The challenge of parasitic bulk doping in Bi-based 3D topological insulator materials is still omnipresent, especially when preparing samples by molecular beam epitaxy (MBE). Here, we present a heterostructure approach for epitaxial BSTS growth. A thin n-type Bi$_2$Se$_3$ (BS) layer is used as an epitaxial and electrostatic seed which drastically improves the crystalline and electronic quality and reproducibility of the sample properties. In heterostructures of BS with p-type (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ (BSTS) we demonstrate intrinsic band bending effects to tune the electronic properties solely by adjusting the thickness of the respective layer. The analysis of weak anti-localization features in the magnetoconductance indicates a separation of top and bottom conduction layers with increasing BSTS thickness. By temperature- and gate-dependent transport measurements, we show that the thin BS seed layer can be completely depleted within the heterostructure and demonstrate electrostatic tuning of the bands via a back-gate throughout the whole sample thickness.

I. INTRODUCTION

Three-dimensional topological insulators (3D TIs), are predicted to feature helical topological surface states (TSS) with linear dispersion and time reversal symmetry protection $^{[1-4]}$. Experimentally, the first 3D TI was realized in Bi$_{1-x}$Sb$_x$ $^{[5]}$, sparking a vast amount of research especially around a whole family of mostly Bismuth-based compounds. The alloy Bi$_2$Se$_3$ (BS) was quickly identified as a promising member of this family. However, while ab-initio calculations showed a prototypical TI band structure $^{[6]}$, angle-resolved photoemission spectroscopy (ARPES) measurements consistently revealed the Fermi energy ($E_F$) to lie in the bulk conduction band because of donor-type Selenium vacancies and/or Se$_{BS}$ anti-sites $^{[7,8]}$. Electronic transport experiments are therefore often dominated by bulk states, making the full utilization of the unique TSS characteristics challenging. The presence of parasitic bulk conduction is generally shared by all Bi-based compounds and the strategies to counteract this issue have been multifold. Successful compensation of unintentional dopants has for example been achieved in single crystalline Bi-Sb-Te-Se solid solutions grown by the Bridgman technique, resulting in suppressed bulk conduction and surface dominated transport $^{[9]}$.

Next to the Bridgman method a widely spread approach to grow crystalline 3D TI samples is molecular beam epitaxy (MBE) that provides crucial advantages for many experimental and possible technological applications. For example, MBE offers quick adjustment of alloy stoichiometries, precise control of sample thickness down to single layers and the capability of in-situ preparation of hybrid devices with well defined interfaces, all while possibly opening a way to wafer-size scalability. However, sample quality has lacked behind significantly compared to other preparation methods and while the issue of parasitic bulk conduction due to structural disorder has not been conclusively solved, research especially concerning the promising quaternary alloy (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ (BSTS) has stalled.

In this contribution, we investigate MBE-grown BS/BSTS heterostructures within a vertical p-n-type concept. We show that BS acts as an excellent seed layer for epitaxial BSTS preparation already reducing unintentional doping due to improved crystallinity. Furthermore, we deliberately tune BSTS into a slight p-type regime via its stoichiometry and use the intrinsically n-type BS to create a band bending within the heterostructure by compensation of opposite excess charges. In a systematic study, we investigate the transport properties of such heterostructures grown on SrTiO$_3$ (STO) and provide a recipe for a highly reproducible growth of BS/BSTS with minimized bulk conduction as-grown. Depending on the respective BS and BSTS thickness, we observe a strong suppression of trivial bulk conduction of the BS layer and a separation of the topological surface states. The choice of highly dielectric STO furthermore allows us to tune the electronic properties of the samples via back-gating leaving the top surface unoccupied for potential surface experiments or interfacing in hybrid devices.
II. EXPERIMENTAL

All samples presented in this work were grown by molecular beam epitaxy. The characterization by ARPES was performed at 77 K with a spot-size of 150 µm and a photo energy of 36 eV for maximum photoemission intensity of the surface states with respect to bulk states. The ARPES samples were protected from oxidation by removable selenium capping layers. The samples for magnetotransport measurements were capped in-situ by 7 nm Al₂O₃. All magnetotransport measurements were carried out at 4.2 K, utilizing a standard 4-point, low-frequency lock-in technique in a Hall bar geometry with the magnetic field applied perpendicular to the film. The Hall bar has a width of w = 20 µm and a length of l = 300 µm. The obtained sheet resistance is defined as 
\[ R_S = \frac{U_{xx}}{I_x} \]
where I is the applied current and \( U_{xx} \) the measured longitudinal voltage. For electrostatic back-gating a voltage was applied between the sample and the bottom of the chip carrier with the STO substrate acting as a dielectric barrier. For additional front-gating the samples were covered by an insulating bilayer of 30 nm SiO₂ and 100 nm of AlOx and a gold electrode.

III. RESULTS

A. BS as seed layer

For Bi-based TI alloys, the optimization of growth quality is crucial since the electronic properties are largely governed by unintentional doping caused by lattice defects. The most widely investigated MBE-grown 3DTI is Bi₂Se₃. Its tetradymite crystal structure is built up by quintuple layers (1 QL ≈ 1 nm), with weak van der Waals (vdW) interlayer bonding between QLs, enabling successful growth on a variety of substrates via vdW epitaxy and high crystallinity was achieved by precise optimization of growth conditions. MBE of related ternary (e.g. Bi₂(Se₁₋ₓTeₓ)₃ or (Bi₃Sb₁₋ₓ)₂Te₃) and especially quaternary compounds like BSTS has been less intensively studied. Expanding the alloy complicates the growth procedure, it increases the amount of atomic disorder naturally occurring in those systems and reduces the amount of suitable substrates since a large lattice mismatch induces crystal defects.

Investigating epitaxial preparation of BSTS directly on the STO(111) substrate, we were unable to find a reliable and reproducible regime of sole single-crystalline order and routinely observed patterns with poly-crystalline features in reflective high energy electron diffraction (RHEED) imaging during growth, as exemplarily shown in Fig. 1h for 6 QL BSTS with \((x/y) = (70/90)\). Using a BST seed layer (Fig. 1b) lead to improvements, but caused 3D features in the RHEED pattern. In addition, different substrates or BSTS stoichiometries compel an adaptation of growth parameters. Introducing a BS seed layer, however, facilitates the growth of high-quality BSTS films, independently of its stoichiometry and the used substrate. Surprisingly, even a single BS layer acts as a highly oriented vdW seed and is sufficient to ease the vdW epitaxy of subsequent BSTS. The protocol to grow the BS seed layers is as follows: saturating the substrate surface by Se at 190 °C for 150 s, growing the BS layers while ramping the substrate temperature from 190 °C to 250 °C within the first 2 QL, followed by annealing under constant Se-flux at 290 °C. At the BSTS growth temperature of 255 °C, the RHEED pattern shows pronounced oscillations and no indication of 3D or poly-crystalline features. Next to STO(111) (see Fig. 1), this protocol has successfully been applied to a variety of substrates, also beyond the common (111)-orientation, without requiring to change the growth protocol. Figures 1c-e exemplarily show RHEED patterns of TI samples (right) and the respective substrate (middle), demonstrating single-crystalline growth on Al₂O₃(0001) (c), GaAs(111) (d), and even disordered C(111) (f). In addition, successful growth was achieved on Al₂O₃ (11-20), GaAs (001) and InP(111).

Crucial for the electronic properties, we found BS to also function as an "electrostatic seed" layer. Selenium vacancies and Se_Bi anti-sites lead to a large bulk donor level in BS, as shown in Fig. 2a) 8,12,13. This pins the Fermi level to the bulk conduction band. It therefore reproducibly fixes the starting point for subsequent layers to an n-type foundation independent of the used substrate. BSTS growth directly on a substrate lead to strong variations of the samples’ electronic properties even for constant stoichiometry. Since the interface potential between sample and substrate is susceptible to minor fluctuations of growth conditions, a controlled positioning of \( E_F \) in the band gap throughout the complete sample thickness has proven to be challenging. Hence, the epitaxial and the electrostatic seed layer functional-
ity of BS dramatically improved the quality, controllability, and especially the reproducibility of crystallographic and electronic sample properties, as we will demonstrate in the following.

B. Heterostructure concept

While the implementation of a BS seed layer proved to be highly favorable for epitaxial BSTS preparation, its prevalent bulk donor level potentially adds a large contribution to the overall bulk conductance of the bilayer. On the other hand, (Bi$_{1-x}$Sb$_x$)$_2$(Te$_{1-y}$Se$_y$)$_3$ allows an engineering of key band structure features, especially the fine tuning of the effective donor to acceptor ratio via the stoichiometric parameters $x$ and $y$ [14,17]. Based on a test series, we chose $x = 70 - 74\%$ and $y = 87 - 91\%$, aiming to maximize the BSTS band gap while creating a slight acceptor surplus (Fig. 2b). A heterostructure with the hence p-type BSTS and n-type BS generates a bending of the system’s electronic bands [15,20], schematically pictured in Figs. 2c)-e). For very thin BSTS, opposite excess charges begin to compensate, but the effect is too small and the Fermi level stays above the conduction band minimum (CBM) (Fig. 2c), as is revealed by ARPES on a heterostructure with 1 QL BS and 3 QL BSTS in Fig. 2f)ii), where an occupation of the bulk conduction band can be observed. Increasing the BSTS thickness enhances the band bending until $E_F$ is pulled below the CBM into the energy gap at the top surface (Fig. 2d ii). The color grading towards iii) in Fig. 2d) indicates the evolution of the shift when increasing the BSTS thickness. This behavior is verified by ARPES in Fig. 2f)iii) and iii). Ideally, at some point, the band bending is sufficient to pull $E_F$ into the band gap almost throughout the whole heterostructure by completely depleting the BS layer (Fig 2e). It is important to stress that while our ARPES measurements follow the trend expected for this thickness-dependent band bending, they only image the energy bands at the very surface of the sample. Electrical transport properties, however, are governed by the complete band structure throughout the whole sample thickness. In the most general case, illustrated in Fig. 2d), the sample can be divided into three segments contributing to transport: a semiconductor-like channel (semiC bulk) where $E_F$ lies in the band gap, a trivial, metal-like bulk channel (m-bulk) for $E_F$ intersecting the conduction band and the non-trivial top and bottom TSS (t-TSS, b-TSS).

C. Magnetotransport characterization

To study the contributions of these channels to electronic transport, systematic BSTS thickness series are investigated with 1, 2 and 4 QL of BS seed layers, in the following referred to as 1+x, 2+x and 4+x series, with the BSTS thickness $x$ reaching from 2 to 43 QL. Figures 3a)-c) show the temperature dependence of the normalized sheet resistance $R_S^{\text{norm}}(T) = R_S(T)/R_S(300\,\text{K}) - 1$ for the three series. The different transport contributions manifest in the measurements due to their different temperature dependencies. For the semiconductor-like channel, activated carriers freeze out upon reducing the temperature and $R_S$ increases. The trivial metal-like bulk conduction and the TSS, on the other hand, act like metals: $R_S$ decreases towards lower temperatures due to the reduction of electron-phonon scattering [21]. The competition of these three transport channels as a function of BSTS thickness is observed for the 1+x (Fig. 3a) and 2+x (Fig. 3b) series. Similar to many observations in bulk conducting TIs, the thinnest samples show a strict metallic behavior due to $E_F$ lying above the conduction band edge, corresponding to Fig. 2c). As expected from the sketch of Fig. 2d), this trivial metallic contribution gradually diminishes with growing BSTS thickness, leading to the semiconductor-like contribution beginning to dominate $R_S(T)$ at high temperatures. For the thinnest samples of Figs. 3a) and b) $R_S$ increases to about 120 K, before a small metallic decrease is observed. This behavior has been reported for fully bulk compensated TIs. There, the drop of $R_S$ at low temperatures is ascribed to dominant TSS transport [9,15]. A stark contrast is presented by the $R_S(T)$ behavior of the 4+x series in Fig. 3c). Here, the thicker BS layer leads to a trivial metal-like bulk channel large enough to dominate transport for all BSTS thicknesses in the complete temperature range. These observations are confirmed by plotting the conductivity $\sigma$ at 4.2 K versus the total sample thickness $t_{\text{tot}}$ (Fig. 3d). All three series show a significant decrease of $\sigma$ with increasing $t_{\text{tot}}$. The dashed line is obtained from the $y$-intercept of the linear fit of the 1+x series in the $1/t_{\text{tot}}$ depiction (inset) and therefore represents the bulk conductivity of BSTS in the limit of $t \rightarrow \infty$ [22]. We find a comparatively low value of $\approx 2500 \, \text{S/m}$. This non-zero bulk conductivity is commonly ascribed to randomly distributed charge puddles and thermally activated carriers from acceptor and donor levels [17,23,20]. Any offset from the dashed line is expected to mainly stem from a trivial bulk contribution caused by the BS seed layer or TSS conduction. The 1+x series (blue circles) approaches the asymptote slightly more quickly than the 2+x samples (red squares), but for thicknesses above $\sim 20$ QL both curves begin to converge. Again, the 4+x series (grey triangles) provides a contrast in showing a significantly larger conductivity for all thicknesses. These observations confirm the conclusions already drawn from the $R_S(T)$ measurements: Using 4 QL of BS induces a large metal-like bulk channel. It dominates the $R_S(T)$ behavior and also substantially contributes to the overall conductivity of all samples at 4.2 K. With 1 QL or 2 QL a qualitatively different behavior is observed: For sufficient
FIG. 2. Schematic band structure and density of states (DOS) of dopant levels in BS (a) and BSTS (b). c) Heterostructure concept: depending on respective BS and BSTS thicknesses, band bending is introduced within the bilayer, leading to different sizes of metal-like (m-bulk) and semiconductor-like (semiC) bulk contribution additional to conduction of top (t-TSS) and bottom (b-TSS) topological surface states. f) ARPES at 77 K imaging the band bending evolution for samples of 1 QL BS and 3 (i), 6 (ii) and 12 QL (iii) BSTS. The horizontal black dashed line represents the Fermi level. The black dashed triangles are a guide to the eye to the position of the t-TSS.

BSTS thickness (> 20 QL) the BS contribution seems to become negligible, yielding almost identical conductivity very close to the value of bulk BSTS. This indicates that we have approached the ideal case of Fig. 2e).

To further characterize the samples, we applied a perpendicular magnetic field B. Figures 4a) and b) compare the absolute magnetoresistance $MR(B) = R_B(B) - R_B(0\,T)$ at 4.2 K of the 1+ and 4+ series. In all measurements a characteristic cusp-like, positive MR around zero magnetic field is observed, commonly described to stem from weak anti-localization [27]. Transport mediated by TSS in TIs is expected to be especially sensitive to this effect, due to their spin helicity and the arising $\pi$ Berry phase [27, 28]. Applying a perpendicular magnetic field breaks time-reversal symmetry and therefore lifts the enhanced delocalization, causing an increase of sample resistance with magnetic field. In addition to the cusp-behavior around zero field, a transition to quadratic or linear behavior at higher magnetic fields is often reported in TIs. Whereas the quadratic behavior is widely accepted to stem from 3D bulk conduction [21], the linear MR is subject to more discussion. In the measurements of Figs. 4a) and b) we never observe signatures $\sim B^2$, again indicating the absence of a sizeable 3D bulk contribution in all our samples. In the 4+x series (Fig. 4b) the MR approaches a linear regime above $\approx 2.5$ T. In contrast, for 1 QL seed layer (Fig. 4a) the cusp-behavior prevails in the complete investigated field range. To explain the origin of such a linear MR (LMR) mainly two models have been proposed: The quantum model of Abrikosov yields an LMR as consequence of linear dispersion, which could link the observation to the linearly dispersive surface states of TIs [29]. The classical model by Parish and Littlewood, however, shows an LMR to emerge in inhomogeneous two dimensional trivial conductors [30, 31]. Since we only observe an LMR in the 4+x series, we conclude the classical model to be a more likely explanation. As evaluated above, 4 QL of BS seed layer lead to a significant, but very thin, metal-like bulk conduction channel largely dominating transport. In the framework of Parish and Littlewood, this channel could be subject to LMR that superimposes with the cusp-like WAL behavior of the TSS. This metallic bulk contribution could furthermore serve as an explanation for the strikingly smaller overall magnetoresistances observed in the 4+x series. It acts as a channel parallel to the TSS and therefore reduces the ratio of transport channels underlying weak anti-localization effects.

For a more detailed analysis of the WAL signature observed in TIs, the theory of Hikami, Larkin and Nagaoka...
(HLN) is commonly applied in the literature to fit the measured data with

\[ \Delta G_{\text{HLN}}(B) = \frac{e^2}{\pi h} \left[ \psi \left( \frac{h}{4eB\ell} + \frac{1}{2} \right) - \ln \left( \frac{h}{4eB\ell} \right) \right], \]

assuming \( \Delta G(B) \approx 1/R_S \) and \( \Delta G_{\text{HLN}}(B) \approx \Delta G(B) \equiv G(B) - G(0) \). Since \( \Delta G(B) \) is directly obtained from the magnetoresistance measurements presented in Fig. 4a), it is important to note that it is, in general, not free from bulk contributions that may not underlie weak anti-localization. The origins and signatures of such additional contributions to MR, as well as their influence on HLN accuracy, need to be subject to a more thorough investigation. In the above equation, \( e \) is the elementary charge, \( h \) Planck’s constant and \( \psi \) the digamma function. The free fit parameters are the phase coherence length \( \ell \) and the dimensionless pre-factor \( \alpha \).

The simplectic case of the HLN theory, distinguished by strong spin-orbit coupling and the absence of magnetic scattering, is usually associated to topological insulators. It is expected to yield a value of \( \alpha = -0.5 \) per independent parallel channel contributing to conduction. Figure 4c) exemplarily shows the HLN fits (white dashed line) to \( \Delta G \) in the 1+ series, demonstrating a very good agreement of the theory and the measured data within \( \pm 1 \text{T} \).

The \( \alpha \)-values for all three series obtained from this fit interval are plotted as a function of the respective BSTS thickness \( t_{\text{BSTS}} \) in Fig. 4d) and a striking resemblance, independent of the seed layer, is observed. For small \( t_{\text{BSTS}} \), \( \alpha \) starts around a value of -0.5, before an increase sets in, approaching -1 above 20 QL. For the smallest BSTS thickness we expect the Fermi level to lie above the conduction band edge throughout the complete heterostructure (see upper inset). Hence, the whole sample effectively acts as one conducting channel and \( \alpha = -0.5 \) is expected. It has furthermore been suggested that below a thickness of approximately 10 QL, \( \alpha = -0.5 \) would even be expected for separated channels due to coupling of top and bottom TSS mediated by tunneling or hopping [33, 34]. This could explain the simultaneous increase in all three series to start around this threshold. The approach of \( \alpha = -1 \) above 20 QL then suggests a true separation of two independent conduction channels.

Contrary to a common interpretation, our data shows that \( \alpha = -1 \) not necessarily allows to conclude a completely insulating bulk, where the TSS at top and bottom each contribute -0.5 to \( \alpha \). We have shown that the 4+ series clearly shows significant bulk conduction for all BSTS thicknesses. However, our analysis indicates that with increasing \( t_{\text{BSTS}} \) the upper TSS still decouples from this bulk channel regardless of seed layer thickness. The lower inset of Fig. 4d) illustrates this more general case with the bottom TSS in direct contact with bulk states and a separated top TSS. In Ref. [28] it has been theoretically predicted that this configuration can also yield \( \alpha = -1 \).

In addition to optimization of as-grown electronic prop-

\[ \text{FIG. 3. Sheet resistance as a function of temperature normalized to room temperature of 1+ (a), 2+ (b), and 4+ (c) series. d) Conductivity of all three series versus total sample thickness. The inset shows the 1+ series versus } 1/t_{\text{tot}} \text{ and a linear fit (light blue dashed line). The y-intercept yields the asymptote (black dashed line) in the main figure.} \]

\[ \text{FIG. 4. Magnetoresistance at 4.2 K for the 1+ (a) and 4+ (b) series. c) HLN fits (white dotted lines) to } \Delta G(B) \text{ for the 1+ series. d) } \alpha \text{ values from HLN fits for all three series versus BSTS thickness at 4.2 K. The insets show band structure sketches for different BSTS thicknesses corresponding to the evolution of } \alpha. \]
FIG. 5. Normalized sheet resistance against back-gate voltage at 4.2 K for the 4+x series (a) with a zoom-in for the thickest samples (b) and the 1+x series (c). (d) Dual-gated measurement of sheet resistance for sample 1+40. The white dashed line is a guide to the eye along the maximum of $R_{S}^{norm}$.

In this study, we have presented an approach to band structure engineering of 3DTI thin films by means of epitaxial MBE growth. Introducing down to a single QL BS seed layer lead to a significant improvement of the BSTS growth quality drastically reducing structural disorder and therefore reducing unintentional bulk doping. By varying the respective thicknesses of the n-type BS and p-type BSTS we were able to substantially tune the as-grown electronic properties of the heterostructures and disentangle the different contributions to the electronic transport of the occurring channels by temperature-,
magnetic field-, and gate-dependent measurements. We have shown that the p-n-type architecture of our samples leads to a compensation of opposite excess charges, culminating in a complete depletion of metal-like bulk conduction for 1 QL BS seed layer and a BSTS thickness above 20 QL. By applying the theoretical framework of Hikami, Larkin and Nagaoka [32], we observed a gradual formation of two separated conduction channels with increasing BSTS thickness, independent of the seed layer thickness, revealing a decoupling of at least the top-TSS from bulk states. The chosen STO substrate allowed the application of back-gating that was shown to be capable of modifying the samples’ electronic properties throughout the whole thickness. This tuning capability, without occupying the top surface, in combination with the decoupling of the top TSS, is particularly attractive for surface experiments or the implementation in hybrid devices.

ACKNOWLEDGMENTS

We acknowledge the financial support of the Deutsche Forschungsgemeinschaft through project ID 422 31495032-SFB1277 (subproject A01). We thank Magdalena Marganska, Klaus Richter, Cosimo Gorini, and Michael Barth for fruitful discussions.

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sample was brought to room-temperature to reset both gates and the procedure was repeated with the back-gate being set into negative direction. Due to this required reset of the gates a small discrepancy between the measurements for positive and negative back-gate direction is unavoidable. To account for this, the $R_S$ values for positive back-gate voltage were shifted by 3.3 V front-gate in Fig. 5d).