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Epitaxy of polar semiconductor Co_3O_4 (110): Growth, structure, and characterization

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The (110) plane of Co_3O_4 spinel exhibits significantly higher rates of carbon monoxide conversion due to the presence of active Co^{3+} species at the surface. However, experimental studies of Co_3O_4 (110) surfaces and interfaces have been limited by the difficulties in growing high-quality films. We report thin (10–250 Å) Co_3O_4 films grown by molecular beam epitaxy in the polar (110) direction on MgAl_2O_4 substrates. Reflection high-energy electron diffraction, atomic force microscopy, x-ray diffraction, and transmission electron microscopy measurements attest to the high quality of the as-grown films. Furthermore, we investigate the electronic structure of this material by core level and valence band x-ray photoelectron spectroscopy, and first-principles density functional theory calculations. Ellipsometry reveals a direct band gap of 0.75 eV and other interband transitions at higher energies. A valence band offset of 3.2 eV is measured for the $\text{Co}_3\text{O}_4/\text{MgAl}_2\text{O}_4$ heterostructure. Magnetic measurements show the signature of antiferromagnetic ordering at 49 K. FTIR ellipsometry finds three infrared-active phonons between 300 and 700 cm^{-1} . © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4885048>]

I. INTRODUCTION

Complex oxides of cobalt find applications in gas sensing,^{1,2} spintronics,^{3–6} batteries,^{2,4} and catalysis,^{7–14} most notably for oxidation of carbon monoxide (CO)^{9,10} and water.^{11–14} At room temperature, the most stable form of cobalt oxide is Co_3O_4 , a semiconductor with a modest band gap of less than 1.6 eV, as compared to the 2.4 eV gap of charge-transfer insulator CoO .^{15–20}

Co_3O_4 assumes the cubic $Fd\bar{3}m$ spinel-type phase, shown in Fig. 1. Cobalt spinels have a history of use as gemstones, and their high stability makes them well-suited for the decorating of ceramics (cobalt-containing spinels, in particular, are responsible for the striking “cobalt blue” pigment).^{21,22} In Co_3O_4 , vertex-sharing tetrahedral Co^{2+} ions carry a magnetic moment, while the nonmagnetic Co^{3+} ions occupy the edge-sharing octahedral sites. Co_3O_4 undergoes an antiferromagnetic phase transition below ~ 40 K.^{23–26}

Studies of crystalline thin film surfaces and interfaces of Co_3O_4 spinel could provide insight into its basic properties and catalytic behavior.^{2,7–13} Of particular interest is the (110) plane that exhibits significantly higher reaction rates due to the presence of active Co^{3+} species at the surface.¹⁰ Though epitaxially grown films offer a natural way to achieve high crystallinity, epitaxy of Co_3O_4 is complicated by the fact that all low-index planes are polar. As shown in Fig. 2, the (110) direction of Co_3O_4 contains two types of

alternating planes: the most stable type-A plane is comprised of units of $\text{Co}_2^{2+}\text{Co}_2^{3+}\text{O}_4$ with a formal charge of +2, while the type-B planes include $\text{Co}_2^{3+}\text{O}_4$, resulting in a charge of –2 per surface unit cell. This polarity further motivates study of polar Co_3O_4 , as polar oxides are of prominent interest due to their increased surface reactivity as compared to the bulk^{27,28} and as a mechanism for the formation of the two dimensional electron gas (2DEG).^{29,30}

Co_3O_4 films have been grown by post-oxidation,^{17,31} atomic layer deposition (ALD),^{32–34} chemical vapor deposition (CVD),^{35–38} pulsed laser deposition (PLD),^{18,39} and molecular beam epitaxy (MBE).^{40–42} A number of substrates, including MgO ,^{18,34,36,38,39} SrTiO_3 ,^{18,34,38,39} MgAl_2O_4 ,^{36,41,42} Al_2O_3 ,^{18,40} LaAlO_3 ,³⁹ Yttria-stabilized zirconia,³⁹ SiO_2/Si ,^{32,33} and iridium³¹ have been studied for the growth of crystalline Co_3O_4 films. Among these substrates, spinel MgAl_2O_4 (110) is an ideal substrate choice not only due to its small lattice mismatch with Co_3O_4 (less than 0.05%) but also due to the fact that it is the only substrate thus far on which Co_3O_4 preferentially grows (110)-oriented.^{41,42} MBE growth offers several advantages including precise control over flux and *in situ* analysis, but reports by Vaz *et al.* have suggested that extensive post-growth *ex situ* annealing is required.^{41,42}

In this work, we report on thin MBE-grown Co_3O_4 films on MgAl_2O_4 substrates. We probe the structure of these as-grown highly crystalline (110)-oriented films by reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), x-ray diffraction (XRD), and transmission electron microscopy (TEM). The film surface roughens at intermediate thickness, but slowly smoothens as growth

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FIG. 1. At room temperature, Co_3O_4 assumes the normal spinel structure. Based on the crystal field splitting, the Co^{2+} ions (tetrahedral, light blue) carry magnetic moment, while the Co^{3+} (octahedral, dark blue) ions are nonmagnetic.

continues, returning to an RMS surface roughness of ~ 1 Å. A valence band offset (VBO) of 3.2 eV is measured for the heterostructure by x-ray photoelectron spectroscopy (XPS). First-principles density functional theory (DFT) calculations optimized to match the shape of the XPS valence band yield a band gap of 0.6 eV for Co_3O_4 . Ellipsometry reveals a direct band gap of 0.75 eV and other interband transitions at higher energies. FTIR ellipsometry finds three infrared-active phonons between 300 and 700 cm^{-1} . Superconducting quantum interference device (SQUID) magnetometry measurements show the signature of antiferromagnetic ordering at an enhanced Néel temperature of 49 K.

II. EXPERIMENTAL DETAILS

MgAl_2O_4 substrates of dimension 5 mm $\times$ 5 mm $\times$ 0.5 mm were degreased in acetone, isopropanol, deionized water, and UV ozone. Substrates were glued with silver paste to a sample holder to ensure good thermal contact. The samples were then introduced into a customized DCA 600 MBE system with a base pressure of 3×10^{-10} Torr. All substrates were outgassed in the chamber at 700 °C for 30 min before

lowering the substrate temperature to 500 °C for growth. The substrate temperature is measured by a thermocouple in close proximity to the substrate heater; the thermocouple is calibrated using a pyrometer measurement of a silicon substrate.

The electron-beam evaporated Co flux was calibrated to a deposition rate of 3–4 Å/min by use of a quartz crystal microbalance. Atomic oxygen was then introduced by means of an RF plasma source at a power of 250 W with an oxygen background pressure of 1×10^{-5} Torr. After growth, the main shutter was closed, and the samples were cooled down in the presence of oxygen. The presence of the film affects the visual appearance of the sample, adding a brown tint as compared to the transparent substrate. This is consistent with the smaller band gap of Co_3O_4 as compared to that of the MgAl_2O_4 substrate.^{18,43} For ellipsometry measurements, a Co_3O_4 film was deposited on a large 2-in.-diameter MgAl_2O_4 substrate to eliminate artifacts due to the size of the sample. The unpolished side of this wafer was coated with Nb metal rather than silver paste before following the steps outlined above.

The samples were monitored during growth by *in situ* RHEED, and then transferred *in situ* to the XPS analysis

FIG. 2. Right: the (110) direction of Co_3O_4 is characterized by a 4-repeat period over a depth of 5.7 Å. The alternating planes are shown from a top view on the left. The type A plane is comprised of units of $\text{Co}^{3+}_2\text{Co}^{2+}_2\text{O}_4$ with a formal charge of +2, while the type B planes include $\text{Co}^{3+}_2\text{O}_4$ resulting in a charge of -2.

chamber (VG Scienta R3000). For the remaining characterization techniques (AFM, XRD, TEM, Ellipsometry, and SQUID), the samples were removed from UHV and exposed to atmosphere.

Spectroscopic ellipsometry measures the complex Fresnel ratio

$$\rho = \frac{r_p}{r_s} = \tan \psi e^{i\Delta}, \quad (1)$$

i.e., the ratio of the p-polarized reflectance r_p to the s-polarized reflectance r_s . ρ is usually expressed in terms of the ellipsometric angles ψ and Δ . For a bulk sample with complex refractive index n , ρ is given by^{44,45}

$$\rho = \frac{(n \cos \phi_0 - \cos \phi_1)(\cos \phi_0 + n \cos \phi_1)}{(n \cos \phi_0 + \cos \phi_1)(\cos \phi_0 - n \cos \phi_1)}, \quad (2)$$

where ϕ_0 is the angle of incidence and ϕ_1 the angle of refraction given by Snell's Law.

The imaginary part of the dielectric function $\varepsilon = n^2$ is related to absorption in the sample by elementary excitations. For example, the absorption in the infrared (IR) spectral region is given by lattice absorption of infrared-active phonons or the free-carrier response in a metal. In the visible and UV spectral region, the absorption is due to interband electronic transitions. The application of this technique to bulk spinel (MgAl_2O_4) has been described recently.⁴³

In the case of a thin film on a substrate, we can still invert Eq. (2) to calculate $\langle n \rangle$ and $\langle \varepsilon \rangle = \langle n \rangle^2$, but these quantities are no longer related to the optical constants of a specific material. Instead, $\langle n \rangle$ and $\langle \varepsilon \rangle$ are determined by the optical constants of the film and the substrate along with the film thickness and surface and interface roughness layer thicknesses. Therefore, $\langle n \rangle$ and $\langle \varepsilon \rangle$ are called the pseudo-refractive index and the pseudo-dielectric function. If the dielectric function ε_s of the substrate and the film thickness are known, then the dielectric function ε_f of the film can be determined by fitting the experimental data using well-established procedures^{44,45} and commercial software (J.A. Woollam Co., Inc., WVASE32). Surface roughness can also be considered within this approach.

For this work, we used two instruments to acquire our data. From 0.76 to 6.5 eV, we measured the ellipsometric angles on a Woollam variable angle-of-incidence spectroscopic ellipsometer (VASE) with computer-controlled Berek waveplate compensator at seven angles of incidence (50° to 80°). For IR ellipsometry, we used a Woollam FTIR-VASE ellipsometer, which is based on a fixed analyzer (0° and 180°) and polarizer ($\pm 45^\circ$) and a rotating compensator. We measured from 250 to 7000 cm^{-1} at five angles of incidence (60° to 80°). In the FTIR experiments, the spectral resolution was set to 8 cm^{-1} to improve the signal to noise ratio. All data sets were merged and fitted simultaneously with the same model, including both lattice absorption and interband electronic transitions. The optical constants for the MgAl_2O_4 substrate were taken from Ref. 43 without adjustments. We assumed a surface roughness of $2 \text{ \AA}$, guided by atomic force microscopy measurements. In the case of a thin absorbing Co_3O_4 layer on a substrate, the layer thickness cannot be

determined. We use a film thickness of $220 \text{ \AA}$ (determined from the growth parameters and confirmed by x-ray reflectance measurements) as an input for our ellipsometry analysis. Small errors in film thickness cause errors in the amplitude of the dielectric function, but do not affect the peak energies and broadenings.

III. RESULTS AND DISCUSSION

The spinel surface was characterized during film deposition using *in situ* RHEED (Fig. 3). The most stable surface of the MgAl_2O_4 (110) substrate is the A-type, which contains both Mg and Al atoms. The RHEED pattern for the substrate (Fig. 3(a)) confirms the crystalline quality of the surface, with sharp diffraction maxima as expected for a periodic surface with negligible roughness. As the Co_3O_4 film grows (Figs. 3(b) and 3(d)), it follows the termination of the substrate to preserve charge neutrality, as is common in polar materials.^{27,41}

The surface roughens with thickness starting between 10 and $20 \text{ \AA}$, causing broadening of the RHEED streaks. However, as the film continues to grow, the surface again becomes smooth, with a crystalline quality approaching that of the substrate at around $100\text{-}\text{\AA}$ -thickness and above (Fig. 3(d)). One possible explanation for these observations is the electrostatic energy of a polar material diverges with increasing thickness.^{27,46} Above a critical field and therefore critical thickness, the surface roughness may develop to compensate

FIG. 3. RHEED patterns along the $[110]$ azimuth at grazing incidence for (a) the MgAl_2O_4 substrate, (b) $\sim 13\text{-}\text{\AA}$ -thick Co_3O_4 film, (c) $\sim 24\text{-}\text{\AA}$ -thick film, and (d) $125\text{-}\text{\AA}$ -thick film. The most stable surface of the MgAl_2O_4 substrate is the A-type, which contains both Mg and Al atoms. The Co_3O_4 film follows the termination of the substrate to preserve charge neutrality, as is common in polar materials. The surface develops roughness at thickness starting between 10 and $20 \text{ \AA}$, causing the observed broadening of the RHEED streaks. The surface again becomes smooth as growth continues, returning to substrate quality around $100 \text{ \AA}$ thickness.

the surface charge density. Once the film can instead compensate by bulk rather than surface reconstruction, the surface can once again become smooth, as seen in the thicker films.

These RHEED observations are supported by *ex situ* AFM measurements for Co_3O_4 samples of varying thickness. Scans of $5 \times 5 \mu\text{m}$ areas are shown for the substrate and three representative films in Fig. 3. For the $\sim 13\text{-}\text{\AA}$ -thick film (Figs. 3(b) and 4(b)), the RMS roughness was $1.26\text{ \AA}$. This is on the order of instrumental resolution; any perceived modulation of the surface is likely due to vibrations of the microscope. For slightly thicker films, such as the $\sim 24\text{ \AA}$ film (Figs. 2(c) and 3(c)), the surface becomes noticeably rougher. In this sample, the RMS roughness increased to $5.26\text{ \AA}$. Finally, the $125\text{ \AA}$ film shown in Fig. 4(d) shows the surface roughness has decreased back down to $1.04\text{ \AA}$; this sample serves as a representative example of the smoothening that occurs in thicker films.

X-ray diffraction measurements were carried out using a Panalytical X'PERT Pro diffractometer (Cu $K\alpha 1$ source, $\lambda = 1.5406\text{ \AA}$) operating at 45 kV and 40 mA . The symmetric $2\theta - \theta$ scan shows strong substrate peaks corresponding to an out-of-plane lattice constant of $8.07\text{ \AA}$. The high-resolution rocking curve of the (440) reflection for a $240\text{-}\text{\AA}$ -thick film Co_3O_4 is shown in Fig. 5(a). Experimental data points are shown by open circles, and a sum of two Voigt functions has been fitted to the data (blue curve). The contribution from the substrate (red curve) is mostly Gaussian, with a width of 0.015° , on the order of instrumental resolution as expected for a single-crystal substrate. The film peak (green curve) has a width 0.03° , not much broader than that of the substrate. The shaded green area outlines values within the uncertainty of the position of the film peak, showing that the film is nearly lattice-matched to the substrate. Spot spacing in RHEED indicates that there is no change in the in-plane lattice constant for the film compared to the substrate up to the thickness that we have grown ($250\text{ \AA}$).

All thicknesses referenced above were first estimated from the quartz crystal microbalance calibration and verified by X-ray reflectivity (XRR). In this geometry, oscillations in

FIG. 4. AFM measurements for: (a) bare MgAl_2O_4 substrate, followed by Co_3O_4 samples of thickness (b) $13\text{ \AA}$, (c) $24\text{ \AA}$, and (d) $125\text{ \AA}$. The RMS roughness measured was $1.52\text{ \AA}$, $1.26\text{ \AA}$, $5.26\text{ \AA}$, and $1.04\text{ \AA}$, respectively.

FIG. 5. (a) Rocking curve data and analysis of the (440) reflection of $240\text{ \AA}$ film (Co_3O_4 on MgAl_2O_4). Experimental data points are shown by open circles, and a sum of two Voigt functions has been fitted to the data. (b) X-ray reflectivity for the same film. The drawn (red) line is a simulation. Oscillations due to the difference in density between the substrate and film persist undamped to high angles, implying a smooth surface and abrupt interface. (c) High-resolution cross-sectional transmission electron micrograph confirms the abrupt interface between the crystalline substrate and film.

the reflected intensity arise due to the difference in density between the substrate and film. An example is shown for the same $240\text{ \AA}$ film (Fig. 5(b)); the black line is experimental data, while the drawn (red) line is a simulation. The simulated oscillations correspond to a film thickness of $240\text{ \AA}$ with $1\text{ \AA}$ roughness. Strong oscillations with minimal damping are indicative of a smooth surface and abrupt interface for the as-grown sample.

To further characterize the interface, Fig. 5(c) shows a cross-sectional transmission electron micrograph taken with a JEOL JEM-4000EX high-resolution electron microscope operated at 400 keV . The image shows a highly crystalline epitaxial Co_3O_4 film on the MgAl_2O_4 substrate with a sharp

and coherent interface, in agreement with the RHEED and XRD results above.

XPS measurements were performed *in situ* using monochromatic Al K α radiation ($h\nu = 1486.6$ eV). To avoid charging due to the highly insulating substrate, a low-energy electron flood gun was used to replace the emitted electrons. Fig. 6 summarizes the core level spectroscopy. A representative survey scan of a bulk-like 250-Å-thick Co₃O₄ film shows the expected peaks of a system dominated by cobalt and oxygen (Fig. 6(a)). Higher-resolution scans of the O 1s

FIG. 6. XPS spectra. (a) Survey scan of representative 250-Å-thick Co₃O₄ film shows a spectrum dominated by cobalt and oxygen. (b) High-resolution Co 2p scan shows characteristic strongly suppressed shake-up satellite peaks at +5.5 eV and +9 eV, as compared to CoO. The O 1s peak shows a slight shoulder, which can be attributed to surface oxygen. (c) To determine the valence band offset, the spectra for pure MgAl₂O₄ (red shading) and Co₃O₄ (blue shading) were scaled, offset, and added together to create a simulated fit (purple line) to the measured valence band spectra for a heterostructure of 13 Å Co₃O₄ on MgAl₂O₄ (black open circles). The residual difference is also plotted (black line).

and Co 2p peaks are shown in Fig. 6(b). Spectra have been artificially shifted to fix the location of the O 1s peak at 530.1 eV. The Co 2p scan shows characteristic strongly suppressed shake-up satellite peaks at +5.5 eV and +9 eV as compared to CoO.¹⁵

Fig. 6(c) displays XPS valence band spectra for the bare MgAl₂O₄ substrate (red shading) and 250-Å-thick Co₃O₄ film (blue shading). The band offset in Co₃O₄ heterostructures may facilitate understanding of the catalytic properties of Co₃O₄; for example, in order to achieve a spontaneous water splitting reaction, both a small band gap and suitable alignment of band edges with respect to the water redox potentials are required.¹⁴ Band offsets were calculated by both core-level¹⁴ and valence band^{47,48} spectroscopy. The valence band maximum (E_{VBM}) for each material was calculated using the linear extrapolation method.⁴⁹ By comparing energy offsets between the Co 2p, Al 2p, and valence band edge positions (as summarized in Table I) using

$$VBO_{CL} = (E_{Co2p} - E_{VBM})_{Co_3O_4} - (E_{Al2p} - E_{VBM})_{MgAl_2O_4} - (E_{Co2p} - E_{Al2p})_{Co_3O_4/MgAl_2O_4}, \quad (3)$$

we calculate a VBO_{CL} of 3.4 eV.

The VBO can also be determined directly from the valence band spectra.^{47,48} For a heterostructure of 13 Å Co₃O₄/MgAl₂O₄, a contribution from the film is visible along with an attenuated contribution from the substrate (Fig. 6(c), black open circles). We simulated a fit (purple solid line) to the heterostructure by scaling and offsetting the pure valence band spectra measured for the MgAl₂O₄ substrate and thick Co₃O₄ film. This method uses an “all at once” fit minimizing χ^2 by the Levenberg-Marquardt algorithm implemented in Igor Pro software (WaveMetrics, Lake Oswego, OR). The difference between the measured and simulated spectra is also plotted (black line). Using this method, we calculate $VBO_{sim} = 3.2$ eV, in good agreement with the offset calculated above by the core levels.

We modeled the electronic structure of bulk Co₃O₄ using the Hubbard-corrected local density approximation (LDA + U) to DFT. The problem is difficult, as two different oxidation states of Co with two different spin states must be described. Because of this, U-values for Co₃O₄ calculations vary widely in the literature.^{18,50–52} The problem is further complicated by the debate over the size of the fundamental band gap of Co₃O₄.

To identify a combination of U which best matches experimental data, we started with the Shirley-background-subtracted XPS valence band (Fig. 7(a), blue open circles) and fit 5 peaks to the data (Fig. 7(a), blue shaded regions). 5

TABLE I. XPS core levels for valence band offset calculation.

Materials	MgAl ₂ O ₄ substrate	~13 Å Co ₃ O ₄ /MgAl ₂ O ₄	Co ₃ O ₄ thick film
Co 2p (eV)	...	777.02	777.87
Al 2p (eV)	74.40	74.65	...
VBM (eV)	3.17	...	0.852

FIG. 7. Valence band structure. (a) Measured XPS valence band for a 250-Å-thick sample is shown by open circles, with the envelope of the 5-peak fit shaded blue. Indicated by the solid black line, calculated DOS for bulk Co_3O_4 with $U(\text{Co}^{2+}) = 4 \text{ eV}$ and $U(\text{Co}^{3+}) = 0 \text{ eV}$ agrees well with experimental features. (b) Site- and orbital-projected DOS for $U(\text{Co}^{2+}) = 4 \text{ eV}$ and $U(\text{Co}^{3+}) = 0 \text{ eV}$.

peaks was the minimum number necessary to acquire a reasonable fit. We then calculated the total density of states (DOS) for 64 combinations of U (from 0 to 7 eV on Co^{2+} and Co^{3+} in 1 eV increments), broadened each DOS by 0.5 eV to account for experimental broadening, and again fit 5 peaks to each DOS. We then compared the overall band width and peak positions with the experimental data, narrowing down from the 64 original possible combinations to 3 best fits: $\{U(\text{Co}^{2+}), U(\text{Co}^{3+})\} = \{0, 0\}$, $\{0, 3\}$, and $\{4, 0\}$. We then checked the magnetization as a function of the two U parameters. Combination $\{4, 0\}$ produced a magnetization of $2.65 \mu_B$ for the Co^{2+} ions, while $\{0, 0\}$ and $\{0, 3\}$ produce lower values of 2.33 and $2.42 \mu_B$, respectively, with the remaining moment on the nonmagnetic Co^{3+} ions. Therefore, based on the peak positions and magnetic moment, we selected $\{U(\text{Co}^{2+}), U(\text{Co}^{3+})\} = \{4, 0\}$ for our calculations.

As shown in Fig. 7(a), after scaling by photoionization cross-section,⁵³ the peak positions, valence band width, and relative peak intensities of the calculated DOS (solid black line) are in good agreement with the XPS valence band. Site- and orbital-projected DOS for $\{U(\text{Co}^{2+}), U(\text{Co}^{3+})\} = \{4, 0\}$ are shown in Fig. 7(b). Comparing with the literature, our $U(\text{Co}^{2+})$ value agrees with the value used by Chen *et al.*,^{51,52} while our $U(\text{Co}^{3+})$ value agrees with that of Qiao *et al.*¹⁸ We calculate a band gap of 0.6 eV, in agreement with the recent transmission measurements from Qiao *et al.*¹⁸ The valence band features are dominated by contributions from Co^{2+} and Co^{3+} d states and O 2p states, with strong hybridization between these orbitals. The top of the valence band is mostly composed of Co^{3+} d and O 2p states, while the main O 2p states lie deeper in the valence band. The bottom of the conduction band has contributions from Co^{2+} and Co^{3+} d states as well as O 2p states. The presence of Co^{3+} d states at the top of the valence band is in agreement with the assignments of Kim and Park.^{19,50} Since both Co^{2+} and Co^{3+} d states are present at the conduction band minimum, we cannot resolve

whether the gap originates from an on-site or cross-site transition.

The pseudo-dielectric function $\langle \epsilon \rangle$ for a 220-Å-thick Co_3O_4 epilayer on spinel is shown in Fig. 8. It is nearly independent of the angle of incidence. Also, the data from both instruments are well matched in the area of overlap near 0.8 eV. As mentioned above, $\langle \epsilon \rangle$ is not representative of the optical constants for Co_3O_4 . Instead, it combines features of the layer and the substrate. For example, at low energies (near 0.5 eV, below the band gap of the film), $\langle \epsilon_1 \rangle = 2.9$, which is determined by the optical constants of the spinel substrate.⁴³ At intermediate energies (between 0.7 and 3 eV), the Co_3O_4 film causes interference effects and the absorption peaks of Co_3O_4 appear as peaks in $\langle \epsilon_1 \rangle$. (In a bulk material, absorption causes peaks in $\langle \epsilon_2 \rangle$.) In the UV region, the absorption of the Co_3O_4 film is very large and interference effects decrease. Therefore, $\langle \epsilon_1 \rangle$ resembles the dielectric function of the Co_3O_4 . We also note that interference effects cause $\langle \epsilon_2 \rangle$ to be negative below 2.5 eV, where the absorption of Co_3O_4 is related to minima of $\langle \epsilon_2 \rangle$. At higher energies, it causes maxima.

The optical constants of the Co_3O_4 epilayer can be determined using well-known procedures,^{44,45} since the film thickness and the optical constants of the spinel substrate are known.⁴³ We write the dielectric function ϵ as a sum of Kramers-Kronig consistent oscillators and vary the oscillator parameters until we reach good agreement between the data (symbols) and model (solid lines) in Fig. 8. The details of the expansion are not important and the fit parameters are not physically meaningful.

The resulting dielectric function ϵ of Co_3O_4 is shown in Fig. 9. These optical constants are available as supplemental material.⁵⁹ We see that Co_3O_4 is an insulator, since ϵ vanishes at low energies. It has a direct band gap (onset of strong absorption) of 0.75 eV. An indirect band gap or defect absorption is not visible with ellipsometry, since the resulting absorption coefficient is very small. The first absorption peak (maximum in the joint density of states for allowed interband optical transitions) occurs at 0.9 eV. Since we merge data sets from two instruments in this spectral region, there is an artifact in the data, which shows a double-peak

FIG. 8. Pseudodielectric function $\langle \epsilon \rangle$ of a 220-Å-thick Co_3O_4 film on spinel. Symbols: Experimental data. Lines: Fit with the dielectric function shown in Fig. 9.

FIG. 9. Real (dashed) and imaginary (solid) parts of the dielectric function ϵ of Co_3O_4 (220-Å-thick film grown by MBE) from the near-IR to the near-UV region, showing peaks due to interband electronic transitions. The band gap for this Co_3O_4 film is 0.75 eV.

structure near 0.9 eV. (A double peak was also suggested in density-functional calculations¹⁸ but we are unable to confirm this with our current experiments. More precise work, including low-temperature ellipsometry measurements optimized for the near-infrared spectral region are needed.) The absorption then drops and reaches a minimum at 1.2 eV. There is a second onset of strong absorption near 1.4 eV, which has been associated with the direct band gap in previous studies.^{19,20} The strong absorption peak at 0.9 eV was not identified in some of the earlier work because of the limited spectral range in some previous experiments. On the other hand, our results are in excellent agreement with those of Ref. 18, where a band gap of 0.74 eV is reported from transmission and photoluminescence measurements. It has been argued¹⁸ that this gap is due to direct dipole-forbidden d-d intraband transitions at tetrahedral-site Co^{2+} cations. These transitions (forbidden in the presence of perfect spherical symmetry) become allowed due to crystal-field splitting in the cubic spinel structure and due to hybridization of the oxygen 2p states with the cobalt 3d states. See the projected DOS shown in Fig. 7(b) for comparison. Our calculations also find substantial Co^{3+} contributions to the valence band maximum and the conduction band minimum. Therefore, we also expect contributions to d to d intraband transitions from the Co^{3+} sites.

The higher-energy peaks at 1.65 and 2.6 eV were previously identified by Kim and Park.¹⁹ Our work shows an additional broad absorption peak at 5 eV, comparable to Ref. 18. At even higher energies, ϵ_2 drops significantly.

The ellipsometric angles in the region of the lattice absorption by infrared active phonons in the Co_3O_4 epilayer and the spinel MgAl_2O_4 substrate are shown in Fig. 10. The data (symbols) can be described with a model (lines) consisting of a spinel substrate and a layer, in which the lattice absorption is written as a sum of Lorentzian lineshapes.⁴³

The spectra are very similar to those of bulk spinel (see Fig. 10 in Ref. 43) with four notable exceptions due to the presence of the Co_3O_4 epilayer: (1) There is a dip in the first reststrahlen band ψ at 555 cm^{-1} because of a strong Co_3O_4 phonon. (2) At 982 cm^{-1} , ψ becomes larger than 45° , where

FIG. 10. Ellipsometric angles for a 220-Å-thick Co_3O_4 film on spinel in the mid-infrared spectral region at five angles of incidence from 60° to 80° . (Symbols: Experimental data. Lines: Fit with a Lorentz oscillator expansion of the Co_3O_4 lattice absorption.)

the dielectric function of the substrate is close to 1 at an LO peak of the substrate. This is an interference effect. For a bulk material, ψ is always below 45° . (3) A Co_3O_4 TO phonon at 655 cm^{-1} causes a tiny modification in the rise of the second reststrahlen band. (4) The fit is not good below 400 cm^{-1} , which was attributed to cation disorder in the earlier work on spinel.⁴³ Nevertheless, we are able to find a small feature in ψ at 395 cm^{-1} , where a Co_3O_4 phonon is expected. In summary, we find Co_3O_4 phonon peaks at 395, 557, and 656 cm^{-1} , in agreement with FTIR reflectance and electron energy loss measurements.^{20,54,55} In the spinel structure, we expect four infrared-active TO phonons.⁴³ For Co_3O_4 , the literature also reports an infrared-active T_{1u} phonon at 214 cm^{-1} , which is below the spectral range of our infrared ellipsometer and therefore was not observed by us.

In Fig. 11, we show an estimate for the mid-IR dielectric function of Co_3O_4 , which was obtained from the fit to the data in Fig. 10. The peak at 395 cm^{-1} is influenced by cation disorder in the substrate. The peak at 656 cm^{-1} is close to a TO mode in the substrate. Therefore, the amplitudes, positions, and broadenings of these peaks are not very accurate. On the other hand, the Co_3O_4 TO peak at 557 cm^{-1} is not influenced by any substrate features and can be determined with good accuracy. The Lorentzian broadening of this TO peak is about 6 cm^{-1} , limited by the spectral resolution (8 cm^{-1}) of our experiment.

We do not observe any signs of a metallic response, which would lead to discrepancies between our lattice-dynamical model and the data at low frequencies. Therefore, we are unable to investigate a two-dimensional electron gas, which might be present at the interface between Co_3O_4 and

FIG. 11. Real (dashed) and imaginary (solid) parts of the dielectric function of Co_3O_4 in the mid-IR, showing lattice absorption by three infrared-active phonons.

MgAl_2O_4 . Also, we do not find any signs of free carriers due to doping in the Co_3O_4 layer. (Other Co_3O_4 layers were reported to be p -type.¹⁸)

Finally, magnetization of a 240-Å-thick Co_3O_4 (110) film was measured as a function of temperature under zero-field-cooled conditions at a constant magnetic field of 1 T oriented in-plane (Fig. 12). Field-cooled measurements were in good agreement with the zero-field-cooled values. The data can be attributed to contributions from the relatively small signal from the sample, the diamagnetic substrate,⁵⁶ backing, and the sample mount. Despite the strong background contribution, a local maximum in the magnetization is clearly visible at 49 K. This value is higher than the Néel temperature $T_N \approx 40$ K for a Co_3O_4 crystal.²³ The T_N enhancement appears due to the stress created by lattice-parameter mismatch between Co_3O_4 and MgAl_2O_4 . Since the lattice parameter of Co_3O_4 is slightly smaller than that of MgAl_2O_4 , the mismatch places Co_3O_4 under a tensile stress. It has been widely observed that T_N in antiferromagnetic oxides including Co_3O_4 increases under high pressure.^{57,58}

FIG. 12. Magnetization of a 240-Å-thick Co_3O_4 (110) film was measured as a function of temperature under zero-field-cooled conditions (blue circles) with constant in-plane magnetic field of 1 T. Field-cooled data show similar characteristics. The onset of antiferromagnetism is labeled at 49 K. Inset image shows G-type antiferromagnetic ordering in the spinel structure. The overall negative magnetization is from the diamagnetic contribution from the substrate.

Why a tensile stress increases T_N in a G-type antiferromagnet deserves further study. Alternatively, an enhanced T_N could be related to variations in the oxygen stoichiometry.

IV. CONCLUSION

In conclusion, we have grown Co_3O_4 films on MgAl_2O_4 (110) using MBE. We investigated surface roughness and smoothing during growth with RHEED and AFM, and further affirm the high quality and sharp interface of the as-grown film by XRD and TEM. Ellipsometry measurements find a small gap of 0.75 eV, in good agreement with DFT calculations based on the shape of the XPS valence band. A valence band offset of 3.2 eV is measured for the heterostructure. Finally, we find that the films are antiferromagnetic with a transition temperature of 49 K, higher than the typical bulk value. These results motivate future study of this material, including DFT/TEM study to determine atomic positions at the interface and surface, low-temperature ellipsometry and optical Hall-effect measurements, and growth on different substrates to study changes in the magnetic properties, band offsets, and catalytic activity.

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