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$_2$O$_3$, and Tb thin films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate</th>
<th>Target</th>
<th>$T_{\text{substrate}}$ [$^\circ$C]</th>
<th>$P_{\text{O}_2}$ [Torr]</th>
<th>$E_{\text{laser}}$ [J/cm$^2$]</th>
<th>Repetition rate [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TbO</td>
<td>CaF$_2$ (001)</td>
<td>Tb$_4$O$_7$</td>
<td>375</td>
<td>-</td>
<td>0.75</td>
<td>15</td>
</tr>
<tr>
<td>Tb$_2$O$_3$</td>
<td>YAlO$_3$ (110)</td>
<td>Tb$_4$O$_7$</td>
<td>250</td>
<td>$5.0 \times 10^{-6}$</td>
<td>0.50</td>
<td>5</td>
</tr>
<tr>
<td>Tb</td>
<td>CaF$_2$ (111)</td>
<td>Tb</td>
<td>R.T.</td>
<td>-</td>
<td>0.70</td>
<td>20</td>
</tr>
</tbody>
</table>
Fig. S1 Tb 4d XPS spectra of TbO, Tb₂O₃ 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$_2$O$_3$ layer of the TbO thin film was removed by Ar$^+$ sputtering. For the quantitative composition analysis, a Tb$_2$O$_3$ 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 \(C_i\) (\(i = \text{Tb}, \text{O}\)) in TbO was obtained by the areal intensity of each atom in TbO and Tb$_2$O$_3$ \(I^\text{TbO}_i / I^\text{Tb2O3}_i\), the IMFP of each atom in TbO and Tb$_2$O$_3$ \(\lambda^\text{TbO}_i, \lambda^\text{Tb2O3}_i\), and the atomic density of each atom in TbO and Tb$_2$O$_3$ \(N^\text{TbO}_i, N^\text{Tb2O3}_i\) as follows, where \(K_i\) is relative intensity \(K_i = I^\text{TbO}_i / I^\text{Tb2O3}_i\).\(^{S2}\)

\[
C_i = \left(\frac{I^\text{TbO}_i}{I^\text{Tb2O3}_i}\right) \cdot \left(\frac{N^\text{TbO}_i}{N^\text{Tb2O3}_i}\right) \cdot \left(\frac{\lambda^\text{TbO}_i}{\lambda^\text{Tb2O3}_i}\right)
\]

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

\[
C^{\text{rel}}_i = \frac{C_i}{\sum C_i} = \frac{(K_i F_i / N^\text{TbO}_i)}{\sum (K_i F_i / N^\text{TbO}_i)} = \frac{(K_i F_i)}{\sum (K_i F_i)}
\]

From the TPP-2M IMFP equation, \(\lambda^\text{TbO}_{\text{Tb}} = 5.68\) Å and \(\lambda^\text{TbO}_{\text{O}} = 7.98\) Å, while \(\lambda^\text{Tb2O3}_{\text{Tb}} = 7.65\) Å and \(\lambda^\text{Tb2O3}_{\text{O}} = 11.5\) Å. In the referential Tb$_2$O$_3$ thin film, \(N^\text{Tb2O3}_i = 0.0496\) mol/cm$^3$ and \(N^\text{Tb2O3}_i = 0.0596\) mol/cm$^3$. Thus, the matrix factor \(F_{\text{Tb}} = 0.0537\) and \(F_{\text{O}} = 0.0861\). Thus,
\[ C_{\text{Tb}}^{\text{rel}} = \left( \frac{K_{\text{Tb}}}{F_{\text{Tb}}} \right)/\left( K_{\text{Tb}} \times F_{\text{Tb}} + K_{\text{O}} \times F_{\text{O}} \right) = 0.513, \]

\[ C_{\text{O}}^{\text{rel}} = \left( \frac{K_{\text{O}}}{F_{\text{O}}} \right)/\left( K_{\text{Tb}} \times F_{\text{Tb}} + K_{\text{O}} \times F_{\text{O}} \right) = 0.486. \]

Therefore, the Tb:O ratio of TbO thin film, \( C_{\text{Tb}}^{\text{rel}}:C_{\text{O}}^{\text{rel}} \), was 1:0.95.
Fig. S2 Typical XRD $\theta$–$2\theta$ patterns of (a) TbO thin film grown on CaF$_2$ (001) substrate (the same data as Fig. 1a) and (b) Tb$_2$O$_3$ thin film grown on YAlO$_3$ (110) substrate.
Fig. S3 (a) Temperature and (b) magnetic field dependence of magnetization for Tb$_2$O$_3$ (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 $T_C$. 

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References
