Tuning the Co/Sr stoichiometry of SrCoO$_{2.5}$ thin films by RHEED assisted MBE growth

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Abstract
Strontium cobaltite (SrCoO$_{2.5+\delta}$, SCO) is a fascinating material because of its topotactic structural phase transition caused by a change in oxygen stoichiometry. In the brownmillerite phase (δ = 0) it is an insulating antiferromagnet whereas in the perovskite phase (δ = 0.5) it is a conducting ferromagnet. In contrast, the impact of the varying Co/Sr stoichiometry on the structure has not yet been studied in SCO thin films. Using molecular beam epitaxy we have fabricated SCO thin films of varying Co/Sr stoichiometry. Films with Co excess exhibit a brownmillerite crystal structure with CoO precipitates within the thin film and on the surface. Co deficient films are amorphous. Only for 1:1 stoichiometry a pure brownmillerite structure is present. We find a clear dependence of the Reflection High Energy Electron Diffraction (RHEED) pattern of these thin films on the stoichiometry. Interestingly, RHEED is very sensitive to a Co excess of less than 12% while x-ray diffraction fails to reveal that difference. Hence, using RHEED, the stoichiometry of SCO can be evaluated and tuned in-situ to a high degree of precision, which allows for a quick adjustment of the growth parameters during a sample series.

1. Introduction
In the last years, strontium cobaltite (SrCoO$_{2.5+\delta}$, SCO) has been studied intensely because its crystal structure exhibits a topotactic phase transformation between two distinct phases. The brownmillerite SrCoO$_{2.5}$ is an antiferromagnetic insulator while the perovskite SrCoO$_{3}$ is a ferromagnetic metal. As a consequence, many studies focus on the oxygen stoichiometry [1, 2] and the manipulation of the topotactic phase transformation by strain [3–5]. SCO is also investigated as a cathode material in solid oxide fuel cells working at reduced temperature [6–8].

Typically, SrCoO$_{2.5+\delta}$ is grown by pulsed laser deposition (PLD) [4, 6, 9]. Inside a vacuum chamber, a high intensity pulsed laser beam is utilized to ablate the target material which results in a plasma plume. After expansion towards a substrate the material finally condenses. Generally, it is assumed that above a certain laser fluence threshold the target stoichiometry is congruently transferred to the film. However, the film stoichiometry depends on various factors like the appropriate gas pressure [10] or the atomic mass of the ejected...
species [11, 12]. For SrTiO$_3$(STO) the stoichiometry results from an intricate interplay of preferential scattering of the light plume element Ti during the propagation towards the substrate and incongruent ablation of STO [13]. For SCO the mass ratio (Co/Sr) is slightly higher than for Ti/Sr in STO. However, one can expect that the mentioned effects will not be negligible for stoichiometric growth of SCO. Until now, however, a study of the stoichiometry in SCO thin films is missing.

Molecular beam epitaxy (MBE) facilitates the control of film stoichiometry by varying the individual deposition rates of the constituents. In co-deposition mode, all elements are deposited simultaneously, while for sequential deposition, the shutters of the constituents are opened alternately [14, 15]. In the latter case Reflection High Energy Electron Diffraction (RHEED) intensity oscillations enable precise stoichiometric growth of e.g. STO [16].

The RHEED pattern itself represents the surface structure and morphology of the thin film sample [17]. The variation of the stoichiometry often relates to a change of the surface structure and therefore opens the opportunity to use the observed change for stoichiometric tuning [18, 19].

Here, we show a correlation of the RHEED pattern of SrCoO$_2$ with Ti during the propagation towards the substrate and incongruent ablation of STO and missing. Only for 1:1 stoichiometry perfect crystallinity is observed. For x-ray diffraction an Oxford plasma source in high brightness mode at 300 W and oxygen flow of 0.12 cm$^3$ min$^{-1}$ was observed during and after growth. The SCO growth rate was cross checked with x-ray reflectivity (XRR) measurements a Bruker D8 Discover diffractometer with a Cu K$_\alpha$ source ($\lambda = 1.5406$ Å) was utilized on samples representative of ideal stoichiometry, Co excess and Co deficiency, respectively. Transmission Electron Microscopy (TEM) in scanning mode was performed with a FEI Tecnai G2 F20 [23], operated at 200 keV, to investigate the crystallinity in depth profile and in combination with Energy-Dispersive x-ray spectroscopy (EDX) to study the composition.

2. Experimental

A set of about 50 SrCoO$_{2.5\pm0.5}$ thin films with varying Co/Sr ratio were grown on 10 mm × 10 mm × 0.5 mm SrTiO$_3$(001) single crystal substrates (CrysTec GmbH) utilizing a DCA M600 molecular beam epitaxy (MBE) system with base pressure of 10$^{-10}$ mbar. For surface cleaning, the substrates were annealed at 1000 °C for 2 hours in ultra high vacuum (UHV). Consequently, Auger electron spectroscopy revealed neither carbon nor other contaminants. Co and Sr were co-deposited from effusion cells. Atomic oxygen was provided with an Oxford plasma source in high brightness mode at 300 W and oxygen flow of 0.12 cm$^2$ min$^{-1}$, which leads to a pressure of 1.6 · 10$^{-3}$ mbar. The deposition rates were monitored before growth by a quartz crystal microbalance (QCM). After thin film deposition, the samples were cooled down with 50 °C min$^{-1}$ at the same oxygen pressure. Reflection high energy electron diffraction (RHEED) was observed in-situ during and after growth. The SCO growth rate was cross checked with x-ray reflectometry (XRR) and is typically 3 Å min$^{-1}$.

Only few reports on MBE grown SCO exist. While for pulsed laser deposition (PLD) a typical growth temperature of 750 °C was used [4, 6, 9], best MBE growth was found at 600°C which is in agreement with Andersen et al [21]. In addition, for bulk systems it is known that SrCoO$_3$ decomposes into the hexagonal Sr$_2$Co$_3$O$_6$ phase at ≈650 °C [22]. MBE growth of SCO growth at 750 °C resulted in high surface roughness rms (root mean square) of about 30 Å with porous structure, independent of the Co/Sr stoichiometry.

To analyse the stoichiometry, Rutherford backscattering spectrometry (RBS) was performed at He-ion energy of 1.4 MeV. For x-ray diffraction (XRD) and reflectivity (XRR) measurements a Bruker D8 Discover diffractometer with a Cu K$_\alpha$ source ($\lambda = 1.5406$ Å) was utilized on samples representative of ideal stoichiometry, Co excess and Co deficiency, respectively. Transmission Electron Microscopy (TEM) in scanning mode was performed with a FEI Tecnai G2 F20 [23], operated at 200 keV, to investigate the crystallinity in depth profile and in combination with Energy-Dispersive x-ray spectroscopy (EDX) to study the composition.
3. Results and discussion

3.1. Variation of the Co/Sr stoichiometry
Various SrCoO$_{2.5+x}$ films were studied covering Co excess (Co/Sr > 1), Co deficiency (Co/Sr < 1) and 1:1 stoichiometry. The stoichiometries are given based on RBS measurements (figure 1) which were fit with the program RUMP [24]. The error of the Co/Sr stoichiometry given by RBS is estimated to be about 10% because of the overlapping Sr signal in both film and substrate. Using e.g. MgO as a substrate would reduce the error due to the separated film and substrate signal because of the light mass of Mg, however MgO was not used due to the large lattice mismatch to SCO. Investigation of simultaneously fabricated SCO films on STO and MgO reveals a disparity of only about 4.5%, so the error for the stoichiometry on STO is likely overestimated (see Supplementary available online at stacks.iop.org/MRX/7/116404/mmedia).

The crystalline structure of the STO substrate and the SCO films were analyzed by in-situ RHEED (see figure 2). The STO substrate is characterized by sharp Bragg reflexes, Laue rings, and Kikuchi lines, which confirm excellent crystallinity and low surface roughness (figure 2(a)). For stoichiometric samples, well defined Bragg spots and a Laue ring are visible, as well as faint indications of Kikuchi lines (figure 2(b)). The intensity of the specular spot shows oscillations during growth which is characteristic of layer-by-layer growth (figure 2(c)).

For large Co excess of 30%, two additional sets of spots emerge in the diffraction pattern. The small and sharp speckles indicate a 3d structure with good crystallinity (figure 2(c): A and in figure 6(a)) while the big, broad spots correspond to small crystalline islands (figure 2(c): B). In contrast, for Co deficiency, here 10% (figure 2(d)), the RHEED pattern reveals only very faint Bragg spots and a washy Laue ring, indicating diminishing crystallinity.

X-ray diffraction was performed to study the crystalline structure and the thickness of the crystalline volume of the SCO thin films from Laue oscillations (see figure 3). The stoichiometric sample reveals only peaks of the brownmillerite phase in c-axis orientation and is single phase, figure 3(b). Assuming a constant unit cell volume equal to the bulk value, the calculated in-plane lattice constant of the film matches the substrate, indicating epitaxial growth. The thickness of the crystalline layer is 25.4 ± 0.3 nm, which is slightly lower than the total film thickness of 28.2 ± 0.3 nm as determined by XRR from Kiessig fringes. From the position of the XRD peaks we see no indication of oxygen vacancies. This is not surprising, since, provided sufficient oxygen partial pressure during growth, SrCoO$_{2.5+x}$ naturally tends to form in the brownmillerite structure grown here, as the Co$^{3+}$ state is the most stable. For high Co excess of 57% the brownmillerite structure peaks remain visible, figure 3(a). A change in peak position towards lower angles indicates an in-plane compressive strain of 0.4%. Additionally, CoO peaks exist in the diffraction pattern. Hence, we may conclude that the surplus Co is precipitated into CoO crystallites. For bulk stoichiometric SrCoO$_{3-x}$, it is known to segregate easily into crystalline Sr$_6$Co$_5$O$_{15}$ and Co$_3$O$_4$ [25]. We take this observation as a strong indication that for Co excess, CoO$_x$ is easily formed. The thickness of the crystalline layer is 31.2 ± 1.6 nm compared to 39.1 ± 0.6 nm film thickness.
In contrast, the Co deficient SCO film of 17% less Co does not reveal any crystalline structure at all, figure 3(c). Throughout the growth study, we have observed only SrCoO$_2.5$ and CoO peaks, no other crystalline phases. In the sample series we grew, we have never found a sample with bad RHEED pattern but good crystallinity in XRD, or vice versa. The methods are consistent. Further x-ray techniques, such as reciprocal space mapping and rocking curve analysis could provide further insight into the collapse of the brownmillerite structure for Co deficiency. But since the aim of this publication is to provide a method to assess the stoichiometry and crystallinity in-situ and fast, further time consuming x-ray characterisation is cumbersome and not in the focus of this publication.

In order to gain information about the surface topography, atomic force microscopy was performed. Figure 4 shows the topography of the samples in figure 2. The topography of the prepared SrTiO$_3$(001) substrate is given in figure 4(a) and reveals a terrace structure with step width of about 0.4 μm and 0.4 nm height, corresponding to the height of one unit cell of STO. The rms roughness is 0.4 nm. The stoichiometric sample exhibits terraces with a length of about 0.2 μm, height of 0.9 nm, which is close to half of a unit cell of SCO, and a rms roughness of 0.45 nm, figure 4(b). The topography is similar to PLD grown SrCoO$_3$−γ thin films reported by Hu et al [26].

Increasing the Co excess destroys the terrace structure, figure 4(c). Instead, a combined layer and island growth is visible, with additional small horizontal and vertical structures of an average length of 50 nm, and diagonal structures of an average length of 163 nm and width of 60 nm. These 3d structures cover about 15% of the surface area. Evidently, the diagonal structures in the AFM image are related to the emergence of the small speckles in the RHEED image (figure 2(c): A) while the small horizontal structures detected by AFM correlate to the broad spots in RHEED. As the films are much less uniform, the rms roughness is increased to 1.4 nm. Neglecting these additional structures, the rms roughness of the underlying film is 0.8 nm which is still higher than for the stoichiometric sample. We may conclude that these diagonal structures in the AFM topograph are CoO islands, which is confirmed later in the manuscript by TEM-EDX measurements. Conversely, for SCO thin films with Co deficit neither terraces nor layered island structures are observed, figure 4(d). The surface is diffuse, with canyon structures of 2–6 nm height, as well as 15 nm high particles.

For a comprehensive picture of the island structures detected by RHEED and AFM, a SCO thin film with about 15% Co excess was studied by TEM and EDX. Figure 5 shows a cross-sectional lamella of the SCO film in the STO[110] direction (this is the diagonal direction in the AFM images). A tungsten cap layer was deposited before cutting the lamella. The lamella was taken from an area that exhibited a large number of the diagonal structures observed in AFM and was identified by EDX as CoO (figure S3 in supplementary). Growth of CoO

Figure 2. RHEED patterns of the SrTiO$_3$(001) substrate (a) and SrCoO$_2.5$ thin films grown on SrTiO$_3$(001) with Co/Sr ratio of (b) Co/Sr = 1.00 representative of ideal stoichiometry, (c) Co/Sr = 1.30 representative of Co excess, and (d) Co/Sr = 0.9 representative of Co deficiency, at 15 keV and with ⟨110⟩ azimuth. The structures marked in (c) correspond to different surface precipitate structures. The contrast of this image has been adjusted to make the structures clearer. (e) shows the RHEED oscillations of the specular beam for the stoichiometric SCO film, indicating layer-by-layer growth.
precipitates is observed on the substrate as well as within the film. The TEM images further confirm an epitaxial film on the substrate, with a mismatch of the in-plane lattice constants of only 0.1%. The c-axis is out-of-plane, as previously measured by XRD. It is possible that the film is not fully single crystalline, as the position of the atoms in the layer is less clearly defined than in the substrate. This could be due to the slightly different in-plane lattice constants for SCO leading to a non-uniform in-plane orientation of the SCO layer. Please note that the SCO film is very sensitive to electron irradiation. After only a few minutes of exposure to 200 keV electrons, the

![Figure 3. XRD 2θ patterns of SrCoO2.5 films grown on SrTiO3 (001) for various stoichiometries; (a) Co/Sr = 1.57 representative of Co excess, (b) Co/Sr = 1.00 representative of ideal stoichiometry, and (c) Co/Sr = 0.83 representative of Co deficiency. The inset in (b) shows the XRR measurement and fit. The peak marked with * in (c) is due to a monochromator issue and not related to the sample. (d) shows a broader range of (b), to show that only BM-SrCoO and STO peaks are present.](image-url)
film exhibits large amorphous regions within the crystalline matrix. The breakdown of the crystallinity seems to start from the surface and propagates downwards to the substrate.

3.2. Fine tuning of the Co/Sr stoichiometry

Previously, we have observed that on approaching the 1:1 stoichiometry of Co and Sr from Co excess the CoO (002) peak of the thin film vanishes in the XRD pattern before the perfect stoichiometry is reached. Figure 6(c) gives a more detailed comparison of XRD patterns corresponding to 12% Co excess and perfect stoichiometry. For both stoichiometries no CoO peak is visible within the detection limit of the XRD instrument. In contrast, comparing the RHEED patterns of the perfect sample (figure 2(b)) to the ones with 12% Co excess (figure 6(a)) and 30% Co excess (figure 2(c)), there are clear differences: In the RHEED pattern of the sample with Co/Sr = 1.3 there are two types of reflexes present that don’t originate from the brownmillerite SrCoO$_{2.5}$ structure; small and sharp speckles, labelled ‘A’; and broad spots ‘B’. The latter already disappeared for Co/Sr = 1.12 (figure 6(a)). Hence we may conclude that the existence of the broad spots is correlated with large Co excess (Co/Sr $\geq$ 1.3). If these spots are missing and only the sharp, small speckles are present, the stoichiometry is closer to 1. But even for small Co excess, here Co/Sr = 1.12, the speckles are very clearly visible.

Only for the perfect stoichiometric samples the speckles are absent (figure 2(b)). Hence, the RHEED pattern is still correlated with the stoichiometry while XRD became insensitive.

Obviously, the speckles for the film with Co/Sr = 1.12 are related to the elongated CoO islands in the AFM topography and TEM images (figures 6(b) and 5(b)). On the other hand the RHEED pattern of the Co deficient film (figure 2(d)) exhibits worse crystallinity than for the other stoichiometries, which is also mirrored in the disappearance of the SCO film peaks in the XRD (figure 3(c)) and no observable island or terrace structures on the AFM image (figure 4(d)).

Analysing the evolution of the RHEED patterns with varying Co/Sr stoichiometry is the method of choice for quick and easy determination of Co excess or deficiency in the SCO film. Indeed, RHEED is extremely
sensitive to even small amounts of Co excess and, because it is an in-situ technique, it can be used during film growth for adjusting the growth parameters. This is especially helpful since one of the major advantages of MBE growth is the ability to adjust the stoichiometry at will and study the influence of stoichiometric variation on the properties of the film. It should be emphasized that utilizing only a small cutout of the RHEED screen as typically presented in other publications, e.g., [27], is not sufficient for the distinction of the stoichiometry in SCO.

4. Summary

In this publication strontium cobaltite (SrCoO$_{2.5+\delta}$, SCO) thin films were fabricated by molecular beam epitaxy (MBE) with different Co/Sr ratio and were studied in-situ by Reflection High Energy Electron Diffraction (RHEED).

RHEED analysis provides a simple and quick way to evaluate the stoichiometry and crystallinity of the SCO films in-situ, without the need for time consuming ex-situ methods. This allows for the quick adjustment of the growth conditions during a sample series. Obviously, RHEED is no replacement for bulk crystalline methods such as x-ray diffraction (XRD), but its advantage as a way of guiding the growth parameters towards stoichiometric samples already during or subsequent growth is invaluable.

The RHEED observations were supported by studying the crystallinity by XRD and Transmission Electron Microscopy (TEM) while the stoichiometry was identified after growth by Rutherford Backscattering Spectrometry (RBS). The surface quality was characterized by Atomic Force Microscopy (AFM).

Films with Co excess are characterized by a brownmillerite crystal structure with CoO precipitates within the thin film and on the surface. Co deficient films are amorphous. Only for 1:1 stoichiometry a pure brownmillerite structure is present. There is a clear dependence of the RHEED patterns of these thin films on the stoichiometry. By RHEED even less than 12% Co excess is detected while XRD does not reveal any difference to a stoichiometric thin film. Hence, during deposition of SCO the growth can be tuned with high precision by RHEED.

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