Sensing Performance of Gas Sensors Fabricated from Controllably Grown ZnO-Based Nanorods on Seed Layers

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ABSTRACT

ZnO nanorods (NRs) grown on different ZnO seed layers deposited at various Ar–O₂ ambient conditions and the morphologies of the seed layers that affect their response to nitric oxide (NO) gas were investigated. The sensing performance of the devices fabricated with the seed layers deposited under an O₂-rich condition tends to deteriorate. We believe that the surface roughness, grain size, and defect concentration of the seed layer are responsible for this phenomenon. Despite the response to the gas was found to be less dependent on NR length, the gas sensing response is significantly dependent on the oxygen vacancy concentration and the exposure of the NR structure to the NO gas ambient surface. Excellent gas response (57.5% at 1 ppm and 7.1% at 100 ppb of NO gas) was achieved at room temperature—superior to the response presented by other proposed methods. This study not only proposes the potential of ZnO-NRs for high-performance NO gas sensor devices but also offers a simple and low-cost method to optimize the response without using any catalyst and additional treatment.

Keywords: gas sensor device, NO gas sensing, hydrothermal growth, ZnO, nanorod.
Introduction

Nitric oxide (NO) is a common air pollutant that is exhausted by car engines, boilers, and other combustion processes on a daily basis [1]. Inhalation of NO gas causes detrimental functional changes in the lungs, causes asthma, degrades the immune system, and facilitates blood-borne cancer cell metastasis [2,3]. Therefore, designing reliable and highly responsive NO gas sensor devices to monitor NO leakage to the environment is crucial.

Numerous designs of NO gas sensors employing ZnO oxides have been proposed [4,5]. ZnO is mostly used as a gas-sensing material because of its high sensitivity, low-temperature fabrication, low cost, and environment friendliness, excellent chemical and thermal stability, and unique ability to form one-dimensional (1D) nanostructures [6]. The employment of 1D nanostructures [e.g., nanorods (NRs), nanocombs, nanotetrapods, and nanobelts] improves the gas-sensing performance [7,8]. In particular, ZnO-NRs reveal a high surface to volume ratio that enables the exchange of charge carriers during the oxidation–reduction mechanism and enables rapid electron transport along the NRs that greatly enhance the charge concentration [11].

The hydrothermal growth technique is a solution-based process used to synthesize ZnO-NRs, which has several advantages such as easy fabrication, low cost, and environment friendly processes, that is beneficial for mass production [10,11]. Various techniques have been explored for enhancing the sensing performance of ZnO-NR sensor devices, such as dopant addition [12,13], quantum dot use [14], annealing [15], and UV light treatment [16]. Despite these proposed techniques being able to enhance the sensing performance, we argue that suitable optimization of the ZnO-NR growth should be considered before employing these techniques; by considering that all the proposed techniques are expensive and time-consuming. Moreover, an effortless method for fabricating a high-performance gas sensor without using a catalyst and without involving any
additional treatment is urgently required to significantly reduce the processing time and cost as well as to encourage the realization of ZnO-based sensors for use in future sensing devices.

The hydrothermal growth technique requires a seed layer to provide ZnO nucleation sites during the growth of the ZnO-NRs. Consequently, the properties of the seed layer defines NR morphology in terms of the diameter, length, density, and alignment [10,17–21]. Thus, a fine tuning on the seed layer is crucial for determining the sensing behavior of the devices. However, the importance of the seed layer to the sensing performance is still overlooked. In this study, we studied the morphology of the ZnO-NRs grown on sputtered seed layers that are deposited at various gas ambient conditions, and the influence of such a modification on the sensing performance of the ZnO-NRs was investigated.

Experimental Method

Sensor device fabrication

Approximately 260-nm-thick indium–tin–oxide (ITO)-coated glass substrates were cleaned using acetone and DI water for 10 min. Then, ZnO seed layers were deposited on the ITO-substrates by using radio-frequency magnetron sputtering at room temperature at various Ar–O₂ gas ratio ambient conditions. The Ar–O₂ gas ratios employed are 1, 0.67, 0.33, and 1 with a flow rate of 30:00, 20:10, 10:20, and 00:30 sccm, respectively. The total gas flow was maintained at 30 sccm. Deposition time was carefully controlled to fabricate the seed layer with a thickness of 50 nm. The deposition rate of the ZnO seed layer at various gas ratio conditions is presented in Fig. 1(a). Then, the ZnO-NRs were synthesized on the ZnO seed layer by employing a precursor aqueous solution of zinc chloride (ZnCl₂) and ammonium hydroxide (NH₃OH), and the hydrothermal process was maintained at 95°C for 10 min. The hydrothermal growth procedure adopted the method that was explained in our previous studies [11,22]. To fabricate the top electrode, drop- cast method is used,
and silver nanowires dispensed in isopropanol (IPA) with concentration as 0.5 wt%. The average
diameter of silver nanowire is about 12–15 nm and an average length is about 80 nm. Silver (Ag)
nanowires were dropped on top of the active areas of the ZnO-NRs. A 40-nm-thick Al film was
deposited as an auxiliary electrode by using a thermal evaporator. The schematic of the fabricated
device is illustrated in Fig. 1(b). The devices, seed layers, and NRs are denoted as Dx, SLx, and
NRx, respectively. Here, x is denoted as 1, 2, 3, and 4. These values represent the gas ambient (Ar:
O\(_2\)) flow of 30:00, 20:10, 10:20, and 00:30 sccm, respectively, for the sputtered seed layer.

Response measurement set-up

The schematic of the gas-sensing measurement setup is shown in Fig. 1(c). An electrical syringe
pump was used to inject the target gas (NO, purity 99.999%) into a tube to mix the gas with the
background dry ambient air. The gas mixture then entered the microfluid system. The background
air was passed into the detection chamber. A moisture absorber (dryer) was first used to filter out
the water in the air. The air in the system was controlled in a low-humidity environment with a
relative humidity of 10% to prevent the components from being affected by room humidity
fluctuations. The current values of the ZnO-NR devices were measured using an electrical
measurement system (model 2400, Keithley Source Meter). The measurement setup was adopted
from a previous study [23].
Fig 1. (a) Deposition rate of the ZnO seed layer grown in various ambient conditions. (b) Schematic of the fabricated device (AgNWs/ZnO-NRs/ZnO/ITO/glass substrate). (c) Gas-sensing measurement system.

Material analysis

The morphology of the ZnO-NRs was examined by using scanning electron microscopy (SEM; Hitachi SU8010). The crystal structures of the ZnO-NRs and the seed layers were investigated through X-ray diffractometry (XRD; D1. Bede Plc.). The X-ray source is Cu K-alpha 1.5406 A. The defect concentrations in the ZnO-NRs and the seed layer were evaluated using an X-ray
photoelectron spectroscopy (XPS; PHI Quantera SXM). A C1s peak with a binding energy of 284.5 eV was taken as a reference.

Results and discussion

Effect of seed layer on ZnO NRs morphology

The surface roughness of the seed layer serves a significant role in the ZnO-NR growth. Therefore, the topography of the ZnO seed layer deposited at various Ar–O₂ gas ratios was obtained, and the result are depicted in Figs. 2(a)–2(d). The surface roughness of the seed layer increases as the O₂ portion increases. This is due to the higher energetic bombardments of the oxygen ions on the growth films, thus resulting in surface degradation [24]. Figures 2(e) and (f) present the XRD patterns of the ZnO seed layer (ZnO-SL) grown at various Ar–O₂ gas ratios and the related ZnO-NRs, respectively. The crystal structure of the ZnO-SL and ZnO-NRs is a hexagonal wurtzite structure and reveals a preferred orientation of (002) (JCPDS, No. 36-1451). The grains of the seed layer that grows in the (002) direction is beneficial in terms of the nucleation sites for NR growth [17,25]. Therefore, the (002) grain size was calculated using the Scherer equation [26], and the result is shown in Fig. 2(g). The grain size of (002) of the ZnO-SL decreases after introducing O₂ gas. The introduction of the neutral oxygen atoms enhances the growth of the grains in various directions (Fig. 2(e)). Thus, the grain size of the (002) grains decreases due to the growth competition process [27,28]. Consequently, the grain size of the NRs grown on the corresponding seed layer decreases (Fig. 2(g)).
**Fig 2.** AFM surface topography of the seed layer deposited under an Ar–O$_2$ gas flow of (a) 30:00 (pure Ar), (b) 20:10, (c) 10:20, and (d) 00:30 (pure O$_2$) sccm. XRD pattern of (e) the deposited ZnO seed layer and (f) the ZnO-NRs. (g) (002) grain size of the seed layer and ZnO-NRs calculated from (e) and (f).

To further evaluate the microstructure of the NRs, an SEM analysis was conducted, and the results are displayed in Figs. 3(a)–3(e). EDX spectrum of the fabricated device is shown in Fig. 3(f). That confirms the presence of all the metal oxide in the composite and quantitatively, as well as silver (Ag) presence is also observed, which is used as a top electrode. The SEM analysis affirms that all NRs are successfully grown vertically regardless of the various seed layer conditions. The top-view SEM images depict the decrease in the diameter of the NRs grown on the O-rich seed layer. This result corroborates with XRD analysis results (Fig. 2(g)). It was also found that the average length and the density of the NRs have a direct dependency on the seed layer condition.
The increase in the number of nucleation sites due to the higher surface roughness of the seed layer (Fig. 2(a)–2(d)) may induce this phenomenon [29,30]. An electrical test was conducted to investigate the sensing performance of the various NR structures.

Fig 3. Cross-sectional SEM images of (a) NR1, (b) NR2, (c) NR3 (d) NR4. Insets in (a)–(d) display the top view of the NRs (e) Length and density of the ZnO-NRs grown on various seed layers and
Gas sensing property

The sensing performance of these various NR microstructures toward NO gas was then assessed. Figures 4(a)–4(d) show the resistance (ohm) and time (sec) curves of the gas-sensing performance of device D1, D2, D3, D4 and inset images shows I-V curves of the device, respectively. The gas-sensing measurements were conducted at room temperature (~26°C) by employing a bias voltage of 5 V, and the nitric oxide gas concentration was 100 ppb to 1 ppm. The calculated response is denoted as $R$ and presented in Figs. 4(a)–4(d), and the device response is summarized in Fig. 4(e). The results reveal that from low to high concentration, there is an increment in the gas-sensing response with respect to the NO gas. We found that the gas response of the device with NRs grown on the seed layer made at pure Ar ambient(D1) is far superior than the response of all other devices. The D1 sensor (fabricated on ZnO-SL-1) presents the highest response with values of 57.5%, 34.9%, and 7.1% at NO concentrations of 1 ppm, 500 ppb, and 100 ppb, respectively. On the other hand, the response significantly decreases in the other devices (Fig. 4(e)). It is worth noting that the four sensors’ resistances are very different in air as shown in Fig. 4. We suggest the possible reason that the variation of the pristine resistance of the devices is due to the conductivity of Ag nanowires top electrode (TE). Since the TE was fabricated employing a drop coating technique, thus, the actual weight of Ag onto the nanorods may slightly different in each drop. Consequently, it may lead to varying amount of Ag nanowires in TE between devices and the resistance variation of the devices. Nevertheless, the Ag(TE)/nanorods contact is following ohmic contact which may not have significant role in the sensing mechanism. Under the comparison with other reported sensors demonstrating good response toward NO gas, the sensing response of our sensors proposed
in this work is better than those made by several other methods and sensing materials listing in Table 1.

![Figures](attachment:figures.png)

Fig 4. Resistance-time curves of (a) D1, (b) D2, (c) D3, and (d) D4 devices and inset I-V results of (a) D1, (b) D2, (c) D3, and (d) D4 devices, respectively. (e) Gas-sensing response results of the various devices measured at room temperature.

This result indicates that the property of the ZnO seed layer determines the microstructure of the NRs; thus, the property of the ZnO seed layer may significantly affect the sensing performance of the NRs. The seed layer has no sensing capability (data not shown), which indicates that the sensing behavior is only from the NR layer. Although the NRs grown on a seed layer deposited with a less amount of Ar gas have greater lengths, the sensing performance of such NRs tends to decrease. This finding suggests that the sensing performance does not always dependent on the height of the NRs, as is commonly observed [9,23]. Therefore, we conducted materials analysis to understand this phenomenon.
Chemical analysis (XPS)

Oxygen vacancy defects serve a significant role in ZnO-based sensor devices [31]. Figures 5 (a)–5(d) show the XPS analysis results of the O1s core level of the ZnO-NRs grown on various seed layers. The O1s spectra were fitted to two Gaussian-resolved peaks—a low binding energy peak (O$_{\text{i}}$) that corresponds to the O$^{2-}$ ions on the hexagonal ZnO structure and a high binding energy peak (O$_{\text{ii}}$) that is attributed to the oxygen-deficient region (oxygen vacancy-rich region) and the chemisorbed or dissociate oxygen species on the surface of ZnO [32,33]. The concentration of oxygen vacancy $V_0$ is represented by the $O_{\text{ii}}$–$O_{\text{Total}}$ ratio [22], as depicted in Fig. 5(e). The ZnO-NRs grown on seed layers deposited with a higher Ar portion have a higher $V_0$ concentration. This may be because a seed layer deposited at ambient conditions with a low amount of oxygen may contain a higher $V_0$ concentration (data not shown). Moreover, the NRs prefer to grow in a condition that requires the lowest formation energy corresponding to the seed layer properties [34]. Therefore, we can assume that the NRs may grow based on the lattice condition of the seed layer to grow with the lowest energy.
Fig 5. XPS spectra of the O1s core level of the ZnO-NRs grown on (a) SL1, (b) SL2, (c) SL3, and (d) SL4 films. (e) Oxygen vacancy concentration in the NRs.

Selectivity and stability test for NO sensing

Selectivity and stability are very essential parameters to check the performance of the gas sensor device. The Device D1 was fabricated to perform the selectivity and stability test. The gas
selectivity test was carried out by using NH$_3$, CO, H$_2$S and acetone gases and the results are depicted in Fig 6(a). It is indicated that the fabricated sensors have no response to 500-ppb CO and H$_2$S gases at room temperature. When detecting 500-ppb acetone and NH$_3$ for 30 sec, the sensors are observed 4.6% and 1.2 % gas responses, respectively, as shown in Fig. 6(a). It is worth noting that, the sensor exhibits a 34.9% sensing response when being exposed to 500-ppb NO indicating that sensor can be selective in detection of NO from above mentioned gases at room temperature.

Furthermore, the effect of relative humidity on the gas sensing performance of the device D1 was studied at room temperature and the results are depicted in Fig 6 (b). The sensing response is decreased in high humidity (55-65% RH) environment due to absorption of water molecule from the humidity atmosphere. This phenomenon reduces the absorption rate of NO molecule at the sensing layer [35].

Sensor stability is also critical characteristic to be used in practical application. To acknowledge the stability test, the device D1 was measured at 500-ppb NO gas under the same test conditions as before for up to 5 days and the observed responses are 33.9, 30.6, 31.2, 28.2 and 26.0% as exhibited in Fig 6(c), indicating a small downward trend in gas response. Nevertheless, the gas response is decreased just a few percent within 5 days confirming that the sensor has good stability at room temperature.
Fig 6. (a) The selectivity performance of the sensor to NH$_3$, acetone, CO and H$_2$S at room temperature, (b) Sensing response of Device D1 in high humidity environment (RH ~ 55-65 %) and (c) The D1 stability results up to 5 days.

Gas sensing mechanism

The sensing mechanism of the various devices is proposed and depicted in Fig. 7. The sensing mechanism is based on the adsorption–desorption reaction of the gas molecules at the surface of the NRs. When the sensor is exposed to air, oxygen molecules are easily absorbed on the sensor surface and captures the electrons from conduction band. The gas sensor response varies due to different morphology structure and absorption rate at the sensing layer. After oxygen adsorption
process, a depletion layer is formed at the outer surface of sensing nanorods layer and results the higher resistance [36]. The reaction induces a change in the electrical property (conductivity or resistance) of the device. This change indicates a response toward the target gas [37]. As shown in Fig. 7, the introduction of NO gas (in an ambient of dry air as the background gas) to the sensor devices results in the adsorption of the NO molecules on the surfaces of the NRs. The NO molecules are ionized at the surface by capturing the electron from the ZnO. The formula of this reaction is as follows:

\[ \text{NO}/\text{NO}_2^{(\text{gas})} + e^- \rightarrow \text{NO}^-/\text{NO}_2^{(\text{ads})} \]  

Hereafter, the \( \text{NO}^-/\text{NO}_2^{(\text{ads})} \) reactant forms a depletion layer on the surface of the NRs. Thus, the electron concentration on the surface of the NRs decreases. This decrease results in an increase in the resistance of the devices [31]. The oxygen vacancy is an electron donor; therefore, the concentration of the oxygen vacancy influences the amount of NO absorbed on the surface of the NRs.

**Fig 7.** Schematic of the gas sensor mechanism in (a) D1, (b) D2, (c) D3, and (d) D4 devices.
The NRs of the device D1 (Fig. 7(a)) exhibit a high oxygen vacancy concentration (Fig. 5(a)) with a high openness structure (low density, Fig. 3(a)). These chemical and structural properties enable the abundant absorption of NO on the surface of the NRs, thus inducing a high response toward the gas target (Fig. 4(a)). Moreover, the NRs of the device D2 (Fig. 7(b)) have a lower oxygen vacancy concentration (Fig. 5(b)) and higher density (Fig. 3(b)) than the NRs of the device D1. Therefore, less NO molecules can be absorbed by the NRs of the device D2, which causes a lower sensing response (Fig. 4(b)). Similarly, the NRs of the devices D3 and D4 (Fig. 7(c) and 7(d)) have very low oxygen vacancy concentrations (Fig. 5(c) and 5(d)) and a low openness structure (Fig. 3(c) and 3(d)). Thus, the sensing response of these devices is significantly lower than the other devices (Fig. 4(c) and 4(d)). However, the device D4 presents a slightly higher gas response than that of the device D3 (Fig. 4(e)). We suggest that this behavior is attributed to the oxygen vacancy concentration of NR4 is slightly lower than that of D3, but the length of NR4 is much longer than that of NR3 (Figs. 3(c) and 3(d)). Thus, this condition helps to increase the area that can be exposed to the NO molecules [21,38].

Conclusions

In conclusion, we investigated the influence of the seed layer on the gas response. The ZnO-NRs that are grown on a seed layer deposited with a low amount of O2 gas were found to be more sensitive toward NO gas. The concentration of the oxygen vacancy defects and the microstructure of the NRs determine the sensing performance. Although the NRs grown on a seed layer deposited with a low amount of O2 gas have a shorter length, the high oxygen vacancy concentration and the loose structure of NRs provide high sensitivity. A sensing response superior than that provided by several other methods can be achieved by simply adjusting the seed layer. It worth noting that the devices require various times to recover the original condition (pristine resistance) after the
exposure to the gas. This phenomenon may be related to the surface area effect and the NO releasing mechanism from the surface of the nanorods. It is very interesting to be explored in our future investigation. Nevertheless, this study suggests that the property of the seed layer cannot be overlooked when designing ZnO-NR-based sensor devices.

Acknowledgment

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Conflicts of interest

The authors declare no conflicts of interest.

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Table Caption
Table 1. Performance comparisons of the NO gas sensors between those from published papers and that of present study.
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<th>Sensing material</th>
<th>Operating Temp.</th>
<th>Sensing Response (%)</th>
<th>Conc. (ppm)</th>
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<td>[40]</td>
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