

CATALYTIC HYDROGEN PEROXIDE DECOMPOSITION ON La_{1-x}Sr_xCoO_{3-δ} PEROVSKITE OXIDE

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ABSTRACT

Lanthanide perovskite oxides are mentioned as material for hydrogen peroxide sensor because they can catalytically decompose hydrogen peroxide in an aqueous medium. The catalytic properties of these perovskite oxides to hydrogen peroxide are suggested due to their oxygen vacancies influenced by the oxide non-stoichiometry. In this paper, we investigate the catalytic hydrogen peroxide decomposition of a La_{1-x}Sr_xCoO_{3-δ} thin film with x=0.7 for sensing application. The oxygen vacancy concentration in the oxide is estimated via the work function measurement using an electrolyte metal oxide semiconductor field effect transistor (^EMOSFET) with a platinum remote gate. The experimental results show the catalytic properties of this oxide to hydrogen peroxide increases with increasing its non-stoichiometry, x.

Keywords: La_{1-x}Sr_xCoO_{3-δ}, hydrogen peroxide, work function.

INTRODUCTION

La_{1-x}Sr_xCoO_{3-δ} belongs to perovskite oxide group A_{1-x}A'_xBO_{3-δ}, where A is a trivalent rare earth element, A' is an alkaline-earth metal and B is a transition metal. This oxide group has widely been used in many applications due to large variety in the oxide composition and stoichiometry.

By doping the alkaline-earth metal in the oxide that generates a positive charge, the charge neutrality is maintained by a change in the valence state of the transition metal and the formation of oxygen vacancies. The oxygen deficiency in the oxide, δ, is mainly determined by the non-stoichiometry of the oxide and redox properties of the transition metal.

Due to the presence of oxygen vacancies, these perovskite oxide types are able to selectively adsorb oxygen [1]. The high catalytic activity of perovskite oxides to oxygen reduction and oxidation is widely applied in solid oxide fuel cells (SOFC) [2], oxygen separation membranes [3] and sensors such as carbon monoxide, hydrocarbons (CH₄, C₄H₁₀) [4] and nitrite oxide [5,6] sensors at an elevated temperature. Especially in sensing applications, some lanthanide perovskite oxides are mentioned as material for hydrogen peroxide sensor because they can catalytically

decompose hydrogen peroxide in aqueous medium. A first hydrogen peroxide sensor has been demonstrated by Shimizu [7]. It has been suggested that the catalytic hydrogen peroxide decomposition of the lanthanide perovskite oxides is due to the oxygen vacancies. However there is no direct method to estimate the oxygen vacancy concentration in the oxide and how is influenced by on the hydrogen peroxide decomposition.

In this paper, we investigate the role of the oxygen vacancy and the influence of the oxide oxygen deficiency on the catalytic hydrogen peroxide decomposition of a La_{0.3}Sr_{0.7}CoO_{3-δ} thin film (LSCO0.7) for sensing application. Because the oxygen vacancy concentration of the oxide, which is seen as a doping level in the oxide, can be estimated via the work function measurement using an Electrolyte MOSFET (^EMOSFET) [8], we use La_{0.3}Sr_{0.7}CoO_{3-δ} as a gate material for the ^EMOSFET.

EXPERIMENT

The ^EMOSFET structure presented in this paper was fabricated using standard NMOS processing steps without a metal gate electrode [9]. The FET has a gate of 500 μm wide and 15 μm long and a gate oxide layer of tantalum oxide. Further a 200-nm thick platinum remote gate electrode with dimensions of 1.5 mm × 1.5 mm was deposited around the Ta₂O₅ gate oxide using sputtering (see Fig. 1).

For measuring the work function of La_{0.3}Sr_{0.7}CoO_{3-δ}, a 110-nm thick La_{0.3}Sr_{0.7}CoO_{3-δ} film obtained by the pulsed laser deposition (PLD) technique, is deposited on a gate area of the ^EMOSFET including the platinum remote gate as seen in Fig. 2.

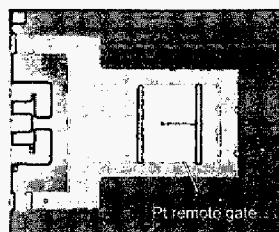


Fig. 1: An ^EMOSFET chip with a platinum remote gate.

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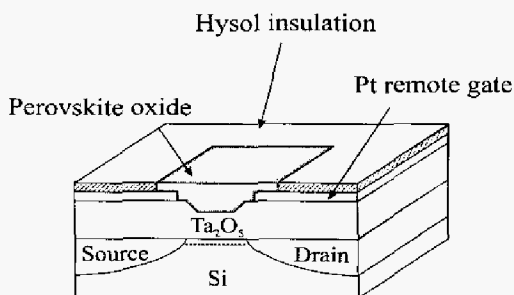


Fig. 2. Cross-section of an ^EMOSFET for measuring the work function change of $\text{La}_{0.7}\text{Sr}_{0.3}\text{CoO}_{3.5}$.

The benefits of using the PLD technique include proper control of the oxide stoichiometry, which plays a crucial role in the sensitivity of the sensor.

During the deposition process, a metallic shadow mask was placed on top of the ^EMOSFET to shield the electrical contacts from undesired deposition of the perovskite oxide. The ablation process of the oxide is realized by a spatial uniform 248 nm excimer laser beam as shown in Fig. 3. After deposition, the sample was slowly cooled down to room temperature in an oxygen flow to maintain a stable oxide composition and to create oxygen vacancies in the oxide.

Before packaging the sensor with Hysol[®] epoxy resin, a tantalum oxide film, formed by sputtering, and a polyimide film, formed by spin coating, are applied on top of the sensor to improve the adhesion of the epoxy resin. Finally, the wafer is diced and the single chip is mounted on a piece of PC board and encapsulated with epoxy.

The work function of the $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ thin film is monitored by measuring the threshold voltage of the FET using a FET amplifier. The hydrogen peroxide sensitivity of the threshold voltage is determined in a phosphate buffer (pH=7) containing 0.1M KCl as a supporting electrolyte. During measurement, the solution is continuously stirred at a constant rate while small known volumes of the hydrogen peroxide stock solution are added. In order to increase the exchange current between $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ and solution a nano-current source is used as described earlier in [8].

The work function of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ during its reaction with H_2O_2 is investigated by means of monitoring the threshold voltage, V_T , of this FET structure using an FET amplifier.

RESULT AND DISCUSSION

Figure 4 shows the threshold voltage, V_T , measured in phosphate buffer while small amounts of hydrogen peroxide solution are added. The reaction between

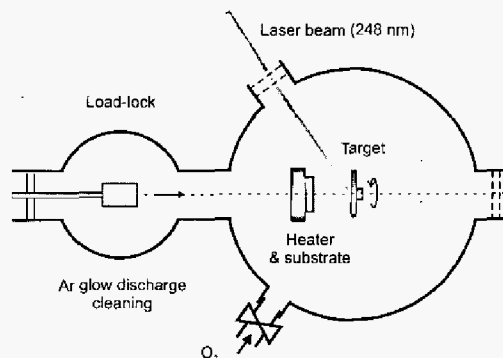
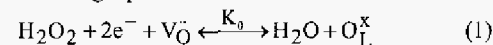


Fig. 3. Pulsed Laser Deposition system.

hydrogen peroxide and the oxide is proposed by the following equation:



where $V_O^{\cdot\cdot}$, O_L^x and K_0 are oxygen vacancy, bound lattice oxygen and the reaction constant, respectively. According to this equation, the decomposition of H_2O_2 rises with increasing oxygen vacancy concentration. The threshold voltage, which is determined by the oxygen vacancies in $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$, is increased as the H_2O_2 concentration increases (see Fig. 5).

Although the $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ gate is relatively thin, the response time of the V_T to the change in the H_2O_2 concentration is still in the order of minutes due to a low exchange current between the oxide and the solution. To accelerate the diffusion and exchange process of H_2O_2 with the oxide, an external DC nano-current has been applied between $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ and the solution. The external current is applied between the remote gate electrode and a counter electrode while independently monitoring the V_T response to the change in hydrogen

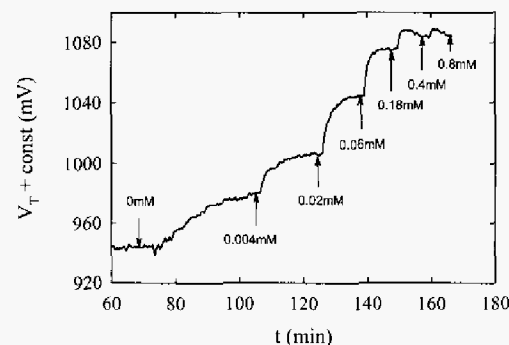


Fig. 4. Threshold voltage of the FET having a $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ gate as function of time when a small amount of H_2O_2 solution is added.

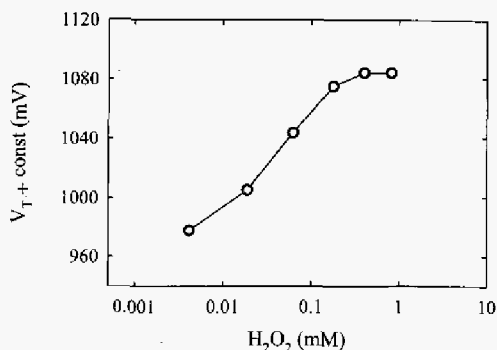


Fig. 5. Threshold voltage of the FET having a $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ gate as function of time when a small amount of H_2O_2 solution is added.

peroxide concentration in the same solution [8].

Dependence of the V_T on the H_2O_2 concentration when a current of 25 nA is applied is shown in Fig. 6. The sensitivity of the threshold voltage to the H_2O_2 concentration increases due to an increase in the exchange current between H_2O_2 and $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$. In case of applying current, the decomposition of hydrogen peroxide still follows Eq. 1, however the reaction constant is changed due to applying the external current. Similarly to the case without applying current, the threshold voltage increases with increasing of the hydrogen peroxide concentration. The sensor shows a higher sensitivity to hydrogen peroxide because in this case the electrons involved in Eq. 1 are partly supplied by the current.

Comparing with a similar lanthanide perovskite oxide but with a different stoichiometry, $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3.5}$ [10], the $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ shows a lower detection limit. It shows that the oxygen deficiency in the oxide is influenced by the oxide stoichiometry.

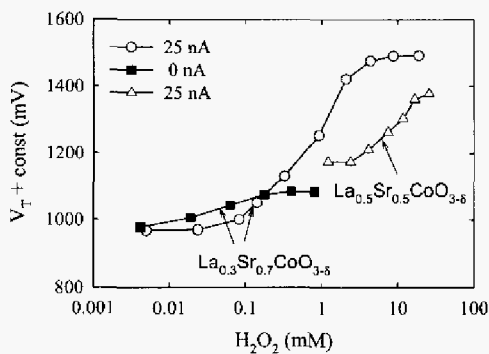


Fig. 6. Dependence of V_T on H_2O_2 concentration at different values of the applied current for different types of gate material.

CONCLUSIONS

We have investigated the oxygen vacancy concentration of $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3.5}$ and its catalytic properties to hydrogen peroxide via the work function measurement by using an FET . The experimental results show that the exchange current between the oxide and hydrogen peroxide is rather low even when the oxide layer is quite thin. The exchange process of hydrogen peroxide with the oxide can be accelerated by applying an extra current between the oxide and the solution. This current enhances the H_2O_2 decomposition and increases the sensitivity of the sensor to hydrogen peroxide. The work function measurement also shows that the oxide is more sensitive to hydrogen peroxide when the x value increases, i.e. when the oxide has the higher oxygen deficiency.

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