 Supplementary Information

Nature of the band gap and origin of the electro-/photo- activity of Co$_3$O$_4$

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Film epitaxy and structural characterization

Figure 1a shows x-ray diffraction (XRD) $\theta$-2$\theta$ scan of a 35-nm epitaxial Co$_3$O$_4$(111) film on Al$_2$O$_3$(0001) substrate. The film exhibits (111) orientation and a fully relaxed structure due to the moderate lattice match (~2.2%) between Co$_3$O$_4$[100] and Al$_2$O$_3$ [1100]. No other impurities, e.g. Co or CoO, are determined indicating a single-phase of the obtained epitaxial film. Notice the epitaxial Co$_3$O$_4$(111) exhibits clear thickness fringes around film (222) Bragg peak due to flat film surface and density contrast between film and substrate. The reflective high-energy electron diffraction (RHEED) image show well-defined shape spots along substrate [1100] direction. The presence of both finite thickness fringes and shape RHEED patterns indicate the high quality of the obtained epitaxial Co$_3$O$_4$(111) films. Figure 1b is a high-resolution atomic force microscopy (AFM) image of the film surface. Clear growth-induced step-terrace structure is observed with a minimum height of ~4.6 Å, which corresponds well to the $d$-spacing for a Co$_3$O$_4$ (111) layer.

Figure 1 (a) XRD $\theta$-2$\theta$ scan a 35 nm epitaxial Co$_3$O$_4$(111) film on Al$_2$O$_3$(0001) substrate. Inset shows the RHEED pattern of the film along [1100] crystallographic direction of the Al$_2$O$_3$ substrate. (b) AFM image of the film surface. (c) Extracted line scan of the rectangular region in AFM image.
**Ellipsometry measurement**

Figure 2 shows the determined film refractive index ($n$) and extinction coefficient ($k$). Overall the obtained $k$ function mimics the absorption lineshape, e.g. asymmetric peak near 1.6 eV, a broad absorption peak near 2.8 eV, knee-like features at 3.7 eV and 4.5 eV, and a generally increasing trend in absorption for higher energies. These features also qualitatively match the reported complex dielectric function in the literature [1,2]. It is shown that the obtained $n$ for film in the low energy range ( < 2.5 eV ), is significantly larger than that of the Al$_2$O$_3$ substrate, which approaches a constant 1.7 across the whole IR-VIS-UV range [3]. Also, the peak at 1.6 eV determined by ellipsometry is less asymmetric than the same peak in absorption spectrum. Therefore, the broad feature of peak 10 in the absorption measurements originates not from absorption, but from the index mismatches at the various interfaces based on Fresnel theory [4-6]. Similar phenomena have also been reported in other layered organic and oxide systems [7-9].

![Figure 2 Determined refractive index and extinctive coefficient for epitaxial Co$_3$O$_4$ film from polarized spectroscopy ellipsometry.](image)

**Substrate choice and optical isotropy of the epitaxial film**

The film orientation depends on the choice of substrate. Epitaxial Co$_3$O$_4$ film exhibits (111) orientation on Al$_2$O$_3$(0001) substrates, but exhibits (001) orientation on SrTiO$_3$(001) and MgO(001) substrates. We show in Figure 3 the obtained optical absorption spectra for Co$_3$O$_4$ films grown on different substrates, e.g. 35nm Co$_3$O$_4$(111) on Al$_2$O$_3$(0001), 20 nm Co$_3$O$_4$(001) on SrTiO$_3$(001) and 20 nm Co$_3$O$_4$(001) on MgO(001) substrates, respectively. It is seen that film absorption is greatly affected by substrate band gap excitation when grown on low band gap substrate SrTiO$_3$ (3.2 eV). Even grown on MgO, which has an intermediate band gap of 7.8 eV, the film absorption is still overlapped with that of the substrate since MgO starts to absorb far below (~5 eV) its nominal band gap. In this case, Al$_2$O$_3$ is a good substrate choice because of its extreme large band gap (~9 eV), which permits isolation of the film absorption. Comparison of the absorption spectra for Co$_3$O$_4$(111) and Co$_3$O$_4$(001) reveals almost identical features, indicating an optical isotropy for this material.
Figure 3. Room temperature optical absorption spectra for 35nm Co$_3$O$_4$(111) on Al$_2$O$_3$(0001), 20 nm Co$_3$O$_4$(001) on SrTiO$_3$(001) and 20 nm Co$_3$O$_4$(001) on MgO(001) substrates.

**Effect of Hubbard $U_{\text{eff}}$ correction on the band gap and structural properties**

We show in Figure 4a the obtained fundamental gap as a function of different $U_{\text{eff}}$ values for both Co ions. Figure 4b shows the calculated lattice constant as a function of different Hubbard U corrections for both Co$^{2+}$ and Co$^{3+}$ ions. It is seen that zero U correction for both Co ions yields a lattice constant agreeing well with the experimental value, and larger U values for Co$^{2+}$ and Co$^{3+}$ results in increasing deviation of the lattice constant from the experimental one.

Figure 4. Calculated band gap (a) and lattice constant (b) as a function of different Hubbard U corrections for both Co ions. Dashed line is the corresponding experimental values.