Supporting Information

Fabrication and characterization of ReO_3-type dielectric films

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Materials synthesis and characterization

TaO_2F and NbO_2F thin films were synthesized following a hydrothermal method.[1] Before the hydrothermal synthesis, Nb or Ta films were deposited on (001)-oriented Al_2O_3 substrates (Shinko-sha) via radio frequency magnetron sputtering at room temperature. Metal films prepared on the Al_2O_3 substrate (M/Al_2O_3, M = Nb, or Ta) and 2 mL of HF solution (0.1-1%) were placed in a Teflon cup. Basically, Nb/Al_2O_3 substrates were more reactive than Ta/Al_2O_3 in HF vapor oxidation. The substrate was held in the inner Teflon holder so as not to directly touch the solution (Also see Fig. 1 in manuscript). The Teflon cup was then placed in a steel autoclave and heated at 413 K for a certain period of time (60-150 min). After heating, the autoclave was cooled in water to room temperature. The films were then washed with distilled water and dried at 353 K for 10 min. The obtained films are denoted as $MO_2F/M/Al_2O_3$ (M = Nb, or Ta).

Samples were characterized using X-ray diffraction (XRD; D8 discover, Bruker, λ = 0.154 nm), UV-vis diffuse reflectance spectroscopy (DRS; JASCO, V-670DS, 200 <λ< 600 nm), and field-emission scanning electron microscopy (FE-SEM; Hitachi, S-4800, and Hitachi, S-5500 with EDS module). The diffuse reflectance (R) data were converted to the Kubelka-Munk function using the equation $f(R) = (1-R)^2/(2R)$. The relative dielectric constants and dielectric losses were measured using an impedance analyzer (4194A, Hewlett Packard) while sweeping the oscillation frequency from 0.2 to 2000 kHz and voltage of 1.0 V. Pt top electrodes (100 nm thick) were deposited using electron beam evaporation.

DFT calculations

All first principles calculations in this work were performed with the projector augmented wave (PAW) method[2,3] based on the density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP) code.[4,5] Generalized gradient approximation parameterized with the Perdew–Burke–Ernzerhof (GGA-PBE) functional was used for exchange-correlation interactions. Nb $4s^2\,4p^6\,5s^1\,4d^4$, O $2s^2\,2p^4$, and F $2s^2\,2p^5$ were treated as valence electrons. A plane-wave kinetic energy cutoff of 500 eV and a $3 \times 3 \times 3$ k-point mesh for sampling the Brillouin zone were used. All calculations were performed using $3 \times 3 \times 3$ supercells (containing 108 atoms) of the MO_2F unit cell. Supercell volumes were held fixed as the experimental value reported by Dabachi et al.[6] in all cases. Structure optimizations were truncated by 0.02 eV/Å. For precise calculations, the electronic density of states (DOSs) was calculated using the HSE06 hybrid functionals.[7]

Table S1. Calculated relative energy of TaO_2F using various structural models.

Entry	Structure	Cell size	Relative energy (meV / f.u.)
1	Uni-axial -Ta-O-Ta-O-Ta-F- chain (Fig. S1 (a))	3 × 3 × 3	0
2	Uni-axial -Ta-O-Ta-O-Ta-F- chain (Fig. S1 (b))	3 × 3 × 3	-31.4
3	SQS structure (Fig. S1 (c))	3 × 3 × 3	323.4

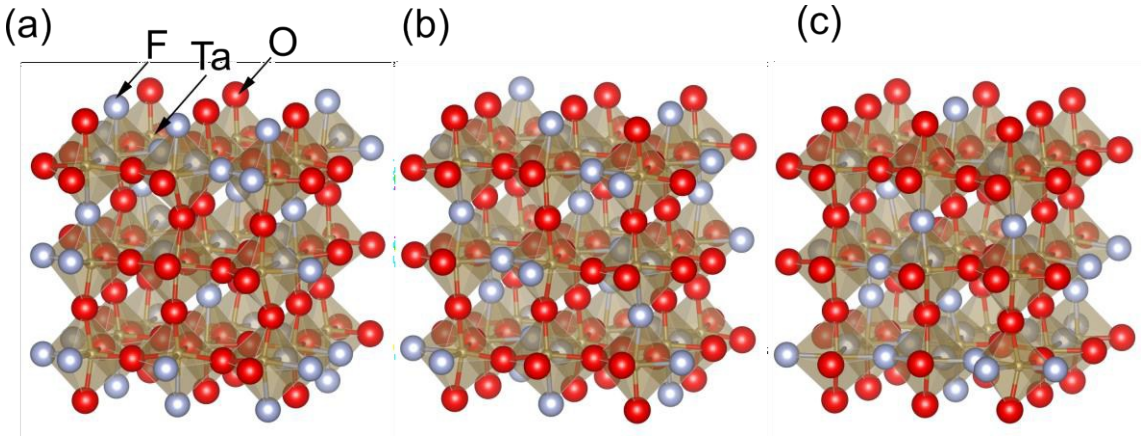

Figure S1. Calculated crystal structures of TaO_2F. (a) 3 × 3 × 3 TaO_2F supercell with uniaxial -Ta-O-Ta-O-Ta-F- chain proposed by Dabachi et al.[6] (b) 3 × 3 × 3 TaO_2F supercell with uniaxial -Ta-O-Ta-O-Ta-F- chain. In this model, each unit cell contains four O atoms and two F atoms (TaO_4F_2). (c) SQS structure calculated with CLUPAN code.[8,9] VESTA was used for structural model visualization.[10]

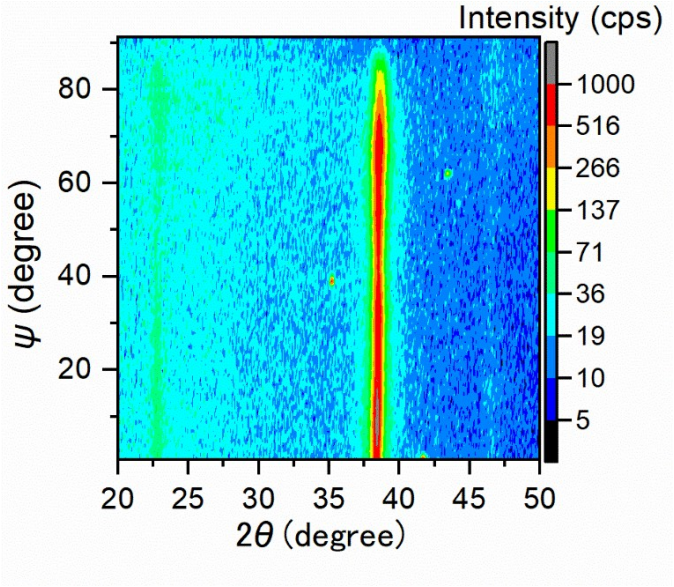

Figure S2. A 2θ-ψ mapping of XRD measurements for NbO_2F/Nb/Al_2O_3 hydrothermally treated at 413 K with 0.2% HF solution for 120 min.

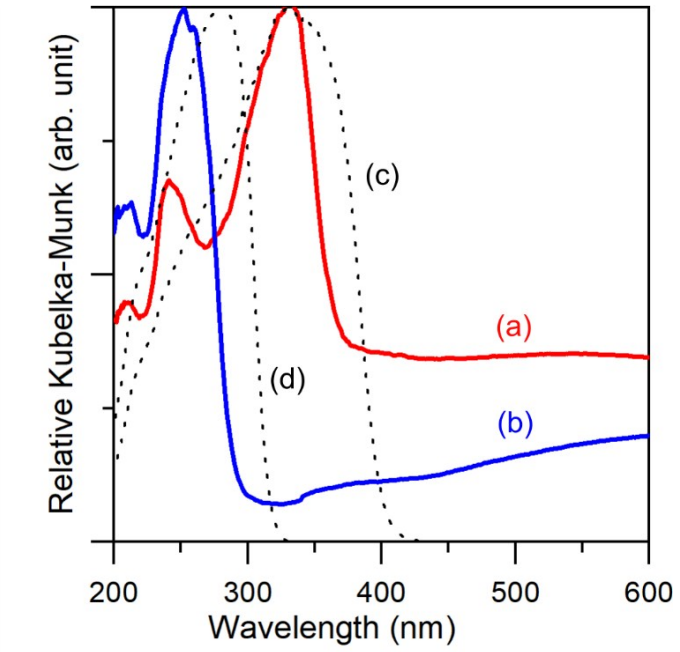

Figure S3. Diffuse reflectance spectra of (a) NbO_2F/Nb, (b) TaO_2F/Ta, (c) Nb_2O_5 powder, and (d) Ta_2O_5 powder.

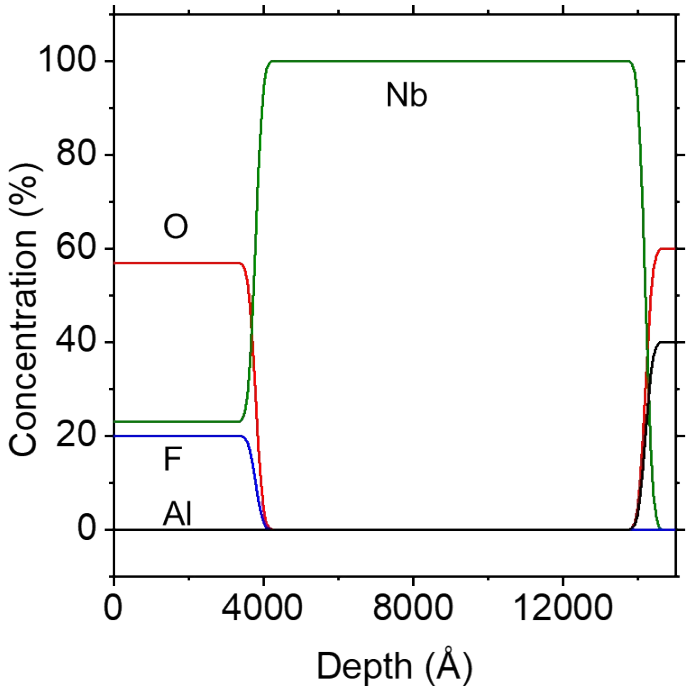

Figure S4. Estimated depth profile for $NbO_2F/Nb/Al_2O_3$ hydrothermally treated at 413 K with 0.2% HF solution for 120 min by Rutherford backscattering spectrometry. Composition of NbO_2F thin film was estimated to be $Nb_{1.00(1)}O_{2.46(17)}F_{0.87(6)}$.

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