Ultrafast dynamics in 2D materials investigated by time-resolved photoemission electron microscopy

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NANYANG
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ULTRAFAST DYNAMICS IN 2D
MATERIALS INVESTIGATED BY
TIME-RESOLVED PHOTOEMISSION
ELECTRON MICROSCOPY

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SCHOOL OF PHYSICAL AND
MATHEMATICAL SCIENCES

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Ultrafast Dynamics in 2D Materials
Investigated by Time-Resolved Photoemission
Electron Microscopy

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Abstract

This thesis includes my four-year researches on ultrafast dynamics on 2D materials using time-resolved photoemission electron microscopy (TR-PEEM). Our aim is to spatially investigate the dynamics on the atomic-layer thick materials. In Chapter 1, the background introduction of the ultrafast dynamics on 2D materials by different optical methods are discussed. While the applications of PEEM on surface science and the time resolved researches of the plasmonics of metal nanostructures are reviewed. At last, our motivation using TR-PEEM to investigate the ultrafast dynamics in semiconductor 2D materials is discussed. In Chapter 2, we briefly introduce our instrument firstly, then extract a 55-fs temporal resolution and an 80-nm spatial resolution through our delicate characterization of our instrument. we show that the apparatus can be used to investigate the sub-100-fs electronic relaxation dynamics. The time constant mapping result not only recovers the ensemble-averaged electronic relaxation time constant, but also directly yields the extent of spatial heterogeneity of the observed dynamics. In Chapter 3, we study the dynamics of WSe₂ pumped by 2.41-eV light, find the spatial heterogeneity. The results help us to understand the influence of structural heterogeneities on the carrier dynamics of two-dimensional materials. In Chapter 4, the research on 4-layer MoS₂ material by TR-PEEM reveals two Auger processes including Auger-mediated exciton formation and exciton-exciton annihilation process. In Chapter 5, we summary all the results discussed in Chapter 2 – 4, put forward some suggestions to further improve our experiments in future.

Chapter 1

Introduction

1.1 The properties and ultrafast dynamics research of two-dimensional materials

Graphene as one-atomic-thin layered material, was discovered in 2004 by Novoselov and Geim,¹ it is a benchmark of two-dimensional (2D) materials. The extremely high mobility $\sim 2.5 \times 10^5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ and the maximum bearing current density at room temperature exhibits its electronic and electric applications in industry.²⁻³ Besides what we mentioned before, the high thermal conductivity⁴, high resistance to gas permeation⁵ and mechanical properties⁶ are all superior than traditional bulk materials. The unique linear dispersion and gapless electronic band structure near K point, also known as Dirac cone structure, demonstrates massless fermions and half-integer, fractional and fractal quantum hall effects.⁷⁻⁹

Despite of the gapless structure in graphene, the photoexcited electrons relaxation process has been investigated by ultrafast optical/IR pump-probe spectroscopy¹⁰⁻¹¹. Although the high energy tail of carrier distribution, the thermalization of the photoexcited carrier finishes within few tens femtoseconds. Then the cooling process of these hot distributed carriers via optical phonon emission lasts hundreds of femtoseconds. Subsequently, the carrier cooling slows down due to the equilibrium temperature of carriers and optical phonons. The exchange rate of energy between the carriers and the optical phonons and anharmonic decay of optical phonons into acoustic phonons will be the bottleneck.¹² Even for the well-established carrier cooling model, there are several underlying dynamic processes. Interband recombination and generation mechanism such as Auger scattering,¹³ plasmon scattering¹⁴ and optical phonon scattering,¹⁵ also play important roles in carriers cooling process in graphene with different time scales. Rather large optical phonon energies (~ 0.162 and 0.196 eV), very

Figure 1.1 Calculated band alignment for MX₂ monolayers. Solid and dashed lines are obtained by PBE and HSE06, respectively. The dotted lines indicate the water reduction (H⁺/H₂) and oxidation (H₂O/O₂) potentials. Reprinted with permission from American Chemical Society.²⁰

slow cooling process in doped graphene occurs via acoustic phonon emission when the energy distribution of most carriers is below the optical phonon energy.¹⁶⁻¹⁷

During the exploration to open bandgap in graphene and make graphene suitable for the optoelectronic devices, the discovery of 2D hexagonal boron nitride (hBN) substrate that can induce a bandgap in graphene¹⁸⁻¹⁹, attracts lot efforts putting into the semiconducting 2D materials. Many layered materials such as transition-metal dichalcogenides depicted in Figure 1.1,²⁰ monoelemental 2D semiconductors (phosphorene, silicene, germanene) and monochalcogenides (GaSe etc.) are discovered successively. The band structure of these materials changes drastically, from indirect bandgap in multilayers to direct bandgap in monolayer.²¹ At the direct bandgap point, the imbalanced carriers in different valley selectively pumped by laser pulse can induce the valley polarization, which demonstrates the viability of optical valley control.²²⁻²³ Different from bulk materials, the bonding energies of exciton in

Figure 1.2 Potential applications for 2D materials and associated changes. ① The lack of current saturation and low gain of graphene transistors. ② Relatively low mobility ($<200 \text{ cm}^2/\text{s}$) of 2D transition metal dichalcogenides. ③ Cleaning method to remove polymer/PR residue without using O_2 plasma. ④ Pinhole-free dielectric formation. ⑤ Single crystalline/larger grain size. ⑥ Reusable substrate, waste handling. ⑦ Control of contact resistance/Schottky barrier/Fermi level pinning. ⑧ Effective doping methods stable in air and/or hermetic packaging. ⑨ Reducing defects from thermal coefficient mismatch of the film and the substrate during CVD. ⑩ Low temperature ($<400^\circ\text{C}$) CVD synthesis for direct growth and integration. ⑪ Clean, repeatable interface after wet/dry transfer or direct synthesis without using metal catalyst. ⑫ Toxicity. Reprinted with permission from Royal Society of Chemistry.³³

WS_2 , trion in MoS_2 and biexciton in WSe_2 are 320 meV ,²⁴ 20 meV ²⁵ and 52 meV ²⁶, respectively. Strong nonlinear optical phenomena emerge in 2D materials, specially at the edges of atomic-thin-layer crystals.²⁷ With these novel properties, they have been applied in many possible applications, such as light-emitting diodes,²⁸ solar cells,²⁹ integrated circuits,³⁰ photodetector³¹ and field-effect transistors³² and so on. Figure 1.2 is the summary of the

Figure 1.3 Evolution of photocarriers after instantaneous interband excitation. Reprinted with permission from John Wiley and Sons.³⁵

potential applications and challenges of 2D materials, and it is divided into two regions: electronics (More Moore) and applications except electronics (More than Moore).³³

Although it is a long way for 2D materials to be applied in real life like traditional bulk materials, 2D materials will be an important component for real world use with continued improvement in large-scale integration and synthesis. Herein, the fundamental research makes a greater contribution to this process, the investigations of ultrafast carrier dynamics in 2D materials provide a way to reveal the physical principles of what we observed. As we discussed before, the carriers' relaxation process in graphene after photoexcited by ultrashort laser pulse. Different from the gapless band structure in graphene, most of the 2D materials behavior as a semiconductor with 1~2 eV bandgap as depicted in Figure 1.1. After photoexcited carriers generated through interband excitation indicated as 'Excitation' in Figure 1.3, the nonthermal distribution of electrons and holes in conduction and valance band becomes the thermal distribution by carriers' self-interaction drawn as 'Thermalization' in Figure 1.3. The initial energy distribution of photocarriers follows the pump spectrum, the thermalization is expected

to be very fast in 2D materials due to the reduced screening effect. Relying on 10-fs time resolution, Nie et al. firstly reported the thermalization happens within 20 fs and it follows non-Markovian quantum kinetics from the fluence dependent measurement in few-layer MoS₂³⁴. But the temperature of Fermi-Dirac distribution carriers is still significantly higher than the lattice temperature, the excess energy will transfer into lattices via phonon emission until the temperature quasi-equilibrium realization between carrier and lattices drawn as ‘Cooling’ in Figure 1.3. The cooling of hot carriers in few-layer MoS₂ lasts about 500 fs and the hot phonon effect is also observed at fluence dependent measurement. Due to the large exciton binding energy originated from strong confinement in z direction, free carriers form excitons in 2D materials exhibited as ‘Exciton Formation’ in Figure 1.3.³⁵ The hundreds meV binding energy has been confirmed in absorption and photoluminescence experiments,^{24, 36} Ceballos et al. investigate the formation process by using transition-absorption measurement.³⁷ Exciton is much less sensitive than free carriers at inducing transition signal changing, with more and more free carrier pairs forming excitons, the transition absorption signal decreases along with delay time increasing. The typical time scale for monolayer to few-layer 2D materials is about 0.3 to 0.5 ps.³⁷⁻³⁸ At last these excitons will recombine by radiative or nonradiative way shown as ‘Recombination’ in Figure 1.3. Usually the exciton-exciton annihilation will dominate the recombination process when the exciton density is larger than 10¹¹ cm⁻²,³⁵ the released energy dissipates as phonon generation or excites carriers in intraband. This process can be described as

$$\frac{dN}{dt} = \frac{1}{\tau}N - \gamma N^2 \quad 1.1$$

where γ and τ are the exciton-exciton annihilation rate and exciton lifetime, respectively. Here are some reports about the annihilation rate in monolayer 2D materials: 0.043 cm² s⁻¹ in MoS₂,³⁹ 0.14 cm² s⁻¹ in WS₂,⁴⁰ 0.13 cm² s⁻¹ in WSe₂⁴¹ and 0.33 cm² s⁻¹ in MoSe₂.⁴² When exciton density

reduces to certain level, the effect of exciton-exciton annihilation is much weaker than previous. The time constant in this region can be treated as exciton lifetime, but the discrepancies can be observed in different sample, even in same sample using different techniques. For example, the MoSe₂ get a lifetime of 150 ps from pump-probe measurement⁴² but 3 ps from time-resolved PL experiment.⁴³ Lots of factors can influence the lifetime of excitons, the first of these is defects. The exciton lifetime mentioned before is not the radiative recombination lifetime of exciton. According to the time-resolved mid-infrared experiment⁴¹ and optical 2D Fourier transform spectroscopy,⁴⁴ the lifetime of radiative recombination is within 200 fs. The theoretical model reveals that most of thermalized excitons are out of the light cone, then excitons need much longer time to recombine via radiative channel.⁴⁵ Here, we emphasize that all processes we talk before, would not happen in sequence. They proceed simultaneously but with different decay rate.

Other ultrafast phenomena such as photocarrier diffusion, spin and valley dynamics and ultrafast carrier transfer in heterostructure 2D materials using ultrafast microscopy and polarization-resolved measurement. After the generation of photocarriers, these carriers are concentrated in laser spot and follow an lateral distribution in ideal condition. Carriers and quasi-particles start to drift away from the high-density region, this process can be described by the diffusion equation

$$\frac{\partial \phi(\mathbf{r}, t)}{\partial t} = \nabla \cdot [D(\phi, \mathbf{r}) \nabla \phi(\mathbf{r}, t)] \quad 1.2$$

Where $\phi(\mathbf{r}, t)$ is the density of photocarriers and $D(\phi, \mathbf{r})$ is the diffusion coefficient. $\mathbf{r}$ and t are the position and time. If we simplify the model as the density of photocarriers is Gaussian lateral distributed with a full width at half maximum w and the diffusion process is isotropic. Then the equation can be solved as

$$w^2(t) = w_0^2(t) + 16 \ln(2)Dt \quad 1.3$$

where w_0 is the initial width of Gaussian distribution. The ultrafast microscopy monitors the carriers profile at different delay time, Gaussian width can be extracted through the Gaussian function fitting. The square of w can be fitted into equation.3, then we can get the diffusion coefficient. Here is a summary of diffusion coefficients of electron-hole pairs or excitons in several 2D materials and some bulk materials as reference. The diffusion coefficients of 2D materials are labelled as solid symbols in Figure 1.4, which are plotted against the optical bandgap. Most of them locate in the range from 10 to 50 $\text{cm}^2 \text{s}^{-1}$, which are much smaller than graphene and black phosphorus. At the same time, more effects have been directed to the research of spin and valley dynamics in 2D materials for the potential application in spintronics. Through several experiments, a typical few picoseconds spin lifetime have observed in monolayer MoS_2 ,⁴⁶ WSe_2 ⁴⁷ and WS_2 ⁴⁸. Low temperature⁴⁸ and doped sample⁴⁹⁻⁵⁰ can

Figure 1.4 Summary of diffusion coefficient of exciton or electron-hole pairs in monolayer 2D materials. Reprinted with permission from John Wiley and Sons.³⁵

significantly enhance the spin lifetime to 100 ps, even nanosecond range. The 2D material heterostructure is formed by two different 2D materials, which has plenty combinations. Different from the heterostructure made of bulk materials requiring the lattice constant match, these two 2D materials are coupled by weak van der Waals force and form an atomic-thin-layer heterostructure. The processes of interface charge transfer have been investigated by several groups. The transfer time from MoS₂ to WS₂ is about 50 fs reported by Hong et al.⁵¹ And in other reports,⁵²⁻⁵³ the time constants for carrier transfer between 2D heterostructure are within 1 ps. The ultrafast transfer processes indicate that effective coupling exists between these two atomic-thin-layer materials, but the physics mechanism remains unknown. With the large pulse width in time-resolved optical microscope, it hinders the further investigation, and scientists need a new way to reveal the secret here with better spatial and temporal resolution.

1.2 Photoelectron emission microscopy (PEEM) and Time-resolved PEEM (TR-PEEM)

PEEM collects the photoelectrons emitted from materials, the high voltage is applied at the entry to increase collection efficiency. Then these photoelectrons transmit through a set of electrostatic lenses, are amplified by a microchannel plate. Finally, these electrons are projected onto the phosphor screen, these images will be captured by charge coupled device (CCD) camera. The lateral resolution of PEEM nowadays has been significantly improved to few nanometers,⁵⁴ but the practical resolution is counted on many factors, such as sample morphology,⁵⁵ photo polarization⁵⁶, multiphoton excitation⁵⁷ and aberration correction^{54, 58-59} et al. Benefiting from the high spatial resolution, PEEM has shown its unique abilities on surface science,⁶⁰ metallurgy,⁶¹ catalysis,⁶⁰ semiconductor physics⁶² and magnetism⁶³. During these applications, the most used irradiation light sources are mercury lamp, synchrotron light and laser pulse. Different light source has its own advantages and will be chosen by experiment requirement and budget. Mercury lamp as a small and cheap light source with 4.9 eV maximum light energy can be mounted to PEEM vacuum chamber directly, it is very convenient to get a

Figure 1.5 PEEM images of 50 nm thick Au triangle with different polarization. White scale bar is 200 nm. Reprinted with permission from American Chemical Society.⁵⁶

high-resolution image in laboratory. The synchrotron light source spanning from UV to X-ray range with high photon flux, provide a powerful way to map elemental composition⁶⁴ and magnetic domain⁶⁵ et al. But the expenditure of synchrotron is extremely high, it cannot be affordable by most countries in the world. While ultrafast laser with moderate price and the ability to investigate ultrafast surface dynamics, it draws more attentions in PEEM community.

With the specific light polarization of laser pulse, it has been applied to the plasmonics research. Plasmonics is the interaction between electromagnetic field and free electrons in a metal. Both the localized surface plasmons (LSP) and surface plasmon polaritons (SPP) in plasmonics are investigated by the combination of ultrashort laser pulse and PEEM. The enhanced electric field caused by excitation of surface plasmons can greatly increase the nonlinear photoemission. Stuckless et al.⁶⁶ reported the signal counts from some regions on rough silver films are orders-of-magnitude enhancement than those on smooth surface. An n-step cascade photon absorption model is put forward to explain the increase of photoemission yield closed to a plasmon energy.⁶⁷ Several refined models are published to describe the plasmon assisted multiphoton emission.⁶⁸⁻⁷¹ The field manipulation through plasmonics is demonstrated by PEEM's high resolution near-field mapping, Figure 1.5 depicts the images taken by PEEM with different polarization excitation light.⁵⁶ The in-plane electric field aligned

Figure 1.6 Near-field manipulation at subwavelength length. Reprinted with permission from American Chemical Society.⁷²

along the edges can display two spots near the triangle's apexes, otherwise only one spot is observed for excitation along triangle altitudes. All these spots are corresponding to certain plasmonic modes. Full control of the SPP field is desired for nanophotonics, the interference mechanism have been exploited in this process.⁷² The bowtie shaped nanostructure with 350 nm edge length and 40 nm gap is irradiated by two orthogonally polarized light pulses. As depicted in Figure 1.6, the photoemission maxima at outer corners of the bowtie switches its position at two different delay times, the simulation of field distribution for TM- and TE-polarized excitations at $+\pi/2$ and $-\pi/2$ relative phase confirms the plasmonic mode. Electric field adaptive method is another way to control spatiotemporal behavior by shaping the laser pulses' amplitude, phase and polarization. Aeschlimann et al.⁷³ exhibited the adaptive polarization shaping of femtosecond laser pulses changes the nanooptical near-field distribution on Ag islands. An evolutionary algorithm is employed to optimize the adaptive control of the field.

Figure 1.7 (a) Interferometric two-photon correlation measurement of the photoelectron emission intensity as a function of the relative time delay. (b) A detailed comparison of the temporal variation of the photoemission signal for four different hotspots. Reprinted with permission from American Chemical Society.⁷⁴

Researching the ultrafast dynamics with nanometers spatial resolution is expected by scientists, PEEM combining with pump-probe method can realize this goal. A first experiment was reported in 2005,⁷⁴ the silver grating structure irradiated by two identical 400 nm, 10 fs replica laser pulse is monitored by PEEM. From the interferometric time-resolved two-photon photoemission of hot spot, the researcher can observe the evolution of localized surface plasmon field as a function of time as shown in Figure 1.7. Initially the intensity of these hot spots oscillates as the exciting laser field, they converged to their plasmonic eigenfrequency up to their dephasing time. Later the dynamics of SPP waves were also investigated by Kubo et al.⁷⁵. Two-path interference scheme is depicted in the left part of Figure 1.8, the light field excite SPP wave at the Ag surface step edge. The polarization wave $P_{spp}(x,t)$ along the vacuum/Ag interface as path 1, the external light field creates a second local polarization component at the interface $P_{light}(x,t)$ as path 2. The total polarization is the combination of P_{spp} and P_{light} , behaves as an interference beating pattern as shown in the right part of Figure 1.8. The quantitative determination of the polariton characteristics is important not only in the fundamental interest

Figure 1.8 Dynamics of a SPP wave propagation investigated by pump-probe experiment. Reprinted with permission from American Chemical Society.⁷⁵

but also the forthcoming technological application. Keiki et al.⁷⁶ used the TR-PEEM to direct image electron recombination and transport on the surface of semiconductor material. The electrons are excited from valence band to conduction band by a 2.4 eV pump pulse, then another 4.8 eV pulse is applied to generate photoelectrons from GaAs drawn in Figure 1.9 (e). Three images of electron spatial distribution on sample surface are displayed in Figure 1.9 (a) – (c), the time trace of this dynamic process is extracted from a series of PEEM images in the

Figure 1.9 (a) – (c) Time-resolved PEEM images at different delay time. (d) Time trace of the ROI labeled in (b). (e) Schematics of the GaAs band structure and experimental method. Reprinted with permission from AIP Publishing LLC.⁷⁶

region labeled in Figure 1.9(b). Through the two-exponential fitting, a 1.5-ps fast decay and 60-ps slow decay process are observed. Michael et al.⁷⁷ image the electron motion in a type-II 2D InSe/GaAs heterostructure. The photoelectrons will accumulate in InSe sample at the instant of photoexcitation, these nonequilibrium carriers will induce the spatial redistribution and internal electric field. Then these photoexcited electrons will start to move and eventually recombine in the sample, the whole processes described above are corresponding to the PEEM images in Figure 1.10.

Figure 1.10 Electron transport over time in the InSe/GaAs heterostructure showing the initial accumulation (red) and eventual recombination (blue). Reprinted with permission from Nature Publishing Group.⁷⁷

1.3 Nanoscale investigation on two-dimensional material

For the atomic-thin-layer 2D materials, their properties are very sensitive to structural defects, strain, electric fields, and molecular adsorbates. Depending on the targeted applications, these factors can be either detrimental or beneficial to 2D materials' properties. These effects can be utilized to control and manipulate the local optoelectronic functionality. Thus, the thorough understanding of the influence of these effects in 2D materials is key to realize unprecedented devices.

Structural defects is very serious in 2D materials, the internal QY of 2D materials is very low, the typical value of QY is in the range of 0.1% - 1% for MoS₂²¹ and about 5% - 20% for WS₂⁷⁸. Conventional optical microscopy is limited by diffraction limit, the resolution is a few hundred nanometers in the visible range, which is much lower than exciton diffusion length and inter-defect spacing. The nanoscale tip can be used as surface plasmonic antenna to amplify the light-matter interactions in tens nanometers. The surface plasmonic modulation technique combining with spectroscopy can provide spatial related information, the nanoscale tip-enhanced Raman scattering has been performed to correlate the local strain and structure to optoelectronic variation.⁷⁹⁻⁸⁰ Nano-optical probe with nanoscale gap at the apex of optical fiber can simultaneously excite sample and collect the luminescence. This technique can effectively

Figure 1.11 (a) and (b) The nano-optical image and spectral median of monolayer MoS₂. (c) The correlation between emission intensity and spectral median. Reprinted with permission from AIP Publishing LLC.⁸¹

eliminate the far-field background and retain the spectral information of the collected emission. The CVD-grown monolayer MoS₂ exhibits a peripheral 300 nm wide edge that is different from the interior region shown in Figure 1.11 (a) reported by Bao et al.⁸¹. Even within the interior region, the population ratio of exciton and trion components varies in nanoscale length, which indicates the spatial fluctuation of local carrier density plotted in Figure 1.11 (c). The quenching processes of other 2D materials are also investigated by the nano-optical imaging techniques,⁸²⁻⁸⁴ but the exact explanation for the observed phenomenon remains unknown.

These two techniques with tens-nanometer resolution have shown the importance and necessity of spatial analysis on 2D materials. However, the strong electric field induced by the tip-enhanced PL or Raman will modulate samples' intrinsic properties through the surface plasmonics. Moreover, the time-resolved information extracted by spatial scanning over whole sample is a time-consuming process. TR-PEEM as a tool combining high spatial and temporal resolution is very suitable to spatially investigate the ultrafast dynamics in 2D materials.

1.4 Reference

1. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306* (5696), 666-669.
2. Mayorov, A. S.; Gorbachev, R. V.; Morozov, S. V.; Britnell, L.; Jalil, R.; Ponomarenko, L. A.; Blake, P.; Novoselov, K. S.; Watanabe, K.; Taniguchi, T.; Geim, A. K., Micrometer-Scale Ballistic Transport in Encapsulated Graphene at Room Temperature. *Nano Letters* **2011**, *11* (6), 2396-2399.
3. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A., Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **2005**, *438* (7065), 197-200.

4. Balandin, A. A., Thermal properties of graphene and nanostructured carbon materials. *Nat. Mater.* **2011**, *10* (8), 569-581.
5. Bunch, J. S.; Verbridge, S. S.; Alden, J. S.; van der Zande, A. M.; Parpia, J. M.; Craighead, H. G.; McEuen, P. L., Impermeable Atomic Membranes from Graphene Sheets. *Nano Lett.* **2008**, *8* (8), 2458-2462.
6. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J., Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* **2008**, *321* (5887), 385-388.
7. Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P., Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **2005**, *438* (7065), 201-204.
8. Du, X.; Skachko, I.; Duerr, F.; Luican, A.; Andrei, E. Y., Fractional quantum Hall effect and insulating phase of Dirac electrons in graphene. *Nature* **2009**, *462* (7270), 192-195.
9. Dean, C. R.; Wang, L.; Maher, P.; Forsythe, C.; Ghahari, F.; Gao, Y.; Katoch, J.; Ishigami, M.; Moon, P.; Koshino, M.; Taniguchi, T.; Watanabe, K.; Shepard, K. L.; Hone, J.; Kim, P., Hofstadter's butterfly and the fractal quantum Hall effect in moire superlattices. *Nature* **2013**, *497* (7451), 598-602.
10. Lui, C. H.; Mak, K. F.; Shan, J.; Heinz, T. F., Ultrafast Photoluminescence from Graphene. *Phys. Rev. Lett.* **2010**, *105* (12), 127404.
11. Huang, L.; Hartland, G. V.; Chu, L.-Q.; Luxmi; Feenstra, R. M.; Lian, C.; Tahy, K.; Xing, H., Ultrafast Transient Absorption Microscopy Studies of Carrier Dynamics in Epitaxial Graphene. *Nano Lett.* **2010**, *10* (4), 1308-1313.
12. Strait, J. H.; Wang, H.; Shivaraman, S.; Shields, V.; Spencer, M.; Rana, F., Very slow cooling dynamics of photoexcited carriers in graphene observed by optical-pump terahertz-probe spectroscopy. *Nano Lett.* **2011**, *11* (11), 4902-6.
13. Winzer, T.; Knorr, A.; Malic, E., Carrier Multiplication in Graphene. *Nano Lett.* **2010**, *10* (12), 4839-4843.

14. Rana, F.; Strait, J. H.; Wang, H.; Manolatou, C., Ultrafast carrier recombination and generation rates for plasmon emission and absorption in graphene. *Phys. Rev. B* **2011**, *84* (4), 045437.
15. Rana, F.; George, P. A.; Strait, J. H.; Dawlaty, J.; Shivaraman, S.; Chandrashekhara, M.; Spencer, M. G., Carrier recombination and generation rates for intravalley and intervalley phonon scattering in graphene. *Phys. Rev. B* **2009**, *79* (11), 115447.
16. Tse, W.-K.; Das Sarma, S., Energy relaxation of hot Dirac fermions in graphene. *Phys. Rev. B* **2009**, *79* (23), 235406.
17. Bistritzer, R.; MacDonald, A. H., Electronic Cooling in Graphene. *Phys. Rev. Lett.* **2009**, *102* (20), 206410.
18. Giovannetti, G.; Khomyakov, P. A.; Brocks, G.; Kelly, P. J.; van den Brink, J., Substrate-induced band gap in graphene on hexagonal boron nitride: Ab initio density functional calculations. *Phys. Rev. B* **2007**, *76* (7), 073103.
19. Dean, C. R.; Young, A. F.; Meric, J.; Lee, C.; Wang, L.; Sorgenfrei, S.; Watanabe, K.; Taniguchi, T.; Kim, P.; Shepard, K. L.; Hone, J., Boron nitride substrates for high-quality graphene electronics. *Nat. Nanotechnol.* **2010**, *5* (10), 722-726.
20. Kang, J.; Tongay, S.; Zhou, J.; Li, J.; Wu, J., Band offsets and heterostructures of two-dimensional semiconductors. *Appl. Phys. Lett.* **2013**, *102* (1), 012111.
21. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105* (13), 136805.
22. Mak, K. F.; He, K.; Shan, J.; Heinz, T. F., Control of valley polarization in monolayer MoS₂ by optical helicity. *Nat. Nanotechnol.* **2012**, *7* (8), 494-498.
23. Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X., Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **2012**, *7* (8), 490-493.

24. Chernikov, A.; Berkelbach, T. C.; Hill, H. M.; Rigosi, A.; Li, Y.; Aslan, O. B.; Reichman, D. R.; Hybertsen, M. S.; Heinz, T. F., Exciton Binding Energy and Nonhydrogenic Rydberg Series in Monolayer WS₂. *Phys. Rev. Lett.* **2014**, *113* (7), 076802.
25. Mak, K. F.; He, K.; Lee, C.; Lee, G. H.; Hone, J.; Heinz, T. F.; Shan, J., Tightly bound trions in monolayer MoS₂. *Nat. Mater.* **2013**, *12* (3), 207-211.
26. You, Y.; Zhang, X.-X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F., Observation of biexcitons in monolayer WSe₂. *Nat. Phys.* **2015**, *11* (6), 477-481.
27. Yin, X.; Ye, Z.; Chenet, D. A.; Ye, Y.; O'Brien, K.; Hone, J. C.; Zhang, X., Edge Nonlinear Optics on a MoS₂ Atomic Monolayer. *Science* **2014**, *344* (6183), 488-490.
28. Pospischil, A.; Furchi, M. M.; Mueller, T., Solar-energy conversion and light emission in an atomic monolayer p-n diode. *Nat. Nanotechnol.* **2014**, *9* (4), 257-261.
29. Bernardi, M.; Palummo, M.; Grossman, J. C., Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials. *Nano Lett.* **2013**, *13* (8), 3664-3670.
30. Wang, H.; Yu, L.; Lee, Y.-H.; Shi, Y.; Hsu, A.; Chin, M. L.; Li, L.-J.; Dubey, M.; Kong, J.; Palacios, T., Integrated Circuits Based on Bilayer MoS₂ Transistors. *Nano Lett.* **2012**, *12* (9), 4674-4680.
31. Baugher, B. W. H.; Churchill, H. O. H.; Yang, Y.; Jarillo-Herrero, P., Optoelectronic devices based on electrically tunable p-n diodes in a monolayer dichalcogenide. *Nat. Nanotechnol.* **2014**, *9* (4), 262-267.
32. Yuan, H.; Bahramy, M. S.; Morimoto, K.; Wu, S.; Nomura, K.; Yang, B.-J.; Shimotani, H.; Suzuki, R.; Toh, M.; Kloc, C.; Xu, X.; Arita, R.; Nagaosa, N.; Iwasa, Y., Zeeman-type spin splitting controlled by an electric field. *Nat. Phys.* **2013**, *9* (9), 563-569.

33. Lee, S.; Zhong, Z., Nanoelectronic circuits based on two-dimensional atomic layer crystals. *Nanoscale* **2014**, 6 (22), 13283-13300.
34. Nie, Z.; Long, R.; Sun, L.; Huang, C.-C.; Zhang, J.; Xiong, Q.; Hewak, D. W.; Shen, Z.; Prezhdo, O. V.; Loh, Z.-H., Ultrafast Carrier Thermalization and Cooling Dynamics in Few-Layer MoS₂. *ACS Nano* **2014**, 8 (10), 10931-10940.
35. Ceballos, F.; Zhao, H., Ultrafast Laser Spectroscopy of Two-Dimensional Materials Beyond Graphene. *Adv. Funct. Mater.* **2016**, 27 (19), 1604509.
36. He, K.; Kumar, N.; Zhao, L.; Wang, Z.; Mak, K. F.; Zhao, H.; Shan, J., Tightly bound excitons in monolayer WSe₂. *Phys. Rev. Lett.* **2014**, 113 (2), 026803.
37. Ceballos, F.; Cui, Q.; Bellus, M. Z.; Zhao, H., Exciton formation in monolayer transition metal dichalcogenides. *Nanoscale* **2016**, 8 (22), 11681-8.
38. Thilagam, A., Exciton formation assisted by longitudinal optical phonons in monolayer transition metal dichalcogenides. *J. Appl. Phys.* **2016**, 120 (12), 124306.
39. Sun, D.; Rao, Y.; Reider, G. A.; Chen, G.; You, Y.; Brézin, L.; Harutyunyan, A. R.; Heinz, T. F., Observation of Rapid Exciton–Exciton Annihilation in Monolayer Molybdenum Disulfide. *Nano Lett.* **2014**, 14 (10), 5625-5629.
40. Yuan, L.; Huang, L., Exciton dynamics and annihilation in WS₂ 2D semiconductors. *Nanoscale* **2015**, 7 (16), 7402-7408.
41. Poellmann, C.; Steinleitner, P.; Leierseder, U.; Nagler, P.; Plechinger, G.; Porer, M.; Bratschitsch, R.; Schuller, C.; Korn, T.; Huber, R., Resonant internal quantum transitions and femtosecond radiative decay of excitons in monolayer WSe₂. *Nat. Mater.* **2015**, 14 (9), 889-893.
42. Kumar, N.; Cui, Q.; Ceballos, F.; He, D.; Wang, Y.; Zhao, H., Exciton-exciton annihilation in MoSe₂ monolayers. *Phys. Rev. B* **2014**, 89 (12), 125427.

43. Wang, G.; Palleau, E.; Amand, T.; Tongay, S.; Marie, X.; Urbaszek, B., Polarization and time-resolved photoluminescence spectroscopy of excitons in MoSe₂ monolayers. *Appl. Phys. Lett.* **2015**, *106* (11), 112101.
44. Moody, G.; Kavir Dass, C.; Hao, K.; Chen, C. H.; Li, L. J.; Singh, A.; Tran, K.; Clark, G.; Xu, X.; Berghauser, G.; Malic, E.; Knorr, A.; Li, X., Intrinsic homogeneous linewidth and broadening mechanisms of excitons in monolayer transition metal dichalcogenides. *Nat. Commun.* **2015**, *6*, 8315.
45. Wang, H.; Zhang, C.; Chan, W.; Manolatou, C.; Tiwari, S.; Rana, F., Radiative lifetimes of excitons and trions in monolayers of the metal dichalcogenide MoS₂. *Phys. Rev. B* **2016**, *93* (4), 045407.
46. Mai, C.; Barrette, A.; Yu, Y.; Semenov, Y. G.; Kim, K. W.; Cao, L.; Gundogdu, K., Many-Body Effects in Valleytronics: Direct Measurement of Valley Lifetimes in Single-Layer MoS₂. *Nano Lett.* **2014**, *14* (1), 202-206.
47. Zhu, C. R.; Zhang, K.; Glazov, M.; Urbaszek, B.; Amand, T.; Ji, Z. W.; Liu, B. L.; Marie, X., Exciton valley dynamics probed by Kerr rotation in WSe₂ monolayers. *Phys. Rev. B* **2014**, *90* (16), 161302.
48. Mai, C.; Semenov, Y. G.; Barrette, A.; Yu, Y.; Jin, Z.; Cao, L.; Kim, K. W.; Gundogdu, K., Exciton valley relaxation in a single layer of WS₂ measured by ultrafast spectroscopy. *Phys. Rev. B* **2014**, *90* (4), 041414.
49. Hsu, W. T.; Chen, Y. L.; Chen, C. H.; Liu, P. S.; Hou, T. H.; Li, L. J.; Chang, W. H., Optically initialized robust valley-polarized holes in monolayer WSe₂. *Nat. Commun.* **2015**, *6*, 8963.
50. Yang, L.; Sinitsyn, N. A.; Chen, W.; Yuan, J.; Zhang, J.; Lou, J.; Crooker, S. A., Long-lived nanosecond spin relaxation and spin coherence of electrons in monolayer MoS₂ and WS₂. *Nat. Phys.* **2015**, *11* (10), 830-834.

51. Hong, X.; Kim, J.; Shi, S.-F.; Zhang, Y.; Jin, C.; Sun, Y.; Tongay, S.; Wu, J.; Zhang, Y.; Wang, F., Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures. *Nat. Nanotechnol.* **2014**, *9* (9), 682-686.
52. Ceballos, F.; Bellus, M. Z.; Chiu, H.-Y.; Zhao, H., Ultrafast Charge Separation and Indirect Exciton Formation in a MoS₂–MoSe₂ van der Waals Heterostructure. *ACS Nano* **2014**, *8* (12), 12717-12724.
53. Bo, P.; Guannan, Y.; Xinfeng, L.; Bo, L.; Xiao, L.; Lei, B.; Longjiang, D.; Tze Chien, S.; Kian Ping, L., Ultrafast charge transfer in MoS₂ /WSe₂ p–n Heterojunction. *2D Mater.* **2016**, *3* (2), 025020.
54. Könenkamp, R.; Word, R. C.; Rempfer, G. F.; Dixon, T.; Almaraz, L.; Jones, T., 5.4nm spatial resolution in biological photoemission electron microscopy. *Ultramicroscopy* **2010**, *110* (7), 899-902.
55. Wang, Y.; Singh, S.; Kruse, P., Ordered nano-scale dimple pattern formation on a titanium alloy (Ti-6Al-4V). *AIP Adv.* **2012**, *2* (3), 032101.
56. Awada, C.; Popescu, T.; Douillard, L.; Charra, F.; Perron, A.; Yockell-Lelièvre, H.; Baudrion, A.-L.; Adam, P.-M.; Bachelot, R., Selective Excitation of Plasmon Resonances of Single Au Triangles by Polarization-Dependent Light Excitation. *J. Phys. Chem. C* **2012**, *116* (27), 14591-14598.
57. Jingquan, L.; Nils, W.; Adrian, W.; Soo Hoon, C.; Matthias, E.; Michael, M.; Matthias, F. K.; Mark, I. S.; Ferenc, K.; Ulf, K., Time of flight-photoemission electron microscope for ultrahigh spatiotemporal probing of nanoplasmonic optical fields. *J. Phys.: Condens. Matter* **2009**, *21* (31), 314005.
58. Koshikawa, T.; Shimizu, H.; Amakawa, R.; Ikuta, T.; Yasue, T.; Bauer, E., A new aberration correction method for photoemission electron microscopy by means of moving focus. *J. Phys.: Condens. Matter* **2005**, *17* (16), S1371.

59. Feng, J.; Forest, E.; MacDowell, A. A.; Marcus, M.; Padmore, H.; Raoux, S.; Robin, D.; Scholl, A.; Schlueter, R.; Schmid, P.; Stöhr, J.; Wan, W.; Wei, D. H.; Wu, Y., An x-ray photoemission electron microscope using an electron mirror aberration corrector for the study of complex materials. *J. Phys.: Condens. Matter* **2005**, *17* (16), S1339.
60. Rotermund, H. H., Real time imaging of catalytic reactions on surfaces: Past, present and future. *Surf. Sci.* **2009**, *603* (10), 1662-1670.
61. Kang, T.-H.; Ihm, K.; Hwang, C.-C.; Jeon, C.; Kim, K.-j.; Kim, J.-Y.; Lee, M.-K.; Shin, H.-J.; Kim, B.; Chung, S.; Park, C.-Y., Direct image observation of the initial forming of passive thin film on stainless steel surface by PEEM. *Appl. Surf. Sci.* **2003**, *212*, 630-635.
62. F., K.; O., K.; Y., Y.; M., T.; M., T.; T., S.-i.; K., S.-y., Femtosecond time-resolved photoemission electron microscopy for spatiotemporal imaging of photogenerated carrier dynamics in semiconductors. *Rev. Sci. Instrum.* **2014**, *85* (8), 083705.
63. Li, J.; Tan, A.; Moon, K. W.; Doran, A.; Marcus, M. A.; Young, A. T.; Arenholz, E.; Ma, S.; Yang, R. F.; Hwang, C.; Qiu, Z. Q., Tailoring the topology of an artificial magnetic skyrmion. *Nat. Commun.* **2014**, *5*, 4704.
64. Scholl, A.; Liberati, M.; Arenholz, E.; Ohldag, H.; Stöhr, J., Creation of an Antiferromagnetic Exchange Spring. *Phys. Rev. Lett.* **2004**, *92* (24), 247201.
65. Farhan, A.; Derlet, P. M.; Kleibert, A.; Balan, A.; Chopdekar, R. V.; Wyss, M.; Anghinolfi, L.; Nolting, F.; Heyderman, L. J., Exploring hyper-cubic energy landscapes in thermally active finite artificial spin-ice systems. *Nat. Phys.* **2013**, *9* (6), 375-382.
66. Stuckless, J. T.; Moskovits, M., Enhanced two-photon photoemission from coldly deposited silver films. *Phys. Rev. B* **1989**, *40* (14), 9997-9998.

67. Wiemann, C.; Bayer, D.; Rohmer, M.; Aeschlimann, M.; Bauer, M., Local 2PPE-yield enhancement in a defined periodic silver nanodisk array. *Surf. Sci.* **2007**, *601* (20), 4714-4721.
68. Banfi, G. P.; Ferrini, G.; Peloi, M.; Parmigiani, F., Anomalous photoemission from Ag(100) in the femtosecond regime. *Phys. Rev. B* **2003**, *67* (3), 035428.
69. Pfeiffer, W.; Kennerknecht, C.; Merschdorf, M., Electron dynamics in supported metal nanoparticles: relaxation and charge transfer studied by time-resolved photoemission. *Appl. Phys. A* **2004**, *78* (7), 1011-1028.
70. Gloskovskii, A.; Valdaitsev, D. A.; Cinchetti, M.; Nepijko, S. A.; Lange, J.; Aeschlimann, M.; Bauer, M.; Klimenkov, M.; Viduta, L. V.; Tomchuk, P. M.; Schönhense, G., Electron emission from films of Ag and Au nanoparticles excited by a femtosecond pump-probe laser. *Phys. Rev. B* **2008**, *77* (19), 195427.
71. Ferrini, G.; Banfi, F.; Giannetti, C.; Parmigiani, F., Non-linear electron photoemission from metals with ultrashort pulses. *Nucl. Instrum. Methods Phys. Res., Sect. A* **2009**, *601* (1), 123-131.
72. Melchior, P.; Bayer, D.; Schneider, C.; Fischer, A.; Rohmer, M.; Pfeiffer, W.; Aeschlimann, M., Optical near-field interference in the excitation of a bowtie nanoantenna. *Phys. Rev. B* **2011**, *83* (23), 235407.
73. Aeschlimann, M.; Bauer, M.; Bayer, D.; Brixner, T.; Garcia de Abajo, F. J.; Pfeiffer, W.; Rohmer, M.; Spindler, C.; Steeb, F., Adaptive subwavelength control of nano-optical fields. *Nature* **2007**, *446* (7133), 301-304.
74. Kubo, A.; Onda, K.; Petek, H.; Sun, Z.; Jung, Y. S.; Kim, H. K., Femtosecond Imaging of Surface Plasmon Dynamics in a Nanostructured Silver Film. *Nano Lett.* **2005**, *5* (6), 1123-1127.

75. Kubo, A.; Pontius, N.; Petek, H., Femtosecond Microscopy of Surface Plasmon Polariton Wave Packet Evolution at the Silver/Vacuum Interface. *Nano Lett.* **2007**, *7* (2), 470-475.
76. Fukumoto, K.; Yamada, Y.; Onda, K.; Koshihara, S.-y., Direct imaging of electron recombination and transport on a semiconductor surface by femtosecond time-resolved photoemission electron microscopy. *Appl. Phys. Lett.* **2014**, *104* (5), 053117.
77. Man, M. K. L.; Margiolakis, A.; Deckoff-Jones, S.; Harada, T.; Wong, E. L.; Krishna, M. B. M.; Madéo, J.; Winchester, A.; Lei, S.; Vajtai, R.; Ajayan, P. M.; Dani, K. M., Imaging the motion of electrons across semiconductor heterojunctions. *Nat. Nanotechnol.* **2017**, *12* (1), 36-40.
78. Vega-Mayoral, V.; Vella, D.; Borzda, T.; Prijatelj, M.; Tempira, I.; Pogna, E. A.; Dal Conte, S.; Topolovsek, P.; Vujicic, N.; Cerullo, G.; Mihailovic, D.; Gadermaier, C., Exciton and charge carrier dynamics in few-layer WS₂. *Nanoscale* **2016**, *8* (10), 5428-5434.
79. Park, K. D.; Khatib, O.; Kravtsov, V.; Clark, G.; Xu, X.; Raschke, M. B., Hybrid Tip-Enhanced Nanospectroscopy And Nanoimaging Of Monolayer WSe₂ With Local Strain Control. *Nano Lett.* **2016**, *16* (4), 2621-2627.
80. Su, W.; Kumar, N.; Mignuzzi, S.; Crain, J.; Roy, D., Nanoscale Mapping Of Excitonic Processes In Single-Layer MoS₂ Using Tip-Enhanced Photoluminescence Microscopy. *Nanoscale* **2016**, *8* (20), 10564-10569.
81. Bao, W.; Borys, N. J.; Ko, C.; Suh, J.; Fan, W.; Thron, A.; Zhang, Y.; Buyanin, A.; Zhang, J.; Cabrini, S.; Ashby, P. D.; Weber-Bargioni, A.; Tongay, S.; Aloni, S.; Ogletree, D. F.; Wu, J.; Salmeron, M. B.; Schuck, P. J., Visualizing nanoscale excitonic relaxation properties of disordered edges and grain boundaries in monolayer molybdenum disulfide. *Nat. Commun.* **2015**, *6*, 7993.

82. Lee, Y.; Park, S.; Kim, H.; Han, G. H.; Lee, Y. H.; Kim, J., Characterization of the structural defects in CVD-grown monolayered MoS₂ using near-field photoluminescence imaging. *Nanoscale* **2015**, 7 (28), 11909-11914.
83. Bao, W.; Melli, M.; Caselli, N.; Riboli, F.; Wiersma, D. S.; Staffaroni, M.; Choo, H.; Ogletree, D. F.; Aloni, S.; Bokor, J.; Cabrini, S.; Intonti, F.; Salmeron, M. B.; Yablonovitch, E.; Schuck, P. J.; Weber-Bargioni, A., Mapping Local Charge Recombination Heterogeneity by Multidimensional Nanospectroscopic Imaging. *Science* **2012**, 338 (6112), 1317-1321.
84. Ogletree, D. F.; Schuck, P. J.; Weber-Bargioni, A. F.; Borys, N. J.; Aloni, S.; Bao, W.; Barja, S.; Lee, J.; Melli, M.; Munechika, K.; Whitlam, S.; Wickenburg, S., Revealing Optical Properties of Reduced-Dimensionality Materials at Relevant Length Scales. *Adv. Mater.* **2015**, 27 (38), 5693-5719.

Chapter 2

Femtosecond Time-Resolved Photoemission Electron Microscopy for Imaging the Spatially Heterogeneous Carrier Relaxation Dynamics of Semiconductors

2.1 Introduction

The ultrafast carrier dynamics of solid-state materials have been investigated by a variety of methods, such as transient absorption,¹⁻³ time-resolved luminescence,⁴ and time-resolved photoemission spectroscopy.⁵ These investigations have uncovered various elementary carrier dynamics occurring on the sub-picosecond to picosecond timescales, such as carrier thermalization, cooling, and trapping.⁶⁻⁷ At the same time, developments in materials science have led to the emergence of technologically important materials, such as graphene, transition metal dichalcogenides, and perovskites, whose growths can lead to samples that exhibit significant spatial heterogeneity. Along these lines, nanomaterials prepared by colloidal synthesis, such as semiconductor nanocrystals and metallic nanoparticles, exhibit size dispersity and the ultrafast carrier dynamics of individual particles are therefore expected to be size-dependent. For such samples, traditional time-resolved measurements that rely on ensemble averaging overlook the heterogeneous response that arises from the size dispersion. The detailed investigations of these samples call for ultrafast microscopy techniques that either simultaneously resolve their dynamics in both space and time or are capable of performing time-resolved measurements at the single-nanoparticle level.

To date, several approaches to ultrafast microscopy have been proposed and demonstrated. The most widely used technique is optical pump-probe microscopy, which combines transient absorption with microscopy objective lenses to access ultrafast dynamics

with few-hundred nanometer spatial resolution, limited by the optical diffraction limit. This approach reveals carrier diffusion in real space in two-dimensional materials⁸⁻⁹ and perovskites.¹⁰⁻¹² As a result of the highly dispersive nature of the optical materials used in microscope objectives, the majority of the time-resolved optical microscopy studies reported to date^{2, 13-14} have a time resolution that is limited to >100 fs. The delivery of 10-fs ultrashort pulses to the sample can be achieved, however, with either careful dispersion pre-compensation up to fourth order¹⁵⁻¹⁶ or by using all-reflective objectives.¹² An additional complication introduced by optical pump-probe microscopy is the need to raster scan the sample in order to reconstruct its image over an extended area (tens of micrometers). Circumventing the optical diffraction limit, the recently demonstrated combination of superresolution microscopy with optical pump-probe spectroscopy provides access to ultrafast dynamics with resolutions of ~ 100 fs in time and ~ 100 nm in space.¹⁷ Another approach to ultrafast microscopy that provides tens of nanometer spatial resolution is to combine scanning near-field optical microscopy (SNOM) with the pump-probe technique.¹⁸⁻¹⁹ Time-resolved SNOM has been used, for example, to observe the beating of plasmon modes in a metal nanowire with 10-fs time resolution²⁰ and spatially resolve the insulator-to-metal phase transition of VO_2 microcrystals.²¹ Recently, scanning tunnelling microscopy combined with terahertz pump and probe pulses have resolved the low-frequency vibrational motion of single molecules with ~ 200 -fs time resolution.²² While these tip-based methods do not require any dispersive objectives and are therefore compatible with ultrashort laser pulses, the need to raster-scan the sample can lead to extended image acquisition times. Moreover, the introduction of a metal tip in the near-field vicinity of the sample could prevent the observation of field-free dynamics.²³

Photoemission electron microscopy (PEEM) is compatible with ultrashort pulses and offers a spatial resolution on the order of 10 nm while preserving a large field-of-view of tens of micrometers, hence circumventing some of the limitations of optical pump-probe

microscopy and tip-enhanced near-field microscopy. This technique relies on imaging the photoelectrons that are emitted from the sample when it is irradiated by light with photon energy exceeding the work function of the material. PEEM is highly suited for nanoscale imaging because its spatial resolution can reach a few nanometers after aberration correction in the magnifying electron optics.²⁴⁻²⁵ Moreover, PEEM is compatible with ultrashort laser pulses because it does not employ any dispersive microscope objective lenses; indeed, the combination of attosecond extreme ultraviolet pulses with PEEM has been proposed.²⁶ Following the pioneering work of Petek and coworkers that led to the first demonstration of femtosecond time-resolved PEEM (TR-PEEM),²⁷ TR-PEEM performed with interferometric scanning of the pump-probe time delay has been extensively used to visualize plasmon-polariton propagation and resolve plasmon dephasing dynamics in metal nanostructures.²⁸⁻³⁰ Aside from pump-probe, femtosecond four-wave mixing has also been combined with PEEM detection to spatially resolve plasmon coupling and dephasing dynamics.³¹ Recent extension of TR-PEEM to the study of semiconductors have elucidated carrier transport in bulk GaAs³² and atomically thin semiconductor heterojunctions³³ on the 1 – 10-ps timescale as well as the sub-picosecond defect-mediated carrier recombination dynamics of a GaAs surface.³⁴

To date, the majority of the TR-PEEM instruments employ a Ti:sapphire oscillator as the light source because the high repetition rate (~100 MHz) minimizes degradation of the spatial resolution due to space charge while preserving a high overall count rate. At the same time, the Ti:sapphire oscillator can furnish sub-10-fs pulses whose spectral coverage is well-suited for the study of plasmonic phenomena in metal nanostructures with exquisite time resolution.^{27, 29-30} Yb fiber laser systems, with their high repetition-rate and high-energy output, have recently emerged as an attractive alternative light source for ultrafast spectroscopy. Some drawbacks of such systems, however, include the narrow gain spectrum of the Yb(III) ion and the higher-order dispersion introduced by the fiber medium, both of which result in relatively

long pulse durations that typically exceed 100 fs. Fortunately, noncollinear optical parametric amplifiers (NOPA) pumped by fiber lasers provide access to ultrashort pulses with durations as short as <15 fs; such a fiber laser-based NOPA light source was recently applied to TR-PEEM microscopy.³⁵

Here, we report the implementation of TR-PEEM microscopy by interfacing a megahertz repetition-rate femtosecond Yb fiber laser to a PEEM microscope. As an alternative to using a NOPA, we employ spectral broadening in a gas-filled hollow-core fibre followed by chirped mirror compression and harmonic generation to produce laser pulses of ~50-fs duration or shorter for TR-PEEM microscopy. The resultant setup furnishes photon energies of 1.20 eV, 2.41 eV, 3.61 eV, 4.81 eV, and 6.02 eV, from which various combinations can be selected for pump and probe, yielding typical time resolutions of ~50 – 60 fs FWHM. When interfaced to a PEEM microscope, a spatial resolution of ~80 nm is achieved (16 – 84% criterion). We process the data to obtain the spatial distribution of time constants for the carrier relaxation dynamics. In analogy to the information provided by fluorescence lifetime imaging microscopy, these decay constant maps provide a means of visualizing the spatially heterogeneous ultrafast carrier dynamics of the sample. As an example, we resolve, in both space and time, the sub-100-fs relaxation dynamics that follow the 3.61-eV excitation of silicon at the Γ valley.

2.2 Experimental details

2.2.1 Overview of the experimental apparatus

The schematic illustration of the TR-PEEM instrument is shown in Figure 2.1. The experimental apparatus consists of two main parts: the optical setup for ultrashort pulse generation and the photoemission electron microscope. An Yb-doped fiber laser (Amplitude Systemes) is used as the primary light source. The laser output is 30 W at a maximum repetition rate of 2 MHz. In our experiments, we employ a repetition rate of 0.6 MHz, hence giving a pulse energy of 50 μ J. The output wavelength is 1030 nm and the pulse duration is 320 fs

Figure 2.1 Schematic illustration of the TR-PEEM setup, including ultrashort pulse generation and a PEEM mounted in a high-vacuum chamber.

FWHM. The photoemission electron microscope (Focus GmbH) is equipped with an integrated sample stage and is housed in a vacuum chamber. A 300 L/s turbomolecular pump (Leybold MAGW300iP) yields a base pressure of 3×10^{-8} mbar in the vacuum chamber. In the following, we provide a detailed description of the various components of the experimental apparatus.

2.2.2 Laser pulse spectral broadening and compression

The output spectrum from the Yb-doped fiber laser is centered at 1030 nm and has a bandwidth of 9 nm [Figure 2.2(a)]. Single-shot autocorrelation reveals a pulse width of 320 fs (FWHM) for the laser output [blue line in Figure 2.2(b)]. Such a pulse duration is not optimal for resolving the elementary carrier dynamics that occur on the sub-picosecond timescale. One possible approach to pulse compression is to employ spectral broadening in a noble gas-filled

Figure 2.2 (a) The spectrum of laser before and after gas-filled hollow-core fiber (HCF) gas cell. (b) Autocorrelation traces of the laser pulse before and after optimal dispersion compensation. (c) The transform-limited pulse shape of the HCF-output spectrum depicted in panel (a). (d) Autocorrelation traces of the output laser pulse with different number of chirped-mirror reflections.

hollow-core fibre followed by temporal compression by using either chirped mirrors³⁶ or prism pairs.³⁷

In the experimental setup, the fiber laser output is focused into a 1-meter-long, 200- μm inner diameter hollow-core fibre filled with Xe gas. The gas cell that houses the hollow-core fiber is surrounded by a cooling water jacket to dissipate the heat that is generated by the 30-W input beam. Efficient self-phase modulation is achieved due to the high nonlinear refractive index n_2 of Xe.³⁸⁻³⁹ The optimal Xe gas pressure is 5.6 bar, for which an overall transmission of 54% is obtained. The spectrum obtained after dispersion compensation is shown in Figure 2.2(a). The spectrum spans 999 – 1064 nm at the –10 dB level and its corresponding transform-limited pulse shape is shown in Figure 2.2(c). Without any dispersion compensation, the pulse width of the output of the hollow-core fiber is ~600 fs FWHM [Figure 2.2(d)]. Optimization of the dispersion compensation is performed by varying the number of reflections of chirped mirrors (Ultrafast Innovations GmbH, -1000 fs^2 per reflection). From Figure 2.2(d), it is evident that the shortest pulse is obtained between -2000 fs^2 and -3000 fs^2 . By varying the insertion of a pair of large-angle fused silica wedges (30° apex angle) into the laser beam, we obtain a minimum autocorrelation width of 77 fs when the total dispersion compensation is $-2.54 \times 10^3 \text{ fs}^2$ [Figure 2.2(b)]. From the computed deconvolution factor of 1.41, we obtain a pulse duration of 55 fs FWHM, $1.2\times$ larger than the transform-limited pulse width. We note that all the autocorrelation traces exhibit obvious satellite features at approximately ± 500 fs, which originate from residual high-order dispersion present in the laser output. Because of their low peak intensity, these satellite pulses do not undergo self-phase modulation and therefore remain even after the spectral broadening and pulse compression.

2.2.3 Harmonic generation and their pulse compression

The central wavelength of the compressed laser pulse is 1030 nm, which corresponds to a photon energy of 1.20 eV. This photon energy is lower than the typical work functions and

Figure 2.3 The schematic of harmonics generation of (a) SHG and THG, (b) 4HG, and (c) 5HG. GDC represents group delay compensation.

band gaps of solid materials, and therefore cannot be used as the pump or probe pulse in TR-PEEM experiments. We employ nonlinear frequency upconversion in beta barium borate (β -BBO) crystals to produce the second (2ω) to the fifth (5ω) harmonic of the 1030-nm fundamental light (Figure 2.3). Third- and fifth-harmonic generation involve sum-frequency generation, which require the use of alpha barium borate (α -BBO) crystals to compensate for the group delay of the individual input frequency components. All the nonlinear frequency conversions occur at the focus of a 50-cm focal-length lens, which is characterized by a confocal parameter of 4 cm. The 2ω beam is produced in a 0.3-mm thick, Type I β -BBO crystal cut at 23.4° [Figure 2.3(a)]. Third-harmonic generation (THG) is accomplished by passing the second harmonic and the residual fundamental beam through a 0.3-mm-thick α -BBO crystal ($\theta = 47.4^\circ$) to compensate for the group velocity mismatch introduced by the first β -BBO

crystal, before sending both beams into a 0.05-mm-thick, Type II β -BBO ($\theta = 40.0^\circ$) to produce the third harmonic by sum-frequency generation [Figure 2.3(a)]. As an alternative to THG, fourth-harmonic generation (4HG) is achieved by positioning a second Type I SHG crystal (0.04-mm-thick, $\theta = 50.0^\circ$) after the first SHG crystal [Figure 2.3(b)]. Finally, to produce the fifth harmonic, a 0.5-mm-thick α -BBO ($\theta = 53.4^\circ$) is positioned between the first SHG crystal and the 4HG crystal. Subsequent mixing of the fourth harmonic with the residual fundamental beam in a 0.03-mm-thick Type I BBO crystal ($\theta = 54.2^\circ$) yields 5ω [Figure 2.3(c)]. In this configuration, the α -BBO crystal positioned after the SHG crystal introduces a suitable delay to the second harmonic, hence pre-compensating for the group velocity mismatch between the fourth harmonic and the fundamental beam in the 4HG crystal.

Dielectric mirrors are used to separate the laser beams of different wavelengths, with the exception of the 5ω output, which is separated from the other harmonics and the fundamental frequency by employing a fused silica prism. The output spectra of the various harmonics are shown in Figures 2.4(a) – 2.4(d) and their corresponding Fourier transform-limited temporal profiles are shown in Figures 2.4(e) – 2.4(h). The second- to fourth-harmonic beams are recompressed by using fused silica prism pairs; temporal compression of the 5ω output was not attempted because it is not routinely used in the pump-probe experiments. Temporal characterization of the 2ω beam is done via second-harmonic intensity autocorrelation, whereas the durations of the 3ω and 4ω beams are obtained via cross-correlation based on difference-frequency mixing of these beams with a compressed 2ω beam. The measured time traces are shown in Figures 2.4(i) – 2.4(k). Assuming that the 2ω beam has a Gaussian temporal profile, the autocorrelation width $\tau_{2\omega}^{\text{ac}}$ yields the pulse width $\tau_{2\omega}$ of the 2ω beam via the relation $\tau_{2\omega} = \tau_{2\omega}^{\text{ac}}/\sqrt{2}$. Similarly, by assuming a Gaussian temporal profile for all the input and output beams, the width of the cross-correlation signal $\tau_{N\omega}^{\text{xc}}$ obtained from

Figure 2.4 The spectrum of (a) SHG, (b) THG, (c) 4HG, and (d) 5HG, along with their corresponding transform-limited pulse shapes, shown in panels (e) – (h), respectively. The correlation time traces of the (i) SHG, (j) THG, and (k) 4HG beams after dispersion compensation.

difference-frequency mixing between the N th harmonic ($N = 3$ or 4) and the 2ω beam is given by $\tau_{N\omega}^{\text{xc}} = \sqrt{\tau_{2\omega}^2 + \tau_{N\omega}^2}$, where $\tau_{N\omega}$ is the FWHM of the N th harmonic. The retrieved FWHM pulse widths of the 2ω , 3ω , and 4ω beams are 46 fs, 40 fs, and 28 fs, respectively. The inter-prism separations correspond to dispersion compensation values of -4390 fs^2 , -4590 fs^2 , and -11570 fs^2 for the 2ω , 3ω , and 4ω beams, respectively. Finally, the average powers of the 2ω , 3ω , and 4ω beams that can be delivered to the sample target for experiments are 2 W, 0.2 W, and 20 mW, respectively.

2.2.4 Spatial resolution of the PEEM microscope

Multiple factors limit the achievable spatial resolution of a PEEM microscope. These include, for example, the existence of residual aberration in the electrostatic lens system,⁴⁰ chromatic aberration caused by the finite spectral bandwidth of the light source, space charge induced by

the use of lasers of ultrashort pulse durations and/or high energy fluences,⁴¹ electron scattering due to residual gases in the vacuum chamber,⁴² and the presence of mechanical vibrations.⁴³ The PEEM microscope that is used in our setup is capable of furnishing a lateral resolution of 26 nm, according to the factory acceptance test performed by irradiating a lithographically prepared silver grid on silicon with a mercury arc lamp.

In our laboratory, we employ the same silver grid sample to determine the spatial resolution of the PEEM microscope under our operating conditions. The sample is illuminated with either the 3ω or the 4ω beam. Long focal-length lenses yield beam diameters ($1/e^2$) of 1.16 mm and 1.02 mm for the 3ω and the 4ω beams at the sample position, respectively. These large beam diameters, being larger than the maximum field of view (FoV) of the PEEM (900 μm), provide a relatively uniform illumination across the sample; note that images acquired at the highest magnification has a FoV of only 30 μm . Furthermore, because the angle of incidence on the sample is 65° , the projection of the laser beam on the sample yields a focal spot size that is $2.4\times$ larger in the tangential direction. Irradiation of the test sample with the 3ω beam at a fluence of $1.3 \mu\text{J}/\text{cm}^2$ yields the PEEM image as shown in Figure 2.5(a). This image is obtained with an exposure time of 10 s. A lineout of the image taken perpendicular to an edge [see the white line in Figure 2.5(a)] is fit to an error function [Figure 2.5(b)], which arises from the convolution of a step function with the instrument response. The latter originates from the work function contrast of the lithographically prepared sample. According to the 16 – 84% criterion, the fit to an error function yields a lateral resolution of 77 nm under 3ω irradiation. Note that the work function of silver (4.5 eV)⁴⁴ requires more than one 3ω photon (3.61-eV photon energy) to eject an electron from the sample. This is confirmed by fluence dependence measurements, which show that the photoemission count rate increases quadratically with the fluence of the 3ω beam [Figure 2.5(c)], in agreement with the expected two-photon nature of the photoemission process. On the other hand, the 4.81-eV photon energy

Figure 2.5 (a) PEEM image of a silver grid on Si substrate illuminated by 3ω light. (b) The corresponding line profile of the white line drawn in panel (a), fit to an error function to extract the spatial resolution. The horizontal dashed lines indicate the 16 – 84 % criteria and the vertical dashed lines show the projection onto the x-axis, giving a spatial resolution of 77 nm. (c) The photoemission signal plotted as a function of fluence shows a quadratic dependence. (d) – (f) correspond to the results obtained with 4ω light. In this case, the resolution is 86 nm and a linear power dependence is observed.

of the 4ω beam is higher than the work function of Ag. The PEEM image of the lithographically

prepared silver sample, taken with 8 nJ/cm^2 of 4ω light and an exposure time of 10 s, is shown in Figure 2.5(d). The line profile of the white mark in Figure 2.5(d) is shown in Figure 2.5(e), from which a resolution of 86 nm is obtained. The PEEM signal collected under 4ω irradiation shows a linear fluence dependence [Figure 2.5(f)]. Comparing Figures 2.5(a) and 2.5(d), it is evident that the morphology of the sample that is reflected in the PEEM image is dependent on the illumination wavelength, as reported previously.⁴⁵⁻⁴⁶

2.2.5 Data acquisition and processing

The operating parameters of PEEM microscope are set via either the remote-control panel or the ProNanoESCA software provided by Focus GmbH. PEEM images are acquired by using the ProNanoESCA software. Time-resolved PEEM measurements employ a home-built LabVIEW program, which interfaces the 14-bit camera of the PEEM (PCO Pixelfly) to a computer-controlled motorized translation stage (Physik Instrumente M-511.DD). The translation stage is positioned in the path of either the fundamental or the second-harmonic beam to introduce a variable optical delay between the pump and probe beams. The minimum step size of $0.10 \text{ }\mu\text{m}$ for the translation stage corresponds to a minimum time delay of 0.67 fs.

The LabVIEW program automatically records a series of PEEM images at various time delays, following the sequence of time points i that is provided as an input to the program. In order to correct for long-term power drifts, acquisition alternates between an image that is recorded at a given time point i (Img_i) with a reference image that is recorded at 100-ps time delay ($\text{Img}_i_{100\text{ps}}$). The typical exposure time used in the pump-probe measurements is 10 s. The dark count rate of each pixel of the camera is about 40 counts/s; the image of the dark counts (Img_{dark}) is recorded for use in subsequent background correction.

Due to the effect of laser heating of the substrate, the PEEM images exhibit a slow drift of $\sim 1 \text{ }\mu\text{m/hour}$. Given that each TR-PEEM measurement typically takes 1 – 2 hours, it is

essential to correct for this drift. This correction is implemented by using the built-in MATLAB function “imregtform” to determine the vector that characterizes the drift between two consecutive reference images (Img_i_100ps and Img_i+1_100ps). To negate the image drift, the opposite drift vector is applied to the PEEM image and reference image at time point $i+1$ by another built-in MATLAB function “imwarp” to yield Img_i_corr and Img_i_100ps_corr , respectively. After the drift correction, Img_i_100ps_corr and Img_dark are both subtracted from Img_i_corr to yield the PEEM image at time point i . The sequence of images collected as a function of time delay is saved as a three-dimensional matrix for further analysis.

A home-built MATLAB program is used to extract information regarding the photoemission count as a function of time delay for a given region of interest (ROI). The ROI can take on different shapes, e.g., line, circle and polygon. Furthermore, the spatial distribution of parameters, e.g., time constants and decay amplitudes, that characterize the ultrafast dynamics can be retrieved by automatically fitting the time trace obtained for each pixel to a convolution of the expected sample response, e.g., a monoexponential decay, with the instrument response function. Each fitting parameter is stored as a two-dimensional matrix. The two-dimensional matrix of the time constants corresponds to a spatial map of time constants, analogous to images obtained from fluorescence lifetime imaging microscopy (FLIM).⁴⁷⁻⁴⁸ To increase the signal-to-noise ratio, the program can set different bin sizes prior to generating the time constant map. In this case, a square selector comprising $N \times N$ pixels moves through the entire image, one pixel at a time, and sums all the counts in the square selector to form a new image.

2.3 Mapping the time constant of electron relaxation in silicon

To demonstrate the capability of the TR-PEEM apparatus, we employ it to investigate the ultrafast electronic relaxation dynamics of bulk silicon. The experiment utilizes 3.61-eV pulses

Figure 2.6 (a) PEEM image taken at -3 ps time delay. (b) Histogram of the photoemission counts of the PEEM image shown in panel (a). (c) Spatially integrated photoemission counts as a function of time delay for the PEEM image shown in panel (a) and its fit to an exponential decay convolved with a Gaussian instrument response function (red line). (d) The band structure of Si, with blue vertical arrows indicating the electronic transition induced by 3ω light. The black dashed arrows denote electronic relaxation from the Γ valley. The red dashed line shows the vacuum level and the green shaded region shows the 2ω probe window.

as pump and 2.41-eV pulses as probe, and a p-doped silicon wafer oriented along the $\langle 100 \rangle$ direction as the sample. The fluences of the pump and probe pulses are 9.4 and $3.6 \mu\text{J}/\text{cm}^2$, respectively. The PEEM image collected at -3000 -fs time delay [Figure 2.6(a)] suggests that the surface of the silicon is not entirely homogeneous over the entire $12 \times 12\text{-}\mu\text{m}^2$ ROI. The heterogeneity can be quantified by examining the histogram of photoemission counts for the ROI, which reveals a normalized root-mean-square deviation of 18.1% [Figure 2.6(b)]. The

pump-probe time trace obtained from plotting the photoemission counts integrated over the entire ROI as a function of time delay is shown in Figure 2.6(c). The time trace, equivalent to one that is obtained from a pump-probe two-photon photoemission (2PPE) measurement, can be fit to a convolution of the instrument response function with a monoexponential decay that is characterized by a time constant of 69 ± 2 fs.

The observed sub-100-fs dynamics can be explained with the aid of the band structure of silicon [Figure 2.6(d)].⁴⁹ The red dashed line indicates the vacuum level of silicon. The green shaded region denotes the probe window, dictated by the requirement to conserve lateral momentum in photoemission, within which an electron can be ejected by the 2.41-eV probe pulse. The 3.61-eV pump pulse promotes electrons across the 3.4-eV direct band gap of silicon at the Γ point [see the blue arrows in Figure 2.6(d)], where the valence band maximum is located. (Note that even though photoexcitation by the 3.61-eV pump also occurs in other regions of k space, such as the L valley, those regions lie beyond the probe window and the TR-PEEM measurement does not report on the ultrafast electron dynamics of those regions.) Following this initial excitation, the electrons in the Γ valley of the conduction band undergo ultrafast relaxation to either the L and/or the X valleys [see the black dashed arrows in Figure 2.6(d)]. In doing so, the electrons leave the probe window, resulting in the decay of the photoemission signal. Given that the probe window is located primarily around the Γ valley, our results suggest that the photoexcited electrons leave the Γ valley on the 70-fs timescale. This measurement, which allows the direct determination of the lifetime of electrons at the Γ valley, should be contrasted with previous studies of the ultrafast electron dynamics of silicon,⁵⁰⁻⁵³ which focused primarily on the dynamics that follow photoexcitation of the phonon-assisted indirect transition with 1.6-eV pulses. A 2PPE measurement revealed that the electrons at the L valley undergo intervalley scattering to the X valley with a time constant of 180 fs.⁵⁴ The 70-fs lifetime of the Γ valley electrons determined herein is considerably shorter,

Figure 2.7 (a) Time trace of single pixel randomly selected in the ROI of Si. (b) Time constant mapping of each pixel in the ROI. (c) Histograms of the time constant mapping (b).

in accord with the higher density of acceptor electronic states that participate in intervalley scattering.

Finally, the time traces acquired at individual pixels can be fit to obtain an image of time constants, in analogy to FLIM.^{47,48} A representative time trace is shown in Fig. 2.7(a) and the time constant map obtained for the ROI shown in Fig. 2.6(a) is plotted in Fig. 2.7(b). Such a map, along with its corresponding histogram [Fig. 2.7(c)], provides a direct visualization of the degree of spatial heterogeneity of the ultrafast carrier dynamics. Statistical analysis of the histogram of decay constants yields an average time constant of 71 fs and a standard deviation

of 9 fs, corresponding to a normalized root-mean-square deviation of 13%. Based on the decay amplitude A_i and the decay constant τ_i obtained for each pixel, the amplitude-weighted average time constant is given by the expression $\langle\tau\rangle = \sum A_i\tau_i / \sum A_i$ and the amplitude-weighted standard deviation is given by $\sigma = \sqrt{\langle\tau^2\rangle - \langle\tau\rangle^2}$, where $\langle\tau^2\rangle = \sum A_i\tau_i^2 / \sum A_i$. For the silicon sample investigated herein, we find $\langle\tau\rangle = 71$ fs and $\sigma = 11$ fs. These values are in good agreement with the spatially-integrated time constant of 69 ± 2 fs, hence showing that the time-constant map can recover the spatially integrated measurement results. Further experiments that correlate the various types of defects and their densities with the observed relaxation time constants can potentially shed light on the origin of the observed heterogeneous electronic relaxation dynamics.

2.4 Conclusion and outlook

The experimental setup of a TR-PEEM microscope that uses an Yb-doped fiber laser as the light source is described. Through a series of hollow-core fiber spectral broadening, chirped mirror pulse compression, harmonic generation, and prism pulse compression stages, we have produced a set of optical harmonics spanning $2\omega - 5\omega$ that can be delivered to the sample with cross-correlation widths as narrow as <60 fs FWHM. Along with the 0.6-MHz repetition rate of the light source and the currently achievable spatial resolution of <80 nm (16 – 84% criterion), the TR-PEEM instrument is well-suited to image the ultrafast, sub-100-fs carrier dynamics of nanoscale materials. Furthermore, the high pulse energies available from fiber laser systems make it possible to image the ultrafast carrier dynamics of semiconductors, hence going beyond the conventional application of TR-PEEM to the investigation of plasmonics in metal nanostructures. In the present work, we employ the TR-PEEM setup to visualize the spatially heterogeneous relaxation dynamics of electrons excited into the Γ valley of the silicon conduction band. Analysis of the photoemission count as a function of time delay for each pixel yields a 2D map of the sub-100-fs decay time constants, in analogy with fluorescence lifetime

imaging microscopy. Spatially integrated measurements yield a relaxation time constant of 69 ± 2 fs, whereas spatially resolved measurements performed over the same area reveal the spatial distribution of decay constants, from which an average time constant of 71 fs and a standard deviation of 9 fs are computed. The exquisite spatial and temporal resolution offered by TR-PEEM and the ability to construct lifetime maps from the TR-PEEM data makes it well-suited for investigating the ultrafast carrier dynamics of either emergent materials that exhibit significant spatial heterogeneity or single nanoparticles that are embedded in a heterogeneous environment. Moreover, with recent advances in the development of femtosecond fiber laser sources, resulting in the availability of femtosecond laser pulses approaching the 100-MHz, 10- μ J level,⁵⁵ and even few-cycle pulses that can be used to produce soft X-rays via high-order harmonic generation,⁵⁶ we envision that the combination of fiber lasers with energy- and momentum-resolved PEEM will pave way for the widespread application of TR-PEEM microscopy to investigate the spatially heterogeneous carrier dynamics of materials.

2. 5 References

1. Rana, F.; Strait, J. H.; Wang, H.; Manolatu, C., Ultrafast carrier recombination and generation rates for plasmon emission and absorption in graphene. *Phys. Rev. B* **2011**, *84* (4), 045437.
2. Huang, L.; Hartland, G. V.; Chu, L.-Q.; Luxmi; Feenstra, R. M.; Lian, C.; Tahy, K.; Xing, H., Ultrafast Transient Absorption Microscopy Studies of Carrier Dynamics in Epitaxial Graphene. *Nano Lett.* **2010**, *10* (4), 1308-1313.
3. Nie, Z.; Long, R.; Sun, L.; Huang, C.-C.; Zhang, J.; Xiong, Q.; Hewak, D. W.; Shen, Z.; Prezhdo, O. V.; Loh, Z.-H., Ultrafast Carrier Thermalization and Cooling Dynamics in Few-Layer MoS₂. *ACS Nano* **2014**, *8* (10), 10931-10940.
4. Lui, C. H.; Mak, K. F.; Shan, J.; Heinz, T. F., Ultrafast Photoluminescence from Graphene. *Phys. Rev. Lett.* **2010**, *105* (12), 127404.

5. Haight, R.; Bokor, J.; Stark, J.; Storz, R. H.; Freeman, R. R.; Bucksbaum, P. H., Picosecond Time-Resolved Photoemission Study of the InP(110) Surface. *Phys. Rev. Lett.* **1985**, *54* (12), 1302-1305.
6. Shah, J., *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*. 2 ed.; Springer-Verlag Berlin Heidelberg: 1999; p 522.
7. Sundaram, S. K.; Mazur, E., Inducing and probing non-thermal transitions in semiconductors using femtosecond laser pulses. *Nat. Mater.* **2002**, *1*, 217.
8. Aeschlimann, M.; Bauer, M.; Bayer, D.; Brixner, T.; Cunovic, S.; Dimler, F.; Fischer, A.; Pfeiffer, W.; Rohmer, M.; Schneider, C.; Steeb, F.; Strüber, C.; Voronine, D. V., Spatiotemporal control of nanooptical excitations. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107* (12), 5329-5333.
9. Ruzicka, B. A.; Wang, S.; Werake, L. K.; Weintrub, B.; Loh, K. P.; Zhao, H., Hot carrier diffusion in graphene. *Phys. Rev. B* **2010**, *82* (19), 195414.
10. Guo, Z.; Manser, J. S.; Wan, Y.; Kamat, P. V.; Huang, L., Spatial and temporal imaging of long-range charge transport in perovskite thin films by ultrafast microscopy. *Nat. Commun.* **2015**, *6*, 7471.
11. Guo, Z.; Wan, Y.; Yang, M.; Snaider, J.; Zhu, K.; Huang, L., Long-range hot-carrier transport in hybrid perovskites visualized by ultrafast microscopy. *Science* **2017**, *356* (6333), 59-62.
12. Nah, S.; Spokoyny, B.; Stoumpos, C.; Soe, C. M. M.; Kanatzidis, M.; Harel, E., Spatially segregated free-carrier and exciton populations in individual lead halide perovskite grains. *Nat. Photonics* **2017**, *11*, 285.
13. Hong, X.; Kim, J.; Shi, S.-F.; Zhang, Y.; Jin, C.; Sun, Y.; Tongay, S.; Wu, J.; Zhang, Y.; Wang, F., Ultrafast charge transfer in atomically thin MoS₂/WS₂ heterostructures. *Nat. Nanotechnol.* **2014**, *9* (9), 682-686.

14. Ceballos, F.; Bellus, M. Z.; Chiu, H.-Y.; Zhao, H., Ultrafast Charge Separation and Indirect Exciton Formation in a MoS₂–MoSe₂ van der Waals Heterostructure. *ACS Nano* **2014**, 8 (12), 12717-12724.
15. Jasapara, J.; Rudolph, W., Characterization of sub-10-fs pulse focusing with high-numerical-aperture microscope objectives. *Opt. Lett.* **1999**, 24 (11), 777-779.
16. Müller; Squier; Wolleschensky; Simon; Brakenhoff, Dispersion pre-compensation of 15 femtosecond optical pulses for high-numerical-aperture objectives. *J. Microsc.* **1998**, 191 (2), 141-150.
17. Massaro, E. S.; Hill, A. H.; Grumstrup, E. M., Super-Resolution Structured Pump–Probe Microscopy. *ACS Photonics* **2016**, 3 (4), 501-506.
18. Bao, W.; Melli, M.; Caselli, N.; Riboli, F.; Wiersma, D. S.; Staffaroni, M.; Choo, H.; Ogletree, D. F.; Aloni, S.; Bokor, J.; Cabrini, S.; Intonti, F.; Salmeron, M. B.; Yablonovitch, E.; Schuck, P. J.; Weber-Bargioni, A., Mapping Local Charge Recombination Heterogeneity by Multidimensional Nanospectroscopic Imaging. *Science* **2012**, 338 (6112), 1317-1321.
19. Tizei, L. H.; Lin, Y. C.; Mukai, M.; Sawada, H.; Lu, A. Y.; Li, L. J.; Kimoto, K.; Suenaga, K., Exciton mapping at subwavelength scales in two-dimensional materials. *Phys Rev Lett* **2015**, 114 (10), 107601.
20. Nishiyama, Y.; Imura, K.; Okamoto, H., Observation of Plasmon Wave Packet Motions via Femtosecond Time-Resolved Near-Field Imaging Techniques. *Nano Lett.* **2015**, 15 (11), 7657-7665.
21. Dönges, S. A.; Khatib, O.; O’Callahan, B. T.; Atkin, J. M.; Park, J. H.; Cobden, D.; Raschke, M. B., Ultrafast Nanoimaging of the Photoinduced Phase Transition Dynamics in VO₂. *Nano Lett.* **2016**, 16 (5), 3029-3035.

22. Cocker, T. L.; Peller, D.; Yu, P.; Repp, J.; Huber, R., Tracking the ultrafast motion of a single molecule by femtosecond orbital imaging. *Nature* **2016**, *539* (7628), 263-267.
23. Xu, X. G.; Raschke, M. B., Near-Field Infrared Vibrational Dynamics and Tip-Enhanced Decoherence. *Nano Lett.* **2013**, *13* (4), 1588-1595.
24. Konenkamp, R.; Word, R. C.; Rempfer, G. F.; Dixon, T.; Almaraz, L.; Jones, T., 5.4nm spatial resolution in biological photoemission electron microscopy. *Ultramicroscopy* **2010**, *110* (7), 899-902.
25. Feng, J.; Forest, E.; MacDowell, A. A.; Marcus, M.; Padmore, H.; Raoux, S.; Robin, D.; Scholl, A.; Schlueter, R.; Schmid, P.; Stöhr, J.; Wan, W.; Wei, D. H.; Wu, Y., An x-ray photoemission electron microscope using an electron mirror aberration corrector for the study of complex materials. *J. Phys.: Condens. Matter* **2005**, *17* (16), S1339.
26. Stockman, M. I.; Kling, M. F.; Kleineberg, U.; Krausz, F., Attosecond nanoplasmonic-field microscope. *Nat. Photonics* **2007**, *1* (9), 539-544.
27. Kubo, A.; Onda, K.; Petek, H.; Sun, Z.; Jung, Y. S.; Kim, H. K., Femtosecond Imaging of Surface Plasmon Dynamics in a Nanostructured Silver Film. *Nano Lett.* **2005**, *5* (6), 1123-1127.
28. Kubo, A.; Pontius, N.; Petek, H., Femtosecond Microscopy of Surface Plasmon Polariton Wave Packet Evolution at the Silver/Vacuum Interface. *Nano Lett.* **2007**, *7* (2), 470-475.
29. Gong, Y.; Joly, A. G.; Hu, D.; El-Khoury, P. Z.; Hess, W. P., Ultrafast Imaging of Surface Plasmons Propagating on a Gold Surface. *Nano Lett.* **2015**, *15* (5), 3472-3478.
30. Marsell, E.; Losquin, A.; Svärd, R.; Miranda, M.; Guo, C.; Harth, A.; Lorek, E.; Mauritsson, J.; Arnold, C. L.; Xu, H.; L'Huillier, A.; Mikkelsen, A., Nanoscale Imaging of Local Few-Femtosecond Near-Field Dynamics within a Single Plasmonic Nanoantenna. *Nano Lett.* **2015**, *15* (10), 6601-6608.

31. Aeschlimann, M.; Brixner, T.; Fischer, A.; Kramer, C.; Melchior, P.; Pfeiffer, W.; Schneider, C.; Strüber, C.; Tuchscherer, P.; Voronine, D., Coherent Two-Dimensional Nanoscopy. *Science* **2011**, 333 (6050), 1723-1726.
32. Keiki, F.; Yuki, Y.; Shin-ya, K.; Ken, O., Lifetimes of photogenerated electrons on a GaAs surface affected by nanostructural defects. *Appl. Phys. Express* **2015**, 8 (10), 101201.
33. Man, M. K. L.; Margiolakis, A.; Deckoff-Jones, S.; Harada, T.; Wong, E. L.; Krishna, M. B. M.; Madéo, J.; Winchester, A.; Lei, S.; Vajtai, R.; Ajayan, P. M.; Dani, K. M., Imaging the motion of electrons across semiconductor heterojunctions. *Nat. Nanotechnol.* **2017**, 12 (1), 36-40.
34. Fukumoto, K.; Onda, K.; Yamada, Y.; Matsuki, T.; Mukuta, T.; Tanaka, S.; Koshihara, S. Y., Femtosecond time-resolved photoemission electron microscopy for spatiotemporal imaging of photogenerated carrier dynamics in semiconductors. *Rev. Sci. Instrum.* **2014**, 85 (8), 083705.
35. Dabrowski, M.; Dai, Y.; Argondizzo, A.; Zou, Q.; Cui, X.; Petek, H., Multiphoton Photoemission Microscopy of High-Order Plasmonic Resonances at the Ag/Vacuum and Ag/Si Interfaces of Epitaxial Silver Nanowires. *ACS Photonics* **2016**, 3 (9), 1704-1713.
36. Nisoli, M.; De Silvestri, S.; Svelto, O.; Szipöcs, R.; Ferencz, K.; Spielmann, C.; Sartania, S.; Krausz, F., Compression of high-energy laser pulses below 5 fs. *Opt. Lett.* **1997**, 22 (8), 522-524.
37. Nisoli, M.; Silvestri, S. D.; Svelto, O., Generation of high energy 10 fs pulses by a new pulse compression technique. *Appl. Phys. Lett.* **1996**, 68 (20), 2793-2795.

38. Couairon, A.; Chakraborty, H. S.; Gaarde, M. B., From single-cycle self-compressed filaments to isolated attosecond pulses in noble gases. *Phys. Rev. A* **2008**, *77* (5), 053814.
39. Borzsonyi, A.; Heiner, Z.; Kovacs, A. P.; Kalashnikov, M. P.; Osvay, K., Measurement of pressure dependent nonlinear refractive index of inert gases. *Opt. Express* **2010**, *18* (25), 25847-25854.
40. Fitzgerald, J. P. S.; Word, R. C.; Könenkamp, R., Theoretical estimates of spherical and chromatic aberration in photoemission electron microscopy. *Ultramicroscopy* **2016**, *160* (Supplement C), 252-255.
41. Buckanie, N. M.; Göhre, J.; Zhou, P.; Linde, D. v. d.; Hoegen, M. H.-V.; Heringdorf, F. J. M. z., Space charge effects in photoemission electron microscopy using amplified femtosecond laser pulses. *J. Phys.: Condens. Matter* **2009**, *21* (31), 314003.
42. Bauer, E., A brief history of PEEM. *J. Electron. Spectrosc. Relat. Phenom.* **2012**, *185* (10), 314-322.
43. Rempfer, G. F.; Skoczylas, W. P.; Hayes Griffith, O., Design and performance of a high-resolution photoelectron microscope. *Ultramicroscopy* **1991**, *36* (1), 196-221.
44. Dweydari, A. W.; Mee, C. H. B., Work function measurements on (100) and (110) surfaces of silver. *Phys. Status Solidi A* **1975**, *27* (1), 223-230.
45. Lin, J.; Weber, N.; Wirth, A.; Chew, S. H.; Escher, M.; Merkel, M.; Kling, M. F.; Stockman, M. I.; Krausz, F.; Kleineberg, U., Time of flight-photoemission electron microscope for ultrahigh spatiotemporal probing of nanoplasmonic optical fields. *J. Phys.: Condens. Matter* **2009**, *21* (31), 314005.
46. Gloskovskii, A.; Valdaitsev, D. A.; Cinchetti, M.; Nepijko, S. A.; Lange, J.; Aeschlimann, M.; Bauer, M.; Klimenkov, M.; Viduta, L. V.; Tomchuk, P. M.;

- Schönhense, G., Electron emission from films of Ag and Au nanoparticles excited by a femtosecond pump-probe laser. *Phys. Rev. B* **2008**, 77 (19), 195427.
47. Bastiaens, P. I. H.; Squire, A., Fluorescence lifetime imaging microscopy: spatial resolution of biochemical processes in the cell. *Trends Cell Biol.* **1999**, 9 (2), 48-52.
 48. Suhling, K.; French, P. M. W.; Phillips, D., Time-resolved fluorescence microscopy. *Photochem. Photobiol. Sci.* **2005**, 4 (1), 13-22.
 49. Phillips, J. C., Band Structure of Silicon, Germanium, and Related Semiconductors. *Phys. Rev.* **1962**, 125 (6), 1931-1936.
 50. Rowe, M. W.; Liu, H.; Williams, G. P.; Williams, R. T., Picosecond photoelectron spectroscopy of excited states at Si(111) 3x3 R30 degrees-B, Si(111) 7x7, Si(100) 2x1, and laser-annealed Si(111) 1x1 surfaces. *Phys. Rev. B* **1993**, 47 (4), 2048-2064.
 51. Goldman, J. R.; Prybyla, J. A., Ultrafast dynamics of laser-excited electron distributions in silicon. *Phys. Rev. Lett.* **1994**, 72 (9), 1364-1367.
 52. Jeong, S.; Bokor, J., Ultrafast carrier dynamics near the Si(100) 2x1 surface. *Phys. Rev. B* **1999**, 59 (7), 4943-4951.
 53. Sabbah, A. J.; Riffe, D. M., Femtosecond pump-probe reflectivity study of silicon carrier dynamics. *Phys. Rev. B* **2002**, 66 (16), 165217.
 54. Ichibayashi, T.; Tanimura, K., Ultrafast Carrier Relaxation in Si Studied by Time-Resolved Two-Photon Photoemission Spectroscopy: Intravalley Scattering and Energy Relaxation of Hot Electrons. *Phys. Rev. Lett.* **2009**, 102 (8), 087403.
 55. Eidam, T.; Hanf, S.; Seise, E.; Andersen, T. V.; Gabler, T.; Wirth, C.; Schreiber, T.; Limpert, J.; Tünnermann, A., Femtosecond fiber CPA system emitting 830 W average output power. *Opt. Lett.* **2010**, 35 (2), 94-96.
 56. Rothhardt, J.; Hädrich, S.; Klenke, A.; Demmler, S.; Hoffmann, A.; Gotschall, T.; Eidam, T.; Krebs, M.; Limpert, J.; Tünnermann, A., 53W average power few-cycle

fiber laser system generating soft x rays up to the water window. *Opt. Lett.* **2014**, 39 (17), 5224-5227.

Chapter 3

Unraveling Spatially Heterogeneous Ultrafast Carrier Dynamics of Single-Layer WSe₂ by Femtosecond Time-Resolved Photoemission Electron Microscopy

3.1 Introduction

Transition metal dichalcogenides (TMDs) exhibit exotic properties such as the emergence of a direct bandgap in monolayer samples,¹⁻² valley polarization,³ and the existence of a large range of bandgaps associated with the extensive library of TMDs.⁴ TMDs have found applications in light harvesting,⁵ sensitive photodetectors,⁶ field-effect transistors⁷ and light-emitting diodes.⁸ However, the quantum efficiencies of TMDs-based light detector and emitter are poor despite its direct bandgap.^{6, 9-10} The low efficiency is attributed to the nonradiative recombination and/or trapping of electrons and holes that are mediated by defects in TMDs.¹¹⁻¹² While chemical vapor deposition (CVD) can furnish wafer-scale samples,¹³ CVD-grown samples have a higher density of defects compared with those obtained from the mechanical exfoliation.¹⁴

Ultrafast spectroscopy provides a route to understanding the fundamental properties of semiconductors by elucidating their ultrafast carrier dynamics.¹⁵ In the case of TMDs, ultrafast spectroscopy measurements reveal dynamics such as the formation of excitons,¹⁶⁻¹⁷ biexcitons¹⁸ and trions.¹⁹ Studies performed with sub-10-fs pulses reveal sub-20-fs carrier thermalization and sub-picosecond carrier cooling.²⁰ Ultrafast dynamics of band-selective carrier relaxation,²¹ valley depolarization,²²⁻²³ defect-assisted carrier trapping,²⁴⁻²⁶ and exciton-exciton annihilation^{12,27-28} have also been reported. Optically initialized valley-polarized holes²⁹ and exciton valley coherence³⁰ in monolayer WSe₂ are discovered.

The majority of time-resolved studies of TMD materials reported to date employ ensemble-averaged measurements. By combining pump-probe spectroscopy with optical microscopy, different regions of interest within a TMD sample can be selectively probed in time-resolved experiments.³¹⁻³² The time-resolved optical microscopy investigation of exciton dynamics of an exfoliated MoS₂ sample with regions of different layer numbers reveals that intravalley relaxation rates can be enhanced 40-fold in a monolayer sample relative to a thick sample.²⁵ However time-resolved optical microscopy has its drawbacks. First, the spatial resolution of conventional optical microscopy is limited by diffraction to several hundred nanometers. Second, the higher-order dispersion introduced by high numerical-aperture microscope objectives limits the typical achievable temporal resolution to ~ 100 fs. Third, producing a differential transmission map of the sample requires raster scanning. Imaging techniques such as tip-enhanced microscopy³³ and scanning near-field optical microscopy (SNOM)³⁴ offer few tens-of-nanometer spatial resolution, although their pump-probe implementation remains to be applied to TMD materials.

Here, we employ femtosecond time-resolved photoemission electron microscopy (TR-PEEM) to investigate the sub-picosecond to picosecond carrier dynamics of monolayer WSe₂. In TR-PEEM, a pump pulse of photon energy $\hbar\omega_{\text{pu}}$ injects electrons into the conduction band, following which electrons that lie within the probe window are ejected into the continuum³⁵⁻³⁸ after a variable time delay. The ejected photoelectrons pass through several electrostatic lenses to form a magnified image of the sample surface at the two-dimensional array detector. Recording the PEEM image as function of pump-probe time delay yields the time evolution of the population of conduction band electrons. TR-PEEM has recently been applied to image carrier transport and recombination occurring on the 1 – 10-ps timescale in both bulk³⁹ and atomically-thin semiconductors.⁴⁰ In the present work, we focus on imaging the sub-picosecond to picosecond carrier dynamics of TMDs with 80-nm spatial- and 60-fs time

resolution. Spatially integrated analysis of single flakes yields a timescale of 0.12 ± 0.01 ps for carrier cooling via intervalley scattering and a Auger rate constant of 0.075 ± 0.001 cm²/s for exciton-exciton annihilation. Fitting the time traces obtained at different positions within a single flake yields a spatial map of the ultrafast carrier relaxation time constants. The pronounced spatial heterogeneities of these time constant maps suggest the need to go beyond ensemble-averaged measurements in the study of the ultrafast carrier dynamics of TMDs.

3.2 Results and discussion

Figure 3.1 shows the static PEEM image of monolayer WSe₂ flakes that is acquired by irradiating the sample with 40-fs, 3.61-eV UV laser pulses. Most of these WSe₂ flakes have a triangular shape, characteristic of TMDs, with large intensity contrast ($\sim 5.4:1$) to the background from the SiO₂/Si substrate. Each flake is labelled a number for the convenience of further discussion. A magnified image of a single WSe₂ flake (No.1 flake) is shown in Figure 3.2(a) exhibiting pronounced spatial heterogeneity. A heterogeneity on the surface that can also be observed in fluorescence images (Figure 3.3). Previous research on strain⁴¹ and structure heterogeneity in atomic layers MoS₂ suggests that it could be induced by the same reason.⁴² Photoelectron spectroscopy of WSe₂ yields a range of 4.5 – 5.5 eV for the ionization potential,

Figure 3.1 Static PEEM image of monolayer WSe₂ sample illuminated by 343-nm light. The flakes discussed in this work are labelled with numbers.

Figure 3.2 (a) The enlarged static PEEM image of No.1 monolayer WSe₂ flake illuminated by 343-nm light. (b) The photoemission signal plotted as a function of fluence showing a quadratic dependence. (c) The band structure of monolayer WSe₂ and 343-nm two-photon probe windows with (yellow region) and without (green region) momentum conservation. The vertical blue lines exhibit the electron transition from conduction band to valance band.

dependent on the type of substrate and the layer number.⁴³ The absorption of a single 3.61-eV photon is therefore insufficient to eject an electron from the valence band maximum of the WSe₂ sample. Fluence dependence measurements show that the photoemission signal scales quadratically with fluence (Figure 3.2b), suggesting the formation of the static PEEM image via two-photon photoionization. Taking into account the conservation of lateral momentum in photoionization, Figure 3.2c shows the region of the band structure that is accessible by the two-photon photoionization probe.

To investigate the ultrafast dynamics of the monolayer WSe₂ flakes, we employ 46-fs, 2.41-eV visible laser pulses for single-photon photoexcitation of electrons from the valance band to the conduction band. Following a variable time delay, 40-fs, 3.61-eV UV pulses eject electrons from the conduction band to yield the photoemission signal. To determine the photon order during the pump-probe experiment, further fluence dependent measurements are performed. The signal counts of the time traces at 0 fs are plotted in Figure 3.4(a) as a function of the 343-nm light fluence. The probe fluences increase from 2.5 to 16 μJ/cm² while the pump

Figure 3.3 Optical and fluorescence image of WSe₂ flakes. (a), (c), and (e) are optical images taken with different magnification. (b), (d), and (f) are corresponding fluorescence images of the optical images in left panel.

fluence remains $6.5 \mu\text{J}/\text{cm}^2$. From the quadratic fitting, it reveals a two-photon detection process for 343-nm light during the pump-probe experiment. However, the fluence measurement on 515-nm light displays a linear relation when the pump fluences increase from 10.5 to 21.1 $\mu\text{J}/\text{cm}^2$ can be observed in Figure 3.4(b).

Figure 3.4 (a) The signal counts at 0 fs time delay of the WSe₂ time trace plotted as a function of the pump fluence of 343-nm laser pulse. The red line is the quadratic fitting line. (b) The relationship between the pump fluences of 515-nm light and their corresponding signal counts at 0 fs. The signal points show a linear dependence (red line).

TR-PEEM resolves the photoemission signal in both space and time, hence furnishing the temporal evolution of the photoemission signal for different spatial regions of the WSe₂ flake. To compare the ultrafast dynamics observed herein with those obtained from ensemble-averaged measurements, however, we first plot the spatially-integrated photoemission signal as a function of time delay. Figure 3.5(a) shows the time traces obtained at pump fluences of

Figure 3.5 (a) The spatially-integrated time traces of the single flake at different pump fluence. (b) The time constants of a fast decay at negative times (τ_-), fast decay (τ_1) and slow decay (τ_2) at positive times plotted as a function of pump fluence.

11 to 21 $\mu\text{J}/\text{cm}^2$; the probe fluence in all cases remains fixed at 2 $\mu\text{J}/\text{cm}^2$. The time traces can be fit to a double-sided exponential decay convolved with the instrument response function; the TR-PEEM signal at negative time undergoes a single exponential decay, whereas the signal at positive time exhibits a biphasic decay. The resultant time constants obtained from the fits to the data collected at different pump excitation fluences are summarized in Figure 3.5(b). The decay dynamics observed at negative times is characterized by a time constant τ_- of ~ 73 fs, independent of pump fluence. In the positive time regime, the ~ 0.1 -ps decay component τ_1 is relatively independent of pump fluence, whereas the picosecond decay component τ_2 decreases monotonically from 2.61 ps to 2.29 ps with increasing pump fluence.

The biphasic decay dynamics observed at positive time delays can be explained as follows. The 2.41-eV photon energy of the pump pulse spans the band gap of monolayer WSe₂ and lies beyond its A and B exciton transition energies of 1.6 and 2.1 eV, respectively.⁴⁴⁻⁴⁵ Photoexcitation therefore initially furnishes a non-thermal distribution of free carriers. Carrier thermalization occurs within the 60-fs instrument response of our experimental setup to yield a hot Fermi-Dirac distribution.²⁰ Through the involvement of intervalley electron-phonon scattering of carriers from the K valley to the adjacent Q valley, carrier thermalization generates a significant electron population in the Q valley, within the window of the 2×3.61 eV probe process as shown in Figure 3.2(c), hence giving rise to the large photoemission signal at time zero. The 0.1-ps decay component (τ_1) is attributed to carrier cooling via intervalley electron-phonon scattering of electrons from the Q valley, which lies within the probe window, to the K valley, where the minimum of the conduction band resides. The observed fluence dependence for τ_2 , on the other hand, suggests that the picosecond decay originates from exciton-exciton annihilation. These assignments are supported by previous time-resolved two-photon photoemission (2PPE) and optical pump-probe studies of TMDs, which reveal sub-picosecond and picosecond timescales for electron cooling and exciton-exciton annihilation,

respectively. Based on previous report,⁴⁵ the exciton density can be calculated at each pump fluence. The signal counts at 500 fs time delay is plotted as a function of exciton density showing a linear relation in Figure 3.6(a). The dynamic of exciton can be expressed as

$$\frac{dN}{dt} = \frac{1}{\tau}N - \gamma N^2 \quad 2.1$$

where N , γ and τ are exciton density, exciton-exciton annihilation rate and electron radiative lifetime. The electron radiative lifetimes varying from tens to hundreds ps are reported from the recombination of electrons and holes,⁴⁶⁻⁴⁷ and much longer than the time range that we focus here. So we can ignore the contribution of τ , the equation (1) can be rewritten as

$$\frac{N_0}{N(t)} - 1 = \gamma N_0 t \quad 2.2$$

where N_0 is the initial exciton density. Through the extracted linear signal-exciton relation in Figure 3.6(a), the quantities $N/N_0 - 1$ at different pump fluences are shown in Figure 3.6(b) and exhibiting a clear straight tendency at all pump fluences from 500 fs to 5 ps. A further global

Figure 3.6 (a) The relation between exciton density and the signal counts at 500 fs showing a linear dependence (red line). (b) The quantity $N/N_0 - 1$ plotted as a function of time delay. The red lines are the linear global fits from 500 fs to 5 ps.

analysis of the time traces over the range of 0.5 – 5 ps for multiple pump fluences yields an exciton-exciton annihilation rate of $0.075 \pm 0.001 \text{ cm}^2/\text{s}$, similar to the exciton-exciton annihilation rates reported previously for MoS_2 ($0.043 \pm 0.011 \text{ cm}^2/\text{s}$)¹² and WS_2 ($0.089 \pm 0.001 \text{ cm}^2/\text{s}$).²⁸ Compared to these earlier studies, which probe the dynamics of excitons confined at the K valley, however, it is important to note that the exciton-exciton annihilation dynamics most likely involves intervalley excitons, i.e., excitons with non-zero center-of-mass momenta. The deviation in the present study arises from the finite probe window of the two-photon ionization probe and the insufficient excess energy of the hole to populate regions beyond the K valley in the carrier thermalization process. In our case, the intervalley exciton comprises an electron in the Q valley bound to a hole in the K valley. The formation of such intervalley excitons in monolayer WSe_2 was recently inferred from time-resolved mid-infrared probing of intraband electron dynamics.¹¹ There, it was found that intervalley excitons, being optically dark, could undergo rapid nonradiative relaxation via Auger-type exciton-exciton annihilation. In fact, the reported annihilation rate of $0.065 \pm 0.005 \text{ cm}^2/\text{s}$ is in excellent agreement with the results of our measurements.

At negative time delays, the sequence in which the visible and UV pulses are incident on the sample is reversed compared to positive time delays. The TR-PEEM signal at negative time delays therefore reports on the dynamics that are induced by 3.61-eV UV excitation and probed by the 2.41-eV visible pulse. As can be seen from the band structure of monolayer WSe_2 , high-energy UV photoexcitation can occur across multiple regions in the Brillouin zone [see dashed lines in Figure 3.2(c)], including in the vicinity of the Γ point, which resides in the probe window for 2.41-eV, single-photon ionization [see hatched area in Figure 3.2(c)]. The 73-fs decay therefore characterizes the timescale for the scattering of electrons away from the Γ point, out of the probe window, to lower-energy regions of the conduction band. The large

Figure 3.7 The time constant mapping of the fast component (a) and slow component (b) and their corresponding histogram (c) and (d).

density of electronic states that exists in high-energy region of the conduction band facilitates the observed ultrafast electron relaxation dynamics.

Analyzing the time traces acquired at the individual pixels of the TR-PEEM image yields information on the spatially resolved ultrafast dynamics of single-layer WSe₂. The resultant spatial distributions of the time constants, analogous to lifetime maps obtained from fluorescence lifetime imaging microscopy, are shown in Figures 3.7(a) and 3.7(b) for the fast and slow decay components extracted from the time traces at positive time delays, respectively. These lifetime maps are obtained with a pump (probe) fluence of 10 $\mu\text{J}/\text{cm}^2$ (2 $\mu\text{J}/\text{cm}^2$). The corresponding histograms of the fast- and slow-decay time constants are shown in Figures 3.7(c) and 3.7(d), respectively. The spatial heterogeneity of the observed ultrafast dynamics is evident

from the lifetime maps and their associated histograms. For the fast (slow) decay component, we obtain an average time constant of 108 fs (2.90 ps) and a standard deviation of 43 fs (1.28 ps). The amplitude-weighted fast- and slow-decay time constants of 107 fs and 2.67 ps, respectively, are in good agreement with those furnished by the spatially integrated analysis (123 ± 6 fs and 2.61 ± 0.17 ps for the fast and slow decay, respectively).

The most striking features of the lifetime maps are the smaller τ_1 and larger τ_2 lifetimes that appear along the edges of the flakes. Because the WSe₂ sample used in the present work were transferred onto the SiO₂/Si substrate, a procedure that is known to release the tensile strain that accumulates during CVD growth,^{42, 48} we eliminate strain fields as a source of heterogeneity. Instead, we ascribe these observations to the presence of increased disorder along the peripheral edges of the WSe₂ flake. Structural disorder is known to yield new zone-edge phonon modes in the Raman spectra⁴⁹⁻⁵⁰ of MoS₂ and WSe₂ as well as increased linewidths for the A_{1g} and E_{2g}^1 phonon peaks due to phonon confinement. In addition, ab initio simulations reveal the broadening of the phonon density of states due to structural disorder.⁵¹ The appearance of disorder-induced phonon modes accelerates electron-phonon scattering rates, thereby facilitating electronic relaxation and resulting in smaller τ_1 values along the edges of the WSe₂ flake. The larger τ_2 lifetimes along the edges can also be explained in terms of slower exciton diffusion⁵² resulting from increased disorder, which in turn leads to longer timescales for exciton-exciton annihilation.

The observed differences in the ultrafast carrier dynamics between the peripheral edge and the interior of the WSe₂ flake are consistent with previous results obtained from hyperspectral imaging of TMDs by near-field photoluminescence (PL) microscopy.³³⁻³⁴ Those studies reveal that the edges of TMD flakes exhibit significantly different spectral characteristics from the interior of the flakes. In the case of MoS₂ and WSe₂, the length scales

Figure 3.8 The time constants (τ_-) at negative times of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.35 is shown as a red line.

of these spectrally distinct edges are found to be 300 nm and 30 – 80 nm, respectively. The edges are characterized by reduced PL intensities and the appearance of a high-energy tail in the PL spectra, both of which are signatures of a disordered, inhomogeneously broadened ensemble of emitters, such as those encountered in organic conjugated polymers⁵³ and quantum dot solids.⁵⁴

Aside from the pronounced differences in electron lifetimes between the edge and interior of the WSe₂ flake, it is noteworthy that the interior of the flake itself also exhibits noticeably heterogeneous carrier dynamics. Previous studies by hyperspectral PL imaging⁵⁵ and Raman microscopy⁵⁶ have attributed the observed heterogeneity to the presence of substrate-induced charge puddles, originally uncovered for graphene.⁵⁷ Charge puddles form as a result of the inhomogeneous doping of the substrate or charge transfer from impurities that are trapped between the WSe₂ monolayer and the SiO₂/Si substrate. In addition, a combination of atomic force microscopy and scanning tunneling spectroscopy have elucidated the existence of bandgap puddles,⁵⁸ which arise from nanoscale distortions of the TMD flake induced by the ~1-nm surface roughness of the SiO₂/Si substrate. The spatially heterogeneous carrier density and band gap of WSe₂ modulates electron-phonon coupling strengths and exciton transport.

The former explains the heterogeneity observed in the electron cooling dynamics (τ_1), whereas the latter yields a distribution of exciton-exciton annihilation times (τ_2). Future experiments that correlate hyperspectral PL and Raman microscopy with TR-PEEM microscopy will enable us to ascertain the effect of charge puddles on the ultrafast carrier dynamics.

Finally, we address the spatial heterogeneity observed in the case of the static PEEM image (Figure 3.2(a)). The PEEM image is collected under two-photon UV irradiation conditions. Because the 3.61-eV photon accesses the conduction band at the Γ point, the two-photon ionization process proceeds via an intermediate electronic state, i.e., the two-photon ionization is resonantly enhanced. If the lifetime of the electron at the Γ point is longer than the 40-fs temporal duration of the UV pulse, the absorption of an additional photon by the intermediate state would result in ionization of the sample. On the other hand, if the intermediate state undergoes ultrafast relaxation to a region of the conduction band that lies beyond the probe window, ionization would be suppressed. The ionization yield, and hence the PEEM signal, is therefore expected to scale with the lifetime of the electron at the Γ point. This lifetime is reflected in the dynamics observed at negative time delays (see above), when the UV pulse precedes the visible pulse. Figure 3.8 shows that the photoemission signal is indeed correlated with the lifetime τ_- , with a Pearson correlation coefficient of 0.35.

3.3 Analysis on flakes

Same analyses are applied on other flakes shown in Figure 3.1, and these results are listed in following Figures 3.9, 3.10, 3.11 and 3.12 for No.2, No.3, No.4 and No.5 flake, respectively. A enlarged static PEEM image of each selected flake is shown in Figures 3.9 – 3.11(a), heterogeneities can be clearly observed on all these flakes. The pump fluence dependent measurement on each flake is plotted in Figures 3.9 – 3.11(b), and the obtained fitting parameters of a fast decay at negative times (τ_-), fast decay (τ_1) and slow decay (τ_2) at positive

times are drawn in Figures 3.9 – 3.11 (c). For the fast decays (τ_-) and (τ_2), the time constants remain at ~ 75 fs and ~ 0.1 ps as the pump fluence increasing in all flakes. The decreasing tendencies from ~ 2.7 ps to ~ 2.2 ps can be seen, which are consistent with our analysis on No.1 flake. At the same time, the Auger rates of exciton-exciton annihilation are calculated on the pump fluence dependent time traces of each flake. Based on the linear relation between exciton density and signal counts at 500 fs [Figures 3.9 – 3.11 (d)], Auger rates can be extracted from the linear global fitting of the quantity $N/N_0 - 1$, each flake gives a constant of 0.080 ± 0.001 , 0.086 ± 0.001 , 0.087 ± 0.001 and 0.071 ± 0.001 cm^2/s for No.2, No.3, No.4 and No.5, respectively. Spatially studies are performed on each flake at the pump fluence of $10 \mu\text{J}/\text{cm}^2$ and probe fluence of $2 \mu\text{J}/\text{cm}^2$. Time constant mapping of fast decay and slow at positive times are demonstrated Figures 3.9 – 3.11 (e) and (f), the histograms of their corresponding time constants are plotted in Figures 3.9 – 3.11 (g) and (h). To better view these parameters, a table (Table 3.1) are used to compare the time constants obtained by different methods. The statistical analysis on spatially resolved time constant mapping exhibits a larger slow decay time constant. When we compare the time constants on different flakes, consistencies by

Table 3.1 Time constants for different flakes

		No.1	No.2	No.3	No.4	No.5
Fast decay (fs)	SI	123 ± 6	124 ± 6	122 ± 6	120 ± 6	131 ± 7
	SR	108 ± 43	104 ± 46	102 ± 43	103 ± 43	106 ± 45
	AW	107	102	104	102	109
Slow decay (ps)	SI	2.61 ± 0.17	2.58 ± 0.16	2.48 ± 0.15	2.59 ± 0.16	2.62 ± 0.19
	SR	2.90 ± 1.28	2.85 ± 1.38	2.97 ± 1.45	2.92 ± 1.33	3.03 ± 1.53
	AW	2.67	2.53	2.67	2.65	2.69

SI: Spatially integrated analysis. **SR:** Statistical analysis of spatially resolved mapping. **AW:**

Amplitude-weighted time constant.

Figure 3.9 (a) Static PEEM image collected with 3.61-eV illumination. (b) Plots of the photoemission signal integrated over the entire flake as a function of time delay at different pump fluences. The colored lines represent fits to a biexponential decay convolved with a Gaussian instrument response function. (c) Time constants as a function of pump fluences. (d) Plots of $[N_0/N_{ex}(t)] - 1$ as a function of time delay for different initial exciton densities N_0 . The red lines are linear global fits over the time delay range of 0.5 – 5 ps. (e) Lifetime map of the fast decay constant. (f) Lifetime map of the slow decay constant. (g) Distribution of the fast decay constant. (h) Histogram of the slow decay constant. (i) Time constants at negative times (τ_-) of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.29 is shown observed as a red line.

different processing ways can be seen. It means the same ultrafast process occurring on

Figure 3.10 (a) Static PEEM image collected with 3.61-eV illumination. (b) Plots of the photoemission signal integrated over the entire flake as a function of time delay at different pump fluences. The colored lines represent fits to a biexponential decay convolved with a Gaussian instrument response function. (c) Time constants as a function of pump fluences. (d) Plots of $[N_0/N_{ex}(t)] - 1$ as a function of time delay for different initial exciton densities N_0 . The red lines are linear global fits over the time delay range of 0.5 – 5 ps. (e) Lifetime map of the fast decay constant. (f) Lifetime map of the slow decay constant. (g) Distribution of the fast decay constant. (h) Histogram of the slow decay constant. (i) Time constants at negative times (τ_-) of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.28 is shown observed as a red line.

different flakes of the CVD grown sample as reported by optical pump-probe experiments.

Figure 3.11 (a) Static PEEM image collected with 3.61-eV illumination. (b) Plots of the photoemission signal integrated over the entire flake as a function of time delay at different pump fluences. The colored lines represent fits to a biexponential decay convolved with a Gaussian instrument response function. (c) Time constants as a function of pump fluences. (d) Plots of $[N_0/N_{ex}(t)] - 1$ as a function of time delay for different initial exciton densities N_0 . The red lines are linear global fits over the time delay range of 0.5 – 5 ps. (e) Lifetime map of the fast decay constant. (f) Lifetime map of the slow decay constant. (g) Distribution of the fast decay constant. (h) Histogram of the slow decay constant. (i) Time constants at negative times (τ_-) of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.29 is shown observed as a red line.

However, the time constant mapping results [Figures 3.9 – 3.11 (e) and (f)] providing by our

Figure 3.12 (a) Static PEEM image collected with 3.61-eV illumination. (b) Plots of the photoemission signal integrated over the entire flake as a function of time delay at different pump fluences. The colored lines represent fits to a biexponential decay convolved with a Gaussian instrument response function. (c) Time constants as a function of pump fluences. (d) Plots of $[N_0/N_{ex}(t)] - 1$ as a function of time delay for different initial exciton densities N_0 . The red lines are linear global fits over the time delay range of 0.5 – 5 ps. (e) Lifetime map of the fast decay constant. (f) Lifetime map of the slow decay constant. (g) Distribution of the fast decay constant. (h) Histogram of the slow decay constant. (i) Time constants at negative times (τ_-) of each pixel plotted as a function of their corresponding static image counts. A linear correlation with a Pearson correlation coefficient of 0.31 is shown observed as a red line.

TR-PEEM can give us a better prospect to research on 2D materials. The correlations between

fast decay at negative times (τ_-) and static PEEM image [Figures 3.9 – 3.11 (i)] are indicated by Pearson correlation coefficient giving values of 0.288, 0.281, 0.286 and 0.313. Here we can find that the results are consistent with each other, which means the analysis on these WSe₂ flakes are robust and reproducible.

3.4 Conclusion

In summary, we have employed femtosecond TR-PEEM to image the ultrafast carrier dynamics of monolayer WSe₂ on SiO₂/Si with ~50-fs time resolution and sub-diffraction-limited spatial resolution. The observed dynamics are assigned to carrier cooling via intervalley electron-phonon scattering of electrons from the Q valley to the K valley, exciton-exciton annihilation involving indirect excitons, and electronic relaxation from the Γ point of the conduction band. The lifetime maps of the ultrafast dynamics exhibit pronounced spatial heterogeneity, most likely associated with structural disorder along the peripheral edges of the WSe₂ flake and the existence of charge puddles in the interior. While the presence of such structural and electronic heterogeneity have been inferred from previous studies of TMDs by time-integrated hyperspectral PL and Raman imaging, our present work directly reveals their effect on the ultrafast carrier dynamics. Future studies that combine TR-PEEM with an array of hyperspectral electron and optical imaging techniques is envisioned to provide insight into how various classes of structural heterogeneities and defects influence the ultrafast elementary carrier dynamics of TMD materials.

3.5 References

1. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F., Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10* (4), 1271-1275.
2. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105* (13), 136805.

3. Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X., Valley polarization in MoS₂ monolayers by optical pumping. *Nat. Nanotechnol.* **2012**, 7 (8), 490-493.
4. Duan, X.; Wang, C.; Pan, A.; Yu, R.; Duan, X., Two-dimensional transition metal dichalcogenides as atomically thin semiconductors: opportunities and challenges. *Chem. Soc. Rev.* **2015**, 44 (24), 8859-8876.
5. Bernardi, M.; Palummo, M.; Grossman, J. C., Extraordinary Sunlight Absorption and One Nanometer Thick Photovoltaics Using Two-Dimensional Monolayer Materials. *Nano Lett.* **2013**, 13 (8), 3664-3670.
6. Baugher, B. W. H.; Churchill, H. O. H.; Yang, Y.; Jarillo-Herrero, P., Optoelectronic devices based on electrically tunable p-n diodes in a monolayer dichalcogenide. *Nat. Nanotechnol.* **2014**, 9 (4), 262-267.
7. Yuan, H.; Bahramy, M. S.; Morimoto, K.; Wu, S.; Nomura, K.; Yang, B.-J.; Shimotani, H.; Suzuki, R.; Toh, M.; Kloc, C.; Xu, X.; Arita, R.; Nagaosa, N.; Iwasa, Y., Zeeman-type spin splitting controlled by an electric field. *Nat. Phys.* **2013**, 9 (9), 563-569.
8. Pospischil, A.; Furchi, M. M.; Mueller, T., Solar-energy conversion and light emission in an atomic monolayer p-n diode. *Nat. Nanotechnol.* **2014**, 9 (4), 257-261.
9. Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A., Ultrasensitive photodetectors based on monolayer MoS₂. *Nat. Nanotechnol.* **2013**, 8 (7), 497-501.
10. Ross, J. S.; Klement, P.; Jones, A. M.; Ghimire, N. J.; Yan, J.; Mandrus, D. G.; Taniguchi, T.; Watanabe, K.; Kitamura, K.; Yao, W.; Cobden, D. H.; Xu, X., Electrically tunable excitonic light-emitting diodes based on monolayer WSe₂ p-n junctions. *Nat. Nanotechnol.* **2014**, 9 (4), 268-272.
11. Poellmann, C.; Steinleitner, P.; Leierseder, U.; Nagler, P.; Plechinger, G.; Porer, M.; Bratschitsch, R.; Schuller, C.; Korn, T.; Huber, R., Resonant internal quantum

- transitions and femtosecond radiative decay of excitons in monolayer WSe₂. *Nat. Mater.* **2015**, *14* (9), 889-893.
12. Sun, D.; Rao, Y.; Reider, G. A.; Chen, G.; You, Y.; Brézin, L.; Harutyunyan, A. R.; Heinz, T. F., Observation of Rapid Exciton–Exciton Annihilation in Monolayer Molybdenum Disulfide. *Nano Lett.* **2014**, *14* (10), 5625-5629.
 13. Kang, K.; Xie, S.; Huang, L.; Han, Y.; Huang, P. Y.; Mak, K. F.; Kim, C.-J.; Muller, D.; Park, J., High-mobility three-atom-thick semiconducting films with wafer-scale homogeneity. *Nature* **2015**, *520*, 656.
 14. Lin, Z.; McCreary, A.; Briggs, N.; Subramanian, S.; Zhang, K.; Sun, Y.; Li, X.; Borys, N. J.; Yuan, H.; Fullerton-Shirey, S. K.; Chernikov, A.; Zhao, H.; McDonnell, S.; Lindenberg, A. M.; Xiao, K.; LeRoy, B. J.; Drndić, M.; Hwang, J. C. M.; Park, J.; Chhowalla, M.; Schaak, R. E.; Javey, A.; Hersam, M. C.; Robinson, J.; Terrones, M., 2D materials advances: from large scale synthesis and controlled heterostructures to improved characterization techniques, defects and applications. *2D Mater.* **2016**, *3* (4), 042001.
 15. Shah, J., *Ultrafast Spectroscopy of Semiconductors and Semiconductor Nanostructures*. 2 ed.; Springer-Verlag Berlin Heidelberg: 1999; p 522.
 16. Ceballos, F.; Cui, Q.; Bellus, M. Z.; Zhao, H., Exciton formation in monolayer transition metal dichalcogenides. *Nanoscale* **2016**, *8* (22), 11681-11688.
 17. Steinleitner, P.; Merkl, P.; Nagler, P.; Mornhinweg, J.; Schüller, C.; Korn, T.; Chernikov, A.; Huber, R., Direct Observation of Ultrafast Exciton Formation in a Monolayer of WSe₂. *Nano Lett.* **2017**, *17* (3), 1455-1460.
 18. You, Y.; Zhang, X.-X.; Berkelbach, T. C.; Hybertsen, M. S.; Reichman, D. R.; Heinz, T. F., Observation of biexcitons in monolayer WSe₂. *Nat. Phys.* **2015**, *11* (6), 477-481.

19. Zhang, C.; Wang, H.; Chan, W.; Manolatu, C.; Rana, F., Absorption of light by excitons and trions in monolayers of metal dichalcogenide MoS₂: Experiments and theory. *Phys. Rev. B* **2014**, *89* (20), 205436.
20. Nie, Z.; Long, R.; Sun, L.; Huang, C.-C.; Zhang, J.; Xiong, Q.; Hewak, D. W.; Shen, Z.; Prezhd, O. V.; Loh, Z.-H., Ultrafast Carrier Thermalization and Cooling Dynamics in Few-Layer MoS₂. *ACS Nano* **2014**, *8* (10), 10931-10940.
21. Nie, Z.; Long, R.; Teguh, J. S.; Huang, C.-C.; Hewak, D. W.; Yeow, E. K. L.; Shen, Z.; Prezhd, O. V.; Loh, Z.-H., Ultrafast Electron and Hole Relaxation Pathways in Few-Layer MoS₂. *J. Phys. Chem. C* **2015**, *119* (35), 20698-20708.
22. Mai, C.; Barrette, A.; Yu, Y.; Semenov, Y. G.; Kim, K. W.; Cao, L.; Gundogdu, K., Many-Body Effects in Valleytronics: Direct Measurement of Valley Lifetimes in Single-Layer MoS₂. *Nano Lett.* **2014**, *14* (1), 202-206.
23. Wang, Q.; Ge, S.; Li, X.; Qiu, J.; Ji, Y.; Feng, J.; Sun, D., Valley Carrier Dynamics in Monolayer Molybdenum Disulfide from Helicity-Resolved Ultrafast Pump-Probe Spectroscopy. *ACS Nano* **2013**, *7* (12), 11087-11093.
24. Wang, H.; Zhang, C.; Rana, F., Ultrafast dynamics of defect-assisted electron-hole recombination in monolayer MoS₂. *Nano Lett.* **2015**, *15* (1), 339-345.
25. Shi, H.; Yan, R.; Bertolazzi, S.; Brivio, J.; Gao, B.; Kis, A.; Jena, D.; Xing, H. G.; Huang, L., Exciton Dynamics in Suspended Monolayer and Few-Layer MoS₂ 2D Crystals. *ACS Nano* **2013**, *7* (2), 1072-1080.
26. Docherty, C. J.; Parkinson, P.; Joyce, H. J.; Chiu, M.-H.; Chen, C.-H.; Lee, M.-Y.; Li, L.-J.; Herz, L. M.; Johnston, M. B., Ultrafast Transient Terahertz Conductivity of Monolayer MoS₂ and WSe₂ Grown by Chemical Vapor Deposition. *ACS Nano* **2014**, *8* (11), 11147-11153.

27. Kumar, N.; Cui, Q.; Ceballos, F.; He, D.; Wang, Y.; Zhao, H., Exciton-exciton annihilation in MoSe₂ monolayers. *Phys. Rev. B* **2014**, 89 (12), 125427.
28. Cunningham, P. D.; McCreary, K. M.; Jonker, B. T., Auger Recombination in Chemical Vapor Deposition-Grown Monolayer WS₂. *J. Phys. Chem. Lett.* **2016**, 7 (24), 5242-5246.
29. Hsu, W. T.; Chen, Y. L.; Chen, C. H.; Liu, P. S.; Hou, T. H.; Li, L. J.; Chang, W. H., Optically initialized robust valley-polarized holes in monolayer WSe₂. *Nat. Commun.* **2015**, 6, 8963.
30. Hao, K.; Moody, G.; Wu, F.; Dass, C. K.; Xu, L.; Chen, C.-H.; Sun, L.; Li, M.-Y.; Li, L.-J.; MacDonald, A. H.; Li, X., Direct measurement of exciton valley coherence in monolayer WSe₂. *Nat. Phys.* **2016**, 12 (7), 677-682.
31. Wang, R.; Ruzicka, B. A.; Kumar, N.; Bellus, M. Z.; Chiu, H.-Y.; Zhao, H., Ultrafast and spatially resolved studies of charge carriers in atomically thin molybdenum disulfide. *Phys. Rev. B* **2012**, 86 (4), 045406.
32. Ceballos, F.; Bellus, M. Z.; Chiu, H. Y.; Zhao, H., Probing charge transfer excitons in a MoSe₂-WS₂ van der Waals heterostructure. *Nanoscale* **2015**, 7 (41), 17523-17528.
33. Park, K. D.; Khatib, O.; Kravtsov, V.; Clark, G.; Xu, X.; Raschke, M. B., Hybrid Tip-Enhanced Nanospectroscopy and Nanoimaging of Monolayer WSe₂ with Local Strain Control. *Nano Lett.* **2016**, 16 (4), 2621-2627.
34. Bao, W.; Borys, N. J.; Ko, C.; Suh, J.; Fan, W.; Thron, A.; Zhang, Y.; Buyanin, A.; Zhang, J.; Cabrini, S.; Ashby, P. D.; Weber-Bargioni, A.; Tongay, S.; Aloni, S.; Ogletree, D. F.; Wu, J.; Salmeron, M. B.; Schuck, P. J., Visualizing nanoscale excitonic relaxation properties of disordered edges and grain boundaries in monolayer molybdenum disulfide. *Nat. Commun.* **2015**, 6, 7993.
35. Stockman, M. I.; Kling, M. F.; Kleineberg, U.; Krausz, F., Attosecond nanoplasmonic-field microscope. *Nat Photon* **2007**, 1 (9), 539-544.

36. Kubo, A.; Onda, K.; Petek, H.; Sun, Z.; Jung, Y. S.; Kim, H. K., Femtosecond Imaging of Surface Plasmon Dynamics in a Nanostructured Silver Film. *Nano Letters* **2005**, *5* (6), 1123-1127.
37. Kubo, A.; Pontius, N.; Petek, H., Femtosecond Microscopy of Surface Plasmon Polariton Wave Packet Evolution at the Silver/Vacuum Interface. *Nano Letters* **2007**, *7* (2), 470-475.
38. Gong, Y.; Joly, A. G.; Hu, D.; El-Khoury, P. Z.; Hess, W. P., Ultrafast Imaging of Surface Plasmons Propagating on a Gold Surface. *Nano Letters* **2015**, *15* (5), 3472-3478.
39. Fukumoto, K.; Yamada, Y.; Onda, K.; Koshihara, S.-y., Direct imaging of electron recombination and transport on a semiconductor surface by femtosecond time-resolved photoemission electron microscopy. *Appl. Phys. Lett.* **2014**, *104* (5), 053117.
40. Man, M. K.; Margiolakis, A.; Deckoff-Jones, S.; Harada, T.; Wong, E. L.; Krishna, M. B.; Madeo, J.; Winchester, A.; Lei, S.; Vajtai, R.; Ajayan, P. M.; Dani, K. M., Imaging the motion of electrons across semiconductor heterojunctions. *Nat. Nanotechnol.* **2017**, *12* (1), 36-40.
41. Amin, B.; Kaloni, T. P.; Schwingenschlogl, U., Strain engineering of WS₂, WSe₂, and WTe₂. *RSC Adv.* **2014**, *4* (65), 34561-34565.
42. Liu, Z.; Amani, M.; Najmaei, S.; Xu, Q.; Zou, X.; Zhou, W.; Yu, T.; Qiu, C.; Birdwell, A. G.; Crowne, F. J.; Vajtai, R.; Yakobson, B. I.; Xia, Z.; Dubey, M.; Ajayan, P. M.; Lou, J., Strain and structure heterogeneity in MoS₂ atomic layers grown by chemical vapour deposition. *Nat. Commun.* **2014**, *5*, 5246.
43. Christopher, M. S.; Rafik, A.; Stephen, M.; Christopher, L. H.; Robert, M. W., WSe₂-contact metal interface chemistry and band alignment under high vacuum and ultra high vacuum deposition conditions. *2D Mater.* **2017**, *4* (2), 025084.

44. Kozawa, D.; Kumar, R.; Carvalho, A.; Kumar Amara, K.; Zhao, W.; Wang, S.; Toh, M.; Ribeiro, R. M.; Castro Neto, A. H.; Matsuda, K.; Eda, G., Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides. *Nat. Commun.* **2014**, *5*, 4543.
45. Li, Y.; Chernikov, A.; Zhang, X.; Rigosi, A.; Hill, H. M.; van der Zande, A. M.; Chenet, D. A.; Shih, E.-M.; Hone, J.; Heinz, T. F., Measurement of the optical dielectric function of monolayer transition-metal dichalcogenides: MoS₂, MoSe₂, WS₂, and WSe₂. *Phys. Rev. B* **2014**, *90* (20), 205422.
46. Cui, Q.; Ceballos, F.; Kumar, N.; Zhao, H., Transient Absorption Microscopy of Monolayer and Bulk WSe₂. *ACS Nano* **2014**, *8* (3), 2970-2976.
47. Yan, T.; Qiao, X.; Liu, X.; Tan, P.; Zhang, X., Photoluminescence properties and exciton dynamics in monolayer WSe₂. *Appl. Phys. Lett.* **2014**, *105* (10), 101901.
48. Kataria, S.; Wagner, S.; Cusati, T.; Fortunelli, A.; Iannaccone, G.; Pandey, H.; Fiori, G.; Lemme, M. C., Growth-Induced Strain in Chemical Vapor Deposited Monolayer MoS₂: Experimental and Theoretical Investigation. *Adv. Mater.* **2017**, *4* (17), 1700031.
49. Mignuzzi, S.; Pollard, A. J.; Bonini, N.; Brennan, B.; Gilmore, I. S.; Pimenta, M. A.; Richards, D.; Roy, D., Effect of disorder on Raman scattering of single-layer MoS₂. *Phys. Rev. B* **2015**, *91* (19), 195411.
50. del Corro, E.; Terrones, H.; Elias, A.; Fantini, C.; Feng, S.; Nguyen, M. A.; Mallouk, T. E.; Terrones, M.; Pimenta, M. A., Excited Excitonic States in 1L, 2L, 3L, and Bulk WSe₂ Observed by Resonant Raman Spectroscopy. *ACS Nano* **2014**, *8* (9), 9629-9635.
51. Şopu, D.; Kotakoski, J.; Albe, K., Finite-size effects in the phonon density of states of nanostructured germanium: A comparative study of nanoparticles, nanocrystals, nanoglasses, and bulk phases. *Phys. Rev. B* **2011**, *83* (24), 245416.

52. Akselrod, G. M.; Deotare, P. B.; Thompson, N. J.; Lee, J.; Tisdale, W. A.; Baldo, M. A.; Menon, V. M.; Bulović, V., Visualization of exciton transport in ordered and disordered molecular solids. *Nat. Commun.* **2014**, *5*, 3646.
53. Laquai, F.; Park, Y.-S.; Kim, J.-J.; Basché, T., Excitation Energy Transfer in Organic Materials: From Fundamentals to Optoelectronic Devices. *Macromol. Rapid Commun.* **2009**, *30* (14), 1203-1231.
54. Kagan, C. R.; Murray, C. B.; Nirmal, M.; Bawendi, M. G., Electronic Energy Transfer in CdSe Quantum Dot Solids. *Phys. Rev. Lett.* **1996**, *76* (9), 1517-1520.
55. Borys, N. J.; Barnard, E. S.; Gao, S.; Yao, K.; Bao, W.; Buyanin, A.; Zhang, Y.; Tongay, S.; Ko, C.; Suh, J.; Weber-Bargioni, A.; Wu, J.; Yang, L.; Schuck, P. J., Anomalous Above-Gap Photoexcitations and Optical Signatures of Localized Charge Puddles in Monolayer Molybdenum Disulfide. *ACS Nano* **2017**, *11* (2), 2115-2123.
56. Michail, A.; Delikoukos, N.; Parthenios, J.; Galiotis, C.; Papagelis, K., Optical detection of strain and doping inhomogeneities in single layer MoS₂. *Appl. Phys. Lett.* **2016**, *108* (17), 173102.
57. Zhang, Y.; Brar, V. W.; Girit, C.; Zettl, A.; Crommie, M. F., Origin of spatial charge inhomogeneity in graphene. *Nat. Phys.* **2009**, *5* (10), 722-726.
58. Shin, B. G.; Han, G. H.; Yun, S. J.; Oh, H. M.; Bae, J. J.; Song, Y. J.; Park, C.-Y.; Lee, Y. H., Indirect Bandgap Puddles in Monolayer MoS₂ by Substrate-Induced Local Strain. *Adv. Mater.* **2016**, *28* (42), 9378-9384.

Chapter 4

Ultrafast Dynamics in Four-layer MoS₂ Investigated by Time-Resolved Photoemission Electron Microscopy

4.1 Introduction

Two-dimensional (2D) materials with strong intralayer and weak interlayer interaction attract a lot attention. The strong photoluminescence in 2D materials exhibits their applications in the optoelectronic devices, due to the transition of indirect bandgap to direct bandgap when the layer number decreases from multilayers to single-layers.¹⁻² Extremely sensitive chemical sensors,³ high mobility field-effect transistors with GHz-frequency on/off ratios,⁴⁻⁵ and fast response phototransistors⁶ have been demonstrated using few-layer MoS₂. Excitons and trions are also found in these 2D materials, which is caused by the strong quantum confinement and reduced dielectric screening resulting from substantial Coulomb interactions between carriers even at room temperature.⁷ Researches on exciton formed in 2D materials reveal that excitons can recombine by different pathways (radiative⁸ or nonradiative⁹⁻¹⁰ decay). To better understand and implement applications of 2D materials, the necessity to performance the ultrafast measurement on the dynamics of photoexcited carriers in these few-layer 2D materials has motivated extensive studies.

Most of the ultrafast studies focus on monolayer 2D materials and display complex multiexponential dynamics. The carrier thermalization and cooling occur in the time scale of hundreds femtosecond,¹¹ while much longer time scale in picosecond range is dominated by charge carrier trapping,¹² and electron-hole radiative recombination¹³. Various layer-dependent studies are conducted by experiments¹⁴⁻¹⁶ and theoretical calculation¹⁷⁻¹⁸ to discover the influence of layer number on 2D materials. Wang et al. report the evolution of the carrier

lifetime with the number of layers and indicate the defect-assisted carrier recombination at surface layer.¹⁹ Cunningham et al. using ultrafast transient absorption spectroscopy and time-resolved terahertz spectroscopy reveal that the carriers are trapped at either surface defects or grain boundaries within 600 fs.²⁰ Kar et al. apply the defect-mediated auger scattering model on charge carriers and excitons to describe the fluence dependent optical pump-terahertz data.²¹ Borzda et al. show primary photoexcitation excitons can efficiently dissociate into charges in 700 fs.²² The mixture of charge and exciton in multilayer MoS₂ generated from the above bandgap photoexcitation electrons is considered from exciton dissociation within 1 ps, and the excitons are trapped in picosecond time range.²³ Through these publications, we can see the free carrier generation and defect-assisted auger process are the main dynamic process in multilayer 2D materials. But the mechanism of free carrier generation and the contribution of surface and edge defects to the defects-assisted auger process are still unclear.

In this chapter, time-resolved photoemission electron microscopy (TR-PEEM) is utilized to spatially monitor the intensity changes of MoS₂ flake at different time delays. The hot carriers cool down to conduction band minimum (CBM) via electron-phonon scattering in the time scale of 200 – 300 fs. In the following picosecond time trace, we propose a mixture process of Auger-mediated exciton formation and exciton-exciton annihilation with secondary rates of $0.15 \pm 0.02 \text{ cm}^2/\text{s}$ and $0.047 \pm 0.002 \text{ cm}^2/\text{s}$. During the Auger-mediated exciton formation process, the re-excited (Auger) electron is considered as the free carrier. This is our contribution to the existing debate of the origination of the free carrier observed in few-layer 2D materials. We also notice the hot spot on the surface of MoS₂ flake in the static PEEM image, there is no obvious correlation between the static PEEM image and time constant mapping. The hot spot on MoS₂ flake is due to the much more ejection of electrons in trap states that is caused by defects, while the mechanism we discussed doesn't evolve with any defects. On another view, it proves that our description on MoS₂ dynamics fits our observation

here. In the histogram of slow decay mappings, the long tail distribution suggests a competition between auger-mediated exciton formation and exciton-exciton annihilation within 8 ps. For further larger time constant, the defect-assisted auger process could even involve it.

4.2 Results and Discussion

To confirm the layer number of MoS₂ sample, atomic force microscopy (AFM) is utilized to measure the height of MoS₂ flake. The AFM image of MoS₂ sample is shown in Figure 4.1(a), and the height distribution is plotted in Figure 4.1(b) for better comparison. Two distinct peaks can be seen with a separation of 2.6 nm after Gaussian function fit. According to the difference of sample height, we can conclude that it is a four-layer MoS₂ sample. The intensity of photoluminescence is drawn in Figure 4.2 as a function of photon energy, two Gaussian functions are employed to fit the curve that gives a center photon energy 1.89 eV for A and 2.06 eV for with a A/B ratio of 2.35. The static PEEM image of MoS₂ illuminated by 343-nm pulse is shown in Figure 4.3(a) with a contrast of 4.8 between sample and substrate. The central triangle flake with $\sim 22 \mu\text{m}$ length is the one we studied on, showing a noticeable hot spot near the edge. According to the reports,^{15, 24} the ionization energy of few-layer MoS₂ is ~ 5.6 eV. Two photons are absorbed simultaneously to conquer the ionization energy and eject electrons

Figure 4.1 (a) The AFM image of MoS₂ indicating the height of the sample. (b) The height distribution of the MoS₂ sample. Two Gaussian functions are utilized to fit the distribution.

Figure 4.2 The photoluminescence (PL) of the few-layer MoS₂ sample. Two Gaussian functions are utilized to fit the spectrum.

from MoS₂. The band structure of four-layer MoS₂ that is different from monolayer one is drawn in Figure 4.3(b), the valance band maximum shifts from K valley to Γ valley and the conduction band minimum shifts from K valley to Q valley.^{14, 17-18, 25} The offset between Γ and K valley is few hundreds meV in valance band, while it is negligible between Q and K valley in conduction band.^{17-18, 26} The transition in K valley induced by pump pulse (2.4 eV) is drawn as a blue vertical line in Figure 4.3(a). The second pulse can monitor the electrons population within yellow region as shown in Figure 4.3(b) via a two-photon process.

Figure 4.3 (a) The PEEM image of MoS₂ using 343-nm laser light as irradiation source. (b) The calculated band structure of four-layer MoS₂. Yellow region indicates the two-photon probe window of 343-nm pulse after considering momentum conservation.

Figure 4.4 (a) Time traces of single MoS₂ flake at different pump fluences after subtracting the reference signal counts at 100 ps. The red lines are the fits to the function described in the main text. The time constants of fast decay (b) and slow decay (c) plotted as a function of pump fluence.

To investigate the electron dynamics in four-layer MoS₂ sample, we conduct the TR-PEEM experiment on MoS₂. The spatially integrated signals of the single MoS₂ flake after subtracting the reference signal recorded at 100 ps are plotted as a function of time delays. Fluence dependent measurement is also performed in this experiment, all time traces are plotted in Figure 4.4(a) with pump fluence labelled above each trace. The process is consisted of three components: exponential rising at negative delay time and fast and slow exponential decays at positive delay time. To extract the exact time constants during this process, we convolve the instrument response with the process as the fit function. All data can be fit to the function very well shown as red lines in Figure 4.4(a), the time constants of fast decay and slow decay are

plotted in Figure 4.4(b) and (c) as a function of pump fluence, respectively. The photon energy (2.4 eV) of pump pulse is larger than the direct bandgap at K valley, the photoexcited carriers need to transfer the excess energy to lattices via electron-phonon scattering.^{11, 27} The time constants of fast component display a step increasing in Figure 4.4(b) when boosting the pump fluence. The value of the fast decay is 220 ± 13 fs at the initial pump fluence of $6.8 \mu\text{J}/\text{cm}^2$, then stays at 277 ± 13 , 280 ± 12 and 277 ± 11 fs when fluence ramping up to $16.9 \mu\text{J}/\text{cm}^2$, and reaches 351 ± 20 fs at the pump fluence of $20.3 \mu\text{J}/\text{cm}^2$. For the increasing tendency of fast decay, it can be considered as the hot phonon effect.^{11, 28-29} The time constants of the slow decay are 1156 ± 77 , 1454 ± 96 , 1308 ± 85 , 1486 ± 92 and 1322 ± 147 fs when the sample are pumped at 6.8, 10.1, 13.5, 16.9 and 20.3 fluence, respectively. Here, we assign the slow decay process as the Auger process, similar phenomena have been reported.^{20, 30} The electron dynamics in four-layer MoS₂ can be described as

$$\frac{dN}{dt} = \frac{1}{\tau}N - \gamma N^2 \quad 4.1$$

where the N is the number of exciton in conduction probe window, τ and γ are the exciton recombination time and second order rate. Usually the typical time constant of exciton recombination through radiate process is more than 10 ps.³¹⁻³² In this case, we can ignore the contribution of the first term and find

$$\frac{N_0}{N(t)} - 1 = \gamma N_0 t \quad 4.2$$

where N_0 is the initial exciton number. The absorbance is ~ 0.18 under 515-nm pump light according to the layer-dependent measurement.³³⁻³⁴ The linear relation between exciton density and signal count at 500 fs is plotted in Figure 4.5 with a slope of $(6.9 \pm 0.7) \times 10^{-7}$ and a intercept and $-(9.0 \pm 0.9) \times 10^5$. According to this linear relation, the quantity $N_0 / N(t) - 1$ calculated from the fluence dependent time trace is shown in Figure 4.6, the grey vertical line

Figure 4.5 The relation between signal and exciton density. The red line is a linear fit to the data,

indicates the time zero. The dynamics at positive times can be divided into two regions with different slopes, we extend the red fit line to time zero to clearly show deviation in first 500 fs. The discrepancy between the quantity $N_0 / N(t) - 1$ and linear tendency become smaller, eventually disappear at $20.3 \mu\text{J}/\text{cm}^2$ pump fluence. A turn point around 2000fs can be seen, two different slope lines meet here indicating a transition of dominating ultrafast process. Through the global fitting, the second order rate are $0.15 \pm 0.02 \text{ cm}^2/\text{s}$ (red line) and $0.047 \pm$

Figure 4.6 The quantity $N_0 / N(t) - 1$ calculated from time trace in Figure 4.4. (a). The grey vertical line indicates the time zero point, and the red and blue lines are the linear fits.

0.002 cm²/s (blue line), respectively. For the second order rate process, it could be caused by exciton-exciton annihilation or defect-mediate auger process. Wang et al¹⁹ and Vega-Mayoral³⁰ show the defect-mediated auger process usually happens in the range of tens and hundreds picoseconds. The time-resolved photoluminescence also demonstrates time constant of intravalley radiative recombination is ~3 ps in bilayer WSe₂,³⁵ it means that most electron and hole will stay in K valley, form exciton and radiative recombination within first few picoseconds before electrons are transferred into Q valley via phonon scattering. The calculated second order rate in second region is similar to the reported exciton-exciton annihilation rate (0.043 cm²/s) for monolayer MoS₂ within 10 ps.³⁶ In this case, the Auger type process in second part (blue lines in Figure 4.6) should be the exciton-exciton annihilation process. The over bandgap pumped electrons with excess energy cool down via electron-phonon scattering to form excitons as discussed before, which is believed to cause the deviation from 0 fs to 500 fs (red dash lines) from second to fifth panel in Figure 4.6. When the pump fluence increasing, the quantity $N_0 / N(t) - 1$ and the red fit lines merge together at early time. Due to the hot phonon effect, the excess electron energy cannot be transferred efficiently via electron-phonon scattering. The following auger process play more significant role as the mitigation of electron cooling. At the pump fluence of 20.3 μJ/cm², the data coincide with auger process as shown in the first panel of Figure 4.6. As the second exciton-exciton annihilation process still can be observed, it indicates that the excitons are generated during the auger process (red lines). In four-layer MoS₂ sample, we think there are two routines for hot electrons to form excitons: electron cooling and auger-assisted exciton formation, but with different tendency. The electrons cooling via phonon scattering is efficient way for exciton formation process at low pump fluence or before the occurrence of hot phonon effect. Once the blockage of the electrons cooling via phonon, the auger-assisted exciton formation will dominate the process. The intervalley scattering in the indirect bandgap of four-layer MoS₂ will reduce the carriers in K

valley, then the auger-assisted exciton formation process will also be suppressed. The time constant for electron and hole intervalley scattering is ~ 0.5 and 2 ps when using the same pump fluence as our case.³⁷ In the research of few-layer MoS₂ using transition absorption, a mixture of free carrier and excitons is observed. Borzda et al suggest the charges are generated by the dissociation of the photoexcited excitons within 700 fs.²² However, Tsokkou et al believe that the free charges are generated during the photoexcitation.²³ From their contrary viewpoints, it seems impossible to reconcile the contradiction. But in our picture, we can accommodate both of their phenomenon. The exciton formed by auger-mediated way will transfer the excess energy to another electron that jumps into higher energy state. These electrons with higher energy can break the bounding energy easily and behave as free carriers. During this exciton formation process, the accumulation of such electrons shows the phenomenon observed by Borzda et al. In the case of Tsokkou et al, the carrier cooling and auger-mediated exciton formation process happen simultaneously, the free charges can be generated by auger-mediated exciton formation process instantaneously after photoexcitation. All the processes we discussed above happen simultaneously but dominate different time scale.

The PEEM image of MoS₂ flake taken at -2000 fs using $6.8 \mu\text{J}/\text{cm}^2$ 515-nm pump fluence is shown in Figure 4.7(a), the signal counts of MoS₂ are $40 - 60$ for each pixel while the background is less than 20 . The intensity fluctuation can be observed on the surface of MoS₂ flake, and a hot spot with nearly twice signal counts of normal pixel can be seen. To increase the signal-to-noise of time constants mapping, a 4×4 pixels² square window scanning over the images pixel by pixel. For example, the image of Figure 4.7(a) after processed is exhibited in Figure 4.7(b), black circles are used to mark the hot spot region except Figure 4.7d using yellow circle for better contrast. Figures 4.6(c) and (d) are the time constant mappings of fast decay and slow decay, and Figures 4.6(e) and (f) are the corresponding amplitude mapping of fast and slow decay. Mappings at higher pump fluence are shown in Figures 4.7, 4.8, 4.9, 4.10 and

Figure 4.7 (a) PEEM image of selected MoS₂ flake taken at -2000 fs delay time using 6.8 μJ/cm² pump fluence. (b) PEEM image after 4×4 pixels² square window sampling over the image (a). The black circle indicates the high counts spot. The time constant mapping of fast decay (c) and slow decay (d) component. The amplitude mapping of fast decay (e) and slow decay (f) component. The region marked by the circle in (c) to (f) is the corresponding area described in (b), different colour is applied to increase the contrast.

Figure 4.8 (a) PEEM image of selected MoS₂ flake taken at -2000 fs delay time using 10.1 $\mu\text{J}/\text{cm}^2$ pump fluence. (b) PEEM image after 4×4 pixels² square window sampling over the image shown in (a). The time constant mapping of fast decay (c) and slow decay (d) component. The corresponding amplitude mapping of fast decay (e) and slow decay (f) component.

Figure 4.9 (a) PEEM image of selected MoS₂ flake taken at -2000 fs delay time using 13.5 $\mu\text{J}/\text{cm}^2$ pump fluence. (b) PEEM image after 4×4 pixels² square window sampling over the image shown in (a). The time constant mapping of fast decay (c) and slow decay (d) component. The corresponding amplitude mapping of fast decay (e) and slow decay (f) component.

Figure 4.10 (a) PEEM image of selected MoS₂ flake taken at -2000 fs delay time using 16.9 $\mu\text{J}/\text{cm}^2$ pump fluence. (b) PEEM image after 4×4 pixels² square window sampling over the image shown in (a). The time constant mapping of fast decay (c) and slow decay (d) component. The corresponding amplitude mapping of fast decay (e) and slow decay (f) component.

Figure 4.11 (a) PEEM image of selected MoS₂ flake taken at -2000 fs delay time using 20.3 μJ/cm² pump fluence. (b) PEEM image after 4×4 pixels² square window sampling over the image shown in (a). The time constant mapping of fast decay (c) and slow decay (d) component. The corresponding amplitude mapping of fast decay (e) and slow decay (f) component.

4.11. From the mapping of fast and slow components in Figures 4.6(c) to (f), the surface exhibits quite uniform fluctuation and indicates the defects are homogeneous distributed. Different from monolayer 2D materials, the few-layer MoS₂ has a sandwich structure. The photoexcited electrons are confined in several layers, Wang et al report the defect-assisted auger scattering are surface limited due to the much larger defects density at surface layers than inner layers.¹⁹ Here we can see that the defects on surface plays a more important role than edge part in our reported process. Notably, a ~ 300 nm (FWMH) hot spot can be observed on the surface of MoS₂ flake in Figures 4.6(a) and (b), but there is no any significant sign shown on its time and amplitude mapping. Matin et al found the acid-treated MoS₂ exhibit ~ 100% photoluminescence quantum yield,³⁸ and several acids are utilized on different 2D materials.³⁹⁻⁴¹ These researches show that the defects on the sample surface can significantly trap the free charge carriers and localize excitons. Through the quantum yield of photoluminescence is depending on the exciton recombination, we can know the hot spot is due to the trapped free charge carriers or localized excitons. For the high counts of hot spot, it may be due to the aggregation of a certain number of defects. While we cannot distinguish the difference on time and amplitude mapping, it means the ultrafast process observed here is not relative to defect, which is consistent with our explanation. Both Auger-mediated exciton formation and exciton and exciton annihilation do not rely on defects.

The histograms of the time constant mappings of fast decay and slow decay are plotted in Figure. 12(a) and (b). At the lowest pump fluence of 6.8 $\mu\text{J}/\text{cm}^2$, the distribution of fast decay spreads widely from 0 to 700 fs. With the pump fluence increasing, the shape of the fast decay histograms looks like a normal distribution, the center shift to right side and the width become narrow. But for the slow decay in Figure 4.12(b), the histograms have long tails in right side without obvious peak shift. The statistical analysis of the histogram can be seen in Figure 4.12(c) and (d), the flake integrated value, mean and median of the histograms are plotted as a function

Figure 4.12 The histograms of fast decay (a) and slow decay (b) of MoS₂ flake at different pump fluence. The fluence dependent fast decay (c) and slow decay (d) based on different calculated methods.

of pump fluence. Different from the integrated results, the mean and median lines exhibit a growing tendency as shown in Figure 4.12(c), which is caused by the hot phonon effect. However, the value of fast decay remains almost the same from 10.1 to 16.9 $\mu\text{J}/\text{cm}^2$ in the integrated flake analysis. We can conclude that the positions with higher signal counts on the surface of MoS₂ flake dominate the fast decay time constant that makes the flake integrated result larger than the statistical value. From the fluence dependent slow decay measurement shown in Figure 4.12(d), the median value is very close to the value acquired from flake

integrated analysis with same tendency. Here we also notice that the flake integrated value is larger than the median, which is caused by the same reason as in the fast decay component. However, the mean value of the slow decay histogram is much higher than the value calculated from other methods, which is originated from the long tail in the large value range. The decreasing of the mean value illustrates the fading of the influence of the long tail depicted in Figure 4.12(d). Through the difference between the histograms of fast decay and slow decay, we can see the fast decay process or the carrier cooling process via phonon scattering is less sensitive to the surface state and exhibits a nearly normal distribution here. But in the slow decay process, it contains two competing processes: auger-assisted exciton formation and exciton-exciton annihilation in the range of 0.5 to 8 ps. Different time constant will be extracted due to the competition of these two processes. And the defect-assisted auger process with larger time constant also can extend time constant.

4.4 Conclusion

We are using TR-PEEM to spatially monitor the intensity change of MoS₂ flake at different time delays. Through the conduction band electrons' variation within our probe window, we can fit the time traces with exponential functions after convolution with instrument response. A hot phonon effect can be observed in the fluence dependent measurement. Later in the plots of the quantity $N_0/N(t) - 1$ calculated from the fluence dependent time trace, we can distinguish three different processes: carrier cooling via phonon scattering, Auger-mediated exciton formation process and exciton-exciton annihilation. The Auger-mediated exciton formation process is first time reported here with 0.15 ± 0.02 cm²/s rate. The rate of following exciton-exciton annihilation is 0.047 ± 0.002 cm²/s, which is consistent with reported exciton-exciton annihilation in monolayer MoS₂. The proposed dynamic process can explain the remaining debate about the generation of free carriers in few-layer sample. The time constant and amplitude mappings of the few-layer MoS₂ exhibit quite homogeneous surface, even at the hot

spot region that could be induced by the aggregation of defects. On another way, it indicates that the ultrafast processes we observed here are less sensitive to the defects' influence in our experiment. The distribution of slow decay with long tail in large value range compared with nearly normal distribution of the slow decay shows the potential competition with auger-mediated exciton formation and exciton-exciton formation, which could even involve the defect-assisted auger process.

4.5 Reference

1. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F., Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, *10* (4), 1271-1275.
2. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C., Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. *ACS Nano* **2014**, *8* (2), 1102-1120.
3. Li, H.; Yin, Z.; He, Q.; Li, H.; Huang, X.; Lu, G.; Fam, D. W. H.; Tok, A. I. Y.; Zhang, Q.; Zhang, H., Fabrication of Single- and Multilayer MoS₂ Film-Based Field-Effect Transistors for Sensing NO at Room Temperature. *Small* **2012**, *8* (1), 63-67.
4. Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J., High Performance Multilayer MoS₂ Transistors with Scandium Contacts. *Nano Lett.* **2013**, *13* (1), 100-105.
5. Kim, S.; Konar, A.; Hwang, W.-S.; Lee, J. H.; Lee, J.; Yang, J.; Jung, C.; Kim, H.; Yoo, J.-B.; Choi, J.-Y.; Jin, Y. W.; Lee, S. Y.; Jena, D.; Choi, W.; Kim, K., High-mobility and low-power thin-film transistors based on multilayer MoS₂ crystals. *Nat. Commun.* **2012**, *3*, 1011.
6. Choi, W.; Cho, M. Y.; Konar, A.; Lee, J. H.; Cha, G.-B.; Hong, S. C.; Kim, S.; Kim, J.; Jena, D.; Joo, J.; Kim, S., High-Detectivity Multilayer MoS₂ Phototransistors with Spectral Response from Ultraviolet to Infrared. *Adv. Mater.* **2012**, *24* (43), 5832-5836.

7. Lin, Y.; Ling, X.; Yu, L.; Huang, S.; Hsu, A. L.; Lee, Y.-H.; Kong, J.; Dresselhaus, M. S.; Palacios, T., Dielectric Screening of Excitons and Trions in Single-Layer MoS₂. *Nano Lett.* **2014**, *14* (10), 5569-5576.
8. Palummo, M.; Bernardi, M.; Grossman, J. C., Exciton Radiative Lifetimes in Two-Dimensional Transition Metal Dichalcogenides. *Nano Lett.* **2015**, *15* (5), 2794-2800.
9. Shi, H.; Yan, R.; Bertolazzi, S.; Brivio, J.; Gao, B.; Kis, A.; Jena, D.; Xing, H. G.; Huang, L., Exciton Dynamics in Suspended Monolayer and Few-Layer MoS₂ 2D Crystals. *ACS Nano* **2013**, *7* (2), 1072-1080.
10. Kozawa, D.; Kumar, R.; Carvalho, A.; Kumar Amara, K.; Zhao, W.; Wang, S.; Toh, M.; Ribeiro, R. M.; Castro Neto, A. H.; Matsuda, K.; Eda, G., Photocarrier relaxation pathway in two-dimensional semiconducting transition metal dichalcogenides. *Nat. Commun.* **2014**, *5*, 4543.
11. Nie, Z.; Long, R.; Sun, L.; Huang, C.-C.; Zhang, J.; Xiong, Q.; Hewak, D. W.; Shen, Z.; Prezhdo, O. V.; Loh, Z.-H., Ultrafast Carrier Thermalization and Cooling Dynamics in Few-Layer MoS₂. *ACS Nano* **2014**, *8* (10), 10931-10940.
12. Wang, H.; Zhang, C.; Rana, F., Ultrafast dynamics of defect-assisted electron-hole recombination in monolayer MoS₂. *Nano Lett.* **2015**, *15* (1), 339-345.
13. Lagarde, D.; Bouet, L.; Marie, X.; Zhu, C. R.; Liu, B. L.; Amand, T.; Tan, P. H.; Urbaszek, B., Carrier and Polarization Dynamics in Monolayer MoS₂. *Phys. Rev. Lett.* **2014**, *112* (4), 047401.
14. Dhakal, K. P.; Duong, D. L.; Lee, J.; Nam, H.; Kim, M.; Kan, M.; Lee, Y. H.; Kim, J., Confocal absorption spectral imaging of MoS₂: optical transitions depending on the atomic thickness of intrinsic and chemically doped MoS₂. *Nanoscale* **2014**, *6* (21), 13028-13035.

15. Keyshar, K.; Berg, M.; Zhang, X.; Vajtai, R.; Gupta, G.; Chan, C. K.; Beechem, T. E.; Ajayan, P. M.; Mohite, A. D.; Ohta, T., Experimental Determination of the Ionization Energies of MoSe₂, WS₂, and MoS₂ on SiO₂ Using Photoemission Electron Microscopy. *ACS Nano* **2017**.
16. Yu, Y.; Yu, Y.; Cai, Y.; Li, W.; Gurarslan, A.; Peelaers, H.; Aspnes, D. E.; Van de Walle, C. G.; Nguyen, N. V.; Zhang, Y.-W.; Cao, L., Exciton-dominated Dielectric Function of Atomically Thin MoS₂ Films. *Sci. Rep.* **2015**, *5*, 16996.
17. Zhao, W.; Ribeiro, R. M.; Toh, M.; Carvalho, A.; Kloc, C.; Castro Neto, A. H.; Eda, G., Origin of Indirect Optical Transitions in Few-Layer MoS₂, WS₂, and WSe₂. *Nano Lett.* **2013**, *13* (11), 5627-5634.
18. Huang, W.; Luo, X.; Gan, C. K.; Quek, S. Y.; Liang, G., Theoretical study of thermoelectric properties of few-layer MoS₂ and WSe₂. *Phys. Chem. Chem. Phys.* **2014**, *16* (22), 10866-10874.
19. Wang, H.; Zhang, C.; Rana, F., Surface Recombination Limited Lifetimes of Photoexcited Carriers in Few-Layer Transition Metal Dichalcogenide MoS₂. *Nano Lett.* **2015**, *15* (12), 8204-10.
20. Cunningham, P. D.; McCreary, K. M.; Hanbicki, A. T.; Currie, M.; Jonker, B. T.; Hayden, L. M., Charge Trapping and Exciton Dynamics in Large-Area CVD Grown MoS₂. *J. Phys. Chem. C* **2016**, *120* (10), 5819-5826.
21. Kar, S.; Su, Y.; Nair, R. R.; Sood, A. K., Probing Photoexcited Carriers in a Few-Layer MoS₂ Laminate by Time-Resolved Optical Pump–Terahertz Probe Spectroscopy. *ACS Nano* **2015**, *9* (12), 12004-12010.
22. Borzda, T.; Gadermaier, C.; Vujicic, N.; Topolovsek, P.; Borovsak, M.; Mertelj, T.; Viola, D.; Manzoni, C.; Pogna, E. A. A.; Brida, D.; Antognazza, M. R.; Scotognella,

- F.; Lanzani, G.; Cerullo, G.; Mihailovic, D., Charge Photogeneration in Few-Layer MoS₂. *Adv. Funct. Mater.* **2015**, 25 (22), 3351-3358.
23. Tsokkou, D.; Yu, X.; Sivula, K.; Banerji, N., The Role of Excitons and Free Charges in the Excited-State Dynamics of Solution-Processed Few-Layer MoS₂ Nanoflakes. *J. Phys. Chem. C* **2016**, 120 (40), 23286-23292.
 24. Berg, M.; Keyshar, K.; Bilgin, I.; Liu, F.; Yamaguchi, H.; Vajtai, R.; Chan, C.; Gupta, G.; Kar, S.; Ajayan, P.; Ohta, T.; Mohite, A. D., Layer dependence of the electronic band alignment of few-layer MoS₂ on SiO₂ measured using photoemission electron microscopy. *Phys. Rev. B* **2017**, 95 (23), 235406.
 25. Yeh, P.-C.; Jin, W.; Zaki, N.; Zhang, D.; Liou, J. T.; Sadowski, J. T.; Al-Mahboob, A.; Dadap, J. I.; Herman, I. P.; Sutter, P.; Osgood, R. M., Layer-dependent electronic structure of an atomically heavy two-dimensional dichalcogenide. *Phys. Rev. B* **2015**, 91 (4), 041407.
 26. Wallauer, R.; Reimann, J.; Armbrust, N.; Gddde, J.; Hfer, U., Intervalley scattering in MoS₂ imaged by two-photon photoemission with a high-harmonic probe. *Appl. Phys. Lett.* **2016**, 109 (16), 162102.
 27. Ceballos, F.; Cui, Q.; Bellus, M. Z.; Zhao, H., Exciton formation in monolayer transition metal dichalcogenides. *Nanoscale* **2016**, 8 (22), 11681-11688.
 28. Shah, J.; Pinczuk, A.; Gossard, A. C.; Wiegmann, W., Energy-Loss Rates for Hot Electrons and Holes in GaAs Quantum Wells. *Phys. Rev. Lett.* **1985**, 54 (18), 2045-2048.
 29. Breusing, M.; Kuehn, S.; Winzer, T.; Malić, E.; Milde, F.; Severin, N.; Rabe, J. P.; Ropers, C.; Knorr, A.; Elsaesser, T., Ultrafast nonequilibrium carrier dynamics in a single graphene layer. *Phys. Rev. B* **2011**, 83 (15), 153410.

30. Vega-Mayoral, V.; Vella, D.; Borzda, T.; Prijatelj, M.; Tempira, I.; Pogna, E. A.; Dal Conte, S.; Topolovsek, P.; Vujcic, N.; Cerullo, G.; Mihailovic, D.; Gadermaier, C., Exciton and charge carrier dynamics in few-layer WS₂. *Nanoscale* **2016**, 8 (10), 5428-5434.
31. Cui, Q.; Ceballos, F.; Kumar, N.; Zhao, H., Transient Absorption Microscopy of Monolayer and Bulk WSe₂. *ACS Nano* **2014**, 8 (3), 2970-2976.
32. Yan, T.; Qiao, X.; Liu, X.; Tan, P.; Zhang, X., Photoluminescence properties and exciton dynamics in monolayer WSe₂. *Appl. Phys. Lett.* **2014**, 105 (10), 101901.
33. Andres, C.-G.; Jorge, Q.; Herko, P. v. d. M.; Nicolás, A.; Gabino, R.-B., Spatially resolved optical absorption spectroscopy of single- and few-layer MoS₂ by hyperspectral imaging. *Nanotechnology* **2016**, 27 (11), 115705.
34. Li, Y.; Chernikov, A.; Zhang, X.; Rigosi, A.; Hill, H. M.; van der Zande, A. M.; Chenet, D. A.; Shih, E.-M.; Hone, J.; Heinz, T. F., Measurement of the optical dielectric function of monolayer transition-metal dichalcogenides: MoS₂, MoSe₂, WS₂, and WSe₂. *Phys. Rev. B* **2014**, 90 (20), 205422.
35. Wang, G.; Marie, X.; Bouet, L.; Vidal, M.; Balocchi, A.; Amand, T.; Lagarde, D.; Urbaszek, B., Exciton dynamics in WSe₂ bilayers. *Appl. Phys. Lett.* **2014**, 105 (18), 182105.
36. Sun, D.; Rao, Y.; Reider, G. A.; Chen, G.; You, Y.; Brézin, L.; Harutyunyan, A. R.; Heinz, T. F., Observation of Rapid Exciton–Exciton Annihilation in Monolayer Molybdenum Disulfide. *Nano Lett.* **2014**, 14 (10), 5625-5629.
37. Nie, Z.; Long, R.; Teguh, J. S.; Huang, C.-C.; Hewak, D. W.; Yeow, E. K. L.; Shen, Z.; Prezhdo, O. V.; Loh, Z.-H., Ultrafast Electron and Hole Relaxation Pathways in Few-Layer MoS₂. *J. Phys. Chem. C* **2015**, 119 (35), 20698-20708.

38. Amani, M.; Lien, D.-H.; Kiriya, D.; Xiao, J.; Azcatl, A.; Noh, J.; Madhvapathy, S. R.; Addou, R.; KC, S.; Dubey, M.; Cho, K.; Wallace, R. M.; Lee, S.-C.; He, J.-H.; Ager, J. W.; Zhang, X.; Yablonovitch, E.; Javey, A., Near-unity photoluminescence quantum yield in MoS₂. *Science* **2015**, *350* (6264), 1065-1068.
39. Han, H.-V.; Lu, A.-Y.; Lu, L.-S.; Huang, J.-K.; Li, H.; Hsu, C.-L.; Lin, Y.-C.; Chiu, M.-H.; Suenaga, K.; Chu, C.-W.; Kuo, H.-C.; Chang, W.-H.; Li, L.-J.; Shi, Y., Photoluminescence Enhancement and Structure Repairing of Monolayer MoSe₂ by Hydrohalic Acid Treatment. *ACS Nano* **2016**, *10* (1), 1454-1461.
40. Amani, M.; Taheri, P.; Addou, R.; Ahn, G. H.; Kiriya, D.; Lien, D.-H.; Ager, J. W.; Wallace, R. M.; Javey, A., Recombination Kinetics and Effects of Superacid Treatment in Sulfur- and Selenium-Based Transition Metal Dichalcogenides. *Nano Lett.* **2016**, *16* (4), 2786-2791.
41. Amani, M.; Burke, R. A.; Ji, X.; Zhao, P.; Lien, D.-H.; Taheri, P.; Ahn, G. H.; Kiriya, D.; Ager, J. W.; Yablonovitch, E.; Kong, J.; Dubey, M.; Javey, A., High Luminescence Efficiency in MoS₂ Grown by Chemical Vapor Deposition. *ACS Nano* **2016**, *10* (7), 6535-6541.

Chapter 5

Summary and Outlook

5.1 Summary

Two-dimensional (2D) materials with many potential applications have attracted lots attentions, many experimental methods have been applied on these materials. Due to the tens micrometres size scale, it is very hard for traditional methods without spatial resolution to locate the sample. Even more, the properties of monolayer 2D materials are very sensitive to surface defects, strains, impurities and even the substrate. The nanometres scale resolution become essential in 2D materials' research. To achieve better performance in applications, the ultrafast measurement is very necessary in these materials. In this thesis, the home-build time-resolved photoemission electron microscopy (TR-PEEM) can provide sub-80-nm spatial resolution along with 46-fs temporal resolution, which is suitable to the researches on the 2D materials.

In these TR-PEEM experiments on 2D materials, a pump pulse of photon energy $\hbar\omega_{pu}$ injects electrons into the conduction band, following which a probe pulse of photon energy $\hbar\omega_{pr}$ ejects electrons with energies that lie within $\hbar\omega_{pr}$ of the vacuum level into the continuum. The photoelectrons that are ejected by this two-photon photoemission process pass through several electrostatic lenses to form a magnified image of the sample surface at the detector. Recording the PEEM image as function of pump-probe time delay yields the time evolution of the population of conduction band electrons that is present within $\hbar\omega_{pr}$ of the vacuum level. First, we employ femtosecond time-resolved photoemission electron microscopy (TR-PEEM) to investigate the sub-picosecond to picosecond carrier dynamics of monolayer WSe₂. Spatially integrated analysis of single flakes yields timescales of 0.1 ps for exciton formation and 1 ps for Auger-mediated trapping and/or recombination. And the time constant and amplitude mapping of WSe₂ flake are presented here to investigate the spatially relative influence. The

edge region and nucleation site show their influence on local density of state and ultrafast dynamic process. The inhomogeneous displayed on WSe₂ flakes' PEEM images caused by defects also demonstrate their influence on ultrafast process. Then the investigation on few-layer MoS₂ materials is also performed still by TR-PEEM, we find the auger-mediated exciton formation process along with exciton-exciton annihilation. The rate for the auger-mediated exciton formation and exciton-exciton annihilation process are $0.15 \pm 0.02 \text{ cm}^2/\text{s}$ and $0.047 \pm 0.002 \text{ cm}^2/\text{s}$, respectively. In the spatial analysis, the hot spot that could be caused by the aggregation of defects shows no obvious correlation in time and amplitude mapping, which means that the process we observed is not very sensitive to the defects. The long tail in the histogram of slow decay process suggests the competition between auger-mediated exciton formation and exciton-exciton annihilation within 8 ps. For even larger decay time, it could even involve the defect-assisted auger process.

5.2 Outlook

The lack of energy resolved ability in our TR-PEEM limits us to further reveal the unknown ultrafast process. Hope my supervisor can get new funding to upgrade our instrument. The photon energy of probe pulse is too low to monitor the electron dynamics far away from Γ region in K space. In our case of missing energy resolved ability, the limit probe window makes us focus on narrow probe window and get rid of other distractions from other valleys. After the upgrade of PEEM instrument, the higher probe energy would help us distinguish the electrons dynamics in a wider K space. For example, the photon energy of probe pulse should be more than 16 eV^{1-3} to monitor the electron dynamics in K valley. Another possibility of combining PEEM and attosecond pulse with EUV photon energy have been demonstrated in Germany.⁴⁻⁵ In this case, we can monitor much fast electron motion in 2D materials. The fixed pump wavelength is another limitation on our experiment, but we have started to set up a NOPA to tune the pump wavelength.

As an important research tools, PL and Raman mapping on 2D materials have been reported.⁶⁻⁹ During 2D materials' study, a comparison between the results of TR-PEEM and PL or Raman is missing, I think we could have a more profound finding.

Other experiments on different materials such as perovskite, metals and hybrid system of metal and 2D materials can also be investigated.

5.3 Reference

1. Wallauer, R.; Reimann, J.; Armbrust, N.; Gdde, J.; Hfer, U., Intervalley scattering in MoS₂ imaged by two-photon photoemission with a high-harmonic probe. *Appl. Phys. Lett.* **2016**, *109* (16), 162102.
2. Grubišić Čabo, A.; Miwa, J. A.; Grnborg, S. S.; Riley, J. M.; Johannsen, J. C.; Cacho, C.; Alexander, O.; Chapman, R. T.; Springate, E.; Grioni, M.; Lauritsen, J. V.; King, P. D. C.; Hofmann, P.; Ulstrup, S., Observation of Ultrafast Free Carrier Dynamics in Single Layer MoS₂. *Nano Lett.* **2015**, *15* (9), 5883-5887.
3. Hein, P.; Stange, A.; Hanff, K.; Yang, L. X.; Rohde, G.; Rossnagel, K.; Bauer, M., Momentum-resolved hot electron dynamics at the 2H-MoS₂ surface. *Phys. Rev. B* **2016**, *94* (20), 205406.
4. Hentschel, M.; Kienberger, R.; Spielmann, C.; Reider, G. A.; Milosevic, N.; Brabec, T.; Corkum, P.; Heinzmann, U.; Drescher, M.; Krausz, F., Attosecond metrology. *Nature* **2001**, *414* (6863), 509-513.
5. Stockman, M. I.; Kling, M. F.; Kleineberg, U.; Krausz, F., Attosecond nanoplasmonic-field microscope. *Nat. Photonics* **2007**, *1* (9), 539-544.
6. Yore, A. E.; Smithe, K. K. H.; Crumrine, W.; Miller, A.; Tuck, J. A.; Redd, B.; Pop, E.; Wang, B.; Newaz, A. K. M., Visualization of Defect-Induced Excitonic Properties of the Edges and Grain Boundaries in Synthesized Monolayer Molybdenum Disulfide. *J. Phys. Chem. C* **2016**, *120* (42), 24080-24087.

7. Su, W.; Kumar, N.; Mignuzzi, S.; Crain, J.; Roy, D., Nanoscale mapping of excitonic processes in single-layer MoS₂ using tip-enhanced photoluminescence microscopy. *Nanoscale* **2016**, 8 (20), 10564-10569.
8. Park, K. D.; Khatib, O.; Kravtsov, V.; Clark, G.; Xu, X.; Raschke, M. B., Hybrid Tip-Enhanced Nanospectroscopy and Nanoimaging of Monolayer WSe₂ with Local Strain Control. *Nano Lett.* **2016**, 16 (4), 2621-2627.
9. Andres, C.-G.; Jorge, Q.; Herko, P. v. d. M.; Nicolás, A.; Gabino, R.-B., Spatially resolved optical absorption spectroscopy of single- and few-layer MoS₂ by hyperspectral imaging. *Nanotechnology* **2016**, 27 (11), 115705.

Publication list

1. **Lin Wang**, Shu-Zee Alencious Lo, Ce Xu, and Zhi-Heng Loh, Femtosecond time-resolved photoemission electron microscopy for imaging the spatially heterogeneous carrier relaxation dynamics of semiconductors. (Submitted)
2. **Lin Wang**, Ce Xu, Ming-Yang Li, Lain-Jong Li, and Zhi-Heng Loh, Unraveling Spatially Heterogeneous Ultrafast Carrier Dynamics of Single-Layer WSe₂ by Femtosecond Time-Resolved Photoemission Electron Microscopy. (Ready to submit)
3. **Lin Wang**, Ce Xu, Ming-Yang Li, Lain-Jong Li, and Zhi-Heng Loh, Ultrafast Dynamics in four-layer MoS₂ Investigated by Time-Resolved Photoemission Electron Microscopy. (In preparation)
4. Zhengrong Wei, Jialin Li, **Lin Wang**, Soo Teck See, Mark Hyunpong Jhon, Yingfeng Zhang, Fan Shi, Minghui Yang and Zhi-Heng Loh, Elucidating the origins of multimode vibrational coherences induced by intense laser fields. *Nature Communications* **2017**, 8, 735