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Toluene sensing characteristics of tin oxide-based gas sensor deposited with various amounts of metalloporphyrin

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Abstract

In this study, the sensing characteristics of tin oxide-based gas sensors deposit with different amounts of metalloporphyrin, which is a functionalization substance, are evaluated. The mass of metalloporphyrin deposited is 3, 10, 20, 30, and 40 mg for 5 different sensors prepared. The deposition of 3 mg of metalloporphyrin result in an island form of functionalization instead of a thin film; meanwhile, thin films with thicknesses of 25, 35, 74, and 92 nm are formed for the other four cases. As the deposition amount of metalloporphyrin increase, the performance of the sensor deteriorate. The samples are prepared by subdividing the amount of metalloporphyrin source to determine the optimized deposition amount. A sample is prepared with deposition amounts ranging between 1 to 10 mg. The sensors deposit with 3–5 mg metalloporphyrin has excellent response, response, and recovery time characteristics.

Keywords: Metalloporphyrin, Gas sensor, Functionalization, Volatile organic compounds, Optimization

Introduction

Not only are different harmful gases (CO, NOx, volatile organic compounds (VOCs), etc.) generated due to the development and diversification of modern society, their emissions are also increasing [1–4]. To manage the emissions of such harmful gases, government agencies have limited the level of emissions; however, as real-time monitoring and control are required to efficiently manage this, research on gas sensors is actively progressing. In particular, resistive gas sensors have a simple structure; therefore, their manufacturing cost is very low [5, 6]. Thus, they have been attracting the attention of many researchers. However, when a single material is used as a sensing material, there is a disadvantage in that the response, recovery characteristics, and selectivity are weak [5, 6]. To overcome this, attempts have been made to improve the performance of the sensor and secure selectivity by adding a functionalized material to the sensing material [7–16]. In particular, a substance called metalloporphyrin is an excellent functionalizing substance for detecting VOCs. Metalloporphyrin acts as an excellent oxygen reduction catalyst to help generate sufficient oxygen ions on the surface of metal oxides and provides adsorption sites that can be bonded to VOCs in various ways including hydrogen, polar, and coordination bonds [17–19]. However, in the case of metalloporphyrin, there is a lack of consideration of the performance of gas sensors depending on the amount of the functionalized material. If a small amount of metalloporphyrin is functionalized, it will not provide a sufficient adsorption site. When a large amount of metalloporphyrin is functionalized, there are many adsorption sites. However, the movement of electrons to the sensing channel will be restricted by the thick metalloporphyrin layer, then the sensing performance of the sensor will deteriorate. In this study, the performance of a gas sensor for toluene was evaluated according to the amount of functionalized material using sensors in which various amounts of metalloporphyrin, a functionalized material, were deposited on tin oxide.

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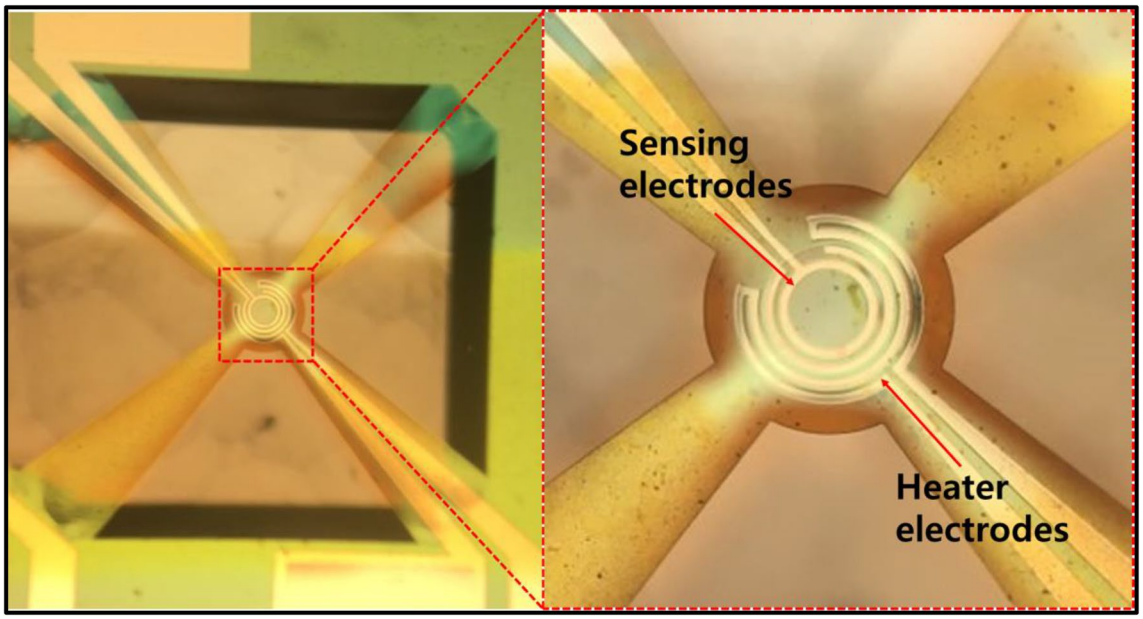

Fig. 1 An optical image of the sensor platform. Ti/Pt electrodes (sensing and heater electrodes) are formed on the suspended $SiO_2/Si_3N_4/SiO_2$ membrane

Materials and methods

This experiment was performed by coating a sensing material on a previously manufactured sensor platform. The sensor platform was fabricated as described in a previous paper [20–22]. The previous paper contains the characteristics of the sensor platform, including configuration, process flow diagram, and heater operating characteristics. Figure 1 shows an optical micrograph of the fabricated sensor. The materials were purchased from Sigma-Aldrich [tin oxide pieces, 5.10.15.20–Tetraphenyl-21H,23H-porphine cobalt(CoTPP)]. The channel material of the sensor was tin oxide, and a 50 nm-thick thin film was deposited using the electron beam vapor deposition method. The functionalized material, metalloporphyrin (CoTPP), was deposited by electron beam vapor deposition, and the amount of deposited metalloporphyrin was 3, 10, 20, 30, and 40 mg. Table 1 lists the thicknesses according to the amount of metalloporphyrin deposited. The thickness of the deposited thin film was measured using a white light interferometer (Zygo NV6300). When 10, 20, 30, and 40 mg of metalloporphyrin were deposited, metalloporphyrin thin films with thicknesses of 25, 35, 74, and 92 nm were obtained, respectively. When 3 mg metalloporphyrin was deposited, the deposited thickness was very thin; therefore, it could not be measured using the white light interferometer. Figure 2 shows an SEM image of the 3 mg of metalloporphyrin source deposited. As the amount of the deposited metalloporphyrin was very small, a thin film could not be formed.

Table 1 The thickness of the metalloporphyrin thin film according to the mass of the deposited metalloporphyrin

Mass of deposited metalloporphyrin	Thickness of the film
3	–
10	25
20	35
30	74
40	92

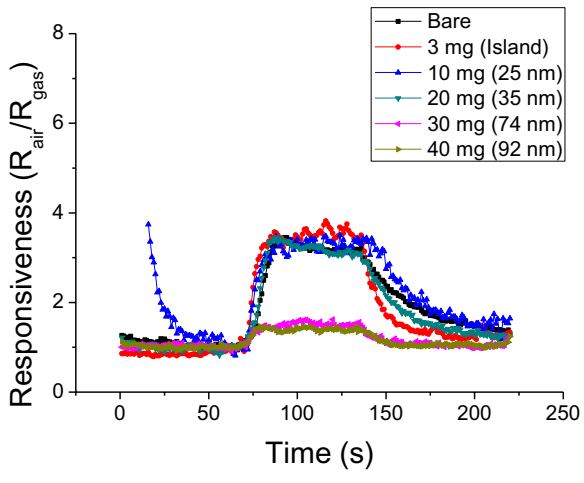

Fig. 2 Transient response characteristics of the fabricated sensors

Therefore the metalloporphyrin remained in the form of an island. A total of 6 sensors for each amount of metalloporphyrin were prepared.

Experimental details

The sensor was placed inside a quartz tube, and the gas type and flow rate were controlled by a mass flow controller. The gas flow rate was maintained at 500 sccm so that the sensor signal was not affected by the flow rate or pressure change. 10 ppm of toluene was used as the target gas to evaluate the characteristics of the sensor. A DC power supply (E3647A Agilent) was connected to the two electrodes of a microheater and heated by applying a voltage of 2.5 V. The temperature of the sensing area at this time was approximately 248 °C. 248 °C is the lowest experimentally confirmed temperature at which a difference in response between bare SnO_2 and functionalized SnO_2 begins to appear. The resistance of the sensor was measured by reading the change in current at 3 V using a source meter (2400. Keithley).

Results and discussion

Figure 2 shows a graph of the transient response characteristics of the fabricated toluene sensor. The response was defined as R_{air}/R_{gas}. The same data were obtained for 6 sensors, and the response, response time, and recovery time are summarized in Fig. 3. Figure 3a–c is a graph showing the response, response time, and recovery time according to the amount of metalloporphyrin deposited on each manufactured sensor. Each data point is an average of data collected from six sensors, and the error bars are displayed. The response time was defined as the time until 90% of the maximum resistance was reached after toluene injection, and the recovery time was the time until 80% of the original resistance was reached after stopping toluene injection. In the case of responsivity, the sensor with 3 mg of deposited metalloporphyrin showed the highest response at 3.55, and the sensor with 40 mg of deposited metalloporphyrin showed the lowest response at 1.26. In the case of response time, the sensor responded the fastest in 11.1 s, and the sensor that was not functionalized responded the slowest in 25.0 s. Compared to bare SnO_2, the sensor functionalized with 3 mg of metalloporphyrin are improved the response by 55.6%. In the case of recovery time, the sensor showed the fastest recovery at 26.6 s, and the sensor that was not functionalized showed the slowest recovery at 167.3 s. Compared to bare SnO_2, the sensor functionalized with 3 mg of metalloporphyrin improved recovery time by 84.1%. In this experiment, it was confirmed that functionalization treatment with a small amount of metalloporphyrin further improved the sensor performance. When 10 mg or more of metalloporphyrin was deposited,

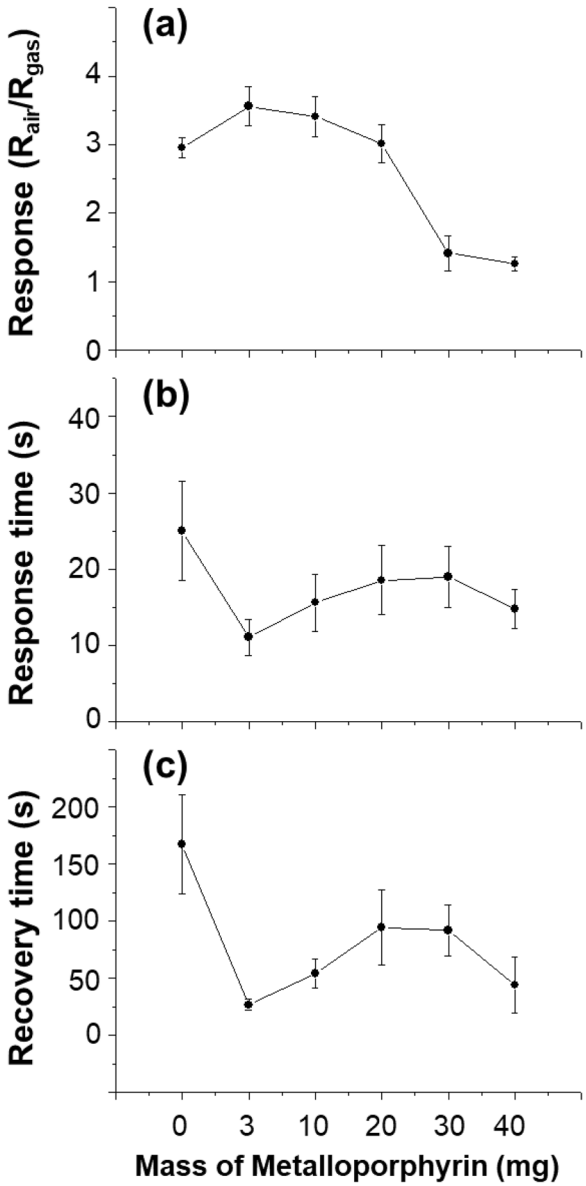

Fig. 3 The response, response time, and recovery time according to the amount of metalloporphyrin deposited on each fabricated sensor. The amount of deposited metalloporphyrin was 3, 10, 20, 30, and 40 mg

as shown in Table 1, a thin film was formed that could be observed using a white light interferometer; however, the deposition of 3 mg of metalloporphyrin did not lead to the formation of a thin film. The metalloporphyrin was expected to have been deposited in the form of an island. Figure 4 shows a field emission scanning electron microscope [FE-SEM(IT-500HR)] image of the 3 mg of metalloporphyrin source deposited. As can be seen from the figure, metalloporphyrin particles of several nanometers

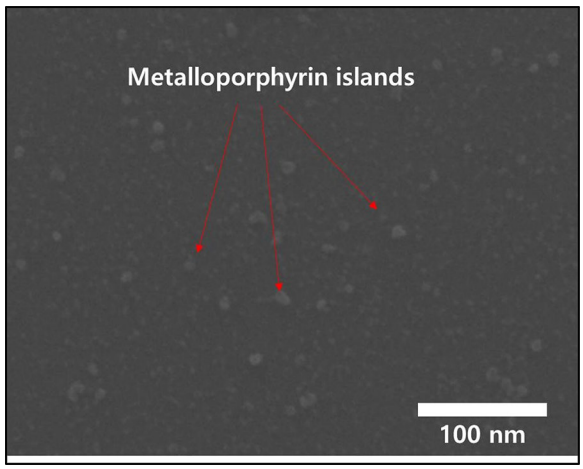

Fig. 4 A SEM image of the metalloporphyrin islands. As the amount of the deposited source was very small, a thin film could not be formed, and the source remained in the form of an island

are evenly distributed. When nanometer-sized metalloporphyrin particles are evenly distributed, sufficient oxygen ions are formed on the surface of the metal oxide [18]. Because they actively participate in the reaction, they have a significant effect on performance improvement. In contrast, in the case where metalloporphyrin is deposited as a thin film, the metalloporphyrin does not act as an electrical channel. Therefore the movement of electrons may be limited. Since the surface of the metal oxide is covered with metalloporphyrin, the formation of oxygen ions required for reaction with the gas may be difficult. Even if a low concentration of oxygen ions is formed, the reaction time may inevitably increase because they participate in the reaction only depending on diffusion.

Samples were prepared by subdividing the amount of metalloporphyrin source to determine the optimized deposition amount. A sample was prepared with deposition amounts ranging between 1 and 10 mg, and signals were confirmed by exposure to 10 ppm of toluene. Figure 5a–c shows the response, response time, and recovery time according to the amount of metalloporphyrin deposited on each manufactured sensor. As in the previous experiment, each data point is an average of data collected from six sensors, and error bars are displayed. In the case of responsivity, the sensors deposited with 3–10 mg of metalloporphyrin showed a similarly high response, and the sensor deposited with 1 mg of metalloporphyrin showed the lowest response. In the case of response time, the error was somewhat large; however, the sensors deposited with 3–4 mg of metalloporphyrin responded the fastest in less than 20 s, and the sensor deposited with 1 mg of

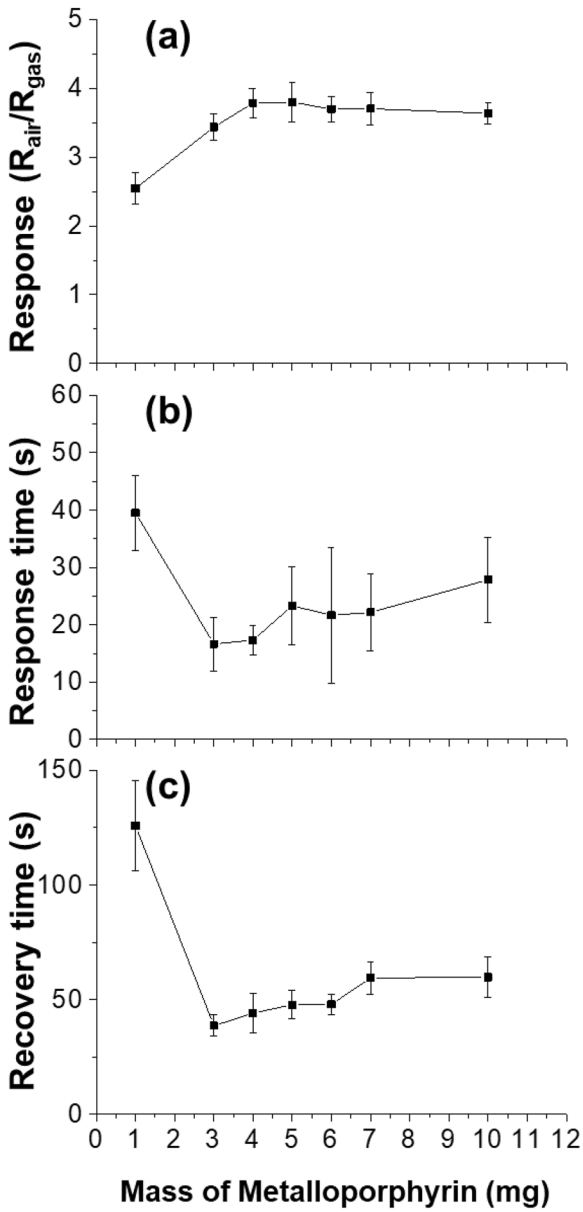

Fig. 5 The response, response time, and recovery time according to the amount of metalloporphyrin deposited on each fabricated sensor. The amount of deposited metalloporphyrin was between 1 and 10 mg

metalloporphyrin responded the slowest in 40 s. In case of recovery time, the sensor deposited with 3 mg of metalloporphyrin showed the fastest recovery at 37 s, and the sensor deposited with 1 mg of metalloporphyrin showed the slowest recovery at 125 s. As a result, it was confirmed that the detection performance was the best when 3–5 mg of metalloporphyrin was deposited.

Conclusions

In this study, a tin oxide-based sensor was functionalized with different amounts of metalloporphyrin, and the characteristics of the sensor were investigated. The sensing material of the sensor was coated using electron beam evaporation to ensure the reliability of the manufactured sensor. In the case of the sensor deposited with 3–5 mg of metalloporphyrin, the response, response time, and recovery time all showed the best performance. This sensor appeared to have a high responsivity as it could provide a sufficient number of adsorption sites for the gas to respond; moreover, the use of 3–5 mg of metalloporphyrin did lead not to interference with the movement of electrons, enabling the sensors to achieve a fast response time and recovery time. Compared to bare SnO_2, the sensor functionalized with 3 mg of metalloporphyrin are improved the response and recovery time by 55.6% and 84.1%, respectively.

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Authors' contributions
CB performed the experiments, analyzed the data, and wrote the manuscript. KJ supervised the research and reviewed the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
All data generated or analysed during this study are included in this published article.

Declarations

Competing interests
The authors declare that they have no competing interests.

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