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Magnetotransport and Photocurrent Spectroscopy in 2D materials

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Abstract

This thesis falls within the broad research field of 2D van der waals materials. The isolation of single-layer graphene and the subsequent discovery of several of these materials has led to the emergence of a new platform to study different physical phenomena, pushing the limits in condensed matter physics. In this thesis I present two research lines, both within this field.

The first part focuses in the study of the quantum hall effect at high temperature in graphene encapsulated with h-BN. Prior to the isolation of graphene, the quantum Hall effect in 2D systems was typically observed only at low temperatures. However, the irruption of graphene allows for investigating the quantum Hall effect up to room temperature due to its large Landau level separation. In this study, through the analysis of thermally-activated transport at filling factor 2 up to room temperature in high quality graphene devices, we reveal a new transport regime where electron-phonon scattering is the main source of dissipation in the quantum hall phase. Furthermore, we establish a link between the activation of the quantum hall effect and the quality of our devices. Thanks to van der waals heterostructures of hBN and graphene we give a further notion of the quantum hall effect, even 40 years after its discovery.

The second part centers on the study of excitons in transition metal dicalchogenides (TMDs) using low temperature photocurrent spectroscopy. 2D transition metal dichalcogenides shows strongly bound excitons that largely influences its optoelectronic response. The binding energy of excitons in these materials reaches values of two orders of magnitude larger than conventional semiconductors. Therefore, 2D-TMDs are a perfect system to study excitons. Before this dissertation the main part of the research of excitonic phenomena are commonly explored using photoluminescence spectroscopy, nevertheless, this technique may not reveal non-radiative excitons. Hence, we propose the use of low temperature photocurrent spectroscopy to study excitonic physics in 2D-TMDs based devices, concretely MoS_2 , MoSe_2 and ReS_2 . Photocurrent spectroscopy is a powerful technique that allows us to obtain transition linewidths of roughly 10 meV, similar to previous photoluminescence studies. Furthermore, using this technique we reveal excitonic peaks not reported in previous literature, demonstrating the potential of this technique. With our investigation we provide new insights on the excitonic physics of 2D-TMDs and we provide an experimental tool with huge possibilities in the future. Finally, I present future research topics that can be developed using low-temperature photocurrent spectroscopy.

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Chapter 1

Introduction and Motivation

In this dissertation I will show our results in the fabrication and experimental characterization of several devices based on different 2D materials.

We start by studying the transport properties, at high magnetic fields and room temperature, of h-BN encapsulated graphene devices to understand why the quantum hall effect could be observed at room temperature in low-mobility graphene samples over SiO₂ and surprisingly the quantization reduces in high mobility samples. As a consequence, we find a new transport regime mediated by phonons in graphene, paving the way to understand this intriguing question.

The main part of the thesis will center on low temperature photocurrent spectroscopy, a new spectroscopy technique for the study of the optoelectronic properties of transition metal dichalcogenides, and concretely excitonic transitions. To perform the spectroscopy measurements, we have developed a completely new experimental setup. This thesis presents the photocurrent spectroscopy characterization of different 2D materials, concretely MoS₂, MoSe₂ and ReS₂ showing the remarkable possibilities of this new technique to study and reveal new excitonic states in 2D transition metal dichalcogenides. I have included also theoretical and numerical studies supporting our experimental results thanks to our collaboration with the QNS group of the Complutense University. Finally, I present two future research lines exploiting the possibilities of photocurrent spectroscopy; the generation of helicity dependent photocurrents in ReS₂ and the study of twisted heterostructures of 2D materials to reveal moiré excitonic states using photocurrent spectroscopy.

In this chapter, I provide a brief introduction about the emergence of 2D materials and motivate the experimental work performed in this thesis, using the van der Waals materials as the cornerstone of our research. Next, I introduce the electronic and optoelectronic properties of the 2D materials characterized in this dissertation, graphene and TMDs. To conclude this chapter, I provide the structure followed in this thesis, with a concise summary to outline the upcoming chapters, emphasizing our findings and their implications.

1.1 Emergence of 2D-materials

The discovery of two-dimensional (2D) materials has opened new perspectives in condensed matter physics. 2D materials are defined by their nanometer-scale thicknesses, leading to quantum confinement in one dimension highly influencing their physical properties. In this group of materials, it is possible to find crystalline [1], amorphous [2] or quasicrystalline [3, 4] materials.

Most studied 2D materials are layered van der Waals materials, which are a group of crystals, characterized by their bulk structure formed from stacks of atomically thin layers. These layers are bonded by weak interlayer interactions, called van der Waals forces. The weak nature of van der Waals forces allows for the crystal to be thinned down to the atomic layer limit.

For many years, it was believed that 2D materials were thermodynamically unstable [5] until the discovery of graphene. The isolation of mechanically exfoliated monolayer graphene in 2004 [6] supposed a milestone in materials science and sparked research on 2D materials. After two decades of intensive research, it can confidently be stated that the potential applications for these materials have only expanded due to the continuously growing catalogue of diverse 2D materials. Nowadays, this family has grown incredibly, to the point where, more than 1500 stable 2D materials have been identified [1, 7]. Among the wide spectrum of 2D materials, one can find semimetals (graphene), insulators (h-BN), semiconductors (MoS_2 , MoSe_2 , ReS_2), magnetic metals (FGTs), magnetic semiconductors (CrPS_4 , CrI_3), and even superconductors (NbSe_2 , NbS_2). Furthermore, the properties of these materials strongly depend on the number of layers. For instance, thick graphite behaves as a conventional semimetal, while monolayer graphene is a semimetal with outstanding quantum electronic properties [8]. Another interesting example is that of the transition metal dichalcogenides (TMDs), such as MoS_2 , MoSe_2 , WS_2 , and WSe_2 . These materials exhibit an indirect to direct bandgap transition at the monolayer limit [9]. Therefore, the monolayers show an improvement, in comparison with bulk crystal, in their absorption and emission mechanisms of light [10], which leads to enhanced optical and optoelectronic properties. Besides, 2D-TMDs optical response is largely influenced by the presence of excitons [11], that are quasiparticles present in semiconductors, formed by electrons and holes bound by the attractive Coulomb interaction.

Another point of great interest, regarding 2D materials, is the possibility of combining and stacking atomically thin layers together in so-called heterostructures, offering a wide range of applications [12, 13, 14]. In particular, h-BN has been extensively used in the field for making heterostructures. h-BN is an insulator with excellent dielectric properties [15, 16], therefore, is usually used as an atomically flat substrate to enhance the properties of various van der Waals materials [17, 18].

1.2 Motivation of the research

Given their variety and their outstanding properties, 2D van der Waals materials have irrupted as a platform to develop a wide range of applications and study several physical effects that are enhanced in this materials. This thesis is centered on exploiting 2D materials to shed light on distinct physical phenomena. In this context, we characterized the electronic and optoelectronic properties of devices based on 2D van der waals materials using magnetotransport and low temperature photocurrent spectroscopy. On the one hand, we study the quantum hall effect at high temperatures in h-BN encapsulated graphene and on the other hand the low temperature photocurrent spectroscopy characterization of transition metal dichalcogenides based devices.

In the nanotechnology group of the university of Salamanca one of the main research lines is devoted to the fabrication and characterization of h-BN graphene heterostructures using electronic transport [19] or THz [20]. The use of h-BN suppress extrinsic disorder originated by defects, for instance ripples. In this framework, we focused in the research of the quantum hall effect using encapsulated graphene. The quantum hall effect [21] is a quantum transport regime where the presence of disorder was necessary to explain the arising of quantized plateaus in the transversal conductivity [22, 23]. This motivate our investigation trying to understand the role of disorder in the quantum hall regime in this high-quality samples. Furthermore, graphene supports quantum hall effect up to room temperature under high magnetic fields [24], however, prior to this dissertation all the studies up to room temperature were performed using graphene over SiO_2 . The quantum hall effect could be observed at room temperature in low-mobility graphene samples over SiO_2 and the quantization reduces in high mobility samples when the graphene is stacked between hBN layers. Suppressing the disorder using h-BN encapsulated graphene reduces the amount of localized states leading to a suppression of the quantization in this regime in comparison with previous literature. Nevertheless, the measurements were not completely conclusive in quantitative terms. However, we find that the suppression of disorder can arise the presence a novel transport regime mediated by electron-phonon scattering in the quantum hall effect at room temperature.

Besides the transport measurements mentioned above, during this thesis we started a new research line in the group, focused on using low-temperature photocurrent spectroscopy to analyze excitonic states in transition metal dichalcogenides. In previous literature, photoluminescence spectroscopy have been the most used technique to characterize excitonic transitions. This technique allows to obtain detailed information about the properties of light-emitting excitons. However, photoluminescence spectroscopy might not reveal non-radiative excitonic states, which needs to be studied using different techniques. The primary motivation of this research line consists in exploiting photocurrent spectroscopy a novel technique to complement the use of photoluminescence spectroscopy, largely used in previous works. To the best of our knowledge, by the beguining of our research only two works [25, 26] used photocurrent spectroscopy for exciton characteri-

zation in 2D materials. Therefore, we developed a new experimental setup to perform photocurrent spectroscopy measurements including a system to reach cryogenic temperatures to improve the spectral resolution. The low temperature photocurrent spectroscopy setup is described at the end of Chapter 3 and it is largely used throughout this dissertation. With our work in this dissertation we demonstrate that phototocurrent spectroscopy is a simple, powerful and yet underused technique for studying excitonic transitions in 2D-TMDs.

1.3 Graphene

In 2004, Novoselov and Geim successfully isolated the first graphene monolayer through the mechanical exfoliation of bulk graphite. Graphite is composed of layers of carbon atoms ordered in a hexagonal pattern and weakly bound together by van der Waals forces. Each individual layer is known as graphene. Graphene is a single atomic layer of carbon atoms arranged in a honeycomb lattice. Figure 1.3.1 a) shows the atomic structure of graphene. This singular atomic structure leads to extraordinary properties and to a wealth of new physical phenomena to be explored, even 20 years after its discovery.

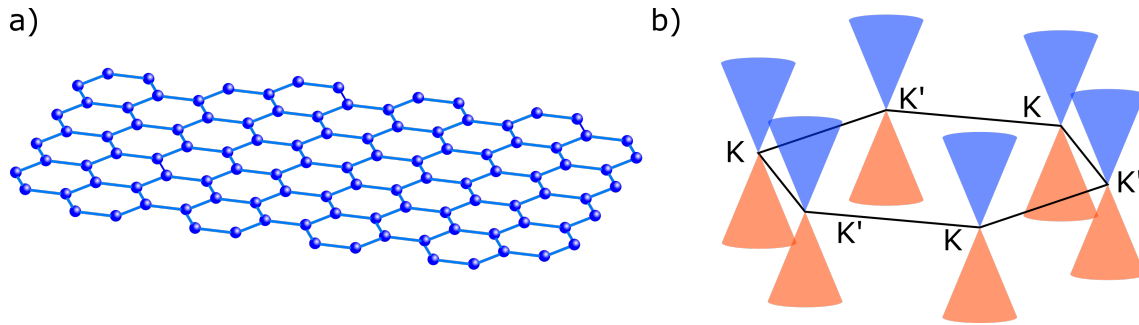


Fig. 1.3.1: Graphene atomic and band structure. a) Schematic of the carbon atoms in graphene showing a honeycomb lattice. b) Simplified low energy band structure of graphene with the Dirac cones in the K valleys.

Regarding its electronic properties, graphene is a semi-metal, characterized by the absence of a band gap. Figure 1.3.1 b) shows the hexagonal Brillouin zone of graphene featuring six K and K' points, also known as Dirac points. This figure also shows the low energy band structure of graphene with the electronic bands crossing near the Dirac points. Notably, the relation between the energy and the momentum of the carriers, known as dispersion relation, is linear around the K points, and is represented as cones corresponding to the well-known Dirac cones [27]. The orange and blue cones indicate the valence and conduction bands, respectively. Due to the linear dispersion, charge carriers near the Dirac points behave as massless relativistic particles, known as Dirac fermions. Such characteristic band structure has given rise to new physics, including Klein tunneling [28], room temperature quantum hall effect [24], fractional quantum hall effect [29] or quantized ballistic transport [19]. Moreover, graphene exhibits high carrier mobilities

[30], long spin diffusion length [31] and unmatched thermoelectric [32] or optoelectronic properties [33].

However, the interaction between the graphene layer and its substrate significantly modifies these properties. The substrate flatness is crucial, because any irregularities can lead to ripples in graphene, potentially causing unwanted effects, for example a huge reduction of the mobility. Thus, to optimize the graphene capabilities by minimizing scattering sources researchers have investigated several methods, such as the fabrication of suspended graphene [34] or the use of hexamethyldisilazane (HMDS) to treat the substrate [35, 36]. Currently, the best approach is the use of h-BN as an atomically flat substrate [17]. Devices based on heterostructures of h-BN/graphene have demonstrated remarkable field-effect mobilities of $10^5 \text{ cm}^2/\text{Vs}$ [19, 37], reducing the possible scattering sources to the minimal.

1.4 Transition metal dichalcogenides

Transition metal dichalcogenides (TMDs) belong to the large family of 2D van der Waals materials and have generated substantial interest in the scientific community [38]. Initially, graphene attracted great attention from the researchers due to its huge mobility and the presence of exotic electronic and transport properties. Nevertheless, the discovery by Novoselov et al [1] of 2D crystals that could be exfoliated to obtain atomically thin layers, like graphene, attracted the researchers to start the investigation on different 2D materials. Furthermore, the absence of an electronic band gap in graphene can be a severe limitation for its use in certain applications. Therefore, great efforts were made to open a bandgap in graphene [39, 40] or in looking for new 2D materials with a band gap.

In 2010 the discovery of 2D semiconducting TMDs [9, 10, 41] with band gaps in the visible range supposed a new revolution in the 2D materials field. Currently, tenths of new 2D-TMDs have been experimentally isolated, featuring band gaps that cover a broad spectrum of energy, ranging from millielectronvolts (meVs) to several electronvolts (eV) [42]. Therefore, in the compilation of TMDs, it is possible to find insulating, semiconducting, metallic or semimetallic materials. Due to this broad catalogue of materials, it is usually possible to find a TMD that is optimal for a certain application.

Furthermore, some semiconducting TMDs in their bulk form show an indirect band gap. By reducing the number of layers to a monolayer, the band structure changes, leading to a direct band gap [43, 44, 45]. The direct band-gap nature of these semiconductors opens the possibilities of developing competitive devices such as, ultrasensitive photodetectors [46, 47], phototransistors [48] or light emitting devices [49, 50].

Every individual layer of the TMDs is composed by three atomic layers forming a X-M-X structure, being M a transition metal layer (Mo, W, Re, Ta) sandwiched by two chalcogen layers X (S, Se, Te). Moreover, these layers can be arranged in different crys-

talline phases like hexagonal (1H/2H), rhombohedral (3R) or tetragonal (1T and 1T'). In this thesis, a significant focus is applied on semiconducting TMDs and the relevant crystalline phases are the 2H-hexagonal of the MoS_2 and MoSe_2 and the tetragonal 1T distorted of the ReS_2 . Figure 1.4.1 shows the crystalline structure of MoS_2 and MoSe_2 (panel a)) and of ReS_2 (panel b)).

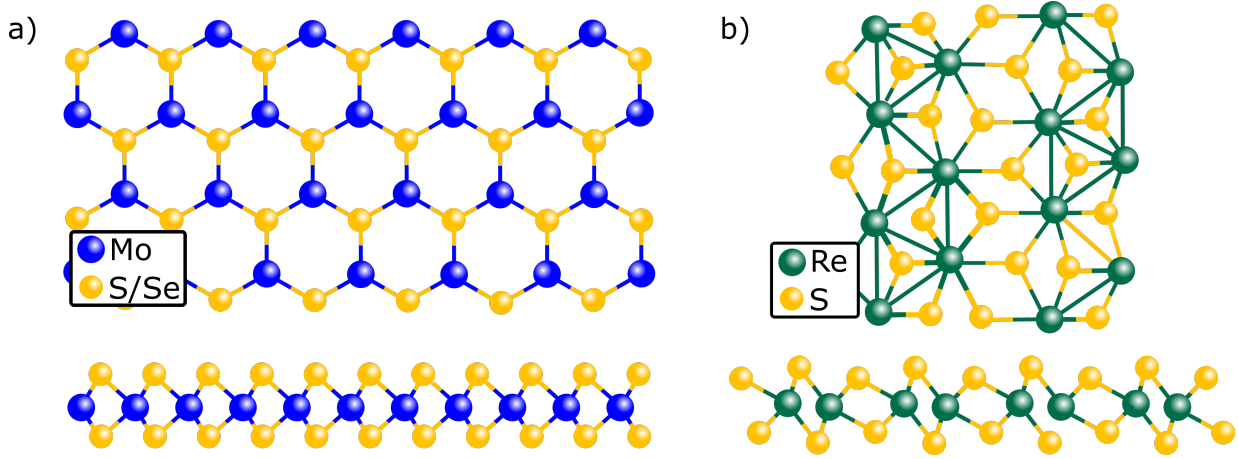


Fig. 1.4.1: MoS/Se_2 and ReS_2 atomic structure. a) Schematic of the top and side view of the atomic structure of MoS/Se_2 with 2H crystalline structure. b) Schematic of the top and side view of the atomic structure of ReS_2 with 1T distorted crystalline structure.

Firstly, I focus on monolayers of 2H-TMDs (MoS_2 , MoSe_2 , WS_2 and WSe_2) which feature a direct band gap in the visible range, 1-2 eV. Figure 1.4.2 a) shows the band structure of the monolayer Mo-based 2H-TMDs calculated using density functional theory (DFT) [51]. This diagram highlights the direct band gap in the K-point. Moreover, the valence band appear splitted into two subbands, v_1 and v_2 . This splitting is caused by the strong spin-orbit interaction present in 2H-TMDs, which results in an energy shift between spin-up and spin-down states in the valence band. Figure 1.4.2 b) shows the schematic of the low energy band structure of Mo-based TMDs. As they have a honeycomb lattice (see figure 1.4.1 a)), similar to graphene, the brillouin zone is also hexagonal, with the band edges located at the K and K' valleys. The red and blue bands in the figure denote the spin-up and spin-down subbands respectively. Panels c) and d) depicts the detailed band structure near the K and K' valleys for WX_2 and MoX_2 , being X=S or Se. There are differences between both W-based and Mo-based TMDs, for instance, the spin splitting in the valence band is roughly 0.2 eV in Mo-based and 0.4 eV in W-based [52, 53]. Besides, the sign of the spin orbit coupling in the conduction band is different for both materials, being positive in the W-based and negative in the Mo-based.

The presence of split spin-up and spin-down bands has several implications in the optical transitions of these materials, such as the arising of two main excitons denoted by excitons A and B. Furthermore, as depicted in figure 1.4.2 c) and d), both valleys, K and K', have different optical selectivity rules for right (σ^+) and left (σ^-) handed circularly

polarized light. Hence, these materials enable the manipulation of spin and valley degrees of freedom using light as an experimental knob to control spin population, opening the opto-spintronics field [54, 55, 56, 57].

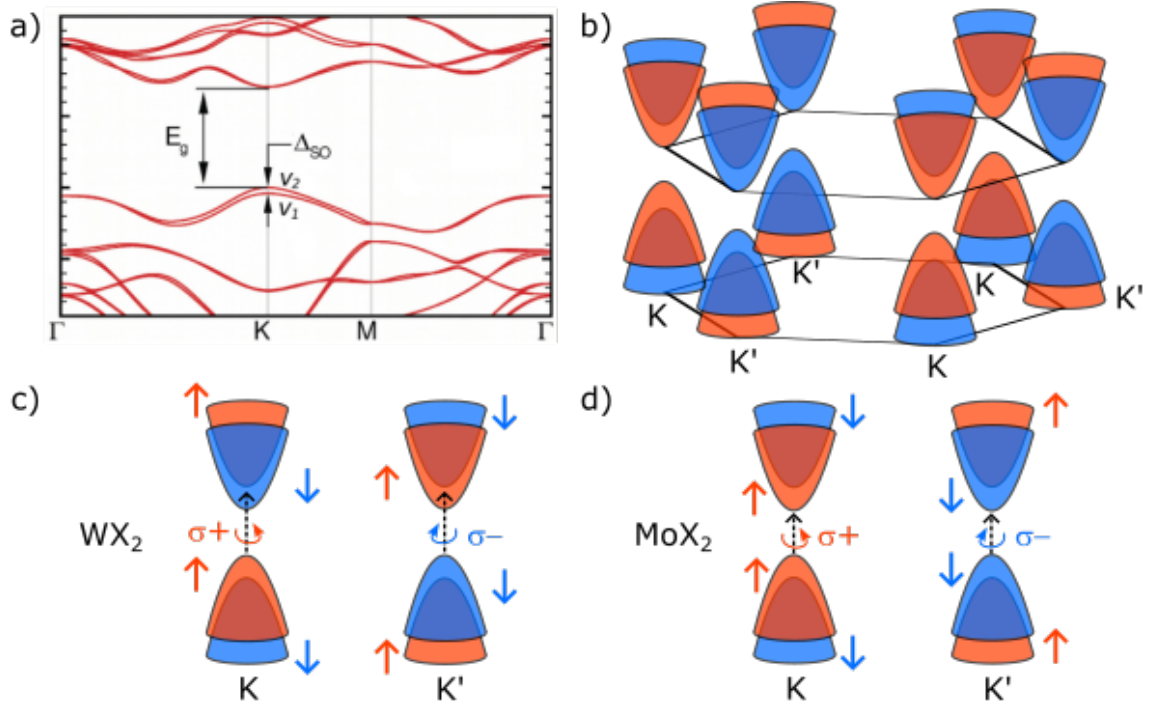


Fig. 1.4.2: 2H-TMDs bands structure. a) Band structure of the Mo-based 2H-TMDs calculated using density functional theory (DFT) [51]. b) Simplified low energy band structure of 2H-TMDs with the direct band gap in the K and K' valleys. c) WX₂ and d) MoX₂ K and K' valleys detail of the band structure [58]. Red and blue band denote the spin up and spin down subbands respectively. The splitting of the conduction band is opposite in both materials. Also is highlighted the optical selectivity rules of each valley.

Secondly, I introduce another 2D-TMD, the ReS₂. ReS₂ is a semiconducting TMD with 1T-distorted crystalline structure, in stark contrast with MoX₂ or WX₂ (see figure 1.4.1). The 1T-distorted structure provides ReS₂ with interesting anisotropic properties of both scientific and technologic importance. Specifically, high anisotropy of ReS₂ may lead to the development of integrated inverters [59], polarization sensitive light detectors [60] or emitters [61].

Figure 1.4.3 a) depicts the band structure of monolayer and bulk ReS₂ [62]. Conversely to 2H-TMDs, ReS₂ lacks of indirect to direct band gap transition in the monolayer limit, and the multilayer flakes of ReS₂ behave similar to the monolayer, due to weak coupling between the stacked layers [62]. Moreover, the band structure of ReS₂ shows a direct band-gap in the Γ -point of the brillouin zone. This indicates one main electronic transition and theoretically would yield an unique excitonic transition. Nevertheless, in experimental works two different excitons are observed, and both excitons are dependent on the angle between the linear polarized incident light and the ReS₂ [62, 63]. The presence of two

different excitonic transitions have been explained by the existence of an indirect gap in the M-point along with the direct band gap in the Γ -point. In the literature, some Ab-initio studies reveal that ReS₂ features two direct bandgap minima at the K1 and Z points of the reciprocal lattice, exhibiting very similar energies [64], as it is depicted in figure 1.4.3 b). In stark contrast, a recent work [65], proposed a different origin for the presence of two excitons, suggesting two non-degenerated excitons originated by the same optical transition and splitted by spin-orbit interaction. Furthermore, figure 1.4.3 c) shows the calculated band structured in a seminal work [66], where it is suggested that spin-orbit coupling can influence the band structure of ReS₂.

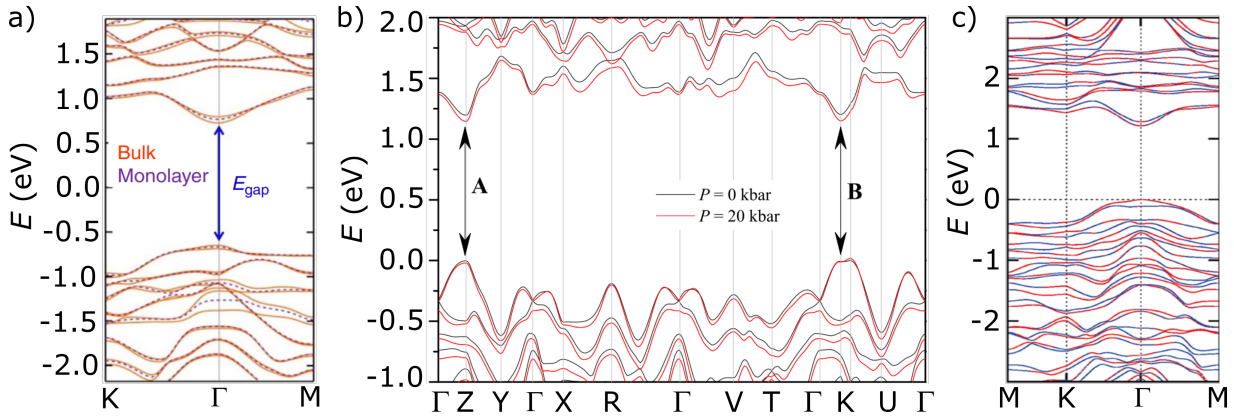


Fig. 1.4.3: Proposed band structure of ReS₂ in literature. a) DFT calculation of the electronic band structures of bulk (orange solid lines) and monolayer (purple dashed lines) ReS₂ with direct bandgap at the Γ point [62]. b) DFT calculation with meta-GGA SCAN functional of the pressure dependent band structure of ReS₂ with two direct band-gap at points Z and K1 [64]. c) DFT calculation of optB86b-vdW functional including spin-orbit coupling with a direct band-gap in the Γ point [66]

1.5 Structure of this thesis

As explained before, 2D materials open new opportunities for exploring physical phenomena and developing new functionalities in optoelectronic devices. In this dissertation, graphene is studied in depth using electronic measurements consisting in magnetotransport, while TMDs are characterized using optoelectronic measurements, specially photocurrent spectroscopy. The thesis is organized as follows:

- Chapter 2 provides the theoretical background required to understand the experimental research performed during this thesis in 2D van der waals materials. It explores the quantum Hall effect in 2D systems, particularly in graphene, highlighting its unique quantization. The chapter also explains the influence of excitons on the optoelectronic properties of 2D-TMDs remarking the role of photocurrent spectroscopy in analyzing excitonic transitions in these materials.

- Chapter 3 presents the details of the experimental methods and facilities used in my doctoral thesis for the fabrication and characterization of devices based in 2D van der waals heterostructures. Furthermore, all the measurement setups and procedures for the optoelectronic measurements, followed in all chapters, are described in depth.
- Chapter 4 provides a study of the quantum hall effect in high quality devices of h-BN encapsulated graphene, at temperatures up to room temperature and using strong magnetic fields. Comparing the activation of the quantum hall effect in h-BN-graphene heterostructures with previous studies in graphene supported on SiO₂ we provide new insights of the electronic transport in the quantum hall regime.
- Chapter 5 presents an insight of the mechanisms responsible for photocurrent generation in 2D transition metal dichalcogenides using a monolayer MoS₂ phototransistor. We clearly distinguish two different regimes, the photoconductive and the photogating effects, and in contrast with previous literature, we associate the photogating effect with intrinsic defects of the semiconductor.
- In chapter 6, using low temperature photocurrent spectroscopy, we characterize the spectral photoresponse of an encapsulated monolayer MoS₂ transistor revealing neutral excitons, trions, and excited states that corresponds with the rydberg series of the neutral excitons. The relative intensities of neutral excitons and trions are modulated using electrical fields, while optical parameters of the device, as the energy band gap or the spin orbit splitting between spin subbands are obtained from the characterization of excitonic rydberg states.
- Chapter 7 presents the low temperature photocurrent spectroscopy characterization of a monolayer MoSe₂ phototransistor identifying excitonic states corresponding with neutral excitons, trions and rydberg states. In this case, the focus is on the study of the influence of the doping level in the trion and neutral exciton energy position, observing a change in the dominant trion species from positive to negative, and the energy splitting between the neutral exciton and negative trion as the doping is increased due to many body effects.
- Chapter 8 focuses on the characterization of the polarization dependent of the spectral photoresponse of few-layer ReS₂ devices. Low symmetry of the material leads to the modulation with the polarization of the main neutral excitons and its corresponding rydberg series in photocurrent spectroscopy measurements. Furthermore, we identify one neutral exciton not reported previously in the literature.
- Chapter 9 presents the perspectives and the possible future work after this dissertation. Firstly, a preliminary characterization of circularly polarized dependent measurements in few layer ReS₂ device is showed, observing the presence of circular photocurrents in the device. Secondly, a moiré homobilayer of MoSe₂ with a twist angle of 0° is characterized using photoluminescence spectroscopy to observe interlayer excitonic states, and photocurrent spectroscopy to preliminary describe signatures of correlated intralayer excitonic states in the moiré pattern.

- Chapter 10 consists in a compilation of the conclusions obtained in this dissertation, summarizing all the work done and drawing the possible future work that can be performed in line with this research.

Chapter 2

Theoretical background

In this thesis, the physical phenomena studied using 2D materials are the quantum hall effect and the physics of excitonic transitions using low temperature photocurrent spectroscopy. This chapter sets the theoretical background essential for a complete understanding of our experimental research.

It begins with an overview of the quantum Hall effect, to understand its origin in 2D systems and the arising of this effect in magnetotransport measurements. Furthermore, I present a theoretical analysis of the quantum hall effect in graphene, that shows an unconventional quantization in comparison with typical 2D systems, being the perfect platform for study quantum hall effect at high temperature due to its huge landau level separation.

Subsequently, I explain the origin of excitons in semiconductors and its impact on the optical properties of 2D-TMDs. 2D-TMDs exhibit enhanced excitonic transitions due to the presence of tightly bound excitons with binding energies reaching hundreds of meVs. This makes them an ideal platform for studying the physics of these quasiparticles. The final part of this chapter introduces different mechanisms of photocurrent generation in 2D-semiconductors and the possibility of using photocurrent spectroscopy as a tool to investigate the spectral optoelectronic response in TMDs.

2.1 Quantum Hall effect in conventional 2D systems

This section introduces the quantum hall effect (QHE) in 2D systems. Firstly, I introduce the classical hall effect. Subsequently, introducing quantum mechanics, I explain the manifestation of the QHE in transport measurements, with the appearance of quantized levels in the transversal resistivity attributed to the presence of Landau levels.

2.1.1 Classical Hall effect

When an electrical charge moves at a constant speed within a uniform magnetic field, it experiences the Lorentz force, which acts perpendicularly to both the magnetic field and the direction of motion. Passing a current through an electrical conductor, as depicted in figure 2.1.1, results in the Hall effect, first identified by Edwin Hall in 1879. The accumulation of charge in one side of the sample leads to a transversal resistivity known as Hall resistivity. Classical hall effect in conductors is easily explained by employing the stationary Drude model in solids, considering the Lorentz force acting on electrons due to an electromagnetic field

$$\frac{\mathbf{v}}{\tau}m = e(\mathbf{E} + \mathbf{v} \times \mathbf{B}) \quad (2.1.1)$$

being τ the characteristic scattering time, $\mathbf{v}$ the velocity of the charge carriers, $\mathbf{E}$ the electric field and $\mathbf{B}$ the magnetic field, that is perpendicular to the hall bar.

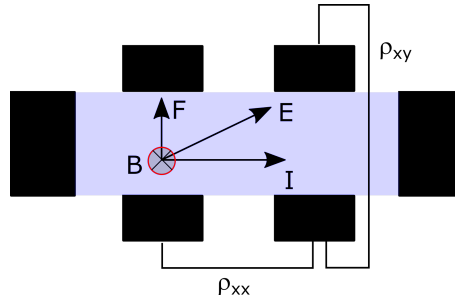


Fig. 2.1.1: Schematics of standard Hall bar device for magnetoresistivity measurements. Magnetic field ($\mathbf{B}$) is perpendicular to the plain and arrows indicate the direction of force ($\mathbf{F}$), current ($\mathbf{I}$) and electric field ($\mathbf{E}$). ρ_{xx} and ρ_{xy} corresponds with the longitudinal and transversal resistivity respectively.

Introducing matrix formalism allows us to derive resistivity values from the current density definition, $\mathbf{E} = \rho \mathbf{J}$

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \begin{pmatrix} m/ne^2\tau & B/ne \\ -B/ne & m/ne^2\tau \end{pmatrix} \begin{pmatrix} J_x \\ J_y \end{pmatrix} \quad (2.1.2)$$

obtaining expressions for the longitudinal resistivity, $\rho_{xx} = \frac{m}{ne^2\tau}$, and for the Hall resistivity, $\rho_{xy} = \frac{B}{ne}$. Observing the resistivity values, it is remarkable that the Hall resistivity depends solely on the magnetic field and the charge carrier density [67].

2.1.2 Quantum Hall effect

The quantum hall effect arises when two dimensional conductors with low carrier density are subjected to low temperatures and high magnetic fields, showing a strong deviation from the classical behaviour of the hall effect. As we can observe in figure 2.1.2. Hall resistance, denoted as $\rho_{xy}(B)$, exhibits flat plateaus at fixed values, corresponding to multiples of the universal constant h/e^2 (panel a)), while longitudinal resistivity $\rho_{xx}(B)$ vanishes (panel b)) [21].

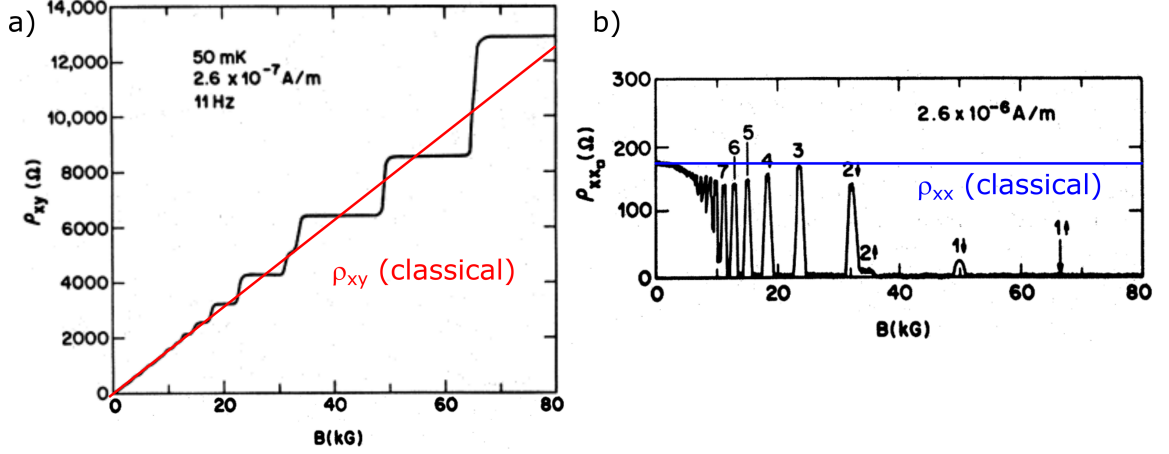


Fig. 2.1.2: Comparison between the classical hall effect (red and blue lines) and the quantum hall effect. Measurements of the quantum hall effect in GaAs-Al_xGa_{1-x}As heterojunctions taken from ref. [68]

This quantization in the Hall resistance can be theoretically predicted by considering a 2D system with a magnetic field applied perpendicular to the sample. When a perpendicular magnetic field is applied to a 2D conductor, the density of states splits into discrete levels of energy [69], predicting theoretically the possibility of the appearance of quantized levels in experimental measurements. To study this 2D system, we use a 2D electron gas model and we introduce the effect of the magnetic field selecting a vector potential using the well-known Landau gauge [67]. These assumptions results in a Hamiltonian that corresponds to

$$H = \frac{\mathbf{P}^2}{2m^*} = \frac{(p - e\mathbf{A})^2}{2m^*} \quad \mathbf{A} = \begin{pmatrix} 0 & xB \end{pmatrix} \quad (2.1.3)$$

With the selection of the landau gauge we have that the hamiltonian results

$$H = \frac{p_x^2}{2m^*} + \frac{(p_y - eBx)^2}{2m^*} \quad (2.1.4)$$

where it is possible to observe that p_y commutes with the hamiltonian, thus its possible to replace the operator p_y by its eigenvalue obtaining

$$H = \frac{p_x^2}{2m^*} + \frac{(\hbar k_y - eBx)^2}{2m^*} \quad (2.1.5)$$

$$H = \frac{p_x^2}{2m^*} + \frac{1}{2}m^*\omega_c^2 (x - l_B^2 k_y)^2 \quad (2.1.6)$$

being $\omega_c = \frac{eB}{m}$ the cyclotron frequency, $l_B = \sqrt{\frac{\hbar}{eB}}$ the magnetic length. The hamiltonian corresponds with an armonic oscillator with quantized energy levels and eigenfunctions

$$E_{n,k_y} = \hbar\omega_c \left(n + \frac{1}{2} \right) \quad \psi(x, y) = H_n(x - x_k) e^{-(x-x_k)^2} e^{ik_y y} \quad (2.1.7)$$

determining that the energy splitting between levels remains constant and exhibits a linear dependence on the magnetic field. Now, if we suppose that the shape of our sample is a rectangle with dimensions (L_x, L_y) , we obtain $k_y = \frac{2\pi}{L_y} n_y$ because we apply the periodic boundary conditions in the y-direction, due to the electrons are confined inside of the sample.

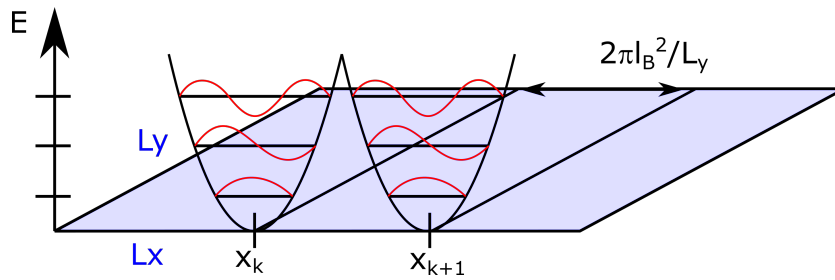


Fig. 2.1.3: Schematics of the different landau levels in the 2D system

From this, we can obtain the degeneracy of the landau levels just counting the number of states, D , that are inside the sample obtaining

$$D = \frac{L_x}{l_B^2 k_y} = \frac{L_x L_y B e}{h} = \frac{\Phi}{\Phi_0} \quad (2.1.8)$$

being $\Phi_0 = h/e$ the quantum flux and Φ the magnetic flux in the sample.

Defining the filling factor as the number of Landau levels filled as a function of the density of electrons $\nu = n_e \Phi_0 / B = n_e h / e B$, we can obtain the value of the transversal resistivity using the classical formula and the density of electrons as a function of ν

$$\rho_{xy} = \frac{B}{n_e e} = \frac{B}{e} \frac{h}{\nu e B} = \frac{1}{\nu} \frac{h}{e^2} \quad (2.1.9)$$

obtaining the values of the different plateaus. In this regime, experimentally is observed that the longitudinal resistivity, ρ_{xx} , vanishes. It is possible to reasonably argue that when Landau levels are completely filled or empty, the system is in a collisionless regime. In this regime, the electrons cannot suffer scattering because the energy between empty states and fully filled states is $\frac{1}{2} \hbar \omega_c$. Due to absence of longitudinal scattering, the characteristic scattering time of the system tends to be infinite, $\tau \rightarrow \infty$. Substituting in equation 2.1.2 we obtain that ρ_{xx} and ρ_{yy} are 0, corresponding with experimental observations.

$$\begin{pmatrix} E_x \\ E_y \end{pmatrix} = \frac{1}{\nu} \frac{h}{e^2} \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} \begin{pmatrix} J_x \\ J_y \end{pmatrix} \quad (2.1.10)$$

This theory comprehensively explains the values of $\rho_{xx}(B)$ and $\rho_{xy}(B)$ when the Landau levels are either completely full or empty. However, in real 2D systems, the Hall resistivity exhibits flat plateaus of varying widths, while the longitudinal resistivity displays different maxima or minima. This phenomenon arises due to disorder in real samples [22], leading to the broadening of Landau levels. Figure 2.1.4 shows a comparison between the theoretical Landau levels (panel a)) and the Landau levels in a real sample (panel b)), where the disorder introduces a broadening, Γ , in the extended states. The presence of disorder also introduces localized states. Electrons in extended states can move freely in the sample and suffer scattering, contributing to the electrical conduction. Meanwhile, electrons in localized states do not contribute to the electronic transport. Figures 2.1.4 c) and d) show the correlation between the experimental measurements (panel c)) and the Landau levels distribution in a real sample. Different positions of the Fermi energy respect to the Landau levels are indicated in panel d). The red, green, and blue dots in panel c) represent different Fermi energy positions in comparison with the measurement. When the Landau levels are not completely full or empty, a dissipation regime is observed, where

the longitudinal resistance is nonzero, and the Hall resistivity is not locked in a multiple of $\frac{h}{e^2}$.

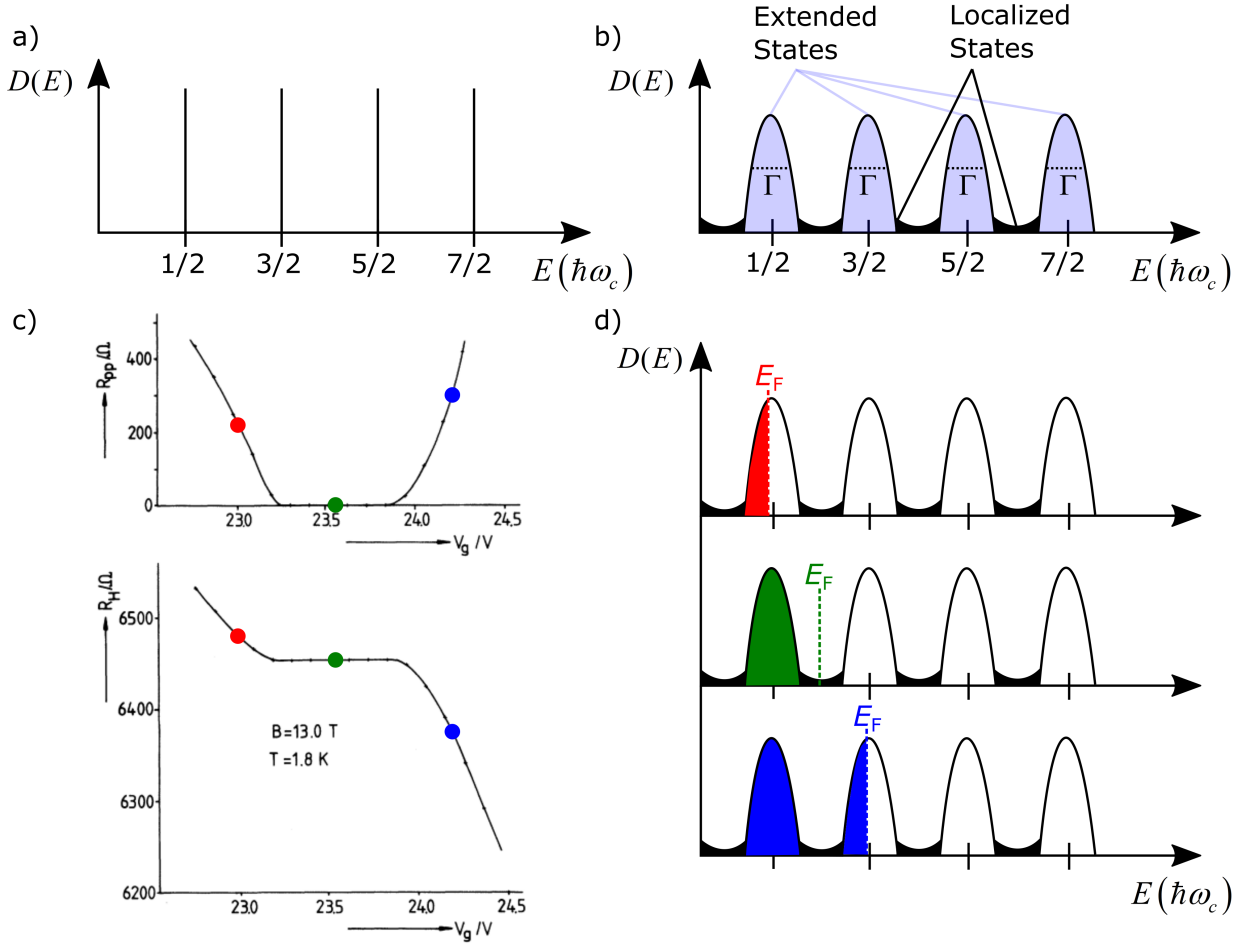


Fig. 2.1.4: Density of states of a 2D electron gas in a perpendicular magnetic field. a) Density of states of an ideal device, corresponding with dirac deltas in the Landau levels. b) Density of states of real device with a broadening Γ in the Landau Levels and the presence of and localized states due to the disorder. c) Measurement of ρ_{xx} and ρ_{xy} in a real device (Measurement taken from ref. [21]). d) Fermi level for each position highlighted in the panel c)

The introduction of disorder allows to explain the experimental measurements in terms of the Landau quantization. However, a key question remains unanswered for fully understand the QHE. In scenarios where the Landau levels are completely filled or empty, and the system operates in a collisionless regime due to the absence of extended states, which states are responsible for conducting current through the sample? The answer is the edge states, that carry the electrical current without electrical resistance [70, 71]. To illustrate the presence of these states, I use a semiclassical picture of free electrons in a magnetic field drawing a cyclotron orbit.

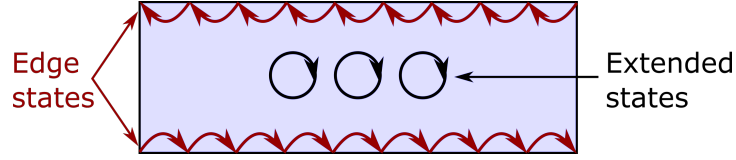


Fig. 2.1.5: Semiclassical picture of the edge states.

Figure 2.1.5 shows a rectangular sample with a perpendicular magnetic field applied. The electrons in the extended states of the Landau levels are represented drawing cyclotron orbits. In a real sample, a confining electrostatic potential ensures the electrons remain within the sample. This confinement, along with a magnetic field in the bulk, generates trajectories at the edges that are open. Near the edges, electrons are forced to reflect back internally resulting in so called skipping orbits. These skipping orbits correspond to the classic interpretation of the chiral edge states. Moreover, the edge states are topologically protected and transport the current through the sample without scattering [72].

2.2 Quantum-Hall effect in graphene

Monolayer graphene can be studied using the relativistic Dirac equation. The electrons and holes behaviour can be described as relativistic massless particles with a linear energy-momentum dispersion relation, $E(\mathbf{k}) = \hbar v_F |\mathbf{k}|$, near the K and K' valleys (see section 1.3). Hamiltonian of this system corresponds with a 2D Dirac equation $H = \hbar v_F \boldsymbol{\sigma} \cdot \mathbf{k} \Psi$ being $\mathbf{k} = (\partial_x \partial_y)$ and $\boldsymbol{\sigma}$ the Pauli matrix. As explained previously, the quantum Hall effect arises when a perpendicular magnetic field is applied to the 2D system. To introduce the magnetic interaction in the system we select a vector potential using the Landau gauge following the similar procedure done in the section 2.1.2, obtaining the Hamiltonian of the system

$$H = \hbar v_F \boldsymbol{\sigma} \cdot \left(\mathbf{k} - \frac{e}{\hbar} \mathbf{A} \right) = \hbar v_F \begin{pmatrix} 0 & k_x - ik_y - i\frac{e}{\hbar} Bx \\ k_x + ik_y - i\frac{e}{\hbar} Bx & 0 \end{pmatrix} \quad (2.2.1)$$

As k_y commutes with the Hamiltonian we can substitute the operator by its eigenvalue and the wave function can be written as $\Psi(x, y) = e^{iky} \phi(x)$. Defining the magnetic length as $l_B = \sqrt{\frac{\hbar}{eB}}$ and the variable $\hat{x} = x + kl_B^2$, the Hamiltonian can be diagonalized defining ladder operators $a = \frac{1}{\sqrt{2}} \left(\frac{\hat{x}}{l_B} + il_B k_x \right)$ as follows

$$H = \hbar v_F \begin{pmatrix} 0 & k_x - i \frac{\hat{x}}{l_B^2} \\ k_x + i \frac{\hat{x}}{l_B^2} & 0 \end{pmatrix} = \frac{\sqrt{2} \hbar v_F}{l_B} \begin{pmatrix} 0 & -ia \\ ia^+ & 0 \end{pmatrix} \quad (2.2.2)$$

obtaining quantized energy levels

$$E_N = \text{sgn}(N) \sqrt{2ev_F^2 \hbar B |N|} \quad (2.2.3)$$

In contrast with conventional semiconductors with parabolic bands ($E \propto k^2$), where the landau levels (LLs) are equispaced in energy showing a linear dependence with B , in graphene the gap between LLs follow a square root relation with B and N . Moreover, in graphene the valleys are degenerated adding an extra twofold degeneracy to spin. These facts yields in an unconventional hall conductivity in graphene with values $\sigma_{xy} = \pm 4e^2/h(N+1/2)$, confirmed in early studies in Gr/SiO₂ [1, 73, 74]. The observation of the unconventional quantum hall effect was a milestone in graphene, confirming the relativistic nature of dirac fermions.

Despite the strongest states in graphene occurring at filling factors, ν , corresponding with the previous σ_{xy} values, devices of high quality display states at all integer values of ν due to the breaking of spin and valley degeneracies. Experimental research on this integer quantum hall states energy gaps were surprising, as they revealed the complex origin of these states. Zeeman spin splitting is three orders of magnitude lower than the cyclotron energy of these states. Moreover, studies on the spin and valley g-factors in these states are significantly higher than predictions from single-particle theories, indicating that new integer states may arise from another mechanisms [75].

Additionally, graphene is a 2D system specially suitable for the observation of the quantum hall effect. Fermi velocity in graphene reaches values of $v_F = 10^6 \text{ ms}^{-1}$, resulting in a landau level separation, Δ_{LL} between $N=0$ and $N=1$ of one order of magnitude bigger than the thermal energy at room temperature ($\Delta_{LL} \approx 2000\text{K}$ at $B = 30\text{T}$) due to the relativistic nature of carriers in graphene (see equation 2.2.3). Furthermore, large scattering times and the possibility of reach very high carriers concentration allows to fully populate the LLs even at very high magnetic fields.

All this characteristics makes graphene the perfect candidate to study QHE under relaxed experimental conditions [76], even at room temperature [24]. In fact, nowadays is still the unique material where QHE have been observed at room temperature. Until now, the QHE at room temperature has only been measured in Gr/SiO₂, where extrinsic disorder dominates the transport regimes.

2.3 Excitons in transition metal dichalcogenides

Excitons are quasi-particles formed by electrons and holes in semiconductors (or insulators) bonded by Coulomb interaction. In a semiconductor, following the absorption of a photon with suitable energy, an electron is promoted to the conduction band, leaving behind a hole in the valence band. The different sign of electrical charge between holes and electrons causes a coulomb attraction leading to the creation of excitons. The scenario of a electron-hole pair in a semiconductor with parabolic bands is analogous to the hydrogen atom, with the hole assuming the role of the proton. In semiconductor physics, this analogy is obtained by the Wannier equation, a version of the Schrödinger equation modified for electrons and holes. The solution to this equation, known as Wannier-Mott excitons, represents the bound states of electron-hole pairs [77]. While the hydrogen atom has a binding energy of approximately 13.6 eV, excitonic binding energy is roughly within a few to hundreds of meVs, significantly lower due to the reduced effective masses of electrons and holes compared to free electrons and protons. Additionally, the semiconductor dielectric constant weakens the Coulomb interaction to about an order of magnitude lower in comparison with hydrogen, further decreasing the exciton binding energy.

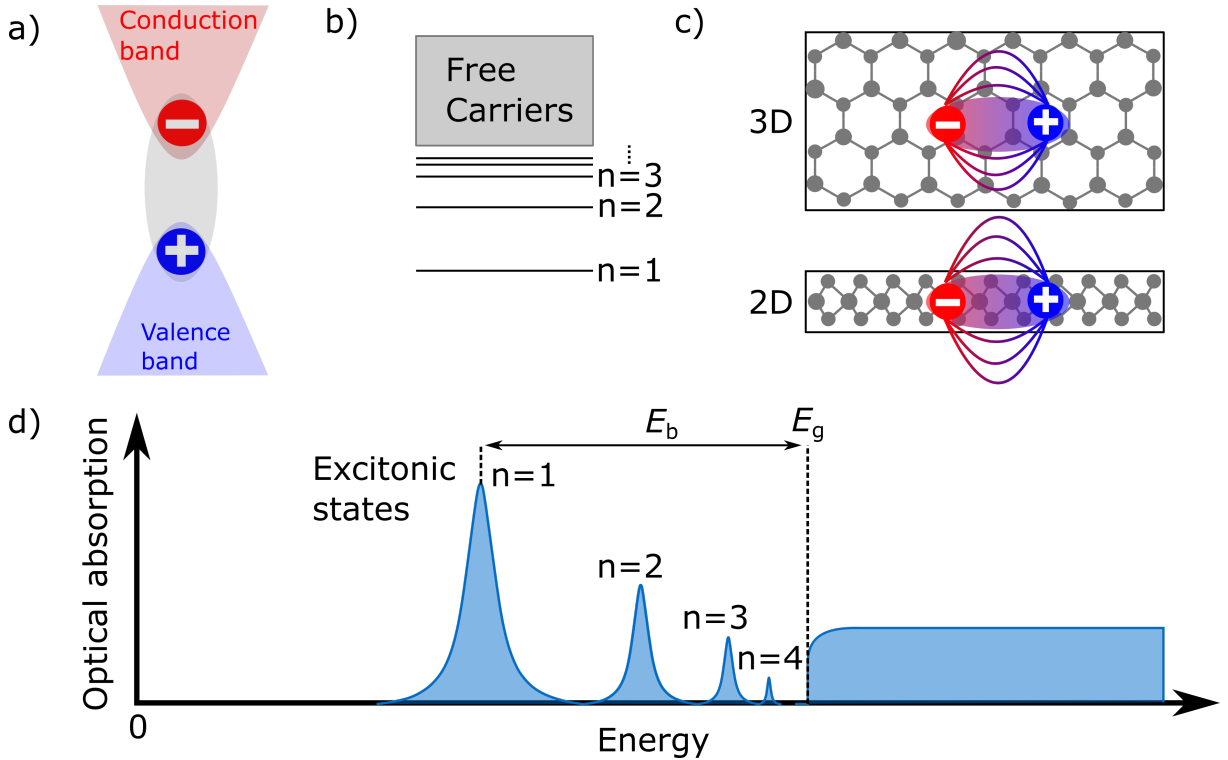


Fig. 2.3.1: Schematic of excitons in 2D materials. a) Electron-hole pair bounded forming an exciton in the reciprocal space. b) Representation of excitons in three-dimensional bulk versus in a two-dimensional monolayer. c) Energy level diagram of the ground and excited states of the excitons and the free carriers band. Panels b) and c) extracted from [78]. d) Illustration of the optical absorption in an ideal 2D semiconductor, highlighting a sequence of excitonic transitions occurring below the band gap, E_g . E_b denotes the exciton binding energy. Panel d) extracted from [58]

In conventional semiconductors, exciton binding energy is relatively low. For instance, in gallium arsenide (GaAs), its value is only 4.2 meV. However, in monolayer TMDs this binding energy is roughly two order of magnitude larger [58]. In atomically thin TMDs, electrons and holes are strongly attracted producing tightly bound excitons with binding energies of hundreds of meVs [11, 79, 80]. Figure 2.3.1 shows a general overview of excitons in 2D-TMDs. Figure 2.3.1 a) depicts a schematic of an electron in the conduction band and a hole in the valence band bonded by the coulomb interaction forming a neutral exciton. Figure 2.3.1 b) shows a representation of the energy levels of an exciton below the conduction band. Similarly to a hydrogen atom, neutral excitons shows a spectra of excited states, commonly known as Rydberg states, denoted with the quantum number, n . Figure 2.3.1 c) displays a schematic of excitons in the real space in a 3D and a 2D crystal. In 2D materials the exciton is strongly confined in the monolayer, and it is similar to a 2D hydrogen atom. The binding energy of the hydrogen atom in 2D is 4 times larger than in 3D [81]. Moreover, the electric field between the electron and the hole is increased by the lower dielectric screening outside the 2D semiconductor. These effects enhance the binding energy of the excitons in 2D semiconductors and in low dimensional systems [82, 83]. In spite of the analogy between excited states in excitons and the Rydberg series of the hydrogen atom, there is a strong deviation due to the influence of the electrical screening in the enviroment of the 2D semiconductor [78]. Figure 2.3.1 d) depicts schematically the optical absorption of a 2D semiconductor, showing the neutral exciton and the excited states, with realistic values depicting a lowering optical absorption sequence between $n=1$ to $n=4$.

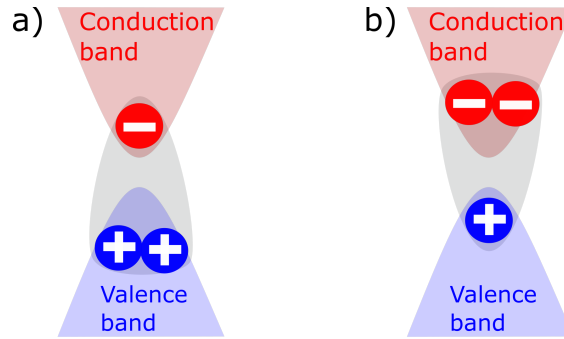


Fig. 2.3.2: Schematic of positive (panel a)) and negative trions (panel b))

Neutral excitons dominate the optical response in TMDs. Nevertheless, the interaction of the excitons with electrons and holes leads to the formation of different excitonic species that play an important role in spectral response of these materials. The interaction of free charge carriers with excitons may create new bound states, such as trions [84] or biexcitons [85]. Trions are charged excitonic states formed by the bond between one exciton and a charge carrier. Figure 2.3.2 displays a representation of the positive (panel a)) and negative trions (panel b)) in the reciprocal space. Trions have either negative or positive charges and in TMDs typically show binding energies of around 10-30 meV. The differences in binding energies between negative and positive trions originate from the different effective masses of electrons and holes. By increasing or reducing the amount of

free carriers in the semiconductor, it is possible to modulate the relative strength of trions in the optical spectra [86]. Moreover, the doping level influences in the energy transition of excitons and trions [87] causing a change in the binding energy of the trions.

2.4 Photocurrent in 2D materials

Optical excitation of semiconductors with photon energies above the bandgap, $E_{\text{exc}} > E_g$, leads to electron transitions from the valence band to the conduction band, resulting in variations in the conductivity of a device. This change in the conductivity is measured as an increase or decrease in the current of the device, commonly known as photocurrent. A key of this thesis is the use of photocurrent measurements as a powerful tool to characterized electronic states in 2D materials.

The devices designed in this thesis to measure photocurrent are based on field effect phototransistors [88], where the channel of the semiconductor is connected by source and drain contacts, alongside a gate that modulates carrier density through the field-effect. Optoelectronic measurements are performed applying a drain-source voltage and illuminating the whole device, obtaining a value of the photocurrent as the difference between the current in the dark and under illumination, $I_{\text{pc}} = I_{\text{on}} - I_{\text{off}}$. The photocurrent setup and the procedure to perform this measurements will be further discussed in chapter 2.

The photocurrent in 2D-phototransistors can be generated by various mechanisms [89]:

- Photoconductive effect: The light absorbed by the phototransistor causes a raise in the free carrier density of the semiconductor through the formation of excited electron-hole pairs. The raise of the carrier density increases the conductivity, resulting in a measurable photocurrent.
- Photogating or photodoping effects: The light absorbed by the phototransistor produces free charge carriers. However, in this case, one type of carrier gets trapped in localized states near the band edge. These trapped charges shift the Fermi level of the semiconductor, changing the effective gate voltage and modifying the current in the phototransistor, leading to a measurable photocurrent. The difference between the photogating and the photodoping effects rely on the characteristic times of relaxation of trapped carriers. The process of relaxation governs the time response of the device, being in the photogating lower than in the photodoping effect.
- Photothermoelectric effects: The light absorbed by the phototransistor causes the device heating, changing the resistance and generating photocurrents through temperature gradients.

The photoconductive and the photogating effects will be discussed in depth in this dissertation, using the gate voltage as an experimental knob to control the dominant photocurrent mechanism in a TMD-based phototransistor.

The polarization of incident light is also a critical factor in photocurrent generation within 2D phototransistors. As illustrated in figure 1.4.2, monolayers of 2H-TMDs exhibit optical selection rules that depend on the helicity of circularly polarized light, which can modulate the photocurrent through circular photogalvanic effects [57]. Additionally, the crystalline structure anisotropy of ReS₂ leads to a photoresponse that depends on the angle between the linear polarization of the incident light and the high-symmetry directions of the ReS₂ crystal. In this thesis we will explore the influence of light polarization on the spectral photoresponse of a ReS₂ phototransistor. Furthermore, we will provide a preliminary characterization of circularly polarized photocurrents in a ReS₂ phototransistor.

2.4.1 Photocurrent spectroscopy

Photocurrent spectroscopy has been largely used to characterize the spectral response of conventional semiconductors such as Si, III-V [90, 91] and even bulk TMDs [92]. Another popular spectroscopy technique is photoluminescence spectroscopy, based on the illumination of the sample with high-energy photons ($E_{\text{exc}} > E_{\text{g}}$) and the subsequent collection of the photons emitted by the sample. In intrinsic semiconductors, electrons move from the valence-band to the conduction band upon absorbing a photon with energy exceeding the semiconductor bandgap. Consequently this transition creates holes in the valence band. Next, both electrons and holes move to lower energy states through non-radiative processes. Finally, the recombination of an electron with a hole results in the emission of a photon with the energy of the involved transition.

In photocurrent spectroscopy the approach is completely different. The excitation wavelength is continuously changed to obtain a photocurrent spectrum, which describes how the photocurrent varies with the wavelength of the incident light. This technique enables the access to high energy states, unlike photoluminescence spectroscopy, as it relies on direct electron transitions without an intermediary recombination.

The spectral photoresponse in 2D-TMDs has been largely studied through a variety of techniques. In previous literature, the main part of the research in this field has employed PL spectroscopy or its different variations such as time-resolved PL[93] and PL excitation[94]. These techniques allow the extraction and detailed analysis of various characteristics associated with light-emitting transitions, including lifetime [95, 96], binding energy[97, 78], and spin and valley polarizations[98, 99].

In photocurrent spectroscopy the phototransistor is the detector of the signal, contrary to the previous spectroscopy techniques. The phototransistor is exposed to monochromatic light and the photoresponse is registered while varying the wavelength. The generated photocurrent depends on the electronic properties of photoexcited states and on the light absorbed by the material. Hence, photocurrent spectroscopy allows to measure radiative and non-radiative excitonic transitions in spite of the existence of non-radiative

relaxation mechanisms, giving a complementary approach to PL spectroscopy. Moreover, as this technique allows us to detect optical transitions via electrical charge, it is well-suited for investigating the transport properties and ionization mechanisms of excitons, which are fundamental for the development of exciton-based optoelectronic devices. Despite its potential, previous to our study in this dissertation, there was only two works that use PCS for exciton characterization in 2D-materials [25, 26]. Furthermore, there was a lack of studies involving measurements at cryogenic temperatures and using high-quality samples. We combine low temperatures, to minimize thermal disorder, with photocurrent spectroscopy achieving resolution bandwidths near 10 meV. This resolution is similar to what is seen in low-temperature PL spectroscopy.

Chapter 3

Equipments and experimental techniques

This chapter describes various methods, tools and facilities used throughout this thesis for the fabrication and characterization of our devices.

In this thesis, all the samples are fabricated using the scotch-tape exfoliation technique of graphene and various TMDs (MoS_2 , MoSe_2 , and ReS_2) to obtain a reduced thickness, even reaching the monolayer limit, due to the weak Van der Waals interaction binding their different layers. Besides, in most of our devices we stacked graphene or TMDs between hexagonal boron nitride (h-BN) flakes to improve their properties using dry-transfer methods. We place our heterostructures onto highly doped Si wafers with a top layer of 300 nm of SiO_2 . By electron beam lithography (EBL) combined with dry plasma etching (RIE/ICP) and e-beam metal evaporation we process our samples in a hall bar geometry with several electrical contacts. Furthermore, the Si/ SiO_2 substrate allow us to use the highly doped wafer as a back gate to control the carrier density in the channel thanks to the field effect. Thus, our devices can be considered as field-effect transistors (FETs).

In this chapter I describe all the equipment and techniques used to fabricate these devices from the exfoliation of the material until last fabrication step the wire bonding in an appropriate chip carrier to be ready for its characterization. In this description I include also the preliminary characterization using raman and photoluminescence spectroscopy to obtain information of the thickness, the quality and the crystalline orientation of the device. After the fabrication I focus on the characterization of the electronic and optoelectronic properties of our devices. I start by detailing the magneto-transport systems used in Salamanca and Nijmegen for our studies of the quantum hall effect in h-BN/graphene/h-BN heterostructures. Next, I describe the photocurrent spectroscopy setup that we installed in the Group of Nanotechnology in Salamanca. We consider this the most relevant original contribution in this chapter of my thesis. This setup has been crucial for the results obtained in the rest of my thesis.

3.1 Characterization equipments of heterostructures

In this section, I describe the profilometer and the micro-Raman spectrometer used to characterize the exfoliated flakes and the heterostructures. This characterization is done previous to the fabrication of the final devices.

3.1.1 Profilometer

Profile measurements were conducted using the DektakXT stylus surface profiler, shown in figure 3.1.1 a). The DektakXT is designed for precise measurement of both thin and thick flake heights with nanometric resolution. The system operates by guiding a diamond-tipped stylus over the sample surface. This stylus is connected to a Linear Variable Differential Transformer (LVDT), which generates electrical signals reflecting the sample surface variations. Using the Vision64 software, the system processes these data points to calculate the height of the flakes. We usually use the profilometer to measure the thickness of h-BN and ReS₂ flakes. As an example, figure 3.1.1 b) displays a ReS₂ flake and a white line that corresponds with the profile shown in panel c). The height of the flake measures approximately 13 nm. Given that a single layer of ReS₂ has a thickness of about 0.8 nm [60], this suggests the flake includes roughly 16-17 layers.

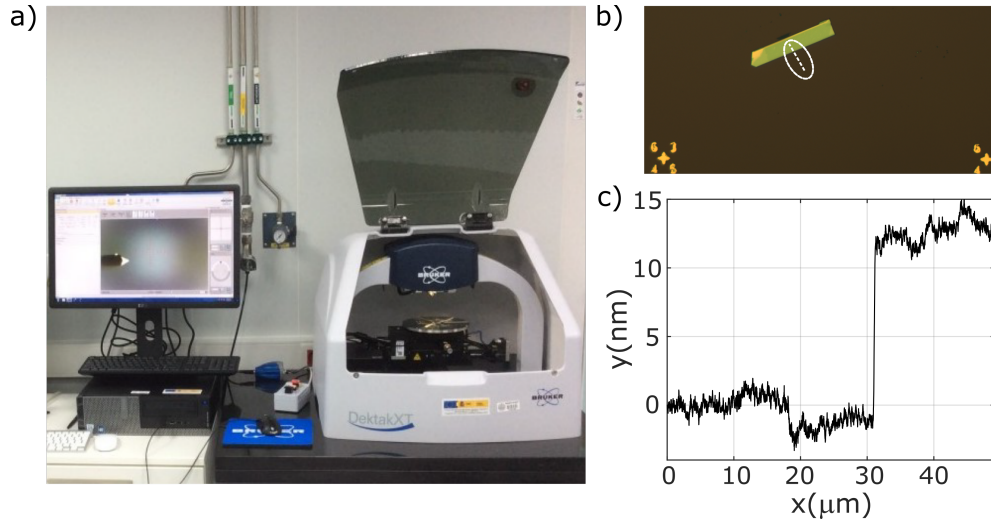


Fig. 3.1.1: a) Profilometer DektakXT stylus surface profiler. b) ReS₂ flake with the line measured by the profilometer. c) Profilometer measurement revealing a height of 13 nm.

3.1.2 Raman spectrometer

The micro-Raman spectrometer used during this dissertation corresponds with the model LAB-HR for Horiba. The use of the Raman spectroscopy is fundamental during this dissertation for the identification of the thicknesses of the exfoliated flakes, confirm the quality of the stacked heterostructures and identify the crystalline orientation of ReS₂ flakes. Furthermore, we also employ the raman spectrometer to perform photoluminescence spectroscopy measurements to preliminary observe the optical transitions in the

2D-TMDs, that will be identified later using photocurrent spectroscopy.

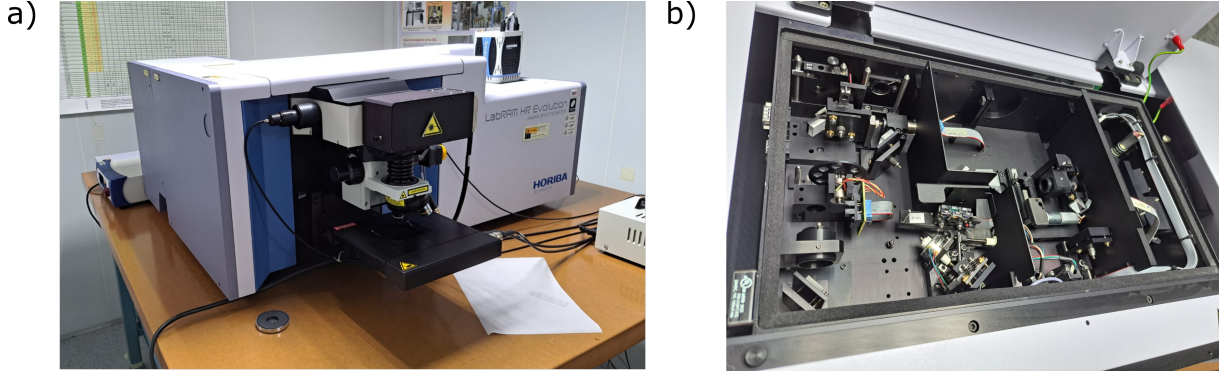


Fig. 3.1.2: Micro-Raman Spectrometer Lab-HR. a) Image of the equipment. b) Internal optical setup of the equipment.

Micro-Raman spectrometer can be operated with three different lasers; Ventus-Solo laser of 532 nm and an output power of 100 mW, He-Ne laser of 633 nm with an output power of 17 mW and a diode laser at 770-795 nm with an output power $> 200\text{mW}$. The incident power can be attenuated as low as 0.01% of its initial power. Figure 3.3.1 shows a picture of the equipment, with three different objectives with magnifications 10X, 50X and 100X optimized to measure micro- and macro- samples. The samples are located in the XY stage with a resolution of microns that allows a perfect alignment between the sample and the lasers. In our particular case, all the spectra are taken with 100X objective due to the 2D nature of the samples. With the 100X objective the laser spot area is around $1\text{ }\mu\text{m}^2$ at the focus point. The measurement range starts in a frequency shift range of 50 cm^{-1} thanks to a cut-off filter of the rayleigh dispersion. To perform the measurements the sample is excited and the back-scattered light is collected by the same objective. The light passes through the spectrometer, which has two different gratings of 1800 lines/mm and 600 lines/mm. Finally, the dispersed light is collected by the synapse CCD detector, cooled by a peltier cell.

For polarization-resolved raman measurements we exploit that the output of the laser is linearly polarized and we placed the rotator stage on the XY stage to rotate the sample and change the polarization angle of incidence. Besides, we place a linear polarizer before the Synapse detector to control also the polarization angle of the back-scattered light.

In photoluminescence spectroscopy the measurement technique is exactly the same but we usually cover longer spectral ranges than in raman spectroscopy. Polarization-resolved photoluminescence measurements are performed fixing the sample position while the linear polarizer before the detector is used to change the polarization angle of the collected light.

3.2 Clean room and fabrication equipments.

In this section I expose the clean room facilities used to fabricate the devices. All the equipments are located into the clean room of the nanotechnology group of the University of Salamanca. The aim of this section consists in give a brief description of the equipments. I will provide more specific information about the fabrication of the 2D FETs in the section 3.4.

3.2.1 FE-SEM with lithography controller

In our devices the definition of different geometries or patterns is performed using standard electron-beam lithography with a scanning electron microscope (SEM). The facility in our clean room is the FE-SEM Sigma of Zeiss with the Raith (elphy plus) nanolithography controller. Figure 3.2.1 shows an optical image of the SEM. FE-SEM is composed by schottky field emission (FE) and GEMINI electron optical column. The electron gun is kept at pressure levels of 10^{-10} while the vacuum in the main chamber is around 10^{-6} . There are two electron detectors to generate an image of the sample, an In-lens detector and a Secondary detector. The apertures ranging from 7.5 to 120 microns and supports a maximum accelerating voltage of 15kV. The SEM is equipped with fully motorized rotary stages across four axes (x , y , z , θ) to move the samples respect electron beam. The nanolithography controller moves the stage automatically to expose the resist and draw the pattern designed in the samples. The electronic resist used in this thesis for the lithography process is always PMMA.



Fig. 3.2.1: FE-SEM Sigma of Zeiss with Raith (elphy plus)

3.2.2 ICP-RIE PlasmaPro 100 Estrelas

Dry etching processes are conducted using the PlasmaPro 100 Estrelas system from Oxford instruments (see figure 3.2.2) that allows Inductively Coupled Plasma (ICP) and Reactive Ion Etching (RIE). With this model is possible to perform dry etching in a variety of materials, including dielectrics, compound semiconductors, metals, and organic substances. It accommodates samples up to 4 inches in diameter and features a cryogenic module for cryoetching at temperatures as low as -120°C . Additionally, an interferometer system integrated into the PlasmaPro 100 Cobra ensures precise control over etching processes. The system supports etching with a diverse range of gases, including Cl_2 , BCl_3 , Ar, SF_6 , C_4F_8 , O_2 , CH_4 , CHF_3 , and H_2 , allowing for the etching of several materials.

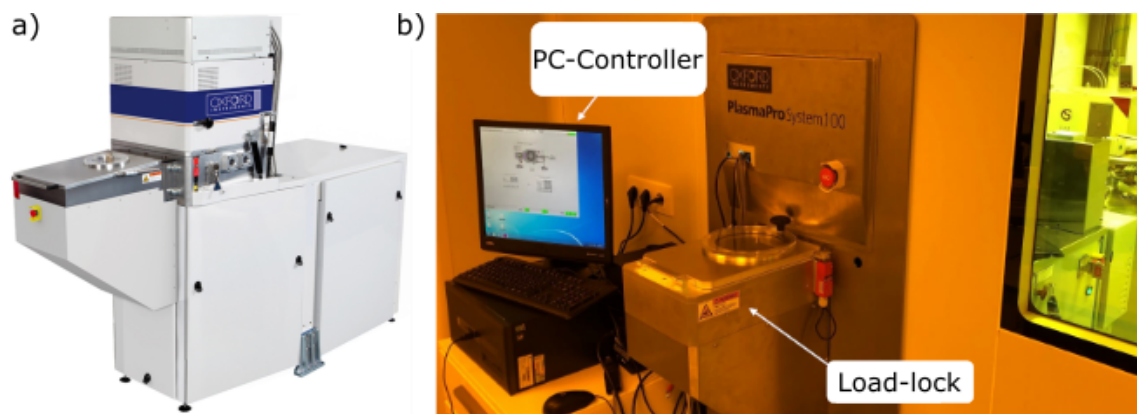


Fig. 3.2.2: a) ICP-RIE PlasmaPro 100 Estrelas. b) Load-Lock and PC controller inside the clean room.

3.2.3 e-Beam evaporator

The metallic deposition of the electrical contacts in our devices is done by using e-beam evaporation. Figure 3.2.3. displays a photograph of the e-beam evaporator in the clean room. This e-beam evaporator was designed by tecnovac using an e-beam gun from telemark. The evaporator has two isolated chambers, one pre-chamber that works as a load-lock reaching levels of vacuum of around 10^{-6} mbar and allows to introduce or remove the samples inside the main chamber without losing the vacuum of the system using a guillotine valve. Metallic evaporations are performed in the main chamber at pressures as low as 10^{-9} mbar. In the main chamber, there are crucibles with different metals. Several metals can be evaporated in this system (Au, Ti, Al, Cr, Co, Ni, Pt) giving versatility to electrically contact different types of materials. Once the sample is introduced into the main chamber and optimal pressure is reached, we begin evaporation by heating the metal with the electron beam. The electron beam is controlled using magnetic fields, manipulated externally with a joystick. When the metal reaches its evaporation temperature, it starts to evaporate, and a quartz crystal monitors the evaporation rate and the thickness of the deposited metal. Finally, upon reaching the desired thickness, a shutter is closed to stop the evaporation.



Fig. 3.2.3: e-beam evaporator designed by tecnovac with telemark e-beam gun.

3.3 Characterization equipments of devices

In this section, I present the equipment used to perform electrical measurements in the final devices. I describe the source measure unit 2600 of keithley and the lock-in amplifier sr830 from stanford research systems. We used these equipments to register the electric and optoelectronic response of the devices. The integration of this equipments will be further discussed in section 3.5.

3.3.1 Sourcemeter keithley 2600 series

A source measure unit, also known as sourcemeter, is a multifunctional instrument designed for precise sourcing and measuring of voltage and current. It integrates various functionalities into one compact device. The sourcemeters used during this dissertation corresponds with the series 2600 of keithley. These sourcemeters have a wide range of operation, allowing to apply voltages up to 200 V and measure currents and voltages as low as 100 fA and 100 nV, respectively.

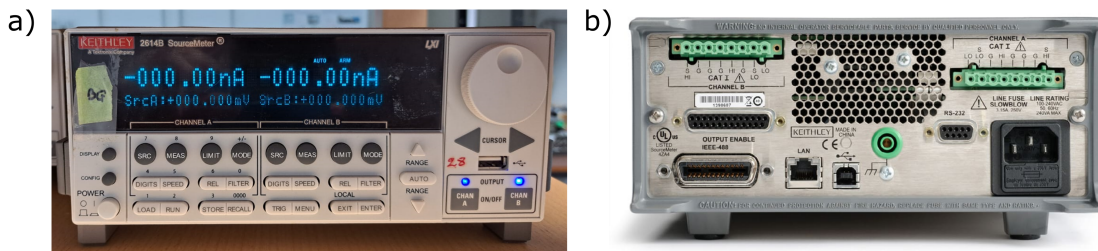


Fig. 3.3.1: Image of the 2614b sourcemeter. a) Front panel and user interface. b) Back panel with the electrical connections.

Figure 3.3.1 shows the front and the back panels of the Keithley 2614B, with two different independent channels (A and B). In this dissertation we always use the sourcemeters in the mode of apply voltage and measure current. In one case to apply a gate voltage and measure the leakage current of the dielectric, and in the other case, to apply a drain-source voltage and measure the drain-source current in the semiconductor channel.

3.3.2 Lock-in amplifier SR830

Lock-in amplifiers are used to measure AC signals (current or voltage) of a determined frequency equal to the reference frequency of the instrument. These equipments allow to eliminate noise or residual signals of other frequencies producing an increase of the signal to noise ratio. The reference frequency in the lock-in amplifier can be internal and directly tuned from the instrument or external modulated, for example, by an optical chopper. The filtering of the signals in the lock-in amplifiers is known as phase-sensitive detection and is based in the multiplication of signals using trigonometry. Considering the reference of the lock-in as $V_{ref} = V_r \sin(\omega_r t + \theta_r)$ and the signal as $V_{sig} = V_s \sin(\omega_s t + \theta_s)$. The lock-in multiplies both signals and the output signal is



Fig. 3.3.2: Image of the lock-in SR830

$$\frac{1}{2} V_s V_r (\cos(\omega_s t - \omega_r t + \theta_s - \theta_r) - \cos(\omega_s t + \omega_r t + \theta_s + \theta_r)) \quad (3.3.1)$$

In the case where ω_s and ω_r are equal ($\omega_s = \omega_r$), we obtain a combination between a DC and an AC signal

$$\frac{1}{2} V_s V_r (\cos(\theta_s - \theta_r) - \cos(2\omega t + \theta_s + \theta_r)) \quad (3.3.2)$$

After that, the signal is passed by a low-pass filter with a cut off frequency lower than 2ω the resulting signal is

$$\frac{1}{2} V_s V_r \cos(\theta_s - \theta_r) \quad (3.3.3)$$

obtaining a value proportional to the signal and to the $\cos(\theta_s - \theta_r)$. The phase is usually adjusted manually in the lock-in to obtain a value near to 0. Finally the output of the lock-in corresponds with the value of V_s and $(\theta_s - \theta_r)$.

3.4 Device fabrication

In the following section I expose the fabrication process of the devices measured during this dissertation. As a substrate for our devices, we use wafers of Si with 300 nm of thermally grown SiO_2 . This thickness of the SiO_2 is optimized to increase the optical contrast of monolayer graphene and TMDs [100]. The size of the substrate is about $1 \text{ cm} \times 1 \text{ cm}$, and it is previously patterned with an array of numbered crosses (markers) separated $400 \mu\text{m}$. This procedure is home-made using optical lithography. Markers are useful to locate the flakes and act as reference coordinates in the process of e-beam lithography. The SiO_2 layer acts as a dielectric to apply electrostatic gating to the channel of the FET using the Si as gate contact.

The first step to start with the fabrication is the cleaning of the substrates. Initially, the substrates are immersed in acetone in an ultrasound bath for 2 minutes and, subsequently, are immersed in isopropanol (IPA) to remove the acetone. Later, they are dried by blowing N_2 and heated up to 110° . Once the substrates are prepared, the device fabrication proceeds through a series of sequential steps:

1. Exfoliation and optical identification.
2. Raman and photoluminescence spectroscopy.
3. Stacking of Van der Waals heterostructures.
4. Shape definition of the device using e-beam lithography and dry etching.
5. Metallic deposition of the contacts using e-beam lithography and e-beam evaporation.
6. Wire-bonding of the devices in a suitable chip-carrier for the different measurement facilities.

It is worth noting that raman and photoluminescence spectroscopy measurements can also be performed after stacking the heterostructures, either to complete the characterization or to check the quality of the heterostructure.

3.4.1 Exfoliation and optical identification

The device fabrication starts with the exfoliation of the van der waals materials. Various methods are available for producing 2D van der Waals materials of different thicknesses, divided into bottom-up and top-down approaches. Bottom-up methods builds the

materials layer by layer, as chemical vapor deposition (CVD) [101]. Conversely, top-down methods start with a bulk crystal and reduce its thickness. Among top-down methods is mechanical exfoliation [102]. Mechanical exfoliation is based in the use of a sticky tape to thin down a bulk crystal of the desired van der Waals material. For graphene and h-BN we have used standard scotch-tape technique, which gives high-quality flakes, using Si/SiO₂ wafers as a substrate. When the substrate are completely cleaned, ambient contaminants are removed from the substrate using an oxygen plasma cleaner. To exfoliate graphene, natural graphite is peeled-off with the scotch-tape several times to reduce progressively the thickness of the graphite flakes. Then, the tape with the flakes is placed onto the substrates applying a light pressure. Subsequently, the substrate is placed on a hot plate while the tape is over it, to melt slightly the glue from the tape and increase the amount of flakes transferred. Following, the tape is removed slowly to release flakes of different thicknesses in the substrate. Exfoliation of h-BN follows a similar procedure. However, instead of searching monolayers, we look for homogeneous flakes of 15-25 nm to encapsulate and isolate properly the graphene or TMDs flakes. Figure 3.4.1 shows examples of the exfoliation of graphene (panel a)) and h-BN (panel b)).

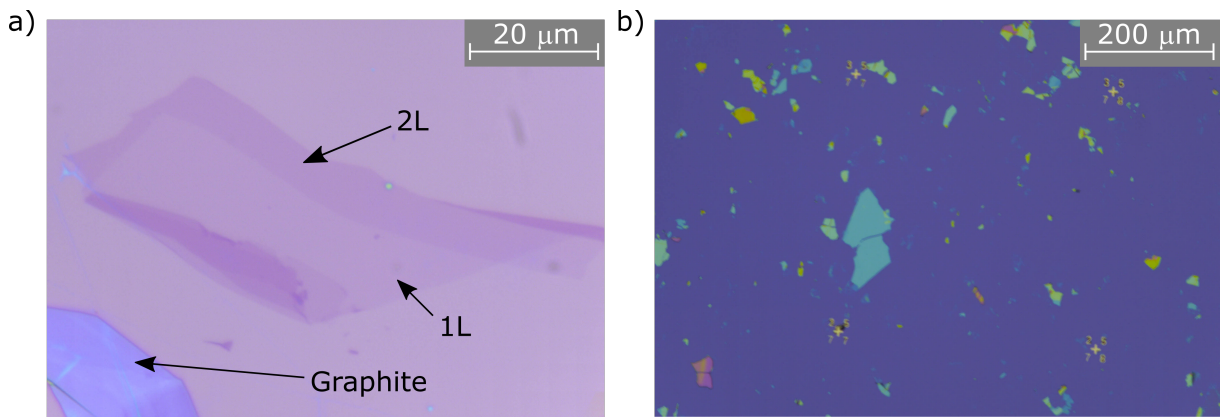


Fig. 3.4.1: a) Exfoliated graphene flakes of different thickness over SiO₂. b) Exfoliated h-BN over a SiO₂ substrate with markers.

Now, focusing on the exfoliation of transition metal dichalcogenides, we used two distinct exfoliation methods during the dissertation. The first method is similar to the procedure described for graphene but using a tape of reduced adhesion (BT-150E-CM, Nitto), and extending the duration of O₂ plasma cleaning to enhance the exfoliation yield on the SiO₂ substrate [103]. This method results in the production of monolayers with lateral dimensions typically ranging from 5 to 10 μm .

In the second method, we used polydimethylsiloxane substrates provided from Gel-Pak (WF-X4) together with the reduced adhesion tape to exfoliate bulk crystals [104]. The inclusion of viscoelastic substrates lead to an increase in monolayer size, typically obtaining lateral dimensions in the range of 30 to 60 μm . This approach is a more effective tool to obtain high-quality monolayers with a larger size.

After the exfoliation, we identify the different flakes thicknesses directly in the microscope by optical contrast. When the materials are directly exfoliated on a SiO_2/Si , the substrate is observed in reflection and the contrast of the monolayers are relatively high, so we can identify approximately the different thicknesses of the flakes. Using PDMS as a substrate we have the possibility of observe the flakes in transmission, because the PDMS films are transparent. This allow us to measure the absorption of red, green and blue (RGB) channels in different flakes using the software of the camera in the microscope. The quantitative examination of the transmission mode RGB channels has demonstrated its effectiveness as an alternative method for determining the number of layers in TMDs [105].

Figure 3.4.2 displays examples of MoS_2 , MoSe_2 and ReS_2 flakes exfoliated onto SiO_2 and PDMS. Panel a) shows a monolayer MoS_2 exfoliated on SiO_2 with lateral dimensions of around $10\ \mu\text{m}$. Panels b) and c) show images taken in the transmission mode of the microscope of monolayers and bilayers of MoSe_2 on PDMS with lateral dimensions of around $60\ \mu\text{m}$. MoS_2 and MoSe_2 monolayers absorbs $10\pm 3\%$ of the light in the blue channel [105]. Panel d) corresponds with an image of few layer ReS_2 flakes on PDMS. Concerning to the exfoliation of the ReS_2 , during this dissertation the flakes of our interest are around 10-20 nm of thickness.

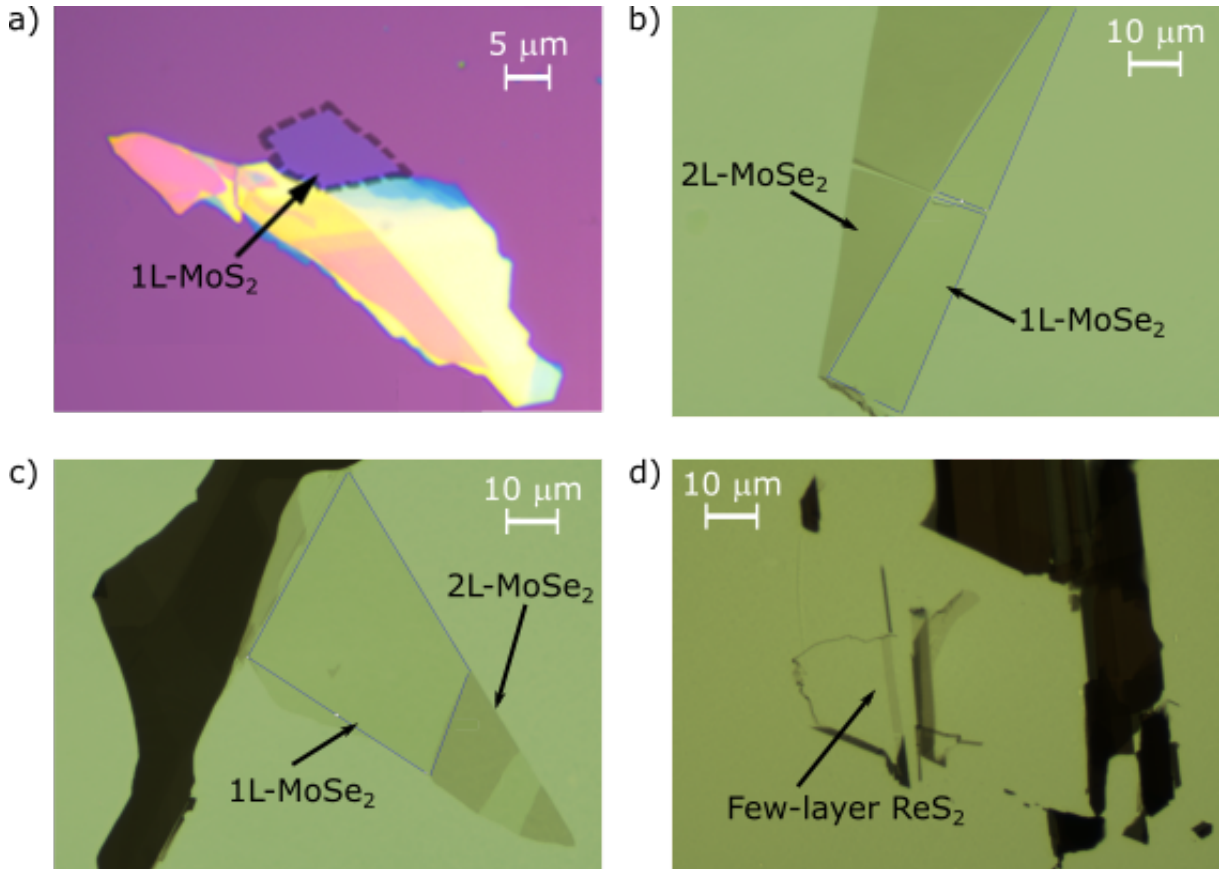


Fig. 3.4.2: a) Exfoliated monolayer of MoS_2 over SiO_2 . b) and c) Exfoliated monolayers of MoSe_2 with lateral dimensions up to $60\ \mu\text{m}$ exfoliated on PDMS substrate. d) Few-layer ReS_2 exfoliated on PDMS substrate

3.4.2 Raman spectroscopy

Raman spectroscopy has demonstrated to be a fast and contactless characterization technique of 2D materials. Raman spectroscopy is based in the inelastic scattering of light when interacts with materials. The material is illuminated with monochromatic light and the photons interact with the lattice vibrations of the sample, also known as phonons or raman modes, resulting in a shift in the energy of the back-scattered photons.

In 2D materials, the lattice vibrations are largely affected by the thickness and the quality of the different flakes. Therefore, raman spectroscopy is a well established technique to identify the thickness of the exfoliated van der waals materials [106]. All the raman spectroscopy measurements are performed using the micro-Raman spectrometer Lab-HR.

3.4.2.1 Raman spectroscopy in graphene

Monolayer graphene exhibits two prominent peaks in the Raman spectrum so called 2D-peak and G-peak. The principal signatures of monolayer graphene are the ratio between the G-peak and the 2D-peak is characterized by a single clear Lorentzian peak.

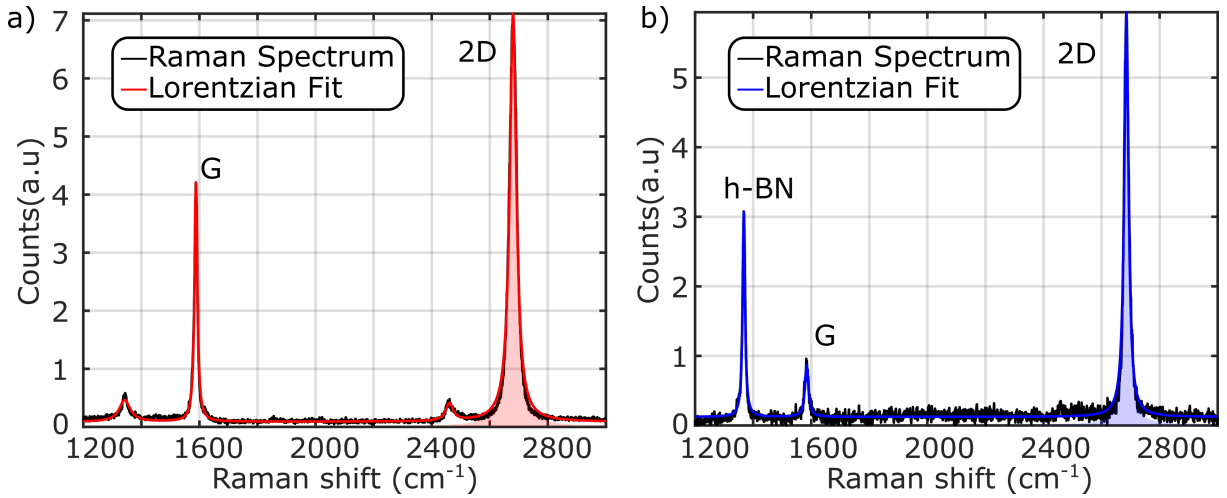


Fig. 3.4.3: Raman characterization of monolayer graphene. a) Raman spectrum of Gr/SiO₂. b) Raman spectrum of h-BN/Gr/h-BN. 2D-peak is depicted in both graphs.

Figure 3.4.3 displays the Raman spectra of graphene on SiO₂ (panel a)) and of graphene encapsulated in h-BN (panel b)). These spectra exhibit the typical characteristics mentioned earlier. Initially, we observe a G-peak to 2D peak ratio (I_{2D}/I_G) greater than 1, and the excellent fit achieved using a single-Lorentzian function of the 2D-peak. Furthermore, a comparison between the two panels reveals an increase in the I_{2D}/I_G ratio when the sample is encapsulated, indicating a noticeable enhancement in the properties of the monolayer graphene.

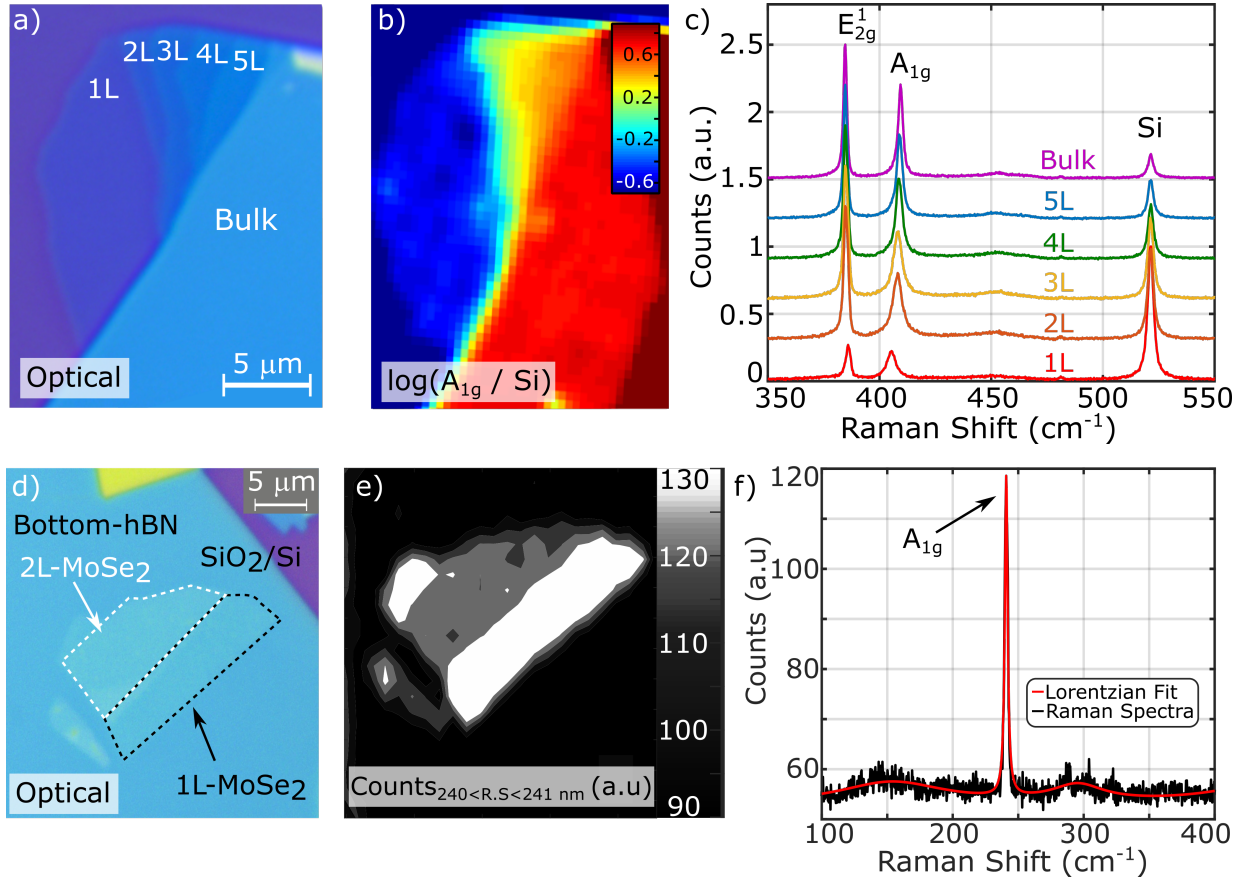
3.4.2.2 Raman spectroscopy in MoS₂ and MoSe₂

Fig. 3.4.4: Raman characterization of the MoS₂ thickness. a) Optical microscopy image of a flake of MoS₂ over SiO₂ with different thicknesses. The labels indicate regions with different thickness. b) False color Raman map of the difference between the A_{1g} and Si peak intensities. c) Raman spectra acquired at the different regions labelled in panel a). The spectra show three prominent peaks corresponding to the A_{1g} and E_{2g}¹ raman modes of MoS₂ and the Si raman mode. d) Optical microscopy image of a flake of MoSe₂ over h-BN. e) False color Raman map of the mean value of the counts in the raman spectra between wavelengths of 240 nm and 241 nm. f) Raman spectrum of the monolayer MoSe₂ flake (black line) and lorentzian fit experimental data (red line). Raman peak A_{1g} is labelled in the figure.

This section centers on Raman characterization of MoS₂ and MoSe₂. Raman spectrum of MoS₂ displays two peaks, associated with the vibration modes A_{1g} and E_{2g}¹, that depend strongly with the thickness of the exfoliated flakes. The relative raman shift distance between the peaks reduces with the reduction of the thickness. Figure 3.4.4 a) displays an optical microscope image of a MoS₂ flake with different thicknesses, while figure 3.4.4 b) presents a false-color map illustrating the ratio of the A_{1g} raman peak of MoS₂ and the intensity of the Si peak, displayed in a logarithmic scale. This representation distinctly reveals the varying thicknesses of the material. Figure 3.4.4 c) shows individual spectra obtained from different regions labeled in the optical image. The number of layers in MoS₂ is confirmed by examining the difference between the spectral positions of the E_{2g}¹

and A_{1g} peaks. In the thinnest region, the distance between the peaks is 19.4 cm^{-1} , a value consistent with those reported in the literature for monolayer MoS_2 [107].

MoSe_2 raman spectrum shows a very prominent peak, associated with the vibration mode, A_{1g} . This peak moves to lower frequencies as the thickness of the flake decreases. Figure 3.4.4 d) shows an optical microscope image a flake with a monolayer and bilayer MoSe_2 . Figure 3.4.4 e) presents a false-color map illustrating the mean value of the counts between frequencies of 240 and 241 cm^{-1} , revealing the monolayer and the bilayer of MoSe_2 . In figure 3.4.4 f) is depicted the raman spectrum of the monolayer MoSe_2 and the fitting of the spectrum to a lorentzian fitting function. The A_{1g} mode is located at 240.82 cm^{-1} , similar to the values in the previous literature for 1L- MoSe_2 [108].

3.4.2.3 Polarized Raman Spectroscopy in ReS_2

ReS_2 is a TMD with different properties to MoS_2 and MoSe_2 . The lack of an indirect to direct band gap transition in the monolayer limit makes few-layer ReS_2 more suitable for photocurrent spectroscopy, thanks to its higher absorption compared to the monolayer. Therefore, to measure the thickness of the flakes, we use the profilometer. Nevertheless, we also use raman spectroscopy in ReS_2 exfoliated flakes. Polarized resolved raman spectroscopy measurements in few-layer ReS_2 allow to reveal the orientation of the crystalline structure of the flakes [109]. To perform polarized resolved raman measurements, we select a parallel polarized configuration between the incident and the collected light, while the sample is rotated along the normal surface to change the relative angle between the ReS_2 flake and the polarization of the light. ReS_2 characterizes by 1T-distorted crystalline structure with two inequivalent perpendicular directions, parallel or perpendicular to the rhenium-chain (b-axis). Figure 3.4.5 a) shows a schematic of the ReS_2 crystalline structure with the b-axis highlighted, while figure 3.4.5 b) is an optical microscope image of a flake of ReS_2 with 13 nm of thickness. Figure 3.4.5 c) shows the Raman spectra of the flake measured at different polarizations with the more representative A_g -like vibration modes highlighted in the figure (modes I to V). The spectra are fitted to a five peak lorentzian function. To observe properly the large modulation of the different raman modes with the polarization angle, we depict in a polar plot the intensity of the raman modes extracted from the lorentzian fitting. Figures 3.4.5 d) and e) shows the intensity of the raman modes as a function of the polarization angle. To fit the experimental data we use the fitting function

$$I = (a \cdot \sin^2(\theta) + b \cdot \sin(2\theta) + c \cdot \cos(\theta))^2 \quad (3.4.1)$$

extracted from the raman tensor of the ReS_2 and the geometry of the experiment, with the incident and collected light in parallel configuration [110].

Mode V modulation provides the direction of the crystalline orientation of the b-axis, giving a maximum signal when polarization of the light is parallel to the b-axis $\theta = 0^\circ$ [109].

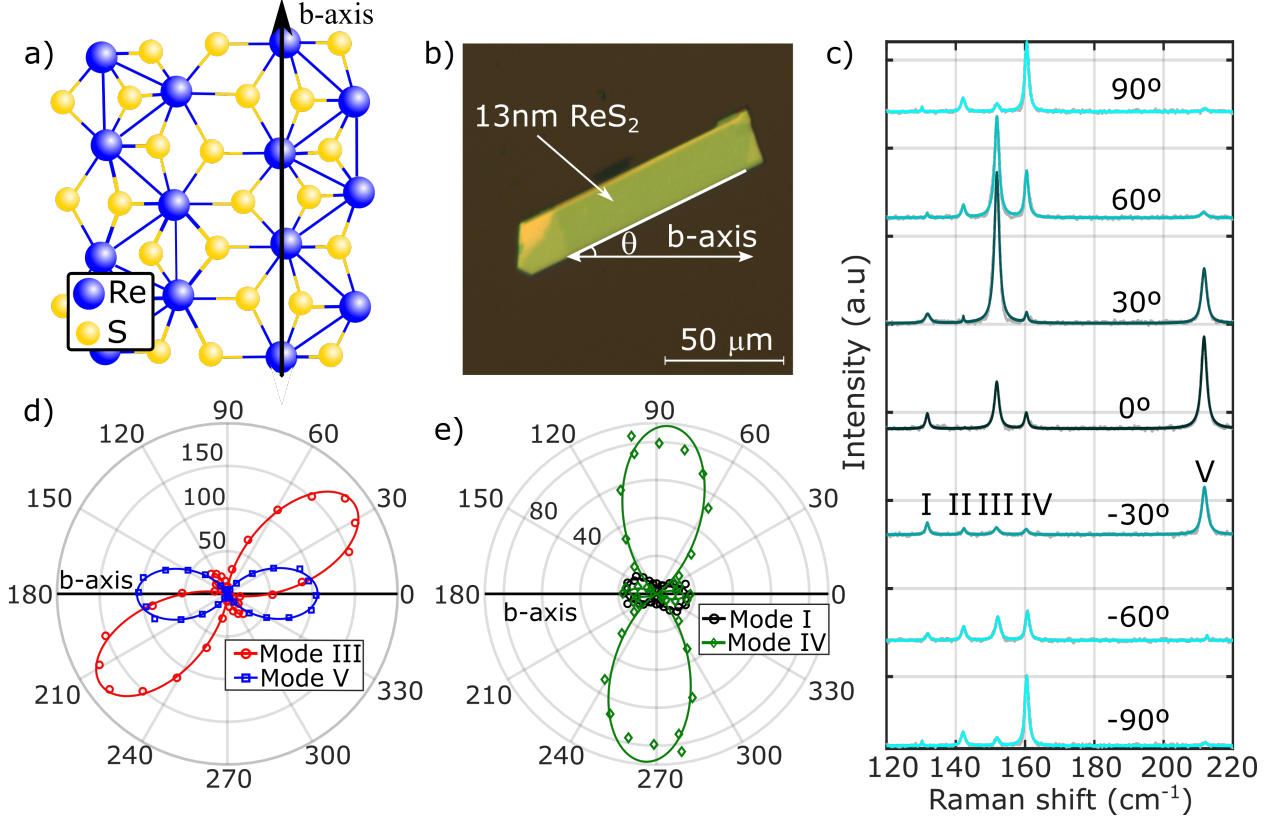


Fig. 3.4.5: Crystal symmetry and polarized resolved Raman spectroscopy in ReS₂. a) Crystalline structure of ReS₂. b) Picture of the few-layer ReS₂ flake transferred on SiO₂. The definition of the angle between the light polarization (white line) and the b-axis (white arrow) is also shown. c) Polarization resolved Raman spectra as function of the sample orientation angle. The spectra taken every 30° between -90° and 90° are vertically offset. Representative modes of ReS₂ are indicated in the figure. d) Raman intensity of modes III (red circles) and V (blue squares) as a function of the polarization angle. e) Raman intensity of modes I (black circles) and IV (green diamonds) as a function of the polarization angle.

Furthermore, another important characteristic of ReS₂, that is possible to identify through raman spectroscopy, is the stacking-order between layers. ReS₂ presents two different stable configurations, named in the literature as AA and AB stacking. For AA-stacked crystals the successive layers are positioned directly on top of each other, while for AB stacking, consecutive layers are shifted by roughly 2.5 Å across the perpendicular crystalline axis to b-axis. In the raman spectra, the main difference between the two stacking configurations is the relative distance between mode I and mode III. In AB-stacking, modes I and III are separated by roughly 18 cm⁻¹, compared to about 13 cm⁻¹ in AA-stacking [111]. Figure 3.4.6 shows the raman spectra of two different flakes of ReS₂ with the light polarization parallel to the b-axis. Modes I and III in panel a) are

separated 13 cm^{-1} indicating an AA-stacked flake, while in panel b) both modes are distanced around 18 cm^{-1} suggesting an AB-stacked flake.

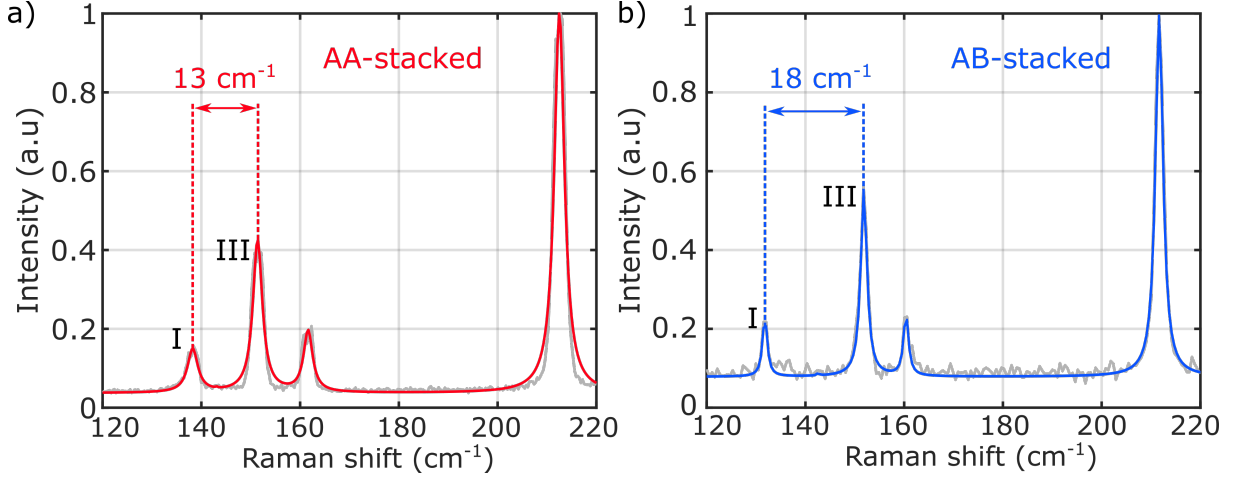


Fig. 3.4.6: AA and AB-stacked ReS₂ Raman spectra measured with linearly polarized light parallel to the b-axis. a) Raman spectrum of AA-stacked ReS₂ flake. b) Raman spectrum of AB-stacked ReS₂ flake.

3.4.3 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is the most used technique to identify excitonic transitions of exfoliated 2D-TMDs. In this dissertation we use the micro-Raman spectrometer to perform room-temperature PL spectroscopy as a complementary characterization. PL spectroscopy in graphene lacks of interest due to the absence of gap in its band structure. In contrast, PL spectroscopy in monolayer semiconducting 2H-TMDs, such as MoS₂, MoSe₂, WS₂ and WSe₂, is significantly more interesting due to its band structure present a direct band gap transition with tightly bound excitons [84, 11]. PL spectroscopy also demonstrates strong excitonic features in the case of 1T-distorted TMDs, such as ReS₂ or ReSe₂. However, contrary to 2H-TMDs, in ReS₂ and ReSe₂ the intensity of PL increases with the number of layers [62].

Figure 3.4.7 shows the PL spectrum of a exfoliated monolayer MoS₂ on SiO₂ substrate obtained with the micro-Raman spectrometer. We fit the PL spectrum using a three-peak lorentzian function. These peaks corresponds with the neutral excitons, A (X_{1s}^A) at 1.87 eV and B (X_{1s}^B) at 2.01 eV, and the trion transition associated to exciton A (T^A) 30 meV below X_{1s}^A . Neutral excitons A and B, and trion A transitions are depicted with blue, green and red peaks respectively. All these values shows a good agreement with the literature confirming the monolayer nature of the exfoliated MoS₂ flake. This flake is used to fabricate the device studied in chapters 4 and 5.

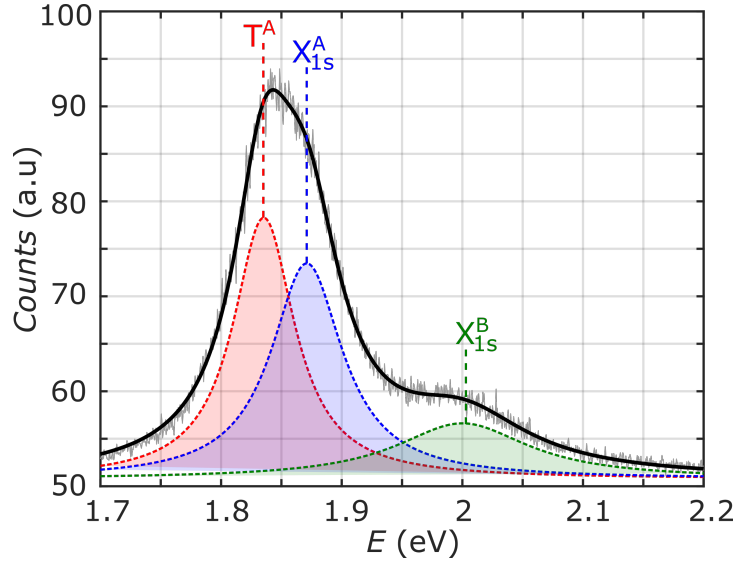


Fig. 3.4.7: Photoluminescence spectrum at room temperature of a monolayer MoS₂ placed on a SiO₂ substrate, excited with 532 nm light. The dashed lines represent the individual spectral contributions from the trion A (T^A), exciton A (X_{1s}^A), and exciton B (X_{1s}^B).

Now, I continue with the use of the PL spectroscopy in ReS₂. In this material PL spectroscopy shows a strong dependence with light polarization because its crystal asymmetry, as shown in raman characterization section. In this case, we use polarization resolved PL spectroscopy to characterize the dichroic nature of the excitons in ReS₂ and have a preliminary characterization of this phenomena prior to the fabrication and the photocurrent characterization of the device.

Figure 3.4.8 a) depicts the ReS₂ flake with the b-axis highlighted. The incident light polarization, depicted with a white arrow, is perpendicular to the b-axis and remains constant in all the measurements. The polarization of the collected light is controlled by placing a linear polarizer in front of the detector. Figure 3.4.8 b) shows the photoluminescence spectra as function of the out-polarization angle. We fit the spectra to a multi-lorentzian peak function (solid multicolor lines). We observe two clear peaks at energies $E = 1.47$ eV and $E = 1.5$ eV, X_1 and X_2 , that are associated with excitons. Another spectral feature, X_3 , is observed at $E = 1.58$ eV and we associate it with excited Rydberg states of the excitons. Intensities of the peaks are modulated as we change the polarizer angle. Figures 3.4.8 c) displays the intensities of the X_1 , X_2 and X_3 extracted from the lorentzian fitting, as a function of the angle, and the fitting of the data to the function $I = I_0 + I_1 \cos^2(\theta + \theta_0)$. I_0 is the minimum intensity of the peaks, I_1 is the difference between the maximum and the minimum intensity and θ_0 is the offset of polarization angle. Modulation reveals the in-plane dipole of the excitons, showing that the optical response of the device is clearly anisotropic. This have been reported in previous literature for few-layer ReS₂ and confirms the hypothesis of excitonic polarization modulation in this material. This flake is used to fabricate the device studied in chapter 7.

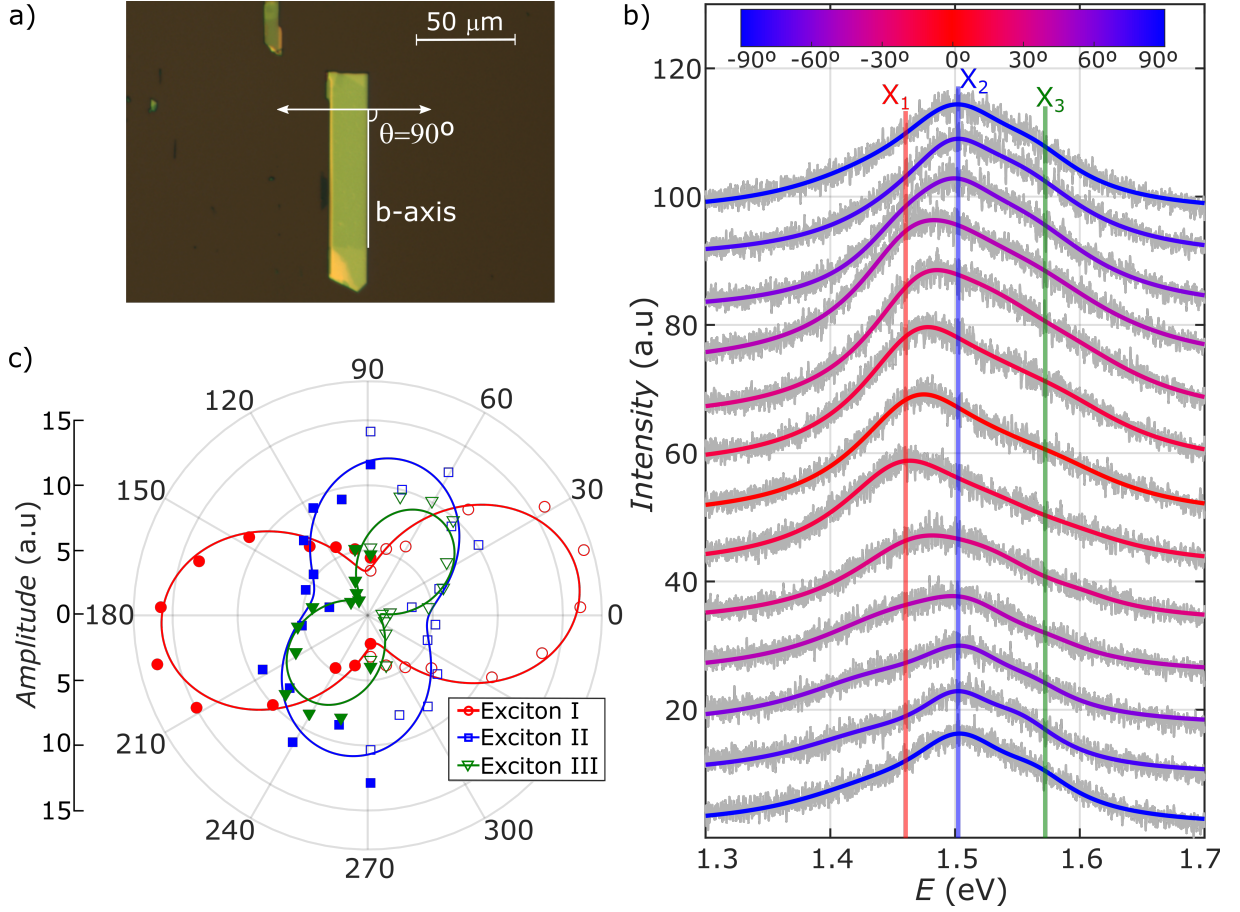


Fig. 3.4.8: Polarization-resolved photoluminescence spectroscopy in ReS_2 . a) Geometry of the experiment. Incident-light polarization is perpendicular to the b-axis while the output polarization is controlled with a polarizer. b) Intensity of exciton X_1 , X_2 and X_3 as function of the polarization angle. Solid lines are the fittings to a dichroic response. c) Photoluminescence spectra at different output polarizations. The spectra taken every 10° between 0° and 180° are vertically offset for clarity. Experimental data (solid grey lines) are fitted to a three-peak lorentzian functions (solid multicolor lines).

3.4.4 Stacking of Van der Waals heterostructures

This section exposes the two procedures of stacking followed in this dissertation. For graphene heterostructures, we use polycarbonate (PC) based transfer method to obtain high quality graphene, encapsulated between two flakes of h-BN. Concerning TMDs, depending on the process of exfoliation, we use the same PC method or PDMS deterministic transfer method.

Both procedures are done in a home-made 2D-transfer system developed by technicians of the nanotechnology group. The optical part of this system comprises an optical microscope (Nikon) complemented with two long working distance objectives (X10, $\text{NA}=0.30$, $\text{WD}=16\text{mm}$ and X20, $\text{NA}=0.40$, $\text{WD}=11\text{mm}$). The substrates are situated on a hot plate, which is placed onto a xy micro-manipulator and a z-stage. The hot plate is complemented with a temperature controller and a vacuum line to fix the sample.

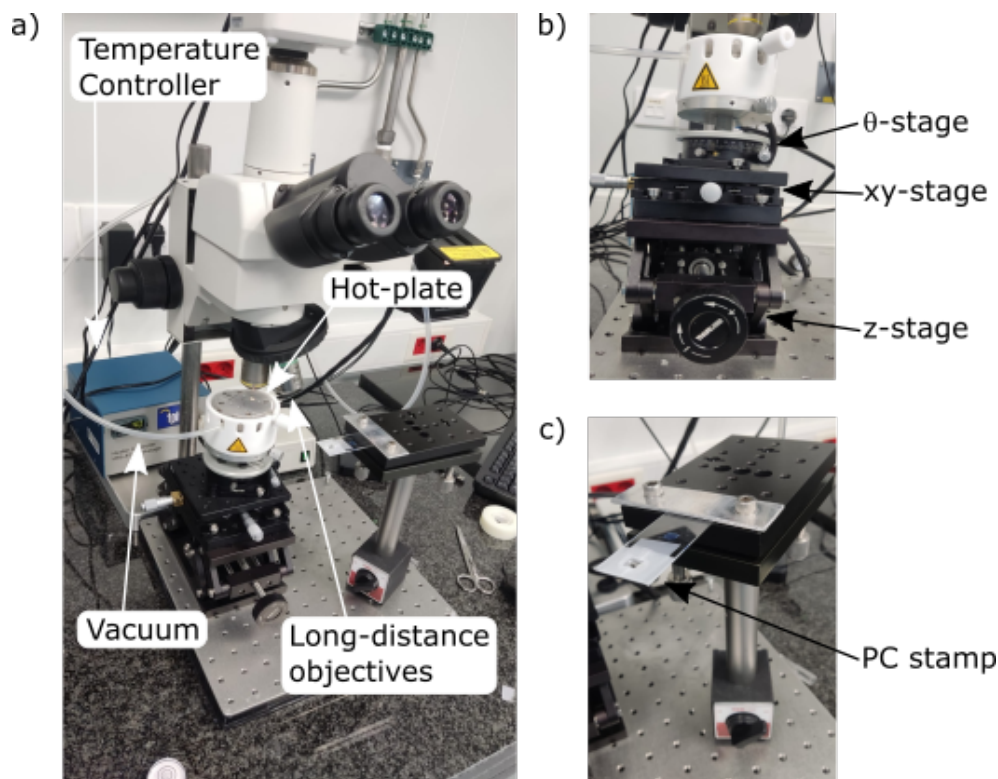


Fig. 3.4.9: Home-made transfer system with the different elements highlighted. a) Picture of the complete transfer system. b) Different stages used to correct the alignment. c) PC stamp placed in the tilted control stage.

Figure 3.4.9 shows an optical image of the transfer system with all the components specified in the picture. The viscoelastic stamp, used to transfer the flakes, is located with the help of a glass slide in the stage with tilted control. Approximately, we situate the stamp over the substrate and the fine adjusting of the landing place is done using the xy micromanipulator.

3.4.4.1 Polycarbonate based transfer method

In this section I describe the transfer method using PC [112, 113] used for fully encapsulated samples of graphene and MoS₂. Firstly, we prepare the PC film to pick-up the flakes. Preparation steps are described in figure 3.4.10. We start by pouring a mixture of chloroform and PC on a glass slide and equally distributing it with another glass slide. Then, the PC becomes solid due to evaporation of the chloroform. Next, we open a small window in a tape. Once the PC is solid, using the tape with the window, we peel off the most homogeneous part of PC-film to obtain a window of PC. Subsequently, the PC window is placed on a small block of home-made PDMS of a thickness of around 0.5 cm. PDMS block helps to land smoothly with the PC-film on the substrates to pick-up or let the desired flakes.

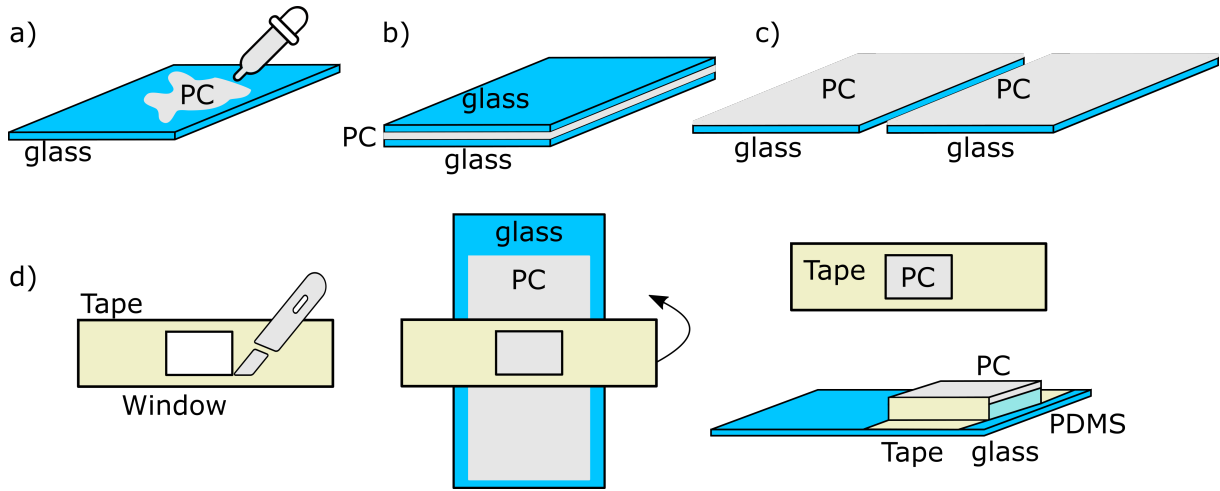


Fig. 3.4.10: Polycarbonate film preparation. a) Mixture of chloroform and PC is poured on a glass. b) and c) Liquid is equally distributed using two glasses. d) After the chloroform is evaporated a tape with a window of PC is prepared and placed on a block of PDMS in a glass slide.

After the preparation of the PC-window and the identification of the desired flakes via optical contrast, raman spectroscopy and profilometer measurements, we start with the stacking process using the described setup. The assembly of heterostructures step by step procedure is indicated in figure 3.4.11.

1. The top h-BN flake is located on a SiO_2 substrate. Using the xy stage and the optical microscope, the h-BN flake is accurately aligned below the PC-film. As the PC-stamp is transparent, the h-BN flake can be seen to perform the alignment. Then, the substrate is heated between $40^\circ\text{--}60^\circ$ and we contact the h-BN flake with the PC. Subsequently, the SiO_2 substrate is lowered and the h-BN flake is picked-up by the PC-film.
2. With the top h-BN in the PC-film, we align the h-BN with the selected flake of graphene or MoS_2 situated in other SiO_2 substrate. In this step the alignment between the flake on the substrate and the h-BN in the PC-film is critical. After the alignment, the substrate is heated up to temperatures of roughly 160° and the contact between the PC film and the substrate is done while the temperature is increased. Then, the PC is melted letting the top h-BN on the flake. Finally, the PC is cleaned using chloroform and acetone.
3. Now, we need to pick-up the stack of the top h-BN and the graphene or MoS_2 and transfer it on the bottom h-BN. Before this step, it is necessary to prepare a new PC window. Following the same procedure explained in the first step, the stack is picked-up. It is important to notice that with this procedure the h-BN is in contact with the PC but the material of interest never touches the PC and is picked-up by the van der Waals interaction with the h-BN.

4. Finally, the stack is accurately aligned above the bottom h-BN using the stages. After making contact with the substrate the PC is melted and subsequently cleaned to finish the final heterostructure.

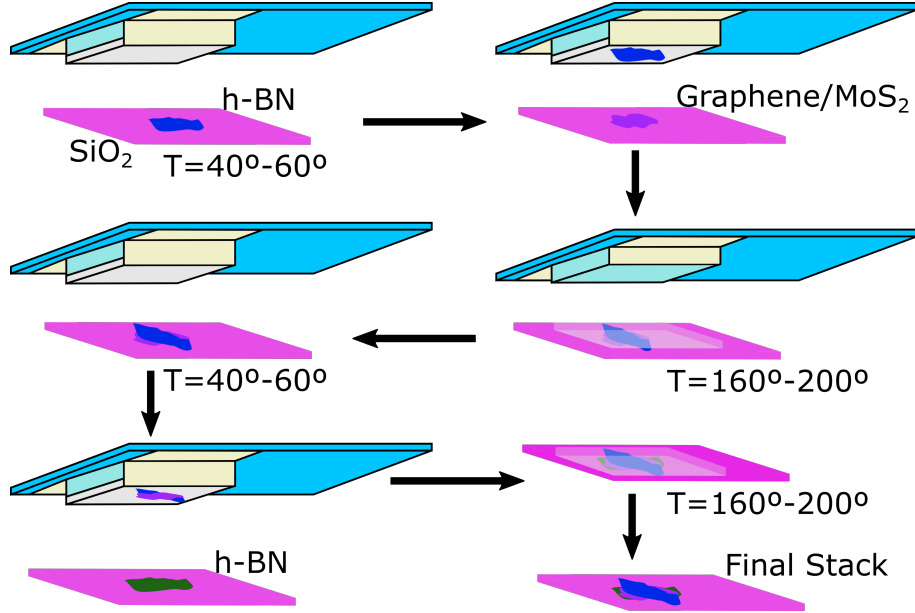


Fig. 3.4.11: Schematic of the PC-based transfer method to complete a heterostructure.

Figure 3.4.12 shows the transfer steps followed to fabricate the heterostructure of the device of 1L-MoS₂ measured in chapters 4 and 5. In panel a), we observe the exfoliated flake on the Si/SiO₂ substrate. Firstly, in panel b) the h-BN is placed over the 1L-MoS₂. Secondly, in panel c) the top h-BN/1L-MoS₂ is picked up and positioned on the bottom h-BN to finish the stack.

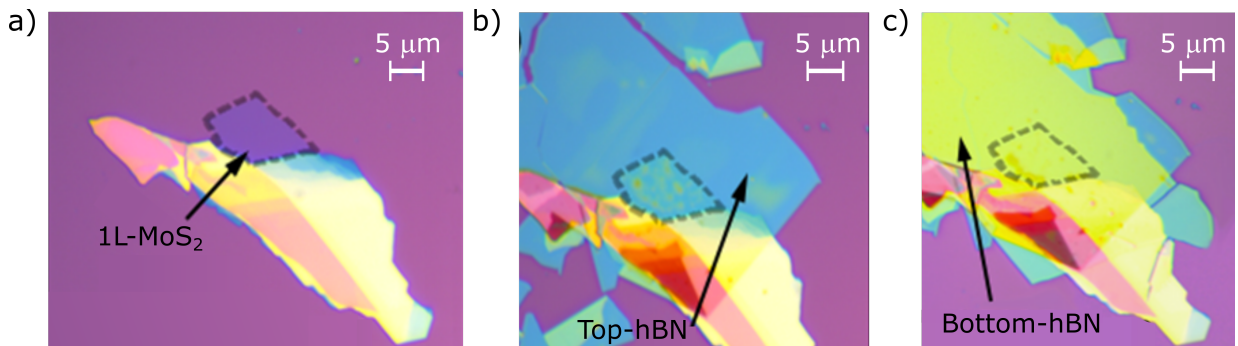


Fig. 3.4.12: Steps to obtain a fully encapsulated 1L-MoS₂. a) Exfoliated 1L-MoS₂ on Si/SiO₂ substrate. b) Top-hBN on the 1L-MoS₂. c) Final heterostructure h-BN/1L-MoS₂/h-BN. All this steps are done using the PC-transfer method.

3.4.4.2 Polydimethylsiloxane based transfer method

In this section I explain the PDMS based transfer method [104]. In contrast with the PC method, the flake is directly exfoliated in the PDMS. In our case, the PDMS is commercial as explained in the exfoliation section. The viscoelastic behaviour of the PDMS makes the material suitable to perform deterministic transfer mechanically of exfoliated flakes. After identifying an appropriate flake to fabricate a device, we start the transfer procedure following the steps depicted in figure 3.4.13.

1. After optical identification of the desired flake exfoliated on the PDMS, the area of interest is isolated by trimming the PDMS stamp to create a strip with the flake near its top edge.
2. With the help of a glass slide and tape the PDMS strip is positioned in the stage of the transfer system. Once the substrate is placed on the hot plate and fixed using vacuum, the substrate and the flake placed on the PDMS are accurately aligned using the stages.
3. Subsequently, using the z-stage the PDMS is stuck to the substrate. This step is critical as occasionally, a gentle tap with the tweezers is required to adhere the PDMS to the substrate. Then, the substrate is heated up to temperatures ranging from 80° - 100° .
4. Finally the PDMS is slowly separated since the viscoelasticity of the material makes it unsticky when the speed of detachment is low. When the PDMS is completely removed the stack is finished. If the flake is still attached to the PDMS after the separation is possible to repeat the process if the flake is in good conditions.

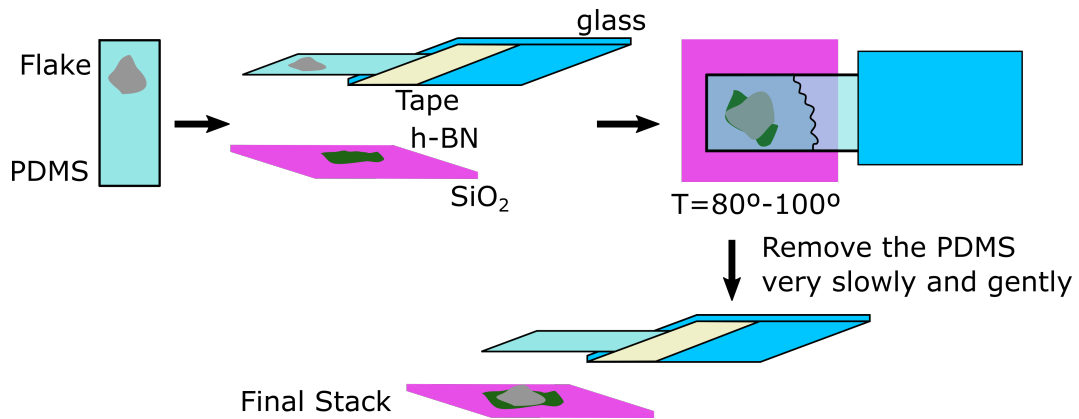


Fig. 3.4.13: Schematic of the PDMS-based transfer method to complete a heterostructure.

Figure 3.4.14 shows different heterostructures done using the PDMS transfer method. Panels a), b) and c) are optical images of transferred flakes of few-layer ReS₂, monolayer WS₂ and monolayer MoSe₂ respectively, on different bottom h-BNs. As the exfoliation

using PDMS is usually used to increase the lateral dimensions of the exfoliated flakes, this flakes can be directly transferred on SiO_2 , so both PC and PDMS methods are complementary. Panel d) shows an optical image of a few-layer ReS_2 flake transferred directly on the Si/SiO_2 substrate.

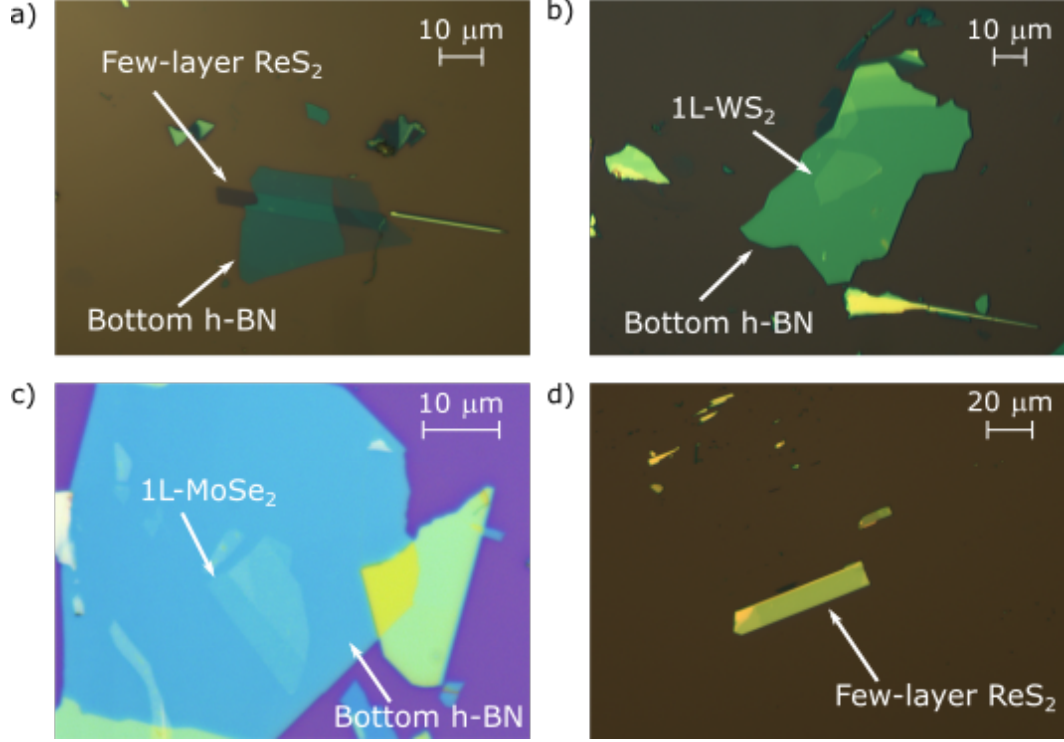


Fig. 3.4.14: PDMS based transfer method heterostructures. a) Few layer ReS_2 transferred on a bottom h-BN stacking. b) 1L- WS_2 transferred on a bottom h-BN. c) 1L- MoSe_2 transferred on a bottom h-BN. d) Few-layer ReS_2 transferred directly on the Si/SiO_2 substrate. Scale bar is in the top-right of all panels.

3.4.5 Design of the device

After finishing the heterostructure, we start with the design of the final device. First step is the definition of the geometry. Usually in our devices, we select a hall-bar like geometry. On the one hand in graphene devices, this geometry is essential to study magnetotransport phenomena and on the other hand, in the TMDs-based devices we select this geometry because we obtain a device with a defined channel and several contacts. We start the design process using the software of the Raith nanolithography controller of the SEM, called Elphy Plus. Elphy Plus is a design software especially developed for electronic lithography, where is possible to define different layers, each layer with the corresponding electronic dose and indicate the markers to obtain a perfect alignment. To start the design of the device we need the dimensions of the useful part of the heterostructure. We have two complementary tools to measure the distances. First, we use the calibrated software of the leica microscope (LAS) to measure the useful part of the heterostructure using the markers as the origin of the axis. After measure all the distances, we take a global picture

of the device with the markers visible. With this picture and using open source software SVGmarks it is possible to couple the picture of the heterostructure with the Elphy Plus software to directly design the device on the picture.

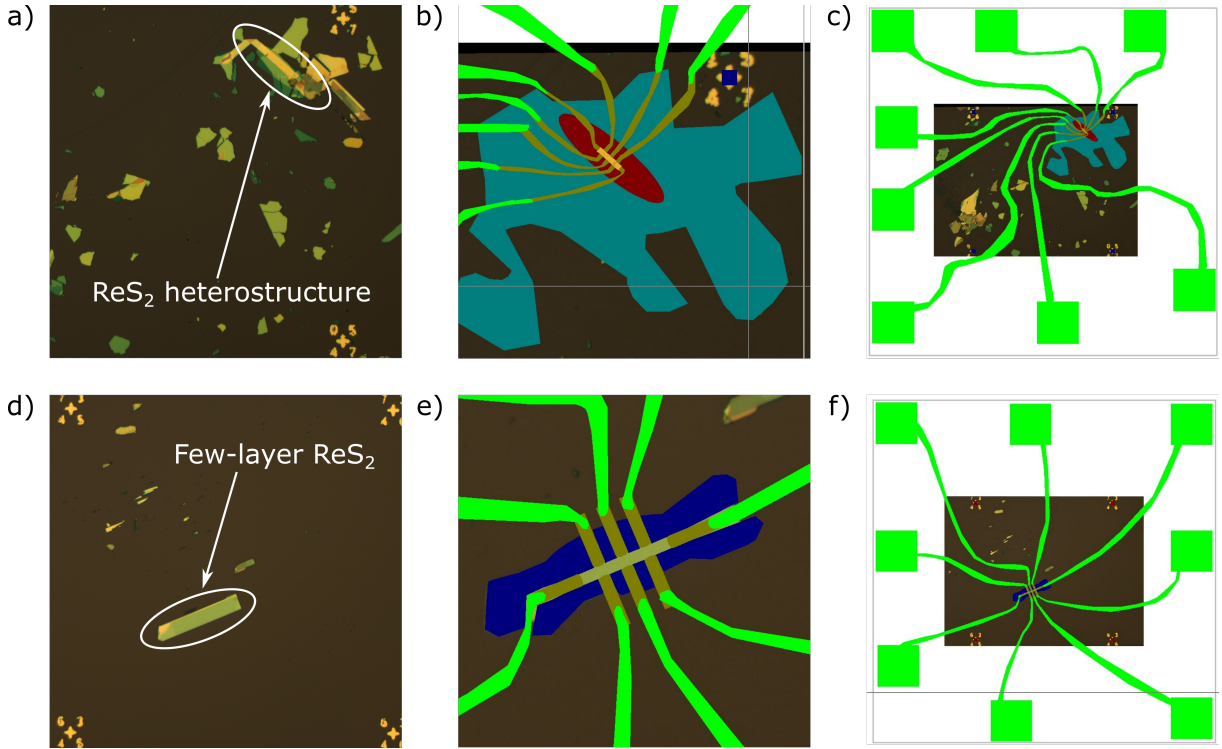


Fig. 3.4.15: Examples of CAD design of the devices. a) Picture used for the design in a heterostructure of h-BN/ReS₂/h-BN. b) Mask (blue and red drawings) for the shape definition and contacts near the sample (yellow drawings) of the device in panel a). c) Pads designing (green drawings) of the device. d) Picture used for the design in a few-layer ReS₂. e) Mask (blue drawing) for the shape definition and contacts near the sample (yellow drawings) of the device in panel d). f) Pads designing (green drawings) of the device.

Figure 3.4.15 shows the designing software with two complete CADs of two devices, with the picture of the device coupled to the software. Panels a) and d) shows two flakes of ReS₂, while panels b), c), e), and f) shows the CAD design of the devices. Use of colours in the designs are related with the definition of different layers. Also is important to notice that we usually define two writing fields to have the possibility of use two different apertures of the SEM. One writing field has an area $500 \times 500 \mu\text{m}^2$ for the definition of the geometry and smaller contacts, where usually is used the $10 \mu\text{m}^2$ aperture. The other one has dimensions of $1000 \times 1000 \mu\text{m}^2$ to define the pads of the sample, where is used the aperture of $60 \mu\text{m}^2$.

3.4.6 Shape definition of the device

Once the design of the device is complete, the subsequent step is the shape definition of the device via electron beam lithography and dry-etching using the SEM and the ICP-RIE previously described. Figure 3.4.16 shows the pictures of the etching process of different

TMDs devices using the procedure described previously. Panels a) and b) displays the PMMA exposed after the e-beam lithography with the shape of the device patterned and the subsequent dry-etching of the h-BN/1L-MoS₂/h-BN heterostructure. Panel c) shows the definition of the h-BN/1L-MoSe₂ heterostructure after the dry-etching process, while panel d) is an optical image of the PMMA exposed after the e-beam lithography for the definition of the geometry of the few-layer ReS₂ on SiO₂.

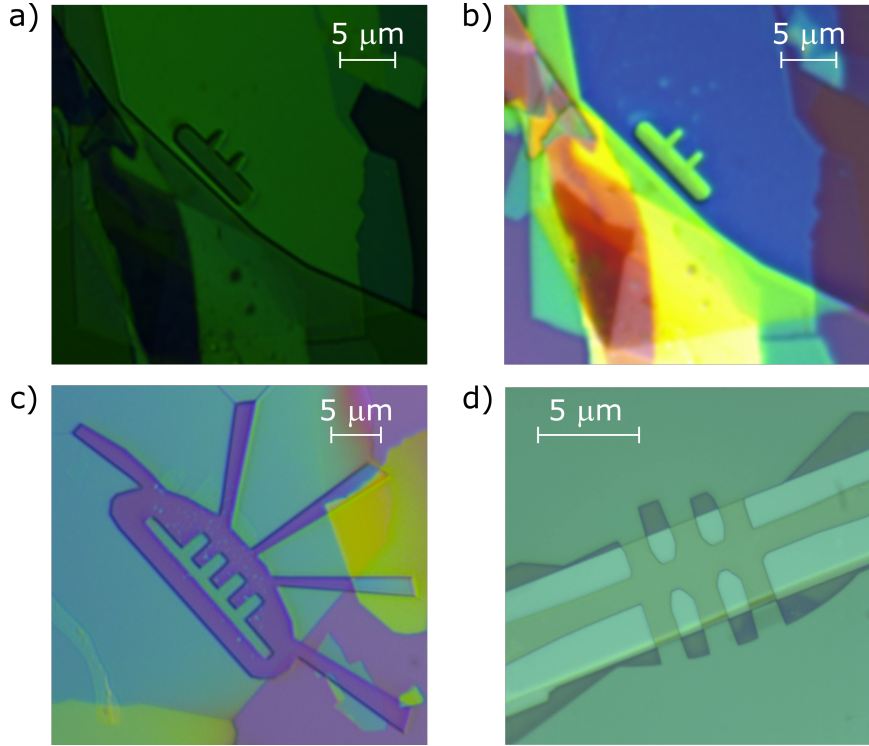


Fig. 3.4.16: Etching of different heterostructures. a) PMMA mask for the definition of the geometry of the h-BN/1L-MoS₂/h-BN heterostructure. b) Dry-etching of the panel a) device. c) h-BN/1L-MoSe₂ device after dry-etching process. d) PMMA mask for the definition of the geometry of the few-layer ReS₂ on SiO₂. Scale bar is present in all panels.

The steps involved in the shape definition of the device are described below:

- First, the samples are covered with a home-made PMMA solution (4% solved in chlorobenzene) and a controlled thickness is obtained by spin-coating the resist. The spinner is set at 4000 rpm/s (with an acceleration of 1000 rpm/s²) for 1 minute and baked at 160° for 10 minutes obtaining a homogeneous resist layer of ≈ 230 nm. The choice of chlorobenzene over commercial PMMA in anisole allows for a more homogeneous and thicker layer due to a better adhesion to the substrate.
- Next, the sample is introduced in the SEM to start the electronic lithography process. Using e-beam lithography, with a 15 kV acceleration voltage and a dose of 250 $\mu\text{C}/\text{cm}^2$, the geometry of the device is defined exposing the resist.

- Subsequently, the sample is removed from the SEM and the resist is developed using a mixture of 1 part of MIBK and 3 parts of isopropanol for 2 minutes and the development process is stopped submerging the sample in isopropanol for 30 seconds.
- Once, the exposed resist is removed the sample is etched using the ICP-RIE in a SF_6 atmosphere (40 sccm, $P = 75$ W, process pressure 6 mTorr and $T = 10$ °C). The etching time varies from 3 to 15 seconds depending on the thicknesses of the flakes. This recipe is specially convenient in encapsulated h-BN samples, leaving a pyramidal profile in the edges of the devices, favouring good electrical side-contacts. This recipe has been used to etch all the samples of this dissertation.

3.4.7 Metallic deposition of the electrical contacts

In order to perform electrical measurements, the devices need conductive contacts through which current or voltages can be applied and measured. After defining the geometry of the devices, the metallic contacts are deposited following the subsequent steps:

- First, the samples are again covered with a home-made PMMA solution. In this case, a 5% solved in chlorobenzene is selected. The 5% allows to obtain a larger thickness to avoid problems to remove the resist after the evaporation of the electrical contacts. The removal of the resist is known as lift-off process. After that, the sample is spin-coated at 4000 rpm/s (with an acceleration of 1000 rpm/s²) for 1 minute and baked at 160° for 10 minutes obtaining resist thickness of ≈ 300 nm.
- Next, the sample is introduced in the SEM to start the electronic lithography process. The definition of the electrical contacts using e-beam lithography is done in two steps. First, the small contacts near the sample are exposed in a small writing field of $500 \times 500 \mu\text{m}^2$ with a $10 \mu\text{m}$ aperture and a dose of $270 \mu\text{C}/\text{cm}^2$. Secondly, the larger parts of the contacts and the pads for the wire-bonding are exposed in a larger write field of $1000 \times 1000 \mu\text{m}^2$ with a $60 \mu\text{m}$ aperture and a dose of $400 \mu\text{C}/\text{cm}^2$.
- Subsequently, the sample is removed from the SEM and the resist is developed using a 1:3 MIBK to isopropanol mixture for 2 minutes. After that, the development process is stopped using isopropanol as explained before.
- Once, the exposed resist is removed the sample introduced in the load-lock of the e-beam evaporator for the metallic-deposition of the contacts. When the pressure in the load-lock reaches values of 10^{-6} mbar, the sample is introduced in the main-chamber. Metallic deposition of the electrical contacts is done at pressures of 10^{-9} mbar. In our devices the contacts are composed by an adhesion layer of Ti or Cr of 5 nm and 60 nm of Au. Combination selected for graphene devices is Cr (5 nm)/Au (60 nm), while in TMDs usually is used Ti(5 nm)/Au(60 nm) contacts. The evaporation rates are kept around $1.5 \text{ \AA}/\text{s}$.

- Finally, when the evaporation is finished, the deposited layers of Ti or Cr, and Au on the PMMA are lifted off by dissolving the PMMA layer acetone. Long distance microscope is used to check the lift-off process. Next, the sample is cleaned with isopropanol and dried with nitrogen gas. If all goes well, only the metallic layer in direct contact with the Si/SiO₂ substrate remains in the sample.

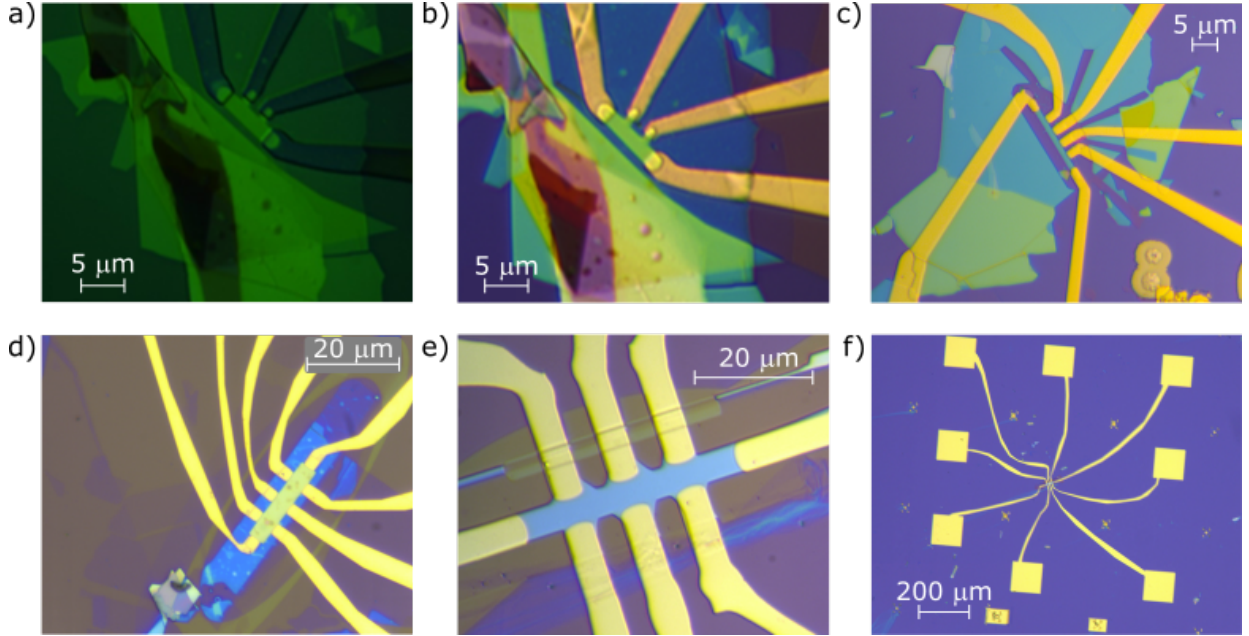


Fig. 3.4.17: Evaporation of metallic contacts in different heterostructures. a) PMMA mask for the evaporation Ti/Au contacts in the h-BN/1L-MoS₂/h-BN heterostructure. b) Ti/Au deposited contacts after the lift-off process in the same device of panel a). c) h-BN/1L-MoSe₂ device after the metallic contacts of Ti/Au deposition. d) Heterostructure of h-BN/ReS₂/h-BN with Cr/Au contacts deposited. e) Deposited Cr/Au contacts on the few-layer ReS₂ flake on SiO₂. f) Zoomed out image of the device in panel e) to observe the pads of the device. Scale bar is present in all panels.

Figure 3.4.17 displays examples of metallic contact deposition in different devices. Panels a) and b) shows the PMMA pattern and the subsequent metallic deposition of Ti/Au contacts in the h-BN/1L-MoS₂/h-BN heterostructure. Panel c) depicts an optical image of the deposited contacts of Ti/Au in the h-BN/1L-MoSe₂ heterostructure. Panel d) shows an optical image of a h-BN/few-layer ReS₂/h-BN heterostructure, while panel e) displays a few-layer ReS₂ on SiO₂, both with Cr/Au contacts deposited. Finally, panel f) shows a zoomed out image of the ReS₂/SiO₂ device with the bonding pads visible. Bonding pads are designed as squares of area 120 × 120 μm in all devices fabricated.

3.4.8 Wire-bonding of the devices

The final step before beginning the characterization of the devices in the measurement setups is the wire-bonding to a chip-carrier. The chip carriers compatible with the equipments used are dil-8, dil-16, and LCC-20, which have 8, 16, and 20 contacts, respectively.

Figure 3.4.18 a) presents the semiautomatic bonding machine, the tpt-HB10, used for wire bonding all devices. This machine features a hot plate that reaches up to 200°C for bonding and a tip with a 25 μm gold wire inside. Figure 3.4.18 b) displays an optical image of a device that has been wire-bonded into a dil-8 chip carrier.

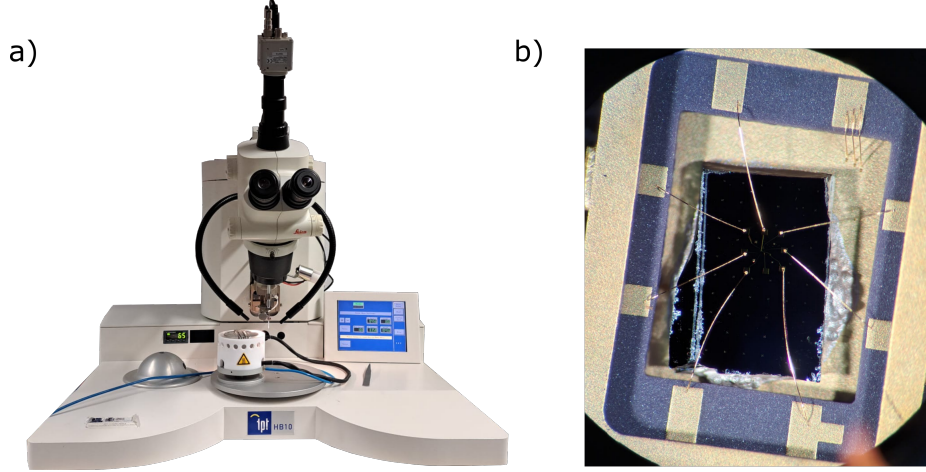


Fig. 3.4.18: Wire-bonding of the devices. a) Semi-automatic bonding equipment tpt-HB10. b) Example of a bonded device.

3.5 Magnetotransport equipments

Magnetotransport consists in the study of the electronic transport when a device is subjected to a magnetic field. This section describes the two magnetotransport equipments used to perform measurements of the quantum hall effect in high-quality graphene, presented in the chapter 3. A bitter solenoid with a cryostat in the High Field Magnet Laboratory (HFML) and the teslatron in the low temperature laboratory (LBT) of the University of Salamanca.

3.5.1 High Field Magnet Laboratory

High magnetic field measurements (up to 30 T) were performed in the HFML in Nijmegen using a cryostat refrigerated with a continuous flow of liquid helium, that reaches temperatures from 1.4 K to 300 K, inside a bitter solenoid with a maximum magnetic field of 33 T (see figure 3.5.1 a)). The liquid helium is collected again using a recovery line, but the helium losses are considerable. The sample, bonded in a 20-pin holder, is placed inside the cryostat using a home-made stick with the electrical connections.

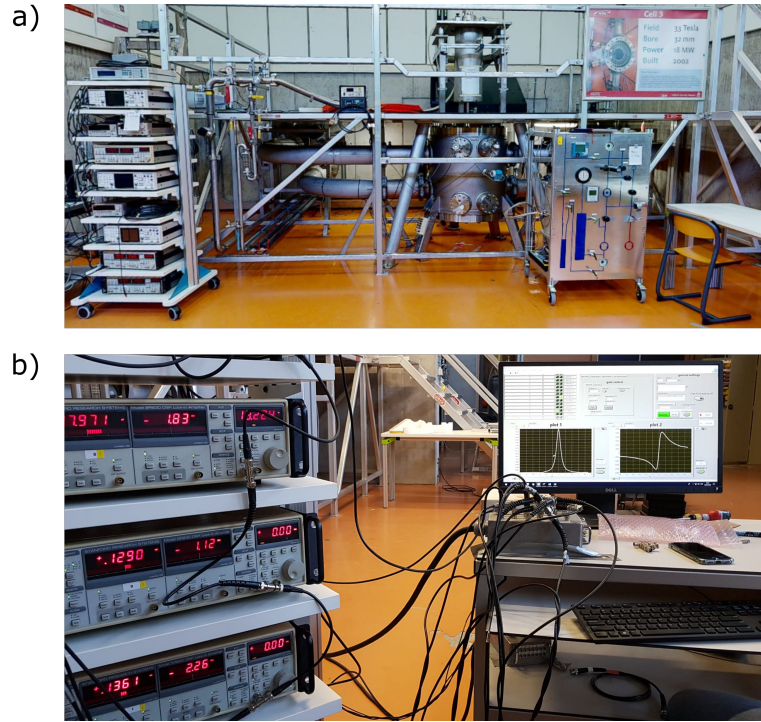


Fig. 3.5.1: a) Bitter solenoid of cell 3 with 33 T of maximum field in the HFML with the sourcemeters and lock-ins placed on the left. b) Measurement setup controlled using a labview program.

To perform the measurements, we had available lock-in amplifiers and source-meters to perform standard electronic transport measurements. In figure 3.1.1 b) it is possible to observe all the equipments controlled using a labview program during a measurement.

3.5.2 Low temperature laboratory in Salamanca

For measurements of magnetotransport at lower magnetic fields we use the teslatron present in the low temperature laboratory (LBT) of the University of Salamanca. Figure 3.5.2 a) shows a picture of the laboratory with different equipments to perform electrical measurements. The main facility in the LBT is the teslatron, an integrated cryofree (without losses of liquid helium) superconducting magnet system, appropriate for the study of low dimensional physics, spintronics or electrical transport measurements. The system is cooled down using a close-cycle helium compressor (F-70 sumitomo) and the sample is placed inside the cryostat in a probe stick with a chip-carrier with 16 or 20 contacts. The probe stick is provided with an automatic rotator that allows to change the orientation of the sample respect the magnetic field. In this facility, the devices can be measured at temperatures from 1.5 K to 300 K. Moreover, the superconducting magnet can apply a maximum magnetic field of 12 T. The sample is kept in a constant bath of helium with a pressure of around 10 mBar to maintain the sample in stable conditions. A home-made labview program controls all the system.



Fig. 3.5.2: a) Image of the low temperature laboratory of the university of Salamanca with a measurement equipments rack and the teslatron. b) Detail of the teslatron equipment developed by oxford instruments with a maximum magnetic field of 12 T and range of temperatures between 1.5 K to 300 K.

3.5.3 Lock-in technique for magnetotransport in graphene

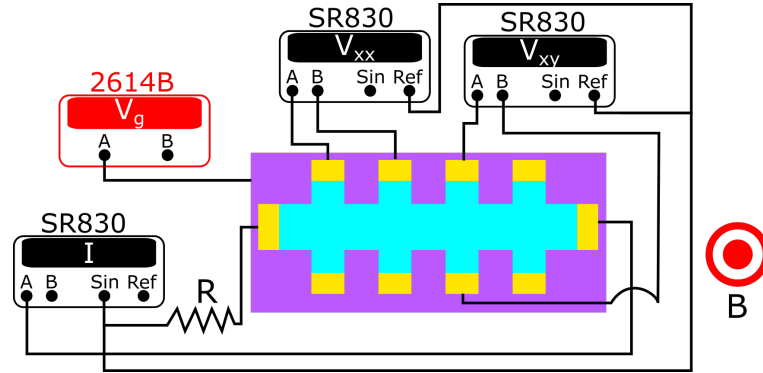


Fig. 3.5.3: Schematic of the lock-in technique to characterize graphene devices. Lock-in amplifiers corresponds with the SR830 equipments and the sourcemeter is the 2614B equipment. R denotes the resistor and the B is the magnetic field.

For measurements in the graphene devices we use the standard 4-probe lock-in technique. Figure 3.5.3 depicts an schematic of the measurement configuration. Firstly, we use the output voltage port of one lock-in amplifier, that generates a sinusoidal voltage of amplitude and frequency desired, with a resistor connected in series, typically between 100-500 M Ω , to inject a sinusoidal current (see fig 3.5.3., lock-in I). We select resistors two order of magnitude higher than the typical resistivity of the graphene, to ensure a constant amplitude of the injected current. Usually, the injected current is selected in a range from 10-20 nA in amplitude, and 10-20 Hz in frequency. The current flowing through the graphene device is measured with the same lock-in using a short-circuit configuration. To measure the longitudinal and the transversal voltages we use two more lock-in amplifiers

(V_{xx} and V_{xy} respectively). Both are synchronized with the lock-in amplifier that injects the constant current (used as the reference). We modulate the carrier density in the graphene devices applying a gate voltage through the Si/SiO₂ using a sourceter.

3.6 Low photocurrent spectroscopy setup

In this section, I describe one of the main achievements of this thesis, the development of a low temperature photocurrent spectroscopy setup. This setup is largely used during this dissertation to characterize the spectral photoresponse of TMD-based phototransistors. Subsequently, I detail briefly the individual components of the setup.

Low-temperature photocurrent spectroscopy is the central part of this dissertation. We have developed an experimental setup that have been widely used during this thesis. All the measurements presented from chapter 4 to 7 have been performed using this setup. Figure 3.6.1 shows a schematic of the low-temperature photocurrent spectroscopy setup used for our measurements. To obtain monochromatic light we use the supercontinuum white laser along the monochromator. The spectrometer is employed to accurately register the wavelength of the monochromatic light.

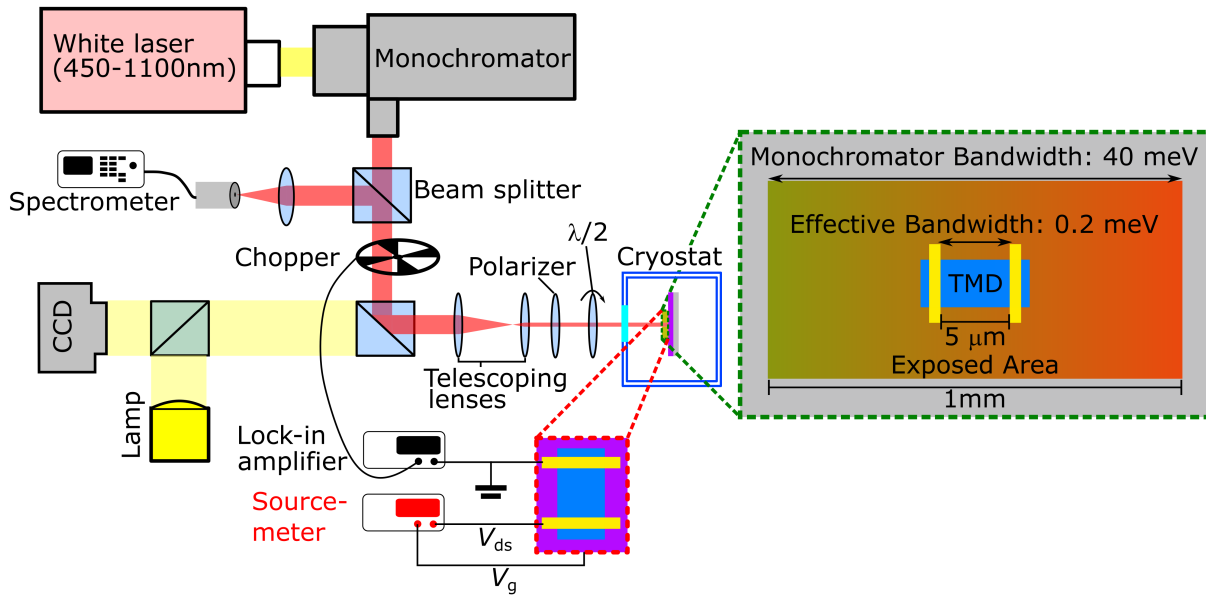


Fig. 3.6.1: Schematic of the low-temperature photocurrent setup. Green inset corresponds with the illumination conditions of the sample and red inset with the electrical measurement setup.

The setup also includes a halogen lamp and a CCD camera, aligned with the laser excitation through two beam splitters, allowing for a direct observation of the sample. Two telescoping lenses are located before the sample to focus and collimate the light. For polarization-dependent measurements, a linear polarizer and a half-wave plate are integrated. Finally, the sample is placed inside the pulse-tube cryostat with optical access. To increase the signal-to-noise ratio in optoelectronic measurements, an optical chopper

modulates the excitation light, while a lock-in amplifier, synchronized to the same modulation frequency, records the device electrical response. To apply the drain source voltage, V_{ds} and the gate voltage, V_g we use the sourcemeter Keithley 2614b (see red inset). A more detailed description of the measurement procedure is exposed in the next section.

To ensure a complete illumination of the device we maintain the output slit of the monochromator fully open. Consequently, this produces a broad, rainbow-like, rectangular light field incident on the device, with a photon energy gradient of about 40 meV across the illuminated region (see green inset). The optically active zone of the device corresponds with the TMD region between the drain and source electrodes and is significantly smaller than the illuminated area, functioning as a secondary slit. Therefore, the spectral measurements effective bandwidth is determined by the photon energy variation from the drain to the source electrode, which is typically in the range of $\Delta E \approx 0.2$ meV.

Supercontinuum white laser

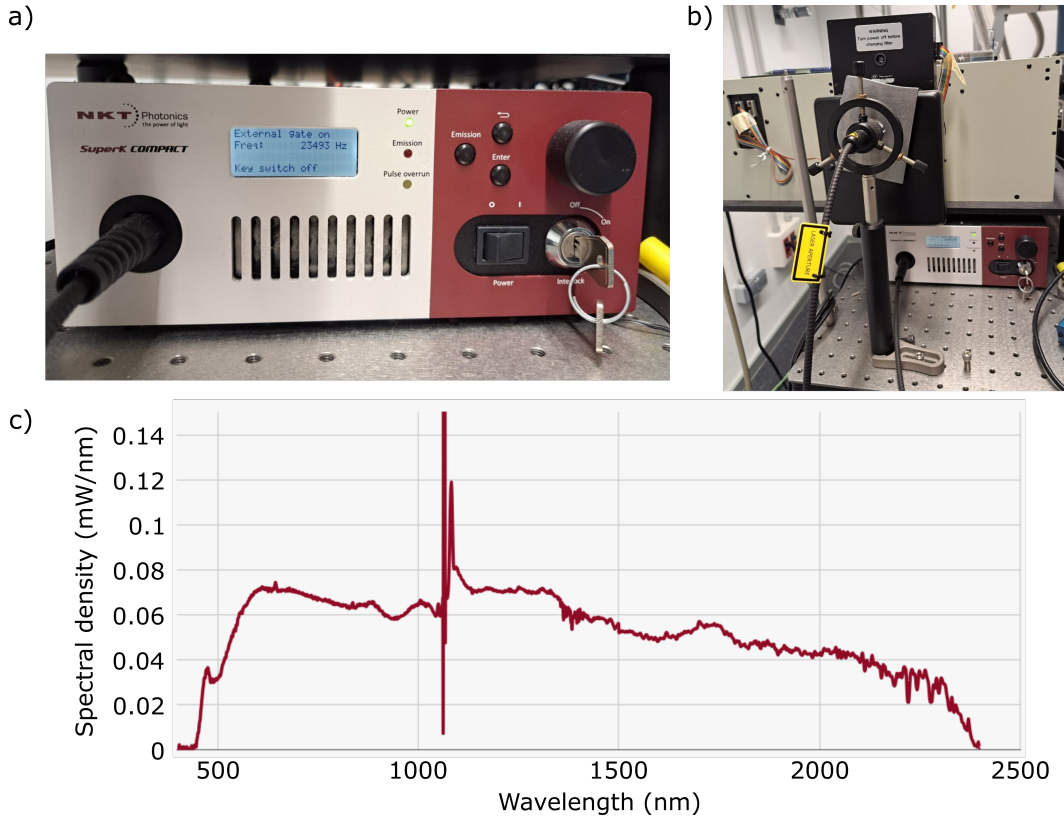


Fig. 3.6.2: a) Image of the SuperK supercontinuum white laser b) Optical fiber with a collimator placed inside the monochromator. c) Spectral density of the laser as a function of the wavelength.

Our light source consists in a white laser from NKT photonics. The model is the SuperK Compact (figure 3.6.2 a)), a compact laser that emits a pulsed supercontinuum light. The laser emits a collimated beam of white light between wavelengths of 450 nm and 2400 nm. The beam is collimated using an optic fiber with a collimator incorporated

in the laser (figure 3.6.2 b)). For our experiments, we used the spectral range from 550 nm to 1060 nm, where the power density is roughly constant (figure 3.6.2 c)).

Monochromator

To select one wavelength of illumination from the white laser we use a monochromator. The model of the monochromator is the Oriel MS257 from Newport with a range of operation from 200 nm to 20 μm . Figure 3.6.3. shows an image of monochromator. In our case, we operate with the monochromator between 550 nm and 1060 nm. In this range the diffraction grating has 1200 lines/mm with a resolution of around 0.1 nm. Oriel MS257 monochromator is programmable and allows to do scans between different wavelengths with various step size, giving the possibility of obtaining the desire resolution.

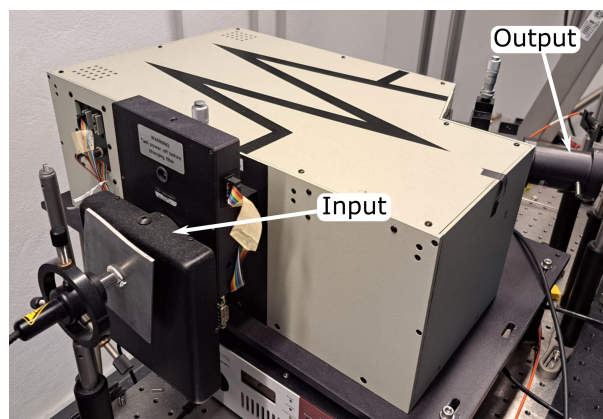


Fig. 3.6.3: Oriel MS257 monochromator with the collimator of the white laser as the light source.

Spectrometer

The wavelength of the output light from the monochromator is registered using an small spectrometer. The model is the bluewave from the company stellarnet (figure 3.6.4). The range of work of this spectrometer goes from 350 nm to 1100 nm. To extract the wavelength, we measure a spectrum and we identificate the maximum using a lorentztian fitting.



Fig. 3.6.4: Bluewave stellarnet spectrometer.

Mirrors and lenses

We collimate and direct the light to the optical window of the cryostat using dielectric mirrors and focal lenses. We use two mirrors mounted in three-axis stages and the focal

lenses are located on a one axis stage to change the spot size to reduce or increase the power density.

Rotator stage and waveplates



Fig. 3.6.5: Electrically controlled thorlabs rotator.

The light polarization can be tuned easily using polarizers, waveplates and a rotator stage. To perform measurements at different polarizations, a linear polarizer is placed before the rotator stage with a half or a quarter waveplate inside. Figure 3.6.5 shows the rotator stage and the programmable electrical controller.

Cryostat with optical access

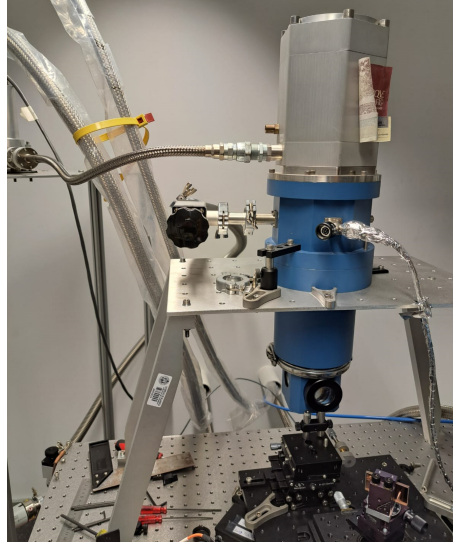


Fig. 3.6.6: Optistat AC-V12 in the optical table where the setup is mounted.

Finally, after all the optical components, we have a closed cycle optical cryostat. The model is the Optistat AC-V12 from oxford instruments (figure 3.6.6) complemented with a close cycle refrigerator connected to a compressor from Cryomech. The system is kept under vacuum at pressures of 10^{-6} mBar using a turbo-pump. The sample is placed into the cryostat using Dil-8 pin holder. The cryostat has four optical windows with a diameter of 12.7 mm. One of the four optical windows is located in line with the light beam and the sample to ensure a correct incidence of the light over the device. The operating temperature range of this system goes from 5 K - 325 K with an stability of ± 0.3 K allowing us to measure at low temperature for long periods of time. The temperature is

registered using a temperature controller that allows to monitorize and change the sample temperature using a calibrated heater.

3.6.1 Electrical configuration used in photocurrent measurements

In photocurrent measurements we use a 2-probe measurement configuration. Figure 3.6.7 shows the schematic of the electrical configuration used in photocurrent measurements. We measure in a short-circuit configuration applying in one contact a drain-source voltage and measuring the DC current (channel A of the sourcemeter). We ground other contact using a current/voltage preamplifier (SR570), that converts the current in voltage amplifying the signal. The output of the amplifier is connected to an oscilloscope, that allows us to observe directly the current flowing in the device, and to the lock-in amplifier, that is synchronized with the optical chopper and gives the value of the photocurrent suppressing the DC signal and possible sources of noise.

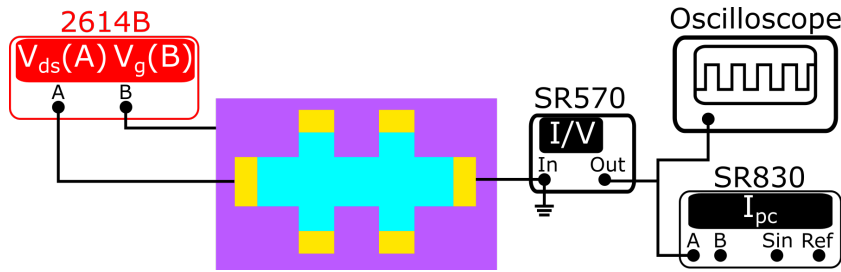


Fig. 3.6.7: Schematic of the electrical configuration in photocurrent measurements. Lock-in amplifiers corresponds with the SR830 equipments and the sourcemeter is the 2614B equipment. Current-voltage preamplifier is denoted by SR570.

Chapter 4

Phonon-mediated Quantum-Hall transport in Graphene

This chapter centers on the study of the room-temperature quantum hall effect (QHE) in high quality h-BN-Graphene-h-BN heterostructures at high magnetic fields (up to 30T).

The conventional observation of the QHE in two-dimensional electron systems typically occurs at liquid-helium temperatures ($T \approx 4\text{K}$), where lattice vibrations are significantly suppressed. At this temperatures bulk carrier scattering is usually dominated by disorder scattering. Nevertheless, graphene is a 2D system with huge mobilities ($\mu > 10000 \text{ cm}^2/\text{Vs}$) and a linear dispersion relation resulting in massless charge carriers. These properties provoke a huge landau-level separation ($\Delta_{LL} \approx 2000\text{K}$ at $B = 30\text{T}$), making graphene a perfect platform for the study of high temperature QHE. This have been studied in the previous literature but using devices of graphene on SiO_2 , where disorder dominates the scattering. However, prior our investigation, there was a lack of studies of high temperature quantum hall effect in h-BN/graphene/h-BN heterostructures, where residual disorder is almost suppressed.

In our measurements at room temperature and high magnetic fields up to 30T of graphene encapsulated in h-BN, we observe that the quantization in the resistivity is weak in comparison to previous quantum hall measurements in graphene supported on SiO_2 . The reduction of disorder via h-BN encapsulation leads to a decrease of the localized states suppressing the quantization. This suppression of the quantization in h-BN encapsulated graphene devices indicates clear differences between both generation of devices.

To extend the notion of the activation mechanisms of the quantization in the QHE, in this chapter we study the activation of the filling factor $\nu=2$. We demonstrate that in devices based on high quality graphene, the dissipation in the Quantum Hall phase is dominated by the electron-phonon scattering, revealing a novel quantum transport regime.

4.1 Introduction

Van der Waals heterostructures have recently revolutionized the study of condensed matter phenomena [114]. Particularly, the use of h-BN as an atomically flat encapsulating dielectric notably reduces the extrinsic disorder [115] in graphene devices, enabling the observation of transport regimes at zero-magnetic field dominated by electron-electron [116], electron-hole [117] or electron-phonon (e-ph) interactions [37]. Electron-phonon scattering dominates the transport at room-temperature in encapsulated graphene [118, 119]. In these devices are obtained carrier mobilities up to $10^5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at low carrier concentrations. Nowadays, the reach of mobilities near the acoustic-phonon-limit at zero-magnetic field is firmly established as a generic property of high-quality graphene devices.

As encapsulated devices shows a drastic reduction of the disorder, the access to new transport regimes seems to be straightforward. Nevertheless, in the experimental observation of the plateaus in the quantum hall effect (QHE), the disorder in the samples causes a broadening in the LLs and increases the presence of localized states with negligible contribution to the electronic transport. The presence of localized states is essential for the QHE, as explained in previous sections. The width of the plateaus in doping or magnetic field dependent measurements is directly correlated with the amount of localized states. Thus, in graphene/SiO₂, where the disorder increases the amount of localized states, the quantization in the QHE is easily observed and the activation mechanisms of this regime are dominated by the disorder. In stark contrast, in h-BN/graphene heterostructures the disorder is almost suppressed and could be a non-ideal platform for the observation of the QHE. However, other mechanisms can arise as the origin of localized states, for instance, e-ph scattering. Graphene supports the QHE until room temperature under strong magnetic fields, being the perfect candidate to study the role of the e-ph interaction as activation mechanism of the QHE.

In this study [120], dedicated to investigate the QHE at high temperatures by employing encapsulated graphene, the main objective is to explore distinct transport regime within the quantum Hall phase. We explore the fundamental question if the e-ph mechanism could also play a role in the quantum Hall regime at temperatures near room temperature, where the population of phonons is very remarkable. In this sense, the previous literature on high-temperature QHE effect in graphene exclusively includes experiments on SiO₂-supported devices [24, 121, 122], motivating such investigation. We fabricate four encapsulated samples, D1-3 and D5, using the dry transfer method from mechanical exfoliated flakes of graphene and h-BN, identified using optical contrast and characterized by raman spectroscopy following the procedures explained in the chapter 3. Sample D4 was made in the Aachen university using CVD graphene growth on Cu foil and directly transferred using h-BN via dry transfer pick-up after a controlled oxidation of the Cu substrate [123]. High-magnetic field magnetotransport measurements were performed in the facilities of the HFML in Radboud University of Nijmegen, while measurements below 10

T were performed in the Teslatron of the University of Salamanca. All the measurements were performed using standard lock-in amplifier technique at low frequency (13Hz) under constant current of 12.5 nA (D1-3 and D5), as explained in section 3.5.3, and constant voltage of $300\mu\text{V}$ (D4). Carrier density is controlled applying a gate voltage through the Si/SiO₂ substrate.

4.2 Zero-magnetic field transport measurements

In this section, we study the zero-magnetic field electronic transport in our encapsulated graphene devices to give a general overview of the transport characteristics of graphene and to characterize the dominant mechanisms in our graphene devices. Band structure of graphene gives a characteristic resistivity dependence on the carrier density, commonly known as Dirac-peak. The relation between the gate voltage and carrier density is obtained via geometric capacitance of a plane parallel capacitor using the formulas

$$C = \frac{\epsilon_r \epsilon_0}{d} \quad (4.2.1)$$

$$C_{ox} = \frac{(C_{SiO_2} \cdot C_{hBN})}{(C_{SiO_2} + C_{hBN})} \quad (4.2.2)$$

$$n = C_{ox} \frac{V_g}{e} \quad (4.2.3)$$

being d , the thickness of the dielectric, $\epsilon_r \epsilon_0$ the permeability of the dielectric.

Figure 4.2.1 a) depicts schematically the measurement configuration in the device D1. As explained in chapter 3, a constant current is injected through the device while longitudinal and transversal voltages are measured in a 4-probe configuration. Panel b) shows the dependence of the resistivity as a function of the gate voltage (carrier density) at various temperatures. Arrows in the measurement highlight the different positions of the Fermi energy represented in the inset.

As it is possible to observe, for high carrier densities the resistivity drops to values around 200Ω , while for voltages near 0V the resistivity rises to $2.5 \text{ k}\Omega$ at $T = 125 \text{ K}$. The increase of the resistivity corresponds with the reduction of carriers in the device reaching its maximum when the fermi energy is located in the charge neutrality point (CNP), where the density of states vanishes.

Thermal energy influences graphene resistivity, revealing two distinct trends with temperature. Figure 4.2.1 c) and d) shows the resistivity dependence on temperature at different electron (panel c)) and hole (panel d)) densities. On the one hand, at low carrier

densities ($n < 9 \times 10^{10} \text{ cm}^{-2}$), resistivity increases as temperature decreases, indicative of clear semiconductor behavior. On the other hand, at high carrier densities ($n > 9 \times 10^{10} \text{ cm}^{-2}$), resistivity increases with temperature, demonstrating a metallic behavior. Moreover, for high carrier densities, the resistivity-temperature relationship is linear ($\rho_{xx} \propto T$), being this behaviour consistent for all devices, suggesting high mobility graphene where the primary scattering mechanism is e-ph interaction [124].

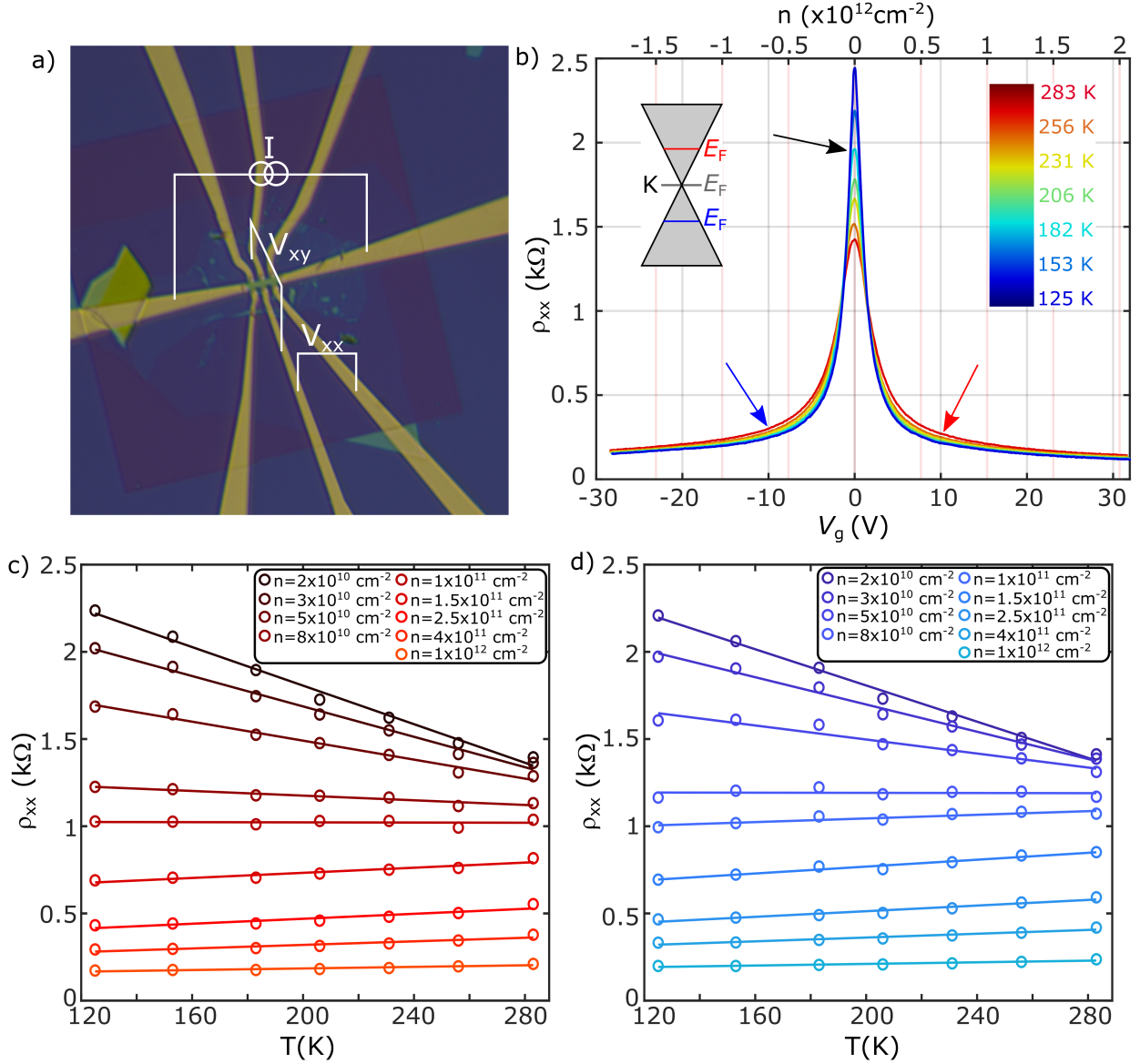


Fig. 4.2.1: Resistivity as a function of the gate voltage at zero magnetic field in high quality graphene. a) Optical microscopy image of hBN-Gr-hBN hall bar. Measurement configuration is marked with white lines. b) Resistivity dependence of the device as function of the gate voltage and the carrier density measured at different temperatures. The inset depicts the band structure of graphene around the K valleys. Different possible positions of E_F that corresponds with V_g pointed with arrows. c) Resistivity temperature dependence for different electrons density. d) Resistivity temperature dependence for different holes density.

Figure 4.2.2 shows zero-magnetic field resistivity for devices D1-3 as function of the temperature, measured in relevant ranges of temperature and carrier density for the study ($T = 160\text{K}-300\text{K}$, $n=1 \times 10^{12} \text{ cm}^{-2}$ (panel a)) and $n=5 \times 10^{11} \text{ cm}^{-2}$ (panel b)). Additionally, in panel a) we include a reference sample from ref. [37]. All samples exhibit a clear linear increase of the resistivity with the temperature, typically attributed to carrier scattering with thermally excited phonons. Linear fits to the data yield slopes within $0.3 \text{ } \Omega/\text{K}$ and $0.48 \text{ } \Omega/\text{K}$. For $n = 5 \times 10^{11} \text{ cm}^{-2}$, values range between $0.5 \text{ } \Omega/\text{K}$ and $0.7 \text{ } \Omega/\text{K}$. Device D3 closely approximates to reference data from ref. [37], suggesting similar sample quality and dominant e-ph scattering. The resistivity of devices D1 and D2 exhibits an offset associated with residual disorder scattering contributing to the e-ph mechanism.

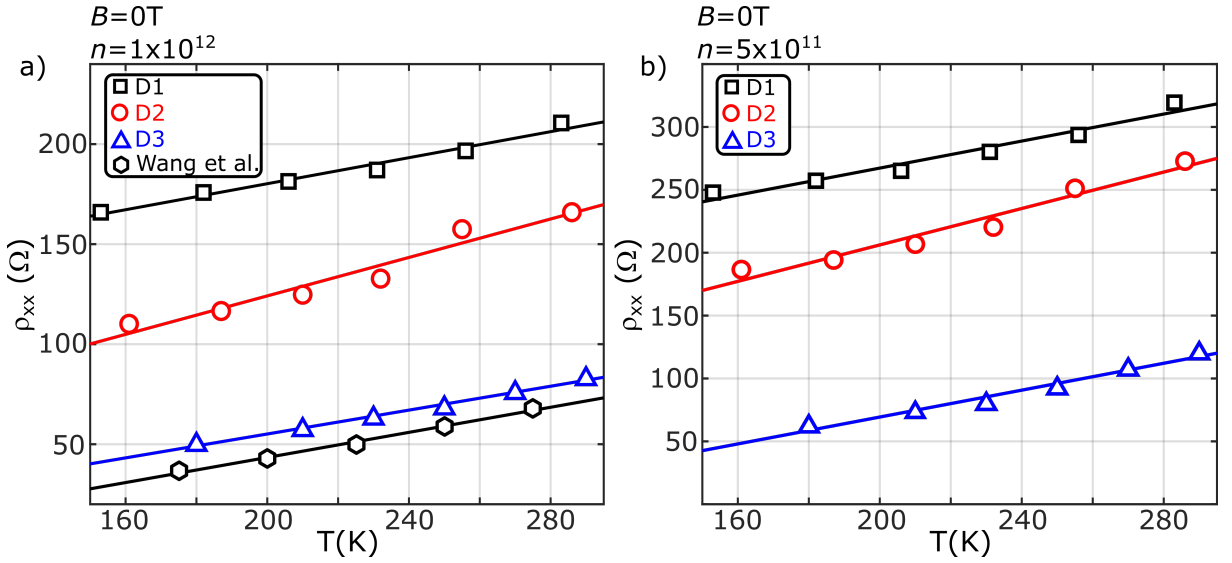


Fig. 4.2.2: Resistivity of samples D1-3 (open symbols), as a function of temperature, measured at $B = 0 \text{ T}$ and $n = 1 \times 10^{12} \text{ cm}^{-2}$ (panel a)) and $n = 5 \times 10^{11} \text{ cm}^{-2}$ (panel b)). Reference data from ref. [37] at the same carrier density are shown as open black hexagons. The continuous lines are linear fits to the data.

Residual disorder is the source of scattering that makes the difference between our devices. The residual disorder in h-BN encapsulated graphene devices has been related with the presence of random strain fluctuations [125]. These fluctuations generate a long-range disorder potential that has been identified as the main source of residual disorder. To identify the influence of the long-range disorder potential and classify the quality of our devices, we calculate the mobility μ and the width of the resistivity peak around the charge neutrality point, n^* . n^* is also known as the carrier density fluctuations and quantify the potential random strain fluctuations in graphene devices.

To obtain the mobility we use two methods, the known drude mobility $\mu = 1/n\rho_{xx}e$ to compute the mobility as function of the carrier density, and the field effect formula for graphene devices, that gives a general mobility for the devices by fitting the resistivity peak to

$$\rho_{xx} = \rho_c + \frac{1}{e\mu\sqrt{n_0^2 + n^2}} \quad (4.2.4)$$

where ρ_c is the contact resistivity, μ the mobility and n_0 the residual doping [126]. Figure 4.2.3 a) shows the fitting to equation 4.2.4 of the resistivity peak measured at 230K in D1 to obtaining a mobility of roughly $6 \times 10^4 \text{ cm}^2/\text{Vs}$.

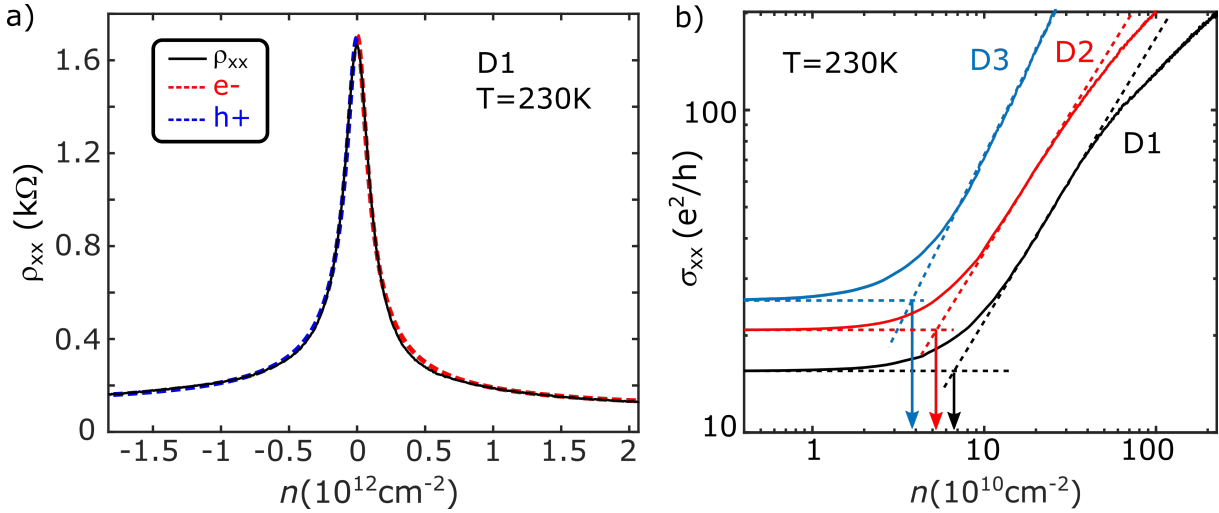


Fig. 4.2.3: Calculation of mobility and n^* . a) Fitting of the resistivity using the field effect formula of D1 at 230K for the electrons side (red dashed line) and holes side (blue dashed line). b) Log-Log plot of the longitudinal conductivity of sample D1 and D3 as a function of the carrier density, exemplifying the extraction of n^* (black and blue arrows).

Figure 4.2.3 b) illustrates estimation of n^* in D1 and D3 through a plot of conductivity, σ_{xx} versus carrier concentration n in a double-logarithmic scale. The n^* value is extrapolated from the intersection between the linear behaviour and the constant value of $\log(\sigma_{xx})$ at low density.

Mobility μ is related with elastic scattering times, while n^* quantifies the potential fluctuations suffered by charge carriers. In previous literature [125] have been demonstrated the linear dependence between $1/\mu$ and n^* for graphene devices. Using this relation between mobilities and carrier density fluctuations we can classify in a proper way the quality of our samples establishing the influence of long-range disorder potentials.

In figure 4.2.4, we present the key transport characteristics previously mentioned of our devices at high temperatures. Figure 4.2.4 a) illustrates the room temperature mobility of D1-3, calculated using the Drude model, plotted against the carrier density, n . All mobility curves consistently surpass typical values for SiO_2 -supported graphene (grey shaded area) across the entire range of n . Notably, sample D3 exhibits a mobility comparable to the data of ref [37] (dash-dotted line), reaching the standard fingerprint of phonon-limited room temperature mobility at zero magnetic field.

It is worth noting that while Wang et al. utilized a 15 μm -wide van der Pauw device, e-ph scattering imposes an approximate 1 μm upper limit to the electronic mean free path at $B = 0\text{T}$ and room temperature. Thus, achieving the zero-magnetic field e-ph limit is feasible with narrow Hall bars, while their channel width exceeds 1 μm (ranging from 1.5 μm to 2.3 μm in our devices).

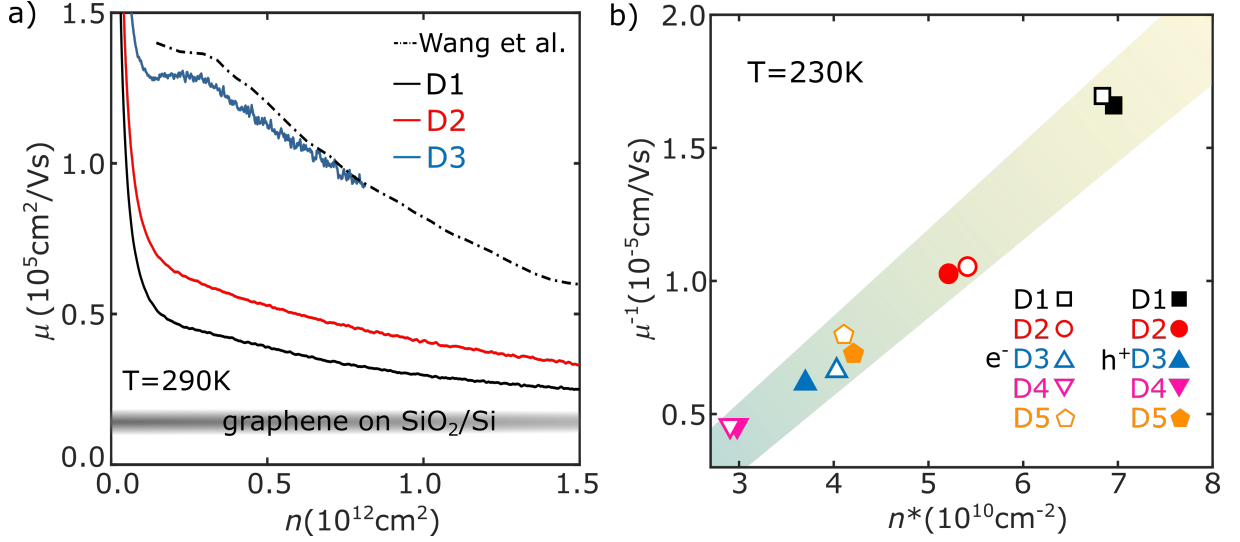


Fig. 4.2.4: Drude mobility and residual disorder at zero magnetic field. a) RT carrier mobility (calculated according to the Drude model) as a function of the carrier concentration, for D1-3. The reference dash-dotted line are data from ref[37], indicating a carrier mobility limited by electron acoustic phonon scattering. The grey-shaded area shows the typical mobility for SiO₂-supported graphene devices, $1\text{--}2 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. b) Inverse of the high temperature (230 K) field-effect mobility as a function of charge inhomogeneity n^* , for D1-5. The shaded area covers a linear fit to the data, $\pm$ one standard error on the best-fit intercept and slope.

Figure 4.2.4 b) shows the correlation between the carrier mobility (calculated using the field-effect formula) and charge inhomogeneity in the CNP region, estimated as the n^* parameter. This analysis considers data at $T = 230 \text{ K}$, where clear thermal activation is observed in the high temperature quantum Hall regime. n^* values, exceeding the intrinsic CNP thermal broadening ($\approx 2.6 \times 10^{10} \text{ cm}^{-2}$ at 230K), quantify residual disorder, which in our devices, remains significantly below typical observations for graphene on SiO₂ (n^* in the few 10^{11} cm^{-2} range). Furthermore, as previously discussed, the linear $\mu^{-1}(n^*)$ dependence (shaded area in figure 4.2.4 b)) indicates that the main scattering sources corresponds with long-range potentials [125, 127], attributed to random strain fluctuations. This scattering is inherent in graphene on substrates [128]. Therefore, we can conclude that the available devices cover a low-disorder range unexplored in previous high temperature QHE experiments and exhibit a well-defined disorder type, with increasing impact along this sequence D4-D3-D5-D2-D1, being D3 and D5 similar between them.

4.3 Activation of the Quantum Hall-Effect in Graphene

As mentioned in the introduction chapter, QHE manifests when the fermi energy lies on the localized states between two LLs (see Fig. 2.1.4). LLs in graphene are separated by Δ_{LL} , corresponding with equation 2.2.3. Graphene shows a huge energy separation between the first LLs $N = 0$ and $N = 1$ in comparison with conventional 2D systems. Between this Landau levels is located the filling factor $\nu = 2$. This filling factor is accesible in graphene devices at room temperature in graphene devices [24, 122] although the high thermal energy.

Thermal energy, $k_B T$, and Δ_{LL} relation governs the fundamental characteristics of the electrical transport in the QH regime. When $k_B T \ll \Delta_{LL}$, no bulk conduction is present in the 2D device, while the chiral edge states conducts the current ballistically vanishing the longitudinal resistivity. As the temperature increases, $k_B T \approx \Delta_{LL}$, thermal excitation of charge carriers in the extended LLs, restores the bulk conduction through the device, activating different scattering mechanisms and showing non-zero longitudinal conductivity in the LLs according to

$$\sigma_{xx} = \sigma_0 e^{-\Delta_{LL}/2k_B T} \quad (4.3.1)$$

This equation is largely employed to estimate the Δ_{LL} using T -dependent measurements of the longitudinal conductivity minimum in the plateau (this method may underestimate Δ_{LL} because of the disorder-induced broadening of the LLs [129]). It is important to notice that the longitudinal resistivity follows a similar behaviour because $\sigma_{xy} \gg \sigma_{xx}^2$ around $\nu=2$.

$$\rho_{xx} = \frac{\sigma_{xx}}{\sigma_{xx}^2 + \sigma_{xy}^2} \approx \frac{\sigma_{xx}}{\sigma_{xy}^2} = \rho_0 e^{-\Delta_{LL}/2k_B T} \quad (4.3.2)$$

being $\rho_0 = \sigma_0 / \sigma_{xy}^2$.

Figure 4.3.1 explains different dissipation regimes in the quantum Hall phase. Panel a) and b) depict the schematic of the transport in the QH regime in conventional systems such as 2DESs in semiconductors. At low temperatures relative to the Δ_{LL} (panel a)), chiral edge states carry the electrical current, resulting in zero longitudinal resistance. At higher temperatures (panel b)), the resistivity becomes finite due to scattering of thermally-excited bulk states. Scattering via e-ph interaction in perpendicular magnetic fields needs lattice vibrations with a wave-vector around the inverse of the magnetic length ($l_B = \sqrt{\hbar/eB}$) [130], introducing a new energy scale, $E_{ph} = \hbar v_s / l_B$, where v_s is the sound

velocity of graphene. In other 2DESs, the low Δ_{LL} cause the suppression the QHE at temperatures insufficient to ensure $k_B T \gg E_{ph}$ [131, 132, 133]. Therefore, the scattering of the bulk in this systems is dominated by disorder with a minimal contribution from lattice vibrations (yellow shading in panel b)). At RT ($k_B T \gg E_{ph}$), graphene exhibits both, the QHE (attributed to the large Δ_{LL}) and predominant e-ph scattering in high-mobility samples. This unique combination enables the presence of a distinct transport regime, characterized by phonon-mediated dissipation at high magnetic fields (dark cyan shading in panel c)).

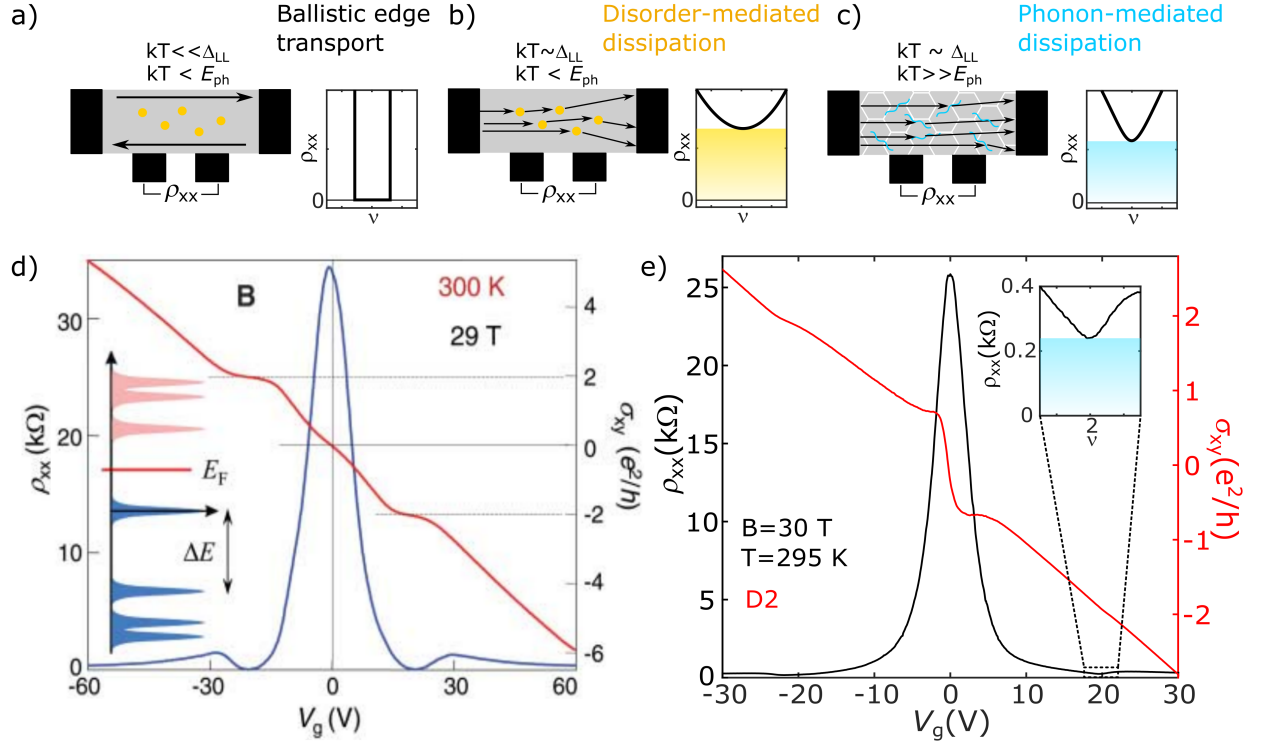


Fig. 4.3.1: Dissipation regimes in the quantum Hall phase. a) and b) Schematics of the temperature-dependent transport in conventional quantum Hall systems, like 2DESs in semiconductors, at thermal energies below (panel a) and comparable (panel b) to Δ_{LL} . c) RT high quality graphene QHE where e-ph scattering is predominant (dark cyan shading). d) Measured ρ_{xx} (blue) and σ_{xy} at magnetic field of 29 T and temperature of 300K as a function of the gate voltage in a graphene device supported on SiO₂. Figure from ref [24]. e) Measured ρ_{xx} (black) and σ_{xy} (red) dependence on back-gate voltage in D2 at a magnetic field of 30 T and temperature of 295K. The inset zooms in on ρ_{xx} near the filling factor $\nu=2$, with the dark cyan shading indicating the finite value of the resistivity minimum in this specific regime.

Panels d) and e) illustrate measurements of the QHE at room temperature in graphene/SiO₂ [24] and encapsulated graphene (device D2) respectively. Measured ρ_{xx} (blue and black lines) and σ_{xy} (red lines) at room temperature and $B \approx 30$ T evidence the presence of the filling factor 2 around $V_g \approx \pm 20$ V showing minima in ρ_{xx} (inset of panel e)) and slope changes in the hall conductivity (σ_{xy}). Significantly, the robustness of room temperature QHE signatures exhibits a marked contrast between high-mobility graphene, D2, and

samples supported by SiO₂. The QHE is stronger in disorder dominated graphene/SiO₂ due to the relation between the QHE and the presence of localized states between the Landau levels. Another difference appears between the samples. For high mobility graphene (panel e)) the shelves-like features around the charge neutrality point arise from the onset of electron-hole coexistence in the highly degenerate LL N=0 [134]. These differences between the two generation of devices indicate that the transport in the QH regime may be governed by distinct scattering processes in the two type of devices.

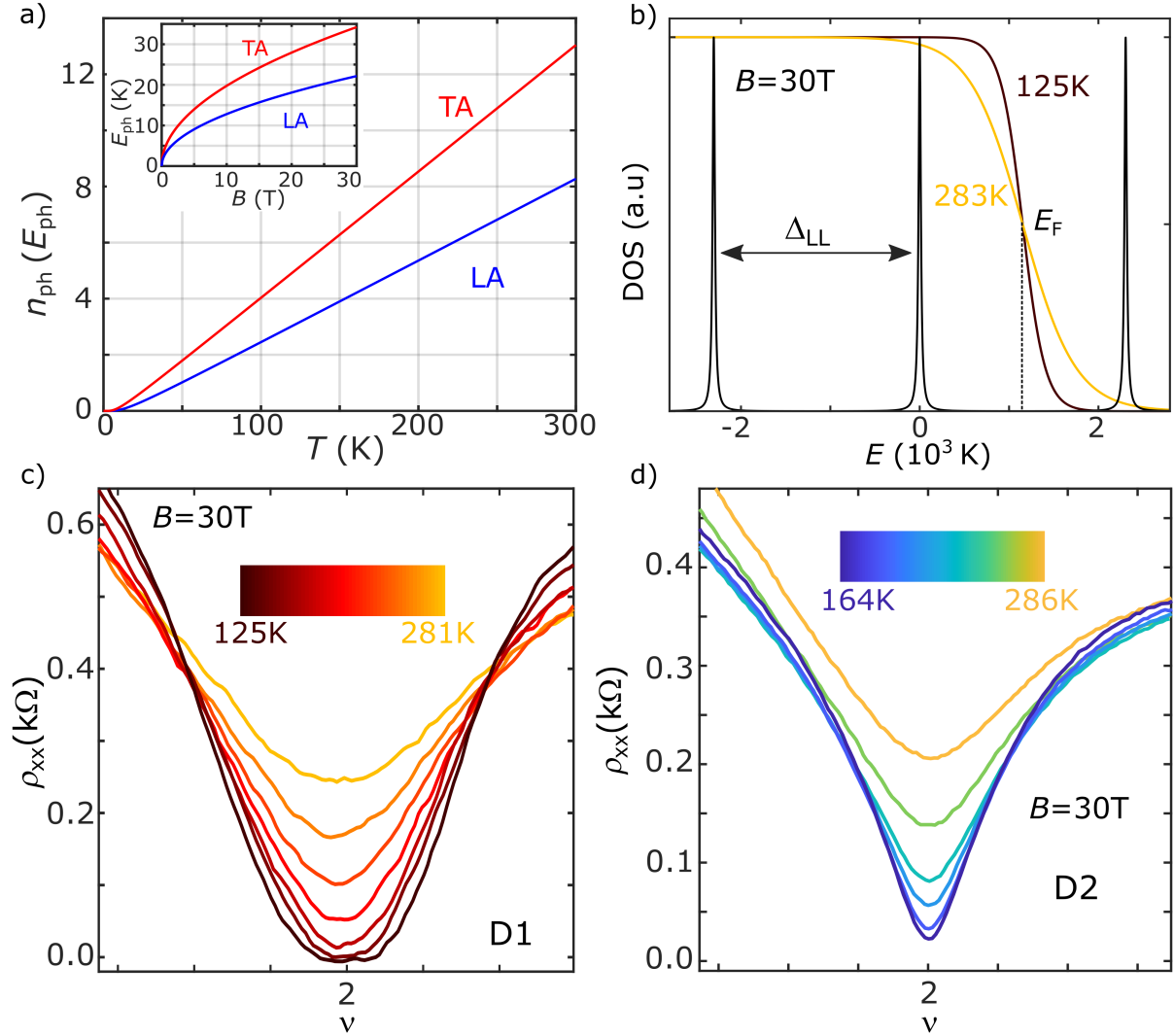


Fig. 4.3.2: Activation of the filling factor $\nu=2$ via temperature controlling. a) Population of longitudinal (LA) and transversal (TA) acoustic phonons in graphene with energy E_{ph} at $B = 30\text{T}$, calculated according to the bose-einstein distribution. Inset: magnetic field dependence of E_{ph} for sound velocities of $v_s=2.1\times 10^4$ m/s and $v_s=1.36\times 10^4$ m/s for LA and TA respectively [135]. b) Graphene density of states (DOS) depicted as a function of energy at $B=30$ T, (with a realistic LL broadening of 15 K). On top of the DOS is the Fermi-Dirac distribution, with the Fermi energy (E_F) situated in the middle between the N=0 and N=1 LLs at two different temperatures. c) and d) Temperature activation of the longitudinal resistivity around filling factor $\nu=2$ at $B = 30\text{T}$ for D1 and D2 respectively.

In the forthcoming analysis, our focus will be on identifying the activation mechanism of the QHE in high-quality graphene, where e-ph interaction is demonstrated to be dominant, as outlined in the previous section. The investigation will primarily center on the magnitude of ρ_{xx} and its variation with temperature. We use the sample temperature as an experimental tool to control the excitation of phonons and electrons in the bulk-extended states to study the activation of the QHE using equation 4.3.2. Figure 4.3.2 a) shows the population dependence with T of longitudinal (LA) and transversal (TA) acoustic phonons with energy $E_{ph} = \hbar v_s/l_B$, calculated following the bose-einstein distribution [135]. As previously mentioned, this phonons contribute to the e-ph scattering in the quantum hall regime at $B = 30$ T. Given the high energy range of optical phonons (1800–2300 K), which leads to small phonon occupation numbers, our consideration is restricted to acoustic phonons [130]. Inset shows the variation of E_{ph} as a function of the magnetic field. Figure 4.3.2 b) depicts the effect of increasing T on the landau quantized electrons in graphene at $B = 30$ T due to the broadening of the Fermi-Dirac distribution around E_F (controlled by V_g). In the figure LLs are depicted with a realistic broadening of 15K. In the case of $T=283$ K it is possible to observe that electrons can promote from the level $N=0$ to $N=1$ causing a contribution of the electrons in the extended states to the longitudinal resistivity in $\nu=2$. As the temperature decreases ($T=125$ K), the excitation of electrons between LLs $N = 0$ and $N = 1$ reduces, leading to a reduction in longitudinal resistivity until it reaches zero, as shown in figures 4.3.2 c) and d) for devices D1 and D2 at 30 T.

By extracting the minima of ρ_{xx} in $\nu=2$, we study the activated longitudinal resistivity of the QHE using our encapsulated devices. Our analysis includes a comparison with the study conducted by Giesbers et al.[122], which explored the activation of the QHE in a graphene sample on SiO_2 .

4.3.1 Arrhenius plots

Firstly, we focus in the activation of σ_{xx} , which follows $1/T$ -exponential trend (equation 4.3.2). Therefore, arrhenius type plots allow us to extract information regarding the activation gaps of our samples and the parameter σ_0 . Value of σ_0 has been predicted in the previous literature for short and long-range disorder scattering obtaining e^2/h and $2e^2/h$ respectively [136, 137]. In the arrhenius fittings, the slope provides the value of Δ_{LL} , while the y-intercept corresponds to σ_0 . Figure 4.3.3 a) to d) shows the arrhenius plots of the minima in the longitudinal conductivity, $\sigma_{xx}(\nu = 2)$, for devices D1-3 and Gr/ SiO_2 device from Giesbers et al. respectively. To fit the data we use a linear fitting with the slope fixed at $\Delta_{LL}/2$. Figure 4.3.3 e) depicts the values extracted of Δ_{LL} from our samples extracted from arrhenius fits leaving the slope as a free parameter, being compatible with the theoretical value of Δ_{LL} , suggesting a residual broadening in LLs in our samples for high magnetic fields. Figure 4.3.3 f) shows the value of σ_0 from the arrhenius plots in panels a)-d) revealing a clear contrast in the behavior between disordered and clean samples. While data from ref [122] approximate the long-range disorder limit ($2e^2/h$

multiplied by the factor 4, accounting for spin and valley degeneracy) [137], our samples exhibit significantly lower values indicating clear differences between both types of devices.

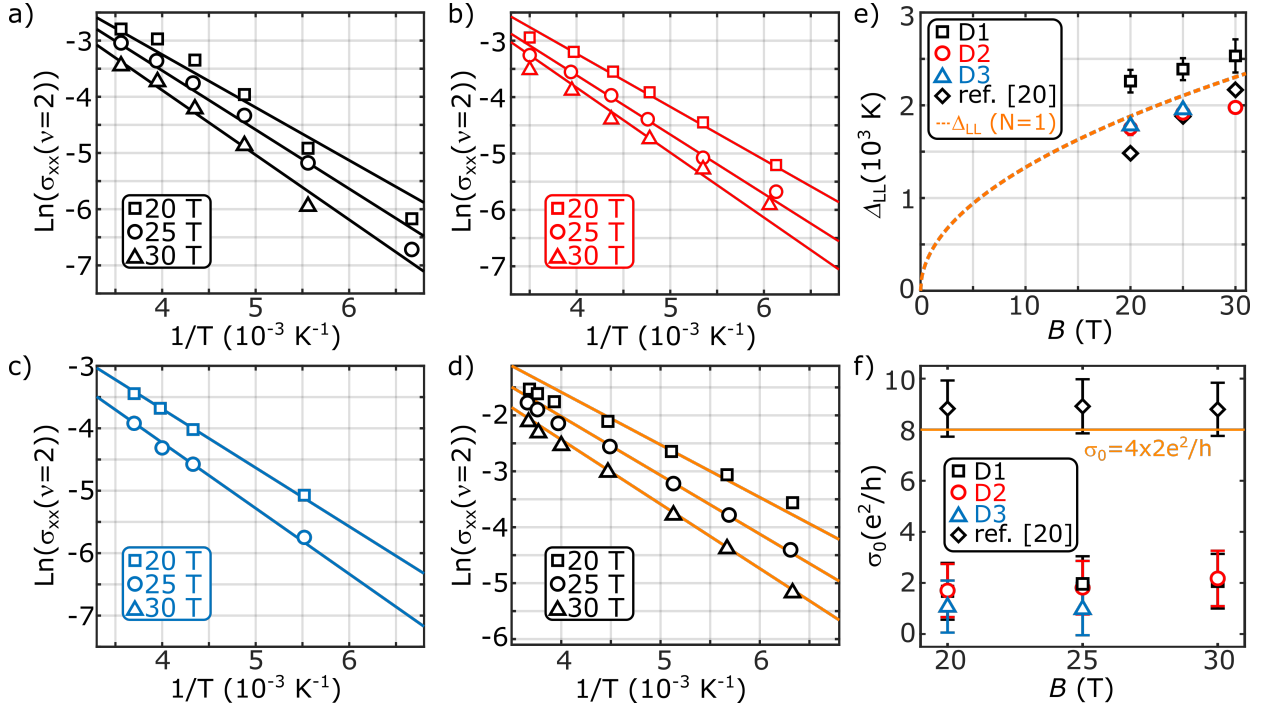


Fig. 4.3.3: Arrhenius plots of the activated conductivity. a) Arrhenius fits $\sigma_{xx} = \sigma_0 e^{-\Delta_{LL}/2k_B T}$ for sample D1 at different magnetic fields. The activation energy is maintained at half of the bare Δ_{LL} . b) Arrhenius fits for sample D2. c) Arrhenius fits for sample D3. d) Arrhenius fits on data from Giesbers et al. e) Δ_{LL} extracted from arrhenius fits leaving the slope as a free parameter in comparison with the theoretical value (orange dashed line) f) Conductivity pre-factors σ_0 from the fits in panels a-d.

4.3.2 Phonon mediated activation of the Quantum Hall Effect

Arrhenius-type fits to the minima of the conductivity, $\sigma_{xx}(\nu = 2)$, highlight the contrasting magnitudes of the pre-factor σ_0 for the two different types of graphene devices, suggesting a different activation mechanism of the QHE in clean graphene from the disorder-mediated. To confirm the different nature of the activation mechanism of the QHE we continue with the analysis of the temperature dependence of ρ_{xx} .

Figure 4.3.4 presents a complete overview of the temperature dependence of T-activated resistivity in the filling factor 2, $\rho_{xx}(\nu = 2)$ for samples D1-4 at selected magnetic fields of 20 T (panel a)), 25 T (panel b)) and 30 T (panel c)). As the electronic structure of graphene exhibits particle-hole symmetry a similar behaviour is observed for $\nu = \pm 2$ (panel d)). In addition to our dataset (D1-4), for comparison of our samples with graphene on SiO_2 , we include $\rho_{xx}(\nu = 2)$ values from ref. [122] in the graphs. The experimental data are plotted along with two theoretical models for scattering in the quantum hall regime (plotted with continuous lines). In both cases, we use an activation energy equal

to $\Delta_{LL}/2$, an assumption corroborated for high magnetic fields in ref. [122]. Furthermore, Arrhenius-type fits to the conductivity shown in figure 4.3.3, confirm the accuracy of the assumed gap size.

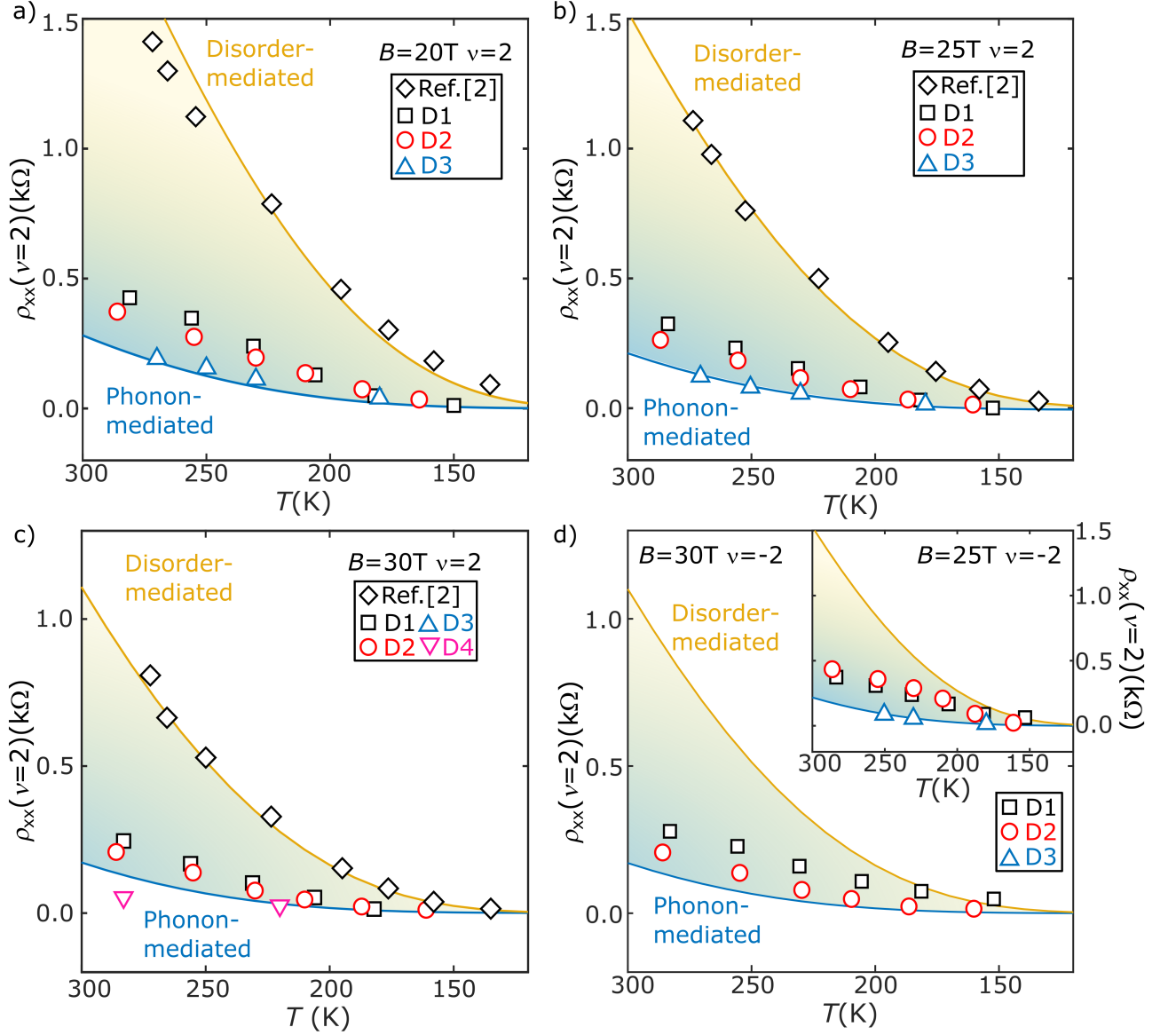


Fig. 4.3.4: Minimum of ρ_{xx} at $\nu=2$ for $B=20\text{ T}$ (panel a)), $B=25\text{ T}$ (panel b)) and $B=30\text{ T}$ (panel c)) and for $\nu=-2$ for $B=30\text{ T}$ and inset $B=25\text{ T}$ (panel d)) as a function of temperature, for the hBN-encapsulated devices. The reference data (black diamonds) are from [122]. The yellow and dark cyan continuous lines are theoretical calculations based on refs. [137, 130] respectively (the shading covers resistivity values within the two theoretical calculations).

The upper line (yellow) assumes an universal conductivity pre-factor correspondent with long-range disorder ($2e^2/h$) [137, 136], multiplied by a factor of 4 to account for the valley and spin degeneracy of graphene. The lower line (dark cyan) is extracted from the work of Alexeev et al. [130], who calculated the conductivity mediated by two-phonon scattering for graphene in the high temperature QH regime.

Here, two-phonon scattering within each Landau Level contributes with a conductivity prefactor $\sigma_0 = \sigma_N(T/300 \text{ K})\sqrt{B/10 \text{ T}}$, which depends on both temperature and magnetic field, in contrast to the constant pre-factor commonly assumed in QH studies. In the $\nu=2$ state, the predominant contribution to the σ_N terms comes from the $N = 0$ and $N = 1$ LL. The contribution to σ_{xx} of $N=0$ is $0.65e^2/h$, one order of magnitude larger than the value coming from $N = 1$, $0.06e^2/h$. Remarkably, the resulting activated behaviour, without any free parameter, aligns well with our devices, while the reference data from graphene on SiO_2 follow the long-range disorder limit. The qualitative agreement between theoretical calculations and experimental data, together with the contrasting behaviour to previous reports, suggests that graphene/hBN heterostructures support electron-phonon dominated transport in the high temperature QH regime.

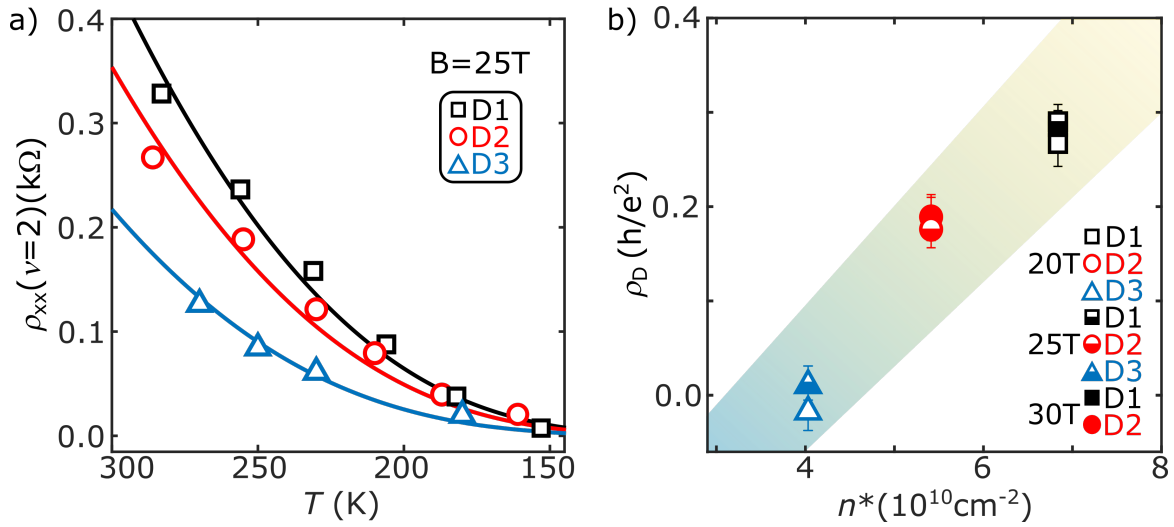


Fig. 4.3.5: Sample-dependent disorder contribution to the activated resistivity. a) Fits to the minimum resistivity as a function of temperature (continuous lines), using the generalized formula including both e-ph and disorder contributions, at $B=25 \text{ T}$. b) Correlation between the T-independent pre-factor to the activated resistivity and $n^*(230 \text{ K})$ for devices D1-3. The shaded area is defined as in Fig. 4.2.4. The error bars correspond to $\pm$ one standard error from the fits shown in the panel a).

In spite of the presence of long-range potentials due to random strain fluctuations (figure 4.2.4), our data clearly show that the e-ph pre-factor goes beyond simply add up to the standard long-range disorder term. To clarify this observation, we systematically analyze the deviation from the phonon-mediated limit in D1-3 (only two high-temperature curves are available for D4 due to experimental limitations). We take a quantitative approach by fitting the data using a generalized relation that incorporates the theoretical e-ph dependence from ref. [130] and introduces an activation part with a constant pre-factor, ρ_D , to account for the impact of residual disorder. Figure 4.3.5 shows the fittings of $\rho_{xx}(\nu=2)$ using the model proposed. Notably, ρ_D is the only free parameter in these fits and allow us to reproduce correctly the experimental data of the T -activated resistivity using the theoretical model proposed.

In figure 4.3.5 b), we depict the extracted values of ρ_D for D1-3 at different magnetic fields, plotted against the broadening of the CNP, n^* (averaged between the electron and hole sides). The observed linear behavior of ρ_D respect n^* , indicated by the shaded area, suggests that random strain fluctuations are responsible for ρ_{xx} surpassing the e-ph limit in the high-temperature QH regime. Notably, the device exhibiting an exact e-ph type dependence (D3, $\rho_D \approx 0$) is also the one with a Drude mobility comparable to the zero-field e-ph limit [37].

4.3.3 Interplay of disorder and e-ph mechanisms

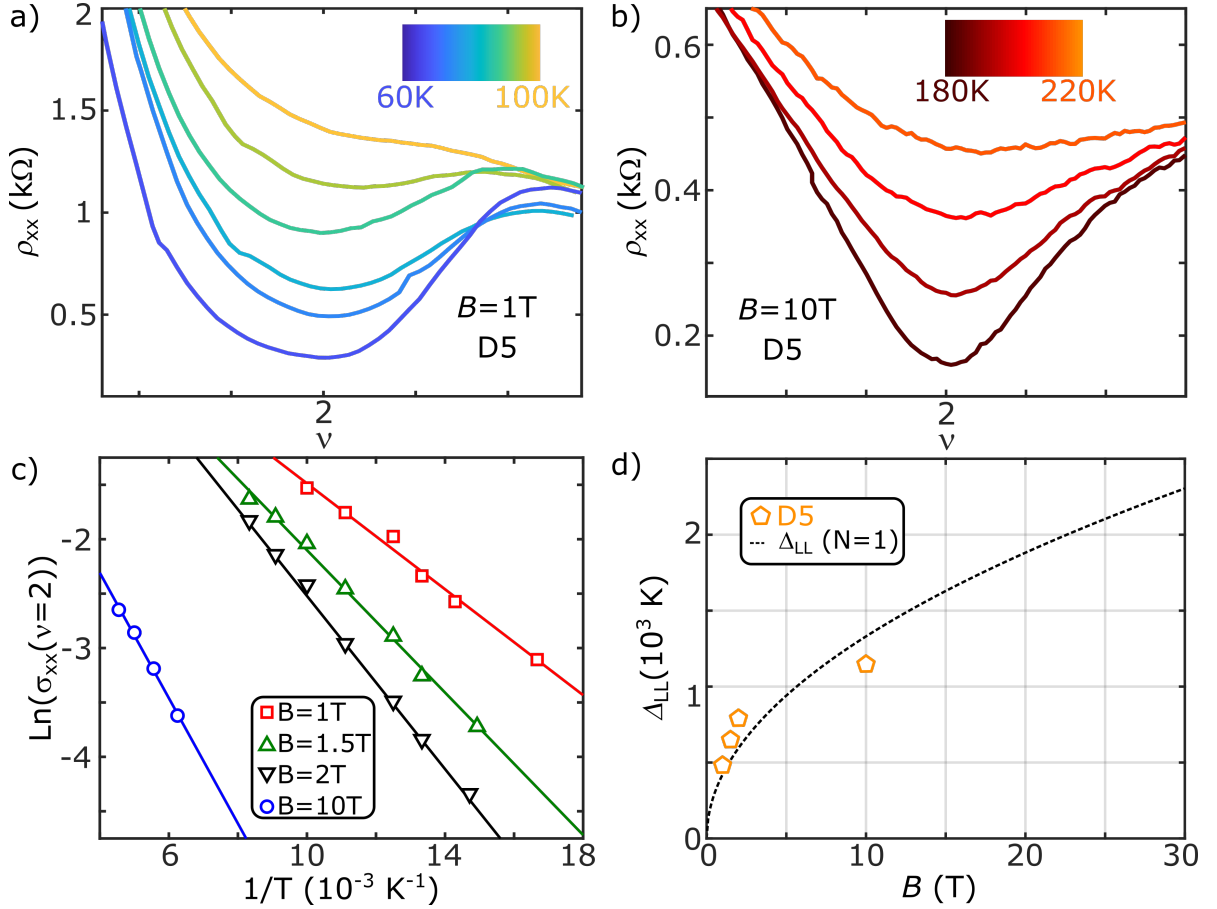


Fig. 4.3.6: T-activated longitudinal resistivity at low magnetic fields. a) and b) Temperature activation of the longitudinal resistivity around filling factor $\nu=2$ for D5 at $B = 1\text{T}$ and $B = 10\text{T}$ respectively. c) Arrhenius fits $\sigma_{xx} = \sigma_0 e^{-\Delta_{LL}/2k_B T}$ for sample D5 at different magnetic fields. d) Estimation of Δ_{LL} in comparison with the theoretical calculation.

To obtain a greater understanding of the interplay between the disorder and e-ph scattering in our clean devices, we use sample D5 to measure the QHE activation at lower magnetic fields (up to 10T in the low temperature laboratory in the University of Salamanca) and correspondingly, lower temperature. D5 transport characteristics are similar to D3 (at $T = 230\text{K}$, $n^* \approx 4.1 \times 10^{10} \text{ cm}^{-2}$ and $\mu \approx 1.3 \times 10^5 \text{ cm}^2/\text{Vs}$), suggesting it is representative of the phonon limit discussed previously.

We measure the T -activated resistivity in $\nu=2$ at selected magnetic fields of $B = 1\text{T}$, $B = 1.5\text{T}$, $B = 2\text{T}$ and $B = 10\text{T}$. We neglect to measure for $B < 1\text{T}$ to ensure the complete development of the QHE at $\nu=2$, as well as an activation gap matching $\Delta_{LL}/2$. Figure 4.3.6 a) and b) illustrate the activation of $\nu=2$ in device D5 at magnetic fields $B = 1\text{T}$ and $B = 10\text{T}$, respectively. This activation occurs over two distinct temperature ranges: between 60K and 100K for $B = 1\text{T}$, and between 180K and 220K for $B = 10\text{T}$. Panel c) displays the arrhenius plots of minima in the longitudinal conductivity $\sigma_{xx}(\nu=2)$ for D5 at magnetic fields of 1T, 1.5T, 2T and 10T. From the fitting we calculate the experimental values of Δ_{LL} . Panel d) depicts the values of Δ_{LL} obtained from the arrhenius and the theoretical value of Δ_{LL} in graphene as function of B . The experimental data demonstrate a good agreement with the theoretical values, even at low magnetic fields, indicating a minimal broadening of the LLs. Following the validation of Δ_{LL} , we proceed to analyze the T -activated longitudinal resistivity, $\rho_{xx}(\nu = 2)$.

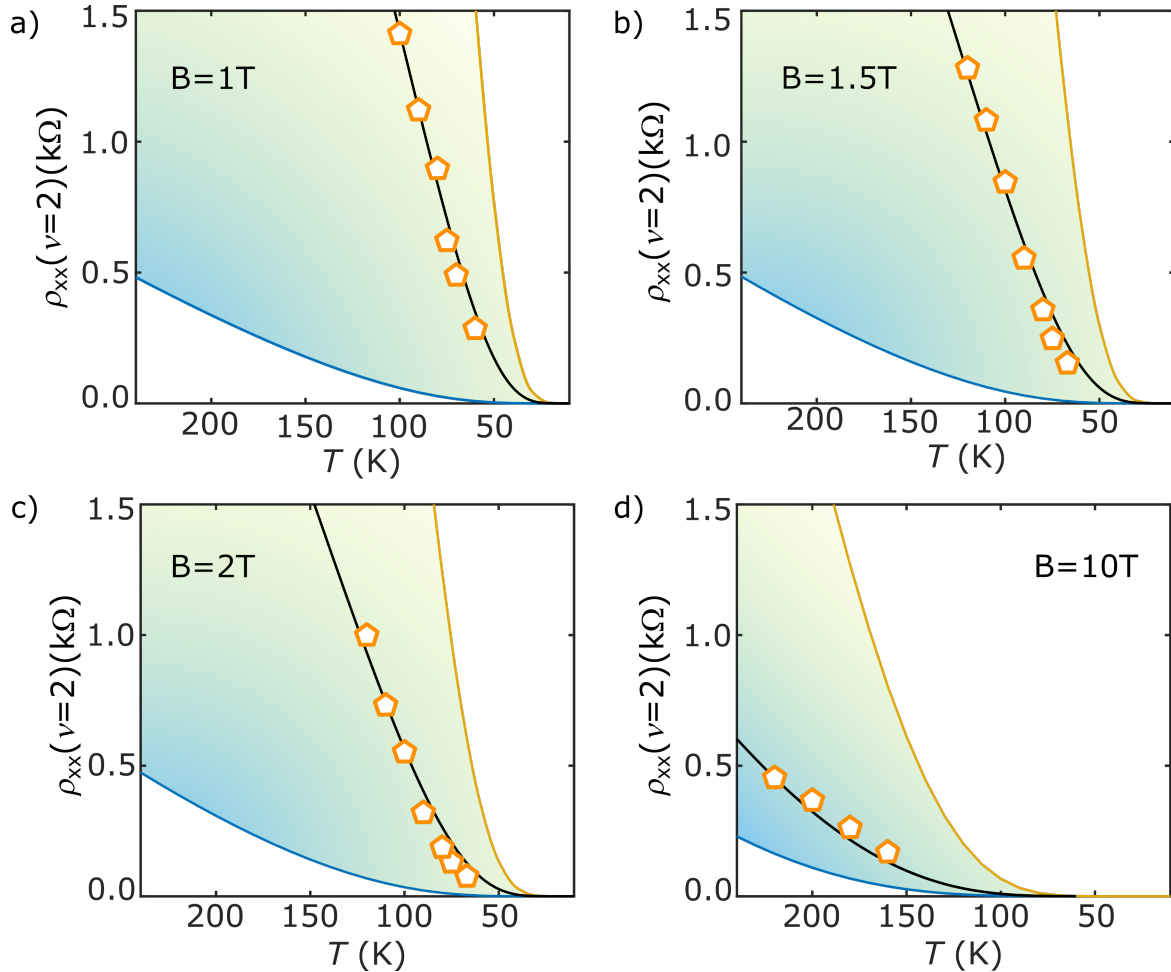


Fig. 4.3.7: T -dependent resistivity at low magnetic fields. a) to d) Activated resistivity at filling factor 2 (depicted as black diamonds) in sample D5 at low magnetic fields of $B = 1\text{T}$, $B = 1.5\text{T}$, $B = 2\text{T}$ and $B = 10\text{T}$. The data are compared to the e-ph (dark cyan line) and long-range disorder (yellow line) limits. Black lines in the plots represent the fits to activated resistivity to extract the parameter ρ_D

Figure 4.3.7 depicts the values of $\rho_{xx}(\nu = 2)$ (orange pentagons) at different temperatures for magnetic fields $B = 1\text{T}$ (panel a)), $B = 1.5\text{T}$ (panel b)), $B = 2\text{T}$ (panel c)) and $B = 10\text{T}$ (panel d)) in comparison with the e-ph (dark cyan) and long-range disorder (yellow line) models. Resistivity values measured for $B = 1\text{T}$ locate around $1.4\text{ k}\Omega$, while the e-ph scattering model predicts values of approximately $100\text{ }\Omega$, highlighting a clear deviation of the data from this model. This fact contrasts with the high-temperature and high-magnetic-field regime, where a negligible deviation from the e-ph limit is observed (figure 4.3.4). As we increase B , and subsequently T , $\rho_{xx}(\nu = 2)$ values drops approximating to the e-ph limit. To compute the deviation at various magnetic fields quantitatively we calculate the parameter ρ_D fitting the data using the procedure previously exposed (black lines).

Subsequently, in order to give a more comprehensive vision of the influence of disorder in clean samples, we compare the value of the ρ_D obtained at different magnetic fields. Figure 4.3.8 shows the ρ_D parameter extracted at different magnetic fields for samples D5 and D3, which have a similar quality. At $B = 10\text{T}$, ρ_D reduces approximately a factor 2 compared to $B = 1\text{T}$. At high magnetic fields beyond $B \geq 20\text{T}$, ρ_D vanishes. The corresponding temperature ranges used in the measurements are depicted in the inset. Throughout the experiments, temperature ranges are adjusted to the applied magnetic field, ensuring alignment with the increase of Δ_{LL} and maintaining comparable conditions of thermal activation for all collected data. In summary, our findings suggest that high-quality graphene devices can manifest both disorder and phonon-mediated contributions to dissipative conductivity in the QH regime. The disorder contribution tends to vanish with rising temperature (and magnetic field) and the e-ph contribution becomes dominant toward room temperature indicating a temperature-driven crossover between the two contributions.

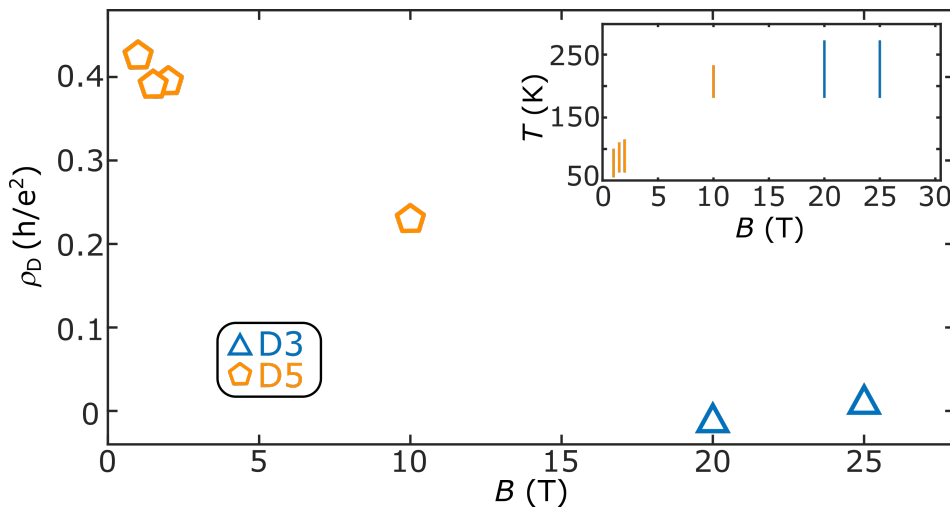


Fig. 4.3.8: Decay of the disorder contribution with temperature. Parameter ρ_D extracted for samples D3 and D5 at various magnetic fields. Inset: Temperature ranges used for the measurements at different magnetic fields.

4.4 Conclusions

Physical phenomena in graphene devices are largely influenced by defects, such as ripples. In graphene on SiO₂, the roughness of the substrate induces inhomogeneity leading to charge carrier density fluctuations in the vicinity of the charge neutrality point and a reduction of the mobility. Specifically, for graphene on SiO₂, the estimated amplitude of this induced inhomogeneity in charge-carrier density is around n^* at $3 \times 10^{11} \text{ cm}^{-2}$, giving samples where the electrical transport is completely dominated by long-range disorder potentials. The use of h-BN as atomically flat encapsulating dielectric suppresses intrinsic ripples increasing the mobility and reducing the charge carrier density fluctuations by an order of magnitude. The improvement of the properties of graphene causes that the electrical transport in these devices is dominated by e-ph scattering at high temperature ranges.

In this chapter, combining strong magnetic fields (up to 30T), high temperatures, and high quality devices of h-BN encapsulated graphene (reaching e-ph limited mobilities) we have presented experimental evidence of phonon-mediated quantum hall transport in graphene.

In section 4.2, we confirmed the prevalence of electron-phonon (e-ph) scattering over disorder, categorizing our samples based on the impact of long-range disorder induced by random-strain fluctuations. In section 4.3, we investigated the activation of the Quantum Hall Effect (QHE) at elevated temperatures, comparing our samples with graphene supported on SiO₂. We observed clear differences between both types of samples. These differences rely on the phonon-mediated activation of the QHE rather than disorder-mediated activation in h-BN encapsulated samples. By introducing a model that integrates both disorder and e-ph mechanisms, we quantified the influence of disorder in our samples using the parameter ρ_D . Furthermore, to better understand the interplay between these two contributions, we measured the activation of the QHE at low magnetic fields and thus, at low temperatures. Our analysis confirmed that in the absence of phonons, long-range disorder activation becomes dominant, suggesting a temperature-driven crossover between the two contributions and confirming the coexistence of disorder and phonon dominated transport regimes in the QH phase.

We can conclude that despite the well-known existence of room temperature QHE in graphene, our work demonstrates that mitigating disorder through van der Waals engineering yields new insights into the transport mechanisms underlying this phenomenon.

Chapter 5

Mechanisms of photocurrent. Fast response photogating in MoS₂

In the following chapters I present the main part of this dissertation that consists in the characterization of the optoelectronic properties of 2D transition metal dichalcogenides (2D-TMDs) phototransistors using photocurrent spectroscopy. To start, this chapter focuses in the study of the photocurrent generation mechanisms of these devices, in particular in a monolayer (1L) MoS₂ phototransistor. Photoresponse in these devices typically arises from a combination of two physical mechanisms: the photoconductive effect (PCE) and the photogating effect (PGE). In previous literature on 1L-MoS₂ phototransistors, PGE is normally attributed to charge trapping by polar molecules adsorbed to the semiconductor channel, resulting in a slow photoresponse with long characteristic times. Therefore, the photoresponse of 1L-MoS₂ phototransistors at high-frequency light modulation is usually assigned to PCE.

In this study, we investigate the photoresponse of a fully h-BN-encapsulated 1L-MoS₂ phototransistor. Contrary to previous understanding, we observe a rapidly responding PGE mechanism that becomes the dominant contribution to the photoresponse under high-frequency light modulation. Using a Hornbeck–Haynes model for the photocarrier dynamics, we fit the illumination power dependence of this PGE and estimate the energy level of the involved traps in the recombination process, obtaining energies compatibles with the presence of shallow traps in MoS₂ induced by the presence of sulfur vacancies.

5.1 Introduction

In 2D-TMDs devices, the photoresponse usually arises from two main mechanisms [89], the photoconductive effect (PCE) and the photogating effect (PGE). In order to properly introduce both effects, firstly we explain the typical behaviour of a transistor.

As mentioned in previous chapters, the devices studied using photocurrent spectroscopy are TMDs-based field-effect transistors with two electrical contacts, drain and source, and a gate contact in the Si/SiO₂ to apply a gate voltage, V_g . V_g controls Fermi energy level, E_F , of the semiconductor. The drain and source contacts allow to apply a drain-source voltage, V_{ds} and measure the current flowing through the semiconductor, I_{ds} .

Figure 5.1.1. summaries the typical operation of a TMDs-based transistor. Panel a) shows the band structure of the semiconducting-TMD with the valence and the conduction bands depicted as blue and red bands respectively. E_F is located in the conduction band, therefore, the semiconductor is doped with electrons (n-doped). Next, panel b) depicts the diagram of the semiconductor with two metallic contacts. The blue and red lines corresponds with the valence and the conduction bands the semiconductor and E_F is drawn as a dashed red line. In the diagram it is applied a voltage bias V_{ds} between the metallic contacts due to the different height between the electrodes. V_{ds} causes a small current flowing through the device I_{ds} . Panel c) shows the dependence of I_{ds} with V_g so called transfer curve. I_{ds} almost vanishes when E_F is located in the gap of the semiconductor. When V_g increases (decreases), E_F reaches the conduction (valence) band edge, the amount of free electrons (holes) increases causing a raise of I_{ds} . Usually, it is difficult to observe conduction in the electrons and in the holes sides in the same device due to dielectric breakdown of the gate.

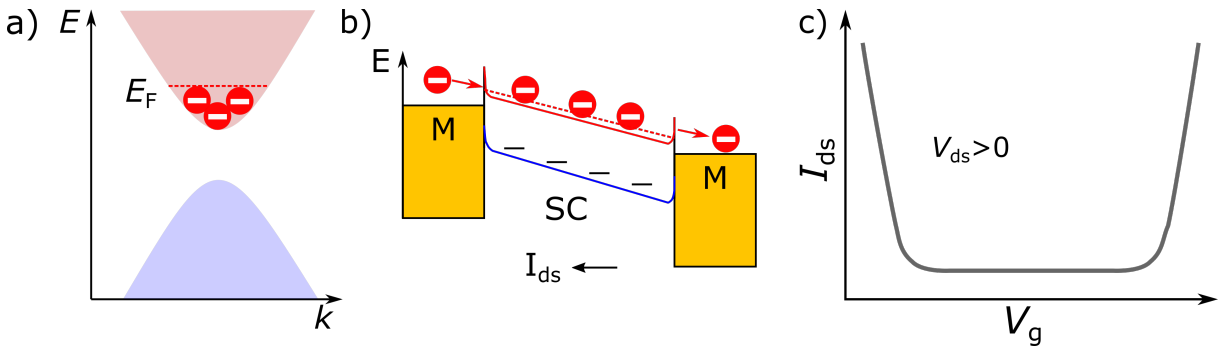


Fig. 5.1.1: Typical operation of a transistor based on 2D-TMDs. a) Band structure showing the conduction and the valence band (red and blue bands respectively) of a semiconductor with E_F in the conduction band. b) Diagram of the transistor with the metallic contacts and the semiconductor channel. A voltage bias is applied between the electrodes, V_{ds} and a current I_{ds} flows through the device. c) Schematic of a transfer curve of a transistor showing the dependence of I_{ds} with V_g .

Next, if the device is illuminated the absorption of photons generate photo-excited carriers. These carriers contribute to the electronic transport changing the value of I_{ds} , by different mechanisms, the PCE and the PGE. We start by explaining the PCE, sketched in the figure 5.1.2. Panel a) shows the band diagram of the semiconductor when it is illuminated with light of an energy $h\nu$. If $h\nu$ is higher than the energy band gap, E_g , the absorption of photon leads to the generation of electron-hole pairs. Panel b) sketches the band diagram of the phototransistor under illumination conditions with the photogenerated electron-hole pairs. The applied bias, V_{ds} , separates the electron-hole pairs, and the resulting photogenerated free electrons and holes move in opposite directions, from the semiconductor to the metallic contacts, causing a net increase in current. Panel c) depicts the schematic of the transfer curve under dark and illumination conditions. I_{ds} increases under illumination the value of the photogenerated current, I_{PC} .

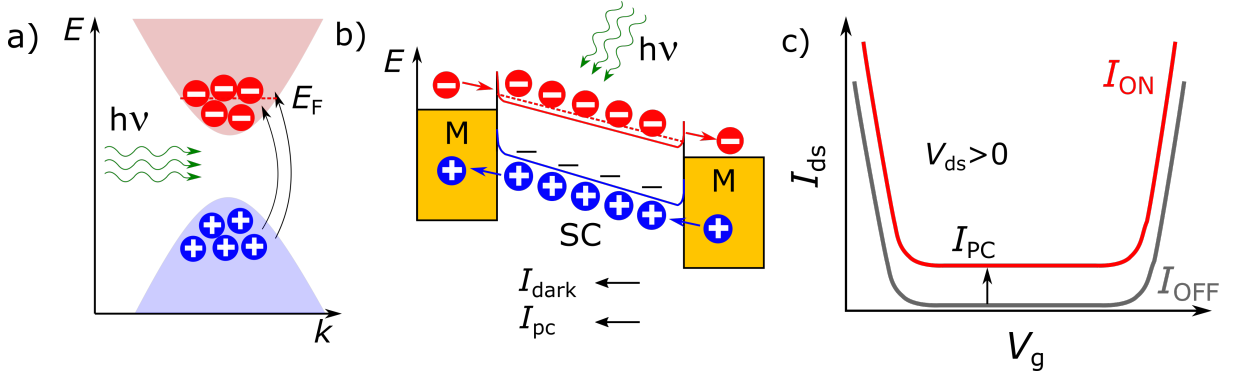


Fig. 5.1.2: Photoconductive effect in a transistor based on 2D-TMDs. a) Band structure showing the conduction and the valence band (red and blue bands respectively) of a semiconductor with E_F in the conduction band. When the semiconductor is illuminated the photon absorption leads to the creation of electron-hole pairs. b) Diagram of the transistor illuminated. The photo-generated electron-hole pairs are separated by an applied external bias, resulting in a photocurrent, I_{PC} , that adds to I_{dark} . c) Transfer curves in the dark (black line) and under illumination (red line) show that illumination leads to enhanced conductivity (vertical shift I_{PC}) and induces a positive I_{PC} across the entire V_g range.

After explaining the PCE, we center the discussion on the PGE. Figure 5.1.3 summarizes the PGE. Panel a) shows the band diagram of the semiconductor illuminated with light of an energy $h\nu > E_g$. In contrast with the PCE, in the PGE, holes or electrons (in this case holes) are trapped in localized states near the band edge. The trapped charge acts as a local gate voltage that shifts E_F and induces an increase of the density of electrons. Panel b) shows the transistor band diagram with the holes trapped in the localized states. The trapped carriers, through electric field effect, shift E_F increasing the electron density. This raise of electrons allows for a higher current I_{PC} . As a result, in panel c), the transfer curve shifts horizontally under illumination compared to in darkness, attributed to the effective gate electric field from the trapped charges. The direction of ΔV_{pge} indicates the charge sign of the trapped carriers (in this case holes). Remarkably, PGE can lead to either a positive or negative I_{PC} , as illustrated in panel c).

When the characteristic relaxation times of the trapped carriers are notably long, can cause shifts in E_F for long times after exposure. In this case, this effect is renamed as photodoping. For instance, in the context of 2D van der Waals photodetectors, this phenomenon can occur between h-BN and SiO₂ interface [138, 139].

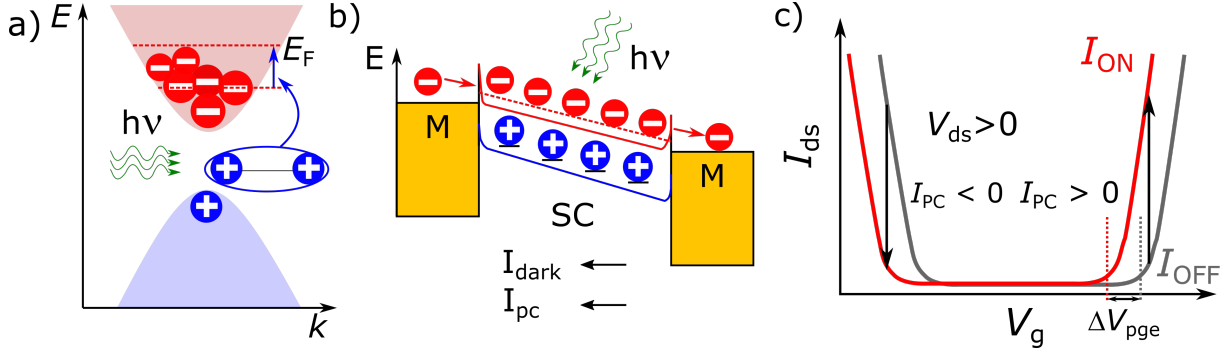


Fig. 5.1.3: Photogating effect in a transistor based on 2D-TMDs. a) Band structure showing the conduction and the valence band (red and blue bands respectively) of a semiconductor with E_F in the conduction band. When the semiconductor is illuminated the photon absorption leads to the creation of electron-hole pairs. The holes can be trapped in localized states near the band edge and act as a local gate shifting E_F and increasing the amount of electrons b) Diagram of the transistor illuminated. The photo-generated trapped holes induces more electrons, resulting in a photocurrent, I_{PC} , that adds to I_{dark} . c) Transfer curves in the dark (black line) and under illumination (red line) show that illumination leads to a horizontal shift ΔV_{pge} and induces a positive or negative I_{PC} .

In this chapter we characterize the photocurrent generation mechanisms in a 1L-MoS₂ phototransistor encapsulated using h-BN. In previous literature, the PGE in 1L-MoS₂ phototransistors has been related to slow recombination processes such as the presence of polar molecules adsorbed on the monolayer surface resulting in an atmosphere-dependent slow photoresponse [140]. Therefore, the previous understanding about the PGE indicated that can be ruled out by modulating the excitation frequency above $f \approx 10$ Hz, while fast response of the device is usually attributed to PCE. However, in our high-quality phototransistor we observe that the PGE appears at modulation frequencies up to 1 kHz.

As discussed in previous chapters, encapsulating van der Waals materials with h-BN enhances their properties and isolates the device from the ambient, reducing the adsorption of polar molecules. In the photoresponse of 1L-MoS₂ phototransistor, the gate voltage and illumination power dependence of the photoresponse indicate that PGE is the dominant mechanism at frequencies up to $f = 1$ kHz, surpassing the frequency response of PGE in previous literature by two orders of magnitude. Moreover, the fast response PGE is still present measuring in vacuum and at cryogenic conditions, where the characteristic response frequencies for charge trapping processes involving adsorbed polar molecules should be notably low, suggesting an intrinsic contribution to PGE related with impurities of the 1L-MoS₂.

PGE contribution to the photoresponse only disappears when gate voltage is well below the threshold voltage (off state). In this regime, the remaining photoresponse dependence with illumination power shows a linear behaviour, as expected for PCE.

5.1.1 Photoconductive vs photogating effect

In this section, we focus on the quantitative difference between the PCE and the PGE. Finally, we explain how to distinguish both effects in experimental photocurrent measurements.

As mentioned before, the photocurrent of 1L-TMD phototransistor is composed by the PCE and PGE, thus can be written as

$$I_{PC} = \Delta I_{PCE} + \Delta V_{PGE} \frac{dI_{ds}}{dV_g} \quad (5.1.1)$$

where ΔI_{PCE} corresponds with the photocurrent generated by the PCE, ΔV_{PGE} corresponds to the effective shift in the threshold voltage caused by PGE and dI_{ds}/dV_g is the transconductance of the device.

Photocurrent generated by PCE is given by the increase in the conductivity of the device.

$$\Delta I_{PCE} = \frac{W}{L} V_{ds} \Delta \sigma_{PCE} \quad (5.1.2)$$

where W/L is the aspect ratio of the device, V_{ds} is the drain source voltage applied and σ_{PCE} is change in the increase in the conductivity via light-excited charge carriers:

$$\Delta \sigma_{PCE} = e(\mu_n n_{ph} + \mu_p p_{ph}) \quad (5.1.3)$$

being μ_n , μ_p the mobilities of electrons and holes respectively and n_{ph} , p_{ph} , the densities of light-excited charge carriers.

Presence of trapped charge carriers can induce PGE. Charge carriers fall into localized or trap states not contributing directly to the electrical transport. However, these trapped carriers screen the V_g applied, inducing photocurrent. Assuming an equilibrium state where the trap carriers are denoted as n_t and using a plane parallel capacitor model the shift in the gate voltage ΔV_{PGE} is

$$\Delta V_{PGE} = \frac{n_t e}{C_{ox}} \quad (5.1.4)$$

being e , the electron charge, C_{ox} the capacitance of the SiO₂ and hBN (see equation 4.2.2). Therefore, the generated photocurrent is

$$I_{PGE} = \frac{n_t e}{C_{ox}} \frac{dI_{ds}}{dV_g} \quad (5.1.5)$$

and I_{PGE} is proportional to the transconductance of the device, $G = \frac{dI_{\text{ds}}}{dV_{\text{g}}}$.

After exposing the two effects, we center on how difference the dominant mechanism in photocurrent generation. In this work, we use two ways to distinguish between their contributions. First, measuring the gate-dependent photocurrent and determining whether I_{PC} is constant or proportional to G [141]. Second, measuring the power dependence of the photocurrent and examining if the trend is linear or sublinear [142]. These characteristic signatures will be discussed in depth in the following sections.

5.2 Photoresponse of monolayer MoS₂ transistor

Figure 5.2.1 a) shows an optical microscopy image of the encapsulated 1L-MoS₂ phototransistor. We fabricate the encapsulated device using the dry transfer method from mechanical exfoliated flakes of MoS₂ and h-BN identified using optical contrast and characterized by raman spectroscopy. Figure 5.2.1 b) depicts schematically the geometry of the device and the measurement configuration. A voltage is applied to the drain contact, while the source contact is grounded using a current-voltage preamplifier connected to a lock-in amplifier. To control the doping level of the semiconductor channel, we apply a gate voltage through Si/SiO₂.

To study the photoresponse of the device we expose the entire device to monochromatic light in our photocurrent setup described in chapter 3. Unless otherwise is stated all measurements are performed in vacuum at $T = 5$ K. Figure 5.2.1 c) illustrates two-terminal I - V curves of the monolayer MoS₂ phototransistor, obtained under dark and uniform illumination with a power density P_{D} of 1 mW/mm² and photon energy $h\nu$ of 1.92 eV (in resonance with the exciton A transition, X_{1s}^{A} , of 1L-MoS₂). I - V curves exhibit a back-to-back diode-like behaviour attributed to Schottky barriers at the contacts, leading to different saturation currents for positive and negative voltages due to asymmetry in the Schottky barrier heights [143].

Figure 5.2.1 d) shows gate transfer characteristics of the device under dark and illuminated conditions at $V_{\text{ds}} = 10$ V for consistency. At low temperatures, the transfer curves exhibit minimal hysteresis, presenting a n-type transistor behaviour (the semiconductor channel conductivity rises with the back-gate voltage, V_{g} surpassing the threshold voltage, V_{th}). In this figure, the two contributions to I_{PC} from equation 5.1.1 are clearly discernible. PGE manifests as a horizontal shift of the transfer curve during illumination by ΔV_{PGE} , while PCE induces a smaller contribution, measurable when the transconductance of the device, G vanishes and a vertical shift, denoted by ΔI_{PCE} , is observed (see inset).

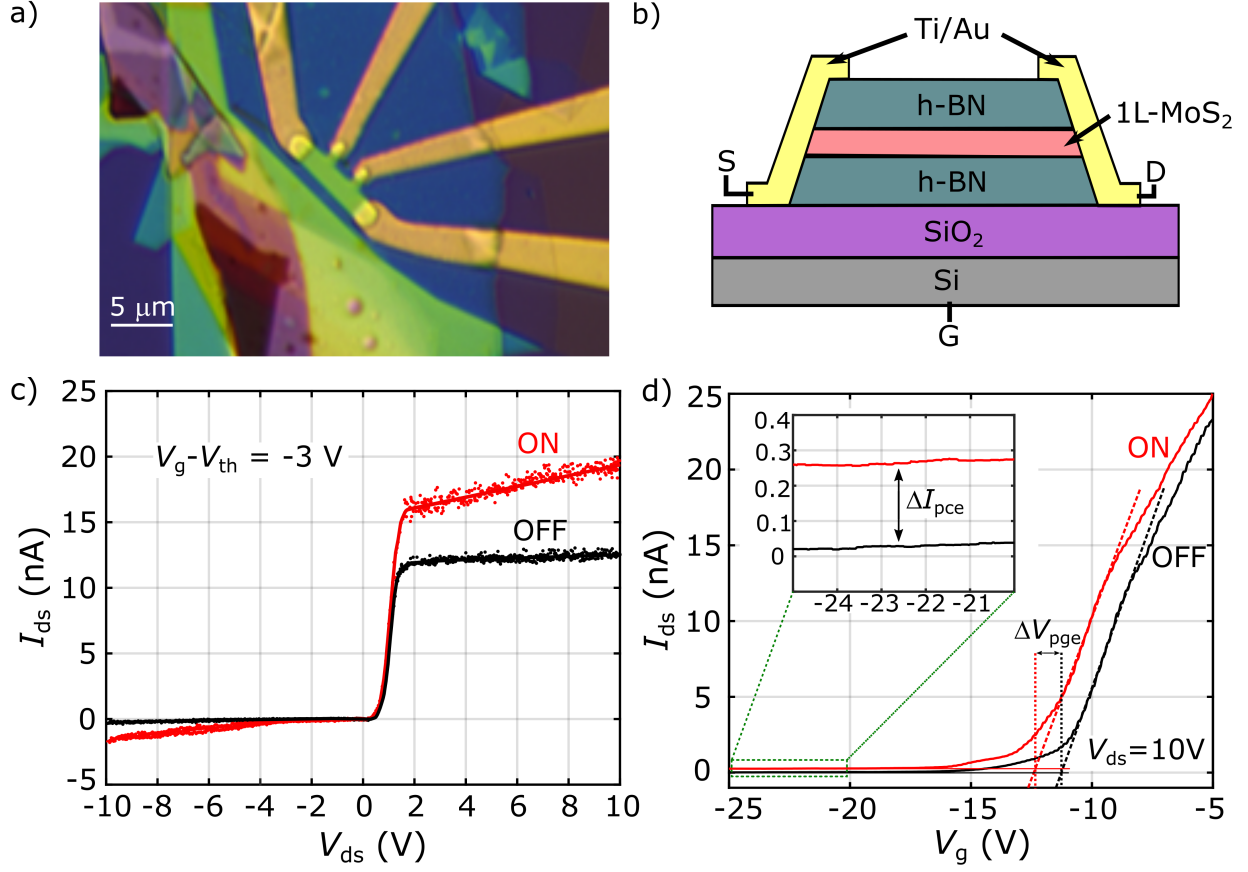


Fig. 5.2.1: Electric and optoelectronic response of the monolayer MoS₂ phototransistor. a) Optical microscopy image of hBN-MoS₂-hBN transistor. b) Schematic drawing of the device with the source, drain and gate contacts highlighted. c) Two-terminal $I - V$ characteristics obtained in both dark and uniform illumination conditions with power density $P_D = 1 \text{ mW/mm}^2$ and photon energy $h\nu = 1.92 \text{ eV}$. Illumination leads to an increase in the drain-source current, I_{ds} , by I_{PC} . d) Gate transfer curves, revealing a threshold gate voltage $V_{th} = -11 \text{ V}$. The inset offers a closer view of the region highlighted by the dashed green rectangle. The contributions to photoresponse of PCE and PGE, denoted by ΔI_{PCE} and ΔV_{PGE} respectively (see equation 5.1.1), are highlighted in the plot.

5.2.1 Spectral photoresponse of the device

Figure 5.2.2 shows the low-temperature photocurrent spectrum of the 1L-MoS₂ phototransistor, measured at 5 K, $V_g - V_{th} = -30 \text{ V}$ and $V_{ds} = 10 \text{ V}$. To measure I_{PC} the illumination was modulated at 31.81 Hz and is registered using a lock-in amplifier at synchronized at the same frequency as described in the section 3.6.1, sweeping the illumination wavelength in the monochromator in 0.1 nm steps. A detailed description of the spectral acquisition procedure can be found in section 3.6 of this thesis.

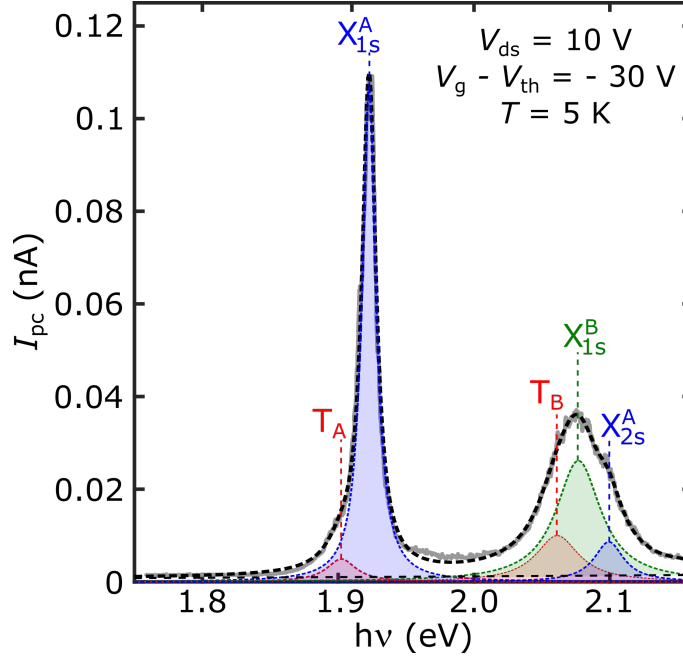


Fig. 5.2.2: Low-temperature photocurrent spectrum of the 1L-MoS₂ phototransistor (grey line) and the fitting to a multi-lorentzian peak function plus an exponential background (black dashed line). Below the spectrum, the Lorentzian peaks are displayed, detailing the neutral excitons X_{1s}^A and X_{1s}^B (shown in blue and green, respectively), charged trions T_A and T_B (in red), and the excited state X_{2s}^A (in blue) of the neutral exciton X_{1s}^A .

For the spectral range of 1.85 eV to 2.15 eV, the I_{PC} spectrum is well-fitted by a multiple Lorentzian peak function plus an exponential background, that accounts for direct interband absorption edge. A quintuple Lorentzian function, with two main (X_{1s}^A and X_{1s}^B) and three smaller peaks at 1.892 eV, 2.035 eV, and 2.090 eV, best replicates the spectral profile. The smaller features are attributed to the A and B trion states, (T_A and T_B), placed 20–30 meV below X_{1s}^A and X_{1s}^B . The 2.090 eV feature is tentatively identified as the first excited Rydberg state of the A exciton, X_{2s}^A . All these excitonic states are labelled using previous literature [144, 145]. In chapter 6 these peaks will be analyzed in deep demonstrating the nature of the transitions and identifying more excited states of X_{1s}^A and X_{1s}^B .

5.2.2 Frequency dependence of the photoresponse

Exploring the photocurrent mechanisms, we study the light modulation frequency dependence of the photoresponse in both regimes: PGE ($V_g > V_{th}$) and PCE ($V_g < V_{th}$). As mentioned before, PGE usually has been associated to slow processes, therefore, the frequency dependence of the photoresponse would reveal if the nature of the photoresponse generated by PGE aligns to the previously reported.

At this point, we compare our results with the work of Furchi et al. [140]. In this work, they measure non-encapsulated 1L-MoS₂ transistor at room temperature, observing a slow response which they attribute to the PGE, caused by charge trapping due to water

molecules on the MoS₂ layer. Using a mechanical chopper for optical excitation and a lock-in amplifier for signal recording, they found a clear drop in photocurrent above light-modulation frequencies of about 1 Hz, indicating the slow response of the trapping process. They concluded that the consistent high-frequency signal was likely due to the PCE.

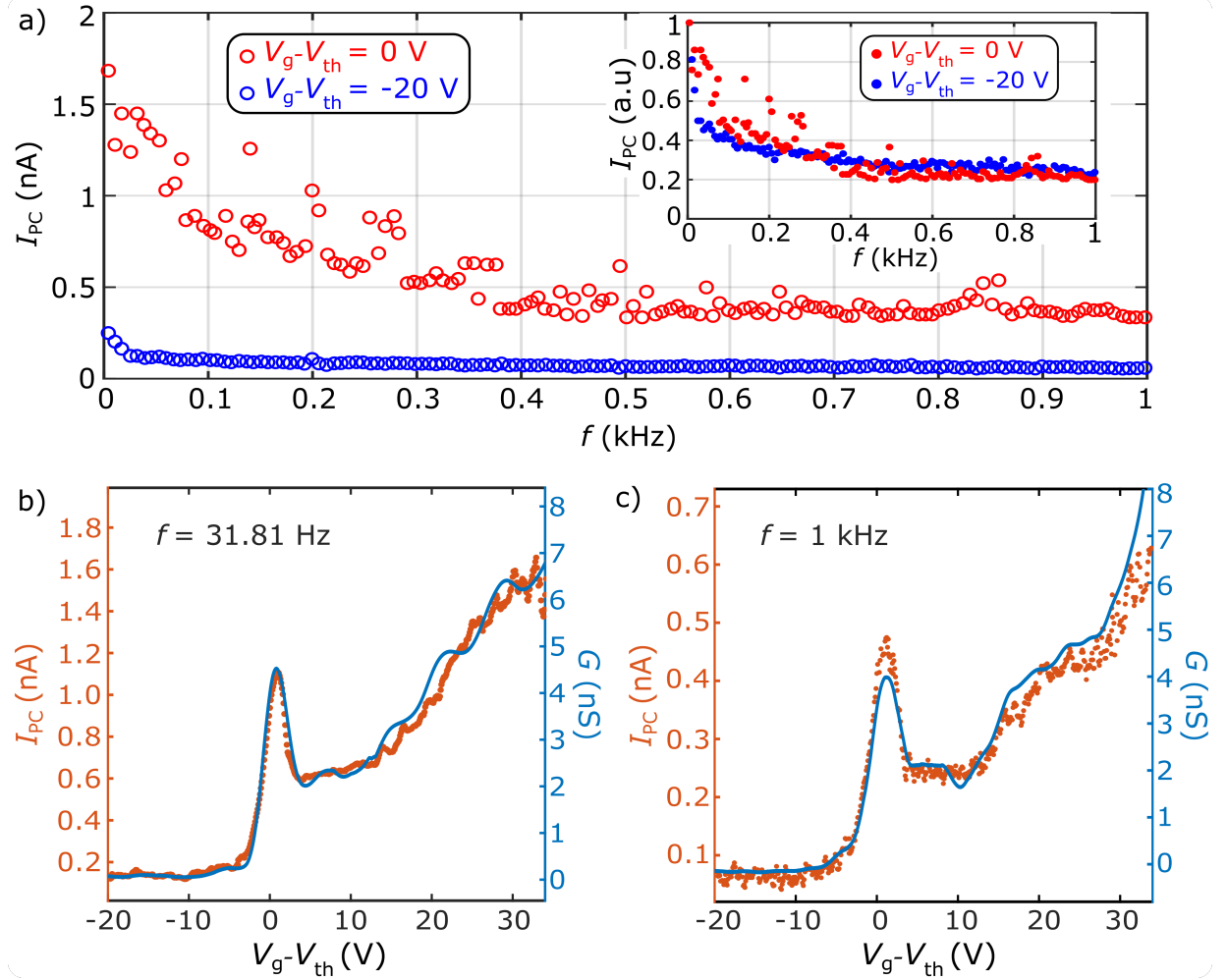


Fig. 5.2.3: Frequency and gate dependent photoresponse. a) I_{PC} as a function of the frequency for $V_g - V_{th} = 0$ V (red dots; corresponding with the PGE regime) and $V_g - V_{th} = -20$ V (blue dots; corresponding with the PCE regime). Inset: Normalized I_{PC} as a function of the frequency for the two regimes. b) and c) Gate dependence of the transconductance of the device (right axis, cyan line) and of I_{PC} (left axis, orange line) measured at $V_{ds} = 10$ V in resonance with X_{1s}^A for $f = 31.81$ Hz and $f = 1$ kHz respectively.

For comparison, we also register the I_{PC} variation with light modulation frequency in our device for a illumination wavelength in resonance with X_{1s}^A for consistency. Figure 5.2.3 a) shows the measured signal for $V_g - V_{th} = 0$ V (red dots), where the PGE is the dominating part of the photoresponse, and for $V_g - V_{th} = -20$ V, where PGE is inexistent because G vanishes and the photoresponse corresponds to PCE. Like in ref [140], the signal decreases at higher frequencies, but the decay is roughly a factor 4 for both regimes (see inset.).

Next, we examine the source of the signal that remains at high-frequency modulation. As mentioned before, previous studies often attribute this fast-response part of the photocurrent to PCE. However, our findings suggest that this fast-photoresponse is also generated by PGE. A key feature of PGE is that the resulting I_{PGE} is proportional to the transconductance $G = \frac{dI_{\text{ds}}}{dV_{\text{g}}}$ of the semiconductor (see equation 5.1.5). This characteristic signature allows us to distinguish PGE from PCE, which should be independent of V_{g} at low carrier densities. Figure 5.2.3 b) depicts the I_{PC} dependence on V_{g} and G (calculated from the I - V_{g} transfer characteristic) in our device at light-modulation frequency of 31.81 Hz, showing a clear proportionality between both magnitudes. In figure 5.2.3 c) we increase the modulation frequency at $f = 1$ kHz and we follow the same procedure comparing G and I_{PC} obtaining the same proportionality than at low frequencies. These findings indicate that PGE is the principal contribution to the photoresponse, even at high frequencies up to 1 kHz, in stark contrast from previous understanding. We attribute this fast-response PGE to charge trapping at sulfur vacancies in the 1L-MoS₂ crystal, as is discussed below in following sections.

When V_{g} is much lower than V_{th} , the device still shows a measurable and constant photocurrent. In this regime, transconductance G is almost zero, reducing the PGE contribution to the photoresponse. Thus, we conclude that the small remaining photocurrent at V_{g} much lower than V_{th} is probably caused by PCE.

5.2.3 Power dependence of the photoresponse

As mentioned before, a characteristic signature of the PCE and PGE is the power dependence of the photoresponse. While PCE shows a linear behaviour with the illumination power, PGE presents a sublinear trend [142]. To further validate our interpretation of the photoresponse in the distinct V_{g} regimes, we use this fingerprint of each regime. We obtain the measurements by changing the power of supercontinuum laser of our setup and measuring I_{PC} .

Figure 5.2.4 displays the power dependence of the photocurrent at different gate voltages regimes. Panels a) and b) depict the behaviour of I_{PC} at $V_{\text{g}}-V_{\text{th}} = -20$ V and $V_{\text{g}}-V_{\text{th}} = 20$ V, respectively, using two illumination wavelengths, each in resonance with the main excitonic transitions of 1L-MoS₂ (see section 5.2.1): X_{Is}^{A} ($h\nu=1.92$ eV) and X_{Is}^{B} ($h\nu=2.07$ eV). Panel a) shows a linear trend I_{PC} respect to the illumination power density while panel b) demonstrates a sublinear behaviour, confirming our previous interpretation: PCE is the main contribution to the photoresponse when $V_{\text{g}} < V_{\text{th}}$, while PGE becomes the dominant mechanism when $V_{\text{g}} > V_{\text{th}}$. To clarify the dominant mechanisms of I_{PC} at different $V_{\text{g}}-V_{\text{th}}$, we take a quantitative approach, based on fitting the I_{PC} power dependence to the phenomenological equation $I_{\text{PC}} \propto P_{\text{D}}^{\alpha}$ [89], allowing us to obtain the value of the parameter α to evaluate the linearity of the behaviour of I_{PC} .

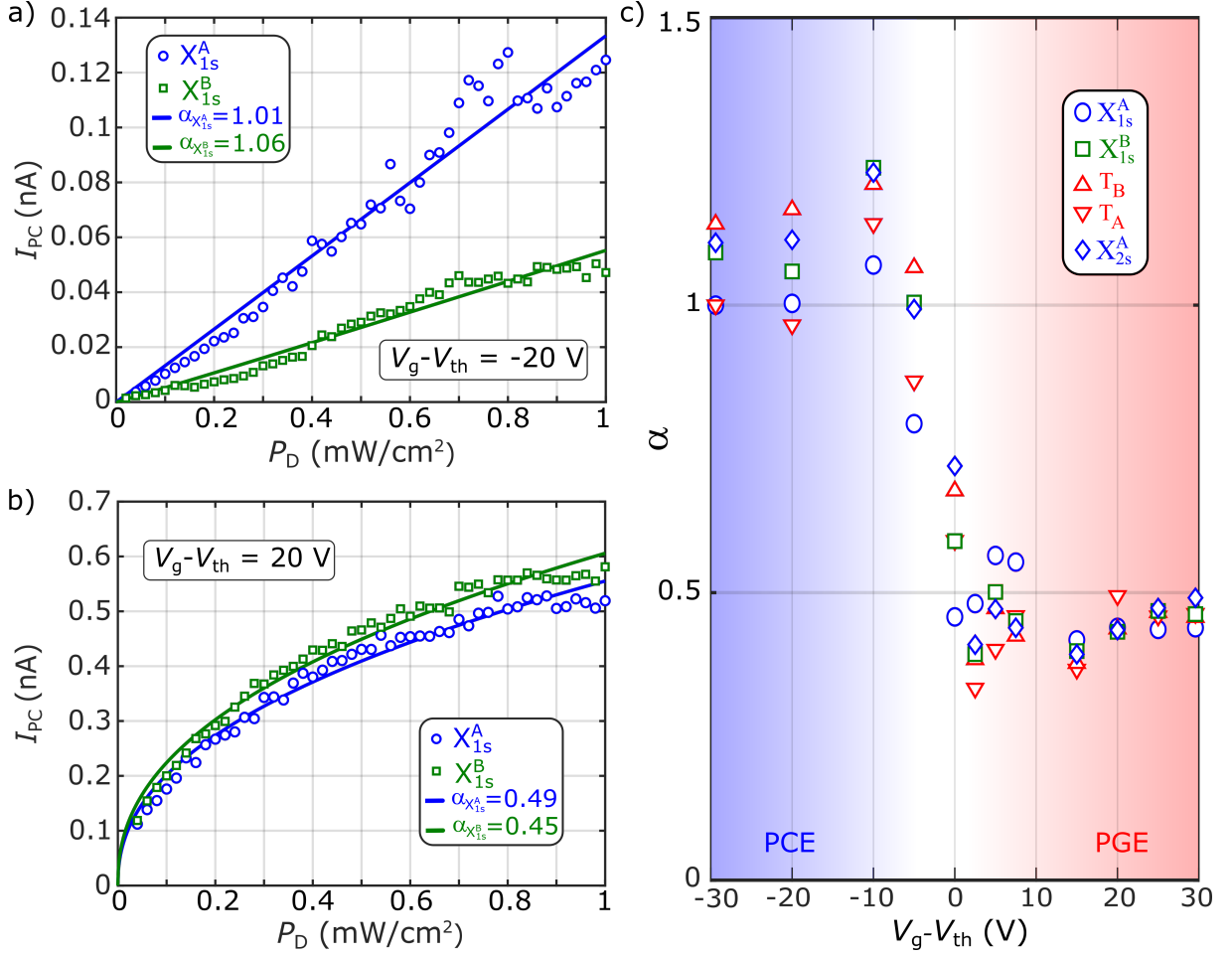


Fig. 5.2.4: Power dependence of the photoresponse at distinct gate voltage regimes. a) Power dependence of I_{PC} at $V_g - V_{th} = -20$ V, measured at photon energies corresponding to the X_{1s}^A and X_{1s}^B excitonic features. The data are fitted to $I_{PC} \propto P^\alpha$ with $\alpha \approx 1$, indicating a linear trend. (b) Similar analysis for $V_g - V_{th} = 20$ V, where the fittings yield $\alpha \approx 0.5$, obtaining a sublinear relation. (c) Fitting parameter, α , variation with $V_g - V_{th}$, evaluated at photon energies matching the five main excitonic features of monolayer MoS₂, indicating the PCE and PGE-dominated photoresponse regimes.

Panel c) displays the extracted parameter α , obtained from the fittings, as a function of $V_g - V_{th}$ across five different illumination energies, corresponding to the five main excitonic transitions, neutral excitons, X_{1s}^A and X_{1s}^B , trions, T_A and T_B , and the rydberg exciton X_{2s}^A . For gate voltages below V_{th} , α approximates to 1 for all selected illumination wavelengths. Nevertheless, for $V_g > V_{th}$, α is observed to be around 0.5. In the following section, we analyze the photocarrier dynamics of the system and establish a correlation with these observed power dependencies.

5.2.4 Dynamics of photoexcited carriers

Building upon these findings, we now explore the possibility of explaining theoretically the photoresponse observed. Following a similar methodology than in previous

literature[140, 146], we analyze the dynamics of photoexcited carriers employing a modified Hornbeck–Haynes model. We consider a scenario where the principal mechanism for photocarrier relaxation is the Shockley–Read–Hall recombination [147, 148], mediated by midgap states. As seen in the previous sections, the shift in V_{th} , $\Delta V_{PGE} = V_{th}^{off} - V_{th}^{on}$, generated by trapped carriers is positive, indicating that these trapped carriers are likely holes. Therefore, we introduce a discrete density of localized states, denoted as D_t , positioned near the valence band edge to account for the presence of the shallow hole traps. Furthermore, in an n-type transistor, it is reasonable to assume that only hole traps near the valence band are relevant, because in equilibrium conditions, electron traps are typically filled. In 1L-MoS₂, midgap states and shallow traps are expected due to the presence of sulfur vacancies within the crystal lattice[149, 150, 151].

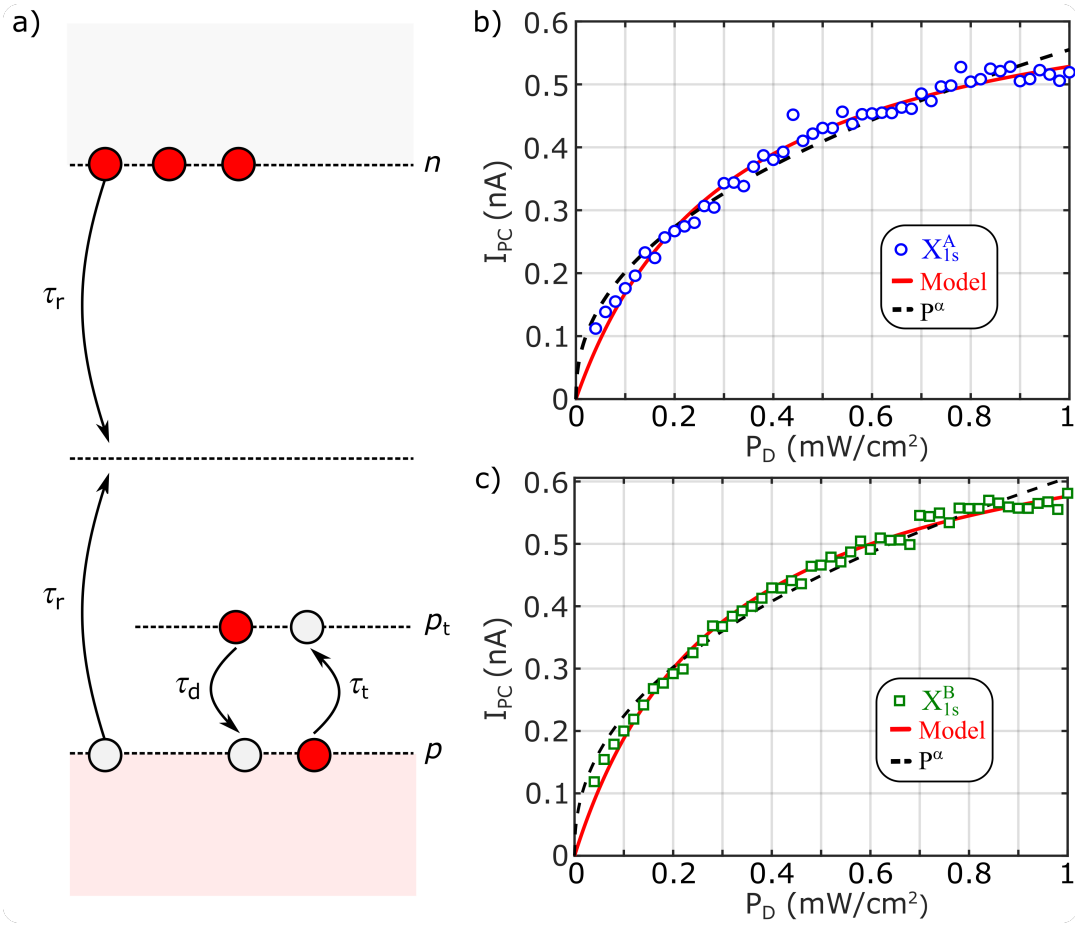


Fig. 5.2.5: Model for photoexcited carrier dynamics. a) Schematic of the simplified energy band diagram, highlighting the excitation and relaxation processes considered in the model. b) Comparative analysis between the power dependence of I_{pc} fitted to P_D^α (black dashed lines) and the fittings to our proposed model (eq. 5.2.13, red solid lines).

Figure 5.2.5 a) depicts a schematic of the energy levels included in our model. The conduction band, labeled as n and depicted in grey, and the valence band, denoted as p and shown in red. The recombination times for the transitions are indicated alongside the

corresponding transition arrows. For simplicity, our model assumes identical recombination times for both electron and hole decays to the midgap states. Thus, the dynamic of the photoexcited carriers can be described by

$$\frac{dn_{\text{ph}}}{dt} = \phi_A - n_{\text{ph}}\tau_r^{-1} \quad (5.2.1)$$

$$\frac{dp_{\text{ph}}}{dt} = \phi_A - p_{\text{ph}}\tau_r^{-1} - p_{\text{ph}}\tau_t^{-1} \left(1 - \frac{p_t}{D_t}\right) + p_t\tau_d^{-1} \quad (5.2.2)$$

$$\frac{dp_t}{dt} = p_{\text{ph}}\tau_t^{-1} \left(1 - \frac{p_t}{D_t}\right) - p_t\tau_d^{-1} \quad (5.2.3)$$

where D_t is the density of localized states, p_t is the density of trapped holes and τ_t and τ_d , the characteristic times of trapping and detrapping of holes in the trap states. Density of absorbed photons is $\phi_A = \frac{\eta P_D \lambda}{hc}$ being η the absorption coefficient for 1L-MoS₂, λ , the illumination wavelength and P_D , the power density. Typical characteristic times of recombination processes are roughly $\tau \approx 10^{-12}$ s, therefore for the chopping frequencies used in the experiment we can consider the system in equilibrium. Solving the equations (5.2.1) - (5.2.3) in this condition,

$$p_{\text{ph}} = \phi_A \tau_r \quad (5.2.4)$$

$$p_t = \frac{\phi_A D_t \tau_r}{\phi_A \tau_r + D_t \left(\frac{\tau_t}{\tau_d}\right)} \quad (5.2.5)$$

From this values of the density of carriers we can obtain the value of the photocurrent for PCE and PGE using the equations (5.1.2)-(5.1.5). Presence of hole traps affects the two mechanism of photoresponse. On the one hand, the increased conductivity via photoexcited carriers can be written as

$$\Delta\sigma_{\text{PCE}} = q(\mu_n + \mu_p)p_{\text{ph}} + q\mu_p p_t \quad (5.2.6)$$

and replacing the value obtained for p_{ph} and p_t

$$\Delta\sigma_{\text{PCE}} = q(\mu_n + \mu_p)\phi_A \tau_r + q\mu_p \frac{\phi_A D_t \tau_r}{\phi_A \tau_r + D_t \left(\frac{\tau_t}{\tau_d}\right)} \quad (5.2.7)$$

The first term of eq. (5.2.7) gives a linear behaviour with the illumination power because $\phi_A \propto P_D$. The second term is more complex giving different behaviours under different assumptions:

- $\phi_A \gg D_t \frac{\tau_t}{\tau_r \tau_d}$

In this case, trap states become saturated due to large illumination power density. Equation 5.2.7 can be written as

$$\Delta\sigma_{\text{PCE}} = q(\mu_n + \mu_p)\phi_A \tau_r + q\mu_p D_t \quad (5.2.8)$$

Resulting in a linear behaviour of $\Delta\sigma_{\text{PCE}}$ with the power density.

- $\phi_A \ll D_t \frac{\tau_t}{\tau_r \tau_d}$

Using low power densities, trap states are very low populated, therefore the presence of localized states is negligible, obtaining again a linear trend of the photoconductivity.

$$\Delta\sigma_{\text{PCE}} = q(\mu_n + \mu_p) \phi_A \tau_r + q\mu_p \frac{\tau_r \tau_d}{\tau_t} \phi_A \quad (5.2.9)$$

- $\phi_A \approx D_t \frac{\tau_t}{\tau_r \tau_d}$

In the last case, for power densities where trap states influence the photoconductivity equation 5.2.7 cannot be simplified obtaining a sublinear behaviour of $\Delta\sigma_{\text{PCE}}$.

On the other hand, density of trapped holes p_t , play a role in partially screening the electric field generated by V_g . This screening contributes additionally to I_{pc} generating the PGE. In the conclusion, we propose that this contribution, which has not been extensively considered in previous studies, is likely responsible for the observed fast-response PGE under conditions of high light-modulation frequencies.

Now, we calculate the influence of the trapped holes in the shift of the gate voltage. First, we start with the relation between the V_g and E_F .

$$\Delta V_g = \Delta E \cdot d + \frac{1}{e} \Delta E_F \quad (5.2.10)$$

being E the electric field between the back-gate and the semiconductor and $-e$ the electron charge. From the plane parallel capacitor we extract the value obtained from the two dielectrics, SiO₂ and h-BN,

$$C_g = \left(\frac{d_{\text{SiO}_2}}{\epsilon_0 \epsilon_{\text{SiO}_2}} + \frac{d_{\text{h-BN}}}{\epsilon_0 \epsilon_{\text{h-BN}}} \right) \quad (5.2.11)$$

and we can write

$$\Delta E \cdot d = \frac{e \Delta n}{C_g} \quad (5.2.12)$$

Substituting in equation 5.2.10 and using the definition of the density of states $\Delta E_F = \frac{\Delta n}{g_{2D}}$ we obtain

$$\Delta V_g = \frac{en}{C_g} = \left(\frac{1}{C_g} + \frac{1}{C_q} \right) e \Delta n \quad (5.2.13)$$

being C_q the quantum capacitance, $C_q = e^2 g_{2D}$. Subsequently, rewriting the previous equation as function of E_F using, $\Delta E_F = \Delta n / g_{2D}$ we obtain

$$\Delta V_g = \left(\frac{1}{C_g} + \frac{1}{C_q} \right) e D \Delta E_F = \left(\frac{1}{C_g} + \frac{1}{C_q} \right) \frac{C_q}{e} \Delta E_F \quad (5.2.14)$$

Therefore, solving for E_F , we obtain

$$\Delta E_F = \frac{e\Delta V_g}{1 + \frac{e^2 g_{2D}}{C_g}} \quad (5.2.15)$$

Density of states of the 2D electron gas g_{2D} can be modeled as a step function at very low temperatures as follows

$$g_{2D} = \begin{cases} \frac{2\mu_{eff}}{\pi\hbar^2} & V_g > V_{th} \\ 0 & V_g < V_{th} \end{cases} \quad (5.2.16)$$

where μ_{eff} corresponds with the effective mass of the electrons in MoS₂ estimated to be around $0.34m_0$, being m_0 the free electron mass. From this considerations, we obtain the relation.

$$\Delta E_F = \frac{e\Delta V_g}{1 + \frac{e^2 g_{2D}}{C_g}} (V_g - V_{th}) \quad (5.2.17)$$

where V_{th} is the threshold voltage at which $E_F = E_{CB}$. In our case, we get $\Delta E_F/(V_g - V_{th}) = 0.28 \text{ meV V}^{-1}$, which for the maximal gate voltages applied here $V_g - V_{th} = 50 \text{ V}$ gives $\Delta E_F = 14 \text{ meV}$. Finally, the density of excess carriers, n can be obtained as $n = \Delta E_F \cdot g_{2D} = 7.17 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1} (V_g - V_{th})$. Once we have the relation of ΔV_g with Δn and ΔE_F we obtain the value of the voltage shift generated by the trapped holes. Substituting into eq. (5.2.13) the density of trapped holes we obtain

$$\Delta V_{PGE} = \frac{ep_t}{C_{ox}} = \left(\frac{1}{C_g} + \frac{1}{C_q} \right) ep_t = \frac{p_t}{\beta} \quad (5.2.18)$$

with $\beta = 7.17 \times 10^{10} \text{ cm}^{-2} \text{ V}^{-1}$. From the value obtained for ΔV_{PGE} , we calculate I_{PGE} using equations (5.1.4) and (5.1.5).

$$I_{PGE} = \frac{D_t}{\beta} \frac{dI_{ds}}{dV_g} \frac{1}{1 + \frac{D_t}{\phi_A \tau_r} \left(\frac{\tau_t}{\tau_d} \right)} = A \frac{1}{1 + \frac{B}{P_D}} \quad (5.2.19)$$

being A and B fitting parameters defined as

$$A = \frac{D_t}{\beta} \frac{dI_{ds}}{dV_g}; \quad B = \frac{D_t \hbar c}{\eta \lambda \tau_r} \left(\frac{\tau_t}{\tau_d} \right) \quad (5.2.20)$$

Using equation 5.2.13 as fitting function we can fit the photocurrent generated by PGE. Figure 5.2.5 b) and c) displays this power dependence of I_{PC} for $V_g - V_{th} = 20 \text{ V}$ alongside the fit to equation 5.2.13, using A and B as fitting parameters. For comparison, we also present the best fit to the widely-used phenomenological equation $I_{PC} \propto P_D^\alpha$. Although both fitting curves exhibit similar shapes, our model demonstrates a better correlation to the experimental data points. The norm of residuals, r , for the fits to equation 5.2.13 yield $r_A = 10 \text{ pA}$ and $r_B = 7 \text{ pA}$ for excitons X_{1s}^A and X_{1s}^B , respectively. These values are

approximately half of those obtained for the fit to $I_{PC} \propto P_D^\alpha$ ($r_A = 20$ pA and $r_B = 20$ pA). From the fitting parameters A and B, we estimate the density of trap states $D_t \approx 1 \times 10^{10} \text{ cm}^{-2}$, and the ratio of characteristic times $\tau_t(\tau_r\tau_d^{-1}) \approx 8.5 \times 10^3 \text{ s}^{-1}$.

From the ratio of characteristic recombination times associated with transitions from shallow hole trap states to the valence band, we calculate the energy difference using the detailed balance principle [146]

$$E_{T,V} = E_T - E_V = k_B T \ln \left(\frac{N_V \tau_d}{D_t \tau_t} \right) \quad (5.2.21)$$

being k_B the Boltzmann constant and N_V the 2D effective density of states in the valence band, $N_V = g_v m^* k_B T / \pi \hbar^2$. In 1L-MoS₂ the valley degeneracy is $g_v = 2$ and the effective mass of the holes is estimated to be $m^* = 0.4m_0$ [152].

Finally, given the strong evidence indicating that the characteristic recombination times of carriers in midgap states, τ_r , of few picoseconds at cryogenic temperatures, we use an approximate value of $\tau_r \approx 5$ ps [153, 154] for estimating the energy of the shallow hole traps relative to the top of the valence band, resulting in $E_{T,V} \approx 8.4$ meV, very close to the valence band edge, suggesting that these shallow hole traps are likely related to the presence of sulfur vacancies in the MoS₂ monolayer, being the most common defects in exfoliated 1L-MoS₂.

5.3 Conclusions

In summary, in this chapter we have clearly distinguished between two separate regimes of photoresponse in 1L-MoS₂, differentiated by their different dependence on illumination power density, P_D and relation of proportionality with the transconductance of the device, G as seen in sections 5.2.2 and 5.2.3. For gate voltage below the threshold voltage, $V_g < V_{th}$, the conduction band of the semiconductor channel based on 1L-MoS₂ is fully depleted and G vanishes, I_{pc} exhibits a linear dependence with P_D indicating a photocurrent generation dominated by the photoconductive effect, PCE. In this regime, $G = 0$, therefore, the contribution of the photogating effect, PGE is completely negligible. Conversely, in the regime where $V_g > V_{th}$, we observe a complex interplay of three mechanisms contributing to the photoresponse: a slow-response PGE, likely due to polar molecules, a fast-response PGE, which we associate with sulfur vacancies, and PCE. In this scenario, the power density dependence of I_{pc} shifts to a sublinear trend, suggesting that the PGE mechanisms are predominant over PCE.

In previous literature [140], the PGE in 1L-MoS₂ devices is attributed to a slow charge-trapping process by polar adsorbates near the 2D channel. Nevertheless, our findings reveal that PGE dominates the device photoresponse even at high frequencies up to 1 kHz. We attribute this fast PGE to charge accumulation in shallow impurities near the valence

band of 1L-MoS₂. In section 5.2.3 by applying a modified Hornbeck–Haynes model that includes this effect, we estimate the trap state density to be approximately $D_t \approx 1 \times 10^{10} \text{ cm}^{-2}$. Thus, even at relatively low trap densities, charge accumulation in shallow impurities emerges as a dominant mechanism for photoresponse.

Furthermore, our fitting methods also allow us to approximate the energy of these trap states $E_{T,V} \approx 8.4 \text{ meV}$ above the valence band edge. We explored various potential sources for these traps, including both intrinsic defects in MoS₂ and extrinsic defects, such as those arising from h-BN encapsulation [138, 155]. Of particular interest are sulfur vacancies, a prevalent defect especially in exfoliated MoS₂. Ab initio simulations [149, 150] of these defects suggest two types of states within the energy gap: one slightly above the middle of the gap and another very close to the valence band edge. The latter, as discussed in [149], exhibits acceptor-like characteristics. Building upon these findings, we believe that the fast-response PGE detected in our experiments is linked to the presence of sulfur vacancies in the 1L-MoS₂ channel.

Chapter 6

Excitonic states in monolayer MoS₂ revealed by low-temperature photocurrent spectroscopy

After the study of the photocurrent generation mechanisms in a monolayer (1L) MoS₂ phototransistor, in the following chapter, we introduce the use of low temperature photocurrent spectroscopy to study the spectral photoresponse of same the device based on 1L-MoS₂ encapsulated on h-BN. We present this technique as an alternative to the widely used techniques, such as photoluminescence, electroluminescence or absorption spectroscopy.

Excitonic physics in two-dimensional semiconductors are typically studied using photoluminescence spectroscopy. Nevertheless, this method only reveals radiative optical transitions. In our research, we use the low-temperature photocurrent spectroscopy technique, that unlike photoluminescence spectroscopy, reveals both radiative and non-radiative excitons, to study the excitonic transitions of a h-BN encapsulated monolayer MoS₂. This technique allows us to observe excitonic peaks, characterized by exceptionally narrow linewidths, as low as 8 meV. Our measurements identify excitonic features consistent with the ground states of neutral excitons (X_{1s}^A and X_{1s}^B) and charged trions (T_A and T_B), as well as up to eight additional spectral lines beyond the X_{1s}^B transition. We attribute these to the Rydberg series of excited states of X^A and X^B . Furthermore, we demonstrate that the excitonic features intensities are controllable via gate and drain-source voltages. Employing an effective-mass theory for two-dimensional excitonic systems based on the keldysh potential, we unequivocally identify spectral features to the Rydberg states of X^A and X^B using a fitting to the solution of the proposed theoretical model.

6.1 Introduction

Excitons in two-dimensional transition metal dichalcogenides (TMDs) have been largely studied through a variety of techniques, being photoluminescence (PL) spectroscopy the most used technique. PL spectroscopy provides access to spontaneous radiative decay of excitonic states, however this technique finds limitations when non-radiative exciton relaxation mechanisms are predominant. These non-radiative processes can significantly suppress or even erase PL peaks, despite being allowed by optical selection rules [156]. For instance, in monolayer (1L) MoS₂, while standard PL spectroscopy efficiently identifies exciton states X_{1s}^A and X_{1s}^B , arising from spin-splitting at the K and K' valleys, it fails in accessing optical transitions of higher energy, such as Rydberg excited states of these excitons. Therefore, alternative techniques like absorption spectroscopy [157, 158, 159, 144] and electroluminescence spectroscopy [160] have become popular for probing excitonic states that remain elusive in PL studies. Figure 6.1.1 shows examples of different spectroscopy techniques used for the study of excitonic states in 2D-TMDs

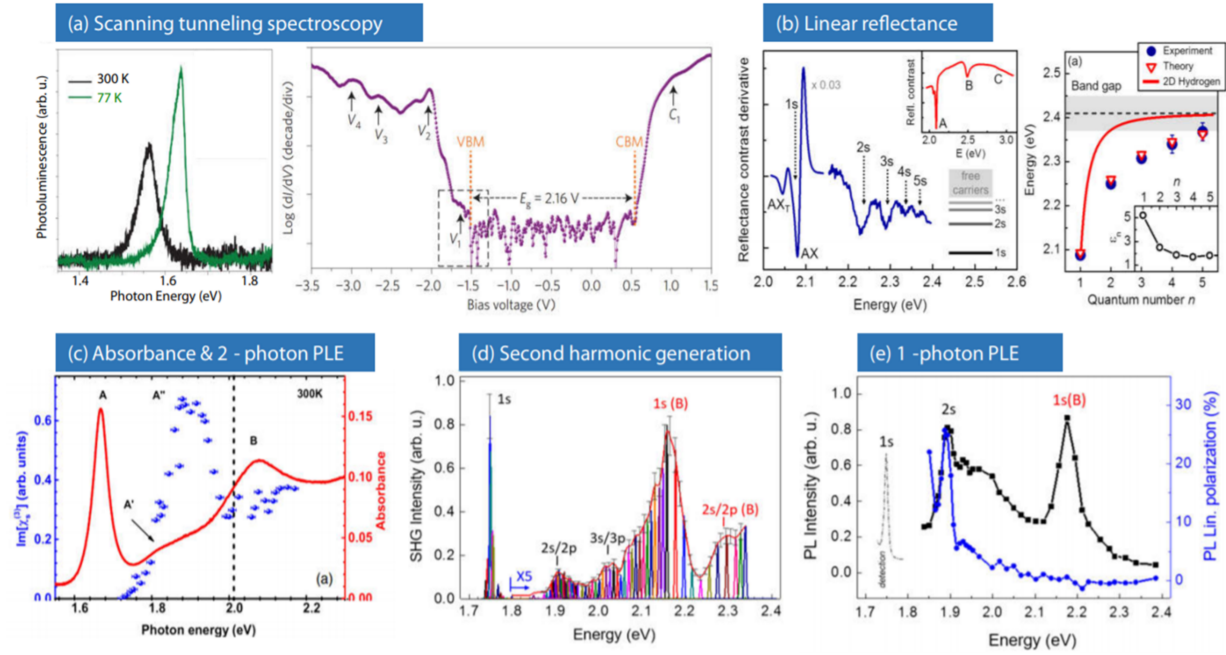


Fig. 6.1.1: Most common spectroscopic techniques to study excitonic properties in TMDs. Figure from ref [58]. a) PL spectroscopy of 1L-MoS₂ on bilayer graphene obtaining a clear optical transition from X_{1s}^A (left panel) combined with the band gap energy measurement via scanning tunneling spectroscopy (right panel) from ref. [97]. b) Excited excitonic states of 1L-WS₂ on SiO₂ measured from reflectance contrast technique in ref. [78]. c) Absorption spectrum of 1L-WS₂ on fused silica from ref. [11]. d) Excitonic features obtained by second-harmonic spectroscopy and e) one photon PL excitation and linear polarization degree of the luminescence 1L-WS₂ of X_{1s}^A and X_{1s}^B from ref. [53]

In this chapter, we use the experimental setup described in section 3.6 to obtain the spectral photoresponse of a high quality MoS₂ phototransistor encapsulated in h-BN using low temperature photocurrent spectroscopy (PCS). Combining the improvement of the

properties of 1L-MoS₂ through the encapsulation using h-BN and cryogenic temperatures ($T = 5$ K), we fully resolve neutral excitons (X_{1s}^A and X_{1s}^B) and their associated charged trions (T_A and T_B), reaching linewidths down to 8 meV (full width at half maximum; FWHM). The FWHM obtained is one order of magnitude lower than in refs [25, 26] and comparable to PL spectroscopy in encapsulated 1L-MoS₂ [161]. After identifying these peaks, we study the effect of the gate voltage in the optoelectronic response, finding that the intensity of the excitons and trions is tuned by the doping level of the phototransistor. Additionally, modifying the drain-source voltage we observe a similar effect in the relative intensity of these spectral features. Beyond these peaks, the photocurrent spectra also reveal eight additional features at higher energies than the X_{1s}^B transition, attributed to the Rydberg series of excited states of X_{1s}^A and X_{1s}^B [94, 144, 145, 162]. Using a theoretical model based on a 2D effective-mass Hamiltonian with a non-hydrogenic Keldysh potential, we replicate the observed rydberg states, labelling correctly the transitions observed.

6.2 Electrical characterization of the device

Firstly, we start our characterization of the encapsulated phototransistor performing an standard electrical characterization of a transistor measuring the transfer and the $I - V$ curves. Figure 6.2.1 a) illustrates schematically the stacking of the h-BN encapsulated 1L-MoS₂ device. Fabrication methods of the device are described in chapter 3. The device is fully encapsulated in two flakes of h-BN. We fabricate the electrical contacts of Ti/Au following an edge geometry [19] and the gate voltage, V_g , is applied through the Si/SiO₂ substrate. All the measurements mentioned in the following sections were conducted in vacuum and at $T = 5$ K, unless specified otherwise.

We start the electrical characterization of the device measuring the gate transfer curve of the device keeping the drain-source voltage fixed, V_{ds} , and sweeping V_g . Figure 6.2.1 b) shows the transfer curve of the device, exhibiting a clear n-type transistor behaviour, with a raise of the drain-source current, I_{ds} , as the gate voltage is increased above of the threshold voltage ($V_{th} = -4$ V). Up next, we characterize the effect of V_{ds} , measuring the $I - V$ characteristics at different V_g . Figure 6.2.1 c) displays the $I - V$ curves of the transistor at different values of V_g . These curves exhibit a diode-like behavior in opposite directions, attributed to the Schottky barriers at the contacts. The observed difference in saturation currents between positive and negative voltages arises from different heights of the Schottky barriers [143, 163]. At $T = 5$ K, thermionic emission can be neglected, therefore, I_{ds} is predominantly produced by tunneling through these Schottky barriers.

Now, we start to characterize the photoresponse of the 1L-MoS₂ transistor illuminating the entire device with an uniform monochromatic light source. Figure 6.2.1 d) presents the variation of I_{ds} over time, measured at different cycles of turned on and off monochromatic light at a frequency of $f = 31.81$ Hz, with $V_{ds} = 10$ V and $V_g - V_{th} = 2$ V. Illumination energy is $h\nu = 1.92$ eV, corresponding to the resonance with the X_{1s}^A exciton (as demonstrated subsequently). Upon illumination, I_{ds} shows an increase from its dark state by a

magnitude I_{pc} , indicating the generation of photocurrent.

As seen in the previous chapter, in 2D-TMDs the photoresponse can be dominated by two different mechanisms [164, 140, 165, 142, 141, 166], the photoconductive effect, that arises from the excitation of electrons from the valence band to the conduction band leading to an increase in the conductivity of the device, and the photogating effect, where trap states in the band gap of the semiconductor are filled resulting in a shift of the fermi energy, E_F . It is important to mention the case when large relaxation times of the trap states present in the h-BN cause long induced shifts in E_F after light exposure, generating the photodoping effect [138]. Our findings indicate that significantly reducing the illumination power density to below 2 mW cm^{-2} can largely mitigate this effect. At these lower power densities, the light-induced shift in V_{th} remains below 0.1 V during spectrum acquisition. To enhance the consistency of the measurements and minimize variations caused by shifts in V_{th} , all spectral data are presented in terms of $V_g - V_{th}$.

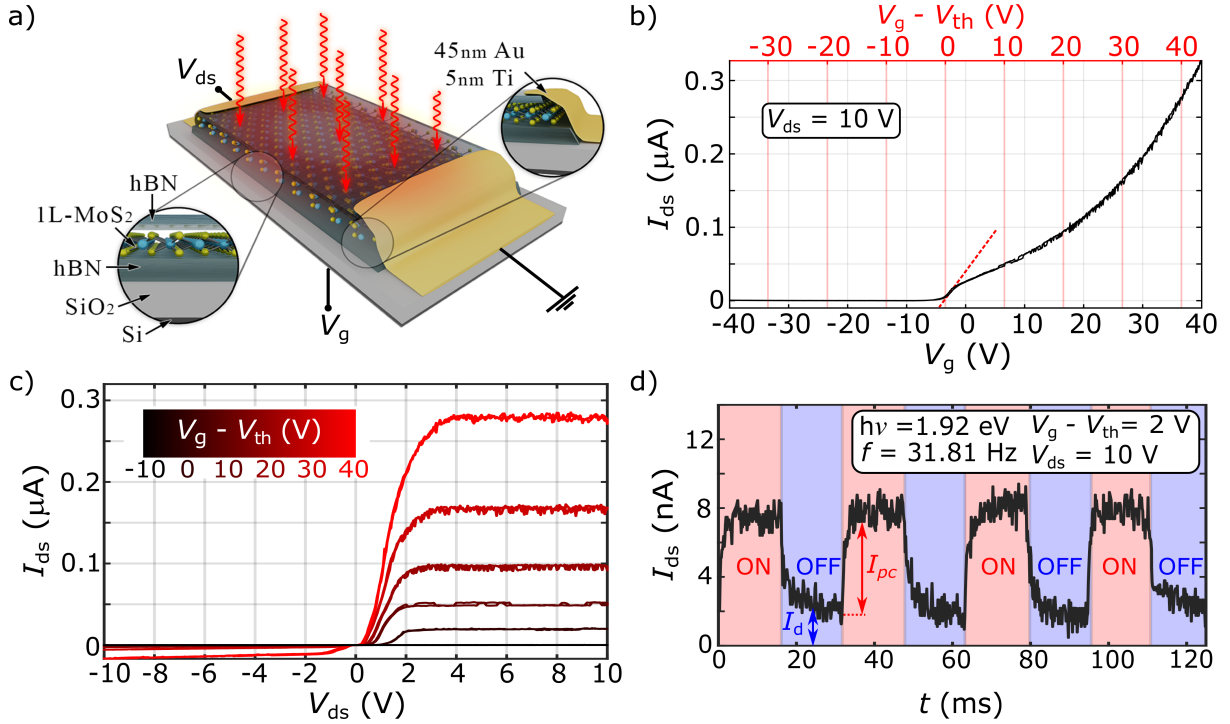


Fig. 6.2.1: Measurement configuration and characterization of the electric and optoelectronic of the 1L-MoS₂ phototransistor at 5K. a) Schematic of the hexagonal boron nitride (h-BN) encapsulated MoS₂ phototransistor with edge contacts. Insets detail contact geometry and the 2D channel. The device is exposed to monochromatic illumination for optoelectronic measurements. b) Gate transfer characteristic at $V_{ds} = 10 \text{ V}$, indicating n-type behavior with $V_{th} = -4 \text{ V}$, estimated from I_{ds} linear region (red dashed line). c) Device I - V characteristics at different gate voltages. d) Drain-source current at $V_{ds} = 10 \text{ V}$ and $V_g - V_{th} = 2 \text{ V}$, showing a 6 nA increase due to light excitation ($h\nu = 1.92 \text{ eV}$).

6.3 Photocurrent spectroscopy in monolayer MoS_2

Figure 6.3.1 illustrates the low-temperature photocurrent spectrum of the 1L- MoS_2 phototransistor, measured at 5 K, $V_g - V_{th} = -20$ V and $V_{ds} = 10$ V. To optimize the signal-to-noise ratio, illumination was modulated at 31.81 Hz and the PC measured using a lock-in amplifier as described in the section 3.6, sweeping the illumination wavelength in 0.1 nm steps.

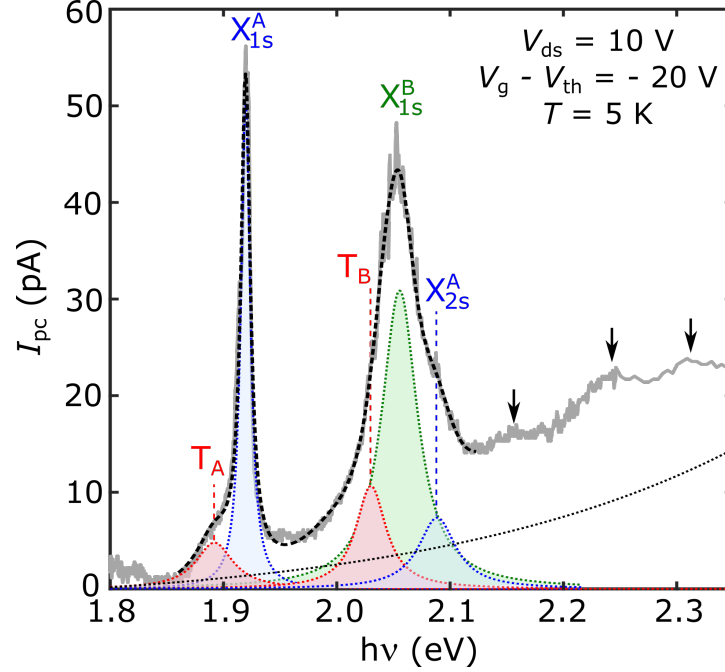


Fig. 6.3.1: Low-temperature photocurrent spectrum of the 1L- MoS_2 phototransistor (grey line) and the fitting to a multi-lorentzian peak function plus an exponential background (black dashed line). Below the spectrum, the Lorentzian peaks are displayed, detailing the neutral excitons X_{1s}^A and X_{1s}^B (shown in blue and green, respectively), charged trions T_A and T_B (in red), and the excited state X_{2s}^A (in blue) of the neutral exciton X_{1s}^A . Black arrows are used to highlight excitonic features occurring above the energy level of X_{2s}^A .

Photocurrent spectrum reveals two prominent peaks at 1.918 eV and 2.060 eV, corresponding to the A and B excitonic ground states (X_{1s}^A and X_{1s}^B) of 1L- MoS_2 , with a 142 meV energy splitting between them. Notably, the X_{1s}^A linewidth is remarkably narrow, 8 meV (FWHM), one order of magnitude lower than in previous studies [25, 26], and comparable to PL [161] indicating the exceptional quality of the 2D semiconductor channel and the power of low temperature PCS as experimental spectroscopy technique.

It is important to note that, unlike optical spectroscopy, PC spectral features manifest only if a specific optical transition alters photoconductivity. Therefore, the observation of neutral excitons requires an effective exciton dissociation mechanism. In TMD phototransistors, this dissociation is markedly enhanced near metal-semiconductor contacts due to strong electric fields giving a significant higher contribution to the photocurrent [167, 168, 169].

For the spectral range of 1.85 eV to 2.15 eV, the experimental PC spectrum closely fits a multi-peak Lorentzian plus an exponential background, that accounts for the direct interband absorption edge. A quintuple Lorentzian function, with two main (X_{1s}^A and X_{1s}^B) and three smaller peaks at 1.892 eV, 2.035 eV, and 2.090 eV, best replicates the spectral profile. The smaller features are attributed to the A and B trion states, (T_A and T_B), placed 20–30 meV below X_{1s}^A and X_{1s}^B . Trions are quasiparticles that can possess either negative or positive charges, depending on the sign of the excess carriers present in the semiconductor (electrons or holes). Given the strong n-doping of the MoS₂ channel, these T_A and T_B features likely represent negatively charged trions.

The 2.090 eV feature is tentatively identified as the first excited Rydberg state of the A exciton, X_{1s}^A , corroborated by low-temperature micro-reflectance and transmission spectroscopy works [144, 145]. Additional spectral features above 2.1 eV, marked by arrows in figure 6.3.1, are associated with the Rydberg series of excited states of X_{1s}^A and X_{1s}^B .

Despite the relative weakness of the T_A , T_B , and X_{2s}^A , these features are consistently replicated in multiple spectra at various gate voltages. These features become more prominent when V_g increases, raising the E_F above the conduction band edge, as it is possible to observe in section 6.3.2.

6.3.1 Effect of temperature in photocurrent spectroscopy

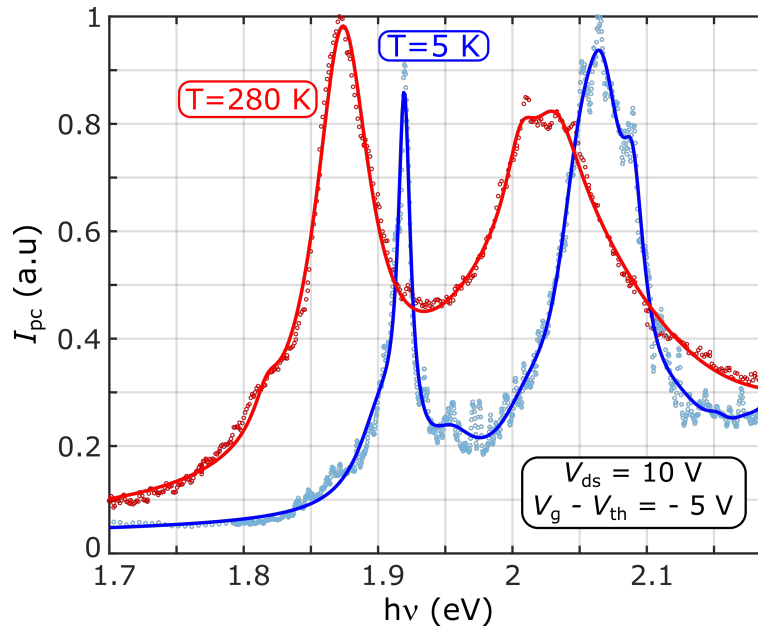


Fig. 6.3.2: Photocurrent spectra of the 1L-MoS₂ phototransistor at $T = 280$ K (red line) and $T = 5$ K (blue line) measured at voltage conditions of $V_g - V_{th} = -5$ V and $V_{ds} = 10$ V.

Now, we analyze the effect of the thermal energy in the photocurrent spectra of our device. Figure 6.3.2) displays the photocurrent spectra of the 1L-MoS₂ phototransistor at $T = 280$ K and $T = 5$ K under similar electrical conditions, $V_{ds} = 10$ V and $V_g - V_{th} = -5$ V, highlighting two key differences. At 280 K, excitonic spectral features are red-shifted by 45 meV due to enhanced electron-phonon interactions [170]. Also, thermal energy at this temperature causes peak broadening, yielding in a FWHM of 53 meV in X_{1s}^A at 280 K, about four times broader than at 5 K.

Reduction of T is critical to improve the spectral resolution of PCS, reaching optical transitions linewidths of few meVs giving the possibility of fully resolve different excitonic features.

6.3.2 Gate and drain-source voltage modulation of the spectral features

Having addressed the excitonic features in 1L-MoS₂ through low-temperature PCS, we now shift our focus to examine how these excitonic peaks are modulated by V_g and V_{ds} . Our initial analysis centers on the modulation effects of V_g on these peaks. As discussed previously, V_g controls the charge carrier density and the Fermi level, E_F , position. This is illustrated in figure 6.2.1 b), which depicts a pronounced n-type transistor behavior. As V_g is increased, E_F enters into the conduction band, leading to an increase in the electron density of the semiconductor channel.

Figure 6.3.3 a) depicts the I_{pc} as a function of $V_g - V_{th}$ under illumination with a photon energy $h\nu = 1.92$ eV, corresponding to the resonance with exciton X_{1s}^A . Notably, I_{pc} increases rapidly when $V_g > V_{th}$, while for $V_g < V_{th}$, the photocurrent almost vanishes. This observation is initially counterintuitive. Under conditions where $V_g < V_{th}$, the electronic states at the conduction band are expected to be depleted, increasing the probability of interband exciton absorption. Certainly, in absorption spectroscopy experiments, the signal typically maximizes when E_F is in the band gap and decreases at higher gate voltages, when the states in the conduction become populated, due to the Pauli blockade effect[84].

In our case, the underlying mechanisms of I_{pc} are more complex. Optical transitions result in observable changes in device conductivity, mainly through photoconductive or photogating effect. The reduction of I_{pc} observed at $V_g < V_{th}$ in our device implies a predominant photogating effect, as previously described in chapter 5. In this scenario, optically excited carriers decay to localized states within the 1L-MoS₂ bandgap, causing an E_F shift due to charge accumulation. A characteristic signature of the photogating effect is that the generated I_{pc} is proportional to the transconductance, $G = \frac{dI_{ds}}{dV_g}$, of the semiconductor channel. Figure 6.3.3 a) clearly presents this correlation, showing the transconductance of the transistor, measured in darkness at $V_{ds} = 10$ V, accurately following the V_g dependence of I_{pc} confirming the phenomena observed in chapter 5.

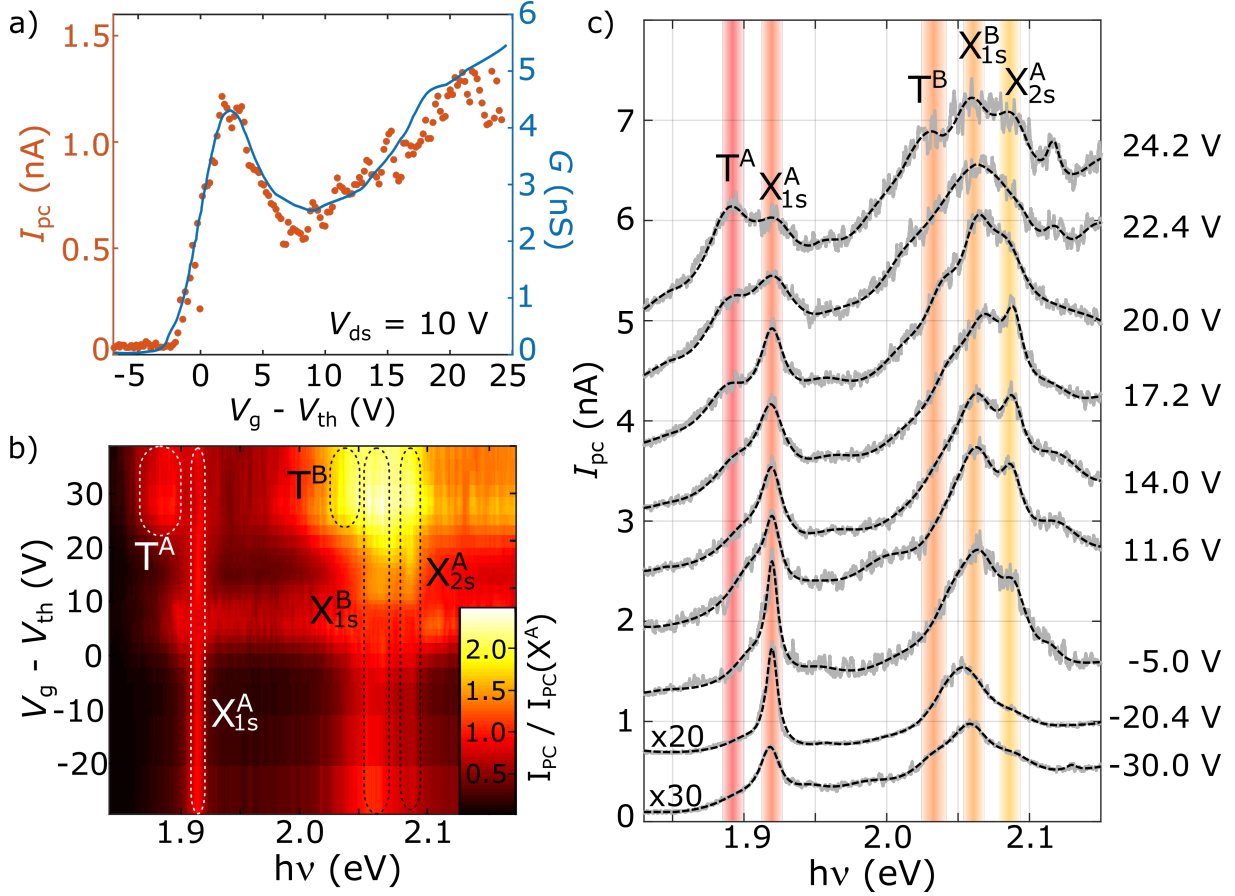


Fig. 6.3.3: Gate modulation of the measured photocurrent. a) Gate dependence of the transconductance of the device (right axis, cyan line) and of I_{pc} (left axis, orange line) measured at $V_{ds} = 10$ V in resonance with X_{1s}^A for $f=31.81$ Hz. b) colormap of the photocurrent, derived from spectra obtained across varying gate voltages, each normalized to the resonance with exciton X_{1s}^A ($h\nu = 1.92$ eV). c) individual spectra (grey line) for a range of $V_g - V_{th}$ between -30 V and 24.2 V, along with their Lorentzian fits (dashed black line). Main spectral peaks are highlighted for clarity (shaded lines) and the spectra are vertically shifted by 0.6 nA for visibility.

Following, we examine the impact of the level of doping on the spectral features using V_g to control the carrier density. We limit our analysis to the main five spectral lines previously discussed, with the higher-energy spectral features to be explored in the next section. Figure 6.3.3 b) presents a color map of I_{pc} as a function of the excitation energy and V_g . For each $V_g - V_{th}$, the I_{pc} data is normalized to the value at $h\nu = 1.92$ eV, in resonance with the X_{1s}^A transition. Here, the five excitonic features previously identified are evident, and their intensities vary significantly with $V_g - V_{th}$, as further illustrated in the individual spectra in figure 6.3.3 c). Notably, as $V_g - V_{th}$ increases, the trion transition intensifies, even surpassing the X_{1s}^A at $V_g - V_{th} = 24.2$ V. This modulation of X_{1s}^A and T_A spectral features has been observed in 1L-TMDs through various techniques like photoluminescence [171, 86], electroluminescence [160], and absorption spectroscopy [84]. Typically, the T_A feature is more pronounced when E_F exceeds the conduction band edge, because the excess of electrons enhances the possibility of formation of bound states between excitons and electrons. Similarly, the T_B transition also becomes more prominent as we increase V_g and the electron density raises in the conduction band.

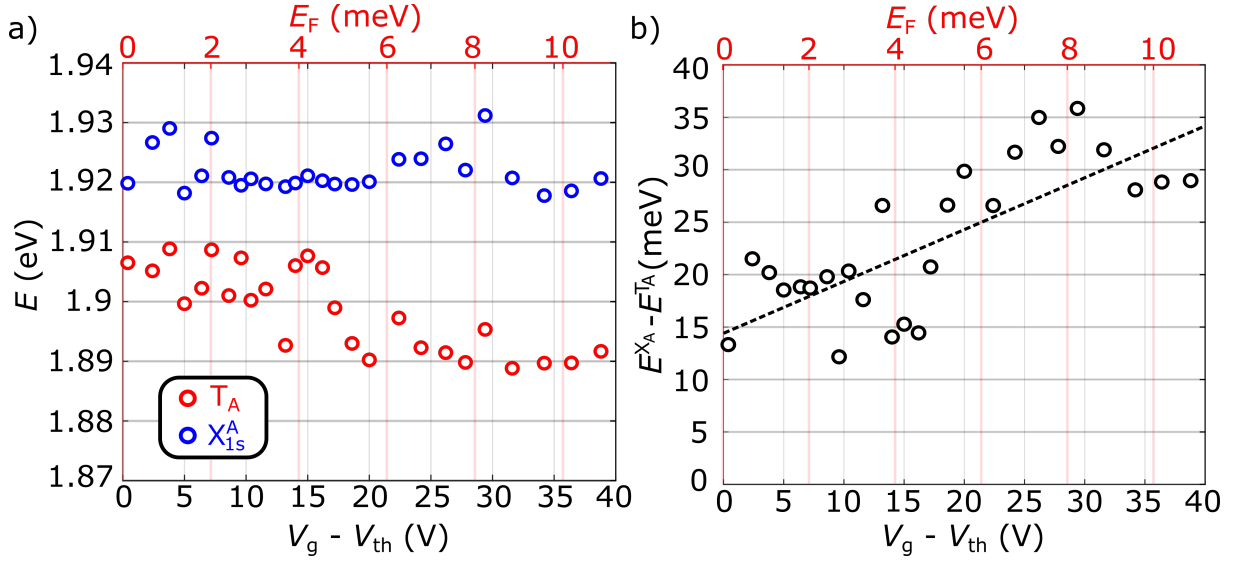


Fig. 6.3.4: Gate voltage modulation on X_{1s}^A - T_A splitting. a) Spectral positions of the X_{1s}^A (blue dots) and T_A (red dots) peaks, derived from multi-Lorentzian fits of the photocurrent spectra within a gate voltage range of $V_g - V_{th} = 0$ V to $V_g - V_{th} = 40$ V. The top axis denotes the corresponding E_F , relative to the conduction band edge. (b) Energy separation between the X_{1s}^A and T_A transitions (black dots) and the linear fitting of the data (black dashed lines).

Now, we focus on the energy position X_{1s}^A and T_A transitions. In the previous studies on 1L-TMDs have shown that applying a gate voltage $V_g > V_{th}$ leads to a greater energy separation between X_{1s}^A and T_A absorption peaks, showing a linear dependence with E_F . First, we need the relation between E_F and $V_g - V_{th}$ calculated in the previous chapter (see equations from 5.2.10 to 5.2.17), where we obtained the relation among $V_g - V_{th}$, E_F and n in our 1L-MoS₂ device. The relation between $V_g - V_{th}$ and E_F is

$$\Delta E_F = \frac{e}{1 + \frac{e^2 g_{2D}}{C_g}} (V_g - V_{th}) \quad (6.3.1)$$

where V_{th} is the threshold voltage at which $E_F = E_{CB}$. As seen in the previous chapter, we get $\Delta E_F / (V_g - V_{th}) = 0.28$ meV V⁻¹, which for the maximal gate voltages applied here $V_g - V_{th} = 50$ V gives $\Delta E_F = 14$ meV. Finally, the density of excess carriers, n can be obtained as $n = \Delta E_F \cdot g_{2D} = 7.17 \times 10^{10}$ cm⁻² V⁻¹ ($V_g - V_{th}$). Thus, the maximal carrier densities reached here are of $n = 3.58 \times 10^{12}$ cm⁻².

Once we have the relation between E_F and $V_g - V_{th}$, we analyze the position of the excitonic transitions X_{1s}^A and T_A as a function of the fermi energy. Figure 6.2.4 b) illustrates the exciton-trion energy splitting. In the voltage range from $V_g - V_{th} = 0$ V to $V_g - V_{th} = 40$ V, corresponding to a $\Delta E_F \approx 11$ meV, the exciton-trion splitting is observed to increase by approximately 15 meV, aligning with findings from ref. [84]. However, our

measurements reached Fermi energies only up to 14 meV, due to leakage problems in our sample, considerably less than the 50 meV observed in [84], leading to a less pronounced observation of this effect. Even the effect is less pronounced, the trend of the splitting between X_{1s}^A and T_A is clear as denoted by the linear fitting performed, confirming T_A as a negatively charged trion in accordance with the modulation of the spectral features intensity previously presented. In chapter 7, we analyze in deep this effect in a 1L-MoSe₂ encapsulated sample, performing a comprehensive characterization using low temperature photocurrent spectroscopy modulating V_g .

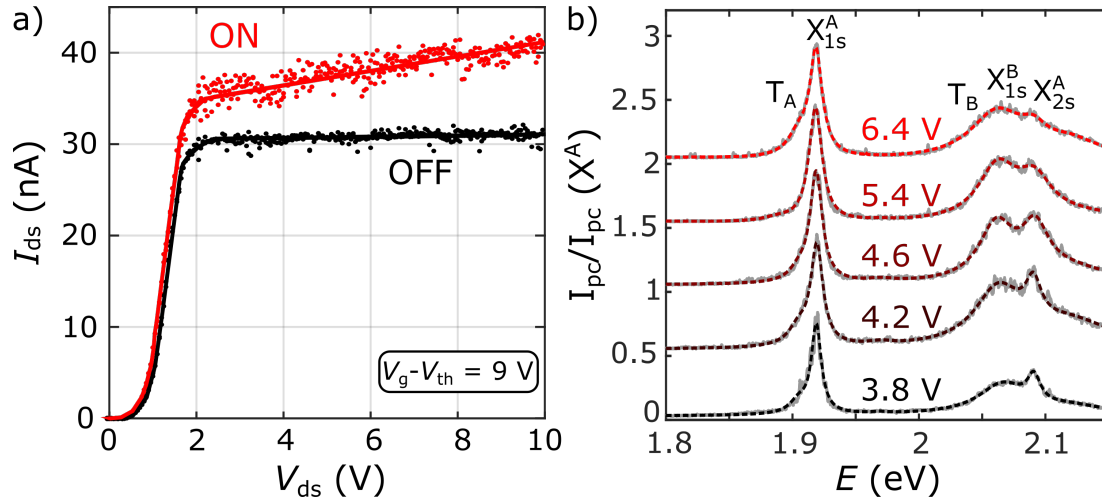


Fig. 6.3.5: Influence of the drain-source voltage in the photocurrent. a) $I - V$ curves of the 1L-MoS₂ phototransistor measured in the dark and under optical excitation on resonance with the X_{1s}^A transition. b) Photocurrent spectra measured at different V_{ds} normalized to the value of $I_{pc}(X_{1s}^A)$

Now we turn on the analysis of the influence of V_{ds} in the photocurrent spectra. Figure 6.3.5 a) displays two $I - V$ characteristics for the same gate voltage, comparing the 1L-MoS₂ device in darkness and under light in resonance with the X_{1s}^A transition. The light exposure effect is similar to an increase in V_g , aligning with the expected behaviour when the current is generated by the photogating effect. Notably, beyond a certain saturation current ($V_{ds} \approx 1.7$ V), the photocurrent stabilizes, differing from the expected increase. Figure 6.3.5 b) presents photocurrent spectra, normalized to I_{pc} measured in X_{1s}^A transition, at $V_g - V_{th} = 9$ V for different V_{ds} , showing that the relative strength of X_{1s}^B and T_B features changes with V_{ds} , with T_B increasing at higher voltages. This behaviour is also seen in X_{1s}^A and T_A features. Additionally, the changes in V_{ds} significantly influences the intensity of the X_{2s}^A peak, which is notably stronger at lower voltages. This effect likely arises from the lower binding energy of this excited state, requiring less ionization energy to contribute to the photocurrent.

6.3.3 Rydberg series of neutral excitons

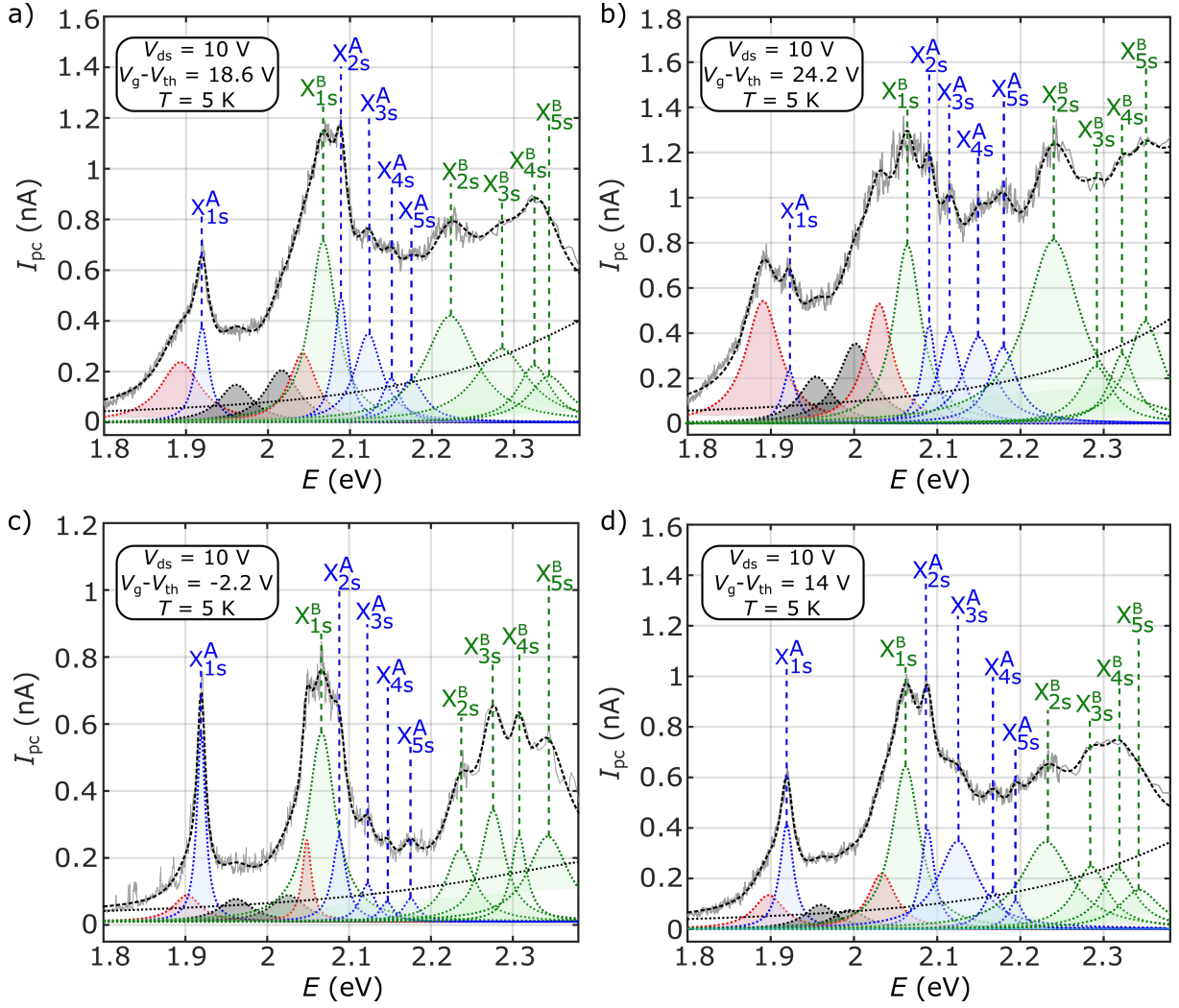


Fig. 6.3.6: Photocurrent spectroscopy of excited Rydberg states at different gate voltages. Panels a), b), c) and d) show photocurrent spectra at $V_g = 18.6, 24.2, -2.2, 14$ V respectively. Experimental data (gray line) are fitted to a multiple-peak Lorentzian plus an exponential background (black, dashed line). The individual Lorentzian functions in blue and green correspond to Rydberg series of excitons A and B respectively. Peak positions of the experimental data observed across different gate voltages fluctuates by up to 6 meV.

As mentioned before, different spectral features appear in the photocurrent spectra at energies above 2.1 eV. We now turn on the study of these excitonic states that are associated to excited states of the neutral excitons, commonly denoted as Rydberg states due to the similarity between an exciton and a hydrogen atom.

Figure 6.3.6 displays photocurrent spectra under different gate voltages, $V_g - V_{th} = 18.6, 24.2, -2.2, 14$ V, at 5 K with a $V_{ds} = 10$ V, revealing consistent appearances of Rydberg excited state peaks across different spectra. Besides, the peaks related to X_{1s}^A , X_{1s}^B , T_A , and T_B , there are eight additional peaks, tentatively identified as part of the Rydberg

series of X^A and X^B excited states, as labeled in the figure. It is important to note that only s-type transitions, being dipole-allowed, are observable in linear photocurrent spectra [172]. Therefore, our analysis will focus exclusively on these s states. It is remarkable that the intensities of these peaks exhibit complex variations with $V_g - V_{th}$. Additionally, minor shifts in peak maxima positions are observed across different voltages, possibly due to changes in electrostatic screening from conduction-band electrons and neighbouring environment. Remarkably, at higher $V_g - V_{th}$, these excited states become increasingly pronounced relative to the fundamental states.

To confirm these spectral assignments, we use an effective-mass theory for excitons in 2D-TMDs [173]. We resolve numerically the effective-mass Schrödinger equation for the radially symmetric exciton states, denoted as ns , to determine their energy levels, E_n .

$$H\Psi_{ns}(r) = (E_n - E_g)\Psi_{ns}(r) \quad (6.3.2)$$

where E_g corresponds with the quasiparticle bandgap and H is the hamiltonian of the system written for the radial coordinate $r = |\mathbf{r}_e - \mathbf{r}_h|$

$$H = -\frac{\hbar}{2\mu} \frac{d^2}{dr^2} + V(r) \quad (6.3.3)$$

For the effective masses of X^A and X^B excitons, we adopt values of $\mu_A = 0.27m_0$ [145] and $\mu_B = 0.27m_0$ [173] respectively, with m_0 being the free electron mass. In the context of thin semiconductor layers, the interaction between electrons and holes, denoted as $V(r)$, deviates from a simple Coulomb potential due to significant nonlocal screening effects from the surrounding environment. Consequently, a more accurate representation of the electron-hole interaction in these environments is provided by the Keldysh potential [174]

$$V(r) = -\frac{\pi e^2}{2r_0} \left[H_0 \left(\frac{\kappa r}{r_0} \right) - Y_0 \left(\frac{\kappa r}{r_0} \right) \right] \quad (6.3.4)$$

In this context, H_0 and Y_0 represent the zero-order Struve and Bessel functions, respectively, while κ denotes the dielectric constant of the embedding medium, which is h-BN in our study, and the parameter r_0 , that is related with the screening length attributable to the 2D polarizability of the 1L-MoS₂. It is remarkable that at large distances ($r \gg r_0/\kappa$), the Keldysh potential converges towards the Coulomb potential, approximated as $V(r) \approx -e^2/\kappa r$. Conversely, at shorter distances ($r \ll r_0/\kappa$), the potential diverges logarithmically [175]. This behaviour allow us to properly describe the nature of the 2D excitons in TMDs, in contrast with the 2D hydrogenic model, that can be solved analitically giving an energy spectrum of the eigenstates

$$E_n = E_g - \frac{\mu e^4}{2\hbar^2 \kappa^2} \frac{1}{(n - 1/2)^2} \quad (6.3.5)$$

This model can describe properly high energy excited states with large radius but for low energy states where the radius is lower than the screening length the model fails (see figure 6.3.7 b)).

As discussed, nonlocal screening effect significantly influences in the energy levels, particularly of the lower energy states where the exciton radius is comparable to the screening length. This results in a logarithmic divergence when the electron and hole are in close proximity instead of the traditional $1/r$ Coulomb interaction. This characteristic behavior in thin semiconductors is typically analyzed through Keldysh approach [176]. The Keldysh potential describes properly the logarithmic divergences in the low energy excited states where $r < \approx r_0$, and the typical coulomb behaviour for high energy states $r \gg r_0$. Equation 6.3.2 for the potential in equation 6.3.4 can be diagonalized in terms of the adimensional coordinate $z = \kappa r/r_0$, leading in the effective mass equation

$$\left(-\frac{d^2}{dz^2} - u_0 f(z)\right) \psi_{ns}(z) = \epsilon_n \psi_{ns}(z) \quad (6.3.6)$$

being $u_0 = \pi\mu/m_0\kappa z_B$ and $\epsilon_n = (\mu/m_0 R_y z_B^2)(E_n - E_g)$ with $z_B = \kappa a_B/r_0$. z_B corresponds with the value of the dimensionless coordinate when the electron-hole separation equals the atomic Bohr radius $a_B = \hbar^2/e^2 m_0 = 0.0529$ nm and $R_y = e^4 m_0 / 2\hbar^2 = 13.605$ eV is the ionization energy of the ground state in the hydrogen atom.

We discretize the equation to solve it numerically, defining z_{max} as the highest value of the relative coordinate in the numerical solution of equation 6.3.6. A grid comprising $N + 1$ points equally space, is established, denoted by $z_l = lh$, where h is defined as z_{max}/N and $l = 0, 1, \dots, N$. For brevity, we express $f_l = f(lh)$ and $\psi_l^{(n)}$ as $\psi_{ns}(lh)$. Thus, the discretized representation of the effective-mass problem is

$$(2 - h^2 u_0 f_l) \psi_l^{(n)} - \psi_{l+1}^{(n)} - \psi_{l-1}^{(n)} = h^2 \epsilon_n \psi_l^{(n)} \quad (6.3.7)$$

with boundary conditions $\psi_0^{(0)} = \psi_0^{(N)} = 0$. Therefore, the problem simplifies to determining the eigenvalues of a real, symmetric and tridiagonal matrix, given the parameters E_g , κ and r_0 . After identifying the lowest eigenvalues, denoted as ϵ_n , the exciton energy levels are given by

$$E_n = E_g + \frac{m_0 z_B^2}{\mu} \epsilon_n R_y \quad (6.3.8)$$

Figure 6.3.7 a) displays the photocurrent spectrum of the 1L-MoS₂ device at 5 K, with a $V_{ds} = 10$ V and $V_g - V_{th} = 17.2$ V. Peaks of the Rydberg series are tentatively ordered as labeled in the figure and the energy positions are indicated in table 1. Figure 6.3.7 b) shows the experimental values of the spectral positions of the Rydberg series peaks and their quantum number, n , associated (empty triangles). To corroborate this labelling of the excited states we perform the fitting of the numerical solution of the keldysh model using E_g , κ and r_0 as free parameters. An initial estimation of E_g is obtained from the spectral positioning of highly excited states ($n > 2$). In these states, the exciton radius

is large, $r \gg r_0/\kappa$, and $V(r)$ approximates to $-e^2/\kappa r$, allowing their energy levels to be modeled by using a 2D hydrogenic Rydberg series. Doing a fitting using the dielectrical constant of the h-BN, $\kappa \approx 4.4$, we obtain $E_g^A = 2.203$ eV and $E_g^B = 2.387$ eV (black dashed lines). Then, we use these results as the initial values of the fitting to numerical solution of the Schrodinger equation with the Keldysh potential. Theoretical points calculated are depicted as filled dots and the fit reproduces accurately the experimental values and allows us to extract optoelectronic parameters of the device.

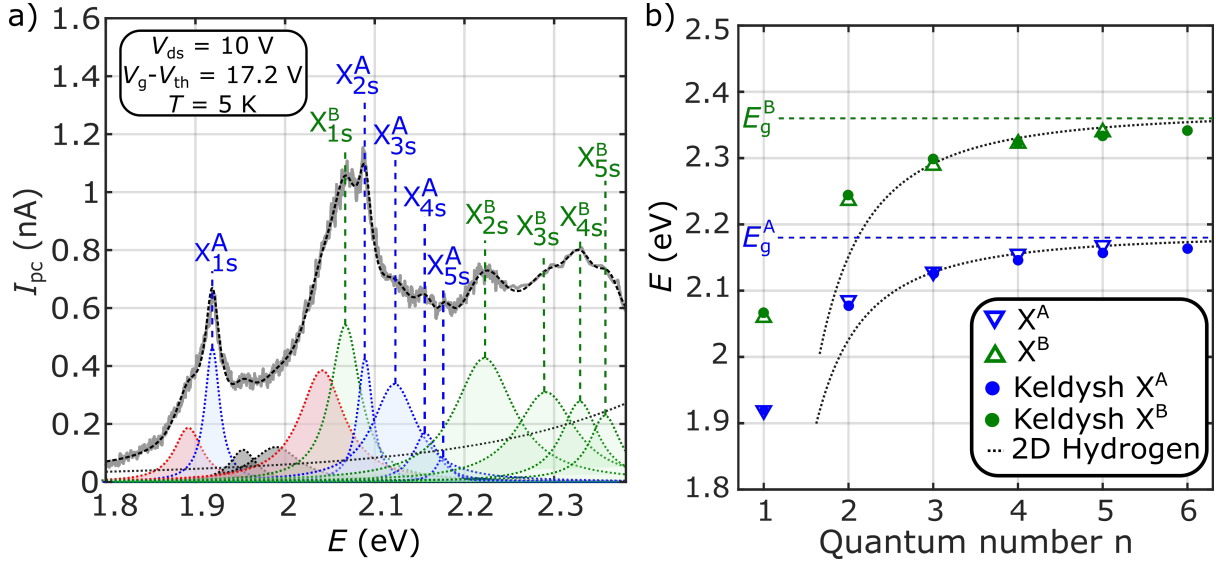


Fig. 6.3.7: Rydberg series of neutral excitons revealed by low temperature PCS. a) Photocurrent spectrum of the 1L-MoS₂ device (grey solid line) and the fit to multi-peak Lorentzian function (black dashed line). Individual Lorentzian functions corresponding with the Rydberg states of the neutral exciton X^A and X^B are depicted below the spectrum (blue and green peaks respectively). b) Experimental (empty triangles) and theoretical (filled circles) energy positions of the excitonic states. Theoretical points are calculated using the Keldysh potential as described in the text. Fits of higher energy states ($n > 2$) to a 2D hydrogen model (black dashed lines) are shown for comparison. The dashed horizontal lines represent the calculated quasiparticle bandgap values, $E_g^A = 2.18$ eV and $E_g^B = 2.36$ eV.

Table 1. Energy position of excited excitonic states in 1L-MoS₂ photocurrent spectrum

T_A	X_{1s}^A	T_B	X_{1s}^B	X_{2s}^A	X_{3s}^A	X_{4s}^A	X_{5s}^A	X_{2s}^B	X_{3s}^B	X_{4s}^B	X_{5s}^B
E (eV)	1.892	1.919	2.041	2.067	2.089	2.127	2.161	2.172	2.231	2.298	2.349

The fitting results, summarized in Table 2, indicate a quasiparticle bandgap of 2.18 eV for the X^A Rydberg series, in a good correlation with measurements using high-magnetic-field absorption spectroscopy on h-BN encapsulated MoS₂ [145]. The dielectric screening parameters obtained are $r_0^A = 3.05$ nm and $\kappa = 4.4$, consistent with previous studies on h-BN encapsulated samples [144, 145]. Binding energy of X_{1s}^A is calculated as $E_b^A = E_g^A - E_{1s}^A$, resulting in E_b^A , in good agreement with micro-reflectance spectroscopy

measurements [144, 145].

For the X^B Rydberg series, limited literature exists, especially for h-BN encapsulated samples. Hill et al. [94] reported the observation of X^B excited states in 1L-MoS₂, estimating an $E_g^B = 2.47$ eV and an exciton binding energy of ≈ 440 meV. Our findings suggest $E_g^B = 2.36$ eV and an exciton binding energy $E_b^B = 290$ meV, remarkably lower.

Finally, using E_g^A and E_g^B , we estimate the MoS₂ valence band splitting ΔE_{VB} . Assuming a conduction band splitting of $\Delta E_{CB} \approx 15$ meV[177, 178], ΔE_{VB} is estimated to be 165 meV, slightly higher than recent ARPES measurements on epitaxial 1L-MoS₂ on gold ($\Delta E_{VB} = 145 \pm 4$ meV)[179]. Using E_g^B from [94] would result in an even larger value $\Delta E_{VB} \approx 275$ meV.

Table 2. Fundamental optoelectronic material parameters of encapsulated 1L-MoS₂

	E_b^A (meV)	E_b^B (meV)	E_g^A (eV)	E_g^B (eV)	r_0^A (nm)	r_0^B (nm)	κ
Goryca et al.[145]	221		2.16		3.40		4.45
Robert et al.[144]	222				2.95		
Hill et al.[94]		440		2.47			
This work[180]	261	290	2.18	2.36	3.05	2.70	4.4

6.4 Conclusions

In this chapter, we have demonstrated that low-temperature PCS is a powerful tool to fully resolve excitonic features, reaching linewidths down to 8 meV (FWHM). This technique is advantageous as it does not require the use of a microscope objective to concentrate the light beam on a small area of the sample ($\approx 1 \mu\text{m}^2$), to avoid peak broadening like in PL or optical spectroscopy methods. The contributing part to the PCS spectrum is instead determined by the spacing between the device drain and source contacts, allowing to illuminate the whole device, largely simplifying both the experimental setup and the process of optical alignment.

Low temperature PCS has allowed us to study spectral features that are typically elusive in PL spectroscopy due to their relatively low PL emission intensity. Remarkable, we could measure the gate voltage modulation of the X_{1s}^A and T_A transitions, well-documented in PL, and extended this to include the X_{1s}^B and T_B transitions, which to our knowledge, was not previously reported.

Moreover, using low temperature PCS we have clearly revealed the excited Rydberg series of X^A and X^B , up to $n = 5$. While similar excitonic features have been observed in earlier experiments using PL spectroscopy, PL emission, and micro-reflectance[94, 144, 181], as well as predicted in theoretical studies [182, 172, 173, 183], these experiments generally revealed excited states of either X^A or X^B Rydberg series, but not both. The PC spectra

in this chapter shows excited states of both X^A and X^B , providing a more comprehensive understanding and constraining the possible spectral assignments reducing possible mistakes.

Additionally, our theoretical analysis using an effective mass model to address the quantum number of the rydberg series has allowed us to obtain optoelectronic material parameters for encapsulated 1L-MoS₂ that align well with both theoretical and experimental literature, further supporting our peak assignments. With PCS, we have also estimated the valence band splitting of 1L-MoS₂, a measurement not previously calculated by the measurement of simultaneous rydberg series of X^A and X^B , obtaining a value of $\Delta E_{VB} = 165$ meV. This result is in close agreement with earlier theoretical works, which suggest a ΔE_{VB} range of 140-170 meV [184, 51], and a slightly lower value measured by ARPES for epitaxial 1L-MoS₂ on gold [179]. Nevertheless, the discrepancy in the value could be explained by the effect of enhanced screening by the gold substrate[182].

In conclusion, low temperature PCS is a promising and yet underused tool to characterize the optoelectronic and excitonic properties of 2D materials [180]. The diversity of excitonic features measured in this chapter highlight the potential of this technique as a good tool compared to other spectral methods, as we demonstrate in the following chapters of this dissertation.

Chapter 7

Excitonic features and gate voltage modulation of the low-temperature photocurrent spectrum in monolayer MoSe₂

In this chapter, we continue with the characterization of the spectral photoresponse of 2D transition metal dichalcogenides (TMDs) using low temperature photocurrent spectroscopy studying a phototransistor based on monolayer MoSe₂ encapsulated in h-BN.

As mentioned in chapter 6, the spectral response characterization of 2D-TMDs has been performed via photoluminescence, absorption or electroluminescence spectroscopy. Nevertheless, there was a lack of work in the literature where the spectral optoelectronic response of a device of MoSe₂ is characterized.

In the following, we investigate the optoelectronic response of exciton transitions in encapsulated monolayer MoSe₂. We successfully identified spectral features corresponding to the main exciton and trion transitions, achieving spectral bandwidths as low as 15 meV. We also explore the Fermi level influence in the position and intensity of these excitonic spectral features, confirming that the splitting between a neutral exciton and the trion associated depends linearly of the Fermi level. This allows us to find values of the band effective mass of electrons and trion binding energies in 1L-MoSe₂. Notably, we found a major change in the photocurrent, even changing the sign when the Fermi level crosses the charge neutrality point. These findings confirm the potential of low-temperature photocurrent spectroscopy in the study of excitons in low-dimensional materials, providing new insights into excitonic transitions in monolayer MoSe₂.

7.1 Introduction

In this chapter, we study the spectral photoresponse of a high-quality MoSe₂ monolayer phototransistor using low-temperature photocurrent spectroscopy (PCS). We identify the main exciton (X_{1s}^A and X_{1s}^B) and trion (T_A and T_B) transitions in 1L-MoSe₂, achieving spectral bandwidths down to 15 meV. Additionally, we examine how the photoresponse evolves with changes in the position of the Fermi energy, E_F . A remarkable observation is the significant modulation of the photocurrent, which even shifts from positive to negative as the Fermi level nears the valence band edge. We also observe a large modulation of the spectral positions of X_{1s}^A and T_A that allows us to confirm the large effective band mass of MoSe₂, compatible with recent studies [185], using many body theory [186]. In the case of T_A we observe an abrupt change in the position, denoting a change of the dominant trion species as the photocurrent signs change from positive to negative.

7.2 Electrical characterization of the device

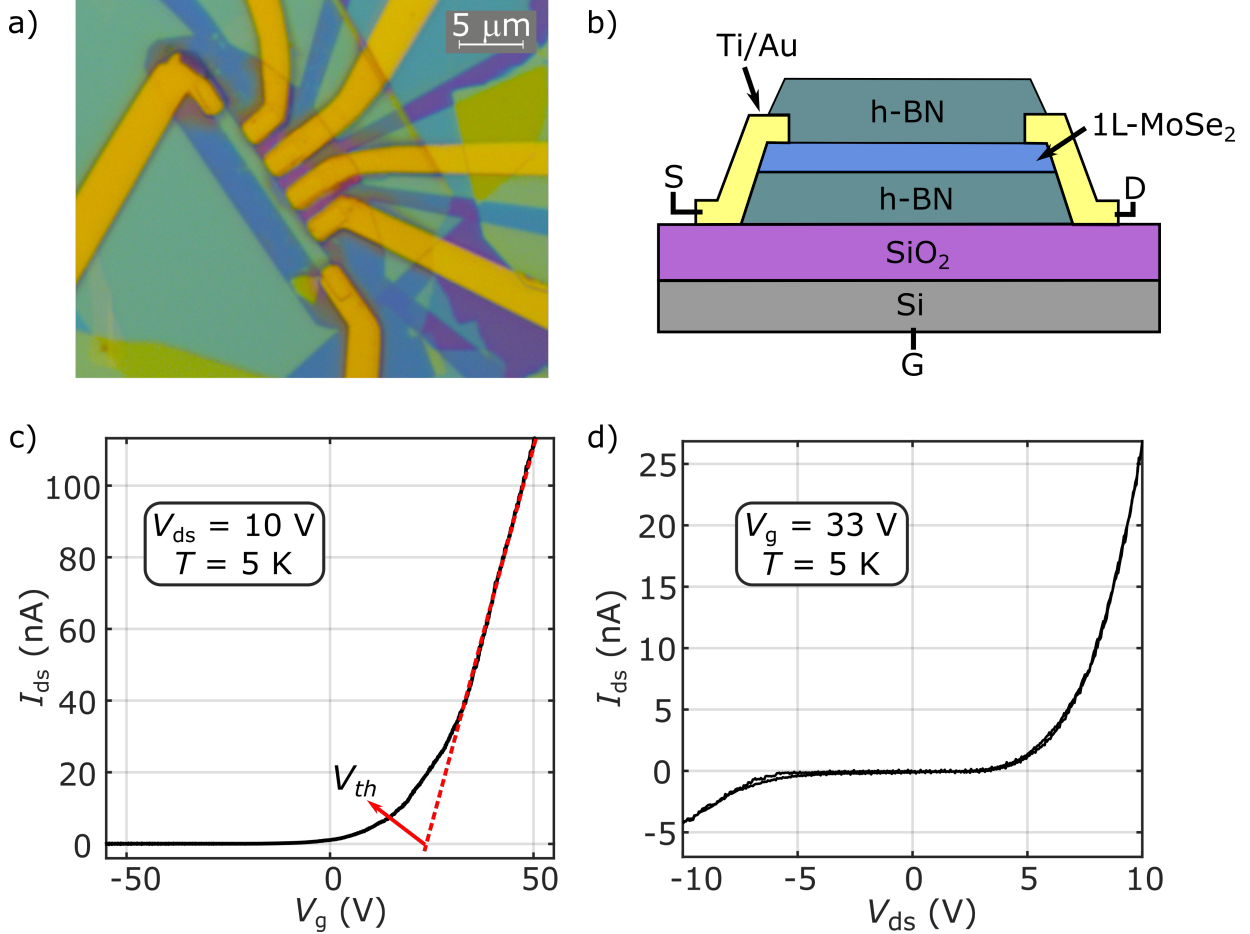


Fig. 7.2.1: Electrical characterization of the monolayer MoSe₂ phototransistor. a) Optical microscopy image of hBN-MoSe₂-hBN transistor. b) Schematic drawing of the device with the source, drain and gate contacts highlighted. c) Gate transfer characteristic at $V_{ds} = 10$ V, indicating n-type behavior with $V_{th} = 23$ V, estimated from the linear part of I_{ds} (red line). d) Device I - V characteristic at $V_g = 33$ V ($V_g - V_{th} = 10$ V).

We start the characterization examining the electrical properties of the device. All measurements, unless stated otherwise, were carried out in vacuum and at $T = 5$ K. Figure 7.2.1 a) shows an optical microscope image of the h-BN encapsulated 1L- MoSe_2 device. We fabricate the sample via mechanical exfoliation of the h-BN flakes on SiO_2 and 1L- MoSe_2 using PDMS. In contrast with the 1L- MoS_2 presented in chapters 5 and 6, with a 1D-edge contact geometry, in MoSe_2 we use a planar contact geometry of Ti/Au prior the total encapsulation of the with the top h-BN. More details of the fabrication of this device are in chapter 3. Figure 7.2.1 b) depicts an schematic of the geometry of the device and the measurement configuration, we apply a V_{ds} between two contacts and the V_g through the Si/ SiO_2 substrate. Figure 7.2.1 c) displays the gate transfer curve of the 1L- MoSe_2 phototransistor with $V_{ds} = 10$ V, revealing clear n-type behaviour and a threshold voltage of $V_{th} = 23$ V. Figure 7.2.1 d) shows $I - V$ characteristic at a fixed V_g of 33 V ($V_g - V_{th} = 10$ V), showing a nonlinear response attributed to asymmetric Schottky barriers at the contacts. Both measurements exhibit minimal hysteresis.

7.3 Photocurrent spectroscopy in monolayer MoSe_2

Subsequently, to study the spectral photoresponse of the device, we illuminate the entire device with a tunable monochromatic light source using the spectroscopy setup developed during this thesis, described in chapter 3.6. We modulate the illumination with an optical chopper at a frequency of $f = 31.81$ Hz and the photocurrent I_{pc} is registered with a lock-in amplifier while the monochromator sweeps in steps of 0.2 nm.

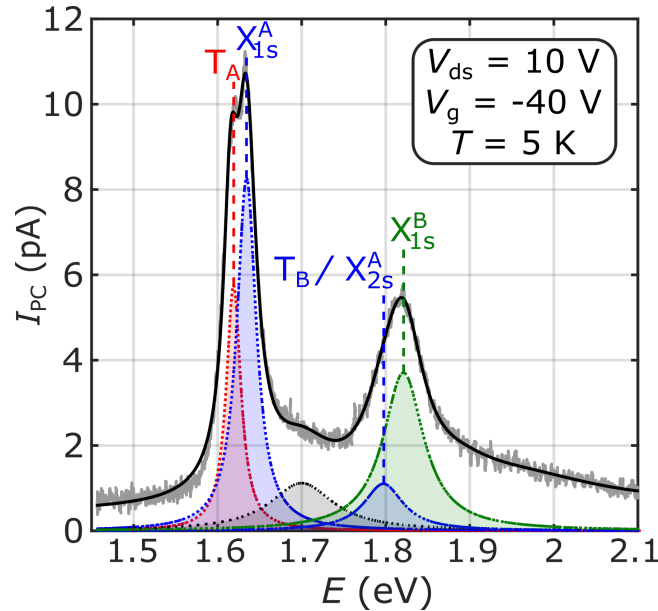


Fig. 7.3.1: Low-temperature photocurrent spectrum of the 1L- MoSe_2 phototransistor (grey line) and the fitting to a multi-lorentzian peak function plus an exponential background (black dashed line). Below the spectrum, the Lorentzian peaks are displayed, detailing the neutral excitons X_{1s}^A and X_{1s}^B (shown in blue and green, respectively), charge trion T_A (in red), and the excited state X_{2s}^A of the neutral exciton X_{1s}^A or T_B (in blue).

Figure 7.3.1 shows a characteristic photocurrent spectrum of the 1L- MoSe_2 phototransistor, measured at $V_{\text{ds}} = 10$ V and $V_g = -40$ V ($V_g - V_{\text{th}} = -63$ V). Photocurrent spectrum is well fitted using a multi-peak Lorentzian function. We observe three primary sharp spectral peaks at 1.616 eV, 1.634 eV, and 1.822 eV, along with two smaller features at 1.799 eV and 1.705 eV. The peaks at $E = 1.634$ eV and $E = 1.822$ eV align with the A and B excitonic ground states (X_{1s}^A and X_{1s}^B) of 1L- MoSe_2 [145]. The peak at $E = 1.616$ eV, located 19 meV below X_{1s}^A , is consistent with the A trion transition T_A [93]. The feature at $E = 1.799$ eV can be attributed to the B trion transition T_B , but it could also include a component from the first excited Rydberg state of the A exciton, X_{2s}^A . The origin of the final feature at 1.705 eV remains uncertain, as it is not observable in the typical low-temperature PL spectroscopy features for 1L- MoSe_2 . However, a similar exciton-like feature between the X_{1s}^A and X_{1s}^B transitions is observed in PCS measurements in chapter 6 for the h-BN encapsulated 1L- MoSe_2 device. This transition might be a nonradiative interlayer exciton formed at the 1L- MoSe_2 and h-BN interface. As we will discuss further in the next sections, these spectral features appear consistently across various spectra at different values of V_g .

7.3.1 Gate modulation of the photocurrent

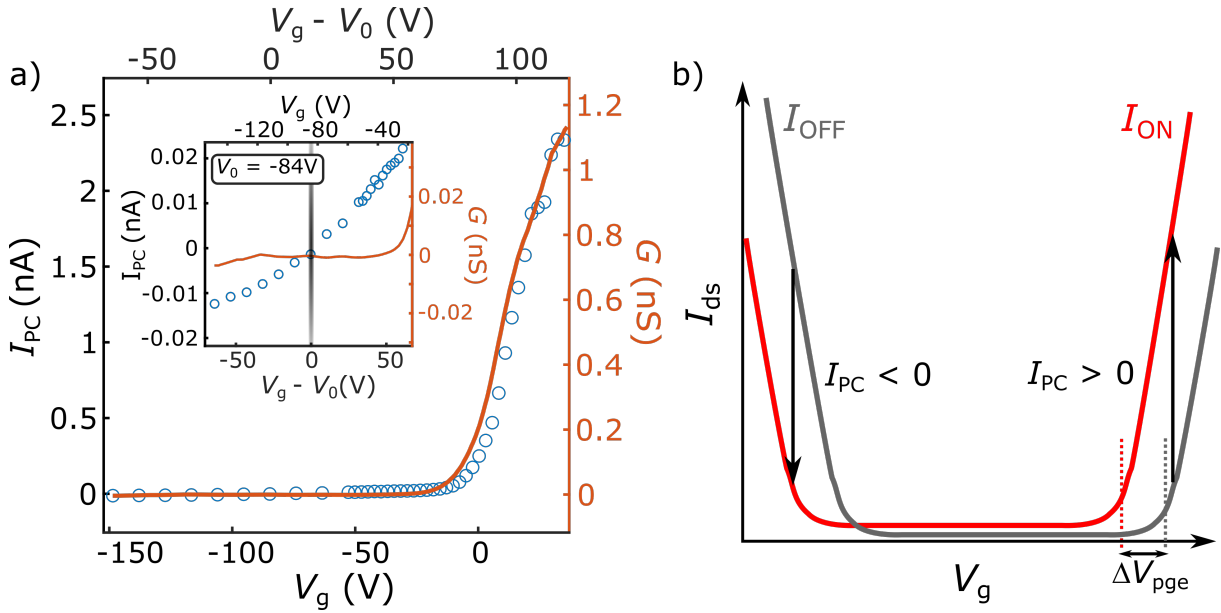


Fig. 7.3.2: Gate dependence of the observed photocurrent. a) Transconductance of the device (orange line, right axis) and gate dependent photocurrent measured at $V_{\text{ds}} = 10$ V, in resonance with the exciton X_{1s}^A transition, at a modulation frequency of $f = 31.81$ Hz. The inset shows a zoom in of the region where the channel is closed. b) Schematic gate ramps of an ambipolar transistor, under illumination and no illumination. The contribution photoresponse of ΔV_{pge} is depicted in the plot.

Now, we analyze the V_g dependence of the device photoresponse. As studied in deep in chapter 5, in TMD-based phototransistors, the photocurrent generation stems from two mechanisms, the photoconductive (PCE) and the photogating (PGE) effects

[140, 164, 187]. These mechanisms are distinguishable by their different dependences with V_g . Specifically, I_{pc} generated from PCE shows a weak dependence on V_g , while PGE-generated I_{pc} is proportional to the transconductance $G = \frac{dI_{\text{ds}}}{dV_g}$, exhibiting a more pronounced V_g dependence.

Figure 7.3.2 a) displays the V_g influence on the generated I_{pc} in the 1L- MoSe_2 phototransistor illuminated with energy in resonance with X_{1s}^A ($E = 1.634$ eV). Above the threshold voltage for the electrons side, $V_{\text{th,e}}$, I_{pc} is proportional to the transconductance of the device, indicative of a dominant PGE. Intriguingly, a small photocurrent persists even when V_g is less than $V_{\text{th,e}}$ and the transconductance approaches zero. The inset in figure 7.3.2 a) zooms into the regime where the device channel is closed, showing the current stabilizing around 10 pA, and I_{pc} decreasing as V_g is reduced, eventually vanishing at $V_g \approx -84$ V. Below this voltage, the photocurrent becomes negative, indicating increased resistivity upon illumination. We infer that $V_g \approx -84$ V, the point where the photocurrent changes sign, corresponds to the charge neutrality point of the 1L- MoSe_2 channel, V_0 .

The negative photocurrent regime observed for $V_g < -84$ V is attributable to the dominance of PGE. Figure 7.3.2 b) schematically represents a typical transfer gate ramp in an ambipolar TMD transistor under dark (OFF) and illuminated (ON) conditions. With the Fermi level in the semiconductor band gap, I_{ds} drops to zero due to the lack of free carriers. When gate voltage reaches the threshold voltages $V_{\text{th,e}}$ ($V_{\text{th,h}}$), I_{ds} surges as electrons (holes) fill the conduction (valence) band. Illumination can cause photoexcited carriers to accumulate in localized states within the bandgap, shifting the Fermi energy and causing a horizontal displacement ΔV_{pge} in the transfer $I - V$ curve. I_{pc} generated by this mechanism is given by

$$I_{\text{pc}} = \Delta V_{\text{PGE}} \frac{dI_{\text{ds}}}{dV_g} \quad (7.3.1)$$

where, ΔV_{pge} can be either positive or negative, depending on if the localized states contributing to PGE are electron acceptors or donors. For 1L- MoSe_2 phototransistors, ΔV_{pge} is typically positive [188], as reflected in the schematic from figure 7.3.2 b). Regarding the transconductance G , its sign varies with V_g , being positive when E_F is near the conduction band and negative near the valence band. Therefore, at V_g close to the valence band threshold, PGE is likely to produce a negative photocurrent, as confirmed by our experimental observations.

7.3.2 Gate dependence of the spectral features

After the analysis of the photocurrent dependence with V_g , we now study the variation of the photocurrent spectra and the excitonic features described previously. For consistency we measure the off-current ($I_{\text{ds}}^{\text{off}}$) of the device before every spectral acquisition, and we present the gate-dependent spectra as a function of $V_g - V_0$. Measurement of $I_{\text{ds}}^{\text{off}}$ allows us to compare the data with the off transfer curve of the device and verify that the photodoping effects are negligible in this configuration.

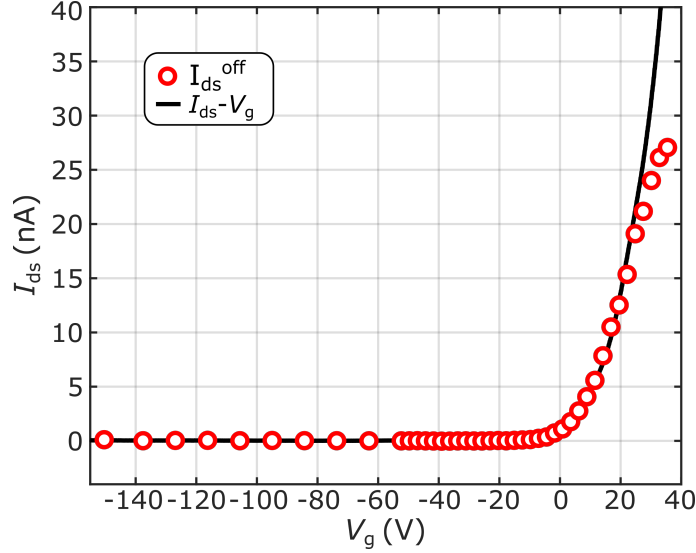


Fig. 7.3.3: Comparison between the off transfer curve of the device (black solid line) and I_{ds} measured before the exposure of the device to the wavelength tunable light source to perform the photocurrent spectroscopy measurements (white and red dots).

Figure 7.3.3 shows the comparison between $I_{\text{ds}}^{\text{off}}$ and the off transfer curve of the device for different V_g , confirming the low influence of the photodoping in the photocurrent spectra. Figure 7.3.4 a) presents the photocurrent spectra at a constant $V_{\text{ds}} = 10$ V across various gate voltages. Consistent with earlier discussion, I_{pc} changes of sign as the gate voltage decreases. The four key spectral features identified earlier (T_A , X_{1s}^A , X_{1s}^B , and T_B X_{2s}^A , as seen in figure 7.3.1) appear consistently in the different spectra. However, V_g influences both the position and intensity of these features. Similar observations regarding the V_g -dependent shifts of excitonic features have been previously reported in PL studies of monolayer TMDs like MoS_2 [144] and WSe_2 [87].

Now, we turn our attention to the evolution of the spectral energy positions X_{1s}^A and T_A with $V_g - V_0$ and E_F . To obtain the relation between these magnitudes we follow a similar procedure to the one explained in chapter 5, from equations (5.2.11) to (5.2.17), where using the quantum capacitance we deduce

$$\Delta E_F = \frac{e}{1 + \frac{e^2 g_{2D}}{C_g}} (V_g - V_0) \approx \frac{C_g \pi \hbar^2}{2e^2 \mu_{eff}} (V_g - V_0) \quad (7.3.2)$$

In this device, the effective mass is $\mu_{eff} = 0.8m_0$ [185] and capacitance of the device with a bottom h-BN of 15 nm is $C_g = 12.53$ nF/cm², yielding in a relation between $V_g - V_0$ and E_F of $E_F / (V_g - V_0) = 0.117$ meV/V.

Figure 7.3.4 b) displays the energy positions of both transitions as function of the $V_g - V_0$ and E_F . We observe that the energy position of the T_A transition experiences an abrupt shift at V_0 , as the sign of I_{pc} inverts. This type of energy shift in the T_A feature for 1L- MoSe_2 , has been observed in previous literature [86, 189], being related to the existence

of two trion species, positively charged (T_A^+) and negatively charged (T_A^-). Modulating $V_g - V_0$ the population of free charged carriers in the 1L- MoSe_2 channel is tuned increasing the amount of holes or electrons, therefore affecting the formation of negative or positive trions through interactions with photogenerated excitons. In this case, under conditions where $V_g < V_0$ and T_A^+ is presumed dominant and the trion transition is observed at $E_{T_A^+} = 1.620 \pm 0.002$ eV. In contrast, for $V_g > V_0$, where T_A^- is likely predominant, the transition is at $E_{T_A^-} = 1.613 \pm 0.005$ eV.

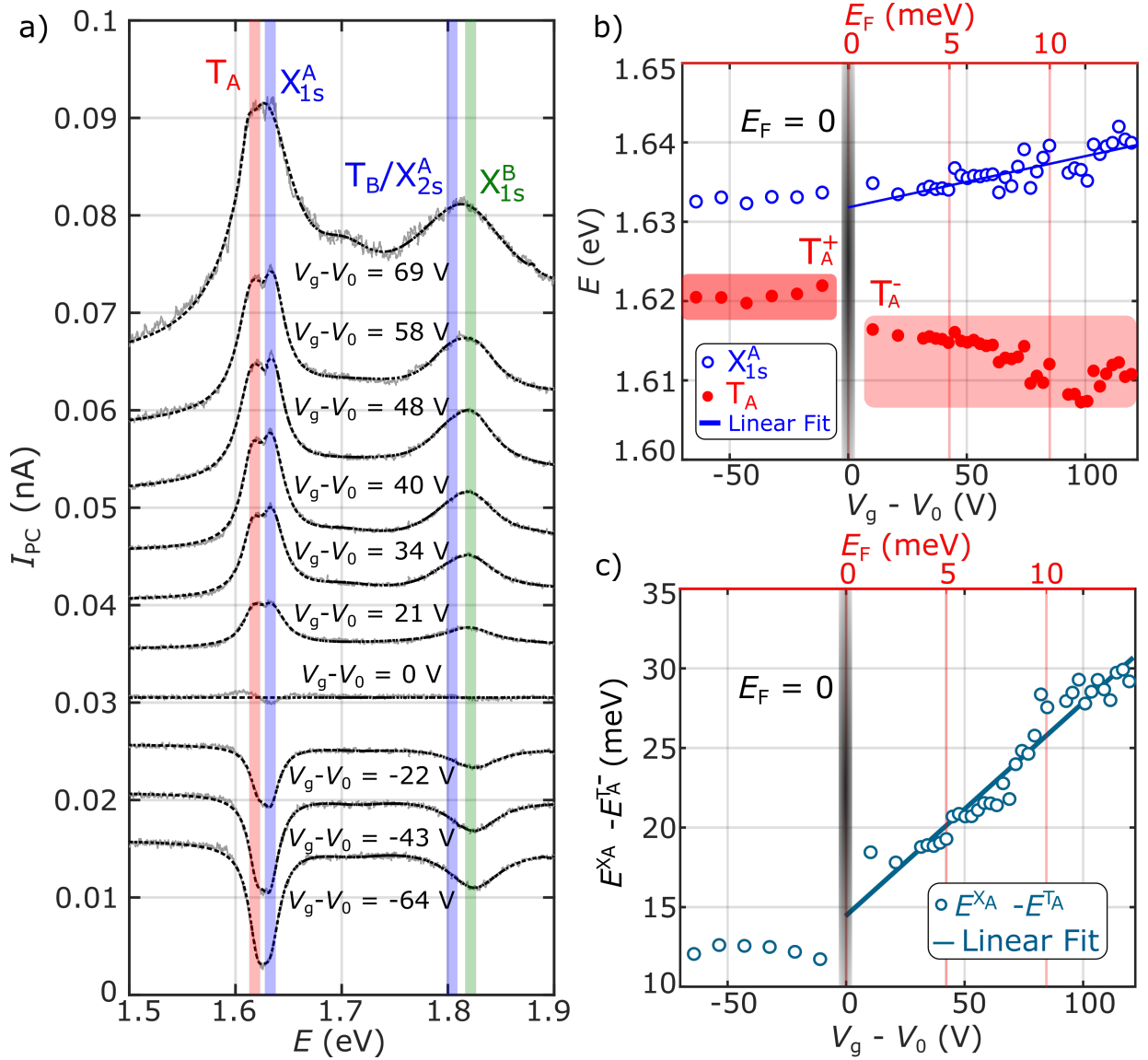


Fig. 7.3.4: Gate dependence of the photocurrent spectra. (a) Individual photocurrent spectra (grey lines) acquired at different gate voltages, $V_g - V_0$, in a range between -64 V and 69 V, fitted to a multi-peak Lorentzian function (dashed black lines). For clarity, the spectra are vertically offset in steps of 0.005 nA. (b) Evolution with gate voltage of X_{1s}^A and T_A (T_A^+ and T_A^-) transition energies. (c) Gate voltage dependence of the energy splitting between the X_{1s}^A and T_A^- transitions.

Moreover, the crossover between trion dominant species, increasing V_g also generates a linear blue-shift of the neutral exciton energy and induces a red shift in trion energy [190, 84, 191, 192]. Both effects are observed in our spectra. We fit the blue-shift of X_{1s}^A using a linear equation to monitorized the behaviour. The slope of the linear fit is 60.1 ± 8.5 meV/V in good agreement with previous observations [190].

Figure 7.3.4 c) illustrates the energy splitting between X_{1s}^A and T_A^- variation with the V_g and E_F . Our findings reveal that this energy difference between the transitions increases linearly in relation to the doping level of the device, following the equation

$$E_{X_{1s}^A} - E_{T_A^-} = E_b^{T_A^-} + cE_F \quad (7.3.3)$$

where $E_{X_{1s}^A} - E_{T_A^-}$ corresponds with the splitting between exciton and trion transitions, $E_b^{T_A^-}$, E_F with the fermi energy and c with the slope of the linear fit, which theoretically predicted value is $c \approx 1$ [186]. This trend aligns with predictions and observations previously reported in literature [84, 186, 193].

By applying equation (7.3.3) to fit the measured energy splitting of between X_{1s}^A and T_A^- , depicted in figure 7.3.4 c), we calculate the binding energy of T_A^- , defined as the energy necessary to form a trion at an infinitesimally small doping level [194]. For this estimation, we consider the charge neutrality point to be at the V_g where the photocurrent vanished and the predominant trion species shifts from T_A^+ to T_A^- , denoted as V_0 [190, 195].

Based on these assumptions, we obtain $E_b^{T_A^-} = 14.54 \pm 0.79$ meV and a slope value of $c \approx 1.14 \pm 0.05$, aligning well with previous studies [84, 196], which suggest that the factor $cE_F \approx E_F$ represents the extra energy required to add the charge from the dissociated trion to the top of the Fermi sea, as required by the Pauli blockade. The determined values for $E_b^{T_A^-}$ and c show a good agreement with the large effective masses observed in recent studies on Mo-based TMDs [145, 178, 185].

Recent studies on 1L- MoSe_2 devices on SiO_2 substrates report slightly higher trion binding energies, around 20 meV [86]. $E_b^{T_A^+}$ has also been quantified through PL in h-BN-encapsulated, CVD-grown MoSe_2 , with an even larger reported value of 27 meV. Comparatively, for 1L- MoS_2 , $E_b^{T_A^+}$ is found to be 18 meV, which is 3.5 meV more than our findings for 1L- MoSe_2 . This energy difference between both materials aligns well with theoretical predictions [197]. The differences observed in our $E_b^{T_A^-}$ results compared to previous studies could rely from variations in substrates [161, 198] and fabrication methods used. Considering that V_g -dependent studies performed only using optical spectral techniques can ignore photodoping effects, potentially leading to systematic errors in estimating the doping level.

7.4 Conclusions

In this chapter, we studied different properties of neutral excitons and various trion species in a h-BN-encapsulated 1L-MoSe₂ phototransistor using low-temperature photocurrent spectroscopy. This technique enabled us to achieve photocurrent spectra with narrow excitonic linewidths, approximately 15 meV, allowing to fully resolve excitonic ground states (X_{1s}^A and X_{1s}^B), trions associated with X_{1s}^A (T_A), and a peak related with T_B and the excited state X_{2s}^A .

We also investigated doping effects on excitonic transitions, by measuring photocurrent spectra at different V_g . We observed a change of the photocurrent sign depending on the Fermi energy level, turning negative below $V_g \approx -84$ V and positive above. Such a change in photocurrent sign is uncommon in TMD phototransistors, due to V_g ranges used in the experiments. Usually, below $V_g = -50$ V is avoided to prevent dielectric breakdown of the SiO₂ layer. Nevertheless, the negative photoresponse is indeed expected when PGE predominates in photocurrent generation and the traps involved in this effect are hole acceptors.

Finally, we investigated the effect of V_g in the spectral position of X_{1s}^A and T_A transitions. T_A shifts abruptly as V_g passes the neutrality point $V_0 \approx -84$ V, suggesting a change from negatively charged (T_A^-) to positively charged (T_A^+) trions. Above V_0 , there was a continuous electrical modulation of transition energies, induced by the increase of the charge carrier density. By analyzing the energy splitting between exciton and trion levels, we estimated the binding energy of negative trions and confirming the large effective mass of electrons in 1L-MoSe₂. Our findings provide novel insights into the exciton-mediated optoelectronic behaviors of 1L-MoSe₂ [199], enhancing the understanding of these systems.

Chapter 8

Polarization tunable excitons in the photocurrent spectra of ReS_2

In the next chapter we turn on the study of rhenium disulphide (ReS_2), a 2D transition metal dichalcogenide (TMD) with an anisotropic crystalline structure, using low temperature photocurrent spectroscopy. Low crystal symmetry of ReS_2 leads to distinctive dichroic optical and optoelectronic behaviours. In contrast with the previous Mo-based TMDs studied during this dissertation, which have an isotropic optoelectronic responses, ReS_2 looks promising for developing light polarization based devices. Prior studies on ReS_2 optical response have primarily performed exclusively with characterization techniques involving optical detection, such as photoluminescence, absorbance, or electroluminescence spectroscopy. Nevertheless, a deep characterization of ReS_2 optoelectronic response with spectral resolution remains scarce in previous literature.

In the following, we investigate the polarization-dependent low temperature photocurrent spectra of two few-layer ReS_2 (AB and AA stacked) devices. Our findings include two main excitonic transitions with energies in agreement with those identified in optical spectroscopy, as well as their excited states. Furthermore, we observe an additional exciton-like feature that is tentatively attributed to a non-radiative transition not previously observed in photoluminescence. The intensity of these excitonic features and their excited states varies with the linear polarization angle of light, showing maximum strength at different polarization angles. This research on the anisotropic photocurrent response contributes novel insights for exploit exotic optoelectronic phenomena and based-polarization applications using ReS_2 -based nanodevices.

8.1 Introduction

Layered transition metal dichalcogenides (2D-TMDs) have been attracting great interest in the last years due to their potential for optics and optoelectronics [10, 44]. The two dimensional confinement and the reduced dielectric screening give an increase of the excitonic binding energies and long lifetimes [84]. To date, the most studied atomically thin semiconductors are those that contain a group VI transition metal, such as, MoS_2 , MoSe_2 , WS_2 and WSe_2 , mainly because they present excitonic transitions with strong oscillator strengths and narrow bandwidths. Furthermore, these 2D-TMDs exhibit valley-dependent optical selection rules, enabling exciton generation in specific valleys via light polarization [200, 201].

However, recently, Re-based TMDs, especially ReS_2 , have drawn attention of the scientific community because of the presence of strong exciton transitions, due to electrical confinement, and optical anisotropy, as a result of their reduced crystal symmetry. Optical anisotropy leads to linear dichroism in their excitonic features, revealed in previous works by photoluminescence, electroluminescence or absorption spectroscopy [61, 109, 202].

Despite the amount of studies on the optoelectronics properties of ReS_2 , there are still unresolved questions about ReS_2 fundamental properties, including the nature of its bandgap (either direct or indirect) and the labeling of different excitonic transitions. Discrepancies in the optical responses observed in ReS_2 may arise from the two different growth directions reported experimentally [203, 204] with similar total energies [205]. Moreover, ReS_2 multilayers can exhibit two different stable stacking orders at room temperature [111, 206], each significantly affecting the optical properties of the material. Additionally, while the optoelectronic properties of ReS_2 are still being unraveled, detailed information on the spectral dependence of photoresponse in ReS_2 -based devices, of crucial importance for several technological applications, remains scarce.

In this chapter, we examine the optoelectronic behaviour of few-layer ReS_2 devices with two different stacking orders (AB stacked device is characterized more in depth). The interplay of strong Coulomb forces and the unique crystalline structure of ReS_2 greatly impacts on the optical behaviour of these photodetectors, which is dominated by excitonic transitions. Building on our previous experience on TMDs we use low-temperature photocurrent spectroscopy to characterize few-layer ReS_2 [180, 199]. In our analysis, we resolve three main excitonic features in ReS_2 . Notably, this includes the identification of a new exciton peak not reported in previous literature. Furthermore, the intensity of these features modulate as a function of the incident light polarization following a dichroic behaviour where each excitonic state reaches its maximum intensity at a different polarization angles.

8.2 Electrical characterization of the device

ReS_2 crystalline structure is characterized by a distorted 1T structure, distinguished by two non-equivalent directions either parallel or perpendicular to the b-axis (see figure 3.4.5 a)). In multilayer formations, ReS_2 exhibits two stable layer stacking configurations, commonly referred to as AA and AB stacking. In AA stacking, layers align directly over each other, whereas in AB stacking, each successive layer shifts approximately $2.5 \text{ \AA}$ along the perpendicular crystalline axis to the b-axis. Few-layer flakes are mechanically exfoliated using PDMS and the thickness is estimated using optical contrast and confirmed by profilometer measurements. We use polarization-resolved Raman spectroscopy of the exfoliated flake to identify the crystalline orientation. All these procedures are described in chapter 3.

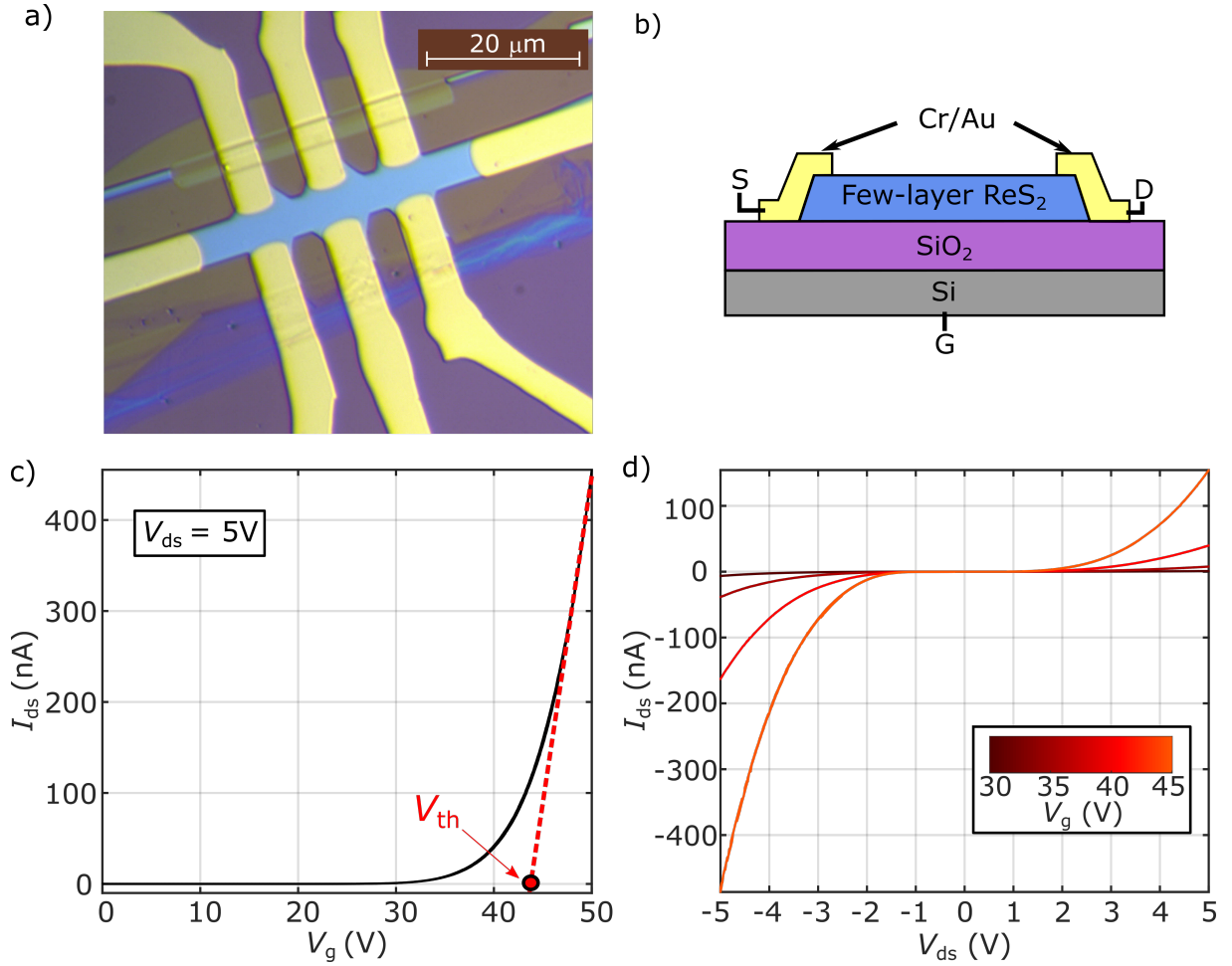


Fig. 8.2.1: Measurement configuration and characterization of the electric response of the few-layer ReS_2 phototransistor at 7 K. a) Optical microscopy image of $\text{ReS}_2/\text{SiO}_2$ transistor. b) Schematic drawing of the ReS_2 device with the source, drain and gate contacts highlighted. c) Gate transfer characteristic at $V_{\text{ds}} = 5 \text{ V}$, indicating n-type behavior with $V_{\text{th}} = 43 \text{ V}$, estimated from I_{ds} linear region (red dashed line). d) Device I - V characteristics at different gate voltages.

Following a similar procedure than in previous chapters, we characterize the electrical response of the device. Figure 8.2.1. a) shows an optical microscope image of the AB-stacked few layer ReS_2 photodetector. Figure 8.2.1 b) displays an schematic of the geometry of the device, indicating the planar contacts of Cr/Au on the flake and the measurement configuration, where we apply a drain-source voltage, V_{ds} between the electrodes and the gate voltage, V_{g} through the Si/SiO₂ flake. In this sample we have omitted the use of h-BN, because the flatness of the substrate in few-layer flake it is not so critical and the photodoping effects on SiO₂ are orders of magnitude lower than on h-BN. Figure 8.2.1 c) presents the gate transfer curve for the ReS_2 phototransistor at $V_{\text{ds}} = 5$ V, showing a clear n-type behaviour with a threshold voltage of $V_{\text{th}} = 43$ V. Figure 8.2.1 d) illustrates the $I - V$ characteristics at various V_{g} , where a nonlinear response is observed, likely due to asymmetric Schottky barriers at the contacts. Notably, both sets of measurements display minimal hysteresis.

8.2.1 Photoresponse of the device

After characterizing the electrical response, we uniformly illuminate the entire device with monochromatic light and measure the I_{ds} at fixed V_{g} and V_{ds} to analyze the photoresponse of the ReS_2 device. Figure 8.2.2 a) shows the cycles of turn on and off of the monochromatic light at a modulation frequency of $f = 31.81$ Hz. Photocurrent, I_{pc} , is obtained by calculating the difference between I_{ds} under light exposure and in dark.

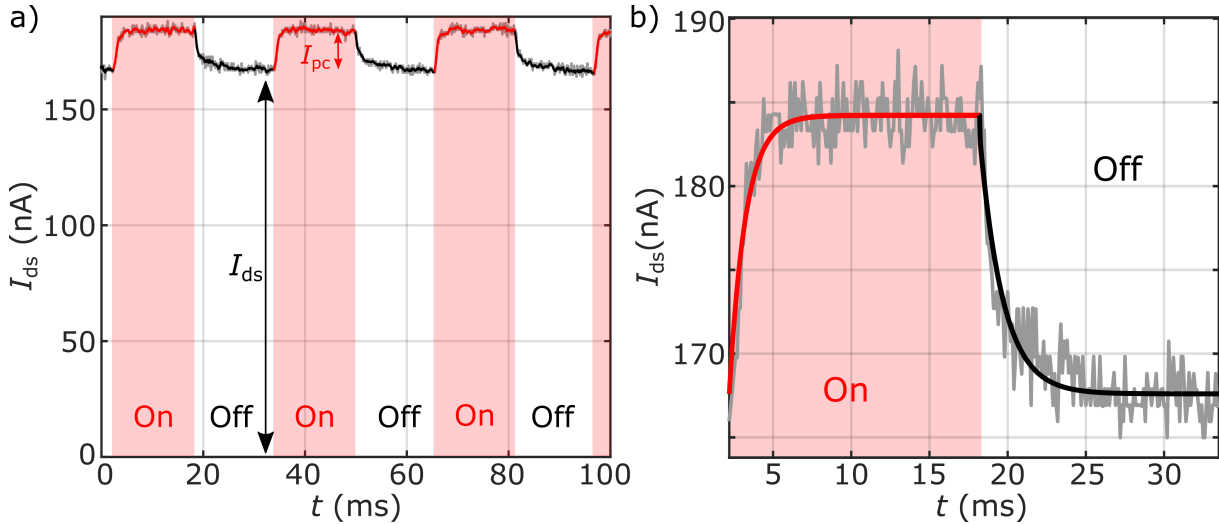


Fig. 8.2.2: Time-dependent photoresponse of the device. a) Drain-source current at $V_{\text{ds}} = 5$ V and $V_{\text{g}} = 45$ V. When the device is illuminated ($E = 2$ eV) the current increases by the photocurrent b) Detail of a single on-off measurement of the device (gray line). Fitting of the on (red line) and off (black line) to an exponential increase and decrease of the photocurrent.

To obtain a complete analysis of the photoresponse we measure the time dependent response of the device. Figure 8.2.2 b) illustrates the temporal evolution of I_{ds} during a single on-off cycle. The optoelectronic response of the device when the illumination is

switched on can be fitted by an exponential decay function with the form

$$I_{\text{ds}}(t) = I_{\text{off}} + I_{\text{ph},1} (1 - e^{-t/\tau_r}) \quad (8.2.1)$$

where I_{off} is I_{ds} before illumination and $I_{\text{ph},1}$, τ_r are used as fitting parameters, being τ_r the response time. In a similar way, the time evolution of $I_{\text{ds}}(t)$ immediately after switching off the light can be modeled as

$$I_{\text{ds}}(t) = I_{\text{off}} + I_{\text{ph},1} e^{-t/\tau_d} \quad (8.2.2)$$

being $I_{\text{ph},2}$ and τ_d the fitting parameters. We calculate the response times of the device $\tau_r = 1.05$ ms for the rise time and $\tau_d = 1.48$ ms for the decay time. As expected, our measurements did not reveal any persistent photodoping effects.

8.3 Photocurrent spectroscopy in few-layer ReS₂

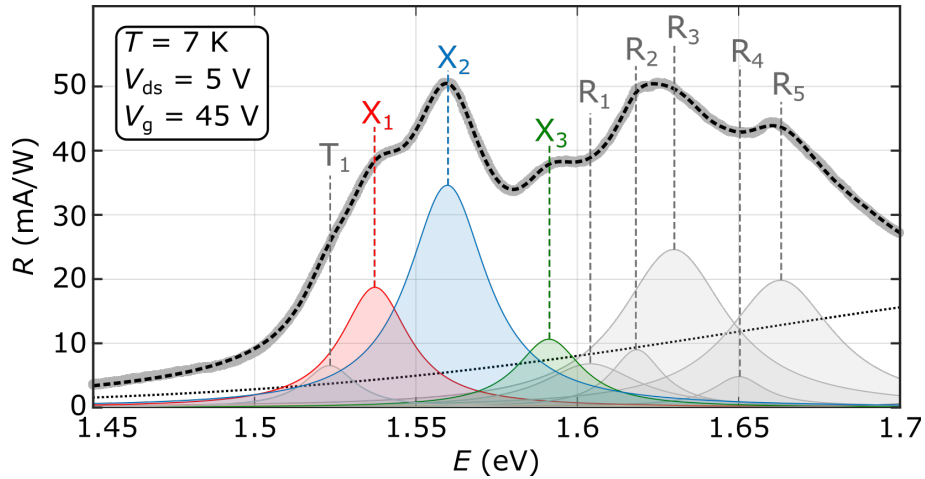


Fig. 8.3.1: Low-temperature photocurrent spectrum of the few-layer ReS₂ phototransistor (grey line) at $V_{\text{ds}} = 5$ V, $V_{\text{g}} = 45$ V and a power density of 500 W/m^2 . The spectrum is acquired for a light-polarization perpendicular to the b-axis. The fitting to a multi-lorentzian peak function plus a background (black dashed line) shows a good correlation. Below the spectrum, the Lorentzian peaks are displayed, detailing the neutral excitons X_1 , X_2 and X_3 (shown in red, blue and green respectively), charged trion T_1 (in grey), and the excited states of the neutral excitons, R_1 - R_5 (in grey).

Now, we focus on the characterization of the spectral photoresponse to reveal the excitonic transitions of few-layer ReS₂ using low-temperature photocurrent spectroscopy. Unless otherwise is stated, all the measurements were performed at 7 K on the AB-stacked ReS₂ device depicted in figure 8.2.1 a). Results at room temperature and for the AA-stacked device are presented in sections 8.3.3 and 8.3.4. Figure 8.3.1 displays a ReS₂ photoresponsivity spectrum, measured at incident light polarization perpendicular to the

b-axis. This spectrum reveals multiple exciton-like features between 1.45 eV and 1.7 eV, aligning well with previous low-temperature photoluminescence spectroscopy findings in ReS_2 [207, 208].

The photocurrent spectrum reveals two main excitons, X_1 and X_2 , located at approximately $E = 1.54$ eV and $E = 1.56$ eV, respectively. These peaks, represented with red and blue peaks, have been previously reported in scientific literature through studies involving low-temperature photoluminescence, electroluminescence, and micro-reflectance spectroscopy [61, 207, 209]. The peaks X_1 and X_2 in our spectra are generally associated with the presence of excitons at the K1 and Z points of the Brillouin zone, where two minima of the band gap appear between the valence and the conduction band [210]. Moreover, a smaller peak is observed at 1.525 eV, placed roughly 14 meV below X_1 . We attribute this peak to the trion state T_1 associated to X_1 [211]. We also resolve a smaller peak at 1.588 eV, which might represent a higher-energy exciton transition, referred to as X_3 . This feature has not been previously reported and we tentatively assign to a non-radiative exciton peak. At higher energies, between 1.6 and 1.7 eV, we observe a group of excitonic peaks. We attribute these peaks to the Rydberg series of the main excitons. The dashed line in figure 8.3.1 illustrates the experimental spectrum fitting using a multi-Lorentzian function. This model incorporates individual Lorentzian peaks for T_1 , X_1 , X_2 , and X_3 , plus five additional peaks (labelled R_1 – R_5) in the 1.6 to 1.7 eV range. It is important to notice that R_1 – R_5 are not fully resolved in our spectra, therefore it is possible that more than one optical transition may be contributing to photoresponse of the assigned peaks. Beyond the multiple Lorentzian peaks, our fitting incorporates a Fermi–Dirac distribution function, positioned at 1.7 eV and depicted as a dotted line in the figure, to account the direct interband transitions on the spectrum.

8.3.1 Gate and drain-source modulation of the spectral features

Now, we focus on electric field influence on the excitonic features. Initially, we analyze the dependence of the photocurrent with V_g and we complete the analysis with the power dependence to extract the main mechanism of I_{pc} generation. After that we focus on the role of the in-plane electric field controlled by V_{ds} . Figure 8.3.2 a) displays the I – V curves of the device measured at $V_g = 45$ V under dark and uniform illumination with a power density P_D of 500 W/m² and photon energy $E = 2$ eV. The inset shows I_{pc} generated as a function of V_{ds} , following a similar trend than the I – V curves. Figure 8.3.2 b) shows gate transfer characteristics of the device under dark and illuminated conditions at E of 2 eV and $V_{ds} = 5$ V for consistency. Figure 8.3.2 c) depicts the I_{pc} dependence on V_g and transconductance G (calculated from the gate transfer curve) in the ReS_2 device at light-modulation frequency of 31.81 Hz, $V_{ds} = 5$ V and photon energy E of 2 eV, showing a clear proportionality between both magnitudes. In these panels, the contribution to I_{pc} of the photogating effect can be clearly distinguished. Photogating effect manifests as a horizontal shift of the transfer curve indicated in the panel b) by ΔV_{th} . As explained in chapter 5, the proportionality between I_{pc} and G indicates that I_{pc} is generated by

the photogating effect. In stark contrast with 1L-MoS₂ device studied in chapter 5 the photoconductive effect is almost negligible. Figure 8.3.2 d) displays the dependence of the photocurrent on illumination power at $V_g = 45$ V, $V_{ds} = 5$ V, and a modulation frequency of $f = 31.81$ Hz, in resonance with the three main excitonic transitions X_1 , X_2 and X_3 . I_{pc} shows a sublinear relationship with the power density, well fitted by the power law $I_{pc} \propto P^\alpha$, where $\alpha \approx 0.6$.

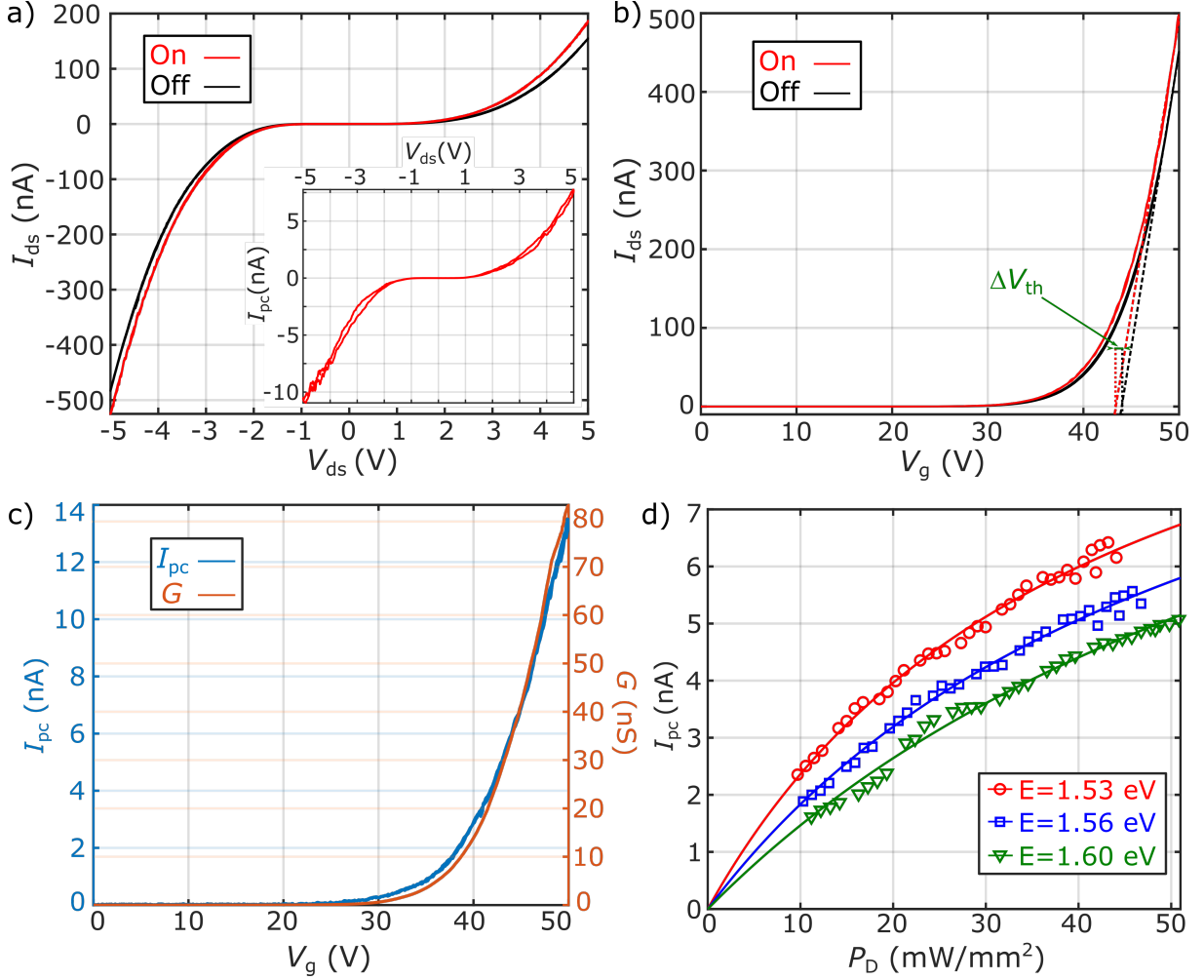


Fig. 8.3.2: Dependence of photocurrent on the power density, gate and drain-source voltages in ReS₂ device. a) $I - V$ curves of the few-layer ReS₂ device measured under dark and with an illumination of $E = 2$ eV at $V_g = 45$ V. Illumination leads to an increase in I_{ds} , by I_{pc} , depicted in the inset as a function of V_{ds} . b) Gate transfer curves measured at $V_{ds} = 5$ V in dark and with illumination conditions, revealing that $V_{th} = 43$ V for the Off trace and a shift, ΔV_{th} in the On trace. c) Gate dependence of the transconductance of the device (right axis, orange line) and of I_{pc} (left axis, cyan line) measured at $V_{ds} = 5$ V for $f = 31.81$ Hz. d) Power dependence of I_{pc} at $V_g = 45$ V, $V_{ds} = 5$ V, and a modulation frequency of $f = 31.81$ Hz measured at photon energies corresponding to the X_1 , X_2 and X_3 excitonic features. The data are fitted to $I_{pc} \propto P^\alpha$ with $\alpha \approx 0.6$, indicating a sublinear trend.

This sublinear trend confirms that the photogating effect is the main I_{pc} generation mechanism in this device.

Subsequently, we investigate the role of the electric field in the excitonic features of the photocurrent spectra. Firstly, we start with the effect of V_g . Figure 8.3.3 a) displays photocurrent spectra obtained at different V_g , in the range between 24 to 50 V, with incident light polarization aligned to the b-axis of the ReS_2 crystal. As expected from photogating, the overall photoresponse drops as V_g decreases. Therefore, for easier comparison, each spectrum is normalized to its photocurrent level at 1.8 eV. b) Ratio of intensities between the X_1 and T_1 spectral peaks as a function of V_g . c) Energy difference between X_1 and T_1 peaks, obtained from multi-Lorentzian fits of the spectra, plotted against V_g . The inset depicts the energy values for X_1 and T_1 .

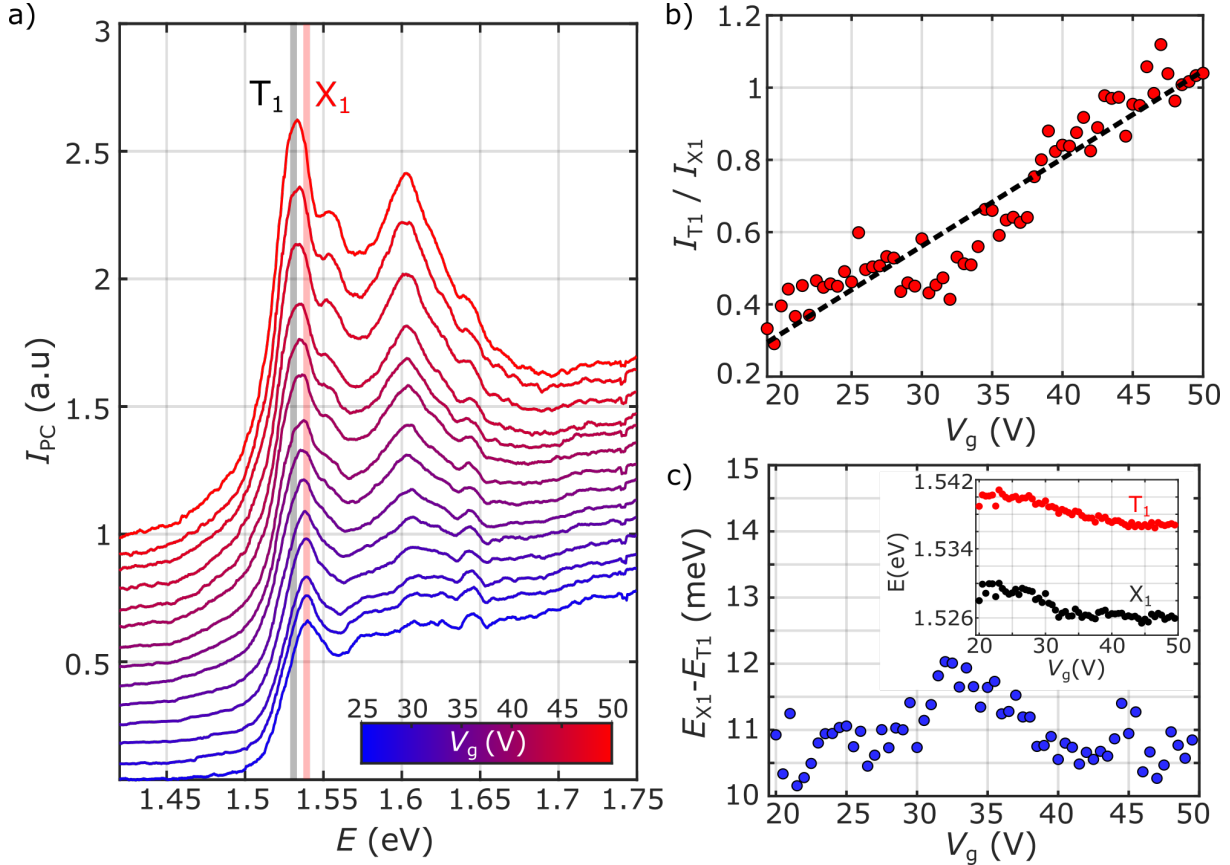


Fig. 8.3.3: Photocurrent spectra dependence on the gate voltage. a) Photocurrent spectra measured at different V_g from 24 V to 50 V, with $V_{ds} = 5$ V, $P_D = 500$ W/m², and light polarization aligned with the b-axis of the ReS_2 crystal. For better comparison, the spectra are vertically offset and each spectrum is normalized to its photoresponse at 1.8 eV. b) Ratio of intensities between the X_1 and T_1 spectral peaks as a function of V_g . c) Energy difference between X_1 and T_1 peaks, obtained from multi-Lorentzian fits of the spectra, plotted against V_g . The inset depicts the energy values for X_1 and T_1 .

Firstly, we observe that the strength of excitonic peaks relative to the baseline increases with V_g , suggesting more effective exciton dissociation at higher voltages due to enhanced electron scattering. Secondly, the higher-energy peaks (R_1 – R_5) show a complex V_g -dependent modulation. Modulation of Rydberg states it is not fully understood, but seems like the increase of V_g favours the dissociation of these states as seen in chapter 6 for photocurrent spectra 1L-MoS₂ device. Finally, V_g modulates the relative intensity of the X_1 and T_1 peaks. Figure 8.3.3 b) illustrates the intensity ratio of T_1 to X_1 , I_{T_1}/I_{X_1} , against V_g , revealing a shift in spectral weight from the neutral exciton to the trion state

as V_g increases, suggesting that T_1 is a negatively charged trion. Figure 8.3.3 c) depicts the energy splitting X_1 and T_1 but in this range of V_g the trend is not clear.

We finish our analysis of the role of the electric field monitoring the influence of V_{ds} in the spectral features. As excitons are neutral quasiparticles formed by a electron-hole pairs, their contribution to photoresponse come from the formation and the dissociation of the bound state. Usually in 2D phototransistors, the exciton dissociation process occurs near the electrodes, where the presence of Schottky barriers leads in strong electric fields [212].

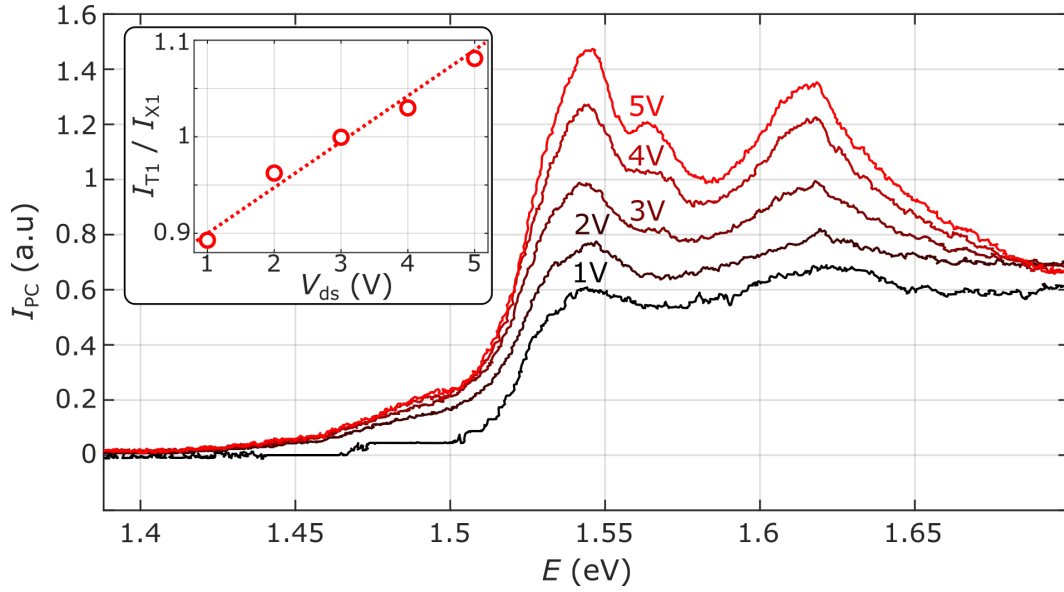


Fig. 8.3.4: Photocurrent spectra measured at V_{ds} from 1 V to 5 V with $V_g = 45$ V, power density at 500 W/m^2 , and light polarized parallel to the b-axis of the ReS_2 crystal. For easier comparison, the spectra are normalized to the photocurrent at 1.9 eV. Inset highlights the changing ratio of photocurrent at 1.54 eV and 1.62 eV, corresponding with peaks X_1 and R_1 . This ratio increases with higher V_{ds} .

Figure 8.3.4 shows photocurrent spectra measured at different values of V_{ds} , in the range from 1 V to 5 V. For clarity, the five spectra have been normalized to the photocurrent value at 1.9 eV, where photoresponse might be mainly produced by direct band-to-band transitions. As expected, the increase in V_{ds} leads in higher probability of exciton dissociation, making excitonic features clearer in comparison to the background caused by interband transitions. Notably, X_2 peak, which is almost invisible at low V_{ds} , becomes fully resolved at $V_{ds} = 5$ V. Moreover, the relative intensity of excitonic features, particularly neutral excitons X_1 - X_3 , become more prominent with the increase of V_{ds} , in comparison with R_1 - R_5 peaks, aligning with the expectation that excited Rydberg states have lower binding energies in comparison with the fundamental states, thus, exciton dissociation for excited states should occur at lower in-plane electric fields. The inset shows the relative intensity of X_1 and R_1 confirming the previous observation.

8.3.2 Polarization modulation of the spectral features

To further understand the exciton behaviour in ReS_2 , we now focus on how the photocurrent spectra are influenced by the polarization of the optical excitation. Figure 8.3.5 a) displays photocurrent spectra measured at multiple polarization angles, between 0° and 180° respect the b-axis. The incident polarization angle strongly influences all previously mentioned spectral features. Figure 8.3.5 b) shows the intensities, extracted from the multi-peak lorentzian fittings, of the three main excitons (X_1 – X_3) against polarization direction. On the one hand, X_1 exciton peaks at a 10° polarization angle relative to the b-axis, while X_2 reaches its maximum at 95° , nearly perpendicular to X_1 . Spectral feature at 1.525 eV aligns with X_1 polarization dependence, supporting its identification as the T_1 trion state. On the other hand, exciton X_3 peaks at a 65° polarization angle, showing a different polarization dependence from X_1 and X_2 , suggesting that X_3 likely represents an exciton transition at a different point in the reciprocal lattice. In all polar plots the dependence of the amplitudes with the polarization angles is fitted to $I = I_0 + I_1 \cos^2(\theta + \theta_0)$ confirming the dichroic behaviour of the transitions.

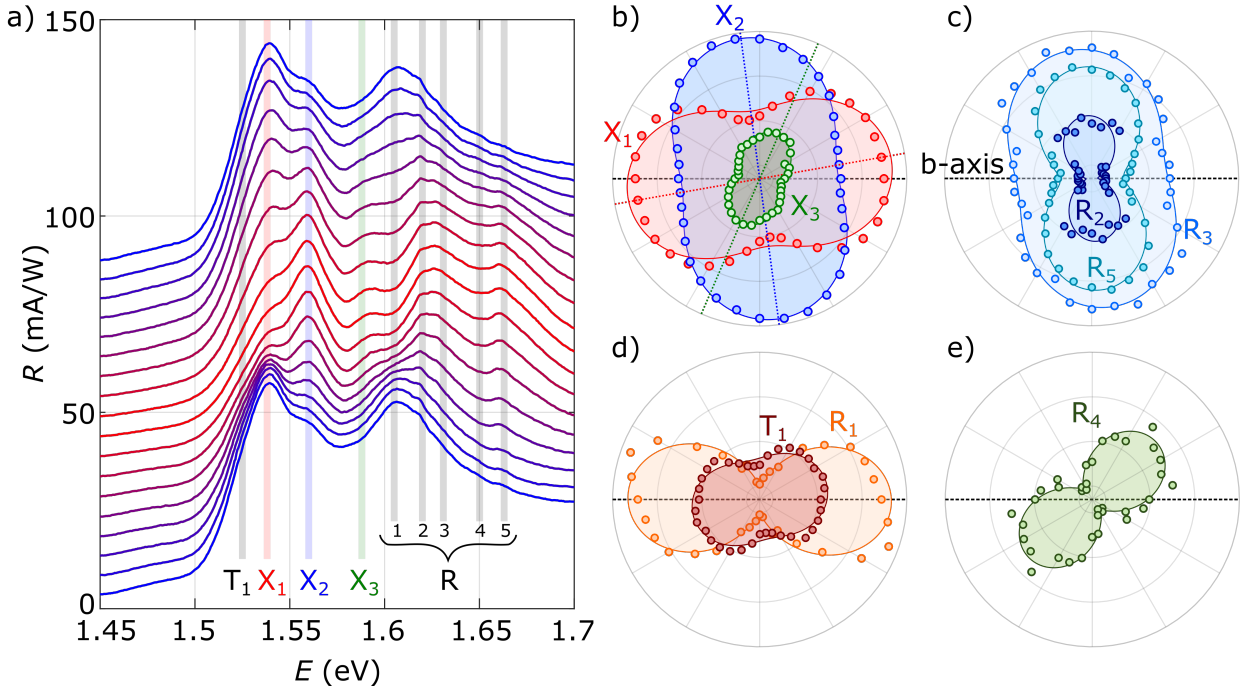


Fig. 8.3.5: Polarization dependent photocurrent spectra in ReS_2 device. a) Photocurrent spectra measured at different light polarization angles, from 0° to 170° relative to the b-axis, with $V_{\text{ds}} = 5$ V, $V_g = 45$ V and a power density of 500 W/m^2 . Consecutive spectra have been shifted vertically in steps of 5 mA/W for clarity. b)–e) Amplitude polar plots of the different spectral features extracted from fittings to multi-Lorentzian curves as a function of the polarization direction, showing a clear modulation.

In panels c) to e) of figure 8.3.2, other spectral features with energies over 1.6 eV display polarization dependence similar to those of the three main exciton peaks, indicating that they are related to these excitons. We associate these states to the rydberg series of neutral excitons. R_1 displays a similar behaviour than X_1 , thus we associate it to an excited state

of X_1 . We link R_2 , R_3 , and R_5 to X_2 because they have a similar polarization behaviour. R_4 , showing a maximum at a 40° polarization angle, seems to involve contributions from the excited states of both X_1 and X_3 . Our findings align well with previous reports on low-temperature PL spectroscopy [208] in few-layer ReS_2 , which identified X_1 and X_2 at energies comparable to ours, and higher-energy features corresponding to their excited states. However, the feature we label as X_3 , not seen in previous PL spectroscopy experiments, shows a different polarization dependence confirming our previous hypothesis of it corresponds with a non-radiative exciton transition.

8.3.3 Room-temperature measurements

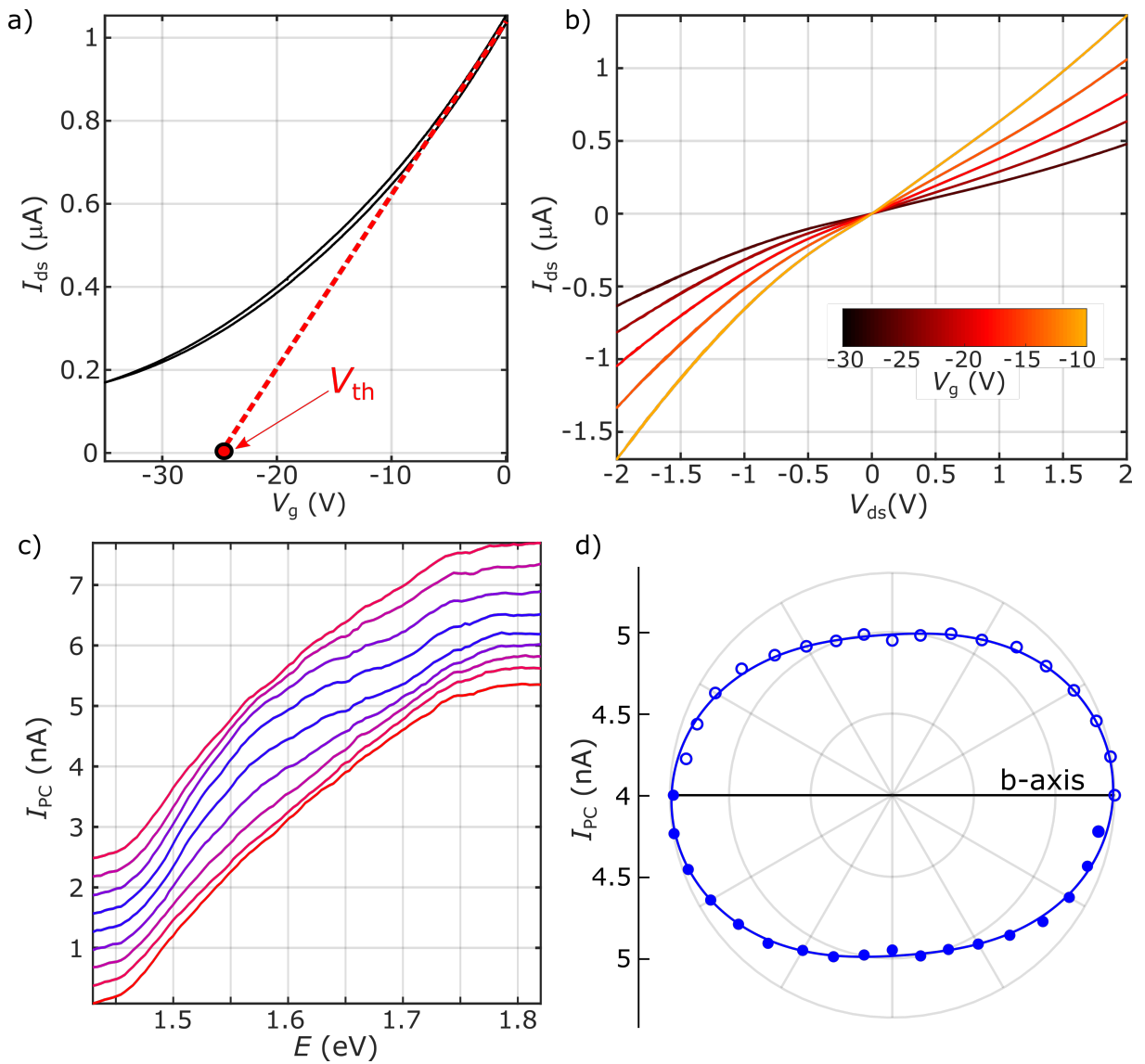


Fig. 8.3.6: Optoelectronic characterization of the device at room temperature. a) Gate transfer curve. V_{th} is calculated extrapolating the linear region of I_{ds} (red dashed line) b) $I - V$ curves at different V_g c) Photocurrent spectra across different polarization angles ranging from 0° to 180° degrees in 20° steps. d) Photocurrent dichroism measured at 1.8 eV.

To obtain a complete picture of the optoelectronic response of the device we repeat the characterization at room temperature. Figure 8.3.6 a) displays the device transfer curve at $V_{\text{ds}} = 2 \text{ V}$, with V_{g} maintained above -35 V due to gate leakage issues. V_{th} is determined by fitting the linear region of the transfer curve. Figure 8.3.6 b) shows the $I-V$ characteristics at different V_{g} . Figure 8.3.6 c) illustrates the photocurrent spectra at different polarization angles, in 20° steps, from 0° to 180° . Here, excitonic features appear broader due to thermal effects, complicating to clearly distinguish different optical transitions. Figure 8.3.6 d) reveals the photocurrent modulation with light polarization at $E = 2 \text{ eV}$, with the blue solid line representing the fit of the data using $I = I_0 + I_1 \cos^2(\theta + \theta_0)$. A clear linear dichroic photoresponse is observed in the device [60].

8.3.4 AA-stacked device

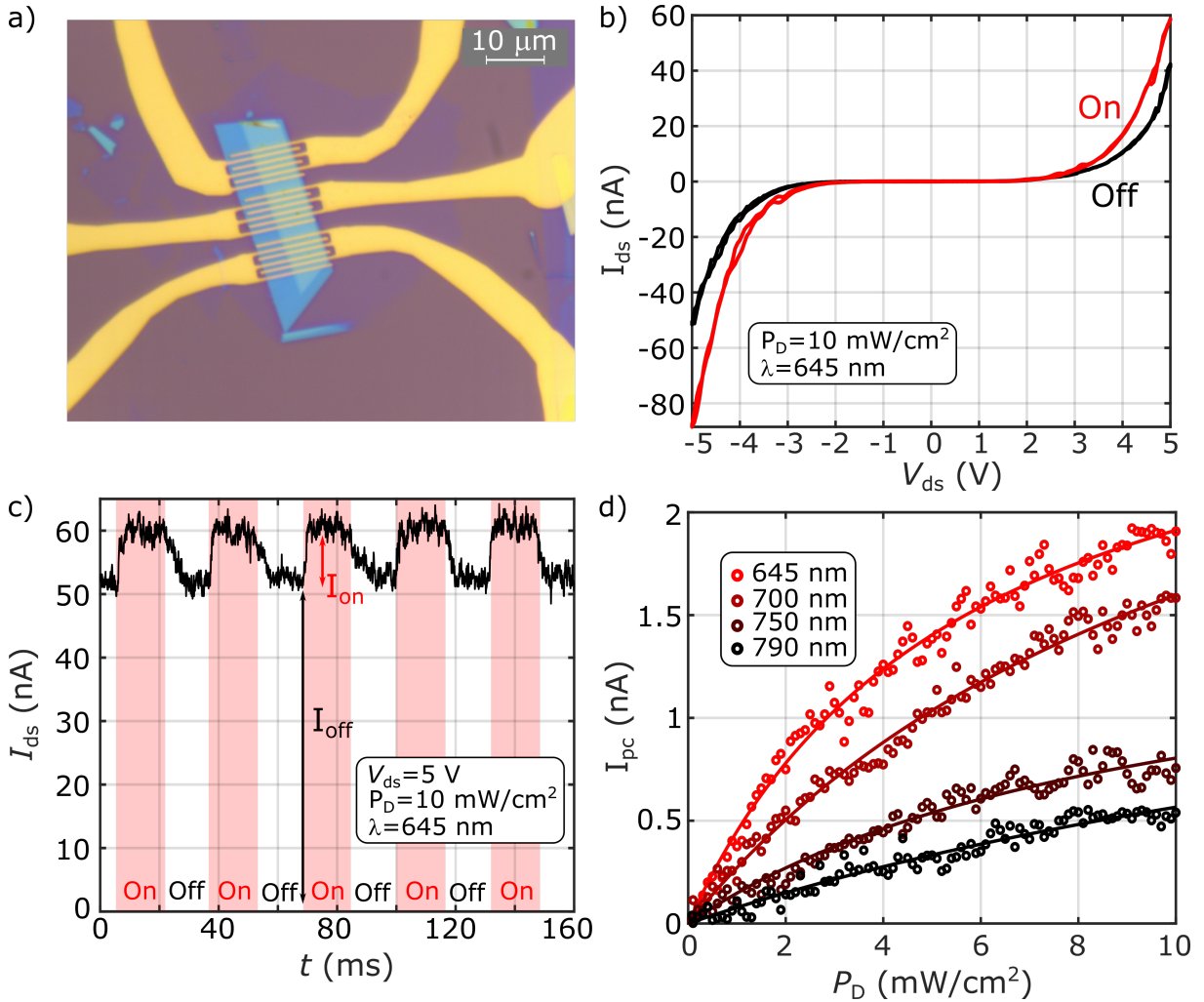


Fig. 8.3.7: Optoelectronic characterization of the device. a) Optical image of the ReS₂ photodetector b) $I-V$ curves with monochromatic illumination of 645 nm (red solid line) and dark (black solid line). c) Drain-source current of the photodetector at $V_{\text{ds}} = 5 \text{ V}$. When the light excitation ($\lambda = 645 \text{ nm}$) is turned on, the drain-source current increases by I_{on} . d) Power dependence of I_{pc} at different wavelength excitation for $V_{\text{ds}} = 5 \text{ V}$. The data are fitted to $I_{\text{pc}} \propto P^{\alpha}$ with $\alpha \approx 0.6$, indicating a sublinear trend.

As mentioned in the introduction, we fabricate a few-layer ReS_2 with an AA-stacking to compare both devices. In this device, we test another geometry to improve the photodetection of the device, but we had problems to do gate voltage dependent measurements due to a leakage in the dielectric of the device.

Figure 8.3.7 a) shows the optical image of the ReS_2 device with an interdigitated geometry of the contacts. We start our electrical measurements by characterizing the optoelectronic response of the device. All the measurements in this device are performed in vacuum at $T = 14$ K. Figure 8.3.7 b) depicts the On (red solid line)-Off (black solid line) $I - V$ curves of the photodetector, presenting a back-to-back Schottky diode behaviour. When the device is exposed to a monochromatic light of 645 nm the current is increased. By modulating the light at a frequency of $f = 31.81$ Hz we characterized the time-dependent photoresponse of the device. Figure 8.3.7 c) shows the time-dependent I_{ds} exposing the device to a excitation wavelength of $\lambda = 645$ nm. When the light is turned on, I_{ds} increases from its value in the dark, I_{off} , by I_{on} . In figure 8.3.7 d), we extract the light power dependent photocurrent of the device at $V_{\text{ds}} = 5$ V and modulation frequency of $f = 31.81$ Hz at different excitation wavelengths. It can clearly be seen that the dependence of the photocurrent is sublinear. We fit the data to the power law $I_{\text{pc}} \propto P^\alpha$, where $\alpha \approx 0.6$. This trend suggests that the main mechanism of the generation of the photocurrent is the photogating. All the measurements show a similar behaviour than in the previous device.

Now we study the spectral photoresponse of the device following a similar procedure of the AB-stacked phototransistor. Figure 8.3.8 a) illustrates the low temperature photocurrent spectra of the AA-stacked ReS_2 photodetector measured at light polarization angles from 0° to 170° every 10° at $V_{\text{ds}} = 5$ V and $f = 31.81$ Hz. The photocurrent spectra is clearly modulated with the polarization angle. In the spectra we can observe three main excitonic peaks at 1.54 eV, 1.575 eV and 1.60 eV, that we attribute to the neutral excitons X_1 , X_2 , X_3 observed in the AB-stacked device. In the spectral range between 1.61 eV to 1.8 eV, appear different peaks that we associate with the Rydberg series of the three neutral excitons.

Figure 8.3.8 b) shows a color map of the photocurrent as a function of the excitation energy and the polarization angle. For each value of the polarization angle, we remove a lineal background between 1.5 and 1.7 eV to highlight the relevance of the spectral peaks in the photocurrent. The three excitonic peaks mentioned before are largely modulated by the polarization angle between the light and the b-axis of the material, following the same trend that in figure 8.3.5. Figure 8.3.8 c) displays the variation of the photocurrent as a function of the light polarization angle at a fixed energy of $E = 2$ eV. Red solid line shows the fitting to $I = I_0 + I_1 \cos^2(\theta + \theta_0)$ of the experimental data. We observe a clear linear dichroic photoresponse of the device as reported in literature [60]. When the polarization is parallel to the b-axis, the photocurrent reaches its maximum and it decreases as the polarization becomes perpendicular to the b-axis. Figure 8.3.8 d) depicts

the intensity of the three neutral excitons as a function of the polarization angle. Solid lines correspond to the fitting of the data. As mentioned before, X_1 , X_2 and X_3 exhibit maximum values at 6° , 86° , 67° from the b-axis, respectively, showing a slightly different behaviour from the AB-stacked devices.

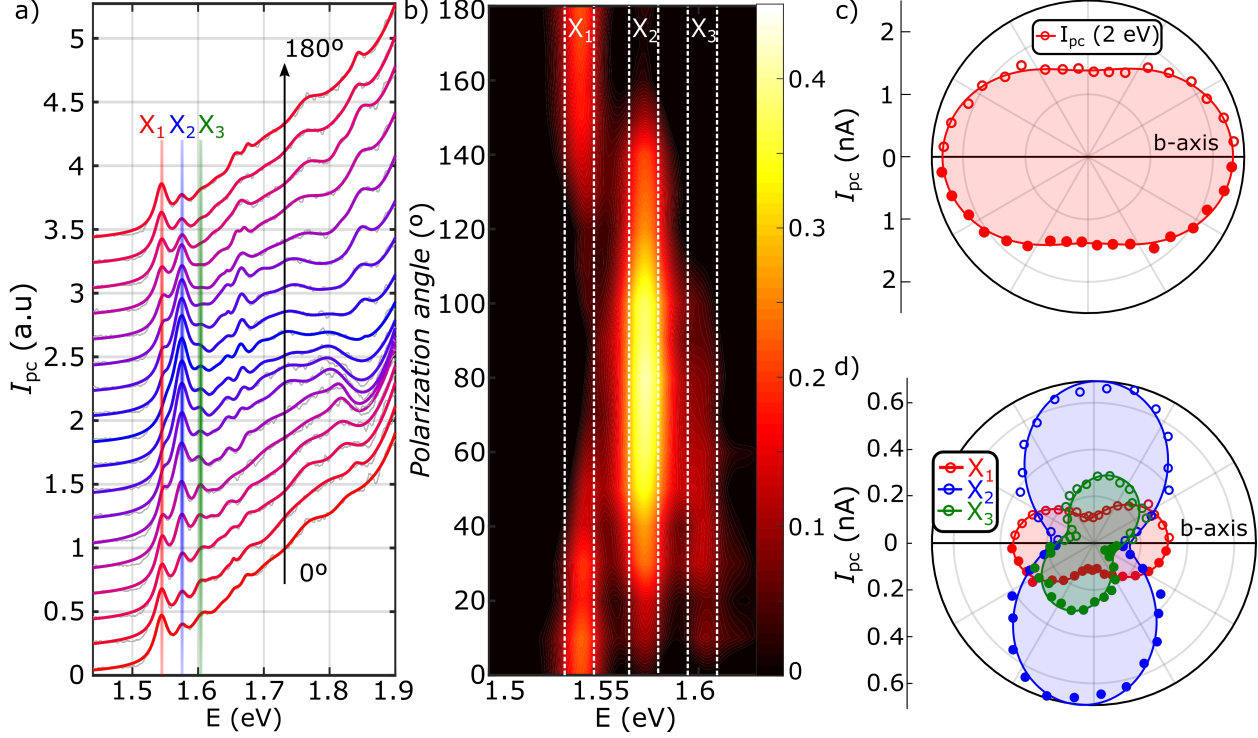


Fig. 8.3.8: Polarized-resolved photocurrent spectroscopy in AA-stacked device. a) Polarized resolved photocurrent spectra as function of the incident polarization light. Red, blue and green lines mark the three neutral excitons. b) Color-map of the excitonic modulation c) Photocurrent as function of the angle of the polarization light with the b-axis at 2 eV. d) Amplitude of the X_1 , X_2 , X_3 as a function angle of the polarization light with the b-axis. Solid lines correspond to the fittings of the data.

8.3.5 Theoretical analysis of the transitions

As discussed previously, in theoretical and experimental works there are a variety of results around the band structure and the origin of the excitonic transitions in ReS_2 . In order to give a more complete picture of the measurements obtained, a theoretical analysis using density functional theory (DFT) is performed thanks to our theoretical colleagues from the quantum nanosystems group from the University Complutense of Madrid. Various exchange-correlation functionals and methods were evaluated, revealing indirect bandgaps ranging from 1.24 eV to 1.26 eV, aligning with previous studies, except for the TB09 functional which indicated a 1.425 eV gap. After comparing the results obtained from different functionals combined with the Bethe-Salpeter equation formalism the TB09 functional accurately captures all significant excitonic features of ReS_2 , including a transition at 1.59 eV, referred to as X_3 . In contrast, the PBE functional more effectively describes the X_2 feature. Therefore, it is concluded that the TB09 and

PBE functionals provide the most accurate results among the functionals evaluated, with TB09 standing out for its detailed representation of experimental observations. Figure 8.4.1 shows the band structure of the bulk ReS₂ obtained using the PBE functional. In comparison with previous literature, we find a direct band gap in X-point of the brillouin zone without a significant influence of the spin-orbit coupling in the location of direct transitions (blue and green lines in figure).

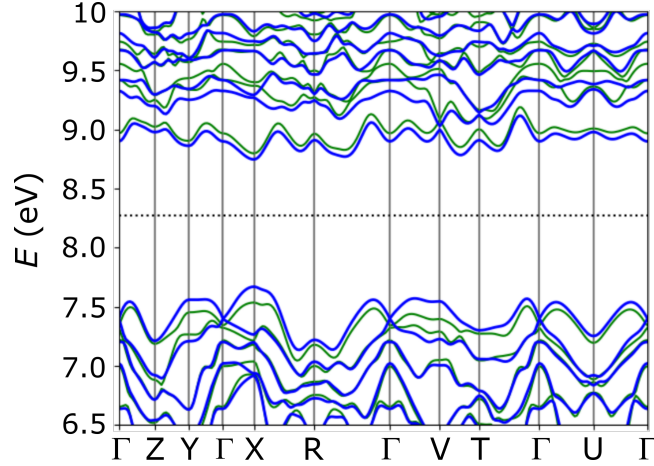


Fig. 8.3.9: Band structure of bulk ReS₂ with (blue) and without (green) spin-orbit coupling along the entire Brillouin zone, using the PBE functional.

8.4 Conclusions

In this chapter, we have presented a comprehensive characterization of the spectral photoresponse of few-layer ReS₂ devices using low temperature photocurrent spectroscopy. We have fabricated phototransistors with AA and AB-stacked ReS₂.

Focusing on the AB-stacked device, we fully characterized the optoelectronic response, obtaining the electrical characteristics and the photoresponse times of the device (around 1 ms). Next, using photocurrent spectroscopy we identified three main excitonic peaks, X₁ and X₂, previously identified in different studies, and X₃, that seems a novel excitonic peak related to a different optical transition. We also observed a set of peaks that we labelled as the Rydberg excited states of the neutral excitons. At lower energies, roughly 15 meV below X₁, another spectral peak is identified as the trion associated to X₁, T₁. We confirm the nature of T₁ and identify the mechanism of I_{pc} as the photogating effect analyzing the gate dependence of I_{pc} and of the spectral features.

Finally, analyzing the polarization dependence of the excitonic transitions, we confirm the novel non-radiative exciton X₃ and the origin of the excited states. The comprehensive characterization conducted in this chapter [213] enhances the understanding of polarization-dependent optoelectronic behaviour of ReS₂, particularly regarding excitons.

A significant aspect of our research is the discovery of a novel exciton transition in the photocurrent spectra, a feature not previously documented in optical spectroscopy studies. Our results also show that ReS_2 is a promising candidate to exploit symmetry dependent effects. Moreover, we demonstrate that photocurrent spectroscopy is a solid and versatile technique to study this effects.

Chapter 9

Circular photocurrents in ReS_2 and excitons in moiré MoSe_2 homobilayers

The main goal of this chapter consists in briefly expose possible future perspectives of the photocurrent spectroscopy in van der waals materials, advancing a step ahead from this dissertation. In this chapter we present preliminary results obtained that encourage the continuation of this research line.

Firstly, we continue with the study of ReS_2 as a possible candidate for the study non-linear optoelectronic phenomena. The crystalline structure of ReS_2 , 1T-distorted, is non-centrosymmetric, and lacks of inversion symmetry while the material posses time-reversal symmetry, being possible the arise of circular polarized light dependent photocurrents as the circular photogalvanic effect. Secondly, we study a moiré homobilayer of MoSe_2 forming a 0° twist angle between monolayers. The formation of a moiré pattern originates exotic excitonic physics. We identify interlayer and intralayer excitons combining photoluminescence and photocurrent spectroscopy. Furthermore, performing gate dependent measurements we tentatively identify strong correlated intralayer excitons in the moiré pattern.

9.1 Circular photocurrents in ReS_2

9.1.1 Introduction

Among 2D materials, monolayer 2H-transition metal dichalcogenides have outstanding properties for the development of valleytronic and spintronic devices. The singular band structure, shown in figure 1.4.2, with two non-equivalent valleys K and K', arises from a lack of inversion symmetry giving an opposite berry phase for the two valleys [214]. For systems with inversion symmetry the berry curvature, $\Omega(k)$, obeys

$$\Omega(k) = \Omega(-k) \quad (9.1.1)$$

and if the system is time-reversal symmetric also

$$\Omega(k) = -\Omega(-k) \quad (9.1.2)$$

From these conditions is possible to conclude that the systems with both inversion and time-reversal symmetry shows a Berry curvature is 0 [214]. However, the breaking of inversion symmetry, combined with conserved time-reversal symmetry, causes the K and K' valleys to respond to light of opposite helicities. When a monolayer TMD is illuminated with circularly polarized light, with photon energy close to the bandgap, only appear optical transitions in one of its two valleys, K or K', dependent on the light helicity. This leads to a light-induced valley population imbalance [98]. Moreover, monolayer 2H-TMDs exhibit significant spin-orbit splitting, with a sign change between the K and K' valleys, coupling the spin and valley degrees of freedom. These characteristic optical selection rules yields in helicity-dependent circular photogalvanic effects (CPGE) [215] at illumination wavelength in resonance with excitonic transitions. Berry curvature have been proposed as the origin of CPGE [216, 217]. However, berry curvature has been ruled out as the dominant mechanism in 2H-TMDs [57] due to the vanishing of CPGE when excitation light is in normal incidence with the crystal.

In the recent years, the interest on the study of non-linear phenomena in non-symmetric materials has increased due to its relation with geometrical and topological properties [218], being possible to explain some of these phenomena using the Berry curvature, even when $\Omega(k)$ vanishes introducing the concept of Berry curvature dipole. Second-harmonic generation [219], non-linear hall effects and CPGE [220] can arise from the lack of inversion symmetry. Recent works have demonstrated large second-harmonic generation in ReS_2 [221, 222] making this material a potential candidate for the presence of CPGE.

In this section, we perform preliminary helicity-dependent photocurrent measurements in a few layer ReS_2 device for different wavelengths to analyze the spectral dependence of the circular photocurrent generation. Similarly to [217, 215, 57] we observe an increase of the circular dependence when the excitation wavelength is in resonance with the excitonic transitions.

9.1.2 Circular photocurrents in ReS_2

Figure 9.1.1 a) displays a sketch of the few-layer ReS_2 device indicating the planar contacts of Cr/Au on the flake and the measurement configuration following the same procedure of previous chapters D, S, and G indicate the drain, source and gate, respectively, of the phototransistor. Unless otherwise is stated the device is kept in the cryostat under vacuum conditions at a temperature of $T = 7$ K. The device photoresponse is characterized using our photocurrent spectroscopy setup, illuminating uniformly the whole device. To obtain circularly polarized light, we use a linear polarizer and a quarter-waveplate, $\lambda/4$ placed in a rotator stage.

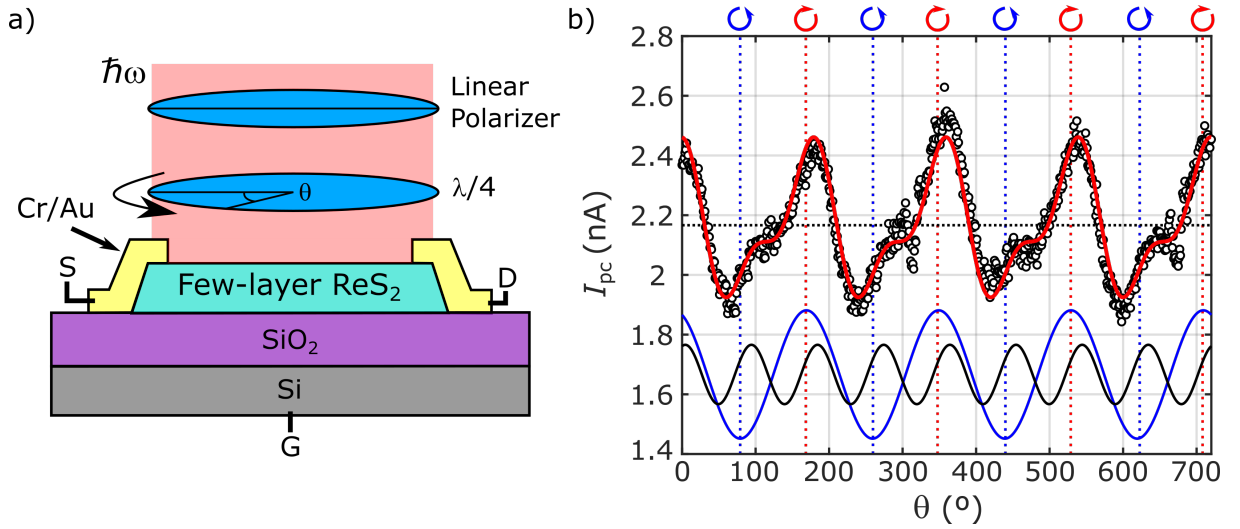


Fig. 9.1.1: Experiment geometry and circular photocurrents in ReS_2 . a) Schematic of the ReS_2 with Cr/Au contacts exposed to circularly polarized light. The quarter waveplate is rotated to change the helicity and the polarization of the excitation light. b) Photocurrent as a function of the waveplate angle depicted as black circles. Red line corresponds with the fitting to phenomenological equation, while constant (black dashed line), circular (blue solid line) and linear (black solid line) contributions depicted individually. Measurement is done at $V_{\text{ds}} = 5$ V, $V_{\text{g}} = 45$ V and illumination energy of 1.57 eV.

Following, for the characterization the helicity-dependent photoresponse of our device, the polarization of the incident light is modulated rotating $\lambda/4$ waveplate. This waveplate modulates the light between left and right circular polarization twice over a 360° rotation. The angle θ represents the orientation of the waveplate fast axis relative to the incoming laser polarization axis. Figure 9.1.1 b) illustrates the helicity-dependent photocurrent at a drain-source voltage, $V_{\text{ds}} = 5$ V, gate-voltage, $V_{\text{g}} = 45$ V and illumination energy $E = 1.57$ eV. The observed dependence of I_{pc} signal can be phenomenologically fitted using

$$I_{\text{pc}}(\theta) = I_0 + C\sin(2(\theta + \theta_0)) + L_1\sin(4(\theta + \theta_0)) + L_2\cos(4(\theta + \theta_0)) \quad (9.1.3)$$

following a similar procedure done in seminal works [57, 215, 217, 223]. In the equation, I_0 is the polarization independent photocurrent, C accounts for the circular dependent I_{pc} , while L_1 and L_2 corresponds with the linear dependent part of I_{pc} . θ_0 corresponds with the misalignment between the linear polarizer and the $\lambda/4$ waveplate. The total linear contribution can be written as $L = \sqrt{L_1^2 + L_2^2}$. It is important to remark that equation 9.1.3 is purely phenomenological and no assumption about the microscopic origin of the circular photocurrents is made for the deduction of the equation. In the particular case of ReS_2 , the presence of a linear component of the photocurrent is expected as the photoresponse depends of the angle of the linear polarization showing a dichroic behaviour [213], while the circular component can arise from different effects such as, berry curvature dipole [220] or the presence of asymmetries arising from the schottky contacts [224, 225].

9.1.3 Spectral dependence of the circular photocurrents

As mentioned in the introduction, the origin of circular photocurrents have been associated with excitonic transitions in 2H-TMDs. In order to shed light about the relation between excitons and a circular photocurrents, we analyze the spectral dependence of the linear and circular components of the helicity-dependent photoresponse.

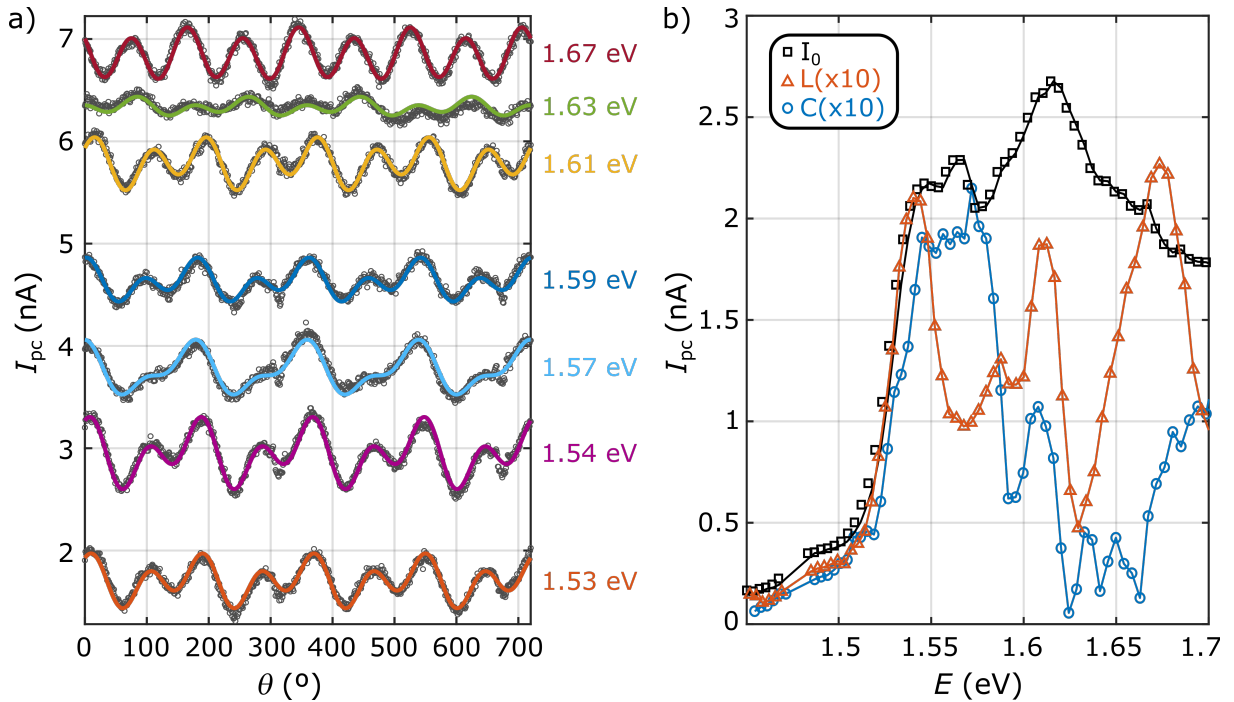


Fig. 9.1.2: Spectral dependence of the circular photocurrent in ReS_2 device. a) Helicity dependence of I_{pc} measured for various illumination energies. Experimental data are depicted using grey circles and the correspondent fittings with solid lines. The measurements are vertically shifted 0.7 nA for clarity. b) Spectral evolution of the fitting parameters, C (orange circles), L (blue triangles) and I_0 (black squares). Values of C and L are multiplied by a factor 10 for visualization. Measurements are done at $V_{\text{ds}} = 5$ V at $V_{\text{g}} = 45$ V.

Figure 9.1.2 a) illustrates the helicity-dependent I_{pc} measured at different excitation energies, alongside the fittings of the experimental data to equation 9.1.3., depicted as dots and solid lines, respectively. The fittings shows a good correlation with the experimental data. Figure 9.1.2 b) displays the spectral dependence of the extracted fitting parameters C , L and I_0 from measurements taken with a step of 2 nm. The polarization-independent component, I_0 , mirrors the photocurrent spectrum of few-layer ReS_2 discussed in chapter 8, being possible to clearly distinguish the excitons X_1 and X_2 at roughly 1.54 eV and 1.57 eV, along with the Rydberg states of the excitons. However, X_3 and Rydberg states are not distinctly resolved due to the larger step size in wavelength. Linear and circular components of I_{pc} shows a pronounced modulation as the illumination energy is tuned. Specifically, L shows two prominent peaks, one at 1.54 eV aligning with X_1 , and another at 1.63 eV corresponding to rydberg state R_1 . Beyond 1.65 eV, L increases with the starting of the absorption band edge. C shows a broad maximum in the range between 1.54 eV and 1.565 eV in resonance with X_1 and X_2 , suggesting a behaviour linked to the excitonic transitions.

9.1.4 Conclusions

In this section, we have performed measurements of the helicity-dependent photoreponse in an AB-stacked ReS_2 phototransistor, characterized in chapter 8, under normal illumination. Moreover, we have covered the spectral range from 1.45 eV to 1.7 eV, to study the spectral dependence of the circular photocurrents. The modulation of the photocurrent with the rotation of the quarter-waveplate is fitted by the phenomenological equation 9.1.3, allowing us to separate the independent, circular and linear polarization components of the photocurrent (I_0 , L , C). Using I_0 is possible to reproduce the photocurrent spectrum of the few-layer ReS_2 , while L and C show a spectral behaviour strongly related with the excitonic transitions of the material. L becomes maximum in resonance with X_1 and R_1 because the polarizer is parallel with the b-axis of the material. Furthermore, L increases as the illumination energy approximates to the absorption band edge. The modulation of the linear component may occur due to the anisotropic nature of the light absorption and the excitonic transitions in ReS_2 . C reaches its maximum in resonance with neutral excitonic transitions, X_1 and X_2 , showing a decoupled behaviour from L . The rise of the circular component at illumination energies correspondent with excitonic transitions have been previously reported in 2H-TMDs monolayers, however the origin of this effect in TMDs have been linked to the presence of opposite berry curvature in the K and K' valleys [217], and ReS_2 band structure lacks of this property, suggesting for a different mechanism behind the helicity-dependent photocurrents. Also, in other works [224, 225, 212], this effect is linked to a symmetry-breaking induced by the schottky contacts. In this characterization we illuminate the whole device, thus, the region near the schottky contacts is also illuminated. A further characterization by using space resolved photocurrent to reduce the effect of the schottky contacts is needed. These preliminary measurements shows the potential of ReS_2 as a candidate for study the origin of nonlinear effects and exploit CPGE for different applications.

9.2 Excitons in moiré MoSe_2 homobilayers

9.2.1 Introduction

One of the most attractive points of 2D materials is the possibility of combine them, stacking atomically thin layers of crystals to form different type of heterostructures. During this dissertation we have used h-BN to encapsulate TMDs and graphene just to improve their properties. However, it is also possible to combine different materials [12, 14]. Due to strong orbital overlap from their close proximity, 2D materials can adopt properties from neighboring layers, a phenomenon known as the proximity effect. This interaction leads to a combination of the materials best properties. For instance, by stacking graphene with transition metal dichalcogenides (TMDs), the strong spin-orbit coupling of TMDs can be transferred to graphene, enabling spin manipulation within graphene [226, 227]. Another example, from a technological point of view, is the combination of TMDs to build p-n junctions for light-detection or light-emitting devices [228, 229]. Furthermore, the stacking of monolayer TMDs to form bilayers opens the possibility of new appearance of excitonic states, such as interlayer excitons, where the electrons and holes are confined in different layers. Figure 9.2.1 shows a schematic representation in the real space of the intra- and interlayer excitons in a TMD/TMD heterostructure.

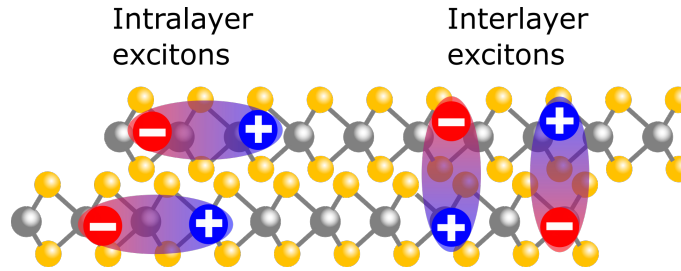


Fig. 9.2.1: Schematic of the inter- and intralayer excitons in the TMDs bilayers.

Beyond from simply creating heterostructures of different 2D materials, the twist angle between layers is a degree of freedom which largely affects the properties of the stack. The discovery of superconductivity in twisted bilayer graphene, at a precisely aligned "magic angle" of 1.1° , highlights the critical role of layer alignment in determining the physical properties of 2D materials [230], opening the research field of twistronics. This observation extends beyond graphene, as other 2D van der Waals materials also exhibit dependent properties on the twist angle. For instance, the interlayer and intralayer excitonic properties of TMDs vary significantly for different values of the twist angle [231, 232]. Stacking layers at a twist angle creates a unique in-plane pattern called moiré superlattice. The period of these moiré patterns depends on both the difference in lattice constants and the twist angle between the layers [233].

Regarding the excitonic properties of TMDs moiré bilayers, interlayer and intralayer excitons shows different signatures of the presence of a moiré superlattice [234]. For in-

stance, interlayer excitons are enhanced when the twist angles between the layers are approximately 0° or 60° [235, 236] due to the larger period of the moiré pattern at this angles. Usually, in literature the moiré TMDs bilayer studied are heterobilayers formed by two different TMDs [235, 237, 238, 239] revealing the formation of moiré excitons in this heterostructures. Nevertheless, the formation of moiré patterns and the presence of moiré excitons are not restricted only to heterobilayers. The stacking of two identical monolayers, so called homobilayers, hosts excitons affected by moiré potentials.

To study the intralayer and interlayer excitons in a moiré sample, we fabricate a phototransistor based on a MoSe_2 homobilayer with a twist-angle between the layers of 0° . In this section, we expose the work performed in the Zernike Institute for Advanced Materials in the University of Groningen. All the measurements were carried in the University of Groningen, while the $\text{MoSe}_2/\text{MoSe}_2$ homobilayer with a twist angle of 0° was fabricated in the clean room of Salamanca.

9.2.2 Experimental setup

The photocurrent spectroscopy setup is similar to previously described in section 3.6. The main differences rely on the use of an 20X optical objective that allows to focus the light beam, reaching a spot size of roughly $2 \mu\text{m}^2$ and the use of a spectrometer aligned after the sample to perform photoluminescence spectroscopy measurements.

Figure 9.2.2 shows the schematic of the low temperature photocurrent and photoluminescence spectroscopy setup in the University of Groningen. A NKT Photonics SuperK EXTREME supercontinuum white light laser, paired with a SuperK Select tunable wavelength filter, serves as the illumination source covering a spectral range of 690 nm - 1100 nm. A chopper modulates the light synchronized with a SR830 lock-in amplifier. The light polarization, initially horizontal, can be modulated using a half-wave plate and directed through a beam splitter cube, dividing the light between the sample and a silicon photodiode (PD36A2) to monitorize the power of the laser. The reflected light is directed through a second beam splitter on a flip mount, guiding light from a white lamp to the sample for illumination, allowing the direct observation of the laser spot and the sample using a CCD camera. Before starting a measurement, the beam splitter is flipped away from the beam path. A motorized quarter-wave plate enables to modulate the light polarization from linear to circular. The light beam is directed to the optical objective mounted in a xyz stage to precisely focus and aligning over the sample. The sample is maintained in vacuum within a LakeShore Janis flow cryostat. In the cryostat the samples are electrically connected in a 24-pin holder. The optoelectronic measurements are performed following the procedure explained in section 3.6.1. Subsequently, the reflected light is collected again by the objective and passes through the beam splitter cube. At this point it is possible to measure the power of the reflected light using a silicon photodiode, allowing to measure simultaneously the photocurrent and the reflectivity to perform scanning photocurrent resolved in space. The photoluminescence spectroscopy measure-

ments are performed coupling a spectrometer in the setup with a flip mirror. The sample is illuminated with monochromatic light at 690 nm wavelength and the light emitted by the sample is collected using a focal lens and an optic fiber coupled to a spectrometer. Before the optic fiber the light of the laser is filtered using a long pass filter of 690 nm.

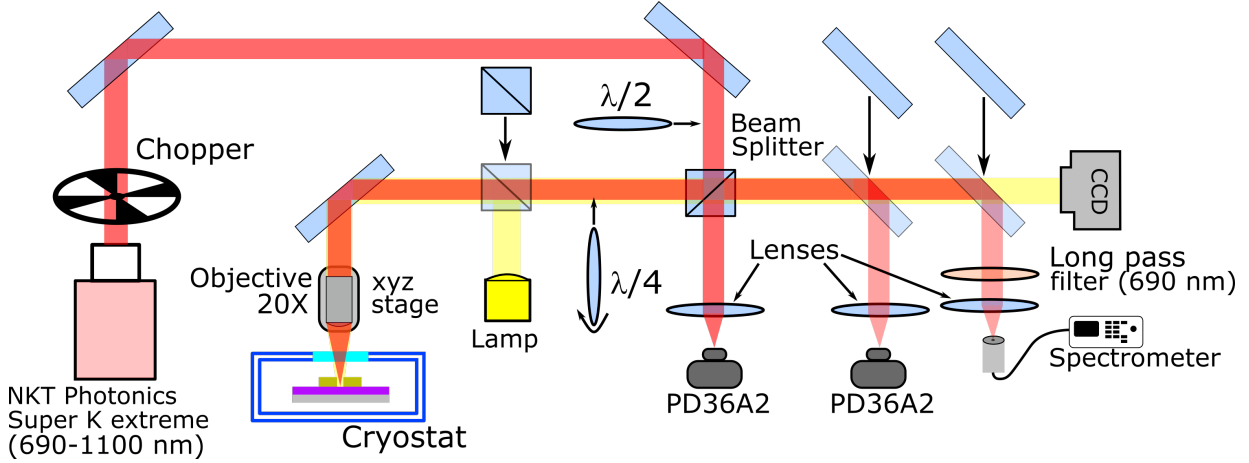


Fig. 9.2.2: Schematic of the low-temperature photocurrent and photoluminescence spectroscopy setup.

9.2.3 Electrical characterization of the MoSe_2 homobilayer

Following a similar procedure explained in the previous chapters, we start with the electrical characterization of the 0° twisted MoSe_2 homobilayer ($\text{t-MoSe}_2/\text{MoSe}_2$) phototransistor. Figure 9.2.3 a) shows an optical image of the device. The monolayer MoSe_2 is exfoliated using PDMS and identified by optical contrast. Then, it is transferred to a dummy Si/SiO_2 substrate. The $\text{hBN}/\text{MoSe}_2/\text{MoSe}_2$ heterostructure was assembled through the PC transfer method, employing the tear-and-stack method [240] to create twisted bilayer MoSe_2 . Subsequently, this heterostructure was placed onto pre-patterned gold contacts on the bottom hBN flake, resulting in the $\text{hBN}/\text{MoSe}_2/\text{MoSe}_2/\text{hBN}$ stacking. Figure 9.2.3 b) displays a schematic of the geometry of the device, indicating the planar contacts of Cr/Au on the flake and the measurement configuration, where we apply a drain-source voltage between the electrodes and the gate voltage through the Si/SiO_2 substrate. In this sample we have deposited the contacts previously on the hBN , to obtain a device with planar contacts after the tear-stack technique. Figure 9.2.3 c) presents the gate transfer curve for the $\text{t-MoSe}_2/\text{MoSe}_2$ phototransistor at $V_{\text{ds}} = 5$ V, showing a clear n-type behaviour with $V_{\text{th}} = 4.5$ V. Figure 9.2.3 d) illustrates the $I - V$ characteristics at various V_{g} , where a nonlinear response is observed, likely due to asymmetric Schottky barriers at the contacts. Remarkably, both sets of measurements present a minimal hysteresis.

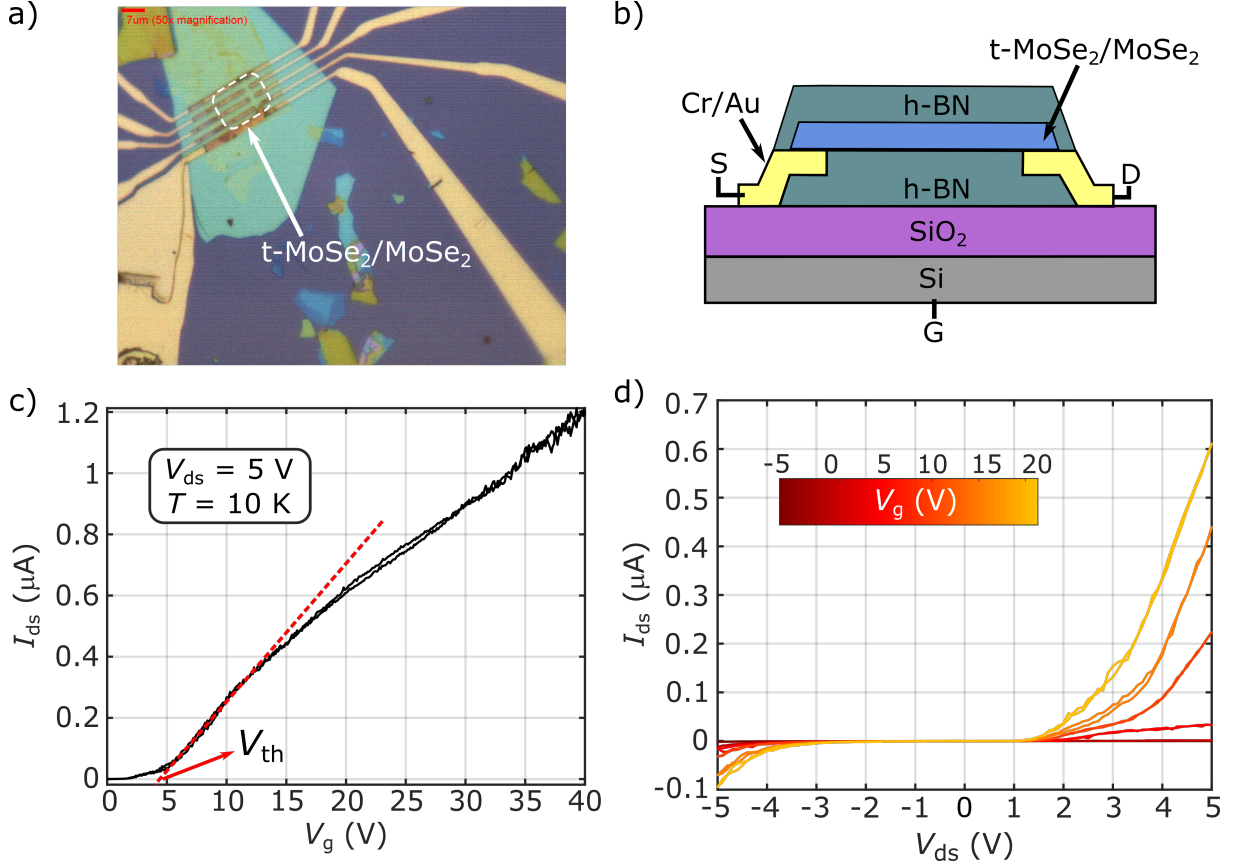


Fig. 9.2.3: Measurement configuration and characterization of the electric response of the t-MoSe₂/MoSe₂ phototransistor at 10K. a) Optical microscopy image of the encapsulated t-MoSe₂/MoSe₂ transistor. b) Schematic drawing of the t-MoSe₂/MoSe₂ device with the source, drain and gate contacts highlighted. c) Gate transfer characteristic at $V_{ds} = 5$ V, indicating n-type behavior with $V_{th} = 4.5$ V, estimated from I_{ds} linear region (red dashed line). d) Device I - V characteristics at different gate voltages.

9.2.4 Interlayer excitonic states using Photoluminescence spectroscopy

After the electrical characterization of the t-MoSe₂/MoSe₂ phototransistor, we start with the characterization of the different excitonic states. Figure 9.2.4 a) shows the origin of the exciton transitions with an schematic of the band structure near the band-gap of the t-MoSe₂/MoSe₂, depicting the two-types of interlayer excitons [241]. Firstly, direct K-K excitons are formed around the K valleys of both MoSe₂ layers. These excitons are intralayer excitons where both electrons and holes are confined within the same layer and interlayer excitons featuring an electron in one MoSe₂ layer and a hole in another. Secondly, another type of interlayer excitons can emerge from indirect optical transitions between the Γ and K valleys of different MoSe₂ layers.

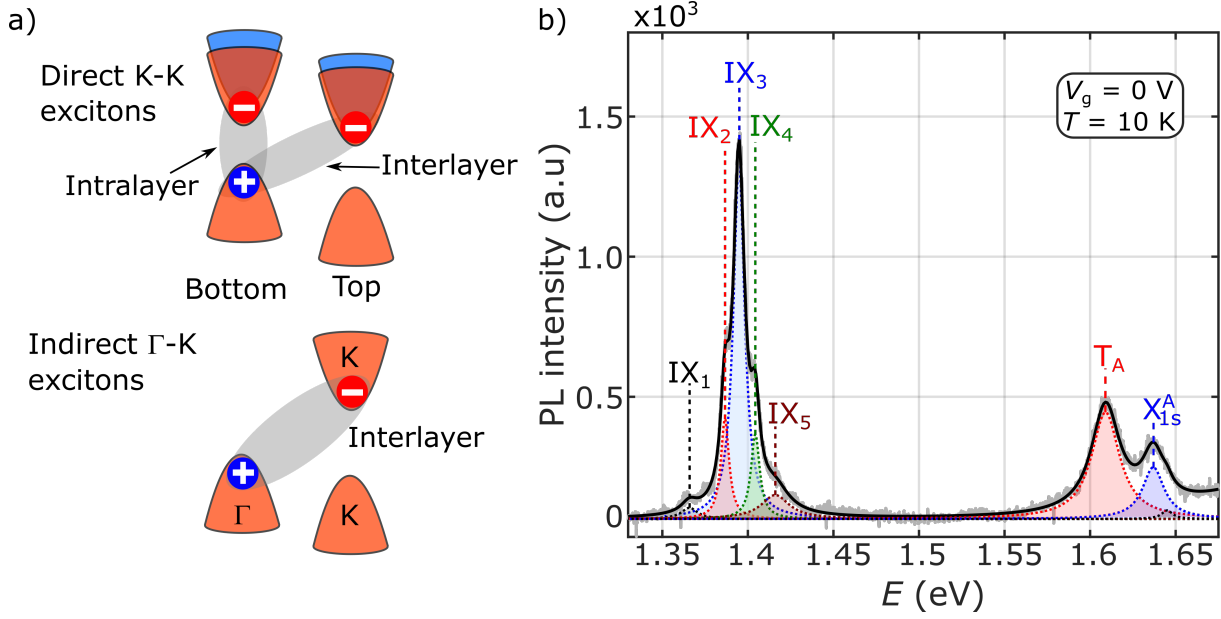


Fig. 9.2.4: Interlayer and intralayer excitons in the $\text{t-MoSe}_2/\text{MoSe}_2$. a) Schematic drawing of the origin of inter- and intralayer excitons in the $\text{t-MoSe}_2/\text{MoSe}_2$. The interlayer excitons can arise from the direct transition between the K valleys or the indirect transition between the Γ -K of the MoSe_2 top and bottom layer [241]. b) Photoluminescence spectrum of the $\text{t-MoSe}_2/\text{MoSe}_2$ measured at $V_g = 0$ V and $T = 10$ K. The inter- and intralayer excitons are highlighted in the plot.

As explained before, we have the possibility to study the excitonic states using photoluminescence (PL) or photocurrent (PC) spectroscopy measurements. The use of PL spectroscopy is convenient for excitonic states of lower energy, such as interlayer excitons. The interlayer excitons presents a high population [232], thus, the PL emission of these states is really strong in comparison with intralayer excitons [228, 242]. Furthermore, the oscillator strength of the interlayer excitons are two orders of magnitude lower than the intralayer [243]. Therefore, the use of photocurrent spectroscopy is not suitable for the study of these states. Figure 9.2.4 b) shows the photoluminescence spectrum of the $\text{t-MoSe}_2/\text{MoSe}_2$ measured at $T = 10$ K and $V_g = 0$ V. The PL spectrum shows peaks at higher energy near 1.6 eV and peaks at lower energy around 1.4 eV. Analogous to observations in other TMD bilayers [244, 245], the peaks around 1.6 eV correspond to momentum-direct intralayer excitons, where both electrons and holes are located in the same layer. Meanwhile, the peaks around 1.4 eV are attributed to momentum-indirect interlayer excitons, involving electrons and holes situated in different layers. In the region associated with interlayer excitons, various peaks are observable. The blue peak, IX_3 corresponds with the main interlayer exciton Γ -K. The broad black and red peaks, IX_1 and IX_5 , shows an energy splitting of 18-20 meV can be related with phonon replicas [241]. Meanwhile, the sharp red and green, IX_2 and IX_4 , showing energy splittings of 6-8 meV from the blue peak, are possibly linked to interlayer moiré excitons that result from the confinement imposed by the moiré superlattice potential [246, 247].

9.2.5 Intralayer excitonic states using Photocurrent Spectroscopy

The small oscillator strength of interlayer excitons complicates their study using methods besides PL [243]. For instance, techniques such as photocurrent and differential reflectivity experiments could yield valuable insights into the intrinsic dynamics of interlayer, however, the resonant excitation and measurement of this excitonic states really difficult.

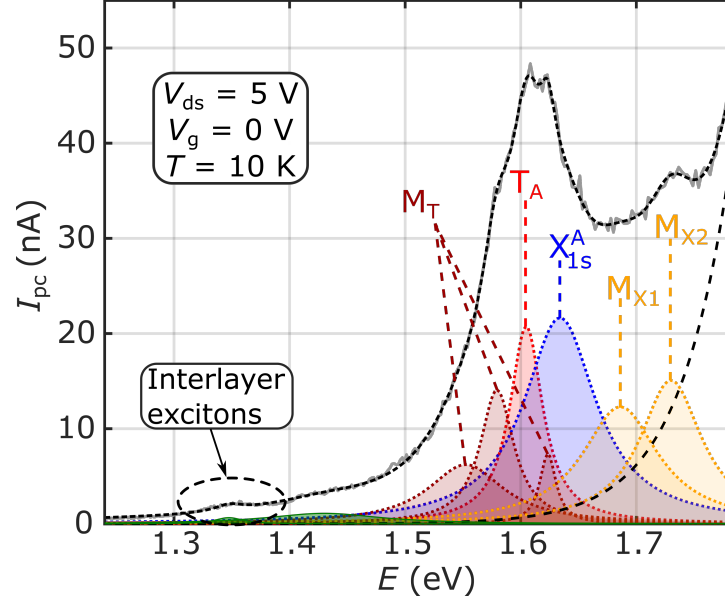


Fig. 9.2.5: Low-temperature photocurrent spectrum of the t- $\text{MoSe}_2/\text{MoSe}_2$ phototransistor (grey line) and the fitting to a multi-lorentzian peak function plus an exponential background (black dashed line). Below the spectrum, the Lorentzian peaks are displayed, detailing the conventional neutral exciton X_{1s}^A (blue), trion T_A (red), the moiré trions, M_T (dark red), and moiré excitons M_{X1} , M_{X2} (yellow).

The interest of using absorption based techniques such as differential reflectivity or photocurrent spectroscopy in moiré heterostructures relies on the study of intralayer excitons. After confirming the moiré nature and the quality of our device using PL spectroscopy and observing clearly the interlayer excitons, we use photocurrent spectroscopy to characterize the intralayer excitons. Figure 9.2.4 shows the photocurrent spectrum of the t- $\text{MoSe}_2/\text{MoSe}_2$ phototransistor measured at $V_{ds} = 5$ V, $V_g = 0$ V and $T = 10$ K. At lower energies a small bump appears at energies of roughly 1.37 eV that can be related with the interlayer excitons. As previously explained the contribution of the interlayer excitons to the photocurrent is almost negligible. The photocurrent spectrum is fitted properly using a multi-peak Lorentzian function. We observe two spectral peaks at 1.604 eV and 1.633 eV that we associate with the interlayer trion, T_A and neutral exciton of the bilayer MoSe_2 X_{1s}^A in accordance with the PL spectrum of figure 9.2.4. In the proximity of these main peaks three peaks appear at energies of 1.552 eV, 1.58 eV and 1.623 eV. In previous literature [236], these peaks have been associated with the presence of moiré trions, denoted as M_T , that arise from the moiré potential formed in the t- $\text{MoSe}_2/\text{MoSe}_2$. Furthermore, two peaks emerge at energies of 1.687 eV and 1.729 eV. These type of peaks

above the main excitons also have been related with intralayer moiré excitons in heterobilayers of TMDs [242, 248]. We labelled these peaks as M_{X1} and M_{X2} . The appearance of moiré excitons significantly highlights the impact of the moiré superlattice on excitonic states, as demonstrated in previous research [249]. In order to confirm the impact of the moiré superlattice, we measure the gate dependence of the photocurrent spectra. Figure 9.2.6 a) shows the gate-dependent normalized photocurrent, $I_{\text{pc}}^{\text{norm}}$, colormap at $T = 10$ K. I_{pc} is normalized to the maximum value of each spectra to avoid the influence of the photogating effect in the analysis. In the colormap it is possible to observe the region around 1.6 eV where we have identified the intralayer excitonic peaks. Figure 9.2.6 b) displays the gate-dependent integrated normalized photocurrent. Integrated $I_{\text{pc}}^{\text{norm}}$ varies with V_g , reaching maximum values at $V_g = 6, 18$ and 34 V. In a seminal work [242] in moiré heterobilayers of TMDs the integrated PL intensity allow the authors identify several correlated electronic phases of the moiré superlattice. Here, using photocurrent spectroscopy we observe a similar effect. Therefore, these maxima in the integrated $I_{\text{pc}}^{\text{norm}}$ could be related with the presence of strong correlated states arising from the moiré potential of the superlattice [250].

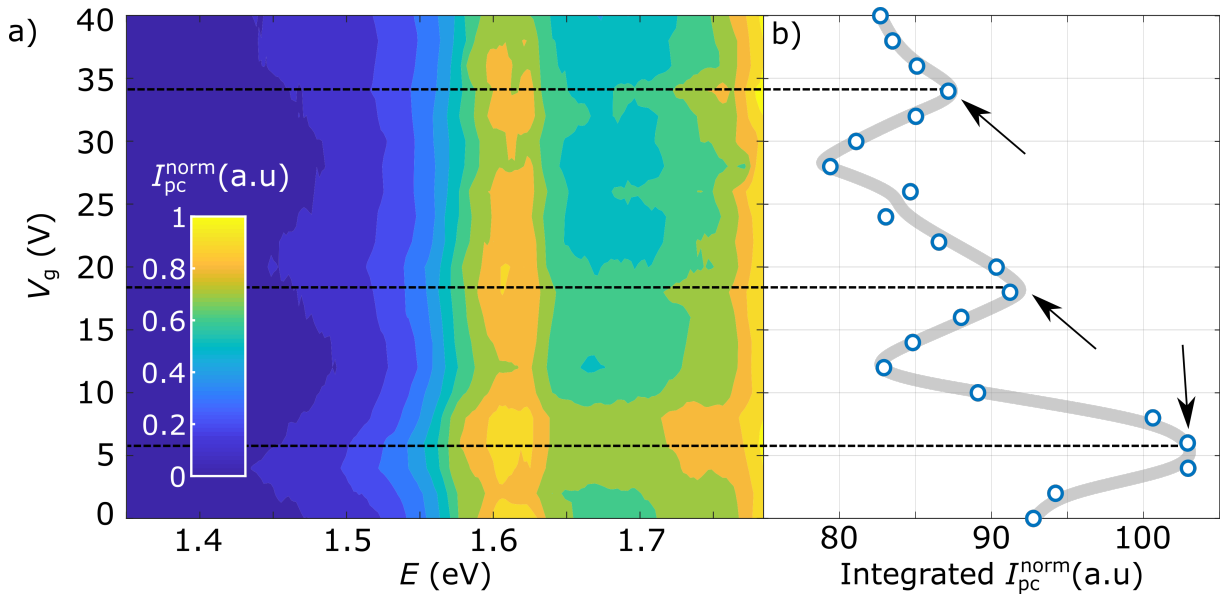


Fig. 9.2.6: Gate modulation of photocurrent spectra of the t-MoSe₂/MoSe₂ phototransistor. a) Gate-dependent photocurrent map b) Integrated $I_{\text{pc}}^{\text{norm}}$ in panel (a) as a function of V_g . The dots corresponds with the $I_{\text{pc}}^{\text{norm}}$ integrated over the whole range depicted and the grey line is drawn guide to the eye for clarity

9.2.6 Conclusions

In this section, we have introduced the concept of moiré superlattices in twisted bilayers of TMDs and the type of excitons that appear in this heterostructures, the interlayer and the intralayer excitons. Furthermore, the excitons are highly affected by the moiré potential of the superlattice. Combining PL and PC spectroscopy we have provided a

general picture of both type of excitons in twisted homobilayer of MoSe₂ with a twist angle between the layers of 0°.

PL spectrum shows prominent interlayer excitons. In previous literature [241] the main interlayer excitons in t-MoSe₂/MoSe₂ have been related with indirect transitions between the valleys Γ and K. Additionally to the main excitonic transition, we observe four transitions, two broad and two sharp transitions. We associate the broad transitions to phonon replicas of the main exciton and the sharp ones to moiré excitons.

PC spectroscopy is a completely different approach and reveal the intralayer excitons of the homobilayer. We observe the presence of the main excitons of the bilayer, T_A and X_{1s}^A . Moreover, we observe three trions related with the moiré superlattice [236] below X_{1s}^A and above this energy two transitions associated with moiré excitons. After identifying the different exciton transitions in the homobilayer based in the previous literature, we study the photocurrent spectra dependence with the gate voltage. Integrating the normalized photocurrent over the whole spectra, we observe a periodic appearance of maxima. In comparison with previous PL studies, where maxima in integrated PL intensity reveal strongly correlated states at fractional filling factors of the moiré superlattice [242], we can infer these maxima in the integrated photocurrent to these correlated states. Nevertheless, a further characterization is needed to confirm if these maxima are a signature of the presence of strong correlated states.

We have extracted valuable information of the behaviour of moiré bilayer of TMDs combining PL and PC spectroscopy, however we need to extend the study of the moiré potential influence in the photocurrent spectral response of moiré heterostructures to more devices. The use of doubled gated devices and the measurements in devices with different twist angle would provide new insights on this topic in the future.

Chapter 10

Summary and conclusions

This thesis included experimental work on two distinct research lines, high temperature quantum hall effect in graphene and low temperature photocurrent spectroscopy in transition metal dichalcogenides (TMDs). While different, they both share the same material platform, namely 2D van der Waals materials. Below, to conclude this dissertation, I analyze the work performed on the high temperature quantum hall effect, and I finish with the discussion on the work regarding low temperature photocurrent spectroscopy. Finally, I design a route of the future work to be done after this dissertation briefly reported in the previous chapter.

The discovery of graphene as a stable material made available a new platform for the study of the quantum hall effect. Graphene shows an unconventional quantization values in the hall conductivity due to its linear band dispersion in the absence of a magnetic field. The quantization of Hall conductivity in graphene is described by $\sigma_{xy} = \pm 4e^2/h(N + 1/2)$, being N the Landau level, in stark contrast with conventional semiconductors [6, 73]. Moreover, the energy separation between the Landau levels Δ_{LL} is proportional to $\pm\sqrt{BN}$, being B the magnetic field, leading to a huge Δ_{LL} .

Since the discovery of the quantum hall effect in the 80s [21], this effect was typically studied in 2D systems at low temperatures of few kelvin, reaching temperatures up to liquid nitrogen in few systems [131, 132, 133]. Graphene changed the rules of the game, allowing the access to study the quantum hall effect under relaxed experimental conditions [76], even up to room temperature (RT) [24] at strong magnetic fields (up to 30T). Nevertheless, the studies involving graphene at temperatures near RT [74, 122] were performed in graphene on SiO_2 , where the roughness of the substrate induces disorder scattering in the electrons. In this samples, the main mechanism of activation of the quantum hall effect is the disorder scattering.

The use of h-BN as atomically flat substrate to encapsulate graphene revolutionized the research in graphene devices [17, 114]. The flatness of h-BN suppresses intrinsic ripples in graphene reducing the disorder scattering. This fact provides access to a regime of electrical transport dominated by electron-phonon scattering at RT[37]. In chapter 3, we fabricated a compilation of 5 encapsulated devices with different influence of disorder in their transport properties, to study the activation of the quantum hall effect. We demonstrate that the quantum hall activation mechanism in encapsulated graphene is dominated by electron-phonon scattering [120] comparing our experimental data with both theoretical studies [137, 130] and graphene supported on SiO₂ devices [122]. Furthermore, we measured the activation of the quantum hall effect at low temperatures (< 100 K), confirming that in the absence of phonons, the disorder activation becomes dominant. Our work demonstrates a new transport regime in the quantum hall effect, 40 years after its discovery, thanks to the use of van der waals materials, concretely graphene and h-BN.

Now, I turn on the main research line of this dissertation, the use of low temperature photocurrent spectroscopy for the study of excitonic transitions in two dimensional transition metal dichalcogenides (2D-TMDs). Similarly to the previous study on the quantum hall effect using graphene, the emergence of 2D van der waals materials, concretely the 2D-TMDs discovery, revolutionize the excitonic physics offering an exceptional platform to study these phenomena [58]. 2D-TMDs such as MoS₂ or MoSe₂ shows a direct band gap and a strong spin-orbit splitting in the valence band states, leading to the presence of two main excitonic transitions, neutral excitons A and B. The binding energy of excitons in 2D-TMDs reaches values of hundreds of meV. Furthermore, in these materials, new excitonic transitions may arise, such as trions [84], rydberg states [78] or biexcitons [85]. These remarkable excitonic effects sparked the research of this phenomena using 2D-TMDs. The most used technique is photoluminescence spectroscopy [93, 94, 95, 97], however, few studies rely on the use of photocurrent spectroscopy [26, 25]. Therefore, we explored the possibility of using this experimental technique to study excitonic physics in 2D-TMDs. Furthermore, we went beyond previous works incorporating low temperature (< 10 K) to reduce thermal disorder and improve the spectral resolution. Besides the identification of different photoexcited states, from a technological point of view photocurrent spectroscopy is crucial for characterizing excitonic devices designed to bridge light-based and electron-based communication protocols by enabling the electrical detection of optically excited exciton states. Despite its importance, the number of studies on photocurrent spectroscopy in 2D-TMDs remained limited in the scientific literature until this dissertation.

In chapter 4, we started our investigation by studying the mechanisms of photocurrent in a h-BN encapsulated monolayer MoS₂ phototransistor to understand the photocurrent generation in 2D-TMDs [164]. Two mechanisms dominate the photoresponse in these devices. First, the photoconductive effect, based on the increase of the conductivity due to the generation of photoexcited free carriers. Second, the photogating effect, based on the shift of the Fermi energy due to the light-induced filling or depletion of localized states

with trapped carriers. Both mechanisms play a role in the photocurrent, however, modulating the gate voltage it is possible to change the dominant mechanism in the device. Moreover, in contrast with previous studies, we conclude that the photogating effect arise from defects associated with sulfur vacancies in the MoS₂ atomic structure [164] contrary to previous studies in MoS₂ [140]. This opens the possibility of modifying the photore-sponse of 2D-TMDs transistor inducing defects.

After understanding the mechanisms of photoresponse, chapters 5 and 6 have shown the low temperature photocurrent spectroscopy characterization of a monolayer MoS₂ and a MoSe₂ encapsulated phototransistors [180, 199]. We combined low temperature photocurrent spectroscopy with the high quality of our devices to resolve several exciton peaks, reaching linewidths as low as 8 meV, similar to previous photoluminescence studies [161]. In both Mo-based transistor we distinguished the two neutral excitons, A and B, and the two trions associated. Furthermore, we modulated the relative intensity of the peaks changing the doping density as done in previous photoluminescence [84, 86]. In MoS₂, beyond these peaks, we resolved four excited states of each exciton, obtaining rydberg series of both excitons simultaneously, identifying unequivocally all the peaks solving the schrodinger equation with the keldysh potential [174]. To the best of our knowledge, the observation of the rydberg states associated with exciton B was not previously reported. In MoSe₂ phototransistor we change the focus to the study of the interaction of excitons with charge carriers in the device. Modulating the gate voltage we observe a crossover in the dominant trion species from negative to positive, depending if the carriers are electrons or holes respectively. Besides, we study the relative positions of the negative trion and the neutral exciton. From many body theory [194, 186] we confirm the effective mass of electrons in MoSe₂ [185].

Finally, in chapter 7 we focus on the study of ReS₂ [213], a 2D-TMD with an anisotropic crystalline structure. Our photocurrent spectroscopy setup is also suitable for the study light polarization influence in the photoresponse. Using two ReS₂ devices with different stacking orders (AA- and AB-stacking), we identified three main excitonic peaks with a dichroic dependence on the angle of the linear polarized light. Moreover, in the photocurrent spectra we resolved a trion and five excited states of the main excitons. We associated the origin of this states by matching the polarization dependence of these peaks with the main excitonic transitions. Two of the main excitons were previously reported in several works [208, 202], while the third peak remained elusive. This highlights the capability of photocurrent spectroscopy to reveal novel optical transitions.

This thesis shed light about the use of low temperature photocurrent spectroscopy for the study of 2D-TMDs. Furthermore, this method offers benefits by eliminating the need for a microscope objective to focus the light beam onto a small sample area. This makes photocurrent spectroscopy quite simple in comparison with previous alternatives. All the findings done highlight the amazing possibilities that offer this technique to access non-radiative transitions in comparison with photoluminescence. Using low temperature

photocurrent spectroscopy we have revealed transitions that remains elusive, even after years of intensive research, such as the rydberg series of exciton B in MoS₂ or the third neutral exciton in ReS₂.

Additionally, there were several experiments that remained unfinished during this PhD. In chapter 8, I have presented two possibilities to continue exploiting the possibilities of photocurrent spectroscopy. Firstly, the study of the possible generation of helicity dependent photocurrents in ReS₂ and its spectral dependence. Secondly, the use of photocurrent spectroscopy to study twisted TMDs heterostructures to reveal moiré excitonic states. Preliminary characterizations of this phenomena seem to be promising, however, a deep and intense work needs to be done to obtain conclusive results.

On the one hand, in the generation of helicity-dependent photocurrents in ReS₂, it is necessary to clarify whether their origin stems from the intrinsic material or from the Schottky contacts of the device. On the other hand, in the study of moiré heterostructures of TMDs, it is essential to characterize heterostructures with different rotation angles and design devices with dual gates to accurately control the doping level of the device.

Appendix A

Abstract

Esta tesis se enmarca dentro del amplio campo de investigación de los materiales 2D de van der waals. El aislamiento del grafeno monocapa y el posterior descubrimiento de varios materiales de van der waals ha hecho que surja de una nueva plataforma para estudiar diferentes fenómenos físicos, superando los límites previos en la física de la materia condensada. En esta tesis presento dos líneas de investigación, ambas dentro de este campo.

La primera parte se centra en el estudio del efecto hall cuántico a alta temperatura en grafeno encapsulado con h-BN. Antes del aislamiento del grafeno, el efecto Hall cuántico en sistemas 2D se observaba típicamente a temperaturas cercanas a la del helio líquido (4 K). Sin embargo, la irrupción del grafeno permite investigar el efecto Hall cuántico hasta temperatura ambiente debido a su gran separación de los niveles de Landau. En este estudio, a través del análisis de la activación del efecto hall cuántico en el factor de llenado 2 hasta temperatura ambiente en dispositivos de grafeno de alta calidad, revelamos un nuevo régimen de transporte donde la dispersión de electrones y fonones es la principal fuente de disipación dentro de éste efecto. Además, establecemos una relación entre la activación del efecto Hall cuántico y la calidad de nuestros dispositivos. Gracias a las heteroestructuras de van der waals del hBN y el grafeno, podemos tener una idea más clara del efecto Hall cuántico, incluso 40 años después de su descubrimiento.

La segunda parte se centra en el estudio de excitones en dicalcogenuros de metales de transición (TMDs) mediante espectroscopía de fotocorriente a baja temperatura. Los dicalcogenuros de metales de transición 2D muestran excitones fuertemente ligados que influyen notablemente en su respuesta optoelectrónica. La energía de enlace de los excitones en estos materiales alcanza valores dos órdenes de magnitud mayores que en los semiconductores convencionales. Por tanto, los 2D-TMD son un sistema perfecto para estudiar excitones. Antes de esta disertación, la mayor parte de la investigación de los fenómenos excitónicos en TMDs se estudiaban mediante espectroscopia de fotoluminiscencia. Sin embargo, esta técnica no puede revelar excitones no radiativos. Por lo tanto, proponemos el uso de espectroscopia de fotocorriente de baja temperatura para estudiar la física de excitones en dispositivos basados en 2D-TMDs, concretamente en MoS₂, MoSe₂ y

ReS₂. La espectroscopía de fotocorriente es una técnica poderosa que nos permite obtener anchos de línea de transición de aproximadamente 10 meV, similares a los anteriores estudios de fotoluminiscencia. Además, al utilizar esta técnica revelamos picos excitónicos no observados en trabajos de espectroscopía anteriores, lo que demuestra el potencial de esta técnica. Con nuestra investigación proporcionamos nuevos conocimientos sobre la física de excitones en los 2D-TMD y proporcionamos una herramienta experimental con enormes posibilidades en el futuro. Finalmente, presento futuros temas de investigación que se pueden desarrollar utilizando espectroscopía de fotocorriente a baja temperatura.

Appendix B

Resumen y Conclusiones

Esta tesis incluye el trabajo experimental realizado en dos líneas de investigación distintas, el efecto Hall cuántico medido a alta temperatura en grafeno y el estudio de espectroscopía de fotocorriente a baja temperatura en dicalcogenuros de metal de transición. Siendo diferentes, ambas comparten la investigación del mismo grupo de materiales, los materiales 2D de van der Waals. A continuación, para concluir esta disertación, analizo el trabajo realizado sobre el efecto Hall cuántico de alta temperatura y termino con una discusión sobre el trabajo relacionado con la espectroscopia de fotocorriente de baja temperatura. Finalmente, diseño una ruta de trabajo futuro a realizar luego de esta disertación reseñada brevemente en el capítulo anterior.

El descubrimiento del grafeno como un material estable puso a disposición una nueva plataforma para el estudio del efecto Hall cuántico. El grafeno muestra valores de cuantización no convencionales en la conductividad Hall debido a que sus bandas muestran una relación de dispersión lineal en ausencia de un campo magnético. La cuantización de la conductividad Hall en el grafeno se describe mediante $\sigma_{xy} = \pm 4e^2/h(N + 1/2)$, siendo N el nivel de Landau, en claro contraste con los semiconductores convencionales [6, 73]. Además, la separación de energía entre los niveles de Landau Δ_{LL} es proporcional a $\pm\sqrt{BN}$, siendo B el campo magnético, dando lugar a un valor alto de Δ_{LL} .

Desde el descubrimiento del efecto hall cuántico en los años 80 [21], este efecto se estudiaba típicamente en sistemas 2D a bajas temperaturas de unos pocos kelvin, alcanzando temperaturas de hasta nitrógeno líquido en pocos sistemas [131, 132, 133]. El grafeno cambió las reglas del juego, permitiendo el acceso al estudio del efecto hall cuántico en condiciones experimentales más amplias [76], incluso hasta temperatura ambiente [24] en campos magnéticos altos (cerca de 30 T). Sin embargo, los estudios que involucran grafeno a temperaturas cercanas a temperatura ambiente [74, 122] se realizaron en grafeno sobre SiO₂, donde la rugosidad del sustrato induce dispersión de los electrones por desorden. En estas muestras, el principal mecanismo de activación del efecto Hall cuántico es la dispersión del desorden.

El uso de h-BN como un sustrato atómicamente plano para encapsular grafeno revolucionó la investigación en dispositivos de grafeno [17, 114]. El h-BN, al ser completamente plano, suprime las arrugas que se pueden producir en el grafeno, reduciendo la dispersión por desorden. Ésto proporciona acceso a un régimen de transporte eléctrico dominado por la dispersión entre fonones y electrones a temperatura ambiente [37]. En el capítulo 3, elaboramos una recopilación de 5 dispositivos encapsulados con diferente influencia del desorden en sus propiedades de transporte, para estudiar la activación del efecto hall cuántico. Demostramos que el mecanismo de activación efecto hall cuántico en grafeno encapsulado está dominado por la dispersión de fonones y electrones [120] comparando nuestros datos experimentales con estudios teóricos [137, 130] y con dispositivos grafeno que utilizan como sustrato SiO₂ [122]. Además, medimos la activación del efecto Hall cuántico a bajas temperaturas (< 100 K), confirmando que en ausencia de fonones el mecanismo de activación por desorden se vuelve dominante. Nuestro trabajo demuestra un nuevo régimen de transporte en el efecto hall cuántico, 40 años después de su descubrimiento, gracias al uso de materiales de van der waals, concretamente grafeno y h-BN.

A continuación, me centro en la principal línea de investigación de esta tesis, el uso de espectroscopía de fotocorriente a baja temperatura para el estudio de transiciones excitónicas en dicalcogenuros de metales de transición bidimensionales (2D-TMDs). De manera similar al estudio anterior sobre el efecto hall cuántico utilizando grafeno, la aparición de materiales 2D de van der waals, en concreto el descubrimiento de los 2D-TMDs, revoluciona la física de excitones y ofrece una plataforma excepcional para estudiar estos fenómenos [58]. Los 2D-TMDs como MoS₂ o MoSe₂ muestran una banda prohibida directa y un fuerte desdoblamiento entre estados de diferente espín en la banda de valencia debido a la interacción espín-órbita, lo que lleva a la presencia de dos excitones principales, los excitones neutrales A y B. La energía de ligadura de los excitones en los 2D-TMDs alcanza valores de cientos de meV. Además, en estos materiales pueden surgir nuevas transiciones excitónicas, como triones [84], estados de Rydberg [78] o biexcitones [85]. Estos efectos excitónicos tan notables impulsaron la investigación de este fenómeno usando los 2D-TMDs. La técnica más utilizada es la espectroscopia de fotoluminiscencia [93, 94, 95, 97], sin embargo, pocos estudios se basan en el uso de la espectroscopia de fotocorriente [26, 25]. Por lo tanto, exploramos la posibilidad de utilizar esta técnica experimental para estudiar la física de excitones en 2D-TMDs. Además, dando un paso más que en trabajos anteriores, incorporamos el uso de baja temperatura (< 10 K) para reducir el desorden térmico y mejorar la resolución espectral. Además de la identificación de diferentes estados fotoexcitados, desde un punto de vista tecnológico, la espectroscopia de fotocorriente es crucial para caracterizar dispositivos excitónicos diseñados para unir protocolos de comunicación basados en luz y electrones al permitir la detección eléctrica de estados de excitones ópticamente excitados. A pesar de su importancia, el número de estudios sobre espectroscopia de fotocorriente en 2D-TMD seguían siendo limitado en la literatura científica hasta esta disertación.

En el capítulo 4, comenzamos nuestra investigación estudiando los mecanismos de la fotocorriente en un fototransistor de MoS_2 monocapa encapsulado en h-BN para comprender la generación de fotocorriente en los 2D-TMDs [164]. Dos mecanismos dominan la fotorespuesta en estos dispositivos. En primer lugar, el efecto fotoconductor, basado en el aumento de la conductividad debido a la generación de portadores libres fotoexcitados. En segundo lugar, el efecto de fotopuerta, basado en el cambio de la energía de Fermi debido al llenado o vaciamiento inducido por la luz de estados localizados con portadores atrapados. Ambos mecanismos juegan un papel en la fotocorriente, sin embargo, modulando el voltaje de la puerta es posible cambiar el mecanismo dominante en el dispositivo. Además, a diferencia de estudios anteriores, concluimos que el efecto de fotopuerta surge de defectos asociados con vacantes de azufre en la estructura del MoS_2 [164] a diferencia de estudios previos en mecanismos de MoS_2 [140]. Esto abre la posibilidad de modificar la fotorespuesta de los transistores basados en 2D-TMDs induciendo defectos.

Después de comprender los mecanismos de la fotorespuesta, en los capítulos 5 y 6 se ha mostrado la caracterización mediante espectroscopía de fotocorriente a baja temperatura de fototransistores de monocapas de MoS_2 y MoSe_2 encapsuladas [180, 199]. Combinamos espectroscopia de fotocorriente a baja temperatura con la alta calidad de nuestros dispositivos para resolver varios picos de excitones, llegando a alcanzar anchos de línea tan bajos como 8 meV, similares a los estudios previos de fotoluminiscencia [161]. En ambos transistores basados en molibdeno distinguimos los dos excitones neutros, A y B, y los dos triones asociados. Además, modulamos la intensidad relativa de los picos cambiando la densidad de dopaje como se hizo anteriormente en estudios que utilizan fotoluminiscencia [84, 86]. En MoS_2 , más allá de estos picos, hemos resuelto cuatro estados excitados de cada excitón, obteniendo las series de Rydberg de ambos excitones simultáneamente e identificando de forma inequívoca todos los picos resolviendo la ecuación de Schrodinger con el potencial Keldysh [174]. Hasta donde sabemos, la observación de los estados de Rydberg asociados con el excitón B no se había realizado previamente. En el fototransistor MoSe_2 pasamos al estudio de la interacción de los excitones con los portadores de carga en el dispositivo. Modulando el voltaje de puerta observamos un cambio en la especie de triones dominante, cambiando de negativa a positiva, dependiendo de si los portadores son electrones o huecos respectivamente. Además, estudiamos las posiciones relativas del trión negativo y el excitón neutro. A partir de teoría de muchos cuerpos [194, 186] confirmamos la masa efectiva de electrones en MoSe_2 [185].

Finalmente, en el capítulo 7 nos centramos en el estudio de ReS_2 [213], un 2D-TMD con una estructura cristalina anisotrópica. Nuestro sistema de medida para realizar espectroscopía de fotocorriente también es adecuado para estudiar la influencia de la polarización de la luz en la fotorespuesta. Usando dos dispositivos ReS_2 con diferentes órdenes de apilamiento (apilamiento AA y AB), identificamos tres picos excitónicos principales con una dependencia dicroica respecto al ángulo de la luz polarizada lineal. Además, en los espectros de fotocorriente observamos un trión y cinco estados excitados de los excitones principales. Asociamos el origen de estos estados comparando la dependencia de la po-

larización de estos picos con las transiciones excitónicas principales. Dos de los excitones principales aparecían previamente en varios trabajos [208, 202], mientras que el tercer pico no ha aparecido en ningún estudio previo. Esto resalta la capacidad de la espectroscopia de fotocorriente para revelar transiciones ópticas nuevas.

Esta tesis da información sobre el uso de la espectroscopía de fotocorriente a baja temperatura para el estudio de 2D-TMD. Además, este método ofrece beneficios al eliminar la necesidad de utilizar un objetivo de microscopio para enfocar el haz de luz en un área pequeña sobre la muestra. Esto hace que la espectroscopía de fotocorriente sea bastante simple en comparación con las alternativas anteriores. Todos los hallazgos realizados ponen en valor las posibilidades que ofrece esta técnica para acceder a transiciones no radiativas en comparación con fotoluminiscencia. En nuestra investigación utilizando espectroscopía de fotocorriente hemos revelado transiciones que permanecían ocultas, incluso después de años de investigación intensiva, como la serie de Rydberg del excitón B en MoS_2 o el tercer excitón neutro en ReS_2 .

Además, hubo varios experimentos que quedaron inacabados durante este doctorado. En el capítulo 8, he presentado dos posibilidades para continuar explotando las posibilidades de la espectroscopia de fotocorriente. En primer lugar, el estudio de la posible generación de fotocorrientes dependientes de la helicidad en ReS_2 y su dependencia espectral. En segundo lugar, el uso de espectroscopía de fotocorriente para estudiar las heteroestructuras de TMDs rotadas para revelar estados excitónicos de moiré. Las caracterizaciones preliminares de este fenómeno parecen prometedoras, sin embargo, es necesario profundizar en este trabajo para obtener resultados concluyentes. En el caso de generación de fotocorrientes dependientes de la helicidad en ReS_2 sería necesario esclarecer si su origen proviene del propio material o de los contactos schottky del dispositivo. En el estudio de heteroestructuras moiré de TMDs, sería necesario caracterizar heteroestructuras con diferentes ángulos de rotación y diseñar dispositivos con dos puertas para controlar correctamente el nivel de dopaje del dispositivo.

Appendix C

List of publications

The results obtained during this thesis have been published in these articles:

1. **Vaquero, D.**, Clericò, V., Salvador-Sánchez, J., Martín-Ramos, A., Díaz, E., Domínguez-Adame, F., Meziani, Y. M, Diez, E. & Quereda, J. (2020). Excitons, trions and Rydberg states in monolayer MoS₂ revealed by low-temperature photocurrent spectroscopy. *Communications Physics*, 3(1), 194.
2. **Vaquero, D.**, Clericò, V., Salvador-Sánchez, J., Díaz, E., Domínguez-Adame, F., Chico, L., Meziani, Y. M, Diez, E. & Quereda, J. (2021). Fast response photogating in monolayer MoS₂ phototransistors. *Nanoscale*, 13(38), 16156-16163.
3. **Vaquero, D.**, Salvador-Sánchez, J., Clericò, V., Diez, E., & Quereda, J. (2022). The low-temperature photocurrent spectrum of monolayer MoSe₂: Excitonic features and gate voltage dependence. *Nanomaterials*, 12(3), 322.
4. **Vaquero, D.**, Clericò, V., Schmitz, M., Delgado-Notario, J. A., Martín-Ramos, A., Salvador-Sánchez, J., Müller, C.S.A., Rubi, K.m, Watanabe, K., Taniguchi, T., Beschoten, B., Stampfer, C., Diez, E., Katnelson, M.I, Zeitler, U., Wiedmann, S. & Pezzini, S. (2023). Phonon-mediated room-temperature quantum Hall transport in graphene. *Nature Communications*, 14(1), 318. **Best article of the Semester in the period October 2022 - March 2023. División de Física de la Materia Condensada, GEFES.**
5. **Vaquero, D.**, Arroyo-Gascón, O., Salvador-Sánchez, J., Alcázar-Ruano, P. L., Diez, E., Perez-Rodríguez, A., Correa, J.D., Domínguez-Adame, F., Chico, L., & Quereda, J. (2023). Polarization-tuneable excitonic spectral features in the optoelectronic response of atomically thin ReS₂. *2D Materials*, 11(1), 015011.
6. **Vaquero, D.**, Clericò, V., Salvador-Sánchez, J., Quereda, J., Diez, E., & Pérez-Muñoz, A. M. (2021). Ionic-liquid gating in two-dimensional TMDs: The operation principles and spectroscopic capabilities. *Micromachines*, 12(12), 1576.

Appendix D

Other publications

1. Pérez-Martín, E., González, T., **Vaquero, D.**, Sánchez-Martín, H., Gaquière, C., Raposo, V. J., Mateos, J. & Iniguez-De-La-Torre, I. (2020). Trap-related frequency dispersion of zero-bias microwave responsivity at low temperature in GaN-based self-switching diodes. *Nanotechnology*, 31(40), 405204.
2. Lechaux, Y., Ñiguez-de-la-Torre, I., Novoa-López, J. A., García-Pérez, Ó., Sánchez-Martín, H., Millithaler, J. F., **Vaquero, D.**, Delgado-Notario, J. A., Clericò, V., González, T. & Mateos, J. (2020). Comprehensive characterization of Gunn oscillations in $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ planar diodes. *Semiconductor Science and Technology*, 35(11), 115009.
3. Pérez-Martín, E., **Vaquero, D.**, Sánchez-Martín, H., Gaquière, C., Raposo, V. J., González, T., Mateos, J. & Iniguez-De-La-Torre, I. (2020). Analysis of trap states in AlGaIn/GaN self-switching diodes via impedance measurements. *Microelectronics Reliability*, 114, 113806.
4. Ersu, G., Munuera, C., Mompean, F. J., **Vaquero, D.**, Quereda, J., Rodrigues, J. E. F., Alonso, J.A, Flores, E., Ares, J.R, Ferrer, I.J, Al-Enizi, A.M, Nafady, A., Kuriakose, S. Island, J.O, & Castellanos-Gomez, A. (2024). Low-Cost and Biodegradable Thermoelectric Devices Based on van der Waals Semiconductors on Paper Substrates. *Energy & Environmental Materials*, 7(1), e12488.
5. Salvador-Sánchez, J., Canonico, L. M., Pérez-Rodríguez, A., Cysne, T. P., Baba, Y., Clericò, V., Vila, M., **Vaquero, D.**, Delgado-Notario, J.A., Caridad, J.M., Watanabe, K., Taniguchi, T., Molina, R.A., Domínguez-Adame, F., Roche, S., Diez, E., Rappoport, T.G, & Amado, M. (2022). Generation and control of non-local chiral currents in graphene superlattices by orbital Hall effect. *arXiv preprint arXiv:2206.04565*.

Appendix E

Posters and Oral contributions

Posters

1. *Fast response photogating in monolayer MoS₂ phototransistors*. Workshop and Summer School in Basics and Applications of Nanolithography, Salamanca, (Spain).
2. *Phonon-mediated room-temperature Quantum-Hall transport in Graphene*. Graphene2023 Conference, Manchester, (England)
3. *Phonon-mediated room-temperature Quantum-Hall transport in Graphene*. 2D quantum matter summer school 2023, Lucca (Italy). **Best Poster Award**.

Oral Contributions

1. *Excitons, trions and Rydberg states in monolayer MoS₂ revealed by low-temperature photocurrent spectroscopy*. CMD 2020 GEFES, Madrid (Spain).
2. *Excitonic states in monolayer transition metal dichalcogenides revealed by low-temperature photocurrent spectroscopy*, 16th International Conference on Nanostructured Materials 2022, Sevilla (Spain).
3. *Fast response photogating in monolayer MoS₂ phototransistors*. XII Reunión de la División de Física de la Materia Condensada de la RSEF (GEFES2023), Salamanca (Spain).
4. *Excitonic states in monolayer transition metal dichalcogenides revealed by low-temperature photocurrent spectroscopy*. CMD 30 - FisMat 2023 conference, Milano (Italy).

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