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Epitaxial growth of γ -CoV₂O₆ thin films: Structure, morphology, and magnetic properties

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We report on the epitaxial growth of 100 nm thick triclinic γ -CoV₂O₆ thin films deposited by pulsed laser deposition on TiO₂(100) substrate. The layers were grown in narrow experimental conditions, at 600 °C and 0.1 millibar oxygen pressure. X-ray diffraction and transmission electron microscopy evidenced the presence of two variants and the following epitaxial relation between the layers and the substrate: $[001]\text{TiO}_2(100) \parallel [0\pm10]\gamma\text{-CoV}_2\text{O}_6(100)$. Besides the magnetization steps expected in γ -CoV₂O₆, low temperature magnetic measurements performed along different crystalline axes show the existence of a strong anisotropy compatible with that expected from a one dimensional system, with the easy magnetization axis lying along the *b* direction (i.e., the Co chains). © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4808205>]

Low-dimensional compounds are of increasing interest because of their peculiar magnetic properties such as the field-induced magnetic plateaus or the strong anisotropy.^{1–6} CoV₂O₆ is one of the most interesting oxides presenting such features. It exists in two allotropic phases generally called α and γ -CoV₂O₆. Both are composed of edge sharing CoO₆ octahedra forming one dimensional chains. These chains form magnetic planes separated by V oxide non-magnetic planes. The monoclinic α -CoV₂O₆ was intensively investigated in the last few years especially for its well defined field induced plateaus^{7,8} and a lot of efforts were recently carried out in order to solve the magnetic structure in the ground and field induced states^{9–11} and understand the magnetic interactions leading to the magnetization plateaus.^{12–14} The ground state is characterized by an antiferromagnetic (AF) interaction between the Co atoms of different chains while the interaction inside the chains is ferromagnetic.

The triclinic γ -CoV₂O₆ seems to show the same kind of magnetic behavior with magnetic plateaus at 1/3 of the saturation magnetization.¹⁵ Its magnetic structure was also investigated by neutrons powder diffraction by Kimber *et al.*¹⁶ who showed the existence of a $k = (1/2, 0, 0)$ propagation vector. However, some magnetic peaks could not be indexed, which was attributed to the existence of a long-wavelength modulation of the magnetic structure. Nevertheless, the crystalline structure has been correctly described and agreed well with the early work of Müller-Buschbaum and Kobel.¹⁷ In this triclinic phase (Fig. 1), the Co chains composed by edge sharing CoO₆ octahedra are aligned along the *b* direction. The *bc* magnetic planes are separated by non-magnetic planes constituted of VO₄ tetrahedra and VO₆ octahedra. The space group is P-1 and the bulk cell parameters are $a = 7.164 \text{ \AA}$, $b = 8.872 \text{ \AA}$, $c = 4.806 \text{ \AA}$, $\alpha = 90.29^\circ$, $\beta = 93.66^\circ$, and $\gamma = 102.05^\circ$.¹⁷

It is important to note that although γ -CoV₂O₆ single crystals could be obtained,¹⁷ there are no reports on the magnetic anisotropy (while such study exists nevertheless for the α phase⁷). Moreover, while there are many reports on the thin

film growth of other low dimensional magnetic oxides,^{18,19} there are no reports on the thin film growth of CoV₂O₆ (neither α nor γ phases). This is probably due to its particular crystalline structure, the difficulty to find an appropriate substrate, the possibility to exhibit different allotropic phases, and the rather low decomposition temperature ($\sim 750^\circ\text{C}$).

In this context, the aim of our work is to show that epitaxial γ -CoV₂O₆ thin films can be obtained and that a strong magnetic anisotropy is present in this material. Contrary to the α phase where the easy magnetization axis is perpendicular to the Co chains,^{7,9} this axis lies along the chain direction in γ -CoV₂O₆.

γ -CoV₂O₆ thin films were deposited by pulsed laser deposition using a KrF excimer laser from a sintered target. The target (polycrystalline γ -CoV₂O₆) was prepared by solid state chemistry as described in Ref. 15. We remind here that the target powder was obtained from a V₂O₅ + CoC₂O₄ mixture, ground, and heated successively several times at 640 °C. The powder was then pressed into target form under 100 bars and heated for one week at 640 °C. The layers were deposited at 600 °C under 0.1 millibar of pure O₂ atmosphere on TiO₂(100) substrates. The laser frequency and energy density were kept at 10 Hz and 1.5 J/cm², respectively. All layers are about 100 nm thick. The choice of the TiO₂(100) substrate was motivated by the small lattice mismatch (0.15% and 4.5%) with respect to the *b* and *c* lattice parameters of the γ -CoV₂O₆ phase.

The crystalline structure of the films was investigated by X-ray diffraction using a Rigaku Smartlab (9 kW) diffractometer equipped with a Cu $k\alpha_1$ source ($\lambda = 1.54056 \text{ \AA}$) and a Ge(220) 2-bounce front monochromator. Further details were obtained by transmission electronic microscopy (TEM) using a JEOL 2100 F microscope Cs corrected at the probe level, with a point to point resolution of 2.2 Å. The composition of the layers was checked using an energy dispersive X-ray spectroscopy (EDS) analyzer coupled to the TEM microscope and showed for all samples a ratio V/Co = 2. The surface morphology was checked by atomic force microscopy (AFM) using a Nanoscope Dimension 3100

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FIG. 1. Crystalline structure of γ -CoV₂O₆. In violet, orange, and yellow are represented the CoO₆ octahedra, the VO₆ octahedra, and the VO₄ tetrahedra, respectively.

instrument and scanning electron microscopy (SEM) using a JEOL JSM-6700F microscope. The magnetic measurements were carried out on a Quantum Design SQUID-VSM magnetometer down to 1.8 K and maximum applied field of 7 T. The magnetization curves were recorded parallel to the sample surface along the [010] and [001]TiO₂ directions (i.e., c and b directions of γ -CoV₂O₆, respectively). Magnetization measurements performed with the applied field perpendicular to the substrate were unsuccessful because of the very weak magnetic signal originating from the low thickness and strong anisotropy.

The X-ray diffraction pattern recorded in symmetric $\theta - 2\theta$ mode of a γ -CoV₂O₆ film (Fig. 2) shows only the $h00$ peaks of TiO₂ and γ -CoV₂O₆. This result indicates that the bc plane, and, therefore, the Co chains of γ -CoV₂O₆ are parallel to the sample surface. The absence of other orientations along with the small width of the peaks suggest that γ -CoV₂O₆ is epitaxially grown on the TiO₂(100) substrate. In order to check if the film is indeed epitaxially grown on the substrate or if it is just textured, ϕ scans were carried out.²⁰ For γ -CoV₂O₆ and TiO₂, the $\{2,0,-1\}$ and $\{3,1,0\}$ plane families were analyzed, respectively. If we keep in mind that the TiO₂ space group is P42/mnm (i.e., rectangular lattice in the (100) plane which is parallel to the sample surface), two reflections separated by 180° corresponding to TiO₂(310) and (3-10) are expected. This is indeed what is observed in Fig. 3. As for γ -CoV₂O₆, due to its P-1 space group, only one peak should be observed upon a complete rotation of the

FIG. 2. X-ray diffraction pattern recorded in $\theta - 2\theta$ mode on a γ -CoV₂O₆ film.

FIG. 3. ϕ scans of the γ -CoV₂O₆ $\{2,0,-1\}$ and TiO₂ $\{3,1,0\}$ planes showing 180° periodicities for the multivariant γ -CoV₂O₆ and monovariant TiO₂, respectively.

samples around the axis normal to the sample surface. However, in our case, two reflections are observed suggesting the presence of two variants (see Fig. 3). This observation was confirmed by analyzing additional out-of-plane peaks of TiO₂ and γ -CoV₂O₆ (not shown here). According to the $\theta - 2\theta$ and ϕ scans, the b and c directions in γ -CoV₂O₆ are parallel to the c and b directions in TiO₂, respectively. The layer is, therefore, epitaxially grown on the substrate according to the relation $[001]\text{TiO}_2(100) \parallel [0\pm10]\gamma\text{-CoV}_2\text{O}_6(100)$. This is compatible with the similar parameters of the substrate ($3 \times c = 3 \times 2.953 \text{ \AA}$) and the layer ($b = 8.872 \text{ \AA}$) giving a lattice mismatch of 0.15%.

In order to have precise values of the lattice parameters, six interplanar distances of independent X-ray out-of-plane reflections were measured. We solved a six equation system of the type $d_{hkl} = f(a, b, c, \alpha, \beta, \gamma, h, k, l)$, where f is the function relating the interplanar distance, the associate hkl indices, and the cell parameters.²¹ For given hkl indices, the cell parameters were estimated at $a = 7.17 \text{ \AA}$, $b = 8.84 \text{ \AA}$, $c = 4.81 \text{ \AA}$, $\alpha = 90.3^\circ$, $\beta = 93.7^\circ$, and $\gamma = 101.7^\circ$, in good agreement with the values reported in the bulk.¹⁷

Further details on the crystalline structure were observed by TEM. Fig. 4 shows a low magnification cross section

FIG. 4. Cross section bright field TEM image of a 100 nm thick γ -CoV₂O₆ film: low magnification (main image) and high resolution (inset). The high resolution image was recorded along the $[001]\text{TiO}_2$ azimuth.

image of a 100 nm thick γ -CoV₂O₆ film. This image shows that the layers are continuous, homogeneous, with a limited roughness. A closer look allows visualizing the atomic planes inside the layer. When observed along the b direction, the (100) and (001) planes are well visible, in agreement with the very good crystalline quality shown by the XRD measurements.

The selected area electron diffraction (SAED) recorded on the cross section along the γ -CoV₂O₆ b and c directions are shown in Figs. 5(a) and 5(b). The pattern shows intense spots corresponding to the TiO₂ substrate and less intense spots corresponding to γ -CoV₂O₆. The two variants of CoV₂O₆ are clearly observed in Fig. 5(b). The epitaxial relation can be easily evidenced from Fig. 5(a), in agreement with that deduced from the XRD data.

Atomic force microscopy and scanning electron microscopy (not shown here) indicated that the film surface is flat, homogeneous, with a roughness of about 2.2 nm rms. It is important to note that the structural and morphological

FIG. 5. Selected area electron diffraction patterns of γ -CoV₂O₆ recorded along the γ -CoV₂O₆ b (a) and c (b) azimuths. The TiO₂ pattern is indexed in white. The two variants of γ -CoV₂O₆ are indexed in yellow and blue. The unit cell in the reciprocal space is also represented for each variant.

quality of these layers are strongly dependent on the deposition conditions. Thus, if the deposition temperature is raised to 680 °C or above, the layer decomposes, spurious phases are observed, and no continuous layers are observed anymore. On the other hand, if the deposition temperature is too low (below about 500 °C), a poorly crystallized (even amorphous at 200 °C) film is obtained. These films can be further crystallized by annealing at 600 °C and the expected (h 00) orientation is obtained. Note also that by using an α -CoV₂O₆ target, a γ -CoV₂O₆ film is obtained, although the deposition temperature is below the transition temperature between the α and γ phases (about 680 °C) and although the transition from the α to γ phase is carried out very slowly for the bulk material. This underlines the importance of the substrate nature on the stability of the γ phase of the film. Indeed, for other complex oxides, it was already shown that strains from the substrate can lead to different phases with respect to the one of the target.^{22,23}

Magnetic measurements recorded at 1.8 K show that along b axis the magnetization behavior is similar to that observed in oriented powder samples.¹⁵ A small magnetization pseudo plateau is observed around 0.4–0.5 T applied field (Fig. 6). The magnetization corresponding to this plateau is about 1/3 of the magnetization at 0.7 T. Over 0.7 T, the magnetization continues to increase slowly towards the value of $3 \mu_B/\text{Co}^{2+}$ ion observed in polycrystalline samples.¹⁵ This continuous magnetization increase can be also due to a possible misalignment of the b axis of our sample with the field direction during its mounting in the SQUID setup or to the existence of structural defects. The variations of the magnetization at 0.1 T with temperature recorded after a zero field cooling (ZFC) and field cooling (FC) procedure (H parallel to the b direction) are shown in the inset of Fig. 6. As observed, the two curves are superimposed and show a maximum at 7 K. This behavior indicates the presence of antiferromagnetic interactions characterized by a Néel temperature T_N of 7 K. This is in agreement with the magnetization curves recorded between 1.8 and 9 K (see supplementary material²⁴), which show a progressive disappearance of the magnetization plateau. Since the α angle of the γ -CoV₂O₆ lattice is close to 90° and since the bc plane is parallel to the substrate (see XRD

FIG. 6. Magnetization curve at 1.8 K of γ -CoV₂O₆ recorded along the b (black) and c (blue) directions. The inset shows the field cooling and zero field cooling variation of the magnetization with temperature under 0.1 T constant magnetic field.

and TEM data), the magnetic properties along the c direction can be easily measured by rotating the sample by 90° on the SQUID probe. This provides information on the magnetic anisotropy, which is expected to be large in such one-dimensional compounds. The magnetization curve measured along the c direction of γ -CoV₂O₆ shows a very weak signal slowly increasing with the magnetic field. At 3 T, this signal is four times weaker along the c direction than along b , confirming, therefore, the strong magnetic anisotropy. The slow increase of the magnetization showing no magnetization steps is related to the antiferromagnetic coupled moments which rotate slowly towards the field direction. The same conclusion can be also drawn from the ZFC/FC measurements. Although the curves are again superimposed with a maximum at 7 K, the magnetic signal is much smaller along with the peak characterizing the AF order. It is interesting to point out that contrary to the monoclinic α -CoV₂O₆ in which the easy magnetization axis and the magnetic moments lie perpendicular to the Co chains,⁹ in the γ phase the easy axis lies along the chain axis. Such behavior was also reported for other one dimensional structures as the ones of Ca₃Co₂O₆.²⁵ Along the a direction, the magnetic measurements could not be performed. This is first due to the β and γ angles very different from 90° and, second, due to the existence of two variants, i.e., of two different a axes. Nevertheless, when the field is applied perpendicular to the sample surface, the magnetization curve (not reported here) shows a variation typical for a hard magnetization axis (such as the c axis).

In conclusion, we have obtained epitaxial layers of γ -CoV₂O₆ on TiO₂(100) substrates. The layers are constituted of two crystalline variants which have in common the bc plane. The b and c axes of γ -CoV₂O₆ are parallel to the c and b axes of the TiO₂ substrate, respectively. The magnetic measurements have shown that the easy magnetization axis lies in the film plane along its b axis (i.e., the chain direction). The magnetic measurements along the c axis allowed to evidence the existence of a large anisotropy in γ -CoV₂O₆, compatible to the one expected from one dimensional systems. Finally, the possibility to obtain thin films of γ -CoV₂O₆ allows the investigation of spin dependent transport properties in this material and their correlation to *ab initio* calculations.

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