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Supplementary Information

Nature of the band gap and origin of the electro-/photo- activity of Co_3O_4

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Film epitaxy and structural characterization

Figure **1**a shows x-ray diffraction (XRD) θ-2θ scan of a 35-nm epitaxial Co_3O_4(111) film on Al_2O_3(0001) substrate. The film exhibits (111) orientation and a fully relaxed structure due the moderate lattice match (~2.2%) between Co_3O_4[100] and Al_2O_3 $[1\bar{1}00]$. No other impurities, e.g. Co or CoO, are determined indicating a single-phase of the obtained epitaxial film. Notice the epitaxial Co_3O_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 $[1\bar{1}00]$ direction. The presence of both finite thickness fringes and shape RHEED patterns indicate the high quality of the obtained epitaxial Co_3O_4(111) films. Figure **1**b 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_3O_4 (111) layer.

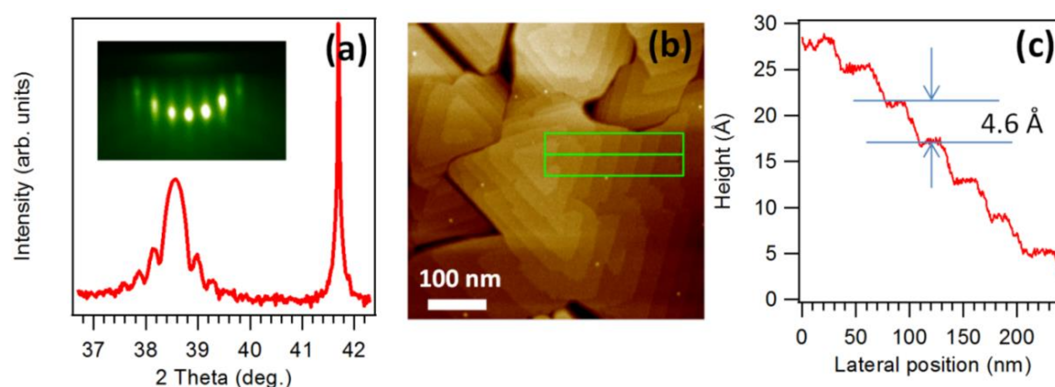

Figure **1** (a) XRD θ-2θ scan a 35 nm epitaxial Co_3O_4(111) film on Al_2O_3(0001) substrate. Inset shows the RHEED pattern of the film along $[1\bar{1}00]$ crystallographic direction of the Al_2O_3 substrate. (b) AFM image of the film surface. (c) Extracted line scan of the rectangular region in AFM 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_2O_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].

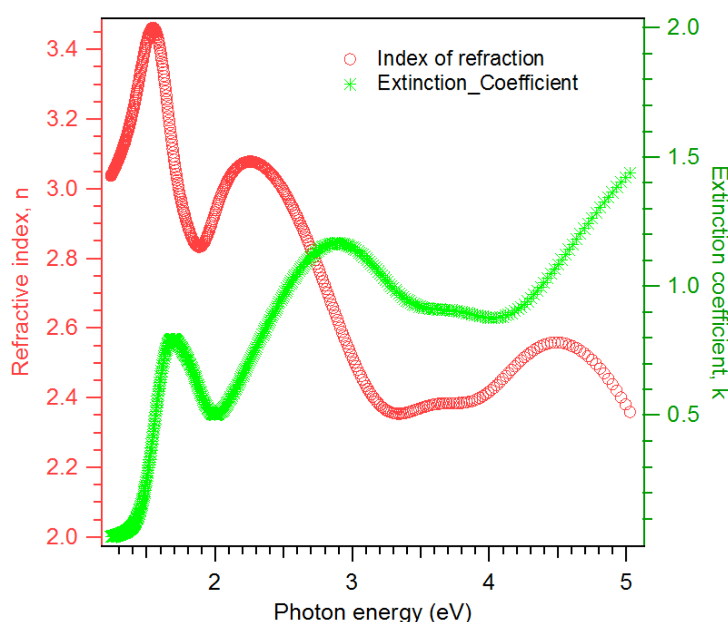

Figure **2** Determined refractive index and extinctive coefficient for epitaxial Co_3O_4 film from polarized spectroscopy ellipsometry.

Substrate choice and optical isotropy of the epitaxial film

The film orientation depends on the choice of substrate. Epitaxial Co_3O_4 film exhibits (111) orientation on Al_2O_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_3O_4 films grown on different substrates, e.g. 35nm Co_3O_4(111) on Al_2O_3(0001), 20 nm Co_3O_4(001) on $SrTiO_3$(001) and 20 nm Co_3O_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_2O_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_3O_4(111) and Co_3O_4(001) reveals almost identical features, indicating an optical isotropy for this material.

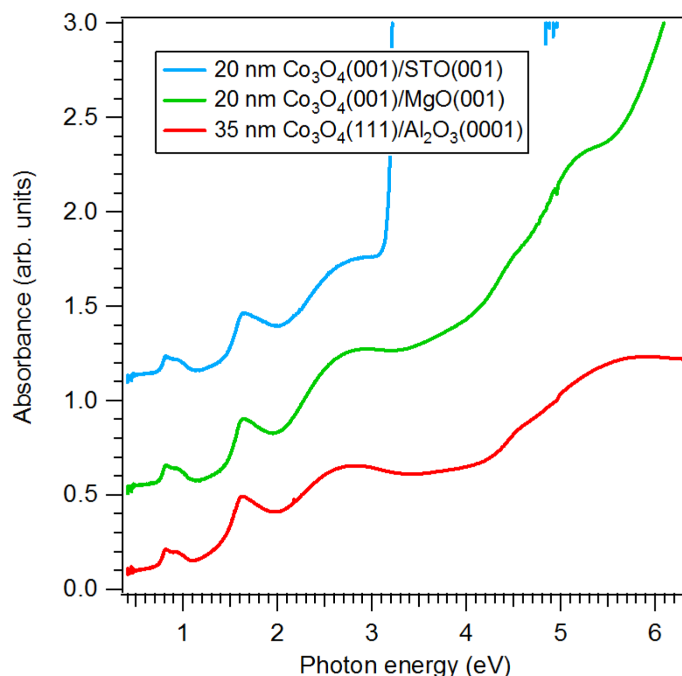

Figure **3**. Room temperature optical absorption spectra for 35nm Co_3O_4(111) on Al_2O_3(0001), 20 nm Co_3O_4(001) on $SrTiO_3$(001) and 20 nm Co_3O_4(001) on MgO(001) substrates.

Effect of Hubbard U_{eff} correction on the band gap and structural properties

We show in Figure **4**a the obtained fundamental gap as a function of different U_{eff} values for both Co ions. Figure **4**b 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.

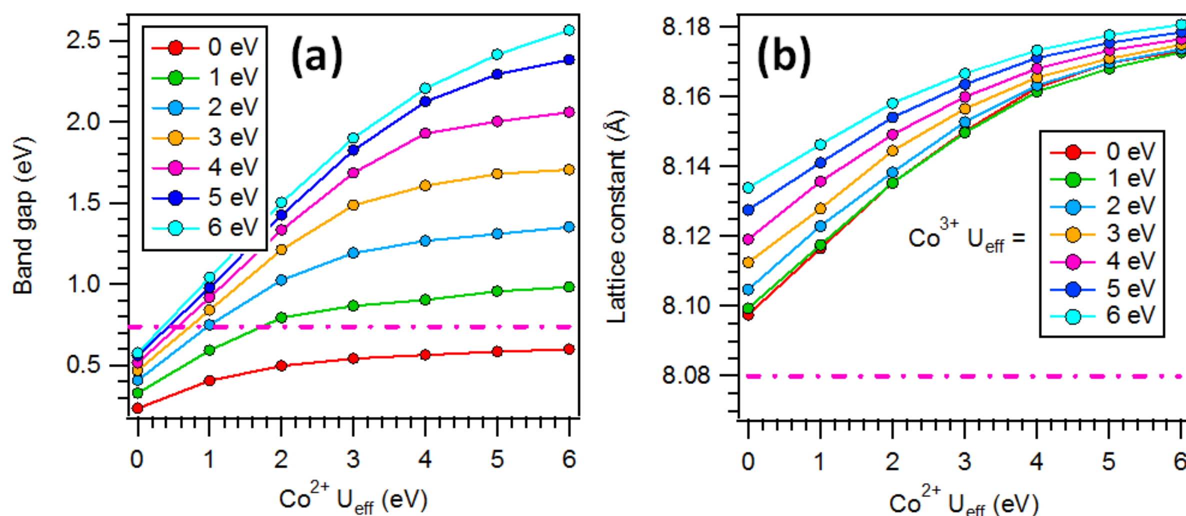

Figure **4**. Calculated band gap (a) and lattice constant (b) as a function of different Hubbard U corrections for both Co ions. Dashed line is the corresponding experimental values.

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