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CO₂ sensor combining a metal-insulator-silicon carbide (MISiC) capacitor and a binary carbonate

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Abstract

A solid-state CO₂ sensor device using a metal-insulator-silicon carbide (MISiC) capacitor combined with a Li₂CO₃–BaCO₃ auxiliary layer was fabricated and tested for its basic sensing properties. The MISiC-based CO₂ sensor attached with the carbonate showed typical capacitance–voltage (*C–V*) properties in air at 400°C, and the sensor device responded well to changes in CO₂ concentration in air at 400°C. The sensor signals were directly proportional to the logarithm of CO₂ concentration. The results suggested that an electrochemical reaction of CO₂ occurred at the interface between the carbonate layer and the electrode, causing the applied voltage to shift in response to CO₂.

Introduction

Development of compact, cheap sensing devices capable of measuring CO₂ concentrations in a parts per million range has been pursued owing to increasing demands for monitoring and controlling CO₂ concentrations in the indoor atmosphere. So far, potentiometric,¹⁻⁶ amperometric,^{7,8} resistive,⁹⁻¹¹ and metal-insulator-semiconductor (MIS)-type^{12,13} solid-state CO₂ sensors have been investigated. Among these sensors, NASICON (Na₃Zr₂Si₂PO₁₂:Na⁺ conductor)-based potentiometric sensors attached with a binary carbonate (Li₂CO₃–BaCO₃) are one of the candidates for practical use because of their

excellent properties such as high sensitivity, high selectivity and fast response.¹⁴ In this case, the binary carbonate is solid electrolyte and acts as an auxiliary layer on the electrochemical reaction at the interface contacting with metal electrode (sensing electrode). The devices attached with a carbonate auxiliary layer are operated at around 400–500°C to ensure the efficient detection of CO₂. However, the sensor of this type needs a counter (or reference) electrode, which makes the sensor structure rather complicated and large. In addition, the use of a counter electrode sometimes degrades the stability of the device if the counter electrode reacts with target gases.

In contrast, MIS-based devices combined with a solid electrolyte as an auxiliary layer have advantages over solid electrolyte-based gas sensors, i.e., elimination of the counter electrode and high-input impedance of the sensor. These features allow for the signal stabilization and device miniaturization. Zamani et al. reported that a Si-based MIS capacitor attached with a NaNO₂-based solid electrolyte showed fairly good NO₂ sensing properties at 160°C.¹⁵ The results indicated the possibility of developing various solid-state gas sensors by combining an MIS capacitor and a solid electrolyte. However, a Si-based MIS device cannot be applied to the high temperature detection of CO₂ because of its low thermal stability at higher than 200°C. The detection of CO₂ with a carbonate-based auxiliary layer usually needs high operating temperatures around 400–500°C. In contrast, a silicon carbide

(SiC)-based MIS device has high thermal stability and thus can be operated up to around 800°C due to its wide bandgap¹⁶. Indeed, some SiC-based MIS devices have been used at high temperatures for the detection of gaseous compounds.¹⁷⁻²¹ In this study, we developed an MISiC capacitor-type CO₂ sensor attached with a binary carbonate and investigated its basic CO₂ sensing properties at 400°C. A binary carbonate (Li₂CO₃–BaCO₃) was used as an auxiliary layer because of its good CO₂ sensing capability and high stability under humid conditions.¹⁴

Experimental

A schematic structure of the SiC-based CO₂ sensor attached with a binary carbonate Li₂CO₃–BaCO₃ (solid electrolyte) as an auxiliary layer is shown in Fig. 1a. An *n*-type 4H-SiC wafer with an *n*-type epitaxial layer (ca. 5 μm) purchased from Cree, Inc., USA, was used as a base material. An insulator layer (SiO_x/Si₃N₄/SiO₂) was formed on the SiC substrate, and then an ohmic contact electrode (Ni/Ti/Pt) was deposited on the back side of the SiC substrate by dc magnetron sputtering. A MgO layer (ca. 100 nm) was deposited on the insulating layer as a passivation layer via thermal evaporation to prevent Li ions from penetrating into the insulating layer during the deposition of the carbonate auxiliary layer. The MgO layer was annealed in O₂ at 400°C for 1 h. A bonding pad (Pt/Ti) was attached

onto the MgO layer by dc magnetron sputtering. A porous gate electrode (Pt) as a sensing electrode ($1\text{ mm} \times 1\text{ mm}$) was deposited on the MgO layer via thermal evaporation. The bonding pad was partly covered with the Pt sensing electrode. Au wires were connected to both the bonding pad and the ohmic contact electrode. A $\text{Li}_2\text{CO}_3\text{--BaCO}_3$ (1:2 in molar ratio) composite powder was prepared as reported elsewhere.¹⁴ The carbonate auxiliary layer was deposited over the area covering the Pt sensing electrode and the MgO layer at 750°C by a melting-and-quenching method. Finally, the sensor chip was fixed on a heater substrate fitted with a temperature sensor, as shown in Fig. 1b.

Capacitance–voltage ($C\text{--}V$) properties were measured with an LCR meter (Boonton 7200, Boonton Electronics, USA) at 400°C . Variations in the applied gate voltage (V_G) at a constant capacitance were used as a sensor signal. Scan speed and frequency of ac voltage applied for $C\text{--}V$ measurements were set to 0.2 V s^{-1} and 1 MHz , respectively. The gas sensing properties of the device were measured in a conventional gas-flow apparatus. Dry sample gases containing CO_2 (1–20%) were prepared by mixing a parent CO_2 gas (100%) with synthetic air ($\text{O}_2\text{--N}_2$). The total gas flow rate was set to 50 mL min^{-1} .

Results and Discussion

Stability of an insulator layer of MIS devices is critical to obtaining stable sensor

responses. There is a possibility that the carbonate auxiliary layer may react with the insulating SiO_2 layer at the fabrication temperature, which causes irreversible degradation of device characteristics. Zamani et al. used Ta_2O_5 as a passivation layer to protect the insulating layer on an MIS capacitor from reacting sensor response.¹⁵ Mizuhata et al. reported that MgO in molten Li_2CO_3 was chemically stable even at 1097 K.²² According to these results, we selected MgO as a passivation layer for the MISiC-based CO_2 sensor.

We first investigated the reactivity of the MgO passivation layer with the Li_2CO_3 – BaCO_3 auxiliary layer by X-ray diffractometry (XRD). Figure 2 shows XRD patterns of (a) Li_2CO_3 – BaCO_3 , a physical mixture of a MgO powder and a Li_2CO_3 – BaCO_3 powder (1:2 by weight) (b) before and (c) after heat-treatment at 750°C for 5 min under atmospheric conditions. No changes occurred in the XRD pattern of the powder mixture after the heat-treatment. These results indicate that MgO does not react with the carbonate even under such severe conditions. Thus, we concluded that a MgO layer is suitable as a passivation layer that can prevent the reaction of the auxiliary layer with the insulating layer on an MISiC.

C – V characteristics of the MISiC-based CO_2 sensor after the deposition of the auxiliary layer (Li_2CO_3 – BaCO_3) were measured to examine its capacitive characteristic. Figure 3 shows C – V properties of the CO_2 sensor device at 400°C in air. The sensor showed

C - V properties typical of an n -type MIS capacitor; i.e., the capacitance varies from an accumulation state to an inversion state with decreasing applied gate voltage. The results suggest that the MgO layer worked well as a passivation layer for the insulating layer on MISiC even after the deposition of the carbonate layer.

Figure 4a shows response transients of the MISiC-based device to 1–20% CO₂ in air at 400°C. Variations in the applied voltage (V_G) at a constant capacitance of 337 pF in response to CO₂ were measured as a sensor signal, because a steeper capacitance change was observed around that capacitance value according to the C - V curve in Fig. 3. The sensor responded to CO₂ and the applied voltage changed depending on CO₂ concentration. It has been reported that for an MIS capacitor attached with NaNO₂, differences in the electric potential between the Au gate electrode and the NaNO₂ auxiliary layer were generated in response to NO₂ due to its electrochemical reaction taking place at the Au/NaNO₂ interface.¹⁵ Thus, such an electrochemical reaction of CO₂ likely occurred at the Pt/carbonate interface in the developed device. The resulting electric potential caused the applied voltage to shift in response to CO₂.

Figure 4b shows the dependence of the applied potential on CO₂ concentration at 400°C. The applied potential was linear to the logarithm of CO₂ concentration, showing a Nernstian behavior frequently observed in potentiometric sensors using solid electrolytes.¹⁻⁶

Thus, we postulated that the following electrochemical reaction 1 occurred at the interface of Pt and the carbonate

However, the reaction electron number (n) calculated from the slope of the linear curve was 1.5, different from the theoretical value of 2.0. In other words, the slope (87.1 mV/decade) of the linear curve was larger than the theoretical value (66.8 mV/decade). A possible reason for the discrepancy is as follows. In the sensor configuration, the porous Pt sensing electrode and the bonding pad were deposited on both the MgO layer and the carbonate auxiliary layer. Thus, the voltage was applied to not only the auxiliary layer but also the MgO layer through the sensing electrode and the bonding pad, i.e., capacitance component between the sensing electrode, the bonding pad and MgO layer is involved in the sensor signals (V_G) measured. Because the MgO layer is believed to be insensitive to CO_2 , it is possible that the applied voltage is not fully associated with the potential differences generated at the Pt/carbonate interface in response to CO_2 . Accordingly, the optimization of the electrode configuration in the device is expected to yield the theoretical responses to changes in CO_2 concentration. In fact, modifications of the structure of the sensing layers including a Pt sensing electrode and the carbonate auxiliary layer by inserting the sensing electrode into the auxiliary layer, which eliminates contact of the sensing electrode to the

insulating layer, or attaching the sensing electrode on top of the auxiliary layer are needed. Such modifications seem to give the theoretical gas response and CO₂ detection of lower concentration.

Conclusions

We fabricated a CO₂ sensor based on an MISiC capacitor combined with a binary carbonate (Li₂CO₃–BaCO₃) as an auxiliary layer and tested its basic sensing properties. A MgO layer as a passivation layer was formed on an insulating SiO₂ layer of an MISiC capacitor. The XRD measurements suggested that the MgO layer could prevent the binary carbonate auxiliary layer from reacting with the SiO₂ layer and avoid destabilizing the capacitive behavior of the MISiC device. The CO₂ sensor attached with the auxiliary layer showed typical *C–V* properties in air at 400°C. The sensor responded well to 1–20% CO₂ in air at 400°C, and the sensor signals (*V_G*) were directly proportional to the logarithm of CO₂ concentration. The obtained results clearly indicated the promising feasibility of SiC-based capacitive sensors fitted with solid electrolytes for the high temperature detection of gaseous compounds.

Acknowledgments

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Figure captions

Figure 1. (Color online) (a) Schematic drawing of an MISiC capacitor-based CO₂ sensor attached with a binary carbonate (Li₂CO₃-BaCO₃) auxiliary layer. (b) A photograph of the fabricated sensor device mounted on a small heater.

Figure 2. (Color online) XRD patterns of (a) Li₂CO₃-BaCO₃ and a mixture powder of MgO and the carbonate (b) before and (c) after heat treatment at 750°C for 5 min in air.

Figure 3. Capacitance-voltage (*C-V*) properties of the MISiC-based CO₂ sensor attached with a Li₂CO₃-BaCO₃ auxiliary layer at 400°C in air.

Figure 4. CO₂ sensing properties of the MISiC-based CO₂ sensor. (a) Response transients to 1-20% CO₂ in air at 400°C. (b) Dependence of the applied voltage (*V_G*) at a constant capacitance (337 pF) on CO₂ concentration in the range of 1-20% at 400°C.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.