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Structural, magnetic and electric properties of $HoMnO_3$ films on $SrTiO_3(001)$

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ABSTRACT

$HoMnO_3$ films were grown on pure and Nb-doped $SrTiO_3$ (001) substrates by pulsed laser deposition. The films grew epitaxially with the *c*-axis along the substrate normal. Varying the deposition temperature between 650 and 850 °C did not significantly affect the structural and magnetic properties of the films, whereas growth in oxygen partial pressures below 0.01 mbar lead to a degradation of the structural properties. Some of the films had a ferromagnetic-like magnetic phase transition at about 45 K, probably related to Mn_3O_4 precipitates; this magnetic response was isotropic. The Ho sublattice was found to be paramagnetic down to 5 K, but showing a pronounced anisotropy with the *c*-axis being the hard axis. The films showed a distinct dielectric anomaly at 16 K that depended on voltage and slightly on frequency in the range between 1 kHz and 1 MHz. The magnetoelectric effect was large with an in-plane field of 8 T suppressing the dielectric anomaly completely.

1. Introduction

$HoMnO_3$ films grow in the orthorhombic Pbnm structure on substrates that provide appropriate templates [1–5]. The orthorhombic $HoMnO_3$ is isostructural with nearly identical lattice constants to orthorhombic $YMnO_3$ that has been used for exchange biasing adjacent ferromagnetic layers [6–8]. Although both compounds have an antiferromagnetic transition at about 42 K, o-$HoMnO_3$ has a much more complex multiferroic structure [9], since the ferroelectricity in o-$HoMnO_3$ is induced by the magnetic order in the Mn sublattice [10–12] and since the Ho sublattice also shows magnetic order. In comparison to hexagonal $HoMnO_3$ [13–19] the study of orthorhombic $HoMnO_3$ is of particular interest, since it allows for the growth of functional heterostructures with other magnetic or ferroelectric perovskites.

In this work the structural, magnetic and magnetoelectric properties of o-$HoMnO_3$ films grown on $SrTiO_3$ (001) were studied. The focus of this study is on the magnetic properties of the films in relation to the structural and deposition parameters. In some of the films we found a ferromagnetic-like transition as already reported for o-$HoMnO_3$ [2,20], o-$YMnO_3$ [21] and o-$TbMnO_3$ [22] films. From the isotropic behavior of this transition and its modification by deposition pressure we conclude on the presence of Mn_3O_4 precipitates. The films still show a strong magnetodielectric coupling and are therefore antiferromagnetic.

2. Experimental

o-$HoMnO_3$ films were grown by pulsed laser deposition from a stoichiometric polycrystalline target onto $SrTiO_3$ (001) substrates. An excimer laser (Lambda Physik) operating at a wavelength of 248 nm (KrF), a repetition rate of 10 Hz and a fluence of about 1.5 J/cm^2 was used for the ablation. Three series of films (henceforth called series I, II and III) were made; in series I the substrate temperature was kept constant at 850 °C and the oxygen partial pressure was varied between 3×10^{-4} and 0.1 mbar; in series II the oxygen partial pressure was kept constant at 0.1 mbar and the substrate temperature was varied between 650 and 850 °C; in series III films were deposited on 0.5% Nb-doped $SrTiO_3$ substrates with temperature and oxygen partial pressure kept constant at 800 °C and 0.1 mbar, respectively, whereas the number of laser pulses was varied between 1250 and 40 000. For extensive magnetocapacitance measurements another $HoMnO_3$ film was deposited at 750 °C and 0.1 mbar O_2 onto a 0.5% Nb-doped $SrTiO_3$ substrate. The thickness of the films was estimated from the deposition time and calibrated by placing half-covered Si pieces close to the $SrTiO_3$ substrates during deposition and measuring the height of the resulting step by atomic force microscopy. The thickness of the films of series III was proportional to the number of laser pulses; most of the films presented here have a thickness of about 200 nm corresponding to 20 000 laser pulses.

Structural characterization of the films was made by X-ray diffraction (XRD) with a Philips X'pert system using Cu $K_{\alpha1}$ radiation. Magnetic characterization of the films was made by SQUID magnetometry (Quantum Design model MPMS-7). The capacitance and magnetocapacitance was measured in an Oxford Instruments flow cryostat equipped with a 8 T superconducting

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solenoid either using an Andeen-Hagerling capacitance bridge (model AH 2500A) operating at 1 kHz or using an Agilent impedance analyzer (model 4294A) operating between 1 kHz and 1 MHz. Assuming a parallel circuit between capacitance C and resistance $R=G^{-1}$, where G denotes the conductance, the Andeen-Hagerling bridge measures the inverse complex impedance $Z^{-1}=i\omega C+G$. Here the complex capacitance $\hat{C}=(i\omega Z)^{-1}\equiv C'-iC''=C-iG/\omega$ is reported. In case of the Agilent impedance analyzer only the capacitance C could be reliably determined in the whole frequency range and therefore only its values are reported here. The top contact was made by evaporating a circular gold contact of about 0.5 mm diameter onto the $HoMnO_3$ film and contacting this with gold wire and silver paint; the bottom contact was made with gold wire and silver paint directly on the unpolished backside of the Nb:$SrTiO_3$ backside.

3. Results

3.1. Structural characterization

Bulk orthorhombic $HoMnO_3$ crystallizes in the $GdFeO_3$-type structure (Pbnm) with lattice constants $a=0.527$ nm, $b=0.584$ nm and $c=0.736$ nm [23]. Compared to the cubic $SrTiO_3$ cell with lattice parameter of $a_{STO}=0.3905$ nm, the lattice mismatch in all orthorhombic directions is rather large with $(a/\sqrt{2}-a_{STO})/a_{STO}=-4.6\%$, $(b/\sqrt{2}-a_{STO})/a_{STO}=+5.7\%$ and $(c/2-a_{STO})/a_{STO}=-5.8\%$. Similar to the case of $SrRuO_3$ films grown on $SrTiO_3$ substrates one might expect two epitaxial relationships between the o-$HoMnO_3$ film and the $SrTiO_3$ substrate: (i) either the films are grown in $(110)_o$ or (ii) in $(001)_o$ orientation, where the subscript o refers to the orthorhombic axes of $HoMnO_3$. In case of strained films one might expect severe lattice distortions in either case, i.e. a monoclinic distortion for the $(110)_o$ orientation and either a tetragonal distortion or severe twinning for the $(001)_o$ orientation. Twinning was indeed found in $TbMnO_3$ films which are isostructural to $HoMnO_3$ films grown on $SrTiO_3$ [24]. Fig. 1(a) and (b) shows $\theta-2\theta$ scans around the $SrTiO_3$ (002) reflection. At about $2\theta=49.2^\circ$ an o-$HoMnO_3$ film reflection appears. Indexing this as the o-$HoMnO_3$ $(004)_o$ reflection yields c-axis constants between 0.740 and 0.746 nm slightly larger than the bulk value; indexing this reflection as $(110)_o$ would lead to $\sqrt{2}ab/(a^2+b^2)^{1/2}=0.524$ nm considerably smaller than the bulk value of 0.553 nm. Therefore we conclude that the o-$HoMnO_3$ films grow with the c-axis along the substrate normal; this is consistent with literature results [2,25]. The c-axis lattice parameter is independent of the oxygen partial pressure, but shows a trend towards a linear increase with the substrate temperature, see Fig. 2; further the c-axis lattice constant is independent of the film thickness up to about 200 nm, above which it decreases slightly.

Fig. 1 clearly shows that the growth of o-$HoMnO_3$ films at oxygen partial pressures below 0.03 mbar is detrimental to the film quality, since the intensity of the $(004)_o$ reflection strongly decreases at lower pressures. This is expected, since manganite films tend to be incompletely oxygenated if grown at too small oxygen partial pressures. The substrate temperature, on the other hand, does not have any significant influence on the intensity of the $(004)_o$ reflection. For the series I films grown at 0.1 and 0.03 mbar oxygen partial pressure φ scans of the $(116)_o$ reflection were recorded, see Fig. 1(c). These show a fourfold pattern consistent with orthorhombic symmetry. The intensity variations between the four reflections might be due to some angular misalignment of the goniometer. θ-2θ scans of the $(116)_o$ reflection (not shown) yield $\sqrt{2}ab/(a^2+b^2)^{1/2}=0.550\pm0.002$ nm in good agreement with the bulk value of 0.553 nm. This indicates that the $HoMnO_3$ films of thickness 200 nm investigated here are strain relaxed.

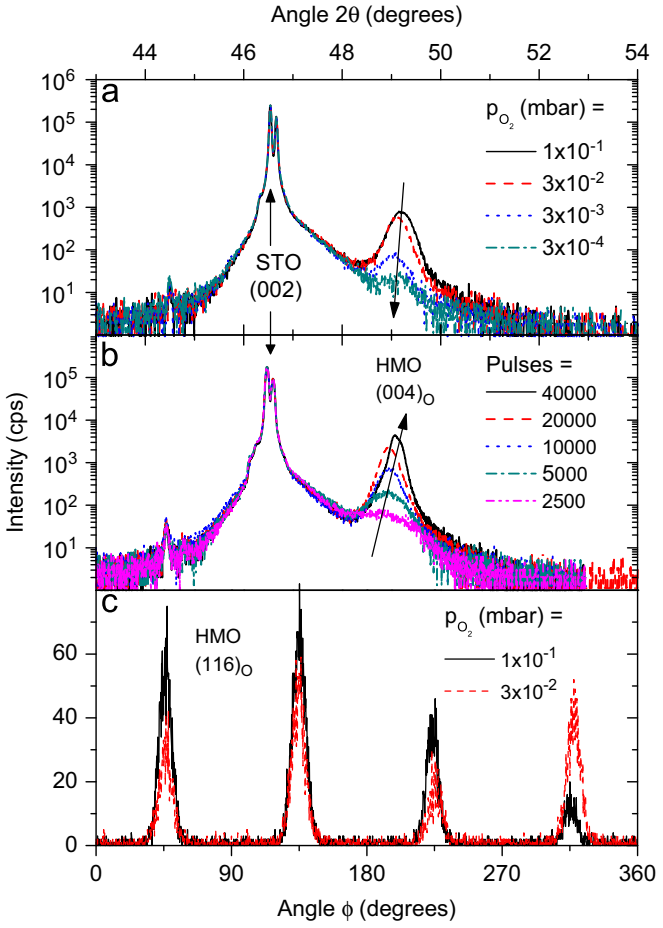

Fig. 1. $\theta-2\theta$ scans of the $HoMnO_3$ films from (a) series I and (b) series III. (c) φ scan of the $HoMnO_3$ $(116)_o$ reflection of the films from series I made at oxygen partial pressures of 0.1 and 0.03 mbar.

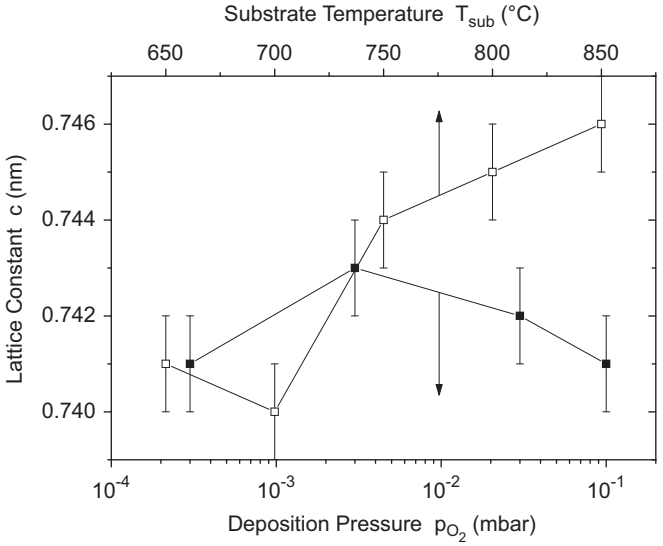

Fig. 2. The c-axis lattice constants of the $HoMnO_3$ films of series I as a function of oxygen partial pressure (bottom axis) and of series II as a function of substrate temperature (top axis).

3.2. Magnetic characterization

For each film the zero-field cooled (ZFC) and field cooled (FC) magnetization with a magnetic field of 0.1 T applied parallel to