{peak}) and average signal (V_{exp}) detected in the measurements. (b) Power dependence of the carrier temperature and carrier energy in graphene at plasmonic contact under longitudinal and transverse polarization.

Next, following [106], we integrate equation (6.2), obtaining,

$$T_c = \sqrt{(T_0)^2 + 2(|V_{PTE-ch}/k|)}, \quad (6.3)$$

where $k = -\frac{\pi^2 k_B^2}{3q} \frac{1}{\sigma} \frac{d\sigma}{dE_F}$ as derived from equation (2.2). As mentioned before, the condition under interest is back gate bias of $V_g = 25$ V, where PV and PTE-ch effects are cancelled. At this back gate bias, $k \approx 63$ nV/K². Taking into account plasmonic contact response at $V_g = 25$ V and its linear power dependence, we can finally estimate the carrier temperature (Figure 6.18). Under illumination with longitudinal polarization, resonance conditions can be reached leading to the carrier temperature of 1000 K established at the plasmonic contact. Interestingly, the transverse polarization still results in a significant carrier heating reaching 550 K. The extracted temperatures are in good agreement with our previous studies of ultrafast carrier heating in graphene/plasmonic nanoparticle complexes where carrier temperatures of 1500 K were reached [267]. Furthermore, similar hot carrier temperatures have been observed for graphene pn junction where the photothermoelectric effect is known to be dominant [78]. In this experiment [78], under illumination conditions of 3.5×10^{12} photons/cm² (100 μW in our experiment), the hot carrier temperature of approximately 200 K was observed demonstrating a temperature raise of $\Delta T \approx 190$ K compared to initial bath temperature of $T_{bath} \approx 10$ K. Interestingly, in our experiment under same illumination conditions, carrier temperatures as high as 1100 K are expected resulting in a temperature rise of $\Delta T \approx 800$ K that is almost 4 times higher compared to the pn junction experiment. This

provides additional confirmation that the presence of plasmonic nanostructures significantly enhances carrier heating efficiency in the graphene channel even without direct hot electron injection from the metal.

6.3.12 Graphene destruction in presence of electromagnetic field

It is well-known that pulsed-laser exposure can lead to defect formation in graphene followed by material ablation and can be used for graphene patterning [268–270]. Therefore, the laser power should be carefully controlled in ultrafast experiments. For graphene the single-shot damage threshold fluence of 200 mJ/cm^2 has been reported for 790 nm laser wavelength [269]. In our experiment, 700 nm wavelength is mostly used due to its resonant condition with the nanoparticles. To be well below the threshold value, $50 \mu\text{W}$ average laser power was used with a focused laser spot width ($\sim 1 \mu\text{m}$) resulting in fluence of 0.02 mJ/cm^2 , that is 4 orders of magnitude lower than the threshold. However, measurements demonstrated very weak photoresponse of contacts with plasmonic nanoparticles. SEM studies revealed that graphene was partially removed in the areas close to plasmonic nanoparticle (Figure 6.19). Since other areas of graphene over the metal contact remained undamaged, partial removal can be attributed to local electromagnetic field enhancement facilitated by plasmonic nanoparticles under resonant excitation.

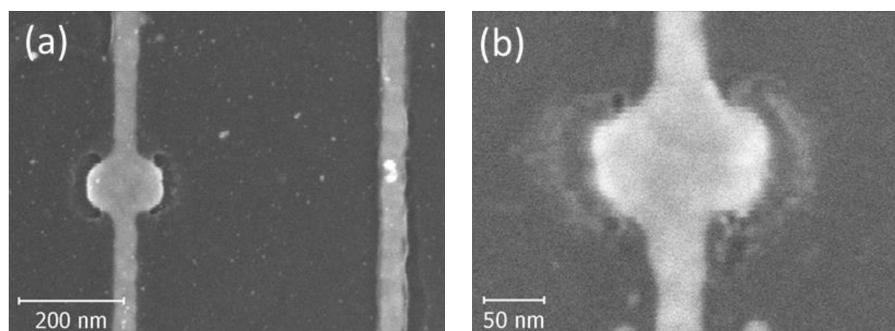


Figure 6.19. Graphene destruction in presence of plasmonic nanoparticles.

Despite very high heat conductivity of pristine graphene, the burning effect appears to be a very local phenomenon as demonstrated in Figure 6.19 (b) where only areas within 50 nm from the nanoparticle are damaged. Recent studies propose that graphene under pulsed laser excitation becomes involved in a chemical reaction with atmospheric oxygen to form CO_2 [270]. The exact temporal evolution of the process is currently unknown. Stöhr et al. suggested the following mechanism of graphene burning process. Due to graphene's high heat conductivity [271], initially undamaged graphene can efficiently drain out the laser-induced heat. However, ultrafast pulse exposure leads to defect formation where atoms

extracted from the crystal lattice create CO₂. Since this process significantly damages the graphene lattice, a reduction in the heat conductivity should be observed increasing the probability of further destruction. Simultaneous heating and lattice damage lead to an avalanche process of burning. Local burning of graphene can be potentially used to identify field enhancement in the presence of plasmonic nanostructures.

6.4 Conclusions

In this chapter, we have studied graphene's optoelectronic properties, firstly, by analysing a typical metal-graphene-metal photodetector. The observed photoresponse has been confirmed to demonstrate high sensitivity to local inhomogeneities, such as doping variation and grain boundaries typically present in CVD graphene material. Next, a plasmonic contact has been introduced into the device to facilitate the study of plasmon-induced carrier heating and its impact on the device photoresponse. Incorporation of the plasmonic contact results in strong photoresponse enhancement that closely follows the spectral characteristic of the plasmonic resonance. Compared to a nonplasmonic contact, approximately 5 time increase in photovoltage is observed at the plasmonic contact under resonant illumination conditions. Furthermore, the peak responsivity of 0.125 mA/W is only one order of magnitude lower than the best reported result for the metal-graphene-metal photodetector of 6.1 mA/W [1,18]. Analysing the gate dependent photoresponse, we successfully unravelled the contribution from photovoltaic and thermoelectric mechanisms. In fact, our results demonstrate that the plasmonic enhancement of graphene photoresponse is primarily due to the increased thermoelectric effect over the device channel. Using the measured device response time of 4 ps, the ultrafast peak voltage was deduced from the measured average response facilitating analyses of ultrafast carrier temperatures. It has been demonstrated that carrier temperatures in excess of 1000 K can be reached in the presence of plasmonic structures even under low power densities. In fact, carrier heating is expected to be 4 times more efficient in the presence of plasmonic nanostructures than for bare graphene. However, extreme local heating has been shown to result in graphene destruction. The detector responsivity could be further improved by utilizing high quality crystalline graphene that enables detector operation with higher Seebeck coefficients [25]. The demonstrated device is expected to facilitate the development of free space compact and ultrafast photodetectors for a range of wavelengths due to plasmon enabled spectral tunability.

7 Conclusions and future work

This chapter summarizes the key findings of the thesis and discusses the implications with regards to the use of hybrid plasmonic structures in optoelectronic devices. Promising research projects based on results from the thesis are also discussed.

7.1 Summary

The primary goal of this thesis was to study the optical properties of graphene/plasmonic-nanostructure complexes, explore the ultrafast carrier dynamics in hybrid systems and understand the generation mechanisms of hot carriers and their contribution to the photocurrent observed in the hybrid devices. The results presented in this thesis show that the strong electromagnetic fields generated in close proximity to plasmonic nanoparticles (NP) can strongly influence the optical response of graphene-based plasmonic hybrids. In particular, the observed absorption enhancement in graphene results in a local generation of hot carriers in the presence of the plasmon-induced near fields with minimal contribution from a charge transfer mechanism from the NPs at the graphene/NP interface. Furthermore, the spatial inhomogeneity in the hot carrier population leads to strong electron temperature gradients that effectively enhances the thermoelectric current in the device leading to the channel based photothermoelectric effect being the dominant process for the asymmetric graphene based plasmonic photodetectors studied here.

To facilitate high efficiency CVD graphene based devices, an effective graphene transfer method from a metallic growth substrate to a target substrate is crucial with a major requirement to preserve properties of the graphene material. Therefore, the thesis begins with the investigation of effects of the transfer methods and subsequent device fabrication techniques on the electronic and structural properties of the resultant graphene films. Particular attention was paid to the study of the source of the extrinsic doping where polymer and substrate induced doping were analysed separately. The use of a polymethylmethacrylate (PMMA) supporting film was demonstrated to induce additional extrinsic doping on the order of $\sim 3 \cdot 10^{12} \text{ cm}^{-2}$. Although PMMA residues were removed by thermal annealing, the extrinsic doping did not reduce, but on the contrary increased by additional $\sim 2 \cdot 10^{12} \text{ cm}^{-2}$ due to higher graphene/SiO₂ interaction. To study the substrate induced doping, various routes to surface engineering were considered including O₂-plasma treatment, a self-assembled monolayer

(SAM) and an hBN layer coating. While the substrate engineering was demonstrated to significantly improve graphene's adhesion to the substrate facilitating dry transfer methods and photolithography contact fabrication, the carrier density in the graphene layer was strongly modified. The SAM layer (ODTS) resulted in the lowest extrinsic doping of the graphene film consistent with the screening effect of the charged states present on the SiO₂ surface, while the highest extrinsic doping was observed for O₂-plasma treatment due to increased density of silanol groups on the SiO₂ surface. The hBN layer resulted in the higher extrinsic doping due to polymer residues left on the surface after material transfer. This effect was reduced by thermal annealing of the hBN layer prior to graphene transfer.

To improve graphene quality during the transfer method, a novel hBN-assisted transfer technique was developed to avoid contact between the graphene and the polymer film [272]. This transfer method resulted in much lower doping concentrations and improved carrier mobility in the graphene compared with the results of the conventional wet transfer method for untreated SiO₂, SAM-modified and hBN covered SiO₂. Moreover, the top hBN layer facilitated large scale encapsulation of the graphene layer leading to greater stability during ambient exposure. It is anticipated that full encapsulation of the graphene layer with hBN layers will further improve its properties. Additionally, high resolution characterization, such as transmission electron microscopy, could provide additional information on the structural properties of the resulting van der Waals heterostructures with the possibility to analyse the density of induced defects created due to surface morphology mismatch of the stacked films. It should be stressed that the novel transfer technique can be applied to other CVD-grown 2D materials enabling the preparation of van der Waals structures with polymer-free interfaces.

Following the optimised graphene transfer process, graphene/plasmonic-NP structures were fabricated and analysed. It was confirmed that the graphene layer created conformal contact with the underlying plasmonic nanostructures. However, the induced mechanical modifications of the graphene layer in the presence of plasmonic nanostructures resulted in a higher defect concentration and tensile strain compared to the relaxed graphene. Additionally, reduced doping concentration was observed for graphene/NP complexes, which was attributed to partial decoupling of graphene from the substrate.

The thesis goes on to explore carrier dynamics in graphene and graphene/NP complexes using differential reflection (DR) spectroscopy. The sign of the DR signal was shown both experimentally and theoretically to be highly sensitive to the graphene doping variation and

substrate interference effects. Using this observation, spatial variation of the DR signal was used to identify local modifications in the graphene doping level by scanning DR imaging. Next, the plasmon induced hot carrier dynamics were studied in the graphene/NP complexes by analysing samples with and without an insulating hBN barrier between the graphene/gold interface. Hot carrier generation in the graphene was demonstrated to be significantly enhanced in the presence of the plasmonic NPs, as confirmed by increased amplitude of the DR signal. However, this effect can now be primarily attributed to the direct photo-excitation processes enhanced by the intense electromagnetic fields surrounding plasmonic NPs, with only a minimal contribution from charge transfer between gold and graphene. Furthermore, inhomogeneity of the plasmon-induced fields resulted in the generation of a highly localised hot carrier population in graphene, which was further confirmed by an observed nonlinear anisotropy in the DR signal. The next step of this work could be to study graphene/NP complexes with a vertical tunnel barrier of varying thickness (number of hBN layers) to precisely assess the contribution of the charge transfer process. Since CVD films are typically characterized by defects such as tears and holes, multilayer material will ensure that tunnelling properties of the CVD hBN layer are preserved. Additionally, the substrate interference would change in the presence of gold NPs and, thus, influence the overall DR signal observed for graphene/NP complexes. Therefore, development of a theoretical model to take into account one more layer partially filled with gold material (~20%) would be beneficial to fully understand enhancement of the DR amplitude.

Finally, the thesis explores the strong electronic temperature gradients generated by the plasmon-induced highly localised hot carrier population in graphene in asymmetric photodetector device. For this purpose, a plasmonic contact with nanobars was introduced in metal-graphene-metal photodetector to facilitate inhomogeneous carrier heating. The plasmonic contact demonstrated a strong photoresponse enhancement closely following the spectral characteristics of the plasmonic resonance. Under resonant illumination conditions, the photovoltage was increased approximately 5 times compared to a nonplasmonic contact, corresponding to a peak responsivity of 0.125 mA/W. This value is only one order of magnitude lower than the best reported result for a metal-graphene-metal photodetector of 6.1 mA/W [1,18]. The detector responsivity could be further improved by utilizing high quality crystalline graphene that enables detector operation with higher Seebeck coefficients [25]. It should also be noted that the suggested device geometry has an advantage of non-zero photoresponse under full illumination due to higher signal produced at the

plasmonic contact. The effect can be further enhanced using asymmetric metallization where different metals are used at source/drain electrodes [18].

Next, the photodetection mechanism of the asymmetric plasmonic device was studied by separately analysing the gate-dependent photoresponse of nonplasmonic and plasmonic contacts. The observed results suggested that the plasmonic contact demonstrated a photoresponse with a dominant photothermoelectric effect originating from electronic temperature difference across the device channel. To further investigate the established carrier temperature profile in the device, the photovoltage generation could be measured at various points away from the injection plasmonic contact by using multiple detector leads or by studying devices with varying channel length. Theoretical model could be further developed to calculate the established carrier temperature profile. Additionally, plasmon-enabled spectral tunability could be investigated by simply increasing the nanobar length. Twice longer (~ 350 nm) nanobar particles are anticipated to provide resonance conditions at telecom wavelength 1500 nm.

Finally, the asymmetric plasmonic device was characterised with time resolved photovoltage spectroscopy to identify its response time. Using the extracted response time of 4ps, the ultrafast peak voltage was deduced from the measured average response facilitating analyses of ultrafast carrier temperatures. It was demonstrated that peak carrier temperatures in excess of 1000K can be reached in the presence of plasmonic structures even under low power densities. It is estimated that the presence of plasmonic nanostructures results in a four times more efficient carrier heating compared to bare graphene. The asymmetric plasmonic devices developed in this thesis could be used to determine the carrier temperature and the cooling length for hot carrier propagation, which are key parameters for a variety of new devices relying on hot-carrier injection and transport.

7.2 Outlook

7.2.1 Imaging ultrafast hot carrier transport

Imaging the motion of photoexcited carriers during their relaxation process is of high importance as it provides insight into carrier transport. The conventional time resolved techniques yield intrinsic carrier relaxation times in the material providing the upper bound on operational speed [74]. However, the actual device response time is determined by the

photo-carrier transient time that is crucial for ultrafast photodetector development. A spatial and time resolved photocurrent microscopy technique can be used to image the transit of ultrashort carrier pulses across photodetectors of various materials with planar contact geometry. In contrast with the conventional time-resolved pump-probe method previously used in this thesis, the modified technique utilizes independent control of the spatial position for both pump and probe laser beams. In this way, the physically separated probe can be used to monitor the evolution of carriers as they transit across the device (Figure 7.1).

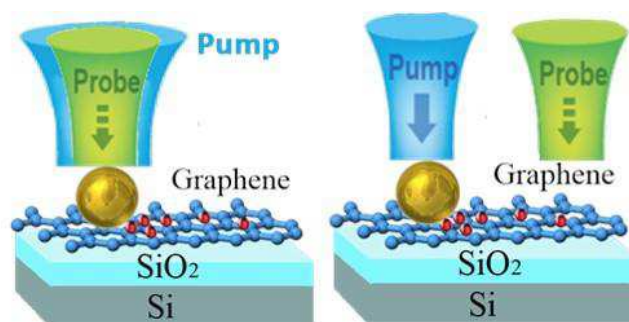


Figure 7.1. Conventional (left) and new (right) time-resolved scanning technique. Red dots represent plasmon-induced hot carriers.

The novel technique can be used to visualize carrier transport in the asymmetric plasmonic photodetectors discussed previously. Of particular interest is the case when the device is under source-drain bias, since the external electric field is expected to influence a hot carrier pulse and potentially facilitate carrier injection from the plasmonic nanostructures. Furthermore, the effect of back gate bias on the carrier pulse is another important parameter to study, since it controls the relative contribution from photo-thermoelectric and photovoltaic mechanisms, as previously discussed. By using an optical cryostat, the influence of the bath temperature on the carrier transient times could be further analysed. This study would deepen our understanding of photodetection principles of graphene based plasmonic devices.

7.2.2 Hot carrier injection

As discussed in Section 2.1, plasmon decay can occur non-radiatively through electron-hole excitation [48]. Our studies demonstrated that hot carrier injection in the graphene layer from the metal is negligible under unbiased conditions (Chapter 5 and 6). Therefore, it is important to consider a device structure where external electric field can be applied to promote carrier injection. Figure 7.2 shows the device structure where an external bias can be applied between the graphene and plasmonic nanostructures that are separated by an hBN layer

serving as a vertical tunneling barrier: (a) plasmonic nanostructures are part of the contact and thus the bias can be directly applied between this contact and the graphene layer; (b) the individual nanoparticles are connected by the underlying graphene contact and thus the bias can be applied between the graphene layers. In this layered structure, the photoexcited electrons from plasmonic NPs can travel vertically to the top graphene layer through the thin middle hBN layer. By applying an interlayer bias voltage, the tunneling barrier can be effectively reduced controlling the amount of injected carriers. In this way, the hot carrier population generated in plasmonic structures can be studied by analysing the corresponding interlayer current under optical excitation that corresponds to plasmonic resonance. Furthermore, the plasmon structure geometry can be adjusted to provide favourable conditions for hot carrier generation such as utilizing Fano resonances [49].

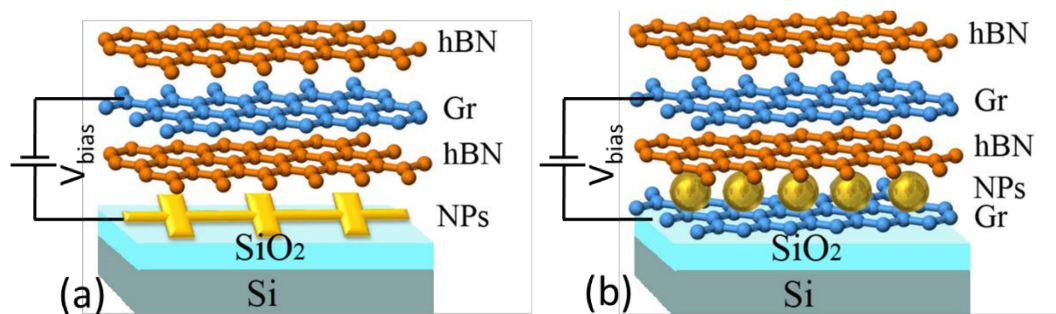


Figure 7.2. Schematics of hot carrier injection devices with plasmonic contact (a) and plasmonic nanoparticles (b).

Similar van der Waals heterostructure (without plasmonic antennas) has been recently studied to control thermalization pathways in the graphene layer [273]. It was demonstrated that depending on the bias conditions and photon energy the photoresponse was due to two distinct processes, thermionic emission and direct carrier tunnelling. Similar behaviour can be expected for the plasmon activated heterostructures. It should be stressed that the suggested device geometry has benefits of low dark current and high detection area [273], that is in contrast with previously discussed planar structures of graphene based photodetectors (Chapter 6). This experiment could not only provide valuable insight into the hot carrier dynamics of plasmonic structures, but could also facilitate hot carrier based applications. One potential application is based on hot carrier driven photochemistry. In this case, the top hBN layer would be replaced by an active chemical medium, while graphene provides the source of hot carriers. Due to long lifetime and associated significant diffusion length of hot carriers in graphene, it is expected that graphene can facilitate higher reaction rates compared to isolated NPs. In fact, enhancement of the plasmon-driven surface-catalytic reaction has been

recently demonstrated in presence of the graphene layer [274]. Of course efficiency of ejection of hot carriers from NPs to graphene has to be taken into account. Nevertheless, the suggested device geometry could be a successful controlled platform to study hot carrier photochemistry with a potential to directly control the hot carrier population.

7.3 Publications or papers in progress related to work conducted during the Ph.D. project

Direct Electronic Measurements of Plasmon Induced Hot Carriers in Graphene

Shautsova, V.; Sidiropoulos, T.; Black, N. C. G.; Gilbertson, A. M.; Maier, S. A. et al.
(in preparation)

Time-resolved differential reflectivity studies of graphene-substrate interactions.

Shautsova, V.; Sidiropoulos, T.; Gilbertson, A. M.; Maier, S. A.; Cohen, L. F. et.al.
(in preparation)

Photoresponse of epitaxial graphene

Shautsova V., Panchal V., Maier S. A., Cohen L. F., Kazakova O.;
(in preparation)

Photoresponse of graphene-porphyrin junctions

Gehring P., Shautsova V., Maier S. A., Cohen L. F., Briggs A. D.;
(in preparation)

Hexagonal Boron Nitride Assisted Transfer and Encapsulation of Large Area CVD Graphene.

Shautsova, V.; Gilbertson, A. M.; Black, N. C. G.; Maier, S. A.; Cohen, L. F.
Sci. Rep. **2016**, 6, 30210.

Plasmon-Induced Optical Anisotropy in Hybrid Graphene–Metal Nanoparticle Systems

Gilbertson, A. M.; Francescato, Y.; Roschuk, T.; Shautsova, V.; Chen, Y.; Sidiropoulos, T. et al.
Nano Lett., **2015**, 15 (5), pp 3458–3464

8 Appendix

8.1 Reflection derivation for single layer substrate

In the following, the derivation of reflection is carried out for a single layer substrate covered with graphene (Figure A1). The normal incidence case is considered to reproduce the pump probe experimental conditions, as discussed in Section 3.3. We treat graphene layer as a conductive boundary condition.

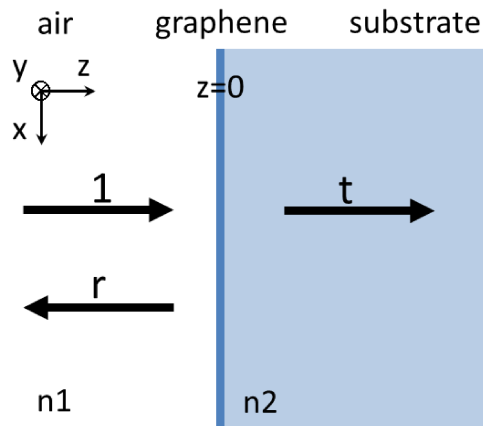


Figure 8.1. Schematic of light interaction with a single layer substrate covered by graphene. Arrows represent the beam directions; n_1 and n_2 are refractive indices of the media and r and t are reflection and transmission coefficients, respectively.

The electric field of the plane wave (before it reflects off the substrate) is then given by

$$E_x = E_{x0} e^{\pm ikz - i\omega t} \quad (4)$$

$$E_y = E_{y0} e^{\pm ikz - i\omega t}$$

where E_{x0} and E_{y0} are the amplitude of the plane wave and the propagation constant k is given by $2\pi n/\lambda$ where n is the refractive index of the medium.

We start with Maxwell's equations in differential form [275]:

$$\underline{\nabla} \times \underline{E} = -\mu \frac{\partial \underline{H}}{\partial t} \quad (5)$$

$$\underline{\nabla} \times \underline{E} = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \\ E_x & E_y & 0 \end{vmatrix} = \hat{x} \left(-\frac{\partial E_y}{\partial z} \right) + \hat{y} \left(\frac{\partial E_x}{\partial z} \right) + \hat{z} \left(\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y} \right) \quad (6)$$

$$\begin{aligned}\frac{\partial E_y}{\partial z} &= \pm ik E_x \\ \frac{\partial E_x}{\partial y} &= \frac{\partial E_x}{\partial y} = 0\end{aligned}\quad (7)$$

$$iw\mu H_y = \pm ik E_x \text{ and } iw\mu H_x = \mp ik E_y \quad (8)$$

$$H_x = \mp n \sqrt{\frac{\epsilon_0}{\mu_0}} E_y \text{ and } H_y = \pm n \sqrt{\frac{\epsilon_0}{\mu_0}} E_x \quad (9)$$

Next, we write the boundary conditions, the requirements for the tangential components of the total vectors $\underline{E}$ and $\underline{H}$ on two sides of the interface to be the same:

$$\underline{n} \times (\underline{E}^1 - \underline{E}^2) = 0 \Rightarrow \underline{E}^1 = \underline{E}^2 \quad (10)$$

$$\underline{n} \times (\underline{H}^1 - \underline{H}^2) = \sigma \underline{E} \quad (11)$$

In the equation (11), σ is the graphene's conductivity function.

$$\underline{n} \times (\underline{H}^1 - \underline{H}^2) = \begin{vmatrix} \hat{x} & \hat{y} & \hat{z} \\ 0 & 0 & 1 \\ H_x & H_y & H_z \end{vmatrix} = \hat{x}(-H_y^2 + H_y^1) + \hat{y}(-H_x^2 + H_x^1) + \hat{z}(0) \quad (12)$$

$$-H_y^2 + H_y^1 = \sigma E_x \quad (13)$$

Matching E-fields at $z=0$:

$$E_0 + rE_0 = tE_0 \quad (14)$$

$$1 + r = t \quad (15)$$

Matching H-fields at $z=0$:

$$-H_y^2 + H_y^1 = \sigma E_x \quad (16)$$

Based on equations (9) and (16), we can obtain:

$$n_1(1 - r) = t \left(n_2 + \sigma \sqrt{\frac{\epsilon_0}{\mu_0}} \right) \quad (17)$$

Finally, using equation (15), reflection and transmission coefficients are given by:

$$r = \frac{n_1 - n_2 - \sigma \sqrt{\frac{\epsilon_0}{\mu_0}}}{n_1 + n_2 + \sigma \sqrt{\frac{\epsilon_0}{\mu_0}}} \quad (18)$$

$$t = \frac{2n_1}{n_1 + n_2 + \sigma \sqrt{\frac{\epsilon_0}{\mu_0}}} \quad (19)$$

29.1 Reflection derivation for multilayer substrate

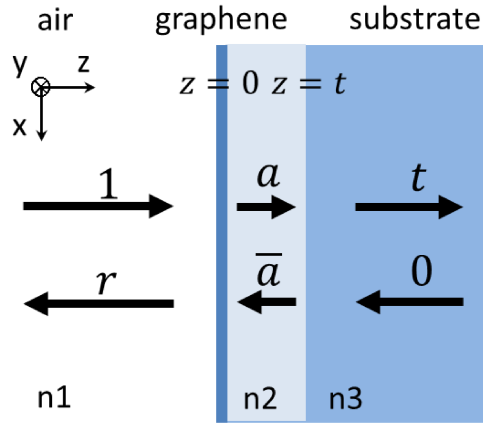


Figure 8.2. Schematic of light interaction with a multilayer substrate covered by graphene. Arrows represent the beam directions; n_1 and n_2 are refractive indices of the media and r and t are reflection and transmission coefficients, respectively.

At the first interface ($z = 0$):

$$1 + r = a + \bar{a} \quad (20)$$

$$n_1(1 - r) = (a - \bar{a})n_2 + (1 + r)\sigma \sqrt{\frac{\epsilon_0}{\mu_0}} \quad (21)$$

At the second interface ($z = t$):

$$ae^{ikt} + \bar{a}e^{-ikt} = te^{ikt} \quad (22)$$

$$n_2(ae^{ikt} - \bar{a}e^{-ikt}) = tn_3e^{ikt} \quad (23)$$

Multiply equation (22) by n_3 :

$$a = \frac{a(n_2 - n_3)}{n_2 + n_3} e^{2ikt} \quad (24)$$

Substituting $\frac{(n_2 - n_3)}{n_2 + n_3} = r_{23}$ and introducing in equation (21):

$$r = \frac{(n_1 - \sigma \sqrt{\mu_0/\epsilon_0}) \cdot (1 + r_{23}e^{2ikt}) - n_2(1 - r_{23}e^{2ikt})}{(n_1 + \sigma \sqrt{\mu_0/\epsilon_0}) \cdot (1 + r_{23}e^{2ikt}) + n_2(1 - r_{23}e^{2ikt})} \quad (25)$$

References

- [1] F.H.L. Koppens, T. Mueller, P. Avouris, A.C. Ferrari, M.S. Vitiello, M. Polini, Photodetectors based on graphene, other two-dimensional materials and hybrid systems, *Nat. Nanotechnol.* 9 (2014) 780–793. doi:10.1038/nnano.2014.215.
- [2] K.F. Mak, J. Shan, Photonics and optoelectronics of 2D semiconductor transition metal dichalcogenides, *Nat. Photonics.* 10 (2016) 216–226. doi:10.1038/nphoton.2015.282.
- [3] G.R. Bhimanapati, Z. Lin, V. Meunier, Y. Jung, J. Cha, S. Das, D. Xiao, Y. Son, M.S. Strano, V.R. Cooper, L. Liang, S.G. Louie, E. Ringe, W. Zhou, S.S. Kim, R.R. Naik, B.G. Sumpter, H. Terrones, F. Xia, Y. Wang, J. Zhu, D. Akinwande, N. Alem, J.A. Schuller, R.E. Schaak, M. Terrones, J.A. Robinson, Recent Advances in Two-Dimensional Materials beyond Graphene, *ACS Nano.* 9 (2015) 11509–11539. doi:10.1021/acs.nano.5b05556.
- [4] F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, Graphene photonics and optoelectronics, *Nat. Photonics.* 4 (2010) 611–622. doi:10.1038/nphoton.2010.186.
- [5] F. Xia, H. Wang, D. Xiao, M. Dubey, A. Ramasubramaniam, Two-dimensional material nanophotonics, *Nat. Photonics.* 8 (2014) 899–907. doi:10.1038/nphoton.2014.271.
- [6] Q. Bao, K.P. Loh, Graphene photonics, plasmonics, and broadband optoelectronic devices., *ACS Nano.* 6 (2012) 3677–94. doi:10.1021/nn300989g.
- [7] A.C. Ferrari, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems, *Nanoscale.* 7 (2014) 4598–4810. doi:10.1039/C4NR01600A.
- [8] P. Avouris, S. Member, M. Freitag, A.S.P. Excitations, Graphene Photonics, Plasmonics, and Optoelectronics, 20 (2014). file:///Users/Niva/Library/Application Support/Mendeley Desktop/Downloaded/Avouris et al. - 2014 - Graphene Photonics, Plasmonics, and Optoelectronics.pdf.
- [9] Z. Sun, H. Chang, Graphene and graphene-like two-dimensional materials in photodetection: mechanisms and methodology., *ACS Nano.* 8 (2014) 4133–56. doi:10.1021/nn500508c.
- [10] T. Low, P. Avouris, Graphene plasmonics for terahertz to mid-infrared applications., *ACS Nano.* 8 (2014) 1086–101. doi:10.1021/nn406627u.
- [11] B.E.A. Saleh, M.C. Teich, Fundamentals of photonics, Wiley-Interscience, 2007.
- [12] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, J. Hone, Boron nitride substrates for high-quality graphene electronics., *Nat. Nanotechnol.* 5 (2010) 722–6. doi:10.1038/nnano.2010.172.
- [13] F. Schwierz, Graphene transistors, *Nat. Nanotechnol.* 5 (2010) 487–496. doi:10.1038/nnano.2010.89.
- [14] N.T.T. Network, I. Laboratories, N.Z.T.P. Laboratories, M.- Wakamiya, High Speed InPDnGaAs Uni-Traveling-Carrier Photodiodes, (n.d.) 3–6.
- [15] Y. Ishikawa, K. Wada, Near-Infrared ge photodiodes for Si photonics: Operation

- frequency and an approach for the future, *IEEE Photonics J.* 2 (2010) 306–320. doi:10.1109/JPHOT.2010.2046026.
- [16] F. Xia, T. Mueller, Y.-M. Lin, A. Valdes-Garcia, P. Avouris, Ultrafast graphene photodetector., *Nat. Nanotechnol.* 4 (2009) 839–43. doi:10.1038/nnano.2009.292.
 - [17] I. Meric, M.Y. Han, A.F. Young, B. Ozyilmaz, P. Kim, K.L. Shepard, Current saturation in zero-bandgap, top-gated graphene field-effect transistors, *Nat. Nanotechnol.* 3 (2008) 654–659. doi:10.1038/nnano.2008.268.
 - [18] T. Mueller, F. Xia, P. Avouris, Graphene photodetectors for high-speed optical communications, *Nat. Photonics.* 4 (2010) 297–301. doi:10.1038/nphoton.2010.40.
 - [19] I. Gierz, J.C. Petersen, M. Mitrano, C. Cacho, I.C.E. Turcu, E. Springate, A. Stöhr, A. Köhler, U. Starke, A. Cavalleri, Snapshots of non-equilibrium Dirac carrier distributions in graphene, *Nat. Mater.* 12 (2013) 1119–1124. doi:10.1038/nmat3757.
 - [20] J.C. Johansson, S.S. Ulstrup, F. Cilento, A. Crepaldi, M. Zacchigna, C. Cacho, I.C.E. Turcu, E. Springate, F. Fromm, C. Roidel, T. Seyller, F. Parmigiani, M. Grioni, P. Hofmann, Direct view of hot carrier dynamics in graphene, *Phys. Rev. Lett.* 111 (2013) 27403. doi:10.1103/PhysRevLett.111.027403.
 - [21] P.J. Hale, S.M. Horne, J. Moger, D.W. Horsell, E. Hendry, Hot phonon decay in supported and suspended exfoliated graphene, *Phys. Rev. B - Condens. Matter Mater. Phys.* 83 (2011) 4–7. doi:10.1103/PhysRevB.83.121404.
 - [22] H. Wang, J.H. Strait, P.A. George, S. Shivaraman, V.B. Shields, M. Chandrashekar, J. Hwang, F. Rana, M.G. Spencer, C.S. Ruiz-Vargas, J. Park, Ultrafast relaxation dynamics of hot optical phonons in graphene, *Appl. Phys. Lett.* 96 (2010). doi:10.1063/1.3291615.
 - [23] J.C.W. Song, L.S. Levitov, Energy flows in graphene: hot carrier dynamics and cooling, *J. Phys. Condens. Matter.* 27 (2015) 164201. doi:10.1088/0953-8984/27/16/164201.
 - [24] J.K. Viljas, T.T. Heikkilä, Electron-phonon heat transfer in monolayer and bilayer graphene, *Phys. Rev. B - Condens. Matter Mater. Phys.* 81 (2010) 1–9. doi:10.1103/PhysRevB.81.245404.
 - [25] J.C.W. Song, M.S. Rudner, C.M. Marcus, L.S. Levitov, Hot carrier transport and photocurrent response in graphene., *Nano Lett.* 11 (2011) 4688–92. doi:10.1021/nl202318u.
 - [26] X. Xu, N.M. Gabor, J.S. Alden, A.M. van der Zande, P.L. McEuen, Photo-thermoelectric effect at a graphene interface junction., *Nano Lett.* 10 (2010) 562–6. doi:10.1021/nl903451y.
 - [27] M. Freitag, T. Low, P. Avouris, Increased responsivity of suspended graphene photodetectors., *Nano Lett.* 13 (2013) 1644–8. doi:10.1021/nl4001037.
 - [28] C.H. Liu, N.M. Dissanayake, S. Lee, K. Lee, Z. Zhong, Evidence for extraction of photoexcited hot carriers from graphene, *ACS Nano.* 6 (2012) 7172–7176. doi:10.1021/nn302227r.
 - [29] M.C. Lemme, F.H.L. Koppens, A.L. Falk, M.S. Rudner, H. Park, L.S. Levitov, C.M. Marcus, Gate-activated photoresponse in a graphene p-n junction., *Nano Lett.* 11 (2011) 4134–7. doi:10.1021/nl2019068.
 - [30] N.M. Gabor, J.C.W. Song, Q. Ma, N.L. Nair, T. Taychatanapat, K. Watanabe, T.

- Taniguchi, L.S. Levitov, P. Jarillo-Herrero, Hot carrier-assisted intrinsic photoresponse in graphene., *Science*. 334 (2011) 648–52. doi:10.1126/science.1211384.
- [31] T. Mueller, F. Xia, M. Freitag, J. Tsang, P. Avouris, Role of contacts in graphene transistors: A scanning photocurrent study, *Phys. Rev. B*. 79 (2009) 245430. doi:10.1103/PhysRevB.79.245430.
- [32] E.J.H. Lee, K. Balasubramanian, R.T. Weitz, M. Burghard, K. Kern, Contact and edge effects in graphene devices., *Nat. Nanotechnol.* 3 (2008) 486–90. doi:10.1038/nnano.2008.172.
- [33] M. Freitag, T. Low, F. Xia, P. Avouris, Photoconductivity of biased graphene, *Nat. Photonics*. 7 (2012) 53–59. doi:10.1038/nphoton.2012.314.
- [34] F. Xia, T. Mueller, R. Golizadeh-Mojarad, M. Freitag, Y. Lin, J. Tsang, V. Perebeinos, P. Avouris, Photocurrent imaging and efficient photon detection in a graphene transistor., *Nano Lett.* 9 (2009) 1039–44. doi:10.1021/nl8033812.
- [35] J. Park, Y.H. Ahn, C. Ruiz-Vargas, Imaging of photocurrent generation and collection in single-layer graphene, *Nano Lett.* 9 (2009) 1742–1746. doi:10.1021/nl8029493.
- [36] M. Engel, M. Steiner, A. Lombardo, A.C. Ferrari, H. V. Löhneysen, P. Avouris, R. Krupke, Light–matter interaction in a microcavity-controlled graphene transistor, *Nat. Commun.* 3 (2012) 906. doi:10.1038/ncomms1911.
- [37] A. Pospischil, M. Humer, M.M. Furchi, D. Bachmann, R. Guider, T. Fromherz, T. Mueller, CMOS-compatible graphene photodetector covering all optical communication bands, *Nat. Photonics*. 7 (2013) 892–896. doi:10.1038/nphoton.2013.240.
- [38] T.J. Echtermeyer, L. Britnell, P.K. Jasnós, A. Lombardo, R. V. Gorbachev, A.N. Grigorenko, A.K. Geim, A.C. Ferrari, K.S. Novoselov, Strong plasmonic enhancement of photovoltage in graphene., *Nat. Commun.* 2 (2011) 458. doi:10.1038/ncomms1464.
- [39] M.L. Brongersma, N.J. Halas, P. Nordlander, Plasmon-induced hot carrier science and technology, *Nat. Nanotechnol.* 10 (2015) 25–34. doi:10.1038/nnano.2014.311.
- [40] Y. Liu, R. Cheng, L. Liao, H. Zhou, J. Bai, G. Liu, L. Liu, Y. Huang, X. Duan, A.K. Geim, K.S. Novoselov, A.H.C. Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, F. Schwierz, F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, P. Avouris, J.H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, R.R. Nair, C. Lee, X. Wei, J.W. Kysar, J. Hone, F. Xia, T. Mueller, Y. Lin, A. Valdes-Garcia, P. Avouris, Y.M. Lin, L. Liao, L. Liao, Y. Wu, J. Chauhan, J. Guo, X. Wang, L. Zhi, K. Müllen, F.N. Xia, S. Bae, Z. Sun, S.F. Shi, X.D. Xu, D.C. Ralph, P.L. McEuen, M. Liu, Q. Bao, T. Mueller, F.N.A. Xia, P. Avouris, J.P. Zheng, K.L. Jiao, W.P. Shen, W.A. Anderson, H.S. Kwok, M.A. Khan, J.N. Kuznia, D.T. Olson, M. Blasingame, A.R. Bhattarai, X.S. Li, A. Reina, K.S. Kim, Z. Li, F. Wang, F. Schedin, E.J.H. Lee, K. Balasubramanian, R.T. Weitz, M. Burghard, K. Kern, A. Hohenau, W. Zhou, T.W. Odom, D. Schaadt, B. Feng, E. Yu, P.K. Jain, W.Y. Huang, M.A. El-Sayed, X. Xu, N.M. Gabor, J.S. Alden, A.M. van der Zande, P.L. McEuen, J. Homola, N.L. Rosi, C.A. Mirkin, T. Echtermeyer, Plasmon resonance enhanced multicolour photodetection by graphene, *Nat. Commun.* 2 (2011) 579. doi:10.1038/ncomms1589.
- [41] Z. Fang, Z. Liu, Y. Wang, P.M. Ajayan, P. Nordlander, N.J. Halas, Graphene-Antenna Sandwich Photodetector, *Nano Lett.* 12 (2012) 3808–3813. doi:10.1021/nl301774e.
- [42] Z. Fang, Y. Wang, Z. Liu, A. Schlather, P.M. Ajayan, F.H.L. Koppens, P. Nordlander,

- N.J. Halas, Plasmon-induced doping of graphene., *ACS Nano*. 6 (2012) 10222–10228. doi:10.1021/nn304028b.
- [43] U. Kreibig, M. Vollmer, *Optical Properties of Metal Clusters*, 1995th ed., Springer, 1995. <http://www.amazon.com/dp/3540578366>.
- [44] B. Lamprecht, J.R. Krenn, A. Leitner, F.R. Aussenegg, Particle-plasmon decay-time determination by measuring the optical near-field's autocorrelation: Influence of inhomogeneous line broadening, *Appl. Phys. B Lasers Opt.* 69 (1999) 223–227. doi:10.1007/s003400050798.
- [45] S.A. Maier, H.A. Atwater, Plasmonics: Localization and guiding of electromagnetic energy in metal/dielectric structures, *J. Appl. Phys.* 98 (2005) 11101. doi:10.1063/1.1951057.
- [46] S.A. Maier, *Plasmonics: Fundamentals and Applications*, 1st ed., Springer, 2007. <http://www.amazon.com/dp/0387331506>.
- [47] V. Giannini, A.I. Fernández-Domínguez, S.C. Heck, S.A. Maier, Plasmonic nanoantennas: fundamentals and their use in controlling the radiative properties of nanoemitters., *Chem. Rev.* 111 (2011) 3888–912. doi:10.1021/cr1002672.
- [48] X. Li, D. Xiao, Z. Zhang, Landau damping of quantum plasmons in metal nanostructures, *New J. Phys.* 15 (2013). doi:10.1088/1367-2630/15/2/023011.
- [49] M.I. Stockman, Nanoscience: Dark-hot resonances., *Nature*. 467 (2010) 541–2. doi:10.1038/467541a.
- [50] A. Manjavacas, J.G. Liu, V. Kulkarni, P. Nordlander, Plasmon-induced hot carriers in metallic nanoparticles, *ACS Nano*. 8 (2014) 7630–7638. doi:10.1021/nn502445f.
- [51] H. Inouye, K. Tanaka, I. Tanahashi, K. Hirao, Ultrafast dynamics of nonequilibrium electrons in a gold nanoparticle system, *Phys. Rev. B.* 57 (1998) 11334–11340. doi:10.1103/PhysRevB.57.11334.
- [52] M. Lisowski, P.A. Loukakos, U. Bovensiepen, J. Stähler, C. Gahl, M. Wolf, Ultra-fast dynamics of electron thermalization, cooling and transport effects in Ru(001), *Appl. Phys. A Mater. Sci. Process.* 78 (2004) 165–176. doi:10.1007/s00339-003-2301-7.
- [53] C. Frischorn, M. Wolf, C. Frischkorn, M. Wolf, Femtochemistry at metal surfaces: Nonadiabatic reaction dynamics, *Chem. Rev.* 106 (2006) 4207–4233. doi:10.1021/cr050161r.
- [54] M.W. Knight, H. Sobhani, P. Nordlander, N.J. Halas, Photodetection with active optical antennas., *Science*. 332 (2011) 702–4. doi:10.1126/science.1203056.
- [55] A. Giugni, B. Torre, A. Toma, M. Francardi, M. Malerba, A. Alabastri, R. Proietti Zaccaria, M.I. Stockman, E. Di Fabrizio, Hot-electron nanoscopy using adiabatic compression of surface plasmons, *Nat. Nanotechnol.* 8 (2013) 845–852. doi:10.1038/nnano.2013.207.
- [56] I. Goykhman, B. Desiatov, J. Khurgin, J. Shappir, U. Levy, Waveguide based compact silicon Schottky photodetector with enhanced responsivity in the telecom spectral band, *Opt. Express*. 20 (2012) 28594. doi:10.1364/OE.20.028594.
- [57] B.Y. Zheng, H. Zhao, A. Manjavacas, M. McClain, P. Nordlander, N.J. Halas, Distinguishing between plasmon-induced and photoexcited carriers in a device geometry, *Nat. Commun.* 6 (2015) 7797. doi:10.1038/ncomms8797.

- [58] K.S. Novoselov, A.K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, A.A. Firsov, Electric Field Effect in Atomically Thin Carbon Films, *Science* (80-.). 306 (2004) 666–669. doi:10.1126/science.1102896.
- [59] A.K.K. Geim, K.S.S. Novoselov, The Rise of Graphene, *Nat. Mater.* 6 (2007) 183–91. doi:10.1038/nmat1849.
- [60] A.H.. Castro Neto, N.M.R.. Peres, K.S.. Novoselov, A.K.. Geim, F. Guinea, The electronic properties of graphene, *Rev. Mod. Phys.* 81 (2009) 109–162. doi:10.1103/RevModPhys.81.109.
- [61] Carbon Nanotube And Graphene Device Physics | Electronic, optoelectronic devices, and nanotechnology | Cambridge University Press, (n.d.). <http://www.cambridge.org/gb/academic/subjects/engineering/electronic-optoelectronic-devices-and-nanotechnology/carbon-nanotube-and-graphene-device-physics> (accessed July 8, 2014).
- [62] R. Saito, G. Dresselhaus, M. Dresselhaus, *Physical Properties of Carbon Nanotubes*, 1998.
- [63] M.O. Goerbig, Electronic properties of graphene in a strong magnetic field, 2011. doi:10.1103/RevModPhys.83.1193.
- [64] P. Venezuela, M. Lazzeri, F. Mauri, Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands, *Phys. Rev. B - Condens. Matter Mater. Phys.* 84 (2011) 1–25. doi:10.1103/PhysRevB.84.035433.
- [65] J. Maultzsch, S. Reich, C. Thomsen, H. Requardt, P. Ordejón, Phonon Dispersion in Graphite, *Phys. Rev. Lett.* 92 (2004) 75501. doi:10.1103/PhysRevLett.92.075501.
- [66] V. Ryzhii, M. Ryzhii, Graphene bilayer field-effect phototransistor for terahertz and infrared detection, *Phys. Rev. B - Condens. Matter Mater. Phys.* 79 (2009) 1–8. doi:10.1103/PhysRevB.79.245311.
- [67] H. Yan, X. Li, B. Chandra, G. Tulevski, Y. Wu, M. Freitag, W. Zhu, P. Avouris, F. Xia, Tunable infrared plasmonic devices using graphene/insulator stacks, *Nat. Nanotechnol.* 7 (2012) 330–334. doi:10.1038/nnano.2012.59.
- [68] R.R. Nair, P. Blake, A.N. Grigorenko, K.S. Novoselov, T.J. Booth, T. Stauber, N.M.R. Peres, A.K. Geim, Fine structure constant defines visual transparency of graphene., *Science*. 320 (2008) 1308. doi:10.1126/science.1156965.
- [69] A. Kuzmenko, E. van Heumen, D. van der Marel, F. Carbone, Universal Optical Conductance of Graphite, *Phys. Rev. Lett.* 100 (2008) 117401. doi:10.1103/PhysRevLett.100.117401.
- [70] F.J. Nelson, V.K. Kamineni, T. Zhang, E.S. Comfort, J.U. Lee, A.C. Diebold, Optical properties of large-area polycrystalline chemical vapor deposited graphene by spectroscopic ellipsometry, *Appl. Phys. Lett.* 97 (2010) 253110. doi:10.1063/1.3525940.
- [71] F. Wang, Y. Zhang, C. Tian, C. Girit, A. Zettl, M. Crommie, Y.R. Shen, Gate-variable optical transitions in graphene., *Science*. 320 (2008) 206–209. doi:10.1126/science.1152793.
- [72] C. Casiraghi, A. Hartschuh, E. Lidorikis, H. Qian, H. Harutyunyan, T. Gokus, K.S. Novoselov, A.C. Ferrari, Rayleigh Imaging of Graphene and Graphene Layers, *Arxiv*.

- (2007) 8. doi:10.1021/nl071168m.
- [73] P. Blake, E.W. Hill, Making graphene visible, *Appl. Phys. Lett.* 91 (2007) 63124. doi:10.1063/1.2768624.
 - [74] E. Malic, A. (Physicist) Knorr, S. Winnerl, Graphene and carbon nanotubes : ultrafast relaxation dynamics and optics, Wiley, 2013.
 - [75] T. Plötzing, T. Winzer, E. Malic, D. Neumaier, A. Knorr, H. Kurz, Experimental verification of carrier multiplication in graphene, *Nano Lett.* 14 (2014) 5371–5375. doi:10.1021/nl502114w.
 - [76] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, Raman spectroscopy in graphene, *Phys. Rep.* 473 (2009) 51–87. doi:10.1016/j.physrep.2009.02.003.
 - [77] R. Bistritzer, A.H. MacDonald, Electronic Cooling in Graphene, *Phys. Rev. Lett.* 102 (2009) 206410. doi:10.1103/PhysRevLett.102.206410.
 - [78] M.W. Graham, S.-F. Shi, D.C. Ralph, J. Park, P.L. McEuen, Photocurrent measurements of supercollision cooling in graphene, *Nat. Phys.* 9 (2012) 103–108. doi:10.1038/nphys2493.
 - [79] K.J. Tielrooij, J.C.W. Song, S.A. Jensen, A. Centeno, A. Pesquera, A. Zurutuza Elorza, M. Bonn, L.S. Levitov, F.H.L. Koppens, Photoexcitation cascade and multiple hot-carrier generation in graphene, *Nat. Phys.* 9 (2013) 248–252. doi:10.1038/nphys2564.
 - [80] L. Huang, G. V Hartland, L.-Q. Chu, Luxmi, R.M. Feenstra, C. Lian, K. Tahy, H. Xing, Ultrafast transient absorption microscopy studies of carrier dynamics in epitaxial graphene., *Nano Lett.* 10 (2010) 1308–13. doi:10.1021/nl904106t.
 - [81] J.M. Iglesias, M.J. Martín, E. Pascual, R. Rengel, Hot carrier and hot phonon coupling during ultrafast relaxation of photoexcited electrons in graphene, *Appl. Phys. Lett.* 108 (2016) 43105. doi:10.1063/1.4940902.
 - [82] J.C.W. Song, M.Y. Reizer, L.S. Levitov, Disorder-assisted electron-phonon scattering and cooling pathways in graphene., *Phys. Rev. Lett.* 109 (2012) 106602. doi:10.1103/PhysRevLett.109.106602.
 - [83] M.W. Graham, S.-F. Shi, Z. Wang, D.C. Ralph, J. Park, P.L. McEuen, Transient absorption and photocurrent microscopy show that hot electron supercollisions describe the rate-limiting relaxation step in graphene., *Nano Lett.* 13 (2013) 5497–502. doi:10.1021/nl4030787.
 - [84] Z. Mics, K.-J.J. Tielrooij, K. Parvez, S.A. Jensen, I. Ivanov, X. Feng, K. Müllen, M. Bonn, D. Turchinovich, K.S. Novoselov, R.R. Nair, A.H.C. Neto, F. Guinea, N.M.R. Peres, K.S. Novoselov, A.K. Geim, S. Das Sarma, S. Adam, E.H. Hwang, E. Rossi, F. Bonaccorso, Z. Sun, T. Hasan, A.C. Ferrari, P. Avouris, Z. Chen, V. Perebeinos, F. Xia, T. Mueller, Y.-M. Lin, A. Valdes-Garcia, P. Avouris, X. Gan, F. Schwierz, Y. Wu, L. Wang, Y. Hao, C.J. Docherty, S. Boubanga-Tombet, M. Mittendorff, X. Cai, L. Ju, P. Alonso-Gonzalez, B. Sensale-Rodriguez, G. Jnawali, Y. Rao, H. Yan, T.F. Heinz, H.Y. Hwang, M.J. Paul, M.J. Paul, T. Kampfrath, K. Tanaka, K.A. Nelson, D. Turchinovich, J.M. Hvam, M.C. Hoffmann, Y. Mukai, H. Hirori, K. Tanaka, R. Ulbricht, E. Hendry, J. Shan, T.F. Heinz, M. Bonn, X. Li, V.N. Kotov, B. Uchoa, V.M. Pereira, F. Guinea, A.H.C. Neto, M. Breusing, D. Brida, K.-J.J. Tielrooij, I. Gierz, J.C. Johannsen, S.A. Jensen, J.C.W. Song, K.-J.J. Tielrooij, F.H.L. Koppens, L.S. Levitov, L.A. Falkovsky, S.S. Pershoguba, A.J. Frenzel, C.H. Lui, Y.C. Shin, J. Kong, N. Gedik, E.H. Hwang, S. Das Sarma, S. Winnerl, J.C.W. Song, M.Y. Reizer, L.S.

- Levitov, S. Tani, F. Blanchard, K. Tanaka, S. Shi, A.J. Frenzel, E. Malic, T. Winzer, E. Bobkin, A. Knorr, T. Winzer, A. Knorr, E. Malic, D. Sun, R. Cheng, N.M. Gabor, M.C. Hoffmann, B.S. Monozon, D. Livshits, E.U. Rafailov, D. Turchinovich, M.C. Hoffmann, D. Turchinovich, Thermodynamic picture of ultrafast charge transport in graphene., *Nat. Commun.* 6 (2015) 7655. doi:10.1038/ncomms8655.
- [85] J.C. Johanness, S. Ulstrup, A. Crepaldi, F. Cilento, M. Zacchigna, J.A. Miwa, C. Cacho, R.T. Chapman, E. Springate, F. Fromm, C. Ridel, T. Seyller, P.D.C. King, F. Parmigiani, M. Grioni, P. Hofmann, Tunable carrier multiplication and cooling in graphene, *Nano Lett.* 15 (2015) 326–331. doi:10.1021/nl503614v.
- [86] P. a George, J. Strait, J. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, M.G. Spencer, Ultrafast Optical-Pump Terahertz-Probe Spectroscopy of the Carrier Relaxation and Recombination Dynamics in Epitaxial Graphene, *Nano Lett.* 8 (2008) 4248–4251. doi:10.1021/nl8019399.
- [87] F. Rana, P.A. George, J.H. Strait, J. Dawlaty, S. Shivaraman, M. Chandrashekhar, M.G. Spencer, Carrier recombination and generation rates for intravalley and intervalley phonon scattering in graphene, *Phys. Rev. B - Condens. Matter Mater. Phys.* 79 (2009) 1–5. doi:10.1103/PhysRevB.79.115447.
- [88] J.M. Dawlaty, S. Shivaraman, M. Chandrashekhar, F. Rana, M.G. Spencer, Measurement of ultrafast carrier dynamics in epitaxial graphene, *Appl. Phys. Lett.* 92 (2008). doi:10.1063/1.2837539.
- [89] K.M. Dani, J. Lee, R. Sharma, A.D. Mohite, C.M. Galande, P.M. Ajayan, A.M. Dattelbaum, H. Htoon, A.J. Taylor, R.P. Prasankumar, Intraband conductivity response in graphene observed using ultrafast infrared-pump visible-probe spectroscopy, *Phys. Rev. B - Condens. Matter Mater. Phys.* 86 (2012) 1–7. doi:10.1103/PhysRevB.86.125403.
- [90] D. Sun, C. Divin, C. Berger, W.A. de Heer, P.N. First, T.B. Norris, Spectroscopic Measurement of Interlayer Screening in Multilayer Epitaxial Graphene, *Phys. Rev. Lett.* 104 (2010) 136802. doi:10.1103/PhysRevLett.104.136802.
- [91] S. Winnerl, M. Orlita, P. Plochocka, P. Kossacki, M. Potemski, T. Winzer, E. Malic, A. Knorr, M. Sprinkle, C. Berger, W.A. De Heer, H. Schneider, M. Helm, Carrier relaxation in epitaxial graphene photoexcited near the dirac point, *Phys. Rev. Lett.* 107 (2011) 2–6. doi:10.1103/PhysRevLett.107.237401.
- [92] T. Limmer, J. Feldmann, E. Da Como, Carrier lifetime in exfoliated few-layer graphene determined from intersubband optical transitions, *Phys. Rev. Lett.* 110 (2013) 1–5. doi:10.1103/PhysRevLett.110.217406.
- [93] S.-F. Shi, T.-T. Tang, B. Zeng, L. Ju, Q. Zhou, A. Zettl, F. Wang, Controlling graphene ultrafast hot carrier response from metal-like to semiconductor-like by electrostatic gating., *Nano Lett.* 14 (2014) 1578–82. doi:10.1021/nl404826r.
- [94] S. Tani, F. Blanchard, K. Tanaka, Ultrafast carrier dynamics in graphene under a high electric field, *Phys. Rev. Lett.* 109 (2012) 1–5. doi:10.1103/PhysRevLett.109.166603.
- [95] B.A. Ruzicka, S. Wang, L.K. Werake, B. Weintrub, K.P. Loh, H. Zhao, Hot carrier diffusion in graphene, *Phys. Rev. B.* 82 (2010) 195414. doi:10.1103/PhysRevB.82.195414.
- [96] B.A. Ruzicka, S. Wang, J. Liu, K.-P. Loh, J.Z. Wu, H. Zhao, Spatially resolved pump-probe study of single-layer graphene produced by chemical vapor deposition [Invited],

- Opt. Mater. Express. 2 (2012) 708. doi:10.1364/OME.2.000708.
- [97] C.W. Luo, P.S. Tseng, H.-J. Chen, K.H. Wu, L.J. Li, Dirac fermion relaxation and energy loss rate near the Fermi surface in monolayer and multilayer graphene., *Nanoscale*. 6 (2014) 8575–8. doi:10.1039/c4nr02205j.
 - [98] J. Yan, M.-H. Kim, J.A. Elle, A.B. Sushkov, G.S. Jenkins, H.M. Milchberg, M.S. Fuhrer, H.D. Drew, Dual-gated bilayer graphene hot-electron bolometer, *Nat. Nanotechnol.* 7 (2012) 472–478. doi:10.1038/nnano.2012.88.
 - [99] G. Konstantatos, M. Badioli, L. Gaudreau, J. Osmond, M. Bernechea, F.P. Garcia de Arquer, F. Gatti, F.H.L. Koppens, Hybrid graphene-quantum dot phototransistors with ultrahigh gain., *Nat. Nanotechnol.* 7 (2012) 363–8. doi:10.1038/nnano.2012.60.
 - [100] L. Ju, J. Velasco, E. Huang, S. Kahn, C. Nosisgia, H.-Z. Tsai, W. Yang, T. Taniguchi, K. Watanabe, Y. Zhang, G. Zhang, M. Crommie, A. Zettl, F. Wang, Photoinduced doping in heterostructures of graphene and boron nitride., *Nat. Nanotechnol.* 9 (2014) 348–52. doi:10.1038/nnano.2014.60.
 - [101] L. Vicarelli, M.S. Vitiello, D. Coquillat, A. Lombardo, A.C. Ferrari, W. Knap, M. Polini, V. Pellegrini, A. Tredicucci, Graphene field-effect transistors as room-temperature terahertz detectors, *Nat. Mater.* 11 (2012) 1–7. doi:10.1038/nmat3417.
 - [102] P.A. Khomyakov, G. Giovannetti, P.C. Rusu, G. Brocks, J. Van Den Brink, P.J. Kelly, First-principles study of the interaction and charge transfer between graphene and metals, *Phys. Rev. B - Condens. Matter Mater. Phys.* 79 (2009) 1–12. doi:10.1103/PhysRevB.79.195425.
 - [103] H. Sojoudi, J. Baltazar, L.M. Tolbert, C.L. Henderson, S. Graham, Creating graphene p-n junctions using self-assembled monolayers., *ACS Appl. Mater. Interfaces*. 4 (2012) 4781–6. doi:10.1021/am301138v.
 - [104] E.C. Peters, E.J.H. Lee, M. Burghard, K. Kern, Gate dependent photocurrents at a graphene p-n junction, *Appl. Phys. Lett.* 97 (2010) 193102. doi:10.1063/1.3505926.
 - [105] Y.M. Zuev, W. Chang, P. Kim, Thermoelectric and magnetothermoelectric transport measurements of graphene., *Phys. Rev. Lett.* 102 (2009) 96807. doi:10.1103/PhysRevLett.102.096807.
 - [106] J.F. Sierra, I. Neumann, M. V Costache, S.O. Valenzuela, Hot-Carrier Seebeck Effect: Diffusion and Remote Detection of Hot Carriers in Graphene., *Nano Lett.* (2015). doi:10.1021/acs.nanolett.5b00922.
 - [107] F. Schedin, E. Lidorikis, A. Lombardo, V.G. Kravets, A.K. Geim, A.N. Grigorenko, K.S. Novoselov, A.C. Ferrari, Surface-enhanced Raman spectroscopy of graphene., *ACS Nano*. 4 (2010) 5617–26. doi:10.1021/nn1010842.
 - [108] J. Mertens, A.L. Eiden, D.O. Sigle, F. Huang, A. Lombardo, Z. Sun, R.S. Sundaram, A. Colli, C. Tserkezis, J. Aizpurua, S. Milana, A.C. Ferrari, J.J. Baumberg, Controlling subnanometer gaps in plasmonic dimers using graphene., *Nano Lett.* 13 (2013) 5033–8. doi:10.1021/nl4018463.
 - [109] A.M. Gilbertson, Y. Francescato, T. Roschuk, V. Shautsova, Y. Chen, T.P.H. Sidiropoulos, M. Hong, V. Giannini, S.A. Maier, L.F. Cohen, R.F. Oulton, Plasmon-Induced Optical Anisotropy in Hybrid Graphene–Metal Nanoparticle Systems, *Nano Lett.* 15 (2015) 3458–3464. doi:10.1021/acs.nanolett.5b00789.
 - [110] P. Avouris, C. Dimitrakopoulos, Graphene: Synthesis and applications, *Mater. Today*.

- 15 (2012) 86–97. doi:10.1016/S1369-7021(12)70044-5.
- [111] L. Chen, Y. Hernandez, X. Feng, K. Müllen, From nanographene and graphene nanoribbons to graphene sheets: Chemical synthesis, *Angew. Chemie - Int. Ed.* 51 (2012) 7640–7654. doi:10.1002/anie.201201084.
- [112] D.S. Lee, C. Riedl, B. Krauss, K. Von Klitzing, U. Starke, J.H. Smet, Raman spectra of epitaxial graphene on SiC and of epitaxial graphene transferred to SiO₂, *Nano Lett.* 8 (2008) 4320–4325. doi:10.1021/nl802156w.
- [113] A.J. Van Bommel, J.E. Crombeen, A. Van Tooren, LEED and Auger electron observations of the SiC(0001) surface, *Surf. Sci.* 48 (1975) 463–472. doi:10.1016/0039-6028(75)90419-7.
- [114] X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S.K. Banerjee, L. Colombo, R.S. Ruoff, Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils, *Science* (80-.). 324 (2009) 1312–1314. doi:10.1126/science.1171245.
- [115] K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B.H. Hong, Large-scale pattern growth of graphene films for stretchable transparent electrodes., *Nature.* 457 (2009) 706–10. doi:10.1038/nature07719.
- [116] K.S. Novoselov, V.I. Fal'ko, L. Colombo, P.R. Gellert, M.G. Schwab, K. Kim, A roadmap for graphene, *Nature.* 490 (2012) 192–200. doi:10.1038/nature11458.
- [117] D. Waldmann, J. Jobst, F. Speck, T. Seyller, M. Krieger, H.B. Weber, Bottom-gated epitaxial graphene, *Nat. Mater.* 10 (2011) 357–360. doi:10.1038/nmat2988.
- [118] S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y. Il Song, Y.-J. Kim, K.S. Kim, B. Ozyilmaz, J.-H. Ahn, B.H. Hong, S. Iijima, Roll-to-roll production of 30-inch graphene films for transparent electrodes., *Nat. Nanotechnol.* 5 (2010) 574–8. doi:10.1038/nnano.2010.132.
- [119] Z.T. Wu, W.W. Zhao, W.Y. Chen, J. Jiang, H.Y. Nan, X.T. Guo, Z. Liang, Y.M. Chen, Y.F. Chen, Z.H. Ni, The influence of chemical solvents on the properties of CVD graphene, *J. Raman Spectrosc.* 46 (2015) 21–24. doi:10.1002/jrs.4582.
- [120] T. Yoon, W.C. Shin, T.-S.Y.S. Kim, J.H. Mun, T.-S.Y.S. Kim, B.J. Cho, Direct measurement of adhesion energy of monolayer graphene as-grown on copper and its application to renewable transfer process., *Nano Lett.* 12 (2012) 1448–1452. doi:10.1021/nl204123h.
- [121] E.H. Lock, M. Baraket, M. Laskoski, S.P. Mulvaney, W.K. Lee, P.E. Sheehan, D.R. Hines, J.T. Robinson, J. Tosado, M.S. Fuhrer, S.C. Hernández, S.G. Walton, High-quality uniform dry transfer of graphene to polymers, *Nano Lett.* 12 (2012) 102–107. doi:10.1021/nl203058s.
- [122] P. Gupta, P.D. Dongare, S. Grover, S. Dubey, H. Mamgain, A. Bhattacharya, M.M. Deshmukh, A facile process for soak-and-peel delamination of CVD graphene from substrates using water., *Sci. Rep.* 4 (2014) 3882. doi:10.1038/srep03882.
- [123] J.W. Suk, A. Kitt, C.W. Magnuson, Y. Hao, S. Ahmed, J. An, A.K. Swan, B.B. Goldberg, R.S. Ruoff, Transfer of CVD-grown monolayer graphene onto arbitrary substrates., *ACS Nano.* 5 (2011) 6916–24. doi:10.1021/nn201207c.
- [124] J. Song, F.-Y. Kam, R.-Q. Png, W.-L. Seah, J.-M. Zhuo, G.-K. Lim, P.K.H. Ho, L.-L. Chua, A general method for transferring graphene onto soft surfaces., *Nat.*

- Nanotechnol. 8 (2013) 356–62. doi:10.1038/nnano.2013.63.
- [125] H.H. Kim, Y. Chung, E. Lee, S.K. Lee, K. Cho, Water-free transfer method for CVD-grown graphene and its application to flexible air-stable graphene transistors., *Adv. Mater.* 26 (2014) 3213–7. doi:10.1002/adma.201305940.
 - [126] X. Liang, B.A. Sperling, I. Calizo, G. Cheng, C.A. Hacker, Q. Zhang, Y. Obeng, K. Yan, H. Peng, Q. Li, X. Zhu, H. Yuan, A.R.H. Walker, Z. Liu, L.-M. Peng, C.A. Richter, Toward clean and crackless transfer of graphene., *ACS Nano.* 5 (2011) 9144–53. doi:10.1021/nn203377t.
 - [127] S. Ryu, L. Liu, S. Berciaud, Y.-J. Yu, H. Liu, P. Kim, G.W. Flynn, L.E. Brus, Atmospheric oxygen binding and hole doping in deformed graphene on a SiO₂ substrate., *Nano Lett.* 10 (2010) 4944–51. doi:10.1021/nl1029607.
 - [128] N. Petrone, C.R. Dean, I. Meric, A.M. van der Zande, P.Y. Huang, L. Wang, D. Muller, K.L. Shepard, J. Hone, Chemical vapor deposition-derived graphene with electrical performance of exfoliated graphene., *Nano Lett.* 12 (2012) 2751–6. doi:10.1021/nl204481s.
 - [129] S.J. Kang, B. Kim, K.S. Kim, Y. Zhao, Z. Chen, G.H. Lee, J. Hone, P. Kim, C. Nuckolls, Inking Elastomeric Stamps with Micro-Patterned, Single Layer Graphene to Create High-Performance OFETs, *Adv. Mater.* 23 (2011) 3531–3535. doi:10.1002/adma.201101570.
 - [130] X. Li, Y. Zhu, W. Cai, M. Borysiak, B. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, Transfer of large-area graphene films for high-performance transparent conductive electrodes., *Nano Lett.* 9 (2009) 4359–63. doi:10.1021/nl902623y.
 - [131] M. Ishigami, J.H. Chen, W.G. Cullen, M.S. Fuhrer, E.D. Williams, Atomic structure of graphene on SiO₂., *Nano Lett.* 7 (2007) 1643–8. doi:10.1021/nl070613a.
 - [132] Y.-C. Lin, C. Jin, J.-C. Lee, S.-F. Jen, K. Suenaga, P.-W. Chiu, Clean transfer of graphene for isolation and suspension., *ACS Nano.* 5 (2011) 2362–8. doi:10.1021/nn200105j.
 - [133] Z. Cheng, Q. Zhou, C. Wang, Q. Li, C. Wang, Y. Fang, Toward intrinsic graphene surfaces: a systematic study on thermal annealing and wet-chemical treatment of SiO₂-supported graphene devices., *Nano Lett.* 11 (2011) 767–71. doi:10.1021/nl103977d.
 - [134] Y. Dan, Y. Lu, N.J. Kybert, Z. Luo, A.T.C. Johnson, Intrinsic response of graphene vapor sensors., *Nano Lett.* 9 (2009) 1472–5. doi:10.1021/nl8033637.
 - [135] A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C.W. Magnuson, S. McDonnell, L. Colombo, E.M. Vogel, R.S. Ruoff, R.M. Wallace, The effect of chemical residues on the physical and electrical properties of chemical vapor deposited graphene transferred to SiO₂, *Appl. Phys. Lett.* 99 (2011) 122108. doi:10.1063/1.3643444.
 - [136] W. Regan, N. Alem, B. Alemán, B. Geng, C. Girit, L. Maserati, F. Wang, M. Crommie, A. Zettl, B. Alemán, B. Geng, B. Alemán, B. Geng, C. Girit, L. Maserati, F. Wang, M. Crommie, A. Zettl, A direct transfer of layer-area graphene, *Appl. Phys. Lett.* 96 (2010) 113102. doi:10.1063/1.3337091.
 - [137] W.-H. Lin, T.-H. Chen, J.-K. Chang, J.-I. Taur, Y.-Y. Lo, W.-L. Lee, C.-S. Chang, W.-B. Su, C.-I. Wu, A direct and polymer-free method for transferring graphene grown by chemical vapor deposition to any substrate., *ACS Nano.* 8 (2014) 1784–91. doi:10.1021/nn406170d.

- [138] S. Adam, E.H. Hwang, V.M. Galitski, S. Das Sarma, A self-consistent theory for graphene transport., *Proc. Natl. Acad. Sci. U. S. A.* 104 (2007) 18392–7. doi:10.1073/pnas.0704772104.
- [139] J.-H. Chen, C. Jang, S. Adam, M.S. Fuhrer, E.D. Williams, M. Ishigami, Charged-impurity scattering in graphene, *Nat. Phys.* 4 (2008) 377–381. doi:10.1038/nphys935.
- [140] J.-H. Chen, C. Jang, S. Xiao, M. Ishigami, M.S. Fuhrer, Intrinsic and extrinsic performance limits of graphene devices on SiO₂., *Nat. Nanotechnol.* 3 (2008) 206–209. doi:10.1038/nnano.2008.58.
- [141] S. Fratini, F. Guinea, Substrate-limited electron dynamics in graphene, *Phys. Rev. B.* 77 (2008) 195415. doi:10.1103/PhysRevB.77.195415.
- [142] M.. Katsnelson, A.. Geim, Electron scattering on microscopic corrugations in graphene, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 366 (2008) 195–204. doi:10.1098/rsta.2007.2157.
- [143] S. Morozov, K. Novoselov, M. Katsnelson, F. Schedin, D. Elias, J. Jaszczak, A. Geim, Giant Intrinsic Carrier Mobilities in Graphene and Its Bilayer, *Phys. Rev. Lett.* 100 (2008) 16602. doi:10.1103/PhysRevLett.100.016602.
- [144] W.H. Lee, J. Park, Y. Kim, K.S. Kim, B.H. Hong, K. Cho, Control of graphene field-effect transistors by interfacial hydrophobic self-assembled monolayers., *Adv. Mater.* 23 (2011) 3460–4. doi:10.1002/adma.201101340.
- [145] X. Wang, J.-B. Xu, C. Wang, J. Du, W. Xie, High-performance graphene devices on SiO₂/Si substrate modified by highly ordered self-assembled monolayers., *Adv. Mater.* 23 (2011) 2464–8. doi:10.1002/adma.201100476.
- [146] K.H. Lee, H.-J. Shin, J. Lee, I. Lee, G.-H. Kim, J.-Y. Choi, S.-W. Kim, Large-scale synthesis of high-quality hexagonal boron nitride nanosheets for large-area graphene electronics., *Nano Lett.* 12 (2012) 714–8. doi:10.1021/nl203635v.
- [147] V.E. Calado, S.-E. Zhu, S. Goswami, Q. Xu, K. Watanabe, T. Taniguchi, G.C.A.M. Janssen, L.M.K. Vandersypen, Ballistic transport in graphene grown by chemical vapor deposition, *Appl. Phys. Lett.* 104 (2014) 23103. doi:10.1063/1.4861627.
- [148] L. Wang, B. Wu, J. Chen, H. Liu, P. Hu, Y. Liu, Monolayer hexagonal boron nitride films with large domain size and clean interface for enhancing the mobility of graphene-based field-effect transistors., *Adv. Mater.* 26 (2014) 1559–64. doi:10.1002/adma.201304937.
- [149] S.M. Song, B.J. Cho, Investigation of interaction between graphene and dielectrics., *Nanotechnology.* 21 (2010) 335706. doi:10.1088/0957-4484/21/33/335706.
- [150] K. Nagashio, T. Yamashita, T. Nishimura, K. Kita, A. Toriumi, Electrical transport properties of graphene on SiO₂ with specific surface structures, *J. Appl. Phys.* 110 (2011) 24513. doi:10.1063/1.3611394.
- [151] W. Regan, N. Alem, B. Alemán, B. Geng, C. Girit, L. Maserati, F. Wang, M. Crommie, A. Zettl, A direct transfer of layer-area graphene, *Appl. Phys. Lett.* 96 (2010) 113102. doi:10.1063/1.3337091.
- [152] J.R. Ferraro, K. Nakamoto, C.W. Brown, *Introductory Raman spectroscopy*, Academic Press, 2003.
- [153] A.C. Ferrari, D.M. Basko, Raman spectroscopy as a versatile tool for studying the properties of graphene., *Nat. Nanotechnol.* 8 (2013) 235–46.

doi:10.1038/nnano.2013.46.

- [154] R.J. Nemanich, G. Lucovsky, S.A. Solin, Infrared active optical vibrations of graphite, *Solid State Commun.* 23 (1977) 117–120. doi:10.1016/0038-1098(77)90663-9.
- [155] D.M. Basko, S. Piscanec, A.C. Ferrari, Electron-electron interactions and doping dependence of the two-phonon Raman intensity in graphene, *Phys. Rev. B.* 80 (2009) 165413. doi:10.1103/PhysRevB.80.165413.
- [156] C. Thomsen, S. Reich, Double Resonant Raman Scattering in Graphite, *Phys. Rev. Lett.* 85 (2000) 5214–5217. doi:10.1103/PhysRevLett.85.5214.
- [157] Y. Kawashima, G. Katagiri, Fundamentals, overtones, and combinations in the Raman spectrum of graphite, *Phys. Rev. B.* 52 (1995) 10053. doi:10.1103/PhysRevB.52.10053.
- [158] A.C. Ferrari, J.C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, S. Piscanec, D. Jiang, K.S. Novoselov, S. Roth, A.K. Geim, Raman Spectrum of Graphene and Graphene Layers, *Phys. Rev. Lett.* 97 (2006) 187401. doi:10.1103/PhysRevLett.97.187401.
- [159] D. Graf, F. Molitor, K. Ensslin, C. Stampfer, A. Jungen, C. Hierold, L. Wirtz, Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene, *Nano Lett.* 7 (2007) 238–242. doi:10.1021/nl061702a.
- [160] C.H. Lui, T.F. Heinz, Measurement of layer breathing mode vibrations in few-layer graphene, *Phys. Rev. B - Condens. Matter Mater. Phys.* 87 (2013) 1–7. doi:10.1103/PhysRevB.87.121404.
- [161] F. Herziger, P. May, J. Maultzsch, Layer number determination in graphene using out-of-plane vibrations, *Phys. Rev. B.* 1 (2012) 1–5. doi:10.1103/PhysRevB.85.235447.
- [162] a. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Phys. Rev. B.* 61 (2000) 14095–14107. doi:10.1103/PhysRevB.61.14095.
- [163] L.G. Cançado, A. Jorio, E.H.M. Ferreira, F. Stavale, C.A. Achete, R.B. Capaz, M.V.O. Moutinho, A. Lombardo, T.S. Kulmala, A.C. Ferrari, Quantifying defects in graphene via Raman spectroscopy at different excitation energies., *Nano Lett.* 11 (2011) 3190–6. doi:10.1021/nl201432g.
- [164] M.M. Lucchese, F. Stavale, E.H.M. Ferreira, C. Vilani, M.V.O. Moutinho, R.B. Capaz, C. a. Achete, a. Jorio, Quantifying ion-induced defects and Raman relaxation length in graphene, *Carbon N. Y.* 48 (2010) 1592–1597. doi:10.1016/j.carbon.2009.12.057.
- [165] S. Pisana, M. Lazzeri, C. Casiraghi, K.S. Novoselov, A.K. Geim, A.C. Ferrari, F. Mauri, Breakdown of the adiabatic Born–Oppenheimer approximation in graphene, *Nat. Mater.* 6 (2007) 198–201. doi:10.1038/nmat1846.
- [166] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S.K. Saha, U. V. Waghmare, K.S. Novoselov, H.R. Krishnamurthy, A.K. Geim, A.C. Ferrari, A.K. Sood, Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor, *Nat. Nanotechnol.* 3 (2008) 210–215. doi:10.1038/nnano.2008.67.
- [167] J. Yan, Y. Zhang, P. Kim, A. Pinczuk, Electric field effect tuning of electron-phonon coupling in graphene, *Phys. Rev. Lett.* 98 (2007) 1–4. doi:10.1103/PhysRevLett.98.166802.
- [168] W. Zhao, P.H. Tan, J. Liu, A.C. Ferrari, Intercalation of few-layer graphite flakes with

- FeCl₃: Raman determination of Fermi level, layer by layer decoupling, and stability., *J. Am. Chem. Soc.* 133 (2011) 5941–6. doi:10.1021/ja110939a.
- [169] V. Yu, E. Whiteway, J. Maassen, M. Hilke, Raman spectroscopy of the internal strain of a graphene layer grown on copper tuned by chemical vapor deposition, *Phys. Rev. B - Condens. Matter Mater. Phys.* 84 (2011) 1–5. doi:10.1103/PhysRevB.84.205407.
- [170] Y. Xiao, H. Kim, C. Mattevi, M. Chhowalla, R.C. Maher, L.F. Cohen, Influence of Cu substrate topography on the growth morphology of chemical vapour deposited graphene, *Carbon N. Y.* 65 (2013) 7–12. doi:10.1016/j.carbon.2013.06.090.
- [171] L.S. Schadler, C. Galiotis, Fundamentals and applications of micro Raman spectroscopy to strain measurements in fibre reinforced composites, *Int. Mater. Rev.* 40 (1995) 116–134. doi:10.1179/095066095790326094.
- [172] M. Huang, H. Yan, C. Chen, D. Song, T.F. Heinz, J. Hone, Phonon softening and crystallographic orientation of strained graphene studied by Raman spectroscopy, *Proc. Natl. Acad. Sci.* 106 (2009) 7304–7308. doi:10.1073/pnas.0811754106.
- [173] T. Mohiuddin, A. Lombardo, R. Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D. Basko, C. Galiotis, N. Marzari, K. Novoselov, A. Geim, A. Ferrari, Uniaxial strain in graphene by Raman spectroscopy: G peak splitting, Grüneisen parameters, and sample orientation, *Phys. Rev. B.* 79 (2009) 205433. doi:10.1103/PhysRevB.79.205433.
- [174] M. Huang, H. Yan, T.F. Heinz, J. Hone, Probing strain-induced electronic structure change in graphene by Raman spectroscopy, *Nano Lett.* 10 (2010) 4074–4079. doi:10.1021/nl102123c.
- [175] D. Yoon, Y.W. Son, H. Cheong, Strain-dependent splitting of the double-resonance raman scattering band in graphene, *Phys. Rev. Lett.* 106 (2011) 1–4. doi:10.1103/PhysRevLett.106.155502.
- [176] F. Ding, H. Ji, Y. Chen, A. Herklotz, K. Dörr, Y. Mei, A. Rastelli, O.G. Schmidt, Stretchable graphene: a close look at fundamental parameters through biaxial straining., *Nano Lett.* 10 (2010) 3453–8. doi:10.1021/nl101533x.
- [177] M.A. Bissett, M. Tsuji, H. Ago, Strain engineering the properties of graphene and other two-dimensional crystals, *Phys. Chem. Chem. Phys.* 16 (2014) 11124. doi:10.1039/c3cp55443k.
- [178] O. Frank, G. Tsoukleri, I. Riaz, K. Papagelis, J. Parthenios, A.C. Ferrari, A.K. Geim, K.S. Novoselov, C. Galiotis, Development of a universal stress sensor for graphene and carbon fibres, *Nat. Commun.* 2 (2011) 255. doi:10.1038/ncomms1247.
- [179] O. Frank, M. Mohr, J. Maultzsch, C. Thomsen, I. Riaz, R. Jalil, K.S. Novoselov, G. Tsoukleri, J. Parthenios, K. Papagelis, L. Kavan, C. Galiotis, Raman 2D-band splitting in graphene: Theory and experiment, *ACS Nano.* 5 (2011) 2231–2239. doi:10.1021/nn103493g.
- [180] J. Zabel, R.R. Nair, A. Ott, T. Georgiou, A.K. Geim, K.S. Novoselov, C. Casiraghi, Raman spectroscopy of graphene and bilayer under biaxial strain: bubbles and balloons., *Nano Lett.* 12 (2012) 617–21. doi:10.1021/nl203359n.
- [181] Y.C. Cheng, Z.Y. Zhu, G.S. Huang, U. Schwingenschlögl, Grüneisen parameter of the G mode of strained monolayer graphene, *Phys. Rev. B - Condens. Matter Mater. Phys.* 83 (2011) 1–5. doi:10.1103/PhysRevB.83.115449.
- [182] M. Mohr, J. Maultzsch, C. Thomsen, Splitting of the Raman 2 D band of graphene

- p>subjected to strain,
- Phys. Rev. B.*
- 82 (2010) 201409. doi:10.1103/PhysRevB.82.201409.
- [183] S. Berciaud, X. Li, H. Htoon, L.E. Brus, S.K. Doorn, T.F. Heinz, Intrinsic line shape of the Raman 2D-mode in freestanding graphene monolayers, *Nano Lett.* 13 (2013) 3517–3523. doi:10.1021/nl400917e.
 - [184] M. Lazzeri, F. Mauri, Nonadiabatic Kohn anomaly in a doped graphene monolayer, *Phys. Rev. Lett.* 97 (2006) 29–32. doi:10.1103/PhysRevLett.97.266407.
 - [185] G.-H. Lee, R.C. Cooper, S.J. An, S. Lee, A. van der Zande, N. Petrone, A.G. Hammerberg, C. Lee, B. Crawford, W. Oliver, J.W. Kysar, J. Hone, High-strength Chemical-Vapor Deposited Graphene and Grain Boundaries, *Science* (80-.). 340 (2013) 1073–1076. doi:10.1126/science.1235126.
 - [186] J. Zhang, J. Zhao, J. Lu, Intrinsic strength and failure behaviors of graphene grain boundaries, *ACS Nano.* 6 (2012) 2704–2711. doi:10.1021/nn3001356.
 - [187] J.E. Lee, G. Ahn, J. Shim, Y.S. Lee, S. Ryu, Optical separation of mechanical strain from charge doping in graphene., *Nat. Commun.* 3 (2012) 1024. doi:10.1038/ncomms2022.
 - [188] C. Metzger, S. Rémi, M. Liu, S. V Kusminskiy, A.H. Castro Neto, A.K. Swan, B.B. Goldberg, Biaxial strain in graphene adhered to shallow depressions., *Nano Lett.* 10 (2010) 6–10. doi:10.1021/nl901625v.
 - [189] S. Berciaud, S. Ryu, L.E. Brus, T.F. Heinz, Probing the Intrinsic properties of exfoliated graphene: Raman spectroscopy of free-standing monolayers, *Nano Lett.* 9 (2009) 346–352. doi:10.1021/nl8031444.
 - [190] T. Yager, A. Lartsev, S. Mahashabde, S. Charpentier, D. Davidovikj, A. Danilov, R. Yakimova, V. Panchal, O. Kazakova, A. Tzalenchuk, S. Lara-Avila, S. Kubatkin, Express optical analysis of epitaxial graphene on SiC: Impact of morphology on quantum transport, *Nano Lett.* 13 (2013) 4217–4223. doi:10.1021/nl402347g.
 - [191] D. Ziegler, P. Gava, J. Güttinger, F. Molitor, L. Wirtz, M. Lazzeri, A.M. Saitta, A. Stemmer, F. Mauri, C. Stampfer, Variations in the work function of doped single- and few-layer graphene assessed by Kelvin probe force microscopy and density functional theory, *Phys. Rev. B.* 83 (2011) 235434. doi:10.1103/PhysRevB.83.235434.
 - [192] Y.-J. Yu, Y. Zhao, S. Ryu, L.E. Brus, K.S. Kim, P. Kim, Tuning the Graphene Work Function by Electric Field Effect, *Nano Lett.* 9 (2009) 3430–3434. doi:10.1021/nl901572a.
 - [193] V. Panchal, A. Lartsev, A. Manzin, R. Yakimova, A. Tzalenchuk, O. Kazakova, Visualisation of edge effects in side-gated graphene nanodevices, *Sci. Rep.* 4 (2014). doi:10.1038/srep05881.
 - [194] W. Zhou, Z.L. Wang, eds., *Scanning Microscopy for Nanotechnology*, Springer New York, New York, NY, 2007. doi:10.1007/978-0-387-39620-0.
 - [195] I. Childres, L.A. Jauregui, M. Foxe, J. Tian, R. Jalilian, I. Jovanovic, Y.P. Chen, Effect of electron-beam irradiation on graphene field effect devices, *Appl. Phys. Lett.* 97 (2010). doi:10.1063/1.3502610.
 - [196] D. Teweldebrhan, A.A. Balandin, Modification of graphene properties due to electron-beam irradiation, *Appl. Phys. Lett.* 94 (2009) 13101. doi:10.1063/1.3062851.
 - [197] R. Wiesendanger, H.-J. Güntherodt, eds., *Scanning Tunneling Microscopy II*, Springer

- Berlin Heidelberg, Berlin, Heidelberg, 1992. doi:10.1007/978-3-642-97363-5.
- [198] B. Voigtländer, Scanning probe microscopy : atomic force microscopy and scanning tunneling microscopy, n.d.
 - [199] Witec, Manual for Alpha300 system, (n.d.).
 - [200] W. Melitz, J. Shen, A.C. Kummel, S. Lee, Kelvin probe force microscopy and its application, *Surf. Sci. Rep.* 66 (2011) 1–27. doi:10.1016/j.surfrep.2010.10.001.
 - [201] R.S.R. S. Chen, A.L. Moore, W. Cai, J.W. Suk, J. An, C. Mishra, C. Amos, C.W. Magnuson, J. Kang, L. Shi, R.S. Ruoff, S. Chen, A.L. Moore, W. Cai, J.W. Suk, J. An, C. Mishra, C. Amos, C.W. Magnuson, J. Kang, L. Shi, Raman Measurements of Thermal Transport in Suspended Monolayer Graphene of Variable Sizes in Vacuum and Gaseous Environments, *ACS Nano*. 5 (2010) 321.
 - [202] N. Cernetic, D.O. Hutchins, H. Ma, A.K.-Y. Jen, Influence of self-assembled monolayer binding group on graphene transistors, *Appl. Phys. Lett.* 106 (2015) 21603. doi:10.1063/1.4905595.
 - [203] Z. Liu, A.A. Bol, W. Haensch, Large-scale graphene transistors with enhanced performance and reliability based on interface engineering by phenylsilane self-assembled monolayers., *Nano Lett.* 11 (2011) 523–8. doi:10.1021/nl1033842.
 - [204] R. Wang, S. Wang, D. Zhang, Z. Li, Y. Fang, X. Qiu, Control of carrier type and density in exfoliated graphene by interface engineering., *ACS Nano*. 5 (2011) 408–12. doi:10.1021/nn102236x.
 - [205] J. Golden, H. Miller, D. Nawrocki, J. Ross, Optimization of Bi-layer Lift-Off Resist Process, *Transition*. (2009).
 - [206] V.R. Manfrinato, L. Zhang, D. Su, H. Duan, R.G. Hobbs, E.A. Stach, K.K. Berggren, Resolution limits of electron-beam lithography toward the atomic scale, *Nano Lett.* 13 (2013) 1555–1558. doi:10.1021/nl304715p.
 - [207] V.R. Manfrinato, J. Wen, L. Zhang, Y. Yang, R.G. Hobbs, B. Baker, D. Su, D. Zakharov, N.J. Zaluzec, D.J. Miller, E.A. Stach, K.K. Berggren, Determining the resolution limits of electron-beam lithography: Direct measurement of the point-spread function, *Nano Lett.* 14 (2014) 4406–4412. doi:10.1021/nl5013773.
 - [208] D. Mack, Super-resolution imaging of plasmonic hotspots, (2017). <https://spiral.imperial.ac.uk/handle/10044/1/44115> (accessed September 16, 2017).
 - [209] A. Urich, K. Unterrainer, T. Mueller, Intrinsic response time of graphene photodetectors, *Nano Lett.* 11 (2011) 2804–2808. doi:10.1021/nl2011388.
 - [210] D. Sun, G. Aivazian, A.M. Jones, J.S. Ross, W. Yao, D. Cobden, X. Xu, Ultrafast hot-carrier-dominated photocurrent in graphene., *Nat. Nanotechnol.* 7 (2012) 114–8. doi:10.1038/nnano.2011.243.
 - [211] A. Taflove, S.C. Hagness, Computational electrodynamics : the finite-difference time-domain method, Artech House, 2005. <http://us.artechhouse.com/Computational-Electrodynamics-The-Finite-Difference-Time-Domain-Method-Third-Edition-P1634.aspx> (accessed September 18, 2017).
 - [212] K. Yee, Numerical solution of initial boundary value problems involving Maxwell's equations in isotropic media, *Antennas Propagation, IEEE Trans.* 14 (1966) 302–307. doi:10.1109/TAP.1966.1138693.

- [213] J.W. Suk, W.H. Lee, J. Lee, H. Chou, R.D. Piner, Y. Hao, D. Akinwande, R.S. Ruoff, Enhancement of the electrical properties of graphene grown by chemical vapor deposition via controlling the effects of polymer residue., *Nano Lett.* 13 (2013) 1462–7. doi:10.1021/nl304420b.
- [214] K. Asadi, E.C. Timmering, T.C.T. Geuns, A. Pesquera, A. Centeno, A. Zurutuza, J.H. Klotwijk, P.W.M. Blom, D.M. de Leeuw, Up-scaling graphene electronics by reproducible metal-graphene contacts., *ACS Appl. Mater. Interfaces.* (2015). doi:10.1021/acsami.5b01869.
- [215] H. Okuyama, N. Iwata, H. Yamamoto, Position-selective growth of vertically aligned carbon nanotubes for application of electronic-measuring nanoprobes, *Phys. E Low-Dimensional Syst. Nanostructures.* 37 (2007) 49–53. doi:10.1016/j.physe.2006.10.016.
- [216] J. Fan, J.M. Michalik, L. Casado, S. Roddaro, M.R. Ibarra, J.M. De Teresa, Investigation of the influence on graphene by using electron-beam and photolithography, *Solid State Commun.* 151 (2011) 1574–1578. doi:10.1016/j.ssc.2011.07.028.
- [217] S. Chen, L. Brown, M. Levendorf, W. Cai, S.Y. Ju, J. Edgeworth, X. Li, C.W. Magnuson, A. Velamakanni, R.D. Piner, J. Kang, J. Park, R.S. Ruoff, Oxidation resistance of graphene-coated Cu and Cu/Ni alloy, *ACS Nano.* 5 (2011) 1321–1327. doi:10.1021/nn103028d.
- [218] S. Nie, W. Wu, S. Xing, Q. Yu, J. Bao, S.S. Pei, K.F. McCarty, Growth from below: Bilayer graphene on copper by chemical vapor deposition, *New J. Phys.* 14 (2012). doi:10.1088/1367-2630/14/9/093028.
- [219] Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, P.-W. Chiu, Graphene annealing: how clean can it be?, *Nano Lett.* 12 (2012) 414–9. doi:10.1021/nl203733r.
- [220] N.J. Lee, J.W. Yoo, Y.J. Choi, C.J. Kang, D.Y. Jeon, D.C. Kim, S. Seo, H.J. Chung, The interlayer screening effect of graphene sheets investigated by Kelvin probe force microscopy, *Appl. Phys. Lett.* 95 (2009) 222107. doi:10.1063/1.3269597.
- [221] W. Bao, F. Miao, Z. Chen, H. Zhang, W. Jang, C. Dames, C.N. Lau, Controlled ripple texturing of suspended graphene and ultrathin graphite membranes, *Nat. Nanotechnol.* 4 (2009) 562–566. doi:10.1038/nnano.2009.191.
- [222] D. Yoon, Y.-W. Son, H. Cheong, Negative Thermal Expansion Coefficient of Graphene Measured by Raman Spectroscopy, *Nano Lett.* 11 (2011) 3227–31. doi:10.1021/nl201488g.
- [223] D.B. Asay, S.H. Kim, Evolution of the Adsorbed Water Layer Structure on Silicon Oxide at Room Temperature, *J. Phys. Chem. B.* 109 (2005) 16760–16763. doi:10.1021/jp053042o.
- [224] X. Zhang, J.-P. Raskin, Low-Temperature Wafer Bonding, *Electrochem. Solid-State Lett.* 7 (2004) G172. doi:10.1149/1.1763793.
- [225] D.H. Kim, H.S. Lee, H. Yang, L. Yang, K. Cho, Tunable Crystal Nanostructures of Pentacene Thin Films on Gate Dielectrics Possessing Surface-Order Control, *Adv. Funct. Mater.* 18 (2008) 1363–1370. doi:10.1002/adfm.200701019.
- [226] Y. Wang, S.W. Tong, X.F. Xu, B. Ozyilmaz, K.P. Loh, Interface engineering of layer-by-layer stacked graphene anodes for high-performance organic solar cells., *Adv. Mater.* 23 (2011) 1514–8. doi:10.1002/adma.201003673.

- [227] L. Wang, I. Meric, P.Y. Huang, Q. Gao, Y. Gao, H. Tran, T. Taniguchi, K. Watanabe, L.M. Campos, D.A. Muller, J. Guo, P. Kim, J. Hone, K.L. Shepard, C.R. Dean, One-dimensional electrical contact to a two-dimensional material., *Science*. 342 (2013) 614–7. doi:10.1126/science.1244358.
- [228] Z. Yan, Z. Sun, W. Lu, J. Yao, Y. Zhu, J.M. Tour, Controlled modulation of electronic properties of graphene by self-assembled monolayers on SiO₂ substrates., *ACS Nano*. 5 (2011) 1535–40. doi:10.1021/nn1034845.
- [229] L.-L. Chua, J. Zaumseil, J.-F. Chang, E.C.-W. Ou, P.K.-H. Ho, H. Sirringhaus, R.H. Friend, General observation of n-type field-effect behaviour in organic semiconductors., *Nature*. 434 (2005) 194–9. doi:10.1038/nature03376.
- [230] Y.-W. Tan, Y. Zhang, K. Bolotin, Y. Zhao, S. Adam, E.H. Hwang, S. Das Sarma, H.L. Stormer, P. Kim, Measurement of Scattering Rate and Minimum Conductivity in Graphene, *Phys. Rev. Lett.* 99 (2007) 246803. doi:10.1103/PhysRevLett.99.246803.
- [231] M. Lafkioti, B. Krauss, T. Lohmann, U. Zschieschang, H. Klauk, K. V Klitzing, J.H. Smet, Graphene on a hydrophobic substrate: doping reduction and hysteresis suppression under ambient conditions., *Nano Lett.* 10 (2010) 1149–53. doi:10.1021/nl903162a.
- [232] L. Wang, Z. Chen, C.R. Dean, T. Taniguchi, K. Watanabe, L.E. Brus, J. Hone, Negligible environmental sensitivity of graphene in a hexagonal boron nitride/graphene/h-BN sandwich structure., *ACS Nano*. 6 (2012) 9314–9. doi:10.1021/nn304004s.
- [233] D. Yoon, H. Moon, Y.-W. Son, J.S. Choi, B.H. Park, Y.H. Cha, Y.D. Kim, H. Cheong, Interference effect on Raman spectrum of graphene on SiO₂ / Si, *Phys. Rev. B*. 80 (2009) 125422. doi:10.1103/PhysRevB.80.125422.
- [234] K.M. McCreary, K. Pi, A.G. Swartz, W. Han, W. Bao, C.N. Lau, F. Guinea, M.I. Katsnelson, R.K. Kawakami, Effect of cluster formation on graphene mobility, *Phys. Rev. B - Condens. Matter Mater. Phys.* 81 (2010) 1–5. doi:10.1103/PhysRevB.81.115453.
- [235] S. Huh, J. Park, K.S. Kim, B.H. Hong, S. Bin Kim, Selective n-type doping of graphene by photo-patterned gold nanoparticles, *ACS Nano*. 5 (2011) 3639–3644. doi:10.1021/nn1035203.
- [236] K. Pi, W. Han, K.M. McCreary, A.G. Swartz, Y. Li, R.K. Kawakami, Manipulation of spin transport in graphene by surface chemical doping, *Phys. Rev. Lett.* 104 (2010) 1–4. doi:10.1103/PhysRevLett.104.187201.
- [237] W.S. Leong, C.T. Nai, J.T.L. Thong, What does annealing do to metal-graphene contacts?, *Nano Lett.* 14 (2014) 3840–7. doi:10.1021/nl500999r.
- [238] L.M. Malard, K. Fai Mak, A.H. Castro Neto, N.M.R. Peres, T.F. Heinz, Observation of intra- and inter-band transitions in the transient optical response of graphene, *New J. Phys.* 15 (2013). doi:10.1088/1367-2630/15/1/015009.
- [239] A.Y. Nikitin, F. Guinea, F.J. Garcia-Vidal, L. Martin-Moreno, Fields radiated by a nanoemitter in a graphene sheet, *Phys. Rev. B - Condens. Matter Mater. Phys.* 84 (2011) 1–7. doi:10.1103/PhysRevB.84.195446.
- [240] Y. Francescato, V. Giannini, S.A. Maier, Strongly confined gap plasmon modes in graphene sandwiches and graphene-on-silicon, *Nano-Structures Opt. Photonics Opt.*

- Strateg. Enhancing Sensing, Imaging, Commun. Energy Convers. 63020 (2015) 493–494. doi:10.1007/978-94-017-9133-5_40.
- [241] E.D. Palik, Handbook of optical constants of solids, Academic Press, 1985.
- [242] M.T. Portella, J. -Y. Bigot, R.W. Schoenlein, J.E. Cunningham, C. V. Shank, k -space carrier dynamics in GaAs, Appl. Phys. Lett. 60 (1992) 2123–2125. doi:10.1063/1.107083.
- [243] A. Smirl, T. Boggess, B. Wherrett, G. Perryman, A. Miller, Picosecond transient orientational and concentration gratings in germanium, IEEE J. Quantum Electron. 19 (1983) 690–700. doi:10.1109/JQE.1983.1071920.
- [244] A.J. Sabbah, D.M. Riffe, Femtosecond pump-probe reflectivity study of silicon carrier dynamics, Phys. Rev. B. 66 (2002) 165217. doi:10.1103/PhysRevB.66.165217.
- [245] M. Mittendorff, T. Winzer, E. Malic, A. Knorr, C. Berger, W.A. De Heer, H. Schneider, M. Helm, S. Winnerl, Anisotropy of excitation and relaxation of photogenerated charge carriers in graphene, Nano Lett. 14 (2014) 1504–1507. doi:10.1021/nl404730y.
- [246] E. Malic, T. Winzer, E. Bobkin, A. Knorr, Microscopic theory of absorption and ultrafast many-particle kinetics in graphene, Phys. Rev. B. 84 (2011) 205406. doi:10.1103/PhysRevB.84.205406.
- [247] J.H. Hodak, A. Henglein, G. V. Hartland, Size dependent properties of Au particles: Coherent excitation and dephasing of acoustic vibrational modes, J. Chem. Phys. 111 (1999) 8613–8621. doi:10.1063/1.480202.
- [248] L. Britnell, R. V. Gorbachev, R. Jalil, B.D. Belle, F. Schedin, a. Mishchenko, T. Georgiou, M.I. Katsnelson, L. Eaves, S. V. Morozov, N.M.R. Peres, J. Leist, a. K. Geim, K.S. Novoselov, L. a. Ponomarenko, Field-Effect Tunneling Transistor Based on Vertical Graphene Heterostructures, Science (80-.). 335 (2012) 947–950. doi:10.1126/science.1218461.
- [249] D. Sun, Z.K. Wu, C. Divin, X. Li, C. Berger, W.A. De Heer, P.N. First, T.B. Norris, Ultrafast relaxation of excited dirac fermions in epitaxial graphene using optical differential transmission spectroscopy, Phys. Rev. Lett. 101 (2008) 1–4. doi:10.1103/PhysRevLett.101.157402.
- [250] A. Woessner, P. Alonso-González, M.B. Lundeberg, Y. Gao, J.E. Barrios-Vargas, G. Navickaite, Q. Ma, D. Janner, K. Watanabe, A.W. Cummings, T. Taniguchi, V. Pruneri, S. Roche, P. Jarillo-Herrero, J. Hone, R. Hillenbrand, F.H.L. Koppens, Near-field photocurrent nanoscopy on bare and encapsulated graphene, Nat. Commun. (2016) 1–7. doi:10.1038/ncomms10783.
- [251] G. Rao, M. Freitag, H.-Y. Chiu, R.S. Sundaram, P. Avouris, Raman and photocurrent imaging of electrical stress-induced p-n junctions in graphene., ACS Nano. 5 (2011) 5848–54. doi:10.1021/nn201611r.
- [252] A.M. Gilbertson, Y. Francescato, T. Roschuk, V. Shautsova, Y. Chen, T.P.H. Sidiropoulos, M. Hong, V. Giannini, S.A. Maier, L.F. Cohen, R.F. Oulton, Plasmon-induced optical anisotropy in hybrid graphene-metal nanoparticle systems., Nano Lett. 15 (2015) 3458–64. doi:10.1021/acs.nanolett.5b00789.
- [253] W. Wang, A. Klots, D. Prasai, Y. Yang, K.I. Bolotin, J. Valentine, Hot Electron-Based Near-Infrared Photodetection Using Bilayer MoS₂., Nano Lett. (2015).

doi:10.1021/acs.nanolett.5b02866.

- [254] V. Giannini, A.I. Fernández-Domínguez, Y. Sonnefraud, T. Roschuk, R. Fernández-García, S.A. Maier, Controlling Light Localization and Light-Matter Interactions with Nanoplasmonics, *Small*. 6 (2010) 2498–2507. doi:10.1002/sml.201001044.
- [255] R. Fernández-García, Y. Sonnefraud, A.I. Fernández-Domínguez, V. Giannini, S.A. Maier, Design considerations for near-field enhancement in optical antennas, *Contemp. Phys.* 55 (2014) 1–11. doi:10.1080/00107514.2013.850788.
- [256] T.G. Habteyes, S. Dhuey, E. Wood, D. Gargas, S. Cabrini, P.J. Schuck, A.P. Alivisatos, S.R. Leone, Metallic adhesion layer induced plasmon damping and molecular linker as a nondamping alternative, *ACS Nano*. 6 (2012) 5702–5709. doi:10.1021/nn301885u.
- [257] H. Wang, Y. Wu, C. Cong, J. Shang, T. Yu, Hysteresis of Electronic Transport in Graphene Transistors, 4 (2010) 13. doi:10.1021/nn101950n.
- [258] Y.G. Lee, C.G. Kang, U.J. Jung, J.J. Kim, H.J. Hwang, H.J. Chung, S. Seo, R. Choi, B.H. Lee, Fast transient charging at the graphene/ SiO₂ interface causing hysteretic device characteristics, *Appl. Phys. Lett.* 98 (2011) 98–101. doi:10.1063/1.3588033.
- [259] S. Wolf, R.N. Tauber, Silicon processing for the VLSI era, Lattice Press, 1986.
- [260] X. Cai, A.B. Sushkov, R.J. Suess, M.M. Jadidi, G.S. Jenkins, L.O. Nyakiti, R.L. Myers-Ward, S. Li, J. Yan, D.K. Gaskill, T.E. Murphy, H.D. Drew, M.S. Fuhrer, Sensitive room-temperature terahertz detection via the photothermoelectric effect in graphene., *Nat. Nanotechnol.* 9 (2014) 814–9. doi:10.1038/nnano.2014.182.
- [261] R.-J. Shiue, Y. Gao, Y. Wang, C. Peng, A.D. Robertson, D.K. Efetov, S. Assefa, F.H.L. Koppens, J. Hone, D. Englund, High-Responsivity Graphene–Boron Nitride Photodetector and Autocorrelator in a Silicon Photonic Integrated Circuit, *Nano Lett.* 15 (2015) 7288–7293. doi:10.1021/acs.nanolett.5b02368.
- [262] A. Sherehiy, R. Jayasinghe, R. Stallard, G. Sumanasekera, A. Sidorov, D. Benjamin, Z. Jiang, Q. Yu, W. Wu, J. Bao, Z. Liu, S. Pei, Y. Chen, Thermoelectric properties of CVD grown large area graphene, *Am. Phys. Soc. APS March Meet.* 2010, March 15–19, 2010, Abstr. #Z21.004. (2010). <http://adsabs.harvard.edu/abs/2010APS..MARZ21004S> (accessed August 9, 2017).
- [263] T.J. Echtermeyer, P.S. Nene, M. Trushin, R. V. Gorbachev, A.L. Eiden, S. Milana, Z. Sun, J. Schliemann, E. Lidorikis, K.S. Novoselov, A.C. Ferrari, Photothermoelectric and Photoelectric Contributions to Light Detection in Metal–Graphene–Metal Photodetectors, *Nano Lett.* 14 (2014) 3733–3742. doi:10.1021/nl5004762.
- [264] Z. Sun, T. Hasan, F. Torrisi, D. Popa, G. Privitera, F. Wang, F. Bonaccorso, D.M. Basko, A.C. Ferrari, Graphene mode-locked ultrafast laser., *ACS Nano*. 4 (2010) 803–10. doi:10.1021/nn901703e.
- [265] F.T. Vasko, Saturation of interband absorption in graphene, *Phys. Rev. B*. 82 (2010) 245422. doi:10.1103/PhysRevB.82.245422.
- [266] K.J. Tielrooij, L. Piatkowski, M. Massicotte, A. Woessner, Q. Ma, Y. Lee, K.S. Myhro, C.N. Lau, P. Jarillo-Herrero, N.F. van Hulst, F.H.L. Koppens, Generation of photovoltage in graphene on a femtosecond timescale through efficient carrier heating, *Nat. Nanotechnol.* 10 (2015) 437–443. doi:10.1038/nnano.2015.54.
- [267] V.I. Shautsova, V.A. Zhuravkov, O. V. Korolik, A.G. Novikau, G.P. Shevchenko, P.I.

- Gaiduk, Effect of Interparticle Field Enhancement in Self-Assembled Silver Aggregates on Surface-Enhanced Raman Scattering, *Plasmonics*. 9 (2014) 993–999. doi:10.1007/s11468-014-9706-3.
- [268] R. Sahin, E. Simsek, S. Akturk, Nanoscale patterning of graphene through femtosecond laser ablation, *Appl. Phys. Lett.* 104 (2014). doi:10.1063/1.4864616.
- [269] A. Roberts, D. Cormode, C. Reynolds, T. Newhouse-Illige, B.J. Leroy, A.S. Sandhu, Response of graphene to femtosecond high-intensity laser irradiation, *Appl. Phys. Lett.* 99 (2011) 1–4. doi:10.1063/1.3623760.
- [270] R.J. Stöhr, R. Kolesov, K. Xia, J. Wrachtrup, All-optical high-resolution nanopatterning and 3D suspending of graphene, *ACS Nano*. 5 (2011) 5141–5150. doi:10.1021/nn201226f.
- [271] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Superior thermal conductivity of single-layer graphene., *Nano Lett.* 8 (2008) 902–7. doi:10.1021/nl0731872.
- [272] V. Shautsova, A.M. Gilbertson, N.C.G. Black, S.A. Maier, L.F. Cohen, Hexagonal Boron Nitride assisted transfer and encapsulation of large area CVD graphene, *Sci. Rep.* 6 (2016) 30210. doi:10.1038/srep30210.
- [273] Q. Ma, T.I. Andersen, N.L. Nair, N.M. Gabor, M. Massicotte, C.H. Lui, A.F. Young, W. Fang, K. Watanabe, T. Taniguchi, J. Kong, N. Gedik, F.H.L. Koppens, P. Jarillo-Herrero, Tuning ultrafast electron thermalization pathways in a van der Waals heterostructure, *Nat. Phys.* 12 (2016) 455–459. doi:10.1038/nphys3620.
- [274] Z. Dai, X. Xiao, W. Wu, Y. Zhang, L. Liao, S. Guo, J. Ying, C. Shan, M. Sun, C. Jiang, Plasmon-driven reaction controlled by the number of graphene layers and localized surface plasmon distribution during optical excitation, *Light Sci. Appl.* 4 (2015) e342. doi:10.1038/lsa.2015.115.
- [275] C. Gao, X. Zhao, J. Yao, X.-Q. Yan, X.-T. Kong, Y. Chen, Z.-B. Liu, J.-G. Tian, Sign of differential reflection and transmission in pump-probe spectroscopy of graphene on dielectric substrate, *Photonics Res.* 3 (2015) A1. doi:10.1364/PRJ.3.0000A1.

List of figures

Figure 2.1. (a) Permittivity of gold with real ($Re(\epsilon)$) and imaginary ($Im(\epsilon)$) parts. Experimental data is compared to Drude (red line) and Drude-Lorentz (blue) models. (c) Experimental extinction cross section of 50 nm gold NPs in water (green) compared to theoretical calculations performed with the Drude (red) and Drude-Lorentz (blue) models. (d) Electromagnetic field distribution for the 50nm gold NP at resonance wavelength of 535nm. Reprinted with permission from [47]. Copyright 2011 American Chemical Society.22

Figure 2.2. Localised surface plasmon excitation and relaxation. (a) Optical illumination results in plasmon excitation that modified the flow of light (Poynting vector) towards the NP. (b) After Landau damping, the out-of-equilibrium carriers decay radiatively through emission of photons or nonradiatively through carrier multiplication due to carrier-carrier interaction. (c) The hot carrier distribution is formed. Subsequent decay occurs through carrier-phonon interactions to equilibrate the carrier and lattice temperatures. (d) Heat conduction results in heat transfer to the NP surroundings. Reprinted by permission from Macmillan Publishers Ltd: [39], copyright 2015.24

Figure 2.3. (a) Carbon allotropes: graphene (top left), graphite (top right), carbon nanotubes (bottom left) and fullerenes C_{60} (bottom right). Adapted with permission from Ref. [60]. Copyrighted by the American Physical Society. The electron arrangement in (b) elemental carbon and (c) graphene. (d) Illustration of the orbitals in graphene [61].25

Figure 2.4. The honeycomb lattice of graphene (a) and corresponding Brillouin zone (b). Electronic dispersion in the honeycomb lattice: energy dispersion as a function of the wave-vector components k_x and k_y (c) and zoom in of the energy bands close to one of the Dirac points (d). Adapted with permission from Ref. [60]. Copyrighted by the American Physical Society.26

Figure 2.5. Theoretical and experimental phonon dispersion of graphene showing the iLO, iTO, oTO, iLA, iTA and oTA phonon modes. adapted with permission from Ref. [64]. Copyrighted by the American Physical Society.27

Figure 2.6. Graphene's optical absorption. (a) Absorption mechanism: (1) intraband, (2) defect mediated and (3) interband. The red arrow indicates excitation photons. The yellow spheres represent carriers. (b) Typical absorption spectrum of doped graphene.28

Figure 2.7. (a) Photograph of a 50-mm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (Inset) Transmittance of white light as a function of the number of graphene layers. Adapted from [68]. Reprinted with permission from AAAS. (b) Optical absorbance of a monolayer graphene calculated from dispersion model values of n and k . Reprinted from [70], with the permission of AIP Publishing.29

Figure 2.8. Schematic illustration of carrier dynamics in graphene. (a) Photoexcitation results in highly energetic electron-hole pair generation. (b) Part of the carrier energy is transferred to a carrier system via scattering processes. (c) Emission of strongly coupled optical phonons (~ 200 meV) results in the energy transfer to the lattice. (d) The hot carriers cool down through normal momentum-conserving process of low energy ($\approx$ several meV) acoustic phonon emission. (e) The hot carrier cooling is facilitated by a disorder-assisted supercollision process that relaxes momentum restrictions enabling faster cooling through emission of high-energy ($\sim k_B T$) acoustic phonons.31

Figure 2.9. (a) Carrier distribution during relaxation process. The first schematic describes strongly out-of-equilibrium carrier distribution due to photoexcitation. The photocarriers thermalize through carrier-carrier scattering and optical phonon emission to create a relatively long-lived hot carrier distribution (the second schematic). The hot carrier distribution relaxes back to equilibrium (the third schematic). Adapted from [23]. (b) Electronic temperature evolution. The experimental data is fitted using a three temperature model with (solid black line) and without (dashed amber line) the supercollision (SC) term. Additionally, the temperatures of the optical phonons (solid blue line) and the acoustic phonons (solid red line) are included. Reprinted with permission from [20]. Copyright 2013 by the American Physical Society.32

Figure 2.10. (a) Schematic of a pump-probe experiment. The sample is excited with a strong pump pulse while being monitored with a weak probe pulse. The time delay between pulses (τ) is varied. (b) The pump pulse creates carrier inversion in graphene. The relaxation of photocarriers is monitored by the probe pulse. (c) Differential transmission (DT) signal of monolayer graphene at various photon energies from 88 to 138 meV demonstrating the sign change close to the Fermi energy [91]. (b) The Fermi-Dirac distribution $f_{FD}(E)$ at different carrier temperatures representing equilibrium distribution (blue line) and distribution after carrier thermalization (red line). Blue and orange arrows indicate regions with negative and positive DT signal, respectively.35

Figure 2.11. (a) Schematic representation of the photovoltaic mechanism where electron-hole (solid and open circle) pairs are separated by an internal electric field. (b, c) Photocurrent response of a graphene transistor: scanning photocurrent image (b) and peak photocurrent magnitude around source and drain contacts as a function of the gate bias (c). The incident excitation laser power is about 30 μ W, and the wavelength is 632.8 nm. Adapted with permission from [34]. Copyright 2009 American Chemical Society.36

Figure 2.12. (a) Schematic representation of the photothermoelectric (PTE) mechanism where $S_{1,2}$ and $\mu_{1,2}$ Seebeck coefficients and chemical potential in graphene areas. (b,c) Calculation of the photocurrent from PTE and PV effects. The PV contribution changes sign only once due to the change of the electrical field direction, while the PTE contribution changes sign twice. Adapted with permission from [25]. Copyright 2011 American Chemical Society.38

Figure 2.13. (a, b) Numerical finite element simulations of local electric field in the presence of gold finger structure (finger width 110 nm, pitch 300 nm) and the corresponding photogenerated signal (normalized to laser power) as a function of the position of the illumination spot (514nm, transverse polarization, spot size $\sim$ 1.5 μ m; Gate voltage 90 V. Colour scale from 0 μ V (blue) to 20 μ V (red)). Adapted by permission from Macmillan Publishers Ltd: [38], copyright 2011. (c, d) Schematics of hot carrier injection from plasmonic nanoparticle in graphene and the Dirac point shift for antenna/graphene transistor under different excitation lasers with a 1mV source-drain bias. Adapted with permission from [42]. Copyright 2011 American Chemical Society.40

Figure 2.14. Summary of methods for graphene production with estimated quality and price indicated for possible applications. Reprinted by permission from Macmillan Publishers Ltd: [110], copyright 2012.42

Figure 2.15. (a-c) Schematic illustration of the transfer procedures used in [114–116], respectively. (d) Optical image of the transferred CVD graphene grown on Cu [116]. (a) Adapted with permission from [114]. Copyright 2012 American Chemical Society. (b) Adapted with permission from [115]. Copyright 2012 American Chemical Society.44

Figure 2.16. (a) Schematic illustration of the PDMS stamp method in combination with the self-release layer. Optical images of successful and failed transfers with and without the self-release layer, respectively. Reprinted by permission from Macmillan Publishers Ltd: [118], copyright 2013. (b) Schematic illustration of PDMS frame method. SEM image of single layer graphene suspended over 2 μm deep well with 5.1 μm diameter. Adapted with permission from [117]. Copyright 2011 American Chemical Society. (c) Schematic illustration of the polyimide tape frame method used by Petrone et. al. Optical image of large-grain CVD graphene transferred on SiO_2 . Adapted with permission from [122]. Copyright 2012 American Chemical Society.46

Figure 2.17. The optical microscopy images of graphene films wet transferred on SiO_2/Si using PMMA as supportive polymer with and without double coating [124]. adapted with permission from [124]. Copyright 2009 American Chemical Society.47

Figure 2.18. (a) Schematic illustration of the polymer-free transfer process used in Ref. [130]. Optical images of the transferred CVD graphene. Scales are 10 μm and 0.5 μm . Adapted from [130], with the permission of AIP Publishing. (b) Schematic illustration of the polymer-free transfer process used in Ref. [131]. STM image of the transferred graphene on the Si (1 1 1) substrate. Adapted with permission from [131]. Copyright 2014 American Chemical Society.48

Figure 2.19. (a) Γ -point phonon-displacement pattern for graphene. Empty and filled circles represent inequivalent carbon atoms. Red arrows show atom displacements. Atom displacements (red arrows) for the A_{1g} mode at K. (b) Raman spectra of pristine (top) and defected (bottom) graphene. Adapted by permission from Macmillan Publishers Ltd: [147], copyright 2013.50

Figure 2.20. Electron and phonon interactions responsible for the common peaks in graphene Raman spectrum: (a) intravalley one-phonon G peak, (b) defect-assisted intravalley one-phonon D' peak, (c) intravalley two-phonon 2D peak, (d) defect-assisted intervalley one-phonon D peak, and (e) intervalley two-phonon 2D peak. Vertical solid arrows represent interband transitions accompanied by photon absorption (upward arrows) or emission (downward arrows) (the photon wave vector is neglected). Dashed arrows represent phonon emission. Horizontal dotted arrows represent defect scattering. Reprinted with permission from [149]. Copyright 2009 by the American Physical Society.....51

Figure 2.21. (a) Comparison of Raman spectra at 514 nm for bulk graphite and graphene (scaled to have similar height of the 2D peak) [152]. (b) Evolution of the ratio of the integrated intensities for the G and 2D peaks at 532 nm with the number of layers [153]. (c) Evolution of the 2D peak at 514 nm with the number of layers [152]. (d) Phonon wave vectors corresponding to the 2D peak in BLG [152]. (e) Combination modes close to the G peak as a function of the number of layers [154,155]. (a,c,d) Adapted with permission from [152]. Copyright 2006 by the American Physical Society. (b) Adapted with permission from [153]. Copyright 2007 American Chemical Society. (e) Adapted by permission from Macmillan Publishers Ltd: [147], copyright 2013.52

Figure 2.22. (a) Raman spectra of five ion bombarded single layer graphene measured at 514.5 nm. The respective $I_{\text{D}}/I_{\text{G}}$ and L_{D} values are indicated for each spectrum. (b) Amorphisation trajectory $EL4[I(\text{D})/I(\text{G})]$ as a function of L_{D} for different excitation energies E_{L} . The dashed blue line is obtained from the empirical model [158]. The solid black and red lines are L_{D}^{-2} and L_{D}^2 dependences, respectively. The shaded area accounts for the upper and lower limits given by the 30% experimental error. (c) Full width at half

maximum of G peak as a function of L_D . (a-c) Adapted with permission from [157]. Copyright 2011 American Chemical Society.	54
Figure 2.23. (a) Pos(G), (b) FWHM(G), (c) Pos(2D) and (d) I(2D)/I(G) as a function of electron and hole doping. Adapted by permission from Macmillan Publishers Ltd: [160], copyright 2008.	56
Figure 2.24. (a) One-phonon processes responsible for the G peak can be eliminated by doping, such as the one that is crossed out. (b) Schematic diagram of 2D Raman processes in doped graphene. (c) Raman spectra of highly doped graphene monolayer measured at 488, 514 532, 561, 593 and 633 nm, normalized to have the same I(G) [162]. (a) Adapted by permission from Macmillan Publishers Ltd: [147], copyright 2013. (b) Adapted with permission from [162]. Copyright 2011 American Chemical Society.	57
Figure 2.25. Graphene's Raman spectrum under strain. (a) G peak of graphene at 0% (grey) and 1% (black) strain. Inset shows the origin of the G+ and G- peaks due to the angle between strain axis and lattice. (b) Dependence of G+ (empty squares) and G- (filled squares) frequency on increasing uniaxial tensile strain. Inset shows an optical image of the measured flake with 10nm scale bar, arrows indicate the strain direction. Adapted from [172]. (c) 2D peak modification with increasing tensile strain applied in parallel to the polarisation of incident laser excitation. The 2D peak has been fitted with two Lorentzian peaks in each spectrum. (d) Dependence of 2D frequency on increasing strain with filled and empty squares representing the two individual Lorentzian components for the 2D peak. Red and black colours correspond to different laser polarization being parallel and perpendicular to the applied stress. The perpendicular data points are offset by -4cm ⁻¹ for clarity. Adapted with permission from [173]. Copyright 2011 American Chemical Society.	58
Figure 2.26. Correlation between the G and 2D peak positions. (a) A vector model decomposition of the effects of hole-doping and strain. The green dot (denoted O) is the peak position for a freestanding graphene sample that is not affected by strain or charge doping. The dashed magenta and black lines represent the summary of observed peak shifts for increasing hole doping and randomly oriented uniaxial stress, respectively. The vectors eH and eT corresponds to strain-free and charge-neutral unit vectors, respectively. (b) The scatter plot represents data obtained from Raman mapping of three graphene samples before (+) and after (×) thermal annealing at 400 °C. The theoretical and experimental trajectories of G and 2D peak positions affected by strain and doping are presented by black and magenta lines, respectively. Adapted by permission from Macmillan Publishers Ltd: [182], copyright 2012.	61
Figure 2.27. Back gate modulation of work function (a) and Fermi energy (c) for single layer (filled symbols) and bilayer (open symbols) graphene. (b) The energy levels for KFM tip and graphene samples. Adapted with permission from [187]. Copyright 2009 American Chemical Society.....	62
Figure 3.1. Optical microscopy image of graphene on SiO ₂ /Si before (a) and after contrast enhancement (b).....	64
Figure 3.2. (a) Schematic of AFM operation. Adapted from [194]. (b) The dominating forces during AFM measurements.....	66
Figure 3.3. Schematic of electronic energy levels for the sample and AFM tip for three different cases: (a) tip and sample are not interacting due to distance d and no electrical contact, (b) tip and sample are brought in electrical contact, and (c) external bias (V_{dc}) is applied between tip and sample to cancel the contact potential difference and thus the tip-sample electrical force. Adapted from [195].	67

Figure 3.4. (a) Schematic illustration of the beam path in Witec Alpha300 system. (b) Schematic of a confocal microscope. Adapted from [194].	68
Figure 3.5. (a) Schematic of measurement set up for FET characterization. (b) Typical resistance dependence for graphene devices demonstrating ambipolar behaviour with n-type and p-type carriers dominating for $V_G > 0$ and $V_G < 0$, respectively [59]. The inset shows the Fermi energy position.	70
Figure 3.6. (Left) Photolithography process: (1) Coat and soft-bake first layer SF6. (2) Coat and soft-bake imaging resist S1805. (3) Expose imaging resist through photolithography mask. (4) Develop S1805/SF6. (5) Deposit metal film. (6) Lift-off bi-layer stack and residual deposition. (Right) SEM image of bi-layer lift-off in gold metallization. The presence of undercut allows complete lift-off removal of resist and residual deposition. Adapted from [200].	71
Figure 3.7. Schematic diagram of a resistive thermal evaporation system. SM – Sample Mount, S – Sample, Sh – Deposition Shutter, GM – Growth Monitor, CM – Crucible Mount, C – Crucible, M – Material. Adapted from [203].	73
Figure 3.8. Schematic diagram of the scanning photocurrent microscopy. Electronic devices are mounted on piezo-stage and modulated optical illumination from various laser sources is focused on the device.	74
Figure 3.9. Schematic diagram of the time resolved measurements.	75
Figure 3.10. Schematic of dark field microscopy and spectroscopy. (a) Principles of dark field microscopy. (b) Reflection beam path towards the detectors: spectrometer and single photon counter (SPC). T – tungsten filament lamp, F – optical fibre, DF-O – dark-field objective, S – sample, Lx – lenses, LPF – linear polarising filters. Adapted from [203].	76
Figure 3.11. Schematic of a Michelson interferometer. Adapted from [50].	78
Figure 4.1. Schematic of the wet/dry transfer process.	81
Figure 4.2. (a) Schematic of “shadow effect” caused by poor contact between the substrate and the mask pattern. Adopted from [210]. (b) Optical microscopy image of the Cr/Au contact fabricated on graphene layer; Shadow region ($\sim 20\mu\text{m}$) can be clearly seen in the top part of the image by the change in colour.	83
Figure 4.3. Optical microscopy images of graphene films after photolithography lift-off step for untreated (a), O_2 -plasma-treated (b) and hBN-covered (c) SiO_2 substrates. Raman spectroscopy results for graphene before and after photolithography (PL) processing: 2D histograms describing correlation between the $I(2\text{D})/I(\text{G})$ ratio and the G-peak position (d,e) and representative Raman spectra (f).	84
Figure 4.4. SEM images of graphene/Cu and hBN/Cu. Bright areas are tears, while darker areas in graphene are multilayers.	85
Figure 4.5. (b) Optical microscopy image of graphene/Cu, the oxidised areas are clearly visible (black cross). (a, c) Raman spectroscopy results for areas with/without oxidation. Raman spectroscopy measurements have been performed using 473nm laser excitation at $200\mu\text{W}$ power.	86
Figure 4.6. AFM images of graphene (a,b) and hBN (c,d) transferred on SiO_2/Si substrates.	87
Figure 4.7. Optical microscopy (a, c, e) and Raman spectroscopy (b, d, f) for PMMA free (a, b), PMMA supported (c, d) and pretransferred graphene (e, f).	89

Figure 4.8. Raman spectroscopy results for PMMA free (a-c), PMMA supported after 5h Acetone treatment (d-f) and 24h Acetone treatment (g-i) and pretransferred graphene (j-l). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the $I(2D)/I(G)$ ratio and the G-peak position, respectively.	90
Figure 4.9. Correlation between the G and 2D peak positions for PMMA free (black), PMMA supported after 5h Acetone treatment (green) and 24h Acetone treatment (blue) and pretransferred graphene (orange). The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.	91
Figure 4.10. AFM images of hBN/SiO ₂ before (a, b) and after thermal annealing for 5 hours at 350°C in vacuum (c, d).....	92
Figure 4.11. AFM (a, d) and KFM (b-f) results of graphene/SiO ₂ before (a-c) and after thermal annealing for 5 hours at 350°C in vacuum (d-f).	94
Figure 4.12. AFM (a, d) and KFM (b-f) results of graphene/SiO ₂ before (a-c) and after thermal annealing for 5 hours at 350°C in vacuum (d-f). The cross-section over a multilayer is presented.	94
Figure 4.13. Correlation between the G and 2D peak positions for graphene before (black) and after thermal annealing in vacuum for 5h at 350°C. The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.....	95
Figure 4.14. Graphene transferred with dry transfer technique on untreated (a), O ₂ -plasma treated (b), SAM-modified (c) and hBN covered (d) SiO ₂ substrate. Only small-size graphene flakes are transferred in the case of the untreated SiO ₂ substrate	96
Figure 4.15. Raman spectroscopy results for graphene transferred using a wet transfer technique on untreated SiO ₂ (a-c), SiO ₂ after O ₂ -plasma treatment (d-f), SAM modified SiO ₂ (g-i) and hBN covered SiO ₂ with (m-o) and without thermal annealing (j-l). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the $I(2D)/I(G)$ ratio and the G-peak position, respectively.	97
Figure 4.16. Correlation between the G and 2D peak positions for graphene transferred using a wet transfer technique on untreated SiO ₂ (black), SiO ₂ after O ₂ -plasma treatment (red), SAM modified SiO ₂ (green) and hBN covered SiO ₂ with (orange) and without thermal annealing (blue). The data is separated in two graphs to avoid overlaps. The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm^{-2} . The O point represents suspended exfoliated graphene.	98
Figure 4.17. Effect of hBN multilayer areas in graphene transferred on hBN-covered SiO ₂ after thermal annealing. (a) Raman spectroscopy map demonstrating spatial variations of 2D and G peak ratio. The multilayer area effect is highlighted by the circle. (b) AFM image of the surface topography confirming presence of hBN multilayer areas underneath of continuous graphene layer.	99
Figure 4.18. Schematic of the hBN-assisted transfer process.....	100

Figure 4.19. Optical microscopy images of the graphene transferred using a WT technique on hBN covered SiO ₂ (a) and using AT method resulting in hBN/Gr (b) and hBN/Gr/hBN stacks (c).....	101
Figure 4.20. Raman spectroscopy results for graphene transferred using a wet transfer technique on hBN covered SiO ₂ (a-c) and using hBN-assisted transfer method resulting in hBN/Gr (d-f) and hBN/Gr/hBN stacks (g-i). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the G and 2D peak positions and the $I(2D)/I(G)$ ratio and the G-peak position, respectively.	102
Figure 4.21. Conductivity of the graphene FETs obtained after wet transfer on untreated SiO ₂ , SiO ₂ after O ₂ -plasma treatment, SAM- and hBN- covered SiO ₂ and from hBN-assisted transfer after preparation (a) and after 1 month storage in ambient conditions (b).	104
Figure 5.1. Sample schematic (first row) and optical microscopy images of bare graphene films (second row) and graphene/NP arrays (R=100nm P=400nm).....	109
Figure 5.2. Representative SEM and AFM images of Gr/NP/hBN/SiO ₂ sample.....	110
Figure 5.3. Plasmonic response of graphene/NP hybrids. (a) Experimental reflectance spectra of the graphene/NP/substrate system with periods of 400 and 300nm. The graphene/substrate response is included for comparison. (b) The simulated reflectance spectra for substrate with/without NPs. Calculated near-field intensity enhancement indicating plasmon resonance at ~780 nm.....	111
Figure 5.4. (a,b) Optical microscopy image of sample Gr/NP/SiO ₂ with NP-array/graphene interface and corresponding spatial map of G-peak position. The NP array period is P=300nm. (c) Representative Raman spectra of the bare graphene and graphene/NP structure with NP period of 300 and 400nm.	112
Figure 5.5. Raman spectroscopy results for sample Gr/NP/SiO ₂ with bare graphene (a-c) and graphene/NP complexes with P=400nm (d-f) and P=300nm (g-i). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio ($I(D)/I(G)$). The second and third rows are 2D histograms describing correlations between the $I(2D)/I(G)$ ratio and the G-peak position and the G and 2D peak positions, respectively. ...	113
Figure 5.6. Correlation between the G and 2D peak positions for bare graphene (black) and graphene/NP complexes with P=400nm (blue) and P=300nm (green). The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping. The indicated doping levels are in cm ⁻² . The O point represents suspended exfoliated graphene.....	115
Figure 5.7. Raman spectroscopy results for the Gr/NP/SiO ₂ , Gr/NP/hBN/SiO ₂ and Gr/hBN/NP/SiO ₂ samples. Spatial variation of the G-peak position and the 2D and G peak intensity ratio $I(2D)/I(G)$ are presented in the first and the second row, respectively.....	116
Figure 5.8. Raman spectroscopy results for Gr/NP/SiO ₂ (a-c), Gr/NP/hBN/SiO ₂ (d-f) and Gr/hBN/NP/SiO ₂ (g-i) samples with bare graphene (Gr) and graphene/NP complexes with P=400nm (Gr/NP). The first row describes defect density in the graphene films by presenting the D and G peak intensity ratio $I(D)/I(G)$. The second row shows the $I(2D)/I(G)$ ratio. The third row presents 2D histograms describing correlation between the G and 2D peak positions.	117

Figure 5.9. AFM and KFM images of Gr/NP/SiO ₂ (a,b) and Gr/NP/hBN/SiO ₂ (d,e) samples. The distributions represent contact potential difference measured for bare graphene and graphene/NP areas for Gr/NP/SiO ₂ (c) and Gr/NP/hBN/SiO ₂ (f) samples.....	118
Figure 5.10. High resolution AFM and KFM images with corresponding cross sections of Gr/NP/SiO ₂ (a, b, c) and Gr/NP/hBN/SiO ₂ (d, e, f) samples.	119
Figure 5.11. Time-resolved DR response for Gr/SiO ₂ (a, b) and Gr/SiO ₂ /Si (c, d) samples with/without O ₂ -plasma treatment of the substrate.....	121
Figure 5.12. Graphene conductivity following the pump pulse (T=600K) is compared to the equilibrium case. The optical probe position is indicated by vertical green arrows; the “-” and “+” indicators mark the sign of the resulting DT signal. Inset: the graphene band structure for a doped layer; probe excitation is indicated by the vertical red arrow.....	122
Figure 5.13. (a) Schematic of graphene on a multilayer substrate. (b, c) FTIR reflection spectra of different multilayer substrates and corresponding calculation results. The break in the experimental data at ~950nm is due to a change in the detector used.	123
Figure 5.14. Amplitude of DR signal calculated for Gr/SiO ₂ (a, b) and Gr/SiO ₂ /Si (c, d) samples with different carrier temperature and fixed Fermi energy at 0.2eV (a, c) and 0.4 eV (b, d) corresponding to effect of O ₂ -plasma treatment.....	124
Figure 5.15. Comparison of calculated and experimental results for Gr/SiO ₂ sample with O ₂ -plasma treatment. Continuous lines present calculation results for different carrier temperature present in the system after pump excitation. Experimental data points are extracted at varying delay time from DR traces in Figure 5.11 (b).	125
Figure 5.16. Time-resolved DR response for Gr/NP/SiO ₂ (a), Gr/NP/hBN/SiO ₂ (b) and Gr/hBN/NP/SiO ₂ (c). The $\Delta R/R_0$ signal for bare graphene (Gr) is compared to Gr/NP structure with NP period of 400nm. All the measurements are performed with parallel () pump and probe beams. Solid lines are guide for the eye.	127
Figure 5.17. (a) Time resolved DR response for Gr/NP structures with varying NP lattice periods (P) obtained with parallel pump–probe polarizations. (b) DR amplitude dependence on the NP period (metal fill factor), solid line is guide for the eye. The measurements are performed on Gr/NP/hBN/SiO ₂ sample.....	127
Figure 5.18. (a) Time resolved DR signal dependent on the probe polarization angle θ for Gr/NP structure with period of 400nm. (b) Dependence of the DR amplitude. Polarization-independent response of bare graphene is included for comparison. The measurements are performed on Gr/NP/SiO ₂ sample. (c) Spatial distribution of near-field intensity enhancement for a gold NP in the array with period of 400nm. The NP is excited with x-polarized light at 840 nm demonstrating the dipole mode of the plasmon resonance.	128
Figure 5.19. Spatial variation of DR amplitude for bare graphene of the Gr/NP/SiO ₂ sample (a) and for graphene/NP-array interface of the Gr/NP/hBN/SiO ₂ sample (b). The scanned area is 20x20 μm	131
Figure 6.1. (a) Photovoltage scanning microscopy results. Left to right: optical microscopy, optical reflection and photovoltage images of the graphene nanoribbon device. (b) Micro-Raman maps of the device (10x2.5 μm). Left to right: spatial distribution of position of the G- and 2D- peaks and of intensity ratio of 2D- and G- peaks.....	133
Figure 6.2. Schematic of the graphene device with plasmonic (<i>Thot</i>) and nonplasmonic (<i>Tbath</i>) contacts.	134

Figure 6.3. (a) Electromagnetic field distributions for the longitudinal and transverse resonance and (b) corresponding cross-section for the longitudinal resonance at 740 nm excitation. The structure parameters are: NP of 150x100 nm, NP period 500 nm and contact spacing 300 nm.	135
Figure 6.4. Results of numerical calculation. (a) Shift of longitudinal resonance with NP length, NP width is 100nm. (b-d) Influence of contact width (b), NP period (c) and Cr adhesion layer (d) on NP field enhancement.	135
Figure 6.5. Structural characterization of the fabricated devices with SEM (a) and AFM (b) techniques.	136
Figure 6.6. Optical microscopy images of the devices tested in Section 6.3. The scale bar is 5 μ m.	137
Figure 6.7. Raman spectroscopy characterization of graphene over the substrate (SiO ₂) and the gold contacts. (a) Representative spectra. (b) Correlation between the G and 2D peak positions. The solid lines of different slope indicate trajectories of equal strain (black and red are used for uniaxial and biaxial strain, respectively) and equal hole doping (see Section 2.6). The indicated doping levels are in cm ⁻² . The O point represents suspended exfoliated graphene.	138
Figure 6.8. Photovoltage response of plasmonic and nonplasmonic contacts at $\lambda = 740$ nm as a function of time (a), laser power (b) and polarization (c).	139
Figure 6.9. (a, b) Scanning dark field microscopy image and corresponding reflection spectra for plasmonic and nonplasmonic contacts and substrate. (c, d) Wavelength dependent photovoltage response measured with elliptical laser spot of 40 μ W power under longitudinal polarization. (e, f) FDTD calculation results.	141
Figure 6.10. Typical gate dependent photovoltage measurements with gate bias ranging from -35 V to 0 V and step size of 5 V. Each bias value is applied for 30 s to let the measurement to settle down.	142
Figure 6.11. Gate dependent photovoltage response of plasmonic (PI) contact under longitudinal and transverse polarization and nonplasmonic (NonPI) contact under longitudinal polarization. The gate bias is tuned from positive voltage towards negative (a,b) and reverse (c,d) as indicated by arrows. The photovoltage measurements are performed with elliptical laser spot at 700 nm with 40 μ W power.	143
Figure 6.12. Gate dependent photovoltage response of representative device 4 with nonplasmonic contacts under longitudinal polarization. The gate bias is tuned from positive voltage towards negative (black) and reverse (blue) as indicated by arrows. The photovoltage measurements are performed with elliptical laser spot at 700nm with 40uW power.	144
Figure 6.13. Transport measurements of representative two contact graphene device 4. (a) Gate dependent source-drain current measured with 10 ms stabilization time per 1V step. (b) Temporal dynamics of source-drain current at gate bias ranging from 35 to 0V with 5V step and 30s stabilization time. (c) Gate dependent source-drain current extracted from (b). All measurements are performed with 1mV source-drain bias.	145
Figure 6.14. Experimental and theoretical conductivity (a) and corresponding Seebeck coefficients (b).	146
Figure 6.15. (a, c) Gate dependent thermoelectric voltage and square resistance. Inset in (a): optical microscopy image of the device with the laser position marked by red dot. The measurements performed with 750nm at 3mW power. (b, d) Photovoltage response of	

plasmonic (longitudinal and transverse polarizations) and nonplasmonic contacts normalised to the maximum value. For comparison purposes normalised thermoelectric voltage is included. The gate bias is tuned from positive voltage towards negative (a,b) and reverse (c,d) as indicated by arrows..... 148

Figure 6.16. (a) Band diagram of the device with graphene/Au interface and graphene channel. Black dash line represents the Fermi level; black fine dash line represents the Dirac point of the graphene. The illumination is located at graphene/Au interface resulting in higher carrier temperature (TH). (b) Calculated gate dependent Fermi level difference (top) and Seebeck coefficient difference (middle) between the Gr/Au and Gr/SiO₂ areas and gate dependent Seebeck coefficient (bottom) for graphene channel. The contributing currents are indicated by arrows. Vertical dash line corresponds to band flattening point observed at 25 V. 149

Figure 6.17. (a, b) Probe-induced photovoltage at plasmonic and nonplasmonic contacts as a function of pump–probe pulse delay time. Probe at 750 nm and 100 μ W power, pump at 650 nm and power as indicated; both beam spots have elliptical shape. Insets are SEM images of the contacts. (c,d) Probe-induced photovoltage at zero time delay point and response time, extracted from bi-exponential decay of the dip in (a) as a function of pump power. 152

Figure 6.18. (a) Schematic diagram of an excitation laser pulse train with $\nu_0 = 80$ MHz and $\tau_0 = 150$ fs and corresponding photovoltage (PV) response with $\tau = 4$ ps including photovoltage peaks (V_{peak}) and average signal (V_{exp}) detected in the measurements. (b) Power dependence of the carrier temperature and carrier energy in graphene at plasmonic contact under longitudinal and transverse polarization. 154

Figure 6.19. Graphene destruction in presence of plasmonic nanoparticles..... 155

Figure 7.1. Conventional (left) and new (right) time-resolved scanning technique. Red dots represent plasmon-induced hot carriers. 161

Figure 7.2. Schematics of hot carrier injection devices with plasmonic contact (a) and plasmonic nanoparticles (b). 162

Figure 8.1. Schematic of light interaction with a single layer substrate covered by graphene. Arrows represent the beam directions; n_1 and n_2 are refractive indices of the media and r and t are reflection and transmission coefficients, respectively. 164

Figure 8.2. Schematic of light interaction with a multilayer substrate covered by graphene. Arrows represent the beam directions; n_1 and n_2 are refractive indices of the media and r and t are reflection and transmission coefficients, respectively. 166

List of tables

Table 2.1. Summary of contributing effects: ✓ – the effect is active and ✕ – the effect is cancelled.	39
Table 2.2. Properties of graphene material obtained by different fabrication methods. Adapted by permission from Macmillan Publishers Ltd: [110], copyright 2012.....	43
Table 4.1. Graphene film properties based on Raman spectroscopy data presented in Figure 4.16.....	98
Table 4.2. The position of the Dirac point and hole/electron mobility for graphene transistors measured after preparation and after 1 month of storage in ambient conditions.....	105
Table 5.1 Details of the samples discussed in this section including the substrate structure and treatment. The Fermi energy is extracted from Raman spectroscopy data (not shown). See Section 4.5 for detailed discussion of the doping induced by engineering of the substrate surface.....	120
Table 5.2 Parameters for the DR response observed for the Gr/NP/hBN/SiO ₂ and Gr/NP/hBN/SiO ₂ samples obtained with parallel () and perpendicular (⊥) pump–probe polarizations. A_2 is the amplitude of the secondary decay component. The ratio A_1/A_2^* is normalised to the bare graphene value extracted for each sample.....	129
Table 6.1. Summary of contributing effects under different gate bias: ✓ – the effect is active and ✕ – the effect is cancelled.....	150

Permissions



ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Plasmonic Nanoantennas:
Fundamentals and Their Use in
Controlling the Radiative
Properties of Nanoemitters
Author: Vincenzo Giannini, Antonio I.
Fernández-Domínguez,
Susannah C. Heck, et al

Publication: Chemical Reviews
Publisher: American Chemical Society
Date: Jun 1, 2011

Copyright © 2011, American Chemical Society

LOGIN

If you're a **copyright.com**
user, you can login to
RightsLink using your
copyright.com credentials.
Already a **RightsLink** user or
want to [learn more?](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

If credit is given to another source for the material you requested, permission must be obtained from that source.

BACK

CLOSE WINDOW

Copyright © 2017 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
Comments? We would like to hear from you. E-mail us at customercare@copyright.com

**NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS**

Sep 23, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4194971385229
License date	Sep 23, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Plasmon-induced hot carrier science and technology
Licensed Content Author	Mark L. Brongersma, Naomi J. Halas, Peter Nordlander
Licensed Content Date	Jan 6, 2015
Licensed Content Volume	10
Licensed Content Issue	1
Type of Use	reuse in a dissertation / thesis
Requestor type	non-commercial (non-profit)
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables /illustrations	1
High-res required	no
Figures	Figure 2.2
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
Requestor Location	Imperial College London Prince Consort road London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice
Billing Address	Imperial College London Prince Consort road London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD

AMERICAN PHYSICAL SOCIETY ORDER DETAILS

Sep 23, 2017

Order Number	501312837
Order date	Sep 23, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Reviews of Modern Physics
Licensed Content Title	The electronic properties of graphene
Licensed Content Author	A. H. Castro Neto et al.
Licensed Content Date	Jan 14, 2009
Licensed Content Volume	81
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print, Electronic
Portion	image/photo
Number of images/photos requested	3
Portion description	Fig 1, Fig 2, Fig 3
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	yes
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	0 to 499
The requesting person/organization is:	Imperial College London
Order reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Expected size (number of pages)	200
	Imperial College Prince Consort Lonodn road
Requestor Location	London, SW7 2AZ United Kingdom Attn: Imperial College Lonodn
Total	Not Available

AMERICAN PHYSICAL SOCIETY ORDER DETAILS

Sep 23, 2017

Order Number	501312838		
Order date	Sep 23, 2017		
Licensed Content Publisher	American Physical Society		
Licensed Content Publication	Physical Review B		
Licensed Content Title	Theory of double-resonant Raman spectra in graphene: Intensity and line shape of defect-induced and two-phonon bands		
Licensed Content Author	Pedro Venezuela, Michele Lazzeri, and Francesco Mauri		
Licensed Content Date	Jul 25, 2011		
Licensed Content Volume	84		
Type of Use	Thesis/Dissertation		
Requestor type	Student		
Format	Print, Electronic		
Portion	image/photo		
Number of images/photos requested	1		
Portion description	Figure 4 bottom		
Rights for	Main product		
Duration of use	Life of Current Edition		
Creation of copies for the disabled	no		
With minor editing privileges	yes		
For distribution to	Worldwide		
In the following language(s)	Original language of publication		
With incidental promotional use	no		
The lifetime unit quantity of new product	0 to 499		
The requesting person/organization is:	Imperial College London		
Order reference number			
Title of your thesis / dissertation	Graphene based plasmonic photodetection		
Expected completion date	Sep 2017		
Expected size (number of pages)	200		
	Imperial Prince	College Consort	London road
Requestor Location	London, United	SW7	2AZ Kingdom
	Attn: Imperial College London		
Total	Not Available		

THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE LICENSE
TERMS AND CONDITIONS

Sep 24, 2017

This Agreement between Imperial College Londn -- Viktoryia Shautsova ("You") and The American Association for the Advancement of Science ("The American Association for the Advancement of Science") consists of your license details and the terms and conditions provided by The American Association for the Advancement of Science and Copyright Clearance Center.

License Number	4195530390244		
License date	Sep 24, 2017		
Licensed Content Publisher	The American Association for the Advancement of Science		
Licensed Content Publication	Science		
Licensed Content Title	Fine Structure Constant Defines Visual Transparency of Graphene		
Licensed Content Author	R. R. Nair,P. Blake,A. N. Grigorenko,K. S. Novoselov,T. J. Booth,T. Stauber,N. M. R. Peres,A. K. Geim		
Licensed Content Date	Jun 6, 2008		
Licensed Content Volume	320		
Licensed Content Issue	5881		
Volume number	320		
Issue number	5881		
Type of Use	Thesis / Dissertation		
Requestor type	Scientist/individual at a research institution		
Format	Print and electronic		
Portion	Figure		
Number of figures/tables	1		
Order reference number			
Title of your thesis dissertation	/ Graphene based plasmonic photodetection		
Expected completion date	Sep 2017		
Estimated size(pages)	200		
Requestor Location	Imperial Prince	College Consort	Londn road
	London, United	SW7	2AZ Kingdom
	Attn: Imperial College Londn		
Billing Type	Invoice		
	Imperial Prince	College Consort	Londn road
Billing Address	London, United Kingdom	SW7	2AZ
	Attn: Imperial College Londn		
Total	0.00 USD		

This Agreement between Imperial College Lonodn -- Viktoryia Shautsova ("You") and AIP Publishing LLC ("AIP Publishing LLC") consists of your license details and the terms and conditions provided by AIP Publishing LLC and Copyright Clearance Center.

License Number	4195530848415		
License date	Sep 24, 2017		
Licensed Publisher	Content	AIP Publishing LLC	
Licensed Publication	Content	Applied Physics Letters	
Licensed Content Title	Optical properties of large-area polycrystalline chemical vapor deposited graphene by spectroscopic ellipsometry		
Licensed Content Author	F. J. Nelson, V. K. Kamineni, T. Zhang, et al		
Licensed Content Date	Dec 20, 2010		
Licensed Content Volume	97		
Licensed Content Issue	25		
Type of Use	Thesis/Dissertation		
Requestor type	Student		
Format	Print and electronic		
Portion	Figure/Table		
Number of figures/tables	1		
Title of your thesis / dissertation	Graphene based plasmonic photodetection		
Expected completion date	Sep 2017		
Estimated size (number of pages)	200		
Requestor Location	Imperial Prince	College Consort	Lonodn road
	London, United	SW7	2AZ Kingdom
	Attn: Imperial College Lonodn		
Billing Type	Invoice		
	Imperial Prince	College Consort	Lonodn road
Billing Address	London, United Kingdom	SW7	2AZ
	Attn: Imperial College Lonodn		
Total	0.00 USD		

Order Details

Journal of Physics : Condensed Matter

Billing Status:
N/A

Order detail ID: 70686998
ISSN: 0953-8984
Publication Type: Journal
Volume:
Issue:
Start page:
Publisher: IOP Publishing

Permission Status:  **Granted**

Permission type: Republish or display content

Type of use: Thesis/Dissertation

Order License Id: 4195531382413

 [View details](#)

Note: This item was invoiced separately through our **RightsLink service**. More info

\$ 0.00

This Agreement between Imperial College Lonodn -- Viktoryia Shautsova ("You") and American Physical Society ("American Physical Society") consists of your license details and the terms and conditions provided by American Physical Society and Copyright Clearance Center.

License Number	4195540305913			
License date	Sep 24, 2017			
Licensed Content Publisher	American Physical Society			
Licensed Content Publication	Physical Review Letters			
Licensed Content Title	Direct View of Hot Carrier Dynamics in Graphene			
Licensed Content Author	Jens Christian Johannsen et al.			
Licensed Content Date	Jul 9, 2013			
Licensed Content Volume	111			
Type of Use	Thesis/Dissertation			
Requestor type	Student			
Format	Print, Electronic			
Portion	image/photo			
Number of images/photos requested	1			
Portion description	Figure 3 (a)			
Rights for	Main product			
Duration of use	Life of Current Edition			
Creation of copies for the disabled	no			
With minor editing privileges	no			
For distribution to	Worldwide			
In the following language(s)	Original language of publication			
With incidental promotional use	no			
The lifetime unit quantity of new product	0 to 499			
The requesting person/organization is:	Imperial College London			
Order reference number				
Title of your thesis / dissertation	Graphene based plasmonic photodetection			
Expected completion date	Sep 2017			
Expected size (number of pages)	200			
	Imperial Prince	College Consort	Lonodn road	
Requestor Location	London, United Kingdom	SW7	2AZ	
	Attn: Imperial College Lonodn			
Billing Type	Invoice			
	Imperial Prince	College Consort	Lonodn road	
Billing Address	London, United Kingdom	SW7	2AZ	
	Attn: Imperial College Lonodn			
Total	0.00 USD			

Special Orders

[Learn more about how Special Orders work](#)

Nanoscale

Order detail ID: 70686999
Job Ticket: 501312982

ISSN: 2040-3372
Publication Type: e-Journal

Volume:

Issue:

Start page:

Publisher: RSC Pub

Author/Editor: National Center for Nanoscience and
Technology ; Royal Society of Chemistry
(Great Britain)

Permission Status:  Special Order
Special Order Update: Checking availability

Permission type: Republish or display content
Type of use: Thesis/Dissertation

[View details](#)

Note: This item will be managed through CCC's **RightsLink service**. [More info](#)

TBD

**Title:**Photocurrent Imaging and
Efficient Photon Detection in a
Graphene Transistor**Author:**Fengnian Xia, Thomas Mueller,
Roksana Golizadeh-Mojarad, et
al

Logged in as:

Viktoryia Shautsova
Imperial College London

Account #:

3001198162

LOGOUT

Publication: Nano Letters**Publisher:** American Chemical Society**Date:** Mar 1, 2009

Copyright © 2009, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

ACS Publications
Most Trusted. Most Cited. Most Read.**Title:**Hot Carrier Transport and
Photocurrent Response in
Graphene**Author:**Justin C. W. Song, Mark S.
Rudner, Charles M. Marcus, et al**Publication:** Nano Letters**Publisher:** American Chemical Society**Date:** Nov 1, 2011

Copyright © 2011, American Chemical Society

Logged in as:

Viktoryia Shautsova
Imperial College Londn

Account #:

3001198162

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS

Sep 25, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4195830893855
License date	Sep 25, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Communications
Licensed Content Title	Strong plasmonic enhancement of photovoltage in graphene
Licensed Content Author	T.J. Echtermeyer, L. Britnell, P.K. Jasnós, A. Lombardo, R.V. Gorbachev et al.
Licensed Content Date	Aug 30, 2011
Licensed Content Volume	2
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	Fig 2.13
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
	Imperial College London Prince Consort road
Requestor Location	London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD
Terms and Conditions	

ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Plasmon-Induced Doping of Graphene
Author: Zheyu Fang, Yumin Wang, Zheng Liu, et al
Publication: ACS Nano
Publisher: American Chemical Society
Date: Nov 1, 2012

Logged in as:
Viktoryia Shautsova
Imperial College London
Account #:
3001198162

[LOGOUT](#)

Copyright © 2012, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS
Sep 25, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4195831461903
License date	Sep 25, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature
Licensed Content Title	A roadmap for graphene
Licensed Content Author	K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim
Licensed Content Date	Oct 10, 2012
Licensed Content Volume	490
Licensed Content Issue	7419
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	Figure 2.14 Table 2.2
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
Requestor Location	Imperial College London Prince Consort road London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD
Terms and Conditions	


ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Direct Measurement of Adhesion
Energy of Monolayer Graphene
As-Grown on Copper and Its
Application to Renewable
Transfer Process

Logged in as:
Viktoryia Shautsova
Imperial College London

Account #:
3001198162

Author: Taeshik Yoon, Woo Cheol Shin,
Taek Yong Kim, et al

[LOGOUT](#)

Publication: Nano Letters

Publisher: American Chemical Society

Date: Mar 1, 2012

Copyright © 2012, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

ACS Publications
Most Trusted. Most Cited. Most Read.**Title:** High-Quality Uniform Dry
Transfer of Graphene to
Polymers**Author:** Evgeniya H. Lock, Mira Baraket,
Matthew Laskoski, et al**Publication:** Nano Letters**Publisher:** American Chemical Society**Date:** Jan 1, 2012

Copyright © 2012, American Chemical Society

Logged in as:
Viktoryia Shautsova
Imperial College LondonAccount #:
3001198162[LOGOUT](#)**PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE**

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.



Title: A facile process for soak-and-peel delamination of CVD graphene from substrates using water

Author: Priti Gupta, Pratiksha D. Dongare, Sameer Grover, Sudipta Dubey, Hitesh Mangain et al.

Publication: Scientific Reports

Publisher: Nature Publishing Group

Date: Jan 24, 2014

Copyright © 2014, Rights Managed by Nature Publishing Group

Logged in as:
Viktoryia Shautsova
Imperial College London
Account #:
3001198162

LOGOUT

Creative Commons

The request you have made is considered to be non-commercial/educational. As the article you have requested has been distributed under a Creative Commons license (Attribution-Noncommercial), you may reuse this material for non-commercial/educational purposes without obtaining additional permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged (please see the article itself for the license version number). You may reuse this material without obtaining permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged, as per the terms of the license. For license terms, please see <http://creativecommons.org/>

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS
Sep 25, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4195840924537
License date	Sep 25, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	A general method for transferring graphene onto soft surfaces
Licensed Content Author	Jie Song, Fong-Yu Kam, Rui-Qi Peng, Wei-Ling Seah, Jing-Mei Zhuo, Geok-Kheng Lim
Licensed Content Date	Apr 28, 2013
Licensed Content Volume	8
Licensed Content Issue	5
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	Figure 2.16
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
	Imperial College London Prince Consort road
Requestor Location	London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	
	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD



RightsLink®

Home

Account
Info

Help



ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Transfer of CVD-Grown
Monolayer Graphene onto
Arbitrary Substrates
Author: Ji Won Suk, Alexander Kitt, Carl
W. Magnuson, et al
Publication: ACS Nano
Publisher: American Chemical Society
Date: Sep 1, 2011

Logged in as:
Viktoryia Shautsova
Imperial College London
Account #:
3001198162

LOGOUT

Copyright © 2011, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

**Title:**Chemical Vapor Deposition-
Derived Graphene with Electrical
Performance of Exfoliated
Graphene**Author:**Nicholas Petrone, Cory R. Dean,
Inanc Meric, et al**Publication:** Nano Letters**Publisher:** American Chemical Society**Date:** Jun 1, 2012

Copyright © 2012, American Chemical Society

Logged in as:

Viktoryia Shautsova
Imperial College London

Account #:

3001198162

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Transfer of Large-Area Graphene
Films for High-Performance
Transparent Conductive
Electrodes

Author: Xuesong Li, Yanwu Zhu, Weiwei
Cai, et al

Logged in as:
Viktoryia Shautsova
Imperial College London

Account #:
3001198162

LOGOUT

Publication: Nano Letters

Publisher: American Chemical Society

Date: Dec 1, 2009

Copyright © 2009, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

AIP PUBLISHING LLC LICENSE
TERMS AND CONDITIONS
Sep 25, 2017

This Agreement between Imperial College Lonodn -- Viktoryia Shautsova ("You") and AIP Publishing LLC ("AIP Publishing LLC") consists of your license details and the terms and conditions provided by AIP Publishing LLC and Copyright Clearance Center.

License Number	4195860641815
License date	Sep 25, 2017
Licensed Content Publisher	AIP Publishing LLC
Licensed Content Publication	Applied Physics Letters
Licensed Content Title	A direct transfer of layer-area graphene
Licensed Content Author	William Regan, Nasim Alem, Benjamín Alemán, et al
Licensed Content Date	Mar 15, 2010
Licensed Content Volume	96
Licensed Content Issue	11
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print and electronic
Portion	Figure/Table
Number of figures/tables	2
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
Requestor Location	Imperial College Lonodn Prince Consort road London, SW7 2AZ United Kingdom Attn: Imperial College Lonodn
Billing Type	Invoice Imperial College Lonodn Prince Consort road
Billing Address	London, United Kingdom SW7 2AZ Attn: Imperial College Lonodn
Total	0.00 USD

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS
Sep 27, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4196961058434
License date	Sep 27, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Raman spectroscopy as a versatile tool for studying the properties of graphene
Licensed Content Author	Andrea C. Ferrari, Denis M. Basko
Licensed Content Date	Apr 4, 2013
Licensed Content Volume	8
Licensed Content Issue	4
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	3
High-res required	no
Figures	Fig. 2.19, 2.21
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
Requestor Location	Imperial College London Prince Consort road London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD

ACS Publications
Most Trusted. Most Cited. Most Read.

Title: Tuning the Graphene Work
Function by Electric Field Effect

Author: Young-Jun Yu, Yue Zhao, Sunmin
Ryu, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: Oct 1, 2009

Copyright © 2009, American Chemical Society

Logged in as:
Viktoryia Shautsova
Imperial College London

Account #:
3001198162

[LOGOUT](#)**PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE**

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

AMERICAN PHYSICAL SOCIETY LICENSE
TERMS AND CONDITIONS
Sep 27, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and American Physical Society ("American Physical Society") consists of your license details and the terms and conditions provided by American Physical Society and Copyright Clearance Center.

License Number	4196961311976
License date	Sep 27, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Physical Review B
Licensed Content Title	Electron-electron interactions and doping dependence of the two-phonon Raman intensity in graphene
Licensed Content Author	D. M. Basko, S. Piscanec, and A. C. Ferrari
Licensed Content Date	Oct 16, 2009
Licensed Content Volume	80
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print, Electronic
Portion	image/photo
Number of images/photos requested	1
Portion description	Fig1
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	0 to 499
The requesting person/organization is:	Imperial College London
Order reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Expected size (number of pages)	200
	Imperial College London Prince Consort road
Requestor Location	London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD

AMERICAN PHYSICAL SOCIETY LICENSE
TERMS AND CONDITIONS
Sep 27, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and American Physical Society ("American Physical Society") consists of your license details and the terms and conditions provided by American Physical Society and Copyright Clearance Center.

License Number	4196970136093
License date	Sep 27, 2017
Licensed Content Publisher	American Physical Society
Licensed Content Publication	Physical Review Letters
Licensed Content Title	Raman Spectrum of Graphene and Graphene Layers
Licensed Content Author	A. C. Ferrari et al.
Licensed Content Date	Oct 30, 2006
Licensed Content Volume	97
Type of Use	Thesis/Dissertation
Requestor type	Student
Format	Print, Electronic
Portion	image/photo
Number of images/photos requested	2
Portion description	Fig.2 and Fig 3
Rights for	Main product
Duration of use	Life of Current Edition
Creation of copies for the disabled	no
With minor editing privileges	no
For distribution to	Worldwide
In the following language(s)	Original language of publication
With incidental promotional use	no
The lifetime unit quantity of new product	0 to 499
The requesting person/organization is:	Imperial College London
Order reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Expected size (number of pages)	200
	Imperial College London Prince Consort road
Requestor Location	
	London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice
	Imperial College London Prince Consort road
Billing Address	
	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD



RightsLink®

Home

Account
Info

Help



ACS Publications
Most Trusted. Most Cited. Most Read.

Title:

Spatially Resolved Raman
Spectroscopy of Single- and
Few-Layer Graphene

Author:

D. Graf, F. Molitor, K. Ensslin, et
al

Publication:

Nano Letters

Publisher:

American Chemical Society

Date:

Feb 1, 2007

Copyright © 2007, American Chemical Society

Logged in as:

Viktoryia Shautsova
Imperial College London

Account #:

3001198162

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.



Title: Quantifying Defects in Graphene
via Raman Spectroscopy at
Different Excitation Energies

Author: L. G. Cançado, A. Jorio, E. H.
Martins Ferreira, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: Aug 1, 2011

Copyright © 2011, American Chemical Society

Logged in as:
Viktoryia Shautsova
Imperial College London

Account #:
3001198162

LOGOUT

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS
Sep 27, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4196971025864
License date	Sep 27, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Nanotechnology
Licensed Content Title	Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor
Licensed Content Author	A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha et al.
Licensed Content Date	Mar 30, 2008
Licensed Content Volume	3
Licensed Content Issue	4
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	Fig. 2.23
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
	Imperial College London Prince Consort road
Requestor Location	
	London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice
	Imperial College London Prince Consort road
Billing Address	
	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD

**Title:**

Intercalation of Few-Layer
Graphite Flakes with FeCl₃:
Raman Determination of Fermi
Level, Layer by Layer
Decoupling, and Stability

Logged in as:

Viktoryia Shautsova
Imperial College London

Account #:
3001198162

Author:

Weijie Zhao, Ping Heng Tan, Jian
Liu, et al

[LOGOUT](#)**Publication:**

Journal of the American
Chemical Society

Publisher:

American Chemical Society

Date:

Apr 1, 2011

Copyright © 2011, American Chemical Society

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.



Title: Development of a universal stress sensor for graphene and carbon fibres

Author: Otakar Frank, Georgia Tsoukleri, Ibtisam Riaz, Konstantinos Papagelis, John Parthenios et al.

Logged in as:
Viktoryia Shautsova
Imperial College London

Account #:
3001198162

LOGOUT

Publication: Nature Communications

Publisher: Nature Publishing Group

Date: Mar 29, 2011

Copyright © 2011, Rights Managed by Nature Publishing Group

Creative Commons

The request you have made is considered to be non-commercial/educational. As the article you have requested has been distributed under a Creative Commons license (Attribution-Noncommercial), you may reuse this material for non-commercial/educational purposes without obtaining additional permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged (please see the article itself for the license version number). You may reuse this material without obtaining permission from Nature Publishing Group, providing that the author and the original source of publication are fully acknowledged, as per the terms of the license. For license terms, please see <http://creativecommons.org/>

BACK

CLOSE WINDOW

Copyright © 2017 Copyright Clearance Center, Inc. All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
Comments? We would like to hear from you. E-mail us at customercare@copyright.com

NATURE PUBLISHING GROUP LICENSE
TERMS AND CONDITIONS
Sep 27, 2017

This Agreement between Imperial College London -- Viktoryia Shautsova ("You") and Nature Publishing Group ("Nature Publishing Group") consists of your license details and the terms and conditions provided by Nature Publishing Group and Copyright Clearance Center.

License Number	4196980281187
License date	Sep 27, 2017
Licensed Content Publisher	Nature Publishing Group
Licensed Content Publication	Nature Communications
Licensed Content Title	Optical separation of mechanical strain from charge doping in graphene
Licensed Content Author	Ji Eun Lee, Gwanghyun Ahn, Jihye Shim, Young Sik Lee, Sunmin Ryu
Licensed Content Date	Aug 28, 2012
Licensed Content Volume	3
Type of Use	reuse in a dissertation / thesis
Requestor type	academic/educational
Format	print and electronic
Portion	figures/tables/illustrations
Number of figures/tables/illustrations	2
High-res required	no
Figures	2.26
Author of this NPG article	no
Your reference number	
Title of your thesis / dissertation	Graphene based plasmonic photodetection
Expected completion date	Sep 2017
Estimated size (number of pages)	200
Requestor Location	Imperial College London Prince Consort road London, SW7 2AZ United Kingdom Attn: Imperial College London
Billing Type	Invoice Imperial College London Prince Consort road
Billing Address	
	London, United Kingdom SW7 2AZ Attn: Imperial College London
Total	0.00 USD