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Impact of epitaxial strain on crystal field splitting of $\alpha$-Cr$_2$O$_3$(0001) thin films quantified by X-ray photoemission spectroscopy

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ABSTRACT
The influence of epitaxial strain on the electronic structure of $\alpha$-Cr$_2$O$_3$(0001) thin films is probed by combining X-ray photoemission spectroscopy and crystal field multiplet calculations. In-plane lattice strain introduces distortions in the CrO$_6$ octahedron and splits the 3d orbital triplet $t_{2g}$ into $a_1 + e$ orbitals. For relaxed thin films, the lineshape of the Cr 2p core levels are well reproduced when the $t_{2g}$ subset is fully degenerated. In-plane tensile strain stabilizes $a_1$ with respect to $e$ orbitals, whereas compressive strain destabilizes $a_1$ orbitals. Understanding these crystal field variations is essential for tuning the physical properties of $\alpha$-Cr$_2$O$_3$ thin films.

IMPACT STATEMENT
The alliance of X-ray photoemission spectroscopy with crystal field multiplet simulations provides a convenient tool to analyze the electronic structure of $\alpha$-Cr$_2$O$_3$(0001) thin films under epitaxial strain.
This relationship is crucial to predict changes in the magnetic and electronic properties of $\alpha$-Cr$_2$O$_3$ when a certain amount of internal strain is considered.

XPS is an analytical technique very sensitive to modifications of the surface chemistry of any compound. Theoretical works [10] have long predicted that changes in the local geometry of the transition metal may lead to changes in the multiplet splitting features of the XPS spectrum. In this regard, Cr$_2$O$_3$ is a very challenging compound since its 2p photoemission structure is known to have a particularly complex spectral shape due to the coupling between the 2p core-hole and the unpaired electrons in the 3d outer shell [11]. Thus, even if studies [12–14] have shown that the spectral shape of the Cr 2p XPS spectrum is related to the cation local environment, a thorough investigation to quantitatively link these changes with the crystal field strength is still lacking.

The main aim of our study is to explore line-shape differences of the Cr 2p core-level spectra in order to quantify changes in the crystal field around the Cr$^{3+}$ cation induced by different epitaxial strains. To do so, we have investigated epitaxial ultrathin films of $\alpha$-Cr$_2$O$_3$ (0001) directly on $\alpha$-Al$_2$O$_3$ (0001) substrate or on $\alpha$-Fe$_2$O$_3$ (0001) buffer layer grown on the same sapphire substrate. These three oxides have a corundum-like crystal structure with in-plane lattice parameters ($a$) equal to 0.476, 0.492 and 0.503 nm for $\alpha$-Al$_2$O$_3$ (0001), $\alpha$-Cr$_2$O$_3$ (0001), and $\alpha$-Fe$_2$O$_3$ (0001), respectively [15]. The in-plane lattice mismatch is $+3.36\%$ for $\alpha$-Cr$_2$O$_3$ on $\alpha$-Al$_2$O$_3$ and $-2.19\%$ for $\alpha$-Cr$_2$O$_3$ on $\alpha$-Fe$_2$O$_3$. Hence, we were able to analyze the photoemission spectra of Cr$_2$O$_3$ thin films under either compressive (for $\alpha$-Cr$_2$O$_3$ on $\alpha$-Al$_2$O$_3$ substrate) or tensile (for $\alpha$-Cr$_2$O$_3$ on $\alpha$-Fe$_2$O$_3$ buffer) in-plane strain.

All samples were grown by Oxygen-plasma-assisted Molecular Beam Epitaxy (O-MBE) on $\alpha$-Al$_2$O$_3$(0001) substrates pre-cleaned in a H$_2$O$_2$/NH$_3$OH/H$_2$O solution and then in situ by exposure to the oxygen plasma. During the growth, the sample holder temperature was around 450°C and the metal evaporation rate was 0.03 nm·min$^{-1}$. Connected to the ultrahigh-vacuum O-MBE chamber, a Reflection High-Energy Electron Diffraction (RHEED) gun allow us to monitor in real time the diffraction patterns and the evolution of the in-plane lattice parameter of each oxide layer. These RHEED images were acquired with the primary beam aligned parallel to [1100] azimuth. The O-MBE setup is described in detail elsewhere [16]. Following growth, the thickness of each sample was measured ex situ by X-ray reflectivity. Ex situ XPS analyses were then carried out for each sample at room temperature with an Escalab 250 XI using a monochromatic Al K$_\alpha$ source ($h\nu = 1486.6$ eV). As the substrate is an insulator, we used a low-energy electron flood gun during spectral acquisition to avoid charge effects.

We started by depicting the evolution of the in-plane lattice parameter vs. coverage (dotted lines in Figure 1) extracted from the RHEED images. For simplicity sake, the spacing between the (11) and (11) streaks in pixel is normalized to a value of 100% for $\alpha$-Al$_2$O$_3$. Thus, values of 96.64% and 94.33% are obtained for bulk $\alpha$-Cr$_2$O$_3$ and $\alpha$-Fe$_2$O$_3$ (dashed lines in Figure 1), respectively. As expected for $\alpha$-Cr$_2$O$_3$ single layers grown on $\alpha$-Al$_2$O$_3$ substrate [15], the strong in-plane compressive strain observed at very early stages of the growth gradually relaxes with deposition time (Figure 1(a)). Therefore, we selected three $\alpha$-Cr$_2$O$_3$ single layers with thicknesses of 1.1, 5.3 and 16.7 nm to evaluate the Cr 2p XPS spectrum of $\alpha$-Cr$_2$O$_3$ under high, moderate and low compressive strain, respectively. Then, we turned our attention to $\alpha$-Cr$_2$O$_3$ layers grown on $\alpha$-Fe$_2$O$_3$ buffer. In this bilayer, Cr$_2$O$_3$ should remain under lateral tension up to several Angstroms, exhibiting similar in-plane lattice parameter as the $\alpha$-Fe$_2$O$_3$ buffer [15]. The growth of the $\alpha$-Fe$_2$O$_3$ buffer was optimized years ago [17,18]. Herein, we selected a $\alpha$-Fe$_2$O$_3$ film thickness of 5.7 nm associated to a fully relaxed state (Figure 1(b)). On this relaxed buffer layer, an ultrathin film of 3.0 nm thickness of $\alpha$-Cr$_2$O$_3$ was grown successfully. As predicted, we clearly observed an in-plane tensile strain in the Cr$_2$O$_3$ layer (Figure 1(b)).

For all samples, the RHEED patterns (inset in Figure 1(a,b)) exhibit sharp streaks without spots or extra streaks, indicating a bidimensional growth mode and layers of high crystalline quality without secondary phases. A perfect epitaxial growth is mandatory for the study of strain evolution as structural defects (e.g. grain boundaries) promote relaxation phenomena and disturb the analysis [19].

We focused then on the description of the Cr 2p XPS spectra of $\alpha$-Cr$_2$O$_3$ samples in different strain scenarios. In $\alpha$-Cr$_2$O$_3$ single layers (Figure 1(c1–c3)), the Cr XPS spectrum have two broad peaks: one centered at 576.5 eV for the Cr 2p$_{3/2}$ peak and the other centered at 586.5 eV for the Cr 2p$_{1/2}$ peak. The Cr 2p$_{1/2}$ envelope exhibits minor changes in all strain scenarios, whereas the multiplet splitting features of the Cr 2p$_{3/2}$ envelope steadily evolve with the in-plane lattice parameter. For high compressive strain (Figure 1(c1)), the multiplet peak at 575.5 eV (A) is less intense than the one at 577.0 eV (B) and the splitting of the Cr 2p$_{3/2}$ envelope is indistinct. Meanwhile, for moderate compressive strain or for relaxed films (Figure 1(c2 and c3)), we observed a remarkable splitting of the Cr 2p$_{3/2}$ envelope where the multiplet peaks A and B have almost the same intensity. In the case of the bilayer, i.e. for high tensile strain
Figure 1. Evolution of the relative RHEED streak spacing and Cr 2p XPS spectra during the growth of \( \alpha \)-Cr\(_2\)O\(_3\)(0001) under (a) compressive (\( \alpha \)-Cr\(_2\)O\(_3\) on \( \alpha \)-Al\(_2\)O\(_3\) substrate) and (b) tensile (\( \alpha \)-Cr\(_2\)O\(_3\) on \( \alpha \)-Fe\(_2\)O\(_3\) buffer) in-plane strain. The inset RHEED images were acquired with the 30 keV beam aligned along the [1\,\bar{1}\,0] azimuth. Examples of high-resolution Cr 2p core level spectra are depicted for \( \alpha \)-Cr\(_2\)O\(_3\) samples under high (c1) and moderate (c2) compressive strain as well as for a fully relaxed film (c3) and under high tensile strain (c4). A Shirley-type background subtraction was used for all spectra.

of Cr\(_2\)O\(_3\) (Figure 1(c4)), the multiplet peak A is also less intense than B; however, contrary to the high compressive strain scenario (Figure 1(c1)), we observed in Figure 1(c4) a prominent shoulder at 578.5 eV (C).

In order to account for all these subtle changes in the multiplet splitting features of the Cr 2p\(_{3/2}\) XPS spectra, we performed semiempirical Crystal Field Multiplet (CFM) [20,21] calculations. The Cr 2p XPS spectra were simulated by solving Green’s functions in second quantization using the quantum many-body program QUANTY [22–24] within the graphical interface CRISPY [25]. The CFM calculations describe the transitions for a single Cr\(^{3+}\) cation from the 3\( d^3\) initial state to the 2\( p^5\)3\( d^3\) final state. They result in atomic multiplets, described by the Coulomb and exchange interactions, the spin–orbit coupling and the crystal field. The 3\( d^3\)–3\( d^3\) and 2\( p^5\)–3\( d^3\) Coulomb and exchange interactions are parametrized in Slater-Condon integrals \( F_{dd}^k \), \( F_{pd}^k \) (Coulomb) and \( C_{pd}^k \) (exchange), whereas the 2\( p^5\) and 3\( d^3\) spin–orbit coupling are parametrized as \( \xi_{2p} \) and \( \xi_{3d} \) for \textit{ab initio} Hartree–Fock calculations. In the corundum structure, the Cr\(^{3+}\) cations lay on the center of a slightly distorted octahedron [26], where a C\(_3\) rotation axis traverses the cation and the center of the two equilateral triangles formed by the oxygen ions. Thus, the crystal field is parametrized in terms of the C\(_3\) point group by \( Dq \), \( D\sigma \) and \( D\tau \) parameters [27].

The treatment of the above-mentioned parameters is described in detail elsewhere [28]. In brief, we reduced the Hartree–Fock values of the Slater-Condon integrals to impute the ionic-covalent behavior of the Cr–O chemical bond. The reduction factors of \( F_{dd}^2 \) (54%) and \( F_{dd}^4 \) (81%) were determined using the experimental Racah B and C parameters \( B = 0.057 \) eV and \( C = 0.433 \) eV [29]) through the relationship:

\[
B = 9F_{dd}^2 - 5F_{dd}^4 \quad \text{and} \quad C = 5F_{dd}^4 / 63.
\]

\( F_{pd}^2 \) and \( G_{pd}^1 \) were scaled to 80% of the associated atomic values, while \( G_{pd}^3 \) was scaled to 90% to fit the distance between multiplet peaks. For the crystal field parameters, \( Dq \) was set to the experimental value of 0.208 eV [29], \( D\sigma \) to 0.600 eV and \( D\tau \) was optimized to fit each photoemission spectrum. For all calculated spectra, the ground state was populated with the Boltzmann distribution at 298 K. The resulting sharp peaks were convoluted with a Lorentzian and Gaussian function (FWHM = 0.3 and 0.6 eV) to mimic the broadening of the experimental spectra.

The CFM model considers the crystal field surrounding the metal ion in terms of symmetry reduction. The introduction of an octahedral field (O\(_h\)) breaks the degeneracy of the spherical 3\( d \) orbitals into two subsets of \( t_2g \) and \( e_g \) orbitals. The symmetry reduction from O\(_h\) to C\(_3v\) is associated to a further splitting of the \( t_2g \) orbital subset into \( a_1 + e \). The energy splitting (\( \delta \)) between the geometric centers of \( a_1 \) and \( e \) orbitals is therefore proportional to distortions in the CrO\(_6\) octahedral center. For instance, \( \delta \) is calculated as \( \sim 2 \) meV in a fully relaxed Cr\(_2\)O\(_3\) crystal [29]. However, this value may increase as a strain is applied.
In the basis of the $C_{3v}$ symmetry, $\delta$ is related to the crystal field parameters through the relationship: $\delta = 3D\alpha + 20/3D\tau$ [30,31]. Since the value of $D\alpha$ is fixed in our study, $\delta$ depends only on the $D\tau$ value obtained by adjusting the calculated $Cr\,2p_{3/2}$ envelope to the experimental one. Figure 2 describes the results of the CFM simulations for $\alpha-Cr_2O_3$ thin films under high (Figure 2(a)) and moderate (Figure 2(b)) in-plane compression, fully relaxed (Figure 2(c)) and under in-plane tension (Figure 2(d)). For a fully relaxed film, the Cr $2p$ XPS spectrum is well fitted with $D\tau = -0.270 \pm 0.005$ eV for which the $t_{2g}$ orbital subset is fully degenerated ($\delta = 0$). When an in-plane compression is applied, $D\tau$ value decreases and $\delta$ increases proportionally to the amount of strain. For instance, the spectrum of 1.1 nm $\alpha-Cr_2O_3$ film, highly compressed through mismatch with $\alpha-Al_2O_3$ substrate, is well fitted with $D\tau = -0.295 \pm 0.005$ eV for which $\delta = 170$ meV. In turn, the spectrum of partial relaxed 5.3 nm film is well fitted with $D\tau = -0.280 \pm 0.005$ eV for which $\delta = 70$ meV. For these samples, the $3d$ orbital diagrams (inset in Figure 2) showed that the higher the in-plane compression, the more destabilized is $a_1$ in relation to $e$ orbitals. Interestingly, the tension scenario showed an opposite tendency: the in-plane tension increases the $D\tau$ value, which decreases $\delta$ by stabilizing $a_1$ in relation to $e$ orbitals. For instance, the spectrum of 3.0 nm $\alpha-Cr_2O_3$ film, strained through mismatch with $\alpha-Fe_2O_3$ buffer,
of $\delta$ appears in $\alpha$-Fe$_2$O$_3$-buffered Cr$_2$O$_3$ layers under 1.6% of lateral tension (Figure 3), for which an enhanced magnetocrystalline anisotropy energy is known [35,36].

In conclusion, we have grown epitaxial $\alpha$-Cr$_2$O$_3$(0001) thin films under different strain scenarios from compressive, tensile to fully relaxed state. The subtle line-shape differences of the Cr 2p X-ray photoemission spectra were explored via Crystal field multiplet calculations in order to extract the crystal field parameters and retrieve the 3d orbital diagram of Cr$_2$O$_3$ in each strain scenario. The careful analysis of the Cr photoemission spectra allowed us to interpret the multiplet features of Cr 2p$_{3/2}$ envelope in the light of deformations in the CrO$_6$ octahedron. This convenient methodology provides a structural tool for understanding the influence of strain on the electronic structure of complex oxides.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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