Supporting Information

Indium-Free Amorphous Ca-Al-O Thin Film as a Transparent Conducting Oxide

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Optical transmittance simulation

We performed optical transmittance simulation, which shows that the obtained electrodynamic parameters of the CAO thin film can reproduce the optical features of experimental transmittance spectra. We constructed optical dielectric functions of the CAO layer based on a simple Drude model as shown in Figure S2(a). The carrier concentration and mobility values were $n = 3 \times 10^{22}$ cm^{-1} and $\mu = 6$ cm^2/Vs, respectively, adopted from the transport measurements of the CAO thin films. We obtained the effective mass value of 5 m_e from the MD calculation. The simulated transmittance spectra of the CAO thin film with different thicknesses on the STO substrate are shown in Figure S2(b). Interestingly, the simulated transmittance spectra closely resemble those obtained from the experiments (Figure 2(a)), especially for the films with thin thicknesses.

Chemical composition characterization

We performed the X-ray photoelectron spectroscopy (XPS) to examine the binding energy of Ca and Al, which leads to the estimation of the chemical concentration of the elements within the CAO thin films (Figure S2(a)). The binding energies of 346.2, 349.7, and 72.95 eV correspond to the Ca $2p_{3/2}$, $2p_{1/2}$, and Al $2p$ orbitals, respectively. Calculation of the spectral weight of corresponding orbital peaks for each element provides the chemical composition. We obtained the atomic concentration ratios of 9.1 ± 0.5 (Figure S2(b)) and 14.2 ± 0.5 (Figure S2(c)) for Ca and Al, respectively.

Density functional calculation

By applying the melt-quench method, we constructed amorphous structures for the representative chemical structures, i.e., the stoichiometric supercell of $Ca_9Al_{14}O_{30}$ (CAO_{30}, 159 atoms), and the oxygen-deficient supercells of $Ca_9Al_{14}O_{29}$ (CAO_{29}), $Ca_9Al_{14}O_{28}$ (CAO_{28}), and $Ca_9Al_{14}O_{22}$ (CAO_{22}). For the sake of computational efficiency, we used a soft pseudopotential for O atoms, which reduces the cut-off energy of the plane wave down to 300 eV, and the gamma point is selected for the **k**-point sampling. First, the atomic positions were randomized by premelting at 5000 K for 2 ps. Then, each sample was melted at 2500 K for 10 ps and quenched from 2500 K to 300 K with a cooling rate of 250 K/ps. Finally, the atomic positions of the amorphous structures were optimized until the atomic forces converged to 0.02 eV/Å. During the relaxation process, we used the standard potential for O atoms with a cutoff energy of 450 eV. Notably, the CAO_{30} and CAO_{29} exhibit a considerably large band gap, consistent with the experimental results shown in Figure 3. Meanwhile, the more defective CAO_{28} (Figure S3(a)) and CAO_{22} (Figure S3(b)) show the generation of in-gap states, resulting in a narrower band gap.

Determination of the thin film transparency

For an accurate comparison between the transmittance of the CAO thin film with other TCO materials, it is essential to exclude the substrate contribution to the optical transmittance spectra. Based on the transmittance results of CAO/STO in Figure 2(a), we obtained the quantitative values of the dielectric functions, i.e., the refractive index (n)

and the extinction coefficient (k) of the CAO thin film. The transmittance for a thin film with thickness t can be calculated by Fresnel equation using n and k as[S1, S2]

$$Tr = \frac{I}{I_0} = \frac{(1-R)^2 + 4R\sin^2\psi}{e^{\alpha t} + R^2 e^{-\alpha t} - 2R\cos 2(\phi+\psi)}, \qquad (1)$$

where the reflectivity R and the absorption coefficients α, ψ, and ϕ, are defined as:

$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$, $\alpha = \frac{4\pi k}{\lambda}$, $\phi = \frac{2\pi n t}{\lambda}$, and $\psi = \tan^{-1}\frac{2k}{n^2 + k^2 - 1}$, respectively.

Using the relation, we obtained the transmittance spectra of a free-standing CAO film with thickness t, as illustrated in Figure 2(b).

References

(S1) L. Zhang, Y. Zhou, L. Guo, W. Zhao, A. Barnes, H.-T. Zhang, C. Eaton, Y. Zheng, M. Brahlek, H. F. Haneef, N. J. Podraza, Moses H. W. Chan, V. Gopalan, K. M. Rabe, R. Engel-Herbert, Correlated Metals as Transparent Conductors. *Nat. Mater.* **2015**, *15*, 204.

(S2) H. Y. Fan, Infra-red Absorption in Semiconductors. *Rep. Prog. Phys.* **1956**, *19*, 107.

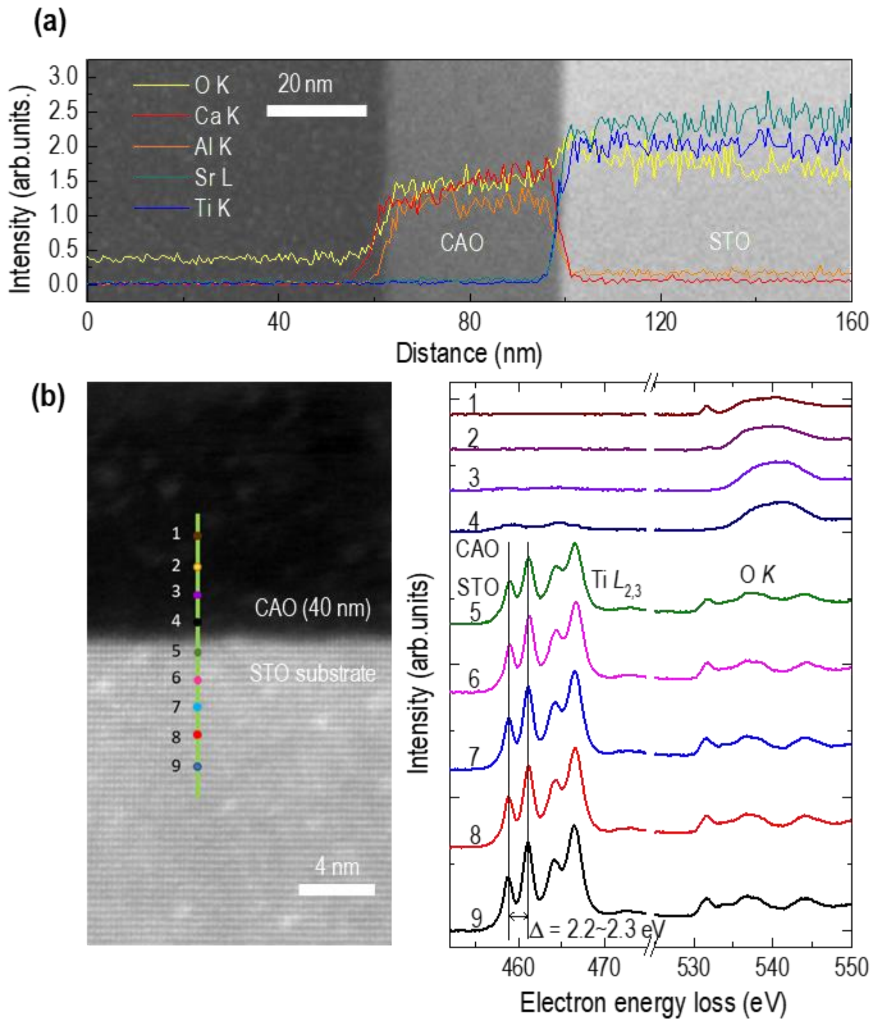

Figure S1. Electron microscopy measurements for the chemical composition investigation. (a) TEM-EDS results on the CAO thin film on STO substrate. Both the CAO thin film and the STO substrate exhibit the elemental homogeneities. (b) STEM-EELS results on the CAO thin film on STO substrate. The Ti $L_{2,3}$- and O-K edges EELS spectra indicate the insulating state of the STO substrate with the absence of oxygen vacancies.

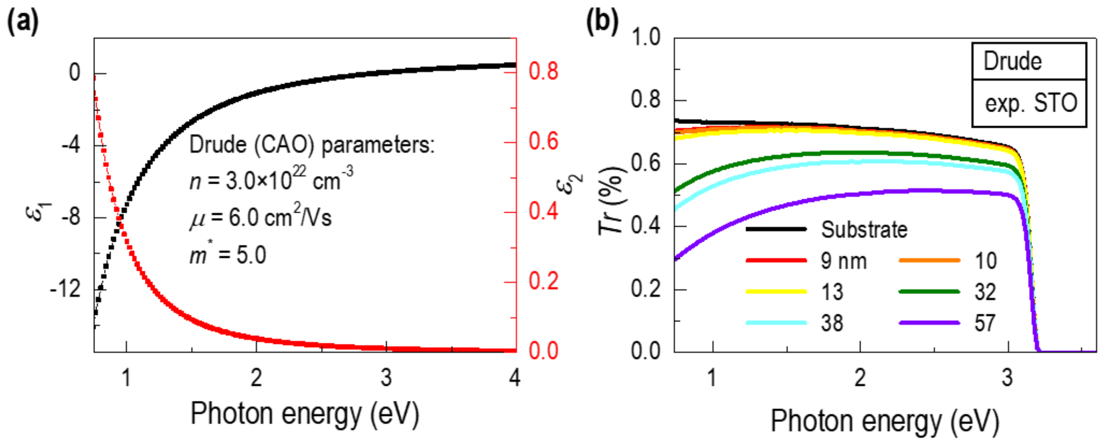

Figure S2. Simulated transmittance spectra of CAO thin films on STO substrate. (a) The real and imaginary parts of the dielectric function of the CAO layer based on simple Drude parameters of $n = 3 \times 10^{22}$ cm^{-1}, $\mu = 6$ cm^2/Vs, and $m^* = 5\ m_e$. (b) The simulated transmittance spectra. The insets show the model layers used for the simulation.

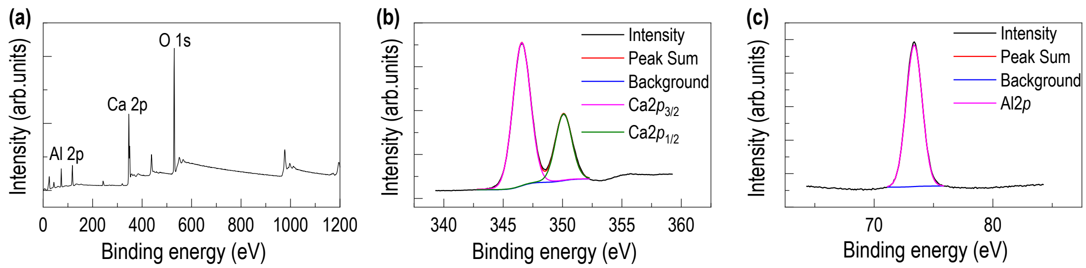

Figure S3. Characterization of the chemical structure. (a) The results of x-ray photoelectron spectroscopy (XPS) measurement for the Ca-Al-O thin film. The XPS spectra of (b) Ca 2*p* and (c) Al 2*p* were used to obtain the chemical composition of the thin films.

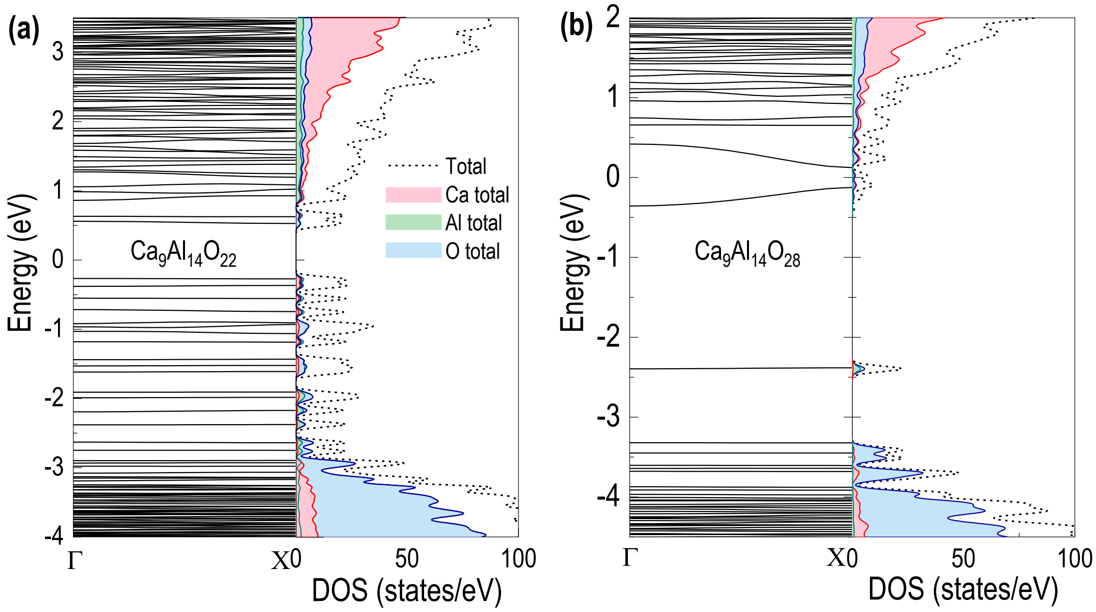

Figure S4. Theoretical calculation results for oxygen deficient $Ca_9Al_{14}O_{22}$ and $Ca_9Al_{14}O_{28}$. (a) The energy band dispersion and the projected density of states for $Ca_9Al_{14}O_{22}$. The defect states within the band gap results in the reduction of the band gap size, which indicates opaqueness. (b) The energy band dispersion and the projected density of states for $Ca_9Al_{14}O_{28}$.