

Sensing properties of perovskite oxide $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ obtained by using pulsed laser deposition

Dam T.V. Anh*, W. Olthuis, P. Bergveld

MESA+ Research Institute, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands

Available online 1 June 2004

Abstract

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ 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_2O_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 $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x = 0.5$) perovskite oxide is deposited on a Pt electrode by using the pulsed laser deposition (PLD) 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.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Perovskite oxide; $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$; Pulsed laser deposition; Hydrogen peroxide

1. Introduction

$\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ 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). 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 $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$, a positive charge is generated. Because the Co^{z+} 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^{z+} ions. Therefore, the oxide has an oxygen deficiency, δ , due to the high oxygen vacancy concentration.

Because of the mixed conductive properties and a large variety in the oxide composition by choosing different A, A', and B elements and oxide stoichiometry x , the perovskite oxides $\text{A}_{1-x}\text{A}'_x\text{BO}_{3-\delta}$ have been used in many applications such as magnetic sensors, super capacitors, solid oxide fuel cells (SOFC) [1–3], and oxidation catalysts. Besides these applications, the perovskite oxides $\text{A}_{1-x}\text{A}'_x\text{BO}_{3-\delta}$ ($\text{A} = \text{La}$, $\text{A}' = \text{Ca}$, Sr , $\text{B} = \text{Co}$, Fe , etc.) have also been used

as a sensing material in oxygen [2], carbon monoxide, hydrocarbon [3], and nitrite oxide [4,5] sensors. The sensing principle of these sensors is mainly related to the catalytic oxidation of the compounds to be analyzed in the presence of the oxygen vacancies.

Due to the presence of oxygen vacancies, some perovskite oxides have a high catalytic activity to oxygen reduction and oxidation, and are also suitable for a H_2O_2 decomposition. The catalytic H_2O_2 decomposition of these perovskite oxides is not determined by the surface metal A, A', and B concentrations nor by the transition metal surface ratio [6]. Especially for La perovskite oxides, the catalytic H_2O_2 decomposition increases with increasing oxygen deficiency, δ . The higher the value of x , the higher the catalytic properties of the perovskite oxides to hydrogen peroxide can be obtained due to the increase in the oxygen deficiency. A first hydrogen peroxide sensor has been demonstrated by Shimizu et al. [7]. The response time of the sensor is quite low: about 20 min due to the very thick perovskite oxide sensing layer which was made by a chemical method. This problem can be solved by using physical deposition techniques such as reactive evaporation, metal–organic chemical vapor deposition (MOCVD) [8], RF sputtering [9], and laser evaporation. Among the existing deposition methods, the pulsed laser deposition (PLD) shows a large rate of deposition and a possibility to grow at relatively high oxygen background pressure, which guarantees stability of the composition of

* Corresponding author. Tel.: +31-53-489-2722; fax: +31-53-489-2287.
E-mail address: d.v.anh@el.utwente.nl (D.T.V. Anh).

the perovskite oxides [10]. Especially, the deposition temperature in the pulsed laser evaporation method is normally not higher than 700 °C. At this temperature, the perovskite deposition process is still compatible with the fabrication of the devices having Si based p–n junctions [11]. In this paper, we show the possibility to obtain a thin $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ perovskite oxide film by using the PLD technique and its sensing properties to hydrogen peroxide in relation with the presence of oxygen vacancies in the oxide.

2. Experiments

The $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ thin film is deposited on platinum electrodes which were sputtered on a $\text{Ta}_2\text{O}_5/\text{SiO}_2/\text{Si}$ 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 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$. The deposition process of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ 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 110 nm after 7 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 $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ to hydrogen peroxide is investigated by studying the potential of an $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode. The investigation of the oxygen vacancy concentration in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ during its reaction with hydrogen peroxide is done by means of the corresponding work function measurement. For this purpose, a thin layer of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ has been used as a gate material for an E^{MOSFET} (see Fig. 2). The working principle of the FET and the setup for the work function measurements have previously been reported in [12].

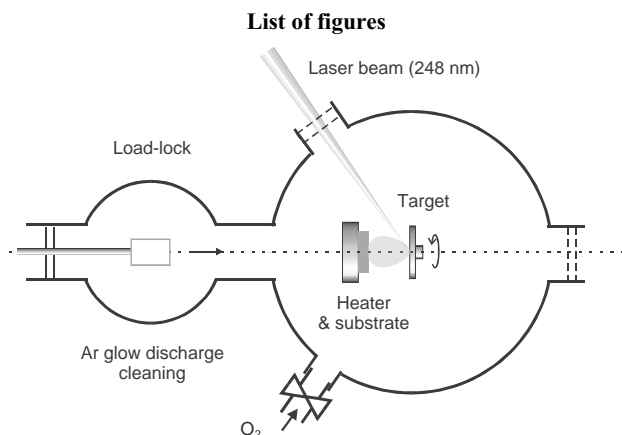
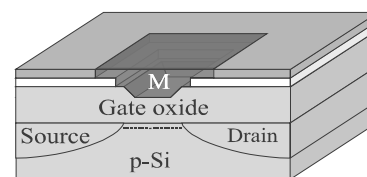


Fig. 1. Pulsed laser deposition system.



■ Perovskite oxide gate (M) ■ Insulation □ Pt

Fig. 2. The E^{MOSFET} with a perovskite oxide gate.

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

3. Results and discussions

The sensing properties of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ to hydrogen peroxide is investigated by measuring the potential of an $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode which contains the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ thin film deposited on a platinum electrode, while changing hydrogen peroxide concentration. The potential response has been measured with respect to a saturated calomel electrode (SCE) and is shown in Fig. 3. The $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ thin film shows catalytic properties to hydrogen peroxide at a concentration of hydrogen peroxide higher than 1 mM. Although the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ layer only has a thickness of 110 nm, the response time of the electrode potential to hydrogen peroxide is still quite long, which is estimated to be about 15 min due to a low exchange current density between hydrogen peroxide and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$.

The sensitivity of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ to hydrogen peroxide is suggested to be caused by a change in the oxygen vacancy concentration in $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ during its reaction with hydrogen peroxide according to Eq. (1):

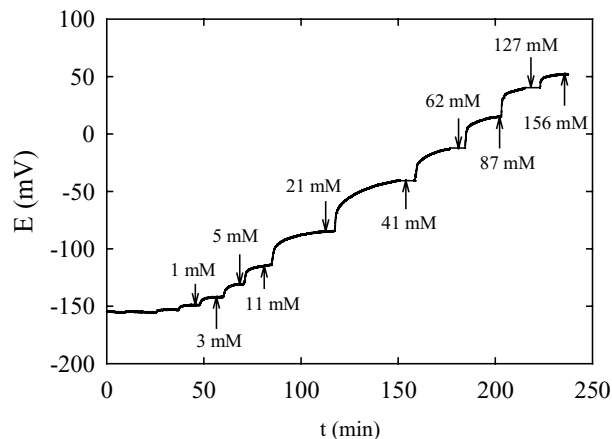
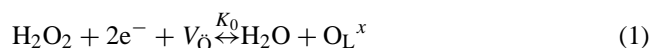


Fig. 3. Potential of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode as a function of the hydrogen peroxide concentration.

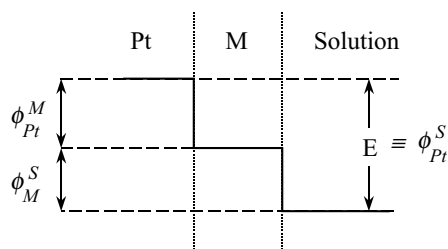


Fig. 4. Potential distribution of a sensing electrode which is in contact with solution.

where V_{O} and O_{L}^x are the oxygen vacancy and the bound lattice oxygen, respectively. The reaction constant, K_0 , of reaction 1 depends on the catalytic properties of the perovskite oxide, which is strongly influenced by the strontium doping level in the perovskite oxide.

It has been analyzed in [13] that the electrode potential, E , is established by two terms: ϕ_M^S and ϕ_{Pt}^M (Fig. 4). The first term, ϕ_M^S , can generally be called the interfacial potential. The second term, ϕ_{Pt}^M , is the contact potential determined by the difference in the work function in the sensing material, which is $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ in this case and the platinum. During the reaction between $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and hydrogen peroxide, variation of this contact potential gives a contribution to a change in the standard potential of the electrode, and thus results in a change in the electrode potential, E . As seen in Fig. 5, the electrode potential response depends on the logarithm of the hydrogen peroxide concentration with a slope of 130 mV/dec, which is higher than the Nernstian value. The super-Nernstian dependence is suggested to be caused by the variation of the oxygen vacancy concentration in the perovskite oxide during the reaction with hydrogen peroxide and is investigated by means of the work function measurement using the E^{MOSFET} .

Using the E^{MOSFET} based structure, which has a $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ gate, the change in the work function of $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ due to the presence of hydrogen peroxide can be measured as a change in the threshold voltage, V_T ,

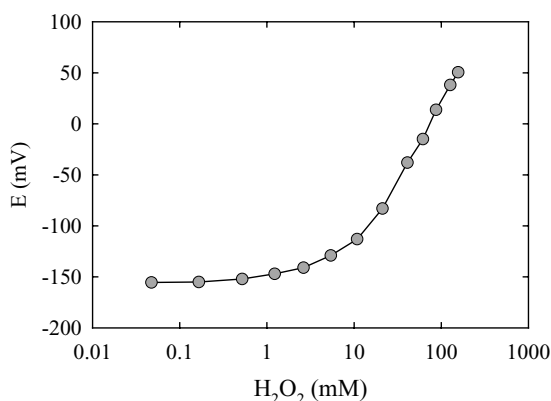


Fig. 5. Potential of the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ electrode as a function of the hydrogen peroxide concentration.

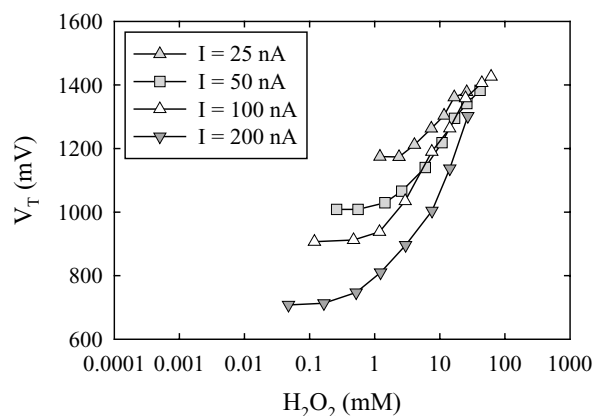


Fig. 6. Threshold voltage of the FET having a $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ gate as a function of H_2O_2 concentration at different values of the applied positive currents.

of the FET. In addition, due to the low exchange current density between hydrogen peroxide and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$, a small external DC current is used to accelerate the hydrogen peroxide decomposition, and therefore, to force the reaction between hydrogen peroxide and $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$. Consequently, the reaction constant of reaction 1 will be changed depending on the applied external current.

Firstly, the threshold voltage of the E^{MOSFET} having a $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ gate has been measured as a function of the hydrogen peroxide concentration when positive currents are applied. Fig. 6 shows that the threshold voltage, V_T , of the FET rises when the H_2O_2 concentration increases. This dependence is a function of the value of the applied positive currents. When the current is applied, in fact, the current influences the input electrochemical reaction between $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ and hydrogen peroxide that results in a high overpotential while the chemical reaction between the oxide and hydrogen peroxide stays the same. The reduction of H_2O_2 can easier occur when a higher positive current is applied. However, the detection limit of the threshold voltage has only been shifted slightly to a higher value when the value of the applied positive current rises. It can also be seen in the same figure that the sensitivity of the sensor based on $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ to H_2O_2 increases depending on the increase in the applied positive current. The sensitive range becomes wider when the applied positive current rises.

A similar measurement has also been done with a negative current. Fig. 7 shows the hydrogen peroxide dependence of the threshold voltage of the FET when a negative current of 25 and 50 nA is applied. At the negative applied current, the threshold voltage decreases to a lower value when the H_2O_2 concentration in solution increases.

The detection limit of the sensor is shifted to a higher value when the value of the applied negative current increases. The obtained result is different from the case when the positive current is applied in which case the detection limit is only slightly shifted. The sensitive range of the sensor when the negative current is applied is narrower than in

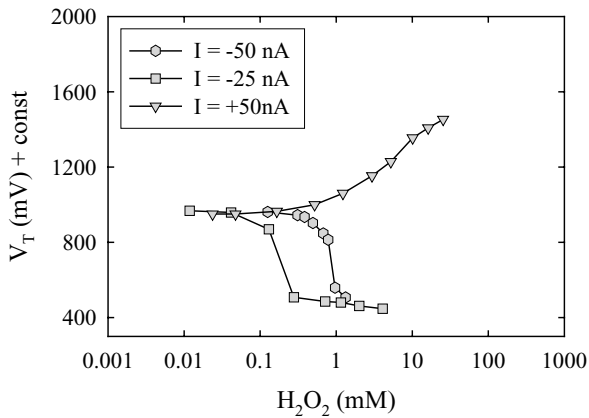


Fig. 7. Threshold voltage as a function of H₂O₂ concentration at different applied currents.

the case of applying the positive current. This can be explained by the different nature of the sensing reaction: reduction of hydrogen peroxide to water ($I > 0$) or oxidation of hydrogen peroxide to oxygen ($I < 0$).

4. Conclusions

This paper has shown the procedure for deposition of La_{0.5}Sr_{0.5}CoO_{3-δ} thin film by using the pulsed laser technique that is an advantage for sensing applications. The sensing property of La_{0.5}Sr_{0.5}CoO_{3-δ} to hydrogen peroxide has been studied by investigating the electrode potential response as well as monitoring the work function during its reaction with hydrogen peroxide. Experimental results show that the work function of the oxide, which is in relation with the oxygen vacancy concentration in the oxide is changed depending on the hydrogen peroxide concentration. This material can be used to detect hydrogen peroxide at milli-molar level.

Acknowledgements

The authors would like to thank Johan Bomer and Frank Roesthuis for technical support. The Dutch Tech-

nology Foundation (STW) is acknowledged for financial support.

References

- [1] S.J. Skinner, Recent advances in perovskite-type materials for SOFC cathodes, *Fuel Cells Bull.* 4 (33) (2001) 6–12.
- [2] P. Lukaszewicz, N. Miura, N. Yamazoe, A LaF₃-based oxygen sensor with perovskite-type oxide electrode operative at room temperature, *Sens. Actuators B Chem.* 1 (1990) 195–198.
- [3] E.L. Brosha, R. Mukundan, D.R. Brown, F.H. Garzon, J.H. Visser, M. Zanini, Z. Zhou, E.M. Logothetis, CO/HC sensors based on thin films of LaCoO_{3-δ} and La_{0.8}Sr_{0.2}CoO_{3-δ} metal oxides, *Sens. Actuators B Chem.* 69 (1–2) (2000) 171–182.
- [4] C. Tofan, D. Klvana, J. Kirchnerova, Decomposition of nitric oxide over perovskite oxide catalysts: effect of CO₂, H₂O and CH₄, *Appl. Catal. B* 36 (4) (2002) 311–323.
- [5] H.J. Hwang, M. Awano, Preparation of LaCoO₃ catalytic thin film by the sol-gel process and its NO decomposition characteristics, *J. Eur. Ceram. Soc.* 21 (10–11) (2001) 2103–2107.
- [6] Y. Ng. Lee, R.M. Lago, J.L.G. Fierro, J. González, Hydrogen peroxide decomposition over Ln_{1-x}A_xMnO₃ (Ln = La or Nd and A = K or Sr) perovskites, *Appl. Catal. A* 215 (1–2) (2001) 245–256.
- [7] Y. Shimizu, H. Komatsu, S. Michishita, N. Yamazo, N. Miura, Sensing characteristics of hydrogen peroxide sensor using carbon-based electrode loaded with perovskite-type oxide, *Sens. Actuators B Chem.* 34 (1–3) (1996) 493–498.
- [8] J.A. Rebane, O.Yu. Gorbenko, S.G. Suslov, N.V. Yakovlev, I.E. Korsakov, V.A. Amelichev, Y.D. Tretyakov, CVD synthesis and SNMS characterization of thin films of ABO₃ perovskite-type materials (PbTiO₃, La(Sr)CoO₃, La(Sr)MnO₃, LaNiO₃), *Thin Solid Films* 302 (1–2) (1997) 140–146.
- [9] C.M. Chiu, Y.H. Chang, The influence of microstructure and deposition methods on CO gas sensing properties of La_{0.8}Sr_{0.2}Co_{1-x}Ni_xO_{3-δ} perovskite films, *Sens. Actuators B Chem.* 54 (3) (1999) 236–242.
- [10] E.A.F. Spans, F.J.G. Roesthuis, D.A.H. Blank, H. Rogalla, Pulsed laser ablation of La_{0.5}Sr_{0.5}CoO_{3-δ}, *Appl. Surf. Sci.* 150 (1999) 171–177.
- [11] S. Zhao, J.K.O. Sin, B. Xu, M. Zhao, Z. Peng, H. Cai, A high performance ethanol sensor based on field-effect transistor using a LaFeO₃ nano-crystalline thin-film as a gate electrode, *Sens. Actuators B Chem.* 64 (1–3) (2000) 83–87.
- [12] P. Bergveld, J. Hendrikse, W. Olthuis, Theory and application of the material work function for chemical sensors based on the field effect principle, *Meas. Sci. Technol.* 9 (1998) 1801–1808.
- [13] Dam.T.V. Anh, W. Olthuis, P. Bergveld, Electroactive gate materials for a hydrogen peroxide sensitive E⁺MOSFET, *IEEE Sens. J.* 2 (1) (2002) 26–33.