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Spray-pyrolysis deposition of $LaMnO_3$ and $La_{1-x}Ca_xMnO_3$ thin films

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Abstract

Ethylene glycol solutions of La–Mn(II) and La–Ca–Mn(II) citric complexes has been used as a starting material for spray-pyrolysis deposition of $LaMnO_3$ and $La_{1-x}Ca_xMnO_3$ thin films on β-quartz, fused quartz, Si(0 0 1) and $SrTiO_3$(1 0 0) substrates heated during the deposition at 380 °C. At suitable post-deposition heating conditions highly uniform films, 0.1–1 μm in thickness, with good crystal structure were obtained. Highly textured $LaMnO_3$ films are obtained on $SrTiO_3$(1 0 0) substrate. Interaction between the layer and Si-containing substrates is observed during the post-deposition heating in static air.

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1. Introduction

Lanthanum manganites are used as catalysts, heating elements, semiconductor ceramic materials, ferromagnets and cathode material for solid oxide fuel cells (SOFC). Materials from the type $Ln_{1-x}A_xMnO_3$ (Ln, lanthanide; A, bivalent cation as Ca, Mg) have attracted a great deal of interest since in 1993 they were shown to display colossal magnetoresistance (CMR). Films of these materials are used in different devices as magnetic field sensors, electric field devices, etc. A review about the CMR manganite films (concerning the deposition procedures, the structural and physical characteristics, the substrate effects as well as some devices on their base) is made in [1].

Numbers of methods are applied for deposition of $LaMnO_3$ and doped manganites. Popular deposition techniques are: magnetrone sputtering [2–7], laser ablation [8,9] and MOCVD [10]. Spin-coating using

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toluene solution of the metal naphthalenes is used in [11]. At the latter method the sample is post-deposition heated at 500 °C for 10 min. The procedure is repeated few times to reach a film thickness of 500 nm. The final product is obtained after heating for 5 h at 1000–1600 °C.

Epitaxial and polycrystalline films are obtained by these methods with thickness between 100 and 200 nm [2–4,6,7] and 400–500 nm [5,10]. $LaAlO_3$(1 0 0), MgO(1 0 0), Si(1 0 0), YSZ(0 0 1), $SrTiO_3$(0 0 1), sapphire(1 0 0), polycrystalline YSZ [3,5], SiO_2 on Si(1 0 0) [2] and YSZ buffered Si(1 0 0) [3,6] have been used as substrates. Their influence on the film crystal structure and morphology has been studied.

In the available literature we did not found data for spray-pyrolysis deposition of films from $LaMnO_3$ and its doped derivatives. In our previous works [12–14] we show that ethylene glycol (EG) solutions of citric complexes of the respective metals can be successfully used as a starting material for spray-pyrolysis deposition of mono- and poly-metallic oxide films. The main advantage of this approach is based on the fact that in many systems of the type M–M′–citric acid (CA)–ethylene glycol (EG), mixed metal complexes are formed (M, M′-metal cations). Using such a precursor (in which the metals are mixed on an atomic level) it is easier to obtain at relatively low temperatures and short time of heating stoichiometric, phase homogeneous multicomponent oxides. In a recent study [15] it was shown that a mixed metal complex with equimolar ratio of the metals is formed in La–Mn–CA–EG-system when metal chlorides are used as metal sources. That is why the solution of these complexes seems to be promising starting material for deposition of $LaMnO_3$ films by spray-pyrolysis. The complexation processes in La–Ca–Mn–CA–EG is obviously more complicated [15] and it was interesting to check also the applicability of the respective system for $La_{1-x}Ca_xMnO_3$ films deposition.

2. Experimental

2.1. Materials

Anhydrous CA (extra pure), $LaCl_3{\cdot}6H_2O$, $MnCl_2{\cdot}4H_2O$, $CaCl_2{\cdot}2H_2O$ and EG—all of p.a. grade were used for the preparation of the starting solutions. The exact content of the metals in the used salts was determined by titration with EDTA.

$LiKAl_2SiTi_4O_{12}$ (called β-quartz), fused quartz, Si(0 0 1) or $SrTiO_3$(1 0 0) (10 × 10 × 1 mm in thickness) were used as substrates. Before the film deposition, they were treated consecutively with trichloroethane, ethanol and acetone in an ultrasonic bath for 10 min.

2.2. Preparation of the starting solution

CA was dissolved in EG at 35–40 °C and the respective metal salts were added to the solution so as mole ratios La^{3+}:Mn^{2+}:CA:EG = 1:1:10:40 and La^{3+}: Ca^{2+}:Mn^{2+}:CA:EG = 0.7:0.3:1:10:40 to be adjusted. The solutions were heated at 120 °C for 40 min. Under the applied conditions formation of complexes with the following proposed formulae [15] was found:

$$LaMnCl_{2.3}{\cdot}[HCit(ROH)_2{\cdot}R \cdot Cit(ROH)_2{}^{-}]_{1.1}{\cdot}[HCit(ROH) \cdot RCit(ROH)_2{}^{2-}]_{0.8}{\cdot}0.1HOROH \cdot 5.0H_2O;$$

$$LaCa_{0.3}Mn_{0.7}Cl_{1.4}(HCit(ROH)^{2-})_{0.8}Cit(ROH)_2{}^{2-}{\cdot}1.5HOROH \cdot 3.3H_2O$$

where HCit = $CH_2COOC(OH)COOCH_2COO$, Cit = $CH_2COOC(O)COOCH_2COO$, R = $CH_2)_2$

2.3. Films deposition

The deposition was carried out by means of a device, shown in [12] with a nebulizer with a nozzle of 0.7 nm in diameter. Pressurized O_2 was used as carrier gas (flow rate of 1 dm^3/min). The substrate was heated at (380 ± 20) °C and was placed 20 cm apart from the nozzle. The pulverization was performed at an angle of 45 °C for 30 s. The film thickness was controlled by the number of the spray procedures keeping constant the substrate temperature, gas flow rate and pressure. After the deposition, the samples were annealed at