

Degradation Mechanism and Expected Lifetime of SnO₂-based Gas Sensor Stored at High Temperatures

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SnO₂-based gas sensors have been widely accepted in hydrocarbon gas industries to detect gas concentration and leakage. They have already been installed at many gas facilities, including in arid climate regions. However, the degradation mechanism and expected lifetime of commercialized gas sensors at high temperatures have not been intensively studied in terms of resistance and response time, making it difficult to maintain and operate the sensors. Hence, we systematically examined the degradation mechanism of commercialized gas sensors and derived their expected lifetime under high temperatures. As the sensor is exposed to heat for more than 25 h, its response time begins to be delayed. After that, its maximum output voltage decreases, resulting in inaccurate gas concentration detection. This phenomenon occurs much faster as the temperature rises. This might be attributed to the poor mechanical adhesion of the SnO₂ film after heat exposure. Reliability tests at various temperatures revealed that the commercialized gas sensors are expected to degrade 10–88 times faster than those stored at room temperature. Therefore, the more frequent monitoring and calibration of the gas sensor operating at high temperatures are highly recommended to reduce the risk of explosive and asphyxiant gases.

1. Introduction

Gas sensors detect the concentration of flammable or toxic gases, providing safe working and living spaces for humans. Gas sensors must accurately measure gas concentration and respond rapidly to changes in gas concentrations. Among the many proposed gas sensors, semiconducting oxide (SnO₂)-based gas sensors have been widely adopted in the industry because of their low cost, ease of manufacturing, high sensitivity, and rapid responses to concentration change.⁽¹⁾ As the hydrocarbon gas enters the SnO₂ film, a chemical reaction occurs between the gas and oxygen vacancies in the SnO₂ film. As a result, the resistance of the SnO₂ film decreases under hydrocarbon gas atmosphere. The introduction of dopings, surface modifications, and nanostructures in the SnO₂ film leads to the improved sensitivity and selectivity of the SnO₂

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film to target gases.^(2–12) In commercially available SnO₂-based gas sensors, the SnO₂ film combines a voltage source with a reference resistor to convert the gas concentration into the output voltage of the system. Simple yet effective SnO₂-based gas sensors have been widely adopted to monitor concentrations of gases in the oil, gas, and petrochemical industries (e.g., methane, butane, propane, and gasoline) because of their reliable performance with high sensitivity.^(13,14) Sensor-incorporated safety systems ensure the safety of flammable gas facilities, such as refineries, oil wells, storage tanks, and gas stations. Considering the importance of gas sensor reliability, the characteristics of sensors have been monitored at room temperature for several months, which gave us an insight into the sensor's lifetime.^(15–17)

Unfortunately, many gas oil wells and related facilities are located in arid climate regions (e.g., the Middle East and Northern Africa), with an annual high temperature of 45 °C or higher.⁽¹⁸⁾ SnO₂-based gas sensors are likely to operate and be stored at very high temperatures, considering the location of the facility. Moreover, the sensors will be exposed to a very high temperature with poor ventilation during shipping and storage.⁽¹⁹⁾ As the temperature of insulated shipping and storage containers is normally higher by 20–30 °C compared with ambient conditions,⁽²⁰⁾ the heat during the shipping and storage affects the sensors. Generally, the performance of the semiconducting-film-based device is degraded much faster owing to the accelerated chemical reaction under high temperatures.^(21–23) Thus, the degradation mechanism and lifetime of the SnO₂ gas sensor under high temperatures would differ from those under room temperature. As a result, intensive studies have been conducted to determine the relationship between heat and the premature aging of SnO₂ gas sensors, revealing that elevated temperature plays an important role in sensor degradation. Yuan *et al.*⁽²²⁾ and Sun *et al.*⁽²³⁾ systematically studied the SnO₂ gas sensor's degradation after heat exposure, indicating that heat is one of the most severe factors in changing the resistance of gas sensors. In addition, it has been shown that the response time of the gas sensor was delayed under high temperatures.⁽²³⁾

Despite the intensive studies of the sensor's lifetime under high temperatures, the acceleration factor for the sensor's lifetime from high temperatures is still vague owing to a lack of long-term experimental data. Long-term exposure to heat is expected in the working and storage conditions of field-installed gas sensors in arid regions. The missing information for long-term exposure to heat makes it difficult to predict the lifetime of a sensor under high temperatures. Moreover, the comprehensive analysis of the gas sensor's lifetime in terms of resistance and response time has been hardly carried out. Although some works clearly indicated that the surrounding conditions affect the resistance and dynamic response of a SnO₂ gas sensor, the predicted lifetime based on response time has not been fully elucidated. Since SnO₂ gas sensors are used to detect some suffocating gases, the delayed response of the sensor will be critical in some applications.⁽²⁾ Despite the importance of a rapid and accurate response to the target gas in the SnO₂ gas sensor, the lack of a comprehensive understanding of the SnO₂-based gas sensor's reliability and expected lifetime under actual operating and storage conditions makes it difficult to establish guidelines for their maintenance and inspection, increasing the risk of systems monitored by them. Hence, it is required to clarify how fast and when the degradation of gas sensors occurs under high temperatures.

In this study, we aimed to systematically predict the lifetime of a SnO₂ gas sensor under high temperatures. Throughout reliability tests of commercially available SnO₂ gas sensors at various temperatures, we found that the degradation mechanism of SnO₂ gas sensors consists of two stages: (i) delayed response time and (ii) decreased resistance. On the basis of the reliability test, we derived the acceleration factor for the sensor, showing that the delay of response time is much faster than that of resistance change. The result shown here indicates that more frequent calibration and monitoring are recommended for SnO₂ gas sensors stored and installed at high temperatures. Moreover, the characteristics of the sensor stored at high temperatures should be checked before its installation. We believe that the result shown here contributes to maintaining and operating sensors installed at high temperatures.

2. Experiments

Commercially available SnO₂-based gas sensors (MQ-4 from Hanwei Electronics) were used to analyze their reliability. These sensors can detect various hydrocarbon gases (e.g., propane, methane, and butane) and are widely used in the gas industry to detect flammable gas leaks. In addition, their detection concentration range is 300–10000 ppm. The sensor system consists of a voltage source, a load resistor, and a SnO₂-based sensor-mounted printed circuit board, as shown in Fig 1. The SnO₂ film is deposited on the Al₂O₃ substrate, incorporating an electrically resistive heater to facilitate a chemical reaction between the SnO₂ film and hydrocarbon gases. Both sides of the SnO₂ film are attached with electrodes for electrical contact. When the SnO₂ film reacts with the target gas, the SnO₂-film-based resistance (R_{SnO_2}) decreases. Accordingly, under high concentrations of target gases, the voltage applied to a load resistor, displayed as an output voltage of the sensor, will increase. It means that the decreased voltage of the sensor indicates the increased resistance of the SnO₂ film. To monitor the dynamic and static responses of the SnO₂-based gas sensor to hydrogen gases, the output voltage is recorded by an oscilloscope (DS-1054Z from Rigol Ltd.). Here, the target gas is butane, whose concentration is 10000 ppm. It also applies an external voltage of 5 V to the sensor for operating the heater and collecting output data. For accurate measurement, we repeatedly measured the sensor five times in each case and used the average. To minimize error from residual gas, the sensor is exposed to fresh air (without hydrocarbon gas) for 5 min at each measurement.

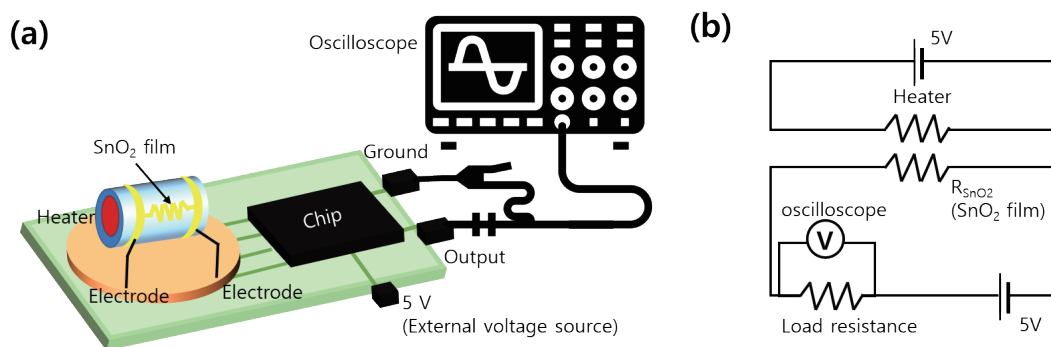


Fig. 1. (Color online) (a) Schematic and (b) circuit diagram of SnO₂-based gas sensor.

After the initial measurement, each sensor is stored at high temperatures (70, 80, 90, and 100 °C). The uniformity of the temperature chamber (MRU-408 from Neuronfit) is within ± 0.5 . In this report, we denote the gas sensors stored at A degrees as GS_A . For instance, the sample stored at 70 °C is marked as GS_{70} . After that, samples were repeatedly analyzed every 25 h until they lost their gas detection characteristics at the point of output voltage and response time. Before each measurement, the samples were cooled at room temperature for 30 min. Considering the deviation of reliability between samples, the average from 10 samples was taken in each case.

3. Results and Discussion

3.1 Degradation mode of SnO₂-based gas sensor

Figure 2 shows the output voltage of the load resistor in the SnO₂ gas-based sensor system and R_{SnO_2} that responds to the concentration of butane. When the gas enters the sensor without exposure to high temperature, the SnO₂ film typically reacts with the gas, decreasing R_{SnO_2} . Thus, the voltage applied to the SnO₂ film decreases from ~ 700 to 1–2 k Ω , while the voltage applied to the load resistor increases. As the output of the MQ-4 sensor represents the voltage applied to the load resistor [see Fig. 1(b)], the output voltage of the sensor system increases under highly concentrated butane (~ 10000 ppm). Under highly concentrated butane, the average maximum voltage (V_{MAX}) for 30 different MQ-4 sensors is 4.76 ± 0.05 V. Owing to the required time for the chemical reaction between butane and the SnO₂ film, it takes 0.35 s to reach 90% of V_{MAX} , called the rising time (T_{Rise}) of the sensor. As the gas is removed from the sensor, the SnO₂ film becomes less conductive by detaching the absorbed gas molecules from it. Accordingly, the output voltage of the system decreases to ~ 0 V and R_{SnO_2} increases to ~ 700 k Ω under fresh air. By measuring the output voltage of the sensor, it is possible to detect the flammable gas rapidly and reproducibly. The sensor operates stably at room temperature for up to 1000 h without significant degradation in T_{Rise} , R_{SnO_2} , and V_{MAX} .

However, its T_{Rise} is delayed, and V_{MAX} decreases when its storage time under high temperature (T_{HT}) increases. Figures 2(b) and 2(c) show two different degradation modes of the sensor under high temperatures. First, the degraded sensor responds to the gas slowly. Its T_{Rise} is

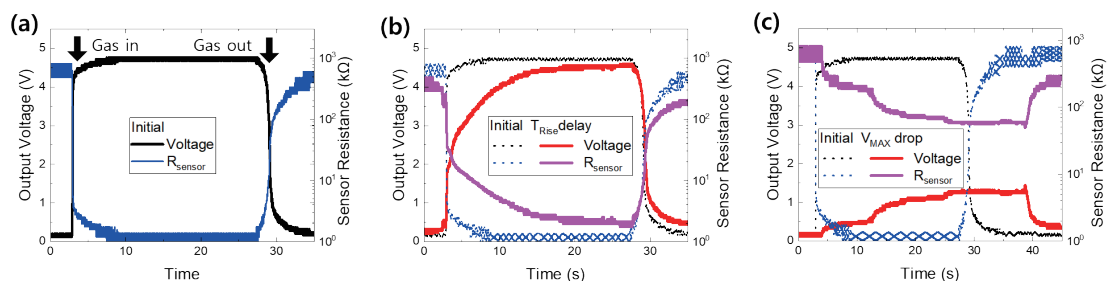


Fig. 2. (Color online) (a) Output voltage characteristics of SnO₂-based gas sensor system and corresponding resistance of SnO₂ film (R_{SnO_2}) under butane (~ 10000 ppm) before exposure to heat. (b) The delayed response and (c) decreased output voltage of gas sensor (increased resistance of SnO₂ film) were observed after long-term exposure to heat.

delayed to 5–10 s after a long T_{HT} compared with the initial measurement. In the worst case, exposure to heat delays its T_{Rise} by more than 10 s. The R_{SnO_2} of high temperature stored sensors also indicates that the long-term exposure of the sensor to high-temperature-postpones the reaction between the target gas and the SnO_2 film. The delayed response of the sensor to the gas might cause serious situations when toxic or flammable gases are leaked to nearby workers and ignition sources. After that, its output voltage decreases significantly. As shown in Fig. 2(c), the V_{MAX} of the sensor drops to below 1.5 V after a long T_{HT} . In consistent, the increase in R_{SnO_2} is observed after long-term heat exposure. The drop of V_{MAX} hinders the sensor from determining the gas concentration accurately, which is critical to controlling the chemical reaction and flammable limit of gases. In our experiment, both phenomena, delayed T_{Rise} and V_{MAX} drop (elevated R_{SnO_2}), are exhibited by every sensor exposed to heat for a long time. In addition, similar trends are observed under a liquefied petroleum gas, a mixture of propane, propylene, and isobutene (see Fig. S1). This reveals that the sensor becomes less reactive to various hydrocarbon gases after heat exposure.

3.2 Degradation of gas sensor under various high temperatures

Despite the common degradation mechanisms of SnO_2 -based gas sensor systems, the T_{HT} for degradation varies depending on the storage temperature. Figure 3 shows the representative output voltage characteristics of GS₇₀, GS₈₀, and GS₉₀. Although these conditions are beyond the maximum allowable temperature suggested by the manufacturer, the over-temperature can frequently happen in real working places and shipping owing to intense solar light irradiation and poor ventilation. The V_{MAX} values of all samples are initially above 4.7 V (4.72–4.95 V). However, such values start to decay as their T_{HT} increases. At GS₇₀, the sensor maintains its V_{MAX} above 4.5 V up to T_{HT} of 400 h. After that, it gradually decreases its V_{MAX} and finally declines below 1.5 V after the T_{HT} of 750 h. That means that its R_{SnO_2} increases above 50 k Ω after prolonged exposure to heat under highly concentrated butane, which is 50 times higher than its initial value. GS₈₀ and GS₉₀ also exhibit similar degradation trends; however, the time for maintaining V_{MAX} above 4.5 V and V_{MAX} drop below 1.5 V becomes much shorter owing to increased heat stress. For example, GS₈₀ and GS₉₀ hold their V_{MAX} above 4.5 V for the T_{HT}

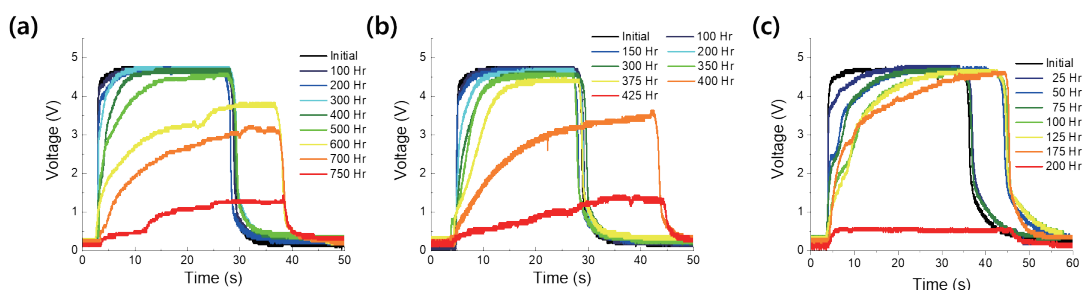


Fig. 3. (Color online) Output voltage characteristics of SnO_2 -based gas sensor system stored at (a) 70, (b) 80, and (c) 90 °C under high butane concentration (~ 10000 ppm). As the samples are stored at high temperatures longer, V_{MAX} becomes smaller, and T_{Rise} is more delayed.

values of 375 and 175 h, respectively. In addition, it takes 425 and 200 h to degrade V_{MAX} below 1.5 V in the case of GS₈₀ and GS₉₀, respectively. These values are much shorter than those derived from GS₇₀.

For statistical analysis, we investigated the average V_{MAX} and its deviation of samples depending on T_{HT} , as shown in Fig. 4. Here, the average and its deviation are achieved from 10 different samples. After short-term heat exposure, all the sensors maintain their initial V_{MAX} (>4.5 V), and then the average V_{MAX} of the sensor starts to decline. As the storage temperature of the sensor elevates, its average V_{MAX} rapidly decreases. For example, the V_{MAX} of GS₁₀₀ drops within 25 h of heat exposure. Furthermore, GS₉₀ starts to diminish its V_{MAX} after 100 h of T_{HT} . In contrast, GS₈₀ and GS₇₀ maintain their initial V_{MAX} values up to 200 and 375 h of T_{HT} , respectively. The T_{HT} values for V_{MAX} drop below 4 V in GS₇₀, GS₈₀, GS₉₀, and GS₁₀₀ are 540, 330, 220, and 110 h, respectively. Moreover, it takes 670, 400, 285, and 155 h to decrease V_{MAX} below 2.5 V ($LT_{2.5V}$) in the cases of GS₇₀, GS₈₀, GS₉₀, and GS₁₀₀, respectively. After 200 and 400 h of T_{HT} , the V_{MAX} values of GS₁₀₀ and GS₉₀ fall below 1.5 V, indicating that they no longer accurately detect gas concentrations. Similarly, GS₈₀ and GS₇₀ are degraded under elevated temperatures with reduced speed. The result clearly indicates that a SnO₂-based gas sensor is susceptible to heat stress, and its degradation correlates with its storage temperature. Moreover, its output voltage drops become more severe and faster under high temperatures, indicating that heat and temperature play an important role in determining the possible operation time of the gas sensor.

In addition, more time is required to reach V_{MAX} , as the sensors are exposed to higher temperatures. As the sensor is exposed to a high temperature for more than 50 h, its T_{Rise} gradually increases. Finally, T_{Rise} saturates around 15 s in our experiment. Although the T_{HT} for delaying T_{Rise} differs depending on the surrounding temperature, all samples follow similar trends. For example, the T_{Rise} of GS₇₀ is less than 5 s until 400 h of T_{HT} . Additionally, the average T_{Rise} of GS₇₀ is maintained within 10 s (7.5 ± 2.2 s) for 500 h of T_{HT} . Its value saturates around 15 s after 700 h of T_{HT} . On the other hand, the T_{Rise} values of GS₈₀ and GS₉₀ increase much faster than that of GS₇₀. The T_{Rise} of GS₉₀ is 3.9 ± 1.1 s after 100 h of T_{HT} . Even worse, its T_{Rise} increases to 8.5 ± 4.7 s at 200 h of T_{HT} . Finally, it takes 400 h of T_{HT} to saturate T_{Rise} . Similar

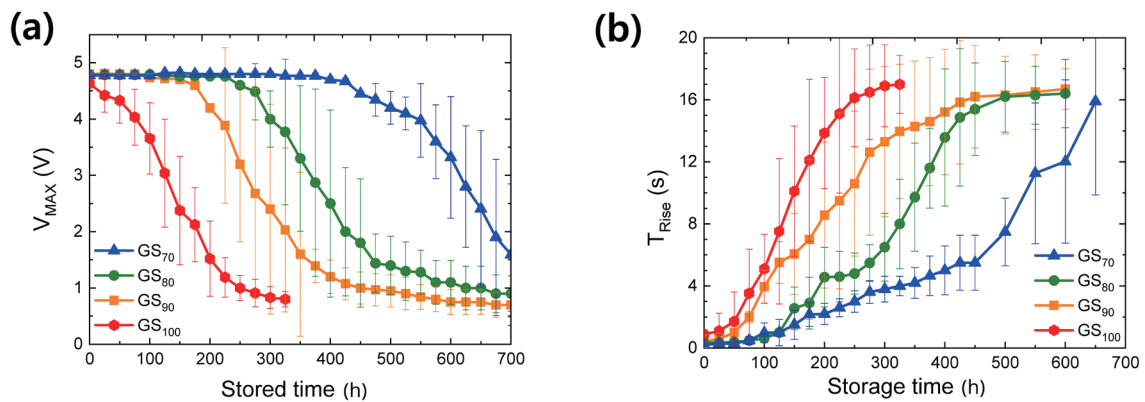


Fig. 4. (Color online) Average (a) V_{MAX} and (b) T_{Rise} of SnO₂-based gas sensor system stored at 70, 80, 90, and 100 °C.

trends in T_{Rise} are also observed in the cases of GS₈₀ or GS₁₀₀, but the required T_{HT} to saturate T_{Rise} varies depending on the surrounding temperature (500 h for GS₈₀ and 250 h for GS₁₀₀). The results reveal that the sensor exposed to a higher temperature for a long time is no longer adequate for a system requiring a rapid response to the leak of toxic and flammable gases. Moreover, this phenomenon is worse when the surrounding temperature is elevated.

3.3 Origin of gas sensor degradation under high temperatures

We believe that the delayed response of a heat-exposed SnO₂ film to hydrocarbon gases is attributed to the deteriorated mechanical adhesion of the SnO₂ film. There are three possible factors used to determine the T_{Rise} of a SnO₂-based gas sensor: (i) the resistance and capacitance of the sensor system except for R_{SnO_2} , (ii) the change in heater temperature, and (iii) the change in the rate of reaction between the gas and the sensor. If the sensor system's resistive and capacitive elements increase, V_{MAX} 's T_{Rise} and falling time will be delayed simultaneously following an inverse relationship with the resistive and capacitive values.^(24–26) The increase in T_{Rise} is distinctive in our experiment, but the falling time, the time for decreasing the output voltage from V_{MAX} to 0, remains constant despite heat exposure. Thus, the increased T_{Rise} might be unaffected by the changes of the resistive and capacitive elements in the sensor circuit except the SnO₂ film. Another plausible reason for the delayed gas sensor response after heat exposure is the decreased heater temperature. Usually, the heater is supposed to facilitate the chemical reaction between a SnO₂ film and the target gas.⁽²⁾ A heater is also implemented in MQ-4. However, the temperature of the heater is constant without any delay independent of heat exposure (see Fig. S2). Regarding the factors mentioned above, the only possible reason for the delayed T_{Rise} is that the SnO₂ film becomes less reactive to hydrocarbon gases. The film might be damaged either physically or chemically under high temperatures.

We monitored its microstructure and chemical composition to estimate the origin of the less sensitive and delayed response of the SnO₂ film after heat exposure. According to previous studies, the absorbed hydrocarbon molecules remaining on the surface of the SnO₂ film deteriorate R_{SnO_2} by replacing the chemical composition.^(27–30) In addition, the microstructure of the SnO₂ film affects R_{SnO_2} and V_{MAX} .^(2–12) However, there are no distinctive changes in the microstructure and crystallinity of the heat-exposed film, as shown in Figs. S3 and S4. The film itself is relatively reliable under high temperatures. The mechanical adhesion of the film becomes weaker after heat exposure. Figure 5 shows photographs of the gas sensor after the mechanical exfoliation test using a conventional sticky tape.⁽³¹⁾ The freshly laminated film, firmly bonded to the substrate with a binder, does not peel off. The electrical connection among the SnO₂ film and two electrodes, directly related to V_{MAX} , remains intact at the room-temperature-stored R_{SnO_2} . Moreover, the SnO₂ particles are interconnected in both parallel and series configurations. As a result, R_{SnO_2} decreases to below 1 k Ω , and V_{MAX} increases to 4.7 V under high gas concentrations.

However, the film is easily detached from the substrate after heating during a mechanical exfoliation test using a conventional sticky tape.⁽³¹⁾ Long-term exposure to heat makes the film brittle, potentially causing poor mechanical and electrical contact among SnO₂ particles. Some

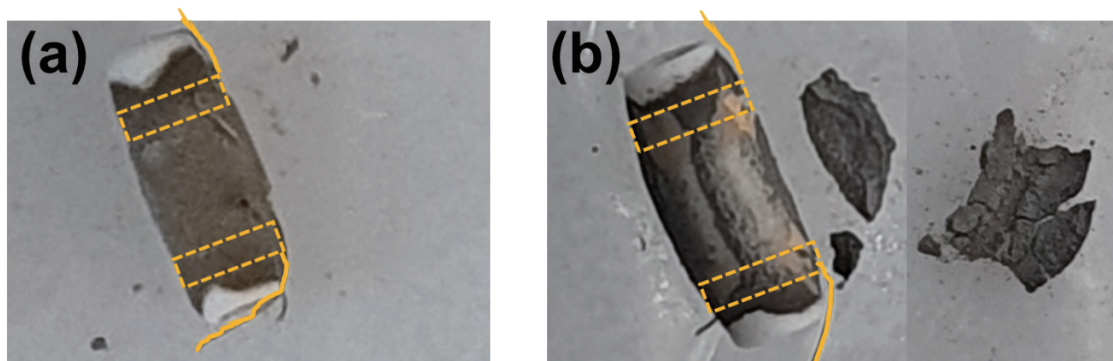


Fig. 5. (Color online) Photographs of (a) as-fabricated and (b) degraded (stored at 90 °C for 300 h) gas sensors after mechanical exfoliation test using conventional sticky tape. Here, the white substrate is a heater-incorporated Al_2O_3 layer, and the dark gray region is a SnO_2 film for detecting gas. Furthermore, the dashed yellow boxes are two electrodes attached to SnO_2 film. The SnO_2 film is firmly attached to the Al_2O_3 substrate before exposure to a high temperature. Moreover, the fresh film tends not to delaminate from the substrate. On the other hand, the SnO_2 film is easily exfoliated by a conventional sticky tape after heat exposure. The right side of (b) is a separate SnO_2 layer from the substrate after long-term heat exposure.

portions of the SnO_2 film may become disconnected and isolated from the sensor after heat exposure, which limits their contribution to the reduction in R_{SnO_2} in highly concentrated gases. We believe that the degradation of the film mainly originates from the degraded binder that connect each SnO_2 particle firmly. As the binder mainly consists of polymer, it is susceptible to a high temperature and loses its mechanical adhesion properties after long-term exposure to heat. The poor adhesion of the binder affects the electrical connection between SnO_2 particles, resulting in the decreased V_{MAX} after heat exposure. Also, the thickness of the SnO_2 film attached to the electrode might decrease compared to its initial status. Moreover, as parts of R_{SnO_2} are disconnected, the chemical reaction time for gas penetration into the SnO_2 film increases. This phenomenon has been reported under film-fabricated unoptimized process conditions.⁽³²⁾ Therefore, we believe that the poor adhesion between the substrate and the SnO_2 film causes an output voltage drop and a slow response of the conventional SnO_2 -based gas sensor after heat exposure. Further research aimed at improving the mechanical adhesion of the SnO_2 film, through adjustments to manufacturing processes and binder materials, could enhance the sensor's thermal stability.

3.4 Predicted lifetime of SnO_2 gas sensor under high temperatures

The output voltage characteristics of GS_{70} , GS_{80} , GS_{90} , and GS_{100} indicate that gas sensors degrade faster under high temperatures. On the basis of the experimental results, we predicted the predicted lifetime of gas sensors under high temperatures to develop its regular monitor planning, as shown in Fig. 6. Since the V_{MAX} and T_{Rise} of gas sensors degrade at different speeds, the predicted lifetimes based on V_{MAX} and T_{Rise} were separately derived. We set the required T_{HT} for reaching V_{MAX} values of 4 and 2.5 V as LT_{4V} and $LT_{2.5V}$, respectively. In addition, the required T_{HT} values for reaching T_{Rise} of 5 and 10 s are defined as LT_{5S} and LT_{10S} , respectively. Then, the

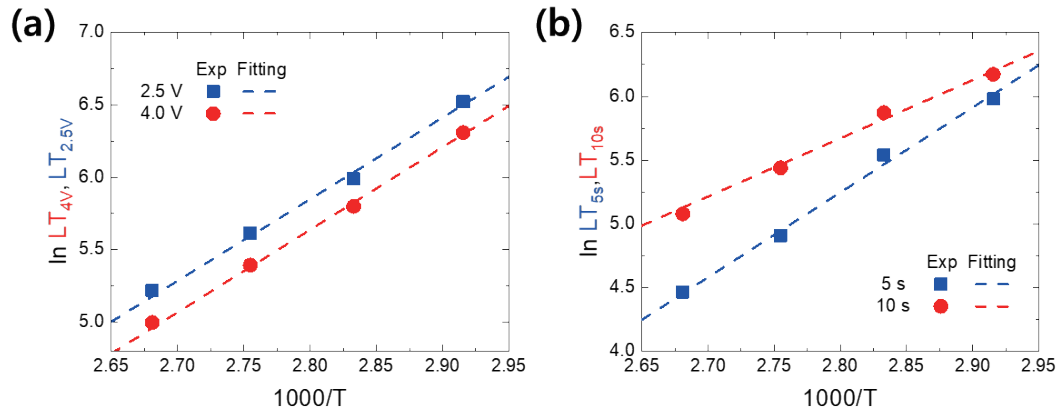


Fig. 6. (Color online) Lifetime-storage temperature characteristics of gas sensor considering its (a) V_{MAX} and (b) T_{Rise} . The dashed line is derived from the experimental results obtained using the Arrhenius equation.

predicted lifetime of gas sensors was calculated through the Arrhenius equation. According to this equation, the lifetime of a gas sensor is an inverse function of the stored temperature:

$$LT(T) = A \exp\left(-\frac{E_a}{KT}\right), \quad (1)$$

where $LT(T)$ is the lifetime of the gas sensor under a specific absolute temperature (T), A is a constant, K is the Boltzmann constant, and E_a is the activation energy of the sensor's lifetime. E_a is negative since the chemical reaction is inversely proportional to the lifetime. The E_a values of LT_{4V} , $LT_{2.5V}$, LT_{5S} , and LT_{10S} are 0.453, 0.459, 0.550, and 0.484 eV, respectively.^(33,34) The derived LT_{4V} and $LT_{2.5V}$ of the gas sensor are 15000–20000 h (1.7–2.2 years) at 20 °C, which is close to its commonly guaranteed working hours (2–3 years) provided by the manufacturer.⁽³⁵⁾ The difference between them might be attributed to the difference in assumption that the temperature is changed to day and night under the actual operating condition, but the same temperature is applied in the experiment. On the basis of the model, we calculated the relative LT_{4V} , $LT_{2.5V}$, LT_{5S} , and LT_{10S} summarized in Table 1. The gas sensors under high temperatures degrade 10–36 times faster than those stored at room temperature at the point of V_{MAX} . The LT_{4V} of gas sensors stored at high temperatures is shorter by 10.48–36.55 times than those of GS₂₀. Moreover, the elevated temperature accelerates the $LT_{2.5V}$ of GS₇₀, GS₈₀, GS₉₀, and GS₁₀₀ by more than 9.23, 14.77, 20.89, and 35.16 times, respectively. It is clear that an elevated temperature plays an important role in decreasing the lifetime of SnO₂-based gas sensors, which are more accelerated at higher temperatures. Thus, the V_{MAX} of gas sensors operating and stored at high temperatures should be more frequently monitored and calibrated to avoid inaccurate gas concentration measurements. Moreover, gas sensors operating under elevated temperatures should be replaced earlier than those at room temperature.

Even worse, they exhibit a much shorter lifetime at the point of T_{Rise} than the sensor at the point of V_{MAX} . As summarized in Table 1 and shown by the derived activation energy, the

Table 1

Expected relative LT_{4V} , $LT_{2.5V}$, LT_{5S} , and LT_{10S} of gas sensors (inverse of acceleration factors) compared with the sensor stored at 20 °C.

Temperature	V_{MAX}		T_{Rise}	
	LT_{4V}	$LT_{2.5V}$	LT_{5S}	LT_{10S}
GS ₇₀	1/10.48	1/9.23	1/19.56	1/12.22
GS ₈₀	1/17.15	1/14.77	1/30.30	1/18.24
GS ₉₀	1/24.82	1/20.89	1/57.24	1/30.27
GS ₁₀₀	1/36.55	1/35.16	1/88.79	1/43.77

sensor's response time is more susceptible to heat than its output voltage. For example, the acceleration factors of LT_{5S} and LT_{10S} are 88.79 and 43.77 at 100 °C, respectively. In addition, the LT_{5S} and LT_{10S} of GS₉₀ are 57.24 and 30.27 times shorter than those of gas sensors at room temperature, respectively. These values are more significant than those of LT_{4V} and $LT_{2.5V}$. Moreover, the LT_{5S} and LT_{10S} of GS₇₀ are 19.56 and 12.22 times shorter than those of gas sensors stored at room temperature. The LT_{5S} and LT_{10S} of gas sensors under high temperatures are 1.32–2.31 times shorter than their corresponding LT_{4V} and $LT_{2.5V}$, indicating that the response time of gas sensors is more susceptible to heat. Therefore, more careful and frequent inspections of the response time of a gas sensor should be conducted at high temperatures. Moreover, it is recommended to replace SnO₂-based gas sensors with other types of sensor in facilities that require a rapid response to gas concentrations at high operating temperatures.

Owing to the temperature change throughout the day and a significant temperature drop after sunset, the actual lifetime of the gas sensor would be longer than the result. However, the result shown here would be constructive for facilities with flammable gas to make guidelines for operating and maintaining SnO₂-based gas sensors. If further lifetime analysis of gas sensors under a temperature cycle is conducted, a more accurate lifetime of gas sensors will be obtained.

4. Conclusions

In this work, we systematically analyzed the degradation of commercialized SnO₂-based gas sensors. As they are exposed to high temperatures for more than 100 h, the sensors respond to the gas more slowly. As a result, a significant increase in T_{Rise} is observed. After that, their maximum output voltage decreases and reaches below 1.5 V within 700 h of heat exposure above 70 °C. The time required for the degradation decreases as the surrounding temperature increases. We believe that the primary degradation mechanism of the sensors is the degradation of the SnO₂ film rather than other heating and circuit elements. The degradations of GS₇₀, GS₈₀, GS₉₀, and GS₁₀₀ are accelerated 10 to 88 times or more than those of gas sensors stored at room temperature. Specifically, the response time of a gas sensor degrades faster at high temperatures than its V_{MAX} drop. Hence, more frequent monitoring and calibration are recommended for a SnO₂-based sensor installed and stored at high temperatures.

Acknowledgments

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Supplementary information

Response of gas sensor to liquefied petroleum gas

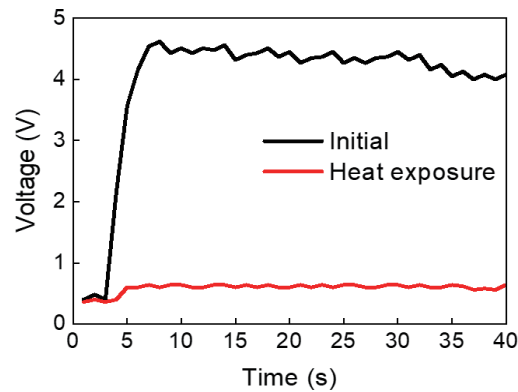


Fig. S1. (Color online) Output voltage characteristics of the SnO₂-based gas sensor system under liquefied petroleum gas (~1000 ppm). After 300 h of heat exposure (90 °C), the V_{MAX} of the gas sensor dropped significantly (<1 V). This is in good agreement with the experimental result of the gas sensor under highly concentrated butane.

Temperature of heater after long-term heat exposure

Figure S2 shows the heater's temperature inside the SnO₂ gas sensor. The heater elevates the sensor's temperature, facilitating the chemical reaction between the SnO₂ film and the gas. The temperature will decrease if T_{Rise} is delayed from the damaged heater after heat exposure. Moreover, its temperature increases slowly. However, the thermography and temperature-time graph of the heater is in the same range after heat exposure. Thus, the delayed T_{Rise} does not originate from the damaged heater.

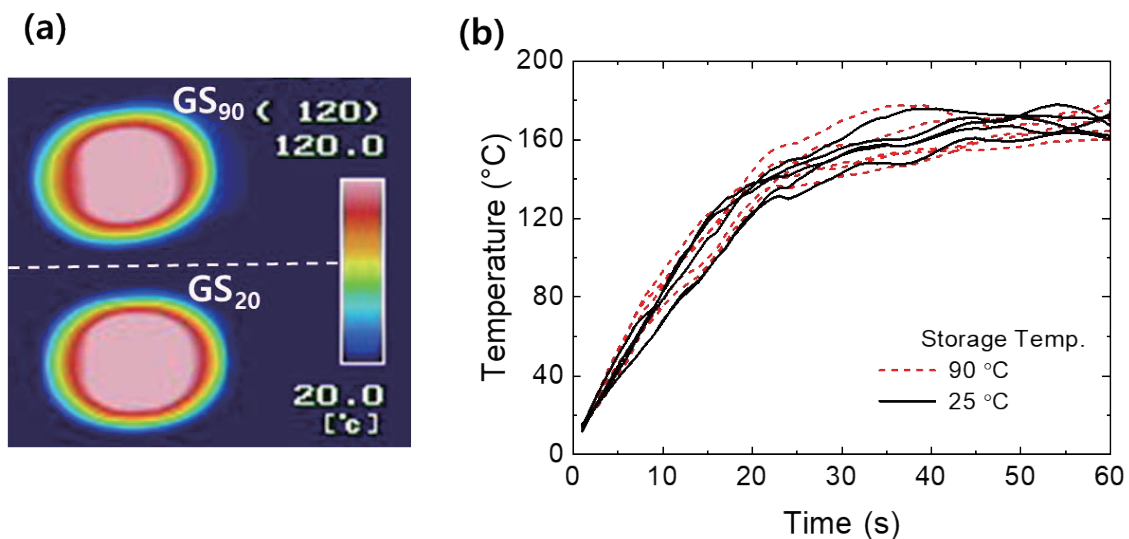


Fig. S2. (Color online) (a) Thermography image of SnO₂-based gas sensor after applying 5 V for 1 min. (b) Heater temperature-time characteristics of the sensor. Here, the sensor was stored at 90 °C and room temperature for 500 h. The temperature of the sensor is independent of heat exposure. All samples are in a similar range.

Microstructure and crystallinity of SnO₂ film after heat exposure

The microstructure and crystallinity of the SnO₂ film were investigated before and after heat exposure to estimate the origin of sensor degradation through scanning electron microscopy (SEM) images and X-ray diffraction (XRD), respectively. Despite significant changes in output voltage and response time in a gas sensor after annealing, the microstructure and crystallinity of the SnO₂ film do not markedly change. These results confirm that the SnO₂ film does not change its chemical bonding and microstructure after long-term heat exposure.

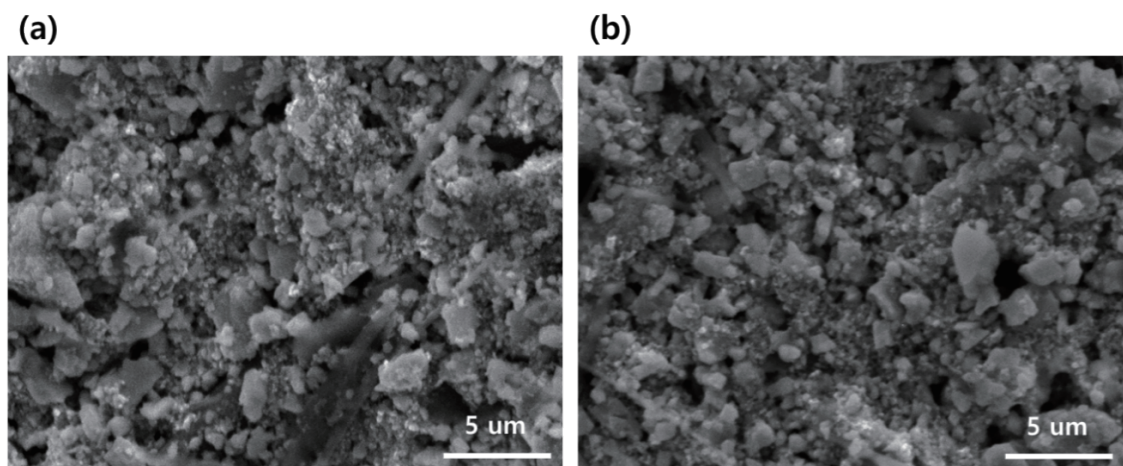


Fig. S3. SEM images of SnO₂ film (a) before and (b) after 300 h of heat exposure (90 °C).

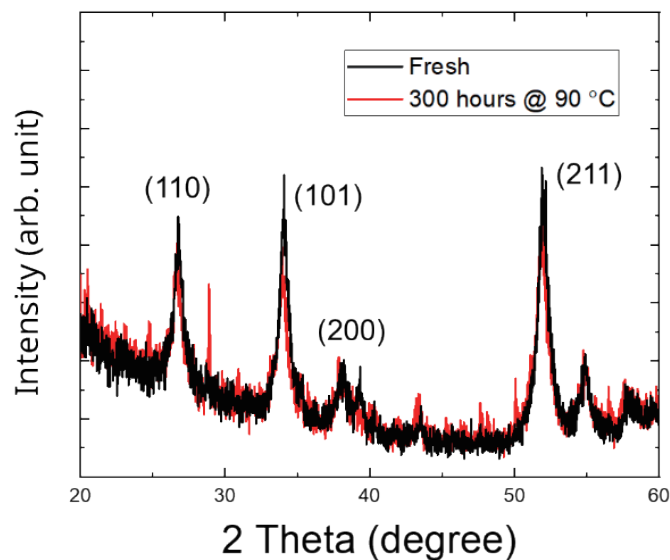


Fig. S4. (Color online) X-ray diffraction patterns of SnO₂ film before and after 300 h of heat exposure (90 °C).