Stacked Type Potentiometric Solid-State CO₂ Gas Sensor for Miniaturization

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Abstract:

A stacked type photentiometric solid-state (S-PSS) carbon dioxide (CO_2) 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 $^{\circ}$ C and between 16~5000 ppm CO_2 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 increasedconsiderably due to continuous damage to the environmentand 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 monitoring and control $[2].CO_{2}$ increasingimportance in environmental pollution and processcontrol and automation as well as applications inagricultural and biotechnological fields [3]. Until now, manyworks have been carried out to develop carbondioxide 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 convenienceto 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 Electrochemical potentiometricCO₂ sensors using solid electrolytesare the most promising among the various methodsfor the detection of carbon dioxide because of their compactstructure, high selectivity, low cost, and the ability of continuousmonitoring [7]. Planar type photentiometric solid-state(P-PSS) type has been utilized for CO₂ 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 photentiometricsolid-state (S-PSS) CO₂ sensor to reduce the active area without the reference material. Furthermore, their responses to CO₂ 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.

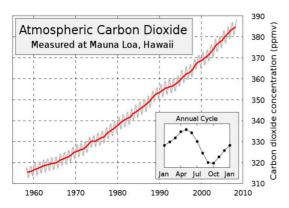


Fig. 1. (a) Planar type and (b) stacked type design of potentiometric solid-state CO₂ sensors.

Design of Stacked CO₂ Sensor Without Reference Electrode

Schematics of two types PSS CO₂ sensor were shown in Fig. 2. Planar type PSS commercially used is shown in Fig. 2(a) and stacked type PSS designed to reduce the active area is shown in Fig. 2(b). S-PSS can reduce the 70% of active area because no reference material is required.

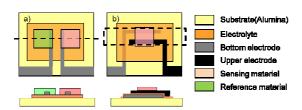


Fig. 2. (a) Planar type and (b) stacked type design of potentiometric solid-state CO₂ sensors.

Fabrication of CO₂ Sensors

Fabrication process and pictures of planar type and stacked type CO_2 gas sensors was shown in Fig. 3.Ptpattern as heater and electrode with thickness 10 um was deposited on alumina substrate (4.5X4.5mm²) using screen printing. Above and below the electrodes are connected through a via-hole. Electrolyte based on Liionwas 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 byheat treatment. Finally, fabricated sensors were packaged on TO-5 can.

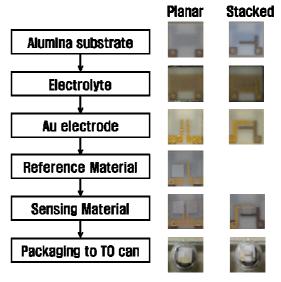


Fig. 3. Fabrication process and pictures of planar type and stacked type CO₂ gas sensors.

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 control to temperature precisely. Air as balanced gas was used at 2000 cc/min flow rate and CO2 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 CO₂ gas of sensing material was shown in Fig. 4. The electromotive force (EMF) of the sensor material was measured by using acquisition board (DAQ) which simultaneously able to acquire 24 channels of analog inputs and internal impedance of over 10 G Ω .

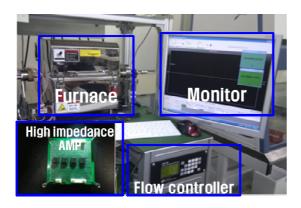
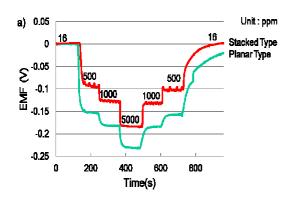


Fig. 4. Measurement apparatus to measure to CO_2 gas of sensing material.

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) at500 °Coperating 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 concentration for twotype sensors was shown in Fig. 5(b). Two sensors showed about 80 mV for decade concentration change.



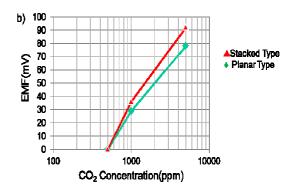
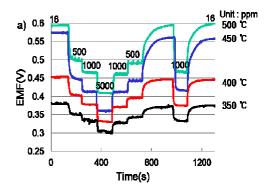
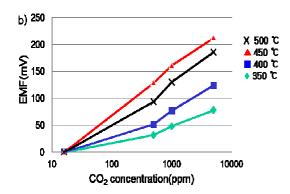


Fig. 5. (a) Response transients and (b) abbreviation curve of planar type and stacked type sensors to various CO_2 concentrations at 500 $^{\circ}$ Coperating temperature.

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 concentrationswere increased. the responseswere increased logarithmically. Repetition measurement for CO₂ 1000 ppm was very good within5 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.





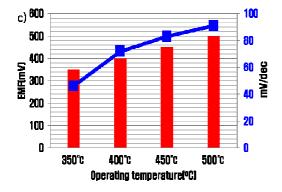


Fig. 6. (a) Response transients and (b) abbreviation curve of stacked type sensor to various CO₂concentrations and (c) Initial EMF and EMF change by decade at different operating temperatures.

The fabricated gas sensor showed good performance to CO₂ gas and proved that it could be adaptable to ubiquitous sensor network applications because of possibility of miniaturization.

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