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Study on Oxygen-Sensing Properties of $LaNiO_3$ Thin Films

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Abstract. The synthesis of rare-earth perovskite-type composition thin films of $LaNiO_3$ by means of the inorganic-sol-gel (ISG) method was studied. The structural stability under high temperature in reducing atmospheres and the oxygen-sensitivity mechanism of the $LaNiO_3$ thin films were examined. It is shown that under the experimental conditions, $LaNiO_3$ decomposes and the valance states of nickel are +2 and +3.

Keywords: $LaNiO_3$ thin film, perovskite, inorganic-sol-gel (ISG) method

1. Introduction

As environmental pollution, caused by the exhaust gas from automobiles, becomes more and more serious, controlling exhaust emissions has generated great interest in governments all over the world. Therefore, sensing materials for automotive waste gases are widely studied and exploited. At present, two different types of automotive oxygen air/fuel (A/F) sensors have been developed for this application in order to increase the engine's efficiency, increase its useful life, save energy and reduce pollution. One type is an electrochemical oxygen-concentration cell based on ZrO_2, the other is a semiconducting resistive device made from TiO_2 [1, 2]. Besides ZrO_2 and TiO_2, materials such as SnO_2, Nb_2O_5, CeO_2, CoO, $Co_{1-x}Mg_xO$ and $SrMg_xTi_{1-x}O_3$ are commonly used. Because of the complexity and the high cost associated with some materials, scientists continue to be interested in new, low cost and simple electronic gas sensing elements. The defect structure and electrical properties of $LaNiO_3$ have been examined, but studies of $LaNiO_3$ ceramics as oxygen sensitive materials are only preliminary [3, 4]. In this paper, the rare-earth perovskite oxide $LaNiO_3$ was examined as a new kind of gas sensing material for automotive waste gases. The structural stability under high temperature in reducing atmospheres and the oxygen-sensitivity mechanism were studied.

2. Experimental

$LaNiO_3$ thin films were prepared on Al_2O_3 substrates by means of a sol-gel method in which lanthanum nitrate [$La(NO_3)_3{\cdot}6H_2O$] and nickel nitrate [$Ni(NO_3)_2{\cdot}6H_2O$] were used as raw materials. They were dissolved in deionized water, and then mixed in a ratio of La:Ni = 1:1. Citric acid was added to the water solutions as a chelating agent to form a clear and stable sol. A polycrystalline Al_2O_3 substrate was dipped into the solution and the solution was coated on the substrate surface uniformly. The sol was then dried under vacuum at 120°C to remove water, and the citrate component formed a film on the substrate. Afterwards, the dried samples were heated at 800°C with a heating rate of 20°C $\cdot min^{-1}$, and decomposed after 1 hour. The above steps were repeated until the $LaNiO_3$ thin film reached an appropriate thickness (usually for 6–7 cycles, the thickness is about 1 μm). Finally, the films were sintered at 800°C for 2 hours.

The crystal structure of the $LaNiO_3$ films was analyzed by X-ray diffraction (XRD) with Cu K_α radiation. Temperature-programmed reduction (TPR) was carried out in a microbalance operated to an accuracy of 0.01 mg. The sample was pumped for 1 h at room temperature and then put in contact with 1.67 mole% H_2/N_2 flow. After this, the temperature was linearly increased at 4 K min^{-1} to the desired temperature. The observed weight loss was taken as a measurement of

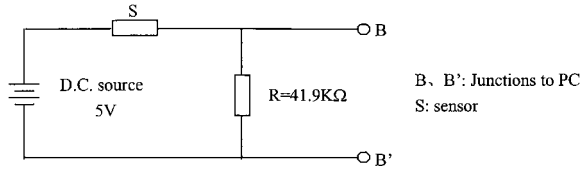

Fig. 1. Electric circuit diagram for testing gas-sensing properties.

its degree of reduction in term of electrons (e^-) per molecule. For $1e^-$ per molecule Ni^{3+} is reduced to Ni^{2+}, the weight loss of the sample being 3.26%. For $3e^-$ per molecule Ni^{3+} is reduced to Ni^0, the weight loss of the sample being 9.77%. Oxygen-sensitivity tests were conducted under flowing gas conditions. The oxygen content was switched between H_2/N_2 and O_2/N_2 atmospheres. The composition of H_2/N_2 and O_2/N_2 used in this paper is 1.67 mole%, chosen to imitate the exhaust conditions in car engines. The oxidizing atmospheres—1.67 mole% O_2/N_2 simulated the lean-burn region and the reducing atmospheres simulated the rich-burn region. The flow rate of the test gas mixture was 1000 cm^3/min. The electric circuit for measuring conductivity changes is shown in Fig. 1. A fixed resistance R [41.9 kΩ] was connected in series with the thin film, and the electric current flowing through the film was measured with a personal computer as the potential drop across R.

3. Results and Discussion

3.1. *Stability of the Perovskite Phase $LaNiO_3$ Thin Films*

Lanthanum nickelate ($LaNiO_3$) exhibits a high concentration of defects in the oxygen sublattice that involves both oxygen deficit at low oxygen partial pressure (Po_2) and oxygen excess at higher Po_2 values. Accordingly, the correct formula of this compound is $LaNiO_{3-\delta}$, where the oxygen nonstoichiometry (δ) may be negative or positive. In this paper oxygen vacancies become the exclusive defects and δ is positive, for oxygen partial pressures $<10^3$ Pa. At low values of the deviation from stoichiometry ($\delta \approx 0$), the defects in crystal form an ideal solid solution [5], and $LaNiO_3$ exhibits high conductivity. However, it is expected that at high defect concentrations, the perovskite structure will be destroyed, and the bulk resistance of $LaNiO_3$ will increase

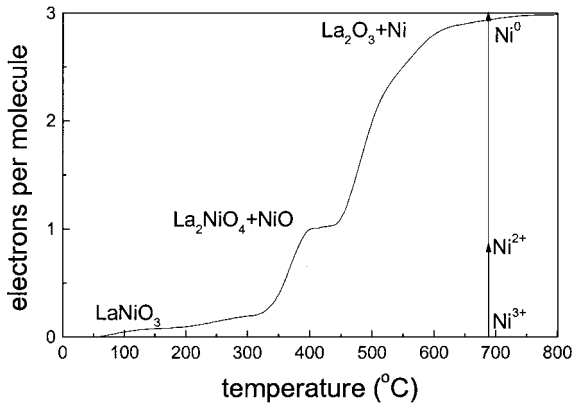

Fig. 2. Temperature-programmed reduction of $LaNiO_3$.

rapidly. For $LaNiO_3$ thin films, as the degree of reduction increases, chemisorption oxygen (O^-) decreases, oxygen vacancy concentration increases, and surface resistance rapidly increases. Therefore $LaNiO_3$ would appear to be a promoting candidate for use as a gas sensing material.

The TPR diagram of $LaNiO_3$ in terms of electrons per molecule against temperature is given in Fig. 2. Two reduction steps are observed. The first step of 1e per molecule takes place between 573 and 723 K; the second step of 3e per molecule occurs between 773 and 1073 K. Similar reduction steps were found for $PrCoO_3$ [6].

XRD patterns of the $LaNiO_3$ sample treated at different temperatures in 1.67 mole% H_2/N_2 for 1 hour (shown in Fig. 3) indicate that the equation of the overall reduction reaction above can be written as follows:

$$LaNiO_3 + \delta H_2 \rightarrow LaNiO_{3-\delta} + \delta H_2O \quad (1)$$

$$2LaNiO_3 + H_2 \rightarrow La_2NiO_4 + NiO + H_2O \quad (2)$$

$$NiO + H_2 \rightarrow Ni + H_2O \quad (3)$$

$$La_2NiO_4 + H_2 \rightarrow La_2O_3 + Ni + H_2O \quad (4)$$

Curve (a) in Fig. 3 is the XRD spectrum of the as-prepared perovskite $LaNiO_3$. The patterns obtained after reduction to 1e per molecule show only peaks of $LaNiO_3$ (curve (b)), although these are less intense than those of the starting samples (curve (a)). It appears that the concentration of oxygen vacancies produced in the first reduction step does not destroy the perovskite structure. The reduction reaction corresponds

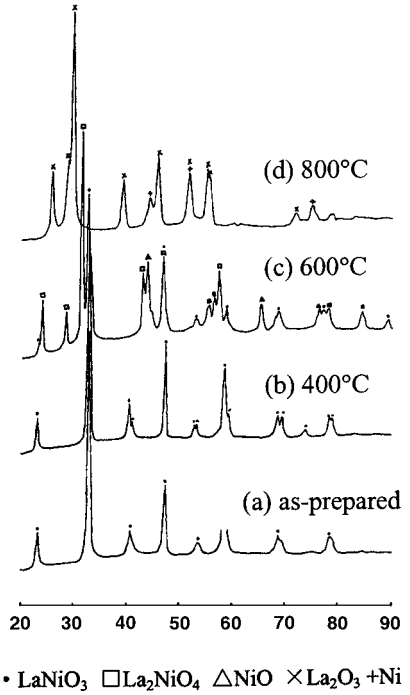

Fig. 3. XRD of the $LaNiO_3$ treated sample at different temperatures under 1.67% H_2/N_2.

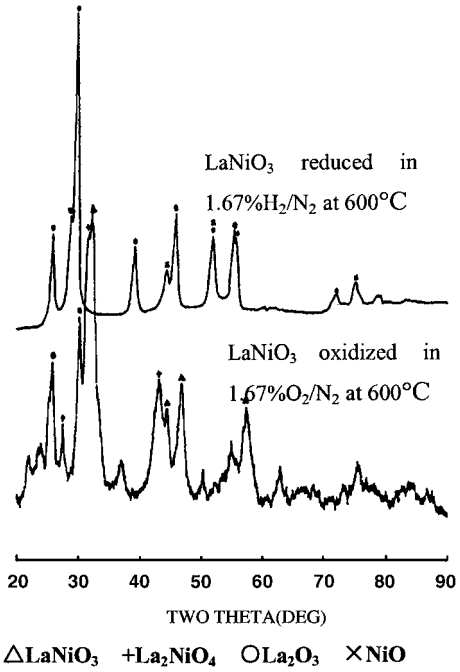

Fig. 4. XRD pattern of the reduction product of $LaNiO_3$ treated in 1.67% O_2/N_2 at 600°C.

to Eq. (1). After reoxidation a spectrum equivalent to that in curve (a) is obtained. The patterns of $LaNiO_3$ reduced to 3e per molecule $LaNiO_3$ (curve (c) and curve (d)) include the peaks of La_2NiO_4, NiO, La_2O_3 and Ni. The perovskite structure was completely destroyed and corresponding reactions are shown in equations of (2), (3) and (4). By reoxidation, the reactions can be written as follows:

$$Ni + 1/2O_2 \rightarrow NiO \tag{5}$$

$$La_2O_3 + Ni + 1/2O_2 \rightarrow La_2NiO_4 \tag{6}$$

$$La_2NiO_4 + NiO + 1/2O_2 \rightarrow 2LaNiO_3 \tag{7}$$

Equations of (5), (6) and (7) reflect complete reactions of the oxides to perovskite (sintering at 800°C for 2 hours in air). However, under our experimental conditions (between 500–800°C for 30 seconds in 1.67 mole% O_2/N_2), only partial reaction of these oxides to perovskite occurs. Because the particle size of NiO and La_2NiO_4 formed in reactions of (5) and (6) are too large, complete reaction of the oxides does not occur. As a result, full conversion to perovskite becomes difficult (Fig. 4).

The temperature range of the automobiles exhaust gas is from 400–800°C, under this range, $LaNiO_3$ is apparently unstable and decomposes to a mixture of La_2NiO_4 and NiO. In the system of $LaNiO_3$-La_2NiO_4-NiO, the valence states of nickel are +2 and +3, so these componds can be represented by the general formula $La(Ni^{3+}_{1-2x}Ni^{2+}_{2x})O_{3-x}$ $(0 \leq x \leq 0.5)$.

3.2. *Oxygen-Sensitivity Mechanism of $LaNiO_3$*

The resistance of metal oxide semiconducting sensors changes with the concentration of oxygen in the test gas mixture. Figures 5 and 6 show the electrical response of a $LaNiO_3$ thin film to 1.67 mole% H_2/N_2 and 1.67 mole% O_2/N_2 atmospheres at selected temperatures in the range 500–800°C. The higher the potential drop across the fixed resistance R, the smaller the resistance of the $LaNiO_3$ thin film, and vice versa. One can observe that there is a decrease in conductivity upon the introduction of H_2. As H_2 is a reducing gas, this confirms that $LaNiO_3$ behaves as a p-type semiconducting oxide. The electrical response of a $LaNiO_3$ thin film in an atmosphere containing O_2, which is an

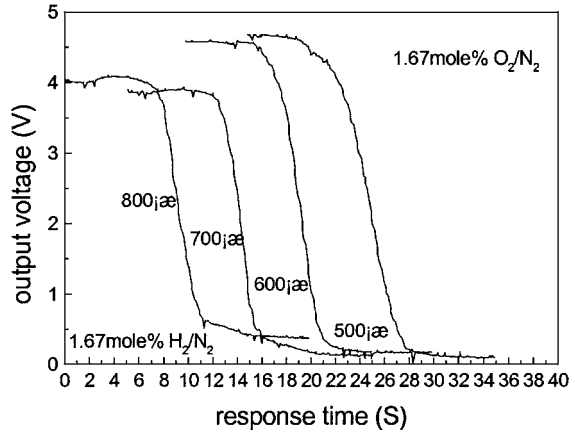

Fig. 5. Response time for $LaNiO_3$ from O_2 to H_2 atmosphere.

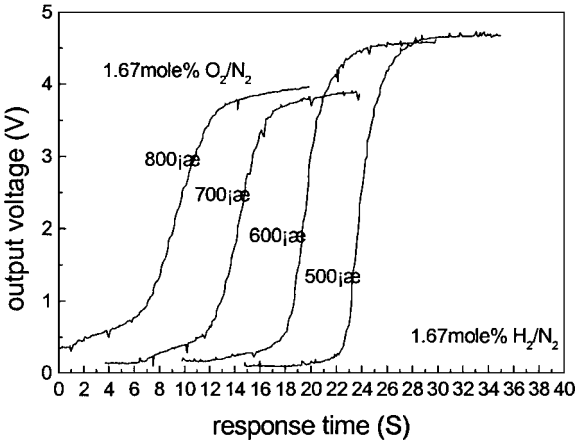

Fig. 6. Response time for $LaNiO_3$ from H_2 to O_2 atmosphere.

oxidizing gas, is also consistent with p-type semiconductor behavior. The conductivity of $LaNiO_3$ films increases upon exposure to 1.67 mole% O_2/N_2 gas flow.

The H_2 response sensitivity of the sensors was larger at lower temperatures, however the response time was longer (larger than 4 seconds at 500°C). The response time (from 30% to 70% of the maximum value) turned shorter at higher temperatures, being about 1 second at 700°C. The O_2 response sensitivity of the $LaNiO_3$ films was larger at lower temperatures, and the response speed also became faster (from 30% to 70% of the maximum value), being about 2 seconds at 500°C.

On the basis of the experimental results, we propose a mechanism for gas sensing on $LaNiO_3$. The process of the resistivity change in $LaNiO_3$ thin films with ambient atmosphere can be divided into two steps. First, surface conductivity is changed by absorption, a fast process. When O_2 is absorbed, it removes electrons from $LaNiO_3$.

$$1/2O_{2(g)} + ne^- \rightarrow O^{n-}_{(ads.)} \tag{8}$$

As O_2 is absorbed in the forms of O^{2-}, O^-, O_2^-, it causes the surface band of semiconductor to bend upward and the surface conductivity increases. When reducing gas (H_2) was absorbed, it donates electrons to $LaNiO_3$.

$$1/2H_{2(g)} \rightarrow H^+_{(ads.)} + ne^- \tag{9}$$

The surface band bends downward and the surface conductivity decreases.

Second, the equilibrium between lattice oxygen and ambient O_2 makes the bulk resistance change.

$$O^{2-}_{ad} \Leftrightarrow O^{2-}_L (O^{2-}_L : \quad \text{lattice oxygen in } LaNiO_3) \tag{10}$$

At low Po_2, the lattice oxygen will move to the surface and reacts with the adsorbed hydrogen:

$$2H^+_{(ads.)} + O^{n-}_{(ads.)} \rightarrow H_2O + (n-2)e^- \tag{11}$$

In this case the perovskite structure is damaged according to Eqs. (2), (3) and (4), and the conductivity of $LaNiO_3$ thin films decreases.

At high Po_2, the adsorbed oxygen diffuses into the body and the perovskite structure is recovered according to Eqs. (5), (6) and (7), then the conductivity increases.

From the results of Fig. 7, it can be observed that the $La(Ni^{3+}_{1-2x}Ni^{2+}_{2x})O_{3-x}$ thin film exhibits a fairly good reproducibility, but only in a short time basis. This is consistent with oxidation-reduction

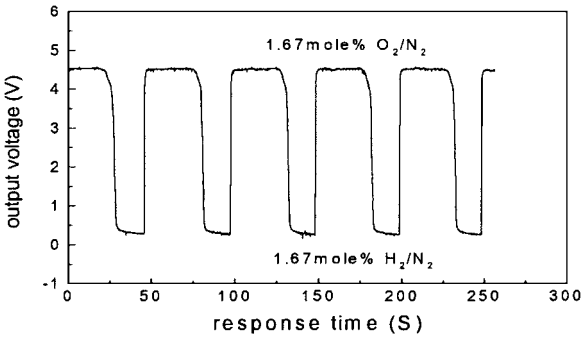

Fig. 7. Reproducibility of $La(Ni^{3+}_{1-2x}Ni^{2+}_{2x})O_{3-x}$ thin film at 600°C.

characteristics of $La(Ni^{3+}_{1-2x}Ni^{2+}_{2x})O_{3-x}$ under our experimental condition.

4. Conclusion

Rare-earth perovskite type oxide $LaNiO_3$ thin films were prepared using inorganic-sol-gel (ISG) method and exhibited good gas sensitivity and fast response. Under the experimental conditions of this study, $LaNiO_3$ decomposes and the valence states of nickel in the system of $LaNiO_3$ are $+2$ and $+3$, so these compounds can be represented by the general formula $La(Ni^{3+}_{1-2x}Ni^{2+}_{2x})O_{3-x}$ $(0 \leq x \leq 0.5)$. Due to the reaction of adsorbed oxygen species on the surface of the p-type semiconducting material, the resistance changes with the concentration of oxygen. But as automotive oxygen air/fuel sensor, further improvements in the stability, the gas sensitivity and response time are needed.

Acknowledgment

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