Structural and electrical properties of $La_{0.8}Pb_{0.2}FeO_3$ thin films deposited by rf magnetron sputtering

C. DOROFTEI[a*], F. IACOMI[a], P. D. POPA[b]
[a] *"Al. I. Cuza" University, Faculty of Physics, 11 Carol I Blvd, 7000506 Iasi, Romania*
[b] *Institute of Technical Physics, Bd. D. Mangeron 47, 700050 Iasi, Romania*

The structural and electric properties of some thin films obtained through rf magnetron sputtering using as target the $La_{0.8}Pb_{0.2}FeO_3$ perovskite have been studied. We have investigated the effects of the quartz and alumina substrate, its temperature during deposition, as well as of sputtering gas composition (Ar/O_2 ratio) and subsequent heat treatments. The thin films microstructure was characterized by XRD, SEM, EDX and AFM analyses. The XRD patterns indicate the generation of perovskite phase and the increase of its crystallinity after a heat treatment at 750^{o}C/30min. The micrographs indicate the formation of a uniformly clustered structure of the films after the heat treatment. From the resistivity standpoint, the layers are practically insensitive to environmental humidity up to a value of about 53% RH and presents a good sensitivity to humidity within the range 53% - 98% RH.

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1. Introduction

Lanthanum perovskite $LaFeO_3$ (LFO) is a semi-conducting oxide and has been extensively studied with reference to several potential applications, such as gas sensors, humidity sensors and catalysts [1-4]. This oxide crystallizes in an orthorhombic perovskite structure [3-6]. The electric resistance of the $LaFeO_3$ based sensor is very high, which is a disadvantage in application. The replacement of rare earth element La by Ba, Ca, Sr and Pb in $LaFeO_3$ can diminish the resistance [7].

The specialized literature presents a series of studies on some thin layers obtained through rf magnetron sputtering methods, deposited on various substrates, using as target the $LaFeO_3$ material obtained through different methods [1,3,8,9].

We have studied in this work the structural and electric properties of some thin films obtained through rf magnetron sputtering using as target the $La_{0.8}Pb_{0.2}FeO_3$ (LPFO) perovskite obtained through precursor self-combustion method [4,10-12]. We have investigated the effects of the quartz and alumina substrate and its temperature during deposition, as well of sputtering gas composition (Ar/O_2 ratio) and of subsequent heat treatments. The microstructure of the thin films was characterized by XRD, SEM, EDX and AFM analyses.

The influence of the environmental humidity on the electric resistivity of the obtained films was determined within the 0% - 98% RH interval.

2. Experimental

The LPFO thin films were deposited by rf magnetron sputtering in a high-vacuum system with a base pressure lower than $5 \cdot 10^{-5}$ Torr - magnetron sputtering VUP 5 (13.56 MHz) installation. The target was realized of powder with a nominal composition $La_{0.8}Pb_{0.2}FeO_3$ prepared by precursor self-combustion method [4]. The LPFO films with the dimensions of 10mm x 10mm x 1mm were grown on alumina (Al_2O_3) and quartz (SiO_2) heated substrates by rf magnetron sputtering. Prior to utilization, the films were cleaned with acetone, detergent with ultrasounds, ethyl alcohol, distilled water, and then dried with warm air. The obtained films were heat treated in air at various temperatures 500 – 800 ^{o}C and with heat treatment durations of up to 90 min, then the silver electrodes were applied.

The characteristics and the deposition parameters of the obtained thin films are presented in Table 1.

Table 1. RF magnetron sputtering parameters for the preparation of LPFO thin films.

Sputtering gas	$Ar+O_2$
$O_2/(O_2 + Ar)$	0 – 1/2
Background pressure	10^{-5} Torr
Working pressure	10^{-3} Torr
Target diameter	4 cm
Target-substrate distance	2,5 – 5,5 cm
Substrate temperature	100 – 300 ^{o}C
RF Power	50 – 200 W
Deposition time	30 – 90 min
Film thickness	330 ±10 nm at 90 min.

X-ray diffraction (XRD) studies of the thin films were carried out at room temperature within the Bragg angle range $30^o \leq 2\theta \leq 50^o$ at a scan speed of 2^o/min by a X-ray diffractometer using the CuK$_{\alpha}$ radiation (λ=1.54184 Å). Crystalline phases were identified by using ”Crystallographica” program. The morphology and elemental chemical composition were analyzed by using scanning electron microscope (SEM), equipped with EDX. The thin films thickness was established from SEM micrographs in cross section of the deposited film.

The roughness of the thin films was characterized by AFM analysis.

The film electric properties and resistivity in terms of temperature between 20^{o}C and 310^{o}C were resulted after a heating, a cooling and a reheating.

The influence of the environmental humidity on the electric resistivity of the obtained films was determined within the 0% - 98% RH interval using a heat stabilized device able to produce mediums with pre-established humidity [13,14].

3. Results and discussion

3.1 Structure and morphology

We present in the following the results of our studies concerning the thin films obtained having $La_{0.8}Pb_{0.2}FeO_3$ as a target.

The XRD patterns for the obtained thin films present an amorphous structure for substrate temperatures during deposition ranging within the interval 100^{o}C - 300^{o}C. When the sputtering gas is only argon, small drops appear indicating perovskite phases, while when the sputtering gas includes argon and oxygen, the perovskite phase indicates an increase of crystallinity.

For the thin films deposited for 90 min, at 75 W rf power, target-substrate distance of 40 mm, substrate temperature of 150^{o}C and the gases ratio $O_2/(O_2+Ar)=1/(1+9)$, the XRD patterns (Fig. 1) indicate a slight generation of the perovskite phase after deposition (untreated), and an increase of its crystallinity after a heat treatment at 750^{o}C/30min.

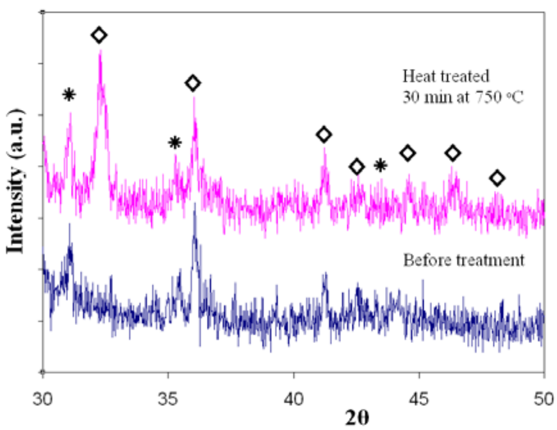

Fig. 1. XRD diffractograms for films deposited on alumina, before and after heat treatment. The identified phases are denoted as follows: (✱) - Al_2O_3; (◇) - $La_{0.8}Pb_{0.2}FeO_3$.

Elemental chemical composition was estimated from the energy dispersive X-ray spectra (EDX). The EDX spectra of the thin film deposited on quartz in the previously specified conditions and considered by us as being optimal are presented in Fig. 2.

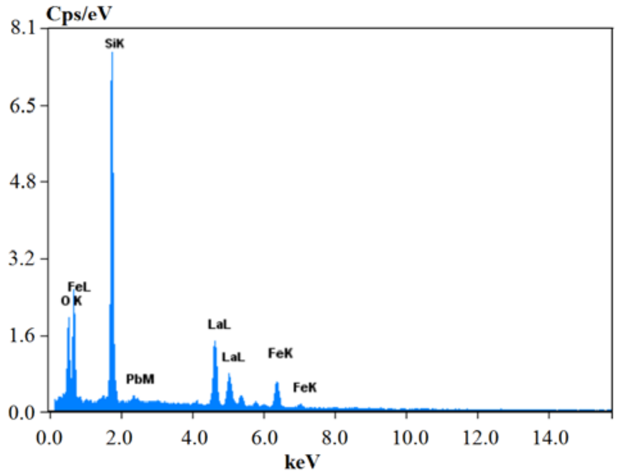

Fig. 2. EDX spectrum for the film deposited on quartz under optimal conditions and heat treated 30min/750^{o}C in air.

For the thin films deposited under specified optimal conditions, their thickness is the same, namely 330 nm ±10 nm (Fig. 3). The films deposited on alumina are a little bit coarser and non-uniform as compared to those deposited on quartz, yet their structural parameters do not differ markedly.

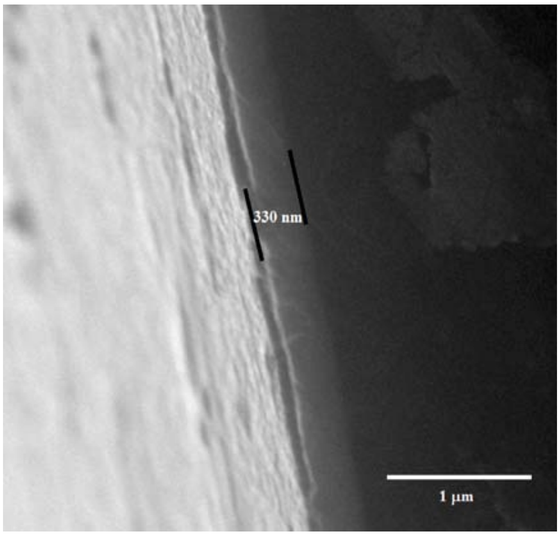

Fig. 3. SEM micrograph in cross sections for thin films deposited on quartz, heat treated 30 min/750^{o}C in air.

The 3D microstructure of the film deposited on alumina is presented in Fig. 4. Following the heat treatment, the crystal size gets modified and one can notice, for the both substrates, the generation of a clustered structure of around 30 nm (Fig. 5).

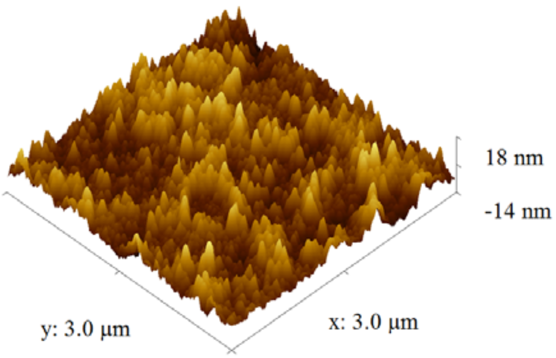

Fig. 4. 3D AFM image for the film deposited on alumina and heat treated 30 min/750°C in air.

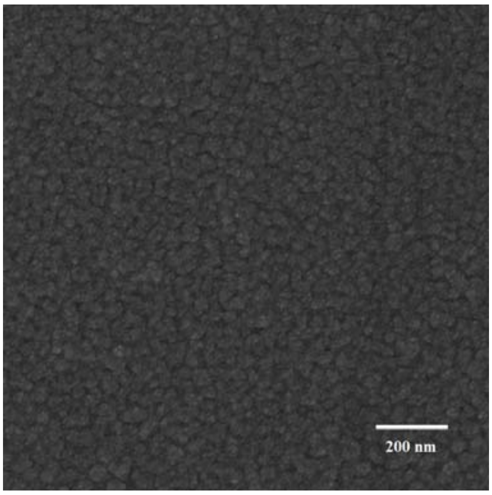

Fig. 5. SEM micrograph for the thin film deposited on alumina and heat treated 30 min/750°C in air.

3.2. Electrical properties

We have also studied the influence of relative environment humidity on the electric resistivity of the obtained films within the range 0% - 98% RH.

The resistivity of the films heat-treated for 30 min at 750°C in air is $3.92 \cdot 10^6$ Ω·cm at room temperature and 0% RH. This decreases down to $6 \cdot 10^2$ Ω·cm at the temperature of 310°C. Figure 6 presents the Log ρ characteristics versus 1000/T during heating, cooling and reheating (5°C/min) for the film deposited on alumina, then heat treated 30 min/750°C in air. These characteristics reveal a good stability (negligible hysteresis) of electric resistivity with temperature during repeated heating and cooling.

The electric behaviour of the films belongs to n-type semiconductors, and the thermal activation energy (E_a) is around 0.5 eV.

The resistivity variation of the film deposited on alumina under previously specified optimal conditions vs. air relative humidity (RH) at the temperature of 25 °C is presented in Fig. 7. From resistivity standpoint, the films are practically insensitive to environment humidity up to a value of around 53% RH.

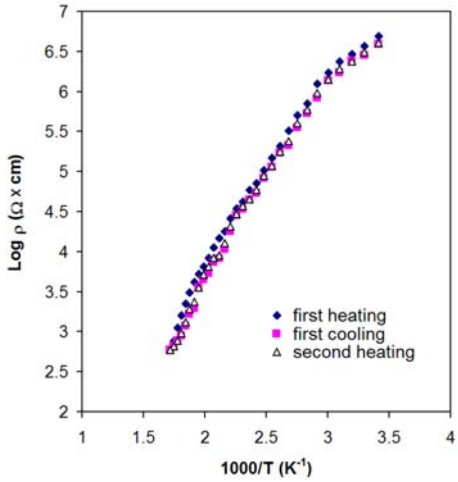

Fig. 6. Log ρ characteristics as functions of 1000/T for the film deposited on alumina and heat treated 30 min/750°C in air.

For higher values of relative humidity, the log ρ characteristic vs. relative environment humidity has a big slope and the film presents a good sensitivity to humidity within the range of the 53% - 98% RH.

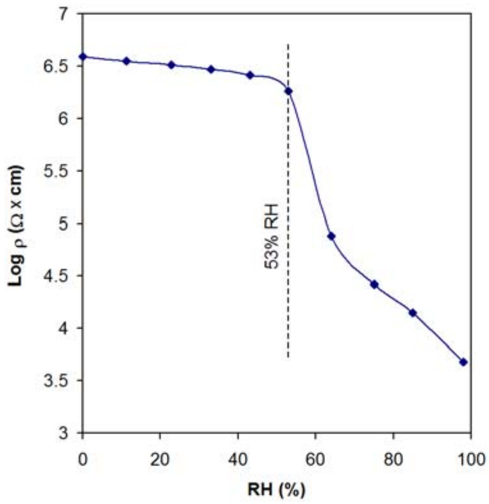

Fig. 7. Rezistivity-humidity characteristic at the temperature of 25 °C for the film deposited on alumina and heat treated 30 min/750°C in air.

4. Conclusions

The most important conclusions are as follows:

- The structural and electric properties of some thin films obtained through rf magnetron sputtering using as target the $La_{0.8}Pb_{0.2}FeO_3$ perovskite, deposited on alumina and quartz substrates have been studied.
- In order to obtain films with a good crystallinity, the deposition conditions considered as optimal are: deposition time 90 min, rf power 75 W, target-substrate distance 40 mm, substrate temperature 150°C and gases ratio $O_2/(O_2+Ar)=1/(1+9)$, while the optimum heat treatment is for 30 min at 750°C in air.

• Following the heat treatment, clustered structures of about 30 nm are formed for both substrates.

• The electric behaviour of the films is that of n-type semiconductors, and the thermal activation energy (E_a) is around the value 0.5 eV. A good stability (negligible hysteresis) of resistivity with temperature during repeated heating and cooling has been found.

• The electric resistivity of the films is less sensitive to environment humidity up to a value of 53% RH, while for higher values (53% - 98% RH), a good sensitivity is present.

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*Corresponding author: docorneliu@yahoo.com