RAPID COMMUNICATION

AlO_x/LiF composite protection layer for Cr-doped $(Bi,Sb)_2Te_3$ quantum anomalous Hall films*

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We have realized robust quantum anomalous Hall samples by protecting Cr-doped $(Bi,Sb)_2Te_3$ topological insulator films with a combination of LiF and AlO_x capping layers. The AlO_x/LiF composite capping layer well keeps the quantum anomalous Hall states of Cr-doped $(Bi,Sb)_2Te_3$ films and effectively prevent them from degradation induced by ambient conditions. The progress is a key step towards the realization of the quantum phenomena in heterostructures and devices based on quantum anomalous Hall system.

Keywords: quantum anomalous Hall effect, AlO_x, LiF, protection layer

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1. Introduction

A topological insulator (TI) is an insulator with topologically protected gapless surface states in its bulk gap.[1–4] This class of materials has received extensive research interests in the past decade for a number of novel quantum phenomena predicted in them.[5–14] The quantum anomalous Hall effect (QAHE), a quantum Hall effect that can occur without external magnetic field, is among the few quantum phenomena that have been experimentally observed.[15–17] The effect is expected to appear in a TI film with its time-reversal symmetry broken by ferromagnetism, introduced via magnetic doping or proximity.[5–7,10,18] The QAHE was experimentally realized in magnetically doped $(Bi,Sb)_2Te_3$ three-dimensional (3D) TI films grown by molecular beam epitaxy (MBE), opening a path toward the observation of many other exotic quantum effects such as topological magnetoeletric effect.[9–11] and chiral topological superconductivity.[13,14]

The magnetically gapped topological surface states play a key role in QAHE in magnetic 3D TI films.[19] Hence QAHE is sensitive to the surface conditions of the films. QAHE was first observed in Cr-doped $(Bi,Sb)_2Te_3$ films with no capping layer.[15] Such bare magnetic TI films cannot hold the QAH property in atmosphere for a long period of time (usually less than one month even in inert atmosphere) and in some microfabrication processes such as electron beam lithography (EBL) and atomic layer deposition (ALD). This greatly impedes studies and applications of QAH-based structures and devices. It is highly desired to find a satisfactory capping layer material capable of preserving the native properties of QAH films and effectively protecting them from degradation under various conditions.

We have tried to protect Cr-doped $(Bi,Sb)_2Te_3$ QAH films by depositing a layer of tellurium on them. Tellurium atoms form a single-crystalline film covering the whole surface of the films,[20] but destroying the QAHE in them. Figures 1(a) and 1(b) show the magnetic field (H) dependencies of the Hall resistance (ρ_{yx}) and the longitudinal resistance (ρ_{xx}) of bare (green lines) and a Te-capped (blue lines) $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films measured at 25 mK, respectively. The bare sample clearly shows the QAHE with its ρ_{yx} up to h/e^2 and ρ_{xx} down to zero. But in the Te-capped film, both ρ_{yx} and ρ_{xx} significantly deviate from the quantized values. The disappearance of the QAHE may be caused by parallel conduction channels brought about by the Te capping layer. Kou *et al*. *in situ* deposited an Al layer of ~ 1 nm on Cr-doped $(Bi,Sb)_2Te_3$ films; the Al layer is oxidized by air into a compact insulating AlO_x film which acts as a capping layer for the underlying magnetic TI film. Although the QAHE is observed in such AlO_x-covered Cr-doped $(Bi,Sb)_2Te_3$ films, the preparation process of AlO_x layer is difficult to control. The coverage of the deposited Al should be carefully chosen to guarantee that it is neither too thick to be completely oxi-

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dized by air nor too thin to protect the film. Besides, the fact that Al electronegativity is much lower than that of Sb and Bi makes Al atoms easily react with the films and modify their properties.

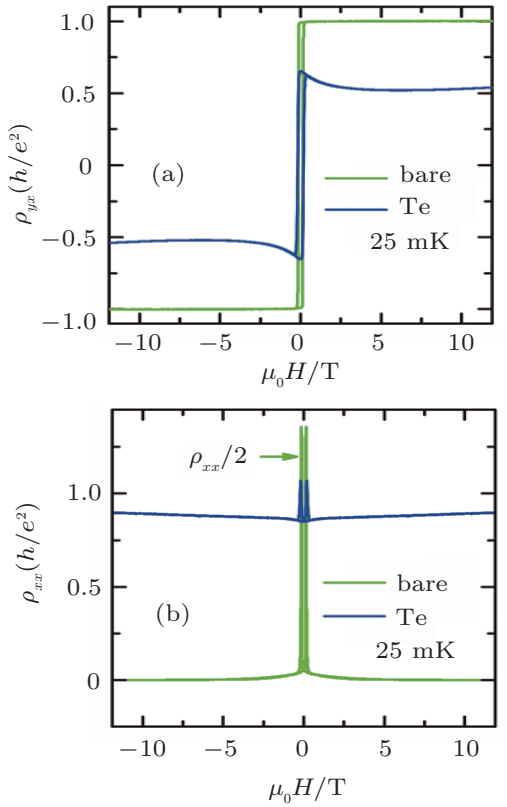


Fig. 1. (color online) Magnetic field dependence of (a) ρ_{yx} and (b) ρ_{xx} for bare (green lines) and Te-capped (blue lines) 5 QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films at 25 mK. The measurement is taken at the CNPs of bare (−6 V) and Te-capped (−32 V) films.

Lithium fluoride is an insulator with rocksalt structure ($a = 4.026$ Å) and a gap of 12.6 eV.[21] The small lattice constant and the big difference between the electro-negativities of Li and F make the compound resistant to diffusion and reaction with atoms in the atmosphere and adjacent layers. So it is a good candidate material for a capping layer of QAH samples. In this study, we investigated the influence of LiF capping layer on the QAHE of Cr-doped $(Bi,Sb)_2Te_3$ films and found that LiF can make an ideal protection layer for the QAH films if covered with a layer of water-resistant AlO_x.

2. Experimental details

The QAH samples used in this study are 5-QL thick $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films prepared on $SrTiO_3$ (111) substrates with MBE. The films were grown in an ultra-high vacuum chamber (base pressure $< 1.0 \times 10^{-10}$ mbar, 1 bar $= 10^5$ Pa) equipped with a reflective high energy electron diffraction (RHEED) facility. Lithium fluoride and Al were prepared by thermal evaporation of LiF powder and Al granules with home-made evaporators, respectively. The QAH films were kept at room temperature for LiF and Al deposition. The transport properties of the films were measured with standard ac lock-in methods. Strontium titanate substrates were used as the dielectric layer of the bottom gate to tune the chemical potential of the films.[22,23]

3. Results and discussion

Figure 2(a) shows the RHEED pattern and atomic force microscope (AFM) map of a bare $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film, which exhibits the typical 1×1 RHEED diffraction streaks and step-terrace morphology as shown before.[15] After depositing $\sim$ 5-nm thick LiF on the film, the 1×1 streaks disappear, and diffraction spots resulting from electron transmission through 3D islands with the same crystalline orientation are observed (Fig. 2(b) top).

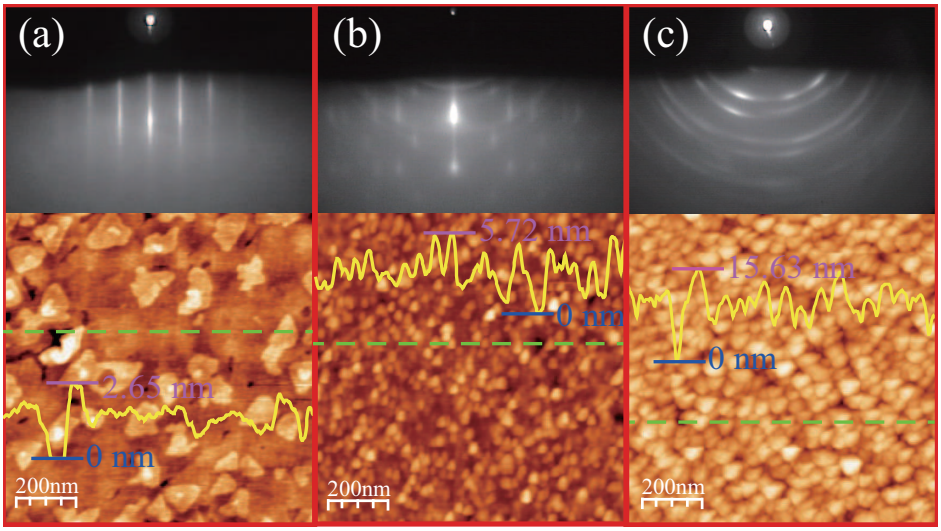


Fig. 2. (color online) (a)–(c) The RHEED pattern (top panels) and 1 μm × 1 μm AFM images (bottom panels) of (a) bare, (b) 5-nm LiF capped, and (c) 40-nm LiF capped 5 QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film. The yellow curves in the AFM images are the line profiles of the AFM images indicated by the green dash lines.

We can also observe diffraction circles indicating existence of islands with different crystalline orientations. With increasing thickness of LiF, the transmission spots gradually disappear, and eventually only the diffraction circles remain (Fig. 2(c) top), which implies a random distribution of crystalline orientation of LiF islands. The AFM images (Figs. 2(b) bottom and 2(c) bottom) indeed exhibit the morphology of 3D islands, consistent with the RHEED observation. The roughness of the surface is ~ 3.26 nm and ~ 10.73 nm when the average thickness of LiF is 5 nm and 40 nm, respectively. Therefore, the Cr-doped $(Bi,Sb)_2Te_3$ film is completely covered by LiF layer in spite of the 3D morphology. This implies that LiF film grows in the Stranski–Krastanov mode on Cr-doped $(Bi,Sb)_2Te_3$.

In Figs. 3(a) and 3(b) we display the H dependencies of ρ_{yx} and ρ_{xx}, respectively, of a bare 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film (green lines) and a film grown under exactly the same conditions but capped with a 40-nm thick LiF (blue lines). The data were taken at 1.5 K. For both of the samples, V_g is tuned to obtain the maximum ρ_{yx}, i.e., at the charge-neutral point (CNP).[15,18] We can see that the Hall traces (ρ_{yx}–H curves) of these two samples basically coincide, and ρ_{yx} reaches $0.75h/e^2$ at 0.3 T. Such a high ρ_{yx} at 1.5 K means that it will reach the quantized Hall plateau at 30 mK.[15] The magnetoresistance (ρ_{xx}–H) curve of the capped film is even a little smaller than that of the bare film, which means better sample quality. Thus LiF capping layer is not detrimental to the QAHE of Cr-doped $(Bi,Sb)_2Te_3$ films. From the V_g dependencies of ρ_{yx} of the two samples (Fig. 3(c)) at zero magnetic field, the CNP (ρ_{yx} maximum) of the LiF-capped film is located at $V_g = 36$ V, larger that of the bare film ($V_g = -1$ V). This suggests that the LiF capping layer dopes holes in the QAH films.

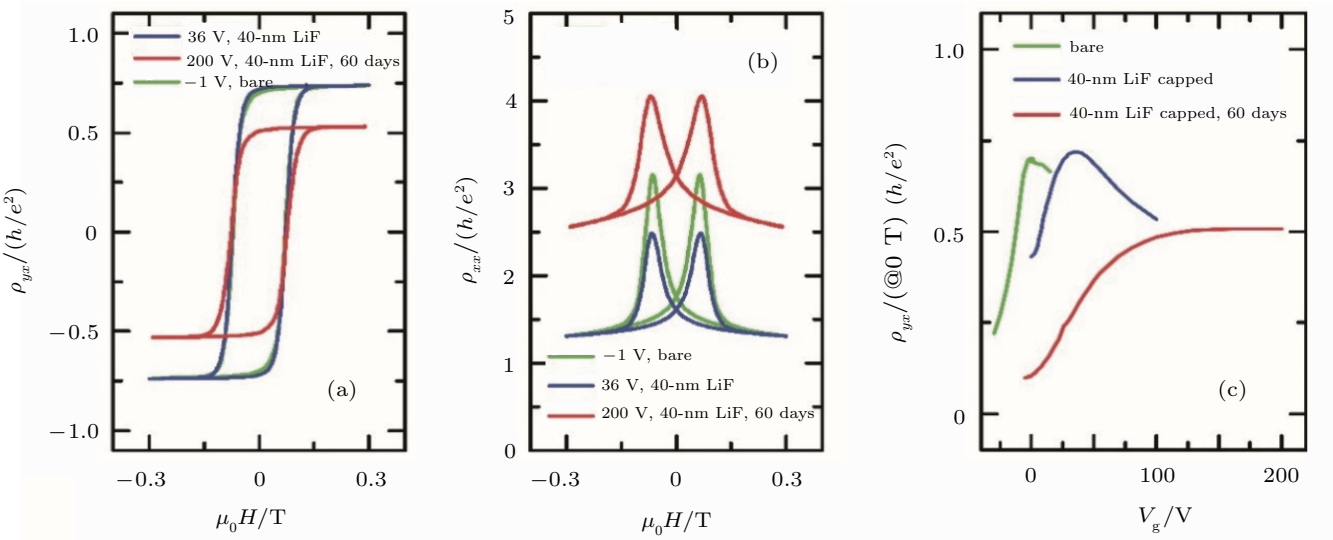


Fig. 3. (color online) Magnetic field dependence of (a) ρ_{yx} and (b) ρ_{xx} for bare (green lines) and 40-nm LiF-capped (blue lines) 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films with gate voltage of -1 V, 36 V. (c) V_g dependence of ρ_{yx} at zero magnetic field for bare (green line) and 40-nm LiF-capped (blue line) 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films. Magnetic field dependence of ρ_{yx} and ρ_{xx} ($V_g = 200$ V), V_g dependence of ρ_{yx} at zero magnetic field of 40-nm LiF-capped 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films, which is kept in argon glove box for 60 days, are shown with red lines in panels (a), (b), and (c). All the measurements are conducted at 1.5 K.

To check if an LiF capping layer can effectively protect the QAHE of Cr-doped $(Bi,Sb)_2Te_3$ films, we measured the LiF-capped $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film after keeping it in an argon glove box for 60 days. The data are plotted with red lines in Figs. 3(a)–3(c). From Fig. 3(c), we can see that the CNP is shifted to $V_g = 150$ V, indicating a heavily p-doping of the film. The maximum ρ_{yx} of the sample at 0.3 T is only $0.51h/e^2$, much lower than $\rho_{yx} = 0.75h/e^2$ of the fresh sample, and ρ_{xx} increases significantly. These observations indicate severe degradation of the film. Hence, although LiF capping layer does not deteriorate the QAHE of Cr-doped $(Bi,Sb)_2Te_3$ films, it is unable to prevent them from aging under ambient conditions.

It is not clear why LiF cannot effectively protect the QAH films with its good chemical stability and compact lattice structure. A fact probably relevant is that LiF is slightly soluble in water (0.132 wt% at 23.7 °C).[24] Thus an LiF layer could adsorb water molecules from the atmosphere and in turn influence the properties of the underlying QAH films. Such a deficiency of LiF can be removed by capping it with a water-resistant layer such as AlO_x.

We deposited 3-nm thick Al on an LiF (5 nm)-covered $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film and had it oxidized into a compact AlO_x layer in air. As shown in Fig. 4(a), the Hall trace of the film with AlO_x/LiF composite capping layer (blue line) is similar to that of the bare film (green line). The maximum ρ_{yx}

of the AlO_x/LiF-capped film is $0.7h/e^2$, only slightly lower than that of the bare film ($0.73h/e^2$), which still keeps the QAH character. ρ_{xx} of the AlO_x/LiF-capped sample is smaller than the bare one (Fig. 4(b)), suggesting an improved sample quality, probably due to avoidance of the exposure of the film surface to atmosphere. After being kept in an argon glove box for 17 days, the AlO_x/LiF-capped film only experiences slight difference in its ρ_{yx} and ρ_{xx} (red lines in Figs. 4(a)–4(c)). Unlike the films capped only by LiF, the V_g for CNP basically remains unchanged with time. Thus the additional AlO_x layer effectively protects the LiF layer and the magnetic TI film from degradation under ambient conditions.

In order to further test the protection effect of the composite capping layer, we attempted using ALD to deposit AlO_x on the AlO_x/LiF-capped samples with ozone (O_3) as the precursor at 70 °C for 2 hours. Such a process is a key step toward the realization of dual-gate structures and tunneling junctions based on quantum anomalous Hall films. The strong oxidation of ozone plus the elevated temperature used in ALD can easily destroy the fragile quantum anomalous Hall states of the magnetically doped $(Bi,Sb)_2Te_3$ films. The black lines in Figs. 4(a)–4(c) represent the transport properties measured in the AlO_x/LiF-capped film after the ALD process. Both the ρ_{yx} and ρ_{xx}, as well as the position of the CNP, show similar values as before ALD deposition, even with a little improvement (larger ρ_{yx}, smaller ρ_{xx} and smaller V_g for the CNP). The improvement probably results from annealing effect of the elevated temperature in the ALD process. This result demonstrates the excellent protection provided by AlO_x/LiF-composite capping layer.

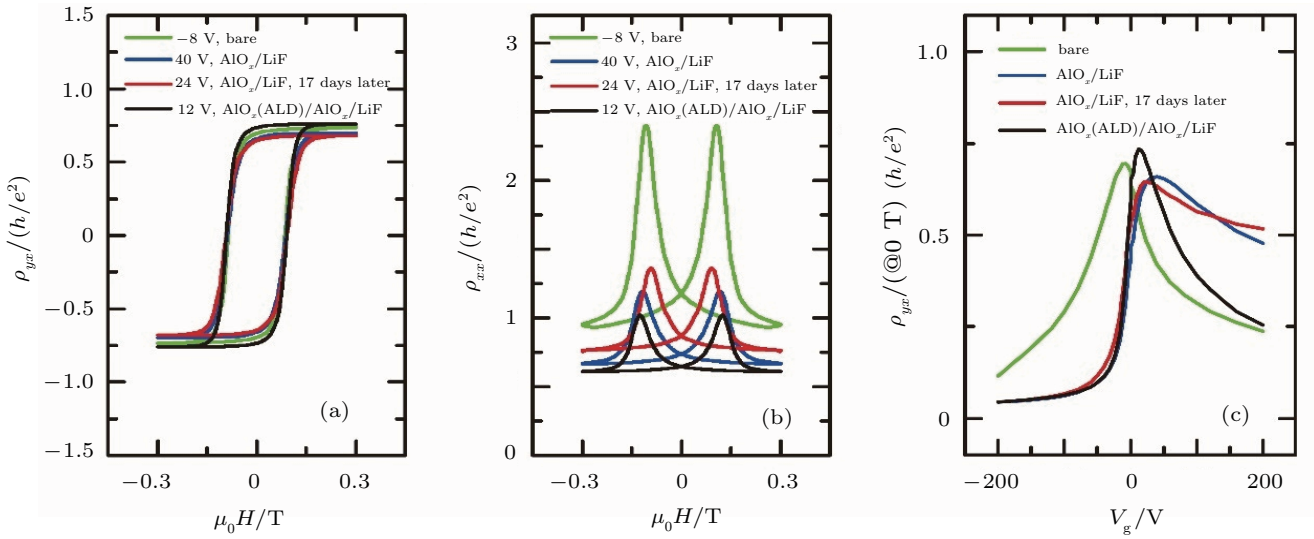


Fig. 4. (color online) Magnetic field dependence of (a) ρ_{yx} and (b) ρ_{xx} for bare (green lines), 3-nm AlO_x/5-nm LiF-capped (blue lines), and 10-nm AlO_x(ALD)/0.5-nm AlO_x/5-nm LiF-capped (black lines) 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films with gate voltage of −8 V, 40 V, and 24 V respectively. (c) V_g dependence of ρ_{yx} at zero magnetic field for bare (green line), 3-nm AlO_x/5-nm LiF-capped (blue line), and 10-nm AlO_x(ALD)/0.5-nm AlO_x/5-nm LiF-capped (black line) 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ films. Magnetic field dependence of ρ_{yx} and ρ_{xx} ($V_g = 12$ V), V_g dependence of ρ_{yx} at zero magnetic field of 3-nm AlO_x/5-nm LiF-capped 5-QL $Cr_{0.15}(Bi_{0.1}Sb_{0.9})_{1.85}Te_3$ film, which is kept in argon glove box for 17 days, are shown with red lines in panels (a), (b), and (c). All the measurements are conducted at 1.5 K.

4. Conclusion

In summary, we found that a LiF capping layer can very well preserve the QAHE of Cr-doped $(Bi,Sb)_2Te_3$ films, but is unable to effectively protect them from contamination of ambient conditions. By covering the LiF surface with an AlO_x layer, we significantly improved the protection effect of LiF, which enabled us to obtain robust QAH samples that survive a longer period of time and endure the harsh conditions of some microfabrication processes. The excellent performance of AlO_x/LiF composite capping layer makes it useful in various studies and applications of QAHE and Bi_2Se_3 family TIs.

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