



Fabrication of NO_x gas sensors using In₂O₃–ZnO composite films

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ABSTRACT

In₂O₃–ZnO composite films were fabricated and their NO_x sensing characteristics were investigated in this study. The content of ZnO in In₂O₃–ZnO film was controlled by adjusting the Zn²⁺/In³⁺ molar ratio (*r*) during the film preparation. With suitable amount of ZnO incorporated into the In₂O₃ films, the responses of the composite films to NO_x at operation temperatures below 200 °C were greatly improved. However, as the ZnO content was further increased, the grain of the composite film started to merge into big ones, thus decreasing the surface area and resulting in lower sensor responses. The detection limit (*S/N*=3) of In₂O₃–ZnO composite film (*r*=0.67) reached 12 ppb at 150 °C. Both pure In₂O₃ (*r*=0) and In₂O₃–ZnO composite films (*r*=0.67) showed no response to CO gas.

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1. Introduction

Sensors for detecting low concentration of nitric oxide (NO) have received progressive attention due to its environmental and health-related importance. NO gas, released from the combustion processes, not only is a precursor of the acid rain, but also is the cause for the depletion of ozone [1]. In the presence of excess oxygen, NO will be oxidized to nitrogen dioxide (NO₂), with the reaction time depending on the NO concentration in air. Frequent exposure to the mixture of NO and NO₂ gas (NO_x) would cause pulmonary edema and fatality. According to the regulations set by the Occupational Safety and Health Administration (OSHA), the permissible exposure limit for NO is at 25 ppm (TWA). It also has been reported that NO has effects on neuron functions, such as transcriptional regulation and ion channel functions, and thus change in NO levels can signify neuron death which is induced by neurodegenerative diseases [2]. Moreover, the exhaled NO concentration has been identified as a biomarker for airway inflammation such as asthma [3] and bronchiectasis [4]. Generally, the exhaled NO level of the patients with asthma is about 34.7–51.1 ppb, which is 3–4 times higher than that of healthy people [3]. It is, therefore,

necessary to develop rugged and reliable NO gas sensors capable of making real-time measurements for public health and security applications.

Solid-state gas sensors, based on thin film's conductivity changes upon interaction with target gas molecules, have widely used as the platform for the detection of some gas molecules. Among the materials used, In₂O₃ is known to be sensitive to some oxidizing gases, such as NO_x [5–8,16] and ozone [9,10]. In order to improve the sensor sensitivity, nanostructured In₂O₃ [11,12] or binary oxide films [13,14] have been used. On the other hand, zinc oxide (ZnO) also has been proposed as a sensing material for the detection of some pollutants [15,16]. Besides, ZnO has been reported as an effective dopant to improve the sensor sensitivity. Yu and Choi [17] reported that the microstructure of SnO₂ was modified after incorporating zinc oxide, resulting in the improvement of sensor sensitivity toward carbon monoxide. Moreover, Miyata et al. [18] reported that the enhanced sensitivity of In₂O₃ based CCl₄ sensor was related to the formation of Zn₂In₂O₃ phase.

In this study, ZnO was used as the doping material of In₂O₃ for enhancing NO_x gas sensing performance. Various amounts of ZnO were incorporated into In₂O₃ film via co-precipitating method. The effect of Zn²⁺/In³⁺ (*r*) ratio during the preparation on the responses of the composite films toward NO_x was investigated. The results showed that the incorporation of ZnO into the In₂O₃ film can improve the composite film's sensitivity of the In₂O₃ film to NO_x gas at low operation temperature (<200 °C).

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Table 1The film thickness and the actual In/Zn ratio of the In₂O₃–ZnO composite films with different values of *r*.

	<i>r</i> values				
	0.00	0.33	0.50	0.67	1.00
Film thickness (μm)	3.83 ± 0.49	3.28 ± 0.62	4.00 ± 1.03	4.75 ± 0.41	4.00 ± 0.35
Actual Zn/In molar ratio	0.00	0.09	0.14	0.25	0.34

2. Experimental

2.1. Preparation of In₂O₃–ZnO films

The mixture of In(OH)₃ and Zn(OH)₂ was formed by carrying out the chemical bath precipitation at 90 °C for 1 h in an aqueous solution containing InCl₃, Zn(NO₃)₂, and hexamethylenetetramine (HMT). To synthesize In(OH)₃–Zn(OH)₂ with different molar ratios, various amounts of 25 mM Zn(NO₃)₂ solution were added in a 25 mM aqueous solution of InCl₃, *i.e.*, with different Zn²⁺/In³⁺ molar ratios (*r*). The concentration of HMT used was 25 mM, and the molar ratio of the sum of Zn²⁺ and In³⁺ ions source to HMT was kept at 1:1.

Thereafter, the In₂O₃–ZnO composite films were fabricated by dropping 60 μl of the In(OH)₃–Zn(OH)₂ solutions with different *r* values on the gold interdigitated electrodes (*n* = 24 fingers, 50 μm spaced, 6 mm long and 50 μm wide). Then the films were dried at room temperature and annealed at 500 °C for 30 min under pure O₂ atmosphere.

2.2. Gas sensing experiment

The electrodes were mounted onto a heater and inside a chamber equipped with gas-flow manifold and mass flow controller (Protec Instruments, Inc.). The mass flow controller offers ±1% full-scale accuracy. The apparatus facilitated automated (PC-DOS) control of temperature and data acquisition of the film resistance using a 2-wire method with a Hewlett Packard 34401A digital voltmeter which permitted resistance (*R*) measurements in the range 0 < *R* < 120 MΩ. Various concentrations of NO_x were tuned by changing the ratio of the flow rate of 484 ppm NO stream (Praxair Inc.) to that of a zero-grade air stream (BOC Canada Ltd.), and were delivered to the chamber at an overall flow rate of 200 cm³ min⁻¹. Since some part of NO would oxidize to NO₂ under air [28], we use NO_x to represent the mixture of NO and NO₂. To clean the surface of the In₂O₃–ZnO films, the In₂O₃–ZnO films were thermally treated from 100 to 500 °C at a heating rate of 10 °C min⁻¹ under zero-grade air environment for 5 cycles.

The response, *S*, is defined by the following equation:

$$S = \frac{R_g - R_{\text{air}}}{R_{\text{air}}} \quad (1)$$

where *R*_{air} and *R*_g are the resistances of the film in zero-grade air gas and in test gas, respectively.

The microstructure of In₂O₃–ZnO composites and the amount of ZnO incorporated into the composites were determined by using a JEOL 840 A scanning electron microscope and an X-ray recorded on a PHI 5000 VersaProbe (ULVAC-PHI, Chigasaki, Japan) system using a microfocussed (100 μm, 25 W) Al X-ray beam, respectively. All photos were taken using an accelerating voltage of 30 kV. The thicknesses of the composite films were determined by cross-sectional SEM. The crystalline phase of the In₂O₃–ZnO films was determined using a General Area Detector Diffraction System (Bruker AXS GADDS) with Co Kα radiation.

3. Results and discussion

3.1. Characterization of In₂O₃ or In₂O₃–ZnO films

The content of ZnO in In₂O₃–ZnO composite film was controlled by adjusting the Zn²⁺/In³⁺ (*r*) ratio during the preparation, and the actual contents of ZnO in the composite film were measured by EDX. The actual Zn/In molar ratio along with the film thickness, prepared using different *r* values, are summarized in Table 1. It was found that the actual Zn/In molar ratio is much lower than that during the preparation, which is possibly resulted from much lower solubility constant of In(OH)₃ than that of Zn(OH)₂ (1 × 10⁻³⁴ M⁴ vs. 3 × 10⁻¹⁷ M³, 25 °C).

The surface morphology of the ZnO–In₂O₃ composite film is quite different from that of the pure In₂O₃ film. As shown in Fig. 1 (a)–(e), the In₂O₃–ZnO composite films showed a bimodal grain size distribution with a major fine and a minor coarse component. The amount, or density, of the coarse component increased as the value of *r* was increased. Fig. 2 shows the top-view of SEM images for the In₂O₃–ZnO composite, prepared with different *r* values, with lower magnification. It can be seen that the coarse component started to merge into bigger ones as the value of *r* was increased from 0.67 to 1.50. This change in the film surface morphology would influence the sensor response, which is discussed in Section 3.2. The growth of the coarse component presumably was resulted from the increase of the Zn²⁺ concentration, namely, the increase of the *r* value, since the precursor concentration would affect the size of the resultant ZnO particles [19].

Fig. 3 shows the X-ray diffraction of the In₂O₃–ZnO films with different *r* ratios. It was found that after the incorporation of ZnO, the rhombohedral phase of In₂O₃ was induced. Besides, the Wurtzite phase of ZnO was observed as *r* value was higher than 0.67.

3.2. Gas sensing characteristics

Fig. 4 shows the gas sensing responses of the composite films to 10 ppm NO_x at different operation temperatures. Note that *R*_{NO_x}/*R*_{air} stands for the ratio of the film resistance in the presence of 10 ppm NO_x to the film resistance in zero-grade air atmosphere. It was found that the responses of all composite films increased as the operation temperature was lowered. Besides, the Zn²⁺/In³⁺ ratio (*r*) has great influence on the sensing responses of the composite films. The sensor response to NO gas, at the operation temperature lower than 200 °C, was much improved as *r* value was increased from 0.33 to 0.67. The grain sizes (*d*) of cubic In₂O₃, rhombohedral In₂O₃, and ZnO, estimated by using the XRD data of Fig. 3 and Scherrer's formula (Eq. (2)), are summarized in Table 2.

$$d = \frac{\lambda}{B \cos \theta} \quad (2)$$

where *λ* and *B* are the wavelength of the X-ray wavelength and full-width at half maximum intensity, respectively.

It was found that the grain size of the cubic In₂O₃ increased from 28.8 to 32.3 nm, as a small quantity of ZnO was incorporated into In₂O₃ film (*r* = 0.33), and decreased from 32.3 to 15.4 nm as the

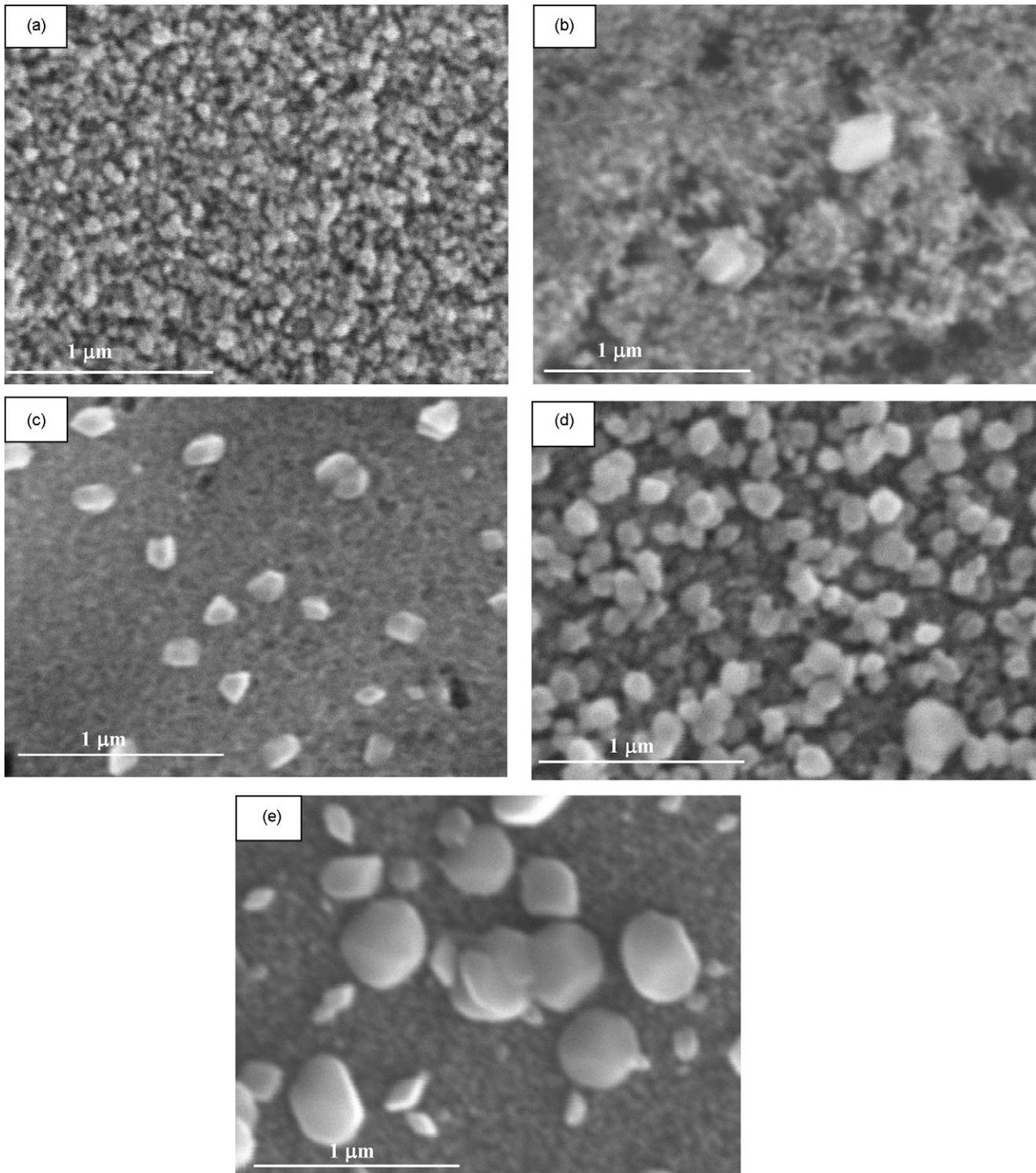


Fig. 1. The top-view of SEM images for the In_2O_3 -ZnO composite film with r values of (a) 0, (b) 0.33, (c) 0.50, (d) 0.67, and (e) 1.00. Scale bar: 1 μm .

content of ZnO was further increased ($0.33 \leq r \leq 0.67$). It has been reported that the grain size has great influence on the sensitivity of the In_2O_3 based NO_2 gas sensor [20], and therefore the decrease in the grain size of In_2O_3 ($0.33 \leq r \leq 0.67$), resulted from the incorporation of ZnO, is one of the factors in enhancing the sensor response. However, as the content of ZnO was further increased ($r=1$), the sensor responses at temperatures lower than 200°C decreased, which could be due to the increase in the grain size of cubic In_2O_3

and the change in the microstructure (see Fig. 2). As a consequence, the optimal r value selected for the later experiments was 0.67.

It is interesting to note that NO_x gas can act as reducing gas at higher temperature and as oxidizing gas at lower temperature, and the response transition temperature ranges, as judged by the transition of $R_{\text{NO}_x}/R_{\text{air}}$ value from greater than 1.0 to smaller than 1.0, depended on the r value. The results are summarized in Table 3. However, the transition in the sensor response was not observed

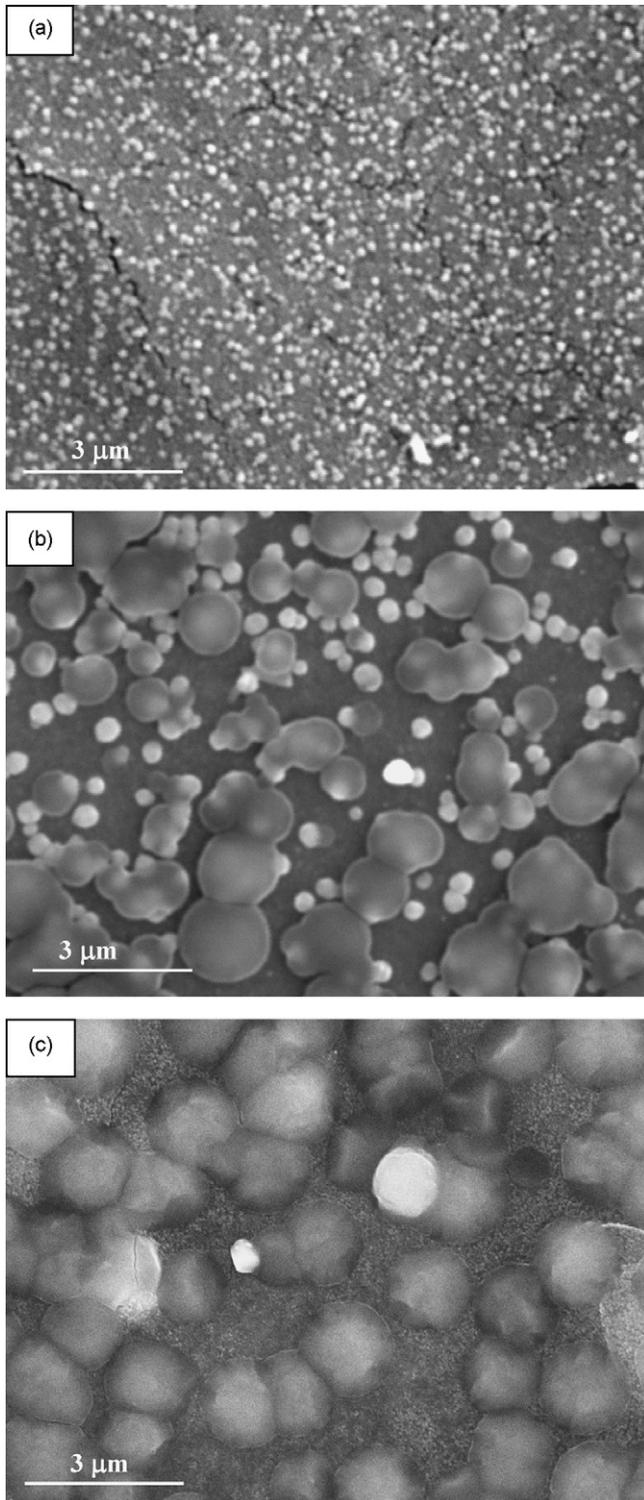


Fig. 2. The top-view of SEM images for the In_2O_3 -ZnO composite film with r values of (a) 0.67, (b) 1.00, and (c) 1.50. Scale bar: $6 \mu\text{m}$.

in the interested temperature range as background zero-grade air was replaced with N_2 (see Fig. 5). Note that $R_{\text{NO}}/R_{\text{N}_2}$ stands for the ratio of the film resistance in the presence of 10 ppm NO to the film resistance in N_2 atmosphere. Since the transformation of NO into NO_2 under N_2 atmosphere is negligible, we use NO instead of NO_x here. Therefore, it can be inferred that the transition in the sensor response is strongly related to the presence of oxygen. The possible mechanisms are discussed in Section 3.3.

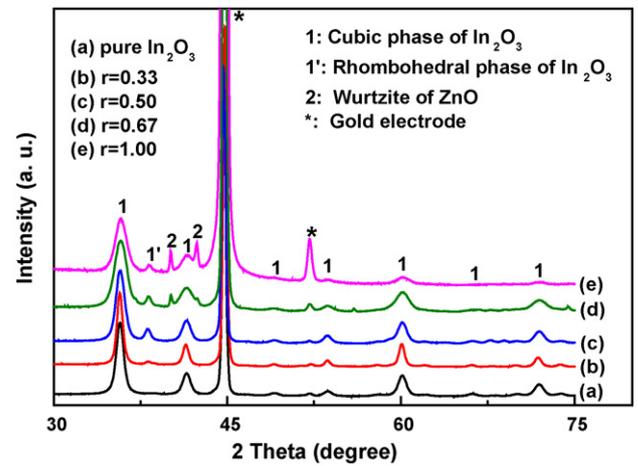


Fig. 3. The XRD patterns of the In_2O_3 -ZnO films with different r ratios.

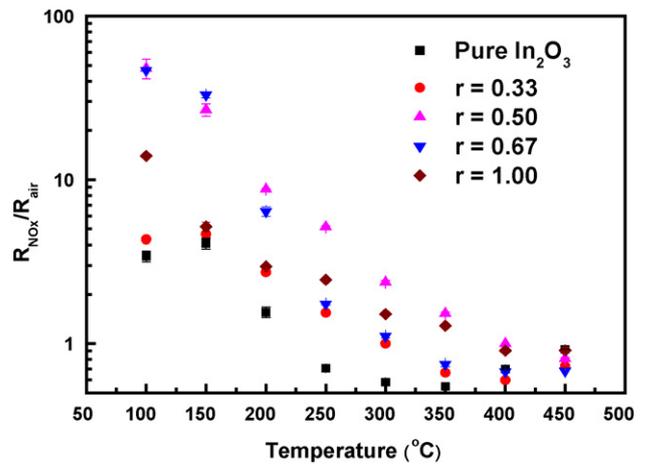


Fig. 4. The changes in the film resistance ratio ($R_{\text{NO}_x}/R_{\text{air}}$) for the pure In_2O_3 and In_2O_3 -ZnO composite films with different $\text{Zn}^{2+}/\text{In}^{3+}$ ratios. All films were exposed to 10 ppm NO in zero-grade air at different operation temperatures.

Table 2

The grain sizes of the cubic $\text{In}_2\text{O}_3^{\text{a}}$, rhombohedral $\text{In}_2\text{O}_3^{\text{b}}$, and ZnO in the In_2O_3 -ZnO composite films with different values of r .

	r values				
	0.00	0.33	0.50	0.67	1.00
Grain size of $\text{In}_2\text{O}_3^{\text{a}}$ (nm)	28.8	32.3	22.2	15.4	17.6
Grain size of $\text{In}_2\text{O}_3^{\text{b}}$ (nm)	N.D.	25.1	26.2	34.1	32.8
Grain size of ZnO (nm)	N.D.	N.D.	N.D.	55.8	61.2

^a Cubic phase.

^b Rhombohedral phase.

3.3. Possible sensing mechanisms

At temperature lower than the transition temperature, the oxygen ions ($\text{O}_{2\text{ads}}^-$) would form at the surface of the In_2O_3 film in a

Table 3

The response transition temperature range for the In_2O_3 -ZnO composite films with different values of r .

r values	Transition range ($^{\circ}\text{C}$)
0.00	200–250
0.33	250–300
0.50	400–450
0.67	300–350
1.00	350–400

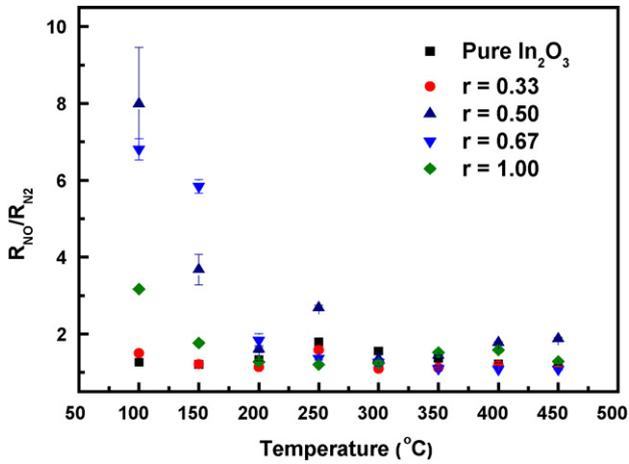
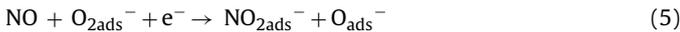
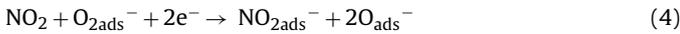


Fig. 5. The changes in the film resistance ratio (R_{NO}/R_{N_2}) for the pure In_2O_3 and In_2O_3 -ZnO composite films with different Zn^{2+}/In^{3+} ratios. All films were exposed to 10 ppm NO in N_2 at different operation temperatures.

sequence of physisorption and charge exchange reactions with the bulk of In_2O_3 grain, as described by Eq. (3). After the In_2O_3 -ZnO film was exposed to NO_x gas, NO_x would react with O_{2ads}^- , via Eqs. (4) and (5), and cause the reduction in the electron concentration, resulting in the increase in the sensor resistance [21].



On the other hand, the adsorbed oxygen ion transformed into atomic oxygen ion (O_{ads}^-), as described by Eq. (6), when the operation temperature was increased to be higher than the transition temperature. After the In_2O_3 -ZnO film was exposed to NO_x gas, NO_x would react with O_{ads}^- , via Eqs. (7) and (8), and cause the increase in the electron concentration, thus lowering the film resistance [22].



As the background zero-grade air was replaced with N_2 gas, the increase in the sensor resistance, as exposed to NO, was simply caused by the NO adsorption in the charged form (NO_{ads}^-) [23], as described by Eq. (9). Since no oxygen exists in N_2 gas, the possibility on the conversion of NO to NO_2 is excluded.



Although the transition behavior has been reported [24], the actual mechanism responsible for this phenomena remains to be clarified. On the other hand, it can also be found from Fig. 3 and Fig. 5 that the response of the In_2O_3 -ZnO films to 10 ppm NO_x in zero-grade atmosphere is larger than that to 10 ppm NO in N_2 atmosphere. As it will be shown latter (Fig. 7), the responses of the pure In_2O_3 film to NO and NO_2 were about the same, but the response of the In_2O_3 -ZnO film to NO_2 was higher than to NO_x . As a sequence, the difference in the sensor response at different atmospheres could be attributed to higher response of the In_2O_3 -ZnO film to NO_2 or difference in the sensing mechanism behind. It should also be noted that although the recovery time and response time for In_2O_3 -ZnO films became much faster as they were exposed to the reducing NO gas at temperatures higher than the transition temperature, the responses were quite small.

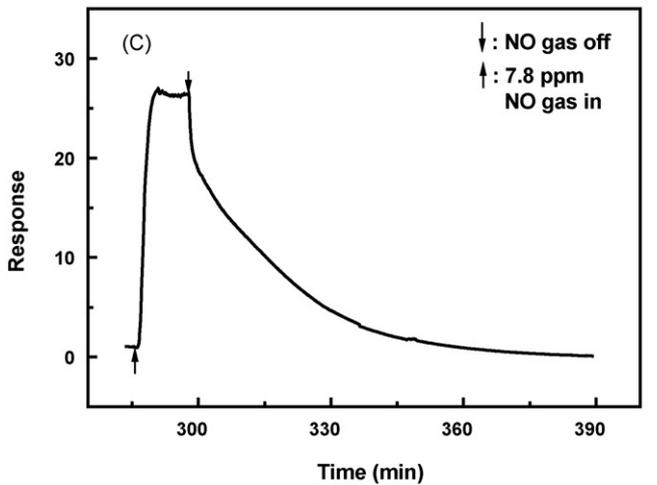
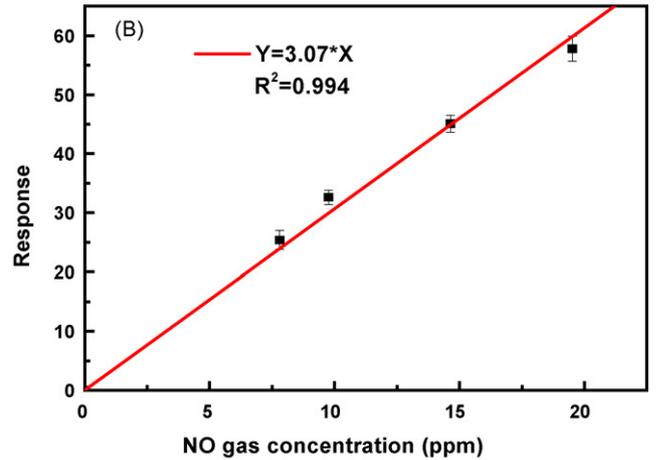
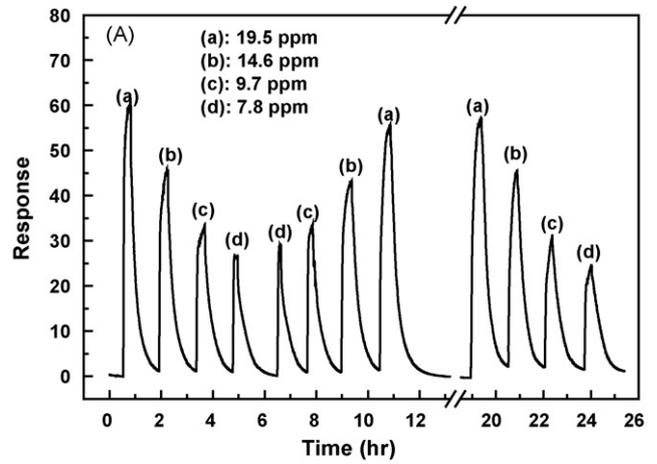


Fig. 6. (a) The transient responses for In_2O_3 -ZnO ($r=0.67$) composite film at $150^\circ C$ to various NO_x concentrations ranging from 7.8 to 19.5 ppm. (b) The resulted calibration curve. (c) The transient response of In_2O_3 -ZnO ($r=0.67$) composite film at $150^\circ C$ to 7.8 ppm.

3.4. NO_x sensing and interference

To develop the NO gas sensor with higher sensitivity and reasonable response and recovery times, we focused on the sensor response at temperature at $150^\circ C$. Fig. 6(a) shows the dynamic responses of the In_2O_3 -ZnO film ($r=0.67$) to various concentrations of NO_x gas at $150^\circ C$. It was found that all the responses are linear with the increase in the concentration of NO_x (Fig. 6(b)). The

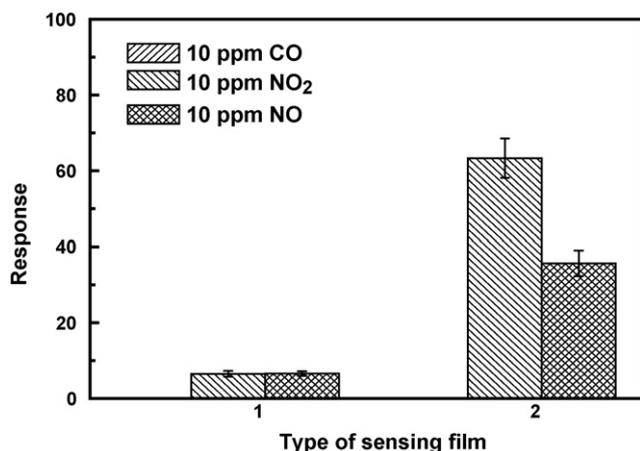


Fig. 7. The responses of the pure In₂O₃ (Type 1) and In₂O₃-ZnO ($r=0.67$, Type 2) films against 10 ppm of NO_x, NO₂ and CO at 150 °C.

limit of detection, based on signal-to-noise ratio of 3, was found to be 12 ppb, which is much lower than that reported in the literature [25]. Moreover, the response time (t_{95}), defined as the time required to reach the 95% of the stable response to NO_x gas, and the recovery time (t_{95}), defined as the time required to reach the 95% of the baseline, for the sensor to detect 7.8 ppm were about 3.5 and 45 min, respectively (see Fig. 6(c)), which are comparable with some In₂O₃ based NO_x gas sensors [25,26]. The long response time and recovery time could be resulted from the low operation temperature [26] and/or the nature of the thick sensing film [27].

The interfering effects of CO and NO₂ were also examined. Fig. 7 shows the responses of the pure In₂O₃ (Type 1) and the In₂O₃-ZnO ($r=0.67$, Type 2) films against NO_x, CO, and NO₂ gases at 150 °C. In fact, both pure In₂O₃ and In₂O₃-ZnO ($r=0.67$) composite films showed no response to 10 ppm CO gas. Thus, the response of CO was not noticed in Fig. 7. On the other hand, NO₂ gas showed significant interfering effect to both pure In₂O₃ and In₂O₃-ZnO ($r=0.67$) films, and the In₂O₃-ZnO film even showed a higher response to NO₂ than NO_x. Further work on the effect of the doping amount of ZnO on the sensing performance of In₂O₃-ZnO film towards NO₂ is under investigation.

Finally, the long-term stability of In₂O₃-ZnO film ($r=0.67$) was investigated by examining the response of the In₂O₃-ZnO ($r=0.67$) film to 10 ppm NO_x, three cycles per once and once per week, for one month. After the test, the electrode was stored in a box, exposed to the ambient air at room temperature with a relative humidity of

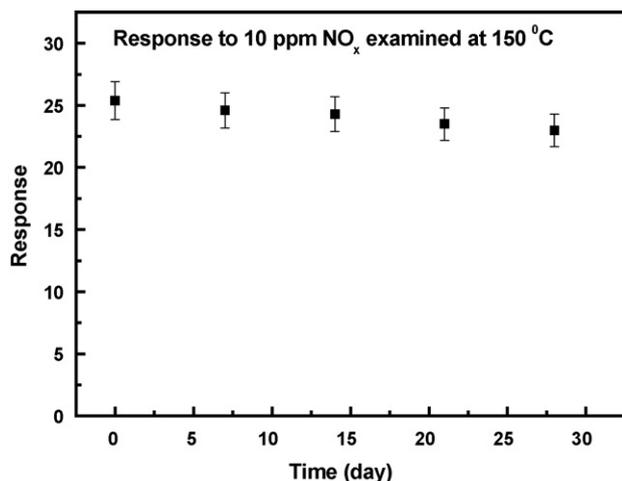


Fig. 8. The responses of In₂O₃-ZnO film to 10 ppm NO_x at 150 °C obtained for different periods.

45%. As shown in Fig. 8, the sensor response remained about 90% after one month use.

4. Conclusions

The In₂O₃-ZnO composite films were synthesized and their NO_x gas sensing characteristics were studied. After incorporating ZnO into In₂O₃ film, the formation of the rhombohedral phase of In₂O₃ and morphological changes were noticed. Besides, with suitable amount of ZnO into the In₂O₃ films ($0.33 \leq r \leq 0.67$), the responses of the resulted composite films to NO_x gas at low temperature (≤ 200 °C) were increased. However, as the content of ZnO was increased ($r \geq 1.00$), the response of the resultant composite film decreased dramatically due to the morphological change. The results suggest that the gas sensors based on the In₂O₃-ZnO composite films have the potential to become candidate for environmental monitoring.

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