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Structural, Magnetic and Transport Properties of $NdBaCo_2O_{5+x}$ Thin Films Deposited by Magnetron Sputtering

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For the first time, thin films of $NdBaCo_2O_{5+x}$ were deposited by RF magnetron sputtering on different substrates. The films deposited on $SrLaAlO_4$(001) substrates exhibited highly textured structure with *c*-axis directed out-of-plane. Magnetic measurements M vs. T of three $NdBaCo_2O_{5+x}/SrLaAlO_4$(001) films revealed successively paramagnetic-ferromagnetic-antiferromagnetic transitions with decrease in temperature. Their paramagnetic Curie–Weiss temperatures were estimated to be in the range of T_C = 100–116 K. Resistivity of the cobaltite thin film exhibited insulating behavior and the best fit was found for the variable range hopping mechanism.

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1. Introduction

Perovskite oxides RBO_3 (where R is a rare-earth element and B is a 3*d*-transition-metal element) are extensively studied materials due to their rich physical properties: high temperature superconductivity, piezoelectricity, colossal magnetoresistance, metal–insulator transitions, as well as prospective applications. The layered cobalt oxides $RBaCo_2O_{5+x}$ (R = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy) have attracted great attention. They offer a possibility to investigate remarkably wide range of doping as well as additional degree of freedom introduced by the ability of Co ions to exist in 3 different spin states [1–7]. However, there are a few studies on thin cobaltite films [8–10].

2. Experimental details

The RF magnetron sputtering setup has been described previously [11]. The deposition procedure used for $NdBaCo_2O_{5+x}$ films was close to that developed for the epitaxial growth of $La_{0.7}Ca_{0.3}MnO_3$ and $La_{0.7}Sr_{0.3}MnO_3$ thin films [11, 12]. The chamber pressure was the same p = 10 Pa, while the substrate temperature T_{sub} was modified over the range from 580°C to 720°C. Following our previous experience some of the deposited $NdBaCo_2O_{5+x}$ thin films (samples NCB1–NCB3) were annealed *in situ* in an oxygen environment at a pressure of 600 Torr. X-ray diffraction measurements have been performed using Cu K_α radiation. Magnetization measurements were performed using a SQUID magnetometer (Quantum Design, MPMS-5). The electrical resistance of the films was measured using a Keithley 617 electrometer.

3. Results and discussion

X-ray diffraction patterns revealed that $NdBaCo_2O_{5+x}$ (NBCO) thin films grown on $Si(100)/SiO_2$ substrates were polycrystalline, while films obtained on $SrLaAlO_4$ (SLA) (001) substrates exhibited only strong 00L reflections (see Fig. 1). Samples NCB1, NCB2 and NCB3 were grown with *c*-axis oriented out-of-plane. It is worth noting that for all of these samples the Bragg peak with indices 003 near 35 degree was registered, pointing out at the ordering of the oxygen vacancies. The c lattice constant for these samples ($c/2 = 3.812$ Å) is larger than the c lattice constants for known bulk $NdBaCo_2O_{5+x}$ samples with variable oxygen stoichiometry (Lobanovskii et al. [4], $c = 7.6052$ Å at $x = 0.72$ and Roy et al. [5], $c = 7.612$ Å at $x = 0.57$). The registered elongation along the c-axis is caused by the in-plane compression due to the significant layer–substrate misfit. For the sample NCB4, an out-of-plane a-axis orientation, due to employing buffer layers of $La_{0.7}Sr_{0.3}MnO_3$ and $PbZr_{0.54}Ti_{0.46}O_3$ (PZT), was found. The registered a-axis value (3.883 Å) implies high oxygen content $x \approx 0.70$, as can be estimated based on calibration data of $GdBaCo_2O_{5+x}$ single crystals (see Fig. 5 of Ref. [6]).

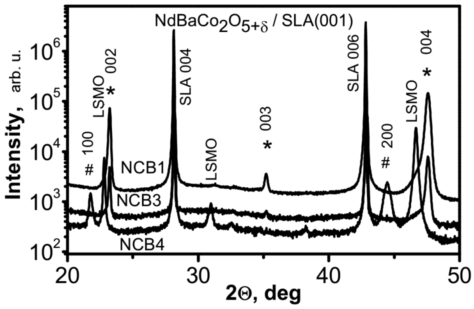

Fig. 1. X-ray diffraction pattern of cobaltite thin film samples NCB1, NCB3, and heterostructure NCB4, deposited by magnetron sputtering on different substrates. Peaks of the substrate SLA(001), c-axis ordered $NdBaCo_2O_{5+x}$, a-axis ordered $NdBaCo_2O_{5+x}$, and $La_{0.7}Sr_{0.3}MnO_3$ are marked by SLA, * , # , and LSMO, respectively.

Temperature variation of magnetization of the samples was measured under a field of 6 kOe in the zero-field-cooled (ZFC) regime. The magnetization M vs. T dependence for three $NdBaCo_2O_{5+x}$ thin films (after subtracting the substrate contribution) is presented in Fig. 2. On decreasing temperature, one can note a magnetization increase at the transformation to the ferromagnetic phase, FM, and followed by predomination of antiferromagnetic, AFM, interactions at lower temperatures, $T < 100$ K, for all three samples. The most pronounced FM response is found for the sample NCB2. This sample shows systematic decrease in magnetization down to lowest temperatures, $T = 4$ K, while other samples exhibit local magnetization enhancement at $T < 20$ K. The observed differences in M vs. T behavior of thin films could be ascribed to variable oxygen content acquired during *in situ* annealing procedure started from different temperature. One can notice that M vs. T behavior of investigated NBCO films resembles that found for bulk samples of the $PrBaCo_2O_{5+x}$ ($x = 0.53$) [5] and $GdBaCo_2O_{5+x}$ ($x = 0.70$) [6] isostructural systems. We fit the Curie–Weiss relation to the paramagnetic, PM, susceptibility of these samples (the contribution of Nd^{3+} ions has been subtracted) and found the reasonable agreement (see inset of Fig. 2). The paramagnetic Curie temperature is estimated as $T_C = 100$ K, 116 K and 103 K, for the samples NCB1, NCB2, and NCB3, respectively. The values of T_C are shifted to lower temperatures in comparison to $T_C \approx 130$ K of bulk $Nd_{0.5}Ba_{0.5}CoO_3$ [7] and such a difference could be ascribed to strained lattice cell of cobaltite thin films.

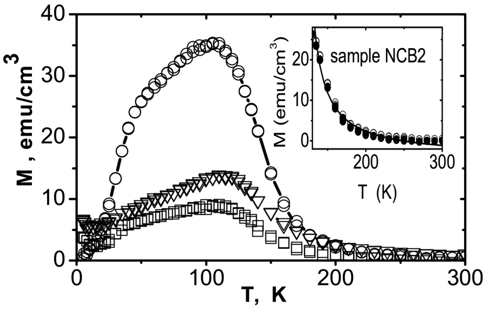

Fig. 2. Temperature dependence of magnetization M for the samples NCB1, NCB2 and NCB3 (marked by triangles, circles and squares, respectively). The inset presents M vs. T dependence for the sample NCB2 (before and after subtracting the contribution of Nd^{3+} ions, presented by empty and full circles, respectively) and a fit to Curie–Weiss expression: M/H (Gs/Oe) $= -6.2 \times 10^{-4} + 0.095(T - 116)$ for the sample NCB2.

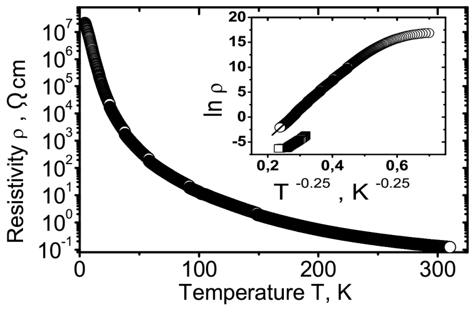

Fig. 3. Temperature dependence of the resistivity ρ of the sample NCB1. The inset presents the fit of the VRH model ($\ln \rho$ vs. $T^{-1/4}$ dependence) for the sample NCB1 (circles) and the bulk $NdBaCo_2O_{5.72}$ sample (squares) (after Ref. [4]).

TABLE

Fit of conducting mechanism of VRH [$n = 4$, Eq. (1)] or hopping dominated by the Coulomb interaction [$n = 2$, Eq. (1)] to the experimental data: values for regression R, standard deviation sd, and appropriate temperature range.

Sample	Model	R/sd	Temp. range
NCB1	$n = 4$	0.99934/0.11789	310–18.5 K
NCB1	$n = 2$	0.99975/0.01754	310–149 K
NCB1	$n = 4$	0.99957/0.07915	130–18.5 K
NBCO [4]	$n = 4$	0.99943/0.02557	226–98 K

The resistivity ρ vs. T dependence is shown in Fig. 3. It reveals insulating behavior over the entire temperature range studied and the resistivity value increases by eight orders of magnitude. The thin films' resistivity values are larger than those of the bulk $NdBaCo_2O_{5.72}$ [4] (by 64 times at room temperature (RT)) and the single crystal $GdBaCo_2O_{5+x}$ [6] (by about 3 orders of magnitude). Such a difference could be ascribed to (i) significantly compressed *ab* plane and tensile strained lattice along the *c*-axis, and (ii) appearance of a shear stress in layer regions located far from the substrate surface, due to lattice relaxation (like in Ref. [9]). In order to elucidate the conduction mechanism we have fit to ρ vs. T data (see Table) the generalized formula for activated hopping model, where ρ is given by

$$\rho = \exp(T_0/T)^{1/n}. \qquad (1)$$

Here, $n = 1$ and 4 correspond, respectively, to Arrhenius and variable-range hopping (VRH) mechanisms, while $n = 2$ corresponds to the Efros–Shklovskii model. For comparison, additional data for a $NdBaCo_2O_{5.72}$ bulk sample are presented as well [4]. The best fits for the resistivity data were found for the VRH model (130 K $< T <$ 18 K) as well as for the Efros–Shklovskii model (310 K $< T <$ 149 K). VRH takes place in disordered systems where charge carriers move by hopping between localized electronic states and its validity is evidenced on cobaltites [6, 8, 9]. One can note (see inset of Fig. 3) that resistivity tends to saturate at lowest temperatures, $T <$ 18 K, which is in agreement with intrinsic mesoscopic phase separation proposed in [6] as well as with structural modelling in [4]. The Efros–Shklovskii model is usually valid when the Coulomb interaction starts to play a key role in carriers hopping, resulting in strong depletion in the density of states (the Coulomb gap) near the Fermi energy. It has been validated for electron-doped $GdBaCo_2O_{5+x}$ ($0.16 < x < 0.44$). The good fit of this model found by us for hole-doped Nd cobaltite film could be understood in the frame of phase separation and the existence of highly elastically strained cobaltite layer close to the substrate surface.

4. Conclusions

For the first time, thin films of $NdBaCo_2O_{5+x}$ have been deposited by RF magnetron sputtering on different substrates. The films deposited on SLA(001) substrates exhibited highly textured structure with *c*-axis directed out-of-plane. Magnetic measurements of M vs. T for three $NdBaCo_2O_{5+x}$/ SLA(001) films revealed successive PM-FM-AFM transitions on cooling. The paramagnetic Curie–Weiss temperatures were estimated to be in the range T_C = 100–116 K. The cobaltite thin film exhibited insulating behavior and best fit was found for VRH mechanism (130 $K < T <$ 18 K).

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