

Chemical and structural investigations of epitaxial Fe-Cr-O thin films

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The Fe-Cr-O ternary system has been studied extensively since the mid-20th century due to its applications in various fields, such as geology, metallurgy, corrosion, and (more recently) spintronics. In this system, solid oxide phases may appear in three different crystallographic structures: the halite, the corundum and the spinel phases. The spinel structure (Fe_{3-x}Cr_xO₄) is a mix of divalent and trivalent cations in the cubic MgAl₂O₄-type structure. Multivalence cations are organized in a geometrically frustrated network of octahedral and tetrahedral sites, termed here Oh-sites and Td-sites respectively. The complexity of the spinel structure opens the way for tailoring the functional properties of these materials (magnetization, Curie temperature, electronic transport by incorporating different metal cations into the host matrix. For instance, substitution of Fe cations for Cr in magnetite converts the half-metal host ferrimagnet into either a semiconductor or an insulator, depending on the x values. Most previous works on the Fe_{3-x}Cr_xO₄ series are based on bulk-like samples, while thin films have received limited consideration. Numerous studies have shown that physical and chemical properties of thin films strongly deviate from the bulk, depending on the growth method, film thickness, and surface and interface effects.

This work presents a comprehensive study of the influence of composition and structural properties of epitaxial Fe-Cr-O thin films.

Thin films were deposited by oxygen-plasma-assisted molecular beam epitaxy (O-MBE) on single crystalline α -Al₂O₃(0001) substrates. This method was chosen as it enables the synthesis with a perfect control of the chromium content (x) by using individual Knudsen effusion cells under a reactive atomic oxygen plasma. During deposition, reflection high-energy electron diffraction (RHEED) patterns were acquired in real time to control the crystalline structure of the oxide formed. Epitaxial growth of 15nm thick Fe_{3-x}Cr_xO₄(1 1 1) thin films of high crystalline quality has been obtained.

Following growth, several characterization techniques were used to obtain chemical and structural information from the thin films. The stoichiometry of the Fe_{3-x}Cr_xO₄ films were verified ex situ by X-ray photoemission spectroscopy (XPS) measurements. The film microstructure was investigated via high-resolution transmission electron microscopy (HRTEM) and complementary quantitative elemental analyses were performed by electron energy loss spectroscopy (EELS) and energy-dispersive X-ray spectroscopy (EDX). X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were carried out on MARS Beamline of synchrotron SOLEIL to resolve the oxidation state and the first cation-neighbors bond distances. Magnetic hysteresis loops and in-plane electrical measurements were conducted. The Cr and Fe cation site distribution was determined by exploring the L_{2,3}-edge X-ray absorption (XAS) and circular dichroism (XMCD) measurements performed on DEIMOS Beamline of synchrotron SOLEIL. Multiplet calculations were used to interpret the dichroism signal.

Stoichiometric series of epitaxial Fe_{3-x}Cr_xO₄(111) thin films were prepared with x varying from 0 to 1.7. The film stoichiometry was first evaluated ex situ by XPS measurements. Since XPS probes only the surface, complementary chemical analyses were performed by STEM-

EELS and STEM-EDX. Those analytical techniques presented similar trends with minimal fluctuations in the Fe and Cr signals throughout the layers and no composition gradient. For $x < 1.4$, RHEED patterns exhibit sharp streaks and no spots, indicating a bidimensional growth mode and layers of high crystalline quality without secondary phases. However, for $x > 1.4$, RHEED images are blurred and the streaks are almost indistinguishable. The layer-substrate interface and structural defects were evaluated by cross-sectional transmission electron microscopy (TEM) images. Figure 1 (left) depicts TEM images of a representative $\text{Fe}_{2.8}\text{Cr}_{0.2}\text{O}_4$ film studied along the [1210] direction. Low magnification TEM image shows that the film is homogeneous and has a constant thickness of about 15 nm. A perfectly flat and abrupt $\text{Fe}_{2.8}\text{Cr}_{0.2}\text{O}_4/\text{Al}_2\text{O}_3$ interface is observed with no noticeable parasite phases at atomic scale. Misfit dislocations, which takes part on the relaxation mechanism of these films, are observed, as already mentioned for other ferrites grown on sapphire substrate by O-MBE (e.g. NiFe_2O_4 and MnFe_2O_4). When comparing HRTEM images of $\text{Fe}_{2.8}\text{Cr}_{0.2}\text{O}_4$ and $\text{Fe}_{2.3}\text{Cr}_{0.7}\text{O}_4$ films, the increasing Cr content seems to induce disorder in the crystalline structure of the film and many stacking defects (e.g., APBs and dislocations) are observed. To investigate further this issue, HRTEM images were acquired for $\text{Fe}_{1.6}\text{Cr}_{1.4}\text{O}_4$ (figure 1 right) and buffer- $\text{Fe}_{1.3}\text{Cr}_{1.7}\text{O}_4$. The increase in the amount of the crystalline nanodomains is unmistakable for both of these layers compared to the first two compositions. These results corroborate well with the decrease in quality of RHEED images. The influence of Cr content on the crystalline quality of the films can be associated to either changes in the cation distribution among tetrahedral and octahedral sublattices or modifications in the growth conditions as the deposition rate is different. For $x < 0.5$ the replacement of Fe^{3+} by slightly smaller Cr^{3+} in Oh-sites does not modify drastically the structure, whereas for $0.6 < x < 1.3$ the displacement of larger Fe^{2+} into Td-sites has a huge influence. Indeed, orbitally active Fe^{2+} cations in Td-sites lead to tetragonal distortions due to cooperative Jahn-Teller effects. For compositions with $x > 1.4$, films are assumed to have the normal type of spinel structure, Fe^{3+} cations are replaced by smaller Cr^{3+} in Oh-sites.

In addition to changing the structural quality, cation disorder has a major impact on the physical properties of the films. The total magnetization and the magnetic anisotropy of $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ thin films decrease as the x values increase. But unlike bulk materials, thin films with high Cr content ($x \geq 1.2$) still show magnetization at room temperature, i.e., near (or above) the Curie temperature of bulk samples. These features were interpreted in the light of the cationic site distribution. For both bulk and thin films, the inversion parameter steadily evolves with composition, ranging from an inverse arrangement (Fe_3O_4) to normal ordering (FeCr_2O_4). Because Cr-rich thin films are still intermediate spinels, while bulk samples are normal spinels, the Curie temperature of these films were increased as they present stronger Td-Oh antiferromagnetic interactions. These results confirm that doping magnetite thin films with Cr is very effective to control the magnetic behavior of this material.

Graphic:

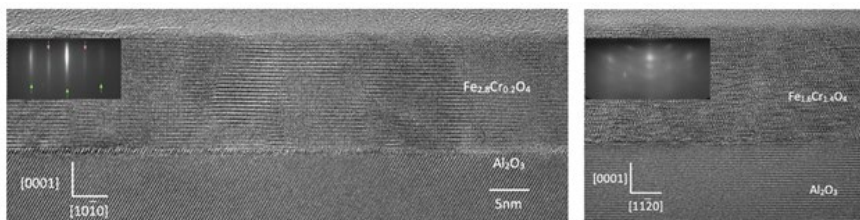


Figure : High resolution TEM image and associated RHEED patterns of $\text{Fe}_{2.8}\text{Cr}_{0.2}\text{O}_4$ films (left), and $\text{Fe}_{1.6}\text{Cr}_{1.4}\text{O}_4$ films (left)

Keywords:

Magnetic materials, EELS, EDS, HRTEM

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P.V.B. Pinho et al. "Stoichiometry Driven Tuning of Physical Properties in Epitaxial $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ Thin Films," Applied Surface Science 615 (2023) 156354