Experimental study of the interfacial cobalt oxide in Co$_3$O$_4$/α-Al$_2$O$_3$(0001) epitaxial films

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A detailed spectroscopic and structural characterization of ultrathin cobalt oxide films grown by O-assisted molecular beam epitaxy on α-Al$_2$O$_3$(0001) single crystals is reported. The experimental results show that the cobalt oxide films become progressively more disordered with increasing thickness, starting from the early stages of deposition. Low energy electron diffraction patterns suggest that the unit cell remains similar to that of α-Al$_2$O$_3$(0001) up to a thickness of 17 Å, while at larger thicknesses a pattern identified with that of Co$_3$O$_4$(111) becomes visible. X-ray photoelectron spectroscopy reveals sudden changes in the shape of the Co 2p lines from 3.4 to 17 Å cobalt oxide thickness, indicating the transition from an interfacial cobalt oxide layer towards [111]-oriented Co$_3$O$_4$. In particular, the absence of characteristic satellite peaks in the Co 2p lines indicates the formation of a trivalent, octahedrally coordinated, interfacial cobalt oxide layer during the early stages of growth, identified as the Co$_3$O$_4$ corundum phase.

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I. INTRODUCTION

The stability of polar surfaces, characterized by a net surface charge, has long been a topic of much interest, since the large electrostatic energies associated with such surfaces are expected to lead to modified electronic and atomic structures, with attendant changes in physical properties. This often leads to surface structures that depart significantly from a simple truncation of the bulk crystal, exhibiting reconstructions, faceting, surface roughening, altered valencies, and atomic structures, with attendant changes in properties, such as the onset of two-dimensional metallic states in ultrathin metallic films.[213] This is a surprising result in that the cobalt sesquioxide, Co$_3$O$_3$, is not the preferred cobalt oxide at the temperatures and pressures attainable in molecular beam epitaxy growth conditions. In fact, the electronic and catalytic properties of Co$_2$O$_3$ have not been studied extensively, possibly due to difficulties in synthesizing this compound.

Recently, we reported the epitaxial growth of Co$_3$O$_4$(110)/MgAl$_2$O$_4$(110) and Co$_3$O$_4$(111)/α-Al$_2$O$_3$(0001) thin films, which were found to exhibit (1×1) surfaces, despite the fact that both surfaces are polar; while the as-grown film surfaces show some degree of disorder, annealing in air results in atomically smooth films for Co$_3$O$_4$(110), and improved morphology for the Co$_3$O$_4$(111) films, while retaining the (1×1) surface structure.[10,11] The stability of these surfaces was attributed to a modified surface valency of the Co cations, corresponding effectively to a surface inversion in the spinel structure; identical conclusions were reached in a study of the growth of twinned (1×1) [111]-oriented Co$_3$O$_4$ films on Ir(001)-(1×1).[22] and in Fe$_3$O$_4$(111)/Pt(111) thin films, which also exhibit a (1×1) surface.[3] One unresolved issue remains the interface structure at the early stages of growth of Co$_3$O$_4$(111)/α-Al$_2$O$_3$(0001). The observation of a significant amount of disorder occurring at the Co$_3$O$_4$/α-Al$_2$O$_3$(0001) interface was tentatively attributed to the possibility of the formation of an off-stoichiometric cobalt oxide, perhaps closer to the corundum Co$_3$O$_4$ phase. In this report, we present the results of a detailed study of the early stages of growth of Co$_3$O$_4$/α-Al$_2$O$_3$(0001) thin films, aiming at understanding the electronic and crystal structure of the interfacial oxide layer.

This is a surprising result in that the cobalt sesquioxide, Co$_3$O$_3$, is not the preferred cobalt oxide at the temperatures and pressures attainable in molecular beam epitaxy growth conditions. In fact, the electronic and catalytic properties of Co$_2$O$_3$ have not been studied extensively, possibly due to difficulties in synthesizing this compound. Chenavas et al.[14] suggest the existence of a high pressure phase with low spin Co$^{3+}$ ($a = 4.882$ Å, $c = 13.38$ Å) and a low pressure phase, with high spin Co$^{3+}$ ($a = 4.782$ Å, $c = 12.96$ Å) based on the observation of a reduction in the unit cell volume upon annealing in air at 400°C for 30 min, where the spin state was inferred from the smaller ionic radius of high spin Co$^{3+}$. Ab initio (ground state) calculations for corundum Co$_2$O$_3$ suggest also that this oxide is energetically stable.[15] The most stable oxides of cobalt include the high temperature rocksalt CoO (cobaltous oxide) phase, where the Co$^{2+}$ ($S = 3/2$) occupy octahedral sites, and the mixed valence cobalt cobaltite, Co$_3$O$_4$, crystallizing in the normal spinel structure ($a = 8.086$ Å) with the Co$^{2+}$ occupying tetrahedral sites and the Co$^{3+}$ occupying octahedral sites.[16,17,18,19] The octahedral Co$^{3+}$ ions are in a low spin state, $S = 0$, while the tetrahedral Co$^{2+}$...
ions are in a high spin state \( (S = 3/2) \), which order antiferromagnetically below about 40 K\textsuperscript{19,22}

II. EXPERIMENTAL

Film growth was carried out in an ultrahigh vacuum (UHV) oxide molecular beam epitaxy deposition system (base pressure of \( 1 \times 10^{-9} \text{ mbar} \)), using conditions identical to those reported earlier\textsuperscript{10,11}. Prior to film growth, the \( \alpha\)-\( \text{Al}_2\text{O}_3 \) substrate was annealed at 600°C in UHV for 60 min, followed by exposure to atomic oxygen at 300°C for 30 min. This procedure results in \( \alpha\)-\( \text{Al}_2\text{O}_3\)(0001) surfaces free of carbon and yielding sharp reflection high energy electron diffraction (RHEED) and low energy electron diffraction (LEED) patterns, characteristic of atomically smooth surfaces (see Fig. 1 and Fig. 2). The only impurities detected by Auger electron spectroscopy (AES) consist of trace amounts of Ca (2%) and K (0.2%). Film growth was carried out at 300°C with partial pressure during growth was set to \( 3 \times 10^{-5} \text{ mbar} \). The Co deposition rate was about 1 Å/min, as measured by a calibrated quartz thickness monitor. Growth rates were monitored before and after deposition throughout this study. The film growth was interrupted at several stages of the deposition process for LEED, AES and x-ray photoelectron spectroscopy (XPS) analysis, namely, after deposition of 1, 2, 10, 20 and 70 Å Co. From \textit{ex situ} x-ray reflectometry of the film carried out after growth, the oxide film thickness was found to be 120 ± 10 Å, where the error bar includes possible systematic errors in the measurement. From this value, the corresponding cobalt oxide film thicknesses are obtained: 1.7, 3.4, 17, 34, and 120 Å. LEED, AES and XPS measurements were performed after transferring the sample under UHV from the growth chamber to a dedicated analysis chamber with a base pressure of \( 1 \times 10^{-10} \text{ mbar} \); typical XPS measurement times ranged from 2-5 h. Before continuation of the film growth, the film surface was exposed to the atomic oxygen beam for 5 min with the sample held at 300°C. \textit{Ex situ} x-ray diffraction (XRD) measurements were performed on the 120 Å film on a Shimadzu diffractometer operating in the parallel beam optics geometry.

III. RESULTS AND DISCUSSION

Film crystallinity was monitored during growth using RHEED, and the diffraction patterns after completion of each layer are shown in Fig. 1 showing \( (1 \times 1) \) diffraction patterns whose overall features agree with the RHEED results. The oblique cell drawn in Fig. 2 (0 Å) corresponds to the \( \alpha\)-\( \text{Al}_2\text{O}_3\)(0001) unit cell (corundum, \( a = 4.7750 \text{ Å}, c = 12.9877 \text{ Å} \) in the hexagonal representation\textsuperscript{23,25,26}). The three-fold symmetric LEED pattern of the \( \alpha\)-\( \text{Al}_2\text{O}_3\)(0001) surface indicates that it is composed predominantly of double-layer atomic steps. The LEED pattern symmetry remains similar to that of the substrate up to 17 Å, while for 34 Å its starts resembling that of \( \text{Co}_3\text{O}_4\)(111)\textsuperscript{11,27}. This evolution in the LEED patterns can also be followed in Fig. 2, which shows the line profiles across the spots labeled A and B in Fig. 2. In order to correct for charging, slight differences in sample positioning, and for the different electron beam energies, the distance between these spots was normalized to the same value for all thicknesses. While for \( \alpha\)-\( \text{Al}_2\text{O}_3\)(0001) no features are present between these

![FIG. 1: RHEED patterns of the cobalt oxide film along two different azimuths of the \( \alpha\)-\( \text{Al}_2\text{O}_3\)(0001) surface at several stages of the film growth, as labeled. The incident electron beam energy is 15 keV.](image)
spots, in Co$_3$O$_4$(111) there is an intermediate diffraction spot, the presence of which can be used to identify the onset of this phase, at about 17 Å. The XRD measurements on the 120 Å film show the presence of the (hhh) planes of Co$_3$O$_4$ at the angle positions corresponding to the bulk values, indicating that the film is fully relaxed. The rocking curve around the (222) plane shows a single gaussian peak, with a width of 0.026°, which corresponds to a characteristic lengthscale in real space of about 180 nm.

Spectroscopic characterization by XPS and AES was performed for each layer thickness, but while XPS could be performed for all cobalt oxide thicknesses, AES could only be performed up to 17 Å, due to sample charging. The XPS spectra were obtained using the Mg K$_\alpha$ line ($h\nu = 1253.6$ eV) of a double anode x-ray source and a double pass cylinder mirror analyzer (PHI 15-255G) set at a pass energy of 25 eV (energy resolution of about 0.8 eV). The XPS data, acquired in energy steps of 0.05 eV, were smoothed using a 5-point adjacent averaging and corrected for the Mg K$_\alpha$ satellite. Charging is always a concern for insulating samples; one common method of calibrating the energy scale against charging is to use the C 1s line from adventitious hydrocarbons but this process cannot be used in these carbon-free samples. X-ray photoelectron emission charges the sample positively, while charging in (electron excited) AES may be of either sign, since the number of ejected electrons may be larger or smaller than the number of incident electrons (secondary electron emission, which is strongly energy dependent). Hence, comparing both the XPS and AES data can provide some information about the extent of charging.

To correct for sample charging in XPS, we consider the Auger and photoelectron spectral features of oxygen, namely, the O 1s peak and the KVV Auger and energy loss peaks, which lie near the Co 2p edge. We set the O 1s peak of α-Al$_2$O$_3$ to the tabulated value of 531.5 eV and the O 1s peak of the 120 Å film, expected to be representative of Co$_3$O$_4$, to the tabulated value of 529.4 eV. For the 1.7 and 3.4 Å films, we assume that most of the O contribution to the photoelectron spectra arises from the substrate, and we tentatively set the O 1s peak to the same energy position as that of α-Al$_2$O$_3$. We find that the KVV Auger loss peaks of O for these films also align with those for α-Al$_2$O$_3$ and that the energy distance from the first O loss peak to the Co 2p$_{3/2}$ is 15.9 eV for both 1.7 and 3.4 Å cobalt oxide films. For the thicker films, both first and second O Auger KVV loss peaks are visible, and shifted to much lower binding energies relative to the Co 2p$_{3/2}$ peak, by 18.9 eV for the first O loss peak and by 5.6 eV for the second O loss peak for the 34 and 120 Å films; for the 17 Å film, the shift is slightly smaller, about 14.4 and 4.2 eV, respectively. Therefore, we can assign the O 1s peak to that of Co$_3$O$_4$ for the 34 and 17 Å films, although for the latter thickness the assignment is less certain. For reference, we also measured the XPS spectra of LaCoO$_3$, where the Co cations are all trivalent; since LaCoO$_3$ is conducting at room temperature ($\sigma \sim 0.1$ Ω$^{-1}$cm$^{-1}$) no charging is expected and no energy corrections have been applied to this XPS spectrum. The LaCoO$_3$ data are from a single crystal wafer cut along one pseudo-cubic (110) plane (mechanically polished to optical flatness and annealed in air at 600°C for 67.5 hours), and were acquired after cleaning in situ in oxygen plasma at 300°C for 30 min. The LaCoO$_3$ single crystal, grown using the floating zone method, is twinned, as shown by Laue and x-ray diffraction, but is otherwise well ordered. The shoulder on the O 1s peak, which was very prominent in the XPS spectra of the sample as-inserted to the analysis system, is due to adsorbed hydroxyl groups that remain on the surface. The XPS spectra for all samples thus calibrated are shown in Fig. 3.

Three distinct features in the XPS spectra as a function of cobalt oxide thickness are apparent: (i) the energy difference between the 2p$_{3/2}$ and 2p$_{1/2}$ peaks remains constant at 15.2 eV with increasing cobalt oxide thickness, and between Co$_3$O$_4$, LaCoO$_3$, and CoO the energy difference between multiplets is sometimes employed to ascertain the ionic valence state, but is not suitable for
The presence and energy position of satellite peaks in the core and valence levels of the photoelectron spectra of the 3d transition metal oxides depend strongly on the ionic environment, cation valency, and electron occupancy. These satellite peaks arise as a consequence of the fact that several channels are available that compete for the final (excited) state. In 2p core level photoelectron emission, the presence of the core hole leads to strong modifications in the energy landscape of the cation and anion (ligand) orbitals that favor screening of the core hole via charge transfer from sp or ligand orbitals. Two processes compete for the final state, one corresponding to the case where charge is transferred from the ligand to the 3d orbital, effectively screening the core hole, which is usually associated with the main line (well screened state, represented by \( |2p^53d^{n+1}L\rangle \), where \( L \) represents the ligand hole)\(^{51,52,53,54,55}\). The other competing process corresponds to a less well screened state (with higher apparent binding energy), where no charge transfer from the ligand takes place and where charge compensation is provided by sp orbitals (unscreened state, represented by \( |2p^33d^n\rangle \)). In a simplified cluster model\(^{51,52,53,54,55}\), the photoemission process is treated as a scattering event from an initial hybridized state

\[
|\psi_f\rangle = \alpha_0 |2p^63d^n\rangle + \alpha_1 |2p^53d^{n+1}L\rangle + \ldots \quad (1)
\]

to final hybridized states of the form

\[
|\psi_f\rangle = \beta_0 |2p^53d^n\rangle + \beta_1 |2p^53d^{n+1}L\rangle + \ldots \quad (2)
\]

The final state with the lowest energy is associated with the main 2p photoelectron line, while the other higher energy states give rise to the satellite lines, although in all cases a strong mixture of orbital states may be present. In particular, for the case of a filled 3d shell \((n = 10, \text{ as in } \text{Cu}_2\text{O})\), charge transfer to the 3d orbital is precluded, and the final state is dominated by the sp-screened state, \( |5p^53d^{10}\rangle \), with no satellite peaks\(^{60}\). In addition, multiplet splitting of the final states due to exchange interaction with the core hole may introduce further features in the spectra\(^{61,62,63,64,65}\). Strong satellite structures occur predominantly in transition-metal and rare-earth cations, and it is generally accepted that charge transfer peaks give the most intense contribution, while multiplet splitting adds to the fine structure, although separation between these contributions is sometimes difficult\(^{52,54,55,66}\).

For our purposes, we are interested in the satellite features that may allow us to identify the ionic state of the cobalt cations, particularly at small cobalt oxide thicknesses, where no satellites are observed. In a simplified relaxation model, the absence of satellite features can be
understood as a consequence of an electronic structure consisting of filled valence levels to which charge transfer from the ligand is precluded. This is expected to be the case for octahedrally coordinated trivalent cobalt, where the crystal field splits the 3d levels into a low energy triplet \( t_{2g} \) level, and to a high energy \( e_g \) doublet, leading to full occupancy of the \( t_{2g} \) states, with a correspondingly low spin state \( S = 0 \). One example where this occurs is in LaCoO\(_3\), whose Co 2p XPS spectrum is shown in Fig. 3. In cluster theory language, this corresponds to the situation where the charge transfer energy \( \Delta \) (difference between the excited \( |2p^63d^6L\rangle \) and ground \( |2p^63d^6\rangle \) initial states of the neutral atom), is larger than the core-hole–d-electron Coulomb energy, \( Q \), such that the screened \( |2p^63d^6L\rangle \) final state remains higher in energy than, and little hybridized with, the unscreened \( |2p^63d^6\rangle \) state. A similar situation occurring in Fe\(^{2+}\) compounds has been analyzed by Kroll et al.\(^{51}\) Hence, in CoO\(_3\), the strongly suppressed satellite peak is explained by the fact that the octahedrally coordinated Co\(^{3+}\) states do not contribute to charge transfer and therefore to shake-up processes; the remaining 1/3 Co cations are tetrahedrally coordinated Co\(^{2+}\) and give rise to shake-up peaks, since the crystal field now leads to a low energy \( e_g \) doublet and a partially filled higher energy \( t_{2g} \) triplet.\(^{1,19,22}\) A comparison of the binding energies of the 2p Co edge peaks for several cobalt oxide compounds (Table I) where we excluded mixed valency oxides other than CoO\(_3\) supports the view that these satellite features may be employed to identify the valence state of cobalt in oxides,\(^{15,63,64,65}\) although exceptions are apparent, including the presence of (strongly suppressed) satellite peaks in the layered LiCoO\(_2\) (where the Co\(^{3+}\) occupy octahedral sites).\(^{10,63}\) For the listed spinels where Co\(^{2+}\) occupy tetrahedral sites, CoAl\(_2\)O\(_4\), CoCr\(_2\)O\(_4\), and the tetragonal CoMn\(_2\)O\(_4\) (stable only at elevated temperatures with parasite phases, including MnCo\(_2\)O\(_4\), known to develop at ambient temperatures)\(^{20}\) the satellite peak splitting is similar to that of divalent cobalt in an octahedral environment, and here CoO\(_3\) seems to be the outlier.

The case of Co\(^{3+}\) in a tetrahedral environment should also give rise to charge-transfer satellite peaks, since in such a crystal field both the low energy \( e_g \) doublet and the higher energy \( t_{2g} \) triplet have empty states.\(^{19,22}\) These observations suggest that the interfacial oxide layer present at low cobalt oxide thicknesses consist of octahedrally coordinated Co\(^{3+}\) cations. We envisage two possibilities that can explain this result: it either corresponds to a fully oxidized cobalt compound with a corundum structure, Co\(_2\)O\(_3\), where all cations are (slightly distorted) octahedrally coordinated; or to the octahedrally coordinated Co\(^{3+}\) layer in the Co\(_3\)O\(_4\)(111) structure, which also would initiate the spinel growth along the [111] direction. The LEED and RHEED patterns for the 1.7 and 3.4 Å films, similar to those of the \( \alpha \)-Al\(_2\)O\(_3\) substrate, seem to support the first interpretation of the spectroscopy data.

Is it now well established that under the preparation conditions used here, the \( \alpha \)-Al\(_2\)O\(_3\)(0001) surface is the non-polar, (1 \( \times 1 \)) Al-terminated surface.\(^{17,18,43,45,50}\) During Co deposition, the cobalt oxide layer is expected to continue the \( \alpha \)-Al\(_2\)O\(_3\) close-packed oxygen sublattice, with either the [AB]A or [AB]C stacking sequences, where the square brackets enclose the hcp stacking of the \( \alpha \)-Al\(_2\)O\(_3\) O sublattice. The first stacking sequence is a continuation of the hcp stacking and contains octahedral interstitial sites only, while the second stacking sequence also contains tetrahedral sites and is expected to mark the onset of the spinel crystal structure. Based on the LEED and XPS results, and considering the atomic configurations expected for the available cationic interstitial sites in the close-packed O sublattice, we propose next a model to explain the epitaxial relationships observed in the spinel(111)/\( \alpha \)-Al\(_2\)O\(_3\)(0001) system. In this model, the transition from the corundum to the spinel structure can occur in two possible ways, schematically shown in Fig. 4. Starting with the stoichiometric corundum (0001) surface, Fig. 3(a), (i) the Co cations oc-

![FIG. 4: Variation of the O 1s XPS peak full width at half maximum (FWHM) as a function of cobalt oxide thickness.](image)

| Oxide | Site | Ion | 2p\(_{1/2}\) B.E. | 2p\(_{3/2}\) B.E. | Ref. |
|-------|------|-----|-----------------|----------------|-----|
| CoO   | o    | 2+  | 780.5 \( \pm 5.9 \) | 796.3 \( \pm 6.7 \) | \cite{39} |
| CoFe\(_2\)O\(_4\) | o    | 2+  | 780.6 \( \pm 5.1 \) | 796.2 \( \pm 6.5 \) | \cite{70} |
| CoFe\(_3\)O\(_4\) | o    | 2+  | 779.9 \( \pm 6.2 \) | 795.7 \( \pm 6.2 \) | \cite{61} |
| LaCoO\(_3\) | o    | 3+  | 780.1 | 795.3 | * |
| CuCo\(_2\)MnO\(_4\) | o    | 3+  | 780.0 | 795.0 | \cite{48} |
| Co\(_2\)O\(_4\) | o    | 3+  | 779.6 | 794.5 | \cite{36} |
| MnCo\(_2\)ZnO\(_4\) | o    | 3+  | 780.4 | 795.4 | \cite{48} |
| LiCoO\(_2\) | o    | 3+  | 779.5 \( \pm 10.6 \) | 794.6 \( \pm 9.5 \) | \cite{66,68} |
| CoAl\(_2\)O\(_4\) | t    | 2+  | 781.0 \( \pm 5.0 \) | 796.7 | \cite{63} |
| CoCr\(_2\)O\(_4\) | t    | 2+  | 780.4 \( \pm 5.3 \) | 796.3 | \cite{61} |
| CoMn\(_2\)O\(_4\) | t    | 2+  | 780.2 \( \pm 5.6 \) | 796.3 \( \pm 6.5 \) | \cite{64,68} |
| Co\(_3\)O\(_4\) | t    | 2+  | 780.7 \( \pm 8.8 \) | 796.0 \( \pm 8.5 \) | \cite{39} |
ocup non-corundum octahedral sites concomitant with
the initiation of the fcc stacking of the O sublattice,
forming the octahedral Co\textsuperscript{3+} layer of the Co\textsubscript{3}O\textsubscript{4}(111)
structure, Fig. 5(b); or (ii) the Co cations occupy both
corundum sites (which are tetrahedrally coordinated in
the fcc stacking of the O sublattice), and octahedral and
tetrahedral non-corundum sites to form the mixed va-

clence Co\textsuperscript{2+}-Co\textsuperscript{3+}-Co\textsuperscript{2+} layer of Co\textsubscript{3}O\textsubscript{4}(111), as shown in
Fig. 5(c). Hence, one finds that the spinel structure can
very naturally continue the corundum structure without
causing undue violence to the cationic distribution at the
interface between the two crystal structures. The differ-
ent possible ways in which the spinel structure can be
generated, and the different equivalent, but not identi-
cal, planes that form the Co\textsubscript{3}O\textsubscript{4} unit cell along the [111]
direction, imply that the presence of stacking faults and
antiphase boundaries are very likely. They may be re-
ponsible, in part, for the surface disorder observed in
the RHEED and LEED patterns.

![Diagram](attachment://diagram.png)

**FIG. 5:** (a) Atomic structure of the stoichiometric corun-
dum (0001) surface. (b) Model for the epitaxial growth of the
Co\textsubscript{3}O\textsubscript{4}(111) structure on the corundum (0001) surface,
showing the formation of the octahedral Co\textsuperscript{3+} layer. (c) Al-
ternative growth model, showing the formation of the mixed
valence tetrahedral Co\textsuperscript{2+}-octahedral Co\textsuperscript{3+}-tetrahedral Co\textsuperscript{2+}
layer of Co\textsubscript{3}O\textsubscript{4}(111) on the corundum (0001) surface. For
each surface, the dashed area indicates the primitive surface
unit cell.

We can, therefore, reconstruct the most likely growth
process in the Co\textsubscript{3}O\textsubscript{4}/\textalpha-Al\textsubscript{2}O\textsubscript{3}(0001) system. We assume
in the following that one unit layer corresponds to the
separation between planes of the close-packed O sublat-
tice, of about 2.3 Å, using the lattice parameter of Co\textsubscript{3}O\textsubscript{4}.

In broad terms, we envisage the cobalt oxide film growth
as follows. At the earliest stage of growth, Co cations fill
the empty octahedral corundum sites of the non-polar \textalpha-\textAl\textsubscript{2}O\textsubscript{3}(0001) surface, resulting in a corundum-like layer
composed of half Al\textsuperscript{3+} cations and half Co\textsuperscript{3+} cations. At 3.4 Å, the cobalt oxide film corresponds to about 1.5
atomic layers, and the observation of octahedrally coor-
dinated Co\textsuperscript{3+} cations in XPS at this thickness could re-
sult from the formation of the octahedrally coordinated
plane of Co\textsubscript{3}O\textsubscript{4} upon the onset of the oxygen C layer of
the fcc stacking. However, the LEED patterns show no
evidence for the formation of the spinel (111) surface up
to about 17 Å. Hence, we conclude that the cobalt oxide
film continues with the corundum structure up to at least
2-3 atomic layers, forming effectively an interfacial cobalt
sesquioxide layer, mediating the transition between the
sapphire and spinel structures. We do not observe sur-
face reconstructions (LEED, RHEED) or changes in va-

clency of the Co cations (XPS) during the initial stages of
growth; this may be expected if the corundum structure
grows in Co-O\textsubscript{3}-Co layer units, which are charge com-
pensated. Since the Co\textsubscript{2}O\textsubscript{3} phase is not thermodynami-
cally the most stable phase, the Co\textsubscript{3}O\textsubscript{4} phase eventually
sets in, with the transition occurring as described in the
model above. This is observed to occur at 17 Å, where
the XPS shows the presence of tetrahedral Co cations,
characteristic of the spinel Co\textsubscript{3}O\textsubscript{4}(111) structure.

**IV. CONCLUSIONS**

We have studied in detail the early growth stages of
epitaxial Co\textsubscript{3}O\textsubscript{4}(111) films grown on \textalpha-\textAl\textsubscript{2}O\textsubscript{3}(0001) sin-
gle crystals. The RHEED and LEED results show that
film growth proceeds via the Stranski-Krastanov mode;
the electron diffraction data, in combination with spec-
troscopic characterization by XPS, indicate the forma-
tion of an octahedrally coordinated, fully oxidized, in-
terfacial cobalt oxide film that mediates the transition
between the corundum and the spinel crystal structures.

These results are a telling example of the strongly mod-
ified structural and electronic properties of metal oxides
that are induced by the change in crystal symmetries at
interfaces.

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