Sensing properties of perovskite oxide
La$_{1-x}$Sr$_x$CoO$_{3-δ}$ obtained by using pulsed laser deposition

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Summary: La$_{1-x}$Sr$_x$CoO$_{3-δ}$ belongs to the group of perovskite oxides of the ABO$_3$ structure, with a trivalent rare earth in the A position (La) and a trivalent metal ion in the B position (Co). Doping with divalent Sr-ions at the trivalent La-positions creates oxygen vacancies which give the oxide catalytic properties to H$_2$O$_2$. However, the conventional techniques which are used to prepare this oxide such as chemical methods, are not suitable for making a thin film. In this paper, a thin layer of La$_{1-x}$Sr$_x$CoO$_{3-δ}$ ($x=0.5$) perovskite oxide is deposited on a Pt electrode by using the Pulsed Laser Deposition technique. The catalytic properties of this perovskite oxide to hydrogen peroxide due to the presence of the oxygen vacancies will be discussed. The results show the possibility to use this perovskite oxide as a sensing material for potentiometric hydrogen peroxide sensors.

Keywords: perovskite oxide, La$_{1-x}$Sr$_x$CoO$_{3-δ}$, pulsed laser deposition, hydrogen peroxide

Category: 2 (Materials and technology) or 5 (Chemical sensors).

1 Introduction

La$_{1-x}$Sr$_x$CoO$_{3-δ}$ belongs to a group of perovskite oxides of the ABO$_3$ structure with a trivalent rare earth in the A position (La) and a trivalent metal ion in the B position (Co). The structure of the LaCoO$_3$ perovskite oxide consists of CoO$_6$ octahedra and the La$^{3+}$ ions, which are inserted between the CoO$_6$ octahedra. When the trivalent La$^{3+}$ ions in LaCoO$_3$ are replaced by divalent earth alkaline ions Sr$^{2+}$ to form La$_{1-x}$Sr$_x$CoO$_{3-δ}$ a positive charge is generated. Because the Co$^{3+}$ ions can have a different oxidation state, the charge neutrality is maintained by the formation of oxygen vacancies and a change in the valence state of the Co$^{3+}$ ions. Therefore, the oxide has an oxygen deficiency, δ, due to the high oxygen vacancy concentration.

This type of perovskite oxides is a promising candidate for solid oxide fuel cells, oxygen separation membranes and sensor material [1]. Different types of the perovskite oxides, which are synthesized by chemical methods, have been used as a material for hydrogen peroxide sensing. However, the response time of the sensor is quite low due to the long time it takes for the hydrogen peroxide to diffuse into the thick layer of the perovskite oxide. Among the existing deposition methods, the Pulsed Laser Deposition (PLD) is a suitable technique for the fabrication of a perovskite oxide thin film. This technique allows the stoichiometric transference of the deposited material from target to substrate [2]. In this paper, we show the possibility to obtain a thin La$_{1-x}$Sr$_x$CoO$_{3-δ}$ ($x=0.5$) perovskite oxide film by using the PLD technique and its sensing properties to hydrogen peroxide.

2 Experiments

The La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ thin film is deposited on platinum electrodes which were sputtered on a Ta$_2$O$_5$/SiO$_2$/Si wafer, using the setup as shown in Fig. 1. During the deposition process, a metallic shadow mask was placed on top of the substrate to shield the platinum electrical contacts from undesired deposition of the La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$. The ablation process of La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ is realized by a spatial uniform 248 nm excimer laser beam. The deposition time was varied from 5 to 7 min depending on the required thickness of the film. The thickness of the film was estimated to be about 75 nm after 5 min of deposition. After deposition, the sample was cooled down to room temperature in an O$_2$ flow. The annealing in the oxygen environment is necessary to obtain a stable composition and to create the oxygen vacancies in the perovskite oxide film. Finally, the wafer was diced in separated devices and encapsulated with Hysol®.

The sensing properties of the La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ thin film to hydrogen peroxide is characterized in a phosphate buffer (pH = 7.1) containing 0.1M KCl. All chemicals used (Merk, Fluka) were of analytical reagent grade.
3 Results and discussions

The La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ thin film shows catalytic properties to hydrogen peroxide. The potential response of the La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ electrode to a change in the hydrogen peroxide concentration has been measured with respect to a saturated calomel electrode (SCE) and is shown in Fig. 2.

The response time of the electrode potential to hydrogen peroxide is estimated to be about 15 min, which is quite long due to a low exchange-current density between hydrogen peroxide and La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$. The electrode potential response depends on the logarithm of the hydrogen peroxide concentration with a slope of 130 mV/dec (see Fig. 3).

The high sensitivity of La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ to hydrogen peroxide is suggested to be caused by a change in the oxygen vacancy concentration in La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ during its reaction with hydrogen peroxide:

$$\text{H}_2\text{O}_2 + 2e^- + V_O^\delta \rightarrow \frac{K}{2} \rightarrow \text{H}_2\text{O} + \text{O}_L^\delta$$

(1)

where $V_O^\delta$ and $O_L^\delta$ are the oxygen vacancy and the bound lattice oxygen, respectively. The reaction constant, $K$, of reaction 1 depends on the catalytic properties of the perovskite oxide, which is influenced by the strontium doping level in the perovskite oxide.

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References

