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Taking topological insulators for a spin

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Chapter 7

Taking topological insulators for their spin: A feasibility study

The experiments reported in this thesis are all directed towards using Bi-based topological insulators as a platform for various applications. However, the progress in understanding phenomena in topological insulators is still ongoing, such that applicability of these materials is difficult to consider yet. Nevertheless, I would like to give an overview of the possibilities of topological insulators in commercial applications. Rather than calling it a 'valorization' chapter, I want to use the term 'feasibility' since the novel properties of topological insulators still require a lot more investigation before one can even think about real applications. In the first part of this chapter, I will discuss the requirements and the implications for producing topological insulators on a large scale. After that, I will discuss the applicability of topological insulators for commercial purposes where I will provide an outlook with respect to the experiments reported in this thesis, in addition to what has been discussed in earlier chapters.

7.1 Production of topological insulator materials

For topological insulators to be used on an industrial scale, one has to look for growth methods to fabricate large-area topological insulator films of which the electrical properties are reproducible and uniform over larger areas of several inches. Furthermore, effects of producing topological insulators on the environment will be discussed as this will become more important in the future.

7.1.1 Mining and purification of raw materials

A first step in the production of topological insulator materials is to inventorize the elements' reserves worldwide and to explore the costs of mining and purification. Most of the topological insulator materials studied so far contain elements including Bi, Sb, Se, and Te[1]. I will discuss the abundance of those elements here, mainly based on studies by the U.S. Geological Survey National Minerals Information Center [3]. The prices of the purified compounds are obtained from Fisher Scientific per August 2017, which give an indication of the intensity of the purification process.

The abundance of Bi in the Earth's crust is about 0.08 ppm by weight, making it two times more abundant than gold, but for example $\sim 10^7$ less abundant than silicon [4]. Bi is mainly obtained from refining process residues in obtaining copper and lead, rather than directly from its ore [5]. It is estimated from the reserves of lead that the reserves of Bi are about 370,000 tons, whereas about 10,000 tons is currently produced every year. This makes the reserves sufficient for another 35 years under current production. Since Bi is obtained as a byproduct, the price of raw Bi is relatively low (around 10 \$/kg; prices can grow when the scarcity increases). In the more purified form, Bi costs between 1400 \$/kg (99.99%) and 6000 \$/kg (99.999+%), reflecting the high costs and intensity of the purification process. Interestingly, Bi has become more popular being a nontoxic substitute for lead and thus obtaining Bi as byproduct of lead is maybe not so feasible anymore in the future. This might change the methods of mining and refining of Bi in the coming years. This is enhanced by the fact that lead is currently the main component in current car batteries, which might change with the rise of electrical cars. However, bismuth minerals are present in insufficient quantities to realize commercial mining at the moment[2]. Recycling of Bi is difficult since it is being used in small amounts for applications (e.g. solders) thereby scattering the Bi in small amounts.

Sb is currently the main component for flame retardants and for alloying with lead in batteries, which makes Sb easier to be recycled than Bi. This yields recycled Sb to contribute ∼15% to the total consumption of Sb in the United States. Sb is mainly obtained from its own ore, but can be obtained as a byproduct from copper and lead production too. Currently, about 130,000–140,000 tons Sb per year is mined, whereas the reserves are estimated to be around 1,500,000 tons (0.2 ppm by weight), and might last for another ten years. The current market price of raw Sb is about 8 \$/kg, whereas purified Sb costs between 1700 \$/kg (99.999%) and 2900 \$/kg (99.9999%).

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[1] A nice overview of topological insulators found/predicted up to 2013 can be found in the review paper by Ando [1]. It was further reported that it is possible to find topological insulators in naturally-occurring minerals, too [2].

[2] This is included in the aforementioned abundance, but not in the estimate for the reserves.

Currently, Se is mostly used for (de)coloring glass and as a catalyst in electrolytic cells for Mn winning such as to reduce the operating power. Furthermore, Se is a human dietary supplement as well as for livestock and is promising for battery applications [6]. Some recycling is being done on earlier photocopiers and electronics where Se had the role of photoconductor and photoreceptor (nowadays it has been replaced with Si or organics). However, for the rest of Se, the use is quite scattered such that recycling is difficult. Se is mainly obtained as a byproduct of refining mostly copper (also lead and nickel) and therefore its supply depends mainly on the copper production. Furthermore, it depends on the request for Mn due to the catalytic properties of Se, which has decreased over the last years. In 2016, the refinery production was around 2,200 tons and the reserves are estimated to be about 100,000 tons (0.05 ppm by weight[3]), giving possibilities for new applications for another 45 years. The price of the raw material varies between 40 and 70 \$/kg and the more purified version costs about 1500 \$/kg (99.999%).

Te is also mainly refined from byproducts in copper and lead production, but Bi_2Te_3 ores also exist in nature. Te is mainly used for CdTe solar cell production and for thermoelectric applications. Recycling of these products is possible, but is currently very small because those products are relatively new. The world production of Te in 2016 was estimated to be about 400 tons while the reserves are estimated on 25,000 tons (0.001 ppm by weight), making it abundant for another 60 years. The price for Te is about 34 \$/kg and in the more purified version the costs are between 1200 \$/kg (99.999+%) and 3800 \$/kg (99.9999+%).

7.1.2 Environmental impact

The described elements above are generally considered to be toxic when humans are exposed to it via inhalation or oral exposure [information obtained from [7–12]]. There is an increased health risk for workers active in the production process of those elements (mining, refining, etc.) and from the abundant (Se) amounts in food which is dangerous when too high quantities are consumed. Such exposures can be easily prevented by improving the safety regulations and protection of the workers and by regulations on food, respectively. Furthermore, care has to be taken that the electrical compounds are well sealed such that the consumer exposure is minimal. Environmental effects based on toxicity for Bi and Te are unknown, but for Sb and Se it is known that it easily pollutes the soil or waters which can affect animals on a local scale [11]. Therefore, it is good to monitor the concentrations of these elements in the soil and ground water to minimize pollution around the production site.

However, the main impact of these elements on the environment is by the production process itself. In 2008, Nuss and Eckelman conducted a life cycle assessment of most of the metals consumed nowadays [13]. First, the authors point out that, based on a report by Graedel et al. [14], recycling rates of the studied 'specialty metals' are rather low: 1–10% for Sb and $< 1\%$ for Bi, Te, and Se. This is due to the fact that such metals are usually integrated in complex products in small amounts and therefore it is difficult to extract those metals for recycling in an economically viable way. Furthermore, products become more durable, i.e. longer lifetimes, and therefore

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[3] Part of which is stored in coal that is difficult to commercially refine at the moment.

recycling shows a low rate. This finding implies that the production of Bi, Sb, Se, and Te has to mainly come from primary production, in agreement with the studies by the U.S. Geological Survey National Minerals Information Center.

As the assessment by Nuss and Eckelman further indicates, the purification and refining of these metals are the most energy-intensive steps in the production process and often require many fossil-fuel-related processes that yield a large CO_2 production already, except for Sb which is mainly a environmental burden by its mining. Looking at the cumulative energy demand to produce the metals (especially for Bi and Te), it can be seen that energy needed for production is relatively high compared to common metals such as Ti, Al, Fe, Cu, and Co. For Sb and Bi, although not produced in large amounts, the global warming potential is already rather high and requires investigation on the environmental impact of producing future devices. However, for future device applications only small amounts of the elements are needed (unless there will be an application on the 'Si scale') such that energy costs and environmental impact per product might be relatively low[4].

7.1.3 Large-area growth

For industrial applications, large-area growth of topological insulator films is required. One obvious candidate to grow such films is by MBE where it is possible to grow topological insulator on wafers up to 3 inch in diameter, as shown in the thesis by Brahlek [15]. Although relatively large wafers can be coated, the required ultra-high vacuum in these systems and the desired low defect density limit the growth rates of the material at the moment (the growth rate is about 1 nm per minute with the settings used in [15]). In GaAs thin-film growth by MBE, many advances have been made where thickness deviations over a 3-inch wafer were already found to be less than 1% in the 1980s [16]. Additionally, multiwafer systems were introduced in the 1990s which then could coat 8,000 4-inch wafers per year [17]. Such upscaling for topological insulators has not been reported yet and the effect of an increase in growth rate on the sample performance is to be investigated. This performance should be benchmarked on the mobility, the charge-carrier density, and corresponding Fermi level position of the system in order to maximize the surface-state contribution for novel applications. As discussed in section 2.4.1, high mobilities can be realized by MBE growth now and is promising for future applications. However, one important limitation is the choice of the substrate and its preparation to reach such record-high properties in Bi-based topological insulators [18]. For example, using Al_2O_3 substrates yields a large defect density and buffer layers are required prior to the growth of Bi_2Se_3. However, the alternative substrate CdS(0001) could resolve the need of a buffer layer, where reasonably high mobilities and a Fermi level inside the bulk band gap were reported when directly grown on that substrate [19]. CdS is a semiconductor with a band gap of $\sim$2.5 eV and a resistivity of 10^7 Ω cm, showing that the influence on the transport properties are supposed to be small. Importantly, it seems difficult to grow topological insulators as interlayers in more complex device architectures and thus should these materials be the starting point/layer of a device geometry.

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[4] One kilogram of Bi can span 10,000 m^2 when a layer of 10 nm is grown, such that the number of devices per amount of Bi might be large.

Other growth techniques, that for example have been used for thermoelectric applications (see also section 7.2.2), produce bulk crystals which yield an arbitrary shape, a low mobility, or a high charge carrier density. Chemical vapor transport growth can yield larger-area films but lack uniformity, although it has the benefit of growing on any arbitrary substrate.

7.1.4 Conclusions

Summarizing, production of topological insulators on an industrial scale requires various considerations. The abundance of some of the elements is limited to 10 to 20 years, based on the current request and known reserves. These numbers can change depending on the request, which might give rise to opening of new mines that suddenly become commercially viable. Based on the current numbers, a long-term business model might be problematic, additionally with regard to the limited recycling rates of the elements that are below 10%. The average costs of $\sim$2000 \$/kg as well as the relatively high environmental impact are mainly related to thorough purification and refining of the elements, whereas the running costs of the actual growth of topological insulators have not yet been considered in this study. The actual growth of topological insulators is at the moment limited by the growth rate of these materials and more understanding is needed on the effects on charge transport by increasing growth rates and changing substrates.

7.2 Applicability of topological insulators

In the experimental chapters of this thesis, I have touched upon (several aspects towards) various potential applications of topological insulators which I would like to discuss here in a bit more detail. Based on the results, I will explore the possibilities of using topological insulators for commercial applications with a low power consumption.

One point of consideration is the behavior of topological insulators when implemented in a larger architecture being connected to different materials. In chapter 3, we have investigated the interface between various metals (for contact leads) and Bi-based topological insulators. Due to the high electron affinity of Bi_2Se_3 and the high electronegativity of the terminating Se layer, it has been theoretically proposed that a charge-accumulation layer is present at the interface with a metal. This will yield Ohmic contacts that are required for low-dissipative device applications. However, hybridization of the metal's states with those of a topological insulator could mask novel properties in the charge transport around the contacts. This problem would require a separation layer (for example a tunnel barrier) that could increase the interface resistance in turn, leading to an increase in power dissipation in future devices. Although this has theoretically been proposed, the hybridization at the interface between a *bulk* metal layer and the topological insulator is difficult to investigate with surface-sensitive techniques such as ARPES and would require transport measurements to elucidate the performance of the surface-state channels. In addition, the potential landscape at the bottom surface, where the material is in contact with a substrate, is unknown. This leads to uncertainty in the performance of the bottom surface which could affect transport through the top surface. One obvious method to investigate the charge-transport properties of the several channels is by studying Shubnikov–de Haas oscillations, as shown in chapter 5. However, the interpretation of the oscillations coming from different channels is scattered in literature, where often limited data due to limitations in the magnetic field are shown to distinguish the various channels. Furthermore, the location of the surface states (top or bottom) is unknown and can be only distinguished in a dual-gate device, which is hampered in turn by the limited possibilities of substrates yielding high-quality growth of topological insulators. Theoretical understanding of the interplay of the different states could contribute to the interpretation of the oscillations from which we for example encountered difficulties to observe a second surface state (and mainly domination by the bulk).

In the efforts to probe the barrier at an interface between a topological insulator and a metal (chapter 3), we observe no clear indication of an interface barrier which would be in line with theoretical proposals and yield transparent interfaces. However, some of the experiments are inconclusive and apparent barriers could be related to fabrication-related issues or limited wetting of the metal under consideration on the topological insulator surface. Nevertheless, beyond our experiments there are hardly reports that point towards non-Ohmic behavior at the interface. One practical issue, as observed throughout the optimization of fabrication recipes for the devices, is that the adhesion between metals and topological insulators is generally poor and requires adhesion layers such as Ti or Cr. Furthermore, Bi_2Se_3 is a soft material and can therefore be easily damaged. This would require an in-situ-grown capping layer that is beneficial for protection of the material against (environmental) doping at the same time. If these issues can be overcome then it is worth to look into potential applications.

7.2.1 Spintronic applications

Our main motivation to study topological insulators is their interesting ambipolar charge-carrier spin texture at the interface where the momentum is locked to the spin orientation of the carriers. This property is strongly protected by the material's topology and yields a decrease in backscattering, enhancing the mobility[5]. The system has a lot of potential for spintronic applications because a spin accumulation can be generated and detected by application of a current bias rather than using ferromagnetic layers to obtain a spin-polarized current. Such a generation of spin current has the advantage that it is unaffected by environmental effects, such as stray fields as is the case for adjacent ferromagnetic layers. Therefore, it allows for further miniaturization of for instance a spin-based field-effect transistor [20], but is bound by a critical minimum thickness at the same time [21]. In addition to the miniaturization possibilities, a full spin polarization of the surface-state charge carriers in topological insulators was predicted, i.e. every out-of-equilibrium charge carrier has the same spin orientation. This would mean that, compared to conventional ferromagnetic layers

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[5] It is to be noted that in Bi-based topological insulators the mobility is only on the order of 2,000 cm^2/Vs (except for some recent results) and that the enhancement is only relative; no high-mobility channels are automatically created.

(with polarizations usually up to ∼40%), spin Hall systems (being 3D systems [22]), and Rashba–Edelstein systems (having a partial cancellation of the spin texture), topological insulators could set a new standard for spin injection. However, the spin polarization is lower as pointed out by Hong et al. An angular-averaging factor has to be included since transverse components contribute to the total charge current (see also section 6.2.2). This gives rise to a maximum polarization of $2/\pi$ [23], but is further reduced by spin–orbit interaction effects to about 50% [24]. Nevertheless, such (ideal) values of spin polarization produced by the topological insulator's surface states are still quite high. Another advantage besides the large spin polarization could be the fact that topological insulators are less metallic compared to ferromagnetic metals, which could be beneficial to partly overcome the conductivity mismatch problem [25]. This conductivity-matched spin injection can be furthermore enhanced by eliminating any bulk contributions, leading to an increase in both the resistance and the surface-state contribution to the spin polarization. However, this gain would have to be weighed against the larger dissipation of the material and requires materials with a higher mobility to compensate for decreasing the charge-carrier density in order to keep the resistivity low.

As discussed in chapter 6, we have tried to detect this spin polarization in sign and magnitude using a ferromagnet contact as detector. Although we have shown that the origin of the observed charge-current-induced, magnetization-dependent voltages in our experiments is unknown, the values for surface-state spin polarization vary between 1.5 and 15%. Here, we take into account unknown factors including the ferromagnet's polarization and the exact ratio between surface states and bulk states. Nevertheless, the higher value seems to correspond well with other reported values for Bi_2Se_3, but in counterdoped compounds with a higher surface-state contribution the spin polarization is unexpectedly lower compared to metallic Bi_2Se_3. A better understanding of the corrections to the ideal case such as the values of the ferromagnet's (tunnel) spin polarization and the bulk and surface-state contributions to the charge transport is needed to determine the actual surface-state spin polarization. Such an understanding can give a reason for the poor performance of the counterdoped compounds, too. Furthermore, the temperature dependence of the spin voltage is an interesting direction for a more detailed investigation since different dependencies are reported. One way to partly overcome such uncertainties is by employing a nonlocal geometry where charge current and spin current can be separated. In this way, most of the spurious effects are removed and an external spin valve can be used to determine the spin polarization of the ferromagnets (see section 6.5).

Provided that the spin polarization of the topological surface states is reasonably large, such materials can be employed for spin-torque-induced magnetization switching in for example magnetoresistive random-access memory (MRAM) [26][6]. Such spin-transfer torque MRAM (STT-MRAM) elements have the advantage that they can be easily downscaled and have a lower power consumption with respect to the earlier generations of MRAM. These advantages come from the different mechanisms that switch the magnetization of the free ferromagnetic layer that serves as the memory element within a magnetic tunnel junction structure. In the earlier generations

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[6] The technology of MRAM is still under development towards commercial applications, mainly because of the relatively large power consumption [27].

of MRAM, a pair of 'bit' lines switch the magnetization of the free magnetic layer by Oersted fields that are generated by application of large current densities ($\sim 10^6$ A/cm^2, depending on the properties of the magnetic layer [28]). Besides the large power consumption, downscaling is limited because too closely packed elements could be influenced by adjacent Oersted fields. Furthermore, in order to generate Oersted fields with smaller strip lines, a larger current density is needed. These issues can be resolved by STT-MRAM where magnetization can be switched by the torque that spins from the first ferromagnetic layer can exert on the ferromagnet's magnetization[7]. This 'direct' way of switching the magnetization is proposed to be more convenient than switching by Oersted fields. The effectiveness comes from the requirement of a smaller current density and further downscaling is possible since such switching depends on the current density rather than the current (as for the Oersted fields)[8]. Furthermore, spin-transfer torque could lead to a new generation of current-tunable oscillators operating at the GHz regime under a static magnetic field and can be useful for wireless on-chip communication [26]. However, this current-controlled switching still shows a considerable inefficiency due to the large power consumption relative to the intrinsic energy of the magnetic state to be competitive in the future [27]. Therefore, the large spin polarization in topological insulators can play a role in order to further lower the required current density to switch the magnetization and can lead to more efficient spin–orbit-torque-based components [30, 31].

It has been shown that topological insulators can exert a torque on a ferromagnet's magnetization by Mellnik et al. [32], where a spin–orbit torque in a Bi_2Se_3/Py heterostructure was measured at room temperature. The spin-torque ratio (the torque strength per unit of charge-current density) in Bi_2Se_3, although shunted by the bulk, has been shown to be an order of magnitude larger than in heavy metals such as Pt and Ta that are relying on the spin Hall effect[9]. Furthermore, it has been reported that the Oersted-field effect is negligible and that the Rashba–Edelstein effect from trivial surface states due to band bending, if at all present, does not dominate the signal when Py is used[10]. A subsequent report where bulk-insulating samples have been used shows an even higher spin-torque ratio [36], mainly due to the suppressed bulk contribution to the charge current. Around the same time, Fan et al. have reported current-induced magnetization switching of a (soft) magnetic topological insulator [37]. It has been shown that current densities below $\sim 10^5$ A/cm^2 are needed to switch the magnetization of the magnetic topological insulator that has a rather low anisotropy field and is only present at temperatures below 10 K. The spin-torque ratio has been found to be another order of magnitude higher at low temperatures compared to the result by Mellnik et al. In a subsequent paper by the same group [38],

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[7] Spin-torque-transfer phenomena are unwanted for future read heads in hard-disk drives, though [26].

[8] It is to be noted in a recent paper that Joule heating could assist an easier switching of the magnetization [29].

[9] Spin Hall effects in a disordered system such as Bi_2Se_3 are expected to be small since such an effect will only occur at the boundary within the mean free path length from the surface [33]. However, there are indications by a recent work that the spin Hall effect from off-stoichiometric materials can exert a strong spin torque on a ferromagnet [34].

[10] However, the exact dispersion of the topological surface state at the interface with a ferromagnet has been theoretically questioned [35].

it has been further reported that the spin–orbit torque from the two nonequivalent surfaces can change the magnetization within the Cr-doped topological insulator itself where the magnetic anisotropy as well as the torque strength can be tuned by an electric field[11]. Although only possible at low temperatures, magnetic topological insulators could therefore serve as magnetic memory element too, but the difference in current between read and write might be an issue. More recently, Han et al. have shown room-temperature switching of a magnetic layer with perpendicular magnetic anisotropy [39], paving the way towards real applications. In this work, it has been further noted that the power consumption is lower than that for spin-Hall-metal-based switching. The outperformance of topological insulators compared to spin Hall metals and Rashba–Edelstein systems makes topological insulators a promising candidate for spin–orbit-torque-MRAM (SOT-MRAM) applications.

One important consideration, as mentioned in the works above, is that the resistance of the topological insulator is relatively high compared to that of ferromagnetic metals, such that main part of the charge current will be shunted through the ferromagnetic layer. Therefore, it is suggested that spin–orbit torque between topological insulators and ferromagnetic insulators should be studied since this will lower the power consumption in future devices. Another point of consideration will be thermoelectric effects as well as Joule-heating effects that originate from the resistive topological insulator and that can interfere with the difference between the reading and writing current of the bits. This will be especially an issue for surface-dominated films where the bulk charge-carrier density is relatively low and the mobility only moderate. Therefore, the balance between power consumption (bulk insulation will yield higher dissipation) and the spin-torque ratio (bulk insulation will yield a larger spin torque) has to be examined.

The actual response time can be extracted from the group velocity of the charge carriers, similar to what has been done in the work by Kastl et al. [40]. From ARPES measurements it is observed that the Fermi velocity for Bi_2Se_3 is $\sim 5 \times 10^5$ m/s which yields response times on the order of ps when the feature size (including leads) is about 1 µm, allowing to perform (spintronic *and* electronic) operations in the THz regime that is supported by ultrafast relaxation dynamics as discussed in chapter 4. However, spintronic operations might be limited to the response time of the magnetic element which depends on the magnon velocity [27][12].

Another potential application of topological insulators is that of spin detection where a spin current is injected into the topological surface states, giving rise to a voltage build-up. Such an effect can be compared with the inverse spin Hall effect in heavy metals and the inverse Rashba–Edelstein effect in for example Ag/Bi systems [22,41]. This spin-to-charge conversion in topological insulators is mainly studied by spin pumping experiments in the group of Saitoh [42,43]. It is found that the bulk states affect this conversion through spin scattering, as predicted from the short mean free path [33]. This yields a reduced spin accumulation in the surface states and ad-

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[11] The actual size of the torque strength has been debated recently by Yasuda et al. [29].

[12] This does not hold for spin-based field-effect transistor because no magnetic states are switched in logic operations [27].

ditionally a negligible inverse spin Hall effect[13]. Furthermore, the generated charge current is easily shunted by the bulk and therefore room-temperature detection using the topological surface states that have a high selectivity is fairly impossible. Upon lowering the temperature, bulk-insulating samples get a more pronounced surface-state contribution. Now, an inverse Rashba–Edelstein length[14] of 0.25 nm at 10 K can be obtained (0.03 nm at room temperature [46]). These values are similar to the model system Ag/Bi at room temperature. More promising topological insulators for the purpose of spin detection are α-Sn and strained HgTe, showing the highest inverse Rashba–Edelstein lengths at room temperature reported so far [47, 48]. Another alternative is switching back to the quantum spin Hall insulator [49] but this requires careful gate control and low temperatures at the moment. Depending on the spintronic device geometry, one has to consider whether the resolution of the spin-to-charge conversion is large enough for realizing a clear on/off-state.

7.2.2 Thermoelectric applications

The studied Bi-based topological insulator materials have been subject of research for thermoelectric applications for decades. Thermoelectrics can be used to generate voltages from heat gradients (and vice versa) and one can think of for example conversion of waste heat from industrial applications or from smaller device structures [50]. Materials suitable for thermoelectrics require a large Seebeck coefficient, a large electrical conductivity, and a low thermal conductivity, yielding a high figure of merit ZT. A large electrical conductivity can be realized from narrow band-gap materials with a relatively high mobility. A higher charge-carrier concentration could lead to improvement additionally but will give rise to a decrease in the Seebeck coefficient. Furthermore, by using heavy elements, the thermal conductivity can be reduced due to a suppression of the phonons which are usually the main contributors to the thermal conductivity. These requirements make Bi-based topological insulators promising to study for thermoelectric applications and, indeed, compounds such as p-type $\mathrm{Bi}_x\mathrm{Sb}_{2-x}\mathrm{Te}_{3-y}\mathrm{Se}_y$, $\mathrm{Bi_2Te_3}$, and $\mathrm{Sb_2Te_3}$ and n-type $\mathrm{Bi_2(Se}_y\mathrm{Te}_{1-y})_3$ are currently used in modern devices that operate at room temperature [51, 52]. The next step is to investigate whether it is possible to use topological insulators for both thermoelectric as well as spintronic applications at the same time.

In order to improve the figure of merit, thin films of crystalline topological insulator compounds can yield an increase in the phonon relaxation due to boundary scattering by the decreased dimensions [52], while preserving good electrical and topological properties. However, as pointed out by Hor et al. [53], the crystallinity gives rise to a larger thermal conductivity in bulk crystals at the same time and the competition between miniaturization and crystallinity has to be investigated. It has to be noted that the thermal conductivity is larger in the plane of the film compared to the conductivity parallel to the surface normal due to a larger lattice scattering. Increased lattice scattering can further be realized by introducing fine grains which leads to an

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[13] However, by limiting the thickness of the topological insulator, one can observe the (bulk) inverse spin Hall effect in $\mathrm{Bi_2Se_3}$ at room temperature [44, 45]. The size of the effect differs considerably between the two experiments.

[14] The ratio between the generated 2D charge current and the injected 3D spin current. This length can be calculated from the velocity of the charge carriers and the scattering time [22].

increase in ZT of Bi_2Se_3 [54]. However, this can eventually lead to destruction of the topological phase [55]. Another possibility of improving ZT is by increasing disorder in the unit cell via alloying binary compounds such as Bi_2Te_3 and having defects in the crystal, which could lead to an improvement of the thermoelectric properties too. However, this will affect the Seebeck coefficient and the conductivity at the same time where the conductivity is being only partially compensated by weak antilocalization effects of the surface states.

Enhancements in ZT via the topological properties have been theoretically predicted by using ultrathin films such that the top and bottom surface hybridize with the cost of losing the novel surface states [56]. Experimental work by Kim et al. has been performed to investigate the power factor σS^2 around the Dirac point (no hybridization), including the conductivity σ and the Seebeck coefficient S [57]. Enhancement of the power factor has been observed around the Dirac point, but it yields a small correction to the best-known bulk power factors for Bi_2Se_3. Similar results have been obtained by using $Bi_xSb_{2-x}Te_{3-y}Se_y$ nanowires (to reduce the phonon scattering) [58], but the absence of an electrostatic gate made it impossible to enhance the power factor when the Fermi level is close to the Dirac point.

In summary, the competition between disorder to improve ZT and crystallinity to probe the topological surface states with reasonably high mobility and low charge-carrier density seems to make it difficult to find high-end topological-insulator-based applications on the border of spintronics and caloritronics. Nevertheless, due to the high Seebeck coefficient in these materials, heat gradients can generate and control the spin accumulation in these materials. Such effects allow for spintronic components that do not require application of a charge current, but rather use heat to generate a spin accumulation. The efficiency of such applications depends on other material parameters such as the thermal conductivity and the physical properties of the environment including substrates or other layers in the stack with for example different Seebeck coefficients. Importantly, heat gradients can affect the charge-current-induced spin polarization too; an effect that has not been studied or considered yet. Understanding heat-related phenomena in topological insulators is crucial to evaluate the efficiency of spintronic devices based on these materials.

7.2.3 Applications for optics

Optically accessing the surface states of topological insulators provides a means to tune their charge and spin-transport properties and allows for future device applications linking optics (photonics) with electronics and spintronics. The initial proposal to study the effect of optical excitation on the transport is based again on spin–momentum locking. It has been proposed that upon excitation with helical light a specific spin species could be excited, which would lead to a resulting photocurrent due to the created spin imbalance. Such photocurrents are expected to move fast, due to the high Fermi velocity, and show relaxation times on the order of picoseconds which make topological insulators ideal for (room-temperature) THz applications. Such an effect could already lead to implementing topological insulators for fast photodetectors of circularly polarized light without the need of a bias [40]. As discussed in this work, the current performance is orders of magnitude worse than that of

GaAs photodetectors. This is attributed to the interfering bulk, which gives room for improvement by for example investigating bulk-insulating compounds. Another interesting consequence of the photogalvanic effect is that a charge current and corresponding spin current can be modulated. By exciting surface-state charge carriers with a certain spin species into the bulk states, a flowing charge current in the topological surface states can be enhanced or suppressed depending on the direction of the generated photocurrent. In this way, helical light can act as a gate in an electrical transistor based on a topological insulator. Furthermore, when the topological insulator is used as a spin generator, helical light can tailor the spin polarization without having to change the applied current, which is useful if the speed of a spintronic device is limited by the electrical modulation of the charge current. In addition to that, it has been shown that spins can be modulated by optical means due to the strong spin–orbit coupling in this material [59], which can improve the control over the spin polarization. However, at the moment the sensitivity to light is rather low. In the experiments reported in chapter 4 as well as in literature, helicity-dependent photocurrents on the order of nA are generated while using reasonable fluences at room temperature, even in bulk-insulating films. Another point of attention is the scalability of optically-gated devices since this is limited by the laser's spot size, as also pointed out by Wunderlich et al. [60].

Besides these issues, it has been reported that a lot of other (bulk-related) effects can interfere with the photogalvanic effect described in chapter 4, which might affect the reliability of future devices. Furthermore, the current understanding of the actual photogalvanic effect in topological insulators is limited, such that it is unclear how to enhance the efficiency of such devices. Relaxation dynamics of excited charge carriers will play an important role in resolving such issues to realize devices similar to the spin Hall effect transistor [60].

Another application using optics worth mentioning is the local control of the electrostatic potential by incident light, which can be realized in two ways. The first method is to optically induce electrical polarization in a $SrTiO_3$ substrate where the semi-transparent topological insulator is grown on, which can be reversibly tuned by UV light and red light [61]. Such electrostatic gating has the advantage that it does not require any supply of voltage and is persistent for over ten hours. Furthermore, the optical control of the local potential can be very convenient when the topological insulator is capped with other semi-transparent layers where an electrical lead might not be possible. This idea can be extended by creating magnetic domains locally via laser-induced lowering of the coercivity such that the writing field of that local domain is lower than the field to switch the magnetization of the full layer [62]. In combination with the current-induced magnetization switching of magnetic topological insulators as described earlier such a magnetic topological insulator can be used for memory applications. Here, writing and erasing can be performed by a combination of laser illumination and application of a current in the topological insulator to switch the magnetization locally. Another method to change the electrostatic potential at the top surface is by inducing a surface photovoltage by light sources that are commercially available [63]. Such photovoltages give rise to an electrostatic potential difference that can be read out by an ARPES-like method. In this way, data can be stored with the memory elements that consist of patches of topological insulator and are stable over several hours. However, a clear erasing procedure is missing at the moment such that the memory elements are inactive until relaxed, but its relatively short lifetime does not make it useful for data storage either. Similar to the optical induction of electrical polarization, this tool can be convenient for local gating applications.

7.3 Conclusions

The interesting properties of Bi-based topological insulators could yield interesting device applications at the border of optics, electronics, and spintronics. Optimizing such materials for thermoelectric applications while maintaining the good topological insulator properties is rather complicated due to the competition between crystallinity and disorder. However, there might be different caloritronic effects in combination with different materials that are worth studying to enhance device performance. Although the potential of the discussed device geometries is high, a full understanding of the material system with its multiple transport channels is lacking and therefore estimates on the device performance are challenging. The distinction between bulk and surface-mediated contributions due to very growth-specific effects requires more investigation, partially due to the limited experimental techniques available.

Another challenge is the energy-intensive refining and purification of the elements needed to construct topological insulators, leaving a considerable environmental footprint at the moment compared to production of common metals. The size of such a footprint cannot be very easily estimated since real device schemes have been hardly proposed. In addition to that, the abundance of some of the commonly used elements for topological insulators is low and necessitates a survey to find new reserves of such elements. Furthermore, searching for new topological insulators or similar phases of matter could open up new possibilities. The moment that a commercial phase is reached depends on experimental and theoretical efforts to understand the interplay between the different transport channels as well as investigations to maintain the growth quality while the throughput is increased.

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