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$Mg_xNi_{1-x}O$-based Gas Sensors with Various Mg/Ni Ratios

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Considering the advancement of contemporary industrialization and urban development, a consequential escalation of air quality deterioration has led to the emergence of diseases and disasters. In this research, we endeavor to harness the properties of MgNiO for the fabrication of a gas sensor designed specifically for the detection of NO_2. In contrast to conventional NiO gas sensors, our findings indicate a noticeable enhancement in the sensor's NO_2 gas responsiveness with increasing proportion of Mg. Remarkably, the utilization of a $Mg_{0.5}Ni_{0.5}O$ film exhibits the most promising outcomes, that is , heightened responsiveness and commendable selectivity. This improvement of performance can be attributed to the increase in oxygen vacancies within the film and consequent alterations in film resistance, which collectively contribute to the overall improvement of sensor responsivity.

1. Introduction

Metal oxide semiconductor gas sensors[1,2] have attracted significant attention in research owing to their cost-effectiveness, high sensitivity, and ease of production.[3,4] Investigations into these sensors have revealed that their sensitivity to gases is influenced by various critical factors, including chemical composition, temperature, morphology, and defects within the sensing layer.[5,6] The fundamental principle underlying metal oxide gas sensors involves altering the resistance of the sensing layer upon exposure to gases.[7] This resistance variation can be attributed to the modification of the energy band alignment resulting from the chemical adsorption of gases. When the sensing layer comes into contact with a target gas, interactions occur between the gas molecules and the sensing film, leading to changes in charge carriers and, consequently, conductivity.

There are a multitude of studies in which gas sensors based on different oxide materials, including ZnO,[8] WO_3,[9] NiO,[10] and TiO_2,[11] have been explored. Furthermore, researchers

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have examined the response of these materials to diverse gases, such as CO, C_2H_5OH, NO_2, SO_2, H_2S, and NH_3. Notably, among these gases, NO_2 is acknowledged as one of the most hazardous, capable of inducing respiratory ailments and tracheal disorders even at low ppb concentrations. Prolonged exposure to elevated NO_2 levels can result in pulmonary edema. Additionally, the corrosive nature of NO_2 imposes stringent requirements on gas sensors used for its measurement. Given the excellent corrosion resistance exhibited by our $Mg_xNi_{1-x}O$ material, we have chosen it as the sensing layer for NO_2 detection.

In our material, which exhibits P-type semiconducting behavior, the sensing layer undergoes a reaction with oxidizing gases, leading to electron loss and an increase in hole concentration, which subsequently cause a reduction in resistance. Numerous studies have highlighted the favorable response of NiO to NO_2.[12] In our investigation, we observed a rising trend in the NO_2 response of MgNiO as the proportion of Mg doping increased, with the optimal response achieved at a Mg:Ni ratio of 5:5. However, further increases in Mg concentration resulted in a diminished response owing to an insufficient Ni presence.

2. Experimental Section

The gas sensor in our study, featuring $Mg_xNi_{1-x}O$ as the sensing layer, was primarily fabricated using a combination of sputtering and electron gun (Egun) deposition techniques. A detailed schematic diagram outlining the fabrication process is depicted in Fig. 1.

Initially, the quartz substrates underwent a thorough cleaning process with acetone, isopropyl alcohol, and deionized (DI) water treatment within an ultrasonicator. Following substrate cleaning, we utilized sputtering to deposit NiO films with various ratios of oxygen concentration onto the substrates. Specifically, in this study, we sputtered NiO films of 150 nm thickness, as well as $Mg_{0.2}Ni_{0.8}O$ and $Mg_{0.5}Ni_{0.5}O$. This allowed us to compare the impact of increasing the Mg concentration on the gas sensing characteristics. The sputtering chamber was maintained at a gas pressure below 5×10^{-6} Torr, by injecting 50 sccm of argon (Ar). The sputtering power was held constant at 80 W, and the substrate was rotated at a rate of 80 rpm. Subsequently, an Egun

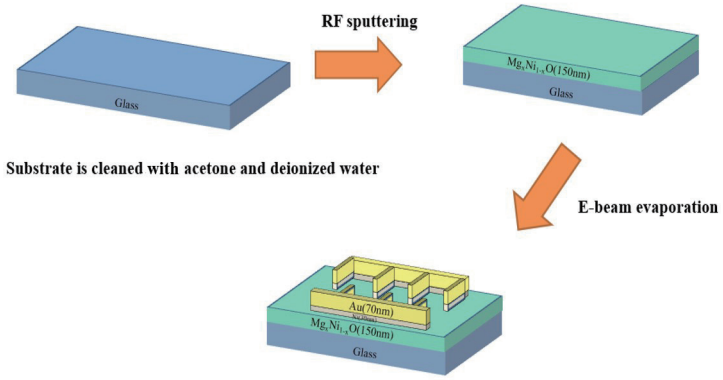

Fig. 1. (Color online) Fabrication process flow of the gas sensor.

was employed to deposit a 30-nm-thick nickel layer followed by a 70-nm-thick gold layer onto the sensing layer as the upper electrode.

Upon the completion of gas sensor fabrication, the samples were placed on a platform and heated to the operating temperature within a sealed chamber. Subsequently, we employed a Keithley 4200 semiconductor parameter analyzer to measure the current–voltage (*IV*) characteristics of the gas sensor element, as illustrated in Fig. 2. By comparing the behavior of the element in air to its response in the presence of the target gas, we were able to determine its responsivity to that specific gas.

3. Results and Discussion

To evaluate the gas response of our sensor, we introduced NO_2 into the sealed chamber and then gradually withdrew it while maintaining a continuous electrical current. For consistency in our measurements, we conducted these tests at a temperature of 150 °C, a temperature known to be optimal for NO_2 measurements. By applying a voltage of 1 V across the sensor via the interdigitated electrodes, we quantified the sensor's responsiveness to gas by monitoring the resulting current. Our measurements confirmed that the MgNiO thin film behaves as a P-type semiconductor. When exposed to air, the oxygen molecules (O_2) dissociate into O_2^- ions and adsorb onto the film surface. Upon injecting the oxidizing gas NO_2, the NO_2 molecules adsorb both electrons and O_2^- ions, becoming ions that adhere to the film, as illustrated by Eq. (3).[12] As NO_2 is introduced, electrons are consumed, leading to a decrease in the resistance of the P-type semiconductor.

The measurement results, depicted in Figs. 3(a)–3(c), represent the current of NiO, $Mg_{0.2}Ni_{0.8}O$, and $Mg_{0.5}Ni_{0.5}O$ thin-film sensors at different NO_2 concentrations ranging from 175 to 3150 ppb. Then, Eq. (4) is used to calculate the responsivity organized and shown in Fig. 3(d). Figure 3(d) clearly demonstrates a substantial increase in NO_2 response with a rise in Mg concentration. Furthermore, we conducted a more detailed investigation with $Mg_{0.5}Ni_{0.5}O$. We

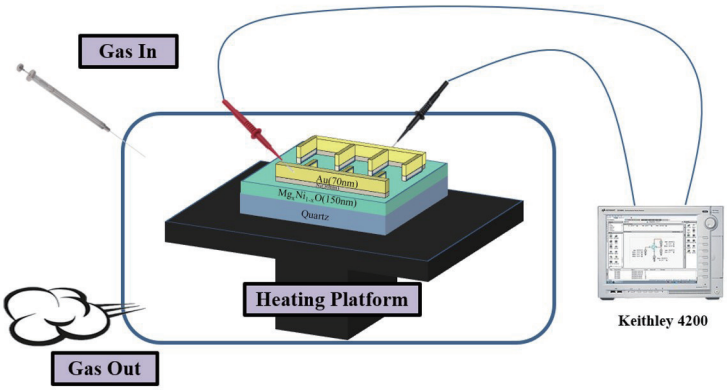

Fig. 2. (Color online) Measurement environment of the gas sensor.

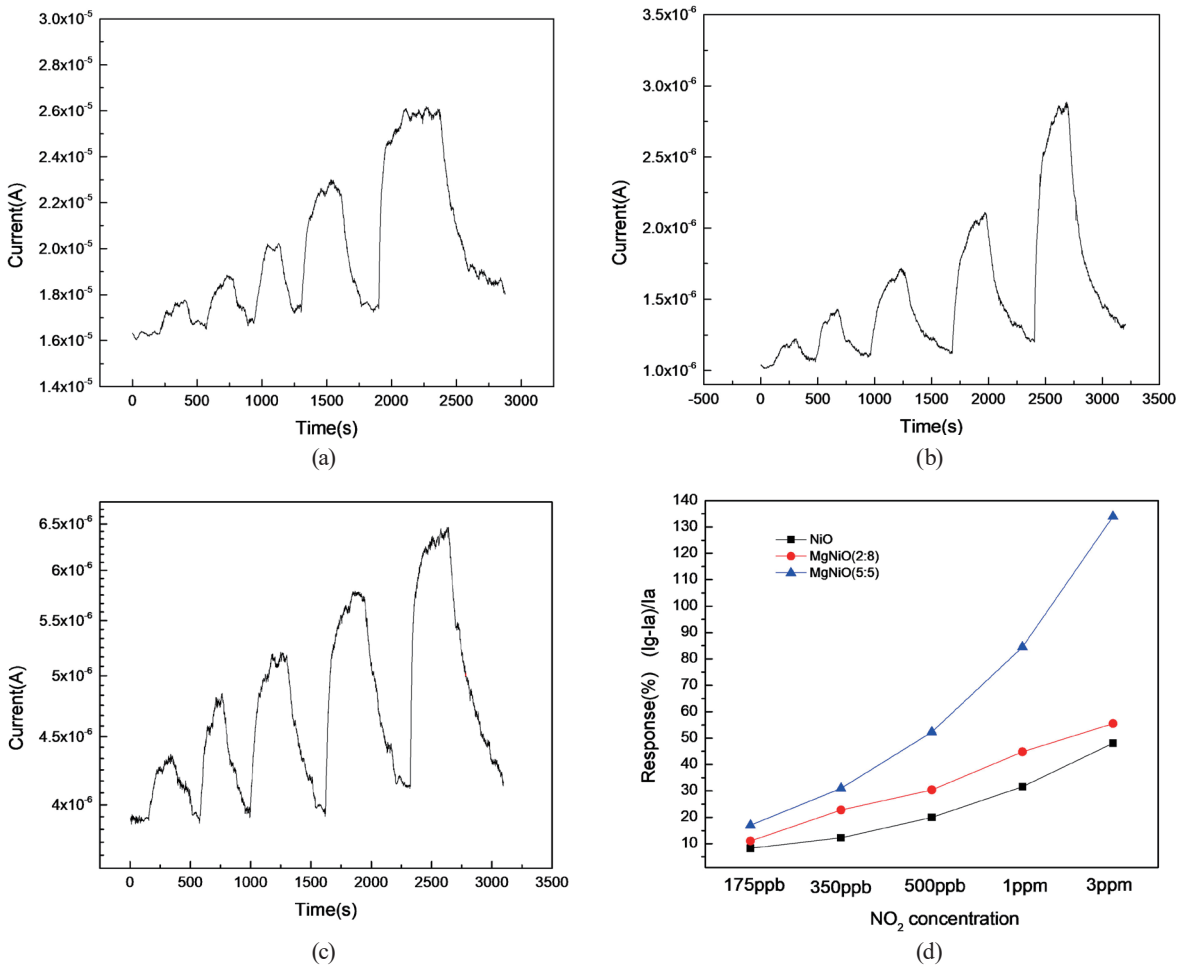

Fig. 3. (Color online) Various measured concentrations of NO_2 using (a) NiO, (b) $Mg_{0.2}Ni_{0.8}O$, and (c) $Mg_{0.5}Ni_{0.5}O$ sensors at 150 °C. (d) Responses of gas sensors with films of different Mg/Ni ratios.

reduced the NO_2 concentration to extremely low levels of 100 and 35 ppb. The results in Fig. 4 reveal that the $Mg_{0.5}Ni_{0.5}O$ sensing film exhibits a pronounced response even at these ultralow NO_2 concentrations.

$$\text{Exposed to air: } O_2(\text{gas}) + e^- \rightarrow O_2^-(\text{ads}) \quad (1)$$

$$\text{Exposed to } NO_2\text{: } NO_2 + e^- \rightarrow NO_2^-(\text{ads}) \quad (2)$$

$$2NO_2(\text{gas}) + O_2^-(\text{ads}) + e^- \rightarrow 2NO_3^-(\text{ads}) \quad (3)$$

$$\text{Response} = [(I_{gas} - I_{dry})/(I_{dry})] \times 100 \quad (4)$$

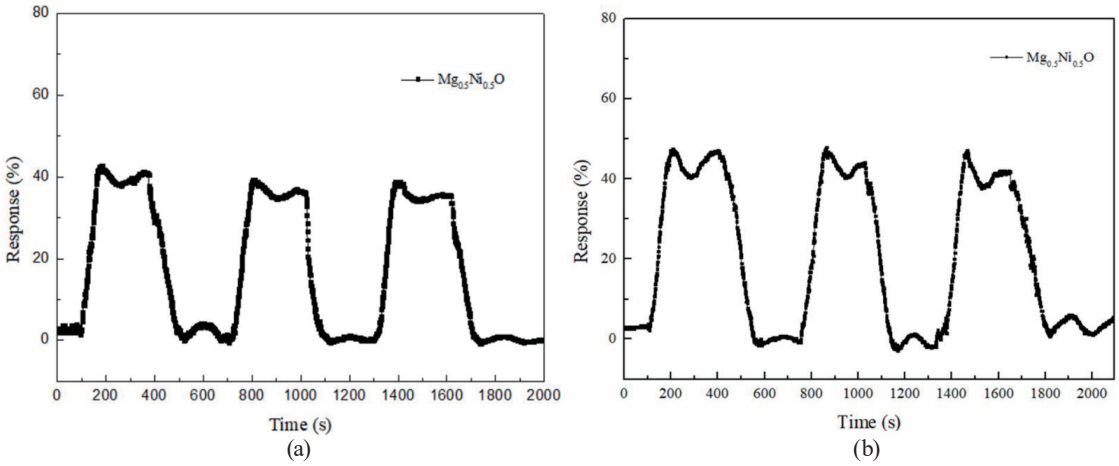

Fig. 4. Responses of $Mg_{0.5}Ni_{0.5}O$ gas sensor to (a) 35 ppb and (b) 100 ppb NO_2.

These findings can be attributed to alterations in oxygen vacancies and electrical resistance, both of which are crucial factors in gas sensor performance. Oxygen vacancies play a pivotal role in gas sensing by enhancing the sensing layer's capacity to adsorb gas molecules. To investigate how the ratio of Mg affects oxygen vacancies, we conducted X-ray photoelectron spectroscopy (XPS) analysis of the film. The results are depicted in Fig. 5.

The O_{1s} peak in the XPS spectrum comprises three subpeaks: M_O peak, V_O peak, and OH− peak. Utilizing Gaussian fitting, we deconvoluted the O_{1s} peak into these three components.[13] Figure 5 shows that as the Mg proportion increases, the oxygen vacancy (V_o) concentration significantly rises. We quantified the proportions of oxygen vacancies by analyzing the M_o (O_I), V_o (O_{II}), and OH− (O_{III}) peaks in Fig. 5. The results are summarized in Table 1. $Mg_{0.5}Ni_{0.5}O$ exhibits the highest concentration of oxygen vacancies, which correlates with its superior gas sensing characteristics.

Furthermore, as Mg possesses a larger bandgap than Ni, the introduction of Mg into NiO leads to a substantial increase in resistance. In the context of gas sensors, a reduction in reference current enhances the response.

Subsequently, we assessed the selectivity of the $Mg_{0.5}Ni_{0.5}O$ gas sensor towards various gases. At an operating temperature of 150 °C, we measured the responsivity to NO, SO_2, CO, and NH_3, each at a concentration of 3150 ppb, and compared these results with the response to NO_2, as sorted and depicted in Fig. 6 and Table 2. The measurements conducted validate the outstanding selectivity of our film to NO_2 at the specified temperature. The MgNiO gas sensor exhibits a notable 168% response to NO_2, followed by a 36% response to NO and an equivalent 36% response to SO_2. Conversely, it demonstrates minimal to negligible responses to CO and NH_3 gases. This comprehensive analysis underscores the viability of utilizing $Mg_{0.5}Ni_{0.5}O$ for NO_2 detection. The $Mg_{0.5}Ni_{0.5}O$ gas sensor exhibited marked selectivity for NO_2 at 150 °C.

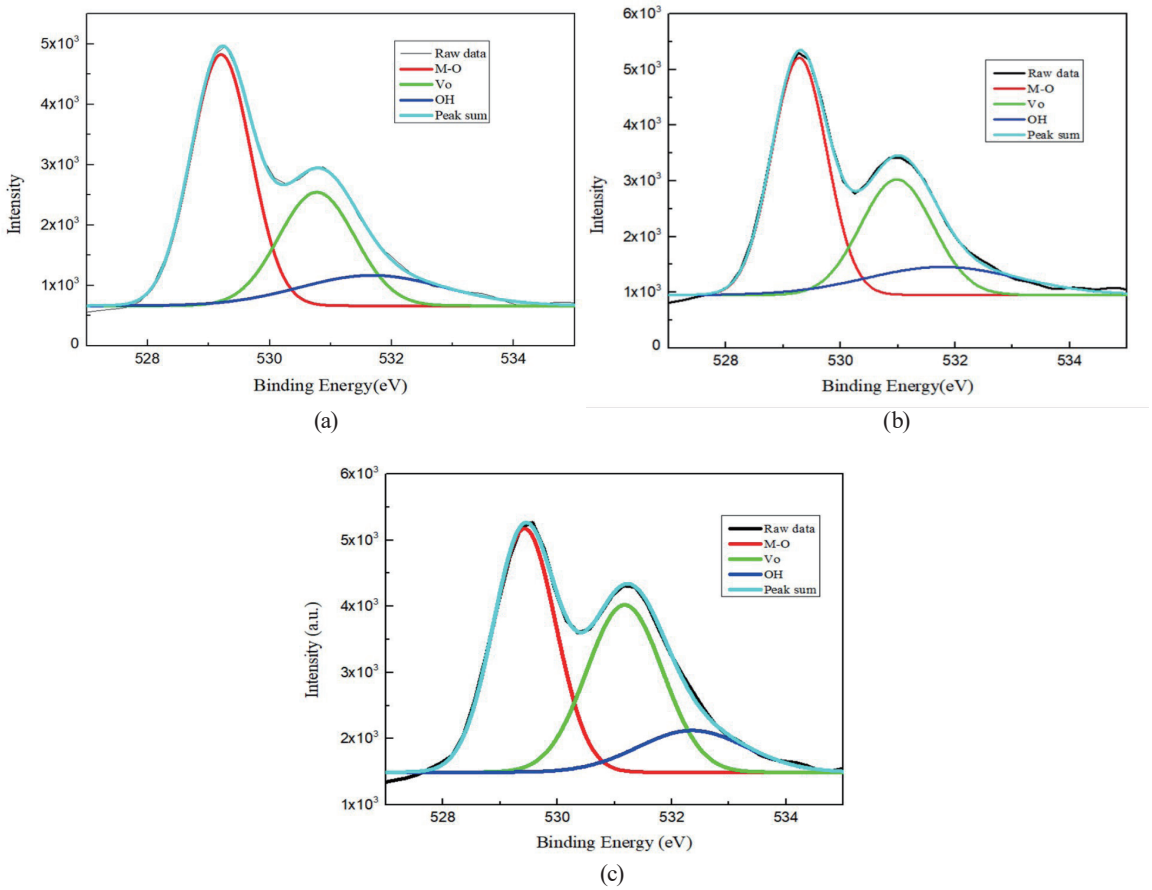

Fig. 5. (Color online) XPS O_{1s} spectra of (a) NiO, (b) $Mg_{0.2}Ni_{0.8}O$, and (c) $Mg_{0.5}Ni_{0.5}O$.

Table 1
Relative ratio of $O_{II}/(O_I + O_{II} + O_{III})$ XPS peaks.

	NiO	$Mg_{0.2}Ni_{0.8}O$	$Mg_{0.5}Ni_{0.5}O$
$O_{II}/(O_I + O_{II} + O_{III})$	29.24%	32.56%	39.16%

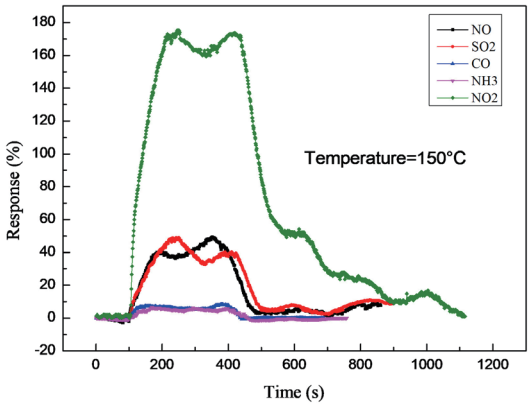

Fig. 6. (Color online) Selectivity of $Mg_{0.5}Ni_{0.5}O$ film to 3 ppm toxic gas at 150 °C.

Table 2
Selectivity of $Mg_{0.5}Ni_{0.5}O$ film to 3 ppm toxic gas at 150 °C.

	NO	SO_2	CO	NH_3	NO_2
Response	47%	36%	7%	3%	168%

4. Conclusions

In this study, we systematically investigated the impact of varying the proportions of $Mg_xNi_{1-x}O$ on the sensing capabilities for NO_2 gas. Initially, with the introduction of Mg, specifically as $Mg_{0.2}Ni_{0.8}O$, we observed a modest enhancement in gas response compared with that to pure NiO. However, as the Mg ratio was further increased to $Mg_{0.5}Ni_{0.5}O$, the gas response exhibited a significant and nearly threefold improvement.

Furthermore, the gas sensor featuring $Mg_{0.5}Ni_{0.5}O$ exhibited exceptional selectivity and displayed a robust response, even at very low NO_2 concentrations. Notably, the response reached an impressive 40% at an NO_2 concentration as low as 35 ppb. These experimental results align with our prior hypotheses, wherein the increase in the Mg proportion led to a substantial increase in oxygen vacancies and, consequently, to a sharp rise in resistance. These dual factors significantly influenced the sensor's characteristics and ultimately contributed to the improved response to NO_2. In summary, we successfully enhanced the gas-sensing properties of NiO films for detecting NO_2.

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