

# Pt Deposition Effect for the Catalyst of the Semiconducting Oxygen Sensor

Seong-Soon Cho and Ho-Gi Kim

Department of Materials Science and Engineering  
Korea Advanced Institute of Science and Technology  
373-1 Kusung-dong Yusung-gu Taejon 305-701 Korea

**Abstract - La-doped SrTiO<sub>3</sub> thick film has been studied from the viewpoint of application for a lambda sensor, especially the effect of Pt deposition as catalyst at low temperature. The as-deposited film was transformed into fine particles less than 0.1 μm and distributed very homogeneously on the surface. The response of the sensor was more symmetric and fastened with aid of Pt particles. But it was difficult to overcome the nonsymmetric behavior perfectly.**

## I. INTRODUCTION

The oxygen sensors have been used to control combustion process, especially in the automobile engineering[1]. SrTiO<sub>3</sub>, which is a nonstoichiometric oxide with perovskite structure, is an oxygen sensor that operates on the principle of the semiconductor[2]. Pure SrTiO<sub>3</sub>, it has large diffusion coefficient originating from coupled motion of ionic charge carriers and electronic charge carriers(ambipolar diffusion phenomena)[3]. So, it was reported that one possible way to realize the measurement and control of fast combustion processes, especially in automobile engineering is the use of resistive oxygen sensors based on thin or thick films of titanates[4, 5]. But in this case, the sensor can be only applicable at higher temperature than at the operating temperature of common electrochemical type oxygen sensors(ZrO<sub>2</sub>)[1]. For detecting the stoichiometric point in automobiles requires those

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materials keep n- or p-type over the whole lambda range. N-type dopants like La can extend the n-type conduction region in a oxygen partial pressure higher than 10<sup>-2</sup>Pa[6]. So it is seemed to be suitable for application as an oxygen sensor. Generally catalysts are added to the sensor both to speed up the reaction, so the response time is reduced to seconds instead of hours and to impart selectivity to the reaction, so some reaction processes are favored over others.

In this study, to speed up the response time of La<sub>2</sub>O<sub>3</sub>-doped(10mol%) SrTiO<sub>3</sub>(Sr/Ti ratio=0.9) thick film lambda sensors, especially at low temperature, Pt particles were deposited at various conditions by DC magnetron sputtering method. The effect of Pt(or catalyst) on the transient response of the SrTiO<sub>3</sub> thick film lambda sensor has not been reported yet.

## II. EXPERIMENTAL

The designated amounts of raw materials (0.9SrCO<sub>3</sub>+TiO<sub>2</sub>+0.1La<sub>2</sub>O<sub>3</sub>, Rare Metal Co., Junsei Chemical Co. Japan) were wet-mixed and calcined at 1150°C for 2hours. The thick film sensors were prepared on Al<sub>2</sub>O<sub>3</sub> substrate(Kyocera A476, Japan) by a screen printing method(6x10mm, 250 mesh). The printed films were sintered at 1300°C for 1 hour. To distribute Pt as catalytic particles on the surface of the sensor, Pt thin film was deposited by DC magnetron sputtering method at room temperature. Table 1 shows the deposition conditions for

TABLE I Sputtering conditions for Pt film.

Base Pressure	< 5 x 10 <sup>-6</sup> torr
Working Pressure	5 ~ 10 x 10 <sup>-3</sup> torr
Power	20~50 Watt
Ar flow	10 sccm
Target	Metal, 3"
Substrate Temp.	Room temp.
Pre-sputter Time	> 10 min

Pt thin film. The deposition time was varied from 30 to 90 seconds. Pt electrodes (TR 7095, Johnson Matthey) were printed on the top of the thick films with an interdigital pattern and sintered at 1050°C for 10 minutes. Response behavior as a lambda sensor was examined by the use of two probe dc technique with the circuit based on short circuit theorem. The excess air/fuel ratio,  $\lambda$ ,  $\lambda = (\text{Air}/\text{C}_3\text{H}_8) / (\text{Air}/\text{C}_3\text{H}_8)_{\text{stoichiometric}}$ , between 0.95 (rich-burn) and 1.05 (lean-burn) was controlled by the use of Yttria-Stabilized ZrO<sub>2</sub> (Bosch, Germany) used in common automobiles operated near 600°C, which is interfaced with main computer. The response behavior of the thick film sensor was analyzed with A/D converter at 366°C.

### III. RESULTS AND DISCUSSION

Fig. 1 shows XRD patterns of the thick film sensor with Pt deposition time. After 90 second-deposition, the thickness of Pt film was considered about 10nm. As-deposited Pt film at room temperature existed mainly amorphous phase, so it is difficult to detect Pt peaks. But after sintering at 1050°C, it became crystalline phase and mainly oriented (111) direction. With longer deposition time, the intensity and crystallinity of Pt (111) direction was increased.

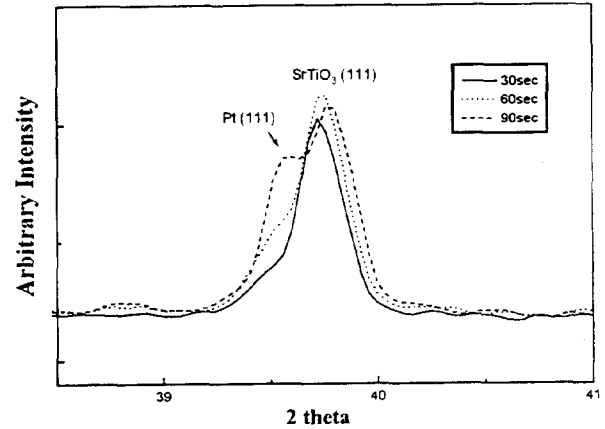


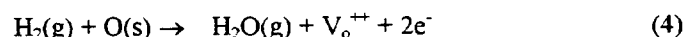
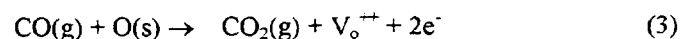
Fig. 1 XRD patterns of the sensors with deposition time.

Fig. 2 shows the SEM photos of sensors with Pt-deposition time. In the case of as-deposited sensor, it was difficult to observe the Pt film or particles on the surface of the sensor, because the film was very thin and not crystallized well at room temperature. After sintering at 1050°C, the Pt film were transformed into fine particles to reduce total surface energy. The particles were distributed very homogeneously and fine less than 0.1  $\mu\text{m}$ . This is a very simple and reproductive method regarding past report[6].

Fig. 3 shows transient response of the La-doped SrTiO<sub>3</sub> oxygen sensor at 366°C with a function of deposition time. Typical rich to lean and lean to rich voltage switching curves are nonsymmetric, because of the difference of the switching mechanisms. When the intake air/fuel mixture is suddenly changed rich to lean condition, the excess oxygen becomes available for the following reactions,



where  $\text{V}_\text{o}^{++}$  is doubly ionized oxygen vacancy. But lean to rich switch, predominant triple-point reactions which governs sensor voltage are



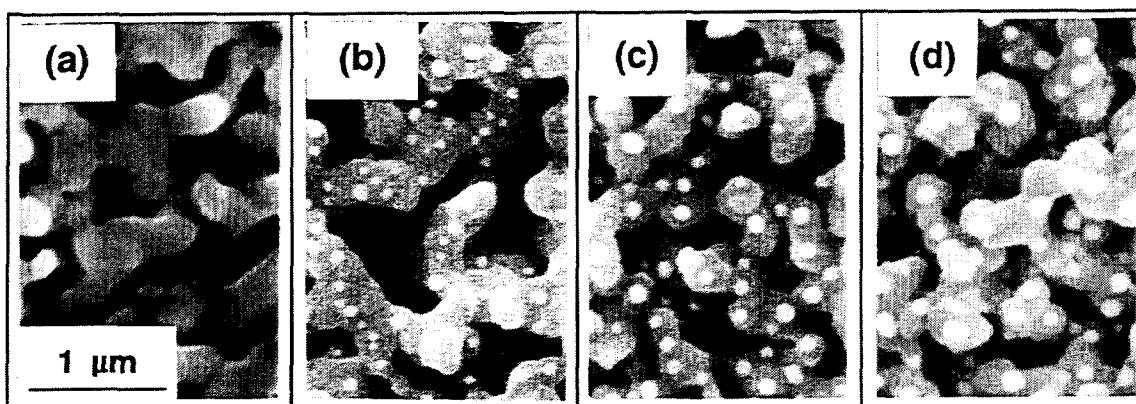


Fig. 2 SEM Photos of the sensors with deposition time.

(a) 0 , (b) 30, (c) 60, (d) 90 seconds

So the sensor without Pt particles(Fig. 3(a)) showed a nonsymmetric and sluggish response. That is the response time( $t_{20\% \text{ of } V_{\max}} \rightarrow t_{80\% \text{ of } V_{\max}}$ ) is 1.2 sec when air/fuel changed from lean to rich transition, but 0.7 sec from rich to lean transition. But increasing deposition time, the sensor showed that response is more fastened and step-wise symmetric. The Pt particles enhanced gas reaction at

sensor/gas/electrode interface and fastened response time of the sensor. So the Pt- deposited sensors (Fig. 3(b) - (d)) shows faster response time shorter than 0.1 second. Regarding [5], this is very fast response especially at low temperature.

But as shown in Fig. 4, the response rate, defined as sensor voltage change rate per time, was nonsymmetric in

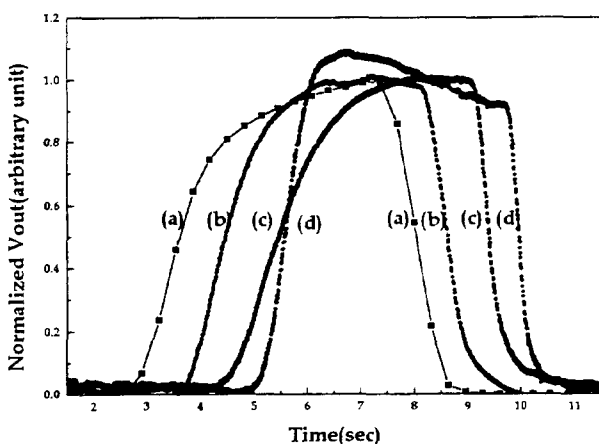


Fig. 3. Response behavior of the sensors with deposition time. (a) 0 , (b) 30, (c) 60, (d) 90 seconds

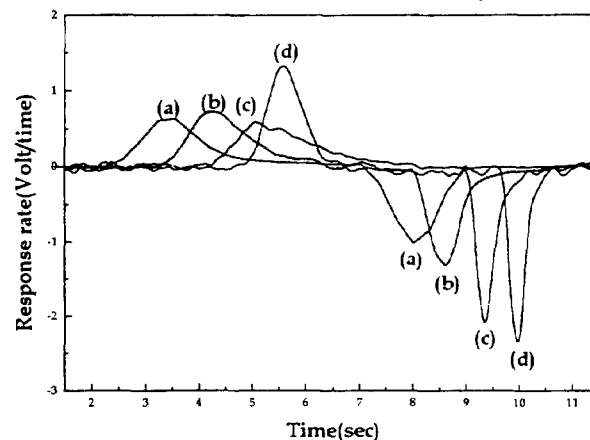


Fig. 4 Response rate of the sensors with deposition time. (a) 0 , (b) 30, (c) 60, (d) 90 seconds

spite of Pt-deposition. The reasons are considered that the reaction rate is different between lean to rich transition and rich to lean. Though it is possible to fasten the response rate but difficult to overcome the nonsymmetric response behavior.

#### IV. CONCLUSIONS

By use of DC magnetron sputtering, it is possible to distribute Pt particles very homogeneously on the top surface of the thick film sensor. After Sintering, the Pt film was transformed into fine particles less than 0.1  $\mu\text{m}$ . The response of the sensor was more symmetric and fastened with aid of Pt particles. But it was difficult to overcome the nonsymmetric behavior perfectly.

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