Consequences of a non-trivial band-structure topology in solids

Investigations of topological surface and interface states

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Abstract

The development and characterization of experimental setups for angle-resolved photoelectron spectroscopy (ARPES) and spin- and angle-resolved photoelectron spectroscopy (SARPES) is described. Subsequently, the two techniques are applied to studies of the electronic band structure in topologically non-trivial materials.

The laser-based ARPES setup works at a photon energy of 10.5 eV and a typical repetition rate in the range 200 kHz to 800 kHz. By using a time-of-flight electron energy analyzer electrons emitted from the sample within a solid angle of up to ±15 degrees can be collected and analyzed simultaneously. The SARPES setup is equipped with a traditional hemispherical electron energy analyzer in combination with a mini-Mott electron polarimeter. The system enables software-controlled switching between angle-resolved spin-integrated and spin-resolved measurements, thus providing the possibility to orient the sample by mapping out the electronic band structure using ARPES before performing spin-resolved measurements at selected points in the Brillouin zone.

Thin films of the topological insulators (TIs) Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ are grown using e-beam evaporation and their surface states are observed by means of ARPES. By using a combination of low photon energies and cryogenic sample temperatures the topological states originating from both the vacuum interface (surface) and the substrate interface are observed in Bi$_2$Se$_3$ films and Bi$_2$Se$_3$/Bi$_2$Te$_3$ heterostructures, with total thicknesses in the ultrathin limit (six to eight quintuple layers), grown on Bi-terminated Si(111) substrates. Band alignment between Si and Bi$_2$Se$_3$ at the interface creates a band bending through the films. The band bending is found to be independent of the Fermi level ($E_F$) position in the bulk of the substrate, suggesting that the surface pinning of $E_F$ in the Si(111) substrate remains unaltered after deposition of the TI films. Therefore, the type and level of doping of the substrate does not show any large influence on the size of the band bending.

Further, we provide experimental evidence for the realization of a topological crystalline insulator (TCI) phase in the narrow-band semiconductor Pb$_{1-x}$Sn$_x$Se. The TCI phase exists for temperatures below the transition temperature $T_c$ and is characterized by an inverted bulk band gap accompanied by the existence of non-gapped surface states crossing the band gap. Above $T_c$ the material is in a topologically trivial phase where the surface states are gapped. Thus, when lowering the sample temperature across $T_c$ a topological phase transition from a trivial insulator to a TCI is observed. SARPES studies indicate a helical spin structure of the surface states both in the topologically trivial and the TCI phase.

**Keywords:** spin- and angle-resolved photoelectron spectroscopy, time-of-flight analyzer, laser based light source, topological insulator, topological crystalline insulator, thin films, surface state, interface state, Bi$_2$Se$_3$, Pb$_{1-x}$Sn$_x$Se.
Publications

List of papers included in this thesis:


List of papers not included in the thesis:

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My first photoemission experiment, performed during the fall of 2008, was a disaster. Apart from not having a clue about what I was doing I also rammed the sample manipulator into the wall of the vacuum chamber bringing the entire experimental station to a halt, for weeks. Since then many more mistakes have been made, some less stupid than others. However, as an experimentalist, I believe the way to success lies in being allowed to make mistakes. Refinement of techniques and processes does not happen over night, but requires repeated, often failed, attempts before paying off. Therefore, I my opinion, I could not have ended up in a more suitable place than in the group of Prof. Oscar Tjernberg. Not that failure comes more frequently here than in other groups, but rather the fact that here freedom under responsibility exists abundantly in addition to the attitude that no experiment is too far fetched not to be tested at least once. Oscar’s expression “Let’s measure!” says it all.

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Magnus H. Berntsen
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Chapter 1

Introduction

1.1 Topology in condensed matter

One of the great achievements within condensed matter physics during the 20th century was the formulation of the band theory of solids [1]. Using this framework the energy distribution of electrons in a material could be described, thus giving a more detailed insight into the origin of macroscopically observable material properties. For instance, categorizing materials based on their electronic transport properties results in three main categories; metals, semiconductors and insulators. What distinguishes the three types of materials from each other is whether or not there is an energy gap in the electronic band structure between the highest occupied (filled) and lowest unoccupied (empty) electronic states\(^1\), as illustrated in Fig. 1.1a). In conductors there is no energy gap and an arbitrarily small amount of energy is needed in order to excite one of the most energetic electrons into a higher energy state. Insulators, on the other hand, have an energy gap between filled and empty states which is so large that it requires a substantial amount of energy to excite an electron across the band gap. Materials which according to their band configuration are classed as insulators are often called band insulators. Semiconductors are in their pure form band insulators but the size of the energy gap is smaller than in the insulators and by creating either acceptor or donor states inside the band gap also these materials can become conducting [2, 3].

Over the past decades, a different classification scheme has been developed which identifies the topological order of a material [4, 5]. The concept of topology, in the context of band structure, can at first glance appear rather abstract. However, the fact is that studies of band structures enable the identification of topological invariants [6, 7], i.e. quantities or properties which are shared by different objects within the same topological “phase” but distinct from that of objects belonging to another phase. In geometry, this can more easily be understood since topology

\(^1\)Here we have not taken into account the Mott insulators, which according to band theory should be conductors but due to electron-electron interactions are insulating.
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Figure 1.1: a) Principle sketch of the band structures of a metals, semiconductors and insulators, respectively. b) Topologically different objects (sphere and torus) can be classified according to their genus (g).

Here deals with the actual shape of an object. A sphere is topologically different from a torus since the torus has a hole in it while the sphere does not. Just by simple deformation of the sphere there is no way of transforming it into a torus, which displays the topologically different nature of the two objects. The topological invariant in this case is its genus \([8]\), i.e. the number of holes in the object. A drinking glass has no holes and therefore belongs to the same topological class as the sphere, although their physical shapes are different. Analogously, a coffee mug belongs to the same class as the torus.

When studying the configuration and appearance of the band structure of materials one is tempted to make a topological distinction between materials based on the presence or absence of an energy gap in the band structure. A question arising in this context is then; are all materials in which there is a finite band gap (insulators and semiconductors) topologically equivalent? If the answer is yes, then one would be able to transform the band structure of any material within this class into any of the other by, in a smooth and continuous fashion, changing the material parameters without closing the energy gap. In recent years, the study of band structure topology has gained popularity after the discovery of materials which at first glance appear to be traditional band insulators but when examined more closely turn out to be of a topologically different character \([9, 10, 11]\). For these materials, a simple, continuous deformation of the band structure does not influence the topological invariants and therefore cannot change the band structure into that of a trivial insulator. In other words, the coffee mug cannot become a sphere by mere deformation. Due to the resemblance with the normal insulators on one hand but the topological difference on the other, these materials are called topological insulators (TIs).

The topological insulating phase was theoretically predicted in 2005 \([12, 9]\) and its existence in real systems was predicted and experimentally verified shortly there-
1.2. EXPERIMENTAL TECHNIQUES PUSHING SCIENCE FORWARD

after [13, 14]. This discovery of a new state of matter has attracted considerable attention from the condensed matter physics community and resulted in numerous publications of the subject [15, 16]. Part of the reason for the great interest in TI is that the non-trivial topology of these materials is not only of theoretical significance, but has concrete, observable physical effects. Although the interior (bulk) of the material is an insulator, the edges or surfaces host conducting states [17]. As a result, if applying a current to a three-dimensional TI, the current will travel only on its exterior. Additionally, these edge or surface states are spin polarized [10], which means that the current will have a well defined direction of the electron’s spin. Due to the latter, TI are predicted to have a great impact on the development of future spin-electronic (spintronic) devices.

Altogether, the fascinating properties of the TIs and the possibility of novel device applications explain the very broad interest in this new state of matter, bringing together theoreticians and experimentalists from both fundamental and applied fields of physics. However, although at present time the most fundamental properties of the TIs have been established, there are many more aspects that remain to be investigated, including detailed studies of how TIs interact with trivial matter, other TIs [18, 19] and superconductors [20, 16].

1.2 Experimental techniques pushing science forward

During the short period of time since the discovery of TI, one of the major experimental techniques deployed in the study of their band structure has been angle-resolved photoelectron spectroscopy (ARPES) [21]. This technique, which will be described in more detail in chapter 4, allows one to directly probe the electronic band structure of a material and is an excellent tool for studying TIs and their surface states in particular.

The field of photoelectron spectroscopy was born in 1907 when P. D. Innes performed the first measurements of the velocity distribution of electrons emitted from core levels in various metals [22]. Since then, this experimental technique has experienced a tremendous development, both technically and resolution wise. The more than hundred fold increase in energy resolution between modern photoemission setups and their early predecessors is partly due to technical refinements in the instruments and detection capabilities themselves but also a result of advances in the excitation or light sources [23].

The continuous development of spectrometers with improved resolving capabilities has been encouraged and partly driven by an increased interest in the low energy electronic structures of metals, semiconductors and other complex systems [24, 25, 26, 27]. Electronic structures with characteristic energy and momentum scales down to the 0.01 eV and $10^{-3}$ Å$^{-1}$ range, respectively, are being studied today [28], which puts high constraints on the instruments used. The wealth of information and knowledge gained from photoemission experiments continues to make the technique one of the principle tools of investigation within many branches
of condensed matter physics. Discoveries of new physical phenomena and the development of new, and the improvement of existing, experimental techniques goes hand in hand and advances within one area open possibilities within the other. For this reason, continuous instrumental developments are highly motivated.

1.3 Aim of the original work

In light of the above discussion, the work included in this thesis can be divided into two major parts:

i) Instrumental development

- The final commissioning of an experimental setup for spin- and angle-resolved photoemission. The setup provides the possibility of extracting information regarding the spin configuration, along with spin integrated angle-resolved measurements, of the electronic band structure of materials (Paper I).

- Development of an experimental setup for angle-resolved photoemission with high angular and energy resolution. The setup uses a newly developed angle-resolving time-of-flight analyzer and is built around a laser-based light source. This setup moves the energy limit of high-repetition rate laser-based sources up to 10.5 eV and demonstrates the advantage of three-dimensional simultaneous acquisition of photoelectron data (Paper II).

ii) Experimental investigations of topological matter

- Topological insulators have been studied using the developed experimental setups. The work has focused on observations of interface states between topologically trivial materials and TI and on TI-TI heterostructures (Paper III), both which are of fundamental interest but also important from a device application point of view. These studied have been performed on thin films and part of the work has therefore been related to gaining the knowledge and expertise needed to manufacture TI thin film samples.

- Verification of the newly predicted topological crystalline insulator phase through angle- and spin-resolved photoemission studies on Pb$_{1-x}$Sn$_x$Se (Paper IV and Paper V).

1.4 Thesis structure

Following this introduction, a background to the subject of topological insulators and topological crystalline insulators is given in chapter 2 and chapter 3, respectively. The description of these topics is far from complete and the reader should see it as an attempt at giving an overall introduction to the field rather than a formal, detailed presentation. Then, in chapter 4, the fundamentals of the experimental
techniques used throughout this work are reviewed. Chapter 5 presents the major results of the instrumental development, including important aspects and details regarding the operation of the laser-based photoemission setup. Results from the experimental investigations of TI and TCI are presented in chapter 6 followed by a summary and conclusions of the work as a whole in chapter 7. In the latter, a discussion related to future work, both of instrumental and experimental character, is included.
Chapter 2

Topological insulators

2.1 An introduction to topological insulators

Topological insulators (TIs) are materials which can neither be classified as pure insulators nor as conductors. Although the interior of the material is an insulator, characterized by an energy gap in the electronic band structure, the edges or surfaces host non-gapped states which cross the bulk band gap, thus enabling conduction on the boundaries of the material [12, 29]. The term “topological” is used since the band structure of these materials possesses a different topology compared to normal band insulators.

Figure 2.1 schematically compares the band structure of an insulator, having surface states extending into the bulk band gap, to that of a topological insulator. The momenta $k_1$ and $k_2$ represent Kramers points, i.e. points in the Brillouin zone where the surface state is doubly degenerate. In the normal insulator one can, by moving the chemical potential, place $E_F$ in such a way that no bands are intersected. Alternatively, imagine that the Kramers crossings can be moved up or down in energy, deforming the surface states, until the bands no longer intersect $E_F$. For the TI, on the other hand, one realizes that no matter where $E_F$ is placed in the band gap, or how the surface state is deformed by moving the Kramers points in energy, the surface state cannot be pushed out of the band gap. Consequently, in the normal insulator the surface state will always intersect $E_F$ an even number of times (alternatively zero times) whereas in the TI there will be an odd number of Fermi-level crossings.

This property of the surface state demonstrates the difference in topology between a normal and a topological insulator. In the TI, the surface states are results of the topology of the bulk band structure and are therefore intrinsic to the TI phase, meaning that they cannot be removed unless inducing a change in the topology. As a result, the surface states are extremely robust, being insensitive to contamination of the surface. In fact, the surface states are protected by time-reversal symmetry, which means they are robust against non-magnetic back-scattering [12].
The special topology of the two-dimensional and three-dimensional TIs, realized in CdTe/HgTe quantum wells [13] and Bi$_2$Se$_3$ [30], respectively, is a result of an inverted band gap of the bulk. An inverted band gap arises when the orbital character of the conduction and valence bands is reversed relative the energy configuration of the atomic orbitals. Figure 2.2 displays the band inversion taking place in Bi$_2$Se$_3$ when starting from pure atomic orbitals and successively including different forms of atomic interactions. Due to the different orbital origin of the conduction and valence band before and after “switching” on spin-orbit coupling the final band structure cannot be “deformed” into that of the non-inverted without first closing the band gap and then reopening it with the reversed sign. Thus, a change between the two cases requires a topological phase transition.

As mentioned in the introduction, when dealing with topology of either geometrical objects or electronic band structure, systems are classified based on specific properties which do not change within a given topological class. Such topological invariants (labeled $\nu$), in the context of band structures, enable us to identify whether a material belongs to the class of trivial insulators or topological insulators [29, 7]. By going back to Fig. 2.1 we see that the trivial insulator in panel a) has either zero or an even number of bands crossing $E_F$. The topologically non-trivial insulator in panel b), on the other hand, has a surface state which must cross $E_F$ an odd number of times. As it turns out, the number of times the surface states intersect $E_F$ is related to the change in the topological invariant ($\Delta \nu$) when crossing the interface between the material and its surroundings. This is called the bulk-boundary correspondence and, loosely speaking, one can say that the topological invariant $\nu$ is given by

$$\nu = N_{E_F} \mod 2$$

resulting in $\nu = 0$ or $\nu = 1$, for the trivial and non-trivial phases, respectively. Here, $N_{E_F}$ is the number of times the surface states intersect $E_F$ along the line in
2.2 Surface electronic states in $\text{Bi}_2\text{Se}_3$, $\text{Bi}_2\text{Te}_3$ and $\text{Sb}_2\text{Te}_3$

When speaking about surface states one refers to electronic states arising from electrons which are spatially confined to the surface, or in a very close vicinity to the surface, of a material. While the reason for their confinement may vary, i.e. the states can be intrinsic or extrinsic [34], a common property of the surface state electrons is that they move only in the direction parallel to the surface and therefore can be labeled by the in-plane crystal momenta $k_x$ and $k_y$. Since there is no motion...

Figure 2.2: Evolution of atomic orbital energy levels in $\text{Bi}_2\text{Se}_3$ when introducing different types of atomic interactions. When spin-orbit interactions are included the band gap is inverted. Adapted from [30].
perpendicular to the surface the electrons do not experience any $k_z$ dispersion and the electronic surface states can be considered as two-dimensional.

The model-TIs Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ have similar rombohedral crystal structures [30] and the SBZ of the (001) surface is hexagonal. Their surface-state band structure can be schematically pictured as in Fig. 2.3a). The nearly linear dispersion of the surface state, connecting the conduction band with the valence band, combined with the degeneracy of the states at the Kramers point at $\Gamma$ makes the surface state appear as a Dirac cone. The crossing point of the two branches is referred to as the Dirac point. In addition to their topologically non-trivial origin, the surface states in these materials possess intriguing spin properties [29, 35, 36]. The states are spin polarized where the direction of the spin is locked to the electron’s momentum and oriented in the plane parallel to the surface, rotating clock-wise around $\Gamma$ (above the Dirac point), indicating the presence of time-reversal symmetry $E(-k, \uparrow) = E(k, \downarrow)$, as illustrated in Fig. 2.3c).

The momentum-locked spin structure partly explains the robustness of these states since non-magnetic back-scattering of an electron described by $E(k, \uparrow)$ into the state $E(-k, \uparrow)$ is prevented due to the lack of such final states. Only when the direction of the spin is also reversed in the scattering process, i.e. $E(k, \uparrow) \rightarrow E(-k, \downarrow)$, can back-scattering occur. Such spin-flip scattering events can only be caused by interactions with a magnetic scattering site and non-magnetic contamination of the surface of a TI will therefore not be able to destroy (scatter) the surface state and, accordingly, nor the topological phase of the material. The momentum-spin-locking has been experimentally confirmed by spin-resolved photoemission studies [37], c.f. chapter 6, although the magnitude of the measured in-plane polarization is $< 1$.
Theoretical predictions suggest that the spin is forced out of the plane due to a hexagonal distortion of the Dirac cone [35], thus giving rise to a $P_z$ component of the polarization. However, at this moment in time the out of plane polarization has only been confirmed in Bi$_2$Te$_3$ [38].

### 2.3 Spintronic applications

The possibility of utilizing not only the charge but also the electron spin in electronic solid-state devices is something which has attracted considerable interest during the past two decades. Magnetoresistive random-access memories (MRAM) [39] and the spin field-effect transistor [40] are some examples of devices which rely on the generation and transport of spin polarized currents.

In some metals [41, 42, 43] spin split surface states exist which could work as sources for spin polarized currents. The inherent difficulty of using such sources is related to their sensitivity to contamination or atomic disorder. For example, although the surface state on Au(111) can be easily prepared in a controlled environment under ultra-high vacuum (UHV) conditions, real devices rely on capping and contacting of the active material rather than atomically clean surfaces. The combination of spin polarization and extreme robustness of the surface states on the TIs makes these materials promising for practical device applications. However, in order to achieve conduction from the surface states alone the chemical potential needs to be placed inside the bulk band gap, something which requires careful control of the amount of bulk defects in these materials. In reality, this has proven cumbersome in the stoichiometric TIs Bi$_2$Se$_3$ and Bi$_2$Te$_3$ due to a large number of Se and Te vacancies which render the materials n-doped, placing the Fermi-level in the conduction band [44, 45, 46]. Chemical reactions at the surface of cleaved single crystalline Bi$_2$Se$_3$ samples also leads to an n-type doping of the surface region [47]. Further, from an application point of view, thin films are more interesting than single crystals since the former can be in-situ grown and interfaced towards other materials, enabling the creating of multi-layers or other structures needed for devices. Thus, studies of TI thin films, and TI-interfaces in particular, are highly motivated.

### 2.4 Experimental realization of TIs

The first observations of the Dirac-like surface states in Bi$_2$Se$_3$ and Bi$_2$Te$_3$ were made on cleaved single crystalline samples [11, 32]. However, by using epitaxial growth techniques high quality crystalline thin films of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ can be achieved on a variety of substrates [48, 46, 49, 50]. Thus, shortly after the initial experiments on bulk crystals a number of different studies on thin films appeared [51, 52, 53]. The electronic state on the vacuum side surface on bulk crystals and thin films is commonly referred to as the surface state. Yet, a thin film grown on a topologically trivial substrate will have an additional surface which
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Figure 2.4: a) Dirac cones on opposite sides of a free-standing TI film. The dispersion of the two states is illustrated in the lower panel. b) Gap opening in surface states due to hybridization between states on top and bottom of film.

faces the substrate. Since the topologically protected states appear on all surfaces of a TI, or more correctly at every interface across which there is a change in the topological invariants, there must also be a state at this additional surface or interface. We therefore refer to this second state as the interface state. Strictly speaking, the surface state is also an interface state due to the fact that it appears at the interface between the TI and vacuum, the latter which is topologically classified as a trivial insulator. However, to simplify the labeling of the states we refer to the two types as surface and interface states, respectively.

If we now imagine having a free-standing thin film of a TI, surrounded by vacuum, we would have identical states on the two surfaces of the film with a uniform chemical potential along the $z$-direction, see Fig. 2.4. At equilibrium there will be no charge accumulation at the edges of the film, thus the helicity of the two states must be opposite. If decreasing the thickness of the film, until the wavefunctions of the states on opposite sides start to overlap, a hybridization gap opens at the Dirac point [54] thus destroying the topological phase, as illustrated in Fig. 2.4b). For Bi$_2$Se$_3$ this happens at film thicknesses $\lesssim 60$ Å. In reality, one rarely works with free-standing films, thus a substrate is always present. Due to band alignment between the film and the substrate, in addition to possible charge transfer to or from the substrate, the chemical potential at the interface will be shifted away from its “free-standing” position. A band bending through the film is thereby generated which shifts the Dirac point of the interface state in energy.
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\[ |V| = 0 \quad \Delta = 0 \quad \Delta = 0 \quad |V| > 0 \quad \Delta > 0 \]

\[ \Delta_{E_0} = 2|V| \]

\[ \Gamma \]

\[ \Gamma \]

\[ \Gamma \]

\[ \Gamma \]

Figure 2.5: Calculated band structure for the surface and interface states using Eq. (2.2) for different values of \(|V|\) and \(\Delta\) illustrating the effect of band bending and hybridization. Red and blue bands have opposite in-plane spin directions.

relative that of the surface state. This situation can be described by a simple two-band model [54]

\[ E_{\sigma\pm}(k) = E_0 - Dk^2 \pm \sqrt{\left(\frac{\Delta}{2} - Bk^2\right)^2 + \left(|V| + \sigma v_F \hbar k\right)^2} \quad (2.2) \]

where \(\sigma = \pm 1\) represents the two spin directions, \(E_0\) is the center energy of the two Dirac points, \(2|V|\) is the band bending through the film, \(\Delta\) is the energy gap at the crossing points away from \(\Gamma\), \(v_F\) the Fermi velocity and \(D\) and \(B\) are coefficients of higher order terms in \(k\). After having introduced a structural inversion asymmetry in the film, generated by the presence of the substrate, we observe that in the ultra-thin limit (where hybridization occurs) an energy gap opens at the momenta where the two states intersect, as shown in Fig. 2.5. From the same figure, we also see that a larger band bending leads to a larger energy offset between the two states, and the two are related as \(\Delta E_D = 2|V|\). Consequently, assuming the Dirac point energies of the surface and interface states can be measured, the magnitude of the band bending can be determined.

2.5 Surface chemical reactions and near-surface band bending

Atomically clean surfaces of materials are difficult to achieve since the atmosphere that surrounds us consists of gas molecules which will stick to or react with all surfaces exposed to it. In the adsorption process the local atomic bonding and charge distribution of the atoms closest to the surface may be distorted from the ideal configuration. Even when surfaces are stored under UHV conditions, residual
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Figure 2.6: a) Adsorption induced charge accumulation at the surface of a TI resulting in a near-surface band bending. b) Formation of quantum well states due to the band bending. Right panel displays real photoemission data on Bi$_2$Se$_3$.

gases adsorb to the surface with a rate determined by the pressure in the vacuum chamber. If charge is transferred between the sample and the adsorbates the local chemical potential is shifted causing a band bending effect close to the surface [34]. The direction of the band bending depends on whether charge is transferred to or from the adsorbates. On Bi$_2$Se$_3$, adsorption of CO, K, H$_2$ and H$_2$O has been shown to induce a downward band bending at the surface [55, 56], as illustrated in Fig. 2.6a). The band bending can be substantial, and as a result, the conduction band may be shifted below the Fermi-level. This creates a potential well which can confine conduction band electrons to the surface. Consequently, a 2D electron gas is formed at the surface, occupying quantum well states (QWS), as seen in Fig. 2.6b). Additionally, due to the potential gradient the QWS experience a Rashba-split, or spin-split, where electrons with opposite spins are separated in energy [47, 56]. Since the adsorption of atoms or molecules only occurs at the surface of a material the described effect will only influence the atomic bonds and charge distribution in a close vicinity of the surface. Buried interfaces, on the other hand, will not be influenced by such adsorption processes. As we will see in Paper III, this knowledge will prove valuable when distinguishing interface states from surface states in cases where both are observed simultaneously.
Chapter 3

Topological crystalline insulators

Inspired by the discovery of topological insulators a search for additional phases of matter has been initiated in which the non-trivial band topology is connected to other types of symmetries than time-reversal symmetry. In 2011, Liang Fu [57] predicted that crystal symmetries in certain systems can replace the role played by TRS in the TIs, resulting in materials with protected surface states accompanied by an insulating bulk. Due to the close resemblance with the TIs and the importance of crystal symmetries, this class of materials has been named topological crystalline insulators (TCIs).

3.1 Distinction between TIs and TCIs

The observable effects of the new TCI phase have many similarities with those of the TIs. The surface states on the TCIs consist of non-gapped states which cross the bulk band gap [57]. Similar to the TIs, the bulk of the TCIs is characterized by an inverted band gap [58]. However, when evaluating the topological invariants used to classify the TIs the TCIs fall into the category of trivial insulators [17]. It turns out that TCIs are described by a different topological invariant, the mirror Chern number [59, 58], which is connected to the mirror symmetry in these materials.

Unlike the TIs, which have protected surface states on all faces of a crystal, TCIs display non-gapped states only on surfaces perpendicular to the mirror planes of the crystal structure. Further, since the states are protected by crystal symmetry the Dirac cones appear at points in the SBZ which are projections of bulk high symmetry points rather than at TRIM as in the TIs. The number of Dirac cones on the surface of a TCI also differs from the TIs. While in a TI the number of Dirac states is always odd, the TCI hosts an even number of Dirac fermions on the surface [17]. Additionally, breaking of time-reversal symmetry, e.g. by introducing magnetic impurities, will not be able to destroy the protected surface states whereas deformation of the crystal breaks its symmetry and consequently gaps the surface states [58].
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3.2 TCI materials

In 2012, Hsieh et al. made the first predictions of the TCI phase in a real material, namely SnTe [58]. Their study showed that SnTe has a band gap which is inverted compared to the closely related material PbTe. The new topological invariant also differs for these two materials suggesting that SnTe is a TCI and PbTe a trivial insulator. By varying the Sn content in the substitutional composition Pb\(_{1-x}\)Sn\(_x\)Te across a certain critical value \(x_c\) one can tune the material into either a non-trivial or trivial phase. When approaching \(x_c\) from the lower side the positive band gap will decrease and at \(x_c\) completely close before reopening with a negative gap for concentrations \(x > x_c\). Subsequent experimental works have confirmed the presence of a TCI phase in SnTe [60] and Pb\(_{0.6}\)Sn\(_{0.4}\)Te [61] as well as the topologically trivial nature of PbTe [60] and Pb\(_{0.8}\)Sn\(_{0.2}\)Te [61]. As will be presented in chapter 6 and in Paper IV, we have also confirmed that Pb\(_{0.77}\)Sn\(_{0.23}\)Se belongs to the newly discovered TCI class of materials.
Chapter 4

Methods and experimental techniques

In this thesis, the electronic structure of ultra-thin TI films and single crystalline TCI samples is examined. By fabricating the thin film samples ourselves we have been in control of the critical parameters related to the film growth, such as film thicknesses and choice of substrate. In the following chapter an overview of the methods used to fabricate and characterize the samples is given. Additionally, a general background of the experimental techniques by which the electronic structure of the films have been determined is also presented.

4.1 Photoelectron spectroscopy

When a crystal is formed, the allowed electronic energy states form seemingly continuous bands rather than discrete atomic energy levels. The collection of all these bands is called the band structure of the material. Studies of the band structure can reveal many fundamental properties of the system even without any prior knowledge of its explicit nature, i.e. a system’s properties are embedded in its band structure. Therefore, by direct observation of the details of the band structure we can learn a great deal about the system at hand. Photoelectron spectroscopy (PES) is a technique which directly probes the band structure of a material by measuring the energy distribution of photoelectrons emitted from a sample. The technique is based on the principle of the photoelectric effect in which energetic radiation (photons) hit a sample and causes electrons to be emitted from the sample surface.

4.1.1 The photoemission process

The photoemission process is a result of interactions between radiation and matter. A photon has a well defined energy $E_{\text{ph}} = h\omega$ which is determined by its wavelength $\lambda$ ($\omega = 2\pi c/\lambda$, where $c$ is the speed of light). The binding energy $E_b$ of an electron
is given by $E_b = E_F - E_i$, where $E_i$ is the energy of the electron’s state and $E_F$ the Fermi energy, i.e. the energy of the highest occupied electronic state. By absorption of a photon the electron gains energy and can be excited into a higher energy state. Since the photon momentum at low photon energies is much smaller compared to the electron momentum one can, as a first approximation, neglect any momentum transfer in the absorption process. If the energy of the photon is larger than $E_b + \Phi$, where $\Phi$ is the work function of the material, the electron can travel to the surface of the material where it can overcome the surface barrier and leave the sample. The emitted electron then has a kinetic energy of $E_{\text{kin}} = h\nu - E_b - \Phi$. By measuring the kinetic energy and angle of emission, relative the surface normal, of the emitted electron its momentum outside the material (in vacuum) is given by

$$K_x = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \theta \cos \phi, \quad (4.1a)$$

$$K_y = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \theta \sin \phi, \quad (4.1b)$$

$$K_z = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cos \theta, \quad (4.1c)$$

where the angles $\theta$ and $\phi$ are defined in a standard spherical coordinate system, see Fig. 4.1a). If the surface of the solid has a periodic well ordered structure, in the photoemission process, the parallel component of the electron momentum is conserved (modulo a reciprocal lattice vector of the surface), giving directly the in-plane momentum $k_{\parallel}$ of the electron in the initial state as

$$|k_{\parallel}| = |K_{\parallel}| = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \theta. \quad (4.2)$$

The momentum component in the $z$-direction is, however, not conserved. By assuming that the electron is excited into a free-electron like final state in vacuum, the perpendicular component of the electron momentum in the material can be expressed as

$$k_{\perp} = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \cos^2 \theta + V_0, \quad (4.3)$$

where $V_0$ is called the inner potential. The inner potential is generally an unknown quantity but can be experimentally estimated by observing the periodicity of the dispersion in the $k_z$ direction.

### 4.1.2 Angle-resolved photoelectron spectroscopy

As explained in the previous paragraph, by measuring the kinetic energy and the emission angle of the photoelectrons the electron momentum of the initial states can be found. Additionally, by determining $E_F$ one can also establish the electron’s binding energy and thus the band structure can be determined. The experimental technique called Angle-Resolved Photoelectron Spectroscopy (ARPES) uses this principle. There are two major ways of performing ARPES measurements, both
4.1. PHOTOELECTRON SPECTROSCOPY

![Figure 4.1](image)

Figure 4.1: a) Photoexcitation of an electron. b) Momentum vector of a photoelectron. The sample surface is parallel to the plane spanned by $K_x$ and $K_y$. c) Principle sketch of the photoemission process.

widely used, which differ primarily by how the kinetic energies of the electrons are determined.

The hemispherical electron analyzer

In the photoemission process, electrons are emitted from the sample surface in all directions. This can be represented by a half-sphere extending out into vacuum, away from the surface. By using an electro-static lens, one can collect electrons emitted within a given solid angle of this half-sphere. Using the lens to image the collected electrons onto a slit, electrons emitted within a narrow strip on the half-sphere are selected and passed on to an energy filter, see Fig. 4.2a) and Fig. 4.3a). The energy filter consists of two capacitor plates formed as half-spheres, thus the name hemisphere, which are separated by a distance $d$. The electrons passing through the slit of the electrostatic lens enters the space between the two capacitor plates. By applying a voltage $U$ across the capacitor the electric field between the plates makes the electrons follow a circular path with a radius of curvature determined by the applied voltage and the kinetic energy of the electrons.

Only electrons with kinetic energy within a narrow range are able to pass through the hemisphere without hitting the capacitor plates. Mounting an electron detector where the electrons exit the hemisphere makes it possible to measure their distribution along two directions. Along the radial direction, the distribution is determined by their energies and along the perpendicular direction the electrons are distributed according to their position along the entrance slit, the latter which
Figure 4.2: a) The angular acceptance of a hemispherical photoelectron spectrometer with a rectangular entrance aperture. Electrons along a line in the BZ are collected. b) An TOF analyzer collects electrons within a solid angle, thus mapping out a plane in the BZ.

represents the emission angle. From the detector one can therefore read out the energy and angular distributions and by tilt and rotation of the sample all emission angles can be covered. Spectra for specific emission angles may then be combined to give a picture of the band structure of the material.

The time-of-flight electron analyzer

Instead of using a hemispherical energy filter to determine the kinetic energy of the electrons one can measure their speeds and thus obtain the kinetic energy through the relation \( E_{\text{kin}} = \frac{1}{2}mv^2 \) (valid for non-relativistic speeds). The speed of an electron is determined by measuring the flight-time \( t \) needed for the electron to travel from the sample to the detector, see Fig. 4.4. Using the simple relation \( l = v \cdot t \) the expression for the kinetic energy becomes \( E_{\text{kin}} = \frac{1}{2}m(l/t)^2 \), where \( l \) is the length of the path which the electron has traveled. An electrostatic lens, similar to the one used in hemispherical analyzers, is used to collect electrons within a certain angular range and image them onto a detector. For all electrons with emission angle \( \theta \neq 0 \) the flight-path through the lens will not be a straight line. Consequently, \( l \) in the expression above is not simply the sample to detector distance. However, if the angular acceptance of the lens is kept small, the flight path of the different electrons will not differ substantially and can be approximated by the distance between the sample and the detector.

In order to accurately determine the flight time of an electron the emission of the electron from the sample and its arrival at the detector must be well defined events. This is achieved by using a pulsed light source which delivers short well defined pulses with a certain amount of time between each pulse. Synchronization of the detector with the light source defines the start (emission) and stop (de-
4.1. PHOTOELECTRON SPECTROSCOPY

Figure 4.3: a) Drawing of a hemispherical electron analyzer. By passing through an electrostatic energy filter (the hemisphere) the electrons are spatially separated on the detector according to their kinetic energies. b) A hemispherical analyzer in combination with an electron spin detector (Mott-detector). Spin up and spin down are separated to the left or right by scattering on a heavy-element target.

Figure 4.4: A TOF analyzer measures the flight time of electrons from the sample to the detector and uses this to determine their kinetic energies.
CHAPTER 4. METHODS AND EXPERIMENTAL TECHNIQUES

tection) signals needed to measure the flight times. Sufficient time between each
light pulse ensures that electrons from one pulse are not associated with electrons
from the next one. Tilting and rotating the sample enables, in a similar manner
as for the hemispherical analyzer, detection of all emission angles. By increasing
the acceptance angle of the lens, and using a two-dimensional detector with high
spatial resolution, the time-of-flight analyzer can also provide angular resolution
over a large angular range without the need of moving the sample. This type of
analyzer has been developed only recently and results and characteristics from our
development of a system using such an analyzer will be presented in chapter 5.

4.1.3 Spin- and angle-resolved photoelectron spectroscopy

By analyzing the spin distribution of the photoelectrons information regarding the
spin states of the electrons in the material can be obtained. The analyzers described
so far are spin integrating, i.e. no distinction between different orientations of the
electron spin can be made. However, analyzers exist in which this distinction can
be made.

In a Mott-detector \cite{62, 63} the photoelectrons are accelerated by a high voltage
(on the order of 30 kV) and subsequently focused onto a target consisting of a heavy
element, such as gold or thorium, resulting in some of the electrons being elastically
backscattered. One can define a scattering plane spanned by the wave vector of
the incoming ($k_i$) and scattered electron ($k_L$ or $k_R$) and a scattering angle $\theta$,
which is the angle between the incoming and scattered wave vector, see Fig. 4.5a).
The probability of scattering through an angle $\theta$ is proportional to the scattering
cross section $\sigma(\theta)$ \cite{63}. When spin orbit interactions between the electron and the
nucleus is included, the scattering cross section will have a spin-dependence. Thus,
one can write $\sigma(\theta) = I(\theta)[1 + S(\theta)P\hat{n}_x]$, where $I(\theta)$ is the spin-averaged scattered
intensity, $S(\theta)$ is the asymmetry or Sherman function, $P$ the polarization of the
incoming electron and $\hat{n}$ a unit vector perpendicular to the scattering plane defined
as $\hat{n}_x = (k_i \times k_x)/|k_i \times k_x|$. Here, $k_x$ with $x = L$ or R is the scattering vector to
the left or right and we define $P > 0$ for $P \parallel \hat{n}_L$.

Let us consider an incoming electron beam and look at electrons scattered to
the left. In that case, electrons with spin up and spin down have a polarization
which is parallel and antiparallel to $\hat{n}_L$, respectively. Consequently, the number
of electrons with spin up scattered to the left is proportional to $1 + S(\theta)$ and the
number of spin down electrons is proportional to $1 - S(\theta)$. For a gold target and a
scattering angle of 120 degrees, a typical angle used in Mott-detectors, the Sherman
function is negative \cite{63}, i.e. $S < 0$. As a result, if the initial beam is unpolarized,
i.e. it contains an equal number of spin up and spin down electrons, the number of
electrons with spin down, scattered to the left, would be larger than the number of
electrons with spin up.

By repeating the arguments above, one realizes that more electrons with spin
up are scattered to the right through the same angle than electrons with spin down.
Placing electron detectors at the left and right positions one would therefore be able
4.2. LIGHT SOURCES FOR PHOTOEMISSION EXPERIMENTS

Figure 4.5: The Mott-scattering process. An incoming electron is preferentially scattered to the left ($k_L$) or right ($k_R$) based on whether its spin is parallel or antiparallel to $\hat{n}_L$.

...to measure an asymmetry in the intensities if the initial electron beam is polarized. The polarization of the initial beam can then be found by

$$P = \frac{I_R - I_L}{I_R + I_L} \times \frac{1}{S},$$

(4.4)

where $I_L$ and $I_R$ are the photoelectron intensities in the left and right detector, respectively. In the convention used here, a positive polarization is defined as parallel to the spin up direction in Fig. 4.5. Using a Mott-detector in combination with a hemispherical electron analyzer one can filter the electrons in energy before passing them on to the spin detector. Consequently, by sweeping the voltages across the hemisphere one can measure spin intensities as a function of kinetic energy of the photoelectrons. As a result, the polarization $P(E_{\text{kin}})$ can be determined.

4.2 Light sources for photoemission experiments

When performing photoemission experiments, ideally, one would like to have an energy resolution which enables even the finest details of the electronic structure of a material to be studied. If the light used to generate photoelectrons consist of photons with a broad range of energies the measured kinetic energies of electrons originating from a well defined electronic energy level $E_i$ would be distributed accordingly. The reason for this is because the kinetic energy of an electron is given by $E_{\text{kin}} = h\nu - \phi - E_i$, where $\phi$ and $E_i$ are fixed quantities for a given electronic level. Thus, the measured electronic structure of the material would appear smeared out. In order to obtain the desired energy resolution a well monochromatized light source is therefore required.

Sometimes, the possibility to either increase or decrease the surface sensitivity in a measurement is desirable. This can be achieved by varying the photon energy since the mean free path of electrons in a material depends on their kinetic energy [64]. In the energy range between 20 eV and 100 eV the electron’s mean free
path experiences a minimum. This implies that if photon energies in this range are used, only electrons originating from a shallow region near the surface are able to escape from the material, thus enhancing the surface sensitivity of the technique. Outside the mentioned energy range, either at lower or higher energies, the bulk sensitivity is increased.

By varying the photon energy one can also map out the band dispersion along the $k_{\perp}$ direction. By using the free-electron like final-state approximation, and setting $\theta = 0$ in Eq. (4.3), the perpendicular component of the momentum can be expressed as $k_{\perp} = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} + V_0}$. This tells us that by varying the incident photon energy, and consequently altering the kinetic energy of the electrons, different $k_{\perp}$-values can be accessed.

The examples discussed above demonstrate that, in many cases, a flexible light source which can deliver a tunable photon energy with a small energy spread is desired. Generally, different types of experiments pose different requirements on the light source. Therefore, there exist a variety of light sources, each serving its own purpose. Two of the most important sources used for the experimental parts of this thesis are presented below.

### 4.2.1 Synchrotron radiation

Synchrotron radiation sources are without doubt the most versatile light sources that exist. These sources consist of a storage ring in which electrons are confined in a circulating path by the use of magnetic fields. When subjected to a magnetic field, an electron in motion will experience a force which can be described by $F = qv \times B$, where $q$ is the electron’s charge, $v$ is the velocity of the particle and $B$ the magnetic field. By applying a magnetic field in the vertical direction, the electrons can complete a circular motion in the horizontal plane. Strictly speaking, a storage ring is not a circle but rather a polygon where straight sections are connected to each other at an angle, see Fig. 4.6a).

Along the straight sections insertion devices, such as the widely used undulator, can be placed. An undulator is a periodic magnetic structure which consists of an array of magnets with alternating directions of the magnetic poles, as drawn in Fig. 4.6b). When moving through the magnetic field of the undulator the electrons are subjected to a magnetic force, however, this time alternating from one side to the other depending on the direction of the magnetic field. This sideways undulating motion results in the electrons emitting synchrotron radiation. Since the electrons are stored in the ring at relativistic speeds the radiation will be focused into a narrow cone along the direction of motion and wavelengths in the IR to X-ray range can be generated. A typical emission spectrum from an undulator is sketched in Fig. 4.6c). It consists of a narrow peak centered at a certain wavelength. The fundamental wavelength and the band width of the radiation are defined by the energy of the electrons together with the magnetic field and periodicity of the undulator. While it is customary to keep the electron energy, the periodicity and undulator length fixed, the magnetic field of the undulator can be
4.2. LIGHT SOURCES FOR PHOTOEMISSION EXPERIMENTS

Figure 4.6: a) In a storage ring the electrons are kept in a circulating motion by the use of bending magnets. b) An undulator is an array of magnets which makes the electrons undulate back and forth thus producing synchrotron radiation. c) Typical emission spectrum from one harmonic of an undulator.

 altered by changing the gap between the two magnetic arrays. Consequently, by changing the undulator gap, the fundamental wavelength of the emitted radiation can be continuously tuned over a large range.

4.2.2 Lasers as light sources

There are certain situations in which one would like to work with other sources of light than the one described above. Photoemission studies of ultra-fast systems, such as life times of excited states [65] or demagnetization processes [66], require a source with ultra short photon pulses. Also, depending on the beamline setup, the energy resolution from a synchrotron might in certain cases be insufficient. In such cases, lasers can provide the necessary time and energy resolution needed.

Laser based light sources deliver coherent radiation, usually with a very narrow bandwidth and pulse lengths down to the femtosecond scale are feasible, making them excellent for high energy and time resolved studies. For TOF electron analyzers, lasers are particularly well suited since this technique relies on a pulsed source. Lasers are considerably less bulky than synchrotrons which make them ideal for use in home-laboratories. However, the major drawback is that lasers only provide a small set of discrete photon energies (or in worst case only one photon energy). Additionally, the photon energy of most high-power lasers is lower than the work function of most materials and lasers in the vacuum ultraviolet (VUV) and X-ray regions are basically non-existent. Therefore, to be able to use lasers as light sources for photoemission the laser light needs to be converted into more energetic
photons. For this purpose, non-linear higher-harmonic generation in crystals or in noble gases can be used to create photons with higher energy. However, also this process is troublesome since HHG in gases requires a certain pulse energy. Reaching sufficient pulse energies often come at the expense of decreased repetition rates of the lasers, thus dramatically reducing the photon flux available for photoemission experiments.

4.2.3 Higher harmonic generation

Higher harmonic generation (HHG) is a process where light of a given wavelength is converted into radiation of shorter wavelengths through interactions with an optically non-linear medium. The medium can be either optical crystals or gases. Since the atoms in the medium consist of positively charged nuclei surrounded by negatively charged electrons the presence of an electric field will tend to displace the two charges in opposite directions, thus polarizing the medium. By considering the light as an oscillating electric field with frequency $\omega_0$

$$E(t) = E_0 \cos(\omega_0 t)$$

the displacement, and consequently the polarization of the medium, also oscillates in time and can be expressed as

$$P(t) = \epsilon_0 (\chi^{(1)} E(t) + \chi^{(3)} E^2(t) + \chi^{(3)} E^3(t) + \cdots).$$

Here, $\epsilon_0$ is the vacuum permittivity, and $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(3)}$ are the linear, quadratic and cubic terms of the susceptibility, respectively.

In weak electric fields, the linear term in Eq. (4.6) is the dominating one. However, if the electric field becomes strong the higher order terms are no longer negligible and have to be taken into consideration. As a result, the polarization will contain terms which oscillate at integer values $n$ of the fundamental frequency $\omega_0$. Since the polarization of the atoms can be viewed as oscillating dipoles, radiation with frequencies $n\omega_0$ (or wavelengths $\lambda = 2\pi/(n\omega)$, $c$ being the speed of light) will be generated in the process.

A commonly used setup for performing HHG is to focus the light from a pulsed laser into a gas cell containing a noble gas. Using a high power laser, in combination with a tight focus, can create a sufficiently high power density at the focus so that a number of higher harmonics are generated in the process. HHG in noble gases reaching wavelengths close to the water-window ($\sim2$-5 nm) has been demonstrated [67]. Experimental setups, with repetition rates and photon flux sufficient for performing photoemission experiments, applying the 27th [68] and the 21st [69] harmonic of 800 nm (resulting from HHG in argon) also exist. However, generation of these high harmonics require power densities on the order of $10^{13} - 10^{15} \text{ W/cm}^2$. Such intensities are currently only achievable using ultra-short pulses, usually in the femtosecond range. Systems capable of providing femtosecond pulses with high
4.2. LIGHT SOURCES FOR PHOTOEMISSION EXPERIMENTS

4.2.4 Principle of monochromation and monochromators

Although the synchrotron radiation produced in an undulator has a limited bandwidth the energy range of the beam is still too large for the light to be directly used in high-resolution photoemission experiments. Also, due to the low conversion efficiency of the HHG process used to convert the light from a laser into higher energies the output from such a process consists of a mixture of the primary frequency and all of the generated harmonics. In both of these cases a filtering of the light, i.e. a narrowing of the bandwidth, is required before passing the light on to the experimental stations. A common way to perform monochromation in the vacuum ultraviolet (VUV) range (10 nm < \( \lambda < 200 \) nm) is to use diffraction gratings. Since radiation incident on a plane laminar grating is diffracted through different angles based on the wavelength of the light, this provides a convenient way of separating the different components of the radiation. The grating equation describes the diffraction of radiation with wavelength \( \lambda \) incident at an angle \( \theta_i \) on a grating with period \( d \),

\[
d(sin \theta_i + sin \theta_m) = m \lambda. \tag{4.7}
\]

Here, \( m = 0, \pm 1, \pm 2, \ldots \) and is an index representing the order of the diffraction maximum, the corresponding angle of the maximum is given by \( \theta_m \). For normal

pulse energies typically have repetition rates < 10kHz. Although providing sufficient flux to enable photoemission experiments, the photoelectron intensities in such laser based systems are much lower than achievable with, for example, synchrotron light sources.
incidence, $\theta_i = 0$, the diffraction angle for the $m$:th order maximum is given by

$$\theta_m = \arcsin \left( \frac{m \lambda}{d} \right). \tag{4.8}$$

From Fig. 4.7b), we see that the diffraction angle for the 1st order maxima increases for longer wavelengths. Thus, for the case of two discrete wavelengths from a HHG process, blocking all angles except from an angular range close to one of the maxima allows one to filter out the desired wavelength. For synchrotron radiation, which consists of continuously distributed wavelengths, the angular width which is selected, in combination with the grating period, determines the band width of the filtered light.

### 4.3 Thin film fabrication techniques

There are several different techniques which can be used for deposition and growth of thin films of various types of materials. The most widely used are sputter deposition, molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) [70]. The choice of growth method depends partly on which materials should be deposited but also on the crystalline requirements of the film. Throughout the work presented here, we have been interested in epitaxially grown thin films of high crystalline quality, thus the MBE technique has been chosen.

#### 4.3.1 Electron beam evaporation

One simple way of performing MBE growth is to use an electron-beam evaporator (e-beam evaporator). In this type of evaporator the source material is heated by a beam of electrons, the latter which is emitted from a filament. As the temperature rises, the source material starts to evaporate and a series of apertures result in a well defined beam of molecules leaving the evaporator. By placing a substrate in the beam path, the evaporated material can be deposited onto the substrate. The evaporator used in this particular work has three independent cells which allows different materials to be co-evaporated onto the same substrate. Flux monitors, measuring the ion current from a cylinder through which the beam passes, enables the rate of evaporation to be monitored.

Since different materials have different melting points and vapor pressures the temperature of the cells need to be set according to the type of material used and the desired rate of evaporation. The heating power is controlled by the emission current, i.e. the current of electrons emitted by the filament which hit the crucible containing the source material. Controlling the emission current is done by adjusting the filament current and the high voltage applied between the filament and the crucible. Table A.1 in Appendix A summarizes the material properties relevant for e-beam evaporation of the elements used to grow the TI thin films in this study.
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4.3.2 Quartz crystal monitor: the microbalance

When using an e-beam evaporator for growth of thin films consisting of several types of elements, both the ratio of the elements and the rate of deposition on the substrate need to be controlled. The former is essential in order to achieve the correct stoichiometry while the latter determines the thickness of the film. For this purpose, a quartz crystal monitor (QCM), or microbalance, can be used. A microbalance is a quartz crystal which is set into a vibrating motion at the resonance frequency by applying an AC voltage across it. The resonance frequency is determined by the shape and mass of the crystal. If a thin layer of a material is deposited onto the crystal its total mass will be slightly altered, thus changing the resonance frequency. The change in frequency allows one to calculate the added mass and if the density $\rho$ of the deposited material is known, the thickness of the layer can be determined. Additionally, one needs to know the $z$-ratio of the deposited material, which is the ratio of the acoustic impedance of the material relative that of quartz and is a measure of the damping of sound waves in a material. Values for $\rho$ and the $z$-ratio for most materials can be found in literature [34, 71]. Table B.1 in Appendix B lists these values for the materials used in our study. A QCM is sensitive to very small changes in the resonance frequency and, consequently, very small masses can be detected, making sub-monolayer depositions feasible.
4.3.3 Low-energy electron diffraction (LEED)

Once the thin films are grown, one would like to check the crystallographic quality of the samples. If a sample is of high quality, the atomic structure is well ordered which means that the position of the atoms on a clean surface of the material also will display a periodic well ordered structure. The arrangement and periodicity can be determined by observing the diffraction pattern created by electrons which are elastically back-scattered from the surface of the sample.

In order to be able to resolve the atomic positions, the de Broglie wavelength $\lambda_{dB}$ of the primary electrons must be on the order of the inter-atomic distances, i.e. $\lambda_{dB} \sim 1$ Å - 2 Å. The de Broglie wavelength of an electron, expressed in terms of its kinetic energy in electron volts, is given by

$$\lambda_{dB} = \frac{h}{mv} \approx \frac{12.3}{\sqrt{E_eV}} \text{ Å}. \quad (4.9)$$

Consequently, the kinetic energies of the incoming electrons can range from approximately 30 eV to a few hundred electron volts.

The geometry of a LEED setup is sketched in Fig. 4.9. The incoming and back-scattered electrons can be described as plane waves with wave-vectors $k$ and $k'$, respectively. Bright diffraction spots appear on the fluorescent screen when the incoming and scattered wave-vectors satisfy the Laue condition, $k' - k = G$, where $G$ is a reciprocal lattice vector. Since the surface is a two-dimensional structure, there will be no diffraction condition in the direction perpendicular to the surface.
The Laue condition can then, more specifically, be expressed as \( k'_\parallel - k_\parallel = G_{hk} \), where \( k_\parallel \) and \( k'_\parallel \) are the in plane components of the wave vectors and \( G_{hk} = h\mathbf{b}_1 + k\mathbf{b}_2 \) is a vector in the two-dimensional reciprocal lattice of the surface with basis vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \). The direct lattice, which describes the real space position of the atoms, is determined by a set of lattice vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \). The reciprocal lattice is then expressed in terms of the direct lattice vectors through the relations
\[
\begin{align*}
\mathbf{b}_1 &= 2\pi \frac{\mathbf{a}_2 \times \hat{e}_\perp}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{e}_\perp)} \quad (4.10a) \\
\mathbf{b}_2 &= 2\pi \frac{\hat{e}_\perp \times \mathbf{a}_1}{\mathbf{a}_1 \cdot (\mathbf{a}_2 \times \hat{e}_\perp)} \quad (4.10b)
\end{align*}
\]
Here \( \hat{e}_\perp \) is a unit vector parallel to the surface normal. Thus, the observed diffraction pattern on the screen reflects the real space configuration of the atoms on the surface of the sample.
Chapter 5

Development of an experimental setup for high resolution laser-based ARPES

As discussed in the introduction, the energy resolution of photoelectron spectrometers has dramatically improved during the past decades. Along with this development there has also been an evolution of the “dimensionality” of the technique. Initially, the analyzers only covered a narrow range of emission angles or alternatively integrating over a broader angular interval. Dispersive features then had to be mapped out point-by-point by rotation of the sample or the analyzer. In the 1980’s, hemispherical analyzers with angle-resolving capabilities were developed [72, 73] providing the possibility to measure a range of emission angles in parallel. As explained in chapter 4, this technique maps out the dispersion along a line in the Brillouin zone and ultimately dramatically improved the achievable momentum resolution. With the latest development of angle resolving Time-of-Flight analyzers, using delay-line detectors with high spatial resolution, the technique has become “three-dimensional”. Electrons emitted within a solid angle can be collected and analyzed in parallel, thus enabling measurement of the energy dispersion over a plane in the Brillouin zone.

In this chapter we present our work related to the development of an experimental photoemission setup (given the name BALTAZAR) with high energy and angular resolutions. The novelty of the instrument stems primarily from two properties; i) the spectrometer is an angle-resolving TOF analyzer with high angular resolution, covering acceptance angles up to ±15 degrees, ii) a high repetition rate laser system in the effective range 0.2 MHz - 1 MHz is used as light source, which after frequency conversion delivers a photon energy of 10.5 eV. In the following sections, an overview of the developed system will be given. Additionally, some of our major findings regarding the characteristics and performance of the system are presented. The latter is meant to give a brief introduction to a few important issues which
CHAPTER 5. DEVELOPMENT OF AN EXPERIMENTAL SETUP FOR HIGH RESOLUTION LASER-BASED ARPES

need to be dealt with when performing angle-resolved measurements with a TOF analyzer.

5.1 Overview of the experimental setup

5.1.1 Light source

The starting point of the light source is a pulsed high-power diode laser, a FUEGO laser from Time-Bandwidth Products. It delivers 10 ps pulses at a wavelength of 1064 nm (IR) with a selectable repetition rate between 0.2 MHz and 8 MHz. At 200 kHz, the maximum average output power from the first stage is 15 W. An amplifier is then used to increase the maximum output IR power to 45 W at 200 kHz. After the amplification, the light is converted from 1064 nm to 355 nm by a two-step process consisting of second harmonic generation (SHG) and sum-frequency generation (SFG) in non-linear crystals. The output from the conversion stage consists of 10 ps pulses of 355 nm photons with a maximum average power of 15 W at 200 kHz resulting in a pulse energy of 75 $\mu$J. The photon energy of the 355 nm light is 3.5 eV which is too low use in most photoemission experiment. Therefore, a second conversion stage follows the laser system, converting the light into photons with sufficient energy to create photoelectrons. This second conversion relies on a higher harmonic generation (HHG) process performed in a Xe-filled gas cell. Since the HHG process requires a certain minimum pulse energy, and taking into account that the pulse energy of the 355 nm light decreases exponentially with increased repetition rate of the system, the repetition rate of the laser is limited to approximately 800 kHz to 1 MHz. Above this rate, the number of photons generated in the HHG process is too low for any high quality photoemission measurements to be made.

5.1.2 Gas cell and monochromator

The laser system is followed by a gas cell filled with Xe gas where the 355 nm light is converted to a different wavelength through a HHG process. By focusing the light into the cell the power density at the focus becomes sufficient to generate the third harmonic of 355 nm, thus producing photons with a wavelength of 118 nm. The energy of the frequency tripled light is 10.5 eV. In the tripling process, not all of the 355 nm light is converted into 118 nm and, therefore, the two wavelengths need to be separated before the light can be used for photoemission. The wavelength separation, or monochromation, is performed using a grating monochromator.

The geometry of the monochromator setup is presented in Fig. 5.1. First, a refocusing mirror is used to reflect the mixed beam of 355 nm and 118 nm light onto a plane, laminar grating. The grating, having a line density of 360 lines per mm, results in the different diffraction maxima of the two wavelengths being well separated in angle. This enables us to let the first-order maxima of the diffracted 118 nm pass through a circular aperture at the exit of the monochromator and
5.1. OVERVIEW OF THE EXPERIMENTAL SETUP

Figure 5.1: Geometry of the monochromator used in the BALTAZAR setup.

subsequently in the direction of the sample. All other diffraction maxima for both
wavelengths are blocked from leaving the monochromator and thus only the 118 nm
light reaches the sample.

Due to the high average output power of the laser, there will be a high heat
load on the optical components in the monochromator. Initially, MgF$_2$-coated
Al mirrors and gratings on silica substrates were used. However, due to the low
thermal conductivity of silica these components experienced beam damages over
time. Therefore, Si substrates with SiC coating (both materials having high thermal
conductivity) have been used for mirrors and grating. Additionally, a 0.5 mm thick
LiF window is used to separate the monochromator from the ultra-high vacuum
(UHV) measurement chamber where the photoemission experiment takes place.
This relaxes the requirements of differential pumping of the monochromator and
contributes to maintain a UHV environment in the analysis chamber, preventing
rapid contamination of the sample. LiF$_2$ is transparent for radiation with energy
below approximately 11 eV, something which enables it to be used as an output
window in our setup with 10.5 eV without absorbing too much of the radiation.

Motorized step motors mounted on the grating enables the beam position in
the analysis chamber to be adjusted. This is important for correct alignment of the
beam spot and the focus of the electron analyzer, something which will be discussed
in more detail below.

5.1.3 Time-of-flight electron analyzer

The most central part of the BALTAZAR system is the electron analyzer, a Themis
1000 from SPECS GmbH. The analyzer consists of a multi-element electrostatic
lens, which collects electrons emitted from the sample within a solid angle of up to
±15 degrees, and a two-dimensional electron detector. Time-of-flight analyzers are
not a new invention; they have been used in the past for photoemission experiments,
mostly for time-resolved studies [74, 75, 76]. However, these have been using either
CHAPTER 5. DEVELOPMENT OF AN EXPERIMENTAL SETUP FOR HIGH RESOLUTION LASER-BASED ARPES

Figure 5.2: a) Flight paths of electrons with different emission angles from the sample through the electrostatic lens. The delay-line detector is capable of determining the striking position and striking time of each electron. b) Definition of emission angles of a photoemitted electron. c) An electron hit on the detector can be described by a radial distance \( r \) and a polar angle \( \phi \) in addition to the striking time \( t \).

single anode or multi-anode detectors which provides only limited angular resolution. It is only very recently that TOF spectrometers, such as the Themis 1000 and the Scienta AR TOF, using two-dimensional electron detectors with a spatial resolution comparable to the ones found in hemispherical electron analyzers have become available.

Since the TOF measures flight times, the detector must be able to detect the striking time of each electron. Therefore, time resolutions on the order of ns or better are desirable. For each electron, the striking position \((x, y)\) on the two-dimensional detector and the striking time \(t\) are stored. This information is then compared to a pre-calculated conversion matrix which transforms the \((x, y, t)\)-coordinates into emission angles and kinetic energies. The lens is assumed to be rotationally symmetric around its center axis, so only the radial distance from the center of the detector and the time of the electron hits are relevant for the conversion. The radial distance is given by \( r = \sqrt{x^2 + y^2} \), where \( x \) and \( y \) are the coordinates on the detector and the conversion center of the detector is set to \((x, y) = (0, 0)\). After comparison of \( r \) and \( t \) values for the electron events with the conversion matrix, the software presents the data in a three-dimensional matrix consisting of one energy and two angular dimensions. The two angles \((\alpha_i)\) are defined as \( \alpha_x = \theta \cos \phi \) and \( \alpha_y = \theta \sin \phi \), where \( \phi = \arcsin(y/r) \). Consequently,
\[ \theta = \sqrt{\alpha_x^2 + \alpha_y^2} \] is the emission angle of an electron relative to the optical axis of the lens. Conversion of the data from angle and energy to parallel momentum \((k_{\parallel})\) and energy can then be done using Eq. 4.2, resulting in

\[
\begin{align*}
k_x &= k_{\parallel} \cos \phi = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \theta \cos \phi \quad (5.1) \\
k_y &= k_{\parallel} \sin \phi = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}}} \sin \theta \sin \phi. \quad (5.2)
\end{align*}
\]

### 5.2 System characteristics and performance

#### 5.2.1 Typical spectrum

As mentioned in the previous section, the measured data are presented in a three-dimensional matrix with one energy and two angular coordinates. Figure 5.3 displays a 3D representation of the data from a measurement of the surface state of Au(111) [41, 24] after conversion to energy and momentum. The data are plotted as constant intensity surfaces. By studying these data one realizes that for the Au(111) surface state, or two-dimensional systems in general, this type of analyzer is particularly advantageous since it allows the entire two-dimensional band structure to be measured in one single “shot”, provided that it is covered by the ±15 degrees angular range of the analyzer. Moreover, using higher photon energies, one can cover the entire Brillouin zone of two-dimensional systems in one measurement.

#### 5.2.2 Photon flux and spot size

The two most important characteristics of the light source are the photon flux of the 10.5 eV photons and the size of the light spot on the sample. We have determined the latter by measurements on a polycrystalline Au sample using the high-magnification lens mode of the analyzer. This lens mode gives the spatial distribution of the origin of the photoelectrons with a magnification of ten times. In this way, the footprint of the photon beam on the sample can be observed and the spot size can be directly determined.

Figure 5.4a) shows a detector image of the light spot on the sample. Intensity profiles along the horizontal and vertical directions through the center of the spot are also presented. We define the spot size as the average FWHM of the intensity profiles. Thus, the spot size for this particular setup is 200 \(\mu\)m.

Figure 5.4b) displays the flux of 10.5 eV photons at the sample position as a function of Xe-gas pressure in the gas cell. The flux has been measured at the lowest repetition rate, i.e. 200 kHz. We observe that a maximum photon flux of \(9 \times 10^{12}\) photons per second is obtained for a Xe pressure of 7 mbar. The flux has also been measured using two different gratings, one Pt-coated and one solid SiC grating. The absolute value of the photon flux has been determined by measuring
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Figure 5.3: Sample spectrum of the surface state on Au(111). a) Three-dimensional plot of constant intensity surfaces extracted from the 3D data matrix. Slices indicated in the figure along the constant energy and energy-momentum directions are displayed in b) and c), respectively. d) Fitted peaks to a momentum-distribution curve (MDC) taken at $E_F$ in c).

Figure 5.4: a) The beam spot on the sample imaged using the high-magnification lens mode of the analyzer. b) Obtained photon flux as a function of Xe gas pressure for the SiC and Pt gratings.
the photocurrent from a Au foil placed in the beam path. The photoelectric yield
of Au at 10.5 eV, needed to translate the value of the photocurrent into photons,
was calibrated using a Si photodiode and a Au mesh with known surface area.

5.2.3 Analyzer-sample work function difference

The time-of-flight analyzer determines the kinetic energy of the photoelectrons
based on their flight time through the system. This technique is therefore sensitive
to any potential difference between the sample and the analyzer. The existence
of a potential difference, arising from different values of the work function for the
spectrometer and the sample, results in an electric field between the sample and the
entrance of the lens. Consequently, the electrons experience either acceleration or
retardation in this region. The resulting change in kinetic energy of the electrons
may render the conversion matrix inaccurate. Therefore, to achieve a field free
environment between sample and analyzer one needs to compensate for any work
function difference by applying a voltage either to the sample or the spectrometer.

In the BALTAZAR system, one has the possibility of applying a so called suction
voltage $U_{\text{suc}}$ to the spectrometer. In order to determine to correct value of $U_{\text{suc}}$
we have used the low energy cutoff $E_{\text{min}}$ which consists of electrons leaving the
sample with very low kinetic energies. In other words, these electrons have binding
energies which are close to $h\nu - \phi$. The low energy cutoff is measured as a function
of positive $U_{\text{suc}}$ and from these values extrapolated to $E_{\text{min}} = 0$ eV. The resulting
value of $U_{\text{suc}}$ then equals the work function difference.

We have systematically investigated the effect of uncompensated work function
difference on the measured dispersion from the Au(111) surface state in order to
establish what are the consequences and with what accuracy the value of $U_{\text{suc}}$ has
to be determined. First, using the approach described above the correct suction
voltage was found to be $U_{\text{suc}} = -0.16$ V. Figure 5.5a) displays the dispersion along
the $k_x$ direction through $\Gamma$ for the suction voltages $-0.16$ V, 0 V and 0.2 V, where
zero on the energy scale refers to $E_F$ in the measurement using the correct suction
voltage. As $U_{\text{suc}}$ is changed, one can observe that the spectrum shifts in kinetic
energy. The left panel of Fig. 5.5b) displays fitted MDC peak positions as a function
of binding energy of the unconverted data from the measurements using different
values of $U_{\text{suc}}$.

The data reveal that the angular range covered by the surface state increases
for the spectrum shifted towards lower kinetic energies (negative $U_{\text{suc}}$). By converting all data sets to momentum and energy using Eq. (4.2) we can extract new
MDC peak positions and plot these as a function of binding energy. The result
is presented in the right panel of Fig. 5.5b) and shows, surprisingly, that there
is no apparent difference in the converted results of the different measurements.
Parabolic fits to the extracted peak positions result in values for the effective mass,
the minimum energy of the surface state (bottom of parabola) and the displace-
ment from $\Gamma$ in momentum of the minimum of the parabola of $0.30m_0$, 480 meV
and 0.0146 Å$^{-1}$, respectively, where $m_0$ is the free electron mass. The discrepancy
Figure 5.5: a) Energy-\( \alpha_x \) spectra (\( \alpha_y = 0 \)) of the Au(111) surface state for different values of \( U_{\text{suc}} \). b) Extracted MDC peak positions and fitted parabolas for both non-converted (left panel) and converted (right panel) data using the indicated values of \( U_{\text{suc}} \).

In these values between the measurement with the correct \( U_{\text{suc}} \) setting and the one with \( U_{\text{suc}} = 0.2 \) V is less than 1 \%. We therefore conclude that, although there is a deviation in the suction voltage of nearly 400 meV, no detectable deviation in the dispersion up to emission angles of \( \pm 10 \) degrees can be detected. However, we expect that a too large deviation between the true and applied value of \( U_{\text{suc}} \) will have an influence on the measured spectrum. At this point in time, no further investigations have been made to find where to draw the limit between an “acceptable” and a “too large” work function discrepancy.
5.2. SYSTEM CHARACTERISTICS AND PERFORMANCE

5.2.4 Defining optical axis and conversion center

The lens used in the electron spectrometer is a so-called electron optical lens, i.e. a lens which collects and focuses (or images) charged particles in the same way as a conventional lens does for visible light. Instead of using lens elements of high-refractive index materials, in the electron lens, electric fields are used to influence the flight path of the electrons, thereby acting as lenses. Similar to an optical lens system, we can define an “optical axis” for the electron lens, which is the trajectory of an electron emitted from the sample with an angle $\theta = 0$ degrees. In a perfect lens, the optical axis and the physical center axis would coincide. However, due to inhomogeneities in the electric fields of a real lens the two are generally not the same. Therefore, in order to be able to use the simulated conversion matrices the optical axis of the system needs to be defined. This is done by defining the position on the detector which corresponds to an emission angle of $(\alpha_x, \alpha_y) = (0, 0)$, or what we call the conversion center. The conversion center might, in other words, differ from the actual center of the detector.

The lens tables of the analyzer are constructed in such a way that electrons can have intermediate foci before hitting the detector. Usually, we are interested in the electronic structure in a material close to the Fermi level. Hence, the kinetic energy and pass energy of the lens are configured in a way so that the electrons in this energy range are spatially distributed on the detector according to their emission angles $\theta$. Outside the conversion “window” (which is roughly determined by $E_{\text{kin}} \pm 0.1E_p$), at lower kinetic energy, electrons with different emission angles can be focused into a single point on the detector. By decreasing the kinetic energy of the lens the conversion window will be shifted towards lower kinetic energies and one can achieve foci both in front (at higher $E_{\text{kin}}$) and after (at lower $E_{\text{kin}}$) the conversion window. If the beam spot on the sample is not aligned with the optical axis of the lens, the high and low kinetic energy foci will be in different positions on the detector. The point on the detector where the two foci are aligned defines the conversion center and the software should use this point as $(\alpha_x, \alpha_y) = (0, 0)$.

5.2.5 Determining correct working distance

If the distance between the sample and the analyzer is not correct, one can still adjust the beam so that the beam spot on the sample lies on the optical axis. However, seen by the analyzer, the sample will be out of focus, something which could compromise the energy and angular resolutions. In order to determine the correct working distance we have used the fact that the kinetic energy of the detected electrons are determined by their time-of-flight along a pre-calculated path between the sample and the detector. Moving the sample closer to the analyzer shortens the effective path length, thus resulting in an apparent increase of the electrons’ kinetic energy. Additionally, the path length also changes when the lens settings, such as kinetic energy and pass energy, are altered. Using the correct working distance, and proper alignment of the beam, the measured kinetic energy of the Fermi level
in a material should be independent of pass energy.

Measurements of the kinetic energy of $E_F$ in a polycrystalline Cu sample as a function of $x$-coordinate on the manipulator are presented in Fig. 5.6. The $x$-axis of the manipulator is parallel to the center axis of the lens and increasing $x$-values indicate that the sample is moved closer to the analyzer. The measurement is repeated for several pass energies. For the wide-angle mode (WAM) with $U_{suc} = 0$ V, the three measurement series intersect at $x = 30$ mm. This value of $x$ is therefore the correct sample position. We also observe that applying a negative $U_{suc}$ voltage changes the correct working distance to $x = 28$ mm.

Worth noting is that when performing measurements it is not the $x$-position itself which is of relevance but rather the actual distance between the sample surface and the analyzer. The measurements presented here were performed using a solid Cu sample holder with a total height of 17.8 mm. Depending on which holder is used, and the thickness of the sample mounted on it, the total height from the bottom of the sample holder to the surface of the sample might be smaller or larger than 17.8 mm. Consequently, the $x$-position setting on the manipulator needs to be adjusted accordingly.

One could also imagine that the spatially resolving lens mode of the analyzer could be used to find the correct working distance. The size of the light spot on the sample experiences a minimum when in focus of the analyzer. However, since the different lens modes are expected to have their foci at different $x$-positions
5.2. SYSTEM CHARACTERISTICS AND PERFORMANCE

Figure 5.7: a) Energy-angle cuts along the $x$ and $y$ directions along with a constant energy cut close to $E_F$ for a measurement of the Au(111) surface state in which the light spot on the sample is not aligned with the optical axis of the lens. b) Illustration of how a misalignment can be generated by not placing the sample at the correct working distance.

we have determined the working distance using the actual lens mode with which measurements are performed.

5.2.6 Effects of misaligned sample and light spot

The procedure of aligning the beam spot on the sample with the optical axis of the analyzer has already been described. Figure 5.7a) presents photoemission spectra from a measurement of the surface state on Au(111) where the beam spot has been deliberately moved away from the correctly aligned position. The observable effect of this misalignment is a “tilt” of the spectrum, as most clearly seen from the upper left panel in Fig. 5.7a), where the Fermi level is not straight. The substantial tilt in the spectrum is also visible in the constant energy slice displayed in the lower panel of Fig. 5.7a), showing a Fermi surface having the shape of a half circle rather than a full circle, which demonstrates the importance of proper alignment.

Misalignments like the one presented here can have a large impact on the apparent energy resolution of the measurement. Imagine, as an example, that one performs a measurement of the Fermi edge of polycrystalline Au with the purpose of determining the energy resolution of the instrument. If the Fermi level is tilted, integration over all angles on the detector will result in a broadening of the edge,
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Figure 5.8: a) The energy resolution of the system determined by measurements of the Fermi edge on polycrystalline Au. b) Detected peak from photoelectrons generated at the detector by scattered light from the sample. The width of the peak represents the time resolution of the detector.

thereby giving a “false” measure of the system’s energy resolution.

The procedure we have used to ensure proper alignment is to first do a rough alignment of the high and low kinetic energy foci, as discussed in section 5.2.4. Then, by using the step motors on the monochromator grating, the beam position on the sample is adjusted until the Fermi level is no longer tilted. Clearly, the light beam cannot enter the system parallel to the optical axis of the analyzer, but rather at an angle. This implies that if the sample is moved closer to or further away from the analyzer (parallel to the optical axis) the beam spot will wander on the sample, see Fig. 5.7b). Hence, the misalignment created in this way has the same effect on the spectrum as the one presented in Fig. 5.7a). Therefore, before starting the alignment procedure, one must make certain that the sample is at the correct working distance.

5.2.7 Energy and momentum resolution

We have determined the overall energy resolution of the system by measuring the width of the Fermi edge of a polycrystalline Au sample, kept at a temperature of $T = 9\, \text{K}$. The result is presented in Fig. 5.8a). When integrating over all angles on the detector, we find an energy resolution $< 5\, \text{meV}$. The resolution is determined by fitting a convolution of a Gaussian function and the Fermi-Dirac distribution (at $T = 9\, \text{K}$) to the measured data. The FWHM of the Gaussian is then taken as the energy resolution of the system.

The time resolution of the detector could possibly influence the energy resolution. Figure 5.8b) displays the measured electron peak generated by photoelectrons created in the detector by light scattered from the sample. We define the time res-
olution $\Delta t$ of the system as the FWHM of the measured peak, consequently giving $\Delta t = 185$ ps. With this time resolution, the simulated energy resolution at a kinetic energy of $E_{\text{kin}} = 5.8$ eV and pass energy $E_p = 2$ eV using the WAM mode is $\Delta E = 2$ meV. To reach an energy resolution of $\Delta E = 5$ meV a time-resolution of $\Delta t = 470$ ps is required. This indicates that the measured energy resolution is not limited by the time resolution of the detector. Further, the estimated energy resolution of the light is $\Delta E_{\text{th}} = k_B T \sim 0.8$ meV. We have discovered that the energy resolution is greatly influenced by the electrical connection between the analyzer and the top of the manipulator which holds the sample. Removing the grounding cable connecting these two parts results in an energy resolution of approximately $20$ meV $- 40$ meV. This suggests that the energy resolution might be limited by poor grounding or by other electrical noise in the system.

The angular resolution is determined by measurements of the surface state of Au(111) (data shown in Fig. 5.3d)). By determining the FWHM of MDC peaks, an angular resolution of 0.8 degrees\(^1\) is found at a kinetic energy of 5.45 eV. This translates into a momentum resolution of $\Delta k = 0.0168$ Å\(^{-1}\).

### 5.2.8 Sample temperature calibration

The BALTAZAR system is equipped with a 4 K closed cycle cryostat. However, the cooling rod is extended with a solid copper rod in order to reach the sample position in the vacuum chamber and thus, the temperature at the sample is expected to be higher. We have measured the temperature at the sample position by attaching a diode sensor to a sample holder and fastening it at the end of the cooling rod. Simultaneously, the temperature at a position approximately 100 mm away from the sample, on the copper rod, is measured by another diode. Since the latter diode is always mounted in the same position this temperature read-out is used as a reference. The sample temperature as a function of the reference temperature is plotted in Fig. 5.9. We see that only below 15 K does the temperature on the sample deviate noticeably from the reference.

\[^2\text{This is the upper limit of the angular resolution. Since the measured MDC width confirms previous measurements on Au(111) [41, 24, 77] the limiting factor in this case could be the sample and not the actual resolution of the instrument. However, as a worst case estimate, we use the obtained MDC width as our angular resolution.}\]
Figure 5.9: Calibration curve of the sample temperature ($T_s$) as a function of reference temperature ($T_{ref}$). The latter is continuously monitored by the temperature controller attached to the sample manipulator.
Chapter 6

Experimental investigations of TIs and TCIs

6.1 Experimental realization of TI thin films

For the purpose of studying interface related phenomena in topological insulators, thin-film samples are ideal for two main reasons. Firstly, the films can be grown on a variety of substrates, thus providing the possibility to create interfaces between TI and either topologically trivial or other TI materials. Secondly, by using ultra-thin films, i.e. films in the thickness range of 1 QL to 8 QL, buried interfaces can be probed directly by photoemission experiments provided that low photon energies and cryogenic sample temperatures are used. In this particular study, thin-film samples of varying thicknesses of the binary compound TIs Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ have been grown. Although the possibility of growing these TIs on a number of different substrates has been demonstrated [48, 46, 49, 50], we here focus on one single type of substrate, namely Si(111), and investigate the effect of the type (p or n) and level of doping of the substrate on the electronic structure of the TI films.

6.1.1 Fabrication of TI thin film samples

Bi$_2$Se$_3$

The process of fabricating TI thin-film samples starts with preparations of the silicon substrate. When exposed to air, the Si(111) surface forms a natural oxide layer which needs to be removed before the TI film can be grown. This is done by repeated cycles of annealing where the substrate temperature is quickly flashed up to approximately 1100 °C. In our case, the heating was controlled by running a direct current through the Si substrate and the temperature was checked using a pyrometer with the emissivity set to 0.57. This procedure resulted in a (7 × 7) reconstruction of the Si(111) surface, which could be observed using LEED, see Fig. 6.1. Subsequently, the reconstructed surface was terminated by an ultra-thin layer of bismuth (1 ML) resulting in a (\sqrt{3} × \sqrt{3})R30° reconstruction. The Bi layer
was deposited using e-beam evaporation while keeping the substrate temperature at 490 °C to 500 °C. The substrate temperature was then lowered to approximately 260 °C to 270 °C and growth of Bi₂Se₃ was initiated by co-evaporation of Bi and Se. Prior to the growth, the deposition rates of Bi and Se was determined using a QCM.

Repeated attempts showed that the $n$-type doping of the films decreased and the spectral quality improved when using a large Se overdose (up to 80 percent more than the stoichiometric 2:3 ratio of Bi and Se) and intermediate substrate temperatures. For substrate temperatures $< 200$ °C diffuse LEED patterns were observed which in some cases could be improved by post annealing. This indicates that there might be an excess of Se which is partly reduced by the annealing process. However, the quality of such films could never match that of films grown at a higher initial temperature.

**Bi₂Te₃**

By substituting Se with Te in the growth recipe described above, we have been able to grow Bi₂Te₃ thin films. Also here, co-evaporation of Bi and Te using a large Te overdose resulted in the best quality and reasonably low $n$-doped samples, c.f. section 6.2. A LEED pattern from a Bi₂Te₃ film is shown in Fig. 6.1d).

**Sb₂Te₃**

Using the same starting point as with Bi₂Se₃ and Bi₂Te₃ we have grown Sb₂Te₃ films on $n$-type doped Si(111) substrates. However, termination of the Si(111)-(7 × 7) surface was done using Sb instead of Bi. Achieving a $(\sqrt{3} \times \sqrt{3})$R30° reconstruction by means of Sb termination is possible by carefully controlling the both the substrate temperature and the amount of deposited Sb [78]. Evaporation of 1 ML Sb,
6.1. EXPERIMENTAL REALIZATION OF TI THIN FILMS

keeping the substrate temperature at 650 °C resulted in the desired reconstruction, as seen in Fig. 6.2. Subsequent deposition of Sb and Te by co-evaporation under Te rich conditions, and at a substrate temperature of 200 °C, was used to grow the Sb$_2$Te$_3$ films.

As seen from the LEED pattern in Fig. 6.2c), there is a weak ring connecting the bright diffraction spots. This ring can also be observed in Bi$_2$Se$_3$ samples where the Bi termination of the Si(111) surface is insufficient or absent [48] and reveals the existence of domains with different in-plane orientation (twinning). The existence of a ring in the LEED pattern of our Sb$_2$Te$_3$ films indicates that twinning is also present in these cases, most likely as a result of a non-complete Sb termination of the Si(111) surface.

6.1.2 Characterization of thin films by ARPES

An indication of the crystalline quality of a TI film directly after growth can be obtained from observations of LEED patterns, as demonstrated in the previous section. However, this technique gives no information regarding the quality of the interface or the level of doping of the film. Therefore, to confirm that our growth process results in samples of high quality we use ARPES to observe the surface state band structure and evaluate the quality of the sample based on the sharpness of the observed spectral features.

Figure 6.3 presents photoemission data of Bi$_2$Se$_3$, Bi$_2$Te$_3$ and Sb$_2$Te$_3$ where each of the spectra are representative for the typical sample quality obtained for the three types of TIs using the described growth procedure. In Fig. 6.3a) we see that Bi$_2$Se$_3$ has a single Dirac cone surface state located at $\bar{\Gamma}$ with the Dirac point at a binding energy of approximately 250 meV. This indicates that the sample is lightly $n$-doped and contains relatively few Se vacancies. Due to the low doping of
the sample the Fermi surface, depicted in the lower panel of Fig. 6.3a), experiences only a small hexagonal warping [79].

The Bi$_2$Te$_3$ sample, on the other hand, has the Dirac point located nearly 700 meV below $E_F$ and is thus highly $n$-doped. This particular sample was grown at a temperature $T < 200$ °C and post-annealed to improve the LEED pattern, something which could possibly explain the high doping level, assuming that the sample loses Te during the annealing process\(^1\). Due to the large doping, the Fermi surface seen in the lower panel of Fig. 6.3b) is clearly hexagonal with the corners of the hexagon pointing in the $\Gamma - M$ direction.

For the Sb$_2$Te$_3$ sample presented in Fig. 6.3c) the situation is different. Whereas both Bi$_2$Se$_3$ and Bi$_2$Te$_3$ become $n$-doped due to Se or Te vacancies, Sb$_2$Te$_3$ grows naturally $p$-doped. Therefore, in the data presented here, only the “lower part” of the Dirac cone is observed which means that the Dirac point is not visible.

From the spectra presented in Fig. 6.3 we can conclude that the quality of the films are good although the general trend is that Bi$_2$Se$_3$ results in films with higher quality than the two other types. Worth noting is that the spectra of Bi$_2$Te$_3$ and Sb$_2$Te$_3$ were acquired at room-temperature whereas the Bi$_2$Se$_3$ was measured at

\(^1\)Bi$_2$Te$_3$ samples which have not been post-annealed, e.g the ones presented in section 6.2.3, show significantly less doping.
a sample temperature of $T = 9$ K. Also, the Bi$_2$Se$_3$ spectrum is measured using 10.5 eV photons, the Bi$_2$Te$_3$ at 22 eV and Sb$_2$Te$_3$ at 17.5 eV. Consequently, the spectral intensity of the surface states should not be directly compared between the different films and a reduced intensity of these states does not necessarily indicate an inferior quality of the film.

6.2 Interface states

The results in the previous section confirm that our fabrication technique produces thin films of high quality. This enables us to take on more advanced studies of TI thin films involving interface states. More specifically, we have studied two main types of interfaces; i) the interface between a TI thin film and the substrate and ii) the interface between two different types of TI thin films. A common experimental challenge for both types of interfaces is that the electronic states, which we would like to access, are not located at the surface of the sample. Using ARPES, probing these states can prove difficult due to the short escape depth of the photoelectrons. However, in spite of these challenges we have, by using low energy photons ($h\nu = 10.5$ eV) in combination with cryogenic sample temperatures, been able to directly measure the electronic structure of buried interface states.

6.2.1 Interface between a TI and a normal insulator

Growing the TI films on Si(111) substrates directly results in a normal insulator-TI interface. This interface should also host helical Dirac fermions similar to the vacuum side surface of the thin film. Previous studies have observed hybridization effects in Bi$_2$Se$_3$ films with thicknesses $< 6$ QL [51, 52]. These effects suggest the presence of interface states, although no direct observation of such states in non-hybridized films have been made. Therefore, it is of fundamental interest to confirm the presence of topological interface states in non-hybridized films and consequently the existence of a topological state at the interface between a normal insulator and a TI.

Figure 6.4a) displays normalized photoemission-intensity plots of a 6 QL Bi$_2$Se$_3$ film grown on a $n$-type Si(111) substrate. In the spectrum, two Dirac-like states are visible. Remembering the discussion from section 2.4, describing how the states on opposite sides of a thin film would be shifted in energy with respect to each other due to the presence of the substrate, we realize that the data suggest that we indeed observe the interface state. The outer, large V-shaped state, is in this case the interface state whereas the inner, smaller state, is the state arising from the surface of the film. Fitting the simple two band model from Eq. (2.2) to our experimental data we see that the data are well reproduced by a band structure without any hybridization gap. In other words, the spectrum shows two Dirac cones, “localized”
Figure 6.4: a) Normalized photoemission intensity spectrum of a 6 QL thick Bi$_2$Se$_3$ film displaying Dirac states at both the surface and the interface. Solid and dotted lines are calculated bands for the two states using Eq. (2.2). b) Second derivative plot (Laplacian) of the corresponding non-normalized spectrum. Dashed line shows the interface state part of the calculated band structure in a).

on opposite sides of the thin film. By calculating the Laplacian$^4$ of the spectrum in Fig. 6.4a), we see that the outer state does not display any obvious deviation from the linear dispersion close to the points where the two Dirac states overlap, see Fig. 6.4b). This is taken as further evidence for the non-hybridized nature of the interface state.

6.2.2 Substrate influence on thin film electronic structure

In the theoretical model used to derive Eq. (2.2) the influence of the substrate is included in the parameter $V$, which represents the potential difference between the interface and surface of the film. This potential difference describes the band bending through the film. In this context, two interesting questions that appear are; 1) What does the band diagram for the Bi$_2$Se$_3$-Si heterojunction look like? 2) What determines the magnitude of the band bending in the film?

From our observations of the interface state in the 6 QL Bi$_2$Se$_3$ film, c.f. Fig. 6.4, we can directly determine the magnitude of the band bending. In this case we have $\Delta E_D = 2V = 0.27$ eV. As a first approximation, we assume a linear band bending throughout the film, which is a reasonable approximation due to its limited thickness (roughly 60 Å). The evolution of the valence and conduction band as a function of distance from the sample surface can then be schematically pictured as

\[ L(k, E) = \frac{\partial^2 I(k, E)}{\partial k^2} + \frac{\partial^2 I(k, E)}{\partial E^2}, \]

where $I(k, E)$ is the intensity in a “pixel” with momentum $k$ and energy $E$. 

$^4$
6.2. INTERFACE STATES

Figure 6.5: a) Band bending through the TI thin film shifts the Dirac point energy of the interface state relative the surface state. b) Pinning of the Fermi level at the surface of Bi-terminated Si(111).

...presented in Fig. 6.5a). Hence, there is a downwards band bending going from the surface towards the interface.

In order to construct the full band diagram for the heterojunction, and thereby answering the first of the questions above, we need to know the band offsets ($\Delta E_c$ or $\Delta E_v$) between Si and Bi$_2$Se$_3$ and the Fermi level position relative the conduction and valence band in the Si substrate. Since a heavily doped $n$-type substrate is used ($\rho = 0.004 \, \Omega \, \text{cm}$) the Fermi level inside the bulk lies close to the conduction band. However, for the Si(111) - (7 x 7) reconstruction the Fermi level at the surface is pinned approximately 0.70 eV above the valence band maximum [80, 81, 82], regardless of the bulk position of $E_F$. After deposition of 1 ML Bi the surface Fermi level position is only slightly reduced to 0.65 eV [83]. Consequently, there is an upwards band bending towards the surface in the substrate as indicated in Fig. 6.5b).

As an initial attempt, if we now simply put the two band diagrams for the Bi$_2$Se$_3$ film and the Bi-covered Si(111) substrate together, aligning the Fermi levels, we get $\Delta E_c = 1.09$ eV, see Fig. 6.6b). This is in fact very close to the value of $\Delta E_c = 1.14$ eV one gets by applying the electron affinity rule [84], using $\chi[\text{Si(111)-(7 x 7)}] = 4.16$ eV and $\chi[\text{Bi}_2\text{Se}_3] \approx 5.3$ eV. Accordingly, the good agreement of $\Delta E_c$ obtained using the two different approaches suggests that the band diagram pictured in Fig. 6.6b) is valid. The Fermi level pinning at the surface of the substrate also implies that the bulk Fermi level position, and thus the bulk doping level, does not influence the band bending in the TI film. This is confirmed by measurements of a 6 QL Bi$_2$Se$_3$ film, also displaying both interface and surface states, grown on a $p$-type substrate ($\rho = 0.0009 \, \Omega \, \text{cm}$), see Fig. 6.6a). In this film, the measured band bending is approximately 0.29 eV and the conduction band offset 1.02 eV. The resulting band diagram for this system is displayed in Fig. 6.6c). The value of

---

5 Determined from measurements of the work function of Bi$_2$Se$_3$. 
\[ \Delta E_c \] is close to what we obtained for the \( n \)-type Si case, thus the validity of our proposed band alignment model is further strengthened.

We are now in a position to answer the second question posed above. From the derived band diagrams presented in Figs. 6.6b) and c) we can conclude that the magnitude of the band bending is determined by a combination of the bulk doping of the TI film and the band offset between the Si substrate and Bi\(_2\)Se\(_3\) together with the Fermi level pinning at the interface. By modifying the bulk doping of the TI film, the band bending can be increased or decreased. However, the binding energy position of the Dirac point of the interface state seems to be fixed at roughly 0.7 eV to 0.8 eV for this particular system.

### 6.2.3 TI-TI heterostructures

The second type of interfaces, which we have been studying, is the interface between two different types of topological insulators. By using a two-step growth process, we have been able to create a layered thin film consisting of Bi\(_2\)Se\(_3\) with an overlayer of Bi\(_2\)Te\(_3\). First, the Bi\(_2\)Se\(_3\) film was grown on a \( n \)-type Si(111) substrate using the procedure described in section 6.1.1. Then, a thin layer of Bi\(_2\)Te\(_3\) was added on top of the first film, resulting in a TI-TI heterojunction. Since both materials in the TI-TI junction are topologically non-trivial, there should not be any topologically protected Dirac state at the interface between them. However, there are theoretical predictions of another state at the interface, consisting of faster-than-light particles (tachyons) [19, 18]. Although the possibility of observing
6.2. INTERFACE STATES

Figure 6.7: Deposition of Bi$_2$Te$_3$ films with increasing thicknesses on top of a 8 QL Bi$_2$Se$_3$ film. From left to right the spectra show; the Bi$_2$Se$_3$ film, sample after deposition of 1 QL of Bi$_2$Te$_3$, after deposition of another 2 QLs of Bi$_2$Te$_3$, after deposition of another 4 QLs of Bi$_2$Te$_3$ (a total of 7QLs Bi$_2$Te$_3$).

tachyons in these structures is intriguing, there are other aspects of a topological insulator heterojunction which also are of fundamental interest.

From a topological point of view, the layered Bi$_2$Te$_3$/Bi$_2$Se$_3$ film can be considered as a single TI having boundaries towards topologically trivial materials in the form of the substrate on one side and vacuum on the other. In this particular case, the interface towards the substrate consists of a Bi$_2$Se$_3$-Si junction, which we studied in the previous section, and the top surface of the film is a plain Bi$_2$Te$_3$-vacuum interface. From our previous results we have established that the Dirac state at the substrate interface of an ordinary Bi$_2$Se$_3$ film exhibits the same linear dispersion and overall Bi$_2$Se$_3$-like behavior as the surface state. The interesting question is what happens to the interface and surface states of a thin film when another TI is deposited on top of it.

Starting with a 8 QL thick Bi$_2$Se$_3$ film the evolution of the surface state has been studied as multiple over-layers of Bi$_2$Te$_3$ were added. ARPES measurements were performed at total layer thicknesses of 1 QL, 3 QL and 7 QL, respectively. The results are presented in Fig. 6.7.

From Fig. 6.7b) one can conclude that already at a total thickness of 1 QL of the Bi$_2$Te$_3$ over-layer, the surface state dispersion has a clear Bi$_2$Te$_3$ character. If grown directly on the Si(111) substrate the electronic structure of a 1 QL thick Bi$_2$Te$_3$ film would be strongly hybridized [85] due to coupling between the two opposite surfaces of the film. The fact that no such hybridization is observed for the 1 QL over-layer is consistent with the absence of a topologically protected state at the interface between the two TIs. Adding additional over-layers of Bi$_2$Te$_3$ has no apparent effect on the observed band structure, although there are variations
in the sample quality and chemical potential for the different thicknesses. This variation is most likely a result of different growth conditions and is not coupled to the actual thickness of the layers. Post-annealing of the sample with the 7 QL thick Bi$_2$Te$_3$ over-layer drastically changes the chemical potential in the film, making it highly $n$-doped similar to what we observed in Fig. 6.3b), something which supports this notion.

In the results presented so far for the TI-TI heterostructure the interface state at the interface towards the Si substrate is not visible. The reason for this might be that the thickness of the film is close to the limit for which the interface state can be directly probed and if the interface is of inferior quality the photoemission intensity from this state will be strongly suppressed. However, in a different sample, consisting of a 6 QL thick Bi$_2$Se$_3$ film with a 2 QL Bi$_2$Te$_3$ over-layer, we observe a “double” band structure consisting of an outer and inner Dirac cone, see Fig. 6.8a). While the latter has a clear Bi$_2$Te$_3$ character and thus arises from the surface, the outer feature appears to be similar to the interface state observed in the pure Bi$_2$Se$_3$ film, presented in section 6.2.1. In fact, the outer state is well described by the calculated band structure for the interface state using Eq. (2.2) and identical model-parameter values as for the Bi$_2$Se$_3$ film, c.f. Fig. 6.8d). A comparison of extracted peak positions of constant energy surfaces, taken at the same energy
6.3. EXPERIMENTAL OBSERVATION OF THE TCI PHASE
IN \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \)

distance above the Dirac point of the interface state, also reveals a good agreement between the outer feature in the heterostructure film and the pure \( \text{Bi}_2\text{Se}_3 \) film, see Fig. 6.8c). We therefore conclude that the outer state is the interface state between the substrate and the \( \text{Bi}_2\text{Se}_3 \) film. Consequently, after deposition of \( \text{Bi}_2\text{Te}_3 \) on top of the \( \text{Bi}_2\text{Se}_3 \) film, the surface state shows a clear \( \text{Bi}_2\text{Te}_3 \) character while the interface state still remains \( \text{Bi}_2\text{Se}_3 \)-like. Additionally, in the data presented here no sign of any tachyon state at the TI-TI interface is observed.

6.3 Experimental observation of the TCI phase in \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \)

The newly proposed TCI phase has been demonstrated to exist in \( \text{SnTe} \) and for the solid solution \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) for \( x \gtrsim 0.4 \) [60, 58, 61]. \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) with \( x \in [0, 0.4] \) share the similar rock-salt (RS) crystal structure as \( \text{Pb}_{1-x}\text{Sn}_x\text{Te} \) and studies show that an inversion of the bulk band gap takes place in both materials, either as a function of temperature or \( (\text{Pb,Sn}) \) content [86, 87, 88]. Therefore, investigations regarding a potential TCI phase in \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) come naturally and since the chemical potential in \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) is tunable during growth of the crystal the realization of \( n \)-type samples is feasible which makes it a good candidate for studying the TCI surface states. Here, we have used ARPES and SARPES to study the surface band structure of \( n \)-type \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) monocrystalline samples with Sn concentrations in the range \( x \in [0.15, 0.30] \).

The RS crystal structure has a face-centered cubic (fcc) direct lattice and the resulting Wigner-Seitz cell of the body-centered cubic (bcc) reciprocal lattice, representing the three-dimensional BZ, is drawn in Fig. 6.9b). \( \text{Pb}_{1-x}\text{Sn}_x\text{Se} \) is a narrow band semiconductor with band gaps located at the eight \( L \) points on the border of the BZ. When projected onto the (001) surface the \( L \) points pair-wise map onto four equivalent \( \bar{X} \) points in the SBZ and the mirror plane drawn in Fig. 6.9b) is mapped onto the \( \bar{\Gamma} - \bar{X} \) line. The bulk band gap is located at the \( L \) points and protected surface states are expected to appear in the vicinity of the \( \bar{X} \) points, thus adding up to a total of four Dirac cones on the (001) surface.

Figure 6.10 displays low-temperature ARPES spectra of the electronic band structure of the surface state in the vicinity of one of the \( \bar{X} \) points on the (001) surface on \( \text{Pb}_{0.77}\text{Sn}_{0.23}\text{Se} \). Panel a) shows the dispersion along the \( \bar{\Gamma}_2 - \bar{X} - \bar{M} \) direction (line I in Fig. 6.9) which reveals that there is a gapless surface state with a Dirac point \( (D_2) \) on the \( \bar{\Gamma}_2 - \bar{X} \) line, slightly shifted away from \( \bar{X} \). Along the \( \bar{X} - \bar{M} \) direction the surface state is gapped. Panel b), in the same figure, presents a cut taken parallel to the \( \bar{M} - \bar{X} - \bar{M} \) direction (line III in Fig. 6.9) through the Dirac point \( D_2 \). Here, a clear \( X \)-like state is visible, confirming that the surface state is a Dirac cone. As seen from the dispersion along the \( \bar{\Gamma}_1 - \bar{X} - \bar{\Gamma}_2 \) direction, presented in panel c), there is another Dirac cone on the near side of \( \bar{X} \) which belongs to the first SBZ.

The fact that the surface state has a minimum (maximum) of the electron (hole)
Figure 6.9: a) Rock-salt (fcc) crystal structure of Pb$_{1-x}$Sn$_x$Se for $x \leq 0.4$. b) Bulk Brillouin zone with symmetry points $\Gamma$, L and X marked, and their projection onto the (001) surface Brillouin zone. Small ellipses in the vicinity of the $\bar{X}$ points represent the Dirac surface states. Lines I to III indicate position of spectra presented in coming figures.

Figure 6.10: ARPES data on Pb$_{0.77}$Sn$_{0.23}$Se ($T = 9$ K) a) Spectrum showing the dispersion along the $\bar{\Gamma}_2 - \bar{X} - \bar{M}$ direction (line I in Fig. 6.9). b) Slice through the Dirac point $D_2$ (line III in Fig. 6.9). c) Dispersion along the $\bar{\Gamma}_1 - \bar{X} - \bar{\Gamma}_2$ direction (line II in Fig. 6.9), showing the two Dirac points $D_1$ and $D_2$ symmetrically placed on each side of $\bar{X}$. 
like “parabolic” band along the \( \bar{X} - \bar{M} \) direction which is shifted away from \( \bar{X} \) indicates that the electronic structure of the surface states close to \( \bar{X} \) is not simply that of two intersecting ideal Dirac cones with Dirac points located at \( D_1 \) and \( D_2 \) respectively. By studying constant energy contours it becomes apparent that the band structure undergoes a change of topology, two separate contours transform into two concentric ones (Lifshitz transition), when moving either up or down in energy from the Dirac points. From the sketch of the observed band structure, see Fig. 6.11, and considering only the upper half of the Dirac cone, one can identify three transition energies where the energy contours change appearance.

First, a constant energy cut at a binding energy between \( E_1 \) and \( E_2 \) will result in two separate contours, as seen in the sketch in Fig. 6.11a) and also in the data in Fig. 6.11b). At the energy \( E_2 \) the Lifshitz transition takes place, resulting in energy contours consisting of concentric “circles” for binding energies \( E_b < E_2 \). In the energy range between \( E_3 \) and \( E_2 \) the inner contour is “hole-like”, decreasing into a point at \( E_3 \) before expanding as an “electron-like” contour for \( E_b < E_3 \). In our experimental data the “hole-to-electron” transition of the inner contour occurs over an energy range approximately covering 20 meV. Due to this small energy range the transition is not directly observable in the current data set. However, the
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![Graph showing ARPES data for Pb$_{1-x}$Sn$_x$Se](image)

Figure 6.12: Low temperature ARPES data ($T = 9$ K) on Pb$_{1-x}$Sn$_x$Se for different Sn concentrations. The panels show the dispersion along the $\bar{\Gamma}_2 - \bar{X} - \bar{M}$ direction.

The overall topological transition of the constant energy contours themselves is visible, see Fig. 6.11b).

With increased Sn content both the Dirac points and the minimum (maximum) of the surface state along $\bar{X} - \bar{M}$ are shifted away from $\bar{X}$, as seen in Fig. 6.12, thus making the Lifshitz transition more pronounced. These results are also confirmed by the calculations presented in Paper IV.

6.3.1 A topological phase transition

Interestingly, Pb$_{1-x}$Sn$_x$Se undergoes a band gap inversion as a function of temperature [86]. The transition $T_c$ varies with Sn content, as seen in Fig. 6.13. Selecting a Sn content $0.2 < x < 0.3$ enables both phases (positive and inverted band gap) to be probed in ARPES experiments when cooling the sample from 300 K to $\sim$10 K. ARPES spectra from Pb$_{0.77}$Sn$_{0.23}$Se for a few sample temperatures in the aforementioned temperature range are presented in Fig. 6.14.

The energy momentum cuts are taken parallel to the $\bar{X} - \bar{M}$ direction and are centered at $D_2$ (c.f. Fig. 6.10b)). At room-temperature the surface state is clearly gapped and consists of electron and hole like parabolic bands. When lowering the sample temperature the gap decreases and at $T < 100$ K the gap is completely closed and the Dirac-like nature of the surface state becomes apparent. From these data we conclude that for this particular concentration of Sn the bulk band gap inversion takes place at $T \sim 100$ K. The transition from gapped to non-gapped surface states therefore signals a phase transition from a trivial insulating phase for $T > T_c$ to a TCI phase at $T < T_c$. According to Fig. 6.13, $T_c$ increases with increased Sn content. This is also confirmed by the data presented in Fig. 6.15.
6.3. EXPERIMENTAL OBSERVATION OF THE TCI PHASE IN Pb$_{1-x}$Sn$_x$Se

Figure 6.13: The evolution of the bulk band gap as a function of temperature and Sn content. The TCI phase exists in the region where the band gap is negative. With increased Sn content the transition temperature between the normal and the TCI phase increases.

Figure 6.14: Temperature dependence of the dispersion along a cut parallel to the $M - \bar{X} - M$ direction (line III in Fig. 6.9b)) in Pb$_{0.77}$Sn$_{0.23}$Se. The spectra display the transition from a normal phase to a TCI phase.
which displays an increasing gap in the surface state at a temperature $T = 150$ K for decreased Sn content.

### 6.3.2 Electronic spin structure of TCI surface states

The theoretical calculations and SARPES studies of the surface states on the (001) face of Pb$_{1-x}$Sn$_x$Se, presented in Paper V, confirm that the states are spin polarized. From the calculations the evolution of the spin structure of the constant energy contours through the Lifshitz transition can be followed. The result is schematically illustrated in Fig. 6.16 for the upper half of the Dirac cones. The indicated binding energies $E_1$, $E_2$ and $E_3$ are the transition energies introduced in Fig. 6.11.

We observe that the inner contour appearing for $E_b < E_2$ reverses its in-plane spin direction when crossing the transition energy $E_3$. However, as already pointed out, the energy scale on which this reversal takes place is too small to clearly resolve, especially in a spin-resolved measurement. Consequently, our experimental results so far only confirm the spin structure of the outer contour in the binding energy range $E_b < E_3$ (and $E_b > E_3$ for the lower part of the Dirac cone). The increased shift away from $\bar{X}$ of the minimum (maximum) of the surface state along $\bar{X} - \bar{M}$ which is observed in samples with larger Sn content makes these samples better candidates for probing the spin structure of the “inner feature”. However, even with the highest possible Sn content the angular and energy scales are still small compared to the available energy and angular resolutions in spin resolved measurements, thus making determination of the inner spin structure challenging. In Pb$_{0.6}$Sn$_{0.4}$Te [61], on the other hand, the angular and energy scales of the surface states are approximately three times as large as in Pb$_{0.77}$Sn$_{0.23}$Se, something which,
6.3. EXPERIMENTAL OBSERVATION OF THE TCI PHASE IN $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$

for the former, has enabled the spin structure in the range $E_1 < E_b < E_2$ to be confirmed.

6.3.3 Surface chemical reactions and near-surface band bending

We discussed earlier in chapter 2.5 that the chemical potential near the surface of a TI (stored in vacuum) experiences a shift caused by adsorbed residual gas atoms or molecules. The rate of adsorption depends on the pressure in the vacuum chamber, thus the time scale of the energy shift varies from system to system. Figure 6.17a) shows the Dirac point binding energy position for $\text{Bi}_2\text{Se}_3$ as a function of time measured in the BALTAZAR system. The observed band bending is downwards and seems to saturate at $\Delta E \sim 0.6 \text{ eV} - 0.7 \text{ eV}$. In Fig. 6.17b) similar data for $\text{Pb}_{0.77}\text{Sn}_{0.23}\text{Se}$ are presented which shows that this material, in contrast to $\text{Bi}_2\text{Se}_3$, experiences an upwards band bending.
Figure 6.17: Energy shift of Dirac point in a) Bi$_2$Se$_3$ and b) Pb$_{0.77}$Sn$_{0.23}$Se as a function of time. The shift is due to band bending close to the surface.
Chapter 7

Conclusions and future work

This thesis has been describing the work related to the development of scientific instruments for photoelectrons spectroscopy in addition to experimental investigations of the low-energy electronic structure in topological insulators and topological crystalline insulators. The major results and conclusions of this work can be summarized as follows:

Instrumental developments

- We have developed a laser-based experimental setup (the BALTAZAR system) for performing ARPES measurements with energy and momentum resolutions reaching 5 meV and 0.02 Å\(^{-1}\), respectively.

- A photon energy of 10.5 eV is generated through HHG in Xe and the repetition rate of the pulsed light source is tunable in the effective range 0.2 MHz to 0.8 MHz. At the lowest repetition rate a photon flux of \(9 \times 10^{12}\) photons/s is reached.

- The three-dimensional detection capability of the TOF analyzer makes the instrument ideal for studies of two-dimensional systems. As we can see from the experimental data on Au(111), the TIs and the TCIs presented in the thesis these systems are particularly well suited since they all have spectral features which at 10.5 eV fit within the angular acceptance of the analyzer.

- Performing high quality ARPES measurements with an angle-resolving TOF analyzer requires careful control over:
  a) Alignment of the beam spot on the optical axis of the lens (crucial)
  b) Determination of correct working distance (important)
  c) Work function compensation (important but not crucial)
CHAPTER 7. CONCLUSIONS AND FUTURE WORK

Topological insulators

- Our studies on interface states in TIs confirm that a Dirac state is present at the interface between a TI thin film and the substrate. The dispersion of the interface state and the energy separation between the surface and the interface state agree well with existing theoretical models.

- From the observed energy offset of the Dirac point at the interface we have been able to construct a model of the band diagram for the Si/Bi$_2$Se$_3$ heterostructure.

- In TI-heterostructures consisting of Bi$_2$Se$_3$/Bi$_2$Te$_3$ we observe an interface state and a surface state of Bi$_2$Se$_3$ and Bi$_2$Te$_3$ character, respectively. No evidence for tachyon states at the Bi$_2$Se$_3$/Bi$_2$Te$_3$ interface is observed.

Topological crystalline insulators

- Our ARPES and SARPES work presented on the narrow band-gap semiconductor Pb$_{1-x}$Sn$_x$Se confirms that this material belongs to the newly proposed TCI phase.

- We have studied the temperature dependent topological phase transition in Pb$_{1-x}$Sn$_x$Se and conclude that the formation of gapless Dirac surface states occurs in agreement with the previously investigated temperature and composition dependent band gap inversion.

Future work

Regarding the BALTAZAR setup, a few important and useful future developments can be identified.

a) The drawback with the system is that only one photon energy is available. This means that there is no “workaround” if running into photoemission cross section issues, leading to low photoelectron count rates for the system under study. One possible way of providing more photon energies could be to install an extra amplification state to the laser (available from the laser manufacturer) thus increasing the power density available for the HHG process. This could enable generation of 17.5 eV photons (5th harmonic of 355 nm). Another possibility would be to use the doubled beam (532 nm) of the fundamental directly in the HHG stage, thus generating 7 eV photons (3rd harmonic of 532 nm).

b) The setup can also be upgraded to include pump-probe capabilities. Using a fraction of the fundamental light (~1.17 eV), the frequency doubled light (~2.34 eV) or the tripled light (~3.5 eV) one can access excited states. Though, due to the relatively long pulse length (10 ps) the application to time-resolved studies might be limited.
For the TIs, studies of normal insulator-TI heterostructures involving other types of substrates are also of interest. The band offsets at the interface can be determined and the effect of the substrate on the band bending through the TI films can be investigated. Also, by H-termination of Si(111)-(7 × 7) the Fermi level at the surface lies close to the bulk value. This could provide a way to manipulate the binding energy of the Dirac point at the interface by using differently doped Si substrates. By creating a thin film having a $n$-type interface state and a $p$-type surface state (or vice versa) the observation of a topological exciton condensate could become possible. This would require careful control over the binding energy position of the Dirac points at the interface and surface, respectively. The latter could be achieved either by substrate induced band bending, bulk doping of the film or possibly by electric gating. Further, in the search for possible tachyon interface states in TI-TI heterostructures, other material combinations than the ones used here can be investigated.

Two future experiments on TCIs which could be of interest related to investigations of the crystal symmetry protected nature of the surface states are:

i) ARPES on magnetically doped Pb$_{1-x}$Sn$_x$Se

ii) ARPES on strained thin films of Pb$_{1-x}$Sn$_x$Se or on crystals compressed along the $x$ or $y$ direction.

Since the surface states are protected by crystal symmetry and not time-reversal symmetry the former experiment should observe gapless surface states (in contrast to the case for TI) whereas the latter deforms the crystal structure and thus should result in a gap opening in the Dirac states.
Appendix A

E-beam evaporation overview

<table>
<thead>
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<th>Element</th>
<th>Melting point (°C)</th>
<th>Temperature in °C at vapor pressure (Torr)</th>
<th>Crucible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>271</td>
<td>330 410 520</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Se</td>
<td>217</td>
<td>89 125 170</td>
<td>Mo</td>
</tr>
<tr>
<td>Te</td>
<td>452</td>
<td>157 207 277</td>
<td>Ta</td>
</tr>
<tr>
<td>Sb</td>
<td>630</td>
<td>279 345 425</td>
<td>Ta</td>
</tr>
</tbody>
</table>

Table A.1: Material parameters relevant for e-beam evaporation [71] along with suitable crucible material.

<table>
<thead>
<tr>
<th>Material Material</th>
<th>High voltage (V)</th>
<th>Typical filament current (A)</th>
<th>Flux (nA)</th>
<th>Crucible size</th>
<th>Deposition rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>825</td>
<td>1.90-2.00</td>
<td>70</td>
<td>Small</td>
<td>0.04</td>
</tr>
<tr>
<td>Se</td>
<td>200</td>
<td>1.60-1.80</td>
<td>350</td>
<td>Medium</td>
<td>0.1</td>
</tr>
<tr>
<td>Se</td>
<td>200</td>
<td>1.45-1.60</td>
<td>450</td>
<td>Large</td>
<td>0.1</td>
</tr>
<tr>
<td>Te</td>
<td>315</td>
<td>1.70-1.80</td>
<td>1150</td>
<td>Medium</td>
<td>0.1</td>
</tr>
<tr>
<td>Sb</td>
<td>730</td>
<td>1.80-1.90</td>
<td>25</td>
<td>Medium</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table A.2: Overview of typical evaporator settings, resulting flux and deposition rates used during growth of TI films.
Appendix B

QCM material parameters

<table>
<thead>
<tr>
<th>Element</th>
<th>$\rho$ (g·cm$^{-3}$)</th>
<th>z-ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>9.75</td>
<td>0.790</td>
</tr>
<tr>
<td>Se</td>
<td>4.81</td>
<td>0.864</td>
</tr>
<tr>
<td>Te</td>
<td>6.24</td>
<td>0.900</td>
</tr>
<tr>
<td>Sb</td>
<td>6.62</td>
<td>0.768</td>
</tr>
</tbody>
</table>

Table B.1: Input parameters to the quartz-crystal monitor for the different elements used to grow the TIs thin films [71].
Bibliography


Summary of contributions


We describe the development of a photoelectron spectrometer, consisting of a hemispherical electron-energy analyzer combined with a mini-Mott electron-spin detector, capable of performing both spin-integrated angle-resolved as well as spin-resolved measurements of photoelectrons from solid samples. The instrument is placed at I3 beamline on the MAXIII storage ring at the MAXlab synchrotron radiation facility at Lund University, Lund, Sweden.

*Contribution:* Performed the final test measurement of the Au(111) surface state, analyzed the spin data, made figures and wrote the major part of the manuscript.


The development and performance of the BALTAZAR system is described; an experimental setup for photoelectron spectroscopy based on the time-of-flight (TOF) principle using a laser as light source. The pulsed light source delivers photons of energy 10.5 eV with sufficient flux to perform high statistics photoemission experiments in the repetition rate range of 0.2 MHz to 0.8 MHz. Energy and momentum resolutions of 5 meV and 0.02 Å⁻¹, respectively, are demonstrated.

*Contribution:* Assembled and commissioned the instrument. Performed all measurements and data analysis. Wrote the manuscript.

Through low photon-energy photoemission experiments we probe the buried TI/substrate interface in Bi$_2$Se$_3$ thin films grown on Si(111). The interface state exhibits a linear dispersion similar to the surface state but is shifted in binding energy due to band bending induced by the presence of the substrate. From the observed band bending we construct a band alignment model for the Si/Bi$_2$Se$_3$ junction. Investigations of Bi$_2$Se$_3$/Bi$_2$Te$_3$ heterostructures show no sign of any state at the interface between the two TIs.

**Contribution:** Manufactured samples, planned and performed the experiments. Analyzed data and wrote the manuscript.


We present evidence for the realization of a topological crystalline insulator (TCI) phase in the narrow band-gap semiconductor Pb$_{0.77}$Sn$_{0.23}$Se. The material undergoes a band gap inversion as a function of temperature which signals a change in topology of the band structure. The topological phase transition occurs at a temperature $T \sim 100$ K and is accompanied by the formation of gapless surface states in the vicinity of the Š points in the surface Brillouin zone of the (001) surface.

**Contribution:** Performed the temperature dependent ARPES studies using the BALTAZAR setup. Analyzed the data, contributed to the physical interpretation of the results, wrote the experimental ARPES part of the manuscript and the supplementary information. Edited the manuscript.

**V. B. M. Wojek, R. Buczko, S. Safaei, P. Dziawa, B. J. Kowalski, M. H. Berntsen, T. Balasubramanian, M. Leandersson, A. Szczerbakow, P. Kacman, T. Story, and O. Tjernberg, Spin-polarized (001) surface states of the topological crystalline insulator Pb$_{0.73}$Sn$_{0.27}$Se.** Physical Review B **87**, 115106 (2013).

By using spin-resolved ARPES we have probed the electronic spin structure of the surface states on the (001) surface of Pb$_{0.72}$Sn$_{0.28}$Se both in the topologically trivial and the TCI phase. The results reveal the existence of spin-polarized helical states both above and below the transition temperature $T_c$. In the TCI phase the spin in the vicinity of the Dirac points rotates clockwise, similar to the case in the topological insulators.

**Contribution:** Took part in the experiment and contributed to the analysis and interpretation of the data. Commented on the manuscript.