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Epitaxial growth of Co_3O_4 on $\text{CoO}(100)$

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Under mildly oxidizing ultrahigh vacuum conditions, it is possible to form on top of $\text{CoO}(100)$ single crystal substrates, thin films that have higher oxygen content but that preserve the overall symmetry of the $\text{CoO}(100)$ low-energy electron diffraction pattern. X-ray photoelectron spectroscopy (XPS) and high-resolution electron-energy-loss spectroscopy (HREELS) data indicate that the epitaxial film grown on $\text{CoO}(100)$ at 625 K and 5×10^{-7} Torr is Co_3O_4 -like in both oxygen content and XP/HREEL spectroscopic characteristics. Both materials are closest packed in lattice oxygen, with the mismatch of bulk O^{2-} - O^{2-} distances of approximately 5%. However, the Co_3O_4 is only able to grow to a thickness of approximately 5 Å before the oxidation process halts. It is proposed that the orientation of Co_3O_4 that forms most readily on the $\text{CoO}(100)$ surface does not present a thermodynamically stable orientation of the bulk Co_3O_4 substrate but is that which grows under the constraint of the best $\text{CoO}(100)/\text{Co}_3\text{O}_4$ epitaxial arrangement. While the mismatch in lattice parameters may in part be to blame for the limitation of higher oxide thickness, thicker oxide films have been grown under conditions with significantly larger mismatch. © 1996 American Vacuum Society.

I. INTRODUCTION

CoO is a rocksalt $3d$ transition metal monoxide with interesting electronic and chemical properties. The material is closest packed in O^{2-} , forming a face-centered cubic arrangement with Co^{2+} -filled octahedral sites. The valence band is primarily comprised of cobalt $3d$ orbitals with some admixture from their neighboring oxygen $2p$.¹ Despite the unfilled character of the valence band, the bonding is localized and the material is a charge transfer insulator with a band gap of approximately 6 eV.² It is antiferromagnetic below temperatures of 289 K.³ The thermodynamically stable surface of CoO is formed along the (100) nonpolar orientation in which cations and anions most favorably balance out electrostatic interactions in interpenetrating square arrays.

Chemically, the metal monoxides find use as partial oxidation catalysts^{4,5} and as gas sensors.⁶ Not coincidental to these applications is the easy accessibility of a second oxidation state of cobalt, Co^{3+} . More highly oxidized cobalt compounds are well known in the solid state. In particular Co_3O_4 is thermodynamically stable under a wide range of substrate temperature and oxygen partial pressure conditions, and may form⁷ on the CoO surface under oxidizing reaction conditions. The oxygen lattice structure of the bulk Co_3O_4 is similar to that of CoO with the closest O^{2-} distances matching to within 5%.⁸ However Co_3O_4 possesses both Co^{3+} and Co^{2+} cations, which are distributed among the fcc octahedral and tetrahedral holes in the normal spinel structure.

In this article, we present x-ray photoelectron spectroscopy (XPS), and high-resolution electron-energy-loss spectroscopy (HREELS) data for both the stoichiometric $\text{Co}(100)$ surface, and for the epitaxially grown, thin film of Co_3O_4 . The O $1s$ and Co $2p$ XPS regions are shown as a function of oxygen exposure, and thickness calculations of the Co_3O_4 overlayer are presented along with a discussion of these phenomena.

II. EXPERIMENT

The $\text{CoO}(100)$ single crystal, approximately $0.5 \times 1 \times 0.2$ cm^3 in size, was obtained from the Atomergic Chemetals Corp. and was grown by the flame fusion method. The crystal surface was oriented to within 1° of the (100) plane by Laue back diffraction and polished with successively finer grades of alumina to 0.03 μm alumina particle size. The crystal was then washed in trichloroethylene, and ultrasonicated in acetone and in methanol. The substrate was placed on a stainless steel backing plate and was held in place by tantalum wires which were placed across the sample edges and spot welded to the backing plate. The mounted sample was then suspended between two tantalum wires and placed between two heating posts to which the tantalum wires were spot welded. Substrate heating was achieved by direct resistive heating of the tantalum wires. The temperature was measured with a Chromel-Alumel thermocouple which had been attached to the backing plate.

The $\text{CoO}(100)$ surface was cleaned by repeated cycles of sputtering with Ar^+ (3×10^{-5} Torr, 2 keV, $3 \mu\text{A}/\text{cm}^2$ for 15 min), annealing in oxygen (5×10^{-7} Torr, 523 K, for 15 min), and annealing in vacuum ($\leq 3 \times 10^{-10}$ Torr, 523 K, for 15 min) until no impurities could be detected by Auger electron spectroscopy. The XPS data were collected at room temperature using a Physical Electronics (Φ) 15-255G double pass cylindrical mirror analyzer. The XPS photoelectrons were generated using Mg $K\alpha$ radiation ($h\nu = 1253.6$ eV) with electron energy analysis done in the constant energy mode with a bandpass of 50 eV. The charging effects in the XPS spectra were compensated for by assigning a binding energy of 529.4 eV to the lattice O $1s$ peak and of 780.5 eV to the CoO Co $2p_{3/2}$ peak.

HREELS data were taken in the specular mode at 60° relative to the surface normal using a single pass 127° sector electron energy analyzer.⁹ The HREELS data were taken

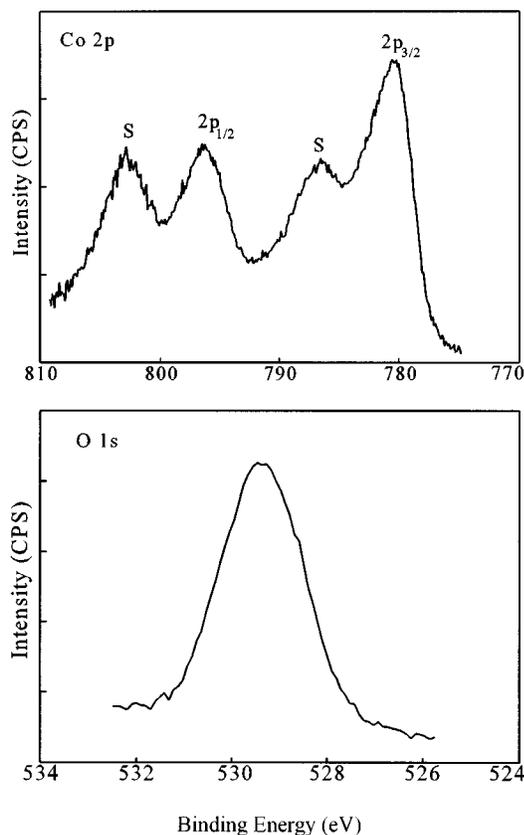


FIG. 1. O 1s and Co 2p XPS spectra for stoichiometric CoO(100).

with a primary beam energy of 3.2 eV, with a resolution of 8.5 meV as measured by the full width at half-maximum of the elastic peak. Charging at the sample surface during the measurements was a problem; thus the HREELS data were collected at a substrate temperature of 500 K, an approach which was used previously with success.¹⁰ No change in the surface composition was detected as a result of HREELS acquisition at this substrate temperature.

III. RESULTS AND DISCUSSION

XPS spectra for the stoichiometric CoO(100) surface are shown in Fig. 1 and a typical HREEL spectrum is given in Fig. 2. Surface stoichiometry was confirmed by the XPS O 1s/Co 2p_{1/2} intensity ratio as well as the Co 2p_{1/2} satellite to Co 2p_{1/2} main peak intensity ratio (Table I). The Co 2p spectrum yields a Co 2p_{3/2} peak at 780.5 eV while the Co 2p_{1/2} peak occurs at 796.4 eV with the corresponding satellites at 787.1 and 803.0 eV, respectively. Among cobalt metal and its oxides, the very intense satellite structure is specific to CoO and results from the charge-transfer band structure characteristic of the late 3d transition metal monoxides. The CoO valence band is primarily comprised of cobalt 3d orbitals. However, a significant admixture of oxygen 2p leads to a hybridized description of the valence band:

$$\Psi_{vb} = \alpha 3d^7 + \beta 3d^8 \bar{L} + \gamma 3d^9 \bar{L}^2,$$

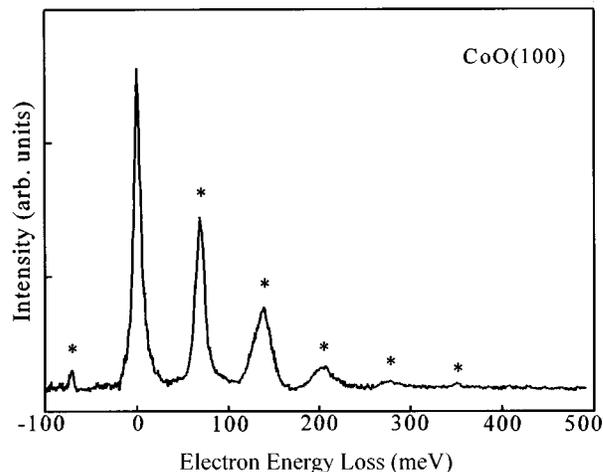


FIG. 2. HREEL Fuchs-Kliwer phonon spectrum of stoichiometric CoO(100) at a primary beam energy of 3.2 eV.

where \bar{L} represents a hole in the oxygen 2p band. Due to the significant admixture of oxygen orbitals, photoexcitation from cobalt 2p core levels has a high probability of creation of both $2p^5 3d^7$ and $2p^5 3d^8 \bar{L}$ final states. Studies of the resonant behavior of the satellite structure² indicate that the lower binding energy $2p_{3/2,1/2}$ features are associated with the $2p^5 3d^8 \bar{L}$ state and the satellite peaks with the $2p^5 3d^7$ state. Co 2p_{1/2} satellite to main peak intensity ratios of ~ 0.9 are characteristic of the cubic cobalt monoxide;¹³ values of ~ 0.3 have been measured for Co₃O₄.¹³

The O 1s peak due to lattice oxygen in CoO(100) is assigned a value of 529.4 eV as an internal binding energy calibration. Previous studies have shown that the lattice O 1s binding energy for transition metal monoxides is relatively insensitive to changes in near-surface stoichiometry.¹⁴ A value of 0.41 was obtained for the XPS O 1s/Co 2p intensity ratio, using the entire Co 2p_{1/2} (satellite plus main peaks) region, and this value is within error of 0.45 reported in the literature for CoO powders.¹¹ No other peaks are visible in the O 1s region.

The HREELS Fuchs-Kliwer phonon spectrum of stoichiometric CoO(100) is shown in Fig. 2. The CoO phonon spectrum comprises a single fundamental loss at 69.4 meV with multiple loss peaks at integral values of the single loss energy. The loss peaks decrease in intensity in a Poisson distribution,¹⁵ indicating that the phonons behave harmonically. The Fuchs-Kliwer phonons are surface analogs of transverse optical bulk modes and thus their energy can be estimated by application of dielectric theory.^{16,17} Using optical and dielectric CoO data available in the literature,¹⁸⁻²⁰ we have previously calculated¹⁵ the fundamental phonon loss energy to be 69.5 meV, in excellent agreement with the present results. The spectrum in Fig. 2 also shows a phonon gain to the high energy side of the elastic peak due to the thermal population of phonons. In order to overcome problems with charging, HREEL spectra were acquired at a substrate temperature of 500 K. The gain to single phonon intensity ratio is in agreement with that anticipated from a

TABLE I. XPS binding energy and intensity data.

| Sample | Co $2p_{3/2}$ (eV) | Satellite (eV) | Co $2p_{1/2}$ (eV) | Satellite (eV) | O $1s^a$ (eV) | Intensity ratio O $1s/\text{Co } 2p_{1/2}$ | Intensity ratio Co $2p_{1/2}$ Sat./Main |
|--|-----------------------|-------------------|-----------------------|-------------------|------------------|---|---|
| CoO(100) (this work) | 780.5 | 787.1 | 796.4 | 803.0 | 529.4 | 0.41 | 0.77 |
| Co_3O_4 (this work) | 779.6 | 787.9 | N.R. ^b | 803.8 | 529.4 | 0.56 | 0.41 |
| | 780.5 | | 796.2 | | 531.2 | | |
| CoO^c | 780.5 | 786.4 | 796.3 | 803.0 | 529.6 | 0.45 | 0.9 |
| | | | | | 531.2 | | |
| Co_3O_4^c | 779.6 | 789.5 | 794.5 | 804.5 | 529.5 | 0.59 | 0.32 |
| | 780.7 | | 796.0 | | 530.8 | | |

^aO $1s$ lattice oxygen set to 529.4 eV.^bN.R.—not resolved.^cReferences 11–13.

Boltzmann population of the 69.4 meV Fuchs–Kliwer phonon at 500 K.

The stoichiometric CoO(100) sample was heated in oxygen (5×10^{-7} Torr O_2 , at 625 K) for increasing lengths of time. Figure 3 shows the Co $2p$ and O $1s$ XP spectra for the series of oxygen exposures. The appearance of a second oxygen component at 531.2 eV is evident in the O $1s$ data after

30 min and the feature continues to increase slowly in intensity to saturate after approximately 300 min. The 531.2 eV peak has previously been detected in a number of studies involving air- or O_2 -exposed CoO,^{12,21} Co_3O_4 powders,^{21–23} and oxidized Co_3O_4 thin films.^{24–26} Absent in stoichiometric CoO O $1s$ XPS, the 531.2 eV species has been attributed to nonstoichiometric near-surface oxygen,²⁶ a more specific

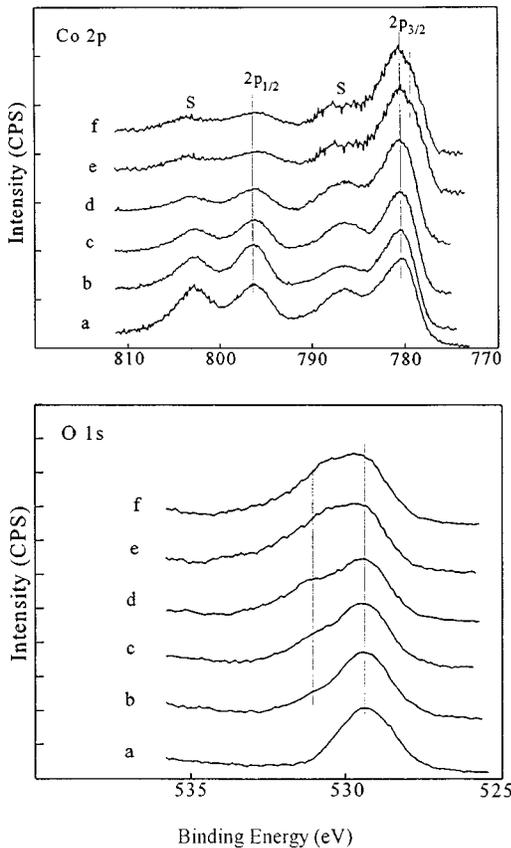


FIG. 3. X-ray photoelectron O $1s$ and Co $2p$ spectra as a function of O_2 exposure at 625 K for (a) 0 min; (b) 30 min; (c) 60 min; (d) 180 min; (e) 300 min; and (f) 360 min.

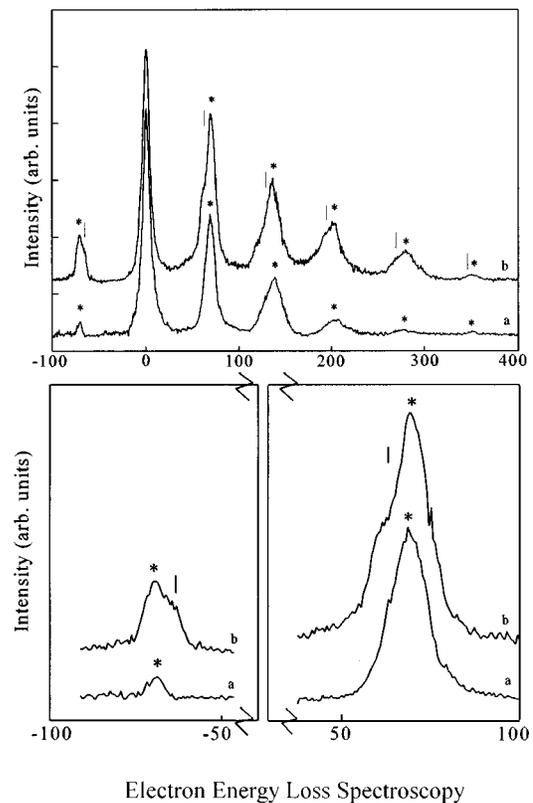


FIG. 4. HREEL Fuchs–Kliwer phonon spectrum of (a) CoO(100) and (b) oxidized CoO(100)– Co_3O_4 . Top panel: full scan. Bottom panel: expanded range for single gain and loss peaks showing new phonon peak to lower gain/loss energy. Asterisks mark CoO phonon structure.

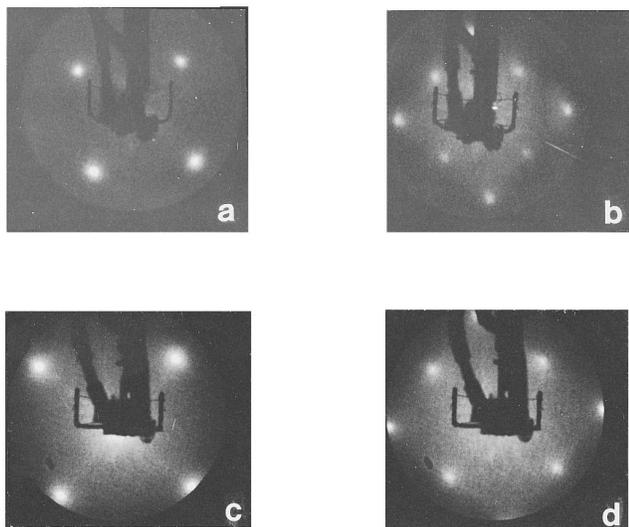


FIG. 5. LEED for $\text{CoO}(100)$ stoichiometric surface at (a) 65 eV and (b) 85 eV, and for the oxidized $\text{CoO}(100)\text{-Co}_3\text{O}_4$ epitaxy at (c) 60 eV and (d) 82 eV.

near-surface O^- ,¹⁰ surface hydroxylation,²⁷ and $\text{Co}(\text{OH})_2$ -like thin film formation.^{22,28}

HREELS of the oxidized $\text{CoO}(100)$ surface (Fig. 4) shows no indication of electron loss to hydroxyl stretching modes (≈ 450 meV) and thus OH-containing species can be discounted as the source of the 531.2 eV O 1s peak. Depending upon the surface pretreatment conditions, the intensity of the 531.2 eV peak can rival that of the 529.4 eV O^{2-} lattice peak from the CoO substrate (Fig. 3, Refs. 12 and 26), precluding the assignment to a surface adsorbate. Additionally, angle-resolved XPS²² has previously shown that the 531.2 eV species is distributed throughout the near-surface region. We, therefore, conclude that the 531.2 eV peak is characteristic of the oxidized $\text{CoO}(100)$ surface and is not due to surface contamination or small quantities of defect oxide resulting from ill-formed oxide overlayers.

The top panel of Fig. 3 shows the Co 2p XPS spectral region as a function of oxygen exposure. Changes in the spectra correlate well with the oxidation of stoichiometric $\text{CoO}(100)$ [Fig. 3(a)] to Co_3O_4 [Fig. 3(f)]. Co 2p peaks broaden due to the formation of an additional cobalt oxidation state ($\text{Co}^{2+}/\text{Co}^{3+}$) and eventually a double Co 2p_{3/2} photoelectron structure is obtained, with binding energies of 779.6 and 780.5 eV, as has been previously obtained for bulk Co_3O_4 samples. It is not possible to resolve the two individual Co 2p_{1/2} components. However, the peak has clearly broadened with oxygen exposure. The Co 2p satellite intensities also decrease substantially and approach satellite/main peak intensity ratios observed for bulk Co_3O_4 . The XPS data are summarized in Table I for $\text{CoO}(100)$ and oxidized $\text{CoO}(100)$ after saturation to 5×10^{-7} Torr O_2 at 625 K (300 min), as well as relevant CoO and Co_3O_4 literature data. The oxidized $\text{CoO}(100)$ surface yields XPS data consistent with the formation of a $\text{CoO}(100)\text{-Co}_3\text{O}_4$ thin film, although satellite intensities and peak positions indicate the oxidation to

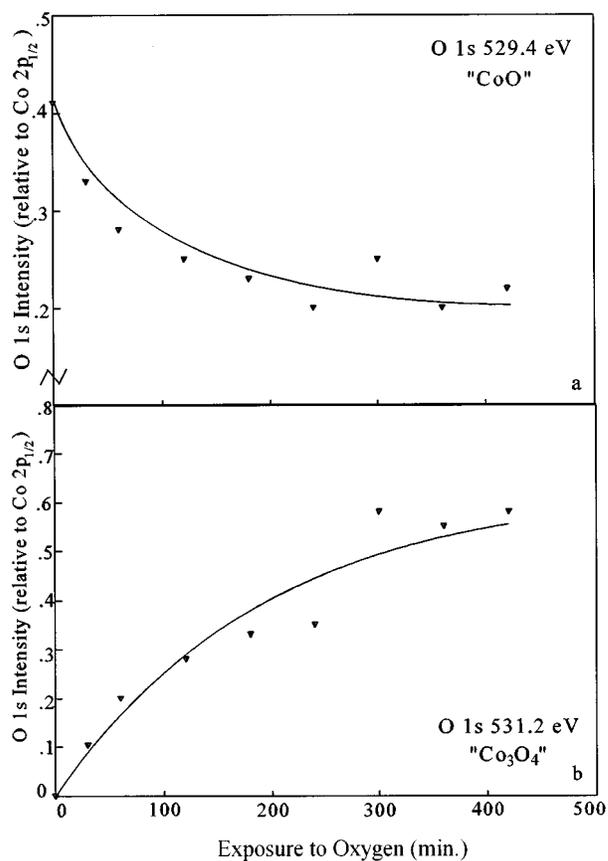


FIG. 6. $\text{CoO}(100)$ O 1s XPS intensity as a function of O_2 exposure for (a) the 529.4 eV peak and (b) and 531.2 eV peak. Oxygen intensities are reported relative to that of Co 2p_{1/2}. The solid line represents a fit to Frank-Van der Merwe layer-by-layer growth (after Ref. 29).

Co_3O_4 is not complete within the sampling depth of the XPS experiment.

The HREELS data shown in Fig. 4 corroborate the presence of a new extended oxide phase on the rocksalt $\text{CoO}(100)$ substrate. The oxidized $\text{CoO}(100)$ spectrum now shows two fundamental Fuchs-Kliwer phonon losses, at 59.8 and 69.8 meV, with multiple loss peaks at integral values of both fundamental phonon losses. The 59.8 meV feature has previously been associated with the formation of Co_3O_4 on $\text{CoO}(100)$.⁷ The spinel structure of Co_3O_4 is lower symmetry than that of the rocksalt CoO lattice and the 69.8 meV feature could potentially represent overlapping Co_3O_4 and CoO phonon losses. However, the HREEL spectrum of Co_3O_4 has not yet been obtained independent of a $\text{CoO}(100)$ substrate and the contribution of Co_3O_4 to the 69.8 meV phonon structure cannot at this point be ascertained.

During oxidation, the low-energy electron diffraction (LEED) pattern obtained from the cobalt oxide surface retains the $\text{CoO}(100)$ two-dimensional symmetry and quality, as shown for LEED from representative $\text{CoO}(100)$ and $\text{CoO}\text{-Co}_3\text{O}_4$ surfaces in Fig. 5. Thus the Co_3O_4 thin film must form in close epitaxy with the underlying $\text{CoO}(100)$ substrate. Other than a slight streaking along $\langle 010 \rangle$ and $\langle 001 \rangle$ directions [Figs. 5(c) and 5(d)], no new diffraction features

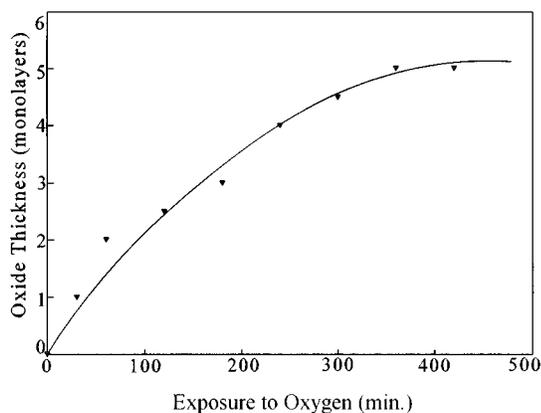


FIG. 7. Thickness of Co₃O₄ layer as a function of oxygen exposure. Thickness calculations are described in the text.

are observed at any point in the oxidation process and both diffuse background intensity and sharpness of the (1×1) diffraction features remain comparable. Sample charging made LEED problematic at 300 K and diffraction patterns could generally not be obtained below about 200 eV at this temperature. The data in Fig. 5 were obtained by heating the

substrate to 625 K under ultrahigh vacuum and turning off the heater current for the approximately 30 s required for LEED acquisition. No changes in either XP or HREEL spectra were detected as a result of the short heating to 625 K.

The O 1s 529.4 and 531.2 eV intensities are plotted as a function of O₂ exposure in Figs. 6(a) and 6(b), respectively. The O 1s data have been normalized to the Co 2p_{1/2} intensity for their particular oxygen exposure to compensate for systematic changes in XPS acquisition among the O₂ annealed surfaces. The 531.2 eV feature, associated with the Co₃O₄-like oxidized surface, saturates after approximately 300 min. Concurrently, the 529.4 eV lattice O²⁻ intensity is attenuated. In order to estimate a minimum thickness for the oxidized layer, we assume that the 531.2 eV O 1s species is characteristic of a Co₃O₄-like oxide which forms epitaxially on top of the CoO(100) substrate and we attribute the entire 529.4 eV intensity to the CoO(100) substrate. The solid lines in Fig. 6 follow intensity changes anticipated for a Frank–Van der Merwe growth mode assuming a constant rate of O₂ adsorption,²⁹ indicating the data are compatible with layer-by-layer epitaxial formation. Attempts to fit the data to Volmer–Weber island growth were unsuccessful.

Calculations of the thickness furthermore assume an exponential attenuation of the XPS photoelectron with a mean free path of 11 Å.³⁰

$$\frac{I_{O,1s(\text{Co}_3\text{O}_4)}}{I_{O,1s(\text{CoO})}} = \frac{S_{O,1s(\text{Co}_3\text{O}_4)} \int_{n=0}^m C_{O,x(\text{Co}_3\text{O}_4)} \exp(-x \cos \theta / \lambda_{O,1s(\text{Co}_3\text{O}_4)}) dx}{S_{O,1s(\text{CoO})} \int_{n=m+1}^{\infty} C_{O,x(\text{CoO})} \exp(-x \cos \theta / \lambda_{O,1s(\text{CoO})}) dx},$$

where m is the thickness of the Co₃O₄ layer, and x is the distance into the surface. S_x are the cross sections of the O 1s photoelectron in Co₃O₄ and CoO, respectively, which are assumed to be the same. $C_{O,x(\text{Co}_3\text{O}_4)}$ and $C_{O,x(\text{CoO})}$ are taken to be constant and equivalent since, in the bulk, both rocksalt CoO and spinel Co₃O₄ are closest packed in lattice oxygen with oxygen–oxygen spacings to within 5%. The spectrometer collection angle, θ , is 42°.

Results of the thickness calculations as a function of oxygen exposure are shown in Fig. 7. The data are given in terms of monolayers, with the average monolayer thickness taken to be 2.13 Å, the distance between layers in the CoO bulk along the <100> direction.³¹ The Co₃O₄ epitaxy is only able to grow to a thickness of 5 monolayers (ML), after which the oxidation of the CoO(100) substrate ceases. Admixture of 531.2 and 529.4 eV oxygen species into the CoO substrate and the Co₃O₄-like overlayer would lead to larger calculated thickness values, and thus a 5 ML limiting thickness should be taken as a lower estimate for the CoO(100)–Co₃O₄ epitaxial growth. However, the limiting thickness is comparable to other constrained oxide epitaxies that have been reported to date, e.g., NiO(111) on Ni(100),³² which form thermodynamically unstable orientations of the oxide and thus do not propagate beyond 3–5 ML.

Assuming bulk termination, the Co₃O₄ orientation that most closely matches the lattice dimensions of the CoO(100) substrate is Co₃O₄(100). Both surfaces have square arrays of oxygen with oxygen–oxygen distances to within 5%. The two surfaces differ primarily in the cobalt ion concentrations and site occupancies. For rocksalt monoxides, the most thermodynamically stable surface orientation is (100), which produces a nonpolar lattice of interpenetrating cation and anion square arrays,⁴ effectively balancing out repulsive and maximizing attractive coulombic interactions. In the spinel structure, coulombic interactions are most favorable for (110) and (111) surfaces,¹⁴ which are the naturally occurring orientations observed on flux-grown Co₃O₄ crystals.³³ While less thermodynamically stable, the Co₃O₄(100) orientation preserves the substrate oxygen lattice arrangement. Under sufficiently oxidizing conditions, a Co₃O₄-like oxide will, therefore, form but it is constrained to do so in the (100) orientation in order to interface with the underlying substrate.

The extent to which this Co₃O₄-like oxide layer accurately reflects a true Co₃O₄(100) surface is by necessity a matter of some speculation, since no studies of single-crystal Co₃O₄(100) have been reported. LEED analysis of these thin films indicate the CoO(100) (1×1) symmetry is preserved

throughout the oxidation process, although some streaking is observed along $\langle 010 \rangle$ and $\langle 001 \rangle$ directions. Since the oxide layer grows to a substantial thickness (≈ 5 ML) the Co₃O₄-like oxide epitaxy must also preserve the (1×1) unit cell structure. According to XPS data, the cobalt ions are comparable in chemical nature to that of Co₃O₄. Oxygen to cobalt XPS intensities also indicate that the oxide composition is close to that expected for Co₃O₄. However, the oxygen in the Co₃O₄-like layer is substantially different than the O²⁻ of the underlying CoO substrate, or from the majority of the oxide ions in powdered Co₃O₄ samples that have been studied by XPS.²¹⁻²³

A simple interpretation of the shift in binding energy from 529.4 eV (CoO 1s) to 531.2 eV (oxide overlayer 1s) is that the oxygen in the Co₃O₄-like layer is less ionic, and is somewhat closer to O⁻ than to the O²⁻ of the typical cobalt oxide lattice oxygen. Al₂O₃ and SiO₂ both have formally O²⁻ valent lattice oxygens with binding energies of >531 eV.²⁷ However, the chemical natures of cations and anions are symbiotic and it is difficult to envision the anion in the oxide overlayer changing without the cations mirroring the change in either their XPS binding energies, anion/cation concentrations, or both. Differences in external relaxation or other final state effects could potentially result in a higher O 1s binding energy, but the present data are insufficient to explain the phenomenon. It is clear that the very intense 531.2 eV O 1s peak is not a result of either defects or hydroxyl contamination, but is characteristic of the oxide layer that forms on CoO(100) under mild oxidation conditions. The oxide layer is substantial in thickness (≈ 5 ML) and has enough long-range order to support cooperative vibrational motions to give rise to HREEL phonon spectra.

IV. CONCLUSIONS

At 625 K and under 5×10^{-7} Torr O₂ CoO(100) oxidizes slowly to produce a Co₃O₄-like oxide overlayer. The orientation of bulk Co₃O₄ that best forms an epitaxial arrangement with the underlying CoO(100) substrate is not that which results in a thermodynamically stable Co₃O₄ surface orientation and the epitaxy is limited to approximately 5 ML in thickness. The oxidized overlayer gives a LEED pattern consistent with the underlying substrate CoO(100)- (1×1) , but with some streaking along $\langle 010 \rangle$ and $\langle 001 \rangle$. O 1s/Co 2p intensities are consistent with the formation of Co₃O₄, as are Co 2p binding energies and satellite structure. However, the O 1s binding energy associated with the overlayer is 531.2 eV. While the feature has been observed previously on oxidized CoO and Co₃O₄ powders, it is considerably higher in binding energy than the 529.4 eV O 1s peak associated with the stoichiometric lattice oxygen. The higher binding energy peak is not a result of water or hydroxyl contamination, since no OH vibrational feature is observed in the HREEL spectrum. The structure of the CoO(100)-Co₃O₄ overlayer must have long-range order, since the LEED is still characteristic of a cubic (1×1) surface. Additionally, phonon structure due to cooperative lattice vibrations is observed in the HREELS,

indicating an oxide with a lower unit cell symmetry but significant enough long-range order to support a very well developed Fuchs-Kliwer phonon spectrum.

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