Studies of ultrafast photocarrier dynamics in spatially heterogeneous transition metal dichalcogenides using time-resolved photoemission electron microscopy

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**STUDIES OF ULTRAFAST PHOTOCARRIER DYNAMICS IN
SPATIALLY HETEROGENEOUS TRANSITION METAL
DICALCOGENIDES USING TIME-RESOLVED
PHOTOEMISSION ELECTRON MICROSCOPY**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

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The *ab initio* calculations reported in the thesis were performed by Prof. Oleg Prezhdo, University of Southern California, USA, and the samples were provided by Prof. Andrea Ferrari, University of Cambridge, UK

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Abstract

Since the discovery of graphene in 2004, two-dimensional (2D) materials have drawn researchers' attention around the world. The applications of 2D materials have been rapidly developed across many disciplines, due to their favourable mechanical, thermal, chemical, electric and optical properties. Transition metal dichalcogenides (TMDs) are among some of the most popular 2D materials. Different from graphene, TMDs have intrinsic bandgaps, which open the door for their application in a variety of ultrathin semiconductor devices. The fabrication of TMDs result in diverse spatial heterogeneities in these materials, which can be either beneficial or detrimental to their properties. Hence, to improve the engineering of these heterogeneities, comprehensive studies of photocarrier dynamics in heterogenous TMDs are required. Here, we harness time-resolved photoemission electron microscopy (TR-PEEM) to investigate effects of heterogeneities on the photocarrier dynamics of TMDs.

In Chapter 1, the atomic layers and band structures of TMDs are described, which play a vital role in their optical and optoelectronic properties. Applications of TMDs in optoelectronic devices will be introduced. The performances of these optoelectronic devices depend largely on the ultrafast carrier dynamics. As such, various ultrafast phenomena that occur in TMDs will be reviewed. The applications of PEEM, especially in studies of the ultrafast dynamics of semiconductors, are introduced. Our motivations for studying the ultrafast dynamics of spatially heterogenous TMDs by TR-PEEM are also discussed.

In Chapter 2, our TR-PEEM instrument is introduced. The TR-PEEM combines ultrafast pump-probe technique and PEEM, achieving 50-fs temporal resolution and 70-nm spatial resolution. The determination of pump/probe photon orders in photoemission experiments is also shown. With the probe photon order determined, we can establish the probe window within the band structure of the measured material. With the excellent spatial

resolution, we obtain not only the temporal evolution of the TR-PEEM signal spatially integrated over the region of interest, but also a lifetime map of the time constant at each pixel of the image. The lifetime map obtained exhibits pronounced spatial heterogeneity. Moreover, the characterization of the output of a home-built noncollinear optical parametric amplifier will be presented.

In Chapter 3, we combine TR-PEEM with atomic force microscopy to investigate the spatially resolved hot-electron transfer dynamics across the monolayer MoS₂/Au interface. A spatially heterogeneous distribution of MoS₂/Au gap distances, along with the excellent temporal and spatial resolution afforded by TR-PEEM, permits the simultaneous measurement of electron transfer rates across a range of MoS₂/Au distances. The spatial distribution of electron transfer time constants is revealed, with a mean of 386 fs and a standard deviation of 54 fs. We show that electron transfer rates decay exponentially as a function of distance, with a small attenuation coefficient of $0.06 \pm 0.01 \text{ \AA}^{-1}$, demonstrating the interfacial electron transport insensitivity against distance fluctuations. *Ab initio* simulations suggest that surface plasmon-like states mediate hot-electron transfer, hence accounting for its weak distance dependence.

Chapter 4 describes the study of ultrafast carrier dynamics in a WSe₂ monolayer/multilayer Type-I homojunction. Investigation of the TR-PEEM signal obtained from the individual components of the homojunction reveals carrier cooling and exciton-exciton annihilation occurring in monolayer WSe₂ with lifetimes of $0.16 \pm 0.01 \text{ ps}$ and $5.13 \pm 0.97 \text{ ps}$, respectively. On the other hand, the electron and hole cooling are observed in multilayer WSe₂ with lifetimes of $0.11 \pm 0.01 \text{ ps}$ and $0.22 \pm 0.01 \text{ ps}$, respectively. Beyond the dynamics confined to the individual components of the homojunction, the TR-PEEM image also revealed the accumulation of holes at the interface of the homojunction; the width of the

depletion zone is found to be $0.60 \pm 0.17 \mu\text{m}$, comparable with the depletion width of traditional silicon p–n junction, which indicates that TMDs are potential replacements of silicon in semiconductor devices. Finally, TR-PEEM reveals electron-hole recombination across the homojunction with a time constant of $96 \pm 3 \text{ ps}$.

In Chapter 5, we investigate electron cooling in a wrinkled multilayer MoS_2 flake. It remains unknown how strain, introduced by wrinkling, impacts the ultrafast photocarrier dynamics of TMDs. Extracting the temporal evolution of the PEEM signal for each pixel, we obtain a time constant map of the wrinkled MoS_2 flake. We find that wrinkled MoS_2 undergoes significantly faster electron cooling, with a lifetime of $97 \pm 2 \text{ fs}$, than flat MoS_2 , with a lifetime of $120 \pm 2 \text{ fs}$. The calculated band structure of strained MoS_2 shows a smaller energy gap for intravalley scattering than unstrained MoS_2 , hence enhancing electron cooling.

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Chapter 1

Introduction

The discovery of graphene started a burgeoning interest in a class of two-dimensional (2D) materials with weak van der Waals force between adjacent layers due to their many fascinating properties.¹⁻³ So far, 2D materials have become a big family consisting of around 500 members,² offering a fertile ground for ultrathin materials researches and attractive applications. Transition metal dichalcogenides (TMDs) have been especially attractive, since the discovery of strong photoluminescence (PL) in monolayer (1L) MoS₂^{4,5} and the fabrication of 1L MoS₂ transistors.⁶ TMDs have favourable electronic and optoelectronic properties, such as high binding energies of excitons and trions,^{7,8} high carrier mobilities,^{9,10} and superconductivity^{11,12}. As a result of these properties, these have found a variety of applications including photodetectors,¹³ transistors¹⁴ and modulators¹⁵. Among the numerous advantages of TMDs, one of the most fascinating characteristics is the tunability of the properties through defect engineering.¹⁶ To comprehend the effects of defect-induced heterogeneities on the electronic and optoelectronic properties, it is crucial to study the ultrafast photocarrier dynamics in heterogeneous TMDs. Time-resolved photoemission electron microscopy (TR-PEEM) is a powerful tool to explore heterogeneities with high temporal and spatial resolutions.

1.1 Transition metal dichalcogenides

TMDs have a long and abundant history. Linus Pauling first determined the crystal structure of TMDs by X-ray crystallography in 1923.¹⁷ By 1969, about 60 types of TMDs had been discovered, two-thirds of them assuming a layered structure.¹⁸ The first report on the exfoliation of 1L MoS₂, by S.Roy Morrison, dates back to 1986.¹⁹ Research of layered materials have been exponentially growing since 2004, following the discovery of graphene. The development of synthesis and characterization techniques stimulated the novel investigations of TMDs, especially their atomically thin flakes.

TMDs are a class of semiconductors with the chemical formula MX₂, where M is a transition metal atom (such as W or Mo) and X is a chalcogen atom (such as S or Se). The transition metals and the chalcogens in MX₂ have valences of +4 and -2, respectively. The coordination of the transition metal atoms results in diverse structural phases in TMDs. Trigonal prismatic (2H) and octahedral (1T) are two of the most commonly observed structural phases in 1L TMDs (Figure 1.1).²⁰ Both of them are made up of a X-M-X sandwich, where two chalcogen atom layers are sandwiched together with one transition metal atom layer. However, the 2H phases are characterized by an ABA stacking, in which all chalcogen atoms occupy same positions vertically aligned along the z-axis. In contrast, the 1T phases are characterized by an ABC stacking, in which chalcogen atoms in one atomic layer are seated at the different positions from that in the other layer. The intralayer bonds are covalent bonds and the interlayer interactions are weak van der Waals forces.

The diversity of TMDs leads to a variety of remarkable electronic and optoelectronic properties. Here, we focus on these semiconducting TMDs composed by group 6 transition metals (such as W, Mo) and chalcogens (such as S, Se, Te). Most of their properties originate from the basic features of their band structures. The band structures of these 2H TMDs from

Figure 1.1. 2H and 1T phases of 1L TMDs. Reprinted with permission from Nature Publishing Group.²⁰

bulk to 1L are shown in Figure 1.2.²¹ The locations of the valence band maximum (VBM) and conduction band minimum (CBM) shift with decreasing layer number. These TMDs have indirect band gaps in the multilayer, changing to direct band gaps in the 1L materials, and the band gaps increasing with decreasing thickness. First-principles calculations of the quasiparticle band structure predicted the large exciton binding energies of TMDs.²² The two-photon PL excitation spectroscopy and linear absorption are employed to investigate the exciton binding energy of WSe₂ on SiO₂, which is determined to be 0.37 eV.²³ The values of the exciton binding energies are 240 meV for either MoS₂ or WSe₂ on sapphire, experimentally characterized by angle-resolved photoelectron spectroscopy and reflectance measurements.²⁴

With the outstanding electronic and optoelectronic properties, TMDs have excellent performances of applications in photodetectors, transistors and light-emitting diodes. Photodetectors based on 1L MoS₂ exhibit a very high photoresponsivity, reaching 880 AW⁻¹.²⁵

Figure 1.2. (a) MoS₂, (b) MoSe₂, (c) MoTe₂, (d) WS₂ and (e) WSe₂ band structures from the bulk to the 1L. Reprinted with permission from American Physical Society.²¹

MoS₂ transistors also have a very high on/off ratio, more than 10^8 at room temperature, setting them up as potential replacements for silicon in semiconductor devices.⁶ TMD-based light-emitting diodes exhibit the quantum efficiency of about 10%.²⁶

1.2 Ultrafast photocarrier dynamics of TMDs

Photocarriers, consisting of free electrons/holes and excitons, dominate the optical and optoelectronic properties of TMDs. Hence, a fundamental understanding of their dynamics in TMDs plays a crucial role in improving the performances of TMD-based optical and

optoelectronic devices. Pump-probe techniques are widely applied in the ultrafast dynamic studies of TMDs, which successfully overcome the response-time limitation of electronic detectors to reveal dynamics on femtosecond or even attosecond timescale.

The typical relaxation processes of photocarriers in conventional semiconductors, including TMDs,²⁷ are shown in Figure 1.3. Upon photoexcitation, the initial energy distribution of photocarriers depends on the spectrum of the excitation light. Thereafter, thermalization rapidly occurs, developing a thermal distribution of the extremely nonthermal carriers via carrier–carrier and carrier-phonon scattering. The thermalization of few-layer MoS₂ was determined to occur within 20 fs, following non-Markovian quantum kinetics.²⁸ After thermalization, the photocarriers have a Fermi-Dirac distribution with a temperature higher than that of the lattice. Therefore, the excess energy of carriers transfers to the lattice via carrier-phonon scattering, a dynamic known as cooling. The cooling of the hot carriers occurs in the few-layer MoS₂ on the ~ 0.6 ps time scale, with an observed hot-phonon effect;²⁸ and a 0.1 ps electron cooling process is observed in the 1L WSe₂.²⁹

Figure 1.3. Typical relaxing processes of photocarriers in semiconductors. Reprinted with permission from John Wiley and Sons.²⁷

1L TMDs have significantly higher exciton binding energies than conventional semiconductors. Hence, excitons in 1L TMDs are stable at room temperature, which play an important role in optical and optoelectronic properties. It was found that exciton formation is a longitudinal optical phonon-assisted process, with a time constant shorter than 1 ps.^{30,31} Following the formation, carriers relax to the ground state via exciton recombination, which can be non-radiative or radiative. Exciton-exciton annihilation, a non-radiative process, observed in TMDs with high exciton densities of more than 10^{11} cm^{-2} , is a second order process whose timescale is determined by the exciton density. The time-dependent exciton density obeys the rate equation

$$\frac{dN_{ex}}{dt} = -\frac{1}{\tau}N_{ex} - \gamma N_{ex}^2, \quad (1.1)$$

where N_{ex} is the density of exciton, τ and γ are the exciton lifetime and the exciton–exciton annihilation rate. The exciton–exciton annihilation only occurs with high exciton density at early recombination times ($t \ll \tau$). Therefore, the term $-\frac{1}{\tau}N_{ex}$ can be ignored to obtain the solution to the second-order rate equation

$$\frac{N_0}{N_{ex}(t)} - 1 = \gamma N_0 t, \quad (1.2)$$

where N_0 is the initial density of exciton. The annihilation rates of 1L TMDs are on the $0.1 \text{ cm}^2\text{s}^{-1}$ scale.³²⁻³⁴ Besides this non-radiative process, exciton recombination can occur radiatively, where the energy of the exciton is converted into a photon. This radiative recombination can be characterized by time-resolved PL measurements. The PL lifetimes of TMDs are affected by the quality of the sample, the layer number and the types of TMDs. The time constants of the radiative recombination range from a few picoseconds to hundreds of picoseconds under diverse experimental conditions.³⁵⁻³⁹

One of the promising aspects of TMDs is that they can be combined with metals or other semiconductors into hybrid materials. Besides the dynamics occurring in single-component TMDs, some unique dynamics have been observed in the hybrids of TMDs, such as charge transfer, which is a key issue in developing their electronic and optoelectronic applications. Ultrafast pump-probe measurements have revealed photocarrier dynamics in these hybrids formed by TMDs. Most popular among them are TMD heterostructures, which can usually be divided into vertical and lateral heterostructures. (Figure 1.4)⁴⁰ Two different TMD components in separate layers bound by weak van der Waals force form vertical heterostructures. On the other hand, two different TMDs connected by covalent bonds in a single layer yield lateral heterostructures. Efficient charge transfer can occur in these heterostructures. Figure 1.5 shows the ultrafast laser spectroscopy results of MoS₂/MoSe₂ vertical heterostructure.⁴¹ The pump and probe were tuned to the resonances of MoSe₂ and MoS₂, respectively. Hence, MoSe₂ was selectively excited by the pump, and the density of electrons in MoS₂ was monitored by the probe. MoSe₂/MoS₂ is a type-II heterostructure, with MoSe₂ having a higher CBM than MoS₂, hence allowing electron transfer from MoSe₂ to MoS₂.

Figure 1.4. Vertical and lateral heterostructures of TMDs. Reprinted with permission from Nature Publishing Group.⁴⁰

Figure 1.5. (a) The pump-probe configuration of MoS₂/MoSe₂ vertical heterostructure. (b) The time trace of differential reflection signal after the photoexcitation of the pump. The rise of $\Delta R/R_0$ infers the electron transfer to MoS₂. Reprinted with permission from American Chemical Society.⁴¹

The rise of $\Delta R/R_0$ is assigned to electron transfer occurring on a sub-picosecond time scale. Charge transfer is also expected to occur in TMD/metal hybrids because PL quenching of TMDs is usually observed when contacted with a metal.^{42,43} Ultrafast laser spectroscopy also reveals the charge transfer from MoS₂ to Au occurring with a time constant ~ 600 fs.⁴⁴

1.3 Photoemission electron microscopy

Photoemission electron microscopy (PEEM) collects local variations of the photoemitted electrons from samples to generate image contrast. In general, PEEM consists of a group of electrostatic lenses and an image acquisition system. The photoemission process is produced by an adequate light source, such as a mercury lamp, a pulsed laser or an X-ray tube. Then,

these photoelectrons are projected onto the image acquisition system by the electrostatic lenses. In the image acquisition system, after the amplification through a microchannel plate, the photoelectrons are converted to visible light signals by a phosphor screen. Finally, a charge-coupled device camera records the signals. The essential principle of PEEM is mostly similar with a conventional optical microscope. Nevertheless, since the imaging process involves electrons, PEEM can overcome the optical diffraction limitation to obtain a spatial resolution of a few nanometers.⁴⁵ In practical PEEM measurements, the spatial resolution can be affected by multiphoton excitation,⁴⁶ light polarization,⁴⁷ and sample morphology.⁴⁸ Moreover, compared with scanning electron microscopy, PEEM avoids using a high-energy electron beam, thereby protecting delicate samples from the beam induced damage. Hence, PEEM gives outstanding performances in diverse research fields such as biology,⁴⁵ surface science,⁴⁹ magnetism,⁵⁰ catalysis,⁴⁹ and semiconductor physics⁵¹.

With the development of ultrafast laser, TR-PEEM, a combination of PEEM and pump-probe techniques, has been employed to investigate ultrafast dynamics of materials. TR-PEEM can achieve a very high temporal resolution, via the utilization of short pulses in a pump-probe instrument. Since the spatial resolution and the temporal resolution of TR-PEEM are respectively determined by the electron microscope and ultrafast laser, TR-PEEM can achieve both the high temporal resolution and the high spatial resolution. With its advantages, the dynamics of metallic surface plasmons have been investigated by TR-PEEM.⁵²⁻⁵⁴ Figure 1.6 shows TR-PEEM images of propagating surface plasmons on a gold surface at different pump-probe delay times.⁵⁴ A lithographically patterned rectangular trench at A was used to couple propagating surface plasmons into gold surface. Pump pulses excited the trench to launch surface plasmon wave packets from A. Then, probe pulses achieved the photoemission from gold surface to obtain images of surface plasmon wave packets. Figure 1.6 (e) displays temporal evolution of the PEEM signal at C. The plasmon wave packet reaches C at 41.3 fs,

Figure 1.6. (a-c) TR-PEEM images of propagating plasmons on a gold surface at different pump-probe delay times. (b) Schematic of pump-probe geometry. The red and blue spots are beam profiles on the gold surface for the pump and the probe, respectively. (c) The time trace of PEEM signal at C. Reprinted with permission from American Chemical Society.⁵⁴

propagating on gold surface with a group velocity of $(0.95 \pm 0.01)c$. Besides the ultrafast dynamics in metals, the electron transfer has been imaged across InSe/GaAs semiconductor heterostructure.⁵⁵ Figure 1.7 displays TR-PEEM images of InSe/GaAs heterostructure taken at a series of time delays. At early time delays, from 2 ps to 10 ps, the accumulation (red) of electrons occurs in InSe, whereas the depletion (blue) is observed in GaAs. Because GaAs has a higher CBM than InSe in this type-II heterostructure, the electrons can transfer from GaAs to InSe. After 10 ps, the decay of the signal, occurring in both GaAs and InSe, is attributed to the recombination of carriers. Recently, TR-PEEM has been employed to reveal the dynamics

Figure 1.7. TR-PEEM images of InSe/GaAs heterostructure taken at different time delays. Reprinted with permission from Nature Publishing Group.⁵⁵

of TMDs. The spatial heterogeneity of the cooling and exciton-exciton annihilation dynamics was observed in 1L WSe₂, which is consistent with the existence of structural disorder and charge puddles in these materials.⁵⁶ Moreover, it was found that the trap states could be induced by laser illumination in WS₂, resulting in the emergence of a defect trapping process under high-intensity illumination.⁵⁷

1.4 Motivations

Spatial heterogeneities play crucial roles in the electronic and optical properties of TMDs. Therefore, it is crucial to visualize and analyze the ultrafast dynamics for a further comprehensive investigation of the alternate properties caused by the presence of heterogeneities, which can inspire defect engineering of TMD-based devices. The challenges are to achieve high spatial resolution for the observation of heterogeneities and high temporal resolution for the analysis of ultrafast dynamics at a femtosecond scale. Thus, we decided to employ TR-PEEM to study ultrafast dynamics of heterogenous TMDs. Here, we performed TR-PEEM measurements on TMD samples prepared by mechanical exfoliation, as TR-PEEM is highly sensitive to the sample qualities. To study the effects of spatial heterogeneities, we should compare heterogenous TMDs with homogenous TMDs under same preparing conditions. With the high spatial resolution of TR-PEEM, we can achieve the comparison on one TMD flake by extracting the signal of pixels with or without the heterogeneities. In this thesis, I will display my work on three different types of heterogeneities: (1) a spatially heterogeneous distribution of 1L MoS₂/Au gap distances, (2) the WSe₂ 1L/multilayer (NL) type-I junction, and (3) the wrinkles of NL MoS₂.

Firstly, to fabricate electronic devices, the TMD layer needs to contact a metal structure as a part of the electrical circuitry. Therefore, electron transport across TMD-metal interfaces significantly affects the performances of the TMD-based devices. Much work has been done to achieve low-resistance metal contacts to TMDs.⁵⁸⁻⁶² Gold is one of the most common candidate to contact with TMDs in devices.^{6,63,64} Thus, we studied 1L MoS₂ on a rough Au substrate, which leads to a spatially heterogeneous distribution of MoS₂/Au gap distances, to understand how interfacial structural heterogeneity influences electron transport efficiency.

Furthermore, one of the most important properties of these TMDs is a significant transition from an indirect bandgap in *NL* to a direct bandgap in *1L*. In addition, *1L* TMDs have a larger bandgap than *NL*. A type-I band alignment has been found in *1L/NL* TMD junction.^{65,66} Hence, charge transfer is expected to occur across the junction, influencing the PL process. Moreover, because interface states resulting in carrier trapping have effects on the electronic performances, the visualization of the depletion region at the interface is desired. TR-PEEM is powerful and appropriate to elucidate the ultrafast photocarrier dynamics of the WSe₂ *1L/NL* junction.

Finally, we employed TR-PEEM to study the wrinkles of *NL* MoS₂, which can result in local strain of TMD flakes. Similar to graphene, TMDs can sustain a high elastic strain before rupturing,^{67,68} and Strain engineering can continuously tune band structures of TMDs^{21,69,70} to modify the performance of TMD-based electronic and thermoelectric devices.^{71,72} To figure out the mechanism of the modulations of properties, it is crucial to study the ultrafast electron dynamics of strained MoS₂.

These studies focus on the diverse heterogeneities, which are common in the design of TMDs devices. However, the traditional optical microscopy is difficult to visualize these heterogeneities without the satisfactory spatial resolution, as the heterogeneities are often in sub-micrometer size scale. Hence, PEEM is a powerful tool to image the heterogenous TMD flakes. Moreover, we combine the femtosecond pump-probe technique with PEEM to perform time-resolved measurements. The spatial details of photocarrier dynamics can be shown intuitively. It is quite easy to extract the effects of the heterogeneities on the photocarrier dynamics.

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Chapter 2

Femtosecond Time-Resolved Photoemission Electron Microscopy

To overcome the limitation of the response time of electronic detectors, ultrashort laser pulses have been employed to elucidate the ultrafast photocarrier dynamics ($<10^{-12}$ s) of solid-state materials. The pump-probe technique, one of the most attractive methods for monitoring the time-dependent population of photocarriers via two time-delayed ultrashort laser pulses, has revealed various photocarrier dynamics, such as thermalization, cooling, exciton-exciton annihilation and radiative recombination.¹⁻³ With developments in materials engineering, it is possible to control the spatial heterogeneities of materials that can improve properties for various design aims.⁴ However, traditional optical pump-probe measurements are conducted over a large region of the sample, overlooking possible spatial heterogeneities. Ultrafast time-resolved microscopy techniques are desired to observe ultrafast dynamics of the heterogeneities. Many different experimental approaches to ultrafast microscopy have emerged. Optical pump-probe microscopy, which is a combination of transient absorption spectroscopy and optical microscopy, has investigated carrier diffusion in materials.⁵⁻⁹ Time-resolved scanning near-field optical microscopy has achieved 10-fs temporal resolution to observe the plasmon dynamics of single gold nanorods.¹⁰ Here, I focus on TR-PEEM, a combination of pump-probe

technique and PEEM. In this chapter, I will introduce the technical specifications of the optical layout and the PEEM in the TR-PEEM setup.

2.1 Overview of the TR-PEEM apparatus

Figure 2.1 shows the schematic illustration of our TR-PEEM apparatus. The TR-PEEM apparatus consists of two parts: a laser setup for the generation of ultrashort pump/probe pulses

Figure 2.1. Schematic illustration of our TR-PEEM apparatus.

and a PEEM for imaging emitted electrons. The light source of the apparatus is a Yb-doped fiber laser with 23-W output power at a maximum repetition rate of 2 MHz. In our measurements, the laser is run with a repetition rate of 600 kHz, thus achieving a pulse energy of about 38 μJ . To obtain short pulses, the primary 1030-nm laser with a pulse width of 320 fs is broadened by a Xe-filled hollow-core fiber, then compressed by a series of chirped mirrors. 55-fs pulses are focused on BBO crystals to generate the harmonics. Then, the laser is split as a pump beam and a probe beam, either of them is compressed again by a prism pair. Both the pump beam and the probe beam are focused onto the sample, giving rise to photoemission. The photoemitted electrons are collected and projected onto an image acquisition system by the PEEM. The PEEM is set in a vacuum chamber, which has a base pressure of 3×10^{-8} mbar yielded by a 300 L/s turbomolecular pump. The vacuum chamber is often baked to obtain a better vacuum degree. The sample stage is integrated with PEEM. The sample is mounted on a sample holder and directly loaded onto the PEEM sample stage. All the TR-PEEM measurements in this thesis are performed at the temperature of 295 K.

2.2 Femtosecond pump-probe technique

2.2.1 Spectral broadening and pulse compression of the 1030-nm fundamental laser output

The primary laser output delivered by the Yb-doped fiber laser has a spectrum centered at 1030 nm, which has a ~ 9 -nm bandwidth. [red line in Figure 2.2(a)] The pulse width of 320 fs for the primary laser is determined by the autocorrelation measurement. [red line in Figure 2.2(b)] To

Figure 2.2. (a) Laser spectra before and after hollow-core fiber broadening. (b) Autocorrelation traces of the 1030-nm laser without compression and with optimal compression. (c) The transform-limited pulse shape of the broadened spectrum. (d) Autocorrelation traces of laser pulses with various dispersion compensations of 0 fs^2 , -1000 fs^2 , -2000 fs^2 , -3000 fs^2 and -4000 fs^2 .

obtain the better temporal resolution for the investigation of sub-picosecond dynamics, shorter laser pulses are desired.

Here, we employ a hollow-core fiber filled with Xe gas to broaden the spectrum, and then chirped mirrors to compress the laser pulses. The output of Yb-doped fiber laser is focused onto a 200- μm inner diameter, 1-m-long hollow-core fiber filled with Xe gas under an optimal pressure of 4.6 bar. The high nonlinear refractive index of Xe promotes an efficient self-phase modulation.^{11,12} The transmission of the hollow-core fiber is around 54%. The spectrum after broadening is displayed in Figure 2.2(a), spanning 1000-1065 nm. Figure 2.2(c) shows a transform-limited pulse shape corresponding to the broadened spectrum. The shortest pulse width of 45 fs can be obtained in ideal conditions. The dispersion compensation is optimized by changing the number of the reflections of chirped mirrors (Ultrafast Innovations GmbH, -1000 fs² per reflection). Figure 2.2(d) shows that the dispersion compensation of the shortest pulses is located between -2000 and -3000 fs². Hence, three chirped mirrors are used to produce -3000 fs² dispersion and a pair of large-angle fused silica wedges is set to compensate the excessive negative dispersion. Finally, the shortest pulses are obtained when the overall dispersion compensation is tuned to $-2.54 \times 10^3 \text{ fs}^2$. The shortest full width at half maximum (FWHM) of the autocorrelation is around 77 fs [blue line in Figure 2.2(b)], thus we can obtain the optimal 1030-nm pulses with a duration of 55 fs.

2.2.2 Harmonic generation and their pulse compression

The 1030-nm fundamental laser has a 1.20-eV photon energy, which is lower than the band gaps and ionization energies of TMDs. Hence, 1030-nm laser is not suitable for use as the pump pulse in TR-PEEM studies of TMDs. I employ a series of beta barium borate (BBO) crystals to generate the second (2ω), the third (3ω) and the fourth (4ω) harmonics of the 1030-

nm laser. The 2ω is generated by a β -BBO crystal (Type I, 0.3-mm thickness, $\theta = 23.4^\circ$). For the 3ω generation, the residual fundamental laser and the 2ω propagate through an α -BBO crystal (0.3-mm thickness, $\theta = 47.4^\circ$) to compensate group velocity mismatch, then another β -BBO crystal (Type II, 0.05-mm thickness, $\theta = 40.0^\circ$) to perform a sum-frequency generation. As an alternative, the 4ω generation is accomplished by doubling the frequency of the 2ω in a β -BBO crystal (Type I, 0.04-mm thickness, $\theta = 50.0^\circ$).

The 2ω , 3ω and 4ω are spectrally isolated by using appropriate dielectric mirrors.

Figures 2.3(a-c) show their spectra and Figures 2.3(d-f) display their corresponding transform-

Figure 2.3. The spectra of (a) 2ω , (b) 3ω and (c) 4ω , and their corresponding transform-limited pulse shapes (d-f). (g) The autocorrelation time trace of 2ω pulses. The cross-correlation time traces of 3ω (h) and 4ω (i) with 2ω .

limited pulse shapes. In our experiments, the 2ω , 3ω and 4ω are recompressed by fused silica prism pairs, with dispersion compensation values of $-4.39 \times 10^3 \text{ fs}^2$, $-4.59 \times 10^3 \text{ fs}^2$, and $-1.16 \times 10^4 \text{ fs}^2$, respectively. The pulse width of the 2ω is obtained via intensity autocorrelation; whereas the durations of the 3ω and 4ω are characterized by cross-correlations with the compressed 2ω . Figures 2.3(g-i) show these time traces. I assume that all the beams have Gaussian pulse shapes. Hence, the pulse width of 2ω is given by

$$\tau_{2\omega} = \tau_{2\omega}^c / \sqrt{2}, \quad (2.1)$$

where $\tau_{2\omega}^c$ is the width of 2ω autocorrelation. The relation between the cross-correlation width and the pulse widths is expressed as

$$\tau_{3\omega/4\omega}^{xc} = \sqrt{\tau_{2\omega}^2 + \tau_{3\omega/4\omega}^2}, \quad (2.2)$$

where $\tau_{3\omega/4\omega}^{xc}$ is the cross-correlation width of $3\omega/4\omega$, $\tau_{3\omega/4\omega}$ is the pulse width of $3\omega/4\omega$. The measurements yield the 2ω , 3ω , and 4ω pulse widths of 44 fs, 33 fs, and 32 fs, respectively. Finally, the compressed 2ω , 3ω , and 4ω are focused onto samples for pump-probe experiments, with maximum pulse energies of 3.3 μJ , 0.33 μJ , and 33 nJ, respectively.

2.2.3 Design and assembly of a noncollinear optical parametric amplifier

I designed and assembled a noncollinear optical parametric amplifier (NOPA) to tune the wavelength of pump pulses. The design of the NOPA follows Ref.13. Figure 2.4(a) shows the design of the NOPA. The 1030-nm laser after the compression is split into two beams by an uncoated fused silica substrate. The $\sim 1\%$ reflection is focused into a 3-mm-thick sapphire plate

Figure 2.4. (a) The layout of the design of the NOPA. (b) Output spectra of the NOPA at different center wavelengths. (c) Interferometric autocorrelation trace (top panel) and intensity autocorrelation trace (bottom panel) of the 740-nm output after the compression by chirped mirrors.

to generate a white light continuum seed before it is re-focused into the NOPA BBO crystal (Type I, 5-mm thickness, $\theta=26.5^\circ$) by a concave mirror. The majority of the 1030-nm beam transmits through the fused silica substrate and is focused into a BBO crystal (Type I, 0.3-mm thickness, $\theta=23.4^\circ$) to generate 2ω , which serves as the NOPA pump. The 2ω beam passes through a translation stage to adjust the time delay between the white light continuum and the 2ω pump, before it is finally focused into the NOPA BBO crystal. The pump pulse energy is $2.0 \mu\text{J}$ and the pump fluence is $1.0 \text{ mJ}/\text{cm}^2$. By adjusting the time delay and the crossing angle ($\sim 3.7^\circ$) between the white light continuum seed and the 2ω pump, we can control the

amplification wavelength and bandwidth. As shown in Figure 2.4(b), the amplified wavelengths span 650 – 950 nm. The output of the NOPA is compressed by 10 reflections off a pair of chirped mirrors (Venteon, DCM9). The interferometric autocorrelation (IAC) and intensity autocorrelation traces (Femtolasers, Femtometer) of the 740-nm output after pulse compression are displayed in the top and bottom panels of Figure 2.4(c), respectively. Both traces are consistent with a FWHM pulse width of 16 fs.

2.3 Photoemission electron microscope

2.3.1 Spatial resolution

The spatial resolution of PEEM is affected by various factors, such as space charge due to emission of a large number of photoelectrons¹⁴, spherical and chromatic aberration¹⁵, and electron scattering with residual gas molecules in the vacuum chamber¹⁶. For our TR-PEEM apparatus, we use a silver grid to characterize the spatial resolution by illuminating the grid with either 3ω or 4ω . The utilization of long focal-length lenses results in large focal spot sizes on the sample; for 3ω and 4ω , the beam diameters are 1.16 mm and 1.02 mm ($1/e^2$), respectively. The beam spot sizes are larger than the maximum field of view (FoV) of 900 μm , thus permitting the uniform illumination of the measured region. Figure 2.5(a) illustrates the PEEM image of the silver grid illuminated by the 3ω with a fluence of 0.67 $\mu\text{J}/\text{cm}^2$. The FoV is 30 μm and the exposure time is 10 s. A line profile of PEEM intensity, taken along the red line in Figure 2.5(a) that is perpendicular to an edge of one grid, is illustrated in Figure 2.5(b). The PEEM signal is fitted to an error function, yielding a lateral spatial resolution of 75 nm with 3ω illumination based on the 16 – 84% criterion. Moreover, Figure 2.5(c) displays the

Figure 2.5. PEEM images of a silver grid illuminated by (a) 3ω and (c) 4ω . (b) The PEEM signal intensity along the red line drawn in (a). (d) The PEEM signal intensity along the blue line drawn in (c).

PEEM image of the silver grid with a FoV of $30\ \mu\text{m}$ and an exposure time of 10 s, illuminated by the 4ω with a fluence of $4.8\ \text{kJ}/\text{cm}^2$. The line profile along the blue mark in Figure 2.5(c) is shown in Figure 2.5(d), which characterizes a lateral spatial resolution of 55 nm under 4ω illumination. Comparing PEEM images illuminated by 3ω and 4ω , it is evident that the light source affects the spatial resolution and the morphology of the sample, consistent with previous reports.^{14,15,17,18} Variations in the images with the light source are due to the different regions of the band structure accessed by photoemission, determined by the photon energy of the light source and the photon order of the interaction, as well as different degrees of chromatic aberration caused by the kinetic energy distributions of emission electrons.

2.3.2 Determination of photon order and photoemission window

Power dependence measurements are carried out to determine the photon order of the interaction of the light sources with the silver grid. The PEEM signal intensity is given as

$$S_{PEEM} = \sigma \cdot F^N, \quad (2.3)$$

where σ is the N -photon ionization cross-section, F is the fluence of the pump pulse, and N is the photon order. Figure 2.6(a) shows that the PEEM signal with the 3ω irradiation has a quadratic fluence dependence, suggesting that the photoemission of 3ω occurs via a two-

Figure 2.6. (a) The PEEM signal of the silver grid plotted as a function of 3ω fluence, fitted with a quadratic function. (b) The PEEM signal plotted as a function of 4ω fluence, fitted with a linear function. (c) The band structure of silver, extracted from ref. 22, with the photoemission windows for two-photon photoemission for 3ω (blue region) and one-photon photoemission for 4ω (purple region).

photon process. One-photon energy (3.61 eV) of 3ω is smaller than the work function of silver $\sim 4.5 \text{ eV}$,¹⁹ thus requiring photoemission via a two-photon process, as observed. In contrast, the work function of silver is smaller than the photon energy of 4ω (4.81 eV). Therefore, the photoemission with the 4ω irradiation can occur via one-photon process, as the linearly 4ω fluence-dependent PEEM signal in Figure 2.6(b) shows.

In pump-probe experiments, similar fluence dependence measurements can be employed to determine the photon order of the interactions of pump pulses and probe pulses with samples. The photoemission intensity as a function of the fluence of pump and probe, is expressed as

$$S = \sigma_{pu} \cdot F_{pu}^{N_{pu}} \times \sigma_{pr} \cdot F_{pr}^{N_{pr}}, \quad (2.4)$$

where S is total photoemission signal, σ_{pu} (σ_{pr}) is the pump absorption (probe ionization) cross-section, F_{pu} (F_{pr}) is the fluence of the pump pulse, and N_{pu} (N_{pr}) is the pump (probe) photon order.

With the photon order determined, the photoemission window can be established based on the requirement to conserve the in-plane momentum in photoemission^{20,21}. With the conservation of the in-plane momentum, ejected electrons in the solid sample should obey

$$E - \frac{\hbar^2 k_{\parallel}^2}{2m} + N\hbar\nu > 0, \quad (2.5)$$

where E is the total energy of the electron referenced to the vacuum level, $\hbar$ is the reduced Planck constant, $k_{\parallel}$ is the in-plane momentum, m is the mass of electron, N is the photon order of the probe, h is the Planck constant and ν is the frequency of the probe photon. Figure 2.6(c) shows the band structure of silver²², with the photoemission windows for the two-photon 3ω

photoemission (blue region) and the one-photon 4ω photoemission (purple region). The electrons below Fermi level within the photoemission windows can be ejected from the silver grid and detected by PEEM. In pump-probe experiments, the probe windows of the measured samples can be determined by using the same method. The probe window defines the regions of the band structures from which electrons can be ejected, hence contributing to the observed PEEM signal.

2.3.3 Data acquisition and processing

The ProNanoESCA software is employed to set the operating parameters of the PEEM and to acquire static PEEM images. A home-built LabVIEW program controls the TR-PEEM measurements, which involves the interface of the 14-bit camera of the PEEM (PCO Pixelfly) and a computer-controlled translation stage (Physik Instrumente M-511.DD). The 2ω and the 3ω beams are often employed as the pump and the probe in my TR-PEEM measurements, respectively. The translation stage is set in the 2ω beam path to introduce a variable time delay between the pump and probe pulses, with a minimum step size of $0.10\ \mu\text{m}$, corresponding to a minimum delay time step of $0.67\ \text{fs}$.

During the TR-PEEM measurements, the LabVIEW program is designed to acquire a series of PEEM images at the programmed time delays with a given exposure time. At each time delay setting, two images are acquired, one at the set time delay (IMG), and the other at a relatively large time delay (IMG_RF), typically $15\ \text{ps}$, with the latter serving as a reference image. Without any illumination, the camera has a dark count rate of $\sim 40\ \text{counts/s}$ for each pixel; therefore, a dark image (IMG_DARK) is acquired for background correction. The laser

heating of the substrate results in a slow drift ($\sim 1 \mu\text{m}/\text{hour}$) of PEEM images and the power of laser may have small fluctuations. Hence, IMG_RFs are employed to correct the drift and the power fluctuations. Both IMG_RF and IMG_DARK are subtracted from IMG to yield the corrected PEEM image at the setting time delay, which is performed by a home-built MATLAB program.

We employ a suite of home-written MATLAB programs to analyze the data. The temporal evolution of PEEM signal can be extracted over any region of interest to track the dynamics occurring in different parts of the sample. Moreover, the MATLAB data analysis program is capable of analyzing the time trace of every pixel within the region of interest by fitting these time traces to a mathematical function that describes the expected sample response. Each fitting parameter can be visualized as an image. For example, an image of the time constants gives a spatial distribution of time constants across the sample, analogous to a PL lifetime map obtained from fluorescence lifetime imaging microscopy^{23,24}.

2.4 Conclusion

Femtosecond TR-PEEM is a combination of the femtosecond laser pump-probe technique and PEEM microscopy. The Yb-doped fiber laser is used as the light source in the pump-probe system. I utilize a Xe-filled hollow-core fiber to broaden the spectrum, followed by chirped mirrors to compress the laser pulses, finally obtaining laser pulses with a duration of 55 fs FWHM. Through harmonic generation in BBO crystals followed by prism-pair pulse compression, I produce the 2ω , 3ω and 4ω harmonics of the fundamental, which are delivered to the sample with pulse widths of ~ 40 fs FWHM, thus supporting a time resolution of ~ 50 fs

for experiments. A home-built NOPA was also assembled to generate wavelength tunable pulses spanning 650 – 950 nm, with the pulses compressed by a pair of chirped mirrors to 16-fs duration. The spatial resolutions are characterized by measurements on a silver grid, and are found to be ~70 nm and ~50 nm with 3ω and 4ω probing, respectively, according to the 16 – 84% criterion. Moreover, power dependence measurements of either 3ω or 4ω are used to determine the photon orders and the photoemission probe windows. As expected, the photon orders of the interactions of the 3ω and 4ω with the silver grid are 2 and 1, respectively. With the photon orders, the photoemission windows for the band structure of silver are determined. Overall, TR-PEEM is a powerful tool for the study of spatially heterogeneous ultrafast dynamics in TMDs due to its outstanding temporal and spatial resolutions.

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Chapter 3

Weak Distance Dependence of Hot-Electron Transfer Rates at the 1L-MoS₂/Au van der Waals Interface

Electron transport across the transition metal dichalcogenide (TMD)–metal interface plays a crucial role in determining the performance characteristics of TMD-based electronic devices. However, the robustness of this elementary process against structural heterogeneity at the TMD-metal interface remains unexplored. Here, we employ a combination of TR-PEEM and atomic force microscopy (AFM) to investigate spatially resolved hot-electron transfer at the 1L MoS₂/Au van der Waals interface. A spatially heterogeneous distribution of 1L-MoS₂/Au gap distances, along with the sub-80-nm spatial- and sub-60-fs temporal resolution afforded by TR-PEEM, permits the simultaneous measurement of electron transfer rates across a range of 1L-MoS₂/Au distances. We show that electron transfer rates decay exponentially as a function of distance, with an attenuation coefficient β of $0.06 \pm 0.01 \text{ \AA}^{-1}$, comparable to those reported for molecular wires. The weak distance dependence of the interfacial hot-electron transfer rate indicates that this process is insensitive with respect to distance fluctuations that exist at TMD-metal interfaces. *Ab initio* simulations suggest that surface plasmon-like states mediate hot-electron transfer, hence accounting for its weak distance dependence.

3.1 Introduction

1L TMDs have unique electronic and optoelectronic properties.¹⁻⁴ Some characteristics of 1L-TMDs that are of technological significance include direct band gaps,^{5,6} large exciton binding energies,⁷⁻⁹ high carrier mobilities,¹⁰ superconductivity,^{11,12} large nonlinear optical susceptibilities,¹³ and the addressability of the energetically degenerate K or K' valleys by valley-selective photoexcitation.^{14,15} As a result of these properties, along with the ability to fabricate TMDs on the wafer-scale,¹⁶ these have found applications in photodetectors,¹⁷⁻¹⁹ photovoltaics,²⁰ phototransistors,^{21,22} and light-emitting diodes.²³⁻²⁵

In TMD-based devices, the TMD layer contacts a metal structure that is part of the electrical circuitry.²⁶ Electronic transport at the TMD-metal interface therefore plays a vital role in the performance characteristics of TMD-based devices.²⁷ While much work has been done to explore means of minimizing the contact resistance at TMD-metal interfaces,²⁸⁻³¹ less known is how interfacial structural heterogeneity influences electron transport efficiency. For example, in TMD-based thin film transistors, irregularities at the TMD-metal interface result in a distribution of voltages across the interface, which in turn leads to contact noise.³²⁻³⁶

Studies of carrier dynamics shed light on the electronic transport properties of materials.^{37,38} While phenomena such as electron-electron³⁹ and electron-phonon scattering,³⁹ bandgap renormalization,⁴⁰ exciton formation,⁴¹ diffusion,⁴² and annihilation,⁴³ and carrier recombination⁴⁴ in TMDs have been extensively investigated by ultrafast spectroscopy,⁴⁵ the dynamics of electron transport across TMD-metal interfaces are still unexplored. Moreover, most time-resolved studies of TMDs are based on spatially averaged measurements, which do not address the effect of spatial heterogeneity induced by the presence of defects on the carrier dynamics. TR-PEEM was extended from studies of plasmon-polariton dynamics of metallic nanostructures⁴⁶ to visualize the spatially heterogeneous carrier dynamics of semiconductors,⁴⁷⁻

⁴⁹ including TMDs.⁵⁰ The spatial resolution of PEEM, as high as ~ 4 nm,⁵¹ makes it well-suited for investigating spatially resolved electronic transport at the TMD-metal interface.

Here, we employ TR-PEEM to investigate hot-electron transfer at a spatially heterogeneous 1L-MoS₂/Au interface. Electrons injected into the conduction band of MoS₂ undergo ultrafast transfer to the Au substrate on a 0.4-ps timescale. The lifetime map reveals spatially heterogeneous hot-electron transfer rates, which correlate to the spatial distribution of 1L-MoS₂/Au distances, as revealed by AFM. The exponential distance dependence of the electron transfer rate is characterized by an attenuation coefficient β of $0.06 \pm 0.01 \text{ \AA}^{-1}$, comparable to those of molecular wires. *Ab initio* simulations shed light on the origin of this unusually small β value for the van der Waals interface.

3.2 Experimental methods

1L-MoS₂ flakes are prepared from micromechanical exfoliation of bulk MoS₂ onto polydimethylsiloxane (PMDS)⁵² followed by transfer to Au film deposited on SiO₂/Si, [Figure 3.1(a)], yielding a 1L region that is the focus of our analysis. Photoexcitation of the 1L-MoS₂/Au sample with the 2.41-eV visible pump pulse leads to the injection of electrons into the conduction band of MoS₂ [Figure 3.1(b)]. These electrons are subsequently ejected by a 3.61-eV UV probe pulse and refocused by a column of electron optics onto a 2D array detector, giving rise to the PEEM signal [Figure 3.1(c)].

Figure 3.1. (a) Optical image of the 1L-MoS₂/Au sample, showing the outline of the region of interest. Broken regions allow access to the Au substrate (brighter areas). (b) 2.41-eV photoexcitation of the MoS₂/Au sample followed by 3.61-eV probe ejects photoelectrons from MoS₂, collected and imaged by the PEEM microscope at different time delays Δt . (c) PEEM image of the 1L-MoS₂/Au.

Power dependence measurements are employed to determine the photon order of the interactions of the 2.41-eV pump and 3.61-eV probe pulses with 1L-MoS₂/Au. The photoemission intensity from the 1L-MoS₂ region is

$$S = \sigma_{pu} \cdot F_{pu}^{N_{pu}} \times \sigma_{pr} \cdot F_{pr}^{N_{pr}}, \quad (3.1)$$

where S is total photoemission signal, σ_{pu} (σ_{pr}) is the pump absorption (probe ionization) cross-section of 1L-MoS₂, F_{pu} (F_{pr}) is the fluence of the pump pulse, and N_{pu} (N_{pr}) is the pump (probe) photon order. We get $N_{pu} = 1.2 \pm 0.1$ [Figure 3.2(a)] and $N_{pr} = 0.8 \pm 0.1$ [Figure 3.2(b)] under our experimental conditions, which suggest that the pump and probe interactions with 1L-MoS₂/Au both occur via a one-photon process. With the probe photon order determined, we proceed to establish the probe window that is relevant to the present study.

Figure 3.2. Fluence dependence measurements for (a) pump and (b) probe pulses. (c) Band structure of 1L-MoS₂ on Au. Excited electrons can be detected within the probe window (blue shaded region). The green arrow shows the pump photoexcitation of electrons from Au Fermi level (the orange line), injecting electrons into the conduction band of 1L-MoS₂.

In photoemission experiments, the probe window arises from the requirement to conserve in-plane momentum in photoemission⁵³ and defines the region of the band structure from which electrons can be ejected. In our calculation of the probe window, we employ the 1L-MoS₂ band structure of Ref. 54, shifting the conduction bands to reproduce the quasi-particle band gap of 1.95 eV, determined by pump-probe angle-resolved photoemission spectroscopy.⁵⁵ The ionization energy of MoS₂ is 5.77 eV.⁵⁶ Another relevant input parameter for the probe window calculation is the PEEM collection angle, which is 90° from the PEEM axis. Figure 3.2(c) displays the band structure of MoS₂ with the probe window superimposed (shaded blue region). The orange line denotes the Fermi level. Considering the location of the probe window, 2.41-eV photoexcitation of MoS₂ itself does not yield electrons in the probe window. As such, the ultrafast dynamics observed in our study is attributed to the injection of hot electrons from Au, which are in turn produced by 2.41-eV photoexcitation of the Au substrate. Photoexcitation of electrons near the Au Fermi level creates hot electrons,⁵⁷ which then undergo ultrafast injection into the high-energy conduction-band states of 1L-MoS₂, from which they can be photoemitted in the instrument probe window (Figure 3.3).

Figure 3.3. Band alignment of the MoS₂/Au, supporting ~10-fs injection of electrons into the MoS₂ conduction band, followed by electron transfer from MoS₂ back to Au. TR-PEEM probes the population of conduction-band electrons in MoS₂ at a series of time delays, from which the rate of electron transfer (k_{ET}) is obtained.

3.3 Results and discussion

The TR-PEEM images acquired at a series of pump-probe time delays are illustrated in Figure 3.4(a). The temporal evolution of the TR-PEEM signal, referenced to the ground state, spatially integrated over a MoS₂ 1L region of interest, is displayed in Figure 3.4(b). The signal exhibits a prompt response at time-zero, coincident with the peak of the signal from the Au substrate, followed by a delayed rise to give a secondary peak that eventually decays on a sub-ps timescale. The signal at time-zero arises from 3.61-eV pump and 2.41-eV probe in the pulse overlap region. The subsequent rise to give a secondary peak, delayed by 0.12 ± 0.01 ps relative to time-zero, reflects the injection of hot electrons from Au into MoS₂ conduction band that resides in the probe window, consistent with the previously observed sub-200-fs hot-electron transfer from Au nanoantennae to 1L-MoS₂.⁵⁸ The TR-PEEM signal subsequently decays with a time constant of 351 ± 6 fs as electrons leave the probe window. The hot-electron injection from Au to MoS₂ is not analyzed in detail in the present study because it occurs on the same timescale as the width of our instrumental response function. The time constant that

Figure 3.4. (a) PEEM images collected in the vicinity of the region of interest shown in Figure 3.1(a). Gaps in the MoS₂ 1L expose the Au substrate, giving rise regions with a large number of counts. (b) Temporal evolution of the TR-PEEM signal (the black dashed line), spatially integrated over the region of interest indicated in Figure 3.1(a). The red line shows the fit. The orange line shows the time trace of the Au substrate.

characterizes the sub-picosecond decay component is independent of carrier density (Figure 3.5), hence ruling out carrier thermalization and carrier-LO-phonon scattering as its possible origins. The former process, in fact, speeds up with carrier density³⁷ whereas the latter decelerates with carrier density due to the hot-phonon effect.³⁷ Instead, based on the conduction-band minimum of MoS₂ being 0.52 eV higher than the Au Fermi level,⁵⁵ we consider the possibility that the sub-ps decay of the TR-PEEM signal arises from the back-electron transfer from the conduction band of MoS₂ to Au (Figure 3.3). This assignment is strongly supported by the ~19-fold reduction of the spectrally integrated PL yield of 1L-MoS₂ on Au as compared to SiO₂ (Figure 3.6). The consistent electron transfer rates at different pump fluences also eliminate the effects of the local laser heating on the observed dynamics.

PL spectra of MoS₂/Au and MoS₂/SiO₂ are shown in Figure 3.6. Both spectra are collected under identical conditions with 514-nm photoexcitation. The PL of MoS₂/Au is strongly quenched, consistent with electron transfer from MoS₂ to Au, thereby suppressing radiative recombination⁵⁹. The spectrally integrated PL intensity of MoS₂/Au is 19× lower than that of MoS₂/SiO₂, i.e., $\Phi_{PL}^{SiO_2}/\Phi_{PL}^{Au} = 19$. That is,

Figure 3.5. (a) TR-PEEM time traces of 1L-MoS₂ supported on Au, obtained for different pump fluences. (b) Time constants retrieved at various pump fluences, showing that the observed ultrafast dynamics is independent of pump fluence.

Figure 3.6. PL spectra of MoS₂/SiO₂ and MoS₂/Au collected under identical experimental conditions.

$$\frac{\Phi_{PL}^{SiO_2}}{\Phi_{PL}^{Au}} = \frac{k_r^{SiO_2} / (k_r^{SiO_2} + k_{nr}^{SiO_2})}{k_r^{Au} / (k_r^{Au} + k_{nr}^{Au} + k_{ET}^{Au})} = 19, \quad (3.2)$$

where $k_r^{SiO_2}$ (k_r^{Au}) is the radiative decay rate of MoS₂ on SiO₂ (Au), $k_{nr}^{SiO_2}$ (k_{nr}^{Au}) is the non-radiative decay rate of MoS₂ on SiO₂ (Au), and k_{ET}^{Au} is the rate of electron transfer. Assuming that the radiative and non-radiative decay rates are independent of substrate, i.e., $k_r^{SiO_2} = k_r^{Au} = k_r$ and $k_{nr}^{SiO_2} = k_{nr}^{Au} = k_{nr}$, equation 3.2 gives

$$\frac{k_r + k_{nr} + k_{ET}}{k_r + k_{nr}} = 19. \quad (3.3)$$

From the reported MoS₂ PL lifetime⁶⁰ $\tau_{PL} = (k_r + k_{nr})^{-1}$ of 7.6 ps, we obtain $k_{ET} = 2.4 \text{ ps}^{-1}$, or $\tau_{ET} = 0.42 \text{ ps}$, in approximate agreement with our measured τ_{ET} value of $351 \pm 6 \text{ fs}$.

Electron transfer from the 1L-MoS₂ conduction band to Au facilitates nonradiative electron-hole recombination through the Au states before they enter the light cone, thus suppressing radiative recombination within 1L-MoS₂ and quenching its PL.⁵⁹ Indeed, optical pump-probe⁶¹ and angle-resolved photoemission⁵⁵ spectroscopies showed ultrafast electron transfer from MoS₂ to Au on a sub-picosecond timescale.

To further investigate the dynamics of electron transfer from 1L-MoS₂ to Au, we extract the time traces for each individual pixel of the TR-PEEM image and fit them after 0.2-ps time delay (after hot electron injection from gold to MoS₂ is completed) to a single exponential decay [Figure 3.7(a)]. The lifetime τ_{ET} obtained from each single-pixel time trace is used to construct a lifetime map [Figure 3.7(b)]. This is analogous to that obtained from fluorescence lifetime imaging microscopy,⁶² and reveals the spatial distribution of τ_{ET} . Figure 3.7(c) shows the corresponding histogram of τ_{ET} values. This has a mean of 386 fs and a standard deviation

Figure 3.7. (a) Representative single-pixel time traces for different locations on the 1L-MoS₂ flake. (b) Map of electron transfer time constants, showing the spatial distribution of time constants and the locations from which the single-pixel traces shown in (a) are extracted. (c) Histogram of electron transfer time constants. (d) AFM image of the region of interest. The Au substrate appears as the darker regions. (e) Distribution of 1L-MoS₂/Au gap distances Δd . The inset shows the height distributions of 1L-MoS₂ and Au regions. (f) FFT power spectra of the time constant map and the AFM image, showing a similar dependence of the FFT power on the spatial frequency.

of 54 fs. The mean is supported by the time constant obtained from fitting the spatially integrated time trace; the slight deviation is due to the fact that the lifetime obtained from the spatially integrated measurement represents an amplitude-weighted average time constant instead of a simple average. The standard deviation, larger than the typical fitting error of ~20 fs for single-pixel time traces, suggests that the observed distribution of time constants originates primarily from the intrinsic spatial heterogeneity of the sample.

In order to elucidate the origin of the spatially heterogeneous τ_{ET} values, AFM measurements are performed [Figure 3.7(d)]. These give the distributions of heights for the 1L-MoS₂ and the adjacent Au substrate regions [Figure 3.7(e) inset]. The Au substrate is prepared by thermal evaporation of a 50-nm Au layer on Si and has nanometer-scale roughness, which translates to roughness of the 1L-MoS₂ atop. The 1L-MoS₂ and Au regions are characterized by mean values of $\langle h_{\text{MoS}_2} \rangle = 0.03$ nm and $\langle h_{\text{Au}} \rangle = -1.23$ nm, respectively, and standard deviations of $\sigma_{\text{MoS}_2} = 1.34$ nm and $\sigma_{\text{Au}} = 1.50$ nm, respectively. To obtain the distribution of 1L-MoS₂/Au gap distances, we assume that the heights of 1L-MoS₂ and Au are correlated, i.e., an elevated 1L-MoS₂ region sits atop a higher part of the Au substrate. The measured heights of the 1L-MoS₂ and Au regions are then sorted in ascending order. The height difference $\Delta h^{(i)}$ for the i th pair of 1L-MoS₂ and Au heights is given by

$$\Delta h^{(i)} = h_{\text{MoS}_2}^{(i)} - h_{\text{Au}}^{(i)}, \quad (3.4)$$

where $h_{\text{MoS}_2}^{(i)}$ is the i th height of 1L-MoS₂ and $h_{\text{Au}}^{(i)}$ is the i th height of Au. To transform this height difference to a distance between the basal S atoms and the Au surface, i.e., the 1L-MoS₂/Au gap distance $\Delta d^{(i)}$, we employ the relation

$$\Delta d^{(i)} = \Delta h^{(i)} - a - 2r_{\text{vdW}}^{\text{S}}, \quad (3.5)$$

where a is the lattice parameter of 1L-MoS₂ (0.316 nm) and $r_{\text{vdW}}^{\text{S}}$ is the van der Waals radius of the S atom (0.180 nm). Figure 3.8 illustrates the relation between these quantities. The resultant distribution of MoS₂–Au gap distances Δd [Figure 3.7(e)] is characterized by a mean of $\langle \Delta d \rangle = 0.59$ nm and a standard deviation of $\sigma_{\Delta d} = 0.22$ nm. Note that the $\langle \Delta d \rangle$ value is consistent with the mean distance gap inferred from the difference between the mean AFM-measured heights $\langle h_{\text{MoS}_2} \rangle - \langle h_{\text{Au}} \rangle - a - 2r_{\text{vdW}}^{\text{S}} = 0.58$ nm.

Beyond characterizing the TR-PEEM lifetime map and the AFM height distribution by the mean and standard deviation values, it is desirable to obtain information on the spatial distribution of the roughness that is evident from both images. We employ the power spectral density (PSD) function to describe the roughness observed for the lifetime map and AFM image. The PSD function can describe complex 2-dimensional geometries, measured by various microscopies, such as AFM and TEM.^{63,64} Going beyond the RMS values of roughness, PSD functions assess signal roughness by considering the lateral distribution over which the signal variation occurs. The PSD for discrete 2D data is expressed as

Figure 3.8. Schematic illustration of 1L MoS₂ on Au.

$$\text{PSD}(f_x, f_y) = \frac{1}{L^2} \times \left[\sum_{m=1}^N \sum_{n=1}^N Z_{mn} e^{-2\pi i \Delta L (f_x m + f_y n)} (\Delta L)^2 \right]^2, \quad (3.6)$$

where L is the length of the region of interest, N is the number of data points in one direction, Z_{mn} is either the AFM profile height or the TR-PEEM decay time constant at position (m, n) , ΔL is distance between adjacent data points, and f_x and f_y are spatial frequencies along the x - and y -axis, respectively.⁶⁵ The resultant $\text{PSD}(f_x, f_y)$ is expressed in polar coordinates before angular averaging as

$$\text{PSD}(f) = \frac{1}{2\pi} \int_0^{2\pi} \text{PSD}(f, \theta) d\theta, \quad (3.7)$$

to obtain a 1-D PSD function, $\text{PSD}(f)$. Figure 3.7(f) shows PSDs of the time constant map and the AFM image. The overlapping PSDs strongly suggest that the spatially heterogeneous lifetime map originates from the surface roughness of the 1L-MoS₂/Au surface.

To shed light on the distance dependence of the electron transfer rate $k_{\text{ET}} = 1/\tau_{\text{ET}}$, we assume,⁶⁶ based on the exponential decrease of through-space electronic coupling with distance, that k_{ET} is inversely correlated with the 1L-MoS₂/Au gap distance Δd . With this assumption, and from the distribution of lifetimes and the distribution of 1L-MoS₂/Au gap distances, we obtain a plot of $\ln k_{\text{ET}}$ vs. Δd (Figure 3.9). This has ~20k data points and suggests a linear relation between $\ln k_{\text{ET}}$ and Δd , i.e., an exponential distance dependence of k_{ET} :

$$k_{\text{ET}} = k_0 \exp(-\beta \Delta d), \quad (3.8)$$

with pre-exponential factor $k_0 = 5.79 \pm 0.53 \text{ ps}^{-1}$ and attenuation factor $\beta = 0.06 \pm 0.01 \text{ \AA}^{-1}$. We note that typical β values for saturated hydrocarbon bridges⁶⁷ are $\sim 0.8 - 1.0 \text{ \AA}^{-1}$ whereas conjugated molecules, such as polyenes,⁶⁸ polyynes,⁶⁹ and phenylene⁷⁰ linkers, span $\sim 0.1 - 0.6$

Figure 3.9. Dependence of the hot-electron transfer rate k_{ET} on the MoS₂-Au gap distance Δd , obtained from a combination of time constant map and AFM maps of the 1L-MoS₂/Au sample. The dots show the data points and is fitted to Eq. 3.8. The density of the data points reflects the density of Δd values from AFM.

$\text{\AA}^{-1}$. Molecular wires with high conjugation lengths and correspondingly small band gaps <1 eV can even have $\beta < 0.1 \text{ \AA}^{-1}$.⁷¹ Our small β , comparable to those observed for molecular wires, is unexpected when one considers the weak electronic coupling that exists at a van der Waals interface.

To explore the origin of the small β , we employ *ab initio* calculations to investigate the nature of the 1L-MoS₂/Au interaction. We consider high-energy conduction-band states of 1L-MoS₂, accessed by photoexcitation and located in the probe window at the Γ point, ~ 1.6 eV higher than the Fermi level. The fragment analysis of the states located 1.6 eV higher than the Fermi level at the various 1L-MoS₂/Au distances yields fractions of the Kohn-Sham orbital localized on 1L-MoS₂ in either isolated 1L-MoS₂ or 1L-MoS₂ interacting with Au (Figure 3.10). Investigation of the partial density of states shows that such states split into two when the Au substrate is brought into the vicinity of 1L-MoS₂. The energy splitting V reflects the 1L-MoS₂/Au coupling strength, and hence, the rate of electron transfer. Increasing the distance between MoS₂ and Au results in an exponential decrease of V with an attenuation factor of $0.21 \text{ \AA}^{-1}$ [Figure 3.11(a)].

Figure 3.10. Fragment analysis of MoS₂ states before and after interaction with Au at various 1L-MoS₂/Au Δd spanning 0.74 to 8.74 Å. A single MoS₂ state splits into a pair of states due to the interaction, with the splitting characterizing the interaction strength.

Plots of the electron density for such a high-energy conduction-band state reveal a significant delocalization from both MoS₂ and Au into the gap [Figure 3.11(b)]. This contrasts the electron density plot for a lower-lying conduction-band state, which shows electrons bound tightly to the individual MoS₂ and Au layers [Figure 3.11(c)]. The electron delocalization is reminiscent of surface plasmon-like states, suggested in Ref. 72 to have effects on the electron transfer dynamics of Au nanorods interfaced to 1L-MoS₂. But these plasmon-like states are not plasmons that are described by a coherent superposition of electron-hole excitations. We believe that the spatial delocalization of the gold electron density into the 1L-MoS₂/Au gap supports the weakly distance-dependent electron transfer observed herein. The calculated β of 0.21 Å⁻¹ is larger than the experimental value because the 8-atom-thick Au slab employed in the simulations may not fully reproduce the spatial extent of the plasmon-like state in the experimental system. Further, high-energy plasmon-like states ($E - E_F > 1.6$ eV) that may be

accessed experimentally extend more into the 1L-MoS₂/Au gap, especially for rough surfaces,⁷³ leading to an experimental β value smaller than the computed one.

Figure 3.11. (a) Plot of the calculated 1L-MoS₂/Au interaction strength V vs. Δd (symbol), and fit to an exponential distance dependence. (b) A plasmon-like state and (c) a non-plasmon-like state exhibit different degrees of delocalization of electrons into the 1L-MoS₂/Au gap, as can be seen from the calculated electron densities (top panel) and their projections (bottom panel). Δd is 0.74 Å.

3.4 Conclusion

In summary, we harnessed the spatial and temporal resolution of TR-PEEM, its large field-of-view, and the spatially heterogeneous distribution of 1L-MoS₂/Au gap distances to determine the distance-dependent hot-electron transfer dynamics across the 1L-MoS₂/Au interface. Our approach seamlessly combines elements of electronic transport measurements performed at single-molecule junctions^{74,75} with ultrafast spectroscopic probing of electron transfer in structurally well-defined donor-bridge-acceptor motifs,⁷⁶ both of which have elucidated distance- and molecular conformation-dependent electron transfer rates. Here, electron transfer likely occurs via incoherent hopping, considering that the probe window lies above the theoretically predicted tunneling barrier height⁷⁷ for the 1L-MoS₂/Au interface and that τ_{ET} exceeds the ~ 10 -fs timescale for carrier dephasing³⁹ in MoS₂. The small attenuation factor suggests that the transport of hot electrons across a 1L-MoS₂/Au interface is robust against surface corrugations and defects. This finding, which contrasts with the interface sensitivity of transport of low-energy charge carriers in TMD-based electronic devices,^{32,33} provides further impetus for realizing optoelectronic devices that harness hot carriers.^{78,79}

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Chapter 4

Visualizing Photocarrier Relaxation Dynamics at the Monolayer-Multilayer WSe₂ Homojunction

The ultrafast charge transfer dynamics at 2D heterojunctions comprising two different TMDs have been extensively studied. However, the ultrafast carrier dynamics of 2D homojunctions, which consist of two chemically identical but electronically distinct TMDs, remain largely unknown. Here, we employ TR-PEEM to elucidate the ultrafast photocarrier dynamics of a type-I 1L–ML WSe₂ homojunction prepared by mechanical exfoliation. The TR-PEEM signals recorded for the individual components of the homojunction reveal the sub-picosecond carrier cooling dynamics of 1L- and ML-WSe₂ as well as few-picosecond exciton-exciton annihilation occurring on 1L-WSe₂. In addition, we observe ultrafast interfacial hole transfer from 1L to ML on the 0.2-ps timescale. The resultant excess hole density on ML-WSe₂ subsequently decays by carrier recombination across the homojunction interface on the 100-ps timescale. Reminiscent of the behavior at a depletion region, the TR-PEEM image reveals the accumulation of hole density on the ML-WSe₂ component at the homojunction interface, characterized by a decay length of $0.60 \pm 0.17 \mu\text{m}$. These results provide a first glimpse into the ultrafast carrier dynamics that occur at TMD homojunctions.

4.1 Introduction

Atomically thin 2D materials have rapidly emerged as a technologically important class of materials. Numerous electronic and optoelectronic properties have been uncovered in semiconducting 2D TMDs, such as layer-sensitive electronic structures,^{1,2} high carrier mobilities,³ high binding energies of excitons and trions,^{4,5} and large nonlinear optical response.⁶ These semiconducting TMDs open up opportunities for the realization of ultrathin nanoelectronics and optoelectronics, with diverse applications such as transistors,⁷ photodetectors⁸ and electroluminescent devices.⁹

Beyond single-component TMDs, heterostructures comprising two chemically distinct TMDs juxtaposed either vertically or laterally have also been prepared. Extensive experimental and theoretical studies have revealed the properties of these TMD heterostructures,¹⁰⁻¹² such as strong photoresponse,¹³ high field-effect ON/OFF ratio,¹⁴ and distinct rectification effect.¹⁵ The behavior of carriers at the heterojunction is dictated by the band alignment of the two TMD components. Both electrons and holes transfer to the same TMD in the case of type-I band alignment, thereby supporting applications that require radiative recombination, such as light-emitting diodes. In the case of type-II band alignment, photocarriers undergo charge separation and transfer across these heterojunctions, giving rise to applications in photodetectors and photovoltaics.^{16,17} Investigations of heterostructures by ultrafast laser spectroscopy reveal charge transfer across type-II vertical heterojunctions within 50 fs.¹⁸⁻²⁴ Time-domain density functional theory and nonadiabatic molecular dynamics simulations suggest that the observed ultrafast interlayer charge transfer is facilitated by quantum coherence and electron delocalization.²⁵ In the case of lateral heterostructures, exciton transfer across a type-I MoS₂-MoSe₂ heterojunction with a velocity of 10⁴ m/s²⁶ and sub-picosecond electron transfer across a type-II composition-graded WS₂-WSe₂ interface have been reported.²⁷

TMD homojunctions have recently emerged as a complement to heterostructures. Homojunctions, unlike heterostructures, comprise the same material at the interface. However, the materials at opposite sides of the interface exhibit distinct electronic band gaps. The band gap can be modulated by varying the phase²⁸ or doping of the material²⁹ or by changing the number of layers.³⁰⁻³³ The lateral type of homojunction can often be found in samples prepared by the mechanical exfoliation of a bulk TMDs. The studies of the homojunction reveal their effects on the electronic and optoelectronic properties of TMDs, which can improve the fabrications of TMD-based devices for various applications. The 1L region of the homojunction possesses a direct bandgap whereas an indirect bandgap exists in *NL* region.^{34,35} In the case of WSe₂, for example, experimental and theoretical studies show that juxtaposing 1L-WSe₂, which has a direct bandgap of 1.64 eV,³⁶ with *NL*-WSe₂, which has an indirect bandgap of 1.44 eV,³⁶ yields an interface with a type-I band alignment.³¹⁻³³ On the other hand, measurements on 1L-*NL* MoS₂ by scanning photocurrent microscopy suggests type-II band alignment,³⁰ whereas Kelvin probe force microscopy gives type-I band alignment.³⁷

Compared to the extensive ultrafast spectroscopy studies that have been performed on TMD heterostructures to date, the ultrafast dynamics of TMD homojunctions remain relatively unexplored. The typical micrometer-scale sizes of TMD homojunctions dictate the need for an ultrafast spectroscopy technique that can simultaneously furnish micrometer to sub-micrometer spatial resolution. TR-PEEM has recently emerged as a complement to ultrafast optical microscopy³⁸⁻⁴⁰ for investigating spatially resolved ultrafast phenomena of semiconductors, resolving the dynamics of trap states in bulk semiconductors²⁹ and perovskite thin films,^{41,42} imaging electron motion in bulk semiconductors⁴³ and atomically thin heterostructures,⁴⁴ and revealing spatially heterogeneous ultrafast dynamics of TMDs.⁴⁵

Here, we employ TR-PEEM to investigate the ultrafast electron and hole dynamics of a 1L–NL WSe₂ type-I homojunction. In addition to sub-picosecond carrier relaxation dynamics occurring within the individual components, we observe ~0.2-ps hole transfer followed by ~0.1-ns charge recombination across the homojunction. Finally, analysis of the PEEM image reveals the width of the depletion region at the 1L–NL interface.

4.2 Experimental methods

The 1L–NL WSe₂ homojunction is prepared from micromechanical exfoliation of bulk MoS₂ onto polydimethylsiloxane (PMDS)⁴⁶. The optical micrograph reveals regions of different layer numbers within the flake (Figure 4.1). Figure 4.2(a) illustrates the AFM image of the 1L–NL WSe₂ homojunction sample. The line profiles taken at two different parts of the homojunction [Figure 4.2(b) and (c)] show that the multilayer regions of the sample are predominantly 6L

Figure 4.1. Optical image of 1L/nL WSe₂ homojunction sample.

Figure 4.2. (a) AFM image of the 1L–NL WSe₂ homojunction. The height profiles along line 1 (b) and line 2 (c) taken across the junction.

and 8L, and that these multilayer regions are separated from the 1L region by a sub-micrometer-wide 4L strip. As the electronic structure is invariant for layer numbers $N \gtrsim 3$,¹ we do not

differentiate the 4L, 6L, and 8L regions in our analysis; instead, we refer to these regions collectively as the *NL* region.

The TR-PEEM setup employs 2.41-eV (515 nm) pump pulses and 3.61-eV (343 nm) probe pulses, with an instrumental response that is characterized by a FWHM of 55 fs. We performed fluence dependence measurements to determine the photon order of the interactions of the 2.41-eV pump and 3.61-eV probe pulses with the 1L and multilayer (*NL*) regions of the WSe₂ sample. The photoemission intensity is given as

$$S = \sigma_{pu} \cdot F_{pu}^{N_{pu}} \times \sigma_{pr} \cdot F_{pr}^{N_{pr}}, \quad (4.1)$$

where S is total photoemission signal, σ_{pu} (σ_{pr}) is the pump absorption (probe ionization) cross-section, F_{pu} (F_{pr}) is the fluence of the pump (probe) pulse, and N_{pu} (N_{pr}) is the pump (probe) photon order. For both 1L- and *NL*-WSe₂, fluence dependence measurements show

Figure 4.3. Fluence dependence measurement results for (a) pump and (b) probe pulses with 1L-WSe₂ and (c) pump and (d) probe pulses with *NL*-WSe₂.

that the photoemission signals scale linearly and quadratically with the pump and probe fluences, respectively [Figure 4.3(a-d)], suggesting that pump photoexcitation is a one-photon process whereas probe photoionization occurs via a two-photon process. The obtained probe photon order is used to establish the probe windows of 1L- [Figure 4.4(a)] and *NL*-WSe₂ [Figure 4.4(b)]. In photoemission experiments, the probe window arises from the requirement to conserve in-plane momentum in photoemission and defines the region of the band structure from which electrons can be ejected.⁴⁷ The WSe₂ band structures are extracted from Ref. 48. According to the electronic band structures of 1L- and *NL*-WSe₂, photoexcitation by 2.41-eV photons is confined to the K valley. The K valley, however, lies beyond the two-photon UV probe window of the PEEM instrument and therefore does not contribute to the PEEM signal. Following our previous TR-PEEM study of CVD-grown 1L-WSe₂,⁴⁵ we believe that the PEEM signals for 1L- and *NL*-WSe₂ most likely originate from their Q valleys. Their Q valleys lie within the probe window and can be populated within the width of the instrument response by carrier thermalization on the ~10-fs timescale.⁴⁹ In the case of *NL*-WSe₂, it should be noted

Figure 4.4. Probe windows for (a) 1L-WSe₂ and (b) *NL*-WSe₂ calculated based on the two-photon probing process with 3.61-eV probe pulses.

that the VBM at the Γ point also lies within the probe window and can therefore contribute to the PEEM signal.

4.3 Results and discussion

The sub-80-nm spatial resolution of the TR-PEEM is well-suited for resolving the layer number-specific carrier dynamics of the 1L–NL WSe₂ homojunction. The TR-PEEM image acquired at 0 fs time delay [Figure 4.5(a)] shows that the signal for the 1L region is ~50% larger

Figure 4.5. (a) PEEM image of 1L/nL WSe₂ sample acquired at 0 fs time delay. (b) Time trace of 1L region. The inset shows the electron cooling and the exciton-exciton annihilation within 1L, which leads to the bi-exponential decay. (c) The time trace of thin nL. The inset shows the electron cooling and the hole cooling within nL, which leads to an exponential rise and an exponential decay, respectively. (d) The zoom-in view of normalized time traces in (b) and (c).

than the multilayer region, which is due to the high ionization cross-sections of 1L WSe₂.⁵⁰ To elucidate the ultrafast dynamics of the homojunction, we measure the spatially integrated time-dependent PEEM signal from the 1L [Figure 4.5(b)] and NL [Figure 4.5(c)] regions of the sample, obtained with pump and probe fluences of 14 $\mu\text{J}\cdot\text{cm}^{-2}$ and 1 $\mu\text{J}\cdot\text{cm}^{-2}$, respectively. The PEEM signal of 1L-WSe₂ exhibits a bi-exponential decay, with time constants of $\tau_1^{1\text{L}} = 0.16 \pm 0.01$ ps and $\tau_2^{1\text{L}} = 5.13 \pm 0.97$ ps, and an amplitude ratio of $A_1^{1\text{L}}/A_2^{1\text{L}} = 24.9 \pm 2.4$. For the NL-WSe₂ region, the PEEM signal shows a delayed rise followed by a decay, with time constants of $\tau_r^{NL} = 0.11 \pm 0.01$ ps and $\tau_d^{NL} = 0.22 \pm 0.01$ ps, respectively. Hence, a decay of 1L signal and a rise of NL signal after time zero are observed in [Figure 4.5(d)].

To better understand the observed dynamics at 1L–NL WSe₂ homojunction, we employ a kinetic model to obtain deeper insight into how the various carrier relaxation channels contribute to the PEEM signal (Figure 4.6). First, we need to identify the states that reside within the probe windows, which will contribute to the TR-PEEM signal. According to Figure 4.4(a), the band extrema that reside within the probe window of 1L-WSe₂ are the conduction-band Q valley ($Q_c^{1\text{L}}$) and the indirect excitonic state ($X^{1\text{L}}$). For the NL-WSe₂ [Figure 4.4(b)], the Q valley of the conduction band (Q_c^{NL}) and the Γ valley of the valence band (Γ_v^{NL}) are located within the probe window. Second, we consider all the possible carrier relaxation and transfer pathways involving states that lie within the TR-PEEM probe windows of 1L- and NL-

Figure 4.6. Schematic illustration of all possible carrier relaxation and transfer pathways involving states that lie within the TR-PEEM probe windows of 1L- and NL-WSe₂.

WSe₂ (Figure 4.6). Electrons in Q_c^{1L} can undergo carrier cooling via $Q \rightarrow K$ intervalley scattering with rate constant k_c^{1L} , indirect exciton formation with rate constant k_f^{1L} , and electron transfer to Q_c^{NL} with rate constant k_{et} . The indirect exciton on 1L-WSe₂ can undergo exciton-exciton annihilation, which we approximate as a first-order process with rate constant k_r^{1L} . (Note that exciton-exciton annihilation is rigorously a second-order process.) For the NL region, electrons (holes) that undergo carrier cooling are funneled to Q_c^{NL} (Γ_v^{NL}) via intervalley scattering with rate constant k_{ec}^{NL} (k_{hc}^{NL}), where the CBM (VBM) resides. At the same time, electrons transferred from Q_c^{1L} arrive at Q_c^{NL} with rate constant k_{et} , whereas holes transferred from K_v^{1L} arrive at Γ_v^{NL} with rate constant k_{ht} .

Following our previous TR-PEEM investigation of CVD-grown 1L-WSe₂, we assign τ_1^{1L} and τ_2^{1L} to depopulation of the Q valley and exciton-exciton annihilation, respectively.⁴⁵ Electrons can leave the Q valley via multiple pathways. First, these electrons can undergo carrier cooling via intervalley scattering to the K valley, where the CBM of 1L-WSe₂ resides. Second, Q valley electrons can transfer across the 1L–NL WSe₂ homojunction interface to the lower-lying Q valley of the NL-WSe₂ component, however, we infer that the electron transfer from 1L to NL (k_{et}) might not occur due to the negligible energy offset of conduction bands of 1L and NL,³⁰ supported by a similar time constant τ_1^{1L} of the isolated 1L WSe₂ (see below). Third, electrons at the Q valley can form dark excitons, comprising electrons at the Q valley and holes at the K valley (VBM), i.e., Q_e - K_h excitons. These dark excitons, which reside in the probe window and have nonvanishing exciton momentum Q , can subsequently undergo exciton-exciton annihilation. Hence, the electron population Q_c^{1L} is expressed as

$$\frac{dQ_c^{1L}}{dt} = -(k_c^{1L} + k_f^{1L} + k_{et})Q_c^{1L}, \quad (4.2)$$

and the population of X^{1L} is expressed as:

$$\frac{dX^{1L}}{dt} = k_f^{1L}Q_c^{1L} - k_r^{1L}X^{1L}. \quad (4.3)$$

The solutions to the above differential equation are

$$Q_c^{1L}(t) = Q_{c,0}^{1L} e^{-(k_c^{1L}+k_f^{1L}+k_{et})t} \quad (4.4)$$

and

$$X^{1L}(t) = \frac{Q_{c,0}^{1L}k_f^{1L}}{k_c^{1L} + k_f^{1L} + k_{et} - k_r^{1L}} e^{-k_r^{1L}t} - \frac{Q_{c,0}^{1L}k_f^{1L}}{k_c^{1L} + k_f^{1L} + k_{et} - k_r^{1L}} e^{-(k_c^{1L}+k_f^{1L}+k_{et})t}, \quad (4.5)$$

where $Q_{c,0}^{1L}$ is the initial electron population in the Q valley of 1L-WSe₂. Hence, the total PEEM signal of 1L-WSe₂ is

$$S_{1L}(t) = \sigma_Q Q_c^{1L}(t) + \sigma_X X^{1L}(t), \quad (4.6)$$

or

$$S_{1L}(t) = \frac{\sigma_X Q_{c,0}^{1L} k_f^{1L}}{k_c^{1L} + k_f^{1L} + k_{et} - k_r^{1L}} e^{-k_r^{1L}t} + \frac{\sigma_Q Q_{c,0}^{1L} (k_c^{1L} + k_{et} - k_r^{1L})}{k_c^{1L} + k_f^{1L} + k_{et} - k_r^{1L}} e^{-(k_c^{1L}+k_f^{1L}+k_{et})t}, \quad (4.7)$$

where σ_X and σ_Q^{1L} are the ionization cross-sections of the indirect exciton and the electron in the Q valley of 1L-WSe₂, respectively. The signal of 1L-WSe₂ can be fitted to a bi-exponential decay to obtain time constants τ_1^{1L} for depopulation of the Q valley and τ_2^{1L} for exciton-exciton annihilation. From Eq. 4.7, we can infer that $\tau_1^{1L} = (k_c^{1L} + k_f^{1L} + k_{et})^{-1} = 0.16 \pm 0.01$ ps and $\tau_2^{1L} = 1/k_r^{1L} = 5.13 \pm 0.97$ ps.

Similar Auger-mediated annihilation dynamics of dark excitons in 1L-WSe₂ was earlier identified by the ultrafast mid-infrared probing of intra-excitonic transitions.⁵¹ Exciton-exciton annihilation is rigorously a second-order process, the relevant rate is expressed as

$$\frac{dN_{ex}}{dt} = -\gamma N_{ex}^2, \quad (4.8)$$

where N_{ex} is the exciton density and γ is exciton-exciton annihilation rate constant. Solving the above differential equation gives

$$N_{ex}(t) = \frac{N_0}{1 + \gamma N_0 t}, \quad (4.9)$$

where N_0 is the initial density of exciton, linearly proportional to the pump fluence. From a global fitting of time traces at different pump fluences ($11 - 21 \mu\text{J}\cdot\text{cm}^{-2}$) to Eq. 4.9, we obtain an annihilation rate of $0.46 \pm 0.02 \text{ cm}^2\cdot\text{s}^{-1}$ (Figure 4.7). This rate constant is consistent with the value of $\sim 0.35 \text{ cm}^2\cdot\text{s}^{-1}$ obtained from a combination of PL spectroscopy and Monte-Carlo simulations of 1L-WSe₂⁵² as well as those obtained from time-resolved optical microscopy for 1L-MoSe₂ ($0.33 \pm 0.06 \text{ cm}^2\cdot\text{s}^{-1}$)⁵³ and 1L-WS₂ ($0.41 \pm 0.02 \text{ cm}^2\cdot\text{s}^{-1}$).⁵⁴

To rationalize the temporal behavior of the TR-PEEM signal recorded for the *ML* region [Figure 4.5(c)], we first note that the CBM and VBM of *ML*-WSe₂, located at the Q valley and Γ point, respectively, both reside within the probe window [Figure 4.4(b)]. The Q valley is located 240 meV below the K valley in the conduction band⁵⁵ while the Γ point is stabilized by 50 meV relative to the K valley in the valence band.⁵⁶ As in the case of 1L-WSe₂, 2.41-eV photoexcitation of *ML*-WSe₂ in the vicinity of the K valley leads to the population of the Q valley by carrier thermalization, hence leading to the TR-PEEM signal at time-zero. Both the carrier transfer from 1L to *ML* and the carrier cooling within *ML* can result in the change of the

Figure 4.7. Time traces of homojunction 1L-WSe₂ over the time delay range of 2 – 15 ps, obtained at different pump fluences.

carrier population in the probe window (Figure 4.6). Therefore, the electron population of Q_c^{NL} is expressed as:

$$\frac{dQ_c^{NL}}{dt} = k_{ec}^{NL} K_c^{NL}, \quad (4.10)$$

where we have neglected electron transfer across the homojunction. The hole population Γ_v^{NL} is

$$\frac{d\Gamma_v^{NL}}{dt} = k_{hc}^{NL}K_v^{NL} + k_{ht}K_v^{1L}. \quad (4.11)$$

The solutions to the above differential equations are

$$Q_c^{NL}(t) = K_{c,0}^{NL}(1 - e^{-k_{ec}^{NL}t}), \quad (4.12)$$

$$\Gamma_v^{NL}(t) = K_{v,0}^{NL}(1 - e^{-k_{hc}^{NL}t}) + K_{v,0}^{1L}(1 - e^{-k_{ht}t}), \quad (4.13)$$

where $K_{c,0}^{NL}$ ($K_{v,0}^{NL}$) is the initial electron (hole) population in conduction-band (valence-band) K valley of NL-WSe₂ and $K_{v,0}^{1L}$ is the initial hole population in valence-band K valley of 1L-WSe₂. Hence, the total PEEM signal of NL-WSe₂ is

$$S_{NL}(t) = \sigma_Q Q_c^{NL}(t) - \sigma_\Gamma \Gamma_v^{NL}(t), \quad (4.14)$$

or

$$\begin{aligned} S_{NL}(t) = & \sigma_Q K_{c,0}^{NL} - \sigma_\Gamma (K_{v,0}^{NL} + K_{v,0}^{1L}) - \sigma_Q^{NL} K_{c,0}^{NL} e^{-k_{ec}^{NL}t} \\ & + \sigma_\Gamma (K_{v,0}^{NL} e^{-k_{hc}^{NL}t} + K_{v,0}^{1L} e^{-k_{ht}t}). \end{aligned} \quad (4.15)$$

In the above expression, σ_Q^{NL} and σ_Γ are the ionization cross-sections of the conduction-band Q valley and the valence-band Γ valley of NL-WSe₂, respectively. From Eq. 4.15, we can see that electron cooling gives rise to an increase in the TR-PEEM signal whereas hole cooling and hole transfer both give rise to a decay of the TR-PEEM signal. Carrier cooling subsequently channels more electrons from the K valley to the Q valley (CBM) via intervalley scattering, resulting in the delayed rise of the TR-PEEM signal with a time constant $\tau_r^{NL} = 0.11 \pm 0.01$ ps, in good agreement with the time constant of 70 ± 15 fs furnished by time- and angle-resolved photoemission spectroscopy of few-layer WSe₂.⁵⁷ At the same time, carrier cooling also results

in the appearance of holes at the VBM via $K \rightarrow \Gamma$ intervalley scattering. Since the TR-PEEM images are referenced to the PEEM image collected in the absence of the pump pulse, the appearance of holes in the probe window leads to a decay of the TR-PEEM signal. Hence, the observed decay of $\tau_d^{NL} = 0.22 \pm 0.01$ ps is assigned to hole cooling. Beyond carrier cooling dynamics, note that the *NL*-WSe₂ signal also reports on charge transfer across the 1L–*NL* WSe₂ homojunction interface. Since the CBM and VBM of *NL*-WSe₂ both reside in the probe window, electron (hole) transfer would lead to the appearance of excess electrons (holes) in the multilayer region, in turn giving rise to a positive (negative) offset in the *NL*-WSe₂ TR-PEEM signal. From Figure 4.4(c), a negative baseline offset at >1-ps time delays is readily apparent, strongly suggesting the presence of sub-picosecond hole transfer across the 1L–*NL* WSe₂ homojunction. According to scanning tunneling spectroscopy, the valence band offset between 1L- and 2L-WSe₂ is 0.12 eV, thus making hole transfer from 1L- to 2L-WSe₂ energetically favorable.³¹ Since the decay of the *NL*-WSe₂ signal is well-described by a single exponential decay with time constant τ_d^{NL} , we infer that interfacial hole transfer and hole cooling both occur on similar timescales of ~ 0.2 ps, $k_{hc}^{NL} \approx k_{ht}$. Note that the few-picosecond decay observed in 1L-WSe₂ and assigned to exciton-exciton annihilation is absent because the small exciton binding energies of multilayer TMDs, typically on the order of 10 meV, do not support the existence of excitons at room temperature.

To elucidate possible ultrafast electron- and/or exciton transfer in addition to hole transfer across the 1L–*NL* homojunction interface, we performed TR-PEEM measurements on an isolated 1L-WSe₂ flake under identical experimental conditions. The isolated 1L-WSe₂ flake cannot exhibit any charge transfer or energy transfer dynamics. Its TR-PEEM time trace (Figure 4.8) can be fitted to a bi-exponential decay function, with a fast decay constant $\tau_1^{1L} = 0.13 \pm 0.01$ ps and a slow decay constant $\tau_2^{1L} = 3.28 \pm 0.10$ ps; the ratio of two decay amplitudes is $A_1^{1L}/A_2^{1L} = 9.0 \pm 0.4$. As in the case of the homojunction 1L-WSe₂, the fast and

Figure 4.8. (a)Optical image and (b)PEEM image of isolated 1L WSe₂. (c)The flake-integrated time trace of isolated 1L-WSe₂.

slow decays are attributed to electrons leaving the Q valley and exciton-exciton annihilation, respectively. Eq. 4.7 also applies to the isolated 1L-WSe₂ flake as well, with the exception that the k_{et} term is omitted because electron transfer cannot occur for an isolated flake. Since the τ_1^{1L} time constants for the isolated 1L-WSe₂ and homojunction 1L-WSe₂ are nearly identical, we can conclude that electron transfer does not occur at the homojunction, i.e., $k_{et} \sim 0$. Global

fitting of the slow decay component at different excitation fluences yields an annihilation rate constant of $0.30 \pm 0.04 \text{ cm}^2 \cdot \text{s}^{-1}$ (Figure 4.9).

The nearly identical τ_1^{1L} values for both the isolated 1L-WSe₂ flake and the homojunction 1L-WSe₂ rules out electron transfer as an additional deactivation pathway for the Q valley electrons of the homojunction 1L-WSe₂. Moreover, compared with the isolated 1L-WSe₂ flake, the larger exciton population decay time τ_2^{1L} of the homojunction 1L-WSe₂ excludes the possibility of ultrafast exciton transfer occurring at the homojunction, which would accelerate

Figure 4.9. Time traces of isolated 1L-WSe₂ over the time delay range of 2 – 15 ps, obtained at different pump fluences.

the decay of the exciton component of the TR-PEEM signal. Instead, the slower exciton population decay of the homojunction 1L-WSe₂ is consistent with ultrafast hole transfer, which depletes the initial density of dark excitons formed, hence decelerating exciton-exciton annihilation. Moreover, a lower initial exciton density also reduces the relative contribution of exciton-exciton annihilation to the overall PEEM signal, thereby accounting for the larger A_1^{1L}/A_2^{1L} amplitude ratio observed for the homojunction 1L-WSe₂. Here we compare the amplitude ratios A_1^{1L}/A_2^{1L} for the homojunction and the isolated flake. For the homojunction 1L-WSe₂, we obtain:

$$A_1^{\text{homo-1L}}/A_2^{\text{homo-1L}} = 24.9 \pm 2.4. \quad (4.16)$$

For the isolated 1L-WSe₂, we obtain:

$$A_1^{\text{iso-1L}}/A_2^{\text{iso-1L}} = 9.0 \pm 0.4. \quad (4.17)$$

As the same pump fluence of $14 \mu\text{J}\cdot\text{cm}^{-2}$ was employed for these two measurements, the initial amplitudes of the signals can be assumed to be the same, i.e.,

$$A_1^{\text{homo-1L}} + A_2^{\text{homo-1L}} = A_1^{\text{iso-1L}} + A_2^{\text{iso-1L}}. \quad (4.18)$$

From Eq. 4.16 - 4.18, we get:

$$A_2^{\text{homo-1L}}/A_2^{\text{iso-1L}} = 0.39 \pm 0.04 \quad (4.19)$$

Hence, we find that the initial exciton density in the homojunction sample is only ~39% that of the isolated flake, due to the hole transfer across 1L/NL homojunction.

The negative baseline offset that appears in the TR-PEEM time trace of the homojunction ML-WSe₂ [Figure 4.5(c)] points to the existence of a long-lived population of holes on the multilayer. Figure 4.10(a) displays the TR-PEEM images at the pump-probe time delays after 1.4 ps. By extending the pump-probe time delay to 250 ps, we find that the negative offset decays with a time constant of 96 ± 3 ps [Figure 4.10(b)], signaling the disappearance of holes from the multilayer on this timescale. We note that TR-PEEM is unable to detect carrier recombination within the multilayer because both its VBM and CBM within the probe window. Instead, the disappearance of holes from the probe window is attributed to carrier recombination across the homojunction. While there have been no reports in the literature of the interfacial carrier recombination times for TMD homojunctions and lateral TMD

Figure 4.10. (a) a serial of ground-state-reference PEEM images with time delays from 1.4 to 44 ps. (b) The time trace of ML with extending time delays to 250 ps, undergoing an exponential rise.

heterojunctions, we note that the ~ 0.1 ns recombination time is in the range observed for vertical TMD heterostructures.^{19,21,58}

Inspection of the TR-PEEM images collected for the *NL*-WSe₂ region at >1 -ps time delays, when carrier cooling no longer contributes to the signal, reveals the accumulation of holes at the homojunction interface [Figure 4.10(a)]. Figure 4.11 illustrates the lineout of the TR-PEEM signal along the black line on the 1.4-ps image in Figure 4.10(a), which reveals a decrease in the hole density with distance from the homojunction interface. Here, we tentatively attribute it to the depletion region that exists at the interface. Fitting the distance dependence of the hole density suggests a depletion width of $0.60 \pm 0.17 \mu\text{m}$. The depletion width for the *NL*-WSe₂ region can be estimated by⁵⁹

$$W_{\text{NL}} = \frac{\pi \epsilon_{\text{WSe}_2} V_{\text{bi}}}{2 \ln(4) q N T} \quad (4.20)$$

where the dielectric constant of *NL* WSe₂ ϵ_{WSe_2} is $16.0\epsilon_0$,⁶⁰ $V_{\text{bi}} = 0.1$ V is the built-in potential of the homojunction,⁶¹ q is the elementary charge, N is the unintentional doping concentration, and the thickness of *NL* WSe₂ T is 6.3 nm. A depletion width of $W_{\text{NL}} \sim 0.6 \mu\text{m}$ corresponds to

Figure 4.11. The lineout of the TR-PEEM signal along the black line on the 1.4-ps image in Figure 4.10(a).

an unintentional doping concentration of $N \sim 10^{16} \text{ cm}^{-3}$. This concentration is consistent with that reported for exfoliated MoS₂.⁶²

4.4 Conclusion

In summary, we have studied the dynamics of photoexcited carriers at the 1L–NL WSe₂ homojunction interface by using TR-PEEM. Beyond the sub-picosecond carrier cooling occurring in the individual components and the few-picosecond exciton-exciton annihilation occurring on the 1L-WSe₂ component, we also observed evidence of an ultrafast interfacial hole transfer from 1L to NL on the 0.2-ps timescale. The resultant excess hole density on NL-WSe₂ eventually decays by carrier recombination across the homojunction interface on the 100-ps timescale. Finally, the TR-PEEM image reveals the accumulation of holes in the NL-WSe₂ component at the homojunction interface, possibly due to the depletion region; this region is characterized by a width of $0.60 \pm 0.17 \text{ }\mu\text{m}$. These results provide a first glimpse into the ultrafast carrier dynamics that occur at an atomically thin homojunction interface.

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Chapter 5

Ultrafast Electronic Relaxation Dynamics of Atomically Thin MoS₂ Accelerated by Strain

Strain engineering of TMDs is one of the most crucial methods to extend their applications, due to the large Young's modulus, high tensile strength, and elasticity of TMDs. The strain provides an exciting opportunity to modify band structures of TMDs. However, the effects of strain on the ultrafast dynamics in TMDs are still unknown. Here, we employ TR-PEEM to study the ultrafast dynamics of a wrinkled, multilayer MoS₂ flake. These micrometer-sized wrinkles result in localized strain of the flake, estimated by AFM to be ~1%. The TR-PEEM signals reveal the relaxation dynamics with a time constant 97 ± 2 fs for wrinkled MoS₂ and 120 ± 2 fs for flat MoS₂. The electronic relaxation rates are enhanced at wrinkles, supported by the lifetime map that reveals the spatial distribution of electronic relaxation times. The fast electronic relaxation on wrinkled MoS₂ is supported by previous *ab initio* studies, which found that the strain decreases relaxation energy distance and enhances electron-phonon coupling strengths.

5.1 Introduction

TMDs are a class of layered materials with favorable electronic and optoelectronic properties, such as high carrier mobilities,^{1,2} valley selectivity in photoexcitation,^{3,4} large exciton and trion binding energies,^{5,6} strong PL,^{7,8} large nonlinear optical susceptibilities,⁹ and superconductivity.^{10,11} These properties of TMDs, along with their atomic thickness and the ability to fabricate high-quality TMD thin films on the wafer scale,¹ open the door to a variety of applications as ultrathin components in photodetectors,¹² light-emitting diodes,¹³⁻¹⁵ transistors,¹⁶ and modulators.¹⁷

The versatility of TMDs and therefore, their range of applications, can further be extended by tuning their electronic band structures.¹⁸ The most obvious approach to tuning band structures is by changing the chemical composition of the sample itself. Various synthesis procedures yield a family of TMDs comprising members with different chemical compositions,¹⁹ each exhibiting a unique band gap and band offsets relative to one another. The properties of different TMDs can be further tuned by chemical doping, e.g., by introducing intercalating metals or molecules²⁰ or by substitutional doping with transition metals,²¹ or even by alloying.^{22,23} For a fixed chemical composition, the band structure can be varied by applying external electric fields,^{24,25} pressure,^{26,27} or strain.^{28,29}

The excellent mechanical properties of TMDs^{30,31} – the large Young’s modulus, high tensile strength, and elasticity – make them amenable to strain engineering. This approach to tuning the band structure³²⁻³⁴ has been exploited, for example, to drive a semiconductor-to-metal transition in TMDs³⁵ and to realize a superlattice of artificial atoms in strain-textured MoS₂,³⁶ and also improve the performance of TMDs in optoelectronic devices.³⁷⁻³⁹ While the effect of strain on the steady-state optoelectronic properties of TMDs has been extensively investigated, less well-known is how strain influences the nonequilibrium carrier dynamics of

TMDs. Information about ultrafast carrier dynamics is pertinent to understanding the high-field carrier transport characteristics of semiconductors.⁴⁰

Here, we employ TR-PEEM to study ultrafast dynamics of a wrinkled, multilayer MoS₂ flake. These micrometer-sized wrinkles result in localized strain of the flake. Resolving its dynamics therefore necessitates the use of an experimental technique with sub-micrometer spatial resolution and sub-100-fs temporal resolution. TR-PEEM combines the femtosecond pump-probe technique with a PEEM microscope to simultaneously achieve high spatial and temporal resolution, making it ideal for investigating the ultrafast dynamics of spatially heterogeneous samples⁴¹. The TR-PEEM measurements show that wrinkled MoS₂ undergoes significantly faster electron cooling than flat MoS₂. These findings are supported by the calculated band structure of strained MoS₂, which shows a smaller energy gap for intravalley scattering than unstrained MoS₂, hence enhancing electron cooling.

5.2 Experimental methods

The MoS₂ flake is grown by chemical vapor transport, exfoliated micromechanically and transferred onto an Au-coated Si substrate. Wrinkles are formed naturally due to the interaction between the MoS₂ flake and the substrate. Figure 5.1 displays the optical image of the wrinkled MoS₂ flake. The wrinkles can be distinguished from flat MoS₂ by their different optical contrasts. In addition, the wrinkles also appear prominently in the topographical map recorded by AFM [Figure 5.2(a)]. These wrinkles are formed from a region of the flake that is ~15

Figure 5.1. Optical image of wrinkled multilayer MoS₂ flake.

layers-thick [Figure 5.2(b)]. I select three wrinkles and take height profiles along three lines for each wrinkle [Figure 5.2(c)]. All height profiles are fit to the function⁴²

$$h(x) = \frac{\delta}{2} \left[1 + \cos \frac{2\pi(x - x_0)}{\lambda} \right] + h_0, \quad (5.1)$$

where δ and λ are the height and width of the wrinkle, respectively; x_0 is the distance of the highest point; h_0 is the height offset. Statistical analysis of 3 height profiles extracted along a 5- μm length of the wrinkle 1 yields a mean (standard deviation) of 2.07 μm (0.02 μm) and 0.50 μm (0.01 μm) for the width and height, respectively. The maximum strain ε that develops on top of a wrinkle can be estimated by^{42,43}

$$\varepsilon \sim \pi^2 h \delta / (1 - \sigma^2) \lambda^2, \quad (5.2)$$

where h is thickness of the MoS₂ flake, δ and λ are respectively the height and width of the wrinkle, and σ is Poisson's ratio ($\sigma = 0.125$)⁴⁴. The maximum strain of the wrinkle 1 is $1.0 \pm 0.1\%$. The strain values of other wrinkles are $\sim 1\%$ (see Table 5.1).

Figure 5.2. (a) AFM image of wrinkled MoS₂. (b) The sketch of a multilayer MoS₂ wrinkle. (c) Height profiles along line 1, 2, 3 (on wrinkle 1); 4, 5, 6 (on wrinkle 2); and 7, 8, 9 (on wrinkle 3). The colored lines are fits to Eq. 5.1.

Table 5.1. Heights δ and widths λ of lines 1 – 9 and the estimated strains ε of wrinkles 1 – 3.

		Line 1	Line 2	Line 3	Mean
Wrinkle 1	Height δ (μm)	0.50	0.50	0.50	0.50 ± 0.01
	Width λ (μm)	2.05	2.08	2.08	2.07 ± 0.02
	Strain ε	$1.0 \pm 0.1\%$			
		Line 4	Line 5	Line 6	Mean
Wrinkle 2	Height δ (μm)	0.34	0.34	0.33	0.34 ± 0.01
	Width λ (μm)	1.75	1.80	1.79	1.78 ± 0.03
	Strain ε	$1.1 \pm 0.1\%$			
		Line 7	Line 8	Line 9	Mean
Wrinkle 3	Height δ (μm)	0.29	0.30	0.31	0.30 ± 0.01
	Width λ (μm)	1.78	1.74	1.82	1.78 ± 0.04
	Strain ε	$1.0 \pm 0.1\%$			

To elucidate the effect of localized strain on ultrafast electronic relaxation dynamics of multilayer MoS₂, we performed TR-PEEM measurements on the wrinkled sample with 2.41-eV pump and 3.61-eV probe. Electrons in the valence band of MoS₂ are excited to the conduction band by the 2.41-eV pump. After a variable time delay, a 3.61-eV probe pulse ejects

Figure 5.3. PEEM signal intensity against the fluences of (a) pump and (b) probe pulses.

Figure 5.4. Band structures of unstrained (black) and strained (red) multilayer MoS₂, with one-photon 2.41-eV pump (green arrow) and one-photon 3.61-eV probe window (shaded regions).

these electrons, which are refocused by a column of electronic lenses onto an array detector to yield the PEEM image. Figures 5.3(a) and (b) show that the PEEM signal varies linearly with pump and probe fluence, respectively. Hence, power-dependent measurements reveal that the pump and the probe interactions with the MoS₂ sample are both one-photon processes. Lateral momentum conservation requirements in photoemission⁴⁵ confines the probe window for 3.61-eV probing to a narrow region around the Γ point of the conduction band (Figure 5.4). Accordingly, we infer that the observed ultrafast dynamics originate from electronic relaxation from the Γ point. The band structure of bulk MoS₂ confirms that the Γ point is readily accessed by 2.41-eV photoexcitation (Figure 5.4).

5.3 Results and discussion

Figure 5.5(a) displays the TR-PEEM images acquired at various pump-probe time delays. The PEEM signal of the wrinkle is $\sim 20\%$ lower than that of flat MoS₂, pointing to the effect of strain on the density of states in the probe window⁴⁶. The conduction band is sensitive to the

Figure 5.5. (a) PEEM images of wrinkled MoS₂ with a series of time delays. Wrinkles have weaker signal intensity than flat MoS₂. (b) Time traces of wrinkled MoS₂ [red box in (a)] and flat MoS₂ [blue box in (a)], fitted by single exponential decay after time-zero convolved with instrumental response function. (c) The schemes of intravalley and intervalley scattering under our experimental conditions.

strain, which shifts states down in energy, towards the Fermi level. Therefore, density of states within the probe window is reduced by the strain. Figure 5.5(b) shows the temporal evolution of the TR-PEEM signals, spatially integrated over wrinkled and flat regions of the multilayer MoS₂. The time traces each exhibit a strong response at time-zero, followed by a single exponential decay with a time constant 97 ± 2 fs for wrinkled MoS₂ and 120 ± 2 fs for the flat MoS₂. The decay of the PEEM signal tracks the relaxation dynamics of the electrons at the Γ

point as they undergo electron-phonon scattering^{47,48} and leave the probe window to populate the lower-lying valleys in the conduction band [Figure 5.5(c)].

To confirm that electronic relaxation rates are enhanced at wrinkles, we extract the time traces for each individual pixel of the TR-PEEM image and fit them to a single exponential decay convolved with the instrumental response function. The time constants obtained at each pixel is used to create a lifetime map that reveals the spatial distribution of electronic relaxation times [Figure 5.6(a)]. Prominent blue stripes in the lifetime map, which encode regions with shorter relaxation times, coincide with the positions of the wrinkles. Figure 5.6(b) shows the histograms of the relaxation time constants on wrinkle 1 and flat MoS₂, extracted from the regions of interest defined in Figure 5.5(a). These histograms have a mean (standard deviation) of 89 fs (14 fs) and 114 fs (14 fs) for the wrinkle 1 and flat MoS₂ regions, respectively. Figure 5.7(a) shows the time traces, spatially integrated over other wrinkles. After time-zero, the PEEM signals of wrinkle 2 and 3 undergo single-exponential decays, with time constants of 94 ± 3 fs and 97 ± 3 fs, respectively. Figure 5.7(b) displays the histograms for other wrinkles,

Figure 5.6. (a) Lifetime map of electron cooling. (b) Histograms of time constants of a wrinkle (marked on lifetime map) and flat MoS₂.

Figure 5.7. (a) Time traces of wrinkles 2 (top panel) and 3 (bottom panel) (b) Histograms of time constants for wrinkles 2 (top panel) and 3 (bottom panel).

extracted from the regions of interest defined in Figure 5.6(a). The distributions of time constants for wrinkles 2 and 3 are characterized by mean values (standard deviations) of 84 fs (13 fs) and 91 fs (14 fs), respectively. All the wrinkles undergo faster electronic relaxation than the flat region. The lifetime map and the histograms both reveal faster electronic relaxation at the wrinkled regions, consistent with the results obtained from the analysis of the spatially integrated time traces [Figure 5.5(b)]; the slight deviation between the two sets of values arises from the fact that the lifetime obtained from the spatially integrated measurement represents an amplitude-weighted average time constant instead of a simple average.

To explain the fast electron cooling in wrinkled MoS₂, we consider the band structure of tensile strained and unstrained multilayer MoS₂ (Figure 5.8).³³ As electron cooling can occur via intravalley and intervalley scattering, the observed decay rate is sum of intravalley scattering rate and intervalley scattering $1/\tau_{\text{obs}} = 1/\tau_{\text{intra}} + 1/\tau_{\text{inter}}$, where τ_{obs} is observed

Figure 5.8. Band structures of unstrained and strained multilayer MoS₂. The small energy distance of intervalley scattering accelerates electron cooling in strained MoS₂. Band structures are reproduced with permission from IOPscience.³³

lifetime, τ_{intra} and τ_{inter} are time constants of intravalley and intervalley scattering, respectively. *Ab initio* studies of MoS₂ reveal that the intravalley $\Gamma \rightarrow Q$ scattering and the intervalley $\Gamma \rightarrow K$ scattering occur primarily via the emissions of the longitudinal optical phonons and the out-of-plane optical phonons, respectively.^{49,50} Optical phonon emission is more efficient relaxation pathway, due to 2 orders of magnitude larger cooling power than acoustic phonons.⁵¹ Considering the changes of band structure with the strain, we find that the conduction band at both K and Γ move towards the Fermi level overall simultaneously. The energy distance of $\Gamma \rightarrow K$ has a negligible change with strain. Hence, the strain has few effects on the rate of the intervalley relaxation $1/\tau_{\text{inter}}$. However, the Q valley of strained MoS₂ has slightly higher energy than unstrained MoS₂, thereby smaller energy distant of $\Gamma \rightarrow Q$ in strained MoS₂. The small energy distance enhances the intravalley phonon scattering, leading to a large intravalley relaxation rate $1/\tau_{\text{intra}}$. As a result, we observe smaller electron cooling lifetime of wrinkled MoS₂ than the flat MoS₂. Moreover, *ab initio* calculations also reveal that compression strain increases the electron-phonon coupling strength, which enhances the electron-phonon scattering rate.⁵²

The different electron cooling time constants of wrinkled and flat MoS₂ is consistent with previous experimental and theoretical studies which show that electron-phonon scattering is significantly sensitive to strain.^{53,54} Thus, strain engineering can modulate the electron-phonon interaction to tune the electron mobilities of TMDs, which has effects on the saturation of drift velocity with implications in high power and high speed field-effect transistors. Moreover, electron cooling in semiconductors is a crucial dynamic in many practical applications. For instance, the fast hot photogenerated electron relaxation is desired for the applications in lasers;⁵⁵ while the utilization of hot electrons before cooling can significantly enhance the efficiency of solar cells.⁵⁶ The strain-induced modulation of electron cooling in TMDs potentially contributes to the material designs for diverse applications.

5.4 Conclusion

In conclusion, we harness the high spatial and temporal resolutions of TR-PEEM to study the spatially heterogeneous ultrafast dynamics of wrinkled multilayer MoS₂. The wrinkles are associated with a maximum strain of ~1%. Probing the ultrafast dynamics at the Γ point reveals markedly faster electronic relaxation for the wrinkled region than the flat region. *Ab initio* simulations suggest that electron-phonon coupling is enhanced by strain, hence facilitating electronic relaxation by dissipation of excess electronic energy to the phonon bath. Our results provide an early glimpse into the effect of strain on the ultrafast dynamics of TMDs, and suggest that applications that require long-lived hot carriers, such as hot-electron-driven photocatalysis⁵⁷, should employ strain-free TMDs.

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Chapter 6

Summary and Outlook

TMDs are an attractive class of two-dimensional (2D) materials with many excellent electronic and optoelectronic properties, such as strong PL,^{1,2} large nonlinear optical susceptibilities,³ superconductivity,^{4,5} high carrier mobilities,^{6,7} valley selectivity in photoexcitation,^{8,9} and large exciton and trion binding energies.^{10,11} These properties open the door for a variety of applications in ultrathin devices including photodetectors,¹² light-emitting diodes,¹³⁻¹⁵ transistors,¹⁶ and modulators.¹⁷ The versatility of TMDs can further be extended by defect engineering with tuning the properties. Studies of ultrafast photocarrier dynamics in spatially heterogeneous TMDs are desired, to improve the performances of their electronic and optoelectronic devices. In this thesis, I harness TR-PEEM with 50-fs temporal resolution and 70-nm spatial resolution to investigate diverse types of heterogeneities in TMDs.

Firstly, spatially resolved hot-electron transfer dynamics at the 1L MoS₂/Au van der Waals interface are studied. AFM reveals a spatially heterogeneous distribution of MoS₂/Au gap distances, which leads to the spatially heterogeneous distribution of electron transfer time constants across MoS₂/Au interface with a mean of 386 fs and a standard deviation of 54 fs. Electron transfer rates decay exponentially as a function of distance, with a small attenuation coefficient of $0.06 \pm 0.01 \text{ \AA}^{-1}$, demonstrating the transport of hot electrons across a MoS₂/Au interface is robust against surface corrugations and defects. *Ab initio* simulations suggest that

surface plasmon-like states mediate hot-electron transfer, hence accounting for its weak distance dependence. Secondly, the dynamics of photoexcited carriers at the 1L–NL WSe₂ homojunction interface are investigated. The 1L–NL homojunction exhibits Type I band alignment, which serves to funnel photocarriers that are originally located on the 1L component to the NL region of the homojunction. Hence, beyond the sub-picosecond carrier cooling occurring in the individual components and the few-picosecond exciton-exciton annihilation occurring on the 1L–WSe₂ component, we also observe evidence of an interfacial hole transfer from 1L to NL on the 0.2-ps timescale and carrier recombination across the homojunction interface on the 100-ps timescale. By harnessing the spatial resolution of the PEEM, we observe the accumulation of holes in the NL–WSe₂ component at the homojunction interface due to the depletion region with a width of $0.60 \pm 0.17 \mu\text{m}$. At last, I perform TR-PEEM measurements on a wrinkled multilayer MoS₂ sample that is subject to 1% strain. Probing the sub-picosecond electron dynamics at the Γ point reveals markedly faster electronic relaxation for the wrinkled region than the flat region. The accelerated relaxation for wrinkled MoS₂ originates from the effect of strain on the band structure and the increased electron-phonon coupling strength.¹⁸

These TR-PEEM results provide a first glimpse into the ultrafast carrier dynamics that occur in spatially heterogenous TMDs. To obtain more detailed information, two updates to our existing TR-PEEM instrument are needed: (1) the generation of extreme ultraviolet (EUV) probe pulses and (2) the ability to resolve the kinetic energy and momentum of the photoemitted electron. In our studies so far, we have focused on the ultrafast dynamics occurring at Γ and Q points in the Brillouin zone of TMDs because these band extrema reside in the probe window¹⁹ of the 3.61-eV probe pulses employed in the experiments. However, many interesting ultrafast dynamics occur at the K valley, such as direct exciton formation,¹ photocarrier transfer in heterostructure,²⁰ and defect-assisted exciton recombination.^{21,22} EUV probe pulses at photon energies of ~ 20 eV are required to access the K valley; for 1L–MoS₂,

for example, a photon energy of 19.7 eV (21.7 eV) is needed to access the CBM (VBM), both located at the K valley. For our setup, we can produce EUV light via high-order harmonic generation.²³⁻²⁵ As EUV probe pulses are used to eject electrons in a large region of the TMD band structure, we need to resolve the momentum and energy of the ejected electrons to map the observed dynamics to regions of interest within the extended probe window. Moreover, with energy and momentum resolved abilities, the energy losses and the momentum changes can be observed during the photocarrier relaxations. Therefore, in the future, the PEEM should be upgraded to include a time-of-flight (TOF) detector and imaging in k -space to achieve energy and momentum resolution, respectively.

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Publication list

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