



# A catalytic combustion-type CO gas sensor incorporating aluminum nitride as an intermediate heat transfer layer for accelerated response time

A. Hosoya, S. Tamura, and N. Imanaka

Department of Applied Chemistry, Faculty of Engineering, Osaka University,  
2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

Correspondence to: N. Imanaka (imanaka@chem.eng.osaka-u.ac.jp)

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**Abstract.** A catalytic combustion-type carbon monoxide gas sensor exhibiting good sensing performance even at moderate temperatures was previously developed by employing a Pt loaded  $\text{CeO}_2\text{-ZrO}_2\text{-SnO}_2$  solid solution as the CO oxidizing catalyst. The addition of aluminum nitride as an intermediate heat transfer layer between the Pt coil and the CO oxidizing catalyst drastically accelerated the response of this device to CO at temperatures as low as 70 °C.

## 1 Introduction

Carbon monoxide (CO) is well known as a highly toxic gas which can act as a severe health hazard if inhaled, even at relatively low concentrations. Because the ability of the CO molecule to bind to hemoglobin is approximately 250 times as high as that of  $\text{O}_2$ , exposure to elevated levels of CO gas (especially over 0.15 %) can be fatal. Since CO gas is both colorless and odorless, detection equipment is typically required to prevent accidental exposure to CO in situations where high levels of the gas may be generated. For these reasons, it is desirable to install compact, inexpensive CO sensors at sites with the potential for elevated CO concentrations in the ambient atmosphere.

To date, various types of compact CO gas monitoring devices have been developed such as those based on semiconductors (for example, Göpel and Schierbaum, 1995; Korotcenkov, 2007), potentiostats (for example, Blurton and Stetter, 1978) and catalytic combustion (for example, Sakaguchi et al., 2009; Ozawa et al., 2005). Semiconductor-type CO gas sensors exhibit stable performance due to their simple construction and a sensing mechanism based on the electrical resistance change caused by CO adsorption on the semiconductor surface. These monitors, however, have a basic deficit in that gases other than CO can also be adsorbed on the semiconductor surface and produce a signal, meaning

that the selectivity of this type of sensor is poor. Potentiostat-type CO sensors allow selective CO detection but cannot operate over prolonged time periods because of the eventual evaporation of liquid electrolyte in the device. In contrast, catalytic combustion-type CO gas sensors have a simple detection system consisting of a Pt coil combined with a CO oxidation catalyst, resulting in both stable and rapid sensing performance over long periods of time. Although catalytic combustion-type sensors detect CO gas via changes in the resistance of the Pt coil, similar to the semiconductor-type sensors, selective CO gas detection can be realized by employing a catalyst that oxidizes only CO gas at a given temperature, since in such cases resistance changes are caused solely by the heat generated from combustion of CO gas on the catalyst loaded on the Pt coil. Moreover, the sensor signal is completely proportional to the resistance change of the Pt coil during CO combustion and this resistance change is precisely correlated with the amount of CO gas oxidized by the catalyst. Therefore, the sensor signal is directly proportional to the CO gas concentration. Unfortunately, a significant problem associated with conventional catalytic combustion-type CO gas sensors remains; the catalysts ( $\text{Pt/Al}_2\text{O}_3$  or  $\text{Pd/Al}_2\text{O}_3$ ) require temperatures over 400 °C for the complete oxidation of CO gas. Because other gases such as methane and volatile organic compounds (VOCs) also combust at such elevated temperatures, these sensors will not be entirely

selective for CO gas. To obtain reliable selectivity, therefore, it is necessary to find novel catalysts which can oxidize CO at lower temperatures at which gases other than CO are not oxidized. Until now, some kinds of low-temperature operating sensors were reported such as the semiconductor-type sensor based on a SnO<sub>2</sub> thin film combined with a Pd/Al<sub>2</sub>O<sub>3</sub> thick film (Tabata et al., 2005) and the catalytic combustion-type sensor applied a Ce-doped cobalt oxide employed as a catalyst (Xu et al., 2008). For the sensor based on a SnO<sub>2</sub> thin film, the low temperature operation at 80 °C was successfully realized, there still remains a possibility of interference of other gases. However, the catalytic combustion-type sensor with Ce-doped cobalt oxide could detect CO selectively at 92 °C in dry atmosphere, but the CO oxidation activity of the catalyst employing a Co-based solid is deteriorated by water vapor. For the practical use of the sensor, the resistance toward water vapor is a concerning problem. Therefore, water-durability is also requested for the catalyst.

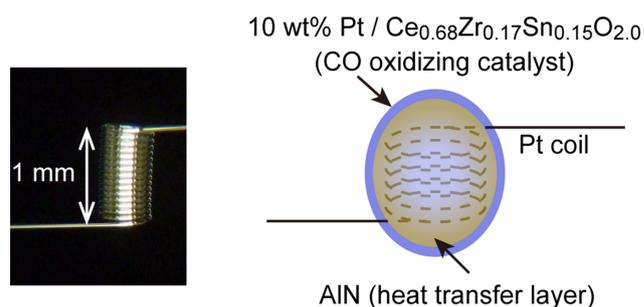
Based on this demand, we have succeeded in developing a low-temperature catalytic combustion-type CO gas sensor, by employing 10 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> as the catalyst (Hosoya et al., 2013). Since this catalyst is capable of completely oxidizing CO at 65 °C, we have achieved sensitive CO detection at temperatures as low as 70 °C. Moreover, since the present catalyst exhibited an excellent CO oxidizing activity even under humid conditions, the sensor also showed responses to CO even in a humid atmosphere. The response time of the device, however, is still sluggish at 180–240 s, due to insufficient heat transfer from the catalyst to the Pt coil, and thus increasing the response time is vitally important in terms of allowing the practical application of this sensor.

In the study reported herein, we improved the response time of a catalytic combustion-type CO gas sensor incorporating a 10 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> catalyst by adding the thermoelectric material aluminum nitride (AlN) as an intermediate heat transfer layer. We subsequently investigated the CO sensing performance of this improved device at 70 °C.

## 2 Experimental

The 10 wt% Pt-loaded Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> solid solution was prepared via the sol–gel method, as described in our previous report (Hosoya et al., 2013), and the sample composition and its CO oxidation activity were confirmed by X-ray fluorescence (Rigaku, ZSX100e) and X-ray powder diffraction (XRD) (Rigaku, SmartLab) analyses as well as by employing a conventional fixed-bed flow reactor.

The CO gas sensor element was fabricated using a Pt coil whose size is 1 mm in length with a 30 μm diameter Pt wire; a schematic illustration of the element is provided in Fig. 1. AlN (Toyo Aluminum K. K.) was dispersed in ethylene glycol to form a slurry which was painted over the Pt coil, and then ethylene glycol was drove off at

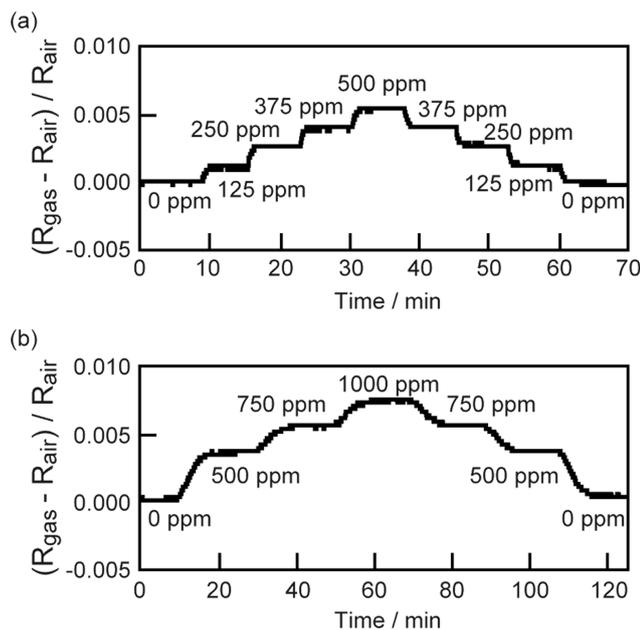


**Figure 1.** Photograph of the Pt coil employed in this work and an illustration of the catalytic combustion-type CO sensor incorporating an AlN interlayer and the 10 wt% Pt loaded Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> catalyst. Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> catalyst.

approximately 150 °C, which was obtained by applying a direct-current voltage of 3 V to the Pt coil, for 30 s. Subsequently, the 10 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> solid catalyst was dispersed in ethylene glycol and was applied over the top of the AlN layer on the Pt coil. The coil was then heated at approximately 150 °C for 30 s to drive off the ethylene glycol and sinter the catalyst. To allow an assessment of the efficiency of the AlN as an intermediate heat transfer layer, the total volume of AlN and catalyst which was applied was almost identical to the total volume of catalyst used in the previous version of the sensor without AlN. The CO sensing performance of the sensor was investigated using an electrometer (Advantest, R8240) to measure the DC voltage generated while passing a DC current of 90 mA through the sensor element to heat the cell up to 70 °C. CO gas concentrations from 0 to 1000 ppm (parts per million) were produced by diluting 1000 ppm CO in air with dry air (O<sub>2</sub> gas concentration in the test gas: 20.95–21.00 %). Regardless of the CO gas concentration, the total gas flow rate passing over the sensor was kept constant at 40 mL min<sup>-1</sup>. The sensor signal in response to exposure to CO gas was defined as  $(R_{\text{gas}} - R_{\text{air}})/R_{\text{air}}$ , where  $R_{\text{gas}}$  and  $R_{\text{air}}$  are the electrical resistances of the sensor when in contact with gas containing CO and with pure air, respectively. The sensor response time was defined as the time required for the electrical resistance of the device to reach 50 or 90 % of the equilibrium value eventually obtained at a given CO gas level.

## 3 Results and discussion

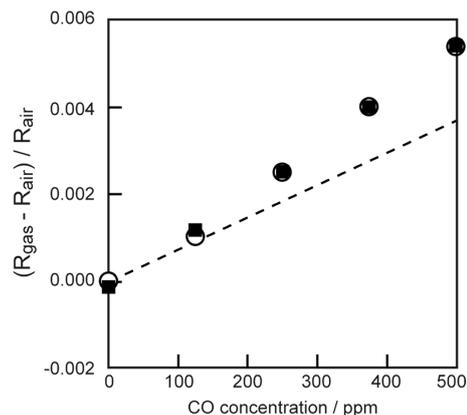
Figure 2 displays a representative response curve for the present sensor with the AlN intermediate heat transfer layer at 70 °C, together with corresponding data for the sensor without the AlN layer (Hosoya et al., 2013). Although similar response curves are observed for both sensors, the sensor without AlN shows slight deviations in its signal even after the signal has plateaued at each CO concentration and, for this reason, over 200 s were required for this sensor to exhibit a 90 % response. In contrast, the sensor with AlN shows



**Figure 2.** Representative response curves at 70 °C for sensors (a) with and (b) without the AlN intermediate heat transfer layer.

more stable output such that the response time is drastically shortened to within 90 s. Furthermore, the time required for the AlN sensor to achieve a 50 % response (based on a meaningful sensor signal to noise or S/N ratio) is approximately 20 s, while the sensor without AlN required over 130 s for a 50 % response. In addition, while the previous sensor without the AlN layer also showed the response to CO at the concentration less than 500 ppm, its sensor signal was quite small compared to the present sensor, indicating that the sensitivity of the sensor was improved by applying the heat-conductive material of AlN having a low heat capacity.

Figure 3 depicts the equilibrium sensor signals obtained at 70 °C in response to various CO gas concentrations. As observed during our previous study of a sensor without AlN, the sensor with AlN produces a signal which varies in a strictly linear fashion with changing CO gas concentrations. Moreover, the sensitivity of the sensor with AlN is higher than that of the sensor without AlN; the response of the sensor with AlN to 500 ppm CO is 1.5 times that of the sensor without AlN. Since the sensor components, except for the presence of the AlN interlayer, are the same for both sensors, acceleration of the response time must be due to improved heat transfer from the CO oxidizing catalyst to the Pt coil. In the case of the sensor without the AlN interlayer, a portion of the heat generated by CO oxidation on the catalyst will be released to atmospheric air before it can be conducted to the Pt coil. As a result, a prolonged time period is necessary to reach a thermal equilibrium state in the Pt coil. In contrast, by applying AlN as an interlayer, due to its excellent thermal conductivity, a greater quantity of heat is effectively



**Figure 3.** Signals at various CO concentrations (○: increasing, ■: decreasing) from a catalytic combustion-type sensor incorporating AlN at 70 °C. Dashed line indicates the sensor signal obtained previously with a sensor without AlN (Hosoya et al., 2013).

and rapidly conducted to the Pt coil through the AlN. This results in both a steadier sensor signal and a more rapid response. The sensitivity was also improved by applying AlN as the heat transfer layer, because the heat capacity of AlN is less than that of the 10 wt% Pt/Ce<sub>0.68</sub>Zr<sub>0.17</sub>Sn<sub>0.15</sub>O<sub>2.0</sub> catalyst. The temperature of a material with a lower heat capacity will increase to a greater extent in response to the same amount of heat energy and therefore the temperature of the Pt coil is further increased as the heat generated in the catalyst is conducted through the AlN layer. Because the sensor signal is dependent on the electrical resistance of the Pt coil, which in turn is directly related to the temperature of the Pt, the sensitivity of the sensor with AlN was improved due to the lower heat capacity of the AlN compared to that of the catalyst. The results in this paper indicate that the high thermal conductivity of AlN can improve CO sensing performance of the catalytic combustion-type sensor when AlN is applied as an intermediate heat transfer layer. This new sensor device should be further studied to prove its potential as a CO detector. The investigation so far lacks information on the influence of humidity and long-term stability, which will be addressed in a future study.

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