Stacked Type Potentiometric Solid-State CO₂ Gas Sensor for Miniaturization

N.-J. Choi¹, H.-K. Lee¹, S. E. Moon¹, W. S. Yang¹ and J. Kim¹

¹Convergence Components & Materials Research Laboratory, Electronics and Telecommunications Research Institute

131, Gajeong-Dong, Yuseung-Gu, Daejeon, 305-700, South Korea
choinj1@etri.re.kr

Abstract:
A stacked type photentiometric solid-state (S-PSS) carbon dioxide (CO₂) sensor based on Li ion was designed and fabricated on alumina substrate by mass production techniques. This design can reduce the 70 % of active area because no reference material is required. All materials were screen-printed except for electrolyte which was deposited thermal evaporation. The prepared materials were characterized by X-ray diffraction analysis and scanning electron microscopy. Gas response characteristics of S-PSS and planar type PSS (P-PSS) were examined at the range of 350~500 °C and between 16~5000 ppm CO₂ gas concentrations. The S-PSS sensor was showed from 40 to 90 mV/decchange at operating temperatures. Repetition measurement was very good within 5 mV in full measurement range.

Key words: Stacked Type, Solid-State, Carbon Dioxide, Gas Sensor

Introduction
Recently, carbon dioxide level in air has been increased considerably due to continuous damage to the environment and the increased use of fossil fuels[1]. The history of atmospheric carbon dioxide concentrations as directly measured at Mauna Loa, Hawaii is shown in Fig. 1. This curve is known as the Keeling curve, and is an essential piece of evidence of the man-made increases in greenhouse gases that are believed to be the cause of global warming [2]. CO₂ monitoring and control is of increasing importance in environmental pollution and process control and automation as well as applications in agricultural and biotechnological fields [3]. Until now, many works have been carried out to develop carbon dioxide gas sensors focused on high sensitivity and stability [4-6]. In implementation, power consumption was not a big problem. However, low-power consumption sensor is able to provide greater convenience to the user. Especially, ubiquitous sensor network (USN) applications, which are needed small size and low power consumption, of sensors are essential to minimize active area. Commercially, carbon dioxide gas is measured by using non-dispersive infrared (NDIR) type with accuracy. NDIR type is difficult to adapt as sensor node because of high power consumption and big size coming from light path. Electrochemical potentiometric CO₂ sensors using solid electrolytes are the most promising among the various methods for the...
detection of carbon dioxide because of their compact structure, high selectivity, low cost, and the ability of continuous monitoring [7]. Planar type phototronic solid-state (P-PSS) type has been utilized for CO$_2$ gas sensor by virtue of its low price but it is composed of a reference and a sensing material. So, there are limits to miniaturization because of two material areas.

Therefore, we designed and fabricated a stacked type phototronic solid-state (S-PSS) CO$_2$ sensor to reduce the active area without the reference material. Furthermore, their responses to CO$_2$ gas were examined with various operating temperatures and gas concentrations. Materials are characterized by optical microscopy, X-ray diffraction (XRD), and scanning electron microscopy (SEM) analysis.

**Fabrication of CO$_2$ Sensors**

Fabrication process and pictures of planar type and stacked type CO$_2$ gas sensors was shown in Fig. 3. Pt pattern as heater and electrode with thickness 10 um was deposited on alumina substrate (4.5X4.5 mm$^2$) using screen printing. Above and below the electrodes are connected through a via-hole. Electrolyte based on Li-ion was deposited overall except for the electrode by thermalevaporation with thickness 1 um and was annealed at 700°C in air. Au electrode, reference and sensing electrodes were screen-printed in turn on electrolyte followed by heat treatment. Finally, fabricated sensors were packaged on TO-5 can.

**Fig. 1.** (a) Planar type and (b) stacked type design of potentiometric solid-state CO$_2$ sensors.

**Fig. 2.** (a) Planar type and (b) stacked type design of potentiometric solid-state CO$_2$ sensors.

**Fig. 3.** Fabrication process and pictures of planar type and stacked type CO$_2$ gas sensors.

**Fig. 4.** The electromotive force (EMF) of the sensor material was measured by using data acquisition board (DAQ) which was simultaneously able to acquire 24 channels of analog inputs and internal impedance of over 10 GΩ.

**Fig. 5.**

**Alumina substrate**

**Electrolyte**

**Au electrode**

**Reference material**

**Sensing material**

**Packaging to TO can**

**Apparatus of Measurement of Gas Response**

Gas sensing properties were measured using a computer-controlled characterization system [8]. Gas sensors prepared on the Alumina substrate were investigated furnace and steel chamber which is possible to control temperature precisely. Air as balanced gas was used at 2000 cc/min flow rate and CO$_2$ gas of 10% was used as an analyte and mixed with balanced gas to adjust desired analyte concentration from 16 parts-per-million (ppm) to about 10000 ppm using mass flow controller (MFC). Measurement apparatus to measure to CO$_2$ gas of sensing material was shown in Fig. 4. The electromotive force (EMF) of the sensor material was measured by using data acquisition board (DAQ) which was simultaneously able to acquire 24 channels of analog inputs and internal impedance of over 10 GΩ.
Results

Response characteristics of alumina sensor were shown in Fig. 5. Raw data curves as function of gas concentration of two type sensors are shown in Fig. 5(a) at 500 °C operating temperature in electric furnace chamber. The figure shows the real response curves acquired by data acquisition system (Agilent 34970A). After stabilizing for 2 min, a gas flow meter was used to inject the test gas every 2 min. The injected gas concentrations were 16, 500, 1000, and 5000 ppm in sequence. The flow rates of balance gas and target gas were 2000 cc/min and 5~100 cc/min, respectively. The transients were sufficiently sharp with the 90% response and recovery times of less than 10 s. Abbreviation presentation graph as function of gas concentration for two-type sensors was shown in Fig. 5(b). Two sensors showed about 80 mV for decade concentration change.

The response characteristics of stacked type sensor for various CO₂ concentrations and different operating temperatures were shown in Fig. 6. Fig. 6(a) and 6(b) show the response transients and abbreviation curve of stacked type sensor to changes in CO₂ concentration in the range of 16~5000 ppm at different operating temperatures, respectively. As operating temperature was increased, electromotive force change was increased. The sensor was showed from 40 to 90 mV/dec change at between 350~500 °C operating temperatures. When the gas concentrations were increased, the responses were increased logarithmically. Repetition measurement for CO₂ 1000 ppm was very good within 5 mV in full measurement range. Blue line and red bar of Fig. 6(c) show initial EMF at 16 ppm CO₂ gas and EMF deviation by decade (500-5000 ppm) at different operating temperatures, respectively. As operating temperature was increased, initial EMF was increased.
The fabricated gas sensor showed good performance to CO\(_2\) gas and proved that it could be adaptable to ubiquitous sensor network applications because of possibility of miniaturization.

**Acknowledgements**

This work was supported by the IT R&D program of MKE/KEIT. [10035570, Development of self-powered smart sensor node platform for smart& green building]

**References**


