Challenges of Topological Insulator Research: Bi$_2$Te$_3$ Thin Films and Magnetic Heterostructures

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1. Introduction

Topological insulators (TIs) are of particular interest in the recent solid-state research because of their exceptional features stemming from the conducting, topologically protected surface states. The exotic properties include the occurrence of novel quantum phenomena and make them promising materials for spintronics and quantum computing applications. Theoretical studies have provided a vast amount of valuable predictions and proposals, whose experimental observation and implementation, to date, are often hindered by an insufficient sample quality. The effect of even a relatively low concentration of defects can make the access to purely topological surface states impossible. This points out the need of high-quality bulk-insulating materials with ultra-clean surfaces/interfaces, which requires sophisticated sample/device preparations as well as special precautions during the measurements. Herein, the challenging work on 3D TI thin films with a focus on Bi$_2$Te$_3$ is reported. It covers the optimization of the molecular beam epitaxy growth process, the in situ characterization of surface states and transport properties, the influence of exposure to ambient gases and of capping layers, as well as the effect of interfacing TI thin film with magnetic materials.

Topological insulators (TIs) are a novel state of matter for which the bulk is insulating, whereas the surface is necessarily metallic. The gapless surface states are a direct consequence of band inversion due to strong spin–orbit interactions and symmetries of the bulk material and are, thus, topologically protected.$^{1-3}$ Bi$_2$Te$_3$ is part of the Bi$_2$Se$_3$ family (Bi$_2$Se$_3$, Bi$_2$Te$_3$, and Sb$_2$Te$_3$ compounds), which share the same rhombohedral, layered crystal structure and belong to the class of 3D strong TIs.$^{4}$ Their surface states represent a new type of a 2D electron system showing a linear energy dispersion. This results in a formation of a single massless Dirac cone in which the spin of the surface electrons is locked perpendicular to its momentum, protecting the electrons against backscattering. Hence, if the Fermi level of the TI is placed in the bulk bandgap, which is relatively large for the Bi$_2$Se$_3$ family ($0.15–0.30$ eV),$^{4}$ the conduction will ideally take place exclusively on the surface of the material. This allows to build advanced devices, which are based on the unusual properties of the topological surface states. For instance, novel transport phenomena, such as the quantum anomalous Hall effect (QAHE), can be induced, and Majorana states can be created in proximity to magnets and superconductors, appealing also for possible applications in room temperature spintronics and quantum computation.$^{5}$

Considering the exciting properties, however, one has to emphasize that the research on TIs carries one inherent issue that potentially hinders experimental investigations and
applications: There is often no unambiguous access by electrical transport measurements to purely topological surface states. Vacancies and anti-site defects are inevitably incorporated in Bi$_2$Te$_3$, Sb$_2$Te$_3$, and Bi$_2$Se$_3$ materials, thereby leading to a considerable enhanced bulk carrier concentration. Both surface and bulk states can then contribute to the experimental results; in fact, the bulk conductivity often even overwhelms the contribution of the surface states, which complicates the explicit interpretation of the observed effects.

An estimate of the required purity can be derived from band structure calculations where the Fermi surfaces enclosed by the TI surface states of the Bi$_2$Se$_3$ family are only a small fraction ($\sim$1%) of the surface Brillouin zones. The topologically relevant carrier densities are, thus, on the order of less than 0.01 electron per surface unit cell, i.e., a few $10^{12}$ cm$^{-2}$ only. Therefore, an extremely low bulk defect concentration of well below ppm (parts per million) level is required.

Several methods have been proposed to counteract the typically n-doped character of bulk Bi$_2$Te$_3$ and Bi$_2$Se$_3$. The most obvious approach is to optimize the sample preparation further to achieve naturally bulk-insulating TIs. As the materials tend to be Te/Se-deficient, one can, for example, try to increase the Te/Se proportion in the starting materials for the crystal synthesis. Another possibility of tuning the Fermi level across the bulk bandgap to realize a surface dominated conduction is counter doping, i.e., the introduction of holes by substituting Bi with, for example, Sn, Mg, or Ca. However, one should note that the required high doping concentrations introduce disorder and scattering, thereby degrading the structural and electronic properties of the topological material. Another route is to utilize the p-type character of bulk Sb$_2$Te$_3$ to modify the bulk carrier type and concentration, namely, by variation of the Sb/Bi ratio in (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ samples.

Also, the TI surface state charge carriers can be changed to be of n- or p-type, namely, by introducing proper non-magnetic dopants directly into the surface. Hereby, the surface states show an unusual robustness and maintain the topological properties due to the protection by time-reversal symmetry. An exposure of a Bi$_2$Se$_3$ surface to small amounts of K, H$_2$, or CO or of Bi$_2$Se$_3$Al$_2$O$_3$ to NO$_2$ was reported to induce n-doping, whereas an exposure of a Sb-deficient Bi$_2$Se$_3$ sample to O$_2$ was observed to induce p-doping. But, this high sensitivity of the TI surface states to surface doping or surface contamination makes the actual access and the manipulation of the TI surface states even more difficult. For example, studies on the degradation of the TI surface states by angle-resolved photoelectron spectroscopy (ARPES) and transport experiments show that the Fermi level can move by hundreds of meV from the bulk bandgap into the bulk conduction band after exposure to ambient conditions. Such a band bending can lead to a parallel shunt or more precisely to a 2D, topologically trivial conductance at the surface masking the contribution of the TI surface states. This is particularly crucial when considering the fabrication of TI devices for research and applications, which is usually done ex situ.

Further methods to minimize the influence of the bulk carrier concentration, which are beyond the optimization of the sample quality, are tuning of the chemical potential by gating or reduction of the bulk to surface ratio using very thin samples, exfoliated nanosheets, or thin films.

Despite all the efforts to improve the quality and to adjust the properties of the samples, the experimental observation of the exotic properties of the TI materials is often still difficult. Thus, there is a strong need for a further improvement of the preparation of samples and devices with sufficiently low bulk conductivities and ultra-clean surfaces and interfaces. In this feature article, we illustrate the challenges in the research on 3D TIs with a focus on Bi$_2$Te$_3$ thin films.

Bi$_2$Te$_3$ is a well-known thermoelectric material. Like Bi$_2$Se$_3$ and Sb$_2$Te$_3$, it crystallizes in a rhombohedral structure consisting of quintuple layers (QLs). The corresponding hexagonal unit cell with the lattice constants of $a = 4.38$ Å and $c = 30.49$ Å is build up of three QLs; i.e., one QL is $\approx$1 nm. The five layers in a QL have strong covalent bonding, whereas the QLs are connected via weak van der Waals forces to each other. Bi$_2$Te$_3$ is, thus, a layered material, which can be easily cleaved between the QLs and can be grown as thin film by van der Waals epitaxy on various substrates even with a large lattice mismatch once the first interface layer has been successfully deposited.

The 3D strong TI material has a relatively large bulk bandgap of about 150 meV, which makes the exotic surface conduction properties observable even at room temperature, as the temperatures of about 1800 K would be necessary to thermally excite electrons from the valence to the conduction band. Its Dirac point is naturally not located freely accessible inside the bandgap, but buried in the valence band. While Te vacancies lead to n-type doping, the presence of Bi$_{\text{Te}}$ anti-sites causes p-type doping. Thus, the conduction of Bi$_2$Te$_3$ can be tuned between n-type and p-type, depending on which kind of defect takes the majority role. For Bi$_2$Te$_3$ thin films, a tuning of the substrate temperature during the deposition has been shown to influence the respective amounts of defects and, hence, to allow for such a conversion from n- to p-type conduction, suggesting that it is indeed feasible to make the material in a thin-film form consistently insulating.

2. Molecular Beam Epitaxy Growth and Structural Characterization of High-Quality Bi$_2$Te$_3$ Thin Films

TIs in thin-film form are attractive not only for possible future device applications but also for the fundamental research. As already pointed out in Section 1, the quality of the TI bulk single crystals often suffers from high bulk conductivities due to an unavoidable presence of vacancies and anti-site defects. Increasing the surface to bulk ratio in thin films thus offers the possibility to enhance the contribution of the topological surface states to the conductivity. Moreover, modern thin-film growth technologies, especially the molecular beam epitaxy (MBE), allow for the preparation of samples with higher carrier mobilities than bulk crystals by defect control, surface protection, and heterostructure engineering. Bi$_2$Te$_3$ thin films have been grown on a variety of substrates, including Si (111), sapphire, SrTiO$_3$, GaAs (001), GaAs (111)B, GaN, graphene, amorphous fused silica, mica (110), and BaF$_2$ (for a review, see, e.g., ref. [25]). The Te content can be precisely controlled by MBE making use of the different evaporation temperatures $T_{\text{Te}}$ and $T_{\text{Bi}}$ of Te and Bi, respectively. In the so-called Te distillation method, more Te is supplied during the deposition than...
nominally required for stoichiometric Bi$_2$Te$_3$ while keeping the substrate at elevated temperature $T_{\text{sub}}$, to re-evaporate the excess of Te$_2$, i.e., $T_{\text{Te}} < T_{\text{sub}} < T_{\text{Bi}}, T_{\text{Bi$_2$Te$_3$}}$.

In the following, we will report on our work on the preparation of bulk-insulating Bi$_2$Te$_3$ thin films using a Te-distillation-assisted MBE growth on single-crystalline Al$_2$O$_3$ (0001) and BaF$_2$ (111) substrates. High-purity (99.9999%) elemental Bi and Te were evaporated under ultra-high vacuum (UHV) conditions from standard effusion cells at the flux rates of 0.5–1 Å min$^{-1}$ for Bi ($\phi_{\text{Bi}}$) and about 1.5–8 Å min$^{-1}$ for Te ($\phi_{\text{Te}}$) onto the heated substrate ($T_{\text{sub}}$ = 160–285 °C). The need for the substantially higher Te flux rates can be explained by the fact that tellurium evaporates preferably as molecule (Te$_2$). Single-crystalline Al$_2$O$_3$ assisted MBE growth on single-crystalline Al$_2$O$_3$ (0001) and BaF$_2$ (111) substrates were chosen as substrates, because they are highly insulating, which is important for transport measurements. Al$_2$O$_3$ (0001) has a very smooth epi-polished surface, it is easy to handle and clean, and it is readily commercially available. The disadvantage is the large lattice mismatch of about 9%. Despite this mismatch, the Bi$_2$Te$_3$ films are known to grow epitaxial on Al$_2$O$_3$ (0001) by van der Waals epitaxy.[28] However, the crystalline structure comprises imperfections, especially multidomain growth, as we will discuss in the following. On the other hand, BaF$_2$ (111) has a perfect lattice match ($<0.1\%$ mismatch), which allows for the growth of single-domain films.[28,29] The drawback of BaF$_2$ is that fluorite substrates can only be produced by chemical–mechanical polishing, which results in much rougher surfaces compared with standard epi-polished substrates such as Al$_2$O$_3$.

Prior to the Bi$_2$Te$_3$ deposition, the Al$_2$O$_3$ substrates were annealed in situ at 600 °C in 1 × 10$^{-6}$ mbar oxygen for 120 min, and the BaF$_2$ substrates were annealed in situ without oxygen at 450 °C for 90 min and at 500 °C for 30 min.

### 2.1. Growth on Al$_2$O$_3$ (0001)

To utilize the Te distillation process, first, the optimum substrate temperature has to be determined. The growth window for Bi$_2$Te$_3$ on Al$_2$O$_3$ was narrowed down to be between 160 °C at which elemental Te starts to re-evaporate and 300 °C at which no deposition of Bi$_2$Te$_3$ takes place for a growth rate of about 0.3 QL min$^{-1}$. The best crystalline quality for Bi$_2$Te$_3$ could be achieved at the substrate temperatures of about 240–250 °C. However, at this temperature, the growth rate is already significantly reduced due to a low sticking probability. Furthermore, for most samples, the Bi$_2$Te$_3$ quality is degraded due to severe twinning and rotational stacking caused by the large lattice mismatch with Al$_2$O$_3$. Atomic force microscopy (AFM) measurements on the first two to three QLS of Bi$_2$Te$_3$ reveal that films grown at high substrate temperature are not continuous, but contain a considerable amount of holes. A reduction of the substrate temperature minimizes the hole concentration and yields the growth of closed layers, but also leads to a poor crystallinity of the film.

To achieve a better quality, a so-called two-step procedure is, therefore, usually used (see also the previous studies[28,30–32]): In the first step, two to three QLS of Bi$_2$Te$_3$ are grown at a low substrate temperature of 160–185 °C, followed by an annealing at the higher temperatures of 240–285 °C in Te atmosphere to crystallize the first layers. In a second step, Bi$_2$Te$_3$ is grown at a higher temperature of 210–260 °C to the desired thickness. The influence of the first-step temperature on the morphology of the Bi$_2$Te$_3$ films is shown in Figure 1. If the first step is grown at the substrate temperatures of about 220 °C or higher, the first layers contain holes that persist throughout the entire layer thickness even when the film is grown thicker, here to about 10 nm. At the lower temperatures of 160–185 °C, the wetting of the substrate becomes better. The film forms a closed layer, showing pyramidal structures at the surface with 1 nm height difference between the terraces, typical for Bi$_2$Te$_3$. A comparison of the AFM results demonstrates further that the lower temperature favors the growth of larger structural domains.

![Figure 1. Influence of the first-step temperature on the morphology of Bi$_2$Te$_3$ films. Ex situ AFM images and corresponding line profiles of ten QL Bi$_2$Te$_3$ on Al$_2$O$_3$ (0001) grown at $\phi_{\text{Bi}} = 1\text{ Å min}^{-1}$ and $\phi_{\text{Te}} = 6\text{ Å min}^{-1}$, and at the substrate temperatures of 220 °C (left) or 170 °C (right) for the first three QLS, followed by an annealing at 270 °C, and a subsequent growth at 250 °C. AFM measurements were performed in tapping mode.](image-url)
In a study on the growth of Bi$_2$Te$_3$ on Si (111), the formation of the twin domains could be fully suppressed using a very slow deposition rate of 2.7 nm h$^{-1}$,[33] whereas we observed that for Al$_2$O$_3$ (0001), the Bi$_2$Te$_3$ films often show a contribution of a second rotated domain for a comparable deposition rate of about 2.2 nm h$^{-1}$ as indicated by RHEED and AFM. The energetics of the growth for the Al$_2$O$_3$ (0001) substrate might, therefore, require an even slower growth rate. The AFM measurements in Figure 3 indeed reveal that the average domain size becomes larger if the films are grown at reduced flux rates, indicating that extremely low deposition rates might support the formation of a single domain layer at the interface with Al$_2$O$_3$ (0001).

2.2. Growth on BaF$_2$ (111)

To avoid the formation of multi-domains, BaF$_2$ (111) substrates with excellent lattice match can be used for the Bi$_2$Te$_3$ growth.[20,29] Utilizing a similar two-step growth process as optimized for Al$_2$O$_3$ (0001), high-quality films can be grown on BaF$_2$ (111). The results of the structural characterization are summarized in Figure 4. The RHEED analysis in Figure 4a reveals clear, prolonged intensity oscillations of the specularly reflected electron beam, which were only very weak, or often not at all, observed for the films grown on Al$_2$O$_3$ (0001). The RHEED oscillations indicate a smooth layer-by-layer growth for the first and second growth steps. From the period of the oscillations, we can determine a Bi$_2$Te$_3$ growth rate of 0.3 QL min$^{-1}$ for a film grown at $\phi_{\text{Bi}} = 1$ Å min$^{-1}$. The corresponding RHEED image in Figure 4b shows intense and narrow streaks with no indication of a rotated domain. The sharp and bright triangular LEED pattern and the 120° in-plane XRD reflections confirm a threefold symmetry; see Figure 4c,d. Also, here, no significant contribution of a rotated domain is observed. In Figure 4e, the topography of the surface is shown as measured by scanning tunneling microscopy. The film consists of pyramidal Bi$_2$Te$_3$ structures similar to the films grown on Al$_2$O$_3$ substrates. In contrast, the triangles are all oriented, indicating the growth of epitaxial, single-domain Bi$_2$Te$_3$ films on BaF$_2$ (111) in agreement with the LEED and XRD results. On the first sight, BaF$_2$ (111) seems to be the ideal substrate for the Bi$_2$Te$_3$ growth. The AFM image displayed in Figure 5, however, points out the drawback of BaF$_2$ substrates. The BaF$_2$ crystals often exhibit deep holes and trenches. Moreover, the substrate surface can be only polished using a chemical–mechanical process, which results in a
considerable roughness, whereas the epi-polished Al₂O₃ (0001) surface is very smooth and clean. The imperfect BaF₂ surface structure can cause the growth of discontinuous Bi₂Te₃ films, which might influence especially the transport measurements.

3. Electronic Structure and Transport Properties: In Situ versus Ex Situ Characterization

Based on the fact that only 1% of doping at the surface due to contaminations can cause a significant change of the magnitude and character of the conduction in the surface region, an investigation of the intrinsic properties of TI materials should be performed under UHV conditions with pressures in the 10⁻¹⁰⁻¹¹ mbar range. A sophisticated UHV system, which combines a growth chamber with in situ characterization tools, is needed to perform reliable measurements. Here, also, controlled contamination experiments can be performed to study the influence of, e.g., exposure to ambient conditions or capping layers. Our unique MBE setup allows for such an in situ study, which includes the sample preparation, structural (RHEED and LEED) and spectroscopic (X-ray photoelectron spectroscopy (XPS), ARPES (all performed at room temperature)) characterization, and temperature-dependent four-probe conductivity measurements.

3.1. In Situ Characterization

After the growth, XPS measurements were performed to determine the exact stoichiometry of the freshly grown Bi₂Te₃ films by comparing the integrated intensities of the Te 3d and Bi 4f core levels and to identify and exclude possible impurities or contaminations. Narrow symmetric core levels of the optimized Bi₂Te₃ films confirm the absence of any Te or Bi excess. Because of the limited resolution at high kinetic energies in XPS, ARPES measurements at lower excitation energy were performed to study the band structure close to the Fermi level. The ARPES measurements in the vicinity to the Fermi level of ten QL Bi₂Te₃ films grown on Bi₂Te₃ (0001) and BaF₂ (111) in Γ–K direction are displayed in Figure 6a,b. The ARPES spectra do not show significant differences when comparing the two substrates. In both cases, the characteristic linear dispersion of the surface states is clearly observable, indicating the presence of mass-less Dirac fermions. The Fermi level lies above the bulk valence band and below the bulk conduction band; i.e., the films are bulk-insulating. Thus, we can attribute the conductance solely to the surface states. It is important to note that no counter doping was required to achieve the bulk charge carrier-free situation.

While the spectroscopic studies are commonly performed in situ, the situation is very different for the characterization of the transport behavior. The vast majority of the transport measurements and/or the device fabrication are done ex situ. In our UHV system, a special sample holder with four spring-loaded point contacts in collinear arrangement and 2 mm spacing was used, allowing for an in situ contacting of the samples. This approach excludes, on the one hand, surface degradation in ambient conditions, or any influence of capping, and on the other hand, minimizes the contact disturbance, as theoretical calculations predict that the deposition of metallic contacts for transport experiments...
Hole sort wrench in the inclusions, one can only speculate about the origin of the offset.

Resistance is extremely sensitive to doping, defects, and contamination.

In situ characterization. ARPES spectra of ten QL Bi$_2$Te$_3$ on a) Al$_2$O$_3$ (0001) and b) BaF$_2$ (111) taken at room temperature using 21.2 eV (He I) photons. c) Corresponding temperature-dependent sheet resistance measurements. a) Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY). [32] Copyright 2020, The Authors, published by AIP Publishing LLC. b,c) Partly adapted with permission.[29] Copyright 2014, National Academy of Sciences of the USA.

Figure 6. In situ characterization. ARPES spectra of ten QL Bi$_2$Te$_3$ on a) Al$_2$O$_3$ (0001) and b) BaF$_2$ (111) taken at room temperature using 21.2 eV (He I) photons. Corresponding temperature-dependent sheet resistance measurements. a) Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY). [32] Copyright 2020, The Authors, published by AIP Publishing LLC. b,c) Partly adapted with permission.[29] Copyright 2014, National Academy of Sciences of the USA.

3.2. Effect of Surface Contamination

High-quality Bi$_2$Te$_3$ thin films do not show aging effects when kept in the UHV system with base pressures in the low $10^{-10}$ to $10^{-11}$ mbar range. Even after several days in UHV, no detectable changes of electronic structure or conductance were observed by ARPES or transport measurements.[20,27,37] This has to be contrasted to reports on bulk TI samples, which show aging effects already within a few hours after cleavage in UHV.[9,13,38] It reveals that the MBE-grown films can be quite inert against small amounts of residual gases.

To study the influence of surface contamination on the TI surface states and conductance, the Bi$_2$Te$_3$ thin films were exposed to a pure oxygen of $1 \times 10^{-6}$ mbar for 10 min. As shown in Figure 7a, the ARPES spectrum shows no effect on the band structure or the position of the chemical potential. Also, XPS measurements (not shown here) do not indicate any change of the Te and Bi core levels upon O$_2$ exposure, which would reveal an oxidation of the surface. These findings are in agreement with other studies by ARPES, XPS, and scanning tunneling spectroscopy,[37,39] but differ from an earlier work where aging effects upon oxygen exposure were reported.[9] Theoretical calculations and simulations argue that a presence of Te vacancies is required for a reaction of oxygen with the Bi$_2$Te$_3$ surface.[40,41] Thus, the inertness of the Bi$_2$Te$_3$ toward oxygen is apparently evidenced for a nearly perfect stoichiometry without Te vacancies at the surface. This also confirms the usefulness of our approach to perform the growth in Te excess and to conduct the annealing in Te atmosphere.

In the next step, the sample was exposed to $1 \times 10^{-2}$ mbar of air for 5 min in the load lock and introduced back into the UHV system. This time, significant changes were observed in ARPES and transport measurements; see Figure 7b,c. Already, the short exposure to air at a pressure far below ambient conditions leads to a shift of the chemical potential by about 50 meV. While the pristine sample has only the TI surface states intersecting the Fermi level, for the air exposed sample, the bulk conduction band moves down, such that its bottom is about 5 meV below the Fermi level and becomes occupied. Although all features of the bands remain intact, this filling of the conduction band clearly changes the conductance of the film. The sheet resistance is reduced by about 200 $\Omega$ after exposure to air. A quantitative estimation of the influence of these extra charge carriers on the film resistance is not straightforward, because the surface carrier mobility will be reduced due to scattering at the adsorbates.[34] The experiments, however, clearly hint toward an
overall reduction of the resistance due to n-type doping caused by air exposure.

When comparing the XPS spectra of the Bi$_2$Te$_3$ thin films before and after exposure to air, the only difference was found to be the appearance of a small carbon peak for the air exposed sample, which is unlikely to cause the band bending effects because of its non-polar character. Less than 1% of a monolayer of adsorbates is sufficient to cause the observed shift of the chemical potential; hence, the amount of the contaminants might be too small to be detected by XPS. As, also, pure oxygen can be ruled out as a source of degradation of the sample surface based on the previous experiment and nitrogen is too inert, water is the most likely candidate to induce the band bending due to its polar character. It should be emphasized that this experiment with the low air pressure, short exposure, and recovery in UHV does not capture the full impact of contamination during ex situ experiments. Thus, the results of real ex situ transport experiments should be affected even much stronger, pointing out the strong need for in situ measurements or protection by an appropriate capping layer for ex situ characterization.

We would like to note that the air exposure has also one welcome side effect, namely, that the appearance of the bulk conduction band due to the surface doping can be used to estimate the indirect bandgap of the Bi$_2$Te$_3$ films. The separation of the bulk valence band and bulk conduction band is \( \approx 145 \) meV consistent with reported experimental and theoretical results.\[^{4,13}\]

3.3. Capping

As not all of the characterization methods can be easily implemented in a UHV system, it is important to develop methods to cap and protect the TI surface states to facilitate ex situ experiments and device fabrication. The surface of Bi$_2$Te$_3$ is naturally Te terminated; thus, Te might be a suitable capping material. Amorphous Te or Se has been already widely used as capping layers for TI materials.\[^{43-46}\] However, it often remains unclear whether the intrinsic topological properties are influenced by the overlayer, but some studies report on alterations of the stoichiometry after the removal of a Te or Se capping layer.\[^{43,44}\]

**Figure 7.** Effect of surface contamination due to exposure to oxygen or air. ARPES spectra of ten QL Bi$_2$Te$_3$ on BaF$_2$ (111) of (a) the pristine sample and after exposure to O$_2$ at \( 1 \times 10^{-6} \) mbar for 10 min and (b) the pristine sample and after exposure to air at \( 1 \times 10^{-2} \) mbar for 5 min. The integrated intensity around \( \Gamma \) is shown for the ARPES spectra in (b). c) Corresponding sheet resistance versus temperature of the pristine sample and after exposure to air. a–c) Partly adapted with permission. Copyright 2014, National Academy of Sciences of the USA.

**Figure 8a** shows the ARPES spectra of a pristine 20 QL Bi$_2$Te$_3$ film, which is covered with one and two unit cells (u.c.) (about 6 and 12 Å) of tellurium. The Dirac cone is still clearly visible after capping. No significant changes of the band structure are observed, indicating that the composition of the sample is not influenced by the capping layer. The surface states are still intact, and also, their filling remains the same. This is remarkable, because the amount of charge carriers with topological properties is only on the order of 0.01 electron per surface unit cell. When the Te capping layer is removed by annealing in UHV, the stoichiometry does not alter as observed by XPS, ARPES, and transport measurements. The resistance of the pristine sample can be recovered after the capping and de-capping procedure; see Figure 8b. Furthermore, we observe that the resistivity decreases gradually but not dramatically for larger thicknesses of the capping layer. The conductivity is, thus, still mainly determined by the surface states of the pristine Bi$_2$Te$_3$. The conductivity of the thin Te layers is, however, larger than expected based on a simple parallel resistance model for which the resistance should be reduced only by a few ohms. One can speculate that this deviation might be caused by screening effects, which might lead to a reduction of the bandgap of the insulating Te layer in proximity to the highly polarizable Bi$_2$Te$_3$ surface.

The quality of the Te layer was found to depend on the Te growth speed. The growth of Te at 1 Å min$^{-1}$ results in an epitaxial, multi-domain layer, as shown by the streaky RHEED pattern in Figure 8c, whereas a higher rate of 8 Å min$^{-1}$ results in a much rougher 3D growth with some polycrystalline contribution as indicated by the spotty RHEED pattern with rings (Figure 8d). The growth mode determines the effectiveness of the capping layer. A 20 unit cell (12 nm) capping layer of ordered Te does not significantly oxidize during a 5 min air exposure and can be fully removed by annealing at 215 °C. The ARPES spectrum and the XPS core levels after de-capping in Figure 9 indicate that the sample surface has essentially the same properties with the pristine sample. This shows that epitaxially grown Te is leakproof against ambient conditions at least for a short exposure. However, a 100 unit cell (60 nm) capping layer of disordered, poly-crystalline Te exhibits a different behavior. The rough
surface of the Te cap seems to be more susceptible to oxidation in air. After the removal of the capping layer at 215 °C from the film, which was exposed to air for 24 h, the ARPES spectrum is blurry, although the Dirac cone is still clearly visible. The XPS measurements reveal the presence of tellurium oxides, such as TeO3, TeO4, or Te(\(\text{OH}\))\(_6\), at about 578 eV binding energy after exposure to air, whereas the Bi core level shows only a tiny change. This indicates that the tellurium oxide is formed by oxidation of the capping layer rather than that of the Bi\(_2\)Te\(_3\) surface. A thin amorphous layer of tellurium oxide seems to remain at the surface after de-capping. We, thus, find that epitaxial Te is a good capping material, which protects the sample against a short exposure to air—new experiments indicate that the exposure to air can be even extended to more than 1 h—and can be fully removed without detectable alteration of the properties of the sample allowing for a reliable ex situ characterization. We would like to add that a recent study on (Bi\(_x\)Sb\(_1-x\))/Co\(_x\) capped with amorphous Te also has shown that the capping can be fully removed after oxidation without changing the properties of the TI.[51]

4. Interfacing Bi\(_2\)Te\(_3\) Thin Films with Ferromagnets

The pursuit for the experimental realization of exotic phenomena, such as the QAHE, has been one of the main focal points of the investigation related to TIs. To this end, the time reversal symmetry, characteristic of TIs, must be broken as to induce a gap at the topological surface states. This can be experimentally achieved by introducing magnetic order in a TI, either by magnetic doping[52–56], or by making use of the proximity effect with a magnetic layer.[31,32,57–65]

The research on the QAHE has been mainly focused on magnetically doped TIs, culminating in its experimental observation, albeit at very low temperatures.[52–54] However, making use of the proximity effect can, in principle, lead to a more uniform magnetization at the interface, which can result in observing the QAHE over a wider temperature range. Here, we would like to infer that ferro- or ferrimagnetic insulators (FIs) are much more promising...
candidates than magnetic transition metals. The relative inert nature of the former makes them more attractive for the use in MBE-grown heterostructures, and, being insulators, one can avoid current shunting in transport measurements.

Here, we report on the interface of Bi2Te3 with EuO (001), Fe3O4 (100), Fe3O4 (111), Y3Fe5O12 (111), and Tm3Fe5O12 (111). EuO is a ferromagnetic insulator with a Curie temperature of 69 K and a large magnetic moment, which makes it an attractive contender for the use in TI/FI heterostructures. Its growth by MBE has been extensively characterized in the recent years,\textsuperscript{[66,67]} but only the top surface but also the interface has also been extensively studied by our group, and Liu et al.\textsuperscript{[68,69]} recently established the optimal growth conditions yielding high-quality films. In addition, Y3Fe5O12 (YIG) and Tm3Fe5O12 (TmIG) are also known for their high Curie temperatures above 860 K and 500 K, respectively. EuO is a good candidate for the use in TI/FI heterostructures. Its growth by MBE has been extensively characterized in the recent years,\textsuperscript{[66,67]} and it was not possible to avoid significant chemical reactions.

4.1. Growth on Various Magnetic Substrates

The magnetic substrates were prepared in various ways: 30 nm thick EuO films were grown in situ on yttria-stabilized zirconia (YSZ) (100) substrates according to the previous studies,\textsuperscript{[66,67]} 30 nm thick Fe3O4 (100) films were grown in situ on MgO (001) substrates following the recipes in the previous studies,\textsuperscript{[68,69]} an Fe3O4 single crystal was grown by floating-zone method and cut and polished along the (111) direction. The substrates were thereafter annealed at 250 °C for 2 h in an oxygen pressure of 1 × 10\textsuperscript{−5} mbar; 16 nm thick TmIG films were grown by off-axis sputtering\textsuperscript{[70,71]} on Gd3Ga5O12 substrates and annealed at 150 °C; YIG substrates were purchased from SurfaceNet GmbH and annealed at 600 °C for 2 h in an oxygen pressure of 1 × 10\textsuperscript{−5} mbar.

To grow Bi2Te3 on EuO thin films, several approaches were attempted. The method described for films grown on Al2O3 (0001) (see Section 2.1) led to a strong reaction between the Bi2Te3 and EuO layers. Further attempts to grow two QLs of Bi2Te3 at room temperature revealed that no strong reactions were present, although this produced an amorphous Bi2Te3 film. This indicates a worse quality of the TI grown on TmIG. Yet, the quality of the thicker films, with six or ten QLs, is similar for all the studied heterostructures.

A subsequent optimization of the growth procedure led to the following recipe: the first two QLS were grown at room temperature, followed by an annealing in Te atmosphere at 240 °C to improve the crystallinity. A second step at 220 °C allowed to grow Bi2Te3 to the desired thickness, keeping the good crystalline quality of the films. This procedure revealed to be quite universal and could also be applied to the growth of Bi2Te3 on Fe3O4 (111), YIG (111), and TmIG (111) without any significant differences in the quality. The RHEED patterns illustrate of the growth of Bi2Te3 on the various magnetic substrates are shown in Figure 12. The panels on the left show the sharp RHEED patterns of the substrates after the cleaning procedure by in situ annealing. The patterns concerning the Bi2Te3 layers (middle and right panels) show streaks indicative of the good crystallinity of the films. An exception should be noted, regarding Bi2Te3 grown on TmIG. For this heterostructure, the RHEED pattern for a two QL film has spots and rings overlapped to the usual streaks. This indicates a worse quality of the TI grown on TmIG. Yet, the quality of the thicker films, with six or ten QLs, is similar for all the studied heterostructures.

XPS and ARPES were used to further characterize the Bi2Te3 layers grown on the magnetic substrates. To investigate not only the top surface but also the interface, XPS and ARPES measurements were performed for two and six or ten QL films. The results are shown in Figure 13 and 14.

The XPS spectra in Figure 13a–c are shifted in energy by 0.06–0.14 eV to overlap with the spectra of the sample grown on Al2O3 (0001). A more detailed discussion on this can be found in the previous study.\textsuperscript{[11]} The Te 3d and Bi 4f spectra of two QL Bi2Te3 show, for all the heterostructures, a slightly altered line shape. This is much more prominent for the film grown on Fe3O4 (100), as shown in Figure 13d. The shoulders located at higher binding energies of both Te 3d and Bi 4f spectra are indicative of Bi–O and Te–O bonds at the interface. It is important to note, however, that no signs of strong chemical reactions between the layers were found, and no metallic Bi or Bi and
**Figure 11.** RHEED patterns of 30 nm Fe$_3$O$_4$ (100) (left), three QL Bi$_2$Te$_3$ grown on top of it at 160 °C (center), and ten QL Bi$_2$Te$_3$ (right). Taken at 20 keV electron energy for Fe$_3$O$_4$ and at 15 keV for Bi$_2$Te$_3$. Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY).[32] Copyright 2020, The Authors, published by AIP Publishing LLC.

**Figure 12.** RHEED patterns of the two-step growth of Bi$_2$Te$_3$ on magnetic layers a) YIG (111), b) TmIG (111), c) Fe$_3$O$_4$ (111), and d) Fe$_3$O$_4$ (100). Taken at 20 keV electron energy for Fe$_3$O$_4$ and at 15 keV for the other materials. Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY).[31] Copyright 2020, The Authors, published by American Physical Society.

**Figure 13.** Te 3d and Bi 4f XPS spectra of two (black) and six QLs (green) Bi$_2$Te$_3$ grown on a) YIG (111), b) TmIG (111), c) Fe$_3$O$_4$ (111), and d) Fe$_3$O$_4$ (100). The spectra of a reference sample of ten QL Bi$_2$Te$_3$ grown on Al$_2$O$_3$ (0001) are shown in orange. Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY).[31] Copyright 2020, The Authors, published by American Physical Society.
Te oxides were identified. Finally, for the thicker films (six or ten QLs), all the line shapes are identical to those of the reference sample.

Figure 14 shows the ARPES spectra for Bi$_2$Te$_3$ grown on the various magnetic substrates. Once again, we show the thickness-dependence of the spectra, and we observe that the topological surface states are present for all the heterostructures. For the thinner films, the surface states are visible on top of a strong background, with contribution from the bulk conduction band. This is similar to previous reports,[27] where the surface states of a Bi$_2$Te$_3$ thin film start to form at a thickness of two QLs. The highly insulating TmIG substrate, together with the poorer quality of the thin TI layer grown on top of it, might explain the impossibility of performing ARPES measurements for such a thin layer. For all the heterostructures, as the thickness increases, the bulk contribution is suppressed, and at a thickness of six to ten QLs, the Fermi level intersects only the topological surfaces states. This is not only a promising indication of the quality of the films, but also demonstrates that the top topological surface states remain intact. The Dirac cone angles are very similar for all the samples, and the Dirac point is located between 0.11 and 0.15 eV, which is in agreement with the samples grown on non-magnetic substrates (see Figure 6a,b). The surface states for the film grown on YIG (Figure 14a) have a rather low intensity, but the Dirac cone angle is still consistent with the remaining samples. The Bi$_2$Te$_3$ layers grown on Fe$_3$O$_4$ (100), Fe$_3$O$_4$ (111), YIG (111), and TmIG (111) have, therefore, consistently high quality, and the characterization techniques used here let us conclude that the quality of the TI is comparable to that of films grown on BaF$_2$ (111) or Al$_2$O$_3$ (0001).

The excellent structural quality of Bi$_2$Te$_3$, Bi$_2$Se$_3$, or (Bi$_x$Sb$_{1-x}$)$_2$Te$_3$ layers grown on YIG (111) has been reported in the literature.[58–62,64,65] RHEED, AFM, and XRD/X-ray reflectivity measurements indicate the good quality of these heterostructures, and scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy has shown that there are no chemical reactions occurring at the interface. High-angle annular dark-field/high-resolution transmission electron microscopy (HRTEM) studies also revealed that a reasonably clean and sharp interface is possible to attain.[59,61,64] There are
considerably fewer reports of TI/FI heterostructures involving TmIG (111). However, these also indicate an excellent structural quality of the TI layer, without the presence of interfacial defects or additional phases, as confirmed by RHEED, AFM, and HRTEM.\textsuperscript{[63,65]} Finally, and to the best of our knowledge, there are no other reports on the use of Fe\textsubscript{3}O\textsubscript{4} as a magnetic layer in thin-film heterostructures. Our investigation emphasizes that the quality of a ten QL interface might be of a poorer quality, as indicated by the Bi–O and Te–O shoulders in Figure 13d.

4.2. Transport Properties of TI/FI Heterostructures

The properties of the heterostructures of Bi\textsubscript{2}Te\textsubscript{3} grown onto Fe\textsubscript{3}O\textsubscript{4} (100), Fe\textsubscript{3}O\textsubscript{4} (111), TmIG (111), and YIG (111) were carefully investigated by transport measurements. All the samples used for the ex situ transport measurements studied in this section were capped with 12 nm of epitaxial Te to avoid contamination from the exposure to air (see discussion in Section 3.2 and 3.3).

Figure 15 shows the sheet resistance as a function of temperature for all the heterostructures. For Bi\textsubscript{2}Te\textsubscript{3}/YIG (111) in Figure 15a, the typical TI metallic-like behavior is observed, with the resistance decreasing with lowering temperature and a minimum at \(\approx 8\) K. The TI grown on TmIG (111) (Figure 15b) has a substantially different behavior, with the resistance increasing by one order of magnitude. Considering that both substrates are substantially different behavior, with the resistance increasing by one order of magnitude. Considering that both substrates are highly insulating, no significant differences should be expected, and they are attributed to the worse structural quality of the TI/TmIG interface, as evidenced by the RHEED pattern in Figure 12b. In contrast to the other magnetic substrates investigated, magnetite undergoes a first-order phase transition, the so-called Verwey transition, at which the resistivity shows a jump of about two orders of magnitude at \(\approx 124\) K. This transition is also observed for the heterostructures of the TI grown on Fe\textsubscript{3}O\textsubscript{4} (111) and (100) (Figure 15c,d). For temperatures above the transition, the substrate dominates the transport properties, such that the total resistance increases as the temperature decreases. In contrast, at temperatures below the transition, the more conducting TI layer dominates the transport.

The magnetoconductance measured at 2 K for all the heterostructures, as well as a reference sample grown on Al\textsubscript{2}O\textsubscript{3} (0001), is shown in Figure 16a. For all the films, a cusp at low magnetic fields is observable, indicative of the predominance of the weak anti-localization (WAL) effect. This can be modeled by the Hikami–Larkin–Nagaoka (HLN) equation,\textsuperscript{[73]} given by

\[
\Delta G_{xx} = \alpha \frac{e^2}{\pi h} \left[ \ln \left( \frac{B}{B_0} \right) + \psi \left( \frac{1}{2} + \frac{B}{B} \right) \right] + \beta B^2
\]

where \(\Delta G_{xx} = G_{xx}(B) - G_{xx}(0)\), \(\alpha\) is a pre-factor, which describes both weak localization (WL) \((\alpha_{WL} < 0)\) and WAL \((\alpha_{WAL} = 1/2\) per independent topological transport channel), \(B_0 = h/(8\pi e l_f^2)\), \(B\) is the applied magnetic field, \(l_f\) is the phase coherence length, \(\psi\) is the digamma function, and \(\beta\) is the coefficient of the magnetic field. \(\alpha, l_f,\) and \(\beta\) are used as fitting parameters of the HLN equation.

The fitting parameters for the measurements at 2 K are included in Table 1. The parameters for ten QL Bi\textsubscript{2}Te\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} (0001) show the expected results for a TI thin film. The value \(\alpha \approx 0.51\) indicates that the top and bottom conducting channels are coupled through bulk carriers, forming one conducting channel.
channel.\textsuperscript{[74]} $\phi$ has a relatively high value, similar to previous studies on Ti thin films.\textsuperscript{[58,75,76]} For the Ti grown on Fe$_3$O$_4$ (100) and (111), only one set of $\alpha$ and $l_\phi$ was used due to the similar phase coherence length of the WAL and WL contributions. In this case, no clear separation can be made while fitting, and the resulting $\alpha$ is then a combination of $\alpha_{\text{WAL}}$ and $\alpha_{\text{WL}}$. A more detailed discussion can be found in the previous study.\textsuperscript{[31]} The heterostructures grown on YIG and TmIG, on the other hand, can be described by two sets of $\alpha$ and $l_\phi$. We note, however, that a negative magnetoresistance was not observed for any of the heterostructures, contrary to Bi$_2$Se$_3$ grown on YIG in the previous study.\textsuperscript{[65]}

The suppression of the cusp-like shape observable in Figure 16a for all the heterostructures, and especially the suppression of $\alpha$ for the Ti grown on Fe$_3$O$_4$ (111), as well as the WL observed for TIs grown on TmIG and YIG are in agreement with a possible gap opening at the topological surface states, caused by the magnetization of the TI at the interface. The more rounded shape of the magnetoconductance for Bi$_2$Te$_3$/Fe$_3$O$_4$ (111) at low magnetic fields results in a less viable fit. Yet, and as the XPS measurements did not indicate any chemical reactions at the interface, the suppressed phase coherence length might also be a consequence of the proximity with the magnetic substrate.

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Figure 16b–d summarizes the Hall measurements, for which a linear background, corresponding to the ordinary Hall effect, was subtracted for all the figures. No AHE was observed for the TI grown on Fe$_3$O$_4$ (100). Adapted under the terms of a Creative Commons Attribution License 4.0 (CC-BY).\textsuperscript{[31]} Copyright 2020, The Authors, published by American Physical Society.

### Table 1. Summary of the parameters obtained from the HLN fit at 2 K for films with six QLs of Bi$_2$Te$_3$ on various magnetic layers. We note that the fits were performed using fields up to 3000 Oe, except for Fe$_3$O$_4$ (111), where fields only up to 500 Oe were used.

| Material       | $\alpha_{\text{WAL}}$ | $l_{\phi,\text{WAL}}$ | $\alpha_{\text{WL}}$ | $l_{\phi,\text{WL}}$ | $R^2$ |
|----------------|-----------------------|------------------------|-----------------------|------------------------|-------|
| Al$_2$O$_3$ (0001) | 0.51                  | 437                    | –                     | –                      | 0.999 |
| Fe$_3$O$_4$ (100) | 0.39                  | 111                    | –                     | –                      | 1.000 |
| Fe$_3$O$_4$ (111) | 0.50                  | 70                     | –                     | 0.983                  |       |
| TmIG (111)      | 0.50                  | 183                    | –0.47                 | 59                     | 0.999 |
| YIG (111)       | 0.50                  | 383                    | –1.00                 | 33                     | 0.998 |

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which might be caused by the dead magnetic layer that has been reported to form on the surface of these films. The increased noise level of the AHE for the film grown on TmIG might be related to the relatively disordered interface as observed by RHEED of the two QL Bi$_2$Te$_3$ layer; see Figure 12b.

The reported values of the anomalous Hall resistance are between 0.1–2Ω, similar to those reported for (Bi$_2$Se$_{1-x}$Te$_x$)$_2$ films grown on TmIG but higher than the ones reported for Bi$_2$Se$_3$ on TmIG. This might be explained by the increased contribution from the bulk conductivity in Bi$_2$Se$_3$, which suppresses the AHE. The more bulk-insulating Bi$_2$Te$_3$ and (Bi$_2$Se$_{1-x}$Te$_x$)$_2$Te$_3$, thus, show an enhanced AHE.

The suppression of the WAL effect and the observation of the AHE for the TI/FI heterostructures indicate the presence of ferromagnetism induced by the magnetic proximity effect between the TI and a magnetic layer, which opens a small gap at the topological surface states. This gap has been predicted to be quite small, below ppm level, not to overwhelm the topological effects. In addition, band bending effects due to doping at the surface can lead to additional topologically trivial conducting states in the surface region. The surface doping as a result of, for example, contamination or adsorption has to be well below 1% of the surface density.

MBE using Te-distillation conditions has been shown to allow for a preparation of high-quality Bi$_2$Te$_3$ thin films. The optimized films are bulk-insulating and show pronounced topological surface states. The choice of the substrate is, however, a compromise. BaF$_2$ (111) has a good lattice match, but a rough surface and other substrates such as Al$_2$O$_3$ (0001) have an epi-polished, smooth surface, but a large lattice mismatch causing structural winning and rotational stacking. Thus, the development of a reliable polishing procedure for BaF$_2$ surfaces would be a great benefit for the growth of Bi$_2$Te$_3$ films with even less structural defects.

Using a slightly modified growth procedure, Bi$_2$Te$_3$ films can also be grown on magnetic substrates such as magnetite and iron garnets with no or minimal chemical reactions at the interface. Transport measurements indicate a gap opening at the topological surface states due to magnetization of the Bi$_2$Te$_3$ induced by the magnetic proximity effect as suggested by a suppression of the WAL effect and the observation of the AHE. Hence, the heterostructures of TIs and magnetic oxides offer a promising playground for further studies.

Due to high sensitivity to air exposure and susceptibility to changes of the composition due to capping layers, it is preferable to keep the samples continuously in UHV for an investigation of the intrinsic properties. However, also carefully developed capping procedures, e.g., with tellurium can be implemented, facilitating ex situ experiments and device fabrications building the basis for an experimental observation of the theoretically predicted quantum phenomena and a possible implementation in future applications.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

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