Stabilization of a honeycomb lattice of IrO$_6$ octahedra in superlattices with ilmenite-type MnTiO$_3$

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Abstract

In the quest for quantum spin liquids, thin films are expected to open the way for the control of intricate magnetic interactions in actual materials by exploiting epitaxial strain and two-dimensionality. However, materials compatible with conventional thin-film growth methods have largely remained undeveloped. As a promising candidate towards the materialization of quantum spin liquids in thin films, we here present a robust ilmenite-type oxide with a honeycomb lattice of edge-sharing IrO$_6$ octahedra artificially stabilized by superlattice formation with an ilmenite-type antiferromagnetic oxide MnTiO$_3$. The stabilized sub-unit-cell-thick Mn–Ir–O layer is isostructural to MnTiO$_3$, having the atomic arrangement corresponding to ilmenite-type MnIrO$_3$ not discovered yet. By spin Hall magnetoresistance measurements, we found that antiferromagnetic ordering in the ilmenite Mn sublattice is suppressed by modified magnetic interactions in the MnO$_6$ planes via the IrO$_6$ planes. These findings lay the foundation for the creation of two-dimensional Kitaev candidate materials, accelerating the discovery of exotic physics and applications specific to quantum spin liquids.
Introduction

Recent progress in the physics of quantum spin liquids has intensified search for new candidate materials. In the materials design, an exactly solvable $S = 1/2$ spin model on a two-dimensional honeycomb lattice has given a rigorous theoretical framework, which was firstly proposed by Kitaev and later reformalized with realistic materials by Jackeli and Khaliullin. The key ingredient of the model is a honeycomb lattice of edge-sharing metal-anion octahedra comprising of Ru$^{3+}$ or Ir$^{4+}$ ions with a $d^5$ electron configuration, which produces bond-specific Ising-like interactions, called Kitaev-type interactions, giving rise to strong quantum fluctuations of (pseudo)spins on the honeycomb lattice. In $\alpha$-RuCl$_3$ and iridates like Na$_2$IrO$_3$, $\alpha$-, $\beta$-, and $\gamma$-Li$_2$IrO$_3$, and H$_3$LiIr$_2$O$_6$ with such a geometry, possibilities of quantum spin liquids via Kitaev-type interactions have been argued intensively. In tandem with theoretical approaches, advanced experiments on bulk crystals, such as magnetic resonant x-ray diffraction (XRD), thermal Hall effect, and nuclear magnetic resonance, have contributed to clarifying complex magnetic phases, as well as identifying the quantum spin liquid state.

One of the major challenges in this research field is to incorporate those materials into thin films, especially atomically thin monolayer forms. Thin-film techniques are not only essential for eventual practical applications but also effective for providing additional degrees of freedom for controlling magnetic interactions in actual materials. For example, epitaxial
strain at the interface and dimensionality control\textsuperscript{16–18} can offer new options to address the issue that the expected Kitaev-type interactions are often broken by the antiferromagnetic ordering due to structural distortion and interlayer coupling\textsuperscript{6–13,19,20}. However, it is quite difficult to prepare high-quality films of $\alpha$-RuCl\textsubscript{3} (refs. \textsuperscript{6,7}) and iridates with H and Li (refs. \textsuperscript{10–14}) that have so far gained attention as the bulk candidate materials. This is because their volatile and/or diffusible nature must entail extremely careful control of stoichiometry and suppression of inter-diffusion for reproducing the bulk properties. Considering these problems in known Kitaev candidate materials, we aimed to find a new crystal system applicable for the thin-film research and focused on ilmenite-type $ABO_3$ compounds (where $A$ and $B$ are metal cations) containing Ir\textsuperscript{19,20}. Recently, Haraguchi et al. reported the bulk synthesis of ilmenite-type ZnIrO\textsubscript{3} and MgIrO\textsubscript{3}, which possess a honeycomb lattice of edge-sharing IrO\textsubscript{6} octahedra in $ab$ plane\textsuperscript{19} (see Fig. 1(a) for the ilmenite-type structure). The authors discussed an XY-like magnetic anisotropy and a tilting magnetic structure that is possibly related to Kitaev-type interactions\textsuperscript{19}.

In this study, starting from ilmenite-type MnTiO\textsubscript{3} for which the single-crystalline film growth on Al\textsubscript{2}O\textsubscript{3}(0001) has been established\textsuperscript{21,22}, we attempted to stabilize Ir at the $B$-site of ilmenite-type Mn$B$O\textsubscript{3}, as shown in Fig. 1(a). By taking advantage of epitaxial strain in superlattices with ilmenite-type MnTiO\textsubscript{3}, which shares the $A$-site MnO\textsubscript{6} plane, we materialized the honeycomb lattice of edge-sharing IrO\textsubscript{6} octahedra in the ilmenite lattice. This ultrathin-film form of iridate will serve as an intriguing two-dimensional platform for pursuing the physics of Kitaev
materials.

Results

Structural characterization by x-ray diffraction (XRD). The films were grown on Al₂O₃(0001) substrates by pulsed-laser deposition using a KrF excimer laser (see Methods). Our early attempt to grow ilmenite-type MnIrO₃ directly on Al₂O₃(0001) was not successful, resulting in phase-separated films of Mn₃O₄ and IrO₂ (see Fig. S1 in Supporting Information for the XRD pattern). We then took a superlattice approach¹⁶⁻¹⁸ based on ilmenite-type MnTiO₃ thin films²¹,²². In the superlattice structure, the common A-site MnO₆ plane is expected to promote the ilmenite-type stacking of MnO₆ and IrO₆ planes along the c-axis direction (the left of Fig. 1(a)). A schematic structure of a typical superlattice is given in Fig. 1(b), where a MnTiO₃ buffer layer with a thickness between 4.3 nm and 7.8 nm is initially grown on Al₂O₃(0001), followed by alternate deposition of much thinner Mn–Ir–O and MnTiO₃ layers. The film thickness of 1.4 nm is roughly equal to typical c-axis parameters of ilmenite-type oxides. In a 0.5-nm-thick Mn–Ir–O (cap)/[4.3-nm-thick MnTiO₃/0.5-nm-thick Mn–Ir–O]₁₅/5.7-nm-thick MnTiO₃(buffer) film (superlattice cycle number 𝑛 = 15 in Fig. 1(b)), the overall chemical composition of the film as evaluated by energy-dispersive x-ray spectroscopy (EDX) was Mn : Ti : Ir = 50.4 : 45.1 : 4.5, in good agreement with the ideal composition of Mn : Ti : Ir = 50.0 : 44.9 : 5.1 expected from the thickness ratio designed. In the out-of-plane XRD pattern shown in Fig. 1(c), four main diffraction peaks are observed from the
film, which are assignable to \((0003n)\) \((n: \text{natural number})\) of the ilmenite-type structure. The appearance of satellite peaks near \((0006)\) and \((00012)\) peaks (indicated by red arrows) reflects periodic modulation in the x-ray scattering cross-section by the superstructure of MnTiO\(_3\) and Mn–Ir–O layers, evidencing that an alloy compound of Mn(Ti,Ir)O\(_3\) is not formed. Assuming the abrupt MnTiO\(_3\)/Mn–Ir–O interface without inter-diffusion, the average in-plane and out-of-plane lattice parameters of the single unit of the superlattice, i.e., \([4.3\text{-nm-thick MnTiO}_3/0.5\text{-nm-thick Mn–Ir–O}]\), are found to be \(a = 5.13\ \text{Å}\) and \(c = 14.29\ \text{Å}\) from the reciprocal space mapping around \((02\overline{2}10)\) (Fig. 1(d)). Since these values differ very little from \(a = 5.1396\ \text{Å}\) and \(c = 14.29\ \text{Å}\) of MnTiO\(_3\) (JCPDS PDF No. 00-029-0902), the lattice parameters of Mn–Ir–O are comparable to those of MnTiO\(_3\). Also, the three-fold symmetry of the \((10\overline{1}4)\) diffraction peak is detected in the in-plane azimuthal \(\phi\) scan measurements (Fig. 1(e)), confirming the epitaxial orientation relationship of the film \([10\overline{1}0](0001) // \text{Al}_2\text{O}_3 [10\overline{1}0](0001)\). Combined together, these results indicate that the film grows as a \(c\)-axis oriented, single-crystalline ilmenite-type oxide with a periodically modulated internal structure.

We examined the critical \(d_{\text{MIO}}\) value for maintaining the single-crystalline film growth by varying the thickness of Mn–Ir–O layers \(d_{\text{MIO}}\) in the \([4.3\text{-nm-thick MnTiO}_3/d_{\text{MIO}}\text{-nm-thick Mn–Ir–O}]_{15}\) superlattice. As shown in Figs. 2(a) and 2(b), the films with \(d_{\text{MIO}} = 0.5\ \text{nm}\) (identical to the sample in Fig. 1) and 1.0 nm exhibit clear (0006) peaks associated with satellite peaks (red arrows). In particular for \(d_{\text{MIO}} = 0.5\ \text{nm}\), thickness fringes appear around the (0006)
peak, which indicate that the total film thickness is uniform over the entire film. Given that the observed satellite peaks are superlattice reflections, the single-unit lengths of the superlattices are calculated to be 4.5 nm for $d_{\text{MIO}} = 0.5$ nm and 5.6 nm for $d_{\text{MIO}} = 1.0$ nm, which coincide well with the designed values of 4.8 nm ($= 4.3 + 0.5$ nm) and 5.3 nm ($= 4.3 + 1.0$ nm), respectively. In the thickest film with $d_{\text{MIO}} = 1.4$ nm (Fig. 2(c)), however, superlattice reflections become indiscernible along with the occurrence of a diffraction peak of segregated IrO$_2$ impurities; the designed superlattice structure is no longer formed for $d_{\text{MIO}} = 1.4$ nm. The concomitant decrease in the (0006) diffraction intensity implies that the basal MnTiO$_3$ layers in the superlattice are also rather disordered. Therefore, the upper bound of $d_{\text{MIO}}$ for stabilizing IrO$_6$ planes in the ilmenite lattice is as thin as 1.0 nm, which is smaller than typical $c$-axis parameters of ilmenite-type oxides (approximately 1.4 nm). This sub-unit-cell thick Mn–Ir–O layer admits two IrO$_6$ planes at most, indicating the fragile crystalline phase of Mn–Ir–O. Sandwiching between stable MnTiO$_3$ layers in the superlattice structure stabilizes the ilmenite-type atomic ordering of Mn–Ir–O ultrathin layers.

**Microstructural characterization by scanning transmission electron microscopy (STEM).**

Our concept to form honeycomb-lattice IrO$_6$ planes was further evidenced by cross-sectional STEM observation (Methods). In a [MnTiO$_3$/Mn–Ir–O]$_8$/MnTiO$_3$(buffer) film (no Mn–Ir–O cap, see Fig. S2 for the XRD pattern), eight bright layers running parallel to the film plane are detected in the wide-area high-angle annular dark-field (HAADF) image, shown in Fig. 3(a).
Owing to the Z-contrast nature (Z: atomic number)$^{23}$, the bright layers must contain much Ir that has the largest Z among the constituent elements (Mn, Ti, Ir, and O). Also, there are tiny bright island-like regions possibly because of segregated Ir-rich impurities. A close inspection on the single unit of the superlattice (Fig. 3(b)) reveals that a Mn–Ir–O layer between MnTiO$_3$ layers contains a couple of bright atomic planes along the [0001] direction. Using the atomically resolved HAADF image of Fig. 3(c) (the area marked by yellow dashed lines in Fig. 3(b)), we compared each atomic site with a model structure (Fig. 3(d)). It was reported for MnTiO$_3$ that the MnO$_6$ (TiO$_6$) plane has a larger (smaller) atomic displacement along the [0001] direction between intra-plane Mn (Ti) ions$^{24}$. By measuring the atomic displacement in the image, we identified that Ir atoms are located at the $B$-site, which is occupied with Ti atoms in MnTiO$_3$, as schematically shown in Fig. 3(d) (also see the left of Fig. 3(c)). In addition, the bright Ir-containing planes are regularly sandwiched between MnO$_6$ planes, with having similar dumbbell-like characteristic atomic arrangement. On the basis of these results, we conclude that a honeycomb lattice of edge-sharing IrO$_6$ octahedra crystallizes in the Mn–Ir–O layer with ilmenite-type atomic ordering. Note here that the Mn–Ir–O layer composed of two pairs of IrO$_6$ and MnO$_6$ planes corresponds to the 2/3 unit cell (u.c.) of the ilmenite lattice (Fig. 1(a)). We also conducted electron energy loss spectroscopy (EELS) for Mn $L$, Ti $L$, and O $K$ edges in the MnTiO$_3$ buffer and Mn–Ir–O layer regions (Fig. S3). While the Mn $L$-edge spectra agree well between the two regions (i.e., Mn$^{2+}$), partial reduction of Ti$^{4+}$ to Ti$^{3+}$ occurs around the
Mn–Ir–O layer$^{25,26}$. Associated with this reduction, the existence of oxygen deficiency is suggested from the O K-edge spectra. We infer that Mn$^{2+}$ and Ir$^{4+}$ are stable under the oxygen pressure of 10 mTorr used for the deposition, whereas Ti$^{4+}$ is slightly reduced to Ti$^{3+}$. Charge transfer between $B$-site TiO$_6$ and IrO$_6$ planes via $A$-site MnO$_6$ planes may be relevant to this point, though it is not clear at this stage.

**Investigation of surface magnetic order by spin Hall magnetoresistance measurements.**

Judging from these structural analyses, a honeycomb lattice of edge-sharing IrO$_6$ octahedra should partly form a two-dimensional network in the superlattice. While some iridates are known to exhibit metallic conduction$^{27-31}$, our superlattice samples were highly insulating (not shown), suggesting the non-metallic electronic structure of Mn–Ir–O as well as the antiferromagnetic insulator MnTiO$_3$. Moreover, with experimental methods applied to bulk crystals$^{10,13-15}$, it is difficult to evaluate magnetism in ultrathin films, particularly for cases of antiferromagnetism and quantum spin liquids. Thus, we studied the surface magnetic order using the spin Hall magnetoresistance (SMR) method, which enables electrical characterization of ferromagnetic$^{32}$ and antiferromagnetic transitions$^{33-35}$, and magnetic anisotropy. By measuring SMR arising at the interface of Pt and MnTiO$_3$ ultrathin films, we have recently demonstrated that the bulk Néel temperature $T_N$ ($\sim 63$ K)$^{36}$ and the uniaxial magnetic anisotropy along the $c$-axis direction persist down to the film thickness of 2.9 nm $\sim 2$ u.c. with six MnO$_6$ planes (thin-MnTiO$_3$ monolayer in Fig. S4)$^{22}$. For the present experiment, we examined five
different heterostructures: Pt/4.3-nm-thick MnTiO₃ (thick-MnTiO₃ monolayer), Pt/1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃ (bilayer), and Pt/1.0-nm-, 1.9-nm-, and 4.3-nm-thick MnTiO₃/1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃ samples (trilayer A, B, and C, respectively). Schematic structures and XRD patterns of the samples are given in Figs. S4 and S5, respectively. As shown in the inset of Fig. 4(a) (Methods), resistances of the two orthogonally arranged Pt channels ($R_1$ for channel 1 and $R_2$ for channel 2) were simultaneously measured under an in-plane magnetic field $H$ applied parallel to channel 1. Figures 4(a), (b), and (c) show the temperature ($T$) dependence of the field-induced resistance variation, $\Delta R = (R_1 / R_2) (\mu_0 H = 0.5 \text{T}) - (R_1 / R_2) (\mu_0 H = 0 \text{T})$, where $\mu_0$ is vacuum permeability. When antiferromagnetic transition takes place in the layer beneath the Pt layer, distinct SMR responses of $R_1$ and $R_2$ below and above $T_N$ result in a kink of $\Delta R$ (refs. 22,33,34). In fact, $\Delta R$ for both the thick-MnTiO₃ monolayer (Fig. 4(a)) and the trilayer C (purple in Fig. 4(c)) exhibits the sudden increase around $T = 60 \text{K}$ upon heating, around which bulk MnTiO₃ undergoes the antiferromagnetic transition36. These results indicate that antiferromagnetic order develops in these 4.3-nm-thick MnTiO₃ top layers (~ 3 u.c. with nine MnO₆ planes) regardless of the underlying Al₂O₃(0001) substrate or the 1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO₃/Al₂O₃(0001) structure. In stark contrast, $\Delta R$ for the bilayer (Fig. 4(b)), and the trilayer A and B (green and light blue in Fig. 4(c)) exhibits the monotonous increase with increasing $T$ without clear anomalies. Although $A$-site spinful MnO₆ planes are common to all samples,
magnetic ordering behavior is thus completely different, which we believe reflects magnetic interactions in Mn–Ir–O, i.e., the unique stacking of honeycomb-lattice IrO$_6$ and MnO$_6$ planes.

**Discussion and Conclusions**

Comparing the SMR results, we discuss possible magnetic properties of Mn–Ir–O. In the thick-MnTiO$_3$ monolayer and the trilayer C terminated with 3-u.c.-thick MnTiO$_3$ top layers, nine MnO$_6$ lie beneath the Pt layer. The clearly detected $T_N$ (the kink in $\Delta R$) in these thick samples is consistent with the robust antiferromagnetic ordering in the thin-MnTiO$_3$ monolayer that we reported previously$^{22}$. The absence of such signatures in the bilayer point to local modification of super-exchange interactions in MnO$_6$ planes by intervening IrO$_6$ planes. Taking into account strong spin-orbit coupling inherent to heavy Ir (refs. $^{1,27–31,37–39}$), the disturbance of the antiferromagnetic order is conceivable. In Fig. 4(d), a tentative picture for spin interactions between the Mn sites (black arrows) in the bilayer is shown schematically, where the antiferromagnetic order develops in the MnTiO$_3$ bottom layer but not in the overgrown Mn–Ir–O layer. In the thin MnTiO$_3$ top layers ($<<$ 2 u.c.) of the trilayer A and B, a similar spin fluctuation is probably caused by the neighboring IrO$_6$ planes.

Extrinsic contributions like the surface roughness and the size effect (refs. $^{40–42}$) to the suppression of antiferromagnetic order in the thin MnTiO$_3$ ($<<$ 2 u.c.) and Mn–Ir–O top layers should also be considered. Firstly, all samples measured have smooth surfaces with root-mean-square roughness values of 0.2–1.0 nm, which cannot not solely account for the distinct SMR
responses. Another support to the negligible role of surface roughness is that the 2-u.c.-thick thin-MnTiO₃ monolayer, despite its island-like film morphology with increased surface roughness, exhibits the bulk-like $T_N$ as in thicker and much flatter samples ($\geq 3$ u.c.)²². Secondly, the total film thicknesses of the heterostructures (including MnTiO₃ and Mn–Ir–O layers) are much thicker than the 2 u.c. so that a sufficiently large volume of the Mn sublattice is ensured for the whole heterostructure. This also helps minimize the possible influence of domain disconnection, which generally becomes pronounced in ultrathin films. In stark contrast, the systematic recovery of antiferromagnetic SMR responses with an increase of the thickness of MnTiO₃ top layer, from the trilayer A (2/3 u.c.), B (4/3 u.c.), to C (3 u.c.), signals the intrinsic origin that is responsible for spin interactions in a characteristic length. Notably, the striking difference between the antiferromagnetic 2-u.c.-thick thin-MnTiO₃ monolayer²² and the non-antiferromagnetic trilayer B (4/3-u.c.-thick MnTiO₃ and 2/3-u.c.-thick Mn–Ir–O (2 u.c. in total) on the MnTiO₃ buffer) manifests that the insertion of honeycomb-lattice IrO₆ planes dramatically affect spin interactions between the nearby Mn sites. Such a spin-disordered (or spin-frustrated) state is possibly linked to quantum spin liquids, though the experimental identification of the featureless magnetic ground state in ultrathin films poses a great challenge⁴³–⁴⁵. Understanding the spin structures (including the Ir sites) and the excited-state properties in Mn–Ir–O with recently advanced diagnostics like Raman spectroscopy¹,⁵,⁴⁶ and in-plane spin transport measurements⁴⁷–⁵⁰ will be the next step. Nevertheless, the suppression
of the strong antiferromagnetic order in the Mn sublattice is promising in showing the feasibility of control of spin interactions by artificially engineering ilmenite-type oxides.

In summary, we have materialized a honeycomb lattice of edge-sharing IrO$_6$ octahedra by superlattice formation with ilmenite-type MnTiO$_3$. The systematic SMR measurements suggested the absence of antiferromagnetic order in the surface Mn–Ir–O layer grown on antiferromagnetic MnTiO$_3$. Even though $A$-site MnO$_6$ planes are common to these oxides, their spin interactions between the Mn sites are quite different. A spin fluctuation induced by strong spin-orbit interactions in IrO$_6$ planes may disturb the antiferromagnetic ordering in the Mn–Ir–O layer and the neighboring regions of the MnTiO$_3$ layers. The stabilization of a two-dimensional IrO$_6$ honeycomb lattice by superlattice technique, as well as potential control of the magnetism via dimensionality and the proximity effect, will trigger the development of ilmenite-based Kitaev materials producing exotic physical phenomena.

Methods

Thin-film growth. A Mn–Ir–O target was prepared from MnO$_2$ and IrO$_2$ powders by spark-plasma-sintering at 50 MPa and 900 °C. The target composition as measured by EDX was Mn : Ir = 0.90 : 1 (atomic ratio). A MnTiO$_3$ buffer layer was grown at a substrate temperature of 850 °C and an oxygen pressure of 10 mTorr using a Mn–Ti–O target. Subsequently, Mn–Ir–O and MnTiO$_3$ layers were alternately deposited for $n$ cycles at 800 °C and 10 mTorr for the formation of a [Mn–Ir–O/MnTiO$_3$]$_n$ superlattice. The crystal structure and composition of the
films were characterized by XRD using Cu $K_{\alpha}$ radiation and EDX, respectively.

**SMR measurements.** A Pt film with a thickness of approximately 2 nm was deposited on the film surface by radio-frequency magnetron sputtering at 150 °C. The heterostructured film was then patterned into an L-shaped multi-terminal device structure using photolithography and Ar-ion milling, followed by electron-beam evaporation of Au/Ti electrodes. Resistance was measured by the four-probe method using a semiconductor parameter analyzer (Agilent 4155C) and nano-volt meters (Keithley 2182A) in a physical property measurement system (Quantum Design Inc.) equipped with a one-axis sample rotator. Details for the measurement scheme and analysis were reported in ref. 22.

**Electron microscopy.** To obtain an electron-transparent thin specimen, the grown thin film with the substrate was mechanically polished, and Ar-ion beam milling was performed at 0.5 kV in the final stage. For the atomic and electronic structure analyses, an aberration corrected STEM system (JEOL ARM300CF) was used, equipped with a DELTA corrector, a cold field emission gun, and an EELS spectrometer (Quantum, Gatan Inc.), operated at 300 kV. The probe forming aperture was 30 mrad and the collection semi-angle for HAADF was 85–200 mrad.
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Author contributions

K.M. grew the films, and performed the SMR measurements along with K.F. K.N., R.I., and N.S. conducted the STEM analysis. K.F., K.M., and A.T. wrote the manuscript with input from other authors. All authors discussed the results. A.T. supervised the project.

Competing interests

The authors declare no competing interests.

Data Availability

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

**Figure 1. Superlattices of ilmenite-type MnTiO$_3$ and Mn–Ir–O.** a, Left: Crystal structure of ilmenite-type MnBO$_3$ viewed along the [1120] direction, drawn by VESTA (ref. 51). Right: Honeycomb lattice formed by edge-sharing BO$_6$ octahedra in $ab$ plane. Black quadrangles represent the unit cell. b, Schematic structure of a Mn–Ir–O(cap)/[d$_{MTO}$-nm-thick MnTiO$_3$/d$_{MIO}$-nm-thick Mn–Ir–O]$_n$/MnTiO$_3$(buffer) film grown on Al$_2$O$_3$(0001). c, Out-of-plane XRD pattern of a film with $d_{MTO} = 4.3$ nm (3 u.c.), $d_{MIO} = 0.5$ nm, and $n = 15$. The thickness of MnTiO$_3$ buffer layer was 5.7 nm (4 u.c.). Red arrows and asterisks indicate superlattice reflections and forbidden Al$_2$O$_3$(0003$_n$) reflections, respectively. d, Reciprocal space mapping around Al$_2$O$_3$ (02110). (e) In-plane $\phi$ scan results for (1014) peaks of Al$_2$O$_3$ substrate (top) and the film (bottom).

**Figure 2. Examination of the critical $d_{MIO}$ value.** a,b,c, Out-of-plane XRD patterns for $d_{MIO}$-nm-thick Mn–Ir–O(cap)/[4.3-nm-thick MnTiO$_3$/d$_{MIO}$-nm-thick Mn–Ir–O]$_{15}$/5.7-nm-thick MnTiO$_3$(buffer) films with $d_{MIO}$ values of (a) 0.5 nm, (b) 1.0 nm, and (c) 1.4 nm.

**Figure 3. Scanning transmission electron microscopy analysis.** HAADF-STEM images of a [MnTiO$_3$/Mn–Ir–O]$_8$/MnTiO$_3$(buffer) film (without a Mn–Ir–O cap layer) viewed along the Al$_2$O$_3$[1120] direction: a, wide area, b, the MnTiO$_3$/Mn–Ir–O/MnTiO$_3$ interface region, and c, the atomically resolved images (the area marked by yellow dashed lines in (b)). d, Schematic crystal structure corresponding to (c).
**Figure 4. Spin Hall magnetoresistance measurements.** a,b,c, Field-induced variation ($\mu_0 H = 0.5$ T) in the resistance ratio of two orthogonally arranged Pt channels, $R_1 / R_2$, for (a) 4.3-nm-thick MnTiO$_3$ monolayer (thick-MnTiO$_3$), (b) 1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO$_3$ bilayer (bilayer), and (c) 1.0-nm-, 1.9-nm-, and 4.3-nm-thick MnTiO$_3$/1.0-nm-thick Mn–Ir–O/4.3-nm-thick MnTiO$_3$ trilayer samples (trilayer A, B, and C, respectively). Inset in (a) shows the measurement setup, where the $R_1$ and $R_2$ are measured simultaneously under an in-plane magnetic field $H$ applied parallel to channel 1 with $R_1$ (perpendicular to channel 2 with $R_2$). $I^+$ and $I^-$ are the electrodes used for current injection. d, Schematic for the spin ordering at Mn sites in the Mn–Ir–O/MnTiO$_3$ bilayer sample expected from the SMR responses. Upper panel: metal-oxygen octahedra in $ab$ plane. Small red spheres represent O ions. Yellow colored octahedra are located above gray colored octahedra. Lower panel: Cross-sectional view along the [11\overline{2}0] direction. Pink, light blue, and brown spheres represent Ir, Mn, and Ti ions accommodated in the oxygen octahedra, respectively. Only localized moments of Mn ions are depicted by black arrows.
Figure 1

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