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Harnessing the Spin-Degree of Freedom of Spin-Orbit Materials in Time, Energy,  
Momentum, and Real-Space

by

Samuel Ciocys

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Physics

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Alessandra Lanzara, Chair

Professor Lane Martin

Professor Zi Qiu

Summer 2022



Harnessing the Spin-Degree of Freedom of Spin-Orbit Materials in Time, Energy,  
Momentum, and Real-Space

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Samuel Ciocys

## Abstract

Harnessing the Spin-Degree of Freedom of Spin-Orbit Materials in Time, Energy,  
Momentum, and Real-Space

by

Samuel Ciocys

Doctor of Philosophy in Physics

University of California, Berkeley

Professor Alessandra Lanzara, Chair

My PhD experience has been focused on identifying and pursuing gaps in the understanding and implementation of spin-based phenomena. I primarily focus on  $\text{Bi}_2\text{Se}_3$ , due to its pervasiveness in the literature, safe and low-cost constituent elements, as well as the fact that its remarkably simple topological band structure functions as an ideal testbed for spin-momentum locked physics.

The ideal spintronic material should have spin-orbit coupling that can be easily and reversibly tuned on ultrafast timescales. From the viewpoint of an ARPES experimentalist, ultrafast infrared pulses are a logical choice for implementing picosecond modifications. Furthermore, the effect of light on Rashba and topological systems has not fully transitioned from material characterization into the realm of engineered systems. For the first portion of my studies, I engineered Rashba-split quantum well states on the surface of a topological insulator and demonstrated the precise control of the spin and energy degrees of freedom as well as the density of states at the Fermi level. Chapters 2 through 5 represent the bulk of my PhD controlling surface band bending to generate ultrafast surface fields in topological insulators. These chapters follow a single coherent and chronological journey from my personal recognition of the effect (Ch. 2) to the exploration of the surface dipole effect on electron trajectory (Ch. 3) to the engineering of the SPV to drive ultrafast electric-field induced changes in quantum well states (Ch. 4 and Ch. 5). The unprecedented control of nearly all aspects of the band structure using photons presents a foundation for coupling spintronic and photonic systems, essential for integrating fiber optic communications with future spin-based devices.

Additionally, I pursue the issue no one wants to talk about for quantum material applications: scaling growth methods while preserving essential properties. This has been one of the main sticking points in not only 2D material fabrication (think mass graphene production or twistrionic applications) but also for 3D bulk systems that depend heavily on single crystal

quality. In my pursuit of understanding spin-orbit coupling in amorphous topological insulators, my collaborators and I discovered spin-momentum locking in amorphous  $\text{Bi}_2\text{Se}_3$  grown through scalable room-temperature thermal evaporation. Chapter 6 details my work investigating strongly dispersive band structures in amorphous materials and the implications to amorphous topology and fermiology. These efforts demonstrate that spin-momentum locking can exist in the amorphous state, and provide an avenue for extracting the same momentum-dependent physics in crystals but for the much larger (and production-feasible) material category of non-crystalline matter.

Finally, Chapter 7 continues in my motivation to expand real-world applications for spin-polarized materials. Solid state spin-filters can be applied to free electrons in vacuum, an intriguing prospect that has implications for spin-resolved microscopy/spectroscopy techniques and has been pursued for decades. I present my work leading a team to design a prototype transmission spin-filter for free electrons. I go over the methods we have developed and optimized to measure electron transmission through membranes and our successful attempts at growing ultrathin free-standing magnetic films, resulting in a groundbreaking spin-filter prototype.

To my wife, Emma

I could not have completed this PhD without your unending support. We met during my second year of graduate studies before either of us knew what we were getting into. We fell in love quickly and it transformed my life and work overnight. Your commitment began at the very beginning, moving to the US to join me on this crazy adventure and you have remained a rock in the final tumultuous half-decade of this busy journey. All of my work has elements of your dedication to my progress, the extra push to achieve something great. We built this together, tusen takk for at du støtter meg.

To my friend, Jagger

Thank you for biting my laptop screen and chewing the hair off my head during our pandemic work-from-home adventures. It wasn't the motivation I needed, but the motivation I deserved. It has been a trying few months at the end here, for us both, but I've enjoyed every second of our journey. You have been more than a cat to me. You always will be.

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# Chapter 1

## Introduction

The irreversibility of society's demand for information is in many ways interconnected to the demand and looming crisis of world-wide energy consumption. As we now are searching for alternative sources of energy that can be scaled to match and exceed fossil fuels while reducing our carbon footprint, we too need to search for new materials that can exceed the limitations of conventional semiconductors to process and send information with reduced losses. World-wide, data centers and information technology contribute to thousands of terawatt hours of energy consumption making up nearly 2% of total human energy consumption [1]. This problem is only exacerbated by predictions, based on the current exponential trend, that captured and consumed data will double nearly every three years starting from the current value of 80 zettabytes [2]; An unthinkable amount of information being processed through lossy traditional semiconductor materials. Unless humans plan to scale back any time soon, the future relies on circumventing classical Joule heating by harnessing quantum properties of novel materials *as much as it depends* on green energy alternatives.

New field effect transistor (FETs) designs that reduce the size and energy consumption of processors are implemented on a sub-yearly basis, but in recent years we have begun to reach the limit of downsizing, achieving only marginal gains [3]. This limitation points to a need to re-design traditional silicon chip architectures in the near future. A promising direction for overhauling data processing hardware is to take advantage of the electronic spin-degree of freedom, or spintronics. One of the major restrictions in implementing spintronic methods is that the full benefit of using the spin-degree of freedom requires a top to bottom re-designing of traditional silicon chip architectures, requiring methods to generate, store, transport, and manipulate spin currents effectively and seamlessly [4]. But the switch may be worth it, since by harnessing the power of spin, additional electronic behaviors emerge that reduce the energy cost of manipulating and transporting information and may even lead to improved energy harvesting.

## 1.1 Spin-Orbit Coupling and the Rashba Effect

Materials with a flexible spin-degree of freedom fall largely into two categories: 1) magnets, exhibiting real-space dependence of electronic spin and 2) spin-orbit coupled materials, exhibiting momentum-space dependence of electronic spin. Though magnetic systems currently serve as an effective means for data storage, spin-orbit materials have a variety of properties that are promising for spin transport and manipulation.

To examine further, we can start by understanding the spin-orbit effect and one of the prime examples of a spin-orbit coupled phenomenon. Spin-orbit coupling in atomic physics is the interaction of the spin of the electron and the orbital magnetic field [5]. The analogy can be held for a solid state system, albeit the orbital calculation becomes a bit more complicated due to the local environment of bonded atoms. From the single atom approach, we can estimate the magnetic field as:

$$\vec{B} = -\frac{\vec{v}}{c^2} \times \vec{E} \quad (1.1)$$

Assuming a spherically symmetric electric potential we can write down the field as:

$$\vec{E}(\vec{r}) = E(r)\hat{r} \quad (1.2)$$

The energy of the interaction is given by the Hamiltonian:

$$H = -\vec{\mu}_s \cdot \vec{B} \quad (1.3)$$

From plugging in the relevant formulas above we get the following relationships:

$$H \propto \frac{E(r)}{r} \vec{\mu}_s \cdot (\vec{r} \times \vec{v}) \quad (1.4)$$

$$\propto \frac{E(r)}{r} \vec{S} \cdot (\vec{r} \times \vec{p}) \quad (1.5)$$

$$\propto \frac{1}{r} \frac{\partial U}{\partial r} \vec{L} \cdot \vec{S} \quad (1.6)$$

Since the Coulomb potential is  $U(r) \propto Z/r$  and we can make a hydrogenic atomic approximation of  $r \sim a_0/Z$ , our resulting difference in energy for two spins from the Hamiltonian has the proportional form of:

$$\Delta E_{\text{SOC}} \propto Z^4 (\vec{L} \cdot \vec{S}) \quad (1.7)$$

From the first equation it is clear that relativistic electrons are more susceptible to spin-orbit coupling. And from the final equation it is clear that spin-orbit coupling is strongly dependent on the atomic mass and strongest in materials with heavy elements (High-Z materials). The result is an energy splitting of the orbital derived bands into separate spin-degenerate bands according to the total angular momentum eigenvalue  $J$ . In many

materials, this results in gaps typically of small energy, “spin-orbit gaps”, that show promise for interesting applications [6, 7, 8].

Achieving a momentum dependent spin-polarization, or a separation in the spin-degree of freedom, requires either the breaking of time-reversal symmetry (magnetic materials) or inversion symmetry. In the case that time-reversal symmetry is preserved and inversion symmetry is not, we are allowed the situation that the energy eigenvalues need only to obey the following symmetry:

$$E(k, \uparrow) = E(-k, \downarrow) \quad (1.8)$$

A standard example of a spin-orbit effect that will help in identifying some of the useful aspects of separating the spin-degree of freedom is the Rashba effect. In the Rashba effect, inversion symmetry is broken, for instance at the surface plane of a cleaved crystal [9]. The broken inversion symmetry at the surface allows for an out-of-plane electric field. This transforms Eq. 1.1 to:

$$\vec{B} = -\frac{\vec{v}}{c^2} \times E_R \hat{z} \quad (1.9)$$

and therefore a Rashba Hamiltonian of the form:

$$H_R = \alpha_R(\vec{k} \times \hat{z}) \cdot \sigma = \alpha_R(k_x \sigma_y - k_y \sigma_x) \quad (1.10)$$

From this last equation, it is clear that the surface state electrons will be split in energy depending on whether the electron’s spin is parallel or antiparallel to the effective magnetic field, resulting in a Rashba energy splitting  $\Delta E_R = 2\alpha_R k_{||}$ .

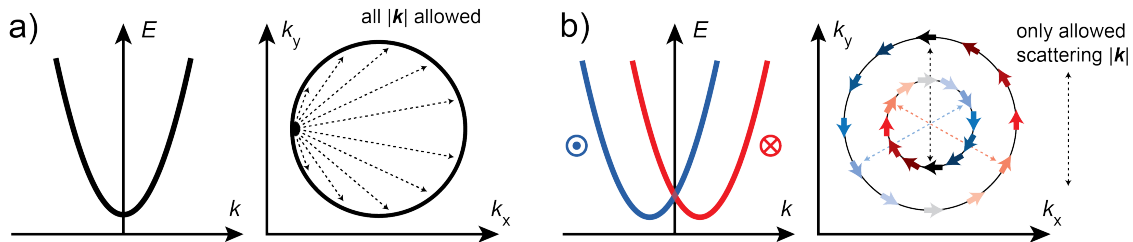


FIGURE 1.1: **Rashba effect and Fermi surface scattering.** **a** Spin-degenerate parabolic band and constant energy surface showing broad spectrum of available scattering  $k$ . **a** Spin-momentum locking in Rashba system reduces available scattering phase space.

The canonical effect on a parabolic dispersion is displayed in Fig. 1.1. Panel a shows the typical parabolic dispersion for a nearly free electron. The Rashba effect (panel b) induces a  $k$ -linear splitting of the spin states in energy, resulting in two identical parabolic dispersions with opposite spin polarization separated in momentum (see blue and red).

Some interesting transport properties emerge upon further inspection of the Rashba dispersion. In the right plot of panel b, we see that the spin of the electron is always perpendicular to the direction of propagation ( $\hat{k}$ ), a property called “spin-momentum locking”. In particular, if the Fermi level is placed at the band bottoms, then left going electrons will always have spin pointing in  $-y$  and right going electrons will have spin in  $+y$ . In this way, Rashba splitting presents an innate ability to generate spin-polarized currents with in-plane electric fields [10]. Moreover, the scattering properties between the spin-degenerate and Rashba cases are significantly different. In the right plot of panel a, an electron scattering from  $(k_x, k_y) = (k_F, 0)$  can scatter to any other  $k$ -state in the Fermi surface since all states are spin-degenerate. This means that a large range of  $\delta k$  scattering channels are available to instigate a scattering event. In contrast, for non-magnetic scattering events, the spin-momentum locking of the Rashba system only allows scattering between matching spin-states. This greatly reduces allowable  $\delta k$  scattering channels offering a level of protection to scattering during transport, increasing the conductivity of the surface state [11].

## 1.2 Rashba Effect in Quantum Wells

The Rashba effect requires broken inversion symmetry breaking and strong spin-orbit coupling. An interesting marriage can be made by combining quantum well structures with spin-orbit coupled materials. In these systems, both the energy degree of freedom and the spin degree of freedom are tied to an underlying potential typically decoupled from the lattice. Lattice potentials are difficult to reversibly modify since they manifest from the tightly bound nuclear cores. Quantum well potentials, on the other hand, are often sourced by geometric confinements that span many crystalline unit cells or charge separation at boundaries. The macro-structure of these potentials makes them more accessible to external stimuli particularly since charge migration plays a role in shaping the potential itself [12].

Quantum wells are also intuitive from a quantum mechanics point of view. The first problem an undergraduate physicist is asked to solve in introductory quantum mechanics is the particle in a box. The confinement potential breaks the continuum spectrum of the free electron into a ladder of energy levels. The effect on material band structures is the same. The top plot of Fig. 1.2a shows a free-electron-like parabolic dispersion (dotted line), measured along the surface plane in momentum-space, reminiscent of a conduction band in a typical semiconductor. The bottom plot illustrates a quantum well potential that confines the conduction band and valence band in a narrow region forming two ladderized quantum well levels. The result is a splitting in energy of the parabolic dispersion into multiple spin-degenerate dispersions (grey). If one can increase the size of the quantum well potential, then the energy splitting is reduced revealing a denser energy packing of energy-split dispersions (panel b). The valence bands are not shown in the above plots, but are shown in real-space in the bottom plots. It can be seen that the energy spacings define the band gap between conduction and valence band edges and form additional gaps between all permutations of conduction band and valence band quantum well levels. These

gaps strongly influence the optical properties of the system without changing the underlying crystal structure. For instance, panel a's primary gap produces a higher energy photon in a lasing condition compare to panel b's primary gap (blue and orange wiggles). This property of quantum well structures serves as the basis for quantum dot applications and quantum well diodes [13, 14].

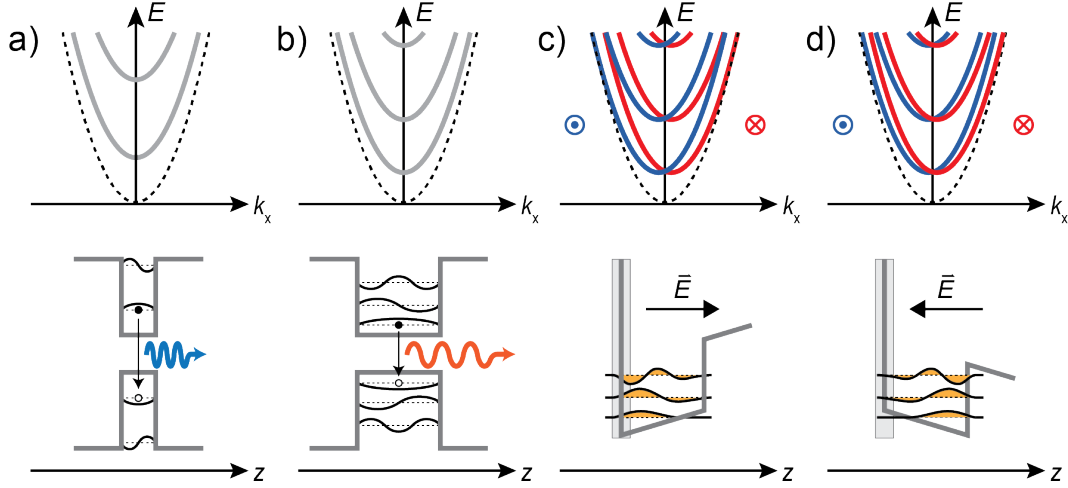


FIGURE 1.2: **Combining quantum wells with the Rashba effect.** **a,b** Width of quantum well determines energy spacing of quantized bands. **c,d** Field at the surface controls wavefunction overlap with inversion symmetry breaking plane, controlling the Rashba effect.

What if we add spin-orbit coupling and inversion symmetry breaking? Panel c illustrates this effect, with the quantum well being terminated at the surface plane (light grey box) and a resulting electric field at the surface enabled by the broken inversion symmetry. The quantum well confinement spin-degenerately splits the parabolas in energy while the Rashba effect spin splits the parabolas in momentum. The strong fields required to induce large Rashba effects are typically not sourced from external fields, but instead the asymmetric nuclear potentials at an inversion symmetry breaking interface. Nevertheless, small applied fields play a critical role in controlling the Rashba effect by migrating the center of mass of the wave-functions towards and away from these nuclear cores [15, 16, 17, 18, 19]. This can be seen in the comparison of panels c and d, where the direction of the applied field determines the strength of the Rashba splitting.

Ultrafast infrared pulses can control the shape of the quantum well potential and therefore the quantization length scale and wave-function overlap with an inversion-symmetry breaking layer (see Ch. 5). In this way, we can control both the energy and spin degrees of freedom as well as the density of states, or in other words, generate an engineered electronic band structure accessible by photons. Manipulation of the energy degree of freedom in quantum wells has produced devices such as quantum well cascade lasers [20]. Controlling the spin-



degree of freedom is crucial for spintronics applications, directly applicable to spin current modulators and spin-logic devices [21, 22, 23]. And, controlling the energy and spin-degree of freedom is a superb mechanism for precisely manipulating the density of states, crucial for engineering emergent phases such as superconductivity, charge density waves, correlated insulators (etc.) in coupled heterostructures such as twistronics [24, 25, 26, 27, 28, 29]. It is clear, that total control of all degrees of freedom in an electronic band structure is ideal for engineering future solid-state devices by tailoring electronic behavior rather than searching for material candidates.

### 1.3 Topological Insulators

Over the last couple of decades, a new class of materials has emerged with promising properties for manipulating the spin-degree of freedom in the solid state: topological insulators. Spin-orbit coupling is essential in the formation of a topological insulator, a distinct state of matter that is defined not by symmetry breaking but by topological invariants that discriminate between topologically inequivalent Hilbert spaces. They exhibit peculiar electronic properties such as an insulating bulk and spin-polarized highly-conductive surface states that are ideal for isolating and manipulating electronic spins. Moreover, the inequivalence of the electronic topology of a topological insulator and the vacuum guarantees the existence of these surface states regardless of the conditions at the surface, promising highly robust room-temperature applications [30, 31, 32, 33]. Three dimensional topological insulators have been realized since the millennium, such as  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$ , with surface state band structures that resemble the first theorized toy-model [34]. They serve as ideal platforms to probe and tune the electronic behavior and spin dynamics of spin-polarized topological surface states.

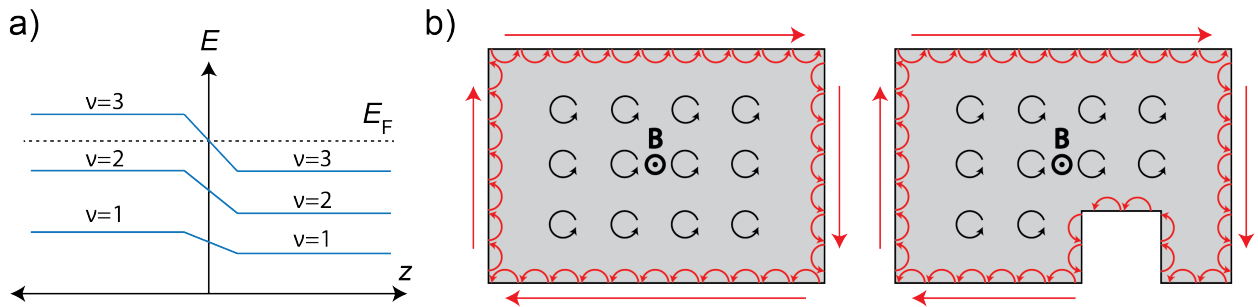


FIGURE 1.3: **Basics of the quantum Hall effect.** **a** At the boundary between two inequivalent Landau quantized bulks, the Fermi level can be tuned to intersect a quantized band leading to a conductive edge state. **b** Classical picture of edge state: bulk is insulating due to cyclotron orbits and electrons skip along the surface in a defined direction. Edge state is robust to back-scattering due to chiral nature.

The quantum Hall effect (QHE) is the typical introductory example to understanding surface states in topological insulators. Though it is not a perfect analogy and the full history of quantized Hall effect is necessary to build a complete picture, it provides a reasonable framework for understanding topology and the presence of chiral edge states. In QHE, a strong magnetic field causes free electrons in a 2D system to form cyclotron orbits, generating Landau levels in the electron spectrum. Fig. 1.3a shows the resulting Landau levels between regions of different field strength, material parameters, or even a vacuum interface (left vs. right z-axis). When a Fermi level is established, two regions of significantly different Landau quantization must form a conductive channel at the interface that intersect  $E_F$ . In panel a, the Fermi level sits in the gap between Landau levels 2 and 3 on the left and Landau levels 3 and 4 on the right. The number of occupied Landau levels is related to the topology of the system by the TKNN formula which defines the quantized Hall conductivity as the “topological invariant” [33]. In panel a, only one channel intersects the Fermi level and this is related to the difference between the occupied Landau levels on the two sides  $\delta\nu = 1$ . This value represents a difference in topology between the two electronic structures which can only be resolved by changing the Landau Level spacing on either side. In the case that the left side is the vacuum barrier, all three channels would intersect the Fermi level at the surface resulting in three populated edge states.

Panel b demonstrates the classical picture for edge conduction. In the bulk of the material, the cyclotron orbits are fully populated localizing the electrons to form an insulating bulk. At the edge, the cyclotron orbits cannot be completed, and instead skip across the surface. The handedness of the orbit, determined by the direction of the magnetic field and sign of the charge carrier, ensures that current can only flow in one direction: a chiral edge state. Flipping the magnetic field direction will result in orbits of the opposite chirality.

In QHE, the edge states are spin degenerate, but by combining spin-orbit coupling and inversion symmetry breaking, the edge state can become spin-polarized due to spin-momentum locking. This is called the quantum anomalous Hall effect (QAHE) [35]. QAHE can be thought of as one half of the topological insulator (at least in 2D). In Fig. 1.4a, I show two QAHE systems with spin-polarized chiral edge states with opposite spin and handedness. The magnetic fields required to form the two systems cancel out when combined, demonstrating the time-reversal symmetry of the 2D topological insulator.

As the band gaps define the topological invariant in the QHE (see Fig. 1.3a), the band gap in a time-reversal symmetric material defines the topology of an insulator. One can ask the question whether a semiconducting or insulating material is topologically equivalent to the vacuum? Or in other words, how does the electron wave-function evolve as it is removed from the crystalline environment into vacuum?

The vacuum looks very much like a material insulator, with a band gap between positrons (holes) and electrons, defined by the rest energy of the electron. The gaps between energy levels of free atoms are topologically equivalent to the vacuum, since you can adiabatically shift the conduction and valence bands for each gap towards the free-electron and positron limit without crossing levels. The first plot in panel b shows the trivial free-atomic conduction and valence band of a particular gap in a trivial semiconductor. In certain materials, local

environment interactions can deform the band structure significantly causing the conduction band and valence band to cross. By turning on spin-orbit coupling (third plot), spin-orbit gaps can form and open a new band gap. This band gap is no longer topologically equivalent to the vacuum, since the valence and conduction band must recross to re-establish the same adiabatic transformation to the electron-positron band gap of the vacuum. The result is a gapped bulk, and at the surface (as the wave-functions approach the vacuum limit) an untwisting of conduction and valence bands to form surface states that cross the gap [30, 33]. This is the 3D topological insulator. The surface states are chiral and spin-polarized, obeying time-reversal symmetry such that  $E(k, \uparrow) = E(-k, \downarrow)$ . The untwisting in real-space and the edge states in  $k$ -space are shown in panel c.

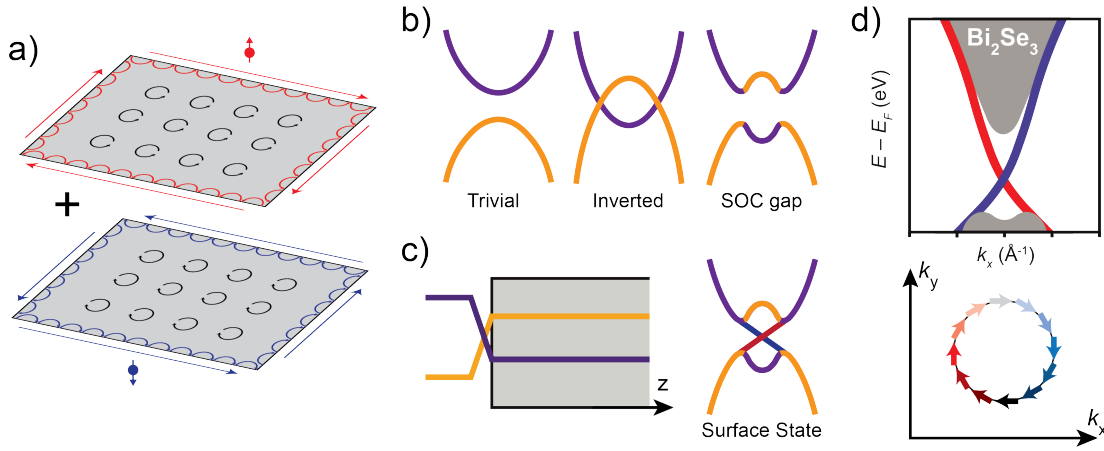


FIGURE 1.4: **Trivial versus topological insulators.** **a** Two copies of QAHE produce time-reversal symmetric topological edge states. **b** Band inversion leads to gap that is inequivalent to the atomic limit. **c** “Untwisting” of gap at surface produces time-reversal symmetric Dirac surface state. **d** Prototypical Bi<sub>2</sub>Se<sub>3</sub> topological insulator surface state and Fermi surface.

The surface states of a topological insulator exhibit the spin-momentum locked characteristics of Rashba states as well as the transport of massless Fermions due to the linear Dirac dispersion [30]. Panel d illustrates the electronic band structure of the realized canonical 3D topological insulator Bi<sub>2</sub>Se<sub>3</sub>. The spin polarized surface states for a Dirac cone (red and blue) span the gap of the bulk valence and conduction bands (grey) [36]. Back-scattering is forbidden without time-reversal symmetry breaking perturbations as can be seen in the Rashba-like spin-texture of the Fermi surface (bottom plot). The surface state then allows for highly-conductive surface channels that are spin-momentum locked and capable of ballistic transport, while the bulk is insulating provided the chemical potential falls in the gap. Moreover, the presence of the surface state is topologically protected in that only a large perturbation that can undo the band inversion throughout the entire bulk can destroy the

spin-polarized states. Magnetic stimuli can gap the surface state, leading to hedgehog spin-textures and 1D chiral edge channels in what are called magnetic topological insulators [37], adding to the richness and potential applications of topological insulators. For these reasons, topological insulators serve as the ideal platform for generating spin-polarized currents, and methods capable of tuning the surface states or adjacent properties are key to developing spin-manipulation devices with low energy cost.

## 1.4 Band Bending in Topological Insulators and Ultrafast Implications

Many of the original ARPES studies on the topological insulator  $\text{Bi}_2\text{Se}_3$  were performed on bulk-conductive samples, n-type doped into the bulk conduction band due to inherent selenium vacancies sequestered during the growth process [38, 39, 40]. Because much of the interesting spin-momentum locking physics occurs at the topological surface state, bulk conducting samples are not ideal for studying surface charge- and spin-dynamics given the strong scattering channels into the conductive bulk, convolving surface and bulk interactions [41, 42, 36]. Alternatively, one can render  $\text{Bi}_2\text{Se}_3$  to be bulk-insulating by introducing small amounts of p-dopants during the growth process such that the surface dynamics are largely isolated from bulk influence. Our studies utilized 1% Mg-doped samples that placed the Fermi level near the bulk valence band.

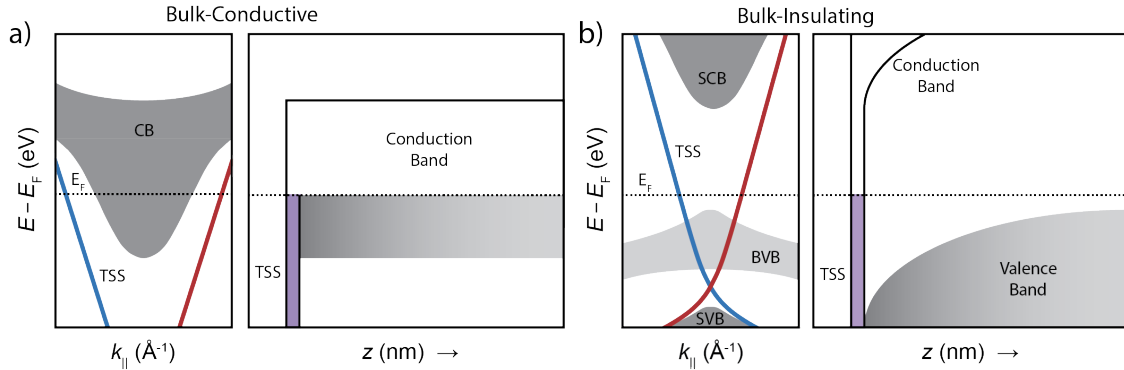


FIGURE 1.5: **Doping-dependent band bending in  $\text{Bi}_2\text{Se}_3$ .** **a** N-type conductive  $\text{Bi}_2\text{Se}_3$ , no band bending. **b** P-type bulk-insulating  $\text{Bi}_2\text{Se}_3$ , surface bands shifted by band bending.

Fig. 1.5 demonstrates the stark difference in surface-to-bulk band structure between n-type bulk-conductive samples and p-type bulk-insulating samples. In the bulk-conductive samples (panel a), the Fermi level cuts through the top of the topological surface state (TSS) and the bottom of the bulk conduction band. This provides a large occupied density of states at the surface and in the bulk and permits a straight forward relaxation channel of

the topological surface state into the bulk conduction band, allowing charge to escape into the bulk easily [41, 43, 44]. On the other hand, the bulk-insulating samples exhibit a Fermi level close to the bulk valence top edge but within the gap. The low carrier concentration in the bulk of the material and the large carrier concentration at the surface creates a p-n junction-like space charge region enabled by the large screening length scale in the bulk. The end result is an in-balance of charge at the surface at equilibrium and a resulting internal electric field that yields significant downward band bending at the surface [45, 46, 47, 48]. Panel b shows how the surface valence band and the bulk valence band are shifted due to this internal band bending. Moreover, the downward band bending effectively n-type dopes the surface band structure revealing more of the Dirac cone above the surface valence band.

In the case of the p-doped samples, the Dirac surface states are the only accessible electrons for transport, and a device can take full advantage of the spin-momentum locking. Moreover, inherent band bending can be controlled by introducing photoexcited carriers via ultrafast infrared pulses. By controlling the band bending, the electric field at the surface (which dictates not only the inversion symmetry breaking of surface states but also localization of such states) can be dynamically modified, presenting an ultrafast means of controlling both the energy and spin degrees of freedom of conductive states.

## 1.5 Applications for Spin-Orbit Devices

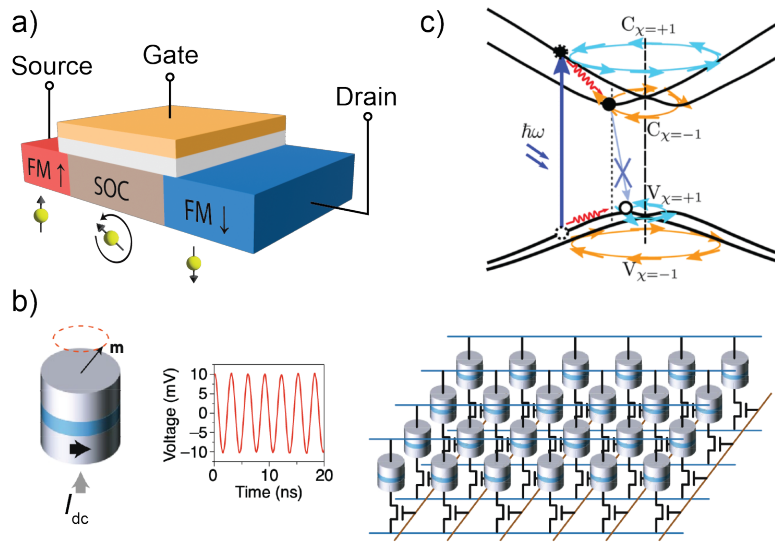
Spintronics is a broad field that encompasses any means of operating with electronic spin rather than electronic charge. The field has mainly been dominated by the use of ferromagnetic and antiferromagnetic materials in order to generate spin-polarized currents and manipulate such currents with the spin-torque effect within heterostructures [22]. However, magnetic materials suffer a variety of drawbacks in real world devices such as miniaturization leading to super-paramagnetism in bulk ferromagnetics, cross-talk from stray fields, and overall weak spin-injection efficiency [49]. Topological insulators and Rashba systems, on the other hand, can reduce the footprint of spintronic elements, decrease joule heating due to diminished back-scattering, and readily produce strong spin-currents as well as exhibit enhanced spin-torque effect [50, 21, 23, 51]. The topological protection of topological surface states also offers a robustness to atmospheric aging providing a stable platform for long-term device operation [52, 53].

There are a myriad of applications for utilizing electronic spin in solid state devices and Fig. 1.6 examines a few of these.

The staple of spintronics devices which motivated an extensive research effort into spin-torque physics is the Datta Das spin-transistor shown in panel a. In 1990, Supriyo Datta and Biswajit Das proposed a transistor based on spin currents that acts as an electronic analog to an electro-optic modulator [54]. The operating principle is that a spin-orbit coupled material is laterally sandwiched between two ferromagnetic materials with opposite magnetization. One ferromagnetic region serves as the source (red region) and injects a spin current aligned to the magnetization vector. The spin-orbit material (brown) rotates the spins via the spin-

torque effect. The second ferromagnetic layer acts as a spin-filter (blue), with the transmitted current dependent on the final alignment of the rotated spin with the magnetization vector. A gate voltage applied to the SOC material tunes the spin-orbit coupling thereby effecting the spin-precession and transmitted current. More recent developments have removed the need for any ferromagnetic materials by using quantum point contacts [55].

Spin-transistors offer incredible theoretical energy savings over charge transfer devices especially when coupled to magnetic storage elements [50]. However, substantial progress is needed to reach optimal efficiencies and can be made through better methods and materials for tuning the Rashba effect and incorporating topological properties.



**FIGURE 1.6: Application of spin and SOC.** **a** Illustration of Datta Das spin modulator: gate voltage controls SOC and therefore spin-precession, FM films act as a polarizer. **b** Neuromorphic STNO element in which spin-precession frequency is controlled by current. Each STNO can influence nearby units and can be easily integrated into large arrays. **c** Rashba effect in perovskite materials enhances lifetimes improving photovoltaic performance. Panel b was adapted with permission from Springer Nature Customer Service Centre GmbH: Springer Nature, Nature Electronics ref. [56] (Neuromorphic Spintronics, Grollier, J. et al.), copyright © 2020. Panel c was reprinted with permission from ref. [57]. Copyright © 2015 American Chemical Society.

Spintronic materials are playing a key role in the development of neuromorphic computation, an exciting application for spin-orbit materials [56, 50, 58]. In a traditional computer, the act of processing and storage are delegated to separate portions of the hardware. In this “von Neumann” architecture, data is continuously transferred between the two branches to achieve desired computation. A neuromorphic computer, so named as it is an attempt to

mimic animal neurons, localizes data processing and memory in the same component. The hope is that neuromorphic computing will reduce energy consumption in intensive applications such as approaching artificial intelligence through machine learning. For instance, the human brain running on 20 W far exceeds our best supercomputers running on 10 MW [59]. State-of-the-art machine learning algorithms already use neural networks with neuromorphic elements simulated on von Neumann machines. A transition to physical neuromorphic elements can reduce the energy cost by removing the intermediate computational step and increase the computing power of neural networks by more effectively utilizing chip footprints [58, 50].

Panel b presents a type of neuromorphic logic element called a spin-torque nano-oscillator (STNO) [56]. The operating principle is very similar to the Datta Das transistor. An applied current passes through a permanent magnet to form a spin-polarized current. The spin-torque effect occurs at a junction interface causing the magnetization of the top magnetic layer to precess. Both the natural frequency and amplitude of the precession is non-linear with current, and the applied current for each element can serve as weights within the neural network. Moreover, the oscillation amplitudes have memory due to the non-zero relaxation time of the magnetization which mimics the leaky integration of biological neurons, a property that makes STNOs ideal for “reservoir computing” by multiplexing the response in time. For instance, a single STNO has been shown to emulate a network of 400 neurons through time-multiplexing to recognize spoken digits with high fidelity [60]. The elements can also be coupled to neighbors through non-local magnetic interactions simulating the synchronization of synaptic connections in the brain (see bottom right panel b)[56].

Arrays of STNOs can be fabricated using existing metal oxide semiconductor techniques and are ultra-compact. Though the neural network architecture provides energy efficiency for particular computational problems, power consumption of STNO elements need to be improved to approach biological neurons or even modern CMOS transistors [21]. This can be achieved through the same solutions as the Datta Das transistor, by improving the spin-torque efficiency and reducing heat generation by incorporating topological insulators or giant Rashba effect materials for the spin-torque process. Preferably, the material would be deposited in a means that is scalable and fits within the current semiconductor chip fabrication paradigm, such as thermal evaporative methods.

Solid state energy harvesting methods typically rely on charges to do work or store energy. Although it is a young field, spin can be a player in the effort of energy production. Methods for spintronic energy production include spin thermoelectric conversion and mechanospin conversion through phonon-magnon coupling [21, 50]. Yet, a relevant example for spin-orbit coupling’s role in energy conversion can be found in perovskite photovoltaics. Though still charge-based energy harvesting, perovskites demonstrate the importance of controlling the spin-degree of freedom for engineering suitable properties for next-generation devices. Panel c showcases the benefit of the Rashba splitting in perovskite band structure in terms of the charge relaxation properties in a photovoltaic material [57, 61]. The spin-texture of the Rashba splitting inhibits direct relaxation of photoexcited carriers and the spin-momentum locking reduces scattering rates, enhancing the lifetime of the carriers and enabling large

photovoltaic power conversion efficiency.

## 1.6 Further Reading on Instrumentation

The completion of my PhD required gaining expertise on a myriad of complicated instrument and experimental methods. For instance, I have performed momentum-resolved measurements using laser-based and synchrotron-sourced equilibrium Angle Resolved PhotoEmission Spectroscopy (ARPES), studied electron dynamics with time-resolved ARPES, and measured spin-polarized band structure in spin-resolved ARPES. I have also studied real-space electronic structure with the MAESTRO  $\mu$ -ARPES endstation, the eV-TEM electron microscope cartridge, and with spin-resolution in the Spin-Polarized Low-Energy Electron Microscope (SPLEEM). The typical ARPES group PhD thesis contains an explanation on the fundamentals of ARPES and its related methods. For the sake of the reader and given the large number of instruments, the plethora of presented data in this thesis, and the already established literature and obligatory thesis entries on the operation and principle for such systems, my thesis contains only limited details of the instrumentation in respective chapters. I instead point the reader to a variety of sources to supplement their understanding of the work in this thesis.

For the ARPES principles of operation, Sobota et al. provides a clear overview of ARPES and its applications [62]. This is followed by Andrea Damascelli with additional basic principles overview and details on momentum-distribution curve (MDC) and energy-distribution curve (EDC) self-energy analysis [63]. And we cannot forget this elegant guide to ARPES matrix elements from Simon Moser [64]. The extension into the time domain with time-resolved ARPES is covered by Smallwood et al [65] and the extension into the spin domain is explained by Jozwiak et al. [66] with the spin time-of-flight spectrometer. Both aforementioned systems from Jozwiak and Smallwood are the same instruments used in this thesis. One can also find overviews for applying multiple ARPES derived experiments on topological systems in the following citations [67, 68]. For the SPLEEM, Rougemaille and Schmid provide a detailed explanation of the principles of spin-polarized magnetic imaging using low energy electrons [69]. And finally, Geelen et al. explain their invention of the eV-TEM microscope in detail [70].

Throughout the thesis, the experiments are described in detail, and ARPES/SPLEEM familiar readers will require very little additional outside information to follow along.



## Chapter 2

# Manipulating Long-Lived Topological Surface Photovoltage in Bulk-Insulating Topological Insulators

I begin this section by stating that topological insulators are an ideal system to host surface photovoltages. The key ingredients to generating the surface band bending required in surface photovoltage materials is an insulating bulk and in-gap states at the surface. Most semiconductors can exhibit an SPV effect; fitting the criteria for an insulating bulk when doped accordingly and hosting in-gap surface states from either the broken translational symmetry at the surface plane or from flat bands generated by dopants, impurities, or atomic vacancies at the surface [71, 46, 45]. But in a traditional semiconductor, these in-gap states are highly susceptible to the surface condition such that atmospheric contaminants, surface topography, and optical aging play a large role in determining the SPV properties in practical applications [46, 72].

On the other hand, topological insulators check both boxes by definition. When intrinsically doped, a topological insulator is insulating in the bulk but it also has topologically protected states at the surface. This ensures that the density of states at the surface is inequivalent to the density of states in the bulk, forcing an in-balance of charge and a band bending space charge region. The large density of states and the topological protection awarded to the surface state fortifies the SPV properties, reducing the effect of extrinsic surface wearing. Moreover, the SPV inherits unique properties from the spin-momentum locking of the surface state. Spin-momentum locking tends to increase photoexcited carrier lifetimes by reducing back-scattering and direct-transition relaxation channels [23, 57, 51]. It also means that charge transport in the surface plane is inherently spin-polarized, making topological surface photovoltages a promising platform for spintronics applications.

This chapter explores my first study on the surface photovoltage in p-type  $\text{Bi}_2\text{Se}_3$  (published in *npj Quantum Materials* in 2020 [48]) discussing the ramifications of fluence dependent ultrafast infrared pulses on the intensity and lifetime of the surface photovoltage. We demonstrate the ubiquity of the SPV effect by comparing bulk-conductive and bulk-

insulating samples of both  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$ . Furthermore, we developed a theoretical framework to understand the long lifetimes by considering the separation of photoexcited charges.

## 2.1 Introduction

The surface photovoltage effect (SPV) in conventional semiconductors is a well-known phenomenon used extensively for semiconductor characterization across a wide range of material properties [71, 46]. The SPV describes an illumination-induced change in the surface potential as a result of photoexcited carriers canceling intrinsic band bending. In conventional semiconductors, broken translational symmetry at the surface results in the formation of in-gap states. As a result, charge redistributes at the surface inducing an internal electric field and subsequent band bending. Upon illumination, charge that was locked in the in-gap states can migrate back to the bulk and cancel the intrinsic field, producing a non-equilibrium potential [71, 46, 45]. The in-gap surface states of a topological insulator are symmetry-protected and spin-momentum locked inhibiting backward scattering, in contrast to the semiconductor SPV [34, 33]. This translates into a highly conductive surface and generation of radial spin currents weakly affected by disorder.

Despite previous predictions [73] and observations of the SPV effect [74, 75, 76, 77] in topological insulators, it is still not clear whether this is an intrinsic property of topological materials and under which conditions it can be realized. Moreover, previous reports rely on narrow temporal ranges and an indirect determination of the time constant, which has led to the misinterpretation of the SPV time-profile [78, 79, 80]. Full characterization of the effect over a larger temporal range is needed in order to directly determine the time constant of the effect.

In this study we reveal that when the prototypical topological insulators  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  are doped into the bulk band gap and are pumped with 800 nm light, a strong, long-lived ( $\sim 10$  ns) and tunable SPV effect develops. We show that both the magnitude and timescale of the SPV can be easily manipulated by changing the fluence, making it very appealing for device applications. These findings were made possible by virtue of Time-Resolved Angle-Resolved PhotoEmission Spectroscopy (TR-ARPES) enabling direct measurement of the chemical potential as a function of pump-probe delay. Furthermore, our study employs a much larger delay range in both negative and positive delay values than any previous SPV study on topological insulators. We argue that the ideal situation to realize such an effect is when the chemical potential falls within the band gap, due to the intricate relation between the existence of a topological surface state, the band bending of the insulating bulk and photoexcited hole trapping in the bulk.

## 2.2 Crystal Growth and Pump-Probe Methods

The  $\text{Bi}_2\text{Se}_3$  single crystals were grown via directional slow solidification with  $\approx 1$  at. % Mg substitution with bismuth to achieve a Fermi energy in the bulk gap. The  $\text{Bi}_2\text{Te}_3$  crystals were grown through the same process with Sn-doping of  $\approx 0.3$  at. % with respect to bismuth. The crystals were cleaved before measurement along the (111) plane at a pressure of  $5 \times 10^{-11}$  Torr to ensure a clean surface for ARPES. Fluence dependent measurements were acquired at the base temperature of our system with liquid nitrogen,  $\sim 80$  K. Temperature dependent measurements were taken using a resistive heater and thermal probe close to the sample stage.

The  $\text{Bi}_2\text{Se}_3$  sample is pumped with 1.5 eV photons generated by a cavity-dumped Ti:sapphire oscillator operating with a repetition rate of 500 kHz. It is then probed with 6 eV photons generated by frequency quadrupling in two stages of BBO crystals. The delay between pump and probe pulses is controlled by a mechanical translation stage that varies the pump path length, with  $\tau = 0$  referring to temporal overlap of the two pulses and positive delays referring to the probe pulse arriving after the pump. The pump and probe beam spot full-width-half-maxes on the sample were  $127 \mu\text{m}$  and  $80 \mu\text{m}$  respectively. The pump beam drifted no more than  $20 \mu\text{m}$  across the entire range of the delay stage determined via CCD camera [65]. In order to achieve fluence dependent measurements, the pump power was filtered to achieve fluences in the range of 0.09 to  $27.5 \mu\text{J}/\text{cm}^2$ . All reported fluence values are for incident fluence on the  $\text{Bi}_2\text{Se}_3$  surface.

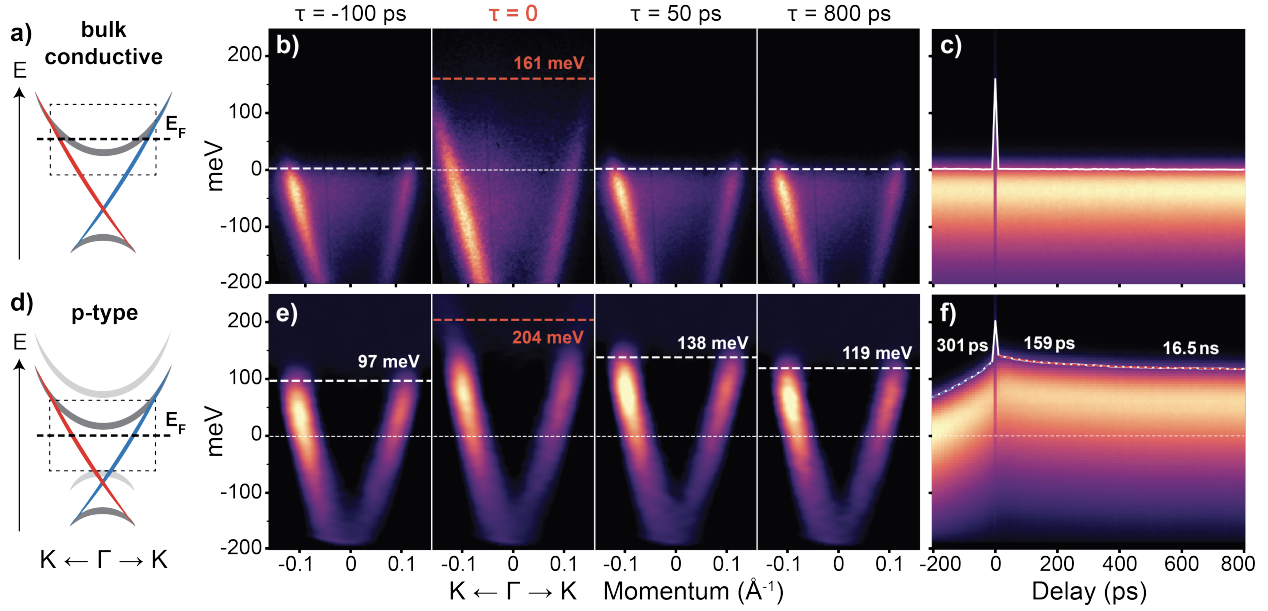
Both the pump and probe were p-polarized incident on the sample. The equilibrium electronic population is imaged with the pump blocked in order to establish the equilibrium Fermi level, when only the bulk valence band and the bottom of the upper topological surface state Dirac cone are populated. With the pump exposed, pump induced excited states above  $E_F$  are imaged at controllable delay times before and after excitation.

The method of growth and time-resolved fluence-dependent characterization are similar through out the following four chapters (Ch. 2 through Ch. 5).

## 2.3 Comparing Bulk-Conductive and P-Type Insulating Dynamics in $\text{Bi}_2\text{Se}_3$

Fig. 2.1 presents transient ARPES spectra showing the distribution of electrons as a function of energy and momentum along a  $\Gamma - \text{K}$  cut through the Brillouin zone for the  $\text{Bi}_2\text{Se}_3$  bulk-conductive and p-type (bulk Mg-doped) topological insulator. The delay of the probe with respect to the pump is represented by  $\tau$ . Spectra were taken with  $\sim 30 \mu\text{J}/\text{cm}^2$  incident fluence. As schematically shown in Fig. 2.1a and 2.1d, the Fermi level,  $E_F$ , of the electron-doped sample intersects the bottom of the bulk conduction band. For the p-type sample (Fig. 2.1d),  $E_F$  lies in the bulk gap near the bulk valence (bulk bands in light grey) and the surface bands are shifted down due to band bending. Band bending does not occur in the bulk-conductive samples, since the metallic bulk forbids a non-uniform potential. For the

bulk-conductive samples at  $\tau = -100$  ps (Fig. 2.1b), photoemission intensity fills the upper Dirac cone up to the Fermi level. After optical excitation with 1.5 eV photons, states above  $E_F$  are populated including the bulk conduction band and surface resonance states [36]. We observe a continuation of the topological surface state linearly dispersing  $> 150$  meV above  $E_F$ . At 50 ps and 800 ps, the excited states have decayed back to equilibrium and states are populated only up to  $E_F$ .



**FIGURE 2.1: Comparison between bulk-conductive and p-type electronic dynamics.** **a-c** presents electron-doped (bulk-conductive) Bi<sub>2</sub>Se<sub>3</sub> data whereas **d-f** presents p-type data. **a, d** Cartoons illustrate the surface state (red and blue) and bulk bands (grey) of Bi<sub>2</sub>Se<sub>3</sub> with the dashed box representing the detector energy-momentum window for the respective dopings. Light grey bands in p-type samples are bulk bands deep in the bulk, and surface bands (red, blue, dark grey) are shifted down due to band bending. **b, e**  $k$ -space slices at  $\tau = -100, 0, 50$ , and  $800$  ps for bulk-conductive (raw data) and p-type (2nd derivative in momentum). **c, f**  $k$ -integrated energy spectra as a function of pump-probe delay. All dynamics from pump excitation of bulk-conductive Bi<sub>2</sub>Se<sub>3</sub> occur within one 10 ps pixel at  $\tau = 0$ . As for p-type, the delay scan exhibits a long 300 ps rise before the presence of the pump, and a slow  $> 10$  ns decay after  $\tau = 0$ . The long 1 ns delay scans that reach  $-200$  ps into the negative delay demonstrate that the negative delay chemical potential shift is separate from the positive delay decay process.

To better extract the timescale associated with such a process, in Fig. 2.1c we show the momentum-integrated spectral intensity across the entire delay range ( $-200$  ps to  $800$

ps). A sudden change of intensity following the pump pulse is observed instantly at  $\tau = 0$ , followed by a decay process that takes less than 10 ps to restore equilibrium. This time scale is in agreement with previous reports [42, 36, 43, 44] and has been discussed in terms of a bottleneck of charge in the bulk state moving through the surface state. In contrast, the p-type samples exhibit a much different response to optical pump as can be clearly seen in Fig. 2.1f. Two main differences are observed: a) persistence of excitation well after  $\tau = 10$  ps; b) apparent presence of excitation even for negative delays. At  $\tau = 0$ , we see population 200 meV above  $E_F$  in both Fig. 2.1e and 2.1f. Strikingly, a non-equilibrium chemical potential persists over a much longer delay window (800 ps), as compared to the bulk-conductive samples (see both panels c and f).

For more than 200 ps preceding pumping, the chemical potential remains above equilibrium  $E_F$  and rises to  $\sim 120$  meV to approach the chemical potential at positive delays as shown by the blue dashed line in Fig. 2.1f. In this case, photoelectrons appear to be affected by a pump pulse that arrives after they have been photoemitted. Previous studies have assumed the chemical potential shift at negative delay is the continuation of the SPV decay from a previous pump pulse, leading to incorrect estimates of the lifetime of the SPV ( $> 4$   $\mu$ s) in similar systems [74, 75, 76, 77]. However, our work reveals over a larger decay range that the negative time decay process is separate from the relaxation of the SPV and therefore unrelated to the previous pulse. This is confirmed by the chemical potential returning to equilibrium towards more negative delays (as can be inferred from Fig. 1f). A 4  $\mu$ s timescale can not explain the reversed decay shape of the negative delay effect. This peculiar behavior is consistent with previous observations of SPV in GaAs [78] in which the chemical potential shift at negative delays has been associated with a SPV generated electric field influencing the photoemitted electrons shortly after leaving the sample surface. Therefore, the negative delay signal is due to in-vacuum electromagnetic interactions with the photoelectron and thus the effect is extrinsic to the material. The timescale of this effect is set by the kinetic energy of photoelectrons propagating away from the sample in vacuum and by the pump spot geometry [78, 79, 80].

By considering a much larger range in both negative and positive delay values we are able to correctly and precisely measure the SPV lifetime. We note that the shorter negative delay range used in previous work [74, 75, 76, 77] is insufficient for observing the reverse decay profile and the negative delay chemical potential shift cannot be attributed to the effect of previous pump pulses. Turning our attention to the positive delay regime (Fig. 1f), two decay mechanisms can be identified due to the wide delay range covered in this experiment. From a two-exponential fit, we extract a timescale of 159 ps and a remarkably long timescale of 16.5 ns at a fluence of  $\sim 30$   $\mu$ J/cm<sup>2</sup>.

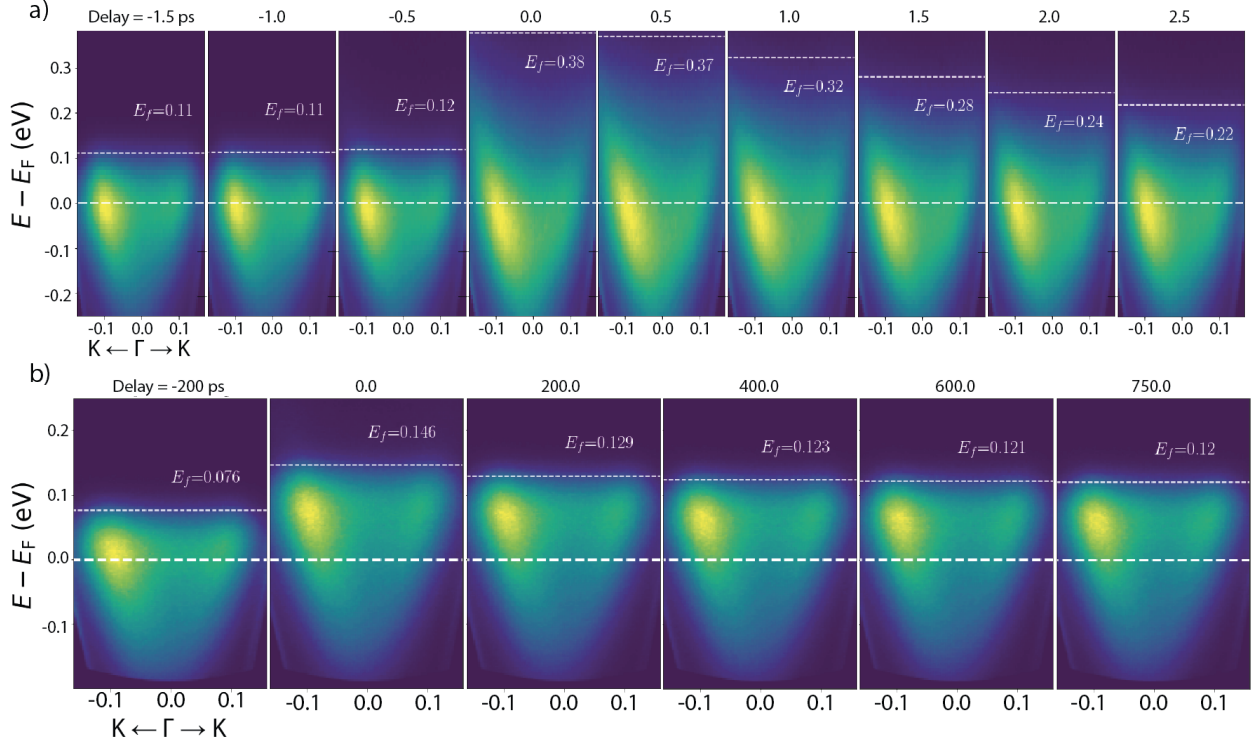


FIGURE 2.2: **Fast and slow dynamics in raw spectra of p-type  $\text{Bi}_2\text{Se}_3$ .** **a** Raw spectra measured every 500 femtoseconds between  $-1.5$  ps to  $2.5$  ps. Clearly shows fast picosecond partial recombination after the onset of the pump at  $\tau = 0$ . The chemical potential fit after excitation is not to be fully trusted since the dynamics are too fast to establish a quasi-equilibrium Fermi level. The chemical potential in the negative delay is above equilibrium and appears constant with respect to negative decay. **b** Raw spectra measured every 200 ps between  $-200$  to  $750$  ps. Long-lived chemical potential shift extends well beyond 800 ps. Chemical potential at  $-200$  ps is lower than the chemical potential near  $-1$  ps.

In Fig. 2.1e, the p-type  $\text{Bi}_2\text{Se}_3$  ARPES spectra have been modified with second derivatives along the momentum axis in order to clearly observe the rigid shift of the Dirac dispersion as a result of the surface photovoltage. For completeness, Fig. 2.2 shows the raw spectra for p-type  $\text{Bi}_2\text{Se}_3$ . In Fig. 2.2a, we present the fast picosecond-timescale spectra in the p-type samples in which the dynamics are of similar timescale to the bulk-conductive dynamics. Fig. 2.2b displays the same data from Fig. 2.1e at 200 ps intervals without second derivatives. The difference in band quality from the bulk-conductive samples to the p-type samples is possibly due to the increased disorder associated with the Mg dopant. From the picosecond data, it is easy to assume that the chemical potential shift at negative delays is constant without further investigation at larger negative delays. This can lead to the wrong assumption that this shift is due to a continuation of the forward decay from the previous

pulse, leading to an incorrect conclusion of a microsecond decay process (accounting for laser repetition rates on the order of microseconds). However, at a larger negative delay of  $-200$  picoseconds, it is clear that the chemical potential shift decays towards more negative delays ruling out the possibility of this phenomenon being associated with a forward decay process.

The fitting function used to determine the chemical potential shift is a Fermi-Dirac distribution plus an affine background multiplied together with a Lorentzian applied on the momentum integrated spectra across all delays for each fluence. Fig. 2.3 displays the typical momenta integrated spectra from the pumped sample at positive delay with the applied fitting model exhibiting very close agreement. This spectra is from delay of 250 ps with  $1.8 \mu\text{J}/\text{cm}^2$  pump fluence.

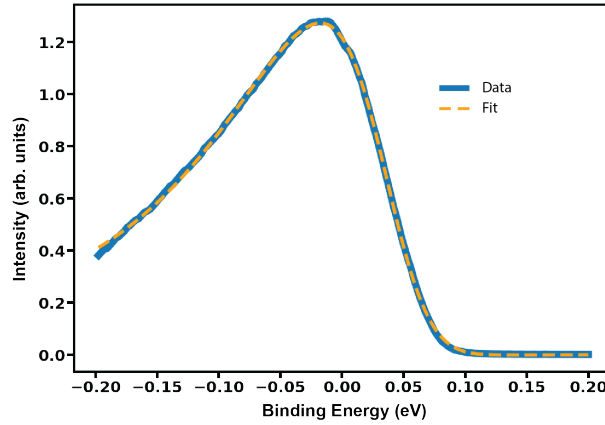


FIGURE 2.3: **Fermi-Dirac and Lorentzian fit to spectra.** Typical momentum integrated spectra with respective fit using a Fermi-Dirac distribution plus an affine background multiplied with a Lorentzian. This spectra is from  $1.8 \mu\text{J}/\text{cm}^2$  fluence data at a delay of 250 ps.

## 2.4 Fluence Dependence of SPV Effect in P-Type $\text{Bi}_2\text{Se}_3$

With the insight that the SPV timescale lasts on the order of 10 ns, we investigate the effects of fluence on the magnitude and decay of the SPV. Figure 2.4 shows the fluence dependence of the SPV effect. Fig. 2.4a displays Fermi energy fits of the momentum-integrated ARPES spectra at each delay for all measured fluences. The Fermi distribution is well-defined adiabatically for all delays except  $\tau = 0$  due to the SPV dynamics being much slower than the typical electron relaxation timescale. The peak excitation at  $\tau = 0$  was removed and replaced by the average value of the neighboring points.

Besides the obvious change in magnitude, the most apparent fluence-dependent feature from this dataset is the shift of the SPV peak to more positive delays as fluence decreases (yellow circles), indicating that the non-equilibrium population requires a finite time to build-up at lower fluences. In order to account for the SPV build-up time at low fluences, the chemical potential versus delay curves were best fitted to a summed three-exponential decay model with one decaying exponential exhibiting a negative amplitude capturing the effect of the SPV build-up, as given by equation 1.

$$F(t) = -|A_{\text{build-up}}|e^{-t/\tau_{\text{build-up}}} + A_{\text{short}}e^{-t/\tau_{\text{short}}} + A_{\text{long}}e^{-t/\tau_{\text{long}}} \quad (2.1)$$

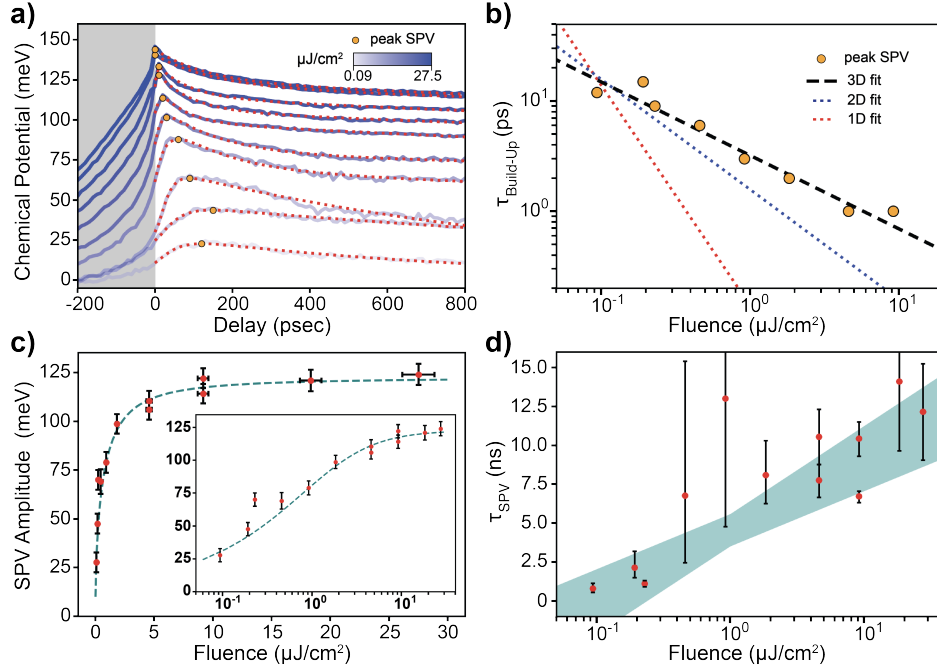
The SPV build-up exponential term takes on a negative amplitude capturing the reduction in a SPV at short delays that would otherwise take on the form of two decaying exponentials alone. It is important to recognize that the time-dependent electric field resulting from the SPV formation affects the positive delay in a similar manner to the negative delay effect. More precisely, the measured chemical potential shift at a given delay is affected by the true chemical potential time profile of the SPV at more positive delays as the photoemitted electron is propagating through a decaying (or growing) electric field. As such, the decay profiles are most affected in delay regions with large time derivatives of the chemical potential shift [80, 79]. Accordingly, the delay regions in which the SPV build-up is dominant are most affected by this phenomenon. This contributes to the non-zero chemical potential shift for the decay curves exhibiting delayed SPV onset. We note that our fit model does not take into account the positive delay effects of the induced time-dependent field but captures the total effect of the SPV build-up, decay, and in-flight time dependence phenomenologically.

We determine the peak SPV onset time ( $\tau_{\text{build-up}}$ ) by the maximum value of the resulting fit function for each fluence. The peak positions are represented by yellow circles in Fig. 2.4a and are summarized in Fig. 2.4b. As the pump fluence is decreased below saturation ( $\sim 10 \mu\text{J}/\text{cm}^2$ ) the onset of the SPV peak occurs at later delays reaching as large as  $\sim 150$  ps near a fluence of  $0.2 \mu\text{J}/\text{cm}^2$ . The long timescale associated with the build-up of this surface field is evidence for diffusive dynamics [81, 82, 83]. Within a diffusive model, the timescale for diffusion scales as  $\tau_{\text{build-up}} \propto \lambda^2$  [84, 85] leading to  $\tau_{\text{build-up}} \propto f^{-\frac{2}{d}}$  where  $\lambda$  is the mean free path,  $f$  is the pump fluence, and  $d$  is the degrees of freedom of travel. The resulting fit for the diffusive models in one, two, and three dimensions is shown as dashed lines in Fig. 2.4b. By letting  $d$  be a free parameter in the fitting, the best fit is obtained for  $d = 3.18 \pm 0.17$ . This is evidence that the delayed build-up of the SPV is due to slow diffusion in the bulk as opposed to a two-dimensional surface effect.

At high fluences, the negative-amplitude decay is nearly absent and the fit is dominated by a two-exponential model with timescales on the order of 100 ps and 1-10 ns, respectively. The amplitude corresponding to the nanosecond timescale represents the SPV amplitude and is presented in Fig. 2.4c. The fluence dependence of the SPV magnitude clearly shows a non-linear trend followed by a quick saturation for fluences above  $10 \mu\text{J}/\text{cm}^2$  up to a maximum of  $\sim 125$  meV. The energy error bars in Fig. 2.4c were determined by combining



the energy variance of the chemical potential fit at a single delay and the variance of the majority component of the SPV amplitude from the exponential fit.



**FIGURE 2.4: Fluence dependence of the SPV.** **a** Fermi edge fits (blue) to delay scan spectra represent the chemical potential as a function of delay at multiple fluences from 0.92 to 27.5  $\mu\text{J}/\text{cm}^2$ . The decay scans are fitted best by the sum of two positive amplitude exponentials and one negative exponential term (red dashed). The SPV peak (yellow dots) occur at later delays with decreasing fluence. **b** The build-up time of the SPV peak log-log plotted as a function of fluence. The data fits best to a 3D diffusion model. Due to discrete delay steps, fluences above 10  $\mu\text{J}/\text{cm}^2$  have peak SPV values at  $\tau = 0$  and are not plotted. **c** SPV magnitude versus fluence as determined by the amplitude of the long  $\sim 10$  ns timescale in the three-exponential model. The teal dashed line depicts the expected trend of the SPV magnitude from the theory discussed in the text. The inset figure demonstrates the same data on a log scale of fluence. **d** SPV decay constant versus fluence as determined by the time constant in the long timescale in the three-exponential model. The error bars are conservative estimates determined by reapplying the fits in the worst case scenarios for variation in pump fluence added in quadrature with the respective covariance from the fits. The teal-shaded region represents two standard deviations of slope and y-intercept of the weighted best fit trend line.

Fig. 2.4d exhibits the SPV decay time as a function of fluence as measured by the longest timescale in the three-exponential fit. As fluence is decreased the SPV timescale trends to 0,

being less than 1 ns below  $0.1 \mu\text{J}/\text{cm}^2$  and greater than 10 ns above  $20 \mu\text{J}/\text{cm}^2$ . The error bars were derived from a conservative consideration of the effect of pump fluctuations on the resulting delay curves added in quadrature to the variances of the long decay fit parameter. The teal region represents the best fit trend line using the fluence variation error bars as weights and accounting for all possible trend lines within two standard deviations of the slope and y-intercept. From Fig. 2.4d, we can conclude that the SPV timescale increases with fluence, reaching 100 ps timescales at low fluences near  $0.1 \mu\text{J}/\text{cm}^2$  and exceeding 10 ns at fluences above  $10 \mu\text{J}/\text{cm}^2$ . The approximately linear trend in the semi-log plot implies a logarithm-like dependence of the SPV time constant with fluence.

## 2.5 Phenomology of SPV Effect from Charge Separation and Bulk Trapping

Fig. 2.5 provides a schematic representation of a possible mechanism for the long-lived SPV in p-type  $\text{Bi}_2\text{Se}_3$  similar to the reported mechanism from Papalazarou et al. [77]. Before pumping, the equilibrium conduction and valence band are expected to bend downwards due to surface state population and redistribution of charge from bulk to surface as seen in Fig. 2.5a. This downward band bending has been confirmed via X-ray photoelectron spectroscopy [86] and is consistent with a p-type semiconductor [46, 87]. After excitation, the top portion of the Dirac cone is populated whilst holes are generated in the bottom cone. Photoexcited electrons above the bulk conduction band and holes below the bulk valence band can quickly disperse into the bulk and recombine until excited states at the surface are mainly below the bulk conduction band bottom, as shown in Fig. 2.5b. Once the excited occupied states of the Dirac cone lie within the bulk band gap, the excited electrons can only recombine with the holes in the bottom cone. This process is already unfavorable due to the spin-momentum locking in the topological surface state. Within this time period, the downward band bending encourages electrons from the bulk to migrate to the upper Dirac cone and holes from the bottom Dirac cone to migrate into the bulk. A dipole field due to this charge migration keeps the holes locked a finite distance from the surface. This reduces the spatial overlap of the electron and hole wave-functions resulting in an even greater enhancement of the photoexcited carrier lifetime. Fig. 2.5c displays how such a dipole localizes holes far from the surface.

It is apparent within this description that bulk-conductive samples in which  $E_F$  intersects the conduction band are incapable of producing an intrinsic SPV. In the metallic regime, the density of states is high both in the bulk and at the surface inhibiting large changes in chemical potential due to the surface state population. Furthermore, recombination of excited carriers is enhanced since the bulk conduction band and surface state are accessible for all energies above  $E_F$ . In contrast, the reported band bending in bulk-conductive  $\text{Bi}_2\text{Se}_3$  is an extrinsic process attributed to adatoms preferentially doping the surface [88, 89, 90, 91] as well as XUV ionization of the adsorbed species [92, 93, 94] explained by the work of

Frantzeskakis et al. [95].

The lower limit on the length scale of the photoinduced dipole is determined by the penetration depth of the surface state wave-function. In fact, the c-axis penetration of the surface state wave-function can be approximated by the minimum thickness in which  $\text{Bi}_2\text{Se}_3$  preserves a bulk boundary correspondence. Previous studies have reported the surface state penetration depth from a single  $\text{Bi}_2\text{Se}_3$  surface to be 2 quintuple layers ( $\sim 2$  nm) [96, 97, 98]. This is consistent with theoretical models that predict a penetration depth of 1-2 nm [99, 100]. Therefore, in order for the hole-dipole distance to play a large role in the long carrier lifetime, this distance would need to be on the order of 2 nm or greater.

To model the fluence dependence of the SPV magnitude, we study photocarrier dynamics at the surface of a topological insulator by utilizing the rate equation. We consider the recombination of the photoexcited carriers in the surface Dirac band and diffusion of holes into the bulk which leads to surface dipole formation and stabilizes long-lived photocarriers. The rate equations are given by

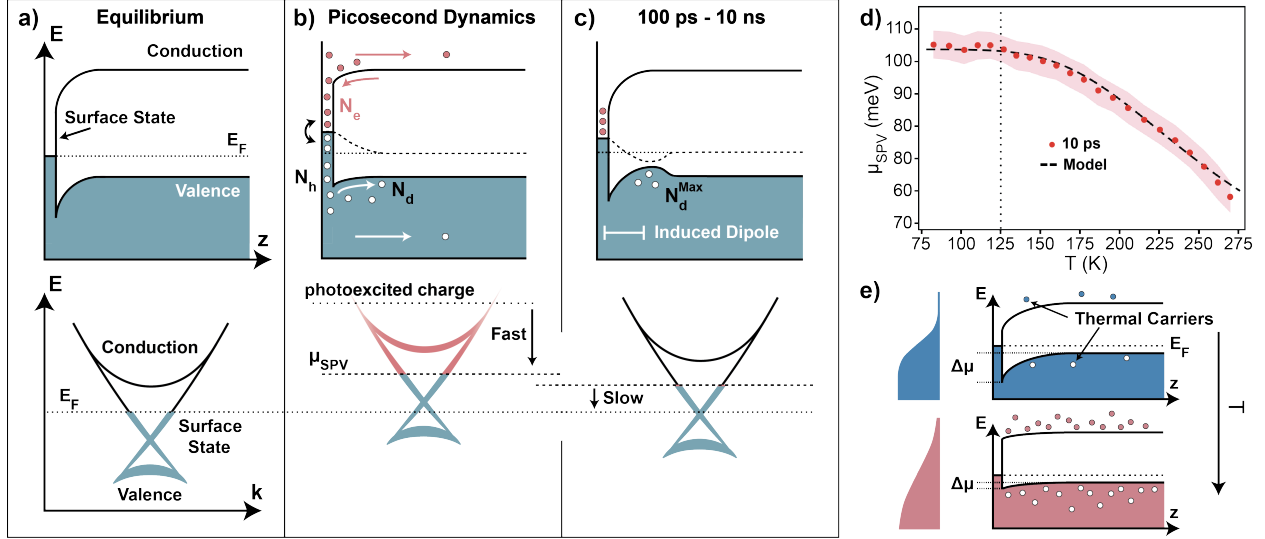
$$\frac{dN_e}{dt} = -\alpha_{\text{rec}}N_eN_h, \quad (2.2)$$

$$\frac{dN_h}{dt} = -\alpha_{\text{rec}}N_eN_h - \alpha_{\text{tun}}(N_d^{\text{max}} - N_d)N_h. \quad (2.3)$$

where  $N_e$ ,  $N_h$  are the electron and hole concentrations in the surface Dirac band, respectively.  $N_d$  is the hole concentration at the top of band bending formed by the excess holes ( $N_d = N_e - N_h$ ).  $N_d^{\text{max}}$  is the maximum hole concentration that the band bending can accommodate.  $\alpha_{\text{rec}}$  is the rate of surface electron and hole recombination and  $\alpha_{\text{tun}}$  is the rate of hole tunneling into the bulk.

The fluence dependence model shown by the dashed teal line in Fig. 2.4c was obtained by solving the rate equations above with the parameters,  $\alpha_{\text{rec}} = 6.5 \times 10^{-16} \text{ m}^2/\text{ps}$ ,  $\alpha_{\text{tun}} = 5.0 \times 10^{-16} \text{ m}^2/\text{ps}$ . As an initial condition, we use  $N_e(t=0) = N_h(t=0) = 0.04N_{\text{ph}}$  with photon density  $N_{\text{ph}}$  determined by the 1.5 eV pump fluence, expressing that 4% of photons create an electron-hole pair. The highest values of  $N_{\text{ph}}$  are on the order of  $10^{18} \text{ m}^{-2}$ . The maximum concentration at the top of the band bending was set to  $N_d^{\text{max}} = 7.1 \times 10^{14} \text{ m}^{-2}$ . This implies that the dipole creating the long-lived SPV (in Fig.3c) is formed by  $\sim 1$ -2% of the initial photoexcited electrons and holes.

The model demonstrates that only the ratio of the two alphas controls the final chemical potential shift due to the SPV. However, we know that recombination must occur on the order of 1 picosecond. The time scale of the initial recombination after excitation is determined by  $(N_e(t=0)\alpha_{\text{rec}})^{-1}$ , locking the order of magnitude of the alphas to  $10^{-16} \text{ m}^2/\text{ps}$ .



**FIGURE 2.5: Photoexcited charge dynamics near the surface of bulk-insulating  $\text{Bi}_2\text{Se}_3$ .** **a** Equilibrium occupation of the bands with intrinsic band bending due to charge in surface states. Upper image demonstrates density of states as a function of distance into the bulk from the surface. Bottom image represents ARPES spectra (surface sensitive). **b** Immediately after photoexcitation, surface state recombination as well as migration into the bulk of photoexcited carriers result in a fast decay of less than 10 ps [42]. **c** However, a small portion of photoexcited holes migrate into bulk due to initial band bending and remain trapped due to their own dipole. Photoexcited holes and electrons are spatially separated and recombination is dramatically reduced. **d** Temperature dependent data taken at a delay of 10 ps confirms that Fermi edge broadening diminishes the SPV effect at high temperatures. The dashed curve is the model fit of the data considering temperature dependence of the Fermi distribution for the migrating holes. Vertical dashed line is an approximate saturation temperature for the SPV. **e** Cartoon representation of diminished band bending as a result of thermal broadening of the Fermi-Dirac distribution. The Fermi-Dirac distributions are illustrated to the left of each cartoon. Temperature-induced additional carriers allow partial re-equilibration of the band bending and therefore a smaller allowable surface-bulk dipole.

The pump pulse creates photoexcited electrons and holes in the surface Dirac bands that evolve in time according to the rate equations. Eventually,  $N_h(t)$  goes to zero due to recombination, while  $N_e(t)$  and  $N_d(t)$  converge into nonzero values which determines the density of the long-lived surface dipole.

From the final value of  $N_e(t)$ , we determine the chemical potential after photoexcitation, by treating the potential difference induced by the spatially separated charge as a capacitor, such that  $V = eN_e(t)l_{\text{dip}}/\epsilon$ . We assume an approximate dipole separation length ( $l_{\text{dip}}$ ) of 10 nm, consistent with previous observations of the band bending depth [86]. The dipole

creating the long-lived SPV (in Fig.3c) is formed by  $\sim 1\%$  of the initial photoexcited electrons as represented by the maximum dipole occupancy  $N_d^{\max}$ . The model suggests that the timescale of hole transport into the bulk and recombination at the surface are comparable. Furthermore, the comparison of the values of the rates and the initial excited carrier concentrations affirms that the majority of excited charge has recombined or has been transported to the bulk within a few picoseconds, consistent with the quick relaxation process between  $\tau = 0$  and 10 ps in both p-type and bulk-conductive samples.

Despite the rapid recombination process, a finite number of holes still diffuse into the bulk to sustain a prolonged dipole. Applying this model and assuming the rates are fixed, the SPV magnitude as a function of fluence closely matches the behavior of the data as seen by the teal dashed line in Fig. 2.4c.

We can further check this model by characterizing the temperature dependence of the SPV. As temperature increases, thermal carriers start to occupy the top of the band bending making tunneling to the bulk less efficient. Additionally, increasing temperature mitigates band bending due to the appearance of extra thermal carriers at the surface [101, 87].

In order to incorporate these effects minimally in our model, we introduced temperature dependence in  $N_d^{\max}$  as  $N_d^{\max} \propto f(\epsilon_d(T))$ , where  $f$  is the Fermi distribution function and  $\epsilon_d$  is the dipole state binding energy. We adopt a phenomenological form for the binding energy,  $\epsilon_d(T) = 86[\text{meV}] - bk_B T$ .

The temperature dependence is written into the model by incorporating a realistic temperature dependent adjustment to the dipole capacity term  $N_d^{\max}$ .

$$N_d^{\max} = \frac{7.1 \times 10^{14} [\text{m}^{-2}]}{1 + \exp[-(1000 - 4T[\text{K}])/T[\text{K}]]}. \quad (2.4)$$

The temperature factor is the Fermi distribution function for the state at the band bending top with energy  $a + bT$ , with  $a = -1000$  and  $b = 4$  chosen phenomenologically. The constant  $a = -1000$  is in units of Kelvin and is placed in more natural units by multiplying by Boltzmann's constant to produce a binding energy of  $\sim 86$  meV. This is a tenable value for the dipole state binding energy, being smaller than the  $\text{Bi}_2\text{Se}_3$  gap.

It is reasonable to expect that increased temperature weakens the band bending reducing the binding energy of the dipole state. This temperature dependence of binding energy is phenomenologically incorporated with linear term  $bk_B T$ . In fact, we can confirm this dependence with experimental data featured in Fig. 2.5d. The temperature-dependence from our model captures the temperature-induced change of band bending profile and thus the SPV magnitude as shown by the black dashed line in Fig. 2.5d. The graph displays the chemical potential shift due to the SPV above the saturation fluence as of 10 ps after the pump as a function of temperature. The SPV weakens at higher temperatures and saturates at temperatures below 125 K. Fig. 2.5e illustrates the mitigation of band bending at higher temperature as a result of additional thermal carriers due to Fermi-edge broadening. The additional holes in the bulk valence partially cancel the band bending field. Our model describes an equivalent picture in that more holes in the bulk valence band at equilibrium result in less room for migrating holes after photoexcitation.

## 2.6 Generalized SPV Effect in $\text{Bi}_2\text{Se}_3$ and $\text{Bi}_2\text{Te}_3$

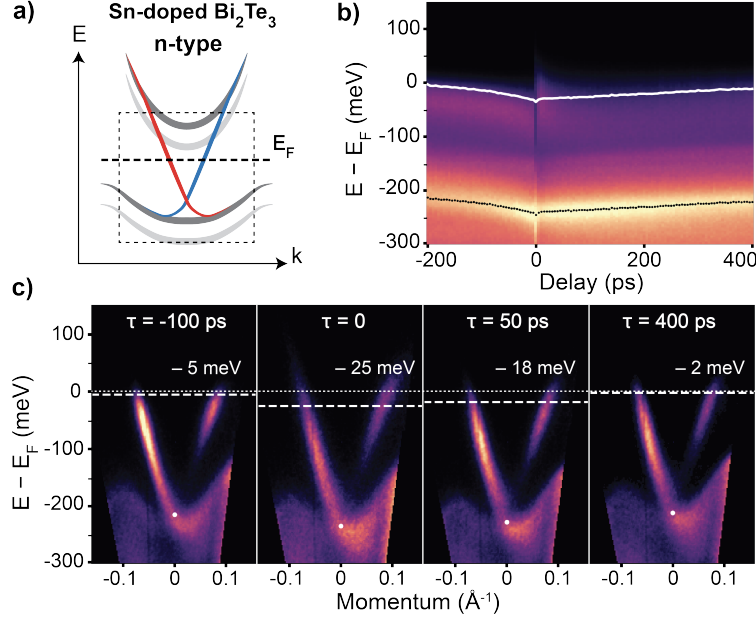


FIGURE 2.6: **SPV effect in Sn-doped  $\text{Bi}_2\text{Te}_3$**  **a** Cartoon depiction of  $\text{Bi}_2\text{Te}_3$  band structure and momentum-energy detection window. Bands at the surface (dark grey, red, and blue) are shifted upward by band bending. **b**  $k$ -integrated energy spectrum as a function of pump-probe delay, Dirac node position and chemical potential are indicated by the black dotted line and white line, respectively. This time, the chemical potential dips downward towards  $\tau = 0$ , returning to equilibrium beyond 400 ps. **c**  $k$ -space slices at  $\tau = -100, 0, 50$ , and 400 ps illustrating the downward chemical potential shift in both the positive and negative delays.

The model described above suggests that the observed SPV might represent a more general property of TIs and provides a general recipe for the effect: chemical potential within the gap and strong in-gap surface states that enable a charge redistribution at the surface. All appropriately doped topological insulators satisfy this condition by definition [31, 102, 103]. To test this idea we have studied Sn-doped  $\text{Bi}_2\text{Te}_3$  when the Fermi energy lies in the gap nearest the bulk conduction band (n-type) as presented in Fig. 2.6. Upon pumping, a SPV effect lasting beyond the delay range ( $> 400\text{ps}$ ) is observed (see Fig. 2.6b and 4c). In contrast to the p-type samples (shown in Figure 1), the surface bands in n-type samples are expected to bend upward, resulting in a SPV with the chemical potential shifting downward upon illumination [46, 45, 87]. This can be observed clearly in Fig. 2.6b, where the Dirac node location is marked in black and the Fermi level is represented in white. The bands rigidly shift downward due to the 800 nm excitation. Near  $\tau = 0$ , the hot-carrier recombination

is visible as a peak above the Fermi level, lasting  $\sim 20$  ps. As is the case for the p-type sample, the decay profile for negative delays points to an extrinsic in-vacuum effect on the photoelectrons. The presence of the SPV in a second topological insulator with a different chemical dopant demonstrates the attainability of this effect and the possible universality among the topological insulators.

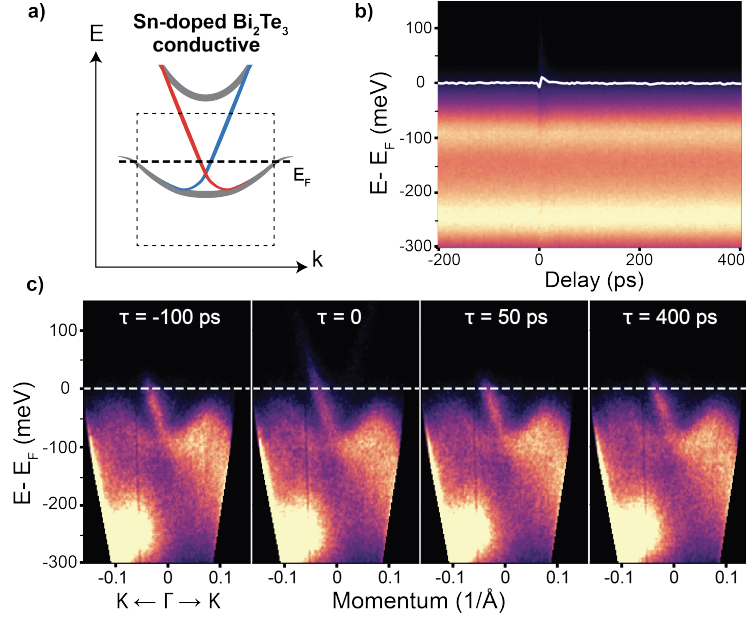


FIGURE 2.7: **Bulk-conductive  $\text{Bi}_2\text{Te}_3$  with no SPV.** **a** Cartoon representation of the  $\text{Bi}_2\text{Te}_3$  band structure with Fermi energy crossing the bulk valence band and detector energy-momentum window. **b**. Momentum-integrated spectra versus delay reveals only quick recombination after excitation. **c**. ARPES spectra at four different delays. The spectra do not experience rigid band shifts in the negative or positive delays as seen in the bulk insulating samples.

$\text{Bi}_2\text{Te}_3$  that is doped with Sn below the bulk band gap into the bulk valence such that the bulk is conductive experiences no surface photovoltage upon excitation. Fig. 2.7 follows the layout of the previously shown Fig. 2.6, and a comparison of the two figures demonstrates the same stark differences in response to 800 nm excitation as the doped and undoped  $\text{Bi}_2\text{Se}_3$  samples. In Fig. 2.7c, the Fermi level appears to approach the valence band along the  $\Gamma - K$  direction, meaning the Fermi level certainly crosses the bulk valence band across the  $\Gamma - M$  direction, rendering the bulk metallic [103, 104]. The quick carrier recombination observed in Fig. 2.7b lasts  $\sim 20$  ps, explaining the initial uprise in Fig. 2.6b as the same mechanism.

## 2.7 Discussion

Our proposed model describing photoexcited hole migration and subsequent dipole trapping matches the SPV response in magnitude versus fluence. Furthermore, the introduction of Fermi-edge broadening to the model captures the temperature response, and the consideration of bulk diffusion dynamics describes the delayed onset of the SPV. However, the model does not take into account decay mechanisms for the non-equilibrium dipole corresponding to the two timescales of the long SPV lifetime. Diffusive spreading of the dipole on the surface is expected and could explain one of these timescales. Further time-resolved measurements with spatial resolution may elucidate the diffusion rates of surface and bulk excited carriers. Understanding the dipole decay mechanisms will be crucial to engineering a topological SPV system with even longer lifetimes.

The presence of a topological SPV in TIs opens up new avenues for applications of the SPV given its unique traits from a conventional SPV such as a spin-momentum locked current at the surface that inherits forbidden backscattering, i.e. ballistic transport [34, 33]. Moreover, the robustness of the topological surface state to contamination ensures an environmentally stable SPV [53]. As the catalogue of known topological insulators expands, time-resolved measurements will determine whether the SPV is truly an inherent property of topological insulators and expound on universal behaviors of the topological SPV.

In order to exploit the topological SPV for spintronics applications, long range spin transport as well as spin manipulation need to be confirmed and developed. We suggest further observation that surface charge is indeed transported far from the region of photoexcitation. This can be resolved via a pump-probe experiment with a spatially resolved probe rastering outside the pumped region. Furthermore, studies are needed to investigate whether optical techniques can be used to manipulate the spin of these long-lived carriers. By weakly breaking time-reversal symmetry such that the system is still topologically non-trivial, one may be able to selectively create decay channels for one spin branch and not the other paving way for long-lived spin current manipulation in topological materials.

## 2.8 Summary

A decade of academic excitement in topological insulators has resulted in few devices and applications. This is partly due to a lack of techniques capable of manipulating the behavior of topological insulators. In this study, we have revealed a large amplitude SPV with a long lifetime on the order of 10 ns. Furthermore, we demonstrate wide range control of the amplitude, timescale, and location of the SPV. The amplitude and lifetime of the SPV in p-type  $\text{Bi}_2\text{Se}_3$  exhibit logarithm-like tunability via fluence. We can manipulate the SPV lifetime over a wide range, from approximately 100 ps to 10 ns. Not only can we control the amplitude and lifetime of the SPV, but we can selectively excite the spin-momentum locked bands spatially with localized illumination. In practice, diffusion of the surface charge from a pump geometry of choice can result in complex spatially dependent spin transport varying



both in magnitude, lifetime, and spin direction. Such extensive manipulation opens up the phase space for new and exciting spintronic devices.

## Chapter 3

# Tracking Surface Photovoltage Dipole Geometry in $\text{Bi}_2\text{Se}_3$ with Time-Resolved Photoemission

In the previous chapter, I discuss how topological insulators exhibit strong and long-lived surface photovoltages when excited by an infrared pump. The ability to generate long-lived potentials on these surfaces provides opportunities to manipulate the spin-momentum locked topological surface states. Moreover, the photo-induced nature of this effect allows for localized excitation of arbitrary geometries. Knowing precisely how these potentials form and evolve is critical in understanding how to manage the effect in applications. The uniqueness of the photoemission experimental geometry, in which the photoelectron must traverse the induced surface field in vacuum, provides an interesting probe of the electric dipole shape generated by the surface photovoltage. In this chapter, I demonstrate how the observed decay of the geometric effect on the photoelectron matches an ab initio electric field model, thereby tracking the fluence-dependent evolution of the induced dipole geometry. By utilizing a standard time-resolved angle-resolved photoemission experiment, we are able to determine real-space information of the dipole while simultaneously recovering time-resolved band structure. The work presented here was published in *Journal of Statistical Mechanics: Theory and Experiment* in 2019 [47], © IOP Publishing Ltd and SISSA Medialab srl. Reproduced with permission. All rights reserved.

### 3.1 Introduction

The negative-delay spectra in time and angle-resolved photoemission spectroscopy (TR-ARPES), in which the photoemitting probe arrives before the pump, are typically used to characterize equilibrium band structure [65, 105, 36, 106, 107]. However, in situations in which the pumped non-equilibrium state hosts a time-dependent electric field, the negative delay exhibits non-equilibrium behavior that is dependent on the magnitude, time-scale, and,

most importantly, the geometry of the excitation [78, 79, 80].

An example of a pump-induced excitation that results in a time-dependent electric field is the surface photovoltage (SPV) effect [76, 108, 74, 78]. An SPV forms in a semiconducting system that exhibits bulk-to-surface band bending. In-gap states at the surface facilitate a charge redistribution between the surface and bulk in order to establish a flat chemical potential. This results in a non-uniform charge distribution and therefore an internal electric field that bends the surface bands. Upon illumination, photoexcited charges cancel the internal field, reversibly reducing the band bending [45, 71].

The necessary ingredients for an SPV are a Fermi level in the bulk gap and in-gap surface states [45, 71]. Topological insulators are ideal SPV candidates. They host topologically-protected in-gap surface states and are bulk-insulating as long as they are doped into the bulk gap [31, 34, 30, 109]. In recent years, many topological insulator systems have been reported to exhibit SPVs via TR-ARPES [76, 108, 74]. During the topological SPV excitation, the surface band bending is mitigated driving a potential difference between the spin-momentum locked surface states inside and outside the excited regions on the surface. This phenomenon opens doors for possible applications such as light-induced spin-current switches or a means to drive localized spin-currents [110, 111, 112].

The pump-induced SPV can be measured directly with TR-ARPES [76, 108, 74, 78, 80]. Upon illumination, the band structure rigidly shifts as the non-equilibrium chemical potential tracks the band bending reduction. For positive delays (in which the probe arrives progressively later after the pump) the excitation decays and the band structure shift diminishes. Naively, one would expect the negative delay to exhibit only equilibrium behavior. However, at negative delays near temporal overlap at delay = 0 ps, the band structure is also shifted and this shift decays at further negative delays. This phenomenon is due to the ARPES geometry, in which the photo-emitted electron must propagate through vacuum to the detector. At negative delays, the photoelectron is emitted first, the pump arrives after the delay time, and the generated field provides an impulse to the traveling electron which shifts the observed binding energy. In this way, the negative delay is governed by the generated electric field shape in vacuum which is in turn determined by the shape of the generated dipole [78, 79, 80].

In this study we examine the fluence-dependent SPV dipole evolution in  $\text{Bi}_2\text{Se}_3$ . We employ the ab initio negative-delay electric field model developed by Yang et al. [78], but with non-Gaussian dipoles and demonstrate that the negative delay is an effective region for determining dipole geometry in TR-ARPES experiments.

### 3.2 Rehashing SPV Effect in P-Type $\text{Bi}_2\text{Se}_3$

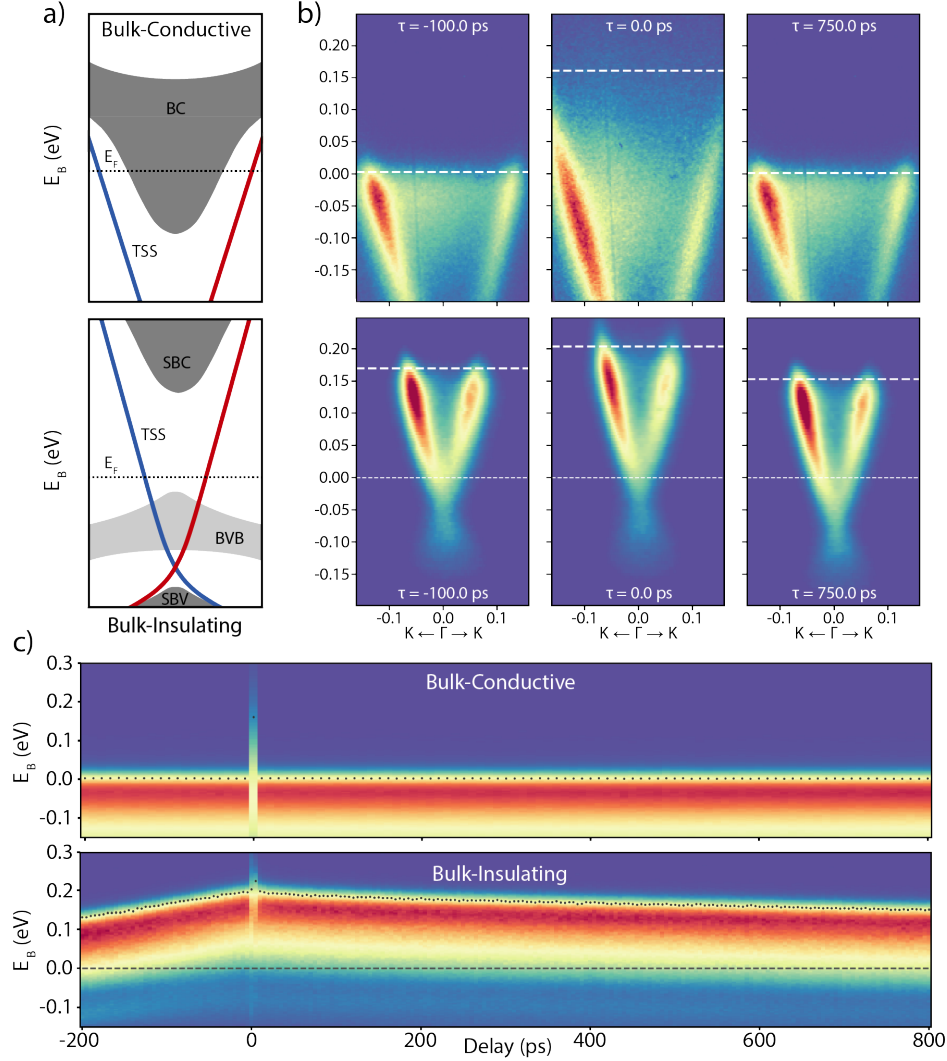


FIGURE 3.1: **Doping specific SPV generation in  $\text{Bi}_2\text{Se}_3$ .** **a** Cartoon band structures for bulk-conductive and bulk-insulating  $\text{Bi}_2\text{Se}_3$ . The insulating films exhibit band bending, shifting the surface valence band (SVB) in dark grey and the topological surface state (TSS) in red and blue. The light grey shape depicts the unshifted bulk valence band (BVB). The bulk-conductive sample experiences no band bending as illustrated by no shifting of the conduction band (CB). **b** ARPES spectra at delays  $-100$  ps,  $0$  ps, and  $750$  ps demonstrating that only the bulk-insulating samples experience long-lived rigid shifts both in positive and negative delay. **c** Momentum-integrated spectra versus delay. The bulk-conductive sample relaxes within  $10$  ps where as the bulk-insulating film exhibits a long forward decay and a shorter decay in the negative delay.

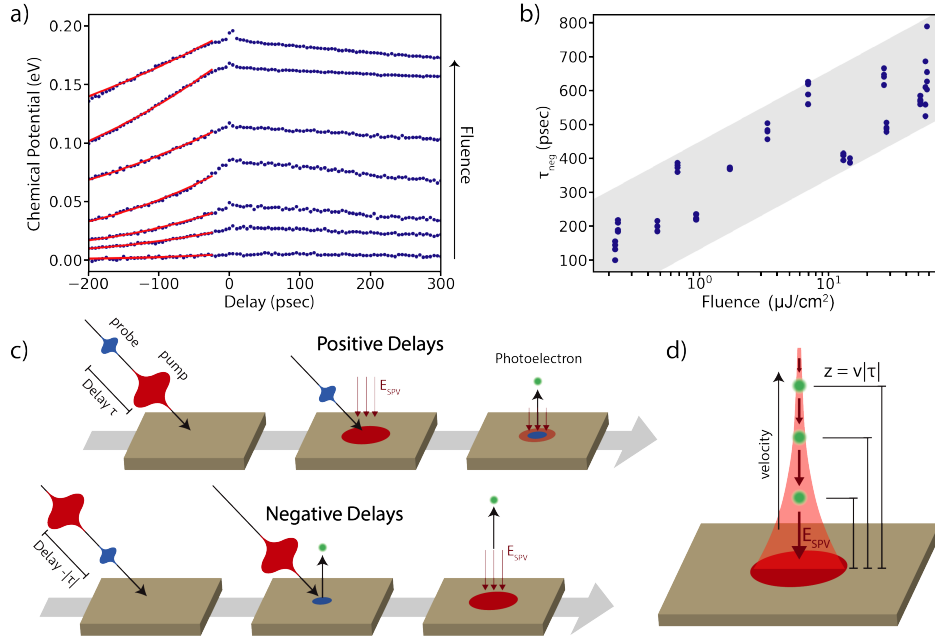
We start our study by examining the difference in pump-probe excitations between bulk-conductive (Fermi level doped into the bulk-conduction band) and bulk-insulating (Fermi level doped into the bulk gap)  $\text{Bi}_2\text{Se}_3$  bulk crystals. The bulk-insulating  $\text{Bi}_2\text{Se}_3$  have been bulk-doped with magnesium to establish an in-gap Fermi level. We utilized 800 nm pump pulses with  $\sim 150$  fs pulse duration. Figure 3.1 demonstrates the markedly different behavior between these two systems. The cartoons in Fig. 3.1a illustrate the difference in doping between the two samples. In the bulk-insulating case (lower cartoon), the Fermi-level is in the bulk gap (bands deep in the bulk shown in light grey), and the bulk bands at the surface (dark grey) as well as the topological surface state (red and blue) are shifted downward by band bending. This can be seen by the offset of the bulk valence band in light grey and the surface valence band in dark grey. Fig. 3.1b displays the pumped behavior of the respective systems. The equilibrium Fermi level was determined with the pump blocked. In the bulk-conductive case, all pump-induced excitation is contained within 10 ps after the pump pulse and no rigid shift of the bands can be observed. In the bulk-insulating case, a rigid shift of the bands occurs at all delays and is maximal at delay = 0 ps, continuing well beyond 750 ps. This is even more clear in Fig. 3.1c. Only a single 10 ps step at delay = 0 is excited in the bulk-conductive samples. The bulk-insulating samples exhibit chemical potential shifts that decay in both the negative-delay direction and in the positive-delay direction. These spectra were taken with a fluence of approximately  $60 \mu\text{J}/\text{cm}^2$ . At this fluence the SPV decay (decay in the positive delay) takes on a two-exponential form with time constants of approximately 50 ps and 5 ns.

### 3.3 Fluence Dependence of Experienced Electric Field in the Negative Delay

We turn our attention to fluence-dependent measurements on the bulk-insulating  $\text{Bi}_2\text{Se}_3$  in order to investigate effects on the negative delay. Figure 3.2 summarizes the negative-delay fits as a function of fluence as well as an explanation for the negative-delay profile. Fig. 3.2a presents Fermi edge fits to the momentum-integrated delay profiles at multiple fluences and represents the chemical potential shift as a function of delay. The fitting function consists of a Fermi-Dirac distribution multiplied by the sum of a Lorentzian and an affine background. By fitting the chemical potential shifts in the negative delays to an exponential for each fluence we generate Fig. 3.2b, negative-delay time constants as a function of fluence. As the fluence increases, the negative-delay time constants increase as well.

Fig. 3.2c compares the pump-probe interaction between the negative-delay and positive-delay regimes. The positive delay response, in which the pump arrives on the sample at a delay  $\tau$  before the probe, is most intuitive. In this paradigm, the pump arrives and generates an SPV induced electric field at the surface. At a time  $t = \tau$  after the pump, the probe arrives and photoemits an electron. With a sufficiently long SPV lifetime, the electron is effectively photoemitted from a non-grounded plane with a voltage equal to the SPV at the

time of photoemission. As a result the spectra at positive delay are rigidly shifted by the magnitude of the SPV at the measured delay, mapping the SPV-decay profile [78, 80]. In the case of negative delays, the photoelectron is emitted first, and after time  $t = |\tau|$  the pump arrives. By the time the pump arrives, the electron is  $z = v|\tau|$  away from the sample surface, where  $v$  is the propagation speed. Therefore, the electron experiences the SPV electric field from a distance as determined by the negative-delay value [78, 80]. Fig. 3.2d demonstrates how three electrons representing three different negative-delay values experience the initial SPV excitation. The width of the red-shaded region corresponds to the strength of the electric field along the propagation axis at a given distance from the sample surface. Each electron samples a different portion of the SPV electric field as they travel to the detector, ultimately leading to a backwards decay profile in the negative-delays of Fig. 3.2a.



**FIGURE 3.2: Fitting the negative-delay profiles.** **a** Fermi energy fits to momentum-integrated delay profiles at multiple fluences. The red lines correspond to exponential fits to the negative-delay features. **b** Time constant of negative-delay exponential fits versus fluence displays positive trend, grey region is a guide to the eyes. **c** Comparison between pump-probe dynamics between negative delays and positive delays. Grey arrows corresponds to chronological order of events. **d** Three electrons demonstrate three separate negative delays at the moment of pump excitation. The width of red-shaded region depicts the electric field strength along the propagation axis. Electrons at larger negative delays sample further segments of the electric field profile.

Since the negative-delay effect is a result of the photoelectron experiencing the SPV

field while enroute to the detector, the SPV-decay time constant might play a role in the fluence dependence of the negative-delay profile, since this would affect the time profile of the observed field. To address this issue, we utilize the model from Yang et al. [78], which calculates the energy shift of the photoelectron due to a pump-induced dipole. The energy shift at each negative delay ( $\Delta E(\tau)$ ) is determined by integrating the electric field across the path of the photoelectron, parameterized in time.

$$\Delta E(\tau) = -ev \int_0^\infty \varepsilon(v(t + |\tau|), t) dt \quad (3.1)$$

Here,  $\varepsilon$  is the electric field intensity as a function of space and time and is assumed to have the same time-dependence as the measured SPV decay, such that  $\varepsilon(t) \propto e^{t/\tau_{SPV}}$ .

The spatial portion of the electric field is determined by directly integrating a given spatial dipole distribution ( $\mathbf{p}(x, y)$ ) and only considering normal emission ( $\hat{\mathbf{z}}$ ), such that:

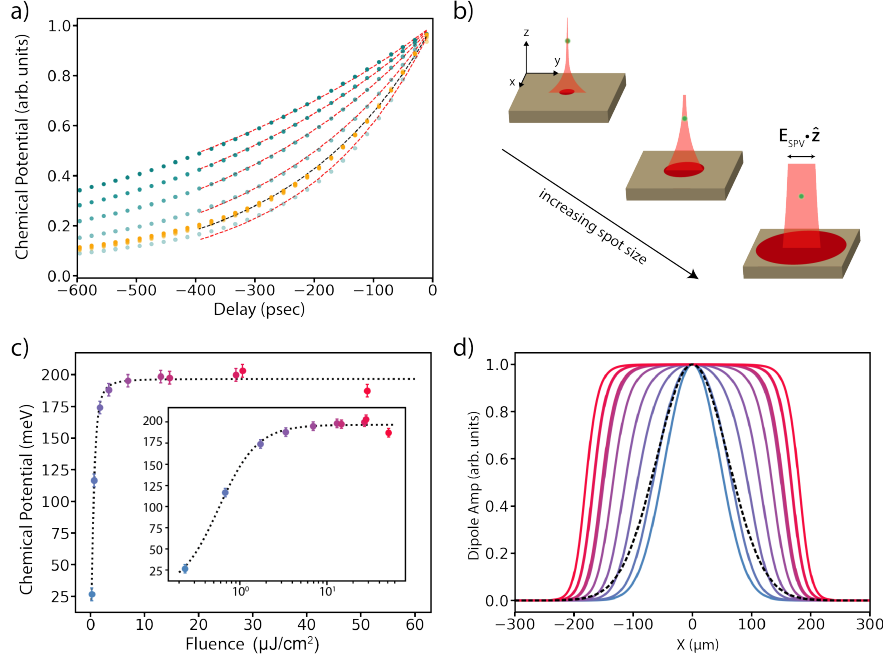
$$\varepsilon(z) \sim \int dx dy \left( \frac{3(\mathbf{p}(x, y) \cdot \hat{\mathbf{r}})\hat{\mathbf{r}} - \mathbf{p}(x, y)}{r^3} \right) \cdot \hat{\mathbf{z}} \quad (3.2)$$

where  $\hat{\mathbf{r}}$  is the vector pointing from a point source  $\mathbf{p}(x, y)$  to the photoelectron at  $(0, 0, z)$ .

### 3.4 Transformation of Dipole Profile from SPV Saturation

We explore this model in Figure 3.3 with multiple pump-beam widths and multiple SPV time constants at a given pump-beam width. Fig. 3.3a demonstrates the negative-delay behavior for Gaussian pump-beam widths of  $\sigma = 50, 75, 100, 125$ , and  $150 \mu\text{m}$  (light green to dark green, respectively) and SPV time constants of  $\tau_{SPV} = 100, 1000, 10000, 100000$  ps (light yellow to dark yellow, respectively). Over many orders of magnitude, there is miniscule dependence of the SPV time constant on the negative-delay profile, implying that the process is mainly driven by the impulse of the initial SPV formation on the photoelectron. On the other hand, the decay profile is significantly modified by small changes in pump-beam spot size as indicated by the evolving green curves and consistent with Yang et al. [78]. Therefore, observed dependence of the negative-delay time constant in the measured system in Fig. 3.1b must be attributed to a fluence-dependent change in the induced dipole geometry.

The scaling of the negative-delay time constant with beam spot size is intuitive. The earlier discussion on the negative-delay response demonstrated that negative-delay values determine the spatial integration region of the electric field. Therefore the negative-delay constant is a measure of the spatial extension of the field [78]. Fig. 3.3b illustrates how the length scale of the field profile depends on the length scale of the dipole feature. In the limiting case that the SPV is an infinite dipole sheet, the field would be constant with respect to distance from the surface.



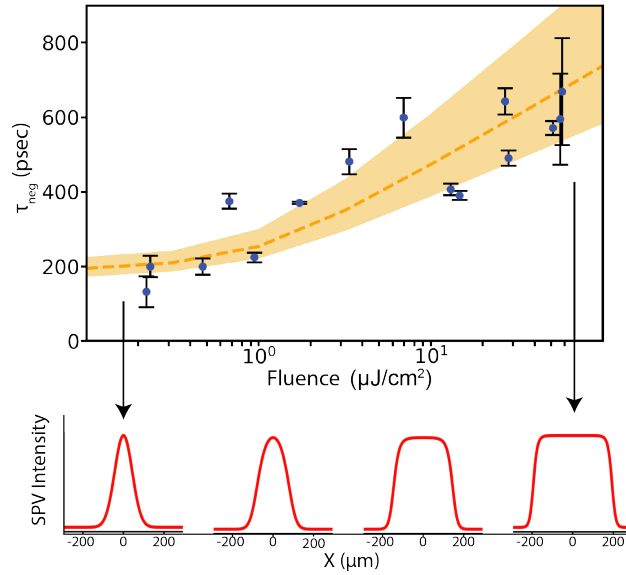
**FIGURE 3.3: Dipole geometry evaluation.** **a** Modeled energy shift versus negative delay as a function of beam size (light green to dark green increasing sigma) and forward SPV-decay constant (light yellow to dark yellow increasing time constant, *indistinguishable*). SPV time constant dependence on the negative delay is weak, beam geometry plays the greatest role. **b** Cartoon depicting SPV field length scale as a function of pump-beam diameter. Width of red-shaded region depicts magnitude of SPV field along z-axis. **c** SPV amplitude as a function of fluence demonstrates heavily non-linear behavior. Dashed black line represents a phenomenological fitting function. Inset: semi-log plot. **d** Dipole profile calculated using SPV amplitude versus fluence response curve. Profile colors correspond to fluences in panel c, black dashed curve corresponds to the initial pump profile with  $\sigma = 60 \mu\text{m}$ .

The generated dipole geometry should in fact be length scale[80]. In the case of a linear dependence of SPV amplitude with fluence, a Gaussian pump beam would generate a Gaussian SPV dipole, since all portions of the beam would uniformly scale into the dipole profile. However, by fitting the positive delay region with a two-exponential model and summing the respective amplitudes, we see that the SPV amplitude is strongly non-linear in fluence as shown in Fig. 3.3c. The black dashed curve represents a phenomenological fit to the fluence of the form  $a/(1+b/x^n)$  ( $a = 0.197$ ,  $b = 0.334$ ,  $n = 1.965$ ). This non-linear scaling of fluence to the SPV dipole would favor top-hat like dipole geometries at high fluence. We can see this clearly by utilizing the SPV fluence response curve from Fig. 3.3c on the known Gaussian pump with size  $\sigma \simeq 60 \mu\text{m}$  and the fluences from the study. The evolution of the dipole geometry with fluence is presented in Fig. 3.3d with colors that correspond to the fluence of



the data points in Fig. 3.3c. The black dashed line depicts the incident Gaussian pump-beam profile. The pump-induced dipole profile transitions from Gaussian-like to top-hat geometry as the fluence is increased.

### 3.5 Observing Gaussian to Top-Hat Dipole Geometry in the Negative Delay



**FIGURE 3.4: Modeling the dipole fluence dependence.** The measured negative-delay time constants as a function of fluence (blue dots) versus the model (yellow region). Errorbars are the standard deviations between multiple measurements at the same fluence. The yellow region was generated by assuming a range of maximal kinetic energies (0.5-0.7 eV) to account for possible changes in work function. The calculated dipole profiles from 0.1, 1, 10, 100  $\mu\text{J}/\text{cm}^2$  demonstrate the evolution of the dipole geometry.

Figure 3.4 demonstrates how a non-linear SPV response to fluence can alter the negative-delay profile, matching the ab initio calculation closely. By performing the same calculation as above but with  $\mathbf{p}(x, y)$  proportional to the augmented dipole profile at fluences ranging between .1 and 100  $\mu\text{J}/\text{cm}^2$ , we are able to determine a realistic model of the negative-delay constant versus fluence, displayed as the yellow region. The orange dashed line represents the calculation given a maximal photoelectron kinetic energy of 0.6 eV, the yellow surrounding region contains the results for 0.5-0.7 eV kinetic energies. The maximal kinetic energy is determined by the difference between the work function of the material and the incident photon energy of the probe. In our case, the material work function is approximately 5.4

eV [113, 114] and our photon energy is 5.93 eV. However, changes in surface chemistry can affect the work function of the material [115, 116]. We expect that some of the scatter in the data is due to sample degradation and subsequent changes in work function. If the surface dipole scaled proportionally with fluence, we would expect a flat response of the decay constant with fluence. The rise in decay constant with increased fluence demonstrates that the non-linear SPV fluence response augments the dipole geometry from approximately Gaussian (left-most red profile) to top-hat (right-most red profile) between the ranges of .1 and 60  $\mu\text{J}/\text{cm}^2$ .

### 3.6 Discussion

The negative delays in time-resolved experiments are often ignored, providing only equilibrium information in most scenarios. However, our study demonstrates that negative delays in time-resolved photoemission experiments provide important real-space information in the case of SPV materials. The time-scale of the negative-delay decay reflects the length scale (from the sample surface) of the pump-induced electric field [78]. In turn, this decay constant can be used to deduce changes in the SPV dipole geometry. The model developed by Yang et al. and employed on Gaussian pump-beams with linear SPV dipole responses [78], can be generally applied to non-Gaussian pump-beams with non-linear responses. Additionally, this method can be used to verify the incident pump-beam diameter during a TR-ARPES experiment. Moreover, with a well calibrated pump beam, it is possible to monitor the work function of an SPV material such as during in situ doping.

The evolution of the SPV dipole profile in  $\text{Bi}_2\text{Se}_3$  from Gaussian to top-hat has strong implications on the dynamics of the excited system. Possible relaxation mechanisms for the SPV excitation include diffusion of the dipole across the surface [74]. Furthermore, free charges can be accelerated along the surface by the potential gradient generated by the SPV, facilitating radial spin-currents. The exact kinetics are strongly influenced by the geometry of the SPV dipole field. By determining the initial state of the SPV excitation, one can begin to conjecture on the forces involved during dipole diffusion or charge transfer. For instance, free charges subjected to a top-hat potential will experience much stronger acceleration near the edges than at the center. In terms of device application, the geometry of the pump-induced field determines the geometry of useful devices. For instance, in applications that utilize the SPV as a photoactivated gate, understanding how to produce a uniform electric field from a given pump geometry is crucial.

### 3.7 Summary

In conclusion, this study establishes that the negative-delay effect resulting from non-equilibrium time-dependent surface fields can be used to determine the pump-induced field geometry by means of TR-ARPES. The ab initio calculation of the energy shift of photoemitted elec-

trons demonstrates that the surface photovoltage geometry on p-type  $\text{Bi}_2\text{Se}_3$  transitions from Gaussian-like to top-hat as a function of fluence as predicted by the non-linear fluence dependence of the SPV amplitude. This technique can be used as a tool to verify the pump-beam geometry at the focus. More importantly, this method allows for simultaneous collection of real-space and momentum-space information in SPV materials from the typical TR-ARPES configuration, introducing a novel procedure to the ARPES tool-kit.

## Chapter 4

# Driving Ultrafast Spin and Energy Modulation in Quantum Well States via Photo-Induced Electric Fields

The future of modern optoelectronics and spintronic devices relies on our ability to control the spin and charge degrees of freedom at ultrafast timescales. Rashba spin-split quantum well states, 2D states that develop at the surface of strong spin-orbit coupling materials, are ideal given the tunability of their energy and spin-states. So far however, most studies have only demonstrated such control in a static way. In this study, we demonstrate control of the spin and energy degrees of freedom of surface quantum well states on  $\text{Bi}_2\text{Se}_3$  at picosecond timescales. Following the work of Ch. 2 and 3, in this chapter, we produce picosecond time-varying electric fields at the material's surface by modulating the band-bending with infrared pulses, thereby reversibly augmenting the quantum well spectrum and Rashba effect. Moreover, we uncover a dynamic quasi-Fermi level, dependent on the Lifshitz transition of the second quantum well. These results open a new pathway for light-driven spintronic devices with ultrafast switching of electronic phases, and offer the interesting prospect to extend this ultrafast photogating technique to a broader host of 2D materials. The work presented here has been recently accepted for publication in *npj Quantum Materials* [117].

### 4.1 Introduction

Quantum well (QW) states in semiconductors are a result of a confining potential that traps electrons (typically in a 2D plane) quantizing their electronic states. These states are easy to produce, have tunable band gaps, and are conceptually simple in terms of quantum systems. For these reasons, they have yielded a plethora of applications such as high-efficiency solar cells, infrared lasers, and qubits [118, 119, 120, 121]. Suitable confinement potentials can be achieved by constructing a multilayer heterostructure, but they can also occur spontaneously on surfaces from an adsorbate induced localized surface potential [122, 123, 124].

When these states appear on the surface, the breaking of inversion symmetry removes the spin-degeneracy resulting in spin-polarized quantum well states [91, 125, 126, 127, 89, 88]. Combining quantum confinement with strong spin-orbit coupling joins the malleable electronic dispersions of quantum well states with the robust spin-polarization of Rashba states, making them extremely promising candidates for spin-based devices, such as the Datta Das spin-transistor [54, 128].

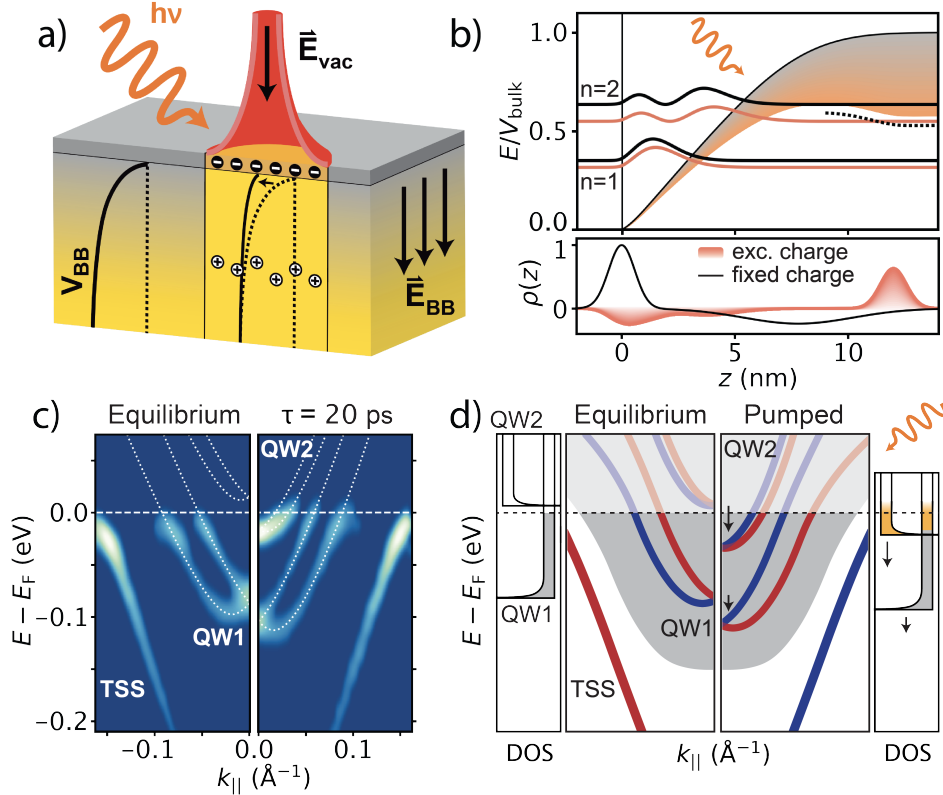
Since the Rashba interaction and quantum well spectrum are both predicated on the underlying electric potential, tuning the electric potential at the surface becomes a powerful method to manipulate both their spin and energy degrees of freedom [129, 130, 131, 124]. Such control has been achieved via in-situ surface chemical doping (irreversible and difficult to implement in devices) [132, 52, 89, 125], and electrostatic gating, (ideal for devices but often limited by the magnitude of the quantum well potential at the surface of bulk samples,  $10^7 - 10^{13}$  V/m)[133, 134, 135]. The real downfall of both methods is in the difficulty to dynamically tune the quantum well states on ultrafast timescales, restricting the ability to study the fundamental mechanisms of electronic relaxation and limiting device application in the time-domain.

Here, by combining the Surface Photovoltage Effect (SPV), a well-studied mechanism to producing reversible surface potentials in many semiconductors, with time and angle resolved photoemission spectroscopy (TR-ARPES), we demonstrate an ultrafast and reversible control of Rashba splitting and energy level spacing, and a subsequent quasi-equilibrium charge storage in correspondence of a photoinduced Lifshitz transition. This is in contrast to proposed methods of spin-current manipulation in topological insulators using the SPV to solely change the local surface potential of the Dirac surface state [77, 136, 108]. These results present a new platform for light-driven spin-orbit modulation and charge manipulation by directly controlling the density of states (DOS) on picosecond timescale. Experiments were performed on p-type  $\text{Bi}_2\text{Se}_3$ , a promising candidate for spin-based devices [54, 128], and ideal since it exhibits a strong SPV effect in the bulk [48, 74] and 2D quantum well Rashba surface states that are readily produced through various surface dopants such as carbon-monoxide, water, potassium, rubidium, or even long exposure to vacuum [127, 88, 89, 90, 137, 138, 40, 52].

## 4.2 Ultrafast Fields from Separation of Excited Charges

The p-type  $\text{Bi}_2\text{Se}_3$  single crystals were grown via directional slow solidification with  $\approx 1$  at. % Mg substitution with bismuth in order to bring  $E_F$  close to the bulk valence band maximum. The crystals were coated in graphite spray then cleaved in vacuum along the (111) plane at a base pressure of  $5 \times 10^{-11}$  Torr. The sample experienced a rapid dosing triggered by initial exposure to the infrared pump resulting in the formation of a clear quantum well spectrum similar to the observations by Lin et al. [91], with no further dosing

occurring after subsequent pumping. This dosing is perhaps due to the presence of trapped gasses in the graphite spray or the crystal itself, and produced results similar to the effects of carbon-monoxide and water surface dosing [88, 89]. We have observed this dosing effect multiple times but only after using graphite spray on specifically p-type  $\text{Bi}_2\text{Se}_3$  samples.



**FIGURE 4.1: Tuning quantum well potentials through charge separation.** **a** Diagram of the band-bending in  $\text{Bi}_2\text{Se}_3$  inside and outside illuminated region. Infrared excitation generates excited electron-hole pairs that are separated by the band-bending, reducing the internal electric field. **b** Photoexcited charge separation decreases the slope of the quantum well potential (grey to orange region). The quantum well energy levels ( $n = 1, 2$ ) before illumination (solid curves) are compressed in energy after the pump (dotted curves). **c**  $\partial^2 I / \partial E^2$  spectra at equilibrium and after pump pulse demonstrating the spectrum modification. **d** Illustration of quantum well level shifts in  $\text{Bi}_2\text{Se}_3$  before and after illumination. The grey parabolic region represents the conduction band before quantization. The DOS of Rashba-split bands exhibits a singularity near the band bottom. The photo-induced spectrum modification enables toggling of a Lifshitz transition.

Figure 4.1 presents a schematic of the experimental setup and the effect of coherent infrared light pulses on the band-bending and quantum well state. In a semiconductor, the

SPV effect occurs when in-gap surface states lead to a redistribution of charge between the bulk and surface at equilibrium. This non-uniform charge distribution is called the space charge region (SCR) and produces an internal electric field that “bends” the bands near the surface, as schematically shown in Fig. 4.1a. In the case of downward band-bending, illumination of the surface via an infrared pulse generates photoexcited electrons and holes that drift to the surface and bulk, respectively. These carriers partially cancel the internal electric field thereby reducing the band-bending and altering the surface potential (solid yellow region) [45, 46]. Equivalently, the downward band-bending potential results in an internal electric field at equilibrium, ( $\vec{E}_{BB}$ ), and this electric field is reduced by an opposing electric field generated by the separated photoexcited charges. The consequence of this is a time-varying electric field in the bulk that decays according to the recombination of separated photoexcited electron-holes. Hence, an SPV semiconductor substrate can serve as a time-dependent electric gate to 2D electronic states at the surface, and the infrared pulse can be focused to gate a specific area of interest. The  $\text{Bi}_2\text{Se}_3$  samples have metallic surfaces due to a topological surface state and host quantum well states which can be modified by the pump-induced time-dependent charge separation. In this way, the surface of the SPV material itself is the subject of the electric field gating and is modified by the time-varying internal field. An added consequence of the photoinduced charge separation is that the resulting finite dipole at the surface also produces an external electric field between the sample and the detector,  $\vec{E}_{vac}$ , that affects the detected kinetic energy of the photoelectron, resulting in a rigid energy shift of the measured dispersion, allowing us to track the SPV in real-time [80, 79, 78, 47, 48].

The  $\text{Bi}_2\text{Se}_3$  samples in this study are p-type doped with a hole-like majority carrier concentration of  $\approx 1 \times 10^{19} \text{ cm}^{-3}$  (see Fig. 4.2), yielding a fairly conductive bulk that generates a narrow SCR at the surface of approximately 10 nm (see discussion). In panel b, we have modeled the effect of an optical pump on the band-bending potential and quantum well energy levels. The lower plot shows the distribution of fixed charges that form the equilibrium band-bending potential (black line) and separated charges following photoexcitation (red gradient). Photoexcited electrons are distributed equally in three parts between the surface and two quantum wells (using the quantum well wave-functions to determine the density profile) and an equal number of photoexcited holes piled at the edge of the SCR. The band-bending length scale is similar to the wave-function spatial extension near the surface, such that only sufficiently separated charge to either side of the SCR can avoid high recombination rates in order to form a persisting SPV effect. [139]. The amplitudes of the excited charges with respect to the fixed charges have been enhanced by  $2\times$  for visibility. The effect of the population of separated photoexcited charges on the quantum well potential is seen in the upper plot (grey to orange). A secondary well forms at the bulk edge of the SCR (see dotted curve in panel b) that limits the ability to trap holes in the bulk such that the quantum well potential is not quenched after SPV saturation at the highest fluence (saturation is shown later in Fig. 4.12b). The squared modulus of the wave-functions and corresponding energies have been calculated for the equilibrium and maximally pumped condition shown as black

and dark orange curves, demonstrating a compression of the energy eigenvalues.

Fig. 4.1c presents  $\partial^2 I / \partial E^2$  ARPES spectra demonstrating the compression of the quantum wells after pump excitation as also schematically summarized in Fig. 4.1d. The strong downward band bending leaves the surface n-type doped, filling a large portion of the upper Dirac cone and the quantized conduction band [48, 89, 126], despite the p-doping in the bulk. The momentum-space picture of the quantum wells in  $\text{Bi}_2\text{Se}_3$  demonstrate more features than the simple cross-section shown in Fig. 4.1b. The first and second quantum wells, QW1 and QW2 are derived from the bulk conduction band (grey parabolic region in panel d) and exhibit near-parabolic dispersions. The strong spin-orbit coupling inherent to  $\text{Bi}_2\text{Se}_3$  as well as inversion symmetry breaking at the cleave-plane generates a Rashba effect that duplicates the quantum well states into momentum-separated spin-polarized pairs (shown in red and blue in panel d)[91, 125, 126]. Furthermore, the momentum splitting transforms the band minimum from point-like to a one-dimensional ring, resulting in a van Hove singularity below the intersection of the Rashba bands [140] for both QW1 and QW2 (see DOS in panel d). At equilibrium, with no pump beam, only QW1 is populated, exhibiting strong Rashba splitting. After pumping with a  $51.8 \mu\text{J}/\text{cm}^2$  820 nm pulse, QW1 and QW2 shift downwards in energy relative to the bulk conduction band minimum. QW1 shifts downward by approximately 25 meV and QW2 emerges below  $E_F$  and is then populated resulting in a sudden increase of the DOS. Therefore, the light-driven modification and subsequent filling of QW2 drives a van Hove singularity below the Fermi level, inducing a Lifshitz transition [141].

### 4.3 Transport Determination of Bulk Carrier Concentration

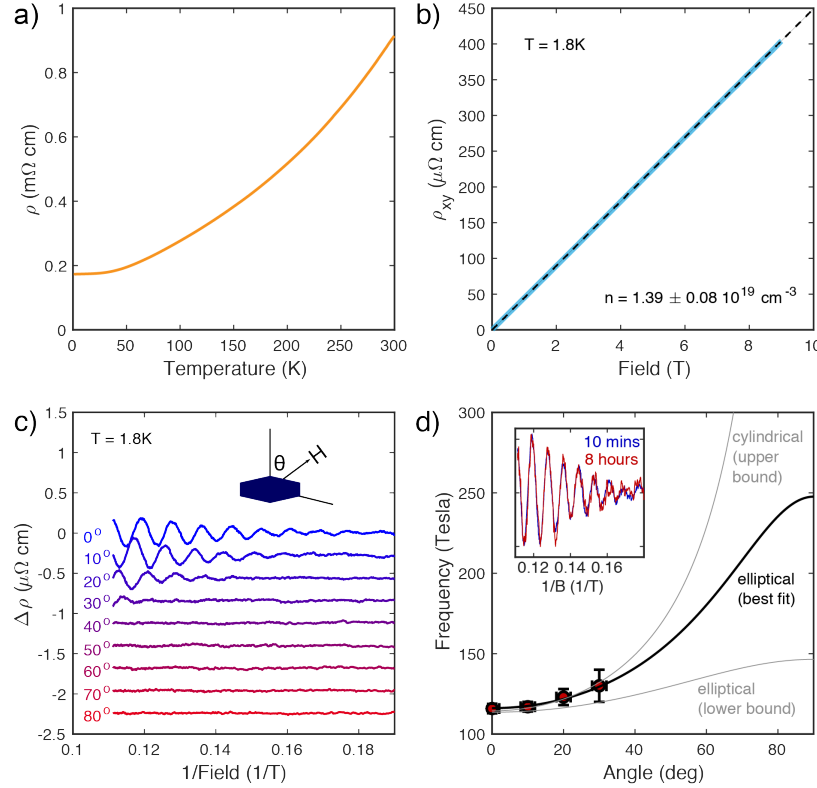
A crystal of  $\text{Bi}_2\text{Se}_3$  from the same growth batch as those used during in the ARPES measurements was cleaved with a scalpel in atmosphere, and electrical contact was made directly to the cleaved surface with gold wires and silver paint over the course of about 10 minutes. The transport measurements were conducted, and then the sample was removed from the cryostat and left in atmosphere for 8 hours, after which it was inserted back into the cryostat and remeasured.

The Hall resistivity at low temperature, as shown in Figure 4.2b gives the most precise measurement of carrier density of  $1.39 \pm 0.08 \times 10^{19} \text{ cm}^{-3}$ . In addition, the overall behavior of the resistivity versus temperature (panel a), and the value of the resistivity at low temperature both give good agreement with those of previous reports in  $\text{Bi}_2\text{Se}_3$  samples with  $10^{19} \text{ cm}^{-3}$  bulk carriers [142, 39].

SdH measurements at low temperature provide an independent method of measuring the carrier density, where the frequency of the SdH oscillation can be correlated to the cross sectional area of the Fermi surface pocket. Extensive work has been done previously in characterizing the Fermi surface of doped  $\text{Bi}_2\text{Se}_3$  crystals [143]. The Fermi surface is shaped



by an elongated ellipsoid with the long axis along the  $k_z$  direction. We therefore measured angle dependence of the oscillation frequency as the magnetic field is rotated from the c-axis direction to the planar direction. The data was then fitted by an ellipsoidal Fermi surface model, and the volume of the modeled Fermi surface was integrated to estimate the SdH carrier density.



**FIGURE 4.2: Transport on p-type  $\text{Bi}_2\text{Se}_3$ .** **a** Resistivity versus temperature. **b** Hall effect at low temperature. The data are well fit by a linear trend, giving a hole-like carrier density of  $1.39 \pm 0.08 \times 10^{19} \text{ cm}^{-3}$ . Uncertainty primarily comes from measurement of the sample thickness. **c** Shubnikov-de Haas (SdH) oscillations at 1.8 K measured in resistivity after background subtraction as a function of magnetic field tilt angle from the crystallographic a-axis to the planar direction (the inset shows geometry). Curves are offset vertically for clarity. **d** Angle dependence of the SdH oscillation frequency. Fits to the elliptical Fermi surface and circular Fermi surface models are shown, which provide upper and lower bounds on the SdH carrier density. Inset shows the magnitude of SdH oscillations for freshly cleaved sample and after 8 hour exposure to atmosphere. Negligible atmospheric effect suggests that oscillations are from bulk carriers. Data and discussion provided by Nikola Maksimovic.

The cross-sectional area of an ellipsoid with short axis  $k_{F,x}$  and long axis  $k_{F,z}$  is,

$$A(\theta) = \pi k_{F,x} [\sin^2(\theta)/k_{F,z}^2 + \cos^2(\theta)/k_{F,x}^2]^{-1} \quad (4.1)$$

The angle-dependent frequency was fitted with the ellipsoidal model with  $k_{F,x}$  and  $k_{F,z}$  as free parameters. The carrier density can be calculated by integrating the volume of the Fermi surface.

$$n_{\text{SdH}} = 1/(2\pi)^3 \pi k_{F,x}^2 k_{F,z} \quad (4.2)$$

The best fit ellipsoidal model results in a SdH carrier density of  $1.1 \times 10^{19} \text{ cm}^{-3}$  in reasonable agreement with the Hall carrier density. To place upper and lower bounds on the SdH carrier density estimate, we model the lower end of the angle-dependent data error bars with an ellipsoidal model (lower bound on SdH carrier density), and model the data with a cylindrical Fermi surface model (upper bound on the SdH carrier density). The cylinder is essentially an ellipsoid in the limit of infinite long axis,  $k_{F,z} \Rightarrow \infty$ . Thus, the angle-dependence of a cylinder is given by  $A(\theta) = \pi k_{F,x}^2 / \cos(\theta)$ . The lower and upper bounds on the estimated SdH carrier density are 0.6 and  $1.9 \times 10^{19} \text{ cm}^{-3}$  respectively. The Hall carrier density falls within this range.

Based on the following arguments, it is likely that the surface carriers have a negligible effect on our measurements, and therefore the carrier density measured by both Hall and SdH reflects that of the bulk. First, it has been previously observed that surface carriers are only detectable in SdH measurements at high fields larger than 10 Tesla and the oscillations associated with the surface states have been observed to disappear if the sample is exposed to atmosphere for more than two hours [142]. Our measurements are taken only up to 9 Tesla, and the SdH oscillation amplitude is essentially unaffected by atmospheric exposure (as seen in Fig. 4.2d inset). Second, the angle-dependent oscillations are best fit by a 3-dimensional ellipsoidal model, rather than a 2-dimensional model, suggesting that the SdH oscillations are associated with a 3-dimensional (i.e. bulk) Fermi surface rather than 2-dimensional surface states. Admittedly, with the amount of data points present it is difficult to distinguish between a cylindrical 2-D scenario and an elliptical 3-D scenario. Nevertheless, the SdH carrier density from the elliptical best fit gives good agreement with the Hall carrier density, suggesting that the SdH and Hall measurements reflect the same bulk carriers. Third, the measured resistivity of the sample is in good agreement with that measured in  $\text{Bi}_2\text{Se}_3$  crystals with  $10^{19} \text{ cm}^{-3}$  bulk carriers. Finally, the surface and bulk carriers on general grounds would be expected to have different mobilities, and as such would produce a nonlinear Hall resistivity in a regime of magnetic field where the two carriers have comparable conductivities. In our measurement, we observe an almost perfectly linear dependence of  $\rho_{xy}$  on field, suggesting that only a single carrier type is detectable over this field range. Based on the above arguments, it is likely that both the SdH and Hall effect measurements probe the bulk carriers in the sample, and that the surface state contribution is negligible.

## 4.4 Dynamic Quantum Well Spectrum and Lifshitz Transition

Figure 4.3 demonstrates the evolution of the quantum well spectrum after ultrafast illumination. Since the SPV decays in time and the effective gating field depends on the SPV strength, a single time-resolved measurement records a continuum of the field effect on the quantum well.

Fig. 4.3a illustrates the field effect on surface confined quantum well as a function of delay. The grey region denotes the quantum well SCR confinement at the surface and the white region represents the near-surface bulk. At equilibrium (I), the band-bending is maximal resulting in an enhanced slope for the quantum well potential and can be represented by an internal electric field  $\vec{E}_{\text{BB}}$ . The maximum reduction in the band-bending is the potential difference between the surface and deep within the bulk at equilibrium, labeled  $V_{\text{BB},0}$ . At  $\tau = 0$  (II), when the pump pulse arrives, separated photoexcited carriers generate an opposing electric field to  $\vec{E}_{\text{BB}}$ , labeled  $\vec{E}_{\text{eff}}$ . The internal field from the separated carriers acts as an effective applied field on the quantum well potential, driving the time-dependent modification to the spectrum. In the illustrated scenario, the pump pulse is significantly strong as to saturate the available hole trap sites altering the surface potential as a function of delay by  $\Delta V_{\text{SPV}}(\tau) = V_{\text{BB},0} - V_{\text{BB}}(\tau)$ , resulting in reduced but non-zero band-bending. At more positive delays (III to IV), the excited charge recombines thus reducing the effective field  $\vec{E}_{\text{eff}}$ , reviving the band-bending potential, and bringing the surface potential back to its equilibrium value.

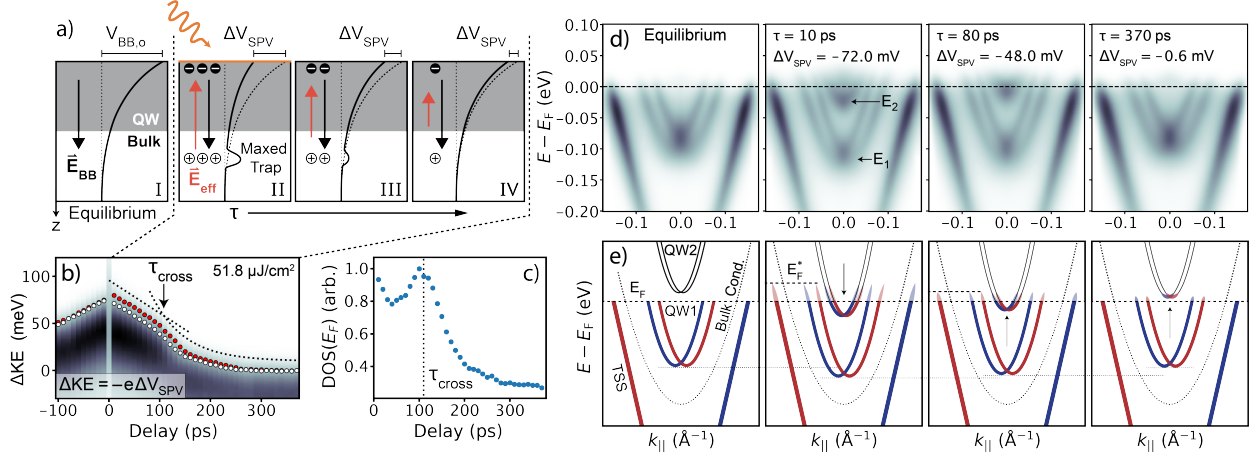
We can monitor the photoexcited charge separation through the energy shift of the ARPES spectrum induced by the in vacuum field produced by  $\Delta V_{\text{SPV}}$ . The change in the surface potential has the effect of increasing the photoelectron kinetic energy at the detector with respect to the equilibrium energy position ( $\Delta \text{KE}$ ). Fig. 4.3b presents the effect of the SPV rigid shift on the topological surface state at the Fermi wavevector as a function of delay. The rigid shift of the spectrum extracted from the shift of the Dirac dispersion at fixed momenta well below  $E_{\text{F}}$  is plotted in white. The Fermi edge as determined by fitting a Lorentzian multiplied by a Fermi-Dirac distribution is plotted in red and denotes the quasi-Fermi level,  $E_{\text{F}}^*$  (See Fig. 4.4). The rigid energy shift is a direct measure of the surface potential as a function of delay since  $\Delta \text{KE}(\tau) = -e\Delta V_{\text{SPV}}(\tau)$ , where  $e$  is the charge of the electron.

Under the center of charge approach [144, 145], the SPV signal can be described by an average displacement of electron and hole sheet charges induced by the band banding such that:

$$\Delta V_{\text{SPV}} = \frac{e}{\epsilon_r \epsilon_0} n_{\text{sep}} d, \quad (4.3)$$

where  $n_{\text{sep}}$  and  $d$  are the charge separation density and separation distance, respectively, and  $\epsilon_r \epsilon_0$  is the dielectric constant of  $\text{Bi}_2\text{Se}_3$ . With the assumption that the separation

distance is fixed and approximately equal to the width of the band-bending region, then the measurement of  $\Delta V_{\text{SPV}}$  is proportional to the charge separation concentration  $n_{\text{sep}}$ , and therefore the charge at the surface [146, 144]. To be clear, this is different than the total photoexcited carriers generated by the pump since significant recombination has taken place after 10 ps, with only sufficiently separated charges surviving (see Fig. 4.13).



**FIGURE 4.3: Time-resolved electric field gating of quantum well spectrum.** **a** Effective applied field,  $\vec{E}_{\text{eff}}$  is generated by separated photoexcited carriers, manifesting as a reduction of the band-bending potential. SPV is maximized before quenching the band-bending due to a finite limit on trapped holes. As photoexcited charge recombines, band-bending returns and the effective field is reduced. **b** Separated surface charge can be monitored by the rigid energy shift of the ARPES spectrum due to the voltage change at the surface ( $\Delta V_{\text{SPV}}$ ). Black open dots correspond to the SPV-induced rigid shift of the band structure relative to equilibrium  $E_F$ , red dots corresponds to the quasi-Fermi level at  $k_F$  of the TSS. **c** DOS at the Fermi level as a function of delay revealing the Lifshitz transition of QW2. **d** Symmetrized ARPES spectra at equilibrium and three non-equilibrium delays demonstrating the pump-induced QW shifts after correcting the SPV shift. **e** Graphic summarizing QW spectrum dynamics corresponding to the spectra in panel d, presenting a delay-dependent field effect on the quantum wells and long-lived quasi- $E_F$ .

Moreover, if the charge is sufficiently separated and localized (a fit assumption based on the long lifetime of the SPV), then the photoinduced charge separation is analogous to a parallel plate capacitor within the probe beam spot and the effective applied field is also proportional to  $\Delta V_{\text{SPV}}$  and the surface charge.

So in the positive delay, as the photoinduced separated charge recombines, as shown in panel a regions II-IV, the  $\Delta KE$  shift of the spectrum decays proportionally to the separated charge density (panel b for  $\tau > 0$ ). Tracking the charge density in this way enables us to map the delay axis to a surface voltage and ultimately an applied field strength (discussed

in Figure 4.7), allowing for a continuous measurement of the field effect by simply allowing the photoexcited recombination to take place.

At negative delays (photoemission occurs before the pump) there is a rigid shift of the recorded ARPES spectrum. This final state effect is due to the photoelectron interacting with an SPV generated field induced by a pump pulse that arrives after photoemission [80, 79, 78, 47]. The rigid energy shift in the negative delay is therefore shifting the unpumped spectrum and can be ignored for the purposes of this study.

In the positive delay, a maximum  $\Delta KE$  shift of 72.0 meV is reached at 10 ps after 51.8  $\mu\text{J}/\text{cm}^2$  illumination. Between 10 ps and 125 ps, the SPV induced shift follows an unusual linear decay profile. After 125 ps the SPV decays exponentially with a time constant of approximately 53 ps. This apparent discrete transition from a linear decay mechanism to an exponential decay is associated with the transit of QW2 above the Fermi level,  $\tau_{\text{cross}}$ . In the absence of surface quantum wells,  $\text{Bi}_2\text{Se}_3$  exhibits a simple exponential decay with no linear region or kink [47, 48]. Panel c shows the DOS at the Fermi level,  $E = (-0.005, 0.005)$  eV, and at zero momentum,  $k = (-0.005, 0.005)$   $\text{\AA}^{-1}$ , demonstrating the crossing of the QW2 band bottom and indicating the Lifshitz transition as QW2 relaxes.

The continuous photo-induced modification of the quantum wells is observed in Fig. 4.3d which displays four spectra of the  $\text{Bi}_2\text{Se}_3$  quantum well spectrum at equilibrium and at three separate delay values. The spectra have been shifted to compensate for the extrinsic delay-dependent rigid energy shift associated with the SPV effect (white circles in panel b) [80, 79, 78, 47]. At equilibrium (far left), only the topological surface state and QW1 are present and occupied below the Fermi level,  $E_F$ . The full band-bending is present creating a steep quantum well potential as we described in scenario I of panel a. This results in a large energy spacing for QW1 and QW2, leaving QW2 unpopulated above  $E_F$ .

For the pumped spectrum, we first look to the data at 10 ps. By this time, nearly all hot carrier recombination has already taken place [41, 42, 36], leaving behind long-lived trapped charges (see Fig. 4.8). QW1 shifts downward in energy and QW2 falls below  $E_F$  as photoexcited charges have reduced the equilibrium band-bending modifying the quantum well potential; States above  $E_F$  are populated resulting in a new quasi-equilibrium Fermi level. At  $\tau = 80$  ps, the quantum well spectrum drifts towards higher energies relative to the topological surface state and  $E_F$ . At  $\tau = 370$  ps, the quantum well spectrum has mostly returned to the equilibrium energy spacing with some charge in QW2 remaining  $\sim 10$  meV above  $E_F$ . For each delay, we can determine the photoinduced change in the surface potential,  $\Delta V_{\text{SPV}}(\tau)$ , from  $\Delta KE$  in panel b, thereby tracking the quantum well modifications as a function of surface voltage.

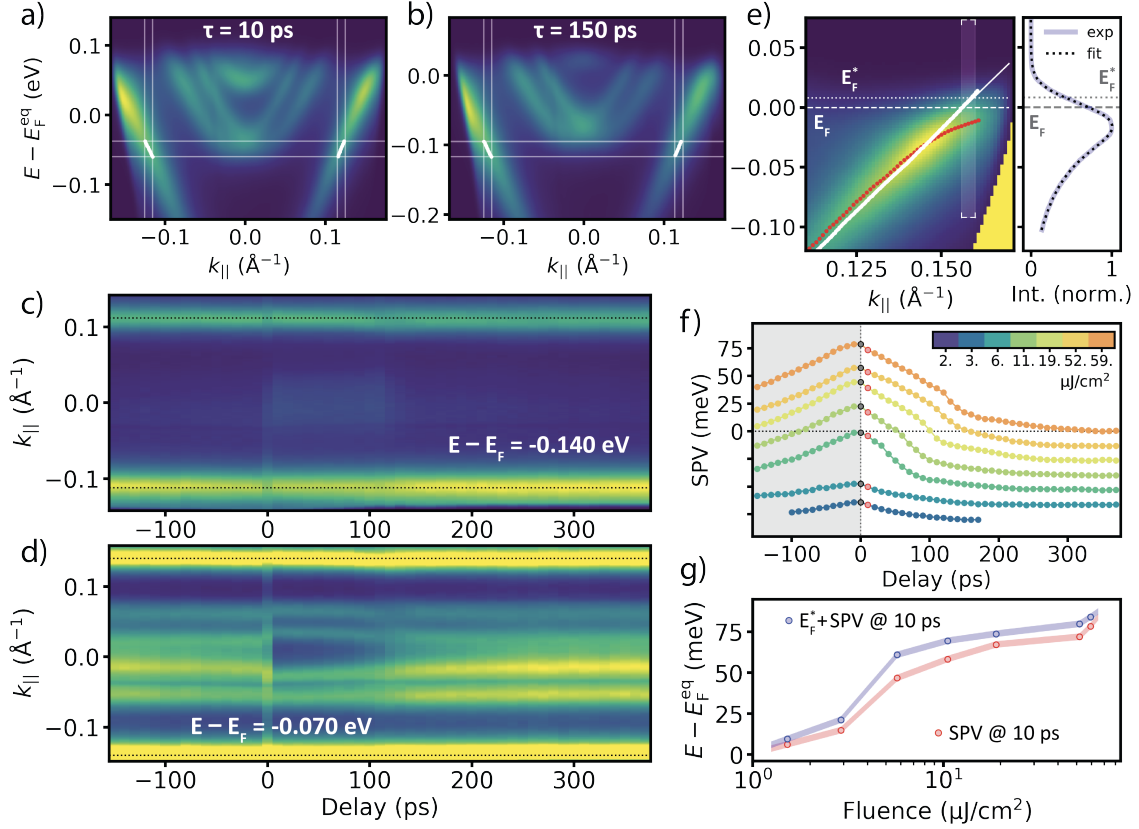
The quantum well spectrum dynamics is summarized in Fig. 4.3e. Only QW1 and QW2 bands are depicted in the quantum well spectrum for simplicity. At equilibrium (far left panel), the second quantum well is unoccupied above  $E_F$  and the quantum well spectrum exhibits large energy spacing due to the full strength of band-bending. After pumping ( $\tau = 0$ ), the band-bending is reduced and the quantum well spectrum contracts bringing QW2 beneath  $E_F$ . As the spectrum modification relaxes, the QW1 band bottom energy (dotted horizontal lines) exhibits a monotonic upward shift, along with the more obvious upward

shift of QW2. Non-equilibrium electrons at the surface are stored in quasi-equilibrium below  $E_F$  in QW1 and QW2 as long as the band-bending remains diminished. The excess electrons stored beneath  $E_F$  are allowed to decay when they are pushed back above  $E_F$  by the return of the equilibrium energy spacings. The competition between the rate of charge being pushed above  $E_F$  by the upward energy shifts and the decay rate of charge above  $E_F$  allows charge to exist above the Fermi level during the course of the spectrum relaxation. This ultimately leads to excess charge remaining in QW2 at  $\tau = 370$  ps even when the quantum well energy spacing has returned to equilibrium.

Though the delay dependence of the band-bending potential is interesting in its own right, this study focuses mainly on the delay-dependent modifications to the quantum well states. As such, we must remove the SPV-induced rigid shift in order to study the relative changes in binding energy of the quantum well spectrum. The negative delays also experience a delay-dependent rigid energy shift as a result of the photoemitted electron's interaction with the generated electric field as it travels in vacuum (grey region Fig. 4.4f)[47, 78].

Figure 4.4 depicts our method for removing the rigid binding energy shift and establishing the Fermi energy at binding energy zero. To determine the delay-dependent rigid shift, we perform Lorentzian centroid fitting of the Dirac surface state in a narrow momentum range on both the negative- and positive-momentum branch ( $|k| = [0.125, 0.135]$ ). (In principle, the Dirac node, rather than the Fermi edge, would be an acceptable choice for determining the delay-dependent rigid shift. However, in our case, the Dirac node coincides with the work function cutoff and is therefore susceptible to small changes in work function and surface stray fields.) Fig. 4.4a,b demonstrate the centroid locations of the unshifted Dirac dispersion for  $51.8 \mu\text{J}/\text{cm}^2$  in the fixed momentum ranges for 10 and 150 ps, clearly showing a large change in energy positions.

Panels c and d demonstrate the validity of the rigid shift determined from panels a and b. In panel c, the rigid shift has been applied to the delay-dependent spectra and integrated over a narrow energy range around  $-0.140$  eV. The constant energy delay map shows that the Dirac dispersion band location is fixed (black dashed lines). In panel d, the constant energy map is centered at  $-0.070$  eV exposing QW1. Again the Dirac surface state is fixed with respect to delay, however QW1 clearly evolves in energy as a function of delay, dipping at small delays and relaxing towards equilibrium at long delays.



**FIGURE 4.4: SPV rigid shift and quasi-Fermi level.** **a,b** Raw spectra at 10 and 150 ps for  $51.8 \mu\text{J}/\text{cm}^2$ . The spectrum at 10 ps is shifted nearly 100 meV above the equilibrium energy position. Rigid shift is determined by fitting the Dirac dispersion in a fixed momentum range for all delays (white dots). **c,d** Rigid shift correction using dispersion shift from panels a,b creates uniform Dirac momentum positions (black dashed lines as visual guide). Panel d demonstrates that, at constant binding energy, QW1 clearly dips while the momentum position of the Dirac surface state remains fixed. **e** Quasi-Fermi level is determined using a Lorentzian multiplied by Dirac distribution at  $k_F$ . White points are MDC peak locations and red points are EDC peak locations. The downturn of the EDC peak locations suggests that  $k_F$  is well within the detector window (yellow region indicates detector edge). **f** SPV shift as a function of fluence determined from dispersion shifts described in panels a,b for all fluences. **g** Quasi-Fermi level compared to SPV shift at maximal measured excitation (10 ps) as a function of fluence. Delay dependence of  $E_F^*$  is shown in Fig. 4.12

In addition to the rigid shift produced by the SPV effect, the Fermi level shifts with respect to the equilibrium Fermi level. Fig. 4.4e displays the Dirac dispersion near  $k_F$  from panel a after applying the SPV rigid shift fix. The white points and the red points indicate the MDC and EDC peak locations, respectively. The downward turn of the EDC peak locations near 0.0 eV is exhibitivite of the energy resolution effect on dispersion fits near the Fermi level [147]. Moreover, the MDC peak locations demonstrate a linear dispersion that is well within the detector window as the dispersion continues on above  $E_F$ . These two factors validate that the momentum fitting region (shaded white region) captures the true  $k_F$  of the Dirac dispersion, thereby providing an accurate determination of the quasi-Fermi level,  $E_F^*$ . The resulting integrated spectral intensity and fit using a Lorentzian multiplied by a Fermi-Dirac distribution with a linear and constant background is displayed in the side plot and closely captures a singular band at  $k_F$  filled above the equilibrium Fermi level.

Panel f displays the SPV shift determined from panels a and b for all measured fluences. The kinked decay profile demonstrates a crossover from linear to exponential-like at a fluence dependent  $\tau_{\text{cross}}$  for fluences greater than  $4 \mu\text{J}/\text{cm}^2$ . Panel g presents the maximal SPV values determined at 10 ps (shaded red dots in panel f) as well as the quasi-Fermi level shift in addition to the SPV shift at 10 ps (blue).

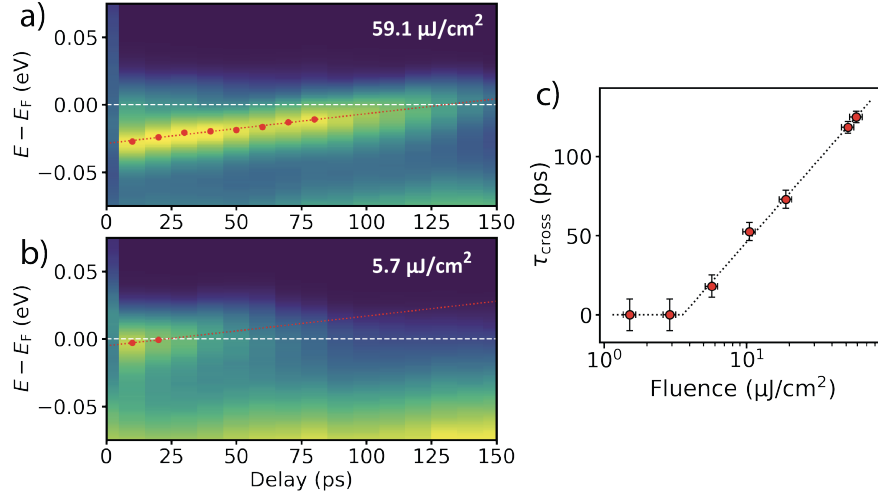


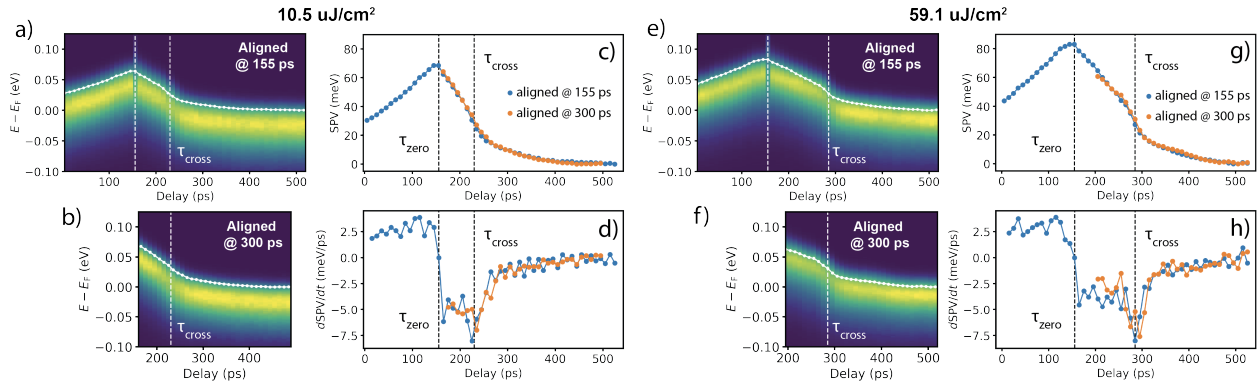
FIGURE 4.5: **QW2 crosses Fermi level.** **a,b** Momentum-integrated spectra at  $\Gamma$  as a function of delay showing QW2 band bottom at highest and lowest fluence in which QW2 is populated below  $E_F$ . Red points and red line represent QW2 peak positions and linear fit. **c** The time at which QW2 crosses  $E_F$  is determined using the linear fit with the error extrapolated from the number of points in the fit and the delay step-size.

The analysis of the decay rate of the electron population in the second quantum well (QW2) relies on knowing the delay value at which QW2 emerges above the Fermi level.



Figure 4.5 demonstrates our method for determining the Fermi level crossing time for the QW2 band bottom. We use the same method to what is shown in Fig. 4.7a, in which the center of mass along the energy axis of the QW2 band bottom is determined for each delay. Then a subsequent linear fit determines the delay time at which the band crosses  $E_F$ .

The resulting values are plotted in Fig. 4.5c. The error bars are an overestimate of the error set to the time step of the delay stage divided by the square root of points in the fit,  $10/\sqrt{(N)}$  ps. This method closely matches the observed crossing time from the SPV decay curves.

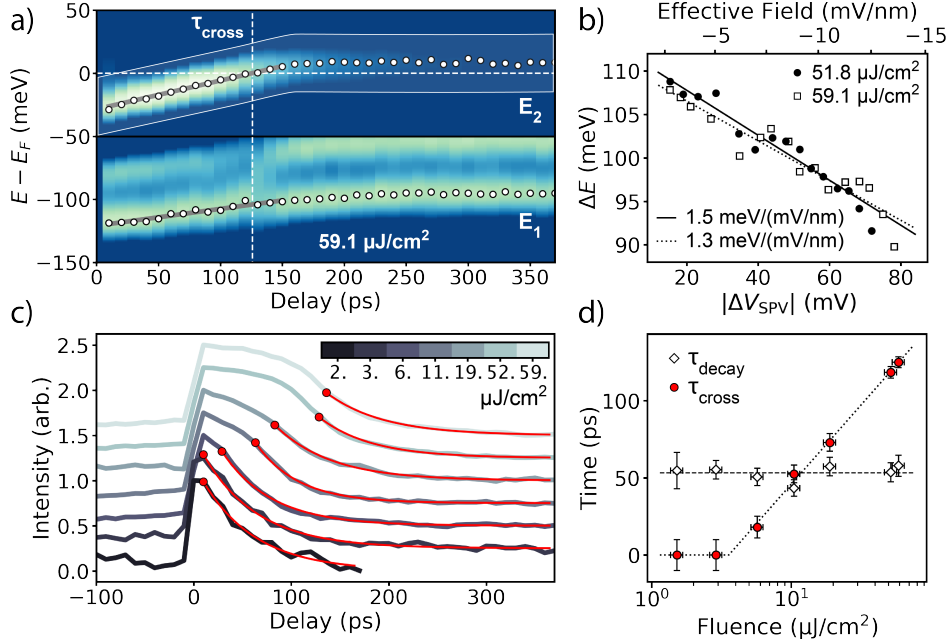


**FIGURE 4.6: Aligning pump-probe spatial overlap before and after kinked feature.**

**a** Rigid shift delay dependence at TSS  $k_F$  for low fluence ( $10.5 \mu\text{J}/\text{cm}^2$ ) with pump spatially overlapped with probe at delay =  $t_0 = 155$  ps in raw delay values. White circles indicate SPV rigid shift determined using method described in Fig. 4.4. **b** Aligning pump with probe at delay = 300 ps in raw delay values. **c** Overlap of SPV profiles from panels a and b. **d** Derivatives of panel c curves with dip indicating kinked feature at  $\tau_{\text{cross}}$ . **e-h** Same as panels a-d at high fluence ( $59.1 \mu\text{J}/\text{cm}^2$ ).

We double checked that the kinked feature in the positive delay of the SPV response is not due to delay stage movement by performing two delay scans at a given fluence and aligning pump-probe spatial overlap before and after the kink. This was performed for all fluences in which a kinked profile is observable. The spatial alignment is performed by scanning the pump pointing mirror in small steps in x and y at a fixed delay value on the delay stage. The pointing position of the mirror that produces maximal excitation according to the live ARPES reading is recorded, ensuring best possible spatial overlap. If the delay stage was causing misalignment that led to a kinked feature, then re-correcting the pointing before and after the kinked feature would lead to large changes in the SPV decay profile. For purposes, of clarity the raw data is shown including the raw delay values (not corrected for  $t_0$ ). The

two delays chosen were  $t_0 = 155$  ps and 300 ps for the figures above. At low fluence ( $10.5 \mu\text{J}/\text{cm}^2$  panels a-d) and high fluence ( $59.1 \mu\text{J}/\text{cm}^2$  panels e-h) the SPV decay profiles are invariant to the readjustment of the pump-probe spatial overlap. This is most clearly seen in panels c-d and g-h where the SPV profile determined using the method in Fig. 4.4 and the differentiated profiles are nearly identical and clearly retain the kinked feature at  $\tau_{\text{cross}}$  for both high and low fluence.



**FIGURE 4.7: Quasi-equilibrium charge and ultrafast intersubband-gap control.** **a**  $\partial^2 I / \partial E^2$  spectra of QW1 and QW2 band bottoms as a function of delay. The band bottom positions are marked by black open dots demonstrating a near-linear recovery up to the moment  $E_2$  crosses  $E_F$ ,  $\tau_{\text{cross}}$ . **b** The intersubband-gap as a function of the SPV determined at each delay for the two highest fluences ( $51.8$  and  $59.1 \mu\text{J}/\text{cm}^2$ ). The effective field on the quantum well system is extrapolated from the average best fit line and the triangular-well approximation. **c** Integrated spectral intensity of the QW2 band bottom using integration window in panel a over a large fluence range.  $E_F$  crossing time, ( $\tau_{\text{cross}}$ ), +10 ps is used as a cutoff (minimum set at 10 ps) for exponential fits (red). **d** QW2 decay rate,  $\tau_{\text{decay}}$ , (black open diamonds) and  $\tau_{\text{cross}}$  (red dots) as a function of maximum SPV at each fluence (and extrapolated effective field on QWs) indicating that the lifetime of QW2 states above  $E_F$  is fixed but quasi-equilibrium lifetime is set by peak field strength.

We further investigate the delay dependence of the quantum well level spacing and charge occupation in order to better understand the pump-induced quantum well state modification. In Fig. 4.3, we demonstrated that the surface potential is a function of delay, and so we are

able to track the quantum well modification with respect to surface voltage. We can take this one step further and estimate the effective field,  $\vec{E}_{\text{eff}}$ , from the energy positions of the QW1 and QW2 band bottoms.

Fig. 4.7a displays momentum integrated  $\partial^2 I / \partial E^2$  spectra for QW1 and QW2 band bottoms as a function of delay. The momentum integration windows for QW1 and QW2 band bottoms are centered at  $k = 0.000 \text{ \AA}^{-1}$  and  $k = 0.023 \text{ \AA}^{-1}$ , respectively, with a width of  $\Delta k = 0.002 \text{ \AA}^{-1}$ . The QW1 and QW2 band bottom positions,  $E_1$  and  $E_2$ , (black open dots) track the evolution of the energy levels as the quantum well spectrum is modified by the field effect and subsequent relaxation. The positions of  $E_1$  and  $E_2$  are displayed in Fig. 4.3d for comparison with the full dispersion. After pump illumination, QW1 and QW2 shift toward higher binding energies, dropping QW1 by  $\sim 25 \text{ meV}$  and QW2 by  $\sim 35 \text{ meV}$  and bringing QW2  $\sim 25 \text{ meV}$  below  $E_F$ . Both quantum wells shift back towards lower binding energies linearly as a function of delay at different rates. For QW2, 126 ps corresponds to  $\tau_{\text{cross}}$  (see vertical dashed line in panel a), the delay time in which the band bottom crosses  $E_F$ . After this point, spectral intensity of the band bottom decreases at an accelerated rate.

An important property of quantum well systems is the intersubband-gap,  $\Delta E = E_2 - E_1$ , which sets important material properties including the optical response. The delay dependence of the quantum well band bottom positions, and therefore the field dependence of the intersubband-gap, demonstrates ultrafast-field tunability. Panel b shows the field dependence of the intersubband-gap, defined as the difference in energy between the QW2 and QW1 band bottom energies  $\Delta E$  for the two highest fluences. We focus on the band-gap values for  $\tau < \tau_{\text{cross}}$  where QW2 is fully populated and the position of the band bottom is not strongly influenced by the Fermi level.

The effective applied field on the quantum well spectrum can be extrapolated from the intersubband-gap. The triangular-well potential is a widely used approximation to describe surface confinement, especially for low-energy wave-functions, and is suited for capturing the effective electric field experienced by the quantum wells (see Fig. 4.9d). A more precise model of the confinement potential may be necessary in the condition of higher-energy wave-functions ( $n > 2$ ) [148, 149, 150, 89].

The triangular-well potential is described by,  $V(z) = eFz$ , in which  $F$  represents the steepness of the well with units of electric field. As such, the quantum well wave-functions take on the form of Airy functions with energy eigenvalues [148, 150]:

$$\epsilon_n = c_n \left[ \frac{(eF\hbar)^2}{2m^*} \right]^{1/3}, \quad (4.4)$$

The energy eigenvalues,  $\epsilon_n$ , are referenced to the bulk conduction band minimum before quantization, which represents the bottom of the quantum well potential. By subtracting  $\epsilon_1$  from  $\epsilon_2$ , the equation can be rearranged to solve for  $F$  using only the intersubband-gap energy, and the known Airy coefficients,  $c_2 \approx 2.338$  and  $c_1 \approx 4.088$ .

$$F = \frac{\sqrt{2m^*}}{e\hbar} \left( \frac{\Delta E}{c_2 - c_1} \right)^{3/2} \quad (4.5)$$

Utilizing the above equation and the average best fit lines from panel b, the x-axis can be rescaled in terms of the effective applied field on the QW states. We use the average effective mass from dispersion fits of  $m^* = 0.45 m_e$ . The total electric field in the quantum well region evaluating the best fit line at equilibrium ( $\Delta V_{\text{SPV}} = 0$ ) is 42.0 mV/nm and 55.7 mV/nm at the maximal SPV ( $\Delta V_{\text{SPV}} = 78.5$ ), reasonable electric field values for surface quantum well systems [135]. This is equivalent to applying a field,  $\vec{E}_{\text{eff}}$  between 0 mV/nm ( $\Delta V_{\text{SPV}} = 0$  mV) and 13.7 mV/nm ( $\Delta V_{\text{SPV}} = 78.5$  mV) opposite to the equilibrium band-bending field  $\vec{E}_{\text{BB}}$ . The field effect on the intersubband-gap shown in Fig. 4.7b exhibits a nearly linear dependence. Yet, equation 3 describes that the band-gap should follow as the electric field to the power of 2/3. Nevertheless, near-linear dependence with respect to field is still expected since the quantum well electric field,  $F$ , is always far from 0, existing in the range of (40 - 60 mV/nm). Since the applied field axis ticks are determined by the y-axis values of the best fit line, they are independent of the surface voltage axis. The even spacing of both x-axis ticks demonstrates that the intersubband gap is near-linear in both surface voltage and effective electric field, as expected from the center of charge separation model in equation 2.

In addition to enabling an ultrafast field effect on the quantum well energy positions and intersubband-gap, the ultrafast gating grants unique access to the dynamics of the quantum well spectrum. In particular we uncover quasi-equilibrium charge occupation and determine recombination timescales, not accessible by any static gating technique. Furthermore, we observe that the crossing of the QW2 band bottom above  $E_F$  (vertical dashed line in Fig. 4.7a,  $\tau_{\text{cross}} = 126$  ps at  $59.1 \mu\text{J}/\text{cm}^2$ ) corresponds to the transition of the SPV relaxation from a linear to an exponential decay mechanism as observed in Fig. 4.3b. Fig. 4.7a now shows that the charge stored in the QW2 band bottom remains stable for delays less than 126 ps, and quickly depopulates the band bottom for delays greater than 126 ps. This behavior can be seen more clearly by integrating the spectral intensity of the raw ARPES spectra using the integration window marked in panel a (shaded region). Fig. 4.7c displays the integrated spectral intensity of the QW2 band bottom as a function of delay for fluences between 1.5 and  $59.1 \mu\text{J}/\text{cm}^2$ . At high fluences the spectral intensity remains stable up until  $\tau_{\text{cross}}$ , after which it transitions into an exponential decay. At the lowest fluences, there is no stable region and only exponential behavior. The decay region in red is fitted with exponential fits, with the start of the fitting range (red dots) set by  $\tau_{\text{cross}} + 10$  ps and a minimum cutoff of 10 ps.

As a function of fluence, the resulting timescales from the exponential fit,  $\tau_{\text{decay}}$ , are plotted in Fig. 4.7d (diamonds) alongside  $\tau_{\text{cross}}$  (red dots). The decay rate of charge in QW2,  $\tau_{\text{decay}}$ , is independent of fluence with an average decay time of 53 ps. On the other hand,  $\tau_{\text{cross}}$  increases logarithmically for fluences above  $4 \mu\text{J}/\text{cm}^2$ , marking a critical fluence for the Lifshitz transition of QW2. For fluences in which the  $\tau_{\text{decay}} = 0$ , QW2 never dips below  $E_F$  after the pump, and therefore does not undergo a Lifshitz transition. All together, this demonstrates that the charge stored in QW2 is stable while it is below  $E_F$  and charge above  $E_F$  decays with a timescale of approximately 53 ps. Moreover, the timescale for stable stored charge in QW2 is a consequence of the dynamic Lifshitz transition and can be controlled by

varying the pump fluence, equivalent to increasing the SPV strength.

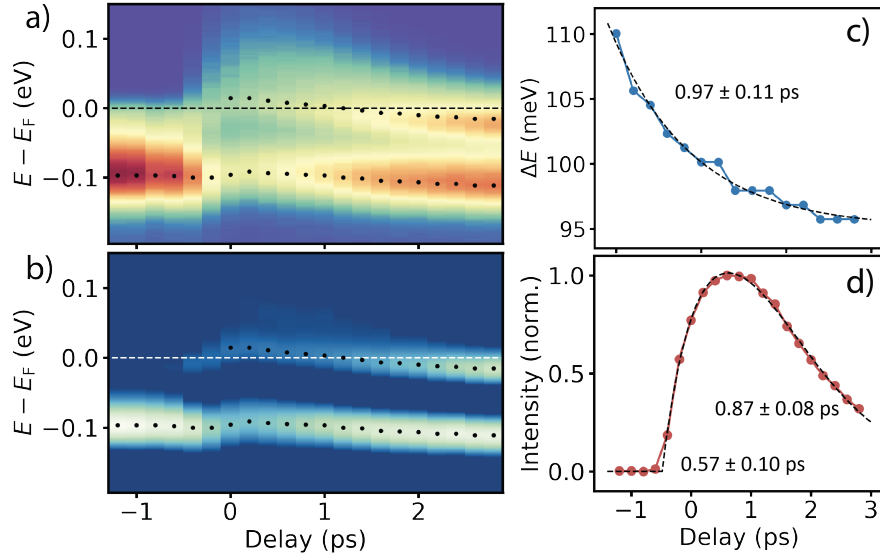


FIGURE 4.8: **Picosecond QW energy-shifts and hot-carrier relaxation.** **a,b** Momentum integrated raw and  $\partial^2 I / \partial E^2$  spectra, respectively, at  $\Gamma$  with QW1 and QW2 peak positions notated in black. **c** intersubband-gap between QW1 and QW2 as a function delay. Time-constant towards maximal applied field is  $\approx 1.0$  ps. **d** Integrated intensity for  $E - E_F > +10$  meV displays build up time of  $\approx 0.6$  ps and decay rate of  $\approx 0.9$  ps.

In Figure 4.8 we present the sub-picosecond dynamics of the QW spectrum with momentum integrated spectrum at  $\Gamma$  as a function of delay. Panels a and b demonstrate the same spectrum in raw data and in  $\partial^2 I / \partial E^2$  after correcting for the SPV shift with black dots corresponding to QW1 and QW2 band bottom peak positions. It is evident that QW2 and QW1 are near equilibrium positions at the onset of the infrared pulse at  $\tau = 0$  ps and evolve downwards in energy towards a “fully-gated” regime.

The time-scale for the onset of the QW spectrum modification can be deduced by observing the intersubband-gap as a function of delay, shown in panel c. Here, the gap trends towards small energy difference exponentially with a time-constant of nearly 1 ps. This serves as a measure of the diffusion timescale at which charge separation occurs. Based on a band-bending length scale and field on the order of 10 nm and 50 mV/nm, we get a c-axis mobility of  $\sim 2 \text{ cm}^2(\text{Vs})^{-1}$ . This is  $1000\times$  less than the in-plane mobility of the charges which is typical in layered materials due to the van der Waals barrier [151].

Panel d shows hot carrier relaxation by integrating the intensity above  $E - E_F = 10$  meV and the full momentum range of the spectrum. The curve is fit by one minus an exponential

times a sigmoid:

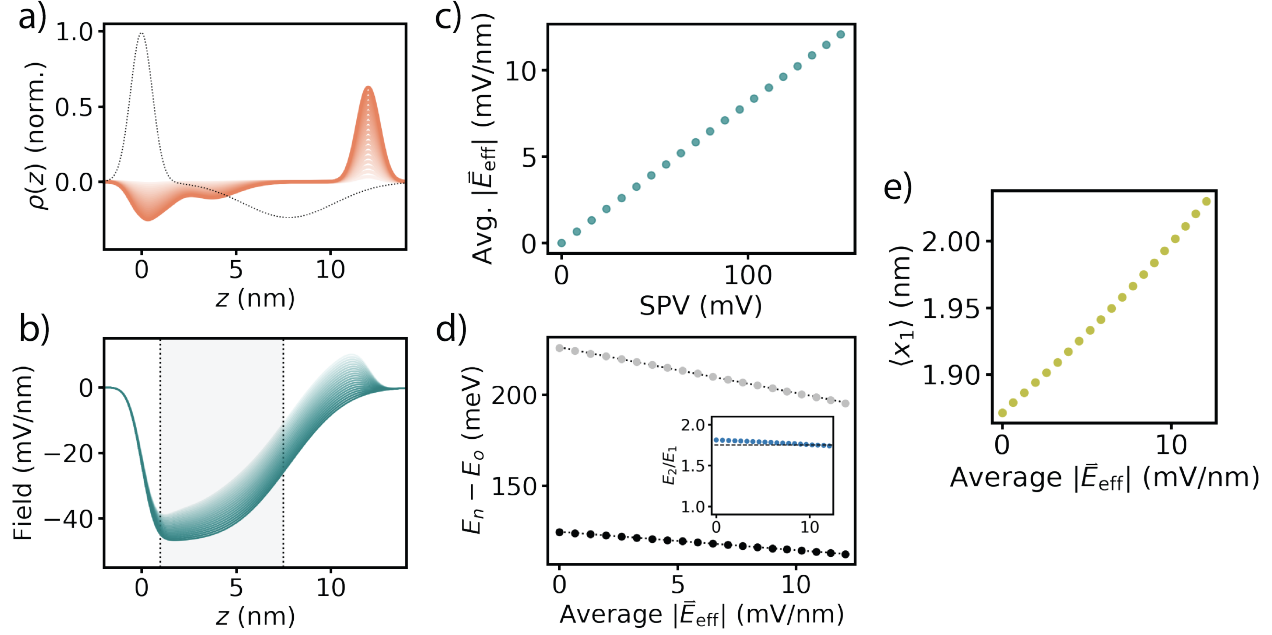
$$I = (1 - e^{-t/\tau_{bu}})(1 + e^{-(t-t_o)/\tau_{relax}}) \quad (4.6)$$

The build-up and relaxation times are approximately 0.6 ps and 0.9 ps, respectively. The build up may be related to high energy photoexcited charges being pushed towards the surface by the band-bending but is also close to the nominal time-resolution of the pump-probe. The relaxation time for hot carriers is clearly much faster than the time scale for the long-lived quasi-Fermi level ( $> 100$  ps).

## 4.5 Field Dependence From Quantum Well Wave-Function Determined Charge Distribution

The potentials and QW wave-functions in Fig. 4.1a were numerically calculated using Schrödinger's equation partially coupled to Poisson's equation. To explain, panel a demonstrates the charge distributions from the calculation. The dashed black line corresponds to the fix charges that generate the equilibrium band-bending and the orange curves represent the photoexcited charge at ten amplitudes (scaled by 2 for comparison with fixed charges). The excited charge is stored in four regions: electrons at TSS, QW1, and QW2 and holes at the edge of the band-bending. The charge distribution is partially calculated using Schrödinger's equation. First, the eigenvalues and eigenfunctions of QW1 and QW2 are calculated in the case of only fixed charges. The squared moduli of the wave-functions from this calculation are used to generate the charge population in the QW1 and QW2 regions at the lowest photoexcited charge amplitude such that electrons are evenly divided between the three surface states and the total electrons equal the hole population at the edge. This procedure is then followed for the next photoexcited charge amplitude by calculating the new eigenvalues and eigenfunctions, and onward for further amplitudes. An effective mass of  $0.45 m_e$  is used in the calculations.

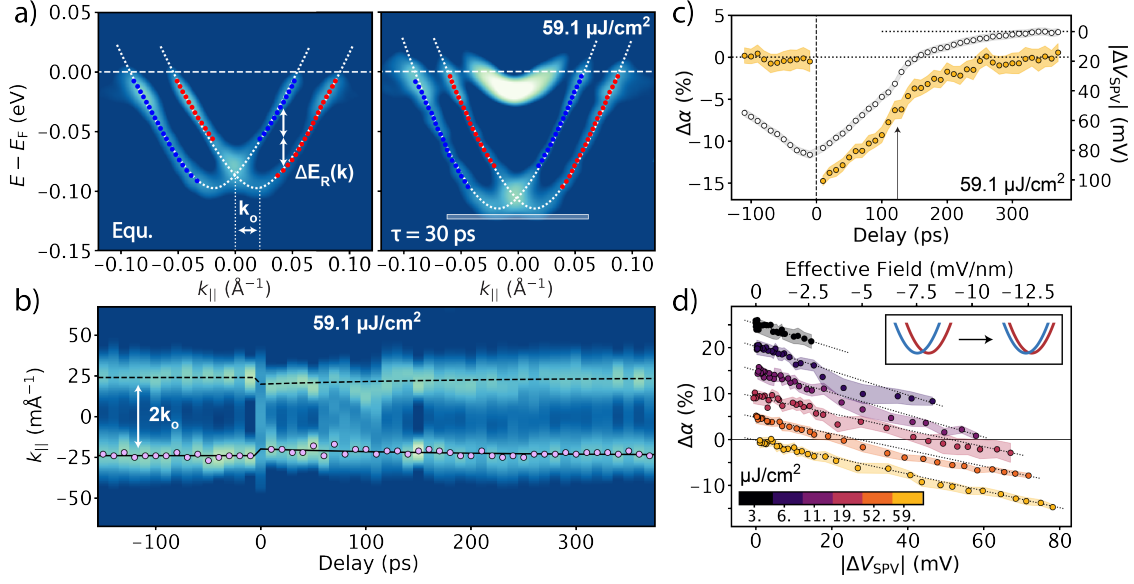
Panel b shows the resulting electric field with an integration region used to produce the average change-in-field, or effective field, in panel c. From panel c it is clear that the applied effective field scales linear with the SPV. Furthermore, we can look at the energy eigenvalues of QW1 and QW2 as a function of this average field. Here, the QW1 and QW2 energy decrease with increasing applied field with values similar to the measured band bottom energies from Fig. 4.7a (noting that the unquantized bulk conduction band minimum is  $\sim 150$  meV below the QW1 band bottom and the intersubband-gap is  $\sim 100$  meV). The inset shows that the ratio between eigenvalues is near 1.75 (dashed horizontal line) over all average effective fields which is consistent with the triangular well approximation, validating the method for retrieving the effective field described in Fig. 4.7. Lastly panel e demonstrates that the expectation value of the electron position in QW1 is linear with effective field and shifts towards the bulk by 5 – 10% at high excitation.



**FIGURE 4.9: Coupled Poisson-Schrödinger model for excited charges.** **a** Charge density profiles of fixed charge (dashed black) and photoexcited charges (light to dark orange) using prior step's wave-functions to determine QW1 and QW2 charge spatial profiles. **b** Electric field from potentials in Fig. 4.1b going from low to high separated charge populations (dark teal to light teal). **c** Average effective field (shaded region panel a) as a function of change in surface potential. **d** Energy eigenvalues of QW1 and QW2 as a function of average effective field. Inset shows ratio of eigenvalues compared to triangular-well approximation (horizontal dashed line). **e** Expectation value of QW1 electron position as a function of applied field showing deeper bulk position as field increases.

This simple model is able to capture the QW1 and QW2 dynamics as a function of charge separation observed in this study within a factor of 2 for the displayed observables such as the change in intersubband-gap and effective field as a function of SPV. This is despite only rough estimates on the length scale of the band-bending and the charge distribution of the fixed charges. A more precise model requires capturing the effective-mass anisotropy in  $k$ -space of the QW dispersion as well as more accurately determining the spatial extension of the fixed charges.

## 4.6 Ultrafast Reversible Reduction of Rashba Effect



**FIGURE 4.10: Ultrafast field effect on Rashba splitting.** **a**  $\partial^2 I / \partial E^2$  non-symmetrized spectra of quantum well states at equilibrium and 30 ps. Red and blue dots correspond to respective spin-split Rashba band positions for QW1. **b**  $\partial^2 I / \partial E^2$  non-symmetrized spectra integrated 15 meV below QW1 band bottom as a function of delay. Pink dots indicate peak positions on the negative- $k$  band bottom, black lines represent 15% reduction in  $k_0$  after pump that relax to equilibrium. **c** Percent change of the Rashba parameter (yellow) as a function of delay (determined by fits in panel a) compared to the delay-dependent SPV (black open dots) at 59.1  $\mu\text{J}/\text{cm}^2$ . After pump excitation, Rashba parameter drops by 15% and experiences a linear onset to exponential recovery (vertical arrow). **d** Percent change of the Rashba parameter versus SPV (and extrapolated effective field) over a large fluence range. Each fluence measurement is spaced by 5% for visibility.

Another appealing capability we can obtain through time-resolved photo-gating is the ultrafast control and tunability of the Rashba splitting. The Rashba effect depends on the inversion symmetry breaking electric field at the surface and can therefore be tuned by an applied field [152, 153, 16]. Note that, the Rashba effect is not a momentum splitting but an energy splitting that is, in the simplest form, linear in momentum, with  $\Delta E_R = \alpha_R k$  where  $\alpha_R k$  is known as the Rashba parameter. In the case of parabolic bands, this leads to a rigid splitting in momentum  $k_0 = \alpha_R m / \hbar^2$  [9, 90]. By directly fitting the bands, we can obtain an accurate determination of  $\alpha_R$ . In Fig. 4.10a, we present band fitting of the Rashba-split QW1 band at equilibrium and  $\tau = 30$  ps after the pump. The momentum positions of the Rashba bands as a function of energy (red and blue dots) were determined by peak fitting



the momentum distribution curves (MDC) along delay-dependent binding energy ranges and avoiding the Rashba crossing at  $\Gamma$ .

In panel b, the delay dependence of the Rashba splitting is clearly seen in the QW1 band bottom momentum positions captured by integrating the second derivative in energy spectra from panel a over a narrow energy range 15 meV below the dispersion, avoiding the increased intensity at the Rashba intersection at  $\Gamma$ . As a guide to the eye a 15% reduction in  $k_0$  at  $\tau = 0$  that returns to equilibrium is overlaid as a black dashed curve. The peak positions for the negative-momentum band bottom are plotted in pink and closely follow the 15% reduction. However, as is apparent from the noise in the peak positions, the direct fits to the dispersions prove to be a more precise method for determining the splitting as a function of delay.

Fig. 4.10c presents the resulting change in Rashba parameter (yellow dots) as a function of delay at high pump fluence ( $59.1 \mu\text{J}/\text{cm}^2$ ) as determined by the dispersion fits. In the negative delay, the Rashba parameter remains constant at its equilibrium value. Upon illumination the Rashba parameter drops  $\sim 15\%$  of the original value and then linearly returns towards equilibrium up until  $\sim 125$  ps (vertical arrow). From then on, the Rashba parameter exponentially returns to the equilibrium value on a timescale of 53 ps. The decay behavior of the Rashba parameter closely matches the SPV decay (black open dots) in which a linear decay transitions into an exponential decay near 125 ps. This implies a linear relationship of the Rashba effect with respect to the surface photovoltage and therefore the applied effective field, and subsequently dependent on the dynamic Lifshitz transition.

Fig. 4.10d plots the percent change of the Rashba parameter as function of the SPV at each delay as well as the extrapolated effective field on the quantum well. The curves are spaced artificially by 5% intervals for clarity. The field effect behavior of the Rashba parameter is linear for all fluences, decreasing as the applied field is driven to more negative values. At the highest applied field of approximately 13.5 mV/nm (experienced when pumped at high fluence) we see the largest decrease in the Rashba splitting of  $\sim 15\%$ . From the average of the fluence measurements, the response of the Rashba parameter versus field strength is  $1.26 \pm 0.21 \text{ } \%/(\text{mV}/\text{nm})$ . This ultimately demonstrates precise control of the Rashba splitting of the quantum well states with ultrafast photo-gating, with the Rashba parameter tuned by the pump pulse intensity and dependent on the Lifshitz mediated relaxation.

The observed field-dependent reduction of the Rashba parameter (Fig. 4.10d) suggests that a shallower quantum well potential leads to a weaker Rashba interaction. This is consistent with the findings in [16, 154] in which the stronger potential gradient polarizes the electron wave-functions, shifting their weight towards the inversion symmetry breaking atomic surface layer. This also explains the stronger Rashba splitting in QW1 versus QW2 (see Fig. 4.1c) and observed in previous studies [125, 90], since the higher order quantum well wave-functions penetrate deeper into the bulk layers.

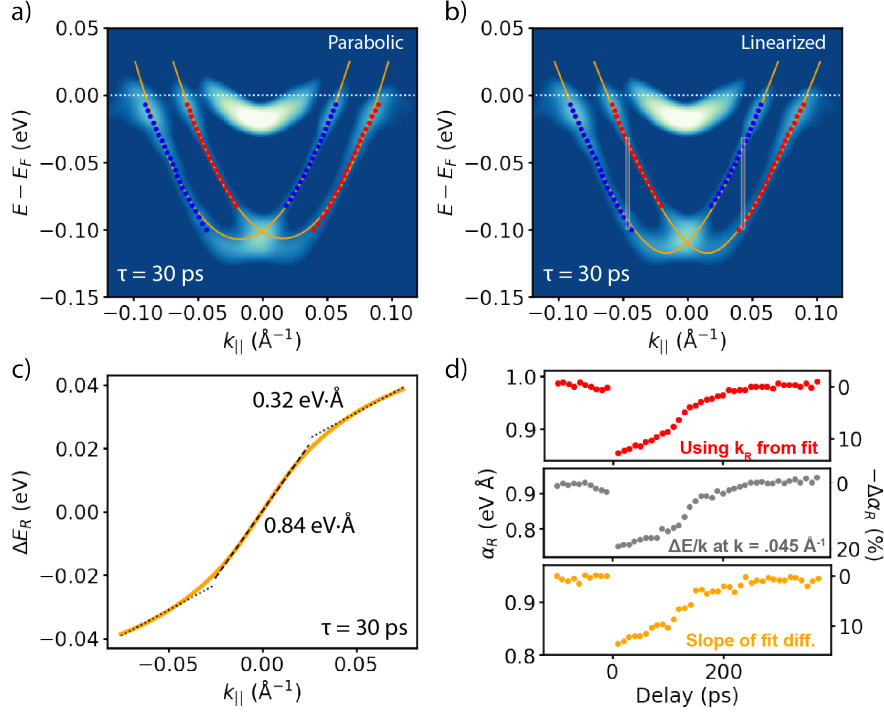


FIGURE 4.11: **Rashba parameter from QW dispersion.** **a**  $\partial^2 I / \partial E^2$  spectrum at 30 ps delay and high fluence. Peak locations of QW1 dispersion (red and blue dots) fitted with parabolas (orange). **b** Same spectrum with linearized parabolic fits. Shaded regions represent points used in panel d for direct measurement of  $\Delta E_R$ . **c** Subtraction of left QW1 fit from right QW2 fit divided by 2, representing  $\Delta E_R$ . The non-parabolic dispersion results in a non- $k$ -linear Rashba splitting. Near- $\Gamma$  splitting is approximately linear and the slope can be used to calculate  $\alpha_R$ . **d** Top panel shows  $\alpha_R$  calculated from  $k_0$  extracted from linearized parabolic fits. Middle panel is  $\alpha_R$  calculated from directly determining energy splitting at  $k = .045 \text{ \AA}^{-1}$  using dispersion peak locations. Bottom panel is  $\alpha_R$  calculated from near- $\Gamma$  slope in panel c.

In the free electron model, the electronic dispersion is parabolic with the form  $E = \hbar^2 k^2 / 2m^*$ , where  $m^*$  is the effective mass. However, electronic interactions in real materials cause dispersions to deviate from parabolic. In the case of the quantum well dispersions in our study, parabolic fits do not match the dispersion at all momentum values. Figure 4.11 panels a and b show two separate fits to the Rashba split QW1 dispersion at high fluence at a delay of 30 ps. Panel a uses a parabolic fit which includes a cubic term to capture asymmetry in momentum:  $E = a(k - k_0)^2 + b(k - k_0)^3 + E_0$ , where  $k_0$  is the location of the band minimum. Panel b uses the fit function utilized in Fig. 4.10 that is quadratic at small

$k$  and linear at large  $k$ :  $E = \frac{a(k-k_0)^2}{1+b|k-k_0|} + E_0$ . The parabolic fit can not capture the dispersion at low momentum, whereas the linearized fit in panel b fits the dispersion at all momenta.

The non-parabolic fit in panel b implies that the Rashba energy splitting is not  $k$ -linear. This can be seen directly by subtracting the left fit result (fit on blue points) with the right fit result (fit on red points) and dividing by 2 (since the Rashba energy splitting,  $\Delta E_R$ , is defined as half the difference in energy). The resulting  $\Delta E_R$  as a function of momentum is plotted in panel c. At small momentum, the dispersion is approximately quadratic leading to a  $k$ -linear energy splitting. At larger momentum, the energy splitting decreases in slope (eventually towards a flat, zero-slope, energy splitting at infinite momentum). For the purposes of this study, we determine the Rashba parameter, or the slope of the energy splitting, by only considering the energy splitting in the near- $\Gamma$  region.

We calculate the Rashba parameter using the momentum splitting parameter,  $k_0$ , from the fit functions. The near- $\Gamma$  Rashba parameter can be approximated by taking the Taylor series expansion of the difference between the left fit result and the right fit result:

$$E(k : a, b, k_0) - E(k : a, b, -k_0) \approx \frac{2ak_0(bk_0 + 2)}{(bk_0 + 1)^2}k \quad (4.7)$$

$$\Rightarrow \alpha_R \approx \frac{ak_0(bk_0 + 2)}{(bk_0 + 1)^2} \quad (4.8)$$

Parameters  $a$  and  $b$  are sensitive to the number of peak positions in the high momentum regime and very low momentum region, which change as a function of delay since the filled region of QW1 is delay dependent. For this reason, the delay averaged values of  $a$  and  $b$  are used to calculate the Rashba parameter. This could have the result of introducing an artificial delay-dependent Rashba parameter. To guarantee this is not the case, we calculate the Rashba parameter with three different methods shown in panel d. The top panel shows the Rashba parameter calculated from  $k_0$  using the Taylor series expansion. The middle panel presents the Rashba parameter calculated directly by subtracting the energy values of the band positions at  $k = 0.045 \text{ \AA}^{-1}$  and dividing by that momentum (shaded region in panel b). The bottom panel is the Rashba parameter calculated from the slope near- $\Gamma$  of  $\Delta E_R$  from the resulting fits, as shown in panel c. All forms of Rashba calculation show a delay dependent Rashba parameter of similar form, suggesting parameters  $a$  and  $b$  do not play a strong role in determining the Rashba parameter.

## 4.7 Lifshitz-Dependent Quasi-Fermi Level Trapping

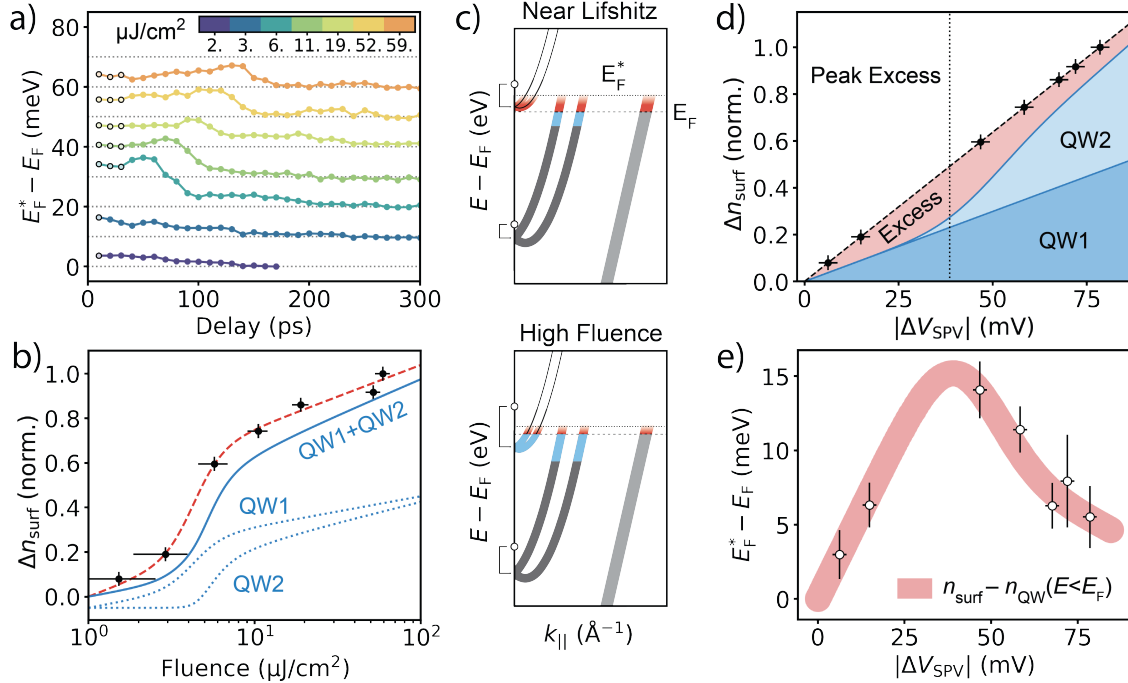


FIGURE 4.12: **Competition between surface state trapping and quasi-Fermi level.**

**a** Quasi-Fermi level as a function of delay for all fluences. Outlined circles indicate averaged points used in panel e. **b** Maximal SPV as a function of fluence indicating separated charge concentration at the surface. Labeled blue curves demonstrate QW1 and QW2 states below  $E_F$  determined from the phenomenological fit (dashed red) and the SPV dependence of the band bottom positions in Fig. 4.7a. **c** Graphical comparison of quasi-Fermi level shifting between medium and high fluence. Medium fluence ( $3 - 7 \mu\text{J}/\text{cm}^2$ ), QW2 photo-carrier generation is significantly larger than available states in shifted QWs. At high fluence, photo-carrier generation has saturated and QW2 provides increased storage below  $E_F$ . **d** Representation of panel b with the x-axis parameterized by SPV surface potential. The only free parameter in this model is the relative amplitude of QW1 + QW2 trapped charge with the total surface charge (black dots). Excess carriers after filling QW trap states contribute to raising  $E_F^*$ . **e**  $E_F^*$  at short delays from panel a and total surface charge minus trapped surface charge (black dashed curve minus solid blue curve in panel d) as a function of surface voltage.

Finally, in Figure 4.12 we report a non-monotonic dependence of the quasi-Fermi level,  $E_F^*$ , with respect to fluence that demonstrates the significance of the Lifshitz transition on the infrared response of the quantum well system.

The delay dependence of  $E_F^*$  for all measured fluences is plotted in Fig. 4.12a.  $E_F^*$  is measured in reference to the equilibrium Fermi level (i.e. the difference between the red fit and white fit from Fig. 4.3b). For fluences above  $4 \mu\text{J}/\text{cm}^2$ ,  $E_F^*$  is offset from equilibrium starting in a plateau region for delays less than  $\tau_{\text{cross}}$  preceding a small peak after  $\tau_{\text{cross}}$  that leads into exponential decay. Curiously, the offset at early delays is non-monotonic with fluence, peaking at  $\sim 15 \text{ meV}$  for  $5.7 \mu\text{J}/\text{cm}^2$  and leveling off towards  $\sim 5 \text{ meV}$  at high fluence. The encircled points indicate the values that are averaged to generate the  $E_F^*$  offset values in panel e. The hump that occurs near  $\tau_{\text{cross}}$ , may be indicative of a large charge transfer from QW2 to the TSS following the reverse Lifshitz transition of the QW2 singularity. This may additionally suggest that the sustained  $E_F^*$  plateau region is also from charge in the QW states leaking into the TSS during relaxation. For the purposes of this study we focus on  $E_F^*$  at early delays. The relatively small offset of  $E_F^*$  is in contrast to previous time-resolved studies on p-type  $\text{Bi}_2\text{Se}_3$ -related samples without quantum wells [77], emphasizing the influence of QW1 and QW2 on the relaxation dynamics.

The behavior of  $E_F^*$  at early delays with respect to pump fluence can be explained within the framework of the stored equilibrium charge in QW1 and QW2 described in Figure 4.7. To start, in Fig. 4.12b we display the fluence dependence of the maximal SPV,  $|\Delta V_{\text{SPV}}(\tau = 10)|$ , which is proportional to the initial net charge at the surface after hot carrier relaxation,  $\Delta n_{\text{surf}} = n_{\text{sep}}$ . Next, the fraction of charge stored below  $E_F$  in QW1 and QW2 is calculated. To do this, we use linear extrapolations of the QW1 and QW2 band bottom positions as a function of SPV from the high fluence data in Fig. 4.7a and the cumulative DOS of Rashba split parabolic bands shown as dashed blue curves (see Fig. 4.14f). The band bottom positions, and therefore the cumulative DOS, are functions of the SPV strength and are calculated from the phenomenological fit of the SPV maximal values (dashed red curve). The sum of the QW1 and QW2 cumulative DOS corresponds to the total available quasi-equilibrium charge states for photoexcited charge (solid blue curve).

Fig. 4.12c depicts two photoexcitation regimes that summarize the role of the Lifshitz transition on  $E_F^*$ . The brackets on the left indicate the pump induced quantum well energy shift from equilibrium positions, the blue and red regions correspond to excited charge below and above  $E_F$ , respectively. At moderate fluences of  $3 - 7 \mu\text{J}/\text{cm}^2$  QW2 undergoes a Lifshitz transition, however only QW1 has significant available states below  $E_F$  leaving excess separated charge to populate above  $E_F$ . At high fluence, QW2 has shifted well below  $E_F$  enabling a large degree of quasi-equilibrium charge storage reducing the burden on states above  $E_F$ .

To further quantify the effect, it is more useful to reparameterize the curves of panel b in terms of the surface voltage to avoid reliance on the SPV phenomenological fit. In this way, the total net charge concentration is a linear function and the QW1 and QW2 band bottoms are linearly dependent on the x-axis. Because the QW1 and QW2 band bottom positions are empirically determined, the only consequential free parameter is the relative amplitude of the total available quasi-equilibrium charge states (blue regions) with respect to  $n_{\text{surf}}$  (dashed black line). The difference between the aforementioned populations represents the excess photoexcited charge at the surface (light red region), which describes the charge

remaining after QW1 and QW2 are filled below  $E_F$  and that must occupy above- $E_F$  states. From panel d, it is clear that the emergence of the QW2 band bottom below  $E_F$ , which acts to enhance the filled DOS contribution of QW2, necessitates a peaked behavior in the excess charge population near the Lifshitz transition, regardless of the fluence dependence of the SPV effect.

The proportionality factor between the charge stored in QW1 and QW2 with respect to  $n_{\text{surf}}$  is chosen such that the excess charge best fits the  $E_F^*$  offset plotted in panel e. The excess charge from the model in panel d (light red curve) closely captures the non-monotonic behavior in the measured  $E_F^*$  values.

## 4.8 Modeling Fluence Dependence of SPV Intensity

High recombination in the quantum wells and at the surface force separated charges to originate in the bulk at the edge of the band-bending region [139]. The two relevant time-scales are  $\alpha_{\text{sep}}$  which determines electron diffusion towards the surface, and  $\alpha_{\text{rec}}$  which determines the recombination in the bulk that reduces the available charge to be separated. This is demonstrated in Figure 4.13a,b at low and high fluence, respectively. At low fluence, electrons are free to separate from the holes by following the band-bending potential, limited by the recombination rate in the bulk. At high fluence, the charge separation occurs rapidly and a potential well forms that pushes electrons and holes in unfavorable directions for reducing the band bending.

As such we can model the formation of the SPV charge separation through a set of rate equations:

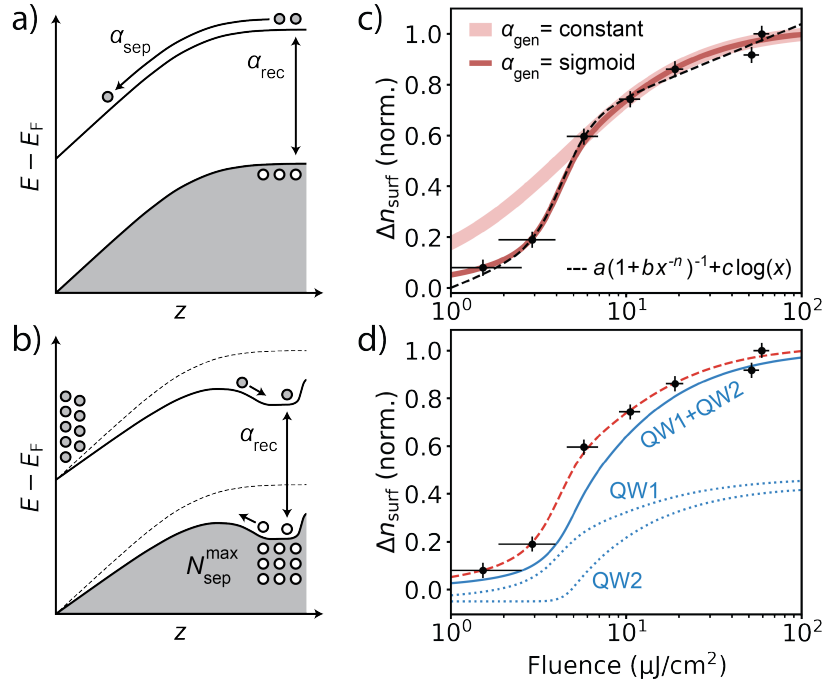
$$\frac{dN_{\text{e,bulk}}}{dt} = -\alpha_{\text{rec}}N_{\text{e,bulk}}N_{\text{h,bulk}} - \alpha_{\text{sep}}(N_{\text{sep}}^{\text{max}} - N_{\text{e,sep}})N_{\text{e,bulk}} \quad (4.9)$$

$$\frac{dN_{\text{e,sep}}}{dt} = \alpha_{\text{sep}}(N_{\text{sep}}^{\text{max}} - N_{\text{e,sep}})N_{\text{e,bulk}} \quad (4.10)$$

where  $N_{\text{e,bulk}}$  are the electrons in the bulk from photoexcitation,  $N_{\text{e,sep}}$  are electrons that are trapped at the surface,  $N_{\text{sep}}^{\text{max}}$  is the maximum charge separation, and  $N_{\text{h,bulk}} = N_{\text{e,bulk}} + N_{\text{e,sep}}$  are the holes after photoexcitation that remain in the bulk. The recombination is assumed to be bimolecular since photoexcited electron-hole pairs are formed in or near the space charge region which is devoid of free charges. The charge migration is dependent on the number of electrons in the bulk and the availability of charge-separated states before maximization. The initial bulk electron population is determined by the fluence,  $N_{\text{e,sep}}(t = 0) = \alpha_{\text{gen}}f/f_{\text{max}}$  and the initial separated population is always zero.

Panel c shows the results of  $\alpha_{\text{gen}} = 1$ ,  $\alpha_{\text{rec}} = 2 \text{ ps}^{-1}$ ,  $\alpha_{\text{sep}} = 2 \text{ ps}^{-1}$ , and  $N_{\text{sep}}^{\text{max}} = 0.035$  evaluated after 10 ps and plotted alongside the normalized SPV maximum at 10 ps. In the case of carrier generation being proportional to fluence (pink), the rate equation closely matches the high fluence data but overestimates the lowest two fluences. This could be explained by the Lifshitz transition which takes place at a critical fluence of  $\sim 4 \mu\text{J}/\text{cm}^2$ . At fluences below the critical fluence, the singularity of QW2 is above the Fermi level, therefore photon

absorption and carrier generation is enhanced towards the surface and rapid recombination in this region inhibits charge separation. This can be phenomenologically captured by incorporating a fluence dependent sigmoidal  $\alpha_{\text{gen}}$  with  $5\times$  reduction in generation rate at low fluence. This is shown in dark red in addition to the phenomenological fit from Fig. 4.12 in dashed black. Panel d shows the analogous plot to Fig. 4.12b using the sigmoidal rate equation model from panel c. The phenomenological fit is used since the analysis in Fig. 4.12d,e is invariant to the fluence dependence and the log-linear regions of the fit demonstrate the QW1 and QW2 cumulative DOS more clearly.



**FIGURE 4.13: Rate equation model of SPV saturation.** **a** At low fluence, excited bulk electrons are unimpeded to follow the band-bending forming a charge separation that generates the SPV. **b** At high fluence, the charge separation occurs rapidly and the excited holes at the edge of the SCR generate a local potential minimum for electrons and local potential maximum for holes, limiting the charge separation. **c** The rate equation model captures the saturation at high fluence well with carrier generation proportional to fluence. To capture low fluence data, a carrier generation rate that is step-like about the critical fluence for the Lifshitz transition is used. **d** Same plot as Fig. 4.12b but using rate equation model.

## 4.9 Net Change in Charge Density

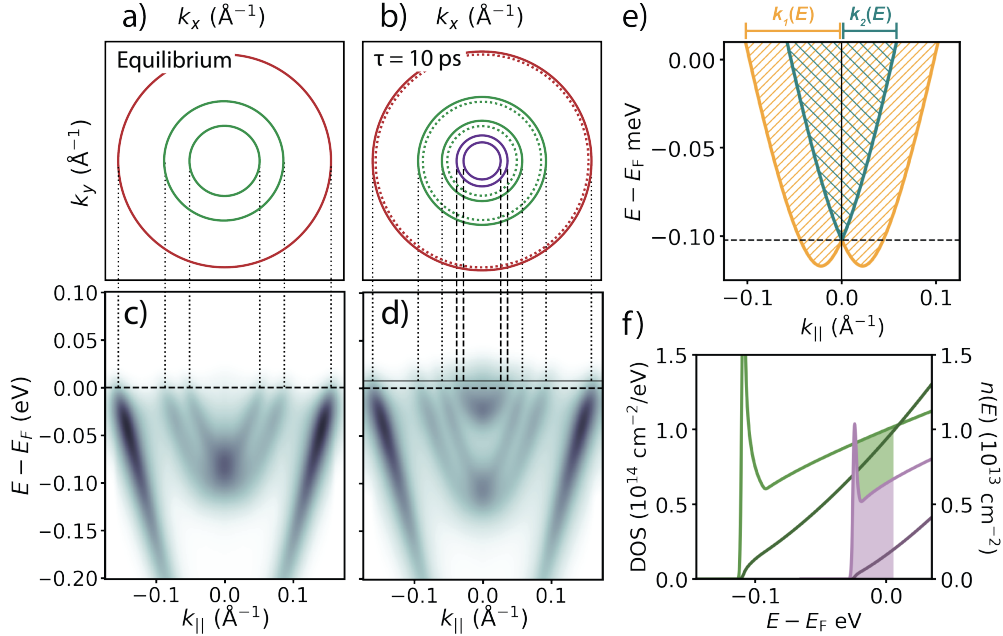


FIGURE 4.14: **Luttinger's theorem and charge storage** **a,b** Fermi surfaces of TSS, QW1, and QW2 before and after pump. QW2 introduces new surface areas after the pump. **c,d** Corresponding ARPES spectra. Fermi wavevectors at the Fermi level and quasi-Fermi level shown with dotted vertical lines. **e** Dispersion of QW1 from fit routine in Fig. 4.10a. DOS is determined using Luttinger's theorem on two separate electron pockets, yellow and teal. Ring-like surface below the Rashba crossing causes a singularity in the DOS. **f** DOS and carrier concentration as a function of energy of QW1 and QW2 (green and purple, respectively) determined from Luttinger analysis in panel e.

Luttinger's theorem says that the carrier density is proportional to the area enclosed by the Fermi surface,

$$n = 2 \int_{\text{FS}} \frac{d^D k}{(2\pi)^D}, \quad (4.11)$$

where  $D$  is the degrees of freedom in  $k$ -space and the 2 prefactor captures spin-degeneracy [155]. We can utilize this theorem to generate a density of states for the quantum well dispersions as well as calculate the stored charge at the surface after excitation.



Figure 4.14 panels a,b,c,d show ARPES spectra and Fermi surface depiction at equilibrium and at 10 ps at high fluence. We can first calculate the stored charge in the topological surface state (TSS) by measuring the change in  $k_F$  after excitation (red rings panels a,b).

Since the TSS is a two dimensional state ( $D = 2$ ) and not spin-degenerate, the change in carrier density is then equal to,

$$\Delta n_{\text{TSS}} = \frac{k_{\text{F},1}^2 - k_{\text{F},0}^2}{4\pi} \quad (4.12)$$

where  $k_{\text{F},0} = 0.155 \text{ \AA}^{-1}$  at equilibrium and  $k_{\text{F},0} = 0.158 \text{ \AA}^{-1}$  after excitation measured at the quasi-Fermi level. This yields a net surface charge of  $0.75 \times 10^{12} \text{ cm}^{-2}$ .

The charge stored in the QWs can be determined in the same fashion, however it is most convenient to calculate the full DOS since it is needed for Fig. 4.12. Panel e shows the dispersion of QW1 determined from the dispersion fits explained in Fig. 4.10. The Rashba split parabolas are again not spin-degenerate and form two separate electron pockets that must be calculated separately then combined. Using Luttinger's theorem as a function of energy we can determine  $n(E)$ , the energy derivative of which is the DOS, both shown in panel f. The momentum-splitting causes an annular pocket at low energies which results in a singularity at energies below the Rashba crossing at  $\Gamma$ . The same analysis has been performed for QW2 using the same dispersion as QW1 but a reduced Rashba splitting of  $k_0 = .012 \text{ \AA}^{-1}$ . The cumulative DOSs,  $n(E)$  from panel f is used in Fig. 4.12b,c,d after broadening by 5 meV [156].

The total stored charge in the QWs can then be calculated by integrating the DOS in the shifted portion of the spectrum up to the quasi-Fermi level, resulting in  $\Delta n_{\text{QWs}} = 2.90 \times 10^{12} + 1.95 \times 10^{12} \text{ cm}^{-2}$ . The total net surface charge is then  $\Delta n_{\text{tot}} \approx 5.6 \times 10^{12} \text{ cm}^{-2}$ . Caution must be taken with this value since the Fermi surface was assumed to be uniformly populated near  $E_F$  and radially symmetric. At these energies above the Dirac node, both the bulk conduction band and TSS take on hexagonal deformations [157] and since we only measure in the  $\Gamma - \text{K}$  directions in this study, it is uncertain whether bottleneck populations of charge exist elsewhere in momentum-space near or above the Fermi level. However, it serves as a good order of magnitude estimate for the maximal stored charge at the surface after excitation.

## 4.10 Discussion

Using the reported dielectric constant of  $\text{Bi}_2\text{Se}_3$  of a nominal  $\epsilon_r \approx 30 - 100$  [158, 38], we can extract an approximate SCR width, describing the spatial extent of the band-bending utilized in Fig. 4.1b,  $d = \sqrt{2 \Delta V_{\text{BB},0} \epsilon_r \epsilon_0 / e n_A} \approx 10 \text{ nm}$  [46], where the acceptor ion concentration,  $n_A$ , is approximately equal to the bulk majority carrier density in the SCR and  $V_{\text{BB},0} \sim 300 \text{ mV}$  based on the observation of the QW3 energy level at short delay and the zero-point energy of the quantum well spectrum. A second independent method is to use charge conservation at the SPV saturation, since band-bending cancellation occurs when the total surface charge

is equal to the volumetric bulk charge times the depth. The maximal surface charge can be calculated by Luttinger's theorem [155] on the QW1, QW2, and TSS bands giving  $5 \times 10^{12} \text{ cm}^{-2}$  (see Fig. 4.14), and since only approximately 1/4 (from  $\Delta V_{\text{SPV}}/V_{\text{BB},0}$ ) of the charge is screened in the SCR we get,  $d = 5 \times 10^{12} \text{ cm}^{-2}/(1 \times 10^{19} \text{ cm}^{-3}/4) \sim 10 \text{ nm}$ . These estimates ignore possible variations in both the dopant concentration and dielectric constant between surface and bulk, as well as hexagonal deformation and possible non-isotropic charge storage at the Fermi surface [157, 52]. However, the approximate SCR width is consistent with the band-bending length scale observed previously in  $\text{Bi}_2\text{Se}_3$  [86].

Initial reports of the Rashba effect on metallic surfaces suggested that applied fields on the order of 1000 mV/nm are insufficient to produce the observed Rashba effect, and that the nuclear core potentials are responsible for large splittings [153, 159]. However, in our experiment we observe a 15% reduction on an approximately 1 eV·Å Rashba effect with fields near 10 mV/nm only. On the other hand, there is a growing body of evidence demonstrating small changes to surface or interface fields generate large changes to the Rashba parameter [152, 18, 160]. A reasonable explanation that has been presented is that the applied field plays an indirect role on the Rashba effect by shifting electrons to and from the nuclear cores at the surface plane [15, 16, 17, 18]. For instance, theoretical studies to explain large spin-splitting in the perovskites have demonstrated surface fields determine the Rashba effect by controlling the spatial overlap of 2DEG wave-functions with the nuclear potentials of surface atoms [17, 16]. With respect to  $\text{Bi}_2\text{Se}_3$ , Eremin et al. presents a debated hypothesis on the origin of the quantum wells from surface modulated van der Waal's gaps [19]. Although the origin of the quantum wells has been further argued to be from surface band-bending [137, 52], their study indirectly demonstrates the role of wave-function overlap with the surface-most quintuple layer as a key ingredient to the Rashba effect. We have shown through our simplified band-bending calculation of the QW wave-functions in Fig. 4.9e that the shift in QW position is field-linear and nearly 2 Å over 10 mV/nm, a significant fraction of the quintuple layer thickness. In totality, our results are consistent with a picture that the origin of the Rashba splitting is largely controlled by wave-function overlap with asymmetric nuclear potentials within the first quintuple layer, controlled linearly by the field. Based on our results and within our interpretation, we recommend a follow-up atomistic DFT approach on the effect of band-bending on Rashba splitting.

One consequence of the ultrafast quantum well modification is a large rapid and reversible change in the DOS at the Fermi level. This is made possible by the emergence of QW2 below  $E_F$  after pump excitation; changing the topology of the Fermi surface and triggering a Lifshitz transition. As the quantum well spectrum relaxes, the QW2 band bottom rises above the Fermi level at  $\tau_{\text{cross}}$ , reversing the Lifshitz transition. The kink in the relaxation of the SPV as well as the Rashba modification is correlated with  $\tau_{\text{cross}}$ , indicating that the reversal of the Lifshitz transition plays a key role in the relaxation. Furthermore, the new states near the Fermi level imply an increase in conductivity at the surface affecting spin-dependent transport properties, and occupation of the QW2 band bottom would influence intersubband optical absorption [161]. As such, this ultrafast field effect device provides many opportunities for applications which are sensitive to the DOS at the chemical potential and

requires further attention exploring the DOS-dependent scattering dynamics.

The SPV photo-gating method relies only on the presence of band-bending in the bulk and a two dimension electronic system-of-interest on the surface. Therefore, this method can be extended to other semiconductor systems with 2D electron gases. In fact, a similar gating method to the one presented here has been utilized successfully in black phosphorous to drive gap renormalization at the surface [162, 163]. Moreover, it may be possible to extend this method to heterojunction systems in which an exfoliated or MBE grown 2D material is placed on top of an SPV substrate separated by a thin insulating layer. In this case, a pump pulse focused on the grounded top layer would result in transient gating of the illuminated surface region. Moreover, SPV time constants can vary significantly from picoseconds to milliseconds depending on the system allowing for a large dynamic range of study [79, 163, 164].

## 4.11 Summary

In conclusion, we have exposed complex quantum well dynamics using a time-resolved SPV-based gate. The phenomenology of the photo-induced quantum well modification is general for surface quantum well systems because it relies on the surface band-bending of not only topological insulators but many semiconducting systems [46]. However, the unique decay profile of both the SPV and Rashba reduction is contingent on the dynamic DOS near the Fermi level and the existence of a van Hove singularity in the Rashba split quantum wells. Accordingly, we have demonstrated local control of the near- $E_F$  DOS; a useful tool for driving electronic phases such as superconductivity [165], magnetism [166], and, more broadly, correlated phases [167]. Furthermore, the ultrafast gating mechanism also revealed dynamically stored charge in QW1 and QW2 that ultimately controls the resulting quasi-Fermi level, impossible to observe using static gating techniques. Lastly, we have demonstrated ultrafast reversible modulation of the Rashba effect on 10-100 picosecond timescales opening up the possibility for GHz spin-current manipulation. The temporary photo-induced Rashba tuning creates a platform for spin-orbit modulation enabling light-driven spintronic devices such as a ultrafast spin-transistors and photo-controlled Rashba circuitry [54, 168, 169].

## Chapter 5

# Ultrafast Electric Fields: Controlling Electron-Phonon Coupling

The density of states at the Fermi surface controls many material properties by influencing the low-energy interactions of conductive electrons. Typically, external tuning knobs generate only small perturbations to the density of states in crystals, since their band structure depends strongly on the lattice potential. On the other hand, quantum well states are contingent on a localized potential extrinsic to the crystal lattice. These potentials can be easily modified with infrared pulses, resulting in substantial dynamic changes to the density of states at the Fermi level, as we have shown in the previous chapter. In this chapter, we investigate the triggering of a reversible Lifshitz transition by driving a quantum well singularity below  $E_F$  at ultrafast timescales. We reveal a substantial ultrafast enhancement of the electron-phonon coupling with repercussions on the relaxation dynamics in the system. Finally, we demonstrate that leveraging the DOS singularity of a quantum well state provides an ideal platform for generating  $> 1 \mu\text{s}$  long-lived excited states.

### 5.1 Introduction

Electron-phonon coupling (EPC) is among the most fundamental interactions in solids, adding to the complexity of electronic behavior beyond the Coulomb interaction. Not only does EPC play an important role in defining the electronic, transport, optical and thermal properties of materials, but it is also fundamental in driving novel quantum phases of matter, such as superconductivity, charge density waves, and 2D Ising materials [24, 25, 26, 27, 28].

Since EPC is strongly dependent on the density of states (DOS) at the chemical potential [170, 171, 26], various methods have been developed to tune the chemical potential in a controlled way and induce changes in the coupling constant. These changes can be particularly relevant in the presence of singularities in the DOS, as is generally the case in the proximity of a Lifshitz transition [141, 172, 173, 174], where very large enhancements of the coupling constant can be realized by placing the chemical potential at the singularity. Most of the

methods adopted so far rely on tuning of static parameters such as temperature, doping, pressure and electrostatic gating [175, 176, 177, 178], with the latter being the most versatile as it does not modify the underlying lattice. 2D quantum well (QW) states, are ideal candidates to controlling Lifshitz transitions, due to their malleable quantized band structure, which in the presence of the Rashba Effect leads to singularities in the DOS [140, 91].

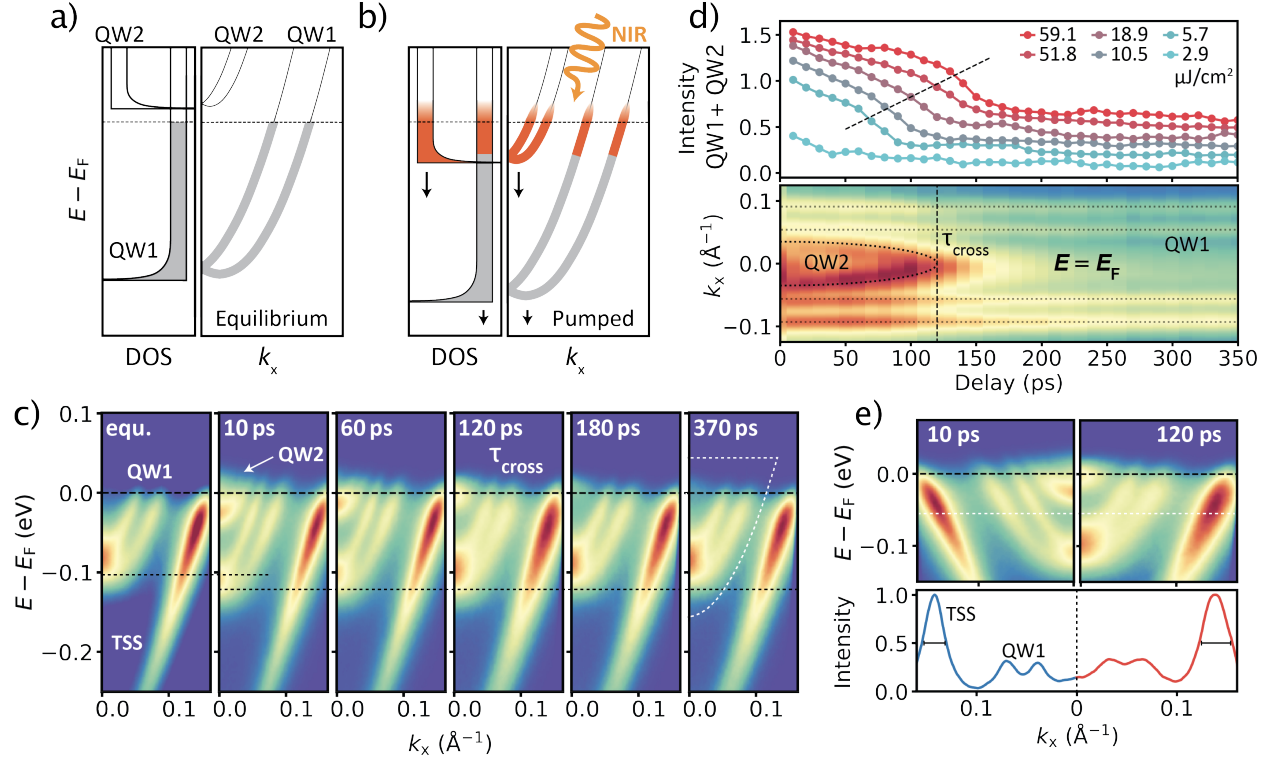
The recent discovery that light can be used to modulate the underlying potential in QWs and to induce a Lifshitz transition [117], opens up the intriguing possibility to tune EPC on ultrafast time scales through DOS alone, and present a new avenue for engineering boson-mediated quantum phases. Time and angle resolved photoemission spectroscopy (TR-ARPES) is ideal to study these effects as it allows a direct measurement of the underlying modification of the band structure and of the electron phonon coupling constant [179, 180].

In this study, we utilize TR-ARPES to drive a Lifshitz transition of a van-Hove-like singularity in the surface quantum wells of  $\text{Bi}_2\text{Se}_3$ . As the singularity returns to the Fermi level, we reveal a transient enhancement of the EPC that effects the electron-hole recombination process and abruptly transfers charge to the surface. Finally, like a bucket pulling charge up from the Fermi Sea, the singularity emerges above  $E_F$ , remaining partially filled on  $\mu\text{s}$  timescales, generating a long lived transient state, inaccessible in equilibrium.

## 5.2 Field-Induced Ultrafast Lifshitz Transition

Fig. 5.1a and 1b present an overall summary of the ultrafast photo-induced Lifshitz transition in the QW spectrum. The infrared pulse generates excited electrons and holes that cancels the surface band bending. Panel a shows the typical spectra of Rashba-split quantum well states before and after infrared illumination. At equilibrium (panel a) only the first quantum well (QW1) is filled, with the two spin-split bands resolved. The corresponding band bottom defines a ring of non-zero radius, in contrast to point-like as in the case of a spin-degenerate band. Consequently, the DOS is no longer a step function, but increases asymptotically in correspondence to the band bottom, akin to a van-Hove singularity [140] (see leftmost panel).

Upon illumination, the surface photovoltage effect is known to modify the potential gradient of the quantum well [117], producing a transient shift of the QW energies that can drive QW2 below the Fermi level (panel b). After the infrared pulse, QW1 and QW2 shift downward and photoexcited charge is stored in the shifted high energy portion of the QW1 dispersion and the singularity in QW2. Accordingly, within this picture, our pump-probe experiment is toggling the DOS singularity of QW2 below and then back above the Fermi level. The downward shifting of QW1 does not affect the Fermi surface topology, but the emergence of QW2 below the Fermi level introduces two new electron pockets, producing a time-dependent Lifshitz transition. This ability to reversibly and continuously control the position of the van Hove singularity with respect to  $E_F$  presents an ideal condition for enhancing electron-phonon interaction.



**FIGURE 5.1: Controlling Rashba singularity with an ultrafast Lifshitz transition.** **a** Schematic of light induced Lifshitz transition and DOS singularities. Before the pump, QW2 is above  $E_F$  and unoccupied. **b** After illumination, QW1 and QW2 shift downwards, QW2 is filled, providing the Fermi surface with additional pockets. **c** Spectra at equilibrium, 10 ps, and 370 ps at  $51.8 \mu\text{J}/\text{cm}^2$  showing the emergence of QW2 below  $E_F$  and subsequent return above  $E_F$  at  $\tau_{\text{cross}}$ . **d** Top: Integrated spectral intensity of full QW1 and QW2 dispersions (dashed white region panel b at  $\tau = 370$  ps) over all measured fluences. At fluences  $> 4 \mu\text{J}/\text{cm}^2$ , charge decay experiences a discrete transition from a linear to exponential decay at  $\tau_{\text{cross}}$  (dashed black line guide to the eye). Bottom: TR-ARPES map at  $E_F$  demonstrating the crossing of the QW2 band bottom (dashed black line). **e** Broadening of dispersions at  $\tau_{\text{cross}}$ . MDCs at  $E = -0.50$  eV show increased linewidths at  $\tau_{\text{cross}}$  versus 10 ps.

Fig. 5.1c displays the raw ARPES spectra of the  $\text{Bi}_2\text{Se}_3$  surface QW states at equilibrium as well as at five representative delays ( $\tau = 10, 60, 120, 180, 370$  ps) pumped at  $51.8 \mu\text{J}/\text{cm}^2$ . At equilibrium, the TSS and the lowest energy quantum well dispersion (QW1) are present and filled below  $E_F$ , with QW1 demonstrating strong Rashba splitting. After pump excitation ( $\tau = 10$  ps), the second Rashba-split quantum well dispersion (QW2) appears below  $E_F$  and is subsequently filled via thermal relaxation. At more positive delays, QW1 and QW2 relax towards their equilibrium energies. In particular,  $\tau = 120$  ps represents

an important moment in the quantum well relaxation, corresponding to the time when the QW2 band bottom and DOS singularity reach the Fermi level. We will refer to this time as

$\tau_{\text{cross}}$ .

The delay time  $\tau_{\text{cross}}$  corresponds to two peculiar phenomena in the delay-dependent spectra represented in panels d and e, respectively: 1) a discontinuity in the decay rate of photoexcited charge (top panel d). 2) a rapid broadening of the TSS and quantum well dispersions (panel e). In the top subpanel of Fig. 5.1d, we present the total spectral intensity of QW1 and QW2 as a function of delay over the fluence range 2.9 - 59.1  $\mu\text{J}/\text{cm}^2$  using the dashed white integration window shown for  $\tau = 370$  ps in panel c. At high fluence, charge is stored adiabatically up until  $\tau_{\text{cross}}$  with the dashed black line serving as a guide to the eye.

The crossing of the QW2 band bottom back above the Fermi level is clearly observed in the time-dependent states at the Fermi level (vertical dashed line) displayed in the TR-ARPES map in the bottom subpanel of Fig. 5.1d. Here, QW1 states that cross  $E_F$  can be seen as continuous lines as a function of delay near  $k_x \approx \pm 0.1$  and  $\pm 0.06 \text{ \AA}^{-1}$ , experiencing slight inward bending as the QW spectrum relaxes. Whereas QW2 states appears at  $k_x \approx \pm 0.045 \text{ \AA}^{-1}$  and approach  $k_x = 0$  as the band bottom crosses the Fermi level at delay  $\tau \approx 120$  ps, marking the reversal of the pump-induced Lifshitz transition.

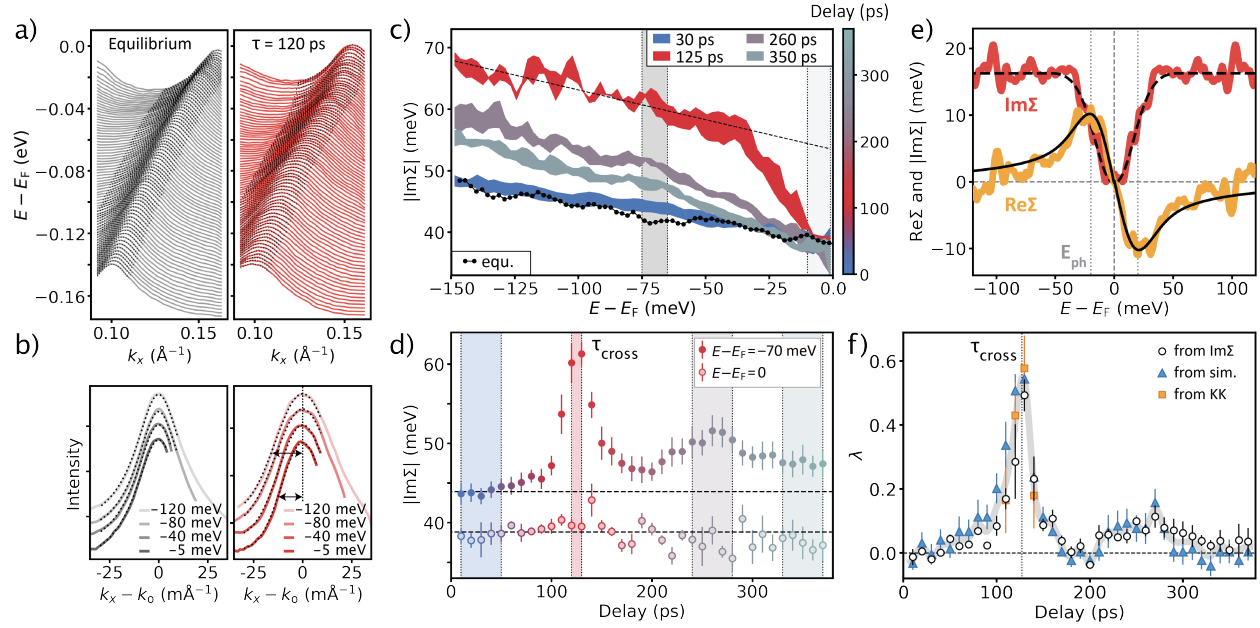
The second effect of rapid spectral broadening is best observed in Fig. 5.1e. The comparison between  $\tau = 10$  ps and  $\tau = 120$  ps of the surface bands including QW1, QW2, and the TSS reveals a significant increase in spectral broadening at  $\tau_{\text{cross}}$ . The bottom panel displays the momentum distribution curves (MDCs) at 50 meV below the Fermi level demonstrating that the spectral linewidth in the momentum direction increases for both the TSS and QW1.

### 5.3 Lifshitz-Mediated Electron Phonon Coupling Enhancement

To better understand the impact of this photoinduced transition on many body interactions, in Figure 5.2 we study its effect on the real and imaginary part of the electron self-energy ( $\text{Re}\Sigma$  and  $\text{Im}\Sigma$ ), quantities that can be directly accessed by ARPES.

The ARPES spectral function is in the form of a Lorentzian with the full-width-at-half-maximum (FWHM) in the energy direction,  $\Gamma_\omega$ , equal to  $2\text{Im}\Sigma(k, \omega)$ , therefore, EDCs provide a direct measure of the  $\text{Im}\Sigma(k, \omega)$ . Similarly, the self-energy can be extracted from the FWHM in the momentum direction for a near-linear dispersion via  $|\text{Im}\Sigma(k, \omega)| = \Gamma_k v_F/2$ . The latter method using MDCs is more precise as it avoids asymmetric effects from the Fermi Dirac distribution [179, 180].

Fig. 5.2a shows the MDCs at equilibrium (grey) and 120 ps (red) with Lorentzian fits (black dashed). Visual comparison of the two plots reveals a dramatic increase of the MDC width at  $\tau_{\text{cross}} = 120$  ps over a large binding-energy range. Fig. 5.2b presents a closer inspection of the MDCs and fits for four evenly spaced binding energies. Particularly at 120 ps, the MDCs dramatically reduce in linewidth as the binding energy approaches  $E_F$  (see arrows).



**FIGURE 5.2: Ultrafast transient self-energy enhancement.** **a** MDCs of TSS at equilibrium and 120 ps demonstrating transient broadening and goodness of Lorentzian fits. **b** MDCs and Lorentzian fits for four binding energies from  $-120$  meV to  $-5$  meV at equilibrium and 120 ps. At 120 ps, there is a clear binding-energy dependence of the width. **c**  $\text{Im}\Sigma$  derived from MDC Lorentzian FWHM as a function of binding energy at equilibrium and four representative delay integration windows (corresponding shaded regions in panel d). **d**  $\text{Im}\Sigma$  as a function delay from dark grey energy window shown in panel d (dark circles) and light grey energy window shown in panel d (light circles). **e**  $\text{Im}\Sigma$  at 120 ps (red) with linear component removed and corresponding  $\text{Re}\Sigma$  from Kramers-Kronig transform (yellow). Dashed and solid black lines correspond to  $\text{Im}\Sigma$  and  $\text{Re}\Sigma$  from 120 ps simulation in Fig. 5.5. **f** The electron-phonon coupling constant,  $\lambda$ , determined from high binding-energy plateau of  $\text{Im}\Sigma$  of panel c (white circles), optimizing MDC centroid locations through simulation (blue triangles), and Kramers-Kronig of measured  $\text{Im}\Sigma$  of panel e (yellow squares).

Fig. 5.2c displays the  $\text{Im}\Sigma$  (extracted from MDCs in the red window of panel a versus binding energy at equilibrium (black dots) and four integrated delay regions (see corresponding shaded colors in panel c) denoted by the average delay value. At equilibrium and 10 ps,  $\text{Im}\Sigma$  is approximately flat and at a minimum. At  $\tau_{\text{cross}}$  and above  $-30$  meV, the self-energy trends sharply downward towards the equilibrium value at  $E_F$ . At longer delays (170 ps and 350 ps) the self-energy remains above the equilibrium position at high binding energies with a downward slope towards the equilibrium value at  $E_F$ .

The energy-dependence of the imaginary part of the self-energy at  $\tau_{\text{cross}}$  is emblematic for electron-phonon coupling, where  $\text{Im}\Sigma$  demonstrates a step-like function that decreases



for energies near the phonon-mode energy [179, 180, 181, 26]. In this specific case, the binding-energy location of the self-energy dip is consistent with the well-known phonon-mode of  $\approx 20$  meV known to couple to both the bulk and surface states at varying degrees [180, 182, 183]. This phonon-mode has been associated with the the optically active  $A_{1g}$  mode [180] as well as polar-type optical modes [184]. The dip near  $E_F$  is suppressed for all other delays, suggesting that EPC from the 20 meV phonon increases at the moment of  $\tau_{\text{cross}}$ . The constant offset for all delays of  $\approx 40$  meV ( $\text{Im}\Sigma$  value at  $E - E_F = 0$ ) is indicative of the electron-disorder interaction and is delay-independent and comparable to previous reports in  $\text{Bi}_2\text{Se}_3$  [180, 185, 186]. Furthermore, overall there is delay-dependent linear component of  $\text{Im}\Sigma$  (dashed line) that could indicate weak electron-electron coupling,  $\beta \approx .0005$ , consistent with previous equilibrium studies of  $\text{Bi}_2\text{Se}_3$  [180, 186] or a previously reported unknown final-state effect [179].

The evolution of the  $\text{Im}\Sigma$  as a function of delay time is shown in Fig. 5.2d. Spectra are shown both at high binding energy represented by dark circles (from dark grey integration window in panel c) and at  $E_F$  represented by lightened circles (from light grey integration window in panel c). The primary feature of the  $\text{Im}\Sigma$  profile at high binding energy is a sharp peak that occurs at  $\tau_{\text{cross}}$ . Moreover,  $\text{Im}\Sigma$  remains raised above the equilibrium value (black dashed) for positive delays beyond the  $\tau_{\text{cross}}$ . However,  $\text{Im}\Sigma$  near  $E_F$  which serves as a measure of the degree of electron-disorder interaction, is delay independent and consistent with previous reports in  $\text{Bi}_2\text{Se}_3$  [180, 185, 186].

These results are consistent with simulated energy vs momentum dispersions experiencing electron-phonon coupling while considering experimental energy and momentum resolutions (see Fig. 5.5). Further confirmation follows from the Kramers-Kronig transformation. Indeed, the real part of the self-energy is related to the imaginary part of the self-energy through the Kramers-Kronig transform. Therefore, from the measured  $\text{Im}\Sigma$  alone we can determine  $\text{Re}\Sigma$  and compare both self-energy components to the best fit self-energies utilized in the simulation of panel b. Fig. 5.2e presents  $\text{Im}\Sigma$  for 120 ps after removing the linear back ground (red) and  $\text{Re}\Sigma$  as determined through Kramers-Kronig analysis (yellow) with the respective self-energies from the simulation overlayed in dashed and solid black, respectively. The Kramers-Kronig analysis reveals a  $\text{Re}\Sigma$  peaked at 20 meV near the expected phonon-mode energy. Both experimental self-energy components closely match the respective self-energies from the simulation.

The results discussed so far suggest an increase of  $\text{Im}\Sigma$  at the characteristic phonon frequency and consequent renormalization of the dispersion indicative of electron-phonon coupling. The strength of this coupling can be directly extracted from the self energy following standard procedure. Specifically, we have adopted three different methods to determine the electron phonon coupling constant and study its evolution as a function of delay time. The results are consistent within each other, as shown in Fig. 5.2f. From the measured  $\text{Im}\Sigma$  in panel b,  $\lambda$  can be determined from the high binding-energy plateau after removing the electron-disorder component and the linear background. The magnitude of  $\lambda$  is determined by the value of the self-energy plateau and the phonon-mode energy being  $\lambda = 2\text{Im}\Sigma(E \ll E_{\text{ph}})/(\pi E_{\text{ph}})$  [25] as shown by white circles. Secondly, we can vary  $\text{Re}\Sigma$

and the corresponding Kramers-Kronig consistent  $\text{Im}\Sigma$  of a 20 meV phonon mode applied to the bare band dispersion through the fitting parameter  $\lambda$  to simulate the measured ARPES spectra (as performed in panel b). The blue triangles correspond to the  $\lambda$  values that best reproduces the measured MDC centroid locations. Lastly, by performing the Kramers-Kronig transform on the background subtracted  $\text{Im}\Sigma$  (as shown in panel e) we can determine  $\lambda$  from the slope of  $\text{Re}\Sigma$  near  $E_F$  [180, 25, 26]. These results are presented as yellow squares for the four delays near  $\tau_{\text{cross}}$  that exhibit a clear dip in  $\text{Im}\Sigma$ .

These observations suggest that the TSS undergoes a sudden increase of the electron-phonon coupling at  $\tau_{\text{cross}}$  reaching a coupling constant of nearly  $\lambda = 0.6$ , much higher than previously reported in equilibrium studies of  $\text{Bi}_2\text{Se}_3$  [180, 187, 184, 188]. Both the TSS and bulk conduction band (of which the QWs are derived) participate in the EPC, with previous studies suggesting that the QWs in  $\text{Bi}_2\text{Se}_3$  are a significant factor in determining EPC strength [189, 183, 190].

## 5.4 Fitting MDCs and Simulating Electron-Phonon Spectral Response

Figure 5.3 demonstrates the fit invariance of the self-energy dip associated with the 20 meV phonon mode. The top panels show the MDCs of the Dirac surface state spectrum at equilibrium and the bottom panels are for  $\tau = 130$  ps near  $\tau_{\text{cross}}$ . Three Lorentzian fitting regimes are used: (Fit 1) symmetric fitting limited by detector window near  $0.165 \text{ \AA}^{-1}$ . (Fit 2) asymmetric fit reducing detector edge contribution (see black arrows). (Fit 3) one-sided fit in which detector edge is not incorporated. All three fitting routines produce the same characteristic curves at equilibrium and at  $\tau_{\text{cross}}$  including the self-energy dip near  $E_F$ . The arrows in panels b show at what binding energy the fit interacts with the momentum-window edge. The edge interaction plays no clearly observable role on the self energy curves observed in panel d.

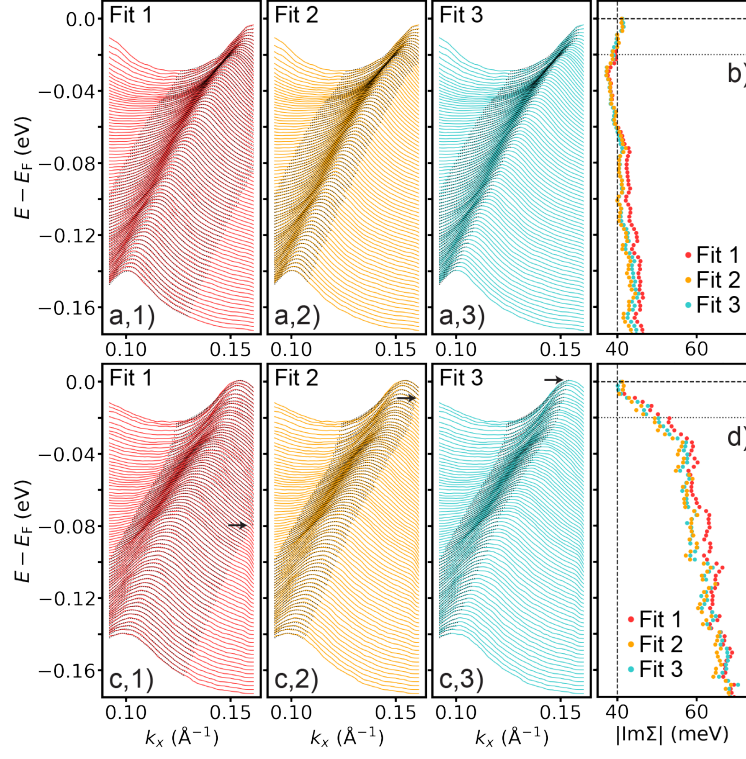


FIGURE 5.3: **Self-energy dip invariant to MDC fitting range.** (a,1-3) MDCs of positive-momentum side of Dirac cone surface state and Lorentzian fits (black) at equilibrium with three different momentum ranges. **b** Extracted self-energy from Lorentzian FWHM for three fitting ranges. (c,1-3) Same as panel a except at  $\tau = 130$  ps near  $\tau_{\text{cross}}$ . **d** corresponding extracted self-energies from panel b.

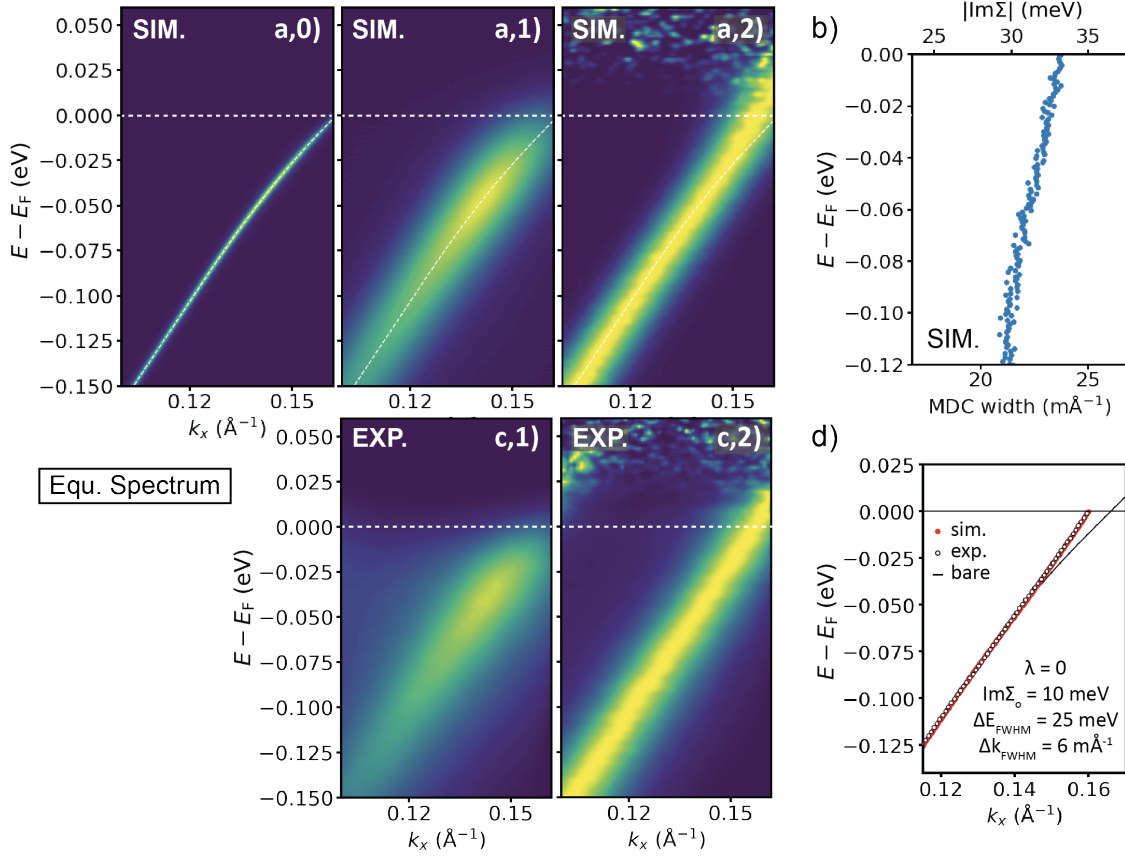


FIGURE 5.4: **Simulated equilibrium spectrum versus experiment.** (a,0) Simulated bare band without energy and momentum detector resolution broadening and reduced self-energy to clearly present dispersion. (a,1) Bare band from (a,0) after energy and momentum resolution convolution and applying energy-independent self-energy of 10 meV. (a,2) Spectrum from (a,1) after normalizing along binding energy and squaring the intensity to clearly show the deviation from the curved bare band dispersion and the nearly constant spectral width. (b) MDC FWHM and extracted imaginary self-energy from the spectrum in (a,1) demonstrating nearly featureless binding-energy dependence. (c,1-2) The experimental data of the equilibrium spectrum for comparison with (a,1) and (a,2). (d) Comparison of the simulated MDC centroids from (a,1) (red) and MDC centroids from the experimental data of (c,1) (open circles).

ARPES measures the single particle spectral function:

$$A(k, \omega) = \frac{1}{\pi} \frac{|\text{Im}\Sigma(k, \omega)|}{(\omega - E_o(k) - \text{Re}\Sigma(k, \omega))^2 + \text{Im}\Sigma(k, \omega)^2} \quad (5.1)$$

where  $k$  and  $\omega$  are the electron momentum and energy, respectively,  $E_o(k)$  is the energy of

the bare band, and  $\text{Re}\Sigma(k, \omega)$  and  $\text{Im}\Sigma(k, \omega)$  are the real and imaginary parts of the electron self-energy.  $\text{Re}\Sigma(k, \omega)$  and  $\text{Im}\Sigma(k, \omega)$  are Kramers-Kronig related and are shaped by many-body interactions. The imaginary part of the self-energy broadens the energy distribution curve (EDC) linewidth whereas the real part modifies the bare band dispersion location. The linewidth and band dispersion can be extracted by either EDCs or MDCs. [179, 180]. In this work we used MDCs to avoid convolution with the Fermi level.

In order to uncover whether the change in the MDC determined dispersions and self-energy dip near  $E_F$  at  $\tau_{\text{cross}}$  are due to electron-phonon coupling at 20 meV, we must carefully simulate the effect of the real and imaginary parts of an electron-phonon contribution to the self-energy with the presence of detector resolution convolution on the measured MDC centroids and widths. Moreover, we must determine the true bare band dispersion before momentum and energy resolution takes effect. In Fig. 5.4, we have determined a bare band dispersion (a,0), that after a constant imaginary self-energy ( $\text{Im}\Sigma_o$ ) and energy and momentum resolution is applied (a,1) reproduces the MDC centroid locations from the experimental data (red vs open circles panel d). In agreement with previous reports [147, 191], the non-zero energy resolution produces an upward distortion of the true dispersion in the energy region  $E - E_F > -\Delta E_{\text{FWHM}}$ . The simulated spectrum (a,1) also qualitatively matches the experimental spectrum (c,1), including after closer inspection by normalizing by binding energy and squaring the intensity ((a,2) and (c,2)). The bare band dispersion was determined by starting with a linear dispersion and applying a polynomial modification above a cutoff binding energy with matching derivatives. The parameters were then varied until the MDC centroids of the simulated data matches the MDC centroids from the experimental data. Fig. 5.4b shows that the MDC widths remain nearly binding-energy independent, exhibiting no dip-like feature near  $E_F$ .

Interestingly, at  $\tau_{\text{cross}}$ , Figure 5.5 demonstrates that the experimental MDC centroid locations (white circles) experience a drastic increase of this upward distortion. Since the energy resolution of the detector is fixed, this reflects a true change in the band structure near  $E_F$ . The spectrum at  $\tau_{\text{cross}}$  is best captured by including an electron-phonon contribution to the bare band dispersion. The contribution to the real-part of the self-energy from electron-phonon coupling produces the characteristic kinked dispersion seen in (a,0) with a kink at 20 meV. The MDC centroid locations (after taking into account energy and momentum resolution (a,1)) reproduces the experimental MDC centroid locations panel d, matching the increased uplift of the dispersion near  $E_F$ . Again the simulated spectrum and the experimental spectrum are qualitatively similar ((a,1) and (a,2) vs (c,1) and (c,2)). Panel b reveals the downward kink produced by the binding-energy dependent imaginary self-energy contribution from the electron-phonon coupling. This dip is only possible given an inherent dip in the true self-energy.

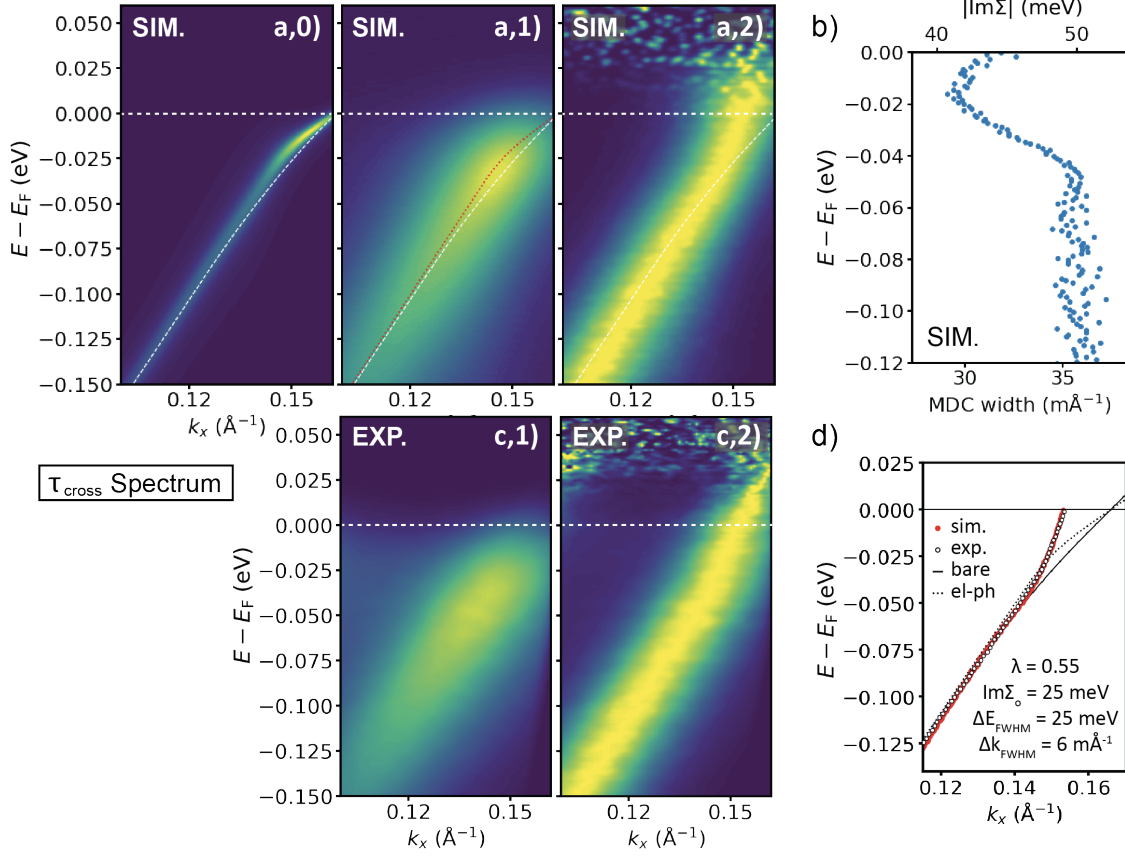


FIGURE 5.5: **Simulated  $\tau_{\text{cross}}$  spectrum versus experiment.** Analogous to Fig. 5.4 but for  $\tau = 130$  ps near  $\tau_{\text{cross}}$ . **(a,0)** We have added an electron-phonon contribution to the real self-energy that produces a kink at 20 meV. **(a,1)** the Kramers-Kronig related imaginary part of the self energy is included in the spectral simulation. **(a,2)** The deviation of the apparent dispersion from the bare band dispersion near  $E_F$  is more apparent. **b** A dip forms near the phonon-kink energy in the measured MDCs widths and extrapolated imaginary self-energy. This was not possible in the case of a binding-energy independent self-energy. **(c,1-2)** and **d** Again, the simulated spectrum closely matches the experimental spectrum both qualitatively and through MDC centroid analysis.

## 5.5 Modeling SPV Decay and Charge Transfer

The Lifshitz transition and the associated self-energy enhancement play a critical role in the recombination of the photoexcited electron-hole pairs. To elucidate their role, we have developed a minimal rate-equation model that incorporates the DOS of QW1 and QW2 as well as enhanced scattering at the moment of the Lifshitz transition. At the surface of the material the conduction band and valence bands bend downwards forming a band bending

potential that generates the quantum well levels. The downward band bending forces holes into the bulk and electrons towards the surface, trapping both populations and generating a separated charge distribution that manifests as (and is proportional to) the measured potential at the surface. Therefore, the decay profile of the this surface potential measures the time-dependence of the photoexcited charge at the surface and it can be directly measured as a function of delay by the delay-dependent rigid shift of the ARPES spectrum according to our previous studies [47, 48]. Since the majority of photoexcited charge at the surface is trapped in the modified quantum well levels, understanding the decay mechanisms of the trapped charge in QW1 and QW2 can reveal the origin of the discontinuous decay profile of the surface potential.

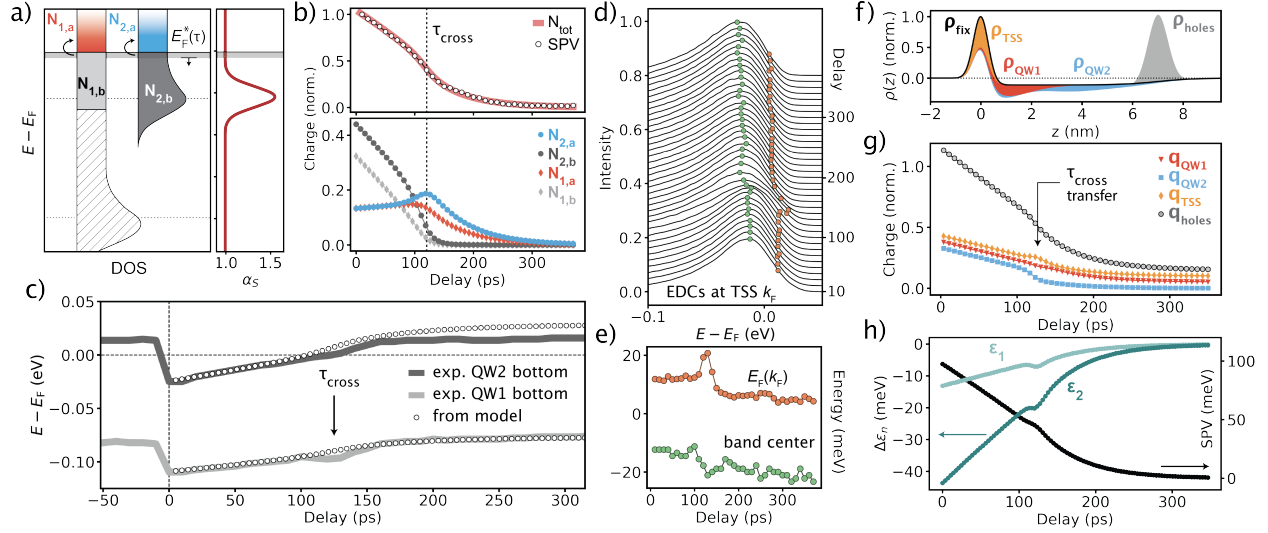
Fig. 5.6a illustrates the electronic filling of QW1 and QW2 after excitation. The equilibrium electron filling is designated by the striped regions whereas the filled regions indicate the excess electron populations created by the pump. For the non-equilibrium charge trapped in the quantum well levels, there are two types of populations: electrons above  $E_F$ : 1) both QW1 and QW2 shift downwards in energy with respect to the Fermi level and establish charge below  $E_F$  ( $N_{1,b}$  and  $N_{2,b}$  respectively) which remains in quasi-equilibrium (no recombination) during their stay below  $E_F$ . 2) photoexcited charges will also populate states in QW1 and QW2 above  $E_F$  ( $N_{1,a}$  and  $N_{2,a}$ ), which can recombine with bulk holes with at a rate  $\alpha_{\text{rec}}$ .

These populations are not static, since QW1 and QW2 relax upward in energy changing the relative position of  $E_F$  with respect to the band bottoms. Our model incorporates this effect by fixing the energy positions of QW1 and QW2 such that  $E_F$  in this energy frame is time dependent,  $E_F^*(\tau)$ . In fact,  $E_F^*$  depends proportionally on the total accumulated charge,  $N_{\text{tot}} = N_{1,a} + N_{1,b} + N_{2,a} + N_{2,b}$ , since the electric field linearly modifies the quantum well level positions and is proportional to the total charge (see Fig. 5.9 and Fig. 4.9).

As  $E_F^*$  shifts downward, charge from  $N_{x,b}$  is transferred to  $N_{x,a}$  according to the respective DOS and  $\Delta E_F^*$ . The DOS of the QWs is broadened by 6 meV, the expected smearing of the DOS at  $T = 80$  K [156]. Finally, we simulate the effect of the sudden increase in  $\lambda$  discussed in Fig. 5.2 through the coefficient  $\alpha_s$  which tracks with QW2; minimum value of 1 and a 6 meV broad Gaussian peak of amplitude +0.5 centered at the QW2 singularity. This has the effect of enhancing the recombination rate,  $\alpha_{\text{rec}} = \alpha_s(E_F^*) \cdot \alpha_o$ , for  $N_{x,a}$  the moment  $E_F^*$  crosses the QW2 singularity as would be expected in the case of increased electron-phonon scattering [192, 26].

Fig. 5.6b plots the results of the model alongside the normalized surface potential profile at  $51.8 \mu\text{J}/\text{cm}^2$ , capturing both the linear decay region as well as the kink towards exponential-like decay. The individual charge populations are shown in the bottom graph. Notably, the charge stored above  $E_F$  in QW1 and QW2 is sustained up until  $\tau_{\text{cross}}$  in which  $N_{2,a}$  exhibits a hump then decay, and  $N_{1,a}$  transitions into exponential-like decay.





**FIGURE 5.6: Singularity mediated relaxation dynamics.** **a** DOS of QW1 and QW2 illustrating rate equation model. Model chooses energy frame in which QW2 band bottom energy is fixed.  $E_F^*$  drifts downward according to total stored charge, while charge  $N_{1b}$  and  $N_{2b}$  are transferred to  $N_{1a}$  and  $N_{2a}$  and allowed to decay with recomb. rate  $\alpha \times \alpha_s$ . **b** Results of model showing good agreement with surface voltage time-dependence. **c** QW1 and QW2 band bottoms from model (light grey and dark grey, respectively) compared to measured EDC centroid band bottom locations at  $\Gamma$  as a function of delay (open circles). **d** EDCs at TSS  $k_F$  as a function of delay with quasi- $E_F$  (orange) and band centers (green), demonstrating short-lived charge accumulation. **e**  $E_F$  and band centers plotted vs delay show peak occurs at  $\tau_{cross}$ . **f** Charge density versus distance into the bulk used in charge transfer model.  $\rho_{fix}$  (black line) is fixed charge that creates band bending potential at equilibrium. Photoexcited electrons  $\rho_{TSS}$ ,  $\rho_{QW1}$ , and  $\rho_{QW2}$  (yellow, red, blue respectively) and photoexcited holes  $\rho_{holes}$  alter the charge distribution after excitation and decay in time. **g** Decay profile of TSS, QW1, QW2, and trapped hole populations, showing charge transfer from QW2 to QW1 and TSS. **h** Charge transfer causes a dip in the relaxation of the QW1 and QW2 eigenvalues (light and dark teal, respectively) at  $\tau_{cross}$ , capturing panel c behavior. Surface potential response (black) is mostly unaffected by charge transfer.

Since  $E_F^*$  measures the relative distance between the QW2 band bottom and  $E_F$ , we can extrapolate the QW1 and QW2 band bottom positions by monitoring  $E_F^*$  versus delay. Fig. 5.6c displays measured band bottom energy positions of QW1 and QW2 as a function of delay determined from the EDC peak positions at  $\Gamma$  (open circles). The model-extrapolated QW2 band bottoms using  $E_F^*$  (dark grey) with the same parameters in panel b matches the measured QW2 band bottom position up until QW2 crosses  $E_F$ . At this point, the EDC peak positions for QW2 no longer capture the true band bottom positions due to convolution with the Fermi level. However, we can see agreement of the model for further delays by



investigating the measured QW1 band bottom position which is unaffected by the Fermi level. Plotted beneath QW2 is  $E_F^*/1.65$  (light grey), offset to match the QW1 energy position at  $\tau = 0$  ps and divided by 1.65 (the empirically determined proportionality constant between QW1 and QW2 energy levels). As verification, we see that the experimentally determined QW1 band bottom positions match the simulation closely across the entire delay range.

However, if one looks closely at panel b, QW1 appears to dip momentarily in energy at  $\tau_{\text{cross}}$  (see arrow). Fig. 5.6d-h presents a reasonable explanation for this phenomenon that again takes into account increased scattering during the Lifshitz transition.

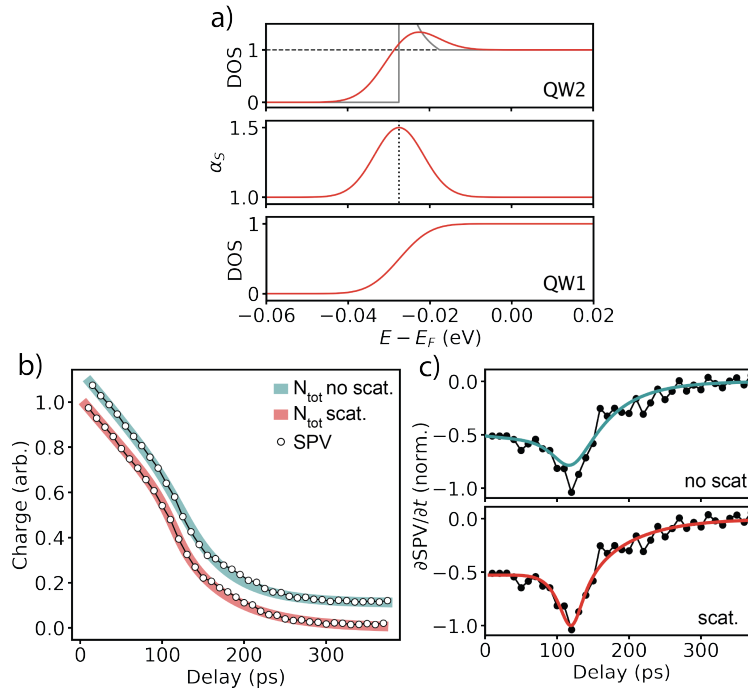
From our earlier discussion of panels a-c, it is clear that the EPC enhancement is associated with an increase in c-axis scattering causing an increase in the electron-hole recombination rate. However, it is likely that this scattering is not unidirectional towards the bulk and due to the intrinsic downward bending in the material, electrons are already pressured towards the surface [48, 46]. In the low-scattering regime before  $\tau_{\text{cross}}$  few electrons participate in indirect scattering to the TSS. However, at  $\tau_{\text{cross}}$  the scattering rate increases driving charge both into the bulk and towards the surface and momentarily producing an excess of charge in TSS.

In fact, this behavior is observed at  $k_F$  of the TSS. In Fig. 5.6d we present EDCs at  $k_F$  that are offset in the y-axis according to their corresponding delay time. The Lorentzian band centers (green) and the quasi-Fermi-level (orange) demonstrate opposing hump-like behavior at  $\tau_{\text{cross}}$ . This can be seen more clearly in Fig. 5.6e in which only the band centers and  $E_F(k_F)$  are plotted versus delay. The sharp increase in the quasi-Fermi-level at  $\tau_{\text{cross}}$  suggests that charge is transferred to the TSS and exists over a short timescale ( $< 20$  ps).

In light of the observed excess charge in the TSS at  $\tau_{\text{cross}}$ , we explore the consequences of such a charge transfer using a partially coupled Poisson-Schrödinger method to simulate charge populations and calculate QW wave-functions (see Fig. 5.9). In Fig. 5.6f, we present the relevant charge densities at the surface and in the bulk used in our model. The equilibrium fixed charge distribution,  $\rho_{\text{fix}}$ , is shown as the black curve and established the equilibrium band bending potential. After the pump pulse, photoexcited charge separation leads to excess electron populations  $\rho_{\text{TSS}}$ ,  $\rho_{\text{QW1}}$ , and  $\rho_{\text{QW2}}$  (yellow, red, and blue, respectively) and an equal number of holes at the bulk edge of the band bending,  $\rho_{\text{holes}}$  (grey). The charge in QW1 and QW2 is determined by the square modulus of the resulting wave-functions confined in the band bending potential (determined by adiabatically introducing charge into the QW states from equilibrium).

The excited charge populations decay according to a simulated surface potential decay profile shown in panel g. The simulated surface potential decay profile can be seen in the excited hole population,  $q_{\text{holes}}$ , which is equal to the summation of the excited QW1, QW2, and TSS populations, maintaining charge neutrality. In order to simulate the charge transfer towards the surface, we introduce a sigmoidal reduction in the charge population of QW2 that is transferred to  $q_{\text{TSS}}$  and  $q_{\text{QW1}}$  asymmetrically, with a Gaussian excess at  $\tau_{\text{cross}}$  given to  $q_{\text{TSS}}$  and the remainder provided to  $q_{\text{QW1}}$ . This produces the effect of a biased charge transfer to the TSS (see arrow) which is then equilibrated with QW1 after  $\tau_{\text{cross}}$ . The curves have been shifted vertically slightly for visibility.

Since the QW wave-functions and eigenvalues are determined at each time step, we can monitor the evolution of the QW spectrum over the course of the surface potential decay and charge transfer event. Fig. 5.6h plots the change in eigenenergy of QW1 (light teal) and QW2 (dark teal) as a function of delay, demonstrating the dipped feature observed in panel b. The model underestimates the shift of QW1 by a factor of two, but closely captures the shape of the time dependence. The surface voltage can be determined in our simulation by the difference in bulk and surface potentials (black) and is only weakly affected by the charge transfer event. This is expected since the change in surface potential is mainly determined by the total population of photoexcited electrons and holes.



**FIGURE 5.7: Decay model details.** **a** QW2 DOS (top), enhanced scattering factor (middle), and QW1 DOS (bottom) used in the simulation. The DOS are broadened by 6 meV Gaussian convolution and  $\alpha_s$  consists of a 6 meV broad Gaussian centered at the QW2 band bottom. The grey line in the top panel represents the singularity in QW2 before broadening. **b** Model results from Fig. 5.6b including QW1 and QW2 populations (top), and model results including only QW2 dynamics (bottom) both for  $51.8 \mu\text{J}/\text{cm}^2$ . **c** Model results for  $N_{\text{tot}}$  with (red) and without (teal) incorporating  $\alpha_s$  compared to measured SPV profile. **d** Time-derivative of model results in panel c with (top) and without (bottom)  $\alpha_s$ . The delay-dependent enhanced scattering is required to fully capture the discontinuous decay rate at 120 ps.

Figure 5.7 presents the QW1 and QW2 DOS, scattering enhancement function, and

alternate results of the decay model. In panel a, we show the DOS for QW2 in red used for all simulations. It is produced from a singularity from Rashba split bands with a 10 meV energy separation between the band bottoms and the Rashba crossing at  $\Gamma$  (grey) broadened with a  $\sigma = 6$  meV Gaussian. The scattering enhancement constant in the middle panel is centered on band bottom position for QW2, so as  $E_F^*$  sweeps downward in energy the peak in  $\alpha_s$  is correlated with the QW2 band bottom. The QW1 DOS is step-like to capture only the photoexcited excess charges at the surface.

In panel b we demonstrate the difference between applying the enhanced scattering (red) and not (teal). The red curve more closely matches the decay of the SPV. This can be seen more clearly in panels c where the time-derivative of the SPV (black dots) and the time-derivative of the decay model results (teal) and (red) are shown. The model with enhanced scattering cannot capture the sharp dip at  $\tau_{\text{cross}}$  in the time-derivative, suggesting that a simple constant decay rate model cannot describe the SPV decay profile.

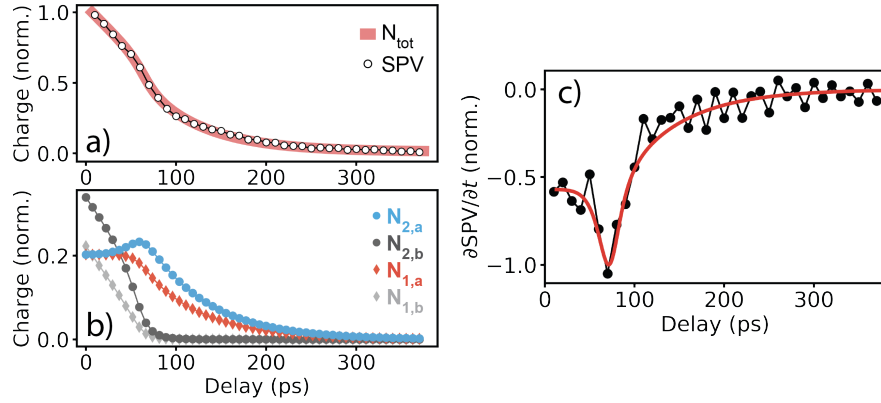


FIGURE 5.8: **Decay model applied to low-fluence SPV.** (a,b) SPV, decay model result, and individual QW populations for  $10.5 \mu\text{J}/\text{cm}^2$ . c Time-derivative of model results in panel a show good agreement with the discontinuous decay feature.

Figure 5.8 demonstrates that the decay model sufficiently captures the decay dynamics at lower fluence. Here, the SPV decay profile at a fluence of  $10.5 \mu\text{J}/\text{cm}^2$  was chosen since the plateau before  $\tau_{\text{cross}}$  is still clearly visible. In panel c, the time-derivative of the decay model reproduces the sharp dip at  $\tau_{\text{cross}}$  well.

## 5.6 Details on Poisson-Schrödinger Model

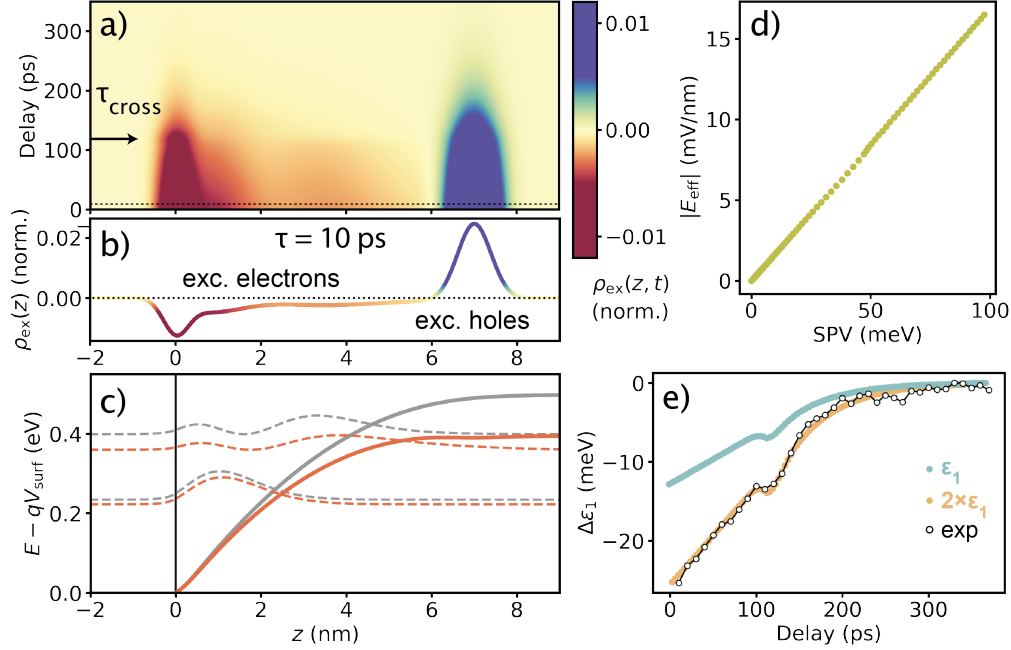


FIGURE 5.9: **Delay-dependent potentials from Poisson analysis.** **a** Delay dependence of photoexcited charge distribution with red regions representing electrons and blue regions representing holes. Charge transfer even is shown by arrow. **b** Charge distribution at 10 ps (black dashed line in panel a). **c** Potential gradient and wave-functions of QWs before and after excitation (grey and orange, respectively). **d** Average potential gradient versus surface potential from simulation in panel a. **e** Energy eigenvalue of QW1 (teal) underestimates measured value from experiment (black open circles) by 2x (beige).

Figure 5.9 presents additional details on the combined Poisson-Schrödinger method for calculating the time dependence of the energy eigenvalues in Fig. 5.6h.

To calculate the quantum well wave-functions and eigenvalues, we first start with a fixed charge distribution that establishes the band bending at equilibrium (see black curve in Fig. 5.6f). This distribution is set to be on a length scale of approximately 10 nm based on the measured bulk hole-like carrier concentration of approximately  $10^{-19} \text{ cm}^{-3}$  and then fine-tuned to produce the observed eigenvalues from the experiment.

This equilibrium distribution leads to the downward band bending potential shown in grey in panel c. The wave-functions for the quantum wells at equilibrium are then calculated using the Schrödinger equation and an effective mass of  $0.45 m_e$  (based on the empirical band fitting of QW1 near the band bottom).

Time-evolution is then incorporated by adding electrons to the surface state (simplified as a Gaussian distribution near the surface) and the quantum wells, using the squared modulus of the wave-functions to define the excited charge density profile into the bulk, in equal proportions for all three states. An equal number of excited holes with respect to the excited electrons are then trapped in a Gaussian profile towards the bulk edge of the band bending. Small time steps of 1 ps are taken in reverse order ( $320 \rightarrow 0$  ps), such that the new potential established by the small addition of excited charge produces a new set of QW wave-functions in turn affecting the charge distribution at the next time step.

The excited electron distribution can be seen in Fig. 5.9 panels a and b. In panel a, the excited charge decays according to Fig. 5.6g, and the charge transfer from QW2 to QW1 and the TSS can be seen at  $\tau_{\text{cross}}$  (see arrow). In panel b, we see the QW wave-functions' effect on the photoexcited charge distribution near the peak excitation after the pump pulse at 10 ps. The effect of the photoexcited charge distribution on the QW wave-functions and eigenvalues is shown in orange in panel c. The eigenvalues are compressed after photoexcitation.

The wave-functions are approximately Airy functions due to the resemblance of the band bending potential to a triangular-well potential. In the triangular-well approximation, the eigenvalues are explicitly dependent on the potential gradient. In panel d, we plot the change in the average potential gradient (averaged between 0 to 4 nm) of the band bending potential which we call the effective applied field ( $E_{\text{eff}}$ ) with respect to the change in the band bending amplitude (SPV), demonstrating the expected linear dependence with SPV.

The charge transfer event depicted in panel a leads to a dip in the relaxation profile of the energy eigenvalues at  $\tau_{\text{cross}}$ . Panel e plots the change in the eigenvalue for QW1 (teal) alongside the change in the measured band bottom energy position from the ARPES experiment (black open circles). Our simulation underestimates the magnitude of the shift, with 2 times the simulated change matching the experimental data closely. The underestimation is not surprising. We have developed a simplistic model that ignores the role of the energy dependent effective mass of QW1, possible polarization of the equilibrium fixed charges, charge migration dynamics, inhomogeneous dielectric constant, and complicated atomic potentials within the  $\text{Bi}_2\text{Se}_3$  quintuple layers and surface adsorbents. However, the model closely captures the qualitative behavior and an atomistic approach can possibly be used to treat the underestimation.

### Long-Lived Photoexcited Remnant Above $E_F$

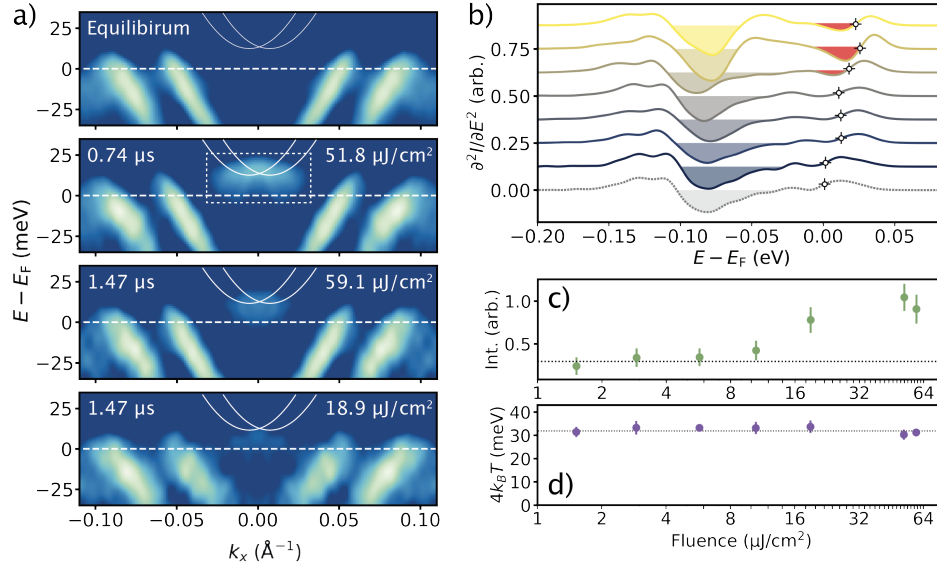


FIGURE 5.10: **Long-lived QW2 excited states.** **a**  $\partial^2 I / \partial E^2$  spectra at equilibrium and at  $-100$  ps before the pump for three fluences ( $51.8$ ,  $59.1$ , and  $18.9 \mu\text{J}/\text{cm}^2$ ), indicating persistent excitation in QW2 from the previous pump pulse ( $0.74$  and  $1.47 \mu\text{s}$  depending on rep. rate). **b**  $\partial^2 I / \partial E^2$  EDCs at  $\Gamma$  and  $-100$  ps for all fluences. Filled regions denote negative band curvature associated with QW1 (blue to yellow) and QW2 (red). Equivalent equilibrium EDC is displayed in grey. **c** Integrated intensity of raw  $-100$  ps spectra in region of excitation (shown in a) normalized to total spectral weight as a function of fluence. Note second highest fluence ( $51.8 \mu\text{J}/\text{cm}^2$ ) has  $2\times$  rep. rate than all other datasets. **d** Fermi-edge broadening as a function of fluence as determined from TSS  $k_F$  at  $-100$  ps. The dashed line represents the Fermi broadening at equilibrium.

We have shown that the QW2 singularity controls the recombination process and generates a transient charge transfer to the surface and that both effects are marked by the characteristic time  $\tau_{\text{cross}}$ . Surprisingly, at high fluence, photoemission intensity remains in the QW2 singularity for remarkably long delay times. In Fig. 5.6d, one can see that charge exists above  $E_F$  at negative delays, before the pump pulse at  $\tau = 0$ . There is only two possibilities that could cause such an effect: Equilibrium heating broadens the Fermi edge partially filling the QW2 singularity above  $E_F$  or quasi-equilibrium photoexcited charge persists in the singularity from the previous pump pulse that occurred at  $\tau = -1/(\text{rep.rate})$ .

In Fig. 5.10a we take a closer look at the singularity at  $\tau = -100$  ps for the three highest fluences and the same region at equilibrium via  $\partial^2 I / \partial E^2$  spectra. The dotted parabolas serve as a guide to the eye for the QW2 dispersion. At equilibrium, we see no charge above

$E_F$ , suggesting that the equilibrium  $E_F$  broadening is not sufficient to populate the QW2 singularity. However, for fluences 18.9, 59.1, and 58.1  $\mu\text{J}/\text{cm}^2$  the singularity is populated above  $E_F$  and the intensity increases in the respective order. The strongest intensity does not occur at the highest fluence, but the second highest. In fact, this spectra was taken at a higher repetition rate than the spectra from the other fluences.

The  $\partial^2 I / \partial E^2$  EDCs at  $\tau = 100$  ps for all measured fluences (blue to yellow in ascending order) are presented in Fig. 5.10b. Negative curvature (indicating populated bands) is designated by the filled regions with the red filled regions corresponding to QW2 population. Due to the low intensity of the QW2 filling, a reliable Fermi level cannot be established, however the inflection point (white circles with crosses) that follows the negative curvature serves as reference for the upper energy limit of the filled singularity. Despite only the three highest fluences demonstrating negative curvature in QW2, the inflection point continuously decreases towards the equilibrium value (near  $E_{F,\text{eq}} = 0$ ) as the fluence is decreased.

If equilibrium heating is the culprit, than the thermal broadening of  $E_F$  in the negative delay would increase with increased fluence and decreased repetition rate over all momentum. In Fig. 5.10c, the integrated intensity from the energy-momentum window in panel a of corresponding raw spectra at  $\tau = -100$  ps are plotted as a function of fluence. Again, we see that higher fluence increases the QW2 intensity monotonically with the exception of 51.8  $\mu\text{J}/\text{cm}^2$  (smallest repetition rate and highest intensity). In Fig. 5.10d, the Fermi-edge broadening at  $k_F$  of the TSS is plotted as a function of fluence with the equilibrium value shown as a dashed line. There is no apparent Fermi broadening as fluence is increased. In particular, the broadening from the highest repetition rate spectrum (which would experience the most heating) remains at the equilibrium value. The increased intensity of the long-lived population with fluence and with reduced rep. rate without a subsequent increase in Fermi level broadening suggests that a metastable population of charge persists above  $E_F$  in the singularity of the QW2 band bottom on timescales greater than 1 microsecond.

## 5.7 Discussion

TR-ARPES suffers from intrinsically poor energy resolution in part due to the Fourier limitation of the bandwidth of the sub-picosecond pulses. The time-resolution can in principle be reduced to improve the energy resolution, however this limits the ability to study typical electronic lifetimes [193]. In this study, we have gone through great lengths to uncover sub-resolution effects (namely the 20 meV phonon kink) by simulating the effect of a kinked dispersion on the MDC centroids. Although, there have been numerous studies on the effect of detector broadening on MDC and EDC fits to dispersions [147, 194, 191, 181], this study is original in the sense that we have focused on non-equilibrium near- $E_F$  modifications to the bare band, leveraging pumped and unpumped spectra to untangle the bare band from the modified band. The power of this technique is demonstrated best in Fig. 5.2e where the  $\text{Im}\Sigma$  and  $\text{Re}\Sigma$  used in the simulation that closely reproduces the MDC centroid locations are nearly identical to the measured  $\text{Im}\Sigma$  and  $\text{Re}\Sigma$  derived from Kramers-Kronig.

As a note, the electron-phonon coupling constant extracted from ARPES experiments can lead to a misrepresentation of the real  $\lambda$ . This limitation is due to the fact that ARPES experiments at equilibrium, do not probe the effective bare band, which is usually either assumed simple in functional form [180], backtracked experimentally [195], or calculated directly [196]. In this experiment, we have treated the unpumped spectra as the bare band reference. In our analysis, we have assumed that  $\lambda$  is near-zero at equilibrium based on similarly doped equilibrium systems from literature [180, 188]. This is consistent with the extrapolated bare band in Fig. 5.2b, which (although it experiences positive curvature) does not demonstrate a kink near 20 meV. This comparative measure between pumped and equilibrium spectra provides certainty of a dynamic real-part of the self-energy and therefore a true time-dependent  $\lambda$ .

Previous studies have demonstrated a large degree of variability in the measured EPC at the TSS [184, 180, 187, 189]. However, it has been shown that  $\lambda$  of the TSS is dependent on the bulk doping and presence of surface QW states [189, 183, 190]. This study helps to untangle the complicated relationship between EPC and the bulk conduction band by demonstrating the sensitivity of  $\lambda$  on the DOS at the Fermi level of the quantized bulk bands. This sensitivity is best seen in Fig. 5.2f where the EPC constant increase dramatically as the QW2 singularity passes the Fermi level. It is possible that the variable electron-phonon coupling seen in previous reports is related to the variable dopings and variable degree of quantization in these samples and the consequential acute responsiveness of the EPC to the DOS at  $E_F$ .

We note that the exact relationship of DOS to EPC appears complicated according to our study. The DOS of QW2 at the Fermi level is only one part of the total DOS of the system which also incorporates the comparable DOS of QW1 and the TSS. It is curious that a fractional change in the DOS would result in tremendous consequences on  $\lambda$ . A possible mechanism to describe the large modification in EPC as a result of the reverse Lifshitz transition is the non-adiabatic filling of the quantum well spectrum. Non-adiabatic effects from Lifshitz transitions have been proposed to explain phonon-mediated superconductivity in TMDs with partially filled valleys [197]. In our system, stored charge in the QW2 band bottom is brought above  $E_F$  at a quicker rate than charge stored in QW1. This results in a substantial change in charge above  $E_F$  from QW2 with reduced filling above  $E_F$  in QW1 and the TSS. We have shown in Fig. 5.6 that this results in charge transfer towards the surface, which equivalently indicates newly accessible states for scattering from QW2. Such a scattering event would impact the phononic DOS leading to the observed EPC enhancement. Moreover, Heid et al. demonstrated that the phonon dispersion relation of Bi<sub>2</sub>Se<sub>3</sub> predicts a large phonon momentum ( $q \approx 0.1 \text{ \AA}^{-1}$ ) suggesting that, near  $E_F$ , the TSS is scattering towards  $k = 0$  and therefore preferencing QW2. However, this is counter to the study's findings that coupling should be strongest at small phonon momenta ( $q = 0.03 \text{ \AA}^{-1}$ ) [184]. Our results suggest that current models to predict EPC in Bi<sub>2</sub>Se<sub>3</sub> and similar topological insulators are incomplete and that focus should be given to the DOS of the bulk/QW states in understanding the phenomenon.

The principle behind the long-lived photoexcited lifetimes for the small fraction of charge



in QW2 is difficult to determine in this study.  $\text{Bi}_2\text{Se}_3$  is known to produce long-lived surface photovoltage effects due to an unknown bulk hole-trapping mechanism, which could partially explain the presence of long-lived excess surface charge [74, 48]. Nevertheless, it is not clear why QW2 demonstrates a Fermi level that is offset from the Fermi level of the TSS and QW1 rather than re-equilibrating the excess charge among all the surface bands, suggesting that the singularity plays a crucial role in the longevity of these excited states. It is possible that the formation of a gap above  $E_F$  with respect to QW2 after  $\tau_{\text{cross}}$  initiates a “phonon bottleneck” in which the photoexcited carriers are in quasi-equilibrium with the high energy phonon modes enabling continued excitation above the gap and thereby inhibiting relaxation [198]. This can be elucidated through a challenging study examining the decay rate of excited charge in QW2 above  $E_F$  as a function of temperature and QW2 band bottom energy. Finally, the differential quasi-equilibrium Fermi level as well as the negative effective mass could indicate exciton formation [199], providing a speculative exotic explanation of the effect. Overall, the long-lived state at the band bottom of QW2 could only be revealed through dynamic actuation of the QW spectrum and solidifies the importance of DOS singularities and Lifshitz transitions in the ultrafast responses of complex materials.

## 5.8 Summary

We have demonstrated an ultrafast control of electron-phonon interaction via a photoinduced Lifshitz transition toggling a van-Hove-like singularity below the Fermi level. The subsequent relaxation of the quantum well spectrum reverses the Lifshitz transition at  $\tau_{\text{cross}}$  triggering a large transient enhancement of the EPC, exceeding previously reported equilibrium values. The interplay of the electron-phonon scattering at the surface and the quasi-equilibrium charge stored in QW1 and QW2 actuates a two-part recombination process characterized by a linear decay before  $\tau_{\text{cross}}$  and an exponential-like decay afterward. Moreover, the electron-phonon scattering momentarily passes charge from the QWs to the TSS, producing an ultrafast modification to the QW potential at  $\tau_{\text{cross}}$ . Finally, a small fraction of excited charge in the QW2 singularity experiences  $> \mu\text{s}$  lifetimes above  $E_F$ . All together, this work establishes a simple means of controlling large changes in the DOS at the Fermi level and enhancement of the electron-boson interaction on ultrafast timescales. It also provides new routes for driving long lived transient states in materials paving the way for novel ultrafast switching devices and DOS-driven quantum phase transitions.

## Chapter 6

# Uncovering Long-Lost Electronic Structure: Glassy Dispersions with Spin-Momentum Locking

An essential facet of engineering materials for next-generation applications is the ability to implement the materials into existing device fabrication procedures, or at least to ensure a scalable process for producing quality devices. Many of the quantum materials studied today are not easily scalable while preserving their unique electronic properties. For instance valleytronics in the transition metal dichalcogenides, twisted heterostructures such as twisted bilayer graphene, or even the well-studied  $\text{Bi}_2\text{Se}_3$  and  $\text{Bi}_2\text{Te}_3$  topological insulators cannot be easily incorporated into silicon chip processing while retaining their highly crystalline two-dimensional van der Waals configuration [200].

An ideal method for producing scalable films for device fabrication is through an evaporative or sputtering process that can produce large area coverage of the material of choice. In many cases, such methods lead to non-crystalline growth. But what if the non-crystalline phase of the material can produce the desired electronic properties? In this situation, thermal evaporation would be an appropriate growth procedure, the energy of producing the films is lowered by using low temperature growth conditions, and the film properties are more robust to substrate selection [201, 202].

In this section, I discuss the findings from a strong collaboration on amorphous topological insulators that formed naturally over the course of our exploration into the band structure of amorphous  $\text{Bi}_2\text{Se}_3$  and its topological implications. I was first contacted by Paul Corbae of the Hellman Group about his interest in examining amorphous analogs of topological insulator crystals in ARPES and together with Quentin Marsal from the Grushin group, Daniel Varjas from Stockholm University, and the respective PIs (Alessandra Lanzara, Frances Hellman, and Adolfo Grushin) we have discovered the first example of spin-momentum locking in an amorphous material as well as uncovered a rich, dispersive momentum-space picture for amorphous systems. Amorphous materials are vastly more common than crystalline systems [203], and our work has unlocked a huge section of material phase space for revealing

novel momentum-dependent electronic behavior. Our manuscript on the subject is currently under review, with a preprint on the arXiv [204].

## 6.1 Introduction

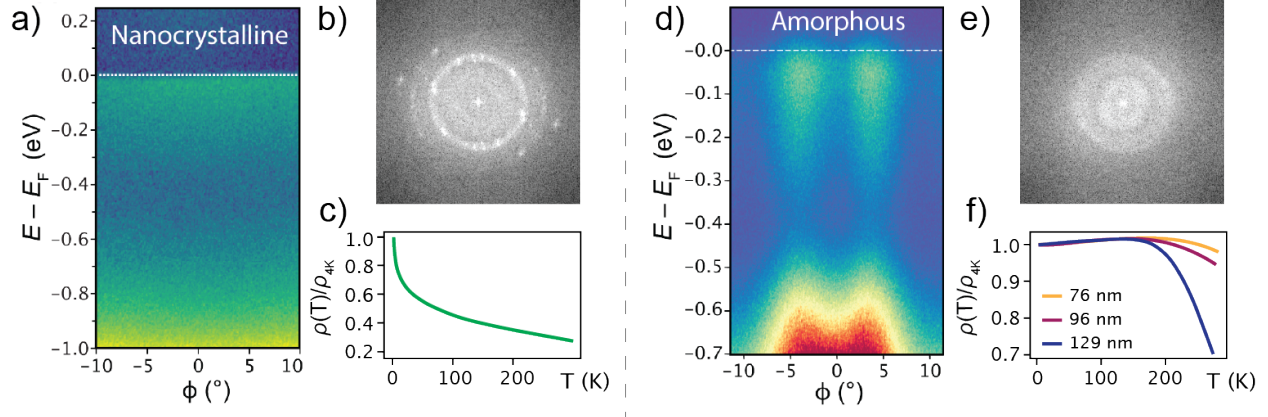


FIGURE 6.1: **Nanocrystalline versus amorphous  $\text{Bi}_2\text{Se}_3$ .** **a** ARPES spectrum of nanocrystalline  $\text{Bi}_2\text{Se}_3$  showing angle-independent intensity. **b** TEM diffraction demonstrating clear randomized diffraction points, indicative of polycrystalline structure. **c** Resistance versus temperature displaying insulating behavior at low-T. **d-f** Same plots as a-c for amorphous  $\text{Bi}_2\text{Se}_3$ : Strong dispersive features, TEM diffraction rings, and metallic behavior at low-T.

When Paul and I began measuring amorphous  $\text{Bi}_2\text{Se}_3$  at synchrotron beamlines, we were often encountered with confused reactions from the surrounding researchers. A common description of amorphous electronic structure assumes that a lack of translational symmetry ensures that momentum is ill-defined. The misconception that the density of states is often assumed to be momentum-independent is pervasive and mainly due to the difficulty to conceptualize band structure without Bloch's theorem [205]. To be quite honest, we ourselves were expecting to see nothing but flat band structure. The expectation being that the momentum dependence would either be washed away by the averaging effect of the  $\sim 100$   $\mu\text{m}$  beam spot or localized by disorder to form flat bands.

Moreover, ARPES scientists (myself included) are very familiar with measuring highly disordered systems, either from poorly grown crystals, bad cleaves, sample decay, or even measuring the Fermi-level reference from polycrystalline copper. In all these cases, the band structure can be blurred to oblivion, revealing an angle-resolved spectrum that may as well have been angle-integrated.

As an example, Paul Corbae produced nanocrystalline  $\text{Bi}_2\text{Se}_3$  via thermal evaporation from bismuth and selenium sources seen in panels a-c in Fig. 6.1. From the ARPES spectrum

in panel a, one can see that the band structure is mundane, showing an energy dependent spectral intensity but a momentum independent response (shown in detector-angle-space). The nanocrystallinity of the sample is confirmed by the sharp but randomly oriented Bragg peaks from electron diffraction in panel b. And transport on the films shows an asymptotic semiconducting behavior towards insulating at low temperature.

In contrast, amorphous  $\text{Bi}_2\text{Se}_3$  was produced by Paul by varying the growth procedure slightly and was then verified by the broad rings in the diffraction pattern (panel e). The ARPES spectrum in panel d is now quite shocking. The flat bands of the nanocrystalline sample are not present, and instead there exists highly dispersive near-vertical features; a strong momentum-dependent band structure. Moreover, the transport properties are significantly different. The insulating regime at low temperature no longer exists, and there is metallic behavior from low temperature that leads to semiconducting behavior near 200 K.

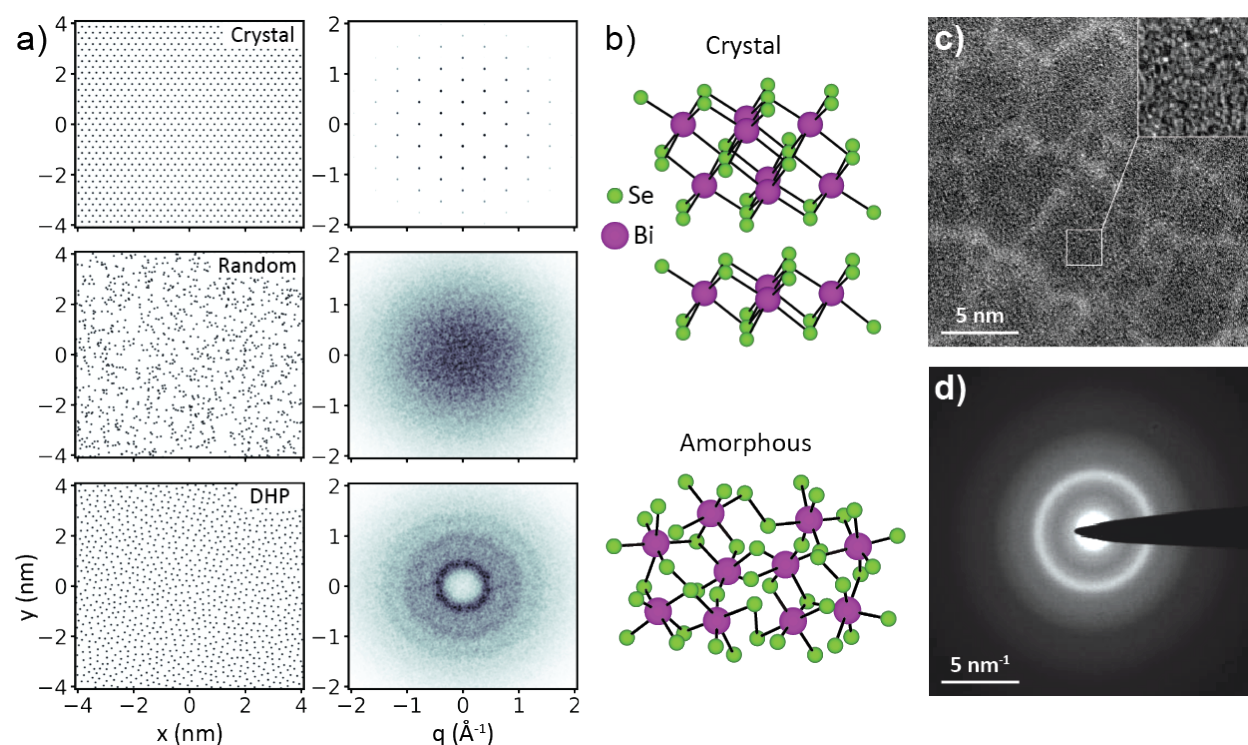


FIGURE 6.2: **Momentum-space structure from real-space length scales.** **a** Real-space (left) and FFT conversion to momentum-space (right) for three different point distributions. **b** Preservation of local ordering of crystalline  $\text{Bi}_2\text{Se}_3$  in amorphous structure. **c** High-resolution TEM of amorphous  $\text{Bi}_2\text{Se}_3$  showing no sign of nanocrystallites and DHP ordering. **d** Characteristic TEM diffraction rings of the amorphous film.

How is it possible that the highly randomized lattice of an amorphous system can demonstrate such strikingly coherent band structure? Let's quickly discuss the basics for the geom-

etry of momentum-space band structure. Fig. 6.2a presents real-space to momentum-space mappings for three different real-space structures. The momentum-space pictures are produced by taking the 2D Fourier transform of the real-space image. In the top images we have a triangular crystalline lattice which transforms into a triangular lattice in momentum-space rotated by 30 degrees. It is always true that a real-space crystal will map into a momentum-space crystal. Bloch's theorem which powers a majority of condensed matter theory is graphically captured in these two images. The wave-functions of electrons in a crystal are constrained by the symmetries of the underlying atomic lattice. This means that the momentum eigenvalues for electrons in the triangular lattice will be periodic and commensurate with the momentum-space lattice in the top right image. This also means that a single unit cell in the momentum-space geometry contains all of the information necessary to define the electronic structure. This single unit cell in momentum-space is called a Brillouin zone, and moving from one identical Brillouin zone to another is performed by translating by an integer multiple of reciprocal lattice vectors. These reciprocal lattice vectors, which define the Brillouin zone size, are inversely proportional to the real-space lattice vectors [64]. In this way, the momentum-space length scales are set by the real-space length scales.

What about an amorphous material? Let's say that we are a bit naive and predict that amorphous materials are comprised of absolutely randomized atomic sites (using normal random distributions in  $x$  and  $y$ ), as can be seen in the middle left image in panel a. In that case, the Fourier transform produces a featureless momentum-space picture, which makes sense since there is zero spatial correlation between any atomic sites. However, this is an un-physical model for a solid state system. The random distribution allows for atomic sites to nearly overlap and leaves large voids which serve as local minima for minimization in the free-energy landscape. Nature abhors voids.

An amorphous material is not a random system. It is defined as having a well-defined local environment and diminishing long-range order [206, 207, 208]. In practice this means that each atomic site looks very similar to every other atomic site, but small local deviations lead to incoherence at large length scales. Take the bottom two images in panel a as an example. Instead of a random distribution, here is what I will call a disordered hard-packed system (DHP), for lack of a consistent general term in the literature. - There is a specific term for amorphous ordering called hyperuniform distributions. It is mathematically specific to prove and for the most part unnecessary for the majority of our arguments, but worth noting to the reader for follow up investigations on the matter. - The DHP model presented in panel a is in fact hyperuniform, but the main importance is the preservation of a real-space length scale, which is not sufficient nor necessary for hyperuniformity.

This DHP lattice is created by incorporating atoms one at a time randomly towards the center (like step-flow island growth around a nucleation point) with a minimum bonding distance, and rotating the position of the atom around its first nearest neighbor until it makes bond length connection with a second nearest neighbor. The end result is a distribution of atomic sites which are mainly 6-fold coordinated with a well defined bond-length. This is the quintessential idea of amorphous materials. Amorphous semiconductors like silicon and germanium or classic glasses like  $\text{SiO}_2$  demonstrate these well-defined nearest neighbor

distances and uniform coordination environments [206, 208]. The FFT in the bottom right corner of panel a shows a structured momentum-space geometry with rotationally-symmetric repeated annuli. The ring radii are determined by the nearest neighbor real-space length scale similar to the Brillouin zone positions in the crystalline case. Since there is no long-range order, the momentum-space structure must be rotational symmetric and is defined simply by a reciprocal lattice scalar defining the distance between rings. So by establishing a well-defined nearest neighbor distance or real-space length scale we have enabled a momentum-space length scale and therefore momentum-space structure in a system with no long-range order. For the case of a solid state amorphous material, the electrons will again obey the annular symmetry in momentum-space, allowing for dispersive features that are commensurate with the ring spacing and rotationally symmetric.

Given this explanation that amorphous systems can have momentum-space structure, we will take a closer look at amorphous  $\text{Bi}_2\text{Se}_3$ . Panel b illustrates the atomic structure of crystalline (top) and amorphous (bottom)  $\text{Bi}_2\text{Se}_3$ . In the crystal, a unit cell is comprised of alternating selenium and bismuth sheets in a quintuple layer structure with each quintuple layer separated by a van der Waal's gap. Each bismuth atom is octahedrally coordinated with selenium atoms. Panel b shows the expected amorphous analog. The local environment is preserved so bismuth is again octahedrally coordinated with selenium but the small deviations in bond angle lead to loss of long-range crystalline order. Peculiarly, there is no easy way to incorporate a van der Waal's gap, an inherently 2D long-range structure, into an amorphous system. In fact, we have observed that stoichiometric amorphous  $\text{Bi}_2\text{Se}_3$  films no longer possess a van der Waal's gap, and instead compensate with increased selenium-selenium bonding [204]. Panel c shows an atomic resolution TEM image of the amorphous  $\text{Bi}_2\text{Se}_3$  films. The zoomed in inset displays the highly packed system lacking voided regions and overall the films possesses no hints of crystalline order. The TEM diffraction pattern reveals the reciprocal-space (or momentum-space) mapping of the atomic sites. Here, we can see the diffuse rings that characterize amorphous structures. The spacing of the rings exhibit higher complexity than the simplistic image in panel a and this is mainly due to the two atomic species present in the  $\text{Bi}_2\text{Se}_3$  unit cell.

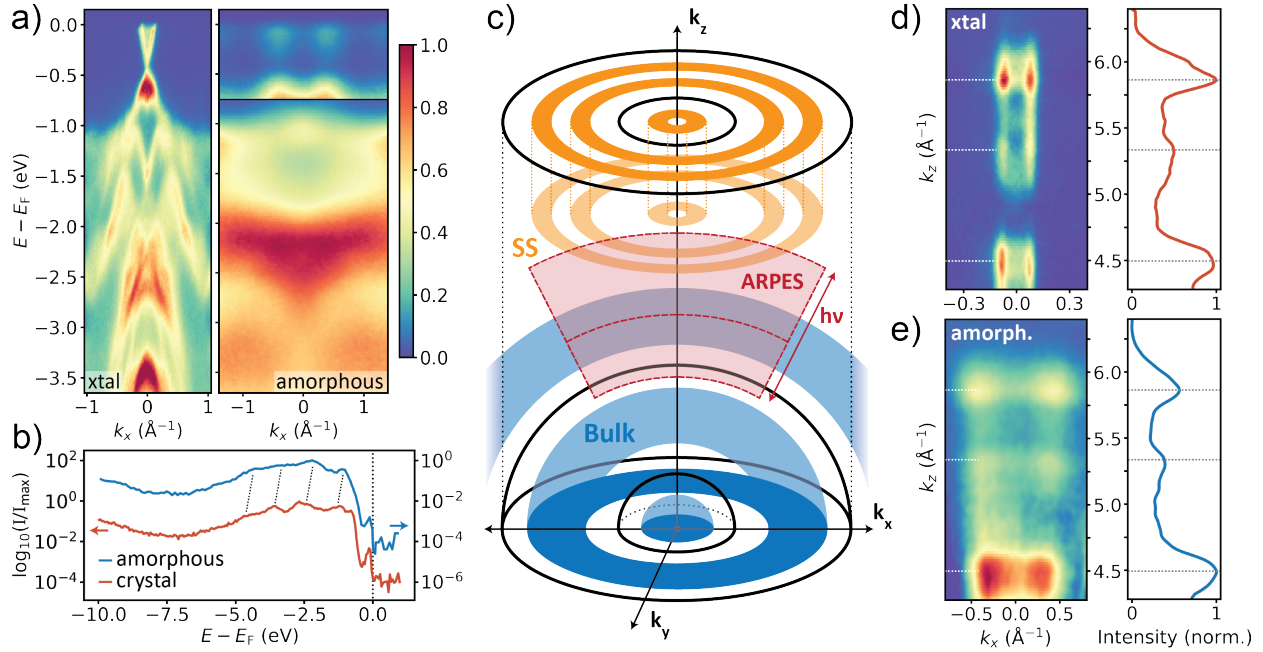
From the TEM data, we have shown that amorphous  $\text{Bi}_2\text{Se}_3$  has a well-defined length scale which translates into well-defined reciprocal space scalars. This is what makes it possible to establish momentum-space structure as we have shown in Fig. 6.1d.

## 6.2 Fermiology of an Amorphous Surface State

We can further explore the momentum-space structure of a- $\text{Bi}_2\text{Se}_3$  (amorphous) by comparison with c- $\text{Bi}_2\text{Se}_3$  (crystalline) and by determining the role of bulk and surface components in Fig. 6.3.

In panel a, we show deep binding-energy ARPES spectra at  $h\nu = 120$  eV for c- $\text{Bi}_2\text{Se}_3$  along the  $\Gamma - \text{K}$  direction and for a- $\text{Bi}_2\text{Se}_3$  radial from  $\Gamma$ . The intensity of the features near the Fermi level in a- $\text{Bi}_2\text{Se}_3$  has been enhanced by  $10\times$  for visibility. Noticeably, the Dirac

state in the crystal and the vertical features in the amorphous system have markedly different Fermi wave vectors ( $k_F$ ),  $0.08 \text{ \AA}^{-1}$  and  $0.4 \text{ \AA}^{-1}$ . Although variable doping can shift the Fermi level along the Dirac cone to linearly change  $k_F$ , a  $5\times$  enhancement points to a fundamentally altered dispersion in a-Bi<sub>2</sub>Se<sub>3</sub> versus c-Bi<sub>2</sub>Se<sub>3</sub> near  $E_F$ . Nevertheless, both near- $E_F$  dispersion demonstrate strong dispersive features characterized by a strong momentum dependence. Deeper in binding energy we see that the crystalline sample maintains strongly dispersive features, whereas the amorphous sample demonstrates flattened and broadened band structure. Notably, there is a broad nearly flat structure near  $-2 \text{ eV}$ .



**FIGURE 6.3: Bulk and surface state comparisons to crystalline Bi<sub>2</sub>Se<sub>3</sub>** **a** Deep binding energy ARPES spectra for c-Bi<sub>2</sub>Se<sub>3</sub> ( $\Gamma - K$ ) and a-Bi<sub>2</sub>Se<sub>3</sub>. **b** XPS on a-Bi<sub>2</sub>Se<sub>3</sub> (blue) and c-Bi<sub>2</sub>Se<sub>3</sub> (red) displays similar spectra for valence bands. Dashed lines indicate corresponding peaks, and the spectral hump of the upper energy portion of the surface state can be seen near  $E_F$  in both samples. **c** Diagram of amorphous band structure geometry. Bulk states form spherical shells around  $\vec{k} = (0, 0, 0)$  (blue), whereas surface states form cylindrical shells around the  $k_z$  axis (orange). For a single photon energy, ARPES probes a section of an approximately spherical shell (red). **d** Surface state spectrum at  $E_F$  as a function of  $k_z$  for c-Bi<sub>2</sub>Se<sub>3</sub>.  $k_x$ -integrated intensity shown to the left with 3 characteristic peaks marked. **e** Same analysis as panel d for a-Bi<sub>2</sub>Se<sub>3</sub> with characteristic peaks in the same  $k_z$  locations.

Even though the curvature of the deep binding energy band structure is reduced in the a-Bi<sub>2</sub>Se<sub>3</sub>, the angle integrated spectral response is intriguingly similar. In panel b we plot



the x-ray photoemission spectroscopy (XPS) spectra for c-Bi<sub>2</sub>Se<sub>3</sub>(red) and a-Bi<sub>2</sub>Se<sub>3</sub>(blue) on shifted y-axes for visibility. The overall intensity as a function of binding energy follows nearly identical dip then hump shapes with a dip near  $-8$  eV and a hump with substructure at  $-3$  eV. The crystalline sample exhibits 4 peaked features in the hump region that correspond to four peaks in the amorphous spectrum shifted by  $\sim 0.5$  eV. The similarity between the spectra indicates that the deep bind energy band structure of the amorphous sample appears as the momentum averaged band structure in the crystal.

The peculiar difference between the highly dispersive bands near the Fermi level and the weakly dispersive bands at high binding energy in a-Bi<sub>2</sub>Se<sub>3</sub> can be largely explained by the unique situation of studying a rotationally symmetric system with ARPES. If we look to panel c, it illustrates the 3D momentum-space structure of bulk bands and surface states given the symmetry of an amorphous system. The bulk bands (blue) are rotationally symmetric and allowed to vary along the radial direction contingent on a well defined reciprocal lattice scalar, thereby forming repeated spherical shells at constant energy within BLZs. Surface states (orange), spatially localized at the surface, are  $k_z$ -independent and form cylindrical shells oriented along the  $k_z$ -axis. ARPES is well suited for studying  $k_z$ -dependence in crystals with Cartesian BZs by varying the photon energy, since:

$$k_z \propto \frac{1}{\hbar} \sqrt{2 * m_e (\hbar\nu - E - \phi + V_0)} \quad (6.1)$$

where  $V_0$  is the fixed inner potential of the material [64]. However, in a spherically symmetric momentum-space ARPES faces an additional challenge to observe  $k_z$ -dependent bulk states. In ARPES,  $k_{x,y} \propto \sin \theta$  and  $k_z \propto \cos \theta$ , where  $\theta$  is the angle of photoemission, such that ARPES probes an approximately spherical cross-section in momentum-space for a given photon energy. The solid red arcs in panel c illustrate variable ARPES cross-sections given fixed photon energies. Moreover, typical inner potentials are of order 10 eV, limiting the minimum probable  $k_z$  to approximately  $2 \text{ \AA}^{-1}$  so that the  $(k_x, k_y)$ -concentric structure at  $k_z = 0$  is out of reach. All in all, this means that ARPES probes along invariant cross-sections of the bulk spherical shells. However, bulk dispersive features can still be revealed along the  $k_z$ -axis by varying the photon energy (shaded red region) but features in  $k_x$  and  $k_y$  will appear flat.

In contrast, surface states are  $k_z$  independent and the concentric structure can be accessed by ARPES at any photon energy (see red shaded region meets orange), revealing dispersive bands in  $k_x$  and  $k_y$  [209]. In panels d and e, we display the  $k_z$ -dependence of the c-Bi<sub>2</sub>Se<sub>3</sub> and a-Bi<sub>2</sub>Se<sub>3</sub> surface states near  $E_F$ , respectively. In the crystalline case,  $k_F$  remains fixed for all  $k_z$  at  $0.08 \text{ \AA}^{-1}$ , manifesting as narrow vertical pillars in  $k_z$  vs.  $k_y$  with variable intensity due to photon energy dependent matrix elements.

Curiously, the amorphous surface state bands expand outward with increasing  $k_z$  (panel e). This is a non-periodic dispersive feature that occurs over the full measured 2.5 inverse angstroms in  $k_z$ . The lack of periodicity over this range indicates that this momentum-space feature cannot be due to a coherent bulk structure since any such structure would be smaller than 2 Angstrom ( $\pi/2.25 \text{ \AA}^{-1}$ ). Moreover, it is definitive that this peculiarity does not affect



the conclusion that these are surface states since, even in the case of a polycrystalline system, bulk states would necessarily form rotationally symmetric shells centered at  $(k_x, k_y, k_z) = (0, 0, 0)$  and would appear nearly horizontal in panel e. Therefore these states must be of surface state origin since they are coherent across many  $k_z$  values.

Crucially, the momentum integrated intensity as a function of  $k_z$  (panels e and d, right plots) are nearly identical, with intensity peaks occurring at the same three  $k_z$  values (horizontal lines). This indicates that the photon energy dependent matrix elements are comparable in the two systems, advocating for similar orbital character stemming from similar surface electronic states.

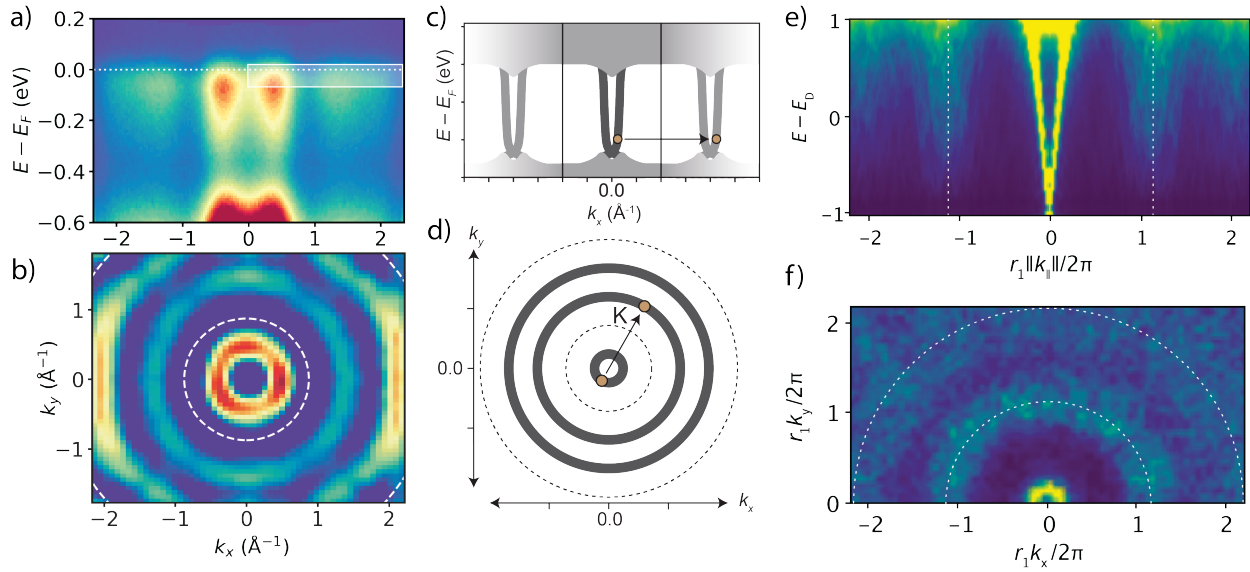


FIGURE 6.4: **Fermiology of the amorphous surface state.** **a** Expanded momentum range of ARPES spectrum uncovers duplicate dispersions approximately  $1.8 \text{ \AA}^{-1}$  from  $\Gamma$ . **b** The Fermi surface ( $\nabla^2 I$  of the raw intensity for visibility) demonstrates rotational symmetry of the primary and duplicated dispersion. **c,d** Illustration of amorphous dispersion and Brillouin zone-like repetition contingent on the reciprocal lattice scalar. **e** Resulting dispersion along  $k_{\parallel}$  through  $\Gamma$  showing duplicated structures. **f** Fermi surface from simulations showing repeated annuli.

As described in Fig. 6.2a and depicted in orange rings in Fig. 6.3c, the well-defined real-space length scale results in a well-defined reciprocal-space scalar which defines a Brillouin-like zone in amorphous momentum-space. The electronic Bloch-waves of a crystalline material produce a repeated band structure in ARPES, such that the same dispersion can be found by translating by a reciprocal lattice vector. An analogous situation occurs in the amorphous system.

Fig. 6.4a shows the amorphous  $\text{Bi}_2\text{Se}_3$  ARPES spectrum extended to further momentum than Fig. 6.1d. The spectrum reveals duplicated paired vertical features on either side of the near zero-momentum dispersion. Panel b shows the Fermi surface (or  $k_x$  vs.  $k_y$  at the Fermi level). If we take the lattice scalar associated with the second nearest neighbor distance (1 bismuth and 1 selenium make up a unit cell in the in-plane direction) determined from TEM diffraction (3.4 Å), this results in a reciprocal lattice scalar of ( $1.8 \text{ Å}^{-1}$ ). The white dotted rings in panel b represent the Brillouin-like zone (BLZ) edge formed by the  $1.8 \text{ Å}^{-1}$  reciprocal lattice scalar and clearly denote the inflection point for the repetitive annuli.

Note that in the first BLZ there exists only one ring, but in the second BLZ there are two. The BZ repetition occurs along the radial direction only, with the band structure duplicated by translating by the reciprocal lattice scalar (see panel c). Rotational symmetry then produces the same effect for all angles creating two annuli in the second BZ (see panel d).

Our theoretical collaborators at the Institut Neel have demonstrated that this BLZ phenomenon is a direct consequence of the nearest neighbor environment and can be reproduced using tight bonding calculations. They employed a Bernevig-Hughes-Zhang (BHZ) model using a 3D arrangement of amorphous sites from thermalized hard packed spheres that are then populated with 6-fold coordinated units. The hopping term of the Hamiltonian depends on the relative position of the two sites  $\mathbf{d}_{ij}$  according to:

$$\langle i|H|j\rangle = it_1(\hat{\mathbf{d}}_{ij} \cdot \boldsymbol{\sigma})\tau_x - t_2\sigma_0\tau_z \quad (6.2)$$

while the onsite energy of a single site reads

$$\langle i|H|i\rangle = M\sigma_0\tau_z \quad (6.3)$$

This model produces a non-trivial gap and a Dirac surface state. From panels e and f, we see that not only does it reproduce the repeated features far from zero momentum, but it further validates that non-crystalline systems can host non-trivial topology.

We have determined in Fig. 6.3 that the vertical features are associated with surface localized states. We have also demonstrated in Fig. 6.1f that the low temperature transport is characteristic of metallic behavior. We further explain in our previous work [204] using magneto-transport and a weak anti-localization calculation that the metallic regime is indicative of non-trivial Berry curvature. All of these observations point towards a non-trivial topology in amorphous  $\text{Bi}_2\text{Se}_3$ , strong evidence for the first solid-state amorphous topological insulator.

As a small note to follow on our discussion of the BLZ repetitions, we in fact see even higher order repetitions when we extend to extreme emission angles in ARPES. By tilting the sample dramatically during photoemission, we can reach well into 45 degree emission at the detector. Fig. 6.5 shows photon energy dependence of the ARPES spectrum from amorphous  $\text{Bi}_2\text{Se}_3$  at large tilt. The angular position of constant momentum as a function of photon energy is plotted in dashed white lines at momenta close to the observed features.

We can see the two features in the second BLZ in the left-center of the plot. On the top-right region of the plot we see two additional features that follow the constant momentum curves. The spectrum below shows a photon energy cut at 120 eV with integer multiples of the reciprocal lattice scalar plotted as vertical white dashed lines. The near-zero momentum BLZ feature is cut-off at the far left, and we see the second and third BLZs in the center and right region (respectively). This data shows the incredible coherence of the electronic states in amorphous  $\text{Bi}_2\text{Se}_3$  despite the lack of long-range order.

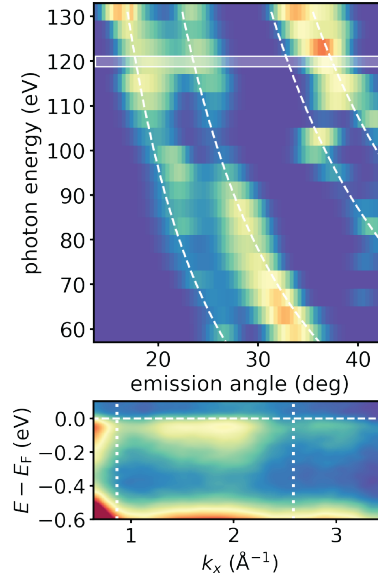


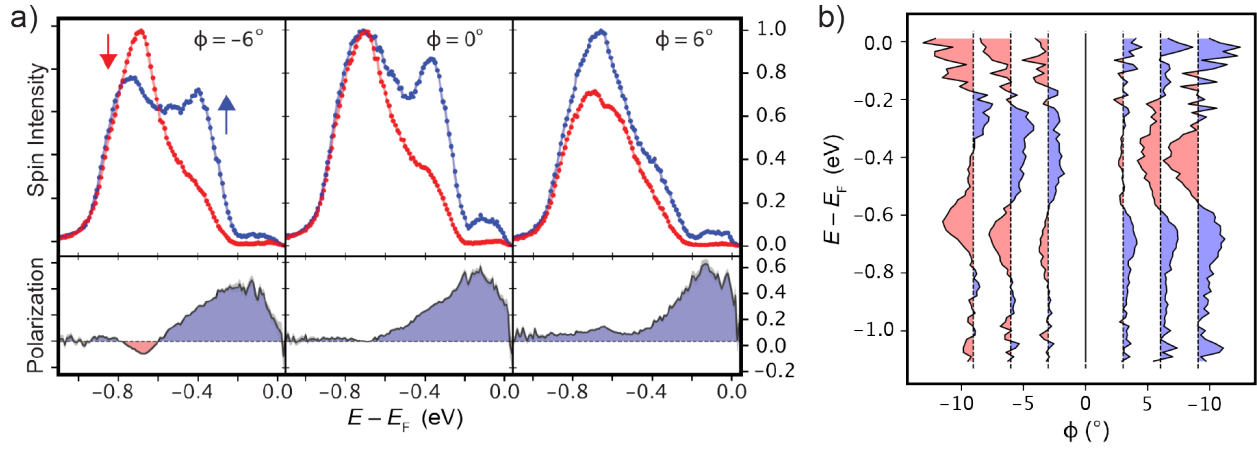
FIGURE 6.5: **Observation of third BLZ.** Photon energy dependence of the 2nd and 3rd BLZ dispersion, obeying  $k_z$ -independent photoemission (dashed white). Lower panel displays dispersion at  $h\nu = 120$  eV with repeated dispersions separated by  $1.8 \text{ \AA}^{-1}$ .

### 6.3 Spin-Momentum Locking of Dispersive Features

I have shown that amorphous  $\text{Bi}_2\text{Se}_3$  exhibits a strongly dispersive band structure manifesting in the surface state electrons. An exciting repercussion of amorphous dispersive band structure is that the momentum *is* well-defined. This means that momentum-dependent effects, typically reserved for discussion of crystalline systems can indeed take place in glassy systems. An acutely momentum-dependent effect is spin-momentum locking. Spin-momentum locking is when the spin of the electron is non-trivial defined by the momentum eigenvalue of the state. A good example of this is the Rashba effect, where spin-orbit coupling produces a linear-in-momentum energy splitting of separate spin branches in an otherwise spin-degenerate band [9]. The split bands are then spin-polarized with a spin-texture that

depends on the momentum direction of the electronic state. Topological insulators also host spin-momentum locked states by way of the Dirac surface state.

I have provided evidence that amorphous  $\text{Bi}_2\text{Se}_3$  may be a topological insulator with the surface state features being related to the Dirac surface state. Additionally, the high-Z bismuth contribution to the atomic structure of the amorphous film means that spin-orbit coupling will play an important role regardless of the topology, suggesting that the Rashba effect most likely emerge [210].



**FIGURE 6.6: Spin-polarized ARPES on amorphous surface state in  $\text{Bi}_2\text{Se}_3$ .** **a** Spin-polarized EDCs with spin-polarization shown below. Above  $E - E_F = -0.6$  eV, there is a large angle-independent 60% polarization due to SME. **b** Removal of the SME produces time-reversal symmetric spin-texture with multiple spin-flippings along the energy axis.

Using spin-resolved ARPES with our spinTOF system, we have measured the spin-polarized band structure of the amorphous films. Fig. 6.6a displays spin-resolved energy distribution curves at three different emission angles. The blue line indicates spin-up counts and the red line indicates spin-down counts, both following Sherman function correction [66, 36]. Spin-up and spin-down are defined by the orthogonal in-plane direction to the measured momentum axis. At  $\phi = -6$  degrees, we are looking at positive momentum electrons. A red peak occurs near  $-0.6$  eV and a blue peak at  $-0.3$  eV. The polarization is shown in the bottom graph and is determined by  $(I_{\text{up}} - I_{\text{down}})/I_{\text{tot}}$ . At  $\phi = -6$  degrees, we are looking at negative momentum electrons, and the red peak is now replaced by a blue peak at  $-0.6$  eV and the blue peak at  $-0.3$  eV is greatly diminished. We are clearly seeing a momentum dependent change in the spin-polarization. One notices from all three polarizations, including in the zero-momentum position of  $\phi = 0$ , that a large spin-up signal (nearly 60%) exists between  $-0.4$  eV up to the Fermi level. This is a result of spin-dependent matrix elements (SME) and has been observed in the crystalline case as well [36]. The signal from the SME is momentum independent and can be removed by subtracting the  $\phi = 0$  polarization as back-

ground from all other angles. The resulting spin-polarized map is shown in panel b. Here we observe a time-reversal symmetric spin-polarized band structure with three separate energy regions of spin-reversal.

The spin-texture is consistent with a spin-polarized topological surface state as we discussed in our previous work [204]. More importantly, it is the first observation of spin-momentum locking in an amorphous material.

## 6.4 Summary

In summary, we have revealed highly dispersive electronic states on the surface of an amorphous material, demonstrating a rotationally symmetric Fermi surface with repeated Bloch-like repetitions. This is made possible by the presence of a well-defined real-space length scale from the hyperuniformly distributed atoms in the amorphous structure which corresponds to a well-defined reciprocal length scale. The amorphous analog to crystalline  $\text{Bi}_2\text{Se}_3$  preserves the angle-integrated XPS spectral features yet exhibits remarkably different valence state behavior, manifesting as vertical-like features with large Fermi wave-vectors. The presence of highly dispersive features in a- $\text{Bi}_2\text{Se}_3$  and the generalization to other amorphous materials enables discussion on momentum-dependent physics in glassy systems including spin-momentum locking and momentum-based pairing in superconductivity. Moreover, it hints at the possibility of overlooked momentum-space structure in highly studied amorphous materials such as silicon and germanium, advocating for retrospective investigation of amorphous systems for dispersive features and heralding new investigations into the largest subsection of materials for quantum effects previously reserved for crystals alone.

## Chapter 7

# Electron Transparent Spin-Filters: Shifting from the Reflection Paradigm

### 7.1 Introduction

The first time I used the SPLEEM system at the National Center for Electron Microscopy at Lawrence Berkeley Laboratory, I was troubleshooting a spin-detection issue of the spinTOF instrument from our own lab. The mechanism for spin-detection in the spinTOF is via reflection exchange-scattering off of a magnetized thin epitaxial film of cobalt grown on tungsten, and its success as a world renowned spin-polarimetry method was a direct result of R&D performed by earlier Lanzara graduate students, Chris Jozwiak and Jeff Graf, about a decade earlier, with ample help from Andreas Schmid, the SPLEEM staff scientist [66]. My task was to check that the tungsten substrate and the method we used to grow the cobalt films in the spinTOF were producing the same results as a decade prior. The answer was yes, and we later discovered the problem to be related to the deposition rate in our system. Nevertheless, it set off a long relationship between me, the SPLEEM Lab, Cobalt exchange-scattering, and the ever-helpful Andreas Schmid. In this chapter, I will go over the progress made to realize a new form of spin-filtering for electron beams, prioritized for the future application of time-of-flight photoemission: A transition from a reflection geometry to transmission.

### 7.2 Challenges and Prospects of Transmission Spin-Filtering of Free Electrons

Spin-polarimeters based on exchange-scattering in the reflection geometry are highly efficient spin detectors with figure of merits for spin-detection orders of magnitude greater than the conventional Mott detector [66]. The first generation of exchange-based spin-polarized ARPES systems utilized time-of-flight spectroscopy to acquire energy resolution and small

circular photoemission entrance apertures which led to 0-dimensional momentum-space acquisitions. This meant that the sample would need to be rotated along two orthogonal axes to retrieve the full Fermi surface. In order to capture larger regions of  $k$ -space simultaneously, more sophisticated geometries for reflection exchange-scattering and Mott detection have since been implemented using hemispheres and complicated electron optics to capture the angle-dependent trajectories following the magnetic target reflection [211].

There is an obvious alternative for reducing the complexity of the electron optics while maintaining the momentum-space throughput of the system: using an exchange-based filter in transmission mode. In this situation a spin-filter can simply be placed at the focal point of an operating angle-resolved time-of-flight (ARTOF) system. The photoelectrons that are transmitted through the magnetic film are filtered according to the same exchange principle as in the reflection geometry and fall into two categories, primary electrons that are unaffected by the film and secondary electrons which have scattered within the film, altering their trajectory and reducing their kinetic energy [212, 69]. The primary electrons will retain the angular and spectroscopic profile of the spin-integrated ARPES spectrum, but will be spin-polarized based on the magnetization of the film, drastically reducing the complexity of the electron optics required in the reflection geometry.

Why hasn't this been developed already? Well, spin-polarized exchange-scattering is most efficient for low energy ( $< 10$  eV) electrons, and low energy electrons have elastic mean free paths on the order of 1 nm [213, 214, 215]. The challenge, then, is in producing large, nanometer thin magnetic films. This is no easy task, and has been attempted for decades with only marginal gains. [214, 215]. However, recent advances in thin film preparation offer us the opportunity to try again. For instance, the progress in graphene synthesis provides the perfect platform to produce large free standing membranes due to its extreme tensile strength [216], and thin-film dry-etch techniques are now common place in many laboratories. We took a multi-prong approach based on our previous experience growing thin cobalt films, our access to world class dry-etch experts at the Center for X-Ray Optics (CXRO), and our relationship with the SPLEEM Lab to develop three separate methods to produce thin free standing magnets. All three methods show great promise as a transmission spin-filter prototype. The third method I will present demonstrates the first working prototype of a transmission spin-filter with sufficient electron transmission for ARPES application.

### 7.3 Thin Film Cobalt Through Intercalation

After my stint troubleshooting the magnetic reflection target of the spinTOF at the SPLEEM Lab, our two labs realized that nanometer-resolved spin-polarized characterization of surfaces using the SPLEEM could compliment momentum-space resolved spin-polarization ARPES experiments, marrying the two worlds of real-space and  $k$ -space in magnetic and spin-orbit coupled studies.

For our first task in conjoining these worlds, I was joined by Samuel Brantly, a recently-graduated undergrad with an immense can-do attitude. We aimed to reproduce the studies

from Andreas Schmid and his colleagues in which highly-oriented atomically thin cobalt films can be grown on ruthenium or iridium crystals via intercalation through CVD grown graphene [217, 218, 219, 220, 221]. Our goal was to grow atomically-thin cobalt with Curie temperatures below liquid nitrogen temperatures such that we could probe the ultrafast demagnetization of the domains using time-resolved spin-resolved ARPES with the spin-TOF. However, it instead served as a starting point for developing ultrathin magnetic films for spin-polarized electron transmission.

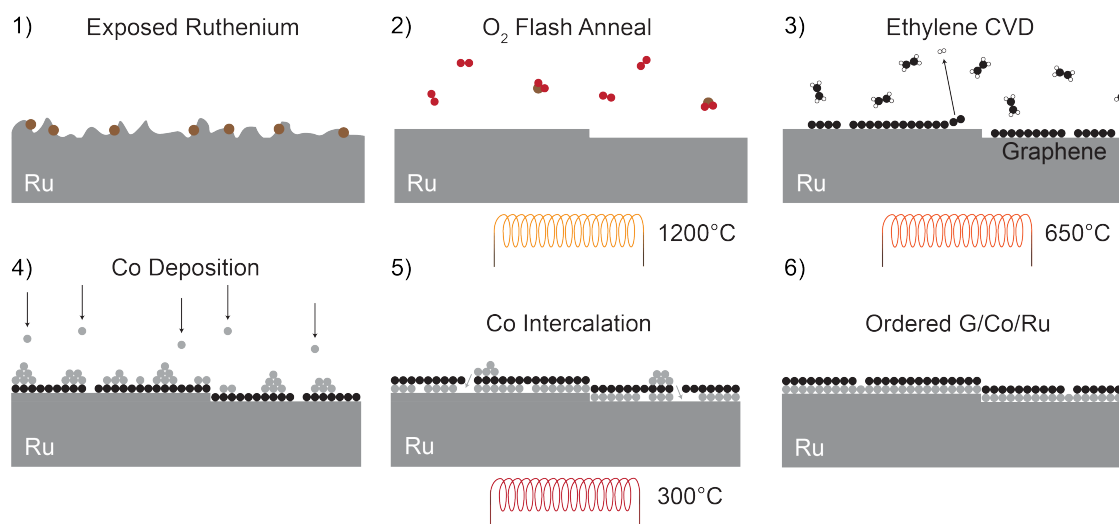


FIGURE 7.1: **Intercalation of cobalt through CVD graphene on ruthenium.** Sample is flash annealed in  $O_2$ , graphene is grown at 650 C using ethylene gas, MBE deposited cobalt is intercalated at 300 C.

Fig. 7.1 outlines the basic recipe for growing atomically thin cobalt films through intercalation demonstrated by Rougemaille and Coraux [217, 218]. Panel 1 shows the initial state of the ruthenium crystal in vacuum in which aging has left the surface pitted on the nanometer scale and atmospheric exposure has introduced chemical contaminants (brown). The crystal surface can be restructured and cleansed through a series of e-beam assisted flashing, panel 2, where the crystal is heated to 1000 Celcius for approximately 10 seconds in  $3 \times 10^{-8}$  Torr  $O_2$ . The oxygen removes the carbon contaminants through combustion like reactions. This is an essential step for even clean ruthenium surfaces since the flashing itself will drive carbon impurities trapped in the bulk to the surface (an alternative method to growing graphene on ruthenium crystals [222]). Following the Rougemaille/Coraux-recipe for chemical vapor deposition (CVD) graphene growth, we heat the cleaned ruthenium crystal to 600 Celcius and introduce ethylene (panel 3). The ethylene undergoes a catalytic reaction on the ruthenium surface, producing a self-terminating graphene monolayer. The key ingredient for successful cobalt intercalation is in this graphene step. The CVD growth is imperfect, forming large



continuous graphene sheets scattered with bond dislocations that form carbon rings greater than 6 atoms. It is believed that these imperfections aid in the mobility of metallic atoms in the otherwise impermeable graphene membrane during the intercalation process [223]. The final steps (panels 4-6) illustrated the molecular beam epitaxy (MBE) of cobalt on graphene, the subsequent intercalation above 300 Celcius, and the final highly ordered cobalt film sandwiched between the bulk ruthenium and graphene cap. Through this method, the cobalt can be grown to arbitrary thickness dependent on the number of cycles of steps 4 and 5.

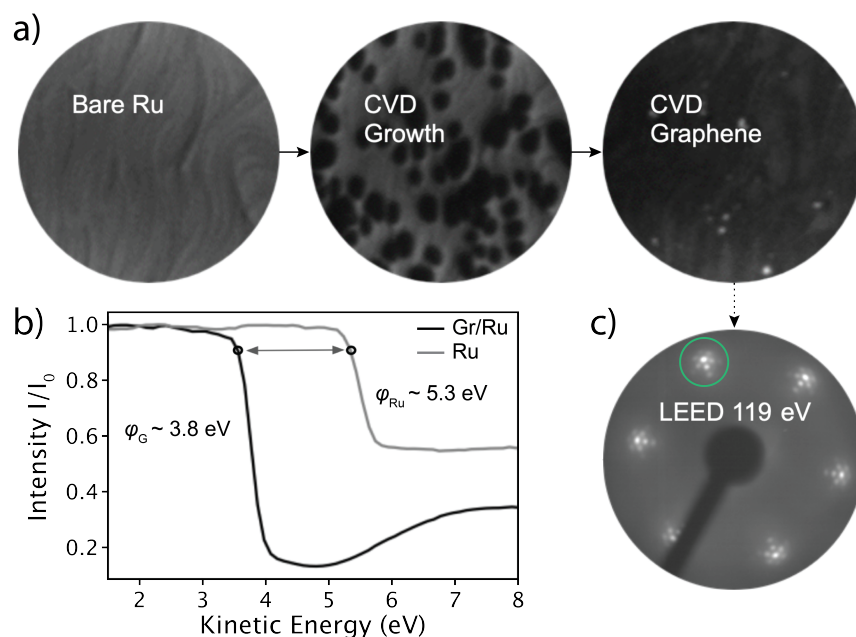


FIGURE 7.2: **Monitoring CVD graphene growth.** **a** LEEM progression of CVD graphene growth. **b** work-function variation between Ru and Gr/Ru. **c** Moire pattern of Gr/Ru from LEED.

The entirety of the process from flashing (panel 2) to CVD graphene growth (panel 3) to cobalt growth and intercalation (panel 4 and 5) can take place in situ to the LEEM measurement. Fig. 7.2 demonstrates the CVD growth through the eyes of the LEEM. The first image in panel a shows the bare ruthenium after flashing with the atomic steps visible as dark wiggly features. The next image shows the graphene growth in action, where disk-like growths form from nucleation centers eventually leading to a full dark film in the final image. By sweeping the kinetic energy of the incoming LEEM electrons we can spectroscopically distinguish between the graphene and ruthenium, shown in panel b. The work-function of the material manifest as a sharp edge. Electrons with kinetic energy below the work-function cannot penetrate the surface and are perfectly reflected in a regime called “mirror-mode”. Above the work-function the electrons are injected or reflected at a ratio dependent on

the band gaps and unoccupied states above the Fermi level and work-function [224, 225]. Therefore, the work-function edge and the shape of the spectrum above the work-function serve as a spectroscopic finger print of the material surface. We can see clearly that the ruthenium and graphene exhibit significantly different LEEM spectra, with the work-function dropping nearly 2 eV and the reflected intensity for high energy electrons reducing drastically upon graphene growth.

Finally the restructuring of the surface is apparent using low energy electron diffraction (LEED), panel c. The typical six diffraction peaks from the 110 ruthenium is preserved but there are an additional six minor diffraction peaks surrounding each major diffraction peak, representing the Moire lattice from the mismatched graphene structure sitting on top [224].

After intercalation, the graphene layer imparts additional properties to the cobalt film over epitaxial cobalt films on ruthenium without graphene. The graphene forms a highly protective layer such that the ruthenium-cobalt-graphene sandwich can be removed from vacuum into atmosphere without reacting with oxygen for long periods of time [218]. This means that the cobalt will not form cobalt-oxide and lose its magnetic character. The magnetic properties are also affected. The graphene coupling to the cobalt leads to increased perpendicular magnetic anisotropy (PMA), acquiring novel domain wall spin-textures and allowing for perpendicular magnetization at greater cobalt thicknesses [220].

## 7.4 Electron Transmission Through Graphene Membranes

The potential for growing thin cobalt films using the intercalation method described above sparked an enthusiasm for attempting to grow ultrathin magnets for spin-filtering applications. Our own lab is home to both a reflection-based spin polarimeter (spinTOF) and an ARTOF with real-space microscopy capabilities. Our hope was that we can manufacture a transmission-based spin-filter, test it in the tried-and-true spinTOF and ultimately use it to transform the ARTOF to an SR-ARTOF by simply placing the filter within the already established electron lens table.

However, to begin this R&D venture, it was crucial that we could measure electron transparency through membranes. This requires methods that can produce electron beams focused on membrane surfaces and count the electrons that make it through. Thankfully, Andreas had at his disposal a sample cartridge capable of producing an electron beam on the backside of the sample while preserving the sample holder footprint necessary for operating in the LEEM system. This enables us to perform LEEM and SPLEEM as usual on the front side of the sample then in situ transition to a backside electron illumination that takes advantage of the LEEM optics to capture a transmission image of the membrane. This device is called an eV Transmission Electron Microscope (eV-TEM) and was developed by Geelen and Jobst et al. and reproduced by Andreas with support from Daniel Geelen [70].

Using the eV-TEM sample cartridge architecture, we employ two separate methods for

measuring electron transmission through thin films in the LEEM system: Measuring electron transmission sourced from the LEEM beam using the eV-TEM as a picoammeter *and* using the eV-TEM as it was designed to measure backside sourced electrons at the LEEM detector. We test these methods on graphene films suspended over TEM grids and we are able to record the electron transmission as a function of electron kinetic energy (at times referred to as start voltage).

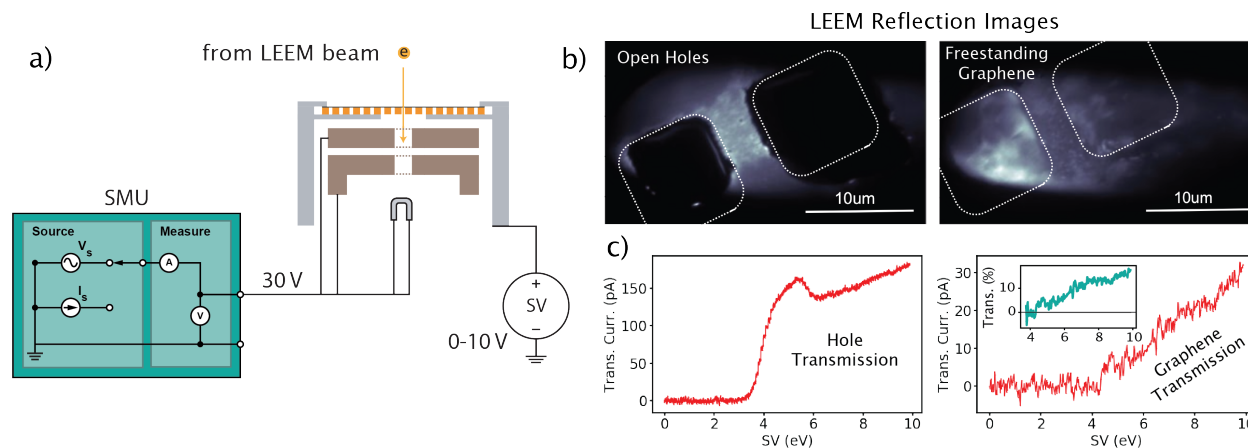


FIGURE 7.3: **Measuring electron transmission from LEEM source.** **a** Experimental setup using SMU to bias filament and read collected current. **b** LEEM images of through-holes (left) and graphene covered holes (right). **c** Transmission as a function of start voltage for above LEEM regions. Inset shows transmission coefficient.

Fig. 7.3 demonstrates the ability to measure electron transmission from electron sourced from the LEEM beam itself. Panel a shows the wiring diagram and eV-TEM cartoon. The electron lenses and filament of the eV-TEM are electrically isolated from the remainder of the cartridge. This allows us to apply a positive bias on the isolated regions behind the graphene membrane that act as an electron catcher's mitt. A source measure unit (SMU) is used to supply the static voltage of 30V. An SMU acts as a highly precise voltage supply and a picoammeter simultaneously. As electrons are transmitted through the graphene membrane and land in the 30V catcher's mitt, the SMU must wick away an equivalent number of electrons to maintain the 30V bias. This current is then read by a computer and serves as the measurement of electron transmission.

A benefit of this technique is that its operation relies on the LEEM beam and the LEEM image can be captured simultaneously during the SMU transmission measurement. The right image in panel b shows a TEM grid with  $10 \times 10 \mu\text{m}$  windows in which the graphene has been blown out as can be seen in the LEEM image. The left graph in panel c now shows the transmission current as function of electron kinetic energy through the open windows. The LEEM image allows us to discern the cross-section of beam that interacts with the voided

regions in order to calculate a relative flux accurately. From the transmission spectrum, we can see a work-function edge, a peak intensity following the work-function, and a slowly increasing plateaued region at higher energy.

The work-function corresponds to the work-function of the surrounding TEM grid region, which generates an effective force field around the holes for low energy electrons. The holes disrupt the normally smooth equi-potentials for uniform samples, resulting in peculiar lensing phenomena around the hole regions seen both in LEEM at energies near the work-function and manifesting as the peaked region in the left graph in panel c.

The right image on panel b presents the LEEM image for TEM grid windows covered by graphene. The footprint of the beam on the windows permits electron transmission through the free standing graphene. The transmission spectrum is shown in the right graph of panel c. It is clear that there is reduced transmission through the graphene membranes versus the open holes. Through examination of the respective beam cross-sections on the windowed regions, a ratio of the electron flux through the graphene versus electron flux through a void hole provides an accurate estimate of the electron transmission coefficient as a function of kinetic energy (see the teal inset in panel c). A transmission coefficient of greater than 20% is reached near 10 eV kinetic energy.

Our results for this particular sample are inconsistent with previous reports on graphene to a degree [213, 226, 227], in which transmission has been observed near 100% at electron kinetic energies near the work-function. This is most likely related to both the cleanliness of the graphene films as well as the geometry of the free standing region. We utilized commercially available graphene films, and we noticed that the transmission spectrum varied greatly between manufacturer and even sample to sample. Moreover, the transmission spectrum through an uncovered hole depends significantly on the shape of the hole, due to the effect of the hole geometry on electron lensing, particularly near the work-function. This means that our study and previous studies that rely on comparing transmission through open holes versus graphene holes would need to either take into account the effect of electron lensing through open holes or use the same hole geometries in order to compare results.

Ultimately, the major benefit of using the LEEM beam to source the electrons for transmission is that we can take advantage of the spin-polarized SPLEEM capabilities to run a spin-polarized electron transmission experiment. In this scenario, the transmission spectrum would be taken with a spin-polarized beam, then again with the spin rotated 180 degrees (perhaps performed multiple times in series). The difference of these two modes would then provide the spin-polarized transmission spectrum. The challenge is that any reasonable magnetic film would add at least 1 nm of material to the graphene thereby reducing the transmission substantially at eV energy scales. The signal to noise ratio of the SMU-based method is already quite low for the bare graphene case as can be seen in the right graph of panel c, and a differenced image with 1 nm extra material would exacerbate this issue. Ideally, a spin-resolved transmission measurement would utilize a single-electron counter such as a multichannel plate (MCP) detector to achieve a high signal to noise ratio.

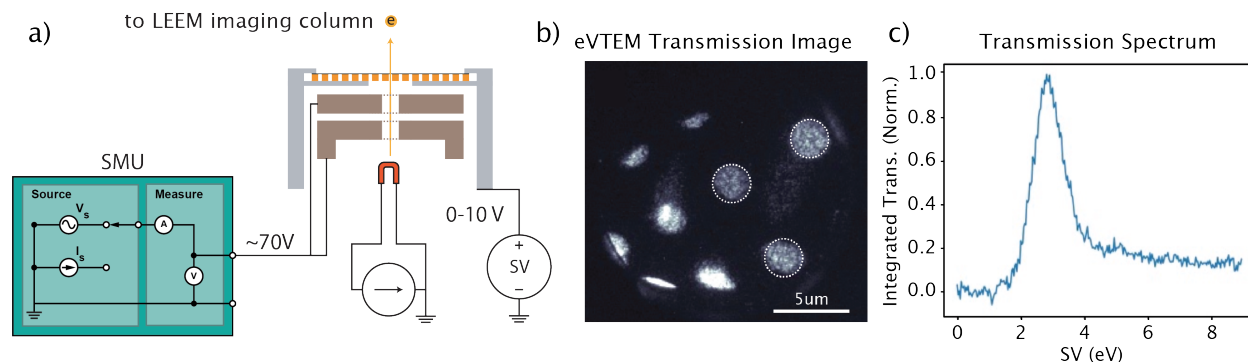


FIGURE 7.4: **Measuring electron transmission with eV-TEM.** **a** Experimental set up using SMU to control eV-TEM lenses and filament current supply to run beam. **b** eV-TEM image on LEEM detector showing 2.5  $\mu\text{m}$  holes covered in graphene. **c** Transmission measured from dashed circles in panel b.

The second method utilizes an MCP but is incapable of spin-resolution. So it serves to provide a much higher signal to noise ratio for electron transmission but is blind to the spin-degree of freedom. This method is the eV-TEM.

The eV-TEM is an ingenious device developed by Daniel Geelen which transforms a typical LEEM sample cartridge into a mini transmission electron microscope [70]. Fig. 7.4a shows the basic operating principle for the eV-TEM assembly at the NCEM SPLEEM Lab. The eV-TEM consists of a small filament that sits in the cartridge behind the sample that sources the electrons for transmission. They are focused onto the backside of the sample through two lenses (brown regions). In our case the lenses were tied together and biased to 70V using the SMU supply. The electrons are then transmitted through the sample and enter the imaging column of the LEEM system. A contrast aperture filters out electrons that are not near-normal to the imaging plane and an image is produced at the MCP detector, in the same fashion as a reflection LEEM experiment.

Panel b shows the eV-TEM transmission image captured at the LEEM MCP for graphene suspended over 2.5  $\mu\text{m}$  circular holes. Since the portion of the cartridge that is holding the sample is isolated from the lenses and filament, the voltage on the sample can be controlled independently which determines the landing energy of the electrons from the filament. In this way, the transmission intensity as a function of electron kinetic energy can be obtained similar to the example in Fig. 7.3 (see panel c).

## 7.5 Producing Free Standing Magnets

Now that we have the tools to be able to measure low-energy electron transmission through thin films, we need a method of producing free-standing magnets thin enough to allow

substantial electron transmission in order to act as an effective spin-filter. For this purpose, we have developed three main thrusts for producing ultrathin free-standing magnets.

The primary challenge is that thin-films ( $< 5$  nm) are typically grown in LEEM systems epitaxially on crystalline substrates. Epitaxial growth is highly dependent on an assortment of external parameters such as lattice matching with the substrate, wetting constraints, growth rate and temperature. However, in order to produce free-standing films, we either need a thin membrane substrate to support the film growth or the capability to etch away the substrate following growth. This constraint greatly restricts the types of available substrates for producing free-standing films. For instance, we utilize three substrates in the following growth examples using silicon nitride (SiN), silicon dioxide (SiO<sub>2</sub>), and graphene; great candidates for free-standing membranes and post-growth etching, but temperamental substrates for producing epitaxial metal growth.

Finally, to preserve the magnetization of the magnetic film for long periods of time (a necessary condition for an operable spin-filter), we must be able to cap the reactive metal film with inert layers. The simplest method would be to deposit a noble metal such as gold, platinum, or iridium. However, uniform coverage of the dense metals requires multiple monolayers of growth, greatly reducing the electron transmission potential. Ideally, graphene would be used as a cap, as it is very electron transparent at low electron kinetic energies, monolayer thin, and impenetrable to atmospheric gases [218]. The methods we have selected below use permutations of both graphene and iridium caps on the top and bottom surface in an effort to determine the ideal scenario between ease of production and efficient spin transmission.

In this section, we will go through the three primary methods in which we are developing (and in one case, have developed) ultrathin free-standing magnets. All of these methods show promise, and have utility to a range of applications including low dimensional data-storage and magnetic heterojunction devices outside of our main goal of developing a transmission-based free-electron spin-filter.

Our first, and perhaps most ambitious method, of producing thin free-standing magnets was based on our previous experience reproducing the results of cobalt intercalation through CVD graphene grown on ruthenium and iridium bulk crystals. Fig. 7.5a presents the basic recipe for growing the device in a manner Andreas has dubbed “The Upside Down Cake Method”. The general concept is to remove the bulk iridium substrate from the previous method and replace it with an ultrathin layer on the backside of graphene to achieve the same intercalation process.

At the start, a commercially purchased graphene film suspended over  $2.5\text{ }\mu\text{m}$  SiN holes is cleaned at  $200\text{ }^{\circ}\text{C}$  for 30 minutes. The graphene covered holes are clearly seen in the LEEM image in the top left corner, exhibiting higher reflectivity above the graphene-on-SiN work-function mainly due to electron lensing from the uneven equi-potential in the holes. The next step is to deposit 10 monolayers of iridium on the back side of the TEM grid (blue outlined panel 1) by loading the sample upside down. After deposition, only the graphene in the holed regions are in contact with the iridium layer. The respective LEEM image shows the graphene covered front side of the grid, now exhibiting reduced reflection in the holed regions

due to a lowering of the work-function for the graphene exposed to iridium on the back side. The sample is then removed from vacuum and reloaded into the chamber right-side-up, a safe procedure since both graphene and iridium are fairly inert towards atmospheric gases. As in the case for cobalt intercalation through graphene on bulk iridium, cobalt is deposited on the top graphene covered side in the orange outlined step 2. The corresponding LEEM image shows uniform coverage of the graphene, as evident by the uniform reflectivity between holed and hole-less regions. However, panel b shows the LEEM reflectivity as a function of start voltage, and the work-function drop for step 2 has become extremely broad. The broadening is most-likely a symptom of sub-resolution regions of varying work-functions, an indication of 3D island growth on the surface leaving regions of exposed graphene [228]. Finally, we perform an intercalation step by heating the sample to 300 C as can be seen in the green outlined step 3. The holed regions again take on decreased LEEM reflectivity with respect to the surrounding regions, but to a lesser degree than step 1.

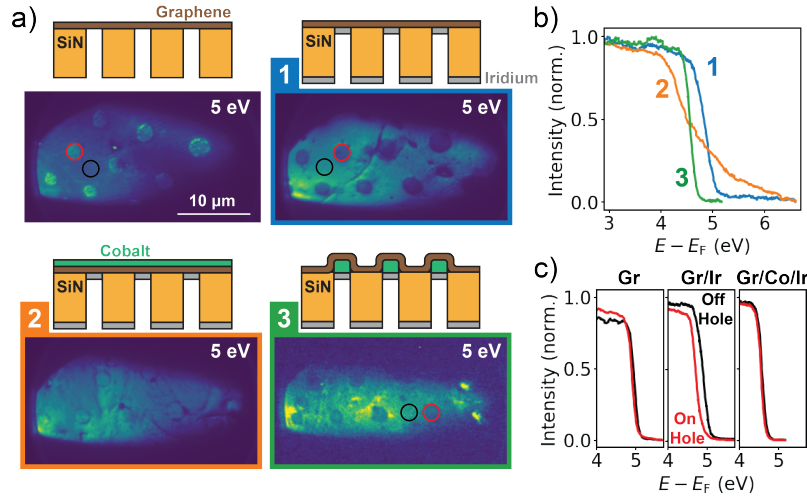


FIGURE 7.5: “The Upside Down Cake Method”. **a** LEEM images of clean graphene, graphene with iridium on the back side (1), cobalt on graphene with iridium backside (2), and after cobalt intercalation (3). **b** work-functions for steps (1-3). Broad work-function in (2) is most likely due to 3D growth. **c** On-hole and off-hole work-functions for bare graphene and steps (1) and (3).

More importantly, panel c shows the evolution of the surface work-function throughout the major steps, comparing both on-hole (red) and off-hole regions (black). After surface treatment of the graphene (prior to step 1, left panel c), the work-function of the two regions are identical at approximately 4.9 eV. Following back-side iridium deposition (step 1, middle panel c), the work-function off-hole and on-hole has split, with off-hole retaining the 4.9 eV work-function, but on-hole reducing by  $\sim 100$  meV. Cobalt growth (step 2) establishes a minimum work-function of  $\sim 4.2$  eV which is subsequently shifted upward to 4.6 eV



following intercalation (see orange curve to green curve in panel b). In right panel c, we see that the on-hole and off-hole work-functions are nearly identical at that value of 4.6 eV, substantially lower than the 4.9 eV from the bare graphene and the 4.2 eV of the cobalt islands. If the cobalt had simply aggregated into larger islands leaving more graphene exposed, we would expect to see the original graphene work-function of 4.9 eV after the heating step. Instead, the unique work-function with a sharp edge indicates that the cobalt is not exposed at the surface and is interacting with the graphene layer, strong evidence for cobalt intercalation at the thin film limit.

Further studies are required, and have been planned, in order to confirm that the intercalation process is indeed occurring. X-ray Photoemission Spectroscopy (XPS) can determine the core level spectroscopic signatures of the elements at the surface and would be able to detect intercalation into the graphene. Furthermore, we need to understand whether cobalt can be intercalated layer-by-layer, as is the case for the bulk substrate method, to produce thicker intercalated cobalt films capable of demonstrating magnetic contrast. Future SPLEEM experiments will focus on reproducing this thin-film intercalation with sequential cobalt depositions and intercalation steps in order to produce a film that exhibits strong magnetic contrast.

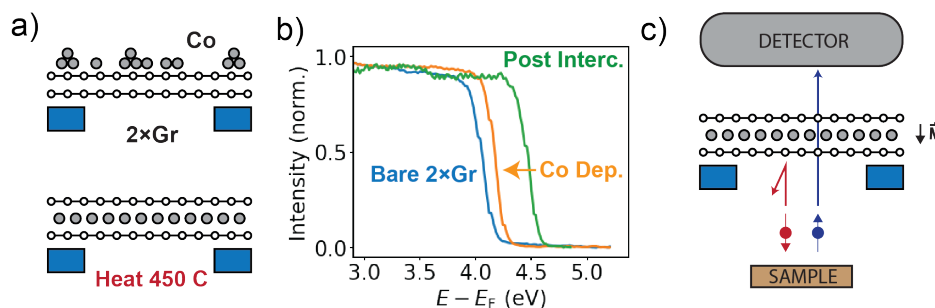


FIGURE 7.6: **Cobalt intercalation of bilayer graphene.** **a** Schematic for growth then heating to achieve intercalation. **b** Work function variation on bare bilayer graphene (blue), after cobalt deposition (orange), and after cobalt intercalation (green). **c** Spin-filter implementation.

In terms of electron transmission, the first approach detailed above is limited by the 10 monolayer iridium base cap, which would provide no magnetic spin-filtering effect and would greatly reduce the proportion of transmitted low-energy electrons. The graphene top cap on the other hand is ideal, since it is the thinnest possible material that is impermeable to ambient contaminants. A natural question would be whether both capping layers could be made from graphene, providing robust protection from the elements (pun intended) while retaining high low-energy electron transmissivity. Perhaps, we could even use the same intercalation process described prior but replace the bottom iridium substrate with another layer of graphene.



There is precedent for this process to work. Graphite (bulk graphene) with intercalated species is common in the literature, but is most often produced through edge transport in liquid solution processes [229]. However, multiple studies have reported that metals and alkali elements can be absorbed or intercalated from the surface into bulk graphite [230, 231]. Yet, to our knowledge, surface intercalation of metals into *bilayer* graphene has never been explored. Our next method attempts to do exactly that.

In Fig. 7.6a we show a diagram of the simple two step process of intercalating cobalt into bilayer graphene, thus producing a thin cobalt film surrounded on either side by the ideal graphene covers (see panel c). 1-2 monolayers of cobalt is deposited on commercially purchased bilayer graphene suspended over  $2.5\ \mu\text{m}$  holes using an e-beam evaporative cell. Then, the sample is heated to 450 C, the temperature at which the LEEM spectrum experiences notable changes. Panel b shows the evolution of the work-function from start to finish. The blue curve indicates the work-function at about 4.1 eV of bare bilayer graphene. Following cobalt deposition (orange curve) the work-function shifts upward to 4.2 eV. Finally, the intercalation step demonstrates a large upward shift of the work-function towards 4.5 eV. Note that this work-function value is very similar to the intercalated graphene work-function in Fig. 7.5a step 3. A reasonable explanation is that the top graphene layer in the initial phase before cobalt deposition experiences a reduced work-function due to its interaction with the lower graphene layer. Following cobalt deposition and intercalation, the cobalt decouples the top graphene layer from the lower layer and instead we measure the work-function of the graphene layer coupled to the newly formed cobalt layer. The three unique sharp work-functions over the course of each stage of the sample growth provides strong evidence for three separate layer-to-layer interactions.

Our final method for producing ultra-thin free-standing magnetic films was our most straight-forward method and primary thrust in the project. The simplicity of the procedure led to the first proof-of-principle for a transmission based spin-filter determined by the successful growth of a thin magnetic film that is substantially electron transparent.

Fig. 7.7a shows the process for growing an iridium-cobalt-iridium sandwich on a 5 nm SiN membrane. The iridium layers protect the cobalt such that the assembly can be moved into vacuum and the SiN layer can be etch away. The etch procedure is selective, using  $\text{CHF}_3$  and  $\text{O}_2$  which rapidly etches SiN stopping at the iridium layer after only 10 seconds of exposure.

Panel b shows two examples of sandwiched films with total thicknesses of 5 nm and 10 nm and  $100 \times 100\ \mu\text{m}$  windows. Most of the membranes are left standing in the 5 nm thick sample and all windows survive the 10 nm thick sample, indicating a sweet spot for minimal etch thickness between 5 and 10 nm. The magnetism of the films can be monitored in situ during growth of the cobalt layer using SPLEEM. Panel c demonstrates that no in-plane magnetic contrast is observable below 5.5 monolayers of cobalt, and clear magnetic domain occur above 5.5 monolayers.

Using the 5 nm thick films, we perform eV-TEM through a film covered window (panel d). The corner of the square window is observable due to the transmission of low energy electrons through the membrane when the electron energy is above the work-function. Panel

e shows the results of a peak finding routine on the data in panel d, displaying the electron counts more clearly. Electron counts exist outside of the free-standing membrane region that are above the dark counts of the detector and could indicate possible secondary (or scattered) electrons that are inelastically transmitted through the film.

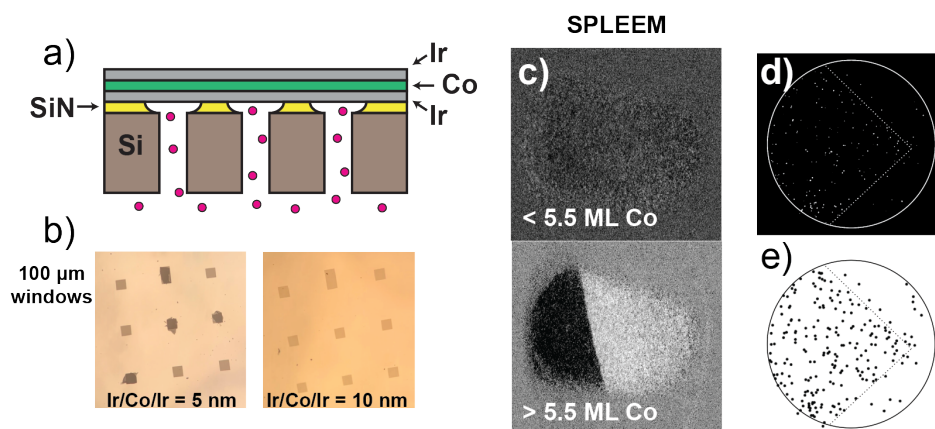


FIGURE 7.7: **Dry-etched sandwiched growth of thin magnetic membranes.** **a** Illustration of dry-etching of SiN, exposing Ir/Co/Ir film. **b** Survival of dry-etch process for 5 nm and 10 nm thick films. **c** In-plane SPLEEM images showing clear magnetic domains above 5.5 monolayers. **d** eV-TEM transmission through 5 nm thick magnetic films. **e** peak locations of electron counts in panel d.

The final stage of determining whether or not these films can be successful spin-filters is to measure the spin-polarized transmission current. This can be performed in two ways. 1) Use a spin-polarized electron source and measure the differential transmitted current between up- and down-spin beams polarized along the magnetization direction of a single-domain magnetized film. 2) Shine unpolarized electrons through a single-domain magnetized film and measure the spin-polarization of the resulting beam using an exchange-scattering spin polarimeter. We plan on performing both of these measurements by 1) using the method described in Fig. 7.3 with the spin-polarized SPLEEM beam and 2) by using an electron source behind the sample in the spinTOF and leveraging the spin resolution of that system. This final check is necessary, however conservation of current suggest that a magnetic film that is electron transparent with good spin-contrast in the reflection geometry must also produce a spin-polarized.

## 7.6 Peculiar Off-Normal SPLEEM Spin Contrast

I want to end this section on a peculiar effect we have observed in our time working with non-epitaxial growth of cobalt films and explained in Fig. 7.8. Typical SPLEEM measurements

are careful to produce highly ordered epitaxial films [69]. Among many reasons for this concern is that non-epitaxial films present many scattering points which greatly reduce the specular-reflected electron intensity and therefore the quality of the resulting LEEM image. Importantly, many LEEM systems (including the one we have used throughout these studies) have fixed contrast apertures with narrow acceptance angles. The contrast aperture acts to accept only normally reflected electrons in the imaging column (top of panel c shows the ideal imaging condition). This means that normally incident electrons that are scattered are not imaged, further reducing the intensity of the collected reflected electrons in the case of heavy scattering.

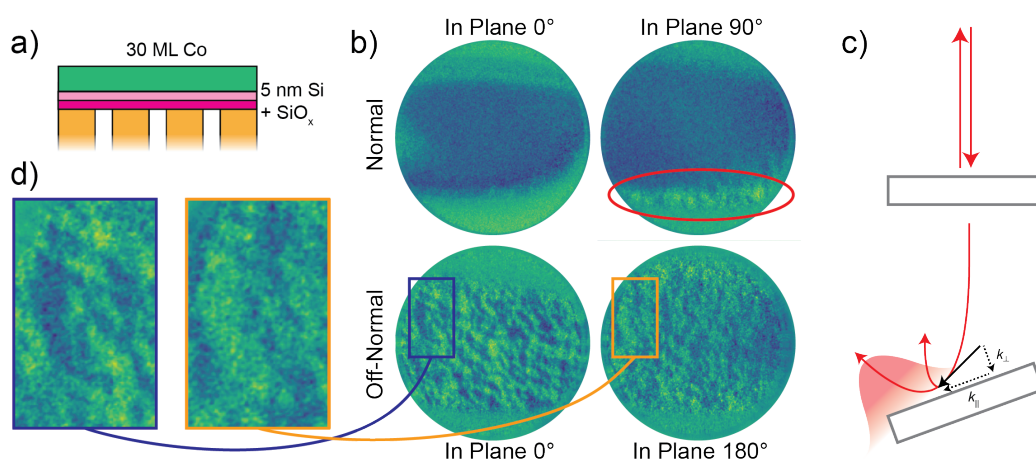


FIGURE 7.8: **Magnetic contrast with off-normal LEEM imaging.** **a** Cobalt magnetic film grown on 5 nm silicon membrane with native oxide. **b** SPLEEM images both in normal reflection and with the sample tilted (rows) at different in-plane spin-orientations. **c** Schematic of normal reflection versus tilted LEEM mode. **d** Zoom-in on off-normal tilted SPLEEM regions showing flipping of domain contrast between 0 and 180 degrees spin-orientation.

We have observed throughout our studies on non-epitaxial cobalt growth a drastic reduction of not only the LEEM intensity but also the SPLEEM spin-contrast. Though the statistics or signal to noise of the spin-contrast depends on the LEEM intensity, the value of the spin-contrast should be unaffected. To elucidate further, panel a shows an example of a 30 monolayer cobalt film grown on 5 nm Si with a native  $\text{SiO}_2$  surface. It is suspected from the reduced LEEM intensity with respect to epitaxial cobalt on tungsten that the cobalt cannot be epitaxial in the system, even more reasonable since the oxide surface is amorphous. From the top SPLEEM images in panel b, we see that there is no clear magnetic contrast in either of the orthogonal in-plane directions when the LEEM is operating in the standard manner with the incident beam normal to the surface.

However the right top image in panel b shows some degree of magnetic contrast at the edge of the beam. At the edge of the electron beam, the normal condition is not fully preserved, meaning electrons are incident on the sample surface with an in-plane component of momentum. This sparked an interesting idea. What if we tilted the sample, such that the main central portion of the beam inherits an in-plane momentum (off-normal incident to the sample)?

This scenario is shown in the bottom cartoon of panel c. By tilting the sample, the deceleration of the beam at the sample surface produces a parabolic trajectory. This means that even a small tilt condition leads to a very large in-plane component of momentum to the incident electrons [224, 225]. The specular-reflected beam cannot be measured by the LEEM imaging column due to the contrast aperture, but finite scattering leads to a broad range of trajectories for the reflected electrons, and a small tail end of reflected electrons will return normal to detection plane. We have measured the magnetic contrast of the non-epitaxial film in this geometry in the bottom two images of panel b. A clear magnetic domain pattern emerges. If we zoom in to identical regions of real-space for flipped spin-polarization of the incident beam (panel d), we see a total reversal of the domain contrast with domain structures preserved, a clear indication of real magnetic structure.

These results are still preliminary, but not without reasonable explanations. The magnetic contrast from SPLEEM is a result of accessing the spin-polarized unoccupied band structure of the magnetic material. A normal incident LEEM electron with kinetic energy above the work-function is injected into a material if an unoccupied state with zero momentum exists at an energy above the Fermi level that corresponds to the electrons kinetic energy. It is reflected when an available state does not exist. This could be due to a band gap at the respective energy or (in the case of spin-polarized band structure and a spin-polarized beam) the electron has the wrong spin character. In the case of a ferromagnetic domain with majority up-spin, the unoccupied states above the Fermi level are largely spin-down polarized, meaning spin-up electrons will be reflected at a higher rate. This description is easily extended to momentum-dependent band structures. Conservation of energy and momentum of the incoming electron means that the in-plane momentum of the electron will map to an in-plane crystalline momentum, and the availability of states in both energy and momentum must be considered for off-normal incident beams. Jobst et al. have demonstrated how tilted LEEM beams can map the electronic dispersions of unoccupied states in graphene using the above principle [224, 225].

Magnetic systems can exhibit momentum-dependent spin-polarized density of states [232]. An acceptable explanation then emerges for our off-normal spin-contrast: The randomized orientations of our non-epitaxial polycrystalline cobalt film could be producing a near zero spin-polarized density of states for electrons with zero in-plane crystalline momentum. Because the films are indeed magnetic, this means the majority and minority spin populations are separated in regions of the band structure away from zero momentum. By tilting the beam, we are able to access the spin-polarized portions of the band structure by introducing an in-plane momentum into the incident electron beam.

Again, these results and theoretical description are preliminary, but it offers an elegant

solution to producing a transmission based spin-filter. By considering that off-normal electrons access non-zero momentum band structure, we can start to consider using non-magnetic materials as spin-filter alternatives, instead using spin-orbit coupled materials. For example, non-magnetic bismuth is a strongly spin-orbit coupled material that exhibits spin-momentum locking with time-reversal symmetry [210]. This means that the zero-momentum density of states is spin-unpolarized, but for non-zero in-plane momentum the density of states *is* spin-polarized with an equal and opposite polarization when the momentum is reversed. Therefore, a spin-polarized beam that intercepts bismuth off-normal is expected to undergo polarized exchange-scattering, given that spin-momentum locking is occurring at accessible energies above the work-function. So by rotating the sample with respect to the incident beam, one could control the sign and magnitude of the spin-filtering effect.

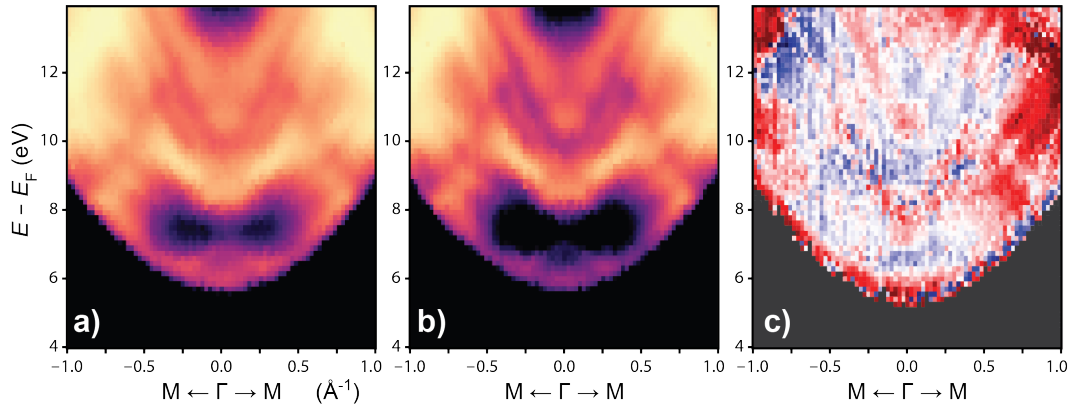


FIGURE 7.9: **Preliminary ARRES on  $\text{Bi}_2\text{Se}_3$ .** **a,b** Light regions correspond to low reflection (unoccupied bands) and dark regions are high reflection (band gaps). **c** Red and blue indicate opposite spin-polarizations. Analysis performed by Jacob Gobbo.

We have begun initial studies for angle-dependent SPLEEM on spin-orbit materials at Andreas' lab using a brand new SPLEEM system with a removable contrast aperture. The removal of the contrast aperture allows us to observe not only the specular reflection, but a large range of reflected angles (a LEED image), enabling off-normal SPLEEM imaging. Jacob Gobbo, Cameron Johnson, and I have begun to expand on the studies of Jobst et al. and report on the observation of *spin-polarized* unoccupied band structure in  $\text{Bi}_2\text{Se}_3$ , to be published by the end of summer 2022. Figure. 7.9 gives a snapshot of the preliminary data. Panels a and b show spin-resolved (low energy) angle-resolved reflected-electron spectroscopy (SR-ARRES) for two opposing in-plane spin orientations of the SPLEEM source beam. The differenced image (panel c) shows clear anti-symmetric spin-texture consistent with time-reversal symmetric spin-orbit coupled materials. The band structure is  $\sim 10$  eV above the Fermi level, never-before-seen in  $\text{Bi}_2\text{Se}_3$ , and high-energy spin-resolved band structure calculations are needed to perform a full analysis.

## Chapter 8

# Concluding Remarks

This dissertation presented novel mechanisms to control the spin-degree of freedom in a mission to develop applicable methods for spintronic devices. I have demonstrated that quantum well states on the surface of bulk-insulating topological insulators expose an ideal platform for engineering band structures with infrared pulses. The result is an ultrafast modification of the quantum well spectrum in energy, a reversible reduction in the spin-orbit coupling at the surface, and a significant effect on the density of states at the Fermi surface due to a transient Lifshitz transition. The Lifshitz transition has subsequent consequences including relaxation dynamics and the enhancement of the electron-phonon coupling of the topological surface state. Next, I revealed a highly dispersive band structure in amorphous  $\text{Bi}_2\text{Se}_3$  that exhibits spin-momentum locking, unveiling momentum-dependent electronic structure in a system with broken translational symmetry. This discovery unlocks a huge portion of material phase space for realizing novel momentum-dependent quantum effects typically reserved for crystals. Moreover, it presents a means for mass producing spin-orbit coupled materials in spintronic applications through simple thermal evaporation. I concluded the thesis by presenting our results on designing, fabricating, and testing transmission-based free-electron spin-filters. I described multiple methods for creating free-standing magnetic membranes and showcased a working prototype for transmission spin-filtering using simple growth and lithography procedures. A method for using spin-orbit materials in place of magnetic materials was discussed, and our preliminary ARRES data on  $\text{Bi}_2\text{Se}_3$  validates the proposal, offering a fundamentally new take on spin-filter design. These discoveries and techniques can be quickly applied to spintronic device design. For instance, the ultrafast Rashba reduction in  $\text{Bi}_2\text{Se}_3$  with quantum well surface states will theoretically act as a photo-gated spin modulator. Moreover, one can imagine using the amorphous  $\text{Bi}_2\text{Se}_3$  as a spin-momentum locked material for angle dependent spin-filtering as described in chapter 8. I hope that the findings from my studies and presented in this thesis will be utilized to create next-generation spin-based devices, enabling a more energy efficient future with more diverse device applications.

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