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The (110) plane of Co₃O₄ spinel exhibits significantly higher rates of carbon monoxide conversion due to the presence of active Co³⁺ species at the surface. However, experimental studies of Co₃O₄ (110) surfaces and interfaces have been limited by the difficulties in growing high-quality films. We report thin (10–250 Å) Co₃O₄ films grown by molecular beam epitaxy in the polar (110) direction on MgAl₂O₄ 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 Co₃O₄/MgAl₂O₄ 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,3,4 batteries,5,6 and catalysis,7–14 notably for oxidation of carbon monoxide (CO)⁹,10 and water.¹¹–¹⁴ At room temperature, the most stable form of cobalt oxide is CoO₂, 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

Co₃O₄ assumes the cubic Fd³m 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 Co₃O₄, vertex-sharing tetrahedral Co²⁺ ions carry a magnetic moment, while the nonmagnetic Co³⁺ ions occupy the edge-sharing octahedral sites. Co₃O₄ undergoes an antiferromagnetic phase transition below ~40 K.²³–²⁶

Studies of crystalline thin film surfaces and interfaces of CoO₂ 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 Co³⁺ species at the surface.¹⁰ Though epitaxially grown films offer a natural way to achieve high crystallinity, epitaxy of Co₃O₄ is complicated by the fact that all low-index planes are polar. As shown in Fig. 2, the (110) direction of Co₃O₄ contains two types of alternating planes: the most stable type-A plane is comprised of units of Co²⁺Co²⁺O⁴ with a formal charge of +2, while the type-B planes include Co³⁺O₄, resulting in a charge of –2 per surface unit cell. This polarity further motivates study of polar Co₃O₄, 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

Co₃O₄ 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),³⁹ and molecular beam epitaxy (MBE).⁴⁰–⁴⁲ A number of substrates, including MgO,³⁴,³⁶,³⁸,³⁹ SrTiO₃,¹⁸,³⁴,³⁸,³⁹ MgAl₂O₄,³⁶,¹⁴,⁴² Al₂O₃,¹⁸,⁴⁰ LaAlO₃,³⁹ Yttria-stabilized zirconia,³⁹ SiO₂/Si,³²,³³ and iridium³¹ have been studied for the growth of crystalline Co₃O₄ films. Among these substrates, spinel MgAl₂O₄ (110) is an ideal substrate choice not only due to its small lattice mismatch with Co₃O₄ (less than 0.05%) but also due to the fact that it is the only substrate thus far on which Co₃O₄ 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 Co₃O₄ films on MgAl₂O₄ 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...
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 Co₃O₄. 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

MgAl₂O₄ substrates of dimension 5 mm × 5 mm × 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 Co₃O₄ as compared to that of the MgAl₂O₄ substrate. For ellipsometry measurements, a Co₃O₄ film was deposited on a large 2-in.-diameter MgAl₂O₄ 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. 1. At room temperature, Co₃O₄ assumes the normal spinel structure. Based on the crystal field splitting, the Co²⁺ ions (tetrahedral, light blue) carry magnetic moment, while the Co³⁺ (octahedral, dark blue) ions are nonmagnetic.

FIG. 2. Right: the (110) direction of Co₃O₄ 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 Co³⁺₃Co²⁺₂O₄ with a formal charge of +2, while the type B planes include Co³⁺₂O₄ 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

\[ \rho = \frac{r_p}{r_s} = \tan \psi e^{i \Delta}, \]

i.e., the ratio of the p-polarized reflectance \( r_p \) to the s-polarized reflectance \( r_s \). \( \rho \) is usually expressed in terms of the ellipsometric angles \( \psi \) and \( \Delta \). For a bulk sample with complex refractive index \( n \), \( \rho \) is given by

\[ \rho = \frac{(n \cos \phi_0 - \cos \phi_1)(\cos \phi_0 + n \cos \phi_1)}{(n \cos \phi_0 + \cos \phi_1)(\cos \phi_0 - n \cos \phi_1)}, \]

(2)

where \( \phi_0 \) is the angle of incidence and \( \phi_1 \) 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\(_2\)O\(_4\)) has been described recently.

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 \( \varepsilon_n \) of the substrate and the film thickness are known, then the dielectric function \( \varepsilon_f \) of the film can be determined by fitting the experimental data using well-established procedures 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 (±45°) 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\(_2\)O\(_4\) substrate were taken from Ref. 43 without adjustments. We assumed a surface roughness of 2 Å, guided by atomic force microscopy measurements. In the case of a thin absorbing Co\(_3\)O\(_4\) layer on a substrate, the layer thickness cannot be determined. We use a film thickness of 220 Å (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\(_2\)O\(_4\) (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\(_3\)O\(_4\) 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.

The surface roughens with thickness starting between 10 and 20 Å, 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-Å-thickness and above (Fig. 3(d)). One possible explanation for these observations is the electrostatic energy of a polar material diverges with increasing thickness. Above a critical field and therefore critical thickness, the surface roughness may develop to compensate...
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$_3$O$_4$ samples of varying thickness. Scans of 5 × 5 μm areas are shown for the substrate and three representative films in Fig. 3. For the ~13-Å-thick film (Figs. 3(b) and 4(b)), the RMS roughness was 1.26 Å. 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 ~24 Å film (Figs. 2(c) and 3(c)), the surface becomes noticeably rougher. In this sample, the RMS roughness increased to 5.26 Å. Finally, the 125 Å film shown in Fig. 4(d) shows the surface roughness has decreased back down to 1.04 Å; 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 Kα source, λ = 1.5406 Å) operating at 45 kV and 40 mA. The symmetric 2θ–θ scan shows strong substrate peaks corresponding to an out-of-plane lattice constant of 8.07 Å. The high-resolution rocking curve of the (440) reflection for a 240-Å-thick film Co$_3$O$_4$ 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 Å).

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 the reflected intensity arise due to the difference in density between the substrate and film. An example is shown for the same 240 Å film (Fig. 5(b)); the black line is experimental data, while 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.
and coherent interface, in agreement with the RHEED and XRD results above.

XPS measurements were performed in situ using monochromatic Al K\textsubscript{α} radiation (hν = 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 Co\textsubscript{3}O\textsubscript{4} film shows the expected peaks of a system dominated by cobalt and oxygen (Fig. 6(a)). Higher-resolution scans of the O 1s 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\textsubscript{2}.\textsuperscript{15}

Fig. 6(c) displays XPS valence band spectra for the bare MgAl\textsubscript{2}O\textsubscript{4} substrate (red shading) and 250-Å-thick Co\textsubscript{3}O\textsubscript{4} film (blue shading). The band offset in Co\textsubscript{3}O\textsubscript{4} heterostructures may facilitate understanding of the catalytic properties of Co\textsubscript{3}O\textsubscript{4}; 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.\textsuperscript{14} Band offsets were calculated by both core-level\textsuperscript{14} and valence band\textsuperscript{47,48} spectroscopy. The valence band maximum (E\textsubscript{VBM}) for each material was calculated using the linear extrapolation method.\textsuperscript{49} By comparing energy offsets between the Co 2p, Al 2p, and valence band edge positions (as summarized in Table I) using

\[
VBO_{CL} = \frac{(E_{Co2p} - E_{VBM})_{Co3O4} - (E_{Al2p} - E_{VBM})_{MgAl2O4}}{(E_{Co2p} - E_{Al2p})_{Co3O4/MgAl2O4}}.
\]

we calculate a VBO\textsubscript{CL} of 3.4 eV.

The VBO can also be determined directly from the valence band spectra.\textsuperscript{47,48} For a heterostructure of 13 Å Co\textsubscript{3}O\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4}, 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 MgAl\textsubscript{2}O\textsubscript{4} substrate and thick Co\textsubscript{3}O\textsubscript{4} film. This method uses an “all at once” fit minimizing \( \chi^2 \) 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\textsubscript{sim} = 3.2 eV, in good agreement with the offset calculated above by the core levels.

We modeled the electronic structure of bulk Co\textsubscript{3}O\textsubscript{4} 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 Co\textsubscript{3}O\textsubscript{4} calculations vary widely in the literature.\textsuperscript{18,30–52} The problem is further complicated by the debate over the size of the fundamental band gap of Co\textsubscript{3}O\textsubscript{4}.

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). The residual difference is also plotted (black line).

### Table I. XPS core levels for valence band offset calculation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>MgAl\textsubscript{2}O\textsubscript{4} substrate</th>
<th>~13 Å Co\textsubscript{3}O\textsubscript{4}/MgAl\textsubscript{2}O\textsubscript{4}</th>
<th>Co\textsubscript{3}O\textsubscript{4} thick film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co 2p (eV)</td>
<td>...</td>
<td>777.02</td>
<td>777.87</td>
</tr>
<tr>
<td>Al 2p (eV)</td>
<td>74.40</td>
<td>74.65</td>
<td>...</td>
</tr>
<tr>
<td>VBM (eV)</td>
<td>3.17</td>
<td>...</td>
<td>0.852</td>
</tr>
</tbody>
</table>

FIG. 6. XPS spectra. (a) Survey scan of representative 250-Å-thick Co\textsubscript{3}O\textsubscript{4} 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 MgAl\textsubscript{2}O\textsubscript{4} (red shading) and Co\textsubscript{3}O\textsubscript{4} (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 Co\textsubscript{3}O\textsubscript{4} on MgAl\textsubscript{2}O\textsubscript{4} (black open circles). The residual difference is also plotted (black line).
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: \(\{\text{U}(\text{Co}^{2+}), \text{U}(\text{Co}^{3+})\} = \{0, 0\}, \{0, 3\}, \text{and} \{4, 0\}\). 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\(^{3+}\) 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\(^{2+}\) ions. Therefore, based on the peak positions and magnetic moment, we selected \(\{\text{U}(\text{Co}^{3+}), \text{U}(\text{Co}^{2+})\} = \{4, 0\}\) for our calculations.

As shown in Fig. 7(a), after scaling by photoionization cross-section, 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 \(\{\text{U}(\text{Co}^{2+}), \text{U}(\text{Co}^{3+})\} = \{4, 0\}\) are shown in Fig. 7(b). Comparing with the literature, our \(\text{U}(\text{Co}^{2+})\) value agrees with the value used by Chen et al.

The resulting dielectric function \(\varepsilon\) of Co\(_3\)O\(_4\) is shown in Fig. 8. These optical constants are available as supplemental material.

The optical constants of the Co\(_3\)O\(_4\) epilayer can be determined using well-known procedures, since the film thickness and the optical constants of the spinel substrate are known. We write the dielectric function \(\varepsilon\) 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 \(\varepsilon\) of Co\(_3\)O\(_4\) is shown in Fig. 9. This optical function is not representative of the optical constants for Co\(_3\)O\(_4\). Instead, it combines features of the layer and the substrate. Therefore, \(\langle \varepsilon_1 \rangle\) resembles the dielectric function of the Co\(_3\)O\(_4\). We also note that interference effects cause \(\langle \varepsilon_2 \rangle\) to be negative below 2.5 eV, where the absorption of Co\(_3\)O\(_4\) is related to minima of \(\langle \varepsilon_2 \rangle\). At higher energies, it causes maxima.

FIG. 7. Valence band structure. (a) Measured XPS valence band for a 250Å-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\(_3\)O\(_4\) with \(\text{U}(\text{Co}^{2+}) = 4\) eV and \(\text{U}(\text{Co}^{3+}) = 0\) eV agrees well with experimental features. (b) Site- and orbital-projected DOS for \(\text{U}(\text{Co}^{2+}) = 4\) eV and \(\text{U}(\text{Co}^{3+}) = 0\) eV.

FIG. 8. Pseudodielectric function \(\langle \varepsilon \rangle\) of a 220Å-thick Co\(_3\)O\(_4\) film on spinel. Symbols: Experimental data. Lines: Fit with the dielectric function shown in Fig. 9.

whether the gap originates from an on-site or cross-site transition.
structure near 0.9 eV. (A double peak was also suggested in density-functional calculations 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. 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 argued 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$^{2+}$ sites.

The higher-energy peaks at 1.65 and 2.6 eV were previously identified by Kim and Park. Our work shows an additional broad absorption peak at 5 eV, comparable to Ref. 18. At even higher energies, $\varepsilon_2$ drops significantly.

The ellipsometric angles in the region of the lattice absorption by infrared active phonons in the Co$_3$O$_4$ epilayer and the spinel MgAl$_2$O$_4$ 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. 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$_3$O$_4$ epilayer: (1) There is a dip in the first reststrahlen band $\psi$ at 555 cm$^{-1}$ because of a strong Co$_3$O$_4$ phonon. (2) At 982 cm$^{-1}$, $\psi$ becomes larger than 45°, where 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, $\psi$ is always below 45°. (3) A Co$_3$O$_4$ 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. Nevertheless, we are able to find a small feature in $\psi$ at 395 cm$^{-1}$, where a Co$_3$O$_4$ phonon is expected. In summary, we find Co$_3$O$_4$ phonon peaks at 395, 557, and 656 cm$^{-1}$, in agreement with FTIR reflectance and electron energy loss measurements. In the spinel structure, we expect four infrared-active TO phonons. For Co$_3$O$_4$, 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$_3$O$_4$, 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$_3$O$_4$ 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$_3$O$_4$ and...
MgAl$_2$O$_4$. Also, we do not find any signs of free carriers due to doping in the Co$_3$O$_4$ layer. (Other Co$_3$O$_4$ layers were reported to be $p$-type.

Finally, magnetization of a 240-Å-thick Co$_3$O$_4$ (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, 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$_3$O$_4$ crystal. The $T_N$ enhancement appears due to the stress created by lattice-parameter mismatch between Co$_3$O$_4$ and MgAl$_2$O$_4$. Since the lattice parameter of Co$_3$O$_4$ is slightly smaller than that of MgAl$_2$O$_4$, the mismatch places Co$_3$O$_4$ under a tensile stress. It has been widely observed that $T_N$ in antiferromagnetic oxides including Co$_3$O$_4$ increases under high pressure.

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$_3$O$_4$ films on MgAl$_2$O$_4$ (110) using MBE. We investigated surface roughness and smoothening 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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