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## Effect of oxygen content „stabilization“ in $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ films at post annealing in air

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The variation of oxygen content in the epitaxial  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  films of 12–75 nm thick onto  $\text{NdGaO}_3$  substrates was quantitatively investigated by indirect method during heat treatment procedure in air at temperature range 873–1073 K. The experimental time dependences of oxygen content variation were investigated theoretically with taking into account the effect of inhomogeneous diffusion of oxygen over the films thickness to provide optimal choice of temperature and duration of the heat treatment procedure. In films 25–75 nm thick, the effect of „stabilization“ of the oxygen content ( $\text{OC} = 3$ ) is revealed, which indicates the presence of an energy barrier that prevents the incorporation of an excess oxygen atom into the near-surface layer of the film at optimal conditions of heat treatment.

**Keywords:** epitaxial films, strain, oxygen index, non-uniform oxygen diffusion.

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### 1. Introduction

Heat treatment of film structures in an oxygen-containing gaseous medium is an important technological procedure that enables to change the oxygen content (OC) in the material of thin epitaxial films based on doped manganites. It is known that OC, as well as the doping level of manganites, radically changes the electrical and magnetic characteristics of the films. The main problems that are solved by varying the OC in doped manganites have fundamental and applied aspects — providing a stoichiometric OC in the material of films intended for studying the properties of strongly correlated systems and demonstrating the effect of colossal magnetoresistance; production of films with maximum achievable values of electrical conductivity, temperature resistance coefficient and key parameter  $T_C$  — temperature of double phase transition (magnetic, between ferromagnetic and paramagnetic state and metal–dielectric transition).

With the development of various film manufacturing technologies, the heat treatment conditions were selected empirically, and the authors of the articles gave recommendations to obtain certain film characteristics [1–4]. Nevertheless, the correct choice of heat treatment conditions to ensure the stoichiometric oxygen content ( $\text{OC} = 3$ ) in films of different thicknesses, in contrast to single crystals [5–7], turned out to be a very difficult task. The main problem is the lack of direct methods of OC control. Since epitaxial films are grown on oxide substrates, it is impossible to control OC in the film material, for example, using energy-dispersive spectrometers with the required accuracy.

The search for alternative approaches led to the development of indirect control methods [8,9], as well as to attempts to select heat treatment conditions based on theoretical concepts. In particular, in the article [10] the results of calculations of the equilibrium state of the film material were provided depending on the temperature and partial pressure of oxygen for several relatively low levels of doping with  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  ( $x = 0.05–0.14$ ). But a film is a more complex object than a single crystal, and to describe its characteristics, additional factors must be taken into account. In particular, the provided calculations do not take into account the mechanically stressed state of the films, which varies with thickness [1,11,12]. The second feature is that the structural quality of films produced using various technologies — by the magnetron method on direct or alternating current, by the laser method, or by the method of chemical vapor deposition of films, also changes with thickness.

Another important uncounted feature, which was found using the indirect method [9,13], is related to the nonlinear properties of oxygen transport in LSMO films. The diffusion coefficient of atomic oxygen significantly and nonlinearly decreases over the film thickness depending on the position between the outer and inner interfaces, and in films of different thicknesses, its value in the vicinity of the outer interface decreases as the film thickness decreases. And this, in particular, leads to the need to select the optimal duration of the heat treatment procedure. It is especially important to take this fact into account during heat treatment of films under conditions of excess oxygen partial pressure, for example, in air. It should be noted that the literature presents numerous results of studies of film characteristics

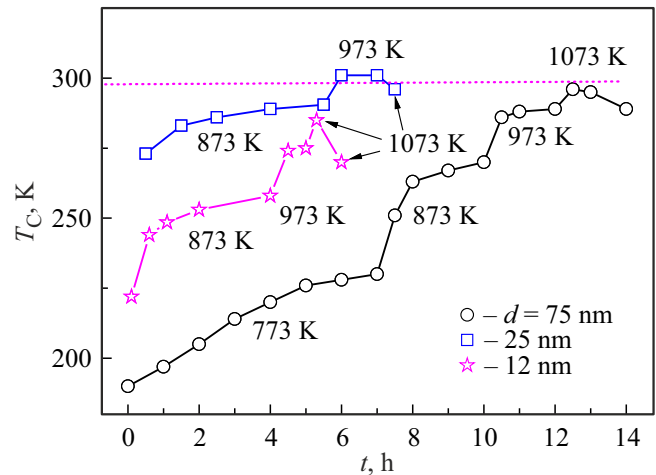
depending on temperature and partial pressure of oxygen in a gaseous medium for a fixed duration of the procedure, for example, 1 h [14]. In this article, using the example of a series of LSMO films of different thicknesses, we show the importance of the optimal choice of heat treatment duration at several fixed temperatures. The use of a step-by-step procedure and an indirect method for estimating the OC enabled to establish an interesting effect of OC = 3 „stabilization“ in films with a thickness of 25–75 nm under optimal heat treatment conditions.

## 2. Experiment details

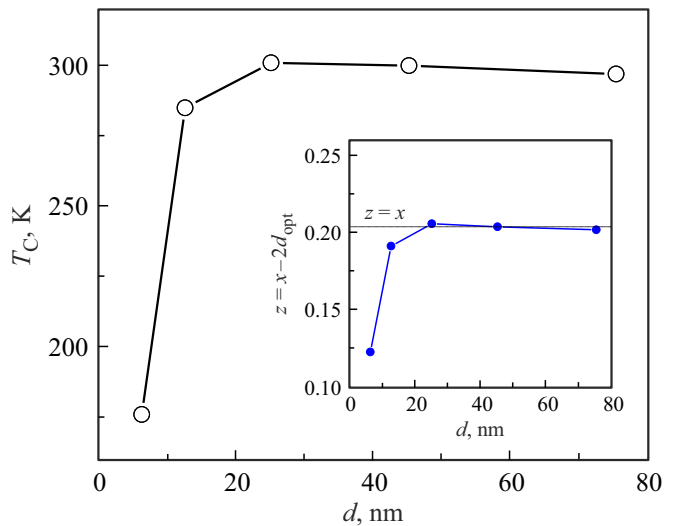
The films were obtained by dc magnetron sputtering of a ceramic target onto high-quality single-crystal substrates (Mateck, Germany) with (110) orientation heated to 873 K in a gas mixture atmosphere (20% oxygen and 80% argon) [15]. The films composition was controlled using an INCA Energy-350 energy dispersive spectrometer. The thickness of the films was controlled by several methods, including the original one [16], based on the calculation of the thickness based on the relative content of heterogeneous cations in the film and in the substrate microscopic layer. To eliminate the oxygen deficiency, the films were subjected to stepwise heat treatment in air. The duration of each heat treatment step at several fixed temperatures in the range of 673–1073 K was 0.5–1 h. After heat treatment, the film was cooled, then contact pads were deposited on it with „Electrolube“ (Germany) silver paint and the temperature dependences of the resistance were measured in the range  $T = 77\text{--}360\text{ K}$  and in a magnetic field  $H = 0\text{--}15\text{ kOe}$ . Before each next heat treatment step, the contact pads were removed. Heating and cooling of the film structures at each heat treatment step was carried out at a rate of about 30 K/min. This enabled to avoid a large mechanical stress of the films. We also note that, taking into account the strong temperature dependence of the diffusion coefficient, the diffusion oxygen transport into the film becomes relatively inefficient for 4–5 min after the start of cooling. The metal–dielectric phase transition temperature  $T_C$  was determined as the temperature minimum of the film conductivity at  $H = 0$ .

## 3. Study results and discussion

A successive change in the values of  $T_C$  during the stepwise heat treatment of three films 12, 25, and 75 nm thick is shown in Fig. 1. As can be seen, within each stage of heat treatment at a fixed temperature, the values of  $T_C$  increase nonlinearly in the form of a dependence that saturates in time. After a stepwise increase in temperature by 100 K, the growth rate  $T_C$  sharply increases and then decreases. Formally, such a dependence is well described theoretically, taking into account a significant decrease in the diffusion coefficient of atomic oxygen over the film thickness [9]. Studies of oxygen transport in



**Figure 1.** Change in the metal-dielectric phase transition temperature in  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  films during stepwise heat treatment in air at several fixed temperatures in the range of 673–1073 K.



**Figure 2.** Dependence of the maximum achievable values of  $T_C$  on the thickness of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  films on  $\text{NdGaO}_3$  substrates. Inset: dependence of parameter  $z = x - 2\delta_{\text{opt}}$  on film thickness.

films of different thicknesses have shown that the diffusion coefficient also decreases significantly with decreasing film thickness [13], which is mainly due to the heterogeneous distribution of mechanical stresses over the film thickness.

Heat treatment of the film structures was carried out in air under conditions corresponding to the equilibrium OC excess in the material of the films [10]. Therefore, as expected, a gradual increase in temperature leads first to a maximum value, and then to a subsequent decrease  $T_C$ . The increase in  $T_C$  is explained by a decrease in the concentration of oxygen vacancies, and the decrease at the last stage of heat treatment is due to the formation of excessive OC, which is associated with the formation of cation-deficient lattice cells. That is, in the process of heat treatment, a decrease in the oxygen vacancies concentration in the film volume

The value of the diffusion coefficients corresponding to the external interface of films of different thicknesses at two fixed temperatures

$d$ , nm	$D \cdot 10^{-19}$ , m <sup>2</sup> /s	
	$T = 873$ K	$T = 973$ K
25	0.516	17
45	1.83	60.4
75	2.5	82.4

and the formation of defective cation-deficient cells in the near-surface layer can occur simultaneously.

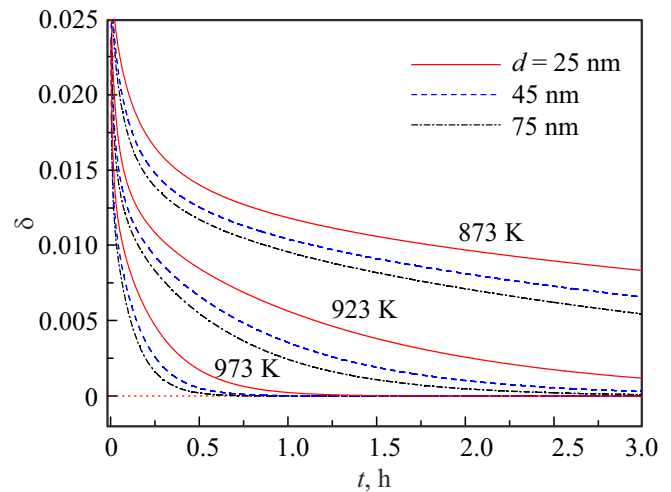
Figure 2 shows the maximum achievable values of  $T_C$  for a series of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  films with a thickness of 6–75 nm on  $\text{NdGaO}_3$  substrates. The values of the parameter  $z = x - 2\delta_{\text{opt}}$  calculated using the indirect method [9] are also presented there. Optimal values  $\delta_{\text{opt}}$  mean the value of the oxygen index corresponding to the maximum temperature of the phase transition.

The most interesting fact is that in films with a thickness of 25–75 nm, the maximum value  $T_C$  corresponds to the stoichiometric oxygen content  $\text{KS} = 3$ ,  $\delta = 0$ . This indicates a rather high quality of the crystal structure in these films, and also that at a temperature of  $T = 873$  K under conditions of a high partial pressure of oxygen, the process of OC excess formation by the formation of additional cation-deficient crystal cells is not implemented. This, in turn, indicates that the crystal structure with  $\text{OC} = 3$  is energetically the most stable, and the incorporation of an excess oxygen atom into the near-surface layer of the film is hindered by an energy barrier that cannot be overcome at this temperature. Indeed, a noticeable decrease  $T_C$ , as it follows from the data in Fig. 1, manifests itself at higher temperatures. As a result, the „stabilization“ effect  $\text{OC} = 3$  is observed. The maximum value of  $T_C$  is achieved at a higher temperature, at 973 or 1073 K, but due to the short duration of heat treatment under these conditions, the increase in the concentration of crystal defects is limited.

Thus, the trade-off in selecting the temperature and duration of the heat treatment procedure is to minimize the number of additional crystal defects that reduce  $T_C$ .

Figure 2 also shows data for a film with a thickness of  $d \approx 6$  nm, which should be considered separately as an object with a significantly weakened exchange interaction [17–19]. Regarding the data for a 12 nm thick film in Fig. 2, it should be noted that the underestimated value of  $z < x$  can be attributed to the inaccuracy of the indirect method, which uses a single correction to take into account the influence of mechanical stresses [13].

Figure 3 shows the calculated time dependences of the oxygen index of LSMO films on  $\text{NdGaO}_3$  substrates during heat treatment at  $T = 873$ , 923 and 973 K. The initial value of the oxygen index in the material of three films corresponds to the value  $\delta = 0.03$ , and the dependence of its values on the thickness and over the thickness of the



**Figure 3.** Time dependences of changes in the oxygen index in LSMO films 25, 45 and 75 nm thick at three fixed temperatures in the range of 873–973 K.

films [13] is taken into account for the diffusion coefficient. The diffusion coefficients at the external interface for three films are given in the table.

As can be seen from the data in Fig. 3, a film with a thickness of  $d = 25$  nm requires a longer heat treatment time than a film with a thickness of 75 nm. This is a consequence of differences in the diffusion coefficient in films of different thicknesses. At  $T = 873$  K, the required heat treatment time exceeds a day, at  $T = 923$  K it decreases to 5–6 h, and at  $T = 973$  K it is approximately 1.5 h.

## 4. Conclusion

The previously established dependence of the diffusion coefficient on the thickness and over the film thickness [9,13] significantly affects the correct selection of the heat treatment parameters for films of different thicknesses. In particular, taking into account this effect shows that the required duration of films heat treatment increases with a decrease in thickness from 75 to 25 nm. To avoid the formation of additional defects in the films material during heat treatment under conditions of excess partial pressure of oxygen, it is important to coordinate the selection of temperature and duration of the procedure. At a temperature of 873 K, in films with a thickness of 25–75 nm, the „stabilization“ effect  $\text{OC} = 3$  is observed, which indicates the presence of an energy barrier that prevents the incorporation of an excess oxygen atom into the near-surface layer of the film.

## Conflict of interest

The authors declare that they have no conflict of interest.

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