



Article

Investigation of High-Sensitivity NO₂ Gas Sensors with Ga₂O₃ Nanorod Sensing Membrane Grown by Hydrothermal Synthesis Method

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Abstract: In this work, Ga₂O₃ nanorods were converted from GaOOH nanorods grown using the hydrothermal synthesis method as the sensing membranes of NO₂ gas sensors. Since a sensing membrane with a high surface-to-volume ratio is a very important issue for gas sensors, the thickness of the seed layer and the concentrations of the hydrothermal precursor gallium nitrate nonahydrate (Ga(NO₃)₃·9H₂O) and hexamethylenetetramine (HMT) were optimized to achieve a high surface-to-volume ratio in the GaOOH nanorods. The results showed that the largest surface-to-volume ratio of the GaOOH nanorods could be obtained using the 50-nm-thick SnO₂ seed layer and the Ga(NO₃)₃·9H₂O/HMT concentration of 12 mM/10 mM. In addition, the GaOOH nanorods were converted to Ga₂O₃ nanorods by thermal annealing in a pure N₂ ambient atmosphere for 2 h at various temperatures of 300 °C, 400 °C, and 500 °C, respectively. Compared with the Ga₂O₃ nanorod sensing membranes annealed at 300 °C and 500 °C, the NO₂ gas sensors using the 400 °C-annealed Ga₂O₃ nanorod sensing membrane exhibited optimal responsivity of 1184.6%, a response time of 63.6 s, and a recovery time of 135.7 s at a NO₂ concentration of 10 ppm. The low NO₂ concentration of 100 ppb could be detected by the Ga₂O₃ nanorod-structured NO₂ gas sensors and the achieved responsivity was 34.2%.

Keywords: field emission scanning electron microscope; Ga₂O₃ nanorods; hydrothermal synthesis method; NO₂ gas sensors; X-ray diffraction; X-ray photoelectron spectroscopy



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1. Introduction

In recent years, due to the rapid development of industries in human society, environmental pollution has become increasingly serious, such as noise, air pollution, water pollution, and nuclear pollution, etc. Among them, the air pollution of nitrogen dioxide (NO₂), causing harm to human health and the environment, is the most serious issue. Even a NO₂ concentration of 3 ppm is enough to cause serious damage and human health problems, including throat irritation, respiratory illnesses, and even death [1,2]. Therefore, to avoid the harm caused by NO₂ gas, it is very important to develop a gas sensor with high responsivity and high selectivity to detect NO₂ gas.

Among several structures of gas sensors, a metal oxide semiconductor (MOS) gas sensor is the most attractive structure due to its inherent advantages of easy fabrication, simple operation, low prices, and a small size [3]. Many metal oxide semiconductor materials have played promising roles in resistive types of MOS-structured gas sensors, such as zinc oxide (ZnO) [4,5], stannic oxide (SnO₂) [6,7], titanium dioxide (TiO₂) [8,9], indium oxide (In₂O₃) [10,11], and gallium oxide (Ga₂O₃) [12,13]. Among the metal oxide semiconductor materials, in view of the advantages of non-toxicity, low prices, and good chemical

stability [14,15], Ga₂O₃ has potential applications in high-temperature gas sensors [16,17]. Moreover, nanostructures have been designed to enhance the performance of gas sensors because of their high surface-to-volume ratio, high specific surface area, and more surface adsorption sites, recently [18–21]. In this work, the GaOOH nanorods were grown on the SnO₂ seed layer by the hydrothermal synthesis method. The resulting GaOOH nanorods were then annealed to convert them into Ga₂O₃ nanorods. The surface morphology of the Ga₂O₃ nanorods was optimized for a high specific surface area, thereby achieving high responsivity and high selectivity in the NO₂ gas sensors.

2. Materials and Methods

2.1. Materials

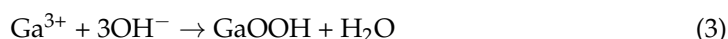
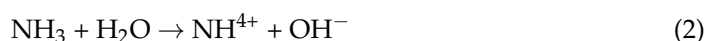
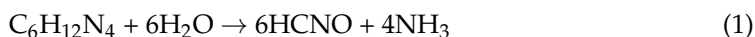
In this work, the SnO₂ target (99.99%) with bonding on a 3 mm Cu plate was purchased from S.P. Alloys Co., Ltd., Keelung, Taiwan. Granules of gallium nitrate nonahydrate (Ga(NO₃)₃·9H₂O, 99.9%) and hexamethylenetetramine (C₆H₁₂N₄, HMT, 99.5%) were, respectively, purchased from Alfa Aesar (Heysham, UK) and Sigma-Aldrich (Darmstadt, Germany). A target-gas NO₂ gas cylinder (1000 ppm) was purchased from Yun Shan Gas Co., Ltd., Tainan, Taiwan.

2.2. Material Characterization

X-ray diffraction (XRD, D8 DISCOVER with GADDS, Bruker AXS GmbH, Karlsruhe, Germany) was used to characterize the seed layers of Ga₂O₃ nanorods. The morphological and structural analyses of the resulting Ga₂O₃ nanorods were performed with a field emission scanning electron microscope (FE-SEM, AURIGA, ZEISS, Oberkochen, Germany). The material characteristics of the annealing-treated GaOOH nanorods were measured using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe III, ULVAC-PHI, Inc., Osaka, Japan). The current–voltage (I–V) characteristics were obtained with an Agilent 4156C (Santa Clara, CA, USA) semiconductor parameter analyzer.

2.3. Experimental Details

Figure 1 shows the schematic configuration of the Ga₂O₃ nanorod-structured NO₂ gas sensors. A radio frequency (RF) magnetron sputtering system was used to deposit SnO₂ films with various thicknesses of 50 nm, 100 nm, and 200 nm on quartz substrates as seed layers for GaOOH nanorods. The RF power, the Ar/O₂ gas ratio, and the chamber pressure were maintained at 75 W, 48/2 sccm, and 5 mtorr, respectively. The growth rate of the SnO₂ films was approximately 6.8 nm/min. After completing the various SnO₂ seed layers, the GaOOH nanorods were grown on quartz substrates using the hydrothermal synthesis method with various concentration solutions consisting of Ga(NO₃)₃·9H₂O and HMT at 180 °C for 4 h using a magnetic stirrer hotplate. The nanorods were then converted from GaOOH to Ga₂O₃ in a pure N₂ ambient atmosphere using a furnace system for 2 h at 300 °C, 400 °C, and 500 °C, respectively. The hydrothermal synthesis processes and the material conversion during the thermal annealing processes are described in Equations (1–4), respectively [22].



The Ni/Au (20/100 nm) metals were deposited on the Ga₂O₃ nanorods as the electrodes of the gas sensors by an electron-beam evaporator.

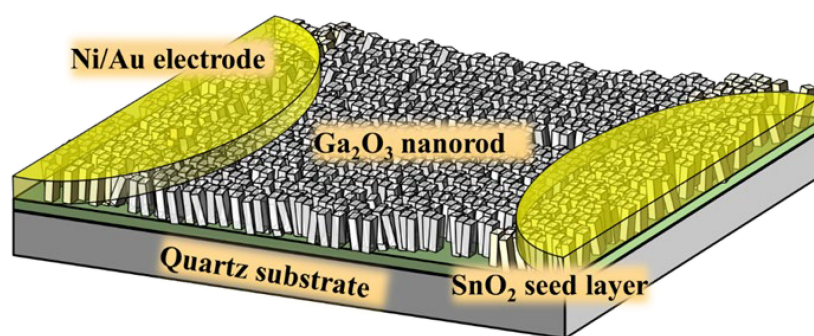


Figure 1. Schematic configuration of NO₂ gas sensors with Ga₂O₃ nanorod sensing membrane.

Figure 2 shows the schematic configuration of the measurement system of the NO₂ gas sensors. A target-gas NO₂ gas cylinder and a mass flow controller (MFC) were installed with a closed chamber to provide a stable NO₂ gas source, and an Agilent 4156C semiconductor parameter analyzer was equipped to measure the current–voltage (I–V) characteristics of the Ga₂O₃ nanorod-structured NO₂ gas sensors. In addition, the closed chamber of the NO₂ gas sensor measurements was equipped with a humidity controller to maintain a relative humidity of 30% during the testing process. When NO₂ gas was introduced into the chamber, the NO₂ molecules would react with the Ga₂O₃ sensing membrane, causing an increase in the resistance of the sensor. This reaction occurred as a result of the NO₂ molecules extracting electrons from the Ga₂O₃ nanorod sensing membrane, which reacted with the O₂[−]_(abs) in the sensing membrane. These reaction processes were as follows in Equations (5)–(8) [23].

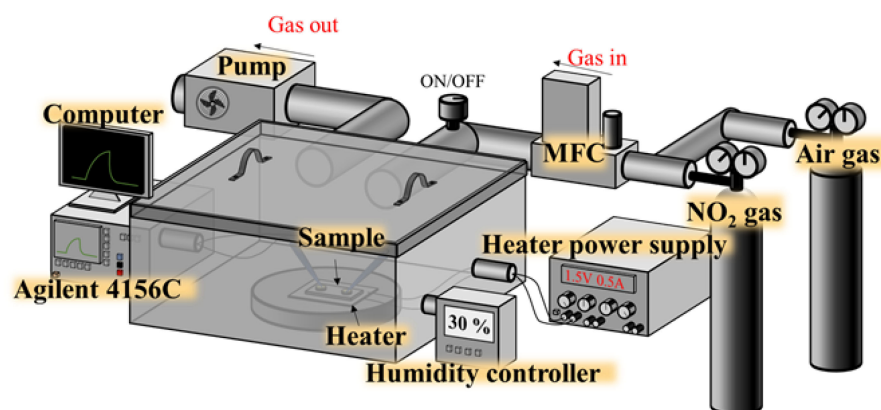
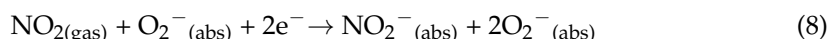


Figure 2. Schematic configuration of measurement system of NO₂ gas sensors.

When the NO₂ gas was removed from the chamber and purged by air, the electrons previously trapped by NO₂ molecules were released back to the conductive band of the material, leading to a decrease in sensor resistance and a return to its initial state.

3. Results

Since the diameter of the resulting nanorods was dependent on the average grain size of the seed layer, which was increased with an increase in the film thickness [24–26], an

amorphous seed layer with a small grain size has become a very important research target to obtain nanorods with a larger surface-to-volume ratio. In this work, to achieve a high surface-to-volume ratio, high specific surface area, and more surface adsorption sites, the surface morphology was optimized by changing the thickness of the SnO_2 seed layer and the mixed solution concentration of the hydrothermal precursors.

Using the measurement of X-ray diffraction (XRD) with $\text{CuK}\alpha$ radiation, Figure 3 illustrates the crystalline characteristics of the SnO_2 seed layers with various thicknesses of 50 nm, 100 nm, and 200 nm. As shown in Figure 3, the 50-nm-thick SnO_2 film did not have any obvious peak in the XRD pattern. Furthermore, for the 100-nm-thick and 200-nm-thick SnO_2 films, three diffraction peaks located at 26.5° , 34.0° , and 51.9° , corresponding to the SnO_2 (110), (101), and (211) planes, respectively, were found [27]. It could be observed that the crystallinity of the SnO_2 film was improved with an increase in the SnO_2 thickness. Consequently, to enable the growth of GaOOH nanorods with a high surface-to-volume ratio morphology, the amorphous structure of a 50-nm-thick SnO_2 film was required for the seed layer in this study.

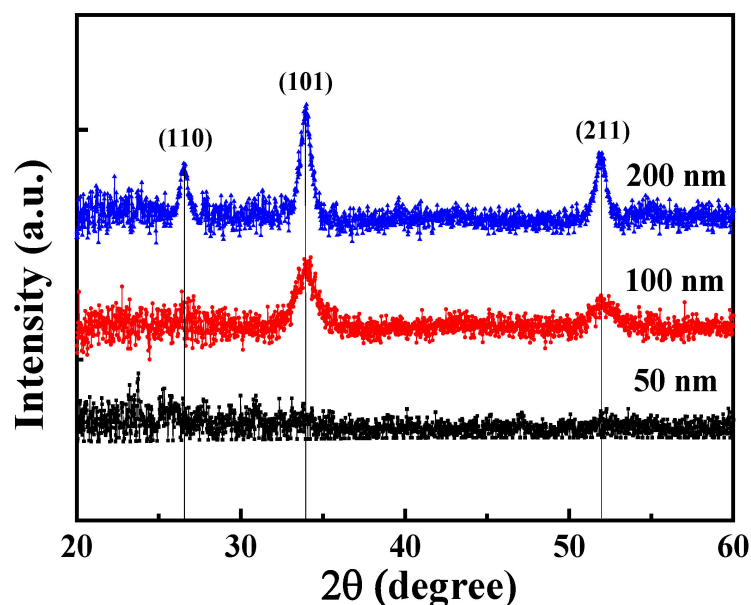


Figure 3. XRD spectra of SnO_2 seed layers with various thicknesses.

Figure 4a–c illustrate the FE-SEM top-view and cross-section images of the GaOOH nanorods respectively synthesized on the various SnO_2 seed layers by the hydrothermal synthesis method with $\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and HMT concentrations of 12 mM and 10 mM. It was seen that the shape of the nanorods was approximately a rhombus and the dimension of the nanorods showed a uniform distribution. However, the size and number of the nanorods were obviously influenced by the thickness of the SnO_2 seed layers. For the GaOOH nanorods grown on the SnO_2 seed layers with various thicknesses of 50 nm, 100 nm, and 200 nm, the average short-side diagonal was approximately 52.0 nm, 60.2 nm, and 72.6 nm, respectively. The average short-side diagonal of the GaOOH nanorods was increased with an increase in the thickness of the SnO_2 seed layers. The height of the resulting nanorods was almost kept at around 320 nm, with no significant difference. Consequently, it could be deduced that the morphology of the GaOOH nanorods was greatly influenced by the thickness of the seed layer. A larger surface-to-volume ratio of GaOOH nanorods was obtained in the thinner SnO_2 seed layer due to the smaller grain size of the thinner seed layer.

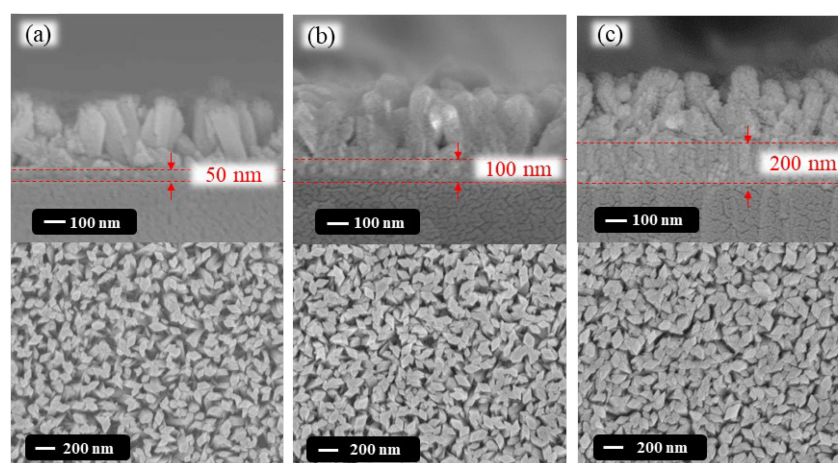


Figure 4. FE-SEM top-view and cross-section images of GaOOH nanorods grown on SnO₂ seed layers with a thickness of (a) 50 nm, (b) 100 nm, and (c) 200 nm.

In the hydrothermal synthesis processes, to obtain an optimized morphology of GaOOH nanorods by changing the concentration of Ga(NO₃)₃·9H₂O and HMT precursors, the various Ga(NO₃)₃·9H₂O/HMT precursor concentrations of 6 mM/5 mM, 12 mM/10 mM, and 18 mM/15 mM were utilized and investigated. The FE-SEM top-view and cross-section images of the various GaOOH nanorods grown on the 50-nm-thick SnO₂ seed layer are shown in Figure 5a–c. The average short-side diagonal of the GaOOH nanorods grown using various Ga(NO₃)₃·9H₂O/HMT precursor concentrations of 6 mM/5 mM, 12 mM/10 mM, and 18 mM/15 mM was 51.5 nm, 52.0 nm, and 70.7 nm, respectively. The corresponding height of the GaOOH nanorods was approximately 195 nm, 320 nm, and 352 nm, respectively. It was found that the average short-side diagonal of the GaOOH nanorods gradually increased with an increase in the concentration of the Ga(NO₃)₃·9H₂O/HMT precursor. Although the smallest average short-side diagonal was obtained in the GaOOH nanorods grown using the precursor concentration of 6 mM/5 mM, the associated nanorods density and height were significantly lower than those grown with the other precursor concentrations. This phenomenon was attributed to the fact that the reactants using 6 mM/5 mM precursors were not sufficient in concentration to deposit at every site where the GaOOH nanorods could be formed. Consequently, the most suitable synthesis conditions for the GaOOH nanorods were the 50-nm-thickness SnO₂ seed layer and the Ga(NO₃)₃·9H₂O/HMT precursor concentration of 12 mM/10 mM, which exhibited the largest surface-to-volume ratio for the GaOOH nanorods.

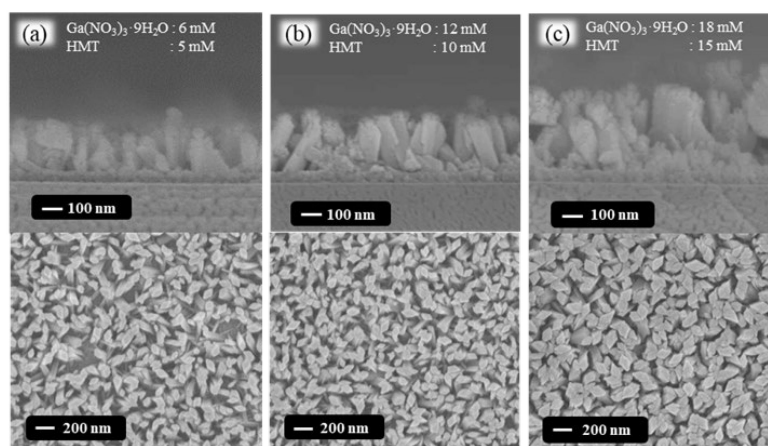


Figure 5. FE-SEM top-view and cross-section images of GaOOH nanorods grown using various precursor concentrations of (a) 6 mM/5 mM, (b) 12 mM/10 mM, and (c) 18 mM/15 mM.

To improve the gas sensitivity of the NO₂ gas sensors, the GaOOH nanorods should be converted into Ga₂O₃ nanorods by annealing treatment. In addition, XPS was carried out to study the existence of oxygen vacancies (O_{vacancy}) and -OH bonds in the Ga₂O₃ nanorod sensing membranes with various annealing temperatures. Figure 6a–d show the O1s core level spectra of the GaOOH nanorods without and with annealing treatment for 2 h at 300 °C, 400 °C, and 500 °C, respectively. The O1s peak was composed of three bands located at the binding energy of 530.8 eV, 532.1 eV, and 533.0 eV, which were, respectively, assigned to the Ga³⁺, O_{vacancy}, and -OH bonds [28]. According to the XPS results, the peak intensity of the -OH bonds was significantly reduced when increasing the annealing temperature. This phenomenon indicated that the thermal energy in the annealing treatment process could cause the dehydroxylation reaction in the Ga₂O₃ nanorods [29]. Moreover, the peak ratio of the Ga³⁺ and O_{vacancy} bonds (Ga³⁺/O_{vacancy}) for the GaOOH nanorods without and with annealing treatment for 2 h at 300 °C, 400 °C, and 500 °C was 11.93, 8.43, 7.38, and 7.01, respectively. It is worth noting that the oxygen vacancies could be effectively increased on the surfaces of the Ga₂O₃ nanorods in the annealing treatment process, thereby increasing the active sites for the NO₂ gas.

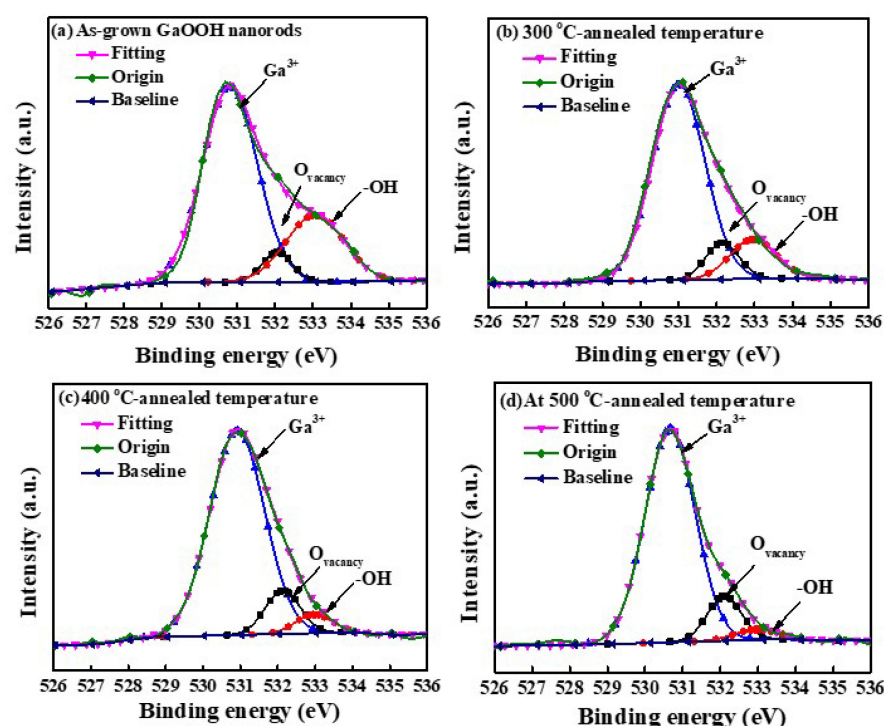


Figure 6. XPS spectra of O1s core-level spectra of (a) as-grown GaOOH nanorods and annealed Ga₂O₃ nanorods treated at (b) 300 °C (c) 400 °C, and (d) 500 °C.

Figure 7 shows the temperature dependence of the resistance ($R_s(T)$) for the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures. In general, the reaction rate and operating temperature were mainly affected by the activation energy (E_A) in the gas sensors. The activation energy of the Ga₂O₃ nanorod-structured NO₂ gas sensors was calculated using the following Arrhenius equation [30]:

$$R_s(T) = R_0 e^{\frac{E_A}{kT}} \quad (9)$$

$$\ln[R_s(T)] = \ln(R_0) + \left(\frac{E_A}{1000k} \right) \left(\frac{1000}{T} \right) \quad (10)$$

where R_0 is the pre-exponential factor, k is the Boltzmann constant, and T is the absolute temperature, respectively. The activation energy is determined by the slope of the Arrhenius

plot. As shown in Figure 7, the activation energy of 248 meV, 214 meV, and 211 meV corresponded to the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at 300 °C, 400 °C, and 500 °C, respectively. In general, the activation energy was inversely proportional to the carrier concentration [31,32], which was also increased with the amounts of oxygen vacancies in the Ga₂O₃ material [33]. According to the XPS results, the oxygen vacancies residing on the surfaces of Ga₂O₃ nanorods were effectively increased during the annealing treatment process. Consequently, it could be deduced that the activation energy was decreased with an increase in the annealing temperature.

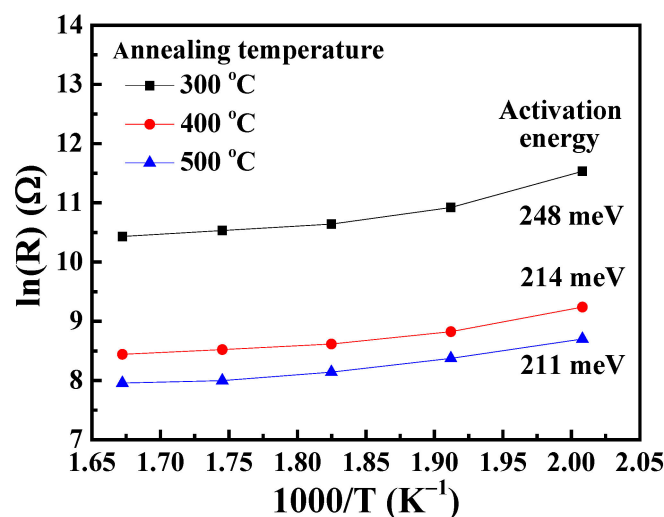


Figure 7. Temperature dependence of resistance for NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures.

In this study, the gas responsivity (R) was calculated using the following equation:

$$R(\%) = \frac{R_g - R_a}{R_a} \times 100\% \quad (11)$$

where R_g and R_a are the resistances of the NO₂ gas sensors in NO₂ gas and air environments, respectively. Figure 8 shows the responsivity versus operating temperature characteristics of the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures. Under a bias voltage of 1 V and a NO₂ gas concentration of 10 ppm, the optimal responsivity of the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at 300 °C, 400 °C, and 500 °C was 225.8%, 1184.6%, and 824.9%, respectively. The corresponding operating temperatures of the optimal responsivity were 300 °C, 275 °C, and 250 °C. It could be found that the responsivity increased with an increase in the annealing temperature until 400 °C and then decreased when further increasing the annealing temperature to 500 °C. The reduction in operating temperature tendency was followed by the activation energy tendency of the annealing temperature of the Ga₂O₃ nanorod sensing membranes. The enhanced responsivity was attributed to the fact that the annealing thermal energy could effectively increase the oxygen vacancies, thereby providing more gas-reactive surface sites. However, the improvement responsivity of the NO₂ gas sensors with 500 °C-annealed Ga₂O₃ nanorod sensing membranes was degraded. It could be deduced that the induced excessive carrier concentration present in the 500 °C-annealed Ga₂O₃ nanorod sensing membranes could reduce the resistance variation [34].

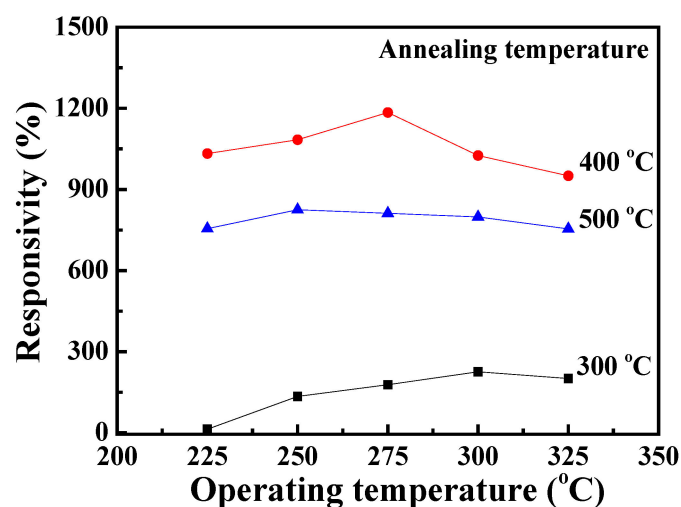


Figure 8. Responsivity versus operating temperature of NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures.

Figure 9a,b show the response time (τ_r) and recovery time (τ_d) of the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures under a bias voltage of 1 V and a NO₂ gas concentration of 10 ppm at their associated individual optimal operating temperatures. In general, the response time and recovery time were calculated as the time from 0% to 90% of the maximum responsivity and from 100% to 10% of the maximum responsivity, respectively [35]. As shown in Figure 9a,b, under the individual optimal operating temperatures of 300 °C, 275 °C, and 250 °C, the response time of the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at 300 °C, 400 °C, and 500 °C was 75.7, 63.6, and 61.5 s, respectively. The corresponding recovery time was 410.4, 135.7, and 125.9 s, respectively. These results indicated that both the response time and the recovery time of the resulting NO₂ gas sensors decreased with an increase in the annealing temperature. This phenomenon was attributed to the fact that lower activation energy of the Ga₂O₃ nanorod-structured gas sensors could be achieved by annealing the sensing membranes at a higher temperature. The reduction in the response time and the recovery time of the resulting gas sensors could be induced by the lower activation energy [36,37].

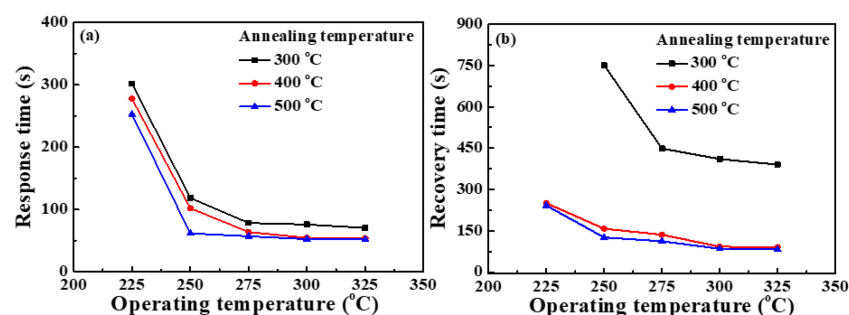


Figure 9. (a) Response time and (b) recovery time of NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes annealed at various temperatures under 10 ppm NO₂ gas concentration.

Figure 10 presents the dynamic gas responsivity of the NO₂ gas sensors with 400 °C annealed-Ga₂O₃ nanorod sensing membranes under various NO₂ concentrations at an operating temperature of 275 °C. It could be found that the responsivity of the gas sensor increased with an increase in the NO₂ concentration, reaching saturation at 50 ppm. The NO₂ gas sensors with 400 °C annealed-Ga₂O₃ nanorod sensing membranes could be effectively detected even at a very low NO₂ concentration of 100 ppb and the achieved responsivity was 34.2%.

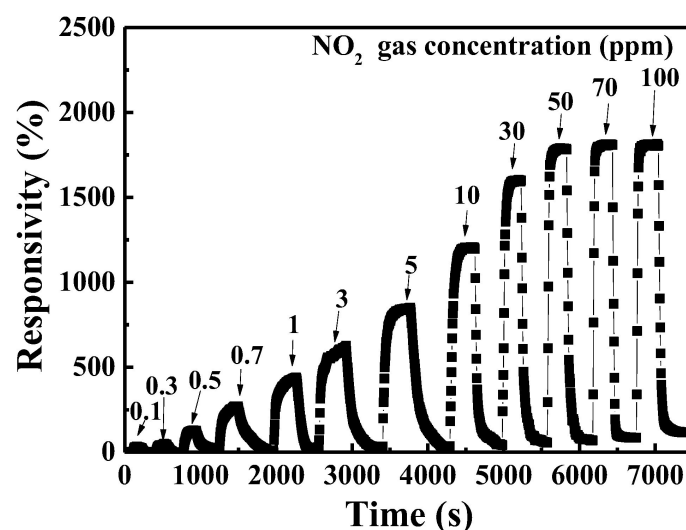


Figure 10. Dynamic gas responsivity of NO_2 gas sensor with 400°C -annealed Ga_2O_3 nanorod sensing membrane under various NO_2 concentrations at an operating temperature of 275°C .

To investigate the gas selectivity of the NO_2 gas sensor with a Ga_2O_3 nanorod sensing membrane, alcohol ($\text{C}_2\text{H}_5\text{OH}$) and ammonia (NH_3) were also used as the target gases in this study. Figure 11 shows the responsivity of the gas sensor with a 400°C -annealed Ga_2O_3 nanorod sensing membrane under various target gases. Under a $\text{C}_2\text{H}_5\text{OH}$ concentration of 100 ppm, a NH_3 concentration of 100 ppm, and a NO_2 concentration of 10 ppm, the responsivity of the NO_2 gas sensors was 154.8%, 187.2%, and 1184.6%, respectively, at an operating temperature of 275°C . This indicated that the gas sensor had certain sensing capability for $\text{C}_2\text{H}_5\text{OH}$ and NH_3 gases, but the responsivity was significantly lower than that of NO_2 gas. Consequently, it could be concluded that the NO_2 gas sensors using the 400°C -annealed Ga_2O_3 nanorods as the sensing membranes had high selectivity for NO_2 gas.

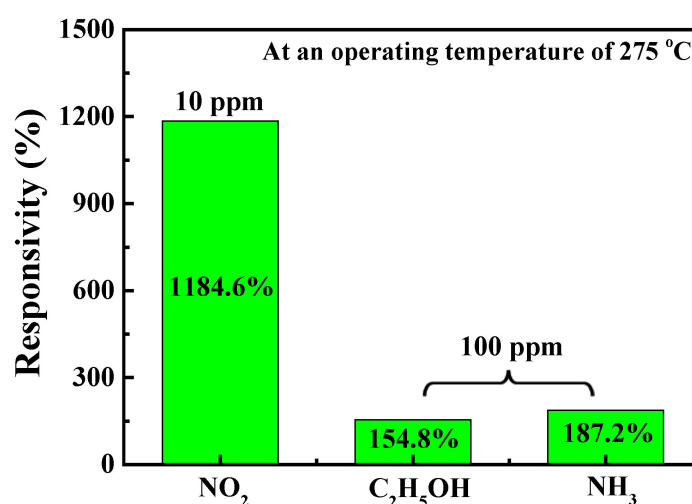


Figure 11. Responsivity of gas sensor with 400°C -annealed Ga_2O_3 nanorod sensing membrane under various target gases.

To further highlight the results of this work, the performance of the NO_2 gas sensors using Ga_2O_3 nanorods as the sensing membranes were compared with other similar studied NO_2 gas sensors reported previously, as listed in Table 1. The performance of the NO_2 gas sensors with Ga_2O_3 nanorod sensing membranes exhibited excellent features.

Table 1. Performance comparison of various structured NO₂ gas sensors.

Materials and Structure	Responsivity	Operating Temperature (°C)	Minimum Concentration of NO ₂ (ppm)	Ref.
TiO ₂ -Ga ₂ O ₃ thin film	~2.4	200	0.5	[38]
ZGO thin film	1.18	300	0.5	[39]
Oxidized galinstan	~1.8%	100	1	[40]
ZnO/ZnS core-shell nanowires	293.29%	300	1	[41]
ZnO nanowalls	9.63	220	5	[42]
Cu-doped ZnO thin film	26%	200	5	[43]
Ga ₂ O ₃ nanorods	34.2%	275	0.1	This work

4. Conclusions

In this study, various Ga₂O₃ nanorods were successfully grown on quartz substrates as sensing membranes of NO₂ gas sensors using the hydrothermal synthesis method and annealing processes. To increase the surface-to-volume ratio of the GaOOH nanorods, the thickness of the SnO₂ seed layer and the concentration of the hydrothermal precursor (Ga(NO₃)₃·9H₂O/HMT) were optimized. The surface-to-volume ratio of the GaOOH nanorods decreased with an increase in the thickness of the SnO₂ seed layer due to the reduction in the resulting grain size. Moreover, by decreasing the concentration of the hydrothermal precursor (Ga(NO₃)₃·9H₂O/HMT), the surface-to-volume ratio of the resulting GaOOH nanorods gradually increased. Although the concentration of 6 mM/5 mM had the highest surface-to-volume ratio, its nanorod density was significantly lower than for the other concentrations. It was found that the surface-to-volume ratio of the GaOOH nanorods could be effectively optimized using the 50-nm-thick SnO₂ seed layer and the Ga(NO₃)₃·9H₂O/HMT concentration of 12 mM/10 mM. The dependence of oxygen vacancies on the annealing temperature of Ga₂O₃ nanorods was verified by the measurements of the XPS experimental results. When the Ga₂O₃ nanorods were annealed at various temperatures, the amounts of oxygen vacancies were increased and the number of -OH bonds was suppressed by the thermal treatment. Consequently, the associated activation energy of the NO₂ gas sensors was decreased from 248 meV to 211 meV when increasing the annealing temperature of the Ga₂O₃ nanorod sensing membranes from 300 °C to 500 °C. The Ga₂O₃ nanorod sensing membrane annealed for 2 h at 400 °C achieved the maximum responsivity of 1184.6%. The response time and recovery time of the NO₂ gas sensors with Ga₂O₃ nanorod sensing membranes were effectively improved by the annealing treatment, which was due to the activation energy tendency of the Ga₂O₃ nanorods. Furthermore, because the Ga₂O₃ nanorod-structured NO₂ gas sensor revealed high sensitivity, it could even detect NO₂ gas with a concentration as low as 100 ppb. Moreover, the gas sensor also exhibited high selectivity towards NO₂ gas, and the responsivity of the gas sensors under the NO₂ concentration of 10 ppm was larger than that under the C₂H₅OH and NH₃ concentrations of 100 ppm. Consequently, it is verified that the low-cost hydrothermal synthesis method can grow GaOOH nanorods that can be converted into Ga₂O₃ nanorods using a thermal annealing process. The resulting Ga₂O₃ nanorods are promising candidates for NO₂ gas sensors.

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