



Article

Annealing Effects on SnO₂ Thin Film for H₂ Gas Sensing

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Abstract: Hydrogen (H₂) is attracting attention as a renewable energy source in various fields. However, H₂ has a potential danger that it can easily cause a backfire or explosion owing to minor external factors. Therefore, H₂ gas monitoring is significant, particularly near the lower explosive limit. Herein, tin dioxide (SnO₂) thin films were annealed at different times. The as-obtained thin films were used as sensing materials for H₂ gas. Here, the performance of the SnO₂ thin film sensor was studied to understand the effect of annealing and operating temperature conditions of gas sensors to further improve their performance. The gas sensing properties exhibited by the 3-h annealed SnO₂ thin film showed the highest response compared to the unannealed SnO₂ thin film by approximately 1.5 times. The as-deposited SnO₂ thin film showed a high response and fast response time to 5% H₂ gas at 300 °C of 257.34% and 3 s, respectively.

Keywords: SnO₂ thin films; metal oxide gas sensor; hydrogen gas sensor; annealing effect



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1. Introduction

Since the industrial revolution, fossil fuels have been used as a major energy source for humanity. However, environmental problems caused by the emission of harmful gases during fuel combustion have emerged, and research on future renewable energy sources, such as solar, nuclear, and wind power, is underway. Among them, hydrogen (H₂) is attracting attention as a renewable energy source used in various fields, such as automobiles, fuel cells, and chemical industries, because of its environmental friendliness and high energy density characteristics [1,2]. However, H₂ has a flame propagation speed of approximately eight times faster than methane, whereas its minimum ignition energy is approximately 0.06 times lower than methane, which can easily cause a backfire or explosion owing to minor external factors [1,3,4]. To use the H₂ gas in the industry environment, H₂ stability should be ensured, and the detection of gases in the environment containing H₂ is inevitable. H₂ is a colorless, odorless, and volatile gas with a relatively high lower explosive limit of 4%. Therefore, detection by concentration at low and high concentrations and fast response time are significant in H₂ sensing [3].

Based on the method of detection, H₂ gas sensors are generally divided into contact (electrochemical, semiconductor, and solid electrolyte sensor), composite (photoionization and total reflection sensor), and optical type sensors (non-dispersive infrared, and photoacoustic sensor) [1,5]. The semiconductor gas sensor detects the target gas by reading a change in the resistance owing to the difference in the electronic density of a semiconductor surface of the sensing unit when gas flows. This sensing method is advantageous because semiconductor gas sensors are inexpensive, can be easily manufactured in large quantities through microelectromechanical system processes, has a simple configuration of detection circuits, and can detect various types of gases. However, because semiconductor

gas sensors are driven at relatively high temperatures, they mainly use a metal-oxide-semiconductor form that is stable at high temperatures. Materials commonly used for metal oxide gas sensors include ZnO [4], SnO₂ [6–8], and TiO₂ [1], among which SnO₂ has been extensively studied as SnO₂ film-structured gas sensors exhibit high response results and fast response rates for specific gases, owing to their unique characteristics. SnO₂ is an n-type semiconductor with a wide energy band gap of 3.6 eV and a tetragonal rutile structure caused by oxygen vacancy. In an n-type semiconductor such as SnO₂, when external thermal energy is applied, an oxygen vacancy layer acts as a donor to change the number of electrons, thereby adjusting the grain boundary that influences the electrical conductivity and gas sensitivity of the semiconductor film. Therefore, SnO₂ is mainly studied to adjust the electrical conductivity and gas sensitivity by controlling the thickness and grain size of the SnO₂ thin film. In 1971, Naoyshi studied the first gas sensor that used SnO₂ as a sensing material [6]. Thenceforth, various studies have been reported for SnO₂ deposition methods, such as the sol-gel method [6], thermal evaporation [9], radio frequency (RF) sputtering [10], chemical vapor deposition [11], and the ion-beam method [12]. Among them, RF sputtering has been extensively investigated with the commercial advantages of a uniform deposition rate, cost-effectiveness, and high reproducibility. However, high energy deposition can result in unevenness or damage to the film. To improve performance and complement disadvantages of SnO₂ film by sputtering, various post-treatment methods, such as annealing [13,14], acid treatment [15], and plasma treatment [16], were studied. Among them, the annealing method influences the shape and size of the crystal grains of the SnO₂ thin film, changes the oxygen vacancy by the injected O₂ gas in the annealing process, and changes the characteristics of the thin film.

In this study, the SnO₂ thin film was deposited on a glass substrate using RF sputtering and applied as an H₂ gas sensor. Our research aims to develop a high-performance sensor that can detect H₂ more sensitively than general SnO₂ sensors by optimizing the annealing time condition of SnO₂ thin films and exploring the sensor operating temperature. In addition, based on the optimization conditions, it was attempted to maximize the H₂ sensing ability by minimizing the problem of interference with other gases, which most metal oxide-based MOS sensors face.

2. Materials and Methods

2.1. Sensor Fabrication

The SnO₂ thin film was deposited using RF sputtering. A glass wafer was used as the substrate, and Au was deposited using E-beam evaporation in advance to form an interdigitated electrode. The 99.99% purity target of SnO₂ was used as a sputtering source under a base pressure of 5×10^{-6} torr. Ar and O₂ gases were used as reaction gases under a flow rate of 10 sccm, and deposition energy of 150 W was applied. The SnO₂ thin film, with dimensions of 2.7×2.85 mm, was deposited on the glass substrate, with a dimension of 5×5 mm. Subsequently, the deposited SnO₂ thin film was annealed at 500 °C under air condition, which was annealed for 1~5 h, with intervals of 2 h. The schematic image of the full fabrication is shown in Figure 1.

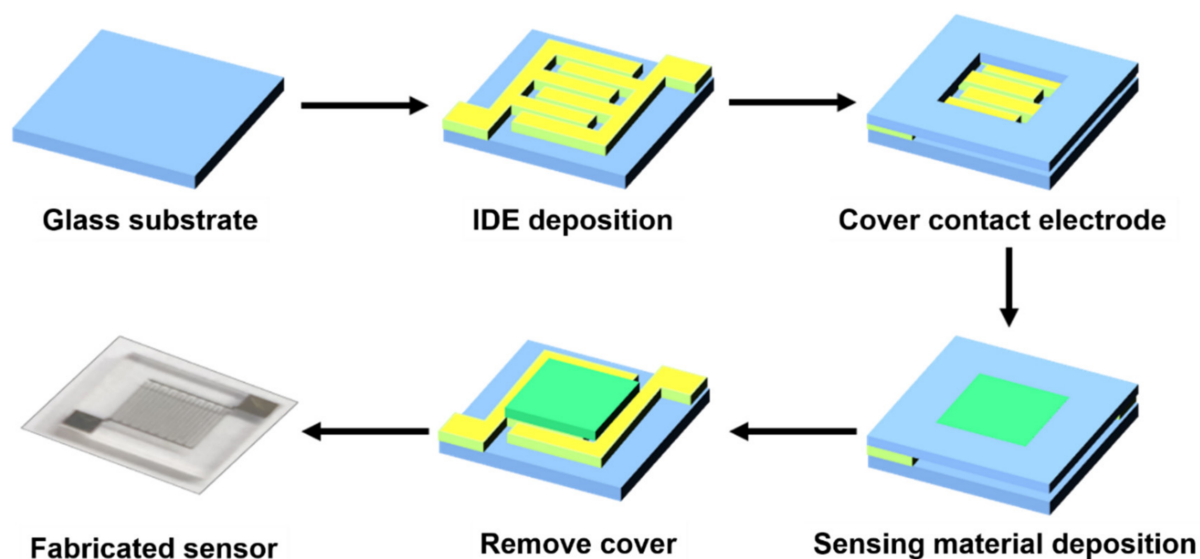


Figure 1. Schematic for SnO₂ gas sensor fabrication.

2.2. Sensor Characterization

The X-ray diffraction (XRD, model Empyrean, Panalytical) was used to analyze the crystal structure before and after annealing of the deposited SnO₂ thin film, and a field emission scanning electron microscope (model SU8220, Hitachi) was used for surface morphology and film thickness analysis. The atomic force microscope (AFM, model NX20, Park Systems) was used for surface characterization, and the hydrogen gas sensing performance was evaluated in the manufactured gas chamber, as shown in Figure 2. In the experiment, H₂ gas concentration was adjusted using a mass flow controller (MFC), and a voltage of 1 V was applied to the gas sensor using a source meter (model B2902B, Keysight) to determine the changes in resistance during sensing caused by changes in the H₂-air environment. The test was performed by fixing the air and H₂ flow rate sum at 400 sccm using an MFC and adjusting the H₂ concentration ratio. The gas detection experiment was performed by placing the sensor on the ceramic heater in the chamber and raising the temperature of the heater from 150 to 300 °C.

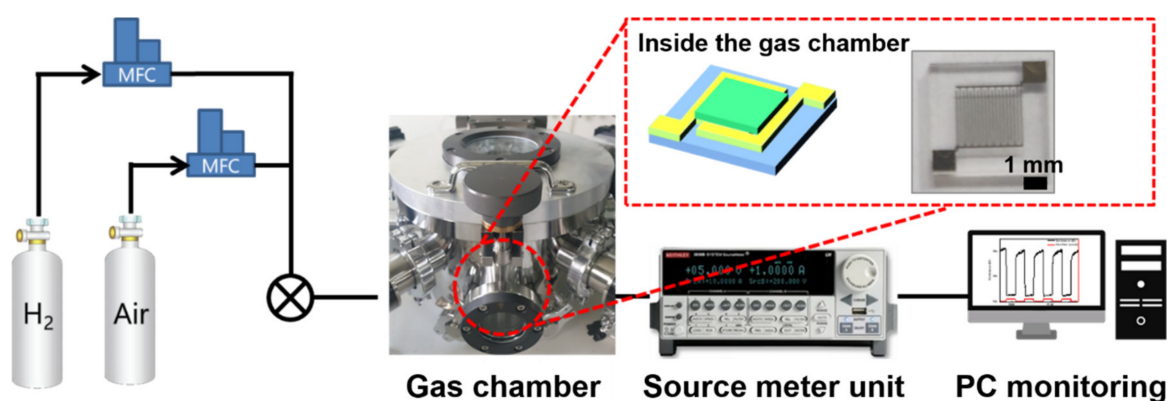


Figure 2. Schematic of gas sensing setup.

3. Results and Discussion

3.1. Structural and Morphological Characteristics

The crystalline structure is closely related to surface morphology. Based on the annealing process, gas sensing properties are influenced by inducing changes in morphology and structure. In addition, because the sensing process is usually operated at high temperatures, sensors that are annealed after deposition are more stable at the operating temperatures.

Metal oxides such as SnO₂ are highly sensitive to annealing, with different crystalline defects, such as oxygen vacancy or lattice disorder [17]. The grain size of the metal oxide shows a grown pattern under conditions of increasing the annealing time at a fixed temperature or changing the annealing temperature. In our case, the grain morphology change of SnO₂ was confirmed by changing the annealing time under the constant temperature condition of 500 °C. The annealing temperature was set through experimental results. SnO₂ thin films were prepared by the RF sputtering method, and these were annealed at a temperature of from 300 to 900 °C per 200 °C, respectively. The optimal temperature condition was set by measuring the response to the hydrogen of this thin film sensor. The finally set annealing optimum temperature was 500 °C. (Figure S3).

XRD patterns show the diffraction peaks of all the samples observed in the SnO₂ pattern (JCPDS no. 41-1445, Figure 3a). From the XRD peaks, the average grain sizes of SnO₂ thin films for different annealing times were calculated using the Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where D is the grain size; K is a constant that depends on the crystalline shape and indices with a value of approximately 0.9; λ is the radiation wavelength; β is the crystalline size, measured at half of the maximum intensity; θ is the Bragg angle at which peaks are observed [18]. From the Scherrer equation, the average grain size of a SnO₂ thin film was calculated and is denoted in Figure 3b.

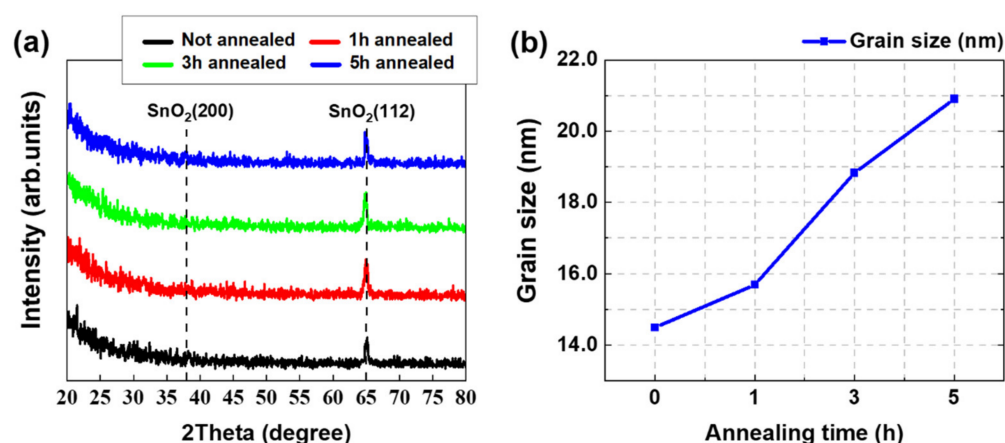


Figure 3. (a) XRD of SnO₂ for annealing time; (b) average grain sizes of the SnO₂ thin film with annealing times.

As shown in Figure 3b, an increase in annealing time increased SnO₂ grain size. Increases in annealing time result in corresponding increases in grain size. This is because smaller grains are combined into larger grains through high-temperature melting. The annealing time results in a rapid decrease in a non-bridging oxygen defects concentration, thereby forming SnO₂ grains [19]. Therefore, an increase in annealing time can be a factor in increasing grain size [20–22].

The surface morphologies of SnO₂ thin films from the as-deposited to 5-h annealed thin films, according to annealing time, are shown by the AFM images. As shown in Figure 4, the surface roughness decreased after the annealing time exceeded 1 h. The decrease was more severe when the annealing time exceeded 3 h. The thickness of film which is not annealed SnO₂ was about 55.6 nm by SEM cross-section image (Figure S1). The surface roughness of the as-deposited SnO₂ thin film was 1.042 nm. After annealing for 1 h, the surface roughness slightly increased to 1.066 nm. However, the surface roughness decreased as the annealing time increased, which was 0.921 nm after annealing the deposited SnO₂ for 3 h. The surface roughness further decreased to 0.399 nm after annealing for 5 h, showing a certain difference compared to the others. After annealing for 1 h, the surface roughness

increased because grains grew in the z-direction to the substrate surface, which occurred preferentially. Notably, island coalescence was absent for 1 h. However, after 1 to 5 h, the vertical surface roughness decreased with an increase in grain size, which became lateral. After being subjected to annealing for 1 h, the surface protrusions melted and grew on the lateral side, meaning the grain size increased. This decrease in surface roughness when the annealing time exceeded 1 h resulted from the island coalescence that created a smaller vertical distance to the top of the island [23].

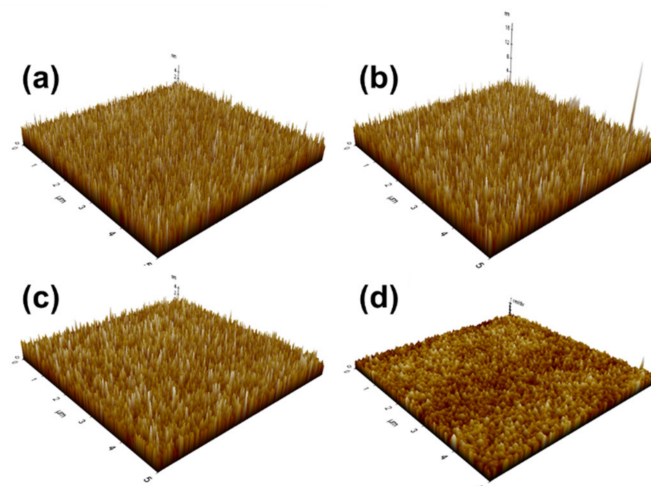


Figure 4. AFM surface image of SnO₂ thin film by annealing time; (a) as-deposited not annealed; (b) 1 h. annealed (c) 3-h annealed (d) 5-h annealed.

The gas sensor based on an n-type metal-oxide-semiconductor, such as SnO₂, is significantly influenced by the grain size. As the electrons flow against the energy barriers formed at the grain boundaries, the number of energy barriers decreases as the grain grows. When a SnO₂ film deposited by sputtering was annealed, the SnO₂ grain crumpled. Thus, the surface of the dense film became porous, increasing the reactive area for H₂ gas that is accompanied by increased sensitivity of the SnO₂ film. After annealing, the grain size of SnO₂ increased, and the energy barriers and grain boundary defects decreased [24].

3.2. Sensing Performance

We validated the effect of SnO₂ thin films on H₂ by adjusting the annealing time and confirmed the optimal conditions in which the sensor will perform under various operating temperatures.

An experiment to evaluate the SnO₂ sensing performance of H₂ gas was conducted inside the gas chamber by adjusting the internal temperature and gas concentration. The sum of the total flow rates of H₂ gas and air was fixed at 400 sccm, and the concentration of H₂ gas was controlled using the MFC. In the experiment, the sensor response for H₂ gas was calculated as follows:

$$\text{Response, } S(\%) = \frac{\Delta R}{R} \times 100 = \frac{R_0 - R}{R} \times 100, \quad (2)$$

R_0 is the resistance of the sensor measured in the air atmosphere before the H₂ gas injection, and R is the resistance of the sensor exposed to H₂ gas. Because SnO₂ is an n-type semiconductor, the resistance at the time of reaction with the H₂ gas is reduced. Therefore, the response of SnO₂ for H₂ gas is calculated as the difference in the resistance before the reaction to the change in the resistance after exposure to H₂.

The sensitivity and response time of the 3 h and unannealed SnO₂ for H₂ gas as conducted in the gas chamber of a fixed internal temperature of 300 °C is shown in Figure 5. According to Figure 5a, the response of both 3-h and unannealed SnO₂ increased with an increase in H₂ concentration; however, the response of the 3-h annealed SnO₂ showed a

higher value than the unannealed SnO₂ for the same hydrogen concentration. The gap between the values of the response of the two conditions increased as the difference in H₂ concentration increased. When the H₂ concentration reached 50,000 ppm, the highest response value was observed in the annealed condition (~378%), which was approximately 1.5 times higher than that of the unannealed (~251%). The H₂ sensing response and recovery time of a 3-h annealed SnO₂ as air and hydrogen flow is shown in Figure 5b. The response and recovery time of the 3-h annealed SnO₂ were approximately 12 and 53 s, respectively, under H₂ gas of 50,000 ppm at a chamber of 300 °C. (The graph of the response and recovery time of the sensor without annealing can be confirmed in the supplementary data, Figure S2). Kang et al. verified that the initial resistance of SnO₂ increases at some point as the annealing temperature increases [25]. In here, we also confirmed that the resistance value increased from the initial annealing value of 35 K to 80 M during the performed annealing time of 1 to 5 hours (Figure S2). The response time was calculated as the elapsed time for the resistance difference between R₀ and R to decrease from 90 to 10% after H₂ gas injection. Similarly, the recovery time was calculated as the time elapsed for the resistance difference to change from 10 to 90%.

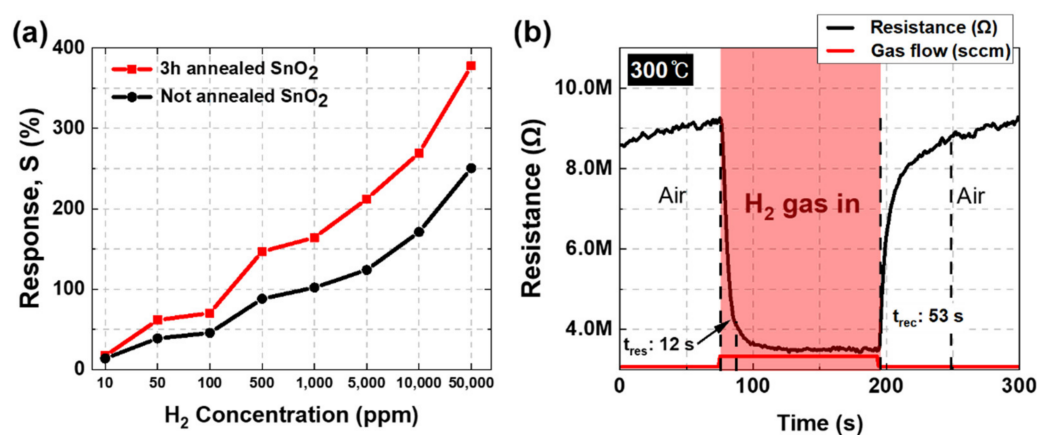


Figure 5. (a) Sensitivity of 3-h annealed SnO₂ and not annealed SnO₂ by H₂ concentration; (b) hydrogen response and recovery time of 3-h annealed SnO₂.

The sensitivity of metal oxides is influenced by many factors, such as the grain size of the material, surface area distribution, and charge carrier on the sensing surface. As shown in Figure 5, the sensitivity gradually increased with the annealing time, and the highest sensitivity was obtained at the 3-h condition. The response time showed a similar tendency to the sensitivity, and the highest value was obtained in the 3-h condition.

The sensitivity is closely related to the surface area and adsorption regions of the sensing gas. With an increase in grain size, the sensitivity of SnO₂ also increases with the surface area. Therefore, the 3-h annealed SnO₂ had a larger surface area and a larger grain size than the unannealed and 1-h-annealed SnO₂ films. This increased the sensitivity (according to the previous measurements, the grain size of SnO₂ increased with the annealing time (Section 3.1)). Figure 6 describes the charge transfer situation when the grain size is increased by performing annealing. In general, the electrical conductivity of semiconducting thin films is increased with annealing because, during the annealing treatment, it is influenced by the tunneling of the charge carriers through the barriers of the grain boundary and the recrystallization of grains [22,26]. The grain size is one of the significant factors that control resistance. The size of the crystallites is determined by directly manipulating the active surfaces (spread-out) of the thin films [22]. An increase in the diameter of the crystallites decreases the spread-out surface of the layer that is formed by the nanocrystallites' decrease. The effect of annealing increases the extended (active) surface at a certain cleavage limit of the resulting crystal, and thus the resistance value decreases [22,27].

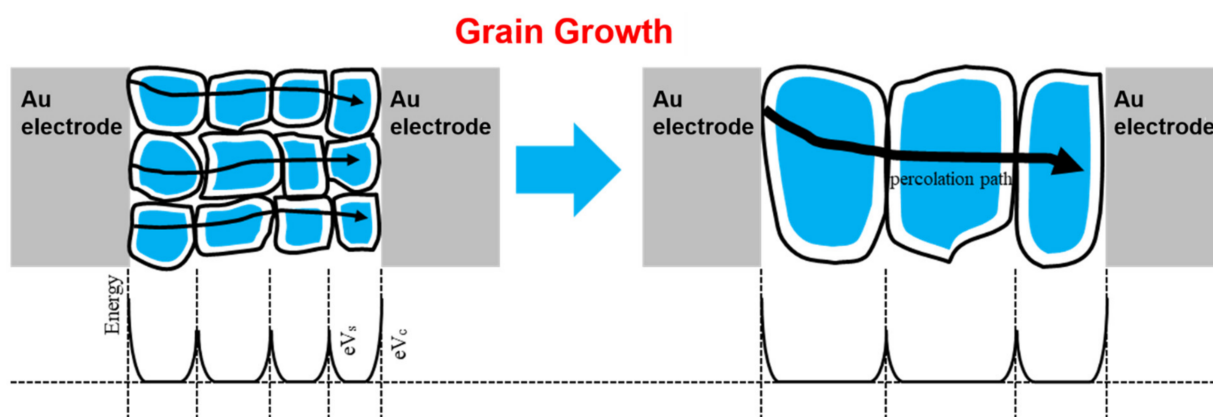


Figure 6. Schematic image of SnO₂ grain boundary and Schottky barrier with Au electrode before and after annealing.

The response and recovery times were also expected to increase with the increasing grain size of SnO₂ because a longer time is required to respond to more adsorption/desorption of H₂ gas on the surface of the sensing materials. Moreover, a larger time is required for saturation and recovery to the initial values, as shown in Figure 7. Lee et al. validated that the heat treatment was essential to induce changes in the gas sensing film morphology that was more stable to be operated at the sensing temperature, and the response time increased when annealing was applied [19].

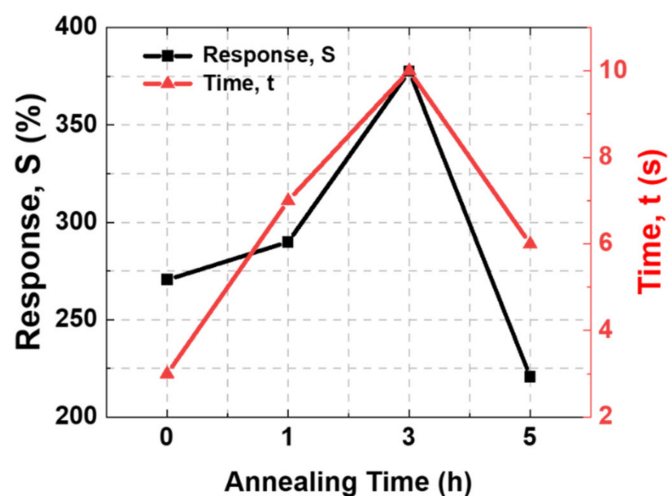


Figure 7. Sensitivity and response time for annealing time of SnO₂ thin film under a 300 °C gas reaction condition.

However, according to Figure 7, the response of the 5-h annealed SnO₂ showed the lowest sensitivity, although the grain size increased. This lowered reactivity is considered to be a phenomenon caused by surface roughness, as shown in Figure 4. The total surface area of SnO₂ annealed for 5 h was reduced compared to others, and the sensitivity to H₂ was also reduced.

Metal oxide-based gas sensors have different performance values according to changes in the operating temperature, owing to their sensing principle. Moreover, the response time is highly influenced by the operating temperature. As shown in Figure 8a, the sensitivities of all the sensors, i.e., the 1, 3, and 5-h-annealed sensors, increased up to the operating temperature of 300 °C. Furthermore, the response time of the 3-h-annealed SnO₂ decreased as the temperature increased, as shown in Figure 8b. Although the sensitivity and response time improved with an increase in operating temperature, the sensing tool was adversely

influenced by the high operating temperature of the gas chamber. Therefore, the experiment was limited to temperatures of at most 300 °C.

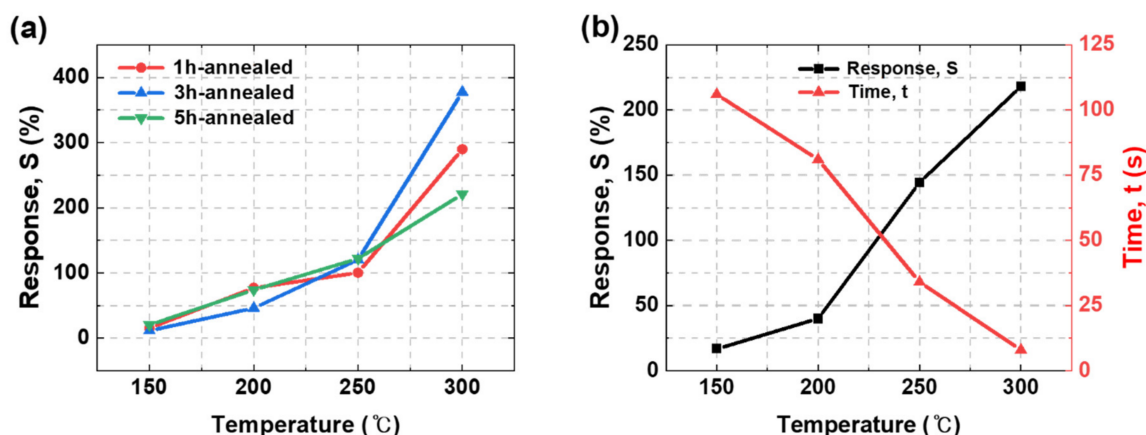


Figure 8. (a) Comparison of response according to the operating temperature of sensors fabricated under different annealing conditions. (b) Comparison of sensitivity and response time according to sensor operating temperature of H₂ sensor fabricated by annealing for 3 h.

Furthermore, we believe that the different optimal working temperatures for the sensors can be explained by assuming that two electron barriers exist between the SnO₂ grains and Au electrodes [28]. One is the barrier between individual SnO₂ grains, and the other is between the SnO₂ and Au electrodes. A charge transfer by gas adsorption/desorption must traverse the two barriers to the measuring device (multimeter). Thus, as the temperature increases, the kinetic energy of the electrons increases, and more electrons can easily jump over the two barriers and move faster than at a lower temperature. Therefore, sensitivity and response time can be improved, as shown in Figure 8.

The selectivity of the SnO₂ thin film to other gases was also validated. In addition to H₂, CO₂, NH₃, and NO₂ were reacted with the SnO₂ thin sensor at 300 °C. The gas sensing mechanism of the metal oxide-based hydrogen detection sensor consists of a chemical reaction between chemically absorbed oxygen and the target gas. The selectivity results for each gas of the SnO₂ thin film are shown in Figure 9. The response to CO₂ with the same concentration of 50 ppm as H₂ was the lowest at 3.89%. In the case of NO₂ and NH₃ gas, the sensor reacted with a low gas concentration of 50 and 20 ppm, respectively, owing to the risk of toxicity. The responses with these gases were 10.99% and 13.76%, respectively. Our gas sensor shows a high response to hydrogen. It is because our hydrogen sensor sets the optimal conditions for the high response, therefore exhibiting excellent reactivity compared to other gases. Another reason is that resistance deviation and the optimized temperature vary depending on the type of sensing gas. For example, NH₃ shows the highest response for SnO₂ thin film at about 100–150 °C. This temperature is much lower than the sensor operating temperature we set for the hydrogen detecting. This selectivity trend has shown that the optimized SnO₂ sensor indicates a better response to hydrogen than NO₂ and NH₃ [28].

In sensor applications, results should be consistent for repeated gas reactions to establish the reliability of the measurement values and product commercialization. Repeatability tests for H₂ gas were performed on a SnO₂ thin film sensor annealed for 3 h. The result is shown in Figure 10. The tests were performed at a reaction temperature of 300 °C for 5% H₂ gas, and a consistent gas response was shown without significant damage to the sensor, even after repeated reactions. A stable and reversible reaction was observed, even in the course of the repeated experiments. Based on these results, the SnO₂ thin film sensor fabricated with the RF sputtering method and treated to an optimal annealing process was stable and suitable for use as a H₂ detection sensor.

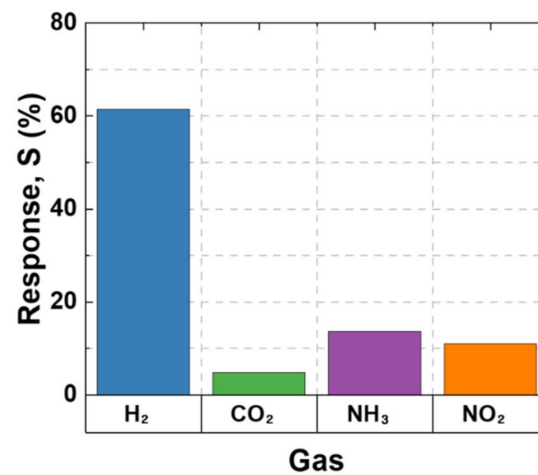


Figure 9. Gas selectivity of SnO₂ thin film.

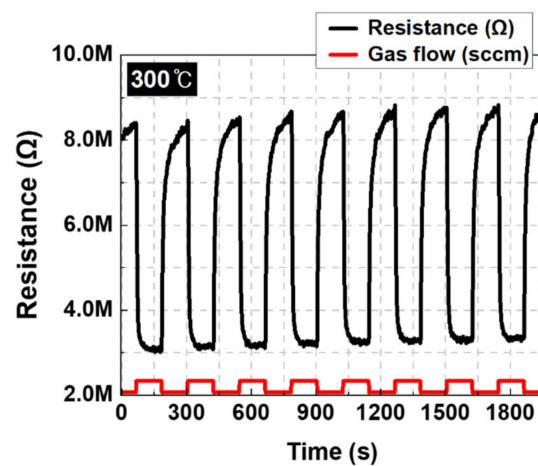
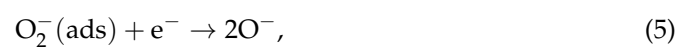


Figure 10. Repeatability tests of 3-h-annealed SnO₂ thin film (5%).

3.3. Sensing Mechanism

Gas sensing of SnO₂ functions on the difference in resistance resulting from the properties of n-type semiconductors caused by free electrons inside. The conductivity of the semiconductor gas sensor is controlled by subsequent reactions, such as chemical adsorption, oxidation, and diffusion of oxygen on the tin oxide's surface. This change occurs by gaining electrons from the reaction between absorbed oxygen and H₂ [24].

If free electrons are activated by applying thermal energy to SnO₂, they are captured on the surface by atmospheric oxygen, as shown in Figure 11a. By capturing the free electrons, the electron depletion layer is formed on the SnO₂ surface, thereby increasing the potential barrier and the internal resistance, as shown in Figure 11b. The chemical equations that explain the capturing of free electrons by oxygen are as follows:



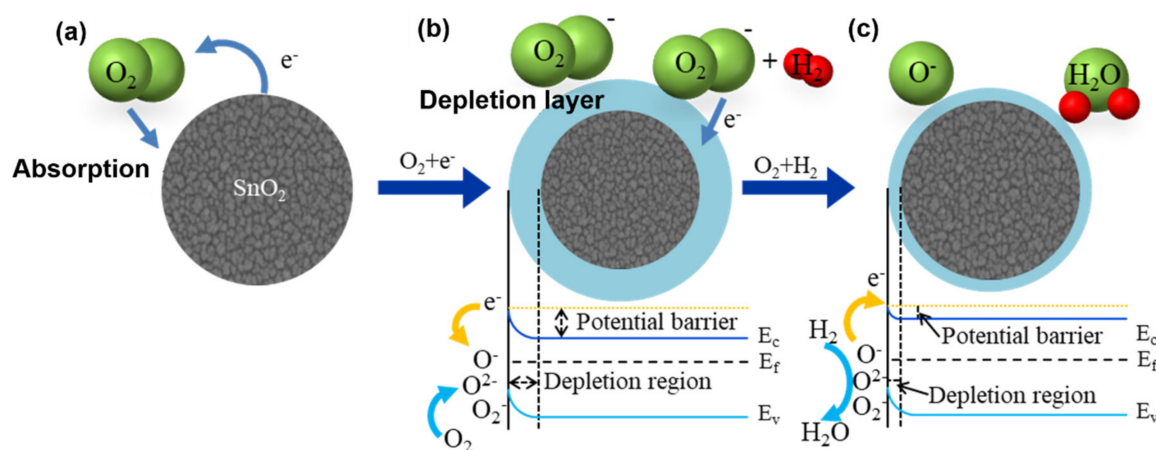
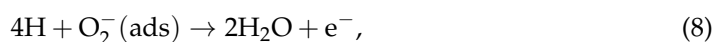
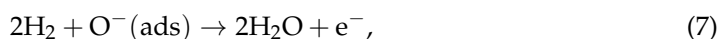
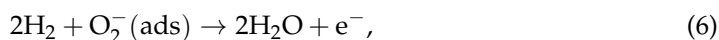


Figure 11. n-type metal oxide hydrogen sensing mechanism; (a) SnO₂ as-deposited; (b) SnO₂ in air; (c) SnO₂ in H₂ reduction gas.

Subsequently, H₂ gas is injected, free electrons react with captured oxygen to form water vapor, the oxygen adsorbed to the surface is removed, the captured free electrons are released, as shown in Figure 11c, potential barriers are lowered, and the internal resistance is reduced. A H₂ sensing reaction is expressed as follows:



4. Conclusions

This study fabricated a SnO₂ thin film gas sensor by depositing a metal oxide-based layer using the RF sputtering technique and annealing under high-temperature conditions. Here, the hydrogen gas detection performance of this SnO₂ thin film sensor, according to the annealing time and gas reaction operating temperature, was demonstrated.

We experimentally validated the H₂ sensing capability of the SnO₂ thin film sensor to improve performance by increasing the metal oxide grain size as the annealing treatment time increased (up to 3 h), which led to the improvement of the surface area for the gas response. In addition, we validated that the improvement of the operating temperature of the gas reaction of the sensor can improve sensor performance and shorten the response time by assisting the electrons to move through the electronic barrier. Our sensor showed excellent selectivity in hydrogen gas compared to other gases. In addition, the sensor could operate without being damaged, even for repeated gas reactions.

This study demonstrated that a robust and stable metal oxide sensor could be manufactured by completing the optimal annealing treatment on the metal oxide thin film introduced by the RF sputtering technique.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/nano12183227/s1>, Figure S1: Cross-section SEM image of unannealed SnO₂, Figure S2: Hydrogen response and recovery time of (a) unannealed SnO₂, (b) 1-h-annealed SnO₂, (c) 3-h-annealed SnO₂, and (d) 5-h-annealed SnO₂, Figure S3: Hydrogen response and time for the annealing temperature.

Author Contributions: Conceptualization, D.J. and H.K.A.; methodology, Y.Y., B.M., D.G.J. and J.L.; software, J.L., J.K. and Y.K.; formal analysis, Y.Y. and B.M.; investigation, Y.Y., B.M. and D.J.; writing—original draft preparation, Y.Y. and B.M.; writing—review and editing, Y.Y., B.M. and D.J.; visualization, Y.Y. and B.M.; supervision, B.M. and D.J.; All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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