

Topological insulators grown by molecular beam epitaxy (MBE) and related quantum devices

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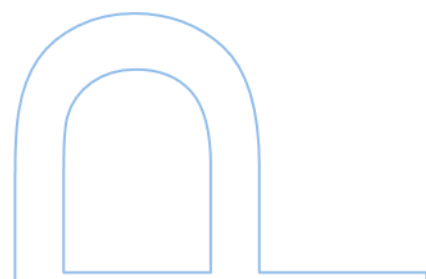
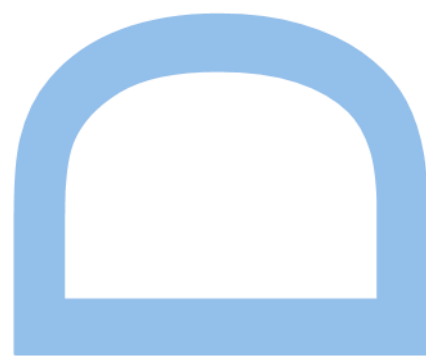
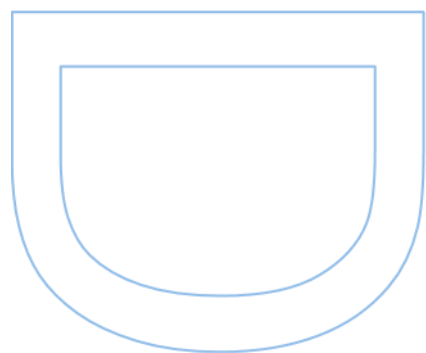
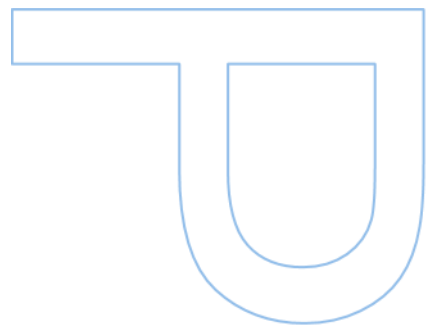
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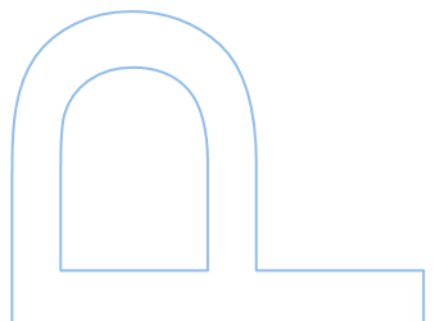
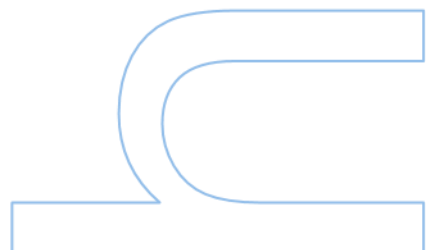
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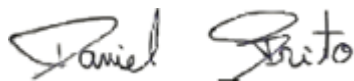
Sworn Statement

I, Daniel Portela de Brito, enrolled in the Doctor's Degree in Physics at the Faculty of Sciences of the University of Porto hereby declare, in accordance with the provisions of paragraph a) of Article 14 of the Code of Ethical Conduct of the University of Porto, that the content of this thesis reflects perspectives, research work and my own interpretations at the time of its submission.

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A handwritten signature in black ink, appearing to read 'Daniel Brito', with a stylized, cursive script.

01/03/2024

Acknowledgments

The journey of a PhD was an evolution as a person, scientifically and mentally. I would recommend everyone to do a PhD. You will face several challenges and emotions. You will learn how life is in the real world. You will develop skills you didn't know you had. Thank you for making me a better person.

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Resumo

Os isoladores topológicos são uma nova classe de matéria caracterizada pela sua estrutura eletrônica única, é isolante no interior e possui estados condutores na superfície. A presença de acoplamento spin-órbita e a simetria de inversão temporal são pré-requisitos para esta nova classe de materiais. Os estados de superfície exibem dispersões do tipo cone de Dirac sem massa e bloqueio spin-momento, o que implica a interação proibida de elétrons de spin oposto e que o spin do elétron muda de acordo com o seu momento. Esta combinação confere a propriedade de condutividade sem dissipação aos isoladores topológicos.

O seleneto de bismuto (Bi_2Se_3) é um isolante topológico promissor devido ao seu hiato energético de 0.3 eV, tornando-o adequado para aplicações à temperatura ambiente. No entanto, uma grande desvantagem é a sua degenerescência do tipo n devido à sua dopagem nativa por vacâncias de Se, que normalmente leva ao transporte no interior, tornando o acesso a estados de superfície condutores uma grande dificuldade. Por conseguinte, a fabricação de Bi_2Se_3 sem contribuição elétrica do interior de alta qualidade com condução ao longo da superfície é de alta relevância. Isto poderia ser obtido deslocando o potencial químico para o seu hiato energético, tornando o transporte dos estados de superfície mais pronunciado.

O presente trabalho contribui para o desenvolvimento da fabricação de filmes de isoladores topológicos de alta qualidade, por epitaxia de feixe molecular. Um dos principais objetivos é investigar a dopagem de Ga e Cu em Bi_2Se_3 , com vista a identificar o seu potencial papel como impurezas aceitadoras. Além disso, a dopagem com elementos exóticos pode oferecer oportunidades para descobrir novos fenómenos físicos, tais como a supercondutividade topológica ou o efeito Hall quântico anômalo. A segunda estratégia centra-se no ajuste do nível de Fermi através da utilização de uma gate eletrostática. Este método reduziu a concentração de elétrons do Bi_2Se_3 , facilitando a deteção do transporte topológico de superfície.

Inicialmente, a investigação começou com a otimização do crescimento filmes finos de Bi_2Se_3 em substratos de safira (0001). Foram otimizados diferentes parâmetros de crescimento, obtendo-se uma temperatura de crescimento de 310 °C, uma abertura da válvula de Se em 2 mm e a implementação de um crescimento em duas fases, designado por tratamento de superfície. A caracterização estrutural demonstraram isolador topológico com boa qualidade estrutural e morfologia com número mínimo de defeitos. Os defeitos de geminação (*twinning*) no plano foram atenuados para menos de 15% com a aplicação do tratamento de superfície. O estudo de duas camadas tampão(*buffer*) diferentes foi abordado, $(\text{Bi}, \text{In})_2\text{Se}_3$ e $\text{In}_2\text{Se}_3 + (\text{Bi}, \text{In})_2\text{Se}_3$, com a última a mostrar um melhor isolamento do Bi_2Se_3 e uma interface ordenada. A camada tampão $\text{In}_2\text{Se}_3 + (\text{Bi}, \text{In})_2\text{Se}_3$ levou a concentrações de elétrons de Bi_2Se_3 de $4 \times 10^{18} \text{ cm}^{-3}$ e mobilidades de elétrons de aproximadamente $600 \text{ cm}^2/\text{Vs}$.

Foram estudadas as propriedades estruturais, elétricas e de transporte da dopagem com Ga e Cu. Os resultados revelam uma expansão da rede c de 28.66 Å (não dopado) para 28.92 Å (Ga: 7 at.%) e uma dopagem do tipo n, seis vezes maior, atingindo valores de aproximadamente $6 \times 10^{19} \text{ cm}^{-3}$. Sugerindo que o Ga possivelmente se intercala no gap de van der Waals. A dopagem de Cu, por outro lado, leva a uma contração da rede c para $\approx 28.60 \text{ Å}$ (Cu: 2 at.%), em que Cu atua como uma impureza aceitadora com uma redução de

duas vezes da concentração de elétrons. Além disso, a medição de magneto transporte mostraram o efeito da anti localização fraca (*WAL*) através da ponta em campos magnéticos baixos de Bi_2Se_3 não dopado. Esta ponta degrada-se após a dopagem com Ga, com uma transição de fase topológica a uma percentagem de Ga de 7 at.%, sugerindo a destruição dos estados de superfície. Por outro lado, a dopagem com Cu mostrou pouca interferência na forma da ponta *WAL*.

As medições de espectroscopia de fotoemissão resolvida em ângulo (*ARPES*) confirmam a presença de estados de superfície em Bi_2Se_3 não dopado, em todas as amostras dopadas com Cu e na amostra dopada com Ga até uma dopagem de 2 at.%, enquanto com 7 at.% de Ga não se observam estados de superfície. A dopagem também levou a uma diminuição do nível de Fermi para a dopagem com Cu e um aumento para a dopagem com Ga.

Além disso, exploramos o fabrico e a caracterização de transístores de efeito de campo (*FET*) baseados em filmes finos de Bi_2Se_3 . A incorporação de uma camada de cobertura de In_2Se_3 e a utilização de alumina como *gate* dielétrica permite a afinação do nível de Fermi e a modulação da concentração de elétrons de $6 \times 10^{12} \text{ cm}^{-2}$ para $4 \times 10^{12} \text{ cm}^{-2}$ com uma tensão de *gate* de -10 V, demonstrando o potencial dos FET para controlar as propriedades de transporte.

Palavras-chave: ARPES, Bi_2Se_3 , dopagem com Cu, dopagem com Ga, efeito de anti localização fraca, epitaxia por feixe molecular, estados de superfície, isoladores topológicos, transístor de efeito de campo.

Abstract

Topological insulators are a new class of matter characterized by their unique electronic structure, which features insulating bulk and conductive surface states. The presence of spin-orbit coupling, and time-reversal symmetry are prerequisites for this new class of materials. The surface states exhibit massless Dirac cone-like dispersions and spin-momentum locking, which implies the forbidden interaction of electrons with opposite spin and that the electron spin changes according to its momentum. This combination confers the property of dissipationless conductivity for topological insulators.

Bismuth selenide (Bi_2Se_3) is a promising topological insulator due to its band gap of 0.3 eV, making it suitable for room temperature applications. However, a major drawback is its n-type degeneracy due to its native doping by Se vacancies, which normally leads to bulk transport, making the access to pure conductive surface states a major difficulty. Therefore, the experimental realization of high-quality bulk-insulating Bi_2Se_3 with pure conduction along the surface is a critical point in the field. This could be obtained by shifting the chemical potential into the bandgap, turning the transport of the surface states to be more pronounced than the bulk counterpart.

The present work contributes to the ongoing effort to grow high-quality topological insulator films by a molecular beam epitaxy. One of the primary objectives is to explore the doping of Bi_2Se_3 with Ga and Cu elements, aiming to identify their potential role as compensating acceptor impurities. Furthermore, doping with exotic elements may offer opportunities to discover novel physical phenomena, such as topological superconductivity or quantum anomalous Hall effect. The second strategy focuses on adjusting the Fermi level through the use of an electrostatic gate. This method reduces the electron concentration of the Bi_2Se_3 , thereby unmasking the topological surface transport.

Initially, the research started with the optimization of the Bi_2Se_3 thin film growth on sapphire (0001) substrates. Different growth parameters are optimized obtaining a growth temperature of 310 °C, Se valve aperture of 2 mm, and the implementation of a two-step growth, denoted as surface treatment. Structural characterization measurements showed thin films with good structural quality and morphology with reduced defects. In-plane twinning defects were mitigated below 15 % by the implementation of the surface treatment. The study of two different buffer layers was addressed, $(\text{Bi}, \text{In})_2\text{Se}_3$ and $\text{In}_2\text{Se}_3 + (\text{Bi}, \text{In})_2\text{Se}_3$, with the latter showing an improved insulation of the bulk of the Bi_2Se_3 and a highly ordered interface. The $\text{In}_2\text{Se}_3 + (\text{Bi}, \text{In})_2\text{Se}_3$ buffer layer led to the Bi_2Se_3 electron concentrations of $4 \times 10^{18} \text{ cm}^{-3}$ and mobilities of approximately $600 \text{ cm}^2/\text{Vs}$.

The structural, electrical, and transport of doping with Ga and Cu were studied. The results reveal a c lattice expansion from 28.66 Å (undoped) to 28.92 Å (Ga: 7 at.%) and six-fold n-type doping reaching values of approximately $6 \times 10^{19} \text{ cm}^{-3}$. Suggesting that Ga possibly intercalates in the van der Waals gap. Cu doping, on the other hand, leads to a c lattice contraction to $\approx 28.60 \text{ Å}$ (Cu: 2 at.%), wherein Cu acts as an acceptor impurity with a two-fold reduction of the electron concentration. Moreover, magnetotransport measurements showed the weak anti-localization (WAL) cusp at low-magnetic fields of undoped Bi_2Se_3 . This cusp degrades upon the doping with Ga, with a topological phase transition at a Ga percentage of 7 at.%, suggesting the destruction of the surface states. Otherwise, the Cu doping showed little interference in the WAL cusp shape.

Angle-resolved photoemission spectroscopy (ARPES) measurements confirm the presence of surface states in undoped Bi₂Se₃, all Cu-doped and Ga-doped up to doping of 2 at.%, whereas at Ga:Bi₂Se₃ 7 at.% no clear surface states are observed. The doping also led to a downward Fermi level shift for Cu doping and an upward shift for doping by Ga.

Furthermore, we explore the fabrication and characterization of field-effect transistor (FET) devices based on Bi₂Se₃ thin films. The incorporation of an In₂Se₃ capping layer and the use of alumina as a dielectric gate allows the tuning of the Fermi level and modulation of carrier concentration from $6 \times 10^{12} \text{ cm}^{-2}$ down to $4 \times 10^{12} \text{ cm}^{-2}$ with a gate voltage of -10 V, demonstrating the potential for FETs to control the transport properties.

Keywords: ARPES, Bi₂Se₃, Cu doping, field effect transistor, Ga doping, molecular beam epitaxy, surface states, topological insulators, weak antilocalization effect.

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List of Abbreviations

AFM	Atomic force microscopy
ARPES	Angle-resolved photoelectron spectroscopy
BEP	Beam equivalent pressure
BIS	(Bi,In) ₂ Se ₃ buffer layer
CB	Conduction band
EBIN	Binding energy
DP	Dirac point
EC	Conduction band minimum
ED	Dirac equation
EF	Fermi level
EV	Valence band maximum
FET	Field effect transistor
FWHM	Full width half maximum
HLN	Hikami-Larkin-Nagaoka
IS-BIS	In ₂ Se ₃ + (Bi,In) ₂ Se ₃ buffer layer
KF	Fermi vector
MBE	Molecular beam epitaxy
QAHE	Quantum anomalous hall effect
QHE	Quantum hall effect
QSHE	Quantum spin hall effect
QL	Quintuple layer
RHA	Rashba splitting
RHEED	Reflection high-energy electron diffraction
SOC	Spin-orbit coupling
RS	Sheet resistance
RT	Room temperature
SS	Surface states
ST	Surface treatment
TEM	Transmission electron microscopy
TI	Topological insulator
TRS	Time reversal symmetry
TSC	Topological superconductor

UHV	Ultra-high vacuum
VB	Valence band
VF	Fermi velocity
VDW	Van der Waals
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectivity
WAL	Weak antilocalization
2DEG	2-Dimensional electron gas

Introduction

In the society we live in, the world is extremely dependent on technology, which has grown exponentially since the discovery of transistors. The transistor is the key to developing new technologies in the modern world because of its efficiency, reliability, and compact size. Even with their compact size, over the years, the world has demanded faster and more efficient electronics. The solution for the problem consisted of transistor size reduction with the purpose of increasing the transistor density in integrated circuits. However, Moore's law predicts that the continuous reduction of the transistor size would eventually approach the physical limit of miniaturization. Simultaneously, the high density and integration of transistors are leading to a high-power consumption. Therefore, alternative materials for semiconductor technologies must be investigated to address this problem. The introduction of topological insulators has attracted considerable attention to the possibility of a dissipationless material, which could minimize the constraints and improve the power consumption of future technologies.

Topological insulators have recently been introduced in the field of condensed matter physics based on the predictions of Kane and Mele¹. The topic increased exponentially after the first experimental discovery due to their promising properties. They are a new class of materials that exhibit insulating behavior in bulk, combined with conductive surfaces or edges. These conductive surfaces arise from strong spin-orbit coupling and are protected by time-reversal symmetry (TRS) to perturbations like disorder or impurities, as long as TRS is preserved. The combination of spin-orbit coupling and TRS leads to the spin-locked momentum of electrons, which implies that electrons with opposite momentum are required to have opposite spin. The spin momentum locking allied with TRS implies the absence of scattering between states with opposite momentum, which leads to a decrease in scattering probability. Hence, the surface states of topological insulator materials assure more efficient transport and can pave the way for the fabrication of electronics with reduced power consumption.

One promising topological insulator candidate is the Bi_2Se_3 compound because of its relatively large band gap (0.3 eV), which is suitable for applications at room temperature. However, a major challenge in exploring the topological properties of these materials is unintentional doping (n-type). Doping leads to bulk conductivity, which masks the effects of dissipationless surface states.

To address this challenge, various strategies have been discovered, such as reverse doping with different elements to compensate (by p-type doping) for unintentional doping by moving the Fermi level of the material into the band gap. This has been implemented by molecular beam epitaxy (MBE) which allows for a controllable composition, a good material quality, and has a crucial advantage for the fabrication of devices on a wafer scale.

The primary goal here is to obtain a material with insulating bulk and conductive surface states on the topological insulator Bi_2Se_3 . Two approaches were used in this study. The first is the study of Bi_2Se_3 doped with Ga and Cu to understand if they could act as acceptor impurities. Additionally, doping could also be beneficial for the discovery of new physical properties such as the anomalous quantum Hall effect or topological superconductivity. The second approach to insulate the bulk by tuning the Fermi level involves the implementation of an electrostatic gate that decreases the electron

concentration of the material and consequently facilitates the exploitation of the topological surface state properties.

The thesis starts (**Chapter 1**) by introducing the topic of quantum topological matter and the state of the art. Here, we explain the theoretical concepts used to understand the subject and the experimental results obtained. Moreover, it shows what has already been obtained to date. This is followed by **Chapter 2**, in which the experimental growth technique (MBE) and several characterization techniques implemented throughout the thesis are explained in more detail.

The experimental results of the thesis start from **Chapter 3**. The research presented in this thesis is as follows (see Fig. 0): Firstly, in **Chapter 3**, the optimization of the growth of the topological insulator Bi_2Se_3 is addressed for the first time at INL by an MBE growth. The substrate temperature, growth rate, and surface treatment were optimized to obtain the best structural properties with minimal defect formation. Moreover, a buffer layer was studied, which leads to a highly oriented interface with the Bi_2Se_3 , and consequently an enhancement of the Bi_2Se_3 electrical and transport properties.

After establishing the procedure for the growth of good-quality Bi_2Se_3 , the doping of Bi_2Se_3 by gallium and copper was studied with the aim of understanding the effect from the structural and electrical points of view (**Chapter 4**). The doped material was studied using Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to obtain information about the structural and compositional evolution upon doping. The Hall effect and weak antilocalization effect were studied to obtain the electrical and transport properties upon doping as a 2D transport effect. Owing to the difficulty in distinguishing the 2D transport from the surfaces and bulk through electrical characterization techniques, ARPES is implemented in **Chapter 5**. An electronic study of the doping effect is achieved, which allows for obtaining detailed information about 2D transport.

Finally, because MBE growth allows the fabrication of several devices on a wafer scale, including heterostructures, the fabrication of field effect transistors (FET) is studied (**Chapter 6**). FET devices have been successfully developed, allowing the tuning of the Fermi level of the material closer to the band gap.

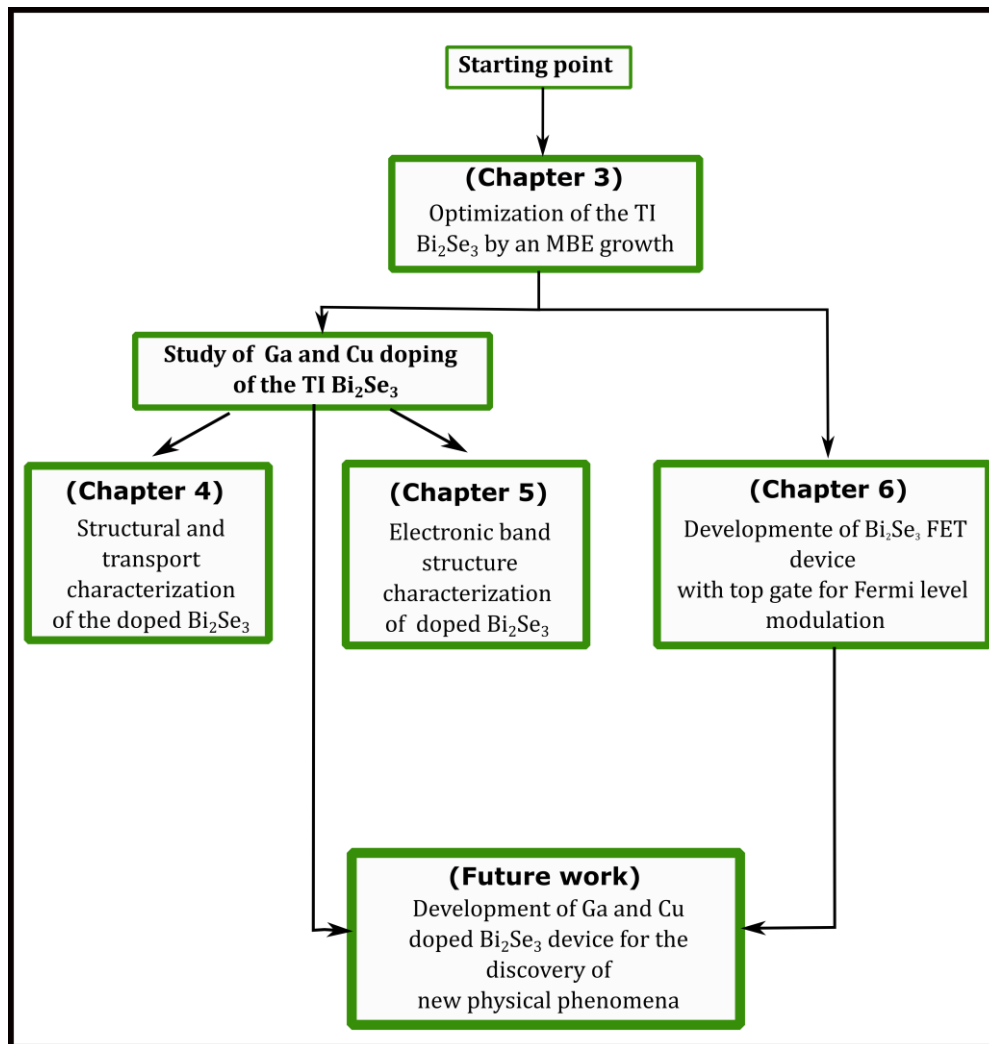


Figure 0 Schematic of the thesis body for the experimental results (Chapters 3-6).

Chapter 1

1. Topological quantum matter

The concept of topology was introduced to condensed matter physics in the 80's by David J. Thouless among others, which led to the Nobel Prize in Physics in 2016. The concept of topological phases of matter has then emerged. These phases are not characterized by local order parameters such as magnetization, polarization, etc.... They are associated with certain properties that are robust to perturbations, meaning there is no spontaneous symmetry breaking. In fact, topological phases are protected by a combination of symmetry and dimensionality, and the robustness of characteristic properties holds as long as, for the given dimensionality, perturbations do not break the protecting symmetry. These properties are characterized by topological invariants, which do not change under smooth, continuous variations of the system's Hamiltonian. Such topological distinct phases can appear in solid-state systems where the topology is related to the crystal's band structure. Topological states were first observed in the quantum Hall effect (QHE)², but most recently the discovery of topological insulators has attracted a lot of attention^{3,4}. This chapter aims to review some aspects to understand the origin of topological matter and its state of the art.

1.1. Quantum Hall effect

In a 2D electron system, within the classical picture, at low temperatures, the presence of a magnetic field perpendicular to the plane of the system and an external electric field, causes electrons to move along circular orbits, due to the Lorentz force. With high magnetic fields, these orbits are localized in the bulk of the material, but close to the edge, these circular orbital motions are incomplete, leading to the movement of electrons along the system edge (Fig. 1.1 a). Quantum mechanically, the system is described by quantized Landau levels, with $n \geq 0$:

$$E_n = \left(n + \frac{1}{2}\right) \hbar \omega_c, \quad n = 0, 1, 2, \dots \quad (1.1)$$

where $\omega_c = \frac{eB}{m}$ is the cyclotron frequency. The Landau levels are illustrated in Fig. 1.1 b). The system behaves as an insulator in the bulk, due to the presence of an energy band gap. However, due to the confining potential, there are states crossing the Fermi level near the edges of the sample, as also indicated in Fig. 1.1 b) by red circles. The presence of an electric

field causes the orbits to drift (classical picture), or the edge states to conduct (quantum picture), which leads to a Hall current along the edges associated with a transverse Hall tension. Experimentally, Von Klitzing et al. ² discovered that the transverse conductivity σ_{xy} is quantized in multiples of e^2/h ⁵:

$$\sigma_{xy} = n \frac{e^2}{h}, \quad n = 0, 1, 2, \dots \quad (1.2)$$

The behavior of the Hall conductivity as a function of the magnetic field is shown in Fig. 1.1 c). The characteristic plateaus associated with the quantized Hall conductivity are observed.

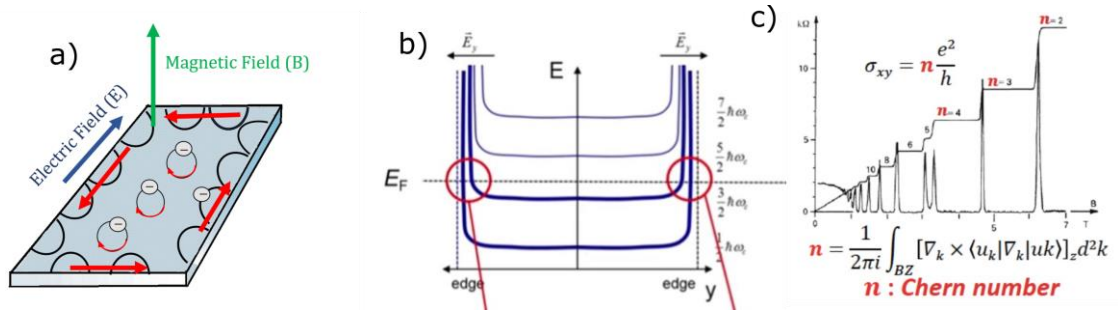


Figure 1.1 a) Representation of Quantum Hall Effect with chiral edge states. b) Representation of the Landau levels. c) Longitudinal and transverse component from the resistivity showing the quantization of conductivity of units of e^2/h . Edited from ².

It was soon realized by Laughlin⁶, Halperin⁷, among others, that the edge states play a determinant role. The presence of a bulk quantized property along with metallic (crossing the Fermi level) boundary states is the hallmark of a topological insulator, known as the bulk-boundary correspondence. Thouless, Kohmoto, Nightingale, and den Njis⁸ made an important further step in this relation, discovering that the quantized conductivity was topological, meaning that it can be described by an integer topological invariant, the first Chern Number (C_n).

$$\sigma_{xy} = C_n \left(\frac{e^2}{h} \right) \quad (1.3)$$

With C_n given by the expression shown in Fig 1.1 c) in terms of the periodic part of the Bloch wave function, u_k . The robustness of the quantized conductivity is explained by the topological invariant, in the sense that it cannot be changed under smooth variations of the Hamiltonian. The topological nature of the quantum Hall effect is characterized by the two-dimensionality of the system and the lack of time reversal symmetry (TRS). For time-reversal symmetric systems, the first Chern number is necessarily zero, implying zero Hall conductivity. In the quantum Hall effect, the time reversal symmetry is broken by the presence of a magnetic field.

1.2. Topological Insulators

Topological phases of matter differ from conventional matter because the former feature a nontrivial topological invariant on its electronic structure. Topological insulators (TIs) are electronic materials with a band gap in the bulk like an insulator material while being electrically conductive along its boundaries, due to topologically unavoidable gapless boundary states⁵.

The formation of conducting edge states in the QHE requires a magnetic field to break the time-reversal symmetry so that the Chern number is different from zero. Topological states can also exist in systems that do not break time reversal symmetry. An important example of an intrinsic effect that causes the formation of nontrivial topological states without the need to break TRS is the spin-orbit coupling.

The spin-orbit coupling allows a different topological class of insulator with TRS unbroken. The presence of spin-orbit coupling leads to a band inversion in the electronic structure of the material between the conduction and the valence band⁵, resulting from the coupling of an electron's magnetic spin to the intrinsic magnetic field set up by the electron's motion around its orbital. The band inversion without TRS breaking is the key ingredient in the new class of topological insulators.

Quantum Spin Hall effect

Kane and Mele¹ proposed a model displaying the so-called quantum spin Hall effect (QSHE), which does not break TRS. It can be understood as two copies of the QHE with spin-filtered (spin current $\neq 0$) counter-propagating (total current = 0) edge states pair (Fig 1.2), where each has a different spin and propagation direction (helical edge states). Considering both edges, a two-terminal conductance of $2 \frac{e^2}{h}$ is expected⁵, but taking into account the spin edge channels, it is expected a nonzero spin Hall conductance of $\frac{e^2}{2h}$ for each channel⁴.

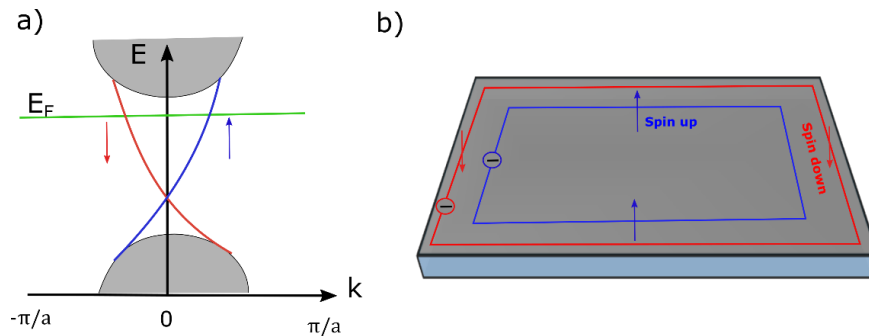


Figure 1.2 a) Schematics of the energy dispersion for a 2D topological system with 1D spin edge states crossing the Fermi level and b) Illustration of the quantum spin hall effect presenting two helical channels around the edges associated for each spin.

Furthermore, due to the absence of a magnetic field, the TRS is maintained. Therefore, backscattering is not allowed since it would require an electron spin to flip. The spin of an electron cannot be changed due to the protection of the TRS, which gives robustness to the edge states. This holds in the presence of disorder or impurities, as long as they do not break TRS. Spin-orbit coupling requires a distinct topological invariant from the Chern number, C_n , because time-reversal invariant systems present a zero Chern number. Thus, a new topological invariant (ν) was introduced for this class of $\mathbb{Z}_2$ topological insulators⁹. A more detailed discussion about the spin-orbit coupling is explained later in the context of 3D topological insulators.

1.2.1. $\mathbb{Z}_2$ topological insulators

2D topological insulators (TIs) with TRS are characterized by a $\mathbb{Z}_2$ topological invariant, ν_0 , which can only take two values, 0 or 1, where 0 would correspond to a topologically trivial and 1 to a topologically nontrivial system¹⁰. This classification derives from the conservation of TRS. The Bloch Hamiltonian should be time-reversal invariant (TRI), consequently, imposing a restriction on the band structure called Kramer's theorem. The theorem states that all eigenstates of a TRI Hamiltonian must be at least two-fold degenerate for spin $\frac{1}{2}$ particles⁵. In particular, at the so-called time-reversal invariant momenta (TRIM) ($k = 0, \pi/a$), two bands must meet corresponding to states related by TRS.

As an example, Fig. 1.3 a) shows the dispersion of spin edge states. The special points $k=0$ and $k=\pi/a$ are degenerate as a consequence of Kramer's theorem, but the spin-orbit coupling splits the degeneracy in momentum as we move away from these points. There are two ways for these states to connect. In Fig.1.3 a) the same pair of edge-state bands are shared between the TRI points. In this case, the edge states can be eliminated with disorder, by tuning the Fermi energy or pushing them out of the band gap, therefore the topological invariant $\nu_0 = 0$ (topological trivial system). In Fig. 1.3 b), the states cannot be removed from the band gap, as there is always an odd number of pairs of states crossing the Fermi level, so that $\nu_0 = 1$ (topological nontrivial system). In conclusion, a topological insulator is characterized by having topologically protected edge states, when there is an odd number of times the states cross the Fermi level.

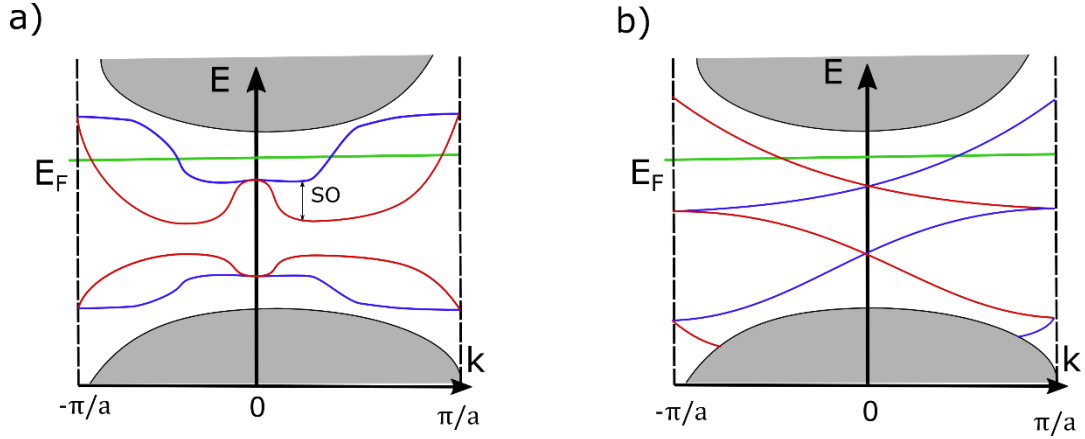


Figure 1.3 Dispersion of spin texture edge states with a) topological trivial and b) topological nontrivial character (Blue and red colors indicate spin species).

1.2.2. 2D Quantum Well HgTe/CdTe

The quantum spin Hall effect was observed experimentally on inverted HgTe/CdTe quantum wells (QWs)³. The compound HgTe is a zero-gap semiconductor with a degeneracy of the valence and conduction bands at the Γ_8 point and which features an inverted band structure, representing a “negative band gap”. This material is combined, as a sandwich, with a semiconductor, $\text{Hg}_{0.32}\text{Cd}_{0.68}\text{Te}$, which has a positive energy gap, meaning that there is no inversion of the conduction and valence bands. Consequently, a QW is formed as illustrated in Fig 1.4. a).

The crucial parameter in the QW is the HgTe layer thickness (d). An evolution of the energy band with the thickness can be seen in Fig. 1.4 b). The s-type band E1 and the p-type H1 band cross each other by increasing the thickness d , reaching a critical value $d_c = 63 \text{ \AA}$, resulting in a zero-gap semiconductor³. For a thickness $d_c < 63 \text{ \AA}$, the material is a normal semiconductor with a valence band below the conducting band and a positive band gap. However, for thickness $d_c > 63 \text{ \AA}$, the band structure is inverted resulting in a “negative band gap”, and a quantum phase transition occurs at $d = d_c$ ³.

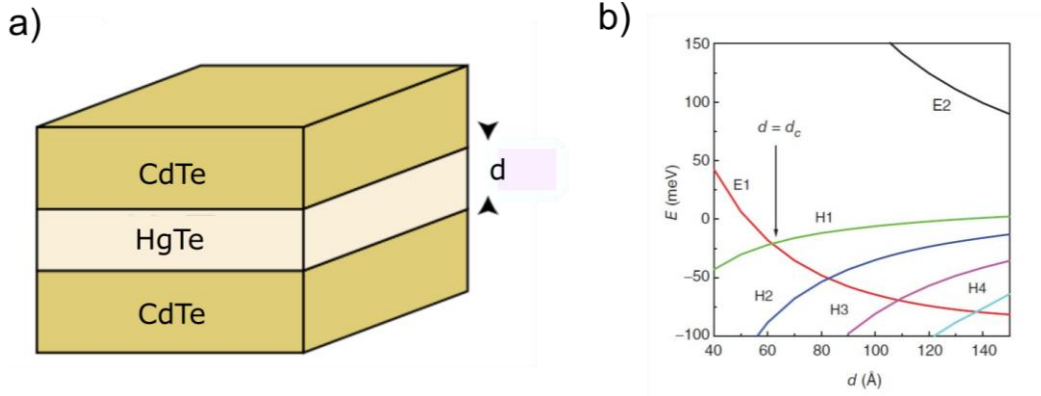


Figure 1.4 a) Quantum Well structure of the HgTe/CdTe heterostructure. b) Electron energy subbands E1 and E2 and heavy-hole subbands (H1-H4) in HgTe QW as a function of thickness d. Edited from ³.

Considering an inverted QW band structure, if the Fermi level is in the bulk band gap, there are edge states crossing the E_F , giving rise to a non-trivial insulator, referred to as the quantum spin Hall effect (QSH). The system is characterized by the existence of two spin-polarized conducting channels at the edge, each one owning a characteristic quantum conductance of $\frac{e^2}{h}$. Furthermore, due to the crossing of states of the inverted band structures, a QSH cannot be adiabatically deformed into a trivial insulating state without closing the gap, so the system is topologically protected.

Experimentally, the $\frac{2e^2}{h}$ conductance, the helical character of the edge channels, and the electrical detection of their spin polarization were demonstrated ³. For the conductance measurement, a four-terminal resistance $R_{14,23} = V_{23} / I_{14}$ of a sample was measured as a function of a gate voltage (Fig. 1.5). The gate voltage enables tuning the Fermi energy from the bulk conduction to the bulk valence band, by shifting the Fermi level.

Sample (I), with a thickness smaller than the critical thickness (d_c), presents a conventional semiconductor behavior, whereas sample (II), with a thickness larger than the critical thickness (d_c) and an inverted band structure exhibits a conductance of $\frac{0.3e^2}{h}$. If the length (L) of the device is shorter, as for samples (III and IV) the conductance reaches the predicted value of $\frac{2e^2}{h}$ and curiously, changing the width (W) does not change the conductance of the material, demonstrating the existence of counterpropagating edge states³.

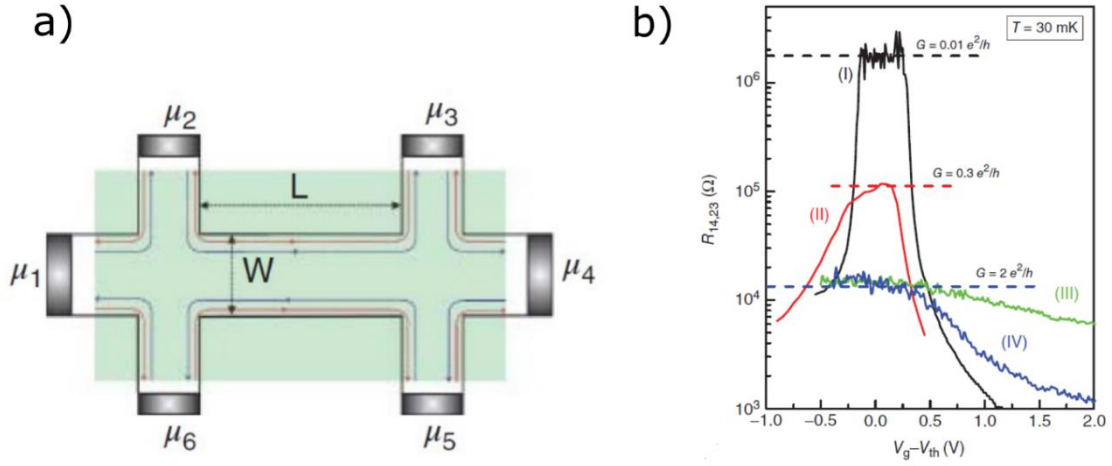


Figure 1.5 a) Hall bar geometry. b) Longitudinal resistance plotted as a function of $V_g - V_{th}$ for 4 different samples at 30mK: (I) QW with $d=45$ Å and (II, III, IV) $d=73$ Å. The device dimensions are (L/W) , (20.0×13.3) μm^2 for devices (I) and (II), (1×1) μm^2 for device (III), and (1×0.5) μm^2 for device (IV) Edited from ³.

1.2.3.3D topological insulator and A_2B_3 Family

Subsequently, it was possible to extend the quantum spin hall insulator to three dimensions (3D), establishing a new bulk topological order and the presence of conducting surface states instead of edge states. 3D TIs are characterized by four $\mathbb{Z}_2$ topological invariants $(\nu_0; \nu_1\nu_2\nu_3)$, where ν_0 is the strong topological invariant and $\nu_1 - \nu_3$ are the weak topological invariants¹⁰. The 2D surface Brillouin zone has 4 different TRIM points. These points give rise to Kramer's pairs, whereas for the rest of the Brillouin zone points the degeneracy is split in momentum due to spin-orbit coupling (SOC). For energy bands connecting these points, it could occur a crossing of the Fermi level an even or odd number of times, corresponding to a trivial insulator and a topological insulator, respectively. Since these TRIM points also belong to other 2D surface Brillouin zones, we arrive at the set of four $\mathbb{Z}_2$ integers, with a single combination guaranteeing the presence of surface states over all the surfaces of the sample¹¹. This combination is identified by the strong topological invariant ν_0 , which can take the values 0 or 1, corresponding to a weak or strong insulator, respectively.

A weak TI ($\nu_0 = 0$) can be seen as a stack of 2D TIs layers (Fig. 1.6 a) left), while the weak topological invariants $(\nu_1\nu_2\nu_3)$ can be seen as the miller indices corresponding to the TI layer. However, the surface states of this type of 3D TI are not protected by TRS and therefore are not robust. A strong TI ($\nu_0 = 1$) presents topologically protected metallic surface states as illustrated in Fig. 1.6 b). Kramer's degeneracy ensures that surface state bands cross at TRIM points, giving rise to the characteristic Dirac cone dispersion shown in Fig. 1.6 c). Furthermore, due to TRS, 3D TIs present opposite spins at opposite momenta, k and $-k$, which leads to the spin-momentum locking also illustrated in Fig. 1.6 c), also referred

to a spin texture. Integrating the phase around the Dirac point, where the spin orientation is fully revolving, gives rise to a Berry phase of π ⁵ and has important consequences for the weak anti-localization effect. This effect is introduced in section 1.2.4.

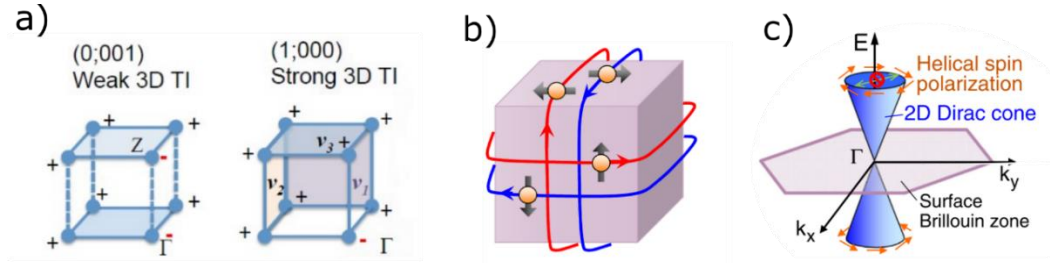


Figure 1.6 a) Illustration of a weak 3D TI being a stack of 2D TI with topological properties and a strong 3D insulator with all surfaces presenting topological properties. b) Full illustration of a Strong 3D TI and the conduction along the TI surface. c) Band diagram of a 3D TI, presenting the topological spin-texture surface states dispersion for 3D systems (Dirac cone) with a spin orientation S rotating along a circle. Edited from ¹⁵⁹.

A_2B_3 Family

It was theoretically proposed by Zhang et al. that binary compounds with elements, such as Bi, Sb, Se, and Te, could lead to a 3D topological insulator with 2D conductive surface states⁴. It was shown that the A_2B_3 family is a candidate for the detection of topological effects with $A = \text{Bi, Sb}$ (Elements of Group V), and $B = \text{Te, Se}$ (Elements of Group VI). Later, these compounds were studied confirming the existence of the topological surface states in Bi_2Se_3 ¹², Bi_2Te_3 ¹³, ... Among them, Bi_2Se_3 offers the potential topologically protected behavior in ordinary crystals at room temperature, due to the large band gap (0.3 eV)⁵.

Bi_2Se_3 presents a rhombohedral crystal structure with a space group ($R\bar{3}m$). The unit cell consists of 15 atomic layers as illustrated in Fig 1.7. 5 atomic layers arranged along the Z-axis are known as quintuple layers (QLs) stacked as $\text{Se1}'\text{-Bi1}'\text{-Se2-Bi1-Se1}$. Two QLs are bound by Van der Waals (VdW) forces, whereas within a QL, intralayers are bonded by strong covalent bonding⁴. A stack of 3 QL forms the unit cell.

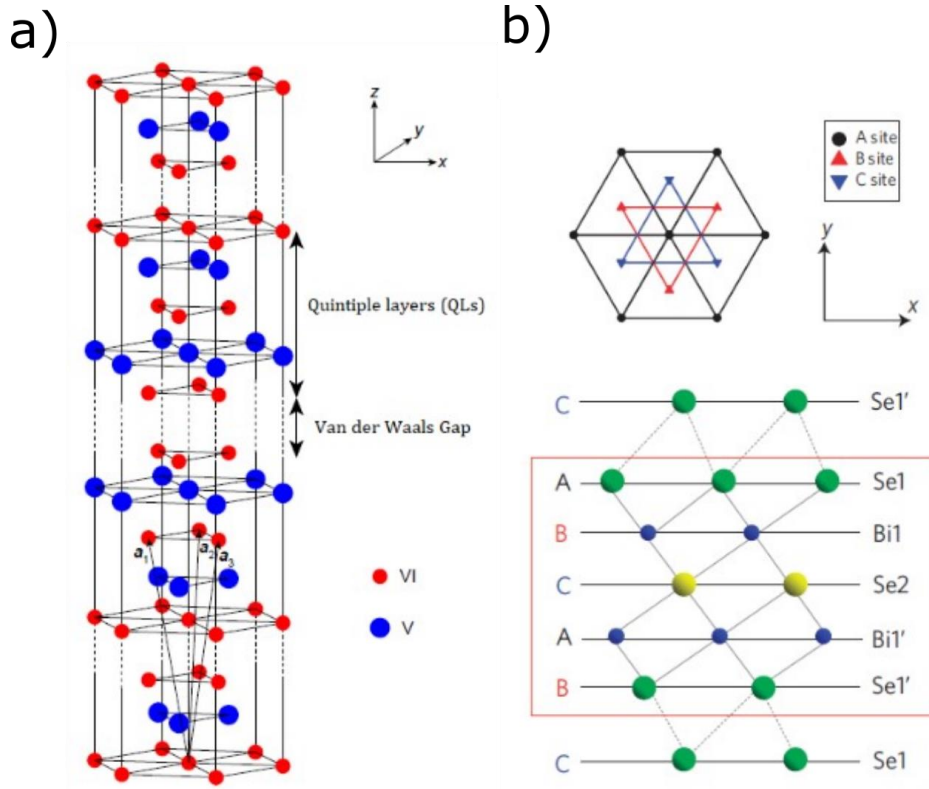


Figure 1.7 a) Crystal structure of A_2B_3 compounds with primitive vectors (a_1, a_2, a_3). b) Illustration of structural organization along the planes YX and ZX of Bi_2Se_3 ¹².

The Bi_2Se_3 band structure is characterized by a large band gap up to 0.3 eV and a robust, almost idealized surface Dirac cone at the Γ point, where the topological surface states are crossing the band gap⁴, see Fig. 1.8 a). The presence of strong spin-orbit coupling, owing to the heavy element Bi, allows the band inversion, splitting the energy levels, and creating the surface states.

Due to the relatively large band gap, Bi_2Se_3 is one candidate suitable for studying the topologically protected states at room temperature ($k_B T = 25$ meV). Furthermore, the surface states are spin non-degenerate and helically spin polarized. The constant energy contour is nearly spherical, while the spin vector is perpendicular to the wave vector. Similar to a 2D TI, where 2 spin channels with opposite spin and propagation directions are present at the edge, for a 3D TI, two opposite spins propagate in opposite directions on a surface instead of a 1D channel. The relation between the spin and the propagation direction is such that the spin direction lies on the surface, but is perpendicular to the propagation direction, an example of the spin-momentum locking. These properties enable efficient spin manipulation for spintronic applications, by modifying the momentum of the electrons.

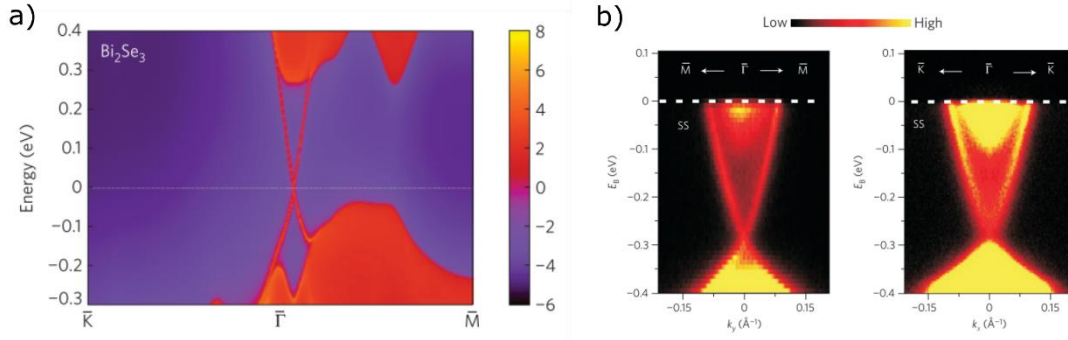


Figure 1.8 a) Energy and momentum dependence of the local density of states (LDOS) for Bi_2Se_3 . b) High resolution ARPES measurements of the surface band structure of Bi_2Se_3 . Edited from ¹².

1.2.4. Weak (anti)localization effect

Weak anti-localization (WAL) is a manifestation of the phase coherence of charge carriers in a material with intrinsic spin-orbit coupling in two-dimensions. For systems in the quantum diffusive regime, the electron maintains its phase coherence after being scattered multiple times, since the mean free path is smaller than the phase coherence length. In a closed time-reversed loop (Fig. 1.9 a), a quantum interference of the phase coherence occurs, causing a quantum correction of the conductivity. In TIs, the time-reversed paths interfere destructively, due to the existence of spin-momentum locking. Whenever an electron is scattered its momentum changes and consequently, the spin rotates accordingly. A phase shift of π (Berry phase) occurs when the electron moves along a closed path, which leads to destructive interference with its original position. This destructive interference increases electron delocalization, meaning that the conductivity is enhanced¹⁰. The application of a perpendicular magnetic field destroys the time-reversal symmetry of the system, and it affects the Berry phase in a way that increases the localization. Therefore, the conductivity decreases sharply, as a cusp, by increasing the magnetic field. This effect is known as the weak anti-localization effect, Fig. 1.9 c). For conventional two-dimensional electron systems with zero Berry phase, a characteristic weak localization is seen instead, as illustrated in Fig. 1.9 b).

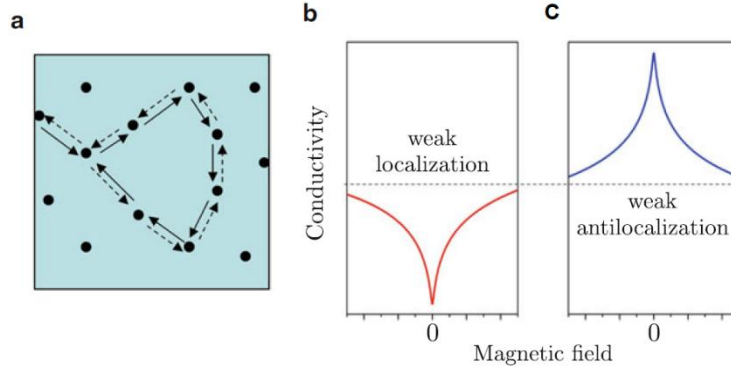


Figure 1.9 a) Illustration of a close loop of an electron path. b) Positive conductance of weak localization (WL) and c) typical weak antilocalization curve showing a decreasing in the conductance with magnetic field ¹⁶⁰.

At low temperatures, in the quantum transport regime, the WAL manifests itself in magnetoresistance (MR) measurements, as a resistance cusp in low fields. This effect arises in TIs due to the presence of strong spin-orbit coupling in the bulk and 2D Dirac-like physics at the edges. The sharp cusp in the magnetoconductance can be described by the following Hikami–Larkin–Nagaoka* (HLN) equation¹⁴:

$$\Delta G(B) = \alpha \frac{e^2}{\pi h} \left[\ln \left(\frac{B\phi}{B} \right) - \psi \left(\frac{1}{2} + \frac{B\phi}{B} \right) \right] + \beta B^2 \quad (1.4),$$

where G is the magneto conductance, e and h are the electron charge and Planck constant, respectively. $B\phi = \frac{\hbar}{4eL_\phi^2}$, where L_ϕ is the phase coherent length and $\psi(x)$ is the digamma function. α “alpha” is the prefactor, a coefficient related to the scattering events that can affect the phase. The value can be either positive for the Weak localization (WL) or negative for the weak antilocalization. For the WAL α is expected to acquire a value of -0.5 per conductive channel. An ideal TI should hold a prefactor of -1 due to the existence of two decoupled surfaces grasping topological surface states. The βB^2 term is representing the magnetic background, being β the quadratic component¹⁴.

*(This equation strictly applies to the variation in sheet conductivity (magnetoconductivity), $\Delta\sigma_{xx}(B)$, of a 2D system, which, in certain geometries, differs from the variation in sample conductance, $\Delta G(B)$, by a dimensionless geometric conversion factor, generally not equal to 1.)

Chapter 2

2. Experimental Techniques

In the following chapter, the experimental setups used here are introduced. Firstly, the molecular beam epitaxy (MBE) is discussed such as all components present in the deposition equipment. *In-situ* characterization is possible by reflection high energy electron diffraction (RHEED). The *ex-situ* characterization techniques applied were X-ray diffraction (XRD), X-ray Reflectivity (XRR), Raman spectroscopy, atomic force microscopy (AFM), magneto-transport measurements, X-ray photoelectron spectroscopy (XPS) and angle-resolved photoemission spectroscopy (ARPES). Finally, the fabrication of the Hall-bar field effect transistors is explained.

2.1. Molecular Beam Epitaxy

There are several deposition techniques for the growth of thin films, such as physical vapor deposition, chemical vapor deposition, and molecular beam epitaxy. Molecular beam epitaxy (MBE) presents several advantages, such as a clean growth environment, good controllability, slow growth rates (1 nm/min), easy to dope, and wafer-scale growth, hence allowing the growth of 2D epitaxial materials¹⁵.

An MBE presents an environment free from contamination due to ultra-high vacuum (UHV) conditions with a low background pressure of 1×10^{-10} mbar and a loading lock pressure of around 1×10^{-9} mbar. Such low pressures are possible due to the combination of a turbo pump, ionic pump, and titanium sublimation pump. Moreover, the low background pressure, in the growth chamber, allows the growth of large-area thin films with good uniformity.

The MBE at INL (Fig. 2.1) (Omicron Nanotechnology EVO-50) has two chambers, the growth chamber, and a loading lock. The latter is used for the storage of substrates before being introduced into the growth chamber, separated by a gate valve. The following elements can be evaporated from the effusion cells: Cu, Bi, Ga, and In. Each element is contained in a non-reactive crucible in Knudsen cells, where a filament surrounding the cell heats the material until it evaporates, creating a molecular beam. The MBE also presents the Se element contained in a valved cracker source. In this case, the Se besides being

evaporated thermally, a cracker at higher temperatures is present to break the large Se molecules into smaller molecules. Subsequently, an adjustable valve is incorporated into the cell, which permits to change of valve aperture from 0 to 5 mm, and consequently changes the Se flux without changing the cell temperature. A beam flux monitor is installed into the system. This movable equipment can be placed directly below the substrate to measure the beam equivalent pressure (BEP) or element fluxes to control the growth rate and the stoichiometry of the deposited compound. Moreover, the substrate holder can be rotated to provide good uniformity throughout the substrate, which can be heated to very high temperatures (max 1000 °C). Finally, an *in-situ* RHEED¹⁶ system is also installed to supply real-time information about the growth, such as crystal structure, and growth rate, as explained in section 2.1.1. The MBE provides good control and high-quality growth of thin films due to the accurate thickness, slow growth rate, and controllable stoichiometry by adjusting the cell temperature. The growth parameters for optimized Bi₂Se₃ were studied in the initial part of the thesis.

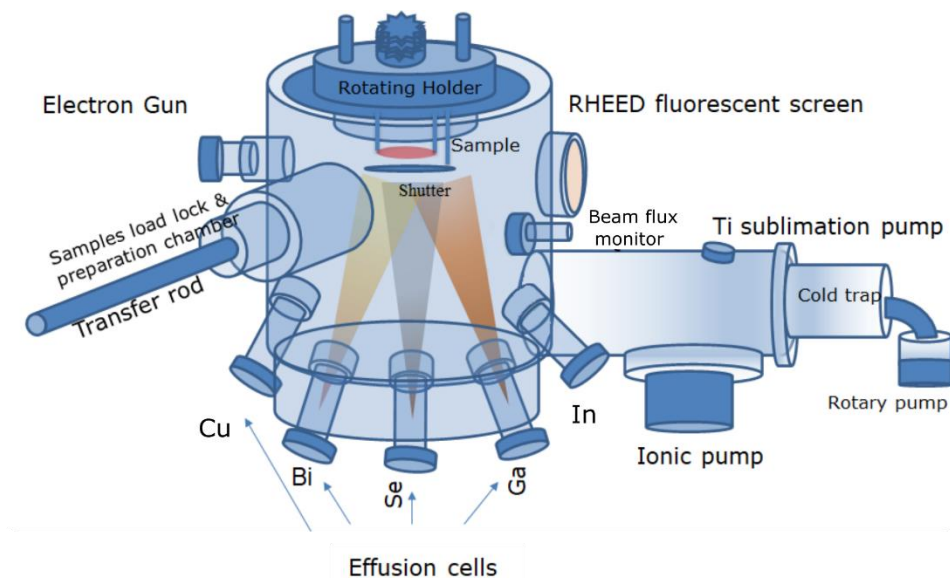


Figure 2.1 MBE diagram showing the growth chamber. This chamber is equipped with 4 Knudsen cells with Cu, Bi, Ga, and In and a valved cracker cell for Se. The system is also equipped with a RHEED and a beam flux monitor.

Epitaxy

MBE allows a slow rate, enabling the epitaxial growth of 2D materials, meaning that the growth material orientation is well-defined concerning the substrate surface, resulting in a single-crystal material¹⁵.

The element flux is controlled by the effusion cell temperature, which either sublimates or evaporates the atoms/molecules of specific elements with low kinetic energy. The growth is dominated by the kinetic energy at the substrate material (substrate temperature). Atoms reaching the surface of the crystal substrate, adatoms, are weakly

bonded to it. They reach with an energy that allows them to move freely parallel to the plane surface to the energetically favorable site of the layer. At this point, they bound and become energetically stable and act as nucleation centers.

There are three distinct growth modes, as presented in Fig 2.2, the Volmer-Weber, the Frank-van der Merwe, and the Stranski-Krastanov¹⁷. These growth modes are dependent on the interface energies and lattice mismatch. However, in lattice-matched systems, the growth modes are mainly dependent on the interface and surface energies.

The Volmer-Weber growth (island growth) (Fig. 2.2 a) takes place as an agglomeration of adatoms in a preferential region on the sample, because the sum of the epilayer surface energy and the interface energy is higher than the energy of the substrate surface, and consequently this nucleation results in 3D islands. On the other hand, Frank-van der Merwe (layer-by-layer) (Fig. 2.2 b) occurs when the energy of the substrate surface is higher, hence the material can be seen as a wet deposition, and a layer-by-layer growth occurs. Finally, the last mode called Stranski-Krastanov, is a mixture of the two previous modes with 2D layers and 3D islands (Fig. 2.2 c), due to a strained epilayer energy with small interface energy.

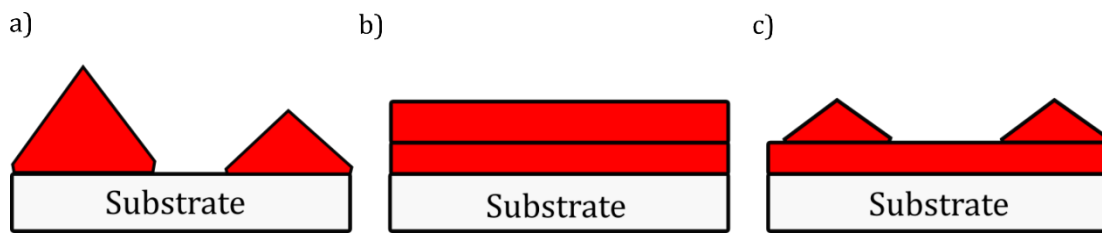


Figure 2.2 Illustration of the three main growth modes a) Volmer-Weber (Island growth), b) Frank-van der Merwe (Layer-by-layer), and c) Stranski-Krastanov.

As introduced in section 1.2.3, the topological insulator studied in the current thesis consists of the A_2B_3 family TI. This family consists of Van der Waals layers stacked by Van der Waals forces. The growth of these materials (Van der Waals) can be understood as layer-by-layer growth (Fig. 2.2 b). Due to the weak bonding of these materials to the substrate through Van der Waals forces, a distinct gap forms. This unique growth characteristic allows for layer-by-layer growth, where each subsequent layer retains structural information from the preceding layer (epitaxial).

Defects

Besides the growth temperature, the substrate surface roughness, lattice mismatch, and other parameters also influence the growth of these thin films, which play an important role in defect minimization. Lattice mismatch is one of the most important factors for the growth of those materials because if the substrate lattice parameter is significantly different from the material lattice parameter, it leads to stress in the thin film. The stress stimulates the formation of defects. As the film is deposited, the formation of defects can accumulate, and consequently, decrease the material quality.

A variety of structural defects exists, such as stacking faults, twin defects, antiphase domain boundaries, point defects, and mosaicity-tilt(twist). As illustrated in Fig 1.7, the stacking sequence of the Bi_2Se_3 in the growth direction would be $ABCABC$, with a rotation of 120° to the previous layer. A stacking fault occurs when a layer is removed or added, leading to a sequence e.g., $ABCBCABC$ or $ABCABBC$ (FIG 2.3a). Studies have shown that stacking faults can be responsible for shifts of the Dirac point concerning the pristine band structure¹⁵. Twin defects occur when two different domains meet, where the stacking sequences are different (Fig 2.3 b). This effect can be in-plane (horizontal twinning) or in the growth direction (vertical twinning). Due to the higher surface/thickness ratio, the probability of an in-plane twinning is larger than a vertical twinning. It can be seen as a triangular rotation between two different domains. Details about the reduction of twinning are studied in Chapter 3.

Finally, point defects are characteristic of single atoms in the lattice sites. There are three types of point defects as shown in Fig. 2.3 c). 1) There are interstitial defects by the nucleation of atoms inside the crystal structure randomly, not adapting to a site of the crystal. 2) If the defect is replacing an element in the lattice, it is called a substitutional defect. In some cases, these defects are introduced on purpose to study doping in the material. 3) In case an element is missing in the site it is called a vacancy.

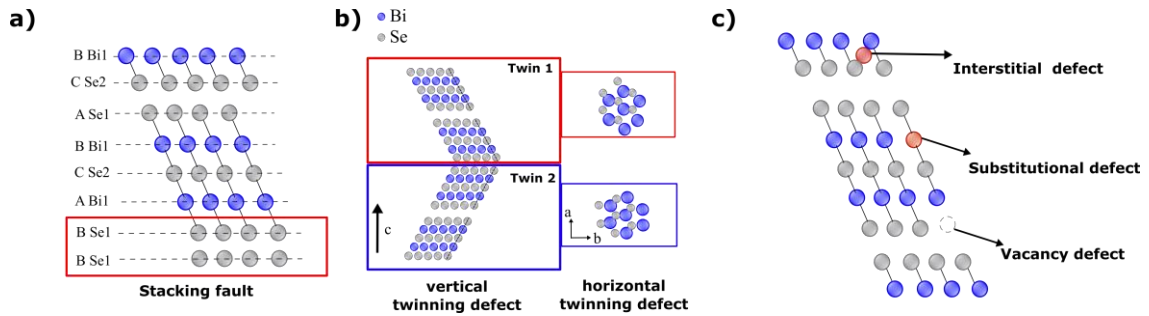


Figure 2.3 Defect representation of a) Stacking fault, b) twin defects (vertical and horizontal), and c) point defects with the representation of interstitial, substitutional and vacancy defects.

Preparation of substrates and growth procedure

Before the 2D material growth, we subjected the substrate to specific annealing steps and surface treatments. Bi_2Se_3 and In_2Se_3 are the 2D materials deposited during the presented thesis. The growth of these materials was optimized on c-oriented (0001) sapphire substrates (Al_2O_3) due to the similar lattice parameter with a lattice mismatch percentage of 15%¹⁵. The substrate is a 2-inch wafer with a thickness of 0.43 mm and a maximum miscut of 0.2° , purchased from University Wafer.

Prior to the material deposition, the substrates are introduced in the UHV system, where they undergo an annealing process at 900°C for 45-60 minutes, to remove all contaminations on the substrate surface.

The Bi_2Se_3 growth procedure optimization is studied in Chapter 3. Bi is evaporated with a cell temperature of 535°C , with a Se cell temperature of 285°C and a Se valve aperture of 2 mm ($\text{BEP} = 1 \times 10^{-5}$ mBar). The Se source also presents a cracker at 900°C to break the large Se molecules into smaller molecules, hence improving the reactivity of the Se atoms. The Bi_2Se_3 growth rate ranges between 1-1.4 nm/min. The Bi cell temperature used for the first growth was around 520°C . After a stabilization of over 5 growths, it was necessary to increase the Bi cell temperature to maintain the growth rate. In Chapter 3, the Bi cell temperature was 520°C , which was increased to 535°C in Chapter 4 and forward. Each element flux is measured by a Bayard-Alpert pressure gauge, beam equivalent pressure (BEP) in front of the substrate. The BEP can be different each growth day which might lead to a small variation in the growth rate.

The In_2Se_3 layer is introduced in Chapter 3 for the implementation of a buffer layer. The growth of In_2Se_3 is of considerable difficulty due to the large phase variety (InSe , $\gamma\text{-In}_2\text{Se}_3$, $\alpha\text{-In}_2\text{Se}_3$, ...) with different crystal forms. Marcel Claro et al. developed the optimization of the $\beta\text{-In}_2\text{Se}_3$ growth by controlling the substrate temperature (550°C) and the Se valve aperture 5 mm ($\text{BEP} = 2.5 \times 10^{-5}$ mBar)¹⁸. The In and Se cell temperatures are 740°C and 285°C , respectively, leading to a growth rate of 1.2 nm/min. $\beta\text{-In}_2\text{Se}_3$ resembles the crystal structure of Bi_2Se_3 with a similar lattice parameter¹⁸. Furthermore, $\beta\text{-In}_2\text{Se}_3$ is a semiconductor material with a 1.38 eV band gap¹⁸ which acts as an insulating material without contributions to the Bi_2Se_3 transport properties when in contact.

2.1.1. In-situ characterization

Reflection high-energy electron diffraction (RHEED)

The growth of epitaxial materials by MBE is commonly monitored by in-situ characterization techniques, such as reflection high-energy electron diffraction (RHEED) to provide good material quality. RHEED is a surface-sensitive technique that offers information about the crystal structure. Fig. 2.4 illustrates the configuration of a RHEED system. It consists of an electron gun to generate a flux of high-energy electrons, which can range between 5-100 keV. Electrons hit the sample at grazing angles ($1\text{-}5^\circ$), which only allows them to interact with the topmost surface layer of the sample. The beam is deflected from the sample surface, and it creates a pattern on a fluorescent screen. Additionally, a rotation stage for the sample is required to allow the azimuthal rotation of the sample for the visualization at different azimuthal directions.

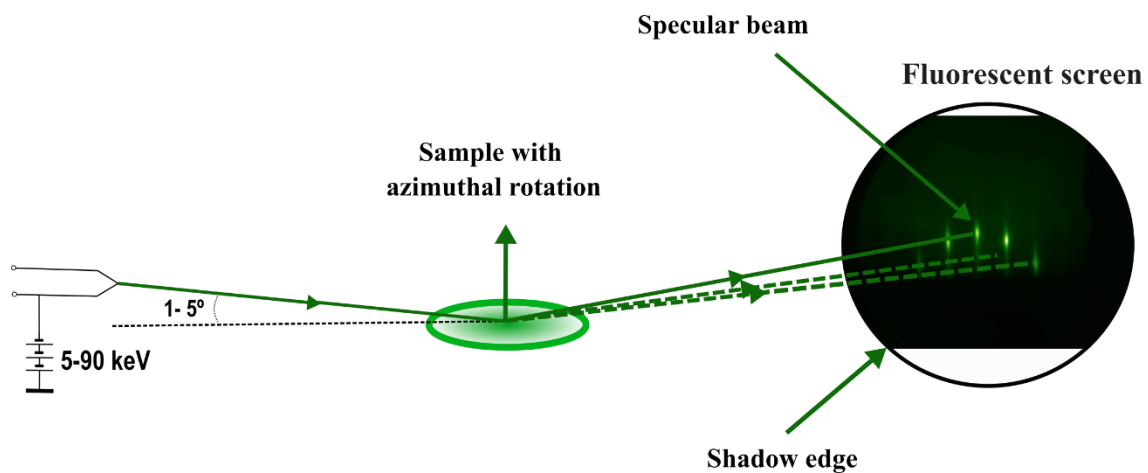


Figure 2.4 Schematic configuration of a RHEED setup.

The Ewald sphere is used to understand the diffraction pattern (Fig 2.5 a). The atoms arranged in the real space are transformed into perpendicular reciprocal planes. The intersection of these planes with the Ewald sphere creates a pattern that is observable on the fluorescent screen. Fig 2.5 b) illustrates possible configurations of realistic surface constructions and their respective RHEED pattern. This information is important for section 4.2.1. For a flat and perfect single crystalline surface, the electron beam diffracts into spots. However, imperfections and the formation of small domains generate an elongation of the spots into streaky lines. On the other hand, if the surface is not flat, e.g. island growth, a regular spot pattern is formed. Finally, if the sample is not a single crystal and presents some polycrystallinity, this leads to the formation of concentric rings.

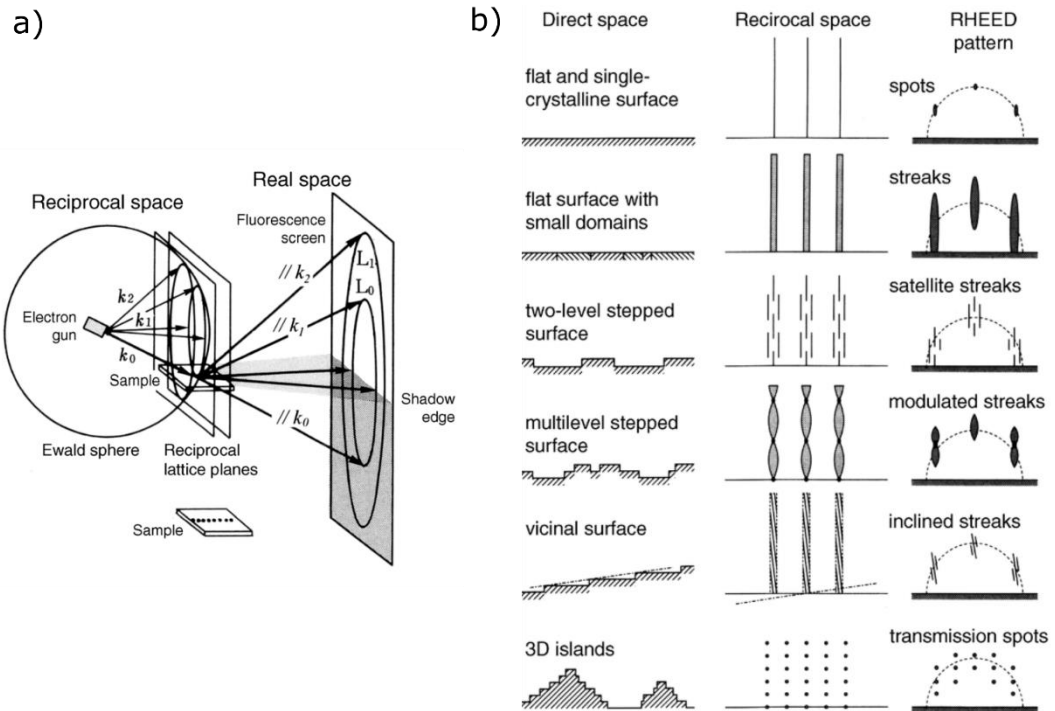


Figure 2.5 a) Reciprocal space and real space of a RHEED. Reciprocal space presents the Ewald sphere construction. b) Schematics of different types of realistic surface growth and correspondent reciprocal space and their RHEED pattern³⁴.

RHEED is also used to monitor the growth in real-time of thin films by measuring the oscillations of the reflection intensity. The oscillations can be used to calculate the growth rate of different materials because a monolayer deposition ($\theta=1$) represents a period oscillation as illustrated in Fig. 2.6.

A KSA from STAIB Instruments is used. The system was operated at a filament current of 1.54 A and accelerating voltages of 15 keV. The RHEED pattern was recorded by a camera.

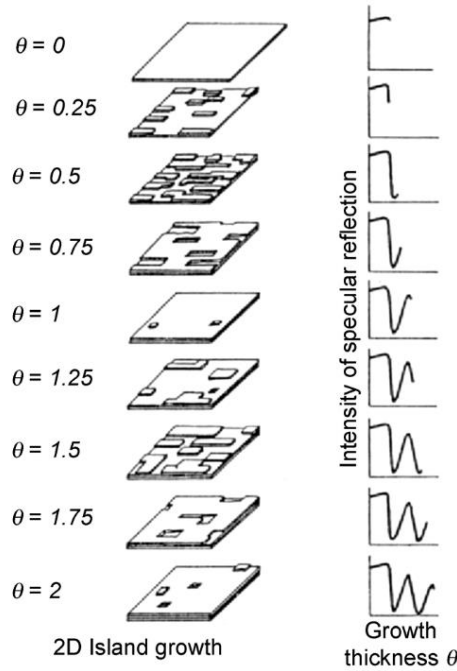


Figure 2.6 RHEED intensity oscillation and crystal growth monitor. θ represents the percentage of the monolayer growth. $\theta=1$ represents 1 monolayer and $\theta=1.5$ represents 1 monolayer and half growth of the following³⁴.

2.2. Ex-situ characterization

2.2.1. X-ray diffraction

X-ray diffraction (XRD) is a common characterization technique used to identify crystal structure, its lattice parameters, material phase, and orientation. The crystal structure study is possible due to the similar range of X-ray wavelength and the inter-atomic distances from the crystal structure, as illustrated in Fig 2.7 a). When an X-ray beam hits a crystalline material, it can be reflected from the material crystalline plane, and consequently interfere with the X-ray beam reflected in the material surface. This process is called diffraction. We have a constructive interference if Bragg's law is satisfied.

$$2d_{hkl} \sin \theta = n\lambda \quad (2.1)$$

where d_{hkl} is the inter-atomic distance between two planes, θ is the incident angle, and λ is the X-ray wavelength. A schematic configuration of the XRD can be seen in Fig. 2.7 b).

Single crystals and epitaxial materials can be identified by XRD, due to the existence of only one set of parallel planes to the surface of the material. These types of materials should present all peaks of the same family (00n, nnn, etc) in the Bragg-Brentano configuration geometry. Epitaxial thin films require different mode XRD geometries for the in-plane lattice

information. In addition to the θ angle, ω , φ , ψ , and χ (Fig 2.7 b) angles are also variable. A φ scan is used to have in-plane information by fixing a ω , θ and χ correspondent to a diffracted plane (hkl), with $h/k \neq 0$ such as the (015) plane. The φ scan is performed by an azimuthal rotation and registers the diffracted intensity. This mode has information about the crystal symmetry, and it can be implemented to study twinning defects.

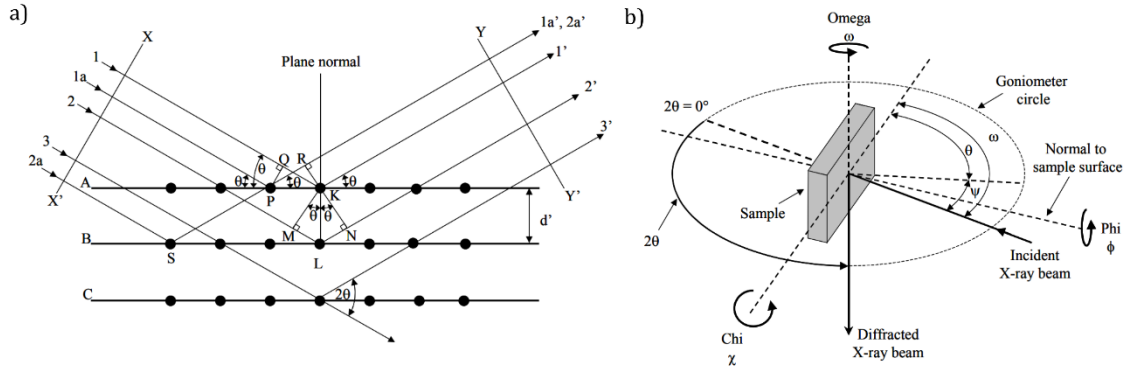


Figure 2.7 a) Inter-atomic planes with diffraction by the crystal structure. b) Angles and axes relevant for all XRD measurement modes ¹⁶¹.

A PANalytical X'Pert system was used to perform the XRD measurements, using a wavelength of 1.54 Å. The Bi_2Se_3 lattice parameter c was calculated with the simplified Eq. (2.2) for a hexagonal crystal structure:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} = \frac{4}{3} \frac{l^2}{c^2} \quad (2.2)$$

Reflectivity

X-ray studies also offer the mode of X-ray reflectivity (XRR) used on flat materials to obtain information about the thickness, roughness, and density of the film. Similar to XRD, an X-ray beam hits the sample at grazing angles, which creates a specular reflected wave. When the incident angle is higher than the critical angle (θ_c) the beam penetrates the material. XRR is focused on the interference at grazing angles which leads to periodic oscillation about the Fresnel reflectivity. Fig. 2.8 explains these oscillations and the respective information acquired.

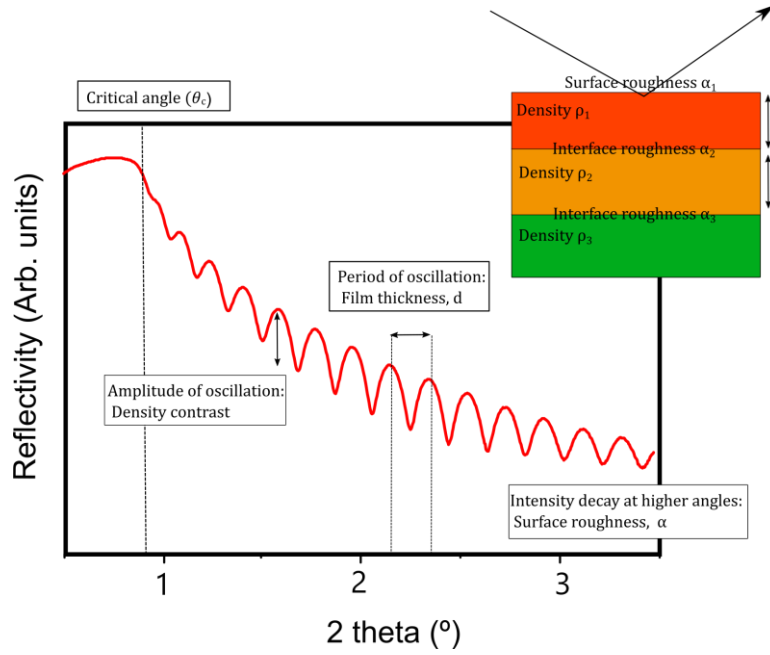


Figure 2.8 Periodic oscillations observed in an XRR scan and information profile.

The reflectivity oscillation period is linked to the thickness of the thin layer, which allows us to estimate the thickness of thin films. The signal amplitude provides information about the materials density, between the thin film and the substrate. Finally, the roughness affects the rate as the oscillation decreases in intensity. Larger roughness leads to a faster decay rate of the reflectivity signal. In case we have more than one layer, the interface roughness also affects the oscillation decay rate. The film thickness can be calculated with the following formula:

$$d = \frac{\lambda}{2(\theta_2 - \theta_1)} \quad (2.3),$$

where θ_1, θ_2 are two consecutive angular positions of maximum or minimum peaks. The fitting analysis of XRR data was achieved by the software REFLEX¹⁹ to obtain an approximate value of the thickness and roughness.

2.2.2. Raman spectroscopy

Raman spectroscopy is a characterization technique to study the vibrational modes of molecules, which permits the extraction of structural information from the material, such as the material phase and symmetry. Raman spectroscopy relies on the measurement of inelastic scattered photons. The vibrational mode of the molecule affects its polarizability. The incident radiation interacts with the polarizability, inducing a dipole moment in the material. This induces the emission of characteristic radiation through the scattering of the

incident radiation. Raman scattering produces two signals, Anti-Stokes and Stokes, symmetrically shifted in frequency relative to the excitation light. The frequency shift correlates directly with the vibrational frequency of the crystal.

The analysis was performed by a confocal Raman microscopy system (WITec alpha300 R) equipped with an optical microscope. The laser wavelength was 532 nm and the power of approximately 0.8 - 2 mW to prevent sample damage. The grating line is 1800 g/mm and the CCD resolution of 0.1 cm^{-1} .

2.2.3. Atomic Force Microscopy

Atomic force microscopy (AFM) is a surface topography mapping technique that allows studying the morphology, growth modes, and surface roughness. A sharp tip supported at the end of a cantilever is used to scan the material surface by measuring the deflection of the cantilever. The beam laser that is reflected in the cantilever moves accordingly and the deflection movement is measured by photodiodes. The tapping mode focuses on a resonance frequency oscillation by a piezoelectric that slightly taps the sample. The force between the sample surface and the tip creates a modulation of the oscillation amplitude, and consequently, a 3D image of the material surface topography is obtained. A configuration of an AFM system can be illustrated in Fig 2.9. The data analysis to obtain the roughness and morphological line profile is obtained with the Gwydion software.

The measurements are performed by a Bruker Dimension AFM in tapping mode.

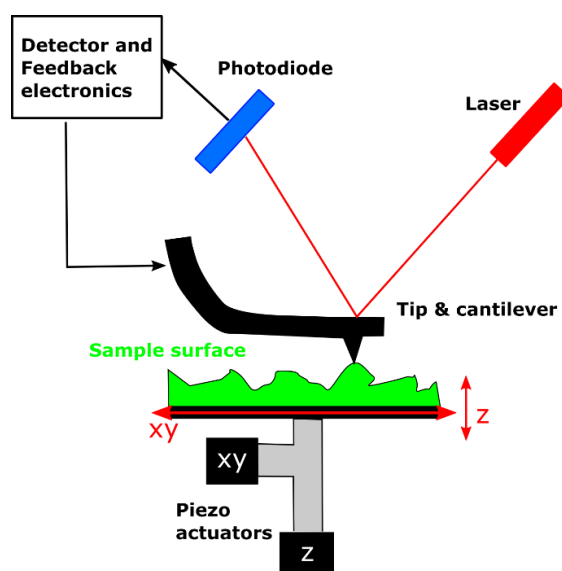


Figure 2.9 Schematic diagram of an atomic force microscope (AFM) setup.

2.2.4. Magneto-transport measurements

To analyze and investigate the electrical and transport properties of topological insulators, magneto-transport measurements are used. Through a variation of the magnetic field at cryogenic temperatures it is possible to obtain topological information. Furthermore, variation in the resistance due to magnetic fields is a crucial characterization for topological insulators to investigate electrical transport.

Geometries

There are two main geometries for these measurements, Van der Pauw and Hall-bar. Both of them were implemented throughout the thesis. Fig. 2.10 shows an example of both geometries. The van der Pauw geometry (Fig. 2.10 a and c) permits the measurement with a smaller preparation time by soldering small indium pellets on top of the material. The Hall-bar geometry (Fig. 2.10 b and d) was implemented by a cleanroom fabrication process, which is explained in section 2.3. This geometry provides a more reliable measurement due to the elimination of contact asymmetries.

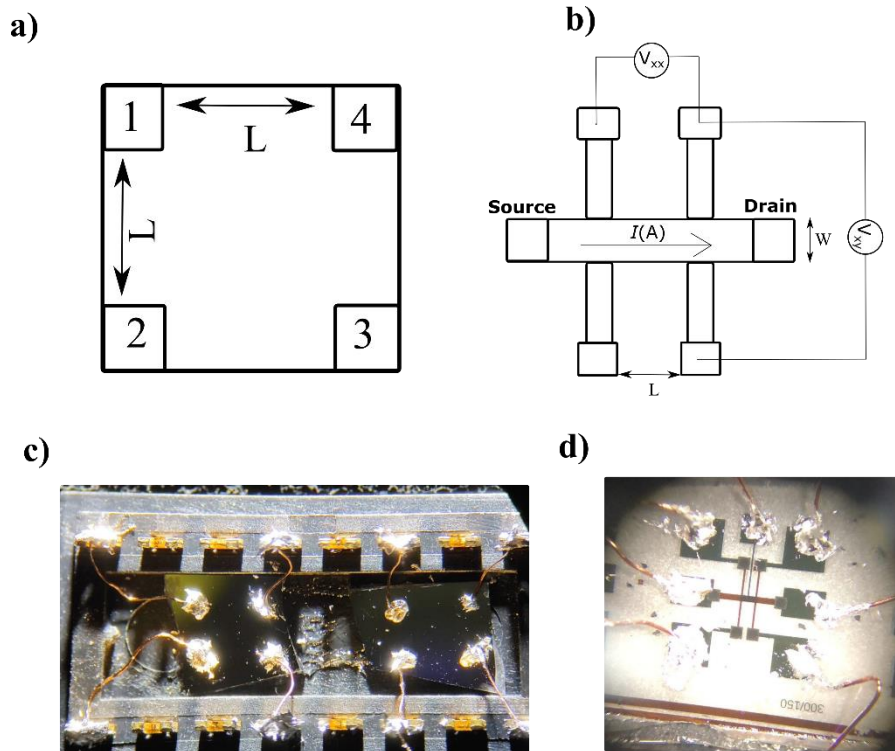


Figure 2.10 a) Van der Pauw geometry. b) Hall-bar geometry with visualization of measured contacts. c) Example Van der Pauw geometry as realized for a Bi_2Se_3 sample. d) Hall-bar example.

Van der Pauw geometry

For a Van der Pauw geometry 4-point contacts (V_1, V_2, V_3, V_4) are considered, where the respective resistances R_A and R_B can be given by:

$$R_A = \frac{1}{2} \left(\frac{V_{43}}{I_{12}} + \frac{V_{12}}{I_{43}} \right) \quad (2.4),$$

$$R_B = \frac{1}{2} \left(\frac{V_{14}}{I_{23}} + \frac{V_{23}}{I_{14}} \right) \quad (2.5),$$

The sheet resistance (R_S) and the resistivity (ρ) are then calculated as follows:

$$e^{\left(\frac{-\pi R_A}{R_S}\right)} + e^{\left(\frac{-\pi R_B}{R_S}\right)} = 1 \quad (2.6),$$

$$\rho = R_S t \quad (2.7),$$

where t is the thin film thickness.

Hall Effect

The transport properties, such as electron concentration and electron mobility, are measured by applying a magnetic field. The magnetic field moves the charged particles perpendicularly both to the field and velocity vector (Lorentz Force). The transverse charge accumulation results in a Hall voltage (V_H). The electron concentration (n_{2d}) and the mobility (μ) are determined as follows:

$$n_{2d} = \frac{|\vec{B}|I}{e|V_H|} \quad (2.8),$$

$$n_{3d} = \frac{n_{2d}}{t} \quad (2.9),$$

$$\mu = \frac{1}{e n_{2d} R_S} \quad (2.10),$$

Where $V_H = \frac{(V^{+24} - V^{-24}) + (V^{+42} - V^{-42}) + (V^{+13} - V^{-13}) + (V^{+31} - V^{-31})}{8}$. The magnetic field is applied in different directions (V^+ and V^-) to obtain a higher resolution of the Hall voltage.

Hall-bar geometry

For the Hall-bar geometry, a different approach can be implemented to calculate the transport properties. As illustrated in Fig. 2.10 b), the current is applied along the source-drain channels. Two different voltages are measured, V_{xx} and V_{xy} to obtain the R_S as follows:

$$R_s = \left(\frac{V_{xx}}{I} \right) \frac{W}{L} \quad (2.11 \text{ a}),$$

$$R_{xy} = \left(\frac{V_{xy}}{I} \right) \quad (2.11 \text{ b}),$$

The electron densities for the Hall-bar geometry were calculated by a linear fitting of the Hall resistance as a function of the magnetic field:

$$n_{2D} = \frac{1}{\left(\frac{\partial R_{xy}}{\partial B} \right) e} \quad (2.12),$$

The equipment used is a Teslatron at the Universidad de Salamanca (through a collaboration). It allows the application of a perpendicular magnetic field to study transport measurements, in a temperature range of 1.5 - 300 K and with magnetic fields up to 10 T. The measurements are performed by a standard lock-in technique with frequencies of 10-20 Hz and a driving current of 0.5 μA , which keeps low heating and good signal detection. All signals proceeded under a low-pass filter in order to minimize the high-frequency noise.

2.2.5. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that relies on the photoelectric effect to obtain quantitative composition and chemical information. The sample is subjected to electromagnetic X-ray radiation. Due to the photoelectron effect, photoelectrons are excited from the material. The kinetic energies of these photoelectrons are measured by a hemispherical analyzer as follows:

$$E_{kin} = h\nu - \phi - E_{bin} \quad (2.13),$$

Where h is Planck's constant, ν is the radiation frequency, ϕ is the work function of the detector, and E_{bin} is the binding energy characteristic of the element present in the sample. The binding energy of each element is unique and depends on the chemical bond to the neighbor atom. Thus, it is possible to identify the elements and chemical compounds. An XPS measurement consists of the collection of these photoelectrons from the spectrometer, based on Eq. 2.13, the spectra show a signal of the photoemission intensity as a function of the binding energy. A schematic diagram of an XPS system is shown in Fig. 2.11.

The XPS system used in this work is an ESCALAB250Xi UHV system (Thermo Fisher Scientific). The samples are treated with a plasma of Ar^+ ions for 2 min to etch any surface oxides. The atomic composition quantification is performed by a fitting of the element peak by a Voigt function and the detection of the signal baseline. The software Advantage (Thermo Fisher Scientific) provides a quantification by the integration of each peak area and the

sensitivity factor provided by the Avantage library.

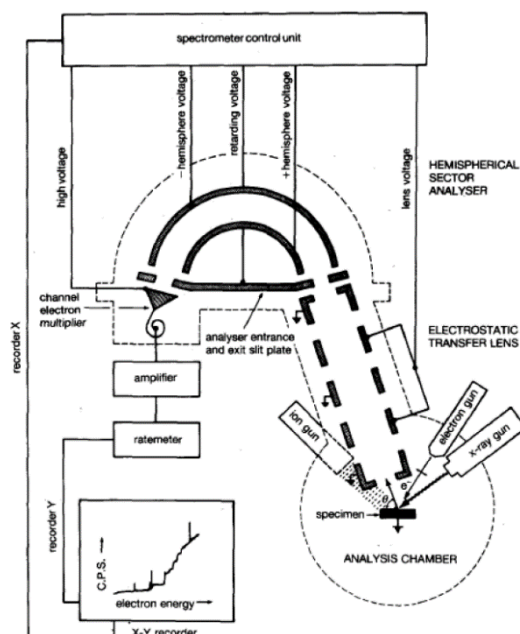


Figure 2.11 Schematic diagram of an XPS instrumentation setup ¹⁶².

2.2.6. Angle-resolved photoemission spectroscopy

Angle-Resolved PhotoEmission Spectroscopy (ARPES) is a characterization technique based on the same principle as XPS, the photoelectric effect. The electronic energy states are studied based on Eq. (2.13), similarly to XPS, with an incorporation of precise measurements of the electron angular distribution. The electron propagation angles (θ , ϕ), (Fig 2.12) carry the information of the electron momenta, which is also connected to the material momentum due to the conservation of momentum laws ²⁰. The electron energy and angle provide information about the material energy and momentum space, and thus a band dispersion is obtained $E(k)$.

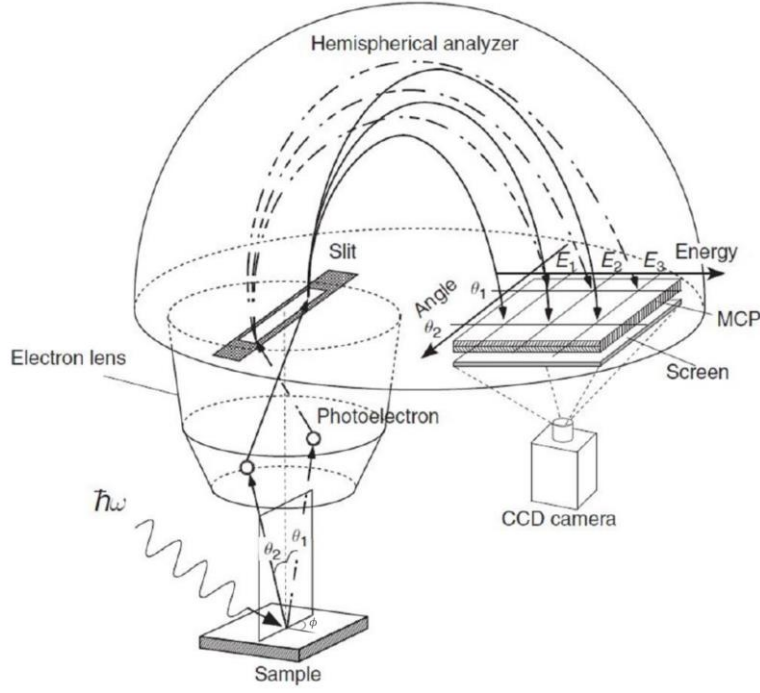


Figure 2.12 Illustration of ARPES geometry experiment with a hemispherical analyzer in angular mode. Adapted from ²⁰.

ARPES starts with a light source with enough energy, typically 20-40 eV, to overcome the work function. Electrons are emitted and collected by electron lenses which collimate the electrons. The slit is used to select the angular ratio of electrons. The hemispherical analyzer can select the specific range of energies by a capacitor voltage. Electrons are then detected by the detector in the multi-channel plate (MCP). The electron position detected by the MCP is transformed into momentum as a function of the angles by the following relations:

$$k_x = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \theta \cos \phi \quad (2.14),$$

$$k_y = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \theta \sin \phi \quad (2.15),$$

$$k_z = \frac{1}{\hbar} \sqrt{2mE_{kin}} \cos \theta \quad (2.16),$$

Where m is the electron mass and θ, ϕ are the polar and azimuthal emission angles, respectively. The photoemission process conserves the momentum, thus the in-plane parallel momentum can be written as:

$$k_{||} = \frac{1}{\hbar} \sqrt{2mE_{kin}} \sin \theta \quad (2.17),$$

For 2D materials, as our topological insulators, the perpendicular dispersion (k_z) can be negligible. Therefore, the electronic dispersion can be determined according to $k_{||}$.

Topological insulators can be compared to semiconductors because the band gap is small to create few electrons in the lowest or highest bands. The unoccupied band is called the conduction band (CB), and the occupied band is called the valence band (VB). These band dispersions can be approximated as parabolic bands as:

$$CB(k) = E_c + \frac{\hbar^2 k^2}{2m_c} + R_{ha} k \quad (2.18),$$

$$VB(k) = E_v - \frac{\hbar^2 k^2}{2m_v} + R_{ha} k \quad (2.19),$$

Where E_c and E_v are the conduction band minimum and valence band maximum, respectively. m_c and m_v are the correspondent electron conduction mass or electron valence mass. Finally, an additional parameter, the Rashba effect contribution (R_{ha}), is characteristic of topological insulators, due to the presence of spin-orbit coupling that splits the bands, known as the Rashba splitting. This effect was visually more pronounced for the valence band here, meaning that this contribution is adjusted only for the valence band.

Another characteristic property of topological insulators is the formation of surface states like Dirac cones. These surface states can also be approximated as a massless Dirac fermion in 2D systems as the Dirac cone equation (E_D):

$$E_D(K) = D_p \pm \hbar V_F |k| \quad (2.20),$$

Where, D_p is the Dirac point and V_F is the electron Fermi velocity. Furthermore, the energy dispersion obtained here is fitted with the previous equations to achieve approximated values for the fermi velocities, electron masses, and band positions.

Additionally, the surface charge carrier density (n_s) can be estimated from the Fermi vector ($k_F^{\square}$) established in the ARPES measurements²¹⁻²³ :

$$n_s = \frac{\pi}{(2\pi)^2} k_F^2 \quad (2.21),$$

The Fermi level is determined by the Fermi-Dirac distribution. The Fermi vector is calculated as observed in Fig 2.13. Electrons occupy the area in the reciprocal space from the lowest energies up to the highest energy, the Fermi level (E_F).

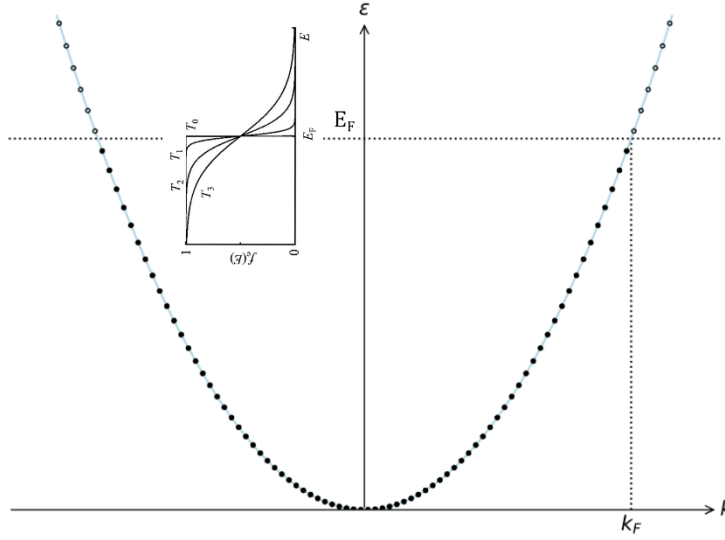


Figure 2.13 Illustration of the energy dispersion relation in 1D representing the Fermi level with the corresponding Fermi vector. The Fermi-Dirac distribution for the concept of the Fermi level position is observed at the Fermi level.

Where the Fermi-Dirac distribution is characterized by $f(E) = \frac{1}{e^{(E-E_F)/k_B T} + 1}$.

All ARPES data in the thesis presented were acquired at the ALBA Synchrotron in Barcelona at the LOREA beamline through the grant “AV-2023027322”. LOREA presents an MBS A-1 hemispherical analyzer with a linear polarization and photon energies ranging between 15 - 40 eV with the optimal condition found to be 18 eV²⁴. The source is an Apple II with a photon flux of approximately 10¹² photons/s and a spot size at the sample of 50×25 μm². The measurements were performed at a base temperature of 12 K and a base pressure of 10⁻¹¹ mbar. The ARPES data is analyzed using a custom Python script to generate ARPES images and to apply the fitting models (Annex S4).

2.3. Device fabrication

In this section, the cleanroom Hall-bar fabrication process to study the electrical and transport properties is presented. Moreover, by deposition of a dielectric material on top of the Bi₂Se₃ channel with a metallic contact (gate), we formed an electrostatic gate to tune the Bi₂Se₃ Fermi level position. This device is a field effect transistor (FET).

Solid gate field effect transistor

Bi_2Se_3 is deposited on sapphire substrates (Al_2O_3) by an MBE following the methods described in section 2.1. Different Bi_2Se_3 thicknesses are used depending on the application of the device. On top of the Bi_2Se_3 layer, a 40 nm capping layer of $\beta\text{-In}_2\text{Se}_3$ is deposited to act as a protective layer (capping layer). Bi_2Se_3 is prone to Se vacancy formation that leads to n-type degeneracy and exposure to air leads to an oxygen diffusion that increases the n-type degeneracy. Our work led to the conclusion that $\beta\text{-In}_2\text{Se}_3$ can be used effectively as a capping layer with an insulating/semiconductor electrical contribution (Chapter 6). The Bi_2Se_3 is the only layer with an electrical contribution for the electrical and transport characterization.

The samples are removed from the MBE system to perform the fabrication process of the Hall-bar structures. All the steps used for the fabrication process are illustrated in Fig 2.14. Usual lithography is performed to create the Hall bar or the metal contacts pattern, by direct laser writing (DWL Heidelberg 2000). Several lithography steps are required to achieve the full working FET device. All steps used the same positive photoresist Az1505 (Merck KGaA) approximately 1 μm thick. The exposure is performed with a laser wavelength of 405 nm and with a laser power within the range of 40-60% of the maximum intensity. The developer used to reveal the pattern is a standard Az400 developer by 30 sec.

The Hall-bar pattern is molded onto the Bi_2Se_3 by a physical etching (Ion milling-Nordiko) with an Ar^+ plasma with an incident angle of 130° to the sample, to avoid the accumulation of material on the sides of the channel. Further etching is performed for 1 min at 174° to remove the extra material accumulated in the channel lateral. This step is crucial to avoid the creation of short circuits between the gate contact and the channel.

The implementation of an electrostatic gate on top of the channel is studied in Chapter 6. Al_2O_3 is the material used for the dielectric layer, due to its good properties as an insulating material with a high dielectric constant. Al_2O_3 is deposited by sputtering aiming at a thickness of 100 nm, and the dielectric layer on the metallic contact area is later removed by a lift-off process.

The metallic contacts, to be in contact with the Bi_2Se_3 layer, require the removal of the $\beta\text{-In}_2\text{Se}_3$ layer selectively without damaging the Bi_2Se_3 layer. Several tests were performed to achieve a wet chemical etch that selectively etched the $\beta\text{-In}_2\text{Se}_3$ ¹⁸. The chemical used is a solution with a volume ratio of HCl (0.5%)+ H_2O_2 (30%) (4:50). The solution etches selectively the $\beta\text{-In}_2\text{Se}_3$ layer in 3-5 min. Additional $\beta\text{-In}_2\text{Se}_3$ samples are used to verify the complete etching of the $\beta\text{-In}_2\text{Se}_3$ layer. An additional 30 s of over-etch is performed to ensure the $\beta\text{-In}_2\text{Se}_3$ is etched completely since the Bi_2Se_3 is not severely affected by the chemical solution. To stop the etch process we perform an immersion of the samples in DI H_2O for a maximum of 30 s to avoid the Bi_2Se_3 oxidation. Studies also predict that water is not as harmful as air or alcohol²⁵.

Finally, the metallic contact can be deposited on top of the Bi_2Se_3 layer and onto the dielectric material for the electrostatic gate. The electrodes are a combination of 15 nm of an adhesion layer of Cr and 35 nm of Au by sputtering.

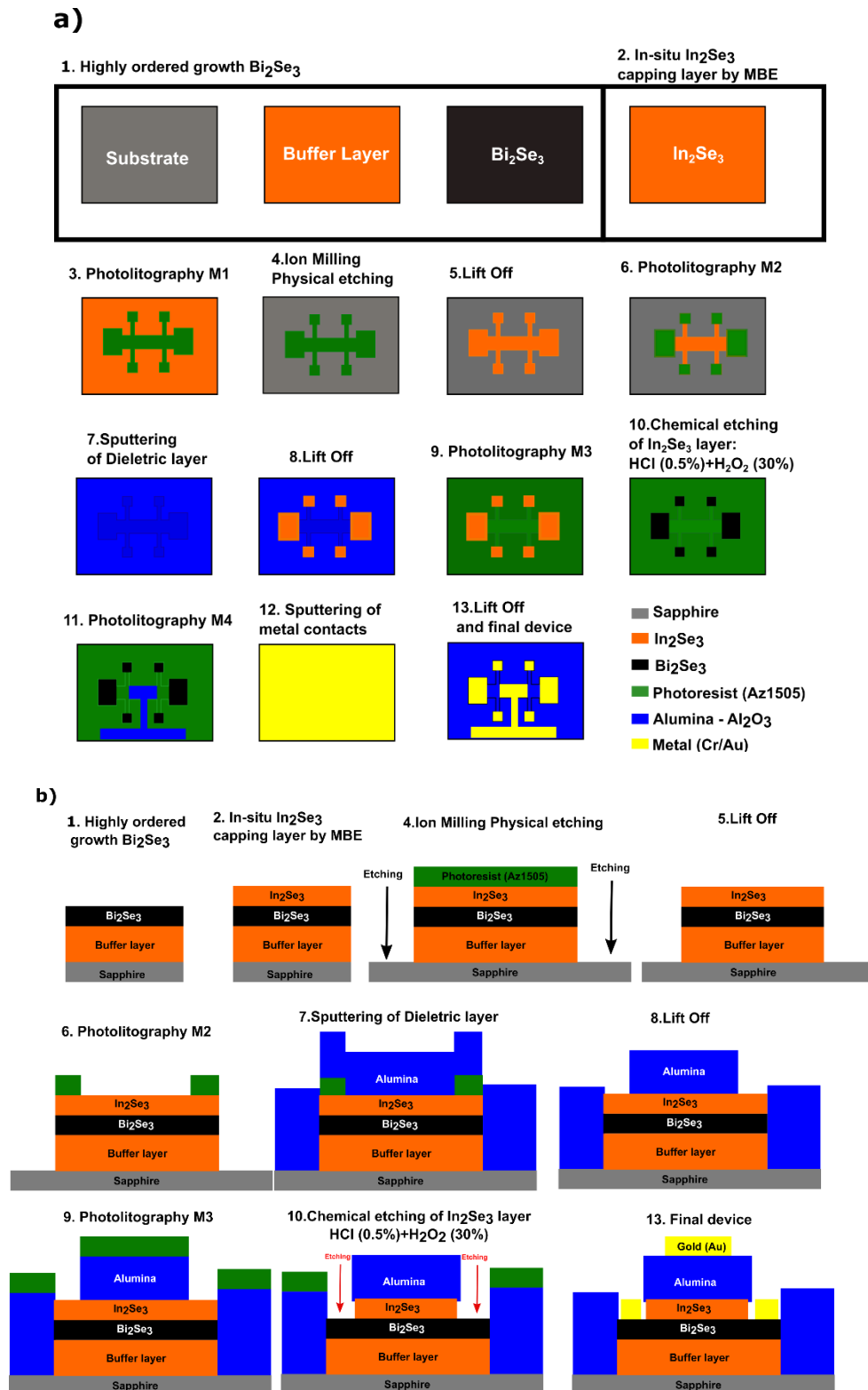


Figure 2.14 a) Top view and b) cross-section view of the cleanroom fabrication process for the Hall-bar structure top gate device.

Chapter 3

3. Bi₂Se₃ growth optimization by molecular beam epitaxy

As mentioned previously, Bi₂Se₃ stands out among the 3D topological insulators due to the large band gap of 0.3 eV and possessing robust semi-Dirac surface states crossing the band gap⁵. The presence of a strong spin-orbit coupling, and the protection of time-reversal symmetry offers the property of a spin-momentum locking of the electron spin, meaning the spin is connected to the momentum space⁵. The surface states similarity to the Dirac cone also resembles the electronic properties of those materials, such as relatively low electron densities and high mobilities¹². The protection offered by the system symmetry leads to the robustness of these properties, which ideally should produce a dissipationless material⁵. Those properties suggest that TIs are relevant in the field of low-power consumption electronics, spintronics, and quantum computation. A key to achieving such good properties is of keen importance that the TI exhibits good crystallinity, minor roughness, low defect densities, and high electron mobility²⁶.

MBE is identified as a deposition technique of high-quality single crystals. The growth of Bi₂Se₃ was reported in several studies showing good properties by MBE^{27–31}. However, Bi₂Se₃ tends to grow with an n-type degeneracy due to the existence of Se vacancies^{29,32}. Se has a low vapor pressure at low pressures and standard temperatures which leads to desorption of the material and acts as a donor impurity. Thus, the bulk material contributes to the electrical properties, which compromises the topological properties of TI and the detection of the surface state properties.

At INL, the growth of TIs was implemented for the first time during this thesis work. This chapter reports the growth of Bi₂Se₃, investigated and optimized by changing different growth parameters such as growth temperature, and Se background. The Bi₂Se₃ growth quality depends on the interface between the layer below and the Bi₂Se₃. To improve the interface a surface treatment (ST) and different buffer layers are studied. The Bi₂Se₃ is studied in terms of structural, electrical, and transport properties.

3.1. Substrate temperature and surface treatment

The first point to consider for the growth was the Se vacancies which represent a critical factor for the growth of a good quality topological insulator with an insulating bulk. Studies have observed that the use of overpressure of selenium reduces the desorption of Se from the deposited material²⁷. The excess Se is re-evaporated due to the relatively high temperatures of the substrate. Theresa Ginley et al. optimized the growth conditions for a selenium cracked source, which allows the use of reduced Se fluxes²⁷. It is reported an optimal ratio Bi/Se of 1:4. Due to the MBE similarities, it is the starting point, where the ratio Bi/Se was kept approximately at 1:4, achieving a growth rate of 1 - 1.4 nm/min.

The growth of Bi₂Se₃ is reported in several substrates, such as InP³³, Si (111)^{31,34,35}, GaAs³⁶, SrTiO₃³⁷, and sapphire (Al₂O₃)^{28–30,38,39}. Van der Waals (VdW) 2D materials possess the ability to couple weakly to the substrate due to the weak VdW forces. It permits the growth of these materials in a large variety of substrates with relatively large lattice mismatch compared to covalent layers. Nevertheless, we selected substrates with small lattice mismatches, chemically compatible, and ideally with a matching hexagonal surface structure.

Table 3.1 shows the lattice parameters of Bi₂Se₃ and the lattice mismatch between Bi₂Se₃ and different types of substrates. The best candidates for the growth of lattice match Bi₂Se₃ are InP and GaAs substrates, but they are commercially expensive. Thus, sapphire substrates are chosen due to their cost-effectiveness while exhibiting a comparable small lattice mismatch (13%) and the inert chemical nature⁴⁰. Furthermore, sapphire substrates are commercially available, extensively studied in the literature with optimized Bi₂Se₃ growth reported and present an electrical insulating behavior that facilitates the study of transport properties without any substrate contribution.

Table 3.1 Lattice constant of Bi₂Se₃ and respective lattice mismatch of different types of substrates¹⁰.

Material	Lattice constants		Lattice mismatch (%)				
	a (Å)	c (Å)	Si (111)	GaAs (111)	InP (111)	Sapphire (0001)	SrTiO ₃ (111)
Bi ₂ Se ₃	4.14	28.64	7.80	3.54	-0.24	-12.9	-25.0

Fig. 3.1 shows the RHEED pattern for the sapphire substrate and the Bi₂Se₃ calibration sample. In Fig. 3.1 a), the sapphire RHEED is shown with the presence of the Kikuchi lines which indicates a high-quality flat surface^{41,42}. The Bi₂Se₃ pattern is observed in Fig. 3.1 b). The pattern confirms the high single crystal quality by the presence of streaky lines with high intensity, corresponding to a flat surface with small domains^{34,43–47}.

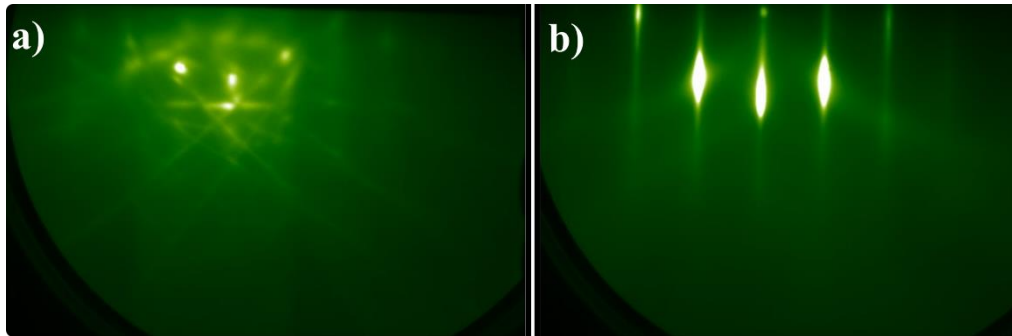


Figure 3.1 a) RHEED pattern of a cleaned sapphire substrate after a 900°C annealing for 45 min. b) RHEED pattern of a 30 nm Bi₂Se₃ layer in the [100] direction.

The first parameter optimization studied is the substrate temperature during the Bi₂Se₃ deposition. Selenium outgasses easily from the thin-film material even at low temperatures between 250-350 °C¹⁵. The consequence of a low substrate temperature is low material mobility and induces defect formation. Consequently, it deteriorates the electrical properties of the film. Conversely, temperatures higher than 400 °C were implausible due to the desorption of Bi and Se atoms. Two different temperatures are used, 270 °C and 310 °C to obtain the best material quality. As mentioned before, the MBE at INL offers a Se flux regulation by the adjustable valve aperture. The valve aperture can vary between 0 – 5 mm. The overpressure of Se is proven to help the Se vacancies minimization. Thus, we decided to implement the higher value of 5.0 mm for the growth of the Bi₂Se₃. The growth time was set to 30 min which led to a 30 nm thick Bi₂Se₃.

Fig. 3.2 shows the AFM image of a 30 nm thick Bi₂Se₃ surface topography for both deposition temperatures with the correspondent line profile. For the first temperature used 270°C (Fig. 3.2 a), it is observed the formation of triangular pyramidal structures characteristic of a hexagonal crystal structure. However, the triangular crystals present a vast number of domains. Furthermore, the crystal size is fairly small with values smaller than 500 nm. Conversely, by increasing the temperature to 310 °C (Fig. 3.2 b), the triangular crystals grew in a more organized orientation showing a formation of small domains. These domains are characterized by the presence of undesired twinning. In terms of the crystal size, there is no visible difference. In Fig. 3.2 c) and d) are shown a random line profile on the Bi₂Se₃ surface. The quintuple layer steps are not easily distinguished due to the poor surface quality. The presence of crystal heights approaching nearly 7 nm height induces a large roughness. Table 3.2 presents the roughness obtained from Gwydion software. At a higher temperature (310 °C) a 0.84 nm roughness is observed, whereas at a lower temperature (270 °C) the roughness is 1.14 nm. Both temperatures showed a roughness similar to the literature, where the temperature of 310 °C demonstrated to be the preferred deposition temperature, because of reduced roughness and twinning.

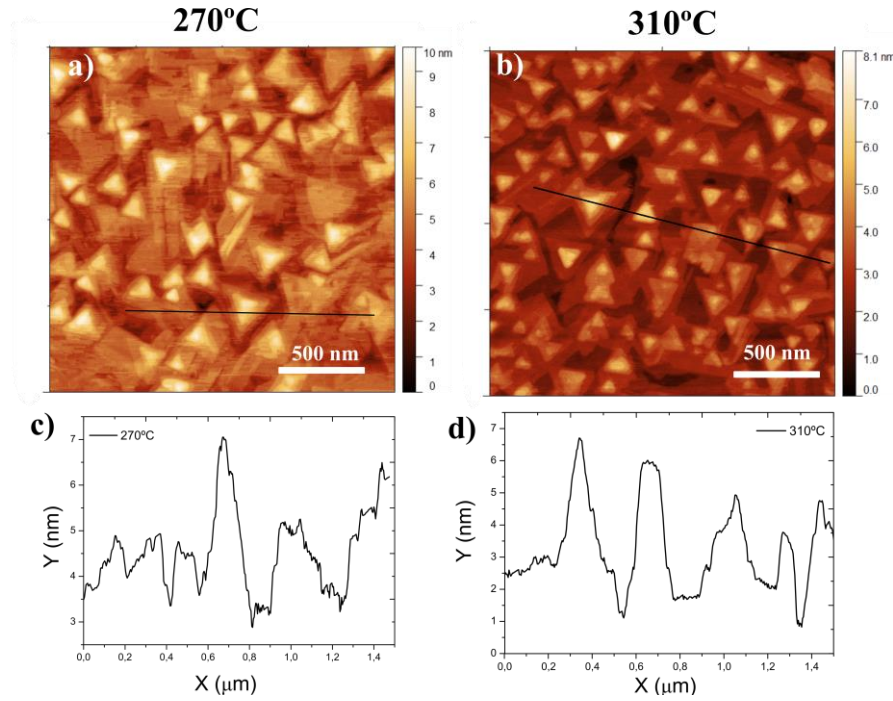


Figure 3.2 AFM image of a 30 nm thick Bi₂Se₃ surface, deposited at a) 270 °C and Se valve: 5.0 mm and b) 310 °C and Se valve: 5.0 mm. Line profile of Bi₂Se₃ surface from c) 270 °C and d) 310 °C, as indicated by the black line in a) and b).

Although the AFM image of the Bi₂Se₃ showed pyramidal structures, there is still room for improvement concerning the twinning in the Bi₂Se₃. Studies concluded that the initial stage or layer is of high importance for the interface quality. The growth of the first layers at lower temperatures increases the uniformity and the larger structural domains³⁴. Ido Levy et al. performed a surface treatment before the Bi₂Se₃ deposition, which led to a twinning suppression. Consequently, the suppression of the twinning can lead to an improvement of the electrical and structural properties²⁸. Here, we implemented this surface treatment by adjusting the conditions reported to our MBE system. The surface treatment consisted of exposure to Bi atoms for 2 min to improve the sapphire interface at 140°C. Subsequently, a sacrificial 2-3 quintuple layers of Bi₂Se₃ are deposited at this low temperature to improve the adhesion to the substrate. The temperature is then increased up to 500°C for the layer to be evaporated from the substrate. The second step is repeated (2-3 quintuple layers of Bi₂Se₃ at 140°C). The Bi₂Se₃ is then deposited after the temperature is increased to 310°C, which is the preferred growth temperature. To prevent the Se evaporation of the initial 2-3 QL Bi₂Se₃ already deposited, the Se shutter is kept open during the substrate warm-up.

The Bi₂Se₃ growth conditions such as growth rates, temperature of the substrate, Se valve aperture, and thin-film thickness are kept the same as before. We observed a significant improvement in the crystal size, reaching up to 1 μm (Fig. 3.3). The twinning seems to be reduced, indicated by the diminished presence of different domains (triangular terraces pointing to the same direction). This effect is described in more detail in section 3.3. The terraces are more defined, and it is possible to identify the QL height of around 1 nm (Fig 3.3 b). On the other hand, the roughness of this sample increased from 0.81 nm to 1.13 nm (Table 3.2), because since more layers are forming at once the crystal size is

increased, and consequently the crystal height, which leads to a slight increase in the roughness.

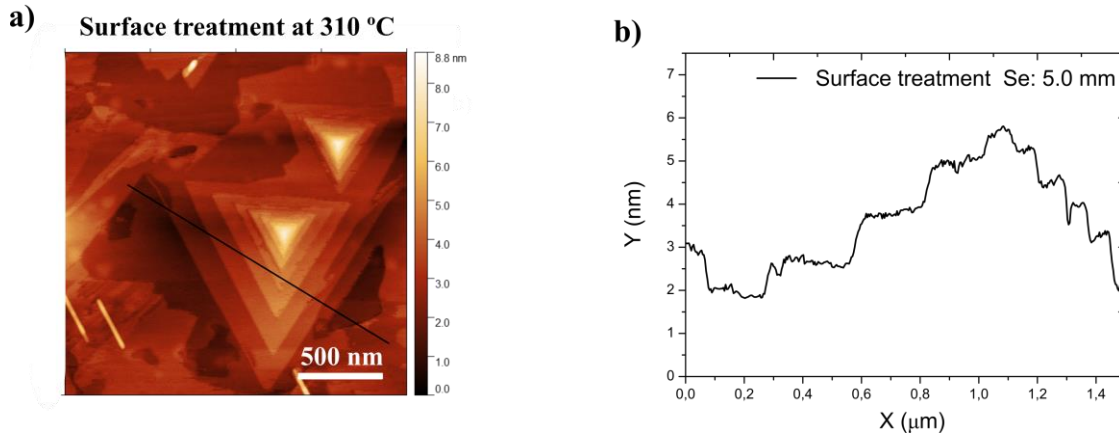


Figure 3.3 a) AFM image of a 30 nm thick Bi₂Se₃ surface with a surface treatment deposited at 310°C, Se valve: 5.0 mm. b) Line profile of Bi₂Se₃ surface as indicated by the black line in a).

Structural characterization of the Bi₂Se₃ layer was performed by X-ray diffraction measurements. The diffractogram (Fig. 3.4) of the Bi₂Se₃ samples deposited at 310°C with and without surface treatment, shows characteristic peaks from the diffraction family {0 0 3n} due to the crystal structure and symmetry of the system. The Bi₂Se₃ presents an epitaxial growth with a rhombohedral crystal structure ($R\bar{3}m$), which is consistent with literature^{34,40,44,48} and without any contaminations. No significant difference is observed for both samples by this scan. However, a φ scan is used in section 3.3 for the quantitative study of twinning.

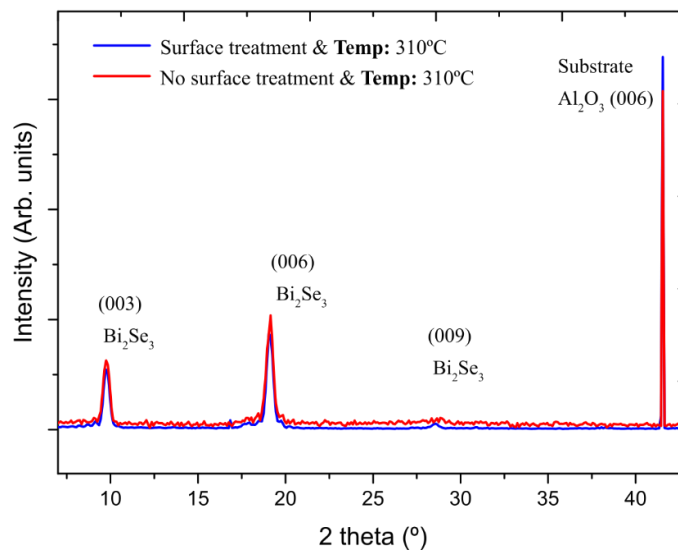


Figure 3.4 XRD diffractogram for the Bi₂Se₃ layer with and without surface treatment.

3.2. Se overpressure optimization

Continuing the growth optimization, the influence of the Se partial pressure is studied. The overpressure of Se has been shown to avoid the formation of Se vacancies. On the other hand, the Se flux could be exaggeratedly higher than it should be.

In the present section, the Bi₂Se₃ is grown with the same optimized conditions reached until now. The sapphire was subjected to surface treatment as explained previously, and the growth temperature was set at 310°C. The Se apertures used are 1 mm and 2 mm to add information to the previous 5 mm.

The AFM images for the three different Se valve settings are shown in Fig. 3.5 with the respective line profile. The AFM image of the Se valve of 1.0 mm (Fig. 3.5 a), presents a similar crystal size as observed previously, but with less defined QLs. The profile line observed in Fig. 3.5 d) indicates the presence of pyramidal triangular islands but with less distinctive single QL steps, as observed in Fig. 3.5 f). Increasing the Se valve to 2.0 mm results in a smoother and more uniform surface as shown in Fig. 3.5 b). The pyramidal growth is maintained, nevertheless, more atomic flat terraces are prone to grow, which indicates a better layer-by-layer growth mode. Furthermore, the twinning can be noticed to be minimized compared to the previous Bi₂Se₃, with a slight proportion of rotated domains. Finally, a profile line shown in Fig. 3.5 e) shows a flat and smooth Bi₂Se₃ surface with well-defined QLs at approximately 1 nm height. The Bi₂Se₃ surface roughness for each sample is shown in Table 3.2. As expected from the AFM images, a lower value of 1.05 nm is observed for the Se valve setting of 2.0 mm. The Se valve setting of 1.0 mm presented the highest value of 1.34 nm, which reveals a relatively rough surface. The optimized Bi₂Se₃ obtained is similar to that reported in the literature with smaller roughness of 0.6 nm and less twinning^{28,36}.

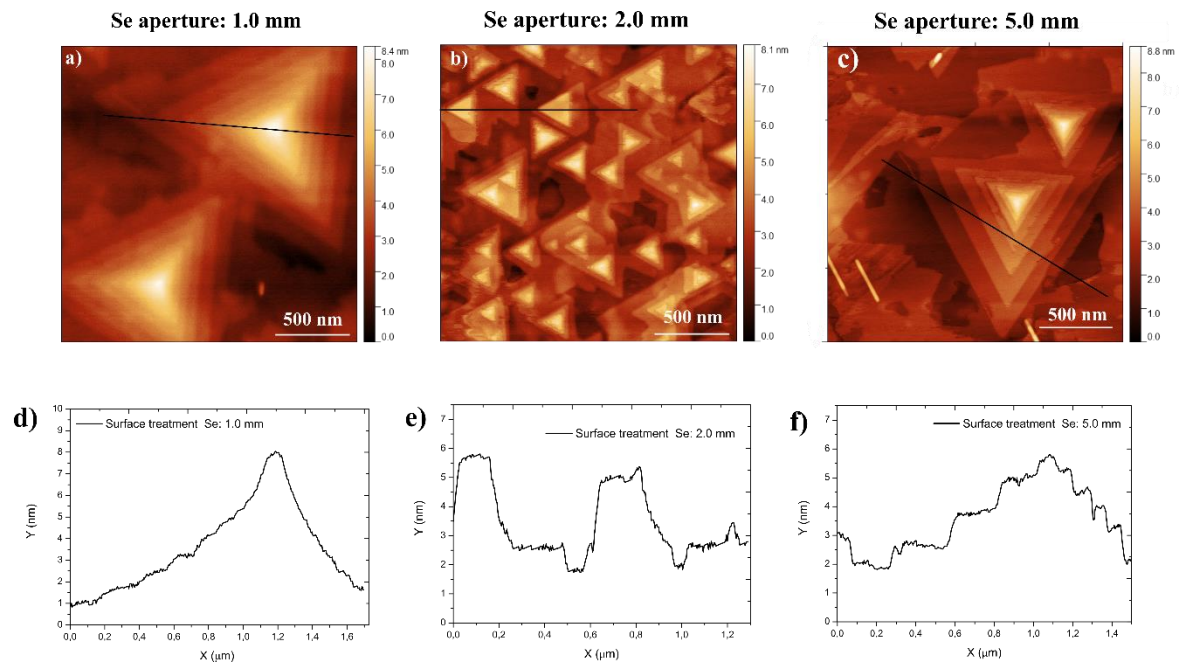


Figure 3.5 AFM images of 30 nm thick Bi₂Se₃ surfaces. The substrates were subjected to a surface treatment. The Bi₂Se₃ growth was performed at 310 °C and with a Se valve aperture of a) 1.0 mm, b) 2.0 mm and c) 5.0 mm. Line profiles of Bi₂Se₃ surfaces grown at a Se aperture of d) 1.0 mm, e) 2.0 mm and f) 5.0 mm, as indicated by the black line.

Table 3.2 RMS roughness of the Bi₂Se₃ surface deposited at 270°C and 310°C, and different Se valve apertures with or without a surface treatment. Data is analyzed by the Gwydion software.

	Samples				
	Se: 5.0 mm without Surface Treatment		Surface treatment at 310 °C		
	270 °C	310 °C	Se: 1.0 mm	Se: 2.0 mm	Se: 5.0 mm
	RMS				
Roughness (nm)	1.14	0.84	1.34	1.05	1.13

3.3. High-resolution x-ray diffraction of Bi₂Se₃

The topological properties of TIs are dependent on the crystalline quality³³, thus, the structural quality of Bi₂Se₃ needs to be studied in detail. A high-resolution X-ray characterization technique, known as XRD rocking curves, can aid in receiving more detailed information. Rocking curves can study the perfection of the crystal when the crystal planes are not parallel. The scan is performed by fixing the angle in a diffraction plane, in our case the most intense peak (006), and afterward, the sample is tilted. A perfect crystal with parallel planes should decrease the intensity of the diffraction peak sharply with a minimal full-width half maximum (FWHM). The presence of defects such as dislocations and mosaicity disrupts the crystal and consequently, the peak intensity is not as sharp as it should be.

Fig. 3.6 displays the rocking curves of the plane (006) for all the Bi₂Se₃ samples grown at 310°C. Due to the reduced quality of the sample grown at 270°C, this characterization was not performed in this sample. By observing the figure, it is possible to conclude that all samples present similar quality by small differences in intensity and FWHM. To compare these values Table 3.3 shows the FWHM for all the presented samples. The only notable difference observed is that performing a treatment of the surface produces a higher-quality crystal. The FWHM for the sample without a surface treatment is approximately 0.23° whereas the samples with a surface treatment exhibit a relatively lower value of approximately 0.22°. Additionally, those samples with a surface treatment obtained good crystal quality with extremely similar results of FWHM. These values are comparable to the literature ranging between 0.003-0.33°. In the best lattice matched substrate, InP, was achieved an FWHM of 0.003°³³. From Table 3.1, the lattice mismatch of InP is 0.24% which explains the highly crystalline quality from the Bi₂Se₃. Whereas on sapphire the values vary between 0.1-0.33°^{28,48-50}, due to the lattice mismatch of 13%. The experimental result suggests that the Bi₂Se₃ quality relies more on the substrate than on the starting layer^{33,49}.

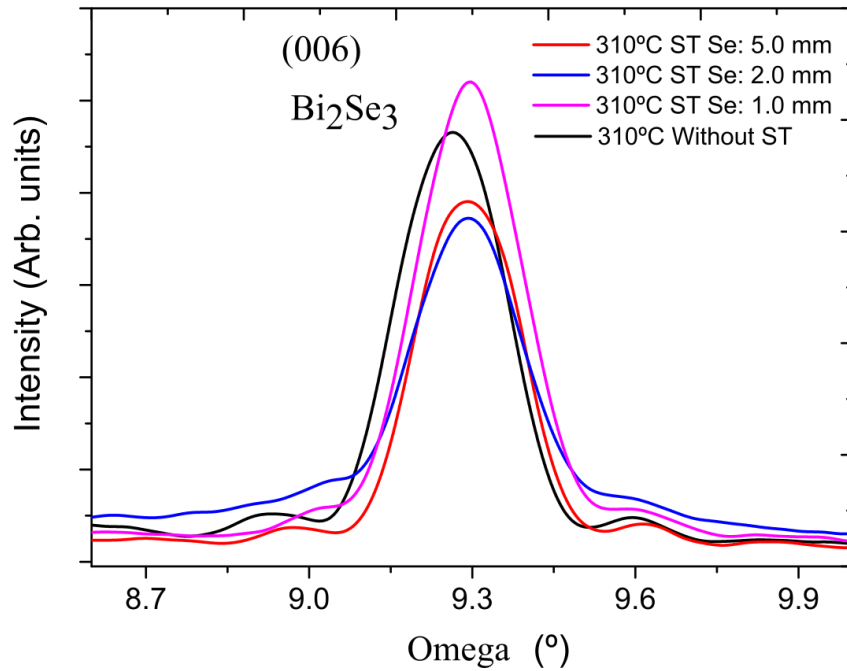


Figure 3.6 XRD rocking curves of Bi₂Se₃ grown at 310°C along the plane (006) of Bi₂Se₃.

Table 3.3 FWHM calculated from the Gaussian fitting of the XRD rocking curves of the Bi₂Se₃ plane (006), for all the Bi₂Se₃ samples deposited at 310°C.

Temperature (°)	Surface treatment	Se valve (mm)	FWHM (°)	Twinning ratio (%)
310	No	5.0	0.229 ± 0.001	44.2
310	Yes	5.0	0.221 ± 0.001	17.5
310	Yes	2.0	0.220 ± 0.001	15.4
310	Yes	1.0	0.219 ± 0.001	18.6

Another characterization technique used to study the crystal quality to give more detail about the percentage of defects in the Bi₂Se₃ layer is φ -scan X-ray diffraction. The φ -scan allows quantifying the percentage of twinning parallel to the surface (in-plane). Similar to the previous characterization technique, the detector is fixed at an angle corresponding to a diffraction spot (of a plane). The φ -scan is performed along the Bi₂Se₃ diffraction spot corresponding to the plane (015), which requires a sample rotation of approximately 57° in the χ axis, as commonly used in the literature^{28,49,51,52}. The sample undergoes a full azimuthal rotation (φ -scan), perpendicular to the sample.

Fig 3.7 shows the φ -scan for all grown samples, which presents a set of high-intensity peaks centered at 0° and repeating every 120° (vertical black dot line) since the system presents a 3-fold symmetry^{28,49}. However, when two different domains are present (twinning), results in the emergence of smaller intensity peaks after 60° of the high-

intensity peaks, as illustrated in Fig 3.7 at -60° , 60° , and -180° (can be understood as a 6-fold symmetry). This minority domain repeats every 120° (vertical green dot line) since the new domain also exhibits a 3-fold symmetry.

An ideal twinning-free crystal would present a minimal intensity for those peaks. By comparing the spectra from all samples, we confirm the existence of twinning due to the presence of the second peak intensity, as expected from the AFM images. The sample without surface treatment (ST) demonstrates a more intense peak at -90° and the remaining peaks every 120° , compared to the other samples that have undergone surface treatment. A small intensity peak is observed at those angles compared to the high-intensity peaks. The ratio of twinning is calculated between both peak intensities and is shown in Table 3.3. The percentage of the twinning of around 44% is reduced to values of around 17.5% by performing the surface treatment, which confirmed the work performed by Ido Levy et al.²⁸. Nonetheless, from all the samples subjected to the ST, the Se valve aperture of 2 mm demonstrates a twinning suppression with a ratio of 15.4%. It can be concluded, taking attention to all the sections studied up to now, that the optimal growth conditions for the Bi₂Se₃ are a growth temperature of 310°C and a Se valve aperture of 2.0 mm.

Henceforward, the sapphire substrates are subjected to the surface treatment to improve the interface sapphire/ Bi₂Se₃. While the Bi₂Se₃ is deposited at 310°C and with a Se valve aperture of 2.0 mm.

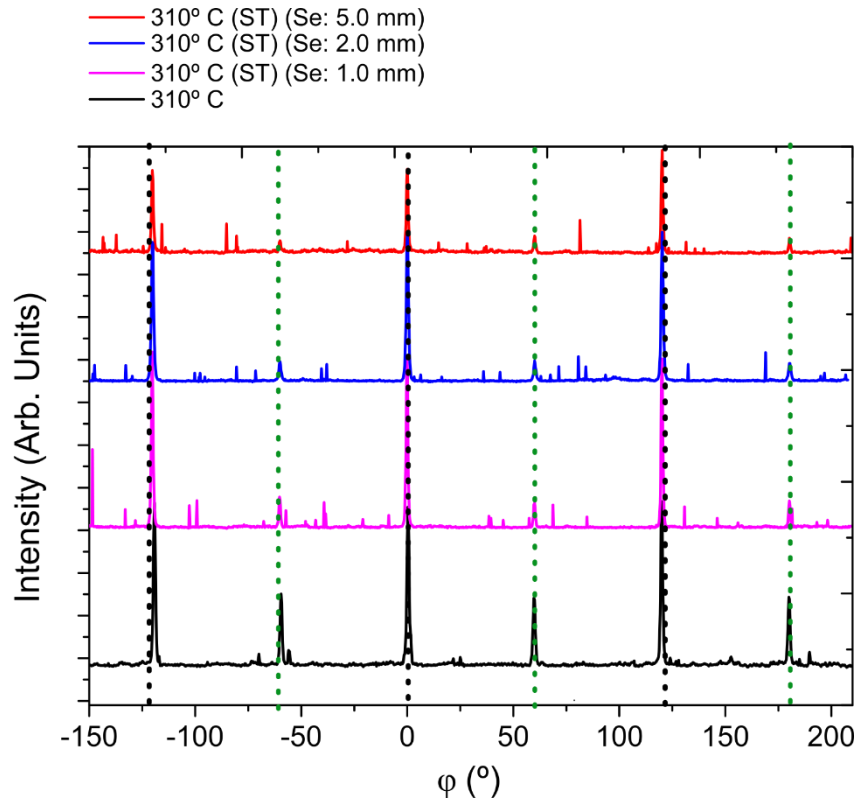


Figure 3.7 XRD ϕ scan of Bi₂Se₃ grown at 310°C along the plane (015) of Bi₂Se₃. The black dotted lines denote the crystal 3-fold symmetry by the repetition of the peak every 120° . The green dotted lines denote the presence of twinning by the appearance of a peak every 60° .

3.4. Buffer layer introduction

The Bi₂Se₃ quality achieved previously showed a low percentage of twinning defects. Nevertheless, there is still room for improvement in terms of interfacial and bulk defects that affect the transport properties of the topological insulator. The growth of these Van der Waals materials requires chemically compatible substrates in preference for lattice-matched ones⁵³. The use of chemically and lattice-matched substrates should lead to the suppression of bulk and interfacial defects, which are the principal cause of low mobilities and high bulk carrier densities in TI films^{54–56}. The use of a buffer layer below the Bi₂Se₃ layer has been shown to lead to a more insulating TI with less bulk electrical contributions^{54–56}.

This section focuses on the reproduction of two research articles where different buffer layers were implemented to achieve a TI with favorable transport properties. In order to analyze the electronic properties of the Bi₂Se₃ layer, the buffer layer is required to not contribute electrically. The key material is the Van der Waals material β -In₂Se₃, which presents a 1.4 eV band gap¹⁸, a trivial band insulator, meaning that it does not contribute to the transport properties. Additionally, the material presents an identical rhombohedral crystal structure and a similar lattice parameter (3.4% lattice mismatch)⁵⁶. The hybridization of the β -In₂Se₃ layer with Bi atoms can lead to an even more chemically stable layer and the “doping” of Bi transforms the lattice parameter to values closer to the Bi₂Se₃ layer. Studies also confirmed that the (Bi_{1-x}In_x)₂Se₃ layer (BIS) is a trivial insulating material as long as the percentage of In is higher than 30%⁵⁶.

Koirala et al.⁵⁵ and Wang et al.⁵⁶ implemented the deposition of a buffer (Bi_{1-x}In_x)₂Se₃ layer prior to the growth of the Bi₂Se₃ layer obtaining the improvement of the transport properties for the TI material. A schematic of each buffer layer growth adapted for the Bi₂Se₃ growth is illustrated in Fig 3.8 a and c. Koirala et al. implemented the growth of a β -In₂Se₃ and a (Bi_{1-x}In_x)₂Se₃ to form the buffer layer IS-BIS (Fig 3.8 a). The initial problem is the large variety of phases of In₂Se₃. Thus, the buffer layer starts with a 3 QL sacrificial layer of Bi₂Se₃ to favor the 20 QL β -In₂Se₃ growth. Later on, the sacrificial layer of Bi₂Se₃ is removed by annealing the substrate to temperatures around 600°C to prevent the creation of electrical shorts between the Bi₂Se₃ layer that is deposited later. After the In₂Se₃ layer, a 20 QL BIS layer is deposited which leads to a highly ordered Bi₂Se₃ layer.

The RHEED pattern was recorded during the buffer growth (Fig 3.8 b). The In₂Se₃ shows the same pattern as the Bi₂Se₃ since they possess an identical crystal structure. The main difference is the intensity of the signal, it presents a more diffuse signal compared to the Bi₂Se₃. The incorporation of Bi atoms leads to a less diffuse signal, where brighter streaky lines are seen for the Bi₂Se₃ RHEED since Bi atoms present a higher atomic number than In atoms. A larger atomic number tends to scatter electrons more effectively, which results in a brighter RHEED signal.

On the other hand, Wang et al. created the (Bi_{1-x}In_x)₂Se₃ layer (FIG 3.8 c) by depositing a 5 QL layer of Bi₂Se₃ and In₂Se₃ separately. This layer is subjected to an annealing process at high temperatures (425°C). The high volatility of Bi₂Se₃ enables the diffusion into the In₂Se₃ layer to form the (Bi_{1-x}In_x)₂Se₃. The RHEED pattern of this buffer layer is shown in

Fig 3.8 d). The pattern of the buffer layer is similar to the previous method. Likewise, the Bi₂Se₃ layer shows the characteristic streaky lines with good single-crystal quality.

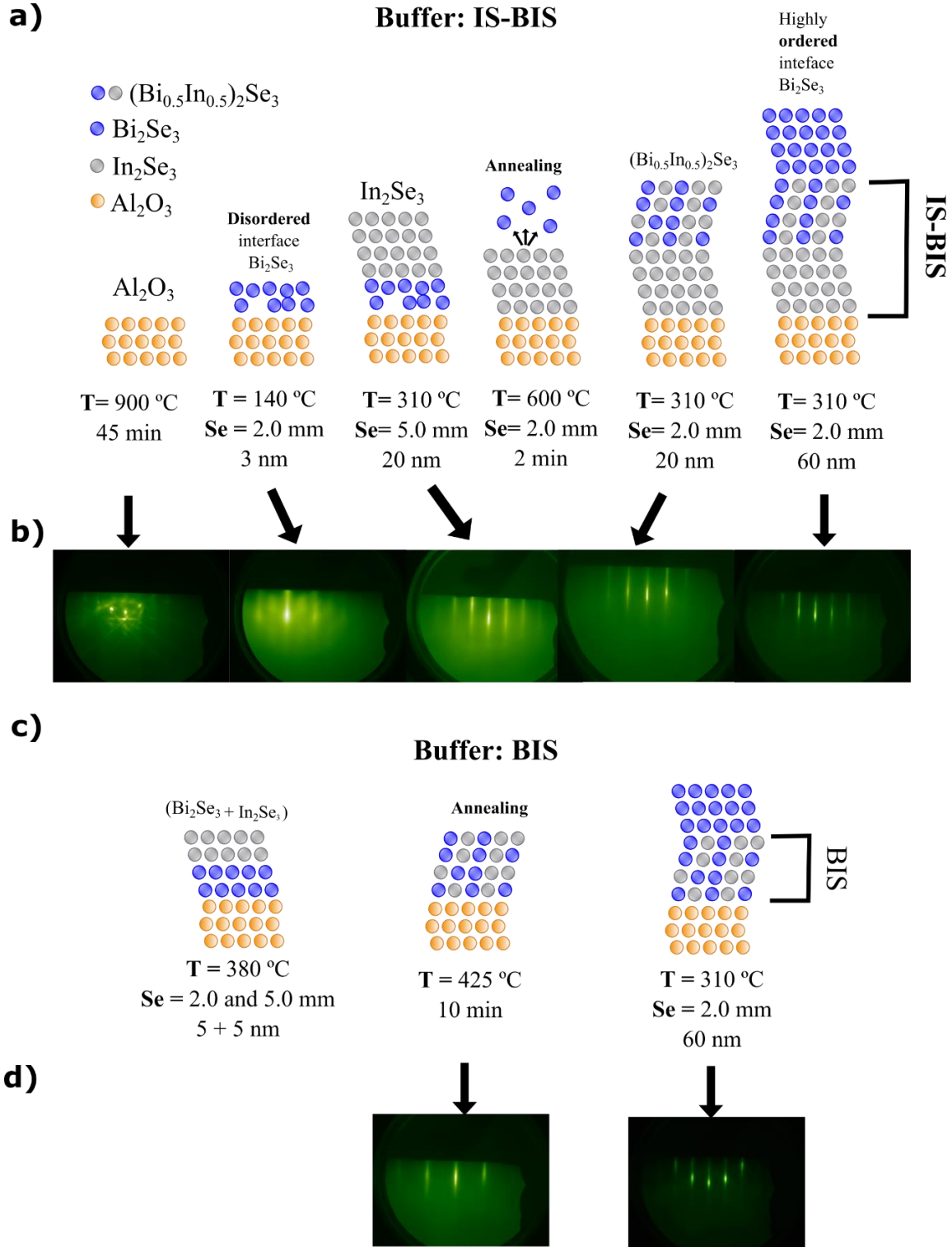


Figure 3.8 Schematic of the IS-BIS buffer layer deposition adapted from Koirala et al. b) RHEED patterns for each individual layer in the direction [100]. c) Schematic of the BIS buffer layer deposition adapted from Wang et al. d) RHEED patterns for each individual layer. The first RHEED is in the direction [110] and the second is in the direction [100], showing that there is a 3-fold rotational symmetry.

Both buffer layers seem to lead to a good Bi₂Se₃ crystal quality concerning the pattern from the RHEED. Following, it is studied in more detail the crystal structure of each Bi₂Se₃ which can be compared to the previous Bi₂Se₃ wherein only a surface treatment is performed before the TI growth. The conditions for the Bi₂Se₃ with a buffer layer had the same growth conditions as the previous Bi₂Se₃, such as a growth temperature of 310°C, and a Se valve opening of 2.0 mm.

3.4.1. Bi₂Se₃ structural properties

The vibrational modes are studied by Raman spectroscopy. The spectra obtained for all three samples are shown in Fig 3.9 a) and an illustration of the characteristic Bi₂Se₃ vibrational modes is displayed in Fig 3.9 b). Three main characteristic peaks of Bi₂Se₃ are detected, A_{1g}^1 , E_g^2 , A_{1g}^2 similar to the literature ^{57–60}. The main difference observed for the signal is the intensity. A pronounced peak intensity Bi₂Se₃ with a buffer IS-BIS is observed whereas a less intense signal is observed for the Bi₂Se₃ with an ST.

The peak position and the FWHM are extracted by a Gaussian fitting (Table 3.4). The Raman modes, A_{1g}^1 , E_g^2 and A_{1g}^2 are detected at approximately 71, 131, and 174 cm⁻¹, respectively. The sample with an ST presents vibrational peak positions closer to the literature ^{57–60}. Conversely, the Bi₂Se₃ growth onto a buffer layer led to a small peak deviation to higher frequencies, a blue shift of 1.9 ± 0.3 cm⁻¹. This deviation could represent a small modification of the lattice parameter due to the buffer layer influence. The reduced FWHM is correlated to an improved crystal quality ⁵⁷. An additional small and broad peak is detected around 250 cm⁻¹ representing atomic Se that is commonly evaporated as reported in the literature ⁶¹.

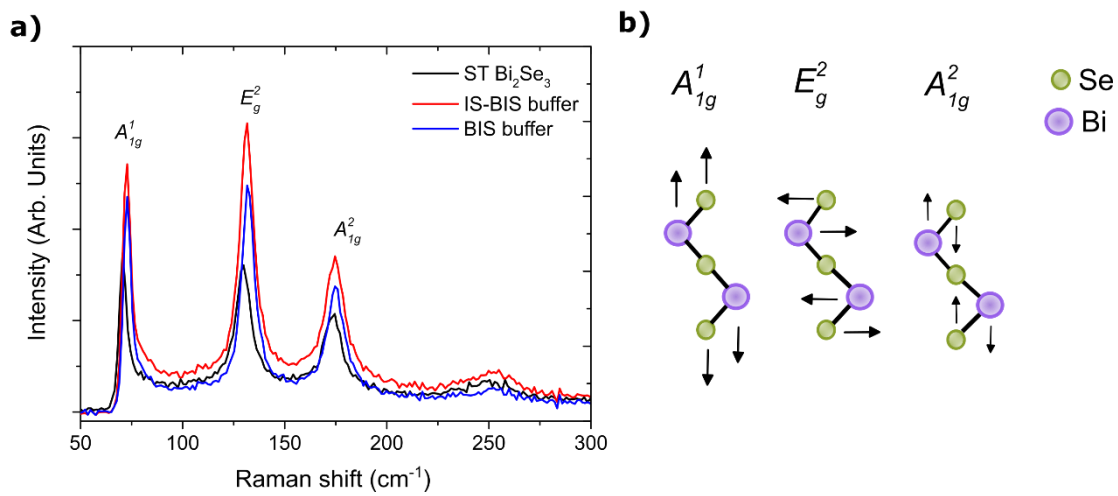


Figure 3.9 a) Room temperature Raman signal of Bi₂Se₃ with a surface treatment and two Bi₂Se₃ samples on a buffer layer showing three characteristic vibrational peaks. b) Illustration of the vibrational modes present in Bi₂Se₃.

Table 3.4 Peak position of each Bi₂Se₃ vibrational mode (A_{1g}^1 , E_g^2 and A_{1g}^2) and correspondent FWHM.

	A_{1g}^1		E_g^2		A_{1g}^2	
	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)	Peak position (cm ⁻¹)	FWHM (cm ⁻¹)
Literature ⁵⁸	71	(4 – 5)	131	(7-8)	174	(9-10)
ST Bi ₂ Se ₃	70.9 ± 0.2	3.7 ± 0.4	129.7 ± 0.2	7.7 ± 0.4	173.3 ± 0.3	10 ± 1
IS-BIS Buffer	72.8 ± 0.3	4.5 ± 0.5	131.3 ± 0.4	6.6 ± 0.2	174.4 ± 0.8	9.2 ± 0.4
BIS Buffer	72.9 ± 0.1	4.2 ± 0.7	132.1 ± 0.1	6.8 ± 0.3	174.9 ± 0.2	8.6 ± 0.5

Further details about the structure of the films can be obtained by X-ray diffraction measurements. The 2θ scan XRD, shown in Fig 3.10 a), exhibits a single crystal family {00L} rhombohedral crystal structure for all samples. There is no relevant difference between the samples confirming the good Bi₂Se₃ quality. However, by performing a high-resolution scan for the (006) plane, small differences can be detected. A peak shift is observed for all the samples due to a difference in the crystal lattice parameters as predicted from the Raman data. The (006) plane is detected at 18.57° for a single ST Bi₂Se₃ whereas for the IS-BIS Bi₂Se₃ it is detected at 18.64°. Additionally, for the buffer layer, IS-BIS an additional peak is also detected at 18.83 ° correspondent to the In₂Se₃ layer. Through the XRD diffraction pattern, the lattice parameter of the Bi₂Se₃ unit cell was calculated (Table 3.5). An additional X-ray scan of the peak (015) is performed to make it possible to calculate the lattice parameter *a*, as described in Eq. (3.1). The uncertainty is calculated by Eq. (3.2) through error propagation.

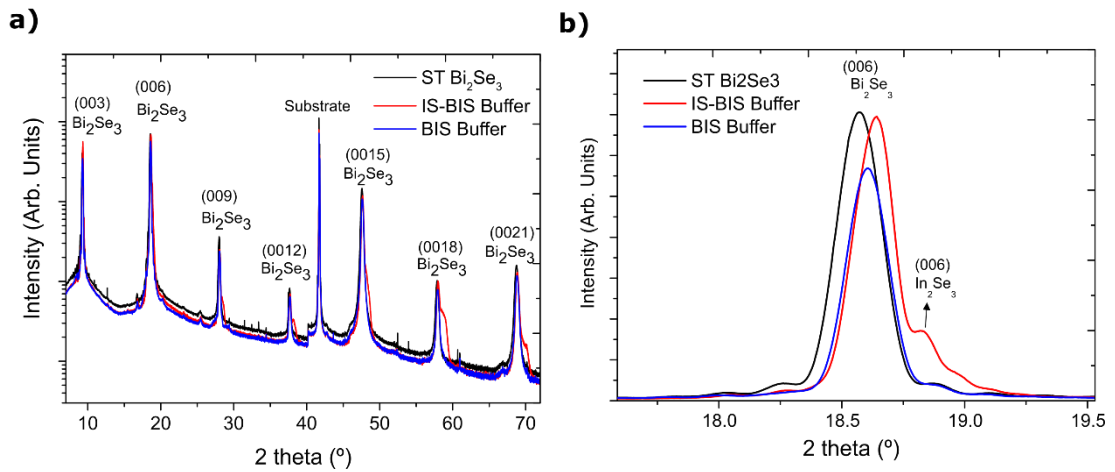


Figure 3.10 a) XRD diffractogram for the Bi₂Se₃ layer with a surface treatment and Bi₂Se₃ grown with an IS-BIS or BIS buffer layer. b) High-resolution x-ray diffraction of the (006) plane of Bi₂Se₃.

$$a = \frac{2\sqrt{3}}{3} \sqrt{\frac{c^2 d^2}{c^2 - 25d^2}} \quad (3.1)$$

$$\Delta_a = \frac{2\sqrt{3} \sqrt{\frac{c^6 \Delta_d^2 + 625d^6 \Delta_c^2}{(c^2 - 25d^2)^3}}}{3} \quad (3.2)$$

Where c and a are the Bi₂Se₃ lattice parameters. d is the interplanar distance correspondent to a diffraction peak position. All parameters present its characteristic error value Δ .

Table 3.5 indicates a decrease in the c lattice parameter as a buffer layer is introduced. A value of 28.66 ± 0.02 Å is obtained for an ST Bi₂Se₃ which is in agreement with the literature $c=28.64$ Å (*ICSD 617072*) and experimental reports ⁶²⁻⁶⁵. This c value changed to a value of 28.6 ± 0.06 Å with an IS-BIS buffer layer and 28.63 ± 0.03 with a BIS buffer layer. Moreover, the a lattice parameter presented a similar value to the literature of around 4.14 Å ^{62,63,65}, whereas for an IS-BIS buffer, there was an increase of 0.4%.

Table 3.5 Crystal lattice parameters a and c of the Bi₂Se₃ layer, for the three types of Bi₂Se₃.

	a (Å)	c (Å)
ST Bi ₂ Se ₃	4.139 ± 0.001	28.66 ± 0.02
IS-BIS Buffer	4.158 ± 0.003	28.60 ± 0.06
BIS Buffer	4.141 ± 0.002	28.63 ± 0.03

X-ray characterization techniques also offer the analysis of the interfaces of each layer through X-ray reflectivity (XRR), which provides information about film thickness and roughness. XRR analysis was performed for the Bi₂Se₃ grown onto the different buffer layers, IS-BIS and BIS. Fig 3.11 shows both spectra (orange lines) and the fitting profiles (blue lines) by the software REFLEX. In addition, the thickness and roughness of all layers from the fitting are presented in Tables 3.6 and 3.7. A thickness of around 20 nm for both layers of In₂Se₃ and BIS is found. In terms of roughness, they present a slightly rough interface. This buffer layer led to a Bi₂Se₃ layer of around 38 nm thick and a roughness of 1.1 nm, which is comparable to previous Bi₂Se₃ roughness (Table 3.2).

Fig 3.11 b) presents the XRR data and the fitting profile for the BIS buffer layer with a Bi₂Se₃ layer on top. Two oscillations are clearly distinguished concerning the BIS and the Bi₂Se₃ layer with different thicknesses. Table 3.7 shows the fitting parameters. The BIS layer was successfully achieved by the annealing of the Bi₂Se₃ and the In₂Se₃, by the accomplishment of a 10 nm thick layer with a low roughness of 0.6 nm. Despite the good buffer layer, the following Bi₂Se₃ layer resulted in a rough film of 1.7 nm and a thickness of 41 nm.

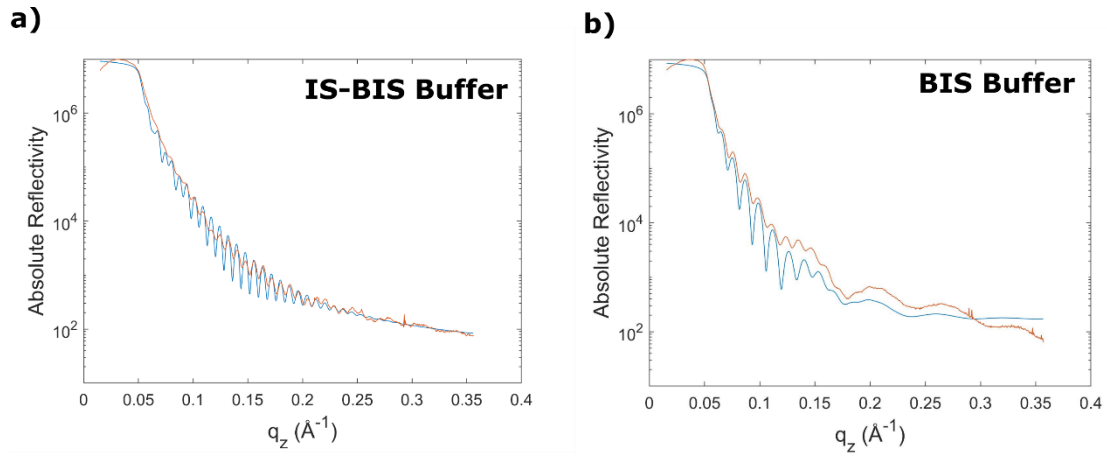


Figure 3.11 X-ray reflectivity measurements for the Bi₂Se₃ grown on a) IS-BIS buffer layer (orange line), b) BIS buffer layer (orange line). Both images present the fitting profile calculated from the software REFLEX extracted in MATLAB (blue lines).

Table 3.6 X-ray reflectivity fitting parameters, thickness, and roughness, for each layer of the IS-BIS buffer sample.

	Roughness (nm)	Thickness (nm)
In ₂ Se ₃	3.5	20
BIS	2.2	17
Bi ₂ Se ₃	1.1	38

Table 3.7 X-ray reflectivity fitting parameters, thickness, and roughness, for each layer of the BIS buffer sample.

	Roughness (nm)	Thickness (nm)
BIS	0.6	10.5
Bi ₂ Se ₃	1.7	41.1

3.4.2. Bi₂Se₃ electrical and transport properties

One important factor of TIs is their electrical and transport properties. An ideal TI should be an insulator in the bulk, have low bulk electron concentration, and possess conductive surface states due to the semi-Dirac-cone surface states, which can be understood as a high electron mobility material. Even in a defective material, the surface

states of a TI are still present due to their robustness. However, some of their transport properties are going to be affected, such as the bulk mobility and the electron concentration.

The transport study of the Bi₂Se₃ layer was performed at room temperature (RT) in a Van der Pauw configuration (Fig 2.10 a). The layer oxidation cannot be avoided since it is exposed to air for a long period of time (one day).

The electrical and transport properties (resistivity, electron concentration, and mobility) of the Bi₂Se₃ with ST and buffer layer are shown in Table 3.8. It can be concluded that the introduction of a buffer layer produces a more resistive layer of Bi₂Se₃ compared to the ST Bi₂Se₃, indicating the growth of a highly ordered layer with fewer defects. The most resistive Bi₂Se₃ film obtained was the sample IS-BIS with a resistivity of $24.83 \pm 0.04 \text{ } \Omega \text{ } \mu\text{m}$. The Bi₂Se₃ can also be affected by an In diffusion into the Bi₂Se₃ layer that reduces the bulk concentration and consequently increases the resistivity, as proposed in the literature⁶⁶. In fact, for the IS-BIS buffer layer sample, the sheet electron concentration is reduced five times compared to the reference ST Bi₂Se₃, from $5.911 \pm 0.003 \times 10^{13}$ to $1.69 \pm 0.04 \times 10^{13} \text{ cm}^{-2}$. In contrast, the BIS buffer sample showed an electron concentration of $2.23 \pm 0.04 \times 10^{13} \text{ cm}^{-2}$. These values are still high, likely because Bi₂Se₃ has the tendency to grow n-type degenerate, due to Se vacancies. These electron concentrations are comparable to the previous research work^{55,56}.

In terms of mobility, the literature demonstrated that Bi₂Se₃ at RT presents values around $600\text{-}1000 \text{ cm}^2/\text{Vs}$ ^{27,39,55,56} with sheet electron concentration values varying between 1×10^{13} and $4 \times 10^{13} \text{ cm}^{-2}$. The ST Bi₂Se₃ exhibited a mobility of $420.7 \text{ cm}^2/\text{Vs}$ which was improved to values closer to $600 \text{ cm}^2/\text{Vs}$ by preparing the Bi₂Se₃ layer on top of a buffer layer. The highest mobility achieved was $592.5 \pm 0.6 \text{ cm}^2/\text{Vs}$ for the IS-BIS buffer sample.

To summarize, the transport properties are enhanced by the buffer layer implementation before the Bi₂Se₃ layer growth. In addition, the IS-BIS buffer layer was demonstrated to achieve better transport properties, such as lower electron concentration and higher mobilities.

Table 3.8 Electrical and transport properties of the Bi₂Se₃ layer, with surface treatment and grown on different buffer layers (IS-BIS or BIS). The measurements are performed at RT.

	Resistivity ($\Omega \text{ } \mu\text{m}$)	Bulk Concentration ($\times 10^{18} \text{ cm}^{-3}$)	Sheet Concentration ($\times 10^{13} \text{ cm}^{-2}$)	Mobility (cm^2/Vs)
ST Bi ₂ Se ₃ (60 nm)	15.06 ± 0.01	9.851 ± 0.005	5.911 ± 0.003	420.7 ± 0.1
IS-BIS Buffer (40 nm)	24.83 ± 0.04	4.23 ± 0.01	1.69 ± 0.04	592.5 ± 0.6
BIS Buffer (40 nm)	19.80 ± 0.04	5.68 ± 0.02	2.23 ± 0.04	554.8 ± 0.4

3.5. Summary

Growth conditions for the topological insulator Bi₂Se₃, are optimized by adjusting growth temperature and the Se valve aperture. The simple Bi₂Se₃ layer presented the best crystal quality for a growth temperature of 310 °C and a Se aperture of 2.0 mm. The twinning defects were successfully reduced by the sapphire surface treatment according to high resolutions of x-ray analysis. The transport properties of Bi₂Se₃ are further enhanced improving the interface between the Bi₂Se₃ and an added semi-insulating buffer layer. The IS-BIS buffer layer technique, previously, studied by Koirala et al. was shown to reduce the electron concentration and increase the Bi₂Se₃ mobilities, which leads to an improved topological insulator overall.

Chapter 4

4. Structural and electrical properties of Ga and Cu doping of Bi₂Se₃

The results presented in this chapter have appeared in the *Daniel Brito et al. Journal of Applied Physics (2022) 132(11)*.

4.1. Motivation

A major difficulty for the exploitation of the Bi₂Se₃ surface states is the n-type degeneracy formed due to Se vacancies. It is of extreme importance to reduce the bulk carrier concentration in order to reduce their contribution to electrical transport. One approach commonly used is through the doping of Bi₂Se₃ with specific elements to achieve p-type doping. The doping of Bi₂Se₃ with Sn⁶⁷, Ag^{68,69}, or In^{66,70}, can shift the Fermi level (E_F) into the band gap and closer to the Dirac point. Sn doping resulted in an E_F shift towards the Dirac point without destroying the surface states, whereas In doping showed a topological phase transition destroying the surface states for doping higher than 7%. The Ag-doped Bi₂Se₃ accomplished a bulk electron concentration reduction with a minimum n_{3d} of $4.7 \times 10^{18} \text{ cm}^{-3}$, which is still higher than the maximum desired value for pure surface state transport at RT (10^{15} cm^{-3})⁷¹.

Furthermore, Bi₂Se₃ has been doped with exotic elements to obtain new physical phenomena such as magnetic dopants to achieve a magnetic topological insulator. Manganese (Mn) brought a lot of attention recently, due to the presence of ferromagnetism that can lead to the quantum anomalous Hall effect (QAHE) in Bi₂Te₃⁷². Instead of an integer quantum Hall effect with a broken time-reversal symmetry by an external magnetic field, the QAHE creates spinful chiral edge states due to doping magnetization and spin-orbit coupling. Other elements, such as Cr⁷³, Co⁶², or Fe⁷⁴ are being studied to achieve the QAHE. From a different perspective, Cu^{75,76}, Sr^{77,78}, and Nb^{79,80} doped Bi₂Se₃ reveal another novel phenomenon: topological superconductivity. This effect takes place due to the rotational symmetry breaking owing to the intercalation of doping atoms in the Van der Waal gap that leads to a zero-resistance material without destroying the surface states. The topological superconductivity (TSC) brought, as well, a lot of interest since it has the capability to host the quasi-particle Majorana fermions^{5,81}, which is a key to the future of quantum computation^{82,83}. The superconductivity achieved by Cu-doped Bi₂Se₃ presented a critical

temperature of approximately 4 K by a melt-growth technique. Likewise, other elements (Sr, Nb) can lead to the superconductivity corresponding to the family $\text{A}_x\text{Bi}_2\text{Se}_3$ (where $\text{A} = \text{Cu, Sr, Nb}$).

The exploration of new doping elements is of meaningful value, which can lead to different physical phenomena. Recently, B. Wiendlocha et al.⁸⁴ predicted resonant levels peaks from the density of states inside the gap in Ga-doped Bi_2Se_3 , which could indicate a p-type doping impurity. In a different approach, Ankita Phutela et al. predicted that GaBiSe_2 should form a strong topological insulator⁸⁵. Considering the lack of experimental data on Ga-doped Bi_2Se_3 , it is of crucial importance to investigate the influence of Ga as a dopant and to provide insight into the theoretical aspect. In the present section, Ga-doping Bi_2Se_3 is implemented due to the lack of previous experimental research. Additionally, in a similar way, the doping of Bi_2Se_3 by Cu is motivated by a lack of experimental studies of doping by Cu in MBE growth⁸⁶. MBE offers the fabrication of wafer-scale and uniform films that are crucial for device fabrication, however, the topological superconductivity in $\text{Cu}_x\text{Bi}_2\text{Se}_3$ was never achieved by MBE growth. Cu doping nematic superconductivity was reported for percentages between 2 – 12 at.%⁸⁷.

4.2. Structural properties

Fig. 4.1 illustrates the unit cell, rhombohedral crystal structure, of the Bi_2Se_3 . The doping element has 3 possible sites in the crystal structure (Fig. 4.1 b, c, d). First, Cu and Ga atoms are prone to replace Bi atoms (Fig 4.1 b) due to their similar valence. Moreover, the Pauling electronegativity of Ga (1.81) or Cu (1.9) is closer to the Bi (2.02) instead of the Se (2.55). The doping element can be interstitial in the quintuple layers sites (Fig 4.1 c) or they can be intercalated in the Van der Waals gap (Fig 4.1 d). It is important to highlight that the topological superconductivity achieved in $\text{Cu-Bi}_2\text{Se}_3$ is attributed to the intercalation of Cu atoms in the Van der Waal gap⁷⁵.

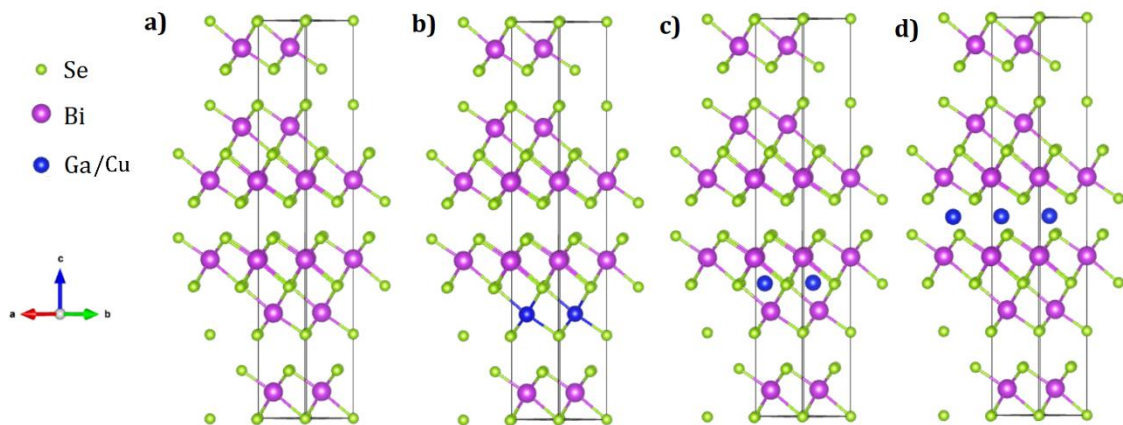


Figure 4.1 Unit cell of a) Bi_2Se_3 crystal structure and possible doping atoms site in the crystal: b) Bi substitution, c) interstitial in the quintuple layer or d) intercalated into the Van der Waals gap. Edited from Daniel Brito et al.¹²⁰.

4.2.1. *In situ* RHEED

To perform the doping of Bi_2Se_3 , Ga or Cu is evaporated simultaneously during the Bi_2Se_3 growth. Different doping percentages are implemented by simply changing the doping element cell temperature. The Ga cell temperature varies from 680 to 765 °C and the Cu cell temperature varies from 830 to 860 °C. The remaining growth parameters are kept the same as in Chapter 3, such as substrate temperature, growth rate, and Se valve. The sapphire substrate is treated with surface treatment as explained in section 3.1 instead of the buffer layer, to prevent the diffusion of In atoms into the Bi_2Se_3 layer. The doping element beam fluxes are measured for each cell (Ga and Cu), by the beam flux monitor to control the doping percentage. Since the substrate temperature (310°C) is higher than the Se cell temperature (285°C), the growth rate depends only on the Bi flux⁸⁸. The doping is controlled by adjusting the (Ga: Bi) or (Cu: Bi) flux ratio, aiming for the nominal doping percentages of (Ga: 0.8 at.%, 2 at.%, 7 at.%, 14 at.%) and (Cu: 2 at.%, 4 at.%, 7 at.%). Further compositional characterization technique (XPS) was used to quantify the doping. A higher doping (14 at.%) of Ga is selected to obtain a systematic study of the Ga doping, and hence comprehend wherein the material starts to deteriorate the Bi_2Se_3 quality. The Ga-doped Bi_2Se_3 film thickness is 60 nm and the Cu-doped Bi_2Se_3 thickness is 40 nm due to a change in the growth rate over time.

During the deposition, the morphology and crystallographic information can be extracted *in situ* by the RHEED. The RHEED patterns are shown in Fig. 4.2 for different doping levels of Bi_2Se_3 for Ga (Fig 4.2 b-d) and Cu (Fig 4.2 f-h). Two distinct undoped samples of Bi_2Se_3 are grown for each doping batch (Fig 4.2 a and e) as reference. The good quality Bi_2Se_3 pattern is characterized by sharp streaky lines and a sixfold symmetry under sample azimuthal rotation. This pattern is preserved with doping up to 2 at.% of Ga Fig 4.2 b. However, at 7 at.% Ga doping Bi_2Se_3 pattern (Fig 4.2 c) starts to exhibit spare dots in the lines, which can be related to a 3D growth or an increase in the film roughness by the incorporation of Ga. When doping increases to 14 at.% (Fig 4.2 d) it destroys the single crystallinity of the Bi_2Se_3 , observed by the presence of concentric rings characteristic of polycrystalline films.

The Cu-doped Bi_2Se_3 RHEED patterns do not show a significant difference upon Cu doping. The pattern is unchanged up to a doping of 7 at.% (Fig 4.2 h). The signal intensity, however, seems to increase upon doping. This effect can be attributed to the doping of metallic elements, which can increase the reflectivity. Thus, it could indicate an accumulation of Cu elemental on the surface. In terms of roughness, the pattern is spot free meaning that the roughness is not altered.

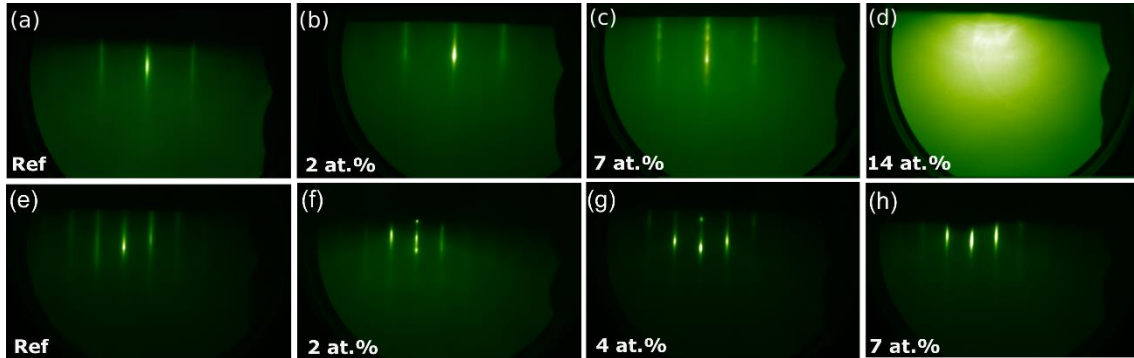


Figure 4.2 RHEED pattern of a) undoped Bi_2Se_3 , Ga-doped with b) 2 at.%, c) 7 at.%, d) 14 at.% in the [110] direction. RHEED pattern of e) undoped Bi_2Se_3 and Cu doped with f) 2 at.%, g) 4 at.% and h) 7 at.% in the [100] direction. Pannels (a)-(d) are edited from Daniel Brito et al. ¹²⁰

4.2.2. X-ray photoelectron Spectroscopy (XPS)

Fig. 4.3 shows high-resolution XPS spectra of Bi_2Se_3 used to quantify the thin film composition of doped samples with different levels of doping. The Ga signal is observed in Fig 4.3 a) for all the Ga- Bi_2Se_3 samples, where the presence of the Ga binding energy (BE) peak confirmed the successful incorporation in Bi_2Se_3 . The BE of Ga $3d$ is detected around 20 eV for all the samples. The peak intensity increases with the percentage of Ga. However, the characteristic oxide BE peak is close to the Ga peak of ≈ 20.5 eV. Furthermore, the surface of Ga-doped Bi_2Se_3 presented a higher concentration of Ga, which indicates a segregation of Ga atoms toward the surface. Annex S1 shows the Ga spectra before and after Ar^+ ion etching.

The XPS peaks of the Bi are presented in Fig 4.3 b) and e), for the Ga-doped and Cu-doped Bi_2Se_3 , respectively. The doublets $\text{Bi } 4f_{7/2}$ and $4f_{5/2}$ are localized at 158.1 and 163.4 eV, respectively. Additionally, for the Cu-doped Bi_2Se_3 (Fig 4.3 e), a shift to higher energies is visible as the doping is increased, which points to a Bi substitution with Cu atoms ⁸⁹. Both signals presented a small percentage of oxides, such as Bi_2O_3 ⁸⁹. The Se $3d$ peak doublet (Fig 4.3 c) and f)) is not discerned due to the superposition of both peaks at ~ 54 eV. Analogous to the Bi signal, the characteristic Se oxides, at 58.9 eV⁶³, were minimal.

Finally, the Cu spectra are shown in Fig 4.3 d) for the Cu-doped Bi_2Se_3 . Two Cu peaks are observed, $2p_{3/2}$ and $2p_{1/2}$ at 932.1 eV and 952 eV, respectively. Similarly to the Ga signal, the intensity increases with the Cu doping. Moreover, a strong and broad Cu^{2+} satellite peak appears approximately at 940 eV, as reported in the literature ⁹⁰. The strong satellite peak presence indicates the existence of divalent Cu^{2+} in the film, which is an indication of the Bi atom being replaced with Cu atoms ^{91–93}.

Table 4.1 shows the composition of each element extracted from the XPS data. The nominal percentages for the Ga and Cu doping agree with the measured doping with a small deviation. From this point forward the nominal percentage is used to facilitate the reading.

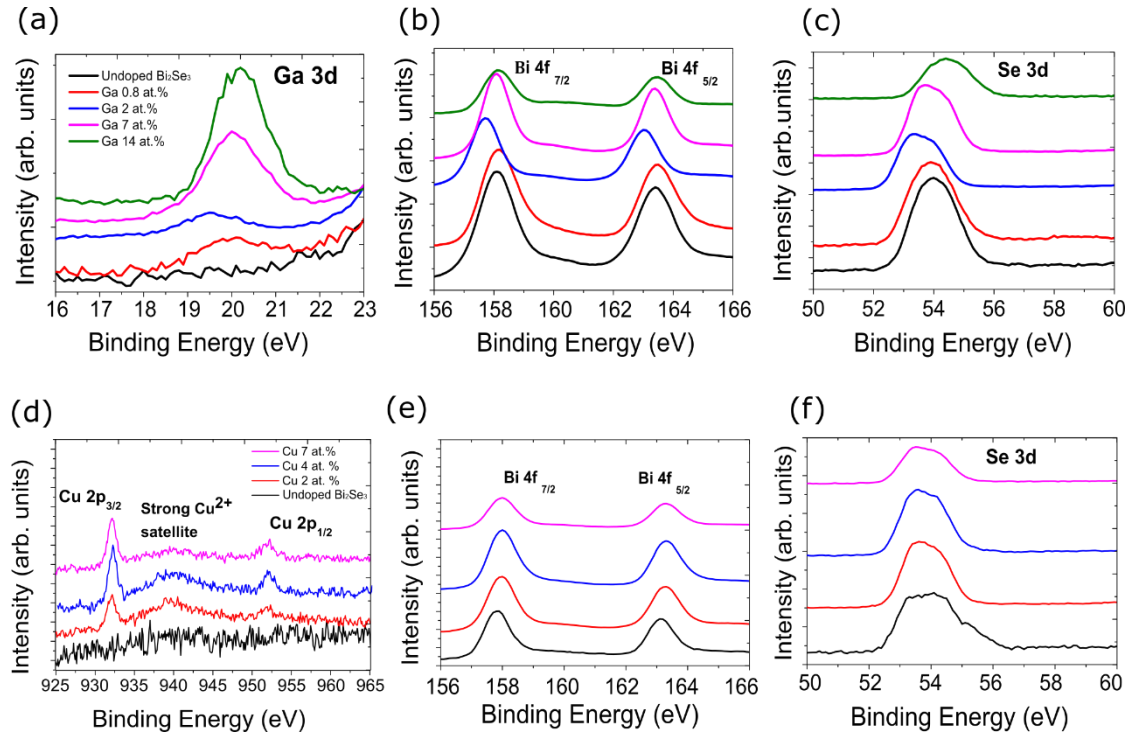


Figure 4.3 XPS spectra for Ga-doped Bi₂Se₃ with the respective high-resolution spectra for a) Ga 3d, b) Bi 4f and c) Se 3d core lines for all doping percentages. XPS spectra for the Cu-doped Bi₂Se₃ with the respective high-resolution spectra for d) Cu 2p, e) Bi 4f and f) Se 3d core lines for all doping percentages. Edited from Daniel Brito et al. ¹²⁰.

Table 4.1 Chemical composition of the Ga/Cu-doped Bi₂Se₃ extracted from the XPS analysis.

Elements	Chemical composition (at.%)							
	Undoped Bi ₂ Se ₃	0.8 at. % Ga	2 at. % Ga	7 at. % Ga	14 at. % Ga	2 at. % Cu	4 at. % Cu	7 at. % Cu
Bi	33.4	35.3	31.8	29.6	21.1	34.8	31.5	32.1
Se	66.6	63.9	66.8	64.5	65.5	63.0	64.1	62.0
Ga	...	0.8	1.4	5.9	13.4	...	...	...
Cu	...	...	...	...	...	2.2	4.4	5.9

4.2.3. XRD and Raman characterization

Fig 4.4 presents the XRD pattern for the Ga (Fig 4.4 a) and b)) and Cu (Fig 4.4 c) and d)) doped Bi_2Se_3 with nominal doping percentage increasing from bottom to top. All the data is performed with the same scan recipe, integration of time, and sample thickness. All the samples presented a single crystal pattern referent to the Bi_2Se_3 as the pure Bi_2Se_3 in the previous chapter and reported in the literature⁷³. Lastly, none of the samples present any contaminations such as GaSe ⁹⁴ ($\theta \approx 12^\circ$, 22° or 46°) or CuSe ⁹⁵ ($\theta \approx 30^\circ$ or 45°). Fig 4.4 b) shows a high-resolution diffractogram of the (0015) plane for the Ga-doped samples to distinguish the Ga doping influence on the lattice parameter with more details. The peak intensity is reduced by more than 50% upon doping, which suggests a deterioration of the crystal quality, in agreement with the RHEED pattern (Fig. 4.2 b-d). Concerning the peak position, there is a shift towards lower angles with the Ga doping. Moreover, for the Ga percentage of 2 and 7 at.% a split double peak towards lower angles occurs. The double peak formation can indicate the formation of a new competing phase while the shift towards lower angles is related to the expansion of the c lattice parameter. The double peak is later converged into a single peak for a Ga doping of 14 at.%.

For the Cu-doped Bi_2Se_3 , the high-resolution diffractogram of the (0015) plane is shown in Fig 4.4 d). Contrary to the Ga-doped Bi_2Se_3 , doping with Cu does not influence the peak intensity. This information supports the RHEED spectra (Fig. 4.2 e-h), where Cu doping leads to brighter streaky lines compared to the Ga-doped samples. Similarly, there is an observable small shift towards lower angles for the Cu-doped samples compared to the reference Bi_2Se_3 .

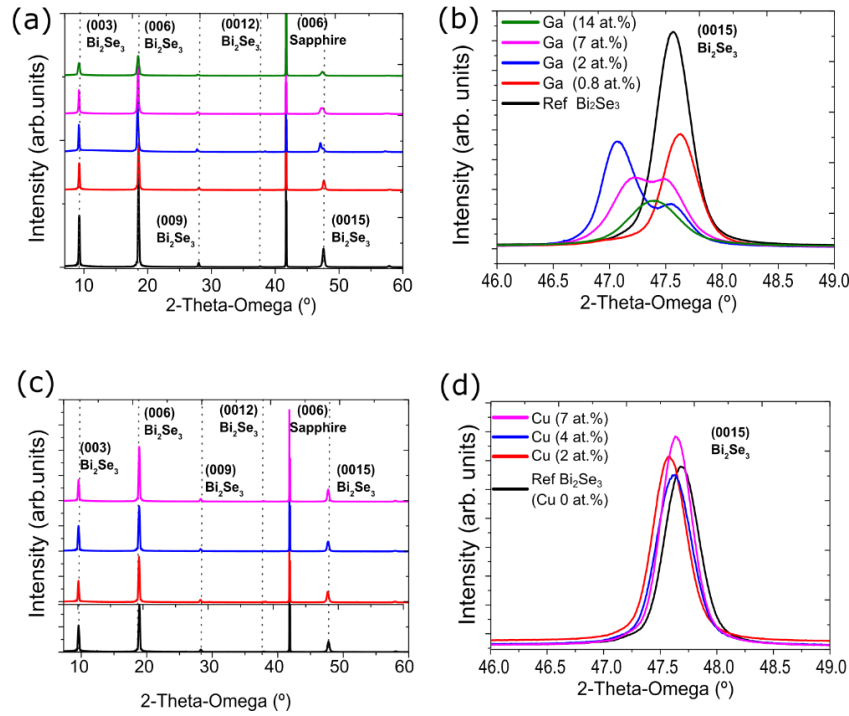


Figure 4.4 XRD pattern for the a) Ga-doped Bi_2Se_3 with b) high-resolution XRD pattern for the (0015) plane. XRD pattern for the c) Cu-doped Bi_2Se_3 with d) high-resolution XRD pattern for the (0015) plane. Edited from Daniel Brito et al.¹²⁰

The XRD peak shift with Ga and Cu doping suggested a modification in the crystal lattice parameter. Based on the XRD data, the c and a lattice parameters are calculated as described in sections 2.2.1 and 3.4.1. The results are shown in Fig 4.5. The Ga-doped Bi_2Se_3 c and a lattice parameter are presented in Fig 4.5 a and b, respectively. An a of 4.14 Å and c of 28.66 Å for the undoped Bi_2Se_3 is obtained, in agreement with the literature^{62–65}. Previous studies from In-doped Bi_2Se_3 reported the decrease in the c lattice parameter due to the Bi atoms substitution with In atoms^{63,64}. Likewise, Ga^{3+} ions exhibit a smaller radius (0.62 Å) compared to the Bi^{3+} (1.03 Å)⁹⁶, then the replacement of Bi atoms with Ga should lead to a decrease in the crystal lattice. The c lattice tends to increase with the percentage of Ga higher than 7 at.%. Furthermore, the second peak formation is treated as a new phase, thus a new lattice parameter is required to be calculated as a different lattice, as illustrated with a blue dot, produces a maximum c lattice parameter of 28.92 Å. The intercalation of Ga atoms in the Van der Waals gap is speculated to be occurring since it would lead to the expansion of the c lattice. The intercalation of different atoms was previously reported for Cu/Ag/Co/Sr- Bi_2Se_3 ^{62,68,78,91}, where an expansion of the lattice is observed. The value starts to decrease compared to smaller doping percentages but is still higher than the reference. For a higher concentration of Ga (14 at.%), the peak is converged to a single one with a value of 28.77 Å. This behavior is hypothesized to be happening because of a mixture of Ga intercalation and substitutional Ga atoms with Bi.

On the other hand, Cu-doped samples presented a similar behavior as the Ga-doping by an increase in the c lattice parameter with Cu doping. Firstly, the undoped Bi_2Se_3 showed a reduced c lattice parameter of 28.60 Å compared to the reference sample of the Ga-doped batch. It is assumed that the high Cu cell temperature ($\sim 900^\circ\text{C}$) can be prejudicial for the Bi_2Se_3 film quality by the evaporation of undesired elements. Fig 4.5 c and d show the lattice parameter evolution with Cu doping. The Bi_2Se_3 unit cell volume decreases as the Cu doping is increased up to 2 at.%, whereas with doping higher than 2 at.%, it starts to increase. Similar to Ga doping there is an increment of the unit cell volume, which indicates an expansion of the crystal structure. However, the values are significantly smaller than the Ga-doped samples. In terms of lower Cu doping (2 at.%), the reduced volume can indicate that the Cu can replace the Bi atoms as observed in the literature⁹⁷.

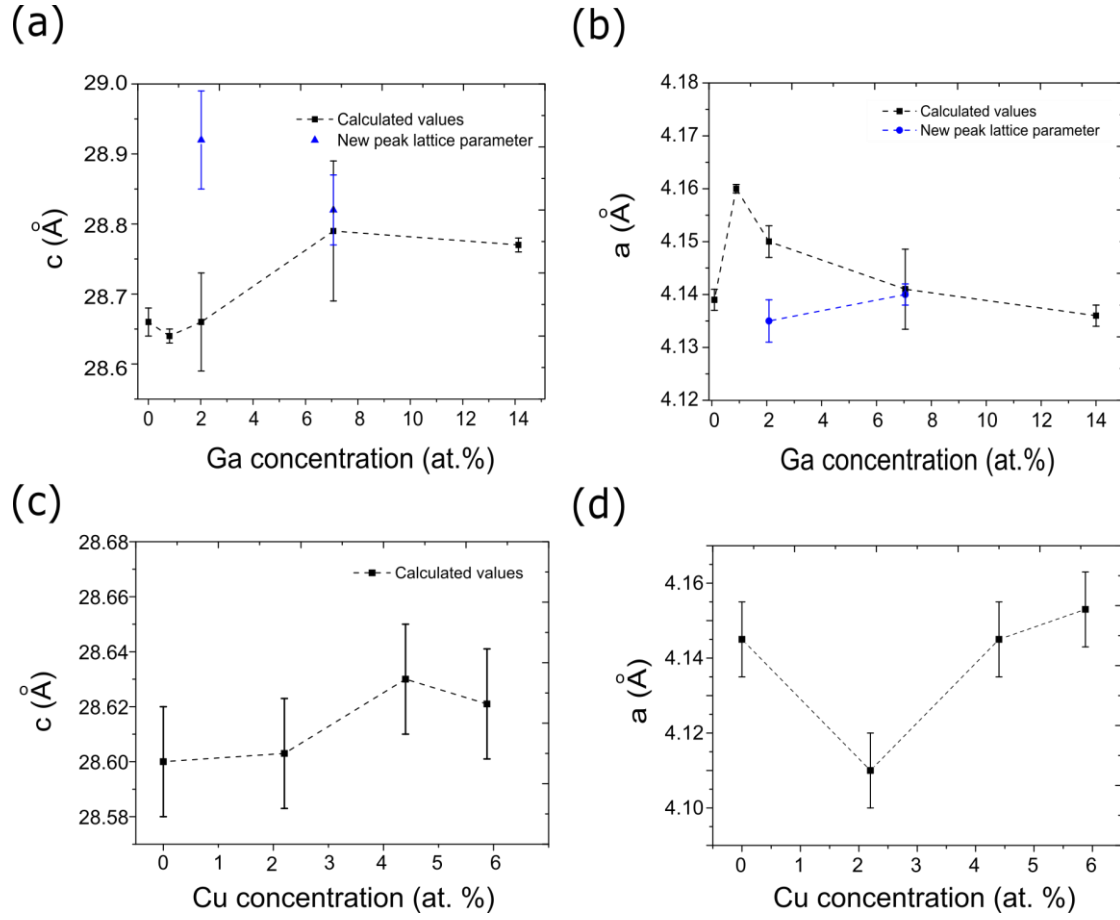


Figure 4.5 Crystal lattice parameters a) c and b) a as a function of the Ga atomic doping percentage. Crystal lattice parameters c) c and d) a as a function of the Cu atomic doping percentage. The calculated values are extracted from XRD by Eq. (2.2) Edited from Daniel Brito et al. ¹²⁰.

Raman spectroscopy is commonly used as a structural and compositional characterization technique. The Bi_2Se_3 vibrational modes are studied by Raman spectroscopy at room temperature and the Ga/Cu doping influence is studied by examining the behavior of the vibrational modes upon doping. Fig. 4.6 shows the Raman spectra for increasing Ga (Fig. 4.6 a) and Cu (Fig. 4.6 c) doping from bottom to top and the evolution of the peak position as a function of the doping concentration (Fig. 4.6 b and d). Three vibrational peaks are observed as characteristic of the Bi_2Se_3 belonging to the A_{1g}^1 , E_g^2 and A_{1g}^2 vibrational modes, at 71, 130, and 174 cm^{-1} , respectively ^{62,98}.

As observed in Fig. 4.6 a), the incorporation of Ga produces a small shift towards lower frequencies. Furthermore, as observed in the XRD pattern, a double peak for the percentage of 2 at.% of Ga forms a small double peak for the E_g^2 vibrational mode at lower frequencies, which leads to a significant new peak deviated of $\approx 7.6 \text{ cm}^{-1}$ (Fig. 4.6 b pink dot) from the reference peak position. For the remaining doping concentrations, no doublet and undesired phase, such as GaSe is observed. The peak position as a function of the Ga doping

is presented in Fig 4.6 b). Earlier studies performed in intercalated Cu- Bi_2Se_3 have shown that the intercalation of Cu in the van der Waals gap leads to a red shift in the vibrational modes ⁹¹. The redshift in Ga doping that we observe corroborates the XRD hypothesis that Ga atoms can be intercalated in the Van der Waals gap, despite the shift being small compared to the error margin.

On the other hand, the shift to higher frequencies in Bi_2Se_3 is reported to occur when Bi atoms are replaced with lighter elements and stronger binding forces ⁶⁴. Both 0.8 at.% Ga and 2 at.% Cu showed a blue shift that can be explained as a competitive substitution of Bi atoms for this small doping. Likewise, Cu-doped Bi_2Se_3 (Fig 4.6 d) showed doping with Cu leads to a blue shift.

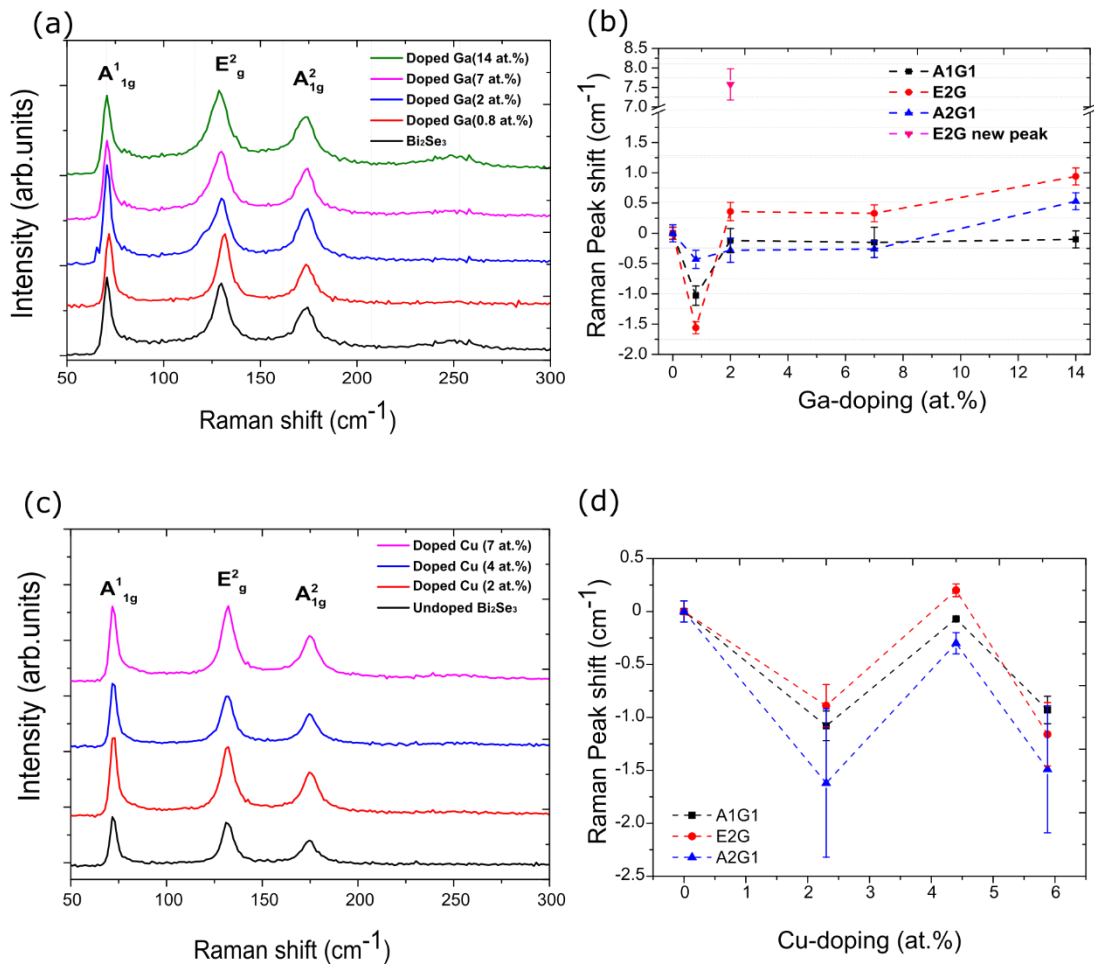


Figure 4.6 Room temperature Raman spectroscopy for a) undoped and Ga-doped Bi_2Se_3 and b) peak position as a function of the nominal Ga percentage. Raman spectroscopy for c) undoped and Cu-doped Bi_2Se_3 and b) peak position as a function of the nominal Cu percentage. Edited from Daniel Brito et al. ¹²⁰.

4.2.4. Transmission electron microscopy (TEM)

Finally, to conclude the structural analysis of the doped Bi_2Se_3 , transmission electron microscopy (TEM) is implemented, which offers a direct visualization of the crystal structure with spatial resolution. Moreover, the dopant localization and distribution can be mapped in conjunction with an energy-dispersive x-ray spectroscopy.

A STEM cross-sectional image of the Cu-doped Bi_2Se_3 for both doping percentages is shown in Fig. 4.7(a) 2 at.% and b) 7 at. %). The samples are prepared with a Ga ion irradiation via FIB to cut a lamella to obtain the STEM images. However, the Ga-doped Bi_2Se_3 is not measured due to the possible contamination during the preparation of the sample with Ga atoms, which can compromise the STEM images.

The Cu- Bi_2Se_3 (Fig. 4.7) reveals an atomically ordered structure by the visualization of a stack of 5 atoms bonded vertically (quintuple layers, QL), separated by a Van der Waals gap, confirming the rhombohedral crystal structure of the Bi_2Se_3 . The images do not present significant defect percentages, such as twinning or dislocations, even at lower magnification.

The good crystallinity of the Bi_2Se_3 is obtained even upon a high Cu percentage of 7 at.%. Thus, the incorporation of Cu atoms in the lattice does not disrupt the crystal quality and does not increase the number of defects. Cu atoms are not distinguished from Bi and Se atoms. Nonetheless, energy-dispersive X-ray spectroscopy can identify atomic localization (Annex S3). As observed in the image in the annex, Bi and Se atoms are well-defined and localized in the crystal structure, whereas Cu atoms are randomly distributed in the crystal structure which reinforces the idea that Cu atoms are replacing Bi atoms in the lattice rather than intercalation.

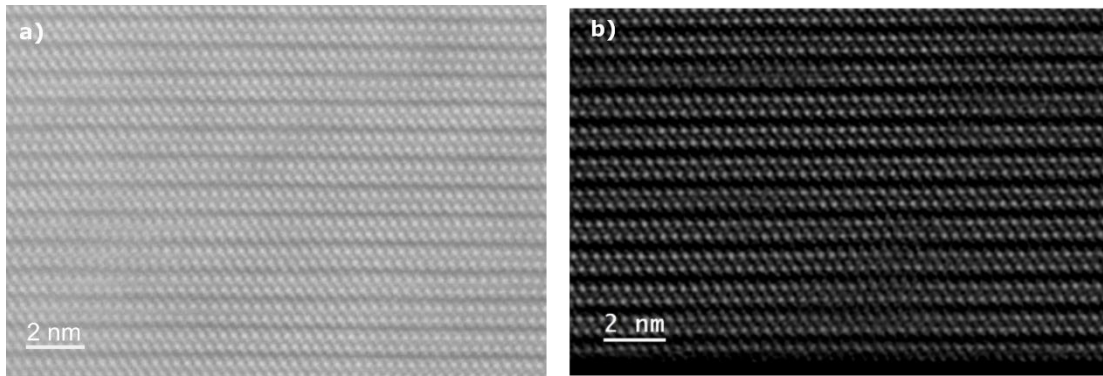


Figure 4.7 STEM images along the [100] direction of Bi_2Se_3 doped with a) 2 at.% and b) 7 at.% of Cu grown on a sapphire substrate.

4.3. Electrical properties

4.3.1. Transport properties

Previously, the Bi₂Se₃ transport properties were only measured at room temperature. To minimize the effect of the bulk contributions, the electrical properties are measured at low temperatures down to 1.5 K. Hall effect measurements can provide information on the level of defects and the impact in terms of the transport properties measurements.

Ga-doped Bi₂Se₃

Fig 4.8 presents the transport properties of undoped and Ga-doped Bi₂Se₃ extracted from Hall effect measurements. The resistivity, bulk, sheet electron concentration, and mobility are shown as a function of the temperature. The doping percentages used are 2 and 7 at.%. The 0.8 and 14 at.% doping samples are not studied due to the reduced effect of the doping on observable properties and the reduced crystal quality of the samples, respectively.

Fig 4.8 a) shows the resistivity as a function of the temperature. Both samples present a metallic behavior, which means a decrease of the resistivity with the decrease of the temperature which suggests that the material conductance is mainly dominated by the bulk conductance. The undoped Bi₂Se₃ exhibits a larger resistivity for temperatures higher than 100 K than the Ga-doped samples, reverted as the temperature decreased. This increase of the resistivity upon doping reveals a greater degree of crystal disorder as the Ga concentration is increased.

In terms of the electron concentration and mobility (Fig 4.8 b) and d)), undoped Bi₂Se₃ shows a sheet concentration of $\sim 7 \times 10^{13} \text{ cm}^{-2}$ and a mobility of $423.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at RT, which is in agreement with previous reports for pure MBE-grown Bi₂Se₃^{39,54,58}. The 60 nm thick Bi₂Se₃ exhibits a bulk electron concentration of $\sim 1 \times 10^{19} \text{ cm}^{-3}$ (Fig 4.8 c), which increases sixfold to $\sim 6 \times 10^{19} \text{ cm}^{-3}$ for both Ga percentages. The high concentration is accompanied by a reduced mobility of $119.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with Ga doping. Therefore, Ga acts as a donor impurity, which reinforces the assumption of the intercalation of Ga atoms in the Van der Waals gap since free Ga atoms in the Van der Waals gap contribute with free electrons for the transport. The substitution of Bi atoms with Ga should not produce such notable influence in the concentration of electrons due to their similar valence. Furthermore, the introduction of defects into the VdW gap, meaning intercalation of atoms, produces potential barriers, leading to a sudden decrease in mobility⁹⁹. Nonetheless, the substitution of Bi atoms with dopant atoms can also decrease the mobility due to ionized impurity scattering. Thus, the decrease in mobility supports the hypothesis of the intercalation of Ga atoms and the substitution in the crystal.

As a function of the temperature the electron concentration and the mobility have

opposite tendencies. The undoped Bi_2Se_3 electron concentration increases with the temperature, whereas the Ga-doped Bi_2Se_3 electron concentration decreases as the temperature increases. This behavior is observed in Sr intercalated Bi_2Se_3 and Nb- Bi_2Se_3 ¹⁰⁰ which are known to exhibit superconductivity at low temperatures^{78,101,102}. This behavior is in accordance with the resistivity since the linear behavior is expected due to the electron-phonon scattering. The Ga- Bi_2Se_3 presented a reduced slope for the resistivity, as a result of the high carrier concentration, producing an increase in the screening of the deformation potential and thus a reduced electron-phonon coupling. Finally, mobility has a similar tendency for all samples, because it decreases with the temperature for the undoped Bi_2Se_3 since the electron-phonon scattering is more pronounced for lower temperatures. Hence, the drift velocity is reduced which reaches a maximum mobility of $1700 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for the undoped Bi_2Se_3 at 10K.

In conclusion, the electrical properties of the Ga- Bi_2Se_3 reinforce the hypothesis of Ga atoms being intercalated, acting as donor impurities. Furthermore, the intercalation of atoms in the VdW gap is known to lead to a rotational symmetry breaking and consequently can lead to superconductivity. The electron concentration trend observed is similar to the previously reported Sr/Nb- Bi_2Se_3 superconductors. However, the zero resistivity is not observed in the resistivity graph down to temperatures of 1.5 K, meaning that the superconductivity is not observed.

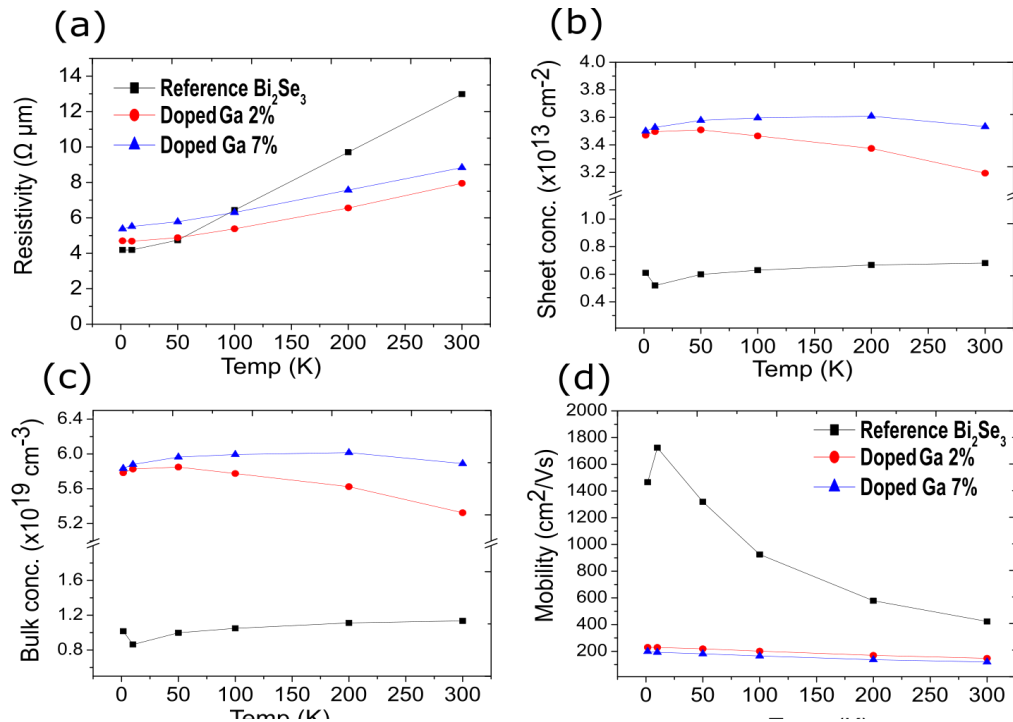


Figure 4.8 a) Resistivity, b) sheet concentration, c) bulk concentration, d) mobility of undoped and Ga-doped Bi_2Se_3 as a function of the temperature extracted from the Hall effect measurements. All samples are n-type. Edited from Daniel Brito et al.¹²⁰.

Cu-doped Bi₂Se₃

Fig 4.9 presents the transport properties of undoped and Cu-doped Bi₂Se₃ extracted from Hall effect measurements in a van der Pauw configuration (Fig. 2.10 a). It shows the resistivity, bulk, sheet electron concentration, and mobility as a function of the temperature up to 100 K. In order to compare the different types of doping, the same doping concentrations (Cu 2 and 7 at.%) are used. As previously observed, all the samples exhibit a decrease in resistivity with a decrease in the temperature Fig 4.9 a). It reveals a weak metallic behavior, which suggests that the transport is controlled by the bulk conductance. As opposed to Ga-doping, doping with Cu produces a systematic increase in resistivity. The increase in resistivity can also be associated with the substitution of Bi atoms with Cu atoms (Cu²⁺), which could act as an acceptor impurity, and consequently increase the resistivity^{95,103,104}. Indeed, as observed for the electron concentration (Fig 4.9 b), the Cu acts as an acceptor impurity. Undoped Bi₂Se₃ presents a sheet concentration of $\sim 8 \times 10^{13} \text{ cm}^{-2}$, which upon Cu doping decreases by almost a factor of 2, to $\sim 5 \times 10^{13} \text{ cm}^{-2}$ with Cu of 7%. The TSC in Cu-doped Bi₂Se₃ requires the intercalation of Cu in the VdW gap, but Cu atoms tend to bind in the crystal structure, replacing Bi atoms^{95,97,103}. The electron concentration shows little dependence on the temperature. The mobility of the undoped Bi₂Se₃ at 100 K is $\approx 450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a maximum of $\sim 625 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 1.5 K. Contrary to the electron concentration, the mobility does not show an improvement upon Cu doping. The mobility was expected to be increased upon Cu doping as a consequence of the lower electron concentration of the Cu-doped Bi₂Se₃. The values are reduced from $625 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $\sim 450 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 1.5 K with a Cu doping of 7 at.%. This can be a consequence of the scattering mechanism due to the presence of Cu impurities.

In conclusion, Cu doping affects positively the transport properties of the topological insulator by reducing the bulk concentration, though, the TSC was not achieved in Cu-Bi₂Se₃ (lack of a 0 Ω resistivity at low temperatures) as the Cu impurity worked as an acceptor replacing Bi atoms and not as an intercalated impurity which is a crucial point to earlier observations of the topological superconductivity⁷⁵.

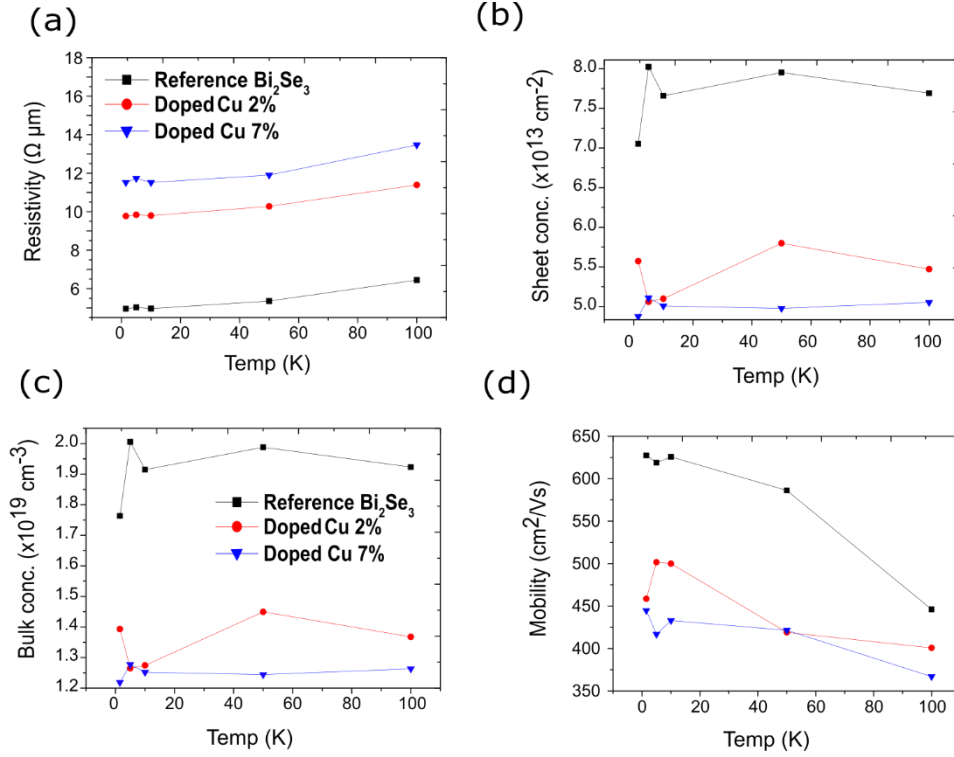


Figure 4.9 a) Resistivity, b) sheet concentration, c) bulk concentration, d) mobility of undoped and Cu-doped Bi_2Se_3 as a function of the temperature extracted from Hall effect measurements. All samples are n-type.

4.3.2. Weak antilocalization effect in doped Bi_2Se_3

As described in section 1.2.4, the weak antilocalization effect (WAL) is a physical phenomenon characteristic of TIs due to the presence of strong spin-orbit coupling in the bulk and 2D Dirac-like physics at the edges^{14,105}. This effect was experimentally observed in Bi_2Se_3 ^{49,67,93}.

Fig 4.10 a and c show the magnetoconductance of the Ga and Cu-doped Bi_2Se_3 , respectively, showing the symmetric cusp typical for a WAL response to small magnetic fields at 1.5 K. The dash lines represent the fitting by the HLN model. The fitting parameters are presented in Fig 4.10 b and d for the Ga and Cu-doped Bi_2Se_3 , respectively. In terms of the Ga doping (Fig 4.10 a and b), the undoped Bi_2Se_3 showed a sharp cusp of the magnetoconductance indicating the presence of conductive surface states. The prefactor (α) obtained is -0.96, which is extremely close to the ideal value of -1, which represents two decoupled surfaces holding topological states. The coherence length (L_ϕ) obtained is 804 nm, which is in agreement with previous reports of Bi_2Se_3 ^{49,61,67,106,107} and denotes good Bi_2Se_3 quality. On the contrary, the undoped sample in the batch of the Cu doping (Fig 4.10 c and d), shows a less pronounced cusp, even though both are undoped Bi_2Se_3 . The principal reason is attributed to the different thicknesses of (60 nm and 40 nm), where studies indicated a transition thickness to occur between 20 and 60 nm referent to the decoupling of the surfaces^{107–109}. Consequently, the decoupling of the surface decreases the value of the prefactor from -0.5 to -1.

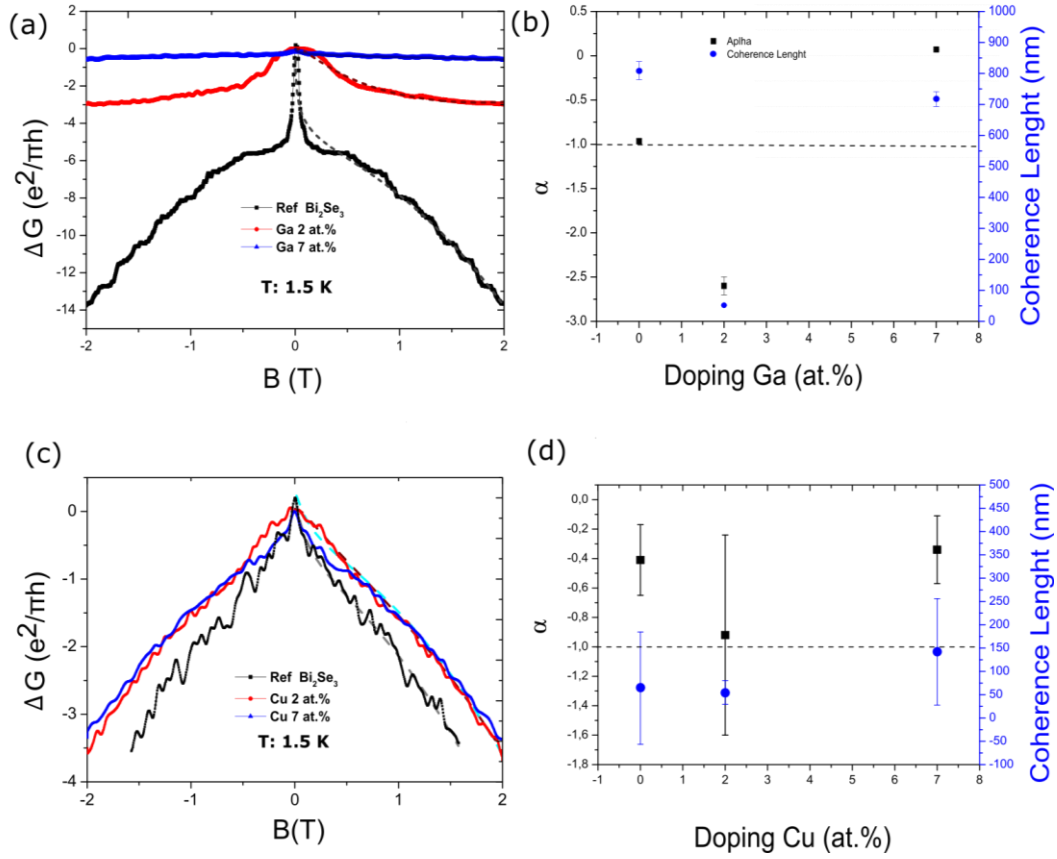


Figure 4.10 WAL measurements for undoped Bi₂Se₃ (black dots) and doped samples with 2 at.% (red dots) and 7 at.% (blue dots) of a) Ga and c) Cu doped Bi₂Se₃, as a function of low magnetic field with the corresponding HLN model fittings (dashed lines). The sharp cusp is a typical feature of the presence of surface states. Fitting parameters α and phase coherence length (L_ϕ) as a function of b) Ga or d) Cu doping level. Edited from Daniel Brito et al. ¹²⁰.

By introducing 2 at.% of Ga (Fig 4.10 a), the WAL cusp becomes less visible compared to the reference. Moreover, the magnetoconductance presents a slight plateau at low magnetic fields, meaning a quantized conductance, that sharply decreases at a critical magnetic field of approximately 0.2 T (Signal before filter is shown annex S2). The presence of a critical magnetic field is commonly observed in superconductors^{79,92,110} (Sc). Moreover, WAL studies in Sc showed higher values than -1 of the prefactor, for temperatures near the superconducting critical temperature ^{111,112}. In our case the α is -2.6 (Fig 4.10 b), suggesting that Ga forms two extra channels with weaker phase coherence compared to the surface states⁶⁷. Castro et al.¹¹³ observed a sudden transition from -0.7 to -2 of the α at a specific critical temperature of 4K in SnTe QWs. It is assumed that the increase in the prefactor is related to the creation of an additional conductive channel. This prefactor increase is accompanied by a reduction of the coherence length with a relatively higher disorder level by doping, presenting a L_ϕ of 52 nm. As a indication concerning the Ga doping, studies on a atomic monolayer of Ga concluded that atomic Ga leads to superconductivity^{114–117} around 4 K, which could explain the superconductor-like behavior of 2 at.% Ga-doped Bi₂Se₃. The intercalation of Ga atoms in the VdW gap might induce superconductivity by a proximity effect with the Bi₂Se₃ layer, which was experimentally realized by Cequn Li¹¹⁵ on Bi₂Te₃.

By increasing the doping to 7 at.% the disordered material is also confirmed by the WAL signal. The cusp has completely vanished with a conductance being unchanged with the magnetic field. The fitting parameters obtained for α is -0.07 and L_ϕ of 717 nm. The higher concentration of Ga and possibly the disorder generated a reduction of the prefactor, and consequently, a disappearance of the surface states, meaning a topological phase transition. This destruction of the surface states is also known to occur in In-doped Bi₂Se₃ for concentrations higher than 7%⁶⁶.

The doping with Cu (Fig 4.10 c and d) produced different behavior compared to the Ga-doped Bi₂Se₃ since all magnetoresistance signals are fairly similar. The fitting parameters obtained for the undoped Bi₂Se₃ are $\alpha = -0.41$ and $L_\phi = 64$ nm. The prefactor value is close to the value corresponding to one conductive surface of -0.5, meaning that there is one coupled conductive surface state. The reduced coherence length indicates the reduced crystal quality. Even though the topological insulator presented lower quality, the surface states are preserved, and the doping influence of Cu can be studied.

Upon Cu doping, the WAL cusp is still present for both doping concentrations. Cu 2 at.% is slightly different from the WAL behavior of Ga-Bi₂Se₃ (2 at%). The signal presents a pronounced quadratic shape but without the presence of the plateau. The fitting parameters obtained are $\alpha = -0.92$ and $L_\phi = 54$ nm. The results suggest a decoupling of the surfaces which produces two decoupled conductive surface states by a α near the ideal value of -1.

Finally, Cu doping of 7 at.% produced fitting parameters $\alpha = -0.34$ and $L_\phi = 141$ nm. Contrary to the Ga doping of 7 at.%, the high concentration of Cu does not produce a phase transition by the destruction of the surface states. The prefactor is relatively close to -0.5, which confirms the presence of a conductive channel. The WAL signal is identical to the reference which indicates a minimal influence of the Cu doping. However, the coherence length is improved from 64 to 141 nm, which might imply the improvement of the material quality. These results are in accordance with the Hall effect measurements, where the TI's 2D transport should be improved by the reduction of the electron concentration and consequently the reduction of the bulk contribution.

4.4. Summary

The epitaxial growth of Ga and Cu-doped Bi_2Se_3 with various doping concentrations is achieved and the influence on the structural, vibrational, and electrical properties is discussed. XPS, Raman, and XRD measurements are used to confirm the effective incorporation of Ga or Cu dopants. The discernible expansion of the crystal lattice and the slight redshift of the vibrational modes suggest that at low concentrations, most Ga atoms can be intercalated in the van der Waals gap between the Bi_2Se_3 QLs. Oppositely, at higher concentrations, the lattice contraction and small blueshift of the vibrational modes observed for the Cu doping suggest a substitution effect, where Cu replaces Bi atoms. Furthermore, n-type doping was observed for all Ga concentrations tested, which excludes Ga as a good candidate for acceptor impurity and reinforces the hypothesis of intercalation. In contrast, the Cu dopant can lead to a reduction of the carrier concentration pointing towards a good acceptor impurity by substitution of Bi atoms.

Finally, as observed for intrinsic band insulators, the lack of WAL suggests the annihilation of the topological surface states as the Ga doping concentration is increased. The persistence of the cusp in Cu-doped samples indicates potential topological behavior. At low Ga doping, the supposed intercalation leads to an increased prefactor, similar to the achieved nematic topological superconductivity. Thus, the present study opens up the possibility of a different dopant to achieve topological superconductivity. Meanwhile, the topological superconductivity of Cu-doped Bi_2Se_3 grown by an MBE is still not achieved.

Chapter 5

5. ARPES measurements of the topological insulator, Bi₂Se₃, and Ga/Cu-doped Bi₂Se₃

5.1. Motivation

Topological insulators (TI) are characterized by massless Dirac surface states (SS). The Bi₂Se₃ band structure is characterized by a large band gap up to 0.3 eV and a robust almost idealized Dirac cone at the Γ point, where the topological surface states are crossing the band gap. The existence of Bi₂Se₃ topological surface states was previously confirmed by Angle-Resolved Photoemission Spectroscopy (ARPES)¹² (Fig 1.8 b). Heretofore, the SS existence was experimentally verified by the WAL effect. However, this 2D transport effect is commonly masked by bulk conductivity due to the Bi₂Se₃ n-type degeneracy. The observation of the WAL effect due to the presence of the SS is necessary but not sufficient to prove the existence of the SS¹¹⁸, since trivial surface states can also produce a WAL effect. Nonetheless, WAL cannot evaluate the SS properties. ARPES, on the contrary, provides direct observation of the electronic structure of the material, which allows the visualization of the SS in the momentum space and the topological properties can be studied (Fermi velocity and Dirac point). ARPES was found to be an ideal characterization technique for the observation of the SS, even for samples with a bulk transport domination¹¹⁹.

Our previous work demonstrated that Ga doping leads to an increase of the electron density by almost six-fold ($n \approx 6 \times 10^{19} \text{ cm}^{-3}$) in Bi₂Se₃¹²⁰. Additionally, Fig. 4.10 showed the WAL upon Ga doping, where the cusp starts to disappear as the Ga concentration increases. These observations could indicate a topological phase transition. We also found evidence that Ga atoms, similarly to Cu, intercalated in the van der Waals gap. Together with the WAL studies, it could predict a new member of the topological superconductivity (TSC) family. Likewise, the WAL upon Cu doping showed the presence of a cusp for both doping and consequently the presence of conductive surface states.

ARPES has been used to study Bi₂Se₃ magnetic dopants¹²¹, rare earth dopants¹²², and other exotic elements^{21,77,79} that can lead to the TSC. Magnetic and TSC dopants may open a gap at the Dirac point of the surface states^{77,123}, which can be observed and confirmed by ARPES measurements, in case it presents enough resolution. The effect of the doping of Ga-Bi₂Se₃ on the surface states was first implemented within this thesis (Chapter 4). Furthermore, ARPES can complement the knowledge about Ga doping and confirm our previous assumptions. Additionally, as previously studied, the growth of topological superconductor Cu-doped Bi₂Se₃ cannot be achieved by an MBE growth. Up to now, ARPES

measurements have been mainly performed on this superconductive doped material^{124–126}. However, ARPES could provide valuable insights into the challenges associated with growing TSC materials via MBE.

This chapter describes experiments with two goals. Firstly, the surface states from the TI Bi_2Se_3 are measured and their topological properties (Fermi velocity, Dirac point, ...) are studied. Secondly, the doping with Ga and Cu is studied to provide additional information about the surface states, such as topological properties and evolution upon doping.

5.1.1. Sample preparation, methodologies, and relevant preliminary information

ARPES is highly sensitive to the surface properties of materials, and thus, meticulous surface preparation is fundamental for accurate measurements. Any impurities, adsorbates, or defects on the surface can significantly influence the observed electronic structure. This sensitivity underscores the need for pristine surfaces to reveal the intrinsic electronic states. Rigorous surface preparation methods, such as in-situ cleaving or annealing, are employed to ensure reliability in ARPES experiments, thereby providing insights into the fundamental electronic properties of materials. Besides the surface sensitivity, the technique is also affected by the material crystallinity, since polycrystalline samples cannot guarantee momentum conservations, thus making it difficult to extract information from poor single crystals.

Sample preparation

The single crystal layers Bi_2Se_3 , Ga-doped Bi_2Se_3 , and Cu-doped Bi_2Se_3 are grown on sapphire substrates (Al_2O_3) by MBE. Ga and Cu doping percentages were chosen to be 2 and 7 at.%. Later on, gold contact pads are deposited on the surface of the sample to prevent charging effects at the detector. The lack of a path for photoexcited charges (worsened by insulating substrate) could lead to a surface charging effect that would jeopardize the ARPES measurements as those surface charges interact with the photoexcited electrons of interest. Even though, the problem can also be easily solved by providing good electrical contact between the film and the sample holder by a *washer*. As shown in Fig. 5.1.

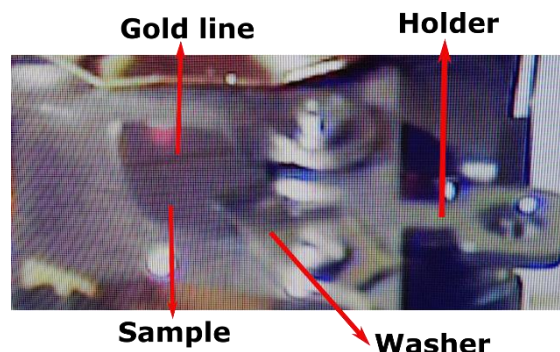


Figure 5.1 Configuration of the Bi_2Se_3 substrate for the ARPES measurements. It is visible the sample with a gold line on the surface of it. The sample is held on the holder by a washer, which also provides the metallic contact to the film surface.

Due to the surface sensitivity of this technique, it is important to protect the surface from any contaminations, impurities, or oxidation reactions. Therefore, the surface of the Bi_2Se_3 is covered with a 20-100 nm amorphous Se capping layer after the MBE growth at a sample temperature of 30-35°C for approximately 10 min. Afterward, the samples are transferred to ALBA synchrotron in Barcelona with the minimal air exposure as possible in a sealed box in vacuum.

After introducing the Bi_2Se_3 samples into the preparation chamber at the LOREA beamline, the Se layer is then removed (Se decapping) by annealing the sample. Several experimental procedures were tested to remove the Se capping layer. The Se capping layer was already implemented in previous studies^{29,127,128}. Nonetheless, the Se decapping depends on various factors such as real temperature, chamber pressure, Se sticking coefficient, and thickness.

Our decapping experiments started by annealing the sample up to 80 °C and staying at this temperature until it is observed a pressure improvement (~2h). Core levels or XPS analysis are implemented to detect the Bi signal to identify the full Se decapping. The core levels could indicate a not-perfect surface cleaning due to the presence of tails in the Bi element peaks, mainly by some Se remnants. Alternatively, a different approach is tested by increasing the temperature to 110 °C and a duration time between 4-6 h. As a result, ARPES intensity showed an improvement in signal-to-noise, and the core level tails were reduced. Finally, a “flash decapping” was performed by annealing at the maximum temperature of 180 °C for the shortest time (5-10 min) wherein the Se seems, by visual inspection, to be fully removed from the surface of the sample. The Se is distinguished by a blueish color. As soon as the surface starts to appear metallic-like the temperature is reduced to avoid the unintentional removal of the Se atoms from the Bi_2Se_3 layer. This last decapping showed to be the ideal annealing where the best signal-to-noise is observed. Therefore, all samples are subjected to a “flash Se decapping” at 180 °C between 5-10 min until an alteration in the surface of the sample is observed.

Preliminary information and results

The ARPES measurements start with the scan of the undoped Bi_2Se_3 band structure at the Γ (gamma point) with different beam source energies (15 – 40 eV). The ideal beam source energy is dependent on the material measured. Thus, different beam source energies from 15 – 40 eV are tested to spot the ideal source energy in order to obtain the best resolution and discern the topological surface states. Lower energies provide the best resolution, and the optimal signal is achieved with a beam source energy of 18 eV.

Furthermore, the beam polarization is studied by using both vertical and planar polarization to understand the preferential polarization. The surface states are detected with a planar polarization, whereas with vertical polarization no signal is detected.

Henceforward, the energy used for ARPES (band dispersion, Fermi map, etc.) is 18 eV. Energies higher than 30 eV showed an increased noise-to-signal and reduced resolution. The temperature of all measurements is about 10 - 15 K to minimize thermal broadening effects allowing a higher energy resolution.

5.2. Bi_2Se_3 electronic band structure concepts

The band structure of the Bi_2Se_3 is composed of a band inversion at the Γ point, related to the non-trivial topology, which creates the crossing surface states. The surface Brillouin zone is composed of a hexagonal structure (Fig 5.2 a), where the Γ point is the center (0,0,0) and the $\bar{K}$ and $\bar{M}$ points are at the corners and the mid-edge of two corners, respectively. The surface states are detected from the gamma point to any momentum direction since the Dirac dispersion is symmetric across different momentum directions.

The energy band dispersion of the Bi_2Se_3 reference sample is shown in Fig 5.2 b). The conduction band (CB) is observed below the Fermi level, demonstrating that the Fermi level resides within the conduction band. This observation confirms the inherent n-type degeneracy attributed to the presence of Se vacancies. The valence band (VB) is observed at higher binding energies as an M-like shape, resulting in the strong split of the band by the spin-orbit coupling. The surface states characteristic of the 3D topological insulator Bi_2Se_3 is observed as a semi-Dirac cone crossing the band gap connecting the CB to the VB, where they merge with the valence band right underneath the Dirac point (D_P), making them only visible on the upper part of the D_P .

Furthermore, the conduction and valence band can be approximated as a parabolic band, the solution of the Hamiltonian for semiconductors. However, the valence band can be approximated as an inverse parabolic with an incorporation of the strong spin-orbit coupling to produce the M-shape. By performing the fitting model, explained previously in section 2.2.6, it is possible to extract the Dirac point position (D_P), Fermi velocity (V_F), the electron mass (m_{ev} , m_{ec}), the conduction band minimum (E_C), and the valence band maximum (E_V). The fitting model is applied to the ARPES of the undoped Bi_2Se_3 (Fig. 5.2 b) and presented in Fig 5.2 c).

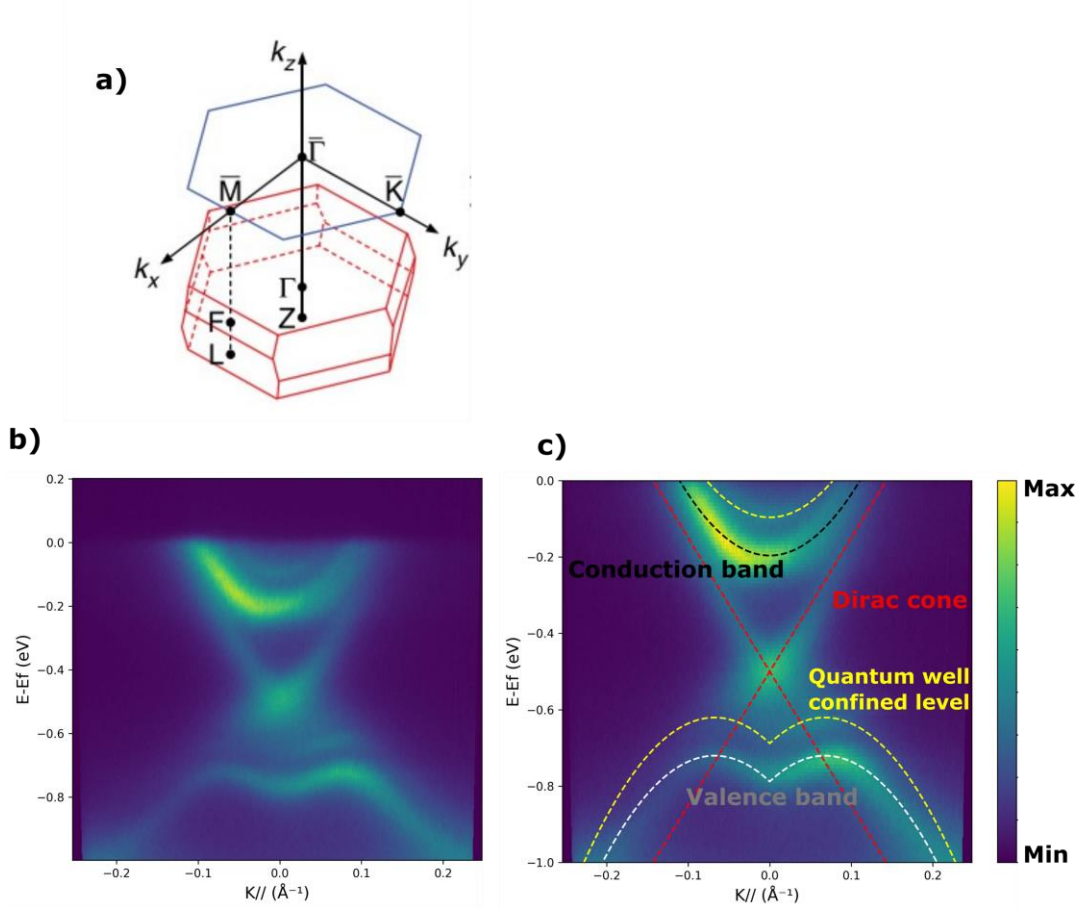


Figure 5.2 a) Bi_2Se_3 surface Brillouin zone with a hexagonal structure with visualization of the relevant symmetry points (Γ , K and M). b) Energy dispersion of Bi_2Se_3 . c) The fitting model applied to the band dispersion of the Bi_2Se_3 , observing the surface states (Dirac cone, red dash), conduction band (Black dash) and valence band (Gray dash). Additionally, as yellow dash line is observed a confined quantum well level, as new conduction and valence bands.

5.2.1. Bands bending and fitting model

Fig 5.2 c) shows sub-bands as quantum well-confined levels by the visualization of extra energy states of the conduction band, and the valence band shifted downwards, which produces an n-type doping of the material.

The downward shift is caused by the Bi_2Se_3 energy band dispersion with scanning time due to the formation of a two-dimensional electron gas (2DEG) on the surface of the material, as illustrated in Fig 5.3 a). The downward shift bending occurs due to an electron accumulation in the surface, by populating metallic states labeled as 2DEG. The 2DEG transforms quantized in discrete levels and the effect can be observed upon a source photoexcitation in Fig 5.2 c) or as a function of the material depth (Fig 5.3 b). It shows the effect as a band shift, with the yellow dash lines being the quantum well-confined level. The black and gray lines correspond to the final conduction and valence band, respectively. This effect is commonly observed in Bi_2Se_3 ^{129–131} and impairs the analysis of the signal.

a)



b)

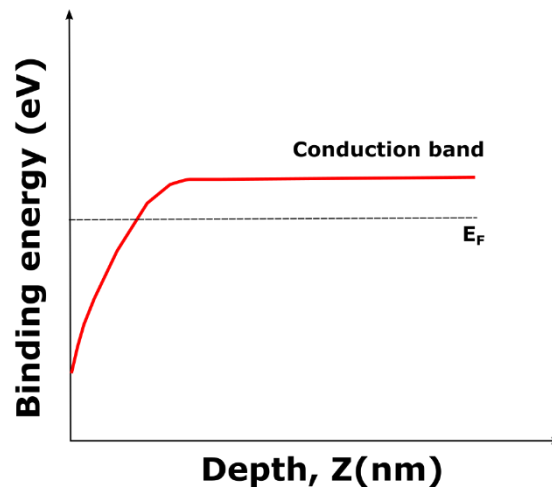


Figure 5.3 a) 2DEG illustration and the respective b) band diagram as a function of the depth of the material.

An alternative scan is used by scanning different spots of the sample and integrating them into a single scan (Fig. 5.4 b), to achieve reliable ARPES data analysis, because the conduction and valence bands are closer to the Fermi level and no sub-bands are visible. This point-integrated signal measurement showed a reduced 2DEG effect contribution. Even though the ARPES becomes more reliable, the signal-to-noise ratio is reduced.

In Fig. 5.4 b) the fitting models are also implemented, where the shift is easier to visualize by comparing the signal to the previous scan (Fig. 5.4 a). The fitting parameters for the reference sample Bi_2Se_3 with both scans (Full scan and point integrated signal) are shown in Table 5.1. Based on the fitting values from Table 5.1, Fig. 5.4 c) presents the simulated signal of the fitting curves as an ARPES data image.

The fitting parameters of both scans are compared. The Fermi velocity from the Bi_2Se_3 surface states are similar, in the range of $3 - 4 \times 10^7$ cm/s, and comparable to the literature^{21,132,133}. The Dirac point position varies from -0.31 to -0.52 eV, by changing the scan mode. As a result, the downward shift is evident, with a 0.21 eV difference. The same effect is visible for the conduction and valence band, where a valence band maximum of -0.67 eV (point scan) and a -0.79 eV (Full scan) is obtained. Likewise, the conduction band minimum

is -0.06 and -0.19 eV for the point scan and the full scan, respectively. There is a shift of approximately 0.13 and 0.12 eV for the conduction band minimum and valence band maximum, respectively.

In terms of the electron and hole effective mass, there is a slight variation, with values varying in the range of 0.11 - 0.31 m_e . Such variation can be associated with the 2DEG which creates an n-type doping and consequently impacts the effective mass. The fitting parameters are in agreement with the literature where the electron effective mass is expected to be around 0.2 m_e ^{21,133} and the Dirac point usually appears at 0.3 eV^{125,126,129,131,132,134}. In conclusion, the point scan presented a more reliable energy band dispersion with a reduced contribution from the 2DEG.

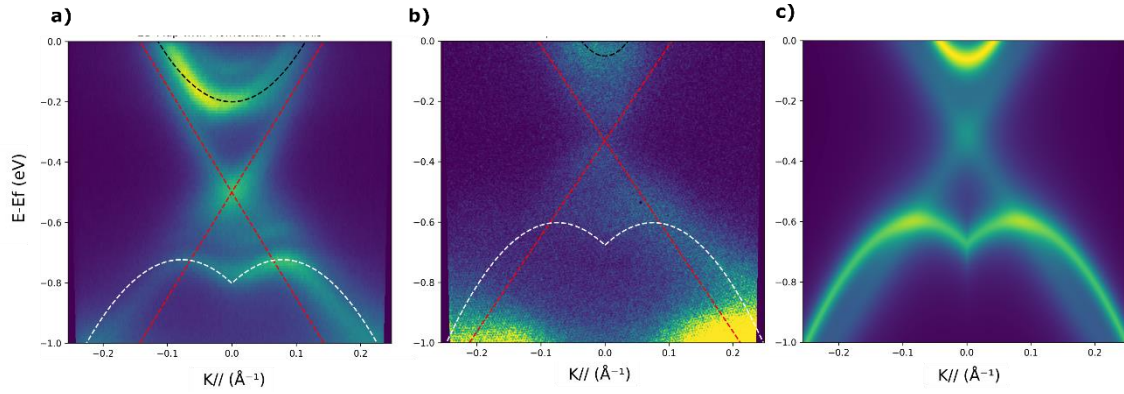


Figure 5.4 Energy dispersion of Bi_2Se_3 with a) long scan mode and b) integrated fast scan in different spots of the sample. The fitting model is applied on both signals where the simulated fitting signal of b) is observed in c).

Table 5.1. Fitting parameters for the Bi_2Se_3 with the 2 different scans, the long scan, and the point integrated scan.

Bi_2Se_3 Sample	V_f ($\times 10^7$ cm/s)	D_p (eV)	m_{ev} (m_e)	m_{ec} (m_e)	E_v (eV)	E_c (eV)
Point scans	3.3 ± 0.2	-0.31 ± 0.05	0.28 ± 0.01	0.11 ± 0.01	-0.67 ± 0.05	-0.06 ± 0.05
Full long scan	4.0 ± 0.1	-0.52 ± 0.05	0.249 ± 0.01	0.31 ± 0.01	-0.792 ± 0.05	-0.191 ± 0.05

5.3. Ga and Cu doped Bi_2Se_3 electronic structure

Core levels are measured for all samples post-Se decapping to determine the material composition (Fig 5.5). This technique is identical to XPS spectroscopy. Unfortunately, the binding energy of the Se peak was not measured due to equipment limitations, which did not allow a precise quantification of each element. The Bi_2Se_3 presents strong Bi $5d$ characteristic peaks for all samples at approximately -25 and -27 eV. Moreover, the Ga signal is detected at -21 eV for the Ga-doped samples, with peak intensity increasing with doping percentage, which confirms the presence and proportionality of the doping element. The Cu-doped Bi_2Se_3 samples do not detect any Cu, because the Cu binding energy is out of the range.

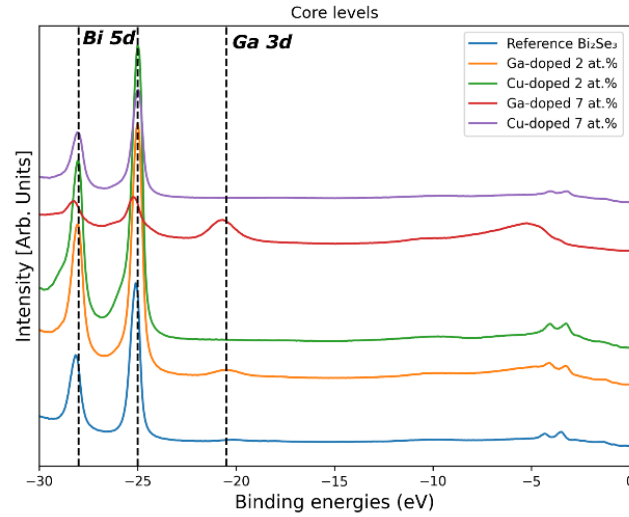


Figure 5.5 Core levels from the Bi_2Se_3 and the Cu/Ga doped Bi_2Se_3 .

In Fig. 5.6, the Ga-doped and Cu-doped Bi_2Se_3 (2 and 7 at.%) energy dispersions are shown. The Ga and Cu doping presented different tendencies of the band structure, corroborating the findings presented in Chapter 4. For a Ga doping of 2 at.% (Fig. 5.6 a), the surface states are not destroyed. The spectrum confirms the existence of surface states crossing the band gap as projected from the Ga-doped Bi_2Se_3 study section 4.3.2 (Fig 4.10). On the other hand, the WAL signal prefactor (α) of -2.5 obtained could suggest the creation of additional surface states (trivial or non-trivial), however, the direct visualization of the band structure rejected this possibility since those states are not observed.

As the Ga concentration is increased to 7 at.% (Fig. 5.6 b) the band dispersion becomes less distinguishable due to the poor crystallinity of the material. The doping with 7 at.% leads to a higher concentration of defects in the material surface that prohibit signal acquisition. The band structure of the Ga-doped Bi_2Se_3 (7at.%) indicates possible

destruction of the surface states, as a consequence of the higher defect concentration. This is in agreement with our previous assumption that the material undergoes a topological phase transition manifested by the lack of the cusp in the WAL effect (Fig 4.10). This destruction of the surface states was also observed for the doping of In with higher percentages than 7 at.%⁶⁶ because In atoms were reducing the spin-orbit coupling and consequently the band inversion was not present in the material.

In the case of Cu doping Bi_2Se_3 (Fig. 5.6 c and d), the surface states are preserved upon the highest concentration of Cu (7 at.%) without deterioration of the signal intensity. The persistence of the surface states even with higher concentrations of Cu is in agreement with the literature^{116,117,136}. The band dispersion quality indicates that the Cu-doped Bi_2Se_3 maintains the single-crystal nature with a low concentration of defects.

In terms of the doping effect, Cu introduction was shown to cause an upward shift of the bands. The conduction band, valence band, and Dirac point move to higher energies by increasing the percentage of Cu, meaning that it moves closer to the Fermi level. This effect is possibly caused by the substitution of Cu atoms with Bi atoms in the crystal lattice, which leads to a reduction of the electron concentration^{95,137,138}. The doping by Cu can improve the topological properties of the topological insulator Bi_2Se_3 by tuning the Fermi level into the band gap as stated in previous reports of Cu-doped Bi_2Se_3 ¹²⁴ and Pb/Sb-doped Bi_2Se_3 ⁸⁸. The high single-crystal quality growth by MBE seems to lead to a substitution of Cu atoms, which can be the cause of the impossibility of achieving the TSC of Cu-doped Bi_2Se_3 .

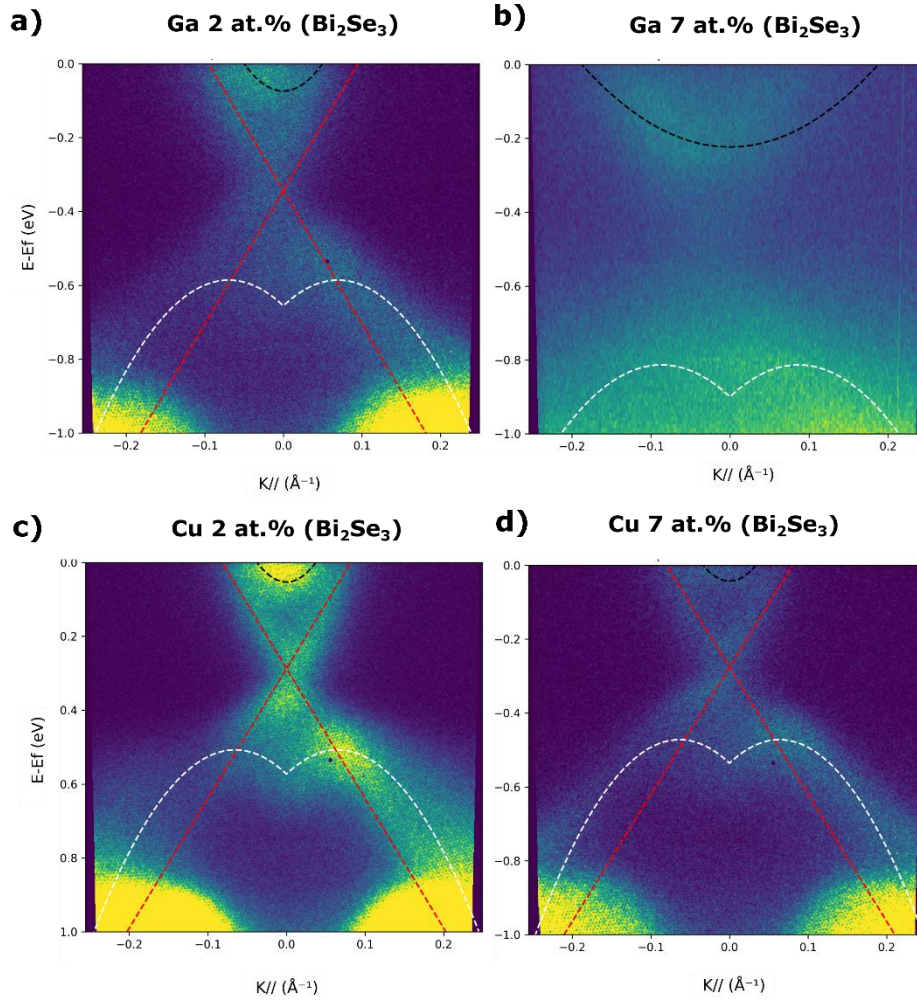


Figure 5.6 Energy dispersion by the point scan of a) 2 at.% Ga-doped Bi_2Se_3 , b) 7 at.% Ga-doped Bi_2Se_3 , c) 2 at.% Cu-doped Bi_2Se_3 and d) 7 at.% Cu-doped Bi_2Se_3 with the fitting model as dashed lines. Black dashed line corresponds the conduction band, red dashed lines to the Dirac surface states and the gray dashed line to the valence band.

The fitting parameters, from the fitting model shown in Fig 5.6, of all the samples are presented in Fig 5.7, Fig 5.8, and Fig 5.9, as a function of the doping. The fitting model is performed for the point-integrated scan where less influence of the 2DEG is found.

The conduction and valence band positions are altered by the introduction of Ga (Fig 5.7 a). The conduction band is moving downwards further from the Fermi level, thus the Fermi level is moving into the conduction band confirming the observation above (Fig 4.8), meaning that the electron concentration is increased. As a consequence, the Dirac point position and the valence band maximum appear to change according to the conduction band. A similar shift in doped Bi_2Se_3 was also observed previously with Co, Mn, Eu^{121} , and Fe^{134} , and in the superconductivity candidates Sr^{77} , and Ag^{21} .

Oppositely, Cu doping (Fig 5.7 b) leads to a conduction band minimum and valence band maximum moving closer to the Fermi level as Cu doping is increased. However, the shift is within the experimental error, which cannot confirm the shift in the conduction band. The shift is more noticeable in the valence band than in the conduction band. Likewise, the Dirac

point also moves towards the Fermi level, which affects positively the transport properties with reduced transport contributions from the bulk conduction band and increased surface states transport. This effect is also stated in the literature^{95,124,137,138} when substitution by Cu atoms occurs.

The conduction and valence electron masses (Fig 5.8) have changed significantly by introducing the doping element. The Ga doping leads to an increase in the hole mass and electron mass. In the case of the conduction electron mass, it changes from approximately 0.11 to almost 0.25 m_e , and the valence electron mass changes from 0.27 m_e up to almost 0.35 m_e . Conversely, the masses in the Cu-doped Bi_2Se_3 decrease by doping with the lower percentage of Cu (2 at.%), and it stays constant up to 7 at.% of Cu. These changes are affected by two factors: the change in the chemical composition and the consequence of changing the crystal lattice parameter. The higher effective electron mass was accompanied by an increase in the crystal lattice parameter (Ga doping), whereas the decrease in the lattice parameter corresponded to the decrease in the effective electron masses (Cu doping). Moreover, the evolution of the effective mass is consistent with the carrier concentration¹³⁹.

The surface states Fermi velocity (Fig 5.9) does not change significantly upon any type of doping, varying between $3.2 - 3.6 \times 10^7$ cm/s. A slight increase is observed for both dopants with 2 at.%, even though the value is within the experimental error. There is the exception of the Ga 7 at.% sample, which does not display a Fermi velocity due to the “non-existence” of the surface states.

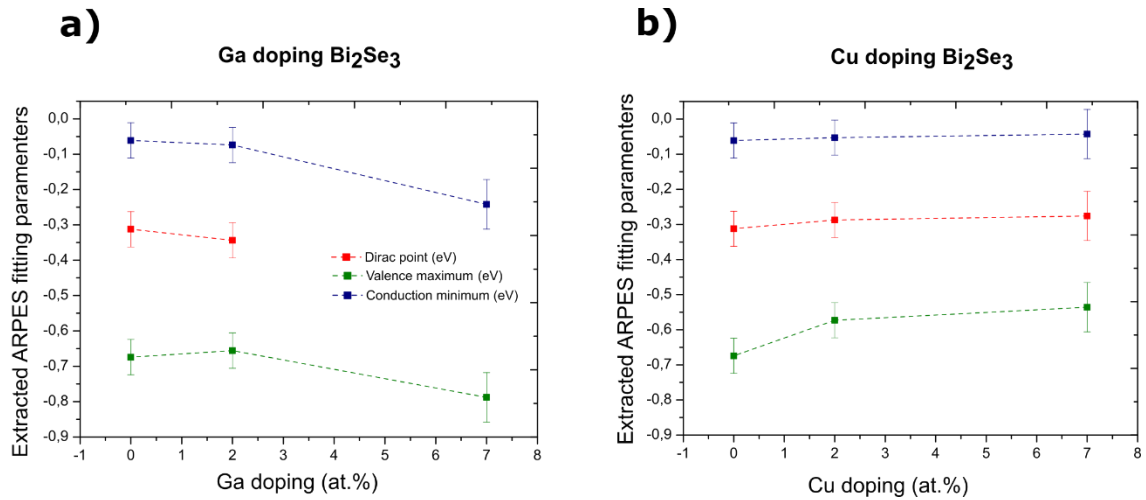


Figure 5.7 Evolution of the conduction band minimum, valence band maximum, and Dirac point of the surface states as a function of a) Ga and b) Cu doping.

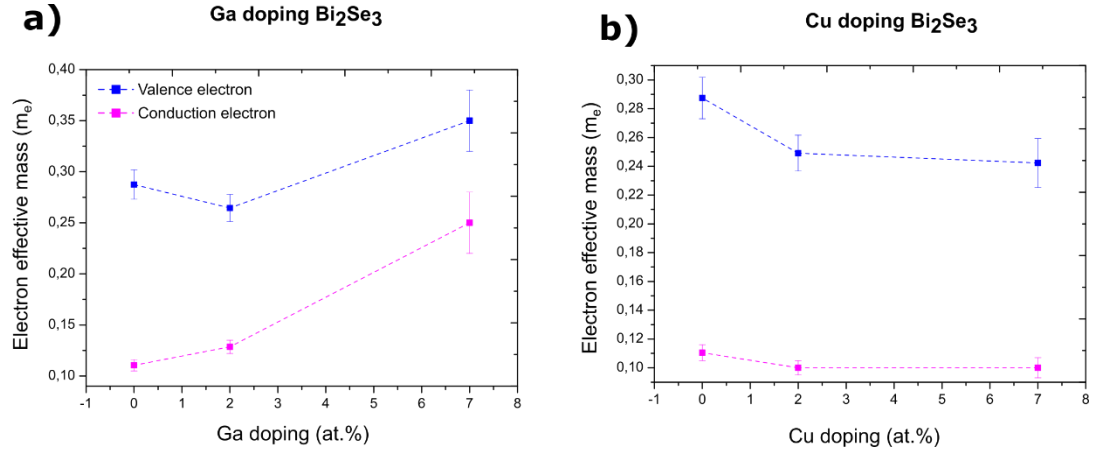


Figure 5.8 Evolution of the conduction and valence electron effective masses as a function of a) Ga and b) Cu doping.

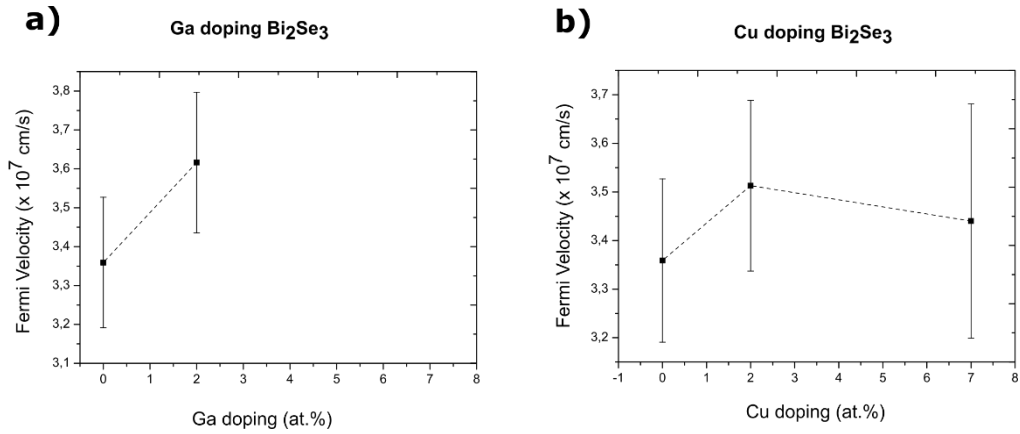


Figure 5.9 Evolution of the Fermi velocity of the surface states as a function of a) Ga and b) Cu doping.

The Bi_2Se_3 and doped Bi_2Se_3 Fermi maps are shown in Fig 5.10. Heretofore, the ARPES band spectrum has been shown in the parallel momentum space ($K_{//}$) with the contribution of K_x and K_y , while the Fermi map is a 3D energy distribution of the electron energy states across different momentum directions (K_x , K_y). The signal is shown for different energy slices 0, -200, -300, -400, -500, and -800 meV related to the Fermi level to have a 2D visualization of the energy distribution as a function of k_x and k_y . However, the Fermi map is measured for a prolonged period, which produces the 2DEG and consequently, the band shift. This full scan produces better signal-to-noise and improves the analysis of the Fermi map.

Overall, the 3D Fermi map is similar for all the samples with minimal differences, similar to the previously observed ARPES data. At the Fermi level, far from the Dirac point, it is observed the conduction band and the Dirac cone contours. The effective Dirac Hamiltonian presents a rotational symmetry in x and y , which should expect a circular Fermi surface for the surface states¹²⁹. However, the Fermi map contours show a hexagonal shape, as a consequence of the hexagonal warping from the 2DEG^{129,121}.

As we move closer to the Dirac point, this previous wrapping effect is less pronounced and the circular shape from the surface states is more noticeable. As a consequence of the full scan, the Dirac point visualization is observed approximately at -500 meV, which explains the difference in the Dirac point position from the previous fitted values. Finally, the Bi_2Se_3 valence band is observed at lower energies (-800 meV). Unfortunately, as explained before, the poor material quality of the Ga-doped Bi_2Se_3 (7 at.%) implies the difficulty in measuring the surface map. As a consequence, the topological phase transition assumption is not possible to confirm due to the non-observed trivial band gap in the Fermi map.

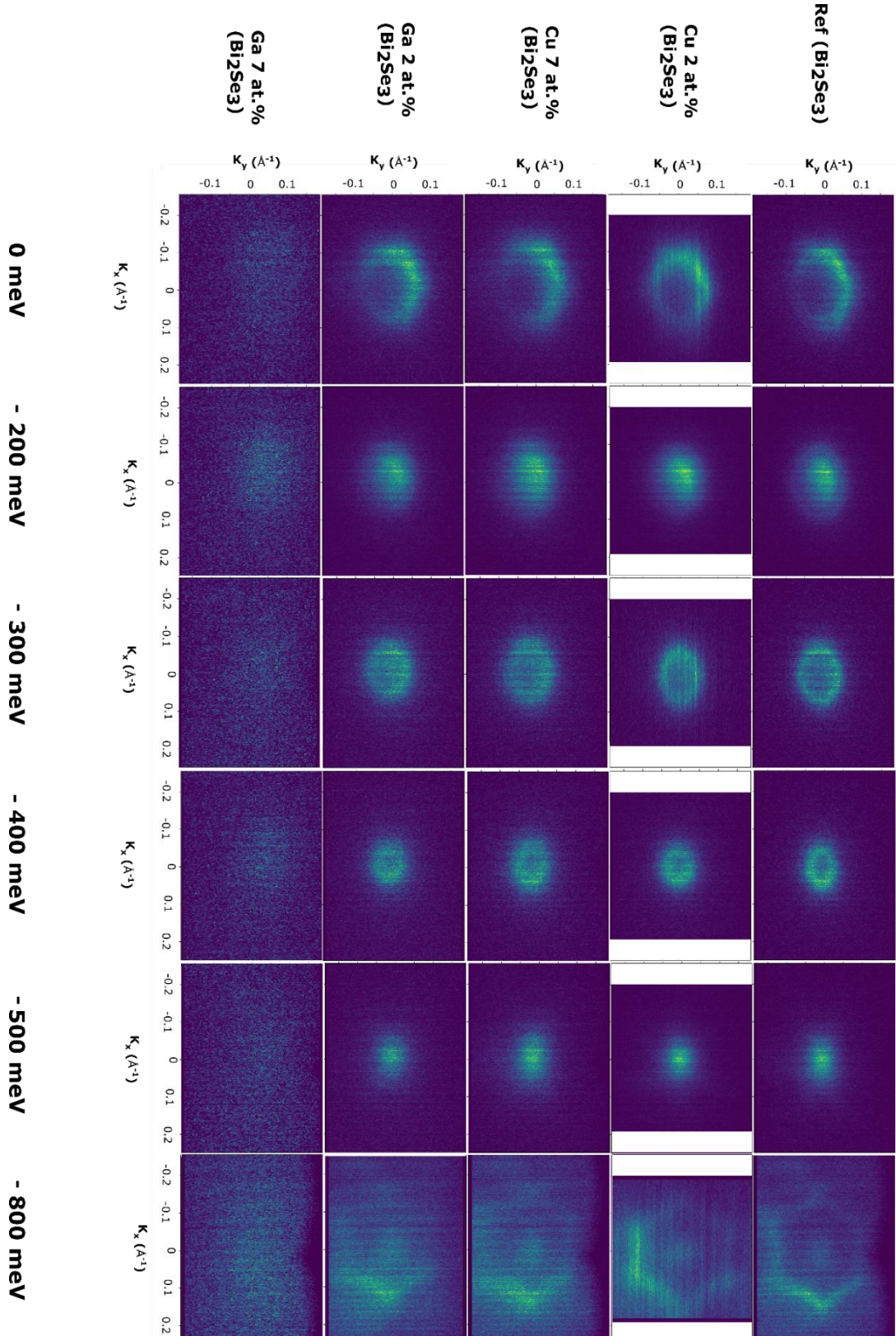


Figure 5.10 Fermi map for the reference Bi_2Se_3 , Ga-doped Bi_2Se_3 and Cu-doped Bi_2Se_3 at energies from the Fermi level (0, -200, -300, -400, -500, -800 meV). The signal is obtained by a long scan to improve the signal-to-noise ratio.

Lastly, as shown in section 2.2.6, Eq. (2.21), the surface charge carrier density (n_s) can be extracted and estimated from the ARPES. In Fig 5.11, the estimated surface carrier density is shown as a function of the Ga and Cu doping.

The concentration for the undoped Bi_2Se_3 is approximately $7 \times 10^{12} \text{ cm}^{-2}$, which is one order of magnitude smaller than that previously obtained in section 4.3.1 of $7 \times 10^{13} \text{ cm}^{-2}$ by Hall effect measurements. This difference demonstrates that the n_{2d} calculated from the Hall measurements presents contributions from the bulk and not only from the surface states. As the doping is increased, the surface electron concentration changes. Ga doping leads to a slight increase up to $\sim 1.3 \times 10^{13} \text{ cm}^{-2}$, for the highest percentage of 7 at.%, which is double the electron concentration of undoped Bi_2Se_3 . The increase in the charge carrier concentration was also observed in Ag- Bi_2Se_3 ²¹. The transport properties extracted from the Hall effect for the Ga doping concluded that there was a six-fold increase, meaning that the electron concentration was mainly increasing the bulk concentration.

In terms of Cu doping, the effect is the opposite, with the electron concentration decreasing slightly up to $\sim 5 \times 10^{12} \text{ cm}^{-2}$, which is in agreement with the previously observed in the hall effect measurements (section 4.3.1).

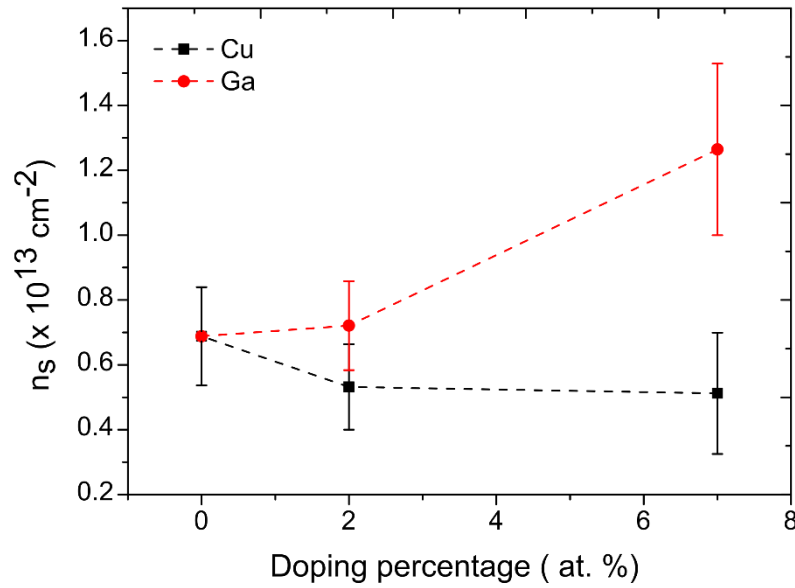


Figure 5.11 Surface charge carrier density of Bi_2Se_3 extracted from ARPES as a function of doping of Cu or Ga.

5.4. Summary

In conclusion, ARPES was conducted on the topological insulator Bi_2Se_3 , including Ga and Cu-doped Bi_2Se_3 , to explore their electronic structures. The experimental procedures involved accurate sample preparation, and annealing, such as systematic annealing experiments to optimize the Se decapping process to enable the ARPES measurements.

The energy spectrum scan of the reference Bi_2Se_3 sample revealed surface states, and subsequent measurements on doped samples demonstrated varied effects. Long scans led to a downward band shift due to the emergence of a 2DEG on the surface, which is reduced by the integration of the measurement at different points on the sample. Cu doping preserved the surface states with an upward Fermi level shift, indicative of improved topological properties by the reduced carrier concentration. Conversely, Ga doping at higher concentrations leads to poor crystallinity and degradation of the signal, suggesting a topological phase transition. The fitting parameters showed an independent variation of the surface states Fermi velocity and electron effective masses. Overall, these findings reinforce our hypothesis that the surface states are destroyed upon concentrations of 7 at.% of Ga. The Cu doping exhibits a systematic topological transport improvement by the Fermi level tuning into the band gap and closer to the Dirac point.

Chapter 6

6. Wafer-scale Bi₂Se₃ top gate field effect devices

A major problem faced in the field of topological insulators is that the bulk is not fully insulating. The use of these materials for applications requires only a residual bulk conductivity. As previously discussed, and concluded in Chapter 3, the use of an IS-BIS buffer layer studied by Koirala et al. improved the transport properties of the topological insulator Bi₂Se₃. Despite the reduction of the electron concentration and increase in mobility, the exploitation of its topological properties at room temperature is still unsuitable. The Mott criteria assign a critical density of carriers for an insulator to become a metal. In the case of the TI Bi₂Se₃, the critical carrier density is relatively low at $n_{3d} = 10^{14}$ - 10^{15} cm⁻³⁷¹ which is orders of magnitude smaller than the previously obtained 10^{18} cm⁻³. Furthermore, air exposure results in the diffusion of oxygen which leads to further n-type doping of the material^{140,141}, and consequently raises the bulk transport contribution.

Another approach to reduce the carrier concentration is by tuning the Fermi level into the band gap by the application of an electrostatic gate¹⁴². This chapter describes the development of a top gate device fabrication process for epitaxial TI Bi₂Se₃ aiming for the reduction of carrier concentration and to reduce bulk contribution for transport.

6.1. Heterostructure growth and field effect transistor fabrication methods

The starting point is the conclusions obtained in section 3.4, where a highly ordered and good interface Bi₂Se₃ topological insulator with improved transport properties is obtained by the prior deposition of an IS-BIS buffer layer. Furthermore, aiming for the fabrication of quantum devices, it is important to protect the surfaces of TI to prevent the deterioration of the surface states. Kong et al. and Edmonds et al.^{140,141} concluded that Bi₂Se₃ exposure to air results in the formation of defects, such as Se vacancies, and it can increase the bulk charge carrier by oxygen diffusion. Thus, the topological states transport properties are suppressed by the bulk contributions.

MBE presents the opportunity to deposit an *in-situ* capping layer after the TI deposition avoiding the detrimental effect of air exposure. There are two possible solutions for the capping layer. Studies demonstrated that amorphous Se is a semiconducting layer with minimal transport contributions and prevents surface oxidation⁴³. The Se layer can be easily

removed by annealing the Bi₂Se₃ at higher temperatures, as discussed previously in section 5.1.1. However, annealing can be harmful to the Bi₂Se₃ layer by the formation of Se vacancies, because Se has high volatility.

The second option, for the capping layer is β -In₂Se₃. It is a semiconductor with a band gap of 1.4 eV¹⁸, thus, in its intrinsic form, it should not contribute to the transport properties. Furthermore, it has good chemical and structural compatibility, which should lead to a highly ordered interface without damaging the TI surface. Thus, a 40 nm β -In₂Se₃ is tested for the first time as a capping layer, and it is studied the feasibility of it for the fabrication of FET devices.

The heterostructure for the fabrication of the FET devices consisted of a 40 nm *IS-BIS* buffer layer, a 12 nm Bi₂Se₃ layer as the FET channel, and finally, the β -In₂Se₃ capping layer, as illustrated in Fig 6.1 a). A complete heterostructure fabricated on a sapphire substrate wafer is observed in Fig 6.1 b), by a blueish color due to optical interference.

The heterostructure crystallography is analyzed by XRD (Fig 6.1 c and d). The reduced thickness of the Bi₂Se₃, compared to the previous section 3.4, reduces the diffraction peak intensity enabling the detection of the In₂Se₃ peaks. Both layers present a rhombohedral crystal structure with a diffraction family {00L} but with different crystal lattice parameters. Fig 6.1 d) shows a high-resolution scan of the (0015) plane of both materials where it is possible to distinguish both peaks.

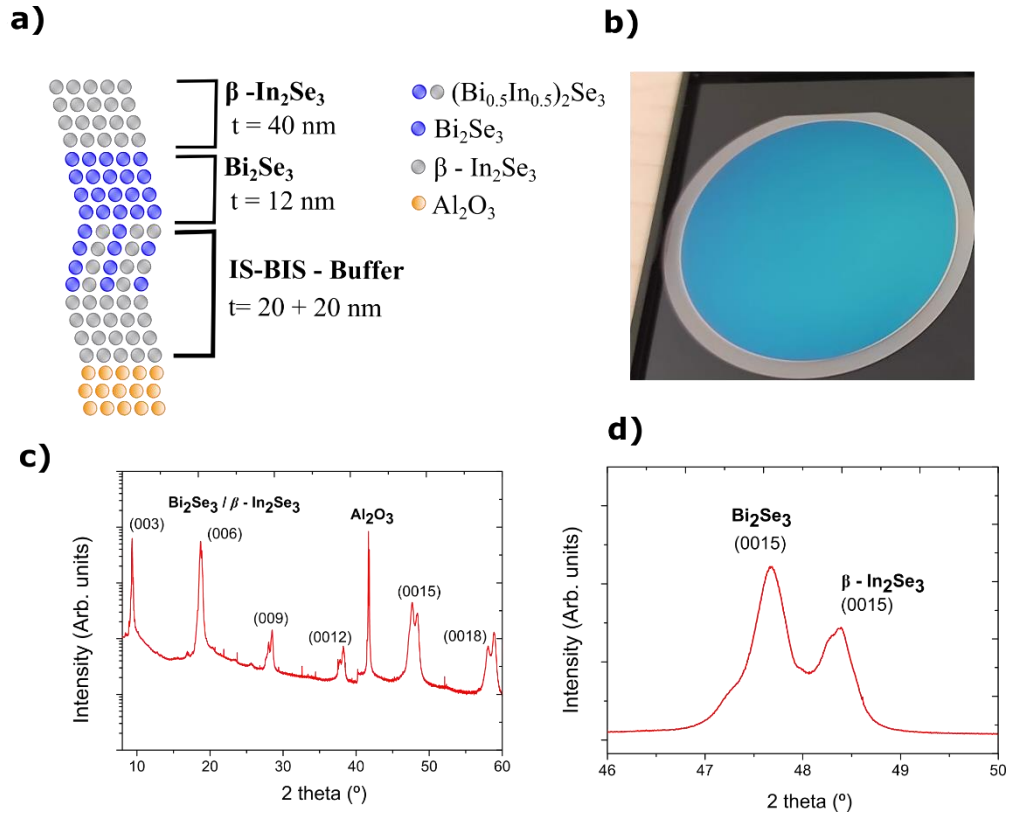


Figure 6.1 a) Devices heterostructure composed by an IS-BIS buffer layer deposition, a 12 nm thick Bi₂Se₃ and a 40 nm thick In₂Se₃ capping layer. b) Photograph of a sapphire wafer with the deposited heterostructure. c) XRD spectrum of the device heterostructure on a sapphire substrate. d) High-resolution XRD for the (0015) diffraction peak.

The capping layer is later removed to provide metallic contact with the Bi₂Se₃. Contrary to the Se capping layer, the β -In₂Se₃ capping layer cannot be removed by increasing the temperature. Diverse etching methods can be used to etch β -In₂Se₃, such as physical etching or wet chemical etching. However, since the thickness of 2D materials does not allow the use of physical etching in a precise condition, meaning that it is extremely difficult to selectively etch the β -In₂Se₃ layer without damaging the Bi₂Se₃. By contrast, wet etching is suitable to remove layers selectively by the use of specific chemicals.

A wet chemical process to etch β -In₂Se₃ was previously developed in the group¹⁸. However, the etching process effect on Bi₂Se₃ was unknown. The etching process uses a diluted solution of 0.5% HCl with 30% H₂O₂ with a proportion of 4:50. The H₂O₂ acts as an In₂Se₃ layer oxidation process while the HCl solution acts in the oxide layer by dissolving it in a liquid form. The etching process is quite fast, within a few minutes to etch 40 nm, and it can be visually monitored by the removal of the In₂Se₃ layer on an additional control In₂Se₃ sample.

The following experiment demonstrates the selectivity of the etching solution. The experiment consisted of two samples, 40 nm β -In₂Se₃ and a 10 nm Bi₂Se₃ being immersed in the etching solution of 0.5% HCl with 30% H₂O₂ (Fig. 6.2 a) for about 30 min. Fig 6.2 b) shows the thinner β -In₂Se₃ and Bi₂Se₃ samples at the end of the etching process. The β -In₂Se₃ is almost completely removed with a few residual layers in some areas of the wafer, whereas the Bi₂Se₃ layer showed to withstand the chemical solution after a 30 min etching process even presenting a reduced thickness when compared to the β -In₂Se₃ layer.

In conclusion, a selective chemical etching is developed to only remove the capping layer without damaging the TI layer. It is important to note that the Bi₂Se₃ layer is only affected by the chemical for a few seconds, due to the over-etching performed to confirm the complete capping layer removal. Furthermore, a recent study presented a TI surface cleaning with diluted HCl to improve the surface¹⁴³ without destroying the surface states.

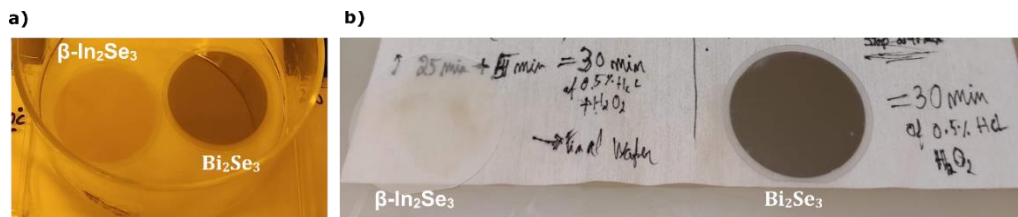


Figure 6.2 In₂Se₃ and Bi₂Se₃ samples a) in a 0.5% HCl + 30% H₂O₂ etching solution (4:50), and b) wafer removed from the etching solution after 30 min.

With an optimized heterostructure deposited, we proceed with the fabrication of the FET device with a top gate. The geometry used for the device is a six-terminal Hall-bar geometry as commonly used in the literature^{43,133,144}. The FET fabrication procedure is explained in detail in section 2.3 and a visual inspection is shown in Fig. 6.3. The fabrication starts with the patterning into a micron-scale Hall bar structure by a physical etching. A 100 nm Al₂O₃ dielectric is deposited by sputtering in order to protect the whole structure from air exposure and to act as the dielectric material in the FET device. The gate dielectric has shown a high dielectric coefficient and is efficient for the fabrication of Bi₂Se₃^{133,143,145–147}. The Al₂O₃ is removed from the contact areas (Fig. 6.3 e) to allow the ohmic contact with the Bi₂Se₃ layer. The etching process discussed previously is successful in removing the capping layer and not affecting the Bi₂Se₃ layer (Fig. 6.3 f). The sample is rapidly transferred to the sputtering system to avoid Bi₂Se₃ oxidation. A 15 nm metal layer (Cr/Au) is deposited as a preliminary contact just to protect the Bi₂Se₃ from air exposure. Gold was shown to be a compatible element to form the ohmic contact without destroying the surface states¹⁴⁸. The top gate FET devices are finalized by the metal deposition with a total thickness of 50 nm, as exhibited in Fig. 6.3 h). The final wafer is observed in Fig. 6.3 i) with 36 FET devices with different dimensions.

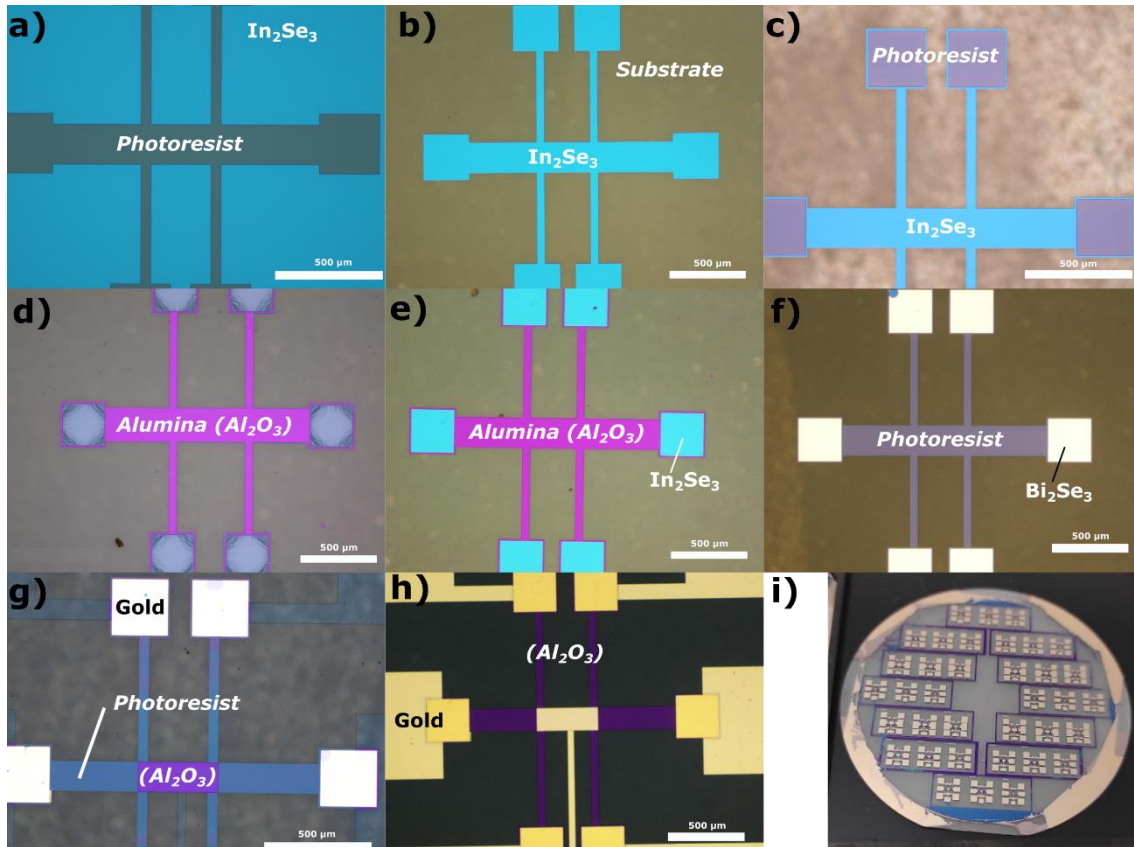


Figure 6.3 Microscope image of the individual steps of the FET device cleanroom fabrication. a) Hall-bar patterning lithography, b) physical etching by ion milling, c) lithography of the metallic contacts, d) dielectric deposition by PVD, e) contact exposure by lift-off, f) chemical etching of the capping layer, g) Gold deposition on the contact area with the lithography for the h) metallic contacts and metallic gate on top of the channel. i) Wafer visualization of the 36 FET devices. The distinct colors are due to the optical interference of the layers.

A cross-section of the Bi₂Se₃ FET device is illustrated in Fig 6.4 a). The Bi₂Se₃ thickness is reduced to 12 nm compared to the previous chapters (40-60 nm) since the bulk transport domination can be reduced by reducing the layer thickness^{107,142,145,149}. The increased surface/bulk ratio suppresses the bulk contribution and highlights the surface state transport.

The following sections describe the electrical measurements of one device as shown in Fig 6.4 b). The measurement of the remaining devices was not performed due to the lack of encouraging results to invest the time of our collaborators in Salamanca. A device from the middle of the substrate is expected to present more uniform layers. The dimensions of this Hall-bar structure are 300/150 μm (L/W), which means that the channel width is 150 μm and the two terminals in the middle have a 300 μm distance from each other, this dimensions are similar to the ones reported in the literature^{150,151}. The electrical measurements are performed at low temperatures (1.5 K) with an indium wire bonding as shown in Fig 6.4 b).

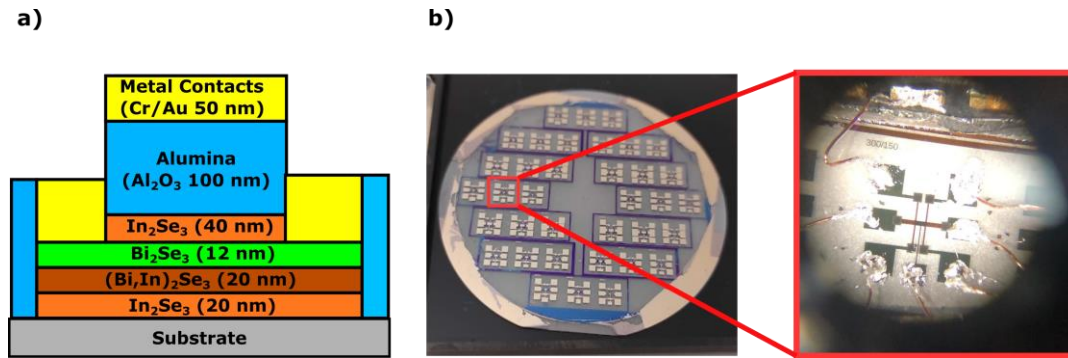


Figure 6.4 Cross-sectional illustration of the Bi₂Se₃ FET devices. b) Full wafer with 36 FET devices and magnification of a 300/150 μm device with the wire bonding configuration, as used for the electrical measurements at low temperatures.

6.2. Field effect transistor electrical measurements

6.2.1. Gate voltage dependence of channel resistance

An operational FET device presents a functional gate without short circuits between the gate contact and the Bi₂Se₃ channel (gate-source I-V curve). The dielectric gate behaves as an insulator, meaning that it should not conduct electricity. Therefore, the application of an electric field should produce a negligible leak current flowing to the channel. However, the application of high electric field or voltages leads to an increase in the oxide layer conductivity, and consequently a dielectric breakdown. This phenomenon can result in permanent damage to the dielectric material and to the functional FET. This gate behavior can be characterized by the Schottky-Frenkel (Eq. 6.1):

$$J = AE^2 e^{\left(\frac{B}{E}\right)} \quad (6.1)$$

Where J is the current density, E is the applied electric field and A and B are constants related to the system geometry and dielectric properties. The gate leak current is negligible until a breakdown voltage where the current starts to increase exponentially like with voltage.

The gate-source I-V was performed at room temperature (RT) in air with different sweeps from 2 - 15 V. It starts with a sweep from -2 V up to 2 V and carefully measures the current flowing along the gate dielectric. The sweep voltage is increased carefully to detect the breakdown voltage, meaning, the maximum voltage that the gate dielectric can withstand without breaking it.

Fig. 6.5 a) shows the gate-source I-V curves for different voltage sweeps. These measurements were performed in a sacrificial device, in order to detect the breakdown voltage, since after reaching the breakdown voltage the device is not operational anymore. As is observed for all curves, an exponential like behavior is successfully achieved confirming the insulating gate behavior. The leak current contribution to the channel current can be disregarded because it is smaller than 10^{-10} A and the channel currents are higher than 10^{-6} A. For a sweep range of 15 V, the leak current starts to increase exponentially between 10 - 12 V, implying that the breakdown voltage is approximately 10 V. The inset image of Fig. 6.5 a) shows the I-V curves with a logarithmic scale to compare with more detail the evolution of the current. The leak current is approximately 1×10^{-12} A and starts increasing up to 1×10^{-11} A as the number of sweeps is increased. Thus, the gate leak current is not stable, and it changes the contribution of the channel with the time of use, due to the defective amorphous insulating layer.

The Bi₂Se₃ channel between the source and drain is also tested to confirm the ohmic contact between the metal contact and the topological insulator (Fig. 6.5 b). An RT linear response is obtained for the channel I-V curve. The gate I-V curve is shown in the same graph to confirm that the leak current does not have short circuits. Thus, the field effect transistor should be functional to modulate the Fermi level position of the Bi₂Se₃ channel by the application of different gate voltages.

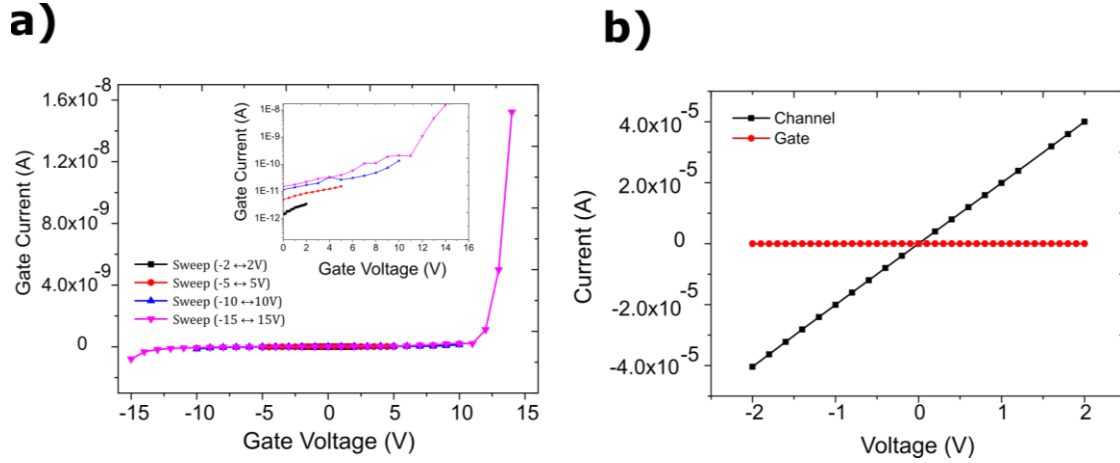


Figure 6.5 a) Gate I-V curves for different sweep voltages. The measurements start with smaller voltage and increase slowly to higher voltage sweeps. b) Bi₂Se₃ channel I-V curve with the gate I-V curve observing a minimal leakage current. The measurements are performed at RT.

The gate voltage is applied to understand the effect that the Fermi level variation has on the Bi₂Se₃ channel. Unfortunately, at RT, residual conductivity is activated thermally creating excited carriers from impurity bands¹⁵², and consequently masking the topological surface states. To reduce the thermal effect in the topological insulator, the electrical measurements were performed at lower temperatures. These measurements were performed in the device shown in Fig 6.4 b), after confirming the insulating behavior of the dielectric layer.

The channel R_{xx} at different temperatures as a function of the gate voltage is shown in Fig 6.6 a). The gate voltage ranges from -5 V to 5 V to avoid gate breakdown. In the temperature range of 200 K - 120 K, the channel resistance is unchanged with voltage, due to the Fermi level lying deep in the conduction band. At a temperature of 90 K (light blue curve), an electrical transition occurs, since the channel resistance starts to be affected by the negative gate voltage. Channel resistivity increases for gate voltages lower than -2 V, which means that the Fermi level is approaching the conduction band minimum. The resistance modulation becomes more pronounced as the temperature is decreased. For temperatures lower than 20 K, the channel resistance can be changed between 12 k Ω to approximately 8 k Ω , a 30% difference, by applying a gate voltage of -5V and 5V, respectively.

At lower temperatures, the gate presents a larger effect on the channel resistance. A full gate sweep from -10 to 10 V is performed at approximately 1.5 K (Fig 6.6 b). The gate after reaching a voltage higher than 10 V showed a large leak current of almost 10^{-9} A. A semi-ambipolar effect is observed for the Bi₂Se₃ resistance as a function of the gate voltage. The resistance is slowly increasing with the application of negative voltages. A sharp increase starts for voltage lower than -5 V, meaning that the Fermi level is approaching the conduction band minimum^{133,153} and the band gap, close to the central neutrality point as observed in the literature by a peak maximum in the resistance^{142,143,146,147}. However, in our FET device, the ambipolar behavior is not achieved due to the limitation of the maximum gate voltage of -10 V. Nevertheless, a resistance modulation of approximately 55% is achieved with a negative voltage of -10 V. Furthermore, the resistance slowly decreases by

applying positive voltages, because the application of a positive gate voltage leads to the n-type doping of the topological insulator and consequently a more metallic film. Additionally, a Bi₂Se₃ resistance curve is shown as a function of the gate voltage, but with the presence of the magnetic field of 2 T. The magnetic field shows a shift in the channel resistance to higher resistances as expected from the WAL effect.

In conclusion, the enhancement of the channel resistance with gating suggests that the Fermi level tuning is successfully achieved in the FET device.

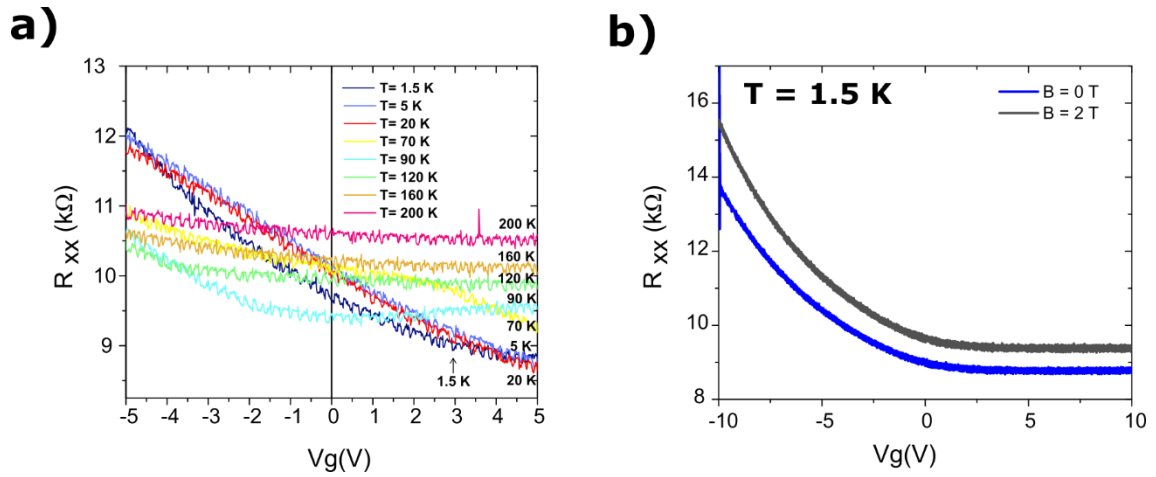


Figure 6.6 Bi₂Se₃ channel resistance as a function of the gate voltage for a) temperatures from 200 K to 1.5 K and b) different magnetic fields of 0 and 2 T at 1.5 K.

6.2.2. Gate Dependence of Weak Antilocalization

WAL is observed in the FET device at 1.5 K as a function of the magnetic field (Fig 6.7) for two different gate voltages of 0 V and -6 V. A clear sharp cusp of the magnetoconductance is visible at both voltages which confirms the existence of the WAL, which indicates the potential existence of surface states in the TI.

Surprisingly, the WAL behavior is identical for both gate voltages even though a large channel resistance is observed at a gate voltage (V_g) of -6 V. The bulk contribution is minimized as the channel becomes more insulating, which should lead to a more pronounced cusp and ideally decoupled surface states from both surfaces (top and bottom). A small deviation in the magnetoconductance is observed at higher magnetic fields than 2T which comes from the contribution of the magnetic field background.

The Bi₂Se₃ WAL effect for both gate voltages is fitted with the HLN model (Eq. 1.4) with the fitting parameters shown in Table 6.1. An α close to -0.1 at $V_g = 0$ V and $V_g = -6$ V is obtained, meaning that the gate voltage does not have a clear influence on the prefactor, as observed in ^{37,149}. At the same time, the prefactor is smaller than the expected -0.5 from coupled surface states, as observed previously for thicker films (section 4.3.2). The reduced

prefactor values can be attributed to the small thickness of the Bi₂Se₃ layer. The prefactor was also observed to decrease as the thickness was decreasing in TIs^{109,154,155}. It was also observed after the maintenance of the MBE system (March 2024) that the In shutter was uncalibrated (partially open when it should be closed) and consequently, could present a small percentage of In in the Bi₂Se₃ layer, which might lead to a weaker WAL.

On the other hand, the coherence length seems to be improved as the negative voltage is applied, from 582 nm to 657 nm. However, a large experimental error might imply that the observed value is statistically consistent with no significant change. The bulk carriers have a reduced contribution to the overall 2D conductivity of the system and, therefore an improved coherence length¹³³. Moreover, the negative voltages reduce the bulk conduction channels by the gate modulation which reduces the surface to bulk scattering.

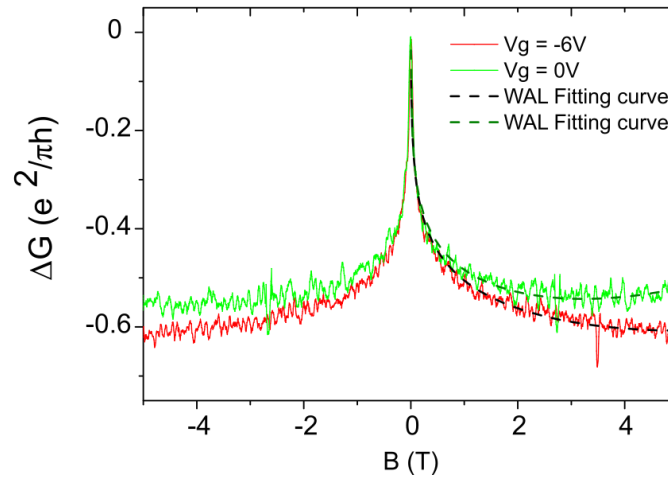


Figure 6.7 Gate dependence of the WAL in the Bi₂Se₃ device for the gate voltage of 0 and -6 V as a function of the magnetic field. The fitting is shown as dashed lines for each gate voltage.

Table 6.1 Estimated WAL fitting values from the Bi₂Se₃ device at 1.5 K for different gate voltages of 0 and -6 V.

Gate (V)	Prefactor (α)	Coherence length (nm)	β
0	-0.08 ± 0.02	582 ± 353	0.004 ± 0.002
-6	-0.09 ± 0.02	657 ± 432	0.002 ± 0.002

6.2.3. Bi₂Se₃ transport properties modulation with gate voltage

Finally, the Bi₂Se₃ transport properties are extracted for the different gate voltages. This characterization of the material is a direct method to prove the effectiveness of the gate effect. The gate dependence of the Hall carrier density (n) is obtained from $n = \frac{1}{R_H e}$, where R_H is the Hall slope. The Hall resistance (R_{xy}) is shown in Fig 6.8 a) for different gate voltages from -10 up to 10 V. R_{xy} shows a linear behavior with the magnetic field as expected, where the Hall slope is extracted to estimate the carrier concentration.

The extracted values, electron density, and mobility are shown in Fig 6.8 b) as a function of the gate voltage. The carrier density is reduced as the gate voltage decreases to negative voltages, which is indicative of a n-type material. Even though the In₂Se₃ capping layer is introduced to prevent oxygen diffusion and at the same time, protect the Bi₂Se₃ layer, the n-type degeneracy can be worsened from unintentional environmental contaminations¹⁵⁶ and by the fabrication process through the chemical reaction between the Bi₂Se₃ and the solvents. At V_g of 0 V, an electron concentration of approximately $6 \times 10^{12} \text{ cm}^{-2}$ is obtained, comparable to the previously observed Bi₂Se₃ with the same buffer layer at RT (section 3.4.2). There is a slight difference from $6 \times 10^{12} \text{ cm}^{-2}$ (1.5 K) to $1.6 \times 10^{13} \text{ cm}^{-2}$ (RT), which is attributed to the temperature since the Bi₂Se₃ electron concentration tends to increase with temperature. The Bi₂Se₃ FET obtained mobility of almost $550 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. The reduced mobility, compared to the previous Bi₂Se₃ on an IS-BIS buffer layer (section 3.4.2: $600 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$) could be associated with the reduced thickness reinforcing the significant effect of the thickness present on the mobility⁴⁰.

In terms of the transport properties modulation with the gate voltage, the electron concentration is reduced from $6 \times 10^{12} \text{ cm}^{-2}$ to $4 \times 10^{12} \text{ cm}^{-2}$ by sweeping the V_g to -10 V, this effect is similarly observed in^{43,133}. Likewise, the mobility is improved from 550 to $750 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ with a V_g of -10 V. The electron concentration decreasing with the gate voltage is also an indication of an n-type material as stated in the literature^{133,150}. The transport properties have a linear tendency with the gate voltage applied.

In conclusion, the gate voltage is shown to affect the Bi₂Se₃ channel by modulating its transport properties, which can be understood as the Fermi level being closer to the band gap or closer to the conduction band minimum.

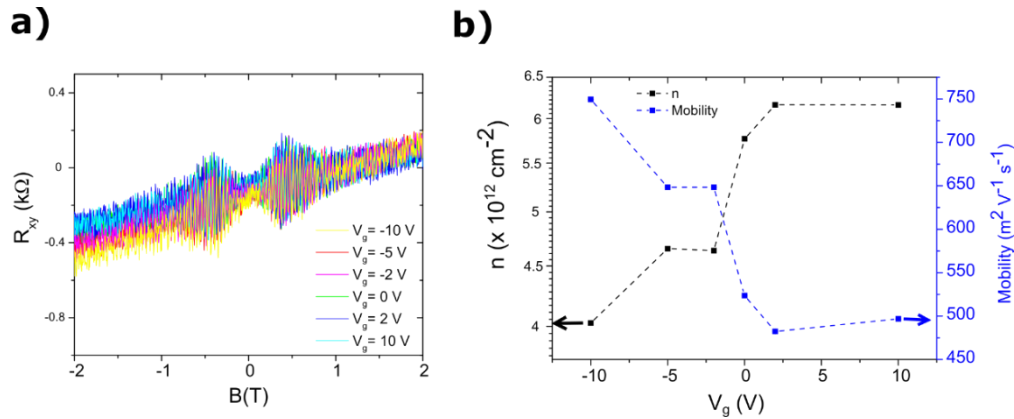


Figure 6.8 a) Linear response of the transverse resistance (R_{xy}) as a function of the magnetic field for different gate voltages. b) Extracted electron concentration and mobility for the different gate voltages. The measurements are performed at a temperature of 1.5 K.

6.3. Summary

In summary, the fabrication of FET devices based on thin-layer MBE-grown Bi_2Se_3 with IS-BIS buffer and In_2Se_3 capping layers is developed at a wafer scale level. Selective In_2Se_3 etching is achieved to allow the ohmic contact with the Bi_2Se_3 with minimal air exposure. A functional gate field effect transistor is achieved by a dielectric behavior of the gate I-V. The negative gate voltage was shown to have a beneficial effect by improving the insulating bulk contributions while improving the transport properties, such as electron concentration and mobility. Furthermore, the WAL was maintained after the fabrication process with a cusp in the magneto conductance.

Conclusion and outlook

In this thesis, MBE was demonstrated to be a robust technique for the deposition of high-quality Bi_2Se_3 thin films. Epitaxial growth on sapphire (0001) substrates has proven feasible for the growth of Bi_2Se_3 at relatively low growth temperatures (310 °C), Se overpressures ($\text{BEP} = 2.5 \times 10^{-5}$ mBar) and slow growth rates (1-1.4 nm/min). Notably, defects created, such as twinning and dislocations, could be mitigated by a substrate surface treatment with two-step growth or by the implementation of an In_2Se_3 -(Bi, In) $_2\text{Se}_3$ buffer layer with improved chemical compatibility. Bi_2Se_3 demonstrated high single crystallography and relatively good electrical and transport properties of the topological insulator with the highest mobility of 592.5 cm^2/Vs and lowest sheet concentration of $1.69 \times 10^{13} \text{ cm}^{-2}$ at room temperature. Furthermore, the topological properties were confirmed by the existence of surface states crossing the band gap (ARPES) and the presence of a weak antilocalization effect cusp in the magnetoconductance. However, the n-type degeneracy obtained after the growth of the TI could not be avoided during growth or after air exposure, impairing the exploitation of the dissipationless surface states at room temperature.

Ga and Cu doping of Bi_2Se_3 was investigated to counterbalance the n-type degeneracy. Ga doping resulted in an expansion of the Bi_2Se_3 crystal lattice parameter by the introduction of Ga atoms in the unit cell. The Bi_2Se_3 lattice parameter c changed from 28.66 Å (reference) to the highest value of 28.92 Å (Ga: 2 at.%). This expansion suggests the Ga intercalation in the van der Waals gap at low Ga concentrations. N-type doping was consistently observed for Ga doping with a sixfold increase of the electron concentration to $\sim 6 \times 10^{19} \text{ cm}^{-3}$ for Ga percentages of 2 at.% and 7 at.%, which supports the interpretation of the intercalation of Ga atoms into the material. ARPES measurements showed an upward Fermi level shift, and consequently, an increase in the electron concentration, which is in agreement with the transport measurements. Moreover, the surface states characteristics of the topological insulator survived upon the lowest concentration of Ga (2 at.%), whereas for the highest concentration of Ga (7 at. %), a destruction of the surface states was observed. Similar conclusions were extracted from the inexistent WAL effect for the doping of the 7 at.% doping with Ga.

In contrast, Cu doping leads to the contraction of the crystal volume as observed by XRD. Moreover, STEM images and energy-dispersive X-rays showed a random distribution of Cu atoms in the crystal. These observations indicate that Cu occupies the Bi sites in the crystal. In terms of transport, Cu doping exhibits characteristics of a good acceptor impurity leading to a two-fold reduction in the carrier concentration by the substitution of Bi atoms. ARPES measurements on Cu-doped Bi_2Se_3 revealed a downward Fermi level shift and consequently, an improved topological transport with a reduction of bulk contributions. Moreover, the surface states are not destroyed upon the highest Cu concentration of 7 at.%.

As an alternative approach to tuning the Fermi level into the band gap, the investigation was extended to the fabrication of FET devices based on epitaxial Bi_2Se_3 , emphasizing the preservation of the TI surface quality by the incorporation of a $\beta\text{-In}_2\text{Se}_3$ capping layer. The fabrication process was developed and successfully achieved, enabling the Fermi level

tuning, closer to the conduction band minimum by the application of negative gate voltages. Tuning of the Fermi level can be seen by the improved transport properties and the semi-ambipolar behavior of the channel resistance while preserving the WAL effect, though with a reduced cusp at low temperatures.

Overall, no evidence of topological superconductivity was found in MBE-grown Bi_2Se_3 doped with Cu atoms. The main reason is attributed to the high-quality thin films provided by MBE growth. The known TSC found in Cu-doped Bi_2Se_3 is achieved by less “cleaner” growth techniques (melt-growth), increasing the concentration of defects in the material, which might be the key to obtaining the TSC. The high-quality growth provided by MBE could thus be a disadvantage for the appearance of TSC, because Cu does not intercalates.

In addition, Ga doping at low concentrations preserved the topological behavior. Moreover, the possibility of Ga being intercalated in the Van der Waals gap and the plateau-like behavior observed in the WAL effect could indicate that Ga might be a possible new dopant for the TSC family. However, high concentrations of Ga doping led to a topological phase transition by the destruction of the surface states since the WAL cusp vanished.

As an outlook for future projects, the growth of the topological insulator Bi_2Se_3 with reduced intrinsic defects and an insulating bulk should be a main goal. The use of different substrates or buffer layers with minimal lattice mismatch should be reconsidered because of the presence of twin domains in the thin-film material and the existence of defects that lead to n-type degeneracy. An interesting approach involves the use of SrTiO_3 (STO) substrates. Despite the larger lattice mismatch of -25% (Table 3.1) compared to sapphire substrates, SrTiO_3 (111) substrates could be used for back-gating, allowing a Fermi-level tuning of the bottom surface³⁷. STO is a dielectric material similar to the Al_2O_3 (sapphire), but with a higher dielectric constant ($\epsilon_r = 300$ at RT¹⁵⁷) compared to the sapphire ($\epsilon_r = 9.3$). Furthermore, the dielectric constant of STO increases at low temperatures ($\epsilon_r = 24000$ at 3K¹⁵⁷), which allows the bottom gate tuning of the Fermi level at low temperatures. The use of both top and bottom gating of the topological insulator can lead to a higher reduction in the carrier concentration and, consequently, the tuning of the Fermi level into the band gap.

The top-gate FET devices developed in this thesis still have room to be improved and achieve an ambipolar behavior characteristic of a Fermi level transition from the conduction band to the valence band. The reduced Fermi level tuning in the FET device is linked to the poor dielectric material used and the deposition technique of Al_2O_3 by sputtering. The use of an ionic liquid gate (TEME-DFSI) would be the focus of the next approach, where a significant tuning effect is achieved even at low gate voltages^{150,158}. Although Ga and Cu-doped Bi_2Se_3 device fabrication was accomplished, the electrical characterization of these devices was not feasible due to time constraints and dedicated tool limitations at the research institute.

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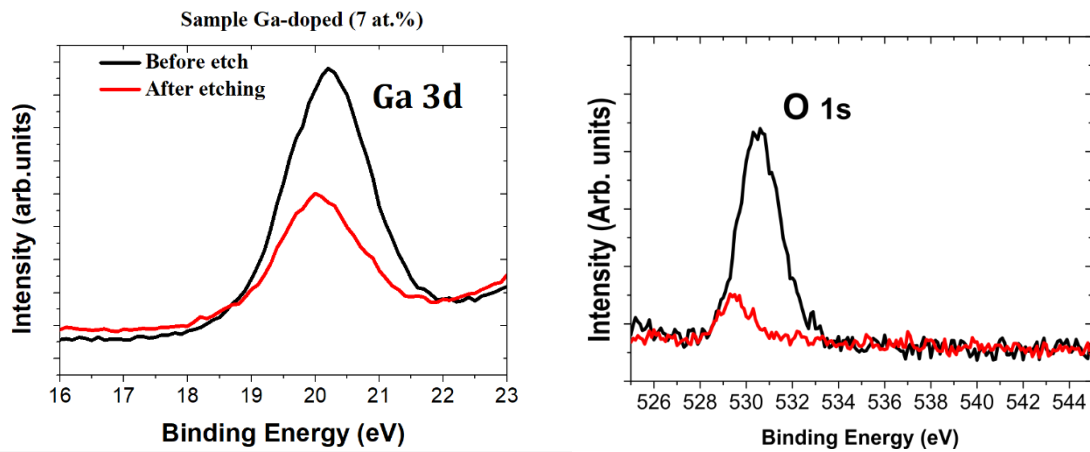
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Annex

S1. Gallium and oxygen segregation towards the surface

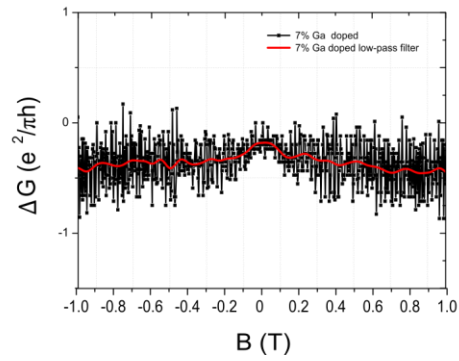
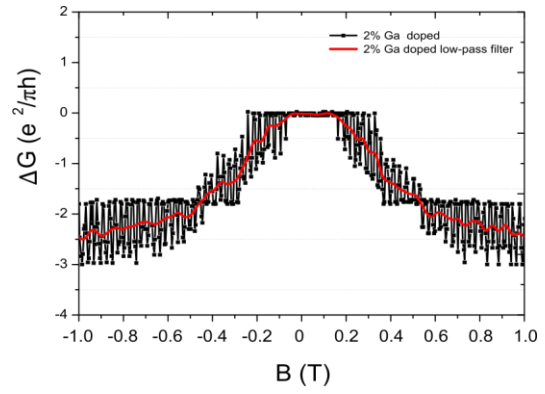
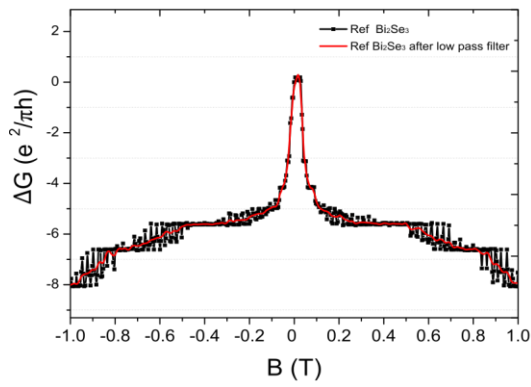
Before performing the etch of the material surface, to remove the oxides, it was observed that there was a higher concentration of Ga atoms in the surface. There is a segregation of Ga atoms towards the surface. The signal before and after the etch is shown in the following image. The signal difference is more perceptible for high compositions of Ga.

Moreover, it was also measured the oxygen signal before and after the etch to confirm that the first layer was oxidized. After the Ar⁺ etching, the signal of oxides was minimal.

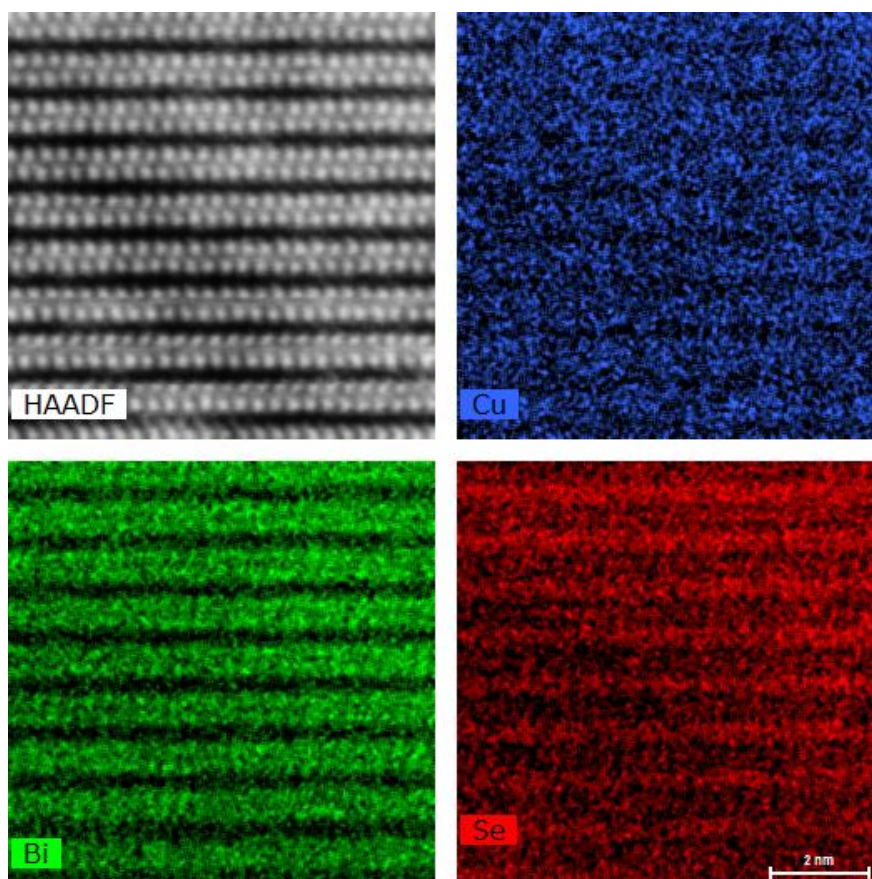


S2. WAL filters and analysis

Application of lowpass filter to remove high frequency noise.



S3. Energy-dispersive x-ray spectroscopy of (7 at.%) Cu-doped Bi_2Se_3



Energy-dispersive x-ray analysis showed an atomic percentage of Cu between 6-7 at.%.

S4. ARPES python code for image creation, analysis and fitting profile

```
from nexusformat.nexus import *
import numpy as np
import matplotlib.pyplot as plt
import matplotlib.colors as mcolors
from ipywidgets import interact, widgets, Layout

def momentum_function(angles, energy):
    # This is just a simple example function, you should replace it with your actual function
    # In this example, we'll assume a linear relationship for demonstration purposes
    return 0.512*(np.sqrt(energy))*np.sin(np.pi*angles/180.0))

from scipy.optimize import curve_fit

# Fermi-Dirac distribution function
def fermi_dirac(E, E_F):
    return 1 / (np.exp(((E - E_F) / (8.617333262145e-05 * 10)) + 1))
```

Single band structure energy dispersion

```
[2]: # Define a function that correlates scattering angle with momentum

from nexusformat.nexus import *
import numpy as np

# Import data
a=nxload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/new_ref/003_new_ref.nxs')

def momentum_function(angles, energy):
    # This is just a simple example function, you should replace it with your actual function
    # In this example, we'll assume a linear relationship for demonstration purposes
    return 0.512*(np.sqrt(energy))*np.sin(np.pi*angles/180.0))

value = np.array(a.entry1.data.data)
angles = np.array(a.entry1.data.angles)
energies = np.array(a.entry1.data.energies)

# Create a new axis for momentum using the defined function
momentum_last = momentum_function(angles, energies[-1])

# Create a new y-axis for momentum
#new_y_axis = np.linspace(np.min(momentum_last), np.max(momentum_last), len(angles))

# Initialize an array to store the remapped values
remapped_values = np.zeros((len(angles), len(energies)))

# Perform the remapping
for i in range(len(energies)):
    momentum = momentum_function(angles, energies[i])
    remapped_values[:, i] = np.interp(momentum_last, momentum, value[:, i], left=0.0, right=0.0)

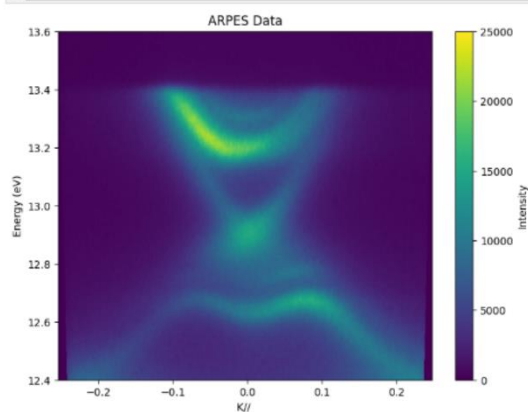
[3]: import matplotlib.pyplot as plt
import matplotlib.colors as mcolors
from ipywidgets import interact, widgets, Layout

# Define the range for the color map scale (adjust these values)
custom_min_intensity = 0
custom_max_intensity = 25000
norm = mcolors.Normalize(vmin=custom_min_intensity, vmax=custom_max_intensity)

# Create a heatmap using Matplotlib
plt.figure(figsize=(8, 6))
plt.imshow(remapped_values.T, cmap='viridis', aspect='auto', origin='lower', extent=[min(momentum_function(angles, energies[-1])), max(momentum_function(angles, energies[-1]))], max(momentum_function(angles, energies[-1]))], max(momentum_function(angles, energies[-1]))])
plt.colorbar(label='Intensity')
plt.title('2D Map with Momentum as Y-Axis')
plt.ylabel('Energy (eV)')
plt.xlabel('K//')
plt.title('ARPES Data')

# Save the plot as a PNG image
#plt.savefig('sample_plot_cu.png', format='png', dpi=300) # 'sample_plot.png' is the desired file name

plt.show()
```



Fitting Fermi dirac function

```
[8]: # Fermi-Dirac distribution function
def fermi_dirac(E, E_F):
    return 1 / (np.exp((E - E_F) / (8.617333262145e-05 * 10)) + 1)

# Example data

actual_E_F = 13.4 # actual Fermi Level for generating example data

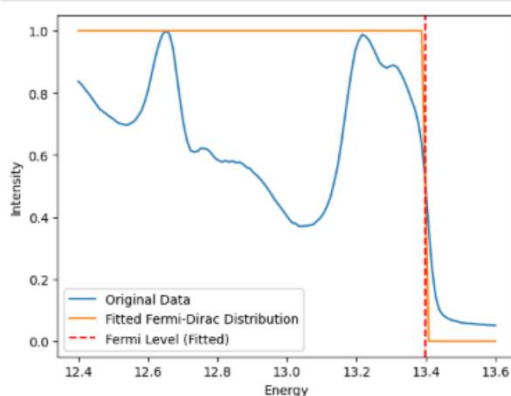
# data integrated
int=np.sum(renapped_values,axis=0)
data=int/max(int)

# Fit Fermi-Dirac distribution to the data
initial_guess = [actual_E_F] # initial guess for fitting parameters
fit_params, Conv = curve_fit(fermi_dirac, energies, data, p0=initial_guess)

# Extract Fermi Level from the fitted parameters
fitted_E_F = fit_params[0]

# Plot the results
plt.plot(energies, data, label='Original Data')
plt.plot(energies, fermi_dirac(energies, *fit_params), label='Fitted Fermi-Dirac Distribution')
plt.axvline(fitted_E_F, color='red', linestyle='--', label='Fermi Level (Fitted)')
plt.xlabel('Energy')
plt.ylabel('Intensity')
plt.legend()
plt.show()

error=np.sqrt(Conv)
print(f"Fitted Fermi Level: {fitted_E_F}")
print(f"Fermi Level error: {error}")
```



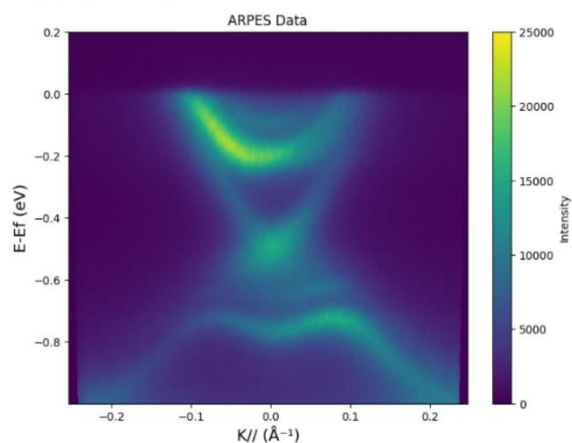
Fitted Fermi Level: 13.398376558002218
Fermi Level error: [[0.001171]]

```
[23]: # Define the range for the color map scale (adjust these values)
#custom_min_intensity = 0
#custom_max_intensity = 35000
#norm = mcolors.Normalize(vmin=custom_min_intensity, vmax=custom_max_intensity)

# Create a heatmap using Matplotlib
plt.figure(figsize=(8, 6))
plt.imshow(renapped_values.T, cmap='viridis', aspect='auto', origin='lower', extent=[min(momentum_function(angles,energies[-1])), max(momentum_function(angles,energies[-1]))])

plt.colorbar(label='Intensity')
plt.title('2D Map with Momentum as Y-Axis')
plt.ylabel('E-Ef (eV)', fontsize=14)
plt.xlabel('K// (Å⁻¹)', fontsize=14)
plt.title('ARPES Data')
#plt.savefig('sample_plot_REF.png', format='png', dpi=300) # 'sample_plot.png' is the desired file name
```

[23]: Text(0.5, 1.0, 'ARPES Data')



For fitting curve

▼ Fitting model

```
[22]: #gen_values = np.zeros((len(angles), len(energies)))
def dograp(Edirac, vel_f, Eval, m_val, Econd, m_cond, momentum_last, energies, remapped_values):

    fitted_E_F=13.4
    x, y = np.meshgrid(momentum_last, energies-fitted_E_F)

    # Parameters for the Lorentzian curve
    linewidth = 0.05 # Lorentzian linewidth
    amplitude = 800.0 # Peak amplitude

    # Create a 2D curve (Line)
    line1 = vel_f * momentum_last + Edirac

    # Calculate the Lorentzian profile perpendicular to the line
    perpendicular_distance = np.abs(y - line1)
    lorentzian = amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line2 = -vel_f * momentum_last + Edirac
    perpendicular_distance = np.abs(y - line2)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line3 = Eval - (3.807/m_val) * momentum_last**2 + rash * np.abs(momentum_last) #+ (1/(4*e_dept)) * ( (3.807/m_val) * momentum_last**2 )**2
    linewidth = 0.05
    perpendicular_distance = np.abs(y - line3)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line4 = Econd + 3.807/m_cond * momentum_last**2
    perpendicular_distance = np.abs(y - line4)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    # New bands
    extravalen = (Eval+0.1) - (3.807/m_val) * momentum_last**2 + rash * np.abs(momentum_last) #from fitting
    extracond = (Econd+0.1) + 3.807/m_cond * momentum_last**2 #From fittings

    # Optionally, visualize the 2D Lorentzian profile perpendicular to the line
    plt.figure(figsize=(8, 6))
    plt.pcolormesh(x, y, lorentzian)
    plt.colorbar()
    plt.show()

    # Create a heatmap using Matplotlib
    plt.figure(figsize=(8, 6))
    plt.pcolormesh(x, y, remapped_values.transpose(), cmap='viridis')
    plt.colorbar(label='Value at Momentum')
    plt.plot(momentum_last, line1, color='red', linestyle='--')
    plt.plot(momentum_last, line2, color='red', linestyle='--')
    plt.plot(momentum_last, line3, color='white', linestyle='--')
    plt.plot(momentum_last, line4, color='black', linestyle='--')
    plt.plot(momentum_last, extravalen, color='yellow', linestyle='--')
    plt.plot(momentum_last, extracond, color='yellow', linestyle='--')
    plt.ylabel('E-Ef (eV)', fontsize=14)
    plt.xlabel('K// (Å⁻¹)', fontsize=14)
    plt.ylim(-1, 0)
    #plt.title('2D Map with Momentum as Y-Axis')
    plt.savefig('sample_plot_REF fitting with all bands.png', format='png', dpi=300) # 'sample_plot.png' is the desired file name
    plt.show()
    return

def curvesfitting(ky, vel_f, Edirac, m_val, m_cond, Eval, Econd):

    linewidth=0.05
    k, y = ky
    amplitude= 1000
    fitted_E_F = 13.4

    # Create a 2D curve (Line)
    line1 = vel_f * k + Edirac

    # Calculate the Lorentzian profile perpendicular to the line
    perpendicular_distance = np.abs(y - line1)
    lorentzian = amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line2 = -vel_f * k + Edirac
    perpendicular_distance = np.abs(y - line2)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line3 = Eval - (3.807/m_val) * k**2 + rash * np.abs(k)
    perpendicular_distance = np.abs(y - line3)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

    line4 = Econd + 3.807/m_cond * k**2
    perpendicular_distance = np.abs(y - line4)
    lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))
    return lorentzian.ravel()
```

```

amplitude=800
fitted_f_f=13.4
mat = np.meshgrid(momentum_last,energies-fitted_f_f)

# Parameters for the Lorentzian curve
x, y = np.meshgrid(momentum_last,energies-fitted_f_f)
linewidth = 0.05 # Lorentzian linewidth
edirac = -0.5
vel_f = 4
eval = -0.5
m_val = 0.25
e_sept = 0.01
rash = 2
fcond = -0.2
m_cond = 0.19

# Flatten the input arrays
x_data_flat = (mat[0]).ravel()
y_data_flat = (mat[1]).ravel()
z_data_flat = (renapped_values.transpose()).ravel()

# Define the region of interest
roi_condition = (x_data_flat > -0.15) & (x_data_flat < 0.15) & (y_data_flat > -1) & (y_data_flat < 0)

# Subset the data
x_roi = x_data_flat[roi_condition]
y_roi = y_data_flat[roi_condition]
z_roi = z_data_flat[roi_condition]

#Bounds
bounds = [(3.5, -0.6, 0.2,0.1,-0.9, -0.2),[5,-0.5,0.35,0.25,-0.4,-0.05]]

# Fit Fermi-Dirac distribution to the data
initial_guess = [vel_f,edirac,m_val,m_cond,eval,fcond] # initial guess for fitting parameters
fit_params, covariance = curve_fit(curvesfitting, (x_roi, y_roi, z_roi), pb=initial_guess, bounds=bounds)

# Extract Fermi level from the fitted parameters
# Create a 2D curve (line)
line1 = vel_f * momentum_last + edirac

# Calculate the Lorentzian profile perpendicular to the line
perpendicular_distance = np.abs(y - line1)
lorentzian = amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

line2 = -vel_f * momentum_last + edirac
perpendicular_distance = np.abs(y - line2)
lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

line3 = eval - (3.887/m_val) * momentum_last**2 + rash * np.abs(momentum_last) # (1/(4*e_sept)) * ((3.887/m_val) * momentum_last**2)**2
linewidth = 0.05
perpendicular_distance = np.abs(y - line3)
lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

line4 = fcond + 3.887/m_cond * momentum_last**2
perpendicular_distance = np.abs(y - line4)
lorentzian += amplitude / (np.pi * linewidth * (1 + ((perpendicular_distance) / linewidth) ** 2.0))

vel_f=fit_params[0]
edirac=fit_params[1]
m_val=fit_params[2]
m_cond=fit_params[3]
eval=fit_params[4]
fcond=fit_params[5]

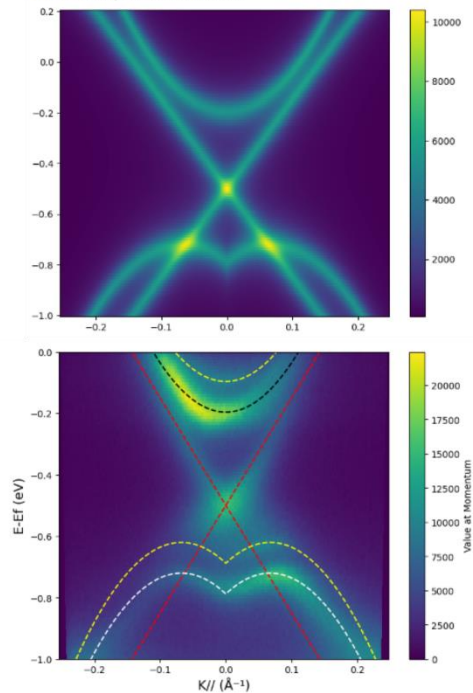
print("Fitted Fermi velocity: {fit_params[0]}")
print("Fitted Dirac point: {fit_params[1]}")
#print("Fitted linewidth: {fit_params[2]}")
print("Fitted Electron mass Valence: {fit_params[2]}")
print("Fitted Electron mass conduction: {fit_params[3]}")
print("Fitted Valence point: {fit_params[4]}")
print("Fitted Conduction point: {fit_params[5]}")

#for i in range(len(fit_params)):
#    for j in range(len(fit_params)):
#        if i==j:
#            print(covariance[i,j])

dagrap(edirac,vel_f,eval,m_val,fcond,m_cond,momentum_last,energies,renapped_values)

Fitted Fermi velocity: 3.58800000000000057
Fitted Dirac point: -0.5000000000000001
Fitted Electron mass Valence: 0.2571758819306135
Fitted Electron mass conduction: 0.237118497462933
Fitted Valence point: -0.7881174126333186
Fitted Conduction point: -0.19624385582749668

```



Core Levels

```

[2]: #Import data
core = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/new_ref/005_new_ref.nxs') # REF
core2 = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Flashed_ref/185_F1_ref.nxs') # Real REF
core3 = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Flashed_Ga_2pc/857_F1_Ga_2pc_core.nxs') # CoreLevels of Ga2%
core4 = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Flashed_Ga_2pc/818_F1_Ga_2pc.nxs') # CoreLevels of Cu 2%
core5 = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Cu_7pc/829_Cu_7pc.nxs') # CoreLevels of Cu 7%
core6 = mload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Ga_7pc/884_Ga_7pc.nxs') # CoreLevels of Ga 7%

anglesc = np.array(core6.entry1.data.angles)
energiesc = np.array(core6.entry1.data.energies)

valuesc = np.array(core.entry1.data.data)
valuesref2 = np.array(core2.entry1.data.data)
valuesga2 = np.array(core3.entry1.data.data)
valuescu2 = np.array(core4.entry1.data.data)
valuescu7 = np.array(core5.entry1.data.data)
valuesga7 = np.array(core6.entry1.data.data)

# Sum along rows (axis 1)
all = np.sum(valuesc, axis=0)

REF = np.sum(valuesc, axis=0)
REALREF = np.sum(valuesref2, axis=0)
ga2one = np.sum(valuesga2, axis=0)
cu2one = np.sum(valuescu2, axis=0)
cu7one = np.sum(valuescu7, axis=0)
ga7one = np.sum(valuesga7, axis=0)

#x-axis
xc = np.zeros(len(energiesc))
for i in range(len(energiesc)):
    xc[i] = energiesc[i] - energiesc[-1] + 1.23 # Where is work function -4.6 eV

# Invert the vector using slicing
#Inverted_vector = energies[::-1]

# Define energy ranges for Bi and Ga peaks
bi_peak_range = (-30, -24)
ga_peak_range = (-21, -19)
in_peak_range = (-19, -17)

# Find indices corresponding to the energy ranges
bi_indices = np.where(xc >= bi_peak_range[0]) & (xc <= bi_peak_range[1])[0]
ga_indices = np.where(xc >= ga_peak_range[0]) & (xc <= ga_peak_range[1])[0]
in_indices = np.where(xc >= in_peak_range[0]) & (xc <= in_peak_range[1])[0]

# Integrate the intensity within the specified energy ranges
bi_intensity = np.trapz(all[bi_indices], xc[bi_indices])
ga_intensity = np.trapz(all[ga_indices], xc[ga_indices])
in_intensity = np.trapz(all[in_indices], xc[in_indices])

ev = bi_intensity + ga_intensity + in_intensity
bipercantage_element = (bi_intensity / ev) * 40
gapercentage_element = (ga_intensity / ev) * 40
inpercentage_element = (in_intensity / ev) * 40

# Print the integrated intensities
print(f"Integrated intensity for Bi (-30 to -24 eV): {bipercantage_element}")
print(f"Integrated intensity for Ga (-21 to -19 eV): {gapercentage_element}")
print(f"Integrated intensity for In (-18 to -17 eV): {inpercentage_element}")

Integrated intensity for Bi (-30 to -24 eV): 36.476294591595696
Integrated intensity for Ga (-21 to -19 eV): 1.9899561621575822
Integrated intensity for In (-18 to -17 eV): 1.6137492462467162

#Last x digits of an array all[-40:]

# Create a core levels
plt.figure(figsize=(8, 6))
plt.xticks([])
plt.ylabel('Intensity [Arb. Units]', fontsize=14)
plt.xlabel('Binding energies (eV)', fontsize=14)
plt.title('Core levels')
plt.xlim(-30, 0)

Offset = 500000
#Plot(xcore[150:600], all[150:600])
plt.plot(xcore, REF, label='Reference Bi,Se')
plt.plot(xcore, REALREF + Offset, label='Referencia Bi,Se')
plt.plot(xcore, ga2one + Offset, label='Ga-doped 2 at.%')
plt.plot(xcore, cu2one + Offset, label='Cu-doped 2 at.%')
plt.plot(xcore, ga7one + Offset, label='Ga-doped 7 at.%')
plt.plot(xcore, cu7one + Offset, label='Cu-doped 7 at.%')

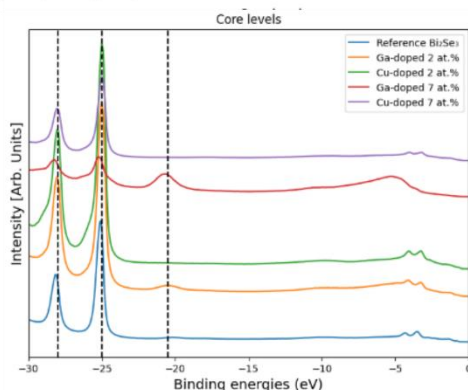
# I cannot believe someone is reading my code! You didn't give up? I would be tired already

# Add a vertical line at x = -25
plt.axvline(x=-25, color='black', linestyle='--')
plt.axvline(x=-28, color='black', linestyle='--')
plt.axvline(x=-18, color='black', linestyle='--')
plt.axvline(x=-20.5, color='black', linestyle='--')
plt.legend()

#
#plt.savefig('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/Analysis/CL/CL.png', format='png', dpi=300)

[3]: cmatplotlib.legend.Legend at 0x109d1795730

```



SEVERAL points

```
[4]: a=nxload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/flashed_ref/001_f1_ref.nxs')

value = np.array(a.entry1.data.data)
angles = np.array(a.entry1.data.angles)
energies = np.array(a.entry1.data.energies)

# All data points?
ss=np.zeros(value[0,0,:].shape)
print(value.shape)

for i in range(9):
    for j in range(9):
        ss+=value[i,i,:,:]

# Create a new axis for momentum using the defined function
momentum_last = momentum_function(angles,energies[-1])

# Initialize an array to store the remapped values
remapped_values = np.zeros((len(angles), len(energies)))

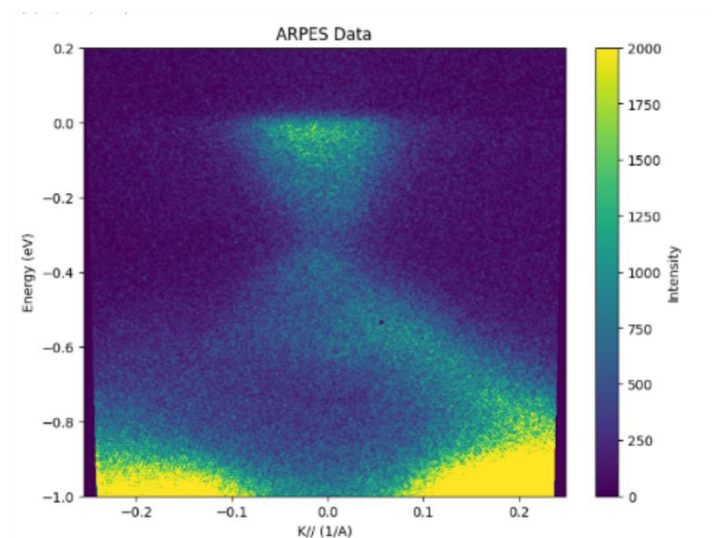
# Perform the remapping
for i in range(len(energies)):
    momentum = momentum_function(angles,energies[i])
    remapped_values[:, i] = np.interp(momentum_last, momentum, ss[:, i],left=0.0,right=0.0)

# Define the range for the color map scale (adjust these values)
fitted_E_F=13.4
custom_min_intensity = 0
custom_max_intensity = 2000
norm = mcolors.Normalize(vmin=custom_min_intensity, vmax=custom_max_intensity)

# Create a heatmap using Matplotlib
plt.figure(figsize=(8, 6))
plt.imshow((remapped_values.T), cmap='viridis', aspect='auto', origin='lower', extent=[min(momentum_function(angles,energies[-1])), max(momentum_function(angles,energies[-1]))])
plt.colorbar(label='Intensity')
plt.title('2D Map with Momentum as Y-Axis')
plt.ylabel('Energy (eV)')
plt.xlabel('K// (1/Å)')
plt.title('ARPES Data')
plt.ylim(-1,0.2)

# Save the plot as a PNG image
#plt.savefig('Band dispersion_REF several points.png', format='png', dpi=300) # 'sample_plot.png' is the desired file name

plt.show()
```



Mapping

```

import matplotlib.pyplot as plt
import matplotlib.colors as mcolors
from ipywidgets import interact, widgets, Layout
from IPython.display import display
from nexusformat.nexus import *
import numpy as np
from nexusformat.nexus import *

# Import data
b=nxload('C:/Users/Utilizador/Desktop/Things to do/Python/DATA/flashed_Cu_2pc/004_f1_Cu_2pc.nxs')

def momentum_function(angles,ener):
    # This is just a simple example function, you should replace it with your actual function
    # In this example, we'll assume a linear relationship for demonstration purposes
    return 0.512*np.sqrt(ener)*np.sin(np.deg2rad(angles))

value = np.array(b.entry1.data.data)
anglesx = np.array(b.entry1.data.angles)
anglesy = np.array(b.entry1.data.def1_angles)
energies = np.array(b.entry1.data.energies)

# Debug the matrix sizes
print(value.shape)
print(anglesx.shape)
print(anglesy.shape)
print(energies.shape)

# Create a new axis for momentum using the defined function
# Create a new axis for momentum using the defined function
momentum_last_x = momentum_function(anglesx,energies[-1])
momentum_last_y = momentum_function(anglesy,energies[-1])

remapped_values = np.zeros((len(anglesy),len(anglesx), len(energies)))

# Perform the remapping
for i in range(len(energies)):
    momentum_x = momentum_function(anglesx,energies[i])
    momentum_y = momentum_function(anglesy,energies[i])
    for k in range(len(anglesy)):
        remapped_values[k,:, i] = np.interp(momentum_last_x, momentum_x, value[k,:, i],left=0.0,right=0.0)
    for l in range(len(anglesx)):
        remapped_values[:,l, i] = np.interp(momentum_last_y, momentum_y, value[:,l, i],left=0.0,right=0.0)

x, y = np.meshgrid(momentum_last_x,momentum_last_y)

print(remapped_values[:, :,5].shape)

# Perform the remapping onto the 2D grid
def update_plot(c=742):
    intensity_data = value[:, :,c] # Intensity data

    # At this point, 'remapped_map' contains the Fermi surface map data

    # Create a heatmap using Matplotlib
    #plt.figure(figsize=(8, 8))
    plt.pcolormesh(y,x,remapped_values[:, :,c], cmap='viridis')
    #plt.colorbar(label='Intensity')
    plt.ylabel('ky (Å⁻¹)')
    plt.xlabel('kx (Å⁻¹)')
    plt.xlim(-0.22,0.24)
    #plt.ylim(-0.18,0.18)
    plt.title(f'ARPES Data for energy: {energies[c]-13.4} eV')
    plt.savefig('Map Cu 2% 0 eV .png', format='png', dpi=300) # 'sample_plot.png' is the desired file name
    plt.show()

# Create an interactive slider for Enval
slider_layout = Layout(width='100%') # Adjust the width as needed
enval_slider = widgets.IntSlider(value=742, min=0, max=943, step=1, description='c', layout=slider_layout)

# Create an interactive plot using ipywidgets
interactive_plot = interact(update_plot, c=enval_slider)
display(interactive_plot)

(161, 617, 943)
(617,)
(161,)
(943,)
(161, 617)
Error displaying widget: model not found
<function __main__.update_plot(c=742)>

plt.pcolormesh(y,x,remapped_values[:, :,520], cmap='viridis')
plt.ylim(-0.18,0.18)
plt.xlim(-0.24,0.24)
plt.savefig('Max Cu 0.4 .png', format='png', dpi=300) # 'sample_plot.png' is the desired file name
plt.show()

```