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CO-sensing characteristics of $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ perovskite films prepared by RF magnetron sputtering

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ABSTRACT

$La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ films have been prepared by RF magnetron sputtering. The structure and carbon monoxide (CO)-sensing characteristics were investigated. The results demonstrated that $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ films showed a preference in orientation of (2 0 2) and (2 2 0). In a wide temperature range 80–300 °C, $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ film-based sensor showed good response to CO gas. An empirical relationship of $R = KC_{CO}^{\alpha}$ with $\alpha = 0.79$ can be obtained.

1. Introduction

Considerable scientific and technological research in solid-state gas sensors has been made due to the need of environmental monitoring and quantification of combustible gases based on their electrical conductivity change [1–3]. Carbon monoxide (CO) is one of the common poisonous gases, which can attach to the haemoglobin and damage the human body by producing a reduction in cellular respiration. The colorless, odorless as well as non-irritating natures of CO make it difficult to be detected, and the hazard of CO is exacerbated by its wide sources. As a result, CO sensors are indispensable in many fields, such as measuring CO concentrations of vehicle emissions, industrial waste, and the indoor atmosphere [4].

It is well known that a number of perovskite oxides (ABO_3, A = lanthanide or alkaline earth metal, B = transition metal) were used as gas-sensor materials because of their stability in thermal and chemical atmospheres. Recently, sensors based on ABO_3-type composite oxides have been studied to detect toxic and combustible gases [5–10]. The sensitivity and selectivity of this kind of sensors can be controlled by selecting suitable A and B atoms or chemical doping as $A_{1-x}A_xB_{1-y}B_yO_3$ materials [11–22].

As a part of our ongoing research on CO sensors, we reported that sensors based on $La_{0.8}Pb_{0.2}Fe_{1-x}Co_xO_3$ and $La_{0.8}Pb_{0.2}Fe_{1-x}Ni_xO_3$ powders showed high sensitivity to CO in a low-temperature range [23–25]. In this paper, $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LPFC) films were prepared by means of RF magnetron sputtering. The structure and CO sensing characteristics were investigated.

2. Experimental

$La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ films were deposited on quartz–glass substrates, the dimension of which was $10 \times 5\,mm^2$, in a JPGF-450 model RF magnetron sputtering system. The stoichiometric amount of La_2O_3, PbO, Fe_2O_3 and CoO were ball milled with ethanol for 12 h, then dried at 105 °C, and pressed in an aluminum holder for a target (diameter 80 mm, thickness 5 mm). The target was calcined for 12 h in air at a temperature of 1100 °C to obtain perovskite phase. The separation between the substrate and the target was 50 mm, a mixture of argon (Ar) and oxygen (O_2) was used as sputtering gas. During film deposition, the partial pressure of Ar and O_2 maintained at 1 Pa, respectively. The power for deposition was 200 W, and the time for deposition was 1 h.

Both ends of the samples were coated with Ag paste and used as electrodes, then calcined at 800 °C for 2 h in air to remove the organic binder. The gas-sensing properties were characterized using a computer-controlled gas-sensing characterization system.

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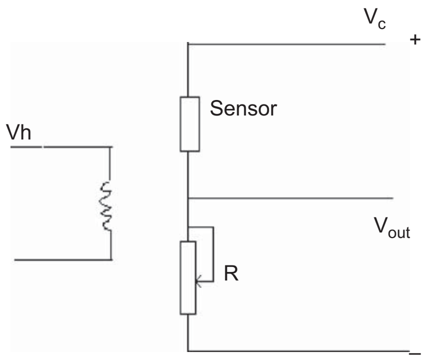

Fig. 1. Graphic of measuring principle.

The sensor resistance was measured by using a conventional circuit in which a sensor element was connected with an external resistor in series at a circuit voltage of 2.5 V. The scheme of the circuit was shown in Fig. 1. The heating voltage (V_h) was supplied to either of the coils for heating the sensors and the circuit voltage (V_c) was supplied across the sensors and the load resistor (R) connected in series. The signal voltage (V_{out}) across the load, which changed with sort and concentration of gas, was measured. The resistance of the load resistor was alternative and the heating voltage could be adjusted within a wide range.

The test gas was CO in dry air with a total flow rate of 500 sccm. Because the $La_{0.8}Pb_{0.2}Fe_{1-x}Co_xO_3$ materials are p-type materials, the electrical resistance of the sensors increases in a reducing gas circumstance. The sensor response S was defined as

$$S = (R_g - R_a)/R_g \times 100(\%) \quad (1)$$

where R_g was the DC (direct current) resistance measured under a working circumstance, while R_a was the resistance in air.

3. Results and discussion

3.1. Phase composition and structure of $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ films

The films were examined by X-ray diffraction (XRD) analysis to obtain the phase and structural composition. Fig. 2 reports the XRD patterns for the LPFC films (a) and the target material (b). It is found that the target material was perovskite phase with orthorhombic structure and the LPFC films by RF magnetron sputtering method showed a preference in orientation of (2 0 2) and (2 2 0). From diffraction peak width, the average crystallite size of LPFC film calculated according to Scherrer's equation [26] is about 32 nm. The morphology of LPFC film was obtained on a Hitachi S2500 scanning electron microscope. It is evident in Fig. 3 that the films show a structure with very small grain sizes, in accordance with the XRD findings. This grain size is approximately two times the Debye length for the depletion layer on the surface. It implies that the surface-sensing mechanism is more effective in these films.

The transmittance spectra of LPFC film was measured at room temperature as shown in Fig. 4. It can be seen that the transmittance spectra of LPFC film are highly transparent in the region from 600 to 800 nm. Rutherford backscattering spectrum (RBS) was used to establish the epitaxial nature of the LPFC film and measure the thickness of the thin film. Fig. 5 shows the RBS/Channeling spectra measured by RBS/Channeling method at the 1.7 MV tandem accelerator at the Shandong University using 2.1 MeV He^{2+} and a scattering angle of 165°. The lanthanum, lead, iron, and cobalt backscattering signals occurred at their expected surface positions as indicated in the figure. The RBS spectrum can be used to estimate the thickness of LPFC film as about 280 nm [27].

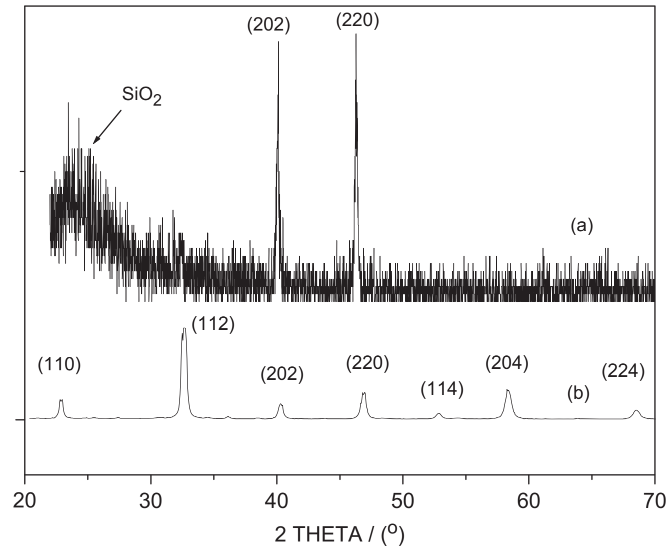

Fig. 2. XRD spectrum of (a) the deposited LPFC film and (b) LPFC sputter target.

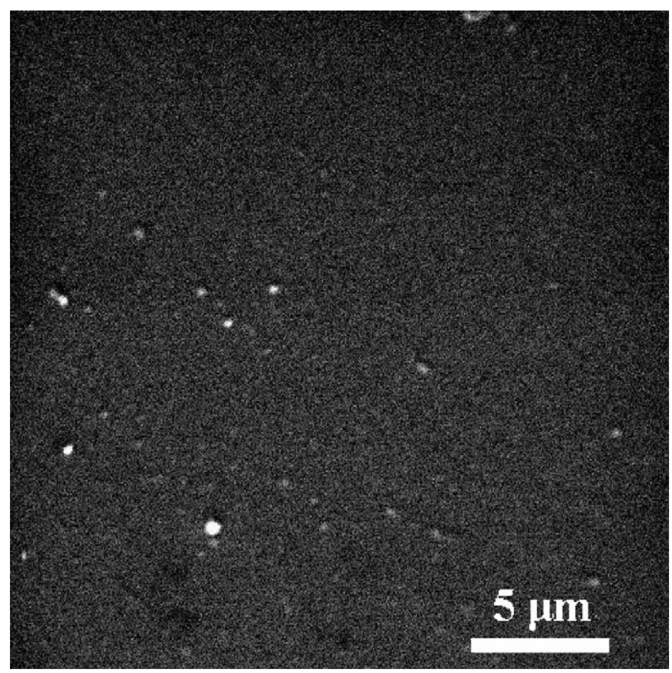

Fig. 3. SEM image of LPFC film.

3.2. Sensor response measurements

Fig. 6 shows the response of LPFC powders and LPFC film-based sensors to 200 ppm CO as a function of temperature. The response of LPFC film-based sensor is obviously higher than that of LPFC powders, and LPFC film-based sensor shows high response to CO with a wide temperature range 80–300 °C. The change in the resistance increases as the effective surface area increases, which results that LPFC film-based sensor has better response to CO gas. From this figure, we can found that the optimal operating temperature of the LPFC film sensor moved to higher operating temperature. This phenomenon can be explained by considering the effects of oxygen species on the film surface. At low