Protective capping of topological surface states of intrinsically insulating Bi$_2$Te$_3$
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We have identified epitaxially grown elemental Te as a capping material that is suited to protect the topological surface states of intrinsically insulating Bi$_2$Te$_3$. By using angle-resolved photoemission, we were able to show that the Te overlayer leaves the dispersive bands of the surface states intact and that it does not alter the chemical potential of the Bi$_2$Te$_3$ thin film. From in-situ four-point contact measurements, we observed that the conductivity of the capped film is still mainly determined by the metallic surface states and that the contribution of the capping layer is minor. Moreover, the Te overlayer can be annealed away in vacuum to produce a clean Bi$_2$Te$_3$ surface in its pristine state even after the exposure of the capped film to air. Our findings will facilitate well-defined and reliable ex-situ experiments on the properties of Bi$_2$Te$_3$ surface states with nontrivial topology.

Topological insulators (TI) form a novel state of matter. They have an electrically insulating bulk, simultaneously, they have a necessarily metallic surface. The surface states have massless Dirac dispersions, and the charge carriers are protected from back-scattering by time reversal symmetry. These properties make TI promising for advanced spintronic applications as well as for the realization of novel quantum particles.

At present, it is very difficult to experimentally measure the topological surface states without being disturbed by signals from the bulk or surface impurities in materials such as Bi$_2$Se$_3$ and Bi$_2$Te$_3$. This is mainly because the Fermi surface enclosed by these surface states forms only a small fraction of the surface Brillouin zone, therefore, the number of charge carriers with interesting topological properties is only of the order of a few $10^{12}$ cm$^{-2}$. This, in turn, sets a very strict constraint in that the concentration of impurities at the surface must be much less than 1%, furthermore, the concentration of defects in the bulk has to be well below the ppm level depending on the thickness of the material.

Recently, we have been able to prepare Bi$_2$Te$_3$ films, using molecular beam epitaxy, whose conductivity is dominated by the surface. Growth, structural characterization using reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED), electronic structure determination by angle-resolved and X-ray photoelectron spectroscopy (ARPES and XPS, respectively), and resistivity measurements were all performed in-situ under ultrahigh vacuum (UHV) conditions. We found that the chemical potential straddles through the surface states and lies inside the bulk band gap, implying that the surface is metallic and the bulk is a good insulator.

Separately, we also discovered that exposure to tiny amounts of air (water) causes the bulk conduction band to get filled with electrons. As a result, the conductivity increases and is no longer determined by the surface states alone. Therefore, to facilitate ex-situ experiments and fabricate devices using the nontrivial properties of surface states, methods need to be developed to cap and protect these surface states. Some studies have attempted to use amorphous Se or Te as a capping material. However, it remains unclear whether the intrinsic properties of the surface states have
been affected. One thing that was clear was that the stoichiometry of the films has been altered after the removal of the capping material.\(^8,9\)

In this study, we report on the use of epitaxially grown Te as a capping material. Our strategy is to deposit the material under UHV conditions in a layer-by-layer fashion and monitor the properties of the Bi\(_2\)Te\(_3\) film, especially those of the surface states using in-situ XPS, ARPES, and conductivity measurements. We also tested whether the Te capping can be removed to restore the Bi\(_2\)Te\(_3\) film with the surface states in their pristine condition and whether this can also be achieved after the exposure of the capped film to air.

Bi\(_2\)Te\(_3\) thin films of typical 20 QL (quintuple layer; 1 QL \(\sim 1\) nm) were grown using molecular beam epitaxy (MBE) under UHV conditions (low 10\(^{-10}\) mbar) on insulating epi-polished and vacuum-annealed BaF\(_2\)(1 1 1) substrates. The details of the growth conditions for the Bi\(_2\)Te\(_3\) films and the experimental setup can be found elsewhere.\(^5\) Te capping was conducted in steps, resulting in a Te overlayer thickness of 1 u.c.(unit cell, \(\sim 6\) Å), 2 u.c (12 Å), 5 u.c. (30 Å), 10 u.c. (60 Å), and 20 u.c. (120 Å). The Te flux rate was set to 1 Å/min with the Bi\(_2\)Te\(_3\) film kept at room temperature.

The RHEED and LEED patterns of a pristine 20 QL Bi\(_2\)Te\(_3\) film for different thicknesses of Te capping are shown in Fig. 1. The LEED of the noncapped sample shows three-fold symmetry as expected for single-domain Bi\(_2\)Te\(_3\). Upon capping with 1 and 2 u.c. Te, additional RHEED streaks and LEED spots appear. The features are sharp, and with the three-fold symmetry still clearly visible in the LEED, we can conclude that the Te overlayer can be epitaxially grown on the Bi\(_2\)Te\(_3\) film. For thicker Te films, e.g. 5 and 20 u.c., multiple LEED patterns appear, and the features become less intense compared to the background. Nonetheless, they remain sharp, as seen in the LEED photographs taken with 26 eV electrons as shown in Fig. S1 of the supplemental material.\(^10\) These observations indicate an epitaxial but multidomain growth mode for thicker Te overlayers, this is probably related to the 1.6% lattice mismatch between Te and Bi\(_2\)Te\(_3\) and the need to relax the strain in the Te overlayer.

XPS measurements reveal very narrow and symmetric Te 3d and Bi 4f core level lines for the pristine Bi\(_2\)Te\(_3\) film, as indicated by the red curve in Fig. 2. With increasing Te thickness, the intensity of the Bi 4f core level decreases without any changes in the line shape or energy position. This decrease is exponential with the 1/e value of 22 Å (\(\sim 3.8\) u.c.), which well fits the typical mean free paths of 1-1.5 keV photoelectrons,\(^11\) indicating that the Te capping forms rather flat overlayers without too many pinholes. The Bi of Bi\(_2\)Te\(_3\) is also chemically not affected by the Te capping. The Te 3d line develops a shoulder at around 0.8 eV higher binding energies upon the deposition of the Te overlayer. This shoulder can be attributed to elemental Te.\(^12\) The 12 nm thick (20 u.c.) Te capping fully suppresses the Bi\(_2\)Te\(_3\) signal; only the elemental Te 3d\(_{3/2}\) and Te 3d\(_{5/2}\) peaks are visible at \(\sim 583\) eV and \(\sim 573\) eV, respectively.

Figure 3(a) shows the ARPES spectra using He I light (21.2 eV) taken along the \(\bar{\Gamma} - \bar{M}\) direction of the pristine 20 QL thick Bi\(_2\)Te\(_3\) film at room temperature and the corresponding spectra with capping layers of 6 Å (1 u.c.) and 12 Å (2 u.c.). One can clearly observe the Dirac cone and the

![Image](image_url)

**FIG. 1.** RHEED and LEED patterns of a pristine 20 QL Bi\(_2\)Te\(_3\) film and the same film at different stages (1 u.c. \(\sim 6\) Å, 2 u.c., 5 u.c. and 20 u.c.) of Te capping. The electron energy is set at 17.5 keV for RHEED and 52 eV for LEED measurements.
topological surface states for the three measurements. Most importantly, for all steps of Te deposition, the Fermi level (zero binding energy) intersects with the surface states only and not with the bulk valence band nor with the bulk conduction band of the Bi$_2$Te$_3$ film. This indicates that surface states of the pristine film are not affected by the Te capping, i.e., not only are the dispersive bands of the topologically nontrivial surface states intact but also their filling remains the same. In particular, the latter is very remarkable in light of the fact that the amount of charge carriers with interesting topological properties is only of the order of a few $10^{12}$ cm$^{-2}$, i.e., of the order of 0.01 per surface unit cell. Thus, our Te capping method does not cause doping of the Bi$_2$Te$_3$ surface. This observation is in agreement with a very recent work on crystalline Te capping of (Bi,Sb)$_2$Te$_3$ thin films.\textsuperscript{13}

For Te capping thicker than $\sim 12$ Å (2 u.c.), we can no longer see the signal from Bi$_2$Te$_3$. This can be attributed to the very small probing depth, of the order of 5 Å, of the ARPES techniques using the He I (21.2 eV) line.\textsuperscript{14} Figure 3(b) shows the angle-integrated UPS (ultraviolet photoelectron spectroscopy) spectrum of pristine Bi$_2$Te$_3$ with different Te capping layers. It is evident that the Bi$_2$Te$_3$ states near the Fermi level are no longer visible for a capping thicker than 30 Å (5 u.c.) and that the spectra for 30 Å (5 u.c.), 60 Å (10 u.c.), and 120 Å (20 u.c.) are similar and essentially given by elemental Te.

![Figure 2](image2.png)

**FIG. 2.** X-ray photoelectron spectroscopy of the Te 3d and Bi 4f core levels of the Bi$_2$Te$_3$ sample with Te cappings of different thicknesses.

![Figure 3](image3.png)

**FIG. 3.** (a) ARPES spectra of a 20 QL Bi$_2$Te$_3$ film and the same film capped with 6 Å (1 u.c.) and 12 Å (2 u.c.), respectively. The data were taken along the $\Gamma - M$ direction at room temperature. (b) Angle integrated UPS spectra of the pristine Bi$_2$Te$_3$ and for different Te capping layers.
FIG. 4. In-situ sheet resistance measurements of the pristine and capped 20 QL thin Bi$_2$Te$_3$ film. The temperature dependent cool-down and warm-up curves are shown for the pristine Bi$_2$Te$_3$ (blue and red) and the film capped with 12 nm Te (violet and orange), respectively. The triangles indicate the room temperature sheet resistance values for Te cappings of different thicknesses. The black crossed circle indicated the room temperature value of the sheet resistance after the removal of the capping layer by thermal desorption at 220°C. The inset displays the sheet resistance versus the Te capping layer thickness at room temperature.

Subsequently, the influence of the Te capping on the electrical transport properties of the Bi$_2$Te$_3$ film were investigated. We conducted the experiments in-situ, i.e., the contacting and temperature-dependent resistivity measurements were all performed under UHV conditions, thereby excluding any external effects that might occur owing to degradation when the film would have been exposed to air. The results are presented in Figure 4. The temperature-dependence of the sheet resistance was investigated for the pristine Bi$_2$Te$_3$ film (blue and red curves) and for the film fully capped with 12 nm Te (violet and orange curves). For the intermediate Te thicknesses only the sheet resistance values at room temperature are shown (triangles). The pristine film shows metallic behavior over the entire temperature range without any sign of degradation of the contacts during the temperature cycle. Upon applying of the Te capping, the resistivity decreases gradually but not dramatically. Most of the conductivity is still determined by the surface states of the pristine Bi$_2$Te$_3$ film.

It should be noted that the extra conductivity owing to the Te capping cannot be accounted for in terms of a simple parallel conductivity due a thin slab of Te with Te bulk properties. The sheet resistance drops, for example, by about 200 Ohm with a 6 nm capping, which is much more than the few Ohm reduction expected on the basis of the specific resistivity of bulk Te ($\rho_{\perp} = 1.5$ mOhm perpendicularly to the c-axis at 20°C). We speculate that the strain or polarizability exerted by the adjacent Bi$_2$Te$_3$ influences the properties of the Te layers closest to the interface in such a manner that those Te layers becomes much more conducting than bulk Te. We note on the other hand that the sheet resistance drop between 6 nm and 12 nm capping is only a few Ohm, well within the expectations for an additional 6 nm thin Te slab having the Te bulk resistivity. We therefore can infer that the Te film is essentially bulk like, except for the Te layers within a few nm from the interface with the Bi$_2$Te$_3$. Since the photoemission data showed no shift of the Fermi level due to the Te capping, we can assume that the resistance of the Bi$_2$Te$_3$ surface states remains to have the $\approx 1$ kOhm value and that the resistance drop is caused by the parallel shunt by the first 6 nm Te having about $\approx 4$ kOhm resistance (with any additional Te layers having the bulk Te properties). In any case, we can be assured that the sheet resistance of the Bi$_2$Te$_3$ with capping is still overwhelmingly given by that of the intrinsic surface states.

The observation that the Te capping does not affect the surface states of the Bi$_2$Te$_3$ film also means that there is no chemical reaction between the Te capping and Bi$_2$Te$_3$. This suggests that it should be possible to remove the capping layer by physical means so as to recover the pristine
state of the Bi$_2$Te$_3$ surface. We have tested this possibility by gradually heating up the capped film while simultaneously monitoring the RHEED pattern. The substrate temperature was first ramped to 180°C and then increased in steps of 10 K with a waiting time of 5 min at each step. At 220°C, the additional RHEED streaks, originating from Te, start to vanish, and after 10 min the original Bi$_2$Te$_3$ RHEED pattern was recovered (cf. Fig. S2). Fig 5(a) shows the ARPES spectrum of this annealed thin film. All features of the pristine Bi$_2$Te$_3$ film are fully restored. The high contrast of the band structure features relative to the background and the similar position of the Fermi level crossings indicate that there are no visible changes in the surface morphology and stoichiometry. It should also be noted that the removal of the Te capping is complete, as evidenced by the XPS measurements shown in Fig. S3 of the supplemental material. The room-temperature sheet resistance of this annealed film (black crossed circle in Fig. 4) is identical to that of the film prior to capping. This serves as further proof that capping and de-capping can be conducted such that the properties of the pristine topologically nontrivial surface states are preserved. In contrast to previous studies, where problems with the stoichiometry were reported, we did not observe changes in the stoichiometry of the Bi$_2$Te$_3$ surface after capping and de-capping Te (see Fig. 5 and Fig. S3).

The issue is now to show that capping does protect Bi$_2$Te$_3$ against degradation upon exposure to ambient conditions. Toward this end, we exposed a capped film to air for at least 5 min at room temperature. After inserting the film back into the UHV system, we conducted the above-described annealing process to remove the Te capping. Figure 5(b) shows the result, where one can clearly observe that the ARPES spectrum is essentially the same as that of the pristine Bi$_2$Te$_3$ film shown in Fig. 5(a).

FIG. 5. ARPES spectra of two different Bi$_2$Te$_3$ films after removal of a 12 nm Te capping. (a) Te capped sample kept in UHV. (b) Te capped sample exposed to air for 5 min.
in Fig. 3(a). This result demonstrates that the capping is leakproof, i.e., the number of pinholes or cracks in the Te overlayer are apparently negligible. It should be noted that our findings are also facilitated by the fact that pure Te thin films are rather inert against oxidation. As has been reported earlier, exposure to air for longer duration does not necessarily result in the formation of TeO,

This also means that if oxidation is occurring, it will be a very slow process and will therefore not affect the properties of the deeply covered Bi₂Te₃ topological surface states during even prolonged ex-situ experiments.

In conclusion, we showed that epitaxially grown elemental Te is an ideal capping material to protect the topological surface states of intrinsically insulating Bi₂Te₃. Our angle-resolved photo-emission experiments established that the Te capping leaves the band dispersions and Fermi level position of the surface states intact. Our in-situ four point contact measurements verified that the electrical properties of the surface states can still be clearly and directly detected despite the presence of the capping. We have demonstrated that the Te capping does indeed protect the Bi₂Te₃ surface against the influence of ambient conditions. Moreover, we have shown that the capping can be easily removed by thermal annealing in vacuum, thereby restoring the Bi₂Te₃ surface to its pristine state. These results will therefore enable a wide range of well-defined and reliable ex-situ and surface/interface sensitive experiments using the Bi₂Te₃ surface states with nontrivial topology.

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