Supplementary Information

A high-T_C heavy rare earth monoxide semiconductor TbO with more than half-filled 4f orbital

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Table S1 Growth parameters of TbO, Tb_2O_3, and Tb thin films.

Sample	Substrate	Target	$T_{\mathrm{substrate}}$ [°C]	P_{O_2} [Torr]	E_{laser} [J/cm^2]	Repetition rate [Hz]
TbO	CaF_2 (001)	Tb_4O_7	375	-	0.75	15
Tb_2O_3	$YAlO_3$ (110)	Tb_4O_7	250	5.0×10^{-6}	0.50	5
Tb	CaF_2 (111)	Tb	R.T.	-	0.70	20

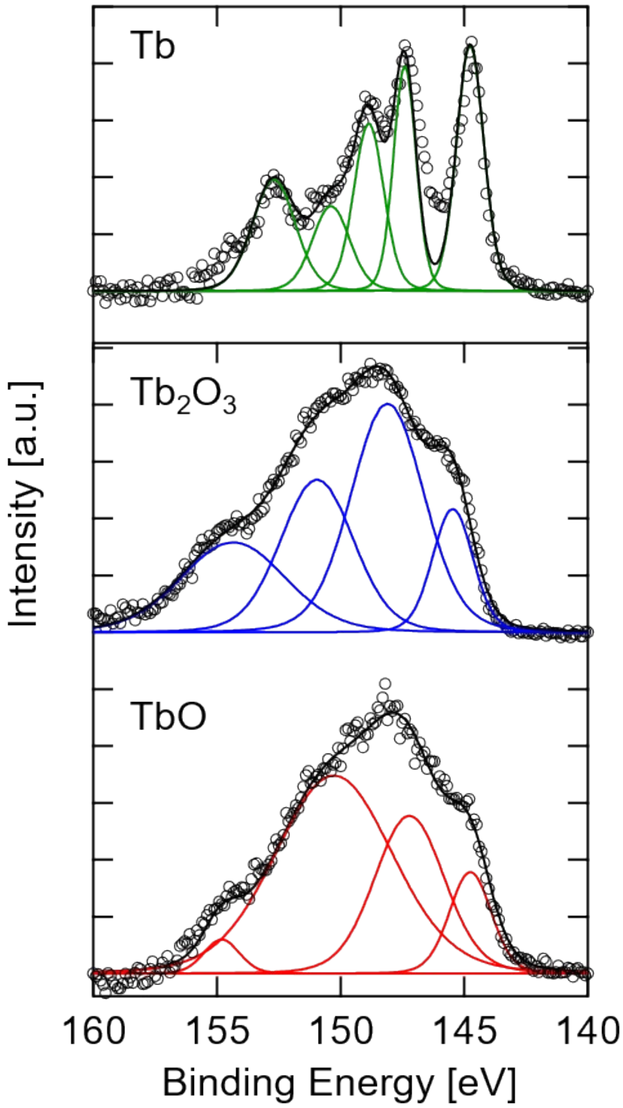

Fig. S1 Tb 4d XPS spectra of TbO, Tb$_2$O$_3$ and Tb thin films. The atomic ratio of Tb:O in TbO thin film was evaluated to be 1:0.95, as described below. Prior to the measurements, capping or surface oxidation layer was removed by in-situ Ar ion sputtering.

Quantitative analysis of TbO layer in TbO thin film by XPS

The composition of a TbO thin film was determined from the areal intensity ratio of Tb 4d and O 1s peaks by XPS measurements. The surface oxidized Tb_2O_3 layer of the TbO thin film was removed by Ar^+ sputtering. For the quantitative composition analysis, a Tb_2O_3 thin film was used as a reference, assuming its stoichiometric composition.

The Tb:O ratio was evaluated by considering the electron inelastic mean free paths (IMFP) with the TPP-2M predictive equation.[S1] The atomic concentration of each atom C_i (i = Tb, O) in TbO was obtained by the areal intensity of each atom in TbO and Tb_2O_3 (I^{TbO}_i, I^{Tb2O3}_i), the IMFP of each atom in TbO and Tb_2O_3 (λ^{TbO}_i, λ^{Tb2O3}_i), and the atomic density of each atom in TbO and Tb_2O_3 (N^{TbO}_i, N^{Tb2O3}_i) as follows, where K_i is relative intensity $K_i = I^{TbO}_i/I^{Tb2O3}_i$).[S2]

$$
\begin{aligned}
C_i &= \left(I^{TbO}_i/I^{Tb2O3}_i\right)/\left\{\left(N^{TbO}_i/N^{Tb2O3}_i\right) \times \left(\lambda^{TbO}_i/\lambda^{Tb2O3}_i\right)\right\} \\
&= (K_i)/\left\{\left(N^{TbO}_i/N^{Tb2O3}_i\right) \times \left(\lambda^{TbO}_i/\lambda^{Tb2O3}_i\right)\right\} \\
&= (K_i) \times \left\{\left(N^{Tb2O3}_i\right) \times \left(\lambda^{Tb2O3}_i/\lambda^{TbO}_i\right)\right\}/N^{TbO}_i
\end{aligned}
$$

The relative intensity (K_i) of Tb and O was calculated to be K_{Tb} = 1.01 and K_o = 0.596. Because of unknown N^{TbO}_i, the relative atomic concentration (C^{rel}_i) was introduced with the matrix factor, $F_i = N^{Tb2O3}_i \times \left(\lambda^{Tb2O3}_i/\lambda^{TbO}_i\right)$[S2]

$$
C^{rel}_i = C_i/\sum C_i = \left(K_iF_i/N^{TbO}_i\right)/\sum\left(K_iF_i/N^{TbO}_i\right) = (K_iF_i)/\sum(K_iF_i)
$$

From the TPP-2M IMFP equation, λ^{TbO}_{Tb}= 5.68 Å and λ^{TbO}_{O}= 7.98 Å, while λ^{Tb2O3}_{Tb}=7.65 Å and λ^{Tb2O3}_{O}= 11.5 Å. In the referential Tb_2O_3 thin film, N^{Tb2O3}_{Tb}= 0.0496 mol/cm^3 and N^{Tb2O3}_{O}= 0.0596 mol/cm^3. Thus, the matrix factor F_{Tb}= 0.0537 and F_O= 0.0861. Thus,

$$C^{rel}{}_{Tb} = \left(K_{Tb}/F_{Tb}\right)/\left(K_{Tb} \times F_{Tb} + K_O \times F_O\right) = 0.513,$$

$$C^{rel}{}_{O} = \left(K_O/F_O\right)/\left(K_{Tb} \times F_{Tb} + K_O \times F_O\right) = 0.486.$$

Therefore, the Tb:O ratio of TbO thin film, $C^{rel}{}_{Tb}$:$C^{rel}{}_{O}$, was 1:0.95.

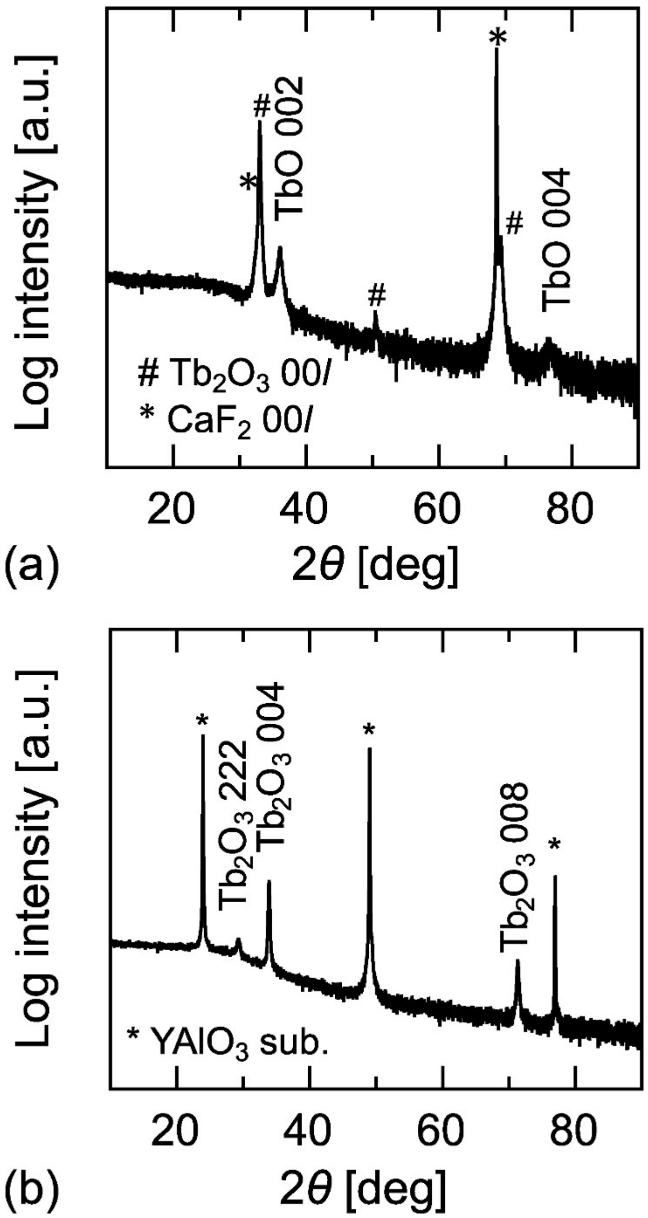

Fig. S2 Typical XRD θ–2θ patterns of (a) TbO thin film grown on CaF_2 (001) substrate (the same data as Fig. 1a) and (b) Tb_2O_3 thin film grown on $YAlO_3$ (110) substrate.

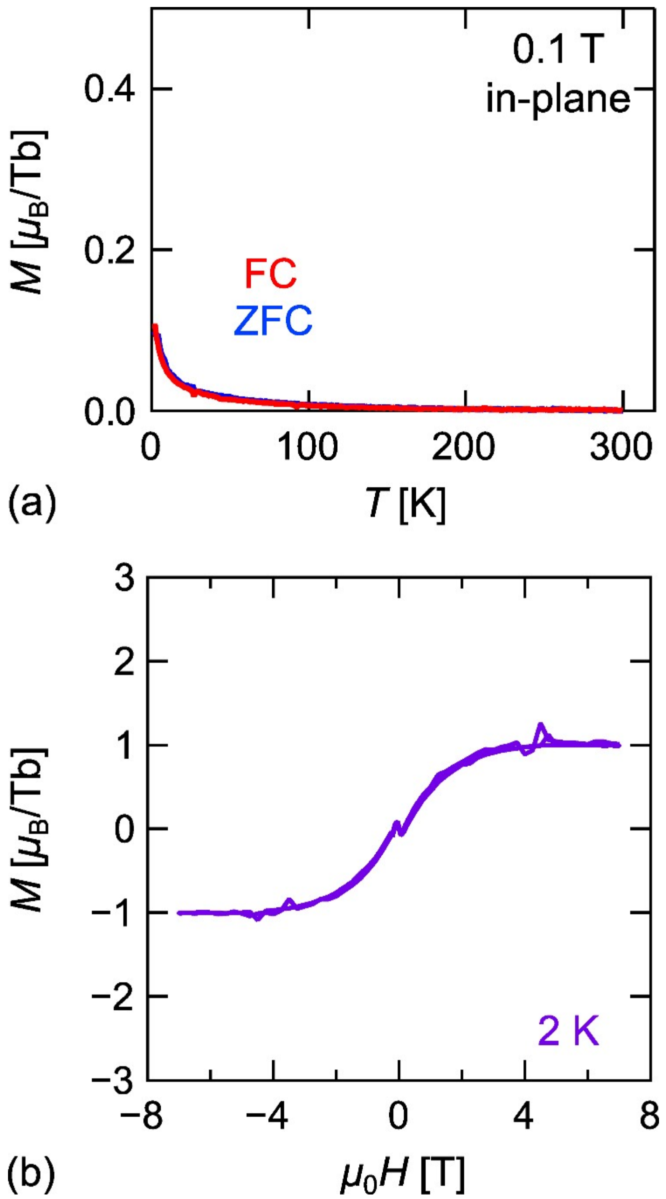

Fig. S3 (a) Temperature and (b) magnetic field dependence of magnetization for Tb_2O_3 (001) epitaxial thin film under in-plane magnetic field.

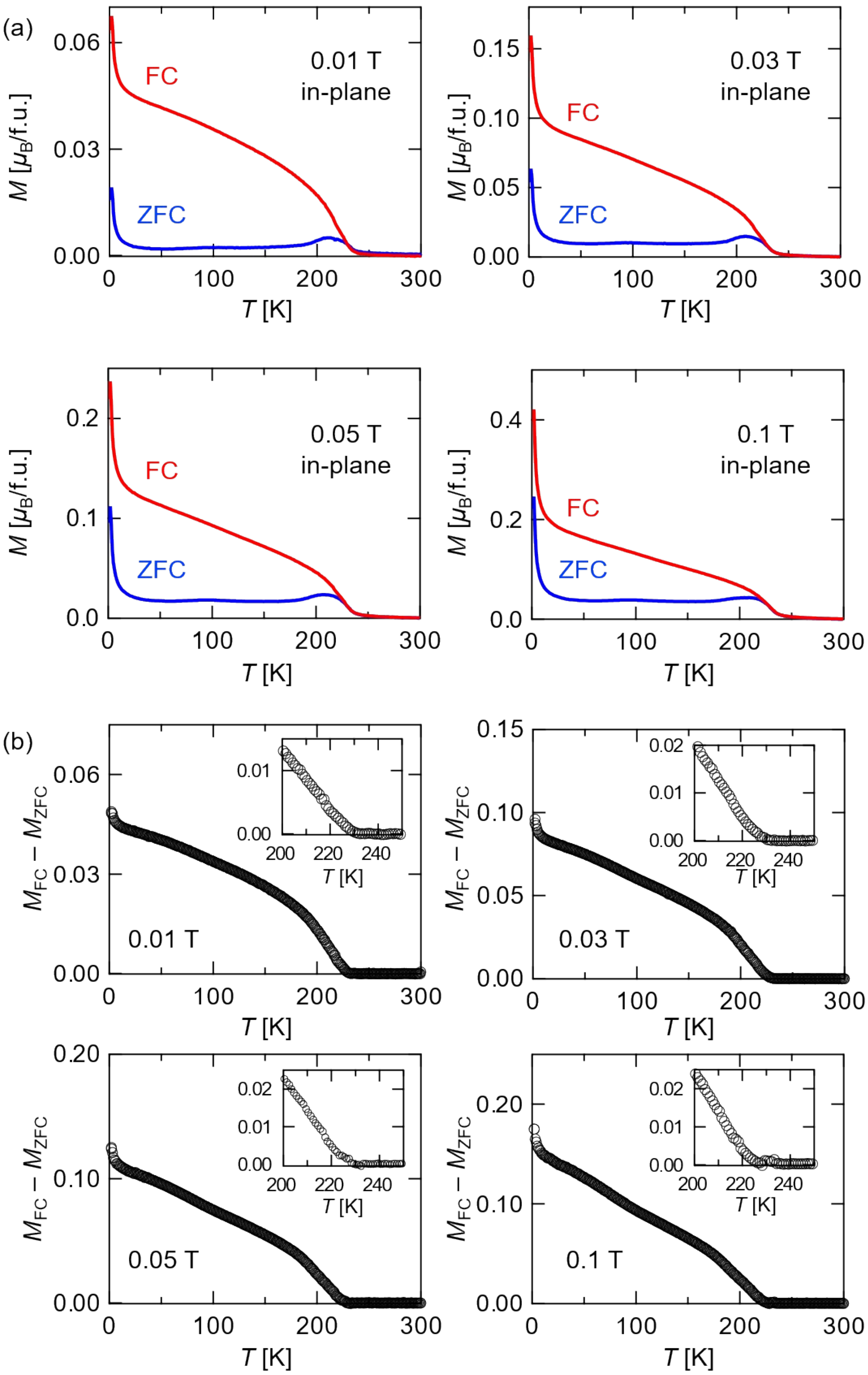

Fig. S2 (a) In-plane M−T curves during ZFC and FC for TbO epitaxial thin film under different magnetic field. (b) The difference between the FC and ZFC curves. Inset shows magnified view around T_C.

References

[S1] S. Tanuma, C.J. Powell and D.R. Penn, Calculation of electron inelastic mean free paths (IMFPs) VII. Reliability of the TPP-2M IMFP predictive equation. *Surf. Interface Anal.*, 2003, **35**, 268−275.

[S2] S. Tanuma, Quantitative Surface Analysis by X-ray Photoelectron Spectroscopy. *J. Surf. Anal.*, 1998, **4**, 20−34.