Interface Engineering Enabled Low Temperature Growth of Magnetic Insulator on Topological Insulator

Nirjhar Bhattacharjee, Krishnamurthy Mahalingam, Alexandria Will-Cole, Yu Yi Wei, Adrian Fedorko, Cynthia T. Bowers, Michael Page, Michael McConney, Don Heiman, and Nian Xiang Sun*

1. Introduction

Realization of the quantum anomalous Hall (QAH) effect has been demonstrated in several magnetic topological insulators (MTIs). MTIs can be synthesized by doping magnetic elements into topological insulators (TIs) or growth of intrinsic MTI compounds. However, these MTI materials require temperatures much lower than their magnetic transition temperature, $T_C$, to achieve quantization in the Hall effect. This deficiency has been attributed to inhomogeneity in magnetic doping which causes localized variation in surface state exchange gaps. Magnetism can also be induced in the surface of TI thin films via proximity exchange effect. This proximity induced magnetization (PIM) is envisioned by coupling TIs with a magnetic insulator (MI). PIM in TIs have been experimentally confirmed in heterostructures of TIs with magnetic insulators such as rare earth garnets and EuS, MTIs, and telluride van der Waals (vdW) magnets. However, recent studies have pointed out the complexities in measuring proximity exchange in these systems, which can be affected by a number of problems such as diffusion at the interface and band bending. Thus, providing a barrier against magnetic diffusion while permitting magnetic exchange in TI/MI heterostructures will be necessary for devices, and it is shown here that a TiO$_x$ interface barrier achieves this goal. Only a single study by Watanabe et al. has shown PIM and QAH in a TI/MI/TI thin film sandwich structure of (Zn,Cr)Te/(Bi,Sb)$_2$Te$_3$/(Zn,Cr)Te. However, even in this material system, the QAH effect was seen at extremely low temperatures of 0.03 K. This low temperature is possibly due to: (1) High-quality MIs which were grown on TI thin films have very low Curie temperature, $T_C$, such as (Zn,Cr)Te with $T_C < 40$ K and EuS with $T_C$ of ~17 K. (2) Even with 20–25% of the magnetic species, Cr in (Zn,Cr)Te, finite localized nonmagnetic nanoregions may exist in the samples. MIs such as rare-earth garnets and ferrites are excellent materials that are magnetically ordered well above room-temperature, making them ideal candidates for QAH materials coupled with TIs. However, growth of MIs on top of TIs using

Combining topological insulators (TIs) and magnetic materials in heterostructures is crucial for advancing spin-based electronics. Magnetic insulators (MIs) can be deposited on TIs using the spin-spray process, which is a unique non-vacuum, low-temperature growth process. TIs have highly reactive surfaces that oxidize upon exposure to atmosphere, making it challenging to grow spin-spray ferrites on TIs. In this work, it is demonstrated that a thin titanium capping layer on TI, followed by oxidation in atmosphere to produce a thin TiO$_x$ interfacial layer, protects the TI surface, without significantly compromising spin transport from the magnetic material across the TiO$_x$ to the TI surface states. First, it is demonstrated that in Bi$_2$Te$_3$/TiO$_x$/Ni$_{10}$Fe$_{20}$ heterostructures, TiO$_x$ provides an excellent barrier against diffusion of magnetic species, yet maintains a large spin-pumping effect. Second, the TiO$_x$ is also used as a protective capping layer on Bi$_2$Te$_3$, followed by the spin-spray growth of the MI, Ni$_{1/2}$Zn$_{1/2}$Fe$_2$O$_4$ (NZFO). For the thinnest TiO$_x$ barriers, Bi$_2$Te$_3$/TiO$_x$/NZFO samples have antiferromagnetic (AFM) disordered interfacial layer because of diffusion. With increasing TiO$_x$ barrier thickness, the diffusion is reduced, but still maintains strong interfacial magnetic exchange-interaction. These experimental results demonstrate a novel method of low-temperature growth of magnetic insulators on TIs enabled by interface engineering.

N. Bhattacharjee, A. Will-Cole, Y. Wei, N. X. Sun
Department of Electrical and Computer Engineering
Northeastern University
Boston, MA 02115, USA
E-mail: n.sun@northeastern.edu
K. Mahalingam, C. T. Bowers, M. Page, M. McConney
Air Force Research Laboratory
Nano-electronic Materials Branch
Wright Patterson Air Force Base
Dayton, OH 05433, USA
A. Fedorko, D. Heiman
Department of Physics
Northeastern University
Boston, MA 02115, USA
D. Heiman
Plasma Science and Fusion Center
MIT
Cambridge, MA 02139, USA

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a high vacuum process is challenging because of their high growth temperatures (>600 °C). At these temperatures, TIs are thermally unstable and can melt or sublimate making them unusable for TI/MI QAH systems. The spin-spray process provides a solution for growth of MIs at much lower temperatures of ≈100 °C. Ferrites are MIs with a high $T_C$ (≈750 °C), which makes them excellent candidates for realization of QAH and spintronic device applications, provided they can be heterostructured with TIs. However, an engineering challenge remains to be solved. TIs have a highly reactive surface, which undergoes reactions promoted by the topological surface states (TSS) electrons. Unfortunately, exposure of TIs to atmosphere leads to rapid oxidation of Bi, Sb, Se, and Te, which is experimentally observed in this work, decouples the MI layer from the adjacent TI. Without a finite exchange interaction between the TSS and the magnetic material, none of the spintronic and quantum properties can be achieved.

In this work, interface engineering of TI/FM and TI/MI heterostructures using an ultra-thin TiO$_x$ interlayer will be presented. The TiO$_x$ interlayer has three important properties: (1) it protects the TI surface against oxidation when exposed to atmosphere after the TI growth; (2) it limits interdiffusion at the TI/FM and TI/MI interface; and (3) it maintains sufficient transparency for spin transport that is crucial for devices. The TiO$_x$ insertion layer acts as a barrier to interfacial diffusion of elements without significantly compromising interaction of magnetic moments with TSSs. First, the interfacial diffusion was examined with and without TiO$_x$ on samples of Bi$_2$Te$_3$/Ni$_{80}$Fe$_{20}$ and spin-spray grown NZFO. Second, the spin-transparency and interfacial exchange-interaction in these heterostructures were examined by measuring the Gilbert damping enhancement using FMR experiments. Further information was obtained from magnetization measurements, TEM images, and EDS scans. From these studies it is evident that low-temperature spin-spray growth of MIs on TIs can be achieved by interface engineering of TIs which is a significant significant result. This is expected to lead to further experimental explorations of interfacial topological properties on the surface of TI/FM, TI/MI, M/MI, and MI/TI/MI heterostructures and their eventual integration of these materials systems into practical quantum and spintronic devices.

2. Experimental Results and Discussion

The experimental section is organized as follows: (2.1) contains results on the effects of TI surface oxidation and interlayer TiO$_x$ on spin-pumping and interdiffusion; (2.2) describes the formation of an antiferromagnetic (AFM) interlayer via atomic diffusion; (2.3) contains results on TI/MI heterostructures grown by nonvacuum, low-temperature spin-spray deposition of NZFO on Bi$_2$Te$_3$.

2.1. Effects of TI Surface Oxidation an Interlayer TiO$_x$ on Spin-pumping and Interfacial Diffusion

2.1.1. Suppression of SOT on TI Surface due to Surface Oxidation

The spin transparency of TI/FM interfaces is conveniently determined in FMR experiments by measuring changes in the Gilbert damping. In high-quality TI/FM interfaces the precessing magnetization in the FM results in spin-pumping into the TI. This is because the strong SOC in TIs, resulting in ISHE and enhanced Gilbert damping. On the other hand, no spin-pumping is seen when the spins are prohibited from transferring from the FM to the TI layer. On exposure to atmosphere, TI surfaces readily oxidize, which leads to topologically trivial insulators on the surface. Almost total loss of spin-pumping was observed in TI/FM heterostructures when the Bi$_2$Te$_3$ thin film was exposed to the atmosphere before deposition of the FM (20 nm thick Py).

To understand the effect of surface oxidation of TI on spin-pumping in TI/FM heterostructures, FMR experiments were performed at room temperature with the following samples: Bi$_2$Te$_3$/Py, Bi$_2$Te$_3$(oxidized in atmosphere)/Py, Bi$_2$Te$_3$/AlO$_x$ (3 nm Al oxidized in atmosphere)/Py, and Al(10nm)/Py (control). For the sample Bi$_2$Te$_3$(oxidized)/Py as the label suggests, Bi$_2$Te$_3$ was exposed to atmosphere before deposition of Py. The FMR linewidths $\Delta H$ were extracted by fitting a Lorentzian function to the FMR field scans (see Experimental Section and Section S1, Supporting Information). The Gilbert damping $\alpha$ was extracted from a linear fit to the $\Delta H$ as a function of frequency using the relation, $\Delta H = H_\gamma + \frac{2\pi}{\gamma} \alpha$, as shown in Figure 1a. Here, $H_\gamma$ is the inhomogeneous linewidth broadening and $\gamma$ is the gyromagnetic ratio ($\frac{2\pi}{\gamma} = 2.8$ MHz Oe$^{-1}$ for metallic films). Figure 1a shows that the Bi$_2$Te$_3$/Py sample has a very large Gilbert damping, $\alpha = 0.060$, compared to all the other samples, indicating that spin transport is nearly eliminated by adding interfacial layers. The sample with Bi$_2$Te$_3$(oxidized)/Py had a much reduced $\alpha = 0.004$, almost the same as a control sample of Al(Py). Note that when the metal-oxide is thick, as with the Bi$_2$Te$_3$/AlO$_x$/Py sample, $\alpha = 0.0101$, which is higher than the control sample but still much lower than that of the Bi$_2$Te$_3$/Py. However, note that in the Bi$_2$Te$_3$(oxidized)/Py sample there is a naturally diffused interlayer of AFM Ni-Bi$_2$Te$_3$ that remains effective for spin transfer and large damping.

Further, the effective magnetization, $4\pi M_{eff}$ was extracted by fitting the FMR frequency, $f_{res}$ as function of FMR, $H_{FMR}$ field plot using the Kittel equation, $f_{res} = \frac{2\pi}{\gamma} \sqrt{H(H_\gamma - H) + 4\pi M_{eff}}$ as shown in Figure 1b. Here, $H_{FMR}$ is the FMR resonance field and $H_\gamma$ is the uniaxial anisotropy field. A significant change in $4\pi M_{eff}$ suggests change in magnetic anisotropy because of interfacial exchange interaction of the FM layer with TSS.

Further, exchange interaction of an FM with a large SOC material should also result in change in $\gamma$. However, due to the large thickness of the FM layer, this change is expected to be negligibly small. Hence, a $\frac{2\pi}{\gamma}$ value of 2.8 MHz Oe$^{-1}$ has been considered for the metallic FMs in this work. The fitting to Kittel equation reveals $4\pi M_{eff}$ values of 12.17 kOe for Py, slightly reduced values of 11.54 kOe for Bi$_2$Te$_3$ (oxidized)/Py, 11.39 kOe for Bi$_2$Te$_3$/AlO$_x$/Py, and a dramatically reduced value of 6.55 kOe for the Bi$_2$Te$_3$/Py heterostructure. This suggests reduced interfacial magnetic interactions in the Bi$_2$Te$_3$(oxidized)/Py and Bi$_2$Te$_3$/AlO$_x$/Py samples because of decoupling of the FM from the TSS of the TI, represented by the schematics in Figures 1c,d. In MBE grown TI thin film samples, surfaces are usually capped with Se or Te which is evaporated by heating in a high-vacuum chamber before growing the FM layer in spin-orbit torque (SOT) devices.
capping layer becomes especially significant for successfully growing MI ferrites using the low-temperature spin-spray process on TIs as substrates are exposed to the atmosphere during deposition. The choice of an effective capping/interface engineered layer is essential as interfacial magnetic interactions and spin transparency must not be allowed to diminish significantly through the barrier for efficient spintronic device applications.

2.1.2. TiOx Interlayer Effects on Diffusion in TI/FM Heterostructures

The atomic interdiffusion in TI/FM samples was investigated as a function of TiOx interlayers. Two cases are illustrated in Figure 2a, one where the Py is grown on the TI without breaking the chamber vacuum and the other where the TI was exposed to atmosphere before depositing the Py. Without breaking the vacuum, the Bi₂Te₃/Py interface develops a topologically non-trivial AFM interfacial layer because of diffusion and reaction of Ni with Bi₂Te₃ and forming NiBi₂Te₄.[42,43] In contrast, oxidizing the surface of the TI prevents reaction and diffusion of Ni or Fe from Py and does not allow forming a topological interfacial layer. To study the effect of surface oxidation of Bi₂Te₃ on the interfacial diffusion and reactions in Bi₂Te₃/Py, room temperature $m(H)$ measurements were performed on the samples of Bi₂Te₃/Py, Bi₂Te₃(oxidized)/Py, and Py (control) samples. Because of interfacial diffusion of Ni, Figure 2b shows that the saturation moment of the Py layer decreases by $\approx 40\%$. This happens because the diffused Ni reacts with Bi₂Te₃ to form compounds which are not ferromagnetically ordered at room temperature.[42] But as expected, no magnetic moment is lost when the Bi₂Te₃ is oxidized before deposition of the Py layer, as the oxide interlayer prevents diffusion of Ni out of the Py layer. Furthermore, as a result of inhibiting diffusion, the oxide interlayer prohibits Ni from reacting with the Bi₂Te₃, which prevents formation of an AFM NiBi₂Te₄ interlayer. The presence of an AFM interfacial layer next to the FM Py was found to induce a large spontaneous exchange bias field, $H_{EB} = 80$ Oe[42] at low temperatures (ZFC 6 K). However, as shown in Figure 2c, samples of Bi₂Te₃(oxidized)/Py didn’t show any exchange-bias effects in contrast to the large exchange bias in Bi₂Te₃/Py heterostructures. These results confirm the suppression of surface reactivity due to atmospheric oxidation of TIs. The oxides formed on the TI surface decouple the TSS chemically from the adjacent FM layer. These results further emphasize the need for interface engineering for integration of TIs with spin-spray grown MIs.

2.1.3. Interface Engineering in TI/FM Heterostructures using TiOx

It is important to investigate how the thickness, $z_{TiOx}$ of interlayers of Ti and its oxide TiOx in TI/FM structures affect the SOT and related magnetic properties. Ti possesses negligible
spin-orbit coupling (SOC) and is highly transparent to spin currents,[45] which makes TiO$_x$ an excellent material for interface engineering of TIs with FM oxides for spintronic device applications. In order to understand the effects of the TiO$_x$ insertion layers in TI/FM heterostructures, crystalline c-axis-oriented Bi$_2$Te$_3$ was grown using magnetron sputtering similar to the work in reference.[42] The growth of high-quality Bi$_2$Te$_3$ was followed by deposition of ultrathin Ti that was subsequently exposed to atmosphere. Py thin films of thickness 20 nm were then grown on the Bi$_2$Te$_3$/TiO$_x$ bilayers to first study their effect on magnetic properties. Figure 3a shows the effects of interfacial diffusion and solid-state reactions by monitoring the reduction of Py moments. Ni and small amounts of Fe diffuse out from the Py and form interfacial compounds due to solid state reactions with Bi$_2$Te$_3$.[42,43] Looking at the saturation moment, it is clear that TiO$_x$ layers with thickness $\leq$1 nm cannot prevent interfacial diffusion of the magnetic species, which is aided by surface reaction with Bi$_2$Te$_3$. Note that the cited TiO$_x$ thickness, $z_{\text{TiO}_x}$, is that of the Ti thin film deposited on a Si/SiO$_2$ substrate. The diffusion of primarily Ni and small amounts of Fe, leads to a moment loss of $\approx$40%, which is comparable to the control Bi$_2$Te$_3$/Py sample.[42] However, TiO$_x$ insertion layers of thickness $\geq$2 nm act as excellent barriers to the diffusion of Ni from Py preventing any loss of magnetic moments.

Next, spin-pumping effect was investigated as a function of TiO$_x$ thickness via the enhancement in Gilbert damping in FMR experiments. A dramatic improvement in spin pumping over AlO$_x$ insertion layers was observed, which can be seen by comparing the results of Figure 1a with those of Figure 3b–d. Table 1 reports the values of various properties for the Bi$_2$Te$_3$/TiO$_x$/Py samples. Values of $\alpha$ obtained for the Bi$_2$Te$_3$/TiO$_x$/Py samples were 0.074, 0.040, and 0.049 for the 1, 2, and 3 nm thick TiO$_x$ layers, respectively, and are comparable to that of 0.061 for the Bi$_2$Te$_3$/Py sample. All these samples hence show significantly enhanced $\alpha$ compared to 0.011 for the control sample of Py, thus confirming a large spin-pumping effect.
where $t_{\text{FM}}$ is the thickness of the FM layer, $\Delta \alpha$ is the enhancement in $\alpha$, $h$ is the reduced Plank’s constant, and $\gamma$ is the gyromagnetic ratio. The enhancement in $\alpha$ for the Bi$_2$Te$_3$/Py and Bi$_2$Te$_3$/TiO$_x$(1 nm)/Py samples may also contain some contributions from the loss of magnetic moments due to the large interdiffusion. But, because of the complexity of the interfaces of these samples, the effect of spin-pumping may not be accurately isolated. The $g_{\uparrow \downarrow}$ values reported for these samples were calculated based on the assumption that the enhancement in $\alpha$ compared to control sample of Py is due to spin-pumping only, which may nevertheless be incorrect. However, as the Bi$_2$Te$_3$/TiO$_x$/Py samples with 2 and 3 nm TiO$_x$ barriers had no noticeable interfacial diffusion of Ni, Fe, they had large $g_{\uparrow \downarrow}$ values as listed in Table 1. These large values indicate that TIs with TiO$_x$ interface-engineered heterostructures can be excellent candidates for efficient SOT devices. Further, Table 1 also lists saturation magnetization, $4\pi M_s \times t_{\text{FM}}$ determined from the $m(H)$ loop measurements in Figure 3a. Using those values, the effective interfacial out-of-plane (OOP) anisotropy field values can be calculated using the relation, $H_{\text{OOP}} = 4\pi M_s - 4\pi M_{\text{eff}}$. The $H_{\text{OOP}}$ values listed in Table 1 show that Bi$_2$Te$_3$/TiO$_x$(2 and 3 nm)/Py samples have $H_{\text{OOP}} = 2.02$ and 2.15 kOe, respectively. The negative $H_{\text{OOP}}$ for the Py sample indicates that the magnetic anisotropy and easy axis of the sample is highly in-plane as expected. The Bi$_2$Te$_3$/TiO$_x$/Py samples on the other hand show a large OOP anisotropy because of the exchange interaction of the interfacial magnetic moments of Py with the TSS of Bi$_2$Te$_3$.

Figure 3. Results of magnetization and FMR experiments on Bi$_2$Te$_3$/Py structures with TiO$_x$ interlayers. a) $m(H)$ loops measured at room temperature, showing no loss of moment for the two thicker TiO$_x$ layers. b) FMR linewidth $\Delta H$ as a function of FMR frequency, showing strong damping for all thickness of TiO$_x$ interlayers. Inset illustrates the spin current passing down thru the TiO$_x$. c) FMR frequency as function of FMR field and Kittel equation fitting. d) Summary of Gilbert damping for Py, and for $z_{\text{TiO}} = 0, 1, 2, 3$ nm thick TiO$_x$ interlayers, which far exceeds that of the Py control sample.

Table 1. Properties for Bi$_2$Te$_3$/TiO$_x$/Py heterostructures for different TiO$_x$ interlayer thickness.

| Material          | $z_{\text{TiO}}$ [nm] | $M_s \times t_{\text{FM}}$ [emu cm$^{-2}$] | $\alpha$ | $g_{\uparrow \downarrow}$ [m$^{-1}$] | $4\pi M_{\text{eff}}$ [kOe] | $H_{\text{OOP}}$ [kOe] |
|-------------------|------------------------|--------------------------------------------|----------|-----------------------------------|-----------------------------|------------------------|
| Py                | –                      | $1.83 \times 10^{-3}$                     | 0.011    | –                                 | 12.6                        | –1.05                  |
| Bi$_2$Te$_3$/Py   | 0                      | $1.33 \times 10^{-3}$                     | 0.061    | $1.70 \times 10^{20}$             | 6.32                        | –                      |
| Bi$_2$Te$_3$/TiO$_x$/Py | 1                      | $1.28 \times 10^{-3}$                     | 0.074    | $2.17 \times 10^{20}$             | 6.56                        | –                      |
| Bi$_2$Te$_3$/TiO$_x$/Py | 2                      | $1.82 \times 10^{-3}$                     | 0.040    | $9.88 \times 10^{19}$             | 9.53                        | 2.02                   |
| Bi$_2$Te$_3$/TiO$_x$/Py | 3                      | $1.75 \times 10^{-3}$                     | 0.049    | $1.29 \times 10^{20}$             | 9.40                        | 2.15                   |

The parameters are described in the text.
2.2. Tuning of Topological AFM Interface with TiO\textsubscript{x} Barrier

Formation of an interfacial topological AFM layer generated by diffusion of Ni and solid-state reaction with Bi\textsubscript{2}Te\textsubscript{3} was shown previously\textsuperscript{[42,43]} The solid-state reaction was found to result in loss of magnetic moment and emergence of a large spontaneous exchange bias in Bi\textsubscript{2}Te\textsubscript{3}/Py heterostructures. The $m(H)$ loop measurements at room temperature in Figure 4a show loss of magnetic moments in the Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/Py sample with the 1 nm thick TiO\textsubscript{x} similar to the Bi\textsubscript{2}Te\textsubscript{3}/Py sample deposited with the same growth conditions. The increase in TiO\textsubscript{x} barrier thickness $z_{\text{TiO}_x}$ was found to prevent the diffusion of Ni across the interface. In order to understand the effect of the interface in the Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/Py samples, $m(H)$ loops were measured at 300 and 6 K in zero-field cooling (ZFC) conditions. The sample with $z_{\text{TiO}_x} = \approx 1$ nm clearly shows a large $H_{\text{EB}} = 56$ Oe and an enhanced $H_c = 66$ Oe, as shown in Figure 4a. This arises from exchange interaction between the FM Py layer with the interfacial topological AFM layer\textsuperscript{[42]} This $H_{\text{EB}}$ was however smaller than the $H_{\text{EB}} = 82$ Oe for Bi\textsubscript{2}Te\textsubscript{3}/Py without a TiO\textsubscript{x} barrier. This is due to the reduction in exchange interaction caused by the insertion of the ultrathin TiO\textsubscript{x} layer between the interfacial AFM Ni-Bi\textsubscript{2}Te\textsubscript{3} and the Py layer. With an increase in thickness of the TiO\textsubscript{x} barrier to $z_{\text{TiO}_x} \geq 2$ nm, there is no diffusion of Ni and hence no $H_{\text{EB}}$ is observed in the samples at low temperatures. This clearly shows the effect of interface engineering on controlling the interfacial properties in Ti/FM heterostructures that will be essential for realization of practical spintronic devices. These results also show the potential of exploring fascinating interfacial phases in TI/FM heterostructures. Figure 5

2.3. Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/NZFO Heterostructures

2.3.1. Interfacial Morphology of Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/NZFO Heterostructures

The following describes results of non-vacuum, spin-spray growth of the magnetic insulator Ni\textsubscript{x}Zn\textsubscript{y}Fe\textsubscript{2}O\textsubscript{4} on Bi\textsubscript{2}Te\textsubscript{3}, which is facilitated using a TiO\textsubscript{x} interlayer. Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/NZFO heterostructures were investigated for their morphology, diffusion, and spin-pumping. The morphology of the Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/NZFO interface was first studied using cross-section transmission electron microscopy (TEM) imaging and energy-dispersive X-ray spectroscopy (EDS). As shown in Figure 6a, the Bi\textsubscript{2}Te\textsubscript{3} is vdW-layered and highly c-axis oriented as expected\textsuperscript{[42]} Figure 5.6a) The TEM image also shows a disordered interfacial layer for $z_{\text{TiO}_x} = \approx 1$ nm that is created by diffusion and solid-state reactions. In contrast, as observed in the TEM images in Figure 6b,c, with increase in thickness of the TiO\textsubscript{x} barrier layer to 2 and 3 nm the thickness of the disordered interface is significantly reduced progressively. The EDS line profiles in Figure 6d–f show the intensity of the EDS signal. With the 1 nm TiO\textsubscript{x} barrier layer there is a clear interfacial layer primarily consisting of Bi, Te, Fe, and O ($z_{\text{TiO}_x} = \approx 1$ nm). This is possibly the primary factor for creation of the highly

![Figure 4](image_url)

Figure 4. Measurements of $m(H)$ loop at 6 K (ZFC) and 300 K showing exchange bias of Bi\textsubscript{2}Te\textsubscript{3}/TiO\textsubscript{x}/Py samples. a) $H_{\text{EB}} = 56$ Oe for $z_{\text{TiO}_x} = 1$ nm at 6 K. b) No exchange bias for $z_{\text{TiO}_x} = 2$ nm, and c) no exchange bias for $z_{\text{TiO}_x} = 3$ nm. d) Comparison of exchange bias at 6 K for the samples. (Inset shows the diffusion-generated AFM layer below the TiO\textsubscript{x} for $z_{\text{TiO}_x} = 1$ nm).
disordered interfacial layer observed in Figure 6a. For the samples with 2 and 3 nm thick TiO x interlayer the thickness of the oxygen diffusion is reduced to ≈5 and ≈0 nm, respectively. Further, thickness of TiO x > 2 nm prevents any Fe diffusion as confirmed by TEM images as well as EDS line profiles. This demonstrates the effectiveness of the thicker TiO x barrier layers in the Bi2Te3/TiOx/NZFO heterostructures.

Diffusion of elements at the interface was analyzed with EDS by extracting the relative concentration of Bi and Te above the TiO x and Fe below the TiO x regions. The concentration of oxygen couldn’t be analyzed accurately as EDS results for light elements are inaccurate. For this analysis of interfacial diffusion only a small thickness of about 5–6 nm above and below the TiO x regions were considered (see Section S4, Supporting Information). As shown in Figure 6h, which is extracted from the Figure 6g, there is a small diffusion of Bi and Te across the TiO x barrier. Concentration of diffused Bi and Te: h) above TiO x barrier and i) below TiO x barrier for comparison. j) Diffused Fe below TiO x barrier in the 1, 2, and 3 nm samples with 1, 2, and 3 nm TiO x, respectively. The values for diffused Te also show a similar trend of 2.6%, 1.4%, and 1.0%, respectively. Interestingly, as shown in Figure 6j, the diffusion of Fe from NZFO to the Bi2Te3 layer was much higher at 11.6% for the sample with 1 nm TiO x and reduces significantly to 5.7% and 4.4% for the samples with 2 and 3 nm TiO x barrier, respectively. The concentrations of Ni and Zn are very small (<2%) throughout the cross-section of the NZFO layer and are within the noise range of EDS signal as shown in Figures 6g,i. Hence, diffusion of these elements could not be determined accurately. Nevertheless, the significant diffusion of Fe in the 1 nm TiO x samples form a disordered interface that results in a fascinating AFM interfacial phase which will be described in Section 2.3.3.

2.3.2. Room Temperature Magnetic Properties of Bi2Te3/TiOx/NZFO Heterostructures

NZFO thin films of thickness ≈250 nm were grown on Bi2Te3/TiO x bilayers using the method described[38, 39] (see Experimental...
The deposition was made at a substrate temperature of \(\approx 100 \, ^\circ\text{C}\), which is not expected to cause any phase change in the Bi\(_2\)Te\(_3\) layer. The Gilbert damping \(\alpha\) extracted from the slope of the FMR linewidth versus frequency in Figure 6a clearly shows a decreasing trend with increasing TiO\(_x\) thickness, shown in Figure 6b and listed in Table 2. The NZFO control sample has \(\alpha\) values slightly less than the values of the Bi\(_2\)Te\(_3\)/TiO\(_x\)/Py samples with 2 and 3 nm TiO\(_x\). The significantly enhanced \(\alpha\) for the 1 nm TiO\(_x\) insertion layer indicates a large spin-pumping and possibly some spin memory-loss (SML) effects in the Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO heterostructure.\[46,56\] Because of the larger thickness of the TiO\(_x\) barrier layers, the overall Gilbert damping enhancement effect is reduced in the Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO with \(z_{\text{TiO}_x} = 2\) and 3 nm samples. This is due to the increase in distance between the MI and TI because of the TiO\(_x\) insertion layer. This is similar to the trend in Gilbert damping change observed in Bi\(_2\)Te\(_3\)/TiO\(_x\)/Py samples as shown earlier, although much more pronounced in case of NZFO samples. This trend in Gilbert damping may also have contributions from the changes in interfacial morphology. However, the exact mechanism cannot be isolated because of the complexity of the interfaces. The enhancement in Gilbert damping indicates that the diffused oxygen in the samples is extremely low and does not significantly affect the interfacial spin transparency and exchange interaction, unlike TIs exposed to atmosphere. In contrast to thick metallic FM films, MIs show more pronounced changes in magnetism because of proximity to large SOC materials.\[46,48\] Fitting the Kittel equation to the \(f_{\text{res}}\) versus \(H_{\text{res}}\) relation, the values of \(2\gamma\) and \(4\pi M_{\text{eff}}\) of the samples as shown in Figure 7c and Table 2. The \(4\pi M_{\text{eff}}\) values for \(z_{\text{TiO}_x} = 2\) and 3 nm were very close to the NZFO control sample.

![Figure 6](image)

Figure 6. Results of FMR experiments on Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO. a) Linewidth \(\Delta H\) as a function of FMR frequency, b) summary of Gilbert damping, and c) FMR frequency as a function of field for NZFO and Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO. d) Comparison of change in \(\gamma\) compared to the control sample of NZFO because of spin-orbit torque (SOT) in the Bi\(_2\)Te\(_3\) layer.

### Table 2. Properties for Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO heterostructures for different TiO\(_x\) interlayer thickness.

| Material               | \(z_{\text{TiO}_x}\) [nm] | 4\(\pi M_{\text{eff}}\) [kOe] | \(\alpha\) | \(\gamma/2\pi\) [MHz Oe\(^{-1}\)] | \(H_{\text{UB}}\) [Oe] | \(H_{\text{C}}\) [Oe] |
|-----------------------|---------------------------|-------------------------------|-----------|-------------------------------|----------------|----------------|
| NZFO                  | –                         | 6.31                          | 0.0118    | 2.81                          | 0              | 161.71        |
| Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO | 1                         | 2.52                          | 0.0313    | 3.05                          | 4.92          | 171.89        |
| Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO | 2                         | 6.57                          | 0.0134    | 2.92                          | 0              | 171.75        |
| Bi\(_2\)Te\(_3\)/TiO\(_x\)/NZFO | 3                         | 6.56                          | 0.012     | 2.79                          | 0              | 175.51        |

The parameters are described in the text.
However, the $z_{\text{TiO}_x}=1$ nm sample showed a dramatic reduction to less than half the other values. This change in $4\pi M_{\text{eff}}$ has possible contributions from: (1) the exchange interaction between the magnetic moments in the MI and TI, as well as (2) new materials phases formed from diffusion and solid-state reactions in the interface, and (3) PIM in the TI due to the adjacent MI. However, these effects could not be isolated in this study and will need further analysis in the future. Furthermore, the $\gamma$ values for the Bi$_2$Te$_3$/TiO$_x$/NZFO samples obtained from the Kittel equation fittings in Figure 6c and listed in Table 2 were significantly different compared to the NZFO control sample. The large changes in $\gamma$ plotted in Figure 6d signify strong exchange interaction effect of the magnetic moments in the MI with the TSSs in the TI surface. The HRTEM and EDS measurements in the earlier section clearly indicated lack of diffusion in the Bi$_2$Te$_3$/TiO$_x$/Py when TiO$_x$ has a thickness larger than 2 nm. This confirms a finite exchange interaction between the TSS and MI even with a finite separation between them.

2.3.3. Interfacial AFM Phase in Bi$_2$Te$_3$/TiO$_x$/NZFO Heterostructures

An AFM interface layer was formed in the Bi$_2$Te$_3$/TiO$_x$/NZFO sample with $z_{\text{TiO}_x}=1$ nm, similar to that discovered in Bi$_2$Te$_3$/Py samples. AFM layers form at the interface in Bi$_2$Te$_3$/Py and Bi$_2$Te$_3$/TiO$_x$/Py samples as a result of interdiffusion and solid state reaction with the TI surface states. In the earlier section clearly indicated lack of diffusion in the Bi$_2$Te$_3$/TiO$_x$/NZFO (and Py) when TiO$_x$ has a thickness larger than 2 nm. This confirms a finite exchange interaction between the TSS and MI even with a finite separation between them.

However, at 6 K the $m(H)$ loop showed a noticeable off-center shift of $\approx 5$ Oe signifying exchange bias from the interaction at the AFM–FM interface. The samples with thicker TiO$_x$ (>2 nm) barrier and the control NZFO sample had a well-centered hysteresis loop at 6 K as well as 300 K, indicating no discernable exchange bias. Table 2 lists values for the exchange bias, $H_{\text{EB}}$ and coercive field, $H_C$. This exchange bias is a clear signature of AFM order in the interface emerging in the ferrite heterostructures, possibly due to solid-state surface chemical reactions promoted by the TSSs of Bi$_2$Te$_3$. The AFM order in the interface may also arise from PIM in the disordered interface composed of Fe, Bi, and Te, similar to V-doped Sb$_2$Te$_3$/EuS interfaces demonstrated by Lee et al. These novel magnetic interfacial layers can have topological nontrivial properties as was shown earlier, but the mechanism is still controversial. It is noteworthy that an effective TiO$_x$ barrier, TI/FM as well as TI/MI heterostructures can be grown without changing the crystalline phase of the TI while still maintaining magnetic interactions between MI (or FM) and TSSs. These experimental results are expected to open further exploration of exotic quantum states in interface-engineered TI/MI and TI/FM heterostructures.

3. Conclusions

Exposure of TI surface to atmosphere was shown to result in formation of oxides on the surface that are impervious to spin currents and coherent electron hopping. The surface oxidation of TI was shown to magnetically decouple FM grown on them and showed suppression of spin-pumping, interfacial solid-state reactions, and exchange interactions. An interface engineering method with TiO$_x$ barrier was presented. An ultrathin layer
(<1 nm) of TiOx was shown to protect the TI surface from oxidation without changing the topological properties. This was verified by coupling the TI, Bi2Te3 with the FM, Py, which showed (1) large Gilbert damping enhancement, (2) interfacial solid-state reaction, and (3) large exchange bias because of formation of topological AFM compounds in the interface. With increase in TiOx thickness beyond 2 nm, the interfacial diffusion can be blocked, while preserving a large spin-pumping effect in Bi2Te3/TiOx/Py heterostructures. Further, low-temperature atmospheric growth of NiZn-ferrite was used as the magnetic insulator in heterostructures. The magnetic properties of NZFO MI on Bi2Te3/TiOx bilayers were studied. Similar to the Bi2Te3/TiOx/Py samples with an ultrathin dusting layer of TiOx (nominally, zTiOx = 1 nm), significant surface reactions were observed for the zTiOx = 1 nm Bi2Te3/TiOx/NZFO samples, which also showed Gilbert damping, large deviation in gyromagnetic ratio and a small but noticeable exchange bias at low temperatures (6 K). However, with higher TiOx barrier thickness, the interface reactions between Bi2Te3 and NZFO was prevented. The results in this study are expected to open a path towards further exploration of interface engineered TI/FM and TI/MI heterostructures for energy efficient spintronic device applications.

4. Experimental Section

Growth of Ti/FM and Ti/TiOx/FM Heterostructures Using Magnetron Sputtering: The TI, Bi2Te3, and Py thin films were grown using the same process conditions as the previous work.[42] For studying the effect of surface oxidation, Bi2Te3 was exposed to atmosphere before deposition of the FM layer. For the interface engineered samples, Ti thin films were grown using DC magnetron sputtering with 30 W power and 3 mT Ar. The growth rate of TI thin films was 0.019 nm s−1, which were oxidized upon exposure to atmosphere. All the samples were capped with 3 nm of Al on top of the FM, which was subsequently oxidized to AIOx on exposure to atmosphere.

Low-Temperature Growth of MI, NZFO Using Spin-Spray Process: Polycrystalline NZFO thin films with thickness of 250 nm were deposited on a Si/SiO2 substrate using a homemade 24° spin spray. The spin-spray growth process for NZFO includes a precursor solution with 1.54 g L−1 of FeCl2, 0.04 g L−1 of ZnCl2, 0.03 g L−1 of NiCl2 and an oxidizer solution with 0.14 g L−1 of NaNO2 and 11.48 g L−1 of CH3COONa. The precursor solution had a pH level of 3–4 and the oxidizer solution had a pH level of 10.8. The process was carried out at a temperature of ≈100 °C with 500 mL volume of solutions. Detailed discussion of the growth of the NZFO films using the spin-spray process is available.[38,39] XPS measurements of the NZFO samples revealed 77.4%, 19.3%, 2.0%, and 1.2% average atomic concentrations of O, Fe, Ni, and Zn, respectively.

Ferromagnetic Resonance: Broad-band FMR experiments were performed using field-sweeping at constant frequencies. The FMR signal was detected using a lock-in amplifier for enhanced sensitivity. The RF field for exciting magnetization in the samples was provided by a coplaner waveguide. A pair of Helmholtz coils which produced an AC magnetic field (500 Hz) was used for the driving field. Control of the experiment and data acquisition was done using national instruments LabVIEW. The parameters, FMR linewidth ΔH and resonance field Hres were extracted by fitting a Lorentzian function to the FMR spectra, given by,

$$\frac{dP}{dH} = \frac{4\pi H}{(4\pi H)^2 + (\Delta H)^2} = \frac{4\pi H}{(4\pi H - H_{res})^2 + (\Delta H)^2} = K H - \Delta H^2 - 4H_{res}^2. $$

Here, K is the absorbed RF power, K = (i = 1, 2) are constants, and H is the applied DC magnetic field.

Measurement of m(H) Hysteresis Loops: Magnetization m(H) measurements were obtained using a Quantum Design MPMS XL-7 superconducting quantum interference device (SQUID) magnetometer.[42,43] Hysteresis loop m(H) measurements were carried out at various temperatures between 6 and 300 K. The ZFC m(T) measurements were obtained while increasing the temperature in an applied field of 50 Oe. Room temperature m(H) measurements were also taken using a vibrating sample magnetometer (VSM).

TEM and EDS Measurements: Samples for TEM investigations were prepared by focused ion beam milling (FIB) using a Ga+ ion source.[42,43] Prior to TEM observation an additional cleaning procedure was performed by Ar-ion milling to reduce a surface amorphous layer and residual Ga from the FIB process. The TEM observations were performed using a Talos 200-FX (ThermoFisher Scientific Inc.) TEM operated at an acceleration voltage of 200 kV. EDS measurements were performed using a ChemiSTEM (ThermoFisher Scientific) and processing of the spectra was performed using Esprit 1.9 (Brucker Inc.) software.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

ferromagnets, interfaces, magnetic topological insulators, topological insulators, van der Waals materials

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