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Ferromagnetic epitaxial Cr$_2$O$_3$ thin films grown on oxide substrates by Pulsed Laser Deposition

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ABSTRACT

Single-phase and single-oriented epitaxial Cr$_2$O$_3$ thin film has been grown on SrTiO$_3$ (111) substrate for the first time. The morphology, epitaxial growth mode and oxygen stoichiometry of the obtained film have been investigated by AFM, XRR, XRD and XPS, and compared to thin film grown on α-Al$_2$O$_3$ under equivalent conditions. The Cr$_2$O$_3$/SrTiO$_3$ system presents a non-coincidence growth based on in-plane rotation of 30° of the Cr$_2$O$_3$ layer respect to the underlying SrTiO$_3$ (111) substrate, while a coincidence growth based on axis-on-axis coupling is present for Cr$_2$O$_3$/α-Al$_2$O$_3$. However, in both cases an in-plane compression occurs in order to match the layer and substrate lattices. The formation of punctual defects in the form of oxygen vacancies have been observed by XPS for the layer grown on α-Al$_2$O$_3$, being the main mechanism for strain alleviation (−4%). However, the 18 nm thick layer grown on SrTiO$_3$ presents stoichiometric oxygen content maintaining an epitaxial strain (−1.6%) accumulated on the lattice. Both epitaxial Cr$_2$O$_3$ layers show soft ferromagnetic response with coercive fields of 60 Oe and 90 Oe for the layer grown on SrTiO$_3$ and α-Al$_2$O$_3$, respectively.

1. Introduction

Chromium trioxide (Cr$_2$O$_3$) is a widely studied oxide, being an important technological material because of its intrinsic properties. It is an antiferromagnetic (AFM, Néel Temperature ($T_N$) = 307 K) and the first discovered magnetoelectric material above room temperature [1–3]. Bulk Cr$_2$O$_3$ also presents uniaxial magnetic anisotropy along the [1 1 1] direction. Additionally, it is a good insulator. The combination of these properties makes this material suitable as a building block in different technological devices. In particular, Cr$_2$O$_3$ has been employed in devices which involve exchange bias effect of coupled ferromagnetic - antiferromagnetic systems [1]. Furthermore, as a result of its good insulating properties, it is also suitable for magnetic tunnel junctions [2]. Cr$_2$O$_3$ is a potential candidate for heterostructures based on epitaxial thin films as it can be easily prepared using a simple growth process. For instance, it has been already implemented as a buffer layer for the growth of other thin films, and has been employed as anode material for Li–ion batteries. However, special attention should be paid to the modification of its intrinsic properties due to the accumulated epitaxial strain. Previous results revealed that the presence of strain induces defects, such as oxygen vacancies, which can infer dramatic changes of its magnetic properties. For instance, unexpected ferromagnetism was found to occur in highly strained Cr$_2$O$_3$ thin films [3,4]. Also, an enhancement of $T_N$ has been directly related to in-plane lattice contraction [5]. Thus, the ability of Cr$_2$O$_3$ to tune its intrinsic properties by artificial strain through epitaxial growth opens the way to the development of complex technological devices. For that, it is mandatory to explore the use of new substrates as templates for the epitaxial growth of Cr$_2$O$_3$ thin films with exotic macroscopic response. Several substrates have been already used, such as sapphire (α - Al$_2$O$_3$) [6,7], graphene [8], Co [9], garnet [10], Cr (110) [11], YAlO$_3$ (001) [12], TiO$_2$ [13], LiNbO$_3$(0001) [14] or Ni(111) with a graphene buffer [15]. However, the use of the well-known SrTiO$_3$ (STO) substrate has been scarcely explored. An attempt of epitaxial growth has been achieved on STO
(001) using CeO$_2$ as buffer layer [16]. However, direct growth of Cr$_2$O$_3$ on STO surface has not been reported yet. The successful epitaxial growth directly on SrTiO$_3$ is of special importance as this material has been widely used for applications in microelectronics due to its high charge storage capacity, chemical stability and its excellent insulating properties [17,18]. Hence, the combination of Cr$_2$O$_3$ and STO intrinsic properties provides a unique possibility to obtain different macroscopic responses on the same heterostructure. In the present work we have successfully grown for the first time epitaxial Cr$_2$O$_3$ thin films on STO (111) substrates. A complete morphological, structural, electronic and magnetic characterization is presented based on a comparison with epitaxial thin films grown on sapphire using equivalent conditions.

2. Experimental section

Cr$_2$O$_3$ thin films were grown on SrTiO$_3$ (111) and $\alpha$-Al$_2$O$_3$ (0001) substrates ($5\times5$ mm$^2$) by Pulsed Laser Deposition (PLD). A Nd:YAG laser ($\lambda = 355$ nm) with 10 Hz and 1 J/cm$^2$ irradiance power was used to ablate a polycrystalline Cr metal target. The deposition was carried out in an oxygen atmosphere of $10^{-4}$ mbar and at a surface temperature of 350 °C. High surface crystallinity was determined by in-situ Reflection High-Energy Electron Diffraction (RHEED) using a primary electron beam of 29 keV. The topography of the samples has been studied by means of a multimode Nanostructure Illa Atomic Force Microscope (Bruker) with a Si tip (Bruker, model TESP), working in tapping mode and operating in air. Images of different sizes were analyzed with WSxM 5.0 software [19].

The structural characterization of the Cr$_2$O$_3$ thin films in both SrTiO$_3$ (111) and $\alpha$-Al$_2$O$_3$ (0001) substrates was investigated by High Resolution Grazing Incidence X-ray Diffraction (HR-GIXRD) in BM25B-SpLine beamline at the ESRF [20]. This end station is composed of a six-circle multipurpose diffractometer in vertical geometry. A photon energy of 15 keV ($\lambda = 0.826$ Å) was used during the experiment to ensure the access to a wide reciprocal space region. Special attention was paid to the study of the growth mechanism of the thin films in the two different substrates, to understand the coupling of the layers lattice with respect to the substrate lattice, as well as to elucidate the possible presence of compressive or tensile stress in the grown films. A layer thickness in the tens of nanometer range, compatible with device manufacturing, in which the epitaxial character still plays an important role but size effects due to ultra-short thicknesses are ruled out has been used for this study. Information about the Cr valence and oxygen stoichiometry was obtained using X-ray Photoelectron Spectroscopy (XPS) methods on the Cr 3s core level using a standard monochromatic X-ray tube, with a Mg K$_\alpha$ radiation anode ($h\nu = 1253.6$ eV).

Scanning Transmission Electron Microscopy (STEM) images of the films were performed in High Angle Annular Dark Field (HAADF) mode using a FEI Titan 60–300 equipped with an aberration corrector for the probe. The convergence angle used was 24 mrad to provide a spatial resolution below 0.1 nm.

The magnetic characterization was performed by Superconducting Quantum Interference Devices (SQUID) Magnetometer at room temperature under a maximum field of 5 T.

3. Results and discussion

During the thin film growth by PLD, in-situ RHEED was used to monitor the evolution of the layers crystallinity. Fig. 1a-d shows representative RHEED patterns of the clean substrates, STO (111) and $\alpha$-Al$_2$O$_3$ (0001) (Fig. 1a and c), and the evaporated Cr$_2$O$_3$ layers (Fig. 1b and d). The RHEED patterns show smooth diffraction stripes, representative of a smooth, homogeneous and crystalline layer. The morphology of the film surface of the different samples has been studied by AFM. Fig. 2a and b show the topography of the Cr$_2$O$_3$ thin films grown on SrTiO$_3$ and $\alpha$-Al$_2$O$_3$, respectively. In both cases a good layer coverage and homogeneity is obtained. AFM profile measurements performed along the surface reveal a flat surface, with root mean square (rms) roughness of approximately 1 nm for the layer grown on SrTiO$_3$ (Fig. 2c). Cr$_2$O$_3$/Al$_2$O$_3$ films show isolated islands on top of a homogeneous coverage. Profile measurements (Fig. 2d) show rms roughness values of 3–4 nm. A similar behavior is obtained from synchrotron-based X-ray reflectivity (XRR) measurements (Fig. 2e and f). Intense Kikuchi fringes are observed for the Cr$_2$O$_3$/SrTiO$_3$ sample, despite the nearly identical densities for the layer (5.22 g/cm$^3$) and substrate (5.12 g/cm$^3$), indicating the presence of abrupt interfaces and flat surfaces, while for the Cr$_2$O$_3$/$\alpha$-Al$_2$O$_3$ sample the rapid attenuation of Kikuchi fringes indicates the presence of a rough surface. Also based on the isostructural character between Cr$_2$O$_3$ and $\alpha$-Al$_2$O$_3$, chemical substitution at the interface is more than probable, which will contribute to the absence of well-defined XRR interference. Thickness values of 18.2(3) nm and 17.7(6) nm have been obtained for the layer grown on SrTiO$_3$ and $\alpha$-Al$_2$O$_3$, respectively from the reflectivity curves.

Bulk sapphire ($\alpha$-Al$_2$O$_3$) (corundum structure) presents in-plane and out-of-plane lattice parameter values of $a = b = 4.76$ Å and $c = 12.99$ Å, respectively [21]. In the case of Cr$_2$O$_3$, isostructural with sapphire, lattice parameters are $a = b = 4.96$ Å and $c = 13.59$ Å. The in-plane lattice mismatch with respect to Cr$_2$O$_3$ is $-4.2\%$ which favors the epitaxial coupling between both lattices. However, SrTiO$_3$ on the (111) orientation, presents lattice parameters of $a = b = 5.5225$ Å and $c = 6.76$ Å implying a lattice mismatch of $+10.2\%$ with Cr$_2$O$_3$, being unfavorable for a coincidence growth. To understand the in-plane coherence between the layers and substrates High Resolution XRD and Reciprocal Space Maps (RSM) measurements were performed. Fig. 3a shows, for the Cr$_2$O$_3$/SrTiO$_3$ system, the RSM around the (022) diffraction peak of the SrTiO$_3$. It can be clearly seen that the diffraction peaks maxima corresponding to the Cr$_2$O$_3$ layer and the SrTiO$_3$ substrate have different in-plane values. Peaks corresponding to STO are those present along the marked yellow line in the figure ($H = 2$), while two peaks associated to the Cr$_2$O$_3$ thin film are aligned along $H = 1.96$ (red line). This XRD pattern can be explained by a non–coincidence epitaxial growth in which the in-plane lattice of the single oriented Cr$_2$O$_3$ (0001) rotates 30° respect to the underlying SrTiO$_3$ (111) plane in order to reduce the lattice mismatch minimizing the epitaxial energy. Such a lattice coupling has been already reported for other transition metal oxides (TM$_2$O$_3$) grown on SrTiO$_3$ (111), for instance for $\alpha$-Fe$_2$O$_3$ [22]. Calculations performed in different diffraction peaks reveal Cr$_2$O$_3$ in–plane lattice parameters of 4.88(4) Å. The difference, in comparison to reported Cr$_2$O$_3$ bulk values ($a = b = 4.96$ Å), results in a compressive strain of $-1.6\%$. Hence, although a non–coincidence growth is present the Cr$_2$O$_3$ layer is strained to match the SrTiO$_3$ lattice. Fig. 3c shows a diagram on the real-space of the Cr$_2$O$_3$ in-plane lattice respect to the substrate lattice in which it can be seen that nearly a perfect coupling between both lattices occurs due to the layer lattice rotation. Out–of–plane scans along the in-plane values for SrTiO$_3$ (Crystal Truncation Rod (CTR) yellow line in the RSM) and Cr$_2$O$_3$ (red line in the RSM) reveal high surface signal between Bragg peaks (Fig. 3b and c) indicating the presence of flat and sharp surface and interface, in agreement with the AFM and XRR measurements. The out–of–plane lattice parameter for Cr$_2$O$_3$ increases to $c = 14.03(3)$ Å respect to the bulk value ($c = 13.59$ Å) maintaining the volume of the bulk unit cell.

In the case of the Cr$_2$O$_3$ layer grown on $\alpha$-Al$_2$O$_3$ (0001), as the former is known to be isostructural to the latter, an axis–on–axis (coherent) growth is expected. Fig. 3d shows the corresponding RSM around the (116) reflection of $\alpha$-Al$_2$O$_3$ (0001) in which it can be seen that the diffraction peak from the Cr$_2$O$_3$ and $\alpha$-Al$_2$O$_3$ has the same in–plane momentum transfer revealing an axis–on–axis coincidence epitaxial growth. The Cr$_2$O$_3$ shrinks its lattice in order to match its in-plane lattice parameter with that of the substrate ($a = b = 4.76$ Å) as shown in the diagram of Fig. 3g. The coincidence growth induces a compressive strain of $-4\%$ to the Cr$_2$O$_3$ lattice. In the out–of–plane direction the Cr$_2$O$_3$ lattice is expanded to $c = 14.18(4)$ Å. In contrast to the layer grown on STO the unit cell volume is not preserved being reduced by
Larger splitting is found for other Cr(III) compounds. In the case of stoichiometric Cr$_2$O$_3$ with formal Cr valence of +3 an energy splitting of 4.1 eV has been reported which coincides with the splitting found for other Cr(III) compounds. Larger splitting values of 5.2 eV has been reported for Cr$^{+2}$ compounds [28] while lower values of 3.5 eV has been found for Cr$^{+4}$ compounds [25]. Fig. 5 shows the Cr 3s XPS spectra obtained in the present work in which the splitting is clearly resolved. The spectra have been aligned to the 3s main peak in order to clearly identify differences in the energy splitting. Slightly different energy splitting is obtained for each sample indicating the presence of faint differences in the Cr oxidation state. An energy splitting of 4.07(4) eV corresponding to a Cr$^{+3}$ valence is obtained for the sample grown on SrTiO$_3$ indicating the presence of stoichiometric Cr$_2$O$_3$ phase. In contrast, larger energy splitting of 4.35(4) eV is obtained for the sample grown on α-Al$_2$O$_3$ corresponding to a lower Cr oxidation state of +2.75. Hence, the formation of 8% oxygen vacancies occurs in the chromium oxide lattice (Cr$_2$O$_{3.9}$ with δ = 0.25) in order to release the strain induced by the epitaxial coincidence growth. An increase of the out-of-plane lattice parameter is then expected in agreement with the results obtained by XRD. From the XPS Cr 3s spectra it can be also seen that the energy width of the satellite peak (higher binding energy) for the layer grown on α-Al$_2$O$_3$ is larger than expected. A value of 2.7 eV is obtained while similar values (2.2 eV at FWHM) for the main and satellite peak should happen [27,28], as is the case of the layer grown on SrTiO$_3$. The broadening of the satellite peak for the layer grown on α-Al$_2$O$_3$ is indicative of the presence of extra interactions with the oxygen ligands that creates extra final states and hence extra satellite structure [29], probably linked to the presence of punctual defects in the form of oxygen vacancies. The experimental integrated intensity of the satellite peak is however very similar for both systems giving rise to nearly equal ratio of intensity of the multiplet peaks for each system. In a simple scenario the intensity ratio of the Cr 3s peaks is dependent on the spin multiplicities [30]. In the case of the Cr$_2$O$_3$ due to the 3d$^3$ high spin configuration of the Cr$^{+3}$ ion with S$_{3d} = 3/2$ the intensity ratio is then given by I (3d ↑↑↑ 3s ↑):I (3d ↑↑↑ 3s ↓) = S$_{3d} + 1$:S$_{3d} = 5$:3, while for the Cr$^{+2}$ ion the intensity ratio is given by 3:2. In the case of a Cr$^{+2.75}$ the ratio is then of 5:3.08 in accordance with the experimental behavior obtained from the measurements.

Fig. 6a shows the measured magnetic response of the studied samples. Both samples show single phase hysteresis loops with very similar coercive field. 60 Oe when deposited on α-Al$_2$O$_3$, and 90 Oe when deposited on SrTiO$_3$ (Fig. 6b and inset). Nevertheless, in the case of the layer grown on SrTiO$_3$ the measured remanence is the double than in the case of the layer deposited on sapphire, maybe due to the energy lost at expenses of rotating domains. These results are consistent with the observed domain size in every sample (140 nm and 8 nm for layers.
grown on $\alpha$-Al$_2$O$_3$ and SrTiO$_3$, respectively). The ferromagnetic response can be attributed to the strain accumulated because of the epitaxial growth, as previously reported [3,4]. In the case of the layer grown on SrTiO$_3$, even if a non-coincidence growth occurs, a remaining strain of $-1.6\%$ has been experimentally observed inducing the ferromagnetic behavior.

4. Conclusions

The successful epitaxial growth of single phase and single oriented Cr$_2$O$_3$ thin films on SrTiO$_3$ (111) has been achieved for the first time. We demonstrate that the use of SrTiO$_3$ (111) substrate is favourable for the growth of high quality Cr$_2$O$_3$ epitaxial thin films. Low surface roughness and absence of oxygen vacancies are found for the layer grown on SrTiO$_3$ while a moderately rough surface coupled to the presence of oxygen defects is found for the layer grown on $\alpha$-Al$_2$O$_3$ (0001). However larger crystallographic domain sizes of 140 nm resulted from the coincidence growth on the $\alpha$-Al$_2$O$_3$ (0001) substrate compared to the moderate values of 8 nm obtained for the layer grown in a non-coincidence way on SrTiO$_3$ (111). Nevertheless the domain sizes obtained for both systems are compatible with nowadays technological requirements. Soft ferromagnetic response has been obtained in both epitaxial layers with very similar coercive field being slightly higher for the layer grown on SrTiO$_3$. Ferromagnetic epitaxial Cr$_2$O$_3$ grown on oxide substrates becomes a potential candidate for the development of complex magnetic based devices.

Authorship contributions

Category 1 - Conception and design of study: María Vila, Juan Rubio – Zuazo, Germán Rafael Castro. Acquisition of data: María Vila, Juan Rubio – Zuazo, Irene Lucas, César Magén, Alicia Prados, Eduardo Salas-Colera, Icíar Arnay and Germán Rafael Castro. Analysis and/or interpretation of data: María Vila, Juan Rubio – Zuazo, Irene Lucas, César Magén, Alicia Prados, Eduardo Salas-Colera, Icíar Arnay and Germán Rafael Castro.
Fig. 3. (a) (H vs L) reciprocal space map at K = 0 for Cr₂O₃ thin film (marked with a red dashed line) grown on STO (1 1 1) (yellow dashed line). Different in-plane values are obtained for Cr₂O₃ and SrTiO₃ revealing an epitaxial non-coincidence growth. (b) CTR and (c) ROD for the layer grown on SrTiO₃. Flat surface and interface are inferred from the surface signal present between the layers Bragg peaks; (d) (H = K vs L) reciprocal space map for Cr₂O₃ thin film grown on α-Al₂O₃. Identical in-plane values are obtained for Cr₂O₃ and α-Al₂O₃ revealing an epitaxial coincidence growth; (e) CTR for the layer grown on α-Al₂O₃. The absence of surface signal reveals the presence of rough surface and interface; Layer and substrate lattice diagrams in real space showing the in-plane coupling for Cr₂O₃ layers grown on (f) SrTiO₃ and (g) α-Al₂O₃.
Fig. 4. HAADF-STEM images of the Cr$_2$O$_3$ films grown on (a) α-Al$_2$O$_3$ (0001) and (b) SrTiO$_3$ (111). The epitaxy relations between the films and their respective films are indicated.

Fig. 5. XPS measurements on the Cr 3s core level. A larger energy splitting is obtained for the layer grown on α-Al$_2$O$_3$ (blue curve) revealing a reduction of the Cr oxidation state as compared to the layer grown on SrTiO$_3$ (red curve). Both spectra have been aligned on the main 3s peak in order to clearly show the difference in energy splitting.

Fig. 6. Comparison of normalized magnetization hysteresis loops of Cr$_2$O$_3$ thin films measured at 300 K on α-Al$_2$O$_3$ and SrTiO$_3$. (a) Complete hysteresis loops up to 50 kOe showing the correct magnetic saturation of the samples (b) Zoom of the hysteresis loops to better compare remanence and coercive fields in every sample.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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