Epitaxial growth and magnetic properties of Sr$_2$CrReO$_6$ thin films

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The double perovskite Sr$_2$CrReO$_6$ is an interesting material for spintronics, showing ferrimagnetism up to 635 K with a predicted high spin polarization of $\approx$ 86%. We fabricated Sr$_2$CrReO$_6$ epitaxial films by pulsed laser deposition on (001)-oriented SrTiO$_3$ substrates. Phase-pure films with optimum crystallographic and magnetic properties were obtained by growing at a substrate temperature of 700°C in pure O$_2$ of 6.6 $\times$ 10$^{-4}$ mbar. The films are c-axis oriented, coherently strained, and show less than 20% anti-site defects. The magnetization curves reveal high saturation magnetization of 0.8 $\mu_B$ per formula unit and high coercivity of 1.1 T, as well as a strong magnetic anisotropy.

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INTRODUCTION

The ferrimagnetic double perovskites $A_2BB'O_6$, with $B$ a magnetic and $B'$ a non-magnetic transition metal ion [1 2 3], are attractive magnetic materials. Of particular interest is Sr$_2$CrReO$_6$ (SCRO) [4 5], as it exhibits a ferrimagnetic transition temperature of $T_C \approx 635$ K well above room temperature, in combination with a quasi half-metallic band structure according to theoretical calculations [6]. This high $T_C$ is strongly correlated to a large induced magnetic spin moment at the non-magnetic Re site [7 8]. $T_C$ can be further increased by electron doping, as demonstrated e.g. in Sr$_2$FeMoO$_6$, Sr$_2$CrWO$_6$, or Sr$_3$CrOsO$_6$ by 5d band filling [9 10 11]. The strong, long-range magnetic interaction is attributed to a kinetic energy driven exchange process, in which the hybridization between itinerant electrons on the $B'$ sites and the localized moments on the $B$ sites leads to an induced magnetic moment of the non-magnetic $B'$ ions [12 13]. Regarding device applications, the strong influence of the growth conditions on the structural, magnetic, and electronic properties of double perovskites is demanding. In particular, it became evident that a key parameter to understand the properties of double perovskites is the amount of anti-site defects ($B$ ions on $B'$ sites and vice versa). It was shown that the saturation magnetization $M_s$ decreases with increasing amount of anti-site defects [14]. Therefore, a thorough understanding of the growth process is a key prerequisite for obtaining thin films with optimum physical properties. While the growth of Sr$_2$FeMoO$_6$ and Sr$_2$CrWO$_6$ thin films has been investigated in detail [15 16 17 18], little is known about Sr$_2$CrReO$_6$ so far [5 19 20].

Here, we report on the epitaxial growth of c-axis oriented SCRO thin films on (001) SrTiO$_3$ (STO) substrates, and discuss the effects of growth temperature, growth atmosphere, and pressure on the film quality. We identify optimal growth parameters leading to SCRO films with excellent crystalline quality as well as magnetic properties comparable to bulk SCRO.

GROWTH AND CRYSTALLOGRAPHIC CHARACTERIZATION

We have used pulsed laser deposition (PLD) [21] to grow the SCRO films from a stoichiometric target, which was fabricated using an oxygen getter control technique to ensure stoichiometry [22]. To identify the optimal growth conditions, we have deposited films (i) in three different atmospheres: O$_2$, Ar, and a mixture of Ar/O$_2$ (99/1 by volume), (ii) at different pressures, and (iii) at different substrate temperatures 450°C $\leq T_S \leq 900$°C. The structural and magnetic properties of the SCRO thin films were analyzed using in-situ reflection high energy electron diffraction (RHEED), high resolution x-ray diffraction (HRXRD), SQUID magnetometry, and high resolution transmission electron microscopy (HRTEM). The film thickness was determined by x-ray reflectometry.

Comparing samples grown in O$_2$, Ar, and Ar/O$_2$, we find that high-quality, phase-pure SCRO films are obtained only in a growth atmosphere containing oxygen. In particular, the presence of oxygen during the growth seems to be essential to achieve Cr/Re sub-lattice ordering [23]. In the following, we therefore focus on films grown in pure O$_2$ atmosphere of $p_{O_2} = 6.6 \times 10^{-4}$ mbar. Higher pressure was found to lead to parasitic phases, lower pressure to a reduced saturation magnetization. Another important deposition parameter is the laser fluence $P_L$ on the target, determining the energy of the ablated particles. We found no significant change of the magnetic and crystalline quality upon varying $P_L$ from 1.0 to 2.5 J/cm$^2$. Moreover, the laser pulse repetition rate $f_L$ also had no noticeable effect on the anti-site disorder in our SCRO films, in contrast to what was
found for Sr$_2$FeMoO$_6$ films [24]. We therefore used a $P_l = 2.0 \text{J/cm}^2$ and $f_L = 2 \text{Hz}$ in all subsequent growth runs.

The influence of the substrate temperature $T_G$ on the structural and magnetic properties of SCRO thin films is summarized in Fig. 1. It is evident that the full width at half maximum (FWHM) of the rocking curve of the SCRO (004) reflection stays almost constant on a low value of about 0.05$^\circ$ for 550°C $\leq T_G \leq$ 750°C. Only at the lowest and highest $T_G$, the FWHM increases up to 0.08$^\circ$. This indicates that SCRO thin films can be grown with low mosaic spread in a large temperature window from 550°C to 750°C. We note that the mosaic spread of the SCRO thin films is close to that of the STO substrate (typically 0.01$^\circ$–0.02$^\circ$). In contrast, the saturation magnetization $M_S$ peaks around $T_G = 700^\circ$C. As a strong correlation between $M_S$ and the sub-lattice order is often observed in ferrimagnetic double perovskites [13], Fig. 1 suggests that SCRO films grown at $T_G \approx 700^\circ$C show a high degree of sub-lattice order and thus a small fraction of anti-site defects. That is, SCRO thin films with optimal structural and magnetic properties are obtained for $T_G = 700^\circ$C in a pure O$_2$ atmosphere of 6.6 x 10$^{-4}$ mbar.

Fig. 2 shows the structural properties achieved for epitaxial SCRO films which were deposited at the optimum growth parameters described above. The $\omega$-2$\theta$ scan reveals no crystalline parasitic phases. As shown in the inset, the observation of Laue oscillations provides evidence for a coherent film growth. Furthermore, the small FWHM of the rocking curve of the SCRO (002) reflection of only 0.05$^\circ$ demonstrates high crystalline quality with low mosaic spread. The Cr/Re sub-lattice order of our SCRO films can be inferred from the intensity of the superstructure (101) reflection shown in Fig. 2(c). This superstructure peak has finite intensity only for a finite amount of ordering on the Cr/Re sublattice. The amount of anti-site defects can be determined from the measured intensity ratio of the (101) and (404) reflections. Comparing the measured intensity to simulations, performed using the software package TOPAS from Bruker company, the amount of anti-site defects is estimated to less than 20%. More detailed information about the mosaicity and the strain state can be obtained from the reciprocal space maps around the (004) and (116) reflections shown in Figs. 2(d) and (e). Clearly no $q_l$-shift of the symmetric (004) and asymmetric (116) SCRO film reflections with respect to the corresponding STO substrate reflections is observed. This demonstrates pseudomorphic growth up to the maximum film thickness of 65 nm. The reciprocal space maps and the in-plane cube-on-cube growth derived from an in-plane $\phi$-scan (not shown) reveal a tetragonal symmetry of the SCRO thin films, with lattice parameters of $a_{\text{SCRO}} = \sqrt{2}a_{\text{STO}} = 5.523$Å and $c_{\text{SCRO}} = 7.90$Å. Comparing the measured in-plane lattice constant to the value $a_{\text{bulk}} = 5.5206$Å of bulk SCRO [2] shows that the tensile epitaxial coherency strain of the SCRO films grown on STO substrates is negligibly small and the films can be regarded as strain-free.

The quality of the interface between the STO substrate and the SCRO film was investigated by HRTEM. The bright-field HRTEM micrograph along the [110]-direction of the STO substrate shown in Fig. 3(a) demonstrates the
perfect epitaxial growth of SCRO on STO. Neither dislocations nor structural defects could be detected. To obtain information on the Cr/Re sub-lattice ordering, electron diffraction was performed, as shown in Fig. 3(b). After foil thickness determination from the intensity ratio \( I(020)/I(000) \), the anti-site defects of the Cr/Re sub-lattice can be estimated to be less than 17\%, e.g. from the intensity ratio \( I(011)/I(020) \). Note that the (011) peak is a superstructure peak with vanishing intensity for complete disorder on the Cr/Re sub-lattice. This provides additional evidence for a highly ordered Cr/Re sub-lattice in our SCRO films.

MAGNETIC PROPERTIES

We finally address the magnetic properties of the SCRO films. Fig. 4 exemplarily shows the \( M(H) \) curves of a 31 nm thick SCRO film recorded at 25 K. For the external magnetic field applied in-plane along [100], the measured saturation magnetization \( M_S = 0.8 \mu_B/\text{f.u.} \) is in good agreement with \( M_S = 0.89 \mu_B/\text{f.u.} \) of our polycrystalline target material and the literature values ranging between 0.8 and 0.9 \( \mu_B/\text{f.u.} \) at low temperature \cite{19}. Recent model calculations including spin-orbit coupling \cite{6} predicted \( M_S = 1.28 \mu_B/\text{f.u.} \) for perfect sub-lattice order. Assuming that \( M_S \) decreases about linearly with increasing sub-lattice disorder, the measured amount of anti-site defects of less than 20\% translates into an expected saturation magnetization larger than 0.77 \( \mu_B/\text{f.u.} \), again in good agreement with the measured value. The measured \( M(H) \) curves also reveal a very large coercive field \( \mu_0 H_c = 1.1 \text{T} \). This value again agrees well with literature data ranging from 1 to 1.5 T at 4.2 K \cite{4, 19}, demonstrating that the SCRO compound is a hard ferromagnet. However, in contrast to a previous study \cite{19} we observe a strong magnetic anisotropy in our SCRO films. This is evident from the \( M(H) \) hysteresis loop with \( H \) oriented perpendicular to the film plane. For this field orientation, the magnetization loop is rectangular-shaped, with a much lower coercive field \( \mu_0 H_c = 62 \text{ mT} \). Furthermore, the field at which the hysteresis loop closes is also reduced to about 0.7 T, as compared to more than 3 T for the magnetic field applied in the film plane. We note that the apparent dependence of \( M_S \) on the field orientation can be attributed to the large saturation field of SCRO, making the unambiguous determination of the diamagnetic contribution of the substrate difficult. Additionally, the large spin-orbit coupling in SCRO is expected to result in strong magnetic anisotropy.

CONCLUSIONS

In conclusion, we have identified the optimal parameters for the epitaxial growth of c-axis oriented SCRO films on (001) STO by pulsed laser deposition. The films have excellent crystalline quality with a high degree of Cr/Re sub-lattice order. The FWHM of the rocking curves is as small as 0.05\(^\circ\), \( M_S \) reaches 0.8 \( \mu_B/\text{f.u.} \), and the coercivity is 1.1 T. These parameters make SCRO thin films an outstanding ferrimagnetic double perovskite for spintronic applications. Financial support by the DFG via the priority programs 1157 and 1285 (project nos. GR 1132/13 and 1132/14), GO 944/3-1, and the Excellence Cluster "Nanosystems Initiative Munich (NIM)" are gratefully acknowledged.

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